Polym. Bull. (2011) 67:251–262
DOI 10.1007/s00289-010-0377-8

ORIGINAL PAPER

Rheological properties of three different microstructures of water-soluble polymers prepared by solution polymerization

Valeria J. González Coronel ·
Enrique J. Jiménez-Regalado

Received: 29 April 2010 / Revised: 18 August 2010 / Accepted: 15 September 2010 /

Abstract Polymer chains consisting of water-soluble polyacrylamides hydrophobically modified with low amount of hydrophobic groups, with varying hydrophobic chain structure (C_{16} and C_{di8}) and with varying localization of the hydrophobe along the chain (telechelic, multisticker, and combined polymers) were investigated. The viscoelastic behavior of these associative polymers has been studied in semidilute solutions using steady-flow and oscillatory experiments. The effect of type and localization of the hydrophobic groups on the viscosity of the associative polymer solution was investigated. It can be inferred that the high viscosity presented by these polymers, is due largely to G_0, which represents the number of associations in the medium at any given time and less so on T_R, which represents the duration time of any given association. On all studied samples, T_R as well as G_0, were affected by the type (di-substituted or linear) and localization of the hydrophobic groups (telechelic, multisticker, or combined).

Keywords Telechelic polymer · Combined polymer · Rheology · Relaxation time

Introduction

Over the past three decades, hydrophobically modified water-soluble polymers (HMWSPs) have attracted increased interest owing to their practical and fundamental importance [1–7]. This system usually consists of a major part of hydrophilic backbone and small proportion of hydrophobic groups. In the semi-diluted regime, intermolecular aggregates prevail over intra-molecular ones and clusters of hydrophobic domains are formed. This leads to a transitional network structure

---

V. J. González Coronel · E. J. Jiménez-Regalado (✉)
Centro de Investigación en Química Aplicada (CIQA),
Blvd. Enrique Reyna #140, 25253 Saltillo, Coahuila, México
e-mail: ejimenez@ciqa.mx

which induces a substantial increase in solution viscosity. HMWSPs 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 [8–14] and (ii) multisticker polymers, in which the hydrophobic groups are randomly distributed as isolated units or as small blocks along the hydrophilic backbone [15–21]. Recently, Jiménez et al. [22, 23] 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. The particular properties of the HMWSPs, as well as the several application possibilities where a rheological control is required in an aqueous system, explains the increasing number of studies on the last years [24–26]. Due to the numerous parameters that influence its properties, the HMWSPs offer a considerable research field. This influence may come from its own polymer parameters (the nature of hydrophobic groups, its chemical constitution, etc.) [27, 28] or from the external factors that influence the association phenomena (shear stress, temperature, and surfactant, etc.) [29, 30].

In this project, we describe a detailed study of the rheological properties in aqueous solutions of three different structures of HMWSP′s (telechelic, multisticker and combined) prepared by solution polymerization using two different hydrophobic groups (di-substituted and linear) of 16 carbon atoms.

Experimental

All copolymers were prepared via solution copolymerization using acetonitrile as solvent in accordance with the procedure previously described [31]. The initial concentration of monomers (acrylamide and hydrophobe) was maintained constant at 3 wt% with respect to the acetonitrile solvent volume. 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, in accordance with the procedure previously described [22, 23]. The polymers obtained were characterized by ^{1}H NMR and light scattering [22, 23]. The polymer characteristics are presented in Table 1.

Sample preparation

Solutions at different polymer 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

Table 1 Polymer characteristics

Type	Polymer	M_w (g/mol)
Homopolymer	PAM	190000
Telechelic	PAM/ACVA$_{di8}$	189000
	PAM/ACVA$_{16}$	190000
Multisticker	PAM-co-DOAM	209000
	PAM-co-HDAM	200000
Combined	P(AM-co-DOAM)/ACVA$_{di8}$	186000
	P(AM-co-HDAM)/ACVA$_{16}$	203000

gap geometry depending on the sample viscosity at temperatures from 25 ± 0.05 °C. 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 wt% $< C <$ 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-HDAM/ACVA16 stands for a poly(acrylamide-co-Hexadecylacrylamide) using an initiator modified hydrophobically with a 16 carbons chain (C_{16}).

Results and discussions

Figure 1 shows the variation of viscosity (η_0) as a function of polymer concentration (C) for PAM, and two associative multisticker copolymers (PAM-co-DOAM and PAM-co-HDAM). Three concentration regimes can be identified for these polymers (although displaced in the concentration axis).

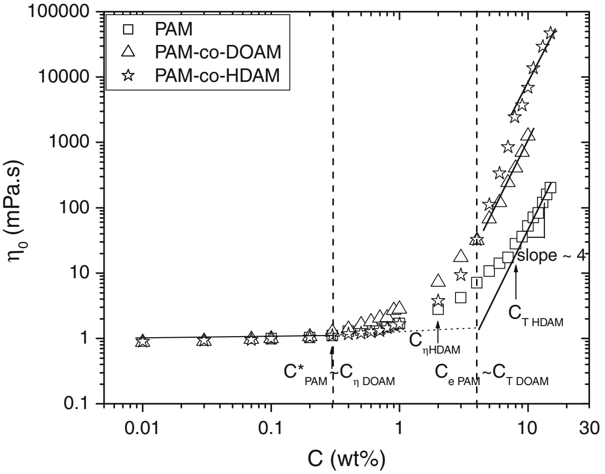

Fig. 1 Variation of zero-shear viscosity (η_0) as a function of polymer concentration (C), for the synthesized multisticker copolymers

(1) When $C < C_\eta$ (C_η is defined as the point in which the viscosity of the associative copolymer surpasses that of the homopolymer). In this 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 [32, 33]. The concentration C_η for the copolymer PAM-co-DOAM (which is 0.3 wt%), is approximately 10 times lower than C_e (which is 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^*. For the case of PAM-co-HDAM, the concentration C_η is 2 wt%. In this case, we assume that C_η is greater for the PAM-co-HDAM that for the PAM-co-DOAM because the linear hydrophobic chain forms intramolecular interactions that greatly decrease the hydrodynamic volume of the chain and need a greater amount of polymer in the solution so that the intermolecular interactions are effective and provide a significant viscosity increase, whereas for the case of the PAM-co-DOAM, the two hydrophobic chains are smaller and, therefore, the intermolecular hydrophobic interactions are weaker and the hydrodynamic volume is not affected as in the previous case and, therefore, needs a smaller amount of polymer for the intermolecular interactions to be effective and the observed viscosity to increase and surpass that of the homopolymer. (2) When the concentration is $C_\eta < C < C_T$ (C_T which will apply for an associative copolymer and is defined in the same manner as C_e). 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 [34, 35]. In the telechelic systems, the linear viscoelastic behavior is Maxwellian [35]. 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, for the copolymer PAM-co-DOAM 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 PAM-co-DOAM, 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 [36]. For the case of the copolymer PAM-co-HDAM, the C_T value is ≈ 7 wt%. (3) When $C > C_T$, in this regime, the viscosity increases as a function of C4. 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. [36], which considers a concentrated solution of a monodisperse chain of N monomers with S stickers attached to each chain.

The variation of viscosity as a function of concentration for PAM and two telechelic polymers with di-substituted and linear 16-carbon atoms hydrophobic groups is presented in Fig. 2. The polymer PAM/ACVA$_{\mathrm{di8}}$ presents the $C_{\eta\mathrm{ACVAdi8}}$ at

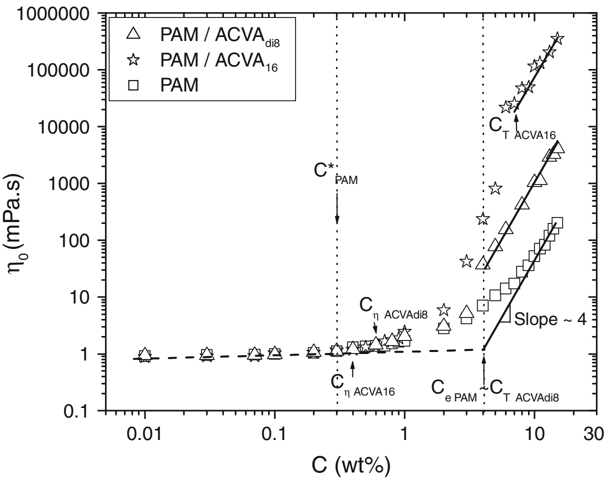

Fig. 2 Variation of η_0 as a function of C for the synthesized telechelic copolymers. The PAM is presented as comparison

0.6 wt%, above that presented by PAM $C^*_{\mathrm{PAM}} \sim 0.3$ wt%; for PAM/ACVA$_{16}$; the $C_{\eta\mathrm{ACVA16}}$ value is $\sim$0.4 wt%. The fact that $C_{\eta\mathrm{ACVAdi8}}$ occurs at a concentration higher than that of $C_{\eta\mathrm{ACVA16}}$ may be because the length of the hydrophobic polymer PAM/ACVA$_{\mathrm{di8}}$ has two hydrophobic chains that are shorter than those of polymer PAM/ACVA$_{16}$ and thus need a higher polymer concentration to be effective and the thickening effect exceeds the viscosity of homopolymer. With regard to semi-dilute regime, it is observed that, $C_{\mathrm{TACVAdi8}} \sim C_{\mathrm{ePAM}} \sim 4$ wt%, whereas $C_{\mathrm{TACVA16}} \sim 6$ wt%, in this case, the polymer PAM/ACVA$_{\mathrm{di8}}$ forms a hydrophobic entanglement concentration lower than that of the polymer PAM/ACVA$_{16}$ because it has two hydrophobic chains while the other only one. Finally, at concentration above C_{T}, the behavior is similar to that observed in Fig. 1.

Figure 3 shows the variation of viscosity (η_0) as a function of concentration for the different synthesized combined polymers. It is seen that the polymer with linear hydrophobic groups (both at the chain ends and along the chain) PAM-co-HDAM/ACVA$_{16}$ has a higher viscosity than its counterpart with the same number of carbon atoms, but di-substituted PAM-co-HDAM/ACVA$_{\mathrm{di8}}$. The C_η of the di-substituted copolymer DOAM/di8, $\mathrm{C}_{\eta\mathrm{DOAM/di8}}$ occurs at a concentration of 0.1 wt%, whereas that of linear copolymer $\mathrm{C}_{\eta\mathrm{HDAM/16}}$ occurs at 0.6 wt%, this is probably because the linear copolymer presents stronger intramolecular links which causes a decrease in the hydrodynamic volume, thus needing a higher polymer concentration to overcome the viscosity of the homopolymer, compared to the di-substituted copolymer which presents weaker intramolecular interactions due to the shorter length of their hydrophobic groups. In the case of C_{T}, the behavior is the same as for C_η, i.e., the di-substituted copolymer ($C_{\mathrm{T}} \sim 6$ wt%) presents a C_{T} slightly lower than the linear copolymer ($C_{\mathrm{T}} \sim 7$ wt%). This may be explained as for the case of C_η.

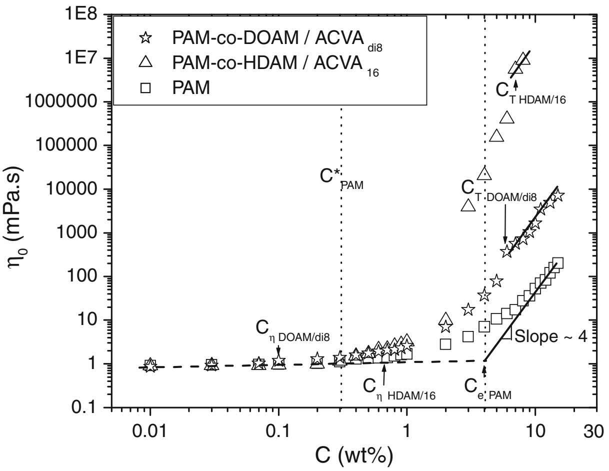

Fig. 3 Variation of η_0 as a function of C for the synthesized combined polymers. The PAM is presented as comparison

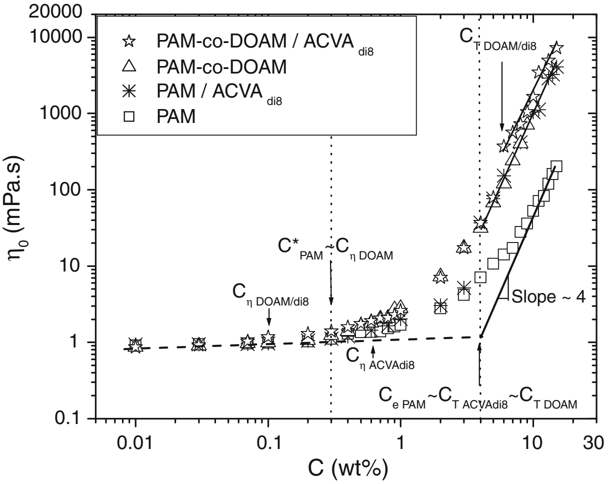

Fig. 4 Variation of η_0 as a function of C for the telechelic, multisticker, and combined polymers using the di-substituted hydrophobic group

Figure 4 compares the viscosity of the combined associative copolymer with that of the telechelic and multisticker ones, for the case where the hydrophobic groups alkyl chain is di-substituted. It is observed that the concentration at which the system passes from the first regime to the second one varies as follows, the combined copolymer PAM-co-DOAM/ACVA$_{di8}$ needs a concentration of 0.1 wt% of polymer to overcome the viscosity of the homopolymer, whereas the multisticker copolymer PAM-co-DOAM requires a concentration of 0.3 wt%, which is the same as that of the homopolymer. In the case of the telechelic PAM/ACVA$_{di8}$ polymer, the required concentration is 0.6 wt%. It can be seen that C_η increases when the amount of hydrophobic groups in the polymer decreases, i.e., C_η [telechelic] > C_η [multisticker] > C_η [combined]. This may be because the more hydrophobic groups in the chain, the more intramolecular interactions that occur, which will cause the hydrodynamic volume of the chain to decrease and, therefore, to require a higher amount of polymer to overcome the viscosity of the homopolymer. In the case of C_T, it was the same for PAM-co-DOAM as well as for PAM/ACVA$_{di8}$, that is, $C_{TACVAdi8}$ is equal to C_{TDOAM}, and equal to 4 wt%. Whereas for the case of PAM-co-DOAM/ACVA$_{di8}$ polymer, C_T occurs up to a concentration of 6 wt%. The viscosity of the combined, telechelic and multisticker associative copolymer for the case where the alkyl chain of the hydrophobic groups is linear, present the same behavior as that presented in the Fig. 4, though these result are not presented.

Figures 1, 2, 3 and 4, 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 the 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 $[C < C_\eta]$ regime, the viscosity of the associative copolymers appears to be somewhat lower than that of the unmodified homopolymer, due ostensibly to the contraction of the hydrodynamic volume caused by the intramolecular associations. In the second (semidilute unentangled) regime, $[C_\eta < C < C_T]$, the viscosity of the associative copolymers starts to increase at a very high rate, this rate being greatly affected by the localization of the hydrophobic groups [higher rate for the combined and telechelic associative copolymers] and by the size of the alkyl chains in the hydrophobic groups [higher rate 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 $[C_T < C]$, the viscosities of the associative copolymers and of the unmodified homopolymer vary 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.

Figure 5 shows the variation of storage (G') and loss (G'') moduli as a function of frequency (ω) for the telechelic PAM/ACVA$_{di8}$ polymer for a concentration of 15 wt%. It is noted that at low frequencies the curves of G' and G'' correspond to the model of Maxwell. At larger frequencies, the curves of G' and G'' (experimental) begin to move away from the theoretical curves, suggesting that in these systems there are several relaxation times (T_R), as the Maxwell model predicts only one relaxation time. Some authors use the value of ω_{cross} to determine the relaxation time ($T = 1/\omega_{cross}$), although this time is smaller than most of the relaxation times in the system. However, considering that some of the analyzed samples did not present ω_{cross}, though the experimental behavior of the G' and G'' curves was in good agreement with the Maxwell model (at least at low frequencies), the T_R was determined using the Maxwell model.

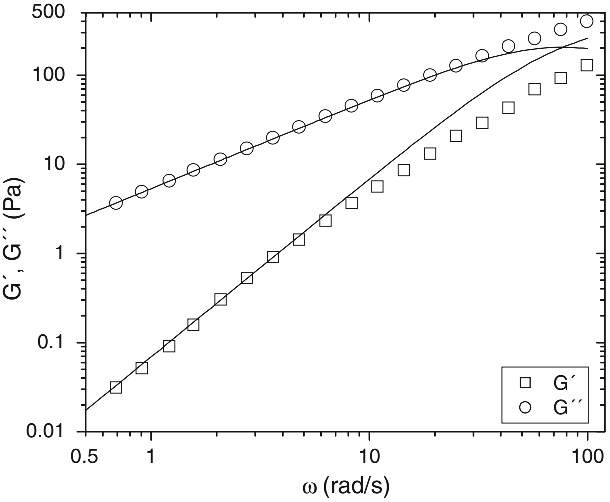

Fig. 5 Storage (G') and loss (G'') moduli as a function of frequency for PAM/ACVA$_{\mathrm{di8}}$ ($C = 15$ wt%). The lines are the fit to one mode Maxwell model ($G_0 = 98$ Pa, relaxation time = 0.013 s)

From the analysis of the data in the low frequency range, we have attempted to determine the longest relaxation time, T_R, and the plateau modulus, G_0, associated with this slowest process. These are obtained from the following relationship:

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

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

T_R is considered as the time when two hydrophobic groups interact and are held together, which is strongly affected by the type and location of these groups.

Figure 6 shows the relaxation times as a function of the polymer concentration for polymers with di-substituted (di8) hydrophobic groups. The combined polymer PAM-co-DOAM/ACVA$_{\mathrm{di8}}$ presents large relaxation times that increase with concentration; and these results are in accordance with the high viscosity conveyed by this associative copolymer. Whereas the telechelic (PAM/ACVA$_{\mathrm{di8}}$) and multisticker (PAM-co-DOAM) polymers, both present much lower relaxation times that increase slowly with concentration. This suggests for these two latter cases, that the time that the hydrophobic association (or link) is maintained is independent of the associative polymer concentration. This result is apparently contradictory, since the effect of both, telechelic and multisticker on the 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 ($\eta = T_R \times G_0$), this would explain the fact of having high viscosity and relative constant relaxation time. In addition, the relaxation time is strongly affected by the type and localization of the hydrophobic groups.

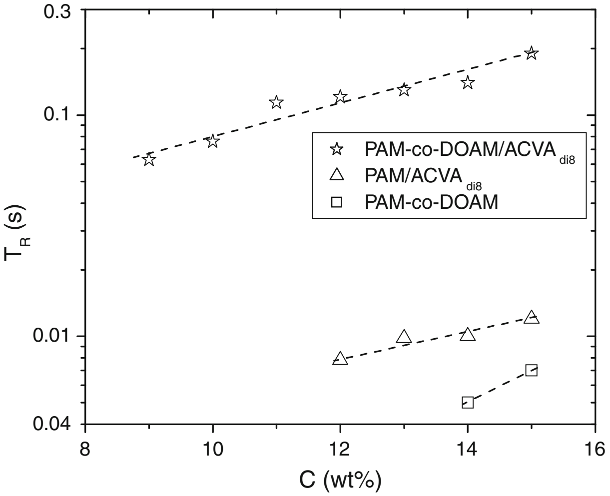

Fig. 6 Variation of the relaxation time T_R as a function of C for the telechelic, multisticker, and combined copolymers using the di-substituted hydrophobic groups (di8)

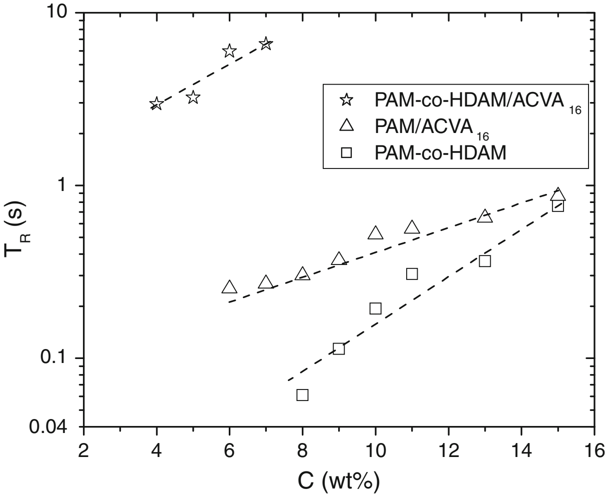

Fig. 7 Variation of the relaxation time T_R as a function of C for the telechelic, multisticker, and combined copolymers using the linear hydrophobic groups (16)

Figure 7 shows the T_R as a function of C for polymers with linear hydrophobic groups (16). Telechelic (PAM/ACVA$_{16}$) and multisticker (PAM-co-HDAM) polymers are those with the longest T_R. The values of T_R found in this work are within the range of those reported by Jimenez-Regalado [2], which reported a clear increase in these values, which coincides with some of the polymers reported here. In the particular case of PAM-co-HDAM and PAM/ACVA$_{16}$ polymers, the T_R remains constant with C, i.e., the lifetime of hydrophobic associations is independent of

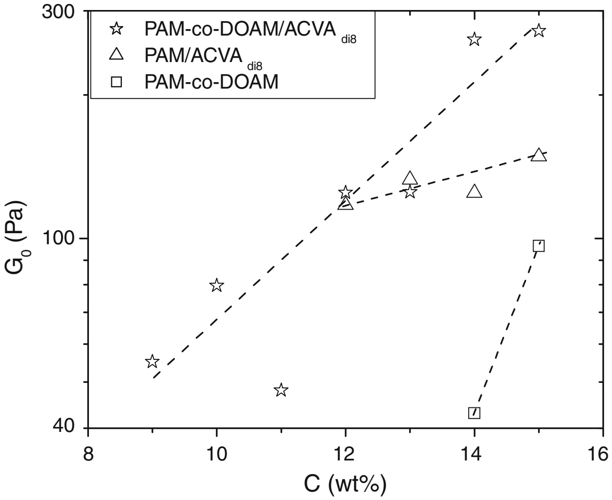

Fig. 8 Variation of the modulus plateau G_0 as a function of C for the telechelic, multisticker, and combined copolymers using the di-substituted hydrophobic groups (di8)

C. For the PAM-co-HDAM/ACVA$_{16}$ polymer, it is reported a slight decrease of T_R, suggesting that the lifetime of associations is shorter.

Figure 8 shows the variation of G_0 as a function of associative polymer concentration for polymers with di-substituted (di8) hydrophobic groups for the same samples presented in Fig. 6. G_0 may be considered as the quantity of hydrophobic links present in the medium at a given time. It can be observed that G_0 increases with the concentration in all the three cases, which indicates that as concentration increases, the number of hydrophobic links also increases. It can be observed that G_0 of PAM-co-DOAM/ACVA$_{di8}$ is higher than that of PAM-co-DOAM and PAM/ACVA$_{di8}$. However, the rate at which G_0 increases with concentration is higher for PAM-co-DOAM than for the other two associative copolymers. For the PAM/ACVA$_{di8}$, the G_0 value increases slightly with the concentration. 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 G_0 values; though it is not very clear why, the PAM/ACVA$_{di8}$ sample, with less hydrophobic groups, but with a larger number of alkyl carbon atoms in the hydrophobic groups, presents G_0 values greater than those of the multisticker associative polymer (PAM-co-DOAM). It seems, therefore, that the value of G_0 is also strongly affected by the type (size) and localization of the hydrophobic groups.

Figure 9 shows the variation of G_0 as a function of associative polymer concentration for polymers with linear hydrophobic groups (16) for the same samples shown in Fig. 7. For the PAM-co-HDAM/ACVA$_{16}$ polymers, it can be observed that G_0 increases strongly with the concentration, while the other two polymers show small increases in G_0 as a function of concentration, this behavior was explained above. From these results, it can be inferred that the high viscosity

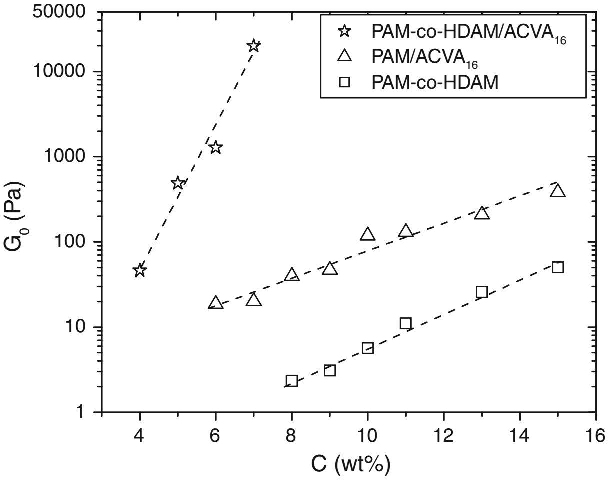

Fig. 9 Variation of the modulus plateau G_0 as a function of C for the telechelic, multisticker, and combined copolymers using the linear hydrophobic groups (16)

presented by these polymers, is due largely to G_0, which represents the number of associations in the medium at any given time and less so on T_R, which represents the duration time of any given association.

Conclusions

The effect of varying hydrophobic chain structure and varying localization of the hydrophobe along the chain on the rheological properties of an aqueous solution of the corresponding associative polymer were investigated.

The relaxation time of all the associative polymers studied in this work, showed a slight variation with concentration, whereas the plateau modulus increased markedly with concentration. It can be inferred that the high viscosity presented by these polymers, is due largely to G_0, which represents the number of associations in the medium at any given time and less so on T_R, which represents the duration time of any given association. On all studied samples, T_R as well as G_0, were affected by the type (di-substituted or linear) and localization of the hydrophobic groups (telechelic, multisticker, or combined).

Acknowledgments The authors wish to thank the Mexican National Council for Science and Technology (CONACYT) for the financial support to this work, through project 46035/A-1.

References

1. Volpert E, Selb J, Candau F (1996) Macromolecules 29:1452
2. Jiménez-Regalado E, Selb J, Candau F (1999) Macromolecules 32:8580
3. Hill A, Candau F, Selb J (1993) Macromolecules 26:4521

4. Stahl GA, Schulz DN (1988) Water-soluble polymers for petroleum recovery. Plenum Press, New York
5. Dubin P, Bock J, Davies RM, Schultz DN, Ties C (1994) Macromolecular complex in chemistry and biology. Springer, Berlin
6. Glass JE (1989) Polymer in aqueous solution: performance through association, Advances in Chemistry Series 223. American Chemical Society, Washington, D.C
7. Shalaby SW, McCormick CL, Butler GB (1991) Water-soluble polymers: synthesis, solution properties and applications, ACS Symposium Series 467. American Chemical Society, Washington, D.C
8. Maechling-Strasser C, Clouet F, François J (1992) Polymer 33:1021
9. Maechling-Strasser C, François J, Clouet F, Tripette C (1992) Polymer 33:627
10. Yekta A, Duhamel J, Brochard P, Adiwidjaja H, Winnik MA (1993) Macromolecules 26:1829
11. Alami E, Almgren M, Brown W, François J (1996) Macromolecules 29:2229
12. Alami E, Almgren M, Brown W, François J (1996) Macromolecules 29:5026
13. Jenkins R, Basset D, Wolf D, Nuyken O (1997) Langmuir 13:6896
14. Rao B, Uemura Y, Dyke L, Mcdonald MP (1995) Macromolecules 28:531
15. Ezzell SA, McCormick CL (1992) Macromolecules 25:1881
16. Branham KD, Shafer GS, Hoyle CE, McCormick CL (1995) Macromolecules 28:6175
17. Ezzell SA, Hoyle CE, Creed D, McCormick CL (1992) Macromolecules 25:1887
18. Feng Y, Billón L, Gras B, Khoukh A, François J (2002) Polymer 43:2055
19. English RJ, Laurer JH, Spontak RJ, Khan SA (2002) Ind Eng Chem Res 41:6425
20. Durand A, Hourdet D (1999) Polymer 40:4941
21. Evani S (1984) U.S. Patent 4,432,881
22. Jiménez-Regalado E, Cadenas-Pliego G, Pérez-Alvarez M, Hernández-Valdez Y (2004) Polymer 45:1993
23. Jiménez-Regalado E, Cadenas-Pliego G, Pérez-Alvarez M, Hernández-Valdez Y (2004) Macromol Res 12:451
24. Tsitsilianis C, Iliopoulos I (2002) Macromolecules 35:3662
25. Semenov N, Rubinstein M (2002) Macromolecules 35:4821
26. Ng WK, Tam KC, Jenkins RD (2001) Polymer 42:249
27. May R, Kaczmarski JP, Glass JE (1996) Macromolecules 29:4745
28. Kathmann EE, White LA, McCormick CL (1997) Macromolecules 30:5297
29. Jiménez-Regalado E, Selb J, Candau F (2000) Langmuir 16:8611
30. Nilsson S, Thuresson K, Lindman B, Nyström B (2000) Macromolecules 33:9641
31. González-Coronel VJ, Jiménez-Regalado EJ (2009) Polym Bull 62:727
32. Abu-Sharkh FB, Yahaya GO, Ali SA, Kazi IW (2001) J Appl Polym Sci 82:467
33. Candau F, Selb J (1999) Adv Colloid Interface Sci 79:149
34. Tanaka F, Edwards SF (1992) Macromolecules 25:1516
35. Annable T, Buscall R, Ettelaie R, Whittlestone DJ (1993) Rheol 37:695
36. Leibler L, Rubinstein M, Colby RH (1991) Macromolecules 24:4701