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ORIGINAL CONTRIBUTION

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Effects of surface charge density on emulsion kinetics and secondary particle formation in emulsifier-free seeded emulsion polymerization of methyl methacrylate

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Abstract Experiments were carried out to investigate the effects of surface charge density on emulsion kinetics and secondary particle formation in emulsifier-free seeded emulsion polymerization. Three monodisperse seed latices with different surface charge densities were prepared from styrene/NaSS comonomers using the two-stage shot-growth process. After purification of the seed latices, they were used in seeded emulsion polymerization of methyl methacrylate. The initial rate of polymerization and the average number of radicals per particle for the high-charged seed latex system were lower than that of the low-charged case. The low rate of polymerization resulted from the low rate of radical adsorption in the beginning of the reaction due to the electrical repulsion between seeds and oligomeric radicals. In this case, because of the secondary particles, particle size distribution became bimodal. The low rate of radical adsorption and the formation of secondary particles reduced the average number of radicals per particle. The rate of polymerization (R_p) increased, but the rate of polymerization per particle (R_p/N_p) decreased.

Key words Surface charge density – electrical repulsion – average number of radicals per particle – rate of polymerization per particle – secondary particle formation

Introduction

In emulsifier-free emulsion polymerization, particle nucleation can be explained by the homogeneous nucleation mechanism or the homogeneous-coagulative nucleation mechanism [1, 2]. In the case of seeded emulsion system, somewhat different reactions take place in the polymerization system. This reaction scheme is illustrated in Fig. 1. Oligomeric radicals are generated from the initiation reaction of monomers and water-soluble initiators in the aqueous phase. As the propagation proceeds, the hydrophobicity of oligomeric radicals increases. They propagate further to become precursor particles or become absorbed by seed particles. Surface-active oligomeric radicals can easily adsorb onto the seeds. Above the critical chain lengths (j_{crit}), coil-conformation transition of oligomeric radicals can occur [2, 3]. These precursors undergo a coagulation process to form colloidally stable particles. The colloidal stability of particles can be achieved by electrostatic repulsion [2]. These competitive reactions (i.e. coil-conformation and adsorption) can be influenced by several factors, such as the weight ratio of monomer to seed solids, the concentration of electrolytes, the polarity of seed particles, the interfacial tension and hydrophilicity of seeds and monomer, and the properties of initiators [4]. For seeded or *ab initio* emulsion systems, Ugelstad, Hansen, Feeny, and Gilbert et al. derived the particle nucleation

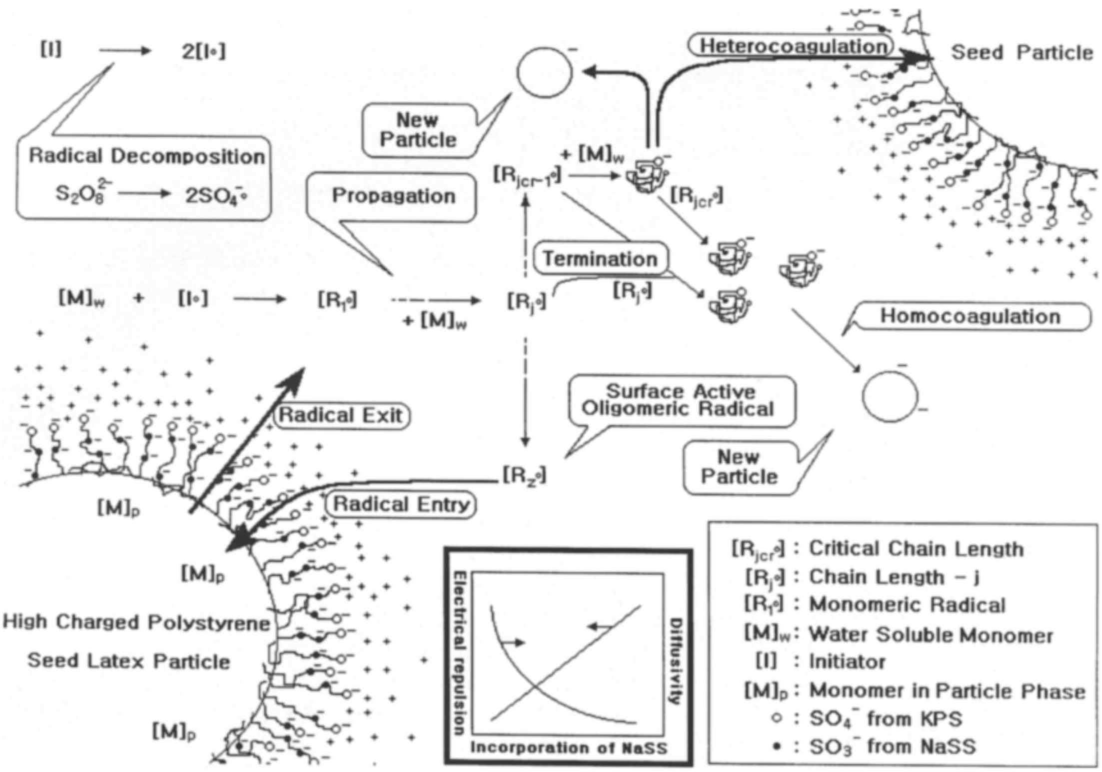


Fig. 1 Schematic diagram of emulsifier-free seeded emulsion polymerization system

model and investigated some important factors affecting particle size distribution [3, 5, 6]. So far, the effects of only the high-charged seeded system has not been studied. Like highly carboxylated polymer particle systems, highly sulfonated systems have both electrostatic repulsion effect and steric effect due to the hydrophilic groups which stretch toward aqueous phase. In this study, the emulsifier-free seeded emulsion system was used to investigate the effects of surface charge density resulted from the incorporated sulfonated groups on polymerization rate, average number of radicals per particle, and formation of secondary particles.

Experimental

Materials

Styrene monomer and methyl methacrylate monomer were obtained from Junsei, Inc., and purified using the inhibitor remover column (Aldrich Chem. Co.). The purified monomers were stored at − 5 °C until use. Sodium styrene sulfonate was obtained from Morton Thiokol Inc. and used as received. Potassium persulfate, sodium bicarbonate, sodium hydroxide, and hydrochloric acid were all of analytical grade and were used without further purification. Double-distilled and deionized water was used throughout.

Preparation of charged seed latices

The seed latex particles were prepared using the two-stage shot-growth process [7–10] because particle size and surface charge density can be controlled independently [9, 10]. The recipe is listed in Table 1. The first-stage copolymerization was carried out with a low concentration of sodium styrene sulfonate (NaSS) to enhance the

Table 1 Shot-growth polymerization recipe for preparation of charged seed latex particles

Component	Initial charge [g]	Shot injection [g]
Styrene	150	Variable[1]
NaSS	0.30	Variable[2]
Potassium persulfate	0.60	0.2
Sodium bicarbonate	0.19	—
DDI water		1600

[1] 19–16 [g].
[2] 1–4 [g].

Table 2 Seeded emulsion polymerization of methyl methacrylate

Component	Charge [g]		
Seed latex	20	20	20
Methyl methacrylate		Variable1)	
Potassium persulfate		Variable2)	
DDI water		40	

1) 1.2–4.5 [g] ratio based on seed solids.
2) 0.1 wt% based on methyl methacrylate monomer.

stability and control the size of the seed particles. Polymerization was carried out in a 4 l water-jacketed glass reactor equipped with a reflux condenser, water circulator, nitrogen inlet, and stirrer. The reactor was thermostated at the reaction temperature by the water circulator. The stirrer speed was maintained at 260 rpm. The second-stage monomer mixture and initiator were added at the appropriate percent conversion of the first-stage monomer. The point of addition of the second-stage monomer was established based on the conversion-time curve determined in separate experiments.

Seeded emulsion polymerization of methyl methacrylate

Seeded emulsion polymerization of methyl methacrylate was carried out with no swelling and under the batch conditions of 3 h at 70 °C. To investigate the effects of surface charge density only, the seed latices were filtered with glass wool to remove coarse particles and steam-stripped to remove any remaining styrene monomer [9]. The latices were cleaned with fivefold excess ion exchange resin (Amberlite MB-604A, mixed bed, Rohm and Hass Co.) for 24 h and then by the serum replacement method [9–13]. The serum was cleaned with pure water to remove free homopolymers dissolved in the aqueous phase or adsorbed on the surface of seed particles until the conductivity of serum was constant. To determine the optimum weight ratio of monomer to seed solids, screening tests were performed because excess amounts of monomer injection can cause secondary particle formation [5]. The recipe is listed in Table 2.

Characterization

Conversion

The conversion was determined by gravitational method. For the determination of conversion, samples were added to 1 cm^3 of a short-stop solution of 1.5 g/dm^3 of hydroquinone in methanol, after which water, methanol, and unreacted monomer were evaporated at 60 °C.

Particle size and particle size distribution

Micrographs and particle size distributions of the latex particles were determined using scanning electron microscopy (SEM, JSM-541LV, JEOL Inc., Japan) and capillary hydrodynamic fractionation (CHDF-1100, Matec Applied Sciences, USA). A drop of 0.1 wt% diluted latex was placed on copper plate and dried at room temperature. The dispersity of the latex particles was defined by the polydispersity index PD[9]

$$\mathrm{PD} = D_\mathrm{w}/D_\mathrm{n} \,, \qquad (1)$$

where D_w is the weight-average diameter of latex particles and D_n is the number-average diameter. For PD less than 1.05, the latex was considered monodisperse [9].

Surface charge density

Surface charge densities of the latex particles were determined using the conductometric titration method [9, 10] after the latices had been rigorously cleaned as above. Conductometric titration was carried out with sodium-hydroxide solutions of concentration 0.02 N in a stirred vessel under nitrogen atmosphere. The surface charge, in term of equivalents of surface groups per gram of polymer particles (N_p) can be expressed [10]

$$N_\mathrm{p} = \frac{\Delta V N}{10^3 W_\mathrm{p}} \,, \qquad (2)$$

where ΔV is the volume of titrant (NaOH), N is the normality of the titrant and W_p the weight of polymer particles titrated. The surface charge density C/cm^2 is calculated from following equation [10]:

$$\sigma = 96500\, N_\mathrm{p} d_\mathrm{p} \frac{D}{6} \,, \qquad (3)$$

where d_p is the particle density and D the particle diameter.

Results and discussion

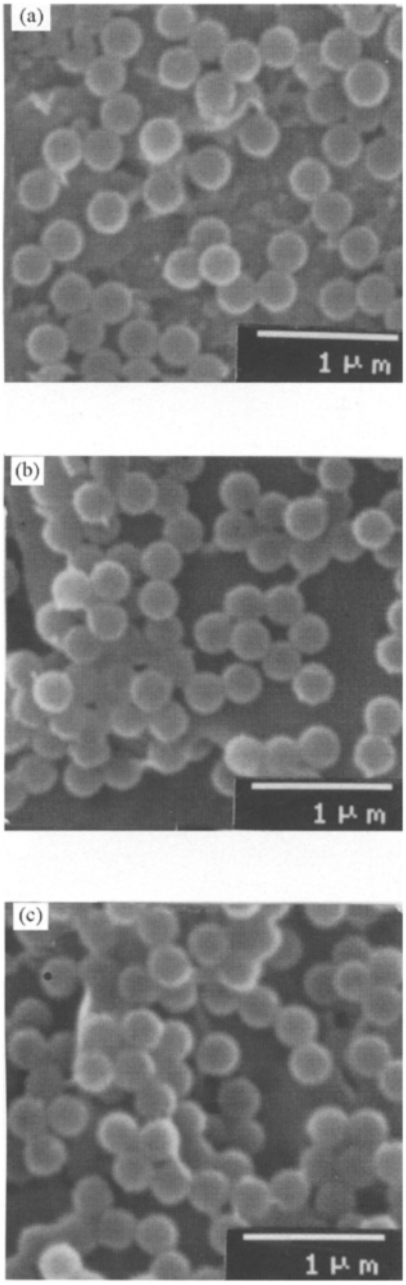
Particle size and surface charge density of seed latex

The data for the prepared seed latices are given in Table 3. The second-stage monomer injection was performed at 90 wt% conversion of the first stage. The number-average diameters of seed latex particles were about 300 nm and the distributions were monodisperse. The total surface areas of seed latex particles (Nxr) were very uniform in order of 10^8 dm^{-2}. The surface charge densities were from

Table 3 Characteristics of charged seed latex particles

No.	S-A	S-B	S-C
D_n [nm]	302	291	300
D_w/D_n	1.01	1.01	1.01
Nxr [dm^{-2}]	3.6×10^8	3.8×10^8	3.6×10^8
σ [μC/cm^2]	12.9	37.9	72.7

Fig. 2 SEM photographs (magnification = 20 K) of charged seed latex particles prepared by shot-growth process (temp.: 70 °C, 24 h, second stage began at the 90% conversion of first stage; (a) S-A, (b) S-B, (c) S-C)



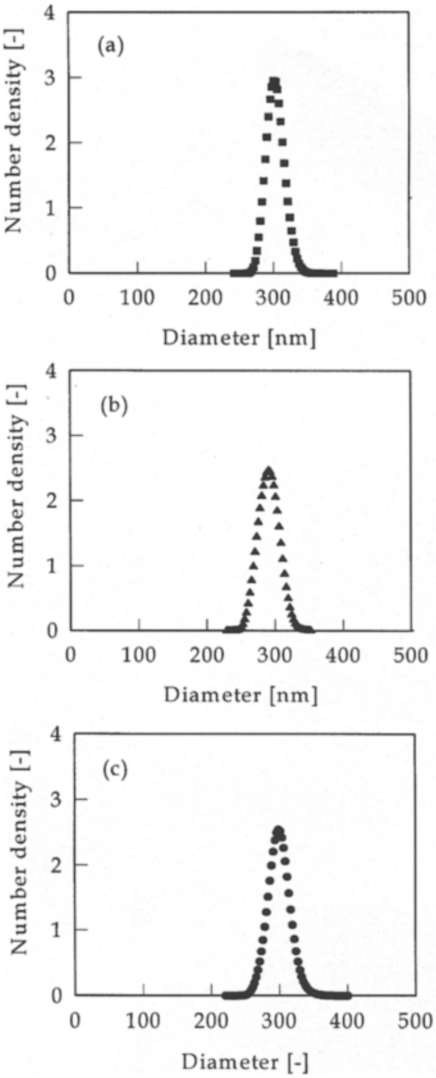


Fig. 3 Particle size distribution of charged seed latex particles ((a) S-A, (b) S-B, (c) S-C)

12.9 to 72.7 μC/cm^2. Considering only five or six sulfonate groups can adsorb onto the area of square nanometers, the surface charge density of 72.7 μC/cm^2 was assumed to be a saturated one. SEM photographs and particle size distributions of the seed latices were shown in Figs. 2 and 3, respectively.

Particle size distribution of PMMA/charged latex

Figs. 4 and 5 shows the SEM photographs and the particle size distributions of PMMA/charged latices. The particle size distributions in Fig. 5 were measured using CHDF-1100. The amount of monomer used in seeded polymerization was fixed as mentioned above. The results

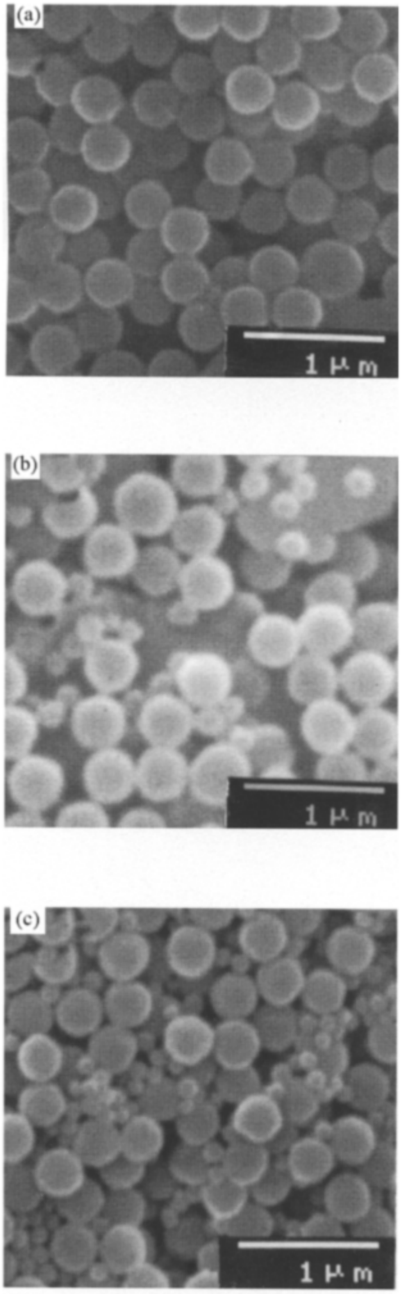


Fig. 4 SEM photographs (magnification = 20 K) of PMMA/charged latex particles (temp.: 70 °C, 3 h, no swelling and batch conditions; (a) S-A, (b) S-B, (c) S-C)

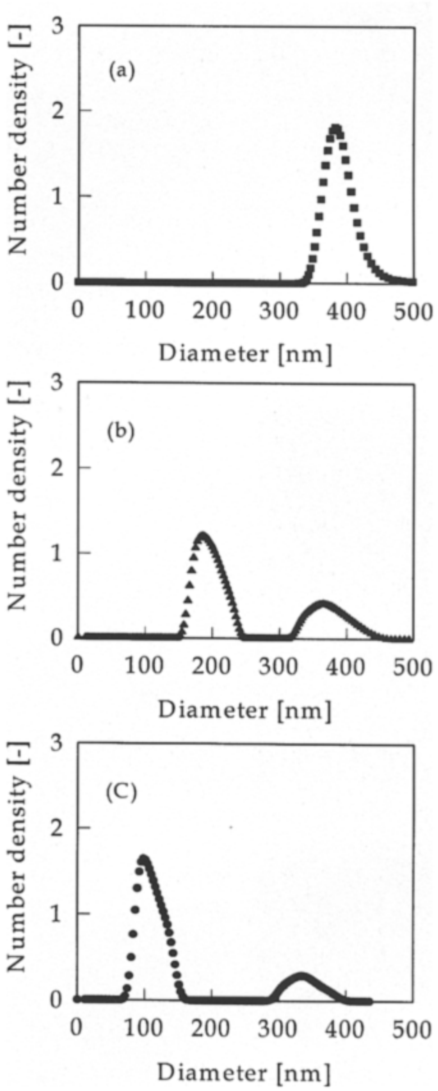


Fig. 5 Particle size distribution of MMA/charged latex particles ((a) S-A, (b) S-B, (c) S-C)

Table 4 Screening test for determination of weight ratio of monomer to seed solid

Monomer/Polymer	S-A	S-B	S-C
1.23	1.01	1.02	1.02
2.20	1.01	1.33 (B)	2.00 (B)
2.75	1.05 (P)	1.34 (B)	2.01 (B)
3.50	1.10 (P)	1.48 (B)	2.11 (B)

P: Polydisperse (Unimodal).
B: Bimodal.

are listed in Table 4. In all the cases from S-A to S-C, the weight ratios of monomer to seed solid were 2.20. Sample S-A is the lowest-charged case and sample S-C is the highest case. In Fig. 4, a high number of secondary particles formed in the case of sample S-C is shown. But in sample S-A, only a few secondary particles formed.

The surface charge density of seed particles reduced the rate of radical adsorption. The rate coefficient of radical adsorption can be obtained from radical balances in the aqueous phase and modified Smoluchowski equation [5]

$$k_c = 4\pi D_w r_{sp} N_A F \ , \qquad (4)$$

$$\rho = k_c [R^*]_{tot} \ , \qquad (5)$$

where, D_w is the diffusion coefficient in water, r_{sp} the swollen radius of the seed, F the reduction factor caused by reversible diffusion and electrostatic repulsion, $[R^*]_{tot}$ the concentration of free radicals in the aqueous phase, and ρ the rate of radical adsorption. If no secondary particles are to be nucleated, then the rate of radical capture by the seed particle, R_c, must exceed the rate of radical generation [15], R_i, i.e.

$$R_c = k_c[R^*]_{tot}N_p/N_A \ , \tag{6}$$

$$R_i < R_c \ . \tag{7}$$

But, in the case of S-B and S-C, the rate of radical capture, R_c, was lower than R_i because the reduction factor, F, decreased due to high electrical repulsion and hydrophilicity of the seed particle [5]. Polydispersity (PD) of the seed and the PMMA/charged latices are listed in Table 4. The PD increased as the surface charge density of the seed particle increased.

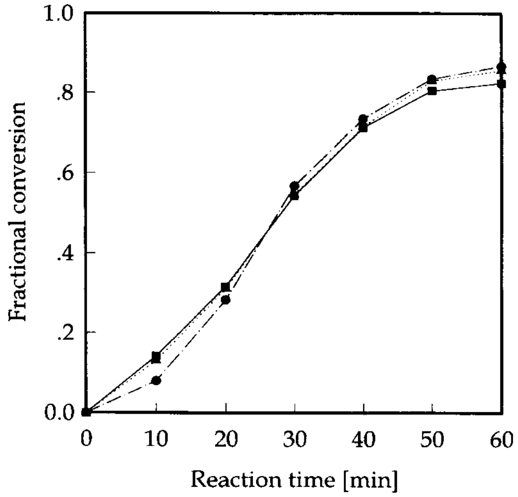


Fig. 6 Effect of surface charge density on fractional conversion of MMA vs. reaction time (■) S-A; (▲) S-B; (●) S-C

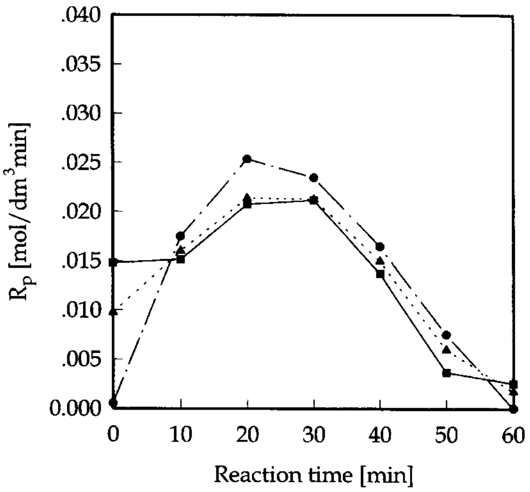


Fig. 7 Effect of surface charge density on rate of polymerization of MMA vs. reaction time (■) S-A; (▲) S-B; (●) S-C

Conversion and rate of polymerization

The fractional conversions of methyl methacrylate are shown in Fig. 6. In relatively low surface charged cases, the plots showed the typical conversion curves of seeded emulsion polymerization. But the highest surface charged case showed an S-shaped curve which is characteristic of micellar nucleation. In *ab initio* polymerization, there are three intervals in the reaction [14]. Interval I is the particle nucleation step, interval II the particle growth step, and interval III the final polymerization step. In first two cases, formation of new particles was minimal. But for the third case, the conversion curve showed a different shape due to the formation of secondary particles resulting from the high surface changed seed. The feature can be explained in two ways: First, in the initial period of the reaction, the electrical repulsion between seeds and oligomeric radicals caused the rate of radical adsorption to decrease. However, the concentration of oligomeric radical in the aqueous phase increases to form new particles easily. As a result, the initial rate of polymerization was low, but increased gradually in the latter period of reaction time. Second, the increase in hydrophilicity of the seeds made the driving force of radical adsorption lower. The rate of polymerization in particles was lower than that in the aqueous phase compared with ordinary-seeded emulsion systems. The rate of polymerization is shown in Fig. 7. The low rate of radical adsorption made the concentration of oligomeric radicals high in the aqueous phase. The oligomeric radicals in the aqueous phase propagate further to coil up and precipitate. These precipitated oligomeric radical are able to capture monomers and other radicals to grow until they achieve colloidal stability. The increase in the rate of polymerization can be explained by the increase of polymerization locus due to the formation of new particles.

Average number of radicals per particle

It is very difficult to estimate the average number of radicals per particle ($\bar{n}$) in emulsion polymerization because the polymerization loci in emulsion polymerization are separated [14]. Although $\bar{n}$ can be calculated by using the solution of Stockmayer-O'Toole, their equation is deduced from the homopolymer system only. So, $\bar{n}$ was calculated from the fitted time-conversion curve as follows:

$$t = ax^5 + bx^4 + cx^3 + dx^2 + ex + f\,, \tag{8}$$

where a, b, c, d, e, and f are fitting parameters. t is reaction time and x is fractional conversion of methyl methacrylate. The above equation was adapted to the following equations to determine $\bar{n}$:

$$\frac{dx}{dt} = \frac{1}{5ax^4 + 4bx^3 + 3cx^2 + 2dx + e}\,, \tag{9}$$

$$\bar{n} = \frac{N_A}{N_p k_p (1 - x)} \frac{dx}{dt}\,. \tag{10}$$

The number of particles includes secondary particles was determined from CHDF allowing secondary and seed particle to be distinguished. The average number of radical per particle ($\bar{n}$) is shown in Fig. 8. In *ab initio* polymerizations, $\bar{n}$ increases abruptly in the beginning of the reaction (i.e. particle formation). After the consummation, $\bar{n}$ decreases and shows comparatively constant value during the period of the particle growth. In the case of seeded systems, however, $\bar{n}$ increases gradually due to the constant number of polymer particle unless there are new particle formations. The increment of $\bar{n}$ results from the decomposition of initiators and radical adsorption onto seed particles. The average number of radicals became smaller as the surface charge density increased. Because of the electrical repulsion between seeds and oligomeric radicals, the rate of radical adsorption decreased and the average number of radicals per particle decreased. The average number of radical varied with the number of particles. Fig. 8 shows the low average number of radicals also resulting from the increase of new particles.

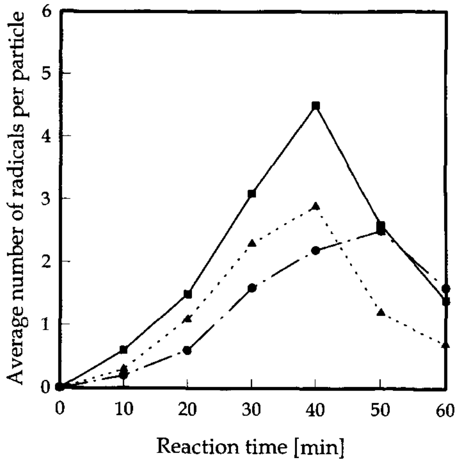


Fig. 8 Effect of surface charge density on average number of radical ($\bar{n}$) vs. reaction time (■) S-A; (▲) S-B; (●) S-C

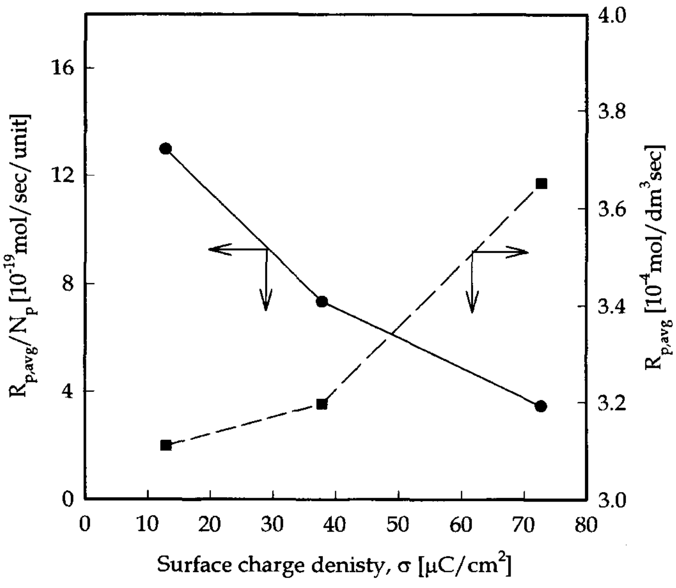


Fig. 9 Rate of polymerization (R_p) and rate of polymerization per a particle (R_p/N_p) vs. surface charge density (-■-) R_p; (----●----) R_p/N_p

Rate of polymerization per particle

The rate of polymerization per particle (R_p/N_p) was introduced to investigate the effect of secondary-particle formation on the rate of polymerization. The rate of polymerization and the rate of polymerization per particle in emulsion polymerization can be expressed, respectively

$$R_p = \frac{k_p[M]_p \bar{n} N_p}{N_A}\,, \tag{11}$$

$$R_p/N_p = \frac{k_p[M]_p \bar{n}}{N_A}\,. \tag{12}$$

Fig. 9 shows that the rate of polymerization per particle decreased as surface charge density increased because of the low value of $\bar{n}$, however, the formation of secondary particles increased. In the high surface charged region ($>20\ \mu C/cm^2$), the rate of polymerization, R_p, increased gradually due to the formation of secondary particles. Secondary particles differ from seed particles in two ways: they have a high exit rate of radicals due to their small size and great curvature [3], and they have a lower swelling rate than the seed particles. The rate of volume growth of the new particle was low compared to that of the seeds. Even though there was a high rate of new particle formation, the secondary particles did not significantly affect the total rate of polymerization.

Conclusions

Emulsifier-free emulsion polymerization of methyl methacrylate was carried out to investigate the effects of surface charged density of seed particles on polymerization rate, radicals per particle, secondary particle formation, and particle size distribution. A low rate of radical adsorption resulted from electrostatic repulsion between the seeds and oligomeric radicals (or precursors). A low rate of radical adsorption caused the rate of polymerization and the average number of radicals per particle to be reduced. In the case of the highest surface charge density (72.7 μC/cm^2), secondary particle nucleation occurred easily in the homogeneous phase. Formation of secondary particles meant an increase in polymerization locus. Therefore, the rate of polymerization (R_p) increased rapidly but the rate of polymerization per particle (R_p/N_p) decreased as the number of particles increased. In the initial period of reaction (i.e. before secondary particle formation), the low rate of radical adsorption resulting from electrical repulsion was a decisive factor in explaining the rate parameters and subsequent nucleation. The low rate of radical adsorption resulted in a low rate of polymerization, a small number of radicals per particle, and secondary-particle formation. After the formation of secondary particles, the number of particle (N_p) was found to be an important factor in determining the rate of polymerization.

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