Phase Behavior and Rheological Properties of Aqueous Solutions Containing Mixtures of Associating Polymers

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ABSTRACT: The phase behavior and the rheological properties of aqueous solutions containing mixtures of multiblock hydrophobically modified polyacrylamides (HMPAM) have been investigated. Mixtures of a HMPAM with a homopolyacrylamide (PAM) phase separate above a given overall polymer concentration and a given PAM content. These results are in qualitative agreement with the predictions of a model based on the entropy changes due to the associations between the hydrophobic units [Annable, T.; Ettelaie, R. *Macromolecules* **1994**, *27*, 5616]. The viscoelastic behavior of semidilute solutions of various series of copolymer mixtures with variable molecular weights ($M_w \approx 10^5$ to 2×10^6), hydrophobe contents ($[H] = 0.5-2$ mol %), and hydrophobic block lengths ($N_H \approx 2-7$ units per block) has been studied using steady-flow and oscillatory experiments. The linear viscoelasticity can be described by a slow relaxation process and other faster complex relaxation processes. When both HMPAM are mutually entangled, the slow relaxation is in agreement with the expectation from a hindered reptation model with in particular a plateau modulus that only depends on polymer concentration. When the two HMPAM are unentangled, the behavior is more complex, the properties being strongly dependent on the hydrophobe characteristics of the two copolymers. In particular, when there is a strong mismatch between the hydrophobic parameters, the viscosity of the system is depressed likely due to a local segregation between the two copolymers.

Introduction

The phase behavior of solutions containing a mixture of two polymers is satisfactorily described by the Flory−Huggins lattice model.[1,2] Phase separation at low or moderate polymer concentration only occurs if there is a strong chemical incompatibility between the two polymers. Phase separation was also observed in solutions containing mixtures of a telechelic associating copolymer with a homopolymer of same molecular weight.[3,4] In that case, the hydrophobic entities located at each end of the associating copolymer contribute to less than 2 wt % toward the molecular weight of this copolymer. Therefore, there is no chemical incompatibility to drive phase separation in the traditional Flory−Huggins sense. It was proposed that the phase separation behavior of this type of systems is an entropically driven phenomenon resulting from the association of the end groups.[3,4]

In this paper, we consider the phase behavior of mixtures of hydrophobically modified polyacrylamides (HMPAM) with homopolyacrylamides (PAM). Another issue that we address concerns the rheological behavior of mixtures of HMPAM differing by their hydrophobic characteristics and/or their molecular weights. One might wonder whether it is possible by an appropriate choice of two HMPAM to tune the rheological parameters of the systems. In addition, a study of HMPAM mixtures differing by their molecular weights is susceptible to bring some information on the effect of polydispersity on the rheological properties. However, the problem is complex as many parameters can be varied: HMPAM molecular weight, hydrophobe content, nature and size of the sticker, concentration regime, etc. It is therefore indispensable to have at one's disposal well-defined samples.

Recently, we have reported a study on the rheological properties of polyacrylamides hydrophobically modified with small amounts of *N*,*N*-dihexylacrylamide (DiHexAM) and prepared by a free radical micellar polymerization technique.[5,6] This process give copolymers in which the hydrophobes are randomly distributed as small blocks along the polyacrylamide backbone.[7−11] The viscoelastic behavior of semidilute aqueous solutions of different series of copolymers with variable molecular weights, hydrophobe contents, and hydrophobic block lengths was investigated as a function of polymer concentration. Two distinct semidilute regimes could be clearly identified. An unentangled regime where the viscosity is controlled by intermolecular hydrophobic interactions and an entangled regime where it is mainly dominated by entanglements. In the latter regime, the results are quite well accounted for by a hindered reptation model.[12]

The multiblock polymers described above are well appropriate to a study of their mixtures because their structural properties can be easily varied in a controlled manner. We report here measurements of linear and nonlinear viscoelasticity of HMPAM mixtures in the various concentration regimes that have been previously identified.

Experimental Section

The synthesis of the samples has been described in detail in previous papers.[6,8,13] The associating copolymers are polyacrylamides hydrophobically modified with a small amount of *N*,*N*-dihexylacrylamide (DiHexAM). They were synthesized in aqueous solution by using the micellar technique of Valint et al.[14] with sodium dodecyl sulfate (SDS) as the surfactant and 4,4′-azobis(4-cyanovaleric acid) (ACVA) as the initiator. In this

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Table 1. Polymer Characteristics

sample[a]	M_w ($\times 10^{-3}$)	$[H]$[b] (mol %)	N_H[c]
1PAM	90	0	0
5PAM	480	0	0
1M1D3.2	115	1.02	3.2
1M2D3.2	140	1.96	3.2
1M2D7	160	2.03	7
5M05D3.2	450	0.48	3.2
5M1D2	425	1.0	2
5M1D3.2	420	1.0	3.2
5M1D5	450	0.96	5
5M1D7	460	1.0	7
5M2D3.2	420	2.0	3.2
14M1D3.2	1400	0.95	3.2
20M1D3.2	2000	1.0	3.2

[a] The sample code refers to the molecular characteristics of the polymer (see Experimental Section). [b] Hydrophobe content in final copolymer. [c] Number of hydrophobes per micelle ≅ hydrophobic block length.

process, the high density of hydrophobic molecules in the micelles favors their incorporation as blocks randomly distributed in the polyacrylamide backbone.[8−11] Note that the use of *N*,*N*-dialkylacrylamides such as DiHexAM instead of *N*-monoalkylacrylamides leads to samples homogeneous in composition.[13]

The characteristics of the samples investigated are given in Table 1. The hydrophobe content in the copolymers (which corresponds within the experimental error to that in the monomer feed) was 0.5, 1, or 2 mol %. The hydrophobe/surfactant molar ratio was adequately adjusted in order to get the number of hydrophobes per micelle, N_H, ranging from 2 to 7. The length of the hydrophobic blocks in the copolymer is assumed to correspond roughly to N_H.[11,13] The molecular weight was varied from $\approx 10^5$ to 2×10^6 by using mercaptoethanol as a chain transfer agent, which behaves like an ideal transfer agent for polyacrylamide (polydispersity index $M_w/M_n \approx 2$).[6] The weight-average molecular weight M_w and the composition of the samples were determined by light scattering and NMR respectively as described elsewhere.[13,15]

The sample code of the copolymers refers to the molecular weight M_w (1, 5, 14, and 20 stand for $M_w \approx 140\,000 \pm 20\,000$, $\approx 450\,000 \pm 20\,000$, 1400 000, and 2 000 000, respectively), to the content in hydrophobic monomer $[H]$, and to the N_H value (i.e., ≅ the length of the hydrophobic block). For example, 1M2D7 stands for a copolymer with a molecular weight of 160 000 containing 2 mol % of DiHexAM and synthesized with a number of hydrophobes per micelle equal to 7 (see Table 1).

Stock aqueous solutions of the pure polymers were first prepared at the desired concentration (1, 2, 3, or 4 wt %) according to the usual procedure.[8,13] Various mixtures of the copolymers were obtained by mixing the required weighted amount of the stock solutions of the same polymer concentration (weight ratio: 0/100, 10/90, 20/80, 40/60, 50/50, 60/40, 80/20, 90/10, 100/0).

Linear viscoelasticity experiments were performed on samples that were viscous enough to provide a meaningful analysis with a Haake RS100 controlled stress rheometer equipped with a cone-plane geometry (angle 1°, diameter 20, 35, or 60 mm depending on the sample viscosity). Flow experiments were carried out with the same rheometer as above or with a Contraves LS30 low shear rheometer, depending on the sample viscosity. More details on the experimental procedures are given elsewhere.[13,16]

NMR experiments were used to determine the HMPAM/PAM content within the phases after separation, after recovery of the polymer by precipitation in methanol.

Reminder

In recent papers, we have presented measurements of the complex shear modulus and the zero-shear viscosity for a series of polyacrylamides containing blocks of *N*,*N*-dihexylacrylamide (DiHexAM).[5,6] The number of hydrophobic blocks per chain, *S*, was tuned by adjusting the molecular weight of the polymer, M_w, the total hydrophobe content, $[H]$, or the length of the hydrophobic blocks, N_H. The latter parameter, which controls the lifetime of the associations, could be varied, owing to the specificity of the free radical micellar copolymerization technique (see Experimental Section).

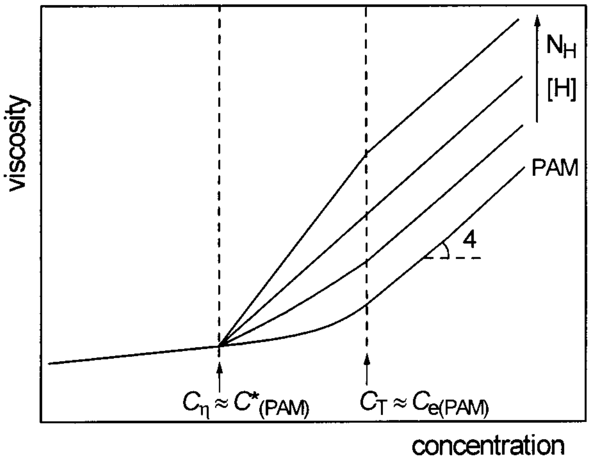

Figure 1. Schematic diagram of the various concentration regimes for multisticker associating polyacrylamides (from ref 6).

Linear viscoelastic measurements performed on these systems revealed the existence of three distinct concentration regimes as in the case of nonassociating polymers. An illustration of this behavior is given in Figure 1.

(i) A dilute regime, $C < C_\eta$, where the chains are isolated and the viscosity is essentially controlled by intramolecular interactions. This regime does not significantly differ from that of unmodified polymers

(ii) A semidilute unentangled regime, $C_\eta < C < C_T$. In this regime, the viscosity is considerably enhanced with respect to that of the unmodified PAM. The break between the first and second regimes is rather sharp with C_η depending on the molecular weight but independent of N_H and/or $[H]$. Note that C_η lies in the vicinity of the overlap concentration C^* of the unmodified polymer analogue. At C_η, one observes for a given molecular weight a set of diverging straight lines whose slopes increase with N_H and/or $[H]$. This regime is dominated by intermolecular hydrophobic associations, and the chains are likely to obey Rouse dynamics, as theoretically described by Rubinstein and Semenov.[17]

(iii) A semidilute entangled regime, $C > C_T$. The break C_T occurs at a concentration close to the critical concentration C_e where the unmodified polymer chains are entangled. The asymptotic behavior is described by parallel straight lines with an exponent of about 4 in the log−log variations of $\eta_0 = f(C)$ whatever N_H or $[H]$.

A similar behavior was observed for HMPAM copolymers with other molecular weights. From the diagram such as that of Figure 1, one can estimate the values of the crossover concentrations C_η and C_T. These are given in Table 2 for polymers with molecular weights of the order of those of the HMPAM investigated in that study.

Linear viscoelastic measurements show that the relaxation mechanism can be described by a slow process more or less separated from faster modes. In the entangled regime ($C > C_T$), the plateau modulus associated with the slow process only depends on the polymer concentration within the experimental ac-

Table 2. Values of C_η and C_T for Acrylamide-Based Polymers with Various Molecular Weights[a]

	$M_w \approx$			
	140 000	450 000	1 400 000	2 000 000
C_η (wt %)	0.8	0.5	0.2	0.15
C_T (wt %)	5	2	0.8	0.6

[a] The concentration C_η represents the crossover between dilute and semidilute unentangled regimes and C_T that between semidilute unentangled and entangled regimes.

curacy. On the other hand, the terminal time rises drastically with either N_H, $[H]$, or M_w.[6]

In the latter regime that corresponds to a much larger density of entanglements than that of hydrophobic associations, the results are quite well described by the sticky reptation model developed by Leibler et al.[12] This model considers a entangled semidilute solution of monodisperse chains of N monomers with S stickers attached to each chain. These stickers, that are at fixed positions, can associate to form reversible cross-links. A given sticker either can be free or is associated, forming a cross-link with other stickers. Two parameters are introduced: the average fraction p of stickers engaged in an association and the average lifetime τ of a sticker in the cross-link. Furthermore, it is assumed that a free sticker can find many sites to attach to, besides the one it was just recently associated with. The linear viscoelastic response of such systems was calculated under the assumption that the tube diameter is fixed by the density of entanglements and that the number of monomers in an entanglement strand, N_e, is much smaller than the average number N_S of monomers along the chain between stickers.

The most striking feature of the rheological behavior predicted in this model is the existence of a two relaxation process. The low-frequency process is characterized by a time T_d, which depends strongly on the chain length, the density of stickers, and τ, according to

$$T_d \cong C^{15/8} N^{7/2} [S]^2 \tau (1 - 9/p + 12/p^2)^{-1} \quad (1)$$

where $[S]$ is the molar ratio of stickers with respect to the total number of monomers.

The plateau modulus associated with the slow process is the same as that of unmodified polymers and scales as

$$G_0 \propto C^{9/4} \quad (2)$$

Finally, the zero-shear viscosity can be approximated by

$$\eta_0 \equiv G_0 T_d \cong C^{33/8} N^{7/2} [S]^2 \tau (1 - 9/p + 12/p^2)^{-1} \quad (3)$$

The main features of the experimental study and notably the scaling behavior of the zero-shear viscosity with molecular weight and polymer concentration were in good agreement with the above theoretical predictions.[6]

Results and Discussion

Phase Diagrams. The phase behavior of a series of polymer mixtures was examined at several overall polymer concentrations ranging from 1 to 4 wt % and for various compositions. Mixtures of two HMPAM with both $[H] \geq 1$ mol % and $N_H \geq 3.2$ were found to be miscible in all proportions in the concentration range investigated ($C \leq 4$ wt %). On the contrary, mixing one of these HMPAM with PAM led to the phase diagrams represented in Figure 2. As can be seen, phase separation occurs at high total concentration and/or low HMPAM content. In this region, the samples separated into two distinct layers both transparent. The upper phase is very fluid whereas the lower one is a gel. Similar features were observed for systems containing weakly associating HMPAM ($N_H = 2$ and/or $[H] = 0.5$ mol %) instead of PAM.

Figure 3 gives the variation of the volume ratio of the two phases as a function of the overall weight ratio of PAM/HMPAM. There is obviously a correlation between these two parameters which suggests that the lower phase is largely HMPAM and the upper phase largely PAM (or weakly associating HMPAM). This was confirmed by NMR experiments on the 1PAM/5M2D3.2 mixtures that show no detectable content of HMPAM in the upper phase. Measurements of the polymer concentration by means of gravimetry experiments indicate that, within the experimental accuracy, the quasi-totality of the PAM is present in the upper phase. Table 3 gives an example of compositions of the separated phases. It can be observed that the systems separated into a dilute PAM solution and a concentrated HMPAM solution, with gel-like properties.

The overall behavior described above is qualitatively similar to that observed by other groups[3,4,18,19] and in particular by Annable and Ettelaie on solutions of poly(ethylene oxide) end-capped at both ends by alkane groups mixed with similar sized unmodified polymers.[3,4] The shape of the phase diagrams reported in Figure 2 as well as the composition of the two phases shows that the phase separation is of segregative type in which the two polymers are enriched in separate phases. In mixtures of nonassociating polymers, this occurs when there is an effective repulsion between the two polymers. In the case of a mixture of an associating polymer with a nonassociating one, the phase separation results mainly from the entropy changes due to the association of the hydrophobic groups rather than from a chemical incompatibility.[3,4] The HMPAM chains are effectively constrained to take on configurations that leave a large number of hydrophobic blocks within aggregates. Increasing the concentration of HMPAM at the expense of the homopolymer in the neighborhood of the chains allows configurations which were not previously available to this chain. The resulting increase of entropy of the HMPAM chains is the driving factor for the phase separation. Annable and Ettelaie have developed a model for telechelic polymers that explains quantitatively this behavior by considering the effect of association of end groups within the Flory−Huggins scheme.[3,4] For the multisticker chains considered here, the effects are more complex, but the thermodynamic arguments developed by these authors apply and allow one to describe qualitatively the main features of the phase separation in the mixture.

Viscoelastic Properties. In previous experimental studies, it was shown that the linear viscoelasticity of semidilute multisticker systems can be described by a main slow relaxation and other faster complex relaxation processes.[6] For entangled systems ($C > C_T$), the slow relaxation is characterized by a plateau modulus that only depends on polymer concentration and a terminal time that strongly depends on the molecular weight of the HMPAM and the density and length of

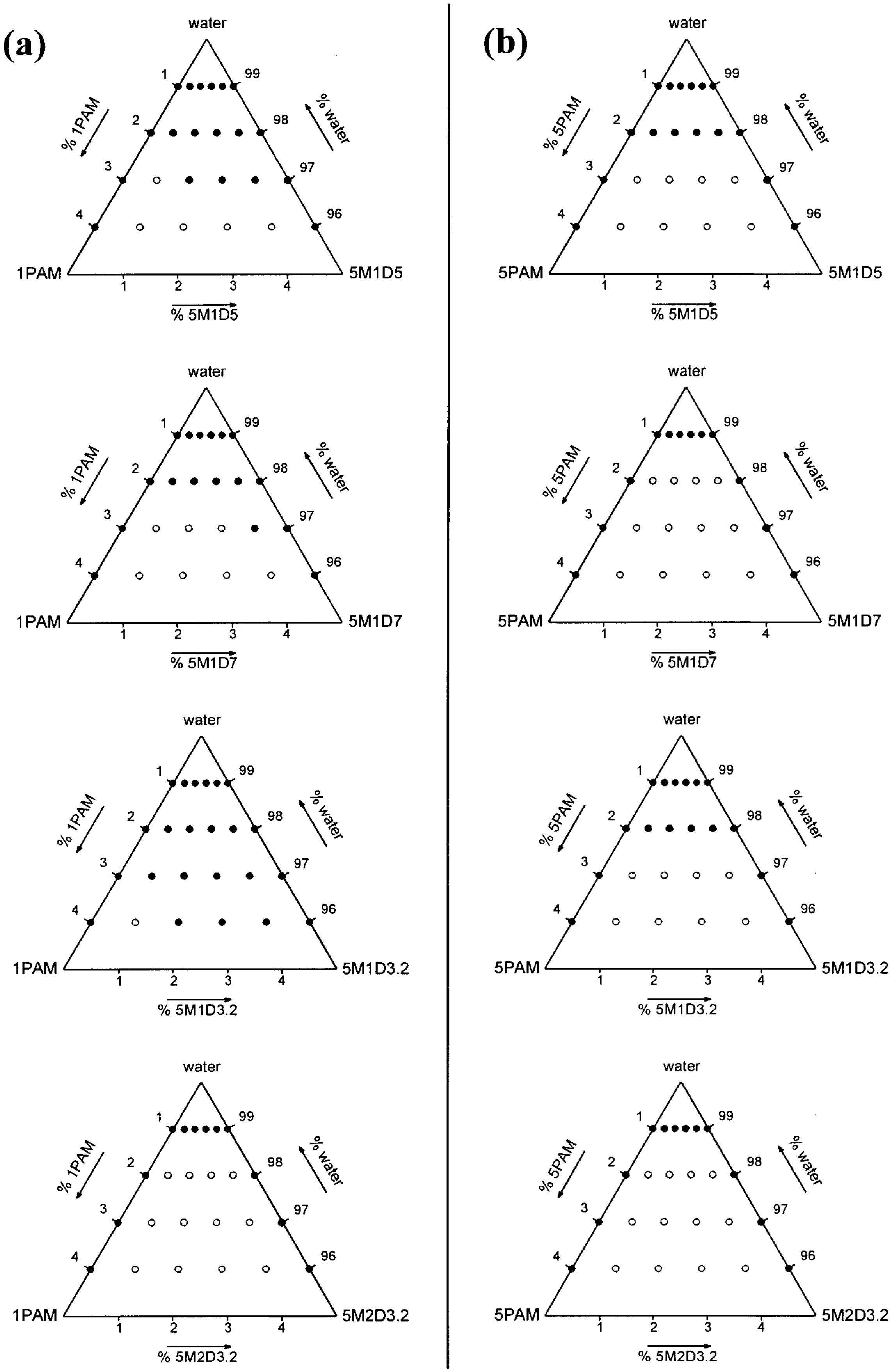

Figure 2. Phase diagrams for mixtures of a homopolyacrylamide (a, M_w = 90 000; b, M_w = 480 000) with different HMPAM of similar molecular weights ($M_w \approx$ 450 000) but different hydrophobe characteristics. Compositions in wt %. (●) Monophasic systems; (○) diphasic systems.

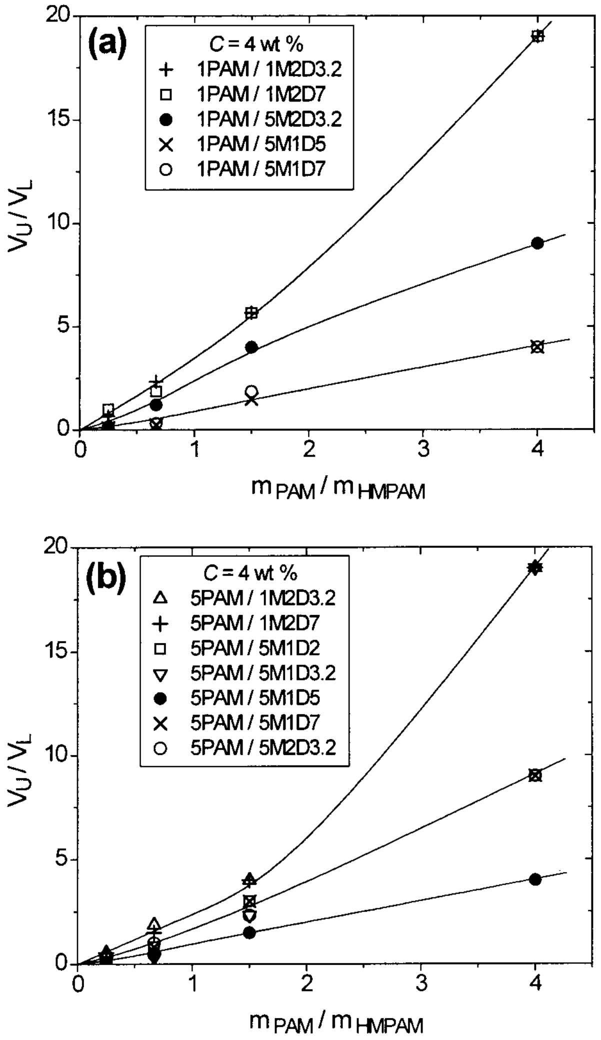

Figure 3. Variation of the volume ratio of the upper phase to the lower phase for demixed systems versus the overall weight ratio of PAM/HMPAM. (a) $M_{w,PAM} = 90\ 000$; (b) $M_{w,PAM} = 480\ 000$).

Table 3. Phase Separation of 4 wt % 1PAM/5M2D3.2 (A/B) Mixtures

m_A/m_b[a] (wt/wt)	V_U/V_L[b] (v/v))	C_U[c] (wt %)	C_L[d] (wt %)
40/60	55/45	2.3	6.1
60/40	80/20	2.6	9.6
80/20	90/10	3	13

[a] m_A/m_B represents the weight ratio of the two solutions before mixing. [b] V_U/V_L represents the volume ratio of the upper phase to the lower phase after separation. [c] C_U is the polymer concentration measured by gravimetry in the upper phase. [d] C_L is the polymer concentration (deduced by difference) in the lower phase.

the hydrophobic blocks. The results related to this process are quite well accounted for by the hindered reptation model.[12] The faster modes involve the local fluctuations as well as the kinetics of association of hydrophobic units. For mixtures of HMPAM, very complex viscoelastic spectra are therefore expected with large distributions of relaxation times. In particular for mixtures of two polymers with largely different molecular weights *M*, the slow relaxation process should be bimodal since the terminal time depends on *M*. In particular, in the entangled regime, it varies as $M^{3.4}$. Such a bimodal behavior was experimentally observed in melts of bidispersed systems[20−22] and theoretically described.[23]

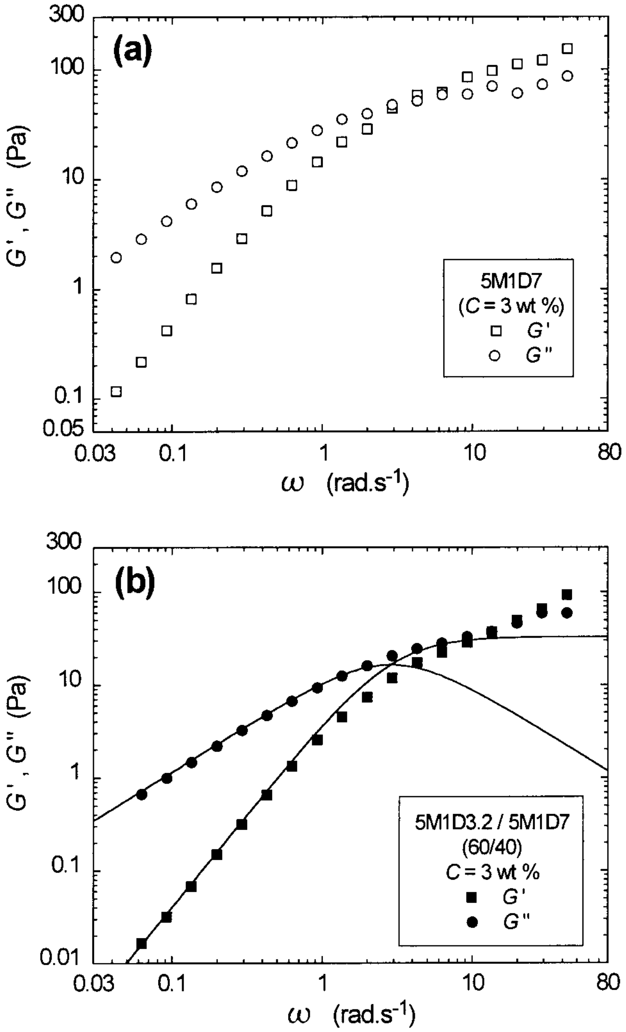

Figure 4. Storage (G') and loss (G'') moduli as a function of frequency for a pure HMPAM (a) and a HMPAM mixture (b). The lines in (b) are the fit to one mode Maxwell model (G_0 = 35 Pa, relaxation time = 0.35 s).

We have investigated mixtures of associating polymers with different molecular weights and/or different hydrophobic characteristics. The overall behavior of the complex shear modulus is that reported in Figure 4. The shape of the viscoelastic spectra obtained for polymer mixtures (Figure 4b) does not qualitatively differ from those of the pure HMPAM systems (Figure 4a). In no case, we found any evidence of bimodal spectra. A detailed analysis of $G'(\omega)$ and $G''(\omega)$ is not feasible. One can note however that in the low-frequency range the variations of $G'(\omega)$ and $G''(\omega)$ versus ω can be described by a Maxwellian model that is they scale like ω^2 and ω, respectively. This scaling behavior can be observed experimentally only when the frequency range accessible experimentally is sufficiently extended below the relaxation frequency. The curves of $G'(\omega)$ and $G''(\omega)$ cross each other at a critical frequency ω_C, but deviations from the Maxwell model appear at frequencies lower than ω_C. The shape of the curves $G'(\omega)$ and $G''(\omega)$ at higher frequencies is indicative of the occurrence of fast modes superimposing on a slow relaxation process. It follows that the relaxation time determined from ω_C is smaller than the longest relaxation time, the latter being the physical quantity relevant for a comparison with the models.

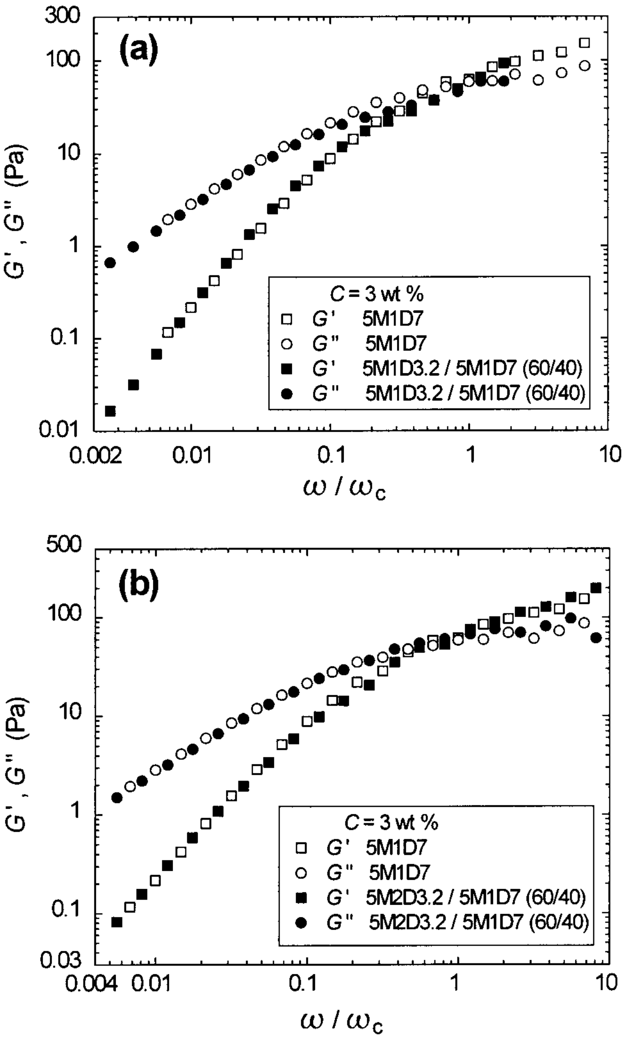

Figure 5. Superposition of the viscoelastic spectra under an horizontal shift for aqueous solutions of entangled HMPAM mixtures. The shift factor is the ratio of the crossing frequencies ω_C. (a) refers to the example given in Figure 4, $\omega_{C,2}/\omega_{C,1} = 2$; (b) $\omega_{C,2}/\omega_{C,1} = 1.3$.

From the analysis of the data in the low-frequency range, we have determined the longest relaxation time T_R and the plateau modulus G_0 associated with this slowest process. These are obtained from the following relationships.

$$T_R = \lim_{\omega \to 0}\left(\frac{1}{\omega}\frac{G'}{G''}\right); \quad G_0 = \frac{1}{T_R}\lim_{\omega \to 0}\left(\frac{G''}{\omega}\right) \qquad (4)$$

The viscoelastic properties of solutions of HMPAM mixtures are expected to depend significantly on both the overall polymer concentration and the composition of the mixture. In the following, we consider three different situations: (i) the two polymers are mutually entangled; (ii) one polymer forms an entangled matrix diluted by the second polymer which is unentangled; (iii) the two polymers are unentangled.

Entangled Systems. Here we consider mixtures of two HMPAM with a total concentration larger than each of the entanglement concentrations C_T of the two polymers. In the case of a mixture of two HMPAM with same molecular weight, the frequency dependence of the complex shear modulus is found to be very similar to that of the pure HMPAM entangled systems. This is illustrated in Figure 5a which shows the master curve obtained by a simple horizontal translation along the frequency axis of the data of Figure 4a,b. The best match between the two viscoelastic spectra is obtained for a shift factor close to the ratio $\omega_{C,2}/\omega_{C,1}$ of the two crossing frequencies ω_C where $G'(\omega) = G''(\omega)$. The good superposition of the data shows that the two viscoelastic spectra differ mainly by their characteristic relaxation frequency.

Such master curves were obtained for the quasi-totality of the entangled systems made from mixtures of HMPAM with same molecular weight. Another example is given in Figure 5b. In that case, the values of the terminal time of each of the two copolymers are close from each other. The master curve is obtained with a very small translational shift ($\omega_{C,2}/\omega_{C,1} = 1.3$), and the two spectra superpose almost perfectly in the whole frequency range.

From the analysis of the $G'(\omega)$ and $G''(\omega)$ curves, it is then possible to determine the first plateau modulus G_0 as well as the terminal time T_R (eq 4) and the zero-shear viscosity $\eta_0 = G_0 T_R$. According to the hindered reptation model, one expects that, in the limit where the density of entanglements is much larger than that of the cross-links, the plateau modulus only depends on the total polymer concentration, irrespective of the hydrophobic characteristics of the two copolymers forming the mixtures. Figure 6 shows the variation of G_0 as a function of the mixture composition for several HMPAM mixtures with similar molecular weights ($M_w \approx 450\,000$) and an overall concentration $C = 3$ wt %. Such solutions are above the entanglement threshold which is $C_T = 2$ wt %. The data are rather scattered due to the uncertainty resulting from the analysis in a limited range of frequencies, but they gather statistically around a value of 30 Pa, which is close to the value obtained for the pure HMPAM solutions at the same concentration.[6] One can also observe quite large deviations from this average value for systems containing predominantly HMPAM with either a low hydrophobe content ($[H] = 0.5$ mol %, 5M05D3.2) or a small block length ($N_H = 2$, 5M1D2) (encircled symbols in Figure 6). In this respect, it must be noted that these mixtures with depressed plateau moduli phase separate at slightly higher concentrations. Therefore, one cannot discard the possibility of local microphase separation, the less associating polymer being excluded from the surrounding more hydrophobic copolymer. This would favor the formation of collapsed microdomains with intramolecular cross-links to the expense of the intermolecular ones, resulting in a smaller value of the modulus.

Let us consider now the behavior of the terminal time and of the zero-shear viscosity, the latter being determined from steady flow measurements with a much better accuracy than the former. Figures 7 and 8 show typical variations of the zero-shear viscosity and of the terminal time as a function of composition for three binary mixtures of HMPAM with similar molecular weights but differing by their hydrophobe content ($[H]$ = 1 and 2 mol %) or their hydrophobic block length (N_H = 3.2, 5, 7). One observes a monotonic variation of η_0 and T_R between the values corresponding to the two pure HMPAM solutions. The observations reported above are in qualitative agreement with the predictions of the sticky reptation model. When mixing two HMPAM with same molecular weights and same N_H but different $[H]$ and assuming binary associations, one modifies mainly the fraction p of close stickers. In

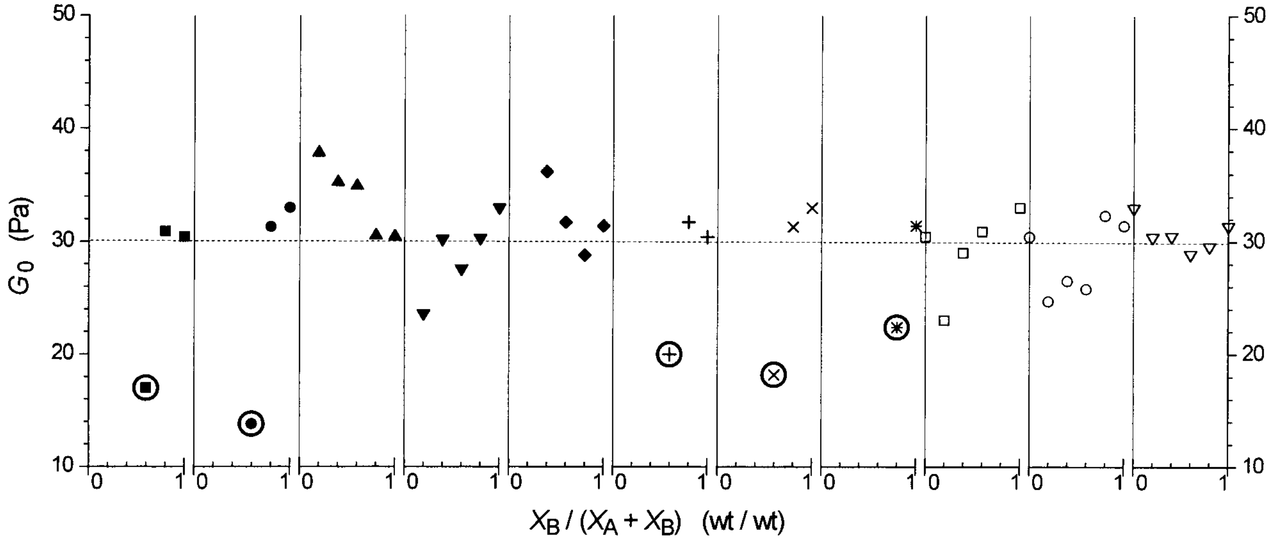

Figure 6. Plateau modulus versus composition for series of aqueous solutions of entangled HMPAM mixtures with same M_w but different hydrophobe content and hydrophobic block length (C = 3 wt %). A/B: 5M05D3.2/5M1D5 (■); 5M05D3.2/5M1D7 (●); 5M1D3.2/5M1D5 (▲); 5M1D3.2/5M1D7 (▼); 5M1D3.2/5M2D3.2 (◆); 5M1D2/5M1D5 (+); 5M1D2/5M1D7 (×); 5M1D2/5M2D3.2 (★); 5M1D5/5M1D7 (□); 5M1D5/5M2D3.2 (○); 5M1D7/5M2D3.2 (▽). For encircled symbols, see text.

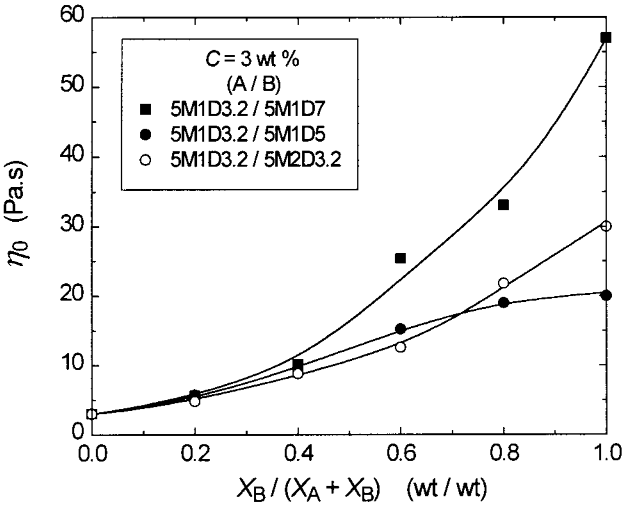

Figure 7. Zero-shear viscosity versus composition for aqueous solutions of entangled HMPAM mixtures with similar molecular weights.

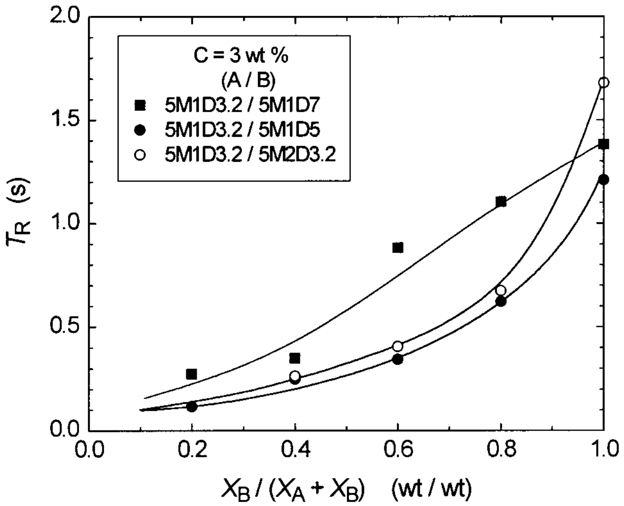

Figure 8. Terminal time versus composition for aqueous solutions of entangled HMPAM mixtures (same systems as in Figure 7).

mixtures of two HMPAM differing only by their N_H, for instance N_H = 3.2 and N_H = 7, three kinds of cross-links form, involving associations 3.2–7, 7–7, and 3.2–3.2. Each of these associations has a different lifetime. But a given chain will be linked to the others through different kinds of cross-links, and in the reptation process, it is likely that an average lifetime will come into play. One can argue that the chain containing blocks with N_H = 7 will reptate more slowly because it will be connected to the others through 7–7 and 7–3.2 associations whereas the chain with N_H = 3.2 will be engaged into cross-links 3.2–3.2 and 3.2–7. In the latter case, the average lifetime will be shorter, thus decreasing the terminal time according to eq 1, but the effect is probably small enough so that it is not detectable in the viscoelastic spectra as shown by the master curves of Figure 5a.

A confirmation of the above picture based on a homogeneous interpenetrated physical network of the two HMPAM is provided by nonlinear viscoelasticity experiments. Figure 9 shows the variation of viscosity versus shear rate for various compositions of a 3 wt % 5M1D3.2/5M1D7 mixture. A shear-thinning behavior is observed similar to that obtained for nonassociating or associating entangled polymers. One can notice however a small shear thickening occurring at intermediate compositions. This could indicate the formation of few intramolecular cross-links.[16,24–26] The reciprocal critical shear rate $\dot{\gamma}_C^{-1}$ corresponding to the onset of shear thinning follows qualitatively the same variation than the terminal time (cf. Figure 8).

Systems with Entangled and Unentangled Chains. For nonassociating polymers, the addition of a low molecular weight polymer to a solution of an entangled high molecular weight polymer amounts to diluting the latter. The case of associating polymers is more complex since bridges between the two unlike polymers may form. It can however be speculated that the main relaxation process is dominated by the reptation of the high molecular weight chains, still hindered by the associations formed between chains of same molecular weight or between unlike chains. As a matter of fact, the viscoelastic spectra can no longer be superposed to those of the pure HMPAM solutions. Generally,

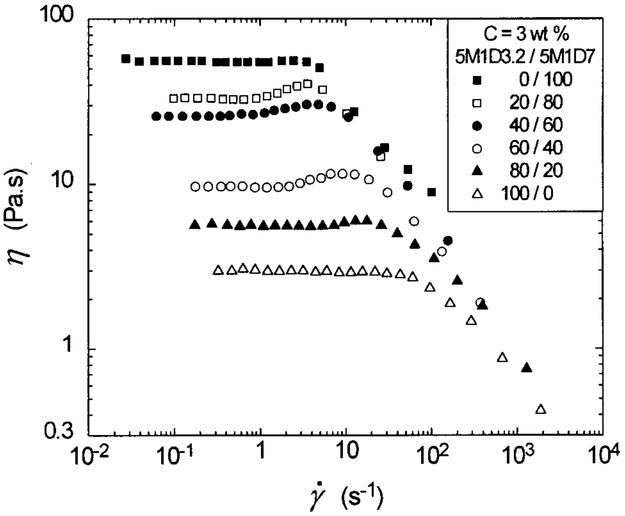

Figure 9. Viscosity versus shear rate for various compositions of aqueous solutions of an entangled HMPAM mixture.

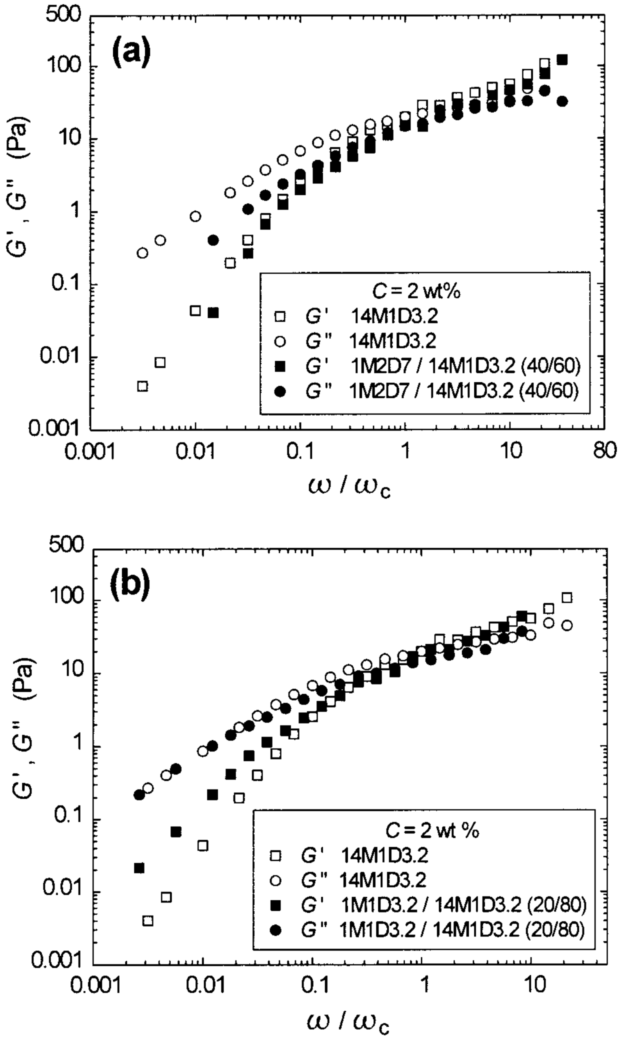

Figure 10. Examples of superposition of the viscoelastic spectra under an horizontal shift for aqueous solutions of 2 wt % HMPAM mixtures: (a) $\omega_{c,2}/\omega_{c,1} = 1.4$; (b) $\omega_{c,2}/\omega_{c,1} = 2.5$.

Table 4. Plateau Modulus and Zero-Shear Viscosity of 3 wt % 5M1D5/P (80/20) Mixtures[a]

	P			
	1PAM	1M1D3.2	1M2D3.2	1M2D7
G_0 (Pa)	18	25	37	50
η_0 (Pa·s)	6.5	9.4	12.4	12.4

[a] For a 2.4 wt % solution of pure 5M1D5: G_0 = 18 Pa and η_0 = 10 Pa·s (calculated from experimental data and power laws of the concentration).[6]

Table 5. Plateau Modulus and Zero-Shear Viscosity of 2 wt % 14M1D3.2/P (80/20) Mixtures[a]

	P		
	1M1D3.2	1M2D3.2	1M2D7
G_0 (Pa)	3	5	7
η_0 (Pa·s)	14	8	22

[a] For a 1.6 wt % solution of pure 14M1D3.2: G_0 = 10 Pa and η_0 = 30 Pa·s (calculated from experimental data and power laws of the concentration).[6]

it is not possible to superpose simultaneously $G'(\omega)$ and $G''(\omega)$ with the same translation of ω as illustrated by the data reported in Figure 10a, which compares the viscoelastic spectra of a 2 wt % 14M1D3.2 pure sample and of a 2 wt % 1M2D7/14M1D3.2 (40/60) mixture. In this mixture, the 14M1D3.2 sample forms an entangled matrix at 1.2 wt % concentration diluted by the low molecular weight sample. Similar results are obtained for the mixture of 14M1D3.2 with another HMPAM of low M_w (Figure 10b).

As a general rule, for systems with entangled and unentangled chains, the plateau modulus of the mixture is depressed with respect to that of the pure entangled system at the same overall concentration. This is shown in Table 4, which gives the G_0 values for 3 wt % mixtures in the ratio 80/20 for a HMPAM with $M_w \approx$ 450 000 (5M1D5) and a PAM or different HMPAM with $M_w \approx$ 140 000. The 5M1D5 sample forms an entangled matrix at a 2.4 wt % concentration, that is, above C_T = 2 wt %. At this concentration, the polymer chains with $M_w \approx$ 140 000 are unentangled, since the corresponding C_T is 5 wt %, but still above C_η ($C_\eta \approx$ 0.8 wt %). The results of Table 4 show that in that case the PAM acts as a simple diluent since the value of G_0 for the PAM/5M1D3.2 mixture is that of the value of the pure 5M1D3.2 solution at 2.4 wt %. However, if the low molecular weight compound is associating, the modulus increases, due to the formation of bridges between the two unlike copolymers. This shows that at the matrix concentration (2.4 wt %), which is slightly above C_T, the cross-links due to the hydrophobic associations still play a role, and the entanglements are not totally dominant. The zero-shear viscosity η_0 follows the same trend as the plateau modulus (cf. Table 4).

The behavior becomes even more complex for systems of lower overall concentration. Table 5 gives the values of G_0 and η_0 for 2 wt % mixtures in the ratio 80/20 for a HMPAM with $M_w \approx$ 1400 000 (14M1D3.2) and a PAM or different HMPAM with a $M_w \approx$ 140 000. The 14M1D3.2 sample forms a matrix at C = 1.6 wt % in which is diluted the HMPAM of lower molecular weight. It can be seen that the G_0 and η_0 values are both smaller than those of the pure 1.6 wt % 14M1D3.2. This can be explained by the fact that the concentration considered is not much larger than the C_η of the polymer with $M_w \approx$ 140 000 ($C_\eta \approx$ 0.8%). Therefore, the sizes of the corresponding chains are approximately that of the mesh size of the semidilute solution of long chains (cf. Figure 11). The former chains will tend to make cross-links, some intramolecular and others with the neighboring strands of the mesh of the long chains, but they will not contribute to the overall elasticity of the system.

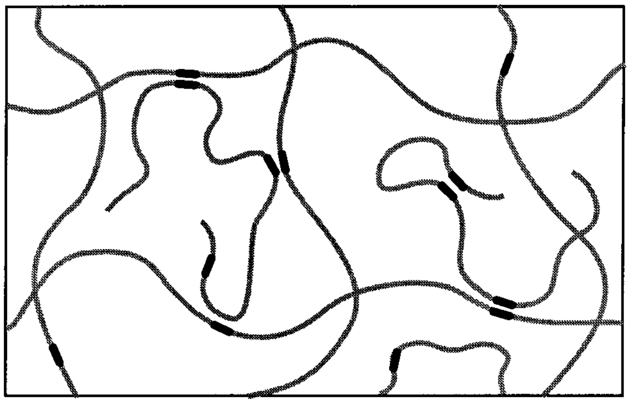

Figure 11. Schematic representation for a mixture containing small HMPAM chains embedded in a matrix of long entangled HMPAM chains.

Even more, they will decrease the number of cross-links between the long chains by occupying some sites located on these chains.

One can also involve another effect linked to a local segregation between two polymers that differ strongly by their molecular weight and/or their hydrophobic characteristics. Such an effect favors the formation of intramolecular links, resulting in lower values of the average plateau modulus and zero-shear viscosity.

A lowering in the viscosity associated with a trend toward phase separation was indeed confirmed by experiments performed on HMPAM/PAM undergoing a macroscopic phase separation (cf. "Phase Diagrams" Section). For some samples, the kinetics of phase separation is very long, sometimes a week or more. It is then possible to perform experiments at the very early stage of the process on systems that are transparent and apparently homogeneous. The viscosity is found much lower than that of the pure HMPAM solution. This trend to phase separation explains the aging phenomena previously reported in the case of samples with a high compositional heterogeneity for which a slow but large decrease of the thickening properties occurs within a few days.[27]

Unentangled Systems. These systems are formed by mixing two HMPAM at a concentration smaller than the entanglement concentration of each of the polymers. In some cases, they are characterized by a nonmonotonic variation of the zero-shear viscosity with the mixture composition. One example is given in Figure 12 showing the variation of the zero-shear viscosity with composition for a 2 wt % mixture of two HMPAM with similar molecular weights but different [H] and N_H (5M1D5/5M2D3.2). It can be seen that the viscosity of the mixture is always less than that of the two pure samples. Such a behavior occurs for unentangled mixtures with very different hydrophobic characteristics. The more plausible explanation is again a slight trend toward segregation between polymers of unlike hydrophobic characteristics. In the example of Figure 12, the difference between the two HMPAM is the spacing between the hydrophobic blocks along the chains and the block length. This mismatch between the block spacing might result in a microphase separation. If this is true, one expects that improving the effective compatibility of the HMPAM should reduce or even suppress this effect. In fact, it was found that for more compatible mixtures (same [H] and N_H) the zero-shear viscosity follows a monotonic variation with the composition. An example is given in Figure 13 showing the results obtained for 1 and 2 wt % mixtures of two HMPAM with [H] = 1 mol %, $N_H = 3.2$, and molecular weights equal to 420 000 and 115 000, respectively. Furthermore, the zero-shear viscosity follows a power law of the number-average molecular weight M_n calculated from the mixture composition and weight-average molecular weight M_w of the copolymers, assuming a polydispersity index $M_w/M_n \approx 2$ for each of the copolymers.[6] The exponent of the power law increases notably with the concentration (Figure 14).

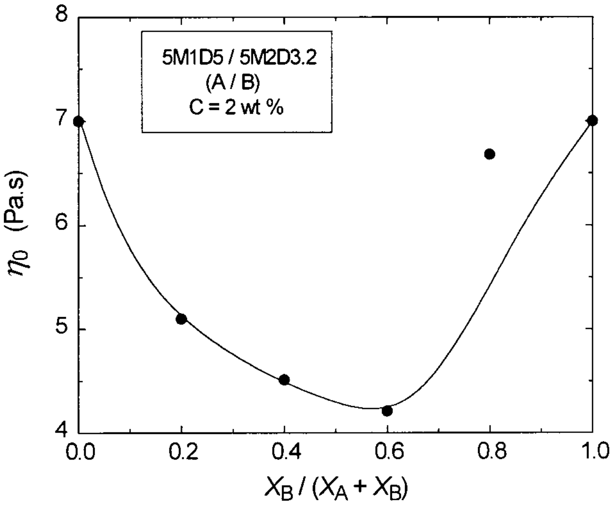

Figure 12. Zero-shear viscosity versus composition for aqueous solutions of an unentangled HMPAM mixture.

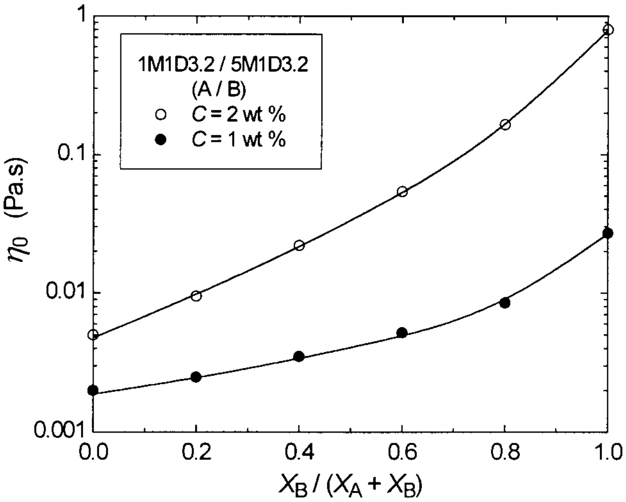

Figure 13. Zero-shear viscosity versus composition for aqueous solutions of an unentangled HMPAM mixture at two concentrations.

The nonlinear viscoelastic experiments provide also a confirmation of the picture of nonhomogeneous interpenetrated mixtures. In previous experiments on pure HMPAM solutions,[6,16] it was shown that, in the range of concentrations extending approximately from C_η to C_T, the solutions exhibited a strong shear thickening at a critical shear rate $\dot{\gamma}_C$ followed by the classical shear thinning. This shear thickening is considered as the signature of the presence of intramolecular cross-links between the associating blocks.[16,24-26] Parts a and b of Figure 15 show the variation of the apparent viscosity versus shear rate for 1 wt % mixtures of a $M_w = 2 \times 10^6$ HMPAM (20M1D3.2) with a $M_w \approx 160\,000$ HMPAM (1M2D7) or $M_w \approx 450\,000$ HMPAM (5M1D5), respec-

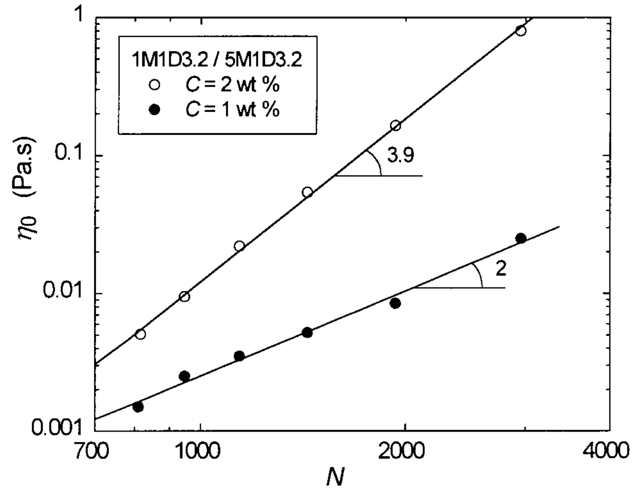

Figure 14. A log−log plot of the zero-shear viscosity versus the average degree of polymerization for aqueous solutions of an unentangled HMPAM mixture at two concentrations (same system as in Figure 13).

tively. The compositions of the mixtures 20M1D3.2/(5M1D5 or 1M2D7) were varied from 100/0 to 0/100. The C_T value for a polymer with $M_w = 2 \times 10^6$ is ≈0.6 wt % so that in the composition range extending from 100/0 to 60/40 this polymer forms an entangled matrix in which the second polymer is diluted. For lower contents of 20M1D3.2, the system is unentangled. For the pure 20M1D3.2 system, one observes the classical shear-thinning behavior of entangled systems with a slight shear-thickening effect. However, as soon as the system is diluted by a low molecular weight HMPAM, the shear thickening becomes significant, no matter whether the system is unentangled (Figure 15a) or entangled (Figure 15b). The inverse critical shear rate is found to decrease continuously with the zero-shear viscosity. This behavior is quite similar to that observed for pure HMPAM solutions in the range $C_\eta \leq C \leq C_T$.

Conclusion

The results presented in this paper show that the phase behavior of solutions containing mixtures of an acrylamide-based multisticker copolymer with a homopolyacrylamide follows the same trends as the systems where the associating polymer is telechelic. In particular, the phase separation of the systems is favored by an increase of the overall polymer concentration and/or of the homopolymer content. The results are in qualitative agreement with the model proposed by Annable and Ettelaie based on the entropy changes due to the associations between the hydrophobic groups.[3,4]

The rheological study shows that the viscoelastic properties of the mixture depends strongly on the concentration regime investigated. In the case of two mutually entangled HMPAM copolymers of same molecular weight, the frequency dependence of the complex shear modulus is qualitatively the same as that of a solution of a pure HMPAM. The terminal time of the stress relaxation has a value between those of the two HMPAM forming the mixture. This is true even if the two HMPAM have hydrophobic blocks of different length. This suggests that the kinetics of the various cross-links susceptible to form can be characterized by an average lifetime, which in turn controls the terminal time. However, in the case of mixtures of strongly associating and weakly associating copolymers, the thickening efficiency as well as the elasticity of the transient network is reduced, likely due to a local segregation which is precursor of the phase separation phenomenon mentioned above.

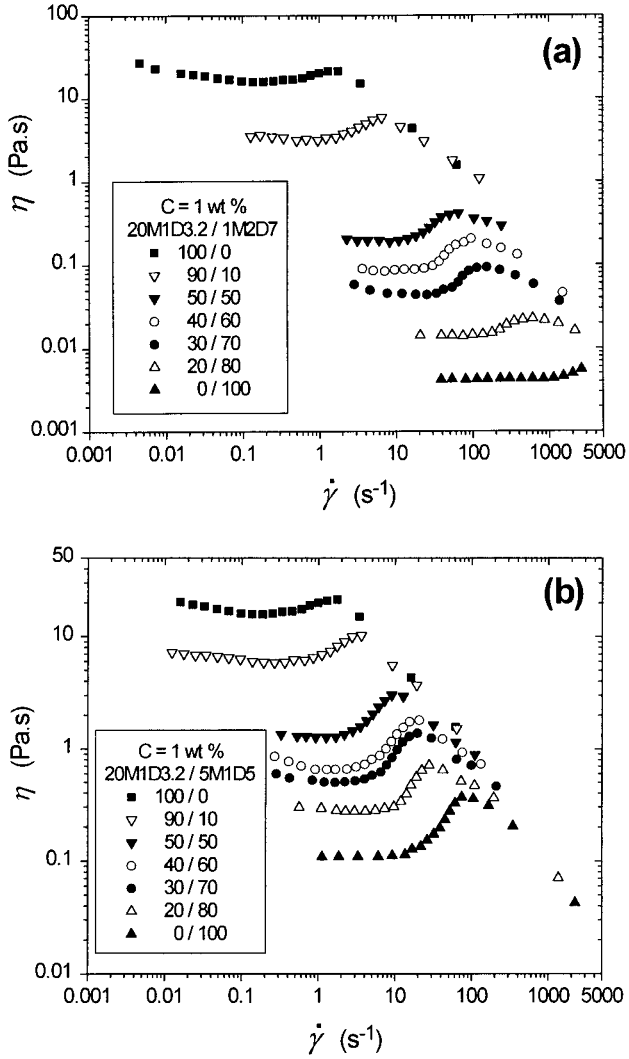

Figure 15. Viscosity versus shear rate for various compositions of aqueous solutions of HMPAM mixtures.

For mixtures made of a matrix of entangled long chains in which are embedded unentangled small HMPAM chains, one observes mainly a dilution effect which decreases the plateau modulus and the zero-shear viscosity, but still the extent of compatibility between the two copolymers seems to play a significant role.

Finally, for mixtures of two unentangled HMPAM, the rheological behavior will strongly depend on the hydrophobic characteristics of the two copolymers. A mixture of two HMPAM with same hydrophobe content, same block length, but different molecular weight will exhibit a zero-shear viscosity that varies monotonically between the values corresponding to each of the HMPAM. Moreover, the zero-shear viscosity follows a power law of the number-average molecular weight of the mixture with an exponent increasing with concentration. On the other hand, a mixture of two HMPAM of the same molecular weight but different hydrophobe characteristics exhibits a zero-shear viscosity that is significantly less than that of the two pure HMPAM. This again can be explained by assuming a local segregation of the two HMPAM.

From the different observations reported above, one can infer that the polydispersity in either molecular weight or microstructure does not play an important role on the rheological behavior of multisticker HMPAM. This holds as long as there is not in the system any homopolymer or any weakly associating copolymer. The presence of the latter may modify the properties of the system because of local segregation or even macroscopic phase separation. On the contrary, no synergetic effects are observed when mixing two HMPAM.

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