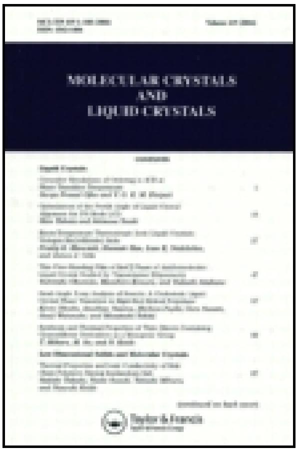

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Micelle Formation and Stabilization of Metal Nanoparticles in Aqueous Solutions of Diblock Copolymers with Monomethyl Ether of Poly(Ethylene Oxide) and Poly(Acrylic Acid)

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Micelle Formation and Stabilization of Metal Nanoparticles in Aqueous Solutions of Diblock Copolymers with Monomethyl Ether of Poly(Ethylene Oxide) and Poly(Acrylic Acid)

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*Double-hydrophilic block copolymers including monomethyl ether of poly(ethylene oxide) and poly(acrylic acid) (MEPEO-*b*-PAAc) with the different ratios of polymer blocks are synthesized by the matrix block-copolymerization and characterized. The intramolecular complex formation (IntraPC) between polymer blocks in MEPEO-*b*-PAAc at low pH (protonated MEPEO-*b*-PAAc) is established. It causes the MEPEO-*b*-PAAc intense micellization in aqueous solutions at pH $\leq$ 4. Water solutions of MEPEO-*b*-PAAc copolymers are used for the synthesis of silver nanoparticles. The stabilizing property of MEPEO-*b*-PAAc solutions by the interaction with the colloid dispersions of silver nanoparticles is shown.*

Keywords Diblock copolymer; intramolecular polycomplex; micelles; nanoparticles; self-assembly; silver

Introduction

The syntheses of metal nanoparticles or clusters are of current interest in the field of materials science, because the unique properties of such nanoparticles can be employed in catalysis, nonlinear optics, and semiconductor and magnetic materials [1–4]. The use of polymeric matrices as a medium for the formation of metal nanoparticles provides the active stabilization and the control over the growth of nanoparticles [3–5]. Various methods for the preparation of metal nanoparticles in a polymeric environment have been suggested [1]. One of the well-known selective methods involves the metal colloid preparation in the cores of amphiphilic block copolymer micelles formed in selective solvents (which thermodynamically favor one of the blocks) [1–3]. In such systems, the nonpolar blocks form the micellar corona surrounding the micellar core including the polar block. The micellar core of such a copolymer micelle can be considered as a nanoreactor, where the solubilization and the growth of metal nanoparticles take place [4]. However, the amphiphilic

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Address correspondence to N. M. Permyakova, Taras Shevchenko National University of Kyiv, Faculty of Chemistry, 64, Volodymyrska Str., Kyiv 01033, Ukraine. E-mail: permyakova@ukr.net block copolymers were successfully employed for binding the metal nanoparticles only in polar organic solvents, while water, as a reaction medium, has a wide range of chemical and physical applications (in particular, of various catalytic reactions). At the same time, the double-hydrophilic block copolymers (where both blocks are soluble in water) with the system of cooperative hydrogen bonds between chemically-complementary polymer blocks form stable regular micelles in aqueous media [6]. This type of micelles contains the hydrophobic core of bonding segments of polymer blocks surrounded by a hydrophilic corona of free segments of polymer blocks [6]. On the other hand, polymer micelles in water media will be prepared by the reaction of double-hydrophilic diblock copolymers with oppositely charged metal cations [4,7]. In this case, the micellar core comprised a network of polyanions/Me complexes surrounded with the hydrophilic nonionic shell. Such a micellization in the systems of poly(ethylene oxide)-*b*-poly(methacrylic acid)/Ca^{2+} complexes [7] and poly(ethylene oxide)-*b*-poly(ethyleneimine)/Pt^{4+} complexes [4] was demonstrated.

In the present work, we have reported on the synthesis of double-hydrophilic block copolymers which consist of monomethyl ether of poly(ethylene oxide) and poly(acrylic acid) with the different ratios of polymer blocks, its self-assembly in aqueous solutions, and the formation of stable colloid dispersions of silver nanoparticles in water solutions of the given copolymers.

Experimental

*Synthesis and Characterization of MEPEO-*b*-PAAcNa and PAAc*

The MEPEO-*b*-PAAcNa samples were synthesized by free radical block copolymerization of acrylic acid (99.5%, "Fluka"), purified under vacuum, with monomethyl ether of poly(ethylene glycol) (MEPEG) $M_{vMEPEG} = 5 \cdot 10^3$ ("Fluka") which were activated by Ce^{IV} ions and used as macroinitiators [8]. The polymerization of MEPEO-*b*-PAAc was performed at the constant $[Ce^{IV}]/[MEPEG] = 1$ mol ratio. The monomer concentration (AAc) in the reaction mixtures was changed from 0.5 to 2 mole AAc/base-mole MEPEG. Sediments of the diblock copolymers were cleansed by deionized water and dissolved in 0.2 N NaOH. Further, the MEPEO-*b*-PAAc samples in the Na^+-form were precipitated into the H^+-form by the addition of HCl to MEPEO-*b*-PAAc alkaline solutions and dissolved in 0.2 N NaOH again, followed by the lyophilic drying. A homopolymer of PAAc was obtained by the free radical homopolymerization of AAc in the presence of C_2H_5OH using Ce^{IV} under the $[AAc]/[C_2H_5OH] = 2$ mol ratio in the reaction mixture under the same experimental conditions. Molecular parameters of diblock copolymers and its chemical compositions of the polymer blocks were determined by ^1H NMR spectroscopy [9]. ^1H NMR spectra were recorded on a Varian Mercury-400 at room temperature using a polymer solution in D_2O. Chemical compositions of the polymer blocks were calculated from the ratio of integrated areas of corresponding ^1H NMR signals [9]. Molecular weights of PAAc samples were determined by viscosimetry data. The concentration of carboxylate groups in the copolymer samples was quantified by the potentiometric titration. The potentiometric titration of the MEPEO-*b*-PAAcNa solutions was performed by using a 1-160 M (Belarus) standard pH meter calibrated with pH buffer standards. The titration was carried out with 0.2 N HCl in a thermostatted cuvette in the argon flow at $T = 298$ K.

Preparation and Characterization of MEPEO-b-PAAc Micelles

MEPEO-*b*-PAAc micelles (the protonated form of PAAc block) with a hydrophobic core formed by bonding segments of polymer blocks and a hydrophilic corona formed by free segments of the polymer blocks were prepared in water solutions of MEPEO-*b*-PAAc at $\mathrm{pH} \leq 4$. The critical micellization concentrations of MEPEO-*b*-PAAc (cmc) at $\mathrm{pH} = 2.5$ and room temperature were determined by static light scattering measurements. The static light scattering measurements were performed on a modernized FPS-3 instrument (Russia). The instrument is equipped with a light diode WP7113VGC/A (520 nm) ("Kingbright"). The value of the Gibb's free energy of the MEPEO-*b*-PAAc micellization at $\mathrm{pH} = 2.5$ was calculated by [10].

Preparation of Ag^+-Containing MEPEO-b-PAAcNa Copolymers

Polymer micelles with ionic cores were prepared by mixing the aqueous solutions of MEPEO-*b*-PAAcNa (deprotonated form of PAAc block) with an $AgNO_3$ solution at various molar ratios of $[Ag^+]$ to $[COO^-]$ groups of the copolymer followed by the 24 h holding at room temperature. The Ag^+ interaction with $\text{-}COO^-$ groups was determined by the FTIR spectroscopy. The FTIR spectra of thin (3–7 μm) films of the copolymer and its mixture with Ag^+ were measured by a Nexus-470 Nicolet FTIR spectrometer (USA) in the range of $1000\text{–}4000\,\mathrm{cm}^{-1}$ at 293 K. The films were cast from aqueous solutions of the copolymer and its mixture with Ag^+ under $[Ag^+]/[COO^-] = 0.4$ on fluorite windows, air-dried, then placed under vacuum above $CaCl_2$ during one week.

Synthesis and Characterization of MEPEO-b-PAAc/Ag Nanoparticles

The synthesis of silver nanoparticles in both types of MEPEO-*b*-PAAc micelles was carried out by the addition of sodium borohydride ($NaBH_4$) (made in China) to the aqueous mixtures, which consist of an $AgNO_3$ solution and a solution of protonated ($\mathrm{pH} = 2.5$) or deprotonated ($\mathrm{pH} = 8.9$) MEPEO-*b*-PAAc ($C_{DBC} = 1\,\mathrm{kg \cdot m^{-3}}$) at the molar ratio $[Ag^+]/[COO^-] = 0.01$. The molar ratio $[NaBH_4]/[Ag^+]$ was equal to 8, which corresponds to the full reduction of Ag^+ by the reaction [11]

$$8Ag^+ + BH_4^- + 8OH^- = 8Ag + H_2BO_3^- + 5H_2O.$$

MEPEO-*b*-PAAcNa/Ag and MEPEO-*b*-PAAc/Ag nanoparticles are identified and characterized, by using the UV-vis absorption spectroscopy [11,12]. The UV-vis spectra of the aqueous solutions of reaction mixtures were recorded on a Varian Cary 50 Scan UV-Visible spectrophotometer, by scanning between 200 and 1000 nm. Dilute aqueous solutions of silver nanoparticles were measured in quartz cuvettes, using a pure solvent as the reference. From the spectral absorption maximum (λ_{max}), the diameter of Ag nanoparticles was calculated, by using the previous measurements correlating nanoparticle sizes with absorption onset data [12].

Results and Discussion

Two deprotonated diblock copolymers were obtained in the above-described manner: MEPEO-*b*-PAAcNa1 (113 MEPEO repeat units and 100 PAAcNa repeat units)

Table 1. Characterization of MEPEO-*b*-PAAcNa diblock copolymers and PAAc

Copolymer	$M_{vMEPEO} \cdot 10^{-3}$	$M_{nPAcNa} \cdot 10^{-4}$	$M_{DBC} \cdot 10^{-4}$[1]	n[2]
MEPEO-*b*-PAAcNa1	5.0	0.9	1.4	100/113
MEPEO-*b*-PAAcNa2	5.0	2.2	2.7	234/113
PAAc	–	2.2[3]	–	–

[1] $M_{DBC} = M_{vMEPEO} + M_{nPAcNa}$.

[2] Units ratio of the polymer blocks (base mole PAAcNa/base-mole MEPEO).

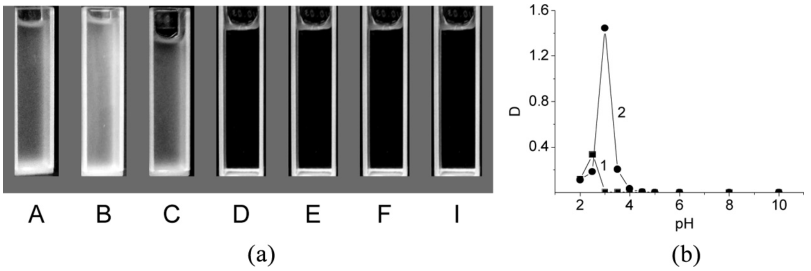
[3] M_{vPAAc}.

and MEPEO-*b*-PAAcNa2 (113 MEPEO repeat units and 234 PAAcNa repeat units) (Table 1).

Earlier, it was revealed that the block copolymerization process has a matrix character because of the formation of hydrogen bonds between grown PAAc chains and MEPEO block [8]. That fact is indicated on the IntraPCs existence in the MEPEO-*b*-PAAc, which is initiated of the MEPEO-*b*-PAAc micellization process by means of hydrophobic interactions between non-polar bound parts of the copolymer blocks in aqueous solutions. The behavior of MEPEO-*b*-PAAc macromolecules in aqueous solutions at various pH can be seen in Figure 1.

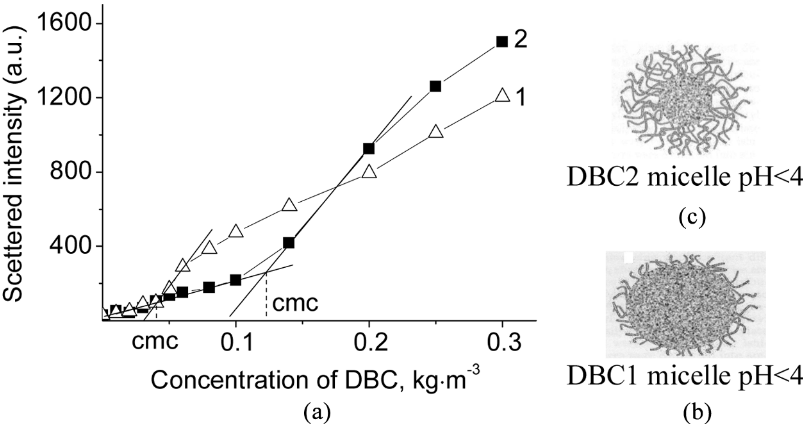
The appearance of the turbidity of MEPEO-*b*-PAAc2 solutions at $pH \leq 4$ indicates the self-assembly of MEPEO-*b*-PAAc macromolecules. As is well known, the micellization process is a function of the concentration [10]. The critical concentration of MEPEO-*b*-PAAc micelle formation (cmc) at $pH = 2.5$ was determined from the dependence of the intensity of the scattered vertically polarized light at an angle of 90^0 on the copolymer concentration (Fig. 2a).

The Gibb's free energy of the MEPEO-*b*-PAAc micellization is calculated using the cmc values by a formula in [10] and is represented in Table 2. It is shown that the MEPEO-*b*-PAAc micellization process develops most intensively when the unit's ratio of the polymer blocks in copolymer is 100/113 (MEPEO-*b*-PAAc1). In this case, the lowest value of the critical concentration of micelle formation (cmc) and the highest value of the Gibb's free energy ($\Delta G°$) of the process were observed (Table 2).



(a) (b)

Figure 1. Photography of the MEPEO-*b*-PAAc2 solutions ($C_{DBC} = 2\,kg \cdot m^{-3}$) (a) and its dependence of the optical density (tubidity) ($C_{DBC} = 1\,kg \cdot m^{-3}$ *–1*, $C_{DBC} = 2\,kg \cdot m^{-3}$ *–2*, $\lambda = 500\,nm$) (b) under various pH: 2 (A), 2.5 (B), 3 (C), 4 (D), 6 (E), 8 (F), 10 (I).



DBC2 micelle pH<4

(c)

DBC1 micelle pH<4

(a)

(b)

Figure 2. Plots of the scattered intensity of the vertically-polarized light at a 90° angle against concentration of MEPEO-*b*-PAAc solutions at the $\mathrm{pH} = 2.5$ (a): MEPEO-*b*-PAAc1 *–1*, MEPEO-*b*-PAAc2 *–2* and MEPEO-*b*-PAAc micelle building (b, c).

Thus, the effect of the strengthening of hydrophobic interactions in the MEPEO-*b*-PAAc1 sample as compared with MEPEO-*b*-PAAc2 sample which depends on the ratio of the polymer blocks lengths is established. For the ratio equal to $n = 100/113$ (MEPEO-*b*-PAAc1), the copolymer form spherical crew-cut micelles with a large hydrophobic core of bonding segments of polymer blocks and short corona of free MEPEO segments (Fig. 2b). The different structure of micelle aggregates for the MEPEO-*b*-PAAc2 which consist of the significant excess of PAAc block relative to the MEPEO block ($n = 234/113$) is represented in Figure 2c. It is shown that the MEPEO-*b*-PAAc2 copolymer form a spherical "hairy" micelle with a large "corona" of free segments of PAAc block [2].

The destruction of IntraPCs in copolymers which was caused by the destruction of micelles at the increasing ionization of carboxylate groups of the copolymer was established using the data of potentiometric titration (Fig. 3).

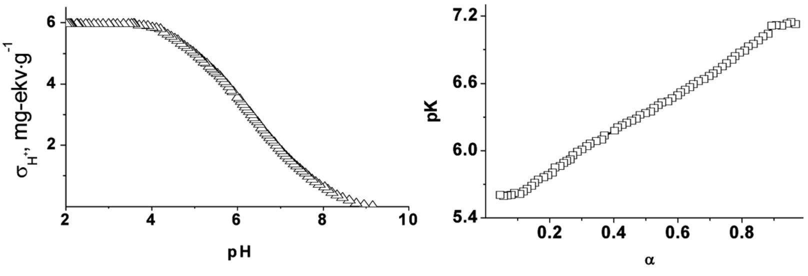
At the increasing ionization of carboxylate groups (at $\mathrm{pH} > 4$), we can see the swelling and the unwinding of MEPEO-*b*-PAAc macromolecules.

The formation of MEPEO-*b*-PAAcNa/Ag^+ micelles is observed by the appearance of the turbidity of the MEPEO-*b*-PAAcNa/Ag^+ aqueous mixtures which increases with $[Ag^+]$. In addition, we observe the strong increase of the intensity of $\nu_{s\,COO^-}$ at $1410\,\mathrm{cm}^{-1}$ and $\nu_{as\,COO^-}$ at $1560\,\mathrm{cm}^{-1}$ (valence vibration bands of carboxylate ions) in the IR spectrum of the given mixture ($[Ag^+]/[COO^-] = 0.4$) as

Table 2. Thermodynamic parameters of MEPEO-*b*-PAAc micellization in water solutions at $\mathrm{pH} = 2.5$

Copolymer	n[1]	$cmc_{295\,K}$, $\mathrm{mol \cdot L^{-1}}$	$-\Delta G_{295\,K}$, $\mathrm{kJ \cdot mol^{-1}}$
MEPEO-*b*-PAAc	100/113	2.85	31.32
MEPEO-*b*-PAAc	234/113	4.56	30.16

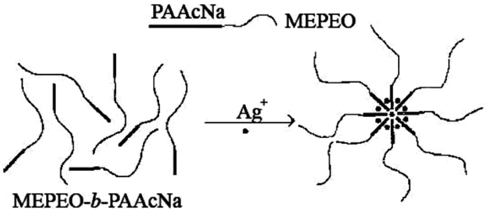
[1] Units ratio of the polymer blocks (base mole PAAcNa/base-mole MEPEO).



(a) (b)

Figure 3. Curves of proton absorption (a) and pK dependence from varying degree of the ionization of the –COOH group in the MEPEO-*b*-PAAc2 (b). $C_{DBC} = 2\,kg \cdot m^{-3}$ $T = 25°C$.

compared with that of individual MEPEO-*b*-PAAcNa. This is caused by the connection of Ag^+ with the $-COO^-$ groups of the copolymer [13]:

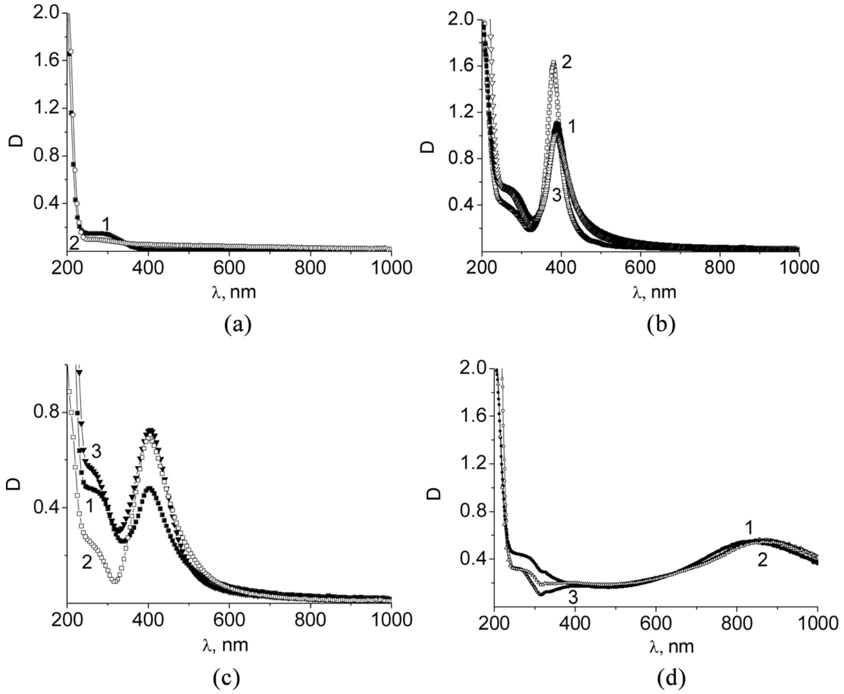


The absorption spectra of the Ag^+-containing MEPEO-*b*-PAAcNa1,2 and Ag^+-containing PAAcNa reaction mixtures at $pH = 8.9$ after the addition of $NaBH_4$ are represented in Figure 4b,c.

It is shown that the absorption band at 381 nm in the spectra of all reaction mixtures in two hours after the addition of $NaBH_4$ is formed (Fig. 4b). The absorption maximum near 400 nm is characterized by the surface plasmon absorbance of the colloid dispersions of silver nanoparticles [11,12]. Since the individual MEPEO-*b*-PAAcNa2 and the MEPEO-*b*-PAAcNa2/Ag^+ mixture without adding $NaBH_4$ are not expected to absorb in the red region of the spectrum (Fig. 4a), the absorption maximum at 381 nm in the spectra of reaction mixtures can be attributed exclusively to silver nanoparticles (Fig. 4b). Through a few days, the position of the absorption peak becomes to be $\lambda_{max} = 408$ nm, and its intensity is lowering (Fig. 4c). Then the position of the absorption peak was invariable during several months. The position of the absorption peaks and their widths depend on the particle size [12]. From the position of the absorption maximum $\lambda_{max} = 408$ nm, we calculate the average particle diameter [12]:

$$d = 9476 - 46.632 \cdot \lambda_{max} + 0.0574 \cdot \lambda_{max}^2$$

So, we obtain the average particle diameter of 5 nm for Ag-containing MEPEO-*b*-PAAcNa2. The narrow width of the absorption maximum indicates a low polydispersity of nanoparticle sizes in the MEPEO-*b*-PAAcNa2 sample. The absorbance spectra of all reaction mixtures at the $pH = 8.9$ contain also the absorption band at $\lambda_{max} = 270–290$ nm which corresponds to silver clusters Ag_4^{2+} [9]. We note that the



(a) (b) (c) (d)

Figure 4. UV-VIS absorption spectra of the individual MEPEO-*b*-PAAcNa2 – *1* and the MEPEO-*b*-PAAcNa2/Ag^+ – *2* solutions at the pH = 8.9 (a), of the MEPEO-*b*-PAAcNa1/Ag^+ – *1*, MEPEO-*b*-PAAcNa2/Ag^+ – *2*, PAAcNa/Ag^+ – *3* reaction mixtures at the pH = 8.9 in a 2 hours after $NaBH_4$ addition (b), in a 72 hours after $NaBH_4$ addition (c), of these reaction mixtures at the pH = 2.5 in a 2 hours after $NaBH_4$ addition. $C_{DBC} = 1\,kg \cdot m^{-3}$, $[Ag^+]/[COO^-] = 0.01$, $[NaBH_4]/[Ag^+] = 8$.

stabilizing properties of MEPEO-*b*-PAAcNa2 copolymer (Fig. 4b, curve 2) in comparing with those of the homopolymer (Fig. 4b, curve 3) at the same length of PAAcNa chains (Table 1) reveal themselves more strongly. The reaction mixture of Ag^+-containing MEPEO-*b*-PAAcNa2 copolymer in two hours after adding $NaBH_4$ includes a much greater amount of silver nanoparticles and a smaller amount of silver clusters than the Ag^+-containing PAAcNa homopolymer under the same experimental conditions (because the absorption peak intensity at $\lambda_{max} = 381$–382 nm is higher by 1.5 times and the absorption peak intensity at $\lambda_{max} = 270$ nm is less by 1.5 times for MEPEO-*b*-PAAcNa2 than that for PAAcNa).

Figure 4d presents the UV-vis spectra of the reaction mixtures of Ag^+ with the micellar solutions of the protonated MEPEO-*b*-PAAc after the addition of $NaBH_4$. The absorption maximum near 400 nm in these spectra is absent. We can see only a small absorption band of Ag_4^{2+} silver clusters ($\lambda_{max} = 270$–290 nm). However, in the absorbance spectra of the Ag^+-containing MEPEO-*b*-PAAc and Ag^+-containing PAAc, we can see the absorption band at $\lambda_{max} > 800$ nm ($\lambda_{max} = 821$ nm for MEPEO-*b*-PAAc1/Ag^+, $\lambda_{max} = 864$ nm for MEPEO-*b*-PAAc2/Ag^+ and PAAc/Ag^+), the so-called "more dark blue silver". It is known that the absorption band at $\lambda_{max} > 450$ nm corresponds to the complexes of silver clusters with a PAAc polyanion [11]. Therefore, in reaction mixtures of Ag^+ with the micellar solutions of protonated MEPEO-*b*-PAAc and PAAc, we observed the partial recovering of Ag^+ to nanoclusters and their interactions with the PAAc polyanion. This fact is caused by a decrease of the $NaBH_4$ redox potential with decrease in pH of the reaction mixtures [1].

Conclusion

The self-assembly of the MEPEO-*b*-PAAc block copolymer in water at $pH \leq 4$ is established. The micellization process of MEPEO-*b*-PAAc macromolecules by means of hydrophobic interactions between the non-polar bound parts of copolymer blocks is developed most intensively when the ratio of the lengths of polymer blocks in the copolymer approaches 1. Silver nanoparticle-containing solutions of the deprotonated MEPEO-*b*-PAAcNa are obtained and studied. It is shown that the stabilizing property of the MEPEO-*b*-PAAcNa copolymers for the silver colloid dispersion is higher in comparison with that of PAAcNa at the same length of PAAcNa chains.

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