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Copolymerization Behavior of an Isobutenyl-Based Surfmer

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Introduction

Surfactants play a crucial role in the production and applications of emulsion polymers, but they can also have adverse effects. For example, when the latex is coated at high application speeds, the surfactant may desorb under the influence of high shear and cause coagulation. Also, when the latex is applied in films and coatings, the surfactant may segregate increasing water sensitivity and migrate to the film−air interface reducing gloss or to the film−substrate interface reducing adhesion. A promising way to reduce the negative effects of the conventional surfactants is to use polymerizable surfactants (surfmers) that are bound covalently to the polymer material so that desorption from the polymer particles or migration in the polymer film is impeded. Surfmers have attracted considerable attention, and several reviews are available.[1−6] In practice, one would like to know what is the ideal surfmer structure for a particular monomer system. Although we are far from being able to make a priori predictions on the optimal structure of the surfmer, it seems clear that the main characteristic of the surfmer is its intrinsic reactivity.[5] Schoonbrood and Asua[7] gave some guidance for the choice of the reactive group of the surfmer. They proposed that in systems with $0.5 < r_{\text{comonomer}} < 10$ and r_{surfmer} close to zero, early polymerization of the surfmer is avoided, which would otherwise result in burying of the surfmer, and a high degree of incorporation at the end of the process can be achieved. The authors stressed that these were rough guidelines because other factors affected the observed reactivity, and they recently suggested that the lower limit (and perhaps the upper limit) of the comonomer reactivity range given above should be increased.[5]

Recently, a new type of sulfonated anionic surfmer with an isobutenyl reactive group was synthesized, and it is reported that it is able to copolymerize alternatingly with fumarates and maleimides.[8] This type of reactive group looks promising for applications in all acrylic latex formulations, which are extensively used for paints and adhesives, because the reactivity ratios are in the range defined above: $r_{\text{isobutylene}} = 0.004$, $r_{\text{MMA}} = 17.9$; $r_{\text{isobutylene}} = 0.005$, $r_{\text{BuA}} = 2.9$; $r_{\text{isobutylene}} = 0.002$, $r_{\text{AA}} = 2.9$ (calculated using the Q−e scheme[9]). Therefore, the copolymerization behavior of this surfmer during the emulsion copolymerization of methyl methacrylate−butyl acrylate−acrylic acid was studied in this work.

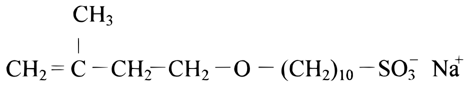
$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_2-CH_2-O-(CH_2)_{10}-SO_3^-\ \ Na^+$$

Figure 1. Surfmer structure.

Table 1. Formulations

	run 1 (PF 186)	run 2 (SDS)
initial charge		
seed[a] (g)	57.267	57.280
KPS (g)	0.250	0.250
$NaHCO_3$ (g)	0.250	0.250
emulsifier[b] (g)	0.051	0.051
water (g)	214.483	214.493
feed 1		
MMA (g)	55.908	55.874
BA (g)	43.023	42.997
AA (g)	0.999	0.998
feed rate (g/min)	0.416	0.416
feed 2		
KPS (g)	0.250	0.250
$NaHCO_3$ (g)	0.250	0.250
emulsifier (g)	0.952	0.951
water (g)	133.0	132.9
feed rate (g/min)	0.56	0.56
temp (°C)	80	80

[a] 8.69 wt % solids, dp = 145 nm; composition: MMA/Sty = 1/1. [b] SDS contained in the seed.

Experimental Section

Methyl methacrylate (MMA) and butyl acrylate (BuA) were cleaned with a 5% NaOH solution, then distilled under nitrogen, and stored at −18 °C until use. Acrylic acid (AA) was used as received. Potassium persulfate (KPS), sodium bicarbonate ($NaHCO_3$), and sodium dodecyl sulfate (SDS) were of analytical grade and used as received. SDS was applied as a reference surfactant. The surfmer (sodium 10-(3-methylbut-3-enyl)oxy decylsulfonate, PF186, Figure 1) was synthesized as described in ref 8. The purity of the surfmer was superior to 98%, and its cmc = 2 g/L. Seeded semicontinuous polymerizations were carried out in a jacketed glass reactor using the recipe given in Table 1. Two separate feeds were used. The first was a mixture of the neat monomers and the second an aqueous solution of emulsifier, buffer, and initiator. The feed flow rates were computer-controlled based on the weight of the storage bottles. After the feeding period of 4 h, the system was left to react for another hour. Samples were taken during the process, the polymerization short-stopped with hydroquinone, and the conversion of the main monomers and surfmer measured. The conversion of the main monomers was determined by gravimetry. Fractional weight-average conversion was defined as the weight of the polymer formed divided by the weight of the monomer fed until that time. Surfmer conversion was determined by two-phase titration of the serum separated by serum replacement.[10] Particle size was determined by dynamic light scattering.

Results and Discussion

Figure 2 presents the evolution of the monomer and surfmer conversions in run 1. The evolution of the monomer conversion in run 2 (using SDS as emulsifier) is also included. Figure 3 presents the evolution of the number of particles, Np, in runs 1 and 2. Figure 2 shows that in the first part of the reaction monomer conversion

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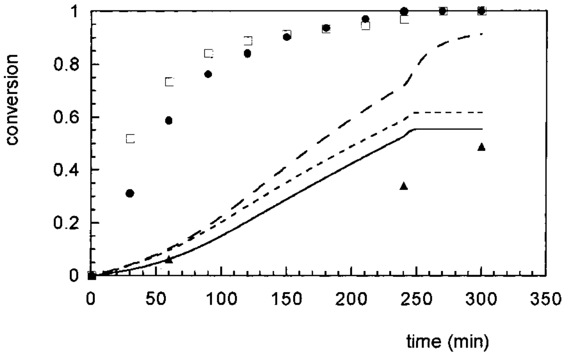

Figure 2. Evolution of monomer and surfmer conversions in runs 1 and 2. Legend: (●) monomer conversion in run 1(PF186); (□) monomer conversion in run 2 (SDS); (▲) surfmer conversion in run 1; (— — —) model 1; (- - -) model 2; (—) model 3.

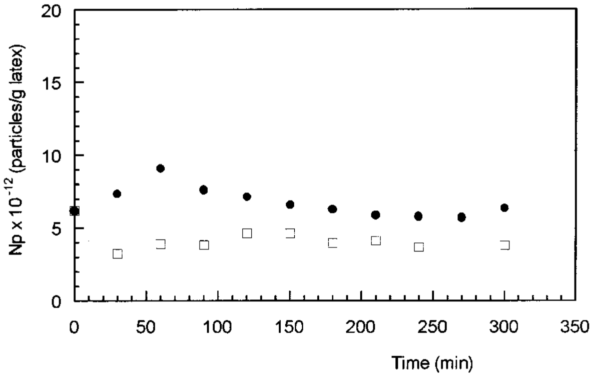

Figure 3. Effect of the type of emulsifier on the number of polymer particles. Legend: (●) PF186; (□) SDS.

was higher when the nonreactive emulsifier was used. The significance of this difference is open to discussion as traces of oxygen often cause changes in the conversion at the beginning of the polymerization.[11] In any case, this difference is not due to a higher number of polymer particles in run 2 because Np was larger in the case of using the surfmer (Figure 3). Figure 2 also shows that only a relatively modest amount of surfmer copolymerized with the monomers. This might be due to its high water solubility (cmc = 2 g/L). This hypothesis is supported by the results reported by Schoonbrood et al.[12] for the batch emulsion copolymerization of styrene with two surfmers based on maleic acid (dodecylsodium sulfopropyl maleate, M12, cmc = 0.5 g/L, and tetradecylsodium sulfopropyl maleate, M14, cmc = 0.12 g/L). They found that M14 copolymerized fast with styrene whereas the more water-soluble M12 presented a significantly lower conversion. On the other hand, PF186 showed a lower incorporation than M12 and M14 even though the reactivity ratios are in the same range. The difference was due to the higher water solubility of PF186. Nevertheless, as desired, incorporation of the present surfmer occurred toward the end of the process, and hence the fraction of the surfmer chemically bound to the polymer material did not become buried. Higher incorporation could be achieved by increasing the length of the hydrophobic part of the surfmer.

Figure 2 presents a comparison between the experimental surfmer conversion and that predicted by integrating the material balance for the surfmer assuming that the reaction mixture was completely homogeneous and using the reactivity ratios calculated for isobutylene (model 1). The time evolution of the product $\tilde{n}$Np ($\tilde{n}$ being the average number of radicals per particle and Np the total number of particles), which is needed to carry out the integration, was estimated from the evolution of the monomer conversion with $kp_{MMA} = 720$ L/(mol s)[13] and $kp_{BuA} = 33\,700$ L/(mol s).[13] In this calculation, it was assumed that the contribution to gravimetric conversion of both surfmer and acrylic acid was negligible. Favresse and Laschewsky[8] reported that PF186 hardly homopolymerizes. Aqueous "solutions" containing up to 50 wt % of surfmer initiated with KPS yielded only 5–6% conversion after 24 h. Therefore, for the calculation of surfmer conversion, a low propagation rate constant was used ($kp_{isobutylene} = 0.1$ L/(mol s)). It can be seen that the surfmer conversion predicted by model 1 was significantly higher than that observed experimentally. It might be argued that the experimental conversion was underestimated because the anionic surface-active oligomers resulting from the initiator were also accounted for as unreacted surfmer during the two-phase titration. However, calculations carried out in a rather nonfavorable scenario (using a large rate constant for initiator decomposition, $k_d = 10^{-4}$ s^{-1}, and assuming that as many as the 20% of the radicals produced formed surface-active oligoradicals) show that at $t = 240$ min surfmer conversion would be underestimated by only a 4%. This is well below to what is needed to reconcile the predicted and the measured surfmer conversions.

Model 1 might overestimate surfmer conversion because it assumed that the reaction mixture was homogeneous. Actually, the surfmer is not homogeneously distributed throughout the particle, but it is located in the outer shell of the polymer particle. To gain some insight into the effect of this limited polymerization region, model 2 was developed assuming that the shell accounts for a 20% of the volume of the particle (a 6 nm thick shell in a particle 172 nm in diameter). Copolymerization of the surfmer and the monomers occurs in the shell whereas only copolymerization of the monomers takes place in the core. The reactivity ratios used in this model were the same as in model 1. Figure 2 shows that the surfmer conversions predicted by model 2 are lower than those obtained with model 1 and agree better with the experimental observations.

A further improvement can be achieved by considering also the partitioning of the surfmer between polymer particles and aqueous phase (model 3). This partitioning is ruled by the adsorption isotherm, which is unknown and likely varied during the process because the characteristics of the surface of the particles varied along the reaction as a result of the incorporation of the acrylic acid and the covalently bound surfmer. As a first approximation, the parameters of the adsorption isotherm of SDS on clean styrene/butyl acrylate polymer particles were used[14] ($k = 244$ L/mol; $a_s = 2.56 \times 10^9$ cm^2/mol). These values probably overestimated the amount of surfmer adsorbed on the polymer particles. Figure 2 shows that the agreement between experimental results and model predictions was further improved.

The results presented above suggest that the localization of the surfmer polymerization in the outer shell of the polymer particles, as well as the partitioning of the surfmer between the particles and the aqueous phase, has a critical influence on the surfmer incorporation. The net result is a reduced incorporation. This indicates that a surfmer with the same reactive group but lower cmc would perform better. Alternatively, a surfmer with a different reactive group (lower $r_{\mathrm{comonomer}}$) and the same cmc could be used. These results further stress that the guide given by Shoonbrood and Asua[7] for the choice of the reactive groups is just a rough estimation.

Figure 2 shows that, on a weight basis, the surfmer stabilized the polymer particles more efficiently than the SDS. This difference is even more acute on molar basis as the molecular weight of the surfmer is higher than that of the SDS ($M_{\mathrm{PF186}} = 328.5$ vs $M_{\mathrm{SDS}} = 288.4$). The mechanical stability of the final latexes was assessed by subjecting them to high shear (14 000 rpm). It was found that the latex obtained with the surfmer was stable for the duration of the test (15 min). The test using the latex produced with SDS could not be completed as extensive foaming occurred after 6 min. On the other hand, the adhesivity of the film formed from the latex obtained with surfmer PF186 was found to be better (higher resistance to peel) than that of the film formed with the latex obtained with SDS.

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