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Synthesis, characterization and rheological properties of three different associative polymers obtained by micellar polymerization

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Summary

We report the synthesis, characterization and rheological properties in aqueous solutions of three different water-soluble associative polymers (AP's) (telechelic, multisticker and combined). Polymer chains consisting of water-soluble polyacrylamides, hydrophobically modified with low amounts of N,N-dihexylacrylamide and a linear hydrophobic initiator. These have been prepared via free radical micellar polymerization. We compare the properties of these different polymers, with respect to the localization of the hydrophobic groups, using steady-flow experiments. In the semidiluted regime we clearly differentiate two different zero-shear viscosity (η_0) -vs- concentration (C) behaviors; a first semidiluted regime unentangled, where the viscosity increases strongly and directly with c and a second regime entangled, where the viscosity increases proportionally to C^4, independently of the localization of the hydrophobic group.

Introduction

Hydrophobically associating water-soluble polymers are a relatively new class of important macromolecules, which are increasingly used in industry due to their ability to impart improved rheological behavior to particulate dispersions [1-10]. Essentially, these polymers consist of a hydrophilic long-chain backbone, with a small number of hydrophobic groups localized either randomly along the chain or at the chain ends, and which usually comprise from 8 to 18 carbon atoms [11-14]. While the nature of their backbone usually renders the polymer soluble in an aqueous media, the intermolecular association of the hydrophobic groups leads to the formation of reversible three-dimensional network structures.

The pronounced thickening behavior observed in these systems arises from interpolymer hydrophobic associations. For example, the viscosity of aqueous solutions of copolymers of acrylamide with small amounts (≤ 1 mol%) of an alkylacrylamide, as the comonomer, shows a pronounced increase at a very low

comonomer concentration “C*”, which is known as the critical overlap concentration [15]. On the contrary, the onset of any similar increase in the viscosity of “pure” polyacrylamide will occur at concentrations much higher than C*.
Hydrophobically modified water-soluble polymers (HMWSP) can be classified into two main classes: (i) telechelic polymers**,** which normally are linear poly(ethylene oxide) (PEO) chains end-capped by long alkyl chains containing from 12 to 18 carbon atoms [16-22]; and (ii) multisticker polymer chains, in which the hydrophobic groups are randomly distributed as isolated units or as small blocks along the hydrophilic backbone [23-29]. Recently Jimenez et al. [30,31] presented a new class of polymer, the combined polymer, which combines the characteristics of both, the telechelic and the multisticker hydrosoluble polymers, that is, a polymer with hydrophobic parts on the chain ends as well as along the macromolecular chain.

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

Experimental

Synthesis of linear hydrophobic initiator. The hydrophobic initiator was prepared through a reaction between 4,4´-azobis(4-cyanopentanoic acid) (ACVA) and the alcohol, 1-dodecanol ($C_{12}H_{25}OH$) (ACVA12) in accordance with the procedure previously described by Belzung [32]. The synthesis and characterization of this initiator has been described in detail in previous papers [30, 31]. The conversion attained in this reaction was 87 %.

Synthesis of the hydrophobic monomers. The hydrophobic monomers were prepared via a reaction of acryloyl chloride with the N,N-Dihexylamine, according to the procedure previously described by Valint et al.[34]. The synthesis and characterization of this initiator has been described in detail in previous papers [1, 2]. The conversion was 70 %.

Synthesis of the associative polymers. The associative polyacrylamides were obtained by micelar copolymerization [35, 29, 36-37]. The total concentration of monomers was of 3 wt% (99.5 % mol acrylamide and 0.5 % mol of N,N-dihexylacrylamide), the hydrophobic initiator concentration was 1×10^{-3} mol/L (in the case of homopolymer (PAM) and the multisticker polymer (PAM-co-DHAM), ACVA was used without modifier), the reaction temperature was 68°C and the total reaction time was 7 h. In this process, the hydrophobic monomer and the hydrophobic initiator are solubilized within sodium dodecyl sulfate (SDS) micelles (in the case of the telechelic and the combined polymers), whereas acrylamide is dissolved in the aqueous continuous medium. The polymers obtained were purified with methanol and dried under reduced pressure at 40°C. In figure 1 we present a scheme of the three different polymers obtained.

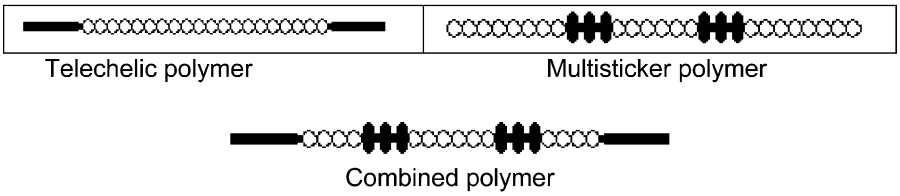

Figure 1. Scheme of the three different associative polymers obtained by micellar polymerization.
OOOO hydrophilic monomer sequence, ▬ hydrophobic initiator,
⧫⧫⧫ hydrophobic monomer sequence

Due to the termination mechanisms that occur in polymerization reactions, such as combination and disproportion, 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 then to be separated by fractionation as follows: the copolymer mix is solubilized in water at a 5 wt%, then cooled and a gel, constituted essentially by triblocks (telechelic) is formed. Finally, the gel is separated and precipitated in methanol and filtered, washed and vacuum dried.

The characteristics of the samples investigated are given in Table 1. The hydrophobe content in the polymers [H] (which corresponds, within the experimental error, to that in the monomer feed) was 0.5 mol %. The hydrophobe / surfactant molar ratio was adequately adjusted in order to obtain the desired number of hydrophobes per micelle, N_H, which was 3. N_H was calculated from the following relationship:

$$N_H=([H]\times N_{agg})/([SDS]-cmc_{SDS})$$

were [SDS], cmc_{SDS} and N_{agg} are respectively, the molar concentration of the surfactant, its critical micelar concentration and its aggregation number (cmc_{SDS} is equal to 0 9.2×10^{-3} mol/L and N_{agg} is equal to 60 at the polymerization temperature of 65°C) [3,38]. The weight-average molecular weight M_W and composition of the samples were determined by light scattering and NMR as previously described [39].

Table 1. Polymer characteristics

Sample	Conversion wt%	M_w ($x10^{-5}$)	$[H]^{a)}$ (mol %)	$S^{b)}$
PAM/ACVA	98	7.34	0	-
PAM-co-DHAM/ACVA	96	8.30	0.48	~ 9.3
PAM/ACVA12	73	7.44	0	-
PAM-co-DHAM/ACVA12	78	6.00	0.47	~ 6.6

a) Hydrophobe content in the polymer
b) Number of hydrophobic blocks per chain (see Experimental)

These amphiphilic copolymers cannot be characterized by size exclusion chromatography (SEC) in water, due to aggregation phenomena. However, homopolyacrylamide prepared under identical experimental conditions, but without hydrophobe, have a polydispersity index M_W/M_n determined by SEC around 2. Thus, a similar molecular weight distribution can be assumed for the copolymers. On the basis of the above considerations, the average number of hydrophobic blocks (i.e. stickers) per macromolecular chain, S, was calculated from the following relationship:

$$S = (M_W/2m) \times [H]/N_H$$

Where m is the molecular weight of the monomer unit (g/mol) (acrylamide m=71 g/mol) and $M_W/2m$ corresponds to the number-average degree of polymerization, N. The sample code of the copolymers refers to the hydrophilic monomer, hydrophobic monomer 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 with a 12 carbon atoms linear chain (ACVA12).

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, the measuring system was enclosed with a solvent trap. The zero-shear viscosity (η_0) was obtained by extrapolation of the apparent viscosity at very low shear rates. The range of concentrations of the associative polymer aqueous solutions was 0.002 wt % < C < 10 wt %. Linear viscoelasticity experiments were performed on samples that were viscous enough to provide meaningful analysis.

Results and discussions

The associative polymers

The ^1H NMR spectrum of PAM-co-DHAM / ACVA12 is presented in Figure 2.

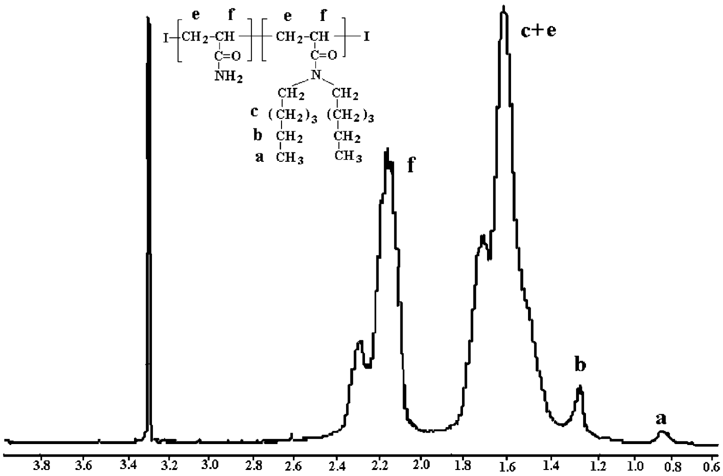

Figure 2. The ^1H NMR spectrum of the PAM-co-DHAM / ACVA12 in D_2O.

The ratio of the two monomers in the copolymer, was determined by integrating the signals of the methyl proton (~ 0.8 ppm), and of ethylene proton attached to the backbone (2 to 2.4 ppm), the ratio was found to be 0.49 mol% with respect to the feed ratio. The NMR spectrum does not show the signals of the hydrophobe initiator, which can be due to the small quantity of initiator used.

Figure 3 shows the variation of the steady-state viscosity η as a function of shear rate $\dot{\gamma}$ for a PAM-co-DHAM associative copolymer at different concentrations, in aqueous solution. At concentrations ≤ 1 wt % the system is Newtonian; that is, there is no detectable variation of η with $\dot{\gamma}$. Upon further increasing the concentration, the zero-shear viscosity increases drastically, and the samples exhibit a stronger shear thinning behavior. The crossover shear rate, $\dot{\gamma}_C$, where the viscosity departs from the limiting plateau value, is a decreasing function of the concentration.

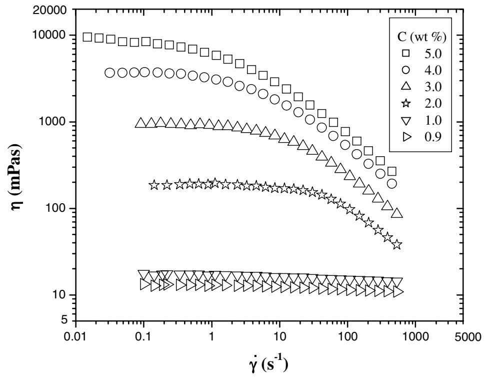

Figure 3. log-log variation of the viscosity versus shear rate of the copolymer PAM-co-DHAM at different concentrations.

Figure 4 presents the variation of the η_0 as a function of the polymer concentration, in a log-log plot, for the multisticker associative copolymer and the homopolymer. Three regimes can be identified:

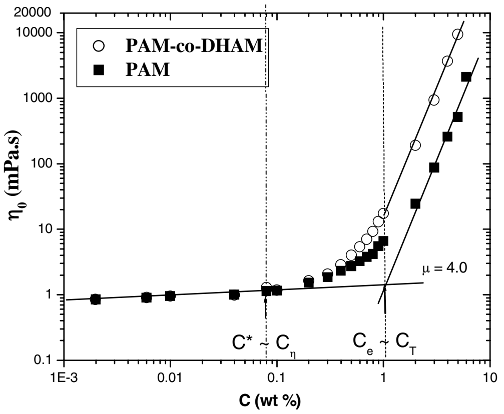

Figure 4. log-log variation of the zero-shear viscosity, η_0, as a function of the polymer concentration for the multisticker associative copolymer.

When $C < C_\eta$. In this dilute regime, the viscosity is slightly depressed, as compared to that of the corresponding unmodified polymer. This is due to the chain concentration

resulting from intramolecular associations [4, 35]. The concentration C_η (which is 0.08 wt%), is approximately 10 times lower than C_e (which is 1.4 wt%), which in turn is the concentration at which the entanglements become effective in the unmodified polymer. These results suggest that C_η is rather close to the overlap concentration C^*.
When the concentration is $C_\eta < C < C_T$; this regime is characterized by a rapid viscosity increase. It can be speculated that at the overlap concentration C* (which is very similar to C_η), intermolecular links form. These hydrophobic associations must be the main cause of the viscosity increase, according to the mechanism similar to that observed with telechelic associating polymers. This mechanism involves the disengagement of an associating sequence from a crosslink, followed by Rouse relaxation [40, 41]. In the telechelic systems the linear viscoelastic behavior is Maxwellian [41]. In this regime, the viscoelasticity is possibly controlled by the effect of intermolecular hydrophobic associations, and it can be considered as the equivalent to the semidilute unentangled regime observed in unmodified polymers. In this respect, it is striking that C_T closely coincides with the C_e value of the corresponding unmodified polymer. It should be noted that, for the multisticker chains such as these studied here, the disengagement of one hydrophobic block from a cross-link does not permit the relaxation of the entire chain, since the chain is still "anchored" by many other stickers even in the absence of entanglements. Therefore, the chain cannot diffuse very far between two consecutive sticker releases [42].
When $C > C_T$. In this regime, the viscosity increases as a function of C^4. In fact, it can be safely assumed that, in the concentration range considered, the density of entanglements is much larger than that of hydrophobic associations. This is the case which has been treated in the sticky reptation model developed by Leibler et al. [42], which considers a concentrated solution of a monodisperse chain of N monomers with S stickers attached to each chain.

In Figure 5 we present the log-log variation of the η_0 as a function of the polymer concentration, for the associative telechelic polymer PAM/ACVA12 with 12 carbon atoms hydrophobic groups at the chain ends -that arise from the initiator- as well as for the unmodified homopolymer.

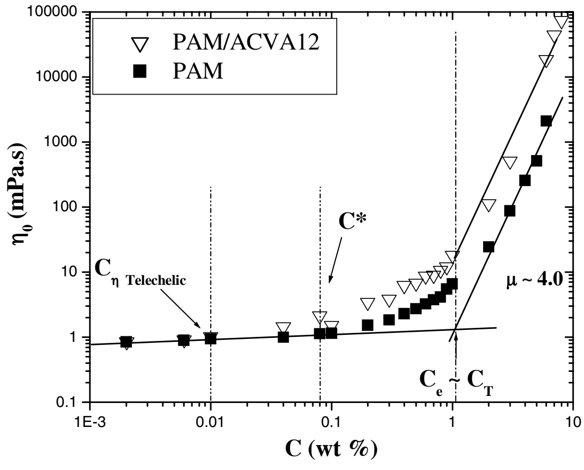

Figure 5. Variation of the zero shear viscosity η_0 as a function of the polymer concentration for the telechelic polymer.

It is observed that PAM/ACVA12 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, $C_{\eta telechelic}$ (0.01 wt %) versus C^* (0.08 wt %). This means that the intermolecular interactions in the PAM/ACVA12 system start to be effective at a concentration lower than that corresponding to the polyacrylamide homopolymer ($C_{\eta telechelic}$ versus C^*_{PAM}). That is, the amplitude of the first (dilute) regime is reduce, whereas that of the second (semidilute unentangled) regime is greatly extended from $C_{\eta telechelic}$ to C_T. Finally, at concentrations above C_T, the behavior is similar to that observed in Figure 4.

In Figure 6 we present the log-log variation of the zero-shear viscosity, η_0 as a function of the polymer concentration for all the systems investigated. Comparing the viscosity of the combined associative copolymer with that of the telechelic and multisticker**,** it is observed that the concentration (C_η) at which the system passes from the first regime to the second one is the same for both the combined and the telechelic, whereas that for the multisticker is higher, that is, [$C_{\eta(combined)} = C_{\eta(telechelic)} = 0.01$wt%] < [$C_{\eta(multisticker)} = 0.08$wt%]. From this, it can be concluded that, for the case of the combined polymer, the localization of the hydrophobic groups at the end of the macromolecule have a much greater influence on the C_η, as compared with the hydrophobic groups along the chain. The concentration needed to pass from the unentangled to the entangled regime is the same for all the synthesized associative polymers (C_T) and for the unmodified homopolymer (C_e). However, above the concentration $C_{\eta(combined)}$, that is, in the second and the third regimes, the viscosity of the combined polymer is markedly superior than that of the telechelic and the multisticker polymers, due to the synergistic effect of the hydrophobic groups located along the chain as well as those located at the chain ends.

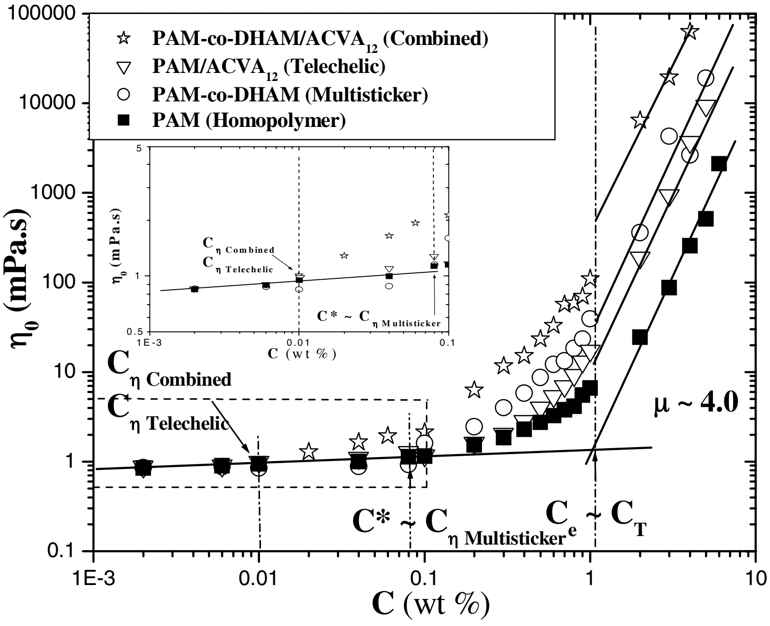

Figure 6. log-log variation of the zero-shear viscosity η_0.as a function of the polymer concentration for all the systems investigated. Inset: zoom of the region presented in dash.

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 by a free radical micellar 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:

A dilute regime, in which $C<C_\eta$, where the chains are isolated and the viscosity is essentially affected by intramolecular interactions. The amplitude of this regime varied according to the localization of the hydrophobic groups.
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.
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 close to 4, independently of the 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 combined polymer presents a synergic effect due to the presence of the hydrophobic chain ends as well as those located along of the macromolecule.

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