Synthesis in Inverse Emulsion and Associating Behavior of Hydrophobically Modified Polyacrylamides

Martial Pabon,[1,*] Jean-Marc Corpart,[2] Joseph Selb,[1] Françoise Candau[1]

[1]*Institut Charles Sadron (CRM), 6 rue Boussingault, 67083 Strasbourg Cedex, France*
[2]*AtoFina, Centre de Recherche Rhône-Alpes (CRRA), rue Henri Moissan, BP 63, 69493 Pierre-Bénite Cedex, France*

ABSTRACT: An inverse free-radical emulsion polymerization technique was used to prepare copolymers of acrylamide and two different hydrophobic comonomers: *N,N*-dihexylacrylamide (diC6) or *N,N*-diphenylacrylamide (diPh). The products of the reaction were high molecular weight hydrophobically modified water-soluble polymers (HMWSPs) encapsulated within water droplets dispersed in an organic medium. A comparison of the copolymer compositions prepared under different experimental conditions showed that the level of incorporation of diPh in the final copolymer depended strongly on its localization in the emulsion (aqueous or oil phase) and on the nature of the redox initiator pair (water-soluble or oil-soluble). The rheological properties of the HMWSPs in aqueous solution were investigated as a function of the comonomer content and the nature of the initiator, using steady-flow experiments. The thickening properties were found to be directly correlated to the conditions of synthesis and were optimal when the initiator and the hydrophobic comonomer were located in two distinct phases. An examination of the viscosity as a function of shear rate showed that these solutions exhibit typical characteristics of hydrophobically associative polymers. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 916–924, 2004

Key words: inverse emulsion polymerization; hydrophobically associative polymers; water-soluble polymeric thickeners; rheology; redox initiators

INTRODUCTION

In the past decade, extensive studies in academic and industrial laboratories have focused on the development of water-soluble associative polymers[1–6] for their use as thickeners in many fields of applications, including fracturing and drilling fluids, latex paint technology, coatings, and cosmetics. Their thickening properties in aqueous solution are attributed to the association of a few hydrophobic units incorporated into a hydrophilic backbone. Over the years, several classes of associative polymers have been developed: depending on the method of synthesis, the hydrophobes can be end-attached (telechelic polymers) or distributed either statistically or as small blocks in the hydrophilic polymeric backbone (multisticker polymers). They are usually obtained either by chemical modification of a precursor polymer or by free-radical copolymerization of the appropriate monomers. However, a major drawback in the latter process comes from the insolubility of the hydrophobic comonomer in water. This problem can be overcome by carrying out the polymerization reaction in a mixture of solvents where both monomers are soluble[7–10] or by using a micellar polymerization technique in which the presence of a surfactant in the micellar state ensures solubilization of the hydrophobe in the aqueous medium.[7,11–13] The latter process that we investigated in detail[10,13–16] was shown to lead to multiblock copolymers in which the hydrophobic blocks are of tunable length and number, according to the experimental conditions.[10,13,16—20] The design of such materials with controllable rheological properties is quite attractive, although the low solid contents achieved at full conversion (a few wt %) may restrict their potential applications. In a recent study,[21] we showed that the use of an inverse emulsion polymerization route allows one to increase considerably the solid contents in the final products (up to 25 wt %). The associative copolymers were formed of an acrylamide/sodium acrylate backbone hydrophobically modified with small amounts (<0.5 mol %) of a series of amphiphilic comonomers, isooctylphenoxy–poly(oxyethylene)(n) methacrylates (with $1 \leq n \leq 12.5$). This process yields high molecular weight polymers encapsulated within water droplets dispersed in an organic medium, which facilitates their subsequent use in many potential applications. Such copolymers exhibit good thickening properties and a direct correlation could be established between their efficiency and the conditions of synthesis (nature of

initiator, localization of the amphiphilic comonomer, etc.).

In the present study, we propose an alternative for the synthesis of associative polymers by inverse emulsion polymerization. In this case, acrylamide is copolymerized with a conventional hydrophobic comonomer, that is, *N,N*-dihexylacrylamide (diC6) or *N,N*-diphenylacrylamide (diPh), instead of the amphiphilic comonomers previously investigated. The choice of these comonomers was dictated by the fact that the use of *N,N*-dialkylacrylamides instead of *N*-monoalkylacrylamides leads to copolymers that not only are homogeneous in composition but also have a more efficient thickening ability.[16] The presence of UV-active phenyl rings on one of these monomers was intended to facilitate the determination of the copolymer composition. We examine first the general criteria requested to achieve an optimal formulation of the emulsions and the parameters that control the incorporation of the hydrophobe into the water-soluble polymeric backbone. In a second part, we investigate the rheological behavior of these associative polymers in aqueous solution, and show how it can be related to the conditions of synthesis.

EXPERIMENTAL

Materials

Acrylamide (AM; Aldrich, France) was recrystallized from chloroform. Acryloyl chloride, dihexylamine, diphenylamine, triethylamine, anhydrous toluene, anhydrous ether, sodium hydrogencarbonate, sodium chloride, and sodium sulfate from Aldrich and hydrochloric acid from Prolabo (France) were the materials and solvents used for the synthesis of diC6 and diPh. All were used as received.

The oil was an isoparaffinic mixture (Isopar M from Exxon, Courbevoie, France). The surfactants were a nonionic block copolymer [Hypermer B246, hydrophile–lipophile balance (HLB) = 6.0], sorbitan monooleate (Span 80, HLB = 4.3), sorbitan sesquioleate (Arlacel 83, HLB = 3.7), and poly(oxyethylene) sorbitol hexaoleate with 50 ethylene oxide residues (Atlas G1096, HLB = 11.4), all from ICI (Everberg, Belgium). Cumene hydroperoxide, sodium metabisulfite, and thionyl chloride (all from Aldrich), and *tert*-butyl hydroperoxide, 75 wt % in water (Société Chalonnaise des Peroxydes, Chalon sur Saône, France), were used as received.

Synthesis of diC6 and diPh

The two acrylamide derivatives were synthesized by the reaction of acryloyl chloride with the corresponding amine according to the procedure of Valint et al.,[7] in which 0.15 mol of the amine and 0.18 mol of triethylamine were solubilized in 400 mL of an anhydrous organic solvent (ether when diC6 was used and toluene for diPh). Acryloyl chloride (0.34 mol) solubilized in 100 mL of the organic solvent were added dropwise at 5°C in the reactive medium under nitrogen. When the reactive medium achieved room temperature, 250 mL of a 10% HCl aqueous solution was added. The organic phase was separated from the aqueous phase and then washed successively with a 10% NaHCO$_3$ aqueous solution until neutral pH was reached, and with a saturated NaCl aqueous solution. The organic phase was dried over Na$_2$SO$_4$ and the solvent was evaporated. diC6 was purified by distillation under vacuum (bp = 105–108°C at $\approx 10^{-2}$ mmHg). diPh was purified by chromatography on silica gel 60 (70–230 mesh ASTM) with heptane/ethyl acetate (70/30 v/v) as the eluent. In spite of this careful purification, the presence of some undetectable residual impurities could not be excluded, as inferred from the results on copolymerization reactions (see Results and Discussion).

Polymerization

Two different redox iniators were used: the hydrophilic *tert*-butyl hydroperoxide/sodium metabisulfite couple (TBH) and the lipophilic cumene hydroperoxide/thionyl chloride couple (CUM). In all the experiments, the aqueous phase/oil phase ratio, the AM/sodium acetate ratio, and the total monomer content in the recipe were kept constant (70/30 and 82/18 w/w, and 25 wt %, respectively), except for sample diPh-2–CUM-O (aqueous phase/oil phase ratio 60/40). The aqueous and oil phases were prepared independently before emulsification. The procedure used for the preparation of the emulsion differed slightly according to the nature of the hydrophobic comonomer. The diC6 comonomer was directly solubilized with Arlacel 83 in Isopar M to form the oil phase, whereas the diPh comonomer was first solubilized in cyclohexane at 45°C before the addition of Isopar M and Arlacel 83. Then, the oil phase was emulsified with the aqueous phase (water, acrylamide, sodium acetate, G1096). Alternatively, diC6 was solubilized in a 75/25 water/methanol mixture (overnight at 40°C), before emulsification with the Isopar M containing the surfactants (Hypermer B-246 and Span 80). In all cases, the aqueous and the oil phases were emulsified with an Ultra-Turax mixer (Jankel & Kunkel, IKA Labortechnik, Staufen, Germany) at 13,500 rpm. The stirring was stopped when the emulsion reached a viscosity of about 500 mPa s^{-1} (measured with a Rheovisco-ELV-8 viscometer, 30 rpm, spindle No. 2, Champlan, France). It should be noted that this viscosity can be reached only when an electrolyte such as sodium acetate is added to the aqueous phase. As shown by Holtzscherer and Candau,[22] the use of an

electrolyte is necessary to avoid the formation of co-agulum during the polymerization of acrylamide in inverse microemulsion. The same is true for the inverse emulsion system investigated here.

The polymerizations were carried out at 18 ± 1°C except for diPh-2–CUM-O, for which a higher temperature (45°C) is required to solubilize the hydrophobic comonomer in the oil phase. The details of the experimental procedure of the polymerization were presented in a previous study.[21] Recall that the final latex was diluted twofold with hexane and poured into an excess of methanol. The precipitated polymer was recovered by centrifugation and then repeatedly washed under stirring with the following solvents: methanol, isopropanol, and acetone. This washing procedure was shown to be more efficient than dialysis in removing residual surfactant.[10,23] After the last cleaning operation, the polymer was dried *in vacuo* at 40°C for 48 h.

The sample code refers to the conditions of synthesis (see Table I). For example, diPh-2–TBH-O corresponds to a polymer obtained with diPh as the hydrophobic comonomer, the amount of the comonomer in the initial monomer mixture is 2 mol %, and TBH is the redox system used for the polymerization. The eventual additional symbol (O) means that the hydrophobic monomer (diPh) is initially solubilized in the oil phase; alternatively, when it is solubilized in the aqueous phase, the symbol W is used.

Molecular weight

The molecular weights of the copolymers were determined in formamide, by light scattering using a multiangle spectrophotometer (AMTEC, $\lambda = 633$ nm, angle = 30–150°), after clarification of the solutions by centrifugation. Previous studies on other hydrophobically modified polyacrylamides have shown that formamide is a suitable solvent to avoid aggregate formation.[10,14,16] The polymer concentration range was $3–5 \times 10^{-5}$ to $1.5–3 \times 10^{-4}$ g/mL. As previously reported,[14,23,24] the presence of a small amount of N-alkylacrylamide comonomer does not significantly affect the refractive index increment (dn/dc) of polyacrylamide (PAM) in formamide. Therefore, the same value of $dn/dc = 0.109$ mL/g[25] was used for all the AM/diC6 and AM/diPh copolymers prepared in this work.

UV measurements

The raw spectra of the diPh-containing copolymers did not show any characteristic maximum because the absorbance arising from the phenyl rings coincides with that of the PAM backbone present in large proportions. By using as a reference a PAM solution at the same concentration as that of the copolymer solution,

it was possible to detect a maximum in absorbance at $\lambda \approx 231$ nm. No calibration curve was established because of the lack of a suitable low molecular weight homolog (N,N-diphenylpropionamide). Therefore, UV measurements did not give the exact diPh content in the copolymers but provided a qualitative estimation on how the copolymer composition varies with the conditions of the synthesis.

Rheological measurements

The purified polymer samples were dissolved in deionized water and then gently stirred for 3 days. Copolymer solutions at the highest concentrations ($C_p \geq 0.4$ wt %) were very viscous and contained bubbles that were eliminated by centrifugation (4 min at ≈ 350 g). All the polymer solutions were perfectly clear and transparent.

Rheological measurements were conducted at 25°C with a Haake RS100 controlled stress rheometer (Champlan, France) equipped with a cone–plate geometry (diameter 35 or 60 mm, angle 1°). To prevent evaporation of water, the measuring system was surrounded by a solvent trap. All flow curves were measured by increasing the shear stress by regular steps and waiting at each step until equilibrium was attained. The zero-shear viscosity η_0 was obtained by extrapolating the apparent viscosity measured at various shear rates ($\dot{\gamma} \approx 10^{-2}–10^3$ s^{-1}).

Note that the final latices can be inverted upon addition of a large amount of water containing a high HLB surfactant (Triton X-100 or Atlas G1096). The rheological properties of the inverted systems were not investigated in the present study.

RESULTS AND DISCUSSION

AM/diC6 copolymers

Formulation and synthesis

The diC6 comonomer was fully soluble in Isopar M. As shown in Table I, the recipe used in the formulation for AM/diC6 copolymers (diC6–1–TBH and diC6–2–TBH samples) is nearly identical to that used for the synthesis of homopolyacrylamide (PAM). It can be noted that the presence of the hydrophobic comonomer does not affect the initial viscosity of the emulsion (500 ± 20 mPa s^{-1}). This result means that the particle size in the emulsion is not modified, and thus indicates that diC6 is not located at the oil/water interface but in the oil phase. Indeed, if diC6 was present at the interface, the interfacial tension and therefore the particle size would be modified, which in turn should affect the viscosity of the emulsion. The kinetics of the copolymerizations are quite similar to that of the AM homopolymerization. In all cases, the

TABLE I
Formulations Used for Copolymer Syntheses[a]

Sample code[b]	Monomers			Hydrophilic solvents		Hydrophobic solvents		Initiator	Surfactants				
	diC6	diPh	AM	Water	Methanol	Isopar M	Cyclohexane		Na acetate	G1096	Arlacel 83	Span 80	Hypermer B246
PAM (TBH)	—	—	24.3	39.7	—	27.7	—	TBH	5.3	0.71	2.33		
diC6-1–TBH	0.81		24.3	39.7		26.9		TBH	5.3	0.71	2.33		
diC6-2–TBH	1.61		24.3	39.7		26.1		TBH	5.3	0.71	2.33		
diPh-05–CUM-O		0.37	23.4	37.4		19.6	10.3	CUM	5.1	0.64	3.16		
diPh-2–CUM-O		1.42	22.1	28.9		22.4	16.6	CUM	4.8	0.64	3.13		
diPh-2–TBH-O		1.43	22.4	34.0		16.7	16.7	TBH	4.9	0.64	3.17		
diPh-2–TBH-W		1.46	22.8	30.9	10.7	22.4		TBH	5.0			5.1	1.7

[a] Units are in wt %.
[b] The sample code refers to the conditions of the synthesis (see Experimental).

TABLE II
Weight-Average Molecular Weight, Second Virial Coefficient, and Radius of Gyration Determined by Light Scattering for PAM and Various AM/diC6 and AM/diPh Copolymers in Formamide Solution

Sample	M_w ($\times 10^{-6}$)	A_2 ($\times 10^4$) (mol L g^{-2})	R_G (Å)
PAM (CUM)	5.3	—	—
PAM (TBH)	4.9	1.7	1530
diC6-1–TBH	5.2	4.7	1510
diC6-2–TBH	5.6	5.2	1530
diPh-05–CUM-O	2.2	2.2	1070
diPh-2–CUM-O	3.3	1.6	1290
diPh-2–TBH-O	2.1	2.1	1050
diPh-2–TBH-W	1.7	2.7	1150

degree of conversion was high (>96–99%) and no coagulum was present in the final latex.

Molecular weight

The values of molecular weight (M_w), second virial coefficient (A_2), and radius of gyration (R_G) are reported in Table II for two AM/diC6 samples and the corresponding PAM, as determined by light scattering in formamide. The results obtained for the homopolymer and the two copolymers are similar, which confirms the ability for formamide to solubilize hydrophobic sequences without the formation of inter- or intramolecular interactions.[10,14,16] Moreover, the values obtained for A_2 indicate that formamide is a good solvent for the hydrophobically modified samples.

Copolymer composition

Previous studies on AM/diC6 copolymers prepared by micellar polymerization have shown that ^{1}H-NMR was a suitable technique for the determination of their composition, with good accuracy to 0.4 mol % of diC6.[16] Recall that in this process, the hydrophobe is entrapped within conventional micelles, whereas acrylamide is solubilized in the aqueous continuous phase. By varying the number of hydrophobes per micelle (N_H), it is then possible to tune the length of the hydrophobic blocks that are randomly distributed along the PAM backbone from one (statistical microstructure) to approximately seven (multiblock microstructure). In this case, the hydrophobe content was calculated from the integration of the peaks of the terminal methyl group of the alkyl side chains (0.6 ppm) and the CH group in the polymer backbone (2 ppm).

Unfortunately, in the case of AM/diC6 samples prepared in inverse emulsion, no peak could be detected from the protons of the alkyl chains. The hypothesis that no hydrophobe is incorporated into the copoly-

mer is not satisfactory, given that (as shown later) the samples exhibited significant associating properties, which revealed the formation of hydrophobic interactions.

Another explanation based on the copolymer microstructure seems the most plausible. As mentioned above, in the case of multiblock AM/diC6 samples with short hydrophobic sequences (N_H < 4), the protons of the alkyl chain were easily detectable in the ^{1}H-NMR spectrum.[16] However, for homologous copolymers with a stronger hydrophobic character (N_H > 4 or [diC6] > 1 mol %), unreliable results were obtained from NMR measurements in pure D_2O (the measured diC6 content in the copolymers was lower than the real content).[26]

From these results, we can conclude that if the length of the hydrophobic blocks is too large, the protons of the alkyl chains cannot be seen by ^{1}H-NMR in D_2O because of a "freezing" effect: the hydrophobic microdomains are not sufficiently solvated and the alkyl chains do not have the mobility required to produce an NMR signal. A similar behavior was also reported for polyacrylamides hydrophobically modified with fluorocarbon groups[27] or with a polymerizable surfactant,[28] and for block copolymers in a poor solvent of one block.[29,30] In some cases, this problem can be overcome by increasing the temperature or by using a (co)solvent able to solvate the hydrophobic blocks.[26] Unfortunately, for the samples investigated here, attempts to use such procedures were unsuccessful. It is therefore very likely that the hydrophobic blocks are rather long (>7–8 units).

This difficulty in determining the incorporation of diC6 in the final copolymers led us to study in more detail associative PAM prepared in inverse emulsion but with a UV chromophore-containing hydrophobic comonomer, diPh.

AM/diPh copolymers

Formulation and synthesis

In contrast with diC6, the hydrophobic comonomer diPh was not soluble in the organic solvent (Isopar M) used in this study. The use of adequate cosolvents allowed its solubilization either in the organic continuous phase or in the dispersed aqueous phase. Below we discuss the incorporation of diPh in the final copolymer as a function of its localization in the emulsion and/or of the nature of the redox initiator used.

Methanol and cyclohexane are both good solvents for diPh. Methanol, which is miscible with water but not with Isopar M, was used to solubilize diPh in the aqueous phase. Conversely, cyclohexane, miscible with Isopar M but not with water, allowed the solubilization of diPh in the organic phase. The recipes used in the formulations are reported in Table I. In

both cases, because of the presence of a new component in the reaction mixture, the composition of the surfactant mixture must be chosen in such a way that it ensures the required viscosity for the starting emulsion and therefore the best stability (see Experimental section). More particularly, when diPh was solubilized in the aqueous phase (diPh-2–TBH-W sample) the surfactant mixture used was Hypermer B-246/Span 80 instead of G1096/Arlacel 83.[31] When diPh was solubilized in the oil phase (diPh-2–CUM-O sample), the composition of the surfactant mixture G1096/Arlacel 83 must be modified to operate at a slightly different HLB value (5.0 instead of 5.5) to take into account the presence of cyclohexane.

Molecular weight

Values of M_w, A_2, and R_G of AM/diPh copolymers and the corresponding PAM homopolymers prepared with the two types of initiator (CUM or TBH), as determined by light scattering in formamide, are reported in Table II. Note that PAM with nearly identical molecular weights (5.1 ± 0.2 × 10^{6} g/mol) were obtained by using either CUM or TBH. Again, the values obtained for A_2 confirm that formamide is an adequate solvent for both hydrophobically modified and unmodified PAM.

One can also note that in contrast with AM/diC6 copolymers, the M_w values of the four modified samples were systematically lower than those of the PAM. In the case of diPh-2–TBH-W, this lowering could be mainly attributed to the presence of methanol, which is known to act as a chain-transfer agent. However, this explanation does not hold for the three other samples that were synthesized without methanol, given that cyclohexane is not an efficient chain-transfer agent. Another possible explanation could be the presence in the medium of some residual impurities, such as N,N-diphenylamine used for the synthesis of diPh, leading to a degradative chain transfer. This assumption is supported by the fact that lower final conversion degrees are generally obtained with diPh, in spite of higher initiator concentrations.

Incorporation of diPh in the copolymer as a function of the conditions of synthesis

UV absorption measurements carried out on aqueous solutions of AM/diPh copolymers indicate the presence of diPh in the final materials (see Experimental section), allowing us to estimate how the copolymer composition varies with the conditions of synthesis.

Examination of the UV spectra *a*, *b*, and *d* reported in Figure 1 shows that the three corresponding copolymers (diPh-2–TBH-W, diPh-2–CUM-O, and diPh-2–TBH-O, respectively) have quite different compositions in spite of a similar diPh content in the monomer
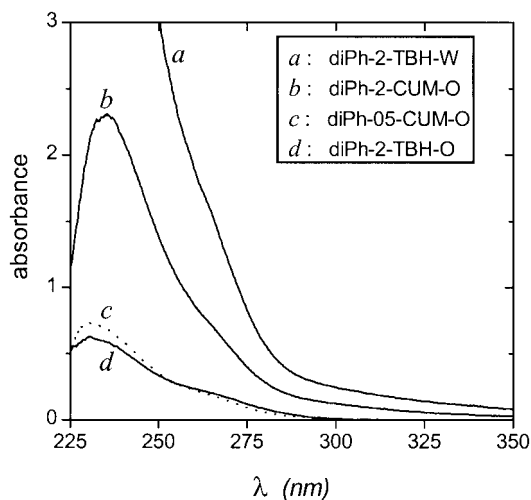
Figure 1 UV spectra for various AM/diPh copolymers in aqueous solution (C_p = 0.3 wt %) after subtraction of the PAM absorption.

feed (2 mol %). This behavior can be explained by taking into account the different distributions of the various components in the reaction medium for these three copolymers, as schematically shown in Figure 2.

1. The copolymer with the highest diPh content (diPh-2–TBH-W, curve *a*) was obtained by solubilization of the hydrophobe in the dispersed phase where most of the acrylamide is present. This case is most favorable to good incorporation of diPh in the copolymer because all the components are in the same phase, likely resulting in a statistical copolymer in which the hydrophobes are randomly distributed as isolated units along the PAM backbone.
2. The diPh-2–TBH-W and diPh-2–TBH-O samples (curves *a* and *d*, respectively, in Fig. 1) were prepared with the same initiator (TBH) and same diPh content, the polymerization reactions differing only by the location of the hydrophobic monomer (cf. Fig. 2). However, the hydrophobe content in diPh-2–TBH-O was 8 times lower than that in diPh-2–TBH-W. In contrast with the case of diPh-2–TBH-W discussed above, the conditions of synthesis of diPh-2–TBH-O were quite unfavorable to good incorporation of diPh, which was not located in the aqueous dispersed phase where the reaction takes place.
3. For the diPh-2–CUM-O and diPh-2–TBH-O samples, the nature of the initiator was different but the initial molar content of diPh, solubilized in the organic phase, was the same (2 mol %). The copolymer prepared with the lipophilic CUM contained about four times more diPh than that prepared with water-soluble TBH (curves *b* and *d* in Fig. 1). This result can be accounted for by a

different polymerization mechanism as already discussed for water-soluble polymers prepared by the same process but using an amphiphilic comonomer with a strong hydrophobic character.[21] We briefly recount below the main features of this mechanism, although more details are given in Pabon et al.[21] When the lipophilic CUM initiator was used, the radicals generated in the organic phase added the diPh molecules and some AM molecules solubilized in this phase (low solubility of AM in Isopar M) to yield a polymer chain. Note that after having added a few diPh units in the organic phase, the growing radical can also react at the water/oil interface with the AM molecules located there (recall that AM acts as a cosurfactant). It can subsequently propagate in aqueous droplets and terminate with a radical present in this phase. This mechanism implies that the associative polymers thus formed possess a hydrophobic comonomer-rich terminal group. When the hydrophilic TBH initiator was used, the radicals generated were localized in the aqueous phase and therefore reacted preferentially with the AM molecules, accounting for the lower incorporation level of the diPh comonomer.
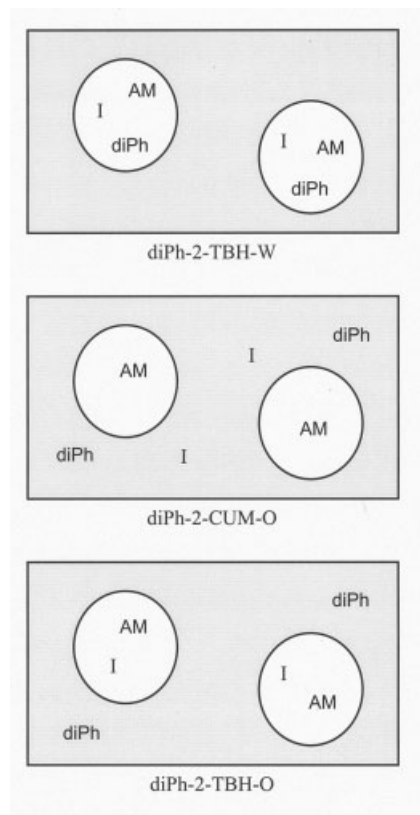

Figure 2 Schematic representation of the localization of the reagents within the emulsion for the synthesis of AM/diPh copolymers under different experimental conditions (the symbol I represents the initiator).
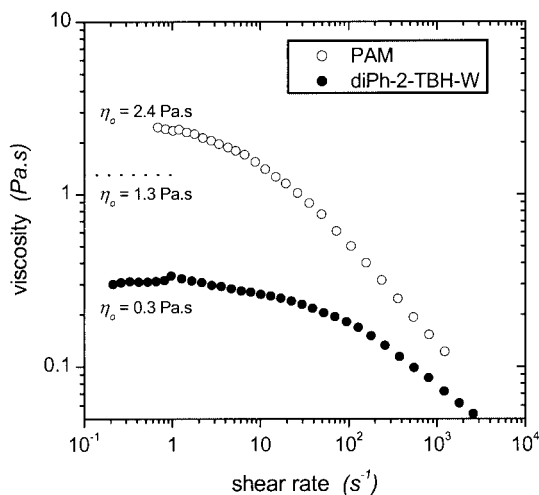
Figure 3 Viscosity as a function of shear rate for the diPh-2–TBH-W copolymer and a PAM ($M_w = 2 \times 10^6$) in aqueous solution ($C_p = 3$ wt %). The dotted line corresponds to the zero-shear viscosity calculated for a PAM with $M_w = 1.7 \times 10^6$.

4. The composition of diPh-05–CUM-O and diPh-2–TBH-O samples is quite similar (curves *c* and *d*, respectively, in Fig. 1) in spite of a strongly different diPh content in the monomer feed (0.5 and 2 mol %, respectively). This result confirms that the incorporation of diPh solubilized in the organic phase is increased by a factor of 4 when a lipophilic initiator is used instead of a water-soluble one. The fact that these two copolymers have similar compositions and similar molecular weights will allow us to determine the effect of the nature of the initiator and copolymer microstructure on their rheological behavior in aqueous solution (see next section).

Rheological behavior in aqueous solution

Polymers hydrophobically modified with diPh

Figure 3 shows a log–log plot of the viscosity versus shear rate for the diPh-2–TBH-W sample. The curve obtained for a PAM with a close molecular weight (2×10^6 versus 1.7×10^6 g/mol) is shown for comparison. Unexpectedly, the Newtonian viscosity (η_0) of the modified PAM is lower (0.3 Pa s^{-1}) than that of PAM (2.4 Pa s^{-1}). This difference in η_0 cannot be attributed to that in molecular weights, as shown by the dotted line of Figure 3, which gives the Newtonian viscosity (1.3 Pa s^{-1}) of a 1.7×10^6 g/mol PAM. This viscosity value was calculated from the experimental value corrected by using the exponent of the power law proposed by Kulicke et al.[32] for PAM in water ($\eta_0 \propto M^\alpha$ with $\alpha = 3.6$ for $C_p = 3$ wt %). It is clear here that the PAM modified with diPh does not show any significant thickening ability. In fact, its diminished viscosity

with respect to that of PAM reflects even the existence of strong intramolecular interactions, resulting in a collapse of the polymer chains. This result can be drawn together with other studies on associative polymers, which showed that excessive hydrophobicity (case of diPh-2–TBH-W sample, which has the highest diPh content of the series; cf. Fig. 1) may favor intramolecular interactions at the expense of intermolecular interactions.[33] Furthermore, the experimental conditions used in the synthesis suggest that the hydrophobic units are randomly distributed as isolated units, and it is now well established that such a microstructure is much less favorable than a blocky microstructure for the design of efficient thickeners.[10,16]

If we now examine the case of diPh-2–CUM-O prepared with the hydrophobic CUM initiator, one observes that in contrast to the previous case, it exhibits a viscosity value about twice that of the corresponding PAM (Fig. 4). A similar result is observed with diPh-05–CUM-O (Fig. 5). Recall that these copolymers have a diPh content about one half and one fourth of that of diPh-2–TBH-W, respectively. Based on the above considerations, it may be assumed that their greater thickening ability is related to their lower hydrophobic character. However, this explanation may be too simplistic and we cannot neglect possible effects of different microstructures and/or compositional heterogeneities because the conditions of synthesis differ: CUM initiator is used instead of TBH and diPh is no longer located in the aqueous droplets but in the continuous phase.

The association degree of these two samples is nevertheless quite limited, compared for example to that of AM/diC6 copolymers in which the hydrophobic units are randomly and singly distributed.[16] The different nature of the hydrophobic groups may account
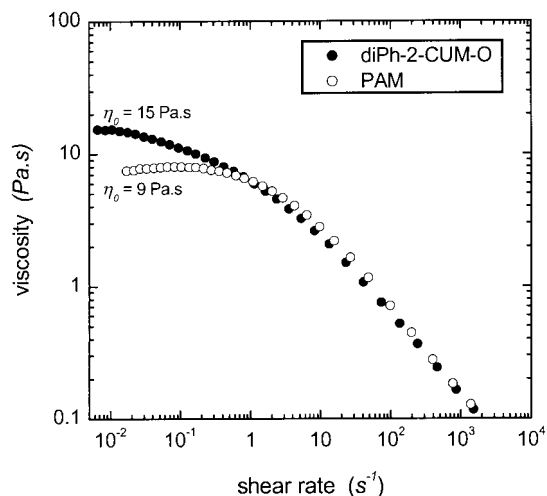

Figure 4 Viscosity as a function of shear rate for the diPh-2–CUM-O copolymer and a PAM ($M_w = 3 \times 10^6$ in aqueous solution ($C_p = 3$ wt %).
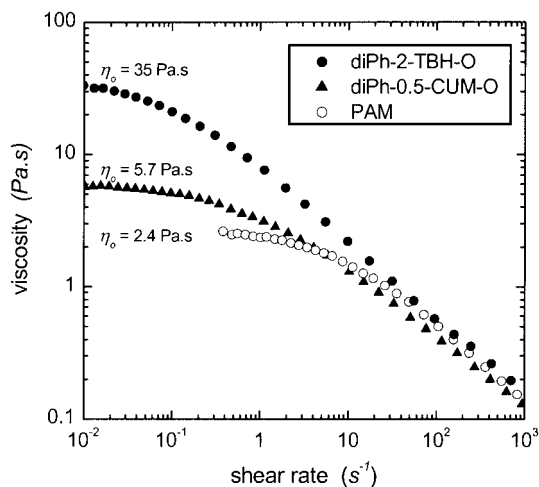
Figure 5 Viscosity as a function of shear rate for the diPh-2-TBH-O and diPh-05–CUM-O copolymers, and a PAM ($M_w = 2 \times 10^6$) in aqueous solution ($C_p = 3$ wt %).

for this result; the hydrophobicity of an aromatic ring is assumed to be equivalent to that of 3 to 4 aliphatic carbons and it is known that a simple variation of ±1 CH$_2$ in the chain may strongly modify the associating behavior of copolymers.[13]

More interesting is the comparison between the diPh-2–TBH-O and diPh-05–CUM-O samples (Fig. 5). These two copolymers have similar compositions (as inferred from UV analysis) and essentially the same average molecular weight (2.15 ± 0.5 g/mol), and in both cases, the hydrophobic monomer is located in the organic continuous phase during polymerization. The two syntheses differ only by the nature of the initiator (see second main section in Results and Discussion). Figure 5 shows a pronounced associating behavior for diPh-2–TBH-O: at the concentration used (3 wt %), its Newtonian viscosity is about 15 times that of the corresponding PAM, compared with about two times for diPh-05–CUM-O. These results are rather unexpected, given that we have seen above that the former situation is the less favorable for good incorporation of the hydrophobe in the copolymer. Again, such behavior can be explained by a different distribution of the hydrophobic units along the polymer backbone, as previously found for other hydrophobically modified polyacrylamides with variable blockiness synthesized by micellar copolymerization.[10,16] The strong shear thinning behavior observed at higher shear rates reflects the rupture of the intermolecular physical links, in good agreement with what is commonly observed for associative polymers.

Polymers hydrophobically modified with diC6

Figure 6 shows the variation of the viscosity with shear rate for diC6–1–TBH and diC6–2–TBH samples

at a 1 wt % concentration in water and for a PAM. Recall that it was not possible to detect the presence of diC6 in these copolymers by ^{1}H-NMR (see first section in Results and Discussion). An enhancement of the Newtonian viscosity of 3.5 and 40 times was observed for these two samples, respectively, compared to that of the PAM analog. This enhancement cannot be attributed to the small difference in molecular weights. A correction of the PAM viscosities based on the power law given by Kulicke et al.[32] ($\eta_0 \propto M^\alpha$ with $\alpha = 2.4$ for $C_p = 1$ wt %) would give viscosity values of 0.21 and 0.25 Pa s^{-1} for PAM of $M_w = 5.2 \times 10^6$ and 5.6 $\times 10^6$ g/mol, respectively, which is still much lower than the viscosities obtained with the copolymers (0.6 and 7 Pa s^{-1}). The increased viscosity can therefore only be ascribed to the associating character of these copolymers, the higher viscosity value being observed for the diC6–2–THB sample, which obviously contains the higher hydrophobe content.

The behavior of AM/diC6 copolymers confirms the findings reported above for AM/diPh copolymers: when the hydrophobic monomer is located in the oil phase, one must use a water-soluble initiator to obtain polymers with enhanced thickening properties. Additionally, the associative character of AM/diC6 copolymers is more pronounced than that with AM/diPh copolymers because it appears at lower concentrations (1 wt % instead of 3 wt %), confirming the higher hydrophobicity of the former with respect to the latter as discussed above.

CONCLUSIONS

In this investigation, we studied the free-radical copolymerization of a water-soluble monomer, acrylamide (AM), with a hydrophobic comonomer, either *N,N*-
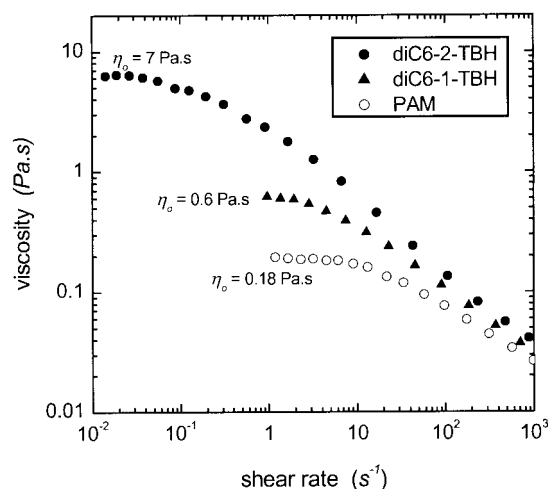

Figure 6 Viscosity as a function of shear rate for the diC6–2–TBH and diC6–1–TBH copolymers, and a PAM ($M_w = 4.9 \times 10^6$) in aqueous solution ($C_p = 1$ wt %).

dihexylacrylamide (diC6) or *N,N*-diphenylacrylamide (diPh), in inverse emulsions, with the aim of designing high solid content materials with controllable thickening properties.

We first defined the best formulation conditions required for the formation of stable emulsions. In particular, in the case of diPh, which is not soluble in either the organic phase or the aqueous phase, the use of cosolvents is required to facilitate its solubilization in either phase. The process leads to stable inverse latices consisting of water droplets swollen with the hydrophobically modified polyacrylamides and dispersed in the organic phase (polymer solids content $\approx$ 25 wt %).

The nature of the redox initiator (hydrophilic or lipophilic) was shown to play an important role on the level of incorporation and on the distribution of the hydrophobic units in the copolymers, which in turn affects their rheological behavior in aqueous solution. The incorporation of diPh in the copolymer was maximized when all of the reaction components are located in the aqueous dispersed phase. The copolymer thus obtained has a statistical microstructure. When diPh was solubilized in the organic phase, the use of a lipophilic initiator enabled increased incorporation into the final copolymer by a factor of 4.

With respect to the copolymers modified with diC6 and synthesized using a hydrophilic redox initiator, they present a more blocky microstructure, which does not allow the determination of hydrophobe incorporation by ^{1}H-NMR attributed to a "freezing effect."

Steady-flow experiments performed on these samples corroborate our previous findings obtained on PAM prepared in inverse emulsion and modified with a polymerizable surfactant[21]: copolymers with a blocky microstructure are more efficient thickeners than copolymers in which the hydrophobic units are statistically distributed. The former microstructure is favored when the hydrophobe and the initiator are located in the oil and aqueous phases, respectively.

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