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NOTE

Rheological Behavior of Bigrafted Hydrophobically Modified Polyelectrolyte

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Introduction

For all of the systems described in the literature, hydrophobically modified water-soluble polymer (HMP) and polyelectrolyte (HMPE) are monografted polymers with only one type of hydrophobic group.[1−13] Generally, the thickening behavior is tuned by modifying the nature of the hydrophilic backbone and/or hydrophobic groups and the blocky structure of the copolymers (with micellar copolymerization[4,12,14]). As far as we are aware, there are no reports in the literature where the associative behavior has been tuned by using bigrafted hydrophobic groups, i.e., one assuring the associativity and other the hydrophilic−lipophilic balance of the main chain. In this study, we have determined, for the first time, the rheological impact of incorporating a large number of short hydrophobic groups (C4) with a small number of classical long chains (C12) in a polymer that maintains solubility in aqueous media. The challenge is to obtain amphiphilic systems that show interesting interfacial properties, in addition to improved rheology. Improving the performances of polymers through the development of smarter molecules represents a key technological challenge for chemical improved/enhanced oil recovery. This Note presents the rheological behavior in 1 M NaCl obtained from the modification of sodium poly(acrylate), PAANa, with *n*-dodecyl (C12) and *n*-butyl (C4) side chains.

Experimental Section

Synthesis and Characterization. A series of mono- and bigrafted hydrophobically modified PAANa polymers with high weight-average molar masses ($M_w = 1.1 \times 10^6$ g/mol, $I_p = 2.0$ and $(\langle S^2 \rangle_z)^{0.5} = 98$ nm in 0.1 M $NaNO_3$) were prepared via one-pot polymer postmodification: monografting with 2 mol % of long C12 alkyl groups and 2 and 10 mol % of short C4 alkyl groups and bigrafting with 2 mol % of C12 and 2 or 10 mol % of C4. Molar mass measurements show that no degradation of chain occurred during these reactions. ^{1}H NMR was carried out at 85 °C on the acidic form of the polymers, wherein the polymer microstructures were observed to agree well with the feed ratio (see Table 1 and Supporting Information for experimental details)

Viscometric Measurements of Dilute and Semidilute Polymer Solutions (NaCl 1 M). The steady shear rheological properties of the polymer semidilute solutions were measured using a Rheometrics ARES shear rheometer with a double-walled Couette fixture ($T = 25$ °C). The intrinsic viscosities ($[\eta]$) of polymers were determined by the ACM technique at room temperature.[15−17] The pH was measured at a constant value of 7.0 ± 0.2.

Results and Discussion

In Dilute Polymer Solution. For the monografted polymer, $[\eta]$ is not modified by the introduction of C4 alkyl groups and is slightly decreased to 245 mL/g with the introduction of C12 alkyl groups (Table 1). For the bigrafted polymers, $[\eta]$ continues to decrease as a function of C4 hydrophobic content down to 180 mL/g. As expected, the C12 alkyl groups induce an intramolecular interaction and explain the decrease of $[\eta]$ for the monografted polymer.[2,6,8−10] This intramolecular interaction is increased with the incorporation of C4 into the bigrafted copolymer, while the introduction of C4 groups alone does not have any effect on the intrinsic viscosity.

In Semidilute Polymer Solutions. The zero-shear viscosities η_0 are plotted in Figure 1. As shown previously, the short C4 alkyl groups incorporated alone into the main chain do not change the rheological behavior in semidilute solutions. Nevertheless, the incorporation of the long C12 alkyl groups increases the viscosity depending on the content of C4 and on the polymer concentration. η_0 values for bigrafted polymers show an unexpected variation: the viscosity sharply increases with a different shape compared to monografted polymers. The viscosifying effect is stronger for the bigrafted polymer with 2 mol % of C4 than for 10 mol % of C4. Both bigrafted polymers exhibit higher viscosities than the corresponding monografted polymer. The critical concentration at which the viscosity increases (C_η) does not depend on the hydrophobic content in the bigrafted polymer and the corresponding C12 monografted polymer. C_η appears at about 2 g/L, which is a concentration lower than the critical

Table 1. Composition of the Feed and Final Compositions of the Copolymers; $[\eta]$ of the Precursor and Grafted Polymers

	compositions (mol %)				
	in the feed		copolymers[a]		$[\eta]$ (mL/g)
sample	C4	C12	C4	C12	NaCl 1 M
precursor[b]					280 ± 22
monografted					
PAA2%C12	0	2	0	2.1	245 ± 20
PAA2%C4	2	0	2	0	285 ± 22
PAA10%C4	10	0	10.9	0	
bigrafted					
PAA2%C12−2%C4	2	2	1.9	1.9	195 ± 16
PAA2%C12−10%C4	10	2	10.5	2.2	180 ± 14

[a] Determined by ^{1}H NMR (see Figures S1 and S2). [b] $M_w = 1.1 \times 10^6$ g/mol, $I_p = 2.0$ (see molar masses measurement in the Supporting Information).

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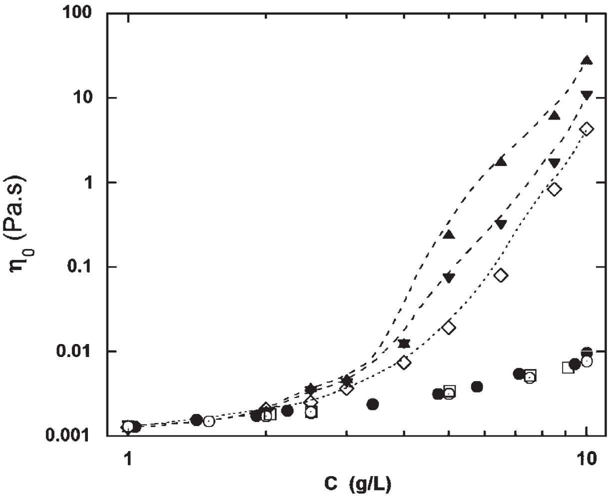

Figure 1. Zero-shear viscosity, η_0, plotted as a function of polymer concentration for precursor (●), monografted polymers with 2% C4 (□), 10% C4 (○), and 2% C12 (◇), and bigrafted polymers with 2% C12−2%C4 (▲) and 2%C12−10%C4 (▼) ([NaCl] = 1 mol/L, lines are guides for the eyes).

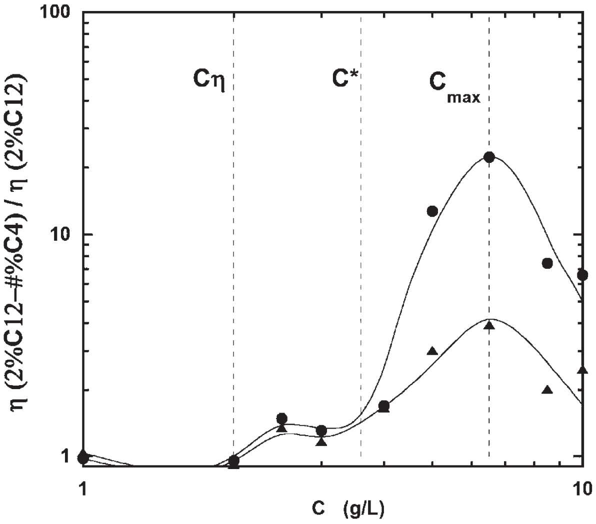

Figure 2. Viscosity ratio between the viscosity of bigrafted polymers in comparison with the corresponding C12 monografted polymer: (●) η(PAA2%C12−2%C4)/η(PAA2%C12) and (▲) η(PAA2%C12−10% C4)/η(PAA2%C12) (the lines are guides for the eyes).

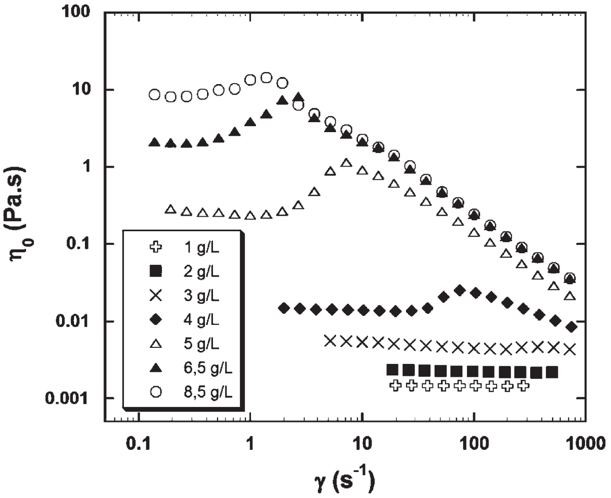

Figure 3. Effect of shear rate on zero-shear viscosity for solutions of PAA2%C12−2%C4 in 1 mol/L NaCl at various polymer concentrations.

overlap concentration (C^*) of the PAANa precursor ($C^* \approx 1/[\eta] = 3.6$ g/L).

Figure 2 compares the evolution of the viscosity ratio of the zero-shear viscosity of the bigrafted polymer to the corresponding C12 monografted as a function of concentration. The observed discontinuous variation of the viscosity ratio shows the following: (i) There is an increase in the viscosity of the bigrafted polymers compared to the corresponding monografted polymer from C_η until a concentration corresponding to the C^* of the precursor. The reported increase of about 30% is larger than the experimental precision. (ii) This first increase is followed by a larger increase in the viscosity until a maximum is achieved (denoted as $C_{\max}$ in Figure 2). The effect is more pronounced for a bigrafted polymer with 2 mol % of C4 than with 10% C4. The viscosities at $C_{\max}$ for PAA2%C4−2%C12 and PAA10% C4−2%C12 are 20 and 4 times larger, respectively, than their corresponding monografted PAA2%C12. (iii) From $C_{\max}$, the viscosity ratio decreases without ever achieving the viscosity of the corresponding monografted polymer in the concentration range explored.

The explanation of this novel behavior is not obvious. This particular shape of the thickening efficiency for bigrafted copolymers could be explained by a cooperative effect of the C4 alkyl groups with the intermolecular association of C12 alkyl chains according to the polymer concentration.

From concentrations higher than C_η, the balance between intra- and intermolecular association changes, and aggregates are formed. These aggregates are initially unentangled, and the increase in the viscosity can be explained by the increase of the aggregate size. This increase is more appreciable in the case of bigrafted copolymers (see Figure 2) and proves the effect of C4 groups on the intra/inter inversion. At concentrations larger than C^*, the inversion of the intra/inter ratio maintains a classical shape to characterize the increase in viscosity of monografted copolymers. The intermolecular binding of alkyl groups at one site increases the affinity for alkyl groups at another site, and therefore, the hydrophobically modified polymer exhibits a positive cooperativity of intermolecular binding of alkyl groups. In the case of bigrafted polymers, and for $C^* < C < C_{\max}$, the intra/inter inversion is strong, and the viscosity sharply increases, particularly for PAA2%C12−2%C4, thus showing a growth of the cooperative effect due to the short alkyl chains; however, this growth of the cooperative effect is not a function of the C4 content, since the viscosity ratio is highest for 2 mol % of C4. It seems that the effect is optimum for a particular value between 0 and 10 mol % of C4 content. At polymer concentrations higher than $C_{\max}$, wherein chain entanglements and the mesh size of the transient network primarily govern dynamic properties, the difference between the mono- and bigrafted polymers becomes negligible.

Shear Thickening Effect. Figure 3 illustrates the influence of the concentration on the rheological responses for the grafted polymers. The most important result is that the increase in concentration promotes a shear-thickening behavior in both mono- and bigrafted copolymers that contain C12 alkyl chains. Several characteristics are evident from these flow curves: at concentrations lower than C^*, the polymer solution exhibits classical behavior with a Newtonian plateau, while at higher concentrations, shear-thickening regions appear in the curves.[18,19] We define some parameters for the assessment of dilatancy: the ratio R between the viscosities at the peak and zero-shear points in

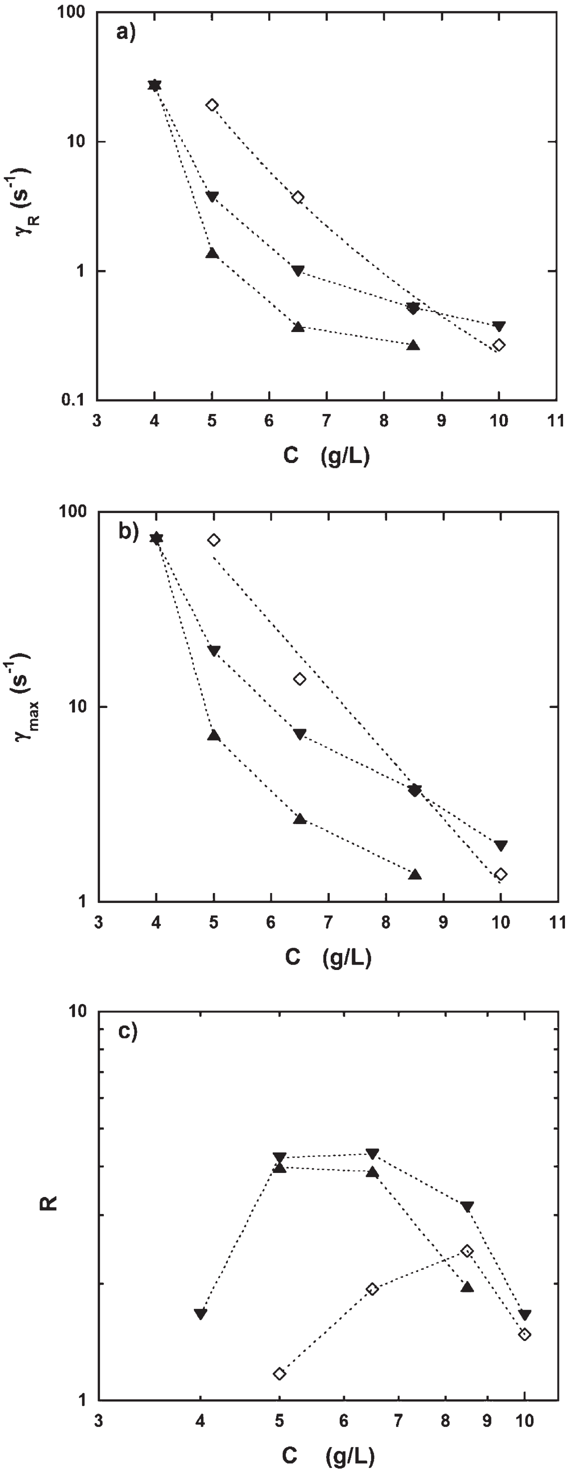

Figure 4. Characteristics of the flow curves for a monografted polymer with 2% C12 (◇) and bigrafted polymers with 2%C12−2%C4 (▲) and 2%C12−10%C4 (▼): (a) $\dot{\gamma}_R$, critical shear rates at which the onset of shear thickening appears; (b) $\dot{\gamma}_{max}$, the shear rate at the maximum viscosities in the flow curves; (c) ratio R between the viscosities at the peak and zero-shear points in the flow curves (the lines are guides for the eyes).

the flow curves; $\dot{\gamma}_R$, the critical shear rate at which the onset of shear thickening appears; and $\dot{\gamma}_{max}$, the shear rate at the maximum viscosity in the flow curves.

The values of these parameters as a function of polymer concentration are reported in Figure 4. The critical shear rates decrease with concentration in all cases. The inverse of $\dot{\gamma}_R$ represents the relaxation time associated with the formation of the transient network induced by shear or the entanglement relaxation time. It is therefore expected that such a relaxation time increases as the polymer concentration becomes higher, since the entanglement density is also increasing. The behaviors of bigrafted polymers are again distinct, and the features are similar to those observed in the zero-shear viscosity values. There is a sharper decrease of the critical shear rates up to a minimum that corresponds to the C_{max} observed previously in Figure 2. The effect is more pronounced for a bigrafted polymer with 2 mol % of C4 compared to that with 10 mol %: The critical shear rates to reach C_{max} for PAA2%C4−2%C12 and PAA10%C4−2% C12 are 22 and 4 times smaller, respectively, than their corresponding monografted PAA2%C12. From C_{max}, the critical shear rates continue to decrease until they achieve the value of the corresponding monografted polymer in the explored range of concentrations. The ratio R also follows this behavior. It is higher for the bigrafted copolymers and tends to the value of the corresponding monografted polymer after C_{max}. It seems that the stress necessary to favor intermolecular bridging depends on the short alkyl chain content in a domain of concentration close to C^* of the precursor.

Conclusion

Rheological measurements in a 1 M NaCl solution carried out in dilute and semidilute regimes show the effects of the incorporation of short alkyl groups (C4) into the HMPE. For monografted copolymer, the C4-modified polymers exhibit similar intrinsic viscosities and zero shear viscosities compared to the unmodified polymer. The C12-modified polymer has the classical behavior of an associative polymer, wherein the intrinsic viscosity is lower than its unmodified analogue, and a viscosifying effect appears at a concentration lower than C^* of the unmodified polymer. For bigrafted copolymers, the C4−C12-modified polymers exhibit a similar trend as the C12-modified polymer, with an unexpected synergistic improvement of the viscosifying effect at low polymer concentrations and a strong decrease in intrinsic viscosity. At relatively low polymer concentrations, as the dynamics involve both inter- and intramolecular associations, the incorporation of C4 alkyl chains to C12 grafted copolymers leads to increases in the zero-shear viscosity and in the shear thickening effect and to decreases in the critical shear rates associated with the latter effect. At higher polymer concentrations, the difference between mono- and bigrafted polymers becomes negligible.

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Supporting Information Available: Synthesis and characterization of HMPEs. This material is available free of charge via the Internet at http://pubs.acs.org.

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