에멀젼 중합에 의한 스티렌-부타디엔 고무의 미세구조 조절과
그의 물성에 관한 연구
(Ⅱ) 유화공중합에서 흡착속도상수

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A Study on the Fine Structure Controls of SBR by Emulsion Polymerization and its Physical Properties (Ⅱ) Entry Rate Coefficients in Emulsion Copolymerization

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요 약 : Penboss등에 의하여 제안된 모델을 기초로 하여, 유화공중합계에서 두 모노머의 속도 상수들로 평균속도상수들을 정의하여 라텍스 입자에 대한 흡착속도 상수가 $\bar{\rho}=\bar{\rho}_a+\bar{\alpha}\,\bar{k}\,\bar{n}$임을 보였다. 입자당 평균 라디칼수($\bar{n}$)를 fate parameter($\bar{\alpha}$)의 양의 함수로서 나타내었다. 이 방법의 적용가능성을 보이기 위하여 stryrene-butadience(St-Bu)계 및 styrene-methyl methacrylate(St-MMA)계를 계산예로 들었다.

Abstract : On the basis of the model proposed by Penboss and coworkers, the rate coefficient for entry into a latex particle for emulsion copolymerization systems can be represented as $\bar{\rho}=\bar{\rho}_a+\bar{\alpha}\,\bar{k}\,\bar{n}$ by use of the appropriate combinations of the kinetic parameters of the comonomers. Average number of radicals per particle ($\bar{n}$) is explicitly presented as a function of the averaged fate parameter ($\bar{\alpha}$) for the zero-one system. Styrene-butadiene(St-Bu) and styrene-methyl methacrylate (St-MMA) systems are given as an example of calculation to demonstrate the applicability of this method.

INTRODUCTION

Smith and Ewart[1] first treated emulsion homopolymerizations quantitatively by assuming that all free radicals resulting from initiator decomposition entered the latex particles and desorption (exit) of free radicals from the latex particles had no kinetic significance once exit had taken placed. It has been pointed out[2,3] that desorbed free radicals may affect the kinetics of emulsion polymerization. Penboss et al.[4] provided a general theoretical treatment of free radical entry into

latex particles, and represented the first-order rate coefficient for entry into a latex particle(ρ) as $\rho=\rho_a+\alpha k\bar{n}$ for the emulsion homopolymeriz ation systems, where ρ_a is the component arising from the aqueous phase initiator and α is the fate parameter expressing the relative importance of heterotermination and re-entry of the exited free radicals. Methodologies[5] have been described for deducing values of these rate coefficients from seeded batch emulsion polymerization kinetic data. For the emulsion copolymerization sysyems, no theory of free radical entry into latex particles has been proposed. This paper shows that the entry rate coefficient in emulsion copolymerization is represented as $\bar{\rho}=\bar{\rho}_a+\bar{\alpha}\,\bar{k}\,\bar{n}$, by extending the model of Penboss et al.[4] to emulsion copolymerization systems. The kinetic equations for copolymerization sysyems can be reduced to equations identical to those of homopolymeriz ation systems by use of the averaged kinetic parameters of comonomers. Average number of radicals per particle($\bar{n}$) is explicitly calculated as a function of the averaged fate parameter ($\bar{\alpha}$).

EXTENSION OF MODEL FOR EMULSION COPOLYMERIZATION

Destription of Model

We consider emulsion copolymerization systems where two comonomers, A and B, are copolymeriz ed, and where new particle generation has been ceased (i.e. after interval Ⅰ). The steps involved in free radical entry into a latex particle are as follows.[4]

(i) The decomposition of initiator.

(ii) Aqueous-phase propagation of the free radical resulting from process (i)to form oligo-meric free radicals (denoted by $R°$), which may eventually become sufficiently surface active to undergo entry into the latex particles.

(iii) Homotermination among the free-radical species formed in processes (i) and (ii).

(iv) Entry of oligomeric free radicals into the latex particles.

(v) Exit of a free radical species from the particles into the aqueous phase.

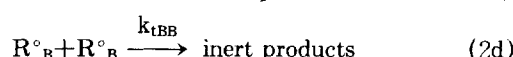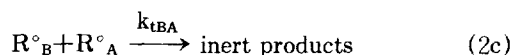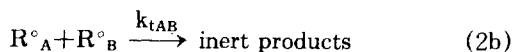(vi) Exited free radicals (denoted by $E°$) subsequently undergoing re-entry into a particle.
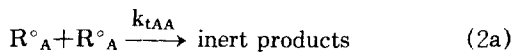
(vii) Exited free radicals undergoing heteroter mination with free radicals arising from processes (i) or (ii).

Penboss et al.[4] employed the concept of an oligomeric free radical, $R°$, to avoid having to take each propagation step into account in pro-cess(ii). Processes (i) and (ii) can then be represented as
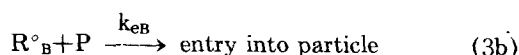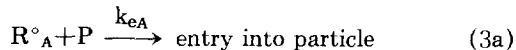
$$I \xrightarrow{k_I} R° \tag{1}$$

where $R°=R°_A+R°_B$, $R°_A$ and $R°_B$ are respec-tively oligomeric free radical of type A and B. k_I is an effective rate coefficient for the produc-tion of $R°$.
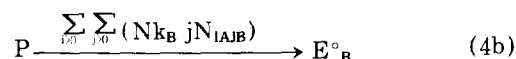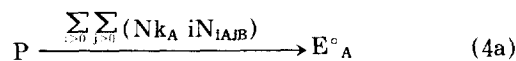
Process (iii) is then represented by

$$R°_A+R°_A \xrightarrow{k_{tAA}} \text{inert products} \tag{2a}$$

$$R°_A+R°_B \xrightarrow{k_{tAB}} \text{inert products} \tag{2b}$$

$$R°_B+R°_A \xrightarrow{k_{tBA}} \text{inert products} \tag{2c}$$

$$R°_B+R°_B \xrightarrow{k_{tBB}} \text{inert products} \tag{2d}$$

where k_{tAB} is the reation rate coefficient of $R°_A$ and $R°_B$ and similarly for k_{tAA}, k_{tBA}, and k_{tBB}.

Process (iv) is represented by

$$R°_A+P \xrightarrow{k_{eA}} \text{entry into particle} \tag{3a}$$

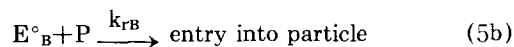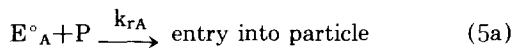$$R°_B+P \xrightarrow{k_{eB}} \text{entry into particle} \tag{3b}$$

where P denotes a polymer latex particle in terms of molar concentration $N=N_c/N_A$, where N_c is the number concentration of latex particle and N_A is Avogadro's constant. k_{eA} and k_{eB} is respe-ctively the rate coefficient of th entry of free radical $R°_A$ and $R°_B$ into the latex particles.
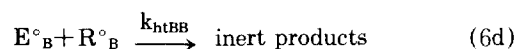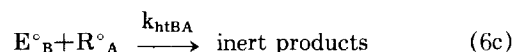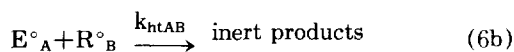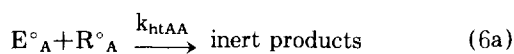
Process (v) is represented as

$$P \xrightarrow{\sum_{i\geq0}\sum_{j\geq0}(Nk_A\, iN_{iAjB})} E°_A \tag{4a}$$

$$P \xrightarrow{\sum_{i\geq0}\sum_{j\geq0}(Nk_B\, jN_{iAjB})} E°_B \tag{4b}$$

where E°_A and E°_B respectively denotes an exited free radical of type A and B. k_A and k_B are respectively the rate coefficients for exit of type A and B free radicals. N_{IAJB} is the relative number of latex particles containing i chains with free radical A and j chains of B.

Exit may affect entry in two ways: through process (ⅵ)

$$E^{\circ}_A + P \xrightarrow{k_{rA}} \text{ entry into particle} \qquad (5a)$$

$$E^{\circ}_B + P \xrightarrow{k_{rB}} \text{ entry into particle} \qquad (5b)$$

and through process (ⅶ)

$$E^{\circ}_A + R^{\circ}_A \xrightarrow{k_{htAA}} \text{ inert products} \qquad (6a)$$

$$E^{\circ}_A + R^{\circ}_B \xrightarrow{k_{htAB}} \text{ inert products} \qquad (6b)$$

$$E^{\circ}_B + R^{\circ}_A \xrightarrow{k_{htBA}} \text{ inert products} \qquad (6c)$$

$$E^{\circ}_B + R^{\circ}_B \xrightarrow{k_{htBB}} \text{ inert products} \qquad (6d)$$

where k_{rA} and k_{rB} are respectively the entry rate coefficient of exited free radical of type A and B into the latex particle, and k_{htAB} is the heteroter mination reaction rate coefficient between E°_A and R°_B and similarly for k_{htAA}, k_{htBA}, and k_{htBB}.

Dervation of Entry Rate Coefficient $\bar{\rho}$

The total rate coefficient of entry of free radicals into a latex particle is given by

$$\bar{\rho} = k_{eA}[R^{\circ}_A] + k_{eB}[R^{\circ}_B] + k_{rA}[E^{\circ}_A] + k_{rB}[E^{\circ}_B] \qquad (7)$$

The mutual aqueous-phase termination between two exited species ($E^{\circ}_A + E^{\circ}_B \rightarrow$ inert products) has been ignored in the above treatment.

The time evolutions of the concentrations of R° and E° are given by

$$d[R^{\circ}]/dt = k_I[\,I\,] - k_{tAA}[R^{\circ}_A][R^{\circ}_A]$$
$$- k_{tAB}[R^{\circ}_A][R^{\circ}_B] - k_{tBA}[R^{\circ}_B][R^{\circ}_A]$$
$$- k_{tBB}[R^{\circ}_B][R^{\circ}_B] - k_{eA}N[R^{\circ}_A]$$
$$- k_{eB}N[R^{\circ}_B] - k_{htAA}[E^{\circ}_A][R^{\circ}_A]$$
$$- k_{htAB}[E^{\circ}_A][R^{\circ}_B] - k_{htBA}[E^{\circ}_B][R^{\circ}_A]$$
$$- k_{htBB}[E^{\circ}_B][R^{\circ}_B] \qquad (8)$$

$$d[E^{\circ}]/dt = \sum_{i>0}\sum_{i>0}(Nk_A i N_{IAJB} + Nk_B j N_{IAJB})$$
$$- k_{rA}N[E^{\circ}_A] - k_{rB}N[E^{\circ}_B]$$
$$- k_{htAA}[E^{\circ}_A][R^{\circ}_A] - k_{htAB}[E^{\circ}_A][R^{\circ}_B]$$
$$- K_{htBA}[E^{\circ}_B][R^{\circ}_A] - k_{htBB}[E^{\circ}_A][R^{\circ}_B] \qquad (9)$$

We define the following averaged rate coefficients:

$$\bar{k}_e = k_{eA}[R^{\circ}_A]/[R^{\circ}] + k_{eB}[R^{\circ}_B]/[R^{\circ}] \qquad (10)$$

$$\bar{k}_r = k_{rA}[E^{\circ}_A]/[E^{\circ}] + k_{rB}[E^{\circ}_B]/[E^{\circ}] \qquad (11)$$

$$\bar{k}_r = k_{tAA}[R^{\circ}_A]^2/[R^{\circ}]^2 + k_{tAB}[R^{\circ}_A][R^{\circ}_B]/[R^{\circ}]^2 + k_{tBA}[R^{\circ}_B][R^{\circ}_A]/[R^{\circ}]^2$$
$$+ k_{tBB}[R^{\circ}_B][R^{\circ}_B]/[R^{\circ}]^2 \qquad (12)$$

$$\bar{k}_{ht} = k_{htAA}[E^{\circ}_A][R^{\circ}_A]/[E^{\circ}][R^{\circ}]$$
$$+ k_{htAB}[E^{\circ}_A][R^{\circ}_B]/[E^{\circ}][R^{\circ}]$$
$$+ k_{htBA}[E^{\circ}_B][R^{\circ}_A]/[E^{\circ}][R^{\circ}]$$
$$+ k_{htBB}[E^{\circ}_B][R^{\circ}_B]/[E^{\circ}][R^{\circ}] \qquad (13)$$

where

$$[E^{\circ}] = [E^{\circ}_A] + [E^{\circ}_B] \text{ and } [R^{\circ}] = [R^{\circ}_A] + [R^{\circ}_B].$$

Using the averaged rate coefficients defined above and substituting the following eqs. (14) ~ (17)[6~8] to eqs. (7), (8) and (9) gives eqs.(18), (19) and (20).

$$P_{ij} = \frac{(i+j)!}{i!j!} \frac{(k_{PBA}C_{MA})^i(k_{PAB}C_{MB})^j}{(k_{PBA}C_{MA} + k_{PAB}C_{MB})^{i+j}} \qquad (14)$$

$$\sum_{i=0}^{s} P_{i(s-i)} = 1, \text{ for } s = 0,1,2,\cdots\cdots \qquad (15)$$

$$\bar{k} = k_A P_{10} + k_B P_{01} \qquad (16)$$

$$\bar{n} = \sum_{i=0}\sum_{j=0}(i+j)N_{IAJB} \qquad (17)$$

$$\bar{\rho} = \bar{k}_e[R^{\circ}] + \bar{k}_r[E^{\circ}] \qquad (18)$$

$$d[R^{\circ}]/dt = k_I[\,I\,] - \bar{k}_e N[R^{\circ}]^2 - \bar{k}_{ht}[E^{\circ}][R^{\circ}] \qquad (19)$$

$$d[E^{\circ}]/dt = N\bar{k}\bar{n} - \bar{k}_r N[E^{\circ}] - \bar{k}_{ht}[E^{\circ}][R^{\circ}] \qquad (20)$$

These eqs(18), (19) and (20) are the same

expressions as the equations for homopolymeriz ation systems derived by Penboss et al.[4]

Penboss et al.[4] treated similar equations as the eqs. (18), (19) and (20) in the case of emulsion homopolymerization, and showed that the entry rate coefficient for an emulsion homopolymeriz ation system may be written in the form: $\rho=\rho_a + \bar{\alpha}k\,\bar{n}$. We can also express the rate coefficient for an emulsion copolymerization system as

$$\bar{\rho}=\bar{\rho}_a+\bar{\alpha}\,\bar{k}\,\bar{n} \tag{21}$$

Here $\bar{\rho}_a$ is the component arising from the aqueous- phase initiator and $\bar{\alpha}$ is the fate para- meter for an emulsion copolymerization system. Eq.(21) is useful for obtaining the capture effi- ciency which is the value of $\bar{\rho}_a / (2k_d\,[\,I\,]\,/\,N_c)$, where k_d is the initiator decomposition rate coefficient. Ballard et al.[6] defined the entry rate coefficient $(\bar{\rho})$ as

$$\bar{\rho}=\rho_A+\rho_B \tag{22}$$

where ρ_A and ρ_B are respectively the entry rate coefficient of type A and B. ρ_A and ρ_B can be expressed as

$$\rho_A=\rho_{OA}+\alpha_A k_A \bar{n}\,P_{10} \tag{23a}$$

$$\rho_B=\rho_{OB}+\alpha_B k_B \bar{n} P_{01} \tag{23b}$$

By combining eqs(22) and (23) and then comparing with eq.(21), $\bar{\rho}_a$ and $\bar{\alpha}$ can be explicitly represented as

$$\bar{\rho}_a = \rho_{OA}+\rho_{OB} \tag{24}$$

and

$$\bar{\alpha}=\frac{\alpha_A k_A P_{10}+\alpha_B k_B P_{01}}{k_A P_{10}+k_B P_{01}} \tag{25}$$

In an emulsion hompolymerization of monomer A, $P_{10}=1$, and $\bar{\alpha}=\alpha_A$ from eq.(25).

DISCUSSIONS

The average number of radicals per paritcle is needed to calculate the rate of emulsion co- polymerization. The number of particles contai-

ning $\bar{n}$ radicals (N_n) fulfills the extended Smit- h-Ewart equation for a copolymer system:

$$dN_n / dt=\bar{\rho}(N_{n-1}-N_n)+\bar{k}[\,(n+1)N_{n+1}-nN_n]$$
$$+\bar{c}[(n+2)(n+1)N_{n+2}-n(n-1)N_n] \tag{26}$$

where $\bar{k}=\bar{k}_A P_{10}+\bar{k}_B P_{01}$ (27)

$$\bar{c}=c_{AA}P_{20}+c_{AB}P_{11}+c_{BB}P_{02} \tag{28}$$

$\bar{c}_{AB}$ is the rate coefficient for bimolecular ter- mination of two growing chains, one with an active A and the other an active B terminal unit, and similarly for c_{AA}, c_{BB} and c_{BA}.

For the zero-one system, eq.(26) can be written as

$$dN_0 / dt=-\bar{\rho}N_0+(\bar{\rho}+\bar{k})N_1 \tag{29a}$$

$$dN_1 / dt=\bar{\rho}N_0-(\bar{\rho}+\bar{k})N_1 \tag{29b}$$

During interval Ⅱ, when the concentrations of monomers within the particles are essentially constant, $\bar{n}$ is derived as

$$\bar{n}=\frac{\bar{\rho}}{2\bar{\rho}+\bar{k}} \tag{30}$$

From eqs.(21) and (30), $\bar{n}$ can be explicitly represented as

$$\bar{n}=\frac{-(2m+1-\bar{\alpha})\pm[(2m+1-\bar{\alpha})^2+8\,\bar{\alpha}m]^{0.5}}{4\bar{\alpha}} \tag{31}$$

where $m=\bar{\rho}_a / \bar{k}$ and $\bar{n}\geqq 0$.

In the special case of the limit $\bar{\alpha}=+1$, eq(31) can be written as

$$\bar{n}=0.5[\,-m+(m^2+2m)^{0.5}] \tag{32}$$

Nomura et al. treated the similar equation as the eq.(32).[9]

Average number of radicals of type A, $\bar{n}_A$, and type B, $\bar{n}_B$, can be found from the following relations:

$$\bar{n}_A=P_{10}\bar{n} \tag{33}$$

$$\bar{n}_B=P_{10}\bar{n} \tag{34}$$

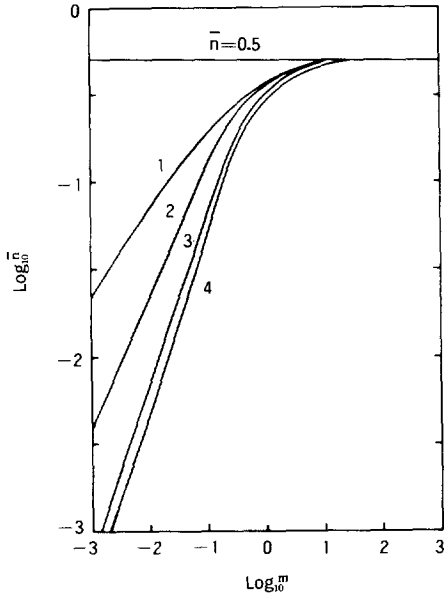Sang-Bo Park, Byung-Kyu Kim, and Young-Jo Shin

Fig. 1. Average number of racdicals per particle $(\bar{n})$ as a function of the parameter m at some specific fate parameters $(\bar{a})$: (1)$+1$, (2) $+0.5$, (3) -0.5, (4) -1 using the kinetic parameters in Table 1.

Fig. 2. Average number of radicals per paricle$(\bar{n})$ and radical number fractions $(\bar{n}_A)$ and $(\bar{n}_B)$ as a function of the parameter m for St-Bu system (A/B).
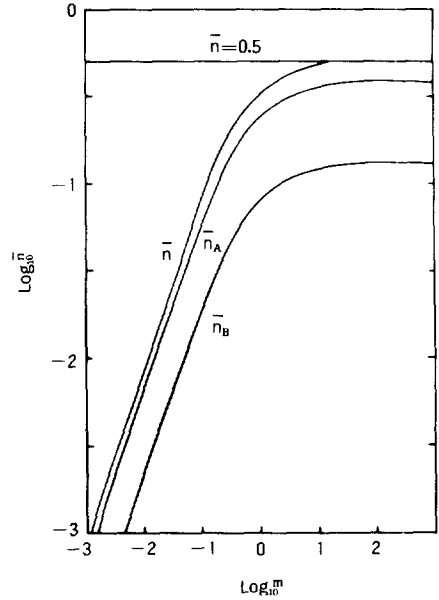

Fig. 3. Average number of radicals per particle $(\bar{n})$ and radical number fractions $(\bar{n}_A$ and $\bar{n}_B)$ as a function of the parameter m for St-MMA system (A/B).
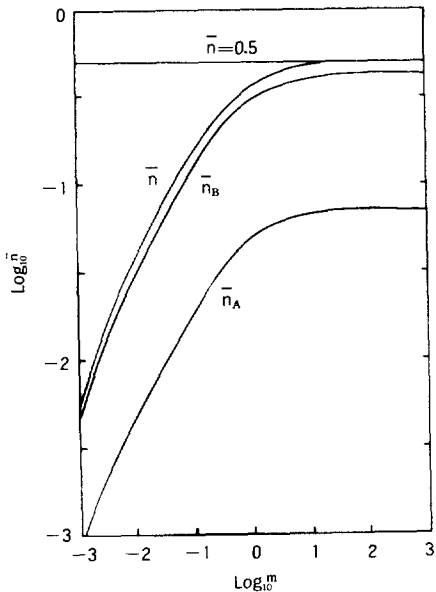
Table 1. Rate Coefficients Used in Calculation

	Monomer		
	A	B	B
	St	Bu	MMA
$k_A, k_B(s^{-1})$	0.0015	0.001	0.001
α_A, α_B	0	$+1$	-1
$k_{PAB}, k_{PBA}(L\ mol^{-1}s^{-1})$	444.8	48.1	
	496		1076
$C_{MA}, C_{MB}(mol.L^{-1})$	3	2	
	4		3

The theoretical value of $\bar{n}$ obtained from eq (32) is plotted against the corresponding value of m on Fig. 1. $\bar{n}=0.5$ in Fig. 1 is the value which was derived by Smith and Ewart[1] in the case of emulsion homopolymerization. Fig. 2 and Fig. 3 show examples of the plot of $\bar{n}, \bar{n}_A, \bar{n}_B$vs. m for St-Bu system and St-MMA system, respectively. Values of the kinetic parameters used in calculations are reported in Table 1.[6]

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