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Synthesis and characterization of telechelic polymers obtained by micellar polymerization

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Summary

The synthesis, characterization and rheological properties in aqueous solution of two telechelic polymers of different structures and size are reported: they are water soluble polyacrylamides, hydrophobically modified with linear and di-substituted hydrophobic initiators. The polymers were prepared via free radical micellar polymerization. The results of static light scattering (SLS), showed similar weight-average molecular weights (M_w) in all of the synthesized polymers. No signal corresponding to the presence of the hydrophobic group of the initiator could be observed by ^{1}H NMR; however, the presence of these hydrophobic groups was demonstrated using rheological measurements.

Introduction

Polymers that associate via physical interactions in solution have received much attention as a replacement for high-molecular weight polymeric viscosifiers. Such associating polymers are now used in a variety of applications because of their unique rheological properties [1-4]. Water-soluble associating polymers are especially interesting because of their role as fluid thickeners in foods, coatings, paints, controlled drug delivery, and inmobilization of enzymes and cells [5-9]. Many of these associating polymers are amphiphilic: they contain a hydrophilic main chain with hydrophobic side chains. For example, polyacrylamides (PAM) and cellulose can be chemically modified by attachment of hydrophobic units along the chain (multisticker polymers) [10-12] or at the chain ends (telechelic polymers) [13-15]. Strong associations between these hydrophobic units lead to the formation of transient networks that depend not only on the structure of the polymer chain (i. e., molecular weight of the main chain, number density, size and distribution of the stickers), but also on external factors such as added surfactants, cosolvents and salts [16-18]. The telechelic polymers are obtained by chemical modification of preexistent polymers [19, 20], but there are some papers that describe their synthesis using a hydrophobic initiator [21, 22].
In this study we report the synthesis and characterization of several telechelic polymers by micellar polymerization using hydrophobic initiators derived from

4,4´-azobis(4-cyanopentanoic acid) (ACVA) with different chain lengths and structure. The hydrophilic monomer was acrylamide. In addition, we carried out a study of the rheological properties of these polymers. Figure 1 shows a schematic representation of the two structures of the telechelic polymers.

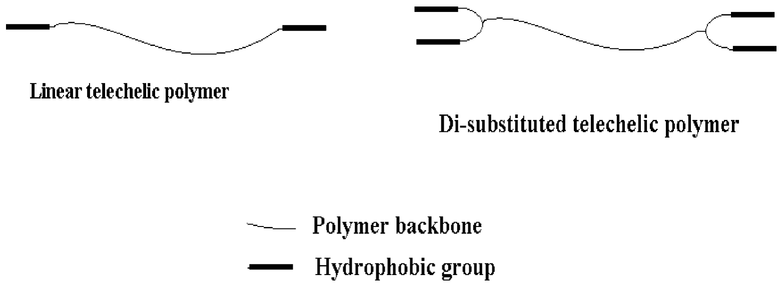
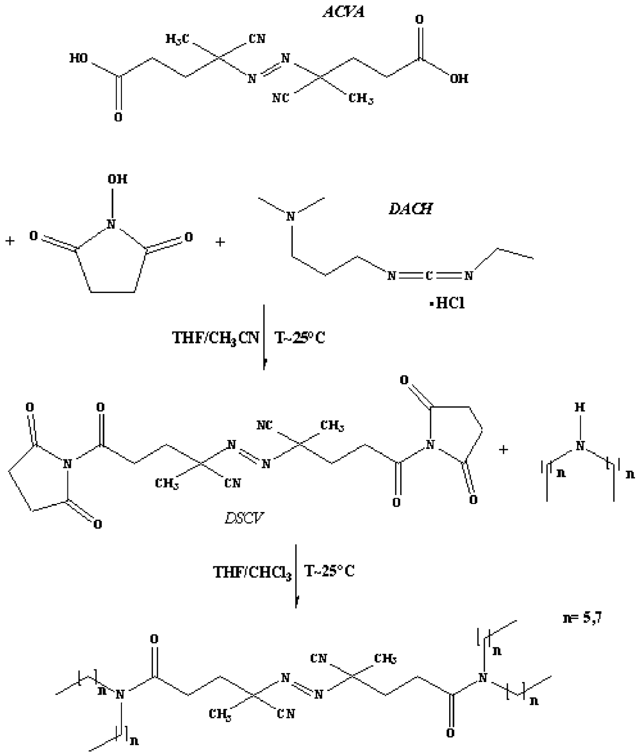


Figure 1. Schematic representation of the two different telechelic polymers obtained by micellar polymerization.

Experimental

Synthesis of the linear hydrophobic initiators. The linear hydrophobic initiators were prepared through a reaction between ACVA and two different alcohols: 1-dodecanol ($C_{12}H_{25}OH$) (ACVA$_{12}$) and 1-hexadecanol ($C_{16}H_{29}OH$) (ACVA$_{16}$), according to the procedure described in a previous paper [23]. The conversions obtained in these reactions were 75.4 and 91 % for ACVA$_{12}$ and ACVA$_{16}$, respectively.

Synthesis of the di-substituted hydrophobic initiators. The di-substituted hydrophobic initiators were synthesized according to the procedure previously described by Kitano et al [24]: 10 g (0.0357 mol) of ACVA, 10.26 g (0.0891 mol) of N-hydroxysuccinimide, 20.50 g (0.1069 mol) of N-(3-dimehylaminoproyl)-N'-ethylcarbodiimide hydrochloride (DACH) and 500 mL of THF/CH_3CN (1:1 v/v) were mixed in a 1000 mL flask equipped with a magnetic stirrer. The reaction was allowed to proceed for 12 h at room temperature. The solvent was eliminated by evaporation and the solid (disuccinimidyl 4,4'-azobis(4-cianovalerate)) (DSCV) was purified with cold water and dried under vacuum for 12 h. To prepare the di-substituted hydrophobic initiator, 25 g (0.0527 mol) of DSCV were placed in a 500 mL flask with the di-alkylamide in 360 mL of THF/$CHCl_3$ (2:1 v/v) and the reaction was allowed to proceed for 24 h at room temperature. The product was purified by silica gel chromatography using a mixture of hexane and ethyl acetate (3:1 v/v). The purified initiator was precipitated in acetonitrile and dried under vacuum for 24 h. The di-substituted hydrophobic initiators were characterized by FTIR and ^{1}H NMR spectroscopy. The conversions obtained in these reactions were 59 and 65 % for ACVA$_{di6}$ and ACVA$_{di8}$, respectively. The reaction is presented in scheme 1 and the ^{1}H NMR spectrum of the di-substituted hydrophobe initiator ACVA$_{di6}$ is shown in Figure 2. The NMR spectrum of the initiator does not show the acid proton of ACVA at 13.2 – 10 ppm; the shift of the alfa carbonyl groups occurs at lower field (i.e. at 2.5 – 2.4 ppm) due to the ester formation, which confirms the occurrence of the expected reaction.



Scheme 1. The synthesis of di-substituted hydrophobic initiator.

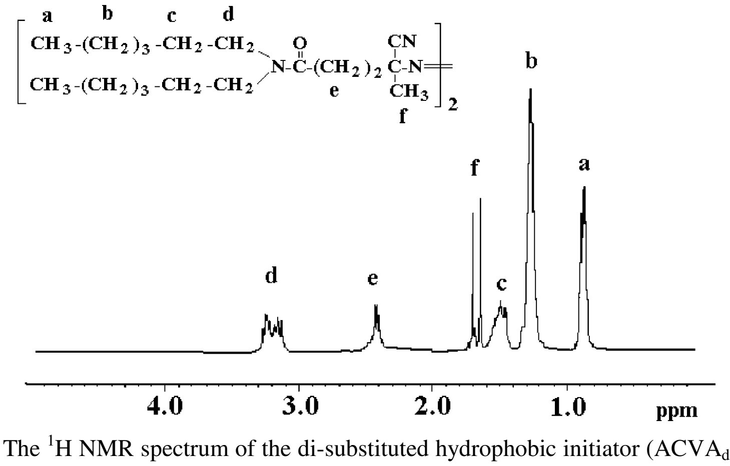


Figure 2. The ${}^{1}H$ NMR spectrum of the di-substituted hydrophobic initiator ($ACVA_{di6}$) in $CDCl_3$.

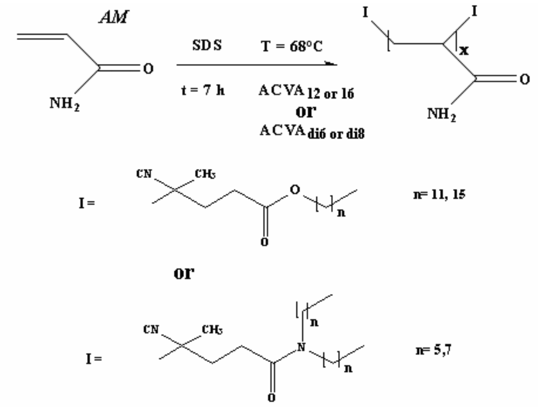
Synthesis of the telechelic polymers. The associating polyacrylamides were obtained by micellar polymerization [1-3]. In this process the hydrophobic initiator is solubilized within SDS micelles, whereas acrylamide is dissolved in the aqueous continuous medium. Firstly it was necessary to find the quantity of SDS to dissolve the hydrophobe initiator, we found this quantity to vary between 1.5 and 4.5 wt% depending on the hydrophobic initiator used. The initial concentration of monomer was maintained constant at 3 wt% based on volume of water, the initiator concentration used was 1* 10^{-3} mol/L, the temperature and reaction time were 68°C and 7 h, respectively. Homopolyacrylamide was prepared under identical experimental conditions using ACVA as initiator (the molar concentrations of the recipes investigated are given in Table 1).

Table 1. Molar concentration of the recipes investigated.

Polymer	**PAM-ACVA$_{di6}$**			**PAM-ACVA$_{di8}$**		
Reagent	**ACVA$_{di6}$**	**AM**	**SDS**	**ACVA$_{di8}$**	**AM**	**SDS**
mol/L	0.0010	0.4221	0.0506	0.0010	0.4221	0.0505
Polymer	**PAM-ACVA$_{16}$**			**PAM-ACVA$_{12}$**		
Reagent	**ACVA$_{16}$**	**AM**	**SDS**	**ACVA$_{12}$**	**AM**	**SDS**
mol/L	0.0010	0.4221	0.1601	0.0010	0.4221	0.1200

A typical example of a micellar polymerization was as follows: SDS 34.61 g (0.12 mol/L), initiator 0.616 g (0.0010 mol/L) and 25 % of total water (242.5 mL) were added to a 1000 mL reactor equipped with thermometer, condenser and mechanical stirrer. The mixture was vigorously agitated and heated (68°C). The acrylamide 30 g (0.4221 mol/L) and the rest of the water (727.5 mL) were mixed separately in another flask. Both solutions were purged with nitrogen for 30 min. This mixture was added to the reactor to start the reaction. Agitation and nitrogen atmosphere were maintained during all the polymerization. The reaction was kept running for 7 h. 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. The reaction is presented in scheme 2.

Due to the termination mechanisms that occur in reactions such as those presented above (combination and disproportionation), these copolymerization 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,



Scheme 2. The synthesis of telechelic polymers.

i.e., telechelic), which have to be separated by fractionation (according to a method described by Belzung et al. [25]) as follows: The mixture of polymer is solubilized in approximately 5 % water, then a non-solvent is added (acetonitrile) until persistent turbidity. The solution was cooled slowly in an ice bath. The presence of two phases was observed, a gel that is essentially constituted by triblock (telechelic) polymers and an aqueous solution essentially constituted by diblock polymer. After the separation of gel, the gel and the aqueous solution were separated, precipited in methanol, filtered, washed and vacuum dried. The polymers obtained were characterized by ^{1}H NMR, and static light scattering (SLS).

Molecular Weight. The weight-average molecular weights, M_w, of the samples were determined by static light scattering (SLS) (using formamide as solvent). The refractive-index increments measured at λ = 633 nm on a Brice-Phoenix differential refractometer in formamide were 0.109 mL/g as described previously [10]. 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 of around 2. It was assumed then, that the polydispersity of the corresponding associative copolymers was the same as the homopolymers.

Characterization. The composition of initiators and polymers was determined by ^{1}H-NMR spectroscopy using 1 wt% solution in $CDCl_3$ (for initiators) or D_2O (for 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 water and stirred gently until the solution was homogeneous.

Rheological measurements. Rheology determinations were performed at 25ºC in a Paar Physical UDS 200 controlled stress rheometer using either a cone and plate geometry (2° angle and 50 mm diameter) or a double gap geometry depending on the sample viscosity . The zero shear viscosity (η_0) was obtained by extrapolation of the apparent viscosity at very low shear rate. The range of concentrations of the aqueous polymer solutions was $0.1 \text{ wt\%} \leq C \leq 5 \text{ wt\%}$.

The sample code used to identify the copolymers refers to the hydrophilic monomer and to the length and structure of the hydrophobic initiators. For example PAM / $ACVA_{di6}$ stands for a polyacrylamide using an initiator di-substituted with a 12 carbons chain (Cdi6). Typical conversions and weight average molecular weights of the samples investigated are given in Table 2.

Table 2. Polymer characteristics.

Type	Polymer	Conversion (wt%)	M_w*10^{-5} (g/mol)
Homopolymer	PAM	97.57	7.3
linear telechelic	PAM/$ACVA_{12}$	67.35	7.4
	PAM/$ACVA_{16}$	72.27	6.9
di-substituted telechelic	PAM/$ACVA_{di6}$	89.74	7.1
	PAM/$ACVA_{di8}$	94.87	6.5

Table 3 presents the results of the polymer separation. It is very important to observe that the triblock chains are the main contributors to the thickening effect of the polymers. The results presented in Table 3 show that the telechelic polymers are constituted mainly by triblocks, which contain two hydrophobic groups situated on each end of the macromolecular chain. It is important to mention that all the polymers studied were separated in diblocks and triblocks, but the characterizations were made just for the triblock polymers.

Table 3. Weight percent of triblocks and diblocks of the polymers investigated.

	Polymer	Triblocks (wt%)	Diblocks (wt%)
Linear telechelic	PAM/ACVA$_{12}$	77.73	22.27
	PAM/ACVA$_{16}$	78.50	21.50
Di-substituted telechelic	PAM/ACVA$_{di6}$	96.15	3.85
	PAM/ACVA$_{di8}$	97.37	2.63

Figure 3 presents the ^{1}H NMR spectrum of the PAM / ACVA$_{di6}$ polymer. The signals of the ethylene proton of the hydrophilic chain can be observed (1.6 and 2.2 ppm). The signals of 0.8 to 1.3 ppm corresponding to the alkylic chain of the hydrophobic initiator were not observed which can be due to the small quantity of initiator used. The telechelic polymers PAM / ACVA$_{di8}$, PAM / ACVA$_{12}$ and PAM / ACVA$_{16}$ present the same signals.

Since no signal corresponding to the alkylic chain of the hydrophobic initiator were observed, we carried out a rheological study to check the presence of the hydrophobic group of the initiator. The viscosities of the telechelic polymers were determined and compared with the viscosity of the homopolymer synthesized with unmodified ACVA.

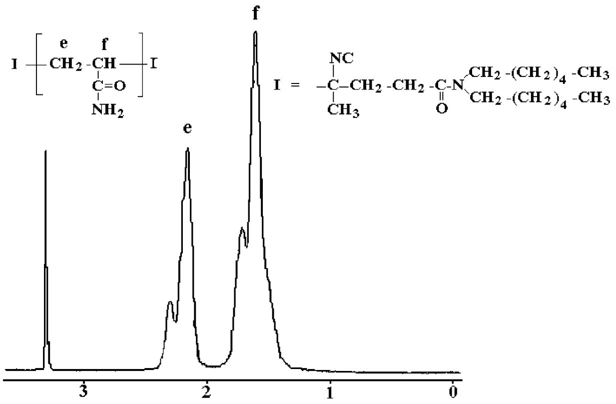


Figure 3. The ^{1}H NMR spectrum of the PAM / ACVA$_{di6}$ polymer in D_2O.

Figure 4 shows the effect on viscosity of diblock and triblocks PAM / ACVA$_{16}$ polymers at a concentration of 1 wt%. The differences among them are clearly seen. These differences are assumed to be because the diblocks can only form micelles, since they have only one hydrophobic end, whereas the triblocks will tend to form transitory networks, which will produce a greater increase in viscosity. It is worth

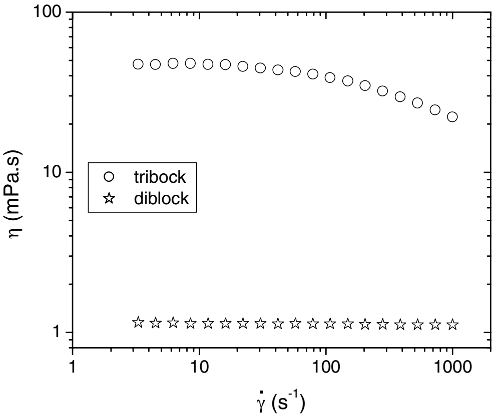


Figure 4. Comparison of the effect on viscosity of the diblock and triblocks PAM / ACVA$_{16}$ polymers at 1 wt%.

mentioning that at 1 wt%, these polymers are above the aggregation concentration, thus, they already present intermolecular hydrophobic interactions.

Figure 5 gives the variation of the steady-state viscosity η as a function of shear rate $\dot{\gamma}$ for the PAM / ACVA$_{12}$ polymer at different concentrations in aqueous solution. In the dilute regime (C ≤ 0.3 wt%), the system is Newtonian; that is, there is no detectable variation of η with $\dot{\gamma}$ within the shear rate studied. However upon further increasing the concentration (0.5 ≤ C), the Newtonian behavior at the lower $\dot{\gamma}$ is followed by a shear thinning behavior; this shear thinning is due to the breakdown of the intermolecular hydrophobic interactions, which produce a decrease in viscosity. We observed a similar qualitative behavior for all the polymers investigated.

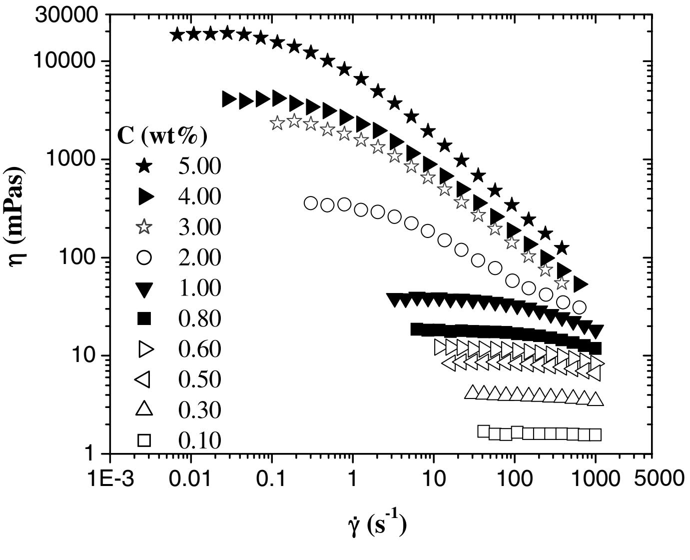


Figure 5. Steady-state viscosity η versus shear-rate for the PAM / ACVA$_{12}$ sample at various concentrations in water.

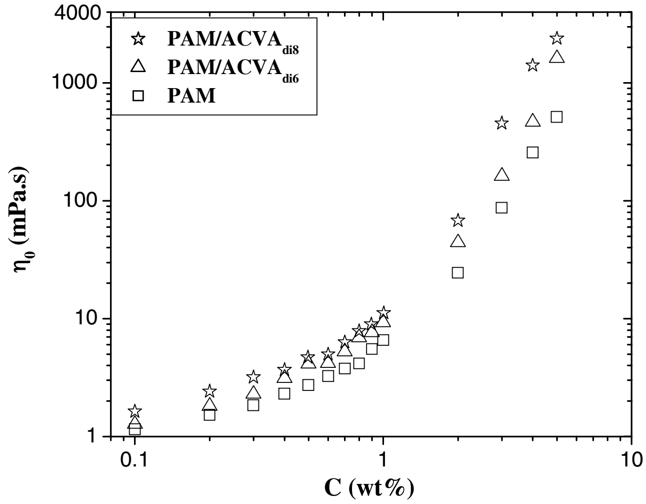


Figure 6. Variation of the zero-shear viscosity of two di-substituted telechelic polymers as a function of concentration.

Figure 6 presents the variation of the zero-shear viscosity (η_0) as a function of C for two di-substituted telechelic polymers (PAM / ACVA$_{di6}$ and PAM / ACVA$_{di8}$) with different length on the alkylic chain (ACVA$_{di6}$ and ACVA$_{di8}$). These polymers are compared with the homopolymer. It is observed that the viscosity of the two di-substituted telechelic polymers is higher than that of the homopolymer. This viscosity increase is due to the presence of the hydrophobic groups at the chain ends and results in the formation of three-dimensional physical networks and an increase in viscosity.

Figure 7 presents the variation of η_0 as a function of C for two linear telechelic polymers (PAM / ACVA$_{12}$ and PAM / ACVA$_{16}$) with different length on the alkylic chain

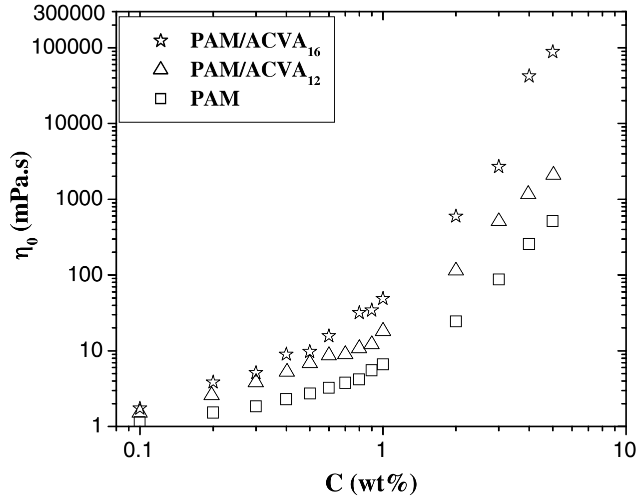


Figure 7. Variation of the zero-shear viscosity of two lineal telechelic polymers as a function of concentration.

(ACVA$_{12}$ and ACVA$_{16}$). These polymers are compared with the homopolymer. For these linear telechelic polymers, we observed qualitatively a similar behavior as in the di-substituted telechelic polymers. That is, the viscosity of these linear telechelic polymers is higher than that of the homopolymer, but in this case, the viscosity presented by the linear telechelic polymers is higher than that of the di-substituted ones. It is important to mention that this rheological study was performed just to determine the presence of the hydrophobic groups situated on each end of the molecular chain, a more extended study will be presented in a forthcoming publication.

Conclusions

The main purpose of this study was the synthesis of telechelic polymers, (linear and di-substituted telechelic polymers), which were prepared by a free radical micellar polymerization. We found that when using the micellar polymerization, most of the polymers obtained were of triblocks telechelic type which presented a higher viscosity as compared to the diblock polymer. M_w of the different polymers, determined by SLS were very similar, even though we used different initiators (ACVA, ACVA$_{12 \text{ and } 16}$, and ACVA$_{di6 \text{ and } di8}$). Unfortunately, it was not possible to determine the polydispersity of the polymers. The ^{1}H NMR spectrum does not present the signals corresponding to the alkylic chain of the hydrophobic initiator in the polymers, but with a rheological study, we could determine the presence of this hydrophobic group in the macromolecule chains. Finally, we observed that the linear telechelic polymers present higher viscosities as compared with the di-substituted ones.

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