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Graphical Evaluation of the Rate Constants of the Elementary Reactions in the Acrolein Polymerization with the Potassium Persulfate - Silver Nitrate Redox System

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A quantitative study was made of the redox-polymerization of acrolein initiated by the potassium persulfate - silver nitrate system. The reaction mechanism of this polymerization was proposed on the basis of the results of the time-conversion, time-molecular weight curves, and also on the basis of the characteristic features of this polymerization, reported in a previous paper. The rate constants of the elementary reactions in this polymerization were estimated by a graphical method. In the early stage, neither the termination nor the transfer reaction is very remarkable as the initiation reaction, but in the later stage the termination reaction by a recombination of the polymer radical and the transfer reaction increase with the reaction time, as does the initiation reaction also.

In a previous paper[1] on the acrolein polymerization with the potassium persulfate - silver nitrate system, it was reported that the polymerization may be classified as a non-stationary state with a slow initiation in both the early and later stages. This paper will attempt to evaluate the rate constants of elementary reactions on the basis of quantitative kinetic measurements and to discuss the mechanism of this polymerization.

Results and Discussion

The Reaction Mechanism. In the previous paper[1], the redox-polymerization of acrolein with a potassium persulfate - silver nitrate catalyst was classified from a kinetic point of view. This polymerization has the non-stationary state showing an accumulation of the propagating species in the early stage (until 0.5∼1.0 hr), and a consumption of the propagating species in the later stage. Moreover, this system is a polymerization with a slow initiation in both the early and later stages. Further, this system was found to show successive polymerization in the early stage, and chain polymerization in the later stage.

The following elementary reactions may, therefore, be assumed for the redox polymerization of acrolein on the basis of the experimental results reported in the previous paper[1] and the results of catalyst decomposition obtained by Bawn *et al.*[2] The respective rate expressions are also shown at the right.

1. Decomposition:

$$\mathrm{Ag^+ + \underset{(C)}{S_2O_8{}^{2-}} + OH^-} \xrightarrow{k_d}$$

$$\mathrm{SO_4{}^{2-} + \underset{(C^*)}{SO_4{}^{-}\cdot} + \underset{(C^*)}{HO\cdot} + Ag^+}$$

$$R_d = k_d[\mathrm{C}] \qquad (1)$$

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[1] T. Kagiya, S. Morita and K. Fukui, This Bulletin, **42**, 2578 (1969).

[2] C. E. H. Bawn and D. Margerison, *Trans. Faraday Soc.*, **51**, 925 (1955).

2. Initiation:

$$C^* + M \xrightarrow{k_i} \underset{(P_1^*)}{CM\cdot} \qquad R_i = k_i[C^*][M] \tag{2}$$

3. Propagation:

$$P_n^* + M \xrightarrow{k_p} P_{n+1}^* \qquad R_p = k_p[P^*][M] \tag{3}$$

4. Termination:

$$P_m^* + P_n^* \xrightarrow{k_t} P_{m+n},\ P_m + P_n$$

$$R_t = k_t[P^*]^2 \tag{4}$$

5. Transfer:

$$P_n^* + XY \xrightarrow{k_{tr}} P_nX + Y^*$$

$$R_{tr} = k_{tr}[P^*][XY] \tag{5}$$

where C represents the potassium persulfate; C*, an anion radical, $SO_4^-\cdot$, and an HO· radical; M, the acrolein monomer; P_n^*, an active polymer chain composed of n monomers; [P*], the total concentration of all the active polymer chains, irrespective of size ($\sum_{n=1}^{\infty}[P_n^*]$); P_n, a dead polymer composed of n monomers; XY, the substance to which the activity of P_n^* is transferred; R_d, R_i, R_p, R_t, and R_{tr} the rates of decomposition, initiation, propagation, termination and transfer, and k_d, k_i, k_p, k_t and k_{tr}, the rate constants of these reactions.

It was reported by Bawn *et al.* that the catalyzed decomposition of potassium persulfate in an aqueous solution by the Ag^+ ion occurs according to:

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^-\cdot + SO_4^{2-}$$

$$Ag^{2+} + OH^- \rightarrow Ag^+ + HO\cdot$$

the second step is very fast compared with the first step, which is the rate-determining step, so that the silver ion (Ag^+) concentration remains constant during the reaction. The rate constant of the decomposition reaction at 0°C was obtained as $k_d = 0.15\ l/\text{hr}$.

The following equations are derived from the elementary reactions described above, when the $SO_4^-\cdot$ and HO· have the same reactivity for initiation:

$$-d[C]/dt = k_d[C] \tag{6}$$

$$d[C^*]/dt = 2R_d - R_i = 2k_d[C] - k_i[C^*][M] \tag{7}$$

$$d[P^*]/dt = R_i - 2R_t = k_i[C^*][M] - 2k_t[P^*]^2 \tag{8}$$

Since the polymer formed has a high molecular weight, the overall rate of polymerization is approximately equal to the rate of propagation:

$$R = d[M_p]/dt \doteqdot R_p = k_p[P^*][M] \tag{9}$$

were R represents the overall polymerization rate, and $[M_p]$, the amount of monomer polymerized. By integrating Eq. (6), the concentration of potassium persulfate is expressed as a function of the reaction time:

$$[C] = [C]_0 e^{-k_d t} \tag{10}$$

were $[C]_0$ represents the concentration of potassium persulfate at a definite reaction time, 0. The rate-determining step of the initiation reaction is the decomposition reaction of the catalyst, as was pointed out in the previous paper[1]; accordingly, Eq. (7) becomes:

$$d[C^*]/dt = 2R_d - R_i = 0 \tag{11}$$

By integrating Eq. (11), and by considering Eq. (10), the sum of polymer chains produced by initiation, $\int R_i dt$, can be expressed by the following equation:

$$\int R_i dt = 2\alpha[C]_0(1 - e^{-k_d t}) \tag{12}$$

where α is an efficiency factor of the catalyst.

The Evaluation of the Rate of Elementary Reactions in the Early Stage. The rate constant of the elementary reaction proposed above was determined by means of a graphical method in the non-stationary polymerization.[3] [P*] is given by Eq. (8):

$$[P^*] = \int R_i dt - 2\int R_t dt \tag{13}$$

From the facts that the polymerization rate and the molecular weight of the polymer increase with the reaction time, the termination rate may be considered to be smaller than the initiation rate.

When R_t is zero, Eq. (13) becomes:

$$[P^*] = \int R_i dt = 2\alpha[C]_0(1 - e^{-k_d t}) \tag{14}$$

By a combination of Eqs. (9) and (14), the rate of polymerization is given as:

$$R_p = 2\alpha k_p[C]_0[M](1 - e^{-k_d t}) \tag{15}$$

In general, the number-average degree of polymerization at a given reaction time is defined by the following:

$$\bar{P} = \int R_p dt \Big/ \left(\int R_i dt + \int R_{tr} dt - \int R_t dt\right) \tag{16}$$

where $\bar{P}$ represents the number-average degree of polymerization. Since, in the early stage, the consumption of the monomer is very small and the value of $k_d t$ is smaller than unity, $\int R_p dt$ without termination and $\int R_i dt$ are given as follows by Eqs. (15) and (12) respectively:

$$\int R_p dt = [M_p] = \alpha k_d k_p [C]_0 [M]_0 t^2 \tag{17}$$

$$\int R_i dt = 2\alpha k_d [C]_0 t \tag{18}$$

If the transfer reaction to the monomer occurs, Eq. (19) is obtained:

$$\int R_{tr} dt = \int k_{tr}[P^*][M] dt = (k_{tr}/k_p)\int R_p dt \tag{19}$$

From a combination of Eqs. (16), (17), (18) and

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[3] T. Kagiya, M. Izu, S. Machi and K. Fukui, This Bulletin, **40**, 1049 (1967).

(19), Eq. (16) becomes:

$$1/\bar{P} = 2/(k_p[\mathrm{M}]_0 t) + k_{tr}/k_p \qquad (20)$$

The following evaluation of the rate constants of elementary reactions was made in the polymerization which was carried out under a monomer concentration of 2.68 mol/*l* and under a redox-pair concentration of 31.5 mmol/*l* (mol ratio 1 : 1). According to Eq. (20), $1/\bar{P}$ is plotted in Fig. 1 against $1/[\mathrm{M}]_0 t$ to give a straight line through the point of origin. This indicates either that the transfer and the termination reaction do not take place or that these reactions compensate each other in Eq. (16). In both cases, k_p was determined from the slope of the straight line in Fig. 1:

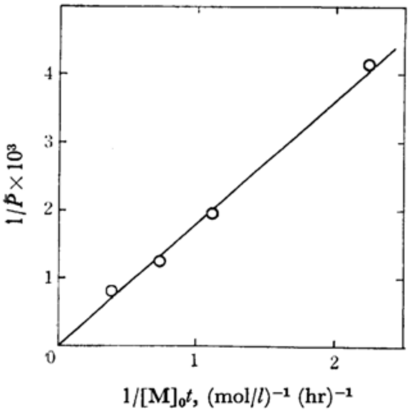

Fig. 1. Reciprocal of degree of polymerization *vs.* $1/[\mathrm{M}]_0 t$
T=0°C; $[K_2S_2O_8]_0=[AgNO_3]_0=31.5$ mmol/*l*; initial monomer concentration, 2.675 mol/*l*

$$k_p = 1.1 \times 10^3\ l/\mathrm{mol{\cdot}hr}.$$

As was reported in the previous paper,[1] it was found, from the results obtained using a two-stage polymerization method, that termination reactions occur both in the early and later stages. It may be concluded, therefore, that the termination reaction compensates the transfer reaction in the early stage.

Equation (21) is derived from Eq. (15):

$$R_p/[\mathrm{M}]=2\alpha k_p[\mathrm{C}]_0(1-\mathrm{e}^{-0.15t}) \qquad (21)$$

The plot of the $R_p/[\mathrm{M}]$ term against the value of $2[\mathrm{C}]_0(1-\mathrm{e}^{-0.15t})$ gives a straight line through the point of origin, as is shown in Fig. 2. From the slope of the line, $\alpha k_p=67.5$ *l*/mol·hr. Since the value of k_p was 1.1×10^3 *l*/mol·hr according to Eq. (20), as has been mentioned above, the efficiency factor of the catalyst is:

$$\alpha = 6.14\times 10^{-2}$$

The value of $\int R_i \mathrm{d}t$ is thus given by the following equation instead of by Eq. (12):

$$\int R_i \mathrm{d}t = 12.28\times 10^{-2}[\mathrm{C}]_0(1-\mathrm{e}^{-0.15t}) \qquad (22)$$

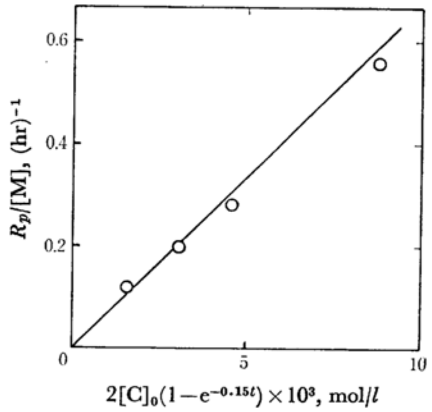

Fig. 2. $R_p/[\mathrm{M}]$ *vs.* $2[\mathrm{C}]_0(1-\mathrm{e}^{-0.15t})$
Reaction conditions are the same as shown in Fig. 1.

The Evaluation of the Rate of Elementary Reactions in the Later Stage. The quantitative evaluation of the rate of elementary reactions in the later stage was continued as follows.

As has been described before, both the transfer and termination reactions take place in this polymerization and compensate each other. When the second-order termination by the polymer radical takes place, the following equation can be derived by integrating Eq. (4):

$$\int R_t \mathrm{d}t = \int k_t[\mathrm{P}^*]^2 \mathrm{d}t = (k_t/k_p^2)\int (R_p^2/[\mathrm{M}]^2)\mathrm{d}t \qquad (23)$$

By combining Eqs. (9), (13), (22) and (23), Eq. (24) is derived:

$$\frac{R_p}{[\mathrm{M}]\int \frac{R_p^2}{[\mathrm{M}]^2}\mathrm{d}t} = \frac{4.25(1-\mathrm{e}^{-0.15t})}{\int \frac{R_p^2}{[\mathrm{M}]^2}\mathrm{d}t} - \frac{2k_t}{1.1\times 10^3} \qquad (24)$$

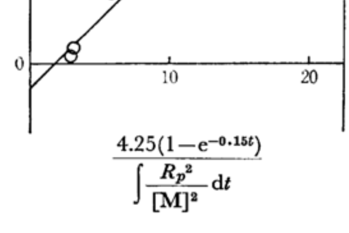

Fig. 3. $\frac{R_p}{[\mathrm{M}]\int \frac{R_p^2}{[\mathrm{M}]^2}\mathrm{d}t}$ *vs.* $\frac{4.25(1-\mathrm{e}^{-0.15t})}{\int \frac{R_p^2}{[\mathrm{M}]^2}\mathrm{d}t}$

Reaction conditions are the same as shown in Fig. 1.

By plotting the value of the left side against the first term on the right side in Eq. (24), a straight line with a slope of unity was obtained, as is shown in Fig. 3. From the value of the intercept of the ordinate axis, k_t was found to be 9.9×10^2 l/mol·hr.

Since the ratio of the consumption of the catalyst is 36% in a reaction period of three hours, it can be assumed that the concentration of the catalyst (potassium persulfate) remains almost constant for about three hours after the start of the polymerization. Eq. (25) can then be derived by combining Eqs. (7), (8) and (11);

$$\mathrm{d}[\mathrm{P}^*]/\mathrm{d}t = 2\alpha k_d[\mathrm{C}]_0 - 2k_t[\mathrm{P}^*]^2 \qquad (25)$$

The following equation is obtained by resolving the differential equation[4]:

$$[\mathrm{P}^*] = (\alpha k_d[\mathrm{C}]_0/k_t)^{1/2}\tanh\left[(4\alpha k_d k_t[\mathrm{C}]_0)^{1/2}t\right] \qquad (26)$$

By substituting the values of k_d, k_t, $[\mathrm{C}]_0$ and α obtained above into Eq. (26), $[\mathrm{P}^*]$ can be plotted against the reaction time as is shown in Fig. 4.

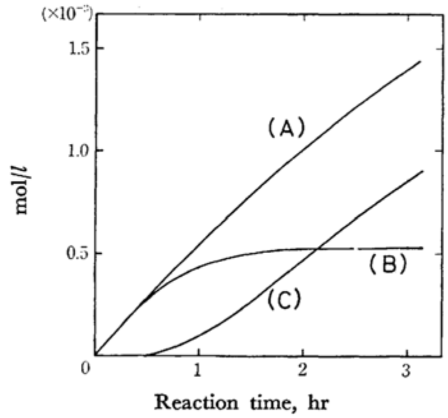

Fig. 4. $\int R_i\mathrm{d}t$, $[\mathrm{P}^*]$ and $2\int R_t\mathrm{d}t$ *vs.* reaction time.
(A), $\int R_i\mathrm{d}t$; (B), $[\mathrm{P}^*]$; (C), $2\int R_t\mathrm{d}t$
Reaction conditions are the same as shown in Fig. 1.

$\int R_i\mathrm{d}t$ [Eq. (22)] and $2\int R_t\mathrm{d}t$ $(=\int R_i\mathrm{d}t - [\mathrm{P}^*])$ are also plotted in the same figure, Fig. 4. When the consumption of the catalyst is negligible, it is found that $[\mathrm{P}^*]$ increases with the reaction time, therefore, the termination reaction becomes remarkable after thirty minutes. Since $[\mathrm{P}^*]$ decreases, however, with the reaction time after about three hours from the start of the polymerization, as was shown in the previous paper,[1] it must be considered in practice that the consumption of the catalyst is not negligible in the later period.

When the recombination between propagating species prevails in the termination, Eq.(27) is derived from Eq.(16):

$$1/\bar{P} = \left(\int R_i\mathrm{d}t - \int R_t\mathrm{d}t\right)\Big/\int R_p\mathrm{d}t + \int R_{tr}\mathrm{d}t\Big/\int R_p\mathrm{d}t \qquad (27)$$

In Eq.(27), when:

$$h(t) \equiv \int R_i\mathrm{d}t - \int R_t\mathrm{d}t \qquad (28)$$

the value of $h(t)$ can be calculated from Fig. 4, assuming that the termination reaction occurs by means of a recombination between propagating species. When a chain transfer to XY (chain-transfer reagent) takes place with a constant concentration,

$$\int R_{tr}\mathrm{d}t = k_{tr}[\mathrm{XY}]\int[\mathrm{P}^*]\mathrm{d}t = (k_{tr}[\mathrm{XY}]/k_p)\int\frac{R_p}{[\mathrm{M}]}\,\mathrm{d}t \qquad (29)$$

By a combination of Eqs. (27), (28) and (29), the following equation is derived:

$$\frac{[\mathrm{M}_p]}{\bar{P}\int\frac{R_p}{[\mathrm{M}]}\mathrm{d}t} = \frac{h(t)}{\int\frac{R_p}{[\mathrm{M}]}\mathrm{d}t} + \frac{k_{tr}[\mathrm{XY}]}{k_p} \qquad (30)$$

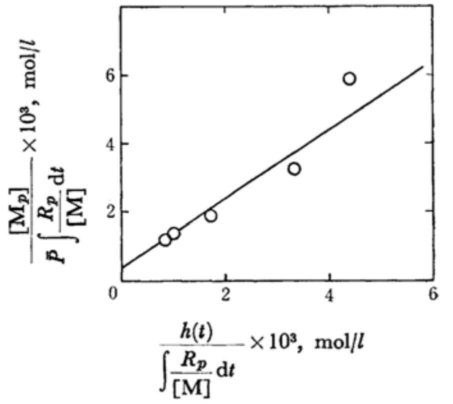

Fig. 5. $\frac{[\mathrm{M}_p]}{\bar{P}\int\frac{R_p}{[\mathrm{M}]}\mathrm{d}t}$ *vs.* $\frac{h(t)}{\int\frac{R_p}{[\mathrm{M}]}\mathrm{d}t}$
Reaction conditions are the same as shown in Fig. 1.

The left side is plotted in Fig. 5 against the first term on the right side to give a straight line with the slope of unity. From the intercept on the ordinate axis, $k_{tr}[\mathrm{XY}]/k_p$ can be obtained. By substituting the k_p value obtained before into $k_{tr}[\mathrm{XY}]/k_p$, $k_{tr}[\mathrm{XY}]$ is obtained as 0.44 $(\mathrm{hr})^{-1}$.

The rate equations and the rate constants of the elementary reactions obtained above are summarized in Table 1.

Comparison of Experimental Results with Theoretical Results. The experimental results on both the polymer yield and the degree of polymerization were compared with the equations which had been theoretically derived from the proposed elementary reactions.

The following relationship on the polymer yield is derived from combining Eqs.(9) and (26):

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[4] M. Magat, *J. Polymer Sci.*, **16**, 491 (1955).

TABLE I. THE RATE EQUATIONS AND THE RATE CONSTANTS OF THE ELEMENTARY REACTIONS

Elementary reaction		Rate equation	Rate constant
Decomposition	$Ag^+ + S_2O_8^{2-} + OH^- \rightarrow$ $SO_4^{2-} + SO_4^{-}\cdot + HO\cdot + Ag^+$	$R_d = k_d[C]$	$k_d = 0.15$ (1/hr)
Initiation	$C^* + M \rightarrow P_1^*$	$R_i = k_i[C^*][M]$	$\int R_i dt = 2\alpha[C]_0(1-e^{-k_d t})$ (mol/l)
Propagation	$P_n^* + M \rightarrow P_{n+1}^*$	$R_p = k_p[P^*][M]$	$k_p = 1.1\times10^3$ (l/mol·hr)
Transfer	$P_n^* + XY \rightarrow P_nX + Y^*$	$R_{tr} = k_{tr}[P^*][XY]$	$k_{tr}[XY] = 0.44$ (l/mol·hr)
Termination	$P_m^* + P_n^* \rightarrow P_{m+n}$	$R_t = k_t[P^*]^2$	$k_t = 9.9\times10^2$ (l/mol·hr)

$$[M_p] = \int k_p(\alpha k_d[C]_0/k_t)^{1/2} \tanh [(4\alpha k_d k_t[C]_0)^{1/2}t][M]dt \tag{31}$$

By substituting various constants, and by graphically integrating with the reaction time, the theoretical value of $[M_p]$ is plotted against the time, and compared with the empirical data, in Fig. 6. A good agreement between observation and theory is observed.

On the other hand, when termination takes place by a recombination of polymer radicals, the following equation can be derived:

$$\bar{P} = \int R_p dt \Big/ \left(\int R_i dt + \int R_{tr} dt - \int R_t dt\right) \tag{16}$$

By substituting Eqs. (31), (12), (29) and (23) into Eq. (16) and by assuming that the [XY] is constant, the following equation is obtained.

The values of each term at various reaction times in Eqs. (32) and (33) are listed in Table 2. Table 2 shows that, in the early stage, both the termination

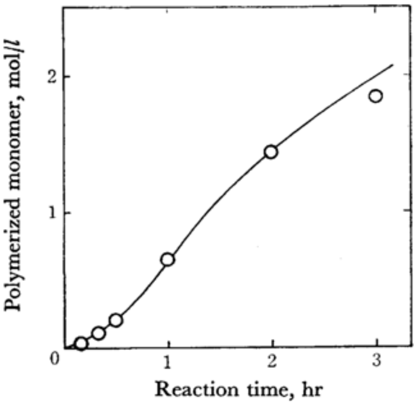

Fig. 6. The amount of polymerized monomer *vs.* reaction time.
(○), experimental data
(—), theoretical curve
Reaction conditions are the same as shown in Fig. 1.

$$\begin{aligned}\bar{P} &= \frac{\int k_p[P^*][M]dt}{2\alpha[C]_0(1-e^{-k_d t}) + k_{tr}[XY]\int [P^*]dt - k_t\int [P^*]^2 dt} \\ &= \frac{(\alpha k_d k_p^2[C]_0/k_t)^{1/2}\int \tanh [(4\alpha k_d k_t[C]_0)^{1/2}t][M]dt}{2\alpha[C]_0(1-e^{-k_d t}) + (k_{tr}[XY]/2k_t)\ln\cosh [(4\alpha k_d k_t[C]_0)^{1/2}t] - \alpha k_d[C]_0 t + (\alpha k_d[C]_0/4k_t)^{1/2}\tanh [(4\alpha k_d k_t[C]_0)^{1/2}t]} \\ &= \frac{595\int \tanh (1.07t)[M]dt}{38.7(1-e^{-0.15t}) + 5.13\log\cosh (1.07t) - 2.9t + 2.71\tanh (1.07t)} \qquad (32) \\ &= \frac{[M_p]\times10^4}{38.7(1-e^{-0.15t}) + 5.13\log\cosh (1.07t) - 2.9t + 2.71\tanh (1.07t)} \qquad (33)\end{aligned}$$

TABLE 2. VARIATION OF $\int R_i dt$, $\int R_{tr} dt$, $\int R_t dt$ AND THE POLYMER YIELD WITH THE REACTION TIME

Reaction time hr	Initiation reaction $\int R_i dt\times10^4$ mol/l	Transfer reaction $\int R_{tr} dt\times10^4$ mol/l	Termination reaction $\int R_t dt\times10^4$ mol/l	Polymer yield mol/l	
	$38.7(1-e^{-0.15t})$	$5.13\log\cosh (1.07t)$	$2.9t-2.71\tanh (1.07t)$	$[M_p]$	$0.595\int \tanh (1.07t)[M]dt$
0.167	0.953	0.035	0.006	0.040	0.022
0.333	1.88	0.139	0.041	0.111	0.086
0.50	2.79	0.304	0.127	0.212	0.193
1.0	5.38	1.09	0.765	0.66	0.625
2.0	10.0	3.25	3.17	1.44	1.46
3.0	14.0	5.60	6.00	1.84	2.06

Reaction conditions are the same as Fig. 1.

and transfer reactions are very small compared with the initiation reaction and that they compensate each other in both the early and later stages. Therefore, in order to evaluate the propagation rate, it is adequate to adopt the method described above, using $R_t = R_{tr} = 0$.

The empirical data is shown in Fig. 7 to agree with the theoretically-derived value. The deviation of the theoretical value in Eq.(32) from the experimental data in the later period is due to the consumption of the catalyst.

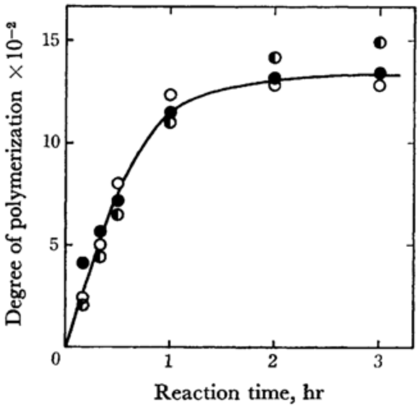

Fig. 7. Degree of polymerization *vs.* reaction time.
(○), experimental data
(◐), theoretical value obtained from Eq. (32)
(●), theoretical value obtained from Eq. (33)
Reaction conditions are the same as shown in Fig. 1.

The values of $k_{tr}[XY]$ in the polymerization at various monomer and catalyst concentrations are summarized in Table 3. The value of $k_{tr}[XY]$ decreases with the initial monomer concentration, independently of the potassium persulfate concentration. The mechanism of the chain-transfer reaction is not clear, but it may be ascribed to impurities in water. The fact that the value of $k_{tr}[XY]$ decreases remarkably with the initial monomer concentration suggests that the activity of XY is markedly decreased by the formation of the polymer.

TABLE 3. THE VALUE OF $k_{tr}[XY]$

Initial monomer concentration (mol/*l*)	$k_{tr}[XY]$ (hr)$^{-1}$
0.449	7.7
1.230[a]	3.0
1.486	2.0
2.272	0.5

Reaction condition: $T = 0°C$,
$[AgNO_3]_0 = [K_2S_2O_8]_0 = 31.5$ mmol/*l*
a) $[K_2S_2O_8]_0 = 15.75$ mmol/*l*

In the view of the fact that the experimental results on both the polymer yield and the degree of polymerization under several reaction conditions coincide with the equation theoretically derived, the proposed elementary reactions and the rate constants evaluated in the non-stationary-state polymerization may be accepted.