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The Effects of the Temperature on the γ-Radiation-Induced Polymerization of Ethylene*

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The gamma-radiation-induced polymerization of ethylene was carried out/over the wide range of temperature from 30 to 200°C at pressure ranging from 100 to 400 kg./cm^2 and at dose rates from 2×10^3 to 4×10^5 rad./hr. It was shown that the rate of polymerization is rapidly accelerated at 30°C, that the degree of acceleration decreases with an increase in the reaction temperature, and that above 100°C the rate is independent of the time. It was correspondingly shown that the molecular weight of the polymer increases with the reaction time, at 30°C, that its increment for a unit of time decreases with an increase in the temperature, and that the molecular weight is independent of the time above 100°C. By means of a kinetical discussion it was concluded that the rate of the termination reaction, which is almost eliminated at 30°C, increases with the temperature and attains a value comparable to that of initiation above 100°C. The dose rate exponents of the polymerization rate and molecular weight were shown to vary with the reaction temperature. Namely, the exponents were evaluated as 0.9 and 0 at 30°C, 0.8 and -0.1 at 100°C, and 0.7 and -0.2 at 140 and 200°C, for the polymerization rate and the molecular weight respectively. It was assumed from these high exponents that the termination may occur above 100°C in a first-order reaction to a considerable extent. Under a constant pressure, the polymer yield was shown to decrease with the temperature from 30 to 60—80°C, and then to increase at high temperatures from 80 to 200°C. On the other hand, the molecular weight of the polymer simply decreases with the temperature from 30 to 200°C. The chain transfer reaction is considered to be almost negligible at 30—70°C. The number of polymer chains for a constant reaction time and monomer concentration is independent of the temperature from 30 to 70°C, while it increases with the temperature from 70 to 200°C. The effects of pressure on the polymer yield and molecular weight were also investigated at 140°C.

In previous papers[1,2] the γ-radiation-induced bulk polymerization of ethylene at normal temperatures was characterized by a steady increase in the polymerization rate and in the molecular weight of polymer with the reaction time. From the kinetic study,[2] the existence of a long-lived radical has been suggested; this has been confirmed by the results of the experiments of the two-stage irradiation method.[3] On the other hand, it was recently shown that the phenomena of the rate acceleration and the increase in the molecular weight with the time vanish, and that the molecular weight is considerably lowered at high reaction temperatures, as has previously been reported briefly.[4] This paper attempts to elucidate the specific influences of the reaction temperature on the γ-radiation-induced polymerization of ethylene in bulk.

Experimental

The reaction vessel, the irradiation facilities, and the experimental procedures are the same as have been reported in a previous paper.[2] The ethylene used was commercially available and 99.9% pure (free of CO and H_2S), containing 21 p. p. m. of acetylene and 0.3 p. p. m. of oxygen. Polymerizations were carried out to low conversion in order to maintain the pressure essentially constant, and the temperature was constant within ±1°C for the duration of the experiment.

Results and Discussion

The Effect of the Temperature on Chain Termination.—A marked acceleration in rate and an increase in the number-average molecular weight with the reaction time have been reported in the γ-radiation-induced polymerization of ethylene at normal temperatures.[1,2] On the other hand, in the polymerization at high temperatures (above 100°C), no increase in the polymerization rate and molecular weight were observed, as has already been reported briefly.[4]

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

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

[3] S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, **A3**, 2931 (1965).

[4] S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, ibid., **A3**, 3029 (1965).

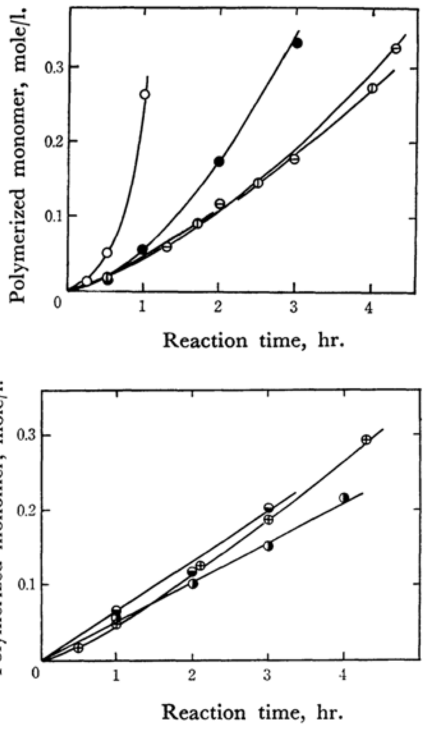

Fig. 1a.

Fig. 1b.

Fig. 1. The amount of polymerized monomer vs. reaction time at various reaction temperatures. (Reaction pressure, 400 kg./cm^2; dose rate, 2.5 $\times 10^4$ rad./hr.; reaction temperature, 30 (○), 58 (●), 62 (⊖), 70 (⦶), 86 (⊕), 100 (◑), 140°C (◒))

The results of the experiments which were carried out at various reaction temperatures from 30 to 200°C, at a dose rate of 2.5×10^4 rad./hr. and at a pressure of 400 kg./cm^2, are summarized in Table I. Figures 1a and 1b show the relation between the amount of the polymerized monomer (i. e., the polymer yield) and the reaction time. They show that the amount of the polymerized monomer increases rapidly with the time at lower temperatures and less rapidly at higher temperatures. In order to show the time dependency of the amount of the polymerized monomer, it is plotted on a logarithmic scale in Fig. 2. The slopes of the line are the time exponents of the polymer yield, which are listed in Table II. It is found that the time exponent at 30°C is 2.1 and that it decreases with the increase in the temperature to unity at temperatures of 100°C and above. In other words, the rate of polymerization increases almost proportionally with the time at 30°C, the increase in the rate for unit time becomes less with an increase in the temperature, and finally the rate becomes independent of the time. Namely, the rate acceleration is observed at 30 to 86°C, its degree decreases with the temperature, and it is not observed at 100 and 140°C.

TABLE I. EFFECTS OF REACTION TEMPERATURE ON POLYMER YIELD AND MOLECULAR WEIGHT

Reaction temp. °C	Reaction time hr.	Polymer yield g.	Molecular weight $\overline{M}_n$ $\times 10^{-4}$
30	0.26	0.03	7.0
	0.53	0.14	14.7
	1.0	0.74	26.6
58	0.50	0.05	6.5
	1.0	0.16	11.5
	2.0	0.49	17.5
	3.0	0.93	23.0
62	0.50	0.05	4.7
	1.3	0.17	7.6
	2.0	0.33	9.9
	3.0	0.50	11.3
	4.3	0.91	14.0
70	0.50	0.06	4.3
	1.7	0.25	6.0
	2.5	0.41	7.4
	4.0	0.76	9.0
86	0.50	0.05	2.4
	1.0	0.14	3.1
	2.1	0.35	3.5
	3.0	0.52	3.6
	4.3	0.82	3.8
100	1.0	0.16	1.8
	2.0	0.28	1.9
	3.0	0.43	2.0
	4.0	0.60	2.1
120	2.0	0.34	1.9
140	1.0	0.18	1.3
	2.0	0.33	1.2
	3.0	0.58	1.2
160	2.0	0.42	0.99
180	2.0	0.54	0.83
200	2.0	0.70	0.64

Reaction pressure, 400±5 kg./cm^2; dose rate, 2.5 $\times 10^4$ rad./hr.; volume of reaction vessel, 100 ml.

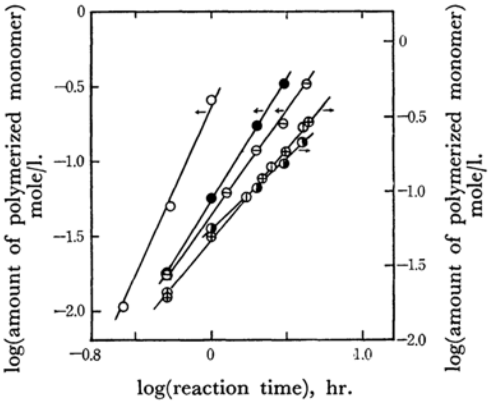

Fig. 2. Relation between the amount of polymerized monomer and reaction time shown in logarithmic scale at various temperatures.
(Notes and reaction conditions are the same as shown in Fig. 1.)

Table II. Time exponent of polymer yield at various reaction temperatures

Reaction temp. °C	Time exponent of polymer yield
30	2.1
58	1.7
62	1.4
70	1.2
86	1.2
100	1.0

Reaction pressure, 400±5 kg./cm^2; dose rate, 2.5 ×10^4 rad./hr.

The effect of the reaction temperature on the increase in the molecular weight with the reaction time is shown in Fig. 3. The molecular weight of polymer formed at 30°C is shown to be proportional to the time. This feature, together with the rate acceleration, have been explained[2)] on the assumption that the termination and transfer do not take place to any appreciable extent. It has been also suggested that the life of the polymer radical is long and that the accumulation of polymer radicals causes the rate acceleration. In the polymerization from 58 to 86°C, it is observed that the molecular weight increases with the time and that the increment for the unit of time decreases with a rise in the temperature. This corresponds to the above fact, i. e., the degree of rate acceleration decreases with temperature. These corresponding facts may indicate that the rate of chain termination increases with rise in the temperature, the average life-time of the polymer radical, therefore, becomes shorter, and the extent of radical accumulation decreases.

Above 100°C the polymerization rate and molecular weight are shown to remain constant, independently of the reaction time, in Figs. 1b and 3. This suggests that the rate of the termination becomes comparable to that of the initiation. The life of the radical is not long, but normal, and the stationary state is realized.

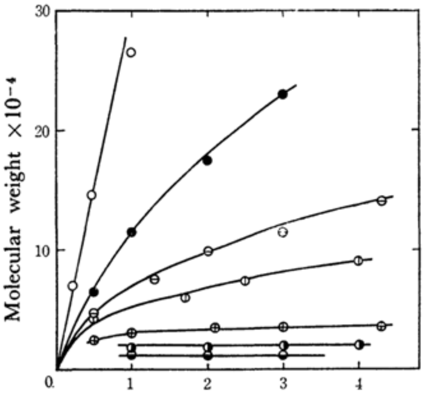

Fig. 3. Molecular weight vs. reaction time at various temperatures. (Notes and reaction conditions are the same as shown in Fig. 1.)

The Order of the Termination Reaction.—In order to elucidate the termination reaction, the dependence of the polymerization rate and the molecular weight on the irradiation dose rate was investigated at various temperatures from 30 to 200°C, the results are summarized in Table III. The rate and the molecular weight are plotted on logarithmic scales against the dose in Figs. 4 and

Table III. Effects of dose rate on polymer yield and molecular weight at various temperatures

Reaction temp. °C	Dose rate rad./hr. ×10^{-4}	Reaction time hr.	Polymer yield g.	Molecular weight $\overline{M}_n$ ×10^{-4}
30	39	0.33	0.73	7.8
	15	0.50	0.63	9.7
	6.3	0.55	0.38	13.2
	0.73	2.0	0.70	42.5
100	39	0.50	0.61	1.2
	15	1.0	0.56	1.2
	6.3	2.0	0.54	1.4
	1.0	5.0	0.37	2.0
	0.50	6.0	0.26	2.2
140	15	1.0	0.56	0.9
	6.3	2.0	0.65	1.0
	1.0	4.1	0.35	1.3
	0.50	5.0	0.27	1.4
	0.19	6.6	0.19	1.9
200	39	0.50	1.15	0.45
	15	1.0	0.90	0.46
	6.3	1.0	0.65	0.47
	1.0	4.0	0.59	0.64
	0.50	6.0	0.62	0.70

Reaction pressure, 400±5 kg./cm^2; volume of reaction vessel, 100 ml. Data for dose rate of 2.5 ×10^4 rad./hr. are listed in Table I.

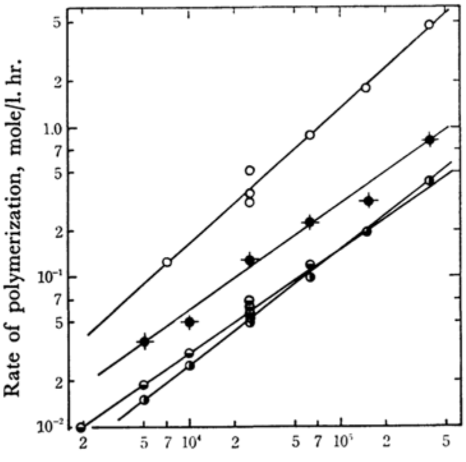

Fig. 4. Effect of dose rate on the rate of polymerization at various temperatures.
(Reaction pressure, 400 kg./cm^2; reaction temperature, 30 (○), 100 (◑), 140 (◒), 200°C (◆))

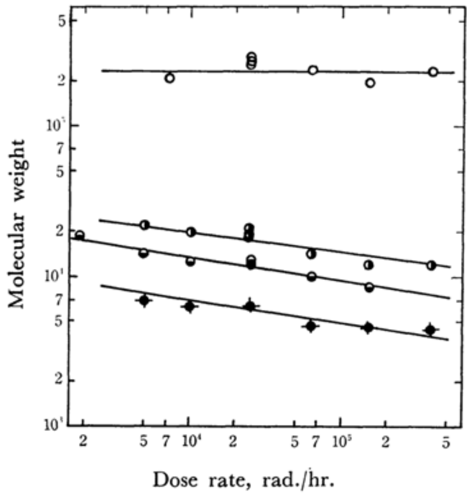

Fig. 5. Effect of dose rate on the molecular weight at various temperatures.
(Notes and reaction conditions are the same as shown in Fig. 4.)

5 respectively. Here, since the rate and the molecular weight increase with the time at 30°C, the data in these figures have been normalized to a fixed reaction time of one hour. The dose rate exponents of the rate and the molecular weight evaluated from the slope of these lines are shown in Table IV. The dose rate exponents for both the rate and the molecular weight are shown to decrease with a rise in the temperature from 30 to 140°C; they remain constant at temperatures from 140 to 200°C.

TABLE IV. DOSE RATE EXPONENTS OF POLYMERIZATION RATE AND MOLECULAR WEIGHT AT VARIOUS TEMPERATURES

Reaction temp., °C	Dose rate exponent of rate	Dose rate exponent of molecular weight
30	0.9	0.0
100	0.8	−0.1
140	0.7	−0.2
200	0.7	−0.2

Reaction conditions are the same as shown in Table III.

It has already been shown in a previous paper[2)] that the exponents at 30°C of 0.9 (approximately unity) for the rate and 0 for the molecular weight coincide with the reaction scheme at normal temperatures; i. e., we may assume no termination reaction. The exponents for the polymerization above 100°C (i. e., 0.8 and 0.7 for the rate, and −0.1 and −0.2 for the molecular weight) are higher than the common exponents of 0.5 and −0.5 for the rate and molecular weight in the case of second-order termination with respect to the polymer radical. These high exponents may indicate that first-order termination with respect to the polymer radical is predominant. The first-order termination is assumed to be brought about by a reaction between the polymer radical and the radical of a low molecular weight which has little effect on the molecular weight of high polymers.

The fact that these exponents decrease with a rise in the temperature indicates that the contribution of the second-order termination, i. e., the mutual termination of the polymer radicals, increases with the temperature from 100 to 200°C.

The Evaluation of the Rate of Termination.—The rates of termination at various temperatures from 58 to 76°C are evaluated by means of the analysis[5)] of the data on the polymer yield on the basis of the following elementary reactions, which have been proposed[2)] for the γ-radiation-induced polymerization of ethylene in bulk:

1. Initiation

$$\mathrm{M} \xrightarrow{k_i} \mathrm{R}_1 \qquad R_i = k_i \rho_{\mathrm{M}} I \tag{1}$$

2. Ethylene excitation and dimerization

$$\begin{gathered}\mathrm{M} \rightleftarrows \mathrm{M}^* \\ \mathrm{M} + \mathrm{M} \overset{K_e}{\rightleftarrows} \mathrm{M}_2{}^* \end{gathered} \qquad f_{\mathrm{M}_2{}^*} = K_e f_{\mathrm{M}}^2 \tag{2}$$

3. Propagation

$$\begin{gathered}\mathrm{R}_1\cdot + \mathrm{M}_2{}^* \xrightarrow{k_p} \mathrm{R}_3\cdot \\ \cdots\cdots\cdots\cdots\cdots\cdots \qquad R_p = k_p[\mathrm{R}\cdot] f_{\mathrm{M}_2{}^*} \\ \mathrm{R}_{n-2}\cdot + \mathrm{M}_2{}^* \xrightarrow{k_p} \mathrm{R}_n\cdot \end{gathered} \tag{3}$$

4. Termination

$$\begin{gathered}\mathrm{R}_n\cdot + \mathrm{Z} \xrightarrow{k_{t1}} \mathrm{P}_n \qquad R_t = k_{t_1}[\mathrm{R}\cdot][\mathrm{Z}] + \\ \mathrm{R}_m\cdot + \mathrm{R}_n\cdot \xrightarrow{k_{t2}} \mathrm{P}_{m+n} \qquad k_{t_2}[\mathrm{R}\cdot]^2 \end{gathered} \tag{4}$$

5. Transfer

$$\begin{gathered}\mathrm{R}_n\cdot + \mathrm{Y} \xrightarrow{k_{tr}} \mathrm{P}_n + \mathrm{Y}\cdot \\ R_{tr} = k_{tr}[\mathrm{R}\cdot][\mathrm{Y}] \end{gathered} \tag{5}$$

where M represents the ethylene monomer; $\mathrm{R}_n\cdot$, an active polymer chain composed of n monomers; [R·] total concentration of all active polymer chains irrespective of size; M*, the excited monomer; $\mathrm{M}_2{}^*$ 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, the 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_{M} the density of ethylene; I, the dose rate; f_{M}, the fugacity of ethylene; $f_{\mathrm{M}_2{}^*}$, the fugacity of the excited dimer, and K_e the equilibrium constant of the 2nd step.

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5) T. Kagiya, M. Izu, S. Machi and K. Fukui, paper presented at the 14th Polymer Symposium, Kyoto, October, 1965.

The rate of polymerization, R, is written:

$$R = k_p K_e [\mathrm{R}\cdot] f_{\mathrm{M}}^2 \qquad (6)$$

where R represents the overall polymerization rate. $[\mathrm{R}\cdot]$ is given in the non-stationary state;

$$[\mathrm{R}\cdot] = \int R_i \mathrm{d}t - \int R_t \mathrm{d}t \qquad (7)$$

Since no second-order termination in the polymer radical takes place below 100°C, Eq. 7 is:

$$[\mathrm{R}\cdot] = \int k_i \rho_{\mathrm{M}} I \mathrm{d}t - \int k_{t_1} [\mathrm{R}\cdot][\mathrm{Z}] \mathrm{d}t \qquad (8)$$

Here, $[\mathrm{R}\cdot]$ on the right side being replaced by Eq. 6,

$$[\mathrm{R}\cdot] = k_i \rho_{\mathrm{M}} I t - (k_{t_1}[\mathrm{Z}]/k_p K_e f_{\mathrm{M}}^2)\cdot \int R \mathrm{d}t \qquad (9)$$

where $\int R \mathrm{d}t$ corresponds to the amount of the polymerized monomer, M_p. By substituting $[\mathrm{R}\cdot]$ in Eq. 6 with Eq. 9, R is written:

$$R = k_i k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 I t - k_{t_1}[\mathrm{Z}] M_p \qquad (10)$$

By integrating Eq. 10 with time,

$$\int R \mathrm{d}t = M_p = (1/2)\cdot k_t k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 I t^2 - k_{t_1}[\mathrm{Z}] \int M_p \mathrm{d}t \qquad (11)$$

$$M_p / \int M_p \mathrm{d}t = (1/2)\cdot k_i k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 I t^2 / \int M_p \mathrm{d}t - k_{t_1}[\mathrm{Z}] \qquad (12)$$

According to Eq. 12, $(M_p/\int M_p \mathrm{d}t)$ is plotted in Fig. 6 against $(t^2/\int M_p \mathrm{d}t)$, where $\int M_p \mathrm{d}t$ is calculated from Fig. 1 by a graphical method. The values of $k_{t_1}[\mathrm{Z}]$, i. e., the rate of termination, are determined from the intercept on the axis of $M_p/\int M_p \mathrm{d}t$; they are summarized in Table V. The rate of termination is shown to increase with the reaction temperature.

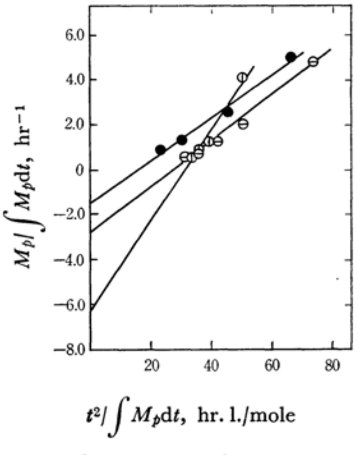

Fig. 6. $M_p/\int M_p \mathrm{d}t$ vs. $t^2/\int M_p \mathrm{d}t$.
(Notes and reaction conditions are the same as shown in Fig. 1.)

TABLE V. RATE OF CHAIN TERMINATION AT VARIOUS TEMPERATURES

Reaction temp. °C	Rate of termination $k_{t_1}[\mathrm{Z}]$ hr^{-1}
58	1.5
62	2.8
70	6.1

Reaction pressure, 400±5 kg./cm²; dose rate, 2.5 ×10⁴ rad./hr.

The Effects of the Temperature on the Polymer Yield and the Molecular Weight.—As is shown in Figs. 1 and 3, the effects of the temperature on the polymer yield and molecular weight are complicated because of their time dependency. Figure 7 shows how the polymer yield at the reaction times of 0.5 and 2.0 hr. varies with reaction temperature. It is shown that the polymer yield decreases rapidly with the temperature from 30 to 60°C, remains almost constant from 60 to 80—100°C, and increases in the higher temperature region (to 200°C). Figure 8 indicates that the molecular weight of the polymer formed at 0.5 and 2.0 hr. under the constant pressure of 400 kg./cm² simply decreases with a rise in the reaction temperature, and that it is very sensitive to the temperature from 30 to 100°C. The effect is shown to become larger as the polymerization proceeds.

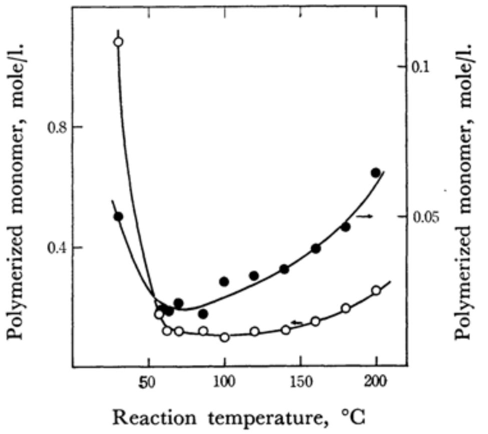

Fig. 7. Effect of reaction temperature on the amount of polymerized monomer.
(Reaction pressure, 400 kg./cm²; dose rate, 2.5 ×10⁴ rad./hr.; reaction time, 0.5 (●), 2.0 hr. (○). Data at 100, 200°C for 0.5 hr., and 62, 70°C for 2.0 hr. are calculated from those at other reaction time.)

The Effects of the Temperature on Chain Initiation and Transfer.—The number-average

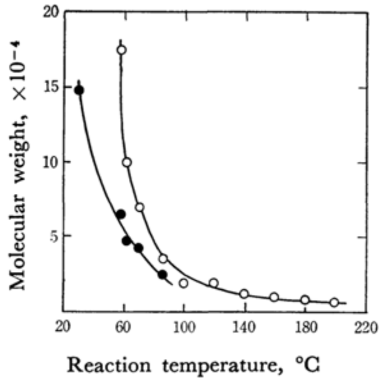

Fig. 8. Effect of reaction temperature on the molecular weight.
(Notes and reaction conditions are the same as shown in Fig. 7. Data at 62, 70°C. for 2.0 hr. are calculated from those at other reaction time.)

degree of polymerization at a given reaction time is written for the polymerization in the non-stationary state, assuming no termination by the recombination of polymer radicals, which is almost realized below 100°C:

$$1/\overline{DP}_n = \int R_i \mathrm{d}t / \int R_p \mathrm{d}t + \int R_{tr} \mathrm{d}t / \int R_p \mathrm{d}t \qquad (13)$$

where $\overline{DP}_n$ represents the number-average degree of polymerization. From the above reaction scheme, Eq. 13 is, then,

$$1/\overline{DP}_n = k_i \rho_{\mathrm{M}} I(t/M_p) + (k_{tr}/k_p)[\mathrm{Y}]/K_e f_{\mathrm{M}}^2 \qquad (14)$$

According to Eq. 14, $1/\overline{DP}_n$ is plotted in Fig. 9 against t/M_p to give an almost linear relation. The fact that the lines in Fig. 9 pass through the point of origin indicates that the transfer reaction does not take place at temperatures from 30 to 70°C.

The relation between the number of moles of polymer chains (N_p) for a unit of ethylene concentration and the reaction time is shown in Fig. 10, where N_p is evaluated as the ratio of the amount of the polymerized monomer to the number-average molecular wight of the polymer, i. e., $M_p/\overline{M}_n$. It is observed that N_p/ρ_{M} (i. e., the number of moles of polymer chains formed divided by the concentration of ethylene) increases almost proportionally with the time at the respective temperatures because of successive initiation by continuous radiation. The number of moles of polymer chains formed per unit of reaction time (i. e., N_p/t, the rate of the increase in number of polymer chains) is shown in Table VI and Fig. 11 for various reaction temperatures. It is shown

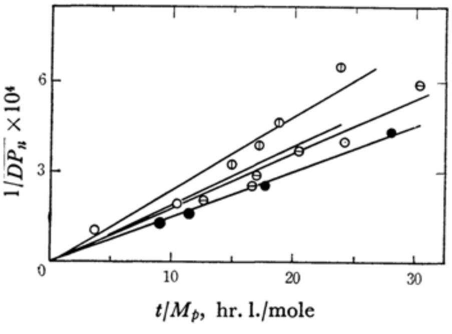

Fig. 9. $1/\overline{DP_n}$ vs. t/M_p.
(Notes and reaction conditions are the same as shown in Fig. 1.)

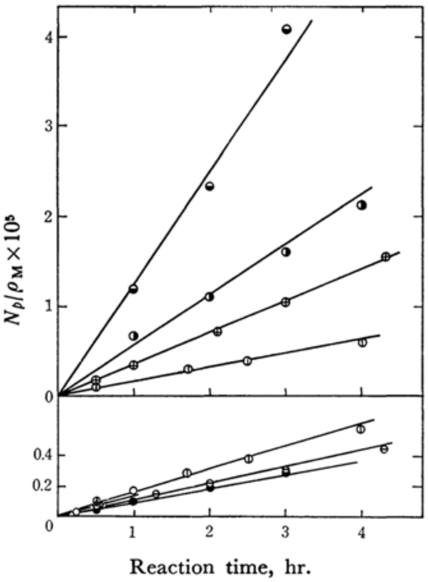

Fig. 10. Number of moles of polymer chains per unit ethylene concentration vs. reaction time at various temperatures.
(Notes and reaction conditions are the same as shown in Fig. 1.)

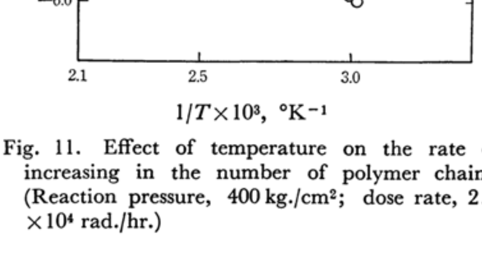

Fig. 11. Effect of temperature on the rate of increasing in the number of polymer chains.
(Reaction pressure, 400 kg./cm²; dose rate, 2.5 ×10⁴ rad./hr.)

TABLE VI. EFFECT OF REACTION TEMPERATURE ON THE RATE OF INCREASING IN THE NUMBER OF MOLES OF POLYMER CHAINS

Reaction temp. °C	$N_p/\rho_M t$ hr^{-1} $\times 10^5$
30	0.13
58	0.10
62	0.11
70	0.16
86	0.33
100	0.57
120	0.71
140	1.23
160	1.92
180	3.10
200	5.55

Reaction pressure, 400±5 kg./cm^2; dose rate, 2.5×10^4 rad./hr.

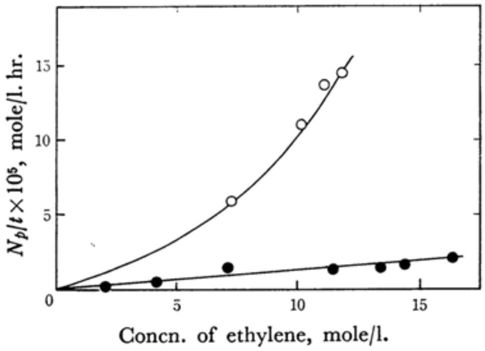

Fig. 12. N_p/t vs. concentration of ethylene. (Reaction temperature, 30 (●), 140°C (○); dose rate, 2.5×10^4 rad./hr.)

that N_p/t is almost independent of the temperature from 30 to 70°C, where the chain transfer does not take place. The rate of initiation is, therefore, known to be independent from the temperature of this range. On the other hand, the higher temperature range, N_p/t is shown to increase with the temperature and an apparent activation energy of about 8 kcal./mole was observed. It is also noted that the polymer yield increases with the temperature over the same range (shown in Fig. 7). Since no evidence for the absence of chain transfer is given in this temperature range, the activation energy may be ascribed not only to the initiation reaction but also to the transfer reaction.

TABLE VII. EFFECTS OF REACTION PRESSURE ON POLYMER YIELD AND MOLECULAR WEIGHT AT 140°C

Ethylene Pres. kg./cm^2	Fugacity kg./cm^2	Concn. mol./l.	Reaction time hr.	Polymer yield g.	Molecular weight $\overline{M}_n$ $\times10^{-4}$
100	80	3.4	46.1	0.25	—
200	144	7.3	6.0	0.23	0.66
300	200	10.1	2.0	0.22	0.99
350	228	11.1	2.0	0.33	1.2
400	261	11.8	listed in Table I		

Dose rate, 2.5×10^4 rad./hr.; volume of reaction vessel, 100 ml.

The Effect of the Pressure on the Polymer Yield and the Molecular Weight at 140°C.—The results of experiments where ethylene pressure varies from 100 to 400 kg./cm^2 are summarized in Table VII. It is shown that the amount of polymerized monomers and the molecular weight per unit of reaction time increase with the ethylene pressure. The number of moles of polymer chains per unit of time is plotted in Fig. 12 against the concentration of ethylene for the polymerization at 140 and 30°C. The direct proportionality which was previously reported⁶⁾ is observed at 30°C. On the other hand, at 140°C with the same concentration of ethylene, N_p is greater than 30°C and is not proportional to the concentration of ethylene. This difference between 30 and 140°C may indicate that additional processes related to ethylene occur at 140°C to increase the number of polymer chains. They may be the additional initiation and/or the transfer with the monomer.

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6) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, *A-1*, **4**, 1517 (1966).