

Kinetic study of the mini-emulsion polymerization of styrene

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A broad particle-size distribution in mini-emulsion polymerization is generally attributed to the long induction period and homogeneous nucleation in the aqueous phase. In this study, the high dissociation rate of the interfacial redox initiator system cumene hydroperoxide/ferrous ion/ethylenediaminetetraacetic acid/sodium formaldehyde sulfoxylate (CHP-Fe²⁺-EDTA-SFS), which could produce hydrophobic radicals and decrease homogeneous nucleation in the aqueous phase, was used to prepare the mini-emulsion polymerization. Polystyrene particles of narrow size distribution were obtained, and their molecular weights were also very narrow (polydispersity index = 1.5–2.0). The effects of the initiator concentration, the ratio of surfactant/cosurfactant (sodium lauryl sulfate/cetyl alcohol, SLS/CA), the styrene concentration and the reaction temperature in the mini-emulsion polymerization of styrene were also investigated. When higher CHP and SFS concentrations or higher reaction temperature were used in the mini-emulsion polymerization, the polymerization rate and conversion became higher. The order of SLS:CA ratios for preparing polymer particles of high stability was 1:3 > 1:10 > 1:1 > 1:6 > 1:0. Copyright © 1996 Elsevier Science Ltd.

(Keywords: mini-emulsion; redox initiator; monodisperse latex)

INTRODUCTION

It has been well characterized^{1–24} that, in a mini-emulsion polymerization with water-soluble initiators, the principal loci of polymerization are the monomer-swollen latex particles. Choi *et al.*⁵ studied mini-emulsion polymerization initiated by an oil-soluble initiator to enhance the polymerization proceeding in the monomer droplets and to avoid homogeneous nucleation in the aqueous phase. However, they concluded that a large number of radicals would desorb from the monomer droplets to the aqueous solution. The reaction behaviours of mini-emulsion polymerization for both water-soluble and oil-soluble initiators were similar. Polymer particles exhibited a wide and skewed distribution to small size range^{19,24}, which resulted from the long nucleation period^{5,21} and homogeneous nucleation in the aqueous phase. Thus, if a narrow particle size distribution in mini-emulsion polymerization is desired, one should shorten the nucleation period and avoid homogeneous nucleation in the aqueous phase.

The redox initiator system cumene hydroperoxide/Fe²⁺/ethylenediaminetetraacetic acid/sodium formaldehyde sulfoxylate (CHP-Fe²⁺-EDTA-SFS) and a new agitation method have been successfully used for the mini-emulsion polymerization of styrene in a previous study²⁵. The redox system had a faster dissociation rate than the thermal initiator, which could lower the nucleation period. The more hydrophobic radicals obtained from CHP could decrease radical desorption to the water phase to avoid homogeneous nucleation in

the aqueous phase. Consequently, polystyrene particles of narrow size distribution were obtained. In this work, a detailed investigation on the effect of each of the reaction components on mini-emulsion polymerization initiated by a redox initiator system was conducted.

EXPERIMENT

Material

The styrene monomers used for the study were commercially available. They were purified by methods described elsewhere². Sodium formaldehyde sulfoxylate (SFS; Katayama Chemical), tetrahydrofuran (THF), cumene hydroperoxide (CHP; Merck Co.), ethylenediaminetetraacetic acid disodium salt (EDTA; Ishisu Pharm. Co. Ltd), ferrous sulfate and cetyl alcohol (CA; Ishisu Pharm. Co. Ltd) were used without further purification. Sodium lauryl sulfate (SLS; Ishisu Pharm. Co. Ltd) was recrystallized twice in methanol before use. Reagent-grade water was obtained using a Waters Millipore purifying system.

Polymerization

The mini-emulsion polymerization of styrene was carried out using the same procedure as the previous study²⁵. The main recipe for mini-emulsion polymerization is shown in *Table 1*.

Particle size measurement

The average diameters of latex particles were measured using an Otsuka DLS700 laser light scattering spectrophotometer. The method used to analyse the diameter of polymer particles is presented in the

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Table 1 The main recipe for mini-emulsion polymerization

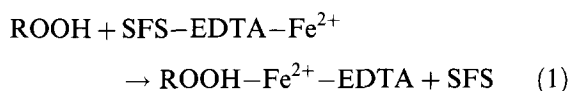
Run No.	SFS (mM)	CHP (mol)	SLS/CA (mM)	Styrene/H ₂ O (ml)
R1	6.61	1.59×10^{-3}	10/30	110/300
R2	7.22	1.59×10^{-3}	10/30	110/300
R3	8.89	1.59×10^{-3}	10/30	110/300
R4	8.89	9.49×10^{-3}	10/30	110/300
R5	8.89	1.38×10^{-3}	10/30	110/300
R6	8.89	2.47×10^{-3}	10/30	110/300
R7	8.89	1.59×10^{-3}	10/10	110/300
R8	8.89	1.59×10^{-3}	10/60	110/300
R9	8.89	1.59×10^{-3}	10/100	110/300
R10	8.89	1.59×10^{-3}	10/30	60/350
R11	8.89	1.59×10^{-3}	10/30	80/330
R12	8.89	1.59×10^{-3}	10/30	140/270

Appendix. The latex particle morphologies were determined by transmission electron microscopy (TEM) using a Hitachi H-700 TEM. The zeta-potential value of the lattices was measured by using a Laser Zee Meter (Penkem Inc., model 510 Laser Meter). The latex sample (0.1 ml) was diluted to 40 ml by using the aqueous solution of 0.05 M potassium biphthalate. The molecular-weight distribution (*MWD*) of the polymers was measured using a Waters Associates HPLC/GPC model 510 gel permeation chromatograph.

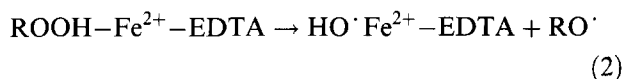
RESULTS AND DISCUSSION

The redox initiator system in this study contained a hydrophobic oxidant (cumene hydroperoxide, CHP), hydrophilic reducing agent (ferrous ion, Fe²⁺, and sodium formaldehyde sulfoxylate, SFS) and chelating agent (ethylenediaminetetraacetic acid, EDTA). The CHP is a radical producer. The SFS is used as a regenerator to get back the Fe²⁺ from Fe³⁺. The chelating agent would complex with Fe²⁺ to prevent Fe²⁺ oxidation in aqueous solution. The main initiation mechanism is described below:

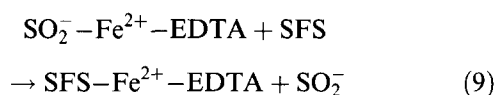
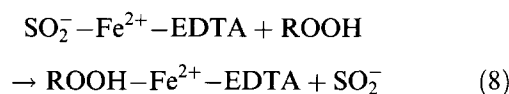
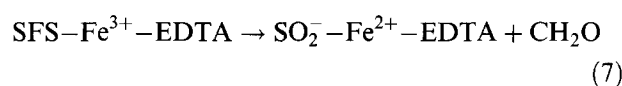
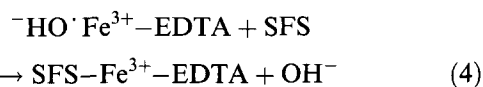
(a) *Diffusion* (The EDTA-Fe²⁺-SFS complex diffused to the interface of monomer droplets from the aqueous phase and reacted with CHP (ROOH))



(b) *Initiation*



(c) *Regeneration*



Reaction (2) is the major element in initiating polymerization. The effects of each component in the mini-emulsion polymerization are described below.

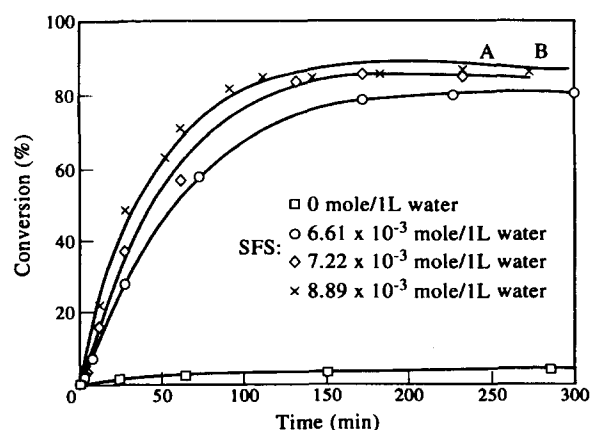
The effect of SFS

The role of SFS was to regenerate the metal oxidants from a higher-valence (Fe³⁺) to lower-valence (Fe²⁺) state, which could then keep on initiating the polymerization. The decomposition rate of CHP was proportional to the Fe²⁺ concentration, and the SFS concentration decreased logarithmically with increasing Fe³⁺ concentration according to the rate equation of the redox reaction, as shown below:

$$-d[\text{CHP}]/dt = k[\text{Fe}^{2+}] \quad (10)$$

$$\ln[\text{SFS}]_0 - \ln[\text{SFS}] = k'[\text{Fe}^{3+}]t \quad (11)$$

In addition, the chelating energy of Fe³⁺ was less than


Figure 1 Conversion vs. time curves for various SFS concentrations

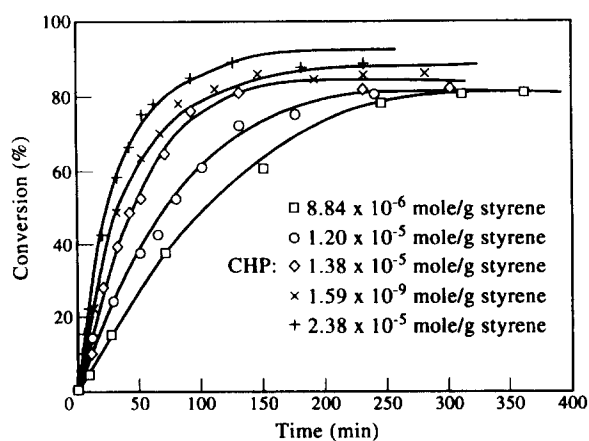


Figure 2 Conversion vs. time curves for various CHP concentrations

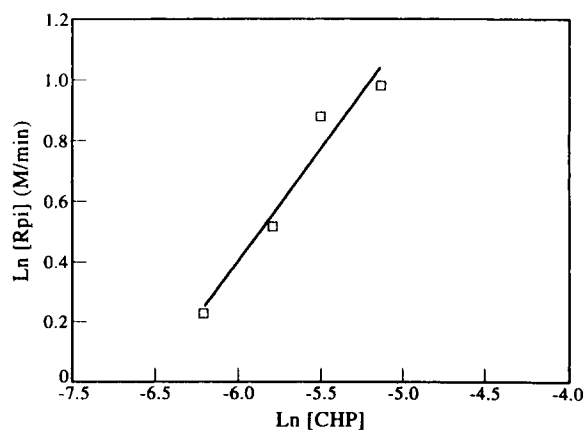


Figure 3 Logarithmic plot of R_{pi} vs. CHP concentration

that of Fe^{2+} . Consequently, if the SFS concentration was not sufficient in the redox system, a large number of Fe^{3+} ions would replace Fe^{2+} to complex with EDTA. In other words, the polymerization should stop under such a circumstance and the monomer would not polymerize completely to polymer at infinite reaction time.

Figure 1 shows the conversion vs. time curves for various SFS concentrations. The polymerization rate obviously decreased with the SFS concentration, and all of the reaction curves did not reach 100% conversion in the same figure. In order to identify whether or not the limiting conversion is due to the insufficiency of SFS,

additional SFS was added to the reaction system when the limiting conversion was reached, which is labelled point 'A' in Figure 1. However, the conversion curves do not increase with additional SFS from point A to point B. The limiting conversions of mini-emulsion polymerization are obviously influenced by other factors. According to the mechanism of mini-emulsion polymerization, one possible explanation is that glassy polystyrene would form gradually in the outer layer of the polymer particle when the monomer conversion increased. This glassy polymer layer should hinder CHP and styrene, which start at the inner region of the particles and diffuse to the surface of the particles for polymerization. Consequently, the limiting conversion is attributed to residual styrene in the inner latex particles.

The effect of CHP

Figure 2 shows that the higher the concentration of CHP, the faster the polymerization rate would be. The polymerization rate was found to depend on the 0.75 power of total CHP concentration from the slope of the straight line in Figure 3, as follows:

$$R_{pi} \propto [CHP]_i^{0.75} \quad (12)$$

It is interesting that no gel effect of polymerization occurred even if a high CHP concentration was used. It means that all of the heat of reaction could be removed effectively in the latex particles. Since there was no accumulation of heat to increase the polymerization rate, so the viscosity of the latex particles did not increase rapidly to gelation. Two possible reasons should be considered. One is that CHP and CA (cetyl alcohol) soluble in the monomer droplets could be used as a plasticizer to plasticize the latex particles when the conversion of polymerization was increased. This could decrease the viscosity of the polymer particles. The other is that most of the polymerization was at the outer layer of polymer particles owing to the interfacial initiator used in our system, and thus the heat of reaction was easily removed by the water phase. In addition, the polymerization rate of the mini-emulsion was lower than that of an emulsion, so the heat of reaction did not accumulate in large quantities in a short time.

The average diameter and size distribution index (D_w/D_n) of polystyrene particles were measured by light scattering, as shown in Table 2. The size distribution of polystyrene particles obtained was very narrow, which is consistent with TEM pictures, as shown in

Table 2 The data of the limiting conversion, zeta potential ($\pm 4\%$), weight-average (D_w) and number-average (D_n) particle sizes ($\pm 3\%$), weight-average (M_w) and number-average (M_n) molecular weights and its distribution ($PDI = M_w/M_n$) for various CHP concentrations of mini-emulsion latex at 70°C; 1000 r.p.m.

CHP (mol)	8.24×10^{-4}	1.20×10^{-3}	1.38×10^{-3}	2.38×10^{-3}
Limiting conversion (%)	80	81	86	88
Zeta potential (mV)	-31	-35	-45	-46
D_w (nm)	135	137	135	123
D_n (nm)	134	136	134	123
D_w/D_n	1.01	1.01	1.01	1.01
$M_w \times 10^5$	2.47	2.32	2.18	2.07
$M_n \times 10^5$	1.43	1.23	1.17	1.24
PDI	1.73	1.89	1.86	1.68

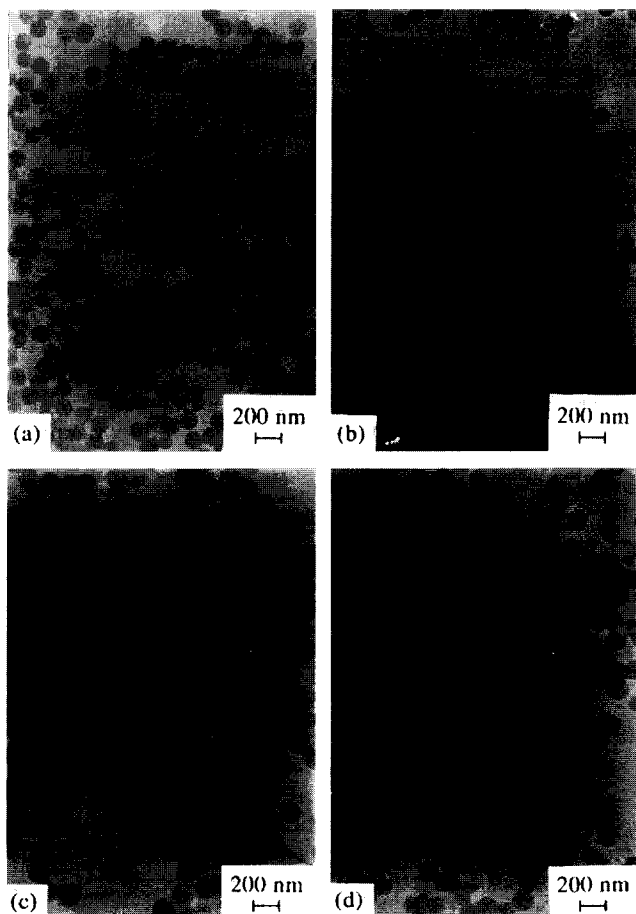


Figure 4 TEM pictures of polystyrene particles prepared by runs (a) R1, (b) R2, (c) R4 and (d) R6 in Table 1

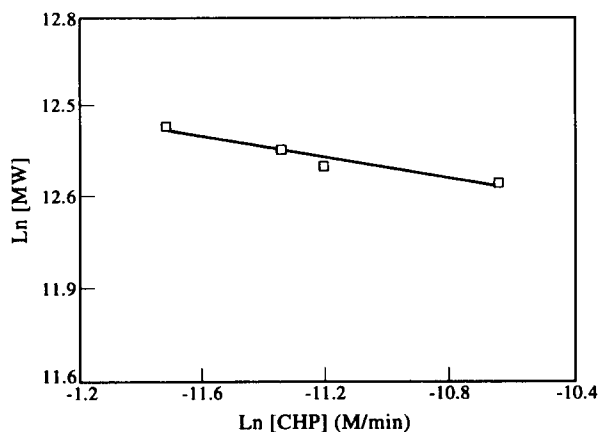


Figure 5 Logarithmic plot of M_w vs. CHP concentration

Figure 4. The diameters of polystyrene particles obtained from this system were very uniform.

Table 2 also shows that the molecular weight of the polystyrene decreased slightly with the CHP concentration. The molecular weight of the polystyrene was found to depend on the -0.15 power of the CHP concentration from the slope of the curves of the logarithm of molecular weight vs. CHP concentration, as shown in Figure 5. That is:

$$M_w \propto [\text{CHP}]_i^{-0.15} \quad (13)$$

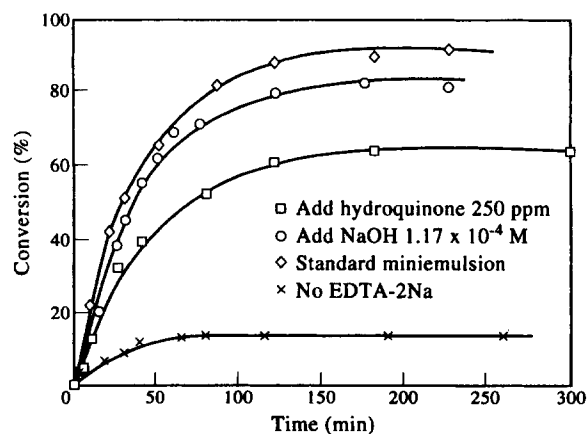


Figure 6 Conversion vs. time curves for different additional substances in mini-emulsion polymerization

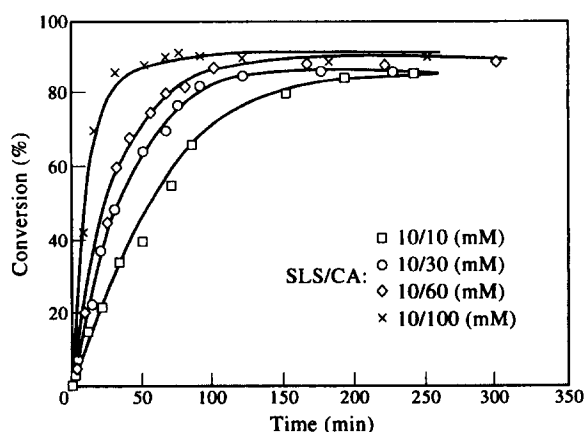


Figure 7 Conversion vs. time curves for various mole ratios of SLS/CA

These results are similar to that reported in the literature^{3,4}. However, the polydispersity index (*PDI*) of the polystyrene obtained from our initiator system was about 1.5–2.0, which was much narrower than the literature value. Consequently, better-quality polystyrene was obtained in our mini-emulsion polymerization system.

The effect of EDTA

The role of EDTA was found to be very important in this redox initiation system. If no EDTA was added in the redox system, the polymerization was slow to proceed, as shown in Figure 6. These results came from the fact that the EDTA– Fe^{2+} complex could avoid Fe^{2+} oxidation to ferric hydroxide ($\text{Fe}(\text{OH})_3$) precipitate, which should lose its reduction ability, and ensure the initiation process in the aqueous solution.

The other conversion curves in Figure 6 represent the effect of the alkalinity of the aqueous solution and hydroquinone (inhibitor) in the aqueous solution for the redox-initiated mini-emulsion polymerization. The Fe^{2+} –EDTA complex should be dissociated when the alkalinity of the aqueous solution was increased, so the increased alkalinity of the aqueous solution should slow down the polymerization rate, as shown in Figure 6. On the other hand, the inhibition effect of hydroquinone in the aqueous solution was less than that reported by

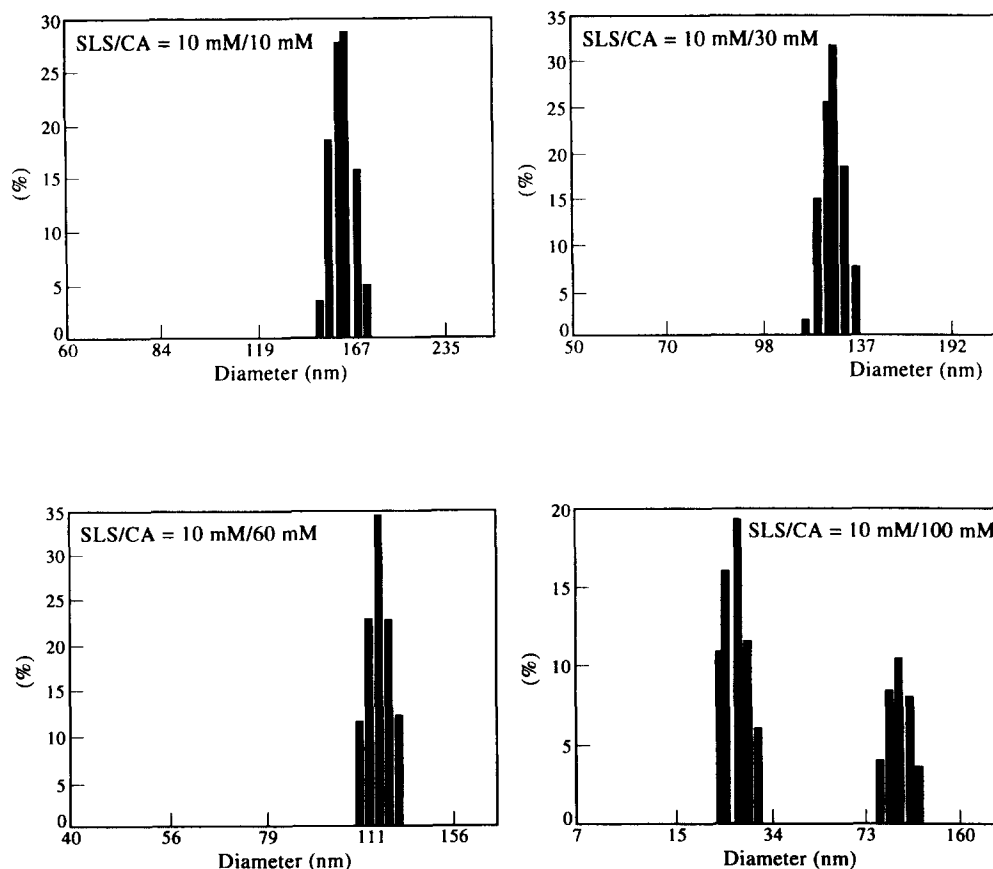


Figure 8 Number-average size distribution of polystyrene obtained at various mole ratios of SLS/CA

Choi *et al.*⁵, whose mini-emulsion polymerization was initiated by an oil initiator (AMBN, azo-bis-2-methylbutyronitrile). Since the radicals obtained with CHP are more hydrophobic than with AMBN from these results, so the radicals in the monomer droplets are scarcely desorbed to the aqueous phase. In other words, a large number of radicals stay on the monomer droplets to polymerization. Consequently, it is appropriate to use this redox initiator system to initiate the mini-emulsion polymerization.

The effect of surfactant/cosurfactant ratio

Figure 7 shows the conversion vs. time for various cosurfactant (CA) concentrations (10, 30, 60 and 100 mM) at the same SLS concentration (10 mM). The polymerization rate was increased with the CA concentration. These results were attributed to the fact that an increase in the CA concentration caused small latex particle size with large surface areas, as shown in Figure 8. The surface areas in the emulsion polymerization are seen to increase with polymerization rate. Therefore, the reaction rate increased with the CA concentration. Since the run with 100 mM CA concentration was over the CMC (critical micelle concentration) from the conductivity meter measurement, a great number of micelles should form in the aqueous solution and compete with the monomer droplets to capture the radicals. These are the reasons why bimodal particle size distributions were obtained.

The stability of mini-emulsions has been studied by many investigators. However, the stability of polymer particles obtained from mini-emulsion polymerization

has been reported less often in the literature. The zeta-potential value is the index of critical coagulation concentration (CCC) of the latex, and the location of CCC is a useful guide to understand the effect of an electrolyte on stability. The value²⁶ of the zeta potential of emulsion solutions is usually correlated with particle mobility, and the particle mobility is primarily dependent on the particle diameters and surface electrical charge densities. The particle diameters can be determined using light scattering or SEM. Therefore, for an emulsion solution with a particular average particle size, the zeta potential may be used qualitatively to correlate with the surface charge densities, which are related to the emulsion stabilities. So, the stability of the polymer particles was measured by using a zeta-potential meter in this study. The result is shown in Table 3. The more

Table 3 The data of the limiting conversion, zeta potential ($\pm 4\%$) weight-average (D_w) and number-average (D_n) particle sizes ($\pm 3\%$), weight-average (M_w) and number-average (M_n) molecular weights and its distribution ($PDI = M_w/M_n$) for different SLS:CA ratios of mini-emulsion latex at 70°C; 1000 r.p.m.

SLS:CA (mM)	10:10	10:30	10:60	10:100
Limiting conversion (%)	85	87	89	90
Zeta potential (mV)	-42	-45	-37	-43
D_w (nm)	150	123	117	48
D_n (nm)	149	122	116	26
D_w/D_n	1.01	1.01	1.01	1.85
$M_w \times 10^5$	3.39	2.17	2.44	2.17
$M_n \times 10^5$	1.46	1.17	1.20	1.22
PDI	2.32	1.86	2.03	1.78

negative the values of the zeta potential, the more stable is the latex. The order of polymer latex stability obtained from various ratios of SLS:CA was $1:3 > 1:10 > 1:1 > 1:6 > 1:0$, which was consistent with the stability of monomer droplets reported by Choi⁵, $1:3 > 1:2 > 1:1 > 1:6 > 1:0$. Furthermore, a two-dimensional hexagonal packing of molecules has been reported to form at a mole ratio of SLS:CA of 1:3 in the system of surfactant/cosurfactant studied by Shah²⁷. The good

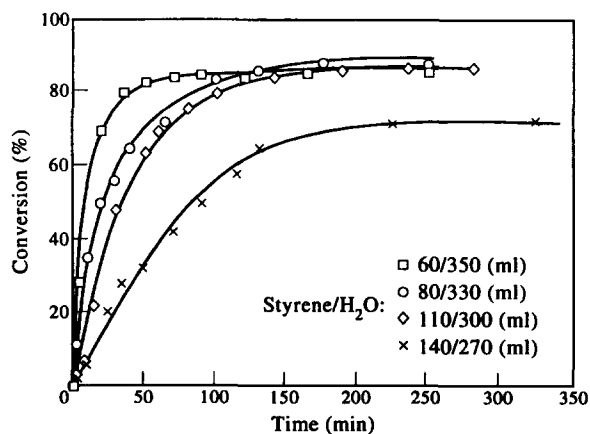


Figure 9 Conversion vs. time curves for various ratios of styrene/H₂O

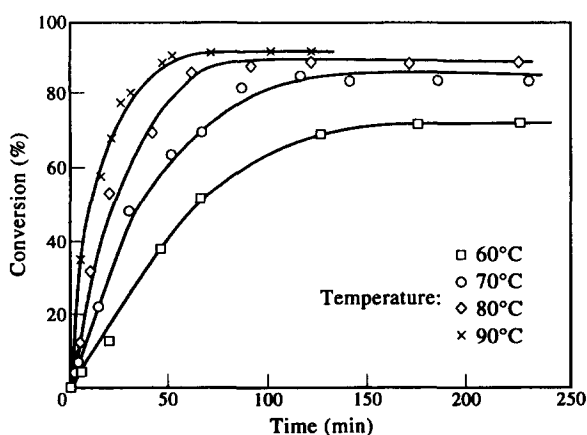


Figure 10 Conversion vs. time curves for different reaction temperatures

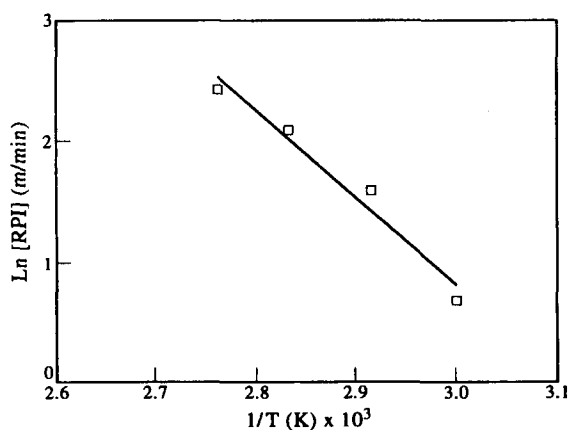


Figure 11 Arrhenius plot for the mini-emulsion polymerization initiated by redox initiator

Table 4 The effect of the different volume ratios of styrene:H₂O on the zeta potential ($\pm 4\%$), limiting conversion and average particle sizes ($\pm 3\%$) at 70°C; 1000 r.p.m.

Styrene:H ₂ O	60:350	80:330	110:300	140:270
Limiting conversion (%)	84	88	87	74
Particle sizes (nm)	92	112	123	152
Zeta potential (mV)	-46	-44	-45	-33

Table 5 The effect of various reaction temperatures on the zeta potential ($\pm 4\%$), limiting conversion and average particle sizes ($\pm 3\%$) at 70°C; 1000 r.p.m.

Temperature (°C)	60	70	80	90
Limiting conversion (%)	76	87	89	92
Particle sizes (nm)	124	123	104	101
Zeta potential (mV)	-38	-45	-46	-43

packing brought excellent stability of monomer droplets, and it remained intact through the polymerization process. Consequently the best stability of polymer latex was obtained with this mole ratio.

The effect of styrene concentration

In conventional emulsion polymerization, the reaction rate was proportional to the monomer concentration. However, different results were obtained according to Figure 9. The higher the monomer concentration, the lower is the polymerization rate in mini-emulsion polymerization. These different results arise because the high monomer concentration should increase the particle size with lower total surface area of latex. The concentration of CHP in the monomer droplets also decreases. Thus, the polymerization rate was decreased with increasing monomer concentration.

Table 4 shows the stability of the polymer particles and the limiting conversion for various monomer concentrations. The particle stability and the limiting conversion of those runs have a similar tendency according to the results in Table 4, except for the 140:270 styrene:water ratio, which yielded the lowest particle stability and limiting conversion. The concentration of the surfactants was obviously not enough to stabilize the polymer particles. The low CHP concentration in latex particles and the long diffusion paths of styrene in large particle sizes should decrease the polymerization rate and the limiting conversion.

The effect of reaction temperature

The reaction rate of mini-emulsion polymerization was increased with temperature, as shown in Figure 10. Following the Arrhenius equation, the apparent overall activation energy was obtained, which was 52.6 kJ mol^{-1} and was in the range of the redox polymerization system, as shown in Figure 11.

Table 5 shows that the reaction temperature would influence not only the polymerization rate but also the limiting conversion. These results showed again that diffusion of the reaction components was the important factor for the limiting conversion. When the reaction temperature increased, the inner viscosity of latex particles should decrease, which could promote the diffusion rate of styrene and CHP in the polymer

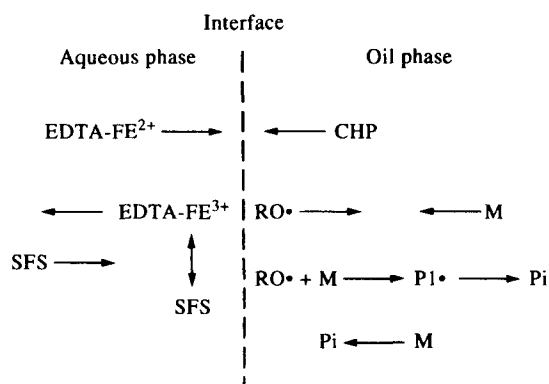


Figure 12 Schematic representation of initiation process at the interface

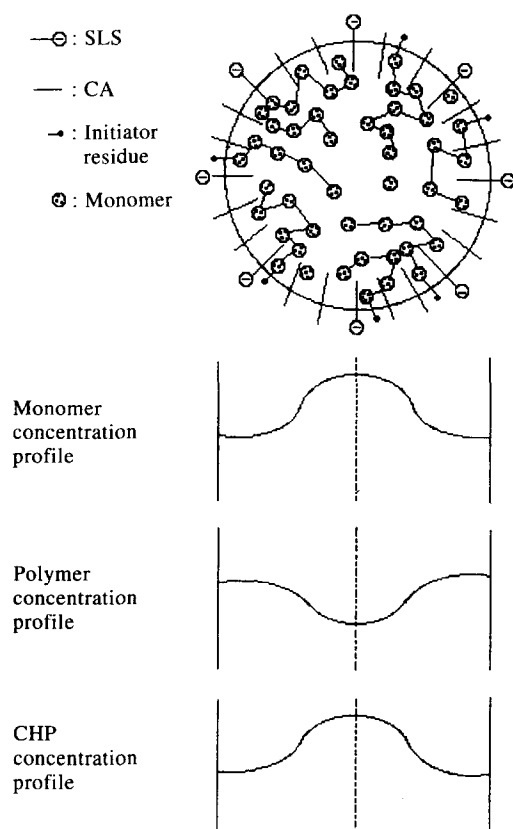


Figure 13 Schematic representation of an event occurring during the mini-emulsion polymerization of styrene, and the concentration profile of content in latex particle

particles. Thus, the conversion of polymerization was higher.

Illustration of reaction behaviour of mini-emulsion polymerization initiated by redox initiator

According to the above results, the reaction behaviour of mini-emulsion polymerization in this study is illustrated as below:

(1) The hydrophobic radicals ($RO\cdot$) were obtained by the redox reaction of CHP and Fe^{2+} . The Fe^{3+} would be regenerated by the reducing agent SFS, which could keep on initiating polymerization.

(2) The hydrophobic radicals ($RO\cdot$) were first to initiate the styrene monomers to oligomer radicals ($P_1\cdot$)

at the surface of the monomer droplets. And, the styrene and CHP gradually diffused out to supply the monomer consumption at the outer layer of the latex particles. The $P_1\cdot$ would also diffuse to inner latex particles to polymerize. The $EDTA-Fe^{3+}$ complex, which was obtained by the reaction of CHP with $EDTA-Fe^{2+}$, would diffuse from the particle interface to the aqueous phase and would be regenerated into $EDTA-Fe^{2+}$ with the reducing agent SFS. The $EDTA-Fe^{2+}$ could diffuse to the particle interface to react with CHP, again. The overall polymerization is illustrated in *Figure 12*.

(3) The concentration distributions of each component in the latex particles are illustrated in *Figure 13*. The initiation polymerization was in the outer layer of polymer particles, and the viscosity of the outer layer of polymer particles increased with reaction conversion. When the viscosity of the polymer layer became higher, the CHP and styrene diffusion rate would slow down. Thus, the concentration of CHP and styrene in the outer layer should be lower than in the inner latex particles, as shown in *Figure 13*. However, the concentration distribution of each reactant should level off gradually.

CONCLUSION

Homogeneous nucleation in the aqueous phase and the gel effect in polymer particles were avoided when an interfacial redox initiator system was used to initiate the mini-emulsion polymerization of styrene. Polystyrene particles with a narrow distribution of molecular weight ($PDI = 1.5-2.0$) were obtained.

The polymerization rate was increased with CHP, SFS and reaction temperature. The CHP and CA soluble in polymer particles could act as a plasticizer to plasticize the polystyrene in the polymer particles, which could decrease the viscosity of the polymer particles and promote the limiting conversion of mini-emulsion polymerization. The high styrene concentrations used would increase the monomer droplet sizes, but decrease the CHP concentration. Thus, the polymerization rate would decrease. The higher stability of the mini-emulsion could produce polymer particles of better stability. The decreasing order of the SLS:CA ratios for preparing high-stability polymer particles was $1:3 > 1:10 > 1:1 > 1:6 > 1:0$.

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APPENDIX A

The method used to analyse particle sizes

The average diameters of polymer particles were calculated using the software of the Otsuka DLS700 laser light scattering spectrophotometer. The correlation function is a cumulative method, as shown below:

$$\ln[g_1(\gamma)] = \sum K_m(\Gamma)(-\gamma)^m m! \quad (\text{A1})$$

$$K_1 = \langle \Gamma \rangle = \int \Gamma G(\Gamma) d\Gamma / \int G(\Gamma) d\Gamma \quad (\text{A2})$$

$$K_2 = \mu_2 - K_1^2 \quad (\text{A3})$$

where $g_1(\gamma)$ = first-order correlation function, γ = correlation time, K_m = m th cumulant, Γ = average decay constant, μ_2 = polydispersity index and $G(\Gamma)$ = Laplace transform of $g_1(\gamma)$.

The K_1 and K_2 are obtained by mathematics analysis and curve-fitting method. Then, the average diameter of polymer particles (D_p) is obtained by the Einstein-Stokes equation, as shown below:

$$D_p = KT/(3\pi\eta D) \quad (\text{A4})$$

$$D = \langle \Gamma \rangle / q^2 \quad (\text{A5})$$

$$q = 4\pi n / [\lambda \sin(\theta/2)] \quad (\text{A6})$$

where K = Boltzmann's constant, T = absolute temperature, η = solvent viscosity, D = diffusion constant of particle, n = refractive index factor of solvent, λ = wavelength of the laser and θ = scattering angle. The D_p is a cumulative average diameter.