



# Effect of temperature on the viscoelastic behaviour of entangled solutions of multisticker associating polyacrylamides

Marie-Rose Caputo, Joseph Selb, Françoise Candau\*

*Institut Charles Sadron, 6 rue Boussingault, BP 40016, 67083 Strasbourg Cedex, France*

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## Abstract

The viscoelastic behaviour of polyacrylamides (PAM) hydrophobically modified with small blocks ( $\approx 3$  monomer units) of *N,N*-dihexylacrylamide (2 mol%) has been investigated in the entangled regime as a function of temperature by steady-flow and oscillatory experiments. The effect of temperature on the rheological behaviour of these systems was also investigated in the presence of surfactant. In both cases, the results were compared to those obtained for the unmodified analogue. The experimental data were analysed using a simple Maxwell model and the time-temperature superposition principle. The results indicate that the main effect of a change in temperature and/or addition of surfactant is to modify the lifetime of the physical crosslinks without changing their density, as inferred from a quasi-constant value of the plateau modulus. The comparison between the plateau moduli of the modified and unmodified systems shows unexpected higher values for the former systems.

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*Keywords:* Associating polymers; Rheological properties; Time-temperature superposition

## 1. Introduction

The incorporation of a few hydrophobic groups in a hydrophilic macromolecular chain results in systems with unique rheological characteristics in aqueous solution [1–7]. Above a certain polymer concentration, the hydrophobic moieties associate and build a transitory three-dimensional network. Recently, we have reported measurements of linear and non-linear viscoelasticity for aqueous solutions of multisticker polymer chains consisting of hydrophobically modified polyacrylamides (HMPAM), in which the number and length of the hydrophobic blocks could be adjusted in a controlled manner [8,9]. This was achieved by free radical copolymerization of acrylamide (AM) with a hydrophobic comonomer solubilised into micelles dispersed in an aqueous continuous medium [10]. An appropriate choice of the hydrophobic comonomer, the *N,N*-dihexylacrylamide (DiHexAM), allowed us to obtain samples homogeneous in composition with an average

copolymer composition independent of the degree of conversion [11].

The main conclusion drawn from the rheological studies performed on these samples was the existence of three distinct concentration regimes: (i) a dilute regime where the viscosity is essentially controlled by intramolecular interactions, (ii) a semidilute unentangled regime, dominated by intermolecular hydrophobic associations, and (iii) a semidilute entangled regime for which the viscoelastic behaviour can be described by a sticky reptation mechanism [12,13]. The results obtained in the latter case suggested that the dynamic properties are strongly dependent on the hydrophobic characteristics of the copolymer whereas the elasticity is mainly controlled by the density of entanglements and only depends on the polymer concentration.

A priori, the above conclusion could be comforted from the comparison between the elastic behaviour of entangled solutions of hydrophobically modified and unmodified polymers, respectively. If entirely controlled by the entanglements, the plateau modulus,  $G_0$ , which is proportional to  $k_B T \nu_e$  (where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\nu_e$  is the entanglement density), should then be the same for both materials.

\* Corresponding author. Tel.: +33-388-41-40-38; fax: +33-388-41-40-99.

*E-mail addresses:* [candau@ics.u-strasbg.fr](mailto:candau@ics.u-strasbg.fr) (F. Candau), [selj@ics.u-strasbg.fr](mailto:selj@ics.u-strasbg.fr) (J. Selb).

Furthermore, the quantity  $G_0/T$  should be independent on temperature for both modified and unmodified polymers.

Some additional information can also be given by studying the samples in the presence of a surfactant susceptible to bind to the hydrophobic blocks contained in the associating polymer. It is indeed well known that the interactions of hydrophobically modified water-soluble polymers with small surfactant molecules affect drastically their rheological behaviour [14–26]. In particular, experiments performed on semidilute solutions of HMPAM showed a strong increase of the terminal time of the stress relaxation at surfactant concentrations around its critical micelle concentration,  $CMC$ , whereas the plateau modulus was found to be constant over an extended range of surfactant concentrations [27].

In this paper, we report measurements of linear and non-linear viscoelasticity of HMPAM solutions in the entangled regime. The temperature dependences of the rheological parameters (terminal time, zero shear viscosity and plateau modulus) have been compared to those obtained for the unmodified parent polyacrylamide. The effect of the addition of surfactant (sodium dodecyl sulfate) on the rheological behaviour of these systems was also studied as a function of temperature.

## 2. Experimental section

The synthesis of the samples has been described in detail in previous papers [9,11,28]. 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. [29] with sodium dodecyl sulfate (SDS) as the surfactant and 4,4'-azobis(4-cyanovaleric acid) (ACVA) as the initiator. In this process, the high density of hydrophobic molecules in the micelles favors their incorporation as blocks randomly distributed in the polyacrylamide backbone [10,28,30–32]. Note that the use of  $N,N$ -dialkylacrylamides such as DiHexAM instead of  $N$ -monoalkylacrylamides leads to samples homogeneous in composition [11].

The characteristics of the samples investigated are given

Table 1  
Polymer characteristics

Sample <sup>a</sup>	$M_w$ ( $\times 10^{-5}$ )	$[H]^b$ (mol%)	$N_H^c$	$S^d$
PAM	11	0	0	
6M2D3.2	6.6	2	3.2	29
11M2D3.2	11	2.1	3.2	51

<sup>a</sup> The sample code refers to the molecular characteristics of the polymer (see Section 2).

<sup>b</sup> Hydrophobe content in the final copolymer.

<sup>c</sup> Number of hydrophobes per micelle  $\equiv$  hydrophobic block length.

<sup>d</sup> Number of stickers per chain (see Section 2).

in Table 1. The hydrophobe content in the copolymers  $[H]$  (which corresponds within the experimental error to that in the monomer feed) was 2 mol%. The hydrophobe/surfactant molar ratio was adequately adjusted in order to get the number of hydrophobes per micelle,  $N_H$ , equal to 3.2 [9,33]. The molecular weight of the polymers was varied by using the mercapto-ethanol as a chain transfer agent, which behaves like an ideal transfer agent for polyacrylamide (polydispersity index  $I_p = M_w/M_n \approx 2$ ) [9]. The average number  $S$  of stickers per chain is calculated from the relationship  $S = (M_w/I_p m) \times ([H]/N_H)$  where  $m$  is the molecular weight of the monomer units [9]. The presence of SDS produces a decrease in the molecular weight of the polymers [34]. Therefore, the homopolyacrylamide (PAM) was also synthesized in the presence of surfactant, allowing a meaningful comparison of the modified and unmodified samples. The molecular weight of the polymers was determined by light scattering in formamide [34], and the composition of copolymers by <sup>1</sup>H NMR in a 85/15 wt/wt DMSO-*d*<sub>6</sub>/D<sub>2</sub>O mixture [11,27].

The sample code of the copolymers refers to the molecular weight  $M_w$  (6 and 11 stand for 660,000 and 1,100,000, respectively), to the content in hydrophobic comonomer  $[H]$ , and to the  $N_H$  value (i.e.  $\equiv$  the length of the hydrophobic block). For example, 6M2D3.2 stands for a copolymer with a molecular weight of 660,000 containing 2 mol% of DiHexAM and synthesized with a initial number of hydrophobes per micelle equal to 3.2 (see Table 1).

For the study of the copolymer/surfactant mixed systems, the solutions were prepared by dissolution of the copolymers, at the appropriate concentration ( $C = 2$  wt%), in stock aqueous solutions of SDS (Acros 99%). These stock solutions were pre-prepared at a range of concentrations between 4 and 20.1 mM. The solutions were homogenized by stirring for 1 day and further centrifugated for 3 h at 3500 rpm at 25 °C in order to remove eventual bubbles resulting from stirring. Note that the aqueous solutions of HMPAM investigated with or without surfactant are in all cases perfectly homogeneous and transparent for the concentration employed. The  $CMC$  and aggregation number ( $N_{agg}$ ) of the SDS at 25 °C are  $CMC = 8$  mM and  $N_{agg} = 75$  [35].

Linear viscoelasticity experiments were performed at various temperatures 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). The dynamic measurements were conducted with a frequency  $\omega$  of  $1 \times 10^{-3}$ –198 rad/s (i.e.  $\equiv 1.8 \times 10^{-4}$ –30 Hz). All measurements were made within the linear viscoelastic region, i.e. under frequencies and strains for which the modulus is independent of strain. Flow experiments were carried out with the same rheometer. For experiments carried out as a function of temperature, the solution was loaded into the rheometer and sufficient time (about 20–30 min) was allowed for the

stresses to relax and to attain thermal equilibrium. In all experiments, a low-viscosity silicon oil was added to the edges of the cone to prevent evaporation of water. More details on the experimental procedures are given elsewhere [11,33].

### 3. Results and discussion

#### 3.1. Data analysis. Oscillatory experiments

Fig. 1 shows typical frequency dependences of the storage modulus  $G'(\omega)$  and of the loss modulus  $G''(\omega)$  for the homopolyacrylamide PAM and the corresponding hydrophobically modified HMPAM. At low frequency, the behaviour of the complex shear modulus is Maxwellian, as ascertained by the variations of  $G'(\omega)$  and  $G''(\omega)$  that scale, respectively, like  $\omega^2$  and  $\omega$ . The curves  $G'(\omega)$  and  $G''(\omega)$  cross each other at a circular frequency  $\omega_c$ . The inverse of  $\omega_c$  is often taken as the characteristic time of the system. As a matter of fact, the comparison between the actual experimental variations of  $G'(\omega)$  and  $G''(\omega)$  and those calculated from the Maxwell model show deviations appearing already before the crossing frequency (Fig. 1). The relatively large polydispersity index of the polymers

(around 2) is partly responsible for these deviations as the terminal time  $T_R$  strongly depends on this parameter ( $T_R \propto N^3$ , with  $N$  the polymerisation degree). The shape of the curves  $G'(\omega)$  and  $G''(\omega)$  at higher frequencies is indicative of the occurrence of fast modes. Indeed, the current models describing the dynamics of both associating polymers and homopolymers predict a multiple relaxation process [12]. It follows that the relaxation time determined from  $\omega_c$  is smaller than the longest relaxation time, the latter being the physical quantity relevant for a comparison with the models. Note that the behaviour reported in Fig. 1 is quite general: slopes of  $G'(\omega)$  and  $G''(\omega)$  close to 1 and 2, respectively, were found for all the samples investigated. From the analysis of the data in the low-frequency range, it is possible to get an estimate of the longest relaxation time,  $T_R$ , and of the plateau modulus,  $G_0$ , associated with this slowest process. These are obtained from the following relationships:

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

##### 3.1.1. Homopolyacrylamides

For entangled systems, the correlations between dynamic and steady-state measurements are generally well described through the empirical method of Cox–Merz [36,37]. This consists in comparing the steady shear viscosity  $\eta(\dot{\gamma})$  as a function of shear rate with the modulus of the complex viscosity  $\eta^*(\omega)$  as a function of the circular frequency. For melts or entangled solutions of polymers, the two functions are found to coincide. In particular, the crossover between the Newtonian plateau and the shear-thinning regime occurs at  $\dot{\gamma}_c \approx T_R^{-1}$  [37–39]. The comparison between  $\eta(\dot{\gamma})$  and  $\eta^*(\omega)$  shown in Fig. 2 for two temperatures (15 and 50 °C) shows that the Cox–Merz rule applies satisfactorily to entangled solutions of polyacrylamides. It is observed that the  $\eta(\dot{\gamma})$  and  $\eta^*(\omega)$  curves coincide in the whole range of the shear rates and frequencies investigated. This result differs

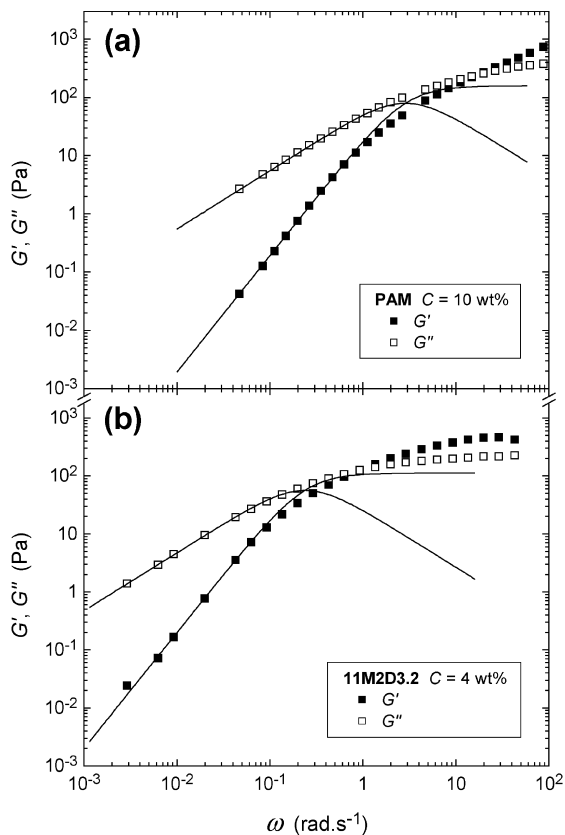


Fig. 1. Storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of frequency at 25 °C for PAM sample in water ( $C = 10$  wt%) (a), and 11M2D3.2 sample in water ( $C = 4$  wt%) (b). The lines are the fit to the one-mode Maxwell model:  $G_0 = 112$  Pa,  $T_R = 4.2$  s (a);  $G_0 = 158$  Pa,  $T_R = 0.35$  s (b).

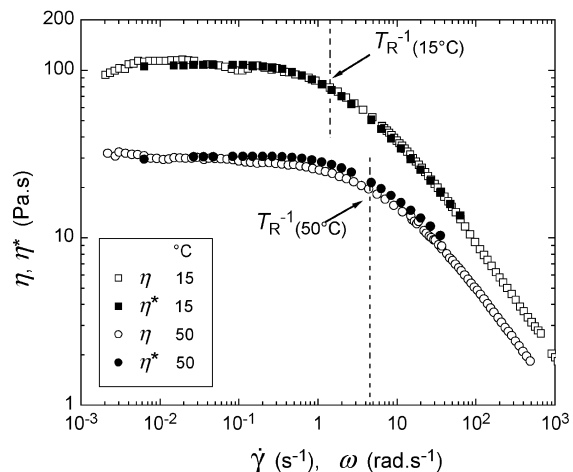


Fig. 2. Steady-state viscosity  $\eta(\dot{\gamma})$  and dynamic complex viscosity  $\eta^*(\omega)$  as a function of shear rate or frequency for PAM sample in water ( $C = 10$  wt%) at 15 and 50 °C.

from that previously reported by Kulicke et al., which found that the Cox–Merz rule does not apply to aqueous PAM solutions [40,41]. As shown in Fig. 2, the departures from the plateau correspond approximately to the terminal time  $T_R$ , as determined by the procedure described above.

Fig. 3 shows the variations of the complex viscosity as a function of frequency for a PAM solution ( $C = 10$  wt%,  $M_w = 1.1 \times 10^6$ ) at various temperatures ranging from 15 to 60 °C. One observes a decrease of the viscosity upon increasing temperature whereas the departures from the plateau is shifted to higher frequencies. The curves are fitted according to the Carreau–Yasuda model [42] normally used for  $\eta(\dot{\gamma})$ , but applied here for  $\eta^*(\omega)$ . Additionally and as shown in Fig. 4, the viscosity curves for the various temperatures and concentrations investigated can be represented by a single master curve by using reduced variables. For each data set, the complex viscosity is normalized by the zero-frequency viscosity  $\eta_0^*$ , and the frequency is normalized by the critical frequency  $\omega_{crit}$  corresponding to the transition between the Newtonian and the power-law regions (the values of  $\omega_{crit}$  were obtained from the Carreau–Yasuda fit parameters).

The shift of the terminal zones to higher frequencies as the temperature is increased can also be observed in the  $G'(\omega)$  and  $G''(\omega)$  curves reported in Fig. 5 for the PAM solutions.

The rheological behaviour of entangled systems is theoretically described by the reptation model [43]. The model gives the following predictions for the main parameters that can be obtained from the rheological experiments:

The terminal time  $T_R$

$$T_R = \frac{N^3 f}{c^3 \xi^6 k_B T} \quad (2)$$

where  $N$  is the degree of polymerisation,  $f$  the friction

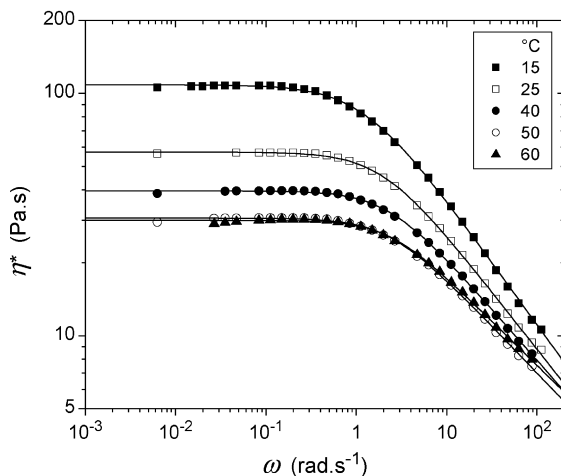


Fig. 3. Complex viscosity versus frequency for PAM sample in water ( $C = 10$  wt%) at various temperatures. The solid lines are the fits to the Carreau–Yasuda model.

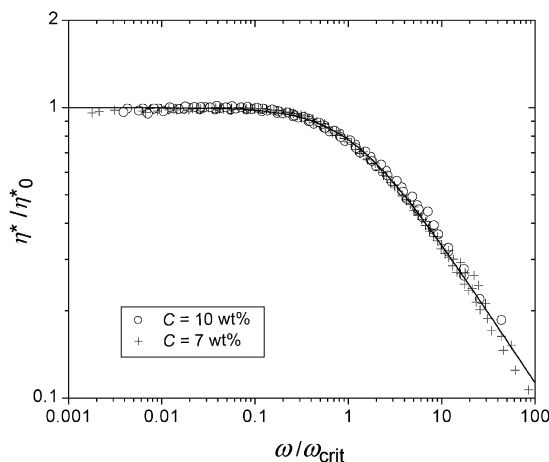


Fig. 4. Normalized plot with reduced variables of the complex viscosity versus frequency for PAM sample in water at two concentrations ( $C = 7$  and 10 wt%) and various temperatures (15, 25, 40, 50 and 60 °C).

coefficient between the monomeric units and the solvent,  $c$  is the number concentration of monomers and  $\xi$  is the correlation length.

The plateau modulus  $G_0$  is given by

$$G_0 = k_B T c / N_e \quad (3)$$

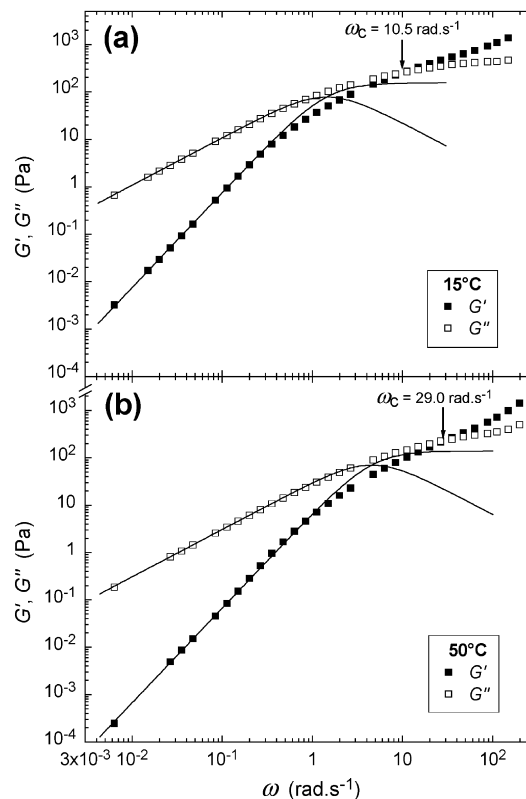


Fig. 5. Storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of frequency for PAM sample in water ( $C = 10$  wt%) at 15 °C (a) and 50 °C (b). The lines are the fit to the one-mode Maxwell model:  $G_0 = 155$  Pa,  $T_R = 0.7$  s (a);  $G_0 = 140$  Pa,  $T_R = 0.22$  s (b).

where  $N_e$  is the number of monomeric units in an entanglement strand.

As for the zero-shear viscosity, it is given by:

$$\eta_0 = T_R G_0 \quad (4)$$

According to Eqs. (2)–(4), the observed decrease of  $\eta_0$  upon increasing temperature can be mostly accounted for by the thermal variation of the friction coefficient between the monomeric units and the solvent, as  $\xi$  and  $N_e$  are not susceptible to vary significantly with temperature.

In most viscoelastic fluids, the  $G'$  and  $G''$  data taken at various temperatures can be combined in a single master curve, according to the classical time–temperature superposition [37,38]. The latter is obtained by shifting the log–log representation of  $G'(\omega)$  and  $G''(\omega)$  obtained at different temperatures horizontally and vertically. In solutions of entangled polymers, according to Eqs. (2)–(4), the vertical shift factor is  $b_T = T_{\text{ref}}/T$ , where  $T_{\text{ref}}$  is a reference temperature (°K). The horizontal shift factor is  $a_T = (T_{\text{ref}}/T)(\eta_T^*/\eta_{T_{\text{ref}}}^*)$  where  $\eta_T^*$  and  $\eta_{T_{\text{ref}}}^*$  are the complex viscosities of the solution at, respectively,  $T_{\text{ref}}$  and  $T$ .

Fig. 6 shows the relaxation spectra of the moduli normalised by  $b_T$  as a function of the circular frequency normalised by  $a_T$ . Within the experimental accuracy, the data gather around a master curve ( $T_{\text{ref}}$  being taken at 298 K) that is fitted in the low frequency range by a Maxwellian model. From this fit, one obtains the following values for the viscoelastic parameters:  $G_0 = 138$  Pa,  $T_R = 0.41$  s (PAM sample at  $C = 10$  wt% and 25 °C).

A similar analysis performed for the same polymer at two other concentrations ( $C = 4$  and  $C = 7$  wt%) gives master curves with the values of  $G_0$  and  $T_R$  reported in Table 2. It should be noted that, in spite of the good superimposition of the different curves on a single master curve, there is

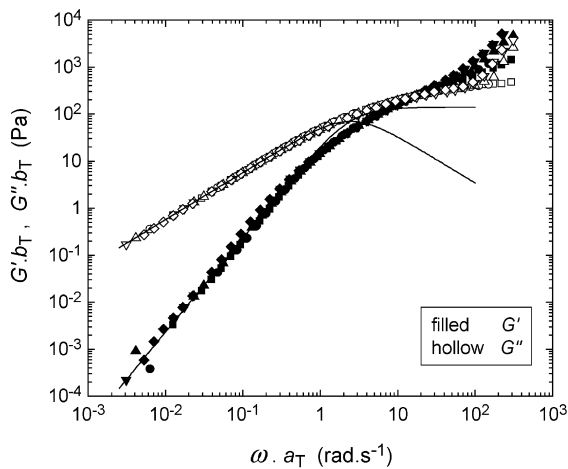


Fig. 6. Superposition of the viscoelastic spectra under horizontal ( $a_T$ ) and vertical ( $b_T$ ) shifts for PAM sample in water ( $C = 10$  wt%) at various temperatures ( $T_{\text{ref}}$  is taken at 298 K) with the corresponding symbols for  $G'$  and  $G''$ , respectively: ■ □ 15 °C; ● ○ 25 °C; ▲ △ 40 °C; ▼ ▽ 50 °C; ◆ ◇ 60 °C. The lines are the fit to the one-mode Maxwell model:  $G_0 = 138$  Pa,  $T_R = 0.41$  s.

Table 2

Variation of  $\eta_0$ ,  $T_R$ , and  $G_0$  for PAM sample as calculated from the master curves for  $T_{\text{ref}} = 298$  K

$C$ (wt%)	$\eta_0$ (Pa s)	$T_R$ (s)	$G_0$ (Pa)
4	0.6	0.045	14
7	8.4	0.16	52
10	56	0.41	138

actually a slight but significant decrease of  $G_0$  when the temperature is increased. A similar behaviour, that cannot be fully explained by the classical scaling concepts on semi-dilute polymer solutions [44], has already been reported for some hydrophobic polymers in organic solvent [45,46]. Further studies on other polymer systems are undoubtedly needed to clarify this point.

Fig. 7 shows the semi-log variation of the shift factor  $a_T$  as a function of  $1/T$  for the PAM sample at  $C = 10$  wt%. According to an Arrhenius law, one obtains an activation energy  $E_a = 30$  kJ/mol from the slope. For  $C = 7$  wt%, the value is  $E_a = 22$  kJ/mol.

The increase of  $G_0$  and  $T_R$  with polymer concentration can be described within the small concentration range investigated, by the following power laws

$$G_0 \propto C^{2.5}, \quad T_R \propto C^{2.5}$$

The scaling exponents theoretically predicted for a polymer in a good solvent are 2.25 for  $G_0$  and 1.5 for  $T_R$  [43]. As a consequence of the behaviours of  $G_0$  and  $T_R$ , the viscosity increases with concentration according to  $\eta_0 \propto C^5$  as compared to the theoretical predictions to  $\eta_0 \propto C^4$  [43, 47]. Such a behaviour has already been reported for PAM investigated over a large concentration range [41,48], as well as for other polymer [45,46,49–55], more especially when there are strong interactions between the polymeric chains as in the case of some polysaccharides [55] or when the quality of the solvent is close to the  $\theta$  conditions [45,46].

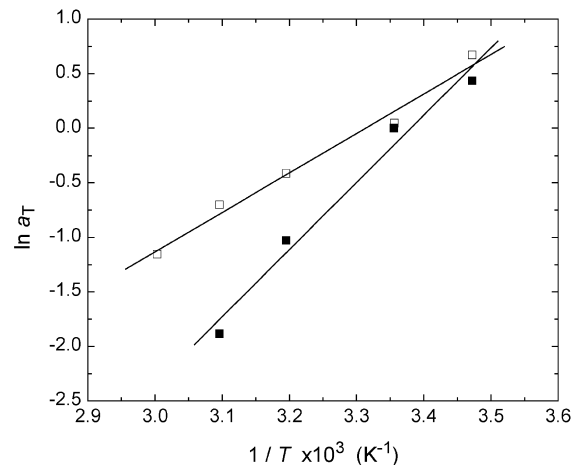


Fig. 7. Variation of the horizontal shift factor  $a_T$  as a function of the inverse temperature for PAM sample (□) in water ( $C = 10$  wt%) and 11M2D3.2 sample (■) in water ( $C = 4$  wt%).

Kulicke et al. have shown that such a behaviour can be explained if it is admitted that the entanglement density for a given concentration in the semi-dilute regime varies with the quality of the solvent [48,54].

### 3.1.2. Hydrophobically modified polyacrylamides

In our previous papers, we have shown that the modification of polyacrylamides with DiHexAM leads to a strong viscosity increase of the polymer solutions [8,9,33]. Also, the viscoelastic behaviour is strongly influenced by the physical crosslinks created by the associations between the hydrophobic units. An interesting observation, already reported by various groups, is that the Cox–Merz rule fails for associating polymers [9,56,57]. In the present case, the  $\eta(\dot{\gamma})$  and  $\eta^*(\omega)$  curves do not coincide, even in the low regime where one would expect a Newtonian behaviour with the same plateau for the two sets of experiments. Also the data obtained upon increasing and decreasing shear rates, respectively, show an important hysteresis. On the contrary, the complex viscosity, which is measured in the linear regime but at finite frequency, shows a well-defined newtonian plateau. In the following, we will use this plateau value for the zero shear viscosity rather than that obtained from the steady-flow experiments.

Fig. 8 shows the  $G'$  and  $G''$  curves for the 11M2D3.2

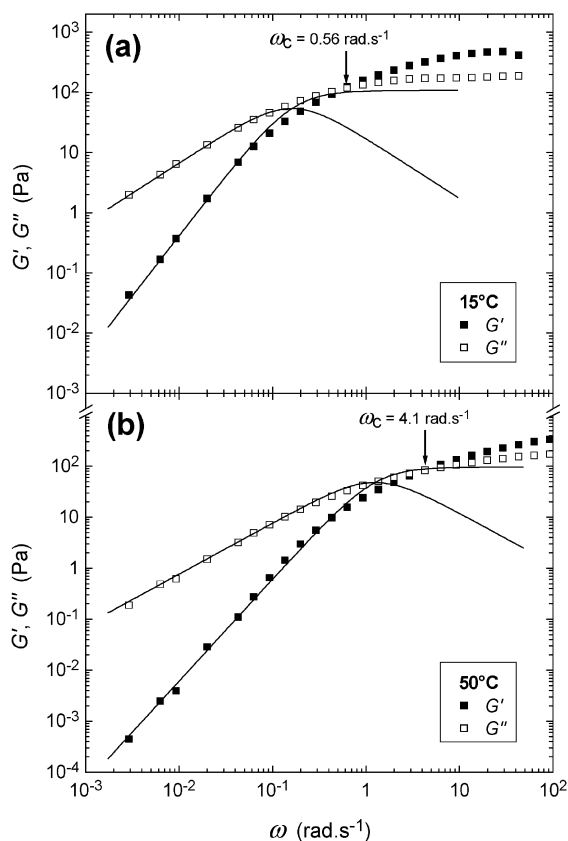


Fig. 8. Storage ( $G'$ ) and loss ( $G''$ ) moduli as a function of frequency for 11M2D3.2 sample in water ( $C = 4$  wt%) at 15 °C (a) and 50 °C (b). The lines are the fit to the one-mode Maxwell model:  $G_0 = 107$  Pa,  $T_R = 6.40$  s (a);  $G_0 = 96$  Pa,  $T_R = 0.80$  s (b).

sample at a concentration  $C = 4$  wt% (that is at  $C/C_e \approx 4$ ,  $C_e$  being the concentration at which the entanglements become elastically effective [9,58]) and at two different temperatures. As the temperature increases, the terminal zone shifts to higher frequencies, which is the signature of the speeding up of the systems dynamics. The data can be treated as previously for the polyacrylamide. Fig. 9(a) shows the master curve obtained from the vertical and horizontal shifts of the data obtained at different temperatures. It is seen that for this system, the moduli can be simply normalised by  $T_{ref}/T$  as for the homopolyacrylamide. This result could be expected from the sticky reptation model developed by Leibler et al. [12] and Rubinstein and Semenov [13] for entangled systems. This model predicts the existence of a two relaxation process and consequently two plateau values for the shear modulus. The lower plateau corresponding to the slower reptation process is at the level of that of the polymer analogue without stickers and scales as:

$$G_0 \propto C^{9/4}$$

As for the terminal time, it depends strongly on the chain

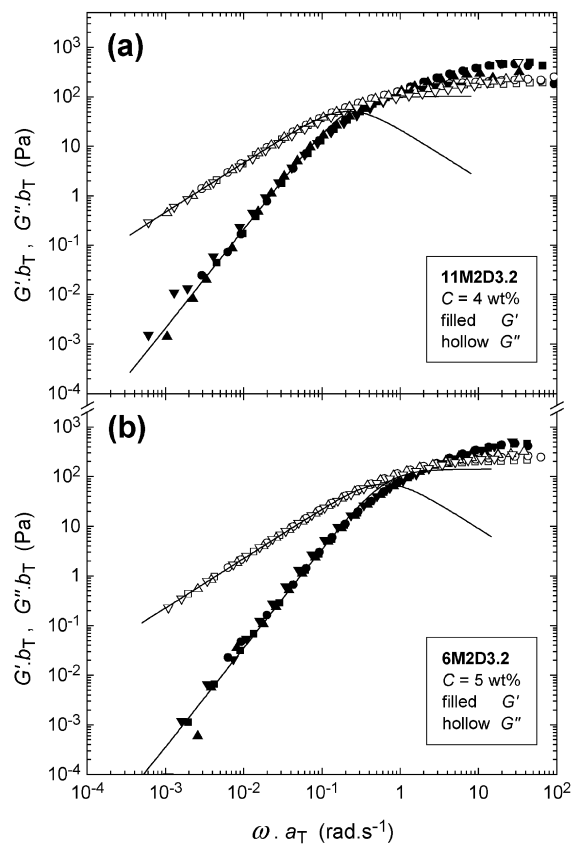


Fig. 9. Superposition of the viscoelastic spectra under horizontal ( $a_T$ ) and vertical ( $b_T$ ) shifts for 11M2D3.2 sample in water,  $C = 4$  wt% (top) and 6M2D3.2 sample in water,  $C = 5$  wt% (bottom) at various temperatures ( $T_{ref}$  is taken at 298 °K) with corresponding symbols for  $G'$  and  $G''$ , respectively:  $\blacksquare$   $\square$  15 °C;  $\bullet$   $\circ$  25 °C;  $\blacktriangle$   $\triangle$  40 °C;  $\blacktriangledown$   $\triangledown$  50 °C. The lines are the fit to the one-mode Maxwell model:  $G_0 = 102$  Pa,  $T_R = 4.55$  s (top) and  $G_0 = 142$  Pa,  $T_R = 1.6$  s (bottom).

length, the density of stickers and the average lifetime  $\tau$  of a sticker in a crosslink according to:

$$T_R \cong C^{15/8} N^{7/2} [S]^2 \tau (1 - 9/p + 12/p^2)^{-1} \quad (5)$$

where  $[S]$  is the molar ratio of stickers with respect to the total monomers and  $p$  is the average fraction of stickers engaged in an association.

Assuming that the factor containing  $p$  in Eq. (5) does not vary significantly with temperature, the temperature dependence of  $T_R$  corresponding to the variation of  $a_T$  is mainly due to that of  $\tau$  and is likely to be Arrhenian. Fig. 7 shows the variation of  $a_T$  vs.  $1/T$ . From this Arrhenius plot, one obtains an activation energy  $E_a = 51$  kJ/mol for the 11M2D3.2 sample, which is much higher than the value for the PAM sample ( $E_a = 30$  kJ/mol) in spite of a lower concentration (4 wt% instead of 10 wt%). Table 3 summarises the values of the different parameters taken from the analysis of  $G'$  and  $G''$  at each temperature for the sample 11M2D3.2.

The results obtained for the 6M2D3.2 sample ( $M_w = 660,000$ ) are quite similar. Fig. 9(b) shows the master curve obtained in normalised coordinates. The activation energy obtained for this sample is quite close to that obtained with the sample of higher molecular weight ( $E_a \approx 46$  kJ/mol).

The above results suggest that the main effect of temperature on this class of associating polyacrylamides is to modify the lifetime of the crosslinks without changing significantly their number [59]. The temperature dependence of the plateau modulus is very weak, which indicates that it is controlled by entanglements and that the additional crosslinks do not play a direct role. However, a puzzling observation is that the plateau modulus which is approximately the same for the two modified samples with different molecular weights (taking into account the difference in concentration), is much larger than that of the analogue homopolyacrylamide at the same concentration (4 wt%):  $G_{0,25^\circ\text{C}} \approx 100$  Pa and  $G_{0,25^\circ\text{C}} \approx 14$  Pa for 11M2D3.2 and PAM samples, respectively.

So, contrary to our expectation, the modulus is not entirely controlled by the entanglements. Considering the large ratio  $C/C_e$ , it is very unlikely that the additional crosslinks formed by association of hydrophobic blocks overcome directly the contribution of the entanglements to  $G_0$ . A possible explanation might be connected with the efficiency of the entanglements. It was shown both

Table 3  
Variation of  $\eta_0$ ,  $T_R$  and  $G_0$  with temperature for 11M2D3.2 sample ( $C = 4$  wt%)

Temperature ( $^\circ\text{C}$ )	$\eta_0$ (Pa s)	$T_R$ (s)	$G_0$ (Pa)
15	687	6.4	107
25	461	4.2	109
40	173	1.5	114
50	76	0.7	103
Master curve	462	4.55	102

theoretically and experimentally that a significant overlap of neighbouring chains is necessary in order for them to constrain each other motion with a ‘universal’ number  $n$  of overlapping chains required for entanglements. This number was estimated to be  $5 \leq n \leq 10$  [60,61]. This means that in entangled solutions, only a fraction of the contacts between chains act as effective entanglements. It could be thought that in associating polymers, this fraction is significantly increased due to the trapping of the contact points between consecutive physical crosslinks. The trapping of entanglements between permanent crosslinks has often been invoked to explain some elastic features in chemically crosslinked gels [62]. Additionally, it can be noted that the difference in the plateau modulus for the hydrophobically modified and the unmodified systems is accompanied by a difference in the activation energy.

### 3.2. Effect of surfactant

The rheological behaviour of the HMPAM solutions in the presence of SDS was found to be qualitatively similar to that reported for many associating systems [14–25]. In particular, the zero-shear viscosity exhibits a flat maximum at a surfactant concentration,  $C_{S,\text{max}}$ , slightly larger than the CMC as shown in Fig. 10. The viscosity decreases rather strongly upon increasing the temperature whereas the position of the maximum is not significantly shifted. The enhancement of the viscosity induced by addition of surfactant is accompanied by a slowing down of the relaxation process. In fact, linear viscoelasticity experiments performed on the samples at the same concentration ( $C = 4$  wt%) as that used in the studies described in the previous paragraph show that the relaxation processes are too slow to be analysed within the frequency range available. Therefore, we studied the 6M2D3.2 sample at a lower concentration ( $C = 2$  wt%) that is at a concentration slightly larger than the entanglement concentration ( $C/C_e \approx 1.3$ ). Based on previous findings on similar HMPAM [9], it

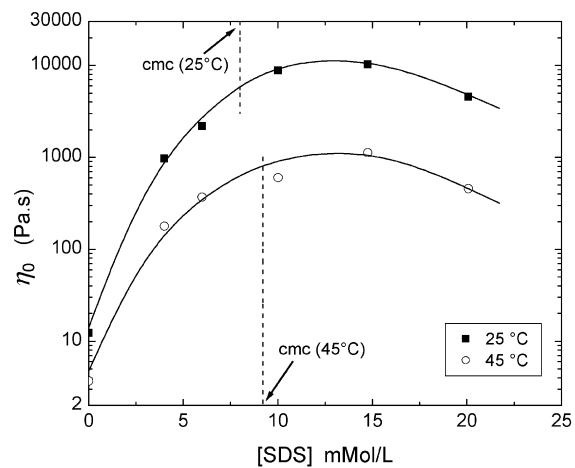


Fig. 10. Effect of SDS concentration on the zero-shear viscosity of 6M2D3.2 sample in water ( $C = 2$  wt%) at 25 and 45  $^\circ\text{C}$ .

can be safely assumed that the system is effectively entangled in this concentration range.

The shapes of the curves representative of  $G'(\omega)$  and  $G''(\omega)$  are quite similar to those obtained for the HMPAM without surfactant. Fig. 11 shows the master curves obtained for systems with surfactant contents ranging from 0 to 20.1 mM, at 25 and 45 °C, with a single horizontal shift (in order to impose the coincidence of the crossing frequencies  $\omega_c$ ). The superposition is quite satisfactory, except in the high frequency range beyond the crossing point, where both local fluctuations and effects of the lifetime of the crosslinks become operative.

Both the enhancement of the viscosity and the slowing down of the relaxation process upon addition of surfactant were generally ascribed to a strengthening of the hydrophobic interactions due to a non-cooperative binding of the surfactant. However, from most of the reported studies, it was not clear on whether the surfactant promotes the formation of new crosslinks or whether it decorates the preexisting crosslinks and increases their lifetimes. We performed recently a study on systems similar to those

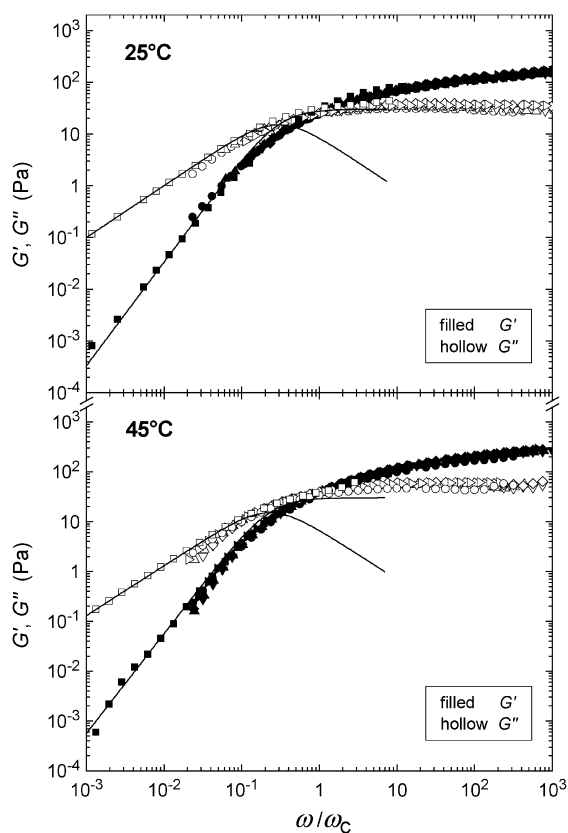


Fig. 11. Superposition of the viscoelastic spectra under an horizontal shift for 6M2D3.2 sample in water ( $C = 2$  wt%) with various SDS contents, at 25 °C (top) and 45 °C (bottom). For each system, the shift factor  $\omega/\omega_c$  is the ratio of the frequency over the crossing frequency. [SDS] and corresponding symbols for  $G'$  and  $G''$ , respectively: 0 mM  $\blacksquare$   $\square$ ; 4 mM  $\bullet$   $\circ$ ; 6 mM  $\blacktriangle$   $\triangle$ ; 10 mM  $\blacktriangledown$   $\triangleright$ ; 14.8 mM  $\blacklozenge$   $\lozenge$ ; 20.1 mM  $\blacktriangleright$   $\triangleright$ . The lines are the fit to the one-mode Maxwell model.

investigated here, which provided arguments in favour of the latter assumption [27]. Similarly, the results presented here, which show that the  $G'(\omega)$  and  $G''(\omega)$  curves can be superimposed on each other at both 25 and 45 °C without any vertical shift when varying the surfactant concentration, tend to indicate as a first approximation that the elastic properties do not depend on the surfactant concentration. This precludes a variation of the crosslink density, whereas the average relaxation time, given by the inverse crossing frequency,  $\omega_c^{-1}$ , goes through a maximum at  $C_{S,max}$  as shown in Table 4. It must be remarked that the relaxation time obtained for these systems are unusually long, as compared with surfactant-free systems investigated up to now ( $\sim 1$  s). This is due to a large increase of the lifetime of the crosslinks, resulting likely from a synergy between the SDS and the DiHexAM hydrophobic units.

For each surfactant concentration, the reciprocal value of the crossing frequency is decreased by increasing the temperature from 25 to 45 °C (see Table 4). This reflects a faster relaxation process, as previously found for the surfactant-free systems. Although experimental data for these polymer/surfactant mixed systems are only available for two temperatures, a rough estimate shows that the activation energy is strongly increased by adding surfactant. For the surfactant concentration corresponding to the viscosity maximum, the value of the activation energy is nearly twice that for the surfactant-free system. This behaviour, in agreement with other studies [23,24,63], reflects the strengthening of the hydrophobic interactions.

The non-linear viscoelasticity experiments also provide interesting information. Fig. 12 shows the variation of the steady-state viscosity at 25 °C as a function of shear stress  $\sigma$  for the same sample 6M2D3.2 ( $C = 2$  wt%) at various surfactant contents. The flow curves exhibit first a slight shear thickening behaviour followed by a discontinuity at a critical shear stress  $\sigma_c$ . Such a behaviour has already been reported for other systems, most often in the presence of surfactant [23,25,64–68]. This phenomenon has been ascribed to a total disruption of the associating interaction network. The reciprocal shear rate just before the discontinuity was assumed to be the lifetime of an intermolecular junction. The fact that such a behaviour is observed in the presence of surfactant might be the

Table 4

Variation of the inverse crossing frequency  $\omega_c^{-1}$  and of the inverse critical shear rate  $\dot{\gamma}_c^{-1}$  with SDS content for the system 6M2D3.2 ( $C = 2$  wt%) at two temperatures

[SDS] (mM)	$\omega_c^{-1}$ (s)		$\dot{\gamma}_c^{-1}$ (s)	
	25 °C	45 °C	25 °C	45 °C
4	21	5	10	2
6	55	12	17	4
10	149	21	37	5
14.8	212	20	81	8
20.1	100	10	30	4



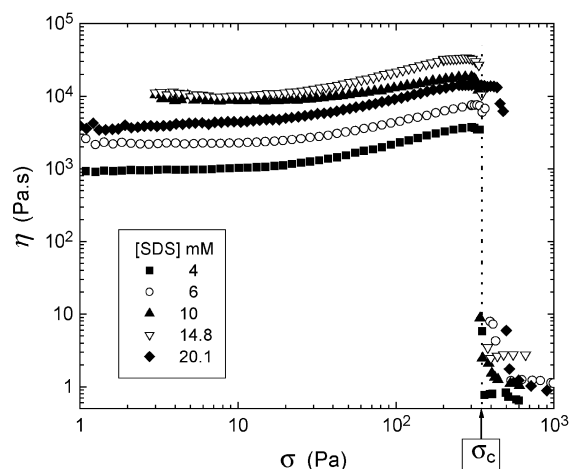


Fig. 12. Steady-state viscosity  $\eta$  as a function of shear stress for 6M2D3.2 sample in water ( $C = 2$  wt%) at 25 °C and for various concentrations of SDS.

consequence of the increased lifetime accessible on the experimental time scale. In Table 4 are given the reciprocal shear rates just before the discontinuity as a function of surfactant concentration at 25 and 45 °C. In both cases, one observes a maximum of this quantity at  $C_{S,max}$ . As already inferred from oscillatory experiments, the lowering of the  $\dot{\gamma}_c^{-1}$  values by increasing the temperature corresponds to shorter average life-times of the hydrophobic associates.

We have also performed experiments on samples containing an excess of surfactant. It is generally believed that at high surfactant concentration, the hydrophobic blocks are singly solubilized by the surfactant micelles, so that the rheological behaviour of the system should be the same as that of the unmodified polymer. The results reported in Table 5 give a quite different picture. This Table shows the comparison between the rheological parameters obtained at 25 °C for the non-modified PAM and the modified one (11M2D3.2) without surfactant, and for the same polymers with an excess of surfactant (500 mM of SDS). It is seen that the viscosity and the terminal time of the hydrophobically modified polymer are decreased in the presence of an excess of surfactant, which suggests a decrease of the lifetime of the associations. On the other hand, the modulus remains approximately the same and is still much larger than that of the unmodified polymer. At such a high SDS concentration, micelles are no more spherical but the viscosity of the solvent is only affected by a

Table 5  
Rheological parameters for the 11M2D3.2 sample and the unmodified analogue PAM in aqueous solution ( $C = 4$  wt%), without surfactant and in the presence of 500 mM SDS (at 25 °C)

Sample	$\eta_0^*$ (Pa s)	$T_R$ (s)	$G_0 = \eta_0^*/T_R$ (Pa)
11M2D3.2	466	4.2	109
11M2D3.2 + SDS	152	1.6	94
PAM	0.59	0.045	14
PAM + SDS	1.03	0.045	23

factor of  $\sim 2.4$  (2.2 mPa s instead of 0.9 mPa s for pure water). This cannot account for the huge difference observed between the respective moduli of the modified and unmodified PAM. This is confirmed by the behaviour of the PAM sample for which the value of  $G_0$  is nearly unaffected by the presence of this high SDS amount (see Table 5). Note also that, by taking into account the modification of the solvent viscosity, the relative viscosity of the associating polymer/surfactant mixture is still much higher than that found for the non-modified PAM. These results go against the common belief and show that, even in the presence of an excess of surfactant, the network created by the intermolecular hydrophobic associations is not fully disrupted. Excimer fluorescence measurements on other associating polyacrylamides bearing hydrophobic naphthyl groups support this view [69].

#### 4. Conclusion

This study shows that in entangled solutions of multi-sticker associating polyacrylamides, a change in temperature or addition of surfactant affects essentially the lifetime of the crosslinks formed by the associating units, whereas the plateau modulus remains roughly unchanged. However, the comparison between the moduli of a hydrophobically modified polymer and the unmodified analogue reveals that the elasticity of the solution is strongly enhanced by the presence of associating units. This surprising result is tentatively explained by an effect of the additional temporary crosslinks on the entanglement efficiency.

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