Polymer 40 (1999) 1359–1366

polymer

Reactive surfactants in heterophase polymerization. XXIV. Emulsion polymerization of styrene with maleate- and succinate-containing cationic surfactants[1]

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Received 6 May 1998; revised 6 May 1998; accepted 6 May 1998

Abstract

A series of alkyl pyridinium bromide maleate and succinate diester surfactants has been used as stabilizers in the free radical emulsion polymerization of styrene. High conversions of styrene were achieved readily with the maleate surfactants, but the succinates gave rise to varying levels of retardation. In two of the latter cases, use of the surfactant at a concentration below its crucial micelle concentration appears to be a key factor, but the other retardations are difficult to account for. Little difference in reactivity and latex properties was found with the maleate surfactants despite the position of the maleate group being very different in the series of molecules examined. Chemical incorporation of the maleate surfmers into the polymer particles appears to occur early on in the polymerizations, but a sufficiently high proportion of groups is on the surface to yield stable latex emulsions. The surface tensions of the final latices produced with both the maleate and succinate surfactants are high, suggesting a large proportion of succinate species are also surface adsorbed. However, the surface tensions of these latices are a little lower than those of latices produced with the maleates, suggesting the proportion of solubilized succinate surfactant is a little higher. This seems to be important in terms of the robustness of the stability of the latices to the addition of electrolytes, the succinate-stabilized species being consistently more tolerant. This suggests that while chemically bound surfactants can improve some of the properties of latices, e.g. the hydrophobicity of films, this might be at the expense of latex stability.

Keywords: Polymerizable surfactant; Maleate surfmers; Emulsion polymerization

1. Introduction

Heterophase polymerizations, especially emulsion polymerizations, are important industrial technologies yielding synthetic elastomers, paints, paper coatings, adhesives, etc. In emulsion polymerizations, the use, or in situ production, of surfactants is necessary in order to achieve stabilization of the latex particles produced during polymerization and indeed later on in the derived products. In the present state of the art, surfactants are adsorbed onto the surface of the latex particles, and as a result, the stabilization they induce can be rather inefficient under certain circumstances, e.g. freeze and thaw cycles, or applied shear stress. Most of these latices are used as film-forming polymers, and then the presence of adsorbed surfactants can confer too much water sensitivity on the film. Thus, high water permeability can arise, which is a major drawback in applications such as paints and other protective coatings. One possible solution to these problems is to covalently attach the surfactant to the polymer so that it cannot be desorbed nor undergo phase separation. There are three main ways to achieve this immobilization: (i) the use of a surface active monomer (surfmer); (ii) the use of a surface active transfer agent (transurf); and (iii) the use of surface active initiators (inisurfs).

Previous studies [1–3], in which different polymerizable functions were tested and screened to demonstrate the best compromise between the overall reactivity and the homopolymerizability, identified the maleate function as a potentially very useful group for incorporation into the surfmer. Maleates are isomers of fumarates, with the fumarate being

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[1] This publication is part of a series of publications from the European Union Program ‘Human Capital and Mobility’ (CHRX CT 930159) on ‘Reactive Surfactants in Heterophase Polymerization for High Performance Polymers’

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PII: S0032-3861(98)00356-5

the *trans* isomer and the maleate being the *cis*. Fumarates can produce homopolymers under typical free radical polymerization conditions, whereas maleates do not. This difference in reactivity from one isomer to the other is attributed to the reduction of the planarity of the maleate due to the presence of the two carboxylate esters in a *cis* configuration [4]. Furthermore, free radical (co)polymerization of 1,2-disubstituted alkenes is generally believed to occur via a *trans* reaction, and in this respect the configuration of fumarates is stereochemically more condusive [5].

Surface active monomers bearing a maleate function have recently attracted some attention. Tauer et al. [6] reported that alkyl sulfopropyl maleates produced latices whose sera contained a lower surfactant concentration, indicating that the surfactant was chemically anchored to the particles. Non-ionic maleates have also been used in emulsion polymerization [7]. In this instance, styrene polymerization was carried out at low solids content (ca. 10%) and 2% surfmer based on monomer. Stable latices were obtained which were monodisperse, with the average particle size being dependent on the EO chain length in the surfmer. However, the latices coagulated when an attempt was made to remove the serum. Recently, this has led Guyot and coworkers [8] to synthesize cationic and zwitterionic maleates. Initial emulsion polymerization experiments produced narrow particle size distributions and small particles, however, it should be pointed out that in some cases an extra conventional cationic surfactant was added to the system. In all cases, the structure of the surfmers was similar, and in particular the position of the maleate group in the hydrophobe. In each case, an alkyl group of variable chain length (from 10 to 18 carbon units) formed one ester of the maleate function, and the hydrophilic head with a short spacer group inbetween the second ester. However, no study has been carried out to date on the effect of the position of the maleate function in a surfmer nor use of such species in emulsion polymerizations. In the previous part of this series [9], the synthesis and surface activity of these monomers was described, we now report their use in emulsion polymerizations.

2. Experimental

2.1. Materials

Styrene (S) [Aldrich] was washed with NaOH (1 M) and distilled before use. It was stored at −18°C. Azo-N,N′-dimethylisobutylamidinium hydrochloride (Wako) was used as received. Water was deionized and distilled. The syntheses of the reactive maleate surfactants and their saturated succinate analogues used in this study are described in the preceding paper [9]. The indicators Disulphine Blue and Dimidium Bromide for the two-phase titration were obtained from Fluka and used as received. Other reagents and solvents were general purpose species, and were used as supplied.

2.2. Emulsion polymerization

Each batch emulsion polymerization was carried out in a 0.3 l jacketed glass vessel fitted with a reflux condenser, nitrogen inlet, sample withdrawal tube and thermocouple. The contents of the reactor were stirred using an impeller-type stirrer. The reactor was heated to 80°C by circulating water from a thermostatic bath through the reactor jacket.

Typically, monomer, surfactant and approximately 90% of the required water were charged into the reactor and thermostated at 80°C under a nitrogen atmosphere with a stirring rate of 350 rpm. After approximately 30 min, the initiator dissolved in the remaining water was added. The composition of the reaction mixture used in these polymerizations is given in Table 1. Approximately 3 g of latex was withdrawn every so often in order to follow the conversion of the main monomer by gravimetry and that of surfmer using the method which is explained in detail later.

2.3. Latex characterization

The surface tension of latices was measured at 22°C on a programmable tensiometer KSV Sigma 70, using a Du Nouy ring. Dynamic light scattering (DLS) was used to measure the particle size of latices in a Malvern System 4700c light scattering instrument. In some cases, transmission electron microscopy (TEM) performed on a Hitachi H-7000 FA was used to determine the polydispersity of the samples.

The amount of coagulum was measured by collecting the solid deposited on the reactor walls and stirrer, and by filtering the latex (mesh 63). It is presented as the weight of coagulum per total weight of monomer added.

2.4. Stability on electrolyte addition

Electrolyte solutions of different concentrations of the following salts: NaCl, Na_2SO_4, $CaCl_2$ and $Al_2(SO_4)_3$, were made up. Aliquots of the most dilute electrolyte concentration (0.01 M) and latex were mixed in a test tube and left to stand. If the latex was stable to that particular concentration, the test was repeated with a more concentrated solution until coagulation occurred.

2.5. Analysis of surfmer conversion

The method used to follow the conversion of the surfmer with time has been described previously [2], however, in

Table 1
Reaction mixture used in emulsion polymerizations

Batch reaction	30% solids content	80°C	350 rpm	N_2 atmosphere
Component		Amount (g)		
Styrene		60		
Surfactant		0.6		
Initiator		0.09		
Water		139.4		

this case some modifications have been employed since the surfmers are cationic in nature.

Polystyrene latices of high conversion were cleaned by centrifugation [10] as follows: 1 g of latex was diluted with 50 ml deionized water and centrifuged at 22 000 rpm for 4 h in a CENTRIKON H-401 apparatus with a A8.24 rotor supplied by Kontron Hermle. The supernatant solution was carefully recovered using a pipette and the latex redispersed in water with the aid of ultrasound. The cycle was performed two–three times, keeping the sera separate after each cycle. For samples of low conversion, the serum replacement technique was used [11]. A portion (2–3 g) of latex was diluted to 450 ml with deionized water, and the dispersion introduced into the cell of an MFS Micro Filtration Systems, consisting of a polycarbonate cylinder with end caps and a stirring polyacetal rod. The cell was used in a semi-continuous way, i.e. the cell was filled with water and most of it allowed to exit before the cell was filled again. The solids content of the latex has to be lower than about 8% to avoid clogging of the membrane. Continuous agitation is necessary to avoid sedimentation of particle aggregates formed as a consequence of the elimination of the surfactants from the particle surface. The process is complete when the conductivity of the effluent water is the same as that of the inlet water. The surfactants (and salts if desirable) can then be identified and quantified by conventional chemical analysis methods. The different batches of sera were kept separately to avoid high dilution of surfactants, typically 6–7 l of water was used to clean a latex sample.

Sera obtained from latex cleaning processes were analysed by a two-phase titration. This is a method described by Rein et al. [12] in 1967 for the determination of most, but not all, anionic surfactants (see original reference for applicability). Briefly, this method is based on the complex formation between cationic and anionic surfactants, and the variation of solubility between the ‘monomeric’ surfactants and the anionic–cationic surfactant complex, the latter being water soluble and the former water insoluble. Two dyes were used as indicators; Disulphine Blue and Dimidium Bromide. Both are water insoluble when in the ‘monomeric’ state; however, they become water soluble when they complex with the oppositely charged surfactant. For the detailed mechanism see the original paper [12] and Ref. [2]. Originally, this method was developed for the determination of anionic surfactants, however, in the present case, the surfactant of interest is cationic and so the procedure was adapted to these circumstances. A solution of known concentration of anionic surfactant, sodium dodecyl sulfate, SDS, was titrated using the cationic surfactant serum as titrant. According to the amount of titrant needed for the known anionic solution, the concentration of cationic surfactant in the serum could be calculated. Since in all cases the concentrations of the sera were expected to be low, in the range of 10^{-5}–10^{-6} M, the interaction between cationic and anionic surfactant was not expected to be 1:1 any more, and therefore a calibration curve had to be generated for each type of surfactant. From the concentration of cationic surfmer (surfactant) remaining in each serum, the amount of reacted surfmer is calculated, and expressed as the conversion (%) of the total amount of surfmer in the original reaction mixture.

3. Results and discussion

In the present study, a series of polymerizable and non-polymerizable surfactants (Fig. 1) has been used in the emulsion polymerization of styrene. The surfmers have a maleate group as the polymerizable function, whereas the non-polymerizable ones possess a succinate function, the saturated analogue of the maleate. In all cases, the head-group is a pyridinium bromide. The same nomenclature has been used as in the preceding paper [9], where the synthesis and surface activity of these novel surfactants is reported. A summary of the results of the characterization of these surfmers is given in Table 2.

These surfactants were used in emulsion polymerizations of styrene in a batch process (Table 1). The amount of surfactant added to the system was low, 1% based on the monomer weight, so that the screening of surfactants could be carried out. Additionally, the weight concentration of surfactant was maintained constant in each polymerization. In the case of c1mc11, c6mc6 and c10mc2, since the molecular weight is the same for all three surfactants, the molar concentration was also the same. As indicated in Table 2, these surfactants show very different aggregation behaviour and, in particular, their critical micelle concentrations (cmc) vary significantly. As a result, with c1mc11 the concentration of surfmer added to the system was slightly lower than its cmc, whilst in the other cases the concentration used was above their respective cmcs. Likewise, for c1sc11 and c6sc6, the surfactant level is below the respective cmc values, but for c10sc2 and c12c2, it is above.

3.1. Surface tension of latices

The results of the emulsion polymerizations are summarized in Table 3. The surface tension of all final latices was observed to be very high and close to that of water,

Table 2
Surface activity data of maleate and succinate surfactants

Surfmer	Mol. wt.	cmc 10^3 mol dm^{-3}	cmc g dm^{-3}	γ_{cmc} mNm^{-1}
c1mc11	442.36	11.1	4.9	45.2
c6mc6	442.36	8.2	3.6	33.7
c10mc2	442.36	1.8	0.79	41.8
c12mc2	471.42	0.68	0.32	41.8
c1sc11	444.37	22.1	9.8	41.8
c6sc6	444.36	48.2	21.4	34.4
c10sc2	444.36	1.21	0.54	27.4
c12sc2	473.42	0.23	0.11	29.5

Table 3
Results of the emulsion polymerizations using maleate and succinate surfactants

Surfactant	Coagulation (%)	Surface tension final solution (mNm^{-1})	Latex particle size (nm)	Appearance of latex
c1mc11	9.2	72.5	101	[b]
c1sc11	—	—	—	[d]
c6mc6	2.1	70	91	[b c]
c6sc6	2.2	63	202	[a]
c10mc2	4.6	70	103	[b]
c10sc2	5.1	70	216	[a]
c12mc2	0.9	62	102	[a]
c12sc2	1.3	60	173	[a]

[a] Typical latex appearance
[b] Some grit appeared in the latex, and a shoulder could be observed in the particle size distribution from DLS
[c] Very thick latex
[d] Emulsion polymerization was not successfully achieved

indicating a low concentration of surfactant/surfmer in the aqueous phase. The reason for this low concentration may be the chemical anchoring of the surfmer to the particles or the physical adsorption of the surfmer onto the particle surface. Latices synthesized with a related maleate surfmer reported in the literature showed similarly high surface tensions [13]. In the latter work, the conversion of the surfmer was determined and a high degree of incorporation of surfmer into the latex polymer was concluded [6]. However, in the present work, the surface tension of latices synthesized

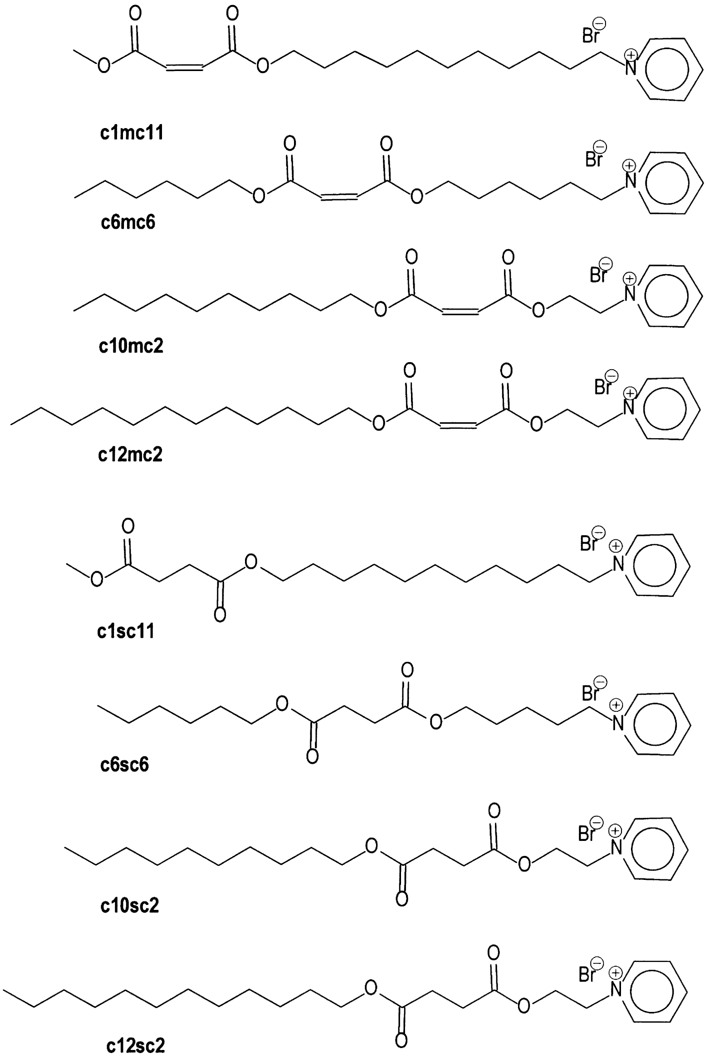

Fig. 1. Structure of maleate surfmers and succinate surfactants used in emulsion polymerizations of styrene.

with the succinate surfactants is also high, albeit slightly lower than with each structurally analogous maleate surfmer. It would appear therefore that the (low) level of residual soluble surfactant is nevertheless somewhat higher with the succinate than the maleates. In the case of the succinates, chemical anchoring via copolymerization of the succinate is not possible, and yet even so final surface tensions are high. One possibility is that the succinates do become chemically bound via a radical transfer reaction, i.e. they function as transurfs. A likely site for hydrogen atom abstraction is the succinate ethylene bridge, since the radical formed would be stabilized to some extent by the adjacent carbonyl group. Additionally, of course, these surfactants may simply be strongly adsorbed to the latex particle surface. Thus, even if the final high surface tension is an indicator of a low concentration of surfactant in the serum, it cannot necessarily be attributed solely to the chemical attachment of the maleate surfmer to the particles from these experiments alone.

3.2. Coagulation

A general requirement for a good surfmer in emulsion polymerization is a limited solubility in water, expressed in terms of its cmc. If the surfmer has a high water solubility, the partitioning of the surfactant could be shifted too much towards the aqueous phase which could lead to decreased stabilization of the polymer particles, and could enhance the probability of unfavourable reactions in the aqueous phase, e.g. polyelectrolyte formation. In Table 3, the data for the amount of coagulum obtained in each emulsion polymerization are given. The level of coagulation occurring in each reaction varied significantly with the surfactant used. The most stable latices (lowest % coagulation) are those produced with the c12/c2 maleate and succinate surfactants, whereas the least stable are those synthesized with the two c1/c11 species. Indeed, in the case of c1sc11, this surfactant was not able to produce a latex at all and the system phase separated during the reaction. The major factor here is probably that the working level of surfactant is below the cmc of these two surfactants. However, this does not appear to be the sole factor, since the behaviours of c6mc6 and c6sc6 are similar, both giving the same level of coagulum, yet the surfactant concentration is such that c6mc6 is above its cmc but c6sc6 is below. The structure of the surfactant is therefore also important.

3.3. Particle size

The particle size of the latices was measured using DLS. Latices produced with maleate surfmers showed smaller particle sizes than those produced with the corresponding succinate series. Furthermore, the particle sizes of the latices in the maleate series were very self-consistent. TEM photographs showed a large polydispersity of all latices. Why the particle size of maleate-derived latices should be lower than those from succinate surfactants is unclear, but it may be related to the chemical incorporation of the maleates and, e.g. in the case of c6sc6, to slow nucleation.

In Figs 2–5, the conversion versus time curves for the styrene polymerizations are shown. In the case of reactions using maleate surfmers, the conversion of surfmer is also reported. The polymerizations involving the maleate surfactants did not produce any large difference in styrene conversion. All the curves are very similar and much as expected in the absence of maleate. In contrast, perhaps somewhat surprisingly, all the succinate surfactants caused retardation of the polymerization of styrene, and while the full explanation of this is not to hand, it may be associated with the possible radical transfer reaction mentioned earlier. With c1sc11, no latex was formed at all and the system phase separated; this is reflected in the very low consumption of styrene (Fig. 2). As mentioned earlier, this is probably due to the rather large cmc of this species. Surfactant c6sc6 was also present fully solubilized below its cmc and,

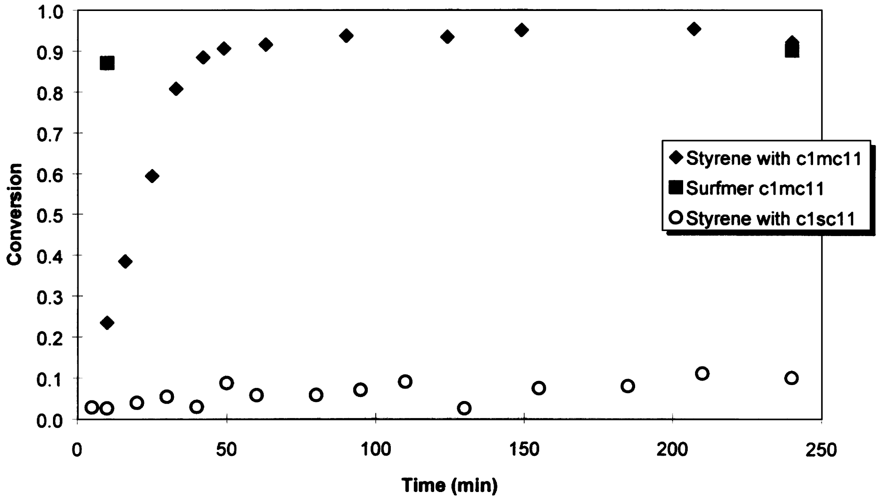

Fig. 2. Conversion versus time for: (i) emulsion polymerization of styrene with: ◆, c1mc11; ○, c1sc11; and (ii) ■, c1mc11.

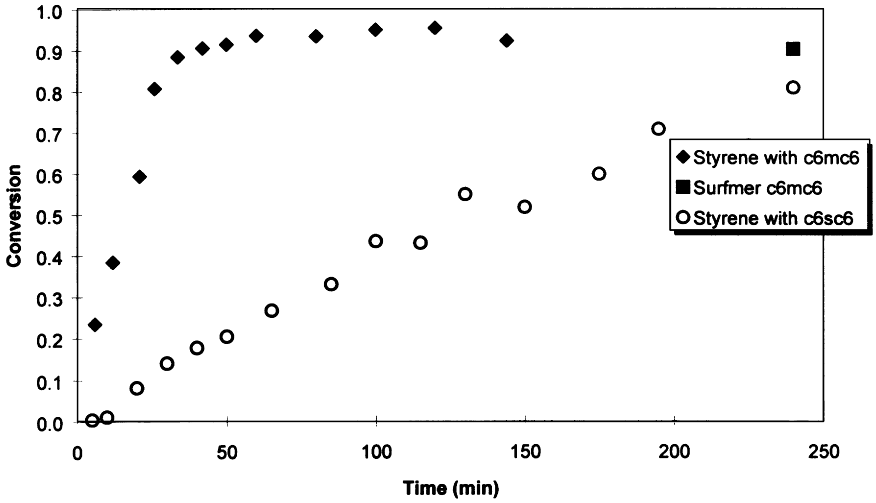

Fig. 3. Conversion versus time for: (i) emulsion polymerization of styrene with: ◆, c6mc6; ○, c6sc6; and (ii) ■, c6mc6.

not surprisingly, styrene conversion was heavily retarded in this case as well (Fig. 3). This probably reflects a long nucleation process and overall the formation of a smaller number of larger particles.

3.4. Surfmer conversion

Latices formed with reactive surfactants were cleaned and the conversion of surfmer determined. In the case of each final latex, these were cleaned using the ultracentrifugation method. This has been proved previously to be valid to clean polystyrene latices [10]. Two latices were also chosen for analysis of the conversion of surfmer at low styrene conversion. These samples were cleaned by the serum replacement method, since the amount of monomer styrene in the sample was high and therefore the precipitation of polymer was more difficult. In addition, ultracentrifugation at low conversions has been found [14] to desorb oligomers which interfere in the subsequent determination of the concentration of surfmer. In all cases, each final latex sample showed that the conversion of surfmer was above 90%. The reactions chosen for the analysis of low conversion were those using c1mc11 and c12mc2, since these represented two extreme cases from the point of view of the position of the maleate function and the cmc of the surfactant. Polymerization with c1mc11 produced the larger amount of coagulum, due to its high cmc. Despite the large difference in cmc, however, it can be observed in Figs 2, and 5 that samples of latices taken at low styrene conversion (20%) showed over 90% of surfmer had already reacted in both cases.

3.5. Surfmer structure and reactivity

In the present study, the maleate surfmers have been studied with the polymerizable function at various positions in the hydrophobic tail. Among the surfmers used previously in emulsion polymerization, tail-type have been the predominant structure [15], however, some studies on head-type have also been carried out [16,17]. Tail-type surfmers in

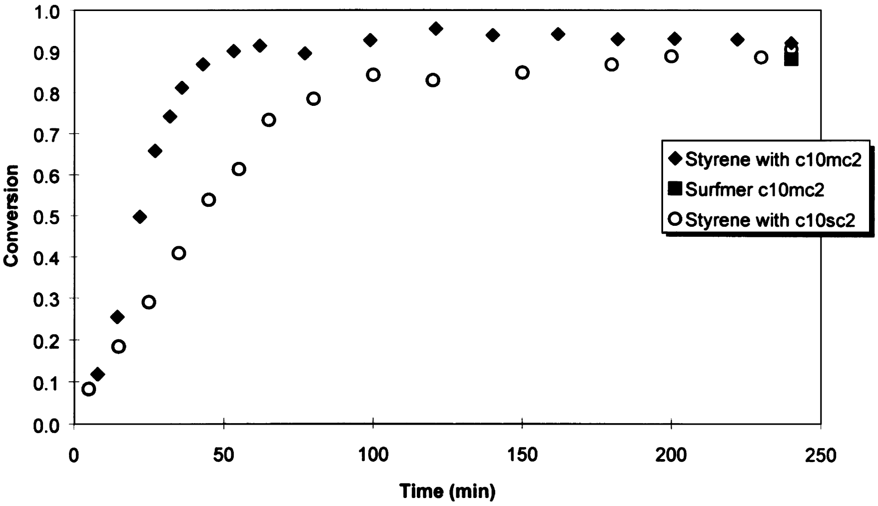

Fig. 4. Conversion versus time for: (i) emulsion polymerization of styrene with: ◆, c10mc2; ○, c10sc2; and (ii) ■, c10mc2.

Table 4
Stability to addition of electrolytes of polystyrene latices produced with maleate and succinate surfactants

Surfactant	0.02 M NaCl	0.1 M NaCl	0.02 M Na_2SO_4	0.02 M $CaCl_2$	0.1 M $CaCl_2$	0.02 M $Al_2(SO_4)_3$
c1mc11	✓✓	x	x	✓	x	x
c6mc6	✓	x	x	✓	x	x
c10mc2	✓	x	x	✓	x	x
c12mc2	✓	x	x	✓	x	x
c1sc11	No latex available for testing					
c6sc6	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
c10sc2	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓
c12sc2	✓✓	✓✓	✓✓	✓✓	✓✓	✓✓

✓✓ Stable on salt addition; ✓ some coagulation on salt addition; x total coagulation on salt addition

principle have a more appropriate structure for emulsion polymerization and the production of stable latices. From the results presented here, it can be concluded that the position of the maleate function along the hydrophobic tail does not significantly affect the reactivity of the surfmer and its incorporation into the latex. c1mc11 is a tail-type surfmer, whereas c12mc2 is a head-type, and yet both appear to be incorporated very efficiently (~90%) into particles even at low styrene conversion (~20%) (Figs 2, and 5). If these monomers are considered simply as diesters of maleic acid, they would be expected to show a rather high tendency towards 1:1 alternating copolymerization with styrene [18]. In addition, the similarity in reactivity is perhaps not surprising, since it has been reported that the polymerization behaviour of fumarate diesters does not seem to be affected by the bulkiness of the ester groups to any considerable extent [19–21], and one might therefore expect similar behaviour with maleates. It has to be kept in mind, however, that the situation could be more complex with the surface active molecules in this work. Nagai and co-workers [22–24] studied the copolymerizability of different surfmers and monomers, and showed that the type of initiator and solvent are also of influence in determining the final structure of the polymers. The presence of micelles in the system, e.g. enhanced the tendency to produce alternating copolymers.

The present observation of the rapid incorporation of maleate surfmers c1mc11 and c12mc2 tends to contradict earlier results. Previously [13], maleates were compared to their fumarate isomers in emulsion polymerization of styrene using AIBN as initiator. The fumarates were reported to have a tendency to produce polyelectrolytes in the aqueous phase, and react very early in the reaction, almost 90% conversion of surfmer was achieved at 20% styrene conversion. In contrast, the maleate analogues did not seem to react until ~80% of the styrene was converted to polymer. More recently, however, it has been reported [2,25] that maleates surfmers do indeed react readily, especially when styrene is present in the system. These apparently contradictory observations probably arise as a result of the use of different initiators, and different latex cleaning and analytical protocols.

3.6. Latex stability and locus of surfmer

The stability to the addition of electrolytes of the latices produced in this work was studied. The composition of the polymerization mixtures was not chosen to produce latices stable to electrolyte addition and therefore it was not expected that the products would be unusually stable in this test. However, it was thought that the test might give a very interesting indication of the extent of surface coverage

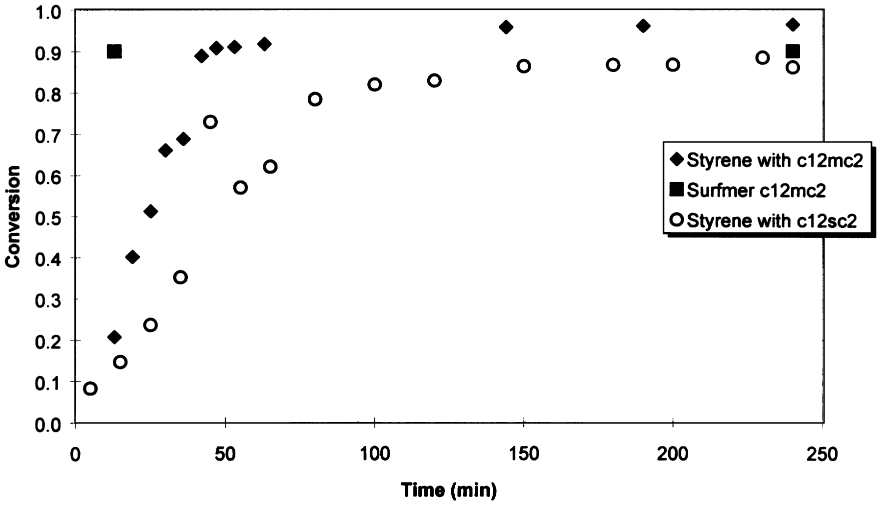

Fig. 5. Conversion versus time for: (i) emulsion polymerization of styrene with: ◆, c12mc2; ○, c12sc2; and (ii) ■, c12mc2.

of the particles by surfactants. The results are shown in Table 4. It is interesting to see that the latices formed with maleate surfmers are generally less stable to the addition of salts than those synthesized using the superficially non-reactive succinate surfactants. This behaviour is in agreement with some earlier cases [26] and in disagreement with others [16]. There are two possible reasons for this behaviour. On the one hand, the reaction of the surfmers early on in polymerizations may be expected to make the burial of surfactant within the particles more probable, and therefore the surface charge would be decreased. In turn, this would make these latices less stable. On the other hand, even if the surfmer was present at the surface, the fact that it is chemically anchored to the particles would produce a change in the whole thermodynamics of the system, since equilibrium between adsorbed surfactant and surfactant in the aqueous phase would no longer be possible.

Since latices produced with the maleate surfmers were stable as formed, there is undoubtedly a sufficiently large proportion of the surfmer residues present on the surface to provide more than adequate charge stabilization. However, it does seem that with these maleates, a large proportion of groups are truly chemically bound, and that little or no equilibrium exists with free surfactant in solution. Consequently, when a change in the external conditions of the system is induced (e.g. an increase in the ionic strength), the system is no longer able to react and shift the equilibrium accordingly. Thus, the tendency to phase separate under these conditions is enhanced. In contrast, the succinate surfactants seem to be more conventional, and for comparable structures, the slightly higher surface tension of each final latex (Table 3) implies a higher level of surfactant solubilized in the aqueous phase, and somewhat less adsorbed or chemically bound by radical transfer reactions than that chemically attached to the case of each structurally analogous maleate (bearing in mind some component of each maleate being buried within latex particles as well). Thus, when the electrolyte is added to the succinate surfactant stabilized latices, a shift in the equilibrium between adsorbed and free surfactant can occur in an attempt to overcome the reduction in the width of the electrical double layer, and hence particle destabilization, triggered by the increase in ionic strength. It seems, therefore, that a component of solubilized ionic surfactant may be crucially important in controlling the robustness of latex stability, and that while chemical binding of all surfactant onto latex particles offers possible advantages in terms of, e.g. the enhanced hydrophobicity of resultant films formed by particle fusion, this may have to be at the expense of reducing the robustness of the latex stability. In technological terms, the combination of a polymerizable surfactant and a lower level of conventional surfactant seems to have much to commend it.

4. Conclusions

Cationic surfactants with reactive maleate groups produce stable latices from styrene emulsion polymerizations. The maleate surfactants are copolymerized readily into the polymer particles and become largely surface bound. Very low levels remain in aqueous solution. Cationic surfactant with analogous succinate structures tends to cause retardation in styrene emulsion polymerizations. Although latices are formed in which a large proportion of the succinate surfactant is adsorbed on particle surfaces, the residual aqueous solution concentration seems to be a little higher than with the maleate surfactants. In turn, this soluble component of surfactant seems to provide the latex with a robustness in stability when challenged with soluble electrolytes.

Acknowledgements

A.M.-G. acknowledges the receipt of a research assistantship from the EU under the ‘Human Capital and Mobility’ programme.

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