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Polymer 45 (2004) 1993–2000

polymer

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Study of three different families of water-soluble copolymers: synthesis, characterization and viscoelastic behavior of semidilute solutions of polymers prepared by solution polymerization

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Received 1 July 2003; received in revised form 1 December 2003; accepted 5 December 2003

Abstract

Polymer chains consisting of water-soluble polyacrylamides, hydrophobically modified with low amounts of *N*,*N*-dialkylacrylamides (*N*,*N*-dihexylacrylamide (DHAM) and *N*,*N*-dioctylacrylamide (DOAM)) have been prepared via free radical solution polymerization, using two hydrophobic initiators derived from 4,4′-azobis(4-cyanopentanoic acid) (ACVA) containing long linear chains of 12 (C12) and 16 (C16) carbon atoms. This procedure resulted in polyacrylamides containing hydrophobic groups along the chain as well as at the chain ends. This class of polymers, termed 'combined associative polymers', has been studied and compared with the multisticker (with hydrophobic groups along the polymer chain) and telechelic (with hydrophobic groups at the chain ends) associative polymers, which were prepared with DHAM or DOAM and with the hydrophobic initiator (ACVA) modified with alkyl chains of two different lengths. The viscoelastic properties of these different families of associative polymers were investigated using steady-flow and oscillatory experiments. The effect of type, localization and concentration of the hydrophobic groups on the viscosity of the associative polymer solution was investigated. All viscosity curves clearly show two different regimes within the semidilute range: a first unentangled regime where the viscosity increases moderately; and a second entangled regime where the viscosity varies according to a power law, proportional to C^4. The relaxation time, T_R, and the plateau modulus, G_0, showed relatively high values which increased with the number of carbon atoms in the hydrophobic groups. The combined associative polymer (PAM-*co*-DHAM/ACVA12) showed relaxation times that remained relatively constant along the concentrations studied, but very high values of G_0.

Keywords: Water-soluble polymers; Hydrophobe; Viscoelasticity

1. Introduction

In the last three decades, many water-soluble polymers (WSP) have become an attractive field of study, due to the properties they confer to the solution. A small amount of WSP introduced in an aqueous mixture, for example, can produce a substantial increase in viscosity [1–3].

Such viscosity modification at very low concentrations can be achieved using polymers that have an important hydrodynamic size, such as a high molecular weight. However, these polymers can present some limitations in use. High molecular weight polymers are susceptible to mechanical degradation when subjected to elevated shear rates, leading to a decrease in viscosity [4].

In order to avoid these difficulties, a new class of macromolecules referred to as hydrophobically modified water-soluble polymers (HMWSP) has been extensively studied over the past few years [5–7].

This type of polymers lead to interactions among the hydrophobic groups, which can result in strong intermolecular associations, that prompt the polymer chains to form superstructures equivalent to a high molecular weight structure and as a result, the effect on viscosity is much larger than it would be with a polymer without any kind of interactions [8–10].

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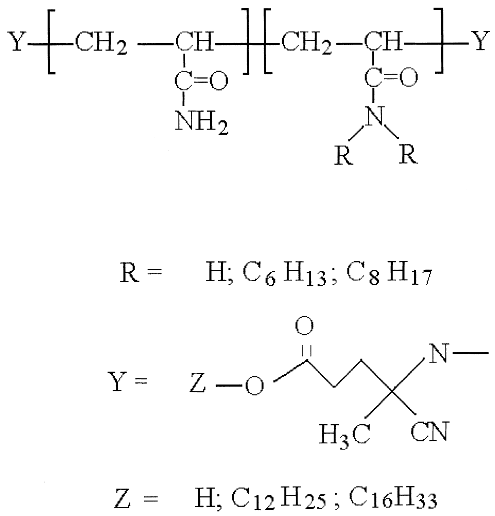
doi:10.1016/j.polymer.2003.12.065



Scheme 1. Chemical structure of the polymers synthesized.

There are two large HMWSP families according to the hydrophobe localization, one is called telechelic, which contains two hydrophobic groups situated on each end of the macromolecular chain [11–14] and the other is called multisticker, which has the hydrophobic groups distributed along the hydrophilic chain either in blocks or at random [10,15–17].

The particular properties of the HMWSP, as well as the several application possibilities where a rheology control is required on an aqueous system, explains the increasing number of studies on the last years [18–20]. Due to the numerous parameters that influence its properties, the HMWSP offer a considerable research field. This influence may come from its own polymer parameters (the nature of the hydrophobic groups, its chemical constitution, etc.) [11,21] or from the external factors that influence the association phenomena (shear stress, temperature, surfactant, etc.) [22,23].

In this study, we have introduced a new HMWSP family, which combines the characteristics of both, the telechelic and the multisticker associative polymers, that is, a polymer with hydrophobic groups at the chain ends as well as along the macromolecular chain. The combined associative copolymers are a very important kind of polymers which can greatly influence the viscosity of a solution, and it is clear that the association process will be enormously dependent on the localization of the hydrophobic groups and their mobility.

In this study, we discuss the synthesis and characterization of three different families of HMWSP (telechelic, multisticker and combined) prepared by solution polymerization. In addition, we present a detailed study of the rheological properties of these three HMWSP.

2. Experimental section

2.1. Synthesis of the hydrophobic initiators

The hydrophobic initiators were prepared through a reaction between ACVA and two different alcohols, 1-dodecanol ($C_{12}H_{25}OH$) (ACVA12) and 1-hexadecanol ($C_{16}H_{29}OH$) (ACVA16), in accordance with the procedure previously described by Belzung [24]. The conversion attained in these reactions was 75.4 and 91% for ACVA12 and ACVA16, respectively.

2.2. Synthesis of the hydrophobic monomers

The hydrophobic monomers were prepared via a reaction of acryloyl chloride with the corresponding *N*-dialkylamine (dihexylamine or dioctylamine), in accordance with the procedure described by Valint et al. [25].

2.3. Synthesis of the copolymers

All copolymers were prepared via solution copolymerization using acetonitrile as solvent. The initial concentration of monomers (acrylamide plus hydrophobe) was maintained constant at 3% (w/w) based on the weight of acetonitrile. The temperature was maintained at 82 °C and the initiator concentration was 0.07 mol% relative to the monomers feed. Copolymerizations were carried out at 1 mol% of hydrophobic monomer relative to the total monomers feed. Homopolyacrylamide was prepared under identical experimental condition (Scheme 1).

Due to the termination mechanisms that occur in reactions such as those mentioned above (combination and disproportionation), these copolymerizations tend to terminate randomly via these two routes and produce both, diblocks (with a hydrophobic group in only one chain end) and triblocks (with a hydrophobic group in each chain end, that is, telechelic), which had to be then separated by fractionation as follows: the copolymer mix is solubilized in 5% water, then a non-solvent is added until persistent turbidity. The mix is then cooled and a gel, constituted essentially by triblocks (telechelics) is formed. Finally, the gel is separated and precipitated in methanol and filtered, washed and vacuum dried.

2.4. Molecular weights

The weight-average molecular weight of the samples M_w was determined by light scattering (using formamide as solvent). The refractive-index increments measured at $\lambda = 633$ nm on a Brice–Phoenix differential refractometer in formamide were 0.109 ml/g. as described previously [16]. It was not possible to characterize these amphiphilic copolymers by size exclusion chromatography (SEC) in water, due to aggregation and adsorption phenomena. However, the homopolyacrylamide prepared under identical experimental conditions, but without hydrophobe, has a polydispersity index M_w/M_n determined by SEC around 2.5. It was assumed that the polydispersity of the corresponding associative copolymers was the same as that of the homopolymers.

Following these considerations, the average number of hydrophobic branches (stickers) per macromolecular chain *'S'*, was calculated from:

$$S = (M_w/2.5m)[H]$$

where m is the molecular weight of the monomer unit (acrylamide, $m = 71$) and $M_w/2.5m$ corresponds to the number-average degree of polymerization *'N'* (see Table 1).

2.5. Characterization

The composition of initiators, monomers and polymers was determined by ^{1}H-NMR spectroscopy, using 1 wt% solution in $CDCl_3$ (for monomers and initiators) or $DMSO/D_2O$ (80/20 wt/wt) (for polymers) at room temperature in a JEOL 300 MHz spectrometer.

2.6. Sample preparation

Solutions at different concentration levels were prepared by directly dissolving a known amount of polymer into deionized distilled H_2O. Each solution was gently stirred until the solution was homogeneous.

2.7. Rheological measurements

Experiments were performed in a Paar Physica UDS200 controlled stress rheometer equipped with a cone and plate geometry (angle 2° and diameter 50 mm) or double gap geometry, depending on the sample viscosity, at 25 °C. To prevent the evaporation of water, we enclosed the measuring system with a solvent trap. The zero-shear viscosity (η_0) was obtained by extrapolation of the apparent viscosity to zero shear rate. The range of concentration of the aqueous polymer solutions was $0.05 < C < 15$ wt%.

The sample code of the copolymers refers to the hydrophilic monomers, hydrophobic monomers and the length of the hydrophobic initiator, for example, PAM-*co*-DHAM/ACVA12 stands for a poly(acrylamide-*co*-dihexylacrylamide) obtained using an initiator modified hydrophobically with a 12 carbon atoms chain (C12). The characteristics of the samples investigated are given in Table 1. The conversion of all samples during synthesis was around 80%. The hydrophobe monomer content in the copolymers [H] was 0.8 mol%, as determined by NMR (although the amount fed was 1.0 mol%; i.e. 20% of the hydrophobe monomer remained without reacting and was washed out). The molecular weight M_w was around 175,000.

Table 1
Polymer characteristics

Polymers	[H]^a (mol%)	M_w (g/mol)	S^b
PAM		185,000	0
PAM/ACVA12		180,000	0
PAM/ACVA16		170,000	0
PAM-*co*-DHAM	0.8	160,000	7.2
PAM-*co*-DOAM	0.78	160,000	7
PAM-*co*-DHAM/ACVA12	0.81	170,000	7.7

[a] Hydrophobe content in the final polymer.
[b] Number of hydrophobes per chain (see Section 2).

3. Results and discussion

3.1. Data analysis. Oscillatory experiments

Fig. 1 shows the variation of the storage $G'(\omega)$ and loss modulus $G''(\omega)$ with frequency. It is observed that at low frequencies, $G'(\omega)$ and $G''(\omega)$ vary in accordance with the Maxwell model, and that the G' and G'' curves cross each other at a point denominated as ω_{cross} and the inverse of ω_{cross} is often taken as the characteristic time of the system. Nevertheless, at higher frequencies, the experimental results exceed those resulting from the Maxwell model. The shape of the G' and G'' curves at higher frequencies is indicative of a fast mode superimposing on a slow relaxation process. This model describing the dynamics of associating polymers predicts a multiple relaxation process (at least two characteristic times). It follows that the relaxation time determined from ω_{cross} is smaller than the longest relaxation time, the latter being the physical quantity relevant for a comparison with the Maxwell model. The behavior observed in Fig. 1 is quite general and is observed for most samples. In fact, the slope of the G'' curves is approximately equal to 1 for all the samples studied, whereas that of the G' curves was found to be approximately

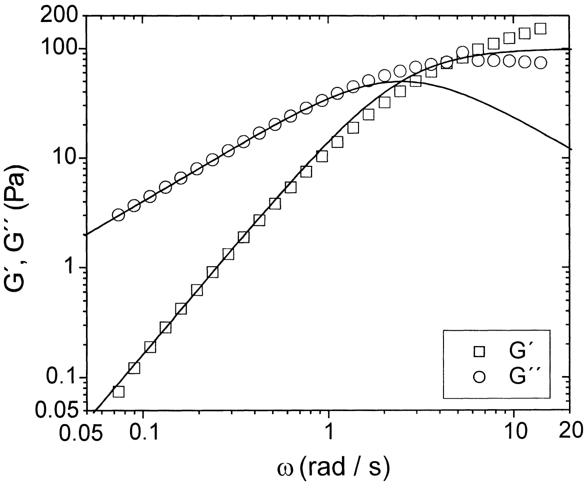


Fig. 1. Storage (G') and loss (G'') moduli as a function of frequency for PAM/ACVA16 sample ($C = 8$ wt%). The lines correspond to the one-mode Maxwell model ($G_0 = 76.7$ Pa, $T_R = 0.0348$ s).

equal to 2 for some samples, but equal to 1.8 for samples with long relaxation times (i.e. at high polymer concentration and/or high length of the hydrophobic chain).

From the data at the low frequency range, we determined the longest relaxation time, T_R, and the plateau modulus, G_0, which are associated with the slowest relaxation process from the following relationships:

$$T_R = \lim_{\varpi \to 0} \left(\frac{1}{\varpi} \frac{G'}{G''} \right) \tag{1}$$

$$G_0 = \frac{1}{T_R} \lim_{\varpi \to 0} \left(\frac{G''}{\varpi} \right) \tag{2}$$

$$\eta_0 = G_0 T_R \tag{3}$$

3.1.1. Linear viscoelastic properties

Zero-shear viscosity. The zero-shear viscosity 'η_0' was determined by extrapolating to zero shear rate (to zero frequency) the viscosity data obtained in the steady-shear flow experiments.

Before further analyzing the results, it is useful to recall the main features of the rheological behavior of *unmodified homopolymers*.

When discussing the dynamical properties of solutions of linear polymer chains, one generally distinguishes four regimes that depend on concentration [9]:

(i) *The dilute (first) regime*. Here, $C < C^*$, where C is the solution concentration and C^* is known as the overlap concentration and is determined as the point in which the viscosity shows a sudden change in slope. In this regime, the zero-shear viscosity of the solution is of the order of that of the solvent.

(ii) *The semidilute unentangled (second) regime*. Here, $C^* < C < C_e$, where C_e represents the concentration at which the entanglements become elastically effective and it is determined as the point where the extrapolation of the viscosity in the first (dilute) regime crosses the extrapolation of the viscosity in the third (semidilute entangled) regime. In this regime, the viscoelasticity of the solution is controlled by the Rouse dynamics and the viscosity increases moderately.

(iii) *The semidilute entangled (third) regime*. Here, $C_e < C < C^{**}$. In this regime, the viscosity properties are described by the repetition model and the viscosity varies according to a power law, that is, viscosity is proportional to C^4.

(iv) *The concentrated (fourth) regime*. This starts beyond C^{**}, where the repetition model still holds but the scaling up becomes different.

Two characteristic parameters can be varied in order to tune up the viscoelastic behavior of the systems investigated in this study. One is the hydrophobe localization along the chain and the other is the hydrophobe chain length. In the following, we discuss the influence of these factors on the zero-shear viscosity η_0, the terminal time of the stress relaxation (i.e. the relaxation time) 'T_R' and the plateau modulus 'G_0', the two latter quantities being obtained from oscillatory experiments using Eqs. (1) and (2).

Figs. 2–5 show the effects of each of these two characteristic parameters on the concentration dependence of the zero-shear viscosity.

Fig. 2 shows the viscosity variation of the two multisticker associative copolymers prepared in this study—using two hydrophobic comonomers of different chain length (dihexyl and dioctyl)—as well as that of the polyacrylamide homopolymer. As with the unmodified homopolymer, we can identify three regimes that depend on the concentration, but which are somewhat displaced along the concentration axis.

For the PAM-*co*-DOAM copolymer, the first (dilute) regime extends up to a point called C_η and defined as the point in which the viscosity of the *associative copolymer* surpasses that of the homopolymer, which in this case occurs approximately at a concentration of 2 wt%, whereas for the homopolymer, $C^*_{(PAM)}$ stands at 0.25 wt%. That is, the viscosity of the solution with the associative copolymer remains the same as that of the homopolymer, even at concentrations as high as 2%. We suppose this is due to the intramolecular interactions of the associative polymer, that apparently tend to shrink its hydrodynamic volume, allowing higher polymer concentrations while maintaining the solution in the first (dilute) regime, before passing C^*, or C_η, and into the second (semidiluted unentangled) regime.

We assume that at C_η, the concentration of the associative copolymer is such that the intermolecular interactions will start to be effective and the viscosity will rapidly start to increase with increasing concentration.

At higher concentrations, in the second (semidilute unentangled) and third (semidilute entangled) regimes, we found that C_T (which will apply for an associative

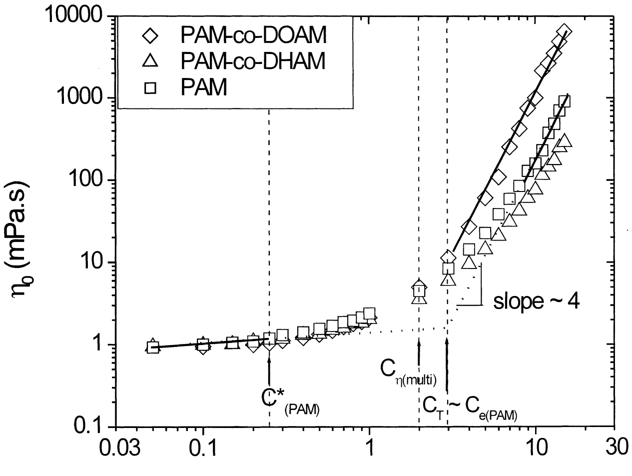


Fig. 2. Variation of η_0 as a function of C for two multisticker associative copolymers with hydrophobic groups of different chain length (diC6 and diC8), (copolymers synthesized using unmodified ACVA as initiator).

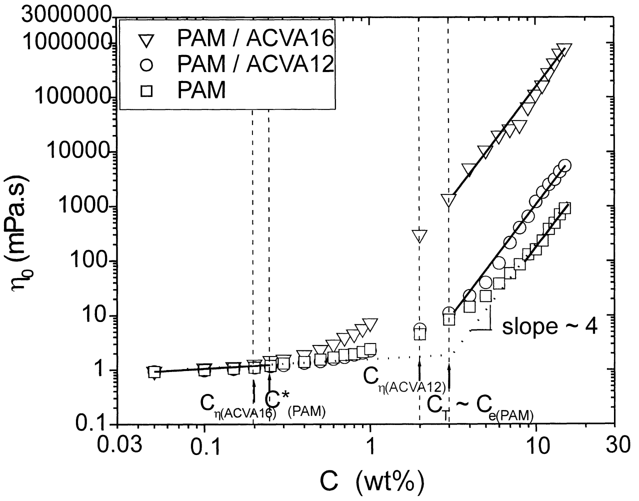


Fig. 3. Variation of η_0 as a function of C for two telechelic associative copolymers with hydrophobic groups of different chain length (C12 and C16), (copolymers synthesized using modified ACVA as initiator).

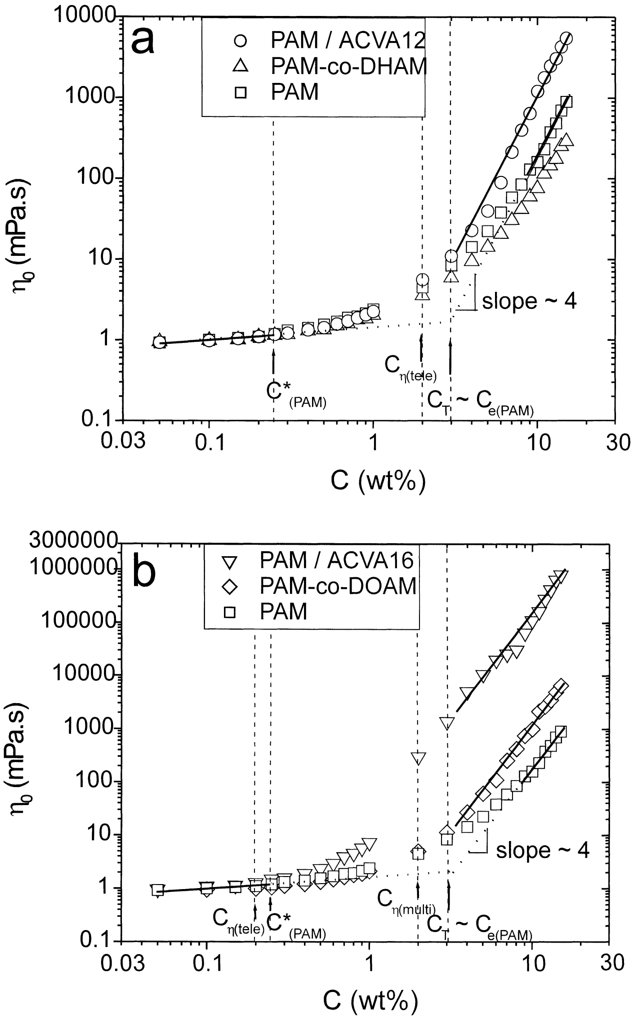


Fig. 4. Comparison between telechelic and multisticker polymers with C12 (a) and with C16 (b).

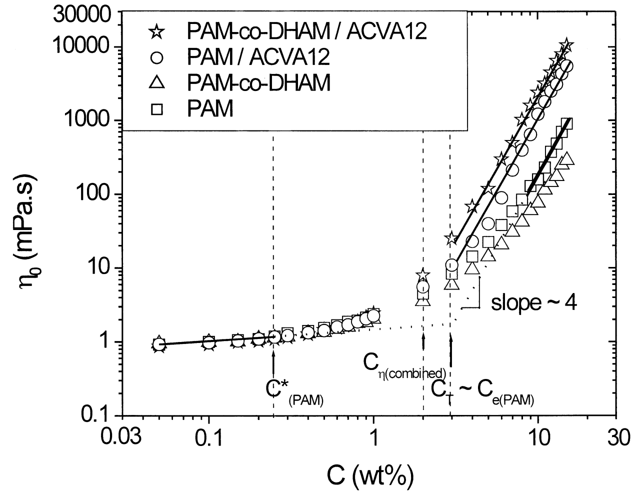


Fig. 5. Comparison of viscosities of telechelic and multisticker polymers with that of the combined type on the series C12.

copolymer and is defined in the same manner as C_e) is approximately the same as $C_{e(PAM)}$ ($C_T \approx C_{e(PAM)} \approx 3 \times$ wt%), where the unmodified homopolymer chains are supposed to start to entangle and the associative copolymers tend to form transitory three-dimensional networks, characteristic of these polymers. At concentrations higher than C_e, the viscosity increases more rapidly, according to a power law, and varies proportionally to C^4. 'C_η' of PAM-*co*-DHAM was not determined, because; we had defined C_η as the point in which the viscosity of the associative copolymer surpasses that of the homopolymer, and in this case the viscosity of the copolymer is always below that of the homopolymer. This behavior is possibly because the hydrophobic chain length (diC6) is too short to have any thickening effect. The fact that the viscosity of the copolymer is lower is simply because it has a lower M_W than the homopolymer (160,000 versus 185,000). On the contrary, PAM-*co*-DOAM do has a very clear point in which its viscosity becomes higher than that of the homopolymer, that is, C_η, which is possibly due to the longer hydrophobic group (diC8) [26].

Fig. 3 shows the variation of (η_0) with concentration for the two associative 'telechelic' polymers with hydrophobic groups at the chain ends of 12 and 16 carbon atoms—that arise from the initiator—as well as for the unmodified homopolymer. It is observed that PAM/ACVA16 passes from the first (dilute) to the second (semidilute unentangled) regime at a concentration a little lower than that corresponding to the unmodified homopolymer, that is, $C_{\eta(ACVA16)}$(0.2 wt%) versus $C^*_{(PAM)}$(0.25 wt%). On the contrary, PAM/ACVA12 passes from the first (dilute) to the second (semidilute unentangled) regime at a concentration as high as 2 wt%.

This means that the intermolecular interactions in the PAM/ACVA16 system start to be effective at concentrations lower than those corresponding to the polyacrylamide homopolymer ($C_{\eta(ACVA16)}$ versus $C^*_{(PAM)}$). That is, the breadth of the first (dilute) regime is reduced (up to $C_{\eta(\mathrm{ACVA16})}$), whereas the second (semidilute unentangled) regime is greatly extended, from $C_{\eta(\mathrm{ACVA16})}$ to C_{T}.

For the PAM/ACVA12 system, it is contrariwise, the breadth of the first (dilute) regime is greatly extended (up to $C_{\eta(ACVA12)}$), whereas the second (semidilute unentangled) regime is reduced from $C_{\eta(ACVA12)}$ to C_{T}.

These results lead us to presume that the length of the alkylic hydrophobic groups at the chain ends, have a great influence on the viscosity of solutions treated with these telechelic polymers. Finally, at concentrations above C_{T}, the behavior is similar to that observed in Fig. 2.

Fig. 4 presents a comparison between telechelic and multisticker associative polymers with hydrophobic groups of 12 and 16 carbon atoms (Fig. 4a and b, respectively). It is observed that the results in Fig. 4a are similar to those on Fig. 2. Additionally, the curves of PAM/ACVA12 of Fig. 2 and that of PAM-*co*-DOAM of Fig 4a are almost identical, with $C_{\eta(\mathrm{tele})}$ from Fig. 4a and $C_{\eta(\mathrm{multi})}$ from Fig. 2 both being equal to 2 wt%. This is interesting, because we have two different associative polymers which differ in the size (C12 and C16) as well as in the localization (multisticker and telechelic) of the hydrophobic groups, but nevertheless, present identical curves. ["It was not possible to determine C_η for the associative copolymer PAM-*co*-DHAM"].

It is also observed in Fig. 4a and b that the viscosity of the telechelic associative copolymers is higher than that of the corresponding multisticker copolymers, and clearly, (Fig. 4b) the viscosity of the telechelic with hydrophobic groups of 16 carbon atoms (instead of 12) presents the highest viscosity of all; two orders of magnitude higher than that of the corresponding multisticker and three orders of magnitude higher than that of the homopolymer.

We suppose that this difference comes from the different arrays that each type of associative copolymer presents while in solution; the multisticker molecules tend to present a very compact conformation due to the many interactions among the larger quantity of hydrophobic groups, whereas the telechelic molecules tend to arrange themselves in what appears to be an array of cloverleaves, occupying thus much larger spaces, and producing thus greater viscosities.

Fig. 5 compares the viscosity of the combined associative copolymer with that of the telechelic and multisticker ones, for the case where the alkyl chain of the hydrophobic groups has 12 carbon atoms. It is observed that the concentration at which the system passes from the first regime to the second one is the same for PAM-*co*-DHAM/ACVA12 as well as for PAM/ACVA12, that is, $C_{\eta(\mathrm{combined})}$ is equal to $C_{\eta(\mathrm{tele})}$, and equal to 2 wt%. This shows that even though the combined polymer PAM-*co*-DHAM/ACVA12 has more hydrophobic groups (along the chain as well as at the chain ends), the combined copolymer concentration needed to surpass the homopolymer viscosity is the same as the one required by the telechelic copolymer PAM/ACVA12. It can be assumed then, that at concentrations below $C_{\eta(\mathrm{combined})}$, the hydrophobic parts located along the chain have not yet any influence on the viscosity increase produced by the combined associative copolymer and only the hydrophobic parts located on the chain ends contribute to the viscosity increase. At concentrations above $C_{\eta(\mathrm{combined})}$, nevertheless, the hydrophobic groups located along the chain as well as those located at the chain ends, both will support the very sharp increase in viscosity.

Figs. 2–5, all show three concentration regimes which are delimitated by C^* and C_{e}, in the case of the unmodified homopolymer and by C_η and C_{T}, in the case of the associative copolymers.

In all cases, the concentration at which C_η occurred depended strongly on the localization of the hydrophobic groups, as well as on the size of the alkyl chains in the hydrophobic groups.

In the first (dilute) regime, $[C < C_\eta]$ the viscosity of the associative copolymers appears to be somewhat lower than that of the unmodified homopolymer, due supposedly to the contraction of the hydrodynamic volume caused by the intramolecular associations.

In the second (semidilute unentangled) regime, $[C_\eta < C < C_{\mathrm{T}}]$ the viscosity of the associative copolymers starts to increase at a very high rate, this rate of increase being greatly affected by the localization of the hydrophobic groups [higher rate of increase for the combined and the telechelic associative copolymers] and by the size of the alkyl chains in the hydrophobic groups [higher rate of increase as the alkyl chains become larger]; whereas the viscosity of the unmodified homopolymer increases just slightly with concentration. Nevertheless, it is striking that C_{T} of the unmodified homopolymer coincides quite well with the C_{e} of the associative copolymers.

In the third (semidilute entangled) regime, $[C_{\mathrm{T}} < C]$ the viscosities of the associative copolymers and of the unmodified homopolymer varies according to a power law, where viscosity is proportional to C^4. In fact, it can be safely assumed that, in the concentration range considered, the density of entanglement is much larger than that of hydrophobic associations.

It has been shown above that, for systems with short relaxation times, the variations of G' and G''—in the low frequency range- are well described by the Maxwell model, that is, they depend on ω^2 and on ω, respectively [9]. In addition, in this low frequency range, it is possible to estimate the relaxation time T_{R} and the plateau modulus G_0 with Eqs. (1) and (2).

Fig. 6 illustrates the variation of relaxation time T_{R} with concentration. Considering T_{R} as the time that two hydrophobic groups interact and maintain a link.

PAM/ACVA16 presents large relaxation times that increase with concentration; and these results are in accordance with the high viscosity conveyed by this associative copolymer. Whereas PAM-*co*-DOAM and PAM-*co*-DHAM/ACVA12, both present much lower relaxation times that increase very slowly with concentration. This suggests for these two latter cases, that the time that the

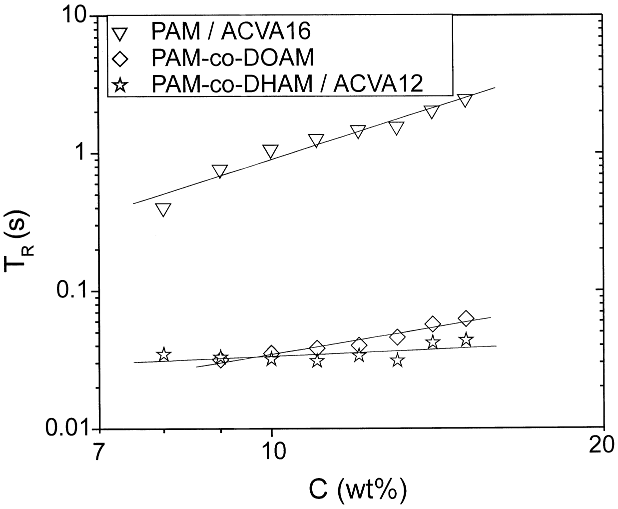


Fig. 6. Variation of the terminal time T_R versus polymer concentration for different samples.

hydrophobic ‘association’ (or link) is maintained is independent of the associative polymer concentration. This result is apparently contradictory, since the effect of PAM-*co*-DHAM/ACVA12 on viscosity is quite marked (as observed in Fig. 5), but if we consider that the viscosity results from the relaxation time multiplied by the plateau modulus, according to Eq. (3), this would explain the fact of having high viscosity and relatively constant relaxation times. In addition, the relaxation time is strongly affected by the type and localization of the hydrophobic groups.

Finally, Fig. 7 shows the variation of G_0 versus the associative polymer concentration for the same samples presented in Fig. 6. G_0 may be considered as the quantity of hydrophobic links present on the environment at a given time. We observe that G_0 increases with concentration in all three samples, which indicates that as we increase the concentration, the number of hydrophobic links also increases. It can be observed that G_0 of PAM-*co*-DHAM/ACVA12 is higher than that of PAM-*co*-DOAM and almost as high as that of PAM/ACVA16. However, the rate at which G_0 increases with concentration is slightly higher for PAM-*co*-DHAM/ACVA12 than for the other two associative copolymers.

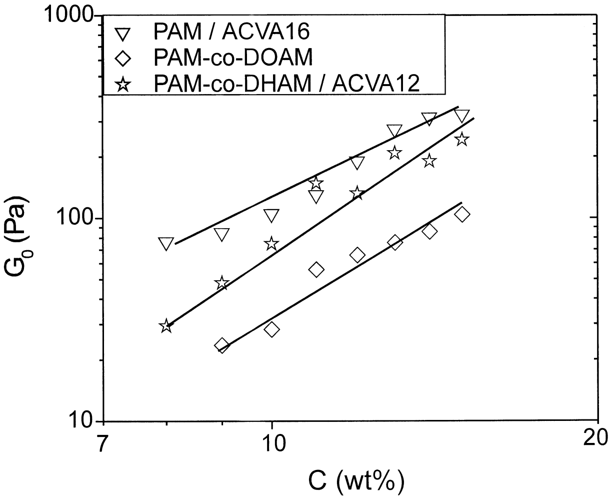


Fig. 7. Variation of G_0 versus polymer concentration for different samples.

This might be due to the larger quantity of hydrophobic groups on this combined associative copolymer (along the chain as well as at the chain ends) which would validate an increased number of hydrophobic links and therefore, higher values of G_0; though it is not very clear why, the PAM/ACVA16 sample, with less hydrophobic groups, but with a larger number of alkyl carbon atoms in the hydrophobic groups, presents values of G_0 superior to those of the combined associative polymer. It seems therefore, that the value of G_0 is also strongly affected by the type (size) and localization of the hydrophobic groups.

4. Conclusions

The results on this study refer to the synthesis of three different types of associative hydrosoluble polymers, (telechelic, multisticker and combined) which were prepared via solution polymerization, were then characterized by NMR and DDL and finally, their influence on the rheological properties of an aqueous solution was examined.

Three concentration regimes were found for all the associative polymers investigated:

(i) a first (dilute) regime, in which $C < C_\eta$, where there is no interaction among chains and the viscosity is controlled essentially by intramolecular interactions. The extent of this regime varied according to the localization and length of the hydrophobic groups.

(ii) a second (semidilute unentangled) regime, in which $C_\eta < C < C_T$. The borderline between the first and second regime is rather sharp at C_η. This regime is dominated by intermolecular hydrophobic associations and the chains would behave according to the Rouse dynamics.

(iii) a third (semidilute entangled) regime, in which $C > C_T$. The borderline C_T occurs at a concentration close to the critical concentration C_e where the unmodified polymer chains are entangled. In a log–log graphic, the variation of η_0 versus C is described by straight lines with an exponent of about 4, independent of the type (size) and localization of the hydrophobic groups. Here, the hydrophobic associations might be completely intermolecular and in addition, the number of entanglements increases strongly with C.

The relaxation time of the associative combined polymer PAM-*co*-DHAM/ACVA12 did not show any variation with concentration, whereas the plateau modulus showed to increase markedly with concentration. On all studied samples, T_R as well as G_0, were strongly affected by the type (size) and localization of the hydrophobic groups.

Acknowledgements

The authors wish to thank the Mexican National Council for Science and Technology (CONACYT) for financial support of this work (project J35155-U). The authors also thank F. Candau and J. Selb for helpful discussions.

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