Radical Entry Mechanisms in Alkali-Soluble-Resin-Stabilized Latexes

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ABSTRACT: Alkali-soluble resins (ASRs) are random copolymers that contain both hydrophobic groups and a large number of carboxylic acid groups, which are widely used as the sole stabilizers in the production of waterborne dispersed polymers because they remarkably improve the end-use properties of the latexes. However, they reduce the radical entry rate. In this work, the mechanisms for radical entry in ASR-stabilized systems have been investigated. It has been found that the mechanism responsible for the reduction of the rate of radical entry depends on the type of ASR used (prone or not prone to suffer hydrogen abstraction), the type of radical produced from the initiator (charged or uncharged, oxygen centered or carbon centered), the phase where the radicals are produced (aqueous or oil phase) and the type of monomer (hydrophobic like styrene or more hydrophilic like methyl methacrylate).

Introduction

Emulsion polymers are widely used as film-forming materials for coatings and adhesives. Because lyophobic colloids are thermodynamically unstable, surfactants are used to provide kinetic stability. However, the conventional (anionic or nonionic) surfactants commonly used as stabilizers in emulsion polymerization create many drawbacks in the final application, including poor wetting, low gloss, high water sensitivity, poor adhesion, mechanical and freeze−thaw instability, shear thinning, and poor physical properties of the resulting film. This poor performance is mainly due to surfactant migration because of the weak hydrophobic interaction between surfactant and polymer phase. The use of polymeric surfactants is an effective method for overcoming most of these problems because they strongly adsorb on the polymer particles.

Alkali-soluble resins (ASRs) are a special type of polymeric surfactants that can be classified as hydrophobically modified anionic polyelectrolytes.[1] They are random copolymers of hydrophobic monomers (e.g., styrene (S), methyl methacrylate (MMA), butyl methacrylate (BMA)) and monomers containing carboxylic acid groups (e.g., acrylic (AA) and methacrylic acid (MAA)). ASRs can be manufactured as low-pH latexes. When neutralized, the polymer becomes water soluble, and it acts as an electrosteric stabilizer (if the pH is higher than the pK_a of the carboxylic acid group). ASR-fortified emulsion polymers provide many advantages such as Newtonian-like flow, low foam production, improved adhesion and wetting properties, excellent mechanical and freeze−thaw stability, and good pigment dispersion.[2,3] In latexes for waterborne printing inks, they provide easy printing machine cleaning, good rewet characteristics, and superior ink transfer efficiency.[4]

Emulsion polymerization stabilized with ASR has not been deeply investigated, and in some cases conflicting results have been reported. Kuo and Chen[5] studied the emulsion polymerization of S by using the polymeric emulsifier poly(dodecyl acrylate-*co*-acrylic acid) (PDA) and also the monomeric emulsifier sodium dodecyl glutarate (SDG). Both a water-soluble initiator (potassium persulfate, KPS) and an oil-soluble initiator (2,2′-azobisisobutyronitrile, AIBN) were used. They found that bimodal particle size distributions were formed with PDA/KPS, PDA/AIBN, and SDG/AIBN, which was interpreted to be an indication that polymerization takes place in both monomer droplets and polymeric surfactant aggregates.

Leemans et al.[6] carried out ab initio emulsion polymerizations of MMA using anionic and cationic water-soluble block polyelectrolytes in combination with negatively charged, neutral, and positively charged entering radicals. They found that the combination of the charge of the entering radical and the charge of the block polyelectrolyte strongly affected the rate of emulsion polymerization, suggesting that the diffusion of free radicals was the rate determining step for the radical entry into the polymer particles.

Kato et al. studied the effect of the molecular weight and copolymer composition of the stabilizer on the kinetics of the emulsion polymerization of S stabilized with a poly(methyl methacrylate-*co*-methacrylic acid) ASR. Both the rate of polymerization and the number of particles slightly depended on the ASR molecular weight, showing a maximum when the molecular weight was in the range of 5000−10 000 g/mol and monotonously decreasing with the content of MAA in the copolymer.[7] However, they reported that the kinetics was quite the same as that observed in the emulsion polymerization of S conducted with sodium dodecyl sulfate (SDS) as emulsifier and KPS as initiator.[8]

Lee and Kim[9] reported that the rate of polymerization of S using a poly(styrene/α-methylstyrene/acrylic acid) alkali-soluble random copolymer was lower than that using a conventional anionic emulsifier. Although a decrease in particle size was observed, the rate of polymerization decreased with increasing ASR concentration. Moreover, a significant decrease in the polymerization rate was observed as the neutralization degree of ASR was increased. These results were explained by the formation of a hairy ASR layer around the particle that made the entry of radicals more difficult and by the solubilization ability of ASR, which could influence the monomer concentration inside the particles. Whereas the polydispersity of the polystyrene particles was not affected by the neutralization degree of the ASR, emulsion polymerization of MMA with the same ASR led to latexes in which the polydispersity increased with the neutralization degree of the ASR.[10] This effect was attributed to the contribution of the homogeneous nucleation enhanced by the higher water solubility of MMA. In addition, grafting of polystyrene to ASR during polymerization was observed and probably resulted from chain transfer to ASR.

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The effect of the monomer type on the emulsion polymerization behavior using a poly(styrene/α-methylstyrene/acrylic acid) ASR has been reported by Hwu and Lee.[11−13] They found that large unstable latexes were obtained for butyl acrylate (BA) because of an inadequate adsorption of the ASR onto the BA particles. For both S and MMA, the average number of radicals per particle was smaller than that for the latexes with SDS, but for S, the difference was smaller than that for MMA. Grafting reactions on the ASR backbone were also observed for S and MMA, indicating that abstraction of hydrogen from ASR by the growing radical probably occurred. The grafting ratio of MMA was less than that of S.[11] Retarding effects have also been reported for emulsion polymerization of BMA.[12] The comparison of several acrylic monomers such as MMA, BMA, and ethyl methacrylate (EMA) shows that the particle size and average radical number per particle were inversely proportional to the hydrophilicity of the monomer. In addition, monomers with lower water solubility favored the grafting reaction onto the ASR.[13]

Reduction in both radical entry and radical exit rate has been reported for the S-seeded emulsion polymerization in electrosterically stabilized seed latexes.[14] The reduction was more acute at neutral pH where significant secondary nucleation was also observed. It has been proposed that the reduction in the radical exit rate is mainly due to a reduction in the diffusion of the monomeric radicals through the polymeric hairy layer.[15] The reduction in the radical entry rate was also attributed to hydrogen abstraction from the AA units of the polymeric hairy layer leading to a tertiary radical, which was thought to be slow to propagate but quick to terminate.[16]

ASRs can be used in both emulsion and miniemulsion polymerization. Compared with standard nonpolymeric emulsifiers, ASRs are commonly used at high levels (>20% on the basis of dry polymer) in emulsion polymerization. Amaral and Asua[17] 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 main difference between conventional emulsion and miniemulsion polymerization is due to the different particle nucleation mechanisms, micellar and homogeneous for conventional emulsion and droplet nucleation for miniemulsion polymerization (although in some cases, homogeneous nucleation cannot be avoided.) Once the particles have been formed, the radical entry and exit mechanisms are expected to be similar in both processes.

The kinetics of miniemulsion polymerization stabilized with ASR has been recently investigated.[18] High-solids miniemulsion copolymerizations of BA and MMA stabilized by a commercial ASR (styrene/α-methyl styrene/acrylic acid) were carried out using two different redox initiators that lead to radicals with different characteristics (anionic sulfate radicals and nonionic *tert*-butoxy radicals). A reduction in the polymerization rate compared with conventional miniemulsion polymerization was reported for both cases, but the effect on the entry of charged radicals was stronger. However, the relative significance of diffusion, charge repulsion, and hydrogen abstraction could not be unambiguously determined.

Considering that the ASR is adsorbed on the particle surface, forming a polymeric hairy layer that contains a high density of negative charges, the mechanisms proposed to justify the reduction of the radical entry are as follows: (1) The hairy layer offers an additional resistance to the diffusion of the entering oligoradicals.[6] (2) The entering anionic oligoradicals are repelled by the negative charges in the hairy layer.[9] (3) The hairy layer acts as a radical sink because the entering oligoradical abstract hydrogens from the ASR in the hairy layer leading to a tertiary radical.[16] Mechanism 1 may act on any type of entering oligomer, mechanism 2 can affect only charged oligoradicals, and mechanism 3 would only be operative for ASRs containing abstractable hydrogens.

Table 1. Formulation Used in the Synthesis of ASRs

component	total charge (g)
MMA	86.70
BMA	112.20
MAA or AA	56.10
CTA (1-octanethiol)	7.65
buffer ($NaHCO_3$)	1.88
emulsifier (SLS)	0.64
initiator (APS)	2.40
water	582.43
total	850

This work is an attempt to clarify the relative importance of contributions of the three mechanisms to the decrease in the radical entry rate. To achieve this goal, initiators producing different radicals and ASRs either prone or not prone to suffering hydrogen abstraction were used. *tert*-Butyl hydroperoxide/ascorbic acid (TBHP/AsAc), ammonium persulfate (APS), and AIBN were used as initiators. We synthesized the ASR that was prone to suffering hydrogen abstraction (ASR_{AA}) by copolymerizing MMA, BMA, and AA. We synthesized the ASR that did not contain easily abstractable hydrogens (ASR_{MAA}) by copolymerizing BMA and MAA. The effect of the type of ASR on the polymerization rate per particle achieved with TBHP/AsAc gives an indication of the relative effect of the hydrogen abstraction on entry rate as compared with diffusional limitations. This initiator yields oxygen-centered radicals that are very efficient at abstracting hydrogen; therefore, a strong effect is expected. However, the effect of the type of ASR on the polymerization rate per particle achieved with APS (which also gives oxygen-centered radicals) will give an indication of the relative effect of the hydrogen abstraction on entry rate as compared with electrostatic repulsion and diffusional limitations. The effect of the ASR type on the polymerization rate per particle when using AIBN will give information about both radical entry and exit because desorption and reentry of initiator radicals from droplets and particles is the key mechanism that controls the kinetics of miniemulsion polymerization and particle growth in emulsion polymerization. For these systems, the contribution of the fraction of the initiator dissolved in the aqueous phase is minor.[19]

Experimental Section

Materials. Technical grade monomers S (Quimidroga), MMA (Quimidroga), BMA (Aldrich), MAA (Aldrich), and AA (Aldrich) were used as received. Sodium lauryl sulfate (SLS, Aldrich), sodium bicarbonate ($NaHCO_3$, Riedel-de Haën), and 1-octanethiol (Aldrich) were used as the anionic surfactant, buffer, and chain transfer agent (CTA), respectively, in the synthesis of the ASRs. TBHP and AsAc were purchased from Aldrich and used as components of the redox initiator system. APS and 2,2-azobisisobutyronitrile (AIBN) were purchased from Aldrich and used as thermal initiators. Hexadecane (HD) was purchased from Aldrich and was used as the hydrophobe in the miniemulsion polymerizations. Double-deionized water was used throughout the work.

Synthesis of the Alkali-Soluble Resins. Semicontinuous emulsion polymerizations were carried out in a 1 L jacketed glass reactor at 70 °C and 200 rpm using the formulation given in Table 1. All of the water, surfactant (SLS), and buffer ($NaHCO_3$) were initially placed in the reactor. When the reaction temperature was reached under a nitrogen atmosphere, the initiator was added, and the mixture of the monomers and CTA was then continuously fed into the reactor at a feed rate of 0.9 g/min for 5 h. After that, the reactor was maintained for 1 h in batch. Two different ASRs were synthesized, varying the type of acid monomer: MAA denoted as ASR_{MAA}, and AA denoted as ASR_{AA}.

The molecular weight of the two resins was measured at the end of the reaction by gel permeation chromatography (GPC, Waters)

Table 2. Characteristics of the ASRs

ASR type	acid number	weight-average molecular weight[a]
ASR_{AA}	171	9200
ASR_{MAA}	145	11 300

[a] Measured using polystyrene standards.

Table 3. Miniemulsion Polymerizations with APS as Initiator

component	initial charge (g)	initiator solution shot (g)
S or MMA	120	
HD	2.40	
ASR_{AA} or ASR_{MAA}	9.60	
APS		1.20
water	256.80	10
total	388.80	11.20

Table 4. Miniemulsion Polymerizations with TBHP/AsAc as Initiator

component	initial charge (g)	stream 1 (g)	stream 2 (g)
S or MMA	120		
HD	2.40		
ASR_{AA} or ASR_{MAA}	9.60		
TBHP			1.02
AsAc		2.16	
water	178	42.84	43.98
total	310	45	45

Table 5. Miniemulsion Polymerizations with AIBN as Initiator

component	initial charge (g)	initiator solution shot(g)
S	110	10
HD	2.40	
ASR_{AA} or ASR_{MAA}	9.60	
AIBN		1.20
water	266.80	
total	388.80	11.20

calibrated with polystyrene standards at ambient temperature. The acid number defined as the milligrams of potassium hydroxide needed to neutralize 1 g of resin was determined by conductometric titration. The characteristics of the two ASRs synthesized are given in Table 2. The ASRs were dissolved by neutralization with ammonia (pH 10) so that they could be used as surfactants.

Miniemulsion Polymerizations. We prepared miniemulsions by mixing the organic phase composed of the monomers (S or MMA) and the costabilizer (HD) with the ASR aqueous solution and forming a dispersion by magnetic stirring for 10 min. Immediately afterward, the dispersion was sonicated in an ice bath. Sonication was carried out with a Branson sonifier 450. The amplitude was set to 80%, and the sonication time was 20 min. To avoid overheating, sonication was stopped every 54 s, and the sample was kept at rest for 6 s.

Tables 3, 4, and 5 show the formulations used for the three types of initiators used, APS, TBHP/AsAc redox system, and AIBN, respectively. The reactions were carried out in batch over 5 h. When thermal initiators were used (APS, AIBN) the initiator solution was added as a shot at the beginning of the reaction. When the redox system TBHP/AsAc was used, the initiator was added to the reactor in separate streams at a feed rate of 0.1875 g/min during 4 h. Then, the system was maintained for an additional 1 h in batch.

All miniemulsion polymerizations were carried out in a 0.5 L glass jacketed reactor at 60 °C and 220 rpm. The solids content was 30% and the initial pH was set equal to 10 by the addition of ammonia. Samples were withdrawn during the polymerization and inhibited with a 1 wt %/wt hydroquinone solution to stop the polymerization. Conversion was gravimetrically determined. Particle size measurements were carried out using a Coulter N4 plus light scattering instrument. Each measurement was taken as the average of three replicates.

Table 6. Radicals from Initiators

initiator	radical
APS	$SO_4^{\bullet -}$
TBHP/AsAc	$(CH_3)_3CO^{\bullet}$
AIBN	$CN(CH_3)_2C^{\bullet}$

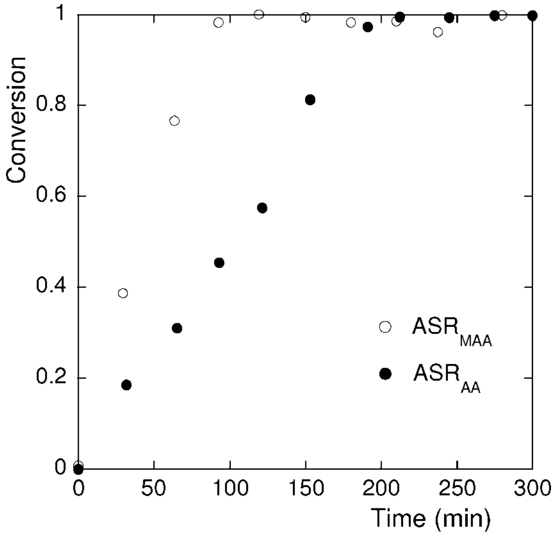

Figure 1. Effect of the ASR type on conversion versus reaction time in miniemulsion polymerization of S using TBHP/AsAc.

Results and Discussion

In this work, three types of initiators are used. Two of them, TBHP/AsAc and APS generate radicals in the aqueous phase. It is worth pointing out that TBHP partitions between the oil and the water phase. At 20 °C, the partition coefficient octane/water is[20] Pow = 5. Therefore, if thermodynamic equilibrium is reached and if a polymer particle behaves as a pure oil phase, then the concentration of TBHP in the oil phase will be 5 times that of the aqueous phase. However, AsAc 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 60 °C, the thermal decomposition rate coefficient of the TBHP[21] is about 5×10^{-11} s^{-1}. For the sake of comparison, at 60 °C, the thermal decomposition rate coefficient of AIBN[21] is 9×10^{-6} s^{-1}, which is more than five 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 60 °C is negligible. Therefore, the system TBHP/AsAc yields noncharged oxygen-centered *tert*-butoxy radicals generated in the aqueous phase. These radicals are hydrophobic enough to enter directly into the monomer droplets and polymer particles. However, APS decomposition leads to water-soluble oxygen-centered anionic radicals that should react with monomer in the aqueous phase to become hydrophobic enough to be able to enter into the monomer droplets and polymer particles. AIBN is an oil-soluble initiator that produces noncharged carbon-centered radicals in the oil phase. Table 6 represents the initiators and free radicals that were used in this work.

Miniemulsion Polymerizations of Styrene with TBHP/AsAc and APS. Four reactions combining the two ASRs synthesized (ASR_{AA} and ASR_{MAA}) and two initiators (TBHP/AsAc, APS) were carried out. Figure 1 presents the effect of the ASR type on the evolution of the monomer conversion in the experiments initiated with TBHP/AsAc. It is worth pointing out that the weight of ASR used in each experiment was the same and that because AA and MAA had different molecular

Table 7. Main Data for Styrene Polymerizations Using TBHP/AsAc

	R_p (g/L s)	d_p (nm)	N_p (particles/L)	R_{pp} (g/particle s)	$\bar{n}$
ASR_{MAA}	0.0561	439	6.5×10^{15}	8.6×10^{-18}	31
ASR_{AA}	0.0255	327	15.6×10^{15}	1.6×10^{-18}	5.7
ASR_{MAA}/ASR_{AA}	2.2	1.3	0.4	5.4	5.4

weights, the ratio between the number of acid groups in ASR_{AA} and ASR_{MAA} was 1.2, namely, ASR_{AA} had a slightly higher content of carboxylic groups. The polymerization rate (R_p) was calculated form the slope of the conversion−time curve. The number of polymer particles (N_p) was determined from the final particle size measured by light scattering. From R_p and N_p, the polymerization rate per particle ($R_{pp} = R_p/N_p$) was calculated. The most relevant data of these reactions are listed in Table 7.

It can be seen that the polymerization rate was higher for the reaction using ASR_{MAA} (Figure 1 and Table 7), even though the number of particles was greater for ASR_{AA} (N_{pMAA}/N_{pAA}= 0.4). Therefore, the polymerization rate per particle was significantly lower for ASR_{AA}, namely, for the ASR that was prone to suffering hydrogen abstraction. This means that under the conditions used in these experiments, the radical entry rate was substantially reduced by the formation of tertiary radicals on the ASR backbone through hydrogen abstraction.

Table 7 shows that the average number of radicals per particle ($\bar{n}$) was well above 0.5, namely, the polymerizations occurred under pseudobulk conditions. Under these circumstances, the polymerization rate is proportional to the square root of the rate of radical entry.[22] Therefore, assuming that the three resistances (diffusion, electrostatic repulsion, and hydrogen abstraction) are in series, the polymerization rate per particle should be inversely proportional to the square root of the overall resistance

$$R_{pp} \propto \left(\frac{1}{R_1 + R_2 + R_3}\right)^{0.5} \tag{1}$$

where R_1 is the resistance to diffusion, R_2 is that of the electrostatic repulsion, and R_3 is that of the hydrogen abstraction.

In the case of TBHP/AsAc, the electrical repulsion did not play any role, and when the ASR_{MAA} was used, hydrogen abstraction was not a significant event. Therefore, the polymerization rates per particle for the two ASRs are as follows

$$(R_{ppMAA})_{TBHP/AsAc} \propto \left(\frac{1}{R_1}\right)^{0.5} \tag{2}$$

$$(R_{ppAA})_{TBHP/AsAc} \propto \left(\frac{1}{R_1 + R_3}\right)^{0.5} \tag{3}$$

The ratio of polymerization rate per particle for the two ASRs is

$$\left(\frac{R_{ppMAA}}{R_{ppAA}}\right)_{TBHP/AsAc} = \left(\frac{R_1 + R_3}{R_1}\right)^{0.5} \tag{4}$$

Because the relationship between the polymerization rates per particle was 5.4 (Table 7), R_3 was substantially bigger than R_1 ($R_3 = 28R_1$), which means that for TBHP/AsAc, the effect of hydrogen abstraction on the reduction of the radical entry rate was 28 times higher than that of the diffusion.

Figure 2 shows the effect of the type of ASR on the evolution of the monomer conversion in the experiments initiated with APS. The most relevant data for these reactions are listed in Table 8.

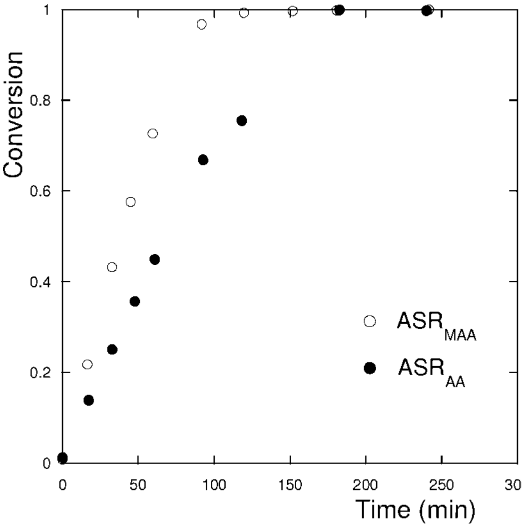

Figure 2. Effect of the ASR type on conversion versus reaction time in miniemulsion polymerization of S using APS.

Table 8. Main Data for Styrene Polymerizations Using APS

	R_p (g/L s)	d_p (nm)	N_p (particles/L)	R_{pp} (g/particle s)	$\bar{n}$
ASR_{MAA}	0.0575	522	3.8×10^{15}	15.1×10^{-18}	54
ASR_{AA}	0.0335	457	5.7×10^{15}	5.9×10^{-18}	21
ASR_{MAA}/ASR_{AA}	1.7	1.1	0.7	2.6	2.6

It can be seen that the polymerization rate was higher for the reaction using ASR_{MAA} (Figure 2 and Table 8), even though the number of particles was greater for ASR_{AA} (N_{pMAA}/N_{pAA} = 0.7). The polymerization rate per particle was lower for ASR_{AA}, namely, the radical entry rate was also lower for the ASR containing easily abstractable hydrogens. These results showed that hydrogen abstraction resulted in a decrease in the entry rate for both TBHP/AsAc and APS. Tables 7 and 8 show that the ratio of the polymerization rates per particle (R_{pp}) for TBHP/AsAc was 5.4, whereas for APS, it was 2.6, and thus the effect was more acute for TBHP/AsAc. This indicates that the rate of entry into the particles of the anionic oligoradicals formed from the APS was lowered by both the negatively charged ASR and the hydrogen abstraction. Equation 1 applied to APS initiator should include the repulsion term (R_2) for the two ASRs. Therefore, the following equations can be obtained

$$(R_{ppMAA})_{APS} \propto \left(\frac{1}{R_1 + R_2}\right)^{0.5} \tag{5}$$

$$(R_{ppAA})_{APS} \propto \left(\frac{1}{R_1 + R_2 + R_3}\right)^{0.5} \tag{6}$$

$$\left(\frac{R_{ppMAA}}{R_{ppAA}}\right)_{APS} = \left(\frac{R_1 + R_2 + R_3}{R_1 + R_2}\right)^{0.5} \tag{7}$$

If it is assumed that the value of R_3 of APS is similar to R_3 of TBHP/AsAc, then it is possible to estimate the ratios between R_2 and R_1 ($R_2 = 3.9R_1$) and between R_3 and R_2 ($R_3 = 7.2R_2$). According to these values, the effect of electrostatic repulsion was 3.9 times greater than that of the diffusion, and the resistance due to hydrogen abstraction was 7.2 times higher than that of the electrical repulsion.

The main conclusion of this section is that the hydrogen abstraction is the major factor in reducing the radical entry rate for S and that electrostatic repulsion also reduces the entry of negatively charged radicals.

Miniemulsion Polymerizations of MMA with TBHP/AsAc and APS. The oxygen-centered radicals are more efficient for hydrogen abstraction than the carbon-centered radicals. Therefore, a more hydrophilic monomer may reduce the

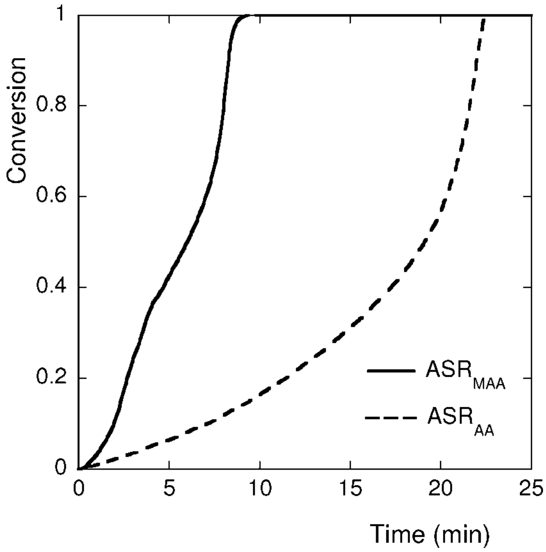

Figure 3. Effect of the ASR type on conversion versus reaction time in miniemulsion polymerization of MMA using TBHP/AsAc.

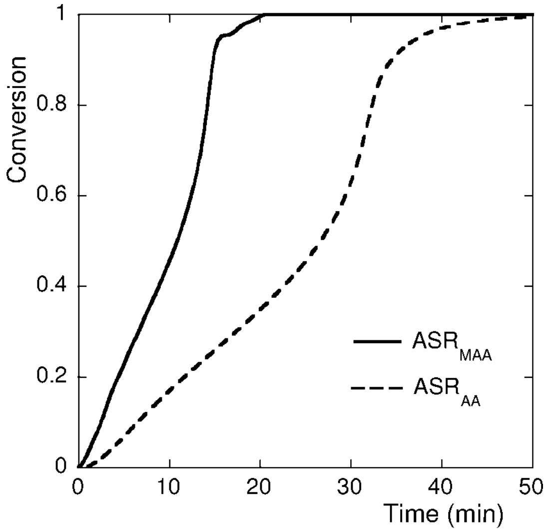

Figure 4. Effect of the ASR type on conversion versus reaction time in miniemulsion polymerization of MMA using APS.

probability of hydrogen abstraction because the oxygen-centered radicals produced in the aqueous phase may more easily react with the monomer, giving carbon-centered radicals. To check this idea, miniemulsion polymerizations of MMA were carried out using the formulations given in Tables 3 and 4 (same formulation as the reactions with S). The miniemulsion polymerizations of MMA were too fast to measure the conversion evolution accurately using gravimetry. Therefore, they were carried out in a calorimeter reactor (Mettler, RC1). In this way, continuous data of conversion were obtained.

Figures 3 and 4 show the results of these reactions. It can be seen that the polymerization rate was higher for the reaction using ASR$_{MAA}$ for both TBHP/AsAc and APS. The most relevant data of these reactions were listed in Table 9 for TBHP/AsAc and in Table 10 for APS.

It can be seen that the polymerization rate per particle was lower for ASR$_{AA}$; that is, the entry rate was lower for the ASR containing easily abstractable hydrogens. Using the same equations as those for S, we calculated the different resistances (R_1, R_2, and R_3). In this case, for the system TBHP/AsAc, $R_3 = 17.5R_1$, and for APS, $R_2 = 39R_1$ and $R_3 = 0.45R_2$. The relative importance of the three mechanisms for the two monomers and the two initiators is presented in Figure 5. It can be seen that when APS was used as initiator, the behavior was strongly affected by the water solubility of the monomer. For S, $R_3 = 7.2R_2$; that is, the effect of the abstraction of hydrogen was 7.2 times higher than that of the electrical repulsion. Conversely, for MMA, $R_3 = 0.45R_2$; that is, the effect of hydrogen abstraction was 2.2 times lower than that of the electrical repulsion. When TBHP/AcAc was used as initiator, the effect of the monomer hydrophilicity was much weaker.

Table 9. Main Data for MMA Polymerizations Using TBHP/AsAc

	R_p (g/L s)	d_p (nm)	N_p (particles/L)	R_{pp} (g/particle s)	$\bar{n}$
ASR$_{MAA}$	0.4080	333	13.0×10^{15}	31.5×10^{-18}	46
ASR$_{AA}$	0.0764	357	10.5×10^{15}	7.3×10^{-18}	10.8
ASR$_{MAA}$/ASR$_{AA}$	5.3	0.9	1.2	4.3	4.3

Table 10. Main Data for MMA Polymerizations Using APS

	R_p (g/L s)	d_p (nm)	N_p (particles/L)	R_{pp} (g/particle s)	$\bar{n}$
ASR$_{MAA}$	0.2165	306	16.7×10^{15}	12.9×10^{-18}	19
ASR$_{AA}$	0.0880	392	8.0×10^{15}	11.0×10^{-18}	16
ASR$_{MAA}$/ASR$_{AA}$	2.5	0.8	2.1	1.2	1.2

These results may be explained as follows. When APS was used in the polymerization of S, the oxygen-centered sulfate radicals, which cannot enter into the polymer particles, had a relatively long life because the monomer concentration in the aqueous phase was very low. Therefore, they could approach the hairy layer abstracting hydrogens. In the polymerization of MMA, the concentration of the monomer in the aqueous phase was much higher; therefore, the life of the oxygen-centered sulfate radicals was shorter. Consequently, the rate of hydrogen abstraction was lower. The effect of the monomer concentration in the aqueous phase was modest for TBHP/AsAc because the *tert*-butoxy radicals could directly enter into the polymer particles.

Miniemulsion Polymerizations of Styrene with AIBN. In this section, the effect of using an oil-soluble initiator that produces carbon-centered radicals was investigated. Figure 6 shows the effect of the ASR type on the monomer conversion for the experiments initiated with AIBN using the formulations given in Table 5. Table 11 presents the most relevant data for these reactions. It can be seen that the polymerization rate was lower for the ASR containing AA even though the number of

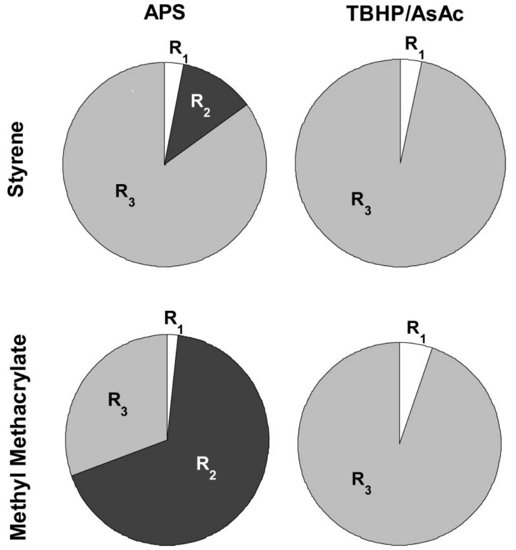

Figure 5. Relative importance of the different entry mechanisms: R_1, diffusion; R_2, electrical repulsion; R_3, hydrogen abstraction.

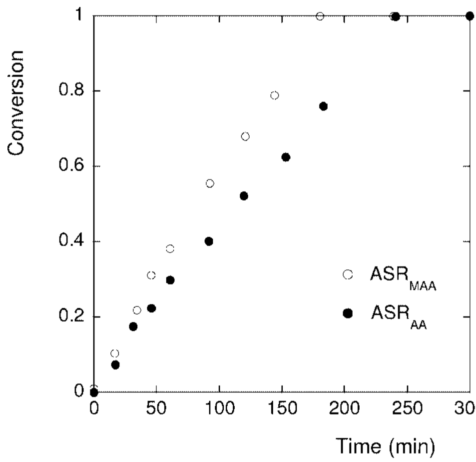

Figure 6. Effect of the ASR type on conversion versus reaction time in miniemulsion polymerization of styrene using AIBN.

Table 11. Main Data for Styrene Polymerizations Using AIBN

	R_p (g/L s)	d_p (nm)	N_p (particles/L)	R_{pp} (g/particle s)	$\bar{n}$
ASR_{MAA}	0.0286	364	1.13×10^{16}	2.5×10^{-18}	8.9
ASR_{AA}	0.0210	352	1.25×10^{16}	1.7×10^{-18}	6
ASR_{MAA}/ASR_{AA}	1.4	1.03	0.9	1.5	1.5

particles was slightly higher for ASR_{AA} ($N_{pMAA}/N_{pAA} = 0.9$). However, the effect was lower than that for the other initiators ($R_{ppMAA}/R_{ppAA} = 1.5$).

The analysis of this system is more complex than that for the previous cases. Thermal decomposition of AIBN gives two radicals inside of the polymer particles. In this case, electrical repulsion does not play any role. Because these radicals are confined in a very small volume, they quickly terminate unless one of the radicals desorbs.[19] Therefore, the polymerization rate is only significant if one radical desorbs. The overall polymerization rate will be that due to the radical that remains in the polymer particle plus the contribution of the radical that desorbs, provided that this one reabsorbs in another particle. The contribution of the desorbed radical will depend on the entry in other particles. Therefore, it should be inversely proportional to the resistance that has to be overcome to enter in the particle. Therefore, the polymerization rate per particle for the two ASRs can be written as follows

$$(R_{ppMAA})_{AIBN} = R_{pp1} + R_{pp2\text{-}MAA} = R_{pp1} + \left(\frac{K}{R_1}\right)^{0.5} \tag{8}$$

$$(R_{ppAA})_{AIBN} = R_{pp1} + R_{pp2\text{-}AA} = R_{pp1} + \left(\frac{K}{R_1 + R_3}\right)^{0.5} \tag{9}$$

where R_{pp1} is the contribution of the radical that remains inside the particle to the polymerization rate per particle, R_{pp2} is the contribution of the reabsorbed radical, and K is a coefficient of proportionality.

In this case, it is not possible to calculate the relative value of R_1 and R_3. Nevertheless, an estimation may be obtained from the mathematical modeling that predicts that the contribution of the radicals that remain in the polymer particle is 36% of the total polymerization rate.[19] Then, we can write

$$R_{pp1} = 0.36\left(R_{pp1} + \left(\frac{K}{R_1}\right)^{0.5}\right) = 0.56\left(\frac{K}{R_1}\right)^{0.5} \tag{10}$$

Therefore,

$$\left(\frac{R_{ppMAA}}{R_{ppAA}}\right)_{AIBN} = \frac{1.56}{0.56 + \left(\frac{R_1}{R_1 + R_3}\right)^{0.5}} \tag{11}$$

The combination of eq 11 and the value of R_{ppMAA}/R_{pAA} from Table 11 gives $R_3 = 3.3R_1$. Therefore, the resistance due to hydrogen abstraction was higher than that of the diffusion, but this value was much lower than the one found for TBHP/AsAc for S. The main reason for this behavior is that AIBN gives carbon-centered radicals that are less effective than oxygen-centered radicals in the hydrogen abstraction from the polymeric chain.

Conclusions

The relative significance of the three mechanisms proposed to justify the reduction of the radical entry in ASR-stabilized latexes was investigated. The three mechanisms considered were the resistance to radical diffusion, the charge repulsion, and the hydrogen abstraction. It was shown that the resistance to the radical entry depends on the type of ASR, the type of initiator, and the type of monomer used. Two monomers of different hydrophobicity (S, MMA), initiators producing different radicals in both aqueous and oil phases, and ASRs either prone or not prone to suffering hydrogen abstraction were used in several miniemulsion polymerizations.

For S (hydrophobic monomer), the polymerization rate when using APS (anionic hydrophilic radicals) was substantially reduced, mainly because the ASR acted as a radical sink (because of hydrogen abstraction), but electrical repulsion was also important. For TBHP/AsAc (uncharged hydrophobic radicals), the effect was due to hydrogen abstraction, and it was substantial.

For MMA (a relatively hydrophilic monomer), the effect of hydrogen abstraction was lower than the electrical resistance for APS. For TBHP/AsAc, the effect of hydrogen abstraction was important (although slightly lower than that for S). The effect of the monomer hydrophilicity was important when APS was used because the sulfate ion radicals must propagate in the aqueous phase before entering into the polymer particles. When the monomer concentration in the aqueous phase was very low (i.e., for S), the oxygen-centered radical had a relatively long life around the hairy layer, and hence it had the opportunity to abstract hydrogens. When MMA, which has a relatively high concentration in the aqueous phase, was used, the life of the oxygen-centered radical was shorter, and the rate of hydrogen abstraction was lower. The effect of the monomer concentration in the aqueous phase was modest for TBHP/AsAc because the *tert*-butoxy radicals can directly enter into the polymer particles.

For the oil-soluble initiator (AIBN), the effect of hydrogen abstraction was similar to that of the radical diffusion because carbon-centered radicals are less effective at abstracting hydrogens.

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