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Synthesis of Hybrid Materials in Polyelectrolyte Matrixes: Control over Sizes and Spatial Organization of Metallic Nanostructures

A. A. Zezin

Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,
Profsoyuznaya ul. 70, Moscow, 117393 Russia

Faculty of Chemistry, Moscow State University, Moscow, 119991 Russia

e-mail: aazezin@yandex.ru

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Abstract—This review is concerned with the synthesis of hybrid materials in solutions, suspensions, and gels of polyelectrolytes with emphasis being placed on the role of interaction between functional groups of macromolecules and ions/surfaces of metals in the control over the processes of nucleation and growth of nanoparticles. The use of several macromolecules carrying nonionogenic groups for the effective control over the sizes and shapes of nanoparticles is exemplified. As the main method for the synthesis of metal nanostructures in colloidal systems, a method based on the reduction of metal ions is discussed. Mechanisms and conditions determining the assembly of metal—polymer nanocomposites of various architectures in polyelectrolyte matrixes and organized polymer systems are considered.

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INTRODUCTION

Metal-containing polymeric compounds possess unique optical, electrophysical, and magnetic properties and high chemical and catalytic activities and serve as an important basis for the creation of various functional devices [1–22]. Nanohybrids based on synthetic and natural polyelectrolytes containing ultradispersed particles of noble metals, silver, and copper manifest antibacterial and fungicidal properties and show promise as materials for medical applications [2, 6, 11, 13, 23–32]. In fact, there is demand for the entire size range of nanoparticles: from nanometers in catalytic systems to tens of nanometers for magnetic materials, nonlinear optical devices, and biosensors. The key problem encountered in the synthesis of nanocomposites consists in the tuning of size, spatial distribution, and morphology of nanoparticles. The stabilization of nanoparticles in polyelectrolyte matrixes makes it possible to prevent their oxidation and aggregation [2–5, 7, 9–12, 18, 19, 31]. The ability of functional groups of polyelectrolytes to bind metal ions provides wide possibilities for their use as precursors in the synthesis of polymer—metal hybrids [3, 5, 7, 9–16, 18, 19, 31–35].

SYNTHESIS OF NANOPARTICLES VIA REDUCTION OF METAL IONS

The assembly of metallic nanoparticles by the reduction of metal ions is a general method for the controlled synthesis of metallic nanostructures in systems based on polyelectrolytes. This method provides precise tuning at the stages of nucleation and growth of nanoparticles owing to variation in thermodynamic and kinetic parameters [3, 5, 9–15, 17, 33, 34].

The formation of nanoparticles may occur via homogeneous or heterogeneous nucleation. In the case of homogeneous nucleation, short-lived charged clusters are formed at the initial stage of reduction of metal ions [12, 36]. The processes of growth and coagulation of clusters assist in the formation of larger structures up to the appearance of quasi-metallic particles (8–15 atoms) [19, 37] that ensure the interfacial boundary for the sorption of metal ions and serve as nuclei for the growth of the metallic phase [12]. The homogenous nucleation [12] includes the stages of formation of neutral metal atoms from ions,

$$\mathrm{Mt}^{x+} \rightarrow \mathrm{Mt}^{(x-1)+} \ldots \rightarrow \mathrm{Mt}^{0}, \qquad (1)$$

and the subsequent aggregation of atoms and ions in clusters,

$$\mathrm{Mt}^{0} + \mathrm{Mt}^{x+} \rightarrow \mathrm{Mt}_2^{x+}. \qquad (2)$$

Coalescence,

$$\mathrm{Mt}_n^{z+} + \mathrm{Mt}_m^{y+} \rightarrow \mathrm{Mt}_{n+m}^{(z+y)+}, \quad (3)$$

and the growth of clusters because of the sorption of metal ions and their successive reduction,

$$\mathrm{Mt}_m^{z+} + \mathrm{Mt}^{x+} \rightarrow \mathrm{Mt}_{m+1}^{(z+x)+}, \quad (4)$$

$$\mathrm{Mt}_{m+1}^{(z+x)+} \rightarrow \ldots . \rightarrow \mathrm{Mt}_{m+1}^{((z+x)-p)+}, \quad (5)$$

entail their enlargement and eventually yield nanoparticles.

At the early stages, when the concentration of charged particles is high, primarily the coalescence of charged clusters, followed by the formation of clusters of a well-defined structure, occurs. At later stages, when the reduction of ions and clusters is exhaustive, the processes of merging neutral clusters prevail and eventually lead to the appearance of nanoparticles with a wide size distribution.

For atoms and clusters built of several atoms, the redox potential is much more negative than that for metals in the colloidal state [12, 38]. The redox potential of silver atoms in water [39], as calculated from the thermodynamic cycle for $\mathrm{Ag}^+/\mathrm{Ag}^0$, is –1.8 V (2.6 V lower than that for the colloidal metal). The potential necessary for the reduction of intermediate oxidation forms of transition metals is extremely high (–2.7 V for the transformation of Cu^+ into isolated atoms of Cu^0 and –2.8 V for the transformation of Ni^{2+} into Ni^+ [38]).

In the case of heterogeneous nucleation, the existing nuclei are involved in the formation of nanoparticles. Although, in this case, the detailed mechanism of formation of nanoparticles frequently remains vague, the assembly processes do not require such high potentials as those in the case of homogeneous nucleation.

The chemical reduction of metal ions in the liquid phase is in most common use for the synthesis of nanoparticles in aqueous and nonaqueous media owing to its simplicity. A wide spectrum of compounds (borohydrides, alcohols, formaldehyde, hydrogen, hydrazine, etc. [3, 5–7, 9–11, 13, 17, 33, 34]) may be employed as reducing agents. The synthesis of noble-metal nanoparticles may be performed via the mechanism of homogeneous nucleation owing to relatively low reduction potentials of the intermediate forms of their ions. The advantageous synthesis of transition-metal nanostructures is discussed in the literature [17, 41–43]. In this case, the assembly of nanoparticles may occur via heterogeneous nucleation. A typical drawback of chemical reduction consists in a wide size distribution of nanoparticles. However, synthesis in the presence of surfactants or polymers makes it possible to obtain nanoparticles with controlled sizes [3, 5, 6, 9–15, 17–19, 22, 33, 34, 44]. Technologies where polymers serve simultaneously as reducing agents of metal ions and efficient stabilizers of the formed nanoparticles have found wide application [45–52].

Radiation-chemical approaches to the synthesis of nanoparticles turned out to be extremely fruitful both for the study of the processes of formation of nanostructures and for the synthesis of metal–polymer nanocomposites [10–12, 23, 27, 36–39, 53–59]. Studies with the use of pulse methods showed that clusters with a certain discrete structure (“magic clusters”) are formed [12, 60] as intermediates of nanoparticles. For example, silver nanoparticles are formed through the intermediate formation of the clusters Ag_2^+, Ag_3^{2+}, Ag_4^{2+}, and Ag_8^{2+} [60].

Metallic nanostructures are as a rule prepared via irradiation of aqueous solutions. The generation of active species during the radiolysis of water may be represented by the following scheme [12, 38].

$$\mathrm{H_2O} \rightarrow \mathrm{e_{aq}^-}, \mathrm{H_3O^+}, \mathrm{H^-}, \mathrm{OH^-}, \mathrm{H_2}, \mathrm{H_2O_2}, \mathrm{HO_2} \quad (6)$$

The main reduction products of radiolysis are hydrated electrons that are generated with the maximum yield. They have an extremely high reduction potential (–2.9 V, [61]) that provides for processes responsible for homogenous nucleation (reactions (1) and (2)) in the reduction of ions of not only noble metals but also transition metals.

The sizes of metallic nanoparticles are controlled by the manipulation of thermodynamic and kinetic factors. In the case of homogeneous nucleation, high reduction potentials of the intermediate oxidation forms of metal cations (reaction (1)) require that strong reducing products should be used. As the sizes of clusters are increased, the potentials decrease abruptly [38, 40] and the growth of nanoparticles (reactions (4) and (5)) may occur in the presence of weak reducing agents [11, 12]. In the case of chemical reduction and UV irradiation [3, 44, 45], an increase in the reduction rate frequently promotes the formation of smaller nanoparticles. This phenomenon may be explained by the fact that an increase in the rate of reduction causes above all a gain in the efficiency of nucleation (reactions (1) and (2)).

When ionizing radiation is applied, an increase in the dose rate ensures acceleration of the formation of atoms; as a result, the ratio between the nucleation of nanoparticles and their growth tends to increase [12] owing to competition between nucleation (reactions (1) and (2)) and coalescence (reaction (3)) processes. The combination of chemical and radiation-chemical approaches exemplifies manipulation of sizes of nanoparticles in the presence of macromolecules. In this case, the radiolysis products are responsible for the nucleation processes. Chemical products having lower redox potentials reduce metal ions adsorbed on clusters and provide the growth of clusters and nanoparticles [12].

However, despite the progress achieved in the synthesis of particles with controlled sizes in polymer systems, the application of formal analysis of kinetic and thermodynamic conditions for estimation of the sizes of nanoparticles is very limited. The interaction of a polymer matrix with metal ions/surfaces of nanoparticles has a crucial impact on the assembly of nanostructures, and the quantitative consideration for this phenomenon is currently impossible. Studies devoted to the synthesis of nanoparticles in multicomponent systems often lack data not only about the mechanisms of nucleation and growth but also about the key conditions of synthesis that determine the immobilization of ions/nanoparticles in polymer systems. The authors often formally compare effects of the rates of processes under different thermodynamic conditions for the reduction of metal ions and the formation of nanoparticles.

FORMATION OF NANOPARTICLES IN POLYELECTROLYTE MATRIXES

The wide application of polyelectrolytes for the synthesis of nanocomposites is associated with the fact that, being a precursor, the polymer matrix should bind metal ions and subsequently should ensure the stabilization of nanoparticles [3, 5, 11, 33, 34]. The majority of studies generally aim to gain insight into the character of immobilization of metal ions in macromolecules and into the influence of interaction between functional groups and the surfaces of nanoparticles on the formation of nanostructures.

During the reduction of metal ions through radiation-chemical approaches in sodium polyacrylate solutions, clusters composed of several silver [54, 55] or platinum [62] atoms were found and their coalescence was absent at low dose rates. An examination of these data made it possible to assume [12, 55] that the interaction of clusters with carboxylate groups is commensurable with strong coordination interactions. The immobilization of polyelectrolytes on the surfaces of nanoparticles hampers their coalescence at the early stage [3, 12, 54, 55, 62–65] and makes it possible to control the sizes of nanoparticles. The sizes of nanoparticles are tuned in many respects by not only electrostatic but also cooperative noncovalent interactions of macromolecules with a metal surface [3, 44, 63–65]. The theoretical model for the formation of nanoparticles (referred to as pseudomatrix processes) was advanced in the 1990s [63–65]; in general, an increase in the energy of interaction of macromolecules with the surfaces of nanoparticles leads to the stabilization of smaller particles. Macromolecules carrying hydrophobic substituents or hydrophobic blocks usually surpass conventional water-soluble polymers in the ability to stabilize metallic nanoparticles [44, 66, 67] and provide the formation of smaller particles. An increase in the molar ratio between macromolecular units and metal ions [3] ensures as a rule more effective control over the sizes of nanoparticles because steric restrictions (related to the insufficient flexibility of chains) to the interaction of macromolecules with nanoparticles are reduced. Discussion of the results showed that the regimes of chemical and radiation-chemical reductions of metal ions affect the sizes and morphologies of nanostructures [3, 9–13, 17, 30, 35, 58, 59, 63–66].

It is reasonable to consider the examples of approaches providing control over the sizes of nanoparticles within the discussion of synthesis of noble-metal and transition-metal nanoparticles in the presence of polyelectrolytes. Gold nanoparticles give rise to the most stable metallic nanostructures, which exhibit well-defined optical, bactericidal, and catalytic properties and high conductivity; therefore, these nanoparticles have found wide use for the manufacture of functional metal-polymer nanomaterials [2–6, 17, 25, 26, 33, 34, 41, 45, 68]. The synthesis of gold nanoparticles clearly demonstrates the effect of polyelectrolyte–metal interactions and assembly regimes of metallic nanostructures [3, 68]. Gold colloids that are negatively charged because of the adsorption of chloride ions may be efficiently stabilized via the addition of cationic polyelectrolytes, such as polyethylenimine (PEI) or poly(*N,N*-diallyldimethylammonium chloride) (PDADMAC) [3]. However, there are examples demonstrating that polyanions may be used for the synthesis of metallic nanostructures. The application of poly(styrenesulfonic acid) leads to the formation of gold colloids stable over several months [3]. At the same time, because of the effective dissociation of functional groups, polystyrenesulfonates are less suitable for stabilization of gold colloids owing to the interaction of negatively charged gold nanoparticles and anionic groups of macromolecules.

Approaches in which polymers may function simultaneously as reducing agents and stabilizing agents have found application for the synthesis of gold nanostructures. Note that the character of interactions of macromolecules with the surfaces of nanoparticles has also a crucial effect on the formation of nanostructures. Stabilized gold particles were successfully prepared in solutions of poly(acrylic acid) (PAA) [45, 46] and linear or branched PEI [47, 49, 50]. As was shown in [50], as the mass ratio between PEI polycations and $HAuCl_4$ in solutions was decreased from 1 : 1 to 10 : 1, steric confinements to the nanoparticle–macromolecule interaction become weaker and the mean size of nanoparticles changes from 20 to 9 nm. When sodium styrenesulfonate–maleic acid copolymers were used [3], ions of gold tetrachloride were reduced and the effect of charge density on the sizes of nanoparticles was revealed. Both 20–25-nm nanoparticles and metal colloids were observed in solutions of the copolymers. In the presence of the copolymer with a higher charge density (sodium styrenesulfonate : maleic acid = 3 : 1), the share of fractions of nanoparticles with sizes up to 25 nm that are stabilized via electrostatic forces dominated.

Butylamine-modified PAA derivatives with various degrees of branching were applied for the preparation and immobilization of gold nanoparticles with sizes of 18–40 nm [45]. The incorporation of side substituents into the polymers, in addition to electrostatic interactions, afforded hydrophobic interactions and affected the sizes of nanoparticles in macromolecular matrixes. The results of [45] suggest that the smallest particles (18 nm) are formed at the optimum ratio of carboxylate and hydrophobic groups. The character of the distribution of nanoparticles within macromolecular aggregates is determined by the balance of steric and electrostatic interactions. In addition, an increase in the temperature at which particles are formed changes the character of interaction between macromolecules and the surfaces of nanoparticles.

Hydrophobic interactions influence the sizes of noble-metal nanoparticles not only in the case of polyelectrolytes. When the solutions of poly(2-hydroxymethyl methacrylate) and poly(2-hydroxypropyl methacrylate) matrixes were used, smaller particles were formed in matrixes of the latter polymer. Nanoparticles of silver, gold, and platinum with sizes in the range 5–20 nm were obtained [44] via reduction by sodium borohydride or ethyl alcohol or under exposure to UV irradiation. These data demonstrated the role of kinetic factors: An increase in the rate of reduction facilitated the formation of smaller particles.

Catalytically active platinum nanoparticles stabilized in polyelectrolyte matrixes were synthesized [18] via the reduction of H_2PtCl_6 by ethanol in the presence of PDADMAC, polyallylamine hydrochloride, polystyrenesulfonate, Nafion, PAA, poly(2-acrylamide-2-methyl-1-propanesulfonic acid), and nonionogenic polyvinylpyrrolidone. Platinum nanoparticles with sizes of 2–4 nm were obtained for all polymer systems. However, in accordance with the electron-microscopy data, nanoparticles give rise to various types of aggregates within associates of polyelectrolyte macromolecules because the conditions of steric and electrostatic interactions are different.

Hybrid materials containing silver nanoparticles show promise for the design of catalytic systems; they have found use in optoelectronics and nanophotonics [2, 4, 5, 7, 9, 14, 15, 17, 19, 31]. Nanocomposite materials [25, 27–32, 69] containing silver nanoparticles have found wide application as effective antibacterial and antiviral preparations. As for the other metal colloids, the size and size distributions of silver nanoparticles and their stability are determined by the nature of the stabilizing polymer matrix, the molecular ratio of metal ions and macromolecular units, and the conditions of reduction of silver ions [13, 17, 23–25, 27–31, 80].

Radiation-chemical approaches made it possible to investigate the stages of formation of silver nanoparticles in polyphosphate solutions [80]. With an increase in the concentration of polyphosphate, the degree of binding of silver ions and charged clusters by functional groups increased. In this case, the probability of reduction of silver ions, the formation of clusters, and the assembly of nanoparticles in the bulk of a solution was reduced. In the efficient binding of silver ions, polyphosphate plays the role of a "microreactor" and ensures the successive assembly of nanostructures through the formation of "magic clusters," and, at the stage of formation of nanoparticles, interaction with their surfaces provides control over sizes within 3 ± 0.5 nm. The synthesis of water-soluble functional nanocomposites with silver particles in the matrix of 1-vinyl-1,2,4-triazole–crotonic acid copolymers showed that an increase in the content of carboxyl groups in the polymer precursor promotes a more efficient stabilization of silver particles at the early stages of their formation and thus hinders coagulation processes [69] and facilitates the formation of smaller nanoparticles with a narrower size distribution.

Copper nanoparticles attract considerable attention owing to their optical, antibacterial, and fungicidal properties [11, 42, 70] and catalytic and electrocatalytic activities [58, 70–73]. Particles of varying sizes are synthesized through different methods, including chemical [17, 41–43] and electrochemical [74, 75] reduction, sonochemistry [76], and γ irradiation [10, 11, 38, 58]. The synthesis of nanoparticles by the chemical reduction of copper ions in a solution of a mixture of two polymers that can form nonstoichiometric soluble interpolymer complexes (IPCs) [77–79] provides better control over the sizes of nanoparticles than that in solutions of the original polymers. Owing to their labile structures, IPCs may be capable of self-tuning to nanometer objects. In this case, triple complexes including nanoparticles and chains of two polymers may be formed [67, 77–79]. X-Ray-initiated reduction of Cu^{2+} ions in aqueous–alcohol suspensions containing polyallylamine and PAA [81] leads to the formation of hybrids with the specific spatial organization of nanoparticles and microdomains (100–200 nm), which are filled with ultrasmall copper nanoparticles (2–4 nm) (Fig. 1).

The synthesis of copper particles vividly demonstrates the formation of metallic nanostructures through the homogeneous or heterogeneous mechanism. Nanoparticles with sizes of nearly 4 nm were obtained in irradiated aqueous–alcohol solutions of PEI–Cu^{2+} complexes through homogeneous nucleation [38]. In this case, irradiation generates two types of reducing particles: hydrated electrons e_{hydr} and alcohol radicals R·CHOH with reduction potentials of −2.9 and −1.5 V, respectively. Both products are involved in the reduction of Cu^{2+} ions to Cu^{+} ions. However, because of the high reduction potential for the formation of individual Cu^0 atoms [38] (precursors of clusters and nanoparticles (reactions (1) and (2)),

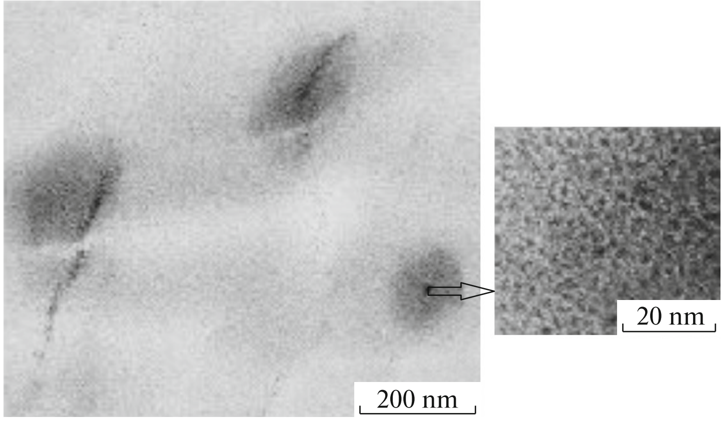

Fig. 1. TEM micrograph of the nanocomposite obtained via the radiation-chemical reduction of Cu^{2+} ions in an aqueous–alcohol suspension of PAA–polyallylamine [81].

Cu^+ ions may be reduced to Cu^0 by only hydrated electrons. The aggregation and growth of clusters cause the appearance of copper nanoparticles. Hence, the reactions of hydrated electrons are responsible for nucleation processes of (reactions (1) and (2)), while the growth of clusters and nanoparticles (reaction (3)) occurs via both types of reactions of reducing particles.

The method of reduction in an aqueous phase was developed for the synthesis of stable copper nanoparticles immobilized in the matrix of polyallylamine. The use of hydrazine as a reducing agent in an alkaline medium made it possible to obtain nanoparticles with controlled sizes of up to 50 nm in polyallylamine solutions [42], which provide the enhancement of surface Raman scattering. As was shown in [42], at the first stage of the chemical process, there is the formation of Cu_2O nuclei, which subsequently transform into metallic particles.

In PAA solutions [35, 79, 82, 83], a change in pH causes a change in the mechanism of the assembly of nanoparticles. At pH 2.8–3.0, copper nanoparticles are formed from the aqua complexes of Cu(II) ions via the mechanism of homogeneous nucleation. An increase in pH to 9 [82] or, in accordance with [35], to 4.3 promotes the binding of Cu(II) ions by carboxylate groups of PAA; in this case, the assembly includes the preliminary formation of CuOH or Cu_2O nanoparticles that subsequently form metallic nanoparticles. The immobilization of copper ions in macromolecules of star-shaped PAAs [35] leads to the situation that, at pH 4.3, macromolecules serve as separate containers for the assembly of nanoparticles: The sizes of nanoparticles are dependent on the contents of copper ions in macromolecules and, accordingly, are determined by the molecular masses of the latter. When nanoparticles are formed from aqua complexes, their size distribution is wider.

The obtainment of nanoparticles with the controlled shape improves the selectivity of catalytic processes and the functionality of optical and sensor materials [17, 41]. The presence of a surfactant changes the values of free energy for crystallographic planes and thus influences the relative growth rate of nanoparticles. The shapes of silver, gold, and platinum nanoparticles may be controlled with the use of polyvinylpyrrolidone as a polymer matrix [17, 41, 84–87]. In accordance with spectroscopic studies, the polyvinylpyrrolidone–metal interaction occurs via the carbonyl group of the pyrrolidone ring.

Polyelectrolytes sometimes contribute to control over the shape of nanoparticles as well. In addition to spherical nanoparticles, which are usually formed via reduction by sodium borohydride, triangular and cylindrical gold nanoparticles were found in the presence of hydrophobically modified PAA [45]. When copper ions were reduced by hydrazine in polyallylamine solutions of a certain concentration [42], nanorods were formed (Fig. 2) along with isotropic nanoparticles.

On the whole, the analysis of the published data suggests wide possibilities for the synthesis of 1–50-nm nanoparticles in polymer systems. In order to tune interactions between macromolecules and ions/surfaces of metals, such methods as change in pH, modification of the chemical structures of functional groups, and the use of copolymers have found wide applications. The efficient interaction of macromolecules with the surfaces of nanoparticles exerts the decisive effect on their sizes; in other cases, variation in the assembly regimes makes it possible to change the sizes of nanostructures over a wide interval. However, studies devoted to the effect of the structures of macromolecules on the specific features of formation of nanostructures are as a rule of an empirical character, and consideration of the mechanisms of nucleation and growth of nanoparticles is frequently beyond the framework of discussion.

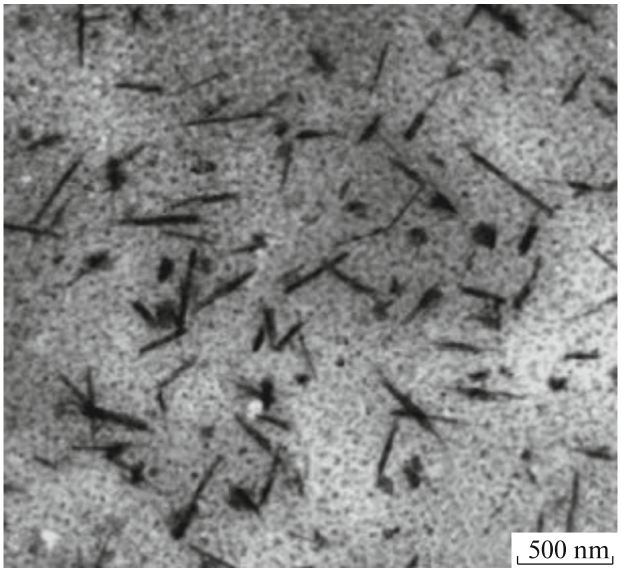

Fig. 2. TEM micrographs of anisotropic copper nanoparticles obtained in a polyallylamine solution via the reduction of Cu^{2+} ions by hydrazine. Reprinted from [42] with the permission of the American Chemical Society. Copyright 2010.

SYNTHESIS OF METALLIC NANOSTRUCTURES OF VARIOUS ARCHITECTURES IN POLYMER MICELLES AND COMPLEXES

At present, there are two main directions in the synthesis of metal–polymer nanocomposites. Micelles of macromolecules of various architectures are employed to prepare soluble nanosized hybrids with the desired spatial organization of nanostructures. In addition, simple one-step methods used for the synthesis of nanocomposites in films or deposited materials by the reduction of metal ions directly in polymer matrixes are of considerable interest.

The interest in the microcapsulation [5, 7, 8, 33, 52, 88] of magnetic or antibacterial nanoparticles is in many respects associated with the development of new drugs and drug-delivery systems. The design of highly dispersed catalysts or electronic devices is another stimulus for the development of the synthesis of metal-containing polymer systems with hierarchical organization [5, 7, 34, 81, 89–98]. The presence of nanostructures in polymer systems allows control over the growth of nanoparticles via tuning of interfacial interactions [5]. The synthesis of block copolymers that carry units able to bind metal ions makes it possible to prepare micelles with the selective localization of precursors suitable for the assembly of nanoparticles. Since the 1990s, copolymers have enjoyed wide application for the synthesis of nanoparticles localized in the core or shell of micelles [5, 33, 34, 89, 90, 99]. The resulting nanohybrids are promising candidates as catalytic systems because of the possibility for the selective transport of reagents and products.

In recent years, the progress in the synthesis of metal–polymer nanostructures with the desired spatial organization has been associated with the use of interpolyelectrolyte complexes (IPECs). Owing to the possibility to control the interaction of functional groups of polyanions and polycations with ions/surfaces of metals in these systems, a wide variety of structures were synthesized [11, 33, 34, 51, 52]. An IPEC based on the PEI–Ag^+ complex, PAA, and the amphiphilic block copolymer PAA-*block*-PS [52] was used as a three-dimensional nanosized template for the synthesis of 20–40-nm-diam nanoparticles in the micelle corona (Fig. 3).

The micelles of IPECs based on terpolymers containing blocks of polybutadiene, quaternized polyvinylpyridine, and poly(methacrylic acid) were used as a basis for the synthesis of polymer–inorganic nanohybrids [33]. The formation of gold nanoparticles (3–4 nm) under exposure to UV irradiation occurs predominantly at the interface between the intermicellar interpolyelectrolyte complex formed between quaternized polyvinylpyridine and poly(methacrylic acid) and the poly(methacrylic acid) corona as well as in the corona of poly(methacrylic acid). Nanoparticles of gold, platinum, and palladium were obtained with the use of UV irradiation or via reduction by $NaBH_4$ in cylindrical micelles of the terpolymer PB-*block*-quaternized polyvinylpyridine-*block*-poly(sodium methacrylate) [34] (Fig. 4).

Another modern trend includes the use of stimulus-responsive polymers for the synthesis of “smart” nanohybrids. Macromolecules of spherical brushes based on thermoresponsive poly(*N*-isopropylacrylamide) may be applied as a basis for biosensors, for the delivery of drugs, or for the separation of metal ions. In matrixes of microgels with the PS hydrophobic core and the poly(*N*-isopropylacrylamide) hydrophilic shell, stable nanohybrids with 2–9-nm particles of gold, silver, platinum, and palladium were obtained [7, 100–105]. The difference in sizes of nanoparticles may be explained by the conditions of complexation of metal ions with the functional groups of microgels. Thermoresponsive core–shell particles with the PS core were used as “smart” carrying systems for catalytically active silver particles. Heating of the suspension above 32°C caused a sharp change in the volume of the poly(*N*-isopropylacrylamide) shell [105] (Fig. 5). Silver nanoparticles were obtained in the micellar IPEC composed of the quaternized polyvinylpyridine–poly(ethylene oxide) block copolymer and the PAA–poly(*N*-isopropylacrylamide) block copolymer [51]. A change in temperature caused the core–shell structural transition in micelles. The units of quaternized polyvinylpyridine and PAA serve as containers for the synthesis of nanoparticles in the cores of micelles at 25°C or coronas of micelles at 60°C. In the polymer

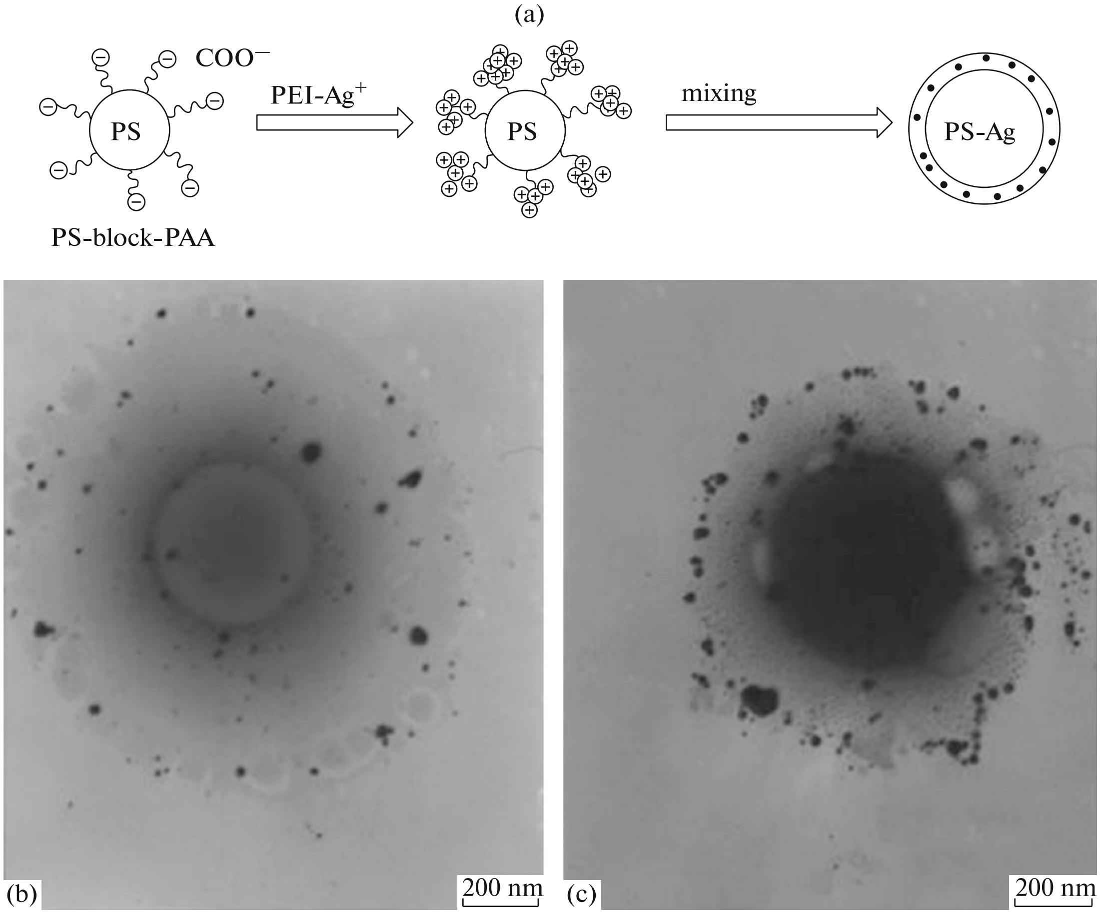

Fig. 3. Synthesis of silver nanoparticles in the corona of the interpolyelectrolyte complex PAA–Ag$^+$–PEI micelles of block copolymer PS-*block*-PAA. (a) Schematic representation of the formation of the metal–polymer nanocomposite in PS-*block*-PAA micelles and (b, c) micrographs of nanocomposites with silver nanoparticles of various sizes: (b) 0.012 wt % PS-*block*-PAA and 0.02 mol/L $AgNO_3$ and (c) 0.012 wt % PS-*block*-PAA and 0.05 mol/L $AgNO_3$. The PAA block provides the reduction of Ag$^+$ ions. Reprinted from [52] with the permission of Elsevier. Copyright 2008.

system, poly(ethylene oxide) plays the role of a reducing agent. The resulting composites may be used as thermoresponsive quantum dots or antimicrobial agents in ship coatings.

Attempts to create accessible methods for the synthesis of metal-polymer nanocomposites stimulated the development of studies on the synthesis of nanoparticles in the media of polymer hydrogels or polyelectrolytes. The reduction or precipitation of metal ions is used to prepare inorganic nanoparticles in swollen polymer matrixes [10, 11, 14–16, 19, 57, 59, 106–121]. The stabilization of inorganic nanoparticles in polymer matrixes makes it possible to prevent aggregation and to provide control over the rate of their growth.

The technique of the so-called “intermatrix synthesis” [15, 19, 106–109] is advantageously used to produce catalytically, electrocatalytically, and magnetically active composites of “zero-valence metals” via the chemical reduction of metal ions in matrixes based on cation-exchange resins. Sulfonated poly(ether ketone) was used as a suitable medium for the intermatrix synthesis of catalytically and electrocatalytically active polymer nanocomposites with nanoparticles of copper, silver, and palladium in the form of membranes, fibers, or resins [15]. Polymeric inks containing nanoparticles are employed to modify the surfaces of electrochemical sensors [19, 108]. After each cycle, the functional group of the polymer component is recycled to the initial ionic state [15]. This phenomenon that makes it possible to obtain nanocomposites with high contents of nanoparticles or to synthesize bimetallic or trimetallic core–shell nanostructures.

The application of sodium borohydride as a reducing agent that cannot penetrate deep into the matrix because of electrostatic repulsion provided conditions for the predominant formation of nanoparticles near the surface of an ion-exchange polymer gel containing sulfonic groups. This spatial distribution is optimum for catalytic and electrocatalytic systems and materials useful for the antibacterial treatment of water [109].

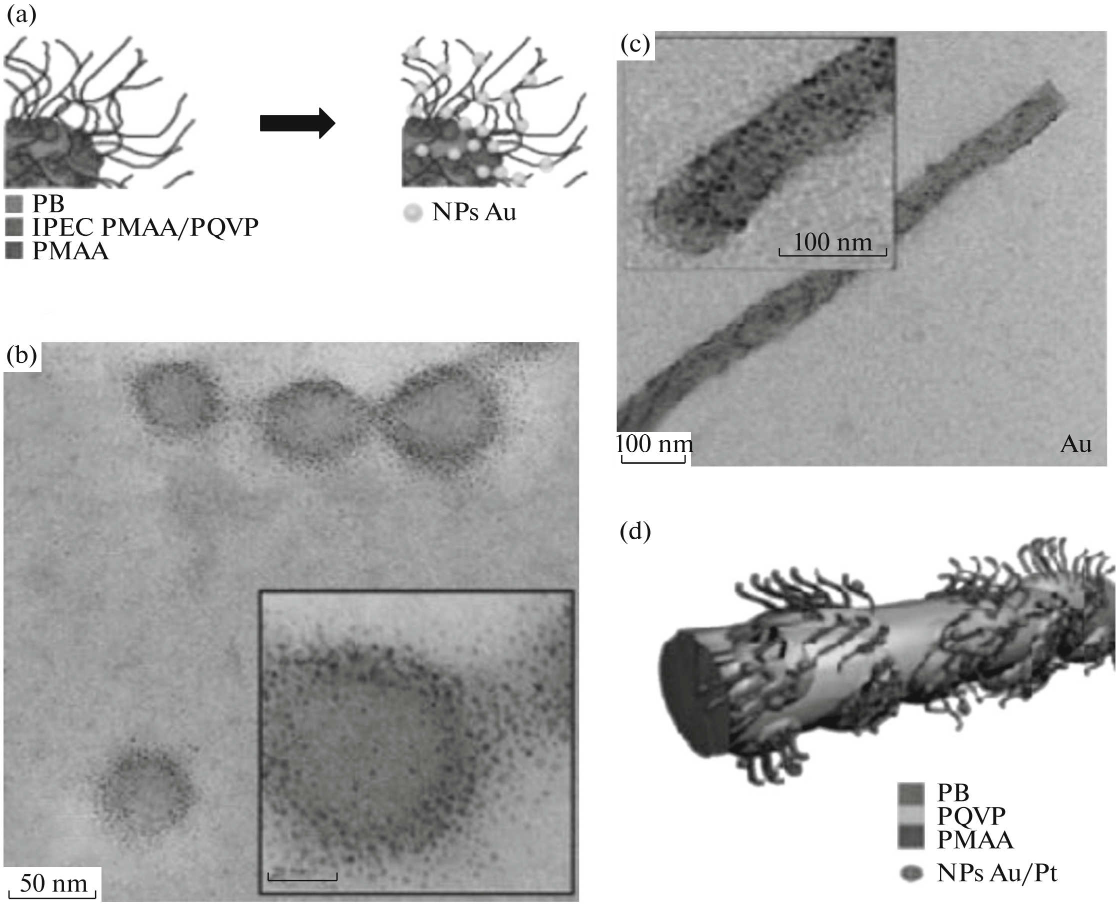

Fig. 4. (a) Schematic representation of the formation of gold nanoparticles under the action of UV radiation in micelles of the terpolymer PB-*block*-quaternized polyvinylpyridine (PQVP)-*block*-poly(methacrylic acid) (PMAA). (b) TEM micrograph of the nanocomposite [33]. (c) TEM micrograph of the nanocomposite obtained via the reduction of gold or platinum ions in the micellar solutions of the terpolymer PB-*block*-PQVP-*block*-PMAA. (d) Schematic representation of the localization of gold or platinum nanoparticles in cylindrical micelles of the terpolymer PB-*block*-PQVP-*block-PMAA* [34]. Reprinted from [33] with the permission of the American Chemical Society, copyright 2009, and [34] of the Royal Chemical Society, copyright 2011.

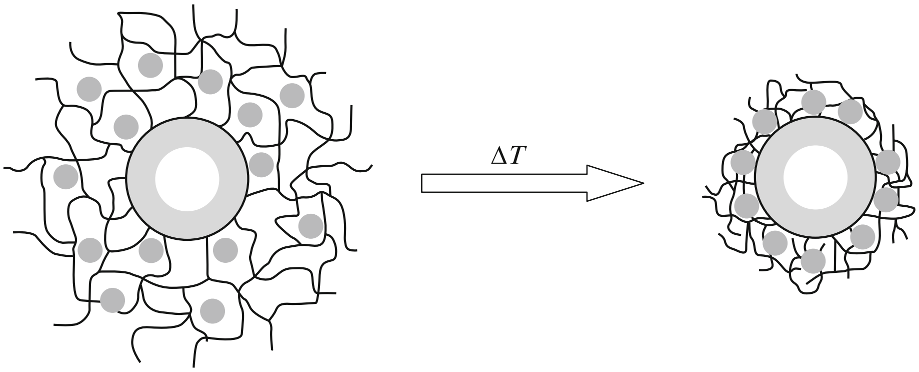

Fig. 5. Nanocomposites based on microgels of the PS-*block*-poly(*N*-isopropylacrylamide) block copolymers. Schematic representation of the effect of temperature on the volume transition of the poly(*N*-isopropylacrylamide) shell containing silver nanoparticles. Reprinted from [105] with the permission of the American Chemical Society. Copyright 2006.

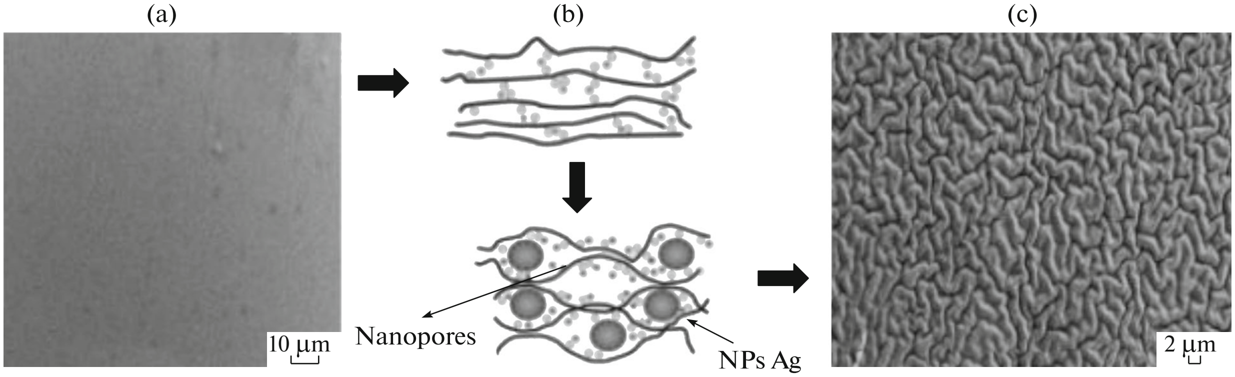

Fig. 6. Scheme illustrating the interaction of silver nanoparticles prepared (b) within the polymer matrix and (a, c) SEM micrographs of the surface of Purolite C100E ion-exchange resin (a) before and (c) after preparation of silver nanoparticles. Reprinted from [109] with the permission of Springer. Copyright 2013.

The interaction of the Ag^+ ions or the formed nanoparticles with the polymer matrix leads to an increase in the degree of crosslinking; as a result, nanopores appear in the polymer gel (Fig. 6).

Polycation–polyanion systems are in wide use for the synthesis of functional nanocomposites [9–11, 14, 16, 59, 110–121]. The advantages and evolution of approaches to the synthesis of metallic nanoparticles in polyanion–polycation multilayer films were discussed in detail in review [9]. As was shown in many publications [14, 16, 111–116], the layer-by-layer deposition of polyelectrolytes containing metal ions and the subsequent reduction of these ions allows preparation of encapsulated nanoparticles with controlled sizes. A similar encapsulation is good because the polymer matrix not only stabilizes nanoparticles but also makes it possible to change the surroundings of catalytic sites and to improve the access to nanoparticles [9]. It was found that the PAA–PEI films with silver nanoparticles exhibit electrocatalytic behavior and antibacterial activity [112]. Recent advances in the synthesis of polymer–inorganic composites from layer-by-layer films are basically determined by the development of membrane catalytic systems [14, 114, 115]. The technology of the polycation–polyanion layer-by-layer deposition was employed to produce core–shell particles and hollow capsules filled with metallic nanoparticles [9, 116]. The feasibility of controlling the precursor structure and varying the modes of reduction of metal ions provided conditions for preparing composites not only with varying sizes of nanoparticles but also with varied spatial ordering of nanostructures [112, 113].

In a wide composition range, polycation–polyanion complexes form water-insoluble or aqueous–organic-media-insoluble samples that feature high dialysis permeabilities to low-molecular-mass polar compounds and ions. Owing to these properties, IPECs may be used as media for the reduction of metal ions and the synthesis of nanoparticles [10, 11, 57, 59, 117–121]. Nanocomposites [10, 11, 57, 59, 117–119] containing nanoparticles of metals or their oxides were obtained in matrixes of interpolymer complexes PAA–PEI via chemical and radiation-chemical approaches. Because of the unique ability of IPECs to stabilize nanoparticles and with the use of radiation-chemical methods, the formation of metallic nanostructures at various stages was investigated [10, 11, 57, 59, 119].

The structures and properties of such polymer–inorganic hybrid materials are determined by the regime of metal-ion reduction [10, 11, 57, 59, 117–119]. When $NaBH_4$ is used as a reducing agent, cuprous oxide nanoparticles nearly 10 nm in size were formed [10]. Metallic nanoparticles of Cu, Ag, Ni, and Pd were obtained via the reduction of metal ions in PAA–PEI interpolymer complexes irradiated in aqueous–organic media with the use of electron accelerators, sources of X-ray radiation and γ radiation [57, 59]. The formation of nanoparticles in irradiated IPEC films is governed by the specific features of formation and transport of radiolysis products and migration of metal ions over the polymer matrix. Under irradiation of films based on interpolyelectrolyte complexes in an aqueous–alcohol medium, clusters are formed via local reactions involving active particles with high reduction potentials, while the growth of nanoparticles is associated with interfacial processes involving stable products of radiolysis [59, 118]. The addition of acetaldehyde (a weak reducing agent) makes it possible to control the ratio between the processes of formation and growth of nanoparticles and to produce nanomaterials with varying structures. The ratio between the rates of generation and growth of nanoparticles in matrixes of interpolyelectrolyte complexes is determined also by the absorbed dose rate and the mechanisms governing the reduction of metal ions and the formation of clusters [57, 59, 118, 119].

Owing to a change in the irradiation parameters, various regimes for the reduction of metal ions on the surface and within polymer films were achieved. This

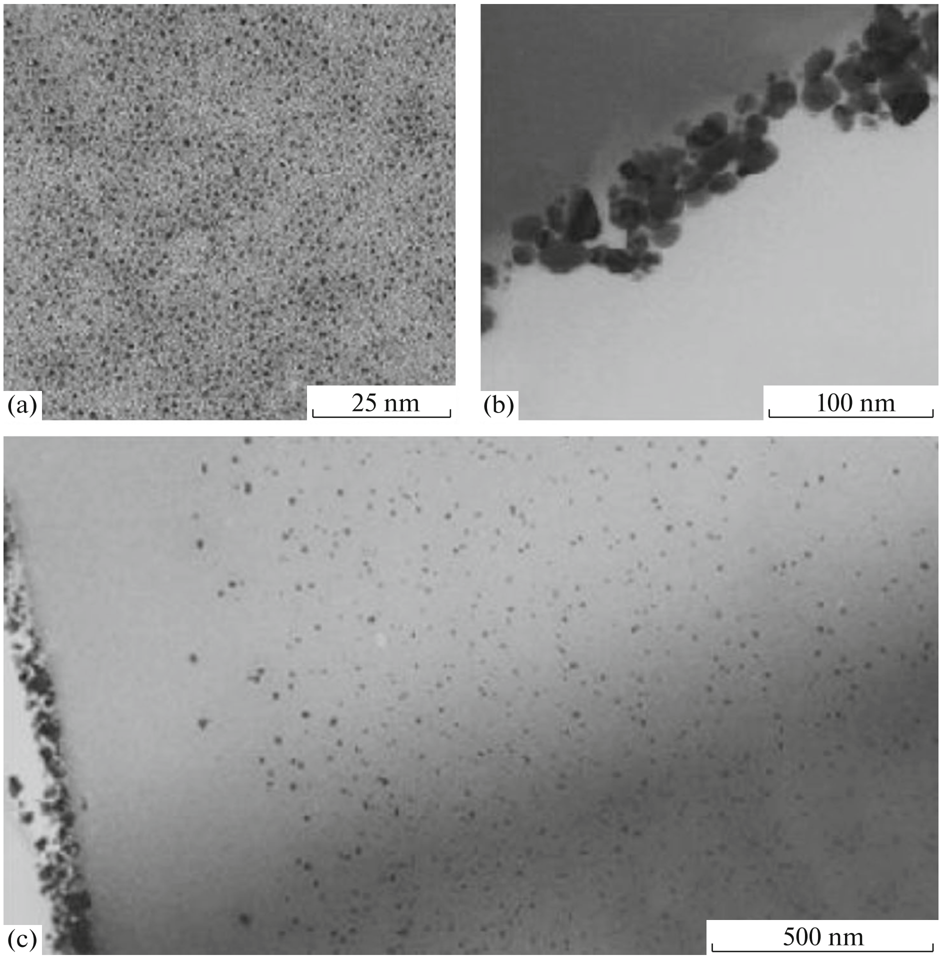

Fig. 7. Synthesis of nanocomposites with the use of radiation-initiated reduction of metal ions in IPEC films. TEM micrographs of PAA–PEI complexes: (a) an initial content of silver ions of 6 wt % and a γ-ray dose rate of 320 kGy, (b) an initial content of silver ions of 6 wt % and an X-ray dose rate of 140 kGy, and (c) an initial content of silver ions of 16 wt % and an X-ray dose rate of 800 kGy.

circumstance made it possible to synthesize composites with nanoparticles randomly distributed in the polymer matrix and materials with the regular spatial distribution of nanoparticles over the film thickness, including materials with the selective localization of nanoparticles in near-surface layers (Fig. 7). A high radiation-chemical yield for the reduction of metal ions [10, 11, 57, 59, 117] provides evidence that IPEC matrixes show promise for the elaboration of one-step methods of producing nanocomposite materials with the use of various kinds of ionizing radiation.

Recent studies demonstrate that the approaches to the synthesis of metallic nanostructures of the desired spatial organization are being intensively developed. In many cases, more and more complex organized micellar templates of copolymers able to selectively include metal ions in their blocks are used. This way is basically determined by achievements in the synthesis of macromolecules of various architectures and the interest in their self-assembly. Another approach involves the use of multiple variants for the deposition of polymer complexes on organic and inorganic membranes and microspheres to prepare nanocomposites or variation in the regimes of reduction of metal ions to control localization of nanoparticles in polymer films and coatings.

CONCLUSIONS

The development of approaches to the reduction of metal ions in matrixes and templates of polyelectrolytes shows that there has been convincing progress in the preparation of metallic nanoparticles with controlled sizes in almost the entire nanometer range. Understanding the conditions that control of macromolecule–ion/metal nanoparticle interactions allows the synthesis of metal–polymer hybrids that are promising for the design catalytic systems, magnetic materials, nonlinear-optical devices, biosensors, microscheme components, etc.

Polyelectrolyte gels, polycation–polyanion multilayer films, or IPECs may be regarded as universal matrixes for the production of metal–polymer functional materials with controlled sizes and spatial organizations of nanoparticles. These materials may be obtained as half-finished materials for conducting inks and in the form of films, membranes, fibers, coatings of porous materials, or microspheres. Recent achievements in the controlled synthesis of macromolecules made it possible to design copolymers of various architectures for use as micellar templates in the synthesis of soluble nanohybrids with the desired spatial organization. In recent years, progress in the design of functional materials has dictated the synthesis of new types of nanosized functional materials based on interpolymer complexes and smart polymers.

General approaches that provide ways to control the tuning of nucleation and growth of nanostructures in polymer matrixes are variation in the rate of reduction, in pH, and in the temperature regime; the use of reducing agents with various potentials; and control over the diffusion of reagents in polymer solutions and gels.

The difference in reduction mechanisms for ions of noble and transition metals and a variety of assembly routes at the stage of nucleation and growth of nanoparticles should be taken into account in the formation of nanostructures. In this situation, the information about the mechanisms of formation of nanostructures in multicomponent polymer systems is the key factor for the controlled tuning of the sizes of nanoparticles and their spatial organization.

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