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Effect of Ionic Strength on the Rheological Properties of Multisticker Associative Polyelectrolytes

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ABSTRACT: The rheology of hydrophobically modified polyelectrolytes containing small hydrophobic blocks randomly distributed along the hydrophilic backbone has been investigated in aqueous salt solutions by means of steady-flow, creep, and oscillatory experiments. The polymers contain acrylamide (≈86 mol %), sodium 2-acrylamido-2-methyl-1-propanesulfonate (≈12 mol %), and *N,N*-dihexylacrylamide units (≈2 mol %). The rheological behavior in the presence of electrolyte for two polymers with two different hydrophobic block lengths ($N_H = 3$ or 7 monomer units per block) was compared to that obtained for salt-free systems. At a fixed salt concentration, the critical concentration at the onset of viscosity enhancement does not depend on the length of the hydrophobic segments in the polymers and is located in the vicinity of the critical overlap concentration of the corresponding hydrophobe-free polymer. This is in strong contrast to the behavior observed for the same polymers in pure water, for which the onset of viscosity enhancement shifts toward lower concentrations as the hydrophobic block length is increased. Below the critical entanglement concentration, the presence of salt influences the dynamics of the polymers, resulting in significant reductions of the zero-shear viscosity and the plateau modulus, the terminal relaxation time being less affected by the addition of electrolyte. In contrast, in the entangled regime, the rheological behavior in salt solutions is not very different from that in the salt-free systems. The properties of these associative polyelectrolytes have been analyzed in the framework of the available theories, that is, either the sticky Rouse model or the sticky reptation model, depending on the concentration range.

Introduction

Associative water-soluble polyelectrolytes contain a few hydrophobic groups incorporated into a charged hydrophilic backbone.[1−18] In aqueous solution, these polymers form intermolecular associations because of hydrophobic interactions, which results in unique rheological properties such as strong viscosity enhancement or gelation,[3−5,10−12,17,19−21] time-dependent effects,[5,22] and marked elasticity.[8,11,13,23] The great variety of the observed effects offers the possibility of tuning and controlling the flow properties of fluids, which has a great importance in various areas such as the petrochemical, cosmetics, and paint industries.[24−30]

The thickening ability of associative polymers can be controlled by changing their molecular weight,[31] the chemical structure of the hydrophilic units,[3,6,7,20,32] the nature and content of the hydrophobic groups,[13,14,33−36] and/or their distribution along the hydrophilic backbone.[22,34,37−40] Acrylamide polymers with a multiblock structure, that is, with small hydrophobic blocks randomly distributed along the main chain, have been widely investigated over the past decade.[41] These polymers are synthesized by micellar free-radical polymerization.[1,41,42] The reaction is carried out in water, the solubility of the hydrophobic monomer being ensured by the addition of surfactant. Under these conditions, the hydrophobic monomers are preferentially located inside the micelles formed by the surfactant, whereas the hydrophilic monomers are solubilized in the continuous aqueous medium. The multiblock structure of the resulting polymers arises from the strong segregation of the monomers between these two microphases, and it is assumed that the length of the hydrophobic segments corresponds roughly to the average number of hydrophobic monomers per micelle (N_H).[34,38,40,41,43] It was shown that even a small increase in the length of the hydrophobic blocks results in a very pronounced viscosity enhancement.[39−41]

The incorporation of ionic units within the polymer backbone ensures a better water solubility, as well as a stronger thickening ability, as a result of coil expansion. The overall behavior of charged associative polymers is governed by the competition between two opposite effects: the attractive association of the hydrophobic groups and the repulsive electrostatic interaction between the charged units. Moreover, charge screening upon salt addition can also have two opposite effects. At the intramolecular level, the chain contraction tends to lower the viscosity. At the intermolecular level, the hydrophobic interactions are less hindered, which promotes enhanced polymolecular associations. As a consequence, depending on which of these effects prevails, a great variety of behaviors can occur.[3,4,6,7,38,44,45] By an adequate choice of the ionic and hydrophobic group contents, it is possible to obtain a synergistic enhancement of the thickening efficiency in a given polymer concentration range.[3,4] Conversely, in some cases, such as with highly charged polymers bearing numerous short hydrophobes, the thickening ability is rather limited because such hydrophobically modified polyelectrolytes exhibit mainly intramolecular associations.[15,35,38,45,46]

Recently, we reported the synthesis of polyelectrolytes of acrylamide (AM), sodium 2-acrylamido-2-methylpropanesulfonate (NaAMPS), and *N,N*-dihexylacrylamide (DiHexAM) using a micellar radical polymerization technique in the presence of a negatively charged surfactant (sodium dodecyl sulfate, SDS).[47] An *N,N*-disubstituted acrylamide derivative (DiHexAM)

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was used as the hydrophobic monomer because it minimizes or even suppresses the compositional drift that is observed when *N*-monosubstituted acrylamide derivatives are used.[34] The choice of a charged monomer bearing a sulfonate group (NaAMPS) was justified by the fact that its presence was found to increase the thermal and chemical stability of the polymers.[48−50]

The properties of these AM−NaAMPS−DiHexAM polymers were studied in pure water.[51] One of the most interesting features of the rheological behavior of these systems concerns the onset of the hydrophobically driven association, which is shifted to lower concentrations as the length of the hydrophobic sequences increases. This was in strong contrast to the behavior of neutral associative poly(acrylamides), for which the critical concentration at which the viscosity increases (C_η) does not depend on N_H or on the hydrophobe content in the polymer.[31] This difference was ascribed to the fact that the concentration range at which the polyelectrolyte chains overlap but are not yet entangled is much broader than for neutral polymers.[52]

The aim of the present study was to investigate the effect of salt on the rheological behavior of these multisticker polyelectrolyte solutions, to gain better insight into the mechanism and the nature of the interactions occurring in these systems.

Experimental Section

Materials. The source and purification of the monomers and other reagents have been previously reported.[47,51]

Polymerization Procedure. The polymers were obtained by micellar copolymerization[1,41] with SDS as described elsewhere.[34,39,47] The monomer concentration in the feed was kept at 2 wt %, and the concentration of the initiator [4,4′-azobis(4-cyanovaleric acid), ACVA] was set to 0.8 mol % with respect to the monomer feed. The molar ratio for AM, NaAMPS, and DiHexAM in the feed was 85.5/10/4.5. The reaction was carried out to 30−40% of conversion (reaction time of about 50 min) in order to obtain polymers with a reduced compositional heterogeneity, as previously shown.[47,51] The polymers were precipitated in acetone and repeatedly washed in an acetone/methanol mixture (9/1 v/v) to remove the surfactant, residual initiator, and monomers. The samples recovered by filtration were dried under reduced pressure at ambient temperature for 48 h. Then, the polymers were dissolved in a water/methanol mixture (1/1 v/v), and precipitation, washing, and drying steps were repeated twice. As previously described,[47,51] the calculation of the initial values of N_H was based on the amount of the surfactant used in the synthesis and on the values of the aggregation number (N_{agg}) and the critical micelle concentration (cmc) reported in the literature for SDS at the same ionic strength as in the reaction medium ($N_{agg} \approx 67$ and cmc = 2.8 mM).[47] The polymer code (N0, N3, or N7) refers to the N_H value (0, 3, or 7, respectively).

Polymer Characterization. The polymer composition was determined by ^{1}H NMR spectroscopy and elemental analysis, as described elsewhere.[34,47,51] The molecular weights of the samples were determined in methanol/water solutions (7/3 v/v) containing 0.1 M NaCl by static light scattering[47,51] with a multiangle photometer (Sofica) at 633 nm. The refractive index increment was measured at the same wavelength on a Brice−Phoenix differential refractometer. The d*n*/d*c* value for the unmodified polymer sample was equal to 0.161 mL/g. The polymer characteristics are reported in Table 1.

Rheological Measurements. The polymer solutions were prepared by dissolution of a known amount of the polymer in NaCl solution. After 48 h of stirring, the solutions were centrifuged for 45 min at 3500 rpm. This procedure allowed us to eliminate the air bubbles trapped in the viscous fluids. No phase separation was observed at this rotation speed. The range of concentrations of the polymer solutions was 0.01 wt % < *C* < 10 wt %.

Rheological measurements were carried out with a Haake RS100 controlled-stress rheometer equipped with a cone−plate geometry (angle = 1°, diameter = 20, 35, or 60 mm depending on sample viscosity). To prevent water evaporation, the measuring system was surrounded with a solvent trap, or for long-time measurements, a low-viscosity silicon oil was added to the edges of the cone. The temperature (25 °C) was controlled with a TC80 Peltier plate system (Haake). The flow curves were recorded in controlled-stress mode, by increasing the shear stress stepwise and waiting at each step until equilibrium was attained (usually 300−1000 s). Note that, during flow measurements, some gellike samples slip away from the measuring system above a certain stress.[51] Linear viscoelasticity and creep experiments were performed on samples that were viscous enough to provide a meaningful analysis. All measurements were made in the linear-response regime. For polymer samples that show a Maxwellian behavior in the low-frequency region of oscillatory spectra, the values of the terminal relaxation time (T_R), the plateau modulus (G_0), and the complex zero-shear viscosity (η_0*) were calculated from dynamic spectra as described elsewhere.[31,51] When the terminal behavior was not observed, creep experiments were performed to determine η_0, G_0, and T_R from the compliance versus time curves, $J_e(t)$, as described earlier.[47,51] Briefly, the values of η_0 and G_0 were obtained from the slope and the intercept of the linear part of the $J_e(t)$ curve (see Figure 5 below) according to the relationship $J_e(t) = 1/G_0 + t/\eta_0$, and T_R was calculated as $T_R = \eta_0/G_0$. As already reported for the same polymers in salt-free solutions,[51] it can be noted that the values of the zero-shear viscosity determined by steady-state, creep, and oscillatory experiments are in good agreement (see Figures 8, 10, and 11 below).

Additional viscometric measurements on dilute solutions were performed on a Contraves LS 30 low-shear rheometer equipped with a Couette 2T−2T measuring system (25 °C). The Newtonian viscosity was determined from the measurements at different shear rates ranging from 0.01 to 110 s^{-1}.

Table 1. Characteristics of the Polymers

		polymer composition (mol %)			
sample	N_H[a]	AM	NaAMPS[b]	DiHexAM[c]	M_w[d] × 10^{-6}
N0	0	87.3	12.7	0	2.1
N3	3	85.5	12.3	2.2	2.1
N7	7	86.1	11.7	2.2	2.0

[a] Number of hydrophobes per micelle ≈ hydrophobe block length. [b] Calculated from elemental analysis data. [c] Determined from ^{1}H NMR spectra. [d] Weight-average molecular weight determined by light scattering in a 0.1 M NaCl methanol/water (7/3 v/v) solution.

Results and Discussion

1. Properties of the Hydrophobe-Free Polyelectrolyte. Before describing the properties of the hydrophobically modified polymers, we discuss first those of the unmodified sample (N0). In Figure 1 is shown the zero-shear viscosity as a function of the polymer concentration for sample N0 in water and in 0.1 M NaCl solution. As discussed earlier,[51] three critical concentrations can be found for the hydrophobe-free polyelectrolyte in aqueous solution. However, the critical overlap concentration (*C**), which is very low for polyelectrolytes in pure water, is not observed here because it is below the range of concentrations investigated (*C** < 0.008 wt %). In a range of concentrations above *C**, the polymer chains can overlap without making effective entanglements. In this regime, the viscosity increases with polymer concentration according to a power law with an exponent of 0.65, slightly higher than the theoretically predicted value (0.5).[52] At the critical entanglement concentration ($C_e \approx$ 1−2 wt %), the chains can be entangled, and finally, above the critical concentration for electrostatic blob entanglements ($C_D \approx$ 3 wt %), the electrostatic interactions are screened, and the system behaves like a neutral polymer in the entangled regime. In this regime, the scaling theory[52] predicts a critical exponent close to 4, whereas a higher value (4.5) is experimentally found here, as also reported for other neutral systems.[53,54]

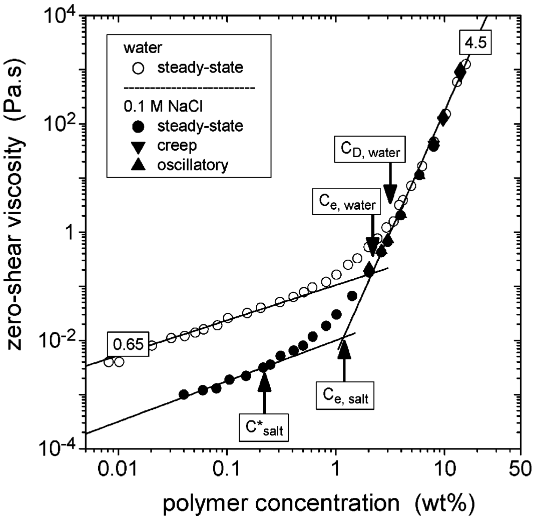

Figure 1. Zero-shear viscosity as a function of concentration for the N0 hydrophobe-free polyelectrolyte in water (open symbols, from ref 51) and in 0.1 M NaCl solution (solid symbols). The labels on the lines are the values of the experimental scaling exponents, and the arrows indicate the approximate crossover concentrations C^*, C_e, and C_D.

At low polymer concentrations ($C < 3$ wt %), the viscosity is reduced upon the addition of salt because of the screening of the charges and the shrinking of the macromolecular coils. However, the difference between the viscosity measured in water and that measured in 0.1 M NaCl becomes negligible as the concentration C_D, associated with the onset of the electrostatic blobs entanglements, is approached. Above this concentration, the viscosity increases with polymer concentration according to $\eta \propto C^{4.5}$ in both water and brine (see Figure 1). In this concentration range, the values of the plateau modulus and the terminal relaxation time are also quite similar in the two solvents (data not shown).

The behavior of polyelectrolytes in salt solution can be analyzed in the framework of the scaling approach, as described by Rubinstein et al.[52,55] When a monovalent salt at a molar concentration of C_s is added to a polymer solution at a concentration $C < C_D$, any property X (zero-shear viscosity, terminal relaxation time, plateau modulus, or diffusion coefficient) can be expressed in terms of the same property X_{water} in the salt-free solution as

$$X/X_{\text{water}} \sim \left(1 + \frac{2AC_s}{C_m}\right)^{\alpha} \tag{1}$$

where C_m is the concentration of monomer units and A is the number of monomer units between charges. At low salt concentrations ($C_s \ll C_m/2A$), one recovers the salt-free behavior. At high salt concentrations, the electrostatic interactions are screened, and the dynamics is analogous to that of neutral polymer solutions. At an intermediate range of salt concentrations, the values of the scaling exponents α depend on whether the polymer concentration is below or above the entanglement concentration (C_e). For the viscosity, the exponent of the scaling law is $\alpha = -0.75$ for $C < C_e$ and $\alpha = -2.25$ for $C_e < C < C_D$.

As shown in Figure 1, the viscosity data in the presence and in the absence of salt vary rather smoothly with polymer concentration, so that there is some uncertainty in the evaluation of the crossover concentrations. In the salt-free systems for which the unentangled regime appears to be well-defined, C_e is on the order of 1−2 wt %. This concentration is rather close to $C_D \approx 3$ wt %. Therefore, the entangled regime, $C_e \leq C \leq C_D$, is very limited, and it is not possible to compare the experimental behavior to the theoretical prediction (eq 1). Such a comparison can, however, be made for the unentangled systems that span a rather extended concentration range. Figure 2 shows the variation of η/η_{water} versus $(1 + 2AC_s/C_m)$ with $C_s = 0.1$ M and $A = 8$.

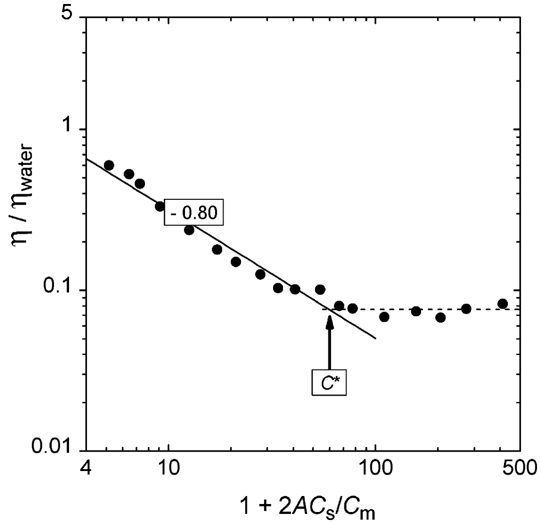

Figure 2. Relative zero-shear viscosity shown in the coordinates according to eq 1 for the N0 hydrophobe-free polyelectrolyte. The label on the line is the value of the experimental scaling exponent.

The data at high concentration (still below C_e) can be fitted by a straight line with a slope of −0.8, in good agreement with the theoretical prediction. At low polymer concentrations ($C <$ 0.1 wt %, i.e., for high values of $1 + 2AC_s/C_m$ in Figure 2), the theoretical predictions probably fail because the system is in the regime within which the coils do not overlap. Thus, the crossover at $C \approx 0.2$ wt % can be regarded as the critical overlap concentration C^*. This value is close to that calculated (0.13 wt %) from the reciprocal of the intrinsic viscosity measured in 0.1 M NaCl. We should also note that the concentration gap between C^* and C_e in salt solution is significantly reduced in comparison to that in pure water (Figure 1). This is mainly due to the fact that C^* in water is very low (<0.008 wt %), because of the chain expansion arising from the electrostatic repulsions between the monomer units.

Because the data for T_R and G_0 at low polymer concentrations were not experimentally available, it was not possible to determine the corresponding scaling exponents below C_e.

2. Rheological Behavior of the Hydrophobically Modified Polyelectrolytes. We present below the results concerning the effect of the ionic strength on the linear and nonlinear rheological behaviors of the investigated hydrophobically modified polymers.

2.1. Linear Viscoelasticity (Oscillatory and Creep Studies). Figure 3 shows the variations of the storage (G') and loss (G'') moduli as a function of the angular frequency (ω) for polymer N3 in water and in 0.1 M NaCl solution. At low frequencies, the behavior of the shear modulus is Maxwellian, as indicated by the variations of $G'(\omega)$ and $G''(\omega)$ that scale as ω^2 and ω, respectively. Above the frequencies at which the curves $G'(\omega)$ and $G''(\omega)$ cross each other, the shape of these curves deviates from Maxwellian behavior, thus indicating the presence of faster relaxation processes that superimpose on the main slow relaxation process. This behavior can be ascribed to the sample

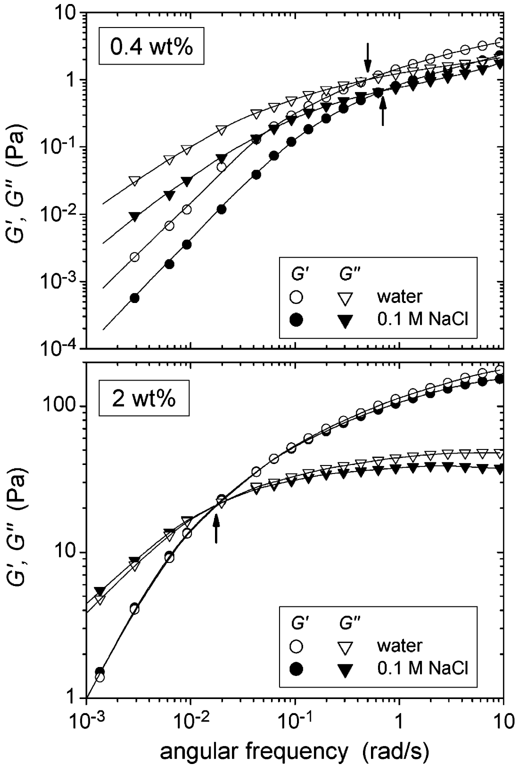

Figure 3. Relaxation spectra of sample N3 at two different concentrations in water and in 0.1 M NaCl solution (the arrows indicate the crossover frequencies).

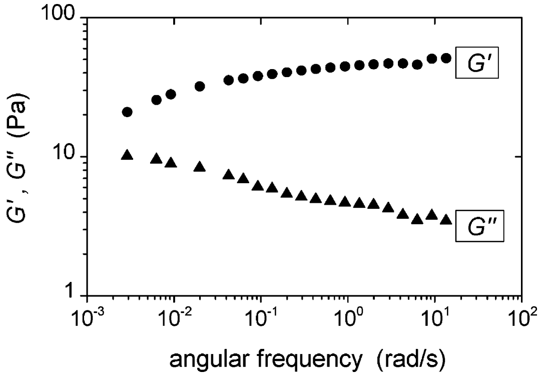

Figure 4. Relaxation spectra of sample N7 in 0.1 M NaCl solution (C = 0.8 wt %).

polydispersity and possible imperfections in the polymer microstructure, which should inevitably broaden the relaxation spectra.

At low polymer concentrations ($C = 0.4$ wt %), the values of both $G'(\omega)$ and $G''(\omega)$ are smaller in salt solution than in pure water. However, the crossover frequency is only slightly affected by the presence of electrolyte (Figure 3, upper panel). As the polymer concentration is increased, the shear moduli increase, and the crossover frequency shifts to lower values. In addition, the viscoelasticity curves almost coincide in both water and 0.1 M NaCl solution (Figure 3, lower panel).

The results obtained for polymer N7 in salt solution (Figure 4) indicate that the frequency dependence of the complex shear modulus corresponds to a gellike behavior, as already observed for the same sample in pure water.[51] In the whole frequency range studied, G' is higher than G'', both moduli being almost frequency-independent. The crossover frequency and the terminal behavior cannot be observed because of the limited range of the experimentally accessible frequencies.

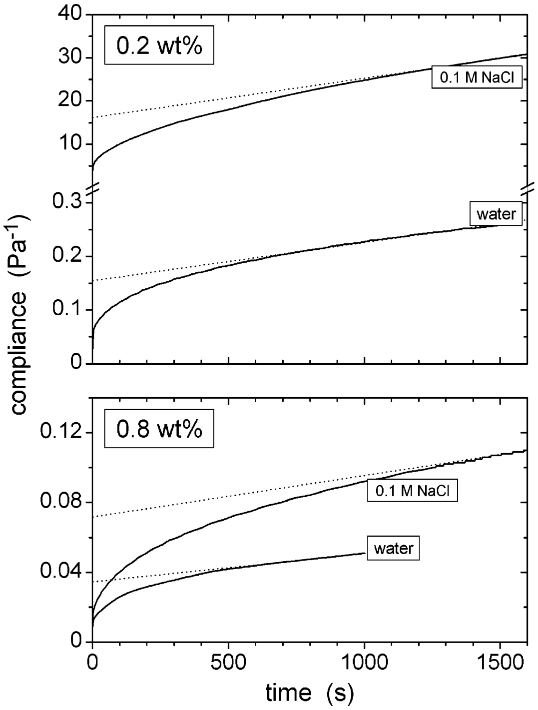

Figure 5. Compliance vs time curves for sample N7 at two different concentrations in water and in 0.1 M NaCl (the dotted lines are the extrapolations of the linear part of the curves).

An alternative way to determine the values of the longest relaxation time (T_R), the plateau modulus (G_0), and the zero-shear viscosity (η_0) is to perform creep experiments in the linear-response limits.[51] As shown in Figure 5, when a sudden stress is applied, a rapid change in the compliance is observed, followed by a smooth increase that becomes linear at longer times. The linear part of the compliance versus time curve provides a determination of the steady-shear viscosity (see Experimental Section). The results of the creep experiments are consistent with those already observed for the oscillatory experiments. When the polymer concentration is low (Figure 5, upper panel), the compliance values in salt solution are much higher than those in water, but the time scales of the initial nonlinear increase of the compliance are about the same in the two solvents. As the polymer concentration is increased, the creep behaviors tend to become similar in the two solvents (Figure 5, lower panel).

The above observations confirm the typical behavior of multisticker associative polymers prepared by micellar polymerization, characterized by a marked slowing of the relaxation process as N_H increases. Thus, the solutions of the polymer that bears long hydrophobic blocks ($N_H = 7$) exhibit extremely long relaxation times, on the order of thousands of seconds, whereas much shorter relaxation times (40−50 s) are observed for the sample with shorter hydrophobic blocks ($N_H = 3$).

From these oscillatory and creep experiments, it can be inferred that the changes in the viscosity values upon addition of salt result mainly from the variation of the plateau modulus, whereas the terminal relaxation time is much less affected. A similar behavior has been also reported for other highly charged associative polyelectrolytes.[56]

2.2. Non-Linear Rheology. Figure 6 presents an illustration of the steady-state flow response for sample N7 at several concentrations in 0.1 M NaCl aqueous solution. The characteristic behavior of associative polymers is observed, that is, the occurrence of a Newtonian plateau at low shear rates, followed by a sharp viscosity drop. As already reported for

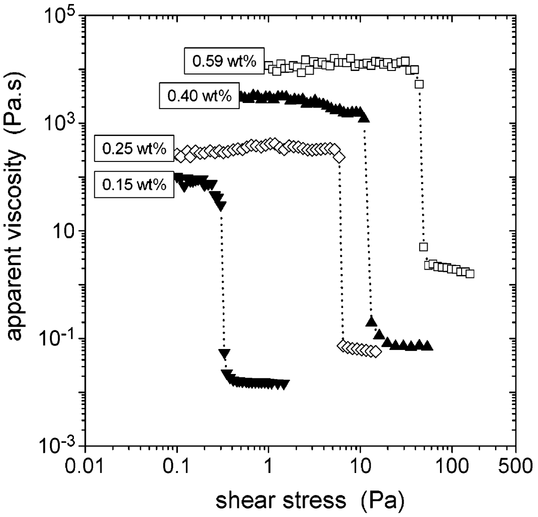

Figure 6. Flow curves for polymer N7 at various concentrations in 0.1 M NaCl solution.

the same sample in salt-free solution,[51] both the zero-shear viscosity (η_0) and the critical stress associated with the viscosity drop exhibit a large increase with the polymer concentration.

It has been proposed that the inverse of the shear rate just before the discontinuity in the flow curves can be identified with the average lifetime of the intermolecular junctions.[57] In the present case, although the critical shear stress increases with polymer concentration (Figure 6), the corresponding critical shear rate does not vary significantly within the experimental accuracy (around $7-10 \times 10^{-3}$ s^{-1}). Therefore, in the unentangled regime (0.15 wt % $< C <$ 1.2 wt %), the lifetime of the hydrophobic associations is nearly constant and can be estimated as $\approx$100−150 s, which is about 3 times smaller than in salt-free solution.[51] This means that the hydrophobic interactions are weakened upon salt addition. Such a finding is rather surprising given that previous studies on related neutral associative polyacrylamides[3,33,41,58] have shown that the thickening efficiency was enhanced in the presence of salt, as a consequence of a "salting-out" effect on the hydrophobic moieties. This suggests an effect of the electrostatic interactions on the lifetime of the hydrophobic junctions. The rigid conformation of the hydrophilic strands that link the hydrophobic junctions possibly affects the number of hydrophobic stickers in a cross-link, thus modifying its lifetime. Of course, this effect should tend to disappear at high polymer concentration, which is indeed experimentally observed.

It can be noted that the relaxation time of the N7 system is 1 order of magnitude longer than the lifetime of the hydrophobic associations. Such a result reflects the typical behavior of multisticker associating polymers. As already reported in previous experimental and theoretical studies,[12,31,51,57,59] this difference in time scales is explained by the fact that the dissociation of one sticker does not permit the relaxation of an entire chain that is still anchored by many other stickers.

A comparison of the flow curves in pure water and in 0.1 M NaCl solution is shown in Figure 7 for samples N0, N3, and N7. For sample N7 (Figure 7, upper panel), the addition of salt leads to two significant effects, more especially at low polymer concentrations. First, the Newtonian viscosity is lowered, although this difference tends to vanish as the polymer concentration is increased. Second, for a given polymer concentration, the discontinuity in the flow curves occurs at a lower critical stress. Once again, this difference vanishes as the polymer concentration increases ($C >$ 0.8 wt %). The above behavior can be explained by taking into account the effect of salt on the size of the macromolecular coil in solution. In the presence of electrolyte, the coil has a more compact conformation than it does in pure water because of the screening of the electrostatic repulsions between units of like charge. This can facilitate the formation of intramolecular hydrophobic associations at the expense of intermolecular junctions. As the intramolecular associations are elastically ineffective, the transient gel formed in the presence of salt is weaker than that in pure water, which will result in a decrease of both the Newtonian viscosity and the critical stress. It should be added that this situation is true only when the dynamics of the system is governed by the properties of individual polymer coils, that is, below C_e. However, above the critical entanglement concentration, when the chains are interpenetrated, the equilibrium is shifted toward the intermolecular associations. Additionally, at this stage, the dynamics starts to be influenced by the entanglements, and the difference between the behaviors in salt and water solutions vanishes.

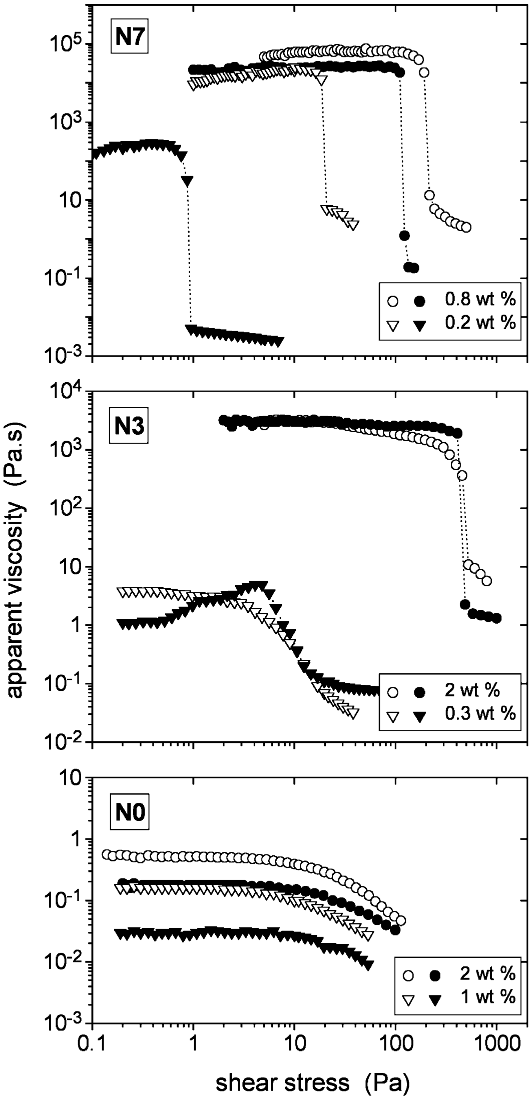

Figure 7. Flow curves at the same concentrations in water (open symbols) and in 0.1 M NaCl solution (solid symbols), for the two hydrophobically modified polyelectrolytes and the hydrophobe-free homologue.

The general behavior of sample N3 with shorter hydrophobic blocks (Figure 7, middle panel) is similar to that of sample N7, but with a significant decrease of the thickening ability, in

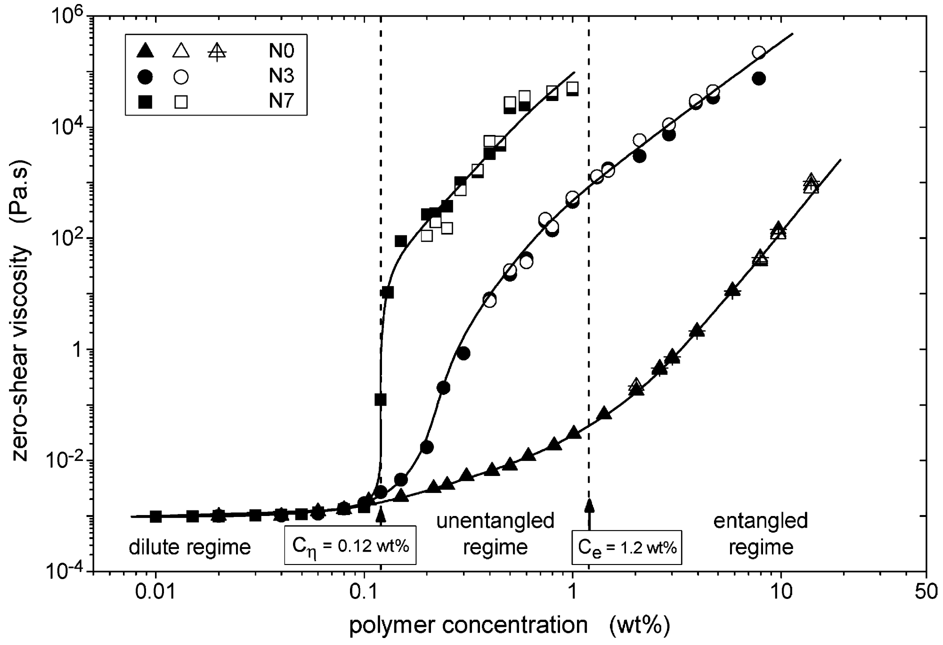

Figure 8. Zero-shear viscosity vs polymer concentration in 0.1 M NaCl aqueous solution for the two hydrophobically modified polyelectrolytes and the hydrophobe-free homologue. Data from steady-state (solid symbols), creep (open symbols), and oscillatory (cross-centered symbols) measurements.

agreement with the well-established influence of N_H on the associating process.[22,31,39−41] Nevertheless, the viscosity is still much higher than that of the hydrophobe-free sample (Figure 7, lower panel).

Another difference between the two associative samples is that the strong discontinuity in the flow curve appears only at high polymer concentrations for sample N3. At lower concentrations, the viscosity decrease at high shear rates is more gradual than for sample N7, and the onset of shear thinning is less defined. In addition, a pronounced shear-thickening effect occurs between the Newtonian plateau and the shear-thinning zone at low polymer concentration in salt solutions. This shear-thickening behavior that is not observed in salt-free aqueous solution will be more thoroughly discussed in a forthcoming publication.

3. Zero-Shear Viscosity Behavior of the Hydrophobically Modified Polyelectrolytes. We present below the effects of the polymer and salt concentrations on the zero-shear viscosity η_0, determined from steady-state, creep, and oscillatory experiments as described above, and we discuss the scaling behavior to dilution of the systems in both the unentangled and entangled regimes.

3.1. Polymer Concentration Regimes. The variations of the zero-shear viscosity as a function of the polymer concentration in 0.1 M NaCl are shown in Figure 8. The viscosity is on the order of that of brine at low polymer concentrations and rises very steeply for the two hydrophobically modified samples beyond a critical concentration C_η. The crossover between the two regimes is well-defined and much sharper for the associative samples than for the unmodified polymer. Within the experimental accuracy, C_η is independent of N_H and equal to 0.12 wt %, which is very close to the C^* value of the hydrophobe-free sample (see Figure 1). Above C_η, the viscosity increase is sharper for the polymer with the longest hydrophobic blocks, for which the viscosity increases by about 4 orders of magnitude as the concentration increases from 0.12 to 0.15 wt % (see Figure 8). In the same concentration range, the viscosity enhancement of polymer N3 is more modest. Upon a further increase of the N3 sample concentration to the critical entanglement concentration (C_e), one observes a second break in the log−log variation of viscosity. The above behavior has already been reported for neutral associating polymers.[31] The concentration range $C_\eta < C < C_e$ was ascribed to the unentangled semidilute regime. Note that the viscosity of polymer N7 in the high-concentration regime ($C > 1$ wt %) was too large to be determined accurately.

The behavior observed in the vicinity of C_η differs from that described for the same hydrophobically modified polyelectrolytes in salt-free solutions, for which C_η decreases as N_H increases.[51] Thus, the associative polyelectrolytes in salt solution behave similarly to their neutral analogues, for which it was observed that C_η is located in the vicinity of C^* of the corresponding unmodified polymer.[31] The value of C_η for polymer N7 in 0.1 M NaCl, (which can be identified here with the gel-point concentration, C_g) is significantly higher (0.12 wt %) than the value of the gel point previously found in pure water (0.05 wt %).[51] A different situation is observed for sample N3, for which the values of C_η are about the same in salt solution and in pure water (≈0.12 wt %). This surprising result indicates that a larger interpenetration of the electrostatically extended chains is required for the association of the shorter hydrophobic sequences in salt-free systems and confirms our previous observation of a coupling between the electrostatic interactions in the strands and the association mechanism (see section 2.2). This effect vanishes at high salt concentration, where the solutions behave as neutral systems.

3.2. Influence of the Salt Concentration. Figure 9 represents the variation of the zero-shear viscosity as a function of NaCl concentration for samples N7 and N0 at two different polymer concentrations (0.1 and 1 wt %). The results are expressed in terms of a reduced variable, that is, the ratio of the viscosity in the presence of salt (η_{NaCl}) to the viscosity in salt-free solution (η_{water}).

The behavior of the hydrophobe-free polymer is the same for the two polymer concentrations studied, as shown by the good superimposition of the η_{NaCl}/η_{water} curves in the whole salt concentration range. The viscosity decreases smoothly as the salt content increases, and finally, at the highest salt level, the

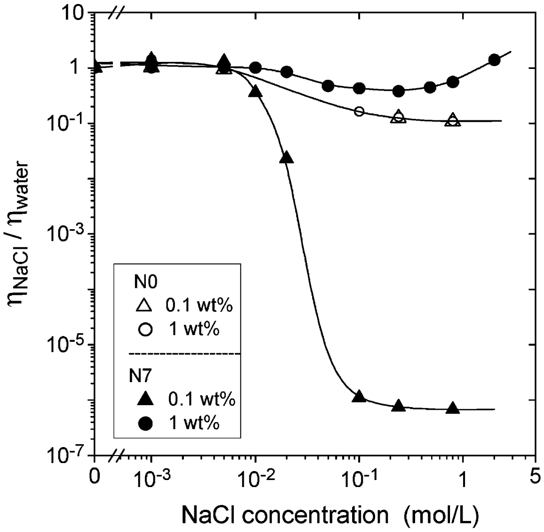

Figure 9. Relative variations of the viscosity with NaCl concentration for polymers N7 and N0 at two different concentrations.

viscosity is reduced to about 10% of its initial value in pure water.

In contrast, for sample N7 in salt solutions, the variation of the viscosity with respect to that in pure water depends significantly on the polymer concentration. For the more dilute solution (0.1 wt %), the viscosity, which is rather high in pure water (≈1700 Pa•s, i.e., about 5 orders of magnitude higher than for sample N0), decreases abruptly (by about 6 orders of magnitude) as the salt concentration increases above 0.01 M, and it finally becomes close to that of sample N0 (≈1.5 mPa•s) at high salt contents (>0.1 M). This observation supports the conclusion that, in the unentangled regime, the thickening properties result from the intermolecular associations between the hydrophobic segments of the overlapping chains. Once the chain dimensions are reduced by charge screening arising from the increase in salt concentration, the transient network structure breaks into a solution of small clusters and isolated macromolecules, and the viscosity is significantly lowered. Conversely, near the critical entanglement concentration (1 wt %), viscosity enhancement is observed in the whole salt concentration range studied. Note also that the viscosity of the sample is rather insensitive to the presence of electrolyte, contrary to what is observed for HASE polymers with a higher charge density than the polymers studied here.[60] The small decrease in viscosity observed for 0.02−0.1 M NaCl can be ascribed to a reduction of the chain dimensions, as was previously discussed. However, at this polymer concentration, the high degree of chain overlap and the entanglements prevent the network from disruption. Finally, above 0.2 M NaCl, the viscosity starts to increase, and simultaneously, a progressive clouding of the solution is observed. This could be ascribed to the previously discussed salting-out effect, that is, to a stronger hydrophobic character of the hydrophobic moieties in the presence of salt, as already found for related neutral associating polymers.[3,33,41,58] With a further increase of the salt content ($C_{\mathrm{NaCl}} > 2$ M), the solution phase separates into a turbid elastic gel and a low-viscosity liquid. Note that, for sample N3, with a lower hydrophobic character, neither clouding nor phase separation is observed, even at high salt concentration (3.5 M NaCl).

The results obtained at various salt contents confirm that the effect of the salt on the rheological behavior appears only at low polymer concentrations. In the unentangled regime, as the dynamics involves both inter- and intramolecular associations, an increase of the ionic strength leads to decreases of the zero-shear viscosity, the plateau modulus, and to a lesser extent, the terminal relaxation time. On the other hand, at higher polymer concentrations, as the dynamic properties are mainly governed by the chain entanglements and the mesh size of the transient network, the difference between pure water and salt solutions tends to become negligible.

3.3. Scaling Laws in Pure Water and in Salt Solution. In this section, we compare the rheological behavior of the polymers to the theoretical predictions in both unentangled and entangled semidilute regimes. Actually, sample N7 could only be studied in the semidilute unentangled regime ($C < 1$ wt %), the measurements in the entangled regime being difficult because of high sample viscosities. For polymer N3, the investigated range of concentrations could be broadened, and meaningful data were obtained in the entangled regime.

(a) Behavior of Polymer N7 in the Semidilute Unentangled Regime. The formation of a transient network for associative polymers in the unentangled regime was recently theoretically discussed in great detail.[61,62] The model assumes that each polymer chain contains a large number of stickers, spaced equidistantly along the chain, and that the stickers are separated by long hydrophilic fragments. The theoretical approach is based on a percolation in the vicinity of a gel point C_g that can be estimated to be close to C_η. The limitations of this approach are that only the pairwise association between stickers is allowed and that it was originally formulated only for neutral polymers. Nevertheless, we have recently shown that this theory can also be applied to hydrophobically associating AM−NaAMPS−DiHexAM polyelectrolytes.[51]

A comparison of the variations of the zero-shear viscosity versus the polymer concentration for sample N7 in water and in 0.1 M NaCl solution is shown in Figure 10a. One observes a large difference between aqueous and salt solutions at low polymer concentrations ($C < 0.5$ wt %). In both solvents, two regimes can be clearly identified above C_η. For the salt solution, the viscosity increases sharply within the 0.12−0.4 wt % concentration range, whereas this dependence levels off within the 0.4−1 wt % range. A similar behavior was observed in pure water, but with a crossover point at a lower value (≈0.15 wt % instead of ≈0.4 wt %). This is consistent with our previous observation that, in the unentangled regime, the viscosity in pure water is enhanced in comparison to that in salt solution because of an extensive chain overlap that favors the intermolecular hydrophobic junctions.

The log−log representation of the viscosity of polymer N7 as a function of the reduced concentration $(C - C_\eta)/C_\eta$ is shown in Figure 10b, with $C_\eta = 0.05$ wt % in pure water and $C_\eta = 0.12$ wt % in 0.1 M NaCl. In both solvents, the data can be fitted by two straight lines with a crossover at a critical reduced concentration of about 2 and 4 for water and 0.1 M NaCl respectively, corresponding to polymer concentrations of about 0.15 and 0.5 wt %. In the presence of salt, the exponents of the experimentally found scaling laws agree very well with the theoretically predicted values for the two regimes, below and above the crossover (3.55 and 1.15, respectively).[61,62] In contrast, in pure water, the scaling relation below the crossover differs from that predicted for neutral systems (≈2 instead of 3.55), as discussed in our recent paper.[51]According to the theory on associative polymers, the crossover can be identified as the transition from the classical gelation regime to the regime in which the strands between the stickers overlap and the fraction of the intermolecular associations remains almost constant. The shift in the value of the critical reduced concentration with increasing ionic strength can be related to the shrinking of the

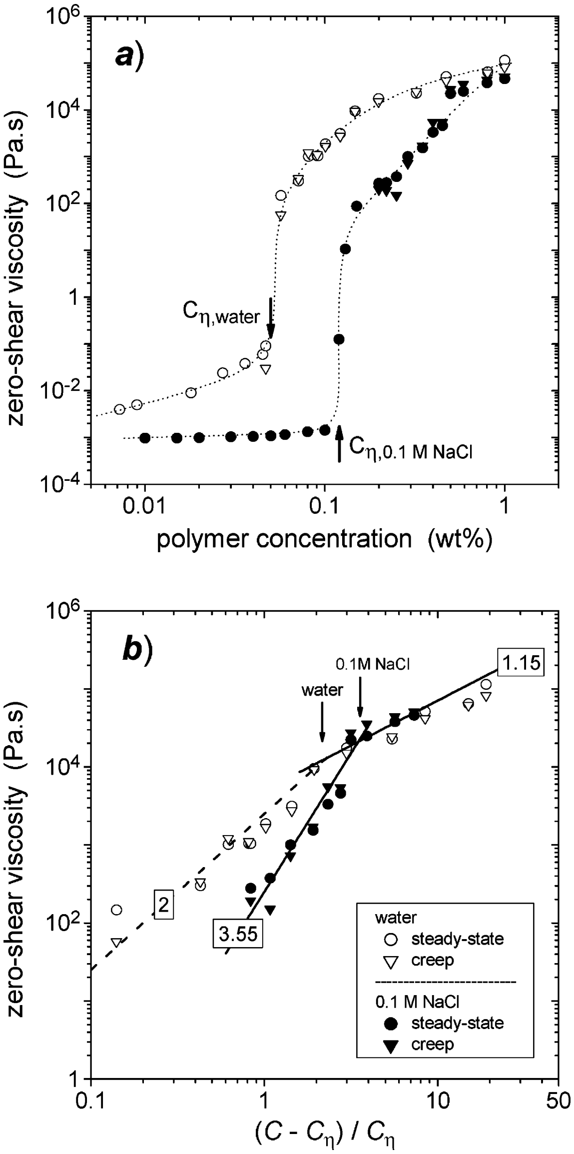

Figure 10. Dependence of the zero-shear viscosity of sample N7 on (a) polymer concentration and (b) relative distance from the gel point, in water (open symbols, from ref 51) and in 0.1 M NaCl solution (solid symbols). The labels on the lines are the values of the scaling exponents, and the arrows indicate the crossover concentrations.

polyelectrolyte chains. In the presence of salt, the strands between neighboring stickers are contracted, so they overlap at a polymer concentration higher than in salt-free solutions.

(b) Behavior of Polymer N3 in the Semidilute Entangled Regime. In the semidilute entangled regime, the dynamics of associative polymers can be described according to the sticky reptation model, in which the chain motion is controlled by the concentration and lifetime of the junction points.[59,63,64] In Figure 11 is shown the zero-shear viscosity of the polymer N3 solutions in water and in 0.1 M NaCl as a function of the polymer concentration.

Viscosity data for the two solvents are superimposed in the concentration range above ≈0.25 wt % (i.e., above C_e). As previously found for neutral associative polyacrylamides,[31,65] the scaling exponent describing the variation of the zero-shear viscosity versus polymer concentration is close to the value of 3.75 theoretically predicted for the entangled regime with unentangled strands between stickers.[63] When the density of entanglements is much larger than that of hydrophobic associations, the stickers simply hinder the reptation, which results in the slowing of the terminal relaxation time, but this process does not influence the concentration dependence of the zero-shear viscosity. It should be noted that the terminal relaxation time and plateau modulus have similar values in water and in salt solutions and their dependence on polymer concentration is not far from predictions of the sticky reptation model (results not shown).[63] However, as shown in Figure 11, at the highest polymer concentrations in both solvents ($C > 5$ wt %), the experimental viscosity data deviate from the theoretical predictions. This could be due to instrumental errors because of the very high viscosity of the samples.

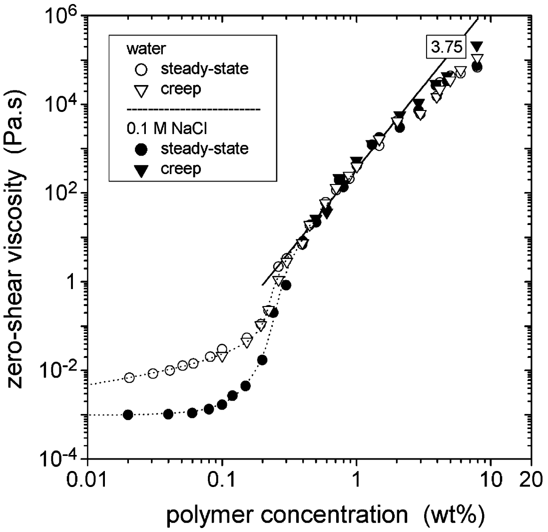

Figure 11. Dependence of the zero-shear viscosity of sample N3 on the polymer concentration in water (open symbols) and in 0.1 M NaCl solution (solid symbols).

Conclusions

The rheological behavior of associative multisticker polyelectrolytes based on AM, NaAMPS, and DiHexAM units was investigated in aqueous salt solution, as a function of the polymer and salt concentrations. Two samples with the same composition ([NaAMPS] ≈ 12 mol % and [DiHexAM] ≈ 2 mol %) and same molecular weight but with hydrophobic blocks of different lengths ($N_H = 3$ or 7) were studied by means of steady-flow, oscillatory, and creep experiments.

It was found that the critical concentration corresponding to the onset of the unentangled semidilute regime (C_η) is very close to the critical overlap concentration of the corresponding hydrophobe-free polymer and does not depend on the length of the hydrophobic sequence. This is in strong contrast to the behavior observed with the same polymers in pure water[51] for which the viscosity enhancement shifts toward lower concentration as the hydrophobic block length is increased.

The effect of the ionic strength on the rheological properties strongly depends on the polymer concentration range. Above C_η (i.e., in the unentangled regime), the addition of salt induces a marked lowering of the zero-shear viscosity and of the plateau modulus, but the relaxation time seems to be only slightly affected. In contrast, above the critical entanglement concentration, the systems tend to behave in a similar way, regardless of the presence of salt. This can be explained by the influence of the electrolyte on the polymer chain size below the entanglement concentration and the fact that, above this threshold, the dynamics is no longer controlled by the coil dimensions but is mainly controlled by the entanglements and the mesh size of the temporary network.

The polymer with the longest hydrophobic segments ($N_H = 7$) was studied in the semidilute unentangled regime, whereas the polymer with shorter sticker blocks ($N_H = 3$) was studied in the entangled regime. In both cases, the association of these multisticker associative polyelectrolytes was found to follow a similar pattern regardless the presence of electrolyte and can be described in the framework of available theories on associative polymers, that is, either the sticky Rouse model or the sticky reptation model, depending on the concentration range.

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References and Notes

(1) Valint, P. L., Jr.; Bock, J.; Schulz, D. N. In *Polymers in Aqueous Media: Performance through Association*; Glass, J. E., Ed.; American Chemical Society: Washington, DC, 1989; Vol. 223, pp 399−410.

(2) Bock, J.; Siano, D. B.; Valint, P. L., Jr.; Pace, S. J. In *Polymers in Aqueous Media: Performance through Association*; Glass, J. E., Ed.; American Chemical Society: Washington, DC, 1989; Vol. 223, pp 411−424.

(3) Biggs, S.; Selb, J.; Candau, F. *Polymer* **1993**, *34*, 580−591.

(4) Lacik, I.; Selb, J.; Candau, F. *Polymer* **1995**, *36*, 3197−3211.

(5) Selb, J.; Biggs, S.; Renoux, D.; Candau, F. In *Hydrophilic Polymers: Performance with Environmental Acceptability*; Glass, J. E., Ed.; American Chemical Society: Washington, DC, 1996; Vol. 248, pp 251−278.

(6) McCormick, C. L.; Middleton, J. C.; Cummins, D. F. *Macromolecules* **1992**, *25*, 1201−1206.

(7) McCormick, C. L.; Middleton, J. C.; Grady, C. E. *Polymer* **1992**, *33*, 4184−4190.

(8) Smith, G. L.; McCormick, C. L. *Macromolecules* **2001**, *34*, 5579−5586.

(9) Wang, K. T.; Iliopoulos, I.; Audebert, R. *Polym. Bull.* **1988**, *20*, 577−582.

(10) Petit, F.; Iliopoulos, I.; Audebert, R.; Szönyi, S. *Langmuir* **1997**, *13*, 4229−4233.

(11) Tsitsilianis, C.; Iliopoulos, I.; Ducouret, G. *Macromolecules* **2000**, *33*, 2936−2943.

(12) English, R. J.; Gulati, H. S.; Jenkins, R. D.; Khan, S. A. *J. Rheol.* **1997**, *41*, 427−444.

(13) English, R. J.; Raghavan, S. R.; Jenkins, R. D.; Khan, S. A. *J. Rheol.* **1999**, *43*, 1175−1194.

(14) Tan, H.; Tam, K. C.; Tirtaatmadja, V.; Jenkins, R. D.; Bassett, D. R. *J. Non-Newtonian Fluid Mech.* **2000**, *92*, 167−185.

(15) Morishima, Y.; Nomura, S.; Ikeda, T.; Seki, M.; Kamachi, M. *Macromolecules* **1995**, *28*, 2874−2881.

(16) Bromberg, L. *J. Phys. Chem. B* **1998**, *102*, 10736−10744.

(17) Bromberg, L. *Macromolecules* **1998**, *31*, 6148−6156.

(18) Feng, Y. J.; Grassl, B.; Billon, L.; Khoukh, A.; Francois, J. *Polym. Int.* **2002**, *51*, 939−947.

(19) Tam, K. C.; Farmer, M. L.; Jenkins, R. D.; Basset, D. R. *J. Polym. Sci. B: Polym. Phys.* **1998**, *36*, 2275−2290.

(20) Noda, T.; Hashidzume, A.; Morishima, Y. *Langmuir* **2001**, *17*, 5984−5991.

(21) Noda, T.; Hashidzume, A.; Morishima, Y. *Macromolecules* **2001**, *34*, 1308−1317.

(22) Branham, K. D.; Davis, D. L.; Middleton, J. C.; McCormick, C. L. *Polymer* **1994**, *35*, 4429−4436.

(23) Tsitsilianis, C.; Iliopoulos, I. *Macromolecules* **2002**, *35*, 3662−3667.

(24) Glass, J. E., Ed. *Water-Soluble Polymers: Beauty with Performance*; American Chemical Society: Washington, DC, 1986; Vol. 213.

(25) Glass, J. E., Ed. *Polymers in Aqueous Media: Performance through Association*; American Chemical Society: Washington, DC, 1989; Vol. 223.

(26) Glass, J. E., Ed. *Hydrophilic Polymers: Performance with Environmental Acceptability*; American Chemical Society: Washington, DC, 1996; Vol. 248.

(27) Glass, J. E., Ed. *Associative Polymers in Aqueous Solution*; American Chemical Society: Washington, DC, 2000; Vol. 765.

(28) Schulz, D. N., Glass, J. E., Eds. *Polymers as Rheology Modifiers*; American Chemical Society: Washington, DC, 1991; Vol. 462.

(29) McCormick, C. L., Ed. *Stimuli-Responsive Water-Soluble and Amphiphilic Polymers*; American Chemical Society: Washington, DC, 2001; Vol. 780.

(30) Winnik, M. A.; Yekta, A. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 424−436.

(31) Jiménez Regalado, E.; Selb, J.; Candau, F. *Macromolecules* **1999**, *32*, 8580−8588.

(32) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Macromolecules* **1996**, *29*, 5273−5278.

(33) Hogen-Esch, T. E.; Amis, E. J. *Trends Polym. Sci.* **1995**, *3*, 98−104.

(34) Volpert, E.; Selb, J.; Candau, F. *Macromolecules* **1996**, *29*, 1452−1463.

(35) Yamamoto, H.; Morishima, Y. *Macromolecules* **1999**, *32*, 7469−7475.

(36) Petit-Agnely, F.; Iliopoulos, I.; Zana, R. *Langmuir* **2000**, *16*, 9921−9927.

(37) Branham, K. D.; Shafer, G. S.; Hoyle, C. E.; McCormick, C. L. *Macromolecules* **1995**, *28*, 6175−6182.

(38) Branham, K. D.; McCormick, C. L. In *Multidimensional Spectroscopy of Polymers*; Urban, M. W., Provder, T., Eds.; American Chemical Society: Washington, DC, 1995; Vol. 598, pp 551−567.

(39) Hill, A.; Candau, F.; Selb, J. *Macromolecules* **1993**, *26*, 4521−4532.

(40) Volpert, E.; Selb, J.; Candau, F. *Polymer* **1998**, *39*, 1025−1033.

(41) Candau, F.; Selb, J. *Adv. Colloid Interface Sci.* **1999**, *79*, 149−172.

(42) Evani, S. (Dow Chemical). U.S. Patent 4,432,881, 1984.

(43) Dowling, K. C.; Thomas, J. K. *Macromolecules* **1991**, *24*, 2341−2347.

(44) Middleton, J. C.; Cummins, D. F.; McCormick, C. L. In *Water-Soluble Polymers: Synthesis, Solution Properties, and Applications*; Shalaby, S. W., McCormick, C. L., Butler, G. B., Eds.; American Chemical Society: Washington, DC, 1991; Vol. 467, pp 338−348.

(45) Branham, K. D.; Snowden, H. S.; McCormick, C. L. *Macromolecules* **1996**, *29*, 254−262.

(46) Noda, T.; Hashidzume, A.; Morishima, Y. *Macromolecules* **2000**, *33*, 3694−3704.

(47) Kujawa, P.; Audibert-Hayet, A.; Selb, J.; Candau, F. *J. Polym. Sci. A: Polym. Chem.* **2003**, *41*, 3261−3274.

(48) Neidlinger, H. H.; Chen, G. S.; McCormick, C. L. *J. Appl. Polym. Sci.* **1984**, *29*, 713−730.

(49) McCormick, C. L.; Elliott, D. L. *Macromolecules* **1986**, *19*, 542−547.

(50) Audibert, A.; Lecourtier, J. *Polym. Degrad. Stab.* **1993**, *40*, 151−165.

(51) Kujawa, P.; Audibert-Hayet, A.; Selb, J.; Candau, F. *J. Polym. Sci. B: Polym. Phys.* **2004**, *42*, 1640−1655.

(52) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *Macromolecules* **1995**, *28*, 1859−1871.

(53) Clasen, C.; Kulicke, W. M. *Prog. Polym. Sci.* **2001**, *26*, 1839−1919.

(54) Caputo, M.-R.; Selb, J.; Candau, F. *Polymer* **2004**, *45*, 231−240.

(55) Rubinstein, M.; Colby, R. H.; Dobrynin, A. V. *Phys. Rev. Lett.* **1994**, *73*, 2776−2779.

(56) Noda, T.; Hashidzume, A.; Morishima, Y. *Langmuir* **2000**, *16*, 5324−5332.

(57) Aubry, T.; Moan, M. *J. Rheol.* **1994**, *38*, 1681−1692.

(58) McCormick, C. L.; Nonaka, T.; Johnson, C. B. *Polymer* **1988**, *29*, 731−739.

(59) Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 4701−4707.

(60) Tam, K. C.; Guo, L.; Jenkins, R. D.; Bassett, D. R. *Polymer* **1999**, *40*, 6369−6379.

(61) Semenov, A. N.; Rubinstein, M. *Macromolecules* **1998**, *31*, 1373−1385.

(62) Rubinstein, M.; Semenov, A. N. *Macromolecules* **1998**, *31*, 1386−1397.

(63) Rubinstein, M.; Semenov, A. N. *Macromolecules* **2001**, *34*, 1058−1068.

(64) Semenov, A. N.; Rubinstein, M. *Macromolecules* **2002**, *35*, 4821−4837.

(65) Candau, F.; Jiménez Regalado, E.; Selb, J. *Macromolecules* **1998**, *31*, 5550−5552.

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