에멀젼 중합에 의한 스티렌－부타디엔 고무의 미세구조 조절과 그의 물성에 관한 연구. 3. 유화중합에 있어서 입경분포의 모델

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A Study on the Control of Fine Structure of SBR by Emulsion Polymerization and its Physical Properties. 3. Modeling of Particle Size Distribution in Emulsion Copolymerization

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요 약 : 유화 공중합을 회분식 반응기에서 행할 경우에 있어서 자유라디칼의 흡착 및 단량체 조성에 따라 달라지는 입경분포를 interval II 영역에서 예측하였다. Styrene-butadiene (St-Bu) 계 및 styrene-methyl methacrylate (St-MMA) 계를 계산의 예로 들었다.

Abstract : The effect of free radical entry and monomer composition on the particle size distribution(PSD) was theoretically analyzed during interval II of emulsion copolymerization in an ideal batch reactor. Styrene-butadiene (St-Bu) and styrene-methyl methacrylate (St-MMA) systems were given as an analytic example.

INTRODUCTION

Since the appearance of the Smith-Ewart theory,[1] it has gained wide acceptance as providing a powerful tool to quantitatively describe free radical homopolymerization. Lichti et al.[2] proposed a mathematical model for describing variation of PSD during homopolymerization by applying the Smith-Ewart theory. Feeney et al.[3~6] treated the model of Lichti et al.[2] together with the coagulative nucleation theory.

In an emulsion copolymerization, Ballard et al[7] proposed a mathematical model for predicting the time evolution of the copolymer composition and copolymer sequence distribution by extending the Smith-Ewart equation[1] to emulsion copolymerization systems. Chen and Wu[8] extended the model of Lichti et al.[2] to predict the conditions for producing bimodal PSD during emulsion copolymerization. No theory dealing with the effect of free radical entry into the latex particle and monomer composition on PSD has been proposed for

emulsion copolymerization.

Recently, Park et al.[9] showed the average rate coefficient for free radical entry into a latex particle($\bar{\rho}$) as $\bar{\rho} = \bar{\rho}_a + \bar{\alpha}\,\bar{k}\,\bar{n}$ for emulsion copolymerization by extending the model of Penboss et al.[10] Here $\bar{\rho}_a$ is the component arising from the aqueous-phase initiator. $\bar{\alpha}$ is the average fate parameter. $\bar{k}$ is the averaged coefficient for exit (desorption) of free radicals. $\bar{n}$ is the averaged number of free radicals per particle.

This paper theoretically deals with the effect of free radical entry into the latex particle and monomer composition on PSD for emulsion copolymerization.

THE TIME EVOLUTION EQUATION OF PSD

Description of Model

We consider the interval II region of an emulsion copolymerization in an ideal batch reactor. Although same model has been introduced by Chen and Wu,[8] its derivation is explained in more detail. For simplicity, we neglect the coagulative nucleation.[3~6]

By extending the model of Lichti et al.,[2] the time evolution of the PSD may be presented as

$$\partial n_{iAjB}(v,t)/\partial t = -[\rho_A + \rho_B + ik_A + jk_B + i(i-1)c_{AA}$$
$$+ 2ijc_{AB} + (j-1)c_{BB} + ir_{AB} + jr_{BA}]n_{iAjB} + \rho_A n_{(i-1)AjB}$$
$$+ \rho_B n_{iA(j-1)B} + (i+1)k_A n_{(i+1)AjB} + (j+1)k_B n_{iA(j+1)B}$$
$$+ (i+1)(i+2)c_{AA}n_{(i+2)AjB} + 2(i+1)(j+1)c_{AB}$$
$$n_{(i+1)A(j+1)B} + (j+1)(j+2)c_{BB}n_{iA(j+2)B} + (i+1)$$
$$r_{AB}n_{(i+1)A(j-1)B} + (j+1)r_{BA}C_M n_{(i-1)A(j+1)B} - \partial/\partial v$$
$$[(ik_{pAA}C_{MA}M_{oA} + jk_{pBA}C_{MA}M_{oA} + jk_{pBB}C_{MB} + ik_{pAB}$$
$$C_{MB}M_{oB})N_A^1 d^{-1}]n_{iAjB} \qquad (1)$$

Here $n_{iAjB}(v, t)$ represents the relative number of latex particles containing $(i+j)$ radicals at volume v and time t, i of which is of type A, and j of which is of type B. ρ_A and ρ_B are the rate coefficients for entry of radical A and B. k_A and k_B are the rate coefficients for exit of radical A and B. c_{AA}, c_{BB} and c_{BA}(with $c_{AB} = c_{BA}$) are the termina-

tion coefficients. r_{AB} and r_{BA} are, respectively, defined as

$$r_{AB} = (k_{pAB} + k_{trAB})C_{MB}C_M^{-1} \qquad (2)$$

$$r_{BA} = (k_{pBA} + k_{trBA})C_{MA}C_M^{-1} \qquad (3)$$

C_{MA} and C_{MB} respectively represent the concentration of monomer A and B within the latex particles and $C_M = C_{MA} + C_{MB}$. k_{pAB} and k_{trAB} are respectively the propagation and transfer rate coefficients for addition of a B monomer to A radical and similarly for others.

N_A is Avogadro number. d is density of the monomer swollen particle. M_{oA} and M_{oB} are respectively the molecular weight of monomer A and B. Note that the definitions of r_{AB} and r_{BA} by Ballard et al.,[7] which is different from ours, are

$$r_{AB} = (k_{pAB} + k_{trAB})C_{MB} \qquad (4)$$

$$r_{BA} = (k_{pBA} + k_{trBA})C_{MA} \qquad (5)$$

in which no C_M^{-1} term is involved.

Here we define the average volume growth rate of unswollen particles containing a radical as

$$(i+j)\bar{K} = \sum_{i=0}^{i+j} P_{ij}(ik_{pAA}C_{MA}M_{oA}N_A^{-1}d_{pA}^{-1}$$
$$+ jk_{pBA}C_{MA}M_{oA}N_A^{-1}d_{pA}^{-1}$$
$$+ jk_{pBB}C_{MB}M_{oB}N_A^{-1}d_{pB}^{-1}$$
$$+ ik_{pAB}C_{MB}M_{oB}N_A^{-1}d_{pB}^{-1} \qquad (6)$$

P_{ij} is defined[7] as the probability of a latex particle containing A and B radicals out of a total of $(i+j)$ radicals. P_{ij} was derived correctly as[8, 11]

$$P_{ij} = \frac{(i+j)!}{i!\,j!}\,\frac{(k_{pBA}C_{MA})^i(k_{pAB}C_{MB})^j}{(k_{pBA}C_{MA} + k_{pAB}C_{MB})^{i+j}} \qquad (7)$$

where d_{pA} and d_{pB} are respectively the densities of polymer A and B. To obtain $\bar{K}$ value of swollen particles, d_{pA} and d_{pB} are replaced by the swollen particle density(d). The relationship between d and concentration of monomers may be presented as (from Appendix)

$$d = 1/v_s = d_{cop}(1 - 10^{-3}C_{MA}M_{oA}d_{MA}^{-1} - 10^{-3}C_{MB}M_{oB}d_{MB}^{-1}) \tag{8}$$

where v_s is the volume of swollen particle. d_{cop} is the copolymer density. d_{MA} and d_{MB} are respectively the density of monomer A and B.

Simplification of Time Evolution Equation of PSD

Ballard et al.[7] defined the following average rate coefficients to simplify eq(1), except the last term

$$\bar{\rho} = \rho_A + \rho_B \tag{9}$$

$$(i+j-1)\bar{k} = \sum_{i=1}^{i+j} P_{ij}(ik_A + jk_B) \tag{10}$$

$$(i+1)(i+j-1)\bar{c} = \sum_{i=1}^{i+j}$$
$$P_{ij}[i(i-1)c_{AA} + 2ijc_{BB} + j(j-1)c_{BB}] \tag{11}$$

Using the definition of P_{ij}, eqs(10) and (11) were simplified as[7,8,11]

$$\bar{k} = k_A P_{10} + k_B P_{01} \tag{12}$$

$$\bar{c} = c_{AA}P_{20} + c_{AB}P_{11} + c_{BB}P_{02} \tag{13}$$

To simplify the last term of eq(1) and eq(6), we define the following average rate coefficients of propagation as

$$\bar{k}_p = \bar{k}_{pA} + \bar{k}_{pB} \tag{14}$$

$$(i+j)\bar{k}_{pA} = \sum_{i=0}^{i+j} P_{ij}(ik_{pAA} + jk_{pBA})C_{MA}C_M^{-1} \tag{15}$$

$$(i+j)\bar{k}_{pB} = \sum_{i=0}^{i+j} P_{ij}(jk_{pBB} + ik_{pAB})C_{MB}C_M^{-1} \tag{16}$$

Using the definition of P_{ij}, eqs(15) and (16) can be simplified as

$$\bar{k}_{pA} = (k_{pAA}C_{MA}P_{10} + k_{pBA}C_{MA}P_{01})C_M^{-1} \tag{17}$$

$$\bar{k}_{pB} = (k_{pAB}C_{MB}P_{10} + k_{pBB}C_{MB}P_{01})C_M^{-1} \tag{18}$$

Using the eqs(15) and (16), eq(6) becomes

$$\bar{K} = \bar{k}_{pA}M_{oA}C_M N_{pA}^{-1}d_{pA}^{-1} + \bar{k}_{pB}M_{oB}C_M N_A^{-1}d_{pB}^{-1} \tag{19}$$

Note that the equation of $\bar{K}$ of Chen and Wu,[8] which is different from ours, is

$$\bar{K} = K_A P_{10} + K_B P_{01} \tag{20}$$

where

$$K_A = (k_{pAA}C_{MA} + k_{pAB}C_{MB}) M_{oA}d_{pA}^{-1}N_A^{-1} \tag{21}$$

$$K_B = (k_{pBB}C_{MB} + k_{pBA}C_{MA}) M_{oB}d_{pB}^{-1}N_A^{-1} \tag{22}$$

K_A and K_B are respectively the volume growth rates of a particle that contains one A-type and one B-type free radical.

Using the definitions of average rate coefficients and from the definition of P_{ij}, eq(1) can be simplified as

$$\partial n_i(v,t)/\partial t = -\bar{\rho}(n_i - n_{i-1}) + \bar{k}[(i+1)n_{i+1} - in_i]$$
$$+ \bar{c}[(i+1)(i+2)n_{i+2} - i(i-1)n_i]$$
$$- \partial/\partial v(i\bar{K}n_i) \tag{23}$$

$n_1(v,t)$ is the relative number of latex particles containing i free radicals at volume v and time t. $n_i(v,t)$ can be derived from the definition P_{ij} as

$$n_{iAjB}(v,t) = P_{ij}n_{(i+j)}(v,t) \tag{24}$$

DISCUSSION

The observed PSD and n(v,t) during copolymerization can be calculated from $n_i(v,t)$ as

$$n(v,t) = \sum_{i=0}^{\infty} n_i(v,t) \tag{25}$$

n_i can be obtained by solving the partial differential equations(23) with appropriate initial conditions. For the 0-1 system, eq(23) can be expressed as

$$\partial n_0/\partial t = -\bar{\rho}n_0 + (\bar{\rho} + \bar{k})n_1 \tag{26}$$

$$\partial n_1/\partial t = \bar{\rho}n_0 - (\bar{\rho} + \bar{k})n_1 - \partial/\partial v(\bar{K}n_1) \tag{27}$$

Lichti et al.[2] solved the similar equations as the eqs(26) and (27) in the case of emulsion homopolymerization by assuming $\bar{\rho}$, $\bar{k}$, and $\bar{K}$ constant with respect to v for simplicity, though they may vary with v.[12~16] Solving eqs(26) and (27) requires a set of initial conditions. For the ab initio[2] emulsion copolymerization in interval II, Lichti et al.[2] took the initial condition as

$$n_0(v, t_0) = (1 - \bar{n}) \, n(v, t) \tag{28}$$

$$n_1(v, t_0) = \bar{n} \, n(v, t) \tag{29}$$

where $\bar{n} = \bar{\rho}/(2\bar{\rho} + \bar{k})$ in interval II. Lichti et al.[2] took $\bar{n} = 0.5$ to determine the kinetic parameters. The expressions for the moments of PSD were obtained by taking the Laplace transform of eqs (26) and (27), and using the method of moment.[17, 18] Moments m_1 and m_2 were obtained as[18]

$$m_k = \int_0^\infty v^k \, n(v, t) \, dv \tag{30}$$

$$m_1 = \bar{n} \, \bar{K} \, t - (1 - \bar{n}) \, \bar{n} \, \bar{K} / \bar{\rho} \tag{31}$$

$$m_2 = (\bar{n} \, \bar{K} \, t)^2 + 2(1 - \bar{n})(\bar{n})^3 \, (\bar{K})^2 / (\bar{\rho})^2$$

Here $\bar{\rho}$, $\bar{k}$, and $\bar{K}$ were assumed constant with respect to v. To characterize the PSD, the number average volume $(\bar{v}_n)$, the weight average volume $(\bar{v}_w)$ and the polydispersity ratio index (P_v) are respectively

$$\bar{v}_n = \int_0^\infty v \, n(v,t) \, dv / \int_0^\infty n(v,t) \, dv = m_1 \tag{33}$$

$$\bar{v}_w = \int_0^\infty v^2 \, n(v,t) \, dv / \int_0^\infty v \, n(v,t) \, dv = m_2 / m_1 \tag{34}$$

$$P_v = \bar{v}_w / \bar{v}_n = m_2 / m_1^2 \tag{35}$$

Number average diameter of a particle is obtained from $(\bar{D}_n)^3 / 6 = \bar{v}_n$. To deal with the effect of free radical entry into the latex particle on PSD, $\bar{n}$ and $\bar{\rho}$ are respectively represented as[9]

$$\bar{n} = \frac{-(2m + 1 - \bar{\alpha}) \pm [(2m + 1 - \bar{\alpha}) + 8 \, \bar{\alpha} m]^{0.5}}{4 \, \bar{\alpha}} \tag{36}$$

$$\bar{\rho} = \bar{\rho}_a + \bar{\alpha} \, \bar{k} \, \bar{n} \tag{37}$$

where $m = \bar{\rho}_a / \bar{k}$. $\bar{\alpha}$ is given by[9]

$$\bar{\alpha} = \frac{\alpha_A \, k_A \, P_{10} + \alpha_B \, k_B \, P_{01}}{k_p \, P_{10} + k_B \, P_{01}} \tag{38}$$

α_A and α_B are respectively the fate parameter of type A and B. Neglecting any background free-radical generating processes, $\bar{\rho}_a$ can be expressed in terms of the initiator concentration as[10]

$$\bar{\rho}_a = 2 \, f \, k_d \, [I] \, N_c^{-1} \tag{39}$$

f is the initiator efficiency. k_d is the decomposition rate coefficient of initiator. [I] is the initiator concentration in the aqueous phase. N_c is the number concentration of latex particle.

To deal with the effect of monomer composition on PSD, we represent eq(19) as

$$\bar{K} = \frac{C_M}{N_A} \frac{\begin{array}{c} k_{pAA} k_{pBB} (r_A f_A^2 M_{oA} d_{pA}^{-1} + f_A f_B M_{oA} d_{pA}^{-1} + \\ r_A k_{pBB} f_A + r_B k_{pAA} f_B \end{array}}{\begin{array}{c} f_A f_B M_{oB} d_{pB}^{-1} + r_B f_B^2 M_{oB} d_{pB}^{-1}) \end{array}} \tag{40}$$

f_A is the mole fraction of monomer A in the particles and r_A is the reactivity ratio and similarly for others.

Fig. 1 and Fig. 2 show the effects of reaction time and $\bar{\rho}_a$ on P_v and $\bar{D}_n$ for St-Bu system and St-MMA system, respectively. P_v values decrease with reaction time.[2,18,19] $\bar{K}$, P_v, $\bar{D}_n$, $\bar{n}$, $\bar{n}_A$ and $\bar{n}_B$ against the monomer composition are plotted in Fig. 3,4,5,6,7 and 9 for St-Bu system and St-MMA system, respectively. $\bar{n}_A$ and $\bar{n}_B$ are respectively the average number of radical of type A and B per particle. They are calculated from $\bar{n}$ by the rela-
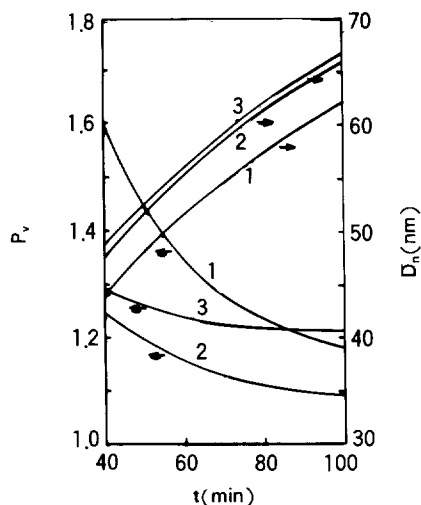

Fig. 1. Polydispersity ratio index (P_v) and number average diameter of particle $(\bar{D}_n)$ vs. reaction time (t, min) at specific values of $\bar{\rho}_a$ for St-Bu system : (1) 0.00107 (2) 0.00214 (3) 0.00428 s^{-1}.

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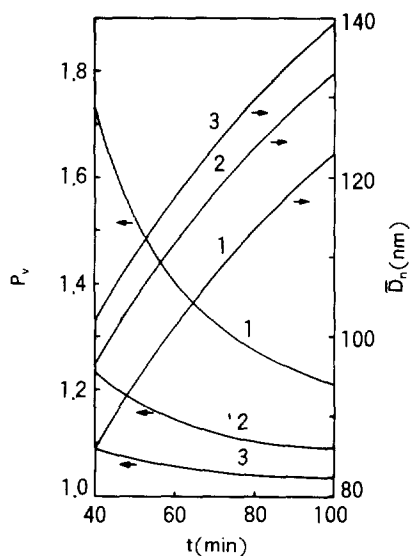**Fig. 2.** Polydispersity ratio indes (P$_v$) and number average diameter of particle ($\bar{D}_n$) vs. reaction time (t, min) at specific values of $\bar{\rho}_a$ for St-MMA system : (1) 0.00107 (2) 0.0214 (3) 0.00428 s^{-1}.
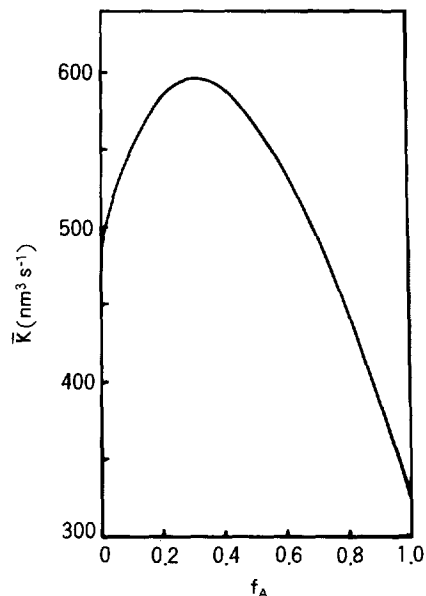

Fig. 4. Average volume growth rate of particle ($\bar{K}$) vs. monomer composition of St (f$_A$), using $\bar{\rho}_a$ / $\bar{k}$ = 1, t = 60 min, for St-MMA system.
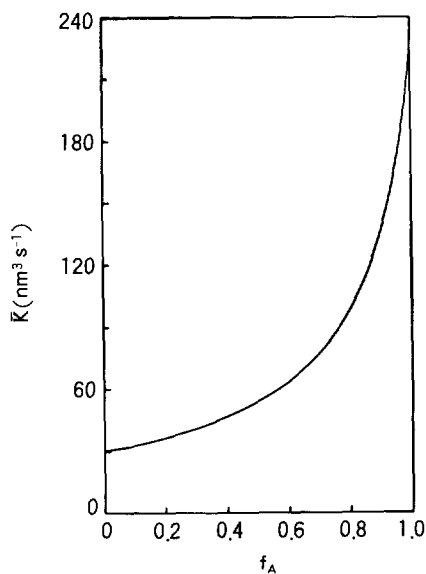

Fig. 3. Average volume growth rate of particle ($\bar{K}$) vs. monomer composition of St (f$_A$), using $\bar{\rho}_a$ / $\bar{k}$ = 1, t = 60 min, for St-Bu system.
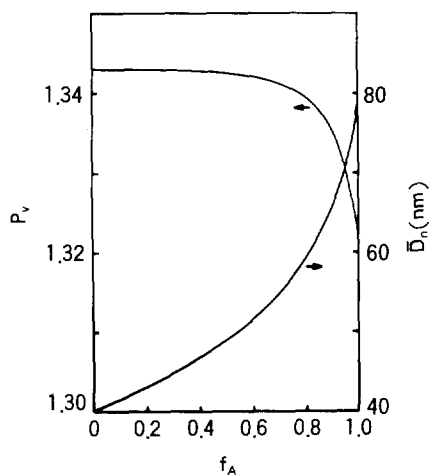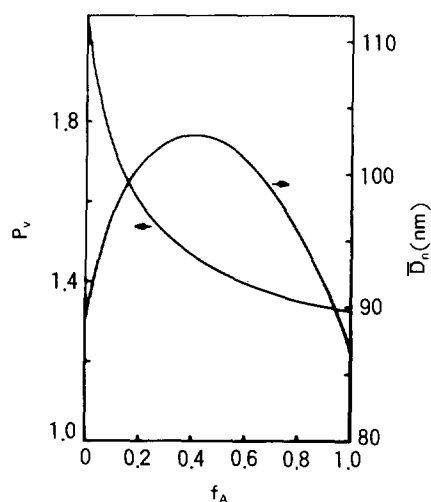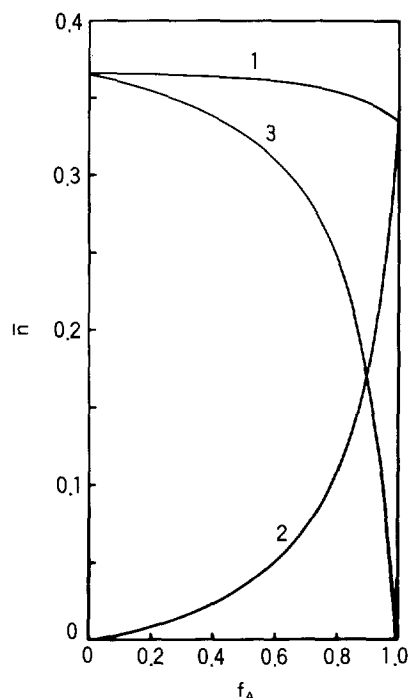

Fig. 5. Polydispersity index ratio (P$_v$) and number average diameter of particle($\bar{D}_n$) vs. monomer composition of St (f$_A$), using $\bar{\rho}_a$ / $\bar{k}$ = 1, t = 60 min, for St-Bu system.
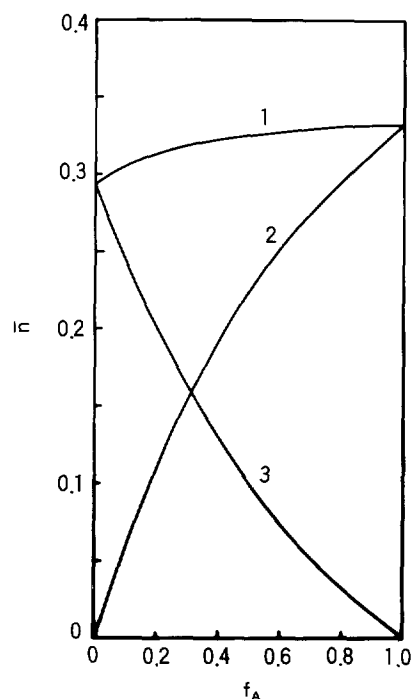
Fig. 6. Polydispersity index ratio (P_v) and number average diameter of particle ($\bar{D}_n$) vs. monomer composition of St (f_A), using $\bar{\rho}_a / \bar{k} = 1$, t = 60 min, for St-MMA system.

Fig. 7. Average number of radical per particle ($\bar{n}$), average number of radical of type A and B per particle ($\bar{n}_A$, $\bar{n}_B$) respectively vs. monomer composition of St (f_A), using $\bar{\rho}_a / \bar{k} = 1$, t = 60 min, for St-Bu system : (1) $\bar{n}$ (2) $\bar{n}_A$ (3) $\bar{n}_B$.

Fig. 8. Average number of radical per particle ($\bar{n}$), average number of radical of type A and B per particle ($\bar{n}_A$, $\bar{n}_B$) respectively vs. monomer composition of St(f_A), using $\bar{\rho}_a / \bar{k} = 1$, t = 60 min, for St-MMA system : (1) $\bar{n}$ (2) $\bar{n}_A$ (3) $\bar{n}_B$.

Table 1. Rate Coefficients Used in Calculation

	Monomer		
	A	B	C
	St	Bu	MMA
k_A, k_B(s⁻¹)	0.0015	0.001	0.001
k_{pAA}, k_{pBB}(L mol⁻¹ s⁻¹)	258	65	495
k_{pAB}, k_{pBA}(L mol⁻¹ s⁻¹)	496		1076
	444.8	48.1	
d_{pA}, d_{pB} (g cm⁻³)	1.05	0.97	1.188
α_A α_B	0	+1	−1
M_{oA}, M_{oB} (g mol⁻¹)	114	54	100

tion : $\bar{n}_A = \bar{n}\,P_{10}$ and $\bar{n}_B = \bar{n}\,P_{01}$. Values of the kinetic parameters used in calculations are shown in Table 1.[7]

APPENDIX

Swollen and Unswollen Latex Particle Parameters in Emulsion Copolymerization System

We assume ideal mixing of monomers and polymer in the particles. Let C_{gA} and C_{gB} denote mass of monomer A and B per mass of polymer inside a latex particle, respectively. For a particle containing 1g of polymer, the mass of monomer A and B solubilized is C_{gA} g and C_{gB} g, respectively. The total volume of this swollen 1 g particle, $V_s(\text{cm}^3\text{g}^{-1})$, is thus given by the following equation

$$V_s = d_{cop}^{-1} + C_{gA}\,d_{MA}^{-1} + C_{gB}\,d_{MB}^{-1} \qquad (A-1)$$

The number of moles of monomer A and B present is respectively $C_{gA}M_{oA}^{-1}$ and $C_{gB}M_{oB}^{-1}$. Thus C_{MA} and C_{MB} (mol dm^{-3}) is respectively given by

$$C_{MA} = 10^3\,C_{gA} / (M_{oA}\,V_s) \qquad (A-2)$$

$$C_{MB} = 10^3\,C_{gB} / (M_{oB}\,V_s) \qquad (A-3)$$

Substituting eqs $(A-2)$ and $(A-3)$ into $(A-1)$, d can be represented as

$$d = v_s^{-1} = d_{cop}(1 - 10^{-3}C_{MA}M_{oA}d_{MA}^{-1}$$
$$- 10^{-3}C_{MB}M_{oB}d_{MB}^{-1}) \qquad (A-4)$$

The volume fraction of copolymer, monomer A, and B is respectively given by

$$\Phi_p = 1 - 10^{-3}C_{MA}M_{oA}d_{MA}^{-1} - 10^{-3}C_{MB}M_{oB}d_{MB}^{-1}$$
$$(A-5)$$

$$\Phi_A = 10^{-3}C_{MA}M_{oA}d_{MA}^{-1} \qquad (A-6)$$

$$\Phi_B = 10^{-3}C_{MB}M_{oB}d_{MB}^{-1} \qquad (A-7)$$

The volume swelling factor f_v is given by

$$f_v = \frac{\text{swollen volume}}{\text{unswollen volume}} = \Phi_\pi^{-1} \qquad (A-8)$$

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