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Morphology of hybrid polystyrene-*block*-poly(ethylene oxide) micelles: Analytical ultracentrifugation and SANS studies

Lyudmila M. Bronstein [a,*], Irina A. Khotina [b], Dmitri M. Chernyshov [b], Peter M. Valetsky [b], Galina I. Timofeeva [b], Lidiya V. Dubrovina [b], Barry Stein [c], Robert Karlinsey [a], Alessandro Triolo [d], A. Weidenmann [e], F. Lo Celso [f], Roberto Triolo [f], Alexei R. Khokhlov [b,g]

[a] *Department of Chemistry, Indiana University, Bloomington, IN 47405, USA*
[b] *A.N. Nesmeyanov Institute of Organoelement Compounds, 119991 Moscow, Russia*
[c] *Department of Biology, Indiana University, Bloomington, IN 47405, USA*
[d] *Istituto per i Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche, via La Farina, 237, 98123 Messina, Italy*
[e] *Hahn-Meitner Institut, Glienicker str. 100, D-14109 Berlin, Germany*
[f] *Dipartimento Chimica Fisica "F. Accascina," Università di Palermo, V.le delle Scienze-Pad. 17, I-90128 Palermo, Italy*
[g] *Physics Department, Moscow State University, Moscow, Russia*

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Abstract

Morphology and structure of aqueous block copolymer solutions based on polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) of two different compositions, a cationic surfactant, cetyl pyridinium chloride (CPC), and either platinic acid ($H_2PtCl_6{\cdot}6H_2O$) or Pt nanoparticles were studied using a combination of analytical ultracentrifugation (AUC), transmission electron microscopy (TEM), and small angle neutron scattering (SANS). These studies combining methods contributing supplemental and analogous structural information allowed us to comprehensively characterize the complex hybrid systems and to discover an isotope effect when H_2O was replaced with D_2O. In particular, TEM shows formation of both micelles and larger aggregates after incorporation of platinic acid, yet the amount of aggregates depends on the $H_2PtCl_6{\cdot}6H_2O$ concentration. AUC reveals the presence of micelles and micellar clusters in the PS-*b*-PEO block copolymers solution and even larger (supermicellar) aggregates in hybrids (with CPC). Conversely, SANS applied to D_2O solutions of the similar species indicates that micelles are spherical and no other micellar species are found in block copolymer solutions. To reconcile the SANS and AUC data, we carried out AUC examination of the corresponding D_2O block copolymer solutions. These measurements demonstrate a pronounced isotope effect on micelle aggregation and micelle size, i.e., no micelle aggregation in D_2O solutions, revealing good agreement of AUC and SANS data.

Keywords: Block copolymer; Surfactant; Hybrid micelles; Isotope effect

1. Introduction

For the last decade, the interaction of various surfactants (anionic, cationic, nonionic) with block and graft copolymers (both nonionic and containing polyelectrolyte block) was extensively studied by a number of researchers [1–20]. Among block copolymers interacting with surfactants, most thoroughly investigated are commercially available poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymers (Pluronics) [1–7,12,13,16], polystyrene-*block*-poly(ethylene oxide), PS-*b*-PEO [10,11,15], poly(ethylene oxide)-*block*-poly(sodium methacrylate [8,9] or acrylate [21]), etc. For all systems containing block (or graft) copolymer and surfactant, the complexation between surfactants and copolymers (either only with hydrophobic part or both with hydrophobic and hydrophilic parts of copolymers) was established; yet, the structure of mixed (or hybrid) micelles was found to depend on the types of copolymers and surfactants and reaction conditions. If a hydrophilic part of a copolymer

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[*] Corresponding author.
E-mail address: lybronst@indiana.edu (L.M. Bronstein).

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is ionic, the main driving force for mixed micelle formation with oppositely charged surfactants is the electrostatic interaction between oppositely charged groups [8,18,21], although hydrophobic interactions should be taken into account as well [6]. Moreover, the hydrophobic interaction should become crucial for mixed micelles of copolymers with charged groups and similarly charged surfactants [14] and for uncharged block copolymers with ionic or nonionic surfactants. On the other hand, if block or graft copolymers contain a poly(ethylene oxide) block (PEO), driving forces should become even more complex and result in more uncertain structures, as interaction of PEO with surfactants may take place: PEO is known to induce micellization of surfactant molecules below the critical micelle concentration (cmc) and to connect micelles by PEO chains [22–27]. When another, more hydrophobic block is present along with PEO, surfactant molecules compete for more preferable interaction sites [28]. As shown in a number of publications, this results in the formation of mixed micelles including both surfactant molecules and copolymer macromolecules [6,7,12,15,29]. In our preceding papers [10,11,15], we described the formation of mixed (hybrid) micellar systems containing PS-*b*-PEO (SE1030, Goldschmidt AG) and cationic surfactant, cetyl pyridinium chloride (CPC), or anionic surfactant, sodium dodecyl sulfate (SDS). These mixed micellar systems are efficient stabilizing media for Pd, Pt, and Rh nanoparticles. Because the nanoparticles are located in the corona of the micelles [10,11,15], they are readily available for substrates [30,31]; this along with their enhanced stability makes these nanoparticulate systems excellent candidates as catalysts for hydrogenation and oxidation of various substrates. Although in our preceding work the given nanoparticles were obtained and characterized, to the best of our knowledge, the behavior of mixed micellar systems under incorporation of bivalent noble metal ions and metal nanoparticle formation was not described so far. In the present paper we report on the structure of mixed micellar systems based on PS-*b*-PEO and CPC with Pt species using a combination of analytical ultracentrifugation (AUC), small angle neutron scattering (SANS) and transmission electron microscopy (TEM). These studies combining methods contributing supplemental and analogous structural information allowed us to comprehensively characterize the complex hybrid systems and to discover an isotope effect when H_2O was replaced with D_2O.

2. Materials and methods

2.1. Materials

Two samples of PS-*b*-PEO, SE1030 (PS of 1000 Da and PEO of 3000 Da, $M_n = 4000$, $M_w = 6200$) and SE0720 (PS of 700 Da and PEO of 2000 Da, $M_n = 2700$, $M_w = 3600$) were received as a gift from Goldschmidt AG (Germany) and used without purification. Cetyl pyridinum chloride monohydrate (CPC, $\geqslant$99.0%) and $NaBH_4$ (98%, powder) were purchased from Aldrich and used as received. $H_2PtCl_6 \cdot 6H_2O$ (99%) was obtained from Reakhim, Russia, and used without purification. Water was purified with a Milli-Q (Millipore) water purification system (18 µS).

2.2. Synthesis

Micellar solutions of PS-*b*-PEO were prepared by direct dissolution of PS-*b*-PEO block copolymer in H_2O or D_2O (1% w/w) under vigorous stirring for 24 h at room temperature and then kept for 24 h in closed vials at 60 °C for further equilibration. CPC was added to the PS-*b*-PEO micellar solutions to reach a concentration of 0.8×10^{-3}–0.14×10^{-2} mol/L and left under stirring for 24 h. $H_2PtCl_6 \cdot 6H_2O$ was added to a mixed micellar solution PS-*b*-PEO/CPC to provide 1 or 6.42 g/L concentrations of platinic acid. This resulted in yellow reaction solutions. After 24 h stirring, Pt nanoparticle formation was carried out by addition of 5-fold molar excess of $NaBH_4$ in the PS-*b*-PEO/CPC-H_2PtCl_6 hybrid micellar solution. In so doing a vigorous gas evolution took place and the yellow solution turned dark gray.

2.3. Characterization

2.3.1. Elemental analysis

Elemental analysis on Pt was carried out using X-ray fluorescence measurements performed with a Zeiss Jena VRA-30 spectrometer equipped with a Mo anode, LiF crystal analyzer and SZ detector. Analyses were based on the Co$K\alpha$ line and a series of standards prepared by mixing 1 g of polystyrene with 10–20 mg of standard compounds. The time of data acquisition was held constant at 10 s. The sample for elemental analysis was prepared by evaporation of ultrafiltrated reaction solution.

2.3.2. AUC

The molecular characteristics such as diffusion (D_0) and sedimentation (S_0) coefficients, absolute molecular weights (M_{SD}), and hydrodynamic radii (R_h) of the sedimenting species were studied using velocity sedimentation in an analytical ultracentrifuge MOM 3180 (Hungary) with Philpot–Svensson optics ($T = 25 \pm 0.1$ °C, $\lambda = 546$ nm). The details of the AUC experiments and the D_0, S_0, M_{SD}, and R_h determination are presented in Supplementary material.

2.3.3. TEM

Specimens for TEM were prepared by placing a drop of reaction solution, diluted to concentration about 2 mg/ml, onto a carbon-coated copper grid. Images were acquired at accelerating voltage of 60 kV on JEOL JEM1010. Images were collected on plate negatives, digitized at 600 dpi and analyzed with the Adobe Photoshop and the Scion Image software packages.

2.3.4. UV–vis

Absorption spectra were recorded on a UVIKON 931 UV–vis spectrometer ("Kontron," USA) in the wavelength range of 200–700 nm.

2.3.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DSC 7 calorimeter. Sample masses var-