Reactive Surfactants in Heterophase Polymerization. 9.[†] Optimum Surfmer Behavior in Emulsion Polymerization

Harold A. S. Schoonbrood[‡] and José M. Asua*

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apartado 1072, 20080 San Sebastián, Spain

Received February 3, 1997; Revised Manuscript Received June 24, 1997[⊗]

ABSTRACT: In an attempt to define the conditions for the optimum use of polymerizable surfactants (surfmers), two anionic maleate surfmers were applied in various emulsion copolymerization systems including styrene/butyl acrylate/acrylic acid, vinyl acetate/VEOVA 10/acrylic acid, vinyl acetate/butyl acrylate/acrylic acid, and methyl methacrylate/butyl acrylate/vinyl acetate. It was found that the reactivity ratios were the most important variable controlling the incorporation of the surfmer into the polymer chains. The surfmer conversion also depended on the particle size: the larger the particle size, the lower the surfmer conversion. It was also found that when the surfmer copolymerized well with the monomers attaining high conversions from the beginning of the process onward, a significant part of the surfmer was buried in the particle interior, leading to unstable latexes. On the basis of the results, an optimum surfmer behavior was defined. Some preferable combinations of surfmer reactive groups and comonomers in terms of reactivity ratios were suggested. Several strategies were proposed to attain the optimum surfmer behavior, and for some of these strategies, experimental examples were given.

Introduction

Surfactants can have negative effects on the properties of the products of emulsion polymer latexes. These negative effects are caused by the fact that the surfactants—when unbound to the polymer material—can desorb from the latex particle surface, causing destabilization, for example, under high shear. The unbound surfactants can migrate through the film, forming aggregates that increase the water sensitivity of the product and cause plasticization by water.[1] The migration of the surfactant[2−4] can also take place toward the air−film interface or even the substrate−film interface. This may have negative consequences for the water sensitivity of the film−air surface and for the adhesion properties of the film at the substrate interface. A solution to these problems can be the use of reactive surfactants. The use of reactive surfactants ensures that the surfactant moiety is bound covalently to the polymer material so that desorption from the latex particle surface or migration in the polymer film is impeded. The more promising possibility lies in the combination of a surfactant and a monomer, referred to as surfmer.[5,6] Examples include anionic surfmers with sulfate or sulfonate head groups,[7−13] cationic surfmers,[14,15] and nonionic surfmers.[16,17] Also a wide range of reactive groups can be found, for example, allylics,[18,19] acrylamides,[13] (meth)acrylates,[18,20] styrenics,[11,21] and maleates. There are also many examples of their use in emulsion copolymerizations, *e.g.*, refs 7, 10, and 21−28. Improvements in properties through the use of surfmers have been reported quite regularly, *e.g.*, in mechanical stability[23] and electrolyte stability of the latex[21] (due to decreased surfactant desorption from the latex surface) and control of surface charge density.[22] In films cast from latexes prepared with surfmers, a decrease of surfactant migration has been reported[10] as well as an improvement of water resistance[9,11,17,22,23] and adhesivity.[11,17,29] An extensive overview of the use of surfmers in polysoaps is given in ref 30. (Note that, in the present work, the focus is on the use of surfmers in emulsion polymerization as comonomers and not to produce polysoaps.)

In two previous publications[7a,b] we reported on the use of several anionic surfmers with varying reactivities. The surfmers were evaluated in the semicontinuous emulsion terpolymerization of styrene (S), butyl acrylate (BA), and acrylic acid (AA) with constant addition rates for monomers and surfmers. The reactions were analyzed with respect to particle size, latex stability, formation of coagulum, and mechanical and electrolyte stability.[7a] The conversions of some of the surfmers (sodium 11-methacryloyl undecan-1-yl sulfate (MET), sodium 11-crotonoyl undecan-1-yl sulfate (CRO), and tetradecyl sulfopropyl maleate (M14)) were analyzed by washing latex samples with water in a serum replacement cell to remove unreacted surfmer.[7b] The concentration of unreacted surfmer in the wash water was determined by means of two-phase titration.[31] It was observed that the conversion of the surfmer depended strongly on the reactivity of the polymerizable group in copolymerization with the main monomers and also strongly on the particle size. If the surfmer was not reactive enough, it did not become incorporated in the polymer material, so that it functioned as surfactant only. On the other hand, if the surfmer was too reactive and its conversion throughout the reaction very high, it could become buried inside the latex particles and be unable to provide stability, or it could form water-soluble polymer chains that can cause bridging flocculation. A surfmer with intermediate reactivities performed more successfully, leaving room for control of its level of conversion. However, at the same time, it was found that the surfmer conversion decreased considerably as the particle size was increased above 100 nm. These studies led to the conclusion that it is not possible to use just any surfmer in a given comonomer system. Moreover, the optimum addition strategy of a given

---

[*] Author to whom correspondence is addressed. E-mail: qppasgoj@sq.ehu.es.

[†] This publication is part of a series of publications from the European Union Programme "Human Capital and Mobility" (CHRX CT 930159) on "Reactive Surfactants for Heterophase Polymerization".

[‡] Present address: Rhône-Poulenc, Centre de Recherches d'Aubervilliers, 52 rue de la Haie Coq, 93308 Aubervilliers Cedex, France.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

S0024-9297(97)00149-6 CCC: $14.00

surfmer in a particular polymerization system may not be a simple matter; *e.g.*, a straightforward, constant addition profile as was used in the previous studies may not be the best procedure.

These results lead to the following questions. Is there an optimum surfmer molecular structure for a particular emulsion polymerization system? Is there an optimum strategy for the use of such a surfmer? Can we give general rules for the choice of a surfmer and its use? In the present paper we will attempt, at least partially, to answer these questions. It has to be pointed out that, although the complete structure of a surfmer is defined by three aspects (its hydrophilic and lipophilic characteristics that control its performance as an emulsifier, the type of reactive double bond, and the position of the double bond within the molecule[32,33]), in this paper we will only refer to the type of double bond, which is the main factor affecting the surfmer reactivity. (The position of the double bond within the surfmer may also have some effect on its reactivity, but this will not be considered in this work.) Regarding the colloidal aspects of the surfmer, some data will be given, but it suffices to say that the surfmer must be able to stabilize the monomer emulsion and the latex particles; *i.e.*, it must be a good emulsifier.

When searching for a good surfmer for a given emulsion polymerization system, perhaps the most obvious route would be to synthesize different surfmers and to evaluate their performance in the emulsion polymerization. However, the synthesis of a surfmer is a tedious and time-consuming exercise. Although some of the work carried out in our laboratory using different surfmers in one emulsion polymerization system will be reviewed and discussed, in this work mainly a different approach is followed. We have chosen one type of double bond (maleate diester) and varied the relative reactivity of the surfmer with the comonomers by using several comonomer systems which display varying reactivities with the surfmer. The maleate double bond has been chosen because, in a previous screening of several different surfmers in a system with S, BA, and AA,[7a,b] sodium tetradecyl 3-sulfopropyl maleate (M14) performed better than the methacrylic acid and the crotonic acid esters. In this work we have also used the dodecyl (Analogue) of M14 (M12). The comonomer systems investigated include the following:

(I) S/BA/AA (49.5/49.5/1 (wt %)). This system has been extensively studied before with M14 as surfmer,[7a,b] and some of those results will be discussed together with new results of reactions with M14 and M12.

(II) Vinyl acetate (VAc)/VEOVA10/AA (69/30/1 (wt %)). VEOVA 10 is a vinyl ester of a highly branched decanoic acid, TM (Shell).

(III) VAc/BA/AA (79/20/1 (wt %)).

(IV) Methyl methacrylate (MMA)/BA/VAc (50/35/15 (wt %)).

Table 1 presents the reactivity ratios between the comonomers and the surfmer.

Based on the performance of the maleate surfmer in the emulsion polymerization of these systems, the optimum surfmer behavior will be defined. Some general rules will be proposed for the reactivity ratios of preferable combinations of comonomers and surfmer types, and ways for inducing the optimum surfmer behavior under industrial-like conditions, namely, high solids content formulations, will be presented.

Table 1. Reactivity Ratios of the M14 (or Corresponding Monomers) with the Main Monomers

surfmer or equivalent monomer	styrene r_S, $r_{surfmer}$	butyl acrylate r_{BA}, $r_{surfmer}$	vinyl acetate r_{VAc}, $r_{surfmer}$	methyl methacrylate r_{MMA}, $r_{surfmer}$
diethyl maleate (M14)	8−10, 0[34]	≫10, 0[a]	0.04, 0.17[34]	354, 0[35]

[a] Estimated on the basis of results of a reaction between BA and M14,[7b] where M14 did not polymerize at all in the presence of BA.

Table 2. Molecular Weight, Purity, and Surface Properties of Surfmers Used[7a]

surfmer	molecular weight	purity (%)	cmc (g/L) tensiometry	cmc (g/L) conductimetry	a_s[a] (Å^2)
M14	456	75	0.12/0.085	0.39/0.2[37]	38
M12	428	92[7c]	0.51[37]	0.68[37]	
SDS	288	91	1.15		42

[a] Water−particle interface.

Experimental Section

Chemicals and Recipes. Styrene, butyl acrylate, vinyl acetate, and methyl methacrylate were distilled before use and stored at −18 °C. VEOVA10 was washed with a 1% NaOH solution and also stored at −18 °C. Acrylic acid (with 10 ppm *p*-methoxyphenol), potassium persulfate (KPS; Fluka, 99%), sodium bicarbonate (Merck, 99.5%), $Na_2S_2O_5$ (Panreac), and sodium dodecyl sulfate (SDS) were used as received. SDS was applied as a reference surfactant. As surfmers we used tetradecyl sulfopropyl maleate (M14)[7a] and dodecyl sulfopropyl maleate (M12, kindly obtained from K. Stähler[36]). The surface-active properties of these surfmers and SDS (used to prepare seed latexes) are given in Table 2. It can be seen that the purity of M12 was approximately 92% and that of M14 76%. The impurities of the surfmers are mainly products coming from the hydrolysis of the maleate groups (long-chain alcohol, sulfonic salts, ...). Although these products are not surface active, the sulfonic salts may become surface active upon reaction with the monomers in the aqueous phase. However, the amount of these species will be small, and they are not therefore expected to influence the overall polymerization behavior.

The reactions were carried out semicontinuously with a 4 h addition period (in 55-I-M14-2-12 this was 12 h). Some of the reactions were carried out with seed latexes. In series I these were latexes prepared with S and BA (50/50 wt %, seed latexes C and D) and in series II with VAc/VEOVA10 (75/25 wt %, seed latex E). These seed latexes were prepared in batch reactions at 80 °C. Recipe (in g) for seed latex C: S, 30; BA, 30; SDS, 2.3; KPS, 6.7; $NaHCO_3$, 2.3; H_2O, 1940. For D and E: S + BA (or VAc + VEOVA10), 60; SDS, 6; KPS, 4; $Na_2S_2O_5$, 2; $NaHCO_3$, 1.7; H_2O, 900. The particle diameters were 39 nm for C and 33 nm for D and E (determined by light scattering, see below). In the seeded reactions no monomer was initially charged, and in the nonseeded reactions the initial monomer charge was allowed to react for 15 min. The polymerizations carried out are summarized in Table 3. The code of each reaction is composed as follows: solids content-monomer system-surfmer-weight % of surfmer; e.g., 30-I-M14-1 refers to the 30 wt % content emulsion polymerization of S/BA/AA using 1 wt % M14 as surfmer. The recipes for the reactions are given in Tables 4−7. In the graphic representation of the results $t = 0$ corresponds to the start of the semicontinuous monomer feed. The polymerizations were carried out in glass reactors with a water jacket for temperature control. A heat exchanger fed with tap water was placed between the reactor and the water bath to control any sudden heat production and to keep the reactor at the set temperature. Two separate feeds were used: the first the neat monomers and the second an aqueous feed with initiator, buffer, and surfmer. The feed flow rates were computer-controlled using an algorithm of proportional integral control. The pumps (ProMinent Gamma/4-RS, feed range 0.1−50 mL/min) pumped the

Table 3. Summary of the Reactions

reaction	monomers (wt %)[a]	recipe	solids content (wt %)	surfmer (wt %)	final particle size (nm)	coagulum (wt %)
30-I-M14-1	S/BA/AA (49.5/49.5/1)	Table 4,[b] 80 °C	30	M14, 1	98	1.3
55-I-M14-2	S/BA/AA (49.5/49.5/1)	Table 5, 80 °C, seed C	55	M14, 2	171	1.0
55-I-M14-2-12	S/BA/AA (49.5/49.5/1)	Table 5, 80 °C, seed C, 12 h	55	M14, 2	181	8[c]
50-I-M14-2	S/BA/AA (49.5/49.5/1)	Table 6, seed D, 80 °C	50	M14, 2	114	1.4
50-I-M12-2	S/BA/AA (49.5/49.5/1)	Table 6, seed D, 80 °C	50	M12, 2	109	1.2
30-II-M12-1	VAc/VEOVA10/AA (69/30/1)	Table 4, 67 °C	30	M12, 1	128	0.6
50-II-M12-2	VAc/VEOVA10/AA (69/30/1)	Table 6, seed E, 67 °C	50	M12, 2	>170	15
54-III-SDS-3.5	VAc/BA/AA (79/20/1)	Table 7, 67 °C	54	SDS, 3.5	146	0.4
54-III-M12-3.5	VAc/BA/AA (79/20/1)	Table 7, 67 °C	54	M12, 3.5		100
30-III-M12-1	VAc/BA/AA (79/20/1)	Table 4, 67 °C	30	M12, 1	109	0.3
30-IV-M12-1	MMA/BA/VAc (50/35/15)	Table 4, 67 °C	30	M12, 1	114	0.9

[a] wt % based on monomers. [b] Surfmer partitioning 30/70. [c] Mainly drying up of latex on the reactor wall.

Table 4. Recipe for the Nonseeded, Semicontinuous Emulsion Polymerizations with 30% Solids Content

	initial charge (g)	feed (g)	partitioning initial charge/feed	total (g)
comonomers[a]	5	95	5/95	100
KPS	0.075	0.075	50/50	0.15
$NaHCO_3$	0.075	0.075	50/50	0.15
H_2O	151.7	81.6	65/35	233.3
surfactant[b]	0.1	0.9	10/90	1.0

[a] The composition of the comonomer mixture was varied in each reaction. [b] This amount pertains to pure surfmer.

Table 5. Recipe for the Seeded, Semicontinuous Emulsion Polymerizations with 55% Solids Content Using System I of Monomers

	initial charge[a] (g)	feed (g)	partitioning initial charge/feed	total (g)
S + BA	1.4	97.6	1/99	99.0
AA	0	1.0	0/100	1.0
KPS	0.07	0.08	50/50	0.15
$NaHCO_3$	0.07	0.08	50/50	0.15
H_2O	48.2	33.3	59/41	81.5
surfactant[b]	0.06[c]	1.9	3/97	2.0

[a] Seed latex C + additional water and surfmer. [b] This amount pertains to pure surfmer. [c] SDS from seed latex C.

Table 6. Recipe for the Seeded, Semicontinuous Emulsion Polymerizations with 50% Solids Content

	initial charge[a] (g)	feed (g)	partitioning initial charge/feed	total (g)
comonomers[b]	2.08	97.92	2/98	100
KPS	0.3	0.3	50/50	0.6
$NaHCO_3$	0.3	0.3	50/50	0.6
H_2O	50	50	50/50	100
surfactant[c]	0.2 + 0.2[d]	1.6	20/80	2.0

[a] Seed latex + additional water and surfmer. [b] The composition of the comonomer mixture was varied in each reaction (see Table 3). [c] This amount pertains to pure surfmer. [d] SDS + surfmer (SDS from seed latex).

two feed streams from bottles (placed on balances, Sartorius Universal U 4100 S, ±0.01 g) whose weight decrease was monitored on-line by a computer. After the feeding period (4 h) the systems were left to react for another hour.

Analysis of Reactions, Particle Size, and Coagulum Formation. During the reactions samples were taken to determine the conversion of the main monomers and surfmers and the particle size. The conversion of the main monomers was determined with gravimetry. This results in values for the fractional weight average conversion (weight of polymer formed divided by weight of monomers added until that time), which will be referred to as fractional conversion or simply conversion. Serum replacement (SR) was used to recover the unreacted surfmer to determine its conversion. The recovery was performed with a UHP-76 of MicroFiltration Systems, by flushing distilled water through in discontinuous mode. The effluent was collected for analysis of the surfmer concentration.

Table 7. Recipe for the Nonseeded, Semicontinuous Emulsion Polymerizations with 54% Solids Content

	initial charge (g)	feed (g)	partitioning initial charge/feed	total (g)
comonomers[a]	5	95	5/95	100
KPS	0.037	0	100/0	0.037
$NaHCO_3$	0.037	0	100/0	0.037
H_2O	28.8	55.7	35/65	84.5
surfactant[b]	1.05	2.45	30/70	3.5

[a] The composition of the comonomer mixture was varied in each reaction. [b] This amount pertains to pure surfmer.

This concentration was determined with two-phase titration, which has been described before.[7b] The particle size was determined with light scattering (LS) with a Malvern System 4700c. This technique gives a z-average particle size ($d_z = \sum n_i d_i^5 / \sum n_i d_i^4$). The amount of coagulum was measured by collecting coagulum on the reactor wall and stirrer and by filtering the latex (mesh 63). It is presented as the weight of coagulum per the total weight of monomer added.

Results and Discussion

Effect of the Reactivity Ratios. System I: Styrene/Butyl Acrylate/Acrylic Acid. In ref 7a,b, several semicontinuous emulsion copolymerizations have been reported with three anionic surfmers having strongly varying reactivities. The methacrylate surfmer (MET) was too reactive for this monomer system, leading to massive coagulation. On the other hand, the crotonate surfmer (CRO) showed a very low reactivity in copolymerization, behaving like a nonreactive surfactant. In the case of maleate (M14), which was investigated in greater detail,[7b] it appeared that the level of conversion was between that of the crotonate and methacrylate surfmers, which is in line with its general copolymerization reactivity. An example of a seeded semicontinuous reaction with M14 (50-I-M14-2) is given in Figure 1. The equivalent reaction with M12 (50-I-M12-2) is shown in the same figure. The recipes of these reactions are given in Tables 3 and 6. The evolution of the total conversion of the main monomers with time was virtually the same for both reactions. The recipes, with the exception of the surfmer, were identical, and the particle number was the same (seeded reactions). It was shown in ref 7b that equivalent reactions with SDS and sodium styrenesulfonate also gave conversion results almost identical with those of 50-I-M14-2. This indicates that the use of the reactive maleate surfmers in these reactions does not affect the kinetics.

Figure 1 also shows that M14 had a relatively high conversion throughout the reaction and a final conversion of 80%. The conversion of M14 was determined by measuring the unreacted surfmer by two-phase

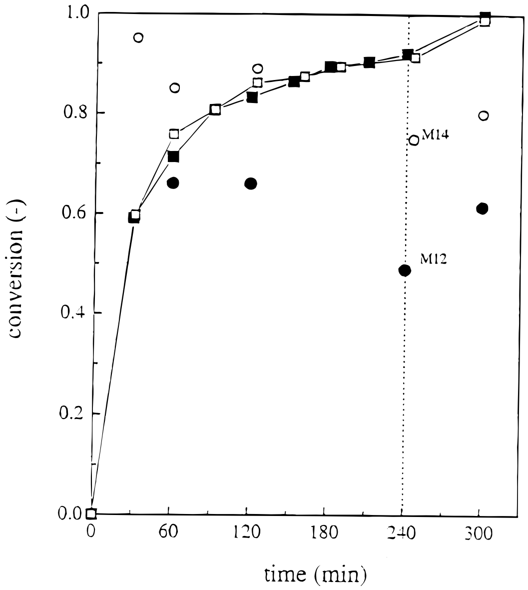

Figure 1. Main monomer conversion (squares) and surfmer conversion (circles) versus time in reactions 50-I-M14-2 (open symbols) and 50-I-M12-2 (closed symbols).

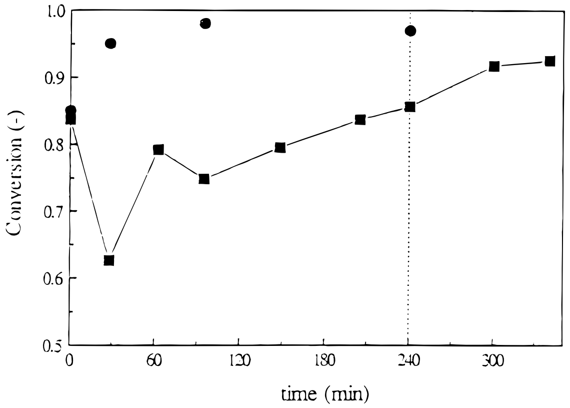

Figure 2. Main monomer conversion (■) and surfmer conversion (●) versus time in reaction 30-I-M14-1.

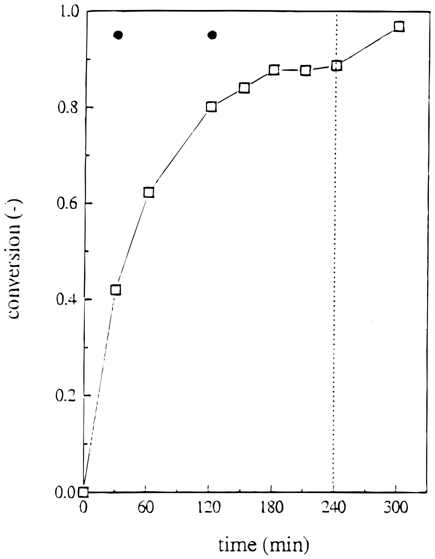

Figure 3. Main monomer conversion and surfmer conversion versus time in reaction 30-II-M12-1 (main monomer, □; M12, ○).

titration. A possible source of errors is the hydrolysis of the surfmer that would make the molecule non-surface-active and hence would not be detected by the two-phase titration method. Unzué^{38} studied the hydrolysis of the M14 at 80 °C and pH 3 (polymerization conditions), finding that after 6 h only 6.5% of the maleate molecules suffered hydrolysis. The conversion of M12 was somewhat lower than that of M14 at equivalent points during the reaction, and its final conversion was 62%. Apart from this difference (which could perhaps be a consequence of the higher water solubility of M12 and hence somewhat lower concentration at the probable main locus for polymerization of the surfmer, the surface of the particle), it can be seen that the pattern of the conversion versus time showed the same characteristics as M14, with a small increase after the end of the feeding period, which corresponds to a batch reaction of the remaining main monomers. These levels of conversion could make these surfmers interesting for this monomer system, as the conversions were high enough to guarantee a high degree of incorporation at the end of the reaction, and, on the other hand, they do not give rise to significant coagulation (the amounts of coagulum in reactions 50-I-M14-2 and 50-I-M12-2 amounted to 1.4% and 1.2%, compared with 1.4% for the equivalent reaction with SDS). Although these amounts are rather high for an industrial recipe, it has to be pointed out that the coagulum was mainly formed by evaporation of water from the latex wetting the reactor wall above the liquid surface, and this coagulum is promoted in small reactors such as the one used in this work. It was observed in a nonseeded reaction with a somewhat smaller final particle size (98 nm, reaction 30-I-M14-1) that the conversion of M14 during the reaction reached levels higher than 95% during the semicontinuous process (see Figure 2). The surface charge density analysis of an equivalent reaction carried out with a water-soluble noncharged initiator (2,2′-azobis(2-methyl-*N*-(2-hydroxyethyl)propionamide) showed that only about 40% of the original M14 surfactant groups were present at the particle surface. This indicates that a large proportion was buried in the particle interior, probably due to the high conversion of M14 from the beginning of the reaction onward. This was corroborated by the results of other reactions, where the surfmers reached very high levels of conversion at low overall conversion. In batch reactions of S with M14^{7c} initiated by $K_2S_2O_8$, the early reaction of the surfmer also led to burying of a significant part of the surfactant groups (65%). This effect decreased the final surface charge density and the stabilizing potential of the surfactant.

All the results combined show that the extent of conversion of the maleate surfmers in comonomer system I can vary considerably, and therefore the maleates may not be optimum surfmers for this system under all circumstances. Before we look at this in more detail, the behavior of the maleates in two other comonomer systems will be discussed.

System II: VAc/VEOVA10/AA (Reactions 30-II-M12-1 and 50-II-M12-2). M12 was used as a surfmer in the monomer system VAc/VEOVA10/AA. The conversion results are shown in Figure 3. It can be seen that in reaction 30-II-M12-1 the conversion of M12 was very high (the concentration of M12 in the effluent of the SR cell was very close to the detection limit) from the beginning onward. The amount of coagulum was not very high, however, and no signs of instability were observed. Since this could be a result of the fact that the solids content was low, reaction 50-II-M12-2 was carried out using seed latex E to ensure a particle size

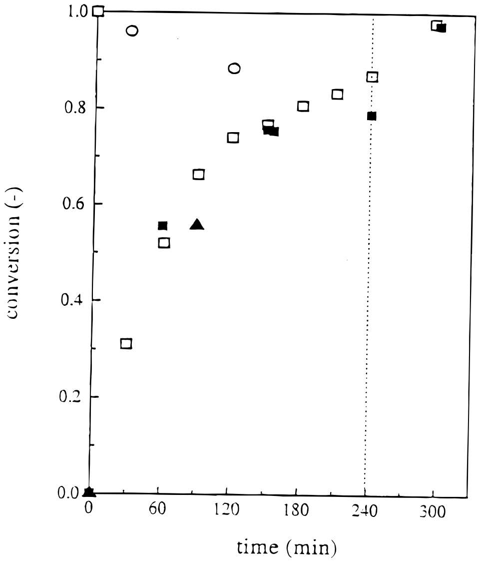

Figure 4. Main monomer conversion and surfmer conversion versus time in reactions 54-III-SDS-3.5 (main monomer, ■), 54-III-M12-3.5 (main monomer, ▲), and 30-III-M12-1 (main monomer, □; M12, ○).

similar to that of 30-II-M12-1. The amount of coagulum produced in this reaction was quite high, and at the same time, the particle size was much higher than expected on the basis of the number of seed particles. This shows the general instability of reaction 50-II-M12, probably caused by the high conversion of the surfmer (in this reaction, the surfmer conversion was not analyzed because the coagulum impeded the recovery of the unreacted surfmer by serum replacement). The high conversion of the surfmer is in agreement with the reactivity ratios between diethyl maleate and VAc: $r_{\text{diethyl maleate}} = 0.04$, $r_{\text{VAc}} = 0.17$,[34] see also Table 1.

System III: VAc/BA/AA System (Reactions 54-III-SDS-3.5, 54-III-M12-3.5, and 30-III-M12-1). In this monomer system, BA is far more reactive than VAc, and at the end of the feeding period there will be a certain amount of VAc left, even under starved conditions. On the other hand, as the M14 does not react with BA,[7b] it was expected that during the feeding time of a semicontinuous process, when there is always some free BA present, the maleate surfmer would not react to high conversion as it does in a system with only vinyl esters, e.g., system II. Consequently, the surfmer would react with the remaining part of the VAc after stopping the feed. Three reactions were carried out with this monomer system, two reactions at 54% solids with SDS and M12 and one at 30% solids with M12 (for conversion results, see Figure 4). The reaction with SDS (54-III-SDS-3.5) gave a stable latex with very little macroscopic coagulum. However, the latex completely coagulated on the shelf after a few weeks. In reaction 54-III-M12-3.5, fine grit formation was observed after 20 min, a strong viscosity increase after 80 min, and total coagulation after 90 min. In order to work under less exigent conditions, reaction 30-III-M12-1 was carried out at 30% solids content. It appeared that the conversion of M12 was very high from the beginning onward, and this probably led to the instability. The conclusion therefore is that the maleate surfmers are too reactive, just as in the previous system, due to the presence of the vinyl esters.

Effect of Other Operational Variables. Based on the above-mentioned results, it can be concluded that the reactivity of the surfmer relative to the main monomers plays an important role in the incorporation of the surfmer at the surface of the particle. However, the reactivity ratios are not the only affecting variable. Thus, Figure 5 shows that, for various semicontinuous reactions carried out with system I, the conversion of M14 decreased with the particle size. This result points strongly in the direction of M14 reacting at the surface of the polymer particle.

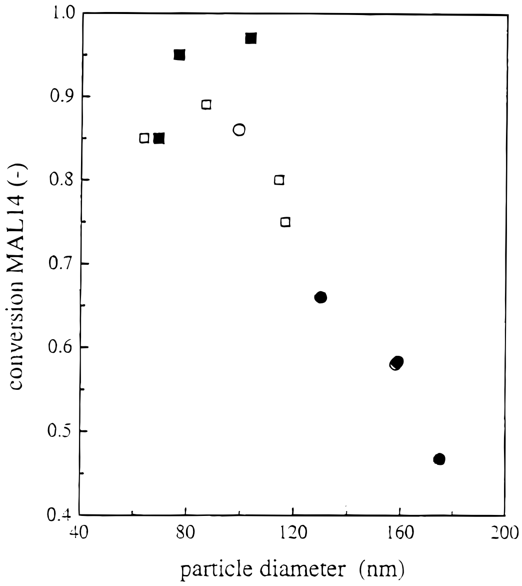

Figure 5. M14 conversion versus particle diameter. Data collected from various seeded, semicontinuous reactions with monomer system I: 30-I-M14-1 (■), 50-I-M14-2 (□), 55-I-M14-2 (○), 55-I-M14-2-12 (●).

In order to further study the influence of the surface area, the effect of the addition of small latex particles at the end of the process was investigated. In reaction 55-M14-2-12 the conversion of M14 at the end of the feeding period was 47%, and during the final batch stage, it increased to 52%. In this batch stage, the conversion of the main monomers increased from 90% to completion. A total of 20 g of the 55-M14-2-12 final latex was mixed with 76 g of seed latex C so that the total area of the polymer particles was doubled. This mixture was diluted with 30 g of water, and then 2 g of S, 2 g of BA, and some KPS were added. This was allowed to react in batch mode at 80 °C (the same temperature as for run 55-M14-2-12). It was found that the M14 conversion increased from 52% to virtually 100%. This also supports the decisive effect of the surface area of the polymer particles on the polymerization of the surfmer.

Optimum Surfmer Behavior. The consequences of the above-mentioned effects are very important. For one, it seems that there is a strong correlation between particle size and surfmer conversion, which implies that, at the beginning of batch reactions and semicontinuous reactions, the instantaneous conversion of the surfmer can be very high and that it decreases if the particle size exceeds 100 nm. If indeed a high level of surfmer conversion (and a consequently high degree of incorporation of the surfactant groups into the polymer chains) is reached when the particle size is still far from its final value, a further increase of the particle size as the reaction of the main monomers continues will lead to burying of part of the surfactant groups at the end of the reaction. On the other hand, the dependence on particle size implies that the conversion of the surfmers added in a later stage of the reaction may be relatively low. This behavior means that only part of the added surfmer will actually have reacted at the end and, at the same time, that the part that has reacted is likely to end up within the particle interior. This completely opposes the purpose of using a reactive surfactant, which should reside at the particle surface and be completely incorporated covalently. At the same time this defines the optimum surfmer behavior:

(1) *To avoid burying of surfactant groups, the surfmer should not react during the initial stages of the reaction where the particle size can still increase significantly.*

(2) *To guarantee a high degree of incorporation at the final particle surface, the surfmer should react to completion toward the final stages of the reaction where the particle size will not increase significantly anymore.*

It has become clear that optimum surfmer behavior in a given emulsion polymerization system is determined by two aspects: the relative reactivity of the surfmer and parameters such as particle size. Since some of the surfmer needs to be present at the beginning of the reaction for stabilization (and especially in nonseeded reactions to provide a sufficient amount of nucleated particles), the problem of an early reaction of the surfmer cannot simply be avoided by starting to feed the surfmer toward the end of the reaction. If no special measures are taken and the surfmer is added in a straightforward manner, the surfmer should not be very reactive to avoid a high conversion, but at the same time it should be reactive enough to reach a reasonable level of incorporation at the end. This has consequences for the possible combinations of comonomers and surfmer types in terms of reactivity ratios, and these are discussed below.

On the other hand, it should be possible to attain the optimum surfmer behavior more closely if a relatively nonreactive surfmer is used from the beginning onward and which is made to react toward the end to obtain a high conversion. Possible ways of achieving this are discussed as well.

(1) Surfmer Reactivity. Although it has been found that the apparent reactivity of a surfmer can decrease with increasing particle size and that it is therefore not easy to treat the effect of reactivity and particle size separately, some general rules for the preferred copolymerization reactivity ratios between surfmer and comonomer will be proposed.

It has already been concluded that the surfmer should not be too reactive in copolymerization with the main monomers to avoid high conversions at the beginning of the reaction. Additionally, on the basis of results with the methacrylate surfmer (MET[7b]), it was concluded that the surfmer should be slow to homopolymerize or, even better, unable to homopolymerize to avoid polymerization and formation of polyelectrolytes in the aqueous phase, a conclusion which had already been reached by Guillaume *et al.*[24] The latter condition means that the reactivity ratio of the surfmer with the comonomer (r_{surfmer}) should be zero or close to zero. The first condition implies that the reactivity ratio of the comonomer with the surfmer ($r_{\text{comonomer}}$) should not be too low.

Examples where the surfmer was clearly too reactive were the methacrylate surfmer in system I[7b] ($0.3 < r_{\text{surfmer}} < 2.6$; $0.3 < r_{\text{comonomer}} < 0.5$) and the maleates in systems II and III (in these systems the reactivities of the maleate surfmers with the vinyl esters were too high: $r_{\text{comonomer}} = 0.04$). This seems to indicate that r_{surfmer} should indeed be close to zero (<0.3) and that $r_{\text{comonomer}}$ should be higher than 0.5.

Table 8. Possible Combinations of Comonomers and Surfmer Reactive Groups

comonomer	surfmer reactive group	$r_{\text{comonomer}}$[a]	r_{surfmer}[a]
vinyl esters	alkyl vinyl ether	3–4	0
vinyl esters	2-alkene	7	0.7
vinyl esters	1-alkene	2	0.34
vinyl esters	crotonate	0.3	0.01
styrene (+ acrylics)	crotonate	26	0.01
styrene (+ acrylics)	maleate	8–10	0
styrene (+ acrylics)	fumarate	0.4	0.055
acrylics	1-alkenes	9	0
acrylics	vinyl esters	5–10	<0.1
acrylics	fumarates	2	0.09

[a] Data obtained from ref 34.

There are also examples of cases where the surfmer was not reactive enough: the crotonate surfmer (CRO[7b]) in system I ($r_{\text{comonomer}} = 26$, $r_{\text{surfmer}} = 0.01$) and the maleate surfmer at high particle diameters in system I ($r_{\text{comonomer}} = 8-10$ or higher). This indicates that $r_{\text{comonomer}}$ should be lower than 10.

In summary, the following conditions can be proposed for the reactivity ratios: $0.5 < r_{\text{comonomer}} < 10$, $r_{\text{surfmer}} \rightarrow 0$. In Table 8 a few possible combinations of surfmer reactive groups and three common comonomer systems in emulsion polymerization are given. This table should only be a rough guideline because (1) it was found that the apparent reactivity decreases with particle size, (2) the reactivity of the double bond might be affected by its position in the surfmer molecules, and (3) as stated above, the optimum surfmer behavior involves an increase in reactivity during the reaction, so that some combinations in Table 8 are useful only in the beginning of the reaction, and an increase in surfmer reactivity at the end of the reaction is required.

(2) Strategies To Induce the Optimum Surfmer Behavior. Several strategies can be proposed to induce the optimum surfmer behavior:

(A) Change in Main Monomer Reactivity. The relative reactivity of a surfmer, which is not very reactive, can be changed toward the end of the reaction by changing the reactivity of the main monomers. This can be done purposefully by adding less reactive monomers, or it is brought about automatically by an intrinsic change in the reacting system:

(A1) Adding Less Reactive Monomers toward the End of the Process. If the main monomers are very reactive and the surfmer does not copolymerize, at the end of the process a less reactive comonomer (or a mixture) can be added so that $r_{\text{comonomer}}$ is decreased and the surfmer will start to copolymerize. This method has the disadvantage that a different polymer is introduced, which could lead to phase separation and consequent loss of performance. Examples could be all acrylic systems with crotonate or maleate surfmers. The surfmers do not copolymerize well in these systems, but the addition toward the end of vinyl esters, with which the surfmers react well, should complete the polymerization of the surfmer.

(A2) Intrinsic Change in Main Monomer Reactivity. In some systems the main monomer reactivity decreases automatically, due to strong composition drift. For example, in systems where one of the main monomers is very unreactive, this monomer will not be incorporated to the same degree as the more reactive monomers, and even in monomer starved semicontinuous reactions a considerable part of it will be left over at the end of the feeding period, when the more reactive monomers have been depleted. Then the unreactive surfmer—which has not reacted considerably up to that point—can start to copolymerize.

(B) Change in Surfmer Reactivity. If a substantial part of the surfactant needs to be present from the beginning of the reaction, the optimum behavior can be brought about if the surfmer is, in principle, not reactive but made to be reactive toward the end. One can think of changes in the structure of the surfactant induced by a change in operation conditions such as temperature, pH, etc. This would mean that the surfactant is not a surfmer at the beginning but turned into a surfmer at the end. This surfmer should be quite reactive (*i.e.*, $r_{\text{comonomer}}$ not too high).

The last two options mentioned below involve not so much an increase in the reactivity of the surfmer but ways to avoid too much burying of surfactant groups.

(C) Surfmer Addition Profile. In systems where the need for stabilizing groups at the beginning of the reaction is not very high due to a low solids content (for example, if all the water is charged at the beginning), a specific addition profile for the surfmer can be used such that the addition rate increases as the solid content increases (in other words, more of the surfmer is added toward the end). In this case the surfmer should be quite reactive to ensure a high degree of incorporation at the end.

(D) Suppressing the Particle Size Growth. The burying of surfmers which have reacted at the beginning of the reaction can be avoided if the particle size is not allowed to increase significantly after the initial stage of the reaction. This can be brought about if the reaction is carried out as a miniemulsion polymerization, where existing monomer droplets are polymerized. In this case the surfmer will be at the particle surface, whether it has reacted or not. The reactivity of the surfmer can be quite high.

In the following we will give examples of options A given above for inducing the optimum surfmer behavior:

(A) Change in Main Monomer Reactivity. (A1) Addition of Less Reactive Monomers toward the End of the Process. In an experiment similar to that described above for the addition of small particles, 3.5 g of VAc and 1.5 g of VEOVA10, which react well with M14, were added to 51 g of latex 55-M14-2-12 together with some additional water and KPS. This was left to react in batch mode at 80 °C. After a few hours a sample was taken and the conversion of M14 appeared to have increased from 52% to 80%.

(A2) Intrinsic Change in Comonomer Reactivity. The MMA/BA/VAc System (Reaction 30-IV-M12-1). Perhaps the most interesting example of a reaction where the optimum surfmer behavior is approached is reaction 30-IV-M12-1. This is a semicontinuous reaction with M12 and with a recipe given in Table 4. The main monomers are MMA (50%), BA (35%), and VAc (15%). This monomer mixture normally gives latexes from which films can be cast easily. From these main monomers VAc is by far the least reactive comonomer. Therefore, during the feeding period, the fractional conversions of both BA and MMA are quite high and that of VAc is relatively low,[39] which means that at the end of the feeding period mainly VAc remains unreacted. This suggests that if a maleate surfmer (M12) is used, this surfmer will not react much during the feeding period during which mainly MMA and BA are reacting, because BA was shown not to react with M14[7b] and the reactivity ratios between MMA and maleates are very unfavorable for copolymerization; see Table 1. At the end of the feeding period, the remaining amount of VAc is expected to copolymerize with M12 (cf. example B1), leading to a high conversion of the surfmer at the end of the reaction. To make sure that the instantaneous conversion of the comonomers (mainly VAc) was not high, the monomer feed flow rate was tripled after 227 min. In Figure 6, the monomer conversion is plotted versus time, and it can be seen that after 227 min of feeding the fractional conversion of the comonomers was roughly 90% and after 240 min even a bit lower (due to the increased flow rate). The M12 conversion was given as well, and it can be seen that after the nucleation period the conversion of M12 was relatively high. This could be due to the fact that the charge was allowed to react in batch mode and at the end of that batch period the monomer mixture was enriched in VAc. Another explanation can be that at this time the particles are very small, leading to an enhanced surfmer conversion, which was also observed in batch reaction with S.[7c] However, after this initial period the fractional conversion drops to a lower level, and at the end of the feeding period it is about 60%. This may indicate that the amount of VAc (15 wt %) was high enough to allow at least some reaction of M12. However, once the feeding has been stopped and the reaction is in batch mode with a large amount of unreacted VAc, the conversion of M12 started to increase rapidly, reaching complete conversion when all main monomers have reacted. Note that in this stage of the reaction, $r_{\text{comonomer}}$ is very low (close to zero), which may not be ideal. If both reactivity ratios are close to zero, alternating copolymers are formed, and the formation of an alternating copolymer of vinyl acetate and M12 is possibly not ideal for stabilization. However, the point of this reaction was to show that, in terms of incorporation, the optimum surfmer behavior can be approached.

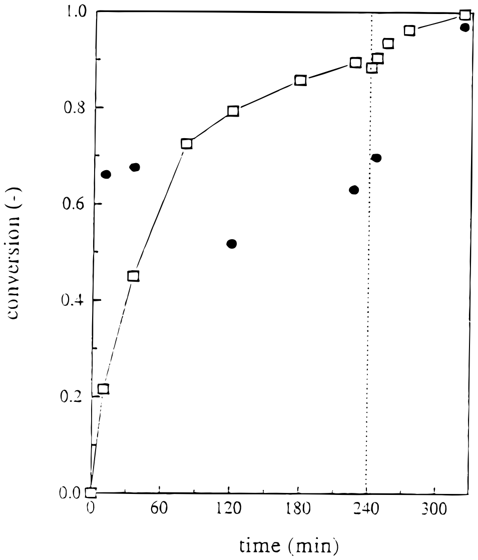

Figure 6. Main monomer conversion and surfmer conversion versus time in reaction 30-IV-M12-1 (main monomer, □; surfmer, ●).

Conclusions

An important conclusion of this work is the realization that, in order to perform well, a surfmer should not be very reactive, in contrast to what had been thought before. If the surfmer copolymerizes quite well with the main monomers, the ensuing latex can become very unstable either due to the formation of water-soluble polymer, causing bridging flocculation, or due to burying of surfactant groups, leading to uncomplete surface coverage. The latter can occur if the polymerizable surfactant reaches high conversions from the beginning of the reaction onward, such as in systems with vinyl ester monomers and maleate surfmers. This has led to the definition of *the optimum surfmer behavior: low conversion (surfmer not reactive) in the beginning and high conversion (surfmer reactive) toward the end of the reaction*. This means that the reactivity of the main monomers in systems with polymerizable surfactants is as important as the copolymerization reactivity of the surfmer itself, and it means that one has to be very careful when choosing the type of surfmer for a given monomer system and the way in which to add this surfmer. In terms of reactivity ratios, it has been concluded that suitable combinations of comonomers and surfmers are those with $0.5 < r_{\mathrm{comonomer}} < 10$ and $r_{\mathrm{surfmer}} \rightarrow 0$. If the used surfmer is not very reactive ($r_{\mathrm{comonomer}}$ high), the optimum behavior could be brought about in various ways: change in main monomer or surfmer reactivity at the end of the reaction, adding most of the surfmer at the end of the reaction, or suppressing particle volume growth in the miniemulsion mode.

Acknowledgment. This work was carried out as part of a European Union sponsored network (CHRX CT 930159). H.A.S.S. acknowledges a grant of the Training and Mobility of Researchers Programme (ERB4001GT953910). The authors express their gratitude to K. Stähler for providing the M12.

References and Notes

(1) Roulstone, B. J.; Wilkinson, M. J.; Hearn, J. *Polym. Int.* **1992**, *27*, 43.
(2) Holmberg, K. *Prog. Org. Coat.* **1992**, *20*, 235.
(3) Zhao, C. I.; Holl, Y.; Pith, T.; Lambla, M. *Colloid Polym. Sci.* **1987**, *265*, 823.
(4) (a) Evanson, K. W.; Urban, M. W. *J. Appl. Polym. Sci.* **1991**, *42*, 2287. (b) Evanson, K. W.; Thorstenson, T. A.; Urban, M. W. *J. Appl. Polym. Sci.* **1991**, *42*, 2297.
(5) Juhuë, D.; Wang, Y.; Lang, J.; Leung, O.-M.; Goh, M. C.; Winnik, M. A. *Polym. Mater. Sci.* **1995**, *73*, 86.
(6) Guyot, A.; Tauer, K. *Adv. Polym. Sci.* **1994**, *111*, 43.
(7) (a) Unzué, M. J.; Schoonbrood, H. A. S.; Asua, J. M.; Montoya Goñi, A.; Sherrington, D. C.; Stähler, K.; Goebel, K. H.; Tauer, K.; Sjöberg, M.; Holmberg, K. *J. Appl. Polym. Sci.*, in press. (b) Schoonbrood, H. A. S.; Unzué, M. J.; Beck, O.-J.; Asua, J. M.; Montoya Goñi, A.; Sherrington, D. C. *Macromolecules* **1997**, *30*, 6024. (c) Schoonbrood, H. A. S.; Unzué, M. J.; Amalvy, J. I.; Asua, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, accepted.
(8) Parker, J. E., III; Alford, J. A. U.S. Patent 5,306,793, 1994.
(9) Onodera, S.; Yamamoto, S.; Tamai, T.; Takahashi, H. Jpn. Patent 06,239,908, 1994.
(10) Chen, S. A.; Chang, H. S. *J. Polym. Sci., Part A: Polym. Chem.* **1985**, *23*, 2615.
(11) Yokota, K.; Ichihara, A.; Shinike, H. U.S. Patent 5,324,862, 1994.
(12) Nagai, K.; Satoh, H.; Kuramoto, N. *Polymer* **1993**, *34*, 4969.
(13) Baumgartner, E.; et al. German Patent DE 32 39 527, 1984.
(14) Kozuka, K.; Kobayashi, S.; Watanabe, A.; Yokoe, M.; Iki, Y. U.S. Patent 3,980,622, 1976.
(15) Cochin, D.; Zana, R.; Candau, F. *Macromolecules* **1993**, *26*, 5765.
(16) Choubal, H.; Ford, W. T. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1873.
(17) Kinoshita, K.; et al. Jpn. Patent 94/49,108, 1994.
(18) Ferguson, P.; Sherrington, D. C.; Gough, A. *Polymer* **1993**, *34*, 3281.
(19) Larrabee, C. E., Jr.; Sprague, E. D. *J. Polym. Sci., Polym. Lett.* **1979**, *17*, 749.
(20) Denton, J. M.; Duecker, D. C.; Sprague, E. D. *J. Phys. Chem.* **1993**, *97*, 756.
(21) Green, B. W.; Saunders, F. L. *J. Colloid Interface Sci.* **1970**, *33*, 393.
(22) Tsaur, S. L.; Fitch, R. B. *J. Colloid Interface Sci.* **1987**, *115*, 450.
(23) Green, B. W.; Sheetz, D. P. *J. Colloid Interface Sci.* **1970**, *32*, 96.
(24) Guillaume, J. L.; Pichot, C.; Guillot, J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 137.
(25) Urquiola, M. B.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2619.
(26) Urquiola, M. B.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 2631.
(27) Urquiola, M. B.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1403.
(28) Tang, R. H.; Chakrabarti, P. M. U.S. Patent 5,296,627, 1994.
(29) Usai, S. Jpn. Patent 94/65,551, 1994.
(30) Laschewsky, A. *Adv. Polym. Sci.* **1995**, *124*, 1.
(31) Reid, V. W.; Longman, G. F.; Heinert, E. *Tenside* **1967**, *4*, 292.
(32) Dais, P.; Paleos, C. M.; Nika, G.; Malliaris, A. *Makromol. Chem.* **1993**, *194*, 445.
(33) Montoya-Goñi, A. Ph.D. Dissertation, University of Strathclyde, 1997.
(34) *Polymer Handbook*, 3rd Ed.; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1989.
(35) Bengough, W. I.; Goldrich, D.; Young, R. A. *Eur. Polym. J.* **1967**, *3*, 117.
(36) Goebel, K. H.; Staehler, K. *Polym. Adv. Technol.* **1994**, *6*, 452.
(37) Goebel, K. H.; Stähler, K.; Von Berlepsch, H. *Colloids Surf. A* **1994**, *87*, 143.
(38) Unzué, M. J. Ph.D. Dissertation, Universidad del País Vasco, San Sebastián, Spain, 1996; pp 42−44.
(39) Urretabizkaia, A.; Asua, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1761.

MA9701494