Effects of Block Length and Structure of Surfactant on Self-Assembly and Solution Behavior of Block Ionomer Complexes

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Several new families of materials have been synthesized on the base of complexes of poly(ethylene oxide)-*b*-poly(sodium methacrylate) (PEO-*b*-PMA) with single-, double-, and triple-tail surfactants. Cetylpyridinium bromide (CPB), didodecyldimethylammonium bromide (DDDAB), dimethyldioctadecyl-ammonium bromide (DODAB), and trioctylmethylammonium bromide (TMAB) were used as the surfactant components. In contrast to complexes of homopolymer PMA with these surfactants, which precipitated from aqueous solutions, PEO-*b*-PMA complexes formed stable dispersions with particle size in the range 100−200 nm. The properties of these systems strongly depended on the lengths of the polyion and nonionic blocks of PEO-*b*-PMA and the structure of the surfactant. In particular, factors governing stability of these complexes in aqueous dispersion include lyophilizing effect of PEO block (increases with increase in PEO chain length), repulsion of PEO chains (increases with decrease in PMA chain length), and packing parameter of the surfactant. Potential applications of these systems include drug delivery.

Introduction

It is well known that single-tail amphiphiles, such as soaps and detergents, form micelles in relatively dilute aqueous solutions. In contrast, double-tail amphiphiles, such as natural phospholipids, normally self-assemble into bilayered lamellae that can close into vesicles. However, in certain cases, lamellae and vesicles form spontaneously from single-tail surfactants.[1] These cases include the mixtures of single-tail cationic and anionic surfactants that produce double-tail anion−cation pairs assembling into vesicles. Lamellar structures on the base of single-tail surfactants can be also obtained by immobilization of surfactant ions on oppositely charged linear or cross-linked polyelectrolytes. In such systems, known as "polymer−surfactant complexes", the ionic headgroups of the surfactant bind to polyelectrolyte units while the surfactant tails segregate into hydrophobic domains.[2] In the solid state, these complexes self-organize into lamellae consisting of alternating layers of polymer chains separated by layers of surfactant molecules.[3]

A new family of polymer−surfactant complexes formed by single-tail ionic surfactants and block copolymers containing ionic and nonionic water-soluble blocks (block ionomers) has recently been described.[4−6] In such complexes, the surfactant molecules are bound to the oppositely charged units of the polyion segment of the block ionomer like in a regular polymer−surfactant complex. However, the solubility behavior of the block ionomer complexes is quite different because of the effect of the nonionic segment. The complexes of block ionomers remain soluble when the polyion charges become neutralized by the surfactant, whereas regular complexes precipitate under the same conditions. Specifically, complexes of an anionic copolymer, poly(ethylene oxide)-*b*-poly(sodium methacrylate) (PEO-*b*-PMA), with single-tail cationic surfactants, spontaneously arrange in aqueous solutions into small vesicles.[5] It is likely that such vesicles are composed of closed bilayers from polymethacrylate anion-bound surfactant with a shell from "grafted" poly(ethylene oxide) chains holding the complexes species in aqueous solution. Another type of morphology was observed for the complexes formed between cationic copolymer poly-(ethylene oxide)-*g*-polyethyleneimine and anionic surfactants.[6] These systems self-assemble in micelle-like aggregates with a hydrophobic core from neutralized polyethyleneimine chains and surfactants and a corona

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from hydrated poly(ethylene oxide) chains. These types of morphologies have been unprecedented for polymer–surfactant complexes and are of considerable theoretical and practical significance. In this work, we performed a comprehensive study of block ionomer–surfactant complexes, focusing on evaluation of relationship between the structure of block ionomer and/or surfactant and physicochemical characteristics of block ionomer complexes formed. In particular, the effects of the block lengths on the solution behavior and macroscopic characteristics of such complexes were investigated using PEO-*b*-PMA with different lengths of PEO and PMA segments. The studies of the effects of the surfactant structure were focused at comparing interactions of PEO-*b*-PMA with single-tail, double-tail, and triple-tail surfactants.

Experimental Section

Materials. The diblock copolymers of *tert*-butyl methacrylate and ethylene oxide used in this study were prepared by sequential anionic polymerization generally following the previously published procedure.[7] The poly(*tert*-butyl methacrylate) segment in these copolymers was hydrolyzed to obtain poly(methacrylic acid) as described in ref 7. The PEO-*b*-PMA copolymers were prepared by redissolving the acid form of the copolymer in a tetrahydrofuran:methanol mixture (95:5 v/v) and adding NaOH in methanol. The precipitate was filtered and washed with methanol, then redissolved in water and freeze dried. The concentration of carboxylate groups in the copolymer samples was estimated by potentiometric titration. Diblock copolymer samples are denoted as PEO(x)-*b*-PMA(y), where x and y represent the degree of polymerization of the PEO segment and PMA segment, respectively. For example, PEO(176)-*b*-PMA(188) represents a diblock copolymer containing 176 ethylene oxide repeat units and 188 sodium methacrylate units. The homopolymer poly(methacrylic acid) (PMA) with a $\bar{P}_w = 930$ was obtained by radical polymerization.[8] Cetylpyridinium bromide (CPB), didodecyldimethylammonium bromide (DDDAB), dimethyldioctadecylammonium bromide (DODAB), and trioctylmethylammonium bromide (TMAB) were purchased from Aldrich Company and used without further purification.[9]

Turbidity Measurements. The turbidity experiments were carried out by titration of aqueous solution of corresponding block ionomer with solution of surfactant in water (CPB) or methanol (DDDAB, TMAB). The transmittance of the mixtures was measured with a Shimadzu UV160 spectrophotometer at 420 nm after equilibration of the system typically for 3 min. The data are reported as turbidity = $(100 - T)/100$, where T is transmittance (%).

Zeta Potential and Sizing Measurements. Electrophoretic mobility (μ_e) measurements were performed at 25 °C with the "ZetaPlus" Zeta Potential Analyzer (Brookhaven Instrument Company) with a 15-mV solid-state laser operated at a wavelength of 635 nm. The zeta potential of the particles was calculated from the electrophoretic mobility values using the Smoluchowski equation:

$$\mu_e = \epsilon \zeta / \eta \qquad (1)$$

where ϵ is the permittivity of liquid, ζ is the zeta potential, and η is the viscosity. In water at 25 °C, one electrophoretic mobility unit corresponds to $\zeta = 12.83$ mV. The effective hydrodynamic diameter was measured by photon correlation spectroscopy using the same instrument equipped with the Multi Angle Option. The experimental error of the effective diameter was <3%. All solutions were prepared using double-distilled water and were filtered repeatedly through a Millipore membrane with a pore

size of 0.45μM. Sizing measurements were performed at 25 °C at an angle of 90°.

Results

Preparation of Complexes. Four different techniques were used to prepare the block ionomer complexes. Complexes from single-tail ionic surfactants were prepared by simple mixing of the aqueous solutions of the block ionomer and surfactant components. Double- and triple-tail surfactants, which are practically insoluble in water, were first dissolved in methanol and then a concentrated methanol solution of surfactant was added into an aqueous solution of corresponding block ionomer at an appropriate ratio. This method was not suitable in the case of DODAB because injection of its methanol solution resulted in immediate precipitation in all cases. Therefore, we first prepared DODAB dispersions by injecting its methanol solutions in water at 60 °C and then mixed these dispersions with aqueous solutions of the block ionomer. Finally, to examine the effect of the mode of preparation of the complex, in some experiments the aqueous suspensions of DODAB (methanol free) were sonicated at 60 °C for 15 min and then mixed with the block ionomer. When methanol solutions of surfactants were used, the concentration of methanol in the final mixtures did not exceed 5 vol %. It is known that at low concentrations of alcohol (<10 vol %) polymer–surfactant complexes remain stable.[10,11]

Potentiometric Study of PEO-*b*-PMA–Surfactant Coupling Reaction. Interaction between cationic surfactant (S^+) and a weak polyacid can be described as an ion-exchange reaction resulting in the release of the protons according to the following scheme:

$$(|-COOH)_n + nS^+ \langle === \rangle [|-COO^- \, S^+]_n + nH^+ \quad (2)$$
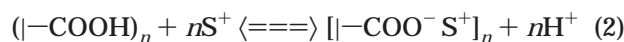
Equilibrium in this reaction at different pH can be studied by potentiometric titration.[12] In this work, we used a potentiometric titration technique to study interactions of the block ionomer with single-tail, double-tail, and triple-tail surfactants. The alkali titration curves were obtained for the mixtures of PEO(210)-*b*-PMA(35) with CPB, DDDAB, and TMAB, as well as of PEO(178)-*b*-PMA(188) and PMA homopolymer with CPB. In all cases, the total concentration of the surfactant was equal to the concentration of the ionizable groups of the polyacid. The degree of conversion, θ, in the ion-exchange reaction (eq 2) was determined from the original titration curves assuming that all alkali is consumed for neutralization of protons released as a result of this reaction. For a weak polyacid, θ at a given pH is expressed in a good approximation as follows[12]

$$\theta = (m_b/V + [H^+] - \sqrt{K_a C_o})/C_o \qquad (3)$$

where m_b is the number of moles of the added base, V is the current volume of the reaction system, K_a is the characteristic dissociation constant, and C_o is the base-molar concentration of the polyacid.

Figure 1 presents the dependencies of θ on pH for the block ionomer–surfactant and homopolymer–surfactant mixtures. The ionization degrees, α, for the PMA segments in block ionomers and PMA homopolymer are also presented in this figure. As is seen with all three types

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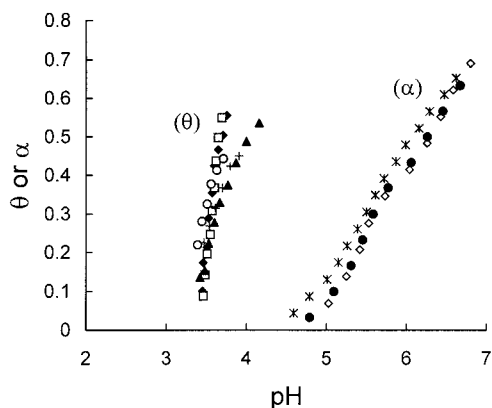(12) Kabanov, V. A. *Polym. Sci. Russ.* **1994**, *36*, 143.

Figure 1. Dependencies of the degree of conversion (θ) in the polyion coupling reactions ($\blacklozenge$, $\bigcirc$, $\square$, $\blacktriangle$, $+$) and degree of ionization (α) of block ionomer samples ($\Diamond$, $\bullet$, $*$) for the following systems: ($\blacklozenge$) PEO(210)-*b*-PMA(35)−CPB; ($\bigcirc$) PEO(176)-*b*-PMA(188)−CPB; ($\square$) PEO(210)-*b*-PMA(35)−DDDAB; ($\blacktriangle$) PEO(210)-*b*-PMA-(35)−TMAB; ($+$) PMA/CPB; ($\bullet$) PEO(176)-*b*-PMA(188); ($\Diamond$) PEO(210)-*b*-PMA(35); and ($*$) PMA.

of surfactant examined, the θ values increase sharply over relatively narrow intervals of pH. The θ−pH curves are shifted to lower pH compared with the α−pH curves of the polyacid. This result demonstrates that the interaction between the cationic surfactants and the polyanion segment of the block ionomers results in formation of a cooperative system of salt bonds. As is seen in Figure 1, there is no major difference between θ−pH curves for all block ionomer−surfactant mixtures examined. This result means that ion pairs between the surfactant cations and anionic units of the block ionomers are not affected by the alterations in the nature of the headgroup of the surfactant molecules. This result is not surprising. In the conditions of the experiment, the surfactant molecules interacting with the polyacid are already assembled into the multimer aggregates. The shift of θ−pH curves compared with the α−pH curve is due to additional stabilization of the ionic form of PMA when COO$^-$ groups of the polyanion are neutralized not by small couterions but the cationic headgroups localized on the surface of surfactant aggregates. At each degree of conversion in reaction 2, the stabilization effect is mainly due to entropy increase caused by the release of simple counterions in the environment, and in the case of strong surfactant bases studied in this work should not depend on the nature of the surfactant headgroups. Furthermore, the θ−pH curves for PEO(210)-*b*-PMA(35)−CPB and PEO(176)-*b*-PMA-(188)−CPB mixtures, which differ in the weight fraction of the PEO chains present in the system, were practically the same as in the case of homopolymer PMA−CPB mixtures. This result suggests that PEO chains do not interfere with the formation of ion pairs between ionized groups of PMA block and surfactant cations.

Solution Behavior of PEO-*b*-PMA−Surfactant Complexes. Turbidimetric titration was used to characterize the solubility of the polymer−surfactant complexes prepared at various compositions of the mixture, $Z_{+/-}$. The composition of the mixture was expressed as a ratio of the surfactant concentration (C_t) to the concentration of ionic groups of the corresponding polyanion:

$$Z_{+/-} = C_t/C_i \qquad (4)$$

(Because the study was performed at pH 9.2, C_i equaled the base-molar concentration of the carboxylate units of the PMA in the system.)
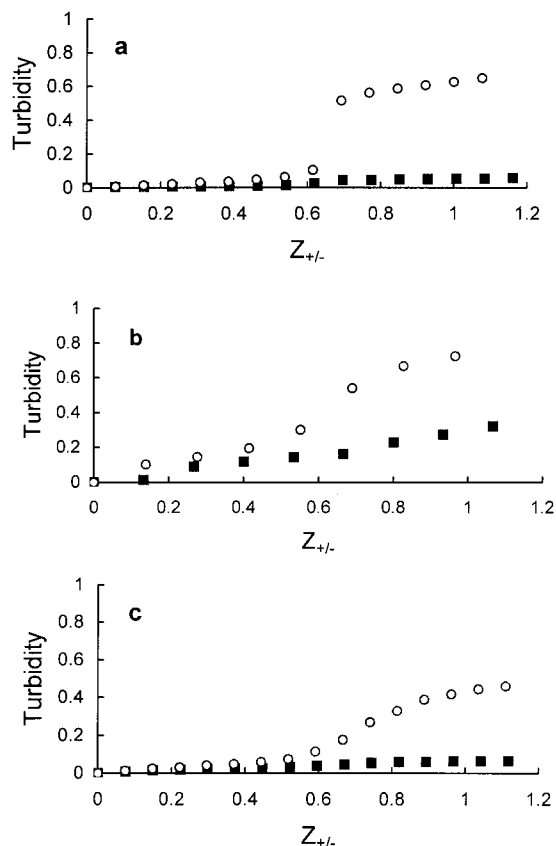

Figure 2. Turbidity in the PEO(x)-*b*-PMA(y)−surfactant systems as a function of the charge ratio in the mixture, $Z_{+/-}$: (a) ($\blacksquare$) PEO(176)-*b*-PMA(188)−CPB; ($\bigcirc$) PEO(210)-*b*-PMA(35)−CPB; (b) ($\blacksquare$) PEO(176)-*b*-PMA(188)−DDDAB; ($\bigcirc$) PEO(210)-*b*-PMA(35)−DDDAB; (c) ($\blacksquare$) PEO(176)-*b*-PMA(188)−TMAB; ($\bigcirc$) PEO(210)-*b*-PMA(35)−TMAB; ($C_i = 6 \times 10^{-4}$ base-mol/L, 25 °C, pH 9.2).

In the initial experiments, the mixtures of the PMA homopolymer and surfactants were examined. High turbidity followed by phase separation was observed after mixing of the components for all surfactants used in this study. This result suggests the formation of polymer−surfactant complexes that are water insoluble. The situation was different for the complexes formed by the PEO(x)-*b*-PMA(y) block ionomers and surfactants. In this case, the solution behavior of the complexes was strongly dependent both on the lengths of the segments of the block ionomer and the structure of the surfactant.

An example of a typical result obtained using mixtures of single-tail surfactants and PEO(x)-*b*-PMA(y) is shown in Figure 2a. The PEO(176)-*b*-PMA(188)−CPB mixtures remain practically transparent or slightly opalescent for all values of $Z_{+/-}$ examined. However, based on the potentiometric titration data already discussed, the complexes are indeed formed under these conditions. Previous studies demonstrated that block ionomer−surfactant complexes form colloidal dispersions in aqueous media stabilized by the hydrophilic PEO blocks.[4−6] Colloidal stability of such dispersions should obviously depend on the length of PEO blocks. Indeed, titration of PEO-(30)-*b*-PMA(147), having the shortest PEO block, with CPB results in phase separation and formation of large visible aggregates. Based on these data, it appears that the PEO segment in PEO(30)-*b*-PMA(147) is not long enough to prevent aggregation of the block ionomer−surfactant complex. More surprisingly, turbidimetric data suggest that the solution properties of the block ionomer−surfactant complex also depend on the length of the ionic

block. Although PEO(210)-*b*-PMA(35)−CPB mixtures formed stable dispersions that did not precipitate, these systems were substantially more turbid than PEO(176)-*b*-PMA(188)−CPB mixtures at $Z_{+/-} > 0.5$.

The solution behavior of the complexes formed by double- and triple-tail surfactants generally was similar to that of the single-tail surfactant systems with the exception of DODAB that will be discussed later. Clearly, like in the case of single-tail surfactant systems, the length of the PEO block plays an important role in the solubility of these complexes. The complexes formed by multitail surfactants and PEO(30)-*b*-PMA(147) immediately precipitated in the entire range of compositions examined. In contrast, mixtures of surfactants and block ionomers containing the long PEO block, PEO(176)-*b*-PMA(188) and PEO(210)-*b*-PMA(35), formed stable dispersions (Figure 2b,c). It is worth mentioning that DDDAB-containing dispersions were more turbid than the single- and triple-tail surfactant systems. Furthermore, as is discussed later, at one composition point, $Z_{+/-} = 0.85$, the PEO(210)-*b*-PMA(35)−DDDAB complexes precipitated.

In general, complexes formed by PEO(210)-*b*-PMA(35) with DDDAB and TMAB revealed the same trend as with the CPB-based systems; that is, the turbidity values at $Z_{+/-} > 0.5$ were increased compared with the complexes formed by PEO(176)-*b*-PMA(188) and corresponding surfactant. Thus, the solution properties of the block ionomer−surfactant complexes depend not only on the length of the PEO segment but also on the ratio of the lengths of the PEO and PMA segments.

Finally, in the case of DODAB, a double-tail surfactant with the longest alkyl radicals, the solution properties of the block ionomer complexes strongly depended on the mode of their preparation. For instance, titration of the block ionomer solution with the surfactant solution in methanol used to prepare other complexes of double- and triple-tail surfactants resulted in precipitation at all compositions examined. At the same time, stable dispersions of PEO(176)-*b*-PMA(188)−DODAB complexes were obtained by mixing the block ionomer with preformed dispersion of DODAB at 60 °C at constant stirring followed by decrease of the temperature to 22 °C. However, these systems precipitated when the components were mixed at ambient temperature. In contrast, mixing of PEO(210)-*b*-PMA(35) and DODAB dispersion both at 60 and 22 °C resulted in immediate precipitation. Finally, the situation was totally different when sonicated DODAB dispersions were used to prepare these complexes. In this case, stable dispersions were obtained with both PEO(176)-*b*-PMA-(188) and PEO(210)-*b*-PMA(35) copolymers. Furthermore, although elevated temperature (60 °C) was critical during sonication of the initial dispersions, mixing of the components could be carried out at either temperature without loss of the colloidal stability of the system. The resulting dispersions were slightly opalescent at all $Z_{+/-}$ ratios examined, with the exception of compositions approximating $Z_{+/-} = 0.8$, when the complexes precipitated.

ζ-**Potential and Size of the Block Ionomer and CPB Complexes.** Stable dispersions of the block ionomer−CPB complexes were further characterized using laser electrophoresis and photon correlation spectroscopy techniques. Figure 3a presents the dependencies of *ζ*-potential of various complexes on $Z_{+/-}$. It is seen that *ζ*-values are negative at $Z_{+/-} < 1$ (range of surfactant deficiency with respect to carboxylate groups) and reach 0 at $Z_{+/-}$ close to unity. This result is consistent with the previous reports suggesting that such behavior is typical for complexes of block ionomers with a variety of oppositely charged single-tail surfactants differing in the length of the aliphatic
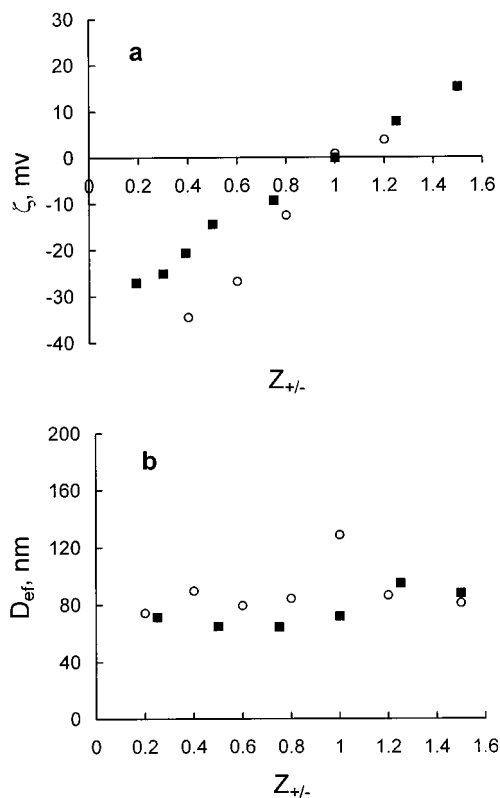

Figure 3. (a) *ζ*-Potential and (b) effective diameter (D_{eff}) of particles formed in PEO(x)-*b*-PMA(y)−CPB systems at various $Z_{+/-}$: (■) PEO(176)-*b*-PMA(188)−CPB; (○) PEO(210)-*b*-PMA-(35)−CPB ($C_i = 6 \times 10^{-4}$ base-mol/L, 25 °C).

radical and type of the headgroup.[5,6] Moreover, one can see in Figure 3a that the net charge of the block ionomer−surfactant particles practically does not depend on the length of the ionic block. This result means that increase in the weight portion of PEO chains in the block ionomer−surfactant complex does not complicate the coupling reaction between copolymer and surfactants ions, which is consistent with the data obtained by potentiometric titration (Figure 1).

At excess of surfactant ($Z_{+/-} > 1$), the particles of the complex become positively charged, which means that at the points where $\zeta = 0$, each carboxylate group of PMA block is coupled with the surfactant ion. The change in the sign of the *ζ*-potential at $Z_{+/-} > 1$ can be attributed to incorporation of the excess of the surfactant cations into the block ionomer complex. Similar behavior was previously described for the complexes of the cationic block ionomers and anionic single tail surfactants.[6]

Figure 3b presents the dependencies of the effective diameter (D_{eff}) of various block ionomer complex particles formed by single-tail surfactants on $Z_{+/-}$. It is important to note that the size of the particles formed by these complexes practically did not depend on the order of mixing of the components (not shown in Figure). The effective diameter of PEO(176)-*b*-PMA(188)−CPB complexes slightly increases with increase in $Z_{+/-}$ but remains rather small in the entire range of the compositions examined. At the same time, the complexes formed by the block ionomer with shorter PMA chains appear to be larger, particularly at $Z_{+/-}$ values close to unity. Furthermore, the systems formed by this block ionomer are more polydisperse. In this case, the polydispersity indexes ranged from 0.1 to 0.2 compared with <0.1 in the case of PEO(176)-*b*-PMA-(188)−CPB complexes.[13]

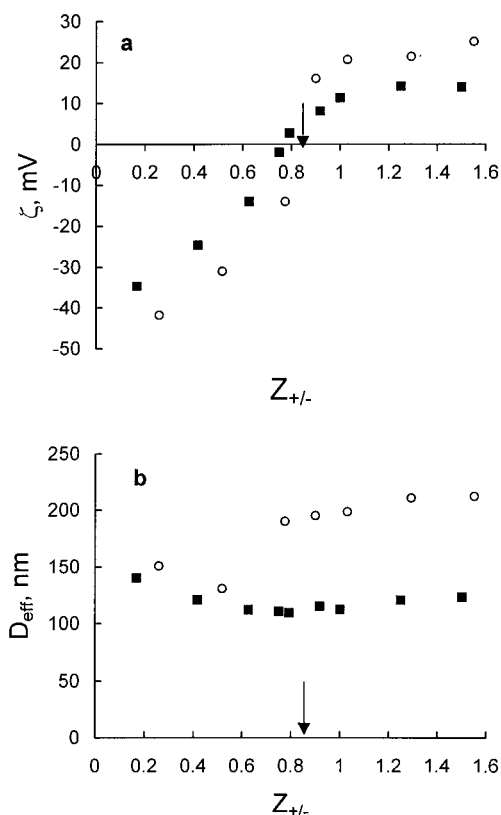**The *ζ*-Potential and Size of the Block Ionomer and DDDAB Complexes.** A somewhat more complicated

Figure 4. (a) ζ-Potential and (b) effective diameter (D_{eff}) of particles formed in PEO(x)-*b*-PMA(y)−DDDAB systems at various $Z_{+/-}$: (■) PEO(176)-b-PMA(188)−DDDAB; (○) PEO-(210)-*b*-PMA(35)−DDDAB. Vertical arrows indicate the point of precipitation for PEO(210)-*b*-PMA(35)−DDDAB system ($C_i = 6 \times 10^{-4}$ base-mol/L, 25 °C).

situation was observed for the block ionomer complexes formed by double-chain surfactants. First of all it is worth mentioning that DDDAB forms positively charged colloid species in water. The size and ζ-potential of DDDAB particles in water practically did not depend on the surfactant concentration in the studied range and were ∼175 nm and 54 mV, respectively. This result is a marked difference compared with the situation with the studied single-tail surfactant forming small micelles above the critical micelle concentration (cmc), which are not detectable by the technique used in this study.

Figure 4a presents the dependency of the ζ-potential on the composition of the mixture for block ionomer−DDDAB systems. These dependencies reveal anomalous behavior compared with those for single-tail surfactant systems. Indeed, the ζ-potential sign changes from negative to positive under conditions of surfactant deficiency: $Z_{+/-} = 0.77$ for PEO(176)-*b*-PMA(188)−DDDAB and $Z_{+/-} = 0.85$ for PEO(210)-*b*-PMA(35)−DDDAB. Interestingly, PEO(210)-*b*-PMA(35)−DDDAB complexes precipitated at this point. At all other compositions, including $Z_{+/-} = 0.8$ and $Z_{+/-} = 0.9$, stable aqueous dispersions were formed in this system, which did not precipitate at least during several days at room temperature. No precipitation was observed with PEO(176)-*b*-PMA(188)−DDDAB complex in the entire range of compositions examined.

Above the electroneutrality point, the complexes were positively charged. This charge might be due to incorpo-

(13) For monodisperse or nearly monodisperse samples, the polydispersity index is close to 0 (0.00 to 0.02); for narrow size distributions, it ranges from ∼0.02 to 0.10, and for broader size distributions it exceeds 0.10.

ration of the positively charged surfactant molecules into the block ionomer complexes. However, in the case of the double-tail surfactants, which form large charged aggregates by themselves, another explanation is also possible. In this case, the neutral block ionomer complexes might coexist with positively charged "free" surfactant aggregates resulting in positive ζ-potential averaged for all species present in the dispersion. The available technique does not allow discrimination of these two possibilities or their combination. However, the fact that PEO(210)-*b*-PMA(35)−DDDAB complexes, which precipitated at the point of electroneutrality, were soluble above this point suggests formation of some mixed aggregates.

Figure 4b shows the dependence of the size of the particles of block ionomer−DDDAB complexes on $Z_{+/-}$. In the range of surfactant deficiency, the size of the particles is sufficiently lower than that of the DDDAB species alone. This result indicates that interaction between the block ionomer and surfactant results in the disintegration of the original surfactant species. The size of PEO(176)-*b*-PMA(188)−DDDAB complexes gradually decreased when composition of the mixture was elevated to $Z_{+/-} = 0.5$, and then remained practically unchanged. In contrast, the size of PEO(210)-*b*-PMA(35)−DDDAB complexes sharply increased from ∼120 to 200 nm at compositions approximating the point of precipitation ($Z_{+/-} = 0.85$). Above this point, the sizes of the complexes increased slightly.

Moreover, in contrast to the complexes from single-tail surfactant, we found that in the case of double-tail surfactant the size of the complex particles strongly depended on the way of preparation of the system, which suggests nonequilibrium behavior. For instance, when the DDDAB solution was added to the PEO(176)-*b*-PMA(188) solution at $Z_{+/-} = 0.5$, the particles of ∼127 nm in diameter were detected. Much smaller particles (∼95 nm) formed under the same conditions when the block ionomer solution was added to the surfactant dispersion.

The ζ-Potential and Size of the Block Ionomer and DODAB Complexes. Like in the case of the DDDAB system, positively charged particles were formed in the aqueous dispersions of DODAB in the absence of the block ionomer. The characteristics of these particles depended on the mode of their preparation. The effective diameters and ζ-potential of the particles were ∼154 nm and 27 mV, respectively, when DODAB dispersions were prepared at 60 °C without sonication and ∼80 nm and 21 mV, respectively, when dispersions were sonicated. In both cases, these aggregates being formed remained stable without changing of macroscopic characteristics even after cooling of the initial dispersion to the room temperature. In the presence of the block ionomers there was a change in ζ-potential and effective diameter of the particles, indicating formation of the complexes.

The dependencies of the ζ-potential on the composition of the mixtures prepared without sonication and using sonicated DODAB dispersions were similar to those observed for DDDAB-based systems. Indeed, as is shown in Figure 5a, the ζ-potential sign in block ionomer−DODAB mixtures changes from negative to positive at surfactant deficiency. The PEO(210)-*b*-PMA(35)−DODAB and PEO(176)-*b*-PMA(188)−DODAB complexes prepared using sonicated DODAB dispersions precipitated at this point (ca. $Z_{+/-} = 0.83$) At all other compositions these systems remained stable in solution.

Figure 5b presents the effective diameters of these complexes. The size of the PEO(176)-*b*-PMA(188)−DODAB complexes prepared without sonication was slightly larger (∼168 nm) in comparison with the pre-
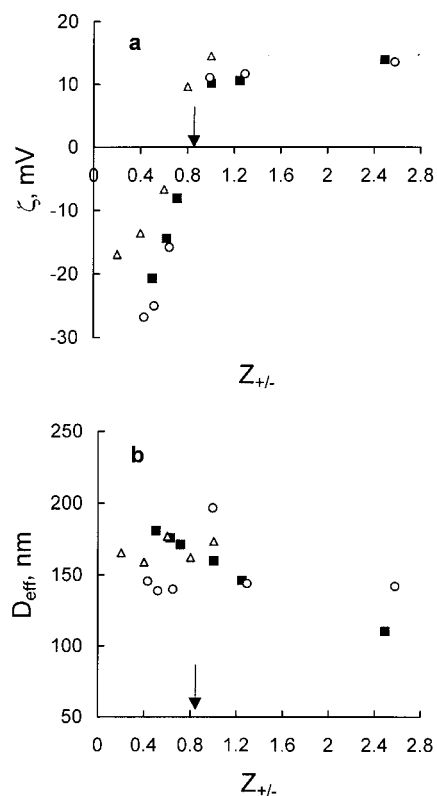
Figure 5. (a) ζ-Potential and (b) effective diameter (D_{eff}) of particles formed in PEO(x)-b-PMA(y)/DODAB systems at various $Z_{+/-}$. Complexes prepared using sonicated DODAB dispersions: (■) PEO(176)-b-PMA(188)−DODAB; (○) PEO-(210)-b-PMA(35)−DODAB. Complexes prepared using non-sonicated DODAB dispersions: (△) PEO(176)-b-PMA(188)−DODAB. Vertical arrows indicate the points of precipitation ([DODAB] = 0.25 mM, 25 °C).

formed DODAB aggregates and practically did not depend on $Z_{+/-}$. In contrast, the PEO(176)-b-PMA(188)−DODAB complexes prepared using sonicated DODAB dispersion were much larger than the initial dispersion particles and their size decreased when $Z_{+/-}$ was elevated. The PEO-(210)-b-PMA(35)−DODAB complexes were also much larger than the initial sonicated DODAB particles, but their size remained practically the same (~140 nm) both at surfactant deficiency and excess with an exception of $Z_{+/-} = 1$ when even larger aggregates (~200 nm) were formed.

The ζ-Potential and Size of the Block Ionomer and TMAB Complexes. As is shown in Figure 6a the ζ-potential of block ionomer−TMAB complexes changes sign from negative to positive upon crossing $Z_{+/-} = 1$. This result means that like in the case of the single-tail surfactant, the electroneutral complexes are formed at $Z_{+/-} = 1$ in which every cationic group of TMAB and carboxylate group of the block ionomer are paired. However, at the excess of surfactant, the absolute values of the ζ-potential are much less than those in the case of CPB systems. This difference could mean that although the triple-tail surfactant incorporates into the block ionomer complexes at $Z_{+/-} > 1$, the extent of its binding is reduced compared with the single-tail surfactant system. An alternative explanation might be stronger binding of the low molecular mass counterions with the headgroups of TMAB molecules incorporated in the complex, resulting in reduced ζ-potential values compared with those for CPB-based systems.

Figure 6b presents the effective diameters of the particles formed in the block ionomer and triple-tail
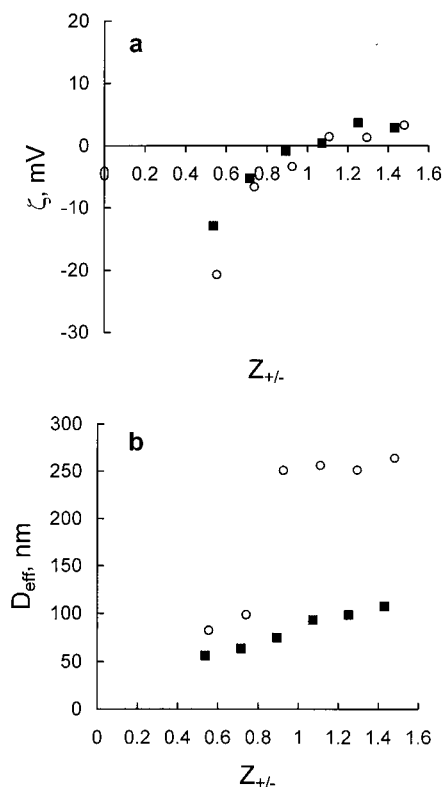

Figure 6. (a) ζ-Potential and (b) effective diameter (D_{eff}) of particles formed in PEO(x)-b-PMA(y)−TMAB systems at various $Z_{+/-}$: (■) PEO(176)-b-PMA(188)−TMAB; (○) PEO(210)-b-PMA(35)−TMAB ($C_i = 7.5 \times 10^{-4}$ base-mol/L, 25 °C).

surfactant mixtures. Like in the case of the single-tail surfactants, we did not detect the aggregates of TMAB in the absence of the block ionomers. However, formation of the particles was observed when TMAB was added to the block ionomer solutions. Comparison of the size versus $Z_{+/-}$ dependencies for PEO(210)-b-PMA(35)−TMAB and PEO(176)-b-PMA(188)−TMAB complexes reveals a trend that is very similar to that of the DDDAB systems; namely, the size of the particles formed by the block ionomer with the shorter ionic block sharply increases at compositions approaching unity, whereas the complexes formed by the block ionomer with longer PMA block do not exhibit such behavior (Figure 4b). At the surfactant excess, the particles of PEO(210)-b-PMA(35)−TMAB complexes are considerably larger (~250 nm) compared with PEO(176)-b-PMA-(188)−TMAB particles, which remain rather small in the entire range of composition and gradually increase in size from ~60 nm to 110 nm when $Z_{+/-}$ is elevated.

Discussion

This study extends our pervious work on the block ionomer−surfactant complexes[4−6] by examining block ionomers with various lengths of blocks and surfactants of different structure. One major result is that the solution behavior and macroscopic characteristics of particles formed in these systems strongly depend on the molecular characteristics of both block ionomer and surfactant components. Specifically, this study suggests that the properties of the block ionomer−surfactant complexes are sensitive to (*i*) length of the nonionic block, PEO; (*ii*) length of the ionic block, PMA; and (*iii*) structure of the surfactant molecule.

Effects of the block lengths on the self-assembly and solution behavior of amphiphilic block copolymers have been studied in detail.[14] In aqueous solutions, hydrophobic

segments of such copolymers segregate in a core of a micelle, whereas hydrophilic segments form a corona preventing phase separation. Generally, stable micelles from PEO-containing diblock copolymers can be produced when (*i*) the molecular mass of PEO segment is between ~1000 to 12 000 g/mol and (*ii*) the length of the PEO segment is greater than or equal to the length of the core-forming block.[15−19] As a first approximation, the block ionomer−surfactant complexes studied in this work can be considered as a special type of a diblock copolymer with a hydrophilic PEO block and a hydrophobic block from polyion−surfactant complex. Using the qualitative rule for the analysis of the solution behavior of PEO(x)-*b*-PMA(y)−surfactant complexes we can conclude that the molecular mass of the PEO block is in the aforementioned range for all block ionomers examined. In this case it appears that the ratio of the lengths of the blocks determines the solution properties of the complexes. For example, PEO(x)-*b*-PMA(y)−CPB complexes are soluble when x ≥ y [PEO(176)-*b*-PMA(188)- and PEO(210)-*b*-PMA-(35)-based systems]. When x < y, as in the case of PEO-(30)-*b*-PMA(147), the block ionomer complexes are water insoluble.

However, the consideration just mentioned of self-assembly for amphiphilic block copolymers does not explain the dependencies of the properties of the block ionomer complexes on the length of the ionic block. Indeed, PEO(210)-*b*-PMA(35)-based complexes generally exhibited higher turbidity and larger size than those based on PEO-(176)-*b*-PMA(188) copolymer with practically the same length of PEO block but significantly longer ionic block. Furthermore, in a number of cases, PEO(210)-*b*-PMA-(35)−surfactant complexes precipitated while corresponding PEO(176)-*b*-PMA(188)−surfactant complexes remained in solution. Such behavior is exhibited to various extents for different surfactants studied in this work and appears to be more pronounced in the case of the double-tail surfactants, particularly, DODAB. This behavior was unexpected and quite unusual because PEO(210)-*b*-PMA-(35)−surfactant complexes appear to have higher content of soluble PEO chains counting per one surfactant molecule in the complex. Indeed, assuming that every carboxylate group of PMA block is paired with surfactant molecule, the molar fraction of PEO block per surfactant molecules incorporated in the PEO(210)-*b*-PMA(35)−surfactant complex is at least ~2.8%, whereas for the PEO(176)-*b*-PMA(188)−surfactant complex, this value is ~0.5%. We believe that just the variation in the PEO content is the key for explanation of the described behavior of the block ionomer−surfactant complexes. One useful analogy might be the behavior of PEO-lipid/lipid dispersions. For these systems, the transition from bilayer structure to micelles as a result of the increase in the PEO-lipid content was theoretically predicted and experimentally verified.[20−23]

The reason for such behavior is lateral tension between the PEO chains grafted to the bilayer surface, which increases with elevation in the PEO-lipid content (and/or molecular mass of PEO chains). At certain PEO-lipid/lipid ratios, this tension reaches the critical tension that the bilayer could support as a material. The increase above this point leads to a spontaneous transition from bilayer to a micellar phase, which balances out the lateral tension due to increase in the curvature of the surface. The relevance of this example to the block ionomer−surfactant complexes is highlighted by our recent observation that some systems, such as complexes of PEO(176)-*b*-PMA-(188) and single-tail surfactants, spontaneously arrange into small vesicles.[5] We can hypothesize that the increase in the content of PEO chains per surfactant molecule can result in destabilization of such morphology in a manner similar to PEO-lipid/lipid systems. In this case, however, formation of normal micelles might be restricted by the cooperative binding of surfactant molecules to the polymer matrix. As a result, formation of some other morphologies, for example, involving larger aggregates, or even pre-cipitation occur.

Furthermore, another important factor determining the behavior and phase transitions in PEO-lipid/lipid systems is lipid polymorphism; that is, the ability of lipids to form different types of aggregates.[22] In our case one should also take into account the short-range structure formation of the surfactant molecules in the hydrophobic domain of the block ionomer−surfactant complexes. Formation of the arrays from polyion-bound surfactant molecules plays a decisive role in the self-assembly of such complexes. One could expect that through alterations in the packing arrangements of surfactant molecules in the polyion-bound arrays, the nature of the surfactant component might very strongly affect both the morphology and solution behavior of the block ionomer complexes.

Indeed, the complexes species formed by the single-tail surfactant are rather small and have narrow size distri-bution (particularly in the case of PEO(176)-*b*-PMA(188)−CPB). Such systems are believed to be in a dynamic equilibrium with the free surfactant in the external solution.[4,6] The equilibrium concentration of the free surfactant, termed "critical association concentration" (cac) is 2−3 orders of magnitude lower than the corre-sponding surfactant cmc. Cooperative electrostatic in-teractions of the headgroups of surfactants and polyion units promote a release of small counterions and self-assembly of surfactant arrays at surfactant concentrations above the cac. The exchange of the surfactant molecules between the particles of the complex and solution is essential for relatively rapid equilibration of such systems, resulting in independence of its properties on the route of preparation.

In contrast, double-tailed surfactants are much less soluble in water and self-assemble into lamellar struc-tures.[24−26] In this case, the polyion chains of the block ionomer interact with the charged headgroups of already preformed surfactant aggregates. The resulting structures exhibit essentially nonequilibrium behavior, which is

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typical for the dispersions of the double-tail surfactants. In such systems, the dependency on the mode of preparation is exhibited not only in variation of the sizes of the species formed (DDDAB) but also in the altered stability of the colloidal particles (DODAB). Interestingly enough, the properties of the block ionomer−DODAB complexes strongly depended on the temperature regime during preparation of the complex. Previous reports suggested that small vesicles can be prepared by sonication of the aqueous suspensions of this surfactant only at temperatures higher than its phase transition temperature (30−50 °C).[27] Sonication of these suspensions at lower temperatures resulted in formation of very large lamellar aggregates.[28] Also, it is known that the size and morphology of vesicles prepared by injecting organic solutions of lipids in water strongly depend on the temperature.[29] This result appears to be due to the kinetic effects involving dependence of the formation of various lipid morphologies on the phase transitions in the lipid bilayer. It quite likely that nonequilibrium behavior underlies the temperature-dependence phenomena observed during preparation of the block ionomer−DODAB complexes.

The rigidity of the structured arrays of double-tailed surfactants might affect not only the macroscopic properties of the formed complexes but also restrict interactions of the polyion chains with the surfactant headgroups. In fact we believe that incomplete binding of polyion carboxylate groups with the surfactant headgroups might be a reason for formation of electroneutral particles of PEO-(176)-*b*-PMA(188)−DODAB complexes at the surfactant deficiency. Indeed, in comparison with single-tail surfactants with the same alkyl radical length, l_c, the double-tail surfactant molecules have larger volume of the nonpolar part, ν_c.[25] As result, whereas the single-tail surfactants can arrange in tight lamellas allowing formation of the ion pairs with every carboxylate group of PMA,[3] the distance between the charged groups of the double-tailed surfactants arranged in lamellas might be too high, leading to the appearance of the mismatches. This assumption is indirectly confirmed by the fact that the points of neutralization for the complexes formed by DDDAB and DODAB are very close ($Z_{+/-} = 0.77-0.85$). Both surfactants have packing parameters ($P = \nu_c/l_c a_c$) close to one and their molecules arrange into bilayer lamella structures having practically the same headgroup areas, (a_c).[24,25,29] As a result, practically the same portions of carboxylate groups of PMA might be unavailable for interacting with the surfactant cations at the surface of the aggregates. These carboxylate groups are possibly condensed with their small counterions (sodium) and not even buried inside the complex, resulting in lowering of the net surface charge density.

Interestingly, the neutralization points are practically the same in the cases of the PEO(176)-*b*-PMA(188)−DODAB complexes prepared without sonication and using sonicated DODAB dispersions. Sonication of DODAB dispersions in the conditions used in this work results in formation of closed vesicles.[27,30] One could expect that in this case the added block ionomer forms ion pairs only with the surfactant molecules at the external leaflet of the vesicles (i.e., ∼50% of the molecules) resulting in charge

neutralization at ca. $Z_{+/-} = 2$.[31−33] However, with the sonicated DODAB dispersions, the charge neutralization was observed at $Z_{+/-} = 0.85$, which suggests that the vesicles undergo structure rearrangements on interaction with the block ionomer, allowing participation of the surfactant molecules from the internal leaflet of the vesicles. This suggestion is also supported by the changes in the diameters of the particles of sonicated DODAB dispersions observed after mixing with the block ionomer. A relevant phenomenon was previously described for the interaction of linear polycation with sonicated liposomes from cardiolopin−phosphatidylcholine mixtures.[31−33] At temperatures above the phase transition temperature, the polycation induced the "flip-flop" of cardiolipin molecules from the inner leaflet of the liposomes, resulting in the asymmetric distribution of cardiolipin in the membrane and its binding with the polycation at the external surface. At temperatures below the phase transition temperature, no flip-flop was observed and only the cardiolipin molecules at the external surface of the liposomes were able to form ion pairs with the polycation. In the case of liquid bilayer, the rupture of the lipid membrane did not occur and vesicles were preserved after removal of the polycation from the liposome surface by the excess of the linear polyanion. However, below the phase transition temperature, the same polycation irreversibly adsorbed[32,33] caused some rearrangements and resulted in disruption of the membrane.[34] In distinction to lipid vesicles where the portion of cardiolipin molecules did not exceed 20% of the total lipid, the sonicated DODAB dispersions might undergo even more drastic morphological transitions on addition of the block ionomer, including membrane rupture and vesicle fusion. A study of the morphologies formed in various block ionomer−surfactant complexes is beyond the scope of this work and it is currently underway in our laboratory.

The final consideration regarding the complexes of the block ionomer and double-tail surfactants deals with the loss of dispersion stability and precipitation observed at least with some of those systems at the compositions approaching the neutralization point. This phenomenon is highly unusual, particularly given the very narrow range of the compositions of the mixture where the precipitation occurs. The complexes of corresponding block ionomers and CPB or TMAB did not precipitate in the entire range of the compositions, including points of electroneutrality. The behavior of the double-tail surfactants is not yet understood and needs further studies, but it is clear that this behavior is related to the peculiarities of the packing arrangements in the double-tail surfactant aggregates bound to the block ionomer. Also, effects of hydration and counterion dissociation can play an important part in the behavior of those systems. As already discussed, even at the points of zero electrophoretic mobility, some portion of carboxylate groups of PMA and, for this matter, ammonium groups of surfactants can form ion pairs with their counterions (sodium and bromide respectively) rather that ion pairs with each other. In this case, dissociation of the counterions, particularly on change in the temperature, may have significant effects on the properties of the complexes. It should be noted in this respect that double-tail surfactants such as DDDAB show significant dissociation of the counterion at elevated temperature,

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which might be one reason the results with this system strongly depend on the preparation.

The triple-tail surfactant used in this study does not reveal critical micellization phenomena characteristic for single-tail surfactants and does not form lamella typical for double-tail surfactants. At low concentrations (less than $\sim 10^{-4}$ M) TMAB forms only loose aggregates, which are much smaller than the conventional micelles. It is remarkable, therefore, that the well-defined species with sizes in the 100–200-nm range self-assemble in the mixtures of this surfactant with the block ionomer. To the best of our knowledge, the polymer–surfactant complexes formed by triple-tail surfactants have not been described before. The structure of such aggregates is unknown, but it is unlikely that they assume lamellar packing. Indeed, the packing parameter of TMAB is >1. Synthetic surfactants and natural lipids having $P > 1$ tend to form reverse micelle structures or hexagonal II phase.[28] Stoichiometric complexes of poly(*N*-ethyl-4-vinylpyridinium) cations and Aerosol OT anions soluble in nonpolar solvents (hexane, octane) have been described.[36] Furthermore, complexes of poly(α-methylstyrene)-*b*-poly(*N*-ethyl-4-vinylpyridinium) and Aerosol OT in selective organic solvent assemble into small micelle-like aggregates with the core from insoluble poly(α-methylstyrene) and a shell from poly(*N*-ethyl-4-vinylpyridinium)–Aerosol OT complex.[37] It is believed that in such systems, the surfactant molecules assume reverse micelle packing with the headgroups bound to the polyion chain surrounded by the alkyl radicals exposed to the organic solvent. The situation might inverse in the aqueous dispersions of the PEO-*b*-PMA–TMAB complexes. In such systems, the particles formed have a core from polyion-bound surfactant and a shell from water-soluble nonionic block. The PMA–TMAB complexes might have reverse micelle or hexagonal II phase packing extending deeply in the core of the block ionomer complex particles. This situation might also explain why the excess of TMAB molecules do not incorporate into the complexes at $Z_{+/-} > 1$, because this would require appearance of the positive charge deeply inside the hydrophobic core of the complexes.

Conclusion

In conclusion, several new families of block ionomer–surfactant materials have been synthesized and characterized. These systems include complexes of PEO-*b*-PMA with single-tail, double-tail, and triple-tail surfactants. A major result is that the solution behavior of these complexes in water and macroscopic characteristics of the aggregates formed by them strongly depend on the lengths of the polyion and nonionic blocks and structure of the surfactant component. Several distinct types of behavior were observed in such systems. Single- and triple-tail surfactants (CPB, TMAB) assemble with PEO-*b*-PMA into macroscopic species that are primarily controlled by the block ionomer structure and composition of the mixture. Depending on the length of the blocks, stable dispersions are formed in such systems with the size of the particles varying from ~ 100 to 200 nm. They do not precipitate in the entire range of composition of the mixture, including stoichiometric compositions when the electroneutral complexes are formed. Complexes of PEO-*b*-PMA and double-tail surfactants (DDDAB, DODAB) strongly depend on the nature of the surfactant aggregates formed in the absence of the polymer as well as the mode of preparation of the systems. The resulting structures exhibit essential nonequilibrium behavior characteristic for the aqueous dispersions of the double-tail surfactants. Overall, the unique self-assembly behavior, the simplicity of the preparation, and the wide variety of available surfactant components make these systems promising in addressing various theoretical and practical problems, particularly, in pharmaceutical drug delivery and other areas where self-assembled nanoparticles are used.

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