# Block Ionomer Complexes with Polystyrene Core-Forming Block in Selective Solvents of Various Polarities. 2. Solution Behavior and Self-Assembly in Nonpolar Solvents

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ABSTRACT: The self-assembly behavior and structural characteristics of the block ionomer complexes from poly(styrene)-*block*-poly(*N*-ethyl-4-vinylpyridinium) (PS-*b*-PE4VP) cations and bis(2-ethylhexyl) sulfosuccinate (AOT) anions in nonpolar solvents were examined by turbidity, viscometry, sedimentation velocity, isothermal diffusion, and dynamic light scattering techniques. The complexes were synthesized by reacting PS-*b*-PE4VP with AOT in aqueous media. The resulting water-insoluble materials contained PS block and PE4VP/AOT complex block. The length of PS block was constant and equal to 100 units, while the length of PE4VP/AOT block was varied (100−500 units). These complexes dissolved in hexane upon addition of small amounts (0.5−10 vol %) of aliphatic alcohols and formed stable dispersions with the size of the particles varying from 50 to 95 nm. The particles represented micelle-like aggregates of PS-*b*-PE4VP/AOT complexes with the core formed by PS chains and the shell formed by PE4VP chains electrostatically bound to AOT ions. The behavior and molecular characteristics of these previously unknown structures (shape, dimensions, chain stretching, and aggregation numbers) resemble those of the micelles formed by nonpolar block copolymers in selective organic solvents. Such systems are unprecedented for the block copolymer aggregates in organic solvents and may have considerable theoretical and practical significance.

## Introduction

Block copolymers containing two immiscible polymer blocks exhibit a number of attractive properties which enable their utilizing in drug delivery systems, chemical synthesis and catalysis, stabilization of colloid dispersions in solution, and many others applications.[1−9] One of the most fundamental properties of block copolymers in dilute solutions is their ability to form micelles in selective solvents. Such micelles consist from the core formed by the insoluble block surrounded by the corona formed by the soluble block. The structure and morphology of such aggregates are determined by multiple factors including the quantity of blocks per chain and their length, the chemical nature of each block, the solvent quality, and the presence of the substances in the solution capable to interact the block copolymer.[8−10]

Amphiphilic block copolymer containing polar (water-soluble) and nonpolar (hydrophobic) blocks commonly form micelles in aqueous solutions. The micelle formation in aqueous media is primarily driven by the entropy contributions due to the hydrophobic interactions of the nonpolar blocks. Conversely, association of block copolymers in organic solvents is solely due to the enthalpy contributions to the free energy change, which is a result of a selective solubility of the blocks in the solvent.[11] Two types of block copolymers forming micelles in organic solvents can be distinguished. First, these are the block copolymers consisting of two different nonpolar blocks: one of that is soluble and another that is insoluble. Second, these are block copolymers containing one nonpolar polar and one polar block, which can be either ionic or nonionic.

Extensive studies of the nonpolar hydrocarbon/hydrocarbon block copolymers in a number of organic solvents were reported.[8,10,12−17] It has been shown that the block copolymer structure, solvent composition, and temperature all considerably influence the unimer−micelle equilibrium, the micelle structure, and the dynamics of the unimer−micelle exchange.[10] Furthermore, solubilization of insoluble homopolymer chains of the same chemical structure as the core-forming block of the block copolymer has been observed.[10,18,19] Typically, such solubilization is possible if the length of the homopolymer does not exceed the length of the core-forming block of the block copolymer.

More recently, the formation of the reverse micelles from block copolymers containing polar, particularly ionic blocks and nonpolar hydrocarbon blocks in relatively nonpolar organic solvents has been described.[20−22] Such micelles are formed only if the length of the ionic block is very small and much less than the length of the hydrocarbon block. Block copolymers with the length of ionic block exceeding the length of the nonpolar block were found to be insoluble in organic solvents of low polarity. The ability of the reverse micelles to solubilize water and other polar substances within the ionic core open possibilities for the application of these systems as microcontainers for chemical synthesis and catalysis.

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An unusual and previously unknown type of micellization of ionic block copolymers in organic solvent has been recently described by our group.[23] Specifically, the stoichiometric complexes of poly(α-methylstyrene)-*block*-poly(*N*-ethyl-4-vinylpyridinium bromide) (PMeS-*b*-PE4VP) with sodium bis(2-ethylhexyl) sulfosuccinate (AOT) were shown to form micellar aggregates with the diameter of ca. 70 nm in selective organic solvents. To produce these systems, as a first stage, the elemental counterions of cationic PE4VP block were displaced for the surfactant anions by titration of PMeS-*b*-PE4VP aqueous dispersion with the AOT solution. This resulted in precipitation of the water-insoluble PMeS-*b*-PE4VP/AOT complex, termed "block ionomer complex", in which the cationic units of PE4VP block were bound electrostatically with the AOT anions. As a second stage, the complexes were dissolved in a hexane:methanol:ethyl ether mixture. In this system PS blocks were insoluble and self-assembled into a core of the micelle-like structures. The AOT-bound PE4VP blocks were soluble and formed a shell, providing for stabilization of these structures in the dispersions.

This work continues the study of the association of block copolymer/surfactant complexes in selective organic solvents and focuses on evaluation of the relationship between the structure of block copolymer and physicochemical characteristics of block ionomer complexes. In particular, the effects of the polyion block length on the self-assembly and structural characteristics of the block ionomer complexes were examined using complexes between polystyrene-*block*-poly(*N*-ethyl-4-vinylpyridinum) cations (PS-*b*-PE4VP) and AOT anions. The length of the PS block was constant and equal to 100 units while the length of the PE4VP block varied from 100 to 500 units. The synthesis of these complexes in aqueous dispersions is discussed in a related paper.[24] The solution behavior of PS-*b*-PE4VP/AOT complexes in a hexane/isopropyl alcohol mixed solvent was studied using turbidity, isothermal diffusion, dynamic light scattering, viscometry, and sedimentation velocity techniques.

## Experimental Section

**Materials.** Block copolymers of styrene and 4-vinylpyridine were synthesized by sequential anionic polymerization as described previously.[25] The block lengths of these copolymer samples were 100 for polystyrene and 100, 200, and 490 for poly(4-vinylpyridine). The polydispersity indexes were 1.12 for all synthesized samples. The 4-vinylpyridine units were exhaustively quaternized by ethyl bromide to obtain cationic PS-*b*-PE4VP block copolymers. The reaction was carried out in 5% copolymer solution in a tetrahydrofuran−methanol (70/30, v/v) mixture for 40 h at 60 °C using a 10-fold excess of ethyl bromide relative to 4-vinylpyridine. The cationic PS-*b*-PE4VP were precipitated in ethyl ether and dried in a vacuum oven at 60 °C for 48 h. The degree of quaternization of PE4VP block was determined by IR spectroscopy using characteristic bands of absorption of quaternized (1640 $\text{cm}^{-1}$) and nonquaternized (1600 and 1415 $\text{cm}^{-1}$) repeating units.[25,26] In all samples the degree of quaternization was above 90%. Diblock copolymer samples are denoted as PS(100)-*b*-PE4VP(*x*), where (100) represents the degree of polymerization of PS and (*x*) represent the degree of polymerization of the PE4VP.

Poly(4-vinylpyridine) homopolymer with $P_w = 480$ was purchased from Polysciences, Inc., and exhaustively quaternized by ethyl bromide to obtain PE4VP(480). The procedure of quaternization was similar to that used for block copolymers, except for using pure methanol as solvent for the synthesis. The degree of quaternization was not less than 90% as determined by IR spectroscopy. AOT, hexane, tetrahydrofuran, ethyl ether, methanol, and isopropyl alcohol were purchased from Sigma-Aldrich Co. and used without further purification.

**Synthesis of Complexes.** Aqueous solutions of PS-*b*-PE4VP samples were prepared by dialysis of PS-*b*-PE4VP solutions in a dimethylformamide−methanol (80/20, v/v) mixture against water at room temperature. The concentration of block copolymers after dialysis was determined by UV spectroscopy using the absorption band of PE4VP repeating units at 259 nm and also by the gravimetric technique. The results of both methods coincide within the experimental error. Samples of PE4VP (480) and AOT were directly dissolved in water.

The procedure of synthesis and characterization of the stoichiometric complex between PMeS(120)-*b*-PE4VP(290) and AOT have been described in detail in our previous publication.[23] Briefly, complexes between PS-*b*-PE4VP (or PE4VP) and AOT were obtained by mixing the equimolar amounts of the components in a 0.2 N NaCl solution at room temperature followed by stirring for 1 h. (Simple salt was added to promote the complete precipitation of the complexes.) The precipitated complexes were separated by filtration, washed several times with water to remove low molecular weight salts, and dried in a vacuum oven at 60 °C until the constant weight of the sample was achieved. The residual content of water in samples was determined by thermogravimetric analysis. It did not exceed 0.7 wt % for PS(100)-*b*-PE4VP(490)/AOT and PE4VP-(480)/AOT, 0.5 wt % for PS(100)-*b*-PE4VP(200)/AOT, and 1.1 wt % for PS(100)-*b*-PE4VP(100)/AOT complexes. The compositions of complexes, $\varphi$ ($\varphi$ is the molar ratio of AOT ions to PE4VP charged units in the complex), were determined by elemental analysis and have values of 1.1, 1.0, 0.9, and 0.8 for PE4VP(480)/AOT, PS(100)-*b*-PE4VP(490)/AOT, PS(100)-*b*-PE4VP(200)/AOT, and PS(100)-*b*-PE4VP(100)/AOT, respectively.

**Turbidity Measurements**. The turbidity measurements were carried out using a Shimadzu UV-160 spectrophotometer at $\lambda = 420$ nm after equilibration of the system typically for 5 min. The data are reported as $\text{Abs}/\text{Abs}_{\text{max}}$, where Abs is the absorbance.

**Viscosity Measurements.** The viscosity measurements were performed using an Ubbelohde viscometer at 22 °C. Each sample was equilibrated at least 10 min before measurements.

**Ultracentrifugation Measurements.** Sedimentation velocity measurements were performed using a Beckman model E analytical ultracentrifuge in the scanning mode at $\lambda = 280$ nm and $\omega = 48\,000$ rpm at room temperature. The partial specific volumes of complexes in hexane/isopropyl alcohol (98/2, v/v) solutions were determined at 22 °C using a pycnometer.

**Dynamic Light Scattering Measurements.** Effective hydrodynamic diameters ($D_{\text{eff}}$) of the particles were measured by photon correlation spectroscopy using a "Zeta-Plus" zeta potential analyzer (Brookhaven Instument Co.) with a 15 mW solid-state laser operated at a laser wavelength of 635 nm and equipped with the multiangle sizing option (BI-MAS). All measurements were performed in a thermostatic cell at 25 °C and at a scattering angle of 90°. Software provided by the manufacturer was used to calculate $D_{\text{eff}}$ values. Particle size measurements were performed in the relatively wide range (from 3 to 10 mg/mL) of the concentration of PS-*b*-PE4VP/AOT complexes.

**Isothermal Diffusion Measurements.** The diffusion coefficients of solute particles in dilute solutions were measured by isothermal diffusion technique, using polarization interferometer at 22 °C. The details of this technique are described elsewhere.[27]

## Results and Discussion

**Solubility of PE4VP/AOT and PS-*b*-PE4VP/AOT Complexes in Hexane.** The PS-*b*-PE4VP/AOT complexes studied in this work and their characteristics are presented in Table 1. The previous report describing the behavior of this type of systems suggested that both the homopolymer and the block ionomer complexes are

**Table 1. Characterization of PE4VP(480)/AOT and PS(100)-*b*-PE4VP(X)/AOT Complexes in Hexane/Isopropyl Alcohol (98/2, v/v) Mixtures**

| | polymer | | | |
|---|---|---|---|---|
| parameter | PE4VP(480) | PS(100)-*b*-PE4VP(490) | PS(100)-*b*-PE4VP(200) | PS(100)-*b*-PE4VP(100) |
| $\varphi$ | 1.1 | 1.0 | 0.9 | 0.8 |
| $[\eta]$, dL/g | 0.14 | 0.21 | 0.09 | 0.08 |
| $K_h$ | 0.32 | 0.38 | 0.50 | 3.30 |
| $D_{mic} \times 10^7$, cm$^2$/s$^a$ | | 1.5 | 2.7 | 3.1 |
| $M_0$, g/mol | $2.6 \times 10^5$ | $2.8 \times 10^5$ | $1.2 \times 10^5$ | $0.7 \times 10^5$ |
| $M_{\eta d}$, g/mol$^a$ | $2.7 \times 10^{5b}$ | $3.1 \times 10^7$ | $1.3 \times 10^7$ | $1.0 \times 10^7$ |
| $N_{\eta d}{}^a$ | $1^b$ | 110 | 107 | 153 |
| $D_{is} \times 10^7$, cm$^2$/s | 8.5 | 7.6 | 13.1 | 6.1 |
| $S \times 10^{13}$, s$^{-1}$ | 32 | 28 | 20.5 | 20.1 |
| $V_0$, cm$^3$/g | 0.825 | 0.842 | 0.875 | 0.904 |
| $M_{sd}$, g/mol | $2.0 \times 10^5$ | $2.0 \times 10^5$ | $0.9 \times 10^5$ | $2.0 \times 10^5$ |
| $N_{sd}$ | 0.8 | 0.7 | 0.8 | 3.0 |

[a] Because of the compositional heterogeneity, the determined structural characteristics refer to the apparent values representing the means for the entire ensemble of particles. [b] Values of $M_{\eta d}$ and $N_{\eta d}$ for PE4VP(480)/AOT complex were estimated using the value of $D_{is}$ at $C = 1$ mg/mL.

soluble in most common organic solvents.[23] One remarkable exception is the aliphatic hydrocarbons. Both PE4VP/AOT and PS-*b*-PE4VP/AOT complexes were found to be insoluble in hexane at room temperature. At elevated temperatures (close to the boiling point of hexane, 68.7 °C) all PS-*b*-PE4VP/AOT complexes were found to be soluble, while the phase separation occurred during the cooling. Even continuous heating of the solutions of these complexes in hexane for various periods of time (up to several days) did not result in formation of the stable colloidal dispersions at the room temperature. These data imply that the poor solubility of the polymer/surfactant complexes in hexane at room temperature reflects the equilibrium behavior of the system, and it is not a result of a slow kinetics of dissolution of the solid phase in the solvent.

Our previous publication has reported that addition of small amounts (about 2.5 vol %) of a polar cosolvent (methanol/ethyl ether mixture, 50/50 v/v) leads to dissolution of both PE4VP(360)/AOT and PMeS(120)-*b*-PE4VP(290)/AOT complexes in hexane.[23] It was shown that pure polystyrene is insoluble under these conditions (both hexane and methanol are nonsolvents for PS and PMeS).[28] Therefore, the solubility of the block ionomer complex was attributed to the interaction of PE4VP/AOT units with the mixed solvent.[23] The two factors likely to affect the solubility of the block ionomer complexes in hexane: (i) the length of ionic segment of block ionomer and (ii) the chemical nature of the cosolvent. To evaluate the influence of these factors, the solubility of the complexes was characterized in terms of the "solubility point". The solubility point was defined as the content of the cosolvent (vol %) necessary to dissolve 3 mg of the polymer−surfactant complex per 1 mL of the solvent at room temperature. Figure 1 presents the dependence of the turbidity of the PS(100)-*b*-PE4VP(200)/AOT/hexane/cosolvent system upon the cosolvent concentration and illustrates the method of determination of the solubility point. Methyl and isopropyl alcohols were used as the cosolvents. In the absence of cosolvent the system was phase-separated: the optically transparent hexane phase coexisted with the swollen insoluble complex. A significant turbidity increase was observed after adding low amounts of the cosolvent, which suggested a limited dispersion of the solid phase of the complex within the solvent. Beyond some critical content of the cosolvent a sharp decrease of turbidity were observed accompanied by complete disappearance of the insoluble complexes. Following addition of the cosolvent practically did not change the turbidity of the system. Such behavior suggested the dissolution of the complexes occurring in a very narrow range of alcohol concentrations above the critical point. The solubility point was defined as the cosolvent content corresponding to a sharp decrease in the turbidity (designated by arrows in Figure 1). The position of the solubility point was practically unaffected by the rate of addition of alcohol to the system, suggesting that this parameter characterizes the equilibrium state of the system.

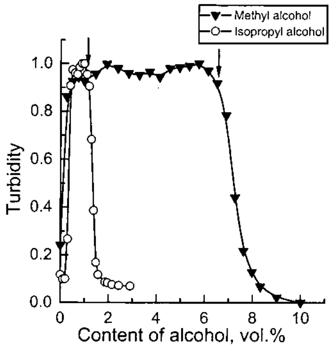

**Figure 1.** Dependence of relative turbidity (Abs/Abs$_{max}$) in PS(100)-*b*-PE4VP(200)/AOT−hexane systems upon the content of cosolvent (methyl or isopropyl alcohol) (vol %) in solution. Methanol was added to the system in the form of a methanol/ethyl ether mixture (50/50, v/v)). Complex concentration was 3 mg/mL, $\lambda = 400$ nm, $T = 22$ °C.

Dependencies of solubility points as a function of the length of the polyion block of the block copolymers in PS-*b*-PE4VP/AOT complexes are presented in Figure 2. These curves can be considered as sections of the "phase diagrams" in the hexane/alcohol solvent at the constant temperature and polymer concentration. The block ionomer complexes are insoluble below these curves and are soluble above them. The analysis of the data presented in Figure 2 reveals that the amount of polar cosolvent required for dispersion of block ionomer complexes in hexane increases in the order

$$\text{PS(100)-}b\text{-PE4VP(490)} < \text{PMeS(120)-}b\text{-PE4VP(290)} < \text{PS(100)-}b\text{-PE4VP(200)} < \text{PS(100)-}b\text{-PE4VP(100)}$$

Since the lengths of the insoluble PS and PMeS blocks were practically the same for all block copolymers, these data suggest that the quantity of the polar cosolvent

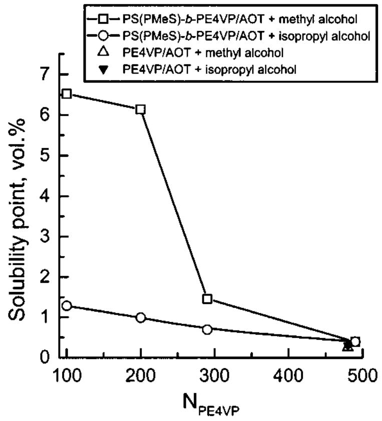

**Figure 2.** Solubility points of PE4VP(480)/AOT and PS(100)-*b*-PE4VP(X)/AOT complexes in hexane–alcohol solvent as a function of the length of PE4VP block. Complex concentration is 3 mg/mL, $\lambda = 400$ nm, $T = 22$ °C.

necessary for dispersion of the block ionomer complex increases as the length of the ionic PE4VP block decreases. Since aliphatic alcohols are good solvents for PE4VP blocks bound with AOT,[23] the addition of these alcohols to hexane increases the quality of the solvent for PE4VP/AOT parts of the block ionomer complex. In fact, the block ionomer complexes studied in this work can be considered as a special type of block copolymers containing insoluble PS or PMeS block and PE4VP/AOT complex "block", which becomes soluble as the quality of the solvent increases. Clearly, the dispersion of the complex was not accompanied by its dissociation because neither free PS(or PMeS)-*b*-PE4VP nor PE4VP homopolymer is soluble in the studied conditions. The role of the PE4VP/AOT complex block in solubilization of the block ionomer complexes is further reinforced by the fact that the complex of the PE4VP(480) homopolymer and AOT exhibits practically the same solubility point as the block ionomer complex having almost the same length of PE4VP chain, PS(100)-*b*-PE4VP(490)/AOT (Figure 2). Furthermore, it is likely that the shorter the PE4VP/AOT block is, the better quality of solvent is required for solubilization of the block ionomer complex in order to compensate for the unfavorable thermodynamic contributions associated with the transfer of insoluble PS(or PMeS) blocks from the condensed phase into the dispersion (Figure 2).

The enhancement of the thermodynamic quality of the solvent with respect to the PE4VP/AOT complex block may be achieved as a result of the increase in the polarity of the solvent and/or enhancement of the specific solvation of the PE4VP/AOT block by alcohol molecules. Taking into account that the total amount of alcohol added to hexane is low (below 10 vol %), and less polar isopropyl alcohol was significantly more effective cosolvent in comparison with more polar methyl alcohol (Figure 2), the contribution of the increasing polarity of the solvent is unlikely. Conversely, the extent of solvation of the PE4VP/AOT complex block by alcohol molecules is a likely main factor contributing to the dispersion of block ionomer complexes. Such solvation effects may include (i) dipole–dipole interactions between ionic PE4VP/AOT bonds and polar hydroxyl groups of alcohol and (ii) additional shielding of polar parts in the PE4VP/AOT complex block from unfavorable contacts with hexane by aliphatic tails of the alcohol molecules. It is possible in this respect that higher efficiency of isopropyl alcohol in dispersing of block ionomer complexes in hexane may be the result of its higher shielding capacity since isopropyl alcohol has a longer and more branched aliphatic group in comparison with methyl alcohol.

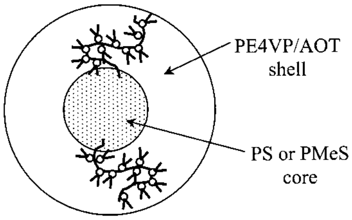

**Figure 3.** Schematic representation of PS(or PMeS)-*b*-PE4VP/AOT micelle-like aggregates.

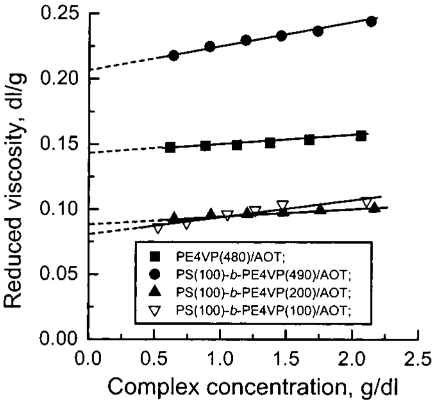

**Figure 4.** Dependence of reduced viscosity of PE4VP(480)/AOT or PS(100)-*b*-PE4VP(X)/AOT complexes vs complex concentration in hexane/isopropyl alcohol (98/2 v/v) mixtures. $T = 22$ °C.

**Association Behavior of PS(or PMeS)-*b*-PE4VP/AOT Complexes in Hexane/Isopropyl Alcohol Solutions.** Since 2 vol % of isopropyl alcohol in hexane was sufficient for formation of the stable dispersions of all PS(or PMeS)-*b*-PE4VP/AOT complexes studied (Figure 2), these complexes were further examined in hexane/isopropyl alcohol (98/2, v/v) mixed solvent. In this solvent all block ionomer complexes at concentrations higher than 5 mg/mL represented opaque dispersions, while the solution of the PE4VP/AOT complex at the same concentration was completely transparent. As previously reported, the formation of the stable dispersions of PS(or PMeS)-*b*-PE4VP/AOT complexes in hexane–isopropyl alcohol mixtures appears to be a result of the arrangement of the block ionomer complex into micelle-like aggregates.[23] In such micelles PS or PMeS segments segregate into an insoluble core while the PE4VP blocks bound with AOT form a shell and stabilize the particles in dispersion (Figure 3).

The structural characteristics of PS(or PMeS)-*b*-PE4VP/AOT complexes were further examined by viscometry. Dependencies of the reduced viscosity ($\eta_{\text{red.}}$) of the PS-*b*-PE4VP/AOT and PE4VP/AOT complexes upon the concentration ($C$) of the complexes are presented in Figure 4. As can be seen in the figure, these dependencies are linear and can be described by the empirical Huggins equation:

$$\eta_{\text{red}} = [\eta] + K_{\text{h}}[\eta]^2 C \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity and $K_{\text{h}}$ is the Huggins constant. These parameters were determined for all block ionomer complexes, and their values are presented

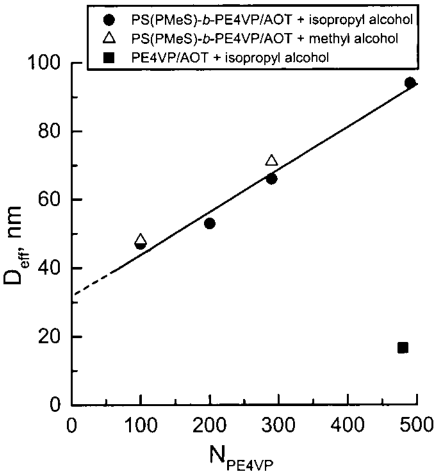

**Figure 5.** Dependence of effective diameter ($D_{eff}$) of particles of PS(or PMeS)-*b*-PE4VP/AOT complexes in (●) hexane/isopropyl alcohol (98/2, v/v) or in (△) hexane/methanol/ethyl ether mixed solvents (the content of alcohol was 10 vol % for PS(100)-*b*-PE4VP(200)/AOT complex and 2 vol % for PMeS-(120)-*b*-PE4VP(290)/AOT complex) upon the length of PE4VP block ($N_{PE4VP}$) of the copolymer. Data for PE4VP(480)/AOT (■) are presented for comparison; $T = 22$ °C.

in Table 1. It is evident that Huggins constants for the block ionomer complexes gradually decreased as the length of the PE4VP block increased. The value of the Huggins constant characterizes the interactions between polymer chains and molecules of the solvent. Typically, $K_h$ diminishes as the thermodynamic quality of the solvent enhances.[28] Therefore, the observed tendency in the change of values of the Huggins constant is consistent with the conclusion that the quality of the solvent (in this case hexane/isopropyl alcohol mixture) for the PS-*b*-PE4VP/AOT complexes increases as the length of PE4VP block increases.

The values of the intrinsic viscosity for the block ionomer complexes were small (0.08−0.21), and the differences between these values were marginal. Since [$\eta$] is a complex function of the molecular weight, dimensions, and shape of the solute particles, it is impossible to make unambiguous conclusions about the molecular characteristics of block ionomer complexes solely on the basis of the viscosity data. Therefore, PS-(or PMeS)-*b*-PE4VP/AOT complexes were further characterized using dynamic light scattering. The effective hydrodynamic diameters of PS(or PMeS)-*b*-PE4VP/AOT particles are presented in Figure 5 as a function of the length of PE4VP segment. The data for the PE4VP/AOT complex are also shown in this figure for comparison. (Since the intensity of scattered light for the PE4VP/AOT complexes was very small, the hydrodynamic diameter for this system was determined by the isothermal diffusion technique.) It is important to note a significant difference in the dimensions between PS(or PMeS)-*b*-PE4VP/AOT and PE4VP/AOT complexes. Such a difference can be explained only by the presence of large micelle-like aggregates in the dispersions of block ionomer complexes. Conversely, the PE4VP/AOT complex, based on the size measurements, appears to exist in the form of random polymer coils or small aggregates.

The sizes of PS(or PMeS)-*b*-PE4VP/AOT aggregates ranged from 47 to 95 nm and increased as the length of the PE4VP block increased. The polydispersity indexes exhibited in these systems were less than 0.1, indicating narrow particle size distributions. Several consecutive size measurements with the same samples showed no changes in the sizes of the particles for at least a week. It is commendable to note that the sizes of the aggregates of the block ionomer complexes were practically independent of the nature and the concentration of the alcohol in the mixture. For instance, the effective diameters of the aggregates formed by PS(100)-*b*-PE4VP(200)/AOT and PMeS(120)-*b*-PE4VP(290)/AOT complexes in hexane/methyl alcohol/ethyl ether solvent practically coincided with the diameters of the aggregates formed by the same complexes in hexane/isopropyl alcohol mixture (Figure 5). The linear regression analysis of the data presented in Figure 5 (solid line) results in the slope of the line of 0.12 nm/PE4VP unit, the intercept of 31 nm, and a correlation coefficient of 0.98. These results were further considered under the assumption that PS(or PMeS)-*b*-PE4VP/AOT complexes formed spherical micellar aggregates with the corona-forming chains being essentially stretched. This assumption is supported by observing a close to spherical morphology for PMeS(120)-*b*-PE4VP(290)/AOT aggregates by electron microscopy as reported in previous work.[23] Assuming that the PS core is spherical, one can estimate the effective diameter of the core from the intercept of the dependence in Figure 5 as approximately equal to 31 nm. This value was close the value calculated using the scaling relations between radius of the core and the length of the core-forming block for starlike copolymer micelles ($R \propto \alpha N^{3/5}$).[21]

It was also of interest to estimate the conformation of the PE4VP/AOT blocks forming the corona of the PS-*b*-PE4VP/AOT micelles. The simplest approach was to compare the experimentally observed dimensions of the micelles with the dimensions obtained from the model assuming that the polymer chains in the corona are in a fully extended conformation. The ratio of the length of the completely extended PE4VP block (which corresponds to the contour length of the block) to the effective end-to-end length in the corona can serve as a measure of PE4VP/AOT segment rigidity. This ratio ($r$) can be roughly estimated using a simple equation:

$$r \approx (0.25N)/(R_{eff} - R_{eff(core)}) \tag{2}$$

where $N$ is the number of repeating units in the PE4VP block, 0.25 nm is the length of the PE4VP unit, and $R_{eff}$ and $R_{eff(core)}$ are radii of the micelle and micelle core, respectively. For all block ionomer complexes studied the value of $r$ varied from 2 to 3. In contrast, for the PE4VP/AOT complex that is likely to have the random coil conformation, the value of $r$ was ca. 14, i.e., several times higher than for the block ionomer based complexes. The small values of $r$ determined for the block ionomer complexes suggest that the surfactant bound PE4VP blocks within the corona of the PS-*b*-PE4VP/AOT micelles have indeed significantly extended conformations.

The molecular weights ($M_{\eta d}$) of the block ionomer complex micelles and the homopolymer based complexes were estimated using the following equation:[29]

$$M_{\eta d} = 10\pi N_A[kT/(6\pi\eta_0 D_{mic})]^3/3[\eta] \tag{3}$$

where $D_{mic}$ is the diffusion coefficient calculated using the Stokes−Einstein equation from light scattering data, [$\eta$] is intrinsic viscosity, $N_A$ is the Avogadro constant, and $k$ is thr Boltzmann constant. The average aggregation numbers of PS-*b*-PE4VP/AOT micelles ($N_{\eta d}$)

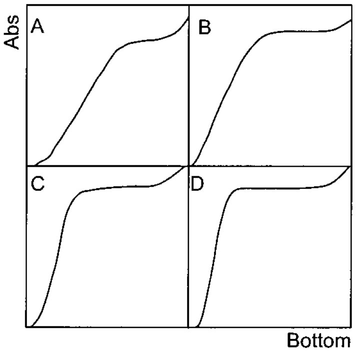

**Figure 6.** Characteristic sedimentation profiles of (A) PE4VP(480)/AOT, (B) PS(100)-*b*-PE4VP(490)/AOT, (C) PS(100)-*b*-PE4VP(200)/AOT, and (D) PS(100)-*b*-PE4VP(100)/AOT complexes in hexane/isopropyl alcohol (98/2, v/v) mixed solvent. Concentration of all polymers is 1 mg/mL; $\lambda = 280$ nm, $\omega = 40\,000$ rpm, $T = 22$ °C.

were estimated from the ratio of $M_{\eta d}$ of the micelles to the molecular weight of the unassociated PS-*b*-PE4VP/AOT complex:

$$N_{\eta d} = M_{\eta d}/M_0 \tag{4}$$

where $M_0$ is the molecular mass of a single PS-*b*-PE4VP/AOT chain, determined using molecular masses of the complex components and compositions of the complexes from the elemental analysis. The values of $M_0$, $M_{\eta d}$, and $N_{\eta d}$ are presented in Table 1. These values suggest that the PE4VP/AOT complexes are present in the solution in the form of single molecules while PS-*b*-PE4VP/AOT complexes indeed self-assemble into micelles. The average aggregation numbers of PS-*b*-PE4VP/AOT micelles were about 100 for PS(100)-*b*-PE4VP(490 or 200)/AOT complexes and about 150 for the PS(100)-*b*-PE4VP(100)/AOT complex.

Interestingly, the dilution of the opalescent solutions of the block ionomer complexes below ca. 1 mg/mL was accompanied by the disappearance of the opalescence. It is likely that after the dilution the aggregates of the PS-*b*-PE4VP/AOT complexes probably dissociated in the single complex species and/or very small aggregates. To evaluate this hypothesis, the solution behavior of PS-*b*-PE4VP/AOT complexes at concentration of 1 mg/mL was studied using the isothermal diffusion technique. The diffusion coefficients ($D_{is}$) determined by this technique are presented in Table 1. As is seen in the table, $D_{is}$ values for PS-*b*-PE4VP/AOT complexes in the dilute solutions were significantly higher than the $D_{mic}$ values determined for the more concentrated systems (>5 mg/mL). This reinforces the conclusion that the self-assembly of the PS-*b*-PE4VP/AOT complexes into large micelle-like aggregates is a concentration-dependent phenomenon. Finally, the block ionomer and homopolymer complexes were characterized by the sedimentation velocity technique. Figure 6 presents typical sedimentation profiles observed in these systems at a low concentration of 1 mg/mL. In all cases only one step was exhibited in these profiles, suggesting that only one type of species was present in PS-*b*-PE4VP/AOT and PE4VP/AOT dispersions. The sedimentation coefficients ($S$) determined using this method are summarized in Table 1. It is seen that $S$ values for PS-*b*-PE4VP/AOT complexes were smaller in comparison with those for the PE4VP/AOT complex. Furthermore, the sedimentation coefficients of the PS-*b*-PE4VP/AOT complexes decreased as the length of the PE4VP block decreased.

The molecular weights ($M_{sd}$) of PS-*b*-PE4VP/AOT complexes at the concentration of 1 mg/mL were estimated from the sedimentation data using the Svedberg equation:

$$M_{sd} = SRT/[D_{is}(1 - V\rho_0)] \tag{5}$$

where $V$ is the partial specific volume of block ionomer complex in the solution and $\rho_0 = 0.657$ g/cm$^3$ is the density of the solvent, both determined by the picnometry technique at 22 °C. Furthermore, the aggregation numbers ($N_{sd}$) for PS-*b*-PE4VP/AOT complexes at the low concentration were calculated from the ratio of $M_{sd}$ to the molecular weight of the PS-*b*-PE4VP/AOT complex, $M_0$:

$$N_{sd} = M_{sd}/M_0 \tag{6}$$

The values of $M_{sd}$ and $N_{sd}$ are presented in Table 1. Comparison of these values with the $M_{\eta d}$ and $N_{\eta d}$ values for the corresponding PS-*b*-PE4VP/AOT complexes determined at higher concentrations directly demonstrates that in the dilute solutions ($C = 1$ mg/mL) the block ionomer complexes are indeed in the form of the single block ionomer chains bound to the AOT molecules (for PS(100)-*b*-PE4VP(490, 200)/AOT complexes) or small aggregates (in the case of the PS(100)-*b*-PE4VP(100)/AOT complex). Therefore, the micellar aggregates of PS-*b*-PE4VP/AOT complexes formed in nonpolar organic mixed solvents dissociate upon dilution. The isolated chains of the block ionomer complexes may be considered as a sort of complex “unimers”. Since the hexane/isopropyl alcohol mixture is a nonsolvent for PS block, it is likely that the PS blocks of the complex unimers collapse and form a condensed monomolecular microphase that is stabilized in the dispersion by PE4VP blocks bound with the AOT counterions. In this case the contribution of the unfavorable interactions between PS block and the solvent should be minimized. A decrease in the shielding efficacy of the PE4VP/AOT block should be expected as the length of PE4VP block decreases. This can explain the formation of small aggregates consisting of several block ionomer complex species for the block copolymers with the short PE4VP blocks, such as the PS(100)-*b*-PE4VP(100)/AOT complex. Indeed as is seen in Table 1, this complex forms small aggregates containing ca. 3 polymer chains.

Overall, although PS-*b*-PE4VP/AOT complexes form very unusual and previously unknown structures, the molecular characteristics of these structures (shape, dimensions, chain stretching, and aggregation numbers) as well as their behavior upon dilution resemble the molecular properties and behavior of conventional nonpolar block copolymers in selective organic solvents. Such systems are unprecedented for the block copolymer aggregates in organic solvents and are in our opinion of considerable theoretical and practical significance and deserve further examinations.

## Conclusions

In conclusion, a new family of block ionomer−surfactant materials consisting of PS-*b*-PE4VP and AOT has been synthesized and characterized. Depending on the length of the polyion block of PS-*b*-PE4VP, stable dispersions in selective organic solvents of low polarity are formed in such systems with the size of the particles varying from 50 to 95 nm. Solvation and additional shielding of polar parts of the PE4VP/AOT complex blocks by alcohol molecules seems to originate from the dispersion of complexes without their dissociation in the organic solvents. Since these systems are quite stable and have sizes close to those of block copolymer micelles,[8,9] they appear to be micelle-like aggregates composed from the core formed by PS segments surrounded by the corona from the PE4VP chains electrostatically bound to AOT ions. Further investigation of the relationship between the structure of the block copolymer and morphology of the PS-*b*-PE4VP/AOT complexes in nonpolar solvents using the electron microscopy technique is needed to reveal the peculiarities of self-assembly in such systems. Despite their unusual structure, molecular characteristics of block ionomer complex micelles (shape, dimensions, chain stretching, and quantity of chains per aggregate) as well as their behavior upon dilution resemble the molecular properties and behavior of conventional nonpolar block copolymers in selective organic solvents. Nevertheless, the existence of arrays of salt bonds hidden within the corona may provide a number of new and peculiar properties to such micelles. These properties may be linked to the ability of micellar corona to extract various polar additives from nonpolar media and to interact with them. Further studies in this field will be subjects of our subsequent publications.

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