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Graphical Evaluation of the Rate Constants of the Elementary Reaction of the Non-stationary Polymerization

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A graphical method for the interpretation of the kinetics of the non-stationary polymerization, and for the evaluation of the rate constants of elementary reactions, was proposed. It was shown that the rates of elementary reactions could be estimated with an extrapolating method using the kinetic data on the polymer yield and the number-average degree of polymerization of the polymer. The graphical method was then applied to some practical examples.

Recently, there have been found many polymerization systems to which a steady-state assumption with respect to the concentration of the propagating species can not be applied. In the kinetic study of these systems, complicated calculations are often required to express the kinetic data as a function of the rate constants of elementary reactions and the concentration of reactants, and to evaluate the rate constants of elementary reactions.

We have previously reported on a classification of polymerization from a kinetic point of view,1) and have clarified the conditions under which nonstationary states are realized. We will present here a general method for the graphical interpretation of kinetic data, and for the evaluation of the rate constants of the elementary reaction of the non-stationary polymerization.

Fundamental Relationship of Polymerization Kinetics

The polymerization reaction is, in general, divided into four elementary reactions: 1) initiation, 2) propagation, 3) chain transfer, and 4) termination. The following two equations connect the kinetic data, *i. e.,* the polymer yield and the number-average degree of polymerization of the polymer formed in a reaction period of from time

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1) T. Kagiya, M. Izu and K. Fukui, This Bulletin, **40**, 1045 (1967).

0 to time t, with the rates of the elementary reactions of polymerization:

$$[\mathrm{P}^*] = \int R_i \mathrm{d}t - \int R_t \mathrm{d}t \tag{1}$$

$$\overline{P} = \frac{\int R_p \mathrm{d}t}{\int R_i \mathrm{d}t + \int R_{tr} \mathrm{d}t} \tag{2}$$

where P^* = the propagating species; $[\mathrm{P}^*]$ = the concentration of P^*; R_i, R_t, R_p, R_{tr} = the rates of initiation, termination, propagation, and chain transfer respectively, and $\overline{P}$ = the number-average degree of polymerization of the polymer formed in a reaction period of from time 0 to time t.

If the recombination between propagating species prevails in the termination, Eq. (2′) is applicable in place of Eq. (2):

$$\overline{P} = \frac{\int R_p \mathrm{d}t}{\int R_i \mathrm{d}t - \frac{1}{2}\int R_t' \mathrm{d}t + \int R_{tr} \mathrm{d}t} \tag{2′}$$

where R_t' = the rate of recombination between propagating species. The rates of the elementary reaction can be expressed as a function of the reaction time and of the concentrations of the reactants. By solving the equations obtained by combining these relationships with the Eqs. (1) and (2), the polymer yield and the number-average degree of polymerization of the polymer formed in a reaction period of from time 0 to time t can be expressed as a function of the reaction time. The rate constants of elementary reactions are evaluated by the use of experimental data on the polymer yield and the number-average degree of the polymerization of the polymer formed.

In non-stationary state polymerization, however, this way of evaluating the rate constants of elementary reactions needs very complicated calculations. The graphical method shown below is useful for the evaluation of these rate constants.

Evaluation of the Rate Constants of Elementary Reactions. *1) Evaluation of the Values of* $\int R_i\, dt$ *and* $\int R_t' dt$. Equation (2) or Eq. (2′) is used in order to evaluate the values of $\int R_i \mathrm{d}t$ and $\int R_t' \mathrm{d}t$ from the kinetic data. The rates of elementary reactions and the integrals of the rates are assumed, or derived and summarized in Table 1. $\int R_i \mathrm{d}t$ is expressed as a general form, *g(t)*. The rate of propagation is assumed to be proportional to the product of $[\mathrm{P}^*]$ and $[\mathrm{M}]$ (M = monomer, and $[\mathrm{M}]$ = the concentration of M). Because the kinetic chain is long enough, the integral is approximately equal to $[\mathrm{M_p}]$ ($[\mathrm{M_p}]$ = the polymer yield counted in polymerized monomer moles). The rate of chain transfer is assumed in each case to be as is shown in Table 1. The integral of the transfer reaction was obtained by eliminating $[\mathrm{P}^*]$ with the use of the relationship of $R_p = k_p[\mathrm{P}^*][\mathrm{M}]$. In the same way, the rate and integral of termination were assumed and derived.

Equation (2) can be modified into the following equation:

$$\frac{1}{\overline{P}} = \frac{\int R_i \mathrm{d}t}{\int R_p \mathrm{d}_t} + \frac{\int R_{tr} \mathrm{d}t}{\int R_p \mathrm{d}t} \tag{3}$$

The following equations are derived by, in each case, substituting the relationship in Table 1 into Eq. (3). a) When chain transfer to the monomer is predominant,

$$\frac{1}{\overline{P}} = \frac{g(t)}{[\mathrm{M_p}]} + \frac{k_{tr}}{k_p} \tag{4-1}$$

b) When chain transfer to the solvent or catalyst is predominant,

$$\frac{[\mathrm{M_p}]}{\overline{P}\int \frac{R_p}{[\mathrm{M}]}\mathrm{d}t} = \frac{g(t)}{\int \frac{R_p}{[\mathrm{M}]}\mathrm{d}t} + \frac{k_{tr}[\mathrm{Y}]}{k_p} \tag{4-2}$$

c) When chain transfer to a by-product is predominant,

$$\frac{[\mathrm{M_p}]}{\overline{P}\int \frac{R_p[\mathrm{M_p}]}{[\mathrm{M}]}\mathrm{d}t} = \frac{g(t)}{\int \frac{R_p[\mathrm{M_p}]}{[\mathrm{M}]}\mathrm{d}t} + \frac{k_{tr}}{k_p} \tag{4-3}$$

In Eqs. (4-1)—(4-3), the second term on the right-hand side is a constant with respect to the reaction time. All the variables except *g(t)* can be evaluated from the experimental data of $[\mathrm{M_p}]$, $\overline{P}$, and R_p and the integral term in each equation can be calculated graphically with the use of the experimental data. Accordingly, if we plot the term of the left-hand side against the first term divided by $g(t)$ in the right-hand side, an upward concave curve or a straight line (when *g(t)* is a constant, that is, in a polymerization with a rapid initiation1)) is obtained. The intercept on the ordinate axis equals the second term on the right-hand side of Eqs. (4-1)—(4-3).

The value of *g(t)* at any reaction time can then be calculated by substituting the value of k_{tr}/k_p or $k_{tr}[\mathrm{Y}]/k_p$ into Eqs. (4-1)—(4-3). The nature of initiation is then determined numerically with the use of the *g(t)* function.

When the mechanism of initiation is known, the rate constant of intiation can be easily obtained. For instance, when $\int R_i = k_i t$ in the case of (b) (for example, in a radiation-induced polymerization), Eq. (4-2) is expressed by the following equation:

TABLE 1. THE RATES AND THEIR INTEGRALS OF THE ELEMENTARY STEPS

Initiation:	R_i	$\int R_i\mathrm{d}t = g(t)$
Propagation:	$R_p = k_p[\mathrm{P}^*][\mathrm{M}]$	$\int R_p\mathrm{d}t = [\mathrm{M_p}]$
Transfer:		
To solvent or catalyst (Y=solvent or catalyst)		
	$R_{tr} = k_{tr}[\mathrm{P}^*][\mathrm{Y}]$	$\int R_{tr}\mathrm{d}t = \frac{k_{tr}[\mathrm{Y}]}{k_p}\int\frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t$
To monomer		
	$R_{tr} = k_{tr}[\mathrm{P}^*][\mathrm{M}]$	$\int R_{tr}\mathrm{d}t = \frac{k_{tr}}{k_p}\,[\mathrm{M_p}]$
To by-product[a]		
	$R_{tr} = k_{tr}[\mathrm{P}^*][\mathrm{M_p}]$	$\int R_{tr}\mathrm{d}t = \frac{k_{tr}}{k_p}\int\frac{R_p[\mathrm{M_p}]}{[\mathrm{M}]}\,\mathrm{d}t$
Termination:		
Mutual termination		
	$R_t = k_t[\mathrm{P}^*]^2$	$\int R_t\mathrm{d}t = \frac{k_t}{k_p^2}\int\frac{R_p^2}{[\mathrm{M}]^2}\,\mathrm{d}t$
Self-deactivation[b]		
	$R_t = k_t t^m$	$\int R_t\mathrm{d}t = k_t\left(\frac{t^{m+1}}{m+1} + C\right)$
Termination with a component of the polymerization system, *e. g.*, solvent, catalyst, or impurity (Z)		
	$R_t = k_t[\mathrm{P}^*][\mathrm{Z}]$	$\int R_t\mathrm{d}t = \frac{k_t[\mathrm{Z}]}{k_p}\int\frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t$
Termination with by-product[a]		
	$R_t = k_t[\mathrm{P}^*][\mathrm{M_p}]$	$\int R_t\mathrm{d}t = \frac{k_t}{k_p}\int\frac{R_p[\mathrm{M_p}]}{[\mathrm{M}]}\,\mathrm{d}t$

a) It was assumed that the amount of by-product was proportional to the polymer yield.

b) In a coordinated anionic polymerization, the catalyst often loses its activity by itself. Because this deactivation is caused by a solid state reaction, the rate can not be expressed as a function of the concentrations of reactants. As has been treated in solid state kinetics the rate, in general, is experimentally expressed as a function of time.

$$\frac{[\mathrm{M_p}]}{\overline{P}\int\frac{\mathrm{R}_p}{[\mathrm{M}]}\,\mathrm{d}t} = \frac{k_i t}{\int\frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t} + \frac{k_{tr}[\mathrm{Y}]}{k_p} \qquad (4\text{-}4)$$

Accordingly, the plot of $[\mathrm{M_p}]\Big/\overline{P}\int\frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t$ against $t\Big/\int\frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t$ gives a straight line, whose slope and intercept on the ordinate axis equal k_i and $k_{tr}[\mathrm{Y}]/k_p$ respectively.

When a termination of the recombination between two propagating species takes place, Eq. (2′) should be used in place of Eq. (2); Eq. (3′) is then derived:

$$\frac{1}{\overline{P}} = \frac{\int R_i\mathrm{d}t - \frac{1}{2}\int R_t'\mathrm{d}t}{\int R_p\mathrm{d}t} + \frac{\int R_{tr}\mathrm{d}t}{\int R_p\mathrm{d}t} \qquad (3')$$

In Eq. (3′), when $h(t) \equiv \int R_i\mathrm{d}t - \frac{1}{2}\int R'_t\mathrm{d}t$, the value of *h(t)* can be obtained from the experimental data at every reaction time, according to a method analogous to that described above. By substituting the relationship of $R_t' = k_t'[\mathrm{P}^*]^2$ and by eliminating $[\mathrm{P}^*]$ by using the relationship of $R_p = k_p[\mathrm{P}^*][\mathrm{M}]$, the following relationship is derived from the equation of $h(t) \equiv \int R_i\mathrm{d}t - \frac{1}{2}\int R'_t\mathrm{d}t$:

$$\frac{2\,h(t)}{\int\frac{R_p^2}{[\mathrm{M}]^2}\,\mathrm{d}t} = \frac{2\int R_i\mathrm{d}t}{\int\frac{R_p^2}{[\mathrm{M}]^2}\,\mathrm{d}t} - \frac{k_t'}{k_p^2} \qquad (3'')$$

Accordingly, with an extrapolating method analogous to that mentioned above, a value of k_t'/k_p^2 can be obtained from Eq. (3″). With the use of this value, $\int R_i\mathrm{d}t$ can be calculated at any reaction time, and the kinetic nature of the initiation can be determined numerically.

2) Evaluation of k_t and k_p. By substituting the relationships in Table 1 into Eq. (1), the following equations are derived:

a) When a mutual termination of the propagating species occurs,

$$\frac{R_p}{[\mathrm{M}]\int \frac{R_p{}^2}{[\mathrm{M}]^2}\,\mathrm{d}t} = \frac{k_p\int R_i\mathrm{d}t}{\int \frac{R_p{}^2}{[\mathrm{M}]^2}\,\mathrm{d}t} - \frac{k_t}{k_p} \tag{5-1}$$

b) When termination occurs from a self-deactivation of the catalyst $\left(\int R_t\mathrm{d}t \equiv k_t f(t)\right)$,

$$\frac{R_p}{[\mathrm{M}]f(t)} = \frac{k_p\int R_i\mathrm{d}t}{f(t)} - k_t k_p \tag{5-2}$$

c) When termination occurs with a solvent, an impurity or a catalyst,

$$\frac{R_p}{[\mathrm{M}]\int \frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t} = \frac{k_p\int R_i\mathrm{d}t}{\int \frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t} - k_t[\mathrm{Z}] \tag{5-3}$$

d) When termination occurs with a by-product,

$$\frac{R_p}{[\mathrm{M}]\int \frac{R_p[\mathrm{M_p}]}{[\mathrm{M}]}\,\mathrm{d}t} = \frac{k_p\int R_i\mathrm{d}t}{\int \frac{R_p[\mathrm{M_p}]}{[\mathrm{M}]}\,\mathrm{d}t} - kt \tag{5-4}$$

The values of $\int R_i\mathrm{d}t$ is obtained according to the method described in Chapter 1).

If the elementary reactions are correctly proposed, a straight line can be obtained by plotting the term on the left-hand side against the first term on the right-hand side divided by k_p. The slope of the straight line gives the values of k_p, and, with the use of the value of the intercept on the ordinate axis, k_t can be estimated.

Examples of the Application of the Graphical Method. *1) Radiation-induced Solid State Polymerization of 3, 3-Bischloromethyloxetane.*[2-4] The polymer yield and intrinsic viscosity of the polymer formed in the presence or the absence of the additive are plotted against the irradiation time in Fig. 1. Figure 1 shows that the rate of polymerization and intrinsic viscosity of the polymer were approximately constant in the absence of the additive, while both of them increased with the irradiation time in the presence of the additive. These results indicate that the steady-state assumption with respect to the propagating species is applicable in the case of the polymerization without the additive, whereas in the presence of the additive the steady-state is not realized. The non-stationary state has been suggested by the present authors as being caused by the depression of the termination arising from the addition of the additive.[4]

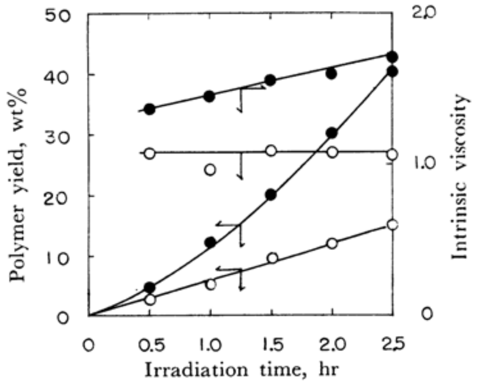

Fig. 1. Influence of the irradiation time on the polymer yield and intrinsic viscosity of the polymer formed by γ-ray-induced solid state polymerization of 3, 3-bischloromethyloxetane:
○ In the absence of the additive
● In the presence of the additive (KOH: 0.5 gr)
Dose rate, 1.5×10^5 rad/hr; irradiation temperature, 0°C; monomer, 6.2 g; monomer crystal prepared at −78°C.

According to the classification from a kinetic point of view previously proposed by the present authors, these polymerizations in the absence and in the presence of the additive are classified, respectively, as a stationary chain polymerization with a slow initiation and a non-stationary successive polymerization with a slow initiation. Accordingly, the kinetic data of the former can be simply interpreted with the steady-state assumption.[4] The kinetic data of the latter are graphically interpreted below.

The elementary steps of this polymerization have been proposed to be as follows by the present authors:

Rate

1. Initiation:

$\mathrm{M} \rightsquigarrow \mathrm{M}^+$ $\qquad R_i = k_i I(\mathrm{M})$

2. Propagation:

$\mathrm{M}^+ + \mathrm{M} \longrightarrow \mathrm{M_2}^+$

....

$R_p = k_p(\mathrm{P}^+)$

3. Termination:

$\mathrm{M}_n{}^+ \longrightarrow \mathrm{M}_n$ $\qquad R_t = k_t(\mathrm{P}^+)$

4. Degradation:

$\mathrm{P} \longrightarrow 2\mathrm{P}$ $\qquad R_d = k_d I(\mathrm{P})$

The $\rightsquigarrow$ sign is used to designate a primary radiation process. Here M = monomer; P = polymer; M^+, $\mathrm{M_2}^+$,$\cdots$, $\mathrm{M}_n{}^+ = \mathrm{P}^+$ = propagating species; R_i, R_p, R_t, R_d = the rates of initiation,

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[2] T. Kagiya, M. Izu and K. Fukui, *Makromol. Chem.*, **78**, 216 (1964).

[3] T. Kagiya, M. Izu and K. Fukui, *J. Polymer Sci.*, **B2**, 779 (1964).

[4] T. Kagiya, M. Izu and K. Fukui, *Makromol. Chem*, **102**, 39 (1967).

propagation, termination, and degradation; k_i, k_p, k_t, k_d = the rate constants of initiation, propagation, termination, and degradation; I = dose rate and (M), (P^+), (P) = mole of M, P^+, and P (counted in monomer moles).

Equation (1) is written in the following form in this case:

$$(P^+) = \int k_i I(M)dt - \int k_t(P^+)dt$$

By combining this equation with the rate equations of the elementary steps, the following equation is derived:

$$\frac{R_p}{(M_p)} = k_i I k_p \frac{\left((M_o t) - \int (M_p)dt\right)}{(M_p)} - k_t$$

where $(M_p) = \int R_p dt$ = the polymer yield counted in polymerized monomer moles, and (M_o) = the initial monomer moles.

$k_i I k_p$ and k_t were evaluated by the plot of $\frac{R_p}{(M_p)}$ against $\left((M_o)t - \int (M_p)dt\right) \Big/ (M_p)$ as is shown in Fig. 2.

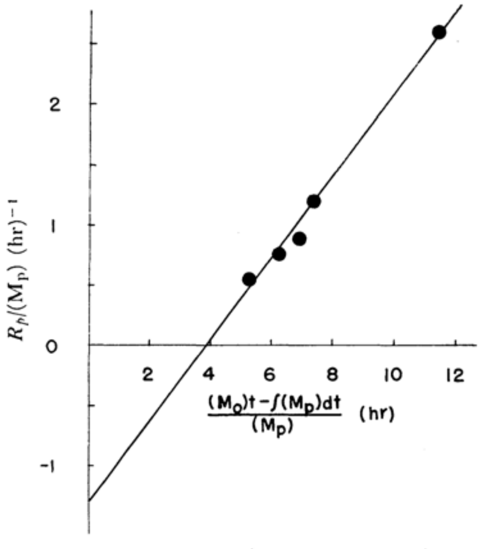

Fig. 2. $R_p/(M_p)$ *versus* $\left((M_o)t - \int (M_p)dt\right) \Big/ (M_p)$ in the γ-ray induced solid state polymerization of 3, 3-bischloromethyloxetane in the presence of the additive.

*2) Polymerization of β-Propiolactone with a Pyridine Catalyst.*⁵⁾ It has been reported by one of the present authors that this polymerization is a successive polymerization with a rapid initiation. This means that the plot of $1/\overline{P}$ against $1/[M_p]$ gives a straight line through the point of origin (Eq. (4-1)). The mole of the polymer chain evaluated from the slope was reported to be equal to the mole of the catalyst used.

The value of $R_p/[M]$, which is proportional to $[P^*]$ if we assume $R_p = k_p[P^*][M]$, decreased with the reaction time. In order to interpret this decrease in the rate, a termination with an impurity was introduced into the elementary steps. The rate was expressed:

$$R_t = k_t[P^*][Z]$$

It has already been shown that Eq. (5-3) is applicable in this case. The plot of $R_p \Big/ [M] \int \frac{R_p}{[M]} dt$ against $1 \Big/ \int \frac{R_p}{[M]} dt$ gives a straight line, as is shown in Fig. 3. From this result, it can be said that one plausible way of interpreting this decrease in the rate is to introduce a termination with an impurity as one of the elementary steps.

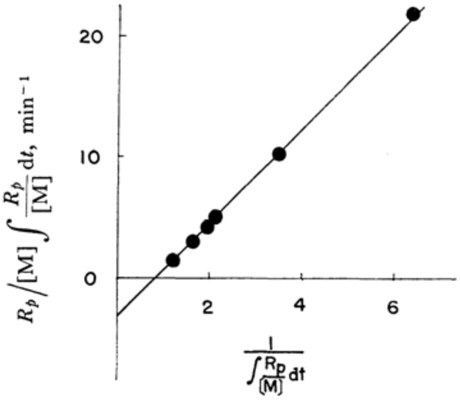

Fig. 3. $R_p \Big/ [M] \int \frac{R_p}{[M]} dt$ *versus* $1 \Big/ \int \frac{R_p}{[M]} dt$ in the polymerization of β-propiolactone with pyridine: $[M_0] = 3.2 \times 10^{-2}$ mol in chloroform solution; temperature, 35°C.

*3) Radiation-induced polymerization of Ethylene.*⁶⁻⁸⁾ The present authors have previously established that the γ-ray-induced polymerization of ethylene at a normal temperature is to be classified as a non-stationary successive polymerization with a slow initiation. On the other hand, this polymerization at a high temperature, above 100°C has been observed to be a stationary chain polymerization with a slow initiation. The kinetics of the non-stationary successive polymerization was studied by the graphical method.

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5) T. Kagiya, T. Sano and K. Fukui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **68**, 1144 (1965).

6) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, **B2**, 765 (1964).

7) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, This Bulletin, **39**, 675 (1966).

8) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, **A3**, 3029 (1965).

The following elementary steps have been proposed for this polymerization⁷⁾:

1. Initiation:

$$M \rightsquigarrow R_1\cdot \qquad R_i = k_i\rho_M I$$

2. Ethylene excitation and dimerization:

$$M \rightsquigarrow M^*$$

$$M + M^* \overset{K_e}{\rightleftharpoons} M_2^* \qquad f_{M_2^*} = K_e f_M{}^2$$

3. Propagation:

$$R_1\cdot + M_2^* \xrightarrow{k_p} R_2\cdot$$

$$\cdots\cdots\cdots\cdots\cdots\cdots \qquad R_p = k_p[R\cdot]f_{M_2^*}$$

$$R_{n-2}\cdot + M_2^* \xrightarrow{k_p} R_n\cdot$$

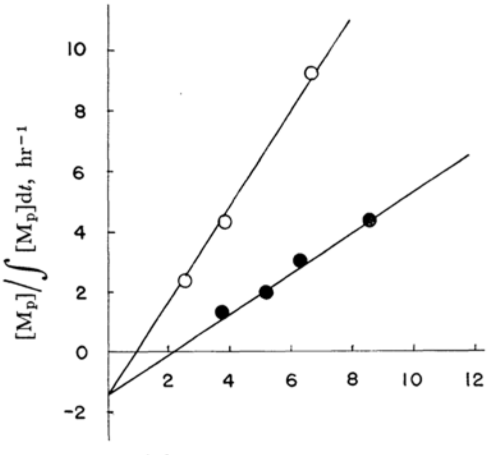
4. Termination:

$$R_n\cdot + Z \xrightarrow{k_t} P_n \qquad R_t = k_t[R\cdot][Z]$$

5. Transfer:

$$R_n\cdot + Y \xrightarrow{k_{tr}} P_n + Y \quad R_{tr} = k_{tr}[R\cdot][Y]$$

where M represents the ethylene monomer; $R_n\cdot$, an active polymer chain composed of n monomers; $[R\cdot]$, the total concentration of all the active poly mer chains, irrespective of size; M*, the excited monomer; M_2*, the excited dimer; Y, the substance with which the activity of the radical is transferred; Z, the substance by which the radical is deactivated; P_n, a dead polymer composed of n monomers; R_i, R_p, R_{tr} and R_t, the rates of initiation, propagation, transfer and termination; k_i, k_p, k_{tr} and k_t, the rate constants of these reactions; ρ_n, the density of ethylene; I, the dose rate; f_M, the fugacity of ethylene; $f_{M_2^*}$, the fugacity of the excited dimer, and K_e, the equilibrium constant of the 2nd step.



$t^2/\int[M_p]dt$, mol/l^{-1} hr

Fig. 4. $[M_p]/\int[M_p]dt$ *versus* $t^2/\int[M_p]dt$ in the ethylene polymerization induced by γ-ray in an agitated state: Reaction pressure, 400 kg/cm²; temperature, 30°C; dose rate, 3.8×10^5 rad/hr; volume of reaction vessel, 1000 m*l*.

○ With agitation
● Without agitation

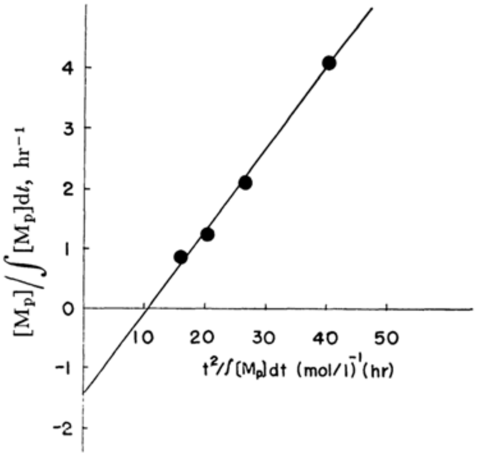


Fig. 5. $[M_p]/\int[M_p]dt$ *versus* $t^2/\int[M_p]dt$ in the ethylene polymerization induced by γ-ray in the presence of CO_2: Reaction pressure, 400 kg/cm²; temperature, 20°C; dose rate, 2.5×10^4 rad/hr; CO_2 molar ratio, 0.314.

Because $g(t)$ is equal to $k_i\rho_M It$, the rates of initiation and chain transfer were estimated by plotting $1/\bar{P}$ against $t/[M_p]$ according to Eq. (4-1). The rate of chain transfer was found to be negligible, because a straight line through the point of origin was obtained by the plot.

The equation for the estimations of k_p and k_t was derived in the same way;

$$\frac{[M_p]}{\int[M_p]dt} = \frac{1}{2}\cdot k_i k_p K_e \rho_M f_M{}^2 I t^2 \int[M_p]dt - k_t[Z]$$

The plots of $[M_p]/\int[M_p]dt$ against $t^2/\int[M_p]dt$ under various reaction conditions are shown in Figs. 4⁹⁾ and 5¹⁰⁾. From the intercept on the ordinate axis and the slope of the obtained straight line, the rate constants were evaluated.

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9) M. Hagiwara, S. Machi and T. Kagiya, unpublished data.

10) W. Kawakami, M. Hagiwara, Y. Hosaki, S. Machi and T. Kagiya, "The Influence of Agitation on the Gas Phase Ethylene Polymerization Induced by γ-Ray," in contribution to *Ind. Eng. Chem.*