For cross-linking long chains

$$\frac{G}{RT} = [\mathrm{A}_4]\{1/2P(F_\mathrm{A}^{\mathrm{out}})[1 - P(F_\mathrm{A}^{\mathrm{out}})]^3 + [1 - P(F_\mathrm{A}^{\mathrm{out}})]^4\} + \epsilon[1 - (1 - \rho)P(F_\mathrm{A}^{\mathrm{out}})]^4 \quad (56)$$

where $[\mathrm{A}_4] = \rho(d_0)/2M_\mathrm{c}$, where d_0 is the initial sample density and M_c is the weight between cross-linkable sites.

It is worth noting that the concentration of effective network chains $\nu_\mathrm{c} + \nu_\mathrm{e}$ can also be applied to predict equilibrium swelling of a rubber network (Flory,[2b] p 579).

Conclusions

The probability of a finite or dangling chain on an ideal polymer network has been derived by a simple recursive scheme. In contrast to the method of Dobson and Gordon[5] probability generating function formalism is not required.

The general result, eq 21, and its specific solutions, eq 23, 24, and 30, give the finite chain probability as a function of reactant type and extent of polymerization. They cover most of the important types of network forming polymerizations.

From the finite chain probability useful property relations such as sol fraction, cross-link density, and the number of elastically effective network chains are developed. Because of their simplicity we expect these relations to be further developed and applied to network polymer property measurements.

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Appendix. Effect of Condensation Products on Sol Fraction

Although the relations for probability of a finite chain and cross-link probability remain unchanged, condensation products do affect the weight fraction solubles. We must modify the weight fraction terms in eq 39. The probability that all arms of an $\mathrm{A}_{f_i}{}^n$ (defined in ref 2a, eq A4) lead to finite chains is $P(F_\mathrm{B}^{\mathrm{in}})^n$. Furthermore the proportion of mass in $\mathrm{A}_{f_i}{}^n$'s and $\mathrm{B}_{g_j}{}^n$'s is $w_{\mathrm{A}_{f_i}{}^n}$ and $w_{\mathrm{B}_{g_j}{}^n}$ as defined in ref 2a, eq A16 and A17. Thus with condensation eq 39 becomes

$$w_\mathrm{s} = \sum_{i=1}^{k} \sum_{n=0}^{f_i} w_{\mathrm{A}_{f_i}{}^n} P(F_\mathrm{B}^{\mathrm{in}})^n + \sum_{j=1}^{l} \sum_{n=0}^{g_j} w_{\mathrm{B}_{g_j}{}^n} P(F_\mathrm{A}^{\mathrm{in}})^n \quad \mathrm{(A1)}$$

For the special case of A_f homopolymerization

$$w_s = \sum_{n=0}^{f} w_{\mathrm{A}_f{}^n} P(F_\mathrm{A}^{\mathrm{in}})^n \quad \mathrm{(A2)}$$

or

$$w_\mathrm{s} = P(F_\mathrm{A}^{\mathrm{out}})^f \left[\frac{2M_{\mathrm{A}_f} - pfM_\mathrm{C}P(F_\mathrm{A}^{\mathrm{out}})^{f-2}}{2M_{\mathrm{A}_f} - pfM_\mathrm{C}}\right] \quad \mathrm{(A3)}$$

For the case A_3, $P(F_\mathrm{A}^{\mathrm{out}}) = (1 - p)/p$ if $p > 1/2$

$$w_\mathrm{s} = \left(\frac{1-p}{p}\right)^3 \left[\frac{2M_{\mathrm{A}_3} - 3(1-p)M_\mathrm{C}}{2M_{\mathrm{A}_3} - 3pM_\mathrm{C}}\right] \quad \mathrm{(A4)}$$

Note that for $M_\mathrm{C} = 0$, the correction factor equals 1 and A3 reduces to eq 38.

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Studies on the Mechanism of Alternating Radical Copolymerization. Quantitative Treatment of the Initial Copolymerization Rate

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ABSTRACT: In the previous paper[1] we have proposed the general mechanism involving the participation of both the free monomers and the charge-transfer complex monomer for the alternating radical copolymerization. This paper describes a quantitative treatment of the initial copolymerization rate to estimate the ratio of the contribution of the charge-transfer complex monomer to the free monomers.

A number of studies have been done concerning the mechanism of the alternating radical copolymerization. As for the propagation process of the copolymerization, the following three mechanisms have been proposed: (i) mechanism considering only the cross reactions of the free monomers, (ii) mechanism of homopolymerization of the charge-transfer complex monomer (CT-complex monomer), (iii) mechanism involving the participation of both the free monomers and the CT-complex monomer. Baldwin et al.[2] has explained the results based on the first mechanism. Yamashita et al.[3] has proposed the second mechanism based on the studies of the terpolymerization, suggesting much higher reactivity of the CT-complex monomer as compared with the free monomers.

The third mechanism has recently been proposed by Tsuchida et al.[4] and by us,[1] although the models are different from each other. The idea of the third mechanism originates from the fact that the initial copolymerization rate does not necessarily maximize at the monomer feed ratio 1:1 where the concentration of the charge-transfer complex is the highest, which is inconsistent with the second mechanism. Litt et al.[5] has independently introduced this concept even to nonalternating systems[6] showing that in some systems the charge-transfer model gives a better explanation of the results than considering the penaltimate and antepenaltimate effect.

In the previous paper[1] describing alternating copolymerization of *N*-vinylcarbazole with the electron-accepting monomer, we have qualitatively shown that the overall initial copolymerization rate is understood as the superposition of the rates of the free monomers $R_p(\mathrm{f})$ and of the CT-complex monomer $R_p(\mathrm{CT})$. Quantitative treatment to evaluate the degree of the participation of the free monomers and the CT-complex monomer in the alternating copolymerization has not been made. In this paper we report a quantitative treatment of the initial copolymerization rate to divide it directly into $R_p(\mathrm{f})$ and $R_p(\mathrm{CT})$ and estimate the ratio of the participation of the CT-complex monomer to the free monomers. The reactivity ratio of the CT-complex monomer to the free monomers toward the growing polymer radical is also evaluated by this method.

Discussion

In the previous paper[1] we have proposed the following mechanism for the alternating radical copolymerization, which involves the cross-reactions of both the free monomers and the CT-complex monomer in the propagation process (eq 6–9).

Initiation Process

$$\mathrm{I} \xrightarrow{k_{\mathrm{id}}} 2\mathrm{R}\cdot \tag{1}$$

$$\mathrm{R}\cdot + \mathrm{M_1} \xrightarrow{k_{\mathrm{i1}}} \mathrm{m_1}\cdot \tag{2}$$

$$\mathrm{R}\cdot + \mathrm{M_2} \xrightarrow{k_{\mathrm{i2}}} \mathrm{m_2}\cdot \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{M_1M_2} \xrightarrow{k_{\mathrm{ic2}}} \mathrm{m_2}\cdot \tag{4}$$

$$\mathrm{R}\cdot + \mathrm{M_2M_1} \xrightarrow{k_{\mathrm{ic1}}} \mathrm{m_1}\cdot \tag{5}$$

Propagation Process

$$\mathrm{m_1}\cdot + \mathrm{M_2} \xrightarrow{k_{12}} \mathrm{m_2}\cdot \tag{6}$$

$$\mathrm{m_2}\cdot + \mathrm{M_1} \xrightarrow{k_{21}} \mathrm{m_1}\cdot \tag{7}$$

$$\mathrm{m_1}\cdot + \mathrm{M_2M_1} \xrightarrow{k_{1\mathrm{c}}} \mathrm{m_1}\cdot \tag{8}$$

$$\mathrm{m_2}\cdot + \mathrm{M_1M_2} \xrightarrow{k_{2\mathrm{c}}} \mathrm{m_2}\cdot \tag{9}$$

Termination Process (I)
(in the case of bimolecular termination)

$$\mathrm{m_1}\cdot + \mathrm{m_1}\cdot \xrightarrow{k_{\mathrm{t11}}} \text{polymer} \tag{10}$$

$$\mathrm{m_1}\cdot + \mathrm{m_2}\cdot \xrightarrow{k_{\mathrm{t12}}} \text{polymer} \tag{11}$$

$$\mathrm{m_2}\cdot + \mathrm{m_2}\cdot \xrightarrow{k_{\mathrm{t22}}} \text{polymer} \tag{12}$$

Termination Process (II)
(in the case of monomolecular termination)

$$\mathrm{m_1}\cdot \xrightarrow{k_{\mathrm{t1}}} \text{polymer} \tag{13}$$

$$\mathrm{m_2}\cdot \xrightarrow{k_{\mathrm{t2}}} \text{polymer} \tag{14}$$

Based on this model we show the quantitative treatment of the initial copolymerization rate to divide R_p into $R_p(\mathrm{f})$ and $R_p(\mathrm{CT})$ respectively and estimate the ratio of the reactivity of the CT-complex monomer to the free monomers toward the growing polymer radical. The method is to examine the total monomer concentration dependence on the overall initial copolymerization rate for each given monomer feed composition.

Evaluation of the Reaction Rates of the Free Monomers $R_p(\mathrm{f})$ and the CT-Complex Monomer $R_p(\mathrm{CT})$

Let us consider first the case where the bimolecular termination occurs. The overall initial copolymerization rate is given by eq 15,[7]

$$R_p = -\mathrm{d}([\mathrm{M_1}] + [\mathrm{M_2}])/\mathrm{d}t = k_{12}[\mathrm{m_1}\cdot][\mathrm{M_2}] + k_{21}[\mathrm{m_2}\cdot][\mathrm{M_1}] + 2\{k_{1\mathrm{c}}[\mathrm{m_1}\cdot][\mathrm{CT}] + k_{2\mathrm{c}}[\mathrm{m_2}\cdot][\mathrm{CT}]\} \tag{15}$$

where $[\mathrm{M_1}]$, $[\mathrm{M_2}]$, and $[\mathrm{CT}]$ represent the concentrations of the free monomers $\mathrm{M_1}$ and $\mathrm{M_2}$ and the CT-complex monomer $\mathrm{M_1M_2}$ ($\mathrm{M_2M_1}$), respectively, and $[\mathrm{m_1}\cdot]$ and $[\mathrm{m_2}\cdot]$ represent the concentrations of the growing polymer radicals with the $\mathrm{M_1}$ and $\mathrm{M_2}$ end, respectively. The equilibrium constant K for the formation of the charge-transfer complex is generally not large in the alternating copolymerization systems; therefore, the concentration of the CT-complex monomer is expressed approximately by eq 16.

$$[\mathrm{CT}] = K[\mathrm{M_1}][\mathrm{M_2}] \tag{16}$$

The steady-state approximation gives eq 17 and 18.

$$k_{12}[\mathrm{m_1}\cdot][\mathrm{M_2}] = k_{21}[\mathrm{m_2}\cdot][\mathrm{M_1}] \tag{17}$$

$$R_\mathrm{i} = R_\mathrm{t} = k_{\mathrm{t11}}[\mathrm{m_1}\cdot]^2 + 2k_{\mathrm{t12}}[\mathrm{m_1}\cdot][\mathrm{m_2}\cdot] + k_{\mathrm{t22}}[\mathrm{m_2}\cdot]^2 \tag{18}$$

As is evident from eq 15 the overall copolymerization rate is expressed as the sum of the reaction rates of the free monomers $R_p(\mathrm{f})$ and the CT-complex monomer $R_p(\mathrm{CT})$.

$$R_p = R_p(\mathrm{f}) + R_p(\mathrm{CT}) \tag{19}$$

$$R_p(\mathrm{f}) = k_{12}[\mathrm{m_1}\cdot][\mathrm{M_2}] + k_{21}[\mathrm{m_2}\cdot][\mathrm{M_1}] \tag{20}$$

$$R_p(\mathrm{CT}) = 2\{k_{1\mathrm{c}}[\mathrm{m_1}\cdot][\mathrm{CT}] + k_{2\mathrm{c}}[\mathrm{m_2}\cdot][\mathrm{CT}]\} \tag{21}$$

Substituting $[\mathrm{M_1}] + [\mathrm{M_2}] = [\mathrm{T}]$ and $[\mathrm{M_2}] = X[\mathrm{M_1}]$, and introducing eq 17 into eq 20 and 21, the ratio of $R_p(\mathrm{CT})$ to $R_p(\mathrm{f})$ will be given by the following equation,

$$R_p(\mathrm{CT})/R_p(\mathrm{f}) = \left(\frac{k_{1\mathrm{c}}}{k_{12}} + \frac{k_{2\mathrm{c}}}{k_{21}}X\right) K \frac{[\mathrm{T}]}{1 + X} \tag{22}$$

where $[\mathrm{T}]/(1 + X) = [\mathrm{M_1}]$. Equation 22 shows that the ratio $R_p(\mathrm{CT})/R_p(\mathrm{f})$ depends on the total monomer concentration and the monomer feed ratio. The rate of the reaction of the free monomers $R_p(\mathrm{f})$ will be expressed as eq 23 by combining eq 17, 18, and 20,

$$R_p(\mathrm{f}) = \frac{2k_{21}k_{12}R_\mathrm{i}^{1/2}X}{\{k_{\mathrm{t11}}k_{21}^2 + 2k_{\mathrm{t12}}k_{21}k_{12}X + k_{\mathrm{t22}}k_{12}^2X^2\}^{1/2}} \times [\mathrm{M_1}] = A(X)[\mathrm{M_1}] \tag{23}$$

$$(R_\mathrm{i} = 2k_\mathrm{d}f[\mathrm{I}])$$

where $A(X)$ should be constant so far as the concentration of the initiator and the monomer feed ratio are fixed. Then, $R_p(\mathrm{CT})$ will be expressed as eq 24 from eq 22 and 23.

$$R_p(\mathrm{CT}) = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[\mathrm{M_1}]^2 \qquad (24)$$

Thus, we have the overall copolymerization rate equation expressed as follows.

$$R_p = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[\mathrm{M_1}]^2 + A(X)[\mathrm{M_1}] \qquad (25)$$

By dividing eq 25 by $[\mathrm{M_1}]$, the following relationship will be derived.

$$R_p/[\mathrm{M_1}] = A(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[\mathrm{M_1}] + A(X) \qquad (26)$$

Equation 26 shows that $R_p/[\mathrm{M_1}]$ is the first-order function with respect to $[\mathrm{M_1}]$ since $A(X)$ and $A(X)K([k_{1c}/k_{12}] + [k_{2c}/k_{21}]X)$ are constant for the fixed X and the initiator concentration. Thus, the plot of $R_p/[\mathrm{M_1}]$ against $[\mathrm{M_1}]$ for each given X (only total monomer concentration is changed in the range where the equilibrium constant K does not change appreciably) should give the straight line. The intercept and the slope of this linear plot give the values of $A(X)$ and $A(X)K([k_{1c}/k_{12}] + [k_{2c}/k_{21}]X)$, respectively. Thus, the values of $R_p(\mathrm{f})$ and $R_p(\mathrm{CT})$ can be obtained for each given monomer feed composition and the given total monomer concentration by use of the eq 23 and 24.

When $R_p(\mathrm{f})$ contributes overwhelmingly to the polymerization rate, the plot of $R_p/[\mathrm{M_1}]$ against $[\mathrm{M_1}]$ will give a straight line with almost no slope for each given X, whereas in the opposite case where $R_p(\mathrm{CT})$ contributes overwhelmingly to the polymerization rate, the linear plot will give a very small value of the intercept, or a very large slope. In the latter case the plot of $R_p/[\mathrm{M_1}]^2$ against $[\mathrm{M_1}]$ for the fixed X would give an approximately straight line with no appreciable slope. It should be mentioned here that the present kinetical treatment based on our model involves the assumption of eq 17 even in the latter case described above, therefore $A(X)$ does not become zero.

Similar treatment can be carried out for the case where the monomolecular termination occurs, to evaluate $R_p(\mathrm{f})$ and $R_p(\mathrm{CT})$, respectively.

In this case eq 18 is replaced by eq 27 and the following equations will be derived.

$$R_i = R_t = k_{t1}[\mathrm{m_1}\cdot] + k_{t2}[\mathrm{m_2}\cdot] \qquad (27)$$

$$R_p(\mathrm{f}) = \frac{2k_{12}k_{21}R_iX}{k_{t1}k_{21} + k_{t2}k_{12}X}[\mathrm{M_1}] = B(X)[\mathrm{M_1}] \qquad (28)^{8}$$

$$R_p(\mathrm{CT}) = B(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[\mathrm{M_1}]^2 \qquad (29)$$

$$R_p = B(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[\mathrm{M_1}]^2 + B(X)[\mathrm{M_1}] \qquad (30)$$

and

$$R_p/[\mathrm{M_1}] = B(X)K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right)[\mathrm{M_1}] + B(X) \qquad (31)$$

Estimation of the Ratio of the Reactivity of the CT-Complex Monomer to the Free Monomers Toward the Growing Polymer Radical End

The ratio of the reactivity of the CT-complex monomer to the free monomers toward the growing polymer chain radicals can be evaluated in the following way. Since the values of $A(X)$ (or $B(X)$) and $A(X)K([k_{1c}/k_{12}] + [k_{2c}/k_{21}]X)$ (or $B(X)K([k_{1c}/k_{12}] + [k_{2c}/k_{21}]X)$) are obtained for each given X, the value of $K([k_{1c}/k_{12}] + [k_{2c}/k_{21}]X)$ can be calculated for each given X. Here, this is defined as $F(X)$.

$$F(X) = K\left(\frac{k_{1c}}{k_{12}} + \frac{k_{2c}}{k_{21}}X\right) \qquad (32)$$

When the value K is obtained from a spectroscopic study, the plot of $F(X)$ against X should give a straight line giving the values of k_{1c}/k_{12} and k_{2c}/k_{21} as the intercept and the slope, respectively. These values indicate the ratio of the reactivity of the CT-complex monomer to the free monomers toward the growing polymer radicals.

Furthermore, the ratio of k_{1c}/k_{12} to k_{2c}/k_{21}, *i.e.*, $k_{1c}k_{21}/k_{2c}k_{12}$, gives the ratio of the relative stability of the growing polymer radicals $\mathrm{m_1}\cdot$ and $\mathrm{m_2}\cdot$.

Information on the Termination Process

The information on the termination process will be given from the dependence of $A(X)$ or $B(X)$ on the monomer feed ratio X. Furthermore, if we define the function $G(X)$ as $G(X) = (X/A(X))^2$ for the bimolecular termination process, we obtain the following equation.

$$G(X) = (X/A(X))^2 = \frac{1}{4R_i}\left(\frac{k_{t22}}{k_{21}^2}X^2 + \frac{2k_{t12}}{k_{21}k_{12}}X + \frac{k_{t11}}{k_{12}^2}\right) \qquad (33)$$

The plot of $G(X)$ against X and the least-squares method will give the relative values of k_{t22}/k_{21}^2, $k_{t12}/k_{12}k_{21}$, and k_{t11}/k_{12}^2, respectively. These three values might offer the information regarding the relative weight of the participation of the three termination reactions. The cross termination factor ϕ is also obtained by combining these three values.

Likewise, the function $H(X)$ is defined as $H(X) = X/B(X)$ for the monomolecular termination process. Then $H(X)$ is expressed as in the following equation.

$$H(X) = X/B(X) = \frac{1}{2R_i}\left(\frac{k_{t2}}{k_{21}}X + \frac{k_{t1}}{k_{12}}\right) \qquad (34)$$

Linear plot of $H(X)$ against X gives the relative values of k_{t2}/k_{21} and k_{t1}/k_{12} from the slope and the intercept, respectively.

As described above the present quantitative treatment of the initial copolymerization rate provides an effective method to estimate the ratio of the reactivity of the CT-complex monomer to the free monomers as well as the ratio of the participation of the CT-complex monomer to the free monomers in the propagation step. We are now applying this kinetical treatment to *N*-vinylcarbazole (NVC)–fumaronitrile[1], NVC–diethyl fumarate[1], vinylferrocene–diethyl fumarate,[9] and other alternating radical copolymerization systems, which will be reported in a later report.

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(6) This means that the copolymer composition is not perfectly 1:1 alternation regardless of the monomer feed composition.

(7) The factor 2 of the latter two terms is introduced since 1 mol of $\mathrm{M_1}$ and 1 mol of $\mathrm{M_2}$ monomer enter at a time by the reaction of 1 mol of the CT-complex monomer.

(8) The monomolecular termination step generally occurs by either k_{t1} or k_{t2} step in a system. If the termination occurs by k_{t1} process, $R_p(\mathrm{f})$ will be reduced as follows:

$$R_p(\mathrm{f}) = (2k_{12}R_i/k_{t1})[\mathrm{M_2}] \qquad (35)$$

If the termination occurs by k_{t2} process, $R_p(\mathrm{f})$ will be reduced as follows:

$$R_p(\mathrm{f}) = (2k_{21}R_i/k_{t2})[\mathrm{M_1}] \qquad (36)$$

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