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Hydrophobically Modified Dimethylacrylamide Synthesis and Rheological Behavior

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ABSTRACT: The synthesis and rheological behavior of hydrophobically modified copolymers based upon *N,N′*-dimethylacrylamide (DMAM) containing dodecyl or octadecyl groups are described. The polymers were synthesized by free radical copolymerization in homogeneous solutions of toluene. This synthesis method ensured that the hydrophobic groups were incorporated individually into the copolymer, i.e., in a nonblocky fashion. This method contrasts with the more commonly produced hydrophobically modified polyacrylamides, synthesized by a micellar polymerization technique, resulting in multiblock structures. Associative behavior of the DMAM copolymers in water was investigated by viscosity measurements. Significant enhancement in viscosity was measured in the semidilute unentangled and entangled regimes. Viscosity enhancement was attributed to the formation of intermolecular hydrophobic aggregates, which act as transitory physical cross-links. While it is well established in the literature that blocky copolymers containing hydrophobic groups can significantly enhance solution viscosity, the same effect produced by hydrophobically modified acrylamide polymers based on randomly copolymerized hydrophobic and hydrophilic monomers is less well-known or understood. The results presented in this paper demonstrate that if long alkyl chains are used as stickers, then hydrophobic aggregation between neighboring chains can promote viscoelastic properties in the semidilute regime. The rheological behavior of these statistical copolymers can be described on the basis of recent theoretical models specially developed for solutions of associating polymers.

Introduction

Hydrophobically modified water-soluble polymers have attracted increasing interest because they exhibit unique rheological properties in aqueous media.[1−4] These polymers consist primarily of a hydrophilic macromolecular backbone with a few percent of hydrophobic groups incorporated within the structure. Hydrophobically modified polymers are usually formed by copolymerization, nonionic copolymerizations generally being based on acrylamide.[5−37]

The majority of hydrophobically modified acrylamides are produced by micellar copolymerization, as reviewed by Candau et al.[5] Micellar copolymerization, first described by Evani and Turner,[6−9] requires the hydrophobic monomer to be solubilized in micelles formed in an aqueous surfactant solution.[5,10−36] Hydrophobic groups could be aliphatic,[10−19] fluorinated,[20−23] or aromatic[24−37] in nature. As polymerization proceeds, hydrophobic monomers are incorporated in the copolymer structure as a series of blocks along the hydrophilic backbone because of the high concentration of hydrophobic units in the micelles. This structure was first proposed by Peer[38] and subsequently demonstrated by the use of fluorescent probes such as pyrene.[18,24,27,28,30,36,37]

Hydrophobically modified water-soluble polymers are of interest because of their useful rheological properties in aqueous solution. The incorporation hydrophobic groups in the hydrophilic network causes the hydrophobes to cluster together into aggregates acting as transitory physical cross-links. In some cases the physical interactions are so strong that physical gels are formed at solution concentrations lower than 2−3 wt %.[14,29]

Macroscopic evidence of interchain aggregation of the hydrophobic groups can be observed by rheology measurements. Above a threshold concentration (C_g), the viscosity of aqueous solutions of hydrophobically modified polymers increases and polymer diffusion slows. The viscosity increases significantly with concentration because the transfer of hydrophobic moieties from intra- to intermolecular associations starts to dominate the rheological behavior. Hydrophobic groups from several polymer chains associate to form aggregates which act as cross-links in a reversible physical network. However, when these solutions are subject to shear, the aggregates, which are stabilized by relatively weak hydrophobic interactions, break down, resulting in a reduction of viscosity (shear thinning). The aggregates easily re-form after shearing, and the solution recovers the initial value of low shear viscosity.[1−5,10−15,17−25,27−29,32−37,39] Careful interpretation of the results is required since rheological properties can be affected by hydrophobe type and content, molecular weight, amount of charge on polymer chain, temperature, salinity of solution, and presence of surfactants.[40]

We report here the synthesis and rheological behavior of hydrophobically modified copolymers based upon *N,N′*-dimethylacrylamide (DMAM) containing dodecyl or octadecyl groups. While hydrophobically modified acrylamides have been widely reported due to the use of the micellar technique, we present an alternative approach whereby DMAM can be copolymerized in a homogeneous reaction medium. Unlike polyacrylamide, poly(DMAM) is soluble in water as well as various organic solvents because it is less polar than PAM.

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Owing to this diverse solubility, DMAM can be co polymerized with hydrophobic monomers in a homogeneous organic medium.

The synthesis and characterization of hydrophobically modified DMAM copolymers have been reported previously; Xie and Hogen-Esch[41] describe synthesis and rheological properties of PDMAM derivatives containing up to 1.5 mol % perfluorinated alkyl side groups, produced by emulsion or bulk polymerization. While the bulk polymers demonstrate that associating polymers can be formed without the use of surfactants, it was found that the emulsion polymers exhibit much stronger associating behavior in aqueous solutions. This was attributed to higher molecular weights, increased blockiness of emulsion polymers, and possible micellar bridging caused by reminant surfactant from the synthesis. Da and Hogen-Esch[42,43] have demonstrated strong association of hydrophobically modified copolymers of PDMAM and perfluorocarbons using poly(ethylene glycol) (PEG) chains to tether the perfluorocarbons to the PDMAM backbone. These copolymers exhibit extremely strong interpolymer association even well below the critical aggregation concentration not only in water but also in many organic solvents, including dioxane. In dioxane the strong associations are due to fluorphilic and hydrophobic interactions and are enhanced by the solution incompatibility of PDMAM and PEG in dioxane, minimizing the mixing of these two polymers and encouraging increased fluorocarbon concentrations in the PEG domains. Uemura et al.[44] synthesized copolymers of DMAM and *N*-(1-(1-pyrene)octadecylacrylamide) but did not study the rheological properties. Of most relevance is a recent study of hydrophobically modified PDMAM reported by Guillaumont et al.[45] The copolymers were synthesized by homogeneous solution polymerization in methanol using hydrophobic comonomers *N*-dodecylmethacrylamide and *N*-octadecylacrylamide. A significant increase in viscosity was observed for aqueous solutions of these polymers at concentrations above 2 wt %. The reaction kinetics were followed by size exclusion chromatography, and it was concluded that the polymer structure was random in nature, not blocky. The increasing viscosity was found to be very similar to that observed by previous workers using micellar polymerized acrylamide copolymers. This is an interesting point, since a prominent theory in the present literature argues that the viscosity enhancement in micellar co polymerized polymers is due not only to the formation of hydrophobic aggregates but also to the fact that these hydrophobic moieties are present in a blocky structure, thereby facilitating the formation of aggregates.[14,24,27,29,46] Indeed, the rheologies of equivalent copolymers prepared from the same proportion of hydrophilic and hydrophobic constituents by micellar and random copolymerization have been directly compared by Ezzel et al.[27,46] and Hill et al.;[24,29] these studies conclude that there was minimal enhanced viscosity in solutions of the random copolymer, due to its nonblocky structure, compared with a large increase in viscosity for micellar copolymer. It should be pointed out that accurate comparison of blocky and statistically random copolymers is difficult because the molecular weights must be very similar, owing to the great dependence of viscosity on MW, and traces of surfactant in the micellar copolymers are very difficult to remove completely, allowing micellar bridging between hydrophobic side chains again increasing viscosity.[41] Even though it is clear that blocky polymers do associate more strongly than random copolymers, this does not necessarily preclude the use of randomly copolymerized hydrophobically modified copolymers if long alkyl chains are used as the hydrophobic moieties.[45] In this case, aggregation in random copolymers is possible due to greater reach and flexibility of the hydrophobic groups. It should be noted that random hydrophobically modified water-soluble copolymers can also be formed by micellar polymerization simply by varying the hydrophobic monomer-to-surfactant ratio.[36] In the present case, however, no surfactant is required due to the solubility of both monomers in the reaction medium. Owing to the simplicity of the polymerization method and the purity of the product (no trapped surfactants), it would appear that consideration of the rheological behavior of these materials, taking into account variables such as molecular weight and mole fraction of alkyl chains over a wide range of polymer concentration in aqueous media, is warranted. Furthermore, a recent study has shown that the mechanical properties of cross-linked structures can be altered by the incorporation of associating groups.[47] Therefore, the present study aims to define a synthesis procedure that can be applied to a wide range of primary structures (both linear copolymers and 3D networks) and to characterize the associating behavior of statistical copolymers. In an attempt to further understand their viscoelastic properties, recent theories developed for solutions of pairwise associating polymers[48,49] will be applied to our copolymers.

Table 1. Copolymer Samples, Synthesis, and Characterization[a]

sample	$f_B = [B]_0/([A]_0 + [B]_0)$	$[A]_0 + [B]_0$, mol/L	$[AIBN]_0$, mol/L	$[A]_0/[B]_0$
1.25DA	0.0125	1	0.01	79
2.5DA	0.025	1	0.01	39
3.75DA	0.0375	1	0.01	26
5.0DA	0.05	1	0.01	19
7.5DA	0.075	1	0.01	12
10.0DA	0.1	1	0.01	9
1.25ODAM	0.0125	1	0.01	79
2.5ODAM	0.025	1	0.01	39
3.75ODAM	0.0375	1	0.01	26

[a] $[A]_0$ is the initial molar concentration of hydrophilic monomer DMAM, $[B]_0$ the initial molar concentration of hydrophobic monomer, and f_B the initial molar feed ratio of hydrophobic monomer. Polymer conversion calculated on a weight by weight comparison with the initial monomer amount was found to be around 90% in all cases.

Experimental Section

Monomers. *N,N*-Dimethylacrylamide (Aldrich), dodecyl acrylate (Polysciences), and octadecylacrylamide (Polysciences) were used as received.

Copolymer Synthesis. Copolymerizations were carried out by a free radical mechanism in toluene in a round-bottomed flask fitted with a condenser and nitrogen gas inlet. Various comonomer ratios were added to toluene in the correct quantity to make 50 mL of 1.0 M solutions (total monomer concentration) (Table 1). The solution was purged for 1 h before raising the nitrogen gas inlet above solution for the duration of the reaction.

During the purge the solution temperature was raised to the reaction temperature, 55−65 °C. After raising the gas purge, 1×10^{-2} mol/L of initiator, 2,2′-azobis(isobutyronitrile) (AIBN), was added, and the solution was left at temperature for 20 h. After the reaction, the solution was allowed to cool to room temperature before the copolymers were precipitated in diethyl ether and dried in a vacuum for several hours at 30 °C.

Characterization of the Copolymers. The polymer samples were characterized by gel permeation chromatography (GPC) in THF at 25 °C using a multidetection system and universal calibration curves. Solutions of approximately 0.1 wt % polymer in THF were prepared several hours before the GPC runs in order to ensure that complete dissolution occurs before measurement.

Proton NMR spectra were recorded for copolymer samples synthesized with various amounts of DA. Spectra were recorded on a Bruker ARX 250 spectrometer operating at 62.9 MHz. Samples were prepared in deuterated methanol at a concentration of 5 wt % and left for at least 24 h before measurement.

Rheological Study. The presence of hydrophobic interactions in the copolymers could be assessed by comparative rheology measurements in both water and a good organic solvent, DMF. A range of rheological measurements were made, as outlined below.

1. Viscosity as a Function of Shear Rate. The prepared copolymers were dissolved in water or DMF in a range of concentrations from 0.1 wt % through to 16 wt %. Solutions were mixed gently for at least 24 h before viscosity measurements were made. The more viscous solutions were then left to stand for at least 24 h to allow bubbles to escape before measurements. The viscosity of each polymer solution in water and DMF was measured as a function of shear rate. Two rheometers were required in order to cover the range of rheological behavior observed. For low-viscosity samples a "Low Shear 30" rheometer (Contraves) was used. This instrument utilizes a Couette cell with coaxial geometry. For more viscous samples, measurements were performed on a controlled strain rheometer, Rheometric RFSII (Rheometrics), equipped with cone–plate geometry. The diameter of the cone–plate was 25 or 50 mm as required. All measurements were conducted at 25 °C, and samples were covered to prevent evaporation during the tests. Analysis of results required that the measurements be normalized with respect to the solvent used; hence, the results shown are in terms of specific viscosity which is defined as

$$\eta_{\mathrm{sp}} = (\eta_{\mathrm{solution}}/\eta_{\mathrm{solvent}}) - 1 \tag{1}$$

2. Viscosity as a Function of Concentration. The viscosity as a function of shear rate was initially measured in all cases. These results were extrapolated to zero shear rate in order to determine the zero shear rate viscosity, which was plotted as a function of polymer concentration to compare the viscosity profile of each polymer over a wide range of concentrations.

3. Complex Modulus Measurement. For the more viscous samples, viscoelastic properties were also investigated by oscillatory measurements on the controlled strain Rheometric RFSII rheometer. First, a strain sweep test was conducted at a frequency of 1 Hz, and the storage (G') and loss modulii (G'') were measured as a function of strain to determine the linear viscoelastic regime. This measurement was stopped before the beginning of the nonlinear regime, and then the modulii were measured in the linear viscoelastic regime at a constant strain ($\gamma = 10\%$) under an oscillating frequency of 0.1–100 rad/s.

Results and Discussion

The proton NMR spectra of copolymers produced from DMAM and DA at various mole percent of DA are compared in Figure 1. Integration of peak areas corresponding to the methylene groups of the backbone and the terminal methyl group of the DA alkyl side chain gives the proportion of each monomer in the copolymer. From Figure 2, it can be seen that the DA monomer reacts effectively with DMAM, resulting in a slightly lower percentage of DA in the copolymer than in the original monomer feed ratio.

Although the reactivity ratios of DMAM and DA or ODAM to our knowledge have not been reported, we can use the $Q-e$ scheme of Alfrey and Price[50] to make some qualitative comments about the copolymerization. This empirical treatment allows a rough estimation of the reactivity ratios of monomers A and B (r_A and r_B) on the basis of the following equations:

$$r_{\mathrm{A}} = (Q_{\mathrm{A}}/Q_{\mathrm{B}}) \exp(-e_{\mathrm{A}}(e_{\mathrm{A}} - e_{\mathrm{B}})) \tag{2}$$

$$r_{\mathrm{B}} = (Q_{\mathrm{B}}/Q_{\mathrm{A}}) \exp(-e_{\mathrm{B}}(e_{\mathrm{B}} - e_{\mathrm{A}})) \tag{3}$$

where Q_x and e_x are measures of the reactivity and polarity, respectively, of monomer i.

These parameters have been calculated for a wide range of monomers from copolymerization data obtained from various pairs of monomers. In Table 2 we report some $Q-e$ values of acrylic monomers and compare the reactivity ratios calculated from eqs 2 and 3 using DMAM as monomer A.

Starting with the acrylate series, one can see that Q values are not very different and close to the Q of DMAM. In that case, the reactivity ratios (see eqs 2 and 3) are mainly controlled by the difference between the polarity parameters (e). By increasing the length of the alkyl group, e_B increases, r_B decreases, and r_A increases, corresponding to a lower reactivity of the acrylate toward itself and also toward DMAM. This reflects the fact that as the side chain length increases there would be an increase in steric hindrance, slowing the approach of the monomer to the active end of a growing chain, irrespective of the character of the chain end. For the monomer in question, dodecyl acrylate, the value of r_B would be expected (from the trend shown for the acrylate series) to be well below unity; hence, the probability of a dodecyl acrylate monomer reacting with another dodecyl acrylate is low, and there would not be expected to be large blocks of these units present in the copolymer structure. The same holds for the system DMAM/ODAM where again a large difference in polarity is responsible for an even smaller value of r_B. From this qualitative discussion we can assume that the copolymerization between DMAM and alkyl acrylate (or acrylamide) results in hydrophobically modified polymers with a statistical distribution of comonomers corresponding to individual incorporation of hydrophobic units into the polymer chain. The instantaneous mean average length sequence of the hydrophobic comonomer B ($\overline{I_{\mathrm{B}}}$), is given by the following equation:

$$\overline{I_{\mathrm{B}}} = 1 + (r_{\mathrm{B}}/x) \quad (\text{with } x = [\mathrm{A}]/[\mathrm{B}]) \tag{4}$$

and remains very close to 1 during most of the conversion extent (using a feed molar ratio $f_B < 0.1$). Applying eq 4, a higher $\overline{I_B}$ value ($\overline{I_B} > 2$, for example) can be expected only for $x < r_B$, i.e., only during the very last step of the conversion (>95%) (Table 1).

Guillaumont et al.[45] have studied the reaction kinetics of DMAM and ODAM by size exclusion chromatography (SEC). By comparing the peak areas of the corresponding monomers and polymer during the course of the reaction, it was shown that the consumption rate of DMAM was higher than that of ODAM. On the other hand, they found similar consumption rates between DMAM and dodecylmethacrylamide (DDMAM) in agreement with the higher reactivity of methacrylate and methacrylamide compared with acrylate and acrylamide.

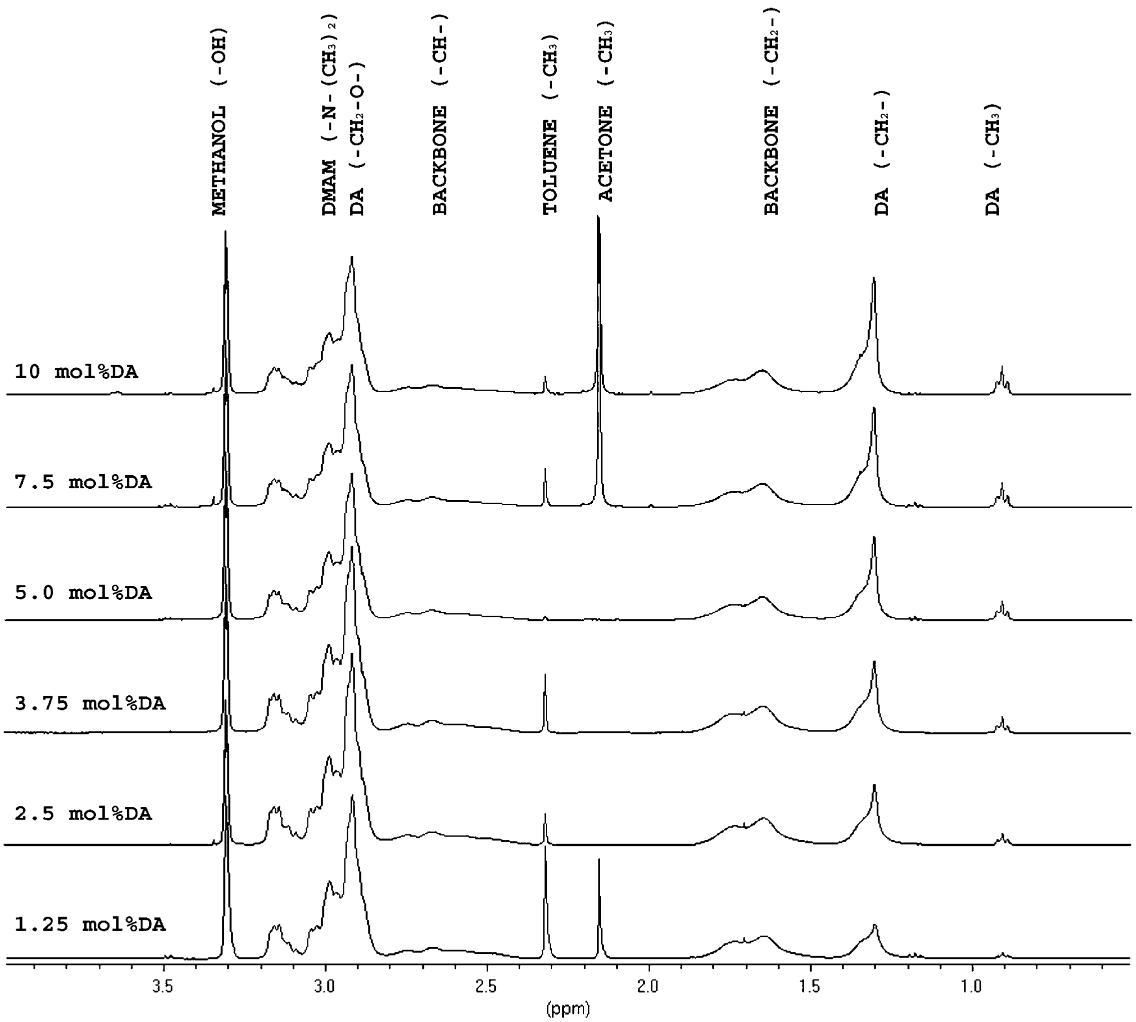

Figure 1. Proton NMR spectra of poly(DMAM-*co*-DA) polymers with various mole percent of dodecyl acrylate (DA).

Figure 2. Molar percentage of DA in copolymers (from analysis of proton NMR results) as a function of initial molar percentage of DA in monomer feed.

Table 2. Reactivity Ratios Calculated from the *Q*−*e* Scheme[a]

monomer	Q	e	r_A	r_B
acrylamide, *N*,*N*-dimethyl (A)	0.41	−0.26		
acrylamide, *N*-octadecyl (B)	0.66	1.64	0.38	0.07
acrylate, methyl (B)	0.45	0.64	0.72	0.61
acrylate, butyl (B)	0.38	0.85	0.81	0.36
acrylate, octadecyl (B)	0.33	1.26	0.84	0.12

[a] Data obtained from *Polymer Handbook*.[51]

Table 3. Macromolecular Characterization of Copolymers by GPC

sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n	$[\eta]_{exp}$,[a] mL/g
1.25DA	28 000	102 000	3.6	29.5
2.5DA	22 000	78 000	3.6	32.1
3.75DA	25 000	96 000	4.0	31.5
5.0DA	48 000	97 000	2.0	34.4
7.5DA	42 000	106 000	2.5	42.1
10.0DA	46 000	117 000	2.6	45.1
1.25ODAM	19 000	90 000	4.7	29.2
2.5ODAM	17 000	82 000	5.0	35.1

[a] $[\eta]$ in THF at $T = 25$ °C.

As expected with similar structures, the solubility of the copolymers in water decreases with the increasing hydrophobicity of the samples. The DA containing samples were soluble with up to 3.75 mol % of hydrophobic monomer while only the ODAM samples containing 1.25 or 2.5 mol % hydrophobic monomer were soluble, reflecting the more hydrophobic character of the side chains in the ODAM samples.

The number-average M_n and weight-average M_w molecular weights as well as the polydispersity index (M_w/M_n) and intrinsic viscosity for copolymers of DMAM−DA and DMAM−ODAM as determined by GPC are shown in Table 3. It is important to note that the GPC measurements were conducted in THF, a good organic solvent for the copolymers. This ensures that there is no specific interactions in the polymers during the analysis; such interactions could introduce some error into the estimation of molecular size. The weight-average molecular weight is comparable and close to 10^5 g/mol in all cases. These values are in good agreement with the molecular weights of the copolymers DMAM/

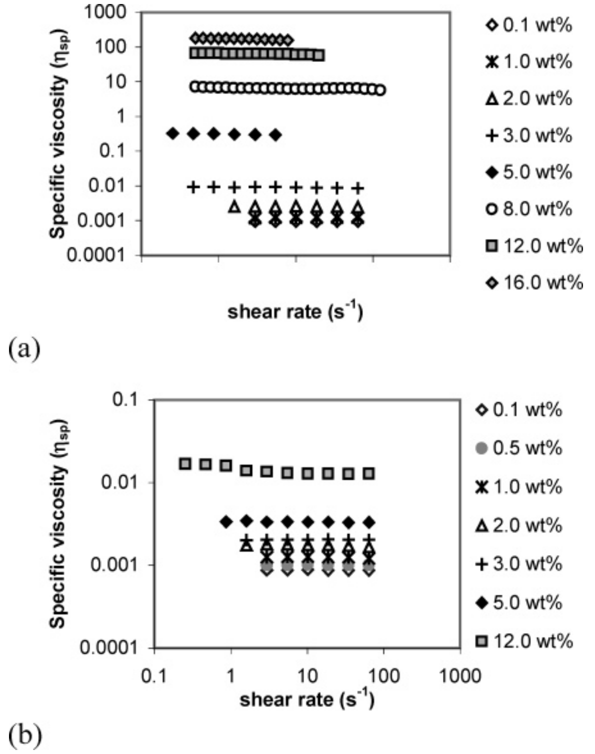

Figure 3. Specific viscosity of 3.75 mol % DA sample (a) in water and (b) in DMF at various concentrations and shear rates.

ODAM and DMAM/DDMAM prepared by Guillaumont et al.[45] in similar conditions in methanol. By comparison, the molecular weights of these statistical copolymers are less than the typical M_w reported for polyacrylamide copolymers produced by micellar copolymerization, which are commonly around 10^6 g/mol.[13,14,24,29] One of the reasons is that in similar conditions of monomer concentration, solvent, initiator, etc., the propagation rate of acrylamide is several times higher than those of acrylic monomers like DMAM.

Rheological Study. To assess the effect of hydrophobic modification on the rheological properties of copolymers, a reference material is required from which enhancement is measured. The best comparison of rheological behavior and hence example of the effects of hydrophobic attachments can be obtained if the rheology of exactly the same polymer is compared in a good organic solvent (DMF) and in water. This allows effects due to differences in molecular weight, polydispersity, comonomer ratios, or contaminants to be eliminated. This comparison would be as explicit and indeed more accurate than a comparison to an unmodified polymer.

1. Steady Shear Flow Measurements. The viscoelastic behavior of associating polymers becomes evident in the semidilute regime above the critical concentration at which intermolecular associations begin to dominate. Steady shear flow measurements can be used to identify the semidilute regime by observing the steady-state viscosity as a function of shear rate at different concentrations in aqueous solutions. Specific viscosity as a function of shear rate was measured for 1.25DA, 2.5DA, 3.75DA, and 1.25ODAM samples. Since the trend in behavior was very similar in all cases, only a typical set of results for the 3.75DA sample, measured in water and DMF, are shown in Figure 3. It is apparent that the viscosity increases with concentration of copolymer, although this effect is much more evident in aqueous solutions. The mole fraction and length of hydrophobic groups also increased the viscosity (see section 2). When the viscosities of the copolymers in DMF are compared to the viscosity of the same copolymers in water (Figure 3), it can be seen that there is little difference until the critical concentration is reached (approximately 2 wt %), above which the viscosity of the copolymers in water is markedly greater than the viscosity of the same copolymer in DMF. The increasing viscosity must therefore be attributed to the aggregation of hydrophobic moieties when the copolymer is dissolved in water.

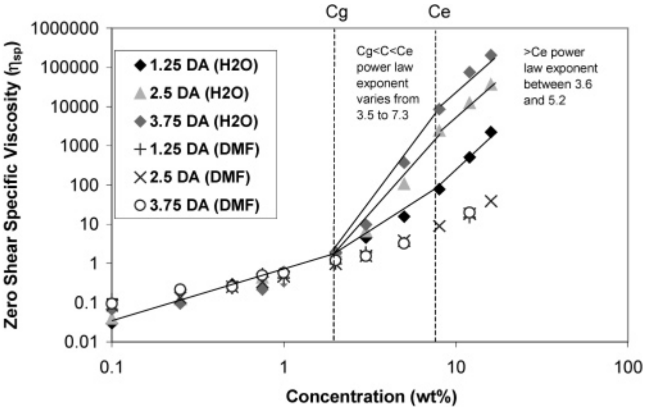

Figure 4. Specific viscosity (at zero shear rate) as a function of concentration for DA-containing polymers.

Below the critical concentration, in the dilute regime, polymer solutions would be expected to act as Newtonian fluids, with no variation in viscosity as a function of shear rate. At concentrations above the critical concentration there would be expected to be a distinct shear thinning effect.[13,14,24,29,52] The shear rate at which shear thinning becomes evident is primarily determined by the molecular weight of the polymers because orientation and disentanglement of the overlapping chains becomes faster than their ability to re-form associations when the shear rate increases.[24,52] For a copolymer containing 1 mol % of hydrophobes and a molecular weight in the order of 10^6, shear thinning has been demonstrated at shear rates between 1 and 100 s^{-1}, depending upon the blockiness[14] and concentration of copolymer in aqueous solutions.[24]

In our studies no significant shear thinning effect was observed over the shear rates examined (up to 500 s^{-1}). The molecular weights of these polymers are approximately 10^5, which is typically an order of magnitude lower than copolymers formed by micellar polymerization of acrylamide.[13,14,24,29] Lower molecular weight results in a shorter relaxation time for the macromolecules and hence the onset of shear thinning would be expected to occur at higher shear rates than in previously published work. Hence, a much wider range of shear rates would need to be studied to observe this effect more explicitly. The aim of the present study, however, was to examine zero shear viscosity as a function of solution concentration for a range of polymers containing different hydrophobic group contents, as discussed below.

2. Viscosity vs Concentration. The viscosities as a function of shear rate were extrapolated to zero shear rate and plotted as a function of polymer concentration (Figures 4 and 5). To describe the viscoelastic behavior of our solutions, we will distinguish three different regimes of concentration, and we will use the recent

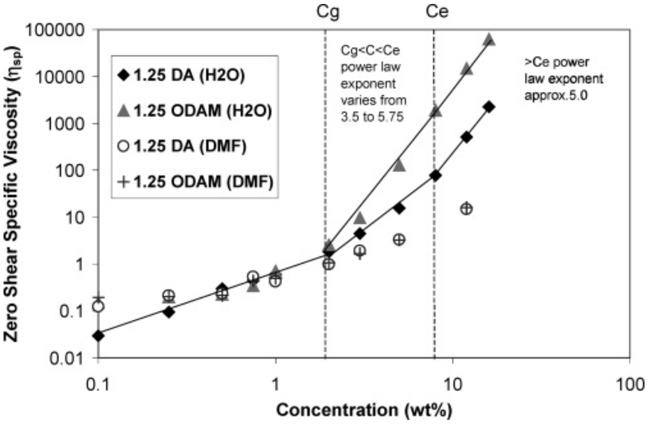

Figure 5. Specific viscosity (at zero shear rate) as a function of concentration for copolymers containing 1.25 mol % DA and 1.25 mol % ODAM, demonstrating the effect of alkyl chain length.

theory of Rubinstein and Semenov discussing the dynamic properties of pair wise associating polymers in semidilute solutions.[48]

(i) *Starting from very low concentrations, we observe a dilute regime,* $C < C_g$, where the rheological behavior is mainly controlled by intramolecular associations. It is undisputed that C_g is closely related and has a very similar value to the overlap concentration, C^*, for the equivalent unmodified polymers. (For an unmodified polymer C^* is simply determined by the molecular weight of the macromolecular chains.) In the concentration regime below C_g the associating polymer chains would act independently, forming intramolecular associations or possibly forming clusters of limited size unable to percolate the whole volume. Hence, the viscosity of the modified polymers would be expected to be either unchanged or lower than that for an unmodified polymer. In Figures 4 and 5 this is typically the case for concentrations below 2 wt %.

(ii) *A semidilute unentangled regime,* $C_g < C < C_e$. The transition from the first to the second regime is abrupt, occurring at a critical concentration $C_g \cong 2$ wt %. There are differing opinions in the literature as to whether C_g is dependent solely on the molecular weight of the chains,[11,53] i.e., $C_g \sim C^*$, or whether the hydrophobic content and block length also have an impact on its value.[14,18,19,43] It is apparent in the present study (Figures 4 and 5) that the value of C_g is very similar in all cases, regardless of the hydrophobic content or chain length in each polymer. The relationship $C^* \sim C_g \sim M_w{}^a$ is generally valid for a given system, as it takes into account the intrinsic flexibility of the macromolecular backbone and long-range interactions due to the conditions of solvation (temperature and solvent). Previously, Regalado et al.[11] have demonstrated a power law exponent ($a \sim -0.8$) for polyacrylamide. Since the solvent/temperature conditions are nearly the same between the present study and the work of Regalado, and a similar flexibility between polyacrylamide and poly(*N,N′*-dimethylacrylamide) chains would be expected, this relation has been applied in the present case. Hence, a weight-average molecular weight of 100 000 should result in a critical aggregation concentration of approximately 2 wt %. From Figures 4 and 5, it is apparent that this analysis is accurate since the upturn in viscosity appears at about 2 wt % for all the copolymers synthesized. On the other hand, C^* of the copolymer in the absence of association (in THF or DMF, for example) can be estimated from the intrinsic viscosities given in Table 3. Using $C^* \sim 1/[\eta]$ and $[\eta]$ values ranging between 30 and 40 mL/g, we get a critical overlap concentration around 2−3 wt %, which is very close to the experimental C_g. In the semidilute regime, viscosity increases significantly with concentration. Considering Figure 4, the polymers which all have very similar molar mass show an increasing slope with increasing hydrophobic content, resulting in a set of divergent straight lines. From Figure 5 it is also apparent that there is an increasing slope with increasing hydrophobic chain length in this regime. This behavior is in agreement with previous work on micellar polymerized acrylamides where the viscosity dependence on concentration increases more dramatically as the hydrophobic content increases and also as the hydrophobic block length increases.[11,13,14,18,19,39,53] The viscosity in the semidilute unentangled regime, $C_g < C < C_e$, is very sensitive to the equilibrium between intramolecular and intermolecular hydrophobic associations; as such, the chains in this region would be expected to obey sticky Rouse dynamics in a good solvent. According to Rubinstein and Semenov,[48] three different scaling relations between viscosity and concentration could be expected in this regime: (1) a first case, with concentration dependence ($\eta \sim C^{4.2}$), mainly due to the interchange from intra- to interassociation, (2) a second case of high conversion intra- to interassociation ($\eta \sim C^{5.9}$), where the lifetime of the associations has to be renormalized in order to take into account the increasing probability (with concentration) for two stickers to associate and dissociate several times together before joining other partners, and (3) a third case ($\eta \sim C^{1.1}$) corresponding to the situation where most of the pairwise associations are interchain. It should be noted that the synthesis conditions governed the amount of experimental results available to be modeled; however, when the experimental data in this regime are compared to the theoretical models discussed above, a reasonable correlation is observed and worthy of discussion. According to Figure 4, we get power law exponents of 3.5, 6.6, and 7.3 for polymer solutions of 1.25 mol % DA, 2.5 mol % DA, and 3.75 mol % DA, respectively. In the first instance, the polymer solution of 1.25 mol % DA appears to behave in good agreement with the first case of sticky Rouse dynamics in a good solvent. As the concentration of hydrophobic monomer increases, the exponent also increases to 6.6 for a solution of 2.5 mol % DA; within experimental error, this is a reasonable fit to the case of high conversion of intra- to interassociation. However, when the concentration of hydrophobic monomer is increased even further to 3.75 mol %, the power law fit was not ideal and yielded an exponent of 7.3, which does not correlate well with the models discussed above. This could be explained by the limited set of data available to model within this regime, and more work may be required to elucidate the behavior of these copolymers as the content of hydrophobes is increased. The results displayed in Figure 5 allow some insight into the influence of the length of the hydrophobic chain on the viscosity vs concentration profile. The power law exponents in the semidilute unentangled regime, $C_g < C < C_e$, were found to be 3.5 for the 1.25 mol % DA copolymer and 5.75 for the 1.25 mol % ODAM copolymer. These exponents correlate very well with the first two predicted cases of sticky Rouse dynamics in a good solvent, essentially indicating that a higher conversion of intra- to interassociation occurs as the length of the hydrophobic chains increase. Even though limited data were available to compare to the theoretical models, it is clear from this brief analysis in the unentangled regime that the dynamics are dominated by the ratio between intra- and intermolecular associations while the primary structure of the associating copolymers also plays a critical role.

(iii) *A semidilute entangled regime*, $C > C_e$. According to Rubinstein and Semenov,[48] a different behavior is expected beyond the entanglement concentration (C_e), a concentration at which entanglements become elastically effective in an unmodified polymer. From Figures 4 and 5, it is clear that this change in behavior occurs above 8 wt %, in agreement with the related literature which states that C_e is typically 5−10 times higher than C^* and more particularly with the work of Regalado et al.,[11] where a ratio $C_e/C^* \sim 4$ was reported. The chain behavior in this regime can be modeled by a sticky reptation model, which can be considered as sticky Rouse motion along the contour of a tube.[48] Essentially, this means that the elastic modulus is controlled by the entanglements between macromolecular backbones with a sticky reptation process at low frequency. In a good solvent, with renormalized bond lifetime, the power law dependence of viscosity on concentration can have two different exponents depending upon whether the polymer strands between stickers are overlapping or actually entangled. If the chains are overlapping, a power law exponent of 3.75 has been predicted between the overlap concentration of the strands between two stickers (C_{l^*}) and below the strand entanglement concentration (C_{le}). Above (C_{le}) they are entangled, and the power law exponent would theoretically increase to 4.72.[48] In good solvent, C_{l^*} can be calculated as follows:

$$C_{l^*} = C^*(N/l)^{4/5} \tag{5}$$

with C^* the overlap concentration of the polymer chain, N the number-average degree of polymerization of the polymer chain, and l the average number of monomer units between two stickers. Using the composition and the molecular weights data of Tables 1 and 3 and considering $C^* \cong C_g = 2$ wt %, one can estimate an overlap concentration of the strands (C_{l^*}) between 5 and 10 wt % for the different water-soluble copolymers. This means that working above C_e, the entanglement concentration of the polymers chains, the polymer strands are close to or above their overlapping concentration (C_{l^*}) but well below their entanglement concentration (C_{le}), since $C^*/C_{l^*} \cong C_e/C_{le}$. In the present work, above C_e, one can estimate, from Figure 4, that the lines tend to be linear with a slope between 3.6 and 5.2 and, from Figure 5, that the slopes are close to 5.0. From the theoretical predictions of Rubinstein and Semenov,[48] a slope of 3.75 would be expected for all the copolymers in this regime. It would seem, therefore, that some of the data analyzed are close to this prediction, but that there is simply not enough information to give quantitative interpretations, and comparisons between the different copolymers synthesized and further work would be required to elucidate the behavior of these copolymers above the polymer entanglement concentration.

3. Complex Modulus. To complement the results obtained in steady shear, the frequency dependence of storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ under oscillating shear were recorded for the most viscous samples. Measurements were made in the linear viscoelastic regime (determined prior to sample measurement) to ensure that the measured properties did not depend on the amplitude of the oscillating shear rate. In this manner the oscillating shear would not cause the rupture of intermolecular associations. The most interesting result was obtained for sample 3.75DA at a concentration of 16 wt % (Figure 6). At this concentration the solution is well within the semidilute entangled regime. The frequency dependence of the complex modulus was found to be similar to those reported by other groups for various types of associating polymers measured in the same regime.[11,13,14,18,54]

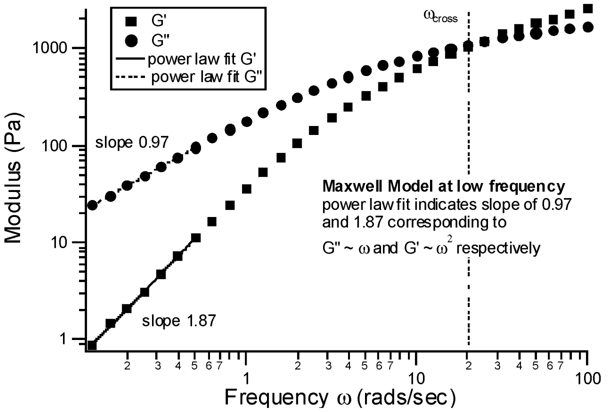

Figure 6. Shear moduli of sample 3.75DA at 16 wt % as a function of frequency of oscillating shear.

It can be seen (Figure 6) that the storage and loss modulii both increase with increasing oscillation frequency. However, the storage modulus G' is increasing at a faster rate than the loss modulus G''. At a particular frequency, denoted ω_{cross}, the storage modulus actually becomes the more dominant of the two. At high frequencies above ω_{cross} the sample acts as a weak viscoelastic gel.

The magnitude of the complex modulus is proportional to the density of mechanically active chains in the network. The network associations act as physical cross-links in hydrophobically modified polymers. Hence, these cross-links have a finite lifetime because the associations act transiently. That is they are in a constant state of disruption and re-formation. Therefore, by monitoring the modulus as a function of increasing oscillating shear frequency, there comes a point where the lifetime of these associations is longer than the time frame in which shear is imposed. Hence, the effect of the hydrophobic interactions becomes more significant at a higher oscillating shear frequency, imparting more elasticity to the system and increasing the storage modulus above that of the loss modulus. The transient network theory predicts that the terminal relaxation time is directly related to the lifetime of these transient cross-links and, hence, inversely related to ω_{cross}.[11,18,54] The relaxation behavior (as indicated by ω_{cross} in Figure 6) is comparable to those reported by other groups for various types of associating polymers.[11,13,14,18,54]

The crossover frequencies observed for a range of copolymer samples are listed in Table 4. The presence of hydrophobic aggregation slows down the dynamics of a polymer system compared to unmodified polymers, as described by Leibler et al.[49] In the case of entangled solutions of associating polymers with unentangled strands between interchain bonds, Rubinstein and

Table 4. Measured Crossover Frequency (ω_{cross}) for a Range of Copolymer Samples with Various Hydrophobicities and Concentrations

hydrophobe content (mol %)	3.75DA	3.75DA	2.5DA	1.25DA	1.25ODAM
total polymer concn (wt %)	12	16	16	16	16
ω_{cross} (rad/s)	40	20	>100	$\gg 100$	50

Semenov[48] predict the following reptation time (τ_{rep}) for a chain in good solvent:

$$\tau_{\mathrm{rep}} \approx \tau_{\mathrm{b}} \mathrm{e}^{\epsilon/2} (f^3/N_{\mathrm{e0}}) \phi^{1.4} \tag{6}$$

with τ_{b} the lifetime of a closed pair of stickers, ϵkT their binding energy, f the number of stickers per chain, N_{e0} the number of monomers between entanglements in the melt, and ϕ the volume fraction of the polymer.

As we can see from this equation, the reptation time of the associating chain, which is related to the terminal relaxation time of the system ($1/\omega_{\mathrm{cross}}$), should increase with the hydrophobicity of stickers ($\tau_{\mathrm{b}}\mathrm{e}^{\epsilon/2}$), the number of hydrophobic groups (f^3), and the concentration of the polymer (ϕ). This correlates very well with the data shown in Table 4.

Consequently, ω_{cross} decreases with the extent of the hydrophobic modification and occurs at a much lower frequency compared to unmodified polymers.[13,14] Although we have not measured the crossover for the equivalent solution in DMF, the difference in viscosity suggests an increase in crossover frequency of 4 orders of magnitude.

At low frequency, the behavior of the complex shear modulus is Maxwellian (i.e., single element viscoelastic model), and the inverse of ω_{cross} can be interpreted as the characteristic relaxation time of the system. The main relaxation process contributing to this characteristic time is due to reptation dynamics. However, at higher frequency, the curves would be expected to deviate from the Maxwell viscoelastic model[11,49] because multiple relaxation mechanisms would begin to operate simultaneously.

Conclusion

Hydrophobically modified water-soluble polymers based on DMAM have been synthesized by a homogeneous free radical solution polymerization method. The hydrophobic comonomers dodecyl acrylate (DA) and octadecylacrylamide (ODAM) were incorporated individually into the polymer in a statistical manner. These copolymers were found to have enhanced viscosities in aqueous solutions as compared to their viscosity in a good organic solvent (DMF), indicating that the aggregation of the hydrophobic side chains results in transient physical cross-links. These results are significant because the polymers are based on a statistical incorporation of hydrophobic groups as opposed to the more commonly synthesized micellar copolymerized block copolymers. In the semidilute entangled regime the hydrophobic aggregations were strong enough to cause the polymer solution to act as a physical viscoelastic gel. The different scaling behaviors of the viscosity with concentration in the semidilute regime are in good agreement with theoretical predictions of Rubinstein and Semenov concerning solutions of associating polymers in a good solvent. According to this model, the dynamics of our copolymer solution is mainly controlled by the transformation from intra- to intermolecular hydrophobic associations in the unentangled regime and by a sticky reptation process in the entangled regime where most of the hydrophobic associations are intermolecular. These results are also in very good agreement with the data reported for hydrophobically modified polyacrylamides with a blocky distribution of the stickers. This demonstrates that the distribution of stickers along the water-soluble backbone is not critical for the associating behavior, but clearly the distribution has a strong impact on the amplitude of the viscosity through the relaxation time of the chain. More generally, this synthesis method which gives rise readily to homogeneous samples is well adapted also to the preparation of hydrophobically modified hydrogels in order to study the influence of additional transient physical cross-links on the properties of chemically cross-linked gels.

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