Kinetics of Electrosterically Stabilized Miniemulsion Polymerization

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ABSTRACT: Alkali-soluble resins (ASRs) are widely used as electrosteric stabilizers as they incorporate advantages in the end-use properties of the waterborne dispersed polymers. The kinetics of the miniemulsion polymerization stabilized with ASRs was studied under industrial-like conditions, using redox initiator systems yielding widely different radicals. It was found that the hairy layer of alkali-soluble resin around the polymer particle reduced the entry rate of hydrophobic radicals formed in the aqueous phase, presumably due to diffusional limitations and/or to the formation of nonreactive tertiary radicals in the ASR backbone by hydrogen abstraction. The entry of anionic radicals formed in the aqueous phase was additionally hindered by the electrostatic repulsion, drastically reducing the efficiency of these radicals to initiate the polymerization.

Introduction

Surfactants play a crucial role in all aspects of the production, storage, and use of emulsion polymers. However, surfactants increase the water sensitivity of the final coating and affect gloss and adhesive properties. In addition, surfactants often fail to adequately stabilize the latex when applied at high speed or when mixed with other colloidal systems (e.g., pigments). The reason for the poor performance is that because of the weak hydrophobic interaction between the surfactant and polymer phase, the surfactant easily desorbs from the particle surface.

Polymeric surfactants overcome most of these limitations because they strongly adsorb on the polymer particles. Alkali-soluble resins (ASRs) are a special type of polymeric surfactants. They are random copolymers of hydrophobic monomers (e.g., styrene (S), methyl methacrylate (MMA), butyl methacrylate (BA)) and monomers containing carboxylic acid groups (e.g., acrylic acid (AA) and methacrylic acid (MAA)). They act as electrosteric stabilizers as they are used at a pH higher than the pK_a of the carboxylic acid group. The incorporation of ASRs brings many advantages, such as more Newtonian rheological behavior, excellent freeze−thaw and shear stability, and good pigment dispersion. In latexes for waterborne printing inks, they provide good wetting behavior, easy printing machine cleaning, and good rewetting characteristics.

Emulsion polymerization stabilized with ASRs has not been deeply investigated, and in some cases conflicting results have been reported. Lee and Kim[1] studied the emulsion polymerization of styrene stabilized with a poly(styrene−α-methylstyrene−acrylic acid) alkali-soluble random copolymer, reporting that the polymerization rate per particle of the system stabilized with ASRs was lower than that when using a conventional anionic emulsifier. In addition, although an increase of the number of particles was observed, the rate of polymerization decreased by increasing ASR concentration. Moreover, the rate of polymerization decreased by increasing the neutralization degree of the ASR. These results were attributed to the formation of a negatively charged hairy ASR layer around the particle, which decreased the rate of radical entry.

Kato et al.[2,3] reported that the emulsion polymerization of styrene stabilized with an MMA−MAA alkali-soluble resin followed a kinetics similar to that characteristic of conventional emulsifiers. Both the number of polymer particles and the rate of polymerization were proportional to the 0.6 power of the ASR concentration and to the 0.4 power of the initial initiator concentration. In addition, they were independent of the initial monomer concentration. On the other hand, the rate of polymerization and N_p slightly depended on the ASR molar mass having a maximum value when the molar mass was in the range of 5000−10000 g/mol. R_p and N_p decreased with the content of the MAA in the ASR. The polymerization rate per particle seemed to increase with MAA content.

The performance of a polymeric emulsifier [poly(dodecyl acrylate-*co*-acrylic), sodium salt, PDA] in emulsion polymerization of styrene was compared with that of a conventional emulsifier of similar structure (sodium dodecyl glutarate, SDG). Both water-soluble ($K_2S_2O_8$, KPS) and oil-soluble initiators (AIBN) were used. Bimodal PSDs were obtained with PDA/$K_2S_2O_8$, PDA/AIBN, and SDG/AIBN, which was interpreted as an indication that polymerization occurred in both PDA micelles and monomer droplets.[4] Emulsion polymerizations of S, MMA, and BA using a poly(styrene−acrylic acid) ASR were compared with those using sodium lauryl sulfate.[5] Large-particle unstable latexes were obtained for BA. For both S and MMA, the average number of radicals per particle was smaller when the ASR was used. Interestingly, the difference was only apparent for conversions greater than 40%.

Reduction of both radical entry and radical exit rate coefficients in electrosterically stabilized latexes has been reported.[6] The reduction was more acute at neutral pH conditions. It has been proposed that this reduction was due to hydrogen abstraction from the ASR in the hairy layer, leading to a tertiary radical, which is slow to propagate but quick to terminate.[7,8]

Compared to standard nonpolymeric emulsifiers, ASRs are commonly used at high levels (>20% based on dry polymer) in emulsion polymerization. This is to provide both good colloidal stability and good product performance, e.g., good rewetting characteristics. do Amaral and Asua[9] reported that high solids content latexes can be obtained by miniemulsion polymerization using a substantially lower amount of ASR than the conventional emulsion polymerization. The latexes obtained through this process presented rewetting properties similar to those obtained through the standard process. However, the kinetics of the process was not studied, which is a serious drawback to develop knowledge-based strategies for the efficient production of high-quality materials.[10] In this work, the kinetics of the miniemulsion polymerization stabilized with ASR was investigated.

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Table 1. Summary of the Miniemulsion Polymerizations

run	BA/MMA (w/w)	surfactant (phm)	initiator (phm)	hexadecane (phm)	solids content (wt %)
1	40/60	ASR (8)	KPS (1.0) NaBs (1.4)	2	20
2	40/60	ASR (8)	TBHP (1.0) AsA (1.4)	2	20
3	40/60	SLS (0.35)	KPS (1.0) NaBs (1.4)	2	20
4	40/60	SLS (0.35)	TBHP (1.0) AsA (1.4)	2	20
5	40/60	SLS (0.35)	KPS (1.0) NaBs (1.4)	2	20
6	40/60	SLS (0.35)	TBHP (1.0) AsA (1.4)	2	20
7[a]	40/60	SLS (0.35)	KPS (1.0) NaBs (1.4)	2	20
8[a]	40/60	SLS (0.35)	TBHP (1.0) AsA (1.4)	2	20
9	40/60	ASR (8)	KPS (1.0) NaBs (1.4)	2	20
10	40/60	ASR (5)	TBHP (0.85) AsA (1.8)	2	50
11	40/60	ASR (8)	TBHP (0.85) AsA (1.8)	2	50
12	40/60	ASR (1.8)	KPS (1.25) NaBs (0.9)	2	50
13	40/60	ASR (8)	KPS (1.25) NaBs (0.9)	2	50

[a] NH_4OH was added to keep the system at basic pH during the whole polymerization.

Experimental Section

Methyl methacrylate, butyl acrylate, hexadecane (HD), and sodium lauryl sulfate (SLS) were purchased from Aldrich and were used as received. The components of the redox initiator systems *tert*-butyl hydroperoxide (TBHP), potassium persulfate (KPS), ascorbic acid (AsA), and sodium bisulfite (NaBs) were purchased from Aldrich and used as received. The ASR (Morez 101E, MZ101E) was supplied by Rohm and Haas and used throughout the entire investigation. It had a molar mass of 6000 g/mol and an acid number of 205, which corresponds to about 17 acrylic acid groups per chain. The acid number of the ASR is defined as the number of grams of KOH needed to fully neutralize all of the AA units present in 1 kg of ASR. Aqueous solutions of the ASR were prepared by placing the solid ASR in a glass reactor and then adding water and a solution of 25 wt % ammonium hydroxide to neutralize and dissolve the ASR. This mixture was held under agitation at 70 °C until visual dissolution had occurred. Enough ammonium hydroxide was added to each ASR solution to ensure a pH greater than 8.0 to guarantee complete neutralization.

Miniemulsions were prepared by mixing the organic phase composed of the monomers and the hexadecane (costabilizer) with the ASR aqueous solution and forming a coarse dispersion by stirring magnetically for 10 min. Immediately afterward, the dispersion was sonicated while being cooled in an ice bath. Sonication was carried out with a Branson sonifier 450. The output power was set to 8, the duty cycle was set to 90%, and the sonication time was 5 min. Both low solids (20 wt %) and high solids (50 wt %) miniemulsions were investigated. Table 1 summarizes the formulations used. All miniemulsion polymerizations were carried out in a 1 L glass jacket reactor at 70 °C under 220 rpm of stirring. In runs 1−4, the reactor was charged with the miniemulsion and the reductant, and the oxidant was added semicontinuously for 6 h. In runs 5−9 all the formulation was included in the initial charge. Runs 10−14 were 50 wt % solids content semicontinuous miniemulsion polymerizations in which the concentration of ASR was varied. The initial charge of the reactor consisted of a miniemulsion of BA and hexadecane containing all the ASR and the reductant. MMA and an aqueous solution of the oxidant were added semicontinuously for 6 h. The reactor was purged with nitrogen during the whole process. Samples were withdrawn during the polymerization and inhibited with a 1 wt % hydroquinone solution to ensure stoppage of the polymerization. Conversion was determined gravimetrically. Droplet and particle size measurements were carried out using a Coulter N4 plus light scattering instrument, and all samples were prepared by placing a single drop of sample in the vial and then filling the vial with DDI water. Each measurement was taken as the average of three replicates.

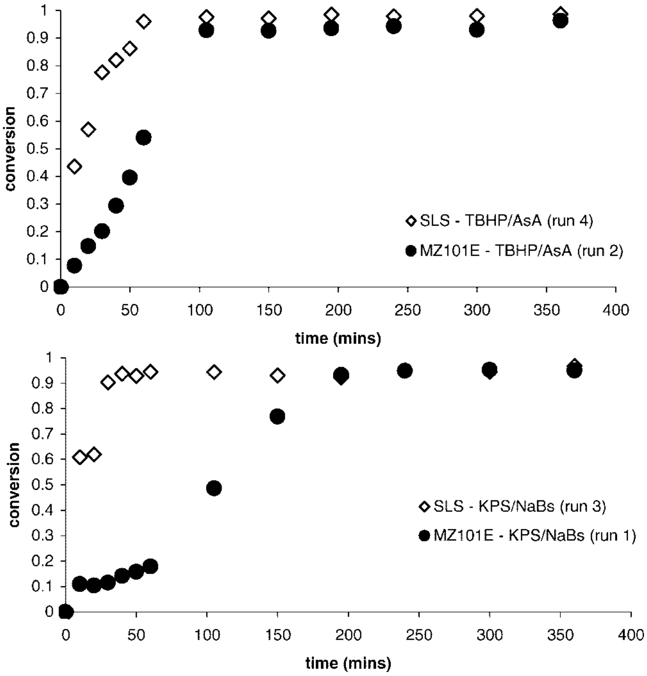

Figure 1. Effect of the initiator system on monomer conversion in miniemulsion polymerization using ASR and SLS (runs 1−4).

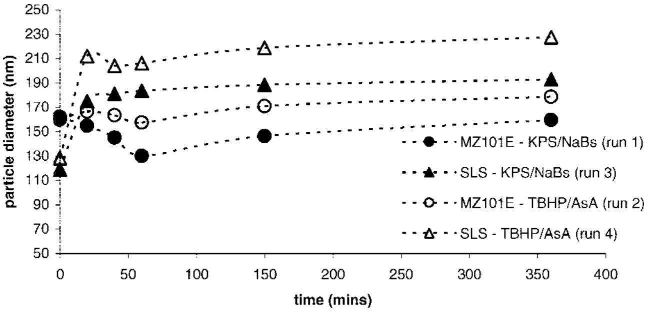

Figure 2. Effect of the initiator system on particle size in miniemulsion polymerization using ASR and SLS (runs 1−4).

Results and Discussion

Figures 1 and 2 present the evolution of monomer conversion and particle diameter, respectively, in runs 1−4. Runs 1 and 3 were carried out using KPS/NaBs, which produces negatively charged water-soluble radicals. In runs 2 and 4, TBHP/AsA was used. TBHP partitions between the oil and the water phase. At 20 °C, the partition coefficient octane/water is $P_{ow} = 5$. Therefore, if thermodynamic equilibrium is reached and if a polymer particle behaves as a pure oil phase, the concentration of TBHP in the oil phase will be 5 times that in the aqueous phase. On the other hand, ascorbic acid is soluble in the aqueous phase. Therefore, two sources of radicals are possible: thermal decomposition of the TBHP in the monomer droplets and redox reaction between TBHP and AsAc in the aqueous phase. At 70 °C, the thermal decomposition rate coefficient of the TBHP is about 10^{-10} s^{-1}. For the sake of comparison, at 70 °C, the

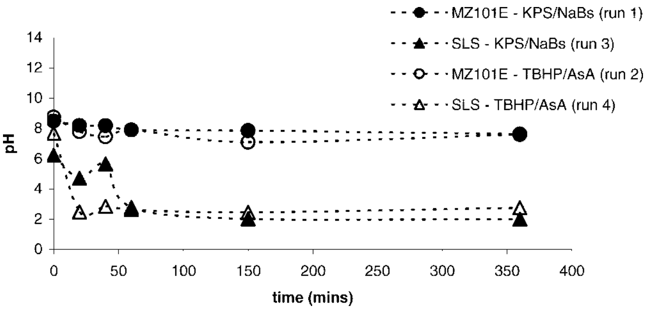

Figure 3. Evolution of the pH in runs 1−4.

thermal decomposition rate coefficient of AIBN is 3.2×10^{-5} s^{-1}, which is more than 5 orders of magnitude faster. Keeping in mind that AIBN is not a particularly fast initiator; this means that the rate of radical production by thermal decomposition of TBHP at 70 °C is negligible. Therefore, the system TBHP/AsAc yields noncharged hydrophobic radicals generated in the aqueous phase. It is worth pointing out that the sulfate ion radicals formed with KPS/NaBs should react with monomer in the aqueous phase to become hydrophobic enough to be able to enter into the monomer droplets and polymer particles.[11−13] On the other hand, the *tert*-butoxy radicals produced by TBHP/AsA are hydrophobic enough to enter directly into the monomer droplets and polymer particles.[14]

Figure 1 shows that the charged persulfate radicals resulted in a much slower polymerization rate compared to the noncharged *tert*-butoxy radicals, even though the number of particles was higher for the KPS/NaBs system (Figure 2). This implies that the average number of radicals per particle was much higher in the miniemulsion polymerized with TBHP/AsA. At first sight this suggests that, as in the case of conventional emulsion polymerization,[1] the negatively charged ASR lowered the rate of entry into the particles of the anionic oligoradicals formed from KPS/NaBs. However, one may argue that the rate of formation of radicals was higher for TBHP/AcA. Therefore, miniemulsion polymerizations using these initiator systems and a conventional emulsifier (SLS) were carried out (runs 3 and 4). Figure 1 shows that, for both initiator systems, the polymerization rate decreased when ASR was used, even though a higher number of particles was produced with the ASR. In addition, the decrease was stronger for KPS/NaBs. Figure 1 also shows that when SLS was used, the polymerization rate was higher for KPS/NaBs than for TBHP/AsA, which was in agreement with the higher number of particles produced with KPS/NaBs. This indicates that the results in Figure 1 were not due to a slow rate of radicals by KPS/NaBs. However, the evolution of pH during these experiments (Figure 3) did not allow a firm conclusion to be reached, because the pH in the SLS experiments was acidic during most of the process (pH ≈ 2) whereas it was basic (pH ≈ 8) when ASR was used. It was therefore possible that the pH affected the radical generation rate. Actually, when using KPS as a thermal initiator, the radical generation rate decreases as pH increases.[15] However, when using KPS as a redox pair with NaBs, the effect may be different.

To check this, runs 5−8 were carried out in batch using SLS as an emulsifier. In runs 7 and 8, NH_4OH was added to ensure a basic pH during the polymerization. Runs 5 and 7 used KPS/NaBs and runs 6 and 8 TBHP/AsA. Figure 4 shows the effect of the pH on the conversion. The initial and final pH values for the experiments are also shown. It can be seen that the pH had no effect on the TBHP/AsA experiments. However, for the KPS/NaBs experiments, the polymerization rate was low in the basic environment. This indicates that the slower KPS/NaBs polymerization rate in run 1 was at least in part due to a basic pH.

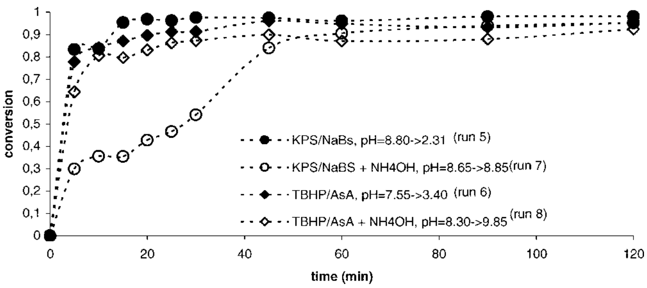

Figure 4. Effect of the pH on monomer conversion in miniemulsion polymerizations stabilized with SLS and initiated with KPS/NaBs and TBHP/AsA.

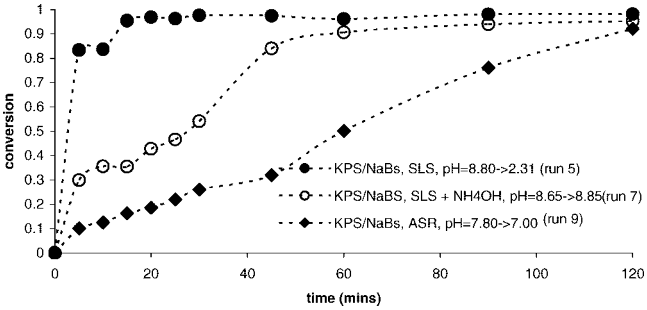

Figure 5. Effect of pH and emulsifier type on monomer conversion in miniemulsion polymerizations initiated with KPS/NaBs (runs 5, 7, and 9).

Comparison of the evolution of monomer conversion in runs 5, 7, and 9 (Figure 5) allows the effect of the pH on radical production and the effect of the ASR on the entry rate of radicals generated by KPS/NaBs to be distinguished. Comparison of runs 5 and 7 shows that a basic pH resulted in a decrease in polymerization rate due to the lower rate of generation of radicals for KPS/NaBs. In addition, the presence of ASR (run 9) caused a further decrease of the polymerization rate. A consequence of practical importance is that KPS/NaBs has a very low efficiency in miniemulsion polymerization stabilized with ASR.

In polymerization in dispersed systems, the efficient use of the radicals produced in the aqueous phase depends to a large extent on the reactions occurring in the aqueous phase and hence on the volume of the aqueous phase relative to the volume of the polymer particles. Therefore, one wonders whether the effects observed at low solids content also occurred at the high solids content typical of commercial processes where radical entry is easier and semicontinuous processes are used.

Experiments 10−13 analyzed the effect of the charge of the radicals produced in the aqueous phase (*tert*-butoxy radicals from TBHP/AsAc and charged persulfate radicals from KPS/NaBs) in high solids miniemulsion polymerization. Figure 6 shows the conversion and particle size achieved with TBHP/AsAc and KPS/NaBs. For each level of ASR, long inhibition periods were observed for KPS/NaBs. In addition, Figure 6 shows that, for KPS/NaBs, the polymerization rate was higher for the lower ASR concentration, even though the number of particles was lower by a factor of 2.5 (estimated using the average particle size and the monomer conversion). On the other hand, the estimated ASR coverage of the particles in run 13 (8 phm of ASR) was 1.3 times that in run 12 (5 phm of ASR), which was enough to overcome the factor of 2.5 in the number of particles.

The results obtained with TBHP/AsA showed a completely different behavior as the polymerization rate increased with ASR concentration. In this case, the number of particles in run 11

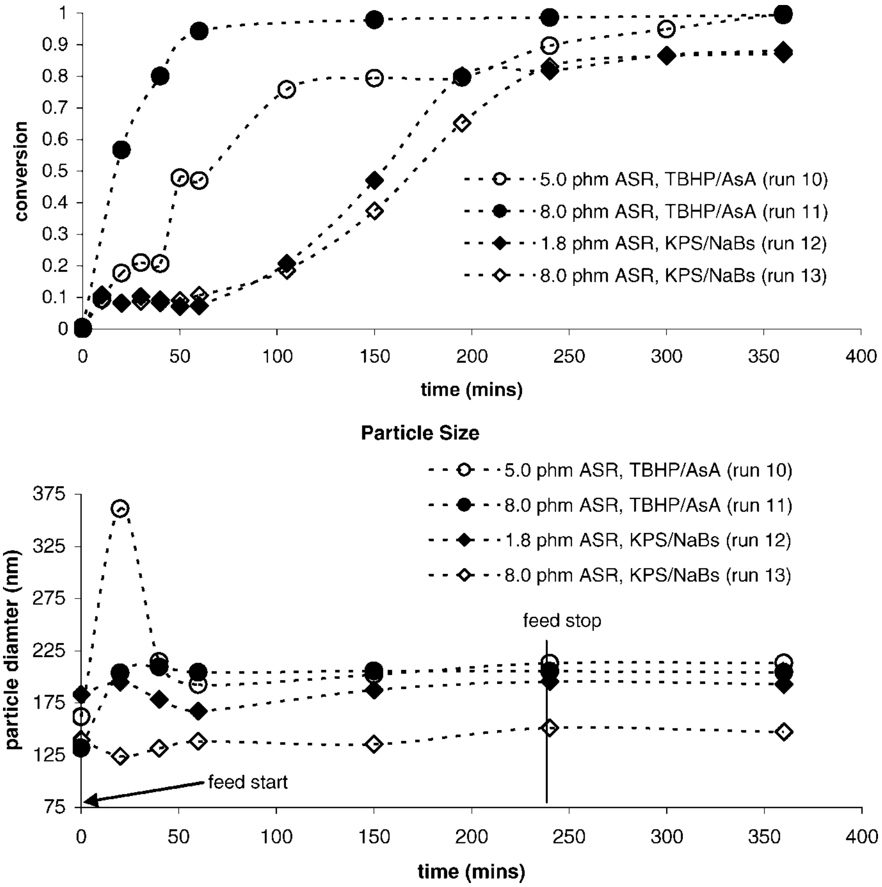

Figure 6. Conversion (upper) and particle sizes (lower) for runs 10−13.

(8 phm of ASR) was about twice that in run 10 (5 phm of ASR), and the particle coverage in run 11 was 0.8 times that in run 10. In addition, the ratio of polymerization rates was $R_{p,8phm}/R_{p,5phm} = 2.2$. This value was close to that of the ratio of the number of particles; namely, the average number of radicals per particle was similar in both experiments, indicating a relatively modest effect of the coverage on the entry of *tert*-butoxy radicals. Comparison with the results obtained with KPS/NaBs shows that the effect on the entry of the charged radicals was stronger. The first obvious reason was the presence of a negative charge on the radicals produced by KPS/NaBs, which would be affected by electrostatic repulsion with the negatively charged ASR. This would be consistent with the effect of the electrostatic repulsion on the rate of entry of anionic radicals that has been described for the seeded emulsion polymerization of styrene initiated with KPS using seeds with different coverages of sodium styrenesulfonate[16] as well as with the effect of the pH on the radical entry rate[6] in electrosterically stabilized latexes.

However, the effect of the formation of midchain radicals by hydrogen abstraction cannot be discarded. TBHP/AsA yields oxygen-centered *tert*-butoxy radicals, which are very efficient in hydrogen abstraction. In addition, they can directly enter into the polymer particles, i.e., without adding any monomer unit. This means that they have to cross the ASR hairy layer and hence have the opportunity of abstracting hydrogens from the ASR backbone. On the other hand, KPS/NaBs yields oxygen-centered sulfate ion radicals that cannot directly enter into the polymer particles. Therefore, in addition to undergoing bimolecular termination, they will react in the aqueous phase with either monomer (giving oxygen-centered radicals which are less efficient in hydrogen abstraction) or ASR (giving tertiary radicals). If the rate of the second process is substantial, radical entry will be reduced. However, the results do not support that for KPS/NaBs the main reason for the slower radical entry rate was the loss of radicals by formation of tertiary radicals by hydrogen abstraction, because the effect would be greater for the *tert*-butoxy radicals produced by TBHP/AsA. Nevertheless, this mechanism cannot be discharged.

Conclusions

In the foregoing, the kinetics of the high solids miniemulsion copolymerization of MMA and BA stabilized with ASR was studied using redox initiators able to give radicals with different characteristics. TBHP/AsAc gives uncharged hydrophobic radicals in the aqueous phase and KPS/NaBs anionic hydrophilic radicals in the aqueous phase. The presence of the hairy layer of alkali-soluble resin around the polymer particle reduced the entry rate of hydrophobic radicals formed in the aqueous phase from TBHP/AsAc, leading to a substantially lower polymerization rate per particle than that obtained with a classical anionic surfactant. This reduction might be due to diffusional limitations and/or to the formation of nonreactive tertiary radicals in the ASR backbone by hydrogen abstraction. For the miniemulsion copolymerization initiated with KPS/NaBs, the use of ASR also led to a lower polymerization rate per particle. However, in this case, two additional effects are operative (in addition to those acting on the hydrophobic radicals). First, the effect of the high pH (the pH should be higher than the pK_a of the carboxylic acid groups of the ASR to maximize the stabilization power of the ASR), which lowers the rate of radical generation from KPS/NaBs. Second, the electrostatic repulsion between the anionic entering radical and the electrosteric ASR has an effect. Comparison between the results obtained with KPS/NaBs and those obtained with TBHP/AsA suggested that these additional effects were the main cause for reducing the entry rate of radicals generated from KPS/NaBs. A consequence of practical importance is that KPS/NaBs has a very low efficiency in miniemulsion polymerization stabilized with ASR.

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