Reactive Surfactants in Heterophase Polymerization. 7.[†] Emulsion Copolymerization Mechanism Involving Three Anionic Polymerizable Surfactants (Surfmers) with Styrene−Butyl Acrylate−Acrylic Acid

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ABSTRACT: The mechanisms of copolymerization of three anionic polymerizable surfactants (surfmers)—a methacrylic ester, a crotonic ester, and a maleic ester—in the emulsion terpolymerization of styrene/butyl acrylate/acrylic acid (S/BA/AA) were investigated. In order to clarify the contribution of each polymerization loci in the process, polymerization in the aqueous phase in the absence of both micelles and monomer droplets and emulsion polymerizations with different solids contents (30, 50, and 55 wt %) and different particle sizes were carried out. It was found that the methacrylic ester surfmer appeared to be extremely reactive and caused premature coagulation. The crotonic ester surfmer reacted only to a small extent and was not incorporated well enough into the polymer latex. The maleic diester surfmer appeared to have intermediate conversions varying between 50% and 95%. It was clearly shown that the degree of conversion of this surfmer depended on the particle diameter, with the conversion decreasing significantly at diameters higher than 100 nm. Although the maleate surfmer was the best of the three surfmers, its optimum use is not straightforward because high conversion of the surfmer led to the burying of a significant fraction of the maleate inside the polymer particles. Suggestions for a more advantageous incorporation are made.

Introduction

A general trend in emulsion polymerization is the search for ways to conduct the process more cheaply and with less negative effects on the environment. Some of the problems encountered in emulsion polymerization and application of emulsion polymerization products are connected with the use of surfactants, needed for stabilization during the production stage and storage. Some problems arise when the surfactant steadily desorbs from the surface of the latex particles during its shelf life or under conditions of high shear[1] of freeze−thaw.[2] This can cause coagulation after the production process. Though most of the surfactant remains adsorbed onto the polymer during intentional flocculation, some can be detected in the serum and therefore in the waste water and create a problem in treatment of the latter.[3] Finally when the latex is applied directly in coatings and films, the surfactant can impede film formation,[4] increase the water sensitivity, or migrate through the film and cause problems connected with sensitivity to water, gloss impairment, and plasticization by water.[3]

These negative features associated with the surfactants may be overcome by binding the surfactant moiety covalently in some way to the polymer material. This might be achieved by modifying the structure and function of the surfactant by incorporating in the surfactant molecule (i) an initiating moiety (inisurfs),[5−9] (ii) a moiety capable of chain transfer (transurfs[10−12]) (or a combination of i and ii, *i.e.*, inifer surfactants[13]), or (iii) a group capable of taking part in the free-radical polymerization. This latter class of molecules, (co)-polymerizable surfactants, is referred to as *surfmers*. In comparison to transurfs and inisurfs, surfmers have the advantage that their incorporation into the polymer chains does not necessarily affect the molecular weight or the rate of polymerization; *i.e.*, the main advantage of emulsion polymerization (combination of high molecular weight and high rate of polymerization) is not affected.

Once the surfmer is incorporated by copolymerization, the “surfactant” cannot desorb from the polymer material under any circumstances, unless the polymer chain in which it is incorporated desorbs or migrates through the polymer material. Holmberg[3] gave a review of polymerizable emulsifiers and listed some applications. The synthesis of surfmers with various polymerizable groups and their homopolymerization in water above and below their critical micelle concentration (cmc), or in other solvents, have been described.[14−24] For an overview see refs 25 and 26. Nigai et al.[27] studied the copolymerization of surfmers in micelles with styrene and methyl methacrylate. Surfmers have also been used to prepare model latex systems.[1,28−31] Although the patent literature presents many examples of the use of surfmers in emulsion polymerization (e.g., refs 32 and

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Table 1. Anionic Polymerizable Surfactants Used

surfactant	structure	M	cmc (g/dm^3)	purity[a] (%)
MET	$NaO_4SC_{11}H_{22}OCOC(CH_3)=CH_2$	358	2.2	64.5
CRO	$NaO_4SC_{11}H_{22}OCOCH=CH(CH_3)$	358	4.9	52.6
M14	$NaO_4SC_3H_6OCOCH=CHCOOC_{14}H_{29}$	456	0.12	76.9
SDS (control)	$NaO_4SC_{12}H_{25}$	288	2	90.6

[a] Contaminants are inorganic salts.

33), the open literature is still relatively scarce.[1,29,30,34−50]

Unzué et al.[45] analyzed the performance of three different surfmers (one was an ester of methacrylic acid (sodium 11-methacryloyl undecan-1-yl-sulfate, MET), the second an ester of crotonic acid (sodium 11-crotonoyl undecan-1-yl sulfate, CRO), and the third a diester of maleic acid (sodium 3-sulfopropyl tetradecyl maleate, M14)) in the emulsion terpolymerization of styrene (S), butyl acrylate (BA), and acrylic acid (AA) at high solids contents (50−55 wt %). Polymerizations using sodium dodecyl sulfate (SDS) as a reference surfactant were also carried out. It was found that at 50 wt % solids content with 1 wt % of surfmer the order of stability of the latexes prepared by unseeded polymerization was SDS $\cong$ CRO > M14 > MET, whereas for 55 wt % solids content latexes prepared by seeded emulsion polymerization with 2 wt % of surfmer, the M14 latex had the highest stability against electrolytes. Films cast from these latexes showed the highest water sensitivity in the case of CRO: CRO $\gg$ SDS > M14. The results of these studies led to the conclusion that the reactivity of the surfmer in copolymerization and, to a lesser extent its water solubility, has a marked effect on its stabilizing efficiency and degree of incorporation. It was speculated that very reactive surfmers could be consumed early in the reaction, leading to burying of the stabilizing moieties in the interior of the particles, and, if water soluble enough, could form water-soluble polyelectrolytes.

In this paper the copolymerization of the three surfmers described above[45] (see Table 1 for the structure and properties) with S/BA/AA was investigated. Emulsion polymerization is a multiphase system, and because of the different partitioning of each monomer and surfmer, their relative concentrations vary from phase to phase. Therefore, their copolymerization will be controlled not only by their reactivity ratios but also by the relative contribution of each polymerization locus to the overall process. In an attempt to clarify the mechanisms of copolymerization of the surfmers, the reactions in the aqueous phase were studied first by carrying out copolymerizations in the absence of both micelles and monomer droplets. Then, emulsion copolymerizations of low (30 wt %) and high (50−55 wt %) solids content were carried out to investigate copolymerization in the polymer particles.

Table 2. Recipes for Aqueous Phase Batch Reactions, Series A (g)

S	BA	AA	surfmer[a]	KPS	$NaHCO_3$	H_2O
0.037	0.081	0.63	1/2 cmc	0.038	0.15	100

[a] Surfmers: MET, CRO, M14.

Table 3. Recipes for Intermediate Solids Content (30 wt %), Semicontinuous Emulsion Polymerizations with Surfmer, Series B (g)

	S	BA	AA	surfmer[a]	initiator[b]	$NaHCO_3$	H_2O
charge	4.95	4.95	0.1	0.3	0.075	0.075	151.7
feed	44.55	44.55	0.9	0.7	0.075	0.075	81.6
total	49.5	49.5	1.0	1.0	0.15	0.15	233.3

[a] Surfmers (and reaction codes): MET (30MET), CRO (30CRO), M14 (30M141, 30M142), SDS (30SDS). [b] $K_2S_2O_8$ (KPS) was used in all runs except in experiment 30M142, in which VA86, a water-soluble nonionic azo initiator, was used.

Table 4. Recipe for High Solids Content (55 wt %), Seeded Semicontinuous Emulsion Polymerizations with Surfmer, Series C (g)

	S	BA	AA	surfmer[a]	KPS	$NaHCO_3$	H_2O
charge[b]	0.7	0.7	0	0.06[c]	0.07	0.07	48.2
feed	48.8	48.8	1.0	1.9	0.08	0.08	33.3
total	49.5	49.5	1.0	2.0	0.15	0.15	81.5

[a] Surfmers (and codes): CRO (55CRO), M14 (55M14 and 55M14-12), SDS (55SDS). [b] Seed latex C; $d_p = 39$ nm. [c] SDS.

Table 5. Recipe for High Solids Content (50 wt %), Seeded Semicontinuous Emulsion Polymerizations with Surfmer, Series D (g)

	S	BA	AA	surfmer[a]	KPS	$NaHCO_3$	H_2O
charge[b]	1.04	1.04	0	0.2 + 0.2[c]	0.3	0.3	50
feed	48.46	48.46	1.0	1.6	0.3	0.3	50
total	49.5	49.5	1.0	2.0	0.6	0.6	100

[a] Surfmers (and codes): M14 (50M14), SDS (50M14), NaSS (50NaSS; all NaSS was fed continuously). [b] Seed latex D; $d_p = 33$ nm. [c] SDS + surfmer (SDS from seed latex).

Experimental Section

Styrene (S) and butyl acrylate (BA) were distilled before use and stored at −18 °C. Acrylic acid (AA, with 10 ppm of *p*-methoxyphenol), potassium persulfate (KPS; Fluka, 99%), sodium bicarbonate (Merck, 99.5%), sodium dodecyl sulfate (SDS), and sodium styrenesulfonate (NaSS) were used as received. NaSS and SDS were used as reference systems. The experimental setup and the reactor have been described in refs 45 and 49. Emulsion polymerizations of different solids contents were carried out: (A) aqueous phase batch reactions (main monomer concentrations equal to their solubilities—experimentally determined—in the aqueous phase in equilibrium with a standard monomer mixture in the absence of surfmer; surfmer concentration equal to half its cmc); (B) unseeded semicontinuous emulsion copolymerizations at low solids contents (30%) to avoid possible interference from coagulation; (C) seeded semicontinuous emulsion copolymerization reactions at 55% solids; and (D) seeded semicontinuous emulsion copolymerization reactions at 50% solids with a smaller particle size than in C. The recipes for all reactions are given in Tables 2−5. The amounts indicated for the surfmers correspond to pure surfmer; *i.e.*, in reality a higher amount was used to account for the impurities (salts). Note that the reactor volume in series A was 2 dm^3 and that in all other reactions 0.5 dm^3. In the semicontinuous reactions (Tables 3−5) feeding was maintained over 4 h with 0.5−1 h postreaction (with the exception of run 55-M14-12, in which a feeding time of 12 h was used). Feeding (an aqueous feed stream and a monomer feed stream) was effected by two pumps (Prominent Gamma 4-RS) and controlled by a PC reading on-line the weight loss of the feed containers. The reaction temperature was 80 °C in all cases. The reactions including AA in the recipe were carried out under acidic conditions (pH = 3−4).

In series C and D seed latices were used to ensure that the final latices obtained with different surfmers had similar particle diameters, which makes comparison of their properties easier. In these reactions part of the weight of the main monomers and water in the recipe was substituted for an equivalent amount in the seed latex. These seed latices were prepared in simple batch reactions at high temperature (80−90 °C). The seed latex for series C was prepared with the following recipe (in g): S, 30; BA, 30; SDS, 2.3; KPS, 6.7; $NaHCO_3$, 2.3; H_2O, 1940. The seed latex for series D was prepared with the following: S, 30; BA, 30; SDS, 6; KPS, 4; $Na_2S_2O_5$, 2; $NaHCO_3$, 1.7; H_2O, 900. The particle diameter of the seed used in series C was 39 nm and that of the seed used in series D 33 nm (light scattering). S, BA, and AA were chosen as the main monomers in the weight ratio S/BA/AA = 49.5/49.5/1 (except in aqueous phase reactions), which leads to a latex from which films can easily be prepared. In series D the amounts of pure surfmers used were equivalent in moles to the mass of M14, being the one indicated in Table 5. As M14 has the highest molecular weight, the other recipes contained less surfmer by weight.

The conversion of the main monomers was determined by gravimetry, but in the aqueous phase reactions (series A) gas chromatography (Shimadzu GC 14-A; column SGE-25QC5/BP20 110) was used, because of the extremely low solids contents. The GC samples were diluted with water containing a known amount of pentanol. Appropiate calibration curves versus pentanol were constructed for each monomer. Particle sizes were determined by light scattering (LS) with a Malvern System 4700c. The amount of coagulum was measured by collecting the coagulum from the reactor wall and stirrer and by filtering the latex (mesh 63). The instantaneous conversions of the surfmers were determined by two-phase titration of the serum separated from the latex particles. Due to the fact that a large part of the unreacted surfmer can be adsorbed on the surface of the latex particles, coagulation or a one-step filtration/centrifugation cannot be applied, because then only the unreacted surfmer in the aqueous phase will be determined. The separation was carried out by serum replacement.

Serum replacement[51,52] (SR) was performed with a UHP-76 from MicroFiltration Systems, by flushing distilled water through in a discontinuous mode and collecting the effluent for later analysis of the surfmer concentration. In order to check the reliability of SR, a terpolymer latex was thoroughly washed, a known amount of M14 or SDS added, and the system left to stand to equilibrate. These latex samples were then washed with SR, and the recovery of surfactant was determined. In both cases 94% of the surfactant was recovered, indicating that SR can be used to remove virtually all unreacted surfactant. Stähler[47] tested ultrafiltration in the case of M14 but concluded that it was not possible to remove all surfactant, but possibly not enough water was used. Instead ultrafiltration with methanol was applied.[47] Surfactants have a higher solubility in methanol than in water, and the equilibrium between adsorbed and dissolved surfactant is shifted considerably to the aqueous/methanol phase, and in case of M14 the shift is dramatic. Stähler[47] found nearly 100% recovery with this technique. However, this method can lead to inaccurate measurements, because surface-active oligomers other than unreacted M14 are extracted by methanol.[50]

To determine the concentration of surfactant/surfmer in the effluent or in the serum recovered from SR, a two-phase titration (TPT) using a mixed indicator solution was applied. This technique was described in a report submitted to the Commission Internationale d'Analyses[53] and is suited for analysis of many, but not all, anionic surfactants. In this method the sample containing the free surfactant or surfmer is mixed with additional water, a mixed indicator solution, and some chloroform. The surfactant combines with the cationic indicator (Dimidium Bromide; Fluka), and this complex is extracted by the organic chloroform phase, giving this phase a pink color. The anionic indicator (Patent Blue V or Disulphine Blue; Fluka) resides in the aqueous phase. When the titrant (Hyamine 1622, *N*,*N*-dimethyl-*N*-[2-[2-[4-(1,1,3,3-tetramethylbutyl)phenoxy]ethoxy]ethyl]benzenemethanaminium chloride; Fluka) is added, this molecule competes effectively with the cationic indicator and starts forming a colorless complex that remains in the chloroform. The cationic dye that is released from the complex returns to the aqueous phase, rendering that phase yellow, while at the equivalent point the excess of the titrant starts combining with the anionic indicator, taking it into the chloroform phase and giving that phase a blue color. At the end point the chloroform just loses its pink color and turns purple/gray before finally turning blue. In the report[53] it is indicated for which surface-active substances the method can be applied and under which conditions. Also a detailed description of the method and of the preparation of the reagents is given. This method was also applied to determine the purity of the synthesized surfmers (see Table 1). For determination of surfmer conversion we applied this method in a slightly modified way, depending on the type of reaction. The modifications are explained in the appropriate places in the Results and Discussion section. In most cases it was found that the concentration of surfactant in the serum was very low, and instead of the 20 mL of serum sample recommended, as described in the report, up to 50 mL had to be added in order to be able to titrate reliably. In all cases appropriate calibration curves were constructed to relate the consumption of titrant to the number of moles of surfactant.

In order to determine the fraction of reacted surfmer that is available for stabilization, namely, the fraction residing at the particle surface and not buried in particle interiors, the surface charge density of some of the latices prepared with M14 was determined by conductimetry. This was applied to latices previously cleaned by SR to avoid interference of any compounds in the serum. After cleaning the latices with water, they were further cleaned by flushing a solution of HCl (10^{-3} M) through the latex until all available cations had been replaced by H^+. This cleaned latex was then titrated automatically with a NaOH solution (0.01−0.05 M) with a Dosimat 665 (Metrohm) connected to a MICRO CM 220 conductimeter (Crison) (for more details see ref 49).

Results and Discussion

Aqueous Phase Batch Reactions (Series A). From literature data one should, in principle, be able to determine the order of reactivity of the three surfmers used. However, most literature data pertain to homogeneous (solvent) systems and to methacrylates, crotonates, and maleates with different ester groups than those used here. Therefore, a set of reactions was performed which might give an idea of the reactivity of the monomers and surfmers in an aqueous phase under reaction conditions similar to those encountered in the aqueous phase of a high solids content S/BA/AA emulsion polymerization. To establish these conditions, the concentrations of the main monomers in the aqueous phase in an emulsion of a 49.5/49.5/1 wt% S/BA/AA mixture in the absence of surfmer were determined at 80 °C by GC. The concentration of the surfmers was equal to half their cmc value measured in the absence of other components in the water; it is acknowledged that the real cmc can be lower in the presence of electrolytes or monomers. The recipes for these reactions have been given in Table 2.

For each surfmer one such reaction was carried out, but for M14 such reactions were also performed in the presence of each of the comonomers separately. The conversions of the comonomers were determined with GC, and the conversion of the surfmer with TPT follows the procedure outlined below. Since TPT is used to characterize the amount of unreacted surfmer, surfmer groups incorporated in polymer chains should be excluded from the sample solution, because they might interfere. When the first reactions were analyzed by TPT, it was noted that, as soon as the sample and the mixed indicator solution were mixed, a slightly brown/pink colored precipitate was formed which remained at the interface between the aqueous phase and the

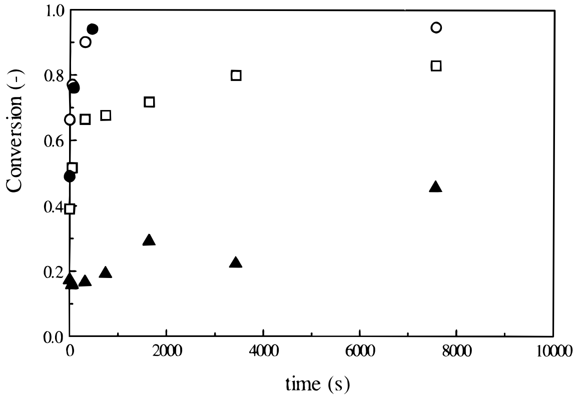

Figure 1. Time evolution of the conversions of S (○), BA (□), AA (▲), and MET (●) in the aqueous phase batch reactions.

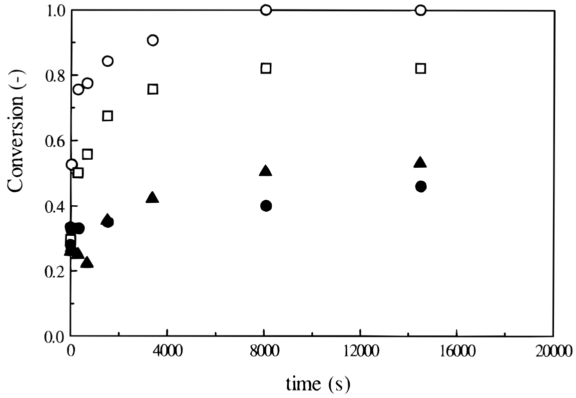

Figure 2. Time evolution of the conversions of S (○), BA (□), AA (▲), and CRO (●) in the aqueous phase batch reactions.

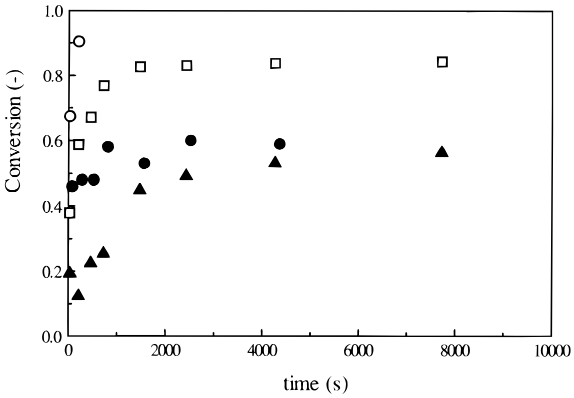

Figure 3. Time evolution of the conversions of S (○), BA (□), AA (▲), and M14 (●) in the aqueous phase batch reactions.

chloroform phase. This indicated that surfmer groups incorporated in polymer chains also combined to a certain extent with the cationic indicator. However, it seemed that this polymer did not dissolve in the chloroform layer but rather formed a precipitate, insoluble in either phase. When the titrant was added to this complex mixture, some of the titrant was consumed by complex formation of the surfmer groups in the precipitate, and this showed up as an extra amount of titrant needed to reach the equivalence point in the case of M14 and CRO but not in the case of MET.

Therefore, all components were first mixed for the titration (including an extra amount of 20 mL of distilled water) in a small separatory funnel using 5−10 mL of chloroform and extracting the surfmer−cationic indicator complex by separating the chloroform layer. By adding another 5−10 mL of chloroform to the funnel, more of the surfmer−cationic indicator complex was extracted, and this was repeated until the chloroform layer no longer contained appreciable amounts of the complex (indicated by the absence of pink color). To the collected fractions of the chloroform, 20 mL of water and 10 mL of mixed acidified indicator solution were added, and the mixture was then titrated. This method was tested by using different amounts of extra added surfmer, and it could be shown that more than 90% of the surfmer was recovered.

The conversions in the three reactions with all comonomers present are shown in Figures 1−3. In all figures corresponding to batch polymerizations, $t = 0$ corresponds to the moment of addition of initiator. As far as the main monomers are concerned, the order of reactivity is as expected; *i.e.*, S is more reactive than both acrylates. The conversion of AA generally lags behind that of S and BA, and the polymerization rate levels off, apparently as soon as S, and to a lesser extent BA, has been depleted. The fact that AA appears to be the least reactive monomer is also due to its high relative concentration. Comparison between these figures shows that in this system the order of reactivity of the surfmers is MET > M14 > CRO. If we ignore the possible heterogeneity of the system occurring during the reaction, the order of reactivity is as expected for systems with styrene and acrylates. Methacrylates are very reactive in the presence of styrene (for instance, $r_S = 0.53$ and $r_{\text{dodecyl methacrylate}} = 0.3$[54]), but r_S can be higher than 1 when copolymerized with methacrylate macromonomers carrying poly(ethylene oxide) side groups.[43] Methacrylates are usually more reactive than acrylates in reactions with styrene (for instance, $r_{MMA} = 2.09 \pm 0.3$ and $r_{\text{methyl acrylate}} = 0.22 \pm 0.05$[55]). It seems also that the crotonate is reacting to some extent, although on the basis of the reactivity ratios of methyl crotonate with styrene one would expect hardly any copolymerization at all ($r_S = 26$, $r_{\text{methyl crotonate}} = 0.01$, at 60 °C in benzene[56]). A similar fact was observed by Urquiola, who copolymerized styrene with the allylic surfmer TREM LF-40 (sodium dodecyl allyl sulfosuccinate) under similar conditions but at much higher monomer concentrations.[57] Unusually it was found that TREM LF-40, which contains an allylic group that is normally very unreactive in homopolymerization and in copolymerizations with acrylates and styrene shows a relatively high rate of polymerization in the presence of these monomers, albeit that its partial conversion remains low.

M14 (Figure 3) shows an interesting behavior in that it copolymerizes quickly as long as S is present, but when this monomer is depleted, the rates of polymerization of the remaining M14 and acrylic acid drop considerably. One could conclude tentatively from these results that M14 reacts to a reasonable extent with S and to a lesser extent with acrylates. This is confirmed in the three reactions with M14 and each of the comonomers individually. The results are shown in Figures 4−6. In Figure 4, it can be seen that indeed M14 reacts rapidly to high conversion with S. Strangely the conversion of M14 seems to decrease at some stage, but this is probably due to formation of surface-active oligomers (S with initiator-derived sulfate groups). The number of moles of persulfate that decompose in this time interval (estimating k_d to be between 10^{-5} and 10^{-4} s^{-1}) is high enough to be able to account for this effect. In the reaction with BA (Figure 5), M14 does not react at all, and even apparently negative conversions can be observed, probably also due to BA-oligomer formation.

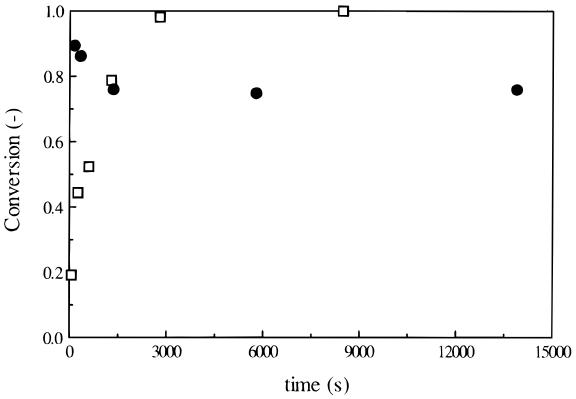

Figure 4. Time evolution of the conversions in the aqueous phase batch copolymerization of S (□) and M14 (●).

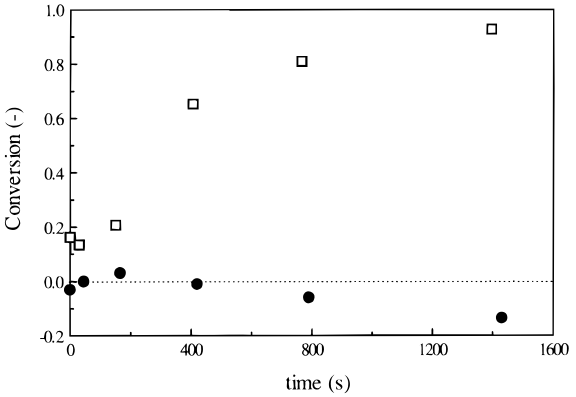

Figure 5. Time evolution of the conversions in the aqueous phase copolymerization of BA (□) and M14 (●).

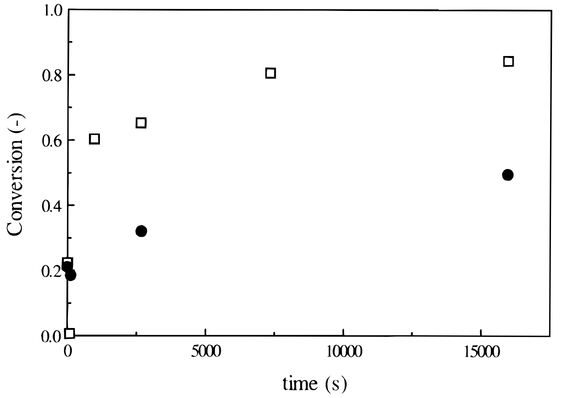

Figure 6. Time evolution of the conversions in the aqueous phase batch copolymerization of AA (□) and M14 (●).

In the reaction with AA (Figure 6) one can see that indeed M14 reacts very slowly with relatively low partial conversion. It may seem that M14 reacts better with AA than with BA, but this is probably due to the very high concentration of AA relative to the concentrations of S and BA.

It is concluded that indeed M14 reacts preferably with S and much less so with acrylates. This is at least qualitatively in agreement with results obtained with the *trans*-fumarate isomer. Various fumarate diesters have been investigated by Otsu *et al.*[58] They list reactivity ratios of diisopropyl fumarate with various comonomers. These data show clearly that the fumarate is quite reactive with S, much less reactive with acrylates, and even less with methyl methacrylate (MMA). This order in reactivity is due to polar factors, with fumarates being strongly electron-accepting. The generally low reactivity of the fumarates is mainly due to steric factors, as the two bulky ester groups cause steric hindrance. This also applies to the maleate, although here it is also thought that the proximity of the two ester groups in the cis-configuration reduces the planarity of the molecule and hence its reactivity.[59] Nevertheless, maleates are electron-accepting monomers as well, and the expected order of reactivity with styrene and acrylates is the same as that with fumarates. This is qualitatively confirmed by reactivity ratios given in the literature between S and diethyl maleate (DEM) ($r_S = 8-10$; $r_{DEM} = 0^{54}$) and between MMA and DEM ($r_{MMA} = 354 \pm 57$; $r_{DEM} = 0$).[60] As far as we know, no reactivity ratios with acrylates have been published. Otsu *et al.*[61] have also shown that there is only a small influence of size of the alkyl groups of dialkyl fumarates on the copolymerizability with S. This is taken as support for the assumption that the order in reactivity of DEM can be extrapolated to the maleate used in this work with its tetradecyl and sulfopropyl groups.

Table 6. Results of Intermediate Solids Content (30 wt %), Series B of Semicontinuous Emulsion Polymerizations: Coagulum and Final Particle Size, d_p

	coagulum (%)[a]	d_p (nm)[b]		coagulum (%)[a]	d_p (nm)[b]
30SDS	0.2	130	30CRO	0.1	222
30MET	0.6	117	30M141	1.3	98

[a] Based on monomer. [b] From light scattering.

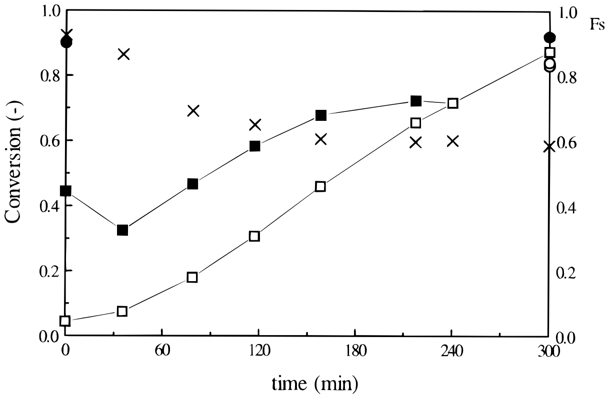

Figure 7. Evolution of the overall (□) and fractional conversions (■) of the main monomers, MET conversion (●), and fraction of S in the polymer (F_S, (×)) in the reaction 30MET.

Semicontinuous Emulsion Polymerizations at 30% Solids Content (Series B). A series of semicontinuous emulsion polymerizations was carried out to analyze the consumption of the surfmers at 30% solids content and 1% surfmer content (see Table 3, series B). Also a control reaction with SDS was carried out. The initial charge was reacted for 30 min. As can be seen in Table 3, the initiator and buffer were partitioned 50/50 over the initial charge and feed, the surfmer 30/70, and the water 65/35. The results show that the amounts of coagulum were low enough to enable analysis of the surfmer conversion (see Table 6).

The overall and fractional conversions of the main monomers (gravimetry) and the fractional conversion of the surfmer (SR) are shown in Figures 7−9. In these figures $t = 0$ corresponds to the start of the feed. The fractional conversion at a certain time is defined as the amount reacted divided by the amount added at that point; the overall conversion is the amount reacted divided by the total amount to be added. Figure 7 shows

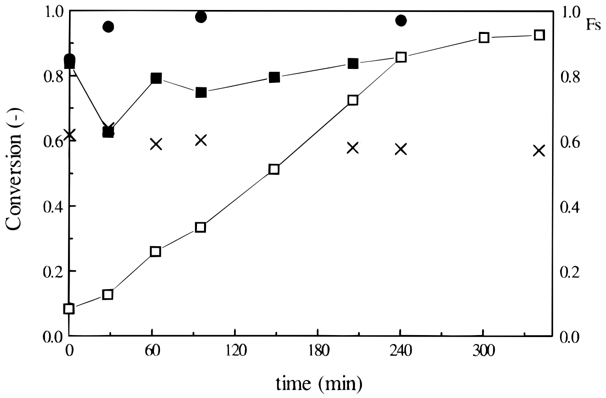

Figure 8. Evolution of the overall (□) and fractional (■) conversions of the main monomers, M14 conversion (●), and fraction of S in the polymer (F_S (×)) in the reaction 30M141.

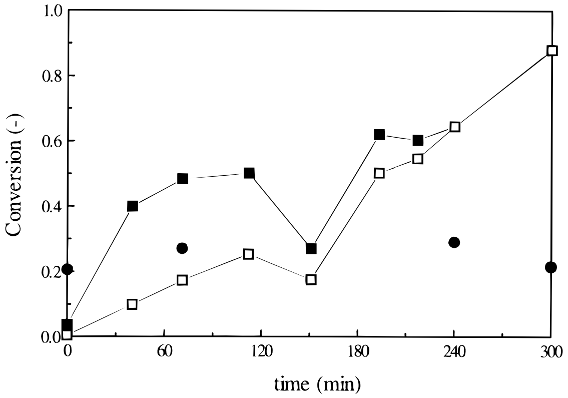

Figure 9. Evolution of the overall (□) and fractional (■) conversions of the main monomer and CRO conversion (●) in reaction 30CRO.

reaction 30MET. It can be seen that the fractional conversion of the main monomers is not very high and steadily increases, which implies that purely starved conditions were not reached. This shows up in the evolution of the overall fraction of S in the polymer (F_S, determined with GC); *i.e.*, there is composition drift at the beginning. The same is observed in reaction 30SDS (not shown). It can also be seen clearly that the instantaneous conversion of MET is very high. This high conversion is in line with the expected reactivity and the results obtained in series A.

Unzué *et al.*[45] reported that, in a similar reaction at 50% solids with 1% of MET, a large amount of coagulum was obtained. In addition, when a nonionic methacrylate surfmer was added to a hitherto stable latex, immediate coagulation occurred. It was suggested that this behavior was a consequence of homopolymerization of methacrylate surfmer in the aqueous phase, leading to the formation of a type of water-soluble polymer capable of causing bridging flocculation. The homopolymerization (or formation of a polymer rich in MET) is certainly possible judging from the expected high reactivity and the results of the aqueous phase reaction. However, it should be recalled that, in the aqueous phase reaction with MET, the preseparation with the separatory funnel in the conversion analysis had little effect: the observed conversion was very high in both cases. This means that the MET is incorporated in a polymer which does not combine with the titrant, so that based on the present results it cannot be concluded whether or not the high amount of coagulation in the reaction with 50% solids was due to bridging flocculation caused by the water-soluble MET-containing polymer. Another explanation could be that the high instantaneous conversion of MET leads to excessive "burying" within the latex particles, so that the surface charge density of the final particles is very low. This is more likely to show up at higher solids contents, as was also shown to be the case for the maleate in another monomer system.[50] Whatever the explanation, due to the large amount of coagulum in the 50% solids reaction, the study of MET was not continued.

Figure 8 shows the results of reaction 30M141. In this case the instantaneous conversions of S and BA are higher, and this shows up in the evolution of F_S, which is constant throughout the reaction. The fractional conversion of M14 is very high as well, starting at 85% at the end of the initial charge period (which is in batch mode) and higher than 95% during the feeding period. The high conversion is in agreement with the results of the aqueous phase reactions. In those reactions it was concluded that M14 reacts preferably with S that, by the very nature of the semicontinuous reaction mode, it is not depleted, and therefore M14 can maintain a high conversion.

For comparison we also performed a batch reaction with M14 and S/BA/AA at a low solids content (5%) and with a relatively high ratio of M14, so that the conversion of M14 could be analyzed by ^{1}H NMR spectroscopy (following the disappearance of the signal of the vinylic protons). In spite of the large amount of M14 (ratios S/BA/M14 = 2/2/1) the relative errors of the vinylic proton signal in the spectrum remained very high, but it could be concluded that the final conversion was high, which is in agreement with the result obtained at the end of the initial charge period in 30M141 (85% conversion of M14).

In Figure 9 it can be seen that again the conversions of S and BA are low but also that the conversion of CRO is low, which is in agreement with the aqueous phase reaction. Although it can be concluded that CRO is not reactive enough in copolymerization with styrene–acrylics, this does not mean that there are no other monomer systems where CRO could be used. It might be expected that CRO is more reactive in copolymerization with vinyl esters (as are crotonates in general[55]), and this is attested to in a 30% solids content batch reaction with 75 wt% vinyl acetate and 25 wt% Veova 10 (vinyl ester of versatic acid (C_{10}), trademark Shell) initiated by 0.3 wt % VA86 (a water-soluble, nonionic azoinitiator; Wako Chemicals) with 1% CRO, in which the CRO had a conversion higher than that of the main monomers.

The final localization of reacted surfmer is as important as the actual degree of conversion. If none of the reacted surfmer is present on the surface of the final particles, the effect of having the surfmer present in the latex is likely to be negative with respect to water sensitivity and zero with respect to latex stability. The latices produced so far were all reasonably stable, even if the conversion was very high as in 30M141, and this suggests that at least a part of M14 is adhered to the particle surface. In order to quantify the fraction of M14 at the particle surface, polymerization 30M142 was carried out using the same recipe as in 30M141, but replacing the anionic KPS with the water-soluble nonionic azo initiator VA86, so as to eliminate any effect of charged initiator groups on the titration. It has to be said that this initiator was not as effective as KPS, and the main monomer conversions were very low during the feeding period. However, the final conversion was

Table 7. Results of High Solids Content (55 wt %), Semicontinuous Emulsion Polymerizations: Coagulum and Final Particle Size, d_p

	coagulum (%)[a]	d_p (nm)[b]		coagulum (%)[a]	d_p (nm)[b]
55CRO	1.3	178	55SDS	0.9	163
55M14	1.0	171			

[a] Based on monomer. [b] From light scattering.

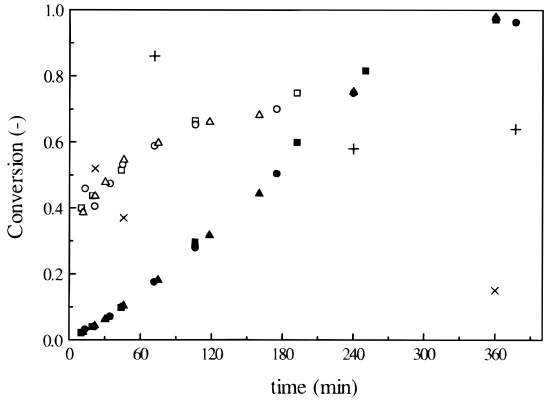

Figure 10. High solids content (55%), semicontinuous emulsion polymerizations (series C): overall (closed symbols) and fractional (open symbols) main monomer conversion versus time in 55SDS (□), 55CRO (△), and 55M14 (○) and surfmer conversion versus time in 55CRO (×) and 55M14 (+).

high, and M14 conversion was close to 100%.

The conductimetric titration revealed that *ca.* 40% of the M14 groups incorporated were situated at the particle surface in the final latex. It follows that the remaining part must be buried in the interior of the latex particle. This is in agreement with the high instantaneous conversion of M14 throughout the reaction 30M141 (see Figure 8).

The fact that only 40% of M14 was found at the particle surface suggests that a high conversion throughout the semicontinuous reaction may not be favorable. On the other hand, a high conversion at the end of the reaction is, of course, very desirable. If the conversion of M14 is determined only by its intrinsic reactivity with the main monomers—mainly styrene—then this may be an unsurmountable problem: addition of the M14 at the end of the reaction should avoid the problem of burying, but this option, of course, deprives the emulsion completely of any stability during the reaction. A certain part of the M14 has to be present in the system from the beginning (especially in nonseeded reactions). However, there might be factors other than copolymerization reactivity that govern the conversion of the M14, and this is investigated more closely below.

Semicontinuous Emulsion Polymerizations at 50–55% Solids Content (Series C and D). A number of reactions were performed at a high solids content in order to study the conversion of the surfmer under industrial-like conditions. These reactions were carried out in two series, using two different seed latexes, C and D. In series C (recipe Table 5) the performance of M14 and CRO versus SDS was tested. MET was not used because, as shown above, it is too reactive for the S/BA/AA system. The seed latexes were used to obtain latex particles of similar final size ($d_p \approx 170$ nm) in each series. With TEM it was shown that there were very few small particles. The results are presented in Table 7 and Figure 10.

Table 7 shows that the amounts of coagulum in these reactions are very similar, around 1%. The type of coagulum observed was more likely to be due to evaporation of water from latex adhering to the reactor wall than to latex instability. The particle concentrations were roughly the same, within 30%, and this was reflected in the conversion–time curves of the main monomers (Figure 10), which were very similar. The fractional conversions of both the main monomers and CRO were rather low. The fractional conversion of CRO seems to be decreasing during the reaction, but calculation of the absolute amount of reacted CRO revealed that this quantity was slowly increasing during reaction. The final conversion was roughly 15%, and this is in accordance with the earlier results. The fractional conversion of M14 also decreased as a function of time. The conversion of M14 was higher than that of CRO but clearly lower than in 30M141. The reason for the latter difference will be addressed in a later section.

Table 8. Results of High Solids Content (50 wt %), Semicontinuous Emulsion Polymerizations: Coagulum and Final Particle Size, d_p

reaction	coagulum wall/stirrer (%)[a]	coagulum (latex) (%)[a]	d_p (nm)[b]
50M14	1.0	0.4	114
50SDS	0.9	0.5	132
50NaSS	1.2	0.6	129

[a] Based on monomer. [b] From light scattering.

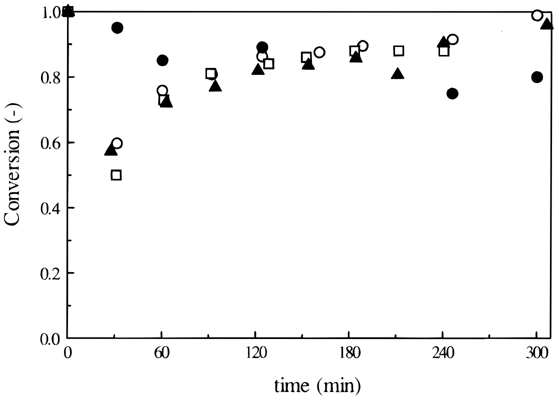

Figure 11. High solids content (50%), semicontinuous emulsion polymerizations (series D): fractional main monomer conversion versus time in 50SDS (□), 50NaSS (▲), 50M14 (○), and M14 (●).

In Table 8 the results of series D of high solids content reactions are shown. In this series CRO was not used, because of the low conversions found in the previous reactions. A reaction with NaSS was also carried out, as this is often used as a reactive stabilizer (it is not surface-active). It was also decided to use another seed latex in order to obtain smaller final particle sizes of around 120 nm, which resulted in a higher number of polymer particles and hence higher fractional conversion. The reaction with NaSS gave the highest amount of coagulum, which could be due to it not being surface-active (if the differences are at all significant).

In Figure 11 the conversions in series D are shown. It can be seen that as with series C the fractional conversion of the main monomers does not depend on the surfmer type. Because of the combined effect of the smaller particle size (higher number of particles) and the higher initiator concentration, conversions are also generally higher than in series C. In addition, it can be seen that the conversion of M14 is quite high, higher than in series C. This will be addressed later.

Toward an Understanding of the Incorporation Mechanism of M14. At first glance it seems that the

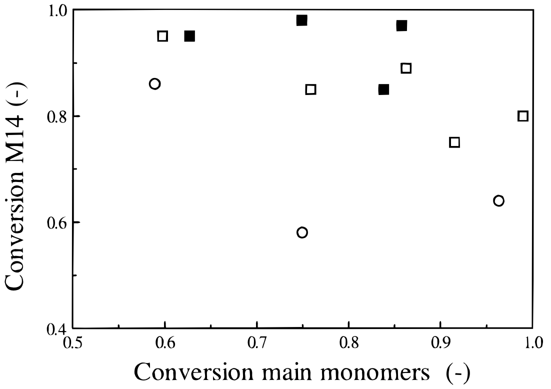

Figure 12. Fractional conversion of M14 in the three reactions at 30, 50, and 55% solids content versus the overall fractional conversion of the main monomers. 30M141 (■), 50M14 (□), and 55M14 (○).

levels of conversion of M14 in the series B–D are all of an intermediate to high level. However, closer inspection reveals that there are also differences in conversion. For example, in 30M141 the M14 conversion is higher than that in 50M14 and much higher than that in 55M14. What causes these differences and what other differences in these reactions are there? The solids contents are different, but it has already been stated[45] that the adsorption isotherm of M14 is such that once particles have been formed, almost all of M14 is situated at the particle surface. Hence, the solids content (and the aqueous phase content) can only have a small effect on the conversion. Another difference could be the amount of initiator in series D, on the one hand, and series B and C, on the other hand. However, the fact that in series B and C the amount of KPS per gram of main monomer is the same excludes this possibility, although there might be a small effect on termination in the aqueous phase. The amounts of M14 in series C and D are the same, so the load of M14 cannot have caused a difference in M14 conversion either. However, two other parameters stand out as different in each case: (a) the main monomer instantaneous conversion and (b) the particle diameter.

Regarding case a, in the type of semicontinuous emulsion polymerization considered here there is normally a positive correlation between the fractional conversions of the individual monomers and the overall fractional conversion. This is so because the ratios of the polymerization rates are determined by the respective reactivity ratios and not by the absolute rate of polymerization. In Figure 12 the fractional conversion of M14 for the three reactions at 30, 50, and 55 wt % solids content is plotted versus the fractional conversion of the main monomers. It can be seen that there is no clear positive correlation with main monomer conversion. If anything, there might be a negative correlation at very high monomer conversions. This may indicate that the incorporation mechanism of M14 is dependent on the presence of other monomers, most notably styrene in this case.

Note that the fractional conversion is strongly correlated with the rate of polymerization and hence the number of particles and the particle size. Thus, when in Figure 12 the main monomer conversion was varied, the particle diameter was as well. In order to find out whether it is the main monomer conversion or the particle diameter that is causing the differences, a second 55% solids polymerization was carried out with M14 (55M14-12) with an addition time of 12 h rather than 4 h. In this way the fractional main monomer conversion could be altered (increased), without changing the particle diameter. The results of 55M14-12 and 55M14 are shown in Figure 13. The fractional main monomer conversion in 55M14-12 is now much higher than that in 55M14, as expected. The final particle diameters are virtually the same (180 and 171 nm). Surprisingly, the conversions of M14 are very similar in both reactions and decreasing with time. The clear increase in main monomer conversion does not lead to an increase in M14 conversion (if anything, it decreased slightly). This is in agreement with the results of Figure 12.

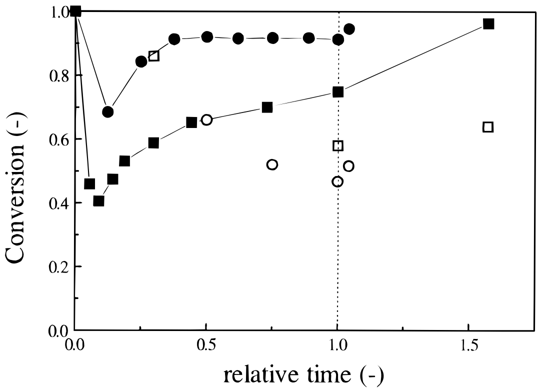

Figure 13. Effect of feeding time on conversion versus relative time (real time divided by total addition time): main monomer (■) and M14 (□) in 55M14; main monomer (●) and M14 (○) in 55M14-12.

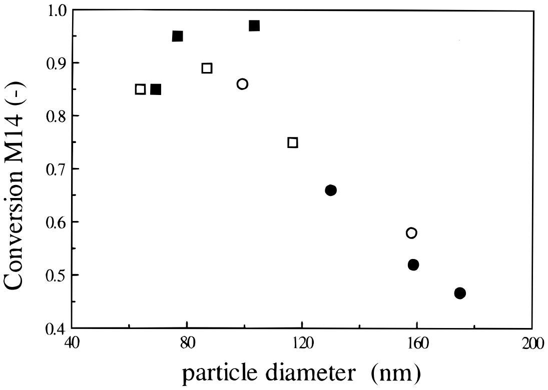

Figure 14. Fractional conversion of M14 versus particle diameter. 30M14 (■), 50M14 (□), 55M14 (○), and 55M14-12 (●).

Regarding case b, in Figure 14 the M14 fractional conversion in the four reactions at 30, 50, and 55% (twice) solids content is plotted versus particle diameter. Note that only data from the feeding period have been plotted (data pertaining to the batch period after the feeding period always show a slight increase in M14 conversion, as can be appreciated in Figures 11 and 13). It can be seen that the fractional conversion of M14 is strongly dependent upon the particle diameter, reaching high levels for small particles up to 100 nm and decreasing steadily at higher particle diameters. When the results of the reactions 50M14, 55M14, and 55M14-12 are analyzed individually, it appears that the fractional conversion of M14 decreases with time within each reaction. In these reactions, the particle diameter increases steadily, whereas the instantaneous conversion stayed constant or increased. This is in agreement with a particle size dependence as observed in Figure 14. This strong particle size dependence may seem logical, since the free unreacted M14 will be present on the particle surface. It is therefore likely that the locus of polymerization for the surfmer is the particle surface. The locus of polymerization for the main monomers is the whole polymer particle volume (except perhaps for AA, but for the polymerization of M14 this is not important). If the M14 reacts only in an outer shell of the particle with a set thickness, one can imagine that an increase in particle diameter is likely to cause a decrease in the extent of reaction of M14, especially since it cannot homopolymerize; *i.e.*, it depends on the presence of other monomers to enable it to polymerize. The strong effect of particle size was further corroborated by the results of the following experiment. To 20 g of the product of 55M14-12 was added 76 g of seed latex C so that the total area of particles of 55M14-12 was equal to that of seed latex C. This mixture was diluted with 30 g of water, and 2 g of S and 2 g of BA were added along with some KPS. This was allowed to react to completion in a batch mode. The conversion of the M14 seemed to increase from 52% in 55M14-12 to virtually 100% in the presence of the small particles of seed latex C, whereas the reaction in batch mode at the end of the feeding period in 55M14-12 led to a conversion increase of only 47−52%.

The conclusion is thus that the extent of conversion of M14 in this system is mainly determined by the particle size and to some extent by the conversion of the main monomers, although the latter dependency is not very clear.

Ideal Surfmers. As stated above, the ideal behavior of a surfmer would be a low conversion throughout the reaction so as to avoid “burying” of surfactant groups, to impart stability to the latex particles, and to emulsify the monomer phase, if present. At the end of the reaction the conversion should reach high levels, binding the surfmer to the particle surface and ensuring a high surface coverage. However, if a surfmer is reactive enough to be able to reach high conversions at the end, it will also reach high conversions during the reaction. This is especially the case in the present system, where small particle diameters give rise to high instantaneous conversions, and a further increase in particle size causes a decrease in instantaneous conversion. In other words, the opposite effect is observed, and this may mean that the M14 may not be the ideal surfmer for the present monomer system.

However, it may be possible, in general, to bring about ideal surfmer behavior, bearing in mind the following:

(a) The surfmer conversion must be low during the reaction: this means that ideal surfmers should, in fact, be unreactive; in some systems where the surfmer is relatively reactive (such as the S/BA/AA−M14 system) this can be attained if high particle diameters are used. If some surfmer addition strategy is applied, the amount of surfactant becoming buried may be limited. This option is limited by the fact that a minimum particle coverage is needed for stability throughout the reaction.

(b) The surfmer conversion has to reach high levels at the end of the main monomers feeding period for which a change in reactivity of the surfmer or main monomers is needed. The latter might be achieved, for example, if at the end of the period of feeding the main monomer mixture, another monomer (mixture) which reacts more favorably with the surfmer is added. Good candidates could be the vinyl esters, which generally react better with crotonates, fumarates,[59] and maleates ($r_{\text{diethyl maleate}} = 0.04$, $r_{\text{vinyl acetate}} = 0.17$[55]) than do any of the (meth)acrylates and styrenes (although the presence of small quantities of styrene will impede reaction of vinyl esters). The example of CRO in Figure 11 shows this clearly. Likewise, there may be monomer systems in which M14 shows a different copolymerization behavior, and where the ideal behavior can be attained. This will be investigated in detail in a forthcoming paper.[62]

Conclusions

On the basis of the reactions described it can be concluded that the maleate surfmer is the most interesting surfmer of the three investigated *for the styrene/butyl acrylate/acrylic acid system* from a point of view of reactivity/copolymerization behavior. The methacrylate surfmer is too reactive, and the crotonate surfmer is not reactive enough. In case of the maleate it seems possible to reach relatively high conversions in the absence of homopolymerization in the aqueous phase which can lead to premature emulsion instability. It was found that a high instantaneous conversion throughout the reaction can lead to significant burying of surfactant in the particle interior. A strong dependence of the maleate surfmer conversion on the particle diameter was found, and although high conversions were reached up to particle diameters of 100 nm, above this value the maleate conversion decreases steadily with diameter. This is in agreement with a reaction at the particle surface. It is also concluded that, although the maleate surfmer may be the best of the three surfmers investigated for the present system, ideal surfmer behavior could not be obtained.

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