Application of Polymer Complexes

Esen A. Bekturov

Institute of High Technologies, 71 Maulenov Str., 050000, Almaty, Kazakhstan

Abstract

Applications of polymer complexes with different low- and highmolecular compounds in catalysis, medicine, environment protection, sorbtion and structurization processes etc. are briefly reviewed.

Introduction

Compositions on the basis of polymer complexes and associates attract great attention from scientific and practical points of view [1, 2]. Polymer complexes have a wide application in different fields: polymer solid electrolytes; macromolecular catalysts; drug delivery systems; membranes; metal and organic ions sorption; matrix polymerization; structure formation of soils; microencapsulation; purification, separation and stabilization of proteins and enzymes [3,4]. Let us consider some of this directions more detailed.

Solid Polymer Electrolytes

Complexes of oxygen-, nitrogen-, sulfur-containing polymers with alkali and alkali-earth metal ions possess remarkable ionic conductance [5,6].

Most famous systems are poly(ethylene glycol) – lithium salts with ionic conductivity of 10^{-4}-10^{-3} ohm/cm order.

The properties of such complexes are well studied in organic solvents, as methanol, acetonitrile, dimethylformamide etc. It is interesting that temperature of melting of complexes obtained from different solvents differ one from other for 30-50 ºC. Melting temperature also influenced by light action during synthesis of complexes.

Ionconducting complexes are forming due to donor-acceptor interaction of electron pair of oxygen, nitrogen atoms of polymer chains with alkali metal cations. Properties of complexes depend on the nature of cations and anions. More stable complexes are forming for lightly polarized anions (J^-, ClO^{4-}, BF^{4-}, SCN^- etc.) and cations of average dimensions (Na^+, K^+), probably, due to adjustable for size of poly(ethylene glycol) spiral. In [7] the effects of stretching on ion transport with LiX-PEO solid polymer electrolytes were studied. The stretching process was found to increase the ion conductivity by about a factor of 5 to 40, depending of nature (cristallinity) of salts.

Ionconducting polymer complexes may be used as solid electrolytes for batteries or accumulators. They have next advantages [6,8]:

1. High mechanical properties, elasticity, technological convenience.
2. Ecological safety, non-leakage.
3. High energy density-270 Wh/dm^3.
4. Low rate of discharge.
5. Wide temperature regime from – 70 to 140 ºC.
6. Absence of passivation.
7. High cyclability.
8. High coefficient of use about 80%.

Some recommendations were elaborated for obtaining good polymer electrolytes:

1. Better to use amorphous flexible polymers with heteroatoms in chain, which are capable to interact with metal ions.
2. Preferably to use alkali metal salts good soluble in polymer matrix with small fast cations, usually Li^+.
3. Better to conduct synthesis in media with low donor ability.

Macromolecular therapeutic systems

Polymer-drug associates attract big attention by

*corresponding author. E-mail: ebekturov@mail.ru

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possibility to regulate the rate of release of drug and prolongation of drug action. Regulation factor may be velocity of dissolving or swelling of polymer matrix, pH, T, etc [9,10].

Compositions of polyvinyl(alcohol) with clofeline (hypotensive drug) were obtained. This composites have such advantage: its release drug slowly (during 24 hours) and not sharp, but gradually [9]. Also thermoresponce systems: hydrogel of polyvinylcaprolactame-pharmazine (antibacterial substance) was obtained. At the room temperature drug release from gel quickly, but at increase of temperature to 37 ºC, rate of release of drug remarkable decreases due to strong shrinkage of gel volume. Very interesting are drug delivery systems with cyclic release of drugs at periodic increase and decrease of temperature [11,12].

Interpenetrating networks of thermosensitive polymer hydrogel comprising poly (dimethyl-acrylamide) and poly (acrylic acid) with possible intermolecular hydrogen bonding was used for pulsatile ("on-off") drug (ketoprofen) release: "on" at higher temperature and "off" at lower temperature [13].

Interpolymer complex poly(methacrylic acid)-poly(ethylene glycol) is used as depo of theophyllinum and chinidine. Drugs going out gradually during 12-24 hours, i.e. prolonged comparably with tablet form (4 hours) [14]. Prolongation of anestetic action of richlokain was obtained by immobilization of drug to carboximethylcellulose and poly(vinylpirrolidone) [15] and to polyacrylate hydrogel [16].

Li J. et al. [17] suggested injectable drug-delivery system based on supramolecular inclusion complexes formed by poly(ethylene oxide) and cyclodextrin.

Medical-biological properties of polymer-metal complexes of vinylpirrolidone-acrylic acid copolymer with Co^{2+}, Zn^{2+}, Fe^{2+} [18] were studied. The investigation of sharp toxicity, immune- and hemo-stimuly activity of this complexes shows, that its toxicity is low possessing ability of simultaneous stimulation of the immunic response and blood creation.

Polyelectrolyte complexes (PEC) from poly (styrenesulfonate) sodium and poly (vinylbenzyltrimethyl ammonium) chloride were used as anticoagulant materials [19]. Surfaces covered by this PEC remarkable reduce adhesion and aggregation of thrombocitas at contact with blood flow. In this case PEC exhibits heparin-like activity, especially at small excess of negative charge. These properties of PEC promote its application in membranes for devices "artificial kidney" or "artificial liver".

One of directions of polymer complexes application is obtaining of artificial blood substitute – oxygen carrier [20]. It is hem complex with polyvinylimidazole. Life time of this complex in solution equal is about 25 min at MM>10^4. It increases up to 5 hours with adding dextran or hialuronic acid. Ability of such complexes to bind oxygen is close to hemoglobin in red blood gulf.

Polyelectrolyte complexes are used as dressing due to its high sorption ability, moisture-supporting properties, low adhesion to wounds [21]. Such material was obtained by treatment of tripsin-containing chitosan film by surfactant. Obtained PEC were examined and show good results: fast healing of wounds with smooth epitelization.

Membranes from PEC

Polyelectrolyte complexes are successfully used as good permeable and selective membranes [3, 22]. Its are perspective in "artificial kidney" and "artificial liver" devices due to its antithrombogenic properties and high dialysis coefficients for blood toxins. Also complex membranes are used in ultrafiltration processes for cleaning of biological liquids (blood, urine). Permeability of PEC membranes is ~ 15 times higher than that of the usual cellulose membranes.

It can be checked that in last decade new methods of obtaining complex membranes were suggested.

1) Film formation on the board of two nonmixing liquids [23]. This process include only one stage and ordered polymer structures are forming.

2) The so-called "the electrostatic self-assembly" method [24]. In this method substrate with charged surface in turn is dipping in dilute solutions of polycations and polyanions. In one cycle two layers (positive and negative charged) are forming. It is possible to obtain film consisting of 200 layers.

It is known macromolecular therapeutic systems for release of insulin at increasing of glucose concentration [25] with use of polyelectrolyte complex as a coat of microcapsule. Complex of poly(acrylic acid) gel with chitosan was used for microcapsulation of laevomycetinum [26].

Matthew H.W.T. et al. [27] reported the use of membrane based on polyelectrolyte complexes between chitosan and anionic polymers in cartilage tissue engineering.

Novel approach to obtain high metal sorbtion capacity was developed [28] utilizing a membrane

containing chitosan and immobilized reactive dye Yellow-2. This composite membrane was used in the removal of heavy metal ions from aqueous solution. The maximal adsorbtion capacities were 64.3 mmol/m^2 for Pb (II); 52.7 mmol/m^2 for Hg (II) and 39.6 mmol/m^2 for Cd (II). More then 95% of adsorbed metal ions were desorbed with HNO^3 solution and adsorbtion capacities of membranes did not significantly changed during 5 cycles.

Polymer catalysts

Complexes of polymers with metal ions are used as catalysts of different processes. Advantage of such systems is uniform distribution of metal particles in catalysts volume and possibility for multiple use of catalysts characterized by turnover number [29,30].

Polymer basis realizes the matrix isolation of catalytic active sites and stabilization of the homogeneous dispersion state. Polymer matrix prevents aggregation of active sites and washing out metal particles by the flow of reagents. It allows the long time function of polymer catalysts without loss of activity, multiple use of the same system. The turnover number for one atom of palladium may reach ten thousands.

In some cases polymer stabilizes colloid dispersions of metal particles. N.Toshima et al. obtained nanosized catalysts by reducing of Pt in alcohol solutions of poly(vinylpirrolidone) [31]. Colloidal palladium (~ 3-4 nm) included in the polyelectrolyte complex of poly(acrylic acid) – poly(ethylene imine) exhibits high selectivity (98%) but shows low activity during hydrogenization of cyclopentadiene.

E. Tsuchida [32] and V. Kabanov [33] groups elaborated method of synthesis of polymer sorbents adjusted to definite metal ions. Complexes of such sorbents with Co^{2+} ions are catalyst of oxidation of styrene and ethylbenzene. Its may be used repeatly without loss of catalytic activity. Active, stable and selective catalysts of allyl alcohol hydrogenization were obtained on the basis of palladium complexes with poly(vinylpyridine), process leads to 98% conversion [34].

V. Kabanov et al. applied a complex of poly (oxyethylene) ether of hystidine with poly (acrylic acid) as catalysts of hydrolysis of complex ether [35].

The catalase-like activity of complexes of amphoteric polyelectrolyte vinylimidazole-acrylic acid with Cu^{2+}, Co^{2+} was studied during hydrogen peroxide decomposition [36]. In the absence of metal ions polyampholyte itself does not exhibite the catalytic effect but in the presence of metal ions forming polyampholyte-metal complex possesses higher catalytic activity than respective low molecular aqua- and hydroxocomplexes.

Biomimetic catalysts with high catalase activity in hydrogen peroxide decomposition were obtained on the basis of ternary complexes: simple or complex ferrum ions – polyethylene imine gel – dodecylbenzylsulfate [36a] and ferrum (III) chloride – polyacrylic acid gel – ethylene diamine [36b]

Polymer catalysts for hydrogenization and oxydation consisting of Pt, poly(ethylene glycole) and metal oxydes sorbents were suggested [37].

Structure formation of soils

Complexes between unlike macromolecules are used for structure formation of soils. Interpolymer complexes of carbomethylcellulose with urea-formaldehyde resins are suggested for structure formation of soils, combat with wind and water erosion, creation of antifiltration screens for economy of irrigating water [38].

It is interesting an example of the use of polymer complex hydrolyzed polyacrylonitrile-poly(dimethyldiallyl ammonium chloride) for sedimentation and cementation of radioactive dust in region of Chernobyl atomic power station [39].

Interpolymer complexes, stabilized by hydrogen bonds poly(acrylic acid)-poly(ethylene glycol), poly(acrylic acid)-poly(vinylpirrolidone) and polyelectrolyte complexes poly(acrylic acid)-poly(dimethyldiallyl ammonium) chloride were used for structurization and extraction of radioactive Sr from soil of Semipalatinsk nuclear polygon [40,41].

Next recommendations were suggested:

1. Solution concentrations must be within 10^{-4}-10^{-2} mol/l.
2. Better one is irrigation method.
3. Desirable to support equimolar ratio of components and pH≤4

Important result is accumulation of Sr in treated soils (9,34 mg/l comparable with control 2,31 mg/l). It may be explained by formation of ternary polymer-polymer-Sr complex in the forming film at soil surface. The same results were obtained for polyelectrolyte complexes.

Sorption processes

Interaction of functional polymers with metal ions with formation of polymer-metal complexes is widely used in waterprepairing, cleaning of drinking water, extraction of metal ions from industry drain water.

It was shown that interpolymer complex of poly(styrenesulfonate) sodium and quoternized poly(vinylpyridine) extracts Cu^{2+} ions more effective than individual components. Adsorption by poly(styrenesulfonate) sodium is equal almost zero, by quoternized poly(vinylpyridine) – 11%, by PEC (1:1) – 91,7% [1].

Use of ternary polyelectrolyte-surfactant-metal complexes remarkably increases the sorbtion ability of polymers [42].

K. Geckeler et al. suggested for extraction and separation of ions of toxic metals LPR method (liquid-phase polymer retention) including sorption of metal ions by water soluble polymers and ultrafiltration of forming complex [43,44]. This method was successfully used for extraction of Ag^{+} and Hg^{+} ions from dirty water. Also above mentioned adjusted sorbents for the definite type of ions are interesting [32,33].

It was shown [45] that Zn, Cu and Pb ions can be included into polyelectrolyte complexes of poly(vinylimidazole) with polyacrilic or poly(methacrylic acides). The reversibility of polymer-polymer complexes precipitation makes promising to use them for concentrating of metal traces in water.

Complex formation of polyampholytes with metal ions may be used for its selective sorption and desorption in the isoelectric point [46]. Very perspective is the use of cross-linked functional polymers-hydrogels for extraction of metal ions, phenols, dyes from dirty water. It was shown that extraction of Cu^{2+} ions from solution by polyethylene imine gel increases in the presence of surfactant [47].

Complex systems consisting of poly(ethylene imine), metal ions and unitiol were studied. On this basis it was suggested polymer-unitiol composition for selective concentration and precipitation of metal ions [48].

Unusual applications of polymer complexes

Polymer hydrogels can sharply change its volume under influence of pH, T and also at complex formation with different high- and low-molecular compounds [49]. So filament from slightly cross-linked poly(methacrylic acid) sharply shrinked by interaction with poly(ethylene glycole), modeling the behavior of muscles. Stripe of polyelectrolyte gel complex with oppositely charged surfactant binds in the electric field. On this basis different molecular machines were demonstrated [50].

Methods of obtaining and properties of artificial muscles based on conducting polymers were considered [51].

The possibility of obtaining of electric current was shown in system hydrogel of poly(ethylene imine) – $CuSO^{4}$ [52].

The gel in solution saturated by Cu2+ ions after the initial deformation in electric field leads to a property to generate electric current of opposite direction after switching an internal electric power. It turn to be a kind of electric current generator or accumulator. It occurs due to asymmetry of electric double layer magnitude at two opposite sides of the gel specimen. The electric current influence leads to network charge changing due to electrophoretic motion of copper ions.

So as one can see, polymer complexes have wide and sometimes unusual fields of application.

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