Solution Behavior and Self-Assembly of Complexes from Poly(α-methylstyrene)-*block*-poly(*N*-ethyl-4-vinylpyridinium) Cations and Aerosol OT Anions

Eugene A. Lysenko,[†] Tatiana K. Bronich,[‡] Adi Eisenberg,[§] Victor A. Kabanov,[†] and Alexander V. Kabanov*,[‡]

Department of Polymer Sciences, M.V. Lomonosov Moscow State University, Leninskie Gory, Moscow V-234, 119899 Russia, Department of Pharmaceutical Sciences, University of Nebraska Medical Center, 600 South 42nd Street, Omaha, Nebraska 68198-6025, and Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

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ABSTRACT: The solution behavior of stoichiometric complexes from poly(α-methylstyrene)-*block*-poly(*N*-ethyl-4-vinypyridinium) cations (PMeS-*b*-PE4VP) and bis(2-ethylhexyl)sulfosuccinate (AOT) anions in a variety of organic solvents with low polarity is characterized. These complexes as well as the stoichiometric complexes between homopolymer poly(*N*-ethyl-4-vinylpyridinium) cations (PE4VP) and AOT were soluble in most common organic solvents except aliphatic hydrocarbons. Both PMeS-*b*-PE4VP- and PE4VP-based complexes dissolve in hexane in the presence of small amounts of mixed methanol−ethyl ether cosolvent. The PMeS-*b*-PE4VP/AOT complex forms stable micelle-like aggregates with an effective diameter of ca. 70 nm under these conditions. Such aggregates are not observed in the solutions of the PE4VP/AOT complex. PMeS segments in the PMeS-*b*-PE4VP/AOT complex segregate into an insoluble core, while the PE4VP segments bound with AOT stabilize these particles in solution. Such a type of morphology has not been described and is unique for polymer−surfactant complexes.

Introduction

Polyelectrolyte−surfactant complexes (PSC) form spontaneously as a result of coupling reactions between polyelectrolytes and oppositely charged low molecular weight surfactants.[1,2] Formation of the salt bonds between ionic units of the polyion and surfactant headgroups and hydrophobic interactions of the aliphatic radicals of the surfactant are major factors that cooperatively stabilize these complexes in aqueous media. Stoichiometric PSC that contain equivalent amounts of the polyion charged units and surfactant counterions are water-insoluble. The properties of the stoichiometric PSC in the solid state as well as their solution behavior in nonpolar organic solvents have recently attracted increased attention.[3−15] Data are available on stoichiometric PSC formed from usual linear[3−9] or slightly cross-linked[10,11] synthetic polyions, polypeptides,[12−14] and DNA.[15] The potential uses of the PSC in the synthesis of new types of ionomers,[6,16] solubilization of polar compounds (including biopolymers) in organic solvents,[9,18] and genetic transfection of living cells[19] have generated significant interest in this field.

The studies and applications of stoichiometric PSC in solution are now limited by relatively poor solubility of these complexes.[5,14] Chloroform appears to be the only universal solvent, which dissolves practically all investigated complexes. Some success in increasing the solubility of certain PSC in organic solvents was achieved by using small amounts (several percent, v/v) of polar cosolvents.[9,14] However, in many cases it is not simple, if at all possible, to find such cosolvents for PSC solubilization. Furthermore, polar cosolvents often induce dissociation of the complex.[6,16,20]

A totally different approach to modifying the solution behavior of polyelectrolyte complexes has recently been advanced.[21−28] This approach consists of using block copolymers containing polyelectrolyte and nonionic segments (block ionomers) for the synthesis of the complexes. These systems were termed "*block ionomer complexes*" (BIC). The solution behavior of the nonionic segments contributes significantly to the overall solubility of the BIC. Particularly, the stoichiometric complexes of poly(ethylene oxide)-*block*-polymethacrylate anions and *N*-alkylpyridinium cations were described that are soluble in water.[27,28] In addition to the increased solubility, the presence of nonionic polymer segments provides for the self-assembly of BIC that is unique for regular polyelectrolyte complexes. It has been shown that these complexes spontaneously arrange in small vesicles with a wall from the surfactant-neutralized polyion surrounded by the hydrophilic ethylene oxide shell.[28] The present paper describes complexes formed between poly(α-methylstyrene)-*block*-poly(*N*-ethyl-4-vinypyridinium) cations (PMeS-*b*-PE4VP) and bis(2-ethylhexyl)sulfosuccinate (aerosol OT or AOT) anions. Such systems are soluble in a variety of organic solvents with low polarity and self-assemble into micelle-like aggregates in selective solvents.

Experimental Section

Materials. The block copolymer of α-methylstyrene and 4-vinylpyridine was synthesized by sequential anionic polymerization generally following the previously described procedure.[29] The segment lengths in this copolymer sample were 120 for poly(α-methylstyrene) (PMeS) and 290 for poly(4-vinylpyridine), respectively. The 4-vinylpyridine units were quaternized by ethyl bromide to obtain PMeS-*b*-PE4VP. The reaction was carried out in a 5% PMeS-*b*-PE4VP solution in a

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* Corresponding author. Fax: (402) 559-9543. E-mail: akabanov@mail.unmc.edu.

[†] Moscow State University.

[‡] University of Nebraska Medical Center.

[§] McGill University.

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Table 1. Solubility of Stoichiometric PE4VP/AOT PSC and PMeS-*b*-PE4VP/AOT BIC and Their Components in Organic Solvents[a]

solvent	bp, °C	dielectric const	AOT	PS	PE4VP	PMeS-*b*-PE4VP	PE4VP/AOT	PMeS-*b*-PE4VP/AOT
chloroform	61.2	4.8	+	+	−	−	+	+
toluene	110.6	2.4	+	+	−	−	+	+
tetrahydrofuran	64.8	7.6	+	+	−	−	+	+
dioxane	101.4	2.2	+	+	−	−	+	+
cyclohexane	80.7	2.0	+	+	−	−	+	+
ethyl ether	34.4	4.3	+	+	−	−	+	+
acetone	56.1	20.7	+	+	−	−	+	+
heptane	98.4	1.9	+	−	−	−	±	±
hexane	68.7	1.9	+	−	−	−	±	±

[a] Solubility was tested in the temperature range from 22 °C to the boiling point of the solvent. The following indexes are used: "+" soluble at 22 °C, "−", insoluble in the whole range from 22 °C to the boiling point of the solvent; "±", swollen but insoluble at room temperature and soluble at the boiling point of the solvent. The concentration of solute was 2−4 mg/mL in all cases.

tetrahydrofuran−methanol mixture (50/50, v/v) for 16 h at 60 °C using a 10-fold excess of ethyl bromide relative to 4-vinylpyridine. PMeS-*b*-PE4VP was precipitated in ethyl ether, washed several times with ethyl ether, and dried in a vacuum at 60 °C for 48 h. The degree of quartenization of the PE4VP segment was ca. 95% as determined by IR spectroscopy.[30] Poly(4-vinylpyridine) homopolymer with $P_w = 360$ was synthesized by anionic polymerization[31] and quaternized by ethyl bromide in methanol. Polystyrene (PS) with $P_w = 200$ having a narrow molecular-weight distribution ($M_w/M_n = 1.05$) was purshased from Polysciences, Inc. Sodium bis(2-ethylhexyl)sulfosuccinate and all orgainc solvents were purchased from Aldrich Co. and used without further purification.

Synthesis of Complexes. Samples of PMeS-*b*-PE4VP were dissolved in water at elevated temperatures (close to the boiling point of water) under continuous stirring for 5 days. Complexes between PMeS-*b*-PE4VP (or PE4VP) and AOT were obtained by mixing the equimolar amounts of the components in a 0.01 N NaCl solution at room temperature. After the mixture was stirred for 1 h, the precipitated complexes were separated by centrifugation, washed several times with water to remove low molecular weight salts, and dried in a vacuum at 45 °C. The extent of solvent removal from the dried samples was determined by thermogravimetric analysis. The composition of the complex was determined by the elemental analysis.

Measurements. The turbidity measurements were carried out using a Shimadzu UV160 spectrophotometer at 420 nm after equilibration of the system typically for 3 min. The data are reported as $(100 - T)/(100 - T_{max})$, where T is the transmittance (%).

The effective hydrodynamic diameter of the solute particles was measured by photon correlation spectroscopy using "ZetaPlus" Zeta Potential Analyzer (Brookhaven Instrument Co.) equipped with the Multi Angle option. A 15 mV solid-state laser operated at a wavelength of 635 nm. The sizing measurements were performed at 25 °C at an angle of 90°.

Negative staining technique was used for the transmission electron microscopy (TEM) studies. A drop of the sample solution was allowed to settle on a carbon grid for 1 min. Excess sample was wicked away with filter paper, and a drop of 1% uranyl acetate solution in methanol was allowed to contact the sample for 1 min. The samples were analyzed using a Hitachi H-7000 microscope.

Results and Discussion

BIC precipitate from aqueous solutions after mixing equimolar amounts of PMeS-*b*-PE4VP and AOT. The molar ratio of the surfactant molecules to the PE4VP charged units in the precipitate equals 1.23; i.e., the complexes contain a small excess of the surfactant. This composition is very close to the compositions previously reported for complexes between homopolymer PE4VP and AOT synthesized under similar conditions.[18]

Table 1 summarizes the experimental data on the solubility of the complexes of the homopolymer (PE4VP/AOT) and block ionomer (PMeS-*b*-PE4VP/AOT) in a variety of organic solvents of low polarity (the solvent dielectric constant varied from 2 to 21). The data on the solubility of the PS and PE4VP homopolymers, the PMeS-*b*-PE4VP block ionomer, and AOT in the same solvents are also presented for comparison. Both the homopolymer and the block ionomer complexes are soluble in most common organic solvents. One remarkable exception is aliphatic hydrocarbons, in which both complex types are soluble only at elevated temperatures. (Poor solubility of the stoichiometric PE4VP/AOT complex in hexane at room temperature (less than 0.7 mg/mL) has been reported previously.[18]) It appears that the dissolution of both complex types in the organic solvents studied is not accompanied by dissociation of the complex, because neither PE4VP nor PMeS-*b*-PE4VP is soluble in these solvents.

Recent studies by Bakeev et al.[5] suggested that the stoichiometric complexes of PE4VP with single-tailed anionic surfactants dissolve in a much narrower range of the solvents compared to the complexes described in the present paper. Particularly, the complex of PE4VP with dodecyl sulfate anions is insoluble in tetrahydrofuran, dioxane, ethyl ether, hexane, cyclyhexane, and acetone both at room temperature and at the boiling point of the solvent.[5] The elevated solubility of PE4VP and PMeS-*b*-PE4VP complexes can be attributed to the difference in the structure of aliphatic chains of dodecyl sulfate and AOT anions. Indeed, while AOT is soluble in every organic solvent studied (Table 1) and forms reverse micelles in many of them,[32] sodium dodecyl sulfate does not dissolve in these solvents at all.

We further studied the effects of cosolvents on the solubility of PSC and BIC in aliphatic hydrocarbons. One particularly efficient cosolvent is methanol mixed with ethyl ether (50/50 v/v). Ethyl ether was used to increase the miscibility of methanol with the hydrocarbon. Figure 1 presents the data on the effects of the cosolvent mixture on the turbidity of the PE4VP/AOT and PMeS-*b*-PE4VP/AOT complexes in hexane. In the absence of the cosolvent, the optically transparent hexane coexists with the swollen insoluble complexes. A significant turbidity increase is observed at very low cosolvent content (ca. 0.5%), followed by the clearing up of the system at ca. 1−2% of the cosolvent. At 2.5% of cosolvent and above, the PE4VP/AOT complex is completely transparent, while the PMeS-*b*-PE4VP/AOT complex is slightly opalescent. Such behavior suggested dissolution of both types of the complexes. Still these complexes do not dissociate because PE4VP and PMeS-*b*-PE4VP alone do not dissolve at up to 50% of the

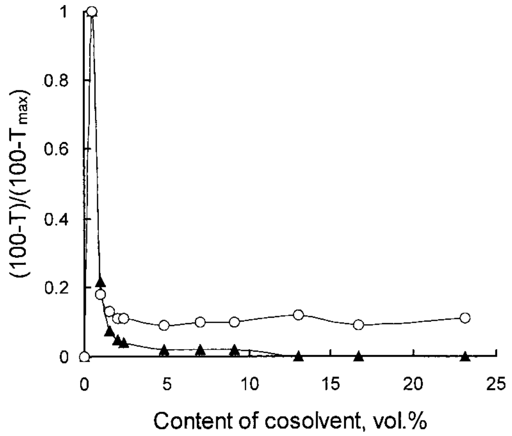

Figure 1. Dependence of relative turbidity (100 − T)/(100 − $T_{\max}$) in PSC/hexane system upon content (vol %) of the cosolvent (methanol/ethyl ether mixture, 50/50 v/v): (▲) PE4VP/AOT; (○) PMeS-*b*-PE4VP/AOT. The concentration of the complexes was 3 mg/mL; T = 22 °C.

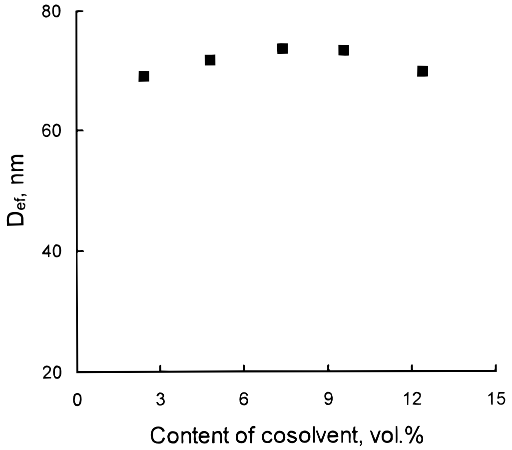

Figure 2. Dependence of effective diameter (D_{ef}) of PMeS-*b*-PE4VP/AOT complexes in hexane/cosolvent mixtures upon content (vol %) of the cosolvent (methanol/ethyl ether mixture, 50/50 v/v). The complex concentration was 3 mg/mL; T = 22 °C.

cosolvent. Interestingly, the addition of up to 30% ethyl ether alone to the hexane did not result in dissolution of the complexes. Therefore methanol increases the complex solubility. A possible reason for that is the solvation of the salt bonds between the polyion units and surfactant. Slight opalescence of the solutions of PMeS-*b*-PE4VP/AOT complexes in hexane−cosolvent mixtures suggested formation of aggregates in these systems. These aggregates are further characterized using dynamic light scattering. As shown in Figure 2, small particles with an effective diameter of about 70 nm are detected in the system in a broad range of the cosolvent contents. In contrast no aggregates are observed in the solutions of the PE4VP/AOT complex. Figure 3 presents the electron microphotograph of PMeS-*b*-PE4VP/AOT particles formed in hexane at 2.5% of the cosolvent. These particles have an ellipsoidal shape and appeared to be relatively narrowly distributed in size. Narrow size distribution is also evident from the light scattering data (polydispersity indexes were 0.05−0.07). The reasons for the ellipsoidal shape of these species are unclear at this time. It will be of interest to study the relationship between the morphology of the particles and the length of the ionic and nonionic segments of PMeS-*b*-PE4VP copolymer.

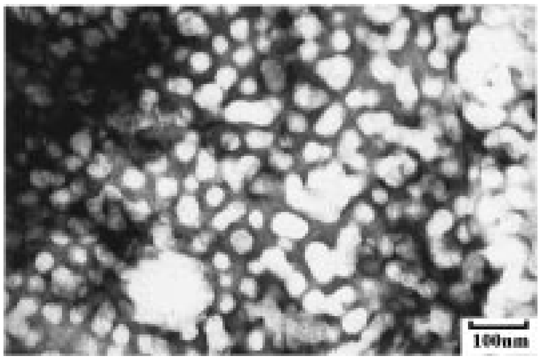

Figure 3. Electron micrograph of PMeS-*b*-PE4VP/AOT particles formed in hexane at 2.5 vol % of the cosolvent (methanol/ethyl ether mixture, 50/50 v/v).

The effect of the PMeS segment in the PMeS-*b*-PE4VP/AOT complex evidently explains the different behavior of the homopolymer and block ionomer complexes. The PMeS homopolymer is insoluble both in pure hexane and in the hexane−cosolvent mixtures studied (data not shown). Therefore in the particles of the PMeS-*b*-PE4VP/AOT complex in the hexane−cosolvent mixtures the PMeS segments segregate into an insoluble core while the PE4VP segments bound with AOT stabilize these domains in solution. Such complexes represent a “reverse” structure compared to the water-soluble complex from the poly(ethylene oxide)-based block ionomer with a core composed of polyion segments neutralized by surfactant and a corona of soluble ethylene oxide segments.[27] To our knowledge this morphology has not been described before and is unique for PSC. We believe that the data obtained in this work warrant further investigation of block ionomer complexes in organic solvents.

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