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Review

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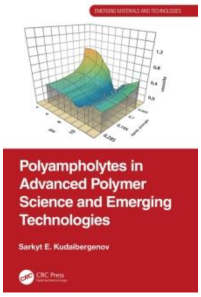
Catalytic Properties of Polyampholytes, Polyampholyte-Metal Complexes, Polyampholyte-Metal Nanoparticles and Polyampholyte-Enzyme Conjugates: a Mini-Review

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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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 chemomechanical 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.

Contents

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 (Fig. 1).

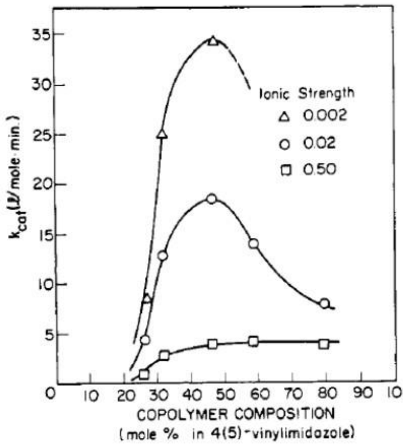


Figure 1. Effects of VI-*co*-AA composition and ionic strength on k_{cat}-catalyzed solvolysis of ATMAI.
Solvent, 28.5 % ethanol–water; pH, 9.0; T, 25 °C.
Reprinted with permission from Ref. [21] (Overberger C. G., Maki H. Esterolytic catalysis by copolymers containing imidazole and carboxyl functions.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

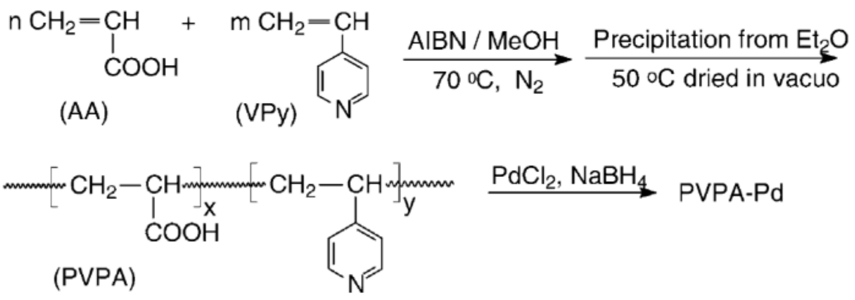


Figure 2. Preparation of poly(4-vinylpyridine-*co*-acrylic acid) copolymer (PVPA) and its palladium complex. Reproduced with permission from Ref. [33]

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 (Fig. 3).

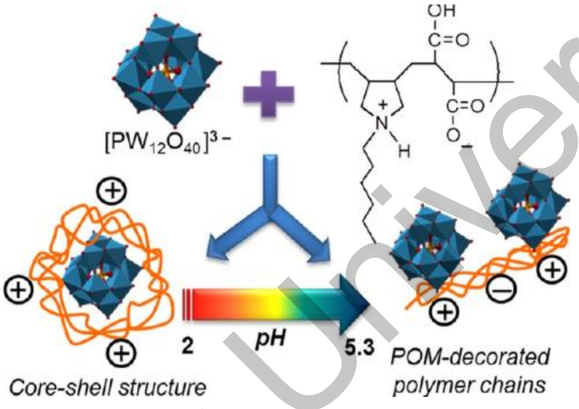


Figure 3. Stabilization of $[PW_{12}O_{40}]^{3-}$ by (poly-N,N-diallyl-N-hexylamine-*alt*-maleic acid) and formation of pH dependent core-shell structure and POM-decorated polymer chains. Reproduced with permission from Ref. [34] (Raj G., Swalus C., Guillet R.A., Devillers M., Nysten B., Gaigneaux E.M. 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.

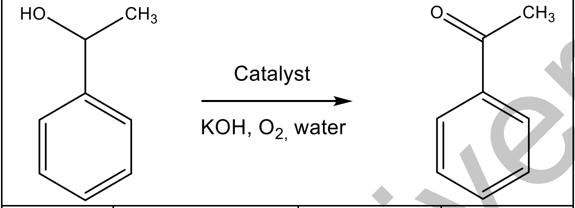
Polyampholyte-Protected Metal Nanoparticles in Catalysis

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] (Fig. 4).

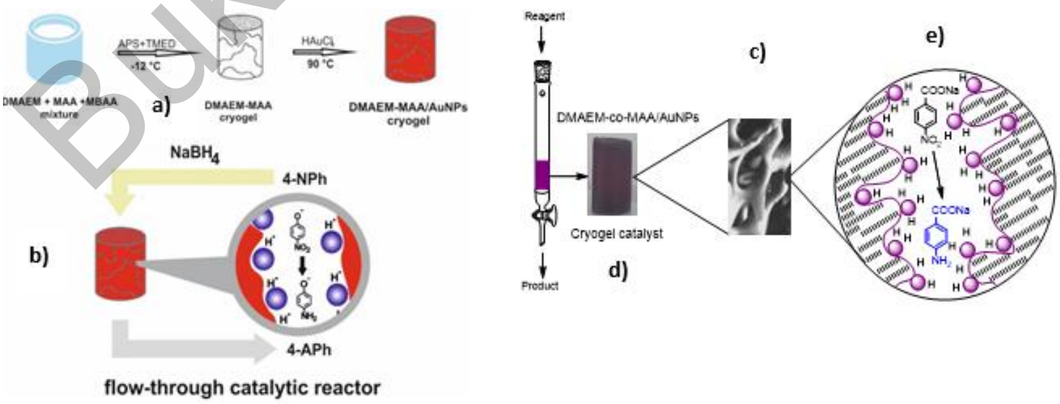


Figure 4. Fabrication of macroporous amphoteric cryogel based on N,N-dimethylaminoethylmetacrylate and methacrylic acid (DMAEM-*co*-MAA) with immobilized AuNPs (*a*) and schematic representation of monolith flow-through catalytic reactor used for hydrogenation of 4-NP (*b*) and *p*-NBA (*c*) over DMAEM-*co*-MAA/AuNPs 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 (Fig. 5).

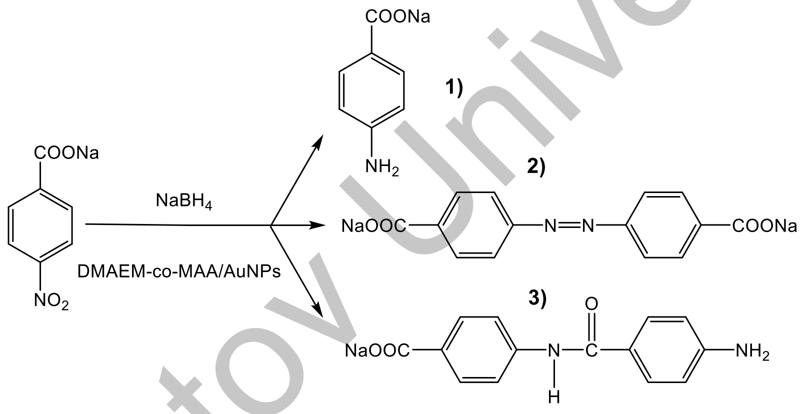


Figure 5. Hydrogenation products of *p*-nitrobenzoic acid sodium salt over DMAEM-co-MAA/AuNPs catalyst. 1) *p*-aminobenzoic acid sodium salt; 2) *p,p*'-azodibenzoate; 3) sodium 4-(4-aminobenzamido)benzoate. Reproduced with permission from Ref. [46]

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 (Fig. 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, iso-propanol 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.

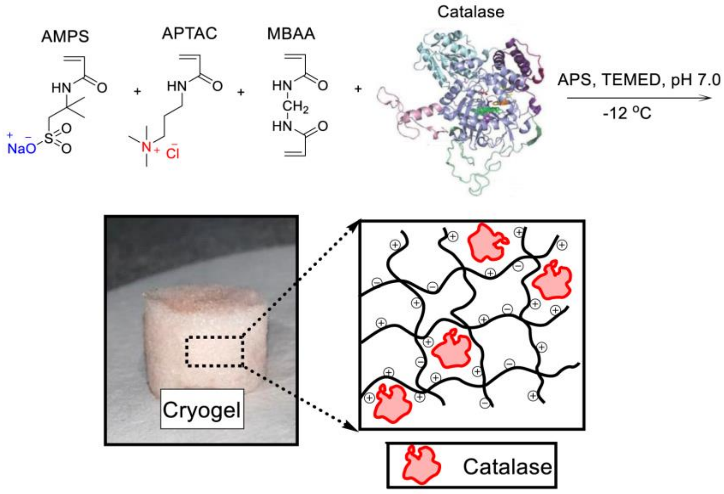


Figure 6. Synthetic protocol of encapsulation of catalase within APTAC-AMPS amphoteric cryogel matrix. Reproduced with permission from Refs. [49, 50]

The batch type reactor was also applied for the oxidation of ethanol by catalase embedded into a polyampholytic 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
$TON \cdot 10^{-7}$ [a)]	18.3	17.9	18.4	18.2	11.3	11.4
$TOF \cdot 10^{-7}$ [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] (Fig. 7).

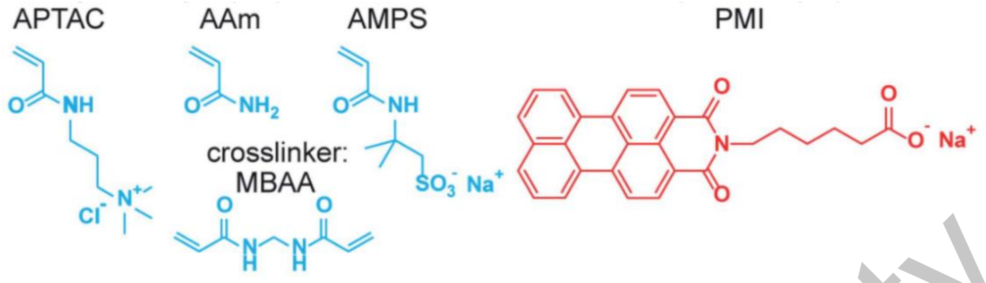


Figure 7. Anionic (AMPS), cationic (APTAC), neutral (AAm) monomers, crosslinker (MBAA) and perylene monoimide (PMI)-based-chromophore used for synthesis of polyampholyte hydrogel. Reproduced with permission from Ref. [54]

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.

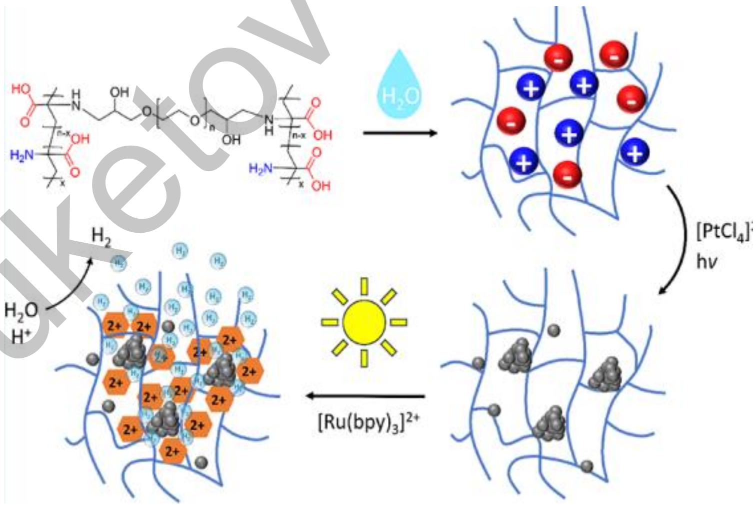


Figure 8. Electrostatic attachment of $[Ru(bpy)_3]_{2+}$ within the PDha-based amphoteric hydrogel, in situ formation of PtNPs and the photocatalytic hydrogen evolution reaction carried out in a polymer network. Reproduced with permision from Ref. [55]

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 μmol· g^{-1}·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 (Fig. 9).

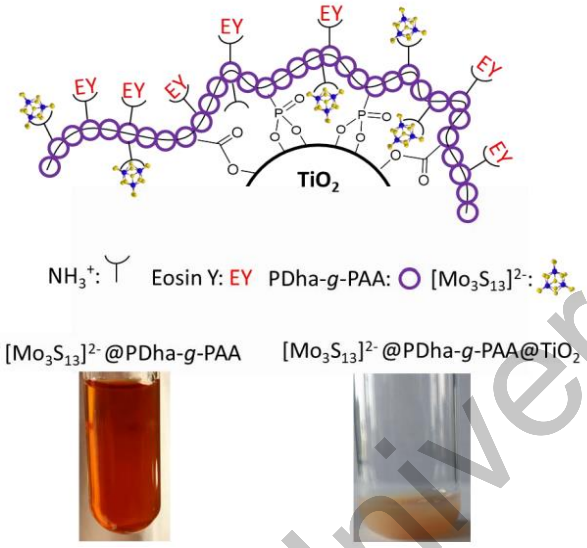


Figure 9. Schematic illustration of proposed interactions between PDha-*g*-PAA and TiO_2, Eosin Y, and $[Mo_3S_{13}]^{2-}$. Reproduced with permision from Ref. [57]

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·g^{-1}·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 porosity, 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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