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Recent advances in associating polymers prepared by micellar polymerization

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SUMMARY: Multisticker polymer chains consisting of polyacrylamides hydrophobically modified with low amounts of *N,N*-dihexylacrylamide (HMPAM) have been prepared by a free radical micellar polymerization technique. The rheological behavior of semi-dilute solutions of HMPAM with variable molecular weights ($M_w \approx 1.15\times10^4$ to 2.2×10^6), hydrophobe contents ([H] = 0.5 to 2 mol%) and hydrophobic block lengths (N_H = 1 to 7 units per block) has been investigated as a function of polymer concentration (C). Two different regimes can be clearly distinguished in the zero-shear viscosity $\eta_0 = f(C)$ curves. A first unentangled regime where the viscosity increase rate strongly depends on N_H and [H]. A second entangled regime where the viscosity follows a scaling behavior of the polymer concentration with an exponent close to 4, whatever [H] or N_H. In this regime, the results can be quite well accounted for by an hindered reptation model.

Introduction

Water-soluble polymers modified with a small amount of hydrophobic groups have become of great interest in the past years.[1-5] Above a certain polymer concentration in aqueous solution, the hydrophobic groups associate and build up a transitory three-dimensional network that induces a strong increase in viscosity. Thereby, these associating polymers exhibit unique rheological properties in solution, due to the reversible dissociation process of the physical cross-links under shear. This particular behavior is of great technological interest in a large number of applications, as for example in oil recovery and latex paint systems. Also the inter- or intramolecular interactions which take place in aqueous solutions lead to the formation of hydrophobic microdomains and this characteristic can be used for the encapsulation of hydrophobic compounds.

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In this paper, we present some recent achievements on the rheological behavior of associating polyacrylamides prepared by micellar polymerization. The results obtained bring some new insight into the nature of the hydrophobic interactions and the mechanism underlying the association.

Experimental Section

The synthesis of the samples by means of a micellar polymerization technique has been described in detail in previous papers.6, 7) In this process, the hydrophobe is solubilized within surfactant micelles (sodium dodecylsulfate) whereas the water-soluble monomer is dissolved in the aqueous continuous medium. Due to their high density in the micelles, the hydrophobic monomers are randomly distributed as small blocks in the hydrophilic backbone.6-11) The associating copolymers are poly(acrylamide)s hydrophobically modified with 0.5 to 2 mol% of *N,N*-dihexylacrylamide (DiHexAM). The molecular weight was varied from 115 000 to 2.2×10^6 by using mercaptoethanol as a chain transfer agent. The initiator was 4,4'-azo-bis(4-cyanovaleric acid), (ACVA). The hydrophobe/surfactant molar ratio was adequately adjusted in order to get the number of hydrophobes per micelle, N_H, ranging from 2 to 7.6, 7) The length of the hydrophobic blocks in the copolymers is assumed to correspond roughly to N_H.11) The molecular weight M_w and composition of the samples were determined as previously described.7) The sample code of the copolymers refers to its molecular weight (1, 5, 15 and 20 stand for ≈ 140 000 ± 25 000, ≈ 440 000 ± 20 000, ≈ 1 400 000 and ≈ 2 000 000 respectively), to the content of hydrophobic monomer and to the N_H value (i.e. the length of the hydrophobic block). For example, 1M1D3.2 stands for a copolymer with a molecular weight of 115 000 containing 1 mol% of DiHexAM and synthesized with a number of hydrophobes per micelle equal to 3.2.

Viscosity experiments were performed on copolymer aqueous solutions (1 wt % < C < 10 wt %) with a Haake RS100 controlled stress rheometer equipped with a cone-plate geometry, or a Contraves LS30 low shear rheometer, depending on the sample viscosity. More details on the experimental procedure are given elsewhere.7, 12)

Results and discussion

We discuss below the effect of the main parameters susceptible to control the rheological behavior of the associating polymers investigated here, i.e. the nature and the content of hydrophobe, the average hydrophobe block length and the copolymer molecular weight.

1. Nature of the hydrophobe

The compositional homogeneity of the copolymers obtained by this process depends on the nature of the hydrophobe. The use of *N*-monosubstituted acrylamide hydrophobes was found to produce a drift in copolymer composition. We could attribute this behavior to the capability of monosubstituted acrylamides to form intramolecular hydrogen bonding. This causes an increased reactivity of the hydrophobe within the micelles due to the low polarity of the microenvironment.7)

On the other hand, the use of *N,N*-disubstituted acrylamide derivatives, for which H-bonding is not possible (because of the absence of N-H group) allowed us to suppress the drift in composition, whatever the number of hydrophobes per micelle. These results led us to use a disubstituted hydrophobe, *N,N*-dihexylacrylamide, (DiHexAM)), which proved to be a very effective thickener and led to samples homogeneous in composition.7, 12)

2. Hydrophobe block length

As seen above, the free radical micellar polymerization technique yields multiblock copolymers in which the hydrophobic blocks are randomly distributed in the hydrophilic backbone.11) It is therefore possible to control the hydrophobe to micelle molar ratio in going from a very blocky structure (high N_H values) to an almost random copolymer in which the hydrophobes are singly distributed ($N_H = 1$). A series of samples was prepared accordingly.

In Figure 1 are reported the log-log variations of the zero-shear viscosity, η_0, versus polymer concentration for samples of similar molecular weight and hydrophobe content but different blockiness (i.e. different N_H values). The corresponding homopolyacrylamide is shown for comparison. One observes in the semi-dilute regime a spectacular effect of the microstructure on η_0 since a variation of N_H from 2 to 7 results in a strong enhancement of the viscosity by almost three decades.

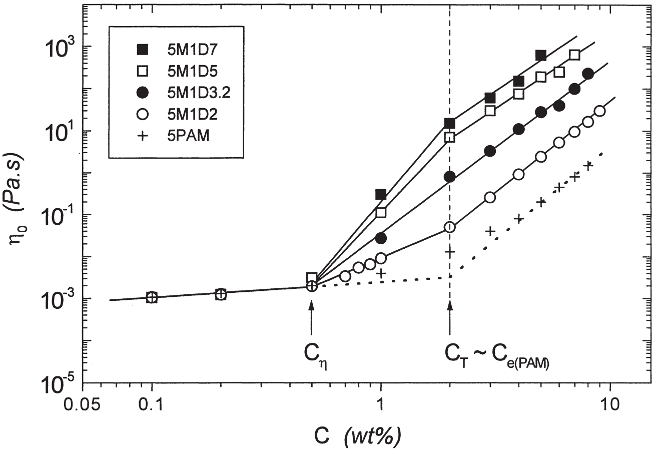

Fig. 1: Zero-shear viscosity versus polymer concentration for a homopolyacrylamide and various AM-DiHexAM copolymers with similar molecular weights ($M_w \approx 450\ 000$) and hydrophobe content ([H] = 1 mol%) but different hydrophobic block length.

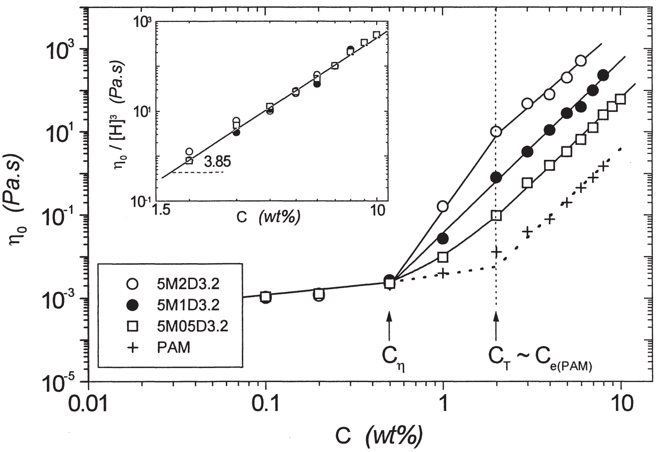

Fig. 2: Zero-shear viscosity versus polymer concentration for a homopolyacrylamide and various AM-DiHexAM copolymers with similar molecular weights ($Mw \approx 450\ 000$) and hydrophobic block length ($N_H = 3.2$), but different hydrophobe contents.

Another interesting feature is the existence of several regimes, as for unmodified polymers:

1) $C \leq C_\eta$. A dilute regime, where the chains are isolated and the viscosity is essentially controlled by intramolecular interactions. This regime does not significantly differ from that of unmodified polymers.

2) $C_\eta \leq C \leq C_T$. Beyond a critical concentration C_η, which is in the vicinity of the critical overlap concentration C* of the unmodified polymer, the viscosity rises very steeply, the higher N_H, the steeper the rise. In this regime, the viscoelasticity is likely controlled by the effect of intermolecular hydrophobic associations. One must also note that this regime corresponds approximately to the semi-dilute unentangled regime observed for unmodified polymers.

3) $C \geq C_T$. For both modified and unmodified polymers, the zero-shear viscosity follows a scaling behavior of the concentration with an exponent close to 4. One can also remark that the break occurs at a concentration C_T, independent of N_H and of the order of that where the unmodified chains are entangled (C_e). The latter is usually defined as the cross-over concentration between the unentangled semi-dilute regime where the viscosity rises smoothly and the entangled regime where the viscosity obeys the power law of the concentration with an exponent close to 4.

3. Hydrophobe content

The effect of hydrophobe content, at constant molecular weight and block length, is illustrated in Figure 2. One observes qualitatively the same behavior as in Figure 1; the cross-over, C_η, between dilute and unentangled semi-dilute regimes is independent of [H]. In this regime, ($C_\eta \leq C \leq C_T$), the exponent of the power law of $\eta_0 = f(C)$ increases with [H].

In the entangled regime ($C > C_T$), parallel straight lines are observed with an exponent close to 4 . In this asymptotic regime, the zero-shear viscosity follows a scaling law of [H] with an exponent of 3 ($\eta_0 \propto [H]^3$) as seen in the inset of Figure 2.

4. Effect of molecular weight

In Figure 3 are given the log-log variations of the zero-shear viscosity versus concentration for four samples of different molecular weight but same hydrophobe content and block length. There is a strong effect of the molecular weight on C_η. In the semi-dilute

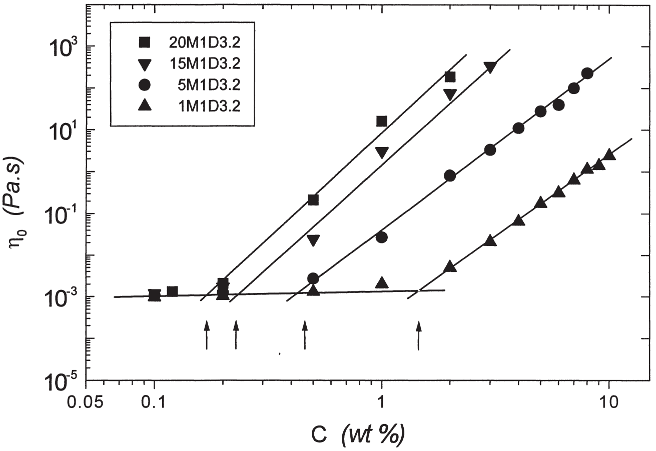

Fig. 3: Zero-shear viscosity versus polymer concentration for various AM-DiHexAM copolymers with the same hydrophobe content ([H] = 1 mol%) and hydrophobic block length ($N_H = 3.2$), but different molecular weights. The arrows indicate the values of C_η.

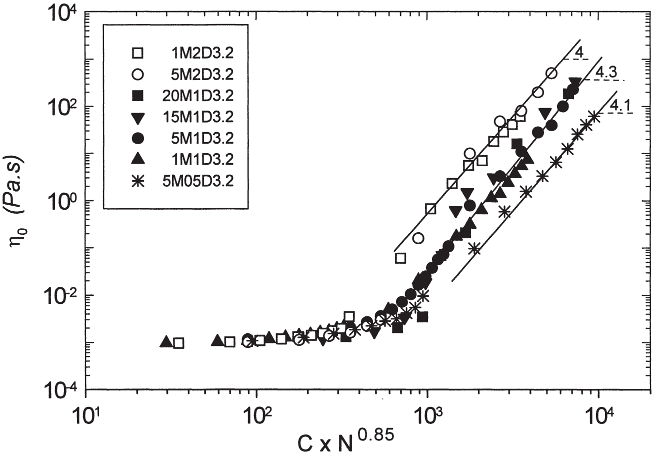

Fig. 4: Variation of the zero-shear viscosity as a function of the scaling variable C × $N^{0.85}$ for various copolymers with the same hydrophobic block length ($N_H = 3.2$), but different molecular weights and different hydrophobe contents: [H] = 2 mol% (open symbols), 1 mol% (filled symbols) and 0.5 mol% (∗).

regime, the viscosity follows a scaling law of the concentration for the four samples with an exponent close to 4. One can gather these curves as a single master curve by using a scaling variable $C \times N^{0.85}$ (N: polymerization degree) (Figure 4, filled symbols). In the same Figure are also reported the log-log variations of $\eta_0 = f(C \times N^{0.85})$ for a series of samples of same hydrophobic block length and variable hydrophobe content ([H] = 0.5 and 2 mol%, $*$ and open symbols respectively).

5. Comparison with the theoretical models

At this stage, one can attempt to compare our results to the theoretical predictions. Obviously, the sticky reptation model proposed by Leibler et al.[13)] for multisticker polymer chains seems the most appropriate, at least in the asymptotic limit where the chain are entangled.

Let us recall that in the reptation model of de Gennes, a given chain is considered as confined into a virtual tube made of the neigboring chains that constitute an uncrossable obstacle.[14)] Therefore, the chain can move only along its own contour length. In the case of associating polymers and as shown by Leibler et al., this scheme is modified by the possibility for the hydrophobic blocks to stick to other chains that comprise the wall of the tube (see Figure 5).

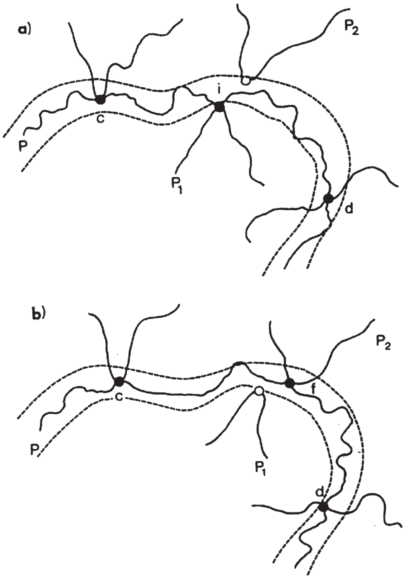

Fig 5: Schematic representation of the sticky reptation. The chain P is initially cross-linked to chain P_1 at point i *(a)*, then the sticker forms a new cross-link with another chain P_2 at point f *(b)*. (Reprinted with permission from Leibler et al.[13)]. Copyright 1991 American Chemical Society).

This results in a hindered reptation with a slowing down of the system dynamics and consequently a much higher viscosity.13) This model was derived under the assumption that the number of entanglements is much larger that the density of stickers and of binary associations between stickers. Another interesting prediction concerns the variation of the zero-shear viscosity which is found to obey the following relationship as a function of polymer concentration:

$$\eta_0 \propto C^{33/8}\, N^{3.5}\, [S]^2\, \tau\, (f(p)) \qquad (1)$$

where N is the degree of polymerization. The parameter [S] is the density of stickers and is directly related to [H] for a given N_H. The parameter τ is the average lifetime of a sticker in a cross-link and p is the average fraction of stickers engaged in an association. From the results reported in Figure 4, we can deduce the following relationship for the zero-shear viscosity dependences.

$$\eta_0 \propto C^x\, N^y\, [H]^3\, f(N_H) \qquad (2)$$

with $4 \leq x \leq 4.3$ and $3.4 \leq y \leq 3.65$.

Equation 2 is very close to the theoretical expression given in Equation (1) as far as the concentration and the degree of polymerization are concerned. On the other hand, the effect of [H] is larger ($\eta_0 \propto [H]^3$) than what is predicted ($\eta_0 \propto [H]^2$). In the theoretical model, it is assumed that the system contains only binary stickers and that the lifetime of the cross-link and the fraction p of stickers are uncorrelated to the other parameters. This assumption might not be fulfilled for the investigated systems, leading to the stronger dependence of η_0 on [H] observed.

Finally, the increase in η_0 observed with N_H is likely associated with the lifetime τ of a cross-link. The rate of disengagement of a hydrophobic sequence from a cluster (possibly binary) is an exponential function of the activation energy for disengagement and therefore can be very sensitive to the length of the blocks.

To conclude, the major progress made in the synthesis by free radical micellar polymerization of multisticker associating polyacrylamides, homogeneous in composition, enabled us to provide a unified description of their rheological behavior. This behavior is remarkably simple and well controlled given the complexity of the systems and can be used to properly design tailored materials according to the end-use envisioned.

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