Kinetics of Emulsion Copolymerization. III. Prediction of the Average Number of Radicals per Particle in an Emulsion Copolymerization System

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Synopsis

This paper develops a simple method for predicting the average number of total radicals per particle and their kinds in emulsion copolymerization systems by extending emulsion homopolymerization theories so far published. The validity and utility of this method is demonstrated by using the experimental data obtained in the emulsion copolymerization of styrene and methyl methacrylate.

INTRODUCTION

It is well known that, in emulsion polymerization, both the rate of polymerization and the degree of polymerization of polymers produced can be increased at the same time. This feature which is characteristic of emulsion polymerization comes mainly from the fact that each polymer particle where polymerization reaction takes place has at most one polymerizing radical. With increasing the average number of radicals per particle from 0.5, the characteristics of this system gradually change from those of emulsion to suspension or bulk polymerizations. It is, therefore, important to know the average number of radicals per particle when the polymers with desired qualities can be produced only by the help of the characteristics of emulsion polymerization.

Thus, the average number of radicals per particle is one of the most important factors which characterize emulsion polymerization. This will be the case for emulsion copolymerization because the mechanism of emulsion copolymerization is essentially the same as that of emulsion homopolymerization.

The present authors have already proposed a method for predicting the average number of total radicals per particle ($\bar{n}_t$) and their kinds in emulsion copolymerization systems.[1] However, it can be applied only in the range where $\bar{n}_t$ does not exceed 0.5. Ballard et al.[2] also proposed a mathematical model for emulsion copolymerization systems which is essentially applicable even in the range where $\bar{n}_t$ is greater than 0.5, but, with increasing the value of $\bar{n}_t$, calculation by their model becomes more and more complex. In this paper, therefore, a simple method which can be applied in all range of $\bar{n}_t$ value is developed by extending emulsion homopolymerization theories so far published.[3-6] Furthermore, the utility of this method is demonstrated by using the experimental data in the emulsion copolymerization of styrene (ST) and methyl methacrylate (MMA).

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KINETIC THEORIES DEVELOPED FOR EMULSION HOMOPOLYMERIZATION

The theories to be used for predicting the average number of radicals per particle in emulsion homopolymerization are briefly reviewed here because these theories are extended to emulsion copolymerization. At steady state, the number of polymer particles containing n radicals (N_n) fulfills the following equation[3]:

$$\frac{dN_n}{dt} = \left(\frac{\rho_e}{N_T}\right) N_{n-1} + k_f(n+1)N_{n+1} + k_{tp}\left[\frac{(n+2)(n+1)}{v_p}\right] N_{n+2}$$
$$- \left(\frac{\rho_e}{N_T}\right) N_n - k_f n N_n - k_{tp}\left[\frac{n(n-1)}{v_p}\right] N_n = 0 \quad (1)$$

The overall rate of radical entry into the polymer particles (ρ_e) involved in eq (1) is expressed by

$$\rho_e = k_a[R_w^*]N_T = r_i + \sum_{n=1}^{\infty} k_f n N_n - 2k_{tw}[R_w^*]^2 \quad (2)$$

Equations (1) and (2) are rewritten in nondimensional forms as follows:

$$\alpha N_{n-1} + m(n+1)N_{n+1} + (n+2)(n+1)N_{n+2}$$
$$= \alpha N_n + mn N_n + n(n-1)N_n \quad (1')$$

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \quad (2')$$

where

$$\alpha = \frac{\rho_e v_p}{k_{tp}N_T}, \quad \alpha' = \frac{r_i v_p}{k_{tp}N_T}, \quad m = \frac{k_f v_p}{k_{tp}}, \quad Y = \frac{2k_{tw}k_{tp}}{k_a^2 N_T v_p} \quad (3)$$

The general solution to eq. (1) for $\bar{n}$ is given by[4,5]

$$\bar{n} = \sum_{n=1}^{\infty} \frac{n N_n}{N_T} = \frac{a}{4}\frac{I_m(a)}{I_{m-1}(a)}, \quad a = (8\alpha)^{1/2} \quad (4)$$

where I_m is the modified Bessel function of the first kind.

Equation (4) is not convenient to use because it involves a parameter α which contains a variable parameter ρ_e. Noting this, Ugelstad et al.[6] solved the simultaneous equations (2') and (4) to eliminate α from the expression for $\bar{n}$, and expressed $\bar{n}$ as a function of the parameters α', m, and Y, which are constituted from accessible constants. They showed the calculated results graphically plotting $\log \bar{n}$ against $\log \alpha'$ over a wide range of m value at several fixed values of Y.[6] Figure 1 is an example of the plot of $\log \bar{n}$ vs. $\log \alpha'$ at $Y = 0$. In emulsion homopolymerization, the condition $Y = 0$ is satisfied because radical termination in the water phase can be neglected under usual conditions. The following empirical equation for $\bar{n}$ predicts almost the same values as the exact solution of simultaneous equations (2') and (4), so that the value of $\bar{n}$ predicted by eq. (5) falls almost perfectly on the solid lines in Figure 1:

$$\bar{n} = \frac{1}{2}\{[(\alpha' + \alpha'/m)^2 + 2(\alpha' + \alpha'/m)]^{1/2}$$
$$- (\alpha' + \alpha'/m)\} + (\frac{1}{4} + \alpha'/2)^{1/2} - \frac{1}{2} \quad (5)$$
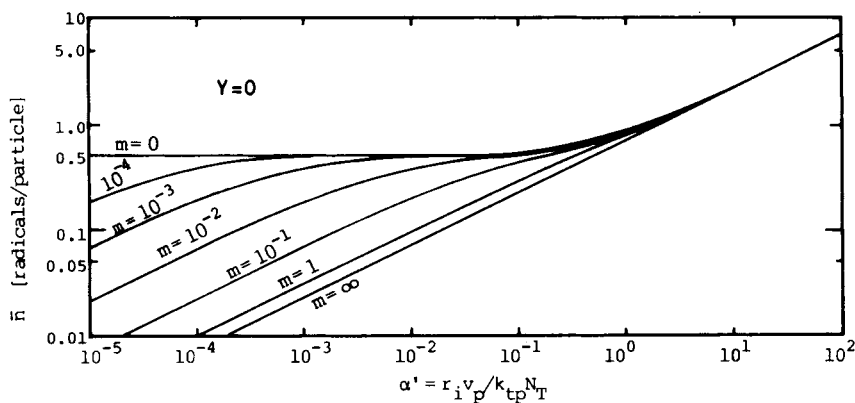
Fig. 1. Average number of radicals per particle, $\bar{n}$, as a function of the parameters α' and m at negligible water-phase termination, $Y = 0$.

Therefore, eq. (5) can be used in place of eqs. (2′) and (4) with satisfactory accuracy. Considering the results shown in Figure 1, it is essential for predicting the average number of radicals per particle that the value of the rate coefficient for radical desorption from the polymer particle, k_f, can be evaluated. The value of k_f can be predicted by the expression;[7–10]

$$k_f = (12 D_w \delta / m_d d_p^2)(k_{mf}/k_p), \quad \delta = (1 + D_w/m_d D_p)^{-1} \qquad (6)$$

The utility of the method mentioned above will be demonstrated in a separate paper using literature data for systems such as styrene, methyl methacrylate, acrylonitrile, vinyl acetate, and vinyl chloride emulsion homopolymerization.

EXTENSION TO AN EMULSION COPOLYMERIZATION SYSTEM

This is the main subject of this paper. For simplicity, let us consider an emulsion copolymerization system where two monomers, A and B, are copolymerized. The rate of emulsion copolymerization can be expressed by

$$\text{for A monomer,} \quad r_{pa} = -\frac{dM_a}{dt} = k_{paa}[M_a]_p \bar{n}_a N_T + k_{pba}[M_a]_p \bar{n}_b N_T \qquad (7)$$

$$\text{for B monomer,} \quad r_{pb} = -\frac{dM_b}{dt} = k_{pbb}[M_b]_p \bar{n}_b N_T + k_{pab}[M_b]_p \bar{n}_a N_T \qquad (8)$$

and the total rate of emulsion copolymerization is given by

$$r_{pt} = r_{pa} + r_{pb} \qquad (9)$$

On the other hand, the degree of polymerization of copolymers instantaneously produced is represented by

$$\bar{p}_N = \frac{r_{pt}}{(r_i/2)\lambda + r_i(1 - \lambda) + r_{mf}} \qquad (10)$$

where r_{mf} denotes the rate of chain transfer to monomer and given by

$$r_{mf} = (k_{maa}[M_a]_p + k_{mab}[M_b]_p)\bar{n}_a N_T$$
$$+ (k_{mbb}[M_b]_p + k_{mba}[M_a]_p)\bar{n}_b N_T \quad (11)$$

Thus, $\bar{n}_a$ and $\bar{n}_b$, the average numbers of A-radicals and B-radicals per particle, are important factors which describe the rate of copolymerization, the average degree of polymerization and copolymer composition in emulsion copolymerization.

Next, equations which predict the values of $\bar{n}_a$ and $\bar{n}_b$ are derived. Let us note a single particle which contains n total radicals, where the number of A-radicals and B-radicals are on the average n_a and n_b, respectively. Then, we have

$$n = n_a + n_b \quad (12)$$

By establishing balance equations on n_a, n_b, and n, and applying a steady state assumption to them, we get

$$\frac{dn_a}{dt} = \left(\frac{\rho_e \omega_a}{N_T}\right) - 2k_{tpaa}\left(\frac{n_a^2}{v_p}\right) - k_{tpab}\left(\frac{n_a \cdot n_b}{v_p}\right) - k_{fa}n_a$$
$$- (k_{pab} + k_{mab})[M_b]_p n_a + (k_{pba} + k_{mba})[M_a]_p n_b = 0 \quad (13a)$$

$$\frac{dn_b}{dt} = \left(\frac{\rho_e \omega_b}{N_T}\right) - 2k_{tpbb}\left(\frac{n_b^2}{v_p}\right) - k_{tpab}\left(\frac{n_a \cdot n_b}{v_p}\right) - k_{fb}n_b$$
$$- (k_{pba} + k_{mba})[M_a]_p n_b + (k_{pab} + k_{mab})[M_b]_p n_a = 0 \quad (13b)$$

$$\frac{dn}{dt} = \frac{d(n_a + n_b)}{dt} = \left(\frac{\rho_e}{N_T}\right) - 2k_{tpaa}\left(\frac{n_a^2}{v_p}\right)$$
$$- 2k_{tpab}\left(\frac{n_a \cdot n_b}{v_p}\right) - 2k_{tpbb}\left(\frac{n_b^2}{v_p}\right) - (k_{fa}n_a + k_{fb}n_b) = 0 \quad (14)$$

It is clear from eq. (14) that the values of the termination and desorption rate terms are at most equal to the value of (ρ_e/N_T). Considering that $\rho_e \simeq r_i \simeq 10^{13}$ molecules/cm^3 water·s, $N_T = 10^{13} \sim 10^{15}$ particles/cm^3 water, and the value of ω_a, the probability of absorbed radicals being or becoming A-radical, is less than unity ($\omega_a + \omega_b = 1$), one can find that the last two terms on the right-hand side of eqs. (13a) and (13b) are dominating. Therefore, eq. (13) can be simplified to

$$(k_{pab} + k_{mab})[M_b]_p n_a = (k_{pba} + k_{mba})[M_a]_p n_b \quad (15)$$

Considering that usually $k_p \gg k_m$, eq. (15) is rearranged to define a parameter A in the form

$$A = \frac{n_b}{n_a} = \left(\frac{k_{paa}}{k_{pbb}}\right)\left(\frac{\gamma_b}{\gamma_a}\right)\left(\frac{[M_b]_p}{[M_a]_p}\right) \quad (16)$$

where γ denotes the monomer reactivity ratio. From eqs. (12) and (16), n_a and n_b can be expressed as follows using n and A:

$$n_a = [1/(1 + A)]n \quad (17)$$

$$n_b = [A/(1 + A)]n \quad (18)$$

On the other hand, the following mean rate coefficients are defined in emulsion

copolymerization so that eqs. (1) and (2) for emulsion homopolymerization can be applied to emulsion copolymerization systems without any modification.

Mean Rate Coefficient for Radical Desorption from Polymer Particles, $\bar{k}_f$

The mean rate coefficient for radical desorption from polymer particles is defined by

$$\bar{k}_f n N_n = (k_{fa} n_a + k_{fb} n_b) N_n \tag{19}$$

Inserting eqs. (17) and (18) into eq. (19), we get a final form for $\bar{k}_f$ as follows:

$$\bar{k}_f = [1/(1 + A)]k_{fa} + [A/(1 + A)]k_{fb} \tag{20}$$

where k_{fa} is the desorption rate coefficient for A-radicals and is given by the following equation[1]:

$$k_{fa} = K_{0a} \left[\frac{\gamma_a C_{maa}[M_a]_p + \gamma_b C_{mba}[M_b]_p}{\gamma_a([M_a]_p + (K_{0a}\bar{n}_t/k_{paa})) + [M_b]_p} \right] \tag{21}$$

where

$$C_{maa} = \frac{k_{maa}}{k_{paa}}, \quad K_{0a} = \left(\frac{12 D_{wa} \delta_a}{m_{da} d_p^2} \right), \quad \delta_a = \left(1 + \frac{D_{wa}}{m_{da} D_{pa}} \right)^{-1}, \quad \text{and} \quad \gamma_a = \frac{k_{paa}}{k_{pab}}$$

Mean Termination Rate Coefficient in Polymer Particles, $\bar{k}_{tp}$

To obtain the mean termination rate coefficient in the polymer particles, it is used that when $n \gg 1$, the following relationship hold approximately:

$$\bar{k}_{tp} \left[\frac{n(n-1)}{v_p} \right] N_n \simeq \bar{k}_{tp} \left(\frac{n^2}{v_p} \right) N_n$$

$$= \left[\frac{k_{tpaa} n_a^2 + k_{tpab} n_a \cdot n_b + k_{tpbb} n_b^2}{v_p} \right] N_n \tag{22}$$

Substitution of eqs. (17) and (18) into eq. (22) leads to a final form of $\bar{k}_{tp}$:

$$\bar{k}_{tp} = [1/(1 + A)]^2 (k_{tpaa} + A k_{tpab} + A^2 k_{tpbb}) \tag{23}$$

Mean Radical Capture Coefficient $\bar{k}_a$ and Mean Radical Termination Rate Coefficient in the Water Phase, $\bar{k}_{tw}$

These rate coefficients need not be defined in this case because $\bar{k}_a$ has not actually appeared explicitly in the necessary equations, and the term involving $\bar{k}_{tw}$ can be neglected under usual reaction conditions.

Using the mean rate coefficients defined above, the steady state balance equation for N_n particles and the overall rate of radical entry into the polymer particle (ρ_e) can be expressed as follows:

$$\frac{dN_n}{dt} = \left(\frac{\rho_e}{N_T} \right) N_{n-1} + \bar{k}_f (n + 1) N_{n+1} + \bar{k}_{tp} \left[\frac{(n+2)(n+1)}{v_p} \right] N_{n+2} - \left(\frac{\rho_e}{N_T} \right) N_n$$

$$- \bar{k}_f n N_n - \bar{k}_{tp} \left[\frac{n(n-1)}{v_p} \right] N_n = 0 \tag{24}$$

$$\rho_e = \overline{k}_a[R_w^*]N_T = r_i + \sum_{n=1}^{\infty} \overline{k}_f n N_n - 2\overline{k}_{tw}[R_w^*]^2 \tag{25}$$

It is clear that these equations are quite the same as eqs. (1) and (2), respectively, except that $\overline{k}_f$, $\overline{k}_{tp}$, and $\overline{k}_{tw}$ are used in place of k_f, k_{tp}, and k_{tw}. Therefore, the method used in emulsion homopolymerization can be applied without any modification to an emulsion copolymerization system for predicting the average number of total radicals per particle, $\overline{n}_t$, and the average number of each radical per particle, $\overline{n}_a$ and $\overline{n}_b$ which are defined by

$$\overline{n}_t = \sum_{n=1}^{\infty} \frac{nN_n}{N_T} = \sum_{n=1}^{\infty} \frac{(n_a + n_b)N_n}{N_T} = \sum_{n=1}^{\infty} \frac{n_a N_n}{N_T} + \sum_{n=1}^{\infty} \frac{n_b N_n}{N_t} = \overline{n}_a + \overline{n}_b \tag{26}$$

where

$$\overline{n}_a = \sum_{n=1}^{\infty} \frac{n_a N_n}{N_T} = \sum_{n=1}^{\infty} \left(\frac{1}{1+A}\right)\frac{nN_n}{N_T} = \left(\frac{1}{1+A}\right)\overline{n}_t \tag{27}$$

$$\overline{n}_b = \sum_{n=1}^{\infty} \frac{n_b N_n}{N_T} = \sum_{n=1}^{\infty} \left(\frac{A}{1+A}\right)\frac{nN_n}{N_T} = \left(\frac{A}{1+A}\right)\overline{n}_t \tag{28}$$

From the discussion given above, it is concluded that Figure 1 and eq. (5) can be used for predicting $\overline{n}_a$, $\overline{n}_b$, and $\overline{n}_t$ if we employ $\overline{k}_f$, $\overline{k}_{tp}$, and $\overline{k}_{tw}$ in place of k_f, k_{tp}, and k_{tw} in the parameters α, α', m, and Y defined by eq. (3).

Furthermore, if we adopt the mean propagation rate coefficients $\overline{k}_p$ defined by

$$\overline{k}_{pa} = \frac{k_{paa} + Ak_{pbb}/\gamma_b}{1+A}, \quad \overline{k}_{pb} = \frac{k_{paa}/\gamma_a + Ak_{pbb}}{1+A} \tag{29}$$

copolymerization rate equations shown by eqs. (7)–(9) are simplified to

$$r_{pa} = -\frac{dM_a}{dt} = M_{0a}\frac{dX_a}{dt} = \overline{k}_{pa}[M_a]_p \overline{n}_t N_T \tag{7'}$$

$$r_{pb} = -\frac{dM_b}{dt} = M_{0b}\frac{dX_b}{dt} = \overline{k}_{pb}[M_b]_p \overline{n}_t N_T \tag{8'}$$

$$r_{pt} = r_{pa} + r_{pb} = M_{0t}\frac{dX_{Mt}}{dt} = (\overline{k}_{pa}[M_a]_p + \overline{k}_{pb}[M_b]_p)\overline{n}_t N_T \tag{9'}$$

The mole ratio of monomer A to B which are instantaneously incorporated into copolymer is given by

$$\frac{dp_a}{dp_b} = \frac{r_{pa}}{r_{pb}} = \frac{[M_a]_p}{[M_b]_p}\left(\frac{\gamma_a[M_a]_p + [M_b]_p}{\gamma_b[M_b]_p + [M_a]_p}\right) = \frac{\overline{k}_{pa}[M_a]_p}{\overline{k}_{pb}[M_b]_p} \tag{30}$$

APPLICATION TO ST AND MMA EMULSION COPOLYMERIZATION SYSTEM

In this section, it is demonstrated by using experimental data obtained in the emulsion copolymerization of ST and MMA that the method mentioned above can be successfully applied for predicting the average number of radicals per particle and their kinds in emulsion copolymerization systems.

TABLE I
Numerical Values of Constants Used (50°C)[1]

Constant	Unit	Styrene (s)	Methyl methacrylate (m)
k_p	(dm³/mol·s)	210	650
γ	(—)	0.52	0.46
δ	(—)	0.16[a]	0.16[a]
C_m	(—)	$C_{mss} = 1.2 \times 10^{-5}$	$C_{mmm} = 2.0 \times 10^{-5}$
		$C_{msm} = 5.0 \times 10^{-5}$ [a]	$C_{mms} = 5.0 \times 10^{-5}$ [a]
D_w	(cm²/s)	1.2×10^{-5}	1.7×10^{-5}
m_d	(—)	1300	50
$\bar{k}_{tp}$	(dm³/mol·s)	6.0×10^7

$\bar{k}_{tp}$ (dm³/mol·s) 6.0×10^7
$k_{tpsm} = 3.6 \times 10^8$
$k_{tpss} = 3.0 \times 10^6$ $k_{tpmm} = 1.8 \times 10^5$
k_{df} (1/s) 6.7×10^{-7} $(r_i = 2k_{df}[I_0])$

[a] Readjusted considering the values of cross-transfer rate constants reported recently by Gold-wasser and Rudin.[11]

Experimental

Commercially available MMA and ST monomers were purified in the way as described in the previous paper.[1] Potassium persulfate and sodium lauryl sulfate of extra-pure grade were used as received as initiator and emulsifier, respectively. All water used was purified by distillation of deionized water in the presence of alkaline potassium permanganate.

The seeded and unseeded emulsion copolymerizations of ST and MMA were carried out using the same experimental apparatus and procedure as shown previously.[1] The preparation of seed latex used in this experiment and the measurement of particle number and monomer concentration in monomer-swollen polymer particles were done in the same ways as described in the previous paper.[1] Conversion of each monomer was determined using gas chromatography. Total monomer conversion was also determined gravimetrically using methanol as precipitant for comparison.

Experimental Results and Discussion

Experimental value of $\bar{n}_t$ is obtained as follows: The values of r_{pa} and r_{pb} are obtained from the slopes of the conversion vs. time curves for each monomer at about 30% conversion where polymer particles are still at equilibrium swelling (monomer–polymer weight ratio, M/P = 1.67).[1] Monomer concentrations in polymer particles, $[M_a]_p$ and $[M_b]_p$ and the value of N_T are measured in the way described above. Propagation rate constants used are literature values listed in Table I. These values are inserted into eqs. (7) and (8), and solved simultaneously for obtaining experimental values of $\bar{n}_a$ and $\bar{n}_b$. The sum of these values gives the $\bar{n}_t$ value. The value of $\bar{n}_t$ thus obtained is plotted against the corresponding value of α' on Figure 1. Figure 2 shows an example of the plot of $\bar{n}_t$ vs. α', which were obtained at the condition of 1:1 weight ratio of ST and MMA monomers in the initial monomer charge.

The solid lines in Figure 2 represent the predicted values for the polymer particles with 100 and 200 nm diameters, respectively. It is seen from this
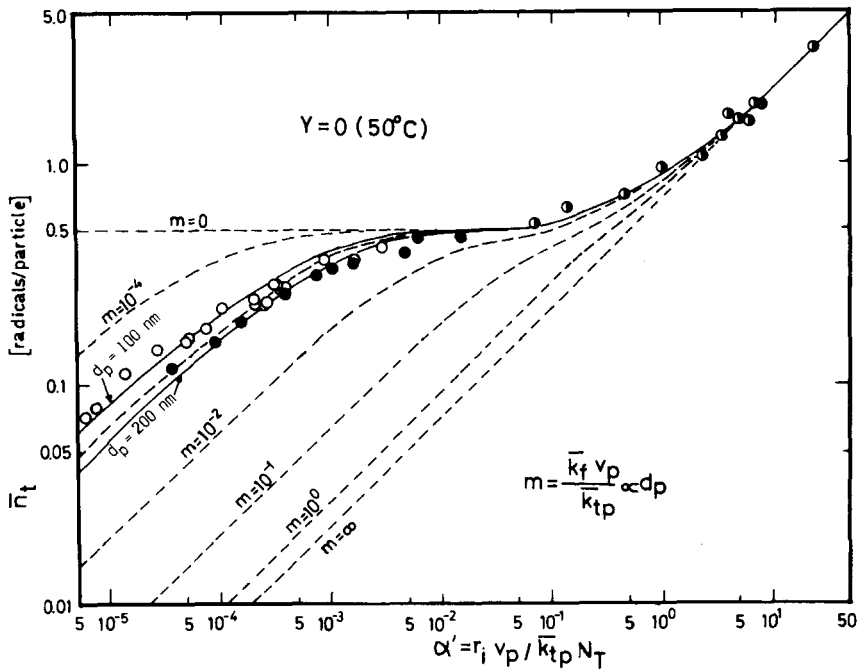
Fig. 2. Comparison between the theoretical and experimental values of $\bar{n}_t$ in emulsion copolymerization of ST and MMA. Experimental $(M_{0m}/M_{0t} = 0.5)$ d_p (monomer-swollen polymer particles) (nm): ($\circledcirc$) 310–590; ($\bullet$) 200–270; ($\circ$) 67–140; theoretical: (——) $d_p = 100, 200$ nm; (- - - -) m = variable (= $\bar{k}_f v_p / k_{tp} \propto d_p$).

comparison that the method developed in this paper can predict very well the average number of radicals per particle in the emulsion copolymerization of ST and MMA. Numerical values used in this calculation are those listed in Table
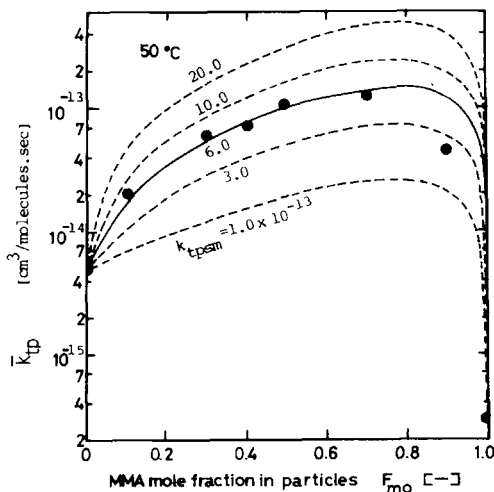

Fig. 3. Effect of mole fraction of MMA monomer in monomer-swollen polymer particles, F_{m0}, on the mean termination rate constant in monomer-swollen polymer particles, $\bar{k}_{tp}$. Theoretical values by eq. (23): (——) $k_{tpsm} = 6.0 \times 10^{-13}$ cm³/molecule·s; (- - -) k_{tpsm} = variable; experimental values: ($\bullet$) F_{m0} = variable.

I. In calculating the value of $\bar{k}_f$, the term, $k_{0a}\bar{n}_t/k_{paa}$ in eq. (21) was neglected for simplicity because neglect of this term did not lead to a serious error.

The value of $\bar{k}_{tp}$ used in this calculation was 6×10^7 dm³/mol·s, as shown in Table I. This value was obtained from analyzing experimental data of $\bar{n}_t$ in the range $\bar{n}_t \gg 0.5$ on the theoretical basis that when $\bar{n}_t \gg 0.5$, $\bar{n}_t$ is expressed by

$$\bar{n}_t = (r_i v_p / 2\bar{k}_{tp} N_T)^{1/2} \tag{31}$$

Figure 3 shows the results of analysis for $\bar{k}_{tp}$. From this figure, the cross-termination rate constant k_{tpab} can be estimated to be 3.6×10^8 dm³/mol·s. The values of $\bar{k}_{tp}$ and k_{tpab} thus estimated seem to be physically reasonable.

CONCLUSION

A method for predicting the average number of radicals per particle and their kinds in emulsion copolymerization systems has been developed by extending emulsion homopolymerization theories so far published. The validity and utility of this method was demonstrated by using the experimental data obtained in the emulsion copolymerization of ST and MMA. This method is very simple but useful because this can be applied without any limitation regarding the range of the value of $\bar{n}_t$. Furthermore, a method was presented for estimating the cross-termination rate constant by using emulsion copolymerization.

APPENDIX: NOMENCLATURE

A	defined by eq. (16)
$C_{mab} = k_{mab}/k_{pab}$	chain transfer constant of A-radical to B-monomer
d_p	particle diameter
D_{wj} $(j = a,b)$	diffusion coefficient of j-oligomer radical in water
k_a	rate constant of radical capture by polymer particles
$\bar{k}_a$	mean rate constant of radical capture by particles
k_d	rate constant of initiator decomposition
k_{fj} $(j = a,b)$	desorption rate coefficient for j-oligomer radicals
$\bar{k}_f$	mean rate coefficient of radical desorption defined by eq. (20)
k_{mf}	rate constant of chain transfer to monomer
k_{mab}	rate constant of chain transfer of A-radical to B-monomer
K_{0j} $(j = a,b)$	desorption rate constant for j-oligomer radical defined by eq. (21)
k_p	propagation rate constant
k_{pab}	propagation rate constant of A-radical to B-monomer
k_{tp}	termination rate constant in polymer particle
$\bar{k}_{tp}$	mean termination rate constant defined by eq. (23)
k_{tpab}	cross-termination rate constant between A- and B-radicals
k_{tw}	termination rate constant in water phase
$\bar{k}_{tw}$	mean termination rate constant in water phase
m_{dj} $(j = a,b)$	partition coefficient of j-oligomer radicals between particle and water phase
M_j $(j = a,b)$	amount of unreacted j-monomer per unit volume of water
$[M_j]_p$ $(j = a,b)$	concentration of j-monomer in polymer particles
M_{0j} $(j = a,b)$	amount of j-monomer initially charged
M_{0t}	total amount of monomer initially charged
n	number of total radicals in a particle
n_j $(j = a,b)$	number of j-radicals in a particle
$\bar{n}$	average number of radicals per particle

$\bar{n}_j$ ($j = a,b$)   average number of j-radicals per particle
$\bar{n}_t$ average number of total radicals per particle ($\Sigma \bar{n}_j$)
N_n number of particles containing n radicals
N_T number of total particles per unit volume of water
p_j ($j = a,b$)   amount of j-monomer incorporated into copolymer
$\bar{P}_N$ number-average degree of polymerization of polymers
r_i rate of radical production in water phase
r_{mf} rate of chain transfer to monomer molecules
r_{pj} ($j = a,b$)   rate of copolymerization of j-monomer
r_{pt} total rate of copolymerization defined by eq. (9)
$[R_w^*]$ concentration of total radicals in the water phase
t reaction time
v_p volume of a particle
X_j ($j = a,b$)   conversion of j-monomer to polymer
X_{Mt} total conversion of monomer to copolymer

Greek Letters

ρ_e overall rate of radical entry into particles defined by eq. (2) or eq. (25)
λ probability of radical termination by combination
ω_j ($j = a,b$)   probability of absorbed radicals being or becoming j-radical
γ_j ($j = a,b$)   monomer reactivity ratio

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