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Miniemulsion polymerization of styrene stabilized by nonionic surfactant and reactive cosurfactant

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Summary A nonionic surfactant, nonylphenol polyethoxylate with an average of 40 ethylene oxides per molecule (NP-40), in combination with a reactive cosurfactant such as dodecyl methacrylate (DMA) or stearyl methacrylate (SMA) was used to prepare stable styrene miniemulsions in this study. Like conventional cosurfactants such as cetyl alcohol (CA) and hexadecane (HD), the reagent DMA or SMA may act as a cosurfactant in stabilizing the homogenized miniemulsions. Furthermore, the methacrylate group can be chemically incorporated into latex particles in subsequent miniemulsion polymerization, as shown by the IR spectra. The rate of Ostwald ripening for these miniemulsions in the decreasing order is: CA > DMA > HD ~ SMA. This trend correlates well with the water solubility of these cosurfactants. The lower the levels of NP-40 and DMA, the greater is the degree of Ostwald ripening. This is because the DMA concentration is not high enough to counteract diffusional degradation of monomer droplets. Polystyrene latex particles were produced via both monomer droplet nucleation and homogeneous (or micellar) nucleation for the system exhibiting strong Ostwald ripening and/or droplet coalescence during the very early stage of polymerization. On the other hand, monomer droplet nucleation becomes more important for the system showing weak Ostwald ripening. Temperature has an important influence on the shelf-life of miniemulsions and subsequent polymerization. This is attributed to the fact that hydrogen bonds between the polyethylene oxide part of NP-40 and water are quite sensitive to changes in temperature.

Key words Miniemulsion polymerization – nonionic surfactant – reactive cosurfactants – styrene – emulsion stability

Introduction

Adequate emulsion stability during storage or miniemulsion polymerization can be achieved by using anionic or nonionic surfactants to prevent coalescence of monomer droplets in combination with a cosurfactant to retard diffusion of monomer from small droplets to large ones (Ostwald ripening) [1–5]. One problem associated with the cosurfactant is the need for removing these small molecules from latex products. For example, the volatile hexadecane (HD) and hydrophilic cetyl alcohol (CA) may cause VOC and water resistance problems, respectively. In a previous report [6], the authors demonstrated that alkyl methacrylates (dodecyl methacrylate (DMA) and stearyl methacrylate (SMA)) can be used as the reactive cosurfactant to prepare stable styrene (ST) miniemulsions. The anionic surfactant, sodium dodecyl sulfate (SDS), which imparts electrostatic repulsion among the interactive monomer droplets or latex particles, was selected as the primary stabilizer. Like conventional cosurfactants CA and HD, the reagent DMA or SMA acts as a normal cosurfactant in stabilizing the homogenized miniemulsions. In subsequent miniemulsion polymerization, the reactive methacrylate group can be chemically incorporated into latex particles, which may eliminate the need for removing these reactive cosurfactants from miniemulsion polymer products. It was also shown that 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.

Latices stabilized by anionic surfactants may become unstable towards added electrolytes due to the greatly reduced Coulombic repulsion between the charged particles. Nonionic surfactants such as nonylphenol polyethoxylate with an average of 40 ethylene oxides per molecule (NP-40) will impart steric stabilization to latex particles [7]. This kind of latex products is quite insensitive to changes in the ionic strength of the aqueous solution and is of great interest to industrial applications. The objective of this work was therefore to study the general features of the stabilizing system NP-40/DMA or NP-40/SMA in ST miniemulsion polymerization.

Experimental

Materials

The chemicals used in this work include styrene (Acros), nonylphenol polyethoxylate with an average of 40 ethylene oxides per molecule (Union Carbide), sodium dodecyl sulfate (J.T. Baker), 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 $<0.057\ \mu$S/cm). Styrene was distilled under reduced pressure before use. All other chemicals were used as received.

Preparation of miniemulsions and polymerization process

Experimental methods regarding the preparation of miniemulsions, shelf-life of miniemulsions, miniemulsion polymerization process, and measurements of average monomer droplet size and latex particle size have been described previously [6].

A typical polymerization recipe comprises 160.56 g water, 0.0356 g sodium bicarbonate (2.64 mM based on total water), 1.580 g NP-40 (5 mM based on total water), 1.079 g SMA (20 mM based on total water), 39.85 g ST, and 0.482 g sodium persulfate (12.57 mM based on total water). The molar ratio of surfactant to cosurfactant was kept constant at 1:4 throughout this work. Polymerization temperature was kept at 80 °C throughout the reaction (reaction time 6 h). The theoretical solid content of the latex product is 21.1%. Conversion of styrene as a function of time was determined by the gravimetric method.

Styrene–water interfacial tension

The styrene–water interfacial tension was determined by a Surface Tensiometer (CBVP-A3, Face) at 25.0 ± 0.2 °C. A sandblasted platinum plate of dimensions $1.95 \times 1.00 \times 0.02$ cm was used. The procedure, for example, involves addition of an aqueous solution of NP-40 into a beaker. The concentration of NP-40 ([NP-40]) is 0.334 mM, slightly above its CMC (0.294 mM at 25 °C [8]). The plate was immersed in this surfactant solution for 10 min and then removed from the solution. This was followed by carefully pouring the DMA containing styrene solution (the molar ratio of NP-40 to DMA was set at 1:4) on the top of the aqueous solution. Subsequently, the treated plate was fully immersed in the oil phase, but not in contact with the aqueous phase. The stage with the styrene–water sample then rose and stopped as soon as the plate came into contact with the aqueous solution. Before taking the data, samples were allowed to equilibrate until the interfacial tension stabilized. The interfacial tension (σ_S) determined in this way should approach a value corresponding to the condition that the styrene–water interface is saturated with surfactant, due to the very small interfacial area generated. This method was verified by comparing the experimental data of the pure styrene–water interfacial tension (35.9 dyn/cm) determined in this work with that reported in the literature (35.5 dyn/cm) [9].

Results and discussion

Monomer droplet size of miniemulsions upon aging

The rate of Ostwald ripening ($\mathrm{d}(d_m^3)/\mathrm{d}t$) can be calculated by the following equation based on the modified LSW theory [5]:

$$\mathrm{d}(d_m^3)/\mathrm{d}t = 32\alpha DS/(9\phi) = 64\sigma V_m DS/(9RT\phi)\,, \tag{1}$$

where d_m is the average monomer droplet size, t the time, α ($=2\sigma V_m/(RT)$) a characteristic length, σ the droplet–water interfacial tension, V_m the molar volume of the substance in the droplet, R the gas constant, T the absolute temperature, D the diffusion coefficient of cosurfactant in water, S the solubility of cosurfactant in water, and ϕ the volume fraction of cosurfactant in the droplet.

Figure 1 shows the data of d_m^3 as a function of t at 35 °C for miniemulsions prepared by the nonionic surfactant NP-40 and various cosurfactants. The concentration of NP-40 ([NP-40]) was kept constant at 5 mM, about one order of magnitude greater than its CMC. The cosurfactant concentration ([SMA], [DMA], [HD] or [CA]) was kept constant at 20 mM. For comparison, the corresponding d_m^3 versus t data at 35 °C for miniemulsions prepared by the anionic surfactant SDS and various cosurfactants taken from ref. [6] are also shown in Fig. 2. Note that the concentration of SDS ([SDS]) was kept constant at 5 mM, only slightly above its CMC (3 mM at 25 °C [8]). The d_m^3 versus t profile is strongly dependent on the type of cosurfactants, and insensitive to the type of surfactants (nonionic versus anionic). 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 (325 nm) > DMA (214 nm) > HD (140 nm) ~ SMA (123 nm). This trend is attributed to the different solubilities of cosurfactants in water. The water solubility of cosurfactants in the decreasing order is CA > DMA > HD ~ SMA) [6]. The greater the solubility of the cosurfactant in water, the less effective is the cosurfactant in retarding diffusion of monomer from small droplets to large ones.

The slope of the least-squares-best-fitted d_m^3 versus t straight line represents the Ostwald ripening rate and the calculated $\mathrm{d}(d_m^3)/\mathrm{d}t$ data are summarized in Table 1. The values of $\mathrm{d}(d_m^3)/\mathrm{d}t$ are 8.30×10^4, 2.56×10^4, 0, and 0 nm^3/min for the miniemulsions stabilized by NP-40/CA, NP-40/DMA, NP-40/HD, and NP-40/SMA, respectively. For comparison, the values of $\mathrm{d}(d_m^3)/\mathrm{d}t$ obtained from Fig. 2 are 1.45×10^5, 6.46×10^4, 0, and 0 nm^3/min for the miniemulsions stabilized by SDS/CA, SDS/DMA, SDS/HD, and SDS/SMA, respectively. As expected, the greater the water solubility of cosurfactants, the more pronounced is the Ostwald ripening effect. Diffusional degradation of monomer droplets is insignificant for miniemulsions prepared by the more hydrophobic cosurfactants HD and SMA. According to Eq. (1), the ratio $\mathrm{d}(d_m^3)/\mathrm{d}t$ (NP-40/CA):$\mathrm{d}(d_m^3)/\mathrm{d}t$ (SDS/CA) = σ (NP-40/CA): σ (SDS/CA) = 8.30×10^4:1.45×10^5, and similarly the

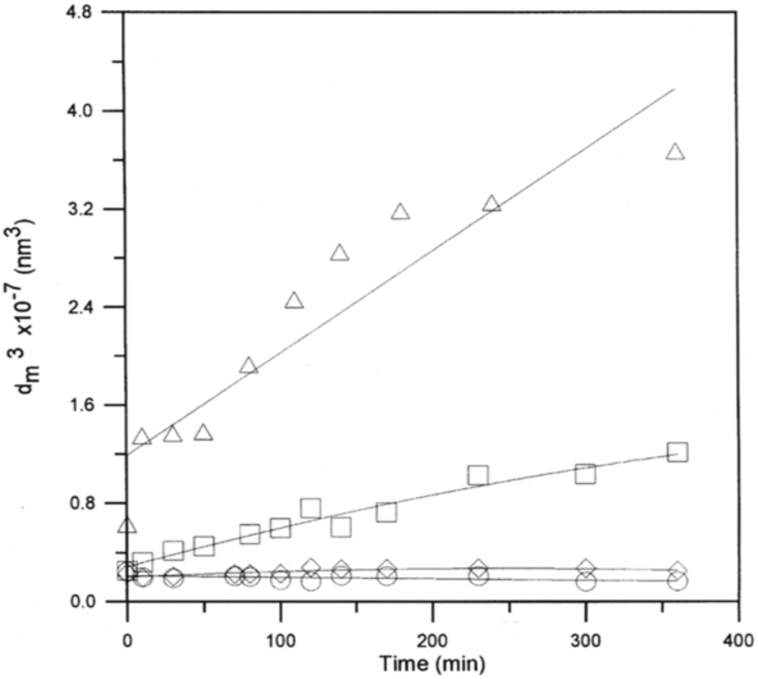

Fig. 1 Average monomer droplet size upon aging at 35 °C as a function of time for miniemulsions prepared by NP-40 and various cosurfactants: [NP-40] = 5 mM; cosurfactant concentration = 20 mM: (◇) HD, (○) SMA, (□) DMA, (△) CA

ratio $d(d_m^3)/dt$ (NP-40/DMA):$d(d_m^3)/dt$ (SDS/DMA) = σ (NP-40/DMA):σ (SDS/DMA) $=2.56\times10^4:6.46\times10^4$. These relationships then lead to the following results: σ (SDS/DMA) = 2.52σ (NP-40/DMA) and σ (SDS/CA) = 1.75σ (NP-40/CA). The trend that the miniemulsion prepared by SDS/DMA (or SDS/CA) shows a higher droplet–water interfacial tension than that prepared by NP-40/DMA (or NP-40/CA) may be explained as follows. Table 2 lists the measured data of styrene–water interfacial tension (σ_S). These data show that cosurfactants have little influence on σ_S. This implies that DMA should be uniformly distributed in the styrene phase. The values of σ_S (NP-40/CA) and σ_S (SDS/CA) were not determined because CA does not dissolve in styrene. The value of σ (NP-40/DMA) should be closer to σ_S (NP-40/DMA) than σ (SDS/DMA) to σ_S (SDS/DMA). This is simply because [NP-40] is one order of magnitude greater than its CMC, whereas [SDS] is only slightly above its CMC. The value of σ (SDS/DMA) is therefore estimated to be greater than $2.52\times5.7=14.4$ dyn/cm, which is much higher than that of σ_S (SDS/DMA) (4.8 dyn/cm). This implies that the amount of adsorbed SDS molecules is not sufficient to completely cover the tremendous droplet surface area generated by homogenization due to the relatively high CMC of SDS. In addition, the initial d_m data shown in Table 1 seem insensitive to the type of cosurfactants. This is primarily due to the same [NP-40] and homogenization condition used in this series of experiments. The slightly scattered initial d_m data are caused by different rates of Ostwald ripening.

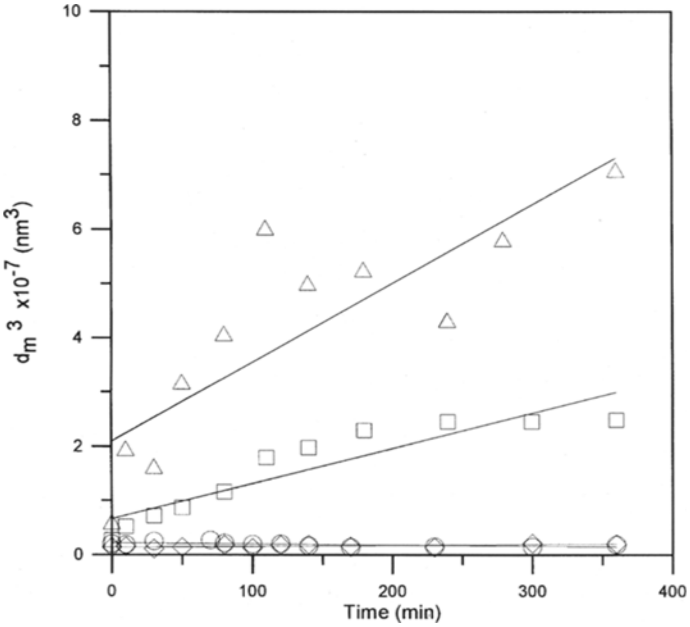

Fig. 2 Average monomer droplet size upon aging at 35 °C as a function of time for miniemulsions prepared by SDS and various cosurfactants: [SDS] = 5 mM; cosurfactant concentration = 20 mM: (◇) HD, (○) SMA, (□) DMA, (△) CA (data taken from ref. [6])

The data of d_m and $d(d_m^3)/dt$ for the miniemulsion with DMA or SMA at various levels of [NP-40] at 35 °C are summarized in Table 1. In this series of experiments, the molar ratio of NP-40 to DMA or SMA was also kept constant at 1:4. At constant surfactant concentration, the initial d_m data seem insensitive to the type of cosurfactants due to the fact that the initial droplet size is principally controlled by the homogenization process. Furthermore, both the initial and steady-state values of d_m decrease rapidly with increasing [NP-40] regardless of the type of cosurfactants (examining the set of experiments (C2, N1, N3) or (C3, N2, N4) in Table 1). This is because more NP-40 is available for stabilizing the droplet surface area generated by shear force. As shown by the $d(d_m^3)/dt$ data in Table 1, the lower the levels of NP-40 and DMA, the greater is the degree of Ostwald ripening. This is because [DMA] is not high enough to counteract diffusional degradation of monomer droplets. According to Eq. (1), the ratio $d(d_m^3)/dt$ (1.52 mM NP-40):$d(d_m^3)/dt$ (5 mM NP-40) = σ (1.52 mM NP-40)/ϕ (1.52 mM NP-40):σ (5 mM NP-40)/ϕ (5 mM NP-40) = σ (1.52 mM NP-40)/1.52:σ (5 mM NP-40)/5 = $5.21\times10^{-3}:2.56\times10^{-3}$. These

Table 1 Data of d_m and Ostwald ripening rate for miniemulsions aged at 35 °C

	C1	C2	C3	C4	N1	N2	N3	N4
Surfactant type	NP-40	NP-40	NP-40	NP-40	NP-40	NP-40	NP-40	NP-40
conc [mM][a]	5	5	5	5	1.52	1.52	0.22	0.22
Cosurfactant type	CA	DMA	SMA	HD	DMA	SMA	DMA	SMA
conc [mM][a]	20	20	20	20	6.08	6.08	0.88	0.88
Initial value of d_m	183	136	136	133	247	242	588	602
Steady value of d_m at 4 h [nm]	325	214	123	140	318	300	560	600
$d(d_m^3)/dt\times10^{-4}$ [nm^3/min]	8.30	2.56	0	0	5.21	0	ND[b]	ND[b]

[a] Based on total water.

[b] Not determined because of the extremely scattered data.

Table 2 Styrene–water interfacial tension data

Surfactant type	NP-40	NP-40	SDS	SDS
Cosurfactant type	—	DMA	—	DMA
Interfacial tension [dyn/cm]	5.8	5.7	5.0	4.8

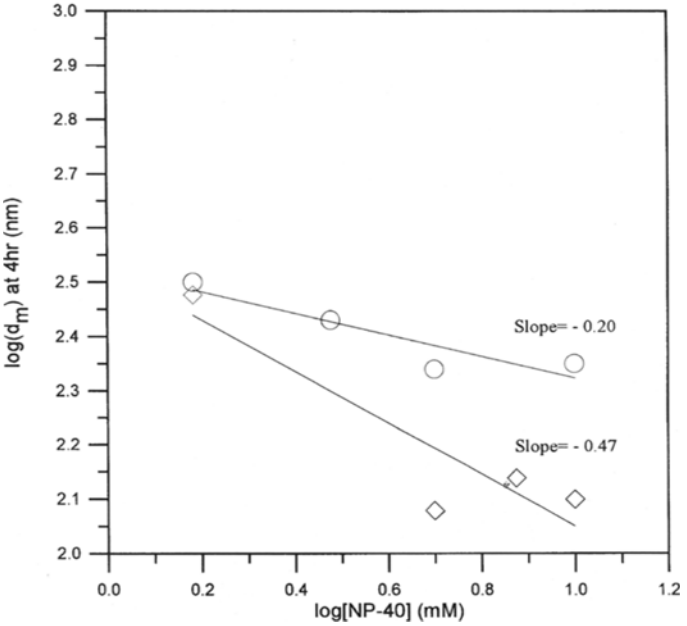

Fig. 3 Logarithmic plot of average monomer droplet size upon aging at 35 °C for 4 h as a function of [NP-40] for miniemulsions prepared by different cosurfactants: cosurfactant concentration = 4 × [NP-40]: (○) DMA, (◇) SMA

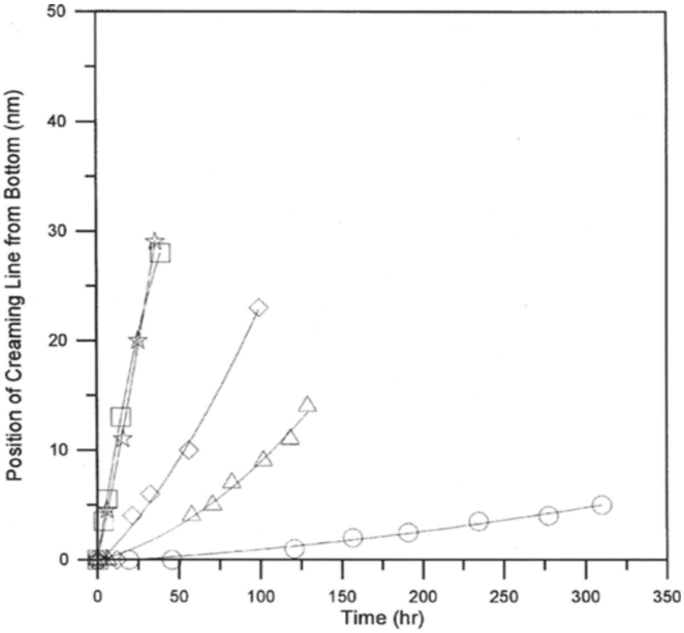

Fig. 4 Position of creaming line from the bottom of the miniemulsion as a function of time: (◇) 5 mM NP-40 + 20 mM CA, (△) 1.52 mM NP-40 + 6.08 mM DMA, (○) 1.52 mM NP-40 + 6.08 mM SMA, (□) 0.22 mM NP-40 + 0.88 mM DMA, (☆) 0.22 mM NP-40 + 0.88 mM SMA

relationships then lead to the following result: σ (1.52 mM NP-40) = 0.62σ (5 mM NP-40). The reason for the lowered σ (1.52 mM NP-40) is attributed to the smaller droplet surface area (or the larger d_m at $t = 0$) produced by homogenization (see the d_m data in Table 1). This may thus result in an increase in the droplet surface coverage by NP-40. Figure 3 shows the logarithmic plot of d_m at 4 h as a function of [NP-40] for miniemulsions with DMA (slope = – 0.20) and SMA (slope = – 0.47), respectively. Although the experimental data of the miniemulsions with NP-40/SMA are quite scattered, these data seem to suggest that d_m is more sensitive to changes in [NP-40] when SMA is chosen as the cosurfactant.

Shelf stability of miniemulsions

The creaming data are shown in Fig. 4, where the ordinate represents the position of the creaming line from the bottom of the sample. These data show that the creaming is greatly retarded as [NP-40] is increased. No creaming phenomenon was observed for the miniemulsions prepared by (i) 5 mM NP-40 + 20 mM SMA and (ii) 5 mM NP-40 + 20 mM HD. In addition, no separate monomer phase on the top of the sample was observed for the miniemulsions investigated in this work. The miniemulsions prepared by (i) 5 mM NP-40 + 20 mM SMA and (ii) 5 mM NP-40 + 20 mM HD remained stable over an observation period of 3 weeks. It can be concluded that at constant surfactant concentration, NP-40 is more effective in preventing the monomer phase separation from occurring upon aging at 35 °C as compared to SDS [6].

Based on the data of the monomer droplet size, creaming rate, and monomer phase separation, 5 mM NP-40 in combination of 20 mM SMA or HD is the best among the cosurfactants studied in this work. The reactive cosurfactants (DMA and SMA) are capable of producing relatively stable miniemulsions with their droplet surfaces covered by a hydrophilic layer of polyethylene oxide. The performance of DMA is similar to that of CA, whereas the performance of SMA is similar to that of HD. These results are consistent with our previous work in which SDS is the primary stabilizer [6].

Miniemulsion polymerization of styrene

The recipes and data for the miniemulsion polymerizations stabilized by various cosurfactants are listed in Tables 1 and 3, respectively (see experiments C1, C2, C3, C3′, and C4). The CMC of the aqueous NP-40 solution at 80 °C is 0.152 mM [8]. In this series of experiments, the concentration of NP-40 and $Na_2S_2O_8$ was kept constant at 5 and 2.66 mM, respectively. The NP-40 concentration is about 30 times greater than its CMC. In the presence of submicron monomer droplets, whether the amount of NP-40 molecules dissolved in water is above its CMC is not clear at this time. This is because a significant fraction of NP-40 molecules can be adsorbed onto the huge monomer droplet–water interfacial area generated during homogenization and the cosurfactant containing styrene–water interfacial area occupied by one molecule of NP-40 is not known. This subject is beyond the scope of this work.

The conversion of styrene (X) versus t profiles are shown in Fig. 5. The rate of polymerization ($\mathrm{d}X/\mathrm{d}t$) increases with an increase in the final number of latex particles ($N_{\mathrm{p,f}}$) (or with a decrease in the final latex particle size ($d_{\mathrm{p,f}}$)) (see Fig. 5 and Table 3). Thus, the rate of polymerization in the increasing order is CA < DMA < HD < SMA.

The particle nucleation mechanism involves capture of radicals by monomer droplets in miniemulsion polymerization. For the polymerization system using CA as the cosurfactant, monomer droplet nucleation may take a long time to be finished (beyond 30% conversion) and only a fraction of these droplets becomes latex particles [10]. 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 the nucleated 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.

Figure 6 shows the d versus t data for miniemulsion polymerizations with various cosurfactants. It is interesting to note that the data of $d_{\mathrm{m,i}}$ taken immediately before the start of polymerization at 80 °C (272–839 nm) is much larger than those of initial d_{m} (133–183 nm) or d_{m} at 4 h (123–325 nm) monitored at 35 °C (see Fig. 6 and Tables 1 and 3). Apparently, this phenomenon cannot be explained by the Ostwald ripening effect alone. It is then postulated

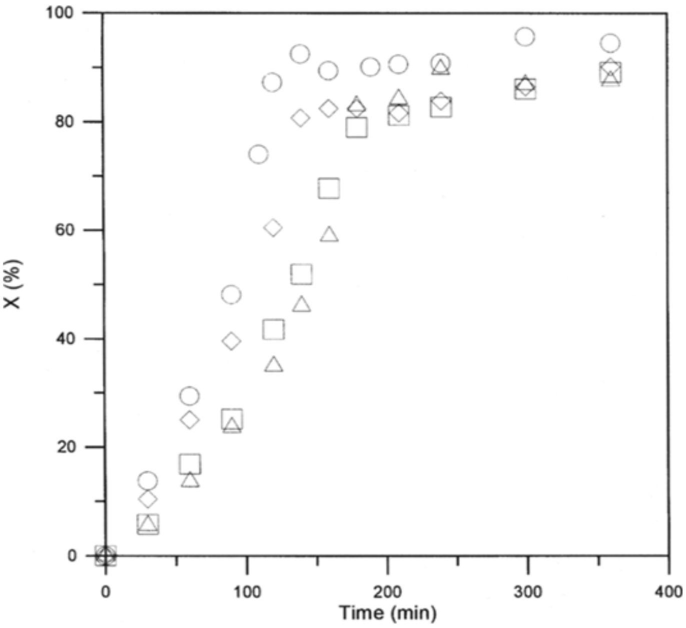

Fig. 5 Conversion of styrene as a function of time for miniemulsion polymerizations prepared by various cosurfactants: [NP-40] = 5 mM; cosurfactant concentration = 20 mM: (◇) HD, (○) SMA, (□) DMA, (△) CA

Table 3 Results obtained from miniemulsion polymerizations stabilized by various cosurfactants

	C1	C2	C3	C4	C3′[a]
$d_{\mathrm{m,i}}$ [nm][b]	839	461	647	272	177
$N_{\mathrm{m,i}} \times 10^{-15}$ [1/L-H_2O][c]	0.84	5.66	2.06	27.51	97.77
$d_{\mathrm{p,f}}$ [nm][d]	314	283	227	248	202
(u/G^2)[e]	2.17×10^{-1}	6.82×10^{-2}	1.11×10^{-1}	6.55×10^{-2}	1.16×10^{-1}
$N_{\mathrm{p,f}} \times 10^{-15}$ [1/L-H_2O][f]	15.2	20.7	40.3	30.8	59.2
$N_{\mathrm{p,f}}/N_{\mathrm{m,i}}$	18.08	3.65	19.56	1.12	0.61
X_{f} [%][g]	87.6	89.2	94.5	90.2	66.2
$\mathrm{d}X/\mathrm{d}t \times 10^2$ [1/min]	0.57	0.60	0.90	0.70	0.17

[a] Recipe C3′ is the same as C3, but polymerized at 60 °C.
[b] Value of d_{m} immediately before the start of polymerization.
[c] Initial number of monomer droplets calculated using the $d_{\mathrm{m,i}}$ data.
[d] Final latex particle size.
[e] Final particle size distribution based on the cumulant method.
[f] Final number of latex particles calculated using the $d_{\mathrm{p,f}}$ and X_{f} data.
[g] Final conversion of styrene.

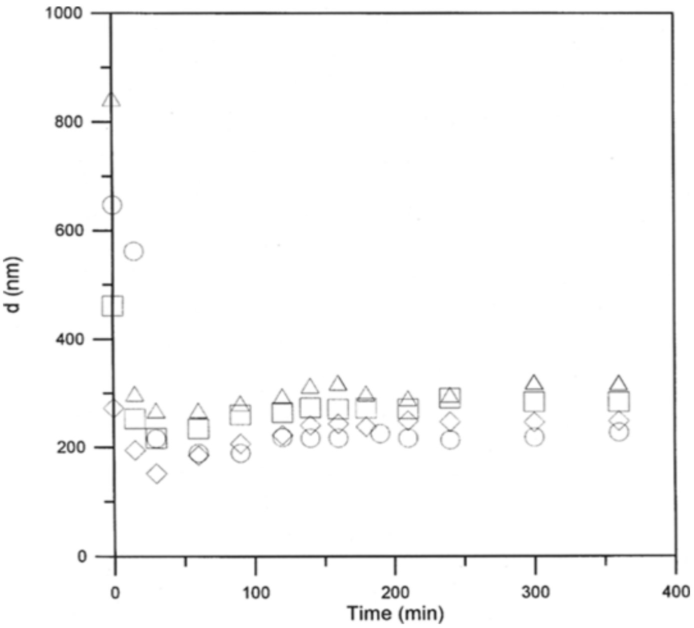

Fig. 6 Average particle/droplet size as a function of time for miniemulsion polymerizations prepared by various cosurfactants: [NP-40] = 5 mM; cosurfactant concentration = 20 mM: (◇) HD, (○) SMA, (□) DMA, (△) CA

that the effect of temperature may also contribute to the rapidly increased $d_{m,i}$. Increasing the temperature from 35 to 80 °C may greatly reduce hydrogen bonds between the polyethylene oxide part of NP-40 and water and, thereby, lower the hydrophilicity of NP-40. This may impair the steric stabilization effect provided by NP-40 and cause coalescence among the interactive monomer droplets to occur immediately before the start of polymerization. The recipe C3 stabilized by 5 mM NP-40/ 20 mM SMA was then chosen to verify this speculation and polymerized at a lower temperature 60 °C (designated as C3′). The resultant X and d versus t data are shown in Figs. 7a and b, respectively, and some kinetic data are also included in Table 3. As shown in Fig. 7b and Table 3, the data of d versus t and $d_{m,i}$ (647 nm at 80 °C versus 177 nm at 60 °C) confirm the proposed mechanisms. Thus, the stabilizing system comprising 5 mM NP-40 and 20 mM SMA can be quite effective in the ST miniemulsion polymerization at a lower temperature (e.g. 60 °C in this work), as observed in the polymerization system stabilized by 5 mM SDS and 20 mM SMA at 80 °C [6]. As expected, the rate of polymerization decreases rapidly when the reaction temperature decreases from 80 to 60 °C (see Fig. 7a and Table 3). Figure 6 also shows that d decreases rapidly to a shallow minimum, followed by a gradual increase to the plateau for miniemulsion polymerizations stabilized by NP-40 and various cosurfactants. The rapidly decreased d is probably due to generation of particle nuclei by some mechanisms other than monomer droplet nucleation. One possible mechanism is homogeneous nucleation [11–13]. 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

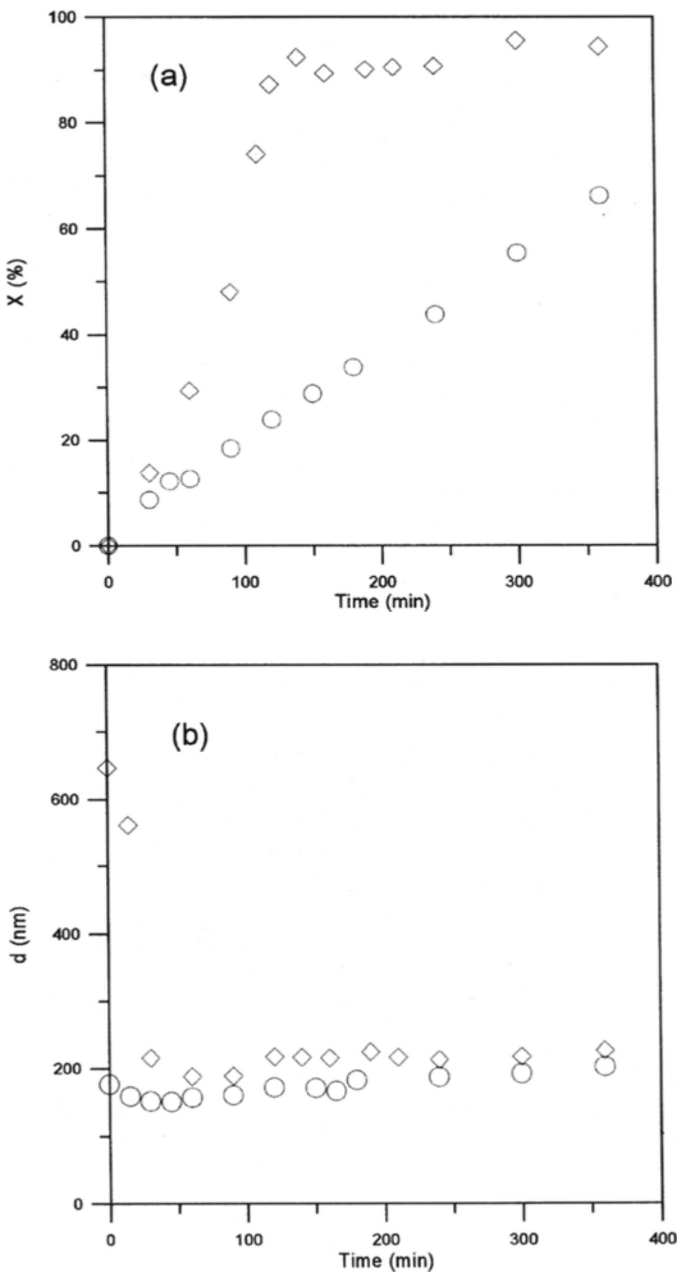

Fig. 7 (a) Conversion of styrene and (b) average particle/droplet size as a function of time for miniemulsion polymerizations stabilized by 5 mM NP-40/20 mM SMA: (◇) 80 °C, (○) 60 °C

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 and droplet coalescence, or even those adsorbed on the monomer droplet surfaces. However, the micellar nucleation mechanism [14–16] cannot be ruled out because [NP-40] is one order of magnitude greater than its CMC and micelles may be present in the polymerization system.

Figure 6 indicates that miniemulsion polymerizations stabilized by NP-40 and various cosurfactants at 80 °C show significant diffusional degradation of monomer droplets and/or droplet coalescence, which results in a reduction in the total droplet surface area. The shrinking droplet–water interfacial area may exclude some of the adsorbed NP-40 species. The desorbed NP-40 may thus contribute to stabilization of these primary particles. Furthermore, the intermolecular complexes of NP-40/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, the value of d decreases significantly during the very 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 origin. The final particle size distribution data shown in Table 3 (see the u/G^2 data) indicate that a quite broad distribution was achieved for the miniemulsion polymerization stabilized by NP-40/CA or NP-40/SMA. On the other hand, the miniemulsion prepared by NP-40/DMA or NP-40/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. Furthermore, the ratio of the final number of latex particles to the initial number of monomer droplets ($N_{p,f}/N_{m,i}$) is much greater than unity for the polymerization system with NP-40/CA or NP-40/SMA, whereas the ratio is quite close to unity for that with NP-40/DMA or NP-40/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. No apparent correlation between the data of u/G^2 and $N_{p,f}/N_{m,i}$ and the water solubility of cosurfactants. It seems that both monomer droplet nucleation and homogeneous (or micellar) nucleation are operative for the system exhibiting strong Ostwald ripening and/or droplet coalescence during the very early stage of polymerization. This may lead to a relatively broad particle size distribution at the end of polymerization. On the other hand, monomer droplet nucleation becomes more important for the system showing weak Ostwald ripening. As a consequence, a narrow particle size distribution is obtained from the miniemulsion polymerization. This is probably due to the temperature effect on the steric stabilization of monomer droplets by NP-40.

Finally, the unreacted ST molecules in the final latex products stabilized by NP-40/SMA and NP-40/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 the pure SMA (1635 cm^{-1}) or DMA (1632 cm^{-1}). Furthermore, absorption of the ester group derived from SMA or DMA (C=O: 1710–1725 cm^{-1} and C–O: 1150–1160 cm^{-1}) was detected in the spectra, as compared to the peaks observed for the pure SMA or DMA (C=O: 1717 cm^{-1} and C–O: 1163 cm^{-1}). As expected, the reactive acrylic cosurfactant SMA or DMA can be effectively incorporated into the polystyrene latex particles.

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