Influence of the Hydrophobe Structure on Composition, Microstructure, and Rheology in Associating Polyacrylamides Prepared by Micellar Copolymerization

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ABSTRACT: Acrylamide polymers modified with low amounts of alkyl- or alkylarylacrylamides (1−5 mol %) have been prepared by an aqueous micellar copolymerization technique. This method is known to lead to multiblock copolymers in which the number and length of the hydrophobic blocks vary with the initial number of hydrophobes per micelle. The incorporation behavior of different types of hydrophobes and their effects on the rheological copolymer properties have been investigated. Interestingly, the use of disubstituted acrylamides leads to an average copolymer composition independent of the degree of conversion, in contrast to what is observed with monosubstituted acrylamides. Solubility measurements of both types of hydrophobes indicate that the micellar dynamics is not responsible for this behavior, but rather the difference in polarity between the bulk phase and the micellar phase. This microenvironment effect modifies the reactivity ratios of those hydrophobes capable of forming hydrogen bonds, whereas the reactivity of the other hydrophobes remains unaffected. The rheological properties of the samples are discussed in terms of copolymer microstructure and type of hydrophobe used (bulkiness, degree of branching, and alkyl chain length). For example, at similar hydrophobe levels, double-chain hydrophobes considerably enhance the thickening efficiency with respect to single-chain hydrophobes.

Introduction

Hydrophobically associating water-soluble polymers have become of great interest in recent years.[1−5] These mainly hydrophilic polymers contain a small proportion of hydrophobic groups, usually in the form of pendant side chains or terminal groups. In aqueous solution, above a certain polymer concentration, intermolecular hydrophobic interactions cause the formation of a transitory three-dimensional network of polymer chains. Thereby, these polymers exhibit particular rheological properties in solution, due to the reversible dissociation process of the physical links occuring under shear. For instance, hydrophobically associating polymers can show interesting behavior as a function of shear rate or shear time, such as shear thinning or thixotropy. The rheological behavior of these compounds is of great technological interest, especially for tertiary oil recovery and latex paint systems.[1−5]

Hydrophobically modified polyacrylamides are an important type of associating polymers. One method to copolymerize acrylamide (AM) with a hydrophobic comonomer is a micellar polymerization technique in which the hydrophobe is solubilized into micelles dispersed in a water continuous medium. This micellar process was shown to be well suited for the preparation of polymers with improved thickening properties.[6−10] However, it was reported by Valint et al.[11] and our group[12] that the solubilization of the comonomer in micelles causes an increased apparent reactivity of the latter. The hydrophobic comonomer indeed is consumed more rapidly than acrylamide, and therefore the hydrophobe content of the polymer chains decreases with conversion, leading to relatively heterogeneous polymer samples. The drift in copolymer composition was found to increase strongly upon increasing the number of hydrophobes per micelle (N_H). It should be noted that such behavior differs much from that observed in homogeneous polymerization, i.e., in a common solvent mixture for both monomers, for which a constant hydrophobe incorporation is observed. Therefore, the monomer pairs investigated were assumed to have similar reactivity ratios.[12,13] The reason for the increased hydrophobic comonomer consumption was thought to be the fast exchange of the solubilizate between the micelles compared to the time required for a polymerization step.[12] However, the results were based on only one type of hydrophobic comonomers, i.e., *N*-(4-butylphenyl)acrylamide (BΦAM)[11] and *N*-(4-ethylphenyl)acrylamide (EΦAM).[12] These monomers have the advantage of being UV active, facilitating the determination of the very low hydrophobe content (≤3 mol %). Recently, we showed in our laboratory, using EΦAM as the hydrophobe, that the micellar effect is also observed with other water-soluble monomers like acrylic acid (AA).[14] In this case, the hydrophobic monomer is less reactive than acrylic acid, and an inverse compositional drift was observed. Playing with N_H, i.e., increasing the apparent reactivity of EΦAM, allowed us to correct for the drift in composition.[14]

The effect of the monomer segregation during synthesis on the copolymer microstructure has been addressed and studied by several authors.[13,15,17−20] The high density of hydrophobic molecules in the micelles should favor their incorporation as blocks in the copolymer backbone. The formation of a blocky structure was first suggested by Peer.[15] Direct experimental evidence was reported by Thomas et al.[16] and McCormick et al.[17−19] from photophysical studies on polyacrylamide derivatives containing either styryl, naphthyl, or pyrenyl groups as hydrophobes. In our laboratory, the copolymer microstructure has been studied by rheological and fluorescence measurements.[13,20] It was clearly established that the copolymer properties are strongly dependent on the hydrophobe/surfactant ratio, i.e., the number of hydrophobes per micelle (N_H).[13,18,19] Despite all of the experimental evidence that the solubilization of the hydrophobe in surfactant micelles leads to a blocky structure, we must point out that no clear

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information exists about the exact microstructure, such as the number and length of the hydrophobic blocks. The drift in composition results in heterogeneous copolymer samples, making it impossible to draw a precise conclusion about the polymer structure.

Other problems are the determination of the hydrophobic content and the control of the polymer properties. In general, the hydrophobe content in hydrophobically associating polyacrylamides is very limited to maintain the solubility in water.[13,21] Consequently, it is often impossible to determine the degree of hydrophobe incorporation, especially for comonomers consisting of alkyl chains. In the latter case, all of the studies assumed implicitly that the hydrophobe content corresponded to the initial feed composition ($[M_H]_i$).[10,16,21,22,23] An additional problem arises from the difficulty to prepare copolymers with both high associativity and good water solubility. McCormick et al. found that dodecylacrylamide cannot be incorporated at a content higher than 0.5 mol %.[21] Comonomers with shorter alkyl chains, such as octylacrylamide, can be used at higher contents, but this results in copolymers with only weak associative properties.[21] As a consequence, the range of hydrophobic modification is rather limited, and therefore the rheological properties cannot be controlled over a large variety.

This paper deals with the effect of the chemical nature of the hydrophobic monomer both on the copolymerization mechanism and on the aqueous solution properties of the resulting copolymers. Various acrylamide derivatives have been considered as hydrophobic monomers. We have especially looked at the behavior of N-disubstituted acrylamides compared to N-monosubstituted compounds. The incorporation behavior as a function of conversion for these two types of monomers has been studied, and a general method to avoid the drift in composition is presented. The influence of the degree of compositional heterogeneity on the copolymer properties was also investigated.

On the basis of these experiments and literature data relative to the copolymerization of acrylamide and monoalkyl- and dialkylacrylamides with other monomers, we propose a general mechanism that accounts well for the results reported so far on the micellar copolymerization of hydrophilic and hydrophobic monomers.

Experimental Section

A. Reagents. Acrylamide (Aldrich) was twice recrystallized from chloroform and stored in the dark at 4 °C until required. Sodium dodecyl sulfate (SDS) (Kodak, 99.9% purity) was used as supplied. The acryloyl chloride and all of the amines used for the comonomer synthesis except methyl-4-ethylaniline, were furnished by Aldrich. The methyl-4-ethylaniline was synthesized by using the procedure of Hughes et al.:[24] an autoclave (volume 100 mL) is filled with 85 g of a 40% aqueous CH_3NH_2 solution, 10 g bromo-4-ethylbenzene and 7 g of CuCl (all Aldrich) as a catalyst. The solution is held at 45 bars and ≈200 °C for 1 h and afterward cooled to room temperature overnight. NaOH (1 M, 40 mL) is added and the aqueous phase is extracted with chloroform. The organic phase is washed with 40 mL of a 10% $NaHCO_3$ solution and 40 mL of a saturated NaCl solution and is distilled under high vacuum (bp = 78−80 °C; yield, 90%).

The hydrophobic comonomers *N*-hexylacrylamide (HexAM), *N*-methyl-*N*-hexylacrylamide (MeHexAM), *N*,*N*-dihexylacrylamide (DiHexAM), *N*-(4-ethyl-phenyl)acrylamide (EΦAM), and *N*-methyl-*N*-(4-ethyl-phenyl)-acrylamide (MeEΦAM) (see Figure 1) were prepared and purified according to the technique of Valint et al.[9] HexAM was crystallized in ether at −20 °C and EΦAM in a hexane/acetone mixture. The monomers MeHexAM, DiHexAM, and MeEΦAM, which are liquids, were purified by distillation with $CuCl_2$ as a polymerization inhibitor under high vacuum at $\approx 10^{-2}$ mmHg (boiling points: 92−93, 105−108, and 122−124 °C, respectively). The purity for all monomers was checked by NMR spectroscopy. A typical ^{1}H NMR spectrum is shown in Figure 2.

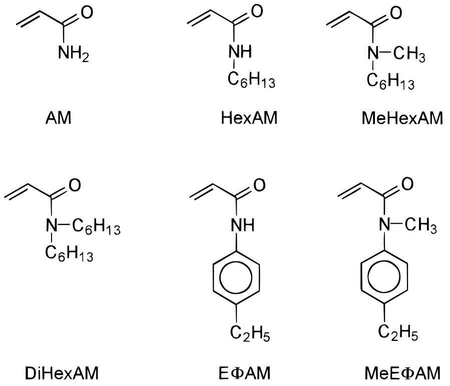

Figure 1. Structures of the monomers investigated.

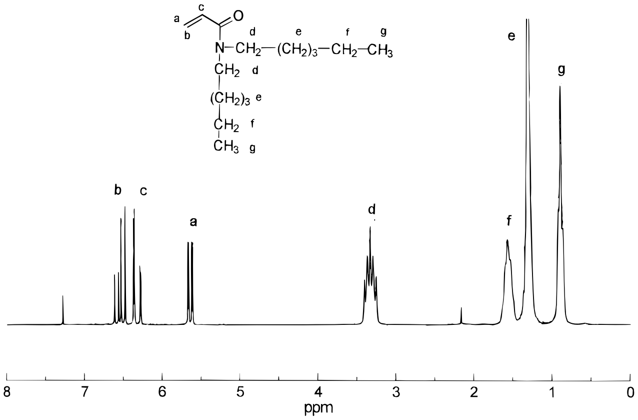

Figure 2. ^{1}H NMR spectrum of dihexylacrylamide (DiHexAM).

B. Polymerization. The copolymers were obtained by micellar copolymerization. In this process, first reported by Evani[6] and Turner et al.,[7] the hydrophobic monomer is solubilized within the surfactant micelles, whereas acrylamide is dissolved in the aqueous continuous medium. The surfactant used in this study was sodium dodecyl sulfate (SDS) at a concentration between 8 and 30 times its critical micelle concentration (CMC). A detailed description of the copolymerization procedure is given elsewhere.[12,13] For some experiments, aliquots were withdrawn at different reaction times, and each recovered polymer fraction was weighed to give the percentage conversion as a function of time.

C. Copolymer Characterization. 1. Nomenclature. The sample codes of the polymers refer to the nature of the hydrophobic comonomer: HAM for a copolymer containing hexylacrylamide, MHAM for MeHexAM, DHAM for DiHexAM ,and MEAM for MeEΦAM. The final number indicates the rounded value of N_H (e.g., MHAM8 stands for a polymer that contains MeHexAM with $N_H = 7.7$).

2. Molecular Weight Determination. The molecular weight of each polymer sample was determined in formamide solution by classical light scattering using a multiangle spectrometer (AMTEC Model MM1). Biggs et al.[12] showed that the presence of a small amount of a hydrophobic comonomer (≤5 mol %) does not significantly affect the refractive index increment, d*n*/d*c*, of polyacrylamide in formamide solution ($dn/dc = 0.111$). All measured values of the molecular weight, M_W, are therefore considered real and not apparent values.

3. Determination of the Hydrophobe Content. The hydrophobe incorporation has been measured by ^{1}H NMR spectroscopy in D_2O for all monomers containing alkyl chains

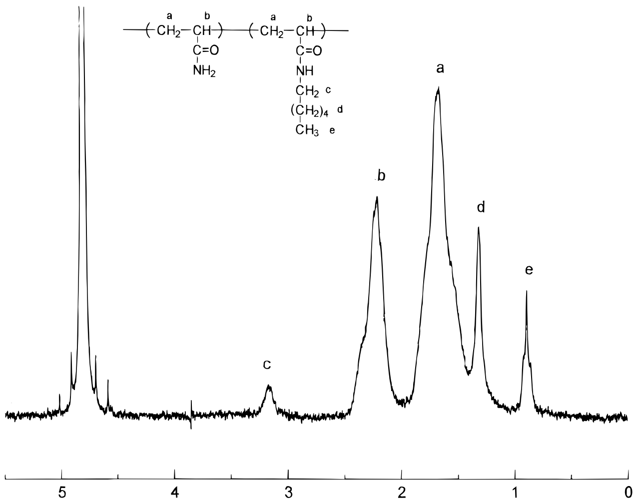

Figure 3. Typical ^1H NMR spectrum for a copolymer containing HexAM (run HAM8: taken at 69% conversion, 6.4 mol % HexAM).

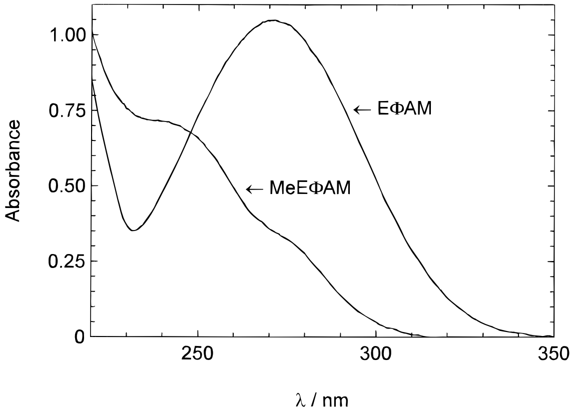

Figure 4. UV spectra for EΦAM and MeEΦAM monomers in water/ethanol (98/2), ($c_{\mathrm{monomer}} = 10^{-4}$ mol/L).

(HexAM, MeHexAM, and DiHexAM). The hydrophobe content was calculated from the integration of the peaks of the terminal methyl group of the alkyl chain and the CH group in the polymer backbone. Examples for an NMR spectrum of a copolymer containing HexAM are shown in Figure 3. The peak of the CH group of the polymer backbone (2.25 ppm) and the peak of the terminal methyl group of the hydrophobe (0.9 ppm) are sufficiently separated to yield the hydrophobe content from their surface ratio.

The incorporation of EΦAM can be measured by UV, as shown by Valint et al.[11] and Biggs et al.[12] It was not possible to measure the incorporation of the MeEΦAM by UV since the methyl group causes a blue shift of about 30 nm compared to the corresponding monomer without a methyl group bound to the nitrogen (see Figure 4). The absence of the double bond after polymerization causes an additional blue shift, so that the absorption lies in the same region as for polyacrylamide, which makes the determination of the hydrophobe content impossible. Therefore the incorporation of this monomer has been determined by ^1H NMR spectroscopy, in comparing the peak of the methyl group bound to the nitrogen with that of the CH group in the polymer backbone. Note that the peak of the CH_3 in the ethyl group was not suited because of a shift to higher frequencies, which led to an overlap of this peak and that of the CH_2 of the polymer backbone.

4. Determination of the Partition Coefficient. The partition coefficient between micelles and the bulk phase for phenyl containing hydrophobes was determined from measurements of their solubility limits in aqueous solution at different SDS concentrations. For each concentration, an excess of monomer was added to the solution, which was subsequently stirred for 1 day at room temperature. After stirring, the unsolubilized hydrophobic monomer was removed by centrifugation. The supernatant, after an appropriate dilution (50−1000 times with a water/ethanol (98/2) mixture), was then analyzed by UV spectroscopy to determine the amount of solubilized monomer. The molar absorption coefficient was initially determined by measuring the absorption at different concentrations in water containing 2% ethanol. The absorption coefficients for EΦAM and MeEΦAM were 10 990 ($\lambda = 270$ nm) and 7990 L mol^{-1} cm^{-1} ($\lambda = 239$ nm), respectively.

From the solubility measurements, it is possible to deduce the partition coefficient between the micelles and the aqueous intermicellar phase, as well as the exchange rate of the hydrophobic monomer. The partition coefficient is defined as

$$K_P = \chi_H^m/\chi_H^w$$

where χ_H^m is the mole fraction of the hydrophobe in the micellar phase and χ_H^m the mole fraction in the aqueous phase. These can be written as

$$\chi_H^m = \frac{c_H^m}{c_{SDS} - \mathrm{CMC} + c_H^m} = \frac{c_{tot} - c_o}{c_{SDS} - \mathrm{CMC} + c_{tot} - c_o}$$

and

$$\chi_H^w = \frac{c_o}{55.6 + \mathrm{CMC} + c_o} \approx \frac{c_o}{55.6}$$

where 55.6 is the number of moles/liter of water, c_H^m is the concentration of the hydrophobe in the micellar phase, c_o the solubility of the hydrophobe in water, c_{tot} is the total concentration of the hydrophobe in the solution, and c_{SDS} is the concentration of SDS (all concentrations are expressed in moles/liter). By using these relationships, the partition coefficient can be expressed as

$$K_P = \frac{(c_{tot} - c_o)\,55.6}{(c_{SDS} - \mathrm{CMC} + c_{tot} - c_o)c_o}$$

Hence

$$c_{tot} = c_o + \frac{K_P c_o}{55.6 - K_P c_o}(c_{SDS} - \mathrm{CMC})$$

Measurement of the solubility of the hydrophobic monomer as a function of surfactant concentration gives the partition coefficient from the slope of the linear plot.

The dynamics of the transfer process of various solubilizates has been studied by fluorescence quenching techniques,[25] the rate of transfer being dependent upon the relative rates of entry and exit (k_+ and k_-) of the solubilizate into and out of the micelle. The following expression relating these entry and exit rate constants to the partition coefficient of the solubilizate between the micelle and the bulk phase has been derived by Almgren et al.:[25]

$$K_P = (k_+/k_-)55.6$$

The exchange is governed by the exit rate k_- of the monomer since the entry rate is diffusion controlled and therefore always in the 10^9−10^{10} M^{-1} s^{-1} range.[26]

The partition coefficient for alkyl-containing hydrophobes cannot be determined by UV spectroscopy. In this case only the solubility in water has been measured using a Total Organic Carbon analyzer (TOC). A measurement of the solubility limit in the presence of surfactant is not possible here because the carbon of the surfactant and that of the monomer cannot be distinguished.

5. Rheological Polymer Characterization. Polymer samples were prepared by swelling the polymer in deionized water for 1 day. Afterward, the polymers were gently stirred

Table 1. Characteristics of the Copolymers

		polymer synthesis			polymer characterization		
sample[a]	hydrophobe	$[M_H]_i$[b] (mol %)	[SDS] (wt %)	N_H[c]	$[M_H]_p$[d] (mol %)	M_W ($\times 10^{-6}$)	conversion (wt %)
PAM						2.5	92
DHAM1	DiHexAM	1	7.5	1	1.1	1.6	92
DHAM2	DiHexAM	1	3	2.7	1.1	2.1	85
DHAM3	DiHexAM	1	2.5	3.2	1.1	2.1	73
DHAM3a	DiHexAM	1	2.5	3.2	1	2.4	26
DHAM4	DiHexAM	1	2.1	4	0.9	2.4	88
HAM8	HexAM	5	4.8	7.7	5.3	1.5	91
MHAM8	MeHexAM	5	4.7	7.7	5.3	1.4	85
MEAM4	MeEΦAM	2	3.8	4.1	1.9	1.2	51

[a] The sample code refers to the nature of the hydrohobe and the value of N_H (cf. Experimental Section). [b] Initial hydrophobe concentration. [c] Number of hydrophobes per micelle. [d] Hydrophobe content in the copolymer determined by NMR.

for 8 days. Solutions at the highest concentrations (≥0.8 wt %) were heated to 40 °C for 15 min to get rid of bubbles.

Viscosity experiments at low concentrations (≤0.5 wt %) were performed on a Contraves LS 30 low-shear rheometer at 25 °C. All other experiments were conducted with a Haake RS100 rheometer equipped with a cone–plate geometry (diameter 35 mm, angle 1°). All flow curves were measured by increasing the shear stress by regular steps and waiting at each step until equilibrium was attained. The shear rate $\dot{\gamma}$ ranged from 0.1–10 to 1000–2900 s^{-1}, depending on the viscometric behavior of the sample. In some cases it was not possible to scan the shear rates over a large range by progressively increasing the shear stress since a slight increase in stress caused a large jump in 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 (CS) and the controlled-rate (CR) modes were well superposed. The dynamic measurements were conducted with a frequency of 0.04–100 rad/s^{-1} (i.e. ~1.6 × 10^{-3}–16 Hz). All measurements were made under frequencies and strains that led to a linear response.

Results and Discussion

A. Synthesis and Characterization. To obtain more information about the incorporation behavior of various monomers containing different alkyl groups (see Figure 1), we have studied the copolymerization of AM with HexAM, MeHexAM, and DiHexAM. HexAM and MeHexAm were chosen because of the rather low hydrophobicity of the C_6 chain. They can thus be incorporated at fairly high contents while still maintaining the water solubility of the copolymer, allowing the determination of the hydrophobe content by ^1H NMR spectroscopy. The monomer DiHexAM was chosen because of its improved sensibility in ^1H NMR spectroscopy due to the number of terminal methyl groups, which is doubled. Its high hydrophobicity should also lead to strong associations. The characteristics of the copolymers prepared by micellar polymerization are reported in Table 1.

Copolymerizations of AM with HexAM (polymer HAM8) and with MeHexAM (polymer MHAM8) were both performed in a 95/5 molar ratio. The number of hydrophobes per micelle was 7.7 in both cases (see Table 1). Figure 5 shows the variation of the hydrophobe content as a function of total monomer conversion. The HexAM monomer shows incorporation behavior very similar to that observed for phenyl-containing monomers.[11,12] The degree in the compositional drift corresponds to that previously observed for EΦAM under the same experimental conditions. The MeHexAM monomer shows a somewhat unexpected result. In contrast to HexAM, no drift in composition is observed (Figure 5). The hydrophobe incorporation remains constant with conversion within the experimental error of the measurement and corresponds to its feed composition.

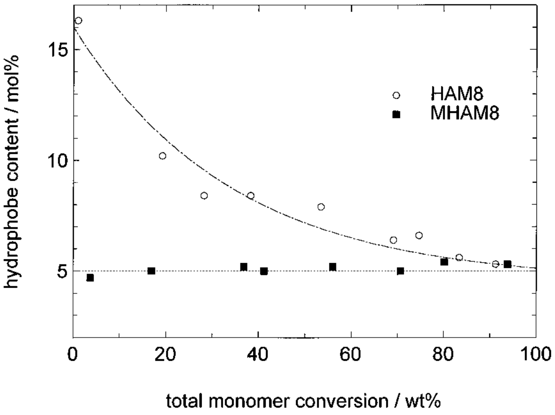

Figure 5. Average content in HexAM or MeHexAM for HAM8 or MHAM8 samples as a function of total monomer conversion ($[M_H]_i$ = 5 mol % and N_H = 7.7).

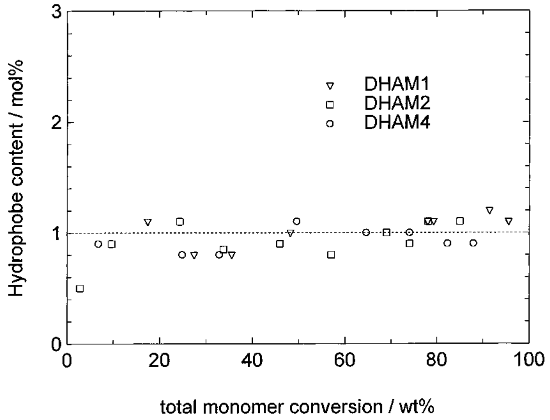

Figure 6. Average DiHexAM content as a function of total monomer conversion for various copolymers prepared at a constant initial hydrophobe level ($[M_H]_i$ = 1 mol %) and different N_H values: DHAM1, N_H = 1; DHAM2, N_H = 2.7; DHAM4, N_H = 4.

Figure 6 presents the hydrophobe incorporation behavior of three copolymerization reactions performed with 1 mol % of DiHexAM in the monomer feed and variable amounts of surfactants in such a way that N_H varies from 1 to 4. For any of the three polymerizations, no drift in composition is observed. Once again we recall that for both EΦAM and BΦAM a strong drift dependency on the hydrophobe to surfactant ratio was observed.[11,12] Apparently, the replacement of the N–H bond by a N–alkyl bond permits one to avoid the drift in composition, since in the case of MeHexAM and DiHexAM no drift is observed, whatever the N_H value.

To verify this assumption, we synthesized the monomer corresponding to the well-studied EΦAM in which

NH was replaced by a NCH_3 group (MeEΦAM). A copolymerization reaction was carried out with an initial MeEΦAM feed of 2 mol % and a hydrophobe to surfactant ratio corresponding to $N_H = 4.1$ (polymer MEAM4). The low degree of conversion and the lower M_W (cf. Table 1) compared to the other samples are possibly due to impurities in the comonomer. Despite the presence of the phenyl ring, the MeEΦAM content in the copolymer could not be determined by UV spectroscopy (see Experimental Section). Although NMR spectroscopy is less accurate than UV spectroscopy, it nevertheless can be used to determine the hydrophobe content. The hydrophobe content was found to be between 1.7 and 1.9 mol % over the whole conversion range, and thus the incorporation can be considered constant with conversion. This supports the assumption that the N−H bond of hydrophobic acrylamide monomers plays an important role in the compositional heterogeneity of copolymers prepared by micellar polymerization.

B. Micellar Copolymerization Mechanism. The data presented above show that the micellar copolymerization of acrylamide with a hydrophobically modified acrylamide does not necessarily lead to an increased apparent reactivity of the hydrophobe solubilized in the micelles and, therefore, to a drift in composition. It seems that the presence of a N−H bond on the acrylamide derivative is the reason for its faster consumption. The replacement of the hydrogen by an alkyl group led, in all cases, to a constant incorporation of the comonomer. In addition to that, no dependence of the incorporation behavior on the number of hydrophobes per micelle was found for disubstituted acrylamides. That means that the reactivity of this hydrophobe type is not influenced by a “micellar effect”. In the case of monosubstituted alkyl- or alkylarylacrylamides, the reactivity is enhanced upon increasing N_H, indicating the existence of a “micellar effect”.[11,12] The consumption of this type of hydrophobe can sometimes be so rapid that, at about 50% conversion, the comonomer is exhausted and only pure polyacrylamide is formed. All of the monomers used in this study, i.e., acrylamide and mono- and disubstituted acrylamides, have very similar chemical and electronic structures. Thus, no strong difference should exist in their reactivity ratios. This supposition is confirmed by a previous study on the copolymerization of AM with EΦAM in aqueous solution containing 10% formamide as cosolvent.[12,13] No drift in composition was found in the homogeneous copolymerization without surfactant. Additional evidence for a “micellar effect” was provided by studies on the copolymerization of acrylic acid with EΦAM in a micellar medium.[14] In this case, the reactivity of the hydrophobe was also enhanced upon increasing N_H.

So far, the micellar dynamics was thought to be responsible for the increased reactivity of the hydrophobe upon an increasing N_H value.[12] The hydrophobes that are solubilized in the micelles exchange very rapidly between the latter by transfer via the continuous bulk medium. The rate of exchange of an EΦAM molecule between two micelles was shown to be 3 orders of magnitude higher than the rate of addition of a monomer to a growing PAM radical.[12] Thus, during the residence time of a radical head group in a micelle, there will be a flux of EΦAM molecules toward this micelle. This should result in faster consumption of the hydrophobe than in a homogeneous polymerization process. The hydrophobic blocks formed at the beginning of the polymerization therefore should be longer than if only the initial content of one micelle was polymerized.

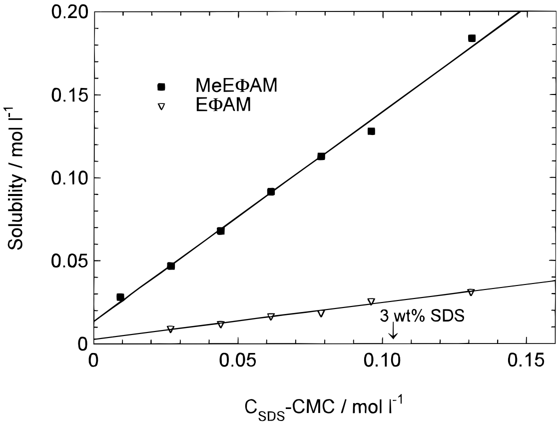

Figure 7. Solubility of EΦ AM and MeEΦ AM in water as a function of SDS concentration.

If this assumption is true, to explain the lack of faster incorporation of the hydrophobes in which the N−H bond is replaced by a NCH_3 group, one should find a decreased exchange rate between the micelles, due to a higher hydrophobicity in the latter case. To verify this, we measured, by UV spectroscopy, the solubility of EΦAM and MeEΦAM as a function of SDS concentration. From the solubility measurements, the partition coefficient between the micelles and the aqueous intermicellar phase is deduced, as is the exchange rate of the hydrophobic monomer (see Experimental Section).

The solubilities of EΦAM and MeEΦAM as a function of SDS concentration are shown in Figure 7. For both monomers, straight lines were obtained. It is somewhat astonishing that the MeEΦAM monomer has a 4 times higher solubility in pure water ($c_o = 1.3 \times 10^{-2}$ mol/L) than EΦAM ($c_o = 3 \times 10^{-3}$ mol/L), which contains a hydrophilic NH group. The solubilities of HexAM, MeHexAM, and DiHexAM ($c_o = 1.8 \times 10^{-2}$, 5.0×10^{-2}, 2.6×10^{-2} mol/L, respectively) measured by a TOC analyzer show the same tendency. This is probably due to the formation of dimers or higher aggregates in water via the carbonyl and the NH group of the latter. This type of structure has been proposed by several authors for acrylamide and monosubstituted acrylamides.[27] In the case of MeEΦAM, the formation of this type of aggregates is not possible due to the absence of a NH group. On the other hand, the solubility of MeEΦAM increases much more rapidly than that of EΦAM, as can be seen from the slopes of the curves plotted in Figure 7. We can conclude from these results that MeEΦAM is more soluble than EΦAM both in the aqueous phase and in the micellar phase.

The analysis of the linear plots leads to very similar partition coefficients: $K_P = 3.6 \times 10^3$ for EΦAM and $K_P = 2.3 \times 10^3$ for MeEΦAM. By using an average value of 7×10^9 M^{-1} s^{-1} for k_+,[25] we obtain exit rates of $k_- = 1 \times 10^8$ and 2×10^8 s^{-1} for EΦAM and MeΦAM, respectively. This means that for both monomers the exchange rate between the micelles is 3 orders of magnitude higher than the rate of addition of a monomer to a growing polyacrylamide radical.[12,28] As only EΦAM shows the phenomenon of increased reactivity in a micellar medium, the fast exchange between the micelles via the aqueous phase cannot be the reason for the drift in composition.

Additional evidence is given by the results of Yeoh et al.[29] These authors polymerized acrylamide with a surfactant containing the same polymerizable group, namely, 11-acrylamidoundecanoate. They found no drift in composition whatever the surfactant/AM ratio. The determination of the reactivity ratios for the monomer pair gave practically the same values for AM and the polymerizable surfactant. This means that no micellar effect leading to an increased reactivity of the hydrophobe takes place in this system. Nevertheless, it should be noted that the comonomer used can be identified as a so-called “bolaform” surfactant due to its two hydrophilic ends. This will result in a different micellar structure than in the case of SDS, especially at the interface. However, the authors found an increased rate of polymerization upon increasing the surfactant/AM ratio, indicating a certain effect of the micellar microenvironment on the polymerization.

On the basis of these results and ours, we can propose a new mechanism occurring in these micellar polymerization systems that accounts for the constant incorporation observed for disubstituted acrylamides, as well as for the drift in composition for monosubstituted acrylamides.

Significant solvent effects have been observed by several authors for free radical-initiated copolymerizations that involve monomers with high dipolar moments or hydrogen-bonding capability.[27,30,31] The copolymerization of acrylamide with styrene or with methyl methacrylate showed a strong solvent dependency on the reactivity ratios. The use of a variety of polar and nonpolar solvents showed that the reactivity of acrylamide increases upon decreasing solvent polarity. The highest reactivity ratio values were found in benzene, and the lowest values were in solvents like ethanol.[31−36] The reason for this behavior was explained through polar effects influencing the amide/enol equilibrium and/or hydrogen bonding. While, for example, in benzene no hydrogen bridging is possible between the solvent and the N−H bonds of acrylamide, there will be a strong influence of such an effect in solvents like ethanol, which will affect the reactivity of this monomer.

Saini et al.[32,37,38] studied the copolymerization of acrylamide, *N*-methylacrylamide (MeAM), and dimethylacrylamide (DMeAM) with styrene or methyl methacrylate. They carried out copolymerizations in a nonpolar solvent (dioxane, $\epsilon = 2.2$) and in a polar solvent (ethanol, $\epsilon = 24.3$). The reactivity ratios of styrene or methyl methacrylate, when copolymerized with one of the three acrylamides, almost were not influenced by the polarity of the solvent. On the contrary, these authors found a strong decrease in the reactivity ratios of AM and MeAM when going from the nonpolar to the polar solvent. These results were in agreement with the observation discussed earlier that the reactivity of acrylamide decreases upon increasing solvent polarity.[31−36] A remarkable result was obtained when DMeAM was copolymerized with styrene or methyl methacrylate. The reactivity ratio of this dialkylacrylamide did not depend on the polarity of the solvent. The reactivity ratios were almost the same in dioxane and in ethanol. The authors attributed this striking difference, compared to the copolymerization of AM or MeAM, to the two electron-donating methyl groups of the amidic nitrogen. In the case of AM or MeAM, hydrogen bonding and the formation of the enolic form of the monomer are possible. This equilibrium between the amidic and enolic forms will be influenced by the solvent and therefore will change the reactivity of the monomer. In the case of a disubstituted acrylamide, H-bonding and/or the formation of the enolic form are not possible due to the absence of the hydrogen atom. The monomer reactivity will not be influenced by the nature of the solvent.

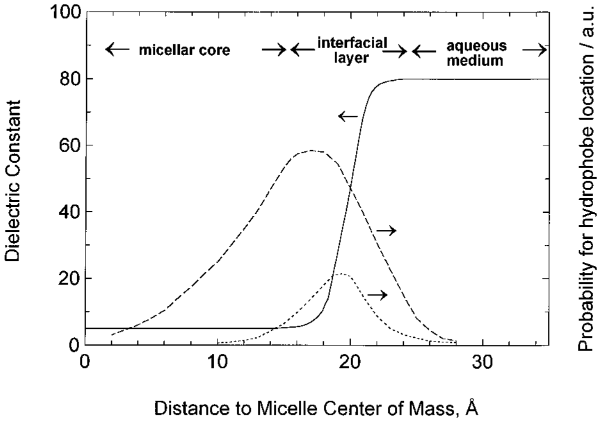

Figure 8. Schematic representation of the dielectric constant (solid line) and monomer distribution for a low (dotted line) and high N_H (dashed line) as a function of the distance of the center of mass for a SDS micelle.

If we apply these results to our system, we can conclude that the reactivity of a monoalkylacrylamide will be higher when localized in the micelle, a medium with a low dielectricity constant, than in the polar aqueous phase. The reactivity of a disubstituted alkylacrylamide will not depend on its locus of solubilization since neither hydrogen bonding nor amide/enol equilibrium can occur. Examination of the interfacial structure of a micelle provides additional information. Figure 8 depicts schematically the dielectric constant as a function of the distance from the micelle center of mass. Such a scheme is based on the well-accepted structure of a micelle. In the micellar interface, a drastic change of the dielectric constant occurs,[39] i.e., from $\epsilon \approx 80$ in the water phase to $\epsilon \approx 5$ in the oil-like micelle phase. Acrylamide is known to act as a cosurfactant in a micellar solution.[40] It can be supposed that a monosubstituted acrylamide, which has a certain amphiphilic character, will also be localized in the micellar interface. Nevertheless, it will be more oriented toward the hydrophobic core than acrylamide, due to its hydrophobic moiety. That implies localization in a medium with a low dielectric constant and no possibility of hydrogen bridging. This should result in an increased reactivity of the hydrophobic comonomer. To better understand this effect, one has to look at the polymerization process in the micellar interface. As already mentioned, the micellar interfacial region can be considered as a mixed monolayer of SDS, acrylamide, and the hydrophobic comonomer. When a growing radical chain encounters a micelle, it will first add some acrylamide monomers, which act as a cosurfactant, facilitating better contact between the hydrophile (AM) and the hydrophobe. The hydrophilic radical chain will tend not to enter very deeply into the micelle. But since the change of the dielectric constant in the interface takes place over a very short distance, the reactivity of the hydrophobe and therefore the kinetics of the hydrophobe incorporation will strongly depend on how deep the radical chain goes into the micelle or, in other words, on the exact localization of the hydrophobic comonomer.

This mechanism can also explain the increased drift in composition upon increasing the number of hydrophobes per micelle. Mukerjee described a model for molecules solubilized in micelles that distinguishes between two extreme states of the solute: the “dissolved state" implying location in the hydrocarbon micellar core, and the "adsorbed state", meaning localization in the micellar interface.[41] He showed that upon increasing the concentration of solute per micelle, the ratio between adsorbed and dissolved states is shifted in favor of the core location. On the basis of this model, the location of the hydrophobic monomer in the micelle can be depicted schematically by the distribution curves shown in Figure 8 for two different N_H values. At very low N_H, the maximum of the distribution curve lies in the interfacial area. As a consequence, only a small amount of the hydrophobic monomers is located in a low-polarity environment. This leads to a slight increase in reactivity and the drift in composition will be rather limited. On the other hand, according to Mukerjee's model, for higher N_H values, the distribution curve will be broadened and shifted toward the micellar core, leading to an increased number of hydrophobic monomers with enhanced reactivity. When the polymer radical enters a micelle, the first hydrophobic monomer will be added in the interfacial layer. Upon an increase in its size, the hydrophobic block enters more deeply into the micelle. Therefore, upon increasing N_H, a larger number of hydrophobes with increased reactivity will be added onto the growing radical in the nonpolar medium of the micellar core. As a result, a rise in N_H leads to an increased drift in composition.

In the case of a disubstituted acrylamide, the process cannot lead to a drift in composition since the reactivity of the monomer will not depend on the polarity of the medium in which it is localized. Nevertheless, it can be supposed that this type of comonomer, which has much lower amphiphilic character, will be more buried in the micellar core than a monosubstituted acrylamide. This could lead to a higher homogeneity of the hydrophobic blocks since the addition of the acrylamide monomers acting as a cosurfactant in the micellar interface will occur to a lesser extent. This different polymerization mechanism will have a profound influence on the copolymer properties, as shown in the following.

C. Rheological Behavior. The influence of a hydrophobic comonomer on the solution behavior of polyacrylamides has already been studied by several authors.[6−8,10,13,17−23,42] The incorporation of a hydrophobe at low content causes drastic changes in the viscometric and rheological behavior. At low polymer concentrations where intramolecular associations are dominant, the hydrophobic interactions produce a decrease in the hydrodynamic radius of the polymer coil. The presence of a low quantity of hydrophobe in the polymer can also induce a strong increase in the solution viscosity already below the critical overlap concentration C^* of the corresponding homopolymer.[21,23] In the semidilute regime, the hydrophobe can considerably enhance the solution viscosity and lead to particular rheological properties (i.e., shear thinning, shear thickening, viscoelasticity, etc.). We tried to investigate the influence of the different types of hydrophobes on the rheological solution behavior in terms of heterogeneity in composition and bulkiness of the comonomer.

1. Viscometric Behavior in Dilute Solution. Figure 9 shows the concentration dependence of the apparent viscosity of a homopolyacrylamide and three hydrophobically modified polyacrylamides containing different hydrophobic comonomers (HexAM, MeHexAM, and DiHexAM). All copolymers are supposed to have a blocky structure (i.e., $N_H \gg 1$ in the synthesis). The viscosities were all measured at a constant shear rate of 10 s^{-1}. In this concentration regime, the DiHexAM/AM polymer (DHAM3) is the only copolymer that shows behavior markedly different from that of the homopolymer. A critical aggregation concentration C_{agg} is found that is far below the C^* of the polyacrylamide. This early upturn of the solution viscosity cannot simply be due to an overlap of the macromolecules, since the overlap is related to the molecular size. On the other hand, the copolymers containing HexAM or MeHexAM (samples HAM8 and MHAM8) show no remarkable difference despite the high hydrophobe content (5 mol %) and the probable large size of the hydrophobic blocks ($N_H = 7.7$ in the synthesis). The solution viscosities of the two polymers lie even under that of the precursor. This can be explained by the formation of intramolecular interactions and the lower molecular weight of the modified polymers. The DiHexAM/AM copolymer (DHAM3), which contains 1 mol % hydrophobe (i.e., 2 mol % hexyl chains), at relatively low concentrations ($\approx$0.3 g dL^{-1}) already shows strong intermolecular interactions, leading to a strong increase in solution viscosity. Apparently, the proximity of the two hexyl chains allows the formation of stronger hydrophobic interactions than what is observed with single hexyl chains.

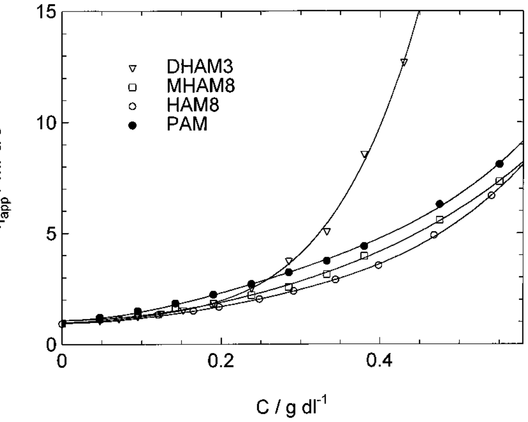

Figure 9. Variation of the apparent viscosity as a function of polymer concentration for DHAM3, MHAM8, HAM8, and PAM.

It was shown in previous studies[13,15,16,18−20] that the blockiness of associative polyacrylamides synthesized by micellar polymerization can be monitored by adjusting the [hydrophobe]/[surfactant] ratio in the synthesis. The thickening efficiency was directly related to the length of the hydrophobic blocks.

Figure 10 shows the concentration dependence of the apparent viscosity of a homopolymer and two copolymers containing 1 mol % DiHexAM, but differing by the N_H value used in the synthesis. For the DHAM1 copolymer ($N_H = 1$), it is expected that the hydrophobes are randomly and singly distributed along the polyacrylamide backbone, while the other copolymer DHAM3 (N_H = 3.2) should have a blocky repartition of the hydrophobic comonomer.

Both copolymers show behavior different from that of the homopolymer. In the low-concentration region, the DHAM1 copolymer shows a lower viscosity than the homopolymer, reflecting its lower mass (see Table 1) and the coil collapse due to intramolecular hydrophobic interactions. At higher concentrations (>0.5 g dL^{-1}), the solution viscosity of the DHAM1 copolymer increases more rapidly than that of the homopolymer. The blocky copolymer (DHAM3) shows much greater as-

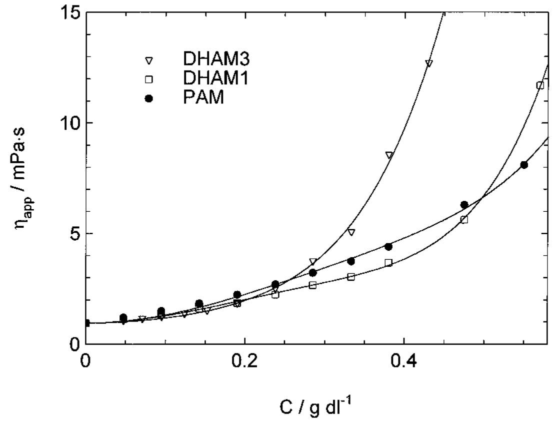

Figure 10. Variation of the apparent viscosity as a function of polymer concentration for DHAM3, DHAM1, and PAM polymers.

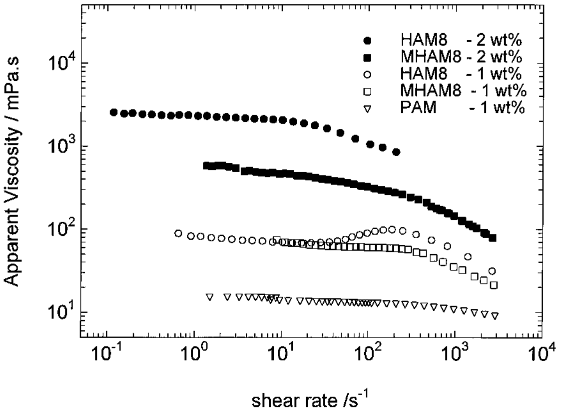

Figure 11. Apparent viscosity as a function of shear rate for HAM8 (heterogeneous in composition) and MHAM8 (homogeneous in composition) at two different concentrations (1 and 2 wt %) and for the homopolymer (PAM, 1 wt %).

sociative behavior than the statistical one. The solution viscosity is slightly lower at low concentrations (<0.25 g dL^{-1}), and afterward a strong upward curvature of the viscosity is found that is largely above the viscosity of the homopolymer. This confirms that the distribution of the hydrophobic comonomer is directly related to the surfactant concentration used in the synthesis, at constant hydrophobe level.

These results suggest that two conditions have to be fulfilled to produce strongly associative polymers with short chains. First, the hydrophobic monomer has to be branched, and second it must have a blocky repartition. Steric effects likely are responsible for this behavior.

2. Rheological Behavior in the Semidilute Regime. The chain overlap concentration C^* of a polymer can be estimated from the onset of the upward curvature of the curve, $\eta_{\text{red}} = f(c)$. For the homopolyacrylamide (PAM) was thus found a value of $C^* \simeq 0.4$ wt %. In this study, the rheological properties under shear have been investigated at polymer concentrations of 1 or 2 wt %, i.e., above C^*.

a. Influence of Compositional Homogeneity. It was shown earlier that AM/dialkyl-AM copolymers reveal no drift in composition, while a strong drift is observed with alkylacrylamides containing a N−H bond (for $N_H \gg 1$). It therefore was interesting to determine how this difference in sample homogeneity could affect the rheological behavior. Figure 11 presents the viscosity/shear rate curves of the copolymers containing HexAM or MeHexAM (samples HAM8 and MHAM8) at concentrations of 1 and 2 wt %, as well as a curve of the homopolymer (PAM) at 1 wt %. Both copolymers recovered at full conversion have nearly the same molecular weight ($M_W \approx 1.5 \times 10^6$, cf. Table 1). The comparison of the data obtained for the homopolymer and for the hydrophobically modified copolymers at the same concentration shows that the incorporation of 5 mol % hexyl chains causes a certain associativity for both copolymers, but the behavior of the two copolymers is different. At 1 wt % concentration and at low shear rates ($\dot{\gamma} < 10\ s^{-1}$), the viscosity values for the two copolymers are similar. However, while the homogeneous sample (MHAM8) exhibits classical rheological behavior, i.e., a shear thinning effect after the newtonian plateau, the heterogeneous copolymer (HAM8) behaves differently. With increasing shear rate, a shear thickening domain is reached first followed by shear thinning. This behavior has already been observed by several groups for associative polymer systems.[10,43,44] The shear thickening was interpreted in terms of the balance between intra- and intermolecular interactions. At a certain shear rate, the shear forces are strong enough to extend the polymer coils and intramolecular hydrophobic associations are disrupted. The hydrophobic domains released can form intermolecular hydrophobic associations, leading to an increase in viscosity. These associations are subsequently broken upon a further increase in the shear rate, and shear thinning behavior is observed. The fact that only the heterogeneous sample shows a shear thickening effect is probably due to a different balance between intra- and intermolecular interactions.

At a higher concentration (2 wt %) no more shear thickening is observed, and both copolymers show classical shear thinning behavior upon increasing shear rate. The theory by Vrahopoulou and McHugh[45] predicts such a disappearance of the shear thickening region with increasing molecular weight and with increasing concentration. Jenkins et al. confirmed this prediction experimentally.[44] It is a somewhat unexpected result that the heterogeneous polymer reveals a considerably higher viscosity than the copolymer without any drift in composition. In addition to its compositional homogeneity, the MHAM8 copolymer contains the comonomer, which should have the higher hydrophobicity due to its additional methyl group. For the HAM8 copolymer, the drift in composition produces at full conversion a polymer sample consisting of copolymer chains whose hydrophobe numbers and sequence lengths are variable, with possibly some homopolymer chains. The large blocks formed in the initial polymer chains (hydrophobe content ≫ 10%) are probably the cause of the higher associativity of the heterogeneous sample.

b. Influence of the Type of Hydrophobe. We have already discussed the different behaviors observed in the dilute regime for hydrophobically modified polyacrylamides containing hydrophobes with one or two alkyl chains. The comonomer DiHexAM causes an early upward curvature of the viscosity, while HexAM and MeHexAM do not show a notable difference compared to the homopolymer in the concentration regime investigated ($c \le 0.5$ wt %). Figure 12 presents the dependence of the viscosity on shear rate in the semidilute regime for a PAM and two hydrophobically modified PAMs (MHAM8 and DHAM3) that have an apparent structural homogeneity in composition due to the constant incorporation of the hydrophobe. The concentra-

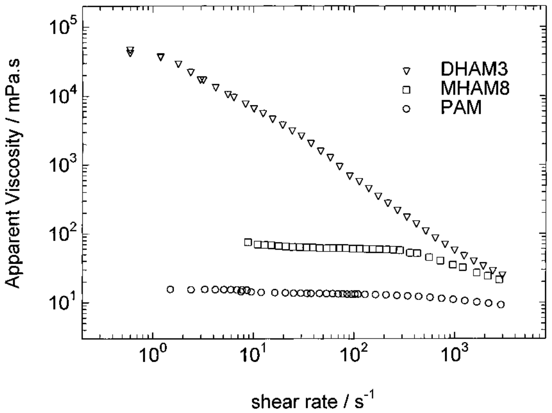

Figure 12. Apparent viscosity as a function of shear rate for homogeneous copolymers containing DiHexAM (DHAM3) or MeHexAM (MHAM8) and for polyacrylamide (polymer concentration: $c_p = 1$ wt %).

tion for all polymers is 1 wt %. While the homopolymer shows rather low viscosity ($\eta_{\dot{\gamma}\to 0} = 15$ mPa·s) and negligible shear thinning, one can observe for the MHAM8 polymer a slightly higher viscosity ($\eta_{\dot{\gamma}\to 0} = 90$ mPa·s) and marked shear thinning despite its lower molecular weight (cf. Table 1). Nevertheless, the thickening effect is relatively small compared to the copolymer containing DiHexAM. Although the copolymer DHAM3 contains 2.5 times fewer hexyl chains than MHAM8, an enormous increase in viscosity ($\eta_{\dot{\gamma}\to 0} \approx$ 50 000 mPa·s) and a remarkable shear thinning effect can be observed. The blockiness of the two copolymers is more or less comparable if one takes into account the fact that DiHexAM has two hexyl chains, which means that the N_H value has to be multiplied by a factor of 2. This leads, for MHAM8 and DHAM3, to a hydrophobic chain per micelle ratio of 7.7 and 6.4, respectively. We also tested copolymers with a HexAM or MeHexAM content (1−3 mol %) lower than in the case of HAM8 or MHAM8. No significant viscosifying effect was observed compared to the homopolymer (results not presented here).

It can therefore be concluded that the positions of the hexyl chains in the dibranched comonomer favor much stronger hydrophobic interactions than acrylamide derivatives containing only one hexyl chain. In the former case, the alkyl chains are closer to each other than in the latter case, especially in a blocky structure, leading to very dense hydrophobic domains. In addition, the DiHexAM blocks are more homogeneous due to the lower acrylamide content than HexAM blocks (see the Micellar Polymerization Mechanism section) and this can also account for the strong hydrophobic interactions.

c. Influence of the Microstructure. As already discussed, the micellar polymerization process allows one to control the microstructure of the resulting copolymer by varying the hydrophobe to micelle ratio in going from a very blocky structure (high N_H values) to an almost random copolymer ($N_H = 1$). Since DiHexAM is incorporated at a constant level with conversion whatever the surfactant content, this compound is a good model for studying the influence of the microstructure on copolymer properties. Figure 13 presents the shear rate dependence of viscosity for three polyacrylamides containing 1 mol % DiHexAM and prepared with different hydrophobe to micelle ratios (copolymers DHAM1, DHAM2, and DHAM3; $N_H = 1$, 2.7, and 3.2, respectively). The homopolymer curve is shown for comparison. The polymer concentration was 1 wt %. Comparison between the various samples is somewhat difficult because of some differences in the molecular weight. However, one can note that each copolymer reveals enhanced viscosity compared to that of the homopolyacrylamide. In particular, the DHAM1 sample shows viscosity higher than that of the homopolymer, in spite of a lower molecular weight. In this case, the distribution of the hydrophobe is random (N_H = 1), but the two hexyl chains contained in each comonomer unit can be considered as a small hydrophobic block. It is clear that the associativity of the polymers increases upon increasing N_H. The two copolymers with more pronounced blockiness show remarkable associativity but their behavior is quite different. DHAM2 shows no real Newtonian plateau, and a shear thickening effect is observed at moderate shear rates followed by shear thinning. The polymer with the larger hydrophobic blocks (DHAM3) reveals much higher viscosity. The shear thickening effect that is not apparent in Figure 13 nevertheless can be seen at a much lower shear rate (cf. Figure 14). Once again, it seems that the incorporation of DiHexAM in the form of blocks facilitates very strong interactions in dense hydrophobic domains.

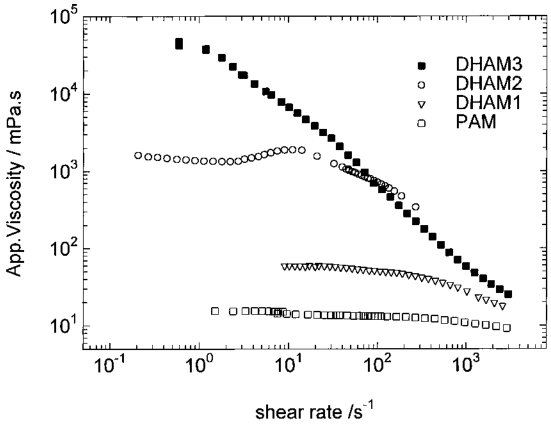

Figure 13. Apparent viscosity as a function of shear rate for various copolymers at a constant DiHexAM level ($[M_H]_i = 1$ mol %) but different N_H values and for a polyacrylamide (polymer concentration: $c_p = 1$ wt %): DHAM1, $N_H = 1$; DHAM2, $N_H = 2.7$; DHAM3, $N_H = 3.2$).

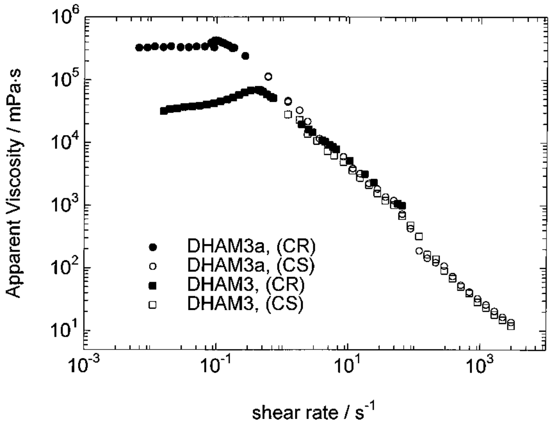

Figure 14. Apparent viscosity as a function of shear rate for DiHexAM/AM copolymers ($[M_H]_i = 1$ mol %, $N_H = 3.2$) taken at two different conversion levels: DHAM3a, 26%; DHAM3, 73% (CS, controlled-stress measurement; CR, controlled-rate measurement).

The difference in behavior of the DHAM2 and DHAM3 copolymers is a little bit surprising. One would not expect that an increase in the N_H value from 2.7 to 3.2 could cause such a difference in polymer properties.

However, Sau and Landoll[46] observed a similar effect with hydrophobically modified (hydroxyethyl)cellulose. An increase in the hydrophobe content by 0.1 mol % enhanced the solution viscosity by a factor of nearly 100. Further increase in the hydrophobe content led to a maximum in viscosity followed by a strong decrease due to incomplete solubility of the polymer. In our case, the large difference observed is caused by a comparable effect. Increasing the average size of the hydrophobic blocks enhances the strength of the interactions between these sequences until a maximum is reached (for about $N_H = 3.5$). This is followed by a decrease in associativity, eventually leading to insoluble samples. For instance, the polymer DHAM4 ($N_H = 4$) could only be dissolved under heating at 40 °C for a few minutes.

d. Influence of Conversion. We have seen that some monomers, for example, dihexylacrylamide, are incorporated at a constant level with conversion, from which it can be inferred that the polymers recovered at full conversion have a macroscopically homogeneous composition. However, this does not necessarily mean that the polymer will have a well-defined microstructure. The average size of the hydrophobic blocks could change as a function of conversion. This will depend on the balance between the number of surfactant molecules in the micellar state and that adsorbed onto the hydrophobic domains in the copolymer. Three cases can be envisioned.

1. After consumption of the hydrophobic comonomer located in a micelle, all of the surfactant forming the micelle adsorbs onto the hydrophobic sequence. This implies that N_H remains constant during the polymerization, leading to a homogeneous microstructure over the whole polymer sample. Therefore, the rheological behavior of the polymer should not depend on the degree of conversion.

2. The hydrophobic blocks adsorb less surfactant than the amount involved in the formation of a micelle. This would lead to a redistribution of the unpolymerized comonomer between hydrophobe-containing micelles and empty micelles. This would cause a decrease in N_H and therefore a decrease in the block size with conversion. In this case, one should observe a lowered thickening capacity of the polymer with conversion.

3. The surfactant has a higher affinity for the hydrophobic blocks than for the unpolymerized comonomer. This should lead to an increase in N_H and in the thickening capacity with conversion.

Rheological measurements performed on samples taken at various degrees of conversion should give us some insight into possible microstructural changes, provided that the molecular weight is not affected in the course of the reaction. Previous studies have indeed shown that the presence of surfactant causes a decrease in molecular weight with conversion:[12] the higher the surfactant concentration, the lower the final molecular weight and the stronger the decrease with conversion.

We synthesized a polymer based on DiHexAM, using a low surfactant concentration in the synthesis, so that the decrease in M_W with conversion should be relatively low. During the polymerization, samples were taken out at 26% (DHAM3a) and 73% (DHAM3) conversion. The molecular weights of the two samples are sufficiently close ($M_W = 2.4 \times 10^6$ and 2.1×10^6, respectively) to allow a meaningful comparison. Figure 14 shows the shear rate dependence of the viscosity for the two samples. To scan a sufficiently large shear rate range, the controlled-stress (CS) mode was used for low shear rates and the controlled-rate (CR) mode was used for higher shear rates (see Experimental Section).

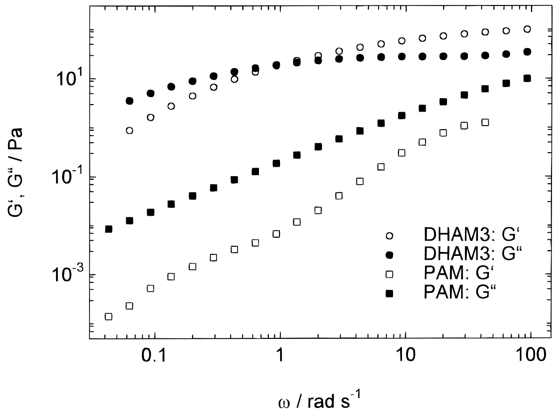

Figure 15. Storage modulus G' and loss modulus G'' as a function of frequency for a hydrophobically modified polyacrylamide containing DiHexAM (DHAM3) and a homopolymer (PAM).

Above $\dot{\gamma} > 1$ s^{-1}, the behavior of the two samples is similar, while at lower shear rates, there is a strong difference. The sample taken at low conversion (DHAM3a) shows a well-defined Newtonian plateau ($\eta_{\dot{\gamma}\to 0} = 300\,000$ mPa·s) over one decade followed by a weak shear thickening region in the range of 0.1 s^{-1}. Afterward, the viscosity decreases constantly. The sample at high conversion (DHAM3) shows essentially the same behavior, but the plateau is found at a much lower level ($\eta_{\dot{\gamma}\to 0} = 40\,000$ mPa·s) and the maximum in viscosity of the shear thickening region is shifted to higher shear rates and is much broader. This tends to indicate that the microstructure of the polymer chains evolves with conversion. The difference in sample behavior cannot be explained by the slight difference in molecular weight. Apparently, the average block size diminishes with conversion since DHAM3 has a much lower zero shear rate viscosity than the sample taken at low conversion. The broader and more marked shear thickening region of the sample at high conversion reflects a wider distribution of relaxation times for the disruption of intramolecular associations. This could mean that the polydispersity of the hydrophobic blocks at the beginning of the polymerization is very narrow, corresponding to the polydispersity of the hydrophobe distribution in the micelles. As the polymerization reaction progresses, a redistribution of the unpolymerized hydrophobic monomers will take place due to the micellar dynamics (case 2 discussed earlier). This causes a diminution of the number of hydrophobes per micelle and correlatively of the size of the built hydrophobic blocks. Small changes in the microstructure, i.e., a small decrease in the hydrophobic sequence length, would be sufficient to cause drastic changes in the copolymer properties, as shown earlier for DHAM2 and DHAM3 samples.

e. Viscoelasticity. The modification of a polyacrylamide by a hydrophobic comonomer considerably increases the viscosity of the polymer solutions. Similarly, the viscoelastic behavior can be strongly influenced by the physical cross-links. For a homopolyacrylamide, the viscoelastic properties above the critical overlap concentration are governed by chain entanglements. In the case of the modified polymer, the hydrophobic associations will probably play the main role. Figure 15 depicts the storage and loss moduli under oscillating shear for the homopolymer (PAM) and a copolymer containing dihexylacrylamide in a blocky repartition (polymer DHAM3). The concentration for both polymers is 2 wt %. A strong increase in G' and G'' are observed for the copolymer due to hydrophobic associations. Under the imposed stress (5 Pa), the high frequencies (>20 Hz) were experimentally inaccessible since the response was no longer linear for the homo- and copolymer.

In the case of the polyacrylamide, the value of the storage modulus is always below that of the loss modulus. The values of the slopes of G' and G'' are not far from 1 and 2, respectively (note that, for a concentration of 3 wt %, these values were equal to 1 and 2; results not presented here). It seems that the curves can be described by the bead−spring model of Zimm and Rouse,[47] which predicts this behavior. For a verification of this assumption, a measurement at higher frequencies would be necessary. The polymer containing a hydrophobic comonomer shows a drastic increase in storage and loss moduli compared to the homopolymer. The high value of G' and the “entanglement coupling” reflect the high elasticity of the associating polymer solution. This indicates that the hydrophobic domains dominate the solution properties. Similar results have been found by other groups for various types of associating polymers. Maerker and Sinton[43] observed a pronounced “entanglement coupling” for solutions of poly(vinyl alcohol) in the presence of sodium borate. The G' and G'' slopes were found to be 1.5 and 1, respectively. Aubry and Moan[48] investigated a hydrophobically modified (hydroxypropyl)guar. They found behavior of the storage and loss moduli that is similar to our case. However, the curves of the homopolymer were more like those of the modified polymer. Investigation over a wider frequency range is required for a better understanding of the viscoelastic behavior. This would permit us to verify the slopes of G' and G'' in the low-frequency region, as well as to study the effect of the hydrophobe at high frequencies. Further work on the viscoelastic properties is in progress.

Conclusion

The results reported in this paper show that a drift in copolymer composition is not an inherent characteristic of the micellar copolymerization of acrylamide with a hydrophobic comonomer. The use of N-disubstituted acrylamides permits one to avoid the drift, and thus the incorporation kinetics of the hydrophobe no longer depends on the number of hydrophobes per micelle in the feed composition.

The examination of the exchange rates of mono- and disubstituted acrylamides resulted in values of the same order for both types of hydrophobes. Thus, the exchange of solubilizates between micelles cannot be the reason, as previously invoked, for the higher incorporation observed in the early stages for the copolymerization of AM with monosubstituted acrylamides. Literature data show that the reactivity of acrylamide and monosubstituted derivatives strongly depends on the solvent polarity. This fact is explained by different degrees of hydrogen-bonding effects in polar and nonpolar solvents. In the case of dialkylacrylamides, no solvent dependence on the monomer reactivity is observed. Hence, monosubstituted acrylamides will have increased reactivity when localized in the nonpolar micellar medium, whereas the reactivity of disubstituted comonomers will not depend on their localization.

Apart from the absence of drift in composition, the use of DiHexAM as a hydrophobic monomer leads to drastically increased associativity of the resulting copolymers, which is not attained with monohexyl compounds. The dibranching of the comonomer permits a higher density of the hydrophobic domains, which facilitates stronger hydrophobic interactions.

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