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ҚҰДАЙБЕРГЕНОВ
Сарқыт Елекенұлы

ҒИБРАТТЫ ҒҰМЫР

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Данный выпуск книжной серии «Ғибратты ғұмыр» посвящен Кудайбергенову Саркыту Елекеновичу, доктору химических наук, профессору, лауреату Государственной премии Казахской ССР в области науки и техники. Кудайбергенов С.Е. признанный в мире ученый в области физической химии полимеров. По результатам общедоступной базы данных, созданной учеными Стэнфордского университета, он по цитируемости входит в топ-2% среди ведущих ученых мира, а по базе данных «Web of Science Clarivate Analytics» является мировым лидером в области синтеза и исследования синтетических полиамфолитов. Его научное направление связано с разработкой и внедрением полимеров специального назначения для нефтяной отрасли, нефтехимии, катализа, нанотехнологии, биотехнологии и медицины. В годы независимости Республики Казахстан, в 1999 г., Кудайбергенов С.Е. организовал и возглавил частное учреждение «Институт полимерных материалов и технологий», которое вносит свой вклад в развитие полимерной науки Казахстана и подготовку высококвалифицированных научных кадров.

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УЧЕНЫЙ. ЛИДЕР. НАСТАВНИК

Казахский национальный университет имени аль-Фараби продолжает выпуск серий «Ғибратты ғұмыр», посвящённых выдающимся личностям, государственным и общественным деятелям, ученым и педагогам, организаторам науки и образования Казахстана.

Очередной выпуск серии «Ғибратты ғұмыр» посвящается 75-летнему юбилею известного ученого, доктора химических наук, профессора, лауреата Государственной премии Казахской ССР в области науки и техники, лауреата премии имени К.И. Сатпаева, Кудайбергенова Саркыта Елекеновича.

Кудайбергенов С.Е. является признанным в мире ученым в области физической химии полимеров. По результатам общедоступной базы данных, созданных учеными Стэнфордского университета (https://doi.org/10.17632/btchxktzyw.2.), он по цитируемости входит в топ-2% среди ведущих ученых мира (Top 2% World Scientists,2023, 2024). По данным Миннауки России С.Е. Кудайбергенов в числе семерых казахстанских ученых входит в научную элиту «Лидеры науки СССР» (1995 г.), а по базе данных «Web of Science Clarivate Analytics» он является мировым лидером в области исследования синтетических полиамфолитов (2018 г.). Тому пример его единолично написанные фундаментальные монографии на английском языке, такие как «Polyampholytes in Advanced Polymer Science and Emerging Technologies», «Recent Advances in the Studying of Synthetic Polyampholytes in Solutions», «Polyampholytes: Synthesis, Characterization and Application» и «Polyampholytes», опубликованные в Германии и США в престижных издательствах «CRC Press», «Springer», «Kluwer Academic/Plenum Publishers» и «John Wiley @ Sons», а также монография «Polyampholytes: Past, Present, Perspectives», изданная в Казахстане. В 2022 году по итогам конкурса Министерства науки и высшего образования

РК ему присуждена премия «Лучший научный работник» за значительный вклад, внесенный в развитие отечественной науки.

В годы независимости Республики Казахстан, в 1999 году, Кудайбергенов С.Е. организовал и возглавил частное учреждение «Институт полимерных материалов и технологий», которое вносит свой вклад в развитие полимерной науки Казахстана и подготовку высококвалифицированных научных кадров.

Его научное направление связано с разработкой и внедрением полимеров специального назначения в нефтяной отрасли, нефтехимии, катализе, нанотехнологии, биотехнологии, медицине и охране окружающей среды. Разработанная им технология полимерного заводнения успешно прошла 12 опытно-промышленных испытаний на месторождениях «Кумколь» и «Карабулак», что позволила значительно увеличить объем дополнительно добываемой нефти.

Кудайбергенов С.Е. обладатель международных грантов фонда Сороса, INTAS-Kazakhstan, открытого конкурса INTAS, руководитель Международного гранта НАТО «Наука для мира и безопасности», проекта коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов», участник Международного проекта Европейского Союза «Horison-2020».

Кудайбергенов С.Е. в 1995 г. прошел трехмесячную стажировку в Национальном научном фонде США и получил сертификат менеджера науки. Он неоднократно представлял казахстанскую науку на различных Международных конференциях и симпозиумах с пленарными, устными и стендовыми докладами в Бельгии, Германии, Греции, Египте, Испании, КНР, Нидерландах, Польше, США, Сингапуре, Турции, Финляндии, Швейцарии, Швеции, Южной Корее и Японии. В качестве приглашенного профессора читал лекции в Университете Хаджеттепе (Турция), Университете Васеда (Япония), Синьцзяньском и Сычуаньском Университетах (КНР), в течение 1 года читал лекции и проводил научные исследования в Институте науки и технологии Квангжу (Южная Корея), подготовил 2 магистров наук из Университета Монпелье (Франция) и Университета Сеул.

Под его руководством защищены 1 докторская, 10 кандидатских и 7 PhD диссертаций. Им организовано 8 Международных семинаров, конференций и симпозиумов, посвященных полимерам специального назначения с участием ученых и специалистов из ближнего и дальнего зарубежья.

В становлении Кудайбергенова С.Е., как ученого большое влияние оказали его научные руководители и консультанты – профессор Шаяхметов Ш.Ш., академик НАН РК Бектуров Е.А., член-корреспондент АН СССР, академик АН КазССР Рафиков С.Р., а также всемирно признанные ученые – академик РАН Кабанов В.А. из МГУ имени М.В. Ломоносова и профессор Ейшун Цушида (Eishun Tsuchida) из Университета Васеда (Япония).

Кудайбергенов С.Е. единолично и в соавторстве опубликовал более 500 научных трудов, в том числе 24 монографии, учебники и учебные пособия на казахском, русском, польском и английском языках,13 глав книг, 37 обзорных и 133 научных статей, опубликованных на английском языке в международных реферируемых журналах с высоким импакт-фактором, 253 статьи в журналах СССР, РФ, СНГ и Казахстана. Он соавтор 45 авторских свидетельств, инновационных патентов, предпатентов и патентов на полезную модель, включая 2 патента Южной Кореи. Его индекс Хирша в базе данных Scopus – 28.

Кудайбергенов С.Е. член редколлегии журналов «Евразийский химико-технологический журнал», «Eurasian Journal of Chemistry», «Узбекский полимерный журнал», «International Journal of Formulation Science», «Shakarim Chemistry & Ecology». В 2021 г. к его 70-летнему юбилею был издан спецвыпуск журнала «Polymers for Advanced Technologies», 2021, V.32, No.7, P.2633-2790. Он член Международных Оргкомитетов IUPAC (Международный Союз чистой и прикладной химии) «MacroMolecular Complexes (MMC)» и «Macro- and Supramolecular Architectures and Materials» (MAM).

Сведения о научно-педагогической деятельности Кудайбергенова С.Е. опубликованы в книге «Ғылым тылсымына жол», энциклопедии «Алматы», «Қазақ Энциклопедиясы»,

справочнике «Кто есть кто в казахстанской науке», в изданиях КазНУ «Наша Элита», «Жүзден жүйрік, мыңнан тұлпар», в журналах «Нефть и Газ», «История Казахстана: преподавание в школе», «Macromolecular Chemistry and Physics», «Polymers for Advanced Technologies», «Вестник КазНУ, Серия химическая», Вестник Карагандинского университета, Серия химическая», Википедия https://ru.wikipedia.org› wiki› Кудайбергенов,_Саркыт_ Елекенович, Farabi University https://farabi.university› news.

В книге содержатся сведения о научно-педагогической и общественной деятельности Кудайбергенова С.Е. в постсоветское время и в период становления независимого Казахстана, научные достижения первого в РК частного научно-исследовательского Института полимерных материалов и технологий, приводятся списки научных трудов – монографий, глав книг, обзорных статей и статей, опубликованных в журналах ближнего и дальнего зарубежья, казахстанских изданиях, перечень авторских свидетельств и патентов, ряд избранных трудов, а также статьи о нем, опубликованные в иностранных и казахстанских журналах.

Творческий путь Кудайбергенова Саркыта Елекеновича и достигнутые успехи в науке и образовании являются замечательным примером для подрастающего поколения.

Жансейіт ТҮЙМЕБАЕВ,
Әл-Фараби атындағы
Қазақ ұлттық университетінің
Басқарма Төрағасы – Ректоры

Е.А. БЕКТУРОВ,
Академик НАН РК

СЛОВО УЧИТЕЛЯ

Во всем мне хочется дойти самой сути.
В работе, в поисках пути, в сердечной смуте.
До сущности протекших дней, до их причины,
До оснований, до корней, до сердцевины.
Все время схватывая нить судеб, событий,
Жить, думать, чувствовать, любить,
свершать открытья…

Борис Пастернак

Эти строки Бориса Пастернака, на мой взгляд, во многом перекликаются с жизненной философией и творчеством моего любимого ученика – Саркыта Кудайбергенова. В них словно заключён тот непростой путь, который ему пришлось пройти. Это будет описано в дальнейшем повествовании.

Он родился в крестьянской семье в далёком ауле. Отец умер, когда ему был всего год, а мать он потерял в четырнадцать лет. Верный её заветам, он всегда хорошо учился и много читал. Благодаря природной любознательности, жажде знаний и огромному трудолюбию в 1968 году он поступил на химический факультет Казахского государственного университета им. С.М. Кирова и успешно окончил его в 1973 году.

Особо хочется отметить его становление как учёного. Мы знакомы и поддерживаем общение уже более сорока лет. Меня всегда поражало его особое отношение к науке. Для него наука – не просто работа, а подлинная среда обитания и способ существования. Он словно погружён в океан знаний и открытий, проявляя при этом редкую дотошность, щепетильность и проницательность. Он с большой ответственностью относится к новым явлениям, исследованиям и открытиям и требует такого же отношения от своих учеников.

Его отличают порядочность, интеллигентность и открытость. Он щедро делится своими знаниями, опытом и научными за-

мыслами с коллегами и учениками. Его научный потенциал далёк от исчерпания: он, как и прежде, полон новых идей и видит широкие возможности для практического воплощения своих научных достижений.

Мне хочется пожелать ему дальнейших успехов на избранном им поприще. С высоты прожитых лет надеюсь, что впереди его ждут новые свершения, а также удовлетворение и радость от признания его достижений и реализации намеченных замыслов.

В.В. ХУТОРЯНСКИЙ,
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Г.С. ИРМУХАМЕТОВА,
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технического университета имени К.И. Сатпаева

КРАТКИЙ ОЧЕРК О НАУЧНО-ПЕДАГОГИЧЕСКОЙ И ОБЩЕСТВЕННОЙ ДЕЯТЕЛЬНОСТИ ДОКТОРА ХИМИЧЕСКИХ НАУК, ПРОФЕССОРА, ЛАУРЕАТА ГОСУДАРСТВЕННОЙ ПРЕМИИ КАЗАХСКОЙ ССР В ОБЛАСТИ НАУКИ И ТЕХНИКИ КУДАЙБЕРГЕНОВА С.Е.

В науке необходима абсолютная честность и преданность.
П.Л. Капица,
лауреат Нобелевской премии

Кудайбергенов Саркыт Елекенович, признанный в мире ученый в области физической химии полимеров, доктор химических наук (1991), профессор (1994), лауреат Государственной премии Казахской ССР в области науки и техники (1987), премии АТ Фонда «Ғылымдағы жетістіктері үшін» (1995), лауреат премии «Парасат», как наиболее публикуемый и цитируемый казахстанский автор за рубежом (2010), лауреат премии имени К.И. Сатпаева «За лучшее научное исследование в области естественных наук» (2019), награжден нагрудным знаком

МОН РК «За заслуги в развитии науки Республики Казахстан» (2012), памятной медалью «5 лет НТЦ АО «КазТрансОйл» (2003), избран почетным профессором Семипалатинского государственного университета имени Шакарима и награжден медалью «Шакарим» «Университетке сіңірген еңбегі үшін» (2011), юбилейными медалями «85 лет Satbayev University» (2019), «Қаныш Сәтбаевтың 125-жылдық мерейтойы» (2024). Он обладатель Государственной научной стипендии для учёных и специалистов, внёсших выдающийся вклад в развитие науки и техники (2020). Министерством науки и высшего образования РК ему присуждена премия «Лучший научный работник» за значительный вклад, внесенный в развитие отечественной науки (2022). Указом Президента Республики Казахстан от 14 августа 2025 г. Кудайбергенов С.Е. включен в состав Национального совета по науке и технологиям при Президенте РК.

По результатам общедоступной базы данных, созданной учеными Стэнфордского университета, он по цитируемости входит в топ-2% среди ведущих ученых мира (Top 2% World Scientists, 2023, 2024 гг.). По данным Миннауки России С.Е. Кудайбергенов в числе семерых казахстанских ученых входит в научную элиту «Лидеры науки СССР» (1995 г.), а по базе данных «Web of Science Clarivate Analytics» (2018 г.) он является мировым лидером в области исследования синтетических полиамфолитов – простых моделей белков и полипептидов.



Участники заседания Национального совета по науке и технологиям при Президенте Республики Казахстан. Акорда, 26 сентября 2025 г.



10 топовых ученых мира, внесших наибольший вклад в развитие научного направления «Полиамфолиты»

Кудайбергенов С.Е. обладатель международных грантов фонда Сороса, INTAS-Kazakhstan, открытого конкурса INTAS, руководитель Международного гранта НАТО «Наука для мира и безопасности», проекта коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов», участник Международного проекта Европейского Союза «Horison-2020», посвященного разработке биоразлагаемых и биосовместимых гелеобразующих полимеров, наногелей и наночастиц для использования в качестве многофункциональных терапевтических агентов в офтальмологии.

Кудайбергенов С.Е. неоднократно представлял казахстанскую науку на различных Международных конференциях и симпозиумах с пленарными, устными и стендовыми докладами в Бельгии, Германии, Греции, Египте, Испании, КНР, Нидерландах, Польше, США, Сингапуре, Турции, Финляндии, Швейцарии, Швеции, Южной Корее и Японии.

Под его руководством защищены 1 докторская, 10 кандидатских и 7 PhD диссертаций. Им организовано 8 Международных семинаров, конференций и симпозиумов, посвященных полиме-

рам специального назначения с участием ученых и специалистов из ближнего и дальнего зарубежья. Его научное направление связано с разработкой и внедрением полимеров специального назначения в нефтяной отрасли, нефтехимии, катализе, нанотехнологии, биотехнологии, медицине, для охраны окружающей среды. Единолично и в соавторстве он опубликовал более 500 научных трудов, в том числе 24 монографии, учебники и учебные пособия на казахском, русском, польском и английском языках,13 глав книг, 37 обзорных и 133 научных статей, опубликованных на английском языке в международных реферируемых журналах с высоким импакт-фактором, 253 статьи в журналах СССР, РФ, СНГ и Казахстана. Он соавтор 45 авторских свидетельств, инновационных патентов, предпатентов и патентов на полезную модель, включая 2 патента Южной Кореи. Его индекс Хирша 28 (Scopus). Общее количество ссылок на его публикации составляет более 5500 статей (Google Академия Sarkyt Kudaibergenov).

Кудайбергенов С.Е. опубликовал единоличные фундаментальные монографии на английском языке в Германии «Recent Advances in the Studying of Synthetic Polyampholytes in Solutions» (1999, изд. Springer), США «Polyampholytes: Synthesis, Characterization and Application» (2002, изд. Kluwer Academic/ Plenum Publishers), «Polyampholytes in Advanced Polymer Science and Emerging Technologies» (2024, изд. CRC Press, Boca Raton, London, New York) и Казахстане «Polyampholytes: Past, Present, Perspectives» (2021, изд. Центр Оперативной Полиграфии, Алматы).

В 1995 г. он прошел трехмесячную стажировку в Национальном научном фонде США и получил сертификат менеджера науки. В качестве приглашенного профессора читал лекции в Университете Хаджеттепе (Турция, 1996), Университете Васеда (Япония, 1998), Синьцзяньском и Сычуаньском Университетах КНР (2015, 2018, 2025 гг.). В 2002-2003 гг. читал лекции и проводил научные исследования в Институте науки и технологии Квангжу (Южная Корея), подготовил 3 магистров наук из Университета Монпелье (Франция) и Университета Сеул.

Он являлся членом диссертационного совета КазНУ имени аль-Фараби по наноматериалам и нанотехнологии (2013-2021 гг.),

председателем диссертационного совета КазНИТУ имени К.И. Сатпаева по специальности «химическая технология органических веществ» (2019-2021 гг.). Член редколлегии журналов «Евразийский химико-технологический журнал», «Eurasian Journal of Chemistry», «Узбекский полимерный журнал», «International Journal of Formulation Science», «Shakarim Chemistry & Ecology». Он гостевой редактор (guest editor) специального выпуска MDPI «Advanced Technologies in Polymer-Protected and Gel-Immobilized Nanocomposites» (2020, https://www.mdpi.com/journal/polymers/special_issues/adv_tech_poly_gel_nano) и специального выпуска «Полимеры специального назначения в нефтяной отрасли, био-, нанотехнологии и медицине» журнала «Вестник Карагандинского университета, Серия химическая» (2022), член Международных Оргкомитетов IUPAC (ИЮПАК) «MacroMolecular Complexes (MMC)» и «Macro- and Supramolecular Architectures and Materials» (MAM).

Кудайбергенов С.Е. обладатель международных грантов фонда Сороса (1994), INTAS (*The **Int**ernational **As**sociation for the Promotion of Co-operation with Scientists from the New Independent States of the Former Soviet Union*) – Kazakhstan (1995), открытого конкурса INTAS (1997, 1999, 2001), INTAS-Kazakhstan (2004). Финансовая помощь Европейского Союза, оказанная в тяжелые годы после развала СССР в виде научных грантов, позволила приостановить «утечку мозгов» многих молодых ученых и удержать их в научной сфере. В 1998-2006 гг. Кудайбергенов С.Е. являлся научным экспертом Международных программ ИНТАС и ИНКО-Коперникус Европейского Союза. В 2011-2014 гг. в рамках Международного гранта НАТО «Наука для мира и безопасности» руководил международным проектом «Устойчивый менеджмент токсичных загрязнителей в Центральной Азии: от региональной модели экосистемы до безопасности окружающей среды». В 2012-2015 гг. руководил проектом коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов» и в 2015-2017 гг. довел до опытно-промышленных испытаний на месторождении «Кумколь». Руководитель 7 научных проектов, финансируемых

по гранту МОН РК (2009-2023 гг.). Помимо этого, проф. Кудайбергенов являлся соруководителем двух совместных проектов между РК и КНР (2015-2016, 2018-2019 гг.), участником Международного проекта Европейского Союза «Horison-2020» (2020-2024 гг.). В 2002-2019 гг. ученый организовал в различных регионах Казахстана 8 Международных семинаров, конференций и симпозиумов, посвященных проблемам реабилитации радиационно-зараженных почв Семипалатинского испытательного полигона и полимерам специального назначения. В 2023 г. проф. С. Кудайбергенов включен в пятилетнюю Программу международного сотрудничества Министерства образования и Государственного управления по делам иностранных специалистов КНР. Программа предусматривает приглашение 1000 талантливых первоклассных ученых из 100 университетов и научных центров со всего мира для чтения лекций и создания тематических инновационных центров с целью поднятия конкурентоспособности, престижа и уровня китайских университетов. В рамках этой Программы Кудайбергенов С.Е. с 28 апреля по 6 мая 2025 г. посетил Сычуаньский университет КНР и прочел несколько лекций по применению природных полимеров в нефтедобыче, биотехнологии и медицине.

В годы независимости Республики Казахстан, в 1999 году, Кудайбергенов С.Е. организовал и возглавил частное учреждение «Институт полимерных материалов и технологий» (ЧУ ИПМТ, www.ipmt.kz), которое вносит свой вклад в развитие полимерной науки Казахстана и подготовку высококвалифицированных научных кадров. Итоги 25-летней деятельности Института опубликована в книге «Ширек ғасыр асулары» (2024). Его научное направление связано с разработкой и внедрением полимеров специального назначения в нефтяной отрасли, нефтехимии, катализе, нанотехнологии, биотехнологии, медицине и охране окружающей среды. Разработанная им технология полимерного заводнения успешно прошла 12 опытно-промышленных испытаний на месторождениях «Кумколь» и «Карабулак», что позволило значительно увеличить объем дополнительно добываемой нефти и снизить обводненность нефтяных скважин.



Первый коллектив Института полимерных материалов и технологий, 1999 г.

В 2021 г. к его 70-летнему юбилею был издан спецвыпуск журнала «Polymers for Advanced Technologies», 2021, V.32, No.7, P.2633-2790, гостевым редактором которого является его талантливый ученик – профессор Хуторянский В.В. (Университет Рединга, Англия). Издание предваряет обзорная статья профессора Хуторянского В.В., посвященная юбиляру, и в нем опубликованы 15 обзорных и оригинальных статей его друзей, коллег и учеников.



Четвертьвековой юбилей Института полимерных материалов и технологий, 2024 г.

Кудайбергенов Саркыт Елекенович родился 20 мая 1951 г. в ауле Жұмыршақ Каргалинского сельского округа (ныне аул Қызыл Жұлдыз сельского округа Келдімұрат) Маканчинского района Семипалатинской области (ныне область Абай) в крестьянской семье. В 1968 году окончил казахскую среднюю школу № 16 имени Абая в г. Семей и в том же году поступил на химический

факультет Казахского государственного университета имени С.М. Кирова. Окончил КазГУ в 1973 г. по специальности «Химия – физическая химия». В 1973-1976 гг. работал в лаборатории физико-химических методов исследования КазГУ в должности инженера. В 1976-78 годы являлся стажером-исследователем кафедры химии высокомолекулярных соединений КазГУ, в 1978-1980 годы – инженер и младший научный сотрудник кафедры химии высокомолекулярных соединений КазГУ. С 1981 по 1993 гг. – младший, старший и ведущий научный сотрудник Института химических наук АН КазССР. В 1994-1996 гг. – заместитель Главного ученого секретаря и начальник управления международных связей Президиума НАН РК. 1996-1998 гг. – профессор кафедры химии высокомолекулярных соединений химического факультета КазГУ имени аль-Фараби. В 2001-2005 гг. работал в НТЦ АО «КазТрансОйл», НТЦ АО «Казахский институт нефти и газа» в должности заместителя директора по научной работе – начальника Центральной лаборатории и Главным химиком в «Институте высоких технологий» АО «НАК «КазАтомПром». С 2005 по 2019 г. работал на кафедре химии и экспертизы Семипалатинского государственного университета имени Шакарима по индивидуальному трудовому договору на 0.5 и 0.25 ставки профессора. С 2008 по 2020 г. руководил лабораторией инженерного профиля Казахского национального исследовательского технического университета имени К.И. Сатпаева.

Кудайбергенов С.Е. в 1980 г. защитил кандидатскую диссертацию под руководством академика НАН РК, Е.А. Бектурова и академика АН КазССР, члена-корреспондента АН СССР, С.Р. Рафикова на тему «Гидродинамические свойства полиэлектролитов на основе винилэтинилпиперидолов-4» в Институте химических наук АН КазССР, а в 1991 г. – докторскую диссертацию на тему «Реакции комплексообразования с участием синтетических полиамфолитов» в МГУ имени М.В. Ломоносова. В 1994 г. ему присвоено звание профессора химии. В 1987 г. он в составе авторского коллектива удостоен звания лауреата Государственной премии КазССР в области науки и техники за цикл монографий «Водорастворимые полимеры и их комплексы».

Кудайбергенов С.Е. проявлял интерес к научным исследованиям будучи еще студентом. В 1973 г. он принимал участие во Всесоюзной научно-студенческой конференции в г. Риге, где выступал с докладом «Ингибирование водород-воздушного пламени тетрафтордибромэтаном». В 1973-1976 годы он в соавторстве с Г.И. Ксандопуло, З.А. Мансуровым и А.А. Сагиндыковым опубликовал ряд статей в «Сборнике работ по химии КазГУ», журналах «Химия и химическая технология», «Горение и взрыв», посвященных изучению водород-воздушного и пропан-воздушного пламени.

Цикл работ по исследованию гидродинамических и конформационных свойств катионных и амфотерных полиэлектролитов на основе винилацетиленовых производных пиперидонов выполнялся в 1976-1980 гг. на кафедре высокомолекулярных соединений КазГУ под руководством к.х.н., доцента Шаяхметова Ш.Ш. и члена-корреспондента АН КазССР д.х.н., проф. Е.А. Бектурова. Впоследствии эти материалы легли в основу его кандидатской диссертации и были включены в главу книги Е.А. Бектурова и З.Х. Бакауовой «Синтетические водорастворимые полимеры в растворах» на русском (1981) и английском (1986) языках, а также в монографию «Катионные полимеры» на русском (1986) и польском (1991) языках в соавторстве с Е.А. Бектуровым и Р.Э. Хамзамулиной. В 1983 г. С.Е. Кудайбергеновым в соавторстве с Е.А. Бектуровым, Ш.Ш. Шаяхметовым, В.В. Рогановым и В.М. Меньшовым опубликовано «Практическое руководство по исследованию полимеров. Метод ультрацентрифугирования» в изд. «Мектеп», Алма-Ата.

В лаборатории физико-химии полимеров Института химических наук АН КазССР он проводил исследования по комплексообразованию неионогенных, анионных, катионных и амфотерных полимеров с ионами переходных и щелочноземельных металлов, комплексными анионами (совместно с Г.М. Жайминой, В.А. Фроловой, С.С. Салтыбаевой, А.А. Курманбаевой, В.Ж. Ушановым, Т.К. Джумадиловым, В.Б. Сигитовым, А.Ш. Чердабаевым), поверхностно-активными веществами и дисперсными частицами (совместно с Г.С. Канапьяновой,

Н.К. Тусупбаевым, К.Б. Мусабековым), полиэлектролитами (совместно с Р.Е. Легкунец, А.Т. Джагипаровой, Д.Е. Нургалиевой, J. Koetz), наночастицами металлов (совместно с А.К. Жармагамбетовой, С.С. Салтыбаевой, С. Г. Мухамеджановой) и белками. Каталитические свойства полимерметаллических комплексов с участием поливинилпиридинов и полиамфолитов в реакциях гидрирования ненасыщенных спиртов, гидролиза сложных эфиров и разложения пероксида водорода изучены совместно с В.Б. Сигитовым, А.К. Жармагамбетовой, Н.А. Доля. Результаты этих исследований были обобщены в монографии «Полимерные комплексы и катализаторы» (1982), «Молекулярные комплексы полимеров» (1988), «Катализ полимерами» (1988), «Catalysis by Polymers» (John Wiley & Sons, 2008). В эти же годы Кудайбергеновым С.Е. впервые показано образование полимерных комплексов на границе раздела фаз двух несмешивающихся жидкостей (совместно с проф. Л.А. Бимендиной, А.Д. Газизовым и Г.Т. Джумадиловой).

В 1996-1998 гг. Кудайбергенов С.Е. работал профессором КазГУ им. аль-Фараби, где инициировал исследования стимулчувствительных свойств водорастворимых и водонабухающих гомо- и сополимеров, интерполиэлектролитных комплексов, интерполимерных комплексов, стабилизированных системой водородных связей, а также интерполимерных пленок и мембран (совместно с В.В. Хуторянским, В.Б. Сигитовым, Г.А. Муном).

Исследования по интерполимерым комплексам в растворе и на межфазной границе двух несмешивающихся жидкостей, а также стимулчувствительным гидрогелям, мембранам и пленкам, адекватно реагирующим на изменение температуры, pH среды, ионной силы раствора, электрического и магнитного поля, были продолжены в ЧУ «Институт полимерных материалов и технологий» с участием проф. Л.А. Бимендиной, Г.Т. Джумадиловой, В.Б. Сигитова, А.Г. Дидуха. Новые полимеры, синтезированные на основе ацетоуксусного эфира и алкиламинов в ЧУ «Институт полимерных материалов и технологий», положили начало разработке целого класса линейных и сшитых полимерных бетаинов с уникальными физико-химическими

и комплексообразующими свойствами. В этих исследованиях наряду с казахстанскими учеными принимали участие проф. Kurt Geckeler (университет Тюбинген, Германия), магистранты и докторанты Института науки и технологии Квангжу (J.G. Noh, Y.I. Sung) и Университета Монпелье (G. Huyghe, J. Mouton). Способность новых полимерных бетаинов образовывать прочные комплексы с ионами переходных металлов и радиоактивным стронцием-90 была апробирована для структурообразования и предотвращения ветровой миграции тяжелых металлов и радионуклидов из поверхностных почв Семипалатинского испытательного полигона. В этих исследованиях принимали участие М.Г. Яшкарова и Л.К. Оразжанова из Университета Шакарима г. Семей. Полученные результаты были обобщены в монографиях «Полимерные комплексы: получение, свойства, применение» (2003, изд. СГУ имени Шакарима) и «Синтез, свойства и применение новых полимерных бетаинов на основе аминокротонатов» (2006, изд. СГУ имени Шакарима).

Взаимопроникающие сетки полиэлектролитов и гидрогелей, гибридные нано- и микрокомпозиты полиэлектролитов с наночастицами диоксида кремния, смешанные пленки Лэнгмюра-Блодже на основе флуоресцентных красителей и полиамфолитов, гидрогель-иммобилизованные биологически активные вещества и наночастицы металлов, водо- и органорастворимые комплексы полиэлектролитов с ПАВ и красителями исследованы (Г.С. Татыханова, Ж.Е. Ибраева) совместно с учеными Потсдамского университета и Института прикладных исследований полимеров имени Фраунгофера (J. Koetz, A. Laschewsky), университета Хельсинки (В.О. Асеев, H. Tenhu) и КарГУ имени Е.А. Букетова (Н.Х. Ибраев, Е.В. Селиверстова).

Для решения проблемы увеличения нефтеотдачи на месторождениях поздней стадии разработки С.Е. Кудайбергеновым и сотрудниками разработана технология гелеполимерной обработки нагнетательных и добывающих скважин путем закачки в пласт водного раствора полисахарида – геллана (А.А. Сагындыков, И.Ш. Гусенов, Б.Ж. Жаппасбаев, А.В. Шахворостов) и гидролизованного полиакриламида (М.С. Сагындиков) с целью снижения проницаемости высокопроницаемых (вымытых) каналов

фильтрации и перераспределения потока нагнетаемого агента в низкопроницаемые нефтенасыщенные каналы, а также для совершенствования технологии полимерного заводнения на месторождении «Каламкас». Технология «WaterBlock+», разработанная в 2011-2014 гг. в рамках проекта коммерциализации при финансовой поддержке Всемирного Банка и МОН РК, защищена многочисленными патентами, авторскими свидетельствами и полезными моделями РК. Отличительной особенностью водного раствора геллана является его способность к образованию геля при контакте с пластовой водой (золь-гель переход). При этом процесс гелеобразования не требует применения дополнительных сшивающих агентов, что значительно упрощает технологию добычи нефти. Полученные результаты опубликованы в коллективной монографии «Полифункциональные полимеры для бурения, добычи, транспортировки нефти и переработки нефтепродуктов» (под редакцией С.Е. Кудайбергенова, 2018). Промысловые испытания технологии «WaterBlock+» проводились в 2013–2017 гг. на месторождении «Кумколь» на 10 нагнетательных скважинах и месторождении «Карабулак» на 2 добывающих скважинах. В 2013 г. закачка водных растворов полисахарида объемом 234 и 160 м^3 в две нагнетательные скважины (№ 3383 и № 3065) в течение 11 месяцев позволила добыть 5890 т дополнительной нефти. В 2015 г. технология «WaterBlock+» прошла также успешный тест по обработке добывающей скважины К-34 на месторождении «Карабулак». После закачки 120 м3 1%-ного раствора геллана обводненность скважины снизилась с 80 до 20 %, в течение последующих 3-х лет она поддерживалась на уровне 50–60 % при незначительном снижении дебита нефти. В проведении опытно-промышленных испытаний технологии «WaterBlock+» кроме сотрудников ЧУ «Институт полимерных материалов и технологий» принимали участие АО «Тургай-Петролеум», ТОО «Институт нефтепромысловой химии», АО «НИПИнефтегаз» и ТОО «ЮВСГ».

По результатам ОПИ, проведенных в 2013-2017 гг. на десяти нагнетательных скважинах месторождения «Кумколь», за 2 года количество дополнительно добытой нефти достигло более 20 000 тонн при общем расходе сухого полимерного реагента 10 тонн.

По результатам ОПИ, проведенных в 2015 г. на месторождении «Карабулак», водоприток к добывающей скважине в течение трех лет снизился в 2 раза (с 80% до 40%).





Проведение опытно-промышленных испытаний технологии полимерного заводнения на месторождении «Кумколь» в АО «Тургай-Петролеум»

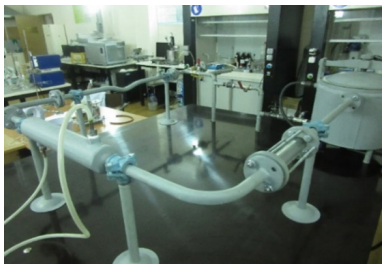
Способность полиамфолитов набухать в коллекторах с высокой минерализацией и тем самым эффективно загущать воду играет важную роль в технологии повышения нефтеотдачи пластов. В указанном направлении под руководством С.Е. Кудайбергенова синтезированы линейные полиамфолиты, а также наногели и микрогели, обладающие соле- и термостойкими свойствами (А.Ш. Шахворостов, И.Ш. Гусенов, Н. Мухаметгазы, А.Е. Аязбаева). Сравнение результатов лабораторных экспериментов по закачке синтетических полиамфолитов и ПААГ в керны и песчаные модели показали, что закачка раствора тройного полиамфолита, растворенного в воде с минерализацией 100-250 г/л, в песчаные модели увеличивает коэффициент вытеснения нефти на 23-28% по сравнению с закачкой ПААГ (18%). Новизна исследований заключается в том, что линейные и сшитые полиамфолиты на основе производных акриламида имеет превосходную нефтевытесняющую способность по сравнению с ПААГ в коллекторах с высокой минерализацией. Результаты лабораторных экспериментов могут привлечь внимание специалистов нефтегазовой отрасли и недропользователей к новым разработкам сотрудников ЧУ «Институт полимерных материалов и технологий» в плане масштабирования синтетических полиамфолитов и проведения опытно-промышленных испытаний.

Результаты обработки нагнетательных скважин на месторождении «Кумколь» в сравнении с другими гелеполимерными системами

Месторождение/ Реагент (год)	Количество нагнетательных скважин	Масса сухого реагента, (тонна)	Масса дополнительно добытой нефти, (тонна)	Технологическая эффективность*, (тонна/тонна)	Время, (месяцы)
Кумколь (Казахстан)/ «WaterBlock+» (2013)	2	2	5890	2945	11
Кумколь (Казахстан)/ «WaterBlock+» (2014)	3	3	8695	2565	8
Кумколь (Казахстан)/ «WaterBlock+» (2017)	5	5	5808	1160	6
Бузачи (Казахстан) / Полиакриламид (2011)	1	42	16 000	380	12
Дацин (КНР)/ Гелепо-лимерная система	4	134	15 000	113	10
Жон-гуан (КНР)/ Гелеполимерная система	2	20,5	3239	158	3
Усинское (Россия)/ Термотропный гель «Галка»	–	117	10 316	88	6

*Технологическая эффективность – это отношение массы дополнительно добытой нефти к массе используемого реагента.

В 2012-2019 гг. в ЧУ «Институт полимерных материалов и технологий» созданы гибкие, эластичные и механически прочные композиционные гидрогелевые материалы для очистки внутренней полости модельных нефтепроводов разного диаметра и сложного профиля от механических примесей, асфальтен-смоло-парафиновых отложений (АСПО), продуктов коррозии, газовых и водно-солевых скоплений, для одновременной транспортировки нефтей и нефтяных фракций, играя при этом роль разделительных поршней, а также для нанесения антикоррозионных растворов на внутреннюю поверхность трубопроводов перед эксплуатацией. Эти исследования проведены совместно с Д.С. Светличным, Ж.Е. Ибраевой, В.Б. Сигитовым, Ж.К. Садакбаевой, Е.В. Благих, А.Н. Кливенко при участии сотрудников НТЦ АО «КазТрансОйл» (А.Г. Дидух, А.Г. Габсаттарова). В 2015-2016 гг. получены инновационный патент РК и Евразийский патент на «Способ получения композиционного гидрогелевого скребка для очистки нефтепровода». В 2015 г. Комитетом индустриального развития промышленной безопасности Министерства по инвестициям и развитию РК выдано разрешение на производство и применение гидрогелевых скребков «ПИГ-1» для очистки нефтепроводов. Этот цикл исследований нашел отражение в монографиях «Композиционные гидрогелевые материалы» (2011), «Композиционные полимерные материалы и технологии на их основе» (2013) и в главе книги «Advanced Separations by Specialized Sorbents» (New York: CRC Press, 2014).



Лабораторный трубопровод



Модельный трубопровод



Очистка трубопровода от АСПО и коррозионных отложений гидрогелевыми «скребками»



ЕВРАЗИЙСКАЯ ПАТЕНТНАЯ ОРГАНИЗАЦИЯ
ЕВРАЗИЙСКОЕ ПАТЕНТНОЕ ВЕДОМСТВО

ЕВРАЗИЙСКИЙ ПАТЕНТ

№ 029431

Название изобретения:
«СПОСОБ ПОЛУЧЕНИЯ КОМПОЗИЦИОННОГО ГИДРОГЕЛЯ ДЛЯ ОЧИСТКИ НЕФТЕПРОВОДА»

Патентовладелец (лицы):
ЧАСТНОЕ УЧРЕЖДЕНИЕ "ИНСТИТУТ ПОЛИМЕРНЫХ МАТЕРИАЛОВ И ТЕХНОЛОГИЙ" (KZ)

Изобретатель (и):
Садыкбаева Жансая Кудайбергеновна, Благих Евгений Владимирович, Жумалы Асия Амангелдыкызы, Нурахметова Жанар Ануарбековна, Кливенко Алексей Николаевич (KZ)

Заявка №: 201600150
Дата подачи заявки: 27 января 2016 г.
Дата выдачи патента: 30 марта 2018 г.

Председатель Евразийского патентного ведомства ТЛЕВЛЕСОВА Сауле Январдековна

1 - 1

"Индустриялық даму және өнеркәсіптік қауіпсіздік комитеті" республикалық мемлекеттік мекемесі

Республиканское государственное учреждение "Комитет индустриального развития и промышленной безопасности"

Астана қ. г.Астана.

Номер: KZ96VEH00003709
Входящий номер: KZ72RDR00004259
Дата выдачи: 04.12.2015

Частное учреждение "Институт полимерных материалов и технологий"
050000, Республика Казахстан, г.Алматы, Бостандыкский район, УЛИЦА САТПАЕВА, дом № 22.

РАЗРЕШЕНИЕ
на применение технических устройств и материалов

Республиканское государственное учреждение "Комитет индустриального развития и промышленной безопасности" Министерство по инвестициям и развитию Республики Казахстан, рассмотрев заявление Частное учреждение "Институт полимерных материалов и технологий" и пакет технической документации к нему, в соответствии со статьей №74 Закона Республики Казахстан "О гражданской защите" и учитывая положительное экспертное заключение ТОО «ТехПромБезопасность» от 30.10.2015 года № 0043-э , разрешает применение на опасных производственных объектах следующих технологий, технических устройств и материалов:

- гидрогелевых скребков «ПИГ-1» производства ЧУ «Институт полимерных материалов и технологий», РК, г/э - 2015.

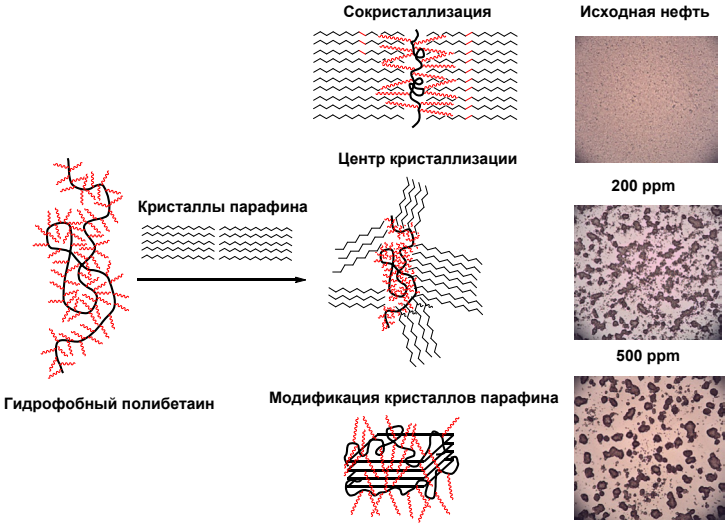
Разрешение действительно при обязательном соблюдении требований законодательства Республики Казахстан в сфере гражданской защиты, а так же технической документации завода-изготовителя.

Заместитель председателя Кушибаев Нурбек

Евразийский патент и разрешение Министерства по инвестициям и развитию РК на производство и применение гидрогелевых скребков «ПИГ-1» для очистки ефтепроводов

Сотрудниками ЧУ «Институт полимерных материалов и технологий» (А.Г. Дидух, А.В. Шахворостов) под руководством С.Е. Кудайбергенова разработан способ предотвращения процессов парафиноотложения в нефтяных резервуарах и снижения температуры потери текучести высоковязких и высокопарафинистых нефтей Казахстана, транспортируемых по нефтепромысловым и магистральным трубопроводам, путем использования полимерных присадок – гидрофобно-модифицированных поли-

мерных бетаинов, содержащих длинноцепные углеводородные «хвосты» (С12-С18) и гидрофильные бетаиновые «головки». Наработаны опытные партии депрессантов и проведены укрупненные лабораторные испытания на экспериментальном стенде НТЦ АО «КазТрансОйл» (А.Г. Дидух). Ингибиторы парафиноотложения, полученные на основе гидрофобно-модифицированных полибетаинов (A.G. Didukh, R.B. Koizhaiganova, L.A. Bimendina, S.E. Kudaibergenov. Synthesis and characterization of novel hydrophobically modified polybetaines as pour point depressants. J. Appl. Polym. Sci. 2003, v.92, p.1042-1048. https://doi.org/10.1002/app.20075), были испытаны в отношении к застывающей при высокой температуре (57 °С) Малазийской нефти (Halim N., Ali S., Nadeem M. N., Abdul Hamid P., Tan I. M. Synthesis of wax inhibitor and assessment of squeeze technique application for Malaysian waxy crude. Society of Petroleum Engineers. 2011. Doi:10.2118/142288-MS) и показали вполне удовлетворительные результаты.



Механизм ингибирования парафиноотложения гидрофобно-модифицированными полибетаинами

Разработаны буровые растворы на основе дисперсной фазы – бентонита, полисахаридов – геллана, ксантана и их смесей,

обладающих хорошими реологическими и флокулирующими свойствами, а также способностью к обратимому золь-гель переходу при изменении температуры и концентрации низкомолекулярных катионов в воде (В.Б. Сигитов, Ж.А. Нурахметова). Определены физико-химические характеристики водных и водно-солевых растворов природных полисахаридов, такие как, плотность, приведенная, эффективная и пластическая вязкость, статическое напряжение сдвига, динамическое напряжение сдвига, седиментационная устойчивость и другие параметры, при варьировании состава и концентрации полимеров, ионной силы раствора, природы солей. На основе смеси геллана, ксантана и крахмала, бентонита и KCl приготовлены различные рецептуры буровых растворов и определены их структурно-механические, фильтрационные и коркообразующие параметры. В 2017 г. проведена апробация рецептур малоглинистых буровых растворов, содержащих полианионную целлюлозу, геллан, ксантан и бентонит, в условиях опытно-промышленных испытаний (ОПИ) в АО «Волковгеология». Результаты применения полимеров специального назначения в нефтяной отрасли, в частности, технология полимерного заводнения, гидрогелевые «скребки», буровые растворы и депрессорная технология, обобщены в коллективной монографии «Полифункциональные полимеры для бурения, добычи, транспортировки нефти и переработки нефтепродуктов» (под редакцией С.Е. Кудайбергенова, 2018).

Исследования в области разработки буровых растворов и флюоресцирующих трассеров с участием термо- и солестойких полиамфолитов на основе производных акриламида проведены И.Ш. Гусеновым, Н. Мухаметгазы, А.В. Шахворостовым.

В 2012-2020 г. в ЧУ «Институт полимерных материалов и технологий» проведен цикл исследований, посвященный полимер-протектированным и гель-иммобилизованным наночастицам металлов – нанокатализаторам, моделирующим действие металлоферментов, а также гетерогенизированным гомогенным катализаторам (Н.А. Доля, Г.С. Татыханова, А.Н. Кливенко, Г. Толеутай, М. Даулетбекова, С. Кабдрахманова, Б.С. Селенова). На основе макропористых криогелей и благородных металлов

получены различные нанокатализаторы, обладающие высокой активностью, селективностью и стабильностью действия в реакциях разложения, гидрирования и окисления в проточном режиме. Успехи в области создания полимер-протектированных и гель-иммобилизованных нанокатализаторов отражены в следующих монографиях: «Полимер-протектированные наночастицы металлов» (2010), «Стабилизация наночастиц металлов гидрофильными полимерами» (2013), «Полимеры в нанотехнологии» (2019).

Серия исследований по контролируемому выходу лекарственных препаратов и белков из матрицы термо- и pH-чувствительных наногелей (Г.С. Татыханова, А.Е. Аязбаева. Т.М. Сейлханов), молекулярно-импринтированных гидрогелей (А.В. Шахворостов) и мукоадгезивных полимеров проведена в рамках Международного проекта Европейского Союза «Horison-2020» (2019-2024 гг.) с участием сотрудников КазНУ имени аль-Фараби (Д.Б. Калдыбеков, Г.С. Ирмухаметова), университета Рединга (В.В. Хуторянский), университета Хельсинки (Х. Тенху, В.О. Асеев), университета Крит (М. Вамвакаки).

Сотрудники ЧУ «Институт полимерных материалов и технологий» совместно с кафедрой биотехнологии КазНУ имени аль-Фараби (Т.Д. Мукашева, Р.Ж. Бекжанова) и ТОО «Bioclean» разрабатывают технологию получения отечественного геллана путем ферментации глюкозосодержащих продуктов, производимых Жаркентским и Бурундайским крахмалопаточными предприятиями, лицензионным штаммом *Sphingomonas paucimobilis* (ATCC 31461) и геллановодобных экзополисахаридов с помощью отечественных штаммов. Проект направлен на импортозамещение пищевого высоко- и низкоацилированного геллана китайского производства дешевым и доступным отечественным продуктом. Область применения геллана – это нефтяная отрасль и пищевая промышленность. Геллан также является перспективным биополимером для медицины в качестве мукоадгезивных материалов, для иммобилизации лекарственных препаратов и стабилизации наночастиц металлов при лечении раковых клеток методом плазмонной фототермической терапии.

Путем химической модификации полисахаридов – кукурузного крахмала, геллана и хитозана получены анионные, катионные и амфотерные полиэлектролиты, которые могут быть использованы в качестве флокулянтов, коагулянтов, комплексонов, добавок к буровым растворам, загустителей пластовой воды, для биотехнологических и биомедицинских целей (Ж. Нурахметова, А. Аязбаева, Р. Тулеева).

Несмотря на достигнутые успехи в химии и физике полимеров, самым любимым предметом проф. С. Кудайбергенова остается класс полиамфолитов, представляющих собой белки – молекулы жизни, состящие из аминокислотных последовательностей. В ряде случаев, с помощью синтетических полиамфолитов, содержащих в макромолекулярной цепи кислотные и основные группы, удается промоделировать некоторые конформационные поведения и функции природных полимеров. В области синтеза и исследования полиамфолитов С. Кудайбергеновым опубликовано три монографии, дюжина обзорных и более 80 оригинальных статей в зарубежных и отечественных журналах.

Сведения о научно-педагогической деятельности Кудайбергенова С.Е. опубликованы в книге «Ғылым тылсымына жол», энциклопедии «Алматы», «Қазақ Энциклопедиясы», справочнике «Кто есть кто в казахстанской науке», в изданиях КазНУ «Наша Элита», «Жүзден жүйрік, мыңнан тұлпар», в журналах «Нефть и Газ», «История Казахстана: преподавание в школе», «Macromolecular Chemistry and Physics», «Polymers for Advanced Technologies», «Вестник КазНУ, Серия химическая», Вестник Карагандинского университета, Серия химическая», Википедия https://ru.wikipedia.org› wiki›, Farabi University https://farabi.university› news.

Творческий путь Кудайбергенова Саркыта Елекеновича и достигнутые успехи в науке и образовании являются замечательным примером для подрастающего поколения во благо процветания Республики Казахстан.

ДИПЛОМЫ, ЗВАНИЯ, НАГРАДЫ, СЕРТИФИКАТЫ



ДИПЛОМ

Ю № 355860

Осы диплом Кудайбергенов Саркыт берілді, ол 1968 жыла Қазақтың Сем Киров атындағы мемлекеттік университетіне түсіп, 1973 жыла осы аталған университеттің толық курсын химия – физикалық химия мамандығы бойынша бітіріп шықты.

Мемлекеттік емтихан комиссиясының 1973 жылғы 30 июндегі қарара бойынша химик деген квалификация берілді.

Мемлекеттік комиссия председателі
Ректор
Секретарь

М. О.

Алматы қаласы 1973 жылға июнь 30

Тіркеу № 586

Кавказский пр.

ДИПЛОМ

Ю № 355860

Настоящий диплом выдан Кудайбергенову Саркыт в том, что он в 1968 году поступил в Казахский государственный университет им. С.М. Кирова и в 1973 году окончил полный курс названного университета по специальности химия – физическая химия.

Решением Государственной экзаменационной комиссии от "30" июня 1973 г. Кудайбергенову присвоена квалификация химик

Председатель Государственной экзаменационной комиссии
Ректор
Секретарь

М. П.

Город Алма-Ата "30" июня 1973 г.

Регистрационный № 586

Московская типография Гослака. 1971.

ДИПЛОМ

ДОКТОРА НАУК

ДТ № 010251

Москва

Решением
Высшей аттестационной комиссии
при Совете Министров СССР
от 20 сентября 1991 г. (протокол № 24/38)
Кудайбергенову Саркыту
 присуждена ученая степень
ДОКТОРА
химических наук

Зам. Председатель
Высшей аттестационной комиссии
Главный ученый секретарь
Высшей аттестационной комиссии

Қазақстан Республикасы
Министрлер Кабинеті жанындағы
Жоғары аттестациялық комиссияның
9 94 жылғы 15 желтоқсандағы шешімімен /№ 7 хаттама/

Кудайбергенов
Сарқыт Елекенұлына
химия
мамандығы бойынша
ПРОФЕССОР
ғылыми атағы берілді

Жоғары аттестациялық
комиссияның төрағасы
ғылыми хатшы

Ө. Әшімов
З. Жәркешова

Ф № 0000325

Алматы

Решением Высшей аттестационной комиссии
при Кабинете Министров Республики Казахстан
от 15 декабря 19 94 года
Кудайбергенову Сарқыту Елекеновичу
присвоено ученое звание
ПРОФЕССОРА
по специальности
химия

By decision of the Supreme Certifying Commission
of the Council of Ministers of the Republic of Kazakhstan
the scientific title of
PROFESSOR
of Chemistry
is conferred upon
Sarkyt Kudaibergenov
as of December 15 19 94

Председатель ВАК
Главный ученый секретарь

Chairman
Principal academic secretary



ҚАЗАҚСТАН КОМПАРТИЯСЫНЫҢ ОРТАЛЫҚ КОМИТЕТІ МЕН
ҚАЗАҚ ССР МИНИСТРЛЕР СОВЕТІНІҢ

1987 жылғы 26 январьдағы қаулысы бойынша

Есім әйгілі академик БЕКТҰРОВКА, Қазақ ССР Ғылым академиясының корреспондент-мүшесі, Қазақ ССР Ғылым академиясының Химия ғылым институтының лабораториа меңгерушісі, жұмыс жетекшісі, Зәуре Хафизқызы БАҚАУОВАҒА, Ларисе Ахметовне БИМЕНДИНАҒА, Сарқыт КҰДАЙБЕРГЕНОВКЕ, химия ғылымының кандидаттары, осы институттың аға ғылыми қызметкерлері, Раисе Ефимовне ЛЕГКУНЕЦКЕ, химия ғылымының кандидаты, Қазақ ССР Жоғары және орталық орта білім министрлігінің С. М. Киров атындағы Қазақ мемлекеттік университетінің аға ғылыми қызметкері, — 1975—1983 жылдарға жарияланған «Сода ерітіндісіндегі кен олардың комплексте-рін» деген монографиялар циклі үшін

ҚАЗАҚ ССР МЕМЛЕКЕТТІК СЫЙЛЫҒЫ БЕРІЛДІ

№ 543 бұл диплом
Сарқыт ҚҰДАЙБЕРГЕНОВКЕ
беріледі

Қазақ ССР Министрлер Советі жанындағы Қазақ ССР Мемлекеттік сыйлықтары жөніндегі комитеттің төрағасы Ж. З. АЙТХОЖИН

Қазақ ССР Министрлер Советі жанындағы Қазақ ССР Мемлекеттік сыйлықтары жөніндегі комитеттің жауапты хатшысы Т. Ә. КЕНЕСАРИН

ПОСТАНОВЛЕНИЕМ ЦЕНТРАЛЬНОГО КОМИТЕТА КОМПАРТИИ
КАЗАХСТАНА И СОВЕТА МИНИСТРОВ КАЗАХСКОЙ ССР

от 26 января 1987 года

ПРИСУЖДЕНА

ГОСУДАРСТВЕННАЯ ПРЕМИЯ КАЗАХСКОЙ ССР

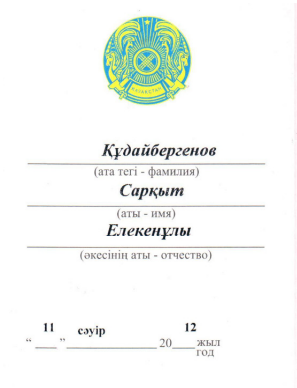
БЕКТУРОВУ Есему Абдиевичу, члену-корреспонденту Академии наук Казахской ССР, заведующему лабораторией Института химических наук Академии наук Казахской ССР, руководителю работы, БАКАУОВОЙ Зауре Хафизовне, БИМЕНДИНОЙ Ларисе Ахметовне, КУДАЙБЕРГЕНОВУ Сарсыту, кандидатам химических наук, старшим научным сотрудникам того же института, ЛЕГКУНЕЦ Раисе Ефимовне, кандидату химических наук, старшему научному сотруднику Казахского государственного университета имени С. М. Кирова Министерства высшего и среднего специального образования Казахской ССР, — за цикл монографий «Водорастворимые полиэлементы и их комплексы», опубликованных в 1975—1983 годах.

Данный диплом № 543 выдан
КУДАЙБЕРГЕНОВУ Сарсыту

Председатель Комитета по Государственным премиям Казахской ССР в области науки и техники при Совете Министров Казахской ССР Ж. З. АЙТХОЖИН

Ответственный секретарь Комитета по Государственным премиям Казахской ССР в области науки и техники при Совете Министров Казахской ССР Т. А. КЕНЕСАРИН





Құдайбергенов
(ата тегі - фамилия)
Сарқыт
(аты - имя)
Елекенұлы
(әкесінің аты - отчество)

11 қаңтар 12
"__" _____ 20__ жыл
год

КУӘЛІК
УДОСТОВЕРЕНИЕ
№ 068

Осы куәлік ғылым беру саласындағы ерекше еңбегі үшін "ҚАЗАҚСТАН РЕСПУБЛИКАСЫНЫҢ ҒЫЛЫМЫН ДАМЫТУҒА СІҢІРГЕН ЕҢБЕГІ ҮШІН" белгісімен марапатталғандығы туралы берілді.

Настоящее удостоверение выдано в том, что он(а) за достигнутые успехи в области науки Республики Казахстан награжден(а) нагрудным знаком "ЗА ЗАСЛУГИ В РАЗВИТИИ НАУКИ РЕСПУБЛИКИ КАЗАХСТАН".

Министр Б. Жұмағұлов





Қазақстан Республикасының
Білім және ғылым министрлігі

ҚҰРМЕТ

Жаратылыстану ғылымдары саласындағы 2019 жылғы үздік ғылыми зерттеуі үшін Қ.И. Сәтбаев атындағы сыйлық

Сарқыт Құдайбергеновке

беріледі

Қазақстан Республикасының Білім және ғылым министрі Ә. Аймағамбетов

Нұр-Сұлтан қаласы








ҚАНЫШ САТБАЕВ
125
№ 086
Кудайбергенов
тегі
Саркыт
аты
Елекенович
әкесінің аты
«ҚАНЫШ САТБАЕВТЫҢ
125-ЖЫЛДЫҚ МЕРЕЙТОЙЫ»
медалімен марапатталды
23.01.24




SATBAYEV UNIVERSITY
85
САТБАЕВ УНИВЕРСИТЕТІ
SATBAYEV UNIVERSITY
Юбилейной медалью
«85 лет КазНИТУ им. К.И. Сатпаева»
награждается
Кудайбергенов
Саркыт
Елекенович
Ректор
Байсанбетов
М.П.
12.04.2019 г.
Регистрационный №
Алматы




СЕМЕЙ
Кудайбергенов
тегі - фамилия
Саркыт
аты - имя
әкесінің аты - отчество
20 маусым 2017 жыл
КУӘЛІК
УДОСТОВЕРЕНИЕ
№ 65
Осы куәлік университетке сіңірген
ерекше еңбегі үшін
«ШӘКӘРІМ»
МЕДАЛІМЕН МАРАПАТТАЛҒАНДЫҒЫ
туралы берілді
Настоящее удостоверение выдано
в том, что он(а) за достигнутые успехи
в университете
НАГРАЖДЕН(А) МЕДАЛЬЮ
«ШАКАРИМ»



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Kudaibergenov Sarkyt Elekenovich

Kazakh National Technical University
named after Satpayev

For his outstanding and continued contribution to global scientific research

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National Centre for Scientific and Technical Information RK



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в научном исследовании



«Лучший научный работник» 2022 г.


This is to certify that

Kudaibergenov

successfully completed

the

National Science Foundation's

Program Management Seminar

April 7, 1995

Date

Instructor

Director

Сертификат о прохождении стажировки в Национальном научном фонде США


FBR 高端讲坛

High-end Rostrum

Key Speaker: *Prof.* Sarkyt KUDAIBERGENOV

Chengdu

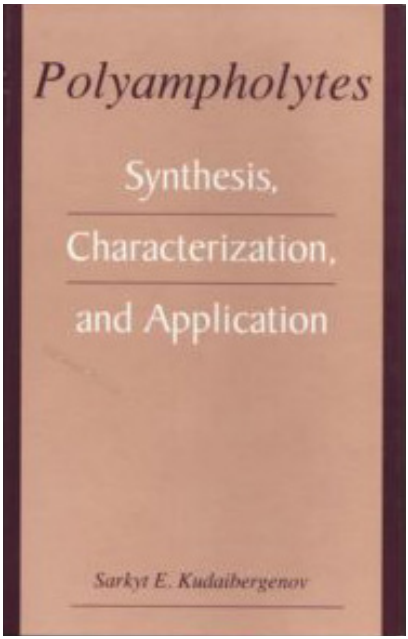
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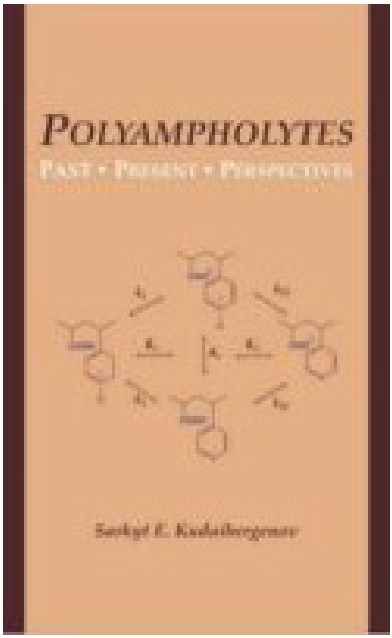
(FBR-HEF0018)

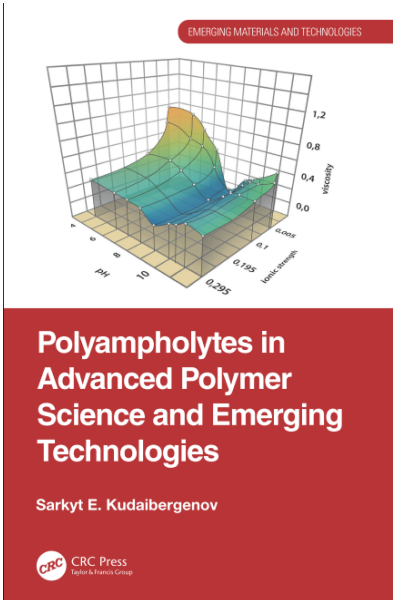
Сертификат «Высококлассная трибуна» Сычуаньского университета КНР

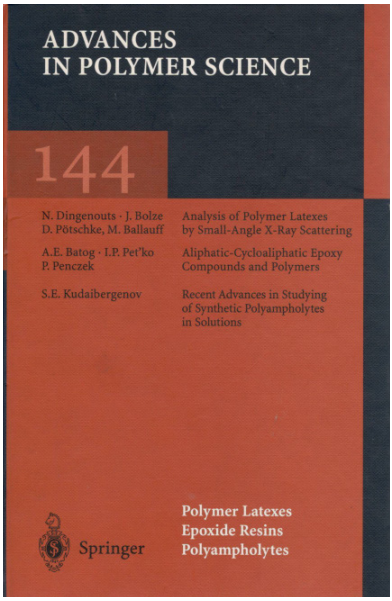
ИЗБРАННЫЕ МОНОГРАФИИ

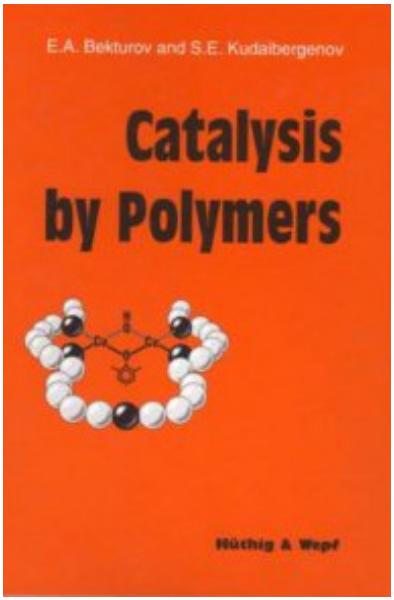


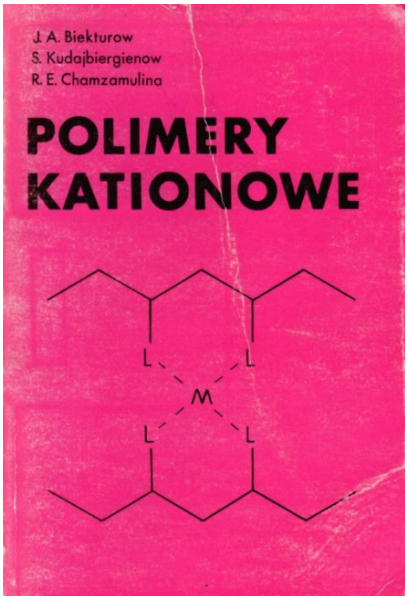

Polyampholytes
Synthesis,
Characterization,
and Application
Sarkyt E. Kudaibergenov


POLYAMPHOLYTES
PAST • PRESENT • PERSPECTIVES
Sarkyt E. Kudaibergenov


EMERGING MATERIALS AND TECHNOLOGIES
1,2
0,8
0,4
0,0
viscosity
pH
ionic strength
Polyampholytes in Advanced Polymer Science and Emerging Technologies
Sarkyt E. Kudaibergenov
CRC Press

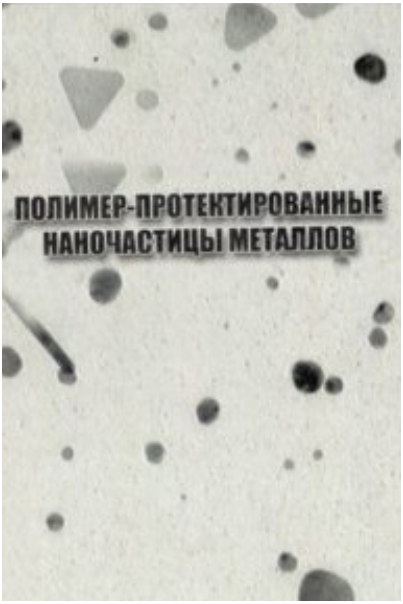

ADVANCES IN POLYMER SCIENCE
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N. Dingenouts · J. Bolze
D. Pötschke, M. Ballauff
Analysis of Polymer Latexes by Small-Angle X-Ray Scattering
A.E. Batog · I.P. Pet'ko
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Aliphatic-Cycloaliphatic Epoxy Compounds and Polymers
S.E. Kudaibergenov
Recent Advances in Studying of Synthetic Polyampholytes in Solutions
Springer
Polymer Latexes
Epoxide Resins
Polyampholytes


E.A. Bekturov and S.E. Kudaibergenov
Catalysis by Polymers
Hüthig & Wepf


J. A. Biekturow
S. Kudajbiergienow
R. E. Chamzamulina
POLIMERY KATIONOWE
L
L
M
L
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ПОЛИМЕРЫ В НАНОТЕХНОЛОГИИ

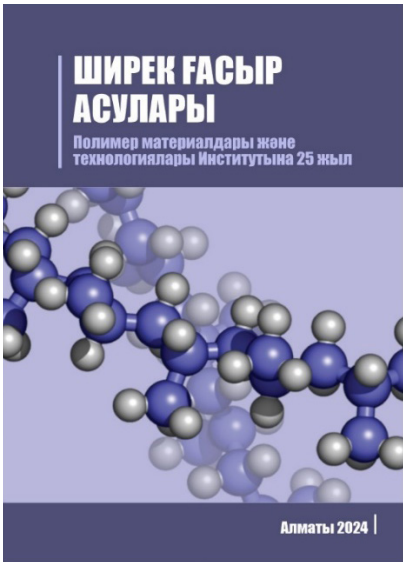

ПОЛИФУНКЦИОНАЛЬНЫЕ
ПОЛИМЕРЫ
В БУРЕНИИ, ДОБЫЧЕ,
ТРАНСПОРТИРОВКЕ НЕФТИ
И ПЕРЕРАБОТКЕ
НЕФТЕПРОДУКТОВ
Под редакцией С.Е. Кудайбергенова

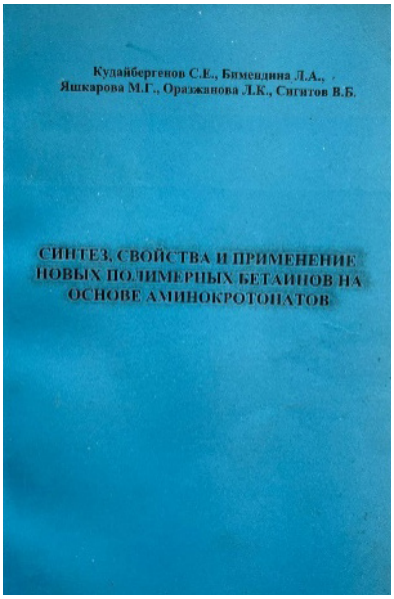

ПОЛИМЕР-ПРОТЕКТИРОВАННЫЕ
НАНОЧАСТИЦЫ МЕТАЛЛОВ


Жанар Ибраева
Сарыт Кудайбергенов
Есен Бектуров
Стабилизация
наночастиц металлов
гидрофильными
полимерами
LAMBERT


КОМПОЗИЦИОННЫЕ
ГИДРОГЕЛЕВЫЕ
МАТЕРИАЛЫ
Композитный гидрогель
Обычный гидрогель


Е.А. Бектуров, С.Е. Кудайбергенов
Краткий курс
ФИЗИКОХИМИИ
ПОЛИМЕРОВ


ШИРЕК ҒАСЫР
АСУЛАРЫ
Полимер материалдары және
технологиялары Институтына 25 жыл
Алматы 2024


Кудайбергенов С.Е., Бимендина Л.А.,
Яшкарова М.Г., Оражанова Л.К., Сигитов В.Б.
СИНТЕЗ, СВОЙСТВА И ПРИМЕНЕНИЕ
НОВЫХ ПОЛИМЕРНЫХ БЕТАИНОВ НА
ОСНОВЕ АМИНОКРОТОНАТОВ


С. Е. Құдайбергенов
ҒЫЛЫМ
ТЫЛСЫМЫНА
ЖОЛ

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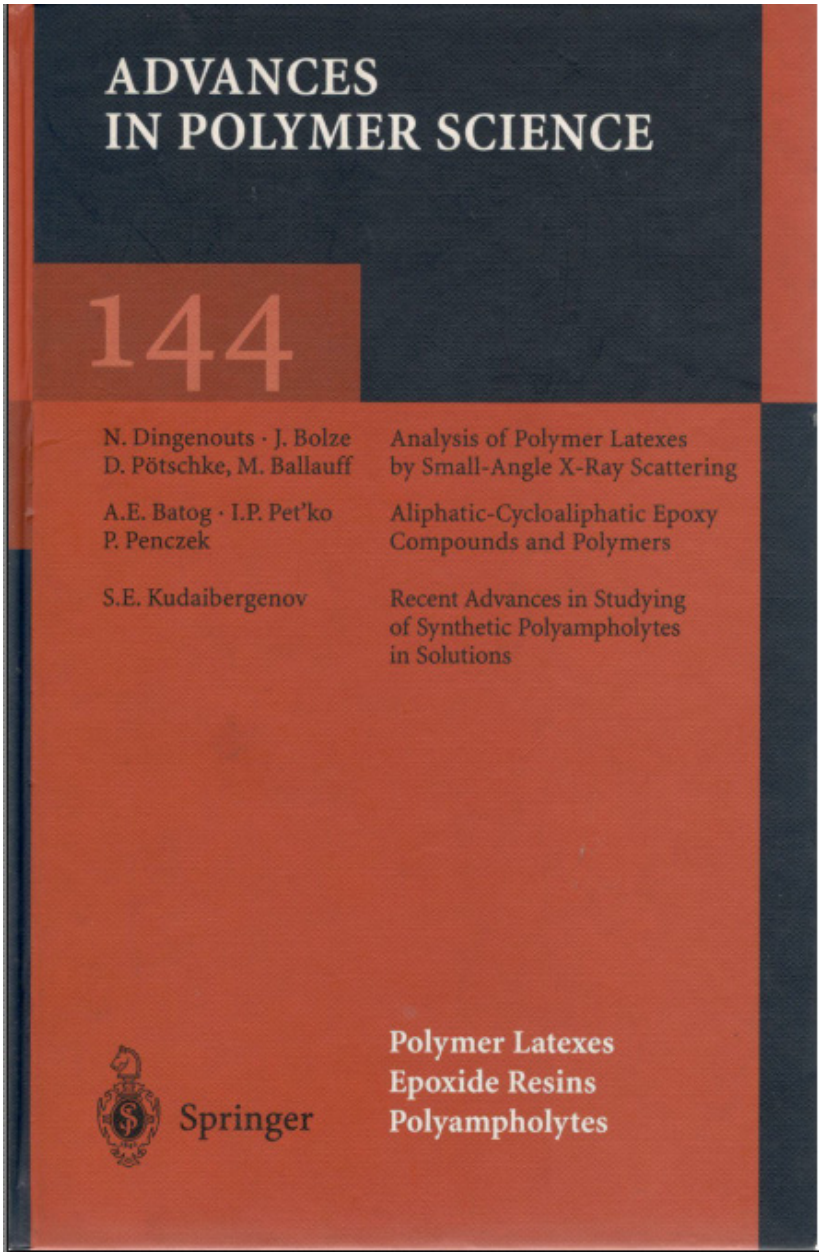
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Recent Advances in the Study of Synthetic Polyampholytes in Solutions

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This article reviews the theoretical and experimental material accumulated in recent years on water-soluble and water-swelling polyampholytes of integral and pendant types. The theory of polyampholytes in comparison with experimental results, acid-base equilibrium, hydrodynamic, conformational, and the molecular and colloidal properties of amphoteric copolymers are considered. The responsibility of Coulomb forces, hydrogen bonds and hydrophobic interactions in the formation of compact structures is shown. Basic attention is paid to the specific structure and behaviour of polyampholytes at or near the isoelectric point (IEP), in particular to the "forcing out" phenomenon found at the IEP. The ability of polyampholytes to associate with various low- and high-molecular-weight substances as well as to be absorbed on dispersed particles is discussed. An attempt to show the closeness of structural organization or molecular recognition of synthetic polyampholytes to natural ones is undertaken.

Keywords: Polyampholytes, Theory of Polyampholytes, Acid-Base Equilibrium, Solution Properties, Associates and Complexes, Zwitterions, Amphoteric Gels, Application

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List of Symbols and Abbreviations

Sect. 3

γ	dimensionless parameter
e	electron charge
b	monomer size
l	Kuhn length
L	chain length
k	Boltzmann constant
T	absolute temperature
N	monomer number
f	fraction of positively charged monomer
g	fraction of negatively charged monomer
k^{-1}	Debye length
l_B	Bjerrum length
k_p^{-1}	screening length
Θ	Flory's Θ temperature
R	Einstein sphere radius
V	excluded volume
V^*	effective excluded volume
N_e	polyelectrolyte blob size
N_1	polyampholyte blob size
$\pm q$	excess of positive or negative charges
Q_c	overall excess charge
N_+	number of positively charged monomers
N_-	number of negatively charged monomers
t	effective temperature
u	ratio of Bjerrum length to bond size
D	electrostatic blob size
σ	charge asymmetry
r_D	Debye volume

Sect. 4

pK'_a	apparent acidic dissociation constant of acidic group
pK'_b	apparent acidic dissociation constant of basic group
α	ionization degree of acidic group
β	ionization degree of g basic group
pK°	intrinsic dissociation constant
E_d	nearest-neighbour electrostatic interaction
E_r	long-range electrostatic interaction
pK°_a	intrinsic dissociation constant of acidic group
pK°_b	intrinsic dissociation constant of basic group
ν	mean number of negative charge
ξ	mean number of positive charge
$\lvert\psi_a\rvert$	electrostatic potential
α_{IEP}	ionization degree of acidic group at the isoelectric point
β_{IEP}	ionization degree of basic group at the isoelectric point
a	molar fraction of acidic units
R	molar ratio of acid to base

Sect. 5

$[\eta]$	intrinsic viscosity
S_0	sedimentation constant
$M_{s\eta}$	average hydrodynamic molecular weight
μ	ionic strength of the solution
η_i/c	reduced viscosity
M_w	weight average molecular mass
R_g	gyration radius
R_h	hydrodynamic radius
C_p	polymer concentration
C_s	salt concentration
d_h	hydrodynamic diameter
d_g	gyration diameter
A_2	second virial coefficient
T_1	spin-lattice relaxation time
τ_c	correlation time

Sect. 6

σ	surface tension
χ	electroconductivity
C_{crit}	critical concentration
G	surface activity
Ω	fraction of precipitated polyampholyte
$C_{PA}{}^d$	concentration of polyampholyte in disperse phase
$C_{PA}{}^s$	concentration of polyampholyte in solution
r_λ	average radius of disperse particles
τ	turbidity

Sect. 7

M	metal ions
L	ligand
k_1, k_2, k_3...	constants of stepwise complex formation
β	stability constant of polymer-metal complexes
n	average number of ligands bound to metal ion
$[L]_t$	total concentration of ligands
$[M]_t$	total concentration of metal ions
[L]	concentration of free ligands
[LH]	concentration of protonated ligands
$g_\perp$	perpendicular g-factor
$g_\parallel$	parallel g-factor
$A_\parallel$	constant of superfine structure
C_{PEC}	concentration of polyelectrolyte complexes

Sect. 9

W	retardation factor
U	potential energy of interaction
R	distance between particles centres
A	optical density
ρ	density of latex particles
C_L	concentration of latex particles
B	optical constant
k_0	rate constant of fast coagulation
V_C	adsorption threshold
$\tilde{A}$	value of specific adsorption
$k_{1,2}$	adsorption constant rate
η	medium viscosity
r_1	average radius of latex particles
r_2	average radius of polyampholyte coils
t_A	adsorption time
f	effectiveness of adsorption
N_1	concentration of latex particles
ζ	electrokinetic potential

Sect. 10

S	sedimentation coefficient
I/I_0	relative fluorescence intensity
Ξ	degree of phase formation

Sect. 11

a	exponent of Mark–Kuhn–Houwink equation
α_e	expansion factor
T_g	glass transition temperature

D	dipole moment
E_A	activation energy

Sect. 12

V/V_0	volume swelling ratio
d	diameter of gel
d_0	initial diameter of gel

Abbreviations

IEP	isoelectric point
pH_{IEP}	pH of the isoelectric point
2VP–AA	2-vinylpyridine–acrylic acid
2VP–MAA	2-vinylpyridine–methacrylic acid
2M5VP–AA	2-methyl-5-vinylpyridine–acrylic acid
1-VI	1-vinylimidazole
DMAEM–MAA	*N,N'*-dimethylaminoethylmethacrylate–methacrylic acid
PDMAEM	poly(*N,N*-dimethylaminoethylmethacrylate)
DMAEM–MMA–MAA	*N,N'*-dimethylaminoethylmethacrylate–methylmethacrylate–methacrylic acid
CM-DEAEC	carboxymethyl-2-diethylaminoethylcellulose
TMVEP–MAA	1,2,5-trimethyl-4-vinylethynylpiperidol–methacrylic acid
CM-HTMAPC	*O*-carboxymethyl-*O*-2-hydroxy-3-(trimethylammonio)propylcellulose
2M5VP–MAA	2-methyl-5-vinylpyridine–methacrylic acid
AMPDAC–SAMPS	2-acrylamido-2-methylpropyldimethylammonium chloride–sodium2-acrylamido-2-methylpropanesulfonate
METMAC–SAMPS	2-methacryloyloxyethyltrimethylammonium chloride–sodium 2-acrylamido-2-methylpropanesulfonate
METMAC–AAm–SAMPS	2-methacryloyloxyethyltrimethylammonium chloride–acrylamide–sodium 2-acrylamido-2-methylpropanesulfonate
PSS-*b*-P2VP	poly(styrene sulfonate)-*block*-poly(2-vinylpyridine)
IPC	interpolyelectrolyte complex
PMAA-*b*-P1M4VPCl	poly(methacrylic acid)-*block*-poly(1-methyl-4-vinylpyridinium chloride)
CCME	chitosan carboxymethyl esters
BSA	bovine serum albumin
SAXS	small angle X-ray scattering
MAA–DMAMA	methacrylic acid–dimethylaminomethacrylate
NaMES–METMAI	sodium 2-methacryloyloxyethanesulfonate–2-methacryloyloxyethyltrimethylammonium iodide

DMVEP–AA	2,5-dimethyl-4-vinylethynylpiperidol–4-acrylic acid
PPG	poly(*N*-propyleneglycine)
PIPCEI	poly(1-isopropylcarboxylethyleneimine)
PEA	poly(ethylenealanine)
EDTA	ethylenediaminetetraacetic acid
VEEA-MAA	vinyl ether of ethanolamine–methacrylic acid
DMF	dimethylformamide
DDSNa	sodium dodecylsulfate
CTMACl	cetyltrimethylammonium chloride
MDAA–MA	*N*-methyldiallylamine–maleic acid
PDMDAAC	poly(*N*,*N*-dimethyldiallylammonium chloride)
DMDAA–MA	*N*,*N*-dimethyldiallylammonium–maleic acid
PAA	poly(acrylic acid)
PEC	polyelectrolyte complexes
PVBTMACl	poly(vinylbenzyltrimethylammonium chloride)
PVPD	poly(*N*-vinylpyrrolidone)
PEG	poly(ethyleneglycol)
C_{PEC}	concentration of PEC
PMAA	poly(methacrylic acid)
MVEP–MAA	1-methyl-4-vinylethynylpiperidol–4-methacrylic acid
m_{HSA}	mass fraction of human serum albumin
m_{PA}	mass fraction of polyampholyte
PSL	poly(styrene) latex
HSA	human serum albumin
IG	immunoglobulins
DLVO	Derjaguin–Landau–Verway–Oberbeek
PEI	poly(ethyleneimine)
ANS	1-anilino-8-naphthalenesulfonic acid
AY	acrylidine yellow
SPSS	sodium poly(styrene sulfonate)
DEAEM–MAA	*N*,*N*-diethylaminoethylmethacrylate–4-methacrylic acid
MKH	Mark–Kuhn–Houwink equation
PDMAAPS	poly[*N*,*N*-dimethyl(amidopropyl)ammonium propanesulfonate]
P2VP-SB	poly(2-vinylpyridinesulfonatopropyl betaine)
P4VP-SB	poly(4-vinylpyridinesulfonatopropyl betaine)
UCST	upper critical soluble temperature
LCST	lower critical soluble temperature
APTAC	acrylamidopropyltrimethylammonium chloride
SA	sodium acrylate
MAPTAC–AA	methacrylamidopropyltrimethylammonium chloride–acrylic acid
SSS	sodium styrene sulfonate

NIPA	*N*-isopropylacrylamide
DC	direct current
TRR	thermoregenerable resins

1 Introduction

In order to adapt the physico-chemical properties of living materials to their biological functions, nature has developed polyelectrolytic polymers with outstanding physical and chemical behaviour. Among the synthetic polyelectrolytes, polyampholytes are very close to biological macromolecules in nature and behaviour [1]. They may provide useful analogs of proteins and are important to modeling some properties and functions of biopolymers such as protein folding and enzymatic activity. The latter has been demonstrated recently [2] and is not considered here.

The dualistic character of polyampholyte chains as compact particles and expanded conformation, as well as the existence of isoelectric point where the net charge of the whole macromolecule is zero and which divides the state of polyampholytes into polyacids and polybases, is also exciting. In spite of our previous publications [3–5], the recent progress in studying the behaviour of synthetic polyampholytes, mainly due to the remarkable works of several research centres and groups on the theory (Edwards, Joanny, Kholodenko, Kardar, Dobrynin, Grosberg and Khokhlov) and the synthesis, characterization and aqueous solution properties of linear and cross-linked polyampholytes (Salamone, McCormick, Candau, Merle, Laschewsky, Tanaka, Katayama), invoked us to systematize and analyze the theoretical and experimental materials in order to predict the perspectives for developing such an interesting class of polyelectrolytes. One of the main purposes of this report is also to bridge the gap between synthetic and natural polymers, between biological materials and the physics and chemistry of macromolecules, and to show a closer relationship between two fascinating worlds.

2 Classification of Polyampholytes

Polyampholytes can comprise chains with combinations of weak acid/weak base, strong acid/weak base, (or else weak acid/strong base) and strong acid/strong base monomers. Typical polyampholytes consisting of weak base and weak acid groups are copolymers of vinylpyridines and acrylic (or methacrylic) acid. While copolymers of *N*-substituted allylamines and vinyl- or styrenesulfonic acids belong to strong base/strong acid polyampholytes, the acidic and basic groups of polyampholytes can also be in salt forms with a low or high charge density along the macromolecules. Independent of the microstructure, polyam-

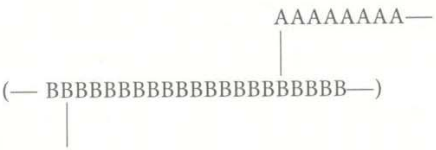
pholyte chains can be divided into a random (1), alternating (2), graft (3), diblock (4) or triblock (5) sequence.

(—ABAABABBBAABAB—) (1)

(—ABABABABABABAB—) (2)



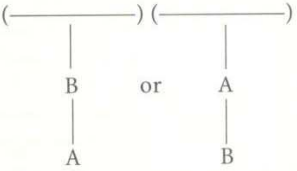
or



(4)

(—AAAAAAAAAAAAABBBBBBBBBBBB—)

(—AAAAAAAAAABBBBBBBBBCCCCCCC—) (5)



(6)

where A, B and C are acidic, basic and neutral monomers, respectively.

In the case of polyampholytes with a betaine structure (6), the acidic and basic groups are situated along the chain backbone. Dependent on the solubility of polyampholytes near the isoelectric point (IEP), they can be water soluble and water insoluble. For instance, the equimolar copolymers of aminoalkyl(meth) acrylates and unsaturated carboxylic acids are water soluble over the complete range of pH-values. On the contrary, copolymers based on vinylpyridines and acrylic (methacrylic, vinyl- or styrenesulfonic) acid are insoluble at the IEP. As a rule most blockpolyampholytes have a wide region of insolubility. Hydrophobic polyampholytes, the behaviour of which is close to "polysoaps", represent the combination of zwitterionic and hydrophobic structures.

3
Theory of Polyampholytes

The theory of solutions of flexible uncharged polymers with excluded volume is at present well developed, but the properties of polyelectrolytes and especially polyampholytes have been considered much less from the theoretical point of view. It is well known that polyampholytes exhibit a change in phase from the extended random flight configuration to a condensed microphase. The polyampholyte theory of Edwards et al. [6] considers the isoelectric state of polyampholytes as a microelectrolyte satisfying a Debye–Huckel-type of structure. The criterion of transition from the collapsed conformation to the extended one is described as follows:

$$\gamma = \frac{e^2 b^2}{kT}(Ll)^{-1/2} \begin{array}{ll} >>1 & \text{collapse} \\ <<1 & \text{open chain} \end{array} \qquad (3.1)$$

where γ is a dimensionless parameter; e is the electron charge; b is the monomer size; l is the Kuhn length; L is the arc length; k is the Boltzmann constant; and T is the absolute temperature.

The concluding remarks of this work are that the addition of salt to the solution will move the collapse point. In the case of charged blockpolyampholytes the existence of a nonuniform dumbbell-like configuration distributed in space is possible. One half of this dumbbell configuration will have a surplus positive and the other half a surplus negative charge.

Higgs and Joanny [7] considered the behaviour of positive and negative charges inside the globule to be similar to that of charges in a small volume of a simple electrolyte. The distribution of the charged monomers within the globule resembles that of the charges in a simple ionic solution rather than those in an ionic crystal. The electrostatic interactions create correlation between the positions in space of the positive and negative charges so that each charge tends to be surrounded by a shell of charge of the opposite sign. The Coulomb interactions are thus screened at long distance and the charges on the polyampholyte chain can be considered as free charges in an ionic solution. The Higgs and Joanny model considers a single chain having a fraction of positively and negatively charged monomers randomly distributed along the macromolecule. Let a chain of N monomers of size b have a fraction f of positively and a fraction g of negatively charged monomers distributed randomly. For a neutral chain (f=g) in pure water it is supposed that there exists a collapsed state of the chain with a volume significantly smaller than the Gaussian chain volume $N^{3/2}b^3$ but significantly larger than the volume of the completely close-packed monomers Nb^3. The chain is at a thermodynamic equilibrium state and can easily change from one configuration to another. If the chain is in a Θ solvent where the second virial coefficient is zero the third virial term will counteract the electrostatic attractions. If the polymer is an Einstein sphere of radius R, the charge concentration

in this region is $\equiv fN/R^3$. By analogy with the Debye–Huckel screening length k^{-1}, one can define a screening length k_p^{-1} due to the charge on the polymer to be given by:

$$k_p^2 \equiv f N l_B / R^3 \tag{3.2}$$

where l_B is the Bjerrum length.

It is necessary to consider different regimes dependent on the dimensions of polymer chains. A long chain collapses into a globule consisting of close-packed blobs of size k^{-1}. The blobs are either Gaussian or swollen depending on the second virial coefficient value. In a Θ solvent, the chain radius in the collapsed state is given by:

$$R \equiv N^{1/3} b (\frac{b}{f l_B})^{1/3} \tag{3.3}$$

In the case of a finite concentration of chains, Higgs and Joanny predict a phase separation between a high concentration phase of interpenetrating polymer chains and a dilute solution in which each chain is a collapsed globule. In the presence of salt, due to the screening of the electrostatic attractive forces by low-molecular-weight ions, the polyampholyte molecules tend to swell and adopt the dimensions of the uncharged chain. Then the electrostatic attractions are treated as a negative contribution to the excluded volume. Therefore a Θ compensation point exists at the salt concentration at which the positive excluded volume interaction V balances the negative electrostatic contribution. The effective excluded volume is given by:

$$V^* = V - 4\pi l_{B^2} f^2 / k b^3 \tag{3.4}$$

At the Θ point ($V^*=0$), the screening length is:

$$k = k_\theta = (l_B f / b)^2 \ (1 / V b) \tag{3.5}$$

This salt concentration marks the transition from collapsed to Gaussian or swollen chains.

Higgs and Joanny also considered a non-neutral polyampholyte with $f-g << f+g$ for the case when $V=0$. In pure water the chain has the characteristics of both a polyelectrolyte (excess of charges: $f-g$) and of a neutral polyampholyte (neutral part: $2g \approx f+g$). The polyelectrolyte blob size is:

$$N_c \sim (\frac{b}{l(f-g)^2})^{2/3} \tag{3.6}$$

Hence, the polyampholyte blob size is:

$$N_l \sim \frac{b^2}{l^2 (f+g)^2} \tag{3.7}$$

The overall conformation of the chain is determined by the relative value of N_1 and N_e. If $N_1 < N_e$ the attractive polyampholyte interaction dominates. The polymer collapses in the same way as a neutral polyampholyte. If $N_1 > N_e$ the repulsive polyelectrolyte interaction dominates and the chain behaves more like a usual polyelectrolyte. The necessary net charge to swell, and thus redissolve the polyampholyte, is therefore:

$$f - g > l_B / b(f+g)^{3/2} \tag{3.8}$$

At a finite salt concentration the polyampholyte effect dominates the polyelectrolyte effect at long distances if:

$$(f-g)^2 < \frac{kl_B}{4}(f+g)^2 \tag{3.9}$$

Hence the chain is expected to collapse for a wider range of $(f–g)$ at higher salt concentrations. For a small net charge case, the reverse of Eq. 3.8, the polyampholyte term dominates at small distances. The main difference between the polyampholyte theory of Edwards et al. [6] and that of Higgs and Joanny [7] is that the former argues that the electrostatic attractions are balanced by the reduction in entropy of the chain due to confinement within a sphere smaller than its natural radius while the latter considers that the third order virial term turns out to be always larger than the confinement entropy for a collapsed chain and must be taken into account. Equation 3.1 also seems to state that short chains collapse and long ones are open which is contrary to that found by Higgs and Joanny. The original Debye–Huckel theory is only valid at low salt concentrations $kl_B < 1$, and, therefore, Higgs and Joanny's theory is not quantitatively accurate for the high salt concentrations needed to dissolve the highly charged polyampholytes.

Two recent studies [8,9] have led to opposite conclusions as to whether the configuration of a polyampholyte is stretched [8,9] or compact [7]. The disagreement between these two conclusions is quite extreme, in that one predicts a compact configuration employing the Debye–Huckel theory, while the other substitutes dimensional arguments for a true renormalization-group treatment. The Debye–Huckel approach implicitly assumes that the polymer is overall neutral (or at least very close to neutrality), while the scaling results rely on typical excess charges in the order of $\pm q_o N^{1/2}$ in the various quenched configurations. It has been proved that the conformation of the polyampholyte is very sensitive to the presence of constraints and the choice of ensemble. A polymer constrained to have a zero net charge collapses to a compact configuration upon reduction in temperature. On the other hand, if N monomers are randomly assigned positive or negative charges, $\pm q_o$ with equal probability, the resulting polymer has an overall excess charge $Q_c \approx \pm q_o N^{1/2}$. Independent of its sign this deviation from neutrality is sufficient to stretch the chain to an extended state at low temperature. Indeed the neutral polyampholyte collapses at low temperatures as predicted by Higgs and Joanny [7]. This result is not particularly sur-

prising for relatively short chains with a moderate excluded-volume interaction, due to the crossover between Gaussian and self-avoiding behaviours. Very different results are obtained when the charges are selected randomly without regard to overall neutrality. As the temperature decreases below T_0, the radii first contract and then reexpand. The explanation of this phenomenon is as follows: at T somewhat smaller than T_0, positive and negative charges start to pair up, thereby reducing the chain size. At lower T the "excess charges" can only reduce their energy by stretching the entire chain, the chain "unfolds" into a stretched linear or branched object with folded "double strands".

In a very recent work, Gutin and Shakhnovich [10] considered the effect of a net charge on chain conformation. They introduced an interesting idea of the elongation of a polyampholyte globule. Their calculations, however, for asymmetric polyampholytes, led to the wrong temperature dependence of the aspect ratio of a polyampholyte chain. According to Dobrynin and Rubinstein [11], the net charge on a typical polyampholyte chain is hardly ever exactly zero because it is usually made by random copolymerization and therefore has some small net charge even if the whole system of chains is, on average, neutral. In this connection the conformation of a single polyampholyte chain was reexamined in the framework of a simple two parametric Flory theory. Let us consider N-mer with $N_+=fN$ positive and $N-=gN$ negative charges. There are three different regimes for polyampholyte chains with charge asymmetry $|N_+-N_-|>|N_+-N_-|^{1/2}$ depending on the effective temperature $t=N/u(N_+-N_-)$ (where u is the ratio of Bjerrum length to the bond size) in a salt-free solution:

i) *Unperturbed regime*: at high effective temperatures $t>t_1$ the electrostatic interactions are unimportant and polyampholyte configuration is controlled by the solvent quality for the uncharged backbone. It is swollen in good solvent, Gaussian in the Θ solvent, or collapsed in a poor solvent (Fig. 1a);

ii) *Polyelectrolyte regime*: at intermediate effective temperatures $t_2<t<t_1$ the repulsion between uncompensated charges $e(N_+-N_-)$ dominates over the charge-fluctuation-induced attraction. The chain is stretched into an array of electrostatic blobs each of size D (Fig. 1b). Inside these blobs the chain statistics are unperturbed by the electrostatic interactions and are the same as in Regime (i). On length scales larger than D the chain is strongly stretched into an array of blobs of total length L. The aspect ratio of L/D of a polyampholyte chain is equal to the number of electrostatic blobs. This aspect ratio is proportional to N and increases with an increase in charge asymmetry $(f-g)$ and with a decrease in temperature T. It should be stressed that the repulsion between uncompensated charges cannot be screened by other charges on the chain.

iii) *Polyampholyte regime* ($t<t_1$): in this regime the aspect ratio of a polyampholyte chain is constant and equal to its maximum value:

$$L/D \approx (N_+ - N_-)^2/(N_+ - N_-) \text{ for } t \le t_2 \qquad (3.10)$$

Fluctuation-induced attraction reduces the chain size (reduces the volume at constant aspect ratio) with decreasing temperature. On length scales small-

er than the Debye radius r_D the polymer configuration is unperturbed [the same as in Regime (i)]. On larger length scales the polyampholyte is a dense packing of Debye blobs which form an asymmetric globule as sketched in Fig. 1c. It is interesting to note that the length L of the polyampholyte globule could be either larger or smaller than the unperturbed size of the chain depending on the reduced temperature range. Chains with smaller charge asymmetries $(N_+-N_-)^2/(N_++N_-)<1$ do not exhibit Regime (ii) (i.e. they do not stretch beyond their unperturbed size) and directly collapse into a globular state [Regime (iii)] from the unperturbed state [Regime (i)] with decreasing temperature. These "almost neutral" polyampholytes form symmetric globules (with aspect ratio $L/D\approx1$). The shape anisotropy of a globule, predicted for

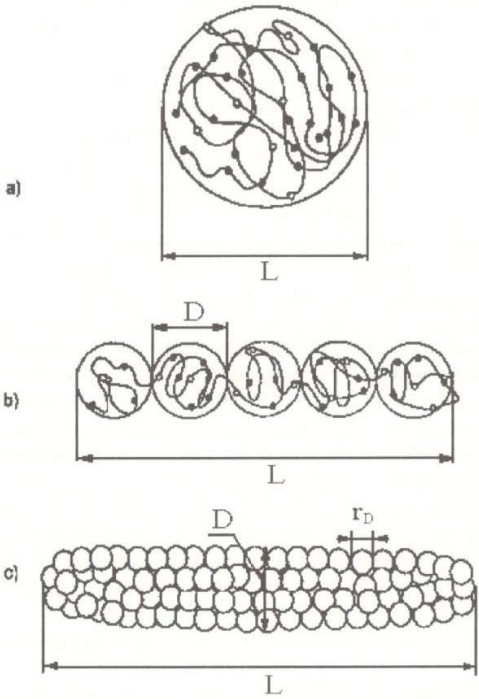


Fig. 1a-c. The three regimes of a polyampholyte chain with charge asymmetry $(N_+-N_-)^2>(N_++N_-)$: **a**) unperturbed regime ($t>t_1$); **b** polyelectrolyte regime ($t_2<t<t_1$); **c**) polyampholyte regime ($t>t_2$) – an elongated globule of Debye blobs (represented by *circles*) [11]

the polyampholyte regime, could be measured in super-cooled polyampholyte solutions. It should also have a profound effect on the polyampholyte phase diagram.

The predictions of references [7] for the case $N_+=N_-$ coincide well with the conclusions of authors [11]. For asymmetric polyampholytes $N_+\neq N_-$, Higgs and Joanny [7] predict that electrostatic repulsion swells the chain only for very large charge asymmetry $\sigma N > t^{-2}$, whereas Dobrynin and Rubinstein [11] found that electrostatic repulsion can stretch the polyampholyte chain with much smaller charge asymmetry $\sigma N > 1$ (of the order of statistical charge fluctuation of the number of charges on the chain).

Qian and Kholodenko [12] studied the conformational properties of polyampholytes according to a Bernoullian type of statistics. It has been shown that the mechanism of collapse transition for the random polyelectrolytes essentially differs from that of uncharged homopolymers. Below the collapse transition temperature, depending on the external conditions, polymer chains can be in one of two globular phases with the possibility of a quasi-first order (due to finite size effects) transition between them. This fact has important biological significance with regard to enzyme-substrate complexes.

The dynamics and conformational properties of polyampholytes have been studied in the presence of external electric fields. In terms of the Rouse model of polymer dynamics, some authors [13] obtained the main-square displacement both of the centre of mass and of individual beads, and the end-to-end distance of the polyampholyte. The equilibrium mean-square end-to-end distance shows an additional elongation which is represented as N^{β}: the exponential equals $\beta=2$ if only one bead is charged or if the charges are distributed in an alternating fashion, $\beta=3$ if the charges are distributed in an uncorrelated fashion, and $\beta=4$ if the correlation length of the charge distribution is large.

Muthukumar and co-workers [14] have studied 20 different randomly charged polyampholytes of length 50 using Monte Carlo simulations. Results for six representative sequences from among the twenty sequences are presented. The mean-squared radii of gyration R_g^2 of the chains are a function of temperature for these sequences. At high temperatures the chains behave as self-avoiding walks and the radii are similar. As the temperature is reduced the radii decrease under the influence of attractive electrostatic interactions. The distribution of the radii and of intrachain energy at three different temperatures for two sequences has been simulated. The location of charges along the chain plays a crucial role in the conformational behaviour of the polyampholytes. In the authors' opinion, the knowledge of merely the energy landscape is insufficient to describe the conformational properties of polyampholytes. The entropy associated with the formation of frustrated conformations needs to be accounted for when trying to understand the conformational properties of heteropolymers with specific sequences. Monte Carlo simulation and variational mean field calculations were used to study the structure of isolated polyampholyte chains at conditions roughly corresponding to dilute solutions [15]. A random distribution of cationic and anionic groups on the chain is assumed and average proper-

ties for samples with restricted or fluctuating net charge on individual chains are computed. The chains swell with increasing net charge while they contract when a balance of positive and negative charges is attained. The variational mean field theory successfully describes the swelling at high net charge while it underestimates the attractive effects characteristic of neutral or nearly neutral chains. This difference is interpreted as the result of spatial correlations among ionized polyampholyte beads in compact coils.

All the above-mentioned theoretical conclusions successfully explain most experimental results as follows:

1) When $f >> g$ or $g >> f$, polyampholyte chains are close to a polycation or a polyanion, respectively, and behave as polyelectrolytes.
2) Polyampholytes at the isoelectric state when the whole macromolecule is neutral tend to collapse, have a small hydrodynamic radius if soluble, and have the phase separation if insoluble.
3) The addition of simple salts leads to swelling of neutral polyampholytes if they are soluble and dissolve the precipitate if they are insoluble ("antipolyelectrolyte" effect).

There are also some discrepancies between the theory and the experimental. All the above-mentioned theories developed for polyampholytes:

1) Neglect the effect of counterions on the conformation of charged chains;
2) are applicable only at low concentration of salts;
3) consider only the diluted solutions;
4) ignore the specific binding of counterions by polyion.

The validity of theories at low salt concentrations is connected with the fact that the Debye–Huckel length k^{-1} is large with respect to the Bjerrum length l_B. The theory cannot be quantitatively accurate for the high salt concentrations needed to dissolve the highly charged polyampholytes, especially blockpolyampholytes. Usually the hydrodynamic properties of amphoteric copolymers are studied in the dilute regime, while the solubility data refer to the semidilute range; NMR or Raman spectroscopic experiments are sometimes performed in the concentrated regime. The preferential binding of anions by polyampholytes usually leads to the shifting of pH_{IEP} to the acidic region or, vice versa, the specific binding of cations shifts the pH_{IEP} towards the alkaline region [16]. The effectiveness of anions to decrease the pH_{IEP} changes mostly as follows: ClO_4^- $>SCN^-$ $>NO_3^-$ $>I^-$ $>Cl^-$ and coincides well with the Hoffmeister series for proteins. In spite of these reservations, the above-mentioned models describe reasonably well the solution behaviour of most polyampholytes.

4
Acid-Base Equilibrium in Polyampholytes

Both the nature of their functional groups and the microstructure of the chain determine the electrochemical properties of polyampholytes. The acid-base properties of amphoteric polyelectrolytes are quite different from the behaviour of both polyacid and polybase due to the fact that near the IEP it is difficult to

titrate the functional groups of polyampholytes [1]. The titration of acidic and basic groups becomes available away from the IEP when positive or negative charges begin to predominate. Then a modification of the Henderson–Hasselbach equation can be used to analyze the acid-base equilibrium of polyampholytes [17–19]:

$$pH = pK_a^{'} + \log\ (\alpha / 1 - \alpha) \tag{4.1}$$

$$pH = pK_b^{'} + \log\ (1 - \beta / \beta) \tag{4.2}$$

where $pK^{'}_a$ and $pK^{'}_b$ are the apparent acidic dissociation constants of acidic and basic groups, respectively, and α and β are the degree of ionization of acidic and basic groups of polyampholytes, respectively.

To determine the dissociation constants of ionizing groups, Katchalsky and Gillis [20] have suggested a theoretical equation based on the model of electrostatic potential smeared along the chain molecule. It takes into account the electrostatic interaction between different chain segments as well as between ionic groups and low molecular weight electrolytes. The theoretical calculations are in good agreement with experimental results obtained for 2-vinylpyridine–acrylic acid (2VP–AA). Analysis of the titration curves of amphoteric copolymers of 2-vinylpyridine–methacrylic acid (2VP–MAA) [21] and 2-methyl-5-vinylpyridine–acrylic acid (2M5VP–AA) [22, 23] of different composition reveals that at low MAA (or AA) content they show a dependence analogous to that of polyvinylpyridines alone but, upon increasing the acid content, the shape of the titration curve changes. The dissociation constant for each copolymer sample depends on its composition: increasing the MAA (or AA) content enhances acid ionization of pyridine groups, while increasing the 2VP content decreases it. The increasing of the 1-vinylimidazole (1-VI) content from 24 to 56,4 mol% enhances the acidity of the AA group's pK_a from 3.97 to 3.25, whereas increasing the AA content from 43.6 to 74 mol% enhances the basicity of 1-VI's pK_b from 10 to 11.4 [4]. This behaviour by polyampholytes is explained by the inductive influence of neighbouring groups. Rice and Harris [24,25] have extended the chain model suggested for polyelectrolytes containing charges of the same sign to alternating polyampholytes. The model takes account of the equilibrium dissociation of acidic and basic groups, counterionic binding, as well as the electrostatic interaction between chain charges. The electrostatic free energy of interaction between nearest-neighbour charges is calculated by the iteration method. Calculations of potentiometric titration curves for a hypothetical copolymer show that the properties of polyampholytes qualitatively approach those of proteins. Katchalsky et al. [17] considered the case when one monomer is present in the copolymer in such abundance that formation of isolated groups in the polymer chain occurs. The results of the theoretical study are compared with the experimental data for 2VP–AA (MAA) synthetic copolymers and for the natural polyampholyte–lysozyme. The agreement between theory and experimental is satisfactory. To extend the utility of the Kachalsky model [17], the nearest-neighbour interaction for a polyampholyte of any composition was com-

puted [19]. The calculated titration curves were compared with the experimental ones. The agreement between them is satisfactory. Ising models have been used to describe the acid-base behaviour of linear polyampholytes and polyelectrolytes [25]. Alternatively, such titration curves are often interpreted in terms of an affinity distribution (pK spectrum). The exact affinity distributions for various Ising models of linear polyelectrolytes and polyampholytes were derived. The acid-base equilibrium of polyampholytes depends also on the microstructure of copolymers. The solubility and titration curves, as well as pH_{IEP}, are different for DMAEM–MAA prepared by radical initiated copolymerization of two monomers (**A**-type), alkaline hydrolysis (**B**-type) or acidolysis of poly-*N*,*N*-dimethylaminoethylmethacrylate (PDMAEM) (**C**-type), although the composition of the copolymers is the same. This is due to different distributions of the sequences of the acidic and basic monomers along the chain. Polyampholytes prepared by the hydrolysis of PDMAEM in concentrated sulfuric acid have a blocklike structure whereas an alkaline-hydrolyzed one tends towards randomness. The apparent pK's of the acidic and basic groups can be expressed by the sum of the intrinsic pK (pK°), the nearest-neighbour interaction (E_d), and the long-range electrostatic interaction (E_r):

$$pK'_a = pK^{\circ}_a + 0.434/kT\,(\partial E_d/\partial \nu)_{\xi} + 0.434/kT\,(\partial E_r/\partial \nu)_{\xi} \tag{4.3}$$

$$pK'_b = pK^{\circ}_b + 0.434/kT\,(\partial E_d/\partial \xi)_{\nu} + 0.434/kT\,(\partial E_r/\partial \xi)_{\nu} \tag{4.4}$$

where ν and ξ are, respectively, the mean number of negative and positive charges on the macromolecule, k is Boatsman's constant, and T is the absolute temperature.

According to Katchalsky et al. [17]:

$$(\partial E_r/\partial \nu)_{\xi} = -(\partial E_r/\partial \xi)_{\nu} = e|\psi_a| \tag{4.5}$$

where $e|\psi_a|$ is the potential on the surface of the polyion. At low ionic strength, the potential $e|\psi_a|$ is the sum of short- and long-range interactions; at high ionic strength only short-range interactions remain. If $pK^{\circ'}_a$ is the sum of the intrinsic pK (pK°_a) and the nearest-neighbour interaction term of the acid, and $pK^{\circ'}_b$ is the difference of the same terms of the base, we have:

$$pK'_a = pK^{\circ'}_a + 0.434\, e|\psi_a|/kT \tag{4.6}$$

$$pK'_b = pK^{\circ'}_b + 0.434\, e|\psi_a|/kT \tag{4.7}$$

Then the modified Henderson–Hasselbach Eqs. 4.1 and 4.2 can be rewritten as follows:

$$pH = pK^{\circ'}_a + \log(\alpha/1-\alpha) + 0.434\, e|\psi_a|/kT \tag{4.8}$$

$$pH = pK^{\circ'}_b + \log(1-\beta/\beta) + 0.434\, e|\psi_a|/kT \tag{4.9}$$

The terms $pK^{o'}_a$ and $pK^{o'}_b$ can be obtained from Eqs. 4.8 and 4.9 if the neutralization is made at high ionic strength. At the IEP when the net charge is zero, $e|\psi_a|$ vanishes and Eqs. 4.8 and 4.9 become:

$$pH_{IEP} = pK^{o'}_a + \log(\alpha_{IEP} / 1 - \alpha_{IEP}) \quad (4.10)$$

$$pH_{IEP} = pK^{o'}_b + \log(1 - \beta_{IEP} / \beta_{IEP}) \quad (4.11)$$

If $pK^{o'}_b - pK^{o'}_a > 2$, the pH_{IEP} of a polyampholyte which contains an excess of acid monomer ($a > 0.5$) is calculated from:

$$pH_{IEP} = pK^{o'}_a + \log(1 - a / 2a - 1) \quad (4.12)$$

and at an excess of base monomer ($a < 0.5$) from:

$$pH_{IEP} = pK^{o'}_b + \log(1 - 2a / a) \quad (4.13)$$

Taking into account that $pK^{o'}_a = 5.15$ and $pK^{o'}_b = 8.58$ for MAA and *N,N*-dimethylaminoethylmethacrylate (DMAEM), respectively, an S-shaped curve of pH_{IEP} vs. the acid content has been obtained theoretically. The theoretical curve fits well with the experimental one for **A**-type copolymers. Small deviations from the theoretical curve are observed for copolymers of type **B** and **C** and can be explained by variations of $pK^{o'}_a$ and $pK^{o'}_b$ due to the nearest-neighbour interaction which depends on the distribution of the acidic and basic monomers. The values of pH_{IEP} of the DMAEM–MMA–MAA triblock copolymer [26] calculated from Eq. 4.14 form the theoretical curves of Fig. 2:

$$pH_{IEP} = pK_b + \log\{1 / 2[(1 - R / R) + (1 - R / R)^2 + (4 / R)\, 10^{pK_a - pK_b}} \quad (4.14)$$

where R is the molar ratio of acid to base.

Similar to a simple amino acid – glycine, a polyampholyte dependent on pH,can change from the cationic to the anionic form, or vice versa, either through the molecular or the bipolar form. Apparently, the existence of full zwitterionic or molecular forms is not realized. The coexistence of both molecular and zwitterionic states is more probable [27]. Combination of potentiometric and conductimetric methods allowed for polyampholytes 2VP–AA and DMAEM–MAA to distinguish between: a) free COOH groups and $>NH^+$ – cations in the alkali titration of copolymers which have the acidic monomer in excess; b) the COO^- anions and >N-groups in the acid titration of copolymers which have an excess of basic monomer; c) COO^- anions of different basic strengths in the acid titration of a copolymer which has the acidic monomer in excess; d) >N-groups of different basic strengths in the acid titration of copolymers which have excess basic monomer [28,29]. The modified titration curves, $pH + \log(\beta/1-\beta)$ vs. β (where β is the degree of ionization of basic groups), for the copolymers show one or two discontinuities which correspond to several extrapolated values of pK^o.

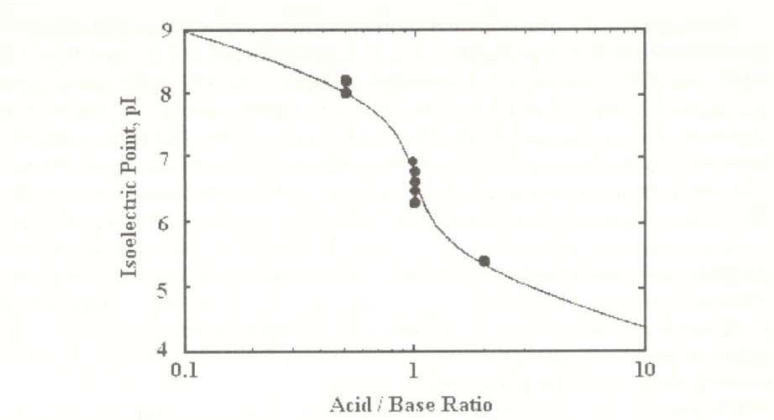


Fig. 2. Theoretical (*solid line*) and experimental (*filled circles*) values of the isoelectric points of DMAEM–MMA–MAA triblock copolymers (Reproduced with permission from [26])

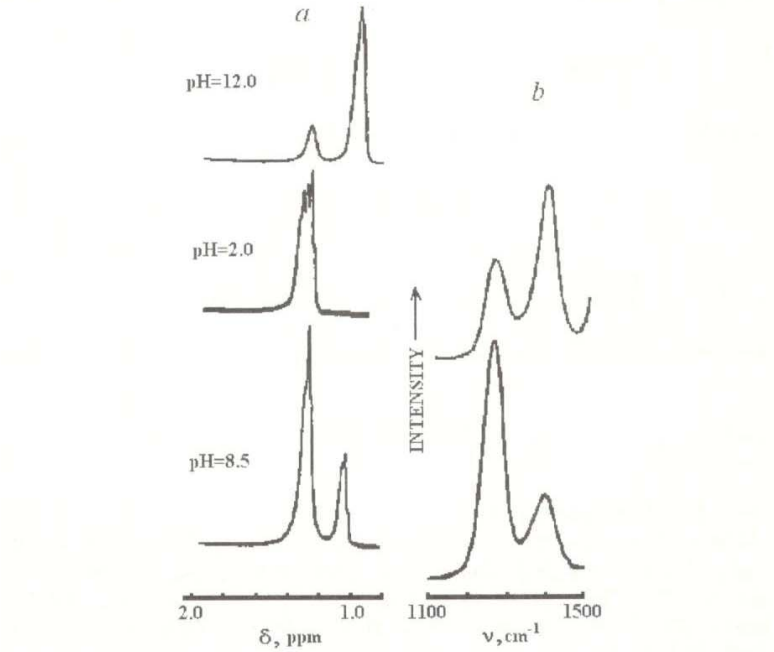
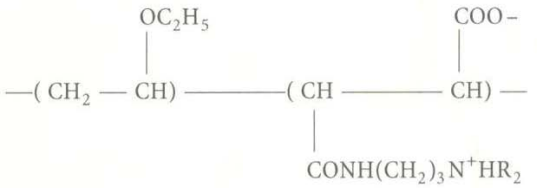


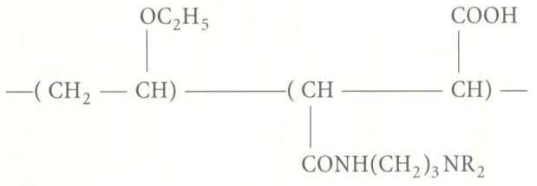
Fig. 3a,b. ^{1}H NMR **a** and FTIR **b** spectra of CM-DEAEC at various pH of the solution [30]

The existence of carboxymethyl-2-diethylaminoethylcellulose (CM-DEAEC) in protonated and non-protonated forms at different pH can be seen from ^1H NMR and FTIR spectra [30]. For methyl protons of DEAEC substituents only one signal is observed at 1.3 ppm in the acidic region whereas another strong signal at 1.05 ppm appears in the alkaline region (Fig. 3a). The former and the latter can be assigned to methyl protons of DEAEC substituents in protonated and non-protonated states. These spectra also indicate that about 80% of DEAEC fragments exist in protonated form at pH=8.5. In spite of the high value pH of 12 some DEAEC groups still exist as cations. The FTIR spectrum of CM-DEAEC has two peaks at ν=1602 and 1740 cm^{-1} that correspond to C=O stretching vibrations of COO^- and COOH, respectively (Fig. 3b). It can be concluded from FTIR measurements that the protonated DEAEC substituents promote the ionization of carboxylic groups through the transfer of protons from carboxylic to amine groups as mentioned earlier.

It has been shown [31] that the presence of hydrophobic groups in polyampholytes can change the equilibrium between the zwitterionic and molecular forms. Alternating copolymers of vinylethyl ether and *N*,*N*-diethylaminopropylmonoamide of maleic acid preferentially exist in the charged form (I) but the replacement of ethyl radicals by two bulky butyl radicals stabilizes the uncharged molecular form (II).



(I)



(II)

where R=C_2H_5 (I) and C_4H_9 (II).

The acid-base properties of alternating comb-like copolymers of α-olefins (C_6H_{12}–$C_{16}H_{28}$) and *N*,*N*-dimethylaminopropylmonoamide of maleic acid [32,33] [where R=C_4H_9 (PA-4), C_6H_{13} (PA-6), C_8H_{17} (PA-8), $C_{10}H_{21}$ (PA-10), $C_{12}H_{25}$ (PA-12) with n=116, 59, 40, 21 and 16, respectively], are changed as shown in Table 1.

Table 1. Acid-Base Characteristics of Comblike Polyampholytes

Polyampholyte	n	pK_a	pK_b	pH_{IEP}
PA-4	116	3.62	10.82	7.22
PA-8	40	3.79	11.23	7.51
PA-10	21	4.24	11.28	7.71
PA-12	16	4.33	11.31	7,82

5
Hydrodynamic, Conformational and Molecular Characteristics of Amphoteric Copolymers

The copolymer composition, charge distribution and density, molecular weight and microstructure are the main parameters for a comprehensive analysis of the structure-properties-function relationships [4,5]. The hydrodynamic properties of polyampholytes are closely related to their conformations that are determined by the intra- or intermolecular interactions between anionic and cationic groups along polymer chains. An intramolecular attraction causes polymer chains to collapse into a globular structure, while an intermolecular one results in an association which behaves like colloid dispersions. A change in the hydrodynamic properties of 1,2,5-trimethyl-4-vinylethynylpiperidinol–4-methacrylic acid (TMVEP–MAA) as a function of pH medium is clearly seen from the data in Table 2 [34–36]. At the IEP the intrinsic viscosity [η] of TMVEP–MAA is minimal whereas the sedimentation constant S_0 has a maximal value. The closely spaced values of the average hydrodynamic molecular weights $M_{s\eta}$ at pH from 4.0 to 11.0 indicate the absence of intermacromolecular association. Figure 4 represents the influence of μ on the hydrodynamic sizes of *O*-carboxymethyl-*O*-2-hydroxy-3-(trimethylammonio)propylcellulose (CM-HTMAPC) [37]. In acidic and alkaline media, polyampholyte molecules behave as polycations and polyanions, respectively; the reduced viscosity value is decreased with the increase in μ. An "antipolyelectrolyte" effect is observed at the IEP: the reduced viscosity η_i/C increases with the increase in μ. These data, together with our previous results [34,35], entirely confirm the prediction of Tanford [1] and theoretical conclusions [7] on the unfolding of water-soluble amphoteric macromolecules at the IEP in the presence of neutral salts.

Table 3 lists hydrodynamic parameters of 2M5VP–MAA copolymers of different composition [38]. At a 90 mol% content of 2M5VP units at pH=1.2 the optical anisotropy of the polyampholyte is negative in sign and approaches the poly(2-methyl-5-vinylpyridine) anisotropy value. A change of the anisotropy sign from negative to positive is observed in the alkaline region. This indicates the formation of compact particles at pH=13, stabilized by the hydrophobic interactions of methyvinylpyridine groups composing the nuclei of the particles. In this case the polyampholyte macromolecule is protected from the precipitation due to hydrophilic carboxylic groups associated with water molecules.

Table 2. Hydrodynamic Characteristics of TMVEP–MAA (54:46 mol-%) at Various pH-Values and Ionic Strength of the Solution μ = 0.1 mol·L^{-1}

pH	[η], (dL·g^{-1})	$S_0 \cdot 10^{13}$ (s)	$M_{s\eta} \cdot 10^{-3}$
4.00	0.40	3.30	90.5
7.25	0.28	4.00	85.6
9.17 (IEP)	0.15	5.88	104.0
11.00	0.26	4.27	92,0

Table 3. Intrinsic Viscosities [η], Weight Average Molecular Weight M_w and Gyration Radius R_g Values of Copolymers 2M5VP–MAA at Various pH-Values of the Solution

[2M5VP] (mol%)	pH	[η], (g·dL^{-1})	$M_w \cdot 10^6$	R_g, (A)
90	1.2±0.05	5.00	0.90	700
	13.0±0.1	0.12	1.00	100
50	1.2±0.10	4.80	0.60	500
	13.0±0.1	4.00	0.60	500

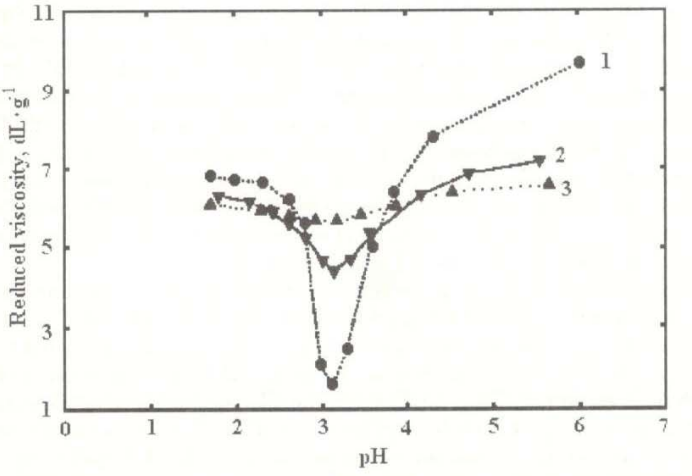


Fig. 4. Reduced viscosities of CM-HTMAPC (C_p=0.060 g·dL^{-1}) at different pH and ionic strengths of the solution μ. μ=0.01 (*curve 1*), 0.03, (*curve 2*) and 0.10 M NaCl (*curve 3*) (Reproduced with permission from [37])

Copolymers of 2-acrylamide-2-methylpropyldimethylammonium chloride and sodium 2-acrylamide-2-methylpropanesulfonate (AMPDAC–SAMPS) were prepared and their dilute solution properties studied as a function of copolymer composition, temperature, time, pH and added low-molecular-weight electrolytes [39–42]. Equimolar copolymers display a minimal viscosity in pure water and a maximal one in concentrated salt solutions. As the copolymer compositions deviate from an equimolar, charge imbalances increase the hydrodynamic volume of the macromolecules.

Corpart and Candau described the synthesis [43], characterization [44] and aqueous salt solution properties [45] of high charge density polyampholytes derived from 2-methacryloyloxyethyltrimethylammonium chloride–sodium 2-acrylamido-2-methylpropanesulfonate (METMAC–SAMPS) monomers. The polyampholytes prepared by means of a microemulsion polymerization have several advantages over other conventional procedures, namely, the process allows the production of very high-molecular-weight polymers (up to 1.7×10^7) and copolymers are more homogeneous in composition, with a microstructure not far from random. Solubility and viscometry experiments show that the solution behaviour of METMAC–SAMPS is essentially controlled by two parameters: the net electrical charge, fixed by the copolymer composition, and the ionic strength. Copolymers with a strong net charge behave more like polyelectrolytes. At intermediate copolymer compositions, the sample behaviour depends on the duality between repulsive (polyelectrolyte effect) and attractive (polyampholyte effect) electrostatic interactions. Depending on the ionic strength, either one of these antagonist effects will dominate. The same authors also reported the study of a low charge density polyampholyte METMAC–SAMPS with an incorporated acrylamide (Aam) monomer [46]. The influence of added salt on the solubility, as well as on the conformational and morphological characteristics of the terpolymer, was analyzed. The hydrodynamic parameters of METMAC–Aam–SAMPS (3.99:92.18:3.88 mol%) in relation to the ionic strength μ are summarized in Table 4. Figure 5 shows the schematic phase diagram of METMAC–AAm–SAMPS at two conditions: 1) when polymer concentration (C_P) is fixed and the salt concentration (C_S) varies; and 2) when the salt concentration is constant and the polymer concentration changes. At low salt content, attractive electrostatic interactions are dominant and the chains collapse. At high salt content, when the Debye–Huckel length becomes short enough so that the Coulomb interactions are screened out, then the excluded volume interactions are dominant and the polymer has a swollen or Gaussian conformation,

Table 4. Weight Average Molecular Weight M_w, Radius of Gyration R_G and Hydrodynamic Radius R_H of METMAC–AAm–SAMPS

μ (mol·L^{-1})	$M_w \cdot 10^{-6}$	R_G (Å)	R_H (Å)
0.2	9.5±1	2400±200	1500±100
0.5	9.1±1	2500±200	1500±100

depending on the quality of the solvent. Below a critical salt content, the chains with zero or small net charge precipitate, due to the polyampholyte effect. The supernatant contains highly swollen oppositely charged molecules. The polymer concentration in the supernatant decreases upon decreasing the salt content, the chains being more and more swollen. In other words, the phase separation observed here represents a fractionation process, not in terms of molecular weight distribution but rather in terms of a net charge distribution. Note that the mass polydispersity can also play a considerable role since the collapse–swollen transition is very sensitive to the molecular weight of the polyampholyte [7]. Various authors [47] have discussed multichain effects in polyampholyte solutions of finite concentration and found that the existing single-chain theories are limited to exponentially small concentrations if the sample contains net charges of both signs. It has been shown that the charged polyampholytes have a strong tendency to form neutral complexes and to precipitate. Stretched chains play almost no role in the ideal case of a neutral sample with nearly symmetric charge; counterions accumulate in the supernatant together with charged, elongated chains and the behaviour of the solution is dominated by "impurities".

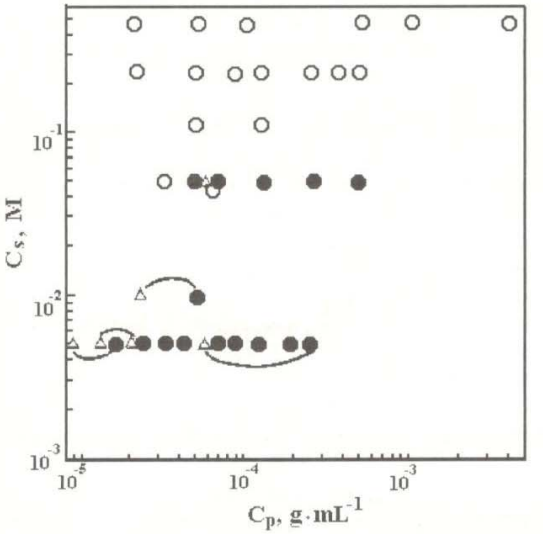


Fig. 5. Actual phase diagram for SAMPS/AAm/METMAC (3.83:92.18:3.99 mol%) copolymer. The *open circles* correspond to soluble samples, and the *filled circles* to samples for which a precipitate could be observed by eye; the *triangles* represent the concentrations of the supernatants estimated from the scattering intensities. The lines connect the initial systems to the corresponding supernatants (Reproduced with permission from [46])

Blockpolyampholytes possess unique physico-chemical properties owing to the combination of acidic and basic blocks in one macromolecular chain. It has been shown [48] that the properties of a linear diblock copolymer poly(styrenesulfonate)-*block*-poly(2-vinylpyridine) (PSS-*b*-P2VP) at the IEP are closely related to those of stoichiometric interpolyelectrolyte complexes (IPC). Depending on the degree of ionization of vinylpyridine blocks, the conformation of the macromolecules is changed as follows. In the uncharged state it is a segregated structure with a nucleus of vinylpyridine blocks maintained in water by hydrating polyacid blocks. At a low degree of ionization it is a coil "frozen" by rare ionic cross-links, at IEP it is a compact structure of IPC stabilized by the intraionic interactions of acidic and basic block units. The addition of a 1:1 type low-molecular-weight electrolyte leads to a narrowing of the precipitation region of a nearly equimolar blockpolyampholyte poly(methacrylic acid)-*block*-poly(1-methyl-4-vinylpyridinium chloride) (PMAA-*b*-P1M4VPCl) [49]. A diagram of the states of PMAA-*b*-P1M4VPCl at various pH and ionic strength is shown in Fig. 6. The dissolution of PMAA-*b*-P1M4VPCl in the presence of KCl may be caused by the rupture of intraionic "bridges" between the oppositely charged blocks near the IEP. The appearance of the precipitation region at high

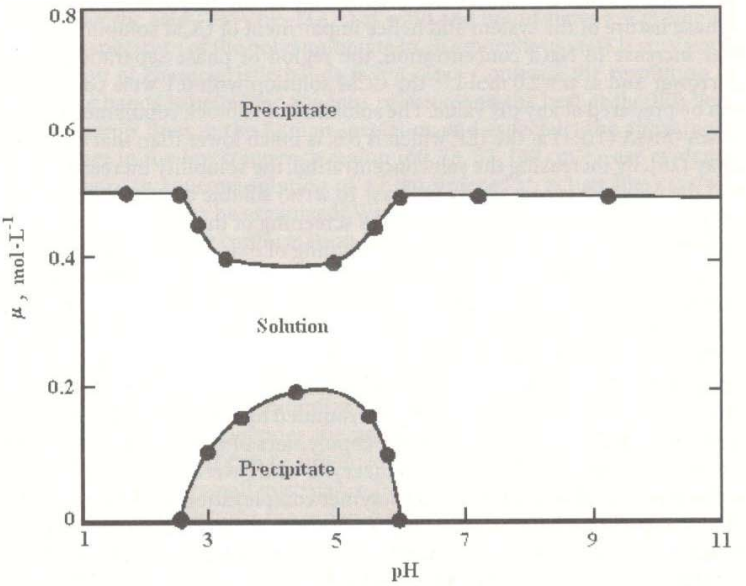


Fig. 6. Phase diagram of PMAA-*b*-P1M4VPCl (45:55 mol%) in aqueous salt solutions. C_{BPA} = 0.045 g·dL^{-1}

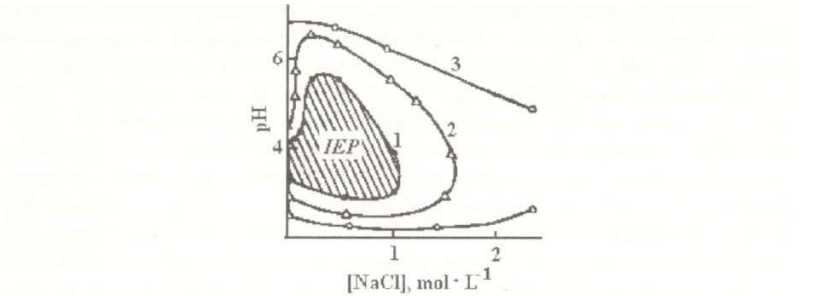


Fig. 7. Phase diagram of CCM-water-salt system as a function of the polymer concentration. C_p=0.05 (*1*), 0.1 (*2*) and 0.5 wt% (*3*)

ionic strength can be explained by the "salting out" effect. Figure 7 presents the phase diagram of chitosan carboxymethyl esters (CCM)/water/salt systems as a function of the polymer concentration, pH and ionic strength of the solution [50,51]. In the centre of the diagram, one can see an isoelectric region where the system is separated into two phases, one of which is solvent and the other a swollen precipitate of IPC. It can be seen from Fig. 7 that increasing the ionic strength up to 0.2–0.3 mol·L^{-1} causes the broadening of the boundaries of the heterophase nature of the system and hence impairment of CCM solubility. On a further increase in NaCl concentration, the region of phase separation becomes narrower and at μ >2.0 mol·L^{-1} the CCM solution with 0.1 wt% concentration can be prepared at any pH value. The solubility of triblock copolymer DMAEM–MMA–MAA (1:1:1) at the IEP, which is 6.6, is much lower than that one pH unit away [26]. By increasing the salt concentration, the solubility increases. At 0.9 M KCl the polymer is completely (at least 10 wt%) soluble even at the IEP. The increase in salt concentration leads to the screening of the attractions of acid and base blocks at the IEP and results in unfolding of macromolecules.

Triblock and random polyampholytes based on DMAEM–MMA–MAA were examined for their phase separation behaviour [52]. Triblock polyampholytes have a much broader phase separation region than the random ones. The specific structure of PMAA-*b*-P1M4VPCl with the excess of cationic or anionic blocks at the IEP is close to the structure of non-stoichiometric IPC. It is suggested that its nucleus consists of intraionic IPC surrounded by cationic blocks protecting it from precipitation [53]. ABC triblock copolymers of polystyrene-*block*-poly(2-(or 4)vinylpyridine)-*block*-poly(methacrylic acid) were synthesized by living anionic polymerization [53a]. Interpolymer complexation of the polyvinylpyridine and poly(methacrylic acid) blocks in the micellar solution was studied in relation to pH in solution by potentiometric, conductimetric and turbidimetric titration and in bulk by FTIR spectroscopy.

Light scattering data of random terpolymer and triblock copolymers DMAEM–MMA–MAA which have the same molecular weight 4000 and compo-

Table 5. Light Scattering Data for DMAEM–MMA–MAA (1:1:1) at pH = 5

Quasielastic light scattering			Static light scattering (Zimm plot)			
copolymer	d_h (Å)	Aggregation no.	M_w	A_2	d_g (Å)	Aggregation no.
random	40		5500			
triblock	110	21	125 000	+20.4	188	23

sition 1:1:1 are presented in Table 5 [26]. The molecular weight of the random terpolymer, as determined by static light scattering, is 5500±500, in reasonable agreement with the expected value of 4000, while the molecular weight of the triblock polymer, as determined by the same method, was found to be 125000±5000, which implies that aggregation occurs. The dependence of the hydrodynamic diameter of triblock polymer on pH shows that around the IEP big aggregates of size 100 nm are formed that are close to colloidal particles.

For self-concentrated aqueous solutions of polyampholytes it is possible to assume the existence of interparticle aggregates to account for the formation of high-ordered structures if polyampholytes are water-soluble at the IEP [54]. Raman spectra of equimolar copolymers of 1,2,5-trimethyl-4-vinylethynylpiperidol–4-methacrylic acid (TMVEP–MAA) at solid and liquid states are presented in Fig. 8. The spectrum of the polyampholyte in an amorphous state is very poor. The resolution of characteristic bands is not clear. Contrary, the resolution of characteristic bands is better for aqueous solution and the best at the IEP. Very sharp and narrow lines in the Raman spectrum, and especially the appearance of several lines in the low frequency region (60, 78, 87, 140 cm^{-1}), are evidence for the existence in aqueous solution of a high-ordered structure like crystals. How can such a structure be organized? When the amorphous copolymer is dissolved in water it takes the conformation of a Gaussian coil. Approaching the IEP compels the acidic and basic groups to interact and to form a globular structure stabilized by ionic contacts, hydrogen bonds and hydrophobic interactions. As a result very compact globular particles similar to the *secondary structure of proteins* are formed. These particles are protected from precipitation by zwitterions replaced on the surface of particles. At moderate concentration such globular particles tend to aggregate to minimize the surface energy (*tertiary structure*). At high concentration of polymer the aggregated macromolecules which are close to colloidal particles can be organized into the ordered crystalline structure. At the same time a small misbalance from the IEP to the acidic or basic region (pH=0.63±0.13) disturbs the ordered structure. The formation of a single crystal for colloidal silica particles as a result of "counterion-mediated attraction" was shown by Ise [55]. Figure 9 shows the SAXS curves for BSA at various pH including IEP [56]. When the solution is acidic or alkaline a peak is seen. However at the IEP (pH=5.06), the peak disappears, e.g. BSA forms an ordered structure in dilute solution.

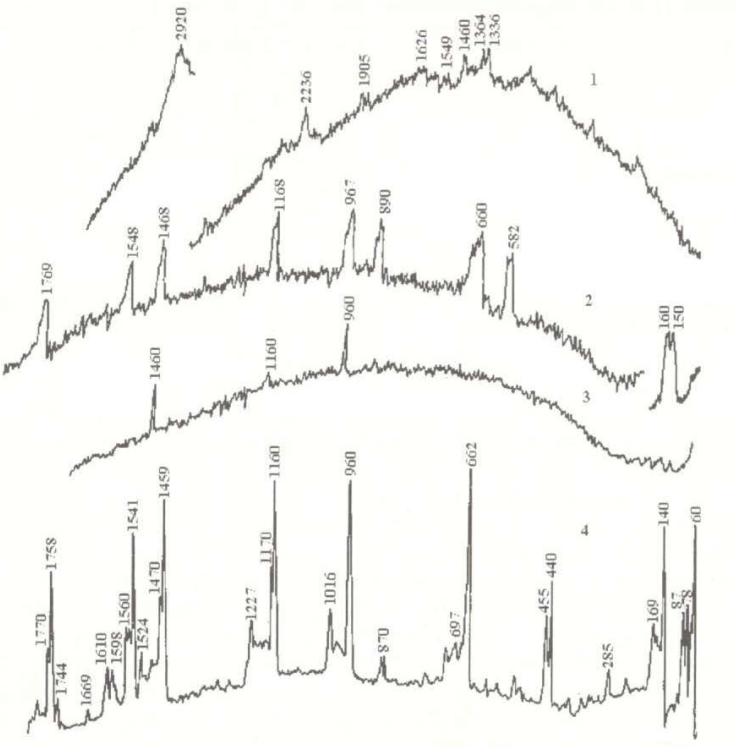


Fig. 8. Raman spectra of MAA–TMVEP in the solid state (*curve 1*) and aqueous solution (*curves 2–4*) at pH=7.5 (*curve 2*), 9.0 (*curve 3*) and 8.25 (IEP) (*curve 4*). C_p=5 g·dL^{-1}

It is also interesting to follow by the behaviour of hydrophobic polyampholytes. The influence of hydrophobic interactions on the solution properties of copolymers of α-olefins and mono-*N*-(3-dimethylaminopropyl)amide of maleic acid has been shown by Tanchuk et al. [32,33]. Especially unusual results were obtained from the dependence of the reduced viscosity on the temperature (Fig. 10). The reduced viscosity of PA-12 (see Table 1) increases with the increase in temperature and at T>340 K the solution transforms into a gel. The cooling of the system leads to the transformation of gel into the liquid state (sol-gel transition). Nature is successful with a large number of thermoreversible sol-gel transitions. For instance, agarose and gelatin undergo a gel-sol transition dependent on temperature. It is interesting to note that the model of amoeboid migration of cells on the surface is also associated with a cyclic sol-gel transition of the actin network [57] (Fig. 11).

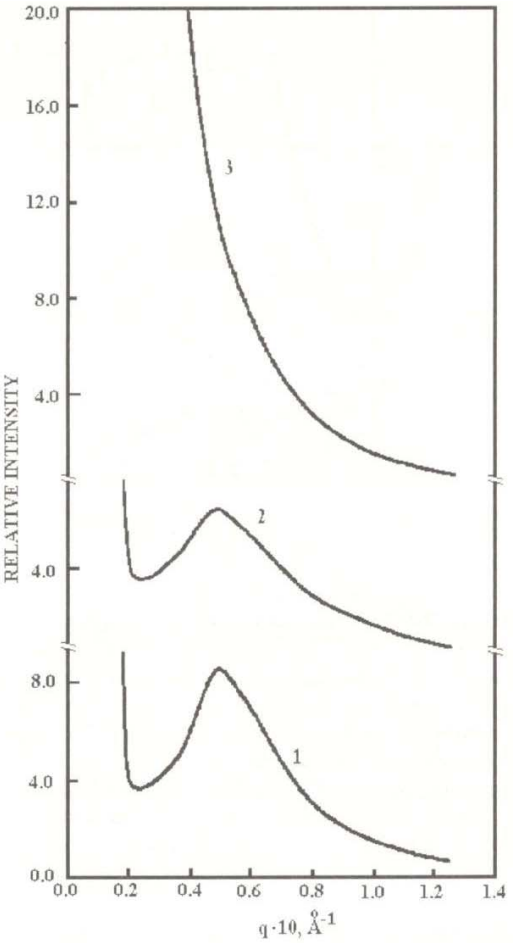


Fig. 9. SAXS curves of BSA at pH=10.94 (*curve 1*), 3.44 (*curve 2*) and 5.06 (*curve 3*). C_{BSA}= 0.075 g·dL^{-1} [55]

An appropriate balance of hydrophilicity and hydrophobicity in the molecular structure of polyampholytes is believed to be a key component in demonstrating the solubilization of organic probes and gelation properties [58]. The existence of hydrophobic clusters consisting of hydrophobic vinylbutyl ether (or styrene) fragments has been shown for alternating copolymers of vinylbutyl ether (or styrene) and *N*,*N*-dimethylaminopropylmonoamide of maleic acid

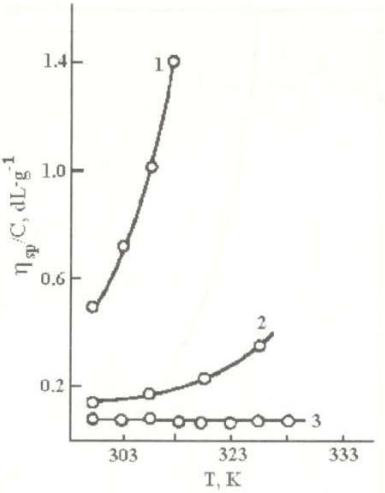


Fig. 10. Change in the reduced viscosity of hydrophobic polyampholyte in relation to the temperature. PA-12 (*curve 1*), PA-10 (*curve 2*), PA-8 (*curve 3*)

[59,60]. The maximal fluorescence intensity of 6-*p*-toluidino-2-naphthalenesulfonic acid was observed at the IEP of hydrophobic polyampholyte [59]. It can be suggested that at the IEP the long alkyl chains replaced inside of compact particles can form hydrophobic domain structures which enhance the solubilization of the organic probes. The macromolecules of hydrophobic polyampholyte PA-12 in aqueous solution near the IEP can also exist in the "helicogen" state by forming a hydrophobic core and a hydrophilic edge similar to natural polymers. At T >340 the formation of interpolyelectrolyte zwitterionic and hydrophobic contacts can take place which in turn cause the gelation of PA-12 (Fig. 12).

Table 6. Spin-Lattice Relaxation Time (T_1)and the Correlation Time (τ_c)Data of ^{14}N for 5 w/v% Aqueous Solutions at 25 °C

Polyampholyte	Without acids or salts		[HCl]/[Monomer]$_{av}$=1		KCl 1 M	
	T_1 (ms)	τ_c (ns)	T_1 (ms)	τ_c (ns)	T_1 (ms)	τ_c (ns)
PSN-25	5.5	0.63	4.3	0.80	4.5	0.77
PSN-50	6.0	0.57	5.5	0.63	4.6	0.75
PSN-75	7.3	0.47	5.5	0.62	4.6	0.75
PSN-100	8.0	0.43	7.2	0.48	6.5	0.53

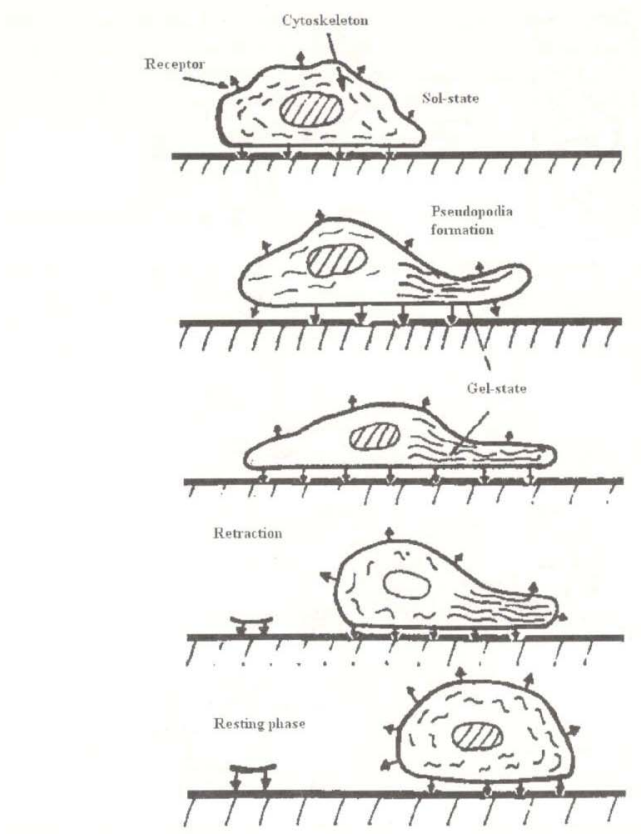


Fig. 11. Model of amoeboid migration of cells on the surfaces associated with cyclic sol-gel transition of the actin network [56]

In polyampholytes the interaction between charged macromolecules and surrounding low-molecular-weight electrolytes is important because the nature of these interactions plays an essential role in understanding the structure of polyampholytes on a molecular level. Authors [61] have reported the ^{23}Na, ^{35}Cl, and ^{39}K NMR relaxation rates and chemical shifts of amphoteric gel MAA-*co*-DMAMA under a variety of water contents and 1 M NaCl and 1 M KCl solution contents.

The dynamic mobilities of the cationic and anionic side chain of amphoteric copolymers of poly(sodium-2-methacryloyloxyethanesulfonate-*co*-2-methacryloyloxyethyltrimethylammonium iodide) (NaMES–METMAI) were estimat-

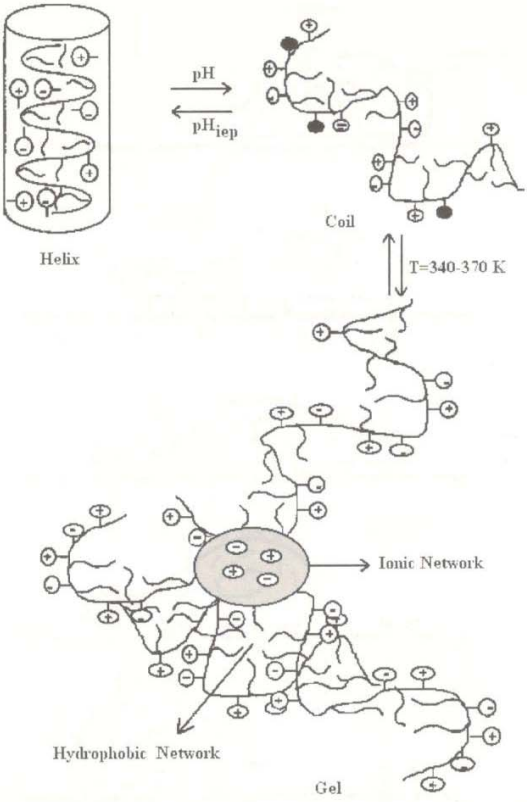


Fig. 12. Helix-coil and sol-gel transitions for hydrophobic polyampholyte PA-12 in relation to pH and temperature

ed with the quadrupolar ^{14}N NMR and ^{23}Na NMR relaxation techniques [62]. From Table 6 some important properties of the NaMES–METMAI copolymer series having the monomer feed ratios 3:1, 1:1, and 1:3 (named PSN-25, PSN-50, and PSN-75, where the numbers following PSN are the mole percents of METMAI in monomer mixtures) in aqueous solution can be ascertained. Firstly, T_1 times of ^{14}N decrease (τ_c becomes longer) as the component METMAI decreases. This means that the sulfonate component acts as a restriction environment to the trimethylammonium group by the attraction between them, and so slows down the motion of the trimethylammonium group. Secondly, τ_c of ^{14}N becomes longer when HCl or KCl is added to the aqueous solution of the PSN series. This

phenomenon is due to the aggregation of the copolymers caused by the charge masking effect of an acid or a salt. The motion of sodium ions studied by Poisson–Boltzmann electrostatic theories and quadrupolar ^{23}Na NMR shows that PSN-0 and PSN-25 behave as typical polyelectrolytes.

6
Colloidal Properties of Polyampholytes

The main peculiarities of phase separation of polyampholytes – random copolymers of 2M5VP-AA that are insoluble at the IEP – were considered by authors [63–65] from the colloid chemical point of view. Tables 7 and 8 summarize some physico-chemical characteristics of polyampholytes used. The surface tension σ, viscosity [η] and electroconductivity χ of PA-3 solution and dispersion are minimal at the IEP (Fig. 13). In the semilogarithmic coordinates the dependence of surface tension σ on lgC has breaking points. They correspond to the critical concentration of polyampholytes C_{crit} that reflects the saturation of the adsorption layer on the liquid-gas boundary. Near the IEP the value of the critical concentration of polyampholytes corresponding to the limited value of σ is low, the surface activity G and the fraction of precipitated particles Ω are also maximal (Table 9). The dependence of C_{crit} on pH can be used to account for the deterioration of solvent quality. At $C=C_{crit}$ the macromolecular coils tend to float from the volume to the liquid-gas surface; at $C < C_{crit}$ the macromolecules are in the

Table 7. Composition, Intrinsic Viscosity, Weight Average Molecular Weight and pH_{IEP} of 2M5VP–AA

Abbreviation	[AA] (mol%)	[η] ($dL \cdot g^{-1}$)	$M_w \cdot 10^{-3}$	pH_{IEP}
PA-1	21.3	1.30	200	6.0
PA-2	27.1	0.73	111	5.9
PA-3	43.0	0.90	-	5.4
PA-4	53.5	0.38	93	5.0
PA-5	66.0	0.28	-	4.35

Table 8. Some Narrow Characteristics of PA-3 Fractions

Abbreviation	[AA] (mol%)	[η] $dL \cdot g^{-1}$	$M_w \cdot 10^{-3}$	pH_{IEP}
PA-31	44.3	1.25	254.4	5.35
PA-32	42.8	0.89	134.3	5.42
PA-33	43.1	0.66	116.9	5.40
PA-34	44.2	0.38	55.1	5,35

Table 9. Influence of pH on C_{crit}, Surface Activity G and the Fraction of Precipitated Polyampholytes Ω^a

pH	5.1	5.2	5.4 (IEP)	5.5	5.75
C_{crit} ($g \cdot dL^{-1}$)	0.09	0.065	0.02	0.065	0.09
$G \cdot 10^3$ ($J \cdot m \cdot kG^{-1}$)	45	180	1110	205	52
W	0.7	1.0	2.8	2.1	0,8

[a] $G=-(\partial\sigma/\partial C)_{C\to 0}$; $\Omega=C_{PA}{}^{d}/C_{PA}{}^{s}$ where $C_{PA}{}^{d}$ is the concentration of polyampholyte in the disperse phase; $C_{PA}{}^{s}$ is the concentration of polyampholyte in solution.

compact and molecular dispersed state, at $C > C_{crit}$ the aggregation of compact particles takes place and the phase separation process occurs. It has been established that the average radius of particle r_λ, turbidity τ and the concentration of disperse phase are also maximal at the IEP of polyampholytes (Fig. 14). The dependence of the hydrodynamic diameter of triblock copolymer DMAEM–MMA–MAA (1:1:1) on pH appears in Fig. 15 [26]. Around the IEP big aggregates of size 100 nm form. At intermediate pH, smaller micellar aggregates of size 11 nm form. At extreme pH the strong electrostatic repulsions destroy the micelles and the polymer molecules occur in solution as separate chains.

The molecular weight and compositional heterogeneity of 2M5VP–AA copolymers having various molecular weights and composition have been studied by spectroturbidimetric titration [66]. The fractionation of copolymers in a mixture of methanol/toluene and methanol/diethyl ether leads to the precipitation

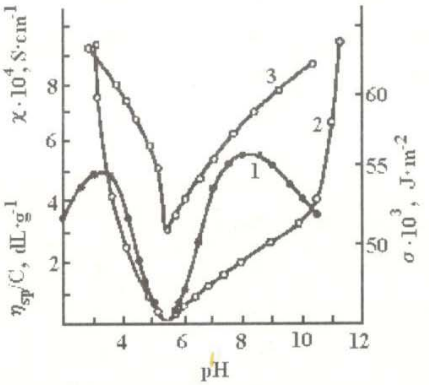


Fig. 13. Dependence of the reduced viscosity (*curve 1*), specific electroconductivity (*curve 2*) and surface tension (*curve 3*) of the solution and dispersion of PA-3 on pH. C_p=0.2 $g \cdot dL^{-1}$

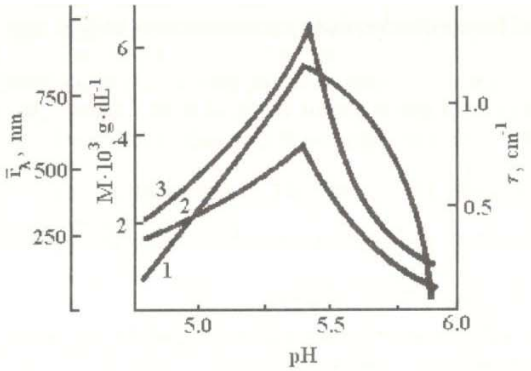


Fig. 14. Dependence of particles size (*curve 1*), concentration of precipitated polymer (*curve 2*), turbidity (*curve 3*) of PA-3 on pH of the solution. C_p=0.1 g·dL^{-1}

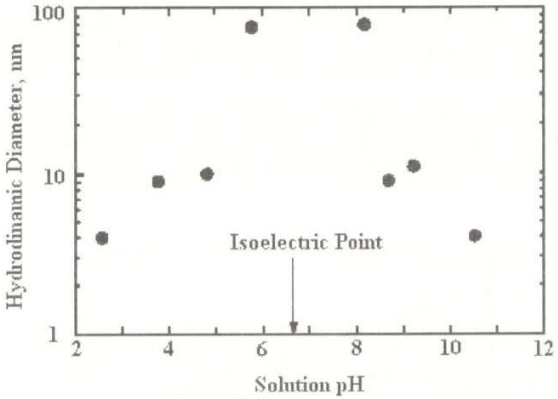


Fig. 15. Hydrodynamic diameter of triblock copolymer DMAEM–MMA–MAA (1:1:1) at different pHs with no added salt (Reproduced with permission from [26])

of polyampholytes by molecular weight and by composition, respectively. To establish the contribution of hydrophobic interactions to the stabilization of disperse particles near the IEP, the influence of simple electrolytes, dioxane, DMF and methanol has been studied. It has been shown that for stabilization of disperse particles of polyampholytes containing less than 25 mol% of AA groups, the hydrophobic interactions between methylvinylpyridine moieties are mostly responsible whereas for the other polyampholytes the driving force that stabilizes the disperse particles is the electrostatic attraction between acidic and basic monomers.

Association of Polyampholytes with Low-Molecular-Weight Ions

The complex formation problems of amphoteric copolymers with metal ions, detergents, dyes and organic probes is also of great interest. The interaction of metal ions M with polymeric ligands L proceeds as follow [67]:

$$M+L \Leftrightarrow ML;\ ML+M \Leftrightarrow ML_2;\ ML_{n-1}+M \Leftrightarrow ML_n$$

The stability constant of polymer–metal complexes β is equal to:

$$\beta_n = k_1\, k_2\, k_3 \ldots k_n = [ML_n]/[M]\,[L]^n$$

Function n, which characterizes the average number of ligands bound to metal ions, is determined from the equation:

$$n = \frac{[L]_t[LH]-[L]}{[M]_t}$$

where $[L]_t$ and $[M]_t$ are the total concentrations of ligand and metal ions; and [L] and [LH] are the concentrations of free (uncomplexed) and protonated ligands, respectively.

The concentrations of [L] and [LH] can be determined from the potentiometric titration curves of polymeric ligands in the absence and presence of metal ions. Figure 16 shows the complex formation curves for the system 2,5-dime-

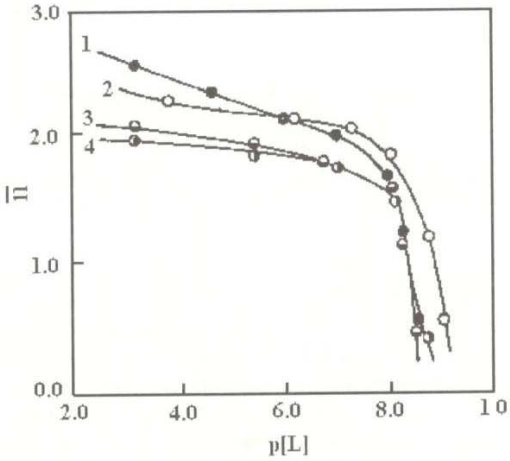


Fig. 16. Complex formation curves for the system DMVEP–AA/metal at μ=0.1 N $NaNO_3$. Cu^{2+} (*1*), Fe^{2+} (*2*), Co^{2+} (*3*), Ni^{2+} (*4*)

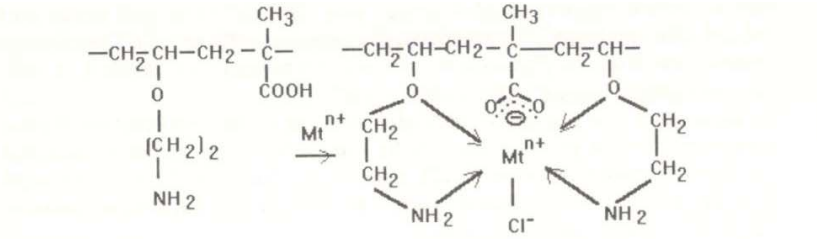
[68,69]. The number of monomeric units complexed with one metal ion is estimated as two from the plateau of the plot n vs. p[L]=–lg[L]. The stability of complexes is changed to $Cu^{2+} > Fe^{2+} > Ni^{2+} > Co^{2+}$.

Joanny and co-workers [70] presented a theory of the complexation of polyanions by divalent cations. The formation of both mono- and dicomplexes is possible. Monocomplexation locally inverts the charge of the polyelectrolyte and transforms it into a polyampholyte. The formation of a dicomplex creates a "bridge" between charged monomers.

Depending on the conditions polyampholytes are able to form several types of complexes and to involve either only acidic (or basic) or acidic and basic groups simultaneously. The chelate complex of Cu^{2+} with the maleic acid-*alt*-vinylamine includes one carboxylic and one amine group [71]. Multidentate polyampholytes, poly(*N*-propyleneglycine) (PPG), poly(1-isopropylcarboxylethyleneimine) (PIPCEI), poly(ethylenealanine) (PEA) are able to form five-membered chelate cycles [72]. The logarithm of complex formation constants lgβ of polyampholytes with respect to bivalent ions changes as follows: $Zn^{2+} > Ni^{2+} > Cd^{2+} > Co^{2+} > Pb^{2+} > Fe^{2+} > Ca^{2+} > Mg^{2+}$ and coincides well with the stability constants of EDTA (Table 10). 2M5VPy–AA can form several types of complexes with copper ions [73]. Analysis of the spectra indicates the existence of several types of complexes that are distinguished by the parameters $g_{\perp}$, $g_{\|}$ and $A_{\|}$. One, with $g_{\perp}=2.058$; $g_{\|}=2.334$ and $A_{\|}=136\cdot10^{-4}\,cm^{-1}$ corresponds to an **A**-type which is stable in the acidic region. The **A**-type complex belongs to cupric ions surrounded by two carboxylic groups with lgβ=7.1, but the line intensity of the **A**-type complex decreases when the pH is increased. In the neutral region pH=6–7.5, the appearance of the **B**-type complex with parameters $g_{\perp}=2.035$; $g_{\|}=2.298$ and $A_{\|}=157\cdot10^{-4}\,cm^{-1}$ occurs. The coordination number of the **B**-type complex in this region is equal to 4 with lgβ=21 that means two extra amino groups can be introduced into the coordination sphere of Cu(II) but the ESR lines of Cu(II) at pH=11.0 disappear. The behaviour of the system is reversible, e.g. the ESR lines appear again when the pH falls. The disappearance of an ESR signal can be ascribed to the formation of binuclear complexes stabilized by OH-bridges. The existence of "ESR undetectable copper" is also well known for copper-containing proteins ("blue" proteins).

Table 10. Stability Constants of Polyampholyte–Metal Complexes

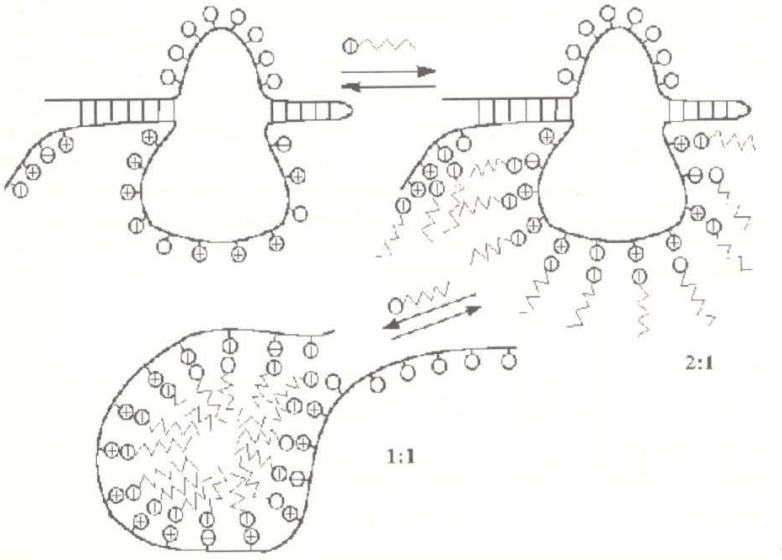
Poly ampholyte	Mg^{2+}	Ca^{2+}	Fe^{2+}	Pb^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Zn^{2+}
PPG	7.2	8.9	17.0	17.4	18.8	18.6	19.0	20.8
PIPCEI	–	–	13.8	13.3	18.8	18.5	19.2	20.8
PEA	7.6	8.9	17.4	16.3	17.6	–	–	–



Scheme a

The stoichiometry of the vinyl ether of monoethanolamine–methacrylic acid/copper(II) (VEMEA–MAA/Cu^{2+}) has been established [74]. A maximum of the dependence of the optical density on the molar ratio of the initial components (Job method) indicates the formation of one type of complex in the pH interval 6–9. The following structure for polyampholyte-copper has been suggested:

Similar to the interaction of individual polyacids and polybases with surfactants, cationic detergents form cooperative complexes with acidic groups of polyampholytes, and anionic ones with their basic groups [75–78]. The addition of detergents leads to considerable variation in pH, electroconductivity, turbid-



Scheme 1. Successive formation of poycomplexes between PMAA*b*-P1M4VPCl and DDSNa

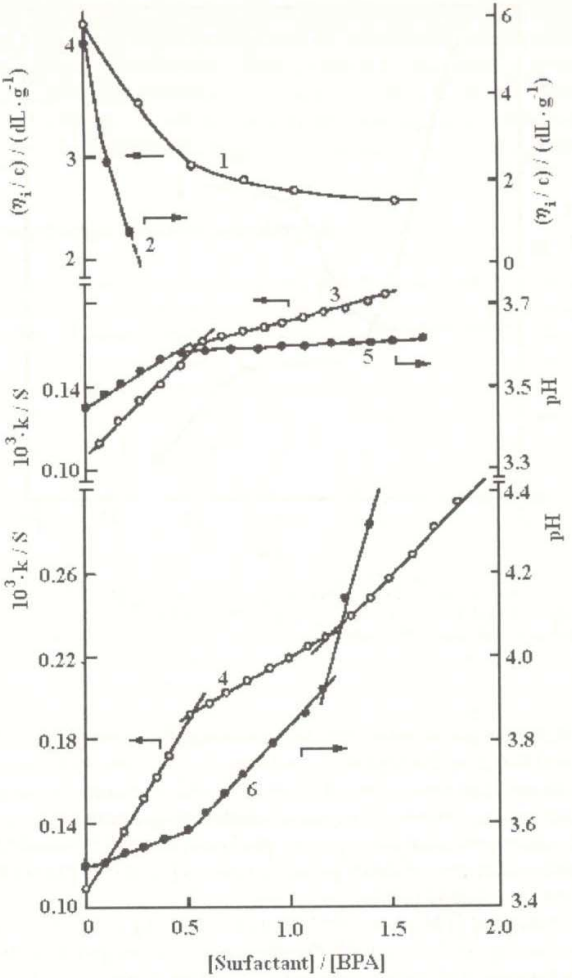


Fig. 17. Variation of reduced viscosity η_i/C (C_p=0.05 g·dL^{-1}) (*curves 1,2*), electroconductivity (*curves 3,4*) and pH (*curves 5,6*) on the composition of blockpolyampholyte/surfactant expressed as a mole ratio of repeating units of the active part of the blockpolyampholyte. [BPA]/[DDSNa] (*curves 1,3,5*), [BPA]/[CTMACl] (*curves 2,4,6*)

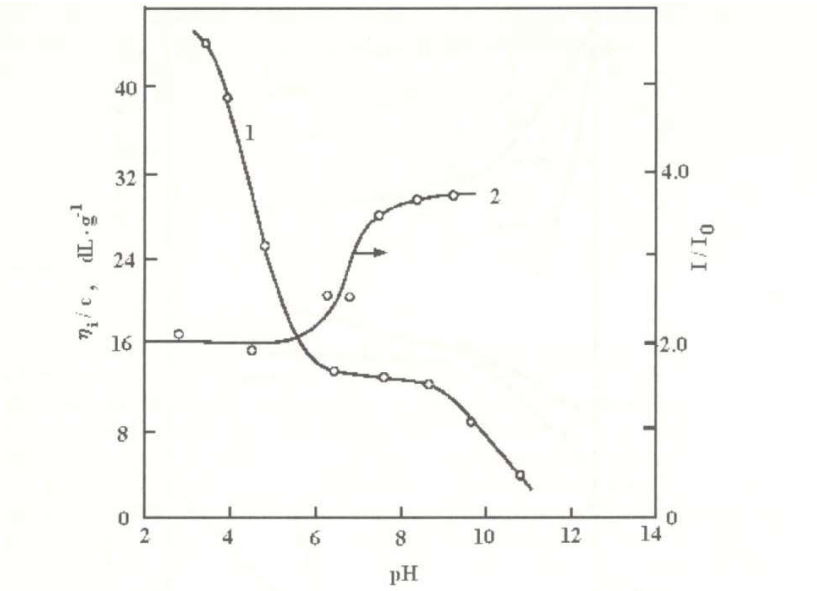


Fig. 18. Dependence of the reduced viscosity η_i/C (C_p=0.05 g·dL^{-1}) (*curve 1*) of block-polyampholyte and relative fluorescence intensity I/I_0 of ANS (*curve 2*) on the pH of the solution. [ANS] = $5 \cdot 10^{-5}$ mol·L^{-1}, λ=320 nm

ity and viscosity of the system. This is connected with the formation of compact particles stabilized by hydrophobic contacts of the long alkyl chain of detergents. These particles are preserved in solution with the help of noncomplexing components of copolymers. The potentiometric and conductimetric titration curves of nearly equimolar blockpolyampholyte (PMAA-*b*-P1M4VPCl) by DDSNa shows the formation of two types of complexes [PMAA-*b*-P1M4VPCl]/[DDSNa]=2:1 and 1:1 (Fig. 17) [79].

The formation of [PMAA-*b*-P1M4VPCl]/[DDSNa]=2:1 can be accounted for by the interaction of DDSNa with the free uncomplexed parts of the cationic block. The formation of the stoichiometric complex is due to the destruction of cooperative ionic contacts between acidic and basic blocks and replacement of them by new cooperative ionic contacts. The successive formation of polycomplexes between PMAA-*b*-P1M4VPCl and DDSNa can be represented by Scheme 1. For the system consisting of PMAA-*b*-P1M4VPCl and CTMACl the formation of [PMAA-*b*-P1M4VPCl]/[CTMACl]=2:1 only is observed. In this case the cationic groups of the surfactant cannot compete with the cationic groups of the blockpolyampholyte and interact only with the carboxylic groups placed on the "loops". Figure 18 shows the variation of relative fluorescence in-

tensity I/I_0 of 8-anilino-1-naphthalenesulfonic acid (ANS) and of the reduced viscosity of PMAA-*b*-P1M4VPCl vs. pH of the solution. A sharp decrease of the reduced viscosity over a small pH interval can be accounted for by the increase of intramacromolecular polyelectrolyte complex formation. The considerable increase of I/I_0 of ANS over pH 6–8 is probably the result of incorporation of dye molecules into the hydrophobic region of intramacromolecular complex.

8
Interpolymer Complexes of Polyampholytes

By now we have rather rich theoretical and experimental materials accumulated for interpolyelectrolyte complexes stabilized by cooperative ionic contacts and interpolymer complexes stabilized by hydrogen bonds. Little attention, however, has been paid to polymer–polymer reactions involving synthetic polyampholytes. The complexes of 2M5VPy–AA with PAA have been studied by various physico-chemical methods [80]. It has been established that the formation of a common cooperative system consisting of ionic and hydrogen bonds between the copolymer and PAA is realized. Authors [81] have considered the interpolyelectrolyte reaction between sulfo derivatives of chitosan – polyampholyte, containing amino and sulfo groups, and 2,5-ionene bromide. The turbidimetric titration curves of 2,5-ionene bromide by chitosan sulfate at pH=2.5 and 11.5 show that the composition of PEC is quite different in acidic and alkaline regions (Fig. 19). In acidic medium only half of the sulfate groups participate in the formation of the nonstoichiometric complex because the rest exist in the form of intramolecular PEC. In the alkaline region the composition of PEC is stoichiometric because all the sulfate groups are involved in the intermolecular PEC formation reaction. The competition between intra- and intermolecular ionic contacts is clearly seen from the comparison of ^{13}C NMR spectra of MDAA–MA and a mixture of MDAA–MA and PDMDAAC at pH=3.9 corresponding to pH_{iep} of the alternative polyampholyte [82] (Fig. 20) Peaks at 180.5 and 180.8 ppm correspond to carboxylate anions of MDAA–MA involved in intramolecular complexes while the shifting of the same peaks up to 181.3 and 181.8 ppm can said to account for the formation of intermolecular complexes between carboxylate anions of MDAA–MA and quaternary nitrogen atoms of PDMDAAC. At the same time at the IEP of DMDAA–MA (pH_{IEP}=4.1), the strength of intramolecular contacts between quaternary ammonium and carboxylate groups is higher than that between the intermolecular ones because the position of carboxylate anions of DMDAA–MA at 182.4 ppm does not change during the addition of PDMDAAC.

As distinct from the statistical and alternative ones, blockpolyampholytes are able to bind both polyacids and polybases as well as non-ionic hydrophilic polymers more cooperatively [83,84]. Figure 21 shows the potentiometric, conductimetric and viscometric curves of titration of PMAA-*b*-P1M4VPCl by PAA, PVBTMACl, PVPD and PEG. The composition of PEC was found from the bend of the curves. All PECs are water-soluble because they are protected from precip-

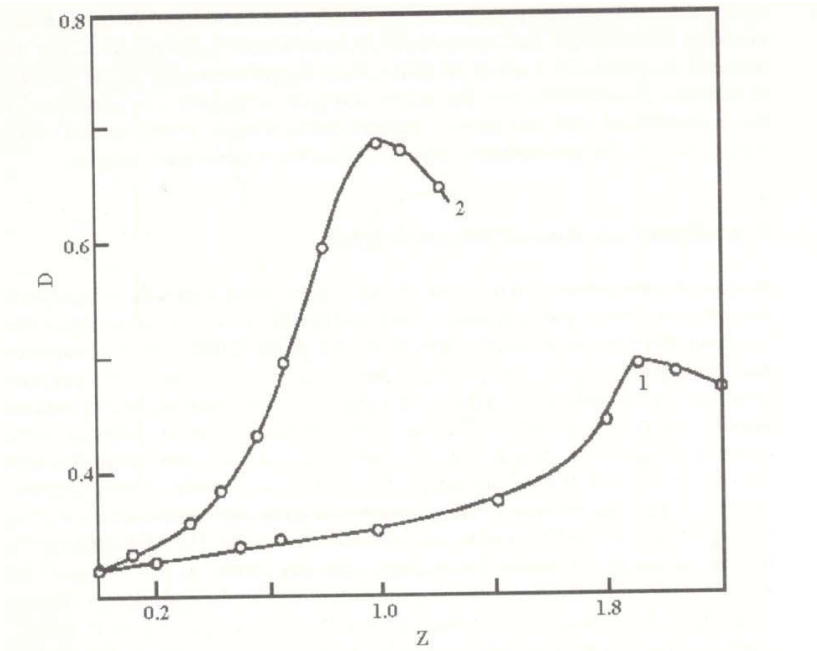


Fig. 19. Turbidimetric titration curves of 2,5-ionene bromide solution by chitosan sulfate (CS) at pH= 2.5 (*curve 1*) and 11.5(*curve 2*). [2,5-ionene]=5 · 10^{-4} mol·L^{-1}. Z=[CS]/[2,5-ionene]

itation with the help of free unloaded parts of PMAA-*b*-P1M4VPCl. The phase diagram of the system PMAA-*b*-P1M4VPCl/PVBTMACl in relation to PEC concentration and pH of the solution is seen from Fig. 22. At C_{PEC} >0.075 g·dL^{-1} PEC has a wide region of insolubility at the interval of pH=2–12. The opaque solution exists at pH >5.0 and C_{PEC} <0.075 g·dL^{-1}. The microgel structure is formed preferentially in the acidic region. Thus we have for this system three phases: solution, gel and precipitate which can be transformed into each other by changing either the PEC concentration or the pH of the solution. This behaviour of PEC can be explained by Scheme 2. At relatively high C_{PEC}, PEC particles aggregate and precipitate. At relatively low C_{PEC}, they are dispersed and form an opaque solution. The phase transition precipitate/microgel and opaque solution/microgel at low pH can be explained by the swelling of PEC particles as a result of suppression by the ionized carboxylic groups of the acidic block which are responsible for PEC formation. The gel formation process is accompanied by the release of a certain amount of PMAA "loops" which form interchain networks with the help of H-bonds.

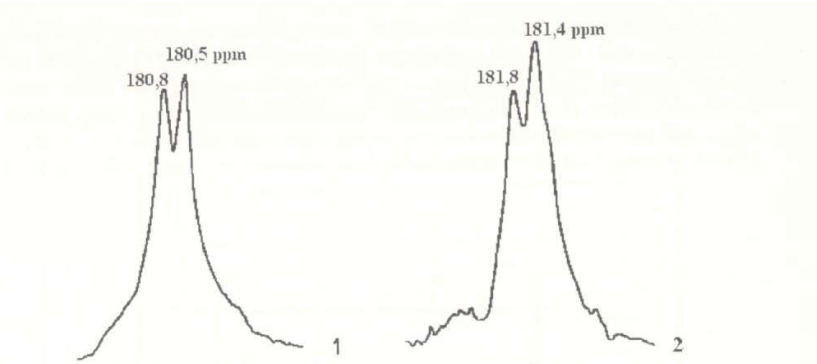
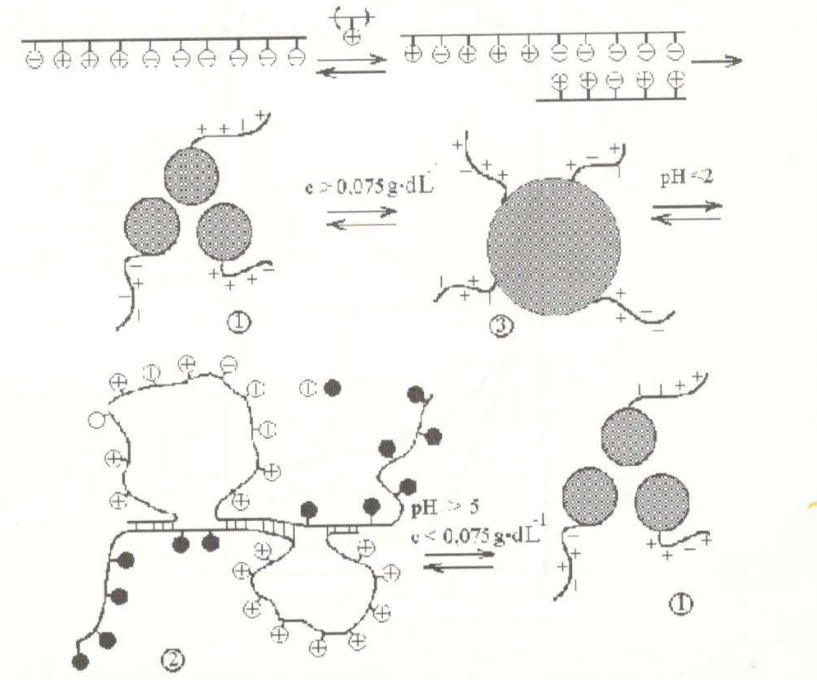


Fig. 20. ^{13}C NMR spectra of carboxylic groups of MDAA–MA (*1*) and a mixture of MDAA–MA and PDMDAAC (*2*) at pH=3.9 that corresponds to the pH_{IEP} of MDAA–MA



Scheme 2. Behaviour of polyelectrolyte complexes

The turbidimetric titration curves of 1-methyl-4-vinylethynylpiperidinol–4-methacrylic acid (MVEP–MAA) by HSA in aqueous solution at various pHs are shown in Fig. 23 [85]. The maximal values of turbidity correspond to the composition of polyampholyte–protein associates expressed as $n=m_{HSA}/m_{PA}$ (where m_{HSA} and m_{PA} are the mass fraction of HSA and the polyampholyte, respectively). As seen from Fig. 24, the most favorable region of interaction of HSA

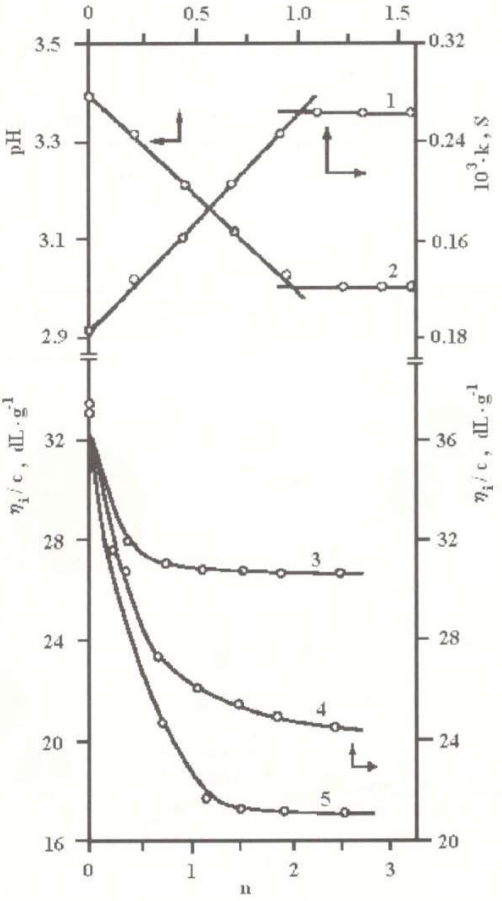


Fig. 21. pH-metric (*curve 1*) conductimetric, (*curve 2*), and viscometric (*curves 3–5*) titration of BPA by PAA (*curves 1,2*), PEG (*curve 3*), PVBTMACl (*curve 4*) and PVPD (*curve 5*). n=[BPA]/[homopolymer]

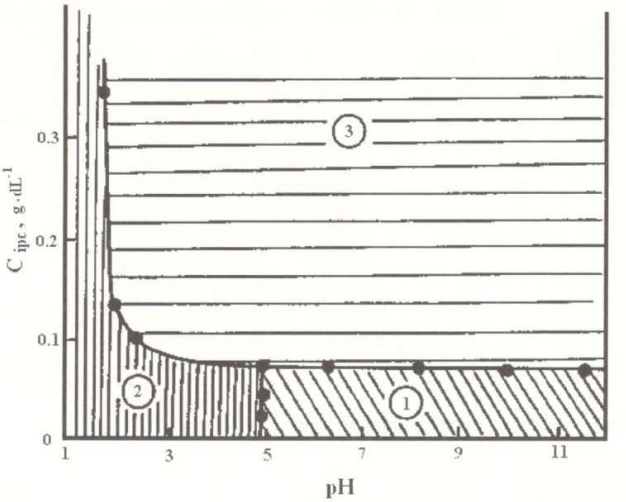


Fig. 22. Phase transition of PEC consisting of BPA and PVBTMACl in water. Opaque solution (*1*), microgel (*2*), precipitate (*3*)

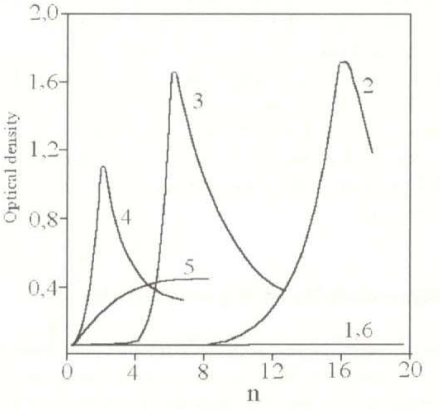


Fig. 23. Turbidimetric titration curves of MVEP–AA by HSA in water at pH=5.1 (*1*), 6.2 (*2*), 7.1 (*3*), 8.5 (*4*), 9.1 (*5*), 10.0 (*6*). $n=m_{HSA}/m_{PA}$

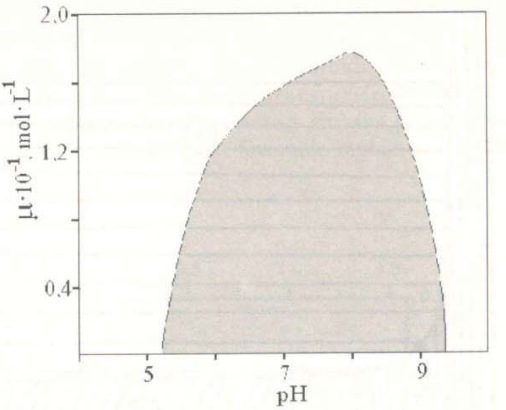


Fig. 24. Stability region of polyampholyte–protein associates

(pH_{IEP}=5.4) and MVEP–MAA (pH_{IEP}=9.4), as also noted by other authors [86], arranges between their isoelectric points. Increasing the ionic strength of the solution makes the association interval of pH narrower.

The complexation behaviour of proteins with dilute solutions of PAA and a random polyampholyte DMAEM–AA–MMA was studied by turbidimetric titration [87]. Polyampholyte–polyampholyte interaction (self-aggregation) and polyampholyte–protein complexation was studied as a function of pH and polymer dosage. Large increases in turbidity were observed for polyampholyte–protein mixtures compared with polyampholyte alone. However, protein analysis of the supernatant and precipitate revealed that only about 10% of the protein precipitates with the random polyampholyte while 90% of the protein remains in the equilibrium liquid. An experiment with PAA and oppositely charged protein shows the opposite trend with 90% precipitation of protein. Hence, great care needs to be taken in the interpretation of turbidimetric titration data. It has been reported that polyampholyte-protein associates behave with lowered immunogenic activity [88].

9
Adsorption of Polyampholytes on Disperse Particles

Regulation of the physico-chemical properties of colloid dispersions by polyelectrolytes is of great interest from the theoretical and practical points of view [89]. A consideration of the peculiarities of absorption of polyelectrolytes on disperse particles can be of help to clarify some aspects of kinetics and mechanism of flocculation, elemental acts of flocculation, as well as to provide the se-

Table 11. Survey of Polyampholytes Employed

Polyampholyte	$Mw \cdot 10^{-3}$	Mole ratio acid/base	pH_{IEP}	Solubility at the IEP*
AA/2M5VP	170	1:1	5.1	S
	–	3:1	4.2	I
AA/VI	20	1:1.3	5.4	S
AA/DMVEP	200	1:1	4.1	S
	100	2:1	4.5	S
MAA/TMVEP	250	2.5:1	5.0	I
PMAA/P1M4VPC	200	1:1.2	5.5	I

*) S: Soluble; I: Insoluble.

lective flocculation of polydisperse particles. The adsorption of HSA, ribonuclease [90,91] and immunoglobulin (IG) [92] on the polystyrene latexes (PSL) was investigated. It has been shown that the maximal adsorption is observed at the IEP of proteins. The influence of synthetic polyampholytes on the stability of cells *Candida lambica* has been investigated [93]. It was established that the decrease of optical density of the system is the result of aggregation of cells due to the simultaneous adsorption of charged macromolecules on several cells. An

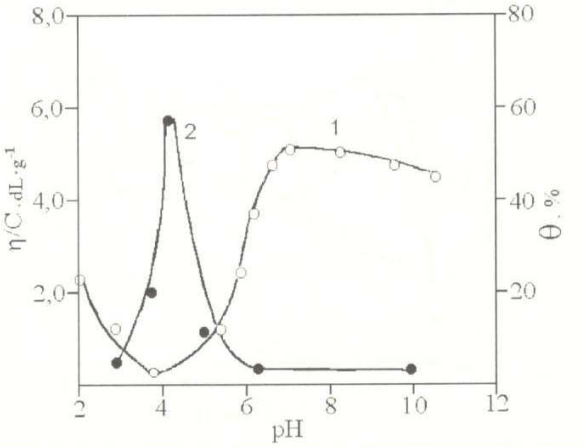


Fig. 25. Dependence of the reduced viscosity of AA/DMVEP (*curve 1*) and the binding degree (θ) of PSL by AA/DMVEP (*curve 2*) on pH of the solution. [AA/DMVEP]=$4.5 \cdot 10^{-3}$ mol·L^{-1}

equation which describes the kinetics of the coagulation process has been found. However, concerning the interaction of synthetic polyampholytes with disperse particles, there is no available information in the literature except for experiments performed by Blaackmeer [94] and Ouali et al. [95]. Joanny [96] has studied theoretically the adsorption of a single random polyampholyte chain on a charged planar surface mimicking the latex particle. His concluding remarks are in good agreement with our experimental results performed recently on the interaction of synthetic polyampholytes with colloid dispersion [97]. Table 11 represents some characteristics of polyampholytes applied for flocculation of disperse particles.

Figure 25 shows the influence of polyampholyte conformation on the binding degree of PSL at various pH. The maximal binding degree takes place at the IEP of AA–DMVEP and coincides well with the behaviour of proteins mentioned elsewhere [90–92].

The dependence of the optical density (A) of PSL on the concentration of various types of polyampholytes is presented in Fig. 26. The flocculating effectiveness of polyampholytes is arranged as follows: PMAA-*b*-P1M4VPCl >AA–VI >MAA–TMVEP >AA–DMVEP and is in good agreement with the sequence of their electrokinetic potential (Fig. 27). The kinetics of flocculation of PSL allow the evaluation of the magnitude of the retardation factor W which characterizes

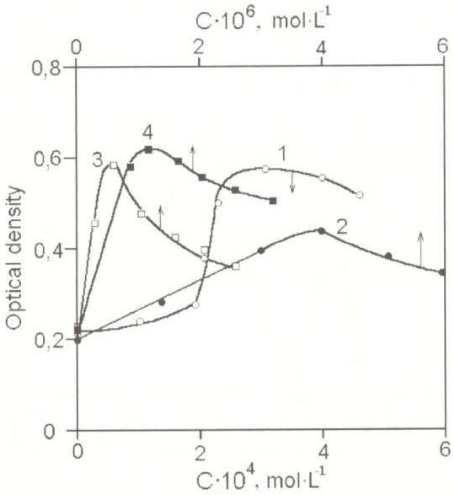


Fig. 26. Dependence of the optical density (D) of PSL on the concentration of added polyampholytes: AA/DMVEP (*curve 1*), MAA/TMVEP (*curve 2*), PMAA-*b*-PMVP (*curve 3*), AA/VI (*curve 4*)

the decrease in the rate of process in comparison to the fast coagulation and is related to the potential energy of interaction U by Eq. 9.1 [98]:

$$W = 2a\int_{2a}^{\infty} \exp\left(U/kT\right)R^{-2}dR \tag{9.1}$$

where a is the radius of particles; k is the Boltzmann constant; T is the absolute temperature; and R is the distance between the particles centres. The factor W can be calculated from the optical density A by Eq. 9.2 [98]:

$$(dA/dt)_{t\to 0} = \frac{Bk_0C_L^2}{2{,}303W\rho^2} = \frac{k'C_L^2}{2{,}303W} \tag{9.2}$$

where ρ is the density of latex particles; $C^2{}_L$ is the concentration of latex particles in g · mL^{-1}; B is the optical constant; k_o is the rate constant of fast flocculation and $k'=Bk_0/\rho^2$.

Since for the same latex particles the values of B, k_o and ρ are constant, the magnitude of k' can be determined from Eq. 9.2 at W=1, e.g. in the region of fast flocculation, while k' is constant for each flocculant and does not depend on the concentration of the system. As seen from Fig. 28 the retardation factor W changes over a wide range of polyampholyte concentration and the theoretical

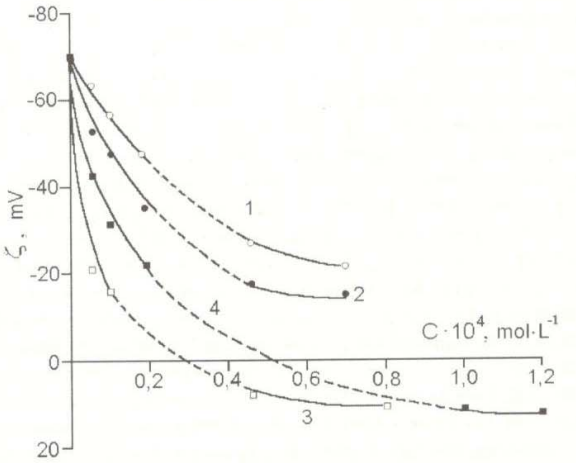


Fig. 27. Variation of the electrokinetic potential of PSL particles on the concentration of polyampholytes: AA/DMVEP (*curve 1*), MAA/TMVEP (*curve 2*), PMAA-*block*-PMVP (*curve 3*), AA/VI (*curve 4*). The dotted lines correspond to lack of stability of PSL

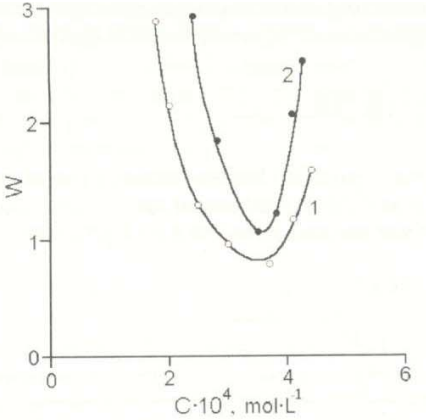


Fig. 28. Dependence of the stability factor of PSL (W) on the concentration of AA/DMVEP. *1* – experimental results, *2* – theoretical calculations

curve does not fit with the experimental one. These results show that another mechanism can be realized that leads to the destabilization of the disperse system in spite of the high energy of the double electric layer which stabilizes the system by electrostatic mechanism. It has been supposed that the flocculation of PSL can be explained by formation of "bridges" between latex and polyampholyte particles [99]. At the same time it is also necessary to take into account the possibility of heterocoagulation as a result of unproportional adsorption of polyampholytes on the surface of PSL leading to the appearance of nonproportional charges and potential on the latex particles.

A comparison of surface area of PSL and macromolecular coils, accepting that the latter is spherical at the IEP, shows that the polyampholyte molecules in dependence of their nature can theoretically involve in the flocs about 28–60 latex particles (Table 12). However, in the case of polyampholytes, the amount of latex particles involved in the flocs is much higher than that theoretically calculated. These data cannot be explained either by DLVO theory [100] or "bridge" or heterocoagulation mechanisms [101]. The mechanism of adsorption of polyampholytes on latex particles can successfully be explained in the framework of theoretical results performed by Joanny [96]. According to Joanny, the polyampholyte solution can adsorb even if its overall charge has the same sign as that of the latex particles. Two cases where the interaction between functional groups of polyampholytes is short range (strongly screened) and long range (unscreened) are considered. For short-range interactions, Joanny, using the replica trick and a Hartree approximation, showed that the adsorption of the chain is

Table 12. Aggregation of PSL by Polyampholytes at Their pH_{IEP} [a]

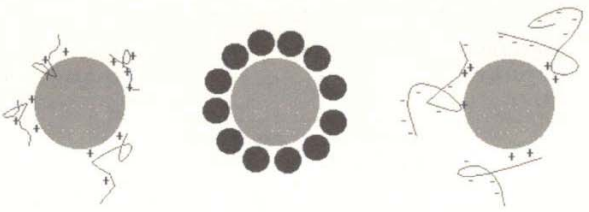
Floc culant	Flocculation effectivity (%)	Number of flocs		Degree of aggregation	Flocculating concentration 10^{-4}mol·L^{-1}
		theoretically calculated	experimentally found		
AA/DMVEP (1:1)	94	60	154	5.6	6–10
MAA/TMVEP (1:1)	65	36	1452	2.2	0.2–0,4
AA–2M5VP (1:1)	92	28	1044	1.8	0.3–0,5
AA–2M5VP (1:3)	82	32	664	3.4	2–4,7

[a] The numerical concentration of latex particles is equal to $4.63 \cdot 10^{17}$ particles/m^3

possible even if it has the same net charge as the surface and if the interaction potential is larger than a critical value, i.e.:

$$V_c = \log\frac{f}{g} \tag{9.3}$$

where V_C is the adsorption threshold; and f and g are the fraction of monomers having, respectively, the same charge and the opposite charge as the surface. If the overall charge of the adsorbing chain is opposite to that of the surface, there is no adsorption threshold ($V_C < 0$). When the total charge is small, which is realized at $f/g \approx 1$, the value of V_C is small. When $f=g$ there is no adsorption threshold, the chain always adsorbs even though the average potential acting on the monomers vanishes. The latter is interpreted as follows: when the monomers oppositely charged to the surface monomers are in contact with the surface, the monomers having the same charge as the surface do not feel the repulsive potential which is assumed here to have an infinitely short range. In other words, for short-range interactions, the redistribution of the charges of the polyampholyte on the surface of charged disperse particles takes place and an entropy penalty must be overcome. It is important to note that, even if the chain is on average repelled by the surface ($f > g$), it can adsorb if the interaction potential V is large enough. Taking into consideration the concluding remarks of Joanny, one can propose the mechanism of interaction of polyampholyte solutions with PSL and suggest the next structure of latex–polyampholyte associates.



Scheme b

The decrease of flocculation effectiveness of polyampholytes on both sides of pH_{IEP} with respect to negatively charged latex particles can be explained by the adsorption of positively charged parts of polyampholytes that protect the floc formation owing to the presence of positively or negatively charged loops dangling on the surface of particles. The continuous contact of polyampholyte molecules (concentration is equal to 0.1 $g \cdot L^{-1}$) with PSL (size of PSL is 120 nm) from 15 min to 24 h increases the value of specific adsorption (Γ) of polyampholytes from 1 to 10 $mg \cdot g^{-1}$. According to Gregory [101] the interaction of polymers with dispersions consists of several stages: a) distribution of macromolecules among the particles; b) adsorption of polymer segments on the surface of particles; c) redistribution of adsorbed chains, e.g. the transition of macromolecular conformation from the initial state to equilibrium; and d) the collision of complex particles with floc formation. Table 13 summarizes the kinetic parameters of adsorption of polyampholytes calculated according to Gregory [101]:

$$k_{1,2} = (2kT / 3\eta)(r_1 + r_2)^2 / r_1 r_2 \tag{9.4}$$

where $k_{1,2}$ is the adsorption constant rate; k is the Boltzmann constant; T is absolute temperature; η is the viscosity of the medium; and r_1 and r_2 are the radius of the latex particles and the polyampholyte coils, respectively. The time t_A that is necessary for adsorption of polyampholyte, f, can be find from Eq. 9.5 suggesting that the concentration of latex particles in the system N_1 is constant and the adsorption rate constant $k_{1,2}$ does not depend on the degree of covering of the surface by polyampholytes.

$$t_A = -\ln(1 - f) / k_{1,2}\, N_1 \tag{9.5}$$

Equation 9.5 represents a rough approximation because both the number of particles and the sum of surface should decrease in the course of adsorption leading to a decrease of $k_{1,2}$. Nevertheless, it allows the calculation of the minimal time which is necessary for adsorption of part of the polyampholytes. From Table 13 it follows that the time taken to adsorb 90% of the polyampholyte reaches 32 s; 50% and 10%

Table 13. Kinetic Parameters of Adsorption of DMVEP–AA by PSL Calculated according to Eqs. 9.4 and 9.5

r_1 PSL (m)	r_2 PA (m)	N_1 particles/m^3	$k_{1,2}$ m^3/s	f (%)	t_A (s)
$6 \cdot 10^{-8}$	$2.1 \cdot 10^{-7}$	$4.63 \cdot 10^{17}$	$1.56 \cdot 10^{-19}$	90	32
				50	9,6
				10	1,46

take 9.6 and 1.4 s, respectively. But the calculated values of t_A are much less than those experimentally observed. For instance to reach the specific adsorption of polyampholytes corresponding to approximately half of Γ_∞ on latex with r=60 nm ($mg \cdot g^{-1}$ over 24 h) it is necessary to spend 20 min. Even to reach 10% adsorption more than 3 min is needed, which is significantly higher than the theoretically predicted value of Γ. Thus the adsorption of polyampholytes by latex particles is not determined by the diffusion of macromolecules to the surface. It could be that the redistribution of adsorbed macromolecules in relation to time is the main factor leading to the displacement of small disperse particles by large ones. The diffusion process proceeds faster and is completed in several seconds dependent on the size of the particles while the redistribution process proceeds slower (from several minutes to

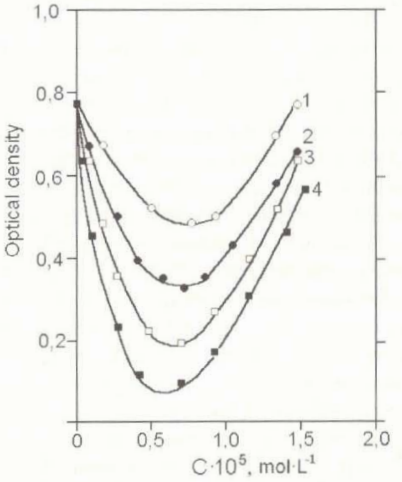


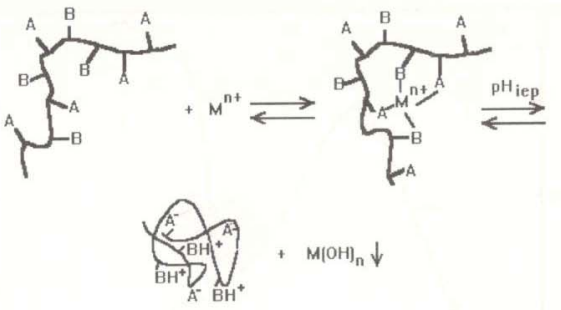
Fig. 29. Dependence of the optical density of barite suspension on the concentration of AA/2M5VP with pH_{IEP}=4.2 (*curves 1–3*) and AA/2M5VP with pH_{IEP}=5.1 (*curve 4*). The fixed time from the precipitation of dispersion is 10 (*curve 1*), 20 (*curve 2*) and 30 min (*curves 3,4*)

several hours) and leads to significant growth of specific adsorption. The marked peculiarities are to be taken into account during the flocculation of latex particles by polymers when the contacting time of macromolecules with dispersions is limited by minutes. The stability of mineral suspension – barium sulfate in the presence of AA/2M5VP – passes through the minimum (Fig. 29). In contrast to latex particles, barite suspension has a rough dispersity. The minimal concentration of polyampholytes causing the flocculation of $BaSO_4$ corresponds to $3–6 \cdot 10^{-5}$ mol·L^{-1}. The addition of polyampholytes at first leads to the aggregation of mineral particles and sedimentation. Therefore, the optical density of the system gradually decreases. A further increasing of the optical density corresponds to the formation of stable disperse particles. At the same time the optimal concentration of one-, two- and three-valent cations (Na^+, Ca^{2+}, Y^{3+}) leading to flocculation of mineral suspension is equal to $20 \cdot 10^{-4}$, $8 \cdot 10^{-4}$ and $1 \cdot 10^{-4}$ mol·L^{-1}, respectively. The optimal size of flocs can be formed only at a definite ratio of concentration of polymers and solid phase. Therefore the dependence of the sedimentation velocity of particles on the concentration of polymers is extremal.

10
"Forcing Out" Phenomenon at the Isoelectric Point of Polyampholytes

At the IEP electrostatic attraction forces between oppositely charged groups are so high that they are condensed into a compact globule squeezing out the solvent. "Force out" phenomenon taking place only near the IEP was at first noted by our research group and afterwards was confirmed by several scientific centres. The main idea of this phenomenon comes from the fact that any low- or high-molecular-weight substances associated with polyampholytes can be released at the IEP as a result of a competition between inter- and intramolecular interactions. In other words if the cooperativity of intrachain interaction of acidic and basic groups within a single macromolecule predominates over those for interchain interaction such phenomenon can be realized. A simple example of this effect is the detachment of amino acids at their zwitterionic or isoionic states from the surface of ion-exchange resins that are applied for separation and analysis of amino acid sequences of proteins. Amphoteric ion-exchangers also act in the same way during the desorption and elution of preliminary absorbed low- and high-molecular-weight ions from the polymeric matrix. However, the realization of "forcing out" phenomenon for a series of water-soluble polyampholytes has been demonstrated by our research group. We have found that these types of polyampholytes are able to bind metal ions, dye molecules and polyelectrolytes at definite pH values and release them quantitatively at the IEP [102–104]. Sorption and desorption processes of transition-metal ions by such polyampholytes can be represented as follows (Scheme c):

If the IEPs of polyampholytes are displaced in the alkaline region, transition metal ions are precipitated in the form of hydroxide and the polyampholyte is found in the solution and can be recovered and used several times. It is interesting to note that a similar effect was observed for a ternary poly(acrylic acid)–



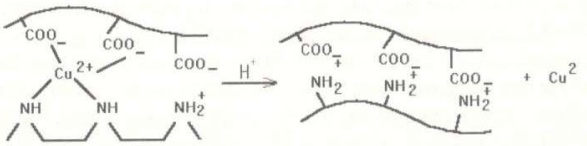
Scheme c

copper(II)–poly(ethyleneimine) system (PAA–Cu^{2+}–PEI) [105]. At definite pH, the displacement of nitrogen–metal coordination bonds and carboxylate–metal ionic bonds by the cooperative polyacid–polybase contacts can probably lead to the precipitation of polyelectrolyte complexes and retaining of metal ions in the supernatant as shown below (Scheme d):

Earlier [106–108] the amphoteric character of the PEC particle dispersion with the IEP, characterized by zero mobility and a minimum in the reduced viscosity, was shown.

The dependence I/I_0 of 1-anilino-8-naphthalensulfonic acid (ANS) and acrydine yellow (AY) bound to DMVEP–AA (pH_{IEP}=7.0) on the pH of the solution is shown in Fig. 30. The maximal value of I/I_0 for ANS at pH=4 is the evidence for the binding of negatively charged dye molecules with cationic parts of polyampholyte. A marked decrease of I/I_0 for ANS and sharp increase for AY near the IEP, approaching those for the ANS and AY solutions alone, can be explained by the release of dye molecules from the macromolecular coils of the polyampholyte. The existence of "forcing out" phenomenon was clearly shown for systems consisting of polyampholyte and anionic or cationic polyelectrolytes [102]. The composition of PEC determined from the breaks of the potentiometric, conductimetric and turbidimetric curves is equal to [polyampholyte]/[polyelectrolyte]=3:1.

Figure 31 shows the pH dependence of the reduced viscosity for the individual components and PEC. Phase separation of products composed of polyam-



Ternary PAA–Cu^{2+}–PEI complex → PEC precipitates

Scheme d

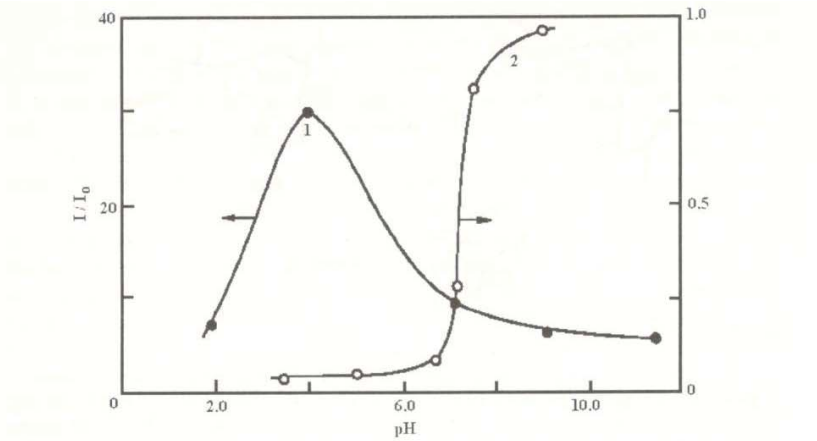
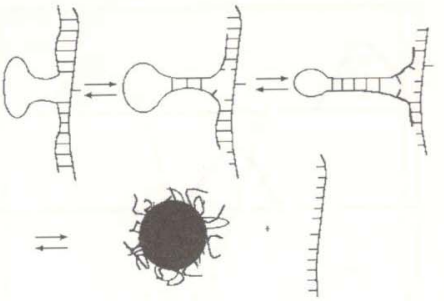


Fig. 30. Dependence of the fluorescence intensity (I/I_0) on pH for the systems polyampholyte–ANS (*curve 1*) and polyampholyte–AY (*curve 2*)

pholyte (DMVEP–AA) and polyacid (PAA) occurs at 3.0< pH <5.5; for PEC consisting of polyampholyte (DMVEP–AA) and cationic polyelectrolyte (PDMDAAC), this process takes place at pH >8.2. Attention should be paid to the fact that near the IEP of DMVEP–AA (pH_{IEP}=7.0), the reduced viscosity of PEC is sharply increased. The only reasonable explanation of this fact is the destruction of PEC particles into individual components. Since the value of reduced viscosity of DMVEP–AA is much lower, near a pH=7, the main contribution to the viscosity should come from the viscosities of anionic or cationic polyelectrolytes.

To confirm a cooperative destruction of PEC particles near the IEP, independent sedimentation experiments were carried out. Figure 32 shows the sedimentation diagrams of DMVEP–AA, PAA and PEC at various pH. The sedimentograms of PEC show one peak with S=4.75 and 4.18 at pH=6.1 and 6.9, respectively. However at pH=7.1 two peaks with S=1.9 ("slow" peak) and 5.6 ("fast" peak) appear on sedimentograms. At the same time the sedimentation coefficients of separate components DMVEP–AA and PAA at pH=7.2 are equal to 3.53 and 1.06, respectively.

The appearance of slow and fast sedimentation peaks at a narrower interval of pH (ΔpH=0.2) change is the result of PEC particle destruction into the individual macromolecules. The structure of PEC composed of polyampholyte and polyelectrolyte can be represented as double-strand sequences of pairs formed with the help of cooperative systems of ionic and hydrogen bonds. Probably near the IEP, some acidic and basic groups of polyampholytes displaced on loops begin to interact with each other cooperatively with the formation of intramolecular complexes. The mechanism of PEC destruction can be represented as follows:



Scheme e

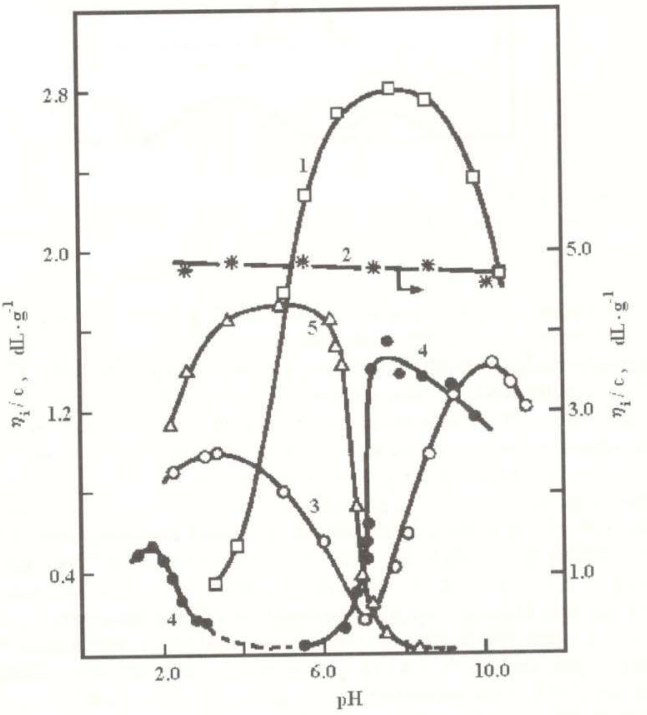


Fig. 31. Influence of pH on the reduced viscosity of PAA (*curve 1*), PDMDAAC (*curve 2*), DMVEP–AA (*curve 3*) and polyelectrolyte complexes composed of DMVEP–AA/PAA (*curve 4*), DMVEP–AA/PDMDAAC (*curve 5*) in water

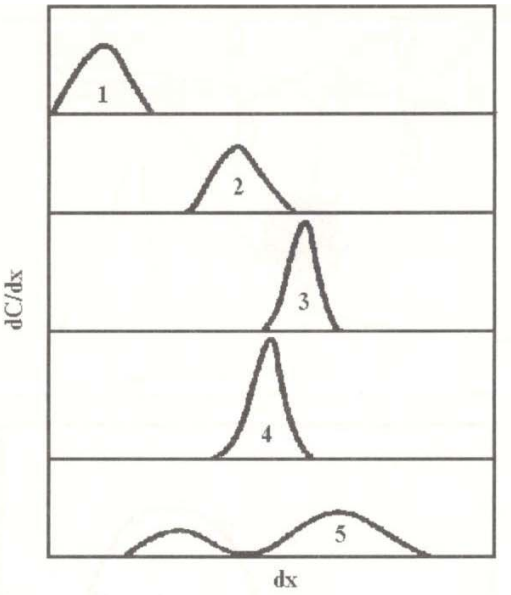


Fig. 32. Sedimentograms of DMVEP–AA (*curve 1*), PAA (*curve 2*) and polyelectrolyte complexes composed of [DMVEP–AA]/[PAA]=3:1 (*curves 3–5*) at various pH in aqueous solution

The dependence of PEC yield on pH shown in Fig. 33 can also serve as additional confirmation of validity of the proposed mechanism [109]. The separate titration curves of polyampholyte by sodium poly(styrenesulfonate) (SPSS) and poly(*N*,*N*-dimethyldiallylammonium chloride) (PDMDAAC) intersect at the IEP where the yield of PEC is also equal to zero. Recently, the realization of the "forcing out" effect in relation to polyampholyte–surfactant complexes was demonstrated [110]. In contrast to the system considered above in the case of polyampholyte–surfactant complexes, polyampholytes (2M5VP–AA, DMAEM–MAA and DEAEM–MAA) at the IEP themselves precipitate and surfactant molecules (CTMA) remain in solution. The phase formation process or "phase rejection" proceeds as avalanche-like. An analysis of precipitate and supernatant shows that the disperse phase is only polyampholyte and the soluble part is pure surfactant. It is interesting to note that the precipitated (after destruction of polycomplexes) polyampholyte 2M5VP–AA becomes insoluble in the alkaline region although the initial polyampholyte itself shows a good solubility in alkaline medium. In other words the "forcing out" effect probably causes the rearrangement of the initial conformation of polyampholyte. The insolubility of polyampholyte particles in the alkaline region can be accounted for by the disposition of preferentially vinylpyridine groups on the surface of aggregates which, after

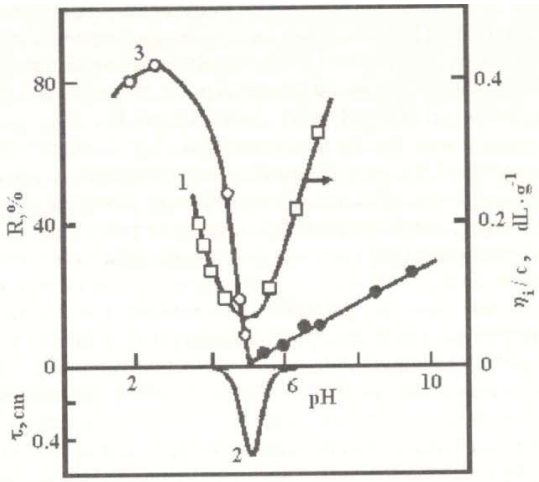


Fig. 33. Dependence of the reduced viscosity (*curve 1*), turbidity (*curve 2*) of TMVEP–MAA and yield of polyelectrolyte complexes (R, %) composed of TMVEP–MAA and PSS (or PDMDDAC). *Open circles* correspond to titration of TMVEP–MAA by PSS. *Closed circles* correspond to titration of TMVEP–MAA by PDMDAAC

Table 14. Comparative Phase Formation of 2M5VP–AA Copolymers at the IEP

AA (mol%)	2M5VP (mol%)	pH_{IEP}	$M_W \cdot 10^{-3}$	C_P (g·dL^{-1})	Ξ_1*	Ξ_2**
44.3	55.7	5.35	254.4	0.1	4.0	62.9
42.8	57.2	5.42	134.3	0.1	2.4	54.9
43.1	56.9	5.40	116.9	0.1	0.9	53.1
44.2	55.8	5.35	55.1	0.1	0.7	52.4

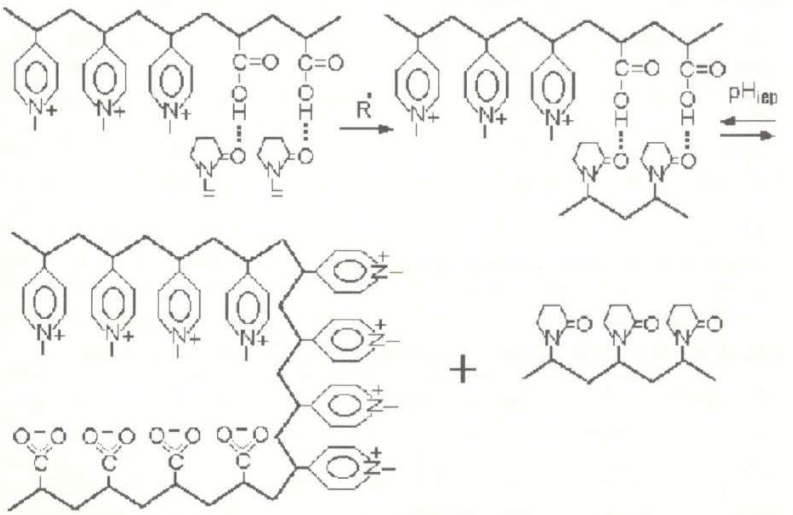
*) Degree of phase formation of polyampholytes before surfactant adsorption;
**) Degree of phase formation of polyampholytes after release of surfactant molecules at the IEP

Table 15. Comparative Phase Formation of DMAEM–MAA Copolymers at the IEP

MAA (mol%)	DMAEM (mol%)	pH_{IEP}	C_P (g·dL^{-1})	Ξ_1	Ξ_2
20.5	79.5	5.5	0.1	-	52.2
42.3	57.7	5.3	0.1	-	62.3
62.3	37.7	4.3	0.1	10.0	75.1

the dissolution of the same polyampholyte in the acidic region, become soluble in the alkaline region as usual and take an initial conformation. The comparison of the degree of phase formation of polyampholytes before (Ξ_1) and after release of surfactant (Ξ_2) shows that the value of Ξ_2 is much higher than Ξ_1 independent of the molecular weight of copolymers (Tables 14 and 15).

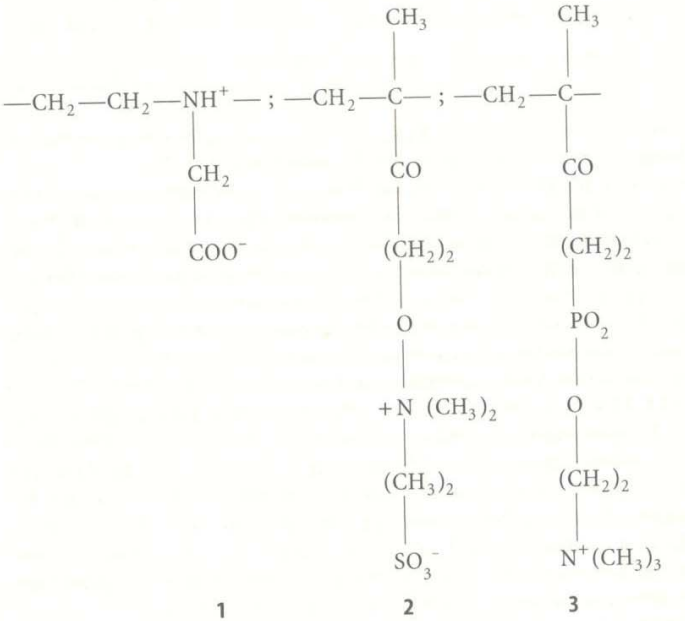
One can suggest that during the interaction of polyampholytes with surfactant molecules the latter prearrange the macromolecular chain so that more suitable conformation of polyampholytes and more profitable arrangement of acidic and basic groups will be provided in order to promote and intensify the cooperative formation of both intra- and interchain contacts between oppositely charged groups. Thus, in the case of polyampholyte–surfactant systems, the mechanism of "molecular recognition" can be realized. The "forcing out" effect can successfully be used in matrix polyreactions [104]. Scheme 3 illustrates the synthesis of poly(*N*-vinylpyrrolidone) on a blockpolyampholyte matrix. The idea of applying a blockpolyampholyte as a matrix offers advantages in comparison with polyacids and polybases alone: 1) matrix polymerization can be carried out on separate blocks; 2) water-soluble products can be protected from the precipitation by free (non-loaded) acidic or basic blocks; 3) easy separation of "daughter" chains from the matrix can be realized as a result of competitive inter- and intramacromolecular complex formation reactions; 4) a narrow molecular weight product can be produced; and 5) the blockpolyampholyte can be reused several times.



Scheme 3. Synthesis of poly(*N*-vinylpyrrolidone) on blockpolyampholyte matrix

11
Properties of Zwitterionic Copolymers

Polymeric betaines or zwitterions are polyampholytes whose oppositely charged groups remote one from another are displaced on one pendant substituent. There are several types of monomers with a betaine structure: carboxybetaines, sulfobetaines and phosphobetaines. Poly-*N*-ethyleneglycine (**1**), poly(*N*-3-sulfopropyl)-*N*-methacryloyloxyethyl-*N*,*N*-dimethylammonium betaine) (**2**) and poly[(2-methacryloyloxyethyl-2-(trimethylammonioethyl-phosphate)] (**3**) are typical examples of this kind of polyampholyte:



1 **2** **3**

The synthesis and solution properties of polymeric betaines were outlined in detail by Salamone and co-workers [111–121], in particular in the vinylimidazole and vinylpyridine series, as well as by other research groups [122–128]. Recently [129–131], the preparation and solution properties of polybetaine, containing the phosphatididylcholine group, poly[(2-methacryloyloxy)ethyl-2-(trimethylammonioethyl phosphate)] which has PO_4^- and $-N^+(CH_3)_3$ groups divided by two methylene groups have been reported. The linear relationship between [η] and 1/μ was observed for the polyampholyte at low μ near pH_{IEP}. When μ is >0.0025, [η] increases due to the release of the attractive interactions between the oppositely charged units. By comparing the μ dependence of the electrostatic expansion factor of the polyampholyte with that of poly(sodium acrylate), it is

Table 16. Hydrodynamic and Molecular Characteristics of Poly(*N*-3-sulfopropyl)-*N*-methacryloyloxyethyl-*N*,*N*-dimethylammonium betaine) in Water-Salt Solutions

Samples	SB-8	SB-9	SB-10	SB-11	SB-12	SB-13
$M_w \cdot 10^5$	11.4	12.2	15.0	26.9	36.7	50.1
C_s (mol·L^{-1})	R_g/R_h (nm)					
0.06	44.6/34.7	47.0/35.8	50.6/39.8	70.2/52.6	81.6/63.0	97.1/72.0
0.08	44.3/36.2	46.7/37.9	52.0/41.8	71.0/65.7	87.5/70.8	100.5/82.0
0.1	45.6/37.0	47.4/38.8	53.6/43.1	80.4/67.4	93.3/80.1	113/95.1
0.3	47.3/39.0	49.7/42.0	56.0/47.0	81.5/70.0	99.8/84.5	128/102.7
1.0	47.0/40.5	49.0/42.5	56.5/47.8	89.5/72.0	101/91.3	135/105.0

suggested that there is a pronounced intramolecular attraction between the oppositely charged segments even when pH deviates from the IEP.

Polymeric betaines are usually insoluble in pure water and have gel characteristics but are soluble in salt-containing solutions. The loss of water solubility and gel-like structure that adopts polybetaines are probably due to the formation of intra- and interchain ion contacts which result in the appearance of cross-linked networks. The intrinsic viscosity [η], second virial coefficient A_2, exponent ***a*** in the MKH equation, the radius of hydration R_g and the hydrodynamic radius R_h increase with the increase in salt concentration C_s [132] (Table 16).

The exponents of the MKH are equal to ***a***=0.5; 0.67; 0.70 and 0.70 for C_s=0.06; 0.3; 1.0 and 4.0 M NaCl aqueous solutions, respectively. The electrostatic expansion factors for polyampholyte effect, α_e, were estimated for the sulfobetaine polymers over a wide range of molecular weights and C_s. It is concluded that the chain expansion for a neutral polyampholyte is controlled by the non-ionic excluded volume effect and the electrostatic excluded volume effect (polyampholyte effect) at moderate added-salt concentration. The electrostatic expansion factor can reasonably be described by a α_e^3-type equation, although no such an equation for the polyampholyte has so far been proposed.

Solubility of polybetaines in aqueous solution depends on the nature of the anions and cations of the added salts. For salts having a common anion (Cl^-) and one-valent cations, an increase in solubility changes as follows: $Li^+ > NH_4^+ > Na^+ > K^+$, while for two-valent cations the solubility increases in the order: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. In the presence of salts with a common cation (K^+), but different anions, the solubility increases in the following order: $ClO_4^- > I^- > Br^- > Cl^-$. Table 17 represents the minimal concentrations ($C_s \cdot 10^{-2}$ mol·L^{-1}) of various salts needed to dissolve poly[*N*,*N*′-diethyl(acrylamidopropyl)ammoniumpropanesulfonate] (PDMAAPS) [133]. Charge/radius ratio, Hoffmeister lyotropic sequences and Pearson theory can successfully be applied to explain the solubility behaviour of polybetaines.

Table 17. Influence of the Nature of Cations and Anions on the Solubility of PDMAAPS

	Cl	Br	I	ClO_4	NO_3	NO_2	SO_4	CH_3COO
Li	4.26							
NH_4	4.09							
Na	3.60			0.77		2.86	4.48	22.11
K	3.57	2.08	0.94	0.86	2.86			
Mg	2.81							
Ca	2.44							
Sr	2.27							
Ba	2.08							

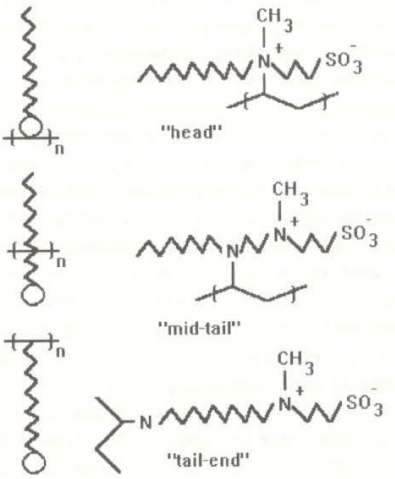
The synthesis [134] and characterization [135,136] of aromatic and aliphatic poly(sulfonatopropylbetaines), together with the binding ability with respect to optical fluorescent and chemically reactive anionic organic probes [137], have been described. The strongly dipolar character of the zwitterionic structure of polybetaines affords a number of specific properties: a) "antipolyelectrolyte" behaviour as typified by increasing chain expansion with increasing ionic strength of the aqueous solution; b) strong binding capacity, with simultaneous dehydration, toward a variety of organic anionic probes in aqueous solution; and c) high solvation power of the glassy polymeric matrixes toward salts of widely different lattice energy leading to completely amorphous blends [138]. Hydration of acrylic (methacrylic) polyzwitterions bearing aliphatic quaternary ammonium-sulfonatopropylbetaine as a side group ($\geq N^+-(CH_2)_3-SO_3^-$) and poly(2-vinyl- and 4-vinylpyridinium sulfonatopropylbetaines) (P2VP-SB and P4VP-SB, respectively) have been studied over a broad range of water content (weight fraction <0.5) [139].

Comprehensive analysis of the first-order transitions and heat capacity of sorbed water, at glass transition temperature (T_g) has allowed the identification of the main common features of the system: a) at 296 K water diffusion is Fickian and the isotherm analysis shows that water sorption occurs according to a multilayer sorption process [140]. It allows discriminating site-bound water (1.5–2.0 water molecules per monomeric unit) and indirectly bound water without great differences of binding energy between these successive solvation layers. Moreover, clustering of water molecules is never observed, not even for the highest water concentrations; b) differential scanning calorimetric measurements [141] allow the quantification of two different types of bound water: non-freezable bound water (type I), 7.7±0.9 molecules per monomeric unit, showing mobility fairly similar to that of bulk water and a strong plasticizing effect on the system; freezable bound water (type II), 6.7±0.9 molecules per monomeric unit, characterized by a complex multipeak melting endotherm occurring in a rather broad

temperature range (242–272 K); and c) the poly(pyridinium zwitterions) display slightly decreased hydrophilicity with respect to their aliphatic quaternary ammonium homologues, e.g. a significantly lower number of non-freezable and freezable bound water molecules per monomeric unit (type I), 5.0 and (type II) 5.5±0.5 showing a two-peak melting endotherm at 267±1 K and 271±1 K.

According to molecular mechanics calculation and dielectric studies [142], triethylammonium-, -pyridinium- and 2,6-dimethylpyridiniumsulfonatopropyl betaines are characterized in dilute aqueous solution by a nearly fully extended conformation with fairly similar intercharge distances (4.8–5.0 Å) leading to dipole moment values of about 23.0–24.2 D. It may also be stressed that the aqueous solutions of aromatic and aliphatic poly(zwitterions) exhibit significantly different phase behaviours: P2VP-SB has an upper critical solution temperature (UCST) at 286 K, poly[*N*,*N*-dimethyl-*N*-[2-(methacryloyloxy)ethyl]-n-(3-sulfonatopropyl)ammonium betaine] shows both UCST at 306 K and an "apparent inverted" lower critical solution temperature (LCST) at 289 K [124,143]. [see also conflicting data of Huglin MB, Radwan MA (1991) Polymer International 26: 97] and P4VP-SB is insoluble over the whole temperature range between 273 and 373 K.

Recently, Laschewsky et al. [144–149] have reported on the synthesis and characterization of zwitterionic polysoaps which combine the advantages of the behaviour of polyzwitterions and micellar polymers. The variation of the polymer geometry produces "head-type" (1), "mid-tail type" (2) and "tail-end type" (3) zwitterionic polysoaps.



Scheme f

The viscosity of the cationic polysoap exhibits polyelectrolyte character whereas the viscosity of the zwitterionic polysoaps behaves as an uncharged polymer. The unusually low viscosities of zwitterionic polysoaps are attributed to the intramolecular aggregation of the hydrophobic side chains, keeping the hydrodynamic radius small. The surface activity and solubilization capacity of amphoteric polysoaps have been studied. The sequence to solubilize hydrophobic dyes is "mid-tail" >"head" >"tail-end" geometry.

The dielectric properties of mixtures of the inorganic salt NaI and zwitterionic polymethacrylates were measured in the frequency range from 10^2 to 10^7 Hz and at temperatures between 110 and 400 K for different salt concentrations (0, 100 and 200 mol%) [150]. One relaxation process is observed whose relaxation rate depends strongly on the length of the aliphatic spacer between the polymethacrylate main chain and the zwitterionic group. Exhibiting an Arrhenius-like temperature dependence with activation energy E_A=47 kJ/mol, this relaxation process is assigned to fluctuation of the quaternary ammonium group in the side chains. At higher temperatures, the dielectric properties and the conductivity are primarily dominated by the mobile inorganic ions: conductivity strongly depends on the salt concentration, showing a pronounced electrode polarization effect. The frequency and salt concentration dependencies of the conductivity can be quantitatively described as hopping of charge carriers being subject to spatially randomly varying energy barriers. For the low-frequency regime, and for critical frequency marking the onset of the conductivity's dispersion, the Barton–Nakajima–Namikawa relationship is fulfilled.

12
Polyampholyte Gels and Networks

A number of studies on the volume phase transition of anionic, cationic and non-ionic hydrogels has been reviewed [151,152]. Little attention, however, has been paid to amphoteric polyelectrolyte hydrogels [153,154]. In contrast to uniform polyelectrolytes the swelling degree of polyampholytes depends on the concentration of the constituent ionic groups or the pH of the external solution [155–159]. The pH response for the secondary structure of amphoteric copolypeptide hydrogels consisting of L-glutamic acid, L-leucine, and L-lysine was investigated through *in situ* monitoring using a Fourier transform IR microscope [160]. The hydrogels were found to exist mainly in the α-helical conformation over the whole pH range studied. Depending on the composition and pH, α-helical conformation was weakened due to the dissociation of their side chains. Amphoteric gels show a minimal swelling degree when the amount of anionic and cationic monomers is equal as in the case of linear polyampholytes considered in previous sections. As the concentration of the anionic and cationic parts deviates from the equimolar ones the swelling ratio increases rapidly (Fig. 34). A reasonable explanation of these results is that the number of osmotically active ions in the hydrogel phase increases as the molar ratio of cationic to anionic groups diverges from unity according to Donnan equilibrium, while, as the mo-

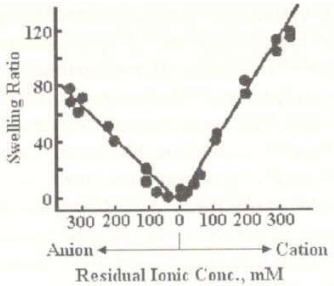


Fig. 34. Plots of swelling ratio (V/V_0) of amphoteric gel MAPTAC–SA as a function of the effective ionic density. The effective ionic density is represented by the residual amount of anionic or cationic groups after a specific binding is formed between the anionic and cationic groups. The numbers of the abscissa indicate an effective ionic density derived by subtracting the anionic group content from the cationic group content [155]

lar ratio of cationic to anionic groups approaches unity, the excess free counterions that are not needed to satisfy the electroneutrality of the chain are effectively "dialyzed" from the hydrogel interior.

Figure 35 combines the temperature-dependent and acetone-content-dependent behaviour of amphoteric gel APTAC–SA [155]. Equimolar polyampholyte gel undergoes a gradual volume change with an increase in acetone composition in an acetone/water mixture. When the content of the cationic groups increases, collapse of gel is observed. On the other hand, the same sample immersed in acetone/water mixtures of 60 and 65% acetone swells in a low

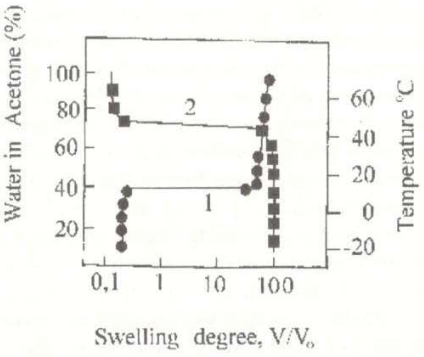


Fig. 35. Volume phase transition of amphoteric gel MAPTAC–SA in relation to temperature (*curve 1*) and acetone content (*curve 2*) [155]

temperature region and collapses in a high temperature region. While the gel in mixtures of 70% acetone or above is observed to maintain a collapsed state over a wide temperature interval, it is concluded that, although the amphoteric gel consists of various proportions of cationic and anionic groups, it exhibits the same pattern of volume phase transition, as did monoionic gels. However, the swelling behaviour observed for equimolar amphoteric gel, e.g. its continuous character, can be attributed to the specific bonding of cationic and anionic parts that act as additional cross-linking agents. It should be noted that the hydrogels containing excess cationic monomers swell more than the hydrogel containing an excess of anionic groups [154]. The "asymmetry" in swelling behaviour can be prescribed to three possible mechanisms: 1) differences in cross-link density caused by different rates of copolymerization; 2) hydrophobicity of moieties, for instance, in the case of styrene moieties that can reduce chain expansion inside the network owing to the hydrophobic interactions; and 3) differences in the activities of counterions to the charged groups, for instance, the attraction between counterions and functional groups will be weaker for MAPTAC or APTAC than for SSS or SA.

Figure 36 shows the deswelling of amphoteric gels as a function of NaCl concentration. Except for the equimolar sample that shows a low sensitivity to ionic strength all other hydrogels with excess of anionic or cationic monomers exhibit a decrease of swelling capacity with the increase of NaCl concentration. The excess of anionic or cationic moieties will require the flow of small ions inside the hydrogel to maintain the electroneutrality and, as a result, the concentration of mobile ions inside and outside of the gel becomes similar; the net osmotic pressure falls and swelling decreases.

The temperature dependence of the swelling ratios of two *N*-isopropylacrylamide (NIPA) based amphoteric gels was measured because the NIPA gel itself

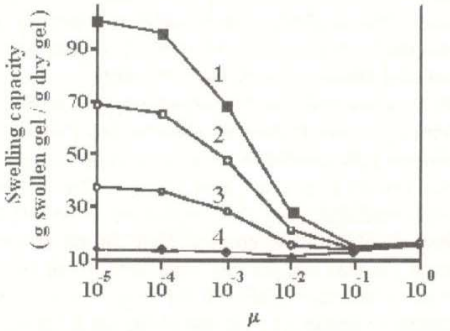


Fig. 36. Swelling equilibria for MAPTAC–SSS amphoteric hydrogels as a function of NaCl concentration. [MAPTAC]/[SSS]=7:1 (*curve 1*), 3.3:1 (*curve 2*),1.8:1 (*curve 3*), 1:1 (*curve 4*) [156]

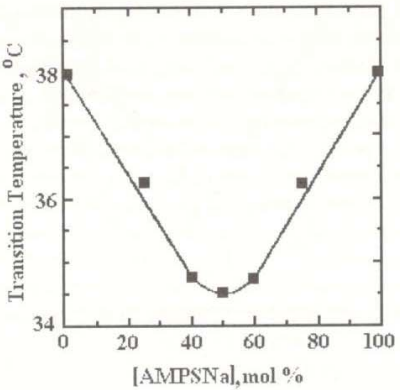


Fig. 37. Plots of the transition temperatures of the NIPA/NDAPD/AMPSNa amphoteric gels against the AMPSNa concentration. The total density of the amphoteric gels are fixed at 1 mol% (Reproduced with permission from [161])

shows a thermosensitive character in water by changing the temperature [161,162]. Figure 37 shows the equilibrium swelling curves of the amphoteric gels in water together with those of NIPA gel. When the content of anionic and cationic groups is equal in NIPA-based gel its swelling behaviour is similar to NIPA gel itself. When the ratio of cationic and anionic groups deviates from 50:50 the transition temperature and the swelling ratio increase. These results were explained by considering that the ionic contacts formed between the cationic and anionic units affect the swelling pressure of the gel. It was also found that the NIPA/betaine amphoteric gels containing an equal constituent in the pendant chain exhibit a similar swelling behaviour to integral type polyampholytes. Amphoteric hydrogel films obtained by subjecting the solution mixture of polyvinylalcohol, polyacrylic acid and polyallylamine hydrochloride to repetitive freezing and thawing swell both in acidic and basic solutions and shrink in neutral pH regions because of polyanion–polycation association [163].

Synthetic polymer gels are known to exist in two phases, swollen and collapsed. Polyampholyte gels should show a re-entrant volume transition in response to pH [164]. Tanaka et al. [165] have reported the existence of more than two phases in randomly distributed polyampholytes of MAPTAC and AA. Let us consider the behaviour of a sample containing 65 mol% of AA and 35 mol% of MAPTAC. At neutral pH this sample has a diameter $d=d_0$ that is referred to as phase 1 ($d/d_0=1$) according to the label in the original paper. At pH=8.5 the gel swells discontinuously to phase 2.7 (Fig. 38). If the pH is lowered from 8.5 to 7.0, the gel returns to phase 1 discontinuously. If instead the pH is increased further from 8.5 to 9.8 and goes back from this point the gel collapses into phase 1 at pH=6.4. The same experiments were done from the acidic side. ^{13}C NMR spectra

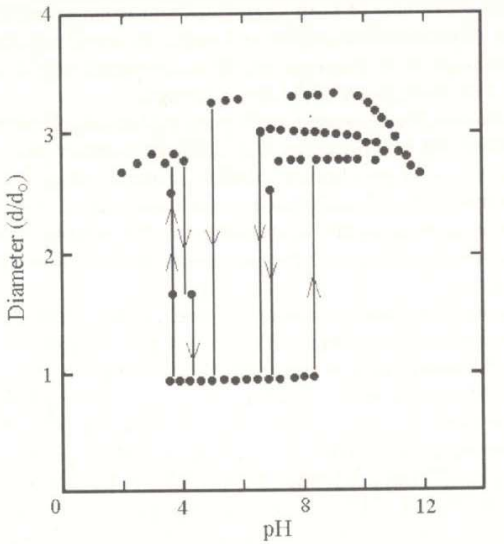


Fig. 38. Equilibrium swelling degree of d/d_0 of AA–MAPTAC (35:65 mol%) copolymer gel in water as a function of pH at 298 K [165]

for different phases at the same pH are clearly distinguishable, indicating that each phase has a different local environment. The nature of multiple phases may be understood if the competition among various interactions: mixing enthalpy and entropy, Coulomb interactions (between acidic and basic groups of polyampholytes, between charged groups and counterions), hydrogen bonding etc. is taken into account. However, more extensive study is needed to identify the microscopic structure of the new phases. Recently, a theoretical description of multiple phases in ionic copolymer gels was presented [166]. The equations for the dissociation equilibrium of the fixed charges in the gel are solved together with a Flory-type swelling model which incorporates both polyelectrolyte and polyampholyte effects. This model correctly predicts the qualitative shape of the gel swelling vs. pH curve.

Polyampholyte microgels METMAC–SAMPS have been synthesized by using an inverse microemulsion route [167]. The swelling properties of so-called "balanced" microgel particles containing variable amounts of the cross-linker were studied by photon-correlation spectroscopy as a function of the ionic strength. The microgel particles flocculate below a certain electrolyte concentration. Above this concentration they are stable and the size of the particles appears to be insensitive to both ionic strength and cross-linker concentration in the monomer feed. Transmission-electron spectroscopy results provided in pure water

show that samples consist of both aggregates and isolated particles. The latter are somewhat ellipsoidal in the collapsed state. The swelling behaviour of "unbalanced" polyampholyte microgel particles displayed only a very small decrease in size with an increase of the ionic strength.

The interaction of high charge density polyampholyte gels formed from sodium methacrylate and *N*,*N*-dimethyl-*N*,*N*-diallylammonium bromide with both ionic surfactants – cetyltpyridinium chloride, sodium dodecylbenzenesulfonate – and organic dyes – alizarin, ninhydrin – has been studied [168]. The efficiency of adsorption of surfactants and dyes leading to the collapse of the gel is determined by the ratio of charges of the polyampholyte network and organic ion concentration.

It is well known that polyelectrolyte gels swell, shrink or bend when DC electric current is applied [169]. These properties of gels are applicable for the construction of chemomechanical devices, artificial muscles, energy conversion systems etc. [170]. Osada and co-workers [171] have constructed an eel-like gel actuator on the basis of poly(2-acrylamido-2-methylpropane sulfonic acid) and studied its chemomechanical properties. Polyampholyte gel is bent to the cathode or anode side if it has predominantly negative or positive charges along the macromolecules (Fig. 39) [172]. As seen from Fig. 39, the amplitude of deflection is gradually decreased with the approach to the IEP. This is probably due to

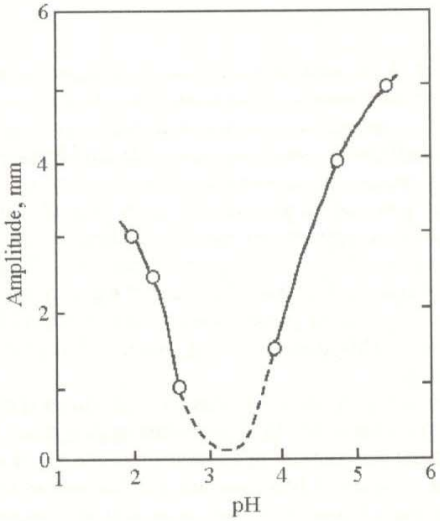


Fig. 39. Dependence of amplitude of deflection on pH of the external solution for polyampholyte gel of the vinyl ether of monoethanolamine–acrylic acid (VEMEA–AA) with pH_{IEP}=4.2

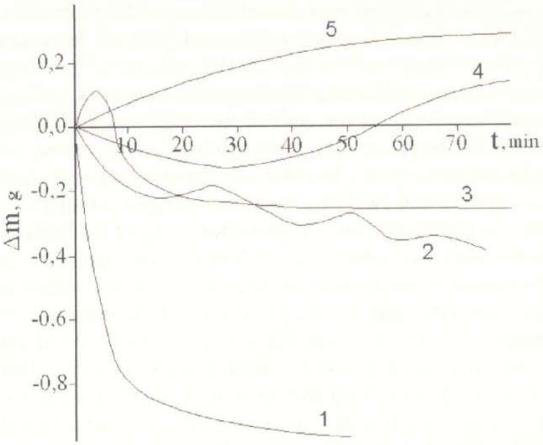
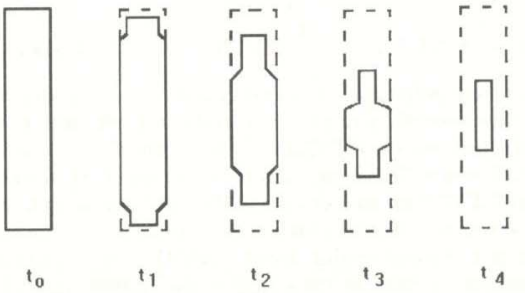


Fig. 40. Relative mass change of polyampholyte gels of the vinyl ether of monoethanolamine–acrylic acid (VEMEA–AA) under the influence of DC electric current at pH=3.0 (*curve 1*), 4.2 (IEP) (*curves 2,4,5*), 6.2. (*curve 3*) at $\mu=1\cdot10^{-2}$ (*curves 1–3*), $1.5\cdot10^{-2}$ (*curve 4*) and $2.5\cdot10^{-2}$ M NaCl (*curve 5*)

the formation of intraionic contacts that decrease the net charge of amphoteric macromolecules. Figure 40 represents the change in polyampholyte weight in relation to time under the influence of DC electric current [173,174].

In cationic (pH=3.0) and anionic (pH=6.2) forms, the hydrogel gradually shrinks from both ends as schematically shown below.

Under the action of DC electric field the redistribution in the double electric layer occurs and shrinking of the specimen from both side takes place. It is interesting to note that the coexistence of three phases (triphasic equilibrium), i.e.



Scheme g

swollen gel, shrunken gel and pure solvent, the so called "bottleneck" macroscopic phase boundary, was observed for ionized NIPA gel rod on heating [175]. Ampholytic gel specimens swell at the IEP (Fig. 40, curve 5). This phenomenon can be interpreted as follows: at the IEP the neutral network under the action of DC is polarized. As a result at the ends of the specimen adjoining the cathode and anode sides the density of the network charge is increased. The increased charges should be compensated by outer counterions that, in turn, cause a water flow inside the system and swelling. It was also observed that, in relation to the ionic strength, the polyampholyte gel oscillates [176]. At the IEP, at intermediate values of ionic strength $2{\cdot}10^{-2} < \mu < 7.5{\cdot}10^{-3}$, polyampholyte gel oscillates (Fig. 40, curves 2 and 4), while anionic and cationic polyelectrolytes only swell or shrink under the same conditions. Faraday law in differential form [176] successfully describes the relaxation-oscillation curves. Gel systems demonstrating rhythmically pulsatile motion similar to that of a heart beat have been developed [177]. Self-oscillations of swelling and deswelling for the poly(*N*-isopropylacrylamide-*co*-acrylic acid) hydrogels were realized by coupling pH and temperature in the external solution media. The pH oscillations were also observed for the system consisting of iodate-sulfite-thiosulfate and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) when polymeric acid was substituted for sulfuric acid [178]. Recently, an analytically tractable model for the description of polyampholytes in an external electric field has been presented [179]. The equilibrium properties of polyampholytes in strong electric fields decisively depend on the charge distribution along the chain.

13
Application of Polyampholytes

Water-soluble and water-swelling polyampholytes are used in a wide number of applications including sewage treatment, flocculation, enhanced oil recovery etc. The desalination of water by cross-linked polyampholytes can be regulated by changing the temperature. Such polyampholytes are called thermoregenerable resins (TRR). To perform the thermoregeneration the next equilibrium should take place in dependence of temperature:

$$R-COOH + R^*-NR_2' + K^+A^- \Leftrightarrow R-COO^-\,K^+ + R^*-N^+HR_2'\,A^-$$

where R and R* are polymer chains; COOH and NR_2' are functional groups; K^+ and A^- are cation and anion, respectively; and R' is a hydrogen or alkyl group.

In principle the function of TRR is as follows: salts absorbed at room temperature (e.g. NaCl) can easily be regenerated by hot water, e.g. the exchange equilibrium is shifted at room temperature to the right and at high temperature to the left. At room temperature the proton is transferred from the acid to the base forming charged ion-exchanging zones ($COOH \rightarrow NR_2' \rightarrow COO^-N^+HR_2'$). The heating of water from 298 K to 358 K leads to the accumulation of H^+ and OH^- due to the ionization of water molecules; the concentration of H^+ and OH^- in-

creases approximately 30 times. Hydrogen and hydroxyl ions suppress the degree of ionization of the amphoteric resin and the equilibrium shifts to the left side.

The salt-rejecting properties in dynamic reverse osmosis membranes made from P2VP-*co*-PMAA were studied by Stille et al. [180,181] The desalination ability of blockpolyampholytes is minimal at the IEP. Cross-linked pentablock-polyampholytes comprising quaternary ammonium residues, styrenesulfonate and neutral cross-linkable isoprene blocks are also applicable as membranes for desalination [182]. An amphoteric ion-exchange membrane was also prepared by chemical grafting of AA and DMAEM on ozonized polyethylene and its physico-chemical properties were compared with those of monofunctional membranes [183]. The amphoteric membrane was characterized by measuring ion-exchange capacity, water and electrolyte content, electrical conductivity, membrane potential and transport number. The ion-exchange capacity of AA–DMAEM membrane determined at various pH is reported in Table 18. Curves of the electrical resistance R as a function of the external pH plotted in Fig. 41 show that the maximal R probably corresponds to the IEP and the value of R is similar for anionic exchange membrane at low pH and cationic exchange membrane at high pH. Potentiometric behaviour of amphoteric membrane prepared from a mixture of the amphoteric chitosan and poly(vinyl alcohol) was studied [184].

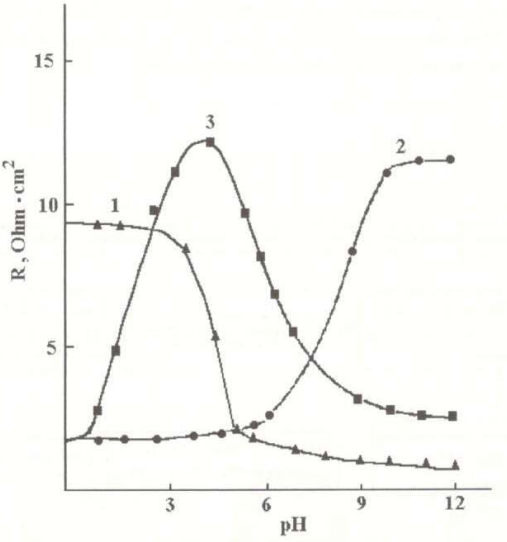


Fig. 41. Variation of the electrical resistance of cationic exchange (*curve 1*), anionic exchange (*curve 2*) and amphoteric exchange (*curve 3*) membranes as a function of the external pH (Reproduced with permission from [183])

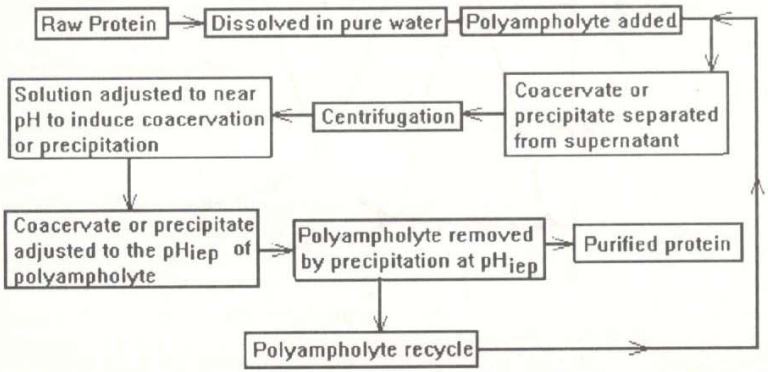
Table 18. Ion-Exchange Capacity of Amphoteric Membranes

Labeled Ion	Cl^-	Na^+	Cl^-	Na^+
External pH	2	6	6	12
Ion-exchange capacity ($meq \cdot G^{-1}$)	0.87	0.24	0.39	0.65

The ability of polyampholyte networks to regulate the water permeability has been shown [185]. The maximal permeability corresponds to the IEP.

Several types of copolymers of methacrylic acid with various quaternary ammonium monomers, terpolymers of these copolymers with methylmethacrylate, were tested for water clarification and decolorization [186]. The polymer is an adjunct to a magnetic iron oxide employed as the primary coagulant, which is recycled after alkaline treatment. Copolymers containing phenolic or amino acid moieties as well as quaternary ammonium sites proved to be the most effective in enhancing water treatment performance with concomitant facile regeneration behaviour.

Protein purification by selective phase separation with anionic and cationic polyelectrolytes has been widely discussed by Dubin et al. [187]. The driving force of such a process is the intermolecular association with the participation of Coulomb interactions, hydrogen bonds and hydrophobic forces. Phase separation with polyampholytes has been described [188,189]. Due to the self-precipitation of polyampholytes at their own IEP in the absence of proteins, they can be used for protein extraction and purification.



Scheme h

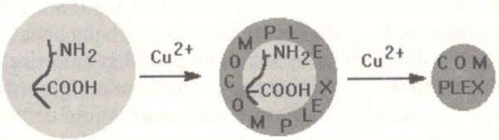
The main advantage of polyampholytes related to the protein separation process is the realization of the "forcing out" effect at the IEP of polyampholytes which will facilitate polymer recycling after protein separation.

The drag reduction behaviour of three classes of polyampholytes having high charge density (copolymers containing NaAMPS and AMPTAC), low charge density (terpolymers containing acrylamide and less than 15 mol% NaAMPS and AMPTAC) as well as betaine copolymers with sulfonate moieties have been examined [190,191]. A dependence of drag reduction effectiveness on copolymer structure, composition and solvation was observed. All polyampholytes exhibit higher drag reduction with increasing ionic strength of the solution. The betaine copolymers have the best drag reduction properties, the low charge density polyampholytes exhibit intermediate drag reduction effectiveness and the high charge density polyampholytes the poorest.

Polyampholyte microcapsule membranes of poly(L-lysine-*alt*-terephthalic acid) were used as self-regulating drug delivery systems [192]. The rate of permeation of 5-sulfosalicylic acid and phenyltrimethylammonium chloride through microcapsule membranes has been found to change depending on the pH and ionic strength of the medium. The drastic change in permeability lies between pH=4 and 6. A remarkable change in microcapsule size was observed in the same way as in the permeability of membranes. At pH >6 (μ=0.0154), the size of the microcapsule was about 60 μm, while it decreased to about 35 μm at pH=4 and increased again to about 45 μm when the pH decreased from 4 to 2.

The formation of coordination and ionic bonds between functional groups of VEMEA–AA and metal ions is accompanied by the gradual shrinking of polyampholyte gel [193]. During the complexation process a shell layer is formed on the surface and moves to the core region of the gel as schematically illustrated below:

It should be noted that the concentration of absorbed copper reaches a constant value after 2 h while the volume contraction of gel continues to change for up to 10 h. This is probably due to the rearrangement of polyampholyte–copper complexes. The complexed layer will probably retard the further penetration of copper ions deep in the gel and the complex formation kinetics are diffusion limited. Figure 42 shows the kinetics of deswelling of polyampholyte gel and desorption of Cu^{2+} at various pH. The desorption of Cu^{2+} from the inside of the gel is accompanied by swelling of the gel. The degree of recovery of copper ions at the IEP of polyampholytes reaches up to 60–70%.



Scheme i

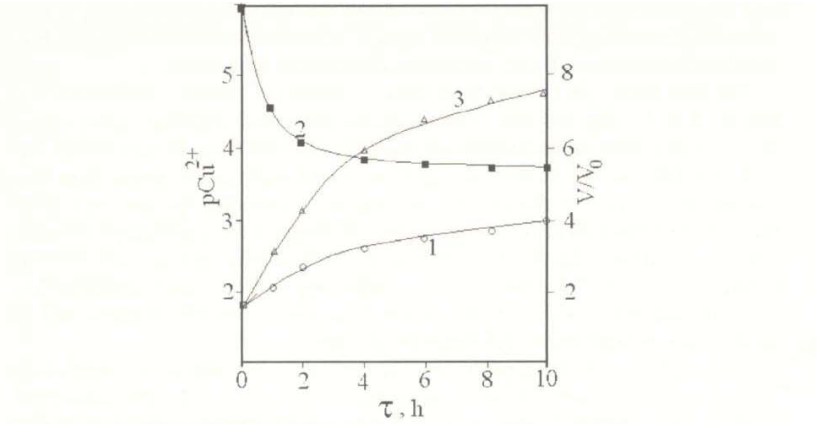


Fig. 42. Time dependence of swelling degree ratio (V/V_0) and concentration of Cu^{2+} at pH= 5.7 (*curve 1*), 5.2 (*curve 2*) and 4.8 (*curve 3*)

14
Concluding Remarks

Polyampholytes have unique electrochemical, hydrodynamic, conformational and complex-forming properties due to the presence of both acidic and basic groups. The ability of linear and cross-linked amphoteric macromolecules to adopt globular, coil, helix and stretched conformations and to demonstrate coil-globule, helix-coil conformational transitions, and sol-gel, collapsed-expanded phase or volume changes in relation to internal (nature and distribution of acid and base substituents, copolymer composition, molecular weight distribution, hydrophobicity etc.) and external (pH, temperature, ionic strength, organic solvents addition etc.) factors, as well as to form superstructures will constantly attract the attention of theorists and experimentalists.

The structures of amphoteric macromolecules, especially at the IEP, fall within eyeshot of several disciplines, at least polymer and colloid sciences, and molecular biology. Here, the ideas, approaches, theoretical calculations and experimental observations of de Gennes [194], Lifshitz et al. [195], Frenkel [196,197], Joanny [96], Burchard [198], Ise [56] and Khokhlov [199] seem to be useful to make some conclusions. According to de Gennes [194], the behaviour of macromolecules is mainly determined by topological and geometrical properties of systems. It is also suggested [195] that the existence of a high-ordered structure inside of globular particles – "Configurational information" or "linear memory" of macromolecular chains – determines the properties of materials [197]. Many similarities exist between covalently bound structures and macromolecular as-

sociates [198]. The high probability of self-organization processes in polyelectrolytes is due to the effective competition between different interaction types [199]. At the IEP, macromolecular chains form a globular structure stabilized by cooperative ionic contacts, hydrogen bonds and hydrophobic interactions, the state of which are close to hydrated globular proteins. In turn, such globular structures can be organized into various types of associates or aggregates stabilized mostly by physical forces. Random association of globules can produce colloid particles. Regular assemblies of globular particles can lead to the appearance of supercrystalline states. The accumulated data imply that polyampholytes can repeat, more or less, the structural organizations of proteins. Having recognized these facts, attempts could be directed to find out the molecular organization levels of amphoteric macromolecules.

The overall chain conformation of polyampholytes with a balanced (same number of negative and positive monomers) and nonbalanced (an excess of positive or negative charges) stoichiometry is essentially controlled by attractive (polyampholyte effect) and repulsive (polyelectrolyte effect) electrostatic interactions. Therefore, depending on the ionic strength, the solution behaviour is dominated by either polyampholyte or polyelectrolyte effects. Polyampholytes with balanced stoichiometry are insoluble in pure water but become soluble upon addition of 1:1 electrolytes owing to the screening of opposite charges and unfolding of the macromolecules, while nonstoichiometric polyampholytes are water-soluble, possess extended polyelectrolyte conformation but have the tendency to be insoluble at a high ionic strength of the solution. An "antipolyelectrolyte" character gives the stoichiometric polyampholytes good swelling in high salinity media and enables them to be used for desalination and enhanced oil recovery.

Analysis of the literature data shows that considerable progress has been made in theoretical considerations in spite of some discrepancies between theory and experiments. In future the quantum-chemical and computer simulations of polyampholyte chains will be developed.

The competition between intra- and interionic contacts is the driving force behind the behaviour that causes the "forcing out" effect near the IEP. This phenomenon can successfully be used in matrix polymerization, and for the recovery and purification of both low- and high-molecular-weight substances. Systematic structural investigations on zwitterionic "polysoaps" that combine the advantages of polyampholytes and micelles are in progress.

A study of complex formation properties of polyampholytes with respect to metal ions, dyes, organic probes, detergents and polyelectrolytes can be of help, on the one hand, in understanding the mechanism of protein denaturation, enzymatic reactions, replication, and, on the other hand, in using such processes in coagulation, purification and enrichment technologies etc.

Evidently, polyampholyte gels belong to multiphase systems due to the ability of macromolecules to adopt different stable conformations in response to changes in environmental conditions. Therefore, more extensive study is needed to identify the microscopic structure of multiphases. Stimuli of the responsive

character of linear and cross-linked polyampholytes can be of help to construct thermoreversible and semipermeable membranes, microcapsules for drugs etc. The development of the oscillating behaviour of gels that will be useful for the design of "muscular" or periodic drug delivery systems, actuators and other devices has just started. According to Tanaka [200] polyampholyte gels are similar to *p-n* junction diodes. The flow of counterions in such gels, corresponding to the flow of holes and electrons in a diode, would be curious to examine.

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Review

Physicochemical, Complexation and Catalytic Properties of Polyampholyte Cryogels

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Abstract: Polyampholyte cryogels are a less considered subject in comparison with cryogels based on nonionic, anionic and cationic precursors. This review is devoted to physicochemical behavior, complexation ability and catalytic properties of cryogels based on amphoteric macromolecules. Polyampholyte cryogels are able to exhibit the stimuli-responsive behavior and change the structure and morphology in response to temperature, pH of the medium, ionic strength and water–organic solvents. Moreover, they can uptake transition metal ions, anionic and cationic dyes, ionic surfactants, polyelectrolytes, proteins, and enzymes through formation of coordination bonds, hydrogen bonds, and electrostatic forces. The catalytic properties of polyampholyte cryogels themselves and with immobilized metal nanoparticles suspended are outlined following hydrolysis, transesterification, hydrogenation and oxidation reactions of various substrates. Application of polyampholyte cryogels as a protein-imprinted matrix for separation and purification of biomacromolecules and for sustained release of proteins is demonstrated. Comparative analysis of the behavior of polyampholyte cryogels with nonionic, anionic and cationic precursors is given together with concluding remarks.

Keywords: polyampholyte cryogels; swelling-deswelling; complexation; protein imprinting; immobilization of metal nanoparticles; catalysis; hydrogenation; oxidation; flow-through catalytic reactor

1. Introduction

The basic terms and definitions [1] together with the history of polymeric cryogels [2,3] including the synthesis, structure-property relationships, and properties [4,5] are comprehensively reviewed and systematized in the fundamental works of V.I. Lozinsky and O. Okay [6]. Preparation protocol, as well as the structural and morphological characteristics of cryogels and their application aspects with regard to biotechnology and biomedicine can be found [7–9]. Among the polymeric cryogels, the most attention has been paid to nonionic, anionic and cationic cryogels [1–9]. Amphoteric nano-, micro- and bulk gels have been the subject of much research [10–17]. Cryogels made of natural polyampholytes—proteins—also belong to amphoteric cryogels. However, in this review we will consider mostly macroporous polyampholyte cryogels of synthetic origin, and mainly focus on recent advances in polyampholyte cryogels prepared from acid–base or anionic–cationic monomer pairs or else betainic monomers in cryoconditions, as listed in Table 1. First, the structural and morphological properties of polyampholyte cryogels in response to pH, temperature, ionic strength and water–organic solvents are discussed. Then the complexation of polyampholyte cryogels with transition metal ions, dyes, surfactants, polyelectrolytes and proteins is outlined. Finally, the design of effective catalytic systems with the help of polyampholyte cryogels within which metal nanoparticles are immobilized will be demonstrated. In the conclusion, the prospects and open problems related to

polyampholyte cryogels is considered. The physicochemical, complexing and catalytic properties of conventional polyampholyte hydrogels are considered only when they are compared with the behavior of polyampholyte cryogels.

Table 1. Examples of various polyampholyte cryogels.

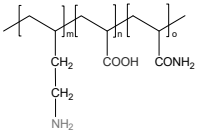
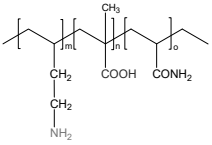
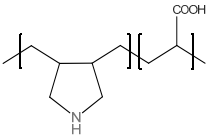
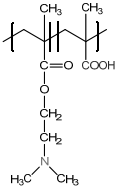
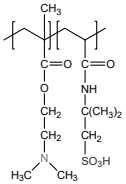
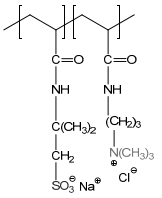
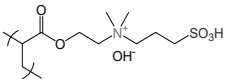
Chemical Structure of Polyampholyte Cryogels *	Name Acronym	Refs
	allylamine-*co*-acrylic acid-*co*-acrylamide, P(AA-*co*-AAc-*co*-AAm)	[18]
	allylamine-*co*-methacrylic acid-*co*-acrylamide, P(AA-*co*-MAA-*co*-AAm)	[19,20]
	diallylamine-*co*-acrylic acid, P(DAA-*co*-AAc)	[21]
	*N*,*N*-dimethylaminoethylmethacrylate-*co*-methacrylic acid, P(DMAEM-*co*-MAA)	[22,23]
	*N*,*N*-dimethylaminoethylmethacrylate-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid, P(DMAEM-*co*-AMPS)	[24]
	2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt-*co*-(3-acrylamidopropyl)trimethylammonium chloride, P(AMPSNa-*co*-APTAC)	[25,26]

Table 1. *Cont.*

Chemical Structure of Polyampholyte Cryogels *	Name Acronym	Refs
	Poly{[2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide}, PMODMSPA	[27]

* Primary, secondary, tertiary amine and quaternary ammonium groups of polyampholytes are in red, carboxylic and sulfonic groups are in blue.

2. Physicochemical Properties of Polyampholyte Cryogels

As seen in Table 1, polyampholyte cryogels can be comprised of primary, secondary and tertiary amine, or quaternary ammonium groups on the one hand, and carboxylic, sulfonic acid or carboxylate, sulfonate moieties on the other. Polyampholyte cryogels, analogous to linear polyampholytes [28], can be defined as pH-dependent "annealed" polyampholyte cryogels in contrast to "quenched" polympholyte cryogels which consist of fully charged monomeric units. When cryogels contain an identical number of pH-dependent acid–base or pH-independent anionic–cationic groups in the same monomer units, they can be referred to as "betainic" or "zwitterionic" cryogels.

The key characteristics of any polyampholytes are the ionization constants of acid–base groups (pK_a or pK_b) and the values of the isoelectric point (IEP) where the whole macromolecule exhibits the quasi-neutral character [28]. Table 2 represents the electrochemical characteristics of allylamine-*co*-acrylic acid-*co*-acrylamide P(AA-*co*-AAc-*co*-AAm) cryogels crosslinked by N,N-methylenebisacrylamide (MBAA) [19,29]. Amphoteric cryogels differ from each other by the content of acid–base and acrylamide (AAm) monomers and are abbreviated as ACG-550, ACG-442, ACG-334, ACG-226 and ACG-118 (Figure 1).

Table 2. Acid–base content, pK_b of allylamine groups and the isoelectric pH (pH_{IEP}) of ACG cryogels. (Reprinted with permission from [29], copyright 2012 Wiley).

Cryogels	–NH_2, mol.%		–COOH, mol.%		pK_b	pH_{IEP}
	Potentiometric Titration	Conductimetric Titration	Potentiometric Titration	Conductimetric Titration		
ACG-550	46.7	41.0	53.3	59.0	5.44	4.0
ACG-442	42.4	37.0	57.6	63.0	5.25	4.1
ACG-334	43.3	33.3	56.7	66.6	5.78	4.2
ACG-226	-	41.4	-	58.6	5.62	4.3
ACG-118	-	38.5	-	61.5	-	3.5

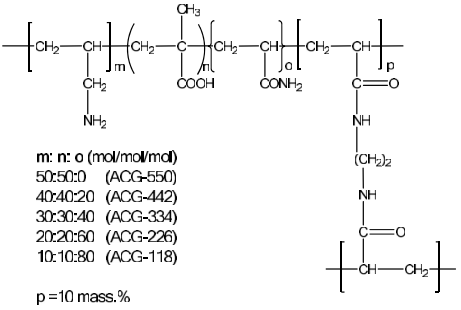


Figure 1. Structure and composition amphoteric cryogel (ACG) cryogels derived from AA, MAA and AAm. (Reprinted with permission from [29], copyright 2012 Wiley).

Both the water flux and swelling rate of the ACG cryogels decreased in the order of ACG-118 > ACG-226 > ACG-334 > ACG-442 > ACG-550 (Figures 2 and 3). This sequence is in good agreement with the gradual transition of low-charge-density cryogel (ACG-118) to high-charge-density cryogel (ACG-550), accompanied by decreasing the pore size of cryogels and hydration of ionic groups by water molecules.

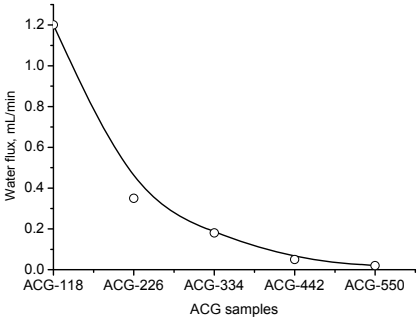


Figure 2. Dynamics of water flux through the ACG samples. (Adapted with permission from [29], copyright 2012 Wiley).

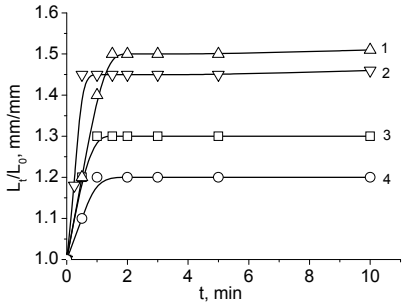


Figure 3. Time dependent swelling of ACG-118 (**1**), ACG-226 (**2**), ACG-334 (**3**) and ACG-550 (**4**) in water. For abbreviation of cryogels please see Figure 1. (Reprinted with permission from [29], copyright 2012 Wiley).

The pH_{IEP} of ACG cryogels were between pH 3.5 and 4.3 (Table 2). Time- and pH-dependent swelling of polyampholyte cryogels is demonstarated in Figures 3 and 4.

Swelling of polyampholyte cryogels of ACG series is fast due to the macroporous structure. Increasing of the acid–base content leads to progressive decreasing of the degree of swelling, water flux and pore size, as a result of formation of strong ionic contacts between the oppositely charged acid–base groups of cryogels.

As seen in Figure 4, the P(DMAEM-co-AMPS) cryogels are in swollen and collapsed states in acidic (pH 2.1) and alkaline (pH 8.0) conditions, respectively. In a narrow interval of pH between 7.7 and 8.0, P(DMAEM-co-AMPS) cryogels exhibit a pH-sensitive phase transition. The values of n found with the equation $kt^n = M_t/M_\infty$, (where k is the swelling rate constant, n is a characteristic exponent describing the mode of penetrant–water–transport mechanism, t is absorption time, M_t is the mass of water absorbed at time t, and M_∞ is the mass of water absorbed at infinite time t_∞) at pH 2.1 are in the

range of 0.14–0.30 based on AMPS content indicating the non-Fickian type of water diffusion into the cryogel volume.

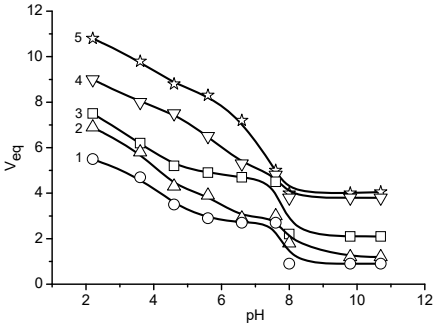


Figure 4. The pH dependent equilibrium swelling (V_{eq}) of P(DMAEM-*co*-AMPS) cryogels. The mole fraction of AMPS is 0 (**1**), 5 (**2**) 15 (**3**), 25 (**4**) and 40 mol.% (**5**). (Updated from [24]).

Figure 5 demonstrates the values of the pH_{IEP} of the ACG series that are arranged between pH 3.5 and 4.3 [29].

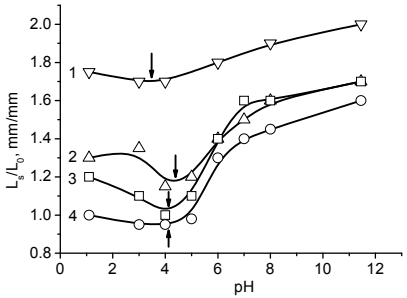


Figure 5. pH-dependent swelling-deswelling of ACG-118 (**1**), ACG-226 (**2**), ACG-334 (**3**) and ACG-550 (**4**). Arrows indicate on the position of the pH_{IEP}. (Reprinted with permission from [29], copyright 2012 Wiley).

The swelling behavior of polyampholyte cryogels was examined in dependence of the ionic strength adjusted by addition of low-molecular-weight salts [24,29]. In acidic and basic media, the swelling degree of P(AA-*co*-AAc-*co*-AAm) cryogels decreases with growth in ionic strength; in contrast, at the IEP the swelling degree of P(AA-*co*-AAc-*co*-AAm) increases as the ionic strength rises (Figure 6).

The gradual decrease of the swelling degree of P(AA-*co*-AAc-*co*-AAm) with an increase in ionic strength, is explained by the screening of similarly charged macroions by low-molecular-weight salts, whereas shielding of the electrostatic attraction between the opposite charges in P(AA-*co*-AAc-*co*-AAm) results in swelling.

The swelling behavior of P(DMAEM-*co*-AMPS) cryogels in aqueous solutions of NaCl, KCl, $MgCl_2$, K_2SO_4, Na_2SO_4, and $MgSO_4$ is demonstrated in Figures 7 and 8 [24]. For salts with a common anion (Cl^-, SO_4^{2-}) and mono- or divalent cations, the swelling decreases in order of $K^+ > Na^+ > Mg^{2+}$, while for salts with a common cations (K^+, Na^+ and Mg^{2+}) but different anions, the swelling decreases in order of $SO_4^{2-} > Cl^-$.

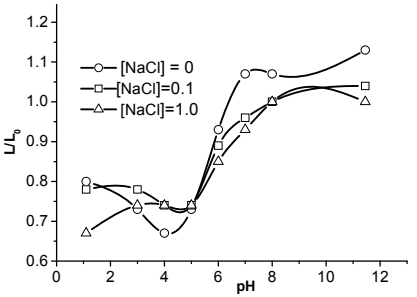


Figure 6. pH-dependent swelling of ACG-334 at various ionic strengths. (Reprinted with permission from [29], copyright 2012 Wiley).

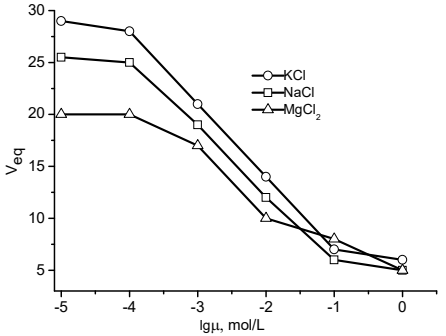


Figure 7. Swelling curves of P(DMAEM-*co*-AMPS) cryogels in aqueous solutions of NaCl, KCl, $MgCl_2$. [AMPS] = 40 mol.%. (Redrawn from [24]).

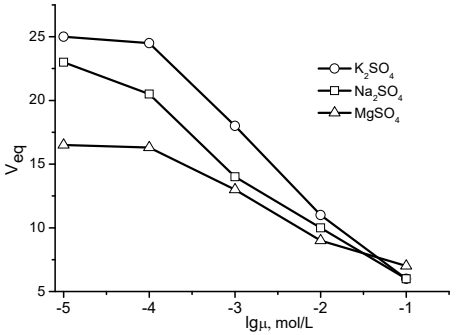


Figure 8. Swelling curves of P(DMAEM-*co*-AMPS) cryogels in aqueous solutions of K_2SO_4, Na_2SO_4, and $MgSO_4$. [AMPS] = 40 mol.%. (Redrawn from [24]).

The behavior of polyampholyte cryogels in water–organic solvent mixture has not been evaluated thoroughly. However, their collapsing in water–acetone mixture is supposed to behave as that of

polyampholyte hydrogels [16,30]. As seen from scanning electron microscope (SEM) pictures, the average pore size of polybetainic gel in pure water is 30–40 μm (Figure 9). In water–acetone mixture the average pore size decreases down to 15–20 μm. In pure acetone, the pores are fully closed, demonstrating the collapse of the gel structure.

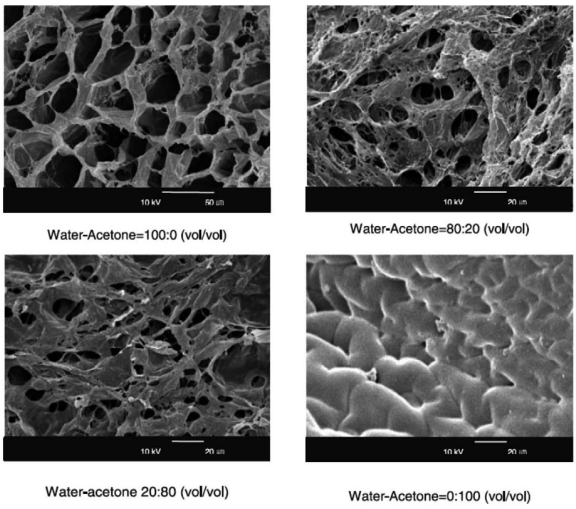


Figure 9. Scanning electron microscope (SEM) pictures of polybetainic gel in water, acetone and water–acetone mixture (Reprinted with permission from [30], copyright 2006 Springer).

The stress-strain curves of P(DMAEM-*co*-MAA) cryogels are presented in Figure 10 [31]. Increasing the concentration of MBAA strengthens the mechanical properties of cryogels.

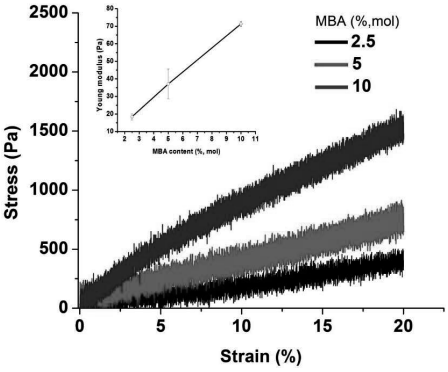


Figure 10. Mechanical properties of P(DMAEM-*co*-MAA) cryogels at different concentrations of MBAA. (Reprinted with permission from [31], copyright 2016 Wiley).

Thus, the swelling-deswelling properties of polyampholyte cryogels with respect to pH, ionic strength, the nature of anions and cations and in the mixture of water–organic solvent do not deviate from the common peculiarities of linear and crosslinked amphoteric macromolecules [28].

3. Complexation of Polyampholyte Cryogels with Transition Metal Ions, Dyes, Surfactants, and Proteins

Due to the presence of acid–base groups, polyampholyte cryogels are able to bind both low- and high-molecular-weight substances. Complexation of polyampholyte cryogels with transition metal ions is accompanied by colorization of samples due to formation of coordination and ionic bonds between metal ions and amine and/or carboxylic groups of cryogels (Figure 11).

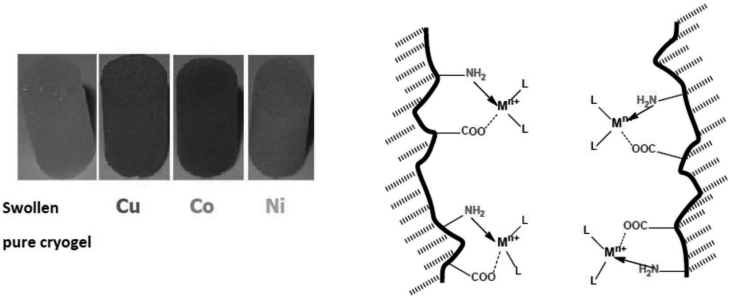


Figure 11. Complexes of ACG-334 with Cu^{2+}, Ni^{2+} and Co^{2+} ions (**left**) and polymer-metal complexation in cryogel pores (**right**). (Reprinted with permission from [29], copyright 2012 Wiley).

As seen in Table 3, the ACG-334 adsorbs up to 99.9% of metal ions but release only 51–67% of metal ions. This is probably due to the capturing of metal ions in dead volumes of networks that are inaccessible for desoprtion. The high adsorption capacity of polyampholyte and polyelectrolyte cryogels can be used for removal of hazardous metal ions [32,33] and dyes [34,35] from waste water.

Table 3. Adsorbed and desorbed amounts of metal ions by ACG-334. (Reprinted with permission from [29], copyright 2012 Wiley).

Transition Metal Ions	Concentration of Metal Ions, mol·L^{-1}	Adsorbed, %	Desorbed, %
Cu^{2+}	10^{-3}	99.9	51.4
Ni^{2+}		99.9	67.2
Co^{2+}		99.9	62.0

The tertiary amine groups of P(DMAEM-*co*-MAA) cryogel bind the sulfonate groups of methyl orange (MO) and sodium dodecylbenzenesulfonate (SDBS) whereas the carboxylic groups interact with amine groups of methylene blue (MB) and quaternary ammonium groups of cetyltrimethylammonium chloride (CTMAC) [31].

Immobilization of CTMAC and SDBS within P(DMAEM-*co*-MAA) cryogel takes place, as shown in Figure 12. The uptake of surfactants by P(DMAEM-*co*-MAA) cryogel is probably accounted for by both electrostatic and hydrophobic interactions of surfactant molecules.

Upon binding of CTMAC, the rate of water flux through the cryogel significantly decreases by 44% in comparison with the initial rate. Hydrophobization of pore surfaces of P(DMAEM-*co*-MAA) cryogel by CTMAC seems to retard the water flux through the pores. According to the conclusion of

authors [36] the surfactant aggregates inside the cryogel matrix, irrespective of whether the attraction mechanism is electrostatic or hydrophobic.

There are two ways of immobilization of proteins within polyampholyte cryogels. The first approach is adsorption of proteins by preliminary prepared cryogels and the second one is imprinting of proteins within a cryogel network in situ cryopolymerization conditions.

It is well known that the binding of proteins by cryogels has an electrostatic nature, and takes place between their isoionic point (IIP) and isoelectric point (IEP) [28]. Figure 13 shows the amount of adsorbed proteins by amphoteric cryogel after one day.

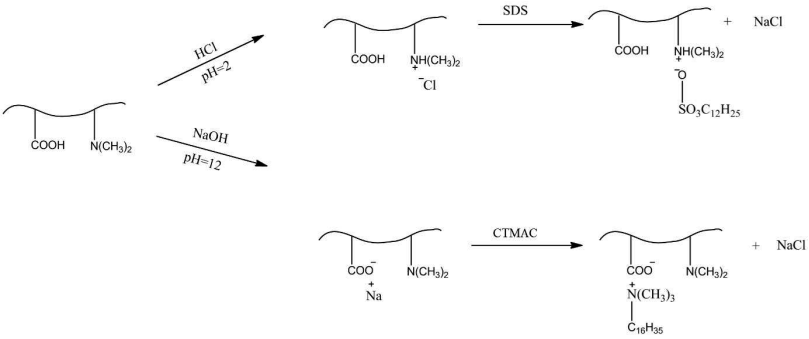


Figure 12. Interaction of SDBS (**upper route**) and CTMAC (**lower route**) with amphoteric cryogel P(DMAEM-*co*-MAA).

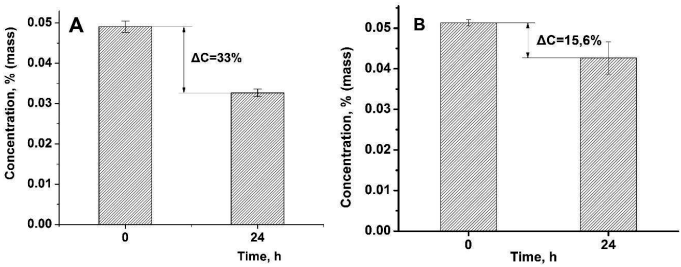


Figure 13. Changing of lysozyme (**A**) and cytochrome C (**B**) concentrations after one day contacting with P(DMAEM-*co*-MAA) cryogel.

The maximal adsorption capacity (q_m) of P(DMAEM-*co*-MAA) cryogel with respect to dyes, surfactants and proteins at different pHs is summarized in Table 4.

Table 4. Adsorption of methylene blue (MB), methyl orange (MO), sodium dodecylbenzenesulfonate (SDBS), and lysozyme by P(DMAEM-*co*-MAA) cryogel. (Reprinted with permission from [31], copyright 2016 Wiley).

Substances	q_m, mg·g^{-1}	pH of Adsorption
Lysozyme	123	9.5
MB	8.3	9.5
SDBS	1313	5.3
MO	27.1	5.3

The binding ability of P(DMAEM-*co*-MAA) cryogel changes in the following order: SDBS > lysozyme >> MO > MB.

One of the unique fundamental property of polyampholytes is the so called isoelectric effect, which takes place at the IEP [28,37–42]. Therefore, the feasibility of utilizing such a phenomenon for polyampholyte cryogels was tested. The IEP of equimolar P(DMAEM-*co*-MAA) found from the flow rate experiments [31] was equal to 7.1 (Figure 14).

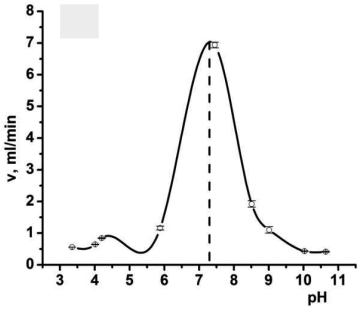


Figure 14. pH dependent change in the flow rate through equimolar P(DMAEM-*co*-MAA) cryogels. The dotted line indicates on the position of the isoelectric point (IEP). (Reprinted with permission from [31], copyright 2016 Wiley).

Table 5 shows the application of the isoelectric effect with respect to SDBS, MB, MO, and lysozyme [31].

Table 5. Detachment of MB, MO, SDBS and lysozyme from P(DMAEM-*co*-MAA) cryogel matrix at different pH. (Reprinted with permission from [31], copyright 2016 Wiley).

Substance	Release, mg/%		
	pH		
	7.1 (IEP)	9.5	5.3
MB	0.04/94	0.003/6	-
MO	0.13/94.5	-	0.0076/5.5
Lysozyme	1.72/98	0.035/2	-
SDBS	17.9/93.2	-	1.3/6.7

At pH 5.3, the amount of MO and MB washed out from the cryogel volume is small, equal to 5.5% and 6.7%, respectively. At pH 9.5, the amount of lysozyme and MB released from the cryogel volume is also small, equal to 2% and 6% respectively. However, at the IEP of P(DMAEM-*co*-MAA) cryogel (pH 7.1), the amount of released MO, MB, SDBS and lysozyme released from the cryogel volume reaches up to 93–98% (Figure 15).

The release mechanism of low- and high molecular compounds at the IEP of P(DMAEM-*co*-MAA) is explained in Figure 16.

At the IEP of P(DMAEM-*co*-MAA) and at pH of 7.1 the cooperativity of intrachain interactions between the acidic and basic groups (formation of inner salt) within a cryogel matrix predominates those of interchain interactions between cryogel and protein (surfactant and dye molecules). As a result, at the IEP of amphoteric cryogel (pH_{IEP} = 7.1) the lysozyme, MB, MO and SDBS are released from the cryogel matrix to the outer solution.

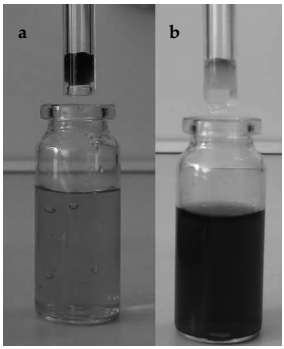


Figure 15. Cryogel samples washed out by buffer solution at pH 9.5 (**a**) and at the IEP pH 7.1 (**b**). (Reprinted with permission from [31], copyright 2016 Wiley).

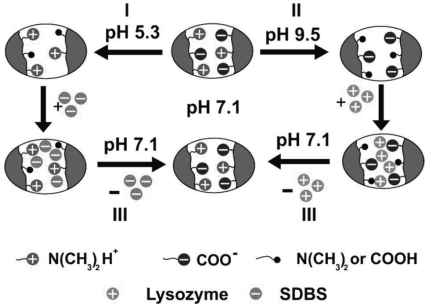


Figure 16. Schematic representation of adsorption of SDBS at pH 5.3 (**route I**), lysozyme at pH 9.5 (**route II**) and their release at pH 7.1, e.g., at the IEP of P(DMAEM-*co*-MAA) (**route III**). (Reprinted with permission from [31], copyright 2016 Wiley).

Molecularly imprinted polyampholyte (MIP) hydrogels and cryogels [43–46] are promising materials for biomedical applications [47–49]. Macroporous amphoteric polymers based on *N*-[3-(dimethylamino)propyl]methacrylate and MAA [46] and *N*,*N*-dimethylaminopropylacrylamide and allylamine (AA) [50] were used as a templates, adsorbents and carriers with respect to bovine serum albumin (BSA) [50] and lysozyme [46]. Macroporous interpenetrating amphoteric cryogels containing methacrylic acid (1st network) and crosslinked chitosan (2nd network) exhibit excellent adsorption-desorption properties with respect to lysozyme [51].

The adsorption capacity of MIP with respect to BSA is much higher (~95%) than nonimprinted polyampholyte (NIP) cryogels (~24%) but the mass transmission resistance is lower in cryogels compared with conventional nonmacroporous materials [45]. As seen in Figure 17, the adsorption saturation for NIP cryogel was reached within 20 min. In the case of MIP, saturation took 50 min because of fitting of template to recognizing sites.

For investigation of the imprinting capability of polyampholyte cryogels, the proteins lysozyme, pepsin, ovalbumin, hemoglobin, and γ-globulin were chosen as templates [52]. The molecular weights of proteins were in the range of (14–210) kDa, the IEPs of proteins varied from 1 to 11 while the IEP of P(AA-*co*-AAc-*co*-AAm) was estimated at about 4.5. An imprinting factor (IF) was calculated by the formula: $IF = k_{MIP}/k_{NIP}$ (where k_{MIP} and k_{NIP} are the retention factors on the molecularly imprinted

polyampholyte—MIP and nonimprinted polyampholyte—NIP) resulting in an IF range of 2–7, which changed in the following order: lysozyme >> ovalbumin > hemoglobin > pepsin > γ-globulin. Thus, polyampholyte cryogels are suitable materials for separation and analysis of proteins and hopefully will play an important role in molecular recognition, separation science and biocatalysis.

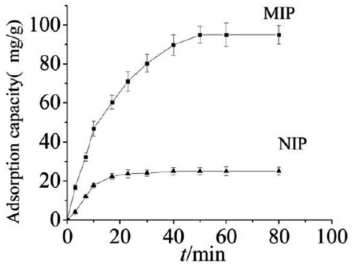


Figure 17. Binding kinetics of bovine serum albumin (BSA) by molecularly imprinted polyampholyte (MIP) and nonimprinted polyampholyte (NIP) based on P(AA-*co*-AAc-co-AAm) cryogels. (Reprinted with permission from [21], copyright 2016 Wiley).

Researchers [53] have prepared lysozyme imprinted polyampholyte hydrogel made of acrylamide, methacrylic acid and *N*,*N*-dimethylaminoethylmethacrylate. The amount of the lysozyme template able to be extracted reached up to 83%. The selective adsoprtion tests showed an IF equal to 3.38 for lysozyme.

Molecularly imprinted polyampholyte hydrogel with respect to BSA was prepared from acrylamide (AAm), *N*-isopropylacrylamide (NIPAM), [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METMAC), and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomers with MBAA as the crosslinker [54]. The reason of selecting such monomers is to provide an opportunity for the protein the hydrogen bond, as the hydrophobic environment and electrostatic interaction increase the selctivity of the hydrogel matrix to recognize the key protein. The morphology of molecularly imprinted polyampholyte hydrogels (MIPAHs) is different from nonimprinted polyampholyte hydrogels (NIPAHs). The pore diameter of MIPAHs is larger than NIPAHs. In order to optimize the structural and functional affinity, the ideal conditions for preparing MIPAHs were found, including AAm concentration, NIPAM/AAm molar ratio, charge densitiy ratio (expressed as METMAC/AMPS molar ratio), and crosslinking density. The maximal binding of BSA (1.97 mg/g) and IF (2.91) was found for equimolar polyampholyte hydrogel. It is suggested that in the case of quenched polyampholyte gels, the specific rebinding and selectively recognition of imprinted proteins becomes tailorable.

Polybetainic (or polyzwitterionic) hydrogels and cryogels based on poly{[2-(methacryloyloxy) ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide}, PMODMSPA with excellent biocompatibility and antofouling properties were prepared by both conventional polymerization at room temperature and under cryopolymerization conditions [27,55]. Polyampholyte cryogels showed high protein loading efficiency at up to 80% and a four-month sustained release rate of a model protein—BSA with very little burst release, whereas the conventional polyampholyte hydrogel showed lower protein loading efficiency (~45%) and a high burst release. The release of BSA from PMODMSPA hydrogel, poly(2-hydroxyethylmethacrylate) (polyHEMA) hydrogel and cryogel matrix continued 4 weeks, whereas the maximal release of BSA from PMODMSPA cryogel reached up to 4 months.

Thus, the adsorption capacity of molecularly imprinted polyampholyte cryogels with respect to proteins is much higher than nonimprinted polyampholyte cryogels. However, the adsorption saturation time for MIP cryogel is longer than nonimprinted polyampholyte cryogel because of

fitting of the template to recognizing sites. Zwitterionic cryogels will prove useful for prolonged macromolecular therapeutic delivery and tissue engineering applications.

4. Immobilization of Metal Nanoparticles within Polyampholyte Cryogel Matrix and Evaluation of Their Catalytic Activity

Cryogel catalysts are promising materials due to the inherent features: macroporous structures, adjustable hydrophilicity and hydrophobility, stimuli-sensitivity and combination of catalytic groups [55–57]. Both polyampholyte cryogel itself [18] and cryogel-immobilized metal nanoparticles [58–64] exhibit unique catalytic properties for various chemical reactions. Nonionic [59,60], anionic [61,62], and cationic [63,64] supermacroporous cryogels and their templated metal nanoparticle composites (Co, Ni, Cu, and Fe) have been used in the redox reaction of $NaBH_4$ and hydrogenation of nitrogroup containing substrates, such as 4-nitrophenol (4-NP), 2-nitrophenol (2-NP) and 4-nitroaniline (4-NA).

Modified polyacrylamide-based amphoteric cryogels were tested as catalytically active substances in transesterification of glyceryl oleate [18]. The highest conversion of glyceride was equal to 88.4% and the yield of methyl oleate is about 64.%.

The catalytic reduction of 4-NP by $NaBH_4$ and oxidation of D,L-dithiotreitol (DTT) by hydrogen peroxide in the presence of AuNPs supported on a cryogel matrix of P(DMAEM-*co*-MAA) was evaluated, and the kinetic parameters, turnover number (TON), turnover frequency (TOF) and activation energy of hydrogenation of 4-NP have been calculated [65–68].

Porous P(DMAEM-*co*-MAA) cryogels with immobilized AuNPs were used as a flow-through catalytic reactor in the reduction of 4-NP and oxidation of DTT. The final hydrogenation product of 4-NP is 4-aminophenol (4-AP), while the final oxidation product of DTT is disulfide (DS) (Figure 18).

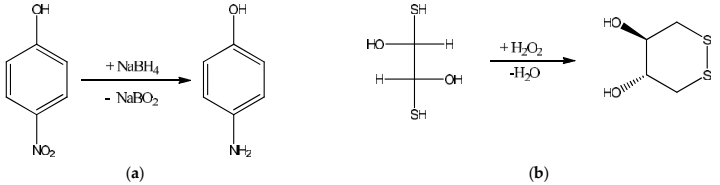


Figure 18. Schemes of reduction of 4-NP by $NaBH_4$ (**a**) and oxidation of D,L-dithiotreitol (DTT) by hydrogen peroxide (**b**).

Both hydrogenation of 4-NP and oxidation of DTT was carried out in a flow-through catalytic reactor, represented in Figure 19.

Passing of the mixture of 4-NP and $NaBH_4$ through P(DMAEM-*co*-MAA) cryogel containing AuNPs leads to reduction of 4-NP to 4-AP [65]. The activation energy of 4-NP reduction in the presence of P(DMAEM-*co*-MAA)/AuNPs is equal to 7.52 kJ·mol^{-1}, which is 2–5 times lower compared to data presented in previous literature [61,62,64]. The AuNPs immobilized cryogel catalyst sustained over 50 cycles without substantial loss of the catalytic activity. The size and shape of AuNPs immobilized within the cryogel matrix are considerably changed after 50 cyclic reductions of 4-NP in comparison with the initial state [65]. The average size of AuNPs accumulated in both surface and longitudinal parts of the cryogel was less than 100 nm. Moreover, the partial leaching out of AuNPs was observed over the course of reduction of sequental portions of substrate [68]. In reduction of 4-NP, the values of TON and TOF of the cryogel catalyst are equal to 38.17 and 21.56 h^{-1} respectively. The cryogel catalyst P(DMAEM-*co*-MAA)/AuNPs also shows the high catalytic activity in oxidation of DTT and sustains 10 cyclic oxidation of substrate with 97–98% conversion. The values of TON and TOF after 10 cyclic oxidation of DTT are equal to 985.2 and 412.2 h^{-1} respectively. The oxidation of DTT proceeds more effectively than reduction of 4-NP due to a high rate constant.

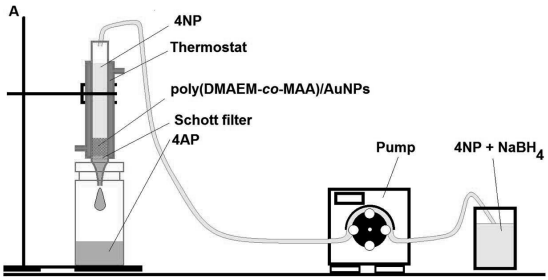


Figure 19. Schematic representation of 4-NP reduction and DTT oxidation by flow-through catalytic reactor based on P(DMAEM-*co*-MAA)/AuNPs. (Reprinted with permission from [67], copyright 2016 Wiley).

Thus cryogel catalysts based on P(DMAEM-*co*-MAA)/AuNPs exhibit a high catalytic activity and conversion in reduction of 4-NP and oxidation of DTT; they can serve as a flow-through catalytic reactor and provide a cascade-type reaction without isolation of intermediate products. The main advantage of the macroporous structure is a large contact area of catalyst and substrate, reusability and simplicity of separation of products from the reaction medium.

The catalytic reduction of *p*-nitrobenzoic acid (*p*-NBA) to *p*-aminobenzoic acid (*p*-ABA) was performed using palladium (PdNPs) and gold nanoparticles (AuNPs) supported on a cryogel matrix of P(DMAEM-*co*-MAA) [69].

Transformation of *p*-NBA to *p*-ABA over DMAEM-*co*-MAA/AuNPs catalyst proceeds via formation of intermediate compounds [70] (Figure 20).

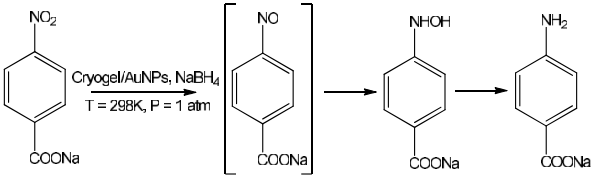


Figure 20. Hydrogenation of *p*-NBA over P(DMAEM-*co*-MAA)/AuNPs catalyst.

It should be noted that in the absence of immobilized AuNPs the mixture of *p*-NBA and $NaBH_4$ fluxed through the P(DMAEM-*co*-MAA) cryogel does not produce *p*-ABA. In the course of *p*-NBA hydrogenation except of *p*-ABA the formation of two additional products was detected. One of them is *p*,*p*′-azodibenzoate, which is the product of catalytic coupling condensation of nitroso compound with hydroxylamine (Figure 21).

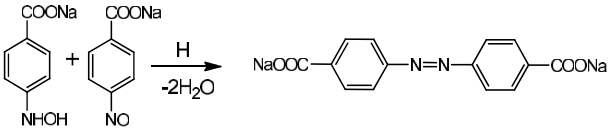


Figure 21. The proposed mechanism of formation of *p*,*p*′-azodibenzoate.

The proposed mechanism of formation of *p,p'*-azodibenzoate on P(DMAEM-*co*-MAA)/AuNPs is confirmed by Raman spectroscopy [71] and is in good agreement with photoreduction of *p*-NBA on nanostructured silver through photoinduced surface catalytic coupling reactions [72].

Another product of *p*-NBA conversion is sodium 4-(4-aminobenzamido)benzoate formed as a result of condensation of amine and carboxylate groups, as demonstrated in Figure 22. A direct condensation polymerization of N-alkylated *p*-ABA has been performed by researcher [73].

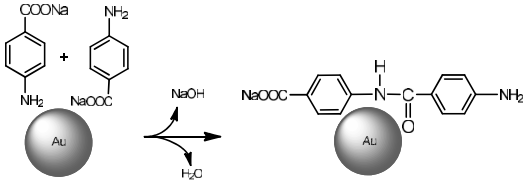


Figure 22. The proposed mechanism of formation of sodium 4-(4-aminobenzamido)benzoate.

Thus, the hydrogenation of *p*-NBA over DMAEM-*co*-MAA/AuNPs produces at least three products: amino-, azo- and amido-derivatives.

In case of P(DMAEM-*co*-MAA)/PdNPs the formation of by-products is not observed. As seen in Table 6, approximately 40% of *p*-NBA is converted to *p*-ABA at [*p*-NBA]:[$NaBH_4$] = 1:50 mol/mol, whereas the conversion is 100% at [*p*-NBA]:[$NaBH_4$] = 1:200 mol/mol.

Table 6. Conversion degree of *p*-NBA to *p*-ABA over DMAEM-*co*-MAA/PdNPs at various molar ratios of substrate to reducing agent. (Reprinted from [69], copyright 2018 Springer).

Cycles	Conversion Degree, %		
	[*p*-NBA]:[$NaBH_4$] = 1:50 mol/mol	[*p*-NBA]:[$NaBH_4$] = 1:100 mol/mol	[*p*-NBA]:[$NaBH_4$] = 1:200 mol/mol
1	0.95	100	100
2	39.02	89.84	100
3	34.73	82.77	100
4	38.10	78.48	100
5	38.40	78.78	100
6	39.63	78.78	100
7	39.94	80.01	100
8	39.94	84.34	100
9	40.55	84.92	100
10	44.23	84.62	100
Average	39.93 *	84.28	100

* Excepting for the first cycle.

The rate constants and activation energy of *p*-NBA reduction over DMAEM-*co*-MAA/PdNPs are represented in Figure 23. The E_a of *p*-NBA reduction on DMAEM-*co*-MAA/PdNPs is equal to 38.83 kJ·mol^{-1}.

Thus, amphoteric cryogels with immobilized palladium and gold nanoparticles may serve as effective flow-through units for continuous hydrogenation or oxidation of various substrates and provide a new strategy for the syntheses of amino compounds, azo dyes, or benzamides from aromatic nitro compounds.

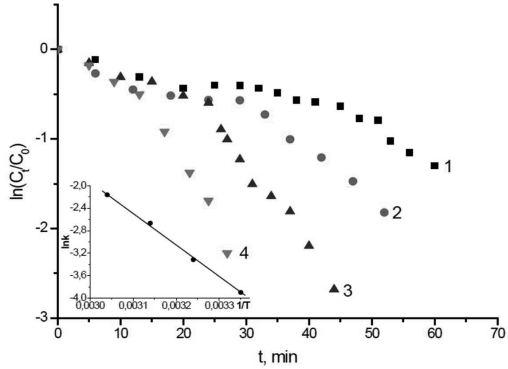


Figure 23. Kinetic curves of *p*-NBA reduction over P(DMAEM-*co*-MAA)/PdNPs are expressed in the graph ln(C_t/C_o) *vs* time. The insert shows lnk *vs* 1/T. T = 298 (**1**), 308 (**2**), 318 (**3**) and 328 K (**4**). (Reprinted from [69], copyright 2018 Springer).

5. Comparative Analysis of Polyampholyte Cryogels with Nonionic, Anionic and Cationic Precursors

Table 1 of the review [3] summarizes the preparation protocol, morphology and physicochemical properties of nonionic cryogels based on AAm, *N*,*N*-dimethyl (or diethyl) acrylamide (DMAAm, DEAAm), NIPAM, 2-hydroxyethylmethacrylate (HEMA); anionic cryogels synthesized using homo- or copolymerization of AAc, MAA, AAm with AMPS, AAm with AAc or itaconic acid (IAc); and cationic cryogels prepared from DMAAm and 2-(diethylamino)ethylmethacrylate (DEAEM). Mostly, the thermo- or pH-sensitive behavior of the above mentioned cryogels were studied. Examples of nonionic, anionic and cationic cryogels prepared from synthetic or natural macromolecular precursors such as poly(vinyl alcohol) (PVA), poly(ethylene oxide) (PEO), poly(*N*-vinylpyrrolidone) (PVP), chitosan, pectin, and cellulose, among others are summarized in Table 2 [3].

In spite of the fact that cryogels of proteins—ovalbumin, serum albumin, gelatin described in Table 3 of [3]—belong to polyampholyte cryogels too, their amphoteric character is weakly exhibited due to a tiny percentage of aminoacids in the macromolecular chain. In contrast, the synthetic polyampholyte cryogels are specific multifunctional objects and have excellent acid–base or anionic–cationic character as well as demonstrate adequate swelling-deswelling, and collapsing behavior in response to external factors such as temperature, pH, ionic strength, metal ions, the nature and charge of low-molecular-weight anions and cations, the mixture of water–organic solvent, and so forth. Some fundamental properties discovered for water-soluble polyampholytes, such as the antipolyelectrolyte effect and the isoelectric effect [37] were clearly demonstarted in the case of polyampholyte cryogels. The antipolyelectrolyte effect that is related to the unfolding of amphoteric macromolecules at the isoelectric point (IEP) upon addition of low-molecular-weight salts was shown for polyampholyte cryogels (see Figure 6). The isoelectric effect that is related to cooperative release of low- or high molecular-weight substances (such as metal ions, dyes, surfactants, polyelectrolytes and proteins) at the IEP of water-soluble polyampholytes also takes place at the IEP of polyampholyte cryogels (see Table 5 and Figure 15). Both phenomena can have practical applications in terms of water desalination, removal of metal ions and organic ions from the wastewater as well as for separation and purification of proteins, and as drug delivery systems.

In future, the closeness of polyampholyte cryogels to cryogels of polyelectrolyte complexes—the products of the interactions between oppositely charged polyelectrolytes might be demonstrated. Polyampholyte cryogels are able to form a very stable metal chelates within macropores due to

formation of both ionic and coordination bonds with acidic and basic groups, and are able to perform specific sorption of metal ions according to stability constants. Recovery of transition metal ions and organic impurities by polyampholyte cryogels is especially important for hydrometallurgy processes and environmental protection. In its turn, the reduction of polyampholyte cryogel-transition metal complexes by reducing agents can produce the nano- and micron-sized particles of metals and/or metal oxides on the inner and surface parts of amphoteric cryogels that might be used as efficient flowing microreactors in catalysis. Passing the mixture of substrate and reducing agent through the cryogel pores provides enough contact time between the catalyst and reaction mixture.

The amphoteric cryogels may retain the amphoteric substrate molecules on the surface of the cryogel matrix, prolonging the contact time between substrate and catalyst. For instance, amphoteric cryogel matrix (DMAEM-MAA) retains the amphoteric product of hydrogenation (p-ABA) much longer and provides more effective catalytic conversion of a substrate. This is the reason of further conversion of amine groups of p-ABA to azocompound and benzamide (see Figures 21 and 22). One can expect that in near future the polyampholyte cryogels may be an effective tool for synthesis of polypeptides from aminoacids in appropriate catalytic conditions. The microstructure of polyampholyte cryogels can be expanded to a random, alternating, graft, block, or dendritic structure with combinations of weak acid/weak base, strong acid/weak base or else weak acid/strong base, and strong acid/strong base.

6. Conclusions

Polyampholyte cryogels as distinct from nonionic, anionic and cationic precursors are unique materials due to the simultaneous presence of acid–base or anionic–cationic monomer units in the macromolecular chain, which considerably expand our opportunities and knowledge about this subject. The behavior of polyampholyte cryogels is not much deviated from the properties of most linear polyampholytes and polyampholyte hydrogels. At the same time, polyampholyte cryogels have many advantages related to applicability. They can be used for removal of metal ions, dyes, surfactants, and drugs from the wastewater. Binding, separation and purification of target proteins from a mixture can also be performed with the help of molecularly imprinted polyampholyte cryogels. Embedding of metal ions or metal nanoparticles within polyampholyte cryogels provides a chance to design active, stable, selective, easy to handle and reusable catalytic systems. To our knowledge the concept of "green chemistry" in the context of catalytic chemistry means reaction behavior in mild conditions, e.g., at atmospheric pressure and low temperature including the easy separation of products from catalysts. These requirements can successfully be realized in case of flow through catalytic reactors made of macroporous polymers within of which metal nanoparticles or enzymes are immobilized. An open problem in the behavior of polyampholyte cryogels is the use of the antipolyelectrolyte effect, i.e., the ability of functional groups of amphoteric cryogels to accumulate low-molecular-weight salts at the IEP, such as for desalination of saline water. Another opportunity is the realization of the "isoelectric" effect for purification and separation of cells, DNA, nucleotides, and proteins from a mixture. Furthermore, theoretical, computational and simulation approaches for better understanding the physicochemical, complexation and catalytic properties of polyampholyte cryogels are required.

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Abbreviations

AA	Allylamine
AAc	Acrylic acid
AAm	Acrylamide
ACG	Amphoteric cryogel
AMPS	2-Acrylamido-2-methyl-1-propanesulfonic acid
4-AP	4-Aminophenol
AuNPs	Gold nanoparticles
BSA	Bovine serum albumin
CTMAC	Cetyltrimethylammonium chloride
DEAAm	*N*,*N*-diethylacrylamide
DEAEM	2-(Diethylamino)ethylmethacrylate
DMAAm	*N*,*N*-dimethylacrylamide
DS	Disulfide
DTT	D,L-dithiotreitol
E_a	Activation energy
HEMA	2-Hydroxyethylmethacrylate
IAc	Itaconic acid
IEP	Isoelectric point
IF	Imprinting factor
IIP	Isoionic point
μ	Ionic strength
MAA	Methacrylic acid
MB	Methylene blue
MBAA	*N*,*N*-methylenebisacrylamide
METMAC	[2-(methacryloyloxy)ethyl]trimethylammonium chloride
MIP	Molecularly imprinted polyampholyte cryogels
MIPAHs	Molecularly imprinted polyampholyte hydrogels
MO	Methyl orange
n	Characteristic exponent describing the mode of penetrant (water) transport mechanism
4-NA	4-Nitroaniline
NIP	Non-imprinted polyampholyte cryogels
NIPAHs	Non-imprinted polyampholyte hydrogels
NIPAM	*N*-isopropylacrylamide
2-NP	2-Nitrophenol
4-NP	4-Nitrophenol
P(AA-*co*-AAc-*co*-AAm)	Allylamine-*co*-acrylic acid-*co*-acrylamide
P(AA-*co*-MAA-*co*-AAm)	Allylamine-*co*-methacrylic acid-*co*-acrylamide
p-ABA	*p*-Aminobenzoic acid
P(AMPSNa-*co*-APTAC)	2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt-*co*-(3-acrylamidopropyl)trimethylammonium chloride
P(DAA-*co*-AAc)	Diallylamine-*co*-acrylic acid
P(DMAEM-*co*-AMPS)	*N*,*N*-dimethylaminoethylmethacrylate-*co*-2-acrylamido-2-methyl-1-propanesulfonic acid
P(DMAEM-*co*-MAA)	*N*,*N*-dimethylaminoethylmethacrylate-*co*-methacrylic acid
PdNPs	Palladium nanoparticles
PEO	Poly(ethylene oxide)
pH_{IEP}	Isoelectric pH
pK_a	Ionization constant of acidic group
pK_b	Ionization constant of basic group
PMODMSPA	Poly{[2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) ammonium hydroxide}
p-NBA	*p*-Nitrobenzoic acid
polyHEMA	Poly(2-hydroxyethylmethacrylate)

PVA	Poly(vinyl alcohol)
PVP	Poly(*N*-vinylpyrrolidone)
q_m	Adsorption capacity
SDBS	Sodium dodecylbenzenesulfonate
SEM	Scanning electron microscope
TOF	Turnover frequency
TON	Turnover number
V_{eq}	Equilibrium swelling

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Advances in Synthetic Polyampholytes for Biotechnology and Medicine

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Abstract—Polyampholytes are unique macromolecules containing acid/base or anionic/cationic groups in the main or side chains that mimic the behavior of proteins, polypeptides or polynucleotides. Water-soluble and water-swelling polyampholytes exhibit salt-tolerant, thermal-resistant, shear-stable, self-healing, anti-fouling, self-assembling, and stimuli-responsive properties that provide broad impact as structural biomaterials, drug delivery and chemo-mechanical systems, biosensors, energy storage devices, supercapacitors, actuators etc. In this review we mainly pay attention to fundamental and applied aspects of synthetic polyampholytes in the context of biotechnology and medicine. Among the outlined topics the role of linear and crosslinked amphoteric macromolecules as well as macromolecular complexes of polyampholytes with polyelectrolytes, DNA, proteins and drugs is highlighted. Cryoprotective behavior of synthetic polyampholytes is shown with respect to cell preservation and viability. Injectable, soft, flexible, stretchable, self-healing and stimuli-responsive physically or chemically crosslinked polyampholyte gels that are promising materials for fabrication of artificial tissue, wound dressing, cartilage, cardiovascular, bone defect repair, regenerative medicine and tissue engineering scaffolds, soft actuators and sensors, soft robotics are also in the eyeshot of this review. Hierarchically structured multi-responsive polyampholytic gels, multilayered films and membranes possessing encapsulation–release and "on–off" behaviors are considered as antibiofouling, anticoagulation, and drug delivery system.

Keywords: Synthetic polyampholytes, biotechnology, medicine, structural biomaterials, biochemo-mechanical systems, anti(bio)fouling, hemocompatibility, cryoprotective properties, drug delivery

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1. INTRODUCTION

Functional, configurational, conformational and behavioral similarity of synthetic polyampholytes to natural ones [1–3] is an emerging platform to protein mimicking [4, 5] and developing of various biocompatible materials, drug delivery systems, tissue-engineering technology, bioreactors etc. Advances in polyampholytes emphasizing biomedical [6–8], medical [9] and antifouling aspects [10] were recently reviewed.

Synthetic polyampholytes can be classified into 3 groups: "annealed," "quenched", and "betainic" (or "zwitterionic") [11–14]. "Annealed" polyampholytes consist of acid-base monomers that are ionized in dependence of pH, while "quenched" precursors containing strongly charged cationic and anionic mono-

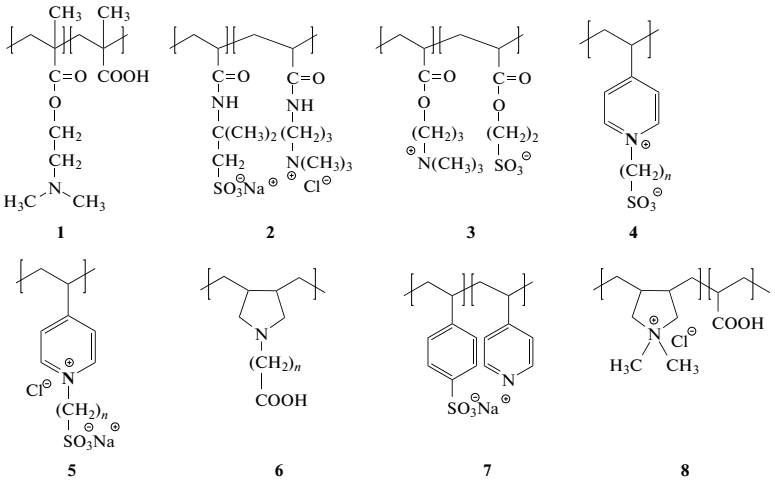


Fig. 1. Repeating monomeric units of annealed (1), quenched (2), zwitterionic (3, 4), quenched betainic (5), annealed betainic (6), and self-annealed (or self-quenched) (7, 8) polyampholytes.

mers retain their respective charges independently on pH. The "semi-annealed" or "semi-quenched" polyampholytes are defined as amphoteric macromolecules that combine the weak acid/cationic or weak base/anionic monomers. "Betainic" (or "zwitterionic") polyampholytes are macromolecules containing identical number of acid-base (or fully charged anionic-cationic) species in the same monomer units [15]. The macromolecules existing via compensation of the cationic-anionic monomer pairs without counterions also belong to "zwitterionic" polymers [16–20] or polyampholytic ionic liquids [21, 22]. Examples of polyampholytes with different chemical structures are shown in Fig. 1.

In the current literature the terms "zwitterionic polyampholytes," "polybetaines," "zwitterionic polyelectrolytes," "polyzwitterions" are also widely used. Lowe and McCormick [12] used the term polyzwitterion for all polymers that possess both cationic and anionic groups. They refer polyampholyte to those polymers that specifically possess the charged groups on *different* monomer units while the term polybetaine is refered to those polymers in which the anionic and cationic groups are replaced on the *same* monomer unit. According to the definition of Laschewsky [16] polyampholytes behave mostly either as polyanionic or as polycationic species, whereas polyzwitterions (or polybetaines) due to their overall charge neutrality exhibit a different, hybrid-like property profile. Sometimes a subtle difference between these definitions is hardly perceptible.

"Annealed," "quenched," and "betainic" type polyampholytes belong to unique macromolecules that can leverage or even manipulate the conformational, physicochemical, physicomechanical and biochemical properties of materials to predictable or desired level. The main difference between the polyelectrolytes and polyampholytes irrespectively of linear or crosslinked (gel state) structure is related to their response to salt addition [23]. Expanded (or swollen) in pure water polyelectrolyte chains shrink in salt solution due to the screened electrostatic repulsion between uniformly charged macroions (polyelectrolyte effect). Collapsed (or shrunken) in aqueous solution "annealed" polyampholyte at the isoelectric point (IEP) and/or charge-balanced "quenched" polyampholyte, including polymeric betaines, in quasi-neutral state, unfold in salt solution due to screening of the electrostatic attraction between oppositely charged monomers ("antipolyelectrolyte" effect). The difference between polyelectrolyte and "antipolyelectrolyte" effects upon salt addition is schematically illustrated in Fig. 2.

Collapsing and expanding of "annealed" polyampholyte chains as a function of pH medium and ionic strength of the solution μ is clearly seen from Fig. 3 [24, 25].

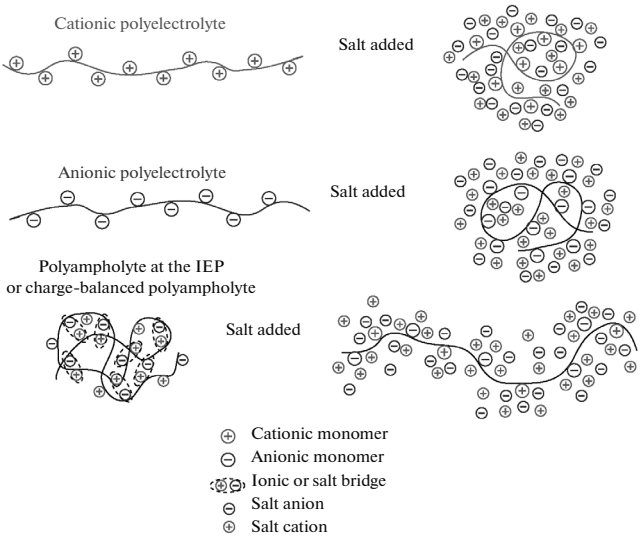


Fig. 2. Schematic illustration of the behavior of polyelectrolyte and polyampholyte in aqueous-salt solution.

From both sides of the IEP, polyampholyte molecules behave like ordinary polyelectrolytes, e.g. the viscosity falls with growth of the ionic strength (blue arrow). An opposite, so-called "antipolyelectrolyte," effect is observed at the IEP, the polyampholyte viscosity increases with increasing of the ionic strength (red arrow). In contrast, the sedimentation constant S_0 is maximal at the isoelectric pH (pH_{IEP}) and diminishes at $pH > pH_{IEP}$ and $pH < pH_{IEP}$ demonstrating the formation of compact conformation at the pH_{IEP}. Thus in contrast to polyelectrolyte effect, the "antipolyelectrolyte" effect is a common phenomenon for "annealed," "quenched," and "betaine" type polyampholytes in aqueous-salt solution.

In recent years the attention of researches is paid to intrinsically disordered proteins (IDPs) also known as intrinsically unstructured proteins that are characterized by their biased amino acid composition and low sequence complexity, as well as by their low proportions of bulky hydrophobic amino acids and high proportions of charged and hydrophilic amino acids [26, 27]. In fact, 75% of IDPs belong to strong polyampholytes [28, 29] and their stimuli-responsive phase transitions functions are governed by relationships between information encoded in their aminoacid sequences and ensembles of conformations [30]. Nature uses polyampholytic IDPs as scaffolds for extracellular matrices, plant cell walls, and other fibrous composites [31, 32]. IDPs can have positive, negative charges or be quasi-electroneutral, exhibit stimuli-responsive conformational and phase behavior, exist as fully expanded, molten globular, pre-molten globular and random coil states [33, 34]. Since the detailed consideration of IDPs is out of the scope of the present review and requires standalone interest, we refer the readers to literature sources [26–34]. Nevertheless, it is obvious that the structural and behavioral similarity between synthetic and natural polyampholytes is due to the presence of positive and negative charges. The location of opposite charges along the macromolecular chain plays a crucial role in the conformational and phase behavior of the polyampholytes. Structural and behavioral similarity between synthetic and natural polyampholytes can expand our knowledge and invoke the renewed interest to polyampholytes in whole and IDPs in particular.

This review is organized as follows. First, the role of polyampholytes to deliver polynucleotides and oligonucleotides to the cell is briefly mentioned. Then perspectives of synthetic amphoteric hydrogels as structural biomaterials are considered. Separate subchapter is devoted to synthetic polyampholytes as macromolecular cryoprotective agents. Drug delivery systems based on polyampholytes are in the fore-

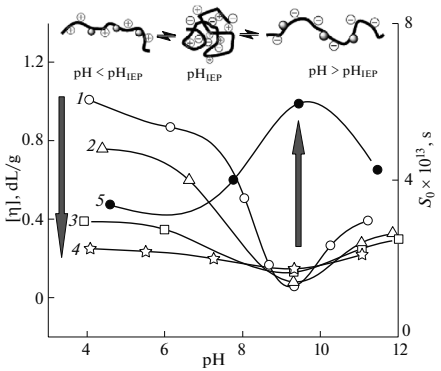


Fig. 3. pH-dependence of the intrinsic viscosity (curves *1*–*4*) and sedimentation constant (curve *5*) of equimolar annealed polyampholyte based on 1,2,5-trimethyl-4-vinylethynylpiperidinol-4-*co*-methacrylic acid TMVEP-*co*-MAA (54 : 46 mol %) in the presence of 0.005 (*1*), 0.01 (*2*), 0.1 (*3*), and 0.3 M KBr (*4*, *5*). Top scheme in Fig. 2 reflects the pH-dependent conformational change of polyampholyte chain. Reprinted from [24].

front of medicine and pharmacy. Concluding parts contain the perspectives of linear and crosslinked polyampholytes for application in biotechnology, medicine and pharmacy.

2. POLYAMPHOLYTES IN DELIVERY OF POLYNUCLEOTIDES AND OLIGONUCLEOTIDES TO CELL

The literature survey reveals that synthetic polyampholytes are less explored subject with respect to gene delivery compared to polycations [35]. Early pioneering works of A.V. Kabanov and V.A. Kabanov [36, 37] laid foundations for accomplishment of polyelectrolytes in delivery of genetic materials in a cell. Formation and dissociation of polyelectrolyte complexes (PEC) formed between DNA and various polyamines [38] as well as polycarboxybetaines [39] was evaluated as a function of ionic strength at different pH using the fluorescence quenching technique. It was shown that the structure of polyamines and polycations is a decisive factor of PEC stability. Polyampholytes are also promising objects to deliver the genetic materials in the treatment of various diseases. Trubetskoy et al. [40–50] patented the complexes of polyampholytes with polynucleotides and oligonucleotides, such as siRNA, or pDNA, to enhance their delivery to cells in vivo or in vitro and to provide therapeutic processes (gene therapy). Delivery of siRNA to cells via formation of interpolyelectrolyte complexes (polyplexes) with cationic polymers proceeds in such a way that such polyplexes having several hundred nanometers are further transferred into cells through endocytosis or a fusion mechanism [51].

Polyampholytes bind nucleic acid to form small complexes which can be utilized in the delivery of nucleic acid to mammalian cells [40–50]. The quintessence of these inventions is closely related to dissociation of preformed DNA–polycation complexes by addition of polyanions [52, 53]. Such principle can definitely be extended to comb-type block polyampholytes (BPA) consisting of anionic and cationic blocks [54]. Cationic block of BPA cooperatively binds DNA and form BPA–DNA complex. If anionic block possesses high charge density, it can displace DNA from its BPA–DNA complex (intra-polyelectrolyte complex) while in case of low charge density anionic block the BPA–DNA complex is not destroyed and surrounded by negatively charged anionic block. In its turn the anionic block replaced on the shell of BPA–DNA complex inhibits interactions of polycomplex with serum proteins. Otherwise binding of negatively charged serum components can significantly decrease gene transfer efficacy of DNA/polycation complexes in vivo. Thus, the charge density of the polyanion or anionic block is of primary importance. The higher the charge density, the more effective is the protective effect against serum proteins. To confirm this principle two types of BPA, namely high charge BPA composed of linear poly(ethyleneimine) (LPEI) and poly(methacrylic acid) (PMAA) and low charge BPA composed of LPEI and poly(glutamic acid) (PGA) were tested with respect to plasmid DNA [40–44]. It was demonstrated

that BPA can substantially enhance gene transfer activity compared to non-polyampholyte mixture. Enhancement of transcriptional activity of DNA complexes was also evidenced for PEG-based polyampholytes [55]. In particular, both polyanions and polyampholytes cause the dissociation of DNA-polycation complexes. A highly charged polyanion enhances the dissociation of DNA–polycation complexes and separation a polycation from a DNA. While BPA induces an effective attraction between a DNA and a polycation and provides a high transcription activity of the DNA–polycation complexes in the presence of polyampholytes [56]. Therefore, one of the important questions is how to design a flexible polyampholyte with maximal effectiveness in dissociation of DNA–polycation complexes. Taking into account that the molecular simulation study arranges the stability of complexes in the following order: block polyampholyte-polyelectrolyte > statistical polyampholyte-polyelectrolyte > alternating polyampholyte-polyelectrolyte [57, 58], depending on charge distribution, nature of solvent and salt, one can expect that the stability of polyampholyte-DNA complexes will follow the same order. Schematic representation of binding of DNA by BPA is shown in Fig. 4. The resulted BPA–DNA polyplex may consist of "core" part represented as interpolyelectrolyte complexes formed between cationic BPA block and anionic DNA, and "shell" part that is the excess of anionic block preserving the solubility of BPA–DNA complexes in water and simultaneously preventing the interaction with proteins (Fig. 4d). In its turn, the "tadpole" shaped "core" part can aggregate into star micelle surrounded by hydrophilic "shell" (Fig. 4e). At or near the isoelectric point (IEP) the cooperative intra-ionic contacts between anionic and cationic blocks of BPA may prevail over the inter-ionic contacts between cationic block of BPA and DNA. As a result, anionic and cationic blocks of BPA can form themselves collapsed intra-ionic polycomplexes and DNA be released (Fig. 4f). A globular "core" of BPA can further be organized into star-like micelle structure surrounded by anionic block of BPA (Fig. 4f).

Release mechanism of anionic, cationic and nonionic polymers at the isoelectric point (IEP) of BPA was discussed for equimolar polycomplexes of BPA–poly(acrylic acid), BPA–poly(*N*,*N*-dimethylallylammonium chloride), and BPA–poly(*N*-vinylpyrrolidone) [59]. As BPA, the block copolymer poly(methacrylic acid)-*block*-poly(1-methyl-4-vinylpyridinium chloride) (PMAA-*b*-P1M4VPyCl) composed of 64 mol % PMAA and 36 mol % P1M4VPyCl was selected. It was found that PMAA-*b*-P1M4VPyCl binds cooperatively both poly(acrylic acid) (PAA) and poly(*N*,*N*-dimethylallylammonium chloride) (PDMAAC) with binding degree $\theta = 38\%$ and 25% respectively at narrow interval of pH 3.3–4.5 (Fig. 5a). While PMAA-*b*-P1M4VPyCl itself forms cooperative intraionic complex in the range of pH 4.5–5.9 with binding degree 32%. It should be noted that PMAA-*b*-P1M4VPyCl can also bind initially anionic and later cationic polyelectrolytes. However, the degree of successive binding of cationic (first) and anionic (second) polyelectrolytes is much lower ($\theta = 22\%$) than the θ values of BPA–PAA ($\theta = 38\%$) and BPA–PDMAAC ($\theta = 25\%$) pairs. These ternary polycomplexes are insoluble and fully precipitate.

As revealed from viscometric data, the pH_{IEP} of BPA based on PMAA-*b*-P1M4VPyCl was placed near pH 6.4 (Fig. 5b). Thus intraionic complexation between anionic and cationic blocks of BPA takes place at pH 4.0–6.1 and is maximal at $pH_{IEP} = 6.4$ which coincides well with viscometric results. The state of BPA at the pH_{IEP} can be represented as "core–shell" structure where the "core" part is a collapsed globule due to compensation of oppositely charged blocks while the "shell" part is an ecess of anionic PMAA block that surrounds the whole macromolecules and preserves from precipitation. Sharp increase in the reduced viscosity at pH > 6.5 is accounted for destruction of intraionic bridges and transformation of BPA into cationic polyelectrolyte. A scaling theory developed for charge imbalanced BPA [60], defined as a "tadpole" shape, with a globular "head" and polyelectrolyte "tail" supports the existence of "core–shell" structure in a charge-asymmetric PMAA-*b*-P1M4VPyCl with an excess of anionic PMAA block. A globular "head" driven by the electrostatic attraction between oppositely charged blocks further aggregates into micelles if the electrostatic repulsion between their "tails" is weaker than the surface energy gain due to aggregation of their "heads." Formation of "core–shell" structures, micelles and aggregates at the pH_{IEP} was observed for proteins [61, 62], block-polyampholytes [63–66], and ampholytic block copolypeptides [67, 68].

Thus, if intra-chain interaction between anionic and cationic blocks of BPA (Intra-PEC) prevails inter-chain interaction between BPA and DNA (Inter-PEC) the latter can be detached from BPA–DNA complex and released at the IEP of BPA. Such phenomenon might be vital because the realization of the "isoelectric effect" was confirmed at the IEP of water-soluble polyampholytes, amphoteric hydrogels and cryogels with respect to polyelectrolytes and proteins [69].

Multi-stimuli-responsive chiral-achiral amino acid-based block copolymers effectively and selectively uptake and release the gene depending on the external stimuli (temperature, pH, NaCl, urea) [70]. Complex (or polyplex) formation between block copolymer poly(A-glu-OH)-*b*-poly(VAm) and DNA was studied by DLS, CD, and gel electrophoresis (Fig. 6).

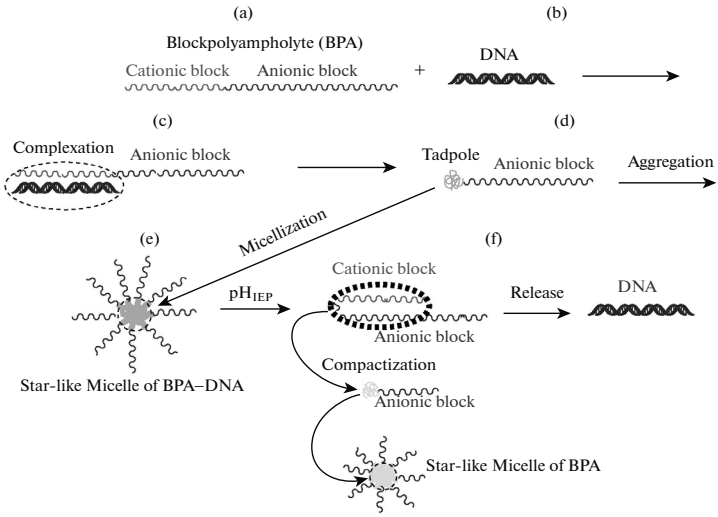


Fig. 4. Schematic routes of BPA–DNA complex formation and proposed release mechanism of DNA at the IEP of BPA.

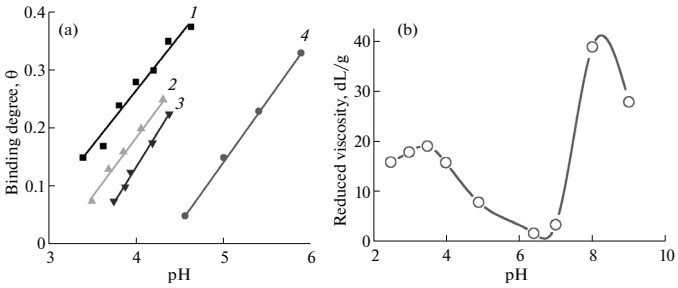


Fig. 5. (a) pH profile of binding degree θ for systems consisting of [PMAA-*b*-P1M4VPyCl]/[PAA] (*1*), [PMAA-*b*-P1M4VPyCl]/[PDMAAC] (*2*), [PMAA-*b*-P1M4VPyCl]/[PDMAAC]/[PAA] (*3*). Curve *4* corresponds to intramolecular complexation within PMAA-*b*-P1M4VPyCl; (b) pH dependence of the reduced viscosity of PMAA-*b*-P1M4VPyCl in aqueous solution. Reproduced from [59].

CD spectra exhibit a strong negative peak at 240 nm and a positive peak at 280 nm that belong to the helicity of B-form DNA. Addition of block polyampholyte decreases both peaks demonstarting that the DNA helicity depends on electrostatic interaction between cationic groups of poly(VAm) and phosphate groups of DNA. The hydrodynamic size of DNA/blockpolyampholyte slightly decreases from D_h = 459 nm to 342 nm with increasing N/P ratios from 1 to 10 confirming the compactization of polyplexes. Insignificant change of zeta-potential of polyplex from −48.9 to −42.5 mV is probably due to the presence of neg-

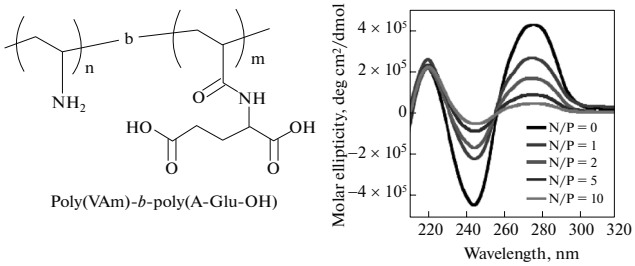


Fig. 6. Structural formula of block copolymer poly(A-glu-OH)-*b*-poly(VAm) and CD spectra of polyplexes formed between DNA and the block copolymer at different cation/anion charge ratio, N/P (where N is nitrogen atoms in poly(VAm), P is phosphate groups in DNA) in potassium phosphate buffer (pH = 7.4, [DNA] = 50 mg L^{-1}). (Reproduced from [70].)

atively charged block of poly(A-Glu-OH) on the surface of polyplex. However, the release of DNA at the IEP of poly(A-glu-OH)-*b*-poly(VAm) was not evaluated.

It was demonstrated [71] that phosphonium salt containing polymers including polyampholyte [72] can effectively bind DNA at lower polymer concentration and mediate good transfections efficiency with low cytotoxicity in comparison with ammonium-based polymers. Table 1 summarizes various types of polybetaines and polyampholytes used as gene delivery vectors [35]. It is seen that polymeric carbo-, sulfo- and phosphobetaines as well as aminocarboxylic and aminophosphonic polyampholytes can be used as effective polyampholyte-mediated gene delivery systems.

Summarizing this section one can conclude that the majority of studies on gene delivery systems are related to polycomplexes (polyplexes) formed between DNA and polycations. Stability of polyplexes is crucial because if the polyplexes are not stable enough, premature dissociation can occur before delivery of the genetic material at the desired place, resulting in low transfection efficiency. If polyplexes are too stable the DNA will not release also resulting in low gene expression. In this connection recharging (coating) of DNA–polycation complexes by polyanions is preferential because the ternary complex effectively protects them from unfavorable interactions with serum proteins. To the best of our knowledge the polyampholytes are less considered subject with respect to gene delivery. A limited number of polyzwitterions (or polybetaines) and comb-like and block-polyampholytes were tested with respect to plasmid DNA. In our mind, the advantage of polyampholytes is due to the variation of their charges as a function of pH. Especially possible release of DNA at the IEP of block-polyampholytes is a promising tool to design the gene delivery systems. Some potential applications can be expected from polyampholytic polypeptides that are able to uptake and release genes depending on external stimuli. Ternary polyplexes composed of natural cationic and anionic polyelectrolytes appear to be promising candidates for gene delivery due to recharging the surface of binary polyplexes as well as reducing the toxicity and enhancing the transcriptional and transfectional efficiency. In its turn the applicability of stimuli-responsive strong polyampholytes – IDPs as gene vector was not tested yet. It is anticipated that in the future a significant number of studies have to be undertaken using stimuli-responsive natural and synthetic polyampholytes with improved in vitro and in vivo tranfection efficiencies [79, 80].

3. AMPHOTERIC HYDROGELS AS PERSPECTIVE STRUCTURAL BIOMATERIALS AND BIOCHEMO-MECHANICAL SYSTEMS

Due to high toughness, excellent bio- and hemocompatibility, anti-biofouling, self-healing ability, cytotoxic and adhesive properties in physiological conditions amphoteric hydrogels are advanced in the forefront of perspective structural biomaterials, such as cartilage, antithrombogenic implants, wound dressing and blood-contacting materials, drug delivery systems [81–84]. Research group of J. Gong et al. [81–90] made remarkable contribution to the development of self-healing, artificial tissue-mimetic and mechanically robust materials based on polyampholyte hydrogels. Recent advances in injectable hydrogels for drug delivery and tissue engineering applications were reviewed in [91].

Table 1. Various polyampholytes applied for complexation with DNA [35]

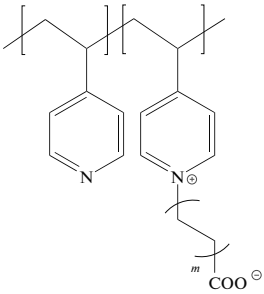
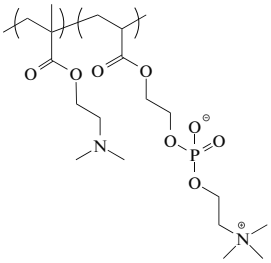
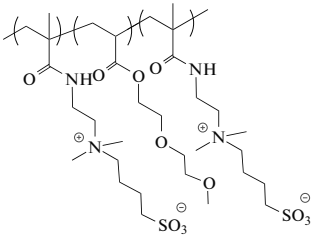
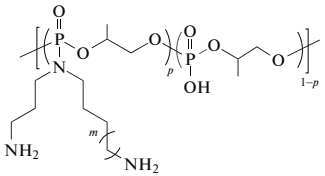
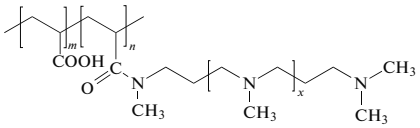
Structural unit	Abbreviation	Description of polymer	Used DNA	Ref.
 Poly(pyridino carboxylate) with various lengths of alkyl chain (*m*) between charges	PCB_m	m = 1,2,3,4,5,8 Degree of substitution >92%, $M_n = (3.5–5.2) \times 10^5$	ctDNA 10 kbp	73
 Poly[2-(dimethylamino)ethyl methacrylate]-*b*-poly(2-methacryloyloxyethyl phosphorylcholine)	PDMAEMA-*b*-PMPC	M_w/M_n = 1.21–1.26; [MPC] = 32, 48, 65, 70%	pDNA 6.7 kbp	74
 Poly(*N*-[3-(methacryloylamino) propyl]-*N*,*N*-dimethyl-*n*-(3-sulfopropyl) ammonium hydroxide-*b*-poly[2-(2-methoxyethoxy)ethyl methacrylate]-*b*- poly(*N*-[3-(methacryloylamino) propyl]-*N*,*N*-dimethyl-*N*-(3-sulfopropyl) ammonium hydroxide	PSB-*b*-POEMA-*b*-PSB	M_w/M_n = 1.23–1.31	ctDNA 5 kbp pDNA 5.3 kbp	75

Table 1. (Contd.)

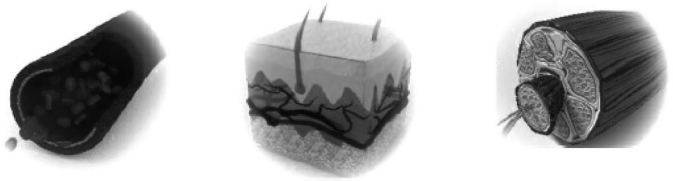
Structural unit	Abbreviation	Description of polymer	Used DNA	Ref.
 Poly(1,2-propylene *H*-phosphonate modified with spermidine (PPA-*g*-SA)	PPA-*g*-SA	$m = 1$, $p = 0.29$, Degree of polymerization 90; $M_w/M_n = 1.43$	pRE-Luciferase, 11.9 kbp; pcDNA3/Bcl-2	76
Poly(1,2-propylene *H*-phosphonate modified with dipropyltriamine (PPA-g-DPA)	PPA-*g*-DPA	$m = 0$, $M_w/M_n = 1.4–2.7$	VR1255C, 6.4 kbp	77
 Polyamines containing tertiary amine groups and acrylic acid (PAM-*co*-AA)	PAM-*co*-AA	$x = 0, 1, 2$ $M_w/M_n = 1.37–1.58$	21-mer DNA oligonucleotide	78

The bending flexibility, high strengths and moduli of the "quenched" polyampholyte hydrogels (QPA) consisting of equimolar amount of strong charged anionic and cationic monomers are similar to soft tissues of vasculature, skin or muscle and can be used as tissue-replacing biomaterials [92]. Figure 7 compares the mechanical properties of polyampholyte hydrogels that can more or less satisfy some requirements of biomaterials.

These data reveal that the mechanical properties of hydrogels derived from interpenetrating and dual-crosslinked networks, macromolecular crosslinking, nanocomposite, thermally conditioned, polyion complexes, and polyampholyte hydrogels reinforced by glass fibers are several orders higher than pristine polyampholyte hydrogels. This fact inspires the design of artificial ligament that can replace the natural one. In case of reinforced by glass fiber polyampholyte hydrogels the driving force of synergistic combination is that the glass fibers play the role of stiff, load bearing, anisotropic matrix while the tough polyampholyte hydrogel acts as extracellular matrix. Namely, the combination of glass fiber woven matter and charge balanced polyampholyte that deswells in water is responsible for strong mechanical properties. Dialysis of counter-ions and co-ions from polyampholyte gel interior to outer environment enhances the adhesion between the gel and the fibers. The highly charged polyampholyte chains after dialysis in deionized water are collapsed or "zipped." In this context, the term "zipped" means multiple cationic/anionic junction zones of polyampholytes with the finite-sized bundles. Microscopic cellular structure of polyampholyte hydrogels in "zipped" form with a pore size ~20 μm after dialysis was directly visualized by field-emission SEM (FE-SEM) and scanning transmission electron microscopy (STEM) [93]. The crucial role of dialysis is that the "zipping" of the polyampholyte chains results in formation of a tough hydrogel that favors the sticking of hydrogel to fibers.

Thermally-healable, hydrophobically modified physical QPA hydrogels based on oppositely charged monomers – sodium salt of 2-acrylamide-2-methylpropanesulfonate (AMPS) and 3-acrylamidopropyltrimethylammonium chloride (APTAC) have recently been prepared via micellar polymerization in the absence of a chemical cross-linker [94]. The resulting hydrogels have mixed micelles composed of sodium dodecyl sulfate (SDS) and *n*-octadecyl acrylate (C18A) units interconnected by AMPS–APTAC copolymer chains, as schematically illustrated in Fig. 8a.

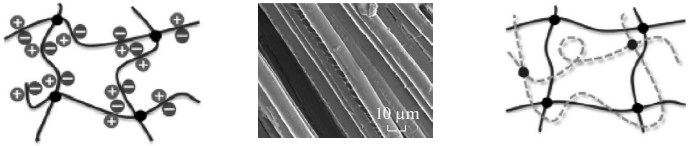
It was shown that the incorporation of even a small amount of C18A into the physical QPA network structure leads to the formation of a macroscopic gel. Cut-and-heal tests revealed that all as-prepared hydrophobically modified QPA hydrogels exhibit healing behavior induced by heating. For instance, the



Vascular tissue
E ~ 100's kPa
σ_f ~ 1 MPa
EWC ~ 70%

Epithelial tissue
E ~ 100's kPa
σ_f ~ 10's MPa
EWC ~ 65%

Muscle tissue
E ~ 10's kPa
σ_f ~ 1 MPa
EWC ~ 75–80%



Crosslinked Polyampholyte hydrogels
E > 8 MPa
σ_f ~ 5 MPa
EWC ~ 40–60%

Fiber reinforced polyampholyte hydrogels
E ~ 600 MPa
σ_f ~ 17 MPa
EWC ~ 50%

Zwitterions containing double networks
E ~ 1.5 MPa
σ_f ~ 23 MPa
EWC ~ 83%

Fig. 7. Comparison of the Young's modulus (E), fracture strength (σ_f), and equilibrium water content (EWC) values of biological tissues and polyampholyte hydrogels. (Compiled from [87, 92].)

hydrogel with 5 mol % C18A shows a complete healing efficiency with respect to Young's modulus, tensile strength, and elongation at break after a healing time at 50 ± 2°C of 1 day (Fig. 7b). Figure 14c presents images of a healed hydrogel specimen with 5 mol % C18A during stretching up to 1200% stretch ratio at which it fractures at any location in the middle as the virgin one.

Thus in the field of polyampholyte hydrogels with enhanced physicochemical properties the advances have been made to improve their mechanical properties. For this purpose, a new class of supramolecular physical hydrogels containing both strong and weak ionic bonds were prepared by random copolymerization of oppositely charged ionic monomers at relatively high monomers concentration and equimolar monomers ratio [82, 86, 90]. Another strategy involves micellar polymerization of strongly charged anionic and cationic monomers as described in [94]. The permanent crosslinks maintain the shape of the gel while the ionic crosslinks as sacrificial network are responsible for elongation, deformation, adhesion, self-healing, shape memory, and other important functions. The hydrogel structures with superior toughness and high fracture energy can be achieved by involving both physical entanglement and chemical bonding.

NIPAM-based polyampholyte hydrogels consisting of acrylic acid and *N*-vinylimidazole monomeric units with co-immobilized glucose oxidase and urease were designed by Kokufuta et al. [95] to develop biochemo-mechanical system, e.g. to convert biochemical energy to mechanical work (swelling-shrinking) as a biocatalyst (regulation of reaction kinetics) in a chemical conversion. Volume changes of poly-

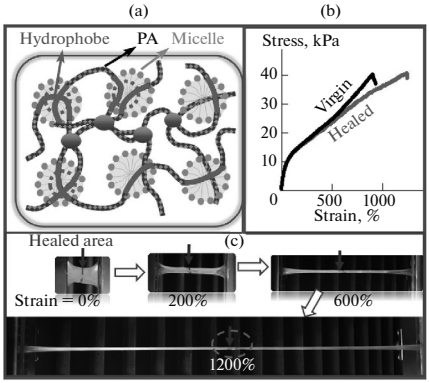


Fig. 8. (a) Cartoon showing the structure of QPA hydrogels formed via micellar polymerization. The green balls represent ionic bonds between polyampholyte chains. (b) Typical stress-strain curves of QPA hydrogels with 5 mol % C18A before (black) and after healing at 50 ± 2°C for 24 h (red). (c) Images of a healed hydrogel specimen with 5 mol % C18A during stretching. Healed area is indicated by arrows. The location of the fracture point is shown by the red dashed circle. Adapted from [94].

ampholyte gels were triggered by enzymatically induced pH of the solution around the isoelectric pH (pI ~ 6–7) of polyampholyte gel. Taking into account that urease catalyzes the hydrolysis of urea to ammonia and carbon dioxide (increasing of pH) while glucose oxidase produces gluconic acid (decreasing of pH) it is expected that addition of glucose leads to swelling of hydrogel due to ionization of imidazole groups of polyampholyte (pI > pH), addition of urea leads to gel swelling because of ionization of carboxylic groups of polyampholyte (pI < pH). The most interesting system is polyampholyte gels that contain co-immobilized enzymes. A swollen gel shrinks or swells upon increasing or decreasing pH passing through the isoelectric point (pI). Figure 9 demonstrates pH-oscillation of amphoteric gel containing both glucose oxidase and urease.

Thus amphoteric gel entrapped enzymes can develop the concept of self-regulating artificial catalytic system with positive feedback mechanism. The pH-coupled with oxygen stimuli on osmotic pressure and electrical potential responses of hemoglobin-loaded polyampholyte hydogel was developed in [96] as biocompatible pH- and oxygen-reactive gas carrier, bio-sensing and actuating materials. Special interest may represent immobilization (or imprinting) of enzymes within the macroporous polyampholyte cryogels [97]. Due to interconnected and large porous structure, polyampholyte cryogels with immobilized enzymes can offer soft and gentle flow-through enzymatic reactors that can operate in mild conditions, e.g. preferentially in aqueous solution, at atmospheric pressure and room temperature including the easy separation of products from enzymatic catalysts.

Composite hydrogels with strongly charged ampholytic nature were prepared by photo-polymerization of the acrylate groups in acrylamide (AA), [2-(acryloyloxy)ethyl]trimethylammonium chloride (AETA), and *N*,*N*′-methylenebisacrylamide (MBAA) in the presence of sulfonate-modified silica nanoparticles $[(SiO_2)_n{-}SO_3^-Na^+]$ [98]. Coulombic interactions between the cationic ammonium side groups along the hydrogel backbone and the anionic sulfonate groups of nanoparticles reinforce the mechanical properties of composite hydrogels and simultaneously improve in tensile modulus, toughness and strain at break compared to neat AA and AETA (Fig. 10). *A priori* we can suggest that such system will behave polyampholyte character similar to remarkable works of Gong [86, 87].

Methodology of 3D printing of highly elastic, transparent and conductive composite polyampholyte hydrogels is perspective to model some human organs and serve as artificial tissue, soft actuators, soft robotics.

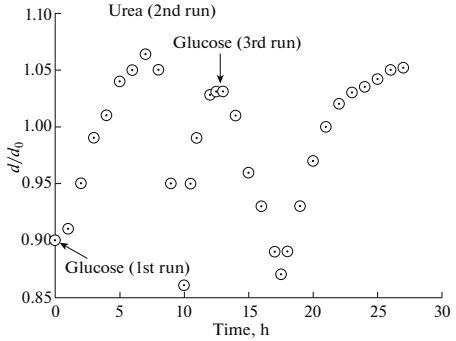


Fig. 9. Shrinking-swelling oscillation of polyampholyte gels with co-immobilized enzymes upon alternative addition of urea and glucose. (Redrawn from [95]).

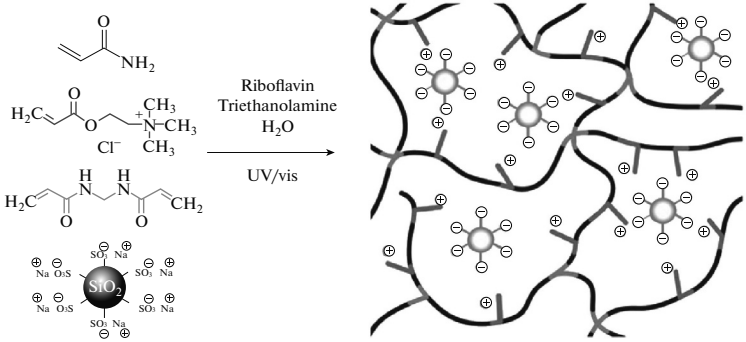


Fig. 10. Synthetic protocol of composite hydrogels via photo-polymerization of AA and AETA in the presence of sulfonate modified SiO_2 (18 nm) using riboflavin:triethanolamine photo-initiator and MBAA crosslinker. (Reprinted from [98].)

4. ANTI(BIO)FOULING PROPERTIES OF POLYAMPHOLYTES

A major challenge in synthetic polyampholytes is prevention of nonspecific protein adsorption, e.g. antifouling behavior due to formation of a nanometer-scale surface containing charged balanced groups from either polybetaines (zwitterionic) or "quenched" polyampholytes that are strongly hydrated through ionic solvation [99]. Due to high charge density, biocompatibility, non-toxicity, protein- and cell repellent properties, antithrombogenic and "antipolyelectrolyte" behavior in saline media poly(zwitterions) attract increased interest in the context of biomedical applications [100, 101]. For biomedical applications, the surface of preliminary activated parent materials is covalently coated by poly(zwitterions) as monolayers, brushes or networks (Fig. 11).

Figure 12 demonstrates different arrangement of anionic and cationic moieties in polysulfobetaines [102]. In case of A and 2 both negative and positive charges are replaced at equidistance from the polymer backbone. Positions B and 3 corresponds to the situation when the positive charge is placed closer to the membrane surface in contrast to positions C and 1 when the anionic group is closer to the surface. Case

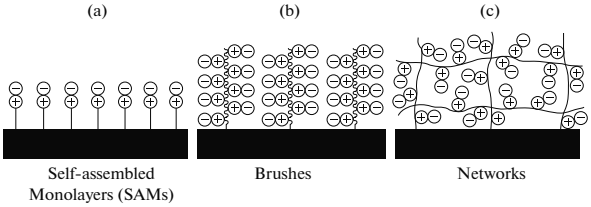


Fig. 11. Replacement of various poly(zwitterions) on the surface. (Reprinted from [100].)

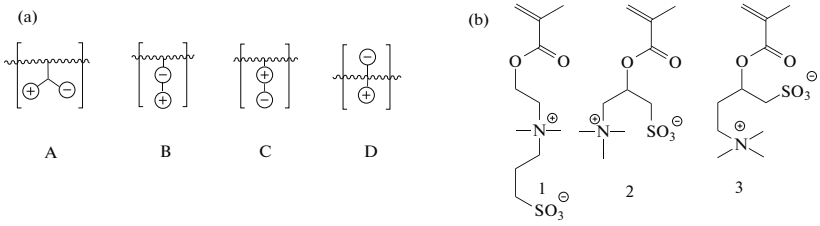


Fig. 12. Different arrangement of anionic and cationic groups in polysulfobetaines. (Reprinted from [102].)

D reflects the position when the positive and negative charges are replaced on the both side of polymer backbone.

Biological effects of polyzwitterionic hydrogel films of about 100 nm thickness prepared from A, B, C, and D were evaluated with respect to model proteins (BSA, lysozyme, fibrinogen) and marine organisms (diatoms *Navicula perminuta*, barnacle cyprids *Balanus improvisus*). The protein-repellent ability of polyzwitterions increases in the following order: fibrinogen > BSA > lysozyme. Fouling resistance of polyzwitterions increases in the order: 1 ≥ 2 > 3 showing the stronger antifouling efficiency of 1 for BSA and fibrinogen. The main conclusions of authors [102] is that among the tested polyzwitterions there is no universal (or champion) antifouling agents and the relative antifouling performance depends on the precise combination of the foulant species and employed polyzwitterions.

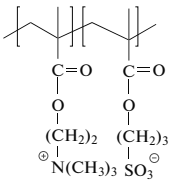
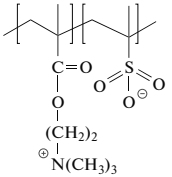
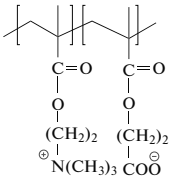
The "non-fouling" behavior of poly(zwitterions) was interpreted by Schlenoff [103, 104] as following: (1) poly(zwitterions) are so strongly hydrated (low interfacial energy with water) and do not disturb the hydrogen bond network of water; (2) strongly swollen polymer chains of poly(zwitterions) are configurationally unfavorable to accommodate large guest biomolecules; (3) there are no sufficiently strong enthalpic or entropic contributions that would favor adhesion of proteins, bacteria or cells to poly(zwitterions).

Anti-fouling, anti-biofouling and antibacterial properties exhibit polyvinilydene fluoride (PVDF) [105], polyethersulfone (PES) [106, 107], or polyamide (PA) [108] ultrafiltration (UF) or reverse osmosis (RO) membranes coated by polyampholytes (Table 2).

Synthetic polyampholytes were used for the construction of biomimetic scaffolds to study the impact of biochemical and physical cues on cell behavior [109]. Microstructured polyampholyte films were fabricated from the polyampholyte p(APM_{10}-*co*-AA_{90}) (where APM is *N*-(3-aminopropyl)methacrylamide hydrochloride, AA is acrylic acid) with comonomer ratio 10 : 90 mol/mol and prestressed polystyrene (PS) by thermal treatment as demonstrated in Fig. 13. Thermal treatment of p(APM_{10}-*co*-AA_{90}) spin-coated onto PS substrate leads to crosslinking of polyampholyte chains through formation of both amide and anhydride groups and formation of wrinkled polyampholyte films that are insoluble in water even at high pH.

Further modification of residual anhydride groups of crosslinked polyampholyte by hydrophilic (D-glucamine) or hydrophobic (decylamine) moieties increases or decreases the attachment of model

Table 2. PVDF, PES and PA membranes modified by polyampholytes

Structural units of polyampholytes used for modification of various membranes	Foulants	Refs
 PVDF membrane bioreactor modified by [2-(methacryloyloxy)ethyl trimethyl ammonium-*co*-3-sulfopropyl methacrylate	Microbial products, Extracellular polymeric substances extracted from municipal wastewater	105
 PES membrane modified by vinylsulfonic acid-*co*-[2-(methacryloyloxy)ethyl]trimethyl ammonium chloride	BSA, humic acid, sodium alginate	106, 107
 Polyamid RO membrane modified by 2-carboxyethylacrylate-*co*-[2(acryloyloxy)ethyl] trimethylammonium chloride	BSA, lysozyme bacteria *Sphingomonas paucimobilis*	108

cells – murine NIH 3T3 fibroplasts on crosslinked thin films in comparison with unmodified polyampholyte films. Figure 14 compares the images of the fibroplasts on PS, unmodified p(APM_{10}-*co*-AA_{90}), and D-glucamine-functionalized p(APM_{10}-*co*-AA_{90}).

It is seen that fibroplasts on both unmodified and functionalized by D-glucamine p(APM_{10}-*co*-AA_{90}) are less spread out on the surface compared to control PS showing the smallest area and more circular morphology. Thus p(APM_{10}-*co*-AA_{90}) film modified by D-glucamine exhibits the best antifouling properties and reduced cell attachment. In future it is planned to synthesize the different compositions of p(APM-*co*-AA) with various crosslinking density and elastic moduli of polyampholyte films. In spite of some achievements in fabrication of antifouling polyampholytes, to date, the application of zwitterionic materials is still at a laboratory level due to high cost of betainic monomers. Moreover the current antifouling polyampholytes contain carbon-carbon backbones and are not biodegradable. Therefore in future biocompatible and biodegradable polyampholytes made of polypeptides or IDPs with superior antifouling properties will be more perspective.

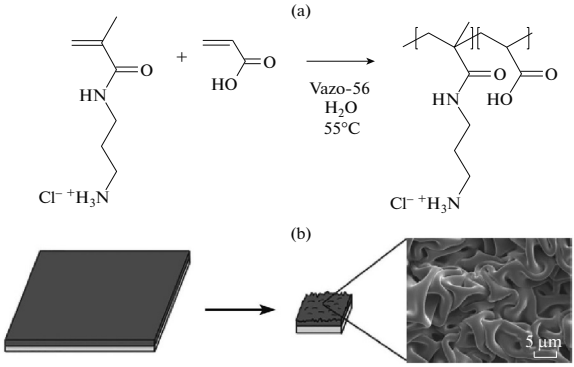


Fig. 13. (a) Copolymerization of *N*-(3-aminopropyl)methacrylamide hydrochloride (APM) and acrylic acid (AA). (b) Formation of microstructured films by thermal shrinking of a p(APM_{10}-*co*-AA_{90})-coated prestressed PS. (Reprinted from [109].)

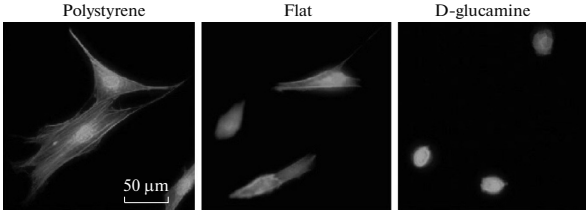


Fig. 14. Epifluorescence images of fibroplasts after 24 h culture on the PS (control) and flat unmodified p(APM_{10}-*co*-AA_{90}) and D-glucamine-functionalized p(APM_{10}-*co*-AA_{90}). (Reprinted from [109].)

5. HEMOCOMPATIBILITY OF SYNTHETIC POLYAMPHOLYTES

Hemocompatibility of linear "quenched" polyampholytes made of 3-sulfopropylmethacrylate (SPMA) and [2-(methacryloyloxy)ethyl]trimethylammonium chloride (METMAC) at various molar ratios of anionic and cationic monomers was evaluated with respect to human blood plasma in order to clarify the influence of charge balance (or imbalance) on plasma-protein association, blood-plasma clotting and blood-cell hemolysis [110]. It was established that SPMA-METMAC copolymers with excess of positive and negative charges enhance polyampholyte-protein associations. The efficiency of SPMA-METMAC copolymers was compared with zwitterionic polymer poly[2-methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium (polySBA). Both the charge balanced SPMA-METMAC copolymer and polySBA effectively resisted protein adsorption onto polymer interfaces and exhibited excellent nonfouling stability. These results suggest that the low protein-adsorption ability of equimolar SPMA-METMAC copolymer and polySBA is related to overall charge neutrality of QPA. Moreover, both polySBA and charge-balanced SPMA-METMAC copolymer under physiological conditions showed very little hemolysis demonstrating the good nonfouling nature and antihemolytic activity in relation to blood cell membranes. The best anticoagulant and antihemolytic activity of equimolar SPMA-METMAC copolymer is attributed to the formation of a highly hydrated layer formed between water molecules and anionic-cationic groups. Thus, hemocompatible nature of SPMA-METMAC copolymer and polySBA has potential application to molecular design of tunable thrombogenic materials for human blood. Polyampholyte brushes composed of amine and carboxylic groups are blood compatible and prevent protein adsorption, cell adhesion and

suppress coagulation/complement activation due to intra and inter-ionic interactions [111]. The adhesion and cytotoxicity tests of P(MAPTAC-*co*-NaSS) hydrogels were carried out with respect to fibroplast cells and macrophages [82, 42]. According to biomedical experiments the nontoxicity and excellent anti-fouling properties for polyampholyte hydrogels was observed towards to macrophages. Tetrapolymer composed of 2-methacryloyloxyethylphosphorylcholine (52.8 mol %), stearyl methacrylate (11.7 mol %), hydroxypropyl methacrylate (31.4 mol %) and trimethoxysilylpropyl methacrylate (4.0 mol %) is one of example of "bioinspired" blood compatible coating for cardiovascular device [112]. Complex formation ability of polybetaines containing cetyl radicals with respect to liposomes based on zwitterionic phosphatidylcholine and anionic diphosphatidylglycerol (cardiolipin) was investigated [113]. The hydrophobic polybetaines irreversibly incorporate into the hydrophobic part of the lipid bilayer and show much lower cytotoxicity. Magnetite nanoparticles coated by amphoteric macromolecules are perspective in biomedical applications, especially as contrast agents in magnetic resonance imaging (MRI) [114–116]. Polyampholyte-coated magnetite nanoparticles (PCMNPs) were used as antifouling and contrasting agent in MRI [117, 118]. The antifouling property of PCMNPs with respect to BSA and lysozyme is effective tool as MRI contrast agent with long in vivo circulation time in blood vessel. The hemocompatibility, in particular, hemolysis, plasma recalcification, dynamic blood clotting, prothrombin time, inflammatory cytokine release and complement system activation assays was investigated. The PCMNPs have no significant effect to vessels and are mainly distributed in the liver and the blood with circulation time 3.77 h. Synthetic strategy of MNP-coated poly(zwitterions) exhibiting antifouling behavior in the context of biomedical applications was reviewed in [119]. Both the hemocompatibility and anti(bio)fouling property of polyampholytes are accounted for a highly hydrated layer formed between water molecules and anionic-cationic groups.

6. CRYOPROTECTIVE PROPERTIES OF SYNTHETIC POLYAMPHOLYTES

Synthetic polyampholytes are suitable materials for inhibition of ice crystallization and can serve as cryoprotective agents (CPAs). Cryopreservation of living cells by polyampholytes is powerful tool in biological, medical, and agricultural research fields as well as in the regenerative, transplantation and reproductive medicine [120]. Successful long-term preservation of stem cells with appropriate differentiation properties is the key technology of cell transplantation. Cryoprotective properties of polyampholytes as antifreezing agents of living cells were demonstrated for the first time by Matsumura and coworkers [121–133]. The commonly recognized CPAs such as glycerol [134] and dimethyl sulfoxide (DMSO) [135, 95] that were used for several decades are proved to be cytotoxic and affected on differentiation of various types of cells. A new polymeric CPAs based on ε-poly-L-lysine carboxylated by succinic anhydride (SA) (COOH-PLL) [120] and hydrophobically modified by dodecylsuccinic anhydride (DDSA) ε-poly-L-lysine (PLL-DDSA) [126], have been developed to reduce physical and physiological damage by cryopreservation in mammalian stem cells (Fig. 15).

It was demonstrated that CPAs based on COOH-PLL, PLL-DDSA, and PLL-DDSA-SA during freezing-thawing process significantly reduces the risks of damage by ice recrystallization and behaves anti-freezing protein-like activities. Figure 16 shows schematically the cryoprotection mechanism NIH 3T3 fibroplast cells with participation of polyampholytes based on *N*,*N*-dimethylaminopropylmethacrylamide and acrylic acid (DMAPMA-AA) by using a standard freeze-rethaw protocol [136].

Upon freezing cell wrapped by polyampholyte chains is concentrated and forms an amorphous pericellular domains consisting of polyampholyte–cell associates. During thawing these polymer-rich pericellular domains are melted and protect cells from damage through ice recrystallization. The polyampholyte chains appear to dehydrate cells during freezing and to decrease cell size. The suggested mechanism of cell cryoprotection by polyampholytes is applicable for viability of certain stem cells [122, 124], mouse oocytes [125], mouse embryos [130], L929 [120, 123, 126, 133].

Systematic investigations clarifying the role of microstructure, acid/base molar ratio, molecular weights, and hydrophobicity of polyampholytes on the ice recrystallization inhibition (IRI) was undertaken by Gibson et al. [137–140]. It was established that the regular polyampholytes are more active than random polyampholytes demonstrating that the distribution of charged units of polyampholytes plays the crucial role in determination of the IRI activity. Hydrophobic modification of both main and side chains of amphoteric macromolecules also changes the IRI activity. However incorporation of 5 mol % hydrophobic monomers – butyl- or octylmethacrylate into the polyampholyte chain *N*,*N*-diemthylaminoethylmethacrylate-*co*-methacrylic acid (DMAEM-MAA) significantly enhances the viability of L929, ADSC and HT-1080 cells [132]. It was demonstrated that functionalized by carboxylic groups poly(aminoethylmethacrylate) (PAEMA-COOH) polyampholyte of equimolar composition gives maximal IRI

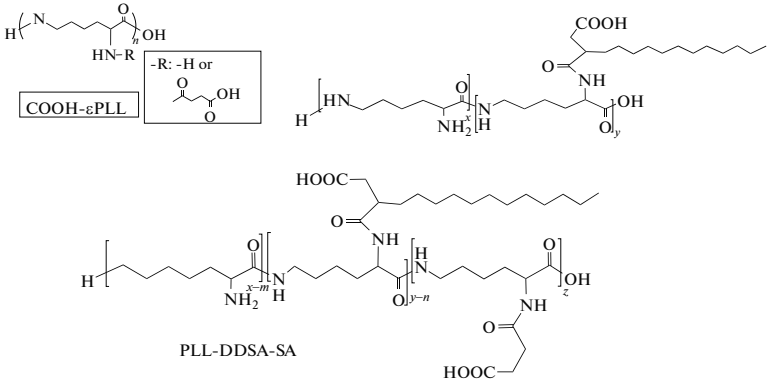


Fig. 15. Repeating monomeric units of CPAs based on COOH-PLL (a), PLL-DDSA (b) and PLL-DDSA-SA (c). (Reprinted from [120, 126].)

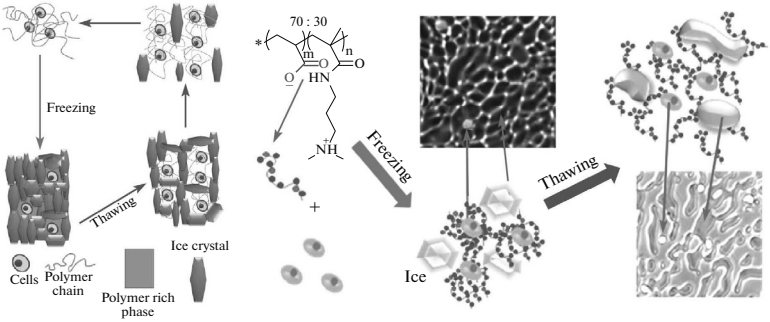


Fig. 16. The proposed mechanism of cryoprotection of cells by synthetic polyampholytes DMAPMA-AA. (Reprinted from [136].)

activity while deviation from the equimolar ratio reduces the IRI activity (Fig. 17a). It is proposed that globular conformation of charge-balanced polyampholytes may be responsible for disrupting the quasi-liquid layer at the ice/water interface and inhibiting ice growth. The molecular weight dependency of PAEMA-COOH polyampholytes containing 50 mol % COOH groups reveals that the IRI activity is higher for high molecular weight polyampholytes (Fig. 17b).

Surprisingly both poly(2-methacryloyloxiethylphosphorilcholine (PMPC) and poly([2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl) (PMEDS) ammonium hydroxide) that belong to poly(phospho- and sulfobetaines) do not exhibit the IRI activity. This phenomenon may be explained by Schlenoff [103] conception of the "non-fouling" behavior of both PMPC and PMEDS that belong to poly(zwitterions). Since poly(zwitterions) do not perturb the surface free energy of water, no molecular rearrangements may occur for zwitterion-modified surfaces or polymers. Water molecules directly hydrated by poly(zwitterions) belong to "nonfreezing water" while water molecules replaced (or located) outside the first hydration shell can be defined as "unassociated," or bulk water. Thus as follows from Schlenoff concept [103]

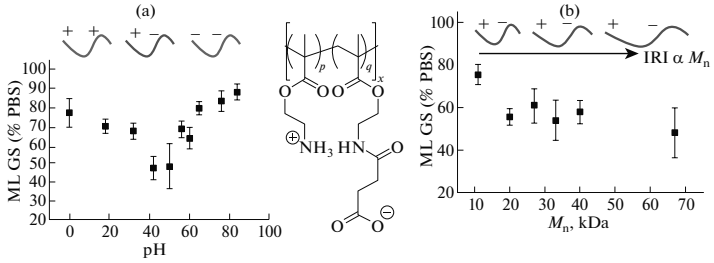


Fig. 17. Dependency of the IRI activity on composition (a) and molecular weight (b) of PAEMA-COOH polyampholytes. (Reprinted from [139].)

poly(zwitterions) can not disorder "bulk water," "semi-ordered water" and hence influence to the rate of ice crystal growth. In spite of the fact that the mode of interaction of polyampholyte chains with ice is still unclear the remarkable experiments of authors [141] might provide insight into this issue. A temperature-dependent evolution of the charge-balanced polyampholyte hydrogel upon cooling was studied by SAXS, WAXS, solid state NMR, field emission SEM (FE-SEM). It was found that a networked globular structure of amphoteric macromolecules effectively prevents the freezing of water in hydrogel. The existence of amorphous water molecules and slushlike, submicrometer-sized ice formation at low temperatures was detected. The hypothesis that a certain fraction of water molecules do not freeze due to confinement with the polymer chains or interactions with these chains was verified by analysis of the shape of the ^{2}H NMR spectra. For better understanding of the ice formation and recrystallization phenomenon in the presence of polyampholytes a variety of experimental materials should be accumulated.

Matsumura et al. [142] invented a novel easily injectable hydrogel composed of synthetic polyampholyte (COOH-PLL) and nanosilicate (laponite) for the cell delivery using cryopreservation methodology developed earlier (Fig. 18).

The uniqueness of the system is that the cells can be preserved both before and after usage without removal of CPA. The composite hydrogels exhibited desirable biocytocompatibility and tunable mechanical properties that are useful for the formulation of new generation of scaffolds.

A new strategy of freeze concentration-mediated cytoplasmic delivery of proteins based on combination of liposomes and hydrophobically modified polyampholytes of PLL-DDSA-SA series (cf. Fig. 10) was developed by Matsumura et al. [143, 144]. The saline property of polyampholyte-modified liposomes is that they can introduce the encapsulated lysozyme into the cell using freeze-thawing strategy of cells (Fig. 19).

The polyampholyte-modified liposomes enhance the interaction between liposomal membranes and L929 fibroplast cells due to hydrophobicity of the former. In future the intracellular delivery of lysozyme proteins by hydrophobically-modified polyampholyte liposomes can be used for cancer trreatment and gene therapy.

7. POLYAMPHOLYTES AS POLYELECTROLYTE, PROTEIN AND DRUG DELIVERY SYSTEMS

Amphoteric nano- and microgels, membranes and thin films are promising platforms in nanomedicine for development of protein and drug delivery system [145, 146]. Uptake of cytochrome C (Cyt-C) by polyampholyte microgels possessing random and "core–shell" microstructures was carried out at pH 8 followed by release of model protein at pH 3.0 and 6.0 [147]. Random polyampholyte microgels consisted of *N*-vinylcaprolactame (VCL), itaconic acid (IA) and *N*-vinylimidazole (VI) at molar ratio of monomers 80 : 10 : 10 or 60 : 20 : 20 mol %. "Core–shell" ampholytic microgel was derived from VCL-IA ("core" part) and NIPAM-VI ("shell" part). Both random and "core–shell" polyampholyte microgels were characterized by FTIR, static and dynamic light scattering, electrophoretic measurement, TEM, and computer simulation. The isoelectric points (IEP) of random and "core–shell" polyampholyte microgels were placed near of pH ~ 6.0. Random and "core–shell" polyampholyte microgels were loaded by Cyt-C at

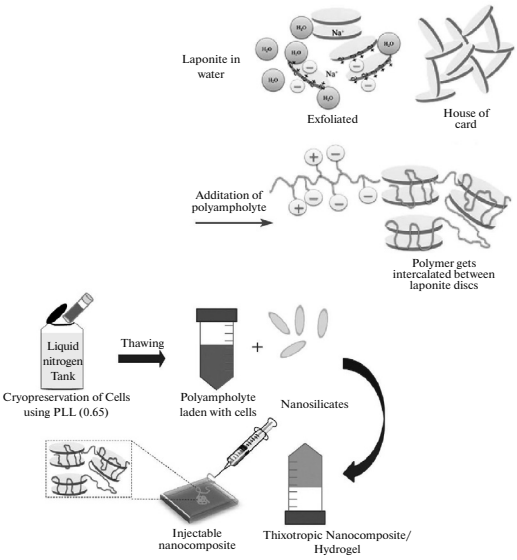


Fig. 18. Schematic representation of thixotropic injectable composite hydrogel formulation. (Reprinted from [142].)

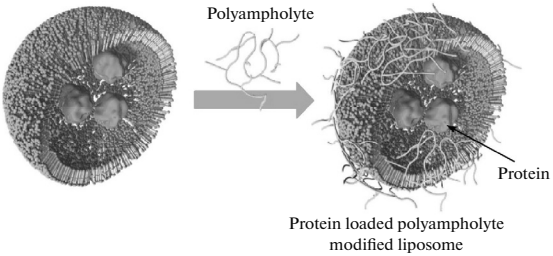


Fig. 19. Schematic representation of protein loaded lipososmes and polyampholyte-modified liposomes. (Reprinted from [143].)

pH 8.0. The results of pH triggered protein release show that Cyt-C much faster releases at the IEP (pH ~ 6.0) for both polyampholyte system due to formation of intrapolyelectrolyte complexes between oppositely charged groups of amphoteric macromolecules. The accelerated and complete release of Cyt-C from the interior of random polyampholyte microgel was observed at pH 3.0 due to electrostatic repulsive forces between protein molecules and positively charged *N*-vinylimidazole fragments. In case of "core-shell" microgel, at the IEP (pH ~ 6.0) only 40% of Cyt-C is released from the microgel interior while in

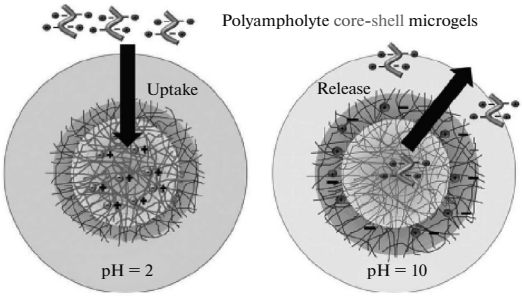


Fig. 20. Schematic representation of uptake of PSSNa at pH 2.0 by a polyampholytic "core-shell" microgel and release of PSSNa at pH 10.0. (Reprinted from [148].)

acidic region, at pH 3.0, the amount of released protein reaches up to 70–80%. These findings are in good agreement with the realization of so-called "isoelectric effect" established for a series of random, block and dendritic water-soluble polyampholytes, amphoteric hydrogels and cryogels that was demonstrated with respect to polyelectrolytes, proteins, metal ions, ionic dyes and surfactants [69].

Also NIPAM-based "core–shell" polyampholyte microgels composed of anionic an itaconic acid monomethyl ether (NIPAM-*co*-MIA) "shell" and cationic *N*-(3-aminopropyl)methacrylamide hydrochloride (NIPAM-*co*-APMH) "core" exhibited sorption and desorption of sodium salt of poly(styrenesulfonic acid) (PSSNa) [148]. In spite of the fact that the core is postively charged while the shell – negatively charged, the polyampholyte "core–shell" microgels were able to uptake the PSSNa and release it (Fig. 20). It was shown that the anionic "shell" did not prevent the release of PSSNs outside. Moreover the anionic "shell" surrounding the cationic "core" improved the colloidal stability of complexed microgel particles in contrast to cationic microgel alone. Such conclusion of authors was confirmed by SANS and computer simulations.

The uptake and release of anionic polyelectrolyte by "core–shell" amphoteric microgels was tested for various molecular weights of $[PSSNa]_{20}$, $[PSSNa]_{200}$, and $[PSSNa]_{2000}$ (where the subscript indicates the polymerization degree). It was revealed that $[PSSNa]_{20}$ penetrates deeply into the "core" of polyampholyte microgels while $[PSSNa]_{200}$ and $[PSSNa]_{2000}$ are mostly accumulated on the periphery of "core". As a result, the long-chain PSSNa releases from the "core" more effectively than that of short chain polyelectrolyte. Gradually penetration of strong anionic polyelectrolyte into the positively charged "core" (NIPAM-*co*-APMH) at low pH 2.0 and formation of stable polyelectrolyte complexes is probably due to suppression of negative charges (NIPAM-*co*-MIA) up to uncharged or neutral state. Liberation of PSSNa from the "core" of polyampholyte microgels at high pH 10 is probably the result of full deprotonation of amine groups of NIPAM-*co*-APMH and partly or full destruction of amphoteric microgel-polyelectrolyte complexes. pH-sensitive polyampholyte of poly(acrylic acid-*co*-vinylamine) (P(AA-*co*-VAm)) was developed as injectable microgels for controlled drug release [149]. Doxorubicin-loaded polyampholyte microgels effectively release the drug (up to 95%) at pH 6.0 during 84 h.

Drug delivery system from nonfouling polyampholyte hydrogels composed of equimolar amount of [2-(acryloyloxy)ethyl]trimethylammonium chloride (TMA), 2-carboxyethylacrylate (CAA) and triethyelene glycol dimethacrylate (TEGDMA) as crosslinker was obtained in the presence of positively charged methylene blue (MB), negatively charged metanil yellow (MY), and neutral caffeine (C) [150]. The drug release kinetics from hydrogel matrix to outer solution was studied as a function of crosslinking degree, pH of the solution and salt concentration. Loading of MB, MY, and C to and releasing from copolymers of *N*,*N*-dimethylaminoethyl methacrylate-acrylic acid (DMAEM-AA) was studied for pH-responsive polyampholytes grafted to poly(2-hydroxyethyl methacrylate) (PHEMA) [151] and PVDF membranes [152]. At pH 5.0 and 7.0 the maximum caffeine release from PVDF modified membrane reached after 3 and 5 h, respectively; however, after 24 h the released amount of caffeine was in the same level. In case of PHEMA-loaded drugs only MB and caffeine incorporated membranes displayed clear pH-responsive release through all coatings.

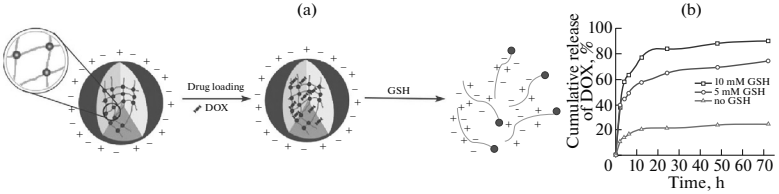


Fig. 21. Zwitterionic poly(sulfobetaine)-based nanogels with loaded DOX for antitumor drug delivery (a) and in vitro drug release profiles of DOX-loaded nanogels with and without GSH treatment (b). (Reprinted from [155].)

The recent progress of non-fouling, biocompatible and bioinert zwitterionic drug carriers derived from phosphorylcholine (PC), carboxybetaine (CB), and sulfobetaine (SB) containing copolymers were discussed in review [153]. Zwitterionic drug nanocarriers are successfully used as a biomimetic strategy for the delivery of chemotherapeutants, DNA, and proteins. Peppas et al. [154] highlighted the recent challenges of stimuli-responsive polymeric nanoparticles in cancer nanomedicine. Among the synthetic polyampholytes, mostly zwitterionic polymers attracted much interest as biocompatible and low fouling nanocarriers for drug delivery. Novel Red/Ox-sensitive zwitterionic poly(sulfobetaine)-based nanogels (<100 nm) loaded by anticancer drug – doxorubicin (DOX) were tested in conditions of in vitro drug release [155] (Fig. 21).

The content of DOX incorporated into nanogel matrix was equal to 24.3%. In vitro drug release kinetics under physiological conditions showed the release of 24.8% DOX, whereas in the presence of 5 mM and 10 mM glutathione, that is similar to tumor cytoplasm environment, 74.4 and 89.9% of DOX released due to degradation of nanogels by glutathione. A series of biodegradable and pH-responsive vesicles (~100 nm) of block copolymers of poly(2-methacryloyloxyethyl phosphorylcholine)$_{50}$-*block*-poly(L-aspartic acid)$_n$ (P(MPC)$_{50}$-*b*-p(AA)$_n$ (n = 10, 25, 50, 75) were exploited as dual-responsive drug delivery vehicles of DOX [156]. In vitro release of DOX from the P(MPC)$_{50}$-*b*-p(AA)$_n$ was tested with respect to mouse embryonic fibroplast (NIH 3T3) and mouse mammary tumor (4T1) cell lines. The DOX-encapsulated vesicles showed the anticancer effect in relation to 4T1 cell lines. The drug release profile of P(MPC)$_{50}$-*b*-p(AA)$_n$ was evaluated at pH 5.5 and 7.4 and at different 1,4-dithiothreitol (DTT) concentrations (5, 10, 15 mmol) over 72 h. Here DTT serves as disassembling agent of vesicles by the cleavage of the S-S linker. At pH 7.4 about 15, 31, and 44% of DOX was released during 72 h in the presence of 5, 10, and 15 mmol DTT respectively. At pH 5.5 the DOX release within 72 h reached up to 61, 70, and 76% in the presence of 5, 10, and 15 mmol DTT, respectively. The highest DOX release was observed at pH 5.5 and addition of 15 mmol of DDT, e.g. when double stimuli was applied. Thus biodegradable and pH-responsive polybetainic vesicles are promising theranostic platform for anticancer treatment. Poly(sulfobetaine)-grafted mesoporous silica nanoparticles (MSN@pSBMA) with enhanced lubrication and sustained drug release behaviors were developed for the treatment of osteoarthrites [157].

Figure 22 shows the MSN nanoparticles with average diameter 100 nm covered with poly(sulfobetaine) chains by grafting.

Aqueous suspension of the MSN@pSBMA nanoparticles as lubricant reduced in 80% of the friction coefficient compared to MSNs alone. The lubrication mechanism of MSN@pSBMA is attributed to the zwitterionic nature of headgroups in the poly(sulfobetaine). The cumulative release of Rhodamine B as a model cargo was in the range of 39.3–49.9% during 52 h.

Sun et al. [158] fabricated a novel enzymatic degradable polyester-based zwitterionic polymer and corresponding polymer-paclitaxel anticancer drug conjugate, which exhibited acid-sensitive drug release for killing of cancer cells (Fig. 23).

Biodegradibility of PLA-SB/PTX was compared in the absence and presence of proteinase K enzyme (Fig. 23b). It is expected that such enzyme-triggered degradation of PLA-SB/PTX will minimize polymer accumulation in the body. pH dependent sustained release of PTX after 120 h was equal to 83.5 ± 4.9% at pH 5.5 and 72.7 ± 4.1% at pH 7.4 and 37°C. Cytotoxicity and cellular uptake studies revealed that the zwitterionic polymer is nontoxic, biocompatible, effective and ready for cellular internalization. A series of zwitterionic polymer membranes coated onto magnetite (Fe_3O_4) nanoparticles were developed to satisfy long-time blood circulation for enhanced photothermal tumor therapy (PTT) [159]. PTT experiments in vivo were performed on A549 tumor models. Seven substances that are PBS (phosphate buffer saline), Fe_3O_4,

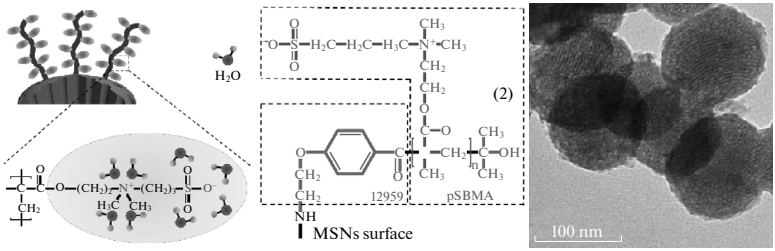


Fig. 22. Schematic diagram demonstrating the structure and morphology of MSN@pSBMA nanoparticles. (Reprinted from [157].)

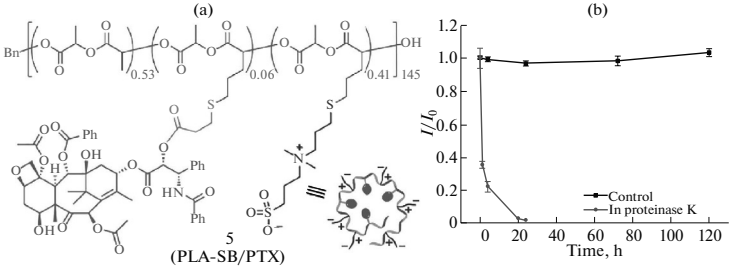


Fig. 23. (a) Structural unit of the biodegradable polymer-drug conjugate based on polylactide (PLA), sulfobetaine (SB), and paclitaxel (PTX). (b) Enzymatic degradation profile of PLA-SB/PTX in water at pH 7.4 and 0.2 mg mL^{-1} of proteinase K in 0.1 M Tris-YCl buffer pH 8.5 at 37°C. (Reprinted from [158].)

Fe_3O_4@RBC (Fe_3O_4 coated by red blood cell), Fe_3O_4@PMPC, Fe_3O_4@PSBMA, Fe_3O_4@PCBMA with 0.1 mL were injected to the tumor volume 100 mm^3, then irradiated by the 808 nm near infrared (NIR) laser for 300 s at 4 h injection. Among the three kinds of zwitterionic polymer membranes coated onto Fe_3O_4 nanoparticles, namely poly(2-methacryloyloxyethyl phosphorylcholine) (Fe_3O_4@PMPC), poly(sulfobetaine methacrylate) (Fe_3O_4@PSBMA), and poly(carboxybetaine methacrylate) (Fe_3O_4@PCBMA) the carboxybetaine-based polymer exhibited the longest blood circulation time ($t_{1/2}$ = 96 h) and superior PTT therapeutic efficacy (Fig. 24). The calculated tumor inhibition rates were equal to 38.4, 63.0, 79.5, 84.9, 98.6% for the Fe_3O_4, Fe_3O_4@RBC, Fe_3O_4@PMPC, Fe_3O_4@PSBMA, Fe_3O_4@PCBMA, respectively. Thus, zwitterionic membrane coated nanoparticles may offer the clinical applications in tumor therapy.

The "isoelectric effect" found at the IEP of polyampholytes is applicable for polyelectrolyte, protein and drug delivery [69]. As mentioned in section 2, any substances bound to polyampholytes may be discharged at the IEP via governing forces among inter- and intramolecular path. Furthermore, as intrachain interactions of acidic and basic groups within a single amphoteric macromolecule are superior to interchain interactions, releasing the loaded substance from the polyampholytes carrier can be fulfilled. The realization of the "isoelectric effect" was shown for pH triggered protein release at the IEP (pH ~ 6.0) of random and "core–shell" polyampholyte microgels [147].

8. CONCLUSION

The role and significance of synthetic polyampholytes in biotechnology and medicine is obvious because amphoteric macromolecules are the closest objects to natural polymers. Uniqueness of synthetic

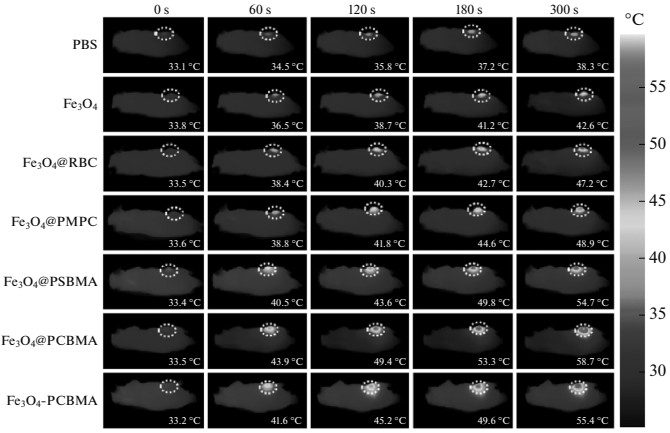


Fig. 24. Infrared thermal images of the bare Fe_3O_4 and coated by polybetaines Fe_3O_4 nanoparticles under 808 nm NIR laser irradiation for 300 s with the injection of 2.5 mg Fe kg^{-1}. White circles highlight the tumor site. (Reprinted from [159].)

polyampholytes is reasonable approximation to intrinsically disordered proteins (IDPs) also known as intrinsically unstructured proteins. Both IDPs and synthetic polyampholytes adopt globular, coil, and stretched conformation and show similar diagram of states as a function of the charge asymmetry expressed, in former case, as the fraction of charged residues FCR = $(f_+ + f_-)$ and net charge per residue NCPR = $|f_+ - f_-|$, in latter case, as $\delta f = |f_+ - f_-|$ and fraction of charged monomers $f = f_+ + f_-$ (where f_+ and f_- are the fractions of positive and negative charges, respectively). Moreover, a number of theoretical studies [160–162] developed to charge fluctuation effects in synthetic polyampholytes highlight the role of electrostatic interactions between oppositely charged monomers in IDPs. The gap between synthetic polyampholytes and IDPs can be bridged by polypeptide-based amphoteric copolymers mimicking the biological activity of natural proteins [163–165]. For example, pH- or charge-dependent conformation of block-polyampholyte and synthetic polypeptide can comprise of double stranded helical conformation and β-sheet that are specific for proteins. The specific feature of proteins, polyampholytic polypeptides, IDPs, and synthetic polyampholytes is existing of the isoelectric point where compaction, globularization, aggregation, coacervation, and precipitation take place. The common phenomenon for all is the "antipolyelectrolyte" effect that leads to dissolution of linear polyampholytes and swelling of polyampholyte gels and IDPs at the pH_{IEP} upon addition of neutral salts. One can hope that both IDPs and protein-mimetic ampholytic polypeptides will fall within eyeshot of several subjects such as polymer chemistry and physics, molecular biology, colloid chemistry, coordination chemistry and catalysis.

The recent studies [147, 148] clearly demonstrated the ability of polyampholyte microgels with random and "core–shell" structures to serve as effective carriers for both polyelectrolytes and proteins with programmed release kinetics. Injectable microgels that are able to switch "on–off" from strong to weak flowable state opens new avenue for cell delivery applications, pH- and oxygen-reactive gas carrier, bio-sensing and actuating materials [91, 97, 142, 149, 166]. Among the synthetic polyampholytes, non-fouling, hemocompatible and biodegradable zwitterionic polymers attract much interest as nanocarriers for delivery of chemotherapeutants, DNA, and proteins, as contrast agents in magnetic resonance imaging. These materials can trigger delivery through a bond cleavage or conformational change under the action of temperature, pH, ionic strength, enzymes, redox potential etc. [167]. Polyampholyte nanoparticles-based photothermal tumor therapy is fast developing and promising theranostic platform that may offer the clinical applications in tumor therapy. Spontaneously physically and chemically crosslinked polyampholyte hydrogels synthesized from strong charged anionic and cationic monomers are proved excellent biomate-

rials as artificial organs due to high toughness, bio- and hemocompatibility, anti-biofouling, self-healing, shear-thinning properties. One of the fast-developing area of synthetic polyampholytes is their cryoprotective properties with respect to living cells, namely, red blood cells, HT-1080, L929, certain stem cells, mouse oocytes and mouse embryos [130, 136, 137]. Application of polyampholytes as cryoprotectants is quite recent and a variety of experimental materials should be accumulated to explore exact mechanisms of the ice formation and recrystallization phenomenon in the presence of polyampholytes. Polyampholytes are also suitable for transport and deliver the genetic materials into the cell. A review [35] gives representative examples of various types of synthetic polyampholytes complexed with DNA in gene delivery. In principle among the synthetic polyampholytes the biodegradable precursors including IDPs can attract much attention and play crucial role for development of next-generation gene-delivery vectors [167]. The advances in cryogel technologies to address challenges in bioseparation, tissue engineering, controlled drug release, biocatalysis etc. were recently reviewed [168]. Application of polyampholyte cryogels as a proten-imprinted matrix for separation and purification of biomacromolecules and for sustained release of biologically active substances was highlighted in [169]. It is anticipated that in the future synthetic polyampholytes will play a great role in solving of biological, biotechnological, bio- and and nanomedicinal problems.

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Synthetic and natural polyampholytes: Structural and behavioral similarity

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The ability of synthetic polyampholytes to adopt globular, coil, helix, and stretched conformations and to exhibit coil–globule, helix–coil, liquid–liquid, sol–gel phase transitions with respect to internal (structure, composition, charge distribution, hydrophobicity, hydrophilicity, and so forth) and external factors (pH, temperature, ionic strength, thermodynamic quality of solvents, and so forth) is very important in duplicating the structural hierarchy of proteins. In this review, the structural and behavioral similarities between synthetic and natural polymers are analyzed, primarily concentrating on synthetic polyampholytes, amphoteric polypeptides, and intrinsically disordered proteins (IDPs) in order to demonstrate the close relationship. The application aspects of polyampholytes and future opportunities are briefly outlined.

KEYWORDS
amphoteric polypeptides, application, conformation, intrinsically disordered proteins, phase transition, synthetic polyampholytes

1 | INTRODUCTION

Pioneering works on synthetic polyampholytes[1,2] and intrinsically disordered proteins (IDPs)[3] first appeared at the beginning of the 1950s. Since then, publications on IDPs have increased exponentially compared to the mere steady increase in those on synthetic polyampholytes. Further, research on polyampholytic polypeptides became the subject of intense development starting from the late 1990s.[4-6]

Synthetic polyampholytes can reasonably be divided into three major classes: annealed, quenched, and betainic (or zwitterionic) (Figure 1).[7,8] Annealed polyampholytes consist of acid-base monomers that become ionized due to changes in pH, whereas quenched precursors containing strongly charged cationic and anionic monomers retain their respective charges independently of pH. Semiannealed and semiquenched polyampholytes are defined as amphoteric macromolecules that combine weak acid/strong base or strong acid/weak base monomers, respectively. Betainic (or zwitterionic) polyampholytes are macromolecules containing identical numbers of acid-base (or fully charged anionic-cationic) species in the same monomer units.[9] Macromolecules formed via compensation of the cationic-anionic monomer pairs without counterions are also zwitterionic polymers[10] or polyampholytic ionic liquids.[11] In the applicable literature, the terms amphoteric polyelectrolytes and amphoteric copolymers are also used.

The theory and basic structures,[12] functions, and applications[13] of natural and synthetic polyampholytes have been reviewed. Their behavior based on Coulombic interactions between complementary charges has been critically analyzed. The properties of polyampholytes in solution and gel state, together with application aspects, have also been assessed. The primary aim of this review is systematization and analysis of the literature in the context of merging the structure-function paradigm of natural and synthetic polyampholytes, focusing on the polyampholyte behavior of biological objects.

2 | STRUCTURAL AND BEHAVIORAL SIMILARITY BETWEEN SYNTHETIC POLYAMPHOLYTES AND INTRINSICALLY DISORDERED PROTEINS

The authors[14] performed a comprehensive review of the applicability of theories of polymer physics developed for the analysis of large macromolecules in order to understand and predict the important properties of intrinsically unstructured proteins (Figure 2).

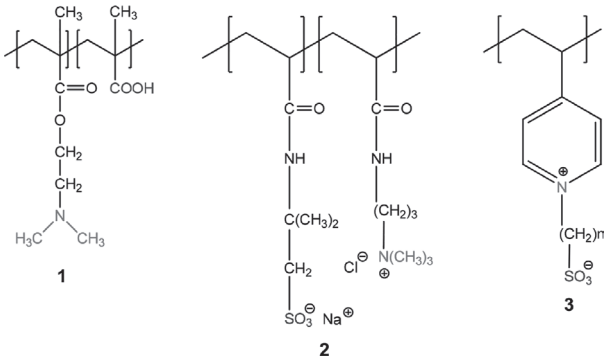


FIGURE 1 Repeating monomeric units of annealed (1), quenched (2), and betainic (or zwitterionic) (3) polyampholytes [Colour figure can be viewed at wileyonlinelibrary.com]

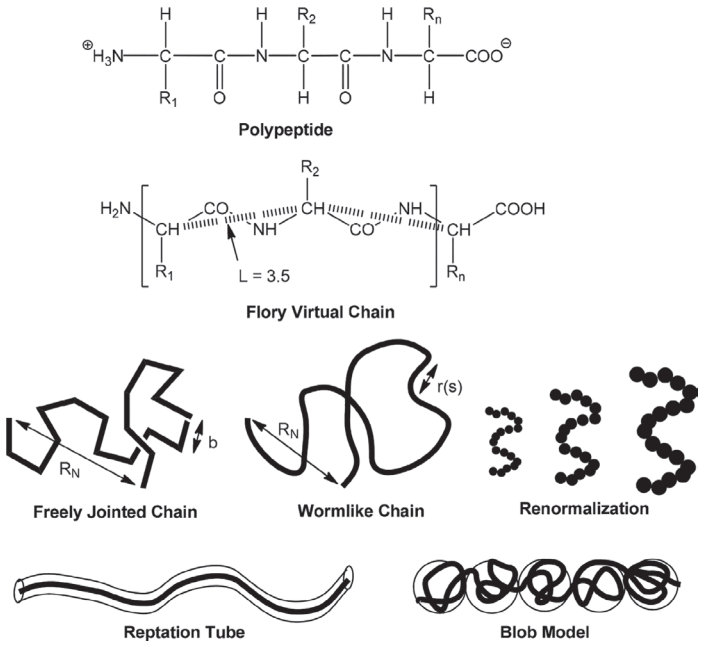


FIGURE 2 Representation of a protein chain in a general polymer framework. Reproduced from Reference 14 with permission from the Elsevier

Firstly, the sequence of amino acids in protein molecules is represented as a virtual chain that is considered to be a freely joined and worm-like chain. These basic models further serve as the basis for higher order models and methods for the analysis of the statistical properties of polymers.

IDPs, also known as intrinsically unstructured proteins, are characterized by their biased amino acid composition and low sequence complexity, as well as by their low proportions of bulky hydrophobic amino acids and high proportions of charged and hydrophilic amino acids[15] (Figure 3). A literature survey shows that there are approximately 1150 validated IDPs. The terms IDPs or intrinsically disordered regions (IDRs) refer to the lack of a well-defined secondary and/or tertiary structure under physiological conditions. The protein quartet model proposes four types of conformations: random coil, premolten globule, molten globule, and folded states, which can transit each other (Figure 4).[16]

In fact, 75% of IDPs are categorized as polyampholytes,[3,17] and their stimuli-responsive phase transition functions are governed by the relationship between the information encoded in their amino acid sequences and their ensembles of conformations.[18] Nature uses polyampholytic IDPs as scaffolds for extracellular matrices, plant cell walls, and other fibrous composites.[19,20]

Charge distribution in IDPs is represented by the fraction of charged residues (FCR) and net charge per residue (NCPR), which are defined as FCR = ($f_+ + f_-$) and NCPR = $|f_+ - f_-|$, respectively, where f_+ and f_- are the fractions of positive (Lys/Arg) and negative (Asp/Glu) charges.[21] IDPs can be positively charged, negatively charged, or quasi-electroneutral, exhibit stimuli-responsive conformational and phase behavior, and exist in fully expanded, molten globular, premolten globular, and random coil states.[22,23] Figure 5A shows the five regions of IDPs as a function of FCR. Here, R1 represents low-FCR sequences with IDPs in a globular conformation, R2 represents globule-coil transformation, R3 belongs to high-FCR sequences with swollen coil or hairpin-like conformations, and R4 and R5 represent expanded completely negatively and positively charged IDPs, respectively. Of note is that the parameter κ reflects the microstructural organization of amino acid sequences, with a low value of κ corresponding to an alternating structure and a large value indicating a block-like structure (Figure 5B). Figure 6 shows a diagram of the states of a polyampholyte chain as a function of the charge asymmetry ($\delta f = |f_+ - f_-|$) and fraction of charged monomers ($f = f_+ + f_-$).[24,25]

According to Dobrynin et al,[25] the overall size and shape of polyampholytes are determined by the balance of several factors: (a) chain entropy that tends to keep the polymer configuration in accordance with Gaussian statistics; (b) fluctuation-induced attractions between charged monomers that tend to collapse the chain into a globule; (c) short-range three-body monomer-monomer interactions that stabilize the size of a globule; and (d) Coulomb repulsion between excess

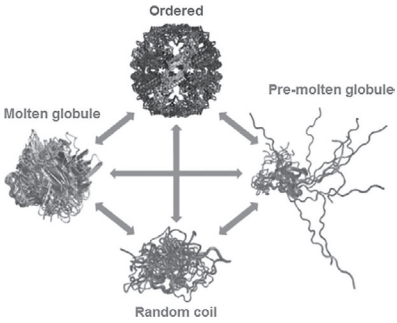


FIGURE 4 Four types of conformations of the polypeptide chain: ordered forms, molten globules, premolten globules, and random coils. Reproduced from Reference 16 with permission from the American Chemical Society [Colour figure can be viewed at wileyonlinelibrary.com]

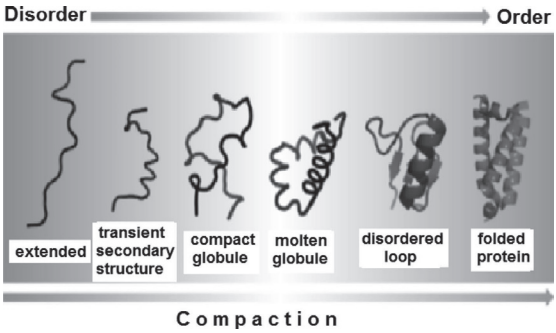


FIGURE 3 Transition of protein molecules from a disordered to a structured state. The color gradient represents a continuum of conformational ensembles (red) to compact, dynamically restricted, fully folded globular states (blue). Reproduced from Reference 16 with permission from the American Chemical Society [Colour figure can be viewed at wileyonlinelibrary.com]

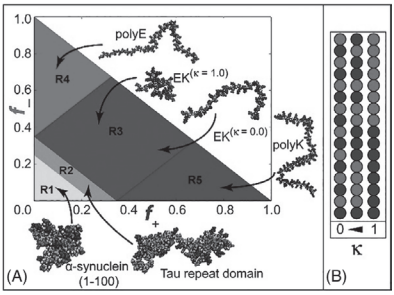


FIGURE 5 (A) Diagram of states for specific IDPs that corresponds to each of the five regions. (B) Schematic depiction of the implication of changing κ values. Red and blue circles represent negative and positive charges, respectively. Reproduced from Reference 23 with permission from the American Chemical Society [Colour figure can be viewed at wileyonlinelibrary.com]

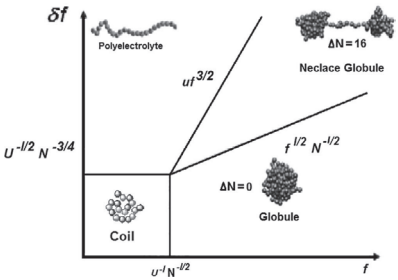


FIGURE 6 Diagram of states of a polyampholyte chain in dilute solution as function of the charge asymmetry $\delta f = |f_+ - f_-|$and fraction of charged monomers $f = f_+ + f_-$. Reproduced from Reference 25 with permission from the Wiley [Colour figure can be viewed at wileyonlinelibrary.com]

charges that tend to stretch the polymer chain. The relative importance of these factors depends on the fraction of positive (f_+) and negative (f_-) charges on the chain, on the charge sequence, on the degree of polymerization (N), and on the ratio of the Bjerrum length (l_B) to the monomer size (b), defining the relative strength of the electrostatic interactions ($u = l_B/b$).

The analogous conformational state is also specific to synthetic block polyampholytes.[24,25] For instance, a balanced polyampholyte with a zero charge ($\Delta N = 0$) forms a dense globule (where ΔN is the difference between the number of positive fN^+ and negative fN^- charges). At the point of definite charge asymmetry ($fN^+ > fN^-$ or $fN^+ < fN^-$), a globule is divided into two parts, with a pearl-like chain connecting double-stranded helical conformations on both ends (Figure 7). The pH-induced collapse and phase diagrams for the IDPs show that collapse takes place at the isoelectric point (IEP), caused by intrapolyelectrolyte complexation between the oppositely charged sequences within single macromolecules, occurring in both synthetic-based random and block polyampholytes.[26]

Polypeptide-based amphoteric copolymers can mimic the biological activity of natural proteins.[27-29] The pH-dependent solution and aggregation behavior of an ABC-type PEO_{42}–$PLLys_{61}$–$PLGlu_{62}$ triblock copolymer with cationic and anionic polypeptide segments was studied in pure water and saline solution[29] (Figure 8).

Stable solutions were prepared at low- and high-pH levels, with precipitation (I) occurring in an intermediate pH range of 4.5 to 10.5. PLGlu adopts a noncharged α-helical conformation at low pH and a charged random coil conformation at high pH. In contrast, PLLys forms a random coil at low pH and turns into an α-helix at high pH. Therefore, at either low- or high-pH levels, half of the polypeptide segments should adopt a random coil conformation and half, an α-helical structure. At an intermediate pH range of ∼4.5 to 10.5, there is evidence for the existence of β-sheet formation, as indicated by a negative CD peak absorption with single minimum at ∼218 nm. Aggregation behavior is controlled by the block sequence and position of the hydrophobic helix block. Vesicles form when the helix block is located at the chain end, whereas single chains are stable when the helix middle block can be wrapped by the two outer hydrophilic blocks and shielded from the water phase (resembling tertiary structure formation in proteins). Polyampholytic polypeptide sequences that form helices in isolation have been identified and extensively studied by the authors.[28] The main conclusion is that the specific patterns of oppositely charged amino acids impart a strong helical propensity to polyampholyte peptide sequences.

Therefore, the structural similarity between IDPs, polypeptide-based, and synthetic polyampholytes can be summarized as follows:

1. Both IDPs and synthetic polyampholytes adopt globular, coil, and stretched conformations. Further, they both show similarities in their states as a function of charge asymmetry, which is expressed in the case of IDPs as the fraction of charged residues, FCR = ($f_+ + f_-$), and net charge per residue, NCPR = $|f_+ - f_-|$, and in the case of synthetic polyampholytes as $\delta f = |f_+ - f_-|$ and the fraction of charged monomers ($f = f_+ + f_-$), where f_+ and f_- are the fractions of positive and negative charges, respectively;
2. pH- or charge-dependent conformation of block polyampholytes and synthetic polypeptides can include double-stranded helical conformation and β-sheet formation, which are specific to proteins.
3. A number of theoretical studies[29,30] devoted to the topic have shown that charge fluctuation affects the shape, phase separation, aggregation, and swelling-deswelling of flexible linear and crosslinked polyampholytes, highlighting the role of electrostatic interactions between oppositely charged monomers in IDPs.

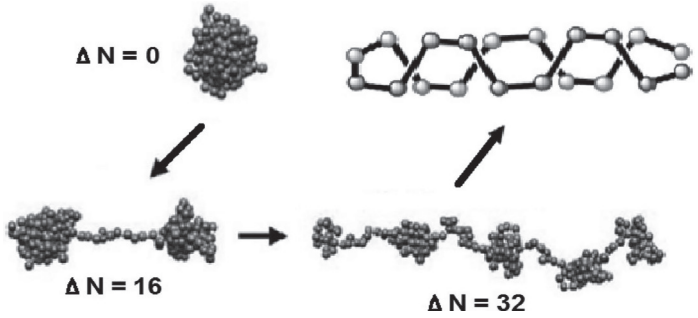
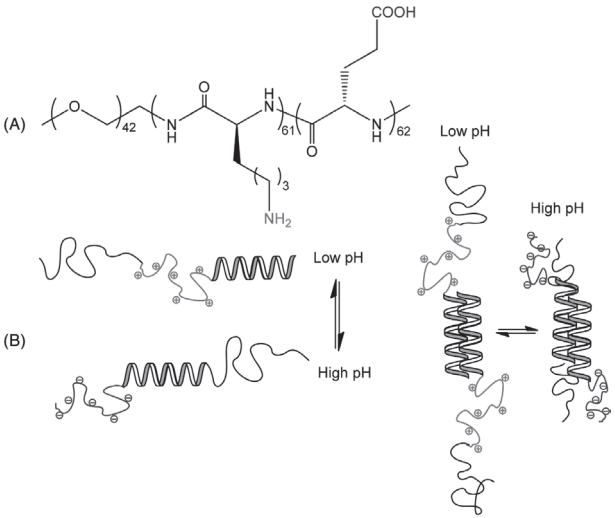


FIGURE 7 Cascade-type transition of a polyampholyte chain due to charge asymmetry and a fragment of double-stranded helical conformation of the ground state of a diblock polyampholyte obtained from Monte-Carlo simulation. Red indicates cationic and blue shows anionic monomers. Reproduced from Reference 25 with permission from the John Wiley & Sons [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 8 Chemical structure (A) and pH-dependent secondary structure (B) of PEO_{42}-$PLLys_{61}$-$PLGlu_{62}$. Schematic illustration of the pH-dependent assembly-disassembly of PEO_{42}-$PLLys_{61}$-$PLGlu_{62}$ in saline solution. Reproduced from Reference 29 with permission from the American Chemical Society [Colour figure can be viewed at wileyonlinelibrary.com]



3 | CONFORMATION AND PHASE BEHAVIOR OF GLOBULAR PROTEINS, AMPHOTERIC POLYPEPTIDES, IDPS, SYNTHETIC POLYAMPHOLYTES, AND INTERPOLYELECTROLYTE COMPLEXES

Complex coacervation, a form of liquid–liquid phase separation (LLPS), is a common phenomenon in globular proteins, IDPs (or IDRs), amphoteric polypeptides, synthetic polyampholytes, and interpolyelectrolyte complexes (IPCs). The simplified molecular design principles developed for synthetic polyampholytes can provide some insights into the more complicated sequences of IDPs and provide an understanding as to how charge-driven LLPS can be designed through tuning of the pattern of charged monomers. Among the synthetic amphoteric copolymers, block polyampholytes are attractive with regard to the study of conformational regimes and phase separation as a function of polymer

concentration, charge balance, pH, ionic strength, and so forth, in order to gain insight into the more complicated system of IDPs.[31] Further, the authors will show that a series of model polyampholytic polypeptides of increasing blockiness undergo self-coacervation due to electrostatic attraction between oppositely charged anionic and cationic blocks along the same polymer chain, which is representative of the classical model system for certain types of IDPs. The similarity between phase separation in both polyampholytic polypeptides[32] and IPCs derived from anionic and cationic polyelectrolyte pairs will expand the understanding of the amphoteric behavior of IPCs.[26]

The phase behavior of a series of lysine-glutamate polyampholytes and IPCs of homopolypeptides is compared in Figure 9.[33] The sequences of block polyampholytes are characterized by their blockiness (τ), which increases from alternating positive-negative monomers (τ = 2) to blocks of 24 positive and negative monomers (τ = 48).

The sequence of charges along these polyampholytic polypeptides plays a significant role in their coacervation ability, as an increase in the blockiness enhances the strength of coacervation. The reason is that the spatial proximity of two oppositely charged blocks leads to a strong Coulomb attraction, small R_g, and higher tendency to phase separation. In contrast, for a strictly alternating sequence, attractive Coulomb interactions require more conformational restriction, resulting in more open, large R_g single-chain conformation, and a lower tendency to phase separation.[30] Differences between the phase diagrams of block polyampholytes and IPCs can be explained by the presence of "charge pattern interfaces" where two segments of oppositely charged blocks merge in polyampholytes, whereas homopolyelectrolytes lack such connectivity, thus leading to different types of salt localization in comparison with block polyampholytes.[34]

Shown in Figure 10 is the LLPS of poly-L-lysine-based betaine-type polyampholyte (PLL-SA50) as a function of temperature and salt addition, including images of liquid–liquid phase separation, coacervation, homogeneous solution, and a microphotograph of coacervate droplets.[35] The phase diagram of aqueous PLL-SA50 solution exhibits LCST-type temperature-responsive LLPS and coacervate formation.

Another example is dual stimuli-responsive polyampholyte poly(L-serinyl acrylate (PSA) in aqueous solution exhibiting LLPS as a response to pH and temperature[36] (Figure 11). At low and high pH, PSA behaves as both a cationic and anionic polyelectrolyte and is fully water soluble. At the isoelectric pH (pH_{IEP} 2.85), PSA exists in zwitterionic form, and in the pH range of 2.3-3.5, PSA is insoluble (two-phase system) due to the formation of intra- and intermacromolecular complexes. The turbid solution of PSA becomes transparent upon heating, but the turbidity reappears upon cooling, indicating the presence of UCST-type phase behavior.

Incorporation of amino acid residues into the structure of synthetic polymers is promising with regard to the design of various nonbiological biomimetic polyampholytes (macromolecular architectures) with stimuli-responsive, self-assembling, tunable chiroptical, catalytic, and optoelectronic properties.[4] Several reviews and research articles have been devoted to the synthesis of amino acid-based synthetic polymers.[5,6]

As regard the behavior of synthetic polyampholytes, amphoteric polypeptides, and IPRs, attention should be paid to the pH-dependent isoelectric state, in which the overall charge of macromolecules is close to zero, the polymer chain is quasi-neutral, with minimal solubility, average size, viscosity, and degree of swelling, while turbidity is maximal, conformation is compact or globular, and electrophoretic mobility is zero.

Commonalities among the phase portraits of proteins, polypeptides, block polyampholytes, and IDPs include pH-dependent globularization, aggregation, precipitation, swelling, and deswelling. In the case of gelatin A and B, the electrostatic attraction between oppositely charged groups

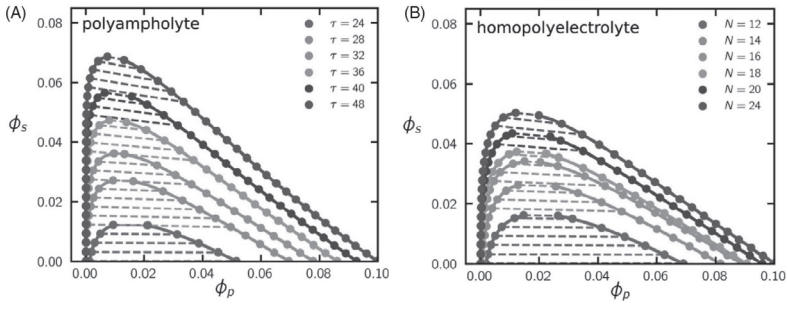


FIGURE 9 Phase diagrams of peptide-based block polyampholytes (A) and IPCs between homopolyelectrolytes (B) for varying values for τ. The homopolyelectrolyte degree of polymerization is denoted as $N_p = \tau/2$. The dotted lines represent the tie lines or the two phases. In these phase diagrams, the bimodal curves demarcate a region of salt-polymer concentrations (ϕ_s vs ϕ_p) within which phase separation occurs. Reproduced from Reference 34 with permission from the Royal Society of Chemistry [Colour figure can be viewed at wileyonlinelibrary.com]

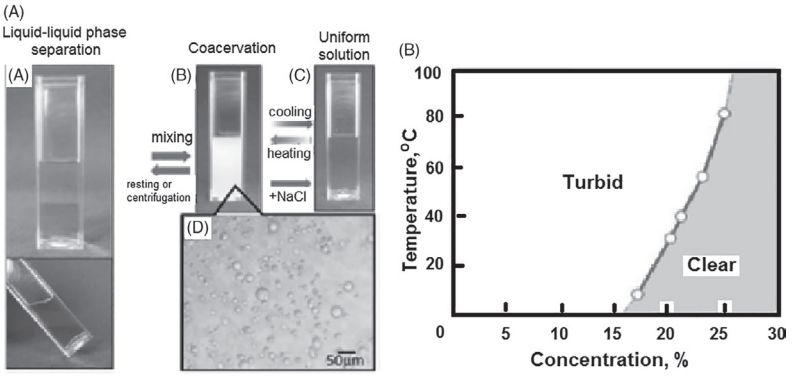


FIGURE 10 Phase behavior (A) and phase diagram (B) of aqueous PLL-SA50 solution. The polymer solution was stained with Alizarin red (10 μg/mL) to enhance visibility. Reproduced from Reference 36 with permission from the John Wiley & Sons [Colour figure can be viewed at wileyonlinelibrary.com]

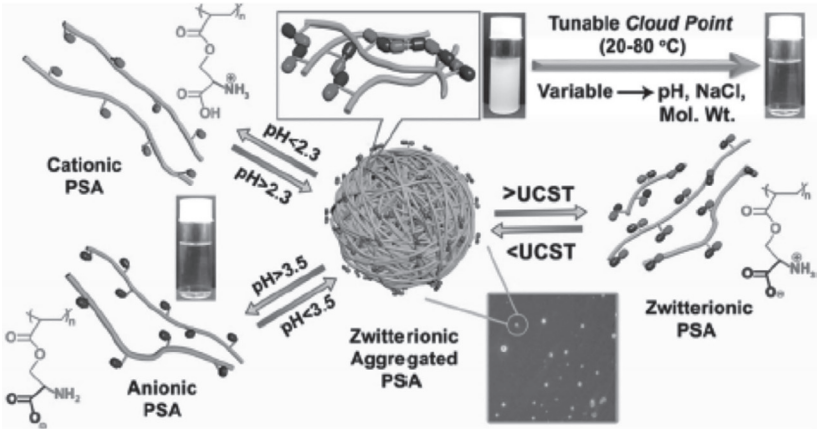


FIGURE 11 Schematic representation of temperature- and pH-induced transition of PSA. Reproduced from Reference 37 with permission from the American Chemical Society [Colour figure can be viewed at wileyonlinelibrary.com]

leads to collapse and self-aggregation of protein molecules at the pH_{IEP}.[37-39] At the isoelectric point of gelatin A (pH_{IEP} = 7.0), the persistence length increases more than two times, leading to expansion of the macromolecular chain in response to an increase in salt concentration.[40] The antipolyelectrolyte effect, related to unfolding of amphoteric macromolecules, at the isoelectric point in the presence of neutral salts is a common phenomenon for annealed, quenched, and betaine-type polyampholytes.[7-10] Nano-sized, micro-sized, and monolithic polyampholyte gels exhibit collapse at the pH_{IEP} and swelling at pH > pH_{IEP} or pH < pH_{IEP}.[41-43]

Temperature- and pH-dependent aggregation of block-copolypeptides based on poly(*N*-isopropylacrylamide)-*block*-poly(L-glutamic acid-*co*-L-lysine) mimics the stimuli-sensitive behavior of polyampholytic biomacromolecules.[44] Their conformation switching between helix and random coil structures was confirmed by CD, NMR, UV-Vis spectroscopy, and DLS. Near the pH_{IEP} of block polyampholytes, the total charge of amphoteric chains is completely neutralized, and aggregation or phase separation (coacervation) takes place.[45,46] Increasing the ionic strength (μ) of the solution through the addition of KCl leads to a narrowing of the precipitation region, and at higher values of μ = 0.3 mol·L^{-1}, block polyampholytes are entirely dissolved.[47] Dissolution of block polyampholytes is due to screening of the oppositely charged blocks on the macromolecules by KCl, which leads to unfolding of the globule into a coil. At pHs below and above the pH_{IEP}, spherical micelles, consisting of either a noncharged acidic block surrounded by a positively charged corona or of a noncharged basic block surrounded by a negatively charged corona, are formed.[46]

IDPs that lack the secondary structure and adopt an extended conformation are also attractive candidates for fabrication of amphoteric polymer brushes.[48] An engineered protein (rNFH-SA) that is classified as an IDP adopts an extended, disordered conformation in solution and can be grafted in an oriented manner to solid supports in order to produce IDP brushes. The influence of pH and ionic strength on IDP brush height was evaluated. At pH > 10.7, the carboxylic groups of glutamic acid are charged, but the lysine groups remain neutral. Electrostatic repulsion between uniformly charged carboxylate ions expands the IDP chain. At pH < 6, the lysine moieties progressively protonate, accumulating positive charges on the IDP chain and the whole macromolecular chain, having become a cationic polyelectrolyte, expands again. At the $pH_{IEP} \approx 6.8$, the electrostatic attraction between oppositely charged side chains along the length of the protein results in collapse of the brush conformation. Polyelectrolyte effects lead to a threefold increase in brush thickness over the pH_{IEP}-centered swelling, which also occurs among synthetic random polyampholytes.[49] The influence of ionic strength on the brush height was evaluated only at extremely high (pH = 10.9) and low (pH = 2.4) pHs, and in both cases, the brush heights decreased with increasing ionic strength. However, studying the effect of ionic strength on IDP brush height at pH_{IEP} would be interesting, as swelling at the pH_{IEP} is a common phenomenon of synthetic polyampholytes. Thermodynamic analysis of the collapse transition profile of polyampholyte gel underpins the similarity of the thermodynamic behavior of globular proteins, emphasizing that the behavior of collapsed polyampholyte hydrogels reproduces the behavior of globular proteins.[50]

Therefore, the specific features of proteins, polyampholytic polypeptides, IDPs, random, regular, and block polyampholytes possessing linear and crosslinked structures are the formation of globular conformations at the pH_{IEP}, stabilized by Coulombic forces between opposite charges within single macromolecules. The location of charges along the macromolecular chain plays a crucial role in the conformational behavior of polyampholytes.[51] Aggregation of globules leads to either precipitation or coacervation. Deviation from the pH_{IEP} transforms polyampholytes into positively or negatively charged polyelectrolytes and consequently results in stretched conformation of macromolecular chains. Swelling of polyampholytes at the pH_{IEP} upon addition of neutral salts demonstrates that the anti-polyelectrolyte effect for proteins and synthetic polyampholytes is a common phenomenon. Expansion of IDPs at (very) high salt concentration was shown by Johner and Joanny.[31] The conformational and phase behavior of IDPs can be understood and predicted using polyampholyte theories to describe the standard properties of macromolecules, such as radius of gyration, height of polymer brush, and so forth. The renewed interest of both theorists and researchers in IDPs is beneficial to advanced theoretical investigations.

4 | APPLICATION POTENTIAL OF POLYAMPHOLYTES

Water-soluble and water-swelling polyampholytes, such as amphoteric cryogels, have found a wide number of practical applications in medicine, biotechnology, nanotechnology, the petroleum industry, water purification, catalysis, desalination, sewage treatment, flocculation, coagulation, and other areas.[52-55] Polyampholyte hydrogels modified by graphene oxide (GO)[56] and magnetic nanoparticles[57] have exhibited good mechanical properties, durability, high sorption capacity, and excellent recyclability, so can be utilized as adsorbents for removal hazardous metal ions in wastewater. The advantages of polyampholyte hydrogel sorbents are: excellent mechanical strength for separation and reusability; fast sorption rate and high sorption capacity; high treatment capacity on fixed-bed columns; efficient removal of toxic metal ions from industrial effluent; and low cost (~US$ 6.3/kg).

Purification of metal ions and dyes from industrial waste is extremely important from an ecological point of view. Removal of Hg(II), Cu(II), methylene blue, methyl orange, and Congo red has been performed with the help of aminocarboxylate-maleic acid-based hydrogels, including linear and crosslinked polyampholytes based on N-acryloyl-N′-ethylpiperzine, using maleic acid and aminocarboxylate-maleic acid as crosslinkers, and chitosan-*g*-poly(acrylic acid) hydrogels modified with clay minerals.[58,59]

Due to their salt and temperature resistance, quenched polyampholytes are widely applied in enhanced oil recovery (EOR) as thickening agents in brine solution.[60-67] Hydrophobically associating polyampholytes may be especially effective viscosity enhancers in high salinity media and at high temperatures, as they combine self-assembly and polyampholytic properties.[68,69] Application of hydrophobically modified and acrylamide-based polyampholytes in EOR has been reviewed.[52,70] Hydrophobically modified polyampholytes have been shown to act as efficient pour-point depressants and for alkaline-surfactant-polymer flooding.[71-75] According to Gou et al,[76] additional oil recovery, equal to 15.46%, has been achieved utilizing hydrophobically modified polyampholytes based on acrylamide, sodium acrylate, 3-(diallylamino)-2-hydroxypropyl sulfonate, and 3-(2-[2-heptadec-8-enyl-4,5-dihydro-imidazol-1-yl]ethyl-carbomoyl)acrylic acid.

Amphoteric hydrogels, due to their high toughness, excellent bio- and hemocompatibility, antibiofouling, self-healing ability, cytotoxic,

and adhesive properties in physiological conditions, have the potential to be at the forefront of advanced structural biomaterials, such as cartilage, antithrombogenic implants, wound dressing, blood-contacting materials, and drug delivery systems.[77,78] Many research groups have made remarkable contributions to the development of self-healing, artificial tissue, including mimetic and mechanically robust materials based on polyampholyte hydrogels.[79-82] Recent advances in injectable hydrogels for drug delivery and tissue engineering applications have been reviewed.[83] The flexibility, high strength, and moduli of quenched polyampholyte hydrogels consisting of equimolar amounts of strongly charged anionic and cationic monomers are similar to the soft tissues of vasculature, skin, or muscle and can be used as biomaterials in tissue replacement.[84]

Due to high charge density, biocompatibility, nontoxicity, protein- and cell-repellent properties, antithrombogenic, and antipolyelectrolyte behavior in saline media, polyzwitterions continue to attract interest in the area of biomedical application.[55,85,86] The biological effects of polyzwitterionic hydrogel films of about 100 nm thickness have been evaluated with respect to model proteins (BSA, lysozyme, fibrinogen). The protein-repellent ability of polyzwitterions increases in the following order: fibrinogen > BSA > lysozyme. Antifouling, antibiofouling, and antibacterial properties have been exhibited by PVDF,[87] polyethersulfone,[88] and polyamide[89] after being applied to reverse osmosis membranes, demonstrating the benefits of anionic and cationic monomers within the polyampholytes.

Synthetic polyampholytes are suitable materials for inhibition of ice crystallization and can serve as cryoprotective agents.[90] The cryoprotective properties of polyampholytes as antifreezing agents for living cells were demonstrated for the first time by Matsumura et al.[91-100] Systematic investigations clarifying the role of microstructure, acid/base molar ratio, molecular weights, and hydrophobicity of polyampholytes on ice recrystallization inhibition were undertaken by Gibson et al.[101-104] A new strategy of freeze concentration-mediated cytoplasmic delivery of proteins based on a combination of liposomes and hydrophobically modified polyampholytes was developed by the authors.[105-107]

5 | FUTURE ADVANCES IN POLYAMPHOLYTES

In 2020, the polymer community celebrates the 100th anniversary of the first article on polymerization, published by Hermann Staudinger. On this occasion, the editors and advisory board members of Macromolecular Chemistry and Physics in a review paper[108] identified the top three areas of future of polymer investigation: (a) new properties and applications, (b) new synthesis methods, and (c) sustainability. In the present work, the authors concentrate their attention on some open problems, properties, and applications of synthetic and natural polyampholytes, without the intention of being exhaustive.

One of the open problems in the behavior of synthetic polyampholytes is to shed light on the internal *globular* structure of amphoteric macromolecules, which are considered to be densely folded three-dimensional nucleations consisting of a core surrounded by a hydrophilic edge from which monomers force out solvents. The discovery of a highly ordered structure of synthetic water-soluble and water-swelling polyampholytes, whether in a solution or solid state, at the isoelectric point (IEP) opens up a challenging task, which requires theoretical, computational, and simulation approaches in order to achieve a better understanding of the driving forces behind the self-organizing structure of polyampholytes at the IEP.[109]

Another open problem is the synthesis of seminatural polyampholytes through modification of natural polysaccharides such as chitosan, cellulose, starch, gellan, dextran, and alginic acid, among others, by introducing either carboxylic (sulfonic) or amine (ammonium) groups, or both, into the macromolecular chains.[110-112] Such biocompatible and biodegradable polyampholytes fabricated from natural polysaccharides can be used in the production of excellent antibiofouling and self-healing materials, bio- and hemo-compatible artificial organs, and drug delivery systems.

The behavior of synthetic polyampholytes in salt-containing solutions is characterized by the existence of the isoelectric effect,[26] the nature of which is that any low- or high-molecular-weight substances associated with polyampholytes can potentially be released at the IEP as a result of competition between inter- and intramolecular interactions. In other words, if the cooperativity of intrachain interactions of acidic (anionic) and basic (cationic) groups within a single macromolecule exceeds interchain interactions, the release of such substances may occur. The isoelectric effect in a series of water-soluble polyampholytes, amphoteric hydrogels, and cryogels has been demonstrated with respect to surfactants, dye molecules, polyelectrolytes, and proteins. However, this phenomenon has not yet been researched with respect to DNA, which could play a crucial role for the development of the next generation of gene-delivery vectors. In this context, some potential applications can also be expected of biodegradable seminatural polyampholytes, amphoteric polypeptides, and IDPs, which might be suitable for transporting and delivering genetic material into cells.

Another future possibility may include immobilization of polymer-metal complexes, metal nanoparticles, metal oxides, or molecularly imprinted enzymes within macroporous polyampholyte hydrogels or cryogels.[113] Due to their interconnected and large porous structures, such gels can be utilized in soft and gentle flow-through catalytic reactors, which can operate under mild conditions (atmospheric pressure, room temperature, and so forth). These reactors may represent a new generation of green macromolecular systems that can be used to provide a sustainable basis for the future development of heterogenized homogeneous catalysts and biocatalysts, in particular for the pharmaceutical industry, where a high conversion rate and pure final product are required. Speculation is even possible with regard to utilization of polyampholyte cryogels in the synthesis of polypeptides from aminoacids in flow-through reactors under appropriate catalytic conditions. Molecularly imprinted polyampholyte hydrogels and cryogels might be utilized as an effective tool for binding, separation, and purification of target proteins.

Crosslinked quenched polyampholytes containing strongly charged cationic and anionic monomers are promising as hydrogel

electrolytes in the development of low-temperature supercapacitors.[114] The main advantage of swollen polyampholyte gel electrolytes over liquid electrolytes is that polymer electrolytes are intrinsically free of leakage-related problems. Polyampholytic ionic liquids made of protic ionic liquid or zwitterionic monomers are another possibility for the development of ion-conducting materials that retain proton conductivity without leaching ions or the requirement of a separate polymer matrix.[11]

6 | CONCLUSIONS

Clearly, the structural and behavioral similarity between synthetic and natural polyampholytes is due to the presence of positive and negative charges. The location of opposite charges along the macromolecular chain plays a crucial role in the conformational and phase behavior of polyampholytes. Diagrams of states for IDPs and synthetic polyampholytes are similar. Commonalities in the phase portraits of proteins, polypeptides, block polyampholytes, and IDPs include pH-dependent globularization, aggregation, precipitation, swelling, and deswelling. Complex coacervation or liquid-liquid phase separation (LLPS) is also a common phenomenon among globular proteins, IDPs, amphoteric polypeptides, and synthetic polyampholytes. The specific feature of proteins, polyampholytic polypeptides, IDPs, and synthetic polyampholytes is the existence of the isoelectric point, at which compaction, globularization, aggregation, coacervation, and precipitation take place. Another common phenomenon is the antipolyelectrolyte effect, which leads to dissolution of linear polyampholytes and swelling of polyampholyte gels and IDPs at the pH_{IEP} upon addition of neutral salts. The structural and behavioral similarities between synthetic and natural polyampholytes can expand knowledge in the field and stimulate renewed interest among both theorists and researchers in advanced theoretical and experimental investigations. Fundamental discoveries in the behavior of linear and crosslinked polyampholytes have been considered with regard to practical applications and future opportunities.

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Application of polyampholytes in emerging technologies

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ABSTRACT

In this brief review the fundamentals of linear and crosslinked polyampholytes including amphoteric cryogels are considered in the light of practical applications. They are widely used in biotechnology, nanotechnology, oil industry, water purification, desalination etc. Some perspectives of polyampholytes as structural biomaterials, biosensors, energy storage devices, supercapacitors are highlighted.
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1. Introduction

Polyampholytes are unique macromolecules containing acid/base and/or anionic/cationic groups in the main or side chains, and are able to mimic the behavior of proteins, polypeptides and polynucleotides. Water-soluble and water-swelling polyampholytes exhibit stimuli-responsive, thermal-resistant, salt-tolerant, shear-stable, self-healing, anti-fouling, and self-assembling properties that provide broad potential as structural biomaterials, drug delivery and chemo-mechanical systems, biosensors, energy storage devices, supercapacitors, and actuators, among others.

One of the fundamental properties discovered in the last century with respect to linear and crosslinked polyampholytes is the so-called *antipolyelectrolyte effect* [1–4] that is related to the unfolding of annealed polyampholytes at the isoelectric point (IEP) or charge-balanced quenched polyampholytes in quasi-neutral state in the presence of salts.

Another phenomenon is the so-called *isoelectric effect* [5–10] that is related to cooperative release (or detachment) of preliminary bonded low- or high-molecular-weight substances at the IEP of annealed polyampholytes or at quasi-neutral state of charge-balanced quenched polyampholytes as a result of competition between inter- and intra-macromolecular (inter-MMC and intra-MMC) complexation.

In the forthcoming sections, the utilization of *antipolyelectrolyte* and *isoelectric effects* will be demonstrated in terms of wastewater purification, water desalination and oil recovery.

2. Application of polyampholytes for wastewater purification and desalination

Fig. 1 illustrates the capturing of transition metal ions by annealed polyampholytes and further recovery from the wastewater [11–13] and soils [14].

If polyampholyte is soluble in water at the IEP (for instance, at high pH 8–10), the metal ions released from macromolecular coils are precipitated in the form of metal hydroxides and the polyampholyte is found in the supernatant. If polyampholyte is insoluble at the IEP (for instance, at low pH 3–5), then the polyampholyte aggregates and precipitates while metal ions are retained in the supernatant. The release of metal ions from macromolecular coils is due to realization of so-called *isoelectric effect* as a result of competition between inter-MMC and intra-MMC [5,9]. The effective removal of metal ions by water-soluble [15–17] and water-swelling [18] polycarboxybetaines (PCBs) is reached up to 97% (Fig. 2). Modified by ethanolamine and glycine PCBs were reused 5 times without the loss of adsorption capacity (99%).

Adsorption of metal ions by PCB hydrogel is accompanied by gradual coloring and shrinking of sample [18] (Fig. 3).

Desorption of metal ions from the gel interior in acidic region is accompanied by decolorization of the gel sample due to release to outer solution.

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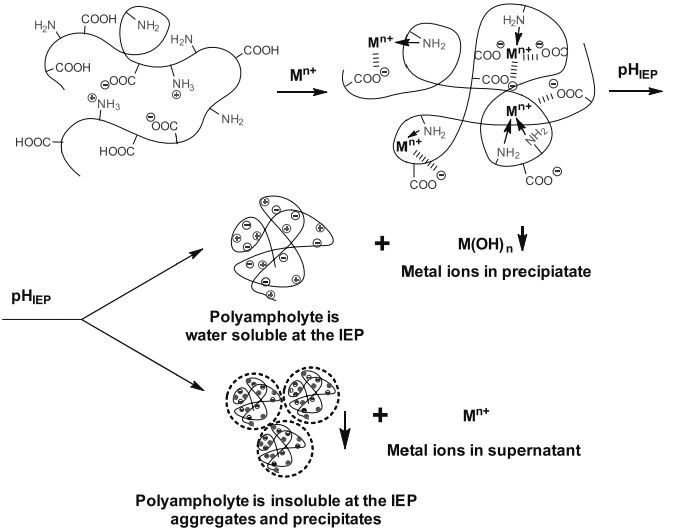


Fig. 1. Recovery of metal ions from the wastewater at the IEP of annealed polyampholytes.

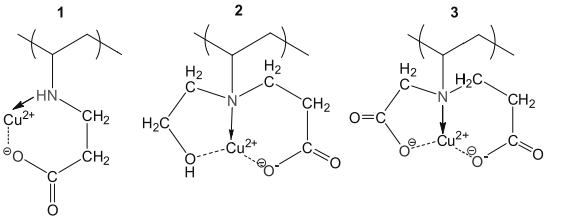


Fig. 2. Chelate complexes of PCB (1) and PCB modified by ethanolamine (2) and glycine (3) with copper (II) ions.

Polyampholyte hydrogel containing amine and carboxylic groups was modified with graphene oxide (GO). It exhibited excellent mechanical strength, fast sorption rate, high sorption capacity, efficient removal of toxic metal ions, and low cost (US$ 6.3/kg) (Fig. 4)[19].

Macroporous amphoteric hydrogels derived from chitosan-g-poly(acrylic acid) containing magnetic particles exhibit high adsorption capacity, easy separation and excellent reusability [20,21] (Fig. 5).

Removal of methylene blue (MB) [22], methyl orange (MO) [23], Congo red [24] was performed with the help of aminocarboxylate-maleic acid based hydrogels [22], linear and crosslinked polyampholytes based on N-acryloyl-N'-ethylpiperzine and maleic acid [23] as well as hydrogels of aminocarboxylate-maleic acid and chitosan-g-poly(acrylic acid) sorbents modified with clay minerals [24,25]. New polysulfobetaine cryogel derived from 2-(N-3-sulfopropyl-N,N-dimethyl ammonium)ethyl methacrylate and water-soluble crosslinker – N,N,N',N'-tetramethyl-N,N'-bis(2-ethylmethacrylate)-propyl-1,3-diammonium dibromide was used for selective sorption of MO from the mixture of MO and MB [26]. The sorption capacity of polysulfobetaine cryogel with respect to individual and mixed dyes after 7 and 24 h revealed that the amphoteric cryogel preferentially adsorbs MO but not MB.

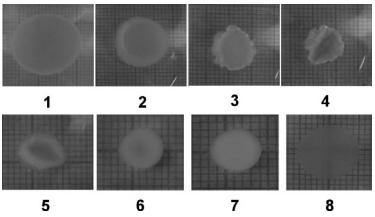


Fig. 3. Adsorption (1–4) and desorption (5–8) of copper(II) ions by PCB hydrogel. Reproduced from Ref. 18.

Block polyampholytes based on poly(2-vinylpyridine-*b*-poly (acrylic acid) (P2VP-*b*-PAA) and poly(2-vinylpyridine-*b*-poly (methacrylic acid) (P2VP-*b*-PMAA) were used for desalination of salted water [27,28]. At the IEP (pH 5.5–6.0) they showed the maximal flux rate and a good salt rejection (60–80%). This behavior is accounted for the formation of intra-MMC between P2VP and PAA (or PMAA) blocks and realization of the *isoelectric effect*. Cross-linked by isoprene polyampholytes composed of quaternary ammonium and styrenesulfonate monomers were used as desalination membranes [29]. The quenched polyampholyte hydrogels

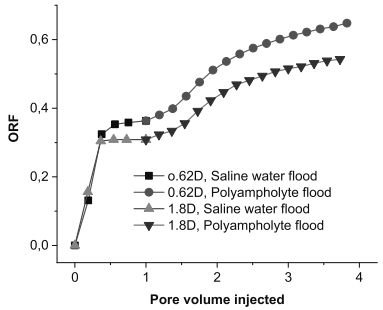


Fig. 6. ORF for water and polymer flooding. Reprinted with permission from Ref. 41.

were used for production of drinking water [30]. Polyzwitterions containing the residues of glycine were used as antiscalant reagents and demonstrated scale inhibition up to 100% [31]. The inexpensive antiscalant has the potential in mitigating scale formation and reject brine in an osmosis chamber.

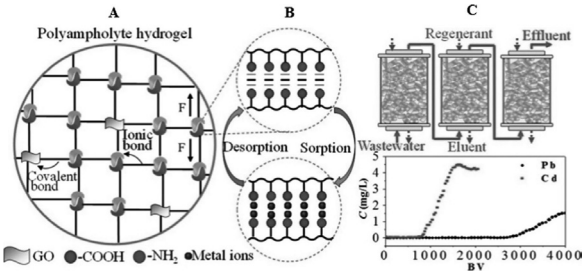


Fig. 4. Polyampholyte hydrogel containing amine and carboxylic groups modified with graphene oxide (A), sorption and desorption of metal ions (B), purification of industrial water from Pb^{2+} and Cd^{2+} ions (C). Reprinted with permission from Ref. 19.

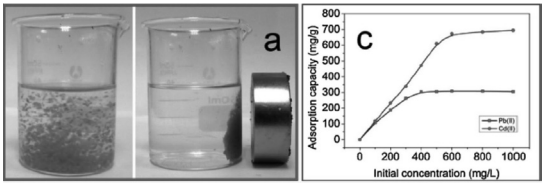


Fig. 5. Separation of metal ions by magnetic macroporous amphoteric hydrogel (a) and adsorption capacity of Cd^{2+} and Pb^{2+} on initial concentration of metal ions (c). Reprinted with permission from Ref. 21.

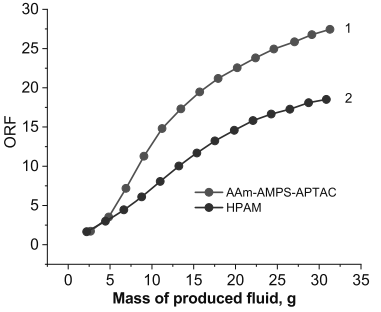


Fig. 7. Comparison of ORF between AAm-AMPS-APTAC (1) and HPAM (2). The permeability of sand pack model is 0.62 Darcy.

3. Application of polyampholytes in enhanced oil recovery and as pour point depressants

The low-charge-density polyampholytes can be used as effective viscosity enhancers in high salinity and high-temperature reservoirs and be utilized in enhanced oil recovery (EOR) processes [32–39]. Recently [40,41] we have synthesized a series of low-charge-density amphoteric terpolymers based on acrylamide (AAm), 2-acrylamido-2-methyl-1-propanesulfonic acid sodium salt (AMPS), and (3-acrylamidopropyl) trimethylammonium chloride (APTAC) and evaluated their viscosifying ability with respect to reservoir saline water (200–300 g L^{-1}) at 60 °C. For polymer flooding experiments the appropriate salt tolerant sample [AAm]:[AMPS]:[APTAC] = 80:10:10 mol.% was selected. The injection of 0.25 wt% polyampholyte dissolved in 200 g L^{-1} brine resulted in a rise of incremental oil recovery factor (ORF) by 28 and 23% for the 0.62D and 1.8D sand pack models, respectively, in comparison with saline water flooding (Fig. 6). The ORF between AAm-AMPS-APTAC and hydrolyzed polyacrylamide (HPAM) was compared, because the latter is the most studied and traditionally used polymer in EOR (Fig. 7). It is seen that the total mass of oil produced in the course of polyampholyte and HPAM injections is around of 28% and 18%, respectively, in comparison with the initial oil mass in the sand packs.

This is explained by an increase in the viscosity of brine solution due to disruption of intra- and interionic contacts between the oppositely charged AMPS and APTAC moieties, demonstrating the *antipolyelectrolyte effect*. This phenomenon leads to a decrease in the mobility factor (M), which is quantitative parameter of oil displacement with water:

$$M = \frac{k_w \cdot \mu_0}{k_0 \cdot \mu_w}$$

where M is mobility factor; k_w is water permeability; μ_0 is oil viscosity; k_0 is oil permeability; μ_w is water viscosity.

In this context the hydrophobically modified polyampholytes (HMPA) may be effective viscosity enhancers in high salinity media and temperature as they combine the advantage of alkaline-surfactant-polymer (ASP) flooding [42–44]. The viscosity of HMPA increases due to intermolecular association of hydrophobic parts [42,43]. Application of HMPA in EOR was reviewed in [45]. According to the results of Gou *et al.* [46] the additional amount of oil recovered by HMPA can reach up to 15–16%. HMPA can be used as efficient pour point depressant and also for ASP flooding [47–52].

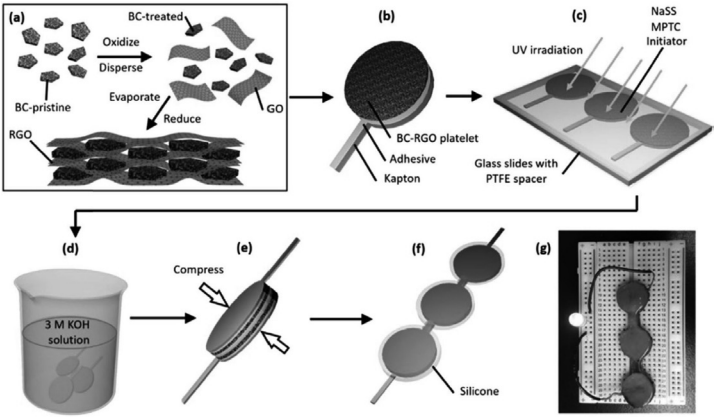


Fig. 8. **a**) Schematic representation of polyampholyte-based supercapacitor assembling. (a) preparation of biochar-reduced graphene oxide (BC-RGO) electrode with high electric conductivity; (**b**) supporting of the BC-RGO electrodes on a Kapton substrate; (**c**) embedding of BC-RGO electrodes within polyampholyte hydrogel based on [P(NaSS-MAPTAC)]; (**d**) The electrolyte dialyzed in 3 M KOH (**e**) compressing the dialyzed electrolyte/electrode pair with the top BC-RGO electrode to fabricate a symmetric supercapacitor; (**f**) 3D supercapacitor encapsulated in silicone to light a green LED (**g**). Reproduced from 53. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Polyampholyte-based supercapacitors, sensors, ionic liquids and structural biomaterials

Authors [53,54] fabricated cost-effective and eco-friendly supercapacitors based on charge balanced sodium 4-vinylbenzenesulfonate (NaSS) and [3-(methacryloylamino)propyl] trimethyl ammonium chloride (MAPTAC) [P(NaSS-MAPTAC)] hydrogel with embedded biochar (BC) and graphene oxide (GO) (Fig. 8). The main advantage of swollen gel polymer electrolytes is that they overcome the leakage problems. The supercapacitor at room temperature showed high energy density of 30 $W{\cdot}h{\cdot}kg^{-1}$ with 90% capacitance retention after 5000 charge–discharge cycles at a power density of 50 $W{\cdot}h{\cdot}kg^{-1}$. At low temperature (-30 °C), the supercapacitor has an energy density of 10.5 $W{\cdot}kg^{-1}$ at a power density of 500 $W{\cdot}kg^{-1}$. Wang et al [55] demonstrated that hydrogel electrolytes with the immobilized pair ions (IPIs) prepared from [2-(acryloyloxy)ethyl]trimethylammonium chloride and sodium salt of 2-acrylamido-2-methyl-1-propanesulfonic acid *via* random copolymerization with poly(ethylene glycol) diacrylate was the most promising electrolyte for supercapacitors and other electrochemical cells. The IPI-Na_2SO_4 system possessed the remarkable energy density of 121.3 $W{\cdot}h{\cdot}kg^{-1}$ and high-power density of 38.4 $W{\cdot}kg^{-1}$ with 5000 charge/discharge cycles.

A bimodal electronic skin (e-skin) sensor array was fabricated from thermochromic liquid crystal dispersed in an elastomer matrix, sandwiched by transparent electrodes prepared from ion conductive and adhesive polyampholyte hydrogels [56]. Combination of elastomer and tough amphoteric hydrogel makes this e-skin mechanically robust and deformable. This device has the potential application in internet-of-things and soft robotics.

The polyampholytic ionic liquids (PILs) were synthesized via reversible addition – fragmentation chain transfer (RAFT) polymerization of monomeric ionic liquids (MILs) [57]. PILs representing tight, elastic, and free-standing films with good mechanical properties were prepared by crosslinking of MILs with poly(ethylene glycol) dimethacrylate [58]. Formation of mobile ionic liquid molecules occurred inside the polyampholyte matrix was responsible for improved ion transport. A self-healing PILs based on acrylic acid, 2-diethylaminoethyl methacrylate and methyl methacrylate were prepared in the presence of ionic liquids containing 1-ethyl-3-methylimidazoliumbis[(trifluoromethyl)sulfonyl]imide ([Emim]TFSI) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) [59]. An ionic liquid-based ionically cross-linked gel polymer electrolyte has not only great potential in traditional electrochromic devices but also can be applied as a new electronic device such as foldable smart windows and stretchable electronic skin. The application area of PILs comprises solar cells, lithium batteries, actuators, light-emitting cells, electrochromic devices, etc. [60].

Polyampholytes can be used as perspective cartilage, antithrombogenic, wound dressing, tissue-replacing, blood-contacting biomaterials due to excellent bio- and hemocompatibility, self-healing, adhesive and low cytotoxicity [61–68]. Recently the advances in injectable hydrogels for drug delivery and tissue engineering applications were reviewed in [69]. Polyampholyte-based artificial biomaterials derived from interpenetrating networks containing zwitterions and amphoteric hydrogels reinforced by glass fibers can replace the natural tissues or muscles.

5. Conclusion

Application aspects of polyampholytes include the environment protection, petroleum industry, biotechnology, electrochemistry, electronics etc. Linear and crosslinked polyampholytes could have a broad impact in the areas of wastewater purification, desalination, enhanced oil recovery, structural biomaterials, energy storage devices, supercapacitors, and actuators, among others. PILs are promising as ion- and proton-conducting materials that retain the conductivity without leaching of ions. Polyampholyte hydrogels can mimic some human organs and serve as artificial tissue, soft actuators, and soft robotics.

CRediT authorship contribution statement

Sarkyt E. Kudaibergenov: Conceptualization, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Review

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Catalytic Properties of Polyampholytes, Polyampholyte-Metal Complexes, Polyampholyte-Metal Nanoparticles and Polyampholyte-Enzyme Conjugates: a Mini-Review

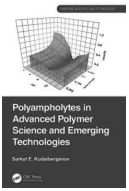
This mini-review briefly discusses the catalytic properties of polyampholytes, polyampholyte-metal complexes, polyampholyte-metal nanoparticles and polyampholyte-catalase conjugates. Polyampholyte-based catalysts can mimic enzyme functions, facilitating reactions like hydrolysis, decomposition, hydrogenation, and oxidation of various substrates. Special focus is given to amphoteric hydrogels and cryogels that encapsulate metal nanoparticles or enzymes. These materials have demonstrated effectiveness in the hydrogenation of nitroaromatic compounds, oxidation of disulfide and aliphatic (or aromatic) alcohols under mild conditions, both in batch and flow-through reactors. Kinetic parameters, turnover numbers (TON), turnover frequencies (TOF), and activation energies are presented for a series of specific catalytic processes. Notably, flow-through reactors exhibit significantly higher catalytic efficiency compared to batch reactors and can be used continuously for extended periods. Additionally, the review explores the potential of light-driven hydrogen and oxygen evolution reactions from water, facilitated by metal nanoparticles within amphoteric hydrogels in the presence of photosensitizers.

Keywords: Polyampholyte-metal complexes, polyampholyte-metal nanoparticles, polyampholyte-enzyme conjugates, catalysis, decomposition, hydrogenation, oxidation, water splitting.



Professor **Sarkyt E. Kudaibergenov** is a prominent Kazakh polymer scientist, known for his research into water-soluble and water-swelling polyampholytes, macromolecular complexes, polymer-stabilized nanoparticles, polymeric catalysis, and stimuli-responsive materials for various applications. Currently he is director of private institution "Institute of Polymer Materials and Technologies" established by him in 1999. He has co-authored 20 monographs and textbooks, published in Kazakh, Russian, Polish and English, as well as over 400 research articles and reviews, more than 150 of which have appeared in international peer-reviewed journals. He has received awards and recognition for his research, including the State Prize of the Republic of Kazakhstan in the field of Science and Technology (1986), the "Parasat" award for being the most published and internationally cited Kazakhstani author (2010), a medal "For merits in the development of science in the Republic of Kazakhstan" from the Ministry of Science and Education of the Republic of Kazakhstan (2012), the K.I. Satpayev Prize for the development of specialty polymers for application in petrochemistry and nanotechnology (2019), and the State Scientific Scholarship for scientists and specialists who have made an outstanding contribution to the development of science and technology (2020). For outstanding achievements in basic science in 2022 he has been recognized as "Best Researcher" by the Ministry of Science and Education of the Republic of Kazakhstan. Despite achieving numerous successes and making significant contributions to the field of physical chemistry of polymers, Professor S.E. Kudaibergenov's enduring interest lies in polyampholytes — a subject he has explored since 1979. He has published several reviews and fundamental monographs on this topic, including "Polyampholytes: Synthesis, Characterization, and Application" (Kluwer Academic/Plenum Publishers, 2002, USA), "Polyampholytes: Past, Present, Perspectives" (2021, Center for Operational Printing, 2021, Kazakhstan), "Polyampholytes in Advanced Polymer Science and Emerging Technologies" (CRS Press, 2024, Boca Raton and London).

Dear Colleagues,



We are pleased to share great news! In September 2024, Professor Kudaibergenov's new book «**Polyampholytes in Advanced Polymer Science and Emerging Technologies**» was just published by CRC Press. This monograph reviews the innovative studies in this field over the past two decades, with the aim to analyze and systematize the literature in the context of emerging technologies.

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1. Introduction. 2. Water-Soluble Polyampholytes. 3. Hydrophobically-Modified Polyampholytes (HMPA). 4. Nanogels, Microgels and Macroporous Gels of Polyampholytes. 5. Macromolecular Complexes of Polyampholytes. 6. Polyampholytes in Biotechnology and Medicine. 7. Polyampholytes in Catalysis. 8. Application of Polyampholytes in Emerging Technologies. 9. Conclusions.

Brief Description of the Book

Polyampholytes are unique polymers containing acid/base and/or anionic/cationic groups in the main or side chains. Water-soluble and water-swelling polyampholytes exhibit properties that provide broad potential as structural biomaterials, drug delivery and chemo-mechanical systems, biosensors, energy storage devices, supercapacitors, and actuators, among others.

This book will appeal to readers who conduct materials research for biomedical, water treatment, and environmental remediation applications.

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Introduction

Synthetic water-soluble polymers, with their abundance of functional groups and conformational flexibility, are prime candidates for designing active and selective catalysts that emulate enzyme functions [1]. The electrostatic interactions, hydrogen bonds, coordination bonds, and hydrophobic entrapment in polyampholytes, polyampholyte-metal complexes, and polyampholyte-metal nanoparticles serve as active and selective centers, catalyzing hydrolysis, decomposition, hydrogenation, and oxidation of various substrates [2]. Polymer-protected nanoparticles [3, 4], porous polymeric gels, surfaces of polymeric thin films/membranes [5–11], and stimuli-responsive polymers [12] are widely used as catalysts. Macroporous amphoteric cryogels, containing metal nanoparticles or enzymes in their pores, can be employed for catalytic reactions in both batch-type and continuous-flow-type reactors [5, 6]. There is significant interest in heterogeneous catalytic hydrogenation of various substrates in continuous-flow reactors [13–16] and the immobilization of enzymes within three-dimensional polymers for use as "green" catalysts [17–20]. These flow-through reactors are catalytically several orders of magnitude more efficient and can be used continuously over long periods. A precise combination of enzymes, mono- and bimetallic nanoparticles within nano-, micro-, and macro-sized polymeric gels, cryogels, and membranes can create synergistic effects in flow-through catalytic reactions.

Catalysis by Polyampholytes

The hydrolysis of the positively charged ester 3-acetoxy-N-trimethylaniline iodide (ATMAI), the negatively charged ester 3-nitro-4-acetoxybenzoic acid (NABA), and the neutral ester *p*-nitrophenylacetate (PNPA) was catalyzed by 4(5)-vinylimidazole-co-acrylic acid (VI-*co*-AA) and 4(5)-vinylimidazole-*co*-maleic acid (VI-*co*-MA) copolymers in a 28.5 vol.% ethanol–water mixture [21]. The results were compared with those obtained using monomeric analogs, specifically imidazole and γ-4(5)-imidazolebutyric acid. For the solvolysis of ATMAI, the catalytic activities of the monomeric and polymeric catalysts increased in the following order: VI-co-MA > VI-co-AA > γ-4(5)-imidazolebutyric acid > imidazole. The strongest catalytic effect was observed with a copolymer containing 42–50 mol.% of imidazole units, attributed to the optimal isolation of acid–base sequences. (Figure 1).

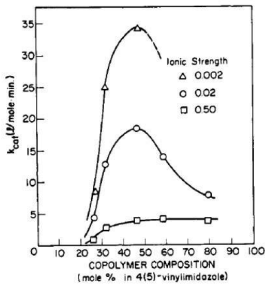


Figure 1. Effects of VI-*co*-AA composition and ionic strength on k_{cat}-catalyzed solvolysis of ATMAI. Solvent, 28.5 % ethanol–water; pH, 9.0; T, 25 °C.
Reprinted with permission from Ref. [21] (Overberger C. G., Maki H. Esterolytic catalysis by copolymers containing imidazole and carboxyl functions. *Macromolecules* 1970, 3, 214–220. Copyright 1970, American Chemical Society)

However, substituting acrylic acid with vinylsulfonic acid significantly reduces the hydrolytic activity of polyampholytes. This decrease is likely due to the high ionization degree of sulfonic acid, which leads to the formation of strong ion pairs between imidazole and sulfonic groups, compared to the weaker interactions with carboxylic groups. The proposed mechanism for ATMAI hydrolysis involves electrostatic interactions between carboxylate anions and the positively charged parts of the substrate, while imidazole molecules attack the ester groups. The catalytic activity of alternating VI-*co*-MA and statistical VI-*co*-AA equimolar polyampholytes was studied in the hydrolysis of *p*-NPA, ATMAI, and NABA. For the alternating copolymer at pH > 9.0, the hydrolysis reaction rate decreases in the following order: NABA > *p*-NPA > ATMAI. In contrast, for the statistical polyampholyte, this order is reversed. The difference in catalytic activity between these copolymers is attributed to the varying pKa values of the carboxylic groups.

The authors of [22–27] used phenylimidazole–acrylic acid (PI-AA), phenylimidazole–methacrylic acid (PI-MAA), and phenylimidazole–N-vinylpyrrolidone (PI-NVP) as polymer catalysts with ATMAI as the substrate. Kinetic analysis indicates that the substrate-binding affinity of the copolymers increases in the order PI-NVP > PI-MAA > PI-AA, which correlates with the hydrophobicity of the comonomers in the order NVP > MAA > AA. ATMAI molecules are bound to PI-NVP primarily through hydrophobic interactions. The PI-AA catalyst interacts with the substrate via both hydrophobic interactions (through PI units) and electrostatic forces (through carboxylate anions). The complex formation between PI-MAA and ATMAI involves contributions from both hydrophobic groups (PI and α-methyl groups of MAA) and electrostatic interactions. The rate of hydrolysis of cationic esters with the general formula S_n^+ in the presence of 5(6)-vinylimidazole and acrylic acid in 40:60 vol.% propanol–water mixtures decreases in the order $S_2^+ > S_7^+ > S_{12}^+ > S_{18}^+$. Once again, copolymers containing 45–55 mol.% of imidazole units exhibit the highest catalytic activity. Substrate molecules with long acyl groups are less efficiently catalyzed due to steric hindrance. However, when the reaction is conducted in a methanol–water (40:60 vol.%) mixture, the opposite effect is observed. Thus, with the catalytic activity of the copolymers increasing as the length of the substrate molecules grows.

Modified polyacrylamide-based amphoteric cryogels were tested as catalytically active substances in transesterification of glyceryl oleate [28]. The highest conversion of glyceride was equal to 88.4 %, and the yield of methyl oleate is about 64 %.

Thus, synthetic polyampholytes actively participate in the hydrolysis of negatively charged, positively charged, and neutral esters, similar to histidine-containing proteins in living organisms. However, when metal ions are coordinated with acid-base groups, the catalytic properties of polyampholyte-metal complexes are significantly enhanced, enabling hydrogen decomposition (catalase-like activity), hydrogenation, oxidation, and isomerization of various substrates. The following subchapter describes the catalysis by polyampholyte-metal complexes.

Catalysis by Polyampholyte-Metal Complexes

Catalysis by polyampholyte-metal complexes typically occurs through the formation of coordination bonds between metal ions and substrate molecules, followed by the creation of intermediate mixed complexes [29]. Polyampholyte-metal (Cu^{2+}, Co^{2+}, Mn^{2+}, Ag^+) complexes were used as catalysts for decomposition of hydrogen peroxide (H_2O_2) [30, 31]. Neither polyampholytes alone nor metal ions exhibit catalytic activity on their own. However, polyampholyte-metal complexes significantly accelerate hydrogen peroxide decomposition, following the Michaelis-Menten kinetic model. Activation of H_2O_2 by polyampholyte-metal complexes was successfully used for the degradation of azo dyes [32].

A palladium complex of poly(4-vinylpyridine-*co*-acrylic acid) (4VP-*co*-AA) was prepared and used for hydrogenation of aromatic nitro compounds, in particular, nitrobenzene, 2-, 3-, and 4-nitroanailines; 2-, 3- and 4-nitrophenols; 2-, 3- and 4-nitroanisols; and 4-nitrobenzaldehyde to corresponding aniline compounds (Figure 2) [33].

The initial hydrogenation rate for all *p*-substituted nitrobenzenes increases in the order *p*-OH > *p*-OCH_3 > > H > *p*-NH_2 > *p*-CHO demonstrating especially good catalytic activity for the hydrogenation of nitrophenols and nitroanisoles. The comparison of hydrogenation rate of different isomers of nitroaniline gives an order of *p*- > *o*- > *m*-substituted nitrobenzenes. The 4VP-co-AA/Pd complex exhibits high stability, sustaining 4-5 cycles of hydrogenation for *p*-nitrobenzene and 4-nitroanisole, with yields 100 % of aniline and 98.8 % of 4-methoxyaniline respectively.

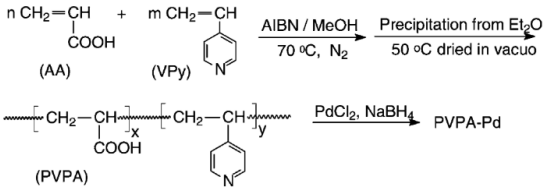


Figure 2. Preparation of poly(4-vinylpyridine-*co*-acrylic acid) copolymer (PVPA) and its palladium complex. Reproduced with permission from Ref. [33]

Raj et al. [34] developed a tunable organic−inorganic hybrid catalyst consisting of a (poly-N,N-diallyl-N-hexylamine-*alt*-maleic acid) and phosphotungstic acid ($H_3PW_{12}O_{40}$) forming polyoxometalate (POM) supramolecular structures (Figure 3).

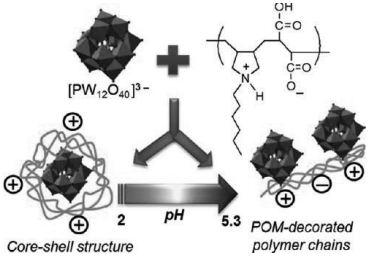


Figure 3. Stabilization of $[PW_{12}O_{40}]^{3-}$ by (poly-N,N-diallyl-N-hexylamine-*alt*-maleic acid) and formation of pH dependent core-shell structure and POM-decorated polymer chains. Reproduced with permission from Ref. [34] (Raj G., Swalus C., Guillet R.A., Devillers M., Nysten B., Gaigneaux E.M. Supramolecular organization in organic–inorganic heterogeneous hybrid catalysts formed from polyoxometalate and poly(ampholyte) polymer. *Langmuir* 2013, 29, 4388−4395. Copyright 2023, American Chemical Society)

The supramolecular organization is driven by electrostatic interactions between the positively charged polyampholyte and anionic POM. Given POM's large size and charge, POM entities are encapsulated by the polymer chains. By tuning the supramolecular assembly of these organic-inorganic hybrids, one can control the catalytic properties of POM heterogeneous catalysts in various chemical transformations. Patent literature [35] also details the use of palladium and platinum nanoparticles stabilized by polymeric carbo-, sulfo-, and phosphobetaines as fuel cell catalysts.

Transforming of metal ions coordinated with the functional groups of polyampholytes into metal nanoparticles is effective tool for creating active, selective, and stable catalysts, particularly because most catalytic reactions occur under mild conditions. In this process, the role of functional polymers is to stabilize the nanoparticles and protect them from aggregation.

Polyampholyte-Protected Metal Nanoparticles in Catalysis

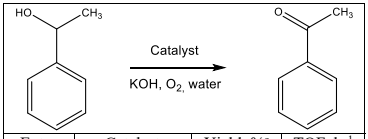
Incorporating noble and transition metal ions into amphoteric nano-, microgels, and macroporous gels as templates during reduction opens new avenues for developing effective catalytic systems [36, 27]. From the relevant literature, it is well known that both hydrogels and cryogels of amphoteric nature can be used for the immobilization of metal nanoparticles [5, 6, 37]. Different shaped gold nanoparticles, i.e., triangular, hexagonal, spherical and rod-like particles in the range of 3–10 μm, can be immobilized within the amphoteric hydrogels and cryogels and distributed at the surface and inner parts of micro- and macropores (40–100 μm). For example, the microgels of poly2-(methacryloyloxy) ethyl] dimethyl (3-sulfopropyl) ammonium hydroxide p(SBMA) containing Ni nanoparticles catalyze the hydrogenation 4-nitrophenol (4-NP),

2-nitrophenol (2-NP), and 4-nitroaniline (4-NA) to corresponding aminophenols [38]. Hereby, the reduction process was monitored by measuring the decrease of the absorption peaks at 414 nm, 400 nm, and 380 nm for 2-NP, 4-NP, and 4-NA, respectively. The activation energy of the hydrogenation of 4-NP and thermodynamic parameters, i.e., enthalpy, entropy, and Gibbs energy were calculated. The cyclic tests for the prepared p(SBMA)-Ni composites were carried out for the reduction of 4-NP. The catalytic activity of p(SBMA)-Ni was decreased to 37 % after the first cycle, and to 10 % after the third cycle. This decrease can be related to structural composite breakdown under release of Ni nanoparticles.

Gold nanoparticles (AuNPs) protected by sulfonated cardo poly(arylene ether sulfone) SPES (abbreviated as Au@SPES) were obtained in the presence of $NaBH_4$ as a reducing agent [39]. The SPES-modified gold nanoparticles were stable at pH between 2 and 14. The TEM micrographs show well-dispersed AuNPs smaller than 4 nm with a relatively narrow size distribution. It is in good agreement with the average AuNPs particles (4.2 nm) determined from the Scherrer equation. The Au@SPES was used as recyclable catalyst in the aerobic oxidation of 1-phenylethan-1-ol (Table 1).

Table 1

Oxidation of 1-phenylethan-1-ol to acetophenone by Au@SPES



Entry	Catalyst	Yield, %[a]	TOF, h^{-1}
1	SPES	0	0
2	AuNPs	25	5
3[b]	Au@SPES	84	16.8
4[c]	Au@SPES	83	16.6
5[d]	Au@SPES	84	16.8

The oxidation reaction takes places in an aqueous solution in mild conditions in the presence of 1 mol.% of Au@SPES and KOH. However, it does not occur with the SPES and only 25 % conversion is observed in the presence of AuNPs (Table 1, entries 1,2). The oxidation of 1-phenylethan-1-ol to acetophenone occurs quantitatively (99 %) maintaining six runs. The Au@SPES precipitates near the isoelectric point (IEP) of the SPES that is convenient to separate and reuse the catalyst.

Macroporous amphoteric cryogels containing metal nanoparticles in pores can be used for catalytic reactions as batch-type and continuous-flow-type reactors [40–45] (Figure 4).

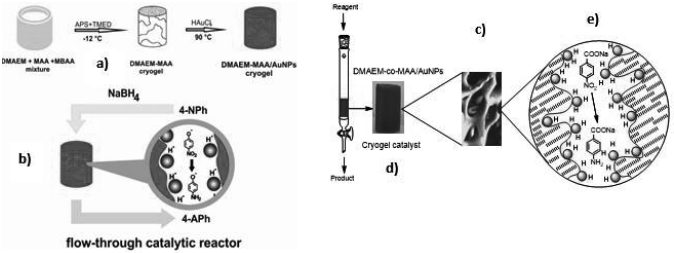


Figure 4. Fabrication of macroporous amphoteric cryogel based on N,N-dimethylaminoethylmetacrylate and methacrylic acid (DMAEM-*co*-MAA) with immobilized AuNPs (*a*) and schematic representation of monolith flow-through catalytic reactor used for hydrogenation of 4-NP (*b*) and *p*-NBA (*c*) over DMAEM-*co*-MAA/AuNPs catalysts. The violet colored sample corresponds to macroporous cryogel DMAEM-*co*-MAA containing AuNPs (*d*) while the violet dots are schematic image of AuNPs (*e*) in cryogel pores. Reproduced with permission from Refs. [42, 44]

Amphoteric cryogel DMAEM-*co*-MAA under heating conditions effectively reduces rhodium, palladium, gold and silver ions and forms fine well-dispersed metal nanoparticles [46]. The DMAEM-*co*-MAA cryogel containing the AuNPs was used as a flow-through catalytic reactor in hydrogenation of 4-nitrophenol (4-NP) and oxidation of D,L-dithiotreitol (DTT) [43]. The DTT forms a stable six-membered ring with an internal disulfide bond once oxidized. The hydrogenation and oxidation products of 4-NP and DTT are 4-aminophenol (4-AP) and disulfide (DS) respectively. The activation energy (E_a), turnover number (TON), turnover frequency (TOF) of hydrogenation and oxidation reactions are presented in Table 2.

Table 2

The activation energy (E_a), TON and TOF at hydrogenation of 4-NP and oxidation of DTT over macroporous DMAEM-*co*-MAA/AuNPs flow-through catalytic reactor

Macroporous flow-through catalyst	Substrate	E_a, kJ·mol^{-1}	TON	TOF, h^{-1}	Run	Ref.
DMAEM-*co*-MAA/AuNPs	4-NP	7.52	38.17	21.56	50	[42]
	DTT	–	985.2	412.2	10	[43]

The catalytic reduction of *p*-nitrobenzoic acid (*p*-NBA) by palladium (PdNPs) and gold nanoparticles (AuNPs) immobilized within DMAEM-*co*-MAA cryogel matrix was also carried out [47]. It should be noted that the DMAEM-*co*-MAA cryogel itself does not produce *p*-aminobenzoic acid (*p*-ABA). The products of hydrogenation of *p*-NBA over DMAEM-co-MAA/AuNPs catalyst are: 1) *p*-ABA, 2) *p,p'*-azodibenzoate and 3) sodium 4-(4-aminobenzamido)benzoate (Figure 5).

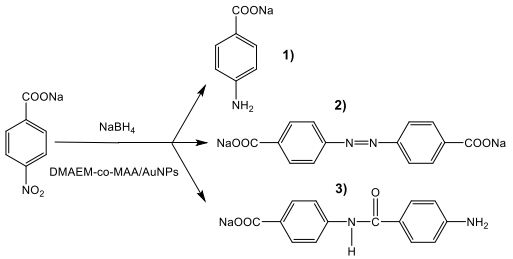


Figure 5. Hydrogenation products of *p*-nitrobenzoic acid sodium salt over DMAEM-co-MAA/AuNPs catalyst. 1) *p*-aminobenzoic acid sodium salt; 2) *p,p'*-azodibenzoate; 3) sodium 4-(4-aminobenzamido)benzoate. Reproduced with permission from Ref. [46]

In case of P(DMAEM-*co*-MAA)/PdNPs the formation of only *p*-ABA with conversion degree 40 % at [*p*-NBA]:[$NaBH_4$] = 1:50 mol/mol and 100 % at [*p*-NBA]:[$NaBH_4$] = 1:200 mol/mol is observed.

Catalytic Properties of Catalase Immobilized within Polyampholyte Cryogels

Special interest may represent physical (adsorption, encapsulation, entrapment) and chemical (covalent attachment, crosslinking) immobilization of enzymes within macroporous gel matrix for obtaining a new generation of flow-through biocatalysts that may have significant potential in biotechnology, fine chemical, food and pharmaceutical industries [47, 48]. The advantages and drawbacks of cryogel-based flow-through catalytic reactor were outlined in [6].

The efficiency of amphoteric catalase encapsulated within amphoteric cryogel matrix in oxidation of ethanol, *iso*-propanol and *n*-butanol by hydrogen peroxide, oxygen and air in batch and flow-through reactor was compared (Figure 6) [49, 50].

The micron-sized cryogel samples (from 10 to 50 μm) provided a free flow of aliphatic alcohol-hydrogen peroxide mixture under the gravity and hydrostatic pressure. The oxidized products of ethanol, isopropanol and *n*-butanol are acetaldehyde, acetone and butyraldehyde with the yields of 97, 87.6 and 80 %, respectively. The optimal conditions for oxidation of aliphatic alcohols are: pH ~ 6.4, temperature range 5–20 °C and volume ratio of substrate to reducing agent 1:1.

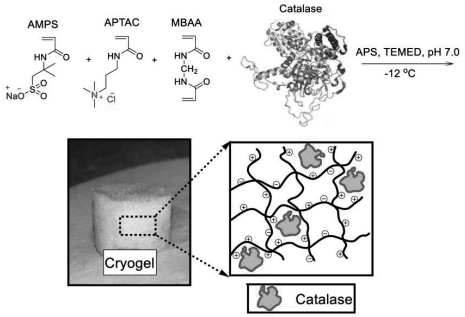


Figure 6. Synthetic protocol of encapsulation of catalase within APTAC-AMPS amphoteric cryogel matrix. Reproduced with permission from Refs. [49, 50]

The batch type reactor was also applied for the oxidation of ethanol by catalase embedded into a poly-ampholytic cryogel matrix using the hydrogen peroxide, molecular oxygen and air as oxidants [50]. The conversion degree of ethanol to acetaldehyde was equal to ~ 97–98 %.

The reusability of cryogel-entrapped catalase in batch reactor was evaluated. It was found that the conversion degree of ethanol to acetaldehyde insignificantly decreases over successive five runs, and after the fifth runs becomes 57.3 %. The calculated TON and TOF values for oxidation of ethanol by hydrogen peroxide, oxygen and air in the presence of monolith and powder cryogels are represented in Table 3.

Table 3

The values of TON and TOF calculated for oxidation of ethanol [50]

Oxidant	H_2O_2		O_2		Air	
	monolith	powder	monolith	powder	monolith	powder
TON·10^{-7} a)	18.3	17.9	18.4	18.2	11.3	11.4
TOF·10^{-7} b)	0.6	0.6	0.6	0.6	0.4	0.4
Notes: a) TON is in mol of product/(mol Cat); b) TOF is in mol of product/(mol Cat·min).						

The TOF value for the flow-through catalytic reactor was six times greater than that of the batch laboratory reactor. The successive oxidation of the isopropanol-hydrogen peroxide mixture resulted in a reduced yield of acetone, likely caused by the collapse of the cryogel matrix. The results of SEM confirmed that the shrinking of cryogel pores in water-organic solvent mixtures reduced the volume of cryogel samples, leading to a decreased flow rate and contact time. UV-Vis spectroscopy revealed that catalase remained within the cryogel matrix without any signs of leaching. After ten cycles of alcohol oxidation, the initial morphology of the cryogel-encapsulated catalase was completely altered. This change is probably due to the oxidative degradation of the cryogel matrix's internal structure by oxygen atoms and/or hydroxyl radicals produced during the hydrogen peroxide decomposition by catalase.

Thus, both monolith and powder cryogels containing the catalase are suitable for the oxidation of aliphatic alcohols into their corresponding carbonyl compounds. The advantages of enzyme-entrapped cryogel samples include the minimal volume of catalyst needed, a high surface-to-volume ratio, high selectivity, increased productivity, energy savings, and adherence to “green chemistry” principles. However, the primary drawback of cryogel microreactors is their weak mechanical properties. A significant issue is the chemical degradation of the cryogel matrix and the leaching of the enzyme from the 3D network, which can lead to contamination of the final products. This problem can be mitigated through the covalent immobilization of enzymes within the cryogel matrix.

Polyampholyte-Based Photocatalytic Systems

Recently new-generation catalysts for water splitting are being developed in combination with light harvesters or photosensitizers [51–53]. One example is entrapping of supramolecular light harvesting assemblies (perylene monoimide (PMI)-based-chromophore) for photocatalytic production of hydrogen within polyampholyte hydrogels [54] (Figure 7).

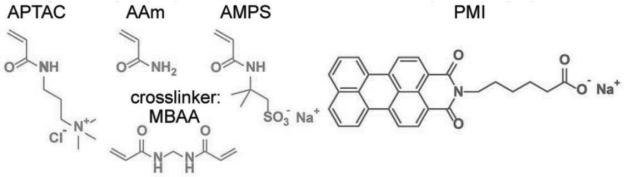


Figure 7. Anionic (AMPS), cationic (APTAC), neutral (AAm) monomers, crosslinker (MBAA) and perylene monoimide (PMI)-based-chromophore used for synthesis of polyampholyte hydrogel. Reproduced with permission from Ref. [54]

Hybrid hydrogels made from PMI and polyampholyte were assessed for their ability to perform photocatalytic proton reduction. When exposed to light, these hydrogels, containing the thiomolybdate catalyst $Na_2[Mo_3S_{13}]$ in an ascorbic acid solution at pH 4, successfully produced hydrogen. Initial experiments indicated that these systems could be reused for multiple photocatalysis cycles after refreshing the small molecule components. Another example is poly(dehydroalanine)-based (PDha) amphoteric hydrogels containing Pt nanoparticles (PtNPs), a thiomolybdate catalyst ($[Mo_3S_{13}]^{2-}$), or a cobalt polyoxometalate catalyst ($Co_4POM = [Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$) and $[Ru(bpy)_3]^{2+}$ which were applied as reusable heterogeneous catalysts for hydrogen evolution (HER) and oxygen evolution reactions (OER) when irradiated under visible light [55, 56]. Formation of hybrid [Ru]@PtNPs@PDha hydrogel and photocatalytic hydrogen evolution reaction carried out in a polymer network is schematically shown in Figure 8.

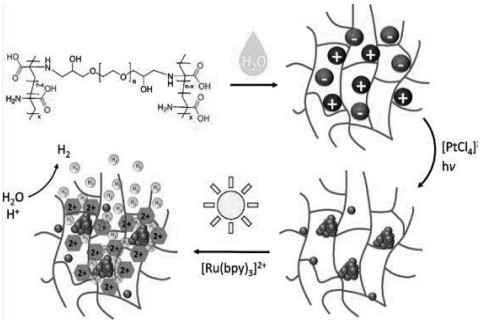


Figure 8. Electrostatic attachment of $[Ru(bpy)_3]_{2+}$ within the PDha-based amphoteric hydrogel, in situ formation of PtNPs and the photocatalytic hydrogen evolution reaction carried out in a polymer network. Reproduced with permision from Ref. [55]

PtNPs can reduce protons and produce hydrogen under visible light if combined with a suitable photosensitizer $[Ru(bpy)_3]_{2+}$. The catalytic activity of [Ru]@PtNPs@PDha for H_2 evolution by visible light irradiation resulted in a H_2 production rate of 28.5 $\mu mol \cdot g^{-1} \cdot h^{-1}$. For $[Ru(bpy)_3]_{2+}$/PtNPs molar ratios of 80, 8, and 0.8 the measured TON was equal to 350, 80, and 52, respectively. This work shows a straightforward approach to hybrid hydrogels for light-driven catalysis, although the presented approach is still prone to photodegradation and leaching depending on the choice of catalyst or photosensitizer.

The creation of core-shell hybrid materials with a TiO_2 core and a shell of polyampholytic poly(dehydroalanine)-*g*-(*n*-propylphosphonic acid acrylamide) (PDha-*g*-PAA@TiO_2) enabled effective immobilization of the photosensitizer Eosin Y (EY) and facilitated electronic interactions between EY and the TiO_2 core [57]. This configuration resulted in significant H_2 generation under visible light. The improved light-driven catalytic activity is credited to the unique core-shell design, where the graft copolymer serves as a bridge, facilitating electron and proton transfer while also preventing EY degradation. Further catalytic enhancement of PDha-*g*-PAA@TiO_2 was achieved by introducing $[Mo_3S_{13}]^{2-}$ cluster anions as a hydrogen-evolution cocatalyst (Figure 9).

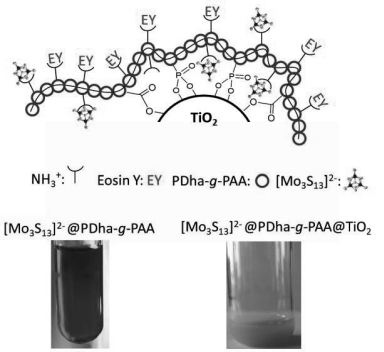


Figure 9. Schematic illustration of proposed interactions between PDha-*g*-PAA and TiO_2, Eosin Y, and $[Mo_3S_{13}]^{2-}$. Reproduced with permision from Ref. [57]

Zwitterionic conjugated polymer is emerging class of organic photocatalyst for light-driven hydrogen production from water due to their photoactive conjugated backbones and hydrophilic ionic side chains [58]. The photocatalytic efficiency of anionic, cationic and amphoteric polyelectrolytes with the thiophene (T)-dibenzo[b,d]thiophene sulfone donor–acceptor backbone was compared. Poly(zwitterionic) photocatalyst behaves the best activity with a hydrogen evolution rate of 55.2 $mmol \cdot g^{-1} \cdot h^{-1}$ under full-arc Xe light irradiation, which is 1.4-, 1.7-, and 10-fold as compared to those of anionic and cationic precursors, respectively.

Table 4 summarizes the activation energy (E_a), turnover number (TON), and turnover frequency (TOF) values of various polyampholyte-based catalysts as reported in the literature. Notably, pure catalase [59] and catalase immobilized within the APTAC-AMPS cryogel matrix exhibit exceptionally high TON in the decomposition of hydrogen peroxide [60] and the oxidation of ethanol [50], both with negative activation energies. Thermodynamically, the negative activation energies can be attributed to the exothermic nature of these catalytic reactions [59].

The main difference between polyampholyte-metal and polyampholyte-metal nanoparticle catalysis lies in the mechanism of the catalytic reaction. In the former case, the reaction proceeds through the formation of coordination bonds between metal ions and substrate molecules, leading to the creation of intermediate mixed complexes [29]. In the latter case, catalytic reactions occur on metal nanoparticles that are immobilized within the polymer matrix. Polyampholyte-metal complexes typically involve transition metal ions such as copper, nickel, and cobalt, which have the ability to form chelate complexes. Conversely, in polyampholyte-metal nanoparticle systems, noble metal ions like silver, gold, palladium, rhodium, and platinum (in cationic or anionic complex forms) are commonly used. It should be noted, however, that polyampholyte-metal complexes can sometimes be reduced to metal nanoparticles during the hydrogenation of substrates. For example, in Ref. 29, a palladium complex of poly(4-vinylpyridine-*co*-acrylic acid) (4VP-*co*-AA) used for the hydrogenation of aromatic nitro compounds can contain both palladium ions and palladium nanoparticles.

It is evident that immobilizing enzymes within hydrogel or cryogel matrices is a promising approach for applications in both batch and flow-through catalytic reactors. Cryogels, in particular, with their tunable po-

rosity, offer an effective and versatile tool for the development of novel biotechnological and industrial applications [50]. The TON and TOF values for hydrogen generation from water using linear and crosslinked polyampholytes containing photocatalysts in the form of metal nanoparticles and photosensitizers [54–57] are lower than those observed for polyampholyte-metal complexes but higher than those for polyampholyte-metal nanoparticles. This discrepancy is likely due to the multicomponent nature of the catalytic system, the complex, multistage processes of electron and proton transfer, as well as issues related to photodegradation and catalyst leaching. In our previous study [42], we detected gradual leaching of palladium and gold nanoparticles from the surface of amphoteric cryogels during sequential hydrogenation of *p*-nitrobenzoic acid (*p*-NBA).

Table 4

The activation energy (E_a), TON, and TOF values for different types of catalysts and catalytic reactions

Catalyst	Substrate	E_a, kJ·mol^{-1}	TON, h^{-1}	TOF, h^{-1}	Ref.
4VP-*co*-AA/Pd^{2+}	*p*-nitrobenzene	–	2000	–	[33]
DMAEM-MAA/PdNPs	*p*-nitrophenol	13.8	–	–	[42]
DMAEM-MAA/AuNPs	*p*-nitrophenol	7.5	38	21.5	[42]
Catalase	H_2O_2	–14.0	$(10–15)\cdot10^{10}$	–	[60]
APTAC-AMPS/Catalase	ethanol	–7.31	$(11.4–18.4)\cdot10^{7}$	$(4–6)\cdot10^{7}$	[50]
AAm-APTAC-AMPS/PMI	H_2O	–	–	107.4	[54]
[Ru]@PtNPs@PDha	H_2O	–	50–350	–	[55, 56]
PDha-*g*-PAA@TiO_2	H_2O	–	> 500	–	[57]

Conclusions

Polyampholytes and their derivatives, including polyampholyte-metal complexes, polyampholyte-metal nanoparticles, and polyampholyte-enzyme conjugates, exhibit remarkable catalytic activity, stability, and selectivity in various chemical reactions, such as the hydrolysis of esters, hydrogenation of nitrocompounds, and oxidation of both aliphatic and aromatic alcohols. Macroporous amphoteric cryogels embedded with metal nanoparticles and enzymes have proven to be effective catalysts in both batch and continuous-flow reactor systems. Comparative analysis of activation energy, turnover number (TON), and turnover frequency (TOF) values indicates that macroporous flow-through reactors demonstrate superior efficiency over their batch-type counterparts. In the realm of photocatalysis, particularly in the context of water splitting — a crucial process for sustainable solar energy conversion — polyampholyte/polyzwitterionic hydrogels represent an advanced scaffold. These hydrogels are capable of immobilizing photosensitizer dyes and catalysts in close proximity, thereby enhancing electron transfer efficiency. Their porous structure allows for the free movement of reactants and products, which is essential for efficient hydrogen and oxygen evolution reactions. Inspired by natural photosynthesis, these innovative hydrogels are poised to play a pivotal role in advancing affordable and efficient solar energy technologies. In the near future, polyampholyte-based nanogels, microgels, and membranes containing metal ions, metal nanoparticles, enzymes, and photosensitive substances could become promising soft materials for applications in the field of catalysis.

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УЧАСТИЕ В МЕЖДУНАРОДНЫХ И РЕСПУБЛИКАНСКИХ ПРОЕКТАХ, СИМПОЗИУМАХ И КОНФЕРЕНЦИЯХ

Под руководством С.Е. Кудайбергенова выполнен ряд Международных проектов, в частности, Международный проект НАТО «Устойчивый менеджмент токсичных загрязнителей в Центральной Азии: от региональной модели экосистемы до безопасности окружающей среды» в сотрудничестве со Стамбульским Техническим Университетом (Турция), Техническим Университетом Иаси (Румыния), Техническим Университетом Мюнхена (Германия), Самаркандским госуниверситетом (Узбекистан) и Институтом химии АН Таджикистана.



Обсуждение Международного проекта НАТО SfP 983931 (Алматы, 8-11 февраля 2009 г.)



Семинар НАТО SfP 983931 в Самаркандском государственном университете, г. Самарканд, Узбекистан, 25-28 апреля 2012 г.



Международный семинар НАТО (NATO SfP 983931) в КазНИТУ имени К.И. Сатпаева, г. Алматы, Казахстан, 17-19 марта 2014 г.

В 2014-2015 гг. и 2017-2019 гг. под научным руководством проф. С.Е. Кудайбергенова и проф. Шимей Сю (Синьцзянский и Сычуньский университеты, КНР) выполнен совместный проект «Разработка композитных гидрогелевых «скребков» для очистки внутренней поверхности трубопроводов».



Визит в Сычуаньский университет, г. Ченду, 2018 г.

В рамках проекта коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов», финансируемого Всемирным Банком и МОН РК (2011-2014 гг), найдено решение проблемы увеличения нефтеотдачи на месторождениях поздней стадии разработки путем использования технологии полимерного заводнения для снижения проницаемости высокопроницаемых (вымытых) каналов фильтрации и перераспределения потока нагнетаемого агента в низкопроницаемые нефтенасыщенные каналы. Закачка в нагнетательные скважины № 3383 и № 3065 месторождения Кумколь 234 и 160 кубических метров раствора полимера в интервале концентраций 0.2-1.0 % позволила увеличить количество дополнительно добытой нефти из 6 добывающих скважин 5890 тонн за период с 1 октября 2013 г. по 1 сентября 2014 г. (за 11 месяцев). По результатам проведения опытно-промышленных испытаний при закачке раствора полисахарида в 5 нагнетательных скважин месторождения Кумколь в течение 19 месяцев добыто дополнительно 14 584 тонн нефти. В проведении опытно-промышленного испытания принимали участие АО «Тургай-Петролеум», АО «Лукойл», АО «НИПИнефтегаз», АО «Институт нефтепромысловой химии», ЧУ «Институт полимерных материалов и технологий» и ТОО «Юго-Восточная Сервисная Группа» (ЮВСГ).

В рамках проекта Европейского Союза «Horison 2020» ЧУ «Институт полимерных материалов и технологий» выполнил совместный проект с Университетом Крит (координатор), Университетом Хельсинки, Национальным центром научных исследований Франции, Институтом макромолекулярной химии АН Чехии, ТОО “BioNavis” (Финляндия), ООО «Делси» (Россия), лабораторией наноматериалов и полимеров (Испания), Университетом Рединга (Англия), Институтом высокомолекулярных соединений РАН (Россия), Федеральным университетом АВС (Бразилия) в области создания мягких биосовместимых полимерных наноструктур для нового поколения нанотехнологий в фармацевтике и офтальмологии. Основной целью инновационного проекта являлась разработка биоразлагаемых и биосовместимых гелеобразующих полимеров, наногелей и наночастиц, предназначенных для ис-

пользования в качестве многофункциональных терапевтических агентов в офтальмологии. Поиск биосовместимых и биоразлагаемых синтетических/природных полимеров. Изучение макромолекул со сложной архитектурой, включая блочные, привитые и звездообразные полимеры в отношении их способности создавать взаимопроникающие сетки с хорошо контролируемыми реологическими и структурными свойствами. Исследовательский план включает также разработку, синтез и характеристику новых макромолекулярных архитектур, продиктованных теоретическими результатами и результатами моделирования свойств материалов, за которыми следует токсичность и испытания материалов/конструкций in vitro/in vivo и промышленные технико-экономические обоснования. Макромолекулярные системы позволят осуществить пролонгированное удержание лекарственного средства в глазу и его контролируемое высвобождение под воздействием таких внешних стимулов, как температура, свет, pH. Синергия, возникающая в результате сотрудничества между мировыми ведущими в своих областях академическими группами и компаниями, позволит обеспечить европейское лидерство в передовых технологиях.

В 2020-2024 гг. в рамках проекта Европейского Союза «Horison 2020» в Хельсинкском университете двух- и трёхмесячные научные стажировки проходили сотрудники ЧУ «Институт полимерных материалов и технологий» Г. Толеутай, М. Даулетбекова, Г.С. Татыханова, А.Е. Аязбаева, Р.Н. Тулеева, Н.Н. Гизатуллина.



HORIZON 2020

Soft Biocompatible Polymeric Nanostructures: A Toolbox for Novel Generation of Nano Pharmaceuticals in Ophthalmology

START PAGE COUNT – MAX 30 PAGES

List of Participants

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			1b. University Hospital – Dept. of Ophthalmology	Miltiadis Tsilimbaris link
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4. CNRS	France	Centre National de la Recherche Scientifique	Institut Pluridisciplinaire de Recherche sur l'Environnement et les Matériaux	Oleg Borisov link
5. IMC CAS	Czech Republic	Ustav Makromolecularni Chemie AV CRVVI	Department of Supramolecular Polymer Systems	Sergej Filippov link
6. BioNavis	Finland	BioNavis Ltd	Non-applicable	Johana Kuncova-Kallio link
7. NanoMyP	Spain	NanoMateriales y Polimeros S.L.	Non-applicable	Antonio L. Medina-Castillo link
TC Partner Organizations	**Country**	**Legal Entity Name**	**Department / Division / Laboratory**	**Scientist-in-Charge**
8. UFABC	Brazil	Fundaçã Universidade Federal Do ABC	Centro de Ciências Naturais e Humanas	Fernando Carlos Giacomelli link
9. IMC RAS	Russian Federation	Institution of Russian Academy of Sciences Institute of Macromolecular Compounds RAS	Laboratory of Anisotropic Polymeric Systems	Andrey Tenkovtsev link
10. IPMT	Republic of Kazakhstan	Institute of Polymer Materials and Technology	Non-applicable	Sarkyt Kudaibergenov link
11. Delsi	Russian Federation	Delsi Ltd.	Non-applicable	Alexander Vilesov link

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Участники Европейского проекта «НАНОПОЛ» в рамках Программы «Горизонт 2020» в Хельсинкском Университете (Финляндия), 2023 г.

Кудайбергенов С.Е. принимал участие в Международных симпозиумах и конференциях с пленарными, устными и стендовыми докладами в Бельгии (1997,1999, 2010), Германии (1987, 1995, 1997), Греции (2017), Египте (1997), Испании (2004), КНР (1987, 2002, 2011, 2018, 2025), Нидерландах (1997), Польше (2001), США (2002, 2013), Сингапуре (2016, 2018), Турции (1994, 1996, 1997, 2008, 2013), Финляндии (1985, 1996, 2011, 2023, 2024), Швейцарии (2000, 2012), Швеции (2002), Южной Корее (1998, 2001, 2002-2003), Японии (1998, 1999, 2017).



Участники Казахско-Узбекского Международного симпозиума «Современные проблемы науки о полимерах». Алматы, 12-13 октября 2023 г.



Участники Международного Симпозиума по макромолекулярным комплексам (ММС-18), Москва, 10-13 июня 2019 г.



Участники Международного Симпозиума по макромолекулярным комплексам (ММС-17), Токио, 28-31 августа 2017 г.



Участники Международного Симпозиума по макромолекулярным комплексам (ММС-14), Хельсинки, 14-17 августа, 2011 г.



Участники восьмого Международного Симпозиума «Полимеры специального назначения», Санаторий «Тастыбулак», Карагандинская область, 23-25 августа 2019 г.





Седьмой Международный семинар по полимерам специального назначения в Satbayev University, Алматы, 7-9 сентября 2017 г.



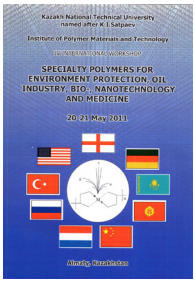
Шестой Международный семинар по полимерам специального назначения в Семипалатинском госуниверситете имени Шакарима, Семей, 17-19 сентября 2015 г.





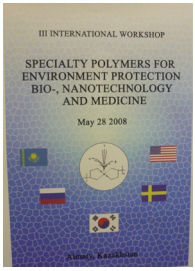
Пятый Международный семинар «Новые материалы и технологии для промышленности, охраны окружающей среды и здоровья человека», Иссык-Куль, 16-20 сентября 2013 г.



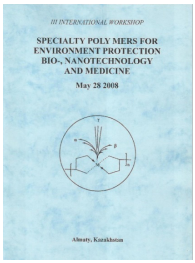


Четвертый Международный семинар «Полимеры специального назначения для охраны окружающей среды, в нефтяной индустрии, био-, нанотехнологии и медицины». КазНТУ имени К.И. Сатпаева, Алматы, 20-21 мая 2011 г.





Третий Международный семинар «Полимеры специального назначения для охраны окружающей среды, био-, нанотехнологии и медицины». Алматы, 28 мая 2008 г.





Второй Международный семинар «Полимеры специального назначения для охраны окружающей среды, био-, нанотехнологии и медицины». Семей, 24-27 сентября 2006 г.





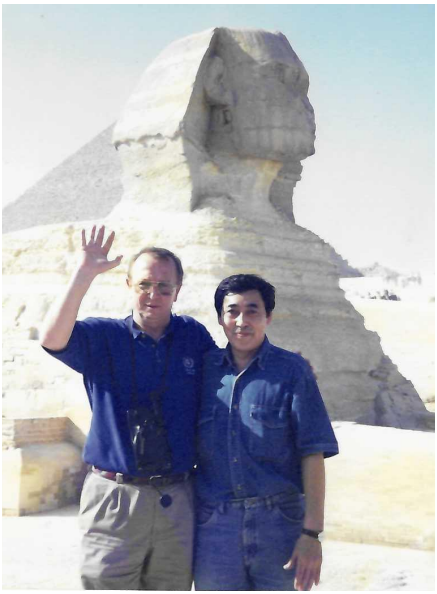
Первый Международный семинар ИНТАС, посвященный Семипалатинскому испытательному полигону. Семей, 21-24 сентября 2002 г.



С профессором Индиана-Пурду университета Полом Дубиным (Paul Dubin), 1995 г.



С профессором Тюбингенского университета Куртом Гекелерем (Kurt Geckeler) и студентами Института науки и технологии Кванжу, Южная Корея, 2002 г.



С профессором Лодзинского технического университета Януш Розиак (Janusz Rosiak) во время очередного заседания МАГАТЭ в Египте, 1998 г.



Участники четвертого Международного полимерного симпозиума тюркоязычных стран в Ближневосточном техническом университете (METU/ ODTÜ), Турция, 1996 г.
Слева направо: проф. Е.А. Бектуров, проф. Нурсели, проф. С. Кудайбергенов, проф. Гюнери Аковали, проф. Сезай Сарач



Участники проекта INTAS в г. Семей, 2002 г.
Слева направо: доцент В. Асеев (Финляндия), проф. Габриэлла Читану (Румыния), проф. Х. Тенху (Финляндия), проф. С. Кудайбергенов (Казахстан), проф. В. Изумрудов (Россия), проф. Ксения Когей (Словения)



Памятник Альберту Эйнштейну в Вашингтоне, расположенный на территории Национальной академии наук США, 1995 г.



Перед зданием Национального научного фонда США, 1995 г.



С ученым-ядерщиком Абдул Кадыр Ханом – «отцом ядерной бомбы» Пакистана – в здании НАН РК, 2005 г.



С узбекскими коллегами на Кок-Тобе



С дочерью Ажар и сыном Амир



С семьей

ПЕРЕЧЕНЬ ВЫПОЛНЕННЫХ ПРОЕКТОВ В ЧУ «ИНСТИТУТ ПОЛИМЕРНЫХ МАТЕРИАЛОВ И ТЕХНОЛОГИЙ»

1) Synthesis and characterization of polyampholyte gels. (INTAS-Kazakhstan 95-0031, 1995-1997)

2) Design of interpolymer membranes for pervaporation processes. (INTAS Open 97-1746, 1999-2001)

3) New generation of smart polymers and polymeric materials for biotechnology. (INTAS Open 00/57, 2000-2001)

4) New polymer systems for bioseparation (INTAS Open 00/113, 2000-2001)

5) Development of rehabilitation methodology of environment of the Semipalatinsk region polluted by nuclear tests (INTAS Monitoring Conference 02-MO-231, 2002)

6) New generation of smart polymers and polymeric materials for biotechnology and environment protection (INTAS Workshop, 2003)

7) Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов (МОН РК и Всемирный Банк, 2011-2013)

8) Разработка методов синтеза полимер-протектированных наночастиц золота и использование их в качестве нанокатализаторов для переработки углеводородного сырья (Национальный научно-технический холдинг «Парасат», 2012-2014)

9) Разработка композиционных гидрогелевых скребков для очистки внутренней полости нефтепроводов (МОН РК, Всемирный Банк, 2014-2016)

10) Фундаментальные и прикладные аспекты макропористых амфотерных криогелей (МОН РК, 2012-2014)

11) Sustainable management of toxic pollutants in Central Asia: Towards a regional ecosystem model for environmental security (NATO-SfP Project 983981, 2012-2014)

12) Development of composite hydrogel “pigs” for cleaning of internal surface of pipelines. (Совместный проект с Синьцзянским университетом КНР, 2015-2016)

13) Обоснование технологии бурения с автоматическим закреплением стенок скважины в сложных горно-геологических условиях (МОН РК, 2015-2017)

14) Разработка технологии получения гидрофобно-модифицированных полимерных присадок для ингибирования парафиноотложения и снижения температуры потери текучести нефти (МОН РК, 2015-2017)

15) Разработка нанокатализаторов и проточного каталитического реактора для переработки углеводородного сырья (МОН РК, 2015-2017)

16) Fabrication and controlled drug release of thermosensitive gradient nanocomposite hydrogels (Совместный проект с Сычуаньским университетом КНР, 2018-2019)

17) Фундаментальные вопросы сильнозаряженных полиамфолитов в изоэлектрической точке (МОН РК, 2018-2020)

18) Изучение процессов производства ванадиевого электролита для проточных редокс аккумуляторов из отечественного сырья (МОН РК, 2018-2020)

19) Синтез и исследование термо- и соле-чувствительных полиамфолитных нано- и микрогелей (МОН РК, 2020-2022)

20) Получение наночастиц золота для лечения раковых клеток методом плазмонной фототермической терапии (МОН РК, 2020-2021)

21) Разработка новых термо- и солестойких амфотерных терполимеров для увеличения нефтедобычи (МОН РК, 2021-2023)

22) Окисление алифатических спиртов каталазой и наночастицами металлов иммобилизованными в матрицу макропористых криогелей (МНиО, 2022-2024гг)

23) Разработка новых лекарственных форм с улучшенными мукоадгезивными свойствами для внутрипузырной химиотерапии (МНиО, 2022-2024гг)

24) Разработка предварительно сформированных гидрогелевых частиц (PPG) для увеличения добычи нефти (МНиО, 2022-2024 гг)

25) Soft biocompatible polymeric NANO structures: A toolbox for novel generation of Nanopharmaceuticals in Ophthalmology “Nanopol” (Horion-2020, 2020-2024)

26) Разработка инновационных технологий добычи нефти для повышения нефтеотдачи, снижения эксплуатационных расходов и углеродного следа (МНиВО, 2024-2026 гг)

27) Опытно-пилотное испытание технологии забойной сегрегации флюидов (ЗСФ) для минимизации добычи избыточной воды и интенсификации притока нефти (Частный фонд «Центр Научно-Технологических Инициатив «Самгау», 2025)

ПОДГОТОВКА КАДРОВ

ДОКТОРСКИЕ, КАНДИДАТСКИЕ, PhD И МАГИСТЕРСКИЕ ДИССЕРТАЦИИ, ПОДГОТОВЛЕННЫЕ ПОД РУКОВОДСТВОМ С.Е. КУДАЙБЕРГЕНОВА

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ОРГАНИЗАЦИОННАЯ ДЕЯТЕЛЬНОСТЬ

В 1999 году Кудайбергенов С.Е. организовал и возглавил частное учреждение «Институт полимерных материалов и технологий» (ЧУ ИПМТ). В стенах Института были подготовлены и защищены 1 докторская, 10 кандидатских и 6 PhD диссертаций, посвященных актуальным проблемам полимерной науки.

Для привлечения внимания правительства, национальных и международных фондов, научного сообщества и местной администрации к экологическим проблемам Семипалатинского испытательного полигона, 21-24 сентября 2002 г. на базе Семипалатинского государственного университета имени Шакарима при финансовой поддержке ИНТАС организована первая Международная конференция «Development of Rehabilitation Methodology of Environment of the Semipalatinsk Region Polluted by Nuclear Tests». В ней приняли участие ведущие ученые и специалисты из США, Южной Кореи, Финляндии, Румынии, Словении, России, Узбекистана и Казахстана.

В 2002 г. Кудайбергенов С.Е. организовал Международный семинар по созданию Программы региональных экспериментальных центров поддержки (Regional Experimental Support Centers Program) для разработки мембранных и гидрогелевых материалов и технологий с участием ЧУ «Институт полимерных материалов и технологий», ТОО «Мембранные технологии», ТОО «Институт нефти и воды», СГУ имени Шакарима, Казахстанско-американского университета.

В 2002 г. в Алмате Кудайбергенов С.Е. активно участвовал в организации Международного полимерного симпозиума тюркоязычных стран, в котором принимали участие ученые и специалисты из Турции, Узбекистана, Кыргызстана, Таджикистана и Казахстана.

С 28 сентября по 4 октября 2003 г. в санатории «Капал-Арасан» был проведен первый Международный семинар ИНТАС по использованию полимерных материалов для охраны окружающей среды, включая проблемы Семипалатинского испытательного полигона и Аральского региона. В нем приняли участие

специалисты из Англии, Швеции, Израиля, России, Узбекистана и Казахстана. Впоследствии проведение таких семинаров стали регулярными. В 2002-2019 гг. он организовал 8 Международных семинаров, конференций и симпозиумов, посвященных полимерам специального назначения для охраны окружающей среды, в нефтяной отрасли, биотехнологии, нанотехнологии и медицине, в СемГУ имени Шакарима, (2002, 2005, 2015), Институте химических наук имени А.Б. Бектурова НАН РК (2008), КазНИТУ имени К.И. Сатпаева (2011, 2017), Кыргызско-Российском Славянском университете (2013), Карагандинском государственном университете имени Е.А. Букетова (2019).

В 2005 г. инициировал создание НИИ химико-экологических проблем (НИИХЭП) при Семипалатинском государственном университете имени Шакарима для решения проблем экологии Семипалатинского испытательного полигона, связанных с ремедиацией радиационно-загрязненных поверхностных слоев почвы и водных источников.

В 2019-2022 гг. совместно с Институтом химии и физики полимеров АН Узбекистана организовал 3 Узбекско-Казахских Симпозиума по современным проблемам науки о полимерах в Ташкенте и Караганде.

Кудайбергенов С.Е. постоянно принимает участие в организации Международного симпозиума «MacroMolecular Complexes (MMC)» в качестве члена Международного Оргкомитета IUPAC (Международный союз теоретической и прикладной химии).

ПУБЛИКАЦИИ О НАУЧНОЙ ДЕЯТЕЛЬНОСТИ С.Е. КУДАЙБЕРГЕНОВА

Sarkyt Kudaibergenov's 60th Birthday

The valuable contributions of Professor Sarkyt Kudaibergenov to polymer science may conveniently be divided into two periods: before and after the collapse of the Soviet regime. The watershed was 1991 - "*... a time to gather stones together*" - because at this time he had already been awarded the Kazakh SSR State Prize in the field of science and technology (1987) for the cycle of monographs "Water soluble polymers and their complexes" and successfully defended a Doctoral Thesis at M.V. Lomonosov Moscow State University (1991). Sometimes the fate of an individual scientist can more or less reflect the development of science history, especially in transition periods. In 1991, most of the Central Asian Republics, including Kazakhstan, became independent; however, very hard times came to science and especially scientists. An internal and external "brain drain" started as a result of trifling financial support, low salaries and a lack of information and communication.

Philanthropists and the worldwide scientific community reacted immediately to preserve the intellectual potential of the former Soviet Union countries. Financial aid, such as individual and long term grants from the Soros Fund in 1994, or gifted journals and books from the American Chemical Society in 1995–2000 were some of the first examples of support to advanced Kazakh researchers like Sarkyt Kudaibergenov. During the period 1995–2004, he received six INTAS grants from the EU (INTAS is the International Association for the promotion of cooperation with scientists from the New Independent States (NIS) of the former Soviet Union) and due to the INTAS financial support, he had the chance to organize (in 1999) the non-governmental Research Institute of Polymer Materials and Technology (IPMT) which since then has found its niche among the governmental research institutes of Kazakhstan.

At the IPMT, he and his co-workers succeeded in publishing more than fifty papers in English in peer-reviewed journals. A total of three Doctors (D.Sc.) and seven Candidates of Sciences (Ph.D.) awards have been achieved within the walls of the IPMT over ten years. At present, most of them have continued their careers as university academics, institute researchers and managers of national companies, while some of them now work in the USA (at the University of Pittsburgh, Pennsylvania) and in South Korea (Korea University, Seoul). Such success was the result of timely change and the adaptation of Sarkyt Kudaibergenov's mentality to market economy and science management, in particular after successful completion of a 3 month program management course at the National Science Foundation in the USA in 1995. In fact, the IPMT is a small research organization; it occupies about 100 m^2 of space, is well equipped and has no permanent staff. As the story goes, "*little bodies may have great souls*" (Мал золотник, да дорог), and it is mostly M.Sc. and Ph.D. students from the various universities of Kazakhstan who perform their research in the warm and creative atmosphere of the IPMT (Figure 1).

Professor Kudaibergenov's first steps into the scientific environment started after obtaining a B.Sc. degree in physical chemistry from Kazakh State University in 1973, and defending his Candidate Thesis (Ph.D.) in polymer chemistry at the Institute of Chemical Sciences, Kazakh Academy of Sciences, in 1980. He received his D.Sc. degree in polymer chemistry from Moscow State University in 1991. From 1980 to



Figure 1. Prof. Kudaibergenov and his Masters students.

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1993, he worked at the Institute of Chemical Sciences, Kazakh Academy of Sciences, as a junior, senior and then leading researcher. From 1994 to 1996 he was deputy scientific secretary and subsequently head of the International Department of Presidium of Kazakh Academy of Sciences. In 1996–1998, as the professor holding the Chair of Macromolecular Compounds of Kazakh National University, he mentored the research projects of M.Sc. and Ph.D. students whose projects were focused on interpolymer reactions, interpolymer complexes and stimuli responsive gels. In 1998, he visited Waseda University, Japan, and in 2002–2003 the Kwangju Institute of Science and Technology, South Korea, as a visiting professor. In 2001–2004, as vice-director and head of laboratory of the "KazTransOil" company Research and Development Center and Kazakh Institute of Oil and Gas, he was engaged in solving the problems of polymer flooding for enhanced oil recovery and polymeric additives for the transportation of crude oils. Since 2008, he has worked as the head of the Laboratory of Engineering Profile at K.I. Satpaev Kazakh National Technical University.

He is the author and co-author of a dozen scientific monographs in Russian, Polish and English, and he has published more than three hundred papers (among them more than one hundred in English). Individually and in collaboration with colleagues from Germany and Italy, he has published several remarkable review articles in the journals Advances in Polymer Science and Macromolecular Rapid Communications, which are devoted to fundamental and applied aspects of linear and crosslinked polyampholytes, as well as their complexes, with various low and high molecular weight compounds. The quintessence of his thirty years of achievements in the field of synthetic and natural polyampholytes is the fundamental monograph "Polyampholytes: Synthesis, Characterization and Application", published by Kluwer Academic/Plenum Publishers in 2002 and the review article "Polyampholytes", published in the Encyclopedia of Polymer Science and Technology in 2008.

During the last five to ten years, his research interests have also covered polymeric complexes and betaines, organic-inorganic composite materials, stimuli responsive hydrogels for drug delivery, protein and enzyme immobilization, polymer protected and hydrogel immobilized metal nanoparticles as catalysts and macroporous amphoteric gels.

Born on May 20, 1951, not far from the Semipalatinsk Nuclear Test Site (SNTS), he always had a patriotic feeling and citizen's responsibility to fight against this nuclear heritage, and in particular, he has paid much attention and made a considerable research contribution to preventing soil migration and the capture of radionuclides from the radioactively contaminated topsoil of SNTS using interpolymer complexes. As a full professor at Semipalatinsk Shakarim State University in 2002, he initiated the organization of the Center for Chemical Ecological Problems in Semipalatinsk. This was followed by several international workshops devoted to "Specialty polymers for environment protection, bio-, nanotechnology and medicine" that were held at the Center.

In 2010, the Thomson Reuters and National Center of Scientific-Technical Information, Kazakhstan, awarded him the "Parasat" Award for international excellence in scientific research and outstanding contributions to global scientific research, recognizing him as the most published and cited Kazakh author abroad. According to the Scopus database, his citation index between 1996–2010 reached up to 462.

His scientific life is tightly connected with his former patron, Professor Esen Bekturov, a distinguished polymer scientist whose eighty year jubilee will be celebrated in December 2011. It is remarkable that the teacher and the pupil have maintained such a fruitful relationship over thirty years for the benefit of their beloved polymer science. His deep respect for both elder and younger scientists is a vital credo of Sarkyt Kudaibergenov. His hospitality and kindness have no limits. Also, at the age of sixty, he continues to work very hard on actively generating new research ideas and inspiring young colleagues. Let us wish him all the best and much success in the future.

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СПЕЦВЫПУСК ЖУРНАЛА «POLYMERS FOR ADVANCED TECHNOLOGIES», ПОСВЯЩЕННЫЙ 70-ЛЕТНЕМУ ЮБИЛЕЮ С.Е. КУДАЙБЕРГЕНОВА



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SPECIAL ISSUE: RESEARCH ARTICLE

polymers advanced technologies WILEY

Happy 70th birthday, Professor Sarkyt E. Kudaibergenov

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In May 2021, the polymer science community of Kazakhstan, numerous former students and collaborators will celebrate the 70th anniversary of Prof Sarkyt E. Kudaibergenov. Prof S. E. Kudaibergenov is a prominent Kazakh polymer scientist, known for his research into water-soluble polymers, polyelectrolytes, polymer complexes, hydrogels, polymer-stabilised colloids, catalysis by polymers and stimuli-responsive materials for various applications. This essay aims to present some highlights of research career of Prof Kudaibergenov with a particular emphasis on his most significant original contributions to polymer science.

Prof Sarkyt E. Kudaibergenov was born on 20 May 1951 in Semipalatinsk region of Kazakh Soviet Socialist Republic, which at that time was a part of Soviet Union. He studied chemistry at Kazakh State University in Almaty from 1968 to 1973; then in 1973 to 1976, he worked as an engineer in the Laboratory of Physicochemical Methods in the Faculty of Chemistry at Kazakh National University. One of his research projects was related to the studies of low-temperature zone of the front of hydrocarbon flames, which resulted in his first publication.[1] In 1980, he joined the Laboratory of Physical Chemistry of Polymers led by Prof E. A. Bekturov at the Institute of Chemical Sciences as a Junior Researcher, and this move led him to a lifelong passion in polymer science. His involvement in the studies of hydrodynamic properties of polyelectrolytes based on vinylethynylpiperidoles-4 resulted in several important publications[2,3] and successful defence of a thesis with the award of a candidate of chemical sciences degree (equivalent to PhD) in 1981. Following his PhD defence, he began expanding the areas of research interests and made contributions to the studies of interactions between poly(ethylene glycols) and alkali metals and ammonium thiocyanates,[4] catalytic properties of complexes of poly(2-vinyl pyridine) and palladium,[5] amphoteric properties of polyelectrolyte complexes[6] and other studies of metal-polymer complexes.[7]

In 1985, he got promoted to a position of Senior Researcher and in 1989 to a position of Leading Researcher. In 1991, he defended a habilitation dissertation on the studies of the complex formation reactions involving synthetic polyampholytes at Moscow State University (Russia) and was awarded a degree of Doctor of Chemical Sciences. In 1994, he received a title of Professor of Chemistry. Two particular highlights of his research in these years are the discovery of the "isoelectric effect" at the isoelectric point of polyampholytes[8] and formation of polyelectrolyte complexes at the dimeric interface between two immiscible liquids.[9]

In the early 90s, he established collaboration with researchers of Kazakh State National University, and in 1996, he was appointed as a Professor and Head of research group in the Department of Macromolecular Chemistry of this University. In these years, he turned his research interests to hydrogen-bonded interpolymer complexes,[10] interpolyelectrolyte complexes,[11] interactions of polyampholytes with disperse particles,[12] stimuli-responsive hydrogels[13,14] and functional membranes.[15] In 1998, he was a visiting professor of Waseda University (Japan) in the group of Prof E. Tsuchida, where he researched ion conductivity of gels based on poly(divinyl ether of diethyleneglycol) in mixtures with lithium perchlorate.[16]

In 1999, he has established and became the Director of the Institute of Polymer Materials and Technologies (IPMT) as a private

research organisation in Almaty (Kazakhstan), which he continues to lead until present. The main research activities of this Institute are focused on the fundamental studies in the field of chemistry and physics of polymers, application of polyfunctional polymers of synthetic and natural origin in oil industry as well as nanomaterials and nanotechnologies. Some of the highlights of Prof Kudaibergenov's research in IPMT include the studies of DNA containing polyelectrolyte complexes,[17] films prepared at the interfaces of immiscible liquids,[18] theoretical studies of salt bonds in polyampholyte chains,[19] and hydrophobically modified polybetaines as pour point depressants.[20] In 2002 to 2003, Prof Kudaibergenov was a visiting professor of Kwangju Institute of Science and Technology (South Korea), where he researched into the development of synthetic strategies and studies the properties of novel polycarbobetaines.[21]

Throughout his entire research career, Prof Kudaibergenov was always open for new opportunities and collaborative links with numerous researchers worldwide. He has made numerous research contributions to various fields of polymer chemistry, materials science and nanotechnology. Some examples of these collaborative projects include the studies of Langmuir-Blodgett films,[22] carbon nanotubes[23] and iron oxide photo-catalyst.[24]

As Prof Kudaibergenov was born in the region that is not far from the Semipalatinsk Nuclear Test Site, he was always feeling an obligation and desire to help with remediation of this radionuclide-contaminated soil. He became an honorary professor of Semipalatinsk Shakarim State University in 2002, initiated the organisation of the Centre for Chemical Ecological Problems in this University and supervised research activities into the use of polymers and their complexes as soil structuring agents to prevent migration of radionuclides and to facilitate their extraction from contaminated soil.[25,26]

In the most recent decade, Prof Kudaibergenov continued active research and turned his attention to a number of new interesting projects, including polymer-protected and hydrogel-immobilised gold nanoparticles[27] and their catalytic applications,[28] macroporous cryogels,[29] hydrophobically modified polymers and hydrogels,[30] application of water-soluble polysaccharides in oil extraction[31] and drug delivery.[32,33]

The breadth of his research interests, desire to explore new avenues of polymer and material science, openness for new collaborations and exceptional hardworking ability continuously lead to new ideas, developments and plans. Despite many successful developments and contributions of Prof S. E. Kudaibergenov in different areas of physical chemistry of polymers, his most favourite topic is the study of amphoteric polymers (polyampholytes). He has been studying polyampholytes since 1979 and published a number of reviews and a fundamental single-author monograph "Polyampholytes: Synthesis, Characterization and Application" (Springer, 2002).

He has co-authored 18 monographs and textbooks published in Russian, Polish and English, over 400 research articles and reviews, with more than 100 of which are in international peer-reviewed journals. His research was recognised through many awards, including the State Prize of the KazSSR in the field of Science and Technology (1986), "Parasat" award as the most published and cited abroad Kazakhstani author (2010), a breastplate "For merits in the development of science of the Republic of Kazakhstan" from the Ministry of Science and Education of the Republic of Kazakhstan (2012) and K.I. Satpayev Prize for the development of specialty polymers for application in petrochemistry and nanotechnology (2019).

He has also organised many international research meetings and workshops, including traditional International Workshop "Specialty polymers for environment protection, oil industry, bio-, nanotechnology and medicine," held in Semey (2006), Almaty (2008), Almaty (2011), Issyk-Kul, Kyrgyzstan (2013), Semey (2015), Almaty (2017) and Karaganda (2019). Numerous former students of Prof S. E. Kudaibergenov currently work as academics and researchers in many universities, research and industrial organisations of Kazakhstan and some other countries.

On behalf of all collaborators, international colleagues, numerous current and former students I congratulate Prof Sarkyt Kudaibergenov with his 70th Anniversary and wish him all the best in his further research activities and personal life.

This special issue of Polymers for Advanced Technologies aims to celebrate Prof Kudaibergenov's anniversary and contains contributions from many of his current and former students, international colleagues and collaborators.

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Открывая новые страницы физической химии гидрофильных полимеров: к 70-летию профессора Саркыта Елекеновича Кудайбергенова

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Данная статья посвящена 70-летнему юбилею выдающегося казахстанского химика – профессора Кудайбергенова Саркыта Елекеновича. Профессор Кудайбергенов С.Е. внес существенный вклад в исследования синтетических и природных полиэлектролитов, их комплексов с различными веществами, полимерных гидрогелей, стимул-чувствительных материалов, наночастиц и нанокомпозитов, а также в работы по использованию различных полимерных материалов и коллоидных систем в качестве катализаторов, реагентов специального назначения и систем доставки лекарств. В статье приведены основные сведения биографического характера, показывающие становление Кудайбергенова С.Е. как ученого, а также рассматриваются его основные научные достижения в области физической химии гидрофильных полимеров и коллоидных систем. Осуществлен обзор наиболее известных работ профессора Кудайбергенова С.Е., опубликованных в журналах, индексируемых Web of Knowledge. Кроме того, приведены сведения о работе профессора Кудайбергенова С.Е. над проектами, финансируемыми различными организациями, членстве в редакционных коллегиях журналов, организации Института Полимерных Материалов и Технологий, участии в работе в диссертационных советах, а также подготовке многочисленных учеников.

Ключевые слова: Кудайбергенов С.Е.; полиэлектролиты; полиамфолиты; полимерные комплексы; наночастицы; гидрогели.

Exploring new avenues in physical chemistry of hydrophilic polymers: to the 70th anniversary of Professor Sarkyt Elekenovich Kudaibergenov

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This paper is dedicated to 70th anniversary of the prominent Kazakh chemist – professor Sarkyt Elekenovich Kudaibergenov. The information of biographical nature, showing the development of S.E. Kudaibergenov as a scientist, as well as his main research contributions to the field of physical chemistry of hydrophilic polymers and colloidal systems are presented in this paper. This is written in the form of a review of the most important and prominent publications of Prof S.E. Kudaibergenov, published in the journals indexed by Web of Knowledge. Professor S.E. Kudaibergenov has made a substantial contribution to the studies of synthetic and natural polyelectrolytes, their complexes with different compounds, polymeric hydrogels, stimuli-responsive materials, nanoparticles and nanocomposites, as well as applications of different polymeric materials and colloidal systems as catalysts, specialty chemicals, and drug delivery systems. This paper also includes information about the research conducted by Professor S.E. Kudaibergenov on various projects, funded by different organisations, his membership in different journals' editorial boards, his role in the establishment of the Institute of Polymer Materials and Technologies, his participation in research councils and committees, as well as supervision of numerous students and researchers. The paper includes some photographs of Professor S.E. Kudaibergenov with several international collaborators.

Keywords: Kudaibergenov S.E.; polyelectrolytes; polyampholytes; polymeric complexes; nanoparticles; hydrogels.

Гидрофильді полимерлер физикалық химиясының жаңа көкжиегіне көз жүгірту: Сарқыт Елекенұлы Құдайбергеновтың 70 жылдық мерейтойы қарсаңында

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Бұл мақала аса көрнекті химик – профессор Сарқыт Елекенұлы Құдайбергеновтың 70 жылдық мерейтойына арналған. Мақалада С.Е. Құдайбергеновтың өмірбаяны туралы ақпаратпен қоса, оның гидрофильді полимерлер мен коллоидты жүйелердің физикалық химиясы саласындағы негізгі ғылыми жетістіктері баяндалады. Талдауға профессор С.Е. Құдайбергеновтың Web of Knowledge басылымдарында жарық көрген аса көрнекті мақалалары негізделе болған. Жасанды және табиғи полиэлектролиттер, олардың әр түрлі заттармен комплекстері, полимерлік гидрогельдер, стимул-сезімтал материалдар, наноөлшектер, нанокомпозиттер, сонымен қатар әр түрлі полимерлік материалдармен қоса коллоидты жүйелердің катализаторлар, дәрі-дәрмекті тасымалдайтын және жер асты мұнайын ығыстырып шығаратын арнайы реагенттер ретінде қолданылатын зерттеулерге қосқан үлесі тілге тиек етілген. Мақалада профессор С.Е. Құдайбергеновтың көптеген жобалары, журналдар алқасының мүшелігі, өзі ұйымдастырған Полимер материалдары және технологиялары институтының жетістіктері, диссертациялық кеңестердегі еңбегі, дайындаған оқушылары туралы ақпарат берілген. Келтірілген фотолар С.Е. Құдайбергеновтың көптеген шет елдік ғалымдармен байланысының куәсі ретінде қарастырылған.

Түйін сөздер: Құдайбергенов С.Е.; полиэлектролитттер; полиамфолиттер; полимерлік комплекстер; наноөлшектер; гидрогельдер.

CHEMICAL BULLETIN
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Открывая новые страницы физической химии гидрофильных полимеров: к 70-летию профессора Саркыта Елекеновича Кудайбергенова

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Мы никогда не прекратим научный поиск,
Но в конце любого исследования обнаруживаем,
Что вернулись к точке старта,
И познаем это место заново.

"Четыре квартета"
Т.С. Элиот, выпускник Гарварда,
Лауреат Нобелевской премии

20 мая 2021 года многочисленные ученики и коллеги будут праздновать 70-летний юбилей выдающегося казахстанского химика – профессора Кудайбергенова Саркыта Елекеновича (рисунок 1).

Кудайбергенов С.Е. – признанный в мире специалист в области физической химии полимеров, доктор химических наук (1991), профессор (1994), лауреат Государственной премии КазССР в области науки и техники (1987 г.), лауреат премии «Парасат», как наиболее публикуемый и цитируемый казахстанский автор за рубежом (2010 г.). Награжден нагрудным знаком МОН РК «За заслуги в развитии науки Республики Казахстан» (2012 г.), юбилейной медалью «85 лет КазНИТУ им. К.И. Сатпаева» (2019 г.), лауреат премии имени К.И. Сатпаева «За лучшее научное исследование в области естественных наук» (2019 г.), обладатель Государственной научной стипендии для учёных и специалистов, внёсших выдающийся вклад в развитие науки и техники (2020 г.).



Рисунок 1 – Проф. С.Е. Кудайбергенов

Кудайбергенов С.Е. окончил химический факультет Казахского Государственного университета им. С.М. Кирова в 1973 году по специальности «Физическая химия». В том же году он поступил на работу инженером в лабораторию физико-химических методов исследования, а с 1976 по 1980 работал стажером-исследователем КазГУ. В эти годы он занимался исследованием низкотемпературных зон горения углеводородов, что привело к его первой серьезной публикации [1]. В 1980 он переходит на работу в Институт химических наук АН РК в лабораторию физической химии полимеров, где под руководством академика Бектурова Е.А. (рисунок 2) занимается исследованиями гидродинамических и конформационных свойств полиэлектролитов [2,3].

В 1980 Кудайбергеновым С.Е. была защищена диссертация на тему «Гидродинамические свойства полиэлектролитов на основе винилэтинилпиперидолов-4» на соискание ученой степени кандидата химических наук. После защиты диссертации, ученый расширяет круг своих научных интересов и занимается исследованиями взаимодействий полиэтиленгликолей с ионами щелочных металлов и тиоцианатами аммония [4], каталитическими свойствами комплексов поливинилпиридинов с палладием [5], амфотерными свойствами интерполи-электролитных комплексов [6], а также исследованиями полимер-металлических комплексов [7]. В Институте химических наук Кудайбергенов С.Е. проработал с 1980 по 1993 годы в качестве младшего, старшего и ведущего научного сотрудника. В 1991 году им была защищена докторская диссертация на тему «Реакции комплексо-



Рисунок 2 – С академиком НАН РК Е.А. Бектуровым

образования с участием синтетических полиамфолитов» в МГУ имени М.В. Ломоносова, а в 1994 он получил ученое звание профессора. Часть результатов его докторской диссертации были опубликованы в виде обзора в журнале «Успехи химии» [8], в котором отражено впервые обнаруженное им явление «изоэлектрического эффекта» выталкивания в области изоэлектрической точки полиамфолитов (рисунок 3).

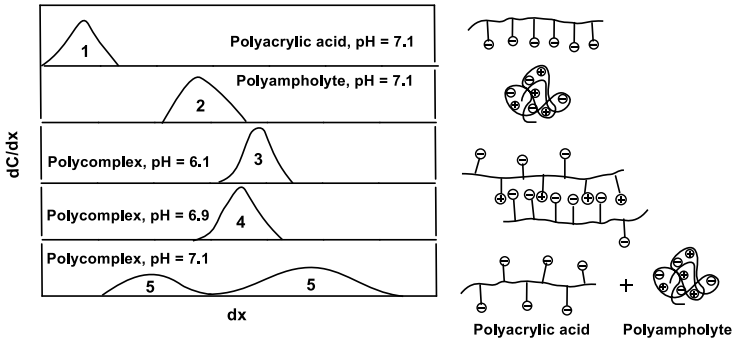


Рисунок 3 – Седиментограммы полиакриловой кислоты (1), полиамфолита (2) и комплексов полиамфолит-полиэлектролит (3, 4) при различных значениях pH среды и проявление «изоэлектрического эффекта» для поликомплекса полиамфолит-полиэлектролит (5) в изоэлектрической точке полиамфолита при pH 7.1. Перепечатано из Russ. Chem. Rev. 1991, 60 (4), 410–419 [8].

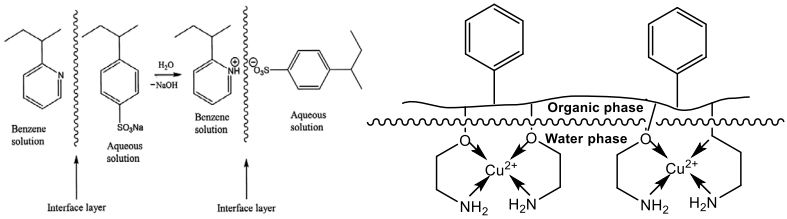


Рисунок 4 – Формирование бислойных интерполиэлектролитных (а) и полимерметаллических комплексов (б) на границе раздела фаз двух несмешивающихся жидкостей. Рисунок (а) перепечатан из [9] с разрешения John Wiley and Sons.

В эти годы Кудайбергеновым С.Е. также было впервые показано образование полиэлектролитных комплексов в виде мембран и пленок на границе раздела фаз двух несмешивающихся жидкостей [9,10] (рисунок 4). Впоследствии получение тонких полиэлектролитных пленок получило бурное развитие при формировании мультислойных (layer-by-layer) мембран и пленок с участием противоположно-заряженных полиэлектролитов.



Рисунок 5 – Профессора С.Е. Кудайбергенов и E. Tsuchida в Японии

В 1993 году он становится начальником отдела химии НИИ Эргономики с ОКБ Министерства образования РК, а с 1994 по 1996 – заместителем главного ученого секретаря и начальником управления международных связей Президиума НАН РК. Существенную роль в становлении Кудайбергенова С.Е. как ученого международного уровня сыграла его трехмесячная стажировка в Национальном Научном Фонде США в 1995 году, где он ознакомился с грантовой системой финансирования науки и стал сертифицированным менеджером науки.

В 1996-1998 гг. Кудайбергенов С.Е. работает профессором КазГУ им. аль-Фараби, где инициирует исследования стимул-чувствительного поведения некоторых водорастворимых сополимеров и их гидрогелей [11], интерполиэлектролитных комплексов [12], интерполимерных комплексов стабилизированных системой водородных связей [13], а также полимерных пленок на их основе [14]. В 1998 проф. Кудайбергенов С.Е. провел 3 месяца в Waseda University (Япония) в научной группе проф. E. Tsuchida в качестве приглашенного профессора (рисунок 5), где занимался исследованиями ионной проводимости гелей на основе поли(дивинилового эфира диэтиленгликоля) в смесях с перхлоратом лития [15].

В 1999 году проф. Кудайбергенов С.Е. организовал и возглавил частное учреждение «Институт полимерных материалов и технологий» (ЧУ ИПМТ) (*www.ipmt.kz*). Параллельно, в 2001-2004 гг., он также работал заместителем директора по научной работе НТЦ АО «КазТрансОйл» и АО «Казахский институт нефти и газа», в 2005-2019 гг. – профессором кафедры химии и экспертизы Семипалатинского государственного университета им. Шакарима, а также в 2008-2020 гг. – руководителем лаборатории инженерного профиля Казахского Национального исследовательского технического университета имени К.И. Сатпаева. В 2002-2003 проф. Кудайбергенов С.Е. также плодотворно работал в Kwangju

Institute of Science and Technology (Южная Корея) в качестве приглашенного профессора, где занимался синтезом и исследованием новых поликарбоксибетаинов на основе (алкил)аминокротонатов [16]. Находясь в Институте науки и технологии Квангжу, он подготовил трех магистров наук из Университета Монпелье (Франция) и Университета Сеула (рисунок 6).

В настоящий момент, Кудайбергенов С.Е. продолжает возглавлять ЧУ ИПМТ и успешно занимается научной работой со своими многочисленными учениками и коллегами. За годы существования Института ученым было опубликовано множество высокорейтинговых публикаций в различных направлениях полимерной и коллоидной химии. Особо хочется отметить такие работы, как исследование комплексообразования катионных полиэлектролитов с ДНК [17], получение полимерных пленок на границе несмешивающихся жидкостей [18], теоретические исследования образования солевых связей в цепях полиамфолитов [19], разработку полимерных композиций как структурирующих агентов для предотвращения миграции радионуклидов и для их извлечения из почв [20,21], получение полимер-протектированных и гель-иммобилизованных наночастиц металлов и исследования их каталитических свойств [22,23] в качестве проточных каталитических реакторов (рисунок 7), синтез и исследования макропористых криогелей [24], синтез гидрофобно-модифицированных полимеров и гидрогелей [25], исследования по применению водорастворимых полисахаридов в нефтедобыче [26], а также создание полимерных систем доставки лекарств [27,28].

Помимо процитированных выше работ, проф. Кудайбергеновым С.Е. в соавторстве было опубликовано 18 монографий на русском, польском и английском языках, свыше 400 научных публикаций, в том числе 17 обзорных статей, 11 глав книг, 145 научных статей, опубликованных на английском языке в международных реферируемых журналах. В 2002 и 2021 гг. он опубликовал фундамен-



Рисунок 6 – Профессор С.Е. Кудайбергенов с магистрантами Университета Монпелье Gregory Huyghe и Julia Mouton в Южной Корее

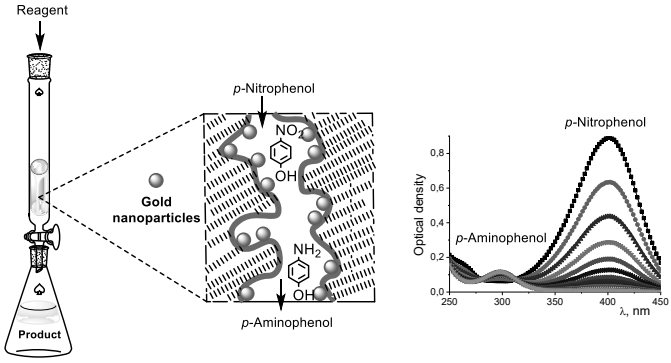


Рисунок 7 – Схема проточного каталитического реактора с криогель-иммобилизированными наночастицами золота

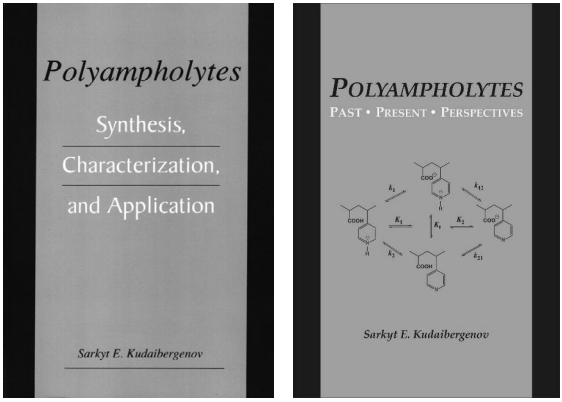


Рисунок 8 – Обложки монографий «Polyampholytes: Synthesis, Characterization and Application» и «Polyampholytes: Past, Present, Perspectives», опубликованных в издательстве «Springer» и казахстанском издательстве

тальные монографии "Polyampholytes: Synthesis, Characterization and Application" в издательстве «Springer» и "Polyampholytes: Past, Present, Perspectives" в казахстанском издательстве (рисунок 8).

Согласно данным базы «Web of Science, Clarivate Analytics», Кудайбергенов С.Е. занимает лидирующую позицию в мире по числу публикаций по направлению «Полиамфолиты». Проф. Кудайбергенов С.Е. является одним из наиболее высокоцитируемых ученых Казахстана, согласно базе данных Scopus его общая цитируемость превышает 1880 и индекс Хирша составляет 20.

Помимо научной работы, проф. Кудайбергенов С.Е. всегда уделял подготовке научных кадров. Под его руководством защищены одна докторская, 9 кандидатских и 3 PhD диссертаций. Он является членом диссертационного совета КазНУ им. аль-Фараби по наноматериалам и нанотехнологии (2013-2021 гг.) и председателем диссертационного совета КазНИТУ имени К.И. Сатпаева по специальности «Химическая технология органических веществ» (2019-2021 гг.). Он также является членом редколлегий журналов «Вестник Карагандинского университета, Серия химическая», «Евразийский химико-технологический журнал», а также гостевым редактором специального выпуска «Advanced Technologies in Polymer-Protected and Gel-Immobilized Nanocomposites» *(https://www.mdpi.com/journal/polymers/special_issues/adv_tech_poly_gel_nano*) и членом Международных Оргкомитетов IUPAC (ИЮПАК) "MacroMolecular Complexes (MMC)" и "Macro- and Supramolecular Architectures and Materials" (MAM).

Кудайбергенов С.Е. является обладателем международных грантов фонда Сороса (1994), ИНТАС - Казахстан (1995, 2004), открытого конкурса ИНТАС (1997, 1999, 2001), ИНТАС-Арал (2003), в 2011-2014 гг. – руководителем Международного проекта НАТО «Устойчивый менеджмент токсичных загрязнителей в Центральной Азии: от региональной модели экосистемы до безопасности окружающей среды». В 2012-2015 гг. он руководил проектом коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов», а также 6 проектами, финансируемыми по гранту МОН РК (2009-2020 гг.). Помимо этого, проф. Кудайбергенов являлся соруководителем двух совместных проектов между РК и КНР (2015-2016, 2018-2019 гг.), а в настоящее время он является участником Международного проекта Европейского Союза «Горизонт-2020» (2019-2022 гг.). В 2002-2019 гг. ученый организовал восемь международных семинаров, посвященных полимерам специального назначения.

Сведения о научно-педагогической деятельности Кудайбергенова С.Е. опубликованы в энциклопедии «Алматы» (1996, с.188), справочнике «Кто есть кто в казахстанской науке» (1999, с.493), а также в таких изданиях, как «Қазақ Энциклопедиясы» (2005, т.6, с.93), «Жүзден жүйрік, мыңнан тұлпар» (изд. КазНУ, 2009), «Нефть и Газ» (2011, №3, с.145), «История Казахстана: преподавание в школе» (2011, №5, с.38-40), «Macromolecular Chemistry and Physics" (2011, v.212, Issue 10, p.1086-1087), «Наша Элита» (изд. «Қазақ университеті», 2014, т.2., с.298-299), Polymers for Advanced Technologies (2020, DOI: 10.1002/pat.5156).

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Congratulations on the anniversary of Professor S.E. Kudaibergenov

The article is dedicated to the 70th anniversary of Sarkyt Elekenovich Kudaibergenov, a prominent Kazakh scientist-chemist. His career and the most significant events of his scientific life are briefly described here. The contribution of Professor S.E. Kudaibergenov to the development of physical chemistry of polymers and his participation in the internationalization of the polymer scientific school are shown.

This article is devoted to the 70th anniversary of Sarkyt Elekenovich Kudaibergenov, a prominent Kazakh scientist-chemist. S.E. Kudaibergenov is an internationally recognized expert in the field of physical chemistry of polymers, Doctor of Chemical Sciences (1991), Professor (1994), Laureate of the Kazakh SSR State Prize in Science and Technology (1987).



Professor S.E. Kudaibergenov is an enthusiastic person who has been inspiring his colleagues and a large number of young researchers working in the field of polymer science for several decades. His fundamental scientific works mainly devoted to the physical chemistry of hydrophilic polymers, stimulated significant progress in this field [1–6].

After graduating from the Faculty of Chemistry at Kazakh State University named after Kirov (now Al-Farabi Kazakh National University) in 1973, Sarkyt Kudaibergenov remained at this university as an engineer and then as a research intern. His academic career continued at the Institute of Chemical Sciences of the Academy of Sciences of the Republic of Kazakhstan in the Laboratory of Physical Chemistry of Polymers led by Academician E.A. Bekturov, a distinguished chemist. A truly important milestone in the career of Professor S.E. Kudaibergenov was the work on a candidate dissertation on the topic "Hydrodynamic properties of polyelectrolytes based on vinylethylpiperidoles-4", which he successfully defended in 1980. This work anticipated his innovative research on the development of the physical chemistry of polyelectrolytes [7, 8]. Studies of polymer complexation reactions were one of the many contributions that S.E. Kudaiberegenov made for the development of polymer science.

One of his first co-authored monographs "Polymer Complexes and Catalysts" describes the interaction of macromolecules with metal ions, explains the mechanisms and conditions of formation of polymer-metal complexes, which have great theoretical interest and practical application [9]. In this book the catalytic properties of some macromolecular compounds in solutions, which are models of biocatalyst-enzymes, are also described. These works formed the basis of the author's further research [10–12]. In 1991 S.E. Kudaibergenov defended his Doctoral Thesis "Complex formation reactions with participation of synthetic polyampholytes" at Lomonosov Moscow State University, in 1994 he has received a title of Professor. After productive work at the Institute of Chemical Sciences, Sarkyt Elekenovich works at responsible positions in the scientific structures of the Ministry of Education and the National Academy of Sciences of the Republic of Kazakhstan. In 1996 S.E. Kudaibergenov was invited to the position of Professor at al-Farabi Kazakh National University, where he organized a scientific group for the production and research of "smart" polymeric materials based on hydrogels and interpolymer complexes. In 1999 Professor S.E. Kudaiberegenov founded a private research organization "Institute of Polymer Materials and Technologies", which successfully operates today and contributes to the development of polymer science in Kazakhstan. The special connection of the scientist with his small motherland is expressed in his cooperation with Semipalatinsk Shakarim State University, where he was a professor of the Department of Chemistry from 2005 to 2019. S.E. Kudaibergenov made a great contribution to the organization of scientific work of Kazakh National Technical University named after K.I. Satpayev, where he permanently headed the Laboratory of Engineering Profile (2008–2020).

As a famous scientist in the field of fundamental science Professor S.E. Kudaibergenov was able to apply the results of theoretical research to solve important practical problems, in particular to increase the efficiency of oil production. The scientist had experience as the head of scientific subdivisions of oil producing companies "KazTransOil" and "KazMunayGas" (2001–2004), headed the commercialization project "Development and implementation of polymer flooding technology to increase oil recovery". These works are important for the development of the economy of Kazakhstan.

In the early days of his scientific career, in 1995, S.E. Kudaibergenov completed a three-month internship at the National Science Foundation in the USA, where he became acquainted with the system of science funding in that country. Then in 1998, as a visiting professor, he researched at Waseda University (Japan) in the research group of Professor E. Tsuchida.

In 2002–2003 Professor S.E. Kudaibergenov was invited as a professor at Kwangju Institute of Science and Technology (South Korea), where he researched and shared his experience with young scientists. He is one of the first scientists in Kazakhstan who received several grants from international foundations, including Soros Fund (1994), INTAS-Kazakhstan (1997, 1999, 2001), INTAS-Aral (2003), NATO (2011–2014), projects with China (2015–2016, 2018–2019), EU Horizon-2020 (2019–2022). Professor S.E. Kudaibergenov is a member of the editorial board of several national English-language scientific journals and was also a guest editor of the special issue "Advanced Technologies in Polymer-Protected and Gel-Immobilized Nanocomposites" for the Polymers journal (MDPI, 2020). He is a regular guest lecturer at international scientific conferences and symposia and a member of the organizing committee of several prestigious scientific forums, including the IUPAC International Symposium on Macromolecule-Metal Complexes (MMC) and the International Symposium on Macro- and Supramolecular Architectures and Materials (MAM). S.E. Kudaibergenov initiated 8 International workshops on polymer specialty that were held in Almaty, Semey and Issyk-Kul (Kyrgyzstan). The last workshop was held at Karagandy University of the name of academician E.A. Buketov in 2019, sponsored by the International Science and Technology Center (ISTC). Invited by S.E. Kudaibergenov, well-known national and international scientists such as Hiroyuki Nishide (Waseda University, Tokyo), Sayora Rashidova (Institute of Physics and Chemistry of Polymers, Uzbekistan), Gulzhian Dzhardimalieva (Institute of Chemical Physics of RAS, Russia), Vladimir Lozinsky (Institute of Elementoorganic Compounds of RAS, Russia), Oguz Okay (Istanbul Technical University, Turkey), Hekki Tenhu (University of Helsinki, Finland), Vitaliy Khutoryanskiy (University of Reading, UK) made plenary reports at the VIII International Symposium on Specialty Polymers. The above mentioned demonstrates that Professor S.E. Kudaibergenov is a scientist of world renown, and the results of his research are recognized in the scientific community. He is also distinguished by his great desire to help young scientists choose their scientific direction, find foreign partners, and use the results for the benefit of the national scientific school.

Professor S.E. Kudaibergenov individually and in collaboration published 19 monographs in Russian, Polish and English languages, he has more than 400 scientific publications, including 17 review articles, 11 book chapters and more than 130 scientific articles published in English in international peer-reviewed journals with a high impact factor. In 2002 and 2021 he published fundamental monographs "Polyampholytes: Synthesis, Characterization and Application" in Springer and "Polyampholytes: Past, Present, Perspectives" in Kazakhstan publishing house. According to the Web of Science, Clarivate Analytics database, S.E. Kudaibergenov is the world's leader in the number of publications in the field of Polyampholytes [13–16]. The annual citation index of his works reaches up to 200 citations. His Hirsch index is 20.

As a member of the editorial board of the journal "Bulletin of the Karaganda university. Chemistry series" Professor S.E. Kudaibergenov contributes to the further promotion of our publication in international scientific bases, his articles and reviews published in the journal are the most demanded among readers. On behalf of the editorial board of the journal we congratulate Professor S.E. Kudaibergenov with his 70th anniversary! We wish you great success in scientific work, good students and followers, new scientific works.

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Е.М. Тажбаев, М.Ж. Бүркеев

Профессор С.Е. Құдайбергеновті мерейтойымен құттықтау

Мақала қазақтың көрнекті ғалым-химигі — Сарқыт Елекенұлы Құдайбергеновтің 70 жылдық мерейтойына арналған. Оның еңбек жолы және ғылыми қызметіндегі маңызды кезеңдері қысқа түрде сипатталған. Профессор С.Е. Құдайбергеновтің полимерлердің физикалық химиясын дамытуға және полимерлер ғылыми мектебін интернационалдандыруға қосқан үлесі көрсетілген.

Е.М. Тажбаев, М.Ж. Буркеев

Поздравление с юбилеем профессора С.Е. Кудайбергенова

Статья посвящена 70-летнему юбилею выдающегося казахстанского ученого-химика — Кудайбергенова Саркыта Елекеновича. В краткой форме описаны его трудовой путь и наиболее значимые события научной карьеры. Показан вклад профессора С.Е. Кудайбергенова в развитие физической химии полимеров и его участие в интернационализации полимерной научной школы.

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С целью презентации своих инновационных идей к нам на предприятие приехали профессора в области исследований нефтепромысловой химии: **Кудайбергенов С.Е. -** *Руководитель лаборатории инженерного профиля КазНТУ имени К.И. Сатпаева, директор Института полимерных материалов и технологий, д.х.н., проф.* **Сагиндыков А.А. -** *Директор ТОО «Институт нефтепромысловой химии», д.х.н., проф.* **Герштанский О.С. -** *Генеральный директор АО «НИПИНефтегаз», д.т.н., проф.*

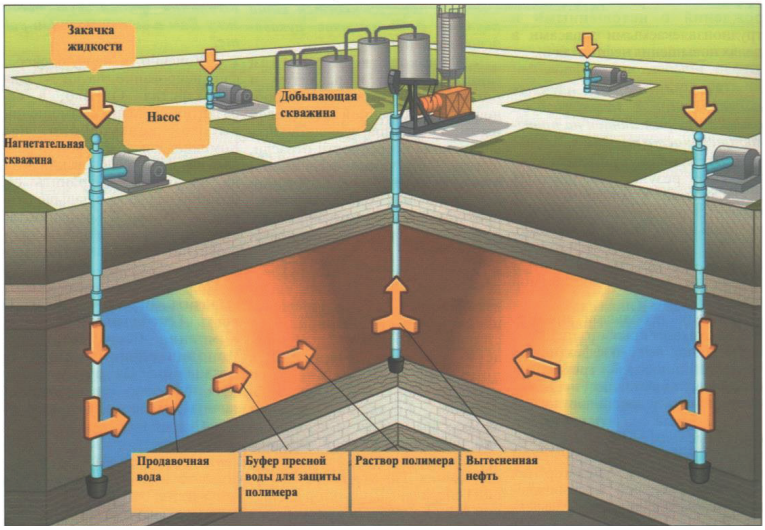
В мировой практике извлечения нефти ведутся разработки, направленные на увеличения нефтеотдачи пластов. Наиболее перспективным методом является метод полимерного заводнения.

Так как, месторождение на контрактной территории АО «ТУРГАЙ ПЕТРОЛЕУМ» находится на последней стадии разработки, основной задачей наших производственников является внедрение более эффективных технологий нефтеизвлечения.

Тема презентации была очень актуальна и интересна, и мы решили вкратце предоставить материалы презентации нашему читателю.

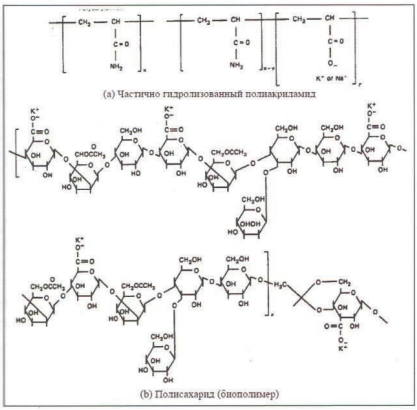
Технология полимерного заводнения заключается в закачке в нефтяной пласт полимерных загустителей или гелеобразующих полимерных систем для увеличения нефтеотдачи путем снижения отношения вязкости нефти и воды ($_0$ = $_{нефти}$/$_{воды}$)

Применение полимеров для повышения нефтеотдачи пластов основано на способности их водных растворов, даже при низкой концентрации полимера, значительно снижать соотношение вязкостей нефти и воды, анизотропию самого пласта и изменять реологические свойства и структуру фильтрационных потоков пластовых флюидов.



Водорастворимые полимеры улучшают нефтеотдачу путем увеличения эффективного охвата водной фазы. Это достигается путем снижения подвижности водной фазы или увеличения вязкости водной фазы. Адсорбция полимера на пористой породе является причиной снижения концентрации полимера в водной фазе и, следовательно, снижение вязкости.

ПОЛИАКРИЛАМИД И ПОЛИСАХАРИД



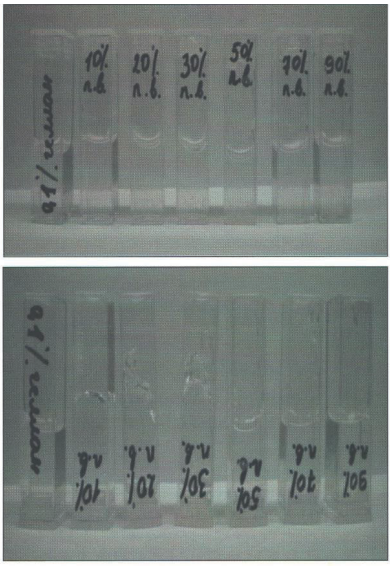
ГЕЛЛАН:

Геллан по химическому строению является анионным внеклеточным бактериальным полисахаридом, пповторяющееся звено которого состоит из остатков 4 полисахаридов: 1,3-β-D-глюкоз, 1,4-β-D-глюкуроновой кислоты, 1,4 - β-D-глюкоз и 1,4 -α-L-рамнозы.

Геллан производится из биомассы путем аэробной ферментации микроорганизмом *Sphingomonas elodea*.

ЗОЛЬ-ГЕЛЬ И ГЕЛЬ-ЗОЛЬ ПЕРЕХОДЫ ГЕЛЛАНА В ПЛАСТОВОЙ ВОДЕ С МИНЕРАЛИЗАЦИЕЙ 73 г/л

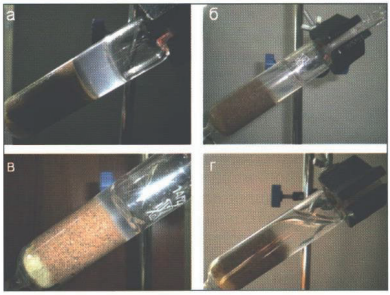
Одним из замечательных свойств геллана, обнаруженных нами впервые, является золь-гель и гель-золь переходы, имеющие место в пластовой воде. Например, 0.1%-ный водный раствор геллана при добавлении 10%, 20% и 30% пластовой воды с минерализацией 73 г/л превращается в гель (золь-гель переход). Однако в присутствии более 50% пластовой воды имеет место переход геллана из состояния геля в состояние золя



(гель-золь переход).

ГЕЛЕОБРАЗОВАНИЕ ГЕЛЛАНА НА ПОВЕРХНОСТИ ПЕСКА, СОДЕРЖАЩЕЙ ПЛАСТОВУЮ ВОДУ

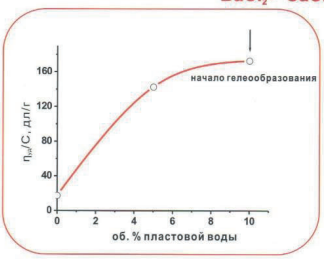
Гелеобразование геллана при контактировании с песком, содержащим пластовую воду, с общей минерализацией 73 г/л. [ГЕЛЛАН] =1.0 (а); 0.5 (б); 0.25 (в) и 0.1% (г).



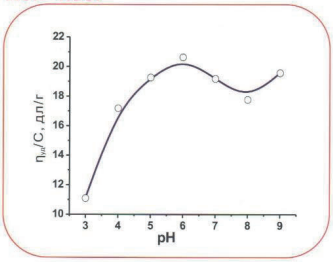
ГЕЛЕОБРАЗОВАНИЕ ГЕЛЛАНА В ВОДНО-СОЛЕВЫХ СРЕДАХ

Гелеобразование геллана в водно-солевых растворах может быть одним из ключевых факторов при вытеснении нефти из пластов. Нами установлено, что эффективность гелеобразования в присутствии солей изменяется в следующем порядке:

$BaCl_2 > CaCl_2\ MgCl_2 > KCl > NaCl$



Изменение приведенной вязкости геллана в воде при добавлении Пластовой воды с минерализацией 73 г/л



Изменение приведенной вязкости геллана в воде в зависимости от pH среды

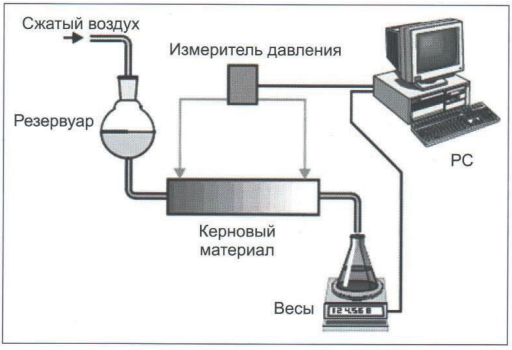
СХЕМА ВЫТЕСНЕНИЯ НЕФТИ ИЗ ПОРИСТОЙ СРЕДЫ ИЗМЕНЕНИЕ ДАВЛЕНИЯ НАГНЕТАНИЯ ПРИ ПРОКАЧКЕ 0.1 %-НЫХ РАСТВОРОВ ГЕЛЛАНА И ПАА ЧЕРЕЗ НАСЫПНУЮ МОДЕЛЬ

После прокачки 3 поровых объёмов (1 поровый объем равен 100 $см^3$) 0.1%-ного раствора геллана, давление резко возрастает. На момент прокачки 315 $см^3$ давление повышается до значения 2.55 МПа. В случае ПАА, кривая монотонно возрастает до значения давления 0.062 МПа и в дальнейшем изменяется незначительно.

Таким образом, при очень близких значениях проницаемости среды (коэффициент проницаемости 3.7-3.8 Дарси) и одинаковой концентрации полимеров (концентрация полимеров 0.1%), на момент прокачки трёх поровых объёмов полимера через модель, геллан повышает давление нагнетания в 40 раз больше, чем ПАА.

За периодическое колебательное изменение давления при фильтрации 0.1%-го водного раствора геллана через пористую среду, насыщенную минерализованной водой, ответственно золь-гель и гель-золь фазовые переходы.

Традиционно используемые для увеличения нефтеотдачи и поставляемые из-за рубежа (в основном из России и Японии) полиакриламид (ПАА) и гидролизованный полиакриламид (ПААГ) в казахстанских условиях оказались малоэффективными при высокой минерализации пластовых вод и высокой температуре.



Основными преимуществами геллана, потенциально используемого для увеличения нефтеотдачи пластов, являются: 1) сопоставимый с ПААГ расход полимера; 2) широкий диапазон регулирования вязкостных свойств рабочего агента; 3) перенаправления фильтрационных потоков; 4) экологическая безопасность из-за способности геллана к биодеградации в пластовых условиях.

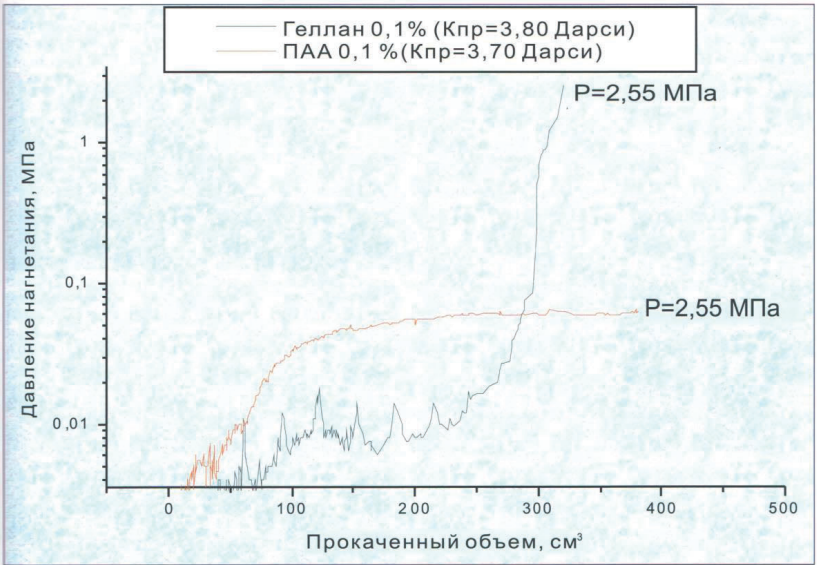
ПЕРСПЕКТИВЫ ТЕХНОЛОГИИ ПОЛИМЕРНОГО ЗАВОДНЕНИЯ :

1. Проведение опытно-промышленных испытаний (ОПИ) технологии полимерного заводнения на нефтяных месторождениях
2. Коммерциализация технологии полимерного заводнения на нефтяных месторождениях РК
3. Успешное внедрение технологии полимерного заводнения в нефтегазовую отрасль позволит на первоначальном этапе использовать импортируемый геллан, а в дальнейшем путем трансферта технологии организовать в Казахстане производство геллана для технологии полимерного заводнения.
4. Разработка и коммерциализация технологии щелочно-мицеллярно-полимерного заводнения (Alkaline/Surfactant/Polymer (ASP) flooding)

P/S : По завершении презентации, профессорам было задано много вопросов от наших сотрудников, что показывает живой интерес к инновационным идеям для дальнейшего их применениями на нашем производстве.

Генеральный директор Есен Кайржан отметил особую важность темы и порекомендовал специалистам нашего предприятия с ответственностью отнестись к предложенным идеям и изучить возможность применения данной технологии полимерного заводнения на месторождении Кумколь.

АБИЛХАИРОВ Даурен
заместитель начальника отдела разработки
к.т.н.





КУДАЙБЕРГЕНОВ САРКЫТ ЕЛЕКЕНОВИЧ

Кудайбергенов Саркыт Елекенович родился 20 мая 1951 г. в ауле Каргалы Маканчинского района Семипалатинской области. В 1963-68 гг. учился в средней школе им. Абая с. Караул Абайского района Семипалатинской области. В 1968 г. окончил среднюю школу № 16 им. Абая в г. Семипалатинске. В 1968 поступил на химический факультет КазГУ и окончил его в 1973 году по специальности - физическая химия. В 1973-1980 гг. работал в лаборатории физико-химических методов исследования КазГУ в должности инженера и младшего научного сотрудника. С 1981 по 1993 гг. работал в Институте химических наук АН РК в должности младшего, старшего и ведущего научного сотрудника. В 1993 - 1994 гг. являлся начальником отдела химии НИИ Эргономики с ОКБ Министерства образования РК. В 1994-1996 гг. занимал должность заместителя Главного ученого секретаря и начальника Управления международных связей Президиума НАН РК. 1996-1998 гг. - профессор КазГУ. В 1999 году он организовал первое в Республике частное учреждение - Институт полимерных материалов и технологий (ИПМТ), директором которого он является и по настоящее время. В 2001-2004 гг. работал в НТЦ АО "КазТрансОйл" и НТЦ АО "Казахский институт нефти и газа" в должности заместителя директора по научной работе - начальником Центральной лаборатории. С 2005 г. он является профессором кафедры химии и экспертизы Семипалатинского государственного университета им. Шакарима. В настоящее время он работает научным руководителем лаборатории инженерного профиля КазНТУ им. К.И. Сатпаева.

Кудайбергенов С.Е. в 1980 году защитил кандидатскую диссертацию в специализированном совете Института химических наук АН Каз ССР, в 1991 году - докторскую диссертацию в специализированном совете МГУ имени М.В.Ломоносова. В 1994 году ему присвоено звание профессора химии. В 1986 году в составе авторского коллектива он удостоился звания Лауреата Государственной премии Республики Казахстан в области науки и техники за цикл монографий "Водорастворимые полимеры и их комплексы".

Кудайбергенов С.Е. представлял научные достижения Республики Казахстан на различных международных симпозиумах и конференциях с пленарными, устными и стендовыми докладами. В качестве приглашенного профессора он читал лекции в Университете Хаджеттепе (Турция, 1996) и Университете Васеда (Япония, 1998). С февраля 2002 г. по январь 2003 г. он в качестве приглашенного профессора находился в Институте науки и технологии Квангжу (Южная Корея), читал лекции и руководил научными работами аспирантов и магистрантов из Франции, Южной Кореи, Непала, Германии. В Институте науки и технологии Квангжу под его научным руководством защищены три диссертации на степень магистра наук из Института науки и технологии Монпелье (Франция) и Университета Сеул (Южная Корея), Института науки и технологии Квангжу (Южная Корея).

Кудайбергенов С.Е. в 1995 году прошел трехмесячную стажировку в Национальном научном фонде США. Он является постоянным экспертом международных программ Европейского союза ИНТАС и ИНКО-КОПЕРНИКУС, рецензентом ряда Международных научных журналов "Journal of Applied Polymer Sciences", "Journal of Polymer Science", "European Polymer Journal", "Polymer". Он является обладателем Международных грантов фонда Сороса (1994), ИНТАС - Казахстан (1995), открытого конкурса ИНТАС (1997, 1999, 2001), ИНТАС-Арал (2003), ИНТАС-Казахстан (2004). В 2002 году он стал победителем гранта ИНТАС по организации и проведению Международной мониторинговой конференции "Разработка реабилитационной методологии по охране окружающей среды Семипалатинского региона, загрязненного

ядерными испытаниями". В 2011 г. он стал обладателем гранта НАТО "Наука для мира". В 2009-2010 гг. за выдающийся вклад в развитие мировой науки Национальный центр научно-технической информации РК и Thomson Reuters присудили ему премию "Парасат", как наиболее цитируемому и публикуемому казахстанскому автору за рубежом. За 1996 по 2010 гг. индекс его цитируемости насчитывает 462 наименования.

Научное направление созданного Кудайбергеновым С.Е. Института полимерных материалов и технологий связано с синтезом и характеристикой новых водорастворимых и водонабухающих полиамфолитов и материалов на их основе для использования в нефтяной промышленности, гидрометаллургии, медицине, решения экологических проблем. В Институте полимерных материалов и технологии под руководством профессора Кудайбергенова С.Е. разработана стратегия получения новых полиамфолитов бетаиновой структуры, которые обладают стимулчувствительными свойствами и обнаруживают уникальные свойства в реакции комплексообразования с различными классами соединений: полимерами, ионами металлов, лекарственными веществами, белками, детергентами. Это открывает широкие перспективы в использовании данного класса полимеров в различных областях промышленности, биотехнологии, медицины, экологии: для извлечения ионов тяжелых металлов; иммобилизации протеинов и лекарственных веществ с целью разделения биополимеров и пролонгации действия лекарств; разделения смесей вода-нефть; увеличения нефтеотдачи пластов; предотвращения водной и ветровой эрозии почвы, зараженной радиоактивными элементами.

В круг научных интересов Кудайбергенова С.Е. входит исследование в области полимер-протектированных и гель-иммобилизованных наночастиц металлов, иммобилизация биологически активных веществ в матрицу стимулчувствительных гидрогелей с целью создания нанокатализаторов и для контролируемой и дозированной подачи биологически активных веществ в окружающую среду.

Кудайбергенов С.Е. является признанным специалистом в области химии и физики полимеров. Он в соавторстве опубликовал 11 монографий, изданных на русском, польском и английском языках, более 300 научных статей и обзоров, одна треть которых (более 100) опубликована на английском языке в международных реферируемых журналах и изданиях. Им получено 10 авторских свидетельств и патентов РК и Южной Кореи. Под его руководством защищены 3 докторские и 10 кандидатских диссертаций и 3 магистерских диссертаций из Франции и Южной Кореи.

В 2002 г. Кудайбергенов С.Е. опубликовал монографию "Полиамфолиты: синтез, характеристика и применение" на английском языке в одном из престижных американских издательств "Клювер Академик/Пленум Паблишерс" (Нью-Йорк, Бостон, Дордрехт, Лондон, Москва). Данная монография представляет собой фундаментальный труд, в котором впервые в мире с начала 1950 г. обобщены и систематизированы работы в области синтеза, исследования и применения уникальных высокомолекулярных соединений, так называемых полимерных амфолитов - простых моделей биополимеров. Отзыв на монографию Кудайбергенова С. Е. опубликован в журнале "Cellulose Chemistry and Technology", v.37, p.517 (2003). По данным анализа "ISI Web of Knowledge", Кудайбергенов С.Е. лидирует среди 25 ведущих ученых мира в области синтеза и исследования полиамфолитов (http://pcs.isiknowledge.com/analyze/ra.cgi).

Сведения о научно-педагогической и общественной деятельности Кудайбергенова С.Е. опубликованы в энциклопедии "Алматы" (1996, с.188), справочнике "Кто есть кто в казахстанской науке" (1999, с. 493) и "Қазақ Энциклопедиясы" (2005, т. 6, с.93), ""Жүзден жүйрік, мыңнан тұлпар" (изд. КазНУ, 2009, с.205-208).

ТАРИХ ПАРАҚТАРЫ

Мақаншы өңірінен шыққан ғалым

Мақаншы ауданындағы Қарғалы ауылдық кеңесіне қарасты Жұмыршақ (қазіргі Келдімұрат ауылдық округі, Қызыл Жұлдыз ауылы) ауылында 1951 жылы туған Құдайбергенов Сарқыт Елекенұлы бүгінде полимерлердің физикалық химиясы саласында әлемге танылған ғалым, химия ғылымдарының докторы, профессор. Әйтсе де оны жерлестеріміздің білуі неғайбыл...

Сарқыттың ғылым мен техника саласындағы материалдары шетелде ең көп жарияланған және ол дәйексөз келтірілген қазақстандық автор ретінде танылды. Қазақ Кеңестік Социалистік Республикасының Мемлекеттік сыйлығының, халықаралық «Парасат» сыйлығының, Қ.И. Сәтбаев атындағы сыйлықтың лауреаты атанды. Оның ғылыми бағыты - мұнай-химия, катализ, нанотехнология, биотехнология, медицина, қоршаған ортаны қорғау салаларында арнайы мақсаттағы полимерлерді өзірлеуге және енгізуге байланысты болды. Ғалымның жеке және бірлескен авторлық еңбектері орыс, поляк және ағылшын тілдерінде 19 монография болып шығарылды, 400-ден астам ғылыми жарияланымдар дайындап, оның ішінде 20 шолу мақаласы, 11 кітап тарауы және 145 ғылыми мақала ағылшын тілінде жоғары импакт-факторлы халықаралық рефераттелған журналдарда жарияланды. Сарқыт Құдайбергенов «Полиамфолиттер» бағытындағы жарияланымдар саны бойынша әлемде жетекші орынға ие ғалым. Оның шығармаларының әлемдік рейтингтегі жалпы дәйексөзділігі 1880 сілтемені құрайды. Ал дәйексөздердің жылдық индексі орта есеппен 150 сілтемеге дейін жетеді. 1995 жылдардан бастап АҚШ-тың Ұлттық Ғылыми қорында үш айлық тағылымдамадан өтіп, шақырылған профессор ретінде Түркиядағы Хаджеттепе университетінде, Жапониядағы Васэда университетінде, Оңтүстік Кореядағы Кванджу Ғылым және технологиялар институтында дәріс оқып, Франциядағы Монпелье университетінен және Сеул университетінен ғылым магистрлерін дайындады.

Тынбай ізденістің арқасында Сарқыт Елекенұлының танымалдылығы артып, Әл-Фараби атындағы Қазақ Ұлттық университетінің наноматериалдар және нанотехнологиялар бойынша диссертациялық кеңесінің мүшесі, Қ.И.Сәтбаев атындағы ҚазҰТУ-дың «Органикалық заттардың химиялық технологиясы» мамандығы бойынша диссертациялық кеңесінің төрағасы, «Өзбек полимер журналы», «Қарағанды университетінің хабаршысы», «Химия сериясы», «Еуразиялық химия-технологиялық журнал» журналдарының редакциялық алқасының мүшесі атанды. Ғылымға сіңірген еңбегінің арқасында оған жүктелген қызметтер де аз болмады. Ол 2011-2014 жылдары НАТО-ның «Ғылым бейбітшілік пен қауіпсіздік үшін» халықаралық гранты аясында «Орталық Азиядағы улы ластағыштарды тұрақты басқару: аймақтық экожүйе моделінен қоршаған орта қауіпсіздігіне дейін» халықаралық жобасын басқарды. Мұнан кейінгі жылдары «Мұнай өндіруді арттыру үшін полимерлі су тасқыны технологиясын өзірлеу және енгізу» коммерцияландыру жобасын басқарды және оны «Құмкөл» кен орнында тәжірибелік-өнеркәсіптік сынақтарға дейін жеткізді. Қазақстан Республикасы Білім және ғылым министрлігінің гранты бойынша қаржыландырылатын 7 жобаның жетекшісі атанып, Қазақстан мен Қытай арасындағы екі бірлескен жобаның тең жетекшісі болды. Қазақстан Республикасының Тәуелсіздік жылдарында, профессор Сарқыт Құдайбергенов «Полимерлі материалдар және технологиялар институты» жеке мекемесін ұйымдастырды және басқарды. Еліміздің ғылымына сіңірген еңбегі үшін Сарқыт Елекенұлы «Жаратылыстану ғылымдары саласындағы үздік ғылыми зерттеулер үшін», «Қазақстан Республикасының ғылымын дамытуға сіңірген еңбегі үшін» Қазақстан Республикасы Білім және ғылым министрлігінің төсбелгісімен, «Қ.И.Сәтбаев атындағы Қазақ ұлттық техникалық университетінің 85 жылдығы» мерейтойлық медалімен марапатталған, ғылым мен техниканың дамуына зор үлес қосқан ғалымдар мен мамандарға арналған мемлекеттік ғылыми стипендияның иегері атанды.

Ол бүгінде қазақстандық жас ғылыми кадрларды даярлауды қамтамасыз ету және оларға жұмыс орындарын құру арқылы Қазақстан ғылымының дамуына өз үлесін қосуда.

Юсбеков Асхат
Қабанбай ауылы

ПОСЛЕСЛОВИЕ

Мне бы хотелось начать послесловие с размышления академика Петра Леонидовича Капицы, выдающегося ученого-физика, лауреата Нобелевской премии. «Человек в своем развитии проходит три стадии, каждая по 25 лет. Первые 25 лет – это животное состояние. Человек думает главным образом о своих страстях и гораздо меньше о науке. Следующие 25 лет – смешанное состояние, с одной стороны, человек продолжает думать об удовлетворении животных страстей, а с другой – о полезной деятельности, например, о науке. И только следующие 25 лет можно считать человеческим состоянием. В человеке уже не бушуют страсти, и он может посвятить себя полностью науке. Ну, а что касается после 75, − то это божественное состояние. Человек становится иконой. Он ничего не делает, но на него молятся». Если следовать саркастическому высказыванию П.Л. Капицы, то я еще не перешел критическую грань, продолжаю заниматься любимой наукой, генерирую новые идеи, пишу книги, статьи, участвую в конференциях, готовлю научные кадры и передаю свои знания молодому поколению.

На жизненном пути любого ученого часто встречаются люди и события, которые впоследствии определяют его дальнейшую судьбу. Хотелось бы рассказать о некоторых из них. В первую очередь, это, конечно, школьный учитель химии – Умыт Касымовна Жумукова, которая окончила факультет химбиологии Семипалатинского пединститута имени Н.К. Крупской с красным дипломом. Она преподавала нам химию в с. Караул Абайского района Семипалатинской области и пробудила мой живой интерес к химии своими увлекательными занятиями, которые сопровождались химическими опытами. На первом курсе учебы в казахском отделении химического факультета КазГУ куратором нашей группы была профессор Танашева Маруан Рахметовна. Поскольку у меня было трехлетнее образование по немецкому языку (5-7 классы), что явно не хватало для продолжения языковой подготовки в университете, то она рекомендовала поступить на

начинающий курс английского языка. Ее совет в моей жизни очень пригодился и сыграл важную роль, т.к. освоение научного английского на достаточно высоком уровне позволило мне издать 3 монографии в Германии и США, опубликовать 13 глав книг, 37 обзорных и 133 оригинальных статьи на английском языке. Я очень благодарен Маруан Рахметовне за ее ценный совет!

Люди старшего поколения хорошо помнят, что в советское время наикратчайшим путем для получения степени кандидата наук являлось 3-х летнее обучение в аспирантуре с обязательным выходом на защиту. Поскольку такой возможности у меня не было, то в 1976-1978 гг. стал стажером-исследователем КазГУ от Усть-Каменогорского строительно-дорожного института, благодаря непосредственной поддержке Шаяхметова Шайсултана Шаяхметовича, в то время доцента кафедры химии высокомолекулярных соединений КазГУ. Об этом выдающемся сыне казахского народа следует говорить отдельно. Шайсултан Шаяхметович – выпускник МГУ имени М.В. Ломоносова (1962 г.), аспирант Института элементоорганических соединений АН СССР (1964-1968 гг.), Министр высшего и среднего специального образования Казахской ССР, Министр народного образования Казахской ССР, а затем Казахстана (1988-1993 гг.). Шайсултан Шаяхметович был очень талантливым и многосторонним человеком, как говорят казахи, «Сегіз қырлы бір сырлы». Он автор сборника лирических стихов на казахском языке, мастер спорта СССР по самбо и чемпион Москвы, составил толковый словарь русско-казахских терминов по химии и химической технологии, автор и соавтор учебников и учебных пособий, посвященных исследованию растворов полимеров. Двухгодичная стажировка на кафедре химии высокомолекулярных соединений КазГУ и последующее продолжение научных исследований под руководством профессора Шаяхметова Шайсултана Шаяхметовича и члена-корреспондента АН КазССР Бектурова Есена Абикеновича при консультационной помощи члена-корреспондента АН СССР Рафикова Сагида Рауфовича дали свои плоды – 4 апреля 1980 г. я успешно защитил диссертацию на соискание ученой

степени кандидата химических наук по специальности «химия высокомолекулярных соединений».

Дальнейшая моя научная карьера целиком и полностью связана с моим учителем – выдающимся ученым, заведующим лабораторией физикохимии полимеров Института химических наук АН КазССР, академиком НАН РК Бектуровым Е.А. В этой лаборатории я проработал с 1980 по 1993 г. в должности младшего, старшего и ведущего научного сотрудника. Руководил группой аспирантов, соискателей и кандидатов наук, состоящей из 6 человек (Жаймина Г.М., Сигитов В.Б., Канапьянова Г.С., Салтыбаева С.С., Курманбаева А.А., Фролова В.А.). Успел опубликовать в соавторстве множество статей, несколько обзоров, 1 учебное пособие и 2 монографии. В 1986 г. за цикл монографий «Водорастворимые полимеры и их комплексы» коллектив авторов (Бимендина Л.А., Бакауова З.Х., Легкунец Р.Е., Кудайбергенов С.Е.) во главе с Бектуровым Е.А. был удостоен звания лауреата Государственной премии КазССР в области науки и техники. Из-за декабрьских событий 1986 г. вручение этой высокой государственной награды состоялось в 1987 г. Я бесконечно благодарен Есену Абикеновичу, что оказался в составе лауреатов несмотря на свой молодой возраст, мне было тогда 35 лет. И тогда впервые стал свидетелем его исключительной порядочности и твердости характера. Некоторые наши уважаемые академики того времени высказывали большие сомнения в отношении меня и в правильности выбора Есена Абикеновича. Даже пренебрежительно говорили: «Мынау кім? (типа «кто он такой?»). Я не знаю, чем тогда руководствовался Есен Абикенович и аргументировал свое твердое решение, но думаю, что он глубоко верил в мою любовь и преданность науке. Такое высокое доверие со стороны Есена Абикеновича побудило меня целиком и полностью посвятить себя науке, что я и делаю до сих пор и небезуспешно. Академик Бектуров Е.А. является одним из первых казахстанских ученых, который поднял «железный занавес» и «прорубил окно в Европу». Он начал публиковаться за рубежом еще в начале 70-х годов прошлого столетия и это продолжается почти полвека. Он уже тогда демонстрировал всему миру, что

в Казахстане есть конкурентоспособная полимерная наука. В этом смысле, по моему мнению, Есен Абикенович опередил свое время. Благодаря его пропаганде достижений казахстанской полимерной науки, лаборатория физикохимии полимеров стала своеобразной «Меккой» для ученых Казахстана, стран ближнего и дальнего зарубежья. Лично мне очень повезло, что я попал в лабораторию Есена Абикеновича. Он мой учитель, наставник и, наверное, можно сказать друг (как никак мы тесно общаемся уже более 40 лет). Это настоящий ученый, человек высочайшей культуры и интеллигентности. Свою благодарность хочу выразить словами Ньютона: «Если я достиг чего-то большего, то благодаря тому, что стоял на плечах гигантов». Без преувеличения адресую эти слова Есену Абикеновичу. Я многому научился у него, как писать обзорные статьи и монографии, относиться к науке с уважением и добросовестно, соблюдать этическую норму ученого, быть щепетильным, скрупулезным, перфекционистом. Такие же требования я предъявляю и к своим ученикам. Быть ученым – значит быть терпеливым, вдумчивым человеком, обладать огромным запасом знаний, не останавливаться на достигнутом, постоянно искать новые, неизведанные подходы и решения, быть примером и вдохновителем для подрастающего поколения! В лаборатории физикохимии полимеров судьба свела меня с моей супругой – Жайминой (Кудайбергеновой) Гульнар Маратовной, которая всю жизнь поддерживала меня в трудные и критические моменты, помогала карабкаться к вершине науки, создавала семейный уют, подарила и воспитала двоих прекрасных детей – сына Амира и дочь Ажар. Гульнар Маратовна проводила уникальные эксперименты, подтверждающие существование так называемых «антиполиэлектролитного и изоэлектрического» эффектов, обнаруженных в поведении линейных и сшитых полиамфолитов. Позднее существование этих явлений было обосновано теоретически и подтверждено экспериментально многочисленными учеными из ближнего и дальнего зарубежья. Наш семейный тандем до сих пор трудится в ЧУ «Институт полимерных материалов и технологий». Вывод такой: именно в науке тесное, дружественное сотрудничество позволяет людям

лучше всего работать и успехи, достигнутые в совместных работах, свидетельствуют о пользе «семейственности» в науке.

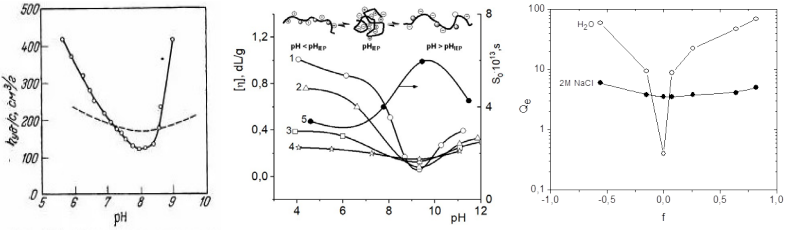
Не могу не рассказать еще об одном выдающемся ученом – докторе физико-математических наук, профессоре Френкеле Сергее Яковлевиче, заведующего лабораторией Института высокомолекулярных соединений АН СССР (г. Ленинград ныне Санкт-Петербург) – большого друга и соратника Есена Абикеновича, официального оппонента моей докторской диссертации, защищенной в 1991 г. на кафедре высокомолекулярных соединений МГУ имени М.В. Ломоносова. Авторитет Сергея Яковлевича был непререкаем среди московских ученых-полимершиков, они снимали шляпу перед ним за его интеллигентность, эрудицию, широкий кругозор и тонкое чувство юмора. Помнится, как он филигранно редактировал наш учебник – «Краткий курс физико-химии полимеров», который несколько раз переиздавался в Казахстане. Еще один штрих. Дело в том, что Сергей Яковлевич и Есен Абикенович были сыновьями выдающихся ученых той эпохи – Якова Ильича Френкеля советского физика, члена-корреспондента АН СССР и лауреата Сталинской премии, и академика Абикена Бектуровича Бектурова – первого заведующего кафедрой общей и неорганической химии и одновременно декана химического факультета КазГУ (1935 г.), а также одного из учредителей АН КазССР, организатора и первого директора Института химических наук в Казахстане (1945-1969 гг). Абикен Бектурович почти четверть века возглавлял Институт химических наук АН КазССР. В 1991 г. Институту химических наук НАН РК было присвоено его имя. Сергей Яковлевич и Есен Абикенович поневоле находились в «тени» своих авторитетных отцов. С одной стороны отцы помогали им, а с другой, как-бы «затрудняли» их продвижение в науке. Успехи сыновей могли быть приписаны к заслугам авторитетных отцов. Но несмотря на такой «отцовский груз», оба смогли доказать себе и окружающим, что они являются самобытными и талантливыми учеными, способными создавать свои научные школы в области физической химии полимеров. И это они сделали, так что честь и хвала им!

Чтобы защитить диссертацию на соискание ученой степени доктора химических наук по специальности «высокомолекулярные соединения», я три года обивал пороги кафедры высокомолекулярных соединений МГУ имени М.В. Ломоносова, начиная с 1989 г. Ежегодно отправлялся в командировку в Москву и докладывал на кафедре основные положения своей диссертации по реакции комплексообразования полиамфолитов и каждый раз получал серьезные замечания либо по части проведения дополнительных экспериментов или по интерпретации полученных результатов. В то время положение осложнялось еще и тем, что между заведующим кафедрой, одновременно председателем научного и диссертационного советов по специальности «высокомолекулярные соединения», членом-корреспондентом АН СССР Кабановым Виктором Александровичем и академиком Бектуровым Е.А. были несколько натянутые отношения. Причина заключалась в том, что Есен Абикенович вместе со своей талантливой ученицей Бимендиной Ларисой Амировной первыми в 1980 г. опубликовали книгу по интерполимерным комплексам на русском языке в издательстве «Наука» АН КазССР, а в 1981 г. – монографию “Interpolymer Complexes” в немецком издательстве “Springer”. Этот факт очень сильно задел самолюбие полимерщиков МГУ, которые считали себя лидерами в области исследования интерполимерных комплексов. В те годы основная конкуренция шла не только между московской и алматинской школой, но и между американским, японским и немецким научными центрами. В сложившихся обстоятельствах у меня часто возникало желание отказаться от защиты докторской диссертации в МГУ. Но я себе говорил так: «Это прежде всего нужно тебе, а не им». Тогда в СССР специализированные советы по защите докторской диссертации по специальности «высокомолекулярные соединения» существовали только в Ташкенте, Уфе и Москве, но я предпочел МГУ. В разговоре с В.А. Кабановым он спросил меня причину моей настойчивости защититься именно в МГУ. Я сказал, что есть такая казахская пословица: «Если падаешь, то лучше с верблюда, т.к. с осла падать больнее» (Түйеден құласаң өркешін төсейді, ал есектен құласаң тұяғын төсейді»). Он смысл моих слов видать интер-

претировал по-своему, т.е. применительно к диссертационному совету МГУ, и согласился. Его согласие стоило мне трех лет мытарств. Вот как вспоминает защиту моей докторской диссертации один из ведущих профессоров кафедры высокомолекулярных соединений МГУ, мой прекрасный друг Изумрудов Владимир Алексеевич. «В те далекие времена защита докторской диссертации была делом трудным и мало кто решался на защиту в МГУ. Но, к чести диссертанта, он решился на этот шаг. Защита действительно была непростой, но после такого чистилища все присутствующие окончательно убедились в силе и торжестве полимерной науки в Казахстане». С тех пор между нами установились самые теплые отношения на долгие годы. При голосовании за присуждение степени доктора наук из 13 членов диссертационного совета, 1 проголосовал против. Тогда председатель диссертационного совета В.А. Кабанов по-отечески похлопал меня по плечу и сказал, что один «черный шар» украшает защиту. До сих пор придерживаюсь его доброго совета продолжать исследования в области полиамфолитов. Удивительно, что защита докторской диссертации состоялась 5 июня 1991 г., а утверждение я получил уже 20 сентября. Дело в том, что высокий уровень полимерной науки в Казахстане и авторитет Есена Абикеновича в области растворов и комплексов водорастворимых полимеров признавали не только в пространстве бывшего СССР, но и во всем мире. В области исследования синтетических полиамфолитов нами экспериментально обнаружено два фундаментальных эффекта, которые впоследствии подтверждены результатами многочисленных исследований.

1. «Антиполиэлектролитный» эффект, суть которого заключается в способности амфотерных макромолекул разворачиваться (или набухать) в солевых растворах вблизи, так называемой, изоэлектрической точки (pH_{IEP}). Существование этого эффекта впервые было предсказано в 1954 г. американскими учеными Ehrlich G., Doty P. Он в интерпретации Ч. Тенфорда (США) вошел в учебник «Физическая химия полимеров» (Москва, изд. «Химия», 1968, Глава 7, с. 575, рисунок слева). В 1979 г. нами экспериментальным путем доказано существование «антиполиэлектролитного» эффекта в поведении водораство-

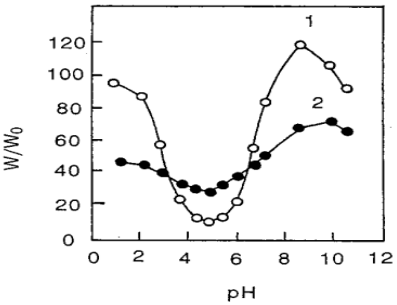
римых синтетических полиамфолитов (С.Е. Кудайбергенов, Ш.Ш. Шаяхметов, Е.А. Бектуров, С.Р. Рафиков. О гидродинамических свойствах амфотерных сополимеров. *Доклады АН СССР*, 1979, т.246, № 1, с. 141-143) (средний рисунок). В те времена Доклады Академии Наук считались самыми авторитетными и престижными журналами СССР.



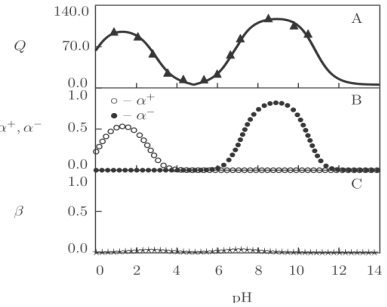
Предсказанный (левый рисунок, штриховая линия), экспериментально подтвержденный нами (средний рисунок) и французскими учеными (правый рисунок) «антиполиэлектролитный» эффект в поведении водорастворимых и водонабухающих полиамфолитов

В 1991 году «антиполиэлектролитный» эффект был теоретически обоснован французскими учеными-теоретиками (Higgs P.G., Joanny J.F. Theory of polyampholyte solutions. *J. Chem. Phys*. 1991, 94, 1543–1554.) и в 1995 и 1999 годах подтвержден для полиамфолитов линейного (G.-Z. Zheng, G. Meshitsuka, A. Ishizu, *J. Polym. Sci. Part B, Polym. Phys*. 1995, V.33, P. 867–873) и сшитого строения (G. Nisato, J. P. Munch, S. J. Candau. Swelling, structure, and elasticity of polyampholyte hydrogels. *Langmuir* 1999, V. 15, P. 4236 – 4244) (правый рисунок). В 2017 г. датские ученые (A.D. Drozdov, J. deClaville Christiansen. The effects of pH and ionic strength on equilibrium swelling of polyampholyte gels. *Int. J. Solids Struct*. 2017, 1–17. http://dx.doi.org/10.1016/j.ijsolstr.2017.01.028) разработали математическую модель для описания набухания полиамфолитного геля в солевом растворе в зависимости от pH среды. Численный анализ показал, что предложенная модель качественно воспроизводит все характерные особенности диаграммы набухания полиамфолитного геля и удовлетворительно описывает наши экспериментальные результаты (S.E. Kudaibergenov, V.B. Sigitov, Swelling, shrinking, deformation and oscillation of

polyampholyte gels based on vinyl 2-aminoethyl ether and sodium acrylate. *Langmuir.* 1999, V.15(12), P.4230-4235. DOI: 10.1021/la981070a).



Экспериментальные результаты зависимости степени набухания полиамфолитного геля (W/W_0) от pH среды в воде (1) и в присутствии 0.1 М раствора KCl (2).



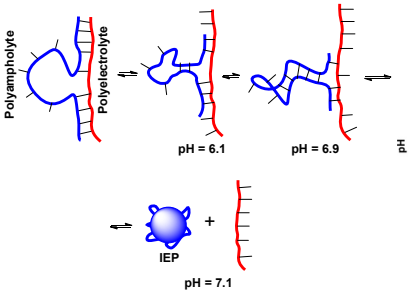
Модель степени набухания (A) и степени ионизации (B) полиамфолитного геля в зависимости от pH среды в воде. Результаты симуляции (C) полностью совпадают с экспериментальными данными.

Впоследствии в 2022 г. на основе «антиполиэлектролитного» эффекта нами разработана и предложена технология добычи нефти синтетическими полиамфолитами из нефтяных резервуаров с высокой минерализацией. Я так подробно описываю этот эффект, чтобы демонстрировать читателям, что зачастую результаты фундаментальных исследований проходят достаточно долгий путь, прежде чем найти практическую реализацию.

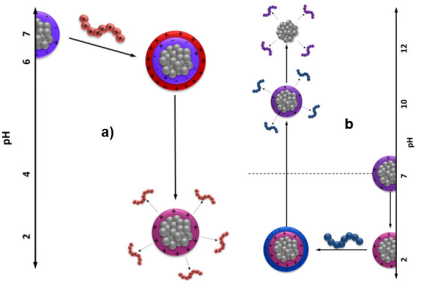
2. Принцип «изоэлектрического» эффекта, впервые обнаруженного нами в 1983-1989 гг. (С.Е. Кудайбергенов, Е.А. Бектуров, Новые свойства синтетических полиамфолитов в изоэлектрической точке. *Вестник АН КазССР,* 1988, № 12, С. 41-44; С.Е. Кудайбергенов, Е.А. Бектуров. Влияние конформационного перехода глобула-клубок в полиамфолитах на сорбцию и десорбцию полиэлектролитов и сывороточного альбумина человека. Высокомол. Соед. Сер. А. 1989, Т.31, С.2614-2617; E. A. Bekturov, S.E. Kudaibergenov. Physico-chemical properties of polyampholytes in solutions. *Makromol. Chem. Macromol. Symp. 1989,* V.26, P.281-295), заключается в том, что при достижении изоэлектрической

точки, электростатические силы взаимодействия между противоположно заряженными звеньями (квазинейтральное состояние амфотерных макромолекул), приводят к «выталкиванию» адсорбированных высоко- и низкомолекулярных соединений (например, белки, полиэлектролиты, ионы металлов, ПАВ, красители, лекарственные препараты и т.д.) из объема глобулярной структуры. Установленный нами «изоэлектрический» эффект позднее подтвержден учеными России, Германии и США (F.H. Schacher et al. *ACS Appl. Nano Mater*. 2018, 1(1), 232-244; F.H. Schacher et al. *Macromol. Rapid Commun. 2018, 39(14), 1800017).*

Здесь следует отметить, что экспериментальное подтверждение фундаментальных открытий независимыми исследователями является критически важным элементом научного процесса. В современной методологии науки это считается одним из ключевых критериев достоверности результата. Экспериментальное подтверждение другими авторами является: 1) фундаментальным критерием научной достоверности; 2) механизмом самокоррекции науки; 3) основой формирования научного консенсуса. Без независимой репликации любое фундаментальное открытие остается лишь гипотезой или предварительным наблюдением.



Схематическое представление механизма разрушения комплекса полиамфолит-полиэлектролит в ИЭТ полиамфолита (С.Е. Кудайбергенов, Е.А. Бектуров. *Высокомол. Соед. Сер. А*. 1989, Т.31, С.2614-2617)



Десорбция поли-(N,N-диметиламиноэтилметакрилата) (а) и поли(стиролсульфоната натрия) (б) в ИЭТ полиамфолита – поли(дегидроаланина). (F. H. Schacher et al. *ACS Appl. Nano Mater*. 2018, 1(1), 232-244)

На основе указанного эффекта нами были предложены способы извлечения ионов переходных металлов из растворов (Бектуров Е.А., Кудайбергенов С.Е., Жаймина Г.М. Способ извлечения ионов металлов из растворов. *Авторское свидетельство СССР* №1086391, 1983; Бектуров Е.А., Кудайбергенов С.Е. Способ извлечения ионов металлов из растворов. *Авторское свидетельство СССР* 1983, №1231810). Однако описанные выше два эффекта – «антиполиэлектролитный и изоэлектрический» в свое время не были заявлены на предмет научного открытия, т.к. в эпоху существования СССР Постановлением Президиума АН СССР регистрация научных открытий была отменена.

Как раз в год защиты моей докторской диссертации случился развал СССР, который нанес непоправимый урон науке в целом и казахстанской, в частности. Начался процесс «утечки мозгов». Ученые стали массово прекращать заниматься наукой и уходить в другие виды деятельности. В эти тяжелые времена финансовая помощь фонда Сороса и Европейского Союза, оказанная в виде научных грантов, позволила временно приостановить «утечку мозгов» множества молодых и маститых ученых Казахстана и оставаться в научной сфере. Фонд Сороса объявлял два типа гранта: индивидуальный и долгосрочный. Критерием отбора служили зарубежные публикации. Мои 36 статьи, опубликованные в различных иностранных журналах, дали прекрасный шанс выиграть индивидуальный грант фонда Сороса в 1994 г. В последующем фонд Сороса объявил двухлетний долгосрочный грант только для ученых СНГ. Оказавшись среди победителей конкурса, наша исследовательская группа под моим руководством в первый год получила финансовую поддержку в размере 25 000 долларов США. В 1995 г. фонд Сороса прекратил финансирование проекта второго года из-за скандальной истории, затеянной некоторыми чиновниками, дескать Запад перехватывает наши передовые идеи и технологии, Сороса обвинили даже в научном шпионаже. После этого фонд Сороса перестал финансировать точные науки и начал поддерживать только социальные науки и неправительственные организации. С системой грантового финансирования я был хорошо знаком с 1995 г. после прохождения трехмесячной стажи-

ровки в Национальном научном фонде США, когда работал начальником Управления международных связей Президиума НАН РК. В то время систему грантового финансирования, принятую в США и Европейских странах, невозможно было внедрить у нас в Казахстане. Бесперебойно работал устоявшийся с советских времен принцип финансирования науки «сверху вниз»: «Государство → Министерство финансов → НАН РК → Отделения наук → Институты → Лаборатории → Научные сотрудники». Фактически финансировались не программы и проекты, а научные организации. Такая бюрократическая схема не позволяла эффективно использовать научный потенциал казахстанских ученых. Только за последние 20 лет у нас появилась возможность полностью перестроить систему бюджетирования науки и ставить ее на рельсы грантового и программно-целевого финансирования.

В 1995 г. Евросоюз впервые объявил совместный конкурс ИНТАС-Казахстан на очень выгодных для Казахстана условиях. С точки зрения Евросоюза это было продиктовано сохранением интеллектуального потенциала в странах СНГ. По условиям конкурса ИНТАС львиную долю научных исследований финансировал ЕС, символическую – Республика Казахстан. При этом исследовательская команда должна была состоять как минимум из 4 участников – двое из университетов стран ЕС и двое из казахстанских университетов или научных учреждений. Размер гранта составлял до 50 000 Евро продолжительностью 12, 18 или 24 месяца. В нашем случае координатором двухлетнего проекта был выбран профессор Хейкки Тенху из университета Хельсинки, руководителем проекта был я, коллаборatorами выступали профессора Иоахим Кетц из университета Потсдам и Ниязбек Хамзаұлы Ибраев из Карагандинского университета имени Е.А. Букетова. Проект был посвящен синтезу и исследованию гидрогелей полиамфолитов. Выделенные Евросоюзом средства в основном расходовались на заработную плату казахстанских участников, для покупки мелкого измерительного оборудования, химреактивов и на командировочные расходы. Перед ИНТАС отчитывались ежегодно, указывая совместные публикации, взаимные поездки, организацию семинаров и участие на

конференциях. Следует отметить, что шанс выиграть грант ИНТАС не превышал 10%. Иностранные эксперты прежде всего обращали внимание на инновационную, техническую и управленческую составляющую проекта. При оформлении заявки на грант ИНТАС самым трудным моментом для казахстанских ученых был поиск координатора и коллаборатора из западных университетов. В этом плане мне сильно повезло. С проф. Хейкки Тенху я был знаком с 1986 г., когда впервые посетил Университет Хельсинки, а проф. Иоахим Кетц в 1987 проходил трехмесячную стажировку в нашей лаборатории по Программе обмена между СССР и ГДР. В 1997-2000 годы был объявлен открытый конкурс ИНТАС (INTAS Open) на исследовательский грант, финансированный Евросоюзом. Наш Институт был вовлечен в состав трех проектов INTAS Open, посвященных «умным» полимерам и полимерным материалам для биотехнологии и новым полимерным системам для биоразделения. В этих проектах принимали участие 14 исследовательских команд из Швеции, Финляндии, Германии, Бельгии, Израиля, России, Казахстана, Словении, Румынии. В 2002-2003 годы на базе Семипалатинского университета имени Шакарима и частного учреждения «Институт полимерных материалов и технологий» было организовано два Международных семинара ИНТАС, посвященных решению экологических проблем Семипалатинского испытательного полигона (СИП) «Development of rehabilitation methodology of environment of the Semipalatinsk region polluted by nuclear tests» и «New generation of smart polymers and polymeric materials for biotechnology and environment protection». Последующий проект ИНТАС-Казахстан (2004 г.) был посвящен предотвращению ветровой миграции радионуклидов из поверхностных почв СИП с участием ученых и специалистов Швейцарии, Германии, России, Украины, Казахстана и Белоруссии. К сожалению, проект не получил дальнейшего развития в связи с несвоевременным выделением финансовых средств правительством РК. В рамках Шестой (2003 г.) и Седьмой (2007 г.) Рамочных Программ Европейского Союза наши проекты не набрали порогового балла. Тем не менее в 2020-2024 годы мы стали участниками

Международного проекта Европейского Союза «Horison-2020». Таким образом, благодаря гранту ИНТАС Европейского Союза, 6 сотрудников ЧУ «Институт полимерных материалов и технологий» стали кандидатами и докторами наук. Следует также отметить гуманитарную помощь американского химического общества для Института. В период информационного голода, начиная с 2001 г. в течение многих лет мы получали книги и журналы по полимерной химии.

В 1994 г. меня пригласили сначала на должность заместителя Главного ученого секретаря Президиума НАН РК, затем предложили должность начальника Управления международных связей. Поработав в Президиуме НАН РК пару с лишним лет, в 1996 г. я был приглашен на кафедру химии высокомолекулярных соединений КазГУ имени аль-Фараби на должность research professor (профессор-исследователь). Как отмечает профессор университета Рединга В.В. Хуторянский в своей статье «Открывая новые страницы физической химии гидрофильных полимеров: к 70-летию профессора Саркыта Елекеновича Кудайбергенова», на кафедре мной были инициированы и проведены широкомасштабные исследования стимул-чувствительных водорастворимых (со)полимеров и их гидрогелей, интерполиэлектролитных комплексов, интерполимерных комплексов, стабилизированных системой водородных связей, а также полимерных пленок на их основе. В этих исследованиях принимали активное участие В.Б. Сигитов, Г.А. Мун, В.В. Хуторянский.

Летом 1998 г. по приглашению профессора Е. Цушида (E. Tsuchida), прекрасного друга и соратника академика Е.А. Бектурова, я находился в университете Васеда (Япония). Несмотря на докторскую степень и профессорское звание в течение трех месяцев занимался исследованием ионной проводимости комплексов гидрогелей поливиниловых эфиров гликолей с ионами щелочных металлов и опубликовал одну совместную статью с японскими коллегами. Профессор Цушида, как активный член химического и полимерного общества Японии, заложил фундамент нового научного направления по макромолекулярным комплексам (**M**acro**M**olecular **C**omplexes (**MMC**) и стал ини-

циатором проведения Международных симпозиумов по ММС под эгидой ИЮПАК (Союз чистой и прикладной химии), начиная с 1985 г. Основал общество кровезаменителей Японии и посвятил свои последние годы созданию и исследованию «искусственной крови». Ко мне он относился с большой теплотой, почти по-отечески. Однажды даже перевел мои имя и фамилию с японского как «талантливый человек, спустившийся с гор». Насчет таланта ничего не могу сказать, но то, что я родился у подножья горы «Тарбагатай» − сущая правда.

Несколько слов о моих талантливых учениках, добившихся больших успехов на научном поприще. В 1997-1998 годы для магистрантов первого года обучения я читал общий курс лекции по организации научных исследований, делился своими знаниями и опытом участия в международных проектах, рассказывал о премудростях написания и публикации научных статей в рейтинговых журналах. Среди магистрантов особый интерес к моим лекциям проявлял мой талантливый ученик Виталий Хуторянский – выпускник КазГУ (1996 г.), ныне профессор школы фармации университета Рединга (Англия). Его научные достижения воистину впечатляют! За достаточно короткий срок своей научной карьеры он достиг очень больших высот: стал научным руководителем года (FindAPhD, 2020), получил награду за лучшую статью в журнале Polymers MDPI (2020), премию Sentinel of Science от Publons за экспертную оценку в области химии (2016). Он является почетным профессором Казанского государственного медицинского университета (2017), Университета имени Шакарима (2014) и Государственного медицинского университета города Семей (2012), Карагандинского университета имени Е.А. Букетова (2024), он член Королевского химического общества (FRSC, 2015), награжден медалью Макбейна (2012) от объединенного комитета Королевского химического общества (группа по изучению коллоидов и интерфейсов и группа по коллоидной и поверхностной химии) и Общества химической промышленности, Великобритания (2012 г.), удостоен премии Национального центра научной информации, как наиболее цитируемый казахстанский автор, живущий за

рубежом (2010). Мои совместные исследования с В. Хуторянским в основном посвящены интерполимерным комплексам, полимер-протектированным наночастицам металлов, мукоадгезивным полимерам и контролируемой доставке лекарственных препаратов с помощью стимулчувствительных полимеров. Он является истинным патриотом Казахстана, подготовил дюжину докторов PhD в качестве иностранного соруководителя. Я очень горжусь им!

Расскажу еще об одном своем талантливом ученике – профессоре Texas Tech University (США) и Назарбаев Университет – Нуршат Нурадже. Мое знакомство с ним состоялось через моего молодого сотрудника – Дидуха Александра Геннадьевича, который в 2001 г. прошел трехмесячную стажировку у хорошо знакомого профессора Пола Дубина (Paul Dubin) в Indiana University-Purdue University, Indianapolis (США). Поездка А. Дидуха в США состоялась при финансовой поддержке американского химического общества, членом которого я являлся в 2001-2003 гг. Поскольку это было его первая заграничная поездка, то Нуршат всячески помогал ему в решении научных проблем, включая житейских. Сам Нуршат попал к П. Дубину через Академию наук КНР, пройдя очень сильный отбор среди претендентов. Нуршат окончил бакалавриат химического факультета Синьцзяньского университета (г. Урумчи) в 1990 г., затем получил степень магистра в 1998 г., работал на месторождении «Карамай», где занимался проблемами увеличения нефтедобычи. Докторскую диссертацию выполнял в Институте физико-химических исследований АН КНР в г. Ланчжоу. В 2000 стал победителем конкурса АН КНР для зарубежной поездки и получил возможность продолжения научных исследований в США в New York City University. С 2001 г. он являлся постдоком и исследователем в Массачусетском институте технологии (г. Бостон), Virginia Tech University, ассистентом профессора в Texas Tech University. Первый раз Нуршат посетил Казахстан в 2011 г. по моему приглашению для участия в Международном семинаре «Полимеры специального назначения для охраны окружающей среды, в нефтяной индустрии, био-, нанотехнологии

и медицины», организованном в КазНИТУ имени К.И. Сатпаева. С этих пор началось наше плодотворное сотрудничество. В 2012-2015 годы я включил его в проект коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов». Результатом наших совместных исследований стали более 20 глав книг, обзоров и статей, опубликованных в журналах с высоким импакт-фактором, таких как *Soft Matters, Polymers*, *Langmuir, Energy Reports, Journal of Materials Chemistry,* Advanced Composites and Hybrid Materials, *Nanoscience & Nanotechnology-Asia, Current Inorganic Chemistry, Polymer Bulletin,* New Journal of Chemistry и в других изданиях, включая казахстанских. С сентября 2019 г. по настоящее время Нуршат работает по контракту в Назарбаев Университет ассоциированным профессором кафедры химической инженерии и цифровых наук, а также руководителем отдела возобновляемых источников энергии и материаловедения Национальной лаборатории Астана. В 2023 г. Нуршат вошел в состав Национального совета по науке и технологиям при Президенте Республики Казахстан, который призван способствовать совершенствованию управления национальной научной системы и выработке рекомендаций по определению приоритетов дальнейшего развития государственной политики в области науки и научно-технической деятельности. Область его научных интересов охватывает синтез функциональных материалов для возобновляемых источников энергии, разработку гетероструктурированных фотокаталитических систем для преобразования солнечной энергии в водородную, проектирование различных электропроводящих полимеров, включая 2D и 3D структуры. В 2008 г. за успешное выполнение докторской диссертации Нуршат награжден «серебряной медалью аспиранта». В 2015 г. за уникальные исследования в области нанонауки журнал *Cognizure* выбрал его лауреатом премии Джозефа Ванга, а журнал *Journal of Materials Chemistry A* в 2018 г. назвал одним из авторитетных исследователей Королевского химического общества. В 2017-2019 годы он удостоен стипендии летнего курса ВВС США. В 2021 году за вклад в казахстанскую науку

награжден Почетной грамотой МОН РК. Советую читателю прочесть газеты «Айқын» (№98 (3170) 1 шілде, 2017 сенбі) и «Egemen Qazaqstan» (2024 ж., 15 қараша, 13 бет), «Түркістан» (№1-2 (1638), 5 қаңтар 2026 жыл, 11 бет), в которых опубликованы статьи о нем «Әлемді мойындатқан Нұршат», «Білікті мамансыз ғылым дамымайды», «Шетелдегі қазақ ғалымдарын шақырудың бірегей» жобасы керек». Со своей стороны я очень рад, что своевременно пригласил Нуршата в Казахстан, ознакомил с некоторыми казахстанскими учебными заведениями, представил многим известным казахстанским ученым, которые способствовали раскрытию его таланта и интеллектуального потенциала. Следует признать, что наших ученых, находящихся за рубежом предостаточно и миссия научного сообщества заключается в возвращении некогда «утекших мозгов» и интеграция их в казахстанскую науку для ускорения научно-технического прогресса и воспитания нового поколения талантливых ученых.

Хотел бы упомянуть самого молодого талантливого ученика-доктора PhD (2018) Искандера Гусенова. Ему всего 30 лет, но он уже добился значительных успехов в области нефтяной инженерии. Будучи еще студентом КазНИТУ имени К.И. Сатпаева, он был вовлечен в науку через руководимую мной лабораторию инженерного профиля. В 2011-2015 годы принимал участие в проекте коммерциализации «Разработка и внедрение технологии полимерного заводнения для увеличения нефтеотдачи пластов» и в проведении опытно-промышленных испытаний на месторождениях «Кумколь» и «Карабулак». В соавторстве имеет более 50 научных трудов, опубликованных в журналах с ненулевым и высоким импакт-фактором и в республиканских изданиях, 7 патентов РК. Владеет английским языком в совершенстве, знает арабский язык, увлекается горным туризмом. В 2016 г. стажировался в Texas Tech University, в 2021-2022 годы – New Mexico Institute of Mining and Technology (США). В 2019 г. подготовил и читал цикл лекции на тему: «Применение природных и синтетических полимеров в процессе интенсификации добычи нефти» для специалистов ТОО «Научно-исследовательский институт технологий добычи и бурения «КазМунайГаз» с

последующей выдачей сертификата. В 2021 г. читал лекцию для студентов университета Хельсинки на тему: «Polyelectrolytes for Enhanced Oil Recovery». Гусенов И.Ш. принимает участие в выполнении 4 грантовых проектов МОН РК. Выступал с устными и стендовыми докладами на Международных и республиканских конференциях в Актау, Томске, Высоких Татрах (Словакия), Лозанне (Швейцария), Шанхае (КНР). В число своих учеников я также причисляю Б.Ж. Жаппасбаева, А.Н. Кливенко, А.В. Шахворостова, А.Е. Аязбаеву, Н. Мұхаметғазы, которые выполняли свои научные исследования в ЧУ «Институт полимерных материалов и технологий» и стали докторами философии (PhD). В настоящее время мои ученики успешно трудятся в Англии, Германии, Саудовской Аравии, США, Национальных компаниях «КазМунайГаз», «КазТрансОйл», казахстанских ВУЗах и НИИ.

Как отмечает лауреат Нобелевской премии, академик П.Л. Капица (см. Афоризмы и размышления П.Л. Капицы. Москва, изд-во Моск. физ.-тех. ин-та, 1994. 152 с.), научная работа относится к той области деятельности человека, которая может успешно развиваться только теми, кто имеет творческие дарования, и только небольшое число людей, обладающих творческими способностями, могут внести неоценимый вклад в науку. Самое ценное в науке достигается творческим процессом, а успех определяется талантом учёного. Самое важное и трудное в организации науки – это отбор действительно наиболее творчески одарённой молодежи и создание тех условий, при которых её талант мог бы быстро развернуться в полную меру. Для этого нужно уметь оценивать творческие способности у молодежи, когда она только начинает свою научную работу. Творчество учёного не может успешно развиваться вне коллектива. Не одни ньютоны и дарвины делают науку. Их достижения были бы совершенно невозможны, если бы они не опирались на целую массу полу-Ньютонов и полу-Дарвинов, имена которых поглотила история, но деятельность которых оставила свой след в науке. Последней приходится решать не одни лишь мировые и основные вопросы; есть множество

менее общих, но важных и крупных задач, для решения которых необходимы эти люди. Научные открытия мирового значения опираются на результаты, полученные этими второстепенными участниками научного дела, они же необходимы, как необходима армия для генерала. И к этим учёным второго, третьего и более низших классов надо подойти внимательно и заботливо; надо учитывать их психологию и создавать для них подходящую почву, а также тщательно подбирать. Их основная характеристика мало чем отличается от характеристики гения, только их творческие силы не так велики и количество не так ограничено. Несомненно, одной из важнейших двигательных сил в развитии науки является справедливая оценка и признание личных заслуг учёного в развитии науки. Надо развивать культуру этого признания. Главную роль тут играет здоровая научная общественность. Очень важно для успешного развития науки создание благоприятных условий для развития природных талантов учёного, для этого надо делать творческую работу привлекательной. Это следует делать общественным организациям, которые, давая правильные оценки достижениям учёных, также давали бы им почувствовать, что их деятельность нужна и полезна человечеству. От себя бы еще добавил, что людям науки нужна творческая свобода, т.к. наука не может работать под постоянным «давлением».

Курьезы случаются и в научном мире, о которых впоследствии вспоминаешь с улыбкой. Один из них связан с моей длинной фамилией, состоящей из 13 букв. Она вызывает определенные трудности в запоминании и произношении для любого иностранца, а для японцев, китайцев и корейцев, тем более. При общении с коллегами из этих стран я часто представлялся, как «Кудай-сан», «Кудай-сэнсей», которые созвучны с широко распространёнными японскими именами, как «Ширай», «Тамай», «Хирай» и очень легко произносятся, и запоминаются. В Китае и Корее я представлялся еще короче, как профессор «Ку». Иногда приходится пойти и на такие маленькие хитрости, чтобы не доставлять людям неудобства и тебя легко запомнили.

Еще один курьезный случай связан с моим обращением к своим молодым сотрудникам. Я часто употребляю крылатое слово «Мырқымбай» из произведения Бейімбета Майлина «Бер қолыңды, Мырқымбай», когда критикую или выражаю свое недовольство несуразным действием в отношении к серьезному делу. Это слово прочно вошло в мой лексикон, и никто на это не обижается. В 1998 году я находился 3 месяца в Университете Васеда (Япония) в качестве приглашенного профессора для чтения лекции и проведения совместных научных исследований. В какой-то момент получил теплое и душевное письмо от своих аспирантов, которое они подписали в конце словами «Ваши Мыркымбаи».

Под конец хочу рассказать курьезный момент, случившийся с Есеном Абикеновичем в Японии (кажется, в 1988 г.). Есен Абикенович будучи в Токио поехал в Киото читать лекции по приглашению проф. Ямада. Но когда он сошел с поезда, то его никто не встретил, и он стоял на перроне пока он не опустел. В этот момент к нему подошел молодой японец и спросил: не вы ли русский профессор Бектуров? Он думал, что Бектуров – это русский ученый и никак не ожидал увидеть азиата. Почему-то японцы в то время всех выходцев из СССР представляли русскими. Это мне напоминает старинную гравюру книги Яна Гевелия «Вестник Астрономии» (1610 г), на которой художник изобразил великих астрономов разных времен, александрийского ученого Клавдия Птоломея, поляка Николая Коперника, датчанина Тихо Брагге, итальянца Джованни Баттиста Риччиоли и узбека Мирзо Улугбека, но последнего с внешностью европейца. Так что азиатов путали с европейцами еще с древних времен.

Оглядываясь на свои прожитые годы, прихожу к выводу о том, что почти полвека были отданы беззаветному служению ее Величеству науке, поиску и раскрытию некоторых тайн полиамфолитов – синтетических аналогов белков. Хотелось бы упомянуть о некоторых «белых пятнах» в химии полиамфолитов, которые вкратце описаны в моей монографии Polyampholytes in Advanced Polymer Science and Emerging Technologies. CRC Press, Boca Raton, London, New York, 2024, 286 p. Одно из них – это образование макромолекул жизни – полипептидов (или белков)

путем конденсации аминокислот. Преодоление законов термодинамики при их синтезе является сложной задачей, т.к. реакция конденсации аминокислот в водной среде, сопровождающаяся выделением молекул воды, «запрещена» как с термодинамической, так и кинетической точек зрения. Если рассмотреть синтез аминокислот в примитивных земных условиях, то важно обратиться к экспериментам Миллера-Урей (Miller-Urey), которые путем пропускания электрического разряда (прообраз молнии) через смесь воды, метана, аммиака, углекислого газа и водорода показали образование 20 аминокислот. Эти эксперименты подтвердили гипотезу Опарина о биохимической эволюции, приводящей к синтезу основных строительных блоков жизни из более простых неорганических и органических предшественников. Но вопрос: как эти аминокислоты конденсировались и образовали белки и пептиды до сих пор остается открытым, несмотря на существование различных гипотез. Читателей, интересующихся этой проблемой, отсылаю к прекрасной книге Cole L.A. Biology of Life: Biochemistry, Physiology and Philosophy. Elsevier, 2016. 184. http://dx.doi.org/10.1016/B978-0-12-809685-7.00004-6.

Полиамфолиты могли бы также представлять интерес для записи, хранения и воспроизведения цифровой информации в компьютерной науке и, в последующем, для кодирования сообщения, аналогично ДНК, хранящей генетическую информацию в виде последовательностей нуклеотидов. В принципе, двоичный код потенциально может быть реализован в структуре амфотерных макромолекул случайного строения с использованием последовательностей кислотных и основных мономеров, определяемых как 0 и 1 бит. Насколько мне известно, возможность «записи» информации на макромолекулярных цепях впервые была упомянута в 1978 году С. Я. Френкелем, который в своей знаменитой статье «Полимеры, перспективы, проблемы и прогнозы» писал, что «Недалеко то время, когда синтетические макромолекулы можно будет использовать для записи информации» (С.Я. Френкель. В книге: «Физика сегодня и завтра». Л., «Наука», 1976, с. 176-270).

Еще одним перспективным направлением в области полиамфолитов является разработка амфотерных гидрогелей, обладаю-

щих высокой ионной проводимостью, гибкостью, адгезивностью и механической прочностью, а также способностью к самозалечиванию для создания гибких, безопасных и долговечных энергетических устройств, используемых в качестве суперконденсаторов, аккумуляторов, солнечных батарей, топливных и сенсорных элементов, хранителей и преобразователей энергии.

Оценку моих достижений в науке о полимерах оставим на суд читателя. Очень надеюсь, что мои неосуществленные идеи, мысли и мечты найдут свое продолжение в трудах моих учеников и последователей. Я очень благодарен каждому, с которым столкнула меня жизнь. Одним – за ценные советы и поддержку, Другим – за пример, Третьим – за урок, Четвертым – за критику. Горжусь тем, что более полувека честно служил и продолжаю служить Ее Величеству – Науке. В завершение своих размышлений привожу такое высказывание англо-американского поэта Томаса Элиота, выпускника Гарварда, лауреата Нобелевской премии:

We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time.

Мы никогда не прекратим научный поиск
Но в конце любого исследования
Обнаруживаем, что вернулись к точке старта
И познаем это место заново.

Біз ешқашан ғылыми ізденістерді тоқтатпаймыз
Бірақ қандай да зерттеулердің соңында
Бастапқы межеге қайта оралып
Оны қайтадан меңгереміз.

Философский смысл этого четверостишья, в моей интерпретации, заключается в стремлении ученого неустанно искать и раскрывать тайны природных явлений, при этом постоянно возвращаясь к стартовой точке уже осознанно, в результате накопленных знаний и опыта, чтобы познать до конца ранее начатое и развивать его дальше.

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