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Scaling Behavior of the Zero Shear Viscosity of Hydrophobically Modified Poly(acrylamide)s

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Introduction. The rheological behavior of associating polymers is generally interpreted from models of transient networks in which junctions are sufficiently weak and recombine in thermal fluctuations.[1−7] Two clearly distinct categories of systems have been considered. The first one refers to unentangled networks in which the molecular weight between neighboring junctions is smaller than the entanglement molecular weight, so that each chain obeys Rouse dynamics modified by sticky trapping centers.[3,5−7] This model describes some of the features of the telechelic associative chains and in particular the Maxwellian behavior of the linear viscoelasticity.[6] The second model is meant for entangled networks made up of linear chains with many temporary cross-links.[2,4] The chain motion is a sticky reptation controlled by the concentration and the lifetime of tie points. Up to now, there has not been to our knowledge any experimental attempt to investigate the rheological behavior of associating polymers in which these two parameters were varied in a controlled manner.

In this letter, we present measurements of the zero shear viscosity for a series of poly(acrylamide)s containing hydrophobic blocks of *N*,*N*-dihexylacrylamide (DiHexAM). The number of hydrophobic stickers per chain, *S*, was tuned by adjusting either the molecular weight of the polymer or the total hydrophobe content. The length of the hydrophobic block that is expected to control the lifetime of the associations was also varied, owing to the specificity of the free radical micellar copolymerization technique. In this process that we have widely investigated in the past years,[8−12] the hydrophobe is solubilized within surfactant micelles whereas acrylamide is dissolved in the aqueous continuous medium (Figure 1). Due to their high density in the micelles, the hydrophobic monomers are randomly distributed as blocks in the acrylamide backbone. Hence, the rheological properties in aqueous solution of these multiblock copolymers are strongly dependent on the hydrophobe/surfactant ratio during the synthesis, i.e., the initial number of hydrophobes per micelle, N_H.[9,11,12]

However, a major problem related to the process was the compositional heterogeneity observed for copolymers based on ***N*-monosubstituted** acrylamide hydrophobes, this type of hydrophobe being the most investigated until recently.[8−10,13] 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.[11]

On the other hand, the use of ***N*,*N*-disubstituted** acrylamide derivatives, for which H-bonding is not possible (because of the absence of a N−H group) allowed us to suppress the drift in composition, whatever the number of hydrophobes per micelle.[11] This breakthrough in the domain of associating polymers prepared by micellar polymerization makes it now possible to perform a relevant study of the various factors affecting their rheological behavior and to provide a more appropriate description of the association mechanism.

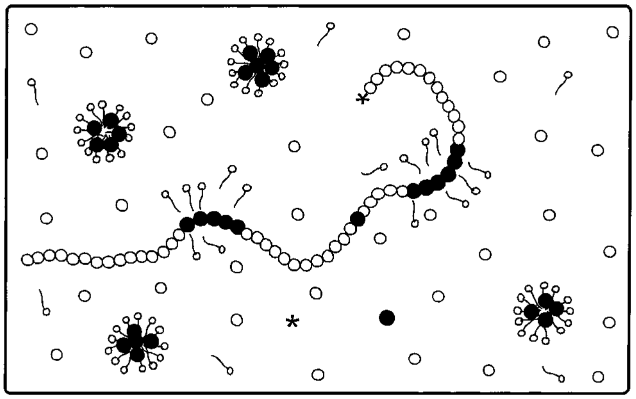

Figure 1. Schematic representation of the micellar copolymerization medium: (○) water-soluble monomer; (●) hydrophobic monomer; (○—) surfactant.

Experimental Section. The synthesis of the samples by means of a micellar polymerization technique has been described in detail in previous papers.[8−12] The associating copolymers are poly(acrylamide)s hydrophobically modified with 1 or 2 mol % of *N*,*N*-dihexylacrylamide (DiHexAM). The molecular weight was varied from 115 000 to 2.7×10^6 by using mercaptoethanol as a chain transfer agent. The initiator was ACVA. The hydrophobe/surfactant molar ratio was adequately adjusted in order to get the number of hydrophobes per micelle, N_H, ranging from 3.2 to 7. The length of the hydrophobic blocks in the copolymers is assumed to correspond roughly to N_H. The molecular weight M_w and composition of the samples were determined as previously described.[9,11,12]

Viscosity experiments were performed on copolymer aqueous solutions (1 wt % < C < 8 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 in refs 11 and 12.

Results and Discussion. In Figure 2a are reported the log−log variations of the zero-shear viscosity, η_0, of three unmodified poly(acrylamide)s (PAM) versus $C[\eta]$, where $[\eta]$ is the intrinsic viscosity. The product $C[\eta]$ is equivalent to the reduced polymer concentration C/C^* where C^* is the overlap concentration of the polymer chains. In this representation, the data obtained for the different molecular weights lie on the same curve within experimental accuracy. The observed behavior is that reported for other polymeric systems,[14−16] namely a dilute regime for $C/C^* < 1$ where η_0 slightly varies with concentration and a crossover regime between $C/C^* \approx 1$ and $C/C^* \approx 6$, in which the chains are overlapped but unentangled. This regime is characterized by a moderate increase of the zero shear viscosity. Finally, in the

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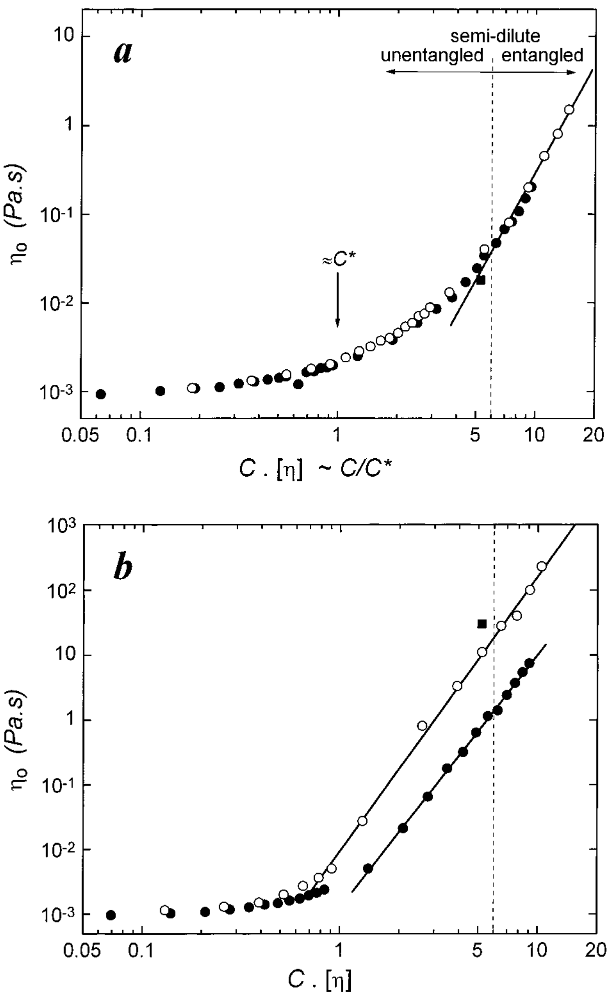

Figure 2. log−log plot of the zero-shear viscosity η_0 as a function of reduced concentration $C/C^* \equiv C[\eta]$ for polymers with different molecular weights: (a) homopoly(acrylamide)s (PAM), M_w = 90 000 (●), 480 000 (○), 2 500 000 (■); (b) copolymers (HMPAM) with the same hydrophobobe content (1 mol %) and blockiness (N_H = 3.2), M_w = 115 000 (●), 420 000 (○), 2 200 000 (■). The dashed lines correspond to the transition between the unentangled and entangled semidilute regimes for the homopolymers.

concentration range $C \gg C^*$ where the system is semidilute and entangled, η_0 follows a power law of the polymer concentration with an exponent of ≈4, close to the theoretical value,[17,18] and in good agreement with those reported for other polymeric systems.[14−16] This corresponds to a scaling of $\eta_0 \sim C^{4}M^{3.4}$.

In Figure 2b are reported the data for hydrophobically modified poly(acrylamide) samples (HMPAM) with three different molecular weights and N_H = 3.2. We have admitted for the values of the intrinsic viscosity those obtained for the unmodified poly(acrylamide)s, assuming that the intramolecular associations become rapidly negligible beyond C^*. Anyhow it was found experimentally that for the copolymers of M_w = 420 000 and M_w = 115 000, the intrinsic viscosity is almost unaffected by the presence of hydrophobic sequences, whereas for the HMPAM sample of $M_w = 2.2 \times 10^6$, $[\eta]$ is reduced by 65% with respect to the unmodified PAM.[12]

It can be observed in Figure 2b that the behavior of η_0 resembles that of entangled systems in a concentration range spanning both entangled and unentangled regimes of the corresponding unmodified PAM. Furthermore, the parameter C/C^* is no more the relevant variable since in this representation the data for different M_w do not superimpose each other. Upon lowering the concentration, one observes a sharp crossover of the viscosity, the latter becoming weakly concentration dependent in the dilute regime. Thus, the results of Figure 2 suggest that in this type of copolymer, the intermolecular associations play a dominant role as soon as the chains start to overlap. These interactions are likely to be closely correlated to the density of junction points, which itself must be directly linked to the concentration of hydrophobic blocks in the solution ($C_{H-block}$). In fact, the zero shear viscosity of samples with the same hydrophobic block length is found to follow a unique scaling law of both hydrophobic block density ($C_{H-block}$) and molecular weight, with an exponent close to 4 (cf. Figure 3). This suggests by analogy with the entangled unmodified samples, that once a tie between two hydrophobic sequences breaks up, this is followed by a motion involving the whole polymer, resulting in an hindered reptation. This supposes that the reptation can take place just beyond C^*, in a regime where the unmodified polymer would be unentangled. This is likely due to the fact that as soon as intermolecular junctions are formed, the bridges between these reversible cross-links contribute effectively to the formation of a tube in which the reptation process can occur. The large increase in η_0 with N_H shown in Figure 3 is likely due to the correlated increase in the lifetime of the junctions. 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.

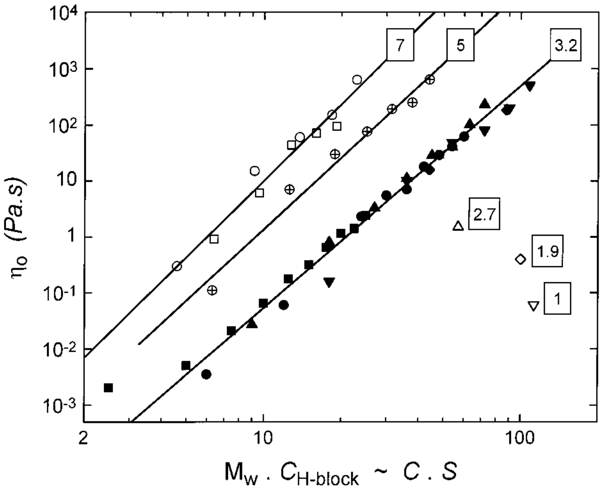

Figure 3. log−log plot of the zero-shear viscosity η_0 as a function of the product ($C \times$ number of blocks per chain) ≡ ($M_w \times$ hydrophobic block density). The labels on the graph refer to the length of the hydrophobic blocks (assumed to be equal to the initial number of hydrophobes per micelle, N_H). The hydrophobe content [H] is given in mol %. M_w = 1 600 000, [H] = 1 (▽); M_w = 2 700 000, [H] = 1 (◇); M_w = 2 200 000, [H] = 1 (△); M_w = 115 000, [H] = 1 (■); M_w = 140 000, [H] = 2 (●); M_w = 420 000, [H] = 1 (▲); M_w = 420 000, [H] = 2 (▼); M_w = 2 000 000, [H] = 1 (◆); M_w = 2 200 000, [H] = 1 (*); M_w = 450 000, [H] = 1 (⊕); M_w = 160 000, [H] = 2 (□); M_w = 460 000, [H] = 1 (○).

At this point, it is interesting to compare our results with the model of Leibler et al.[4] although the conditions under which the model applies do not correspond to the case considered here. In the latter, the reversible cross-links appear to contribute significantly to the formation of the tube. In the model of Leibler et al. it is assumed that the tube diameter is fixed by the density of entanglements and that the number of monomers in an entanglement strand, N_e, is much smaller than the average number N_s of monomers along the chain between stickers. Under these conditions, the zero shear viscosity is found to be described by the following relationship:

$$\eta_0 \cong \frac{CRT}{N_e}\left(\frac{N}{N_e}\right)^{3/2} \frac{2S^2\tau}{1 - 9/p + 12/p^2} \qquad (1)$$

where S is the number of hydrophobic stickers attached to each chain, τ is the average lifetime of the associations, and p is the fraction of stickers that forms a cross-link with other stickers.

The above expression can be rewritten by taking into account the scaling of N_e with polymer concentration, i.e., $N_e \sim C^{5-/4}$ in good solvent.[17,18]

$$\eta_0 \sim C^{33/8}N^{3/2}S^2\tau(1 - 9/p + 12/p^2)^{-1} \qquad (2)$$

To compare this expression with our results, we can remark that the variable $C_{H-block}\, M_w$ is also equal to $C.S$. Therefore, one finds qualitatively the trends expressed in the model of Leibler et al., that is, a large increase of η_0 with polymer concentration and with the number S of stickers per chain. Furthermore, an increase in N_H should lead to a large increase in the lifetime τ of the junctions, thus accounting for the strong enhancement of η_0 with N_H. However, the results of Figure 3 show that η_0 does not depend on M for a given S but, as mentioned above, the experimental conditions are rather different from those in the model. In particular, in the system investigated here, the tube diameter is likely determined by N_s and not by N_e. Actually, it is rather S, the number of stickers per chain, that plays the number of entanglements per chain, N/N_e, appearing in eq 1. The fact remains that the basic assumption of the model, namely that the motion of the chains occurs through Rouse relaxation of strands between two kinetic events (association and dissociation), should also apply to the case treated here. It is remarkable that the viscosity of these apparently complex systems can be described over 6 decades in a large range of molecular weights by a simple scaling behavior of a reduced variable ($C \times$ number of blocks per chain $\equiv M_w \times$ block density) for a given N_H.

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