Solution Properties of Polymers Containing Zwitterionic Moieties in Side Chains

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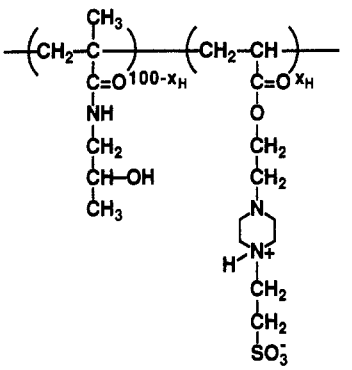
ABSTRACT: The solubility and association of *N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymers containing *N*-(2-hydroxyethyl)piperazine-*N'*-ethanesulfonic acid (HEPES) side chains in aqueous solvents were investigated using light scattering methods. The weight-average molar masses, diffusion coefficients, and hydrodynamic sizes of the copolymer molecules and their aggregates were studied as a function of HEPES content, solvent pH, and copolymer concentration. The copolymers with a high content of HEPES-containing side chains (60–100 mol %) associated in aqueous buffers, forming multichain aggregates (clusters). The formation of these aggregates was strongly dependent on solvent pH. Well-defined aggregates were observed at pH values between 6 and 7 (the hydrodynamic radius, R_h, was about 115 nm), and a broad distribution of large aggregates ($R_h \approx 250$ nm) was found at pH 8 and 10. These aggregates disappeared completely at pH 3. The observed effect of solvent pH on the solution properties of copolymers was explained qualitatively by the well-known electrolyte behavior of HEPES molecules. The aggregation found at solvent pH between 6 and 7 was related to the zwitterionic structure of HEPES-containing side chains which is formed in the vicinity of the half-neutralization point of the copolymers (pH ~6.5). The attractive electrostatic forces among ion pairs (dipoles) of zwitterionic HEPES moieties appeared to be responsible for both the intermolecular and intramolecular association.

Introduction

In recent years zwitterionic surfactants (zwitterionic molecules with hydrophobic alkyl chains) have been investigated with increased attention due to their good solubility in water and low sensitivity to changes in salt concentration and temperature.[1–6] Although electrically neutral in the vicinity of their isoelectric point, they differ from poly(oxyethylene alkyl ether) nonionic surfactants, especially in their thermal behavior.[2] Interactions between head groups are mainly due to electric dipole–dipole repulsions between zwitterionic groups, which set the optimal curvature of a surfactant film at an interface, and the bulkiness of the head groups.[3] For example, zwitterionic surfactants efficiently solubilize latex particles against flocculation with electrolytes.[4] Contrary to low molecular mass surfactants the properties of macromolecules with zwitterionic groups have not, to the best of our knowledge, been systematically studied.

Recently, we have obtained preliminary results on aqueous solutions of *N*-(2-hydroxypropyl)methacrylamide (HPMA) copolymers containing both *p*-nitroaniline, attached to the backbone via oligopeptide side chains, and *N*-(2-hydroxyethyl)piperarazine-*N'*-ethanesulfonic acid (HEPES) side chains.[7] Associative behavior among zwitterionic HEPES-containing macromolecules occurred as a result of attractive electric dipole–dipole interactions. Since the zwitterionic macromolecules represent a new class of polymers possessing attractive electrostatic dipole–dipole interactions, we have started a systematic investigation of their properties. In order to obtain more information about the structure and behavior of water-soluble zwitterionic copolymers, light scattering experiments on dilute solutions of copolymers of HPMA and the acryloyl ester of the HEPES sodium salt (HPMA–AHEPES copolymers) were performed in buffers with different pH values. The aim of the research was to evaluate the role of attractive long-range electric dipole interactions on solution properties of the zwitterionic copolymers.

Chart 1. Chemical Structure of HPMA–AHEPES Copolymers[a]



[a] x_H is the content of AHEPES comonomers.

Experimental Section

Synthesis of Monomers and Copolymers. Monomers *N*-(2-hydroxypropyl)methacrylamide (HPMA)[8] and the acryloyl ester of sodium *N*-(2-hydroxyethyl)piperazine-*N'*-ethanesulfonate (AHEPES)[7] were prepared according to previously described procedures. Copolymers of HPMA and AHEPES were prepared by free radical precipitation copolymerization in acetone containing a small amount of DMSO (to dissolve the monomer mixture) at 50 °C for 24 h using 2,2'-azobis(isobutyronitrile) as the initiator. The ratio of monomers to initiator to solvent in the feed was 12.5:0.6:86.9 (wt %). The stoichiometry of monomers in the feed was manipulated to prepare a variety of HPMA–AHEPES copolymers containing different amounts of HEPES side chains (Chart 1, Table 1). The copolymers were purified by dialysis against water for two days and lyophilized. The weight-average molecular masses, M_w, of these copolymers were estimated by size exclusion chromatography (FPLC) on a Superose 6 column, calibrated with poly(HPMA) fractions (30–300 kDa), using Tris buffer (0.05 M 2-amino-2-(hydroxymethyl)-1,3-pro-

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Table 1. Characterization of HPMA-AHEPES Copolymers

copolymer	[HPMA], mol %	[AHEPES], mol %	M_w, g mol^{-1}
1	95.9	4.1	67 000
2	90.6	9.4	43 000
3	80.6	19.4	35 000
4	61.5	38.5	28 000
5	42.0	58.0	22 000
6	22.5	77.5	17 000
7	00.0	100	16 000

panediol + 0.5 M NaCl, pH = 8.0) as eluent. The molar content of AHEPES comonomer, x_H, was determined by sulfur analysis.

Buffers. Sodium phosphate/citric acid buffers (pH 3–8) were adjusted for ionic strength i = 0.5 or 1.0 by addition of the appropriate amount of potassium chloride. For pH 10 and 11, 0.05 M sodium carbonate/borax buffers were used.

Static Light Scattering (SLS). Integral light scattering measurements were performed with a light scattering goniometer, equipped with a He–Ne laser (vertically polarized, wavelength λ_0 = 633 nm) in the angular range of θ = 30–150° at 25 °C. The processed data were represented as

$$Kc/\Delta R(0) = 1/M_w + 2A_2c \quad (1)$$

where

$$K = 4\pi^2(dn/dc)^2 n_0^2/N_A\lambda_0^4 \quad (2)$$

c is the polymer concentration (g cm^{-3}), $\Delta R(0)$ is the excess Rayleigh ratio, which is proportional to the intensity of light scattered from the copolymer solution when extrapolated to a zero angle of measurement, A_2 is the second virial coefficient, M_w is the true weight-average molecular mass, λ_0 is the wavelength of used light, and n_0 is the refractive index of the solvent. The refractive index increment for solutions of the AHEPES homopolymer (x_H = 100 mol %) in the sodium phosphate/citric acid buffer (pH 6, i = 0.5), $(dn/dc)_\mu$ = 0.120 mL g^{-1}, was measured using a Brice Phonics differential refractometer following equilibration dialysis of copolymer solutions against buffer, as described in ref 9.

Dynamic Light Scattering (DLS). The measurements were made using the dynamic light scattering apparatus previously described.[10] The light source was a 40-mW He–Ne laser, and the light scattering data were analyzed with an ALV-5000 multibit, multisampling time autocorrelator covering approximately 8 decades in delay time t. The samples were thermostated at 25 °C in a refractive index matching liquid.

The multisampling time autocorrelation functions were analyzed by inverse Laplace transform using the REPES[11] method of constrained regularization which is similar in many respects to the inversion routine CONTIN[12] to obtain a distribution $\tau A(\tau)$ of decay time τ. However, REPES directly minimizes the sum of the squared differences between the experimental and calculated intensity time correlation functions using nonlinear programming. This method uses an equidistant logarithmic grid with fixed components (here a grid of 10 components per decade) and determines their amplitudes. From the characteristic decay times τ_i (peak positions of $\tau A(\tau)$) the apparent diffusion coefficients, D_i, were obtained from the equation

$$D_i = 1/\tau_i\,\mathbf{q}^2 \quad (3)$$

where $\mathbf{q}$ is the scattering vector ($\mathbf{q} = 4\pi n_0 \sin(\theta/2)/\lambda_0$). The hydrodynamic radius, R_h, was calculated from the Stokes–Einstein relationship

$$R_{hi} = kT/6\pi\eta D_{0i} \quad (4)$$

where k is Boltzmann's constant, T is the absolute temperature, η is the solvent viscosity, and D_{0i} is the zero angle and concentration limit of D_i.

Results and Discussion

Electrolyte Properties of HPMA–AHEPES Copolymers. The shape of titration curves for the AHEPES homopolymer and HPMA–AHEPES copolymers (not shown) is typical for buffers and can be related to ionization properties of HEPES moieties. From the pH at the half-neutralization point the apparent pK_a = 7.1 was obtained for the AHEPES homopolymer and pK_a = 6.5 for the AHEPES monomer.[13] The pK_a values for HPMA–AHEPES copolymers have been found to be between 6 and 7. Thus, a zwitterionic structure (Chart 1) is formed at the isoelectric point of HEPES moieties[13] in the vicinity of the solution pH ~6.5 for copolymers under study. Positively charged HEPES molecules predominate in aqueous solutions at limiting conditions of pH ≤ 3. An opposite situation takes place on increasing the pH above pH ~6.5. Almost exclusively negatively charged HEPES-containing side chains exist at pH ≥ 10. The electrolyte properties of HEPES-containing side chains are very important for solution behavior of HPMA-AHEPES copolymers as will be demonstrated in the next section. Thus, the transition from regular polyelectrolyte behavior at high (≥10) or low pH (≤3) values to solutions of zwitterionic polymers characterized by attractive electric dipole–dipole interactions in the vicinity of the half-neutralization point of the solutions can be achieved by a variation of solvent pH.

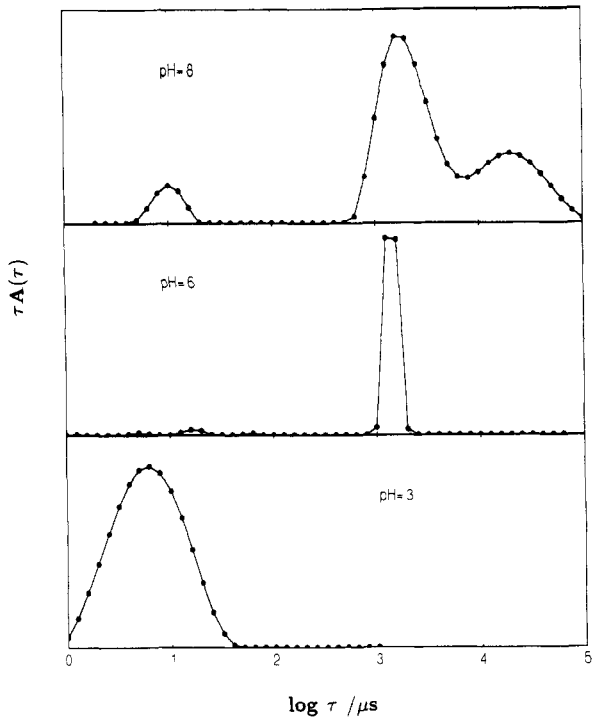

Figure 1. Distribution function of decay times, $\tau A(\tau)$, of the AHEPES homopolymer with x_H = 100 mol % in solvents with different pH values as indicated (c = 0.01 g mL^{-1}, i = 0.5).

Solution Properties. According to our expectations, the solution properties of zwitterionic HPMA–AHEPES copolymers are complex and strongly dependent on solvent pH. This is demonstrated in Figure 1, where the decay time distribution functions $\tau A(\tau)$, obtained by the inverse Laplace transformation of multisampling time correlation functions, are plotted for solutions of the AHEPES homopolymer (x_H = 100 mol %) in three different buffers with pH 3, 6, and 8. The decay time distribution functions can be generally reduced to two main distinct bands centered at the fast decay time, τ_f, and the slow decay time, τ_s. The dynamic processes (fast and slow) characterized by τ_f and τ_s both have a diffusive character (reciprocal values of τ_f and τ_s are $\mathbf{q}^2$-dependent). Hence, it was possible to introduce two diffusion coefficients, D_f (fast process) and D_s (slow process). The existence of two

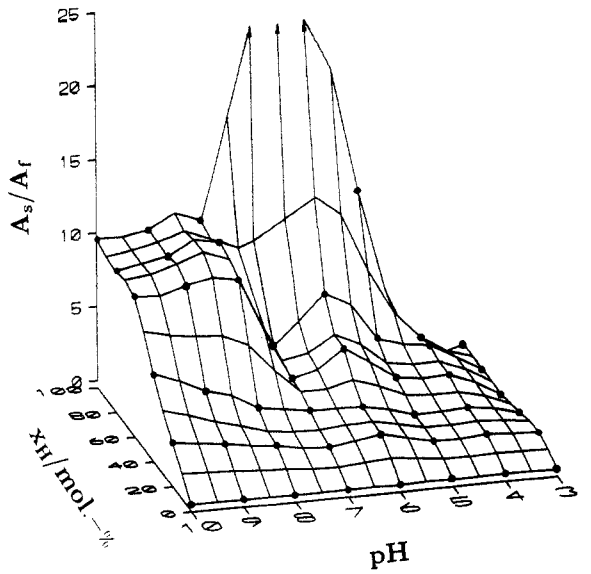

Figure 2. Ratios of scattering amplitudes, A_s/A_f, as a function of pH and content of HEPES-containing side chains, x_H (c = 0.01 g mL^{-1}, i = 0.5).

Table 2. Hydrodynamic Radius R_{hs} (nm) as a Function of the Solvent pH and AHEPES Content x_H (mol %)

	R_{hs}, nm				
pH	x_H = 19.4 mol %	x_H = 38.5 mol %	x_H = 58.0 mol %	x_H = 77.5 mol %	x_H = 100 mol %
10	104	98	122	104	100
8	95	106	256	202	245
7	121	102	105	105	104
6	112	98	92	113	115
5	87	77	96	123	124
4	83	78	97	102	
3	81	87			

diffusion coefficients in dilute solutions generally points to the existence of at least two types of scatterers with different hydrodynamic radii in the system. Only the fast mode is observed at pH 3 (Figure 1), evidently corresponding to polymer coil diffusion. The fairly broad distribution of this mode reflects the polydispersity of a copolymer sample prepared by free radical precipitation copolymerization. In order to support this interpretation, the static light measurements of M_w were made on the same copolymer solutions. A value $M_w = 1.3 \times 10^4$ g mol^{-1} was found which is in reasonable agreement with FPLC data (cf. Table 1) for the AHEPES homopolymer (x_H = 100 mol %). Since the decay time values of τ_f were of the same order of magnitude for all measured samples, they can be related to a diffusion of molecularly dissolved copolymer coils. Well-defined slow modes with a narrow size distribution have been observed at solvent pH values between 6 and 7. The scatterers responsible for the slow diffusion mode have a hydrodynamic radius R_{hs} = 115 nm, and are probably formed by the association of zwitterionic macromolecules. The fast polymer mode was practically undetectable in these solutions. Both the fast and slow (broad) modes were simultaneously observed at high solvent pH values (pH 8 and 10). In this case, the total amount of the AHEPES homopolymer molecules detected in aggregates is several times lower than found in solvents with pH 6–7.

More detailed data on the behavior of HPMA–AHEPES copolymer samples with x_H = 0–100 mol % in solvents with pH 3–10 are shown in the three-dimensional plot in Figure 2 and are listed in Tables 2 and 3. The ratio of scattering amplitudes A_s/A_f, where A_s and A_f are the relative scattering amplitudes for slow and fast diffusive

Table 3. Hydrodynamic Radius R_{hf} (nm) as a Function of the Solvent pH and AHEPES Content x_H (mol %)

	R_{hf}, nm				
pH	x_H = 19.4 mol %	x_H = 38.5 mol %	x_H = 58.0 mol %	x_H = 77.5 mol %	x_H = 100 mol %
10	2.8	2.1	1.3	1.0	0.93
8	3.5	2.6	1.5	1.3	0.91
7	3.5	2.8	1.8	1.4	0.98
6	3.1	2.9	2.2	1.6	
5	3.6	2.8	2.0	1.5	
4	3.6	2.8	2.0	1.5	1.0
3	3.6	2.8	1.7	1.3	0.71

processes, respectively, can serve as a measure of aggregation (association) capability of the HPMA–AHEPES copolymers in respective solvents. The ratio A_s/A_f is strongly pH-dependent with a maximum at solvent pH values between 6 and 7 and decreases with decreasing content of HEPES-containing side chains, x_H, vanishing for $x_H \leq 40$ mol %. Aggregation at higher values of solvent pH also disappear for $x_H \leq 40$ mol %. Since the aggregates were found to be unstable at low concentrations (see Figure 4), the hydrodynamic radii of aggregates, R_{hs}, were calculated from D_{0s} values (eq 4) for infinite dilution obtained by linear extrapolation of D_s values from only the higher concentration range to c = 0, and they are shown in Table 2. R_{hs} values are in the vicinity of 100 nm for all measured samples with an exception of copolymer samples with x_H = 60, 80, and 100 mol % at pH 8 (cf. Table 2) where larger aggregates with a broad size distribution were found (see Figure 1). In order to estimate the association number of aggregates, static light scattering measurements were performed on solutions at pH 6 for the AHEPES homopolymer (x_H = 100 mol %) where well-defined aggregates with a very low scattering contribution of copolymer molecules to the totally scattered light were found (see Figure 1). We have obtained the total molar mass $M_{wt} = 4.1 \times 10^6$ g mol^{-1} by extrapolation (eq 1) using only the higher concentration range, which gives the weight-average molar mass of both aggregates (M_{wa}) and molecularly dissolved copolymer (M_w) in respective solutions. Since we do not know the mass fraction of aggregates and homopolymer molecules in solution, the molar mass of aggregates, M_{wa}, cannot be determined accurately. However, it can only be stated that the aggregation (association) number is higher than the experimental value of M_{wt}/M_w = 320.

As for the hydrodynamic radius of copolymer chains, R_{hf}, the only dependence was on x_H, which was observed within experimental error (see Table 3). This dependence partially reflects a difference in the molar mass of zwitterionic HPMA–AHEPES copolymers. In order to evaluate the molar mass dependence of R_{hf}, the log–log plot of R_{hf} versus M_w of HPMA–AHEPES copolymers at pH 7 is shown in Figure 3. The solid line with the slope of 0.5 represents the molar mass dependence of R_{hf} for copolymers under Θ conditions. Systematical deviations of experimental R_{hf} values from the Θ-like M_w dependence to smaller R_h values at higher values of x_H reveal a collapse of the copolymer chains due to increasing attractive electric dipole–dipole interactions.

The above experimental observations give rise to a question as to why aggregation occurs in HPMA–AHEPES copolymer solutions, particularly at solvent pH values between 6 and 7. To answer this question, the effect of the copolymer concentration, c, and the ionic strength of the solvent, i, on aggregate formation was studied. The concentration dependence of D_s for AHEPES homopolymer (x_H = 100 mol %) at solvent pH 6 is shown in Figure

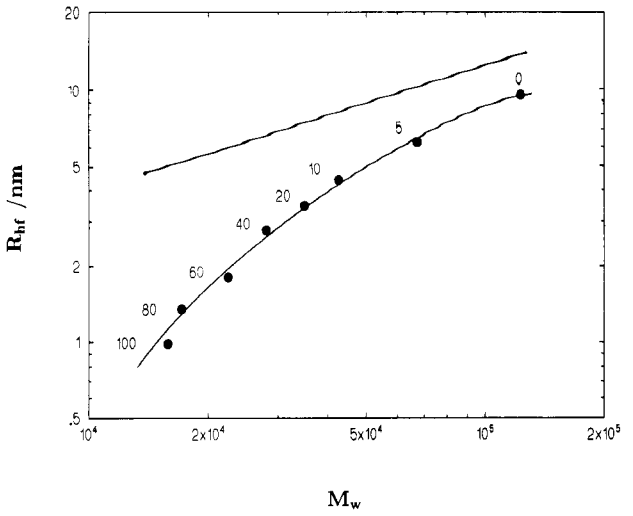

Figure 3. Molecular mass dependence of the hydrodynamic radius R_{hf} of copolymer chains at pH 7. The corresponding x_H values are indicated above the experimental points. The solid line with the slope of 0.5 represents the molar mass dependence of R_{hf} for copolymers under Θ conditions.

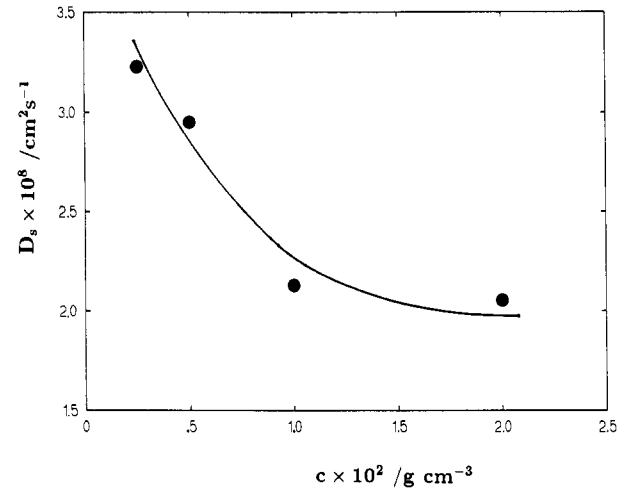

Figure 4. Concentration dependence of D_s for AHEPES homopolymer (x_H = 100 mol %, pH 6).

4. D_s seems to be practically independent of c at higher concentrations ($c \geq 0.01$ g mL^{-1}), and increases with decreasing concentration at lower concentrations. The fact that the aggregates can be disrupted by dilution is especially interesting. The continuous decrease in effective size (increase of D_s) below concentrations of 0.01 g mL^{-1} shows the dynamic nature of the aggregation process, which is probably controlled by open association. Thus, an increase of D_s at low concentrations is due to a decomposition of the aggregates when approaching the critical aggregate concentration.

The effect of the ionic strength on the aggregation of AHEPES homopolymer is demonstrated in Figure 5, where the decay time distribution functions are shown at pH 6 and i = 0.5 and 1. The A_s/A_f ratio decreases with increasing values of i. In other words, the aggregation process can be effectively screened by co-ions presented in the solution. Therefore, interactions responsible for the aggregation should be of an electrostatic nature, and result from charges dislocated on polymer chains; most likely the electric dipole–dipole attractive interactions between different zwitterionic groups are indicated (HEPES-containing side chains). Moreover, the width of the slow peak increases with increasing values of i (cf. Figure 5), reflecting a broadening of the aggregate size distribution. This broadening is probably due to a destabilization of aggregates as a consequence of screening of the electric dipole attractive interactions.

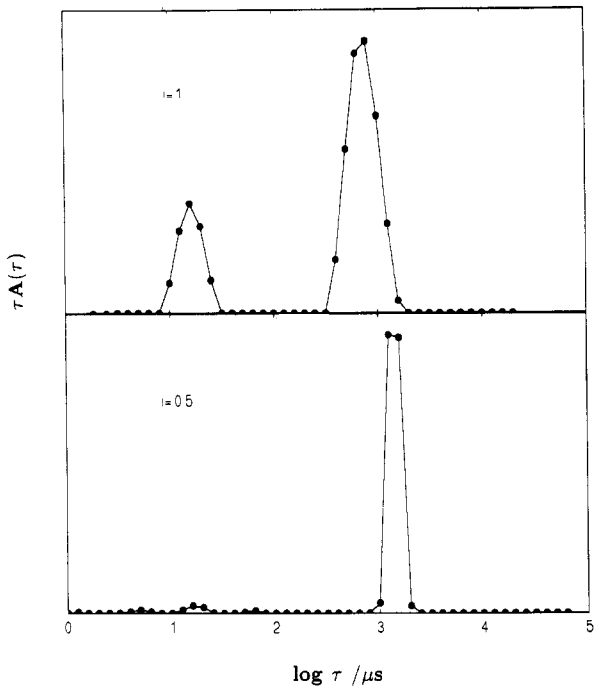

Figure 5. Distribution function of decay times, $\tau A(\tau)$, of the copolymer with x_H = 100 mol % at pH 6 and different ionic strengths i as indicated in the left-hand portion of the figures.

The main experimental results can be briefly summarized as follows: The fast and slow diffusive modes corresponding to diffusion of copolymer chains and aggregates, respectively, were observed. Well-defined aggregates were found in the vicinity of the isoelectric point of HEPES groups, where both positive and negative charges are equally substituted on HEPES-containing side chains (zwitterionic structure) of HPMA–AHEPES copolymers, for $x_H \geq 60$ mol %. The aggregation process has a dynamic character. A collapse of molecularly dissolved chains was observed simultaneously with aggregation. The same attractive electric interactions are responsible for both the collapse of copolymer chains and their aggregation. A weak aggregation was also detected at solvent pH values of 8 and 10 for $x_H \geq 60$ mol %.

The aggregation of zwitterionic polymers in aqueous solvents is a process analogous to cluster formation observed in ionomer solutions in low-polarity solvents. The ionomers are polymers containing a relatively low fraction of ionic groups (≤10 mol %). These polymers have been studied intensively for a long time[14–19] because of their technologically useful properties. In low-polarity solvents practically all the counterions are undissociated and form ion pairs (dipoles) with ions of the polymer chains (free counterions are absent). Among ion pairs attractive forces are operative as a result of electric dipole–dipole interactions. As for the presence of dipoles in polymer solutions an analogical situation exists in solutions of zwitterionic polymers where electric dipoles are borne by zwitterionic molecules, particularly in the vicinity of solvent pH ~6.5. However, an important difference between these two polymeric systems exists. Thus, contrary to the ionomer solutions the electric dipole–dipole interactions in aqueous solutions of zwitterionic polymers are more effectively screened by the high polarity of the solvent, co-ions, and counterions in the solution. A number of models for the morphology of random ionomers have been proposed,[16,20–23] none of which are completely consistent with all of the experimental observations. It is

now generally accepted that the ion pairs are associating to form so-called multiplets.[20] The dipole association is mainly intramolecular at low concentration,[24] and as the concentration increases intramolecular associations are gradually re-formed intermolecularly, resulting in aggregation and eventually gelation.[18,19,25] The extent of aggregation has been shown to be controlled by equilibrium between single contracted chains and multichain aggregates (clusters), and can be modeled by the "open association" model.[26] The contraction of molecularly dissolved chains is thought to be due to intramolecular ion pair association.

Since the solution properties of studied HPMA–AHEPES copolymers ($x_H \geq 60$ mol %) at solvent pH ~6.5 and ionomers in low-polarity solvents are very similar in many aspects, it is plausible to propose the same mechanism of aggregation in both the cases, suggesting multiplet formation even in solutions of zwitterionic polymers. The screening of electric dipole–dipole interactions in solutions of zwitterionic polymers is probably the reason why the association equilibrium is shifted toward a higher molar concentration of ion pairs ($x_H \geq 60$ mol %) in comparison with ionomer solutions (≤10 mol % ionic groups).

The large aggregates observed in DLS experiments at high solvent pH values were probably clusters resulting from the association tendency of AHEPES monomer units. The HEPES moieties at high solvent pH have only negatively charged SO_3^- head groups, and the rest of the side chain is hydrophobic. A consequence of this is an amphiphilicity of AHEPES monomer units at high pH values, which could be responsible for the observed aggregation.

The solution behavior of HPMA–AHEPES copolymers at low pH (~3) should be purely polyelectrolytic. The absence of the slow mode frequently observed in polyelectrolyte solutions in the so-called "extraordinary regime" at low salt concentrations[27–31] is probably due to the high ionic strength of buffers used ($i \geq 0.5$).

Conclusions

It has been found that in dilute solutions of HPMA–AHEPES copolymers with a high content of HEPES side chains (x_H = 60–100 mol %) the fast and slow diffusive modes corresponding to diffusion of single copolymer chains and their multichain aggregates, respectively, are generally observable. Well-defined aggregates were observed in the vicinity of the isoelectric point of HEPES groups in side chains of copolymers, where both the positive and negative charges are equally substituted on HEPES moieties, which form a zwitterionic structure. A collapse of molecularly dissolved chains was observed simultaneously with aggregation. The aggregation process has a dynamic nature characterized by an equilibrium between single contracted chains and multichain aggregates. The intermolecular and intramolecular aggregation, in analogy with the behavior of ionomers in low-polarity solvents, may be due to attractive electric dipole–dipole interactions among different zwitterionic HEPES moieties (ion pairs, dipoles) in side chains of HPMA–AHEPES copolymers.

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