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ORIGINAL PAPER

Synthesis, characterization and rheological properties of three different microstructures of water-soluble polymers prepared by solution polymerization

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Abstract Three different structures were synthesized via solution free radical polymerization. Polyacrylamides hydrophobically modified with small amounts of two different *N′N*-dialkylacrylamides [*N*,*N*-dihexylacrylamide (DHAM) and *N*,*N*-dioctylacrylamide (DOAM)] and two different *N*-alkylacrylamides [*N*-dodecylacrylamide (DAM) and *N*-hexadecylacrylamide (HDAM)] have been synthesized using two linear hydrophobic initiators with 12 ($ACVA_{12}$) and 16 ($ACVA_{16}$) carbon atoms and two di-substituted hydrophobic initiator with two chains of 6 ($ACVA_{di6}$) and 8 ($ACVA_{di8}$) carbon atoms derived from 4′4-azobis(4-cyanopentanoic acid) (ACVA). The polymers obtained were telechelic, multisticker and combined. The initiators, monomers and polymers synthesized were characterized by ^{1}H NMR and light scattering (LS). The rheological properties of these three different associative polymers were investigated using steady-state experiments. The effect of location and structure (linear or di-substituted) of the hydrophobic groups upon the viscosity of the polymer in solution was studied.

Keywords Telechelic polymers · Rheology · Combined polymers · Multisticker polymers

Introduction

Over the past few decades, extensive studies in academic and industrial laboratories have been focused on the development of polymers for use as associative thickeners, in many application areas including fluid drag in latex paints, coatings and cosmetics [1–25]. Its properties in aqueous solution thickeners are attributed to

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the association of small hydrophobic units incorporated within a hydrophilic skeleton [2–4, 12, 17, 19, 24–26]. Over the years, many kinds of associative polymers have been developed, depending on the method of synthesis, or distribution of hydrophilic groups. Two different architectures of associative polymers have emerged: telechelic polymers, in which the hydrophobic modifications are located only in the extremes of the hydrophilic polymer chains [6, 8], and multisticker polymers, in which the hydrophobic groups are distributed along the hydrophilic chain [15, 27, 28]. A large number of researchers have studied the effect of the location of these hydrophobic groups, comparing the two types of polymers, HEUR and HMHEC; the first, containing the hydrophobic groups at the chain ends and the latter with the hydrophobic groups distributed along the hydrophilic chain. These studies however, are somewhat limited because the two water-soluble polymers types may possess a hydrophilic chain of different chemical nature, which makes their comparisons not so valid.

In a previous article, we reported the synthesis of a new structure of associative polymer called combined polymer [29], in which the hydrophobic groups are both, at the chain ends and along the hydrophilic polymer chain. Another parameter that has attracted the attention of researchers in this area, is the type of hydrophobe modification used; some authors have opted for the use of fluorinated groups, although its major disadvantage is its high cost, thus, most authors use hydrocarbon groups as modifiers. For the particular case of polyacrylamides, the structures more commonly studied are the multisticker polymers, with very few studies on telechelic polyacrylamides.

The significance of these hydrophobic groups location lies in its rheological response, which is essentially due to the type of aggregate that each polymeric structure will form in aqueous solution. Much has been written about the formation of networks or micellar flowers (*as some authors call them*) [30–32], which produce the high viscosity characteristic of the telechelic polymers. Aggregates formed by the multisticker polymers are more complicated to understand due to their more complex structure.

The purpose of this study is to obtain polymeric structures, containing hydrophobic groups at the ends and along the water-soluble polymer chain, as well as their precursors (telechelic and multisticker structures) for a comparative study. For this, linear and di-substituted hydrophobic modifiers of different lengths (monomers as well as initiators) were synthesized. In addition, a study of the rheological properties of aqueous solutions of the obtained polymers was carried out.

Experimental

Materials

Acrylamide (AM) (>99%), acetonitrile (>99.9%), chloroform d_6 (99.96 atom % D), deuterium oxide (99.990 atom % D), dimethyl sulfoxide-d_6 (99.96 atom % D), formamide (>99%), triethylamine (>99.5%) and tetrahydrofuran (THF) (99.9%)

were from Aldrich, and acryloyl chloride (>96%), dodecylamine (>99.5%), hexadecylamine (>99%), 4,4′-azobis(4-cyanopentanoic acid) (ACVA) (>98%), dihexylamine (97%), 1-dodecanol (>98.5%), 1-hexadecanol (99%), dioctylamine (>97%), were from Fluka.

Synthesis of the hydrophobic initiators

The linear hydrophobic initiators were prepared through a reaction between ACVA and two different alcohols, 1-dodecanol ($C_{12}H_{25}OH$) and 1-hexadecanol ($C_{16}H_{29}OH$) in accordance with the procedure previously described [29, 33]. The di-substituted hydrophobic initiators were synthesized according to the procedure previously described [34] via a reaction of ACVA and two different *N*,*N*-dialkylamine (dihexylamine or Dioctylamine). Figure 1 shows a schematic representation of these two types of hydrophobic initiators.

Synthesis of the hydrophobic monomers

The di-substituted hydrophobic monomers were prepared via a reaction of acryloyl chloride with the corresponding *N*,*N*-dialkylamine (dihexylamine or dioctylamine) and the *mono*-substituted hydrophobic monomers with *N*-alkylamine (dodecylamine or hexadecylamine) in accordance with the procedure previously described by Valint et al. [35]. Figure 2 shows a schematic representation of these two types of hydrophobe monomers.

Synthesis of the copolymers

All copolymers were prepared via solution copolymerization using acetonitrile as solvent. The initial concentration of monomers (AM and hydrophobe) was maintained constant at 3% (wt/wt) based on volume of acetonitrile. The temperature was fixed at 82 °C and the initiator concentration was 0.07 mol% relative to the

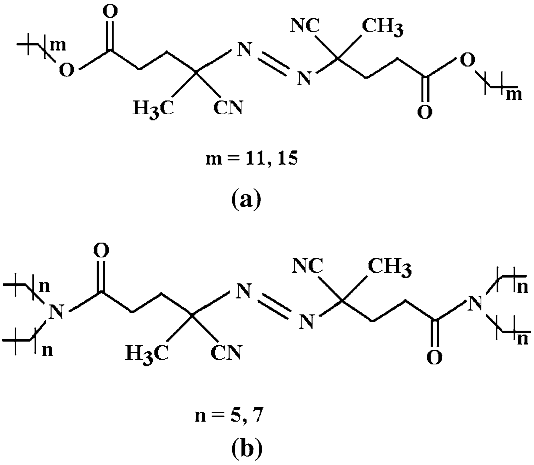


Fig. 1 Schematic representation of two synthesized hydrophobic initiators: **a** linear, **b** di-substituted

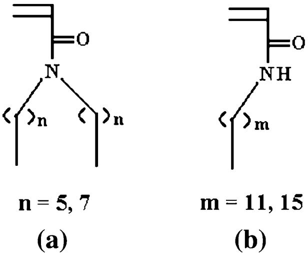


Fig. 2 Schematic representation of two hydrophobic monomers used: **a** *N*,*N*-dialkylamine (di-substituted), **b** *N*-alkylamine (linear)

monomer feed. Copolymerizations were carried out at 1 mol% of hydrophobic monomer relative to the total feed of monomers. Homopolyacrylamide was prepared under identical experimental condition using ACVA as initiator. A typical example of a solution copolymerization was as follows: the AM, the hydrophobic monomer and 468 g of acetonitrile were added, at room temperature, to a 600 mL reactor equipped with thermometer, condenser and mechanical stirrer. The mixture was vigorously agitated, purged with nitrogen during 1 h, and heated to 82 °C under agitation. Then, the initiator was added to the mixture to start the reaction, and bubbling was maintained during all the polymerization reaction, which was run for about 1 h. The polymer obtained was insoluble in acetonitrile. The polymer was recovered by filtration and washed with methanol to remove traces of residual monomer and initiator, and finally filtered and dried under reduced pressure at 40 °C for 48 h. Due to the termination mechanisms that occur in reactions such as 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, i.e., telechelic), which have to be separated by fractionation (according to a method described by Belzung et al. [36]) as follows: the mixture of polymers is solubilized in approximately 5% water, then a non-solvent is added (acetonitrile) until persistent turbidity. The solution is cooled slowly in an ice bath. The presence of two phases is observed, a gel that is essentially constituted by triblock (telechelic) polymers and an aqueous solution essentially constituted by diblock polymer. Thereafter, the gel and the aqueous solution were separated, precipitated in methanol, filtered, washed and vacuum dried. The polymers obtained were characterized by ^{1}H NMR, and light scattering (LS).

The chemical structure of the synthesized polymers is presented in the Fig. 3.

The ^{1}H NMR spectrum of the multisticker polymer PAM-*co*-DAM is presented in Fig. 4. The ratio of the two monomers in the copolymer, was determined by integrating the signals of the methyl proton ($\sim$0.8 ppm), and of the ethylene proton attached to the backbone (1.1–1.8 ppm), the ratio was found to be around 0.82 mol% with respect to the feed ratio.

Molecular weights

The samples weight-average molecular weights M_{w} was determined by light scattering, LS (using formamide as solvent). The refractive-index increments measured at $\lambda = 633$ nm on a Brice–Phoenix differential refractometer in

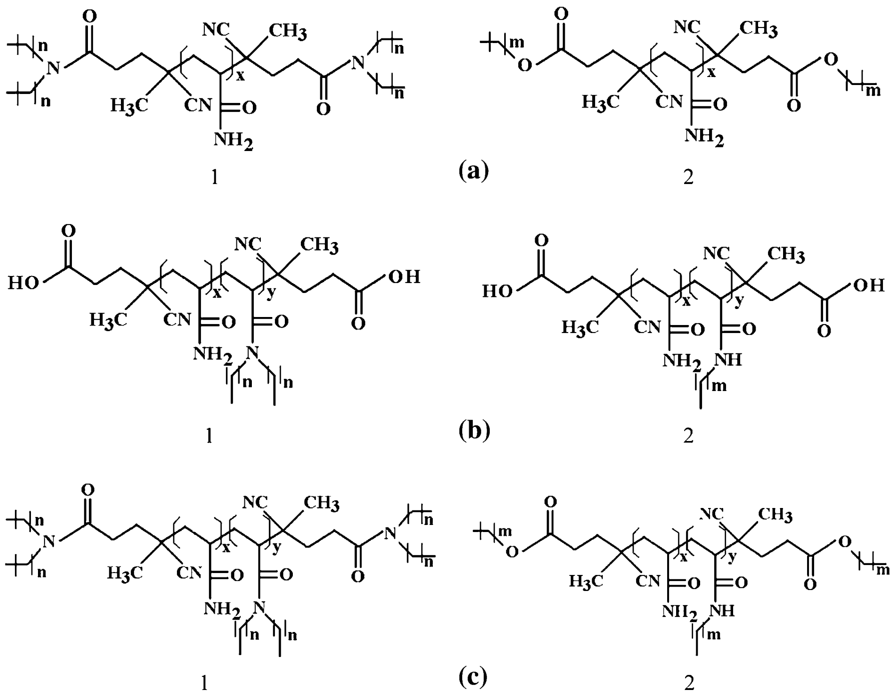
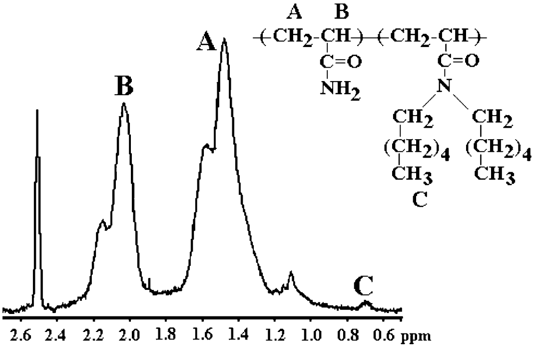


Fig. 3 Schematic representation of the synthesized hydrophobic polymers **a** telechelic, **b** multisticker and **c** combined. *1* di-substituted and *2* linear

Fig. 4 The ^{1}H NMR spectrum of the multisticker PAM-*co*-DHAM polymer. D_2O was used as solvent



formamide were 0.109 mL/g as previously described [37]. These amphiphilic copolymers cannot be characterized 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. Thus, a similar molecular weight distribution can be assumed for the copolymers. On the basis of the above considerations, the average number of hydrophobic groups (i.e. stickers) per macromolecular chain, *S* was calculated from the following relationship:

$$S = (M_W/2.5m) \times [\mathrm{H}] \tag{1}$$

where m is the molecular weight of the monomer unit (g/mol) (AM $m = 71$ g/mol), [H] is the molar concentration of the hydrophobe monomer and $M_W/2.5$ m corresponds to the number-average degree of polymerization, N.

Characterization

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

Sample preparation

Solutions at different concentrations 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.

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 a temperature of 25 ± 0.05 °C. To minimized 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. The range of concentration of the aqueous polymer solutions was $0.01 \text{ wt\%} < \mathrm{C} < 5 \text{ wt\%}$.

The sample code of the copolymers refers to the hydrophilic monomers, hydrophobic monomers and the length of the hydrophobic initiator. For example, PAM-co-HDAM/ACVA$_{12}$ stands for a poly(acrylamide-*co*-hexadecylacrylamide) using a linear initiator hydrophobically modified with a 12 carbons chain (C_{12}). The characteristics of the samples investigated are given in Table 1.

Results and discussion

Figure 5 shows the variation of the zero shear viscosity (η_0) as a function of the polymer concentration [C] for two di-substituted and two linear telechelic polymers synthesized with different initiator length on the alkyl chain [diC_6 and diC_8 (di-substituted) and C_{12} and C_{16} (linear)]. These polymers are compared with the homopolymer. It is observed that for $[\mathrm{C}] < 0.6$ wt%, the viscosity of the PAM/ACVA$_{di8}$ polymer is slightly lower than that of the corresponding unmodified polymer. This is due to the chain contraction resulting from intramolecular associations. But at higher concentrations ($[\mathrm{C}] > 0.6$ wt%) the viscosity is higher than that of the homopolymer; on this region the behavior is controlled by the effect of the intermolecular hydrophobe association effect, this tends to form

Table 1 Polymer characteristics

Type	Polymer	[H] (mol%)	Conversion	M_w (g/mol)	S^a
Homopolymer	PAM		90.32	190,000	
Telechelic	PAM/ACVA$_{di6}$		73.92	232,000	2
	PAM/ACVA$_{di8}$		80.62	169,000	2
	PAM/ACVA$_{12}$		95.76	220,000	2
	PAM/ACVA$_{16}$		96.58	190,000	2
Multisticker	PAM-*co*-DHAM	0.78	87.39	203,000	9
	PAM-*co*-DOAM	0.67	85.43	209,000	8
	PAM-*co*-DAM	0.83	86.41	182,000	9
	PAM-*co*-HDAM	0.8	93.18	200,000	9
Combined	P(AM-*co*-DHAM)/ACVA$_{di6}$	0.76	89.68	195,000	10
	P(AM-*co*-DOAM)/ACVA$_{di8}$	0.84	98.85	186,000	11
	P(AM-*co*-DAM)/ACVA$_{12}$	0.98	82.69	208,000	13
	P(AM-*co*-HDAM)/ACVA$_{16}$	0.92	91.54	253,000	15

[a] Number of hydrophobes per chain obtained with ec. 1

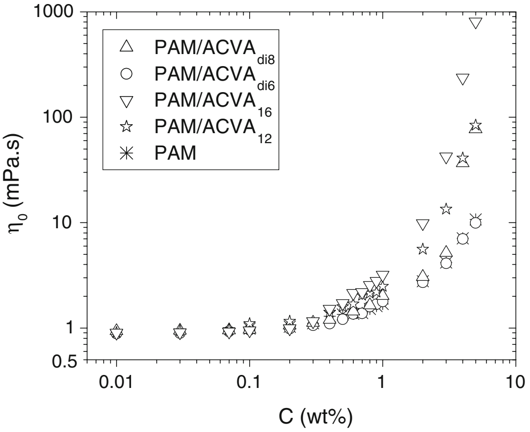
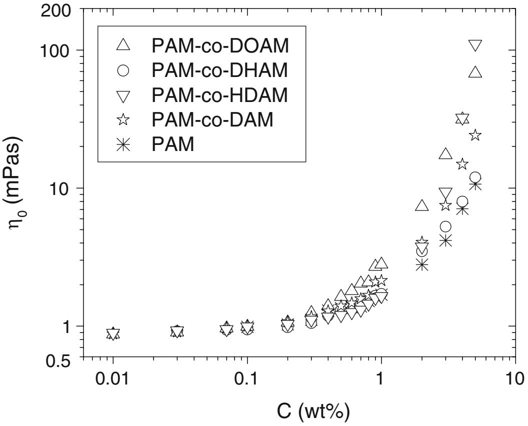


Fig. 5 Variation of the zero shear viscosity η_0 as a function of the polymer concentration for the telechelic polymers

tridimentional physical networks and the viscosity increases [15, 27, 38]. For the PAM/ACVA$_{di6}$, polymer, on the other hand, the viscosity was always lower than that of the corresponding homopolymer at all concentrations studied. A possible explanation could be the short hydrophobic chain length (diC$_6$) localized at each polymer chain end, this can explain the lower viscosity presented by the PAM/ACVA$_{di6}$ polymer. In addition, Volpert et al. [15] showed that hydrophobic groups with short carbon chain lengths (diC$_6$) randomly distributed along the polymer chain do not produce any associative copolymer behavior. For the PAM/ACVA$_{12}$ polymer, a concentration of ~0.5 wt% is necessary in order for the viscosity of the associative polymer to be higher than that of the homopolymer. For the PAM/ACVA$_{16}$, polymer, it is observed that at low concentration (0.3 wt%) the viscosity is about the same as that of the homopolymer, however, at higher concentration

Fig. 6 Variation of the zero shear viscosity η_0 as a function of the polymer concentration for the multisticker polymers



(0.4 wt%) the viscosity becomes higher and it increases markedly with concentration.

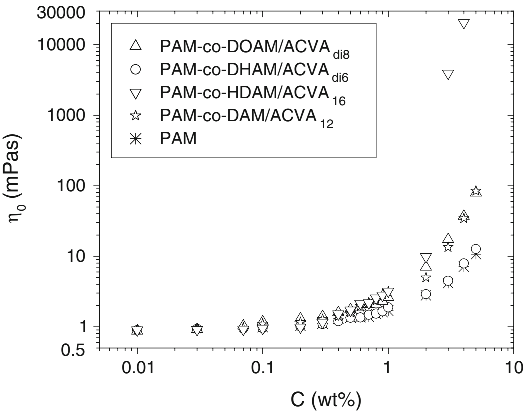
Figure 6 present the variation of η_0 as a function of [C] for two di-substituted and two linear multisticker polymers synthesized with different monomer lengths on the alkyl chain (diC$_6$ and diC$_8$ (di-substituted) and C$_{12}$ and C$_{16}$ (linear)). These polymers are compared with the homopolymer. It is observed that at low concentrations ([C] $<$ 1 wt%), the viscosity of the PAM-*co*-DOAM polymer is about the same as that of the homopolymer, however, at higher concentrations ([C] $\geq$ 0.2 wt%) the viscosity becomes higher and it increases appreciably with concentration. For the PAM-*co*-DHAM polymer, on the other hand, much higher concentrations ([C] $>$ 2 wt %) are necessary in order for the viscosity of the associative polymer to be higher than that of the homopolymer. The global behavior is the result of a transition from a system where the conformation of the macromolecular chains is controlled by the intramolecular interactions at low concentrations to a system where at higher concentrations, the intermolecular interactions have an important role [15, 27, 38]. This is in accordance with the general behavior reported on previews studies for several types of associative polymers [39, 40].

Figure 7 shows the variation of η_0 as a function of [C] for two di-substituted and two linear combined polymers synthesized with different monomer and initiator lengths on the alkyl chain. These polymers are compared with the homopolymer.

For the case of the di-substituted polymers, it is observed that for the PAM-*co*-DOAM/ACVA$_{di8}$ polymer, it is necessary to attain a concentration of 0.07 wt% in order to surpass the viscosity of the homopolymer, whereas for the PAM-*co*-DOAM/ACVA$_{di6}$ polymer this concentration has to be above 3 wt%. For the case of the linear polymers, it is observed that the PAM-*co*-DAM/ACVA$_{12}$ polymer concentration has to reach approximately 0.1 wt%, whereas as that of PAM-*co*-HDAM/ACVA$_{16}$ has to reach approximately 0.4 wt%.

For the di-substituted polymers, their behavior can be explained as mentioned before; it is due to the difference in length of the hydrophobic part, i.e., the longer the chain, the more intermolecular interactions will form at small concentrations.

Fig. 7 Variation of the zero shear viscosity η_0 as a function of the polymer concentration for the combined polymers



The contrary occurs with the linear polymers, i.e., the longer the hydrophobic chain, the higher the concentration needed to surpass the viscosity of the homopolymer for example, a higher concentration of PAM-*co*-HDAM/ACVA$_{16}$ ([C] = 0.4 wt%) would be required to surpass the viscosity of the homopolymer, as compared to the required concentration of PAM-*co*-DAM/ACVA$_{12}$ ([C] = 0.1 wt. This could result from the competition of inter and intra molecular interactions, i.e., the longer the hydrophobic chain, the stronger the intramolecular interactions, and therefore, the higher the concentration of associative polymer needed to increase the viscosity above that of the homopolymer. On the contrary, the shorter the hydrophobic length, the lower the concentration of associative polymer needed to increase the viscosity above that of the homopolymer.

This should also occur with the di-substituted polymers, but due to the hydrophobic short chains, the above mentioned behavior is not observed.

Conclusions

Three different types of associative hydrosoluble polymers (telechelic, multisticker and combined) were prepared via solution polymerization and characterized by NMR and LS. Finally, their influence on the rheological properties of an aqueous solution was studied.

It was found that the linear polymers produced a higher viscosity as compared to the di-substituted polymers. It was also found that the telechelic polymers produce a greater thickening effect than the multistickers, even when the quantity on the hydrophobic groups is lower, which brings out the importance on the localization of these groups on the thickening properties. The combined polymers produce a higher viscosity as compared to both, the telechelic and multisticker polymers which supports the conclusion of a synergistic effect. This gives the associative combined polymers a much higher capacity to form interactions on hydrophobic molecules. A detailed study on the rheological properties for these three polymers will be presented on a future study.

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