Interaction of Polystyrene-*block*-poly(ethylene oxide) Micelles with Cationic Surfactant in Aqueous Solutions. Metal Colloid Formation in Hybrid Systems

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The interaction of the amphiphilic block copolymer, polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO), with cationic surfactant, cetylpyridinium chloride (CPC), in aqueous media was studied by static light scattering and analytical ultracentrifugation. Three well-defined populations of hybrid structures corresponding to micelles, micellar clusters, and supermicellar aggregates were found to exist in the PS-*b*-PEO/CPC aqueous solutions at a block copolymer concentration of 10 g/L. The relative ratio of each type of structure and their parameters strongly depend on the CPC concentration, mobility of the polystyrene micellar core, and chemical composition of the dispersing media. Ion exchange of the surfactant counterions in the hybrid PS-*b*-PEO/CPC system by $PtCl_6^{2-}$ and $PdCl_4^{2-}$ ions resulted in saturation of the micellar structures with noble metal ions. The subsequent reduction of the metal-containing PS-*b*-PEO/CPC/MX_n species with $NaBH_4$ and molecular hydrogen resulted in the formation of metal nanoparticles mainly located in the block copolymer micelles.

Introduction

The tremendous attention paid to metal or metal compound nanoparticles in recent years is explained by their unique properties determined by the high surface areas of small particles and quantization of most electronic properties.[1−3] The use of polymeric matrixes as a medium for metal nanoparticle formation allows controlling the nanoparticle nucleation and growth and also imparting the new properties to polymeric materials.[4−8] There are various methods to form nanoparticles in a polymeric environment.[4−20] One promising approach is the formation of metal nanoparticles in the micelle cores of amphiphilic block copolymer micelles in apolar solvents when the polymeric system is already nanostructured.[10−20] In these systems the nonpolar block is soluble in the solvent, while the polar block forms the core which is able to consume metal compounds due to coordination. The cores can be considered as nanoreactors where under reduction nucleation and growth of metal nanoparticles occur. It seems appropriate to apply a similar approach to aqueous media; however, amphiphilic block copolymers, for example, polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO), in water and other polar solvents form micelles with a

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nonpolar core, which cannot coordinate with metal compounds. At the same time, water is an environmentally friendly solvent and can be used as a reaction medium in catalytic reactions with water-soluble substrates. In this paper we suggest a novel approach for imparting functionality to a nonpolar micelle core formed by an amphiphilic block copolymer. We have assumed that if cationic or anionic surfactants are added to aqueous micellar solutions of amphiphilic diblock copolymers (e.g., PS-*b*-PEO), the surfactants will penetrate the hydrophobic micellar cores of block copolymers. In this case, the surface of the micelle cores will be charged with headgroups of the corresponding surfactants, while the surfactant counterions neutralizing the micellar charge will be preferentially located in the corona of the micelles. By exchanging surfactant counterions (Na^+, Cl^-) with metal ions (either cations, such as $Ag(H_2O)_2{}^{2+}$, $Ni(H_2O)_6{}^{2+}$, or $Cu(H_2O)_4{}^{2+}$, or anions, i.e., $PtCl_6{}^{2-}$, $PdCl_4{}^{2-}$, or others), the latter will saturate the micellar corona. Subsequent reduction of the metal ions with various reducing agents is expected to result in the formation of metal nanoparticles covering the PS micelle cores.

It was concluded that these hybrid PS-*b*-PEO/surfactant systems will provide control over metal nanoparticle formation. On the other hand, several publications describing the interaction of sodium dodecyl sulfate (SDS) with ABA type block copolymers derived from Pluronics (EO_x−PO_y−EO_x) reported the decomposition of block copolymer micelles upon complexation with surfactant molecules.[21−23] The higher the concentration of SDS, the lower the aggregation number of block copolymer micelles, which finally results in micelle decomposition and in a solution where block copolymer molecules are saturated with surfactant molecules at 0.1 mol/L SDS.[23] The present paper is focused on the formation of block copolymer/surfactant micellar complexes, derived from PS-*b*-PEO and cationic surfactant, cetylpyridinium chloride (CPC), and on the synthesis of Pd and Pt nanoparticles in these hybrid systems. To prevent the block copolymer micelles from decomposing upon complexation with surfactant molecules, the CPC concentration was limited to 0.8×10^{-3} to 0.2×10^{-2} mol/L.

In a preceding publication[24] we reported on the structure of PS-*b*-PEO aqueous solutions. By ultracentrifugation, aqueous solutions of PS-*b*-PEO were found to contain micelles and micellar clusters,[24] which agree with the results obtained by other authors.[25,26] The means for decomposing the micellar clusters were also developed.[24]

Experimental Section

PS-*b*-PEO (SE 1030), PS-1000, PEO-3000, $M_n = 4000$, $M_w = 6200$ (by ultracentrifugation), was received from Goldschmidt (Germany) and used without further purification. Toluene and THF were distilled under KOH. KCl (Reakhim), $NaBH_4$ (Reidel-de-Haen), CPC, $H_2PtCl_6 \cdot 6H_2O$, and K_2PdCl_4 (Aldrich) were used as received. Water was purified with a Milli-Q water purification system.

Polymer samples were prepared by dissolution of PS-*b*-PEO block copolymer (concentration of 5−10 g/L or 0.8×10^{-3} to 0.16×10^{-2} mol/L) in H_2O, H_2O/THF (5 vol % of THF), H_2O/toluene (0.5−1.0 vol % of toluene), and H_2O/ethanol (5−10 vol % of ethanol) under vigorous stirring for 24 h. After block copolymer dissolution, CPC was added to the micellar solution to prepare a concentration of 0.8×10^{-3} to 0.2×10^{-2} mol/L. In the case of KCl and $NaBH_4$, the corresponding salt was added to the PS-*b*-PEO/CPC solution to prepare concentrations of 0.66×10^{-2} and 1.68×10^{-2} mol/L, respectively.

Metalation of the PS-*b*-PEO/CPC micelles was performed in air by simple mixing of the PS-*b*-PEO/CPC solution with aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ or K_2PdCl_4. Metal salt concentration was varied in the range 1.2×10^{-3} to 1.7×10^{-2} mol/L. The metalated samples were stirred for 2 h (or 7 days or more) and then reduced with $NaBH_4$ (5-fold excess). H_2 reduction of the Pt- and Pd-containing samples was carried out by a method described elsewhere.[27] Prior to that, solutions were degassed during three freezing−thawing cycles with evacuation in the frozen state and filling with argon at the end.[12,13] $NaBH_4$ reduction was carried out in air.

Viscosity of solutions was measured with an automatic viscosimeter AVS-400 (Germany). Examination of molecular weight and micelle sizes was performed by static light scattering measurements with the Fica-50 (France) goniodiffusometer using vertically polarized light of wavelength $\lambda = 546$ nm in the angle interval 30−150° by standard procedure.[28]

The diffusion and sedimentation rates of the sedimenting species were studied using an analytical ultracentrifuge MOM 3180 (Hungary) with Philpot-Svensson optics ($T = 25 \pm 0.1$ °C, $\lambda = 546$ nm). The total diffusion coefficients D were calculated from the broadening rate of a synthetic boundary formed in the ultracentrifuge cell between the polymer solution and the pure solvent.[29] For micelles and micellar clusters, diffusion coefficients were calculated from the value of the area under the appropriate peak. Having calculated diffusion coefficients, the micelle radii of gyration R_g were calculated from the Stokes equation for the spherical particles.[30] The sedimentation coefficients S_c were calculated from the rate of migration of the concentration zone in the force field of the ultracentrifuge.[29] Values of molecular weights were calculated according to the first Svedberg formula.[29]

The specific partial volume $\bar{V}$ and the solvent density ρ_0 were measured by pycnometry ($T = 25 \pm 0.05$ °C). Before measurement, the pycnometer was calibrated by Hg.

Samples for transmission electron microscopy were prepared by evaporation of 10^{-4} mol/L aqueous solutions containing Pt or Pd nanoparticles in air. A drop of solution was placed on an electron microscope copper grid. After drying, electron micrographs of the sample were taken with an EM-125 electron microscope.

Results and Discussion

1. Characteristics of Micelles and Micellar Aggregates in Aqueous Solutions of PS-*b*-PEO/CPC.

To evaluate the interaction of cationic surfactant molecules with the amphiphilic block copolymer PS-*b*-PEO, viscosimetry, static light scattering, sedimentation, diffusion in ultracentrifuge, and dilatometry were employed. Three different surfactant concentrations were examined: (i) 0.8×10^{-3} mol/L which is below the critical micelle concentration (cmc) value[31] and excludes CPC micelle formation in the PS-*b*-PEO solutions, (ii) 0.14×10^{-2} mol/L which is the cmc for water, and (iii) 0.2×10^{-2} mol/L which is above the cmc. Dilution of the initial PS-*b*-PEO/CPC solutions during sedimentation experiments to a concentration of 5 g/L was carried out with solvent that contained the corresponding amount of CPC in water.

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Table 1. Characteristics of Micellar Structures in the PS-*b*-PEO/CPC Aqueous Solutions[a]

				micelles					micellar clusters					supermicellar aggregates
CPC loading, mol/L	10^{-6} $M_w^{(m)}$	$\bar{V}$, cm^3/g	[η], g/dL	% w_1	10^{13} S_o, s	$10^7 D_o$, cm^2/s	10^{-6} M_{SD}	R_g, nm	% w_2	$10^{13} S_o$, s	$10^7 D_o$, cm^2/s	10^{-6} M_{SD}	R_g, nm	% w_3
0	2.20[b]	0.825	0.14	29	3.7	2.0	0.255	12.8	71	12.5	0.62	2.80	42.1	0
0.8×10^{-3}	2.10	0.863	0.15	61	2.6	1.9	0.260	12.8	30	11.6	0.59	3.75	43.3	9
0.14×10^{-2} (cmc)	2.20	0.871	0.17	55	2.8	1.9	0.325	13.5	34	13.2	0.50	4.3	48.8	11
0.2×10^{-2}	2.56	0.896	0.20	46	3.1	1.7	0.346	14.3	36	17.2	0.48	4.50	50.8	18

[a] Here and in Tables 2 and 3, S_o is the sedimentation coefficient (relative deviation ±1%), D_o is the diffusion coefficient (relative deviation ±1.5%), M_{SD} is the micellar weight of the fraction obtained from sedimentation data (relative deviation ±5%), R_g is the radius of gyration (relative deviation ±5%), $\bar{M}_w$ is the total micellar weight obtained from static light scattering data (relative deviation ±5%), $\bar{V}$ is the partial volume (relative deviation ±5%), and [η] is an intrinsic viscosity (relative deviation ±1%). w_1-%, w_2-%, and w_3-% are the weight fractions of micelles, micellar clusters, and supermicellar aggregates (relative deviation ±2.5%). [b] The total micellar molecular weight of PS-*b*-PEO in water $M_{SD}\Sigma$ obtained from ultracentrifugation data and calculated from the eq 1 is equal to 2.10×10^{-6}.

The interaction of water-soluble amphiphilic AB block copolymers of polystyrene and poly(ethylene oxide) with anionic surfactant, sodium lauryl sulfate (SLS), is described in ref 32. Block copolymers described in that paper that have a very short PS block compared to PEO (PEO/PS > 12) did not form micelles. With NMR and solution viscosity, the authors showed that both the PS and PEO blocks do interact with SLS. Unlike these systems, the PS-*b*-PEO chosen by us has a higher fraction of the PS block (PEO/PS = 3:1), which results in micelle formation in water despite the low molecular weight of blocks. This fact should strongly influence the interaction of block copolymer with surfactant molecules.

The CPC molecules form micelles in water with an aggregation number of 90−100 and average molecular weight of 32×10^3 when their concentration in solution reaches the cmc. PS-*b*-PEO in THF, a good solvent for both blocks, forms a molecular solution. In water, which is a selective solvent for PS-*b*-PEO, i.e., water is a solvent only for the PEO block, the block copolymer forms micellar structures with the average micellar weight M_w of about 2×10^6 and radius of gyration R_g of 60 nm (by static light scattering).[24] By sedimentation in an ultracentrifuge,[24] the PS-*b*-PEO aqueous solution contains 29% (±2.5%) micelles with micellar weight of 0.255×10^6 and 71% (±2.5%) of micellar clusters with micellar weight of 2.8×10^6 (Table 1). From these data, the average micellar weight can be calculated by eq 1

$$M_{SD}\Sigma = w_1 M_{SD(1)} + w_2 M_{SD(2)} \quad (1)$$

where w_1, $M_{SD(1)}$ and w_2, $M_{SD(2)}$ are the weight fractions and the molecular weights of micelles and micellar clusters, respectively. From Table 1 one can see that micellar weight values obtained from two independent methods are in good agreement.

Similarly to aqueous solutions of PS-*b*-PEO,[24] sedimentation in an ultracentrifuge for aqueous systems containing different amounts of CPC shows the presence of two main types of micellar structures: micelles and micellar clusters. Quantitative characteristics of those structures and their ratios are presented in Table 1. Examination of the data implies that the increase of CPC results in an increase in molecular weight for both micelles and micellar clusters and an increase in their sizes as well. This supports a hypothesis that the CPC molecules do incorporate into the block copolymer micelles and micellar clusters. Another independent confirmation is an increase of intrinsic viscosity [η] measured for the system containing CPC compared to the solution without surfactant (Table 1). The increase of intrinsic viscosity can be explained by an increase in size of both micelles and micellar clusters after incorporation of CPC molecules. The higher the CPC concentration, the more the CPC molecules are incorporated into the block copolymer micelles and clusters, thus resulting in the increase of their volume and the [η] values, respectively. If surfactant micelles with size much less than that of the block copolymer micelles (compare the M_w values of 32×10^3 and 255×10^3, respectively) would form in the hybrid solution, the intrinsic viscosity would only decrease.

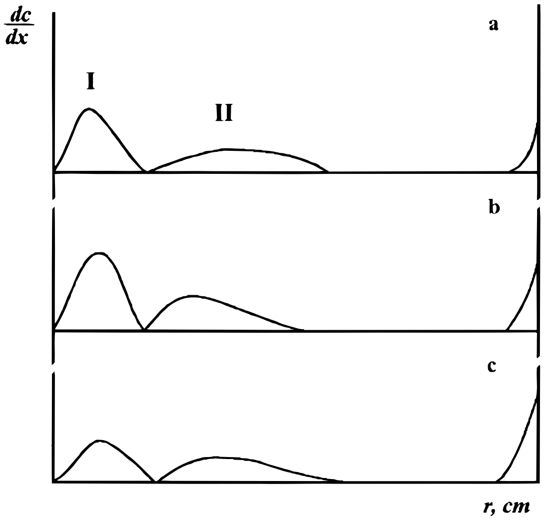

Figure 1. Sedimentograms of PS-*b*-PEO in aqueous solutions containing various amounts of CPC: 0.8×10^{-3} (a), 0.14×10^{-2} (b), and 0.2×10^{-2} (c). The PS-*b*-PEO concentration was 0.5 g/L. Here and in Figure 2, rotation rate was 50 000 rpm and time was 30 min (from the beginning of rotation). Characteristic sedimentation coefficients (S_c) for the main peaks I and II (for Figures 1 and 2) are presented in Table 4.

Sedimentograms of the PS-*b*-PEO aqueous solutions (rotation rate 50 000 rpm) containing 0.8×10^{-3}, 0.14×10^{-2}, and 0.2×10^{-2} mol/L CPC are presented in Figure 1. In sedimentograms, near the bottom of the sedimentation unit one can see the third peak. The area below this peak (that is proportional to fraction) increases with increase of the surfactant concentration in the system. It can be supposed that near the bottom we observe even larger structures than those already characterized as micellar clusters. Appearance of that third peak can be explained by the formation of "supermicellar aggregates" consisting probably of micellar clusters and the CPC molecules. With increase of the CPC loading in the system from 0.8×10^{-3} to 0.2×10^{-2} mol/L, the fraction of aggregates increases from 9 to 18%. For the system containing 0.2×10^{-2} mol/L CPC, we calculated the sedimentation coefficient for the third peak which was 35.0×10^{-13} s, which is twice as much compared to the sedimentation coefficient of the micellar clusters.

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From the discussion above, one can see that surfactant molecules interact both with micelles and micellar clusters. Moreover, with the latter this interaction is apparently more favorable and induces the formation of supermicellar aggregates.

In ref 23 the authors claimed that anionic, cationic, and even zwitterionic surfactants interact with the block copolymers and thereby suppress their micellization However, the data obtained in our experiments show that this generalization seems not quite correct. The interaction of block copolymers with surfactant molecules does not necessarily suppress the micellization of block copolymers. In particular cases, comicellization can be preferable. One can surmise that it depends on both the surfactant and block copolymer structure.

2. The Association of PS-*b*-PEO/CPC in the Presence of Various Additives in Water. After characterization of the PS-*b*-PEO/CPC micellar solutions, we focused on controlling the structure of these solutions. Micellar clusters in aqueous solutions of block copolymers containing the PEO block are supposed to be formed due to various interactions including hydrogen bonding between PEO chains and water and the structure of water and hydrophobic interactions between PEO units of the neighboring chains.[33-35] As published recently,[36] aggregative processes in the PEO solutions can be activated by inhomogeneities, for example, due to impurities, and the tendency for aggregation is strengthened in low molecular weight PEO. In the preceding paper,[24] following general understanding of the formation of these aggregates,[33-35] we discussed two ways to influence the micellization behavior of PS-*b*-PEO in aqueous solutions. One avenue is to affect the interaction of PEO chains with each other, which can be accomplished by several means. Another is to influence the mobility of the PS core by addition of small amounts of solvents, preferably soluble in the micelle core. This approach was derived from the comparison of two block copolymers: PS-*b*-PEO and PB-*b*-PEO.[24] The latter does not form stable micellar clusters in aqueous solutions which can be explained by high mobility of the PB ($T_g^{\mathrm{PB}-1,2} = 12$ °C) micelle core. Similar to PS-*b*-PEO,[24] we examined the hybrid system PS-*b*-PEO/CPC in the presence of various additives.

2.1. KCl and NaBH$_4$ Addition. As mentioned above, the addition of substances which might coordinate with PEO units and disrupt the interpolymer attraction should prevent micellar cluster formation. The influence of ionic species on block copolymer morphology was discussed in refs 37 and 38. We described the influence of NaBH$_4$ and KCl addition on the morphology of a PS-*b*-PEO micellar system in water resulting mainly in decomposition of the micellar clusters, while characteristics of the micelles were not much influenced.[24] The choice of NaBH$_4$ was determined by its use as a reducing agent for metal nanoparticle formation.

To investigate how the presence of these compounds can affect the micelle-to-cluster transformation, we have examined the structural properties of PS-*b*-PEO solutions containing 0.8×10^{-3} mol/L CPC after introduction of NaBH$_4$ and KCl (Table 2). Here, sedimentograms display the complete absence of the peaks corresponding to micellar clusters and supermicellar aggregates, while micelle size and micelle weight slightly decrease in the case of KCl. Such a change of the micellar parameters can be explained by the complexity of the system containing many different ions. In the case of NaBH$_4$, micellar characteristics do not change, though pyridine rings of the CPC molecules can be easily hydrogenated in the presence of NaBH$_4$ with formation of the mixture of reduced pyridines,[39] some of them are not charged yet. One can treat this fact as the change of the chemical behavior of the CPC molecules (stabilization of pyridine rings toward hydrogenation) in the PS-*b*-PEO micellar solutions compared to other surfactant complexes (for example, complex of anionic polyelectrolyte gel with CPC).[40] One can speculate that this is connected with the absorption of the CPC molecules by the block copolymer micelles which makes the hydrogenation less probable.

Table 2. Structural Characteristics of the PS-*b*-PEO and PS-*b*-PEO/CPC (0.8×10^{-3} mol/L CPC) Aqueous Solutions in the Presence of Ethanol, KCl (0.66×10^{-2} mol/L) and NaBH$_4$ (1.68×10^{-2} mol/L)

	micelles[a]				
solvent	$10^{13}S_o$, s	10^7D_o, cm^2/s	10^{-6} M_{SD}	R_g, nm	$\bar{V}$, cm^3/g
5 vol % C_2H_5OH	15.5	3.8	0.320	8.2	0.825
5 vol % C_2H_5OH + CPC	3.4	1.6	0.400	15.3	0.886
10 vol % C_2H_5OH	2.0	4.5	0.058	5.3	0.833
10 vol % C_2H_5OH + CPC	0.9	5.0	0.043	4.5	0.910
NaBH$_4$	3.8	1.8	0.260	14.2	0.798
NaBH$_4$ + CPC	2.8	1.7	0.264	14.4	0.844
KCl	4.0	2.2	0.265	11.7	0.830
KCl + CPC	2.4	2.4	0.155	10.0	0.844

[a] Weight fraction of micelles w$_1$-% is 100%.

2.2. The Toluene Addition. As found previously,[24] the addition of 0.5 vol % toluene, which is a selective solvent for PS, to the aqueous PS-*b*-PEO solution diminishes the micelle cluster fraction to 36%. At the same time, the micelle weight and micelle size were slightly increased due to swelling of the micelle core. Introduction of 0.5 vol % toluene in the hybrid PS-*b*-PEO/CPC solution containing 0.8×10^{-3} mol/L CPC results in further decrease of the cluster content to 27% and decrease of their molecular weight up to 2.23×10^6. At the same time, the values of M_{SD} and R_g of micelles increase and micelles become even less dense: $\bar{V}$ increases, which means that the density in the system decreases (Table 3). However, the addition of 1 vol % toluene to the PS-*b*-PEO solution and to the hybrid PS-*b*-PEO/CPC system yields a completely different result. In the case of PS-*b*-PEO, the micellar clusters still exist and the micelles become larger and less dense (Table 3). In the case of PS-*b*-PEO/CPC, micellar clusters and supermicellar aggregates disappear, while the M_{SD} and R_g values of the micelles strongly decrease.

We suggest the following interpretation of these events. In the absence of surfactants, the addition of toluene only promotes the swelling of the micelle cores. The influence of additives of low-molecular-weight solvent solubilizing the aggregates derived from chain molecules with associating groups was studied by Monte Carlo computer simulations using the bond fluctuation model.[41] As shown, upon the addition of solvent the aggregates adopt a three-

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Table 3. Structural Characteristics of the PS-*b*-PEO and PS-*b*-PEO/CPC (0.8 × 10^{-3} mol/L CPC) Aqueous Solutions in the Presence of Various Modifying Additives

	micelles					micellar clusters					
media	w_1-%	$10^{13}S_o$, s	10^7D_o, cm^2/s	10^{-6} M_{SD}	R_g, nm	w_2-%	$10^{13}S_o$, s	10^7D_o, cm^2/s	10^{-6} M_{SD}	R_g, nm	$\bar{V}$, cm^3/g
5 vol % THF	42	4.1	1.9	0.360	13.0	58	8.8	0.82	2.00	30.0	0.869
5 vol % THF + CPC	34[a]	2.8	2.0	0.400	12.2	46	6.5	0.90	2.07	27.2	0.917
0.5 vol % toluene	64	4.0	1.8	0.340	14.2	36	14.8	0.50	4.65	51.4	0.839
0.5 vol % toluene + CPC	73	3.7	1.7	0.330	15.1	27	11.1	0.90	2.23	28.5	0.863
1 vol % toluene	73	6.2	1.50	0.410	16.3	27	11.1	0.90	2.23	28.5	0.863
1 vol % toluene + CPC	100	3.3	3.2	0.165	7.6						0.839

[a] This solution contains 20% of supermicellar aggregates.

Table 4. Characteristic Sedimentation Coefficients ($10^{13}S_c$, s) for the Main Peaks I and II in Figures 1 and 2

	Figure 1			Figure 2		
peaks	a	b	c	a	b	c
I	2.48	1.77	1.90	2.84	1.97	2.04
II	10.2	9.2	7.39	10.9		

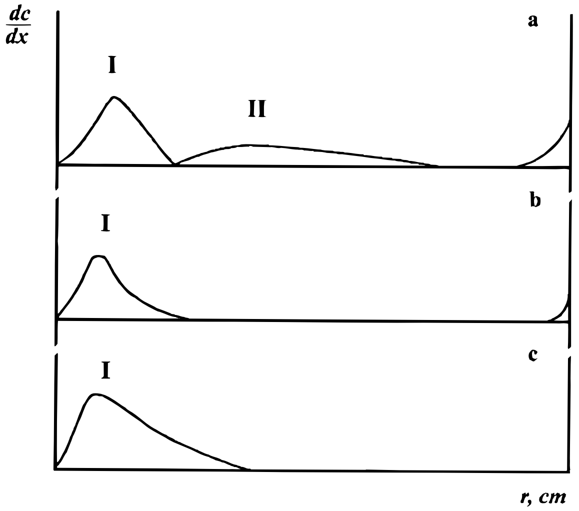

Figure 2. Sedimentograms of the aqueous solutions of PS-*b*-PEO/CPC (0.8 × 10^{-3} mol/L CPC) containing 5 vol % THF (a), 5 vol % C_2H_5OH (b), and 1 vol % toluene (c).

layer structure with the "lake" of the solvent molecules in the central region. Amphiphilic block copolymers are aggregates of this kind, and analogy is relevant. When CPC is loaded, its molecules can easier penetrate in the swollen (due to toluene) micelle cores (the more the toluene loading, the easier the penetration), which results in a higher percentage of charges on the surface of the micelle core. This, in turn, must increase the repulsion between the CPC headgroups and might result in larger micelles. However, the main contribution to the effective repulsion is additional osmotic pressure of counterions in the corona rather than direct electrostatic repulsion of the heads of surfactants. This repulsion must rather generate smaller micelles. Another factor is that attraction due to hydrophobic interactions in the micelle cores will tend to keep the micelles smaller, which can be especially pronounced for short block copolymers (Table 2). The sedimentogram of the PS-*b*-PEO/CPC aqueous solution containing 1 vol % of toluene is presented in Figure 2.

2.3. The Ethanol Addition. Another way we explored for controlling the micellar cluster presence in the PS-*b*-PEO solution[24] was addition of alcohols which were expected to change the hydrophobicity of the solvent. Addition of 5 vol % ethanol to PS-*b*-PEO/CPC results in the decomposition of the micellar clusters and formation of micelles (Figure 2). At the same time, micellar weight and size increase. This can be explained by more active incorporation of surfactants inside the micelle cores in the presence of 5 vol % ethanol. The introduction of 10 vol % ethanol to PS-*b*-PEO/CPC also decomposes the micellar clusters and supermicellar aggregates, but changes proceeding with micelle parameters are completely different and really prominent: micelle weight and size dramatically decrease (Table 2). In the preceding paper[24] we explained this phenomenon, observed in the absence of surfactant molecules, by an increase of hydrophobicity of the PEO chains in water/ethanol which results in the shrinkage of the PEO chains (water becomes poor solvent for more hydrophobic chains) and decrease of the micelle size due to steric hindrances in corona. A similar explanation is possible for PS-*b*-PEO/CPC containing 10 vol % of C_2H_5OH. The sensitivity of micellar parameters to the amount of alcohol (5 and 10 vol %) seems to be really remarkable.

Another possible explanation of the ethanol impact on the morphology of PS-*b*-PEO and PS-*b*-PEO/CPC micelles is that addition of alcohol can significantly lower the surface tension of the polystyrene core, decreasing the aggregation number of micelles. To check this supposition, we examined the influence of THF (which is a much better solvent for PS compared to ethanol and should also diminish surface tension) on the structural characteristics of diblock copolymer solutions (Figure 2). The data presented in Table 3 show that addition of 5 vol % THF to the PS-*b*-PEO micellar solutions in water does not result in any pronounced changes of their morphology: only change of the micelle density ($\bar{V}$ increases) was observed. Furthermore, in contrast to ethanol-containing solutions, THF addition does not disintegrate the micellar aggregates in the system.

3. Metal Nanoparticle Formation in the PS-*b*-PEO/CPC System. Thus, CPC molecules penetrate the PS-*b*-PEO micelles and micellar clusters, forming a hybrid system. According to our supposition, this penetration should charge the PS cores, making them able to attract counterions. At the same time, exchange of surfactant monovalent counterions (Cl^-) for divalent metal anions should be favorable from the viewpoint of entropy. Relying on this hypothesis, we studied the interaction of the PS-*b*-PEO/CPC system with $PtCl_6^{2-}$ and $PdCl_4^{2-}$ anions followed by reduction of metal ions. The formation of Pd, Pt, and gold nanoparticles in the coronas of the PS-*b*-PEO micelles was described in ref 42. The authors observed the formation of small nanoparticles, but solely hydrophobic interactions with the PS core were not sufficient to provide a good stabilization of nanoparticles. In the present paper we report a few details of ion incorporation

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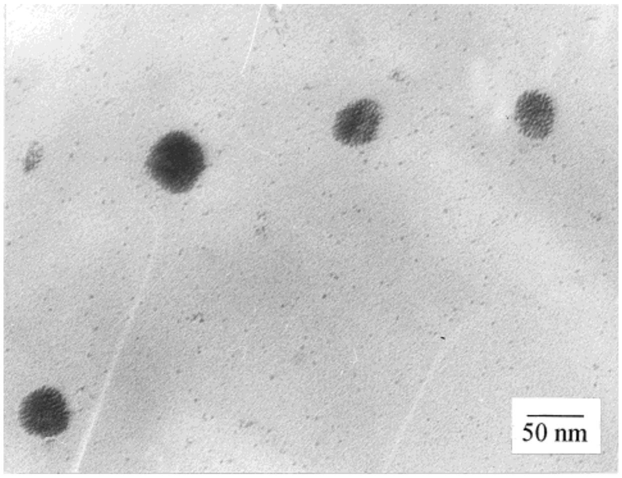

Figure 3. TEM micrograph of Pt nanoparticles stabilized in the PS-*b*-PEO/CPC block copolymer micelles in water and obtained via reduction of $H_2PtCl_6 \cdot 6H_2O$ (1.24×10^{-2} mol/L) with $NaBH_4$.

into the hybrid micelles and demonstrate the possibility of forming nanoparticles in close vicinity of the PS cores in the hybrid solutions.

To clarify how the time of stirring of the hybrid PS-*b*-PEO/CPC/$H_2PtCl_6 \cdot 6H_2O$ system influences the structure and properties of metal nanoparticles, the series of platinum colloids reduced with $NaBH_4$ was prepared in this system after different exposure times. The $NaBH_4$ reduction of $H_2PtCl_6 \cdot 6H_2O$ in 2 h after its dissolution in the PS-*b*-PEO/CPC aqueous solution was found to result in rather big (from 80 to 100 nm in diameter) and unstable aggregates, which precipitate in several days. In the case of 1 week exposure of the PS-*b*-PEO/CPC/$H_2PtCl_6 \cdot 6H_2O$ system, we observed the formation of large nearly spherical aggregates of 26 ± 4 nm in diameter that were densely constructed from small particles of about 2−4 nm in size (Figure 3). We surmise that such aggregates are block copolymer micelles containing Pt nanoparticles in the corona and these micelles become visible due to staining with small Pt particles. Big micellar clusters were not observed, which is in agreement with sedimentation data, because the addition of $NaBH_4$ decomposes micellar clusters (see discussion above for the system containing $NaBH_4$). Similar results were obtained after 3 weeks of stirring of the system before reduction. The stability of Pt nanoparticles prepared in this way was provided when $H_2PtCl_6 \cdot 6H_2O$ loading was varied from 0.16×10^{-2} to 1.24×10^{-2} mol/L. It should be noted that Pt nanoparticles prepared at the same reaction conditions in the PS-*b*-PEO aqueous solutions in the absence of surfactant were stable only for several hours and then precipitation occurred.

Another way to prepare Pt nanoparticles in the PS-*b*-PEO/CPC/$H_2PtCl_6 \cdot 6H_2O$ system is with H_2 reduction. Unlike $NaBH_4$, the advantage of H_2 reduction is the lack of side products which might cover the particle surface.[43] Hydrogen reduction of the PS-*b*-PEO/CPC+$H_2PtCl_6 \cdot 6H_2O$ system after 1 week of stirring results in the formation of stable platinum colloids. In Figure 4a one can see that the sample consists of micellar structures, which are nearly spheres (some cylindrical structures are present) with a mean diameter of 100 ± 15 nm that is close to the average size of the micellar clusters within experimental error. Figure 4b presents the biggest aggregates found in the system which consists of particles of 2−4 nm in diameter. The stability of colloidal solutions was provided when $H_2PtCl_6 \cdot 6H_2O$ loading did not exceed 3.36×10^{-3} mol/L. A careful look on all the micrographs shows that most of Pt particles are located in micelles or micellar clusters, while only a negligible fraction of Pt colloids is formed between them (Figures 3 and 4). In the system where micellar clusters were absent (that is when $NaBH_4$ was used as reducing agent), Pt nanoparticles showed an enhanced stability.

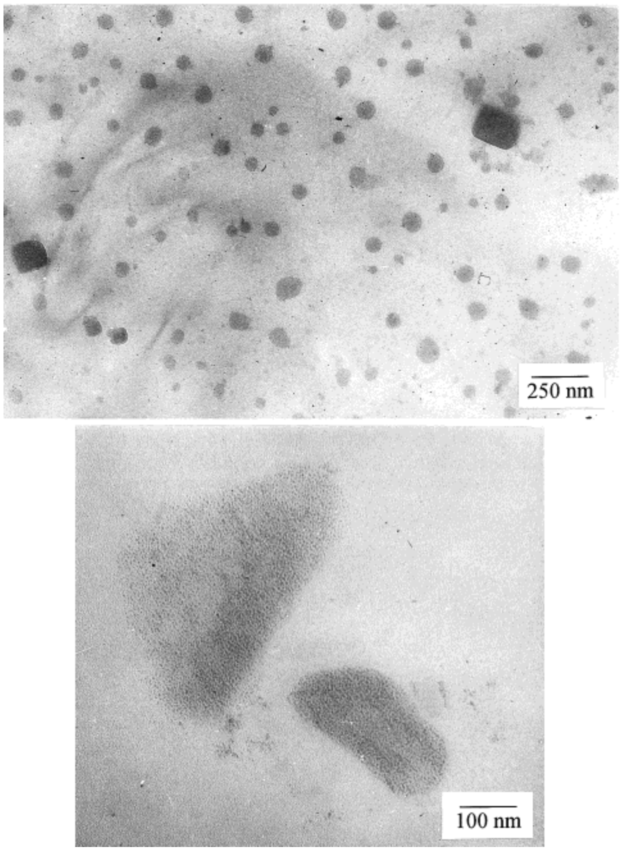

Figure 4. TEM micrographs of Pt nanoparticles stabilized in the PS-*b*-PEO/CPC block copolymer micelles in water and obtained via reduction of $H_2PtCl_6 \cdot 6H_2O$ (3.36×10^{-3} mol/L) with molecular hydrogen.

The formation of Pd colloids proceeds similarly to Pt ones. Dissolution of K_2PdCl_4 in the PS-*b*-PEO/CPC hybrid system and subsequent reduction of metal compound with $NaBH_4$ results in the formation of Pd nanoparticles of 4−6 nm in size which are located in micelles with a mean diameter of 20 ± 5 nm. Pd colloids were very stable in the concentration range of 0.42×10^{-2} to 1.24×10^{-2} mol/L. Thus, $NaBH_4$ reduction of Pt and Pd compounds immobilized in the PS-*b*-PEO/CPC micellar system completely decomposes micellar clusters and results in the formation of solely micelles with embedded metal nanoparticles; i.e., the hybrid PS-*b*-PEO/CPC system does function as a "nanoreactor" for metal nanoparticle formation.

Conclusions

The interaction of the PS-*b*-PEO micellar structures with cationic surfactant, CPC, was studied by static light scattering and analytical ultracentrifugation. Three types of micellar structures were found in this system: micelles, micellar clusters, and supermicellar aggregates. Increase of the CPC loading in the PS-*b*-PEO aqueous solution was

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shown to result in increase of the micellar weight and size of both micelles and micellar clusters and increase of the intrinsic viscosity of the PS-*b*-PEO/CPC solutions. These facts confirm the incorporation of CPC molecules in the block copolymer micelles and micellar clusters with a formation of hybrid systems. Moreover, the interaction of CPC with micellar clusters induces the formation of supermicellar aggregates.

The morphology of the hybrid PS-*b*-PEO/CPC system in water can be controlled in the same way as for PS-*b*-PEO. Decomposition of micellar clusters can be provided by addition of the salts affecting an ability of the PEO units to interact with each other, selective solvents for the PS core (toluene), or solvents capable of changing the hydrophobicity of PEO in water (ethanol).

The morphology and stability of Pt and Pd nanoparticles synthesized in the PS-*b*-PEO/CPC micellar solutions depend on the reducing agent type and metal salt concentration. Reduction of metal salts with $NaBH_4$ results in decomposition of the micellar clusters and formation of micelles with embedded metal nanoparticles. These systems display an enhanced stability. H_2 reduction results in small nanoparticles mainly located in micelles and micellar clusters.

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