Soluble Stoichiometric Complexes from Poly(*N*-ethyl-4-vinylpyridinium) Cations and Poly(ethylene

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ABSTRACT: Block ionomer complexes formed between the block copolymers containing poly(sodium methacrylate) (PMANa) and poly(ethylene oxide) (PEO) segments and poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVP) were investigated. The data obtained suggest that (i) these systems form water-soluble stoichiometric complexes; (ii) these complexes are stable in a much broader pH range compared to the polyelectrolyte complexes prepared from homopolymers; (iii) they self-assemble to form the core of a micelle comprised of neutralized polyions, surrounded by the PEO corona; (iv) they are salt sensitive since they fall apart as the salt concentration increases beyond a critical value; and (v) they can participate in the cooperative polyion substitution reactions. Therefore, these complexes represent a new class of hybrid materials which combine properties of polyelectrolyte complexes and block copolymer micelles.

Introduction

Self-assembly of diblock copolymers in selective solvents has been studied for a number of years. For example, styrene and isoprene diblocks in a solvent like toluene lead to the self-assembly of the isoprene blocks into a spherical micelle, with the styrene chains providing the solubilizing corona.[1] Many other examples of similar self-assembly of diblocks in selective solvents are known. For amphiphilic diblock copolymers, such as styrene and ethylene oxide, the self-assembly is facilitated by the much larger differences in the solubility parameter between the two segments.[2] In such systems, the differential solubility can be maintained even for very short block lengths, which is more difficult for the block copolymers in which both segments are hydrophobic. Ionic block copolymers have also been investigated, i.e. systems in which one of the blocks is ionic and thus hydrophilic, while the other block is hydrophobic.[3]

Independent of the above studies, the field of interpolyelectrolyte complexes (IPEC) has also received considerable attention.[4] IPEC represent special classes of chemical compounds, formed as a result of cooperative electrostatic interactions between oppositely charged polyions. The properties of these complexes depend strongly on their composition, i.e. the base-molar ratio of the polyions. Nonstoichiometric complexes containing an excess of one component have a net charge of the same sign as this excess component and are usually water-soluble. An important property of the soluble complexes is that they participate in highly selective reactions of polyion exchange and substitution.[5] The stoichiometric complexes are electroneutral since the charges of the components are mutually neutralized, and they usually precipitate from solution.

A new class of soluble polyelectrolyte complexes formed between ionogenic block copolymers and oppositely charged polyions has been recently described.[6,7] Specifically, the complexes formed between DNA polyanions and cationic poly(ethylene oxide)-*block*-polyspermine copolymers attracted significant attention because of their capability of delivering nucleic acids to target cells.[7] The formation and solution behavior of such complexes are very poorly studied yet. It is known, however, that these complexes are drastically different from ordinary IPECs formed by homopolymers, since they retain solubility in spite of charge neutralization, because of the presence of the poly(ethylene oxide) segments.[6,7] The solubility of these complexes is a major advantage compared to other cationic systems for DNA delivery which usually have a tendency to precipitate from solution.[8]

The present publication investigates complexes which belong to the same class as the DNA complexes with cationic copolymers. These complexes are formed between poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVP)[9] and diblock copolymer, containing poly(ethylene oxide) (PEO) and poly(sodium methacrylate) (PMANa) segments. In these systems the poly(methacrylate) anion (PMA^-) is complexed with a poly(*N*-ethyl-4-vinylpyridinium) cation ($PEVP^+$). This work suggests (i) that poly(ethylene oxide)-*block*-poly(sodium methacrylate) copolymer (PEO−PMANa) and PEVP react in aqueous solutions to form water-soluble stoichiometric complexes; (ii) that these complexes are more stable compared to IPEC formed by PMANa and PEVP homopolymers; and (iii) that these complexes self-assemble to form the core of a micelle, surrounded by the PEO corona. Further, these complexes are hybrid materials in the sense that they combine properties of IPEC and of block copolymer micelles. Since the microphase in these complexes is formed by the polyion chains, we will call them the "*block ionomer complexes*" (BIC). As with other polyelectrolyte complexes, the stability of the BIC is dependent on the pH and salt concentration in a

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cooperative manner. Furthermore, these complexes will be shown to participate in polyion substitution reactions which are not only characteristic of regular IPEC but are also a hallmark of these materials.

Materials and Methods

PEO-*block*-poly(butyl methacrylate) copolymers were prepared by anionic polymerization using cumyl potassium as the initiator with sequential addition of the two components.[10] The chain lengths in the PEO−PMANa copolymer were 176 for PEO and 188 for PMANa segments. The poly(butyl methacrylate) chain was hydrolyzed to obtain PEO−PMAA,[9] which was then precipitated from a tetrahydrofuran:methanol mixture (95:5 v/v) by adding NaOH in methanol. The precipitate containing the PEO−PMANa copolymer was washed with methanol and dried under vacuum at 60 °C. Poly(4-vinylpyridine) samples were prepared by radical polymerization and fractionated in a methanol−ethyl acetate system.[11] The fractions obtained were further reacted with ethyl bromide to obtain PEVP with a degree of quaternization of 96%, as confirmed using IR spectroscopy.[11] Two samples of PEVP were synthesized using the procedures described: PEVP ($\bar{P}_w = 100$) and PEVP ($\bar{P}_w = 4890$). The PMAA was obtained by radical polymerization[12] and then labeled with 1-pyrenyldiazomethane as previously reported.[13] The labeled PMAA ($\bar{P}_w = 2150$) contained 1 pyrenyl group per 450 units. The sodium poly(styrenesulfonate) ($\bar{P}_w = 340$) was obtained from Aldrich and used without further purification.

All fluorescence measurements were performed at 22 °C and pH 9.0 using a Shimadzu P5000 spectrofluorophotometer. The excitation wavelengths were 333 nm for pyrene and 342 nm for pyrenyl-labeled PMAA. The concentration of pyrene during critical micelle concentration (CMC) measurements and fluorescence polarization experiments was 5×10^{-7} M. For the fluorescence polarization studies the spectrofluorometer was equipped with polarizers in the right-angle configuration. The value of anisotropy was calculated using the relationship

$$r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH}) \tag{1}$$

where $G = I_{HV}/I_{HH}$ is an instrumental correction factor and I_{VV}, I_{VH}, I_{HV}, and I_{HH} refer to resultant emission intensities at 392 nm polarized in the vertical or horizontal detection planes (second subscript index) upon excitation with either vertically or horizontally polarized light (first subscript index). The turbidity measurements were performed using the Shimadzu UV160 spectrophotometer at 420 nm.

Results and Discussion

Polyion Coupling Reactions. Two different samples of PEVP, with a low molecular mass ("short PEVP") and a high molecular mass ("long PEVP") were used in this work. The contour length of the long PEVP ($\bar{P}_w = 4890$) was approximately 24 times higher than that of the PMANa segment of the PEO−PMANa block copolymer. By contrast, the contour length of the short PEVP ($\bar{P}_w = 100$) was almost 2 times smaller than that of the PMANa segment of the block copolymer. The degree of conversion in polyion coupling reactions involving weak polyelectrolytes, such as PMAA, is pH-dependent.[14] One way to investigate the conversion dependence on pH in these reactions is to use potentiometric titration.[14] Therefore, the potentiometric titration curves were obtained for PEO−PMAA and PEVP mixtures (1:1 counting for ionogenic repeating units), as well as for the PMAA homopolymer and PEVP mixture and solutions of individual PEO−PMAA and PMAA. The degree of conversion, θ, in the reaction between PMANa chains and PEVP was determined from the original titration curves assuming that all alkali is consumed only for neutralization of COOH groups which then form ionic pairs with PEVP$^+$ units. For a weak polyacid θ at a given pH is expressed as follows

$$\theta = (m_b/V + [H^+] - \sqrt{K_a C_o})/C_o \tag{2}$$

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.[15]

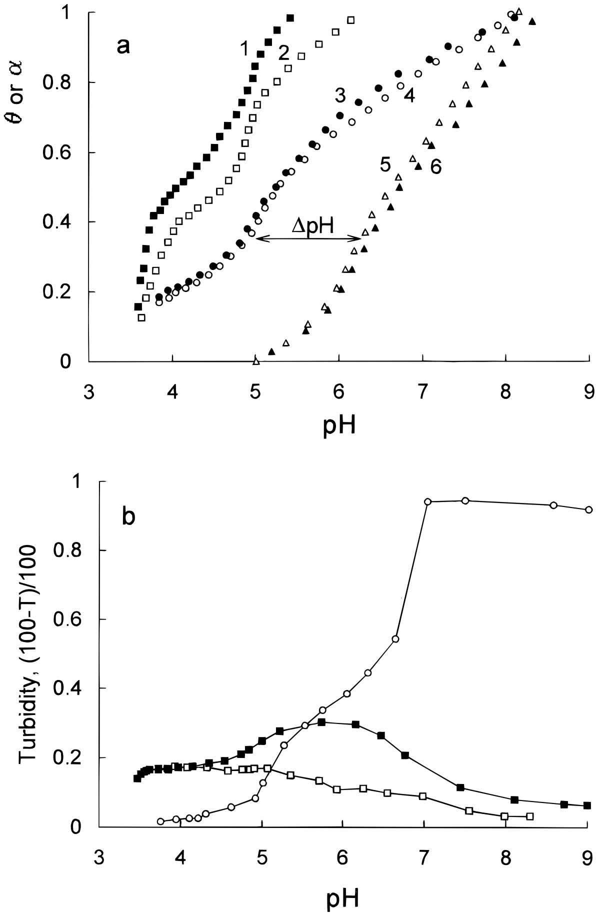

Figure 1. (a) Dependencies of the degree of conversion (θ) in the polyion coupling reactions (■, □, ○, ●) and degree of ionization (α) of polyacid samples (△, ▲) for the following systems: (■) PEO−PMA$^-$ and long PEVP$^+$; (□) PEO−PMA$^-$ and short PEVP$^+$; (○) PMA$^-$ and short PEVP$^+$; (●) PMA$^-$ and short PEVP$^+$ in the presence of PEO; (△) PEO−PMAA; (▲) PMAA. The pH shift, ΔpH, between the θ−pH and α−pH dependencies is shown for the PMAA complex as an example. (b) Turbidity in the systems containing complexes formed between (■) PEO−PMA$^-$ and long PEVP$^+$, (□) PEO−PMA$^-$ and short PEVP$^+$, and (○) PMA$^-$ and short PEVP$^+$. Turbidity is determined as $(100 - T)/100$, where T is transmittance (%). (a, b) The concentrations of polyions and PEO homopolymer (MW 8000) is 7×10^{-4} base-moles/L.

The dependencies of θ on pH represented in Figure 1a are shifted to lower pH compared to the dependencies of ionization degrees, α, for PEO−PMAA and PMAA. This shows that the interaction between the polyanionic components and PEVP has a distinct cooperative character and results in formation of the complexes, in which most of the ionic units are paired. The pH difference, ΔpH, between θ−pH curves of the complexes and α−pH curves of corresponding individual polyacids at each $\theta = \alpha$ is a differential measure of a free energy of cooperative stabilization of the polyelectrolyte complexes, $\Delta G_c(\alpha) = RT\Delta\text{pH}$ (see Annex A). Therefore, the further the θ−pH curve is shifted toward acid pH compared to α−pH curve, the greater is the stability of the polyelectrolyte complex. Importantly, the θ−pH curves for the PEO−PMA$^-$/PEVP$^+$ complexes are much steeper and are drastically shifted to the acid area compared to the curve for the PMA$^-$/PEVP$^+$ complex (compare curves 1, 2, and 4 in Figure 1a at $\theta = \alpha > 0.2$). At the same time, the α−pH curves for the PEO−PMAA and PMAA are very close (compare curves 5 and 6). As a result the $\Delta G_c(\alpha)$ for the complexes formed by the PEO−PMAA copolymers is much higher compared to the $\Delta G_c(\alpha)$ observed for the complex of the PMAA homopolymer. This suggests that the PEO segments of the copolymer significantly stabilize the complexes between the anionic segments of PEO−PMA$^-$ and PEVP$^+$. Further, the PEO−PMA$^-$/PEVP$^+$ complex formed by long PEVP is more stable than that of a short PEVP (compare curves 1 and 2). It is very important that the PEO homopolymer practically does not affect complexes of PMA$^-$ and PEVP$^+$ (compare curves 3 and 4), which clearly shows that the stabilization effects are characteristic only for the block copolymer polyions. These effects increase with the increase in the degree of conversion at $\theta > 0.6$ for both short and long PEVP-based complexes, since at $\theta > 0.6$ the θ−pH curve for the PMA$^-$/PEVP$^+$ complex approximates the α−pH curve (compare curves 4 and 6), while the θ−pH curves for the PEO−PMA$^-$/PEVP$^+$ complexes do not (compare curves 1, 2, and 5). This difference in behavior is probably explained by the precipitation of PMA$^-$/PEVP$^+$ complex at high degrees of conversion (Figure 1b) which may decelerate further coupling of PMA$^-$ and PEVP$^+$ chains and yield nonequilibrium complexes. By contrast, the complexes formed by the block copolymer remain soluble at high degrees of conversion, Figure 1b (see next section for further discussion). At $\theta = \alpha = 0.5$ the $\Delta G_c(\alpha)$ values for the PMA$^-$/PEVP$^+$ complex and PEO−PMA$^-$/PEVP$^+$ complexes formed by short and long PEVP are 3.52, 5.05, and 6.42 kJ·M^{-1}, respectively. Therefore, the stabilization effects of PEO chains at $\theta = \alpha = 0.5$ are 1.53 and 2.90 kJ·M^{-1} for the short and long PEVP-based complexes, respectively.

The nonmonotonous character of the θ−pH curves for the PEO−PMA$^-$/PEVP$^+$ and PMA$^-$/PEVP$^+$ complexes is worth mentioning. It is known that PEO forms cooperative H complexes with PMAA in aqueous solutions at the acidic pH region.[16] The decreased solubility of PEO−PMAA observed at low pH (data not shown) suggests that the copolymer also forms the H-complexes (which are, probably, intramolecular). Therefore the shape of curves 1 and 2 at pH 3.7 to pH 4.5, may be attributed to the transformation of PEO−PMAA H-complexes into PEO−PMA$^-$/PEVP$^+$ complexes. The difference between curves 1, 2, and 3 may reflect the difference in the stability of intramolecular PEO−PMAA and intermolecular PEO and PMAA H-complexes; however, there is no data at this time that independently validate this hypothesis. Nonmonotonous behavior of curves 1−4 at pH 4.5 to pH 5.5 can be attributed to the transformation of the well-known intramolecular clusters of H-bonded PMAA units stabilized by nonpolar interactions of CH_3 groups[17] into PEO−PMA$^-$/PEVP$^+$ or PMA$^-$/PEVP$^+$ complexes, respectively.

Solubility of PEO−PMA$^-$/PEVP$^+$ Complexes. One characteristic of the PEO−PMA$^-$/PEVP$^+$ complexes is noteworthy, specifically, their water solubility. Figure 1b presents the data on the turbidity of the complexes as a function of pH. At θ close to 1 the stoichiometric complexes are formed. Their solutions are either completely transparent (short PEVP-based complex) or only slightly opalescent (long PEVP-based complex). In this respect, these complexes are very different from the normal stoichiometric IPEC which precipitate under comparable conditions, as shown in Figure 1b for the PMA$^-$/PEVP$^+$ complex. Since the PMA$^-$/PEVP$^+$ IPEC is water insoluble at $\theta \approx 1$, yet the PEO−PMA$^-$/PEVP$^+$ BIC is water-soluble, it suggests very strongly that in the case of BIC we are dealing with an aggregated (self-assembled) system which is present in the form of a microphase species solubilized by the PEO chains. The simplest way to describe them is as micelle-like aggregates with a core formed by neutralized polyions surrounded by a PEO corona.

The turbidity data also indicate that some structural rearrangements take place in the PEO−PMA$^-$/PEVP$^+$ complexes at pH 6.0−7.5, since a decrease in turbidity is observed at these pH, which is more pronounced in the case of the long PEVP. As follows from the θ−pH curves, all ionizable groups of interacting polyions are paired in this pH range. Therefore, we hypothesize that these rearrangements are caused by complexation of sodium ions administered to the system during NaOH titration with PEO chains. The complexation of PEO polymers and low-molecular mass cations has been extensively studied.[18] We obtained data suggesting that the binding of monovalent cations with PEO segments of PEO−PMANa copolymer affect properties of both the initial copolymer and its complexes (data not presented). The detailed studies of these effects will be reported elsewhere.

Pyrene Solubilization in BIC. The self-assembly in BIC systems was investigated using pyrene as the fluorescence probe.[19] A fluorescence emission of pyrene is significantly increased in the presence of both short and long PEVP-based complexes. Interestingly, at low wavelengths ($\lambda_{\max} = 363$ nm), a scattering peak is also seen in these systems, which is more intense for the long PEVP than for the short PEVP system. Practically no scattering is observed in the vicinity of I_1 or I_3. At the same time, the quantum yield is increased when the complex concentration increases, which is in complete analogy with the behavior of normal block copolymer micelles. The concentration dependence of the fluorescence intensity (I_1) for the complex based on the short PEVP is shown in Figure 2. The behavior is strongly reminescent of a micellar system in the vicinity of the CMC[19] and thus indeed suggests that a CMC is observed using this technique. The CMC is about 1.4×10^{-3} base-moles/L or 7.4 μM counting per the block copolymer chains. This value lies in the range of the CMC characteristic for such systems as PEO-*b*-poly(propylene oxide)-*b*-PEO or polystyrene-*b*-poly(sodium acrylate) block copolymers and is substantially lower than the CMC usually observed with low molecular mass surfactants.[21] Interestingly, below the CMC, opalescence is observed, which suggests that these systems may be subject to anomalous micellization, which has also been observed for a very wide range of other block copolymer systems and has been investigated to some extent.[22] The fluorescence intensity as a function of concentration for the complex based on the long PEVP is also shown in Figure 2. In contrast to the short PEVP-based system, no CMC type behavior is observed. However, the fluorescence intensity still increases with total complex concentration, suggesting (from the shape of the curve) that in this system a normal partitioning of the pyrene between the complex and the water takes place.

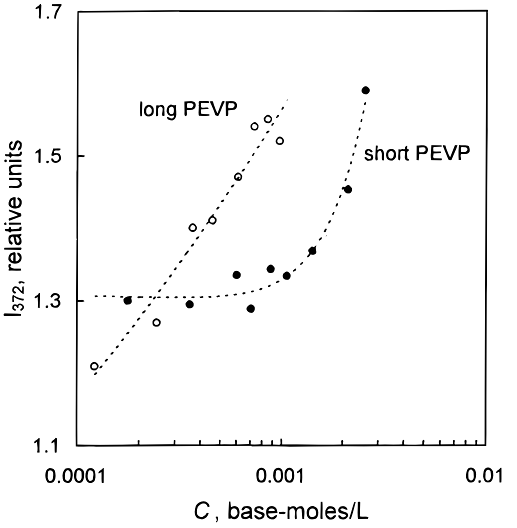

Figure 2. Dependence of the intensity of pyrene fluorescence emission (I_{372}) on the concentration of the complex (C) formed by the short and long PEVP samples at pH 9.5. The concentration of the complex (base-moles/L) equals to the concentration of the reacting polyions since the binding constant of the polyion segments at θ close to 1 is infinitely large.[20]

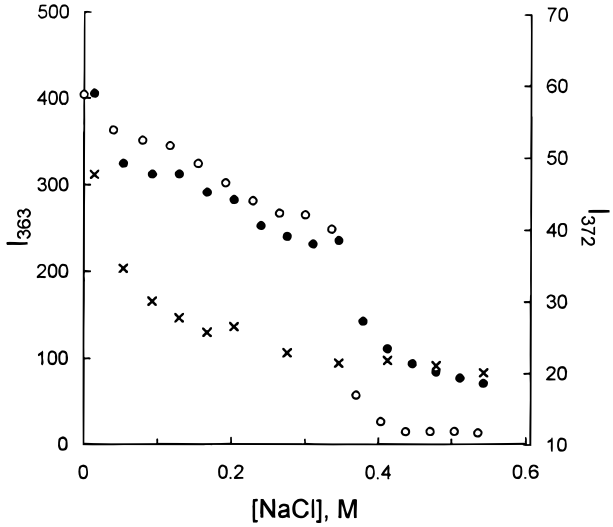

Figure 3. Dependencies of the scattering intensity (I_{363}) of the PEO−PMA$^-$/PEVP$^+$ complex (○) and pyrene fluorescence emission (I_{372}), (●, ×) on the NaCl concentration. Measurements of pyrene fluorescence were performed with (●) or without (×) the complex. Concentration of the complex is 1.12 × 10^{-3} base-moles/L.

The value of I_1/I_3 is of interest because it is frequently associated with a polarity of the environment of the probe molecule.[19] In aqueous solution, the I_1/I_3 value is about 1.7−2.0, while in a nonpolar environment such as hexane, it is about 0.6. In the case of short PEVP, the value changes from 1.72 to 1.44 as the concentration of the complex increases. This confirms that the environment of the pyrene probe goes from polar to nonpolar exactly as it does as one traverses the CMC region in normal micelles. In the case of the long PEVP complex, I_1/I_3 monotonously decreases from 1.92 to 1.81, suggesting less significant changes in polarity. Polarized fluorescence was investigated both for free pyrene and for pyrene in the complex. A dramatic change in the anisotropy, r, was seen: from $r = 0.003$ for the complex-free solution to $r = 0.031$ for the short PEVP-based system and $r = 0.2$ for the long PEVP-based system. The relatively large r value for the long PEVP complex is indicative of a higher rotational relaxation time for pyrene solubilized in this complex compared to that for pyrene in the short PEVP complex.

More detailed structure studies will be needed to better characterize these complexes. However, one possible explanation for the above results is that in the case of the short PEVP complex, we are dealing with a multicomplex aggregate which is solubilized by the PEO chains. By contrast, for the long PEVP complex we are probably dealing with the unicomplex micelle, which apparently contains a hydrophobic backbone formed by the complexed polyions and hydrophilic PEO "grafts" that provide for the complex solubility.

Cooperative Dissociation of BIC. The effect of added salt was investigated for the *long PEVP*-based complex by monitoring the scattering peak intensity at a wavelength of 363 nm. A plot of the scattered intensity as a function of salt concentration is shown in Figure 3. It is seen that at approximately 0.35 M NaCl, the scattered intensity decreases sharply over a relatively narrow salt concentration range. These studies are paralleled by investigations of the pyrene fluorescence, in both the presence and the absence of the complex, which are also shown in Figure 3. In the presence of the complex, the fluorescence intensity goes through a sigmoidal change very similar to the behavior of the scattered intensity. By contrast, the pyrene alone shows no such behavior. This suggests that the observed changes in the scattered intensity are due to the disintegration of the complex when the NaCl content increases to 0.35 M. The behavior is thus analogous to regular IPEC which are known to be salt-sensitive and dissociate at some critical value of the salt concentration.[14] Furthermore, the pyrene probe experiment demonstrates very clearly that it is the microphase that disintegrates in the case of the PEO−PMA$^-$/PEVP$^+$ complexes.

Polyion Substitution Reactions in BIC. The final experiments to be reported here are the polyion substitution reactions. Two types were investigated, one involving sodium poly(styrenesulfonate) and the other PMANa with an attached fluorescent label. It is known that while reacting with soluble IPEC in aqueous solutions, sulfonate-based polyanions substitute carboxylate-based anions in the complex.[14] Thus we expected that poly(styrenesulfonate) anion will substitute the PEO−PMA$^-$ anion if added to the BIC. This type of experiment was indeed performed using the long PEVP-based complex as an example, with the result that the poly(styrenesulfonate)/PEVP$^+$ complex precipitates.

The other experiment involved pyrenyl-labeled PMANa.[14] The starting point was a nonstoichiometric water-soluble IPEC between the short PEVP$^+$ and labeled PMA$^-$ with a base-molar ratio of cationic to anionic units of 0.2. In this complex, the fluorescence of the tag is completely quenched by the PEVP$^+$ units. When the PEO−PMANa block copolymer is added to this complex, a partial restoration of the fluorescence is observed (data not shown). A similar increase in fluorescence is observed when this complex is mixed with the nonlabeled PMANa. This suggested that a substitution reaction takes place between the polyanion segments in the block copolymer and the PMA$^-$ chains attached to the complex, in complete analogy with the exchange reactions studied in regular IPEC.

Conclusion. It was shown that stoichiometric BIC are formed between the PEO−PMANa diblock copolymer and PEVP of both high and low molecular weight. Both these complexes are water-soluble and are thus drastically different from regular IPEC prepared from homopolymers. The complexes based on the short PEVP chains self-assemble in a micelle consisting of a core formed by neutralized polyions and a PEO corona. These micelles undergo a CMC as one changes the BIC concentration. The BIC are salt sensitive since they fall apart as the salt concentration increases beyond a critical value. This aspect of the behavior is unique in the case of block copolymer micelles. We are not aware of any other systems in which the hydrophobic block has been shown to be salt sensitive in this manner. The BIC are subject to substitution reactions in exactly the same way as IPEC based on homopolymers. Therefore, the BIC represent a new class of hybrid materials which combine properties of polyelectrolyte complexes and block copolymer micelles.

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Annex A. Reaction between Weak Polyacid and Strong Polybase

The ionization equilibrium of the weak polyacid (e.g., PMAA) in the absence of the polycation (in our case PEVP$^+$) is described by the following equation

$$\frac{[\mathrm{H}^+]'\alpha}{1-\alpha} = K'_\alpha(\alpha) = \mathrm{e}^{-\Delta G'(\alpha)/RT} \qquad (4)$$

and in the presence of polycation by the following equation

$$\frac{[\mathrm{H}^+]''\alpha}{1-\alpha} = K''_\alpha(\alpha) = \mathrm{e}^{-\Delta G''(\alpha)/RT} \qquad (5)$$

where α is the ionization degree, $K'_\alpha(\alpha)$ and $K''_\alpha(\alpha)$ are the apparent ionization constants, and $\Delta G'(\alpha)$ and $\Delta G''(\alpha)$ are the free energies of ionization in the absence and presence of polycation, respectively. The degree of conversion in the polyion coupling reaction, θ, is determined as the fraction of the units of the polyanion that form ionic pairs with the polycation units. It was previously demonstrated that in the presence of the polycation practically all ionized units of the polyacid participate in the formation of ionic pairs, i.e. $\theta = \alpha$.[14]

Dividing eq 1 by eq 2 and then taking the logarithm of the resultant equation yields the following

$$\Delta\mathrm{pH} = \frac{\Delta G_\mathrm{c}(\alpha)}{RT} \qquad (6)$$

where ΔpH is the pH difference between the θ−pH curves of the complexes and the α−pH curves at each $\theta = \alpha$ and $\Delta G_\mathrm{c}(\alpha)$ is the difference of free energies of ionization of polyacid in the presence and absence of the polycation: $\Delta G_\mathrm{c}(\alpha) = \Delta G''(\alpha) - \Delta G'(\alpha)$. R is the universal gas constant, and T is the absolute temperature. The $\Delta G_\mathrm{c}(\alpha)$ value is a *differential* characteristic of the impact of polycation in ionization of polyacid. The integral free energy, ΔG_total, characterizing the total thermodynamic impact of cooperative interaction of polyions at a given degree of ionization of polyacid $\alpha = \alpha_1$ ($=\theta_1$) is determined as follows

$$\Delta G_\mathrm{total} = \int_0^{\alpha_1} \Delta G_\mathrm{c}(\alpha)\,\mathrm{d}\alpha = RT\int_0^{\alpha_1} \Delta\mathrm{pH}(\alpha)\,\mathrm{d}\alpha \qquad (7)$$

The ΔG_total is a measure of the free energy of the polyion coupling reaction at a given degree of ionization.

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(9) We will use the following abbreviations: PMANa, PMAA, PMA$^-$ for the poly(sodium methacrylate), poly(methacrylic acid), and polymethacrylate anion. Similarly, the salt, acid, and anionic forms of the copolymer are abbreviated as PEO−PMANa, PEO−PMAA, and PEO−PMA$^-$. PEVP and PEVP$^+$ will be used for poly(*N*-ethyl-4-vinylpyridinium bromide) and the poly(*N*-ethyl-4-vinylpyridinium) cation.

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