

Synthesis in Inverse Emulsion and Properties of Water-Soluble Associating Polymers

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ABSTRACT: An inverse, free-radical emulsion polymerization technique was designed for the preparation of copolymers of acrylamide and sodium acrylate modified with low amounts (<0.5 mol %) of a series of amphiphilic comonomers, the isooctylphenoxy-poly(oxyethylene)(*n*) methacrylates ($1 \leq n \leq 12$). The products of the reaction were hydrophobically modified water-soluble polymers (HMWSPs) of high molecular weight encapsulated within water droplets dispersed in an organic medium. Kinetic studies showed that the full-conversion samples were rather homogeneous in composition because of the specificity of the process. A mechanistic scheme is proposed that accounts for the incorporation level of the amphiphilic comonomer as a function of its hydrophile-lipophile balance and the nature of the redox initiator (hydrophilic or lipophilic). The rheological properties of the HMWSPs in aqueous solutions were investigated as a function of the comonomer content and the nature of the initiator with steady-flow experiments. The thickening properties were directly correlated to the conditions of synthesis and were optimal when the initiator and the amphiphilic comonomer were located in two distinct phases. A maximum in viscosity was observed for a hydrophobe content of about 0.3 mol %. An examination of the viscosity as a function of the shear rate and time showed that these solutions had all the characteristics of associating polymers. The complex rheological behavior was the result of the balance between interchain and intrachain hydrophobic liaisons and the kinetics of disorganization and reorganization of the network structure. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1418–1430, 2002; DOI 10.1002/app.10337

Key words: inverse emulsion polymerization; amphiphilic monomers; hydrophobically associating polymers; water-soluble polymeric thickeners; rheology

INTRODUCTION

Water-soluble polymers are presently the subject of extensive research because of their important applications as stabilizers, flocculants, and absorbants.^{1–4} They can also be used as aqueous viscosity modifiers in tertiary oil recovery, latex

paint systems, pigment printing for textiles, coatings, and cosmetics.⁵ For a significant thickening efficiency even at low concentrations, the polymer chains should have large hydrodynamic volumes, which imply the use of high molecular weight polymers. Another way to obtain thickeners is to synthesize water-soluble polymers containing a small number of hydrophobic groups (a few mole percent). Above a certain polymer concentration, the hydrophobic groups associate intermolecularly and build up a transitory three-dimensional network that induces a strong increase in viscosity.^{6–9} These associating polymers exhibit unique rheologi-

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cal properties in solution due to the reversible dissociation of the physical crosslinks under shear.

Hydrophobically modified polyacrylamides form an important class of associating polymers. They are usually obtained by polymerization in solution^{10–13} or by a micellar polymerization technique in which the hydrophobe is solubilized into micelles dispersed in an aqueous medium.^{10,14–16} The latter process has been shown to be well suited to the synthesis of tailored materials with good controllable rheological properties.^{12,16–20} However, a drawback of both processes is the low solid content in the final material (a few weight percent). However, polymerization reactions in inverse emulsions or microemulsions are choice methods for the synthesis of high molecular weight, water-soluble polymers in the form of latexes, that is, water-swollen polymer particles dispersed in an organic, continuous phase.^{21–23} The advantages of the techniques are the high solid contents (25–35 wt %) with low viscosities of the dispersions, good handling, and storage facilities.

The objective of this study was to extend the classical inverse emulsion polymerization technique to the synthesis of hydrophobically modified water-soluble polymers (HMWSPs). The materials investigated here were obtained by the free-radical emulsion terpolymerization of an acrylamide (AM)–sodium acrylate (NaA) mixture with an amphiphilic comonomer (or surfmer), isooctylphenoxy–poly(oxyethylene)(*n*) methacrylate. The number (*n*) of ethylene oxide (EO) units in the comonomer was varied from 1 to 12 so that we could cover a wide range of samples. After a search for an optimal formulation, we established the best polymerization conditions required for the synthesis of associating polymers with a high thickening efficiency. Two different redox initiators were used: the hydrophilic *tert*-butyl hydroperoxide/sodium metabisulfite couple (TBH), and the lipophilic cumene hydroperoxide/thionyl chloride) couple (CUM). A detailed study of the rheological behavior of these polymers in aqueous solutions allowed us to correlate their properties to the synthesis conditions.

EXPERIMENTAL

Materials

AM (Aldrich, France) was recrystallized in chloroform. The inhibitor present in acrylic acid (AA; Aldrich) was removed by the passage of the product through a special column (inhibitor remover from Aldrich).

The amphiphilic comonomers, isooctylphenoxy–poly(oxyethylene)(*n*) methacrylates, supplied by AtoFina were obtained by the reaction of methacrylic anhydride on commercial nonionic surfactants (Triton®). The general formula of these amphiphilic comonomers (surfmers) is given in Figure 1. In this work, four different comonomers were prepared, T1, T5, T10, and T12 with Triton®, with an average number of EO units of 1, 5, 9.5, and 12.5 respectively (Table I). The theoretical hydrophile–lipophile balance (HLB) of the comonomers given in Table I were calculated from the Griffin relation,²⁴ in which the hydrophilic part of the molecule is the carboxyl group and the poly(oxyethylene) chain.

The oil was an isoparaffinic mixture (Isopar M from Exxon, Courbevoie, France). Surfactants other than the surfmers and Triton® (from Union Carbide, Rungis, France) are sorbitan sesquioleate (Arlacel 83, HLB = 3.7) and poly(oxyethylene) sorbitol hexaoleate with 50 EO residues (Atlas G1096, HLB = 11.4), both 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.

Polymerization

Reactions for a total recipe of 70 g were carried out in a 150-mL, double-jacketed glass reactor fitted with a mechanical stirrer, a condenser, a thermometer, a nitrogen inlet/outlet, a rubber septum cap for the injection of the redox initiator, and an outlet at the bottom for sampling during polymerization. In all the experiments, the aqueous-phase/oil-phase ratio and the total monomer content in the recipe were kept constant (70/30 w/w and 25 wt %, respectively). Depending on the samples, the surfactant content ranged from 3 to 11.4 wt % based on the total recipe. The aqueous phase (NaOH, water, AA, AM, and G1096) and the oil phase (Isopar M and Arlacel 83) were emulsified with an Ultra-Turax mixer at 13,500 rpm (note that the T1 comonomer was first solu-

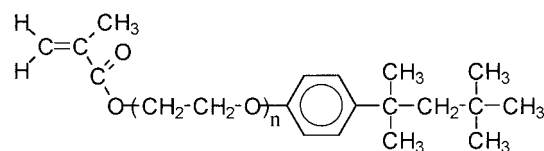


Figure 1 Chemical structure of the amphiphilic comonomers.

Table I Characteristics of the Amphiphilic Monomers

Code	Precursor Surfactant ^a	Average Number of EO Units (<i>n</i>)	Molecular Weight ^b	HLB ^c
T1	Triton X15	1	318	5.5
T5	Triton X45	5	494	10.7
T10	Triton X100	9.5	692	13.6
T12	Triton X102	12.5	824	14.4

^a Registered name.

^b Average value calculated from the average molecular weight of the precursor surfactant.

^c Calculated from the Griffin equation.²⁴

bilized in the oil phase, whereas T5, T10, and T12 were solubilized in water). During this stirring, the emulsion temperature was maintained at 18°C, which was also the polymerization temperature ($\pm 1^\circ\text{C}$). This stirring was stopped when the emulsion reached a viscosity of 500 mPa s (measured with a Rheovisco-ELV-8 viscometer at 30 rpm with a No. 2 spindle). The emulsion (67 g) was introduced into the reactor and deaerated by nitrogen bubbling under stirring (250 rpm) for 60 min. For the hydrophilic redox system (with TBH as the initiator), 1 mL of a solution of *tert*-butyl hydroperoxide aqueous (0.28 g in 40 g of water) was injected into the reactor and then, after 15 min, 2 mL of a sodium metabisulfite aqueous solution (0.106 g in 40 g of water) was injected within 2 h. For the lipophilic redox system (with CUM as the initiator), a solution of cumene hydroperoxide in the isoparaffinic solvent (0.17 g in 20 g of solvent) was injected into the reactor and then, after 15 min, 6.7 mL of thionyl chloride in

the isoparaffinic solvent (0.3 g in 20 g of solvent) was injected within 2 h. At the end of the reducing agent addition, the medium was still stirred under nitrogen for 1 h more. The final product of the reaction was a stable and coagulum-free latex. This 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. After the last cleaning operation, the polymer was dried *in vacuo* at 40°C for 48 h. For kinetic experiments, samples were withdrawn at various reaction times, and hydroquinone was used to stop the polymerization; monomer conversion was determined by gravimetry on the recovered polymer fraction.

The sample code refers to the synthesis conditions (see Table II). For example, E-T10-05-TBH corresponds to a polymer obtained by inverse emulsion polymerization (E) with T10 as the amphiphilic comonomer, 0.5 mol % comonomer in the initial monomer mixture, and TBH as the redox system used for the polymerization. The symbol NP is added to the sample code for the hydrophobe-free homologue polymers synthesized by the replacement of the amphiphilic comonomer with the corresponding nonpolymerizable Triton[®] surfactant with the same average number of EO units.

Polymer Compositions

The hydrophilic polymer backbone contained AM, AA, and NaA. For all the polymerizations, AA was used under its neutralized form (NaA). The presence of AA in the polymer was due to the cleaning operations.²⁵ The weight content in carbon, hydrogen, nitrogen, and sodium were obtained by

Table II Characteristics of the Systems Investigated

Sample Code	Surfmer	Initiator	Surfactants ^a		Monomer Feed (mol %)			Polymer Composition (mol %)			
			G1096	Arlacel 83	Surfmer	AM	NaA	Surfmer	AM	NaA	AA
E-T1-05-TBH	T1	TBH	0.6	3.4	0.67	83.6	15.8	0.02	86.5	12.9	0.6
E-T5-05-TBH	T5	TBH	—	4.3	0.49	83.1	16.4	0.19	84.7	14.6	0.5
E-T10-02-TBH	T10	TBH	—	3.0	0.22	82.0	17.8	0.20	84.0	14.2	1.6
E-T10-05-TBH	T10	TBH	—	7.1	0.50	81.9	17.6	0.30	84.0	15.3	0.4
E-T10-08-TBH	T10	TBH	—	11.4	0.79	81.2	18.0	0.44	82.9	14.1	2.5
E-T12-05-TBH	T12	TBH	—	9.5	0.50	84.0	15.5	0.35	84.2	14.6	0.9
E-T1-05-CUM	T1	CUM	0.6	3.4	0.67	83.6	15.8	0.14			
E-T10-05-CUM	T10	CUM	—	7.3	0.50	81.8	17.7	n.d.			

^a Weight percent of the total recipe.

microanalysis. The ratio between nitrogen and sodium gave the ratio between AM and NaA. The potentiometric titration of carboxylic groups gave the AA content. Data in Table II show that the composition of the polymer backbone was close to that of the hydrophilic monomer feed.

The amphiphilic comonomer content was determined from UV absorption measurements in aqueous solutions. Nonpolymerizable Triton surfactants at concentrations lower than their critical micelle concentration were used as model compounds for the determination of the absorption coefficient of the chromophore: $\epsilon = 1280$ and $1350 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $\lambda = 276 \text{ nm}$ for Triton-X100 and Triton-X102, respectively. These values are in agreement with those reported for other homologue Triton surfactants below the critical micelle concentration.^{26,27} From these results, we assume that the absorption coefficient does not depend on the length of the poly(oxyethylene) chain. For UV measurements performed on copolymers, the corresponding hydrophobe-free polymer was used as a reference to take into account the slight absorbance of the polymer backbone. UV analysis could not be carried out on the E-T10-05-CUM sample because of the very slight turbidity of its aqueous solutions.

Molecular Weights

The molecular weights of the samples were determined in formamide/NaCl solutions by classical light scattering with a multiangle spectrophotometer (Amtec, $\lambda = 633 \text{ nm}$). The polymer concentration range was 3×10^{-5} to $1.5 \times 10^{-4} \text{ g/mL}$. The refractive-index increments measured at $\lambda = 633 \text{ nm}$ on a Brice-Phoenix differential refractometer for the E-T10-05-TBH-NP sample in formamide at 0.1 and 0.2M NaCl were $dn/dc = 0.080$ and 0.085, respectively.

Rheological Measurements

Stock aqueous solutions at $C = 0.25$ and 1 wt % were prepared in deionized water and then gently stirred for 3 days. Solutions at various polymer concentrations were obtained by dilution of the stock solutions. Copolymer solutions at the highest concentrations ($\geq 0.4 \text{ wt } \%$) were very viscous and contained bubbles that were eliminated by centrifugation (4 min at $\approx 350G$). All the polymer solutions, except those with E-T10-05-CUM, were perfectly clear and transparent, in contrast to aqueous solutions of similar polymers without NaA units, which were slightly opalescent.²⁸

Viscosity experiments at low concentrations ($\leq 0.1 \text{ wt } \%$) were performed on a Contraves LS30

low-shear rheometer at 25°C with concentric cylinder geometry (with either 2T–2T or 1–1 as the measuring system, depending on the viscosity range). Experiments at higher concentrations were conducted at 25°C with a Haake RS100 controlled stress rheometer equipped with cone-plate geometry (diameter = 35 or 60 mm, angle = 1°). To prevent the evaporation of water, we surrounded the measuring system with a solvent trap or, for long-time measurements, added a low-viscosity silicon oil to the edges of the cone. We verified that the contact with the silicon oil did not modify the rheological properties of the aqueous copolymer solutions. We measured all flow curves by increasing the shear stress in regular steps and waiting at each step until equilibrium was attained. With both rheometers, the zero-shear viscosity (η_0) was obtained by extrapolation of the apparent viscosity measured at various shear rates ($\dot{\gamma} \sim 10^{-2}$ to 10^2 s^{-1} for the LS30 and 10^{-2} to 10^3 s^{-1} for the Haake RS100).

RESULTS AND DISCUSSION

Formulation

The components and emulsion formulation were selected according to a strategy classically used in inverse emulsion polymerization:²²

1. Aqueous-phase/oil-phase = 70/30 w/w.
2. Oil: Isopar M.
3. Aqueous phase: monomer/water weight ratio = 0.53 (i.e., total monomer content in the recipe = 25 wt %).
4. Surfactants: mixtures of Arlacel 83 and G 1096 at the appropriate HLB (discussed later).
5. Water-soluble monomers: AM/NaA = 83/17 $\pm 1 \text{ mol/mol}$. The incorporation of additives such as electrolytes (either nonpolymerizable such as sodium sulfate or polymerizable such as NaA) were shown in some cases to decrease the amount of coagulum by a factor of 5 or more and to contribute to the emulsion stability.²²
6. Amphiphilic comonomers: a series of isooctylphenoxy-poly(oxyethylene)(n) methacrylates with a variable number of EO units group (from 1 to 12; HLB values ranged from 5.5 to 14.4; see Table I). The choice of these comonomers was guided by the following criteria:

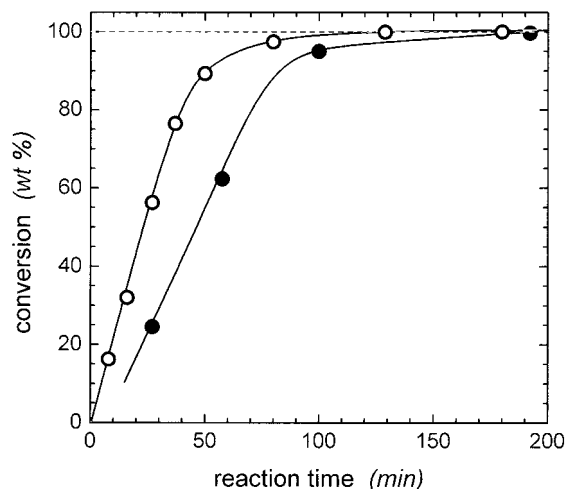


Figure 2 Conversion as a function of time for two samples: (○) E-T10-05-TBH and (●) E-T1-05-CUM.

- The synthesis could be easily performed with nonpolymerizable commercially available surfactants (Triton® series).
- The comonomers were nonionic, like the Arlacel 83/G1096 emulsifier mixture used in the formulation.
- A series of nonionic polymerizable surfactants with a variable number of EO units would allow us to study the effect of the hydrophilic character of the amphiphilic comonomer on its incorporation in the final copolymer.
- The amphiphilic comonomers bore an aromatic ring that could be easily detected by UV absorption in the final polymer.

In inverse emulsion polymerization, the HLB values of the emulsifier mostly used by formulators range between 4 and 6. In this study, we set the HLB at a fixed value of 5.5 for all the experiments. In this case, it was necessary to take into account the presence of the amphiphilic comonomer for the calculation. Although the latter was in low proportions in the system (~ 0.5 mol % of the monomer feed), we nevertheless had to modify the concentrations of G1096 and Arlacel 83 to maintain the HLB of the surfactants at a value of 5.5.

For T10 and T12, which had rather high HLB values (13.6 and 14.4, respectively), the optimum HLB of the polymerization medium could only be obtained with a single surfactant with a low HLB (Arlacel 83, HLB = 3.7) instead of the surfactant mixture (Arlacel 83/G1096). Moreover, the re-

quested viscosity of the initial emulsions and the stability of the final latexes were actually reached for a slightly different HLB value (5.0 instead of 5.5). This could be ascribed to some uncertainties in the calculations of the HLB values of the surfmers.

Polymerization Kinetics

In Figure 2 are reported the conversion–time curves for two samples differing in the nature of the comonomer (T1 or T10) and the initiator (hydrophilic TBH or lipophilic CUM). In both cases, a quantitative yield was reached after about approximately 100 min. Figure 3 shows the variation of the molar percentage of acrylic units and T10 in the E-T10-05-TBH sample as a function of monomer conversion. Figure 4 refers to the incorporation of the hydrophobic T1 comonomer in the E-T1-05-CUM sample. Whatever the system, the rate of incorporation of these monomers did not vary significantly with conversion, an unexpected result if we consider the large difference in the values of the reactivity ratios of the monomers involved. The literature data reported for similar systems in homogeneous polar solutions indicate that alkyl methacrylates [e.g., methyl methacrylate (MMA) or butyl methacrylate (BMA)] are much more reactive than AM and AA ($r_{\text{MMA}} = 2.60$ and $r_{\text{AM}} = 0.44$;²⁹ $r_{\text{BMA}} = 3.67$ and $r_{\text{AA}} = 0.29$ ³⁰). As for the reactivity ratios of AM and AA in aqueous solutions, they are 0.9 and 0.29, respectively, at pH 9.³¹ However, it was shown in previous studies that the reactivity ratios of var-

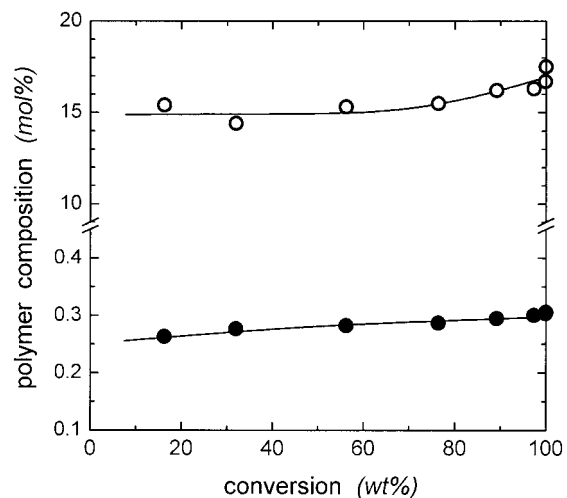


Figure 3 Variation of the molar percentage of (○) acrylic units (NaA + AA) and (●) T10 in the E-T10-05-TBH sample as a function of conversion.

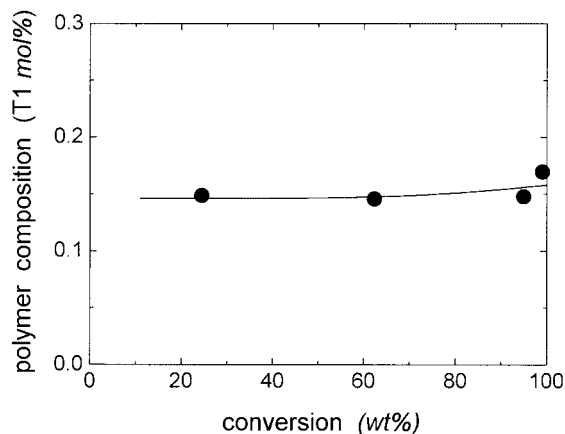


Figure 4 Variation of the T1 content in the E-T1-05-CUM sample as a function of conversion.

ious pairs of water-soluble monomers were affected by the method of polymerization. In particular, it was found that inverse emulsion or microemulsion polymerization of AM and NaA (with Isopar M as the continuous phase) led to reactivity ratio values close to unity.^{32–34} This result was interpreted in terms of the microenvironment (high local monomer concentration, viscosity of the medium, and nature of the interactions) and/or a polymerization mechanism different from that observed in homogeneous media. Our results, although fragmentary, corroborate the conclusions of these studies, that polymerization in dispersed media leads to samples more homogeneous in composition than those prepared in solution.

An additional point to note is that the molar composition of AM used in the feed (83%) was not far from the azeotropic composition determined in solution polymerization (88/12 mol/mol AM/NaA),³¹ and this may also account for the small compositional drift observed.

Copolymer Characteristics

Incorporation of the Amphiphilic Comonomer as a Function of Its HLB

A series of samples were prepared with the water-soluble redox couple. In this series, the average number of EO units of the comonomer was varied from 1 to 12, whereas its amount in the feed was kept constant and equal to 0.5 mol %. Figure 5 shows the amount of comonomer incorporated into the final polymer as a function of the average number of EO units. Let us recall that the higher the number of EO units in the amphiphilic comonomer, the greater the HLB. In all cases, the

comonomer incorporation was incomplete, although it increased with increasing HLB.

To interpret this result, we comment on the incorporation rate obtained for polymerizations reactions carried out in the presence of T12 (highest HLB value of the series) and T1 (lowest HLB value).

Synthesis in the Presence of T12 with a Water-Soluble Initiator (E-T12-O5-TBH Sample). Because the T12 comonomer had a rather high HLB value (14.4), it was assumed to preferentially locate in the aqueous dispersed phase together with the other components and/or at the water–oil interface. This situation was most favorable to good incorporation in the polymer, each droplet acting as a microreactor with kinetics resembling those of solution polymerization.

Synthesis in the Presence of T1 with a Water-Soluble Initiator (E-T1-O5-TBH Sample). The HLB of this comonomer was low (5.5), resulting in a preferential location of T1 in the organic, continuous phase or at the water–oil interface, the other components (AM, NaA, and the initiator) being solubilized in the aqueous dispersed phase. Each droplet was, therefore, the center of a solution copolymerization between AM and NaA with only a small contribution of the T1 comonomer.

Synthesis in the Presence of T1 with a Lipophilic Initiator (E-T1-O5-CUM Sample). Because of these results, we synthesized a sample based on

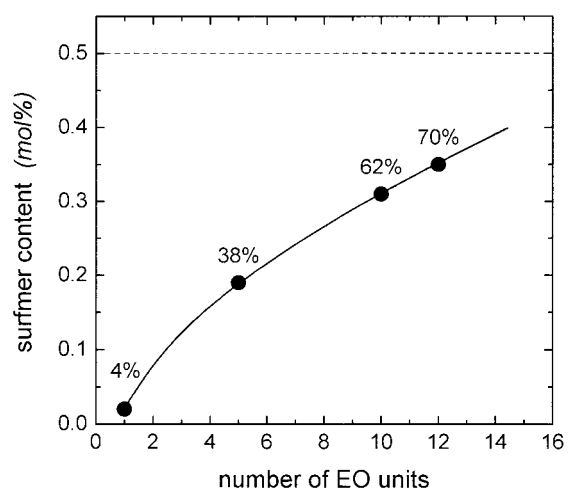


Figure 5 Surfmer content in the final copolymer as a function of the length of the EO spacer in the surfmer. Data-point labels indicate the incorporation level of the surfmers based on the initial surfmer content in the monomer feed (0.5 mol %).

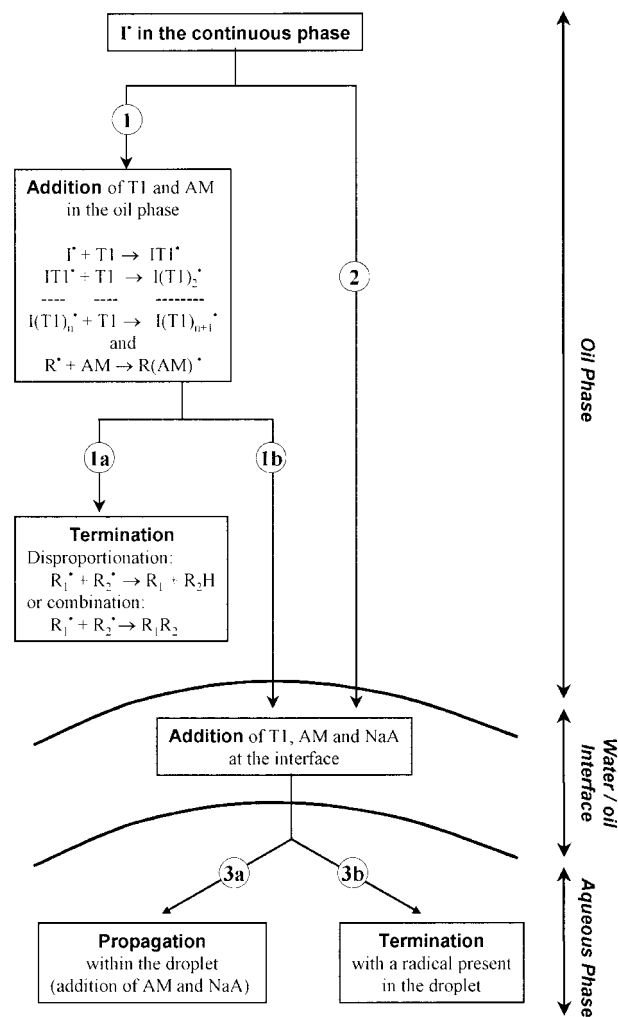


Figure 6 Mechanistic scheme for the inverse emulsion polymerization of AM, NaA, and T1 amphiphilic monomer with the lipophilic redox initiator (CUM).

T1 with the lipophilic CUM initiator instead of the water-soluble TBH. In this case, the T1 content in the final polymer reached 0.14 mol % as opposed to 0.02 mol % with TBH.

Figure 6 sets forth a mechanistic scheme for the inverse emulsion polymerization in the presence of T1 with CUM as the lipophilic initiator. According to this scheme, a radical generated by the initiator in the organic phase can either react with the hydrophobic T1 comonomer (path 1) or diffuse at the water–oil interface (path 2). In the first case, the radical can add other hydrophobic monomers or possibly AM monomers (low solubility in Isopar M) to give rise in the oily phase to a polymer after disproportionation or recombination (path 1a). After a few units are added, the radical can also come into contact by diffusion with the water–oil interface (path 1b). It can then

react with T1 or the AM and NaA molecules located at the interface (cosurfactant role) and subsequently propagates in the aqueous phase (path 3a) or terminates with a radical present in the droplet (path 3b). During the propagating reactions at the water–oil interface, a transfer reaction between the growing radical and the EO units of the nonionic surfactants may occur.³⁵ This mechanism implies that the water-soluble polymers have a hydrophobic comonomer-rich terminal group.

For a polymerization initiated with the TBH redox couple, radicals are essentially generated in the aqueous phase, accounting for the lower incorporation rate of T1. The low but not zero value of the T1 incorporation in the polymer can be accounted for by (1) the TBH redox couple generating a fraction of radicals in the organic phase, facilitating the T1 incorporation; (2) the low fraction of T1 present in the aqueous phase copolymerizing with AM and NaA; and (3) the hydrophobic monomer present at the water–oil interface also copolymerizing with the other monomers. The second and third reasons tend to indicate that the T1 units are statistically distributed along the polymer chain. In light of this mechanism, it seems difficult to discriminate between a blocky or statistical microstructure of the copolymers.

For T10-containing samples, it can be seen in Table II that the level of the surfmer incorporation decreased with an increasing initial T10 content in the monomer feed: the incorporation of T10 was nearly complete for a 0.2 mol % initial content but was only approximately 55% for a 0.8 mol % initial content. To explain this behavior, we must remember that a higher T10 content in the formulation also requires a higher Arlacel 83 content to maintain the HLB of the surfactant mixture at its optimal value. However, the solubility of T10 in the oil phase was enhanced in the presence of an increased amount of Arlacel 83.²⁸ This led to the lower incorporation level observed because, as discussed previously, the comonomers solubilized in the oil phase were less incorporated in the polymer chain.

Molecular Weights

The determination of the molecular weights was complicated because of the complex nature of the samples. They contained three types of monomer units along the backbone, one of which was charged and one of which was hydrophobic. As a result, we can expect that the light scattering measurements lead to an apparent molecular

Table III Molecular Weights of Two Samples Determined by Light Scattering in Formamide/NaCl Solution

Sample	[NaCl]	$M_w (\times 10^{-6})$
E-T10-05-TBH-NP	0.1M	5.7
E-T12-05-TBH	0.1M	5.8
E-T12-05-TBH	0.2M	6.4

weight rather than the true average molecular weight (M_w). A mixture of formamide and 0.1 or 0.2M NaCl was chosen as a solvent to minimize the hydrophobic associations and the ionic interactions. For a rigorous analysis of light scattering data, the refractive-index increment should be measured after the establishment of the osmotic equilibrium between the polyelectrolyte solution and solvent. Such a refinement was not taken into account in this study. However, the error remained limited because the ions of the salt added to the solvent were identical to the counterions of the polyelectrolyte.

In Table III are compared the average molecular weights determined for a sample containing 0.5 mol % T12 at two salt concentrations and for a sample synthesized under similar conditions but with the nonpolymerizable Triton-X100 surfactant instead of the T12 surfmer. The values are close to each other within the experimental error of the measurements and around 6×10^6 , allowing a meaningful comparison of the associating behavior reported in the next section.

Rheological Behavior

The experiments mainly dealt with samples based on T10 as the amphiphilic comonomer. In all cases, the thickening properties were compared to those of polymers without hydrophobes and prepared under similar experimental conditions.

Effect of the Nature of the Initiator

Figure 7 shows the concentration dependence of the Newtonian viscosity for two samples containing the same monomer feed but prepared with either the water-soluble redox initiator (TBH) or the lipophilic one (CUM). The Newtonian viscosities of the polymers prepared under the same experimental conditions but with the nonpolymerizable Triton-X100 surfactant are shown for comparison. Above a critical concentration of about 0.1 wt %, one can observe a strong enhance-

ment of the viscosity for the hydrophobically modified samples with respect to those obtained for the unmodified analogs, which reflects the formation of aggregates caused by hydrophobic intermolecular interactions. The effect was more pronounced for the sample prepared with the lipophilic CUM initiator (e.g., the viscosity was increased by as much as about 2 decades for a 0.2 wt % CUM sample). This result corroborates previous data that we obtained for samples of similar natures and compositions but synthesized in microemulsions.^{28,36}

Because the viscosity of the unmodified polymers does not depend on the nature of the initiator (see the open symbols in Fig. 7), we see no reason to attribute the observed difference in viscosity to a difference in molecular weight. We are rather inclined to believe that the associating behavior of the hydrophobically modified polymers depends on the nature of the initiator. This can occur for the following reasons:

1. A change in the amount of the amphiphilic comonomer effectively incorporated in the polymer. However, this amount could not be determined quantitatively for the E-T10-05-CUM sample (see the Experimental section).
2. A different microstructure, that is, a different distribution of the comonomer units along the polymer backbone.

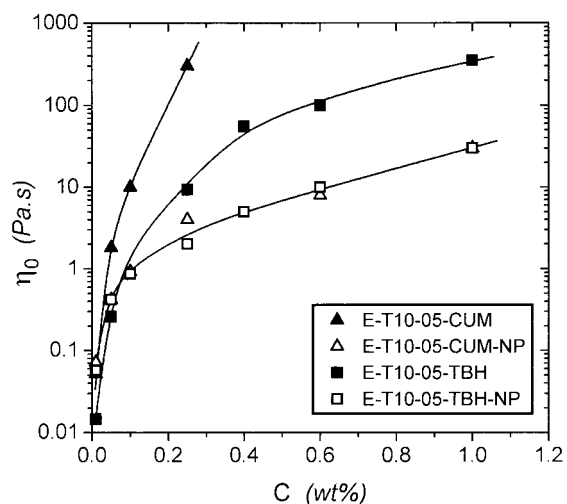


Figure 7 Variation of η_0 as a function of C for two T10-containing copolymers (filled symbols) prepared with CUM or TBH as the initiator at the same T10 content (0.5 mol %) in the initial monomer feed. Open symbols correspond to the surfmer-free homologue polymers.

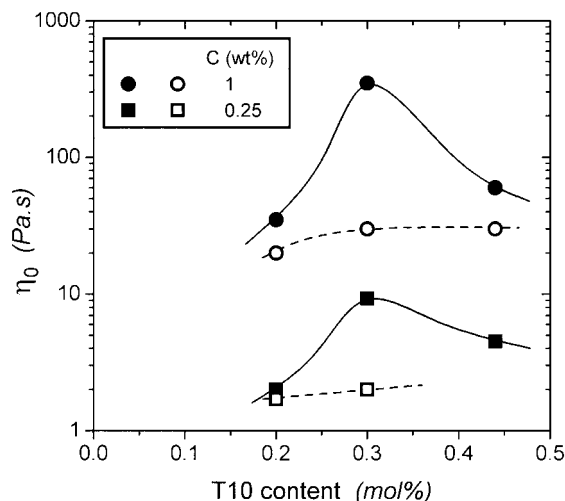


Figure 8 Effect of the surfmer content on η_0 of T10-containing copolymers (filled symbols) at two different polymer concentrations. Open symbols correspond to surfmer-free homologue samples.

The latter explanation seems most likely as several studies have stressed the major influence of the HMWSP blockiness on their associating properties.^{12,18,20,37–39} This assumption is further supported by the aspect of the aqueous solutions, which were opalescent for E-T10-05-CUM but perfectly transparent for E-T10-05-TBH. In addition, Larpent et al.⁴⁰ clearly showed that the nature of the initiator (oil-soluble or water-soluble) in a dispersed system containing styrene and a polymerizable surfactant could modify the apparent reactivity ratios values of the monomers and, consequently, the microstructure of the resulting copolymer.

Effect of the Comonomer Content

The effect of this parameter on the rheological behavior of HMWSP was investigated in the dilute and semidilute regimes.

Figure 8 shows the effect of the T10 content on η_0 for three samples of similar molecular weights but differing in the amount of T10 (from 0.2 to 0.44 mol %). In each case, the viscosity is compared with that of the unmodified polymer. For the hydrophobically modified samples, the viscosity of the solutions went through a maximum for a molar content of about 0.3 mol %. For 0.2 mol % T10, the polymer did not show any associating properties, and when the molar content reached 0.44%, the thickening efficiency was reduced. An optimum in viscosity was also observed by other authors for various HMWSPs.^{41–44} This behavior

is explained by the competition between intermolecular and intramolecular associations, which have opposite effects on the thickening efficiency: the former type of association leads to the formation of a transitory three-dimensional network, whereas the latter is responsible for chain collapse. Therefore, the viscosity decreases beyond a given hydrophobe level because the intramolecular association effect overcomes the intermolecular association effect. In our case, the optimum was located at a very low hydrophobe content (~ 0.3 mol %), whereas it was generally a few percent in other studies.^{41–45} We ascribe this difference to the presence of an hydrophilic poly(oxyethylene) spacer between each hydrophobic group and the polymer backbone. Indeed, it has been reported that the viscosity maximum is shifted toward lower hydrophobe contents (from 2.5 to 0.5 mol %) with the length of the hydrophilic spacer increasing from 0 to 3 EO units.^{43,44} This was explained by a decoupling in the motion of the polymer backbone and hydrophobic side groups that favored both intramolecular and intermolecular hydrophobic interactions. Our results are in agreement with these previous findings: because of a much longer hydrophilic spacer (10 EO units), the viscosity maximum occurred at a very low hydrophobe content.

Experiments were also carried out in the dilute regime for the same series of samples but in the presence of 0.1M NaCl to suppress the polyelectrolyte effect. Figure 9 shows the variation of the intrinsic viscosities ($[\eta]$) and the corresponding Huggins coefficients (k_H) as a function of the T10 comonomer content. A significant decrease in $[\eta]$ was observed with the T10 content in the copolymer increasing above approximately 0.2 mol %. This was due to the formation of intramolecular interactions resulting in a collapse of the chain. Simultaneously, k_H became greater, indicating a lowering of the solvent quality, in good agreement with the behavior often observed for associating polymers in dilute solutions.^{12,15,17,38,46} Note that $[\eta]$ values of the sample with 0.2 mol % T10 and the unmodified polymer are quite close; this reflects the absence of significant hydrophobic interactions, in agreement with the results observed previously in salt-free solutions at higher concentrations.

Effect of the Degree of Conversion

Rheological measurements performed on samples taken at two different degrees of conversion from the same copolymerization experiment (E-T10-

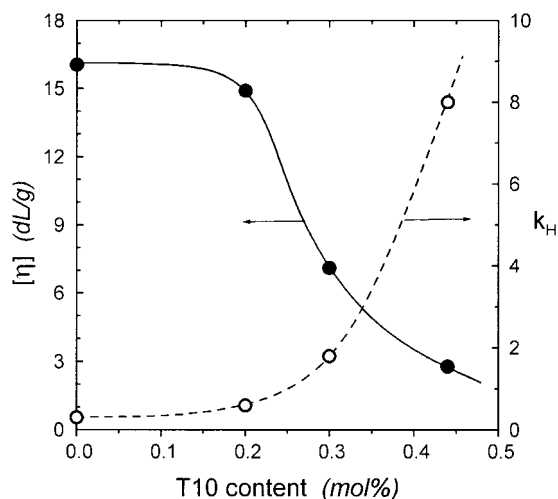


Figure 9 Variation of $[\eta]$ and k_H as a function of the T10 comonomer content.

05-TBH) show that the low-conversion sample (16%) exhibited enhanced thickening properties in comparison with the full-conversion sample, with approximately 100 Pa s instead of approximately 10 Pa s at $C = 0.25$ wt %. This could reflect an evolution of the copolymer microstructure with conversion as previously found for other associating polymers synthesized by micellar copolymerization.^{19,38} Another contribution could be the slightly higher hydrophobe content in the final polymer (0.3 mol % instead of 0.26 mol % for the low-conversion sample), which could be beyond the optimal hydrophobe content as discussed previously.

Shear Thinning Behavior

Under shear, the copolymer solutions exhibited the pronounced shear thinning behavior usually found for associating polymers and caused by the disruption of the temporary physical network. However, for the systems investigated here, the viscosity did not decrease monotonously in the shear thinning regime. Figure 10 shows that there are some transitions that appear more clearly in a plot of the viscosity and shear stress than in a plot of the viscosity and shear rate. Such behavior seems to be typical of some associating systems because Aubry and Moan (for hydroxypropylguar derivatives^{47,48}) and Jenkins and coworkers (for the so-called HEUR⁴⁹ and HASE^{50–52} polymers) also reported similar rheological behaviors. Actually, with our samples, two inflection points often appear in the flow curves, similar to the findings of Jenkins and cowork-

ers.^{49–51} Although some successive rearrangements of the transient physical network could be postulated to account for the nonconventional flow curve shape, a clear explanation of this behavior is still a matter of discussion. By assuming that the sudden drop in viscosity is related to the destruction of the hydrophobe links, we can estimate the average lifetime of the hydrophobic associations from the reciprocal of the shear rate at the transition.^{47,52} In this study, this critical shear rate could be hardly estimated because rather smooth transitions were observed, in contrast with the single and sharp discontinuity reported elsewhere.^{47,52} The broadening of the transition could be ascribed to a slight heterogeneity in the microstructure and composition as already discussed in the previous section. As shown in Figure 10, the discontinuity effect was maximized in the intermediate polymer concentration range (0.4 wt % $\leq C \leq 1$ wt %) and was more difficult to observe at higher polymer concentrations ($C \geq 2$ wt %). This has to be related to the transition between the unentangled semidilute regime and the entangled semidilute regime. Note also that a slight shear thickening effect can be observed on flow curves at intermediate polymer concentrations; this is also typical of unentangled semidilute solutions of associating polymers and is the signature of intramolecular associations.^{17,19,20,52,53}

Influence of the Shear History

Several studies have shown that the rheological properties of associating polymers in aqueous solutions can be strongly dependent on the shear

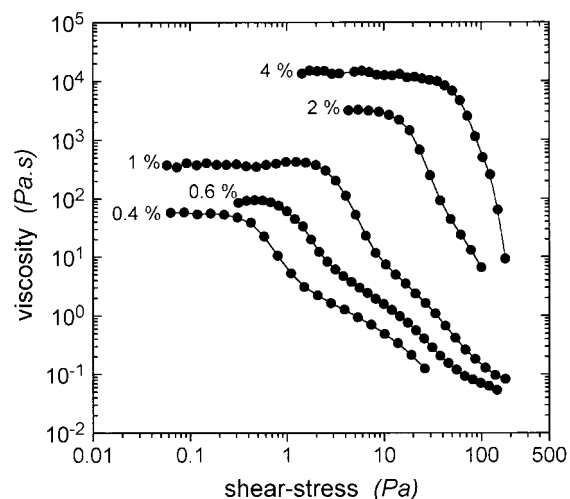


Figure 10 Viscosity as a function of shear stress for the E-T10-05-TBH sample at different concentrations.

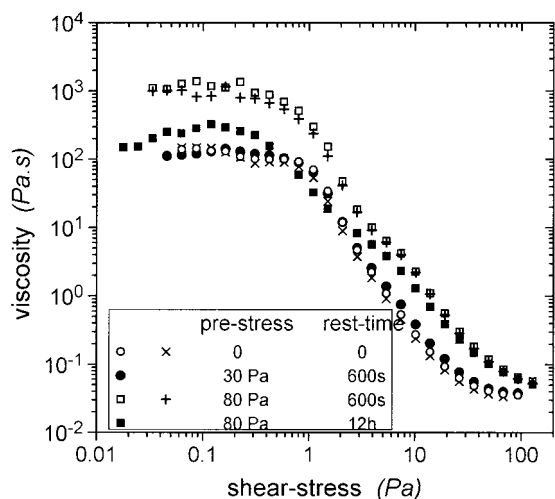


Figure 11 Shear history effect: flow curves recorded after different preshearing stresses and variable rest times (the low-conversion E-T10-05-TBH sample, $C = 0.25$ wt %).

history.^{12,15,48,49,54–58} Various behaviors have been previously observed when the viscosity has been measured as a function of time under constant shear or with alternating shear and rest periods. Therefore, the systems are most often time-dependent (thixotropic and/or rheopectic), and the variations in viscosity could depend on the time and the level of the stress as well as the rest time. Such phenomena have been explained, at least qualitatively, by the kinetics of the disorganization and reorganization of the network structure and, therefore, by more or less complex relaxation processes.

The shear history effect has been investigated here by the application of a given shear stress (30 or 80 Pa) for a given time (10 min), and then the sample was left at rest for a variable time (10 min or 12 h) before the viscosity was measured with a stress sweep according to the usual procedure (equilibrium condition). The resulting flow curves were compared with that obtained for the same sample (E-T10-05-TBH, low conversion) without preshearing (Fig. 11). First, two different measurements without preshearing led to quite reproducible results. The sample subjected to preshearing with $\sigma = 30$ Pa exhibited an identical flow curve. On the contrary, after preshearing with a greater stress value, $\sigma = 80$ Pa, and the same rest time (10 min), the viscosity values were strongly enhanced: the Newtonian plateau was approximately 10 times higher. These results mean that above a critical shear stress and the full destruction of the physical network, the latter reformed

in a different way. Once again, the reproducibility of the rheological properties could be noted by the good superposition of two sets of experimental data with preshearing at $\sigma = 80$ Pa. However, this reorganization, implying a greater number of intermolecular associations, actually corresponded to a metastable state. Indeed, after a long time at rest (12 h), the viscosities came back to values close to the initial ones, an indication that the system recovered its initial structure very slowly.

CONCLUSIONS

In this article, we have describe the synthesis of associating water-soluble polymers with an inverse emulsion polymerization route. The hydrophilic backbone of the copolymers was formed from an AM/NaA mixture. The incorporation of the hydrophobic groups (<0.5 mol %) was achieved by free-radical copolymerization of these water-soluble monomers with a series of amphiphilic comonomers, the isooctylphenoxy-poly(oxyethylene)(n) methacrylates, whose number of EO units was varied from 1 to 12. We have defined the best stability conditions for the production of stable emulsions before and after polymerization. The process yielded high molecular weight polymers ($M_w \sim 6 \times 10^6$) encapsulated within water-swollen droplets dispersed in an organic medium (solid content ≤ 25 wt %). This conditioning facilitated its subsequent use for industrial applications. High yields of conversion were reached (>99%) with, however, a partial incorporation of the minor hydrophobic component in the copolymer. When a hydrophilic redox initiator was used, the incorporation level increased with the HLB of the amphiphilic comonomer, that is, with the number of EO units.

The copolymers formed were quite homogeneous in composition, confirming the specificity of the polymerization mechanism in dispersed media. This was due to monomer partitioning between the dispersed phase and the continuous phase as well as interfacial and microenvironment effects.

These hydrophobically modified polymers exhibited interesting rheological properties in aqueous solutions. In the semidilute regime, the hydrophobic groups associated intermolecularly, which induced a strong increase in the viscosity, even at very low polymer concentrations (~ 0.2 wt %) and hydrophobe contents (≤ 0.5 mol %). The rheological behavior of the samples was directly

correlated to the synthesis conditions. In particular, the degree of association depended on the nature of the redox initiator; the best conditions were obtained when the initiator was located in the phase that did not contain the amphiphilic comonomer, and this result was attributed to a different copolymer microstructure (blocky or statistical), depending on the synthesis conditions.

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