Properties of Hydrophobically Associating Polyacrylamides: Influence of the Method of Synthesis

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ABSTRACT: Hydrophobically modified water-soluble polymers have been prepared by radial copolymerization of acrylamide and ethylphenylacrylamide as the hydrophobic comonomer. Three methods of synthesis in aqueous media have been investigated: (i) a "micellar" process in which the presence of a surfactant ensures the solubilization of the hydrophobic monomer; (ii) a "homogeneous" process wherein a miscible cosolvent is used; (iii) a "heterogeneous" process, without additive to solubilize the insoluble monomer. The properties of the copolymers in dilute and semidilute aqueous solutions strongly depend on the conditions of the synthesis. Copolymers prepared by the homogeneous and heterogeneous processes behave like homopolyacrylamide; i.e., hydrophobic interactions do not occur significantly. Copolymers obtained by micellar copolymerization exhibit improved thickening properties due to intermolecular hydrophobic associations. These differences can be directly related to the copolymer microstructure, i.e., to a random or blocky distribution of the hydrophobic units. The blockiness of the copolymer can be adjusted by varying the [hydrophobe]/[micelle] ratio at a constant hydrophobe level. Thus, it is possible to control the association degree and therefore the rheological properties. Fluorescence studies, using pyrene as a probe, reveal the formation of hydrophobic microdomains which corroborate the rheological results.

Introduction

Hydrophobically associating polymers consist of a water-soluble polymer containing a small number of hydrophobic groups.[1-3] In aqueous solution, above a certain polymer concentration, intermolecular hydrophobic interactions lead to the formation of polymolecular associations. As a consequence, these copolymers exhibit thickening properties equivalent to those observed for higher molecular weight homopolymers. Under increasing shear, the physical links between chains are disrupted but re-form with decreasing shear. This way, it is possible to avoid the irreversible mechanical degradation which occurs for very high molecular weight samples when subjected to high shear stresses.[4] Furthermore, the reversible association/dissociation process gives rise to particular rheological behaviors as a function of shear rate or shear time. Such shear thinning and thixotropic properties are of great technological importance especially in applications on water-based systems which involve a viscosity control.[5-8]

As a consequence, in the past few years, there has been an increasing interest into the synthesis and properties of hydrophobically modified water-soluble polymers. The preparation of such materials can be carried out, as for any copolymer synthesis, either by chemical modification of a preformed polymer or by copolymerization of the appropriate monomers or by a combination of both methods. The former synthesis route has mainly been applied to cellulose derivatives,[9,10] to poly(oxyethylene) (which leads to the so-called HEUR thickeners,[11-13] i.e., Hydrophobically modified Ethoxylated URethane polymers), and, more recently, to poly(acrylic acid).[14] The copolymerization processes concern essentially acrylamide-based copolymers.[15-44] In this case, some difficulties in the copolymer synthesis arise from the insolubility of the hydrophobic monomer in water. To overcome this problem, it was proposed[15,16] to use an aqueous surfactant solution which ensures the solubilization of the hydrophobe within micelles. This "micellar" process was shown to be well suited for the preparation of copolymers with improved thickening properties.[15-18,20,23-30] However, although many published works deal with copolymers synthesized by this micellar technique,[15-37] the specific features of this process have rarely been recognized. An important point which was only recently examined is how the copolymer microstructure is affected by the presence of the surfactant micelles during the synthesis. In the original papers, a random structure was implicitly admitted,[18-20] and in subsequent papers the problem of the structure of the copolymers was sometimes just mentioned[23,27,28] or generally neglected. The formation of a blocky structure was first suggested by Peer.[22] Direct experimental evidence of this blocky structure was reported by Thomas et al.[32] and McCormick et al.[31,37] from photophysical studies on polyacrylamide derivatives containing either styryl[32] or pyrenyl[31,37] groups as hydrophobes. Thus it was shown that samples prepared under micellar conditions exhibit a stronger excimer to monomer fluorescence ratio than samples prepared in homogeneous solution. As excimer formation is favored when fluorescent chromophores are in close proximity, the photophysical behavior of the copolymers prepared using the micellar process was consistent with the presence of adjoining hydrophobic units along the backbone. Using the same photophysical technique on naphthalene-labeled polyacrylamides, McCormick and co-workers have further shown that the length of the hydrophobic blocks was directly related to the hydrophobe-to-surfactant ratio.[36] Additional evidence of the main role of the surfactant was also provided in a concurrent work from our laboratory.[30] In this study we clearly established that the thickening properties of hydrophobically modified polyacrylamides were strongly dependent on the experimental conditions of the synthesis.

In this paper, we present the results of a more detailed investigation on the synthesis–structure–property relationships for acrylamide-based copolymers. *N*-4-Ethylphenylacrylamide (eΦAM) has been chosen as the hydrophobic comonomer because its hydrophobicity is not too high and its UV activity allows the accurate determination of the copolymer composition.[19,30,34,44] Different methods of preparation, with or without surfactant, are compared, and the micellar process is studied in detail by varying the formulation of the initial reaction mixture. The copolymer molecular weights have been carefully

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Table I. Conditions for the Synthesis and Physical Properties of the Polymers

			polymerization parameters[a]			polymer characterization		
copolymerization process	series	sample	[eΦAM][b]	[SDS][c]	other additives	[eΦAM][d]	$M_w \times 10^{-6}$ [e]	solubility in water[f]
homogeneous	I	1-F10	1	0	formamide	0.99	1.2	++
	II	075-S3	0.75	3		0.71	1.8	++
		1-S3	1	3		0.98	1.7	+
		2-S3	2	3		1.85		-
		3-S3	3	3		2.80	1.5	--
micellar	III	1-S1	1	1		1.07	1.7	--
		1-S1.5	1	1.5		0.98	2.9	-
		1-S2	1	2		0.92	2.0	+
		1-S3′	1	3		0.98	1.9	+
		1-S5	1	5		1.00	1.3	++
	IV	1-S3-Na02	1	3	[NaCl] = 0.2 M	0.98	2.1	+
		1-S3-Na05	1	3	[NaCl] = 0.5 M	0.94	1.9	+
heterogeneous	V	1-S0	1	0		1.01	(2.0)	++
		2-S0	2	0		1.86	(1.8)	±
		3-S0	3	0		2.57	(1.5)	●
homopolyacrylamides		PAM-S0	0	0			2.1 (2.1)	++
		PAM-S1	0	1			2.3 (2.2)	++
		PAM-S3	0	3			1.9 (1.9)	++
		PAM-S5	0	5			1.4 (1.6)	++

[a] Total monomer concentration = 3 wt %; $[K_2S_2O_8] = 3.3 \times 10^{-4}$ M; $T = 50$ °C. [b] Mole percent in the feed = [eΦAM]/([AM] + [eΦAM]). [c] SDS weight percent in the feed, based on volume of water. [d] Molar composition = [eΦAM]/([AM] + [eΦAM]), determined by UV analysis. [e] Molecular weight determined by light scattering in formamide. Values in parentheses have been determined by viscometry. [f] ++, easily soluble; +, soluble; ±, cloudy solution; -, difficult to dissolve; - -, ≃insoluble.

determined to provide a valid comparison of the various samples. We have investigated how the experimental conditions of the synthesis could affect the hydrophobe distribution within the copolymer, which in turn should alter the aqueous solution properties. For this purpose, we have studied (i) the viscometric behavior in dilute solution, (ii) the rheological behavior as a function of shear rate and polymer concentration in the semidilute range, and (iii) the formation of hydrophobic microdomains in solution by means of a fluorescence technique.

Experimental Section

The sources and the purification of the monomers and other reagents have been reported elsewhere.[44]

Polymerization. Various series of acrylamide/*N*-4-ethylphenylacrylamide (AM/eΦAM) copolymers were synthesized using three different processes. These are described in detail in the Results and Discussion. The characteristics of the copolymers are reported in Table I. The main variable parameters are either the hydrophobe level or the nature and amount of the additives within the aqueous medium (surfactant, salt, organic cosolvent). All other experimental parameters were kept constant: the overall concentration of monomers (3 wt %), the temperature (50 °C), and the nature and the concentration of the initiator ($K_2S_2O_8$ at 0.3 wt % relative to the monomer feed). The polymerization reactions were always conducted to nearly complete conversion.

For reference, homopolyacrylamides (PAM) were prepared under identical experimental conditions in the presence of variable amounts of surfactant.

The experimental procedure used for the micellar process was as follows. The reaction vessel consisted of a 1-L thermostated double-wall reactor fitted with a condenser, mechanical stirrer, rubber septum cap, and nitrogen inlet/outlet. The reactor, containing sodium dodecyl sulfate (SDS) and eΦAM, was purged with nitrogen during 0.5 h, while nitrogen was also bubbled separately through the aqueous acrylamide solution within a flask connected to the reactor. Then the acrylamide solution was transferred into the reaction flask, and the mixture was heated to 50 °C under stirring. This procedure was preferable to the direct deaeration of the reaction mixture owing to the strong foaming ability of the surfactant solution. When the mixture was homogeneous (within ≃0.5–1 h, depending on the amounts of the hydrophobic monomer and surfactant), the aqueous solution of $K_2S_2O_8$ was injected with a syringe. The reaction was run for 7 h. At this stage, the conversion determined gravimetrically was about 90%, in agreement with literature data on the kinetics of the acrylamide homopolymerization.[45] A more detailed investigation on the kinetics of the micellar copolymerization has been previously published.[44]

For the two other methods of synthesis, the procedure was essentially analogous to that described above. In the homogeneous process, it was important to dissolve first eΦAM in formamide before adding the aqueous AM solution.

After cooling the final reaction mixture, the polymer was precipitated by dropwise addition into an 8-fold excess of methanol. The polymer recovered by filtration was repeatedly washed in methanol under stirring, then dried several days at 40 °C under vacuum, and stored in a desiccator.

Copolymer Characterization. The molecular weight and composition data reported in Table I were determined using classical light scattering and UV spectroscopy according to the procedure previously described.[44] Attempts to determine the molecular weight distribution by size exclusion chromatography were not successful due to the high molecular weight values and adsorption phenomena on the columns. Molecular weights of PAM were also determined from intrinsic viscosity measurements (see below).

Viscometric Study in Dilute Solution. The intrinsic viscosities [η] of the (co)polymers were determined in 0.1 M NaCl aqueous solution at 25 °C. Measurements were carried out using an automatic capillary viscometer (Ubbelohde type) at polymer concentrations in the range 0.02–0.13 g/dL. From molecular weight values ($<2.5 \times 10^6$) and [η] values (<550 cm³/g), it is inferred that the shear rate imposed in the capillary does not affect the viscosity data.[46] In these experiments, care must be taken to avoid foaming of the copolymer solutions, which would result in erroneous flow times.

Rheological Measurements in Semidilute Solution. Viscosity–shear rate measurements were performed at 20 °C in the polymer concentration range 1–3 wt %. Polymer solutions were prepared by dissolution of the samples in pure water at room temperature at appropriate weight/weight concentrations. No agitation was applied during the first day of dissolution (swelling of the polymer); then homogenization was ensured by magnetic stirring for another day. Prior to measurements, the solutions were still kept for 2 more days to eliminate air bubbles.

A Carri-Med CLS-100 controlled-stress rheometer was used with a cone–plate geometry (diameter 6 cm, with either a 1° angle acrylic cone or a 2° stainless steel cone). The instrument was interfaced with a personal computer and driven by a software package (Carri45) supplied by the manufacturer. Flow curves were recorded using the usual stress scanning mode: first by increasing linearly the imposed torque from zero to a predefined maximum and then by varying the torque in the reverse way. The shear rate $\dot{\gamma}$ ranged from 0.1–10 s^{-1} to 1000–2500 s^{-1} depending

on the viscosity of the sample. Generally, a ramp time of 7 min was used for both up and down curves. Inertial effects, which may lead to experimental artifacts in this type of measurement, were taken into account according to the method of correction proposed by Krieger.[47] Additional data points at lower shear rates were obtained by using another method. The latter is a creep measurement under low and constant stress which leads to a linear variation of the strain versus time. The slope of the curve corresponds to the steady shear rate. Thus, the viscosity can be measured at different low shear rates by repeating stepwise measurements at defined stress values.

Fluorescence. A sufficient amount of an ethanolic stock solution of pyrene was evaporated within a flask under a stream of N_2 before adding the polymer solution in such a way that the final pyrene concentration was 10^{-6} M. Solutions were allowed to equilibriate for 24 h prior to fluorescence runs. In an alternative way, the polymer was dissolved in a saturated and previously filtered aqueous solution of pyrene ([pyrene] $\simeq 5 \times 10^{-7}$ M).

Steady-state fluorescence measurements were performed on air-equilibrated solutions at 25 °C using a Hitachi F-4010 spectrophotometer. The excitation wavelength was 335 nm; the first and third peaks of the pyrene emission spectra were situated at 374 and 385 nm, respectively.

It was observed that the pyrene emission spectra of copolymer solutions were progressively modified under continuous illumination (I_3/I_1 decreases by $\simeq$5–10% within 10 min), while this behavior did not appear for other pyrene solutions without polymer. After cutting off the excitation light for a few minutes, the initial I_3/I_1 value was recovered. Therefore correct data were assumed to be those recorded immediately after allowing the sample to equilibrate for 5 min in the apparatus without any excitation light. The origin of this photoprocess also observed by others[48,49] was not pursued.

Results and Discussion

Description of the Copolymerization Processes. The usual way for preparing polyacrylamide is a free-radical polymerization in aqueous solution.[50] However, in the present case, the experimental conditions of the copolymerization are necessarily different, since the hydrophobic monomer is insoluble in water.

In this study, we have investigated three processes which differ mainly in the way the hydrophobic monomer is dispersed within the aqueous medium: (i) it is solubilized by addition of a cosolvent (homogeneous polymerization); (ii) it is solubilized by addition of a surfactant (micellar polymerization); (iii) it is dispersed in the aqueous solution, without any additive (heterogeneous polymerization). The sample code given in Table I refers to the conditions of synthesis. For example, 1-S3 is a sample containing one mol % of eΦAM and prepared by using three wt % of SDS.

Homogeneous Copolymerization. The use of another solvent instead of water is the simplest way to overcome the problem of the insolubility of the hydrophobic monomer in the aqueous medium. There are few common solvents for the two monomers, e.g., methanol, ethanol, chloroform, acetone, and formamide. Furthermore, there are only a small number of solvents for polyacrylamide other than water (formamide, ethylene glycol, and morpholine).[50,51] Note that the case where the initial mixture is homogeneous but the polymer formed is insoluble in the reaction medium[31,32] (precipitation polymerization) has not been considered in this work. Indeed it was previously reported that such experimental conditions preclude the formation of sufficiently high molecular weight polymers.[18] A possibility to achieve the solubilization of the components of the reaction is to use a mixture of solvents, especially those based on water. In the choice of an organic (co)solvent, there is another constraint due to the possibility of chain transfer reactions leading to a lowering of the molecular weights.

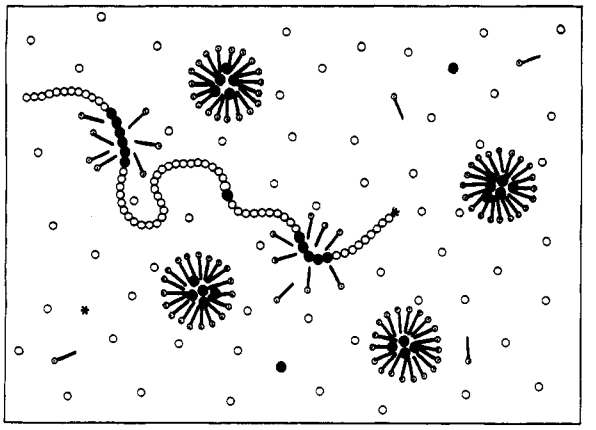

Figure 1. Schematic representation of the reaction medium for the micellar copolymerization: ○, acrylamide; ●, hydrophobic monomer; —⊙, surfactant; *, initiator.

Homogeneous copolymerization has been investigated using water and three different cosolvents: morpholine, ethylene glycol, and formamide. For each system we have attempted to minimize the amount of cosolvent to keep at the lowest level eventual chain transfer reactions.

Morpholine is the best solvent for ethylphenylacrylamide. Even very low morpholine concentrations in water ($\simeq$3 vol %) were sufficient to obtain a homogeneous initial medium. However, whatever the morpholine content, no polymerization occurred.

With ethylene glycol it was important to reduce its proportion in the aqueous mixture because alcohols are known to be efficient transfer agents. On the other hand, relatively large amounts of ethylene glycol ($\simeq$25 vol %) are required to achieve the dissolution of ethylphenylacrylamide. Under these conditions, the molecular weights obtained were too low ($\simeq$200 000) for the purpose of this study.

The water–formamide mixture was found to be well suited for the preparation of high molecular weight polymers ($>10^6$). Although no systematic study of the optimal conditions was performed, the composition of the mixture selected was 90% water/10% formamide (by volume).

Micellar Copolymerization. In this process, initially reported by Evani[15] and Turner et al.,[16] the hydrophobic monomer is solubilized within surfactant micelles, whereas acrylamide is dissolved together with the potassium persulfate initiator in the aqueous continuous medium (Figure 1). The surfactant used in this study was sodium dodecyl sulfate (SDS) at concentrations between 4 and 20 times its critical micelle concentration (cmc). The reaction mixture is optically transparent, but it must be emphasized it is actually a microheterogeneous system. Below are outlined the major differences between this process and the more conventional polymerizations carried out in the presence of a surfactant, i.e., emulsion or microemulsion processes.

(i) In an aqueous emulsion polymerization, the amount of surfactant is low with respect to that of the hydrophobic monomer. On the contrary, in the present micellar process, the surfactant over hydrophobe ratio is quite high (typically in the range 15/1 to 70/1 by weight).

(ii) A direct emulsion (co)polymerization implies a low water solubility of the monomer(s); i.e., the monomers are essentially located in the dispersed phase (large monomer droplets and small micelles). The situation is quite different for the micellar copolymerization, since the major part of the monomeric species, i.e., acrylamide, is soluble in the aqueous continous phase; the hydrophobic monomer

located within the micelles represents only a very small fraction of the total monomer feed (≃2–7 wt %).

(iii) In the micellar process, the two monomers are segregated into two distinct phases due to their very different solubilities. As discussed later in this paper, such a situation affects the mechanism of the copolymerization.

(iv) In the micellar process, the copolymerization reaction occurs in both the continuous phase and the dispersed phase. Therefore, although this process was called "micellar copolymerization", it involves in fact a combination of a micellar polymerization and a solution polymerization. In this respect the name "micellar polymerization" is somewhat ambiguous since a true micellar polymerization actually occurs when all of the monomer is located exclusively in swollen micelles.[52,53]

(v) The final reaction mixture is not a latex (i.e., a fluid dispersion of insoluble polymer particles in water), but a homogeneous, clear, and strongly viscous polymer solution. Besides, the copolymerization of a hydrophilic and a hydrophobic monomer by an emulsion process gives a latex functionalized with hydrophilic groups because of the reverse proportion of the two monomers (examples of such systems are styrene/carboxylic monomers,[54] styrene/acrylamide,[55] and styrene/sodium styrenesulfonate).[56]

Heterogeneous Copolymerization. In this process, ethylphenylacrylamide is dispersed as a fine powder in the acrylamide aqueous solution under stirring. As the polymerization proceeds, the solid particles are progressively consumed while the viscosity of the reaction medium increases. At the end, the aspect of the reaction mixture depends on the initial amount of ethylphenylacrylamide. For a copolymer with a very low hydrophobe content (1 mol %) the final solution appears quite homogeneous. This result shows that the incorporation of the hydrophobe in the polyacrylamide chains is possible, despite its initial rough dispersion in the medium. Attempts to prepare copolymers with a higher hydrophobe content (2–3 mol %) led to somewhat cloudy solutions, due to the presence of a small insoluble fraction. Even when the reaction time was increased, (above 7 h), the insoluble part did not disappear. In fact, this is not surprising because, at this stage, the majority of the acrylamide is already converted to polymer.[44,45] In spite of the strong limitation on the hydrophobe level, this heterogeneous process could appear as an interesting alternative method for the preparation of hydrophobically modified copolymers. However, it is unclear whether an insufficient dispersion of the hydrophobic grains will affect the reproductibility of the experiments.

Proposed Mechanism–Microstructure Relationships. Guided by the specific features of the three copolymerization processes described above, we can postulate a mechanism for each reaction and its influence on the copolymer structure.

Homogeneous Copolymerization. It is expected that hydrophobes are singly and randomly distributed along the polymer backbone. Due to the very small amount of the hydrophobic monomer in the reaction medium, it is obvious that the probability is low for a macroradical terminated by a hydrophobic unit to find another hydrophobic monomer before reacting with any acrylamide molecule. The possibility for a growing polymer chain to add successively two hydrophobic units could only be increased if the reactivity ratios of the monomer pair are strongly in favor of *N*-ethylphenylacrylamide.

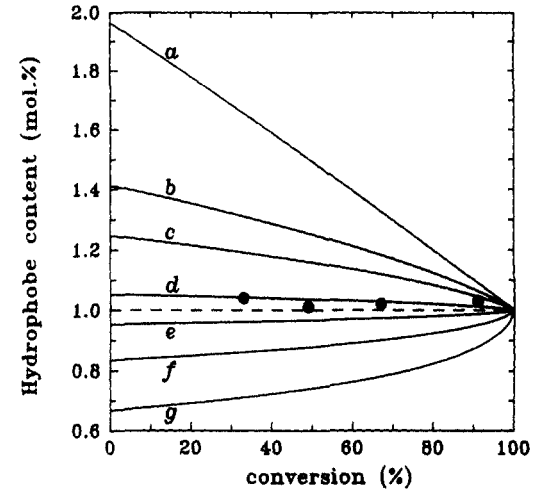

Figure 2. Average cumulative composition of the copolymer as a function of the conversion: (●) experimental data[44] for the eΦAM/AM system (1/99 by moles) in the homogeneous water–formamide mixture (10/90 by volume); (- - -) random copolymerization ($r_A = r_B = 1$); (—) theoretical curves for various reactivity ratio pairs r_A/r_B (a, 1.2/0.5; b, 0.7/0.7; c, 1.2/0.8; d, 1.05/0.95; e, 0.95/1.05; f, 0.8/1.2; g, 0.5/1.5).

These intuitive considerations can be more quantitatively expressed by the following relations:[57a]

$$P_{AA} = \frac{r_A}{r_A + (1/f_A - 1)}$$

$$\bar{n}_A = 1 + \frac{r_A f_A}{1 - f_A}$$

where the subscript A refers to the hydrophobic monomer, P_{AA} is the probability of forming a diad AA, r_A is the reactivity ratio, $\bar{n}_A$ is the number-average sequence length, and f_A is the mole fraction of species A.

As f_A is kept low (<0.03), it can be easily shown that even with an unlikely large value of r_A, the value of P_{AA} is low and $\bar{n}_A$ is always nearly equal to unity; i.e., hydrophobes should be effectively singly distributed.

Although reactivity ratios have not been determined, it is reasonable to assume a rather similar reactivity for both monomers since they bear an identical acrylamide functional group. An indirect evidence of this assumption is given by another study from our laboratory[44] in which it was shown that for the homogeneous copolymerization the copolymer composition is constant as a function of monomer conversion. In Figure 2, the experimental data from Biggs et al.[44] are compared with the theoretical composition–conversion curves. These curves were calculated from the well-known Mayo–Lewis and Skeist equations[57b] using a computing procedure analogous to that proposed by others authors.[58] It is clear that the constancy of copolymer composition with conversion implies that both reactivity ratio values are close to unity.

Micellar Copolymerization. In this particular process, the important question to be addressed is how the initial monomer segregation affects the hydrophobe distribution in the copolymer. In contrast to the previous process, a random distribution cannot be assumed only from criteria based on a low hydrophobe level and similar monomer reactivities; the initial microphase separation of the monomers should be the main factor which controls the monomer sequence distribution. Under the experimental conditions used, the estimated number of hydrophobe molecules solubilized within each micelle is always greater than unity (cf. Table IV). In other words, micelles behave as microdomains with a concentration of hydro-

phobe much greater than that in the bulk solution (Figure 1). Therefore, a random monomer distribution should fulfill the following requirements: (i) the water-borne free radicals should not come into contact with the micelles; (ii) the copolymerization reaction should exclusively occur in the aqueous continuous phase; (iii) the incorporation of the hydrophobic monomer could only result from its progressive migration from the swollen micelles to the aqueous phase. The achievement of all these requirements is unrealistic. The possibility of a copolymerization in the aqueous continuous phase cannot be fully excluded because a small amount of the hydrophobic monomer is always present in the aqueous phase as a result of the partitioning of ethylphenylacrylamide between the micelles and the intermicellar solution. Nevertheless this kind of reaction leading to the incorporation of single hydrophobe units into the polyacrylamide chain should only represent a small part of the copolymerization process. Indeed, due to the large interfacial area between the continuous phase and the dispersed phase, there is a high probability for the growing radical head group to diffuse into the interfacial layer region of the micelles.

From these considerations, the most probable reaction mechanism is the following: (i) potassium persulfate initiates the polymerization of acrylamide in the aqueous phase; (ii) when a growing macroradical head group encounters a monomer-swollen micelle, it adds several hydrophobe molecules inside the micelle to form a short hydrophobe block; (iii) the radical head group may then leave the micelle and the polymerization proceeds with acrylamide until another micelle is encountered to form again a hydrophobic block. These steps are repeated many times because the average lifetime of a growing polyacrylamide radical is relatively high. This is due to a high ratio of the rate constants for propagation over termination and to a small chain transfer constant in water.[45]

The conclusion is that a rather blocky structure will form (Figure 1). A somewhat similar mechanism was also suggested by Peer[22] for a slightly different system. This author used an oil-soluble initiator which was therefore located inside the micelles and not in the continuous aqueous phase as with the water-soluble initiator used here.

According to the above-proposed scheme, the key parameter is the number of hydrophobe molecules per micelle. Both the length and the number of hydrophobic blocks can be modified by varying the surfactant/hydrophobe ratio. A random copolymer structure might even be expected by using a high surfactant/hydrophobe ratio in such a way that each micelle is at the most occupied by a single hydrophobe.

Against such a mechanism, it could be argued that the surfactant layer in the micelle may act as a barrier between hydrophobic and hydrophilic monomers. Another reason to suspect a relative inaccessibility of the hydrophobes is that the initiating radicals are produced in an aqueous acrylamide solution, leading to the formation of polyacrylamide macroradicals; the water-soluble nature of these macroradicals could prevent their penetration into the hydrophobic micellar region, whereas in emulsion and microemulsion polymerizations, primary radicals generated in the aqueous phase can easily diffuse into the micelles. If both arguments were valid, this should prevent a growing polymer chain to consume alternatively the two monomers solubilized within the micelles and in the continuous phase, respectively. In fact, the micellar interfacial region is not a pure monolayer of SDS but actually contains a noticeable amount of both monomers.

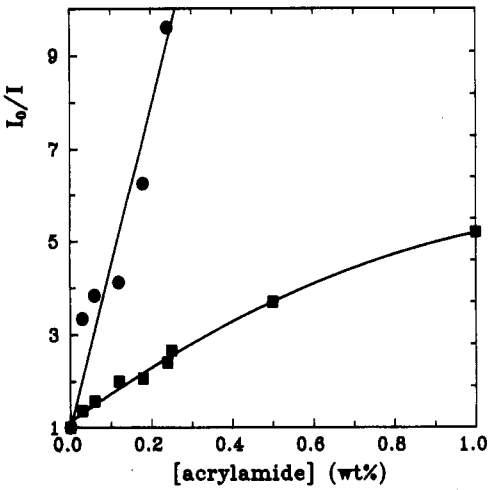

Figure 3. Relative intensity of the pyrene fluorescence as a function of acrylamide concentration in aqueous solution (●) and in SDS aqueous solution, 3 wt % (■). (I_0 and I are the steady-state fluorescence emission intensities without and with acrylamide, respectively. [Pyrene] = saturated aqueous solution, i.e., $\simeq 5 \times 10^{-7}$ M).

This was suggested by a previous work from our laboratory where it was shown that acryalmide behaves as a cosurfactant in some micellar systems.[59] The same should hold for eΦAM, which is probably not exclusively confined in the core of the micelles. Further evidence for the penetration of acryamide into the surfactant layer of the micelle was also obtained from fluorescence measurements using pyrene as a probe. As shown in Figure 3, acrylamide is a strong quencher of the pyrene fluorescence in aqueous solution. In the case of micellar SDS solutions, the quenching is reduced, but still effective. It is well known that pyrene, due to its hydrophobic character, is preferentially located within the micelles in order to get a more favorable hydrophobic environment.[60] Fluorescence results show that the micellar palisade layer does not prevent acrylamide from coming into the vicinity of pyrene solubilized in the micelles. A different behavior was reported by Dowling and Thomas,[32] who infer from similar fluorescence experiments that the penetration of cetyltrimethylammonium bromide micelles (CTAB) by acrylamide was nominal.

The interfacial micellar layer is therefore a region where both monomer species are in close proximity. Such a situation is favorable to the growth of a polymeric chain successively and repeatedly inside and outside the micelles. In any case, it must be emphasized that, as opposed to the emulsion polymerization, a macromolecular chain never penetrates completely inside a micelle. When a growing end encounters a micelle, the greatest part of the chain, i.e., water-soluble polyacrylamide, remains in the aqueous phase while the monomers contained within the micelles are polymerized.

Note that the above mechanism is oversimplified. Other parameters must be taken into account and in particular the dynamics of the micellar system. A more detailed investigation on the kinetics of the reaction and on the way of incorporation of the hydrophobes in the copolymer was previously published.[44] The main conclusions are summarized below: (i) The solubilization of the hydrophobic monomer within the micelles does not reduce its accessibility to growing radicals generated in the bulk solution, but in fact it leads to an apparent greater reactivity. The hydrophobe is more rapidly incorporated into the polymer chain at the early stages of the reaction; the higher the hydrophobe/surfactant ratio, the faster is

the rate. This behavior was accounted for by the hydrophobe transfer between micelles. 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. Consequently, during the residence time of a radical head group in a micelle, there is a flux of eΦAM molecules toward this micelle. This leads to longer hydrophobic blocks than if only the initial content of one micelle was polymerized. (ii) Another question was the future of the surfactant after consumption of the micellar content. It is expected that surfactant–copolymer interactions will compete with a redistribution of the hydrophobes between swollen and empty micelles. If the latter phenomenon is predominant, one should get an additional drift in the length of the hydrophobic blocks toward shorter blocks as a function of the degree of conversion. (iii) A consequence of the partial intermixing of the monomer in the interfacial micellar region is that the hydrophobic blocks of the copolymer are not only formed of pure eΦAM but should also contain a few acrylamide units (tapered structure).

In conclusion, although the average length of the hydrophobic blocks should depend on the initial number of hydrophobic monomers per micelle, there is not a straightforward relationship between these two parameters. It should however be noted that even by taking into account the above refinements on the postulated reactional scheme, the overall mechanism–microstructure relationship is mainly unaffected. The picture of the copolymerization process is still a random walk of the propagating species in the aqueous solution to form long hydrophilic sequences interrupted by more or less short hydrophobic blocks formed during encounters with the micelles.

Heterogeneous Copolymerization. It is believed that the polymerization occurs almost exclusively in the aqueous phase and not within the solid monomer particles (at least in the first stages of the reaction). This assumption is based on the following reasons. First, the initiator is water soluble. Second, the size of the insoluble particles is relatively large and therefore the total area of the solid–liquid interface is small. As a result, the insoluble monomer particles are not very effective in capturing free radicals. This behavior is to be opposed to that of the micellar process where the eΦAM swollen micelles are favorable reaction sites.

From the above considerations, the copolymerization in solution is made possible owing to the slight solubility of the hydrophobic monomer in water. The solubility of ethylphenylacrylamide measured by UV spectrophotometry at 25 °C is 0.36 g/L, and this value should be higher at the temperature of the polymerization (50 °C). In spite of this low solubility a relatively large fraction of the hydrophobe is actually solubilized in water because of the low level of eΦAM in the reaction mixture. For example, at 1 mol % hydrophobe based on the total monomer feed, more than half of the eΦAM molecules are dissolved in the acrylamide solution and these molecules can add onto the growing polyacrylamide radicals. The hydrophobe concentration in water is maintained at the saturation level by diffusion from the solid particles. According to this scheme, one expects a copolymer with a random structure as for the homogeneous process.

The too low solubility of the hydrophobic monomer and the high polymerization rate of acrylamide are nevertheless the limiting factors in this process, as also noted by other authors[18] for monomers with a stronger hydrophobic character like *N*-dodecylacrylamide. In our case, when higher eΦAM content are used, the whole dissolution of the hydrophobe particles cannot be achieved before the completion of the acrylamide polymerization. Under these conditions, in the last stage of the reaction, the possibility of a polymerization within the remaining monomer particles cannot be excluded. Then, the fine insoluble fraction found in the final mixture may well be formed by eΦAM polymer together with the unused hydrophobic monomer. The exact nature of the final insoluble fraction was not further investigated.

Table II. Intrinsic Viscosity [η] (mL/g) and Huggins Coefficient k_H for Copolymers and PAM in 0.1 M NaCl Aqueous Solution

series[a]	sample code	k_H	$[\eta]_{expt}$	$[\eta]_{calcd}$[b]
I	1-F10	0.35	300	340
II	075-S3	0.75	360	460
	1-S3	0.80	320	440
	2-S3	1.20	205	
	3-S3	1.30	160	400
III	1-S3′	0.90	330	480
	1-S5	0.45	340	360
IV	1-S3-Na05′	1.1	300	400
V	1-S0	0.45	490	
	2-S0	0.50	460	
	3-S0	0.40	400	
PAM	PAM-S0	0.42	520	515
	PAM-S1	0.46	530	550
	PAM-S3	0.45	470	480
	PAM-S5	0.42	430	380

[a] Series numbers are defined in Table I. [b] Calculated using the relationship $[\eta] = 9.33 \times 10^{-3} M_w^{0.75}$ established for PAM[46] and the M_w data from light scattering measurements given in Table I.

Polymer Characterization. Molecular Weight. The molecular weight of the modified polymers is a parameter of primordial importance with regard to their viscosifying properties, especially in the semidilute range. The theory predicts that the viscosity η varies as M^α with $\alpha = 1$ and 3.4 in dilute and semidilute solutions, respectively.[61] Experimentally it was found for polyacrylamide in aqueous solution[50] that $\eta \sim M^4$ for $M > 5 \times 10^5$ and polymer concentrations $C_p > 2$ wt %. That means for example that the viscosity is doubled when the molecular weight is just increased by 20%. This effect should be amplified in the case of associative polymers. Therefore, a meaningful comparison of the rheological properties of the various copolymers requires the knowledge of their molecular weights. This point has often been neglected in the previous studies and the molecular weights have rarely been determined accurately. Some authors[28,31a,32,39,62] have estimated molecular weights from intrinsic viscosity measurements in water, using the relationship established for the homopolymer. Such a procedure is questionable as it leads to more or less erroneous results. Indeed it was shown in other studies[10,18,20,31bc,63,64] and in this work (see Table II) that the conformation of a single hydrophobically modified coil is more compact than the unmodified water-soluble coil, due to hydrophobic intramolecular interactions. Therefore, the viscometric molecular weight values are underestimated and the extent of the error depends on the molecular characteristics of the sample. More reliable data can be obtained from light scattering experiments, providing supramolecular aggregates do not exist within the solution. In this respect, we have found[65] that formamide, in spite of a lower refractive index increment dn/dc, is a more appropriate solvent than water, classically used for polyacrylamide. The clarification of the solutions is much easier and Zimm plots exhibit the usual pattern.[44] On the contrary, in water some aggregates still remain even in very dilute solutions, which leads to higher and spurious M_w values.[65]

Examination of the data of Table I leads to the following comments:

(i) The molecular weights of copolymers prepared by micellar polymerization are similar to those of PAM obtained under identical conditions. Thus, a low level (1 mol %) of the hydrophobic comonomer does not noticeably change the acrylamide polymerization process. However, for higher hydrophobe content (sample 3-S3), the lowering in molecular weight may arise from increased radical transfer reactions onto the hydrophobic groups, as discussed elsewhere.[44]

(ii) At the highest surfactant content, both PAM and copolymer exhibit lower molecular weights. This may be ascribed to transfer reactions on the surfactant or to surfactant impurities. Indeed it is known that alcohols are always present within SDS,[66] as residual reagents from the synthesis or as subsequent hydrolysis products of the surfactant. Hydrolysis of SDS probably occurs to some extent under the polymerization conditions (several hours at 50 °C).

(iii) The polymerization in the solvent mixture (1-F10) gives rise to lower molecular weights in accordance with literature data.[67]

(iv) For copolymers prepared by the heterogeneous process, the light scattering data are not reliable due to the presence of large particules with a high hydrophobe content. The molecular weights have been evaluated from viscometric data. This is justified in this case because, as shown later in this paper, such copolymers do not present significant hydrophobic interactions.

Copolymer Composition. In the case of the heterogeneous copolymerization at the highest hydrophobe levels, the incorporation of the hydrophobic monomer is incomplete, as expected from the final aspect of the reaction medium. In all other cases, there is a good agreement between the composition of the monomer feed and the final composition of the copolymer (Table I). However, these average values do not reflect the compositional heterogeneity of the samples. In another study from our laboratory,[44] it was found that the micellar process leads to an inherent polydispersity in composition depending on the [hydrophobe]/[micelle] ratio.

Copolymer Microstructure. NMR spectroscopy is a method commonly used for the determination of copolymer microstructures. In the present case, the technique is not sensitive enough due to the very low hydrophobe content ($\simeq$1 mol %). However, information on the microstructure of copolymers was indirectly obtained from a study on their solution properties, as shown below.

Solubility of Copolymers in Water. A first qualitative indication of the effect of the polymerization procedure on the copolymer microstructure was gained from the preparation of the aqueous polymer solutions.

In the case of micellar copolymerization, the redissolution in water of copolymers recovered by precipitation is often difficult. This is especially true for copolymers of series II (cf. Table I) prepared at variable hydrophobe levels. For the highest hydrophobe contents (>1 mol %), gel-like particules remain in suspension and do not disappear even after prolonged heating under vigorous stirring. Similar dissolution problems were also reported for other types of hydrophobically modified water-soluble polymers.[9,10,23,26,27] However, such a behavior was generally observed for systems with a stronger hydrophobic character because of the presence of either a higher hydrophobe content or longer alkyl chain ($\geq C_{12}$). In the present case, it is evident that a very low number of small hydrophobic units should not induce such hydrophobic properties if these units were randomly distributed along the water-soluble chain. Indeed, for amphiphilic compounds, hydrophobic effects only occur above a certain critical size of the hydrophobic moiety. For example, in the case of polysoaps, side groups longer than a C_8 alkyl chain are generally needed to give rise to significant intramolecular hydrophobic interactions.[68,69] Audebert and co-workers[14] have also shown that the grafting of a small amount of alkyl chains onto a poly(sodium acrylate) modifies the solution properties provided that the alkyl chain exceeds eight methyl groups. In the present study, isolated ethylphenyl groups should not exhibit a strong hydrophobicity, whereas several adjoining units form larger and more hydrophobic sequences which should strongly reduce the solubility of the macromolecular chain in water. The effect of the blockiness on copolymer properties has been extensively investigated for many years. It is well established that di- or triblock hydrophilic/hydrophobic copolymers are very difficult to solubilize in water, even when the hydrophobic part is a small fraction of the polymeric chain;[70] on the other hand, random copolymers of similar composition are fully water-soluble.[71] The solubility properties of copolymers obtained via the micellar process are therefore in agreement with their presumed blocky structure. This is especially apparent for the copolymer series III prepared at constant hydrophobe content and variable amounts of surfactant. Sample 1-S5 prepared at the highest surfactant level is easily soluble in water, while for the lowest surfactant content, the recovered copolymer (1-S1) is insoluble in water. This strong modification of the solubility of polyacrylamide derivatives confirms that the length of the hydrophobic blocks is related to the number of hydrophobic monomers per micelle. In a study on the synthesis of acrylamide/styrene copolymers by a similar micellar process, Dowling and Thomas have reported analogous variations of the copolymer solubility in water as a function of the initial styrene/surfactant ratio.[32]

In the case of copolymers with the same composition but prepared by the homogeneous process, the dissolution in water is much easier, as for homopolyacrylamide. This behavior suggests a more random hydrophobe distribution. This is also true for copolymers obtained by the heterogeneous process, but the solution is slightly turbid due to the presence of a small insoluble fraction as discussed in the Synthesis section.

An interesting feature concerns copolymers with a poor water solubility. The redissolution is greatly facilitated by addition of SDS, which indicates the existence of surfactant/copolymer interactions such that SDS micelles provide the solubilization of the hydrophobic moieties of the copolymer. A similar behavior has been also reported for other hydrophobically modified water-soluble polymers.[9,10,23,72]

The other particularity of the aqueous solution is the high foaming ability, especially for copolymers prepared by micellar polymerization. This cannot be due to the presence of residual surfactant from the synthesis procedure because this behavior subsists even after an extensive purification of samples by repeated dissolution/precipitation cycles. Also, no significant amount of SDS is detected by elemental analysis of sulfur. Furthermore, copolymers obtained from heterogeneous and homogeneous processes also exhibit foaming properties, but to a lesser extent. This behavior reflects the amphiphilic nature of the copolymers.

Viscometric Study in Dilute Solution. In Table II are reported the intrinsic viscosity [η] and the Huggins

coefficient k_H of some copolymer samples. The values of $[\eta]$ for homopolymers of equal molecular weight are also given for comparison. Once again, the properties of hydrophobically modified polyacrylamides are shown to strongly depend on the way the hydrophobes are incorporated within the water-soluble chain. From the viscometric data, two kinds of copolymers can be distinguished: (i) the samples for which the values of k_H (about 0.4) and intrinsic viscosity are close to those of the corresponding polyacrylamides; (ii) the samples that present a k_H value higher than 0.7 and an intrinsic viscosity less than that of polyacrylamides.

The first type comprises copolymer series I and V (i.e., homogeneous and heterogeneous polymerizations, respectively) and the sample prepared in the presence of the highest surfactant content (1-S5). In these cases, viscometric data indicate that, despite the presence of hydrophobic groups, the samples behave as homopolyacrylamide. The values of k_H are similar to those commonly found for polymers in a good solvent (0.4–0.5).

The second type of copolymers corresponds to the samples obtained from the micellar process (series II, III, and IV) (except sample 1-S5). Compared to the former case, the higher values of k_H and the lower intrinsic viscosities reflect a reduced solvent quality. These measurements give quantitative support to the observations on the solubility properties. For a same hydrophobe content, the micellar process leads to copolymers which exhibit a higher hydrophobicity in comparison with the two other processes. The lowering in intrinsic viscosity reflects the contraction of the polymer coil because of intramolecular hydrophobic interactions. As expected, this effect is stronger upon increasing the hydrophobe level (see copolymers of series II).

The behavior in dilute solution confirms the mechanism/microstructure relationship postulated for each of the three processes. The differences in properties are consistently interpreted in terms of differences in hydrophobe sequence distribution. When the small hydrophobic groups are distributed as discrete units (heterogeneous and homogeneous processes), they do not exhibit their hydrophobicity and the conformation of the water-soluble macromolecule is not affected. (Note that a different behavior has been reported for other hydrophobe-containing water-soluble polymers;[31b,c] intramolecular interactions leading to a collapse of the coil were operative even when the hydrophobic units were singly distributed). More interestingly, by using a micellar copolymerization, the extent of the hydrophobic character can be modified while maintaining a constant hydrophobe level. Thus, depending on the micelle concentration, it is possible to obtain copolymers without a noticeable number of intramolecular interactions (sample 1-S5) as well as copolymers for which the hydrodynamic volume of the coil is markedly reduced due to intramolecular interactions (sample 1-S3′). These results provide further evidence that the initial number of hydrophobes per micelle governs the length of the hydrophobic blocks. This is also fully consistent with photophysical studies on copolymers containing fluorescent hydrophobic units and prepared under micellar conditions.[32,36]

Rheological Behavior in Semidilute Solution. The main goal of this study was to examine how the conditions of the synthesis could affect the thickening ability of the copolymers. This implied that we investigate the solution properties in the semidilute range, well above the critical overlap concentration C^*, where the intermolecular interactions significantly contribute to the viscosity. In addition, it was also of primordial importance to compare copolymers with the same overall composition, since the association process strongly depends on the hydrophobe content.[14,20,26–28,39,73]

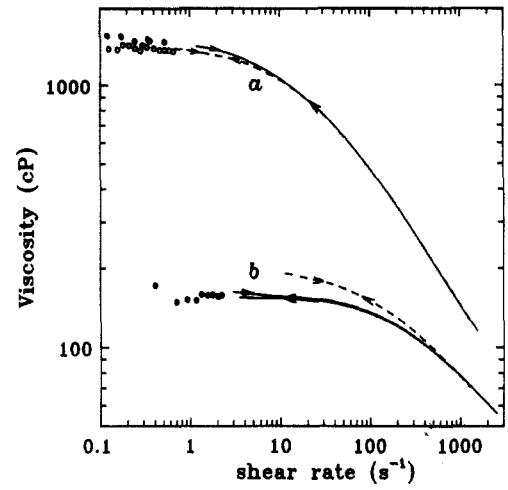

Figure 4. Apparent viscosity as a function of shear rate for solutions of copolymers (solid lines and filled symbols) and homopolymers (dashed lines and open symbols) at a concentration of 3 wt %: (a) copolymer 1-S0, heterogeneous copolymerization (●, —) and PAM (○, - - -) ($M_w = 1.9 \times 10^6$); (b) copolymer 1-F10, homogeneous copolymerization (●, —) and PAM (- - -) $M_w = 1.2 \times 10^6$). (Lines represent the data obtained under increasing and then decreasing shear stress; circles are data from "low-shear" measurements.)

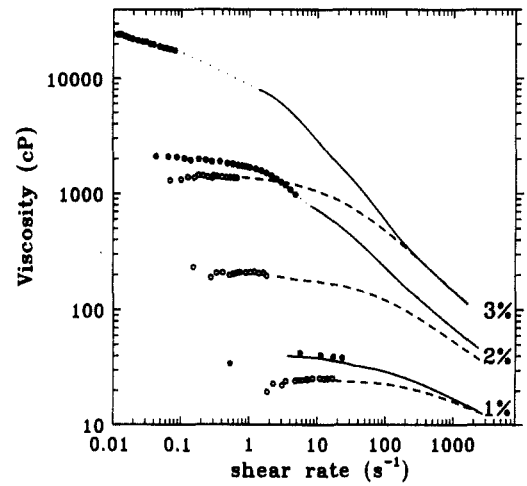

Figure 5. Apparent viscosity as a function of shear rate for solutions at three different concentrations (1, 2, and 3 wt %) in copolymer 1-S3′ synthesized by micellar polymerization (●, —) and homopolymer PAM-S3 (○, - - -). (Lines represent data obtained under increasing shear stress; circles are data from "low-shear" measurements.).

The three processes do not generally provide copolymers of the same molecular weights, so that a direct comparison of their thickening properties is not always possible. Therefore, to test the effect of the method of synthesis, we compared the results obtained for each copolymer with those of a similar molecular weight polyacrylamide. The variation of the apparent viscosity as a function of the shear rate $\dot{\gamma}$ is shown for three copolymers with the same hydrophobe content (1 mol %) synthesized by heterogeneous (Figure 4a), homogeneous (Figure 4b), and micellar copolymerizations (Figure 5), respectively. In each case, the flow curves obtained with the corresponding homopolymer are also given for reference. The data were obtained by using the three successive experimental procedures: (i) at given low shear rates; (ii) upon scanning of increasing shear rates; (iii) upon scanning of decreasing

Table III. Viscometric Data for a Copolymer and a Homopolymer as a Function of Concentration and Shear Rate $\dot{\gamma}$

polymer concn, wt %	copolymer 1-S2			homopolymer PAM-S3			η_{cop}/η_{PAM} at $\dot{\gamma}_0$	η_{cop}/η_{PAM} at $\dot{\gamma}_{1000}$
	η_0[a]	η_{1000}[b]	η_0/η_{1000}	η_0	η_{1000}	η_0/η_{1000}		
1	42	16.5	2.5	24	16	1.5	1.75	1.03
2	2000	65	31	200	55	3.6	10.0	1.18
3	≃30000	150	200	1400	144	9.7	21.4	1.04

[a] η_0 = viscosity (cP) extrapolated to zero shear ($\dot{\gamma}_0$). [b] η_{1000} = apparent viscosity (cP) at $\dot{\gamma}$ = 1000 s^{-1} ($\dot{\gamma}_{1000}$).

shear rates (see Experimental Section). Again, the copolymers prepared by the micellar process exhibit a particular behavior compared to that of either the homopolymers or other copolymers.

In the case of heterogeneous and homogeneous copolymerizations (Figure 4a,b), no improvement in the thickening properties is observed when compared to the polyacrylamides. In both cases, the flow curves correspond closely within the experimental accuracy. The overall rheological behavior corresponds to the classical pattern of semidilute polymer solutions, as previously described, for example, for polyacrylamide in water.[50] Characteristic features are the Newtonian plateau at low shear rates and the shear-thinning effect caused by the orientation and the disentanglement of the macromolecular chains under shear. Additionaly, these results stress the importance of the molecular weight. The lower thickening ability for sample 1-F10 compared to 1-S0 (nearly 1 order of magnitude) is only due to a lower molecular weight (M_w ratio ≃ 0.63). For both samples, the zero shear rate viscosity varies as $M_w^{4.1}$, which is close to the behavior reported in the literature.[50]

On the contrary, the data in Figure 5 show that the copolymer prepared by the micellar process gives rise to enhanced viscosifying properties in the low-shear region; the higher the concentration, the larger is the effect. This is a clear indication that hydrophobic interactions occur between chains, which leads to polymolecular structures with a high hydrodynamic volume. Furthermore, the shear-thinning behavior is much more pronounced since at the highest shear rates, the copolymer and the homopolymer solutions present an identical viscosity. This considerable loss in viscosity for the copolymer corresponds to the progressive rupture of the intermolecular associations upon increasing the shear rate, and these are no longer effective at the highest shear values. The shear-thinning behavior can be expressed by the ratio η_0/η_{1000}, where η_0 and η_{1000} are the viscosities extrapolated to zero shear and measured at $\dot{\gamma}$ = 1000 s^{-1} respectively. The effectiveness of the intermolecular association can also be related to the ratio of the viscosities given by the copolymer and a homopolymer of the same molecular weight. These parameters are reported in Table III for different polymer concentrations. These data show that (i) the degree of association increases strongly with copolymer concentration and (ii) the hydrophobic associations vanish at high shear rate for all copolymer concentrations. Such a typical behavior has been previously described for other associating polymers.[2,3,7,8]

Another interesting feature which has rarely been investigated[23,26,27,30] concerns the reversibility of the rheological measurements under increasing and decreasing shear. For both homogeneous and heterogeneous copolymerizations, the samples exhibit a classical rheological behavior; i.e., the curves obtained under increasing and decreasing ramps are fully superimposed (Figure 4). Note

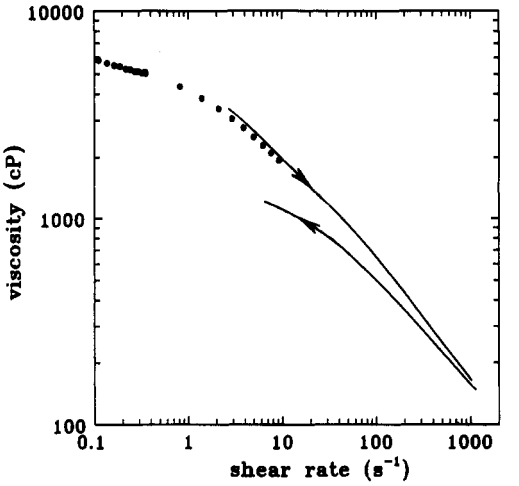

Figure 6. Apparent viscosity as a function of shear rate for solutions of copolymer 1-S2 (micellar polymerization) at a concentration of 3 wt %: (●) "low-shear" data; (→ and ←) increasing and decreasing shear stress, respectively.

also that the data from the "low-shear" procedure are in accordance with the data obtained by the conventional flow procedure. The solutions of the copolymer prepared by micellar copolymerization behave differently, as the down ramp curve lies down the up ramp curve (Figure 6). In addition, at the end of the cycle of increasing/decreasing shear, the viscosity is much lower than the initial value obtained by the "low-shear" procedure. This is not due to a mechanical degradation but to a pronounced thixotropic effect that is a time-dependent behavior. Indeed, the viscosity was restored when the system was left to rest for a sufficient time. This indicates that the destructuration and/or the restructuration of the system are not instantaneous processes. A more detailed investigation on the reversibility and the kinetics of the association/dissociation phenomena will be the subject of a forthcoming paper.

These results confirm those obtained in the dilute regime. The copolymers prepared by the homogeneous or the heterogeneous processes behave exactly like unmodified polyacrylamides. Single ethylphenyl groups are not hydrophobic enough to induced polymolecular associations. For the systems under investigation, the micellar polymerization is the only process which leads to copolymers with associative properties owing to their blocky structure. However, the homogeneous copolymerization could also be a suitable method provided that a hydrophobic monomer with a longer alkyl chain is used. On the contrary, the heterogeneous process does not seem to be a convenient way for preparing efficient associative polymers because this would require a more hydrophobic monomer that cannot be easily dispersed in water.

Further evidence that the micellar copolymerization allows one to control the copolymer structure is given by Table IV. At constant hydrophobe level, the viscosifying properties strongly depend on the surfactant concentration and on the amount of the added salt in the reaction medium. For comparison, viscometric data obtained with PAM are also given (according to the molecular weight values, PAM-S3 is to compare with samples 1-S3-Na05, 1-S3-Na02, 1-S2, 1-S3, and PAM-S5 with 1-S5). The large differences in the copolymer solution properties cannot be ascribed to a molecular weight effect since all samples (except sample 1-S5) have a similar molecular weight. It is clear that the thickening ability is directly related to the initial micelle concentration used during the synthesis. Thus, the viscosity increases upon decreasing the initial

Table IV. Viscosity Properties in Aqueous Solution (Concentration 3 wt %) of Copolymers Prepared by the Micellar Process: Effect of the Initial Micelle Concentration at a Constant Hydrophobe Level (1 mol %)

sample code	conditions of the synthesis	N_H[a]	η_0[b] (cP)	$M_w \times 10^{-6}$
1-S1	1% SDS	9.8	≃insoluble	1.7
1-S3-Na05	3% SDS + 0.5 M NaCl	6.1	33000	1.9
1-S3-Na02	3% SDS + 0.2 M NaCl	4.4	15000	2.1
1-S2	2% SDS	4.1	6000	2.0
1-S3	3% SDS	2.6	2300	1.9
1-S5	5% SDS	1.5	290	1.3
PAM-S3			1400	1.9
PAM-S5			390	1.4

[a] N_H = number of hydrophobes per micelle.[74] [b] Viscosity extrapolated to zero shear.

surfactant concentration. Furthermore, while maintaining a constant surfactant concentration, the number of micelles can also be varied by adding salt, which is known to cause an increase in the aggregation number of micelles. As expected, the addition of NaCl to the reaction medium gives rise to copolymers with enhanced thickening properties. The data in Table IV show a higher degree of hydrophobic interactions upon increasing N_H, which corresponds to the estimated number of hydrophobes per micelle. This behavior is a consequence of longer hydrophobic blocks at a constant hydrophobe level, in agreement with the proposed reaction scheme. Note also that sample 1-S5 prepared at the highest surfactant content ($N_H \simeq 1.5$) behaves nearly like a polyacrylamide.

Figure 7 shows the variation of the viscosity as a function of shear rate at two polymer concentrations for samples prepared at variable micellar concentrations. For all the samples, the viscosity tends to level off at high shear, as a consequence of the breakdown of interchain liaisons. Data in Figure 7 also show that the thixotropic character increases markedly with the initial values of the viscosity. This is depicted by the increasing deviation between the measurements carried out initially at low shear and those obtained at the end of the down ramp flow curve. This behavior means that, after the destructuration of the systems under shear, the recovery of the initial properties with time strongly depends on the extent of hydrophobic interactions. Consequently, the measurement of the viscosity of the solutions may be affected by the shear history.

In a preliminary report, similar conclusions were drawn on the effect of the initial micellar concentration, although a higher thickening ability was found for the same copolymers[30] (the zero shear viscosities were in the range 1500 to >100 000 cP whereas the polymer concentration was only 1 wt %). In fact, this difference in the viscosity data results from the way the solutions were prepared. Data in ref 30 concerned the solutions obtained by dialysis of the final reaction mixture, while here the solutions have been prepared by redissolution of the polymer recovered by precipitation. These two important effects of the history of the samples (method of preparation of the solution and shear history) will be more thoroughly analyzed in a future paper.

Fluorescence Study. Complementary fluorescence studies were performed to provide further insight into the association process. Indeed fluorescence techniques have proved useful in studying various microheterogeneous systems[77] and recently have been applied to associative polymers.[21,25b,28,31,37,44,64,78-81] Pyrene is a widely used fluorescent probe because the ratio I_3/I_1 of the intensities of the third and first peaks of the emission spectrum is sensitive to the local environment of the probe.[60] Thus,

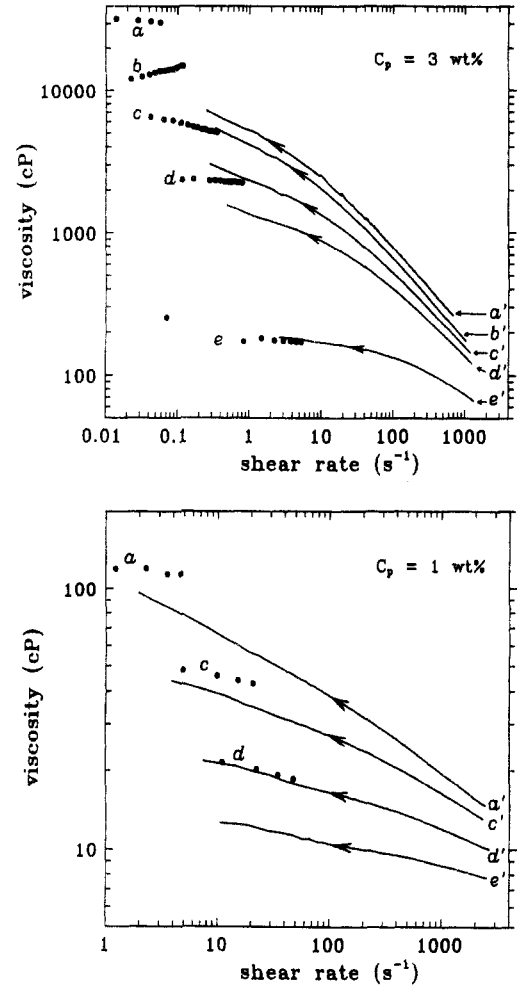

Figure 7. Apparent viscosity as a function of shear rate for various copolymers prepared by micellar copolymerization at a constant hydrophobe level (1 mol %) and variable SDS micelle concentrations. Polymer concentration: 3 wt % (top) and 1 wt % (bottom). (●) (a–e): "low shear" data; (—) a′–e′: measurements under decreasing shear stress (data under increasing shear are not plotted to avoid overlap of curves). Samples: 1-S3-Na05 (a+a′); 1-S3-Na02 (b+b′); 1-S2 (c+c′); 1-S3 (d+d′); 1-S5 (e+e′).

Table V. Fluorescence Intensity Ratio I_3/I_1 of the Pyrene Probe for Various (Co)polymer Samples as a Function of Concentration

	polymer concn (wt %)				
sample code	0.1	0.5	1	2	3
PAM-S3	0.54	0.56	0.58	0.62	0.65
1-F10	0.55				0.68
1-S0	0.55				0.68
1-S1.5	0.59	0.69	0.76		0.90
1-S3-Na05	0.57		0.66		0.74
1-S3-Na02			0.64		0.72
1-S3			0.62		
1-S5			0.59		

the formation of hydrophobic microdomains in an aqueous solution can be evidenced by an increase in the I_3/I_1 ratio. The data are reported in Table V and in Figure 8 for some samples at different polymer concentrations.

For homopolyacrylamide, at low concentration the I_3/I_1 ratio is practically equivalent to that measured in pure water (≃0.53) but increases slightly at higher concentrations. This effect is not observed for an aqueous solution of propionamide, which is the model compound of the polymer and reflects a slight hydrophobicity of the polyacrylamide backbone.

For copolymers prepared by the homogeneous process (1-F10) and the heterogeneous process (1-S0), there are

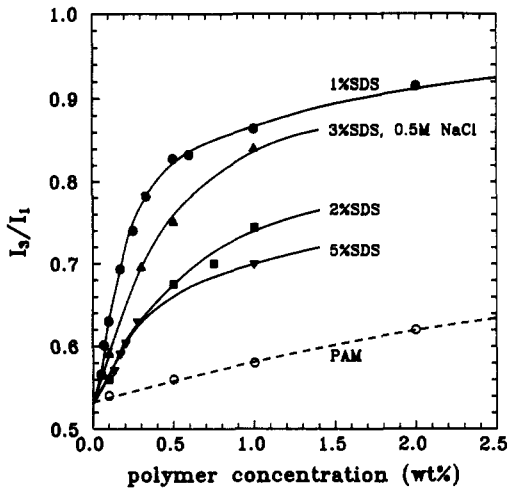

Figure 8. Fluorescence intensity ratio I_3/I_1 of pyrene probe as a function of polymer concentration for various samples synthesized by micellar copolymerization at a constant hydrophobe level (1 mol %) and variable SDS micelle concentration (labels on curves refer to the conditions of the synthesis): (●) 1-S1; (▲) 1-S3-Na05; (■) 1-S2; (▼) 1-S5; (○) PAM as a reference (aqueous solutions obtained by dialysis of the final reaction mixture).

no significant differences in the I_3/I_1 values and those of the homopolyacrylamide at the same concentrations. Fluorescence data confirm again the absence of hydrophobic interactions for these copolymers.

On the contrary, copolymers prepared by the micellar process (except 1-S5) give rise to higher I_3/I_1 values, which supports the formation of hydrophobic microdomains. Fluorescence data in Table V also reveal that an increase of the micellar concentration in the reaction mixture leads to a decrease of the hydrophobic character of the copolymer solution, in parallel with the decrease in viscosity discussed above. However, for a copolymer series at a given concentration, the range of variation of the parameter I_3/I_1 is rather limited (Table V, data at 1 wt %), while large variations of viscosity are observed (Table IV). From simple steady-state fluorescence measurements, it is not possible to distinguish whether the variation of the parameter I_3/I_1 is due to a decrease in the number of hydrophobic domains or to a modification of their hydrophobicity. Probably both processes must be operative. More quantitative information could be obtained from time-resolved fluorescence methods.

The fluorescence study also shows a quite different behavior between the solutions prepared by dialysis of the final reaction mixture and those obtained by redissolution of the precipitated polymer (Figure 8). Let us recall that the former systems possess a higher thickening ability. There is a close correlation between the values of I_3/I_1 and the rheological data. The large variation of I_3/I_1 with copolymer concentration observed in Figure 8 compared to that given in Table V supports the idea that the degree of intermolecular association depends on the way the solutions are prepared. In addition, the data confirm again the important role played by the experimental conditions used during the synthesis.

Conclusions

Most of the previous studies on hydrophobically modified water-soluble polymer have focused on the control of the thickening ability by varying the nature and/or the number of hydrophobes. The results presented in this paper show that the distribution of the hydrophobic units along the backone is also a parameter of prior importance. This monomer sequence distribution is directly related to the experimental conditions used in the copolymer synthesis. As adjoining hydrophobic monomer units in a polymer chains exhibit a higher hydrophobicity than isolated units, the aqueous solution properties strongly depend on the synthesis conditions. Relationships between the copolymerization mechanism, the copolymer microstructure, and solution properties were evidenced using rheological and fluorescence probe techniques. The extent of the intermolecular association process as a function of the copolymer samples, polymer concentration, and shear rate was monitored at a macroscopic level by the viscometric behavior and at a microscopic level by the formation of hydrophobic microdomains in aqueous solution.

While homogeneous solution copolymerization leads to a stastitical copolymer, the use of a micellar polymerization process yields a copolymer with a somewhat blocky structure as a consequence of the microheterogeneous nature of the polymerization medium. Therefore, in the case of the micellar process, the role of the surfactant is twofold: not only does it ensure the solubilization of the hydrophobic monomer in the aqueous medium but it also induces the formation of hydrophobic sequences whose length depends on the micellar concentration. At a constant hydroprobe level, longer hydrophobic sequences give rise to a higher degree of intermolecular interactions and therefore to a greater thickening efficiency.

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