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ORIGINAL CONTRIBUTION

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Miniemulsion polymerization of styrene using alkyl methacrylates as the reactive cosurfactant

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Abstract Stable styrene miniemulsions were prepared by using alkyl methacrylates as the reactive cosurfactant. Like conventional cosurfactants (e.g., cetyl alcohol (CA) and hexadecane (HD)), alkyl methacrylates (e.g., dodecyl methacrylate (DMA) and stearyl methacrylate (SMA)) may act as a cosurfactant in stabilizing the homogenized miniemulsions. Furthermore, the methacrylate group may be chemically incorporated into latex particles in subsequent miniemulsion polymerization. The data of the monomer droplet size, creaming rate and phase separation of monomer as a function of time were used to evaluate the shelf-life of miniemulsions stabilized by sodium dodecyl sulfate in combination with various cosurfactants. Polystyrene latex particles were produced via both monomer droplet nucleation and homogeneous nucleation in the miniemulsion polymerization using CA or DMA as the cosurfactant, with the result of a quite broad particle size distribution. On the other hand, the miniemulsion polymerization with HD or SMA showed a predominant monomer droplet nucleation. The resultant particle size distribution was relatively narrow. In miniemulsion polymerization, the less hydrophobic DMA is similar to CA, whereas the more hydrophobic SMA is similar to HD.

Key words Miniemulsion polymerization – reactive cosurfactants – styrene – alkyl methacrylates – emulsion stability

Introduction

Miniemulsion polymerization [1–4] involves dissolution of a water-insoluble, low molecular weight cosurfactant into monomer, followed by mixing the oil mixture with an aqueous surfactant solution in a high-shear mixer. The resultant miniemulsion comprising submicron monomer droplets is then polymerized by a persulfate initiator. Adequate emulsion stability during storage or polymerization can be achieved by an anionic surfactant to prevent coalescence among the interactive droplets in combination with a cosurfactant to retard diffusion of monomer from small droplets to large droplets (Ostwald ripening). One problem associated with conventional cosurfactants (e.g., hexadecane (HD) and cetyl alcohol (CA)) is the need for removing these compounds from latex products. This is because HD left in latex products evaporates slowly and may thus cause VOC problem. The cosurfactant CA has a hydroxyl group and it may reduce the water resistance of miniemulsion polymers. To overcome these drawbacks, a polymeric hydrophobe has been used as the sole cosurfactant to prepare kinetically stable miniemulsions [5–7]. The resultant miniemulsions are capable of resisting diffusional degradation long enough to allow monomer droplet nucleation to occur.

In this report, we demonstrate the use of a reactive cosurfactant, stearyl methacrylate (SMA) or dodecyl methacrylate (DMA), in styrene (ST) miniemulsion polymerization. Like conventional cosurfactants, alkyl methacrylates may act as a cosurfactant in stabilizing the homogenized miniemulsions. Furthermore, the methacrylate group may be chemically incorporated into polymer particles in subsequent polymerization and, thereby, partially resolve the contamination problem. This is because the residual surfactant (e.g., sodium dodecyl sulfate (SDS)) may also cause problems (e.g., reduction in adhesion of a pressure-sensitive adhesive). As polymerization proceeds, the reactive cosurfactant concentration in the nucleated droplets will decrease. The initial depletion of cosurfactant should not cause any diffusional degradation because the hydrophobic polymer formed inside the droplets can help stabilize the polymerizing miniemulsion. For the moment, we will focus on evaluation of these reactive cosurfactants (SMA and DMA) in comparison with HD and CA. Thus, SDS was selected as the primary surfactant because it has been widely used in ST miniemulsion polymerization. Nevertheless, the reactive surfactant, sodium dodecyl allyl sulfosuccinate studied in our previous work [8, 9], in combination with SMA or DMA was also included in this work to study the feasibility of producing latices free from low molecular weight contaminants.

Experimental

Materials

The chemicals used in this work include styrene (Taiwan Styrene Co.), sodium dodecyl sulfate (Henkel Co.), sodium alkyl allyl sulfosuccinate (Eleminol JS-2) (Sanyo Chemical Industries), stearyl methacrylate (Mitsubishi Rayon), dodecyl methacrylate (Aldrich), hexadecane (Sigma), cetyl alcohol (Osaka Hayashi Pure Chemical Industries), sodium persulfate (Riedel-de Haen), sodium bicarbonate (Riedel-de Haen), nitrogen (Ching-Feng-Harng Co.) and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance $<0.057\ \mu\text{S}\,\text{cm}^{-1}$). Styrene was distilled under reduced pressure before use. All other chemicals were used as received.

Preparation of miniemulsions

The miniemulsion containing SMA, DMA or HD was prepared by dissolving SDS in water and the cosurfactant in the monomer, respectively. The oily and aqueous solutions were mixed with a mechanical agitator at 400 rpm for 10 min. The resultant emulsion was then homogenized by the Microfluidizer-110Y (Microfluidics Co.), operated at 5000 psi outlet pressure and 10 passes. For the CA containing miniemulsion, SDS and CA were first dissolved in water at 65 °C for 2 h, cooled to 25 °C to form a gel phase, and then homogenized by the microfluidizer (5 000 psi, 5 passes) to break up the gel phase. Styrene was then added to the SDS/CA solution subject to mechanical agitation at 400 rpm for 10 min, followed by homogenization using the microfluidizer (5 000 psi, 10 passes).

The shelf-life of a miniemulsion was monitored by placing about 100 mL sample in a capped glass vial at 35 °C for one month. The position of the creaming line from the bottom of the sample and the time necessary for a visible monomer phase on the top of the sample to appear were then recorded.

Polymerization process

Polymerization was carried out in a 250 ml reactor equipped with a four-bladed fan turbine agitator, a thermometer, and a reflux condenser. Immediately after homogenization, the resultant miniemulsion was charged into the reactor and then purged with N_2 for 10 min while the reactor temperature was brought to 80 °C. A typical miniemulsion charge comprises 155.56 g water, 0.0356 g sodium bicarbonate (2.64 mM based on total water), 0.230 g SDS (5 mM based on total water), 1.079 g SMA (20 mM based on total water) and 39.85 g ST. The molar ratio of surfactant to cosurfactant was kept constant at 1:4 throughout this work. The reaction was then initiated by addition of the initiator solution comprising 5 g water and 0.102 g sodium persulfate (2.66 mM based on total water). Polymerization temperature was kept at 80 °C throughout the reaction (reaction time = 4 h). The theoretical solid content of the latex product is 20.6%.

The latex product was filtered through 40-mesh (0.42 mm) and 200-mesh (0.074 mm) screens in series to collect the filterable solids. Scraps adhering to the agitator, thermometer and reactor wall were also collected. Total solid content and conversion of styrene (X) as a function of time were determined by the gravimetric method.

Determination of monomer droplet size (or latex particle size)

The data of average monomer droplet size (or latex particle size) were obtained from the dynamic light scattering method (Otsuka Photal LPA-3000/3100). The sample was diluted with water to adjust the number of photons counted per second (cps) to 8000–12 000. The dilution water was saturated with surfactant and monomer and, consequently, diffusion of SDS and ST from monomer droplets (or monomer-swollen latex particles) into water was prohibited. The reported data represent an average of at least three measurements and the errors have been estimated to be 8% or less.

Results and discussion

Monomer droplet size of miniemulsions upon aging

Figure 1 shows the average monomer droplet size (d_m) data as a function of time (t) for miniemulsions prepared by various cosurfactants. The SDS concentration ([SDS]) was kept constant at 5 mM, slightly above its CMC (3 mM at 25 °C [10]). After homogenization, the SDS concentration in water should be below its CMC because most of the SDS molecules are adsorbed on the huge droplet surface area. The cosurfactant concentration was kept constant at 20 mM. The steady state value of d_m for miniemulsions aging at 35 °C for 4 h (see Table 1) in the decreasing order is: CA (390 nm) > DMA (290 nm) > SMA (125 nm) ~ HD (115 nm). According to the method of Small's group molar attraction constant [11], the solubility parameters (δ) for CA, DMA, SMA, and HD are 18.5, 16.8, 16.7 and 15.9 $(\mathrm{MPa})^{1/2}$, respectively. The group molar attraction constant of the hydroxyl group for CA was estimated from the δ data of octyl alcohol (21.1 $(\mathrm{MPa})^{1/2}$) since it is not available in the literature. For the homologous series of fluorocarbons, however, each additional unit of $-CF_2-$ reduces the water solubility by a factor of 8 [12]. Similarly, the cosurfactant SMA which has 6 more units of $-CH_2-$ should be more hydrophobic than DMA even though the difference in the estimated values of δ is only 0.1 $(\mathrm{MPa})^{1/2}$. Thus, the hydrophobicity of the cosurfactant in the decreasing order: HD > SMA > DMA > CA. Figure 1 shows that the steady state value of d_m remains relatively constant for the miniemulsion prepared by the more hydrophobic cosurfactant, HD or SMA. On the other hand, the steady state value of d_m increases rapidly when the less hydrophobic CA or DMA is used as the cosurfactant. In addition, the initial d_m data (139 ± 28 nm) seem insensitive to the type of cosurfactants. This is due to the same SDS concentration and homogenization condition used in this series of experiments. The slightly scattered data is caused by different rates of Ostwald ripening.

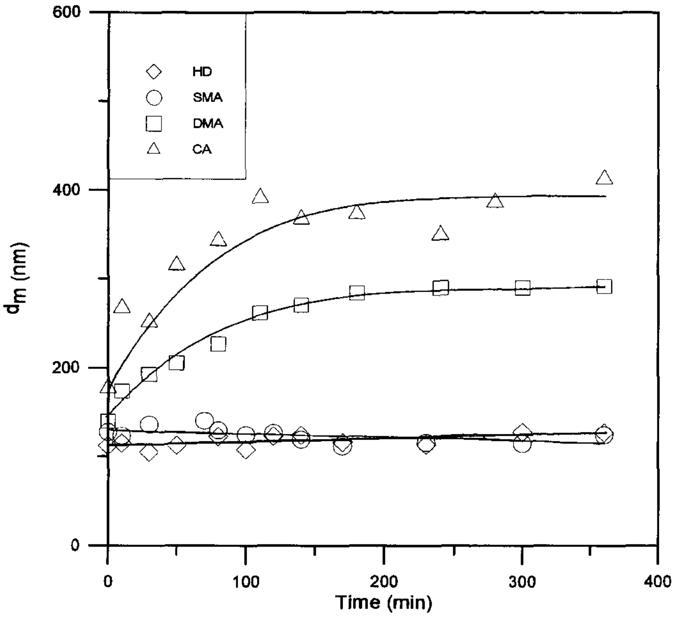


Fig. 1 Average monomer droplet size upon aging at 35 °C as a function of time for miniemulsions prepared by various cosurfactants: [SDS] = 5 mM; cosurfactant concentration = 20 mM. (◇) HD, (○) SMA, (□) DMA, (△) CA

The monomer droplet size increases gradually and then levels off for the miniemulsion with CA or DMA. This is because the initial droplet size distribution is relatively broad. Thus, the monomer in small droplets tends to diffuse into water and then into large droplets because the monomer solubility in water increases with decreasing droplet size (Ostwald ripening). This leads to a gradual increase in d_m with time. Ostwald ripening is counterbalanced by the osmotic pressure built up later in the aging process and, as a result, d_m approaches a steady value (see Fig. 1). On the other hand, for the miniemulsion with HD

Table 1 Steady state values of the monomer droplet size (d_m) for the miniemulsions measured after four hours aging

	CS1	CS2	CS3	CS4	S1	S2	S3	S4	S5	S6
Surfactant type	SDS	SDS	SDS	SDS	SDS	SDS	SDS	SDS	JS-2	JS-2
Conc. (mM)[a]	5	5	5	5	10	10	2.5	2.5	5	5
Cosurfactant type	CA	DMA	SMA	HD	DMA	SMA	DMA	SMA	DMA	SMA
Conc. (mM)[a]	20	20	20	20	40	40	10	10	20	20
Steady value of d_m at 4 h (nm)	390	290	125	115	234	108	350	162	288	162

[a] Based on total water.

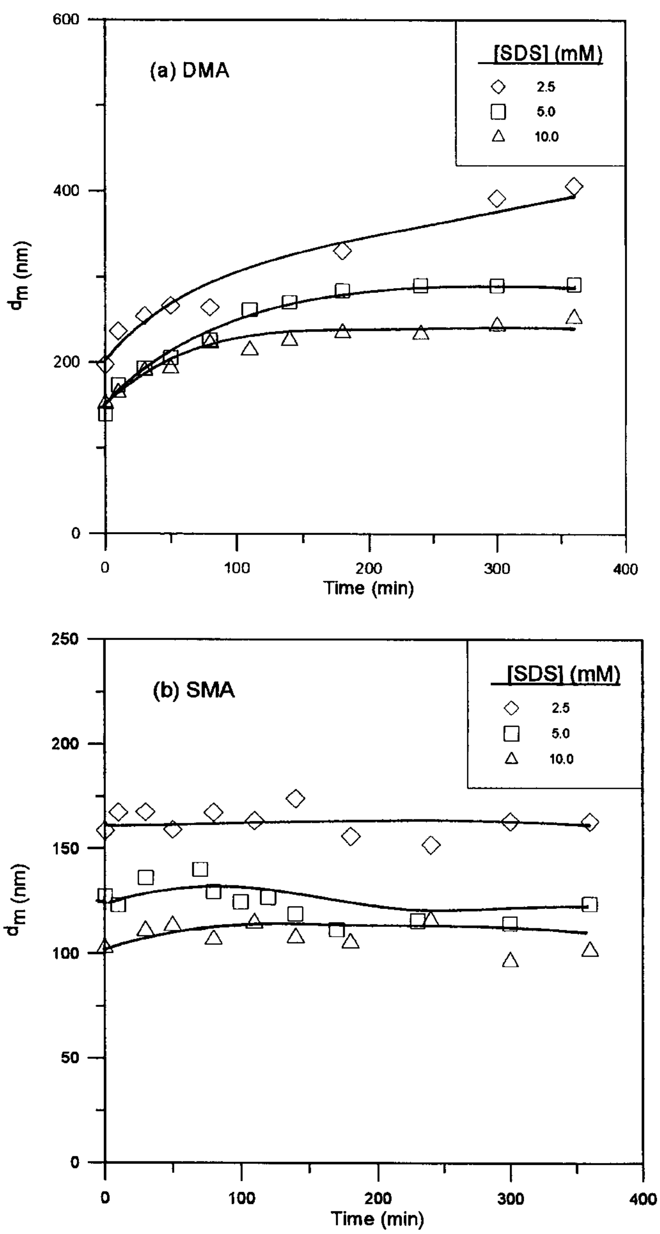


Fig. 2 Average monomer droplet size upon aging at 35 °C as a function of time for miniemulsions prepared by various concentrations of surfactants and cosurfactants. (a): (◇) 2.5 mM SDS + 10 mM DMA, (□) 5 mM SDS + 20 mM DMA, (△) 10 mM SDS + 40 mM DMA; (b): (◇) 2.5 mM SDS + 10 mM SMA, (□) 5 mM SDS + 20 mM SMA, (△) 10 mM SDS + 40 mM SMA

or SMA d_m remains relatively constant due to the extremely hydrophobic cosurfactant.

The d_m vs. t data for the miniemulsion with DMA or SMA at various levels of [SDS] are shown in Fig. 2. The molar ratio of SDS to DMA or SMA was kept constant at 1:4. The steady state value of d_m decreases with increasing [SDS] regardless of the type of cosurfactants. This is because more SDS is available for stabilizing the droplet surface area generated by shear force. Thus, a reduction in d_m is observed when [SDS] increases from 2.5 to 10.0 mM. At constant [SDS], the steady state value of d_m for the miniemulsion with SMA is smaller than that for the miniemulsion with DMA. Furthermore, the degree of Ostwald ripening is the greatest for the miniemulsion prepared by 2.5 mM SDS and 10.0 mM DMA. This is because the DMA concentration is not high enough to counteract diffusional degradation (see the diamond data points in Fig. 2a). Figure 3 shows the logarithmic plot of d_m at 4 h as a function of [SDS] for miniemulsions with DMA (slope = − 0.16) and SMA (slope = − 0.30), respectively. These data suggest that d_m is more sensitive to changes in [SDS] when SMA is chosen as the cosurfactant.

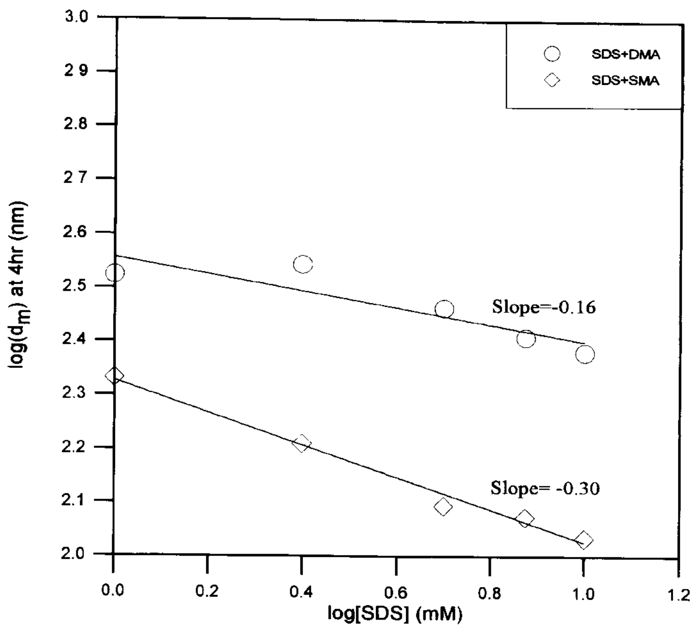


Fig. 3 Logarithmic plot of average monomer droplet size upon aging at 35 °C for 4 h as a function of [SDS] for miniemulsions prepared by different cosurfactants: cosurfactant concentration = 4 × [SDS]. (○) DMA, (◇) SMA

Figure 4 shows the d_m vs. t data for miniemulsions with different combinations of surfactants (SDS vs. JS-2) and cosurfactants (DMA vs. SMA). The concentrations of surfactant and cosurfactant were kept constant at 5 and 20 mM, respectively. The JS-2 concentration is about one order of magnitude greater than its CMC (0.61 mM) [8]. However, the concentration of free JS-2 in water is much lower than 5 mM due to the huge droplet surface area generated after homogenization. The d_m data show that

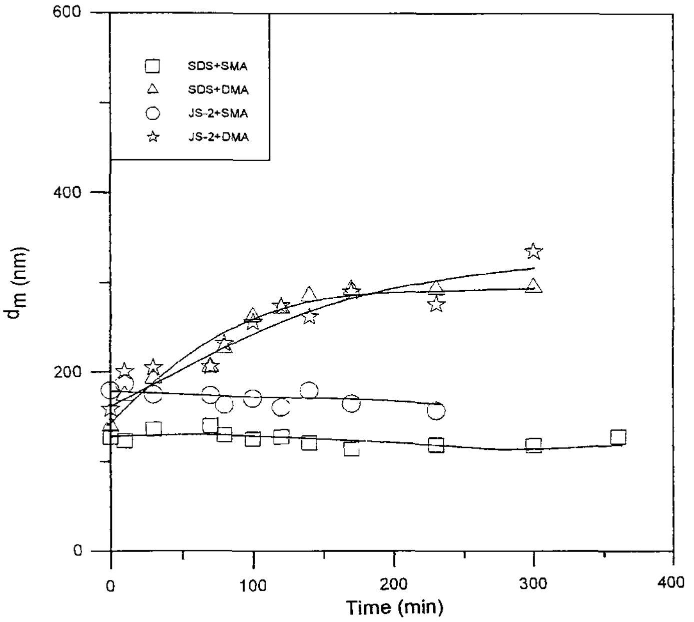


Fig. 4 Average monomer droplet size upon aging at 35 °C as a function of time for miniemulsions prepared by different types of surfactants and cosurfactants: concentrations of surfactant and cosurfactant are 5 mM and 20 mM, respectively. (□) SDS + SMA, (△) SDS + DMA, (○) JS-2 + SMA, (☆) JS-2 + DMA

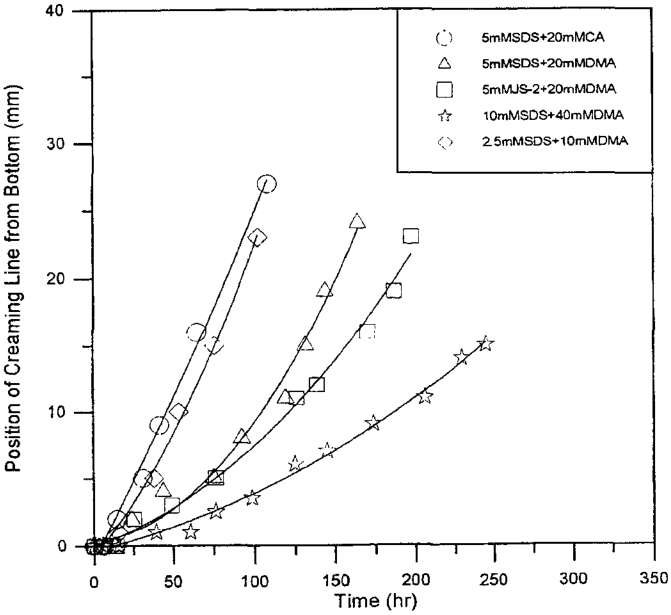


Fig. 5 Position of creaming line from the bottom of the miniemulsion as a function of time. (○) 5 mM SDS + 20 mM CA, (◇) 2.5 mM SDS + 10 mM DMA, (△) 5 mM SDS + 20 mM DMA, (□) 5 mM JS-2 + 20 mM DMA, (☆) 10 mM SDS + 40 mM DMA

SDS is more effective in reducing the droplet size than JS-2 when SMA is chosen as the cosurfactant. On the contrary, no significant difference in the d_m profiles is detected for the miniemulsions with DMA. Again, strong Ostwald ripening was experienced for the miniemulsions containing the less hydrophobic DMA.

Shelf stability of miniemulsions

The creaming data are shown in Fig. 5, where the ordinate represents the position of the creaming line from the bottom of the sample. No creaming phenomenon was observed for miniemulsions prepared by (i) 5 mM SDS + 20 mM HD, (ii) 2.5 mM SDS + 10 mM SMA, (iii) 5 mM SDS + 20 mM SMA, (iv) 10 mM SDS + 40 mM SMA and (v) 5 mM JS-2 + 20 mM SMA. The effect of the cosurfactant type on the creaming rate in the decreasing order is as follows: CA > DMA $\gg$ SMA ~ HD. The creaming rate is relatively insensitive to the surfactant type (i.e., SDS vs. JS-2). The data also show that the creaming rate decreases with increasing surfactant concentration.

Interesting enough, a separate monomer phase on the top of the sample was observed for miniemulsions prepared by (i) 5 mM SDS + 20 mM HD (310 h, 115 nm), (ii) 2.5 mM SDS + 10 mM SMA (21.0 h, 162 nm), (iii) 5 mM SDS + 20 mM SMA (49.5 h, 125 nm), (iv) 10 mM SDS + 40 mM SMA (52.5 h, 108 nm) and (v) 5 mM JS-2 + 20 mM SMA (11.5 h, 162 nm). The numeric values shown in the above parenthesis represent the time (t_s) when a monomer layer on the top of the sample is observed and the steady state value of d_m at 4 h, respectively. The miniemulsion stabilized by JS-2/SMA shows the worst performance in this category. However, even these JS-2 containing monomer droplets are stable enough to become nucleated in the subsequent polymerization. For the miniemulsion with DMA, eventually there was no monomer layer on the top of the sample. One common feature of the samples showing phase separation of monomer is the smaller d_m at steady state (110–160 nm) in comparison with those creamed samples (230–390 nm) (see Table 1). It is postulated that the miniemulsion showing insignificant Ostwald ripening has a huge droplet–water interfacial area. The surface coverage of droplets by surfactant may be insufficient to stabilize these innumerable tiny droplets which are strongly influenced by Brownian motion. The unstable monomer droplets may undergo intensive coalescence and, thereby, lead to a visible monomer layer on the top of the sample due to the gravitational force. To verify this postulation, a miniemulsion stabilized by JS-2/SMA was prepared, followed by post-addition of SDS (6.2 mM) to the miniemulsion. The sample was mixed for 30 min at 25 °C by a magnetic stirrer to ensure that the added SDS became adsorbed on the droplet surfaces. Such a low shear force should not change the monomer droplet size. The sample was then aged at 35 °C and no phase separation of monomer was observed over a period of 48 h. This serves as supporting evidence of the above speculation. For experiments CS3, S2 and S4, t_s increases with increasing [SDS] (i.e., increasing droplet stability against coalescence) (see Table 1). On the other hand, the creamed miniemulsion shows a quite large d_m at steady state due to Ostwald ripening. Thus, droplet surfaces are well covered by surfactant and further coagulation is greatly retarded.

Judging from the data of droplet size, creaming rate, and monomer phase separation, HD with the lowest δ (15.9(MPa)$^{1/2}$) is the best among the cosurfactants studied. Alkyl methacrylates (DMA and SMA) are capable of producing relatively stable miniemulsions. The performance of DMA is similar to that of CA, whereas the performance of SMA is similar to that of HD. The values of δ for ST and water are 19.0 and 47.9(MPa)$^{1/2}$, respectively [11]. The cosurfactant CA ($\delta = 18.5$(MPa)$^{1/2}$) has a hydroxyl end-group ($-$OH) which forms hydrogen bond with water. Thus, CA packs at the interspace between SDS molecules on the droplet surface. The resultant intermolecular complexes at the oil–water interface impart a low interfacial tension and high resistence to coalescence of droplets [13–16]. On the other hand, HD ($\delta =$ 15.9(MPa)$^{1/2}$) containing no polar groups is distributed more uniformly in the droplets. As to alkyl methacrylates, the polar ester group will pull the cosurfactant toward the oil–water interface. The cosurfactant SMA has a longer alkyl chain (i.e., more hydrophobic) and this makes the species more like HD. On the other hand, DMA has a shorter alkyl chain (i.e., less hydrophobic) and the performance of DMA moves away from that of HD.

Miniemulsion polymerization of styrene

The recipes and data for miniemulsion polymerizations stabilized by various cosurfactants are listed in Tables 1 and 2, respectively. The conversion of styrene (X) vs. t profiles are shown in Fig. 6. The initiator concentration was kept constant at 2.66 mM based on total water. Table 2 shows that all miniemulsion polymerizations have comparable polymerization rates (dX/dt) except for the JS-2 stabilized miniemulsion polymerization. In addition to the lower dX/dt, only 62% conversion was achieved at the end of polymerization for the JS-2 stabilized system. This is probably due to chain transfer of radicals to sodium alkyl allyl sulfosuccinate (JS-2) via the α-hydrogen abstraction mechanism. The resultant JS-2 radicals may desorb from latex particles, reduce the average number of radicals per particle and, thereby, decrease dX/dt. Another possible cause is the retarded polymerization of styrene by JS-2 due to their unfavorable reactivity ratios. A reactive surfactant showing improved copolymerizability with styrene is needed to cooperate with alkyl methacrylates in producing miniemulsion polymers free from low molecular weight contaminants.

In miniemulsion polymerization, latex particles are nucleated via capture of radicals by monomer droplets. For the system with CA, monomer droplet nucleation may take a long time to be finished (beyond 30% conversion) and only a fraction of these droplets becomes latex particles [17]. This is attributed to the slower entry rate of radicals caused by intermolecular complexes at the oil–water interface. Note that monomer droplets may coexist with latex particles in the reaction system and, hence, the dynamic light scattering data only represent the average particle size (d) of the mixture comprising latex particles and monomer droplets.

Table 2 Results obtained from the miniemulsion polymerizations stabilized by various types of cosurfactants

	CS1	CS2	CS3	CS4	S6
$d_{m,i}$ (nm)[a]	351	299	138	148	119
$N_{m,i} \times 10^{-17}$ (1/L-H$_2$O)[b]	0.124	0.201	2.062	1.644	3.184
$d_{p,f}$ (nm)[c]	125	148	145	149	186
(u/G^2)[d]	1.17×10^{-1}	1.50×10^{-1}	3.53×10^{-2}	8.5×10^{-2}	—
$N_{p,f} \times 10^{-17}$ (1/L-H$_2$O)[e]	2.386	1.456	1.563	1.409	0.772
$N_{p,f}/N_{m,i}$	19.24	7.24	0.76	0.86	0.24
X_f(%)[f]	98.0	89.4	90.6	89.2	61.5
$dX/dt \times 10^2$ (1/min)	1.43	1.05	1.32	0.93	0.37

[a] Value of d_m immediately before the start of polymerization.
[b] Initial number of monomer droplets calculated using the d_m data.
[c] Final latex particle size.
[d] Final particle size distribution based on the cumulant method.
[e] Final number of latex particles calculated using the $d_{p,f}$ and X_f data.
[f] Final conversion of styrene.

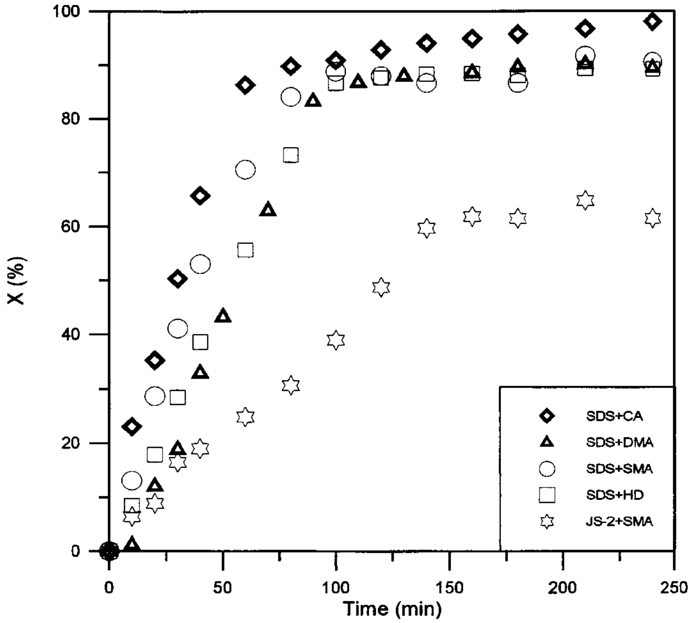


Fig. 6 Conversion of styrene as a function of time for miniemulsion polymerizations prepared by various cosurfactants: [SDS] = 5 mM; cosurfactant concentration = 20 mM. (◇) CA, (△) DMA, (○) SMA, (□) HD, (☆) 5 mM JS-2 + 20 mM SMA

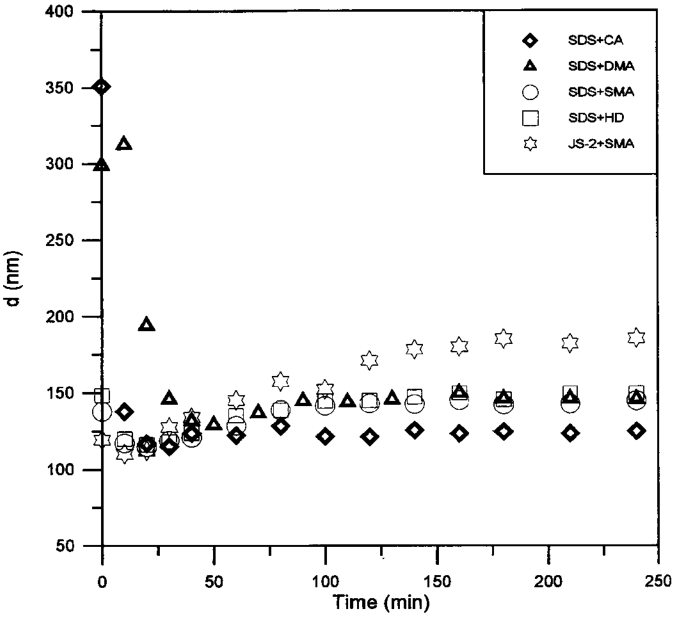


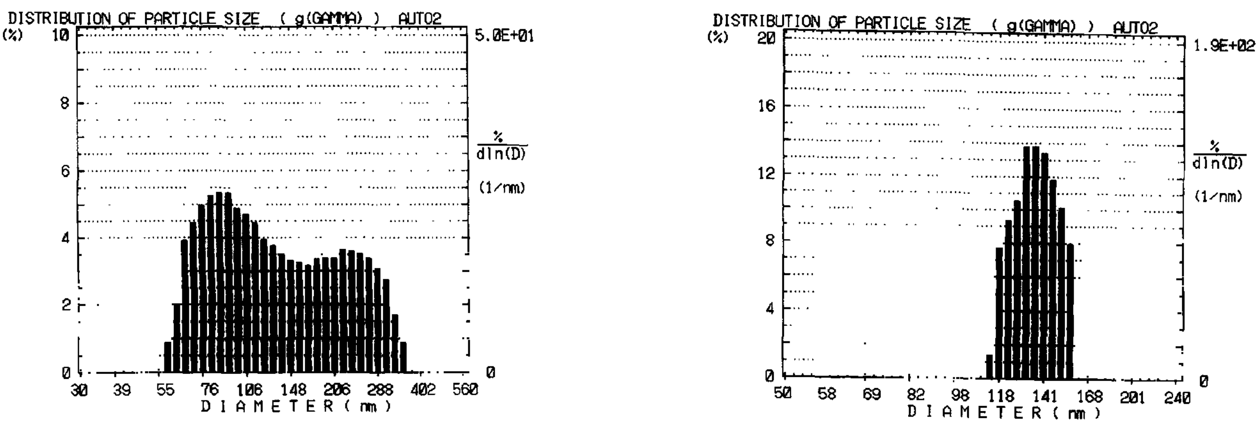
Fig. 7 Average particle/droplet size as a function of time for miniemulsion polymerizations prepared by various cosurfactants: [SDS] = 5 mM; cosurfactant concentration = 20 mM. (◇) CA, (△) DMA, (○) SMA, (□) HD, (☆) 5 mM JS-2 + 20 mM SMA

The *d* vs. *t* data for miniemulsion polymerizations with various cosurfactants are shown in Fig. 7. The average particle size decreases rapidly to a minimum, followed by a gradual increase to the plateau for the system with SDS/CA or SDS/DMA. The rapidly decreased *d* is probably due to generation of particle nuclei by some mechanisms other than monomer droplet nucleation. These particle nuclei are most likely generated by homogeneous nucleation [18–20] because [SDS] is only slightly above its CMC. The majority of SDS molecules may thus be adsorbed at the monomer droplet–water interface. Oligomeric radicals generated in water become insoluble when a critical chain length is achieved. This water-insoluble radical may thus coil up and form a particle nuclei ($\sim 10^0$ nm in diameter). Subsequently, stable primary particles ($\sim 10^1$ nm in diameter) are produced via limited flocculation among the unstable particle nuclei and adsorption of surfactant on their particle surfaces. The surfactant required to stabilize these primary particles comes from those dissolved in water, those released from monomer droplet surfaces due to Ostwald ripening or even those adsorbed on the monomer droplet surfaces. The miniemulsion with SDS/CA or SDS/DMA shows significant diffusional degradation, which results in a decrease in the total droplet surface area. The shrinking droplet-water interfacial area may exclude some of the adsorbed SDS species. The desorbed SDS contributes to stabilization of these primary particles. Furthermore, the intermolecular complexes of SDS/CA at the oil–water interface leads to a slower entry rate of radicals and, thereby, increases the probability of nucleating primary particles in water. Thus, *d* decreases significantly during the early stage of polymerization. Later on, the particle size distribution may become narrower due to long residence time involved in a batch reactor. Long residence time reduces the difference in size for the growing particles with different originations.

The *d* vs. *t* data for the system with SDS/SMA, SDS/HD or JS-2/SMA also show similar trends, but the initial decrease in *d* is not significant (see Fig. 7). This is due to the predominant monomer droplet nucleation for lack of stabilizing species to induce the population of small primary particles. Most particle nuclei formed in water are captured by the growing particles or monomer droplets throughout the reaction. The final particle size distribution data shown in Table 2 (see the u/G^2 data) and Fig. 8 indicate that a quite broad distribution was achieved for the miniemulsion polymerization system stabilized by SDS/CA or SDS/DMA. Note that the SDS/CA system even shows a bimodal particle size distribution (see Fig. 8a). On the other hand, the miniemulsion prepared by SDS/SMA or SDS/HD shows a relatively narrow particle size distribution. The greater the value of u/G^2, the broader is the final latex particle size distribution. These data further support the proposed competitive particle nucleation mechanism. The ratio of the final number of latex particles to the initial number of monomer droplets

(a) CA

(c) SMA



(b) DMA

(d) HD

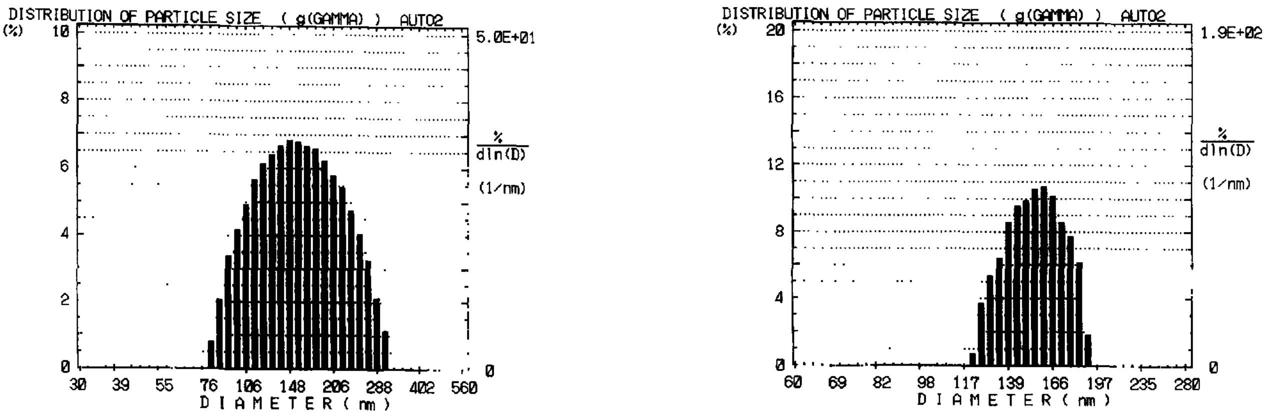


Fig. 8 Final latex particle size distribution data for miniemulsion polymerizations with various cosurfactants: (a) CA, (b) DMA, (c) SMA, (d) HD

($N_{p,f}/N_{m,i}$) is greater than unity for the system with SDS/CA or SDS/DMA, whereas the ratio is approximate 0.8 for that with SDS/SMA or SDS/HD (see Table 2). The former shows that a large proportion of the resultant latex particles are produced by homogeneous nucleation. The latter implies the predominant monomer droplet nucleation. These calculations also show that the alkyl chain length of the ractive cosurfactant (alkyl methacrylate) controls its performance properties.

Finally, the unreacted ST molecules in the final latex products stabilized by SDS/SMA and SDS/DMA, respectively, were removed in a vacuum oven for 24 h. The resultant polymer was then scanned by IR (JASCO IR-700) and there was no evidence of –C = C– derived from SMA or DMA, as shown by the peak observed for pure SMA (1635 cm^{-1}) or DMA (1632 cm^{-1}). As expected, the reactive acrylic cosurfactant SMA or DMA can be effectively incorporated into the polystyrene latex particles.

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