ELSEVIER

PII: S0032-3861(97)00393-5

Associating behaviour of polyacrylamides hydrophobically modified with dihexylacrylamide

Edgar Volpert†, Joseph Selb and Francoise Candau*
Institut Charles Sadron (CRM), 6 rue Boussingault, 67083 Strasbourg Cedex, France
(Revised 24 April 1997)

Polyacrylamides hydrophobically modified with a small amount of dihexylacrylamide (HMPAM) have been prepared by means of an aqueous micellar polymerization technique. This process leads to copolymers in which the hydrophobic molecules are randomly distributed as blocks in the acrylamide backbone. Keeping constant the hydrophobe level (1 mol%), the length of the blocks was adjusted by varying the surfactant content used in the synthesis, i.e. by varying the number of hydrophobes per micelle, N_H. The resulting copolymers are homogeneous in composition, but have a different microstructure (blockiness). The rheological properties of the samples in aqueous solution have been investigated as a function of polymer concentration, polymer conversion, temperature and in the presence of surfactant, using steady flow and oscillatory experiments. The hydrophobic modification of the polyacrylamide backbone induces a slowing down of the reptation movement of the polymer chains. The results stress the major role of the hydrophobe distribution in the copolymer for a good control of the thickening efficiency of associating HMPAM. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: associating polyacrylamides; micellar polymerization; water-soluble polymeric thickeners)

INTRODUCTION

Water-soluble polymers modified with a small amount of hydrophobic groups have become of great interest in recent years[1–4]. In aqueous solution, intermolecular hydrophobic interactions form above a certain polymer concentration, which enhances dramatically the viscosity. Thereby, these polymers exhibit particular rheological properties in solution, due to the reversible dissociation process of the physical links under shear, and this is of great technological interest, especially for tertiary oil recovery and latex paint systems.

Hydrophobically modified polyacrylamides (HMPAM) are an important type of associating polymers. One method to copolymerize acrylamide (AM) with a hydrophobic comonomer is a free radical micellar polymerization technique in which the hydrophobe is solubilized into micelles dispersed in a water continuous medium. This micellar process was shown to be well suited for the preparation of polymers with improved thickening properties[5–13]. An attractive feature was the possibility of controlling the copolymer microstructure by varying the number of hydrophobes per micelle, N_H. It was shown by several authors that the high density of the hydrophobic monomers in the micelles favours their incorporation as blocks in the polymer backbone[11,14–21]. Hence, the copolymer properties are strongly dependent on the hydrophobe/surfactant ratio during the synthesis, i.e. the number of hydrophobes per micelle. However, a major problem related to this process was the increased reactivity of the hydrophobic monomer when solubilized in the

micelles. It was reported by Valint et al.[22] using N-(4-butylphenyl)acrylamide as the hydrophobic monomer and by our group[23] using N-(4-ethylphenyl)acrylamide that the process causes a drift in copolymer composition. The hydrophobic comonomer is consumed more rapidly than acrylamide, and therefore the hydrophobe content of the polymer chains decreases with conversion, leading to relatively heterogeneous polymer samples. It was then difficult to draw definite conclusions about the influence of N_H on the rheological properties because of the sample heterogeneity. In a recent paper[13] we showed that the drift in composition is not a general characteristic of the micellar copolymerization process. We could demonstrate that the increased reactivity of the hydrophobic comonomer caused by its solubilization within micelles only occurs in the case of N-monosubstituted acrylamides. The use of N,N-disubstituted acrylamide derivatives allows one to suppress the drift in composition whatever the number of hydrophobes per micelle. Based on solubility measurements and literature data, we were able to propose a mechanism for the radical micellar copolymerization process which explains the different behaviour of mono- and disubstituted acrylamides[13,24].

An additional problem arises from the difficulty in preparing copolymers with both high associativity and good water solubility. We showed that this can be attained by using dibranched comonomers such as N,N-dihexyl-acrylamide (DiHexAM)[13]. The use of this compound leads to homogeneous samples having strong associative properties and a good water solubility.

In this work, we have studied the rheological properties ofassociating polyacrylamides prepared by micellar copolymerization and containing DiHexAM as the hydrophobic comonomer. In particular we have looked at the effect of the hydrophobe distribution, i.e. the N_H value, on

Table 1 Characteristics of the polymers

| Polymer[a]	$[H]_i$ (mol%)[b]	SDS (wt%)[c]	N_H[d]	Conversion (wt%)	$[H]_P$ (mol%)[e]	M_w ($\times 10^{-6}$)
PAM	—	3	—	92	—	2.5
1DH1	1	7.5	1	96	1.1	1.6
1DH1.9	1	4	1.9	84	1	2.7
1DH2.7	1	3	2.7	85	1.1	2.2
1.5DH2.7	1.5	4.3	2.7	86	1.3	2.0
1DH3.2	1	2.5	3.2	73	1.1	2.2
1DH3.2L	1	2.5	3.2	26	1	2.4

[a]The sample code refers to the hydrophobe level and the value of N_H (see Experimental section). The suffix L corresponds to a low conversion sample.
[b]Initial hydrophobe concentration in the monomer feed.
[c]Surfactant concentration used in the synthesis.
[d]Number of hydrophobes per micelle in the synthesis.
[e]Hydrophobe content in the copolymer.
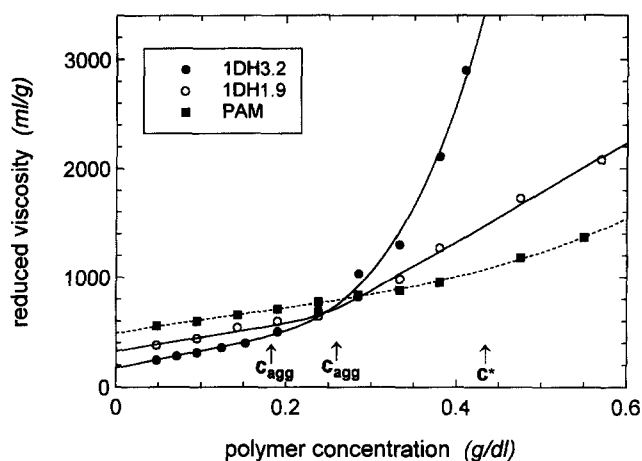
Figure 1 Reduced viscosity as a function of polymer concentration for two AM/DiHexAM copolymers with the same hydrophobe content (1 mol%) and different blockiness ($N_H = 1.9$ and 3.2) and for a homopolyacrylamide (shear rate $\dot{\gamma} 10 \text{ s}^{-1}$; $T = 25°C$)

the rheological copolymer properties. The dependence of the solution viscosity on polymer concentration and shear rate as well as the change in the viscoelastic properties caused by the incorporation of DiHexAM have been examined. A study of the rheological properties has also been performed as a function of polymer conversion, temperature and in the presence of surfactant. The possible reasons for the shear thickening effect observed at intermediate shear rates are discussed.

EXPERIMENTAL

Polymerization method

The synthesis of the samples has been described in detail in previous papers[11,13,23]. The associating copolymers are polyacrylamides hydrophobically modified with a low amount (1–1.5 mol%) of N,N-dihexylacrylamide (DiHexAM). They are obtained through a micellar radical copolymerization in water, with sodium dodecyl sulfate (SDS) as the surfactant and the potassium persulfate ($K_2S_2O_8$) as the initiator. The presence of the surfactant allows the solubilization of the hydrophobic monomer. The use of disubstituted acrylamides as comonomers was shown to lead to samples homogeneous in composition, that is with an average copolymer composition independent of the degree of conversion[13]. The sequence distribution of the hydrophobic monomer in the copolymer chain depends mainly on the initial number of hydrophobic monomers per

micelle, N_H, calculated as follows:

$$N_H = \frac{[M_H]}{([SDS] - CMC)/N_{agg}}$$

where $[M_H]$ is the initial molar concentration of DiHexAM, $[SDS]$ the molar surfactant concentration, CMC its critical micellar concentration and N_{agg} its aggregation number ($CMC_{SDS} = 9.2 \times 10^{-3}$ mol l^{-1} and $N_{agg} = 60$ at the polymerization temperature of 50°C[11]). At high surfactant concentration, i.e. $N_H \leq 1$, the hydrophobes are assumed to be singly and randomly distributed in the copolymer backbone. Keeping constant the hydrophobe level and decreasing the surfactant concentration leads to an increase in N_H which results in a blocky distribution of the comonomer. The presence of SDS produces a decrease in the molecular weight of the polymers[11,23]. Therefore, the homopolyacrylamide (PAM) was also synthesized in the presence of surfactant, allowing a meaningful comparison of modified and unmodified samples. The characteristics of the polymers are given in *Table 1*. The molecular weight of all polymers has been determined by light scattering in formamide[23], and the composition of copolymers by ^{1}H NMR in D_2O as previously described[13].

The sample code of the copolymers refers to the content of the hydrophobic comonomer and to the N_H value. For example, IDHI.9 stands for a copolymer containing 1 mol% of DiHexAM and synthesized with a number of hydrophobes per micelle equal to 1.9.

Rheological measurements

Polymer solutions were prepared by swelling the polymer in deionized water for 1 day, and then gently stirred for 7 days. Copolymer solutions at the highest concentrations ($C_p \geq 0.8$ wt%) were very viscous and were heated up to 40°C for 15 min to remove bubbles. For the study of polymer/surfactant mixed systems, appropriate amounts of SDS (Kodak, 99%) were directly added to the polymer solutions and the mixtures were homogenized by stirring for 1 day.

Viscosity experiments at low concentrations ($C_p \leq 0.6$ wt%) were performed on a Contraves LS 30 low-shear rheometer at 25°C. All other experiments were conducted with a Haake RS100 controlled stress rheometer equipped with a cone-plate geometry (diameter 35 mm, angle 1°) or a double gap concentric cylinder geometry (inner/outer radii 18/21.4 mm and 17.75/21.7 mm for the rotor and stator, respectively, length 55 mm), at 25°C unless otherwise noted. All flow curves were measured by increasing the shear stress σ by regular steps and waiting at each step
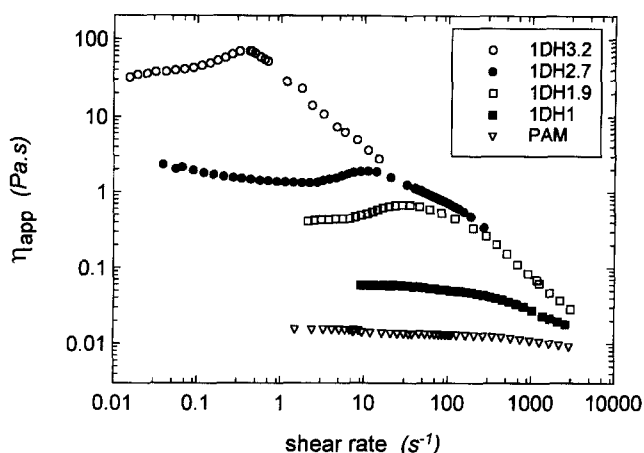
Figure 2 Apparent viscosity as a function of shear rate for AM/DiHexAM copolymers with the same hydrophobe content (1 mol%) and different blockiness (N_H = 1, 1.9, 2.7, 3.2), and for a homopolyacrylamide. Polymer concentration Cp = 1 wt%; T = 25°C

Table 2 Intrinsic viscosity and Huggins coefficient for different polymers in aqueous solution

Polymer	M_w($\times$ 10^{-6})	$[\eta]$ (ml g^{-1})	$[\eta]_{calc}$ (ml g^{-1})^a	k_H
PAM	2.5	530	585	0.4
1DH1	1.6	340	420	0.9
1DH1.9	2.7	330	620	1.2
1DH3.2	2.2	175	530	4.7

^{a}Calculated using the relationship $[\eta] = 9.33 \times 10^{-3} M_w^{0.75}$ established for PAM[66].

until equilibrium was attained. The shear rate $\dot{\gamma}$ ranged from 0.1 to to 2900 s^{-1}, depending on the viscometric behaviour of the sample. In some cases it was not possible to scan the shear stress over a large range by increasing progressively the shear stress, since a slight increase in stress caused a large jump in shear rate. To overcome this problem, we used the controlled rate mode of the rheometer, which permitted us to scan the whole shear rate range without large gaps. In all cases, we checked that the curves measured in the controlled stress and the controlled rate modes were well superposed. For some very viscous samples (for example 1DH3.2 in *Figure 2*), the data recorded at the highest shear rate are questionable and have been discarded because of a possible slipping effect between the sample and the measuring system. The dynamic measurements were conducted with a frequency ω of 0.04–100 rad s^{-1} (i.e.~1.6 $\times$ 10^{-3}–16 Hz). All measurements were made within the linear viscoelastic region, i.e. under frequencies and strains for which the modulus is independent of strain.

For both geometries, the solution was loaded into the rheometer, and sufficient time (about 20–25 min) was allowed for the stresses to relax and to attain thermal equilibrium. In all the experiments, the measuring system was surrounded by a solvent trap to prevent evaporation of water.

RESULTS AND DISCUSSION

Influence of the microstructure

The incorporation of a hydrophobic monomer into a water-soluble polymer leads to two main effects. In the dilute regime where the polymer coils are isolated from each other, the hydrophobic parts can interact intramolecularly,

while in the semi-dilute concentration regime, intermolecular hydrophobic interactions become predominant.

Viscosifying behaviour. The influence of the N_H value, i.e. the hydrophobic block length on intra- and intermolecular interactions is illustrated in *Figure 1*. The reduced viscosity η_{red} is plotted as a function of polymer concentration C_p for two HMPAM samples (IDH3.2, IDHI.9) with the same DiHexAM content but different hydrophobe distributions, and for the corresponding homopolyacrylamide (PAM). At low polymer concentrations the viscosity of the HMPAM is reduced with respect to that of PAM due to intramolecular interactions resulting in a collapse of the chain. This effect is enhanced by increasing the length of the hydrophobic blocks. Above a 'critical' concentration which depends on the sample, one observes an upward curvature in the reduced viscosity. The viscosity increase becomes more pronounced with increasing the hydrophobic block size and shows up at lower concentrations. The upturn of the viscosity in the case of the homopolymer is due to the onset of the coil overlap and is therefore related to the molecular size. In this case, the 'critical' concentration can be identified as C^*, i.e. the chain overlap concentration. The viscosity upturn observed for both HMPAM cannot be attributed to a chain overlap since the samples are within the same range of molecular weights. The viscosity increase is a consequence of the formation of aggregates caused by hydrophobic intermolecular associations. Therefore, the concentration at which the viscosity upturn occurs can be identified as a critical aggregation concentration C_{agg}, which is lower than the coil overlap concentration[8,9,20,25–31].

The intrinsic viscosity $[\eta]$ and the Huggins coefficient k_H of the different polymers calculated from the data in the linear regime are reported in *Table 2*. The experimental values of $[\eta]$ have been compared with those calculated for homopolyacrylamides of equal molecular weight. For all HMPAM samples, $[\eta]$ is lowered with respect to the corresponding homopolyacrylamide, and an increase in N_H, i.e. an increase in the hydrophobic block size, leads to a decrease in the coil size. Simultaneously, the Huggins coefficient k_H becomes greater, indicating a lowering of the solvent quality, in good agreement with the behaviour often observed for associating polymers in dilute solution[7,11,26,30,32–36]. Note, however, that for other associating polymers, increasing values of k_H have been observed while $[\eta]$ remained nearly constant or even increased[8,9,28,34,37]. This behaviour was attributed to the presence of polymolecular associations that may subsist at low polymer concentrations. As both intramolecular and intermolecular effects coexist, one of these effects may outweigh the other, leading to lower or higher $[\eta]$ depending on the system investigated (nature and content of the hydrophobe, compositional heterogeneity, etc.).

Steady flow experiments

In *Figure 2* is reported the shear rate dependence of viscosity for four different polyacrylamides modified with 1 mol% of DiHexAM. The curve of the homopolymer is shown for comparison. At low shear rates, all the samples show a higher viscosity than the unmodified polymer and the viscosity increases with increasing N_H. The influence of N_H on the rheological properties was already observed for other associating polyacrylamides prepared by micellar copolymerization[11], but in this case, the variation of N_H was accompanied by a modification of the compositional heterogeneity. The results obtained here with

AM/DiHexAM copolymers are more relevant since the samples are homogeneous in composition. Note that even 1DH1 sample exhibits improved thickening properties, in spite of the fact that it has a lower molecular weight than homopolyacrylamide and that the hydrophobes are randomly and singly distributed ($N_H = 1$). This result shows the strong efficiency of DiHexAM as the hydrophobe. We previously reported that such strong associative properties cannot be obtained by using single chain hydrophobes[13]. Again, it is noteworthy that the samples presented in *Figure 2* have the same hydrophobe content but different block sizes. Increasing N_H amounts to augmenting the size of the hydrophobic blocks while decreasing their number. Therefore, it can be concluded that the size of the hydrophobic blocks is more effective for the associative properties than their number. It is somewhat surprising to have such a large difference in viscosity between polymers 1DH2.7 and 1DH3.2. The close values of N_H should lead to relatively similar polymer structures. This difference might be due to a strong non-linear increase of the associative properties with N_H. At higher shear rates, copolymers with $N_H > 1$ show a shear thickening effect followed by shear thinning. This effect is shifted to lower shear rates when N_H increases. It can be interpreted by a change of intra- to intermolecular interactions under shear. This point will be discussed later. At the highest shear rates ($\dot{\gamma} \sim 2900$ s^{-1}) copolymer samples still present a higher viscosity than the homopolymer. This means that a complete rupture of the hydrophobic associations will occur above the accessible shear rate range.

Linear viscoelasticity. We have seen that the modification of polyacrylamide with DiHexAM leads to a strong viscosity increase of the polymer solutions. Similarly, the viscoelastic behaviour should be strongly influenced by the physical cross-links. The measurements have been performed in the linear viscoelastic regime. In this regime, no rupture of intramolecular associations occurs, as shown later. In *Figure 3* is reported the storage and the loss moduli (G' and G'') of the homopolyacrylamide and IDHI.9 and IDH3.2 samples. The presence of the hydrophobe increases both moduli and shifts the relaxation spectra to lower frequencies. For the two modified copolymers, G' becomes larger than G'' at a certain frequency illustrating the importance of the elastic part. The crossing point G_c where $G' = G''$, cannot be observed for the homopolymer because of the limited accessible frequency range. The slopes of G' and G'' in the terminal zone for the polyacrylamide are 1.8 and 1, respectively. The value of G' which is smaller than the 'classical' value of 2 is presumably due to the low precision at this concentration. Note that slopes of 1 and 2 where found for G' and G'', respectively, at higher PAM concentrations (≥ 3 wt%). As for HMPAM samples, the slopes are found to be 1.5 and 1 for G' and G'', respectively.

The shift of the terminal zone to lower frequencies that is induced by the hydrophobic modification is a signature of a slowing down of the system dynamics. In the case of a maxwellian behaviour, a characteristic relaxation time τ_r can be estimated from the frequency ω_c corresponding to the crossing point $G_c(\tau_r = 1/\omega_c)$. The results calculated according to this procedure are reported in *Table 3*. An exact value of τ_r cannot be obtained for the homopolyacrylamide because of the limited frequency range. It can, however, be concluded that the dynamics are slowed down by about a factor 10 for the sample 1DH1.9 and by a factor 100 for the sample IDH3.2. This is in agreement with the shift of the
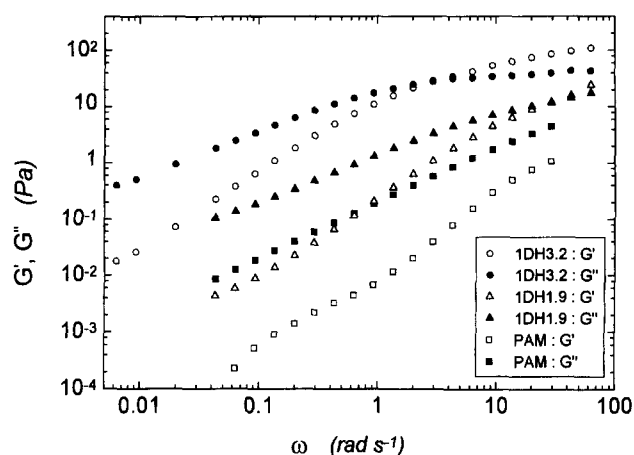
Figure 3 Storage modulus G' and loss modulus G'' as a function of frequency for two AM/DiHexAM copolymers with the same hydrophobe content (1 mol%) and different blockiness ($N_H = 1.9$ and 3.2), and for a homopolyacrylamide ($C_p = 2$ wt%; shear stress $\sigma = 1$ Pa; $T = 25°C$)
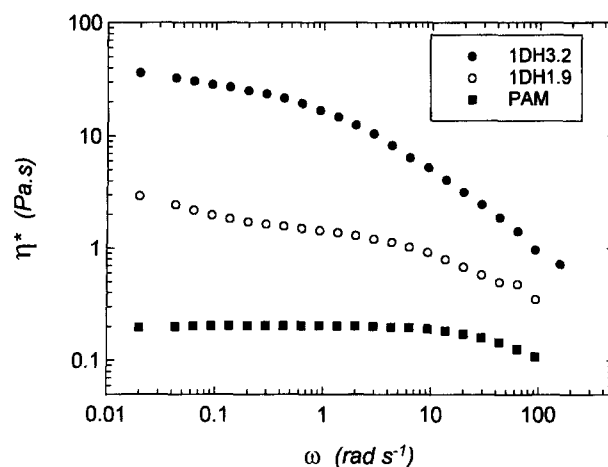
Figure 4 Complex viscosity η^* as a function of frequency for the polymers IDH3.2, IDHI.9 and PAM. The curves have been calculated from the G' and G'' values given in *Figure 3*

Table 3 Characteristic relaxation times τ_r for different samples

Polymer	Concentration (wt%)	τ_r (s^{-1})
1DH3.2	2	0.3
1DH1.9	2	0.03
PAM	2	< 0.01
PAM	3	0.01
PAM	5	0.05

terminal zone by approximately the same factors compared to the homopolymer shown in *Figure 3*.

The complex viscosity $\eta^* = (G'^2 + G''^2)^{1/2}/\omega$ calculated for PAM, 1 DH 1.9 and 1DH3.2 polymers are reported in *Figure 4*. The homopolymer shows a 'newtonian' behaviour over nearly the whole frequency range. At high frequency, the decrease in viscosity corresponds to the viscoelastic relaxation related to the disentanglement of the chains. The evolution of the complex viscosity with frequency is completely different for HMPAM. At low frequencies, the viscosity is much higher and decreases slightly upon increasing frequency while beyond the relaxation frequency, one observes a steeper decrease. At the highest frequencies, the copolymers still show a higher viscosity

than the homopolymer indicating that the hydrophobic associations have not completely relaxed. It can be noted that the shape of the complex viscosity curves differs from that of the steady-shear flow curves. While a region of shear thickening is observed from flow experiments, an equivalent behaviour does not appears in the variation of the complex viscosity. Similar results were reported by Annable *et al.*[38].

To better understand the influence of the hydrophobic domains on the polymer behaviour, two parameters have to be taken into account: the slowing down of the reptation movement of the polymer chain and the number of additional cross-links due to the hydrophobic associations. A theory of 'sticky reptation' was proposed by Leibler *et al.*[39] which applies to this type of polymers. According to this theory, the relaxation of the polymer is governed by the reptation hindered by the hydrophobic associations. The resulting relaxation differs in two points from that of the unmodified polymer. The terminal zone is shifted to longer times, that means $\tau_d > \tau'_d$ where τ_d and τ'_d are the terminal times of the modified and the unmodified polymers respectively. Going to shorter times, i.e. to higher frequencies, the storage modulus G' reaches a first plateau which has the same value as that of the unmodified polymer solution at the same concentration; this plateau is due to entanglements only. At shorter relaxation times $t < \tau$, where τ is the lifetime of the associations, a second plateau arises which comes from the hydrophobic associations. The second plateau is followed by the relaxation of the Rouse-mode which is similar for both modified and unmodified polymers.

The accessible frequency range is probably too limited here to detect the life-time of the hydrophobic associations. Even the first plateau could not be visualized, which is in part due to the polydispersity of the samples. The presence of the hydrophobic sequences nevertheless causes a considerable shift of the terminal zone to lower frequencies illustrating the slowing down of the chain reptation. It would be interesting to make experiments at higher frequencies to see if the storage modulus reaches the same value for all samples. This would mean that the hydrophobic associations do not act as a type of additional entanglements and that the viscosity increase is exclusively due to the slowing down of the reptation dynamics as predicted by Leibler's model. Such a result was for example obtained by Pezron *et al.*[40] in galactomannan solutions cross-linked by borate ions.

Kesavan and Prud'homme[41] have studied polymers of the guar type cross-linked by borate ions. They subtracted the moduli measured for the unassociated polymer (i.e. in the absence of borate) from the moduli obtained in the presence of borate to isolate the relaxation processes resulting from borate associations. The authors found a maxwellian behaviour with a single time constant. We have performed the same procedure using the data reported in *Figure 3*. Subtracting the moduli of the homopolymer from the moduli of the modified polymer gave reduced moduli which differ merely from the unreduced curves. This means that the dynamics of the copolymers are almost completely governed by the hydrophobic associations.

Polymer–surfactant interactions

The effect of adding surfactant to semi-dilute solutions of hydrophobically associating polymers at surfactant concentrations equal to or less than its CMC has been reported by a number of authors[26,30,42–51]. In general the viscosity increases with the addition of surfactant to attain a
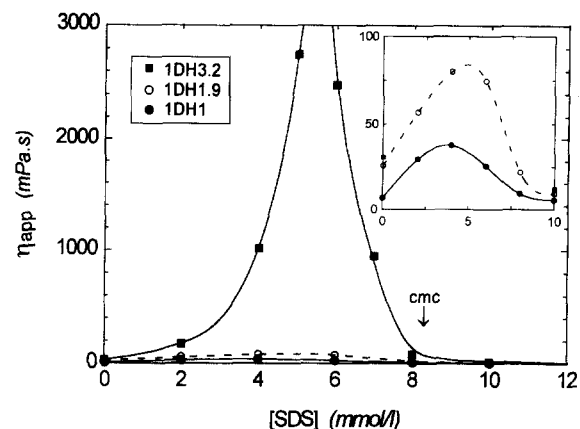
Figure 5 Apparent viscosity as a function of SDS concentration for AM/DiHexAM copolymers with the same hydrophobe content (1 mol%) and different microstructures. The inset corresponds to the same data with an enlarged scale ($C_p = 0.5$ wt%, $\dot{\gamma} = 10$ s^{-1}; $T = 25°C$)

maximum at a certain concentration. Increasing further the surfactant concentration causes a decrease in the viscosity down to the level of the pure polymer solution.

It is now accepted that this behaviour involves the formation of mixed micelles between the surfactant and the copolymer hydrophobe regions. At the highest surfactant concentration, i.e. above its CMC, the lowering of the viscosity can be unambiguously attributed to the disruption of the hydrophobic links between polymer chains because enough surfactant is present to solubilize each hydrophobe sequence within a single micelle. On the other hand, at low surfactant content, the mechanism responsible for the enhanced viscosity is still matter of discussion: the surfactant may promote the formation of additional interchain links[52] or/and contribute to strengthen the existing associations, i.e. to increase their lifetime[53,54].

In previous studies on associating polymers–surfactant interactions, the hydrophobic character of the polymer was varied by modifying the content or the nature of the hydrophobic groups. The effect of the hydrophobe distribution at a constant hydrophobe level was not reported so far. The interaction of surfactant with the hydrophobic microdomains should depend on the length of the hydrophobic sequences. In *Figure 5* is reported the viscosity as a function of SDS concentration for three copolymers (1DH1, 1DH1.9, 1DH3.2) with the same amount but a different distribution of the hydrophobic chains. A considerable effect of the surfactant is observed only for the polymer containing the largest hydrophobic blocks (1DH3.2). The viscosity is increased by about a factor 100 while the increase for the polymers with shorter hydrophobic sequences is limited to about a factor 3–5. At the highest surfactant concentrations, samples 1DH1.9 and 1DH3.2 show a lower viscosity than in the absence of SDS, while the viscosity of sample 1DH1 keeps the same value in both cases. It follows that the degree of association at this polymer concentration is quite weak for the sample with singly distributed hydrophobes (1DH1). The strong upturn of the viscosity observed for the sample 1DH3.2 can be explained by its much higher degree of association. This is consistent with the very strong associativity of this sample compared to that of sample 1DH2.7 (see *Figure 2*) and confirms that the degree of association augments non-linearly with the N_H value.

Data of *Figure 5* seem to indicate that the maximum in

viscosity is shifted toward higher surfactant content with increasing the hydrophobic block size. This means that a larger amount of surfactant is required to disrupt the associations between polymer chains. However, as the fraction of hydrophobic chains in the associated state is not known for the various samples, it is difficult to decide whether this shift is correlated to a change in the number or in the life-time of the hydrophobic interactions.

Influence of conversion

As for all other disubstituted acrylamides, the incorporation of DiHexAM remains constant with conversion during the micellar polymerization reaction[13]. This means the synthesis method leads to samples which are homogeneous in composition, although it does not necessarily imply that the microstructure is independent of conversion. A dependence of microstructure with conversion was recently inferred from steady-flow experiments performed on 1DH3.2L and 1DH3.2 samples taken at two degrees of conversion (26 and 73%, respectively)[13]. The viscosity at low shear rates was found to be much lower in the case of the high conversion sample (~40 Pa-s instead of ~300 Pa-s at $C_p = 1$ wt%) and the shear thickening region was broader (see *Figure 14* in Ref. [13]). This behaviour suggests that the mean block size decreases to some extent as the reaction proceeds and this leads to a broadening of the sequence length distribution.

The variation of the mean block length and its distribution should also influence the viscoelastic properties. In *Figure 6* is shown the evolution of the storage and the loss moduli as a function of frequency for 1DH3.2L and 1DH3.2 samples. Both samples show the same type of curves, but the relaxation spectra of the low conversion polymer (1DH3.2L) are shifted by about 1 decade to lower frequencies and the storage and loss moduli are larger. Furthermore, the value of G' attains a plateau at high frequencies and G'' shows a slight maximum at a frequency of about 1 rad s^{-1}. This maximum can be identified as the retarded terminal time τ_d predicted by Leibler's theory of sticky reptation. From the values of the crossing point G_c, it can be seen that the relaxation time τ_r for the sample 1DH3.2L is ~10 times higher than for 1DH3.2. This is in agreement with the shift of 1 decade observed between the terminal zones of the two samples.

The different shape of the moduli curves obtained for the two copolymers confirms the results previously reported in Ref. [13] using flow experiments, i.e. that at high conversion the mean size of the hydrophobic blocks is lower than at low conversion whereas the size distribution is broadened. As the low conversion sample 1DH3.2L is more efficient in slowing down the reptation dynamics than the high conversion sample 1DH3.2 with a larger number of smaller blocks, we can conclude that the associating properties are more influenced by the size of the hydrophobic blocks than by their effective number on the chain.

Temperature behaviour

The effect of temperature on the rheological behaviour of associating polymers is an important factor to be taken into account for applications as for example in oil recovery processes. It should be mentioned that only few studies[8,28,37,54-56] dealt with the associative behaviour as a function of temperature and the conclusions are still controversial. Some authors claim that an increase in temperature favours hydrophobic interactions[8,28,37], while the reverse situation is suggested by others[55].
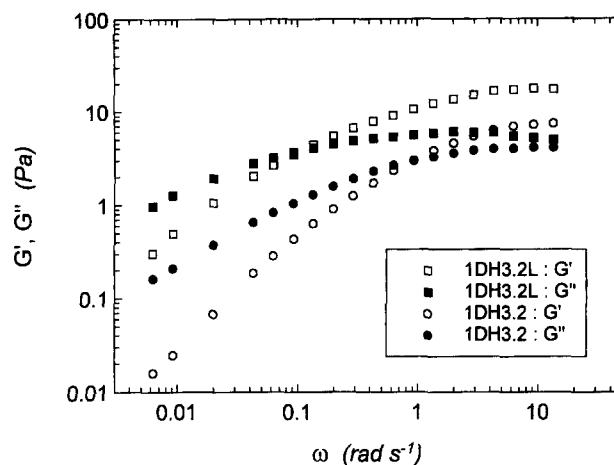
Figure 6 Storage modulus G' and loss modulus G'' as a function of frequency for two AM/DiHexAM copolymers synthesized with the same hydrophobe content (1 mol%) and same N_H (3.2) but taken at two different conversion levels: 1 DH3.2, 73% conversion; 1DH3.2, 73% conversion ($C_p = 1$ wt%, $\sigma = 1$ Pa; $T = 25°$C)
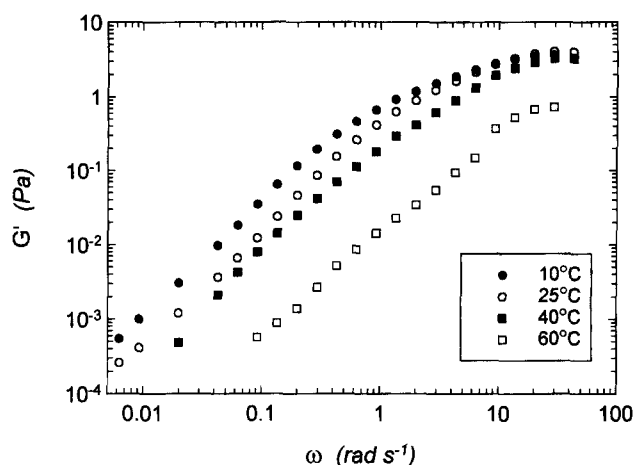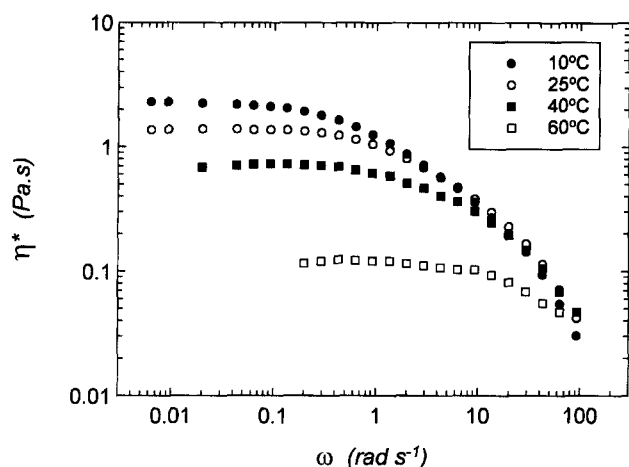

Figure 7 Storage modulus G' and loss modulus G'' as a function of frequency for the copolymer 1DH3.2L at different temperatures ($Cp = 0.75$ wt%, $\sigma = 0.5$ Pa)

Temperature effect was investigated with sample 1DH3.2L (stopped at low conversion) which is homogeneous both in composition and microstructure. While the relative viscosity $\eta_{rel} = \eta_{solution}/\eta_{solvent}$ of PAM solutions does not vary with temperatures[55], η_{rel} decreases steadily upon increasing temperature for the HMPAM samples. For exmple, for $C_p = 0.75$ wt%, the values of η_{rel} (measured at $\dot{\gamma} = 1$ s^{-1}) are equal to 3700, 1500 and 380 at 25, 40 and 60°C, respectively. This viscosity decrease is due to a diminution of the association degree, reflecting an augmentation in solubility of the hydrophobic moieties, in good agreement with previous results on acrylamide/ethylphenylacrylamide copolymers[55].

The storage modulus G' as a function of frequency at four different temperatures is reported in *Figure 7* for the copolymer 1DH3.2L. The loss modulus curves show the same aspect (not presented here). We must remark that the measurements at 60°C are less accurate because of the lower solution viscosity at this temperature and the large inertia correction at high frequencies. The terminal zone shifts to lower frequencies when decreasing the temperature. The shift becomes more pronounced in the high temperature range. The slopes in the terminal region where

Table 4 Characteristic relaxation times τ_r at different temperatures and the corresponding moduli G_c at $G' = G''$ (sample 1DH3.2L, $C_p = 0.75$ wt%)

T (°C)	τ_r (s⁻¹)	G_c (Pa)
10	0.4	1.5
25	0.2	1.9
40	0.09	2
60	< 0.02	—

Figure 8 Complex viscosity η^* as a function of frequency for the copolymer IDH3.2L at different temperatures ($C_p = 0.75$ wt%, $\sigma = 0.5$ Pa)

found to be 1.6 and 1 for G' and G'', respectively. For the first three temperatures, the moduli reach the same plateau value. This could suggest that the number of hydrophobic associations does not vary in this temperature range and that the decrease in thickening efficiency is only due to a shorter association life-time.

The characteristic relaxation times have been determined from the frequency at which $G'(\omega) = G''(\omega)$. The values are reported in *Table 4*. The observed decrease of the relaxation time upon increasing temperature indicates a decrease of the association life-time. This is in agreement with Leibler's model of sticky reptation which predicts that the terminal time τ_d is directly proportional to the average life-time of a hydrophobic sequence in the associated state.

Figure 8 shows the complex viscosity as a function of frequency at the four temperatures. For all temperatures a 'newtonian' plateau is observed at low frequencies while a decrease is observed when going to higher frequencies. In this representation, the displacement of the terminal zone to higher frequencies with increasing temperature is demonstrated by a broadening of the low frequency plateau.

In other studies on different associating systems (polyols–borax[40,41] and hydrophobically modified hydroxyethyllcellulose[54]), it has been shown that G' and G'' data taken at various temperatures could be combined to a single master curve according to the classical time–temperature superposition[57], with a temperature shift factor which obeysan Arrhenius law. In the case of the samples studied here, we found that the time–temperature superposition does not satisfactorily apply to the whole range of temperature investigated, and the shift factor does not show an Arrhenius temperature dependence. This can be ascribed to the strong decrease of the association degree at the highest temperature, as shown by the low values of viscosity and moduli.

Shear thickening effect

In *Figure 2* we have seen that copolymers with $N_H > 1$ exhibit a shear thickening at a shear rate which is a decreasing function of N_H. This phenomenon is immediately followed by shear thinning. The particular behaviour of viscosity enhancement with increasing shear has been known for many years for another class of associating polymers, namely ionomers in nonpolar organic solvents[58] and also with polyols–sodium borate systems[59]. In the case of hydrophobically associating polymers, the same phenomenom has been less often observed and investigated[7,13,60].

The shear thickening effect observed for associating polymers has been treated theoretically by a number of authors. The first theories by Witten and Cohen[61] and by Ballard *et al.*[62] conclude that the viscosity enhancement with increasing shear rates is due to a change from intra- to intermolecular interactions. The probability of binding to an associative group is proportional to the polymer concentration. According to this approach, the shear thickening effect should disappear with increasing concentration. This is in agreement with the results reported for various water-soluble associating polymers[7,13,59,60].

More recently, a somewhat different explanation was given by Wang[63] taking into account the temporary nature of the network. In this theory, it is assumed that not all the polymer chains are bounded to the hydrophobic clusters. A fraction of polymeric chains are dangling or even free and do not participate to the transient network formation. Under shear, free chains are incorporated into the network leading to a higher viscosity.

A quite different process for the shear thickening effect of non-associating systems has been suggested by Vrahopoulou and McHugh[64]. The increase in viscosity under shear is attributed to a supplementary energy dissipation resulting from the extension of the connected chains with a non-gaussian behaviour. In the case of physically cross-linked networks, Marrucci *et al.*[65] proposed two models also based on a non-gaussian behaviour of the chains stretched by the shear. In contrast with the previous theories, the shear thickening can be qualitatively predicted even if the number of effective stickers remains constant. In conclusion, it appears that the reasons for the shear-thickening behaviour are still controversial, although a change from intra- to interchain associations generally accounts for this effect.

The fact that copolymer 1DH1 does not show any shear thickening (see *Figure 2*) can be related to the low degree of intramolecular interactions compared to the other polymers. The viscometric measurements reported in *Table 2* show only a slight coil contraction with respect to that of the corresponding PAM. Consequently, one does not observe an increase in viscosity and the shear dependence shows a classical behaviour. Increasing the N_H value enhances the coil contraction evidenced by the decrease in intrinsic viscosity. The shear rate value at which the shear thickening occurs shows that the relaxation time of the hydrophobic associations augments with N_H.

In *Figure 9* is reported the viscosity-shear dependence for copolymers 1DH2.7 and 1.5DH2.7. Their difference in molecular weights is quite small (see *Table 1*). Both samples have the same microstructure, i.e. the same block size distribution, but the copolymer 1.5DH2.7 contains more hydrophobic sites. Both curves show the same shape and can be superimposed by a simple vertical shift. The shear
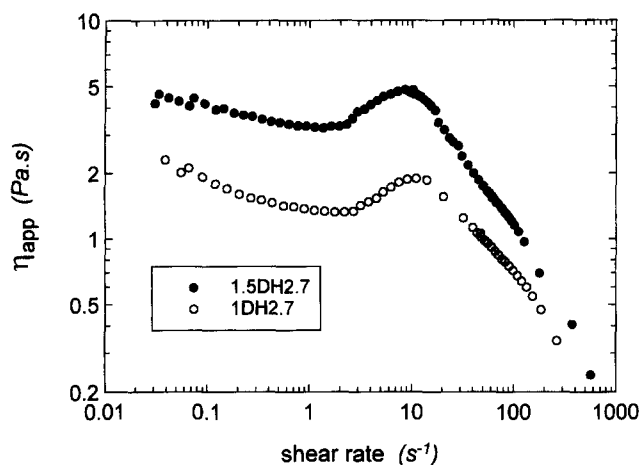
Figure 9 Apparent viscosity as a function of shear rate for two AM/DiHexAM copolymers synthesized with same N_H (2.7), but different hydrophobe levels (1 and 1.5 mol%) ($C_p = 1$ wt%; $T = 25°C$)
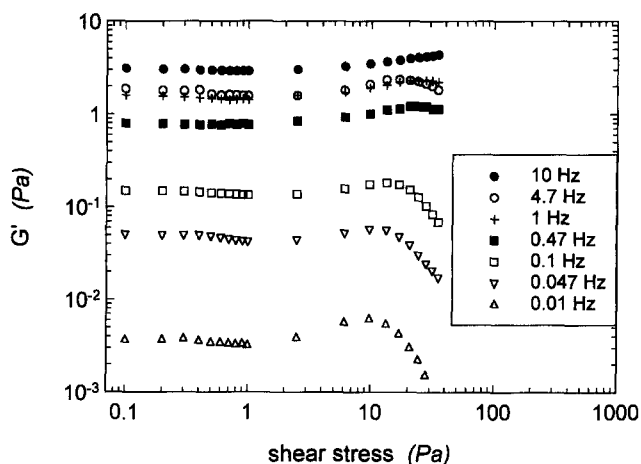
Figure 10 Stress dependence of the storage modulus G' for the copolymer 1DH3.2L at different frequencies ($C_p = 0.75$ wt%; $T = 25°C$)

thickening appears for both samples at the same shear rate value, and this could be an indication that the main factor controlling the intra–inter transition is the average length of the hydrophobic sequences.

However, one cannot entirely discard the possibility that the shear thickening is due to a non-homogeneous distribution of polymer chains with different microstructures. In this respect, it is noteworthy that a sample obtained at high conversion shows a broader shear thickening region than the sample stopped at low conversion degree (see *Figure 14* of Ref. [13]).

We have already mentioned that the measurements in the linear oscillatory regime show exclusively the dynamics of the intermolecular interactions. In *Figure 10* is reported the stress dependence of the storage modulus G' at different frequencies for copolymer 1DH3.2L. It has to be noted that the loss modulus G'' shows the same aspect (not presented here). For all frequencies, a linear behaviour is observed up to a stress of about 1 Pa. Increasing the stress further induces an upturn of the modulus and after having attained a maximum, the modulus drops. This can be interpreted in the same manner as for the shear thickening under flow. At weak stresses, the polymer coil does not deform and only the relaxation of the intermolecular jnctions is observed. Application of sufficiently high

stresses will then deform the chain structure. This induces a rupture of some intramolecular cross-links, subsequently forming intermolecular junctions and the modulus increases. At higher stresses the modulus drops, indicating a rupture of some intermolecular junctions. The maximum in *Figure 10* is shifted to higher stresses with increasing frequency, which amounts to decreasing the strain.

CONCLUSION

The results reported here provide useful information on the rheological behaviour of HMPAM prepared by micellar copolymerization. The samples consist of polyacrylamides modified with 1 mol% of dihexylacrylamide. The length of the hydrophobic blocks in the hydrophilic backbone was modified by varying the hydrophobe/micelle ratio, N_H, in the synthesis. The resulting samples exhibit therefore a different microstructure (blockiness). However, it is noteworthy that all the samples are homogeneous in composition, with an average copolymer composition independent of the degree of conversion, as opposed to those previously prepared by this process and thoroughly investigated. This makes it eventually possible to investigate the true properties of HMPAM and to provide a more appropriate description of their associative behaviour. Steady flow and oscillatory experiments have been used to study the rheological properties in aqueous solution as a function of various parameters such as polymer concentration, polymer conversion, temperature and in the presence of surfactant. The results clearly show that the hydrophobe distribution in the copolymer is the key parameter which controls the thickening ability of HMPAM: at constant hydrophobe level, the longer the blocks, the greater the thickening efficiency. For example, a variation of N_H from 1 to ~3 results in the spectacular enhancement of viscosity by 4 decades. The associating properties are indeed more influenced by the size of the hydrophobic blocks than by their effective number on the chain. Furthermore, the dynamics of the copolymers are essentially controlled by the hydrophobic interactions, with a slowing down of the reptation movement of the chains due to the hydrophobe incorporation. Increasing the temperature is seen to decrease the association degree, while addition of a certain amount of surfactant enhances drastically the viscosity—all these effects being tightly correlated to the length of the hydrophobic blocks. However, supplementary experiments are required to decide whether the observed effects arise from a change in the number or in the life-time of the hydrophobic interactions.

ACKNOWLEDGEMENTS

REFERENCES

1. Glass, J. E. (ed.), *Polymers in Aqueous Media: Performance through Association*. Advances in Chemistry Series, American Chemical Society, Washington, DC, 1989.

2. Shalaby, S. W., McCormick, C. L. and Butler, G. B., (ed), *Water-Soluble Polymers. Synthesis, Solution Properties and Applications.* ACS Symposium Series, American Chemical Society, Washington, DC, 1991.

3. Schulz, D. N. and Glass, J. E. (ed), *Polymers as Rheology Modifiers.* ACS Symposium Series, American Chemical Society, Washington, DC, 1991.

4. Glass, J. E. (ed.), *Hydrophilic Polymers. Performance with Environmental Acceptability.* Advances in Chemistry Series, American Chemical Society, Washington, DC, 1996.

5. Evani, S., European Patent 57 875, 1982.

6. Bock, J., Siano, D. B., Kowalik, R. M. and Turner, S. R., European Patent 115 213, 1984.

7. Bock, J., Siano, D. B., Valint, P. L. Jr and Pace, S. J., in *Water-Soluble Polymers. Synthesis, Solution Properties and Applications,* ed. S. W. Shalaby, C. L. McCormick and G. B. Butler. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 22, p. 411.

8. McCormick, C. L., Nonaka, T. and Johnson, C. B., *Polymer,* 1988, **29**, 731.

9. Flynn, C. E. and Goodwin, J. W., in *Polymers as Rheology Modifiers,* ed. D. N. Schulz and J. E. Glass. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 11, p. 190.

10. McCormick, C. L., Middleton, J. C. and Cummins, D. F., *Macromolecules,* 1992, **25**, 1201.

11. Hill, A., Candau, F. and Selb, J., *Macromolecules,* 1993, **26**, 4521.

12. Branham, K. D., Snowden, H. S. and McCormick, C. L., *Macromolecules,* 1996, **29**, 254.

13. Volpert, E., Selb, J. and Candau, F., *Macromolecules,* 1996, **29**, 1452.

14. Peer, W. J., in *Water-Soluble Polymers. Synthesis, Solution Properties and Applications,* ed. S. W. Shalaby, C. L. McCormick and G. B. Butler. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 20, p. 381.

15. Dowling, K. C. and Thomas, J. K., *Macromolecules,* 1990, **23**, 1059.

16. Branham, K. D., Middleton, J. C. and McCormick, C. L., *Polymer Preparations (American Chemistry Society, Division of Polymer Chemistry),* 1991, **32**(1), 106.

17. Kramer, M. C., Ezzell, S. A. and McCormick, C. L., *Polymer Preprints (American Chemistry Society, Division of Polymer Chemistry),* 1991, **32**(1), 106.

18. Ezzell, S. A. and McCormick, C. L., *Macromolecules,* 1992, **25**, 1881.

19. Ezzell, S. A., Hoyle, C. E., Creed, D. and McCormick, C. L., *Macromolecules,* 1992, **25**, 1887.

20. Branham, K. D., Davis, D. L., Middleton, J. C. and McCormick, C. L., *Polymer,* 1994, **35**, 4429.

21. Branham, K. D., Shafer, G. S., Hoyle, C. E. and McCormick, C. L., *Macromolecules,* 1995, **28**, 6175.

22. Valint, P. L. Jr, Bock, J., Ogletree, J., Zushma, S. and Pace, S. J., *Polymer Preprints (American Chemistry Society, Division of Polymer Chemistry),* 1990, **31**(2), 67.

23. Biggs, S., Hill, A., Selb, J. and Candau, F., *Journal of Physical Chemistry,* 1992, **96**, 1505.

24. Candau, F., Volpert, E., Lacik, I. and Selb, J., *Macromolecular Symposia,* 1996, **111**, 85.

25. Landoll, L. M., *Journal of Polymer Science, Polymer Chemistry Edition,* 1982, **20**, 443.

26. Tanaka, R., Meadows, J., Phillips, G. O. and Williams, P. A., *Carbohydrate Polymer,* 1990, **12**, 443.

27. Howard, P. R., Leasure, E. L., Rosier, S. T. and Schaller, E. J., in *Polymers as Rheology Modifiers,* ed. D. N. Schulz and J. E. Glass. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 12, p. 207.

28. Zhang, Y. X., Da, A. H., Butler, G. B. and Hogen-Esch, T. E., *Journal of Polymer Science, Polymer Chemistry Edition,* 1992, **30**, 1383.

29. Fonnum, G., Bakke, J. and Hansen, F. K., *Colloid Polymer Science,* 1993, **271**, 380.

30. Senan, C., Meadows, J., Shone, P. T. and Williams, P. A., *Langmuir,* 1994, **10**, 2471.

31. Jenkins, R. D., Bassett, D. R., Silebi, C. A. and El-Aasser, M. S., *Journal of Applied Polymer Science,* 1995, **58**, 209.

32. Gelman, R. A. and Barth, H. G., in *Water-Soluble Polymers: Beauty with Performance,* ed. J. E. Glass. Advances in Chemistry Series 213, American Chemical Society, Washington, DC, 1986, Chapter 6, p. 101.

33. Schulz, D. N., Kaladas, J. J., Maurer, J. J., Bock, J., Pace, S. J. and Schulz, W. W., *Polymer,* 1987, **28**, 2110.

34. Magny, B., Iliopoulos, I. and Audebert, R., *Polymer Communications,* 1991, **32**, 456.

35. Sinquin, A., Hubert, P. and Dellacherie, E., *Polymer,* 1994, **35**, 3557.

36. Picton, L., Merle, L. and Muller, G., *International Journal of Polymer Analysis and Characterization,* 1996, **2**, 103.

37. Hwang, F. S. and Hogen-Esch, T. E., *Macromolecules,* 1995, **28**, 3328.

38. Annable, T., Buscall, R., Ettelaie, R. and Whittlestone, D., *Journal of Rheology,* 1993, **37**, 695.

39. Leibler, L., Rubinstein, M. and Colby, R. H., *Macromolecules,* 1991, **24**, 4701.

40. Pezron, E., Ricard, A. and Leibler, L., *Journal of Polymer Science, Polymer Physics Edition,* 1990, **28**, 2445.

41. Kesavan, S. and Prud'Homme, R. K., *Macromolecules,* 1992, **25**, 2026.

42. Gelman, R. A., *International Dissolving Pulps Conference,* TAPPI, 1987. p. 159.

43. Sau, A. C. and Landoll, L. M., in *Water-Soluble Polymers. Synthesis, Solution Properties and Applications,* ed. S. W. Shalaby, C. L. McCormick and G. B. Butler. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 18, p. 343.

44. Lundberg, D. J., Glass, J. E. and Eley, J. E., *Journal of Rheology,* 1991, **35**, 1255.

45. Dualeh, A. J. and Steiner, C. A., *Macromolecules,* 1991, **24**, 112.

46. Winnik, F. M., Ringsdorf, H. and Venzmer, J., *Langmuir,* 1991, **7**, 905.

47. Biggs, S., Selb, J. and Candau, F., *Langmuir,* 1992, **8**, 838.

48. Magny, B., Iliopoulos, I., Zana, R. and Audebert, R., *Langmuir,* 1994, **10**, 3180.

49. Binana-Limbele, W., Clouet, F. and François, J., *Colloid Polymer Science,* 1993, **271**, 748.

50. Chang, Y., Lochhead, R. Y. and McCormick, C. L., *Macromolecules,* 1994, **27**, 2145.

51. Guillemet, F. and Piculell, L., *Journal of Physics and Chemistry,* 1995, **99**, 9201.

52. Aubry, T. and Moan, M., *Journal of Rheology,* 1996, **40**, 441.

53. Thuresson, K., Södennann, O., Hansson, P. and Wang, G., *Journal of Physical Chemistry,* 1996, **100**, 4909.

54. Guillemet, F., Thesis, Université Pierre et Marie Curie, Paris, 1995.

55. Biggs, S., Selb, J. and Candau, F., *Polymer,* 1993, **34**, 580.

56. Caritey, J. P., Thesis, Université de Rouen, 1994.

57. Ferry, J. D., *Viscoelastic Properties of Polymers,* 3rd ed. Wiley, New York, 1980.

58. Lundberg, R. D. and Duvdevani, I., in *Polymers as Rheology Modifiers,* ed. D. N. Schulz and J. E. Glass. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 9, p. 155.

59. Maerker, J. M. and Sinton, S. W., *Journal of Rheology,* 1986, **30**, 77.

60. Jenkins, R. D., Silebi, C. A. and El-Aasser, M. S., in *Polymers as Rheology Modifiers,* ed. D. N. Schulz and J. E. Glass. ACS Symposium Series, American Chemical Society, Washington, DC, 1991, Chapter 13, p. 222.

61. Witten, T. A. Jr and Cohen, M. H., *Macromolecules,* 1985, **18**, 1915.

62. Ballard, M. J., Buscall, R. and Waite, F. A., *Polymer,* 1988, **29**, 1287.

63. Wang, S. Q., *Macromolecules,* 1992, **25**, 7003.

64. Vrahopoulou, E. P. and McHugh, A. J., *Journal of Rheology,* 1987, **31**, 371.

65. Marrucci, G., Bhargava, S. and Cooper, S. L., *Macromolecules,* 1993, **26**, 6483.

66. Frangois, J., Sarazin, D., Schwartz, T. and Weill, G., *Polymer,* 1979, **20**, 969.