

Styrene Emulsion Polymerization in the Presence of a Maleate-Functional Surfactant

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ABSTRACT: Dodecylhemiester of maleic anhydride is a very good anionic stabilizer for the emulsion polymerization of styrene. Rather high solid contents may be produced. Up to about 70% of the surfactant can be grafted onto the surface of the particles. Upon flocculation with calcium salt, only 3% of the surfactant is left in the washing water.
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Key words: emulsion polymerization; styrene; maleic anhydride hemiester; flocculation

INTRODUCTION

In emulsion polymerization, use of reactive surfactants, i.e., surfactants that can be covalently linked to the surface of the particles, are expected to lead to a certain number of advantages. First of all, improvement of the latex stability. Because in conventional emulsion polymerization the surfactants are simply adsorbed onto the surface of particles, they can desorb under certain circumstances, so causing a lack of stability; this is the case when the latex is submitted to high shear, this is also the case when the latex is frozen. In both cases, flocculation takes place.

A second kind of benefit is expected in the case of film-forming latexes; in conventional emulsion, the surfactant being not firmly attached to the particle are able to migrate toward the surface of the films. It may result in defects of adhesion if the film is expected to protect the surface of a substrate, as in the various kind of paints. In addition, it is known that during the process of coalescence, phase separation takes place.¹ Then some

domains containing residual water are formed. These domains also contain a high concentration of surfactants. They may be trapped in the polymer. A part of them may migrate towards the surface of the film, but some of them remain trapped. If the film is exposed to water environment, or just a high level of humidity, the diffusion of water through the polymer film towards these trapped domains make them to swell; this is the main cause of the water rebound of the film, which, again, is detrimental against the protection of the substrate versus corrosion. This is because, if the domain swells enough, a percolation system may occur, so that the film becomes permeable to water.

A third kind of benefit takes place if the latex is expected to give material upon flocculation. Then it may be expected that if the surfactant is covalently linked to the surface of the polymer particles, a smaller amount of it will be rejected in the water phase. So the water left after the flocculation process should be less polluted. This latter kind of benefit is the subject of the present article.

Much work has been done with the use of reaction surfactants in emulsion polymerization. The pioneering work was carried out by Green and Scheetz² for anionic surfactants and Ottewil³ for the nonionic surfactants. In both cases, the reac-

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tion takes place by copolymerization of the reactive surfactant (SURFMERS) with the other monomers. Two industrial processes based on reactive surfactants have been described by ICI.⁴ Most of the work done with surfmer, but also with INISURFS (surfactants reactive as initiators) and TRANSURFS (surfactants reactive as transfer agents) has been reviewed in a recent review,⁵ covering the work published up to 1993. Since that date a few articles have appeared^{6–10} showing the interest paid to the subject, especially for biological purposes.^{9,10} The work by Tauer and Stahler^{11,12} pointed out the interest of compounds functionalized with maleate. It has been shown that the surface tension of the latex produced with such compounds remain that of water even when high amount of surfactants up to 100 times the critical micellar concentration (CMC) were used in the emulsion polymerization of styrene. That means that the maleate compound is fully grafted at the surface of the particles, because no surfactant is left in the serum. These surfactants are produced from fatty alcohol hemiester of maleic anhydride, and further reacted with propane sulfone, which leads to a sodium sulphate ended anionic surfactants.

In the present article, we report a study carried out with the simplest maleic surfactant, i.e., the hemiester coming from the reaction of dodecanol with maleic anhydride, which is neutralized as the sodium salt and engaged in the emulsion polymerization of styrene.

EXPERIMENTAL

Materials

Styrene (Prolabo) is first distilled under vacuum and then stored at -20°C . CO_3NaH and potassium persulfate are commercial products (Riedel–del Haen) as well as maleic anhydride (Jansenn) and dodecanol (Aldrich).

Synthesis of Monododecyl Maleate (MDM)

According to Hamaide and Zicmanis,¹³ maleic anhydride (49.03 g, 0.50 mol) and 1-dodecanol (95.90 g, 0.51 mol) were stirred in a melted state at 80°C for 1 h. Heptane (150 cm^3) was added to the reaction mixture and stirred for some minutes until an homogeneous solution forms. The solution was left at room temperature for 3 h, then at 15°C for 2 h, with mixing from time to time. The

precipitate formed was collected and recrystallized from heptane (150 cm^3). White bright crystals of monododecyl maleate (132.26 g, 93.0%) were obtained.

Critical Micellar Concentration

The analysis of MDM was checked using $^1\text{H-NMR}$ (Bruker 250 Mhz). Its previously defined CMC has been measured either using conductimetric titration or with surface tension measurements (Du Nouy method, Kruss apparatus). The results are respectively 5.8 and 6.0 mM/L (i.e., 1.7 g/L), which is a little smaller than for the Sodium Dodecyl Sulfate (2.3 g/L) often used in emulsion polymerization.

Batch Polymerization

Deionized water (900 g) is changed into a reactor (1.5 L) and degassed under a stream of nitrogen at 70°C . Then CO_3NaH (2 g) are introduced together with the surfactant (0.8 g). While the surfactant is dissolved the pH reaches a value of 8.7 after about 30 min. Potassium persulfate (0.75 g) is then added in 20 g of water, and finally styrene (90°g). A first set of experiments, with this recipe (10% solid contents), has been devoted to the comparison of MDM with more conventional surfactants, i.e., potassium stearate (KS) or sodium dodecyl sulfate (SDS).

A second set of experiments has been carried out with higher solid contents (30%). In this case, more surfactant was needed, and then a second addition of surfactant is carried out after the nucleation period.

Latex Characterization

Sampling was carried out at regular intervals to follow conversion kinetics gravimetrically and particle size using quasi elastic light scattering (QELS) (Brookhaven 8000), or transmission electron microscopy (TEM).

Before titration of the surface functional groups, the latex are diluted to about 1.5% solid contents, and are passed through ion exchange resins several times so that the residual conductivity of the latex are less than 10–20 microsiemens/cm.

Conductimetric titration of strong (SO_4^-) and weak (COO^-) acid groups are carried out upon addition of diluted soda to solution prepared using 5–30 g of washed latex diluted in 100 mL of bipher-

Table I Polymerization Experiments and Results

Run	Sodium Stearate			MDM					
	1	7	8	2	3	4	5	6	9
NaHCO ₃ (g)	1.02	1.0	0	1.01	2.0	2.0	2.0	2.0	2.0
Surfactant g	3.4	0.8	1.5	2.87	1.52	0.8	0.4	0.6	0.82
nmol/l	13.01	3.05	5.73	10.94	5.80	3.04	1.54	2.28	3.13
Ionic Strength nmol/l	70	50	29	80	76	73	71	72	73
Final Conv %	99	100	100	100	100	99	99	100	97
Final Size nm	93	330	82	93.5	75	90	240	109	80
Final part. Nb 10 ¹⁷	2	0.05	3	2.2	4	2.5	0.12	1.3	3.1

Data for styrene polymerization at 70°C with water (900 g), styrene (90 g), and K₂S₂O₈ (0.75 g) in 20 g of water.

mutated water (conductivity less than 1 μs/cm). This method has been preferred to potentiometry, because it is more accurate, although the purity of the reactants (specially bipermutated water) is more demanding.

Other characterization may involve NMR measurements that allow the long alkyl chain of the hemiester to be detected at 0.9 (CH₃) and 1.3 (CH₂) ppm from Tetramethylsilane and also SEC (size exclusion chromatography) for molecular weight measurements.

Floculation

The critical coagulation concentration CCC is measured by turbidimetric titration upon addition of a serum containing 1% of calcium chloride, to a latex diluted to a solid contents of 0.1%. The CCC is determined as the concentration inducing rapid floculation.

For the floculation itself, 400 ML of latex, are used, to which a volume of 1% calcium chloride, slightly larger than the CCC, is added. After stirring, the floc is diluted with 300 mL of bipermutated water filtered, redispersed, and washed three times and finally filtered and dried. The washing water are evaporated slowly at 50°C and then under vacuum at 40°C, allowing the measurement of their solid contents (residual salts and surfactants).

RESULTS AND DISCUSSION

Polymerization Kinetics and Particle Size

A set of experiments have been carried out using the basic recipe with 10% solid contents and varying the amount of surfactant. Some comparative

data were obtained either with MDM or potassium stearate. In some cases the ionic strenght has been changed by using various amount of buffer (NaH CO₃). The corresponding experiments are reported in Table I. The conversion curves are shown in Figure 1. It can be seen that

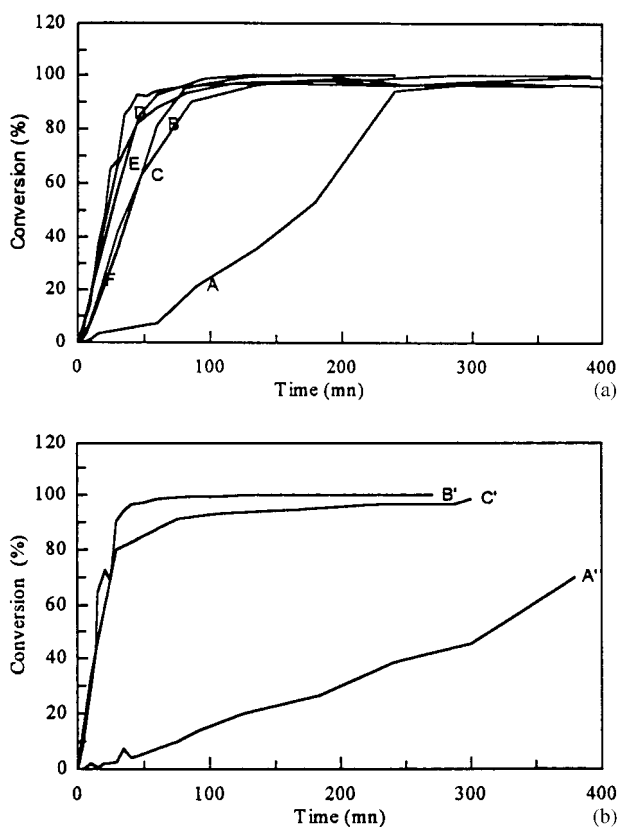
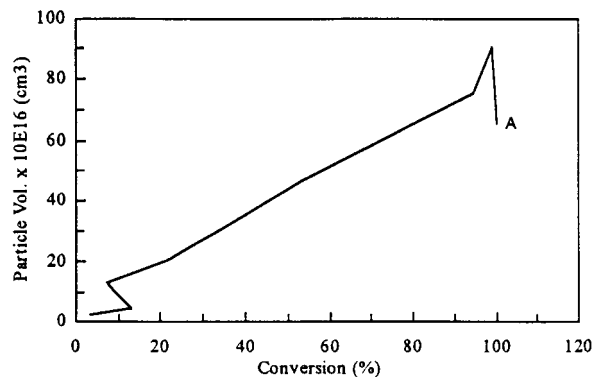


Figure 1 Kinetics of styrene emulsion polymerization with 10% solid contents: (a) with MDM as emulsifier A = 1.54 mmol/L; B = 2.28; C = 3.04; D = 3.13; E = 5.8; F = 10.9 mmol/L. (b) With sodium stearate as emulsifier: A' = 3.05; B' = 5.73; C' = 13.01 mmol/L.



[MDM] : A = 1.54 mmol/l

Figure 2 Volume of polymer produced: variation with conversion (run 5 of Table I).

whatever the amount of MDM rapid conversion takes place, even if the amount of stabilizer is quite low. This is different from the case of potassium stearate where, if the concentration of surfactant is lower than the normal value (3.4 g), the polymerization rate is much slower. The absence of buffer (run 8) cause the latex to flocculate overnight; then the final pH value was 4.5 due to the slow decomposition of the initiator (T-1/2 being 5 h at 70°C). The conversion curves of Figure 1 does not show a definite period of acceleration, due to the nucleation of the particules. The high rates, however, correspond to a large number of particles so that the nucleation is very rapid. In most cases this number is in the range of 2 to 4 10^{17} , corresponding to final sizes ranging from 75 to 90 nm. In just a few cases, when the amount of surfactant is small enough, larger particles are

Table II Evolution of Particle Size with Time for Run 9

Time (mn)	Conversion %	Particles Diameter nm	Particles Number 10^{17}
5	6.7		
10	14.2	61	1.2
15	37.0	74	1.5
20	48.8	77	1.78
25	65.4	72.4	2.85
30	69.1	77	2.51
35	85	75	3.4
40	88	81	2.72
55	93	79	3.15
76	96	80	3.1
110	97	79	3.2

Table III Comparison of Particles Size (nm) by QELS and TEM

Run	1	2	3	5
QELS	93	93	79	240
TEM	83	82	59	227
D_w/D_n^a	1.03	1.08	1.09	1.01

^a Ratio of the weigh average to the number average of particle diameter.

produced (run 5). In such cases the particle volume increases quasi-linearly with the conversion as expected (Fig. 2). When the particules are smaller, there is a general trend for increase with the conversion, but the relationship is less clear. Typical data are shown in Table II (run 9). A few measurements of particle size from QELS have been checked by electron microscopy. The data are show in Table III. As often observed, the values given by TEM are smaller than those by

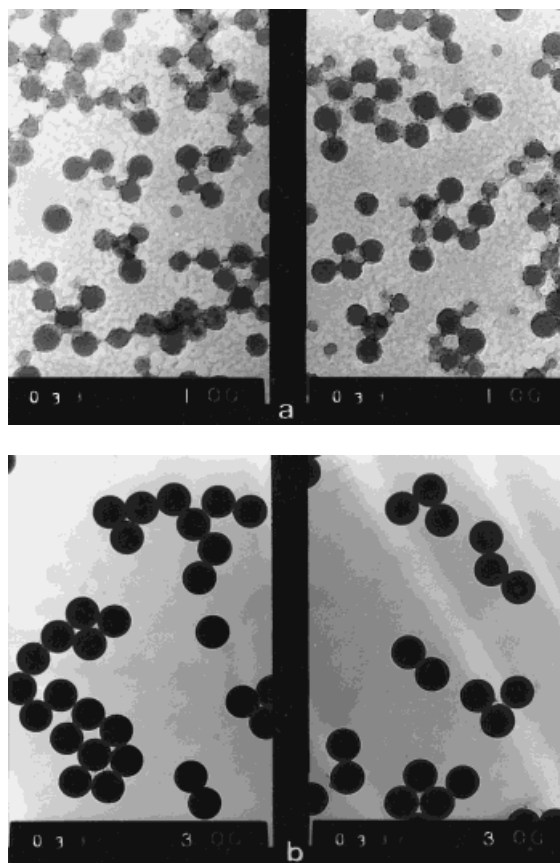


Figure 3 Transmission electron microscopy pictures of particles of run 3 (gain 100,000) and run 5 (gain 30,000).

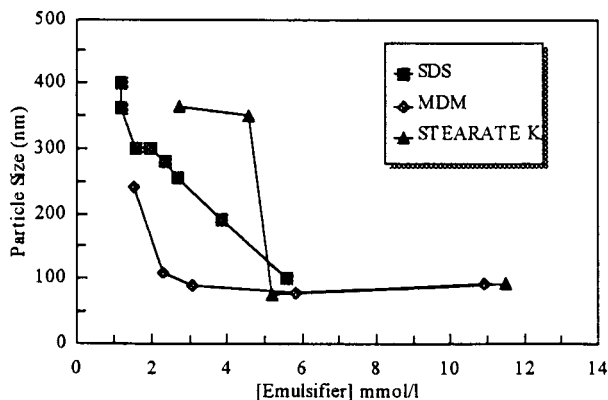


Figure 4 Final particle size (nm) vs. concentration of surfactant in emulsion polymerization of styrene with different surfactants (sodium dodecyl sulfate, SDS, sodium stearate, and monodoceylmaleate (MDM)).

QELS, possibly due to the influence of adsorbed surfactants and electrical double layers, which may become significant for small particle sizes. This diffuse layer is more or less visible in the TEM pictures (Fig. 3). On the contrary, when small amount of surfactants have been used resulting in larger particle size (run 5) well-defined monodisperse particles are produced.

The comparison of MDM with more conventional surfactants such as both sodium stearate on sodium dodecylsulfate, are shown in Figure 4. It is clear that small particle size with less than 100 nm can be obtained using smaller amount of MDM. Larger particle size are observed only if the amount of MDM engaged is lower than 3 mmol/L, instead of 5 and 6, respectively, in the case of KS and SDS. Then it may be concluded that MDM is a very efficient surfactant in emulsion polymerization.

A second series of experiments have been carried out with the purpose to increase the solid

contents of the lattices up to about 30%, i.e., a level more in line with industrial practice. The first run of that new series (run 13) was based on the formulation of run 4, except that the monomer/water ratio was increased. The polymerization was about as fast as for run 4 and the number of particles was the same. At the end of the polymerization the final diameter was increased up to 130 nm instead of 90. This was the expected value, taking into account that the number of particles was kept constant. However, after the polymerization, spontaneous flocculation takes place overnight. A similar run (run 5) was then carried out but stopped after 6 h. It showed an excellent reproductibility in terms of kinetics, particle number, and particle size. But some floc was again produced, although it could be redispersed rather easily. To increase the stability of the latex, without changing the nucleation period and then the number of particles, a few runs were carried out with a second addition of stabilizer after the nucleation period. The corresponding data are reported in Table IV.

The recipe include also $K_2S_2O_8$: 0.75 g and $NaHCO_3$ (2 g).

In run 14 addition of 0.4 g more of MDM took place after the nucleation period and corresponds roughly to the end of step II of the emulsion polymerization (i.e., the disappearance of the droplets) and 40–60% conversion. Then no new crop of particle can be produced. Although the stirring rate has been reduced from 300 rpm to 50 rpm, some flocculation took place after 6 h. But the flocs are easily redispersed in a solution of SDS and the particle size remain close to the expected value, i.e., 130 nm.

In the next run (run 16) a threefold amount of MDM has been used. It results in a larger number of particles $5.8 \cdot 10^{17}$ instead of $2.5 \cdot 10^{17}$, with a

Table IV High Solid Contents Experiments

Run	H ₂ O	Styrene	MDM	I mmol/l	Particles Nb 10 ¹⁷	Particles Size (nm)
4	924	90.5	0.80	73	2.5	90
13	664	300	0.80	100	2.3	131
15	665	300	0.80	110	2.5	128
14	669	300	0.8 + 0.4	102	2.5	129
16	665	300	2.66	111	5.8	97
17	921	300	0.8 + 0.8	76	2.4	132
18	921	385	0.8 + 1.3	78	2.3	143

The recipe include also $K_2S_2O_8$: 0.75 g and $NaHCO_3$ (2 g).

Table V Run 18 Polymerization Data

Time (min)	Conv. %	Particle Size nm	Particle Number 10 ¹⁷	Surface Acid Groups	
				Strong $\mu\text{C}/\text{cm}^2$	Weak $\mu\text{C}/\text{cm}^2$
20	3.1	59	1.04	2.9	<.02
30	7.6	68	1.7		
40	16.4	77	2.5		
50	28.7	82	3.7	0.91	<0.4
60	42.3	93	3.7	0.99	<0.4
76	58.7	107	3.4		
90	71	115	3.3		
120	90	136	2.5		
180	96	144	2.3	0.67	1.44
300	97	149	2.1		
1320	100	153	1.94	0.77	1.7

particle size of 97 nm. The number of particles has been multiplied by 2.6 instead of the value of 1.9 expected from the Smith–Ewart theory of micellar nucleation, and give an expected factor of 1.9. This latex is still lacking stability. Due to the increase of the number of particles the surface to be protected has been multiplied by 3.2 when the amount of stabilizer is compared with the reference run 4 has been multiplied by 3.3. However, going from 10 to 30% solid contents, the ionic strength of the serum has been seriously increased (Table IV), being now more than 0.1 mol/L. For that reason, in the next runs (17 and 18) the volume of water has been increased, so as to keep an ionic strength similar to that of run 4. In both cases, the protocol of delayed addition of a further amount of MDM after the nucleation period has been adopted. The particle number has then remained stable, and the final particle size was as expected. Practically no floc was produced, even after 24 h. Table V reports the regular increase of particle size with conversion. The particle number goes through a slight maximum, up to $3.7 \cdot 10^{17}/\text{L}$ and then decrease slightly due to a very slow flocculation process.

Surface Functionalization

The electrostatic stabilization of these lattices can be studied through surface titration of strong and weak acid groups. The strong acid came from the persulfate initiator, while most of the weak acid came from the grafted hemiester. In the case of run 18, a few data are reported in the last column of Table V. It can be shown that the charge density of the surface is initially due to the strong acids

while, at the end of the polymerization the grafted surfactant accounts for the largest part of the charges. It corresponds to a grafting yield of 38%.

In the first series of experiments (10% solid contents), the final grafting yield of the carboxylic group of the surfactant was shown to be dependent on the amount of MDM engaged. As shown in Table VI, this yield tends to increase when the amount of MDM was decreased. On the other hand, a rather constant amount of strong acid groups is observed. For both strong and weak acid groups, the surface charge density does not change as much as with the MDM concentration. When the amount of MDM is rather large (runs 2, 3, and 4) there is a high surface for the capture of the surfactant, and even if the incorporation yield is low, the surface may be almost saturated in carboxylic groups. Upon decreasing the concentration of the MDM, the number of particles decreases as does the surface. However, the larger particles tend to keep a higher charge density to maintain their stability.

In the second series of experiments (Table VII) upon increasing the concentration of MDM the incorporation yield is almost constant.

Two side reactions may cause some variation of this charge density. First, it is possible that there is some hydrolysis of the ester function. This will cause a loss of carboxylic groups. Some indications for this side reaction come from the NMR analysis of the latex. One may expect a resonance at 4.3 ppm for the CH₂ in α position of the ester group. In fact, in run 2, instead of that resonance, another one is observed at 3.6 ppm, which corresponds more to a CH₂ near an alcohol group. However, experiments have been carried

Table VI Final Surface Coverage with Latex at 10% Solid Contents

Run	5	6	4	3	2
MDM mM	1.54	2.28	3.04	5.80	10.94
Part. Diam nm	240	109	90	79	90
SO ₄ ⁻ %	7	12	10	12.4	11.7
SO ₄ ⁻ % $\mu\text{C}/\text{cm}^2$	1.32	1.05	1.73	0.96	1.07
COO ⁻ %	66.7	70.3	47.1	43.2	16.9
COO ⁻ % $\mu\text{C}/\text{cm}^2$	3.72	2.58	2.01	2.83	2.87

out to test the stability of HEAM vs. hydrolysis. It turns out that, using concentrations of both MDM and NaHCO₃ similar to those used in the polymerization experiments, after 24 h at 80°C, only 43% of the hemiester have been hydrolyzed from the analysis of the water extracted with chloroform. So, it can be concluded that this side reaction cannot be considered as a major event.

The second possible side reaction should be a transfer reaction involving the CH₂ group in α position vs. the ester group. It might account for a further incorporation of the MDM. It is difficult to decide if this reaction can be important or not. However, when using sodium stearate as surfactant, in run 1, a rather high amount of carboxylic group have been found at the surface of the latex (6.3 $\mu\text{C}/\text{cm}^2$). In that case, the best explanation seems to be the transfer reaction.

Floculation

Whatever the amount of MDM used and the solid contents, the CCC was shown to be in between 8 and 20 mM CaCl₂. The floculation test have been carried out as described in the experimental part. A complete analysis of the MDM in each materials and phases allows one to make a precise balance. The surface analysis of the carboxylic groups give the amount of grafted material. Extraction of the residue of the water with chloroform gives the

amount that remains water soluble after the floculation. Extraction from the floc with isopropanol gives that part which was carried by the floc and is adsorbed but not grafted. The part that remains most probably corresponds to carboxylic groups that are buried. Results from one experiment representative of each serie of runs are reported in Table VIII. For the low solid contents the part that may be considered as buried is rather low, and the largest part of the surfactant is just adsorbed onto the surface of the particles, another part being grafted probably at the end of the process. On the other hand, for the high solid contents, a rather large part is buried. Possible reasons are first, the low ionic strength because relatively less surfactant is used, and, second, because a two-step addition protocol has been used for the surfactant. Then, upon progressive growth of the particles, their number being constant but their volume being proportional to the conversion, more chances are available for carboxylic groups to be buried, and it turns that, even if the increasing surface of the particle increases, the probability of capture of the reactive surfactant, the amount of the grafted part of the MDM is about equal to that of the buried groups. With higher solid contents, the yield of the incorporated MDM is quite high and little remains simply adsorbed on the floc. Finally, the amount that remains as pollution in the water is very limited.

Table VII Final Surface Coverage at 30% Solid Contents

Run	15	14	17
MDM mM	4.1	6.3	8.2
Part. Diam nm	129	128	125
SO ₄ ⁻ %	11.9	12.2	13.1
SO ₄ ⁻ % $\mu\text{C}/\text{cm}^2$	0.49	0.49	0.52
COO ⁻ %	40	28	39
COO ⁻ % $\mu\text{C}/\text{cm}^2$	1.25	0.59	1.59

CONCLUSION

A maleate reactive surfactant, able to copolymerize with styrene, has been proven to be a quite efficient surfactant in styrene emulsion polymerization. It is able to stabilize small latex particles with a very limited amount of product. A part of that surfactant remains actually grafted onto the surface of the latex particles or remains strongly adsorbed to them, so that a very small part of

Table VIII Balance of MDM after Flocculation

Run	HEAM g	Grafted %	Adsorbed %	Water Soluble %	Burried %
4	0.8	32.5	49	8.5	10
18	0.8 + 1.3	45.5	6	3	45.5

the surfactant remains in the water phase upon flocculation with ionic salts.

Then a question is raised to know if other reactive surfactants—namely inisurfs, surfmers, or transurfs, which can participate in the radical polymerization process as initiators, comonomers, or transfer agent, the behaviour of which have been recently reviewed⁵—may behave similarly upon flocculation. It seems, however, that the main limitation should be the price of such chemicals. This limitation is not present in the case of the maleate hemiester, which has been chosen for that study, due to its low potential price.

Another point of interest should be to extend this study to actual industrial polymerization, leading to polymer product that are actually recovered upon flocculation. This is the case for the major products of rubber industry such as SBR, NBR, and polychloroprenes, as well as in plastics such as ABS engineering plastics. For the same reason, it should be quite interesting to use these reactive surfactants in the paper-coating industry, where the environmental constraints are a very important problem.

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