

Studies of alkali soluble resin as a surfactant in emulsion polymerization

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Abstract

In this work, alkali soluble resin (ASR) was evaluated as a surfactant in emulsion polymerization of methyl methacrylate (MMA), styrene (SM), and butylacrylate (BA). A decrease in reaction rate was observed with ASR as the surfactant in the MMA system but not in the SM system. Kinetic analysis indicated that ASR retards the reaction rate and reduces the average number of radicals per latex particle in the MMA system. Experimental results also showed that the reaction rate of BA was slow and that the BA latex was unstable with ASR as the surfactant. A grafting reaction was observed in the presence of ASR via gel permeation chromatography (GPC) measurements. The transmission electron micrograph was employed to observe the morphology of latex as well. It depicted that the particles were surrounded by ASR to stabilize the latex particle. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Latex; Polymeric surfactant; Alkali soluble resin

1. Introduction

The ever-tightening regulation control of air quality in the 1990s has resulted in many studies of technologies in place of solvent-based coating. Approaches to reduce volatile organic compound (VOC) include high solid content coating, powder coating, ultraviolet curing coating and water-based coating. Water-based coating is widely used because its processing parameters are similar to those of the solvent-based system. In the water-based system, emulsion polymerization is the most commonly used method and has been adapted to produce commodity products such as polystyrene, polyvinyl chloride and ABS resins.

Anionic and nonionic emulsifiers [1] are usually used as stabilizers in emulsion polymerization. However, emulsifiers create many drawbacks in the final application such as poor water resistance, poor adhesion, slow film formation and altering polymer properties. To overcome those drawbacks, several methods have been used to prepare the latex. The first method is emulsifier-free emulsion polymerization [2–5]. The second method is to employ a reactive surfactant [6]. This method improves the performance of the latex significantly, for the surfactant is capable of reacting with the monomer and anchoring itself onto the particle surfaces. The third method is to use a polymeric surfactant in

emulsion polymerization [7–9]. Owing to its large molecular structure, the polymeric surfactant is able to eliminate the disadvantages associated with surfactant migration. Moreover, due to its steric effect on the particle, the polymeric surfactant can produce latex with other features such as excellent mechanical stability and freeze–thaw stability. Kiehlbauch and Tsaur [10,11] examined the feasibility of using alkali soluble resin (ASR) as a surfactant and concluded that the resin-fortified emulsion polymers offered many advantages, such as substantial Newtonian flow, excellent mechanical stability and freeze–thaw stability, good pigment dispersity and wetting property. Lee and Kim [12] also studied the reaction behaviors of MMA and SM in the ASR aqueous solution. Their investigations used ASR neutralized with sodium hydroxide as a surfactant and showed that ASR formed aggregates in the aqueous solution. Moreover, grafting of polystyrene to ASR during emulsion polymerization was proposed.

In this work, we aim to understand more thoroughly the reaction behaviors with ASR as the surfactant in emulsion polymerization. Methyl methacrylate (MMA), styrene (SM), and butyl acrylate (BA) were the monomers used. The effects of ASR on the reaction rate, particle size and molecular weight were studied. The gel permeation chromatography (GPC) and alkali separation methods were employed to study the grafting reaction. The morphology of latex was observed via TEM as well.

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Table 1
The recipe of emulsion polymerization (the reaction temperature was 70°C)

Ingredients	Amount (g)
Water	679.2
ASR aqueous solution ^a	160 (ASR 25 wt% based on monomer)
Monomer	160
K ₂ S ₂ O ₈	0.8 (0.5 wt% based on monomer)

^a Solid content = 25%, degree of neutralization = 110%.

2. Experimental

2.1. Materials

Reagent grades of methyl methacrylate (MMA, Lancaster), butyl acrylate (BA, Lancaster), styrene (SM, Acros), potassium persulfate (KPS, Acros), hydroquinone (Merck), sodium lauryl sulfate (SLS, T.C.I.) and ammonium hydroxide (TEDIA) were used. Inhibitors of MMA, SM and BA were removed with Al₂O₃ (Fisher A540) prior to polymerization. ASR (a copolymer of SM and acrylic acid (AA); Johnson Co.) was used as received. Water was deionized. Batch reaction was adapted to evaluate reaction behaviors.

2.2. Preparation of the alkali soluble resin solution

250 g of ASR, 63.7 g of ammonium hydroxide and

686.3 g of deionized water were added into a 1 l reactor at room temperature. The mixture was stirred and the temperature was kept at 70°C for 2 h until the solution was completely clear. The concentration of the ASR solution was 25 wt%, and the degree of neutralization was 110%.

2.3. Emulsion polymerization

Emulsion polymerization was carried out in a 1 l four-neck reaction vessel equipped with a mechanical stirrer (Teflon baffle stirrer), a reflux-cooler, a thermometer, a nitrogen flushing and a thermostat jacket to control the temperature. Quantitative monomers and surfactants were added into the reactor at room temperature. The stirring rate was controlled at 400 rpm. Nitrogen gas was bubbled through the reaction mixture. The aqueous solution of the initiator was added into the reactor when the temperature of the system was kept at 70°C for 10 min. After adding the initiator, the reaction was allowed to proceed for 2 h. A sample of the latex was taken out of the reactor at regular intervals and then dried in an oven at 110°C for 4 h. The conversions were calculated based on gravimetric measurements. The ingredients and conditions of emulsion polymerization are tabulated in Table 1. In this system, the concentration of monomer was 16%, the concentration of surfactant was either 25 wt% (based on monomer) of polymeric surfactant (ASR) or 3 wt% (based on monomer) of SLS and the concentration of the initiator (K₂S₂O₈) was 0.5 wt% (base on monomer).

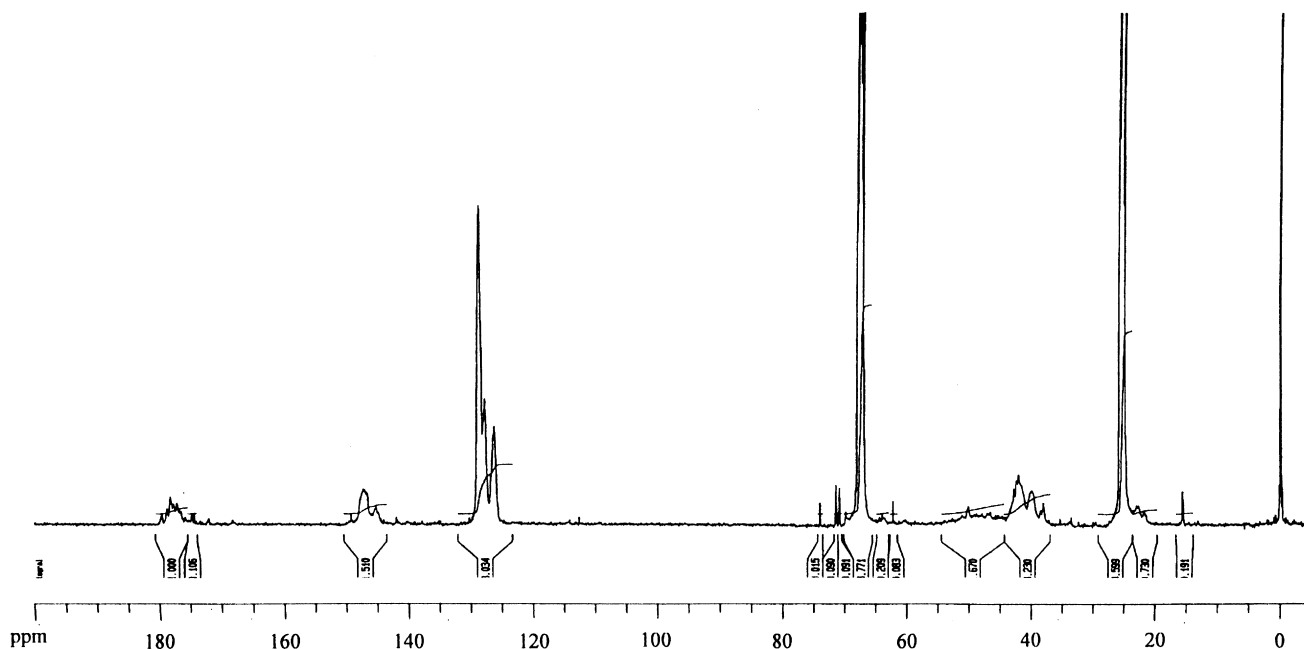


Fig. 1. The ¹³C NMR spectrum of ASR.

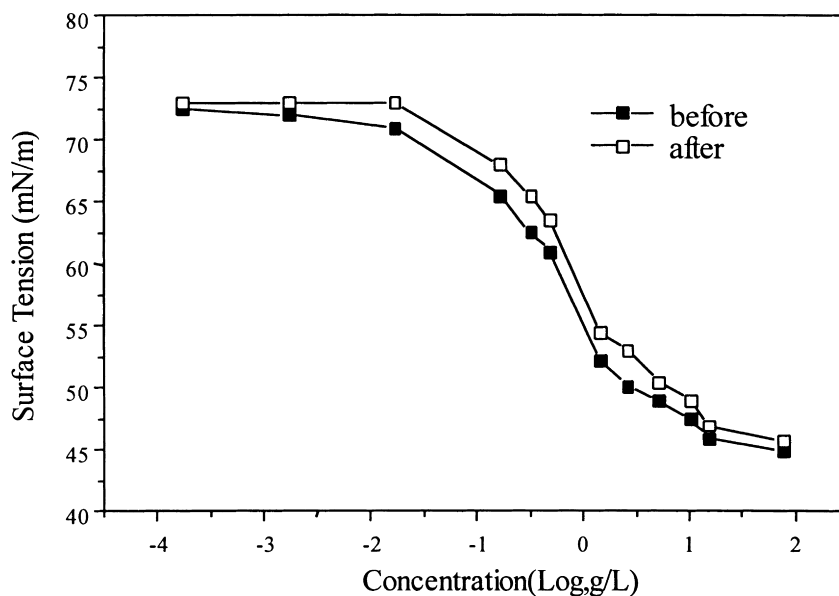


Fig. 2. The Effects of ASR concentrations on surface tensions.

2.4. Characterizations

^{13}C nuclear magnetic resonance (NMR) and acid value titration were used to characterize the ASR composition. NMR spectra were obtained at ambient temperature using a Bruker (DRX-400) spectrometer operating at 100 MHz, and the ASR sample was made up as solution in deuterated THF containing 100 mg polymer in 3 ml solvent. The surface tension of ASR aqueous solution was measured by a surface tension meter (KRUSSTensiometer K6). The average particle size of the latex was determined by light scattering of a laser submicron particle sizer (MALVERN Instruments, Model 270). The morphology of latex was observed via transmission electron microscopy. Particles

were first separated by adding hydrogen chloride solution into the latex, then drying it in the oven and mixing in epoxy resins to fix the samples. RuO_4 was used to stain the unsaturated bond of ASR in the latex.

The grafting ratio of ASR to polymer was determined by the alkali separation method and the acid titration method. The dried latex was dissolved in THF to form a 2.5 wt% solution then mixed with a 1.4% ammonium aqueous solution to form two portions. The grafting content was measured by titrating the alkali insoluble part with 0.1% KOH solution.

The weight-averaged molecular weight of the polymer was measured by GPC with both RI and UV as the detectors. Solutions for GPC analysis were prepared by dissolving the

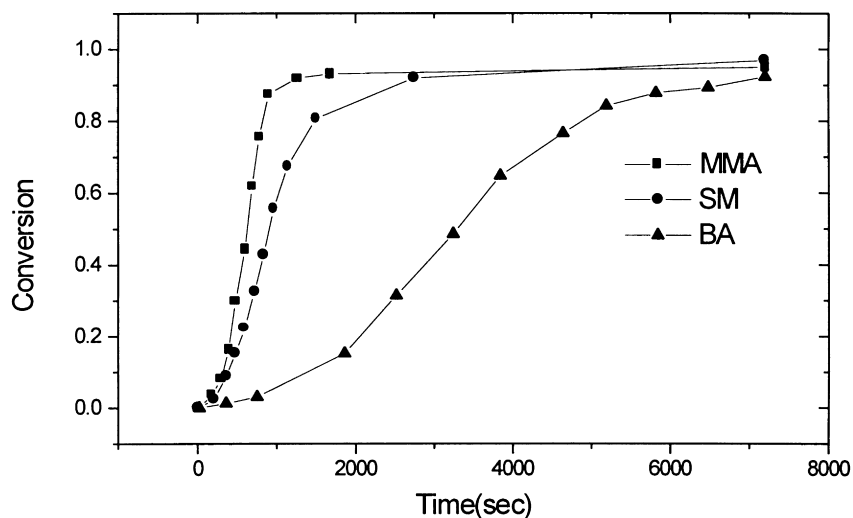
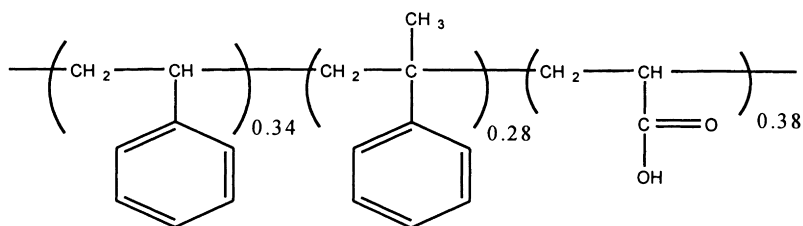


Fig. 3. Effects of ASR surfactant on the reaction rates.

sample with THF to give a polymer concentration of approximately 0.25 wt%. Each solution was injected into the THF flowstream of a GPC system operating at 40°C with 1 cm³/min flow rate. A series of five columns

weight average molecular weight and number average molecular weight determined by GPC were 9800 and 5100, respectively. The chemical structure of ASR is proposed as follows:



(KF805, 804, 803, 802, 801) were equipped with GPC as separation columns and polystyrene standards were used for calibration.

3. Results and discussion

3.1. Structure of ASR

The composition of ASR was determined by Pyrolyzer GC Mass (Finnigan), ¹³C NMR and acid titration, separately. The PGC-Mass results show that ASR is primarily composed of SM, alpha methyl styrene (AMS) and AA. The ¹³C NMR was used to identify each composition quantitatively in the ASR. Fig. 1 shows the NMR spectrum of ASR and its ¹³C peak assignments. The signals comprise CH₃ of AMS at δ c 22.7–23 ppm, COOH of AA at δ c 174.4–179.5 ppm and CH (phenyl) of AMS, SM at δ c 126.2–129.7 ppm. The relative intensities in the ASR spectra were approximately 0.73:1:8.03, i.e. the molar ratio of SM, AMS, AA is 0.34, 0.28, 0.38. The AA content of ASR was about 3.96×10^{-3} mol/g resin. This concentration was also confirmed by the acid titration method that shows an AA content of 3.86×10^{-3} mol/g resin. The

In order to increase the hydrophilicity of this polymer, ammonium base was added to ionize the acid and to form a hydrophilic salt.

3.2. Surface tension of ASR aqueous solution

The ASR polymeric surfactant was dissolved in an alkali aqueous solution to form a clear solution. The relationship between the surface tension and the ASR concentration is shown in Fig. 2. It indicates that the surface tension decreases slowly with increasing ASR concentration in the beginning, then at the concentration above 0.017 g/l, the surface tension drops drastically from 70 to 50 mN/m. As we know, when the surfactant concentration reaches the critical micelle concentration (CMC), a sharp change in the solution properties, such as surface tension, electrical conductivity, viscosity and ion activity will be observed due to the transformation of a solution state to a micelle state. Therefore, Fig. 2 suggests that ASR forms micelle-like aggregates as reported by Lee and Kim [12]. Since ASR is composed of species with various molecular weights (molecular weight distribution is 1.9 from the GPC result), the critical aggregate concentration of ASR ranges from 1.48 to 14.8 g/l. Moreover, Fig. 2 also shows that the surface

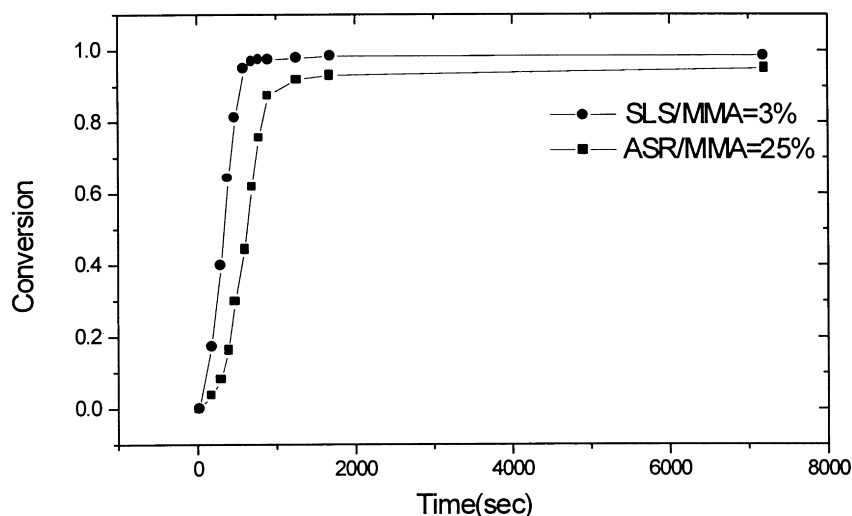


Fig. 4. Comparisons of the reaction rates between ASR and SLS surfactants in the MMA system.

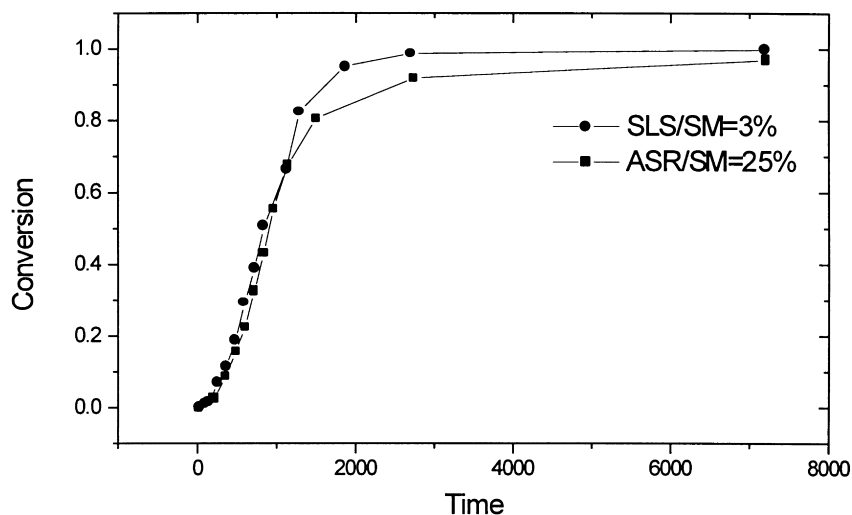


Fig. 5. Comparisons of the reaction rates between ASR and SLS surfactants in the SM system.

tensions of the ASR aqueous solution before stirring are lower than after stirring. This phenomenon is due to the high molecular weight of ASR causing it to diffuse slowly to the surface of the ASR solution. It also explains how the polymeric surfactant can overcome the drawbacks of surfactant migration.

3.3. Effects of ASR on the conversion and reaction rate

In this study, the effects of ASR on emulsion polymerization of various monomers were evaluated. Due to the solubility differences of MMA, SM and BA in aqueous solutions, the mechanism of particle nucleation is expected to be different between these monomers. Generally the mechanism for particle formation of emulsion polymerization proceeds in two simultaneous processes [13]. One is the entry of radicals from the aqueous phase into the micelles. The other is homogeneous nucleation, whereby oligomeric radicals in the aqueous solution polymerize and become insoluble while precipitating onto themselves. The precipitated species are stabilized by absorbing surfactants with subsequent absorption of monomers to form polymer particles. The relative extent of micellar and homogeneous nucleation is expected to vary with the solubility of the monomer and the concentration of the surfactant. High

monomer solubility in water (such as MMA) and low surfactant concentration favor homogeneous nucleation. On the contrary, micellar nucleation is favored by low monomer solubility in water (such as SM and BA) and high surfactant concentration. In this study, the micellar nucleation plays an important role because the concentration (48 g/l) of ASR employed in this study was higher than the critical concentration (1.48–14.8 g/l) of aggregation. Since free radicals are mostly generated in the continuous phase, they must diffuse through the hydrophilic barrier formed by the ASR surfactant, and consequently, reaction between free radicals and ASR is expected. Fig. 3 provides the conversion versus reaction time with ASR as the surfactant. It shows that the reaction rate of BA is the slowest one. The average particle size of BA latex is 177.7 nm and the particle size distribution is much broader than those of the SM and MMA systems. BA latex is also unstable, for precipitation occurs after storing for one month. The above results show that ASR cannot be adsorbed adequately onto the BA particles to stabilize the latex system. Therefore, the particle formation and reaction rate of the BA system is lower than that of the MMA and SM systems.

In order to evaluate the effects of ASR on the MMA and SM emulsion polymerizations, SLS was employed as the surfactant to compare the differences in the reaction behaviors separately. The concentration of SLS was controlled at 3% based on the monomer to maintain the same particle size of the final latex for comparison. The reaction rates of MMA and SM can be calculated from the slopes of Figs. 4 and 5 in both ASR and SLS systems as listed in Table 3. The reaction rate of emulsion polymerization can be expressed as [9,13]:

$$R_p(d[M]/dt) = k_p C_p \bar{n} N_p / N_a \quad (1)$$

where k_p is the rate constant for radical propagation, C_p is the monomer concentration in the polymer particles, \bar{n} is the

Table 2
Numerical constants used in the kinetic study

Parameter	SM	MMA
A (1/mol s)	$10^{7.1}$	$10^{6.4}$
E_a (J/mol)	29×10^3	22.2×10^3
d_p (g/cm ³)	1.044	1.178
d_m (g/cm ³)	0.878	0.909
X_s	0.325	0.3
C_p (mol/l)	6	6.8
M_w (g/mol)	104	100
R (J/mol K)	8.314	8.314

Table 3
Surfactant effects on the particle sizes and the molecular weights of latex particles

Sample	MMA/ASR	SM/ASR	BA/ASR	MMA/SLS	SM/SLS
D_p (nm)	55.4	54.1	177.7 ^a	65.6	65
Particle number $\times 10^{18}$ (1/l)	1.54	1.78	0.043	0.92	1.1
Reaction rate $\times 10^3$ (mol/s l)	2.0	1.1	0.29	5.5	1
Conversion ^b (%)	16.3	15.6	–	17.5	18.8
$M_w^c \times 10^{-4}$ (experimental)	40	45	–	97.4	59.4
t (s)	16	18.5	–	9.6	11.4
$M_w \times 10^{-4}$ (calculation)	1067	607	–	726	374

^a The measurement was not stable.

^b The conversion at which the molecular weight was measured.

^c The molecular weight of ASR not included.

average number of radicals per particle, N_p is the number of particles per unit volume of the continuous phase, and N_a is Avogadro's number. The temperature dependence of the rate constant can be expressed in Arrhenius form [15–17]:

$$k_p = A \exp(-E_a/RT) \quad (2)$$

and the number of particles per unit volume of the continuous phase is expressed as:

$$N_p = 6m_p/\pi D^3 d \quad (3)$$

where m_p is the polymer mass per unit volume of aqueous phase, D is the diameter of swollen particle and d is the density of swollen particle which assume a linear relationship with the composition of polymer and monomer. The density of the swollen particle is calculated as follows:

$$d = d_m(1 - X_s) + d_p X_s \quad \text{as } X < X_s \quad (4)$$

$$d = d_m(1 - X) + d_p X \quad \text{as } X > X_s \quad (5)$$

where d_m is the density of monomer, d_p is the density of polymer and X_s is the conversion of monomer as the droplet

disappeared. Table 2 summarizes the values of parameters for MMA and SM emulsion polymerizations, respectively.

From Table 3, we can find that the reaction rate of MMA in the ASR system is slower than that in the SLS system although the particle number in the ASR system is higher than that in the SLS system. Further, the reaction rate of SM does not show a significant difference in either the ASR or SLS systems. In general, ASR not only functions as a stabilizer, but also acts as a retarder or a chain transfer agent. The abstraction of hydrogen from ASR by the growing chain radical probably occurs. The free radical formed on the ASR chain by hydrogen abstraction may react with the monomer and thus create a branch on the ASR backbone. This grafting reaction may affect the overall polymerization rate, which depends on the mobility of the free radical. This phenomenon was also found in other emulsion polymerization systems such as acrylate monomer with alkyd resin [18] as the surfactant or vinyl acetate with polyvinyl alcohol [9] as the surfactant. Since the structure of ASR contains SM and AMS, ASR should be compatible with SM and the mobility of the transferred free radical would be expected to be the same in the SM systems with ASR and SLS as surfactants, respectively. In other words,

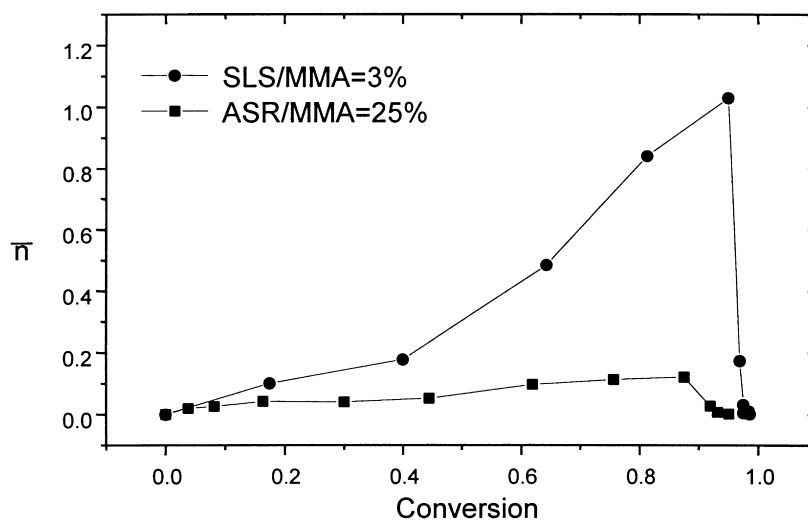


Fig. 6. Comparisons of \bar{n} between ASR and SLS as surfactants in the MMA system.

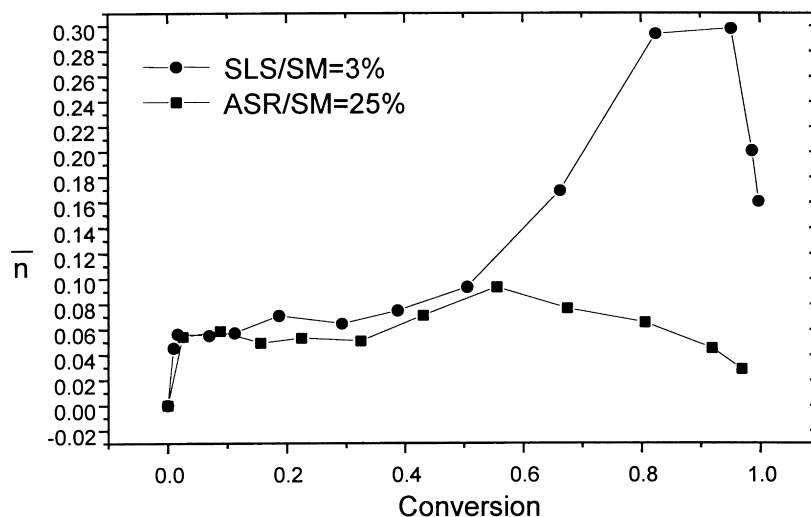


Fig. 7. Comparisons of \bar{n} between ASR and SLS as surfactants in the SM system.

the effective number of free radicals in a particle will not be reduced in the SM system with ASR as the surfactant. However, in the MMA system, the mobility of the free radical is restricted with ASR as the surfactant due to the decreased compatibility between ASR and MMA. Thus, the number of effective radicals in a particle with ASR as the surfactant would be less than that with SLS as the surfactant in the MMA system.

It was also found, from Figs. 4 and 5, that the final conversion of monomer in the ASR system is always lower than that in the SLS system for either monomer. As we know, most radicals are generated in the continuous phase, then react with monomers dissolved in the continuous phase to form macroradicals. However, ASR absorbed on the particle surface forms a barrier layer to retard the radicals reacting with the hydrophobic monomers, which stay in the core area of the particle. Therefore, the frequency of monomer reacting with the macroradical was depressed. Therefore, we observe that the monomer conversion with ASR as the surfactant is lower than that with SLS as the surfactant.

Fig. 6 shows the average radical number per particle (\bar{n}) with ASR or SLS as the surfactant in the MMA system. It shows that \bar{n} with ASR as the surfactant is lower than that with SLS as the surfactant especially at conversions above 40% (reaction proceeded in Interval III). This phenomenon is also observed in the SM system, as shown in Fig. 7, but the difference in \bar{n} is not as large as that in the MMA system. The occurrence of the gel effect [13] caused the value of \bar{n} to increase drastically as the reaction proceeding in Interval III with SLS as the surfactant, but this was not the case with ASR as the surfactant (Figs. 5 and 6). Harkins [19] has postulated a reaction scheme in emulsion polymerization which is divided into three distinct Intervals (I, II, III): Interval I—nucleation of polymer particles in the presence of both micelles and monomer droplets; Interval II—growth of polymer particles in the absence of micelles; and Interval

III—polymerization within the monomer swollen polymer particles in the absence of both micelles and monomer droplets. The gel effect will always be found in Interval III with SLS as the surfactant [14]. This gel effect does not occur with ASR employed as the surfactant. Since the transferred ASR radical is a hydrophilic reaction site, water will still be a plasticizer to maintain the mobility of radicals to collide with each other. It makes the termination reaction easier. The barrier layer formed by ASR also retards the macroradicals into the particles and reduces the radical number of a particle. It also explains why the reaction with ASR as the surfactant is always not as complete as those with SLS as the surfactant (Figs. 4 and 5).

3.4. Molecular weight of polymers

In addition to the influences of ASR on the reaction rate, the effects of ASR on the molecular weight were also studied. The molecular weight of the polymer produced by emulsion polymerization is dominated by chain transfer and bimolecular termination [14]. The degree of polymerization is expressed as [13]:

$$\bar{X}_n = r_p / (r_i + r_t) \quad (6)$$

where \bar{X}_n is the degree of polymerization, r_p is the propagation rate in the particles, r_i is the radical generating rate in the particles and r_t is the rate of transfer to monomer or to the chain transfer agent in the particles. Assuming that the radical is terminated by radical combination only, then the propagation reaction will proceed until another radical is captured by the particle to terminate the propagation reaction. Eq. (6) can be rewritten as [14]:

$$\bar{X}_n = r_p / r_i = k_p C_p / (N_a 2fk_d [I] / N) \quad (7)$$

where f is the initiator efficiency, k_d is the dissociation constant of the initiator and $[I]$ is the concentration of the

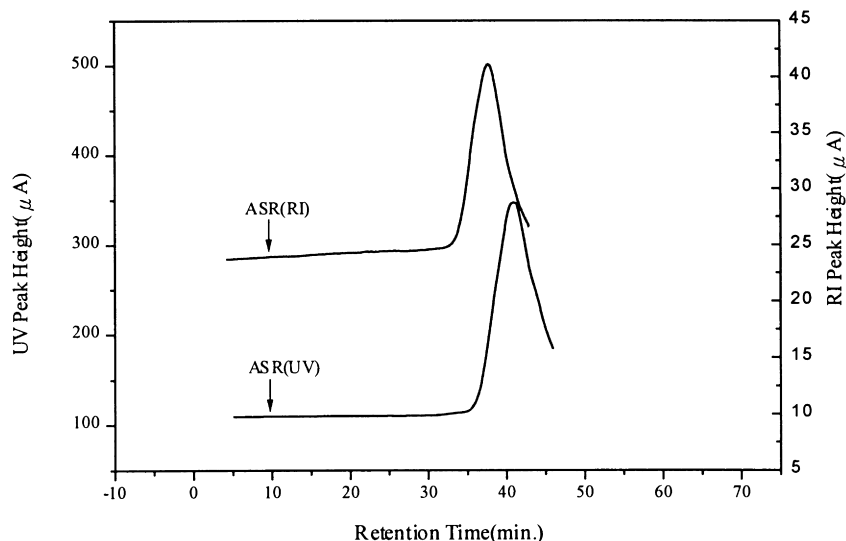


Fig. 8. GPC chromatograms of ASR using RI and UV as detectors.

initiator. In this study, the initiator concentration is 3.6×10^{-3} mol/l, the dissociation constant [20] of $K_2S_2O_8$ at 70°C is 2.21×10^{-5} l/s and the initiator efficiency is assumed to be 1. The free radical generating rate (r_i) can be calculated ($2fk_d[I]$) to be 1.6×10^{-7} mol/l s. The particle numbers are within $0.92\text{--}1.78 \times 10^{18}$ l/l as listed in the Table 3. The average time (t) needed for each particle to capture a radical can be calculated by dividing the particle number by the free radical generating rate. The molecular weight of the polymer should be equal to $k_p \times C_p \times t \times M_w$, and the results are listed in Table 3. The calculated molecular weights of polystyrene are much larger than the experimental values. It indicates that the termination reaction is not dominated by bimolecular termination only and that chain transfer reactions with the monomer, surfactant and polymer play

major roles in the termination reaction. Table 3 presents the molecular weights of the latex at a conversion of about 15% (Interval II). In Interval II, the particle is saturated with monomer and the frequency of reacting with polymer should be limited. In this stage, it can be expected that chain transfer to the monomer or surfactant but not to polymer dominates the growth of molecular weight of latex. Table 3 shows that the molecular weight of polymer with ASR as the surfactant is less than that with SLS as the surfactant. This finding can be accounted for and explained by the chain transfer behavior of ASR. It is known that chain transfer agent or retarder will decrease the molecular weight [13] of the polymer. The above results suggest that ASR functions both as, surfactant and, chain transfer agent in the emulsion polymerization.

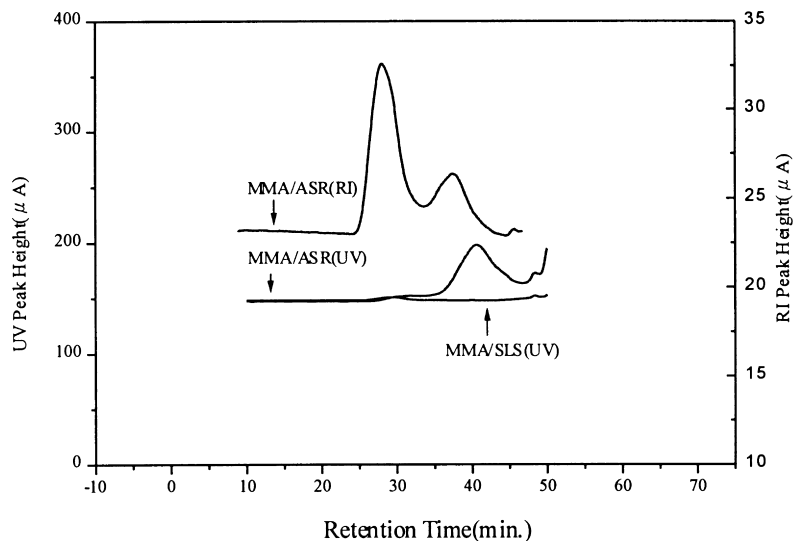


Fig. 9. GPC studies of the MMA/ASR and MMA/SLS systems in the batch reaction.

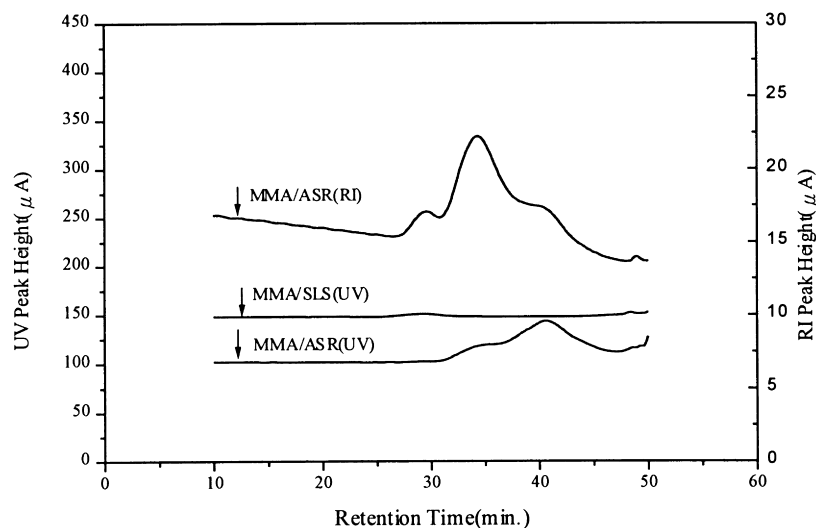


Fig. 10. GPC studies of the MMA/ASR and MMA/SLS systems in the semi-continuous reaction.

3.5. Grafting reaction of ASR

GPC with UV (254 nm) and RI as detectors was used to understand the chain transfer behavior of ASR and the results are shown in Figs. 8, 9 and 10. Fig. 8 depicts that ASR has both RI and UV absorptions (retention time about 40 min). The RI result indicates that the weight-average molecular weight of ASR is 9,800. ASR is composed of SM and AA and therefore the UV absorbance of ASR is induced by the SM structure. Figs. 9 and 10 display the GPC chromatograms of MMA in both the ASR and SLS systems by batch reaction or semi-continuous reaction, respectively. In the semi-continuous reaction, monomers were added gradually into the reactor during a 2 h period. Both high molecular weight (retention time at 32 min) and low molecular weight (retention time at 40 min) absorptions

appear in the GPC chromatograms of the MMA/ASR (RI) system. The low molecular weight fraction represents the ASR surfactant, and the other absorption peak represents either the MMA polymer or the ASR-grafted-MMA copolymer. Since the MMA polymer does not have apparent UV absorption in the SLS system, the molecular weight absorption peak in the UV detector shown in Figs. 9 and 10 must be caused by ASR. This observation suggests that the grafting reaction between ASR and MMA does occur and this reaction causes UV absorption. Additionally, the peak area under the absorption peak in UV spectra of the high molecular weight region (retention time at 32 min) could be used to compare the grafting behavior. In the semi-continuous reaction, the product has a stronger peak (retention time at 32 min) than its counterpart in the batch reaction (Figs. 9 and 10). This observation suggests the possibility

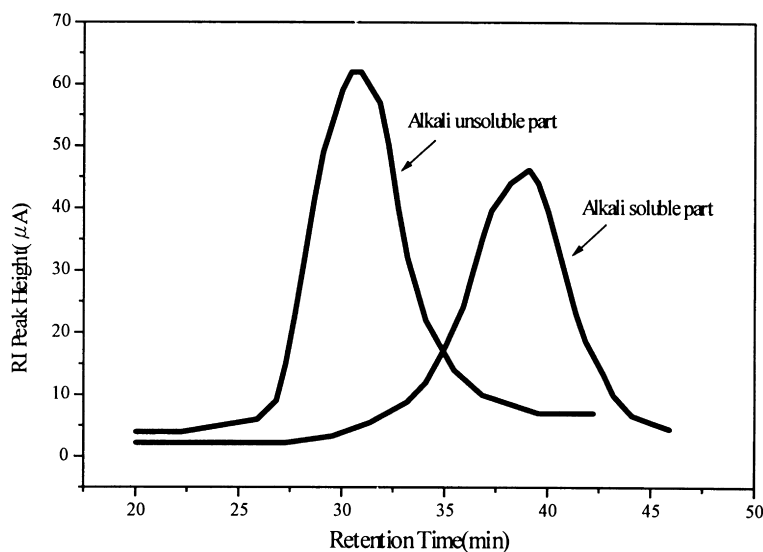


Fig. 11. GPC studies of alkali soluble and insoluble parts of SM/ASR latex.

Table 4
Effects of ASR neutralization degree on the ASR grafting ratio to each monomer

Neutralization degree (%)	PMMA acid content ^a	ASR grafting ratio ^b (%)	PSM acid content ^a	ASR grafting ratio ^b (%)
110	6.6	3	12.2	5.5
90	6.5	3	12.1	5.5
70	6.4	2.9	11	5

^a mg KOH/g resin.

^b ASR grafting to polymer ratio; acid content/44 (the acid content of ASR added in the reaction).

of the grafting reaction, especially in the semi-continuous process in which the added monomers diffuse through the ASR layer and the grafting reaction between monomer and ASR occurs. While in the batch reaction, the monomers stay inside the core region.

In our experiments, the alkali separation method was used to determine the ASR grafting content. This method involves adding an alkali aqueous solution to the latex polymer solution. The ungrafted ASR is then dissolved in the alkali solution and the remaining polymer is titrated with 0.1 N KOH to determine the grafted ASR content. Fig. 11 displays the molecular weight distributions of alkali soluble and alkali insoluble parts of SM latex. Table 4 lists the acid content of the alkali insoluble portion and the grafting ratio of each latex. As described previously, these results also show that the grafting reaction does occur and that about 15–28% of the added ASR was grafted with the monomer. Additionally, the grafting ratio depends more on the monomer structure than on the degree of neutralization of ASR. The grafting ratio of MMA is less than that of SM. This indicates that ASR acts as the chain transfer agent more in the SM system than in the MMA system. The ASR transferred macroradical is easier to propagate with SM than with MMA.

3.6. Morphology

The absorption phenomenon of ASR in the latex particle can be further understood via the particle morphology

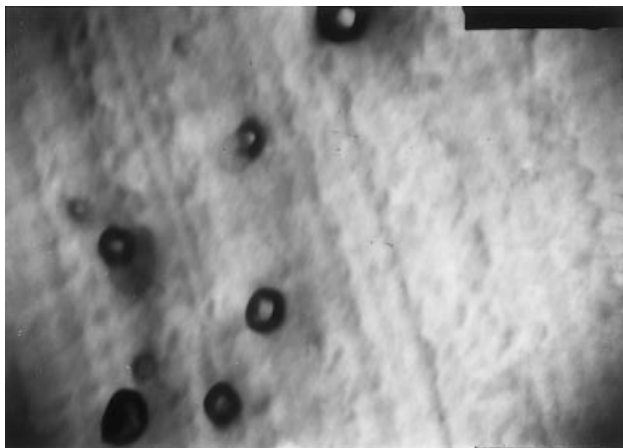


Fig. 12. TEM micrograph of PMMA/ASR latex.

observed by TEM. The major component of ASR is SM, thereby it can be stained with RuO₄. Figs. 12 and 13 show the TEM pictures of the latexes of MMA and BA, respectively. Both latexes were polymerized with ASR as the surfactant. They show that ASR surrounds the particles. The particle morphologies are similar to a core and shell type. These data also prove that ASR adsorbs on the particle surface to form a protecting barrier layer, so that the free radical must diffuse through the protecting barrier layer and therefore the reaction between free radical and ASR does occur. Figs. 12 and 13 also show that the shell thickness of the MMA/ASR system is larger than that of the BA/ASR system. It also explains why the stability of BA is worse than that of MMA with ASR employed as the surfactant.

4. Conclusion

In this study, ASR was used as the surfactant to prepare latex, and its reaction behaviors were compared with SLS and ASR as the surfactants, respectively. In the ASR aqueous solution, a distinguishable ASR aggregate concentration was observed. As considered in this paper, the micellar nucleation plays the role of a major growth mechanism. ASR has a dominant effect on the reaction rate, the size of particles and the molecular weight. In addition, the grafting reaction is observed in the ASR system, which results in a smaller average molecular weight of latex than in the SLS system. TEM studies show that the morphology of latex is core and shell type and the shell

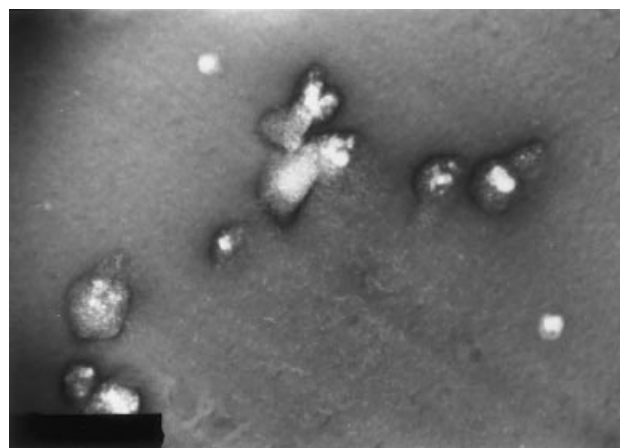


Fig. 13. TEM micrograph of PBA/ASR latex.

thickness of PMMA latex is larger than that of the PBA latex. It also shows that the stability of PMMA latex is better than that of the PBA latex.

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