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Block Ionomer Complexes from Polystyrene-*block*-polyacrylate Anions and N-Cetylpyridinium Cations

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ABSTRACT: Insoluble nonstoichiometric and stoichiometric complexes were formed as a result of reaction between polystyrene-*block*-polyacrylate anions (PS-*b*-PAA$^-$) and *N*-cetylpyridinium cations ($C_{16}Py^+$) in aqueous media. In the presence of water the nonstoichiometric complexes with low content of surfactant represent swollen materials that contain polystyrene fragments, PAA units neutralized by surfactant, and ionized PAA$^-$ chains capable of ion exchange reactions involving regular inorganic and surfactant counterions. In the solid state these complexes represent a special class of complex ionomer material containing a segregated crystalline domain from $C_{16}Py^+$ bound to the polyion, sodium−carboxylate ion pairs, and an amorphous polystyrene segment. Changing the polyion and surfactant ratio as well as lengths of the block ionomer segments can vary the microstructure of such materials and their properties.

Introduction

Stoichiometric complexes of polyelectrolytes with oppositely charged surfactants have attracted increasing attention in the literature during the last several years.[1,2] In such systems the ionic headgroups of the surfactant form salt bonds with the polyion units while the nonpolar tails of the surfactant interact hydrophobically with each other. These complexes are synthesized in aqueous media by simple mixing of the components. The complexes are water-insoluble but can be dissolved in organic solvents.[3−10] In relatively polar solvents (e.g., aliphatic alcohols, *N*,*N*-dimethylformamide, and dimethyl sulfoxide) the dissolution of the complex is commonly accompanied by its dissociation.[7,8] In contrast, in organic solvents with low polarity (e.g. chloroform) the complexes dissolve without disociation.[3−6,9,10] The solubility and conformational state of the complex in solution is dependent on the structure of the surfactant and the polyelectrolyte as well as on the properties of the solvent. These systems are most commonly pictured as “combs” consisting of surfactant-neutralized polyions with surfactant tails exposed into solvent.[3−6,9,10] In the solid state these complexes adopt lamellar structures consisting of alternating layers of polymer chains and surfactant molecules.[7,10−16] In such systems aliphatic radicals of the surfactants arrange in bilayers, which can crystallize when these radicals are sufficiently long (e.g., cetyl or octadecyl groups).[10,13,15] The potential use of the polymer−surfactant complexes for the synthesis of new type of ionomers,[6,17] 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.

A new family of polymer−surfactant complexes formed by ionic surfactants and block copolymers containing ionic and nonionic water-soluble segments (block ionomers) has recently been described.[20,21] 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 and structure of the block ionomer complexes is quite different because of the effect of the nonionic segment. Specifically, the stoichiometric complexes of poly(ethylene oxide)-*block*-polymethacrylate anions and *N*-alkylpyridinium cations were described which are soluble in water.[20] It has been shown that these complexes spontaneously form small vesicles with a wall of the surfactant-neutralized polyion surrounded by the hydrophilic ethylene oxide shell.[21]

The present work investigates a different and as yet unexplored type of block ionomer complex in which the nonionic segment is water-insoluble. In contrast to water-soluble complexes containing ethylene oxide segments, such systems are soluble only in organic solvents. Using an example of the complexes formed between polystyrene-*block*-polyacrylate anions (PS-*b*-PAA$^-$) and *N*-cetylpyridinium cations ($C_{16}Py^+$), we demonstrate that in the solid state the nonionic and surfactant-neutralized polyion segments segregate. The resulting materials have a unique microheterogeneous structure combining sequences of ion pairs formed by surfactant and PAA units, crystalline domains formed by aliphatic surfactant radicals, and amorphous polystyrene.

Experimental Section

Materials. Block copolymers of *tert*-butyl acrylate and styrene used in this study were prepared by sequential anionic polymerization generally following the previously described procedure.[22] Block lengths in copolymer were 86 for poly(styrene) (PS) and 900, 390, 190, and 100 for *tert*-butyl acrylate segments, respectively. The copolymers were hydrolyzed to obtain polystyrene-*block*-poly(acrylic acid) as previously de-

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scribed.[22] Copolymers poly(styrene)-*block*-poly(sodium acrylate) (PS(86)-*b*-PANa(*X*), where *X* is the polymerization degree of the polyacrylic segment) were prepared by redissolving the acid form of the copolymer in methanol and adding NaOH in isopropyl alcohol. The neutralized copolymers were filtered out, washed with isopropyl alcohol, and then dried in a vacuum oven at 45 °C untill constant mass of the samples. Concentration of carboxylate groups in the copolymer was determined (a) on the basis of copolymer composition with polymer amounts determined by thermogravimetric analysis and (b) defined directly using potentiometric titration. Results of both methods coincided within the range of experimental error. The homopolymer poly(acrylic acid) (PAA) with $P_w = 50$ was purchased from Sigma-Aldrich Co. The concentration of carboxylic groups in PAA solutions was estimated by potentiometric titration. Cetylpyridinium bromide monohydrate ($C_{16}PyBr$) and organic solvents were obtained from Sigma-Aldrich Co. and used without further purification.

Synthesis of Complexes. Samples of PS(86)-*b*-PANa(*X*), ($X = 100$, 190, 390, 900) were dissolved in water at elevated temperatures (close to the water boiling point) under continuous stirring during 5 days as previously described.[23] Complexes between PS(86)-*b*-PAA^-(*X*) and $C_{16}Py^+$ were obtained by mixing the components in a 0.01 N NaCl solution, pH = 9.0−9.5. After the mixture was stirred for 1 h, the precipitated complexes were separated by centrifugation. The amounts PS(86)-*b*-PANa(*X*) and $C_{16}PyBr$ remaining in solution after precipitation of the complexes were determined by potentiometric titration and UV spectroscopy at 259 nm, respectively. The complexes were washed several times with water to remove low molecular weight salts and then dried in a vacuum at 45 °C for 36 h. The degree of solvent removal from dried samples was determined by thermogravimetric analysis.

Differential Scanning Calorimetry (DSC). Temperatures (T_m) and enthalpies of melting (ΔH_m) of samples in the solid state were determined using a Shimadzu DSC-50 differential scanning calorimeter at a scanning rate of 5 °C/min in the range of temperatures from 20 to 100 °C. The masses of the samples were from 0.7 to 1.4 mg. Heating scans were performed at least twice for each sample, and in all cases melting temperatures were essentially identical.

Results and Discussion

Synthesis of PS(86)-*b*-PAA^-(*X*)/$C_{16}Py^+$ Complexes. The complexes are synthesized by simple mixing of the components. The composition of the mixture is expressed as a ratio of $C_{16}PyBr$ concentration to the base-molar concentration of ionic groups of the corresponding polyion: $Z = [C_{16}PyBr]/[COONa]$. We also define herein the composition of the complex, φ, as the ratio of the $C_{16}Py^+$ cations to the charged units of polyion in the complex. (It is important to note that the composition of the complex not necessarily equals the composition of the mixture because the complex can disproportionate.) Since the studies are performed at pH 9.0−9.5, the concentration of the charged units equals the base-molar concentration of PANa in the system.

For all studied compositions of the mixture, and all molecular masses of the block ionomer, turbid solutions are formed during mixing of PS(86)-*b*-PANa(*X*) and $C_{16}PyBr$, suggesting the formation of insoluble PS(86)-*b*-PAA^-(*X*)/$C_{16}Py^+$ complexes. The complexes formed by PS(86)-*b*-PANa(100), PS(86)-*b*-PANa(190), and PS(86)-*b*-PANa(390) at $Z < 1$ cannot be easily isolated because of flotation and the fact that the precipitates are too fine to be filtered. At $Z \geq 1$ the complexes precipitate and are isolated by centrifugation. Under these conditions ($Z \geq 1$) all complexes are stoichiometric, i.e., $\varphi = 1.0$, as determined by elemental analysis and analysis of supernatant after separation of the complex.

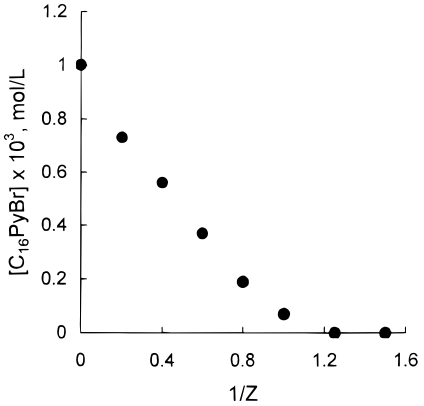

Figure 1. Dependence of the concentration of $C_{16}PyBr$ remaining in the supernatant during titration of the surfactant by PS(86)-*b*-PANa(900) on 1/*Z*. Initial $C_{16}PyBr$ concentration equaled 1×10^{-3} M, [NaCl] = 0.01 M, and $T = 22$ °C.

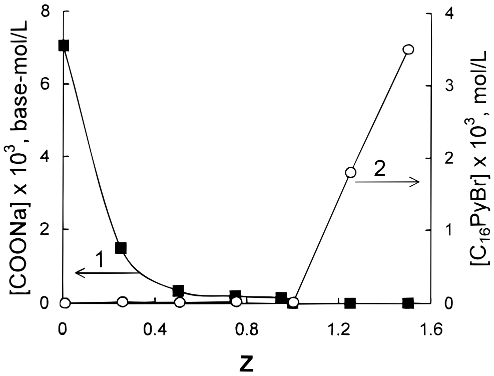

Figure 2. Dependencies of the concentration of the carboxylate groups of PS(86)-*b*-PANa(900) (curve 1) and $C_{16}PyBr$ (curve 2) remaining in supernatant during titration of the block ionomer by surfactant on *Z*. Initial concentration of carboxylate groups of the block ionomer equaled 7.1×10^{-3} base mol/L, [NaCl] = 0.01 M, and $T = 22$ °C.

The complexes formed by PS(86)-*b*-PANa(900) precipitate for the whole range of compositions of the mixture. Therefore, the relationship between the composition of the mixture and the composition of the complex is studied in detail for this system. The amounts of PS(86)-*b*-PANa(900) and $C_{16}PyBr$ found in the precipitate are dependent on the composition of the mixture and do not depend on the order of mixing of the components (surfactant titrated by block ionomer or *vice versa*). Therefore, the distribution of the components between the complex precipitate and solution is consistent with the existence of equilibrium for all studied compositions.

Figure 1 shows the dependence of the concentration of $C_{16}PyBr$ remaining in the supernatant during titration of the surfactant by PS(86)-*b*-PANa(900) on 1/*Z*. The $C_{16}PyBr$ concentration in the supernatant decreases linearly with an increase in the amount of added block ionomer. Complete precipitation of the surfactant is observed at $1/Z = Z = 1$, i.e., at surfactant and polyion equivalency. The potentiometric titration of the supernatant suggested that all block ionomer molecules incorporate in the precipitate in the whole range of compositions $0 < 1/Z < 1$. These data unambiguously suggest the formation of the insoluble stoichiometric PS(86)-*b*-$PAA(900)^-$/$C_{16}Py^+$ complex in this range of mixture compositions.

Figure 2 presents the dependencies of the concentration of $C_{16}PyBr$ and PS(86)-*b*-PANa(900) remaining in solution during titration of the block ionomer by surfactant on *Z*. Relatively small amounts of $C_{16}PyBr$

added to the block ionomer in substoichiometric quantity (e.g. $Z = 0.25$) lead to a sharp decrease in the block ionomer concentration (curve 1). At $Z \geq 0.5$ the precipitation of the block ionomer is complete. In the range of composition $0 < Z \leq 1$ most $C_{16}Py^+$ is included in the precipitate (curve 2) with the residual equilibrium concentration of surfactant in supernatant equaling 2×10^{-5} M. These data suggest that if the block ionomer is present in excess, the nonstoichiometric insoluble PS(86)-*b*-PAA^-(900)/$C_{16}Py^+$ complex is formed and the composition of the complex equals the composition of the mixture. This conclusion is further supported by the elemental analysis suggesting that at $Z = 0.6$ the composition of the PS(86)-*b*-PAA(900)$^-$/$C_{16}Py^+$ complex is ca. 0.57; i.e., the complex is nonstoichiometric.

Formation of the insoluble nonstoichiometric complexes with compositions equaling the composition of the mixture is significantly different compared to the behavior of the complexes formed between the PAA^- homopolymer and surfactant cations.[24] In the homopolymer systems, the insoluble polyelectrolyte–surfactant complexes precipitating from dilute solutions are always stoichiometric. If the degree of polymerization of the polyion is high enough, at $Z < 1$ the precipitate coexists in equilibrium with the soluble nonstoichiometric complex of a characteristic composition φ_{ch}, usually not exceeding 0.25–0.30.[25] The increase in the amount of the surfactant in the range $\varphi_{ch} < Z < 1$ results in a decrease of the soluble complex portion and an increase of the stoichiometric complex portion. At $Z = 1$ all polyion chains become entrapped in the stoichiometric complex, which remains the only product of the reaction.

Such a disproportioning phenomenon is due to the entropy advantage of keeping in solution the maximum possible number of the PAA^- chains, each retaining its translational degrees of freedom.[26] However, this is not the case with the PS(86)-*b*-PAA(900)$^-$/$C_{16}Py^+$ system. In contrast to the PAA^- homopolymer, which forms true solutions in aqueous media, PS(86)-*b*-PAA^-(900) forms micelles.[23] The PS segments of the block ionomer segregate into the hydrophobic core of the micelle with the charged PAA^- chains surrounding the core and stabilizing the micelles in aqueous media. In other words, PAA^- segments in the original micelle solution are already immobilized within the micelle corona, thus losing their translational degrees of freedom. Hence the entropy loss on aggregation of the micelles as a whole and their phase separation involving some PAA^- sequences is relatively insignificant. Therefore, the aggregation proceeds continuously with progressive binding of $C_{16}Py^+$ to PAA^- blocks due to hydrophobic attraction and segregation of the bound $C_{16}Py^+$ aliphatic radicals.

Properties of the Swollen Nonstoichiometric Complexes. The precipitates of nonstoichiometric PS(86)-*b*-PAA(900)$^-$/$C_{16}Py^+$ complexes synthesized at low surfactant contents, e.g. $Z = 0.25$, are highly swollen and friable. The microstructure of this complex is of interest. It apparently contains hydrophobic PS domains, joined by the negatively charged PAA^- segments and domains of PAA^- units bound with the surfactant counterions. Addition of HCl to this system in the amount equivalent to the amount of the free carboxylate groups in the complex results in a drastic contraction of the complex phase. The composition of the complex does not change after addition of the acid as shown by the elemental analysis. Therefore, the change in the state of aggregation of the complex is apparently due to neutralization of the negatively charged PAA^- segments and a decrease in their electrostatic repulsion. The condensation of the complex phase after addition of acid is reversible, since the complex became swollen after the addition of the equivalent amounts of NaOH. Addition of $C_{16}PyBr$ to the swollen nonstoichiometric complex also causes condensation of the precipitate similar to that observed in the presence of HCl. These data suggest that the nonstoichiometric PS(86)-*b*-PAA^-(900)/$C_{16}Py^+$ complex represents a special type of swollen ion-exchange material.

Table 1. Solubility of Stoichiometric Complexes in Low-Polarity Organic Solvents[a]

complex	chloroform	toluene	tetrahydrofuran
PAA^-(50)/$C_{16}Py^+$	+	±	−
PS(86)-*b*-PAA^-(900)/$C_{16}Py^+$	+	±	−
PS(86)-*b*-PAA^-(190)/$C_{16}Py^+$	+	±	−
PS(86)-*b*-PAA^-(100)/$C_{16}Py^+$	+	±	−

[a] The following indexes are used: "+", soluble; "−", insoluble, "±", insoluble, swollen. The complex concentration was 2 mg/mL in all cases.

Table 2. Solubility of Complexes of Varying Compositions in Chloroform[a]

complex	complex composition, φ			
	0.25	0.5	0.75	1.0
PS(86)-*b*-PAA^-(900)/$C_{16}Py^+$	−	−	+	+
PS(86)-*b*-PAA^-(190)/$C_{16}Py^+$ [b]	−	±	+	+

[a] The following indexes are used: "+", soluble; "−", insoluble; "±", insoluble, swollen. The complex concentration was 2 mg/mL in all cases. [b] Nonstoichiometric PS(86)-*b*-PAA^-(190)/$C_{16}Py^+$ complex was separated from supernatant by sedimentation after neutralization of the free carbyxylate groups of the block ionomer with HCl.

Solubility of PS(86)-*b*-PAA^-(*X*)/$C_{16}Py^+$ Complexes in Organic Solvents. Solubility of the stoichiometric complexes formed by homopolymer PAA^- and cetyltrimethylammonium cations in organic solvents with low polarity was previously reported.[5] It was shown that at room temperature such complexes dissolve in chloroform but are insoluble in most other organic solvents. In this work we study the solubility of PS(86)-*b*-PAA^-(X)/$C_{16}Py^+$ complexes in chloroform, toluene, and tetrahydrofuran. The solubility is characterized in the temperature ranges from 22 °C to the boiling points of the solvents. Since for all samples the solubility does not change appreciably within these temperature ranges, we present herein the data obtained at 22 °C. The data presented in Table 1 suggest that the presence of PS segments does not alter the solubility of the stoichiometric complexes in the PS-selective solvents. Indeed these complexes are insoluble in tetrahydrofuran and toluene, which are good solvents for the PS homopolymer but nonsolvents for the PAA^-/$C_{16}Py^+$ complex. The stoichiometric complexes dissolved only in chloroform, in which both PS and the PAA^-/$C_{16}Py^+$ complex are soluble.

The solubility of the complexes of varying compositions in chloroform is studied using the block ionomers with both long and short PANa segments (Table 2). In both cases the nonstoichiometric PS(86)-*b*-PAA^-(*X*)/$C_{16}Py^+$ complexes are soluble at $\varphi = 0.75$. These complexes represent a special class of ionomer materials containing 25% of free carboxylate groups with inorganic counterion. It is likely that the sodium–carboxy-

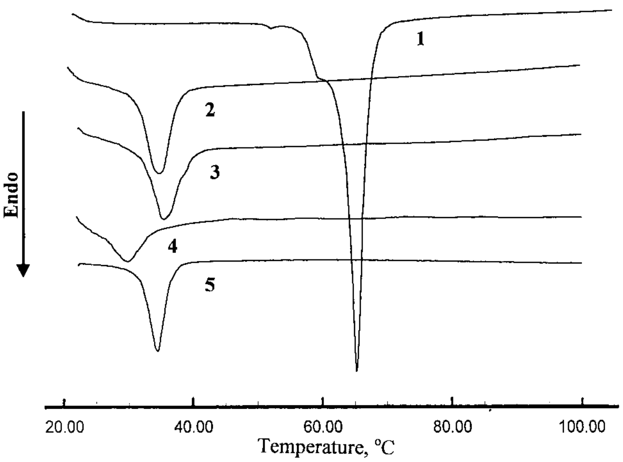

Figure 3. DSC thermograms: (1) C_{16}PyBr; (2) $PAA^{-}(50)/C_{16}Py^{+}$, $\varphi = 1.0$; (3) PS(86)-*b*-$PAA^{-}(900)/C_{16}Py^{+}$, $\varphi = 1.0$; (4) PS(86)-*b*-$PAA^{-}(900)/C_{16}Py^{+}$, $\varphi = 0.5$; (5) PS(86)-*b*-$PAA^{-}(100)/C_{16}Py^{+}$, $\varphi = 1.0$. For the clarity of presentation the thermograms are shifted with respect to each other along the heat axis. The values of the transition temperatures and enthalpies are presented in Table 3.

late ion pairs form some type of ionic clusters to avoid contact with the chloroform. The ionomer behavior of the nonstoichiometric complexes formed by poly(*N*-ethyl-4-vinylpyridinium) cations and dodecyl sulfate anions in chloroform has recently been reported.[6] The present work provides the first evidence on the solubility of nonstoichiometric carboxylate-based complexes in organic solvents.

DSC Study of PS(86)-*b*-$PAA^{-}(X)/C_{16}Py^{+}$ Complexes in the Solid State. The PS(86)-*b*-$PAA^{-}(X)/C_{16}Py^{+}$ complexes in the solid state are characterized using DSC. For most studies the complexes are synthesized in aqueous media as described above and then dried from water admixtures to a constant weight. For select studies the complexes are then redissolved in chloroform and dried in a vacuum. Figure 3 presents typical thermograms of the stoichiometric and nonstoichiometric PS(86)-*b*-$PAA^{-}(X)/C_{16}Py^{+}$ complexes. This figure also shows thermograms of C_{16}PyBr and the stoichiometric $PAA^{-}(50)/C_{16}Py^{+}$ complex for comparison. The thermograms of the block ionomer complexes reveal a single well-pronounced endothermic peak at 32−36 °C. No melting peak characteristic of pure surfactant is observed.

The trace of the thermograms and the positions of the peaks are very similar for the complex samples that are dried from water and chloroform. This suggests that the transition observed corresponds to the melting of some equilibrium structures. The melting temperatures (T_m) and enthalpies (ΔH_m) for the block ionomer complexes are very similar to those for the homopolymer $PAA^{-}(50)/C_{16}Py^{+}$ complex (Table 3). The transition in the homopolymer system was previously related to the melting of the crystalline lamellar phase formed by the aliphatic radicals of the surfactant bound with the polyion.[13,15] Compared to the melting of the free C_{16}PyBr the T_m and ΔH_m parameters for the polymer surfactant complexes are significantly decreased (Table 3). This was explained by defective packaging of aliphatic radicals immobilized on a polyion chain.[13,16] The degree of crystallinity of the surfactant radicals in the complexes is ca. 30% as estimated by comparing the ΔH_m values in Table 3 with those reported for the comblike poly(cetyl acrylates).[27] Hence, the relatively small fraction of methylene groups of the surfactant tails is involved in the crystalline lattice.

Table 3. Phase Transition Temperatures (T_m) and Enthalpies (ΔH) of the Complexes and C_{16}PyBr

sample	complex composn, φ	PS content, mol %	T_m, °C (±3 °C)	ΔH,[a] J/g (±5 J/g)
C_{16}PyBr	n.a.	n.a.	66	95
$PAA^{-}(50)/C_{16}Py^{+}$	1.0	0	36	30
PS(86)-*b*-$PAA^{-}(900)/C_{16}Py^{+}$	1.0	8.7	36	30
PS(86)-*b*-$PAA^{-}(900)/C_{16}Py^{+}$	0.5	8.7	32	24
PS(86)-*b*-$PAA^{-}(390)/C_{16}Py^{+}$	1.0	18.1	36	32
PS(86)-*b*-$PAA^{-}(100)/C_{16}Py^{+}$	1.0	46.2	33	28

[a] The melting enthalpies in the cases of the homopolymer and block ionomer complexes are related to the mass of $C_{16}Py^{+}$, incorporated in the complex.

The identity of the melting behavior of the homopolymer complex and block ionomer complexes with varying relative content of polyions and PS segments is noteworthy. The PS(86)-*b*-$PAA^{-}(X)/C_{16}Py^{+}$ complexes studied in this work contain from ca. 9 to 46 mol % of PS. Still the T_m and ΔH_m values for all these systems are practically the same within the margin of the experimental error (Table 3). This suggests that PS chains are not blended with PAA^{-} segments bound with the surfactant counterions. This can be easily explained by the incompatibility of PS with aliphatic hydrocarbons.[28]

Furthermore, the T_m and ΔH_m values are close for the stoichiometric and nonstoichiometric PS(86)-*b*-$PAA^{-}(900)/C_{16}Py^{+}$ complexes. In the nonstoichiometric complex at $\varphi = 0.5$ half of the carboxylate units are bound to the surfactant counterion, while the remainder forms ion pairs with the sodium ions. The stoichiometric complex does not contain any sodium−carboxylate ion pairs. Therefore, DSC data suggest some kind of segregation of the carboxylate units carrying counterions of different types in the nonstoichiometric complex. It is likely that while the $C_{16}Py^{+}$ ions bound to the polyion units are segregated in the crystalline domain, the units comprising the sodium−carboxylate ion pairs in the nonstoichiometric complex form ionic aggregates. Also, we hypothesize that in this case the contacts of the ionic domains with the PS chains are minimized.

Conclusions

The block ionomer complexes described in this work represent a special class of microheterogeneous amphiphilic materials. Insoluble nonstoichiometric and stoichiometric complexes are formed as a result of reaction between PS-*b*-PAA^{-} anions and $C_{16}Py^{+}$ cations in aqueous media. In the presence of water the nonstoichiometric complexes with low content of surfactant represent swollen materials that contain polystyrene fragments, PAA units neutralized by surfactant, and ionized PAA^{-} chains capable of ion exchange reaction involving regular inorganic and surfactant counterions. In the solid state these complexes represent a special class of complex ionomer material containing a segregated crystalline domain from $C_{16}Py^{+}$ bound to the polyion, sodium−carboxylate ion pairs, and amorphous polystyrene segment. It is likely that changing the polyion and surfactant ratio as well as lengths of the block ionomer segments can vary the microstructure of such materials and their properties.

Further studies will focus on the effect of the nature of the surfactant on the structure and properties of such materials. These complexes in the solid state may possess numerous interesting and useful mechanical and physicochemical properties, resulting from structural microheterogeneity. We believe that the results reported in this work warrant further investigation of these materials.

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