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Association Behavior of Ampholytic Diblock Copolymers

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ABSTRACT: The association of diblock copolymers with oppositely charged, water-soluble poly(dimethylamino)ethyl methacrylate (AMA) and sodium polymethacrylate (SPM) blocks was studied in aqueous solution as a function of pH and the segment ratio of the two blocks. The size and the structure of these copolymer aggregates were characterized by dynamic light scattering, electrokinetic, and potentiometric measurements. The association process is mainly electrostatically driven. At pH values around the isoelectric point, unlimited aggregation or phase separation takes place. The position of this region depends on the segment ratio of the two blocks. If the pH is moved away from the isoelectric point, the net charge of the copolymer molecules leads to charged molecular assemblies. At pH values higher than 10 or lower than 4, i.e., one of the blocks is entirely uncharged, copolymer assemblies still exist. The solution behavior of the corresponding oppositely charged homopolyelectrolyte mixtures was also studied. The size of the charged homopolymer complexes is smaller than that for copolymers although the length of the homopolymer molecules is higher.

Introduction

Block copolymers with two water-soluble, oppositely charged polyelectrolyte blocks form a relatively new class of copolymers that may be exploited for stabilization of colloidal dispersions and microencapsulation in electronic, paint, cosmetics, and pharmaceutical industries. The association behavior of these molecules in solution is a very important aspect for understanding its colloidal stability. Particularly on hydrophilic surfaces, one of the blocks will be able to adsorb due to for example electrostatic interactions or hydrogen bonding, whereas the other block contributes to the stabilization of the particles. It is possible to regulate the charge and, therefore, the association and stabilization behavior of these molecules by changing the segment ratio of the blocks. Ampholytic diblock copolymers can contain strong or weak acid or basic groups. The advantage of weak groups is that it is also possible to regulate the charge by changing the pH of the solution.

The majority of water-soluble diblock copolymers is amphiphilic; i.e., they have one insoluble (hydrophobic) block and one water-soluble block. Depending on the block length ratios and solubilities, such polymers associate in solution to a variety of micellar structures.[1−10] However, the association of polymers consisting of two *soluble* blocks that associate electrostatically has been investigated much less, and little is known about the structures formed in this case. Some studies have been performed with block copolymers of poly(vinylpyridinium) salt and either poly(methacrylic acid) or poly(styrenesulfonate).[11−13] These block copolymers are insoluble at pH values around the isoelectric point (iep). Above and below the iep both the solubility and the viscosity increases. Formation of internal polysalt complexes and conformational changes have been emphasized.

Ampholytic block copolymers with weak acid and basic groups have been prepared and characterized by Creutz et al.[14,15] The dynamics of micellization of these block copolymers of poly(dimethylamino)ethyl methacrylate (AMA) and sodium polymethacrylate (SPM) were studied by steady-state fluorescence spectroscopy and size exclusion chromatography. The exchange rate between aggregates ("micelles") and solution for these block copolymers is more than 1000 times smaller than for simple amphiphilic molecules. The exchange rate can be tuned by changing the block size ratio, the molecular architecture, and the length of the alkyl spacer in the AMA group. In their interpretation the authors treat these block copolymers as amphiphilic whereas both the AMA and the SPM blocks are soluble. In these investigations little attention has been paid to the morphology of the associates.

Block copolymers with oppositely charged polyelectrolyte blocks are to some extent the analogues of mixtures of oppositely charged polyelectrolytes, except that the chemical binding between two blocks leads to a loss of conformational and translational entropy. For mixtures of two oppositely charged polyelectrolytes, complexation and phase separation have been studied extensively.[16−20] A characteristic feature of these systems is a strong tendency toward association of the oppositely charged polyions. In general, Coulombic interactions play a dominant role in their association behavior, but it was emphasized recently that the association of oppositely charged polyelectrolytes is primarily an entropic effect because of the nonuniform distribution of counterions.[18] Salt addition often increases the solubility, and in many cases the ternary system becomes entirely miscible above a certain critical salt concentration.[18,21] Despite the large number of experimental studies on mixed polyelectrolyte systems, their association behavior is still not well understood and, therefore, a matter of intensive investigation.

Recently, Cohen Stuart et al. studied the behavior of a mixture of a polyanion and a block copolymer with a neutral and a cationic block.[22] The polyanion and the two blocks of the copolymer are water-soluble. For a block size ratio of 1:1, a macroscopic phase separation occurs around the isoelectric composition, but with a longer neutral block (ratio 3:1) stable micelles are formed in this region.

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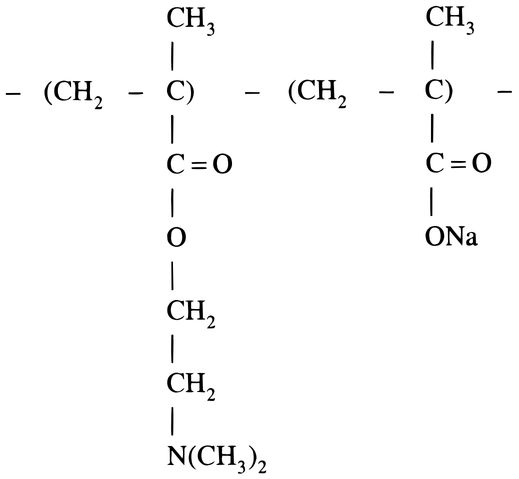

$$-(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C(=O)OCH_2CH_2N(CH_3)_2}{C}})-(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C(=O)ONa}{C}})-$$

Figure 1. Structural formula of poly(dimethylamino)ethyl methacrylate/sodium polymethacrylate copolymer.

Table 1. Molecular Characteristics of the Used Homo- and Copolymers

polymer	*N* [AMA]	*N* [SPM]	*M*	M_w/M_n
AMA	127		19 900	1.1
SPM		240	25 900	1.04
SC240	15	27[a]	5 300	1.1
SC184	24	63[a]	10 800	1.1

[a] These values differ from the corresponding values of Creutz et al.,[15] probably because (erroneously) Cl^- was added to the block molecular weight of SPM.

In the present work we have studied the association behavior of two ampholytic AMA/SPM diblock copolymers of different block ratios by dynamic light scattering, electrokinetics, and potentiometric titrations.

Experimental Section

Materials. A mixture of homopolymers (AMA and SPM) was used to model the corresponding copolymers. AMA homopolymer was synthesized by Dr. Arnold's group in Halle (Germany). SPM was obtained from ROCHROM (polymer standard service). Both homopolymers were made by anionic polymerization.

Two diblock polyelectrolytes of poly(dimethylamino)ethyl methacrylate (AMA) and sodium polymethacrylate (SPM) were used. These have been prepared by Creutz et al.[14,15] from anionically polymerized diblock copolymers of AMA and *tert*-butyl methacrylate by hydrolyzing the *tert*-butyl ester groups. The structural formula of the block copolymers is presented in Figure 1.

The monomer molar masses for AMA and SPM are 157 and 108, respectively. Sample names, degrees of polymerization *N*, molecular weight, and coefficients of polydispersity M_w/M_n for both homopolymers and degree of polymerization of the AMA and SPM blocks in the blockcopolymers are listed in Table 1. At pH = 9 the critical micelle concentration amounted to 11.2 and 2.8 μM for SC184 and SC240 as determined by light scattering.[15] Both AMA and SPM blocks have groups with a pH-dependent charge. The pK_a value for the tertiary amine group of monomeric AMA is about 8.4,[23] and the pK_a value for methacrylic group of SPM is about 4.9.[24]

Water was purified using an Elgastat UHP unit. Sodium chloride was obtained from Merck and was of p.a. quality.

Sample Preparation. Stock solutions of a concentration of 10 mg mL^{-1} were prepared by dissolving the block copolymers in 10 mM NaCl solution which had been filtered through 0.2 μm pore size filters. To obtain concentrations ranging from 10 to 0.5 mg mL^{-1}, further dilutions were performed with filtered salt solutions. The ionic strength was adjusted by addition of a certain amount of 3 M NaCl solution.

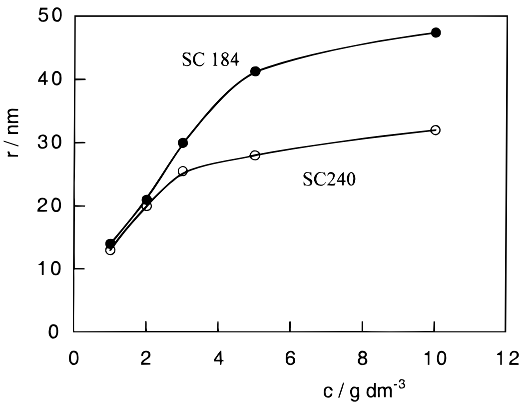

Figure 2. Radius of SC240 and SC184 particles measured at pH 10.2 and 9.1, respectively, as a function of copolymer concentration. c_{NaCl} = 10 mM.

The mixed polymer solutions consisting of both AMA and SPM were prepared by mixing equal amounts of AMA and SPM solutions of concentrations 2 and 2.5 mg mL^{-1}, respectively, at pH 9. The final concentrations of AMA and SPM in the mixture were 1 and 1.25 g L^{-1}, respectively, and the monomer ratio [AMA]:[SPM] was 1:1.8, which corresponds to the block size ratio of the SC240 copolymer.

All stock solutions had initial pH values of 9–11. To adjust the pH value of the solutions, 0.1 M HCl or 0.1 M NaOH was used. For dynamic light scattering measurements the solutions were filtered through 0.2 μm pore size filters (Acrodisc) directly into the cuvette.

Dynamic Light Scattering. Dynamic light scattering was performed with an ALV-light scattering instrument using a 400 mW argon ion laser tuned at a wavelength of 514 nm. All measurements were done at room temperature. To analyze the autocorrelation function, the method of cumulants was used.[25] In this method it is assumed that the scattering particles are spherical and that only the translational diffusion coefficient contributes to the autocorrelation function. The average diffusion coefficient and corresponding hydrodynamic radius of the particles were calculated using the Stokes–Einstein relation for spherical particles.

Microelectrophoresis. Electrophoretic mobilities of block copolymer and polyelectrolyte complexes were measured at 298 K with a Malvern Zetasizer MK III.

Potentiometric Titration. The charge of the copolymer molecules as a function of pH was determined by potentiometric titration. Copolymer solutions of concentration 2 g L^{-1} were titrated between pH 10 and 4 using 0.1 M HCl or NaOH.

Results and Discussion

Block Copolymer Solutions. Traditionally, dynamic light scattering has been applied for the study of self-aggregating amphiphilic block copolymer systems.[10,26–28] It is well-known that these copolymers form micellar structures in aqueous solutions, and a great deal of data about size, structure, influence of solvent, and salt addition is available in the literature.[1–3,6–8] In principle, dynamic light scattering is very sensitive to polydispersity and particle shape. Here, we used this method mainly to estimate the average size of polymer aggregates. The average hydrodynamic radius of SC240 and SC184 in 10 mM NaCl solution as a function of copolymer concentration obtained at pH 10.2 and 9.1, respectively, is shown in Figure 2. The radius of particles measured at a scattering angle of 90° increases gradually up to values of about 30 nm for SC240 and 45 nm for SC184, at a copolymer concentration of 10 g L^{-1}. The particles are rather polydisperse as indicated by the increase in size at scattering angles less than 90°. For comparison, also the hydrodynamic radius of

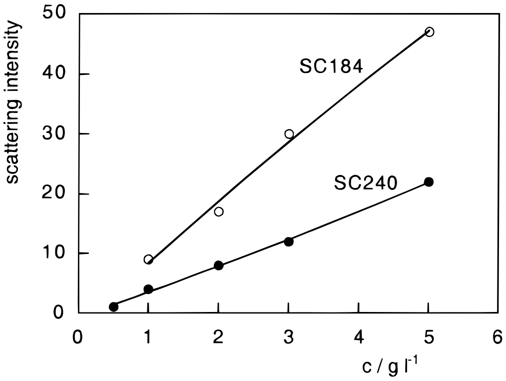

Figure 3. Scattering light intensity (in arbitrary units) of SC240 and SC184 solutions measured at pH 10.2. and pH 9.1, respectively, as a function of copolymer concentration. NaCl concentration is 10 mM.

the homopolymers AMA and SPM has been measured at pH 9 and amounts to about 3–5 nm. The radius does not depend on polyelectrolyte concentration although the length of homopolymers used is 2–5 times that for the diblock copolymers. These results provide strong evidence that in the diblock copolymer solutions we are dealing with some kind of soluble molecular aggregate.

The critical aggregation concentrations (cac) for block copolymer solutions have been estimated from the scattering intensity as a function of the polymer concentration. All values were corrected for the (small) scattering intensity of a pure 10 mM NaCl solution. The results for both SC240 and SC184 are shown in Figure 3. It can be seen that for both copolymers used the intensity is a linear function of the copolymer concentration. The intersection with the concentration axis gives an estimate of the critical aggregation concentrations and are close to the cmc values given by Creutz et al.[15] (15 and 120 mg L^{-1} for SC240 and SC184, respectively, at pH = 9). These values are fairly high; usually amphiphilic diblock copolymers have much lower cmc's, unless the hydrophobic block is very short and the hydrophilic block very long.[3] We therefore conclude that a hydrophobic mechanism is unlikely.

As mentioned before, both blocks of our copolymers have a pH-dependent charge, and therefore, both blocks contribute to the overall charge. From potentiometric titration of the homopolymers it is known that the homopolymer charge for AMA is developed entirely between pH = 5–10 and that for SPM[23,24,29,30] between pH 4 and 9. If the aggregation of these copolymers is electrostatically driven, the size of copolymer aggregates has to be pH dependent between pH 4 and 10. To check this, the average diffusion radius of aggregates and the light scattering intensity have been measured as a function of pH at different salt concentrations. The results for SC240 and SC184 are shown in Figures 4 and 5, respectively. The copolymer concentration in both cases was 2 g L^{-1}. At pH values around neutral both samples have a turbid region of phase separation and at lower and higher pH a transparent region where a homogeneous one-phase system exists. The solution of SC240 is unstable between pH 5.5 and 8; that of SC184 is unstable between 3.5 and 6.5 independent of the salt concentration. Similar phase separations have been observed for the triblock copolymers studied by Hatton et al.[26,27] and with the mixtures of oppositely charged polyelectrolytes. We are dealing here with a region of complex coacervation; i.e., a liquid phase concentrated in both polymers separates from a phase that essentially contains only solvent.[18] The concentration of droplets of the concentrated phase in this region is rather high, which causes the high scattering intensity. Secondary effects such as aggregation and flocculation of the droplets as well as reflection of the scattered light from the particles make it rather difficult to measure the size of the droplets in this region using the light scattering technique. However, independent optical microscopy

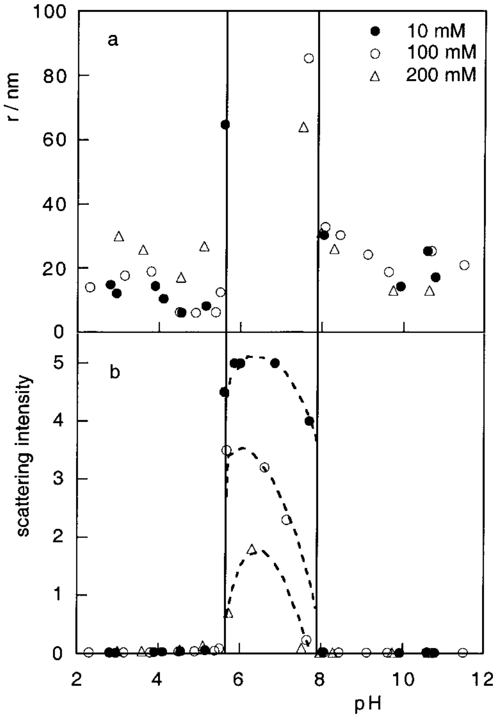

Figure 4. Radius of the particles (panel a) and the scattering light intensity in au (panel b) measured in 2 g L^{-1} solution of SC240 as a function of pH at different NaCl concentrations.

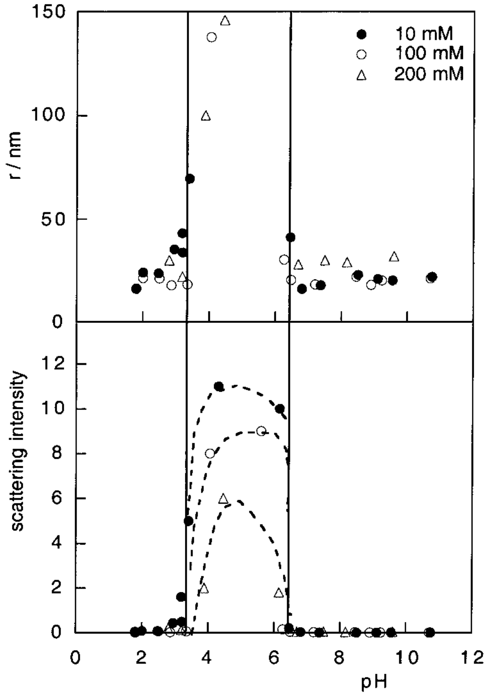

Figure 5. Radius of the particles (panel a) and the intensity of the scattered light in au (panel b) measured in 2 g L^{-1} SC184 solution as a function of pH at different salt concentrations.

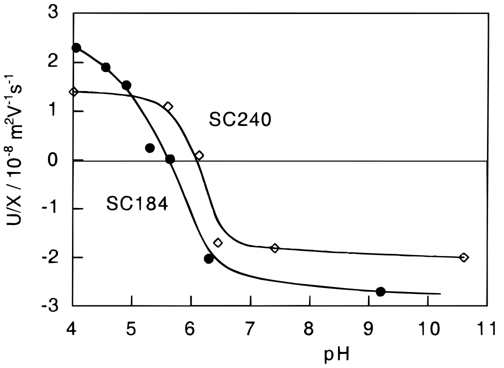

Figure 6. Electrophoretic mobilities of the copolymer aggregates measured in 2 g L^{-1} SC240 and SC184 solutions as a function of pH at 10 mM salt concentration.

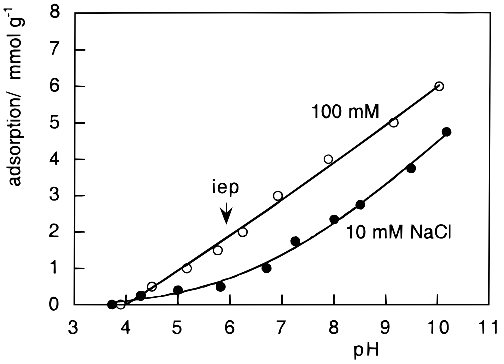

Figure 7. Acid−base titrations of SC240 at two salt concentrations. The relative charge is expressed as amount of acid or based consumed by the copolymer per gram.

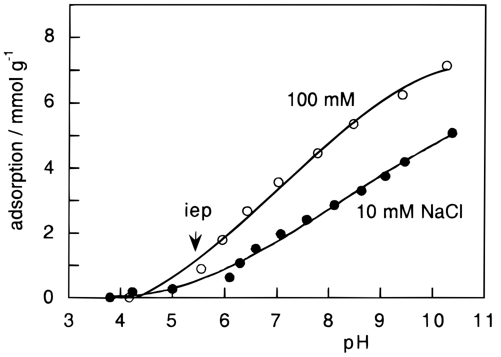

Figure 8. Acid−base titration of SC184 at two salt concentrations. The relative charge is expressed as amount of acid or base consumed by the copolymer per gram.

observations confirm that the size distribution of droplets is rather broad and that the radius of droplets may reach a value of about 500 nm. In the region of pH where the scattering intensity was rather low and solutions seemed to be optically clear, the radius of the particles was (within experimental error and for both copolymer samples) about 20 nm and nearly pH independent. It is remarkable that at a pH higher than 10 and less than 4, where one of the blocks would be entirely uncharged and there would be no longer a driving force for complexation, the aggregates still exist in solution. One reason for this may be a shift in p*K* of the interacting monomer units due to the short mutual distance. Another possibility is the existence of additional nonelectrostatic interactions between the copolymers in order to compensate the existing electrostatic repulsion.

Salt addition (0.1 and 0.2 M) did not change the size of the particles in the stable regions considerably, but as is shown in Figures 4b and 5b, the intensity of the scattered light in the region of phase separation decreases gradually with increasing salt concentration, indicating an increase in miscibility. The response of the soluble polyelectrolyte aggregates to addition of low molecular weight salt may be a result from two counteracting interactions: an electric screening of the attraction within the aggregate and a salting-out effect acting between the particles. The salting-out effect would show up as an increase in particle size, while the screening effect causes the dissolution of the aggregates at a critical salt concentration.[31] A combination of these two opposite effects would determine the polyelectrolyte behavior at different salt concentrations. In our case the screening effect seems to dominate in the region of phase separation, resulting in a decrease of droplet size, whereas in the stable region where the aggregates are rather small, the salting-out effect seems to play a role. Unfortunately, due to the large number of parameters influencing complex formation, a general quantitative model for similar systems is so far absent, and therefore, it is rather difficult to predict the effect of salt addition on the aggregation behavior of oppositely charged polyelectrolytes.

To check the mechanism of aggregation in copolymer solutions, electrophoretic mobilities of both copolymers have been measured as a function of pH at 10 mM salt concentration. The results are presented in Figure 6. If we may assume that mainly the uncompensated charge of aggregates contributes to the charge of the diffuse layer, the electrophoretic mobility as a function of pH provides information about the uncompensated charges of the aggregates. As is shown in Figure 6, the decrease of the solution pH from 10 to 3 causes the uncompensated charge of copolymer aggregates to change from negative to positive. At the isoelectric point (iep), which is 6.0 for SC240 and 5.5 for SC184, the total charge of copolymer molecules is completely neutralized, and unlimited aggregation or phase separation (coacervation) takes place (Figures 4 and 5). For SC184, which contains more negative groups per positive group than SC240, the charge compensation point occurs at lower pH, and the region of coacervation is correspondingly shifted to low pH. As soon as the pH is moved away from the iep, the uncompensated charge of the copolymer molecules increases, and at a critical value the coacervates start to dissolve as stable, charged aggregates of copolymer molecules.

To further characterize the charge of the polyampholytes, potentiometric titrations of both samples have been performed. The relative total charge of SC240 and SC184 expressed in millimoles of acid or base consumed per gram of copolymer as a function of pH at two salt concentrations is shown in Figures 7 and 8. As has been mentioned before, both polybase and polyacid gradually develop their entire charge in the region between pH 4 and 10. By contrast, the copolymer molecules at low salt concentration and at pH around iep's keep the charge nearly constant. The process of coacervation in this region inhibits charge formation of copolymer molecules. Increasing the salt concentration as well as shifting the pH far from the iep causes a gradual change of the charge density. The values of the maximum charge as determined for both copolymers at high salt concentra-

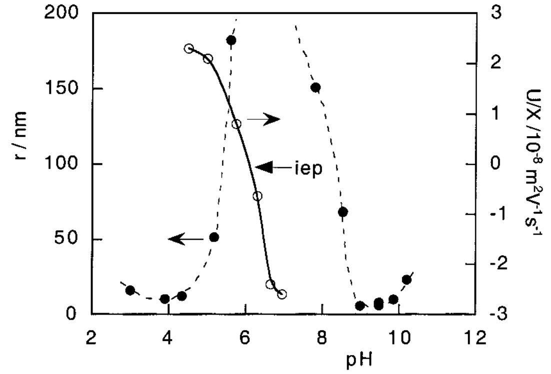

Figure 9. Radius and electrophoretic mobilities of the polyelectrolyte AMA and SPM complexes as a function of pH measured at 10 mM salt concentration. The segment ratio [AMA]:[SPM] = 1:1.8 corresponds to the segment ratio for the SC240 copolymer.

tion are close to the calculated charge capacities, which are 7.8 mmol g^{-1} for SC240 and 8.2 mmol g^{-1} for SC184.

Mixture of Homopolymers. Further insight into the aggregation behavior of copolyelectrolyte molecules can be obtained by comparison to the solution behavior of the corresponding homopolyelectrolyte mixtures. Homopolymers normally do not aggregate in solution and exist in their unimeric form.[31] However, pairs of oppositely charged polyelectrolytes are able to form complexes in aqueous solutions.[16,17,20] Such complexation is mainly due to the electrostatic attractions between the oppositely charged chains. Both stoichiometric and nonstoichiometric complexes may be formed.[31] In stoichiometric complexes (coacervates) the charge is nearly neutralized, so that these aggregates are unstable in solution and separate into a polymer-rich phase and almost pure solvent. Nonstoichiometric complexes stabilized by the uncompensated polymer charge may remain in solution. The stability and the size of these complexes depend on the value of the uncompensated charge and the ionic strength of the solution.

We measured the size and the electrophoretic mobilities of the polyelectrolyte complexes of AMA and SPM as a function of pH at 10 mM salt concentration. The results are shown in Figure 9. The concentrations of AMA and SPM in the mixed solution were 1.0 and 1.25 g L^{-1}, respectively. The monomer molar ratio AMA:SPM was 1:1.8, which corresponds to that of AMA and SPM blocks in the SC240 copolymer. The mixture of oppositely charged polyelectrolytes demonstrates a similar phase behavior as the SC240 copolymer. The iep is about pH 6.0, which is inside the region of phase separation where the uncompensated charge of the polyelectrolyte complexes seems to be small. A comparison of the instability regions for the mixture of homopolymers (Figure 9) and the block copolymer SC240 (Figure 4) shows that for the former the strong complexation already starts at pH < 9, whereas for SC240 it starts only at pH < 8. This fact together with the observation that the pH of the mixed polyelectrolyte solutions always changes considerably during mixing implies that, upon forming the complex, protons are taken up or expelled because ion pairs are formed. These ion pairs are probably stabilized by an additional nonelectrostatic interaction between the two homopolyelectrolytes. Most likely, collective interactions between oppositely charged polyelectrolyte molecules with pH-dependent (flexible) chain charge may induce additional charged groups compared with the normally regulated charge of a single polyelectrolyte. A similar effect is well-known during the formation of surface complexes between, e.g., positively charged polybase and a negative silica surface.[32] This effect does not contribute to the value of the uncompensated polymer charge and the electrophoretic mobility but strengthens the attraction between the two oppositely charged molecules. It leads to complex formation at pH > 10 and pH < 4 where one of the polymers is entirely uncharged, and the electrostatic attraction between the homopolymers would be expected to be too weak to induce aggregation. The size of the stable homopolymer complexes at pH below 4.5 and above pH 9 is smaller than that of the copolymers (Figures 4 and 5) even though the length of the homopolymer molecules is larger.

Conclusions

Ampholytic diblock copolymers with oppositely charged blocks form aggregates in aqueous solutions. The aggregation behavior depends on solution pH and on the length ratio between the two blocks, indicating that the association is mainly due to the electrostatic attraction between the oppositely charged blocks. In the region of pH around the isoelectric point the total charge of copolymer molecules is nearly neutralized, and unlimited aggregation or phase separation occurs. The position of this region depends on the segment ratio of both blocks. As the uncompensated charge of the copolymer molecules increases stable, charged aggregates appear in solution. The size of these aggregates increases with concentration of the copolymer in solution but is almost independent of pH.

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