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A Kinetic Study of the γ-Radiation-Induced Polymerization of Ethylene at a Normal Temperature*

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The gamma-radiation-induced polymerization of ethylene was carried out in the intermediate pressure region from 70 to 400 kg./cm² with a dose-rate from 5×10^3 to 4.3×10^5 rad./hr. and at a temperature of 30°C. An overall *G*-value of the 10^4 order was usually obtained. No induction period for polymerization was observed. The polymerization rate and the molecular weight of the polymer formed were shown to increase almost proportionally with the reaction time and with the pressure of ethylene. The dose-rate exponents of the rate and the molecular weight were found to be 0.9 and 0 respectively. These results indicate that the stationary-state hypothesis, i. e., that the rate of initiation is equal to that of termination, is not realized in this polymerization. From the kinetic discussion of the initial stage of polymerization, where the concentration of monomer remains essentially constant, it was concluded that the rates of termination and transfer reaction are very small; the life of polymer radicals is, therefore, quite long and the growing of polymer radicals proceeds successively under irradiation.

Several studies[1-7] of the γ-radiation-induced polymerization of ethylene have been published during the past ten years. Hayward and Bretton,[1] for instance, reported that the reaction consisted of two parts; the one was strongly inhibited by a trace of oxygen, and the other was not. Laird et al.[2] reported that the rate of polymerization depended on the ethylene pressure (P) and the radiation intensity (I), as the rate$=kP^{2.6}I^{0.9}$, with the overall activation energy of 3.3 kcal./mol. at lower temperatures of 20 to 125°C and at pressures from 473 to 1185 atm., while at higher temperatures (from 100 to 200°C) the rate$=kP^{3.1}I^{0.8}$, with the activation energy of 13.6 kcal./mol. Medvedev et al.[5] observed that the rate of polymerization increased with the reaction time, and that the maximum rate was proportional to the ethylene concentration to the power of 4—5 and to the 0.3 th power of the dose rate. More recently, Steinberg et al.[7] reported the rate equation to be rate$=kP^{1.02}I^{0.42}$ and that the *G*-value was very high.

We are now undertaking a series of investigations of the γ-radiation-induced polymerization of ethylene in order to find its mechanism. We have already communicated briefly[8,9] that the polymerization rate and the molecular weight of the polymer increase with the reaction time, and that the life of the growing polymer radical is long at 30°C under irradiation. In the present work, the polymerization rate and the molecular weight have been measured in the pressure range from 70 to 400 kg./cm², at the temperature of 30°C, and at dose-rates from 5000 to 430000 rad./hr. using ethylene of a high purity. The main topic of this paper is a kinetic discussion of the polymerization at normal temperature.

Experimental

A scheme of the experimental equipment is shown in Fig. 1. The reaction vessel was an unstirred stainless-steel (SUS-27) autoclave with a capacity of 100 ml. The pressure measurements were made by a Bourdon tube gauge. A chromel-alumel thermocouple with a recorder was used for the continuous temperature measurements. The reaction temperature was regulated within 2°C by an automatic controller. The reactions were carried out by the batch stysem.

Before the vessel was filled with ethylene, the system was evacuated and swept out with ethylene three times; then ethyene was introduced from a reservoir to the vessel, which had been cooled in a methanol - dry ice

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1) J. C. Hayward, Jr. and R. H. Bretton, *Chem. Eng. Progr., Symp. Ser.*, **50** (13), 73 (1954).

2) R. K. Liard, A. G. Morrel and L. Seed., *Discussions Faraday Soc.*, **22**, 126 (1956).

3) J. G. Lewis, J. J. Martin and L. C. Anderson, *Chem. Eng. Progr., Symp. Ser.*, **50** (5), 249 (1954).

4) B. G. Bray, R. A. Carstens, O. A. Larson, J. J. Martin and K. K. G. Sikchi, ibid., **55** (27), 33 (1959).

5) S. S. Medvedev, A. D. Abkin, P. M. Khomikovskii, G. N. Gerasimov, V. F. Gromov, Yu. A. Chikin, V. A. Tsingister, A. L. Auer, M. K. Yalovleva, L. P. Mezhirova, A. V. Matveeva and Z. G. Bezzubuik, *Polymer Sci. (USSR) (English Transl.)*, **2**, 457 (1961).

6) Y. Hosaka, M. Takehisa, Y. Urano and M. Yasumoto, *Tokyo Kogyo Shikensho Hokoku*, **56**, 225 (1961).

7) M. Steinberg, P. Colombo, L. Kukacka, R. N. Chapman and G. Alder, *Proc. Intern. Symp. Radiation Induced Polymerization Copolymerization*, Battelle Memorial Institute, 70 (Nov. 29—30, 1962).

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

9) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, ibid., **3A**, 2931 (1965).

TABLE I. EFFECT OF REACTION PRESSURE AND TIME ON POLYMER YIELD AND MOLECULAR WEIGHT

Ethylene*			Reaction time	Polymer yield	Molecular weight	*G*-value molecule/ 100 eV.
Pressure kg./cm²	Fugacity kg./cm²	Concn. mol./l.	hr.	g.	$\times 10^{-4}$	$\times 10^{-3}$
400	116	16.4	0.26	0.03	7.0	3.4
400	116	16.4	0.53	0.14	14.7	8.0
400	116	16.4	1.0	0.74	26.6	22.4
384	112	16.0	2.6	2.62	31.5	31.5
405	117	16.4	4.0	5.52	33.2	42.5
400	116	16.4	8.0	11.72	31.2	43.3
388	113	16.1	20.8	22.79	24.0	34.2
295	90	15.4	0.70	0.16	13.3	7.4
295	90	15.4	1.0	0.27	17.4	8.8
300	91	15.4	1.7	0.71	26.5	13.5
300	91	15.4	4.0	2.52	32.0	20.4
296	90	15.4	20.2	14.84	26.0	23.7
200	70	14.4	0.70	0.08	5.9	4.0
200	70	14.4	1.2	0.12	6.6	3.5
200	70	14.4	2.5	0.50	12.7	7.0
201	70	14.4	4.0	1.50	17.2	13.0
200	70	14.4	8.0	3.89	24.1	16.9
203	71	14.4	20.0	11.42	23.2	19.9
152	61	13.4	1.7	0.19	6.3	4.2
152	61	13.4	2.5	0.31	8.8	4.6
152	61	13.4	4.0	0.79	16.4	7.4
154	61	13.4	8.0	2.29	19.4	10.7
150	60	13.3	20.3	6.79	22.3	12.4
70	45	7.2	15.0	0.39	2.1	1.8
70	45	7.2	20.7	0.50	1.6	1.7
70	45	7.2	44.6	3.07	4.3	4.8

Reaction temperature, 30°C; Dose-rate, 2.5×10^4 rad./hr.
* at initial condition

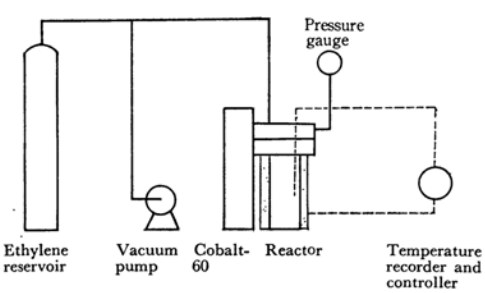

Fig. 1. Experimental equipment.

bath. The vessel was then brought to the desired reaction temperature and pressure. As a source of γ-ray, 400-curie and 12000-curie cobalt-60 were used. The radiation intensity inside the reaction vessel was measured by ferrous sulfate dosimetry. At the end of the irradiation period, the unpolymerized ethylene was purged and the vessel was opened in the air. The amount of polymer formed was determined by direct weighing.

The ethylene used was commercially available and was 99.9% pure (free of CO and H_2S), containing 48 p. p. m. acetylene and 3 p. p. m. oxygen. The density and fugacity of ethylene at a given pressure and temperature are known from Benzler's pressure-enthalpy diagram.[10]

The solution viscosity of the polyethylene formed was measured in tetralin at 130°C. The number-average molecular weight of polymer was estimated by Tung's formula[11]:

$$[\eta] = 4.60 \times 10^{-4} \overline{M}_n^{0.725}$$

Results

The results are summarized in Tables I and II.

The polymer yield is plotted against the reaction time in Fig. 2. In these experiments there is no induction period in which no polymer is formed. The yield of the polymer formed increases rapidly with the reaction time in the early stage, while in the stage of higher conversion, the increasing rate is gradually reduced because of the drop in pressure.

10) H. Benzler and A. V. Koch, *Chem. Ingr. Tech.*, **27** (2), 71 (1955).
11) L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

Table II. Effect of dose-rate on polymer yield and molecular weight

Dose-rate rad./hr. $\times 10^{-4}$	Reaction time hr.	Polymer yield g.	Molecular weight $\times 10^{-4}$	G-Value molecule/100 eV. $\times 10^{-3}$
43	1.0	0.91	4.4	1.8
21	1.0	0.55	5.5	2.2
12	1.0	0.36	5.8	2.6
5.6	1.0	0.25	6.6	3.8
2.5	1.2	0.12	6.6	3.5
1.3	5.0	1.08	24.5	14.2
0.77	4.0	0.54	25.5	15.0
0.50	5.0	0.57	26.0	19.5

Ethylene pressure, 200 kg./cm²
Reaction temperature, 30°C

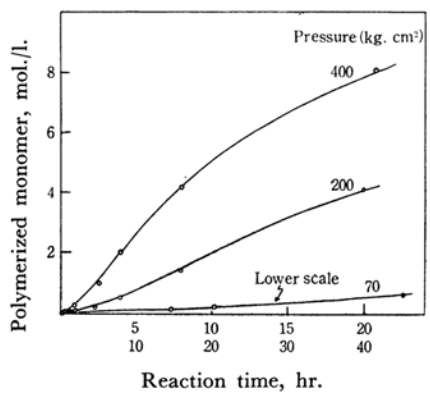

Fig. 2. The amount of ethylene polymerized vs. reaction time.
(Reaction temperature, 30°C; dose-rate, 2.5×10^4 rad./hr.)

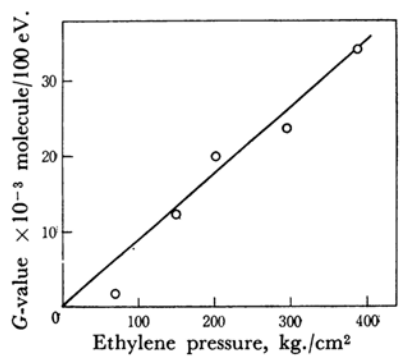

Fig. 3. G-value vs. initial ethylene pressure.
(Reaction temperature, 30°C; dose-rate, 2.5×10^4 rad./hr.; reaction time, ca. 20 hr.)

The G-value (molecules of ethylene polymerized per 100 eV. absorbed in the mass of the monomer and the polymer) is also shown in Tables I and II. The G-value depends on the reaction time, the ethylene pressure, the dose-rate and the reaction temperature; it lies between 1.8×10^3 and 4.3×10^4. Figure 3 indicates that the overall G-value is proportional to the initial pressure of ethylene.

Polymerization under a Low Conversion.—The experiments concerned with kinetic study were carried out under conditions in which the conversion of ethylene to polymer was low and the pressure remained essentially constant during the course of the reaction.

Polymer Yield.—The polymer yield, with a dose rate of 2.5×10^4 rad./hr. under various pressures, is plotted against the time in Fig. 4. No induction period was observed in our experiments. As is shown in Table I, at a pressure of 400 kg./cm² under 30°C, 0.03 g. of polymer is formed in only 16 min. in a 100 ml. reactor. On the other hand, an induction period of more than several hours, as a result of oxygen, was reported in the case of the polymerization of ethylene containing over 60 p. p. m. oxygen by Steinberg et al.[7] and by Hayward et al.[1] The reason for the difference between these results and ours is not clear,

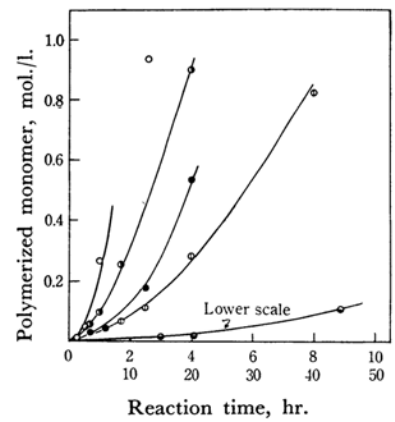

Fig. 4. The amount of polymerized monomer vs. reaction time.
(Reaction temperature, 30°C; dose-rate, 2.5×10^4 rad./hr.; ethylene pressure, 70 (◒), 150 (◑), 200 (●), 300 (◑), 400 kg./cm² (○))

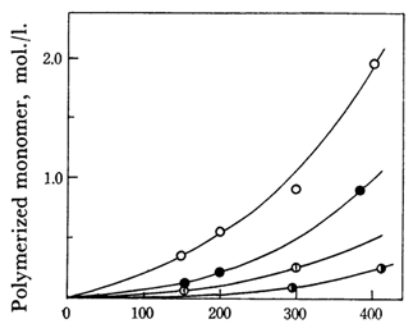

Fig. 5. The amount of polymerized monomer vs. ethylene pressure.
(Reaction temperature, 30°C; dose-rate, 2.5×10^4 rad/hr.; reaction time, 1.0 (◑), 1.7 (◑), 2.5 (●.), 4.0 hr. (○))

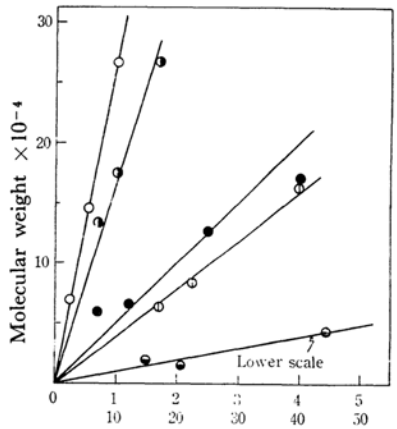

Fig. 6. Molecular weight vs. reaction time. (Reaction conditions and notes are the same as Fig. 4.)

but it may be ascribed to the difference in the amounts of oxygen; i. e., the ethylene used in our experiments contains only 3 p. p. m. oxygen, plus other impurities.

Since the polymer yield increases rapidly with the reaction time, as is shown in Fig. 4, it should be noted that a rate acceleration is observed in this polymerization.

The effect of the intensity was investigated over the dose-rate range from 0.5×10^4 to 43×10^4 rad./hr.; a hundred-fold range was thus covered. In Table II, it is shown that the amount of polymer formed increases with the dose-rate. Figure 5 indicates that the polymer yield at a constant time increases rapidly with the pressure.

Molecular Weight.—In these experiments, the molecular weight falls in the wide range from 20000 to 300000, depending on the reaction conditions.

The molecular weight of the polymer formed in the early stage of less than ca. 3% conversion is plotted against the reaction time at each respective pressure (but these pressures are almost constant during the reaction) in Fig. 6. It is a characteristic phenomenon that the molecular weight of the polymer formed increases proportionally with the reaction time. The increase in ethylene pressure obviously gives the increase in the molecular weight of the polymer.

The dependence of the molecular weight of the polymer on the radiation dose-rate is seen in Table II. It is interesting that the molecular weight at the unit reaction time is almost independent of the dose rate.

Discussion

From the characteristic features—(1) the reaction rate increases with the reaction time; (2) the molecular weight of the polymer formed increases with the reaction time, and a polymer of a very high molecular weight is easily obtained, and (3) the radiation dose-rate has little effect on the molecular weight of the polymer, it can be concluded that the stationary-state hypothesis, that the rate of initiation is equal to that of termination, is not realized in this polymerization.

In our kinetic study experimental results are, therefore, treated without using the stationary-state hypothesis.

Polymerization Rate.—The following elementary reactions are assumed for the γ-radiation-induced polymerization of ethylene in bulk; the respective rate expressions are also shown at the right.

1. Initiation $\mathrm{M} \xrightarrow{k_i} \mathrm{R}_1\cdot$ $R_i=k_i\rho_{\mathrm{M}}I$ (1)
2. Ethylene excitation $\mathrm{M} \rightleftarrows \mathrm{M}^*$
$\mathrm{M}+\mathrm{M}^* \rightleftarrows \mathrm{M}_2^*$ $f_{\mathrm{M}_2^*}=K_e f_{\mathrm{M}}^2$ (2)
3. Propagation $\mathrm{R}_1\cdot+\mathrm{M}_2^* \xrightarrow{k_p} \mathrm{R}_3\cdot$
$R_{n-2}\cdot+\mathrm{M}_2^* \xrightarrow{k_p} \mathrm{R}_n\cdot$
$R_p=k_p[\mathrm{R}\cdot]f_{\mathrm{M}_2^*}$ (3)
4. Termination $\mathrm{R}_m\cdot+\mathrm{R}_n\cdot \xrightarrow{k_{t1}} \mathrm{P}_{m+n}$
$\mathrm{R}_n\cdot+\mathrm{Z} \xrightarrow{k_{t2}} \mathrm{P}_n$
$R_t=k_{t_1}[\mathrm{R}\cdot]^2+k_{t_2}[\mathrm{R}\cdot][\mathrm{Z}]$ (4)
5. Transfer $\mathrm{R}_n\cdot+\mathrm{Y} \xrightarrow{k_{tr}} \mathrm{P}_n+\mathrm{Y}\cdot$
$R_{tr}=k_{tr}[\mathrm{R}\cdot][\mathrm{Y}]$ (5)

where M represents the ethylene monomer; $\mathrm{R}_n\cdot$, an active polymer chain composed of n monomers; $[\mathrm{R}\cdot]$, the total concentration of all the active polymer chains, irrespective of size (i. e., $\sum_{n=1}^{\infty}[\mathrm{R}\cdot_n]$); M^*, the excited ethylene monomer; M_2^*, the excited ethylene dimer; Y, the substance to which the activity of $\mathrm{R}\cdot_n$ is transferred; Z, the substance by which $\mathrm{R}\cdot_n$ 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_{M} the density of ethylene; I, the dose rate; f_{M}, the fugacity of ethylene; $f_{\mathrm{M}_2^*}$ the fugacity of the excited ethylene dimer, and K_e, the equilibrium constant of the 2nd step.

Since the initiation step is brought about by the absorption of the radiation energy by the monomer, the rate of the initiation reaction may be considered to be proportional to the density of ethylene presented in the reactor and to the intensity of radiation. The rate expression 1 is, therefore, given for the initiation reaction. The 2nd step is characteristic in this scheme. The step of the formation

of the excited dimer from the monomer with radiation is introduced because of the following facts; (1) as was reported before,[9] the propagation reaction does not take place without radiation, though it takes place with a radiation of a very low dose rate, and (2) the rate of propagation is proportional to the 2nd power of ethylene fugacity, as will be described later. It is well known that the rates of excitation and energy transfer are very fast in the radiation chemistry. The 2nd step is, therefore, very fast compared with the 3rd step and is in equilibrium.

In the propagation step, the excited dimer adds to the propagating chain. Ordinary chain termination and transfer are assumed. The overall rate of polymerization is approximately equal to the rate of propagation; accordingly, it becomes:

$$R=\mathrm{d}M_p/\mathrm{d}t\simeq R_p=k_p[\mathrm{R}\cdot]f_{\mathrm{M}_2^*}, \qquad (6)$$

where R represents the overall polymerization rate, and M_p, the amount of monomer polymerized. Here, without the assumption of stationary-state, [R·] is given by:

$$[\mathrm{R}\cdot]=k_i\rho_{\mathrm{M}}It-\int R_t\mathrm{d}t \qquad (7)$$

From the facts that the rate of polymerization and the molecular weight of the polymer increase with the reaction time, it can be assumed that no termination reaction occurs, that, namely, R_t is zero. Equation 7 then becomes:

$$[\mathrm{R}\cdot]=k_i\rho_{\mathrm{M}}It \qquad (8)$$

From the combination of Eqs. 2, 6 and 8, the overall rate of polymerization can be expressed by the following equation:

$$R=\mathrm{d}M_p/\mathrm{d}t\simeq R_p=k_pk_iK_e\rho_{\mathrm{M}}f_{\mathrm{M}}^2It \qquad (9)$$

By integrating Eq. 9, the amount of the monomer polymerized is expressed as a function of the density and the fugacity of ethylene, the dose rate, and the reaction time; namely,

$$M_p=(1/2)\cdot k_pk_iK_e\rho_{\mathrm{M}}f_{\mathrm{M}}^2It^2 \qquad (10)$$

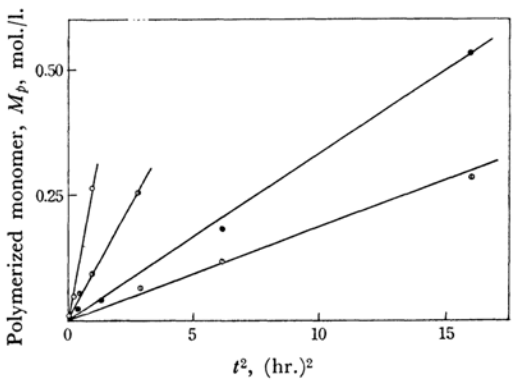

Fig. 7. The amount of polymerized monomer vs. square of reaction time.
(Reaction conditions and notes are the same as Fig. 4.)

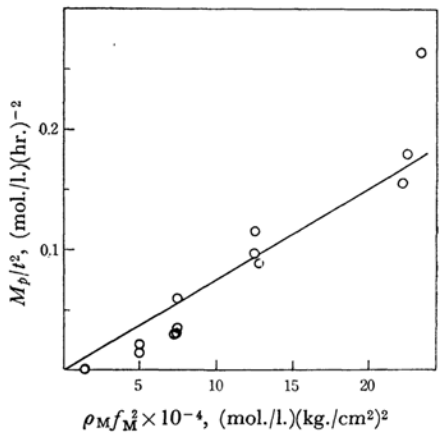

Fig. 8. M_p/t^2 vs. $\rho_{\mathrm{M}}\cdot f^2{}_{\mathrm{M}}$.
(Reaction temperature, 30°C; dose-rate, 2.5×10^4 rad./hr.; ethylene pressure, 70 to 400 kg./cm^2).

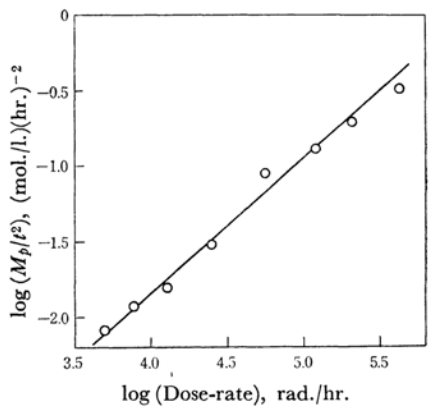

Fig. 9. Logarithmic plots of M_p/t^2 vs. dose-rate.
(Reaction temperature, 30°C; ethylene pressure, 200 kg./cm^2)

A distinct linear relation exists between the amount of monomer polymerized and the square of the reaction time at each respective pressure, as is indicated in Fig. 7. The plot of $\rho_{\mathrm{M}}f_{\mathrm{M}}^2$ versus M_p/t^2 also gives the straight line in Fig. 8. The logarithmic plot of the dose-rate against M_p/t^2 is shown in Fig. 9, from which the dose-rate exponent of M_p/t^2 may be seen to be 0.9.

The results are combined and an empirical expression of amount of monomer polymerized is obtained as:

$$M_p=k_1\rho_{\mathrm{M}}f_{\mathrm{M}}^2I^{0.9}t^2 \qquad (11)$$

The approximate agreement of the empirical expression with the theoretical one (10), derived from the elementary reactions presumed above, is thus shown.

The Degree of Polymerization.—The number-average degree of polymerization at a given reaction time is written for the polymerization with no termination by recombination as follows:

$$\overline{DP}=\left(\int R_p\mathrm{d}t\right)/\left(\int R_i\mathrm{d}t+\int R_{tr}\mathrm{d}t\right) \qquad (12)$$

where $\overline{DP}$ represents the number-average degree of polymerization, and $\int R_p\mathrm{d}t$ is as given in Eq. 10 ($\int R_i\mathrm{d}t$ is also obtained from Eq. 1); accordingly:

$$\overline{DP}=\frac{(1/2)\cdot k_p k_i K_e \rho_M f_M^2 I t^2}{k_i \rho_M I t+(k_{tr}/k_p K_e)\cdot([Y]/f_M^2)\cdot M_p} \qquad (13)$$

then;

$$1/\overline{DP}=(2/k_p K_e f_M^2 t)+(k_{tr}/k_p K_e)\cdot([Y]/f_M^2) \qquad (14)$$

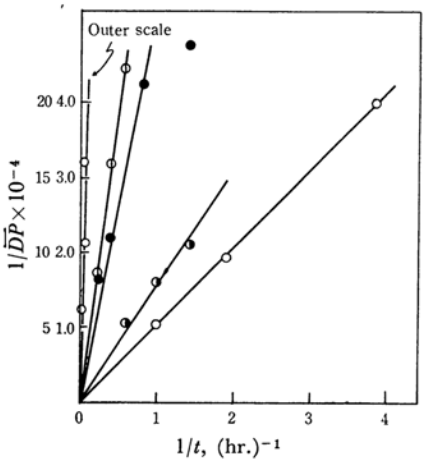

Fig. 10. Reciprocal of degree of polymerization vs. reciprocal of time.
(Reaction conditions and notes are the same as Fig. 4.)

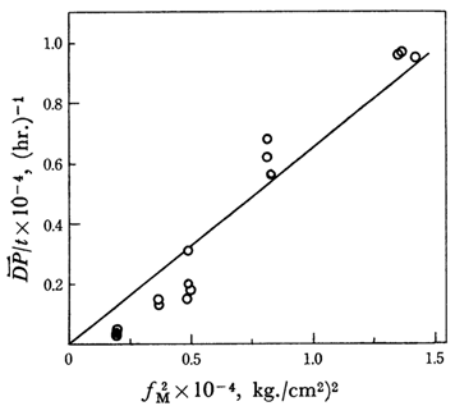

Fig. 11. $\overline{DP}/t$ vs. square of ethylene fugacity.
(Reaction temperature, 30°C; dose-rate, 2.5×10^4 rad./hr.; ethylene pressure, 70 to 400 kg./cm²)

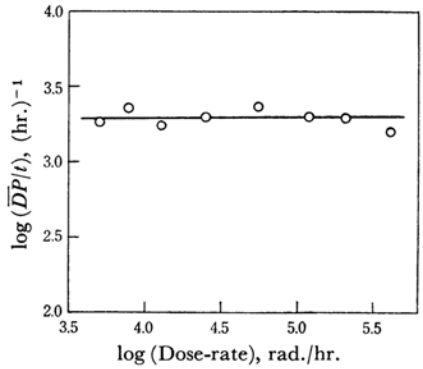

Fig. 12. Logarithmic plots of $\overline{DP}/t$ vs. dose-rate.
(Reaction temperature, 30°C; ethylene pressure, 200 kg./cm²)

The plot of the reciprocal of $\overline{DP}$ against the reciprocal of the reaction time gives a straight line through the origin, as is shown in Fig. 10. The fact that the line goes through the origin indicates that there is no transfer reaction in the polymerization; Eq. 14 thus becomes:

$$\overline{DP}=(1/2)\cdot k_p K_e f_M^2 t \qquad (15)$$

The linear relation between $\overline{DP}$ and the time has previously been shown in Fig. 6. In Fig. 11, it is shown that the ratio of the degree of polymerization to the reaction time is approximately proportional to the square of ethylene fugacity. Figure 12 shows that the dose rate does not influence $\overline{DP}/t$. By combining these results, the following empirical expression of the degree of polymerization is obtained:

$$\overline{DP}=k_2 f_M^2 t \qquad (16)$$

The empirical expression is shown to agree with theoretically derived Eq. 15.

In the view of fact that the experimental results on both polymerization rate and the degree of polymerization coincide with the equation theoretically derived, the proposed elementary reaction and the assumption that the termination is essentially eliminated, and that the stationary state is not realized in this polymerization, may be accepted. In other words, the propagation, proceeds successively, and a long-lived active polymer chain may exist under irradiation. The long life-time of the active chain has been proved by a kind of post polymerization experiment.[9]