Viscoelastic Behavior of Semidilute Solutions of Multisticker Polymer Chains

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ABSTRACT: Multisticker polymer chains consisting of water-soluble polyacrylamides hydrophobically modified with low amounts of *N*,*N*-dihexylacrylamide have been prepared by a free radical micellar polymerization technique. This process gives multiblock copolymers in which the number and length of the hydrophobic blocks can be tuned by varying the surfactant over hydrophobe molar ratio. The viscoelastic behavior of semidilute solutions of various series of copolymers with variable molecular weights ($M_w \approx 4.2 \times 10^4-2.7 \times 10^6$), hydrophobe contents ($[H] = 0.5-2$ mol %), and hydrophobic block lengths ($N_H = 1-7$ units per block) has been investigated as a function of polymer concentration, C, using steady-flow and oscillatory experiments. In the semidilute range, 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. The linear viscoelasticity can be described by (i) a slow relaxation process with a plateau modulus that only depends on polymer concentration and (ii) other faster complex relaxation processes. In the latter regime, the results can be quite well accounted for by a hindered reptation model.

Introduction

The incorporation of a few hydrophobic groups in a hydrophilic macromolecular chain results in systems with unique rheological characteristics in aqueous solutions. Above a certain polymer concentration, the hydrophobic moieties associate and build a transitory three-dimensional network.[1−8] The most salient features of such reversible networks is their significantly different viscoelastic behavior compared to that of polymers without associating groups. This behavior shows up in a slowing down of the polymer diffusion and an increase of the zero-shear viscosity. This rheological behavior is generally interpreted from models of transient networks in which junctions are sufficiently weak and recombine in thermal fluctuations. 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.[9−13] This model describes some of the features of the telechelic associative chains and in particular the Maxwellian behavior of the linear viscoelasticity.[10−12,14,15] The second model is meant for entangled networks made up of linear chains with many temporary cross-links. The chain motion is a sticky reptation controlled by the concentration and the lifetime of the tie points.[16,17] To check the validity of the model as well as to optimize the thickening behavior of associating polymers, it is desirable to have systems in which these two parameters can be varied in a controlled manner.

In a recent letter, we have presented measurements of the zero-shear viscosity, η_0, for a series of poly(acrylamide)s containing hydrophobic blocks of *N*,*N*-dihexylacrylamide (DiHexAM).[18] The number of hydrophobic stickers per chain, S, was tuned by adjusting the molecular weight of the polymer, the total hydrophobe content, or the length of the hydrophobic blocks. The latter parameter, which is expected to control the lifetime of the associations,[18,19] could be varied owing to the specificity of the free radical micellar copolymerization technique.[20] In this process, which we have investigated widely in the past years,[19,21−27] the hydrophobe is solubilized within surfactant micelles whereas acrylamide is dissolved in the aqueous continuous medium. Because of their high local concentration within the micelles, the hydrophobic monomers are distributed as blocks randomly along the polyacrylamide backbone.[19,20,23,26,28−32] It was also shown that the use of *N*,*N*-disubstituted acrylamides (as DiHexAM) led to copolymers homogeneous in composition.[26,27]

The rheological study performed on semidilute aqueous solutions of these multiblock copolymers showed a strong enhancement of η_0 upon increasing the hydrophobe content $[H]$, the polymer molecular weight M_w, the initial number of hydrophobes per micelle, N_H, and the polymer concentration C. The zero-shear viscosity data obtained for a series of samples having the same N_H were found to obey a simple scaling law of the polymer concentration and the number S of hydrophobic blocks attached to each chain.[18] The overall behavior followed qualitatively the trends expressed in the sticky reptation model proposed by Leibler et al.[17] However, a more precise comparison between theory and experiment requires the knowledge of the terminal time of the stress relaxation and that of the plateau modulus.

In this paper, we report measurements of linear and nonlinear viscoelasticity for various series of hydrophobically modified polyacrylamides (HMPAM) including both samples for which the zero-shear viscosity data were previously reported and additional samples. The results obtained allowed us to provide a more accurate scaling behavior and a better understanding of the dynamic properties and of the mechanism underlying the association of these multisticker polymers.

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Table 1. Polymer Characteristics

sample[a]	M_w ($\times 10^{-3}$)	$[H]^b$ (mol %)	$N_H{}^c$	S^d	C^e (wt %)
1PAM	90	0	0	0	0.1−10
5PAM	480	0	0	0	0.1−8
05M2D3.2	42	2	3.2	1.8	15, 20
1M1D3.2	115	1	3.2	2.5	0.1−10
1M2D3.2	140	2	3.2	6	1−10
1M2D7	160	2	7	3.2	1−8
5M05D3.2	450	0.5	3.2	4.9	0.1−10
5M1D2	425	1	2	15	0.1−9
5M1D3.2	420	1	3.2	9	0.1−8
5M1D5	450	1	5	6.3	0.1−7
5M1D7	460	1	7	4.6	0.1−5
5M2D3.2	420	2	3.2	18	0.1−6
14M1D3.2	1400	1	3.2	30	1−3
16M1D1*	1600	1	1	112	1
20M1D3.2	2000	1	3.2	44	0.1−2
22M1D3.2*	2200	1	3.2	48	1
22M1D2.7*	2200	1	2.7	57	1
27M1D1.9*	2700	1	1.9	100	1

[a] The sample code refers to the molecular characteristics of the polymers (see Experimental Section); * = samples from ref 19. [b] Hydrophobe content in the monomer feed. [c] Number of hydrophobe per micelle ≅ hydrophobic block length. [d] Number of hydrophobic blocks per chain (see Experimental Section). [e] Concentration range investigated in rheological measurements.

Experimental Section

The associating polyacrylamides were obtained by micellar copolymerization.[20,33−35] In this process, the hydrophobic monomer, *N,N*-dihexylacrylamide (DiHexAM), is solubilized within sodium dodecyl sulfate (SDS) micelles, whereas acrylamide is dissolved in the aqueous continuous medium. The copolymerization procedure has been described in detail elsewhere.[23,26]

The characteristics of the samples investigated are given in Table 1. The hydrophobe content in the copolymers, $[H]$ (which corresponds within the experimental error to that in the monomer feed) was 0.5, 1, or 2 mol %. The hydrophobe/surfactant molar ratio was adequately adjusted in order to get the number of hydrophobes per micelle, N_H, ranging from 1 to 7. N_H was calculated from the following relationship:

$$N_H = ([H]N_{agg})/([SDS] - cmc_{SDS}) \quad (1)$$

where [SDS], cmc_{SDS}, and N_{agg} are the molar concentration of the surfactant, its critical micellar concentration, and its aggregation number, respectively ($cmc_{SDS} = 9.2 \times 10^{-3}$ mol/L and $N_{agg} = 60$ at the polymerization temperature of 50 °C).[19,23] Owing to the monomer segregation within the micellar reaction medium, it is expected that, when a water-soluble growing macroradical encounters a micelle, all the hydrophobic monomers located within the micelle are consumed to form a short hydrophobic block.[20,23] Furthermore, by using *N,N*-dialkylacrylamides as hydrophobes instead of *N*-monoalkylacrylamides, it was found that the copolymer composition does not depend on the degree of conversion.[26,27] Hence, it can be reasonably assumed that the length of the hydrophobic blocks in the copolymer corresponds roughly to the initial number of hydrophobic monomers per micelles, i.e., N_H.

The molecular weight was varied from 42 000 to 2.7×10^6 by using mercaptoethanol as a chain transfer agent. Note that, in this case, the initiator was 4,4′-azobis(4-cyanovaleric acid) (ACVA) instead of potassium persulfate commonly used in previous micellar copolymerizations,[20,23,26] in order to avoid the redox side reaction between the mercaptan and persulfate.[36,37] For example, the concentration of the transfer agent was 6.9×10^{-5} and 4.8×10^{-4} M for obtaining M_w around 400 000 and 100 000, respectively, with [monomer] = 0.42 M and [ACVA] $= 3.2 \times 10^{-3}$ M. The weight-average molecular weight M_w and composition of the samples were determined by light scattering and NMR as previously described.[26] These amphiphilic copolymers cannot be characterized by size exclusion chromatography (SEC) in water, due to aggregation and adsorption phenomena. However, homopolyacrylamides prepared under identical experimental conditions, but without hydrophobe, have a polydispersity index M_w/M_n determined by SEC around two. That means that mercaptoethanol behaves like an ideal transfer agent for polyacrylamide. A similar molecular weight distribution can be assumed for the copolymers, since both types of samples exhibit close weight-average molecular weight values. On the basis of the above considerations, the average number of hydrophobic blocks (i.e., stickers) per macromolecular chain, S, was calculated from the following relationship:

$$S = (M_w/2m)[H]/N_H \quad (2)$$

where m is the molecular weight of the monomer unit (acrylamide, $m = 71$) and $M_w/2m$ corresponds to the number-average degree of polymerization, N.

The sample code of the copolymers refers to the molecular weight M_w (1, 5, 14, and 20 stand for ≈140 000 (±20 000), ≈450 000 (±20 000), ≈1 400 000, and ≈2 000 000, respectively), to the content in hydrophobic monomer $[H]$, and to the N_H value (i.e., approximately 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 (see Table 1).

The range of concentrations of the aqueous polymer solutions was 0.1 wt % < C < 20 wt %. Linear viscoelasticity experiments were performed on samples that were viscous enough to provide a meaningful analysis (see Table 1) with a Haake RS100 controlled stress rheometer equipped with a cone-plane geometry (angle 1°, diameter 20, 35, or 60 mm depending on the sample viscosity). In some cases, it was not possible to scan the shear rate over a large range by progressively increasing the shear stress since a slight increase in stress caused a large jump in the shear rate. To overcome this problem, we used the controlled-rate mode of the rheometer, which permitted us to scan the whole shear rate range without large gaps. In all cases, we checked that the curves measured in the controlled-stress and the controlled-rate modes were well superposed. The dynamic measurements were conducted with a frequency of 0.04−100 rad/s (i.e., ≈1.6×10^{-3}−14 Hz). All measurements were made under frequencies and strains that led to a linear response. Flow experiments were carried out with the same rheometer as above or with a Contraves LS30 low-shear rheometer, depending on the sample viscosity. More details on the experimental procedures are given elsewhere.[19,26]

Results

A. Data Analysis. Oscillatory Experiments. Figure 1 shows typical frequency dependences of the storage modulus $G'(\omega)$ and of the loss modulus $G''(\omega)$. At low frequency, the behavior of the complex shear modulus is Maxwellian, as ascertained by the variations of $G'(\omega)$ and $G''(\omega)$ versus ω that scale respectively like ω^2 and ω. The curves $G'(\omega)$ and $G''(\omega)$ cross each other at a circular frequency ω_{cross}. The inverse of ω_{cross} is often taken as the characteristic time of the system. As a matter of fact, the comparison between the actual experimental variations of $G'(\omega)$ and $G''(\omega)$ and those calculated from the Maxwell model shows deviations appearing already before the crossing frequency (Figure 1). The shape of the curves $G'(\omega)$ and $G''(\omega)$ at higher frequencies is indicative of the occurrence of fast modes superimposing on a slow relaxation process. Indeed, and as discussed later, the current models describing the dynamics of associating polymers predict a multiple relaxation process (at least two characteristic times). It follows that the relaxation time determined from ω_{cross} is smaller than the longest relaxation time, the latter being the physical quantity relevant for a comparison

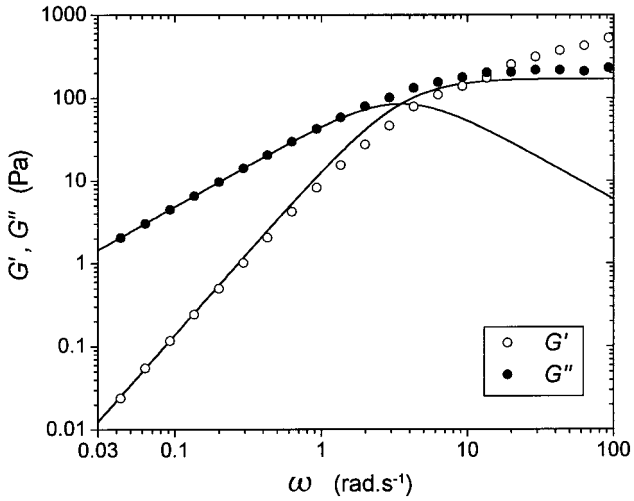

Figure 1. Storage (G') and loss (G'') moduli as a function of frequency for 1M2D7 sample (C = 5 wt %). The lines are the fit to one-mode Maxwell model (G_0 = 170 Pa, relaxation time = 0.285 s).

with the models. The behavior reported in Figure 1 is quite general and is observed for most of the samples. In fact, the slope of the $G''(\omega)$ curves is equal to 1 for all the samples studied, whereas that of the $G'(\omega)$ curves was found to decrease down to 1.8−1.7 for samples with long relaxation times (e.g., at high polymer concentration and/or high N_H).

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 relationships:

$$T_R = \lim_{\omega\to 0}\left(\frac{1}{\omega}\frac{G'}{G''}\right); \quad G_0 = \frac{1}{T_R}\lim_{\omega\to 0}\left(\frac{G''}{\omega}\right) \qquad (3)$$

Steady-Shear Flow Measurements. Figure 2a,b shows typical variations of the steady-state values of the viscosity η as a function of shear rate $\dot\gamma$ for two HMPAM. For sample 5M2D3.2, whose concentration (C = 2 wt %) corresponds to the very beginning of the semidilute regime, one observes a marked shear thickening effect followed by a shear thinning behavior at higher shear rate (Figure 2a). On the other hand, for a strongly entangled solution (sample 1M2D3.2, C = 9 wt %) the shear flow curve shows only a shear-thinning behavior, like in semidilute solutions of nonassociating polymers (Figure 2b).

For entangled systems, the correlations between dynamic and steady-state measurements are generally well described through the empirical method of Cox−Merz.[38,39] This consists of comparing the steady shear viscosity $\eta(\dot\gamma)$ as a function of shear rate with the modulus of the complex viscosity $\eta^*(\omega)$ as a function of the circular frequency. For melts or entangled solutions of polymers, the two functions are found to coincide.[39−41] In particular, the crossover between the Newtonian plateau and the shear-thinning regime occurs at $\dot\gamma_c = \omega_c$, where ω_c is the circular frequency at which $G'(\omega)$ and $G''(\omega)$ cross each other. However, the Cox−Merz rule is usually not reliable for complex structured fluids.[8,11]

The comparison between $\eta(\dot\gamma)$ and $\eta^*(\omega)$ illustrated in Figure 2a,b shows that the Cox−Merz rule fails for associating polyacrylamides even in the case where only

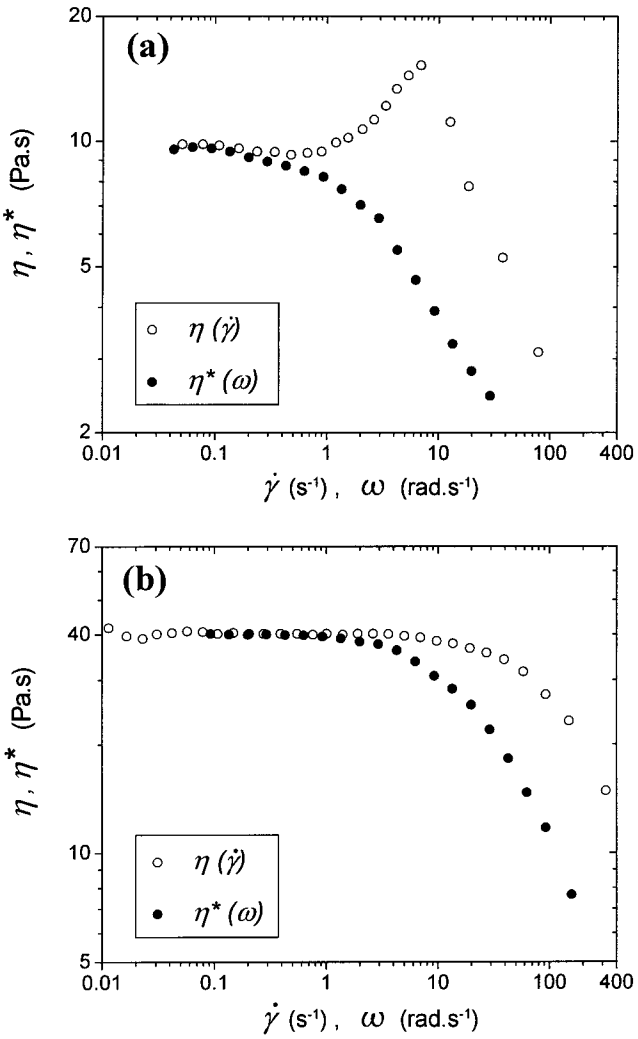

Figure 2. Steady-state viscosity $\eta(\dot\gamma)$ and dynamic complex viscosity $\eta^*(\omega)$ as functions of shear rate or frequency: (a) sample 5M2D3.2 (C = 2 wt %); (b) sample 1M2D3.2 (C = 9 wt %).

shear thinning is observed. The $\eta(\dot\gamma)$ and $\eta^*(\omega)$ curves coincide only in the Newtonian regime. We found in most cases that the shear rate $\dot\gamma_c$ at which $\eta(\dot\gamma)$ departs from the plateau behavior does not correspond to the inverse of the terminal time as determined from the procedure described above. Therefore, shear flow experiments conveniently used for measuring the zero-shear viscosity can only give here qualitative trends for the viscoelastic parameters.

B. Linear Viscoelastic Properties. The viscoelastic behavior of associating polymers shows up in the semidilute regime, that is, beyond the critical concentration C_η at which intermolecular associations form. This concentration is in the vicinity of the overlap concentration of the polymer chains, C^*. Shear-flow experiments allow one to localize the semidilute regime as illustrated in Figure 3, which gives the variation of the steady-state viscosity η as a function of shear rate $\dot\gamma$ for a HMPAM at different concentrations in aqueous solution. In the dilute regime ($C \lesssim 0.55$ wt %), the system is Newtonian; that is, there is no detectable variation of η with $\dot\gamma$. Slightly above the crossover concentration ($C \approx 1$ wt %), one observes the behavior previously mentioned (see Figure 2a), i.e., a shear thickening followed by shear thinning. Upon increasing further the concentration, the zero-shear viscosity in-

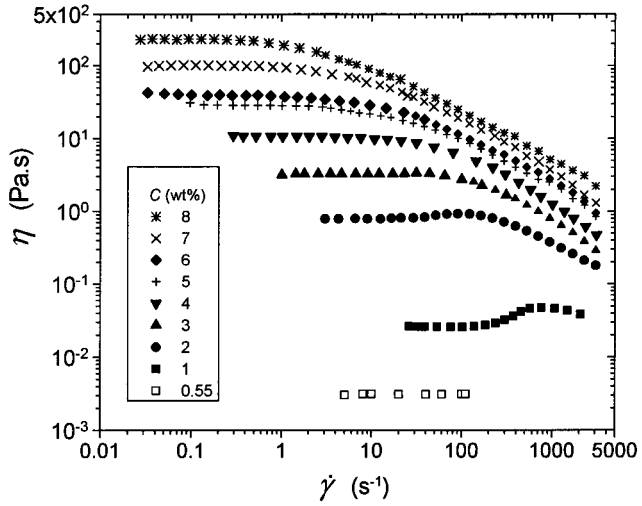

Figure 3. Steady-state viscosity η versus shear-rate for 5M1D3.2 sample at various concentrations in water.

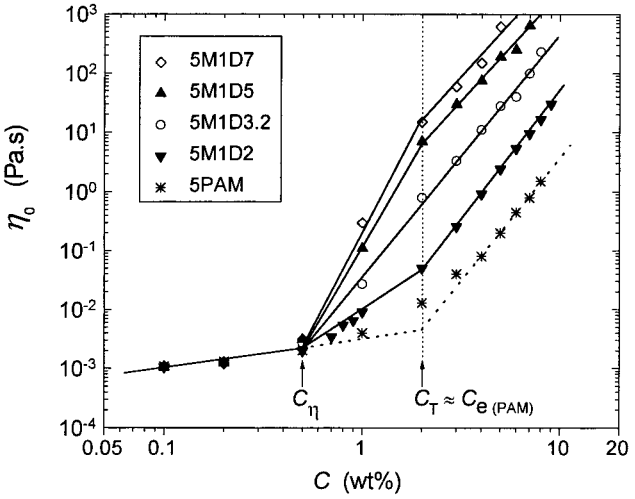

Figure 4. Effect of the hydrophobic block length N_H on the concentration dependence of the zero-shear viscosity for samples with similar molecular weight ($M_w \approx 450\,000$) and hydrophobe content ([H] = 1 mol %).

creases drastically, the shear thickening effect disappears, and the sample exhibits a stronger shear thinning behavior. The crossover shear rate, $\dot{\gamma}_c$, where the viscosity departs from the limiting plateau value, is a decreasing function of the concentration.

Three characteristic parameters can be varied in order to tune the viscoelastic behavior of the systems investigated in this study. One is the length of the hydrophilic backbone (i.e., the copolymer molecular weight M_w or degree of polymerization N), and the two others—hydrophobe content [H] and block length (assumed to correspond roughly to N_H, see Experimental Section)—refer to the hydrophobe characteristics. In the following, we discuss the influence of these factors on the zero-shear viscosity, η_0, the terminal time of the stress relaxation, T_R, and the plateau modulus G_0 associated with the slowest process, the two latter quantities being obtained from oscillatory experiments using eqs 3.

Figures 4−6 show the effects of each of these three characteristic parameters ([N_H], [H], and M_w), keeping constant the two others, on the concentration dependences of the zero-shear viscosity. For all the systems investigated, one observes qualitatively a similar behavior. The viscosity is of the order of that of water at low polymer concentrations C and rises very steeply beyond a critical concentration C_η. The crossover between the two viscosity regimes is well-defined and much sharper than for unmodified polyacrylamides (see Figures 4 and 5). It can also be seen in Figures 4 and 5 corresponding to polymers with same molecular weight, that C_η is independent of [N_H] and [H] within the experimental accuracy. Beyond C_η, the viscosity first follows a power law of the concentration with an exponent that increases with N_H and/or [H]. Interestingly, at a concentration C_T, one observes a second break in the log−log variations of $\eta_0(C)$. This break occurs at a concentration close to that where the unmodified polymer chains become entangled (C_e). The asymptotic behavior at high concentrations is described by parallel straight lines for different values of N_H and [H]. A similar behavior, that is a break at $C_T \approx C_e$, was also observed for polymers of $M_w \approx 150\,000$ and [H] = 2% (series 1M2D3.2, 1M2D7, not shown).

Figure 6 shows the effect of molecular weight on the viscosity behavior for samples with same N_H and [H] (3.2 and 1 mol %, respectively). There is a strong effect of the molecular weight on C_η. In the semidilute regime, the viscosity follows a scaling law of the concentration for the four samples with an exponent close to 4, and there is no detectable second break, whatever the molecular weight, as in the other plots for $N_H = 3.2$ and [H] = 1 mol %.

The effects of the three characteristic parameters, [H], N_H, and M_w, on the terminal time T_R are illustrated by Figure 7, in a log−log representation against polymer concentration for different series of samples. As could be expected from the viscosity results, the relaxation process strongly slows down upon increasing either [H], N_H, or M_w. The variations of T_R with concentration can be described by roughly parallel straight lines with slopes ≈2−3, considering the experimental uncertainty on these measurements.

Finally, in Figure 8 is reported the variation of G_0 versus polymer concentration for all the series investigated. The data are somewhat scattered, but one does not detect any trend with the molecular weight or the hydrophobe characteristics.

Discussion

Before analyzing further the above results, it is useful to recall the main features of the rheological behavior of unmodified polymers. When discussing the dynamical properties of solutions of linear polymer chains, one generally distinguishes four concentrations regimes:[42−44]

(i) The dilute regime $C < C^*$ where C^* is the overlap concentration, for which the zero-shear viscosity is of the order of that of the solvent.

(ii) The semidilute unentangled regime $C^* < C < C_e$ where C_e represents the concentration at which the entanglements become elastically effective. In this regime, the viscoelasticity of the solution is controlled by the Rouse dynamics and the viscosity increases moderately. Note that the ratio of C_e/C^* is generally of the order of 5−10.[43,44]

(iii) The semidilute entangled regime $C_e < C < C^{**}$. The viscosity properties are described by the reptation model, and the viscosity follows a power law of the polymer concentration with an exponent close to 4. The plateau modulus is proportional to the density of entanglements.

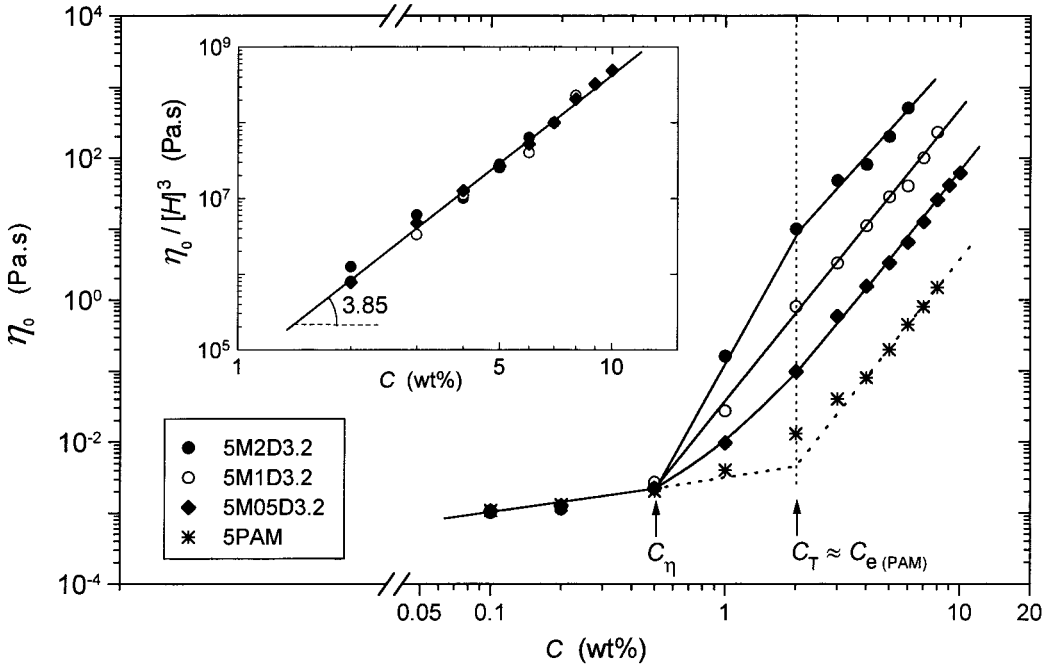

Figure 5. Effect of the hydrophobe content [*H*] on the concentration dependence of the zero-shear viscosity for samples with similar molecular weight ($M_w \approx 450\,000$) and hydrophobic block length ($N_H = 3.2$). Inset: variation of the quantity $\eta_0/[H]^3$ as a function of concentration for the same samples. ([*H*] is expressed in molar fraction.)

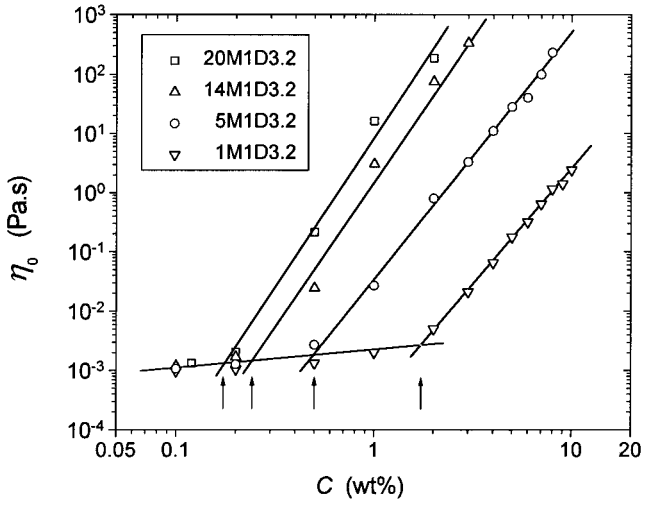

Figure 6. Effect of the molecular weight on the concentration dependence of the zero-shear viscosity for samples with similar hydrophobe content ([*H*] = 1 mol %) and block length (N_H = 3.2). The arrows indicate the value of C_η for each sample.

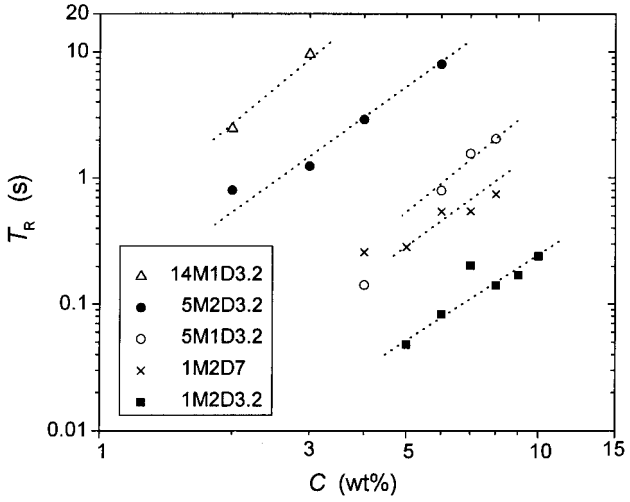

Figure 7. Variation of the terminal time as a function of polymer concentration for various series of samples with variable hydrophobe contents (5M1D3.2 and 5M2D3.2), hydrophobic block lengths (1M2D3.2 and 1M2D7), and molecular weights (5M1D3.2 and 14M1D3.2; 1M2D3.2 and 5M2D3.2).

(iv) The concentrated regime starts beyond C^{**}; the reptation model still holds, but the scaling behavior becomes different.

A remarkable feature of the rheological behavior of polymer solutions is that the zero-shear viscosity is a unique function of the reduced variable $C/C^* \cong C[\eta]$ in the concentration range $C < C^{**}$,[39,42,45] as shown for example for aqueous polyacrylamide solutions.[18,46]

On the contrary, for the associating polymers investigated here, the parameter C/C^* is no more the relevant variable, since for samples with a given molecular weight, the viscosity depends drastically on both N_H and [*H*].[18] From the behavior illustrated in Figures 4−6, we can identify several regimes:

(i) $C < C_\eta$. In this dilute regime, the viscosity is slightly depressed, as compared to that of the corresponding unmodified polymer. This is due to the chain contraction resulting from intramolecular associations.[20,23,47−50] The concentration C_η, which is independent of N_H and [*H*] (Figures 4 and 5), decreases upon increasing the molecular weight of the polymer (Figure 6) and is around 4 times lower than C_e, the concentration at which the entanglements become effective in the unmodified polymer (Figures 4 and 5). These results suggest that C_η is rather close to the overlap concentration C^*. In fact, C_η follows a power law of M_w with an exponent of -0.80 ± 0.05, which is very close to that found for unmodified polymers.[42,51]

(ii) $C_\eta < C < C_T$. This regime is characterized by a fast viscosity increase, whose rate is enhanced upon increasing [N_H] and [*H*] (Figures 4 and 5). It can be speculated that at the overlap concentration C_η intermolecular links form. These hydrophobic associations

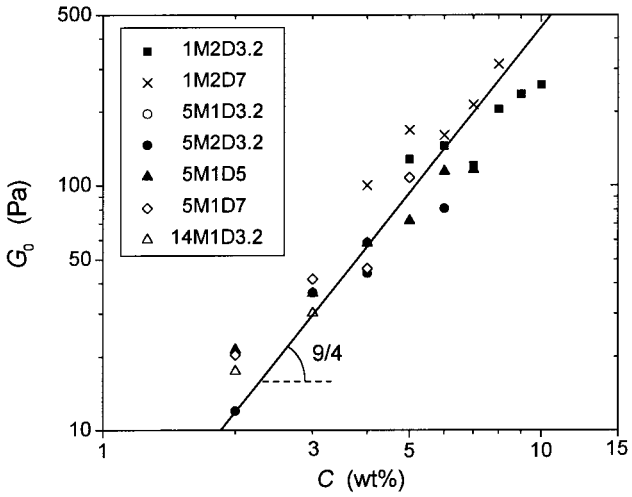

Figure 8. Plateau modulus as a function of concentration for a series of samples with variable molecular weights, hydrophobe contents, and block lengths.

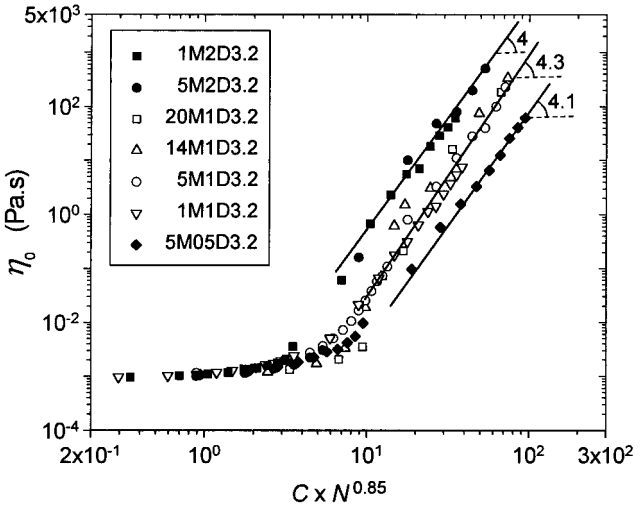

Figure 9. A log−log plot of the zero-shear viscosity versus the reduced variable $CN^{0.85} \cong C/C_\eta$ for a series of samples with variable molecular weights and hydrophobe contents but the same hydrophobic block length (C is expressed in g/g).

must be the main cause of the viscosity rise, according to a mechanism similar to that observed with telechelic associating polymers. This mechanism involves the disengagement of an associating sequence from a cross-link followed by Rouse relaxation.[9−12] In the telechelic systems, the linear viscoelastic behavior is Maxwellian.[11,12,14] In fact, we have noted that the $G'(\omega)$ and $G''(\omega)$ curves obtained for systems with $C < C_T$ fit rather well the Maxwell model in the low-frequency range. Thus, in the regime $C_\eta < C < C_T$, the viscoelasticity is likely controlled by the effect of intermolecular hydrophobic associations, and it can be considered as the equivalent of the semidilute unentangled regime observed in unmodified polymers. In this respect, it is striking that C_T coincides more or less with the C_e value of the corresponding unmodified polymer (Figures 4 and 5). However, the HMPAM exhibit a rate of viscosity increase depending on the values of N_H and $[H]$ that, contrary to the unmodified polymer, can be even faster than in the regime at higher concentration, where the chains are entangled ($C > C_T$). In this respect, it should be noted that, for multisticker chains such as these studied here, 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.[17] This slowing down of the reptation can explain why the rate of viscosity increase with concentration becomes very large upon increasing $[H]$, that is, the number of stickers per chain. This effect is also enhanced upon increasing the sticker size (i.e., the hydrophobic block length $\cong N_H$) which presumably controls the lifetime of an association. The viscosity increase rate is the same for the systems with $[H] = 1$ mol % and $N_H = 3.2$ in the whole concentration range investigated beyond C_η, and the break at the concentration C_T is undetectable experimentally (Figures 4−6). This has no physical meaning and is purely fortuitous since upon decreasing further $[H]$ or N_H, one progressively recovers the behavior characteristic of the unmodified polymers with still an enhanced viscosity, as shown in Figures 4 and 5.

(iii) $C > C_T$. In this regime, the viscosity follows a scaling behavior of the polymer concentration with an exponent close to 4, whatever $[H]$ or N_H (Figures 4−6). Furthermore, the viscosity results obtained for samples with $N_H = 3.2$ and variable $[H]$ (0.5, 1, and 2 mol %) are found to obey a scaling behavior of the polymerization degree. This is shown in Figure 9 where the effect of molecular weight is taken into account through a scaling behavior CN^x with $x \approx 0.85$ for the various series. This scaling behavior is quite close to that found for unmodified polymers in the entangled regime.[18,39,46,52] 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.[17] which considers a concentrated solution of monodisperse chain of N monomers with S stickers attached to each chain. These stickers, which are at fixed positions, can associate to form reversible cross-links. A given sticker either can be free or is associated, forming a cross-link with other stickers. Two parameters are introduced: the average fraction, p, of stickers engaged in an association and the average lifetime τ of a sticker in the cross-link. Furthermore, it is assumed that a free sticker can find many sites to attach to, besides the one it was just recently associated with.

The linear viscoelastic response of such systems was calculated under the assumption 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.

The most striking feature of the rheological behavior predicted in this model is the existence of a two relaxation process. The higher frequency process has a characteristic time equal to τ and is independent of the molecular parameters (N and S). On the other hand, the low-frequency process is characterized by a time T_d which depends strongly on the chain length, the density of stickers, and τ, according to

$$T_d \cong \left(\frac{N}{N_e}\right)^{3/2} \frac{2S^2\tau}{1 - 9/p + 12/p^2} \qquad (4)$$

The above expression can be rewritten by taking into account the scaling of N_e with polymer concentration,

i.e., $N_e \propto C^{-5/4}$ in good solvent[42,51] and assuming, as in the original model, that p is independent of concentration:

$$T_d \cong C^{15/8} N^{3/2} S^2 \tau (1 - 9/p + 12/p^2)^{-1} \quad (5)$$

or in terms of the molar ratio $[S]$ of stickers with respect to the total number of monomers:

$$T_d \cong C^{15/8} N^{7/2} [S]^2 \tau (1 - 9/p + 12/p^2)^{-1} \quad (6)$$

The shear modulus is expected to exhibit two plateau values. At high frequencies, $1/\tau_e > \omega > 1/\tau$, where τ_e is the Rouse time of the entanglement strand, the plateau modulus is given by

$$G_1 \cong CRT\left(\frac{p}{N_s} + \frac{1}{N_e}\right) \quad (7)$$

On the time scale τ where the stickers open, the stress held by the stickers relaxes, and the modulus drops to the level of the identical linear chain system without stickers:

$$G_2 \cong CRT\left(\frac{1}{N_e}\right) \quad (8)$$

This second plateau ends up at the circular frequency of the order of the reciprocal terminal time T_d.

Using the good solvent relation, $N_e \propto C^{-5/4}$, leads to the same scaling behavior as for unmodified polymers:[42,51]

$$G_2 \propto C^{9/4} \quad (9)$$

Finally, the zero-shear viscosity can be approximated by

$$\eta_0 \equiv G_2 T_d \cong C^{33/8} N^{7/2} [S]^2 \tau (1 - 9/p + 12/p^2)^{-1} \quad (10)$$

Looking at eqs 6, 9, and 10, we can note that the predicted scaling behaviors with concentration and polymerization degree are not too different from those corresponding to unmodified polymers. Thus, the zero-shear viscosity scales as $C^{33/8}\, N^{7/2}$ whereas the scaling generally reported for unmodified polymers is $\propto C^4 N^3$.[42,45] The small difference in the exponents for the concentration dependence of η_0 is due to the fact that the Leibler's model is based on the tube model with fluctuations, whereas the prediction for unmodified polymers given above corresponds to the bare reptation model used by de Gennes.[53] The scaling behavior of the plateau modulus is exactly the same for both modified and unmodified polymers. The enhancement of the viscosity and the slowing down of the terminal time come mainly from the parameter τ, lifetime of a cross-link, in the theoretical expression given for modified polymers.

Now, looking back at the experimental data, one finds striking analogies between the theoretical predictions and the results, despite the fact that two well-separated relaxation processes cannot be observed. First, one should note that the relaxation process associated with the sticker disengagment is expected to be out of the frequency range experimentally accessible. A rough estimate of the ratio T_d/τ can be calculated from eq 4 assuming $p \gtrsim 0.6$. Referring back to the example of Figure 1 which corresponds to measurements performed on sample 1M2D7 at $C \approx C_T \approx C_e$ (5 wt %), $S = 3.2$, $T_d \cong T_R = 0.285$ s, and taking $(N_e/N) \approx 10$,[43,44] one obtains $T_d/\tau \gtrsim 30$, confirming that τ is too small ($\lesssim 10^{-2}$ s) to be detected experimentally ($\omega \gtrsim 100$ rad/s).[53] The shape of the stress relaxation is in most cases well described by a slow relaxation followed by a distribution of modes (see Figure 1). It is not surprising to find such a distribution since in addition to possible imperfections due to the chemistry, for instance chain polydispersity and fluctuations in the number of stickers per chain, other mechanisms inherent to the reptation process, such as fluctuations in tube length or constraint release, broaden the spectrum of relaxation times.[17] Furthermore, we have no indication of the nature of the associations and more specifically on the number of hydrophobic blocks engaged in a cross-link. More convincing is the comparison between the model and the experimental data regarding the effects of the molecular parameters N_H, $[H]$, and N on T_R, G_0, and particularly η_0, which is measured with much better accuracy.

As a matter of fact, the results reported in Figure 9 for a series of HMPAM with $N_H = 3.2$ and $[H]$ variable show that η_0 scales with a good accuracy like $C^x N^y$ with $4 \lesssim x \lesssim 4.3$ and $3.4 \lesssim y \lesssim 3.65$. This is very close to the theoretical expression given in eq 10. This means that if we consider a series of HMPAM with a given $[H]$ in which the number of stickers per chain is varied by changing the molecular weight (in other words, by keeping constant the spacing between two consecutive stickers), the experimental results are well described by the theory in the regime $C > C_T$ where the reptation process holds. However, the comparison fails if the number of stickers per chain is varied by changing $[H]$, that is, the spacing between stickers. In that case, the zero-shear viscosity η_0 is predicted to vary like $N^{3/2}S^2 \equiv N^{7/2}[S]^2 \propto [H]^2$ (the parameter $[S] = S/N$ is directly related to $[H]$ for a given N_H, see eq 2). Actually, the results given in the inset of Figure 5 show that the viscosity varies with a good accuracy like $[H]^3$. In the theory, it is assumed that the system contains only binary stickers and that the lifetime of the cross-link τ and the fraction p of stickers are uncorrelated to the other parameters. This seems to be true as far as the spacing between two consecutive stickers is kept constant. This assumption might not hold when varying the spacing.

Finally, the increase in η_0 observed with N_H is likely associated with the lifetime τ of the cross-links. The rate of disengagement of a hydrophobic sequence from a cluster (possibly binary) is an exponential function of the activation energy for disengagement[11,54] and therefore can be very sensitive to the length of the hydrophobic blocks.

The results of dynamic viscoelasticity are also consistent with those of the zero-shear viscosity. For $C > C_T$, it was found (see Figure 8) that G_0 depends only on polymer concentration within the experimental accuracy, which suggests that the elasticity is dominated by entanglements. This behavior is consistent with the theoretical prediction $G_0 \propto C^{9/4}$. Therefore, the terminal time T_R should follow the same variation with N and $[H]$ as the zero-shear viscosity. This is shown in Figure 10, which represents the log−log variation of the quantity $T_R/[H]^3 N^{3.5}$ as a function of concentration. The results are compatible with the theoretical $C^{15/8}$ prediction (see eq 6).

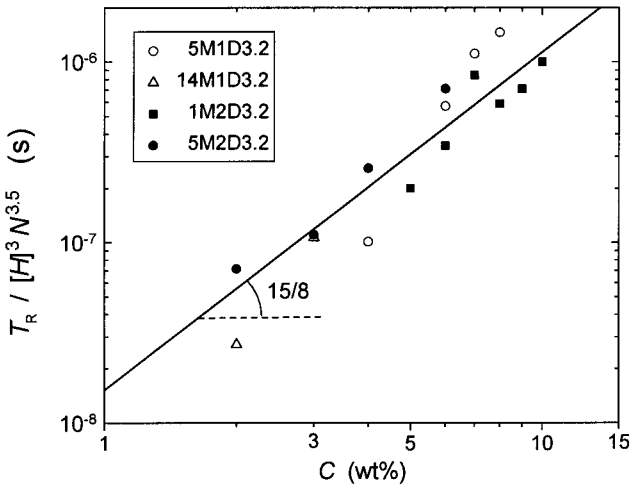

Figure 10. Variation of the quantity $T_R/[H]^3N^{3.5}$ as a function of concentration for a series of samples with variable molecular weights and hydrophobe contents but the same hydrophobic block length ($N_H = 3.2$). ([H] is expressed in molar fraction.)

Up to now, we have discussed the linear viscoelasticity results. The nonlinear behavior is more complex. The shear thickening behavior of our samples is similar to that observed for many associating polymeric systems.[14,15,19,55−58] However, the reasons for this effect are still controversial,[13,59−63] and the mechanism involved could be different depending upon the nature of the associating system (short telechelic polymers or polymers with multiple stickers).[8] In the case of multisticker polymer chains, the shear thickening effect is generally attributed to a shear-induced change in the balance between intramolecular and intermolecular associations. At relatively low polymer concentrations, many of the associations are intramolecular, and therefore only a small fraction of intermolecular associations contributes to the viscosity at low shear rates. Under increasing shear flow, the macromolecular chains are stretched, leading to a higher probability of intermolecular associations and thus to an increase in viscosity. Obviously, such a mechanism can be operative in the concentration regime where both intra- and intermolecular associations are present, that is, just beyond C_η. This is indeed what is observed experimentally (see Figures 2 and 3). However, even at higher concentrations where only the classical shear thinning is observed, there is some effect of the shear flow on the intermolecular associations since the Cox−Merz rule fails. This coupling likely modifies the lifetime of association. In this respect, experiments using the superposition of oscillations to a steady-state shear flow should provide useful information.[15,58,64]

Conclusion

The results reported in this paper bring some new insight into the association mechanism of multisticker polymer chains. The systems investigated here are hydrophobically modified polyacrylamides (HMPAM) in which the number and length of the hydrophobic blocks can be adjusted in a controlled manner. Three characteristic parameters were varied in order to tune the viscoelastic behavior of HMPAM: the molecular weight ($42\,000 \le M_w \le 2.7 \times 10^6$), the hydrophobe content ([H] = 0.5−2 mol %), and the length of the hydrophobic units in the sticker ($1 \le N_H \le 7$). The main conclusion that can be drawn from the measurements of the linear

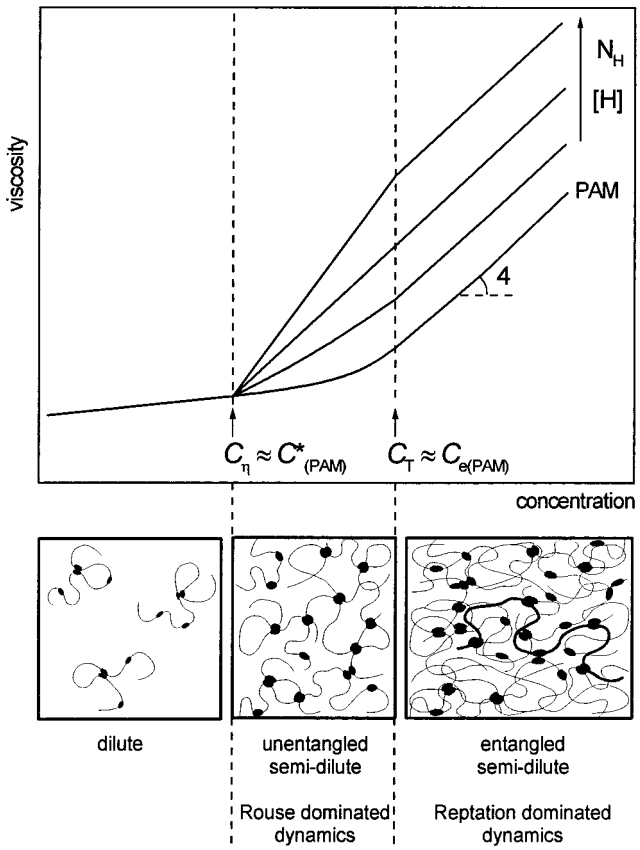

Figure 11. Schematic diagram of the various concentration regimes for multisticker associating polymers.

viscoelasticity of HMPAM is the existence of three distinct regimes, as in the case of unmodified polymers. The schematic diagram of Figure 11 illustrates these different regimes:

(i) A dilute regime, $C < C_\eta$, 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.

(ii) A semidilute unentangled regime, $C_\eta < C < C_T$. The break between the first and second regimes is rather sharp with C_η depending on the molar mass but independent of N_H and/or [H]. Note that C_η lies in the vicinity of the overlap concentration of the unmodified polymer analogues C^*. At C_η, one observes for a given molar mass a set of diverging straight lines whose slopes increase with N_H and/or [H]. This regime is dominated by intermolecular hydrophobic associations, and the chains are likely to obey Rouse dynamics. However, one cannot discard the possibility that in this regime p varies from 0 to a finite value <1 as C increase from C_η to C_T

(iii) A semidilute entangled regime, $C > C_T$. The break C_T occurs at a concentration close to the critical concentration C_e where the unmodified polymer chains are entangled. The asymptotic behavior is described by parallel straight lines with an exponent of about 4 in the log−log variations of $\eta_0 = f(C)$ whatever N_H or [H]. Here the hydrophobic associations might be fully intermolecular, but the number of entanglements increases strongly with C.

Linear viscoelastic measurements show that the relaxation mechanism can be described by a slow process more or less separated from faster modes. In the entangled regime, the plateau modulus associated

with the slow process only depends on the polymer concentration within the experimental accuracy. On the other hand, the terminal time rises drastically with either N_H, [H], or N. The results obtained, in particular those related to the zero-shear viscosity, which is the parameter determined with the best accuracy, are consistent with the theoretical predictions of the sticky reptation model of Leibler et al.,[17] as far as the spacing between two consecutive stickers is kept constant. However, a stronger dependence of η_0 with [H] is found which might reflect changes in the aggregation number of the associating clusters as [H] increases. The huge increase of η_0 and T_R with N_H is likely correlated to an increase of the lifetime of a cross-link.

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