

Effects of carboxylic monomers on the styrene miniemulsion polymerizations stabilized by SDS/alkyl methacrylates

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Abstract

The effects of a small amount of carboxylic monomers (AA and MAA) on the styrene miniemulsion polymerizations stabilized by SDS/DMA or SDS/SMA are studied. A mixed mode of particle nucleation (monomer droplet nucleation and homogeneous nucleation) is operative during polymerization. Formation of particle nuclei in the aqueous phase predominates in the SDS/SMA stabilized polymerization in the absence of carboxylic monomers. The relatively stable monomer droplets exhibiting an extremely large droplet surface area become the primary particle nucleation loci when a small amount of AA or MAA is used as the comonomer. On the other hand, homogeneous nucleation plays a crucial role in the polymerizations stabilized by SDS/DMA. The experiment using the less hydrophilic MAA as the comonomer shows an intermediate behavior in the polymerization kinetics. A mechanistic model is proposed for the enhanced monomer droplet nucleation in the polymerizations containing carboxylic monomers. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Micellar nucleation [1–4] and homogeneous nucleation [5–7] are responsible for the formation of latex particles in emulsion polymerization. Monomer droplets only serve as a reservoir to supply latex particles with monomer and surfactant during the reaction. The pioneering work of Ugelstad et al. [8,9] showed that monomer droplets may become the primary particle nucleation loci provided that these droplets are subjected to intensive homogenization and then become small enough to compete effectively with micelles for the incoming radicals. This was followed by a number of studies which established the groundwork of the particle nucleation and growth mechanisms involved in such a miniemulsion polymerization system [10–18]. Upon aging, the emulsion product undergoes significant diffusional degradation of oil droplets with a relatively broad size distribution (i.e. large droplets grow in size at the expense of small ones, termed the Ostwald ripening effect) [19]. Incorporation of a low molecular weight cosurfactant (e.g. cetyl alcohol or hexadecane) into the colloidal system builds up an osmotic pressure between the large and small droplets and, thereby, retards Ostwald ripening. Therefore, using an appropriate

surfactant (e.g. sodium dodecyl sulfate, SDS) to prevent monomer droplets from coalescence in combination with cosurfactant is the key to a successful miniemulsion polymerization. In our previous work [20,21], the extremely hydrophobic stearyl methacrylate (SMA) and dodecyl methacrylate (DMA) were used to stabilize the miniemulsion polymerization of styrene (ST). The main feature of this approach is that SMA (or DMA) acts as a cosurfactant in the preparation of miniemulsion and it becomes chemically incorporated into the emulsion polymer during the subsequent polymerization. The presence of undesired volatile organic compounds in the latex product is thus minimized.

Incorporation of a small amount of carboxylic monomers such as acrylic acid (AA) or methacrylic acid (MAA) into the emulsion polymer is a common practice in industry. The carboxyl group coupled onto the latex particle surface enhances the colloidal stability and adhesion properties in the coating and adhesive applications. de Arbina and Asua [22] employed the miniemulsion polymerization technique to prepare stable ST/2EHA/MAA latex products with a total solid content close to 60%, where 2EHA represents 2-ethylhexyl acrylate. Such a level of total solid content could not be achieved by emulsion polymerization. Masa et al. [23] examined the difference in the reaction kinetics between the emulsion and miniemulsion polymerizations of ST, 2EHA and MAA. It was shown that the miniemulsion polymerization

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rate is slower in comparison with the emulsion polymerization counterpart. The objective of this work was to study the influence of a small amount of AA and MAA (water solubility: AA > MAA) on the ST miniemulsion polymerization kinetics. Furthermore, an extremely hydrophobic dye was adopted as a probe [24–26] to gain a better understanding of the particle nucleation and growth mechanisms.

2. Experimental

2.1. Materials

The chemicals used in this work include styrene (Taiwan Styrene Monomer), sodium dodecyl sulfate (J.T. Baker, 99%), stearyl methacrylate (Mitsubishi Rayon), dodecyl methacrylate (Aldrich), acrylic acid (Formosa Plastic), methacrylic acid (Mitsubishi Rayon), sodium persulfate (SPS) (Riedel-de Haen), sodium bicarbonate (Riedel-de Haen), potassium hydrogenphthalate (Hayashi), nitrogen (Ching-Feng-Harng Co., Taiwan), water-insoluble dye (Blue 70, molecular weight $\cong 10^3$ g/mol) (Shenq-Fong Fine Chemical Ltd., China), tetrahydrofuran (THF) (Merck), and deionized water (Barnsted, Nanopure Ultrapure Water System, specific conductance <0.057 $\mu\text{S}/\text{cm}$). SMA and DMA were recrystallized in ethanol and ST and AA were distilled under reduced pressure before use. All other chemicals were used as received.

2.2. Miniemulsion preparation and polymerization

The miniemulsion was prepared by dissolving SDS in water and the cosurfactant (SMA or DMA) and dye in the monomer. 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. The miniemulsion sample was cooled by an ice-water bath during homogenization. Miniemulsion 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 consists of 40 g water, 2.66 mM NaHCO_3 , 6 mM SDS, 24 mM SMA, 10 g ST, 0.24 mM dye and 6 mM SPS, in which all the molar concentrations are based on the aqueous phase. The molar ratio of surfactant to cosurfactant was kept constant at 1:4 throughout this work. The concentrations of SDS, SPS, NaHCO_3 and dye were kept constant at 6, 6, 2.66 and 0.24 mM, respectively. Polymerization temperature was kept constant at 80°C. The theoretical solid content of the latex product is about 20%.

2.3. Determination of monomer droplet size (or latex particle size)

The data of average monomer droplet size were obtained from dynamic light scattering (DLS) (Otsuka Photal LPA-3000/3100). The sample was diluted with water to adjust the number of photons counted per second to 8000–12,000. The dilution water was saturated with SDS (critical micelle concentration (CMC) = 8.2 mM) and ST (1.92 mM) to avoid diffusion of SDS and ST from the monomer droplets (or monomer-swollen latex particles) into water. The data of CMC for SDS and the water solubility for ST were taken from Refs. [27,28], respectively. The reported data of the average monomer droplet diameter immediately before the start of polymerization ($d_{m,i}$) represent the average of at least three measurements and the errors have been estimated to be 8% or less. The weight-average diameter (d_w) and polydispersity index (d_w/d_n) of the resultant latex particles were determined by transmission electron microscopy (TEM) (JEOL TEM-1200 EXII). The parameter d_n is the number-average diameter of latex particles. At least 300 latex particles per sample were counted in the particle size measurement. Based on the $d_{m,i}$ and d_w data, the number of monomer droplets per liter water produced immediately before the start of polymerization ($N_{m,i}$) and the number of latex particles per liter water produced at the end of polymerization ($N_{p,f}$) were calculated.

2.4. Characterization of latex products

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 monomer conversion (X) were determined gravimetrically. The zeta potential of the latex particles (ζ) were measured by the Malvern Zetamaster. The latex sample with a volume of 0.1 ml was diluted with 39.9 ml 0.05 mM potassium hydrogenphthalate buffer solution (pH 4) before the ζ measurement. The reported ζ data represent the average of 10 measurements. The weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) of the resultant emulsion polymer were obtained from gel permeation chromatography (Waters Styragel HR2, HR4 and HR6). M_n is the number-average molecular weight of the emulsion polymer. A series of polystyrene standards was used to establish the calibration curve.

The following procedure developed in Refs. [24–26] was modified slightly to determine the dye content in the resultant latex particles. A distinct peak at 678 nm was observed for the solution of 1.7×10^{-4} g dye and 0.5 g dried polystyrene in 20 ml THF by the UV absorbance method (Shimadzu UV-160A). No absorbance was detected at this wavelength for the solution of dried polystyrene in 20 ml THF. The extinction coefficient obtained from the calibration curve of the UV absorbance at 678 nm versus the dye

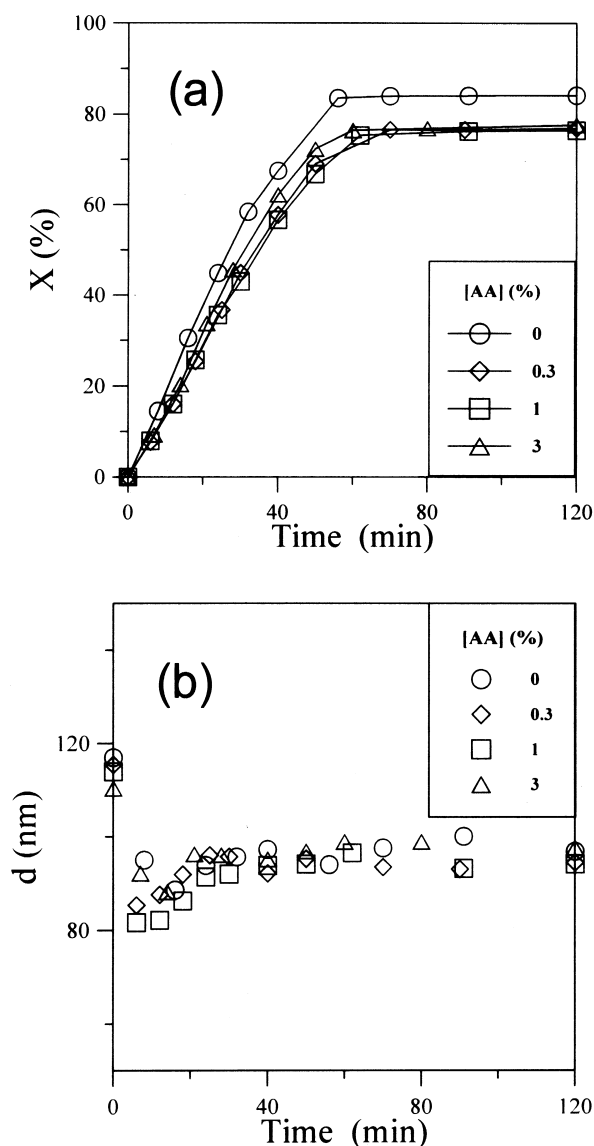


Fig. 1. Effect of the AA concentration on (a) the monomer conversion versus time profiles and (b) the average particle size versus time data for the polymerizations using SMA as the cosurfactant: [AA] = (○) 0 wt%, (◇) 0.3 wt%, (□) 1.0 wt%, (△) 3.0 wt%.

concentration data was determined to be 7.313×10^4 ml/(cm g). To determine the amount of dye incorporated into latex particles, the latex product was allowed to stand at room temperature over 5 days before UV absorbance measurements. In this manner, a thin layer of blue precipitate (originating from the bulk dye suspended in the latex product) can be found on the bottom of the sample. This is followed by centrifugation at 8000 rpm (Beckman J2-21) and filtration to further remove the fraction of dye that was not incorporated into latex particles during polymerization. Approximately 0.5 g dried emulsion polymer was then dissolved in 20 ml THF for determination of the dye content according to the above calibration curve. The reported P_{dye} data, defined as the weight percentage of dye that is

ultimately incorporated into latex particles, represent the average of five measurements.

3. Results and discussion

In the first series of polymerizations, the concentration of AA ([AA]) was varied in the range of 0–3 wt% based on ST. Fig. 1 shows the effects of [AA] on the monomer conversion (X) versus time (t) profiles (a) and the average particle size (d) versus t data (b) for the polymerizations using SMA as the cosurfactant. During polymerization, monomer droplets coexist with the nucleated latex particles and, hence, the dynamic light scattering data (d) represent the average particle size of the reaction mixture consisting of latex particles and monomer droplets. The polymerization rate ($R_p = [M]_0 dX/dt$) data are listed in Table 1 (S1–S4), in which $[M]_0$ is the initial monomer concentration based on water (2.33 mM in this work) and the value of dX/dt is the least-squares-best-fitted slope of the linear portion of the X versus t curve. R_p first decreases to a minimum and then increases when [AA] increases from 0 to 3 wt% (Fig. 1a and Table 1). This cannot be simply attributed to the number of reaction loci ($N_{p,f}$) produced. The larger the population of latex particles, the faster the polymerization rate. Although the data are quite scattered, the $N_{p,f}$ versus [AA] data do not show exactly the same trend as the R_p data (Table 1). The very complicated particle nucleation mechanisms, as will be shown below, may be responsible for this observation.

For the polymerizations stabilized by SDS/SMA, incorporation of a small amount of AA into the reaction mixture results in an insignificant reduction in $d_{m,i}$ (or a slight increase in $N_{m,i}$) (Table 1). Fig. 1b shows that a rapid reduction in d is experienced during the early stage of polymerization. This is most likely due to the generation of tiny particle nuclei by homogeneous nucleation because the SDS concentration is below the CMC. The surfactant required to stabilize these growing particle nuclei comes from those SDS molecules dissolved in water, those released from the monomer droplet surface due to Ostwald ripening (if present) or even those adsorbed on the droplet surface. It was shown that diffusional degradation of monomer droplets (Ostwald ripening) for the ST miniemulsion using SMA as the cosurfactant is not as important as the DMA counterpart [20,21,29]. After the minimum is achieved, d starts to increase gradually to a plateau with the progress of polymerization. The increase of d is caused by the polymerization of the imbibed monomer in latex particles, the limited flocculation between two latex particles or between one latex particle and one monomer droplet, and the coalescence of monomer droplets. All the latex products show comparable values of d_w , but the latex particle size distribution (d_w/d_n) becomes broader when [AA] increases from 0 to 3 wt% (Fig. 2 and Table 1). This suggests that the particle nucleation and growth mechanisms vary significantly for the polymerizations in the

Table 1
Results obtained from the styrene miniemulsion polymerizations with AA or MAA

Exp ID	S1	S2	S3	S4	S5	D1	D2	D3	D5
Cosurfactant	SMA	SMA	SMA	SMA	SMA	DMA	DMA	DMA	DMA
MAA or AA (%)	AA (0)	AA (0.3)	AA (1)	AA (3)	MAA (3)	AA (0)	AA (1)	AA (3)	MAA (3)
$d_{m,i}$ (nm)	117	115	114	113	112	251	230	234	227
d_w (nm)	112	114	111	114	105	122 (121) ^a	– (271) ^a	88 (214) ^a	103
d_w/d_n	1.011	1.025	1.033	1.034	1.025	1.014	–	1.286	1.049
$N_{m,i} \times 10^{-17}$ (l ⁻¹)	3.21	3.34	3.48	3.56	3.70	0.32	0.42	0.40	0.44
$N_{p,f} \times 10^{-17}$ (l ⁻¹)	2.68	2.27	2.47	2.32	3.25	2.18	–	2.90	3.00
$N_{p,f}/N_{m,i}$	0.84	0.68	0.71	0.65	0.88	6.73	–	7.16	6.72
$R_p \times 10^2$ (mol/(l min))	4.26	3.51	3.38	4.08	4.27	3.49	0.47	0.89	2.1
$R_p/N_{p,f} \times 10^{19}$ (mol/min)	1.59	1.54	1.37	1.76	1.31	1.60	–	0.31	0.71
P_{dye} (%)	21.3	53.7	55.8	63.2	66.4	20.6	27.4	38.4	40.9
$N_d \times 10^{-17}$ (l ⁻¹)	0.68	1.79	1.94	2.25	2.45	0.067	0.12	0.15	0.18
$N_w \times 10^{-16}$ (l ⁻¹)	20.00	4.81	5.32	0.72	7.93	21.10	–	27.20	27.90
$N_w/N_{p,f}$	0.75	0.21	0.22	0.03	0.24	0.97	–	0.95	0.94
$-\zeta$ (mV)	31.1	29.9	26.6	24.9	22.4	46.7	–	–	–
$M_w \times 10^{-5}$	1.9	1.7	2.0	2.3	2.9	1.7	3.4	4.3	3.4
M_w/M_n	1.99	1.96	2.08	2.15	2.08	2.23	4.65	5.15	4.64
Total scrap (%)	3.1	1.2	1.1	0.8	0.6	1.0	0.2	0.3	0.3

^a Determined by dynamic light scattering.

presence and absence of AA. The increased particle nucleation period in combination with the mixed mode of particle nucleation (i.e. monomer droplet nucleation and homogeneous nucleation) are probably responsible for the gradually increased d_w/d_n with [AA].

The ratio $N_{p,f}/N_{m,i}$ is lower than unity for the polymerizations with SDS/SMA and it seems to decrease with increasing [AA] (Table 1). This may lead to the false conclusion that monomer droplets are the primary particle nucleation loci in this system. Incorporation of a small amount of AA

into the reaction mixture increases P_{dye} significantly (Table 1). In addition, P_{dye} increases with increasing [AA]. Taking the polymerization with [AA] = 1 wt% as an example, P_{dye} is equal to 55.8% and this implies that about 56% of the monomer droplets initially present in the system can be successfully transformed into latex particles. The remaining droplets only serve as a reservoir to supply latex particles with monomer and surfactant. Thus, monomer droplet nucleation becomes more important when [AA] increases from 0 to 3 wt%. If coalescence among the monomer droplets is negligible during polymerization, then the number of latex particles originating from monomer droplet nucleation (N_d) and the number of particles originating from homogeneous nucleation (N_w) can be calculated according to the following mass balance equations [24–26]:

$$N_d = N_{m,i} P_{dye} \quad (1)$$

$$N_w = N_{p,f} - N_d \quad (2)$$

The calculated N_d , N_w and $N_w/N_{p,f}$ data are also included in Table 1. These data show that N_d increases with increasing [AA] and monomer droplet nucleation plays a crucial role in the SDS/SMA stabilized polymerizations with [AA] = 1–3 wt%. However, homogeneous nucleation cannot be ignored except the run with [AA] = 3 wt% ($N_w/N_{p,f}$ = 0.03) since $N_w/N_{p,f}$ is about 0.2 for the polymerizations with [AA] = 0.3 and 1 wt%. It is also interesting to note that most of the latex particles are generated by homogeneous nucleation for the polymerization in the absence of AA ($N_w/N_{p,f}$ = 0.75). Thus, even the extremely hydrophobic SMA cannot suppress the formation of particle nuclei in the aqueous phase.

It is very difficult to explain why, at relatively constant $N_{m,i}$ (ca. 3.4×10^{17} l⁻¹), incorporation of a small quantity of

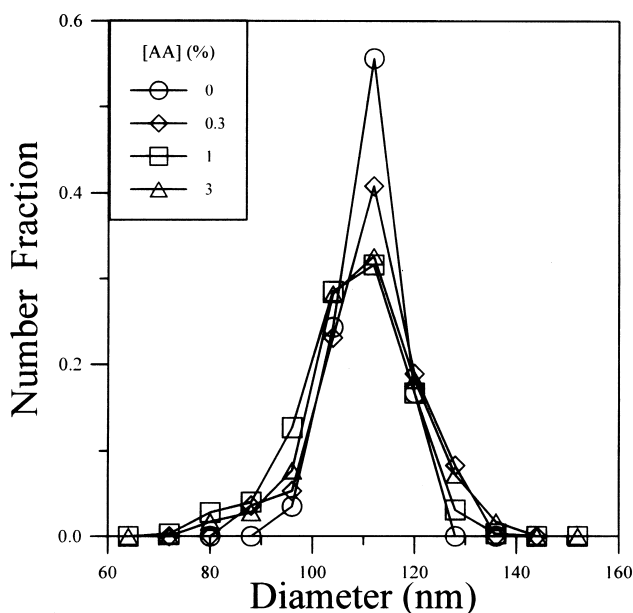


Fig. 2. Latex particle size distribution profiles for the polymerizations using SMA as the cosurfactant: [AA] = (○) 0 wt%, (◇) 0.3 wt%, (□) 1.0 wt%, (△) 3.0 wt%.

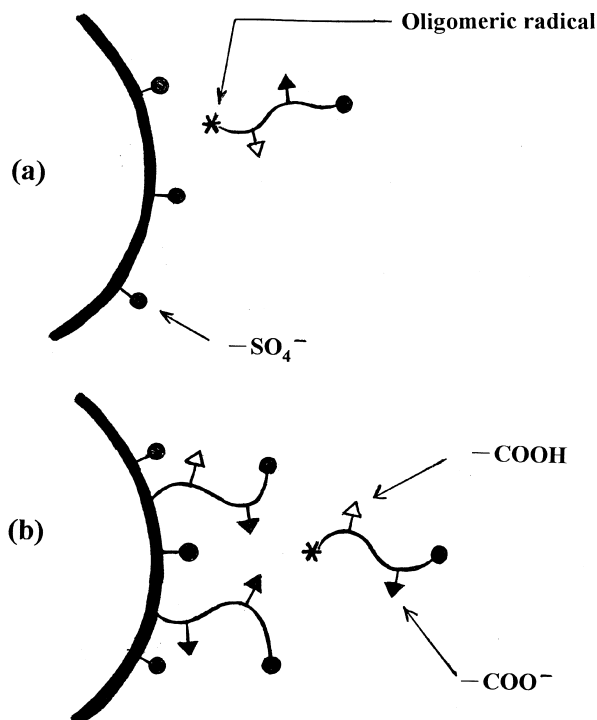


Fig. 3. Oil–water interfacial layer of monomer droplets or latex particles for the polymerization in the absence of AA (a) and latex particles for the polymerizations in the presence of AA (b).

AA into the polymerizations with SDS/SMA promotes monomer droplet nucleation (Table 1). This is because the water-soluble AA enhances the aqueous phase polymerization and it should favor the formation of particle nuclei in water. It is postulated that the composition of oligomeric radicals generated in water is rich in AA. The critical chain length for the AA containing radicals to precipitate out of the aqueous phase should be longer as compared with that obtained from the polymerization in the absence of AA. This will then increase the probability of capturing the relatively hydrophilic radicals by monomer droplets exhibiting a very large droplet surface area ($d_{m,i} = 113\text{--}115\text{ nm}$, $N_{m,i} = 3.34\text{--}3.56 \times 10^{17}\text{ l}^{-1}$ and, hence, the initial oil–water interfacial area is ca. $1.4 \times 10^4\text{ m}^2/\text{l}$ for the polymerizations with $[\text{AA}] = 0.3\text{--}3\text{ wt}\%$). As a consequence, more monomer droplets can be nucleated upon collision with these radicals induced by shear force. Another contributing factor is that the relatively hydrophilic polymer chain segment comprising ST, AA and a sulfate end-group cannot penetrate into the interior part of latex particles and it is extended toward the aqueous phase, as shown schematically in Fig. 3. Such an oil–water interfacial layer may retard the entry of radicals from the aqueous phase due to the electrostatic repulsion force between the negatively charged polymer chain segment extended from the particle surface and the negatively charged radical originating from the persulfate initiator (Fig. 3b). On the other hand, in competition with latex particles, the probability of capturing these radicals by monomer droplets may increase significantly (Fig.

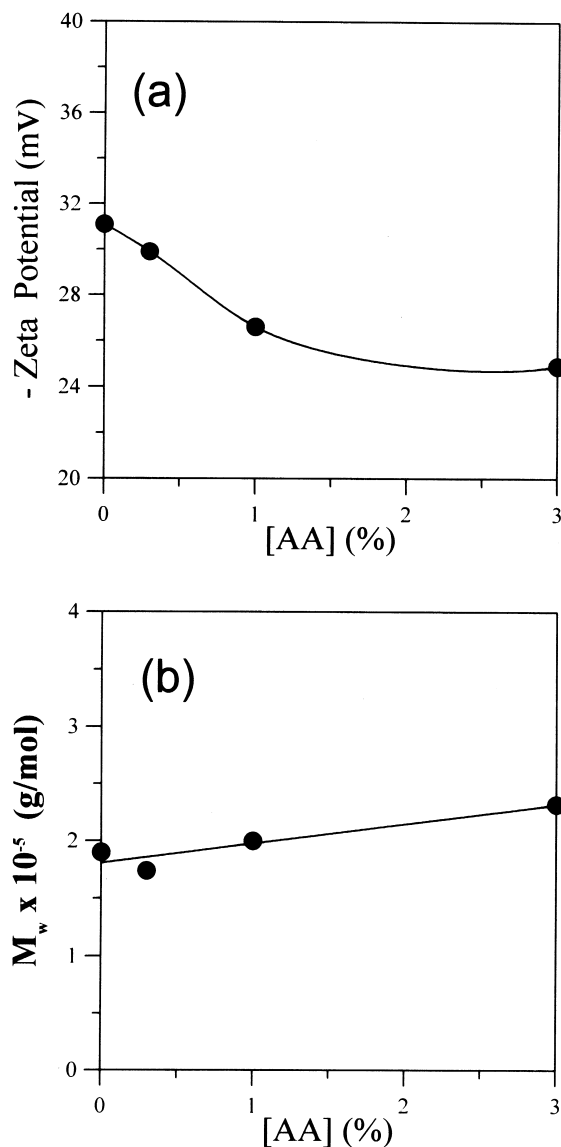


Fig. 4. Zeta potential of latex particles (a) and polymer molecular weight (b) as a function of the AA concentration for the polymerizations using SMA as the cosurfactant.

3a). Therefore, monomer droplet nucleation is greatly enhanced in the AA containing polymerizations. This scenario may also contribute to the reduced R_p for the polymerizations in the presence of AA as compared to the polymerization in the absence of AA. In other words, the rate of capture of radicals by the carboxylated latex particles (or R_p) is slower in comparison with the polymerization in the absence of AA (Fig. 3).

For the polymerizations with SDS/SMA, the absolute value of ζ first decreases rapidly and then levels off when $[\text{AA}]$ increases from 0 to 3 wt% (Fig. 4a). Incorporation of a small amount of AA onto the latex particle surface will increase the particle surface charge density because a certain fraction of AA is in the ionized form dependent on

the pH of the bulk solution. This will then result in the increase of ζ . On the other hand, the carboxylated latex particles are covered by a very hydrophilic polymer layer which can shift the shear plane toward the bulk solution. The ζ of latex particles is thus reduced. It is then postulated that the latter effect overrides the former and, consequently, the ζ of latex particles decreases with increasing [AA]. Besides, the latex particle surface becomes more hydrophilic and the particle surface coverage by SDS (particle surface charge density) decreases when [AA] increases from 0 to 3 wt%. The polymer molecular weight increases gradually with increasing [AA] (Fig. 4b). This is attributed to the retarded entry of radicals into the carboxylated latex particles, thereby leading to the reduced bimolecular termination reaction inside the particles. As expected, the use of AA improves the latex stability and, therefore, the total scrap decreases from 3.1 to 0.8% when [AA] increases from 0 to 3 wt% (Table 1).

Fig. 5 shows the effects of [AA] on the X versus t profiles (a) and the d versus t data (b) for the polymerizations using DMA as the cosurfactant. It is shown that the polymerization is severely retarded when AA is used as the comonomer (see Fig. 5a and the R_p data for D1–D3 in Table 1). The final conversion achieved is only 30 and 44% for the polymerizations with [AA] = 1 and 3 wt%, respectively. For the recipes with SDS/DMA and various levels of AA, $d_{m,i}$ is much larger (or $N_{m,i}$ is much smaller) in comparison with the SMA counterpart (Table 1) because the less hydrophobic DMA is not very effective in retarding the Ostwald ripening effect. For the polymerization in the absence of AA, d decreases rapidly to a plateau and this is again attributed to the formation of particle nuclei in the aqueous phase (see the circular data points in Fig. 5b). On the other hand, d first increases and then levels off ([AA] = 1 wt%) or the d versus t curve shows a maximum ([AA] = 3 wt%) for the polymerizations in the presence of AA (Fig. 5b). During the early stage of polymerization, the increase of d is most likely due to the Ostwald ripening effect. These data imply the retarded homogeneous nucleation (see the above discussion) as compared to the polymerization without AA. Furthermore, the carboxylated latex particle surface layer acts as a barrier to the incoming radicals from the aqueous phase. All these factors contribute to the slow polymerization rate for the runs with [AA] = 1 and 3 wt% (see Fig. 5 and the R_p data in Table 1). Sixty minutes after the start of polymerization, the run with [AA] = 1 wt% does not show a significant reduction in d and the lowest level of final conversion ($X_f = 30\%$) is obtained because of the slowest particle nucleation. Under the circumstances, the authors were unable to determine d_w by TEM and the average particle size of the final latex product determined by DLS was reported instead (see the data in the parentheses in Table 1). After the maximal d has been achieved at $t = \text{ca. } 60 \text{ min}$, d starts to decrease and then levels off for the polymerization with [AA] = 3 wt%. This implies that formation of particle nuclei becomes more

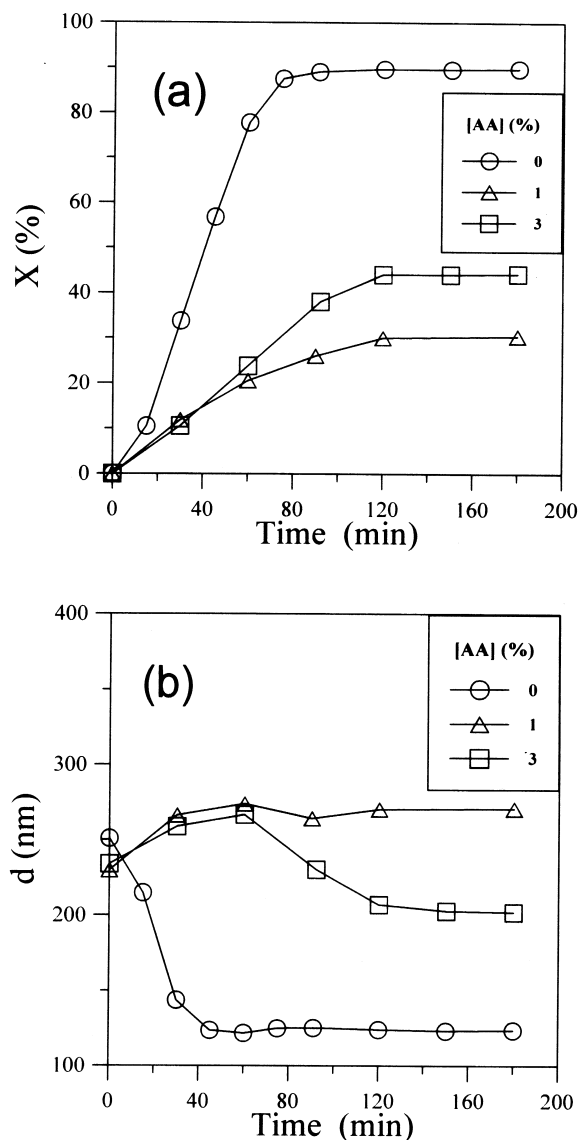


Fig. 5. Effect of the AA concentration on (a) the monomer conversion versus time profiles and (b) the average particle size versus time data for the polymerizations using DMA as the cosurfactant: [AA] = (○) 0 wt%, (△) 1.0 wt%, (□) 3.0 wt%.

important and a larger X_f (44%) is achieved. These speculated mechanisms are supported by (1) $d_{m,i}$: D1 (251 nm) > D3 (234) \cong D2 (230); (2) the average particle size of the final latex product: D2 (271 nm) > D3 (214) > D1 (121); (3) R_p : D1 ($3.49 \times 10^{-2} \text{ mol}/(1 \text{ min})$) > D3 (8.9×10^{-3}) > D2 (4.7×10^{-3}); and (4) $R_p/N_{p,f}$: D1 ($1.6 \times 10^{-19} \text{ mol/l}$) > D2 (3.1×10^{-20}).

The ratio $N_{p,f}/N_{m,i}$ is much greater than unity for both the SDS/DMA stabilized polymerizations with [AA] = 0 and 3 wt%. This indicates that homogeneous nucleation plays an important role in the particle formation process. Indeed, the $N_w/N_{p,f}$ data in Table 1 show that more than 95% of the latex particles are generated in the aqueous phase. The large values of $N_w/N_{p,f}$ are due to the predominant Ostwald

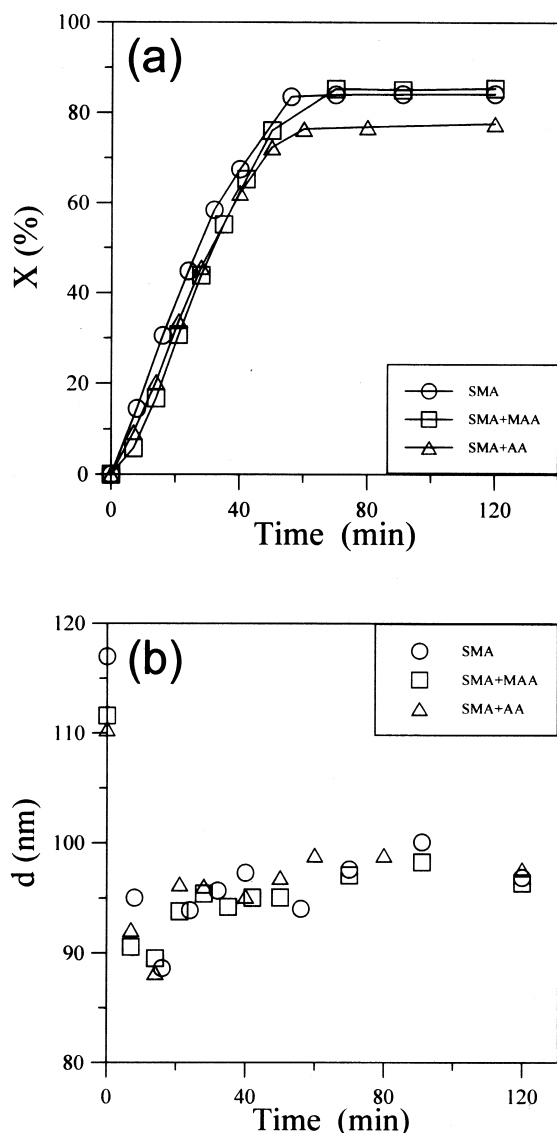


Fig. 6. Effect of the type of carboxyl monomers on (a) the monomer conversion versus time profiles and (b) the average particle size versus time data for the polymerizations using SMA as the cosurfactant. (○) In the absence of carboxyl monomers, (□) MAA, (△) AA.

ripening effect (i.e. the abundant supply of SDS, released from the continuously shrinking monomer droplet surface, for stabilizing the water-borne particle nuclei). Although incorporation of 3 wt% AA into the reaction mixture increases N_d and N_w simultaneously, the polymerization is slower in comparison with the run without AA. This is attributed to the effect associated with the surface structure of the carboxylated latex particles. Just like the SMA series, both M_w and M_w/M_n increase with increasing [AA] and the total amount of coagulum is greatly reduced when a small quantity of AA is used as the comonomer (Table 1).

In the final series of polymerizations, the concentration of AA or MAA ([AA] or [MAA]) was kept constant at 3 wt%. MAA possesses one extra methyl group and, therefore, it is

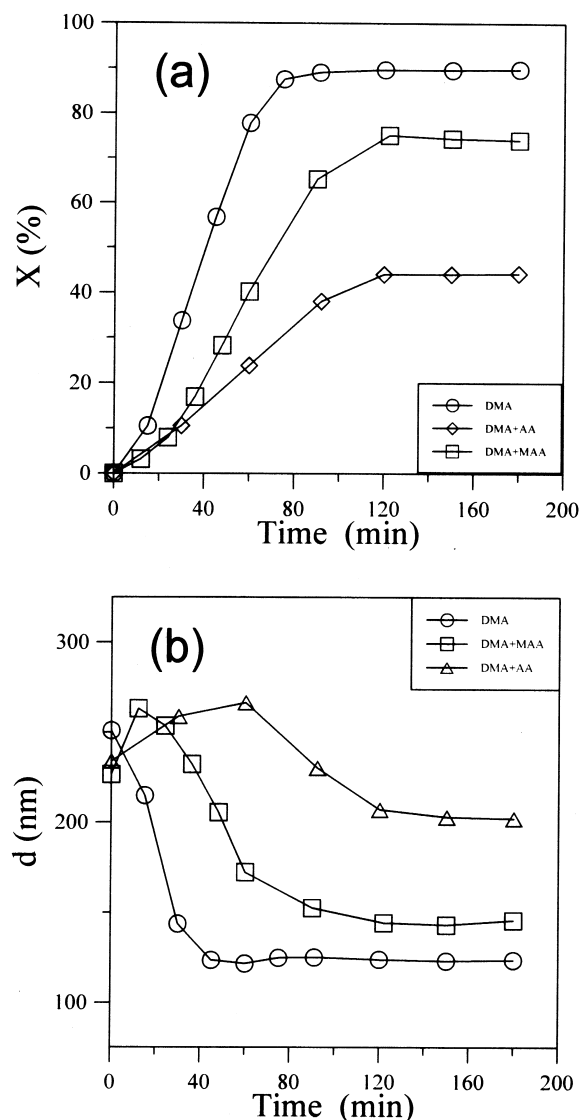


Fig. 7. Effect of the type of carboxyl monomers on (a) the monomer conversion versus time profiles and (b) the average particle size versus time data for the polymerizations using DMA as the cosurfactant. (○) In the absence of carboxyl monomers, (□) MAA, (△) AA.

less hydrophilic than AA. For comparison, the polymerizations in the absence of AA and MAA were also included in this section. The data of X and d as a function of t for the polymerizations stabilized by SDS/SMA and SDS/DMA are shown in Figs. 6 and 7, respectively. Some other experimental data are compiled in Table 1 (S1, S2 and S5; D1, D2 and D5).

Figs. 6 and 7 and the R_p , $R_p/N_{p,f}$ and $N_{p,f}/N_{m,i}$ data in Table 1 show that the influence of the type of carboxylic monomers on the polymerization kinetics for the runs with SMA (S1, S2 and S5) is not as important as the DMA counterpart (D1, D2 and D5). The N_d , N_w and $N_w/N_{p,f}$ data in Table 1 disclose that the degree of monomer droplet nucleation in the decreasing order is:

AA (S2) > MAA (S5) > In the absence of carboxylic monomers (S2)

In fact, most of the latex particles are nucleated in the submicron monomer droplets containing 3 wt% AA or MAA. In addition, the run with the weaker carboxylic monomer MAA shows an intermediate behavior in the ST miniemulsion polymerization stabilized by SDS/SMA. This is probably due to the fact that the probability for the oligomeric radicals comprising ST and MAA to participate the particle formation process in the aqueous phase is increased as compared to the AA counterpart. Another contributing factor is that the comonomer MAA can be distributed more uniformly in the latex particles in comparison with AA [30–32]. This will then alleviate the effect of the retarded entry of radicals into the carboxylated latex particles shown in Fig. 3b. The probability of capturing the incoming radicals by monomer droplets (i.e. monomer droplet nucleation) is reduced accordingly.

While significant diffusional degradation of monomer droplets takes place, formation of particle nuclei in the aqueous phase is delayed in the SDS/DMA stabilized polymerizations with 3 wt% AA or MAA (see the triangular or square data points in Fig. 7b). Fig. 8 and Table 1 clearly show that d_w in the decreasing order is:

In the absence of carboxylic monomers (D1) > MAA (D5) > AA (D2)

In addition, d_w/d_n in the decreasing order is:

AA (D2) > MAA (D5) > In the absence of carboxylic monomers (D1)

AA or MAA tends to extend the period of particle nucleation as a consequence of the suppressed formation of particle nuclei in the aqueous phase (Fig. 3). The size distribution of the resultant latex particles then becomes broader as compared to the polymerization without AA or MAA. Both the R_p and $R_p/N_{p,f}$ data obey the following order (Fig. 7a and Table 1):

In the absence of carboxylic monomers (D1) > MAA (D5) > AA (D2)

Homogeneous nucleation predominates in the SDS/DMA stabilized polymerizations ($N_w/N_{p,f} \geq 0.94$), but the addition of AA or MAA promotes monomer droplet nucleation (see the N_d data in Table 1). For both the SDS/SMA and SDS/DMA stabilized polymerizations, the following trends hold (Table 1):

d_w/d_n AA > MAA > In the absence of carboxylic monomers

M_w AA > MAA > In the absence of carboxylic monomers

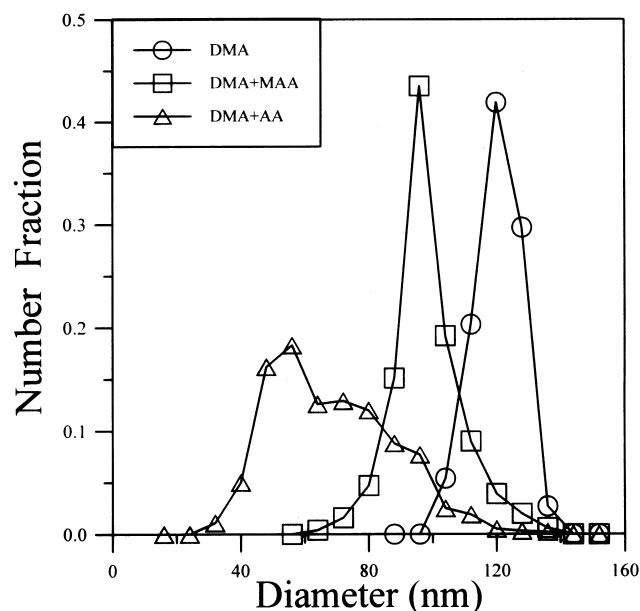


Fig. 8. Latex particle size distribution profiles for the polymerizations using DMA as the cosurfactant. (○) In the absence of carboxyl monomers, (□) MAA, (△) AA.

M_w/M_n AA > MAA > In the absence of carboxylic monomers

ζ In the absence of carboxylic monomers > AA \equiv MAA

As discussed above, all these results are closely related to the very complicated particle nucleation and growth mechanisms involved in both the SMA and DMA series.

4. Conclusions

The influence of a small amount of carboxylic monomers (AA and MAA) on the styrene miniemulsion polymerizations stabilized by SDS/SMA or SDS/DMA is significant. A mixed mode of particle nucleation (monomer droplet nucleation and homogeneous nucleation) was proposed for these polymerization systems. Formation of particle nuclei in the aqueous phase (homogeneous nucleation) predominates in the SDS/SMA and SDS/DMA polymerizations in the absence of carboxylic monomers. Incorporation of a small amount of AA into the reaction mixture results in relatively hydrophilic oligomeric radicals and this makes the formation of the water-borne particle nuclei more difficult. Furthermore, the efficiency of capturing the incoming radicals by the carboxylated latex particles is reduced significantly due to the electrostatic repulsion force between the negatively charged polymer chain segment extended from the particle surface and the negatively charged oligomeric radical originating from the persulfate initiator. The probability of nucleation in the submicron monomer droplets (i.e. monomer droplet nucleation) is enhanced accordingly. The run using the less hydrophilic MAA as

the comonomer shows an intermediate behavior in the polymerization kinetics and mechanisms. For the SDS/SMA stabilized polymerizations with carboxylic monomers, the relatively stable monomer droplets exhibiting a very large droplet surface area become the primary particle nucleation loci. On the other hand, homogeneous nucleation plays a crucial role in the SDS/DMA stabilized polymerizations, in which the Ostwald ripening effect overrides the effect associated with carboxylic monomers. Moreover, formation of particle nuclei in the aqueous phase is severely delayed. The polymerization rate decreases and the particle size distribution of latex particles becomes broader when a small amount of AA or MAA is used as the comonomer.

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