

## Characterization and Rheological Properties of Dilute-solutions of Three Different Families of Water-soluble Copolymers Prepared by Solution Polymerization

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**Abstract:** Water-soluble polyacrylamides hydrophobically modified with small amounts of *N,N*-dialkylacrylamides [*N,N*-dihexylacrylamide (DHAM) and *N,N*-dioctylacrylamide (DOAM)] have been prepared through free radical solution polymerizations using two hydrophobic initiators derived from 4,4'-azobis(4-cyanopentanoic acid) (ACVA) and long linear chains consisting of 12 and 16 carbon atoms (C12 and C16). This procedure resulted in polyacrylamides containing hydrophobic groups along the chain as well as at the chain ends. We compare the properties of this class of polymers, termed "combined associative polymers", with those of the multisticker (with hydrophobic groups along the polymer chain) and telechelic (with hydrophobic groups at the chain ends) associative polymers. These materials were prepared using DHAM or DOAM and a hydrophobic initiator (ACVA) modified with alkyl chains of two different lengths. Polymers having molecular weights ( $M_w$ ) of ca. 175,000 and hydrophobic contents [H] of ca. 0.8 mol% were prepared using 0.07 mol% of initiator relative to the total monomer feed. We investigated the effects that the type, localization, and concentration of the hydrophobic groups have on the viscosities of the associative polymer solutions.

**Keywords:** associative polymers, rheology, combined polymers.

### 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 viscosity increase.<sup>1-3</sup>

Such viscosity modification at 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 be mechanically degraded when subjected to elevated shear rates, leading to a decrease in viscosity.<sup>4</sup>

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.<sup>5-7</sup>

This type of polymers and the larger concentrations achievable at  $C^*$  (critical aggregation concentration) lead to

interactions among the hydrophobic groups, which can produce 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.<sup>8-10</sup>

There are two large HMWSP families according to the hydrophobe localization, there is a polymer group called telechelic, which contains two hydrophobic groups situated on each end of the macromolecular chain<sup>11-14</sup> and a polymer group called multistickers, which has the hydrophobic groups distributed along the hydrophilic chain either in blocks or at random.<sup>10,15-17</sup>

The particular properties on 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.<sup>18-20</sup> 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 hydrophobic groups nature, chemical constitution, etc.)<sup>11,21</sup> or from the external factors that influence the association phenomena (shear stress, temperature, surfactant, etc).<sup>22,23</sup>

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On this study we have introduced a new HMWSP family, which combines the characteristics of both, the telechelic and the multistickers hydrosoluble polymers, that is, a polymer with hydrophobic parts on the chain ends as well as along the macromolecular chain. This is a very important kind of polymer which can greatly influence the viscosity, and it is clear that the association process will be enormously dependent on the localization of the hydrophobic groups and their mobility. Figure 1 shows a schematic representation these three types of hydrosoluble polymers.

We discuss the preparation of hydrophobic initiators with different carbon chain lengths and the synthesis and characterization of three different families of HMWSP (telechelic, multisticker and combined) prepared by solution polymerization, using the acrylamide (AM) as the hydrophilic monomer and two dialkylacrylamides as the hydrophobic monomers, as well as two hydrophobic initiators derived from 4,4'-azobis(4-cyanopentanoic acid) (ACVA) with different carbon chain lengths (C12 and C16). In addition, we carried out a detailed study of the rheological properties of these three HMWSP.

## Experimental

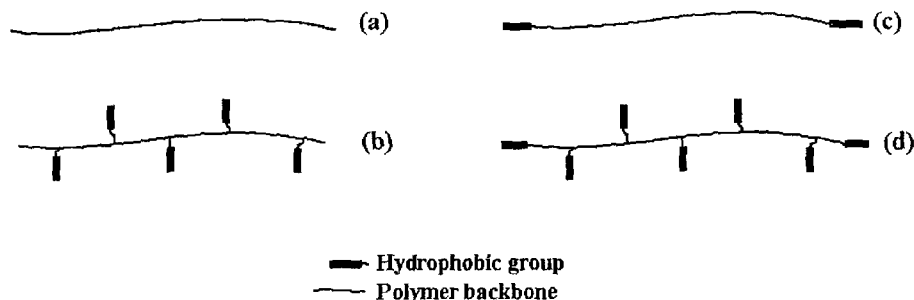
**Materials.** Acrylamide (AM), acetonitrile, chloroform  $d_6$ , deuterium oxide and tetrahydrofuran (THF) were from Aldrich, and acryloyl chloride, ACVA, *N,N'*-dicyclohexylcarbodiimide, 4-dimethyl-aminopyridine, 1-dodecanol, 1-hexadecanol, dihexylamine and dioctylamine, were from Fluka.

**Synthesis of the Hydrophobic Initiators.** The hydrophobic initiators were prepared through a reaction between ACVA and two different alcohols, 1-dodecanol ( $C_{12}H_{25}OH$ ) and 1-hexadecanol ( $C_{16}H_{33}OH$ ). A 500 mL, three-necked flask equipped with a magnetic stirrer and an addition funnel was purged with nitrogen. The ACVA (0.0357 mol) and the respective alcohol (0.075 mol) were dissolved in 300 mL of THF and placed in the flask. Separately, the *N,N'*-dicyclohexylcarbodiimide (0.075 mol) and the 4-dimethyl-aminopyridine (0.0016 mol) were dissolved in 50 mL of THF and then added to the flask drop wise over a period of

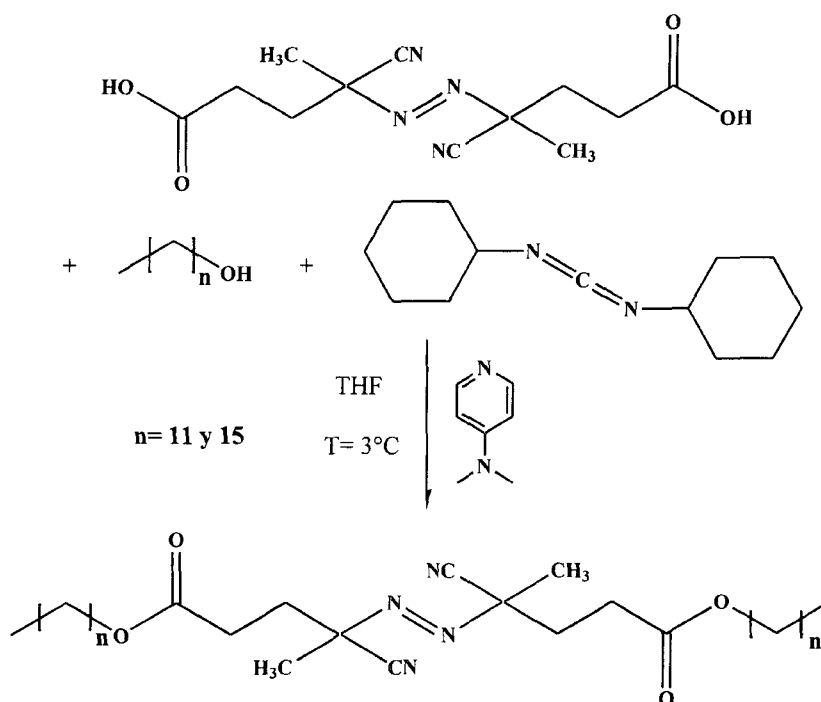
2 h at 3 °C. The reaction was allowed to proceed for 18 h at room temperature. The solution obtained was concentrated under vacuum and the initiator was precipitated in cold with methanol and finally dried. The conversion of the ACVA12 and ACVA16 was 75.4 and 91% respectively. The reaction route is presented in Scheme I and the  $^1H$  NMR spectrum of the hydrophobic initiator ACVA12 in Figure 2. The NMR spectrum of the hydrophobic initiator ACVA12, does not show the acid proton of ACVA at 13.2-10 ppm; the shift of the alfa carbonyls occurs at a lower field (i.e. at 2.5-2.4 ppm) due to the ester formation, which confirms the occurrence of the expected reaction.

**Synthesis of the hydrophobic monomers.** The hydrophobic monomers were prepared via a reaction of acryloyl chloride with the corresponding *N*-dialkylamine (dihexylamine or dioctylamine), according to the procedure previously described by Valint *et al.*<sup>24</sup>

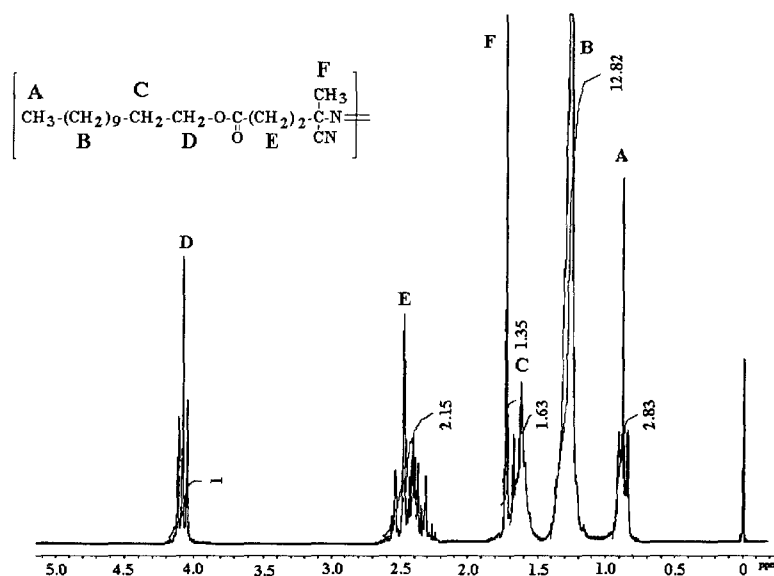
**Synthesis of the Copolymers.** All copolymers were prepared via solution copolymerization using acetonitrile as solvent. The initial concentration of monomers (acrylamide and hydrophobe) was maintained constant at 3% (wt/wt) based on volume of acetonitrile. The temperature was fixed at 82 °C and the initiator concentration was 0.07 mol% relative to the 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 acrylamide, the hydrophobic monomer and 468 g of acetonitrile were added to a 600 mL reactor equipped with thermometer, condenser and mechanical stirrer. The mixture was vigorously agitated and purged with nitrogen during 1 h, the mixture was then heated to 82 °C under agitation. The initiator was added to the mixture to start the reaction, and bubbling was maintained during all the polymerization. The reaction 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. The reaction is presented in the Scheme II.



**Figure 1.** Schematic representation of the configuration of synthetic associative aqueous polymers. (a) homopolymer, (b) multistickers-polymer, (c) telechelic polymer, and (d) combined polymer.



**Scheme I.** The synthesis of hydrophobic initiator.

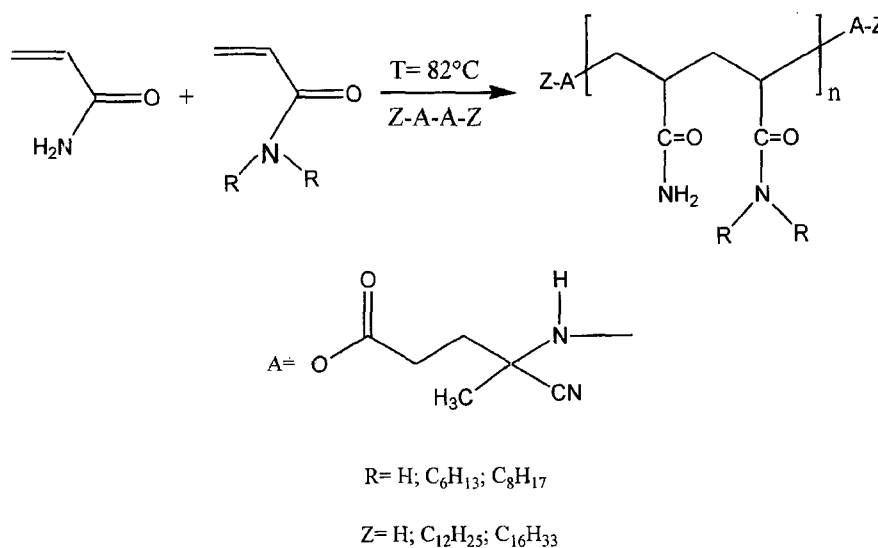


**Figure 2.** The  $^1\text{H}$  NMR spectrum of the hydrophobic initiator ACVA12 in  $\text{CDCl}_3$ .

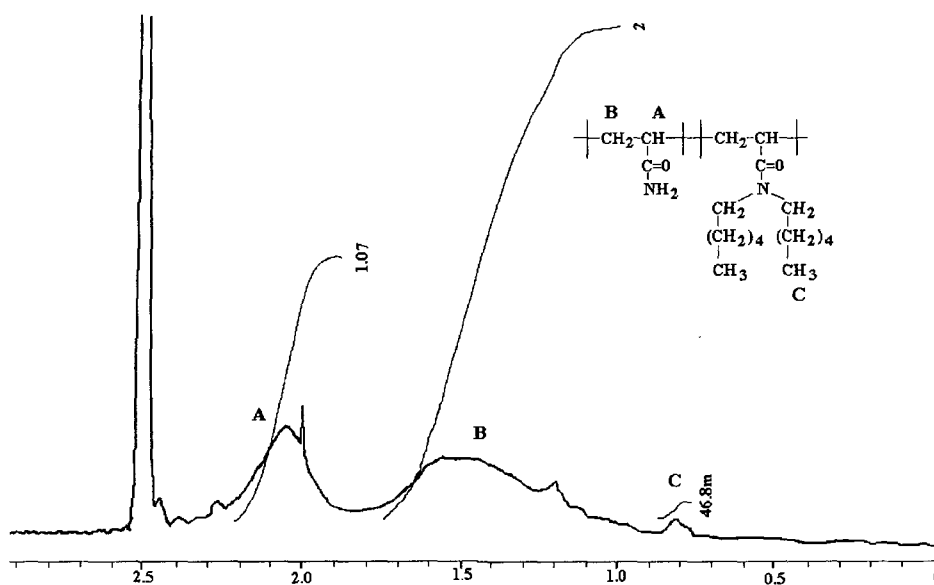
Due to the termination mechanisms that occur, such as combination and disproportionation, these two routes produced both, diblock (with a hydrophobic group in only one chain end) and triblocks (with a hydrophobic group in each chain end, that is, mix telechelic), which had to be then separated by fractionation as follows: the copolymer is solubilized in 5% water, then a non-solvent is added until persis-

tent turbidity by triblocks (telechelic) is formed. Finally, the gel is separated and precipitated in methanol and filtered, washed and vacuum dried.

The  $^1\text{H}$  NMR spectrum of the PAM-co-DHAM is presented in Figure 3. 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



**Scheme II.** The synthesis of polymers.



**Figure 3.** The  $^1\text{H}$  NMR spectrum of the PAM-co-DOAM polymer in DMSO/D<sub>2</sub>O (80/20 wt/wt).

attached to the backbone (1.1 to 1.8 ppm), the ratio was found to be 0.8 mol% with respect to the feed ratio.

**Molecular Weights.** The weight-average molecular weights  $M_w$  of the samples were determined by light scattering. The refractive-index increments measured at  $\lambda = 633$  nm on a Brice-Phoenix differential refractometer in formamide were 0.109 mL/g as previously described.<sup>16</sup> 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.

**Characterization.** The composition of the initiators, monomers and polymers was determined by  $^1\text{H}$ -NMR spectroscopy, using 1 wt% solution in CDCl<sub>3</sub> or DMSO/D<sub>2</sub>O (80/20 wt/wt) 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<sub>2</sub>O. Each solution was gently stirred until the solution was homogeneous.

**Rheological Measurements.** Experiments were performed in a Paar Physica UDS200 controlled stress rheometer

**Table I. Polymer Characteristics**

Polymers	Conversion (wt%)	[H] <sup>a</sup> (mol%)	M <sub>w</sub> <sup>b</sup> (g/mol)
PAM	81.4		185,000
PAM/ACVA12	82.6		180,000
PAM/ACVA16	84.6		170,000
PAM-co-DHAM	83.6	0.8	160,000
PAM-co-DOAM	84	0.78	160,000
PAM-co-DHAM/ACVA12	81.3	0.81	170,000

<sup>a</sup>Hydrophobe content in the final polymer.

<sup>b</sup>Molecular weight determined by light scattering.

equipped with a cone and plate geometry (angle 2° and diameter 50 mm) or double gap geometry depending on the sample viscosity at temperatures from 25 °C. To prevent the evaporation of water, we enclosed the measuring system with solvent trap. The zero-shear viscosity ( $\eta_0$ ) was obtained by extrapolation of the apparent viscosity. The range of concentration of the aqueous polymer solutions was 0.05 wt% < C < 5 wt%.

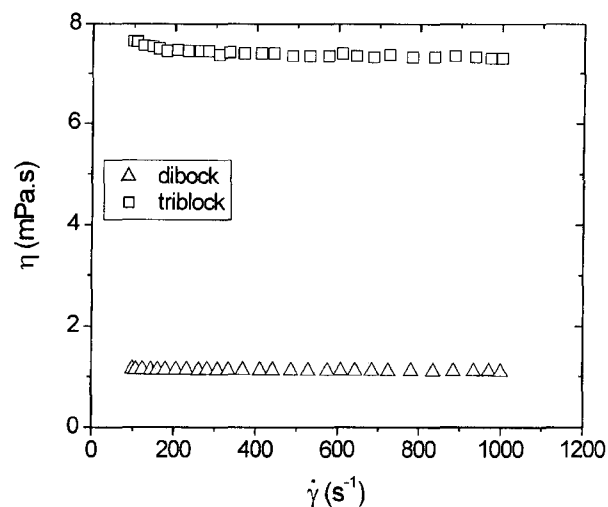
The sample code of the copolymers refers to the hydrophilic monomers, hydrophobic monomers and the length of the hydrophobic initiator. For example, PAM-co-DHAM/ACVA12 stands for a poly(acrylamide-co-dihexylacrylamide) using an initiator modified hydrophobically with a 12 carbons chain (C12). The characteristics of the samples investigated are given in Table I. The conversion of all samples was around of 80%. The hydrophobe content in the copolymers [H] was 0.8 mol%. The molecular weight was  $M_w \approx 175,000$ .

## Results and Discussion

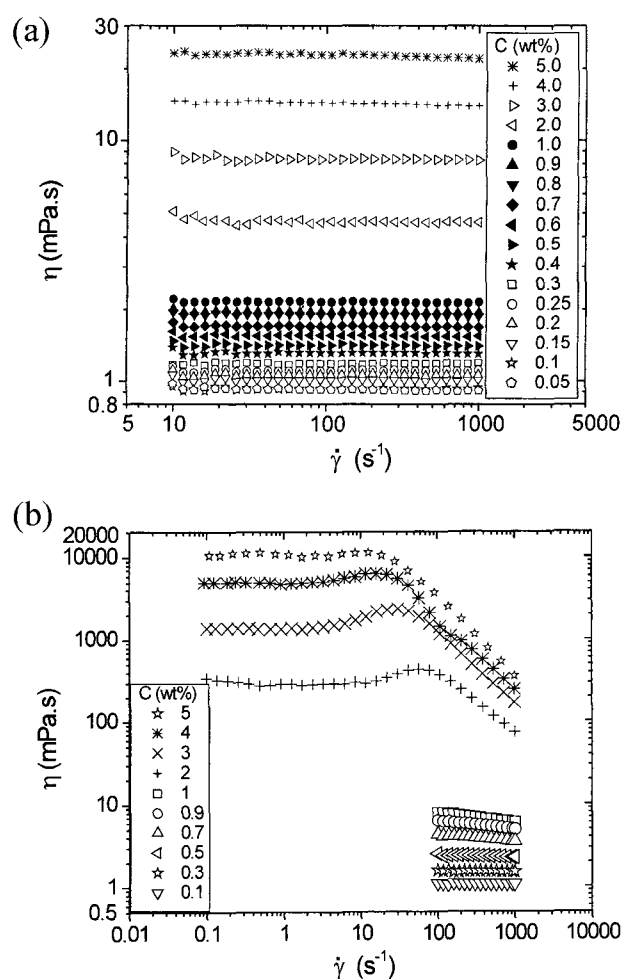
The introduction of hydrophobic groups into a water-soluble polymer will modify the flow behavior of the precursor polymer. This is mainly due to intramolecular associations, intermolecular associations, or both. The net effect of these associations depends, among other factors, on polymer concentration.

Figure 4 shows the effect on viscosity of diblock and triblock PAM/ACVA16 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 mentioning that at 1 wt%, these polymers are above the aggregation concentration, thus, they already present intermolecular hydrophobic interactions.

The results of shear-flow experiments are illustrated in Figure 5, which gives the variation of the steady-state viscosity ( $\eta$ ) as a function of shear rate ( $\dot{\gamma}$ ) for a PAM (Figure



**Figure 4.** Comparison of the effect on viscosity of the diblock and triblock PAM/ACVA16 polymers at 1 wt%.

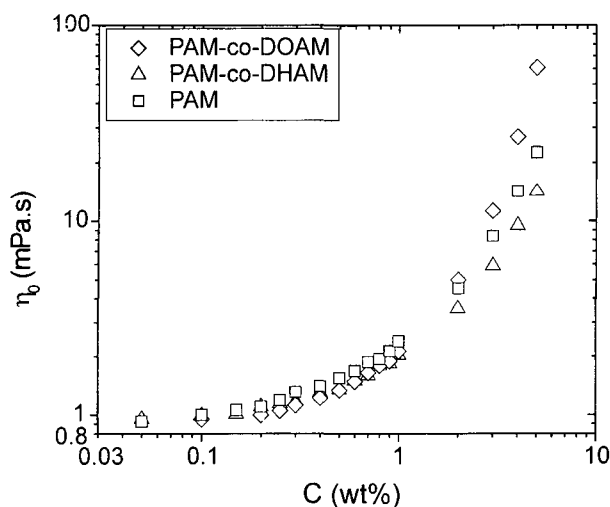


**Figure 5.** Steady-state viscosity versus shear-rate for two sample at various concentrations in water. (a) PAM and (b) PAM/ACVA16.

5(a) and PAM/ACVA16 (Figure 5(b)) at different concentrations in an aqueous solution. As shown in Figure 5(a) PAM presents a Newtonian behavior within the concentrations studied, which means that there is no variation on  $\eta$  as a function of  $\dot{\gamma}$ . From the respective associative polymer (Figure 5(b)) we observe that the system remains Newtonian for ( $C \leq 0.5$ ). However upon further increasing the concentration, ( $0.5 \leq C \leq 1$ ) the zero-shear viscosity increases, that is, the Newtonian behavior is followed by a shear thinning behaviour, this shear thinning is due to the breakdown of the intermolecular hydrophobic interactions, which produce a decrease in viscosity. For higher concentrations, ( $2 \leq C \leq 5$ ) the zero-shear viscosity increases drastically showing a shear-thickening effect. This shear-thickening effect has been observed by different authors and it is explained as the point of equilibrium between the intra- and intermolecular associations.<sup>8,22</sup> At certain shear-rate the hydrophobic intra-molecular associations are broken. These free hydrophobic sequences immediately form intermolecular associations with is obtained. This shear-thickening effect has been described on the Witten and Cohen polymer theory<sup>25</sup> as associations that form ionic interactions. On further increasing the shear-rate, the intermolecular associations start to break down in the same way, producing the observed continuous decrease in viscosity.

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 and the other is the hydrophobe length on the monomer as well as on the initiator.

Figure 6 presents the variation of the zero-shear viscosity ( $\eta_0$ ) as a function of the polymer concentration ( $C$ ) for two synthesized polymers (PAM-co-DHAM and PAM-co-DOAM) with different monomer length on the alkylic chain

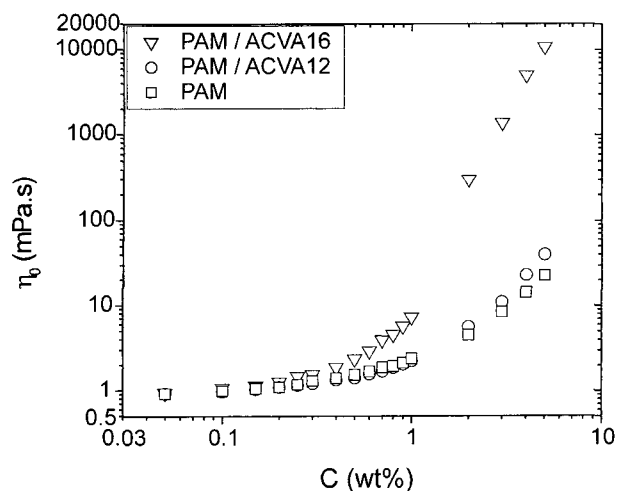


**Figure 6.** Influence of the length of the hydrophobe part of the monomer in the rheological properties.

(diC6 and diC8). These polymers are compared with the homopolymer. It is observed that for  $C < 2$  wt%, the viscosity of polymer PAM-co-DOAM is slightly lower, as compared to that of the corresponding unmodified polymer. This is due to the chain contraction resulting from intramolecular associations. But at higher concentrations ( $C > 2$  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 tridimensional physical networks and the viscosity increases. For the polymer PAM-co-DHAM, 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 difference on molecular weight between the homopolymer and the associative polymer (homopolymer 185,000 and the PAM-co-DHAM 160,000), considering that the hydrodynamic volume is directly proportional to the molecular weight, according to the following expression<sup>10</sup>:  $\eta_1/\eta_2 = A(M_1/M_2)^{3/4}$ .

That is, the homopolymer viscosity would be about 1.5 times larger than that of the associative polymer, this can explain the lower viscosity presented on the polymer PAM-co-DHAM. In addition, Volpert *et al.*<sup>8</sup> showed that hydrophobic groups with short carbon chain length (diC6) randomly distributed along the polymer chain do not produce any associative copolymer behaviour.

Figure 7 shows the variation of ( $\eta_0$ ) as a function of  $C$  for two associative polymers with an alkylic chain length different from that of the hydrophobic initiator (C12 and C16). These polymers are also compared to the original homopolymer, and it is observed for polymer PAM/ACVA16 that at low concentration ( $C < 0.1$  wt%) the viscosity 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 polymer



**Figure 7.** Influence of the length of the hydrophobe part of the initiator in the rheological properties.

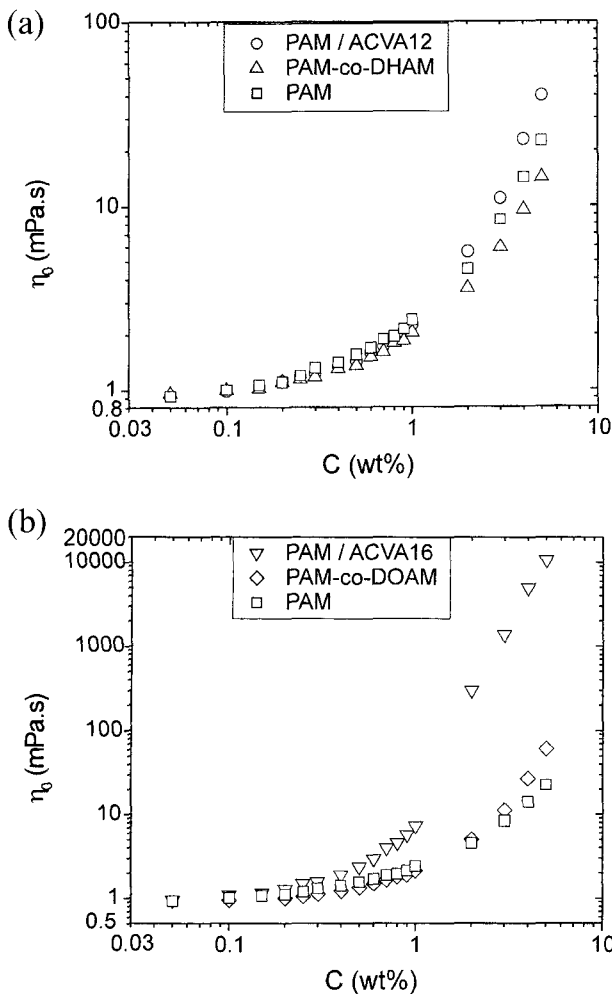
PAM/ACVA12, on the other hand, much larger concentrations ( $C > 2$  wt%) are necessary in order for the viscosity of the associative polymer to be higher than that of the homopolymer. The global behavior is the result of a transition from a system where the conformation of the macromolecular chains is controlled by the intramolecular interactions at low concentrations to a system where the intermolecular interactions have an important role at higher concentrations.<sup>8,10,22</sup>

In accordance with the general behavior presented on pre-views studies on several types of associative polymers.<sup>26,27</sup>

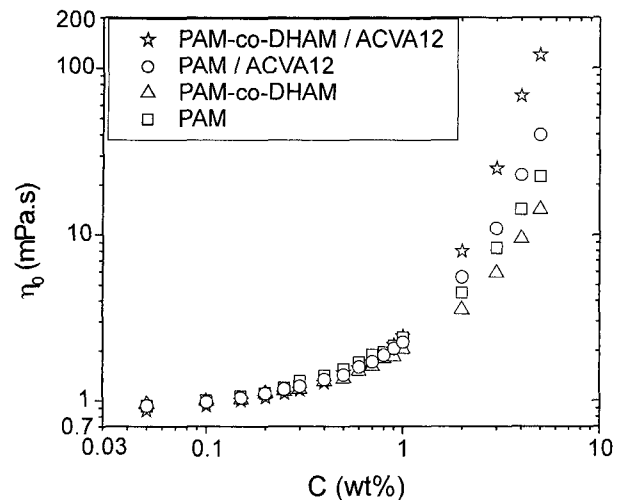
Figure 8 presents a comparison between telechelic and multisticker polymers with C12 (Figure 8(a)) and with C16 (Figure 8(b)). In both cases, the viscosity on the telechelic polymers (PAM/ACVA12 and PAM/ACVA16) at high polymer concentrations is always higher than that of the homopolymer and the same applies for the multisticker polymers. This appears a little strange, because considering the amount of hydrophobe part it is used on the monomer (0.8

mol%) as well as on the initiator (0.07 mol%) it could be thought that the multisticker polymers would have a higher viscosity than that of the telechelic polymers simply because they have a larger concentration of hydrophobe parts. From these results, it appears that the localization of the hydrophobe parts have a great influence on the viscosity of the final associative polymer. This can be explained considering the conformation each polymer adopts in the aqueous solution; while the telechelic polymer (with the hydrophobic groups at the chain ends) adopts a flower shape,<sup>28-30</sup> which favours the increase of the hydrodynamic volume, producing thus a higher viscosity in comparison with the multisticker polymer (with the hydrophobic groups along the chain), which presents a compact volume due to a higher quantity of hydrophobic groups distributed along the chain. And this increase in viscosity becomes greater the longer the carbon chain.

Figure 9 compares the viscosity of telechelic and multisticker polymers with that of the combined type on the series C12. It is observed that at low concentrations, the viscosity of the combined polymer PAM-co-DHAM/ACVA12 is lower than that of the other three polymers, which brings out the strong influence of intramolecular interactions, -due to the high quantity of hydrophobic parts,- which would tend to decrease the hydrodynamic volume, and tend to show a lower viscosity. But at higher concentrations, the viscosity of this polymer that combines the telechelic and multisticker characteristics is higher than that of the other two polymers (PAM/ACVA12 and PAM-co-DHAM), which brings out the synergistic effect of the two hydrophobe parts in the "combined" polymer chain (those along the chain plus those at the chain ends) which results in a higher density stress. These results demonstrate that the associative "combined" polymers have better associative properties in com-



**Figure 8.** Comparison between the telechelic and multisticker polymers: (a) series C12 and (b) series C16.



**Figure 9.** Comparison between the telechelic and multisticker polymers with the combined polymer on the series C12.

parison with the “simple” telechelic and “simple” multisticker polymers.

## 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.

It was found on the telechelic polymers a thicker stress to the ones on multisticker polymers, even when the quantity on the hydrophobic groups is lower, which brings out the importance on the localization of these groups on the thick properties. It was also found that the combined polymer (PAM-*co*-DHAM/ACVA12) presented a higher viscosity as compared to the telechelic (PAM/ACVA12) and multisticker polymers (PAM-*co*-DHAM) individually, 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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