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A Kinetic Study of the Free-Radical Bulk Polymerization of Ethylene

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The bulk polymerization of ethylene was carried out under mild conditions, *i. e.*, pressures of from 183 to 400 kg/cm^2 and temperatures of from 30 to 140°C, using azobisisobutyronitrile as an initiator. In polymerization at the low temperature of 40°C, both the polymerization rate and the molecular weight of the polymer formed increased with the reaction time. At the above temperature, the polymerization rate was shown to be proportional to the amount of initiator, and the molecular weight was found to be independent of it. Furthermore, both the polymerization rate and molecular weight were found to be proportional to the 2.5th power of ethylene fugacity. The dependencies of the polymerization rate and the molecular weight on the reaction time decrease with the rise in reaction temperatures from 30 to 100°C. A kinetical discussion indicated that the rate of termination is almost zero at 30—40°C, but that it increases with the temperature. The polymerization rate and the molecular weight were shown to be proportional to the 0.8 and 0.2th powers of the amount of the initiator. The activation energy of the initiation reaction was evaluated to be *ca.* 27 kcal/mol.

The free-radical polymerization of ethylene has usually been investigated under severe reaction conditions, such as high pressures from 800 to 2000 kg/cm^2 and high temperatures from 130 to 250°C.[1-5] Such conditions are also used in the industrial process. Recently, however, a few studies have been conducted under milder conditions, namely, under lower pressures and at lower temperatures.[6,7] The possibility of the existence of a long-lived polymer radical was first pointed out briefly by Buchdahl[8] in his discussion of the paper by Laird *et al.*[2] Lyubetzky *et al.*[7] studied the polymerization of ethylene at 70°C with azobisisobutyronitrile (AIBN) in benzene, and pointed out that the propagation reaction occurs with the living polymer radical in the polymer crystalline phase.

We have reported several characteristics of the low temperature free-radical bulk polymerization of ethylene in a previous paper.[9] This paper, a continuation of that earlier paper, will be concerned with the kinetic study of ethylene polymerization in bulk with AIBN, at temperatures of from 30 to 140°C and at pressures of from 100 to 400 kg/cm^2.

Experimental

Polymerization was carried out in a static, unstirred, stainless-steel (SUS-27) high-pressure vessel with a capacity of 100 m*l*. After the desired amount of crystalline AIBN had been introduced, the vessel was flushed out six times with ethylene (10 kg/cm^2). The vessel was then cooled in a methanol-dry ice bath, ethylene being introduced from a reservoir. The vessel was warmed to the desired reaction temperature, and a very small amount of ethylene was released from the vessel to adjust the reaction pressure. Since the polymerization was carried out to a low conversion, the pressure, which was measured by a Bourdon tube gauge, was almost constant throughout the reaction. A temperature constant within ±1°C was also maintained by an automatic controller. At the end of the reaction, the unpolymerized ethylene was purged and the vessel was opened. After the unchanged initiator had been extracted by using boiling acetone, the polymer yield was determined.

The ethylene used had been commercially obtained and was 99.9% pure (free of CO and H_2S), containing 21 ppm acetylene and 0.3 ppm oxygen. The density and fugacity of ethylene at a given pressure and temperature were known from Benzler's pressure-enthalpy diagram.[10] AIBN was purified by recrystallization

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[1] S. Kodama, I. Taniguchi, S. Yuasa, T. Ota and Y. Terada, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **57**, 439 (1954).

[2] R. K. Laird, A. G. Morrell and L. Seed, *Discussions Faraday Soc.*, **22**, 126 (1956).

[3] S. Kodama, Y. Matsushima, A. Ueyoshi, T. Shimidzu, T. Kagiya and K. Fukui, *J. Polymer Sci.*, **41**, 83 (1959).

[4] R. O. Symcox and P. Ehrlich, *J. Am. Chem. Soc.*, **84**, 531 (1962).

[5] R. H. Bretton and B. F. Dodge, *Chem. Eng. Progr.*, **58** (No. 8), 50 (1962).

[6] H. N. Friedlander, *J. Polymer Sci.*, **58**, 455 (1962).

[7] B. L. Erussalimsky, S. G. Lyubetzky, W. W. Mazurek, S. Ya. Frenkel and L. G. Shaltyko, *Polymer*, **3**, 639 (1962).

[8] R. Buchdahl, *Discussions Faraday Soc.*, **22**, 150 (1956).

[9] S. Machi, T. Sakai, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, **B3**, 709 (1965).

[10] H. Benzler and A. V. Koch, *Chem. Ingr. Tech.*, **27**, (No. 2), 71 (1955).

from acetone. The molecular weight of the polymer was determined from its intrinsic viscosity in tetralin at 130°C. Tung's formula[11] was used in the calculation of the molecular weight, because the polymer has little branching, like a low-pressure polyethylene.[9]

Results and Discussion

Polymerization at a Low Temperature. The experimental results are summarized in Table 1.

Figure 1 shows the changes in the polymer yield (*i. e.*, the amount of polymerized monomer) and the molecular weight with the reaction time. The polymer yield is found to be proportional to the second power of the time, and the molecular weight, to the first power. The polymerization rate and molecular weight increase with the time. Similar features have been found as distinct characteristics in the low temperature bulk polymerization of ethylene induced by radiation.[12,13] These facts suggest that the rate of termination is very small. The polymer radical, therefore, accumulates as AIBN decomposes to radicals, and the rate of polymerization increases. The steady increase in the molecular weight suggests that the rates of both termination and transfer are very small.

TABLE 1. RESULTS OF THE POLYMERIZATION AT 40°C

Ethylene pressure kg/cm²	Amount of AIBN mmol	Reaction time hr	Polymer yield g	Molecular weight $\overline{M}_n \times 10^{-4}$
400	0.980	1.5	0.24	11.3
		2.0	0.32	13.9
		3.0	0.76	23.7
		4.0	1.35	31.6
183	0.421	4.0	0.11	6.5
210			0.15	9.1
240			0.19	11.9
400			0.54	32.0
400	0.140	4.0	0.20	31.4
	0.412		0.54	32.0
	0.700		0.94	31.4
	0.980		1.35	31.6

Volume of reaction vessel, 100 m*l*

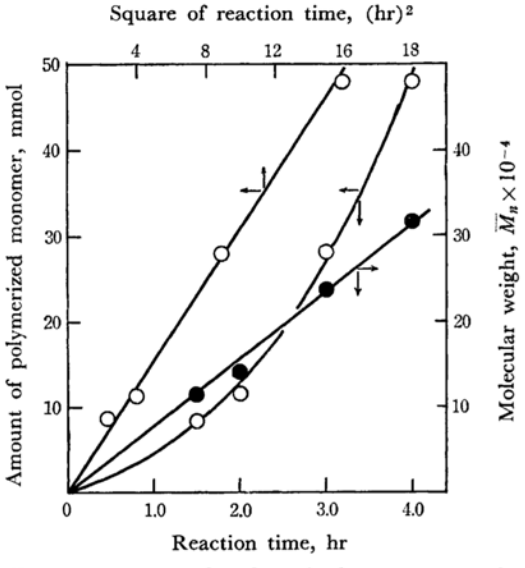

Fig. 1. Amount of polymerized monomer and polymer molecular weight *vs.* reaction time. (Reaction conditions: temperature, 40°C; pressure, 400 kg/cm²; AIBN, 0.98 mmol)

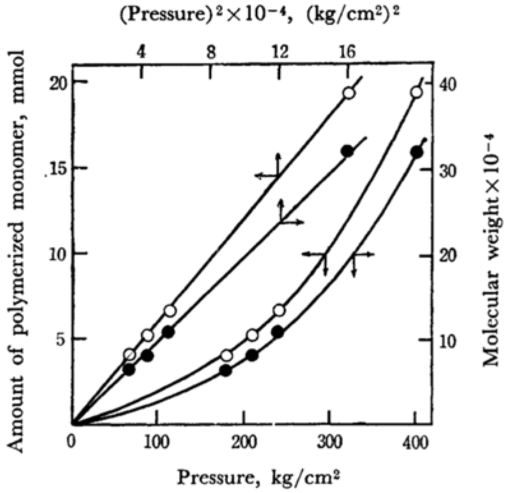

Fig. 2. Amount of polymerized monomer and polymer molecular weight *vs.* reaction pressure. (Reaction conditions: temperature, 40°C; AIBN, 0.42 mmol; time, 4.0 hr)

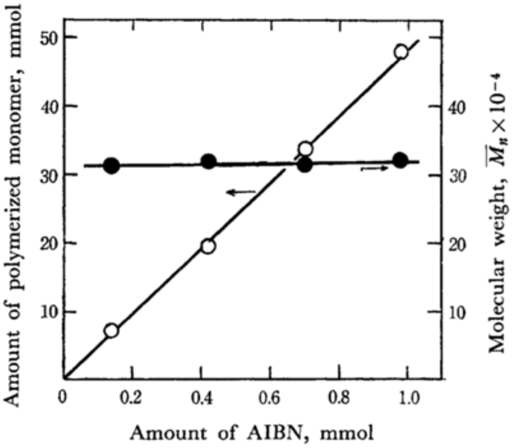

Fig. 3. Amount of polymerized monomer and polymer molecular weight *vs.* amount of initiator.
(Reaction conditions: temperature, 40°C; pressure, 400 kg/cm²; time, 4.0 hr)

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[11] L. H. Tung, *J. Polymer Sci.*, **24**, 333 (1957).

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

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

Figure 2 shows the effects of the ethylene pressure on the polymer yield and the molecular weight. Both the molecular weight and polymer yield increase rapidly with the ethylene pressure at a constant time. Their pressure exponents are found to be approximately two.

Figure 3 shows the influence of the amount of the initiator; the figure indicates that the polymer yield at a constant time is proportional to the number of moles of initiator added, and that the molecular weight of the polymer is independent of it. These facts are in contrast to the dependencies of the rate and molecular weight on the amount of the initiator in a polymerization where rapid bimolecular termination occurs.

The polymerization is considered to consist of the following steps:

Initiation

Decomposition of initiator
$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}\cdot \qquad (1)$$

Addition of a monomer
$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{RM_1}\cdot \qquad (2)$$

Propagation
$$\begin{array}{l} \mathrm{RM_1}\cdot \; + \; \mathrm{M} \xrightarrow{k_p} \mathrm{RM_2}\cdot \qquad (3) \\ \quad\vdots \qquad\quad \vdots \qquad\qquad \vdots \\ \mathrm{RM}_{n-1}\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}_n\cdot \qquad (4) \end{array}$$

Transfer
$$\mathrm{RM}_n\cdot + \mathrm{Y} \xrightarrow{k_{tr}} \mathrm{P}_n + \mathrm{Y}\cdot \qquad (5)$$

Termination
$$\mathrm{RM}_n\cdot + \mathrm{Z} \xrightarrow{k_{t_1}} \mathrm{P}_n \qquad (6)$$
$$\mathrm{RM}_m\cdot + \mathrm{RM}_n\cdot \xrightarrow{k_{t_2}} \mathrm{P}_{m+n} \qquad (7)$$

The initiation step consists of two reactions, *i. e.*, the decomposition of the initiator, I, into free radicals, R·, and the addition of a monomer to form radicals, $\mathrm{RM_1}\cdot$. Since the decomposition of AIBN has been shown to proceed *via* a first-order reaction independent of the reaction media, such as various organic solvents,[14,15] an aqueous solution of dioxane[16] and water[17] where AIBN is not soluble, a first-order decomposition is assumed in this system in the absence of a solvent. Thus, the rate of the primary radical formation at time t is:

$$\mathrm{d}[\mathrm{R}\cdot]/\mathrm{d}t = 2k_dI_0\exp(-k_dt) \qquad (8)$$

where k_d represents the rate constant of the decomposition of the initiator, and where I_0 is the amount of the initiator at the initial stage. Some fraction of the primary radicals may initiate chains according to Eq. (2), and the other fraction tends to disappear through other reactions. The rate of the initiation of chain radicals is, therefore, given by:

$$R_i = \mathrm{d}[\mathrm{RM_1}\cdot]/\mathrm{d}t = 2fk_dI_0\exp(-k_dt) \qquad (9)$$

where f is the fraction of the radicals initiating polymerization chains, the so-called radical yield. Since the number of moles of polymer chains formed at a constant reaction time is independent of the ethylene pressure, as will be described below, the f fraction is not dependent on the monomer concentration.

At a low temperature of 40°C and at the initial stage, since the value of k_dt is much smaller than unity, R_i is approximately expressed as:

$$R_i = 2fk_dI_0 \qquad (10)$$

Propagation proceeds by the addition of monomers to the chain radical to form the growing polymer radical, $\mathrm{RM}_n\cdot$, which has n monomeric units. The rate of propagation, R_p, is:

$$R_p = k_p[\mathrm{RM}\cdot]f_\mathrm{M} \qquad (11)$$

where [RM·] is the total concentration of radicals irrespective of size $(\sum_{n=1}^{\infty}[\mathrm{RM}_n\cdot])$, and k_p, the rate constant of propagation. The ethylene fugacity, f_M, is used as a measured of ethylene activity under high pressure. The concentration of radicals at time t is given as the difference between initiation and termination:

$$[\mathrm{RM}\cdot] = \int_0^t R_i\mathrm{d}t - \int_0^t R_t\mathrm{d}t \qquad (12)$$

where R_t is the rate of termination. As has been mentioned above, the rate of termination is negligible. Thus:

$$[\mathrm{RM}_n\cdot] \fallingdotseq \int_0^t R_i\mathrm{d}t = 2fI_0\{1-\exp(-k_dt)\} \qquad (13)$$

At low temperatures and at the initial stage of polymerization, Eq. (13) is approximately rewritten as:

$$[\mathrm{RM}\cdot] \fallingdotseq 2fk_dI_0t \qquad (14)$$

The rate of polymerization, which is essentially the same as the rate of propagation, is given by combining Eq. (11) and Eq. (14):

$$R \fallingdotseq R_p = R_p[\mathrm{RM}\cdot]f_\mathrm{M} = 2fk_dk_pI_0f_\mathrm{M}t \qquad (15)$$

By integrating Eq. (15), the amount of the polymerized monomer, M_p, at time t is given:

$$M_p = fk_dk_pI_0f_\mathrm{M}t^2 \qquad (16)$$

The experimental correlations described above between the amount of the polymerized monomer and the reaction time, as well as the amount of the initiator (that is, the amount of the polymerized monomer is proportional to the second power of the reaction time and to the first power of the amount of the initiator), have thus been shown to

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14) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949).

15) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

16) K. S. Kwei, *J. Polymer Sci.*, **A3**, 2387 (1965).

17) S. Kodama, Y. Matsushima, A. Ueyoshi, T. Shimidzu, T. Kagiya, S. Yuasa, and K. Fukui, *ibid.*, **41**, 83 (1959).

coincide well with the theoretical equation (16) at the initial stage of polymerization.

The number of moles of polymer chains is calculated as the ratio of the moles of the polymerized monomer to the degree of polymerization of the polymer ($M_p/\overline{DP}_n$). Figure 4 indicates that the number of moles of polymer chains increase proportionally with the reaction time.

The relation between the amounts of the polymerized monomer and the molecular weights of the polymers formed at various ethylene fugacities is shown in Fig. 5. The fact that all the plots ride on the same straight line through the point of origin indicates that the number of moles of polymer chains formed at a constant time (*i. e.*, the initiation rate) is independent of the ethylene fugacity.

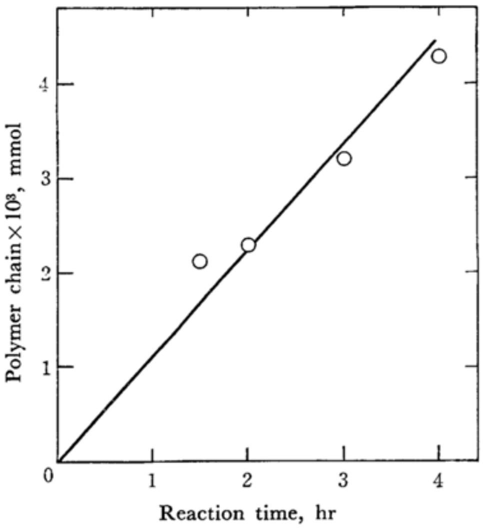

Fig. 4. Number of moles of polymer chains *vs.* reaction time.
(Reaction conditions: temperature, 40°C; AIBN, 0.98 mmol; pressure, 400 kg/cm²)

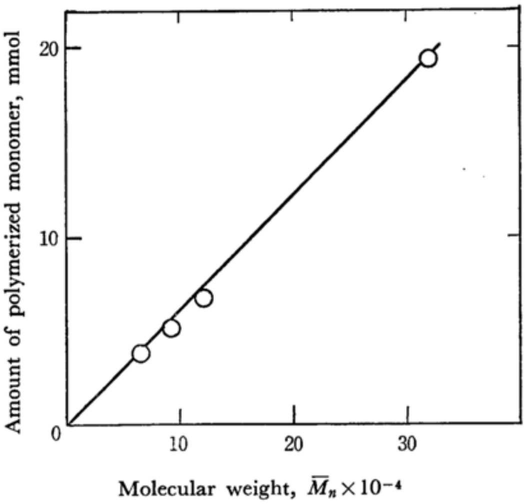

Fig. 5. Relation between amount of polymerized monomer and polymer molecular weight at various pressures.
(Reaction conditons: pressure, 138—400 kg/cm²; temperature 40°C; AIBN, 0.42 mmol)

The effects of the ethylene fugacity on the polymer yield and the molecular weight are shown in Fig. 6, from which the fugacity exponents for them all are found to be the same, *i. e.*, 2.5. This demonstrates that the rate of propagation is linear to the 2.5 th power of the ethylene fugacity. The fugacity dependence of the propagation rate has also been determined to be *ca.* 2 by means of the two-stage polymerization method reported in other of our papers.[18,19] The reason for this high fugacity exponent of the propagation rate is not clear, but one possible reason is that the propagation is brought about by the addition of two or three associated monomer molecules, as will be described below.

The degree of the polymerization of the polymer ($\overline{DP}_n$) is given by the following equation when the termination and transfer are eliminated:

$$\overline{DP}_n = \int R_p \mathrm{d}t \Big/ \int R_i \mathrm{d}t$$
$$= fk_d k_p I_0 f_M t^2 / 2fk_d I_0 t = 1/2 \cdot k_p f_M t \qquad (17)$$

This equation means that the degree of polymerization is proportional to the reaction time and independent of the amount of initiator. The experimental facts, which are shown in Fig. 1 and Fig. 3, agree very well with Eq. (17). As for the dependence of the degree of polymerization on ethylene fugacity, however, the experimental results shown in Fig. 6 indicate that the exponent is *ca.* 2.5, which is higher than that expected from Eq. (17).

The empirical equations of the polymer yield and the degree of polymerization are thus obtained as follows:

$$M_p = k_1 I_0 f_M{}^{2.5} t^2 \qquad (18)$$

$$\overline{DP}_n = k_2 f_M{}^{2.5} t \qquad (19)$$

The fact that the fugacity exponents of both the polymer yield and the degree of polymerization are higher than the theoretical values seems to be due to a higher-order dependence of the propagation rate on the monomer fugacity.

When ethylene reacts with a growing radical as associated form of *n* molecules, the rate of propagation is proportional to the fugacity of the associated

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[18] S. Machi, S. Kise, M. Hagiwara and T. Kagiya, *J. Polymer Sci.*, **B4**, 585 (1966).

[19] S. Machi, S. Kise, M. Hagiwara and T. Kagiya, Mechanism of Propagation, Transfer, and Short-Chain Branching in the Free-Radical Bulk Polymerization of Ethylene, *ibid.*, in press.

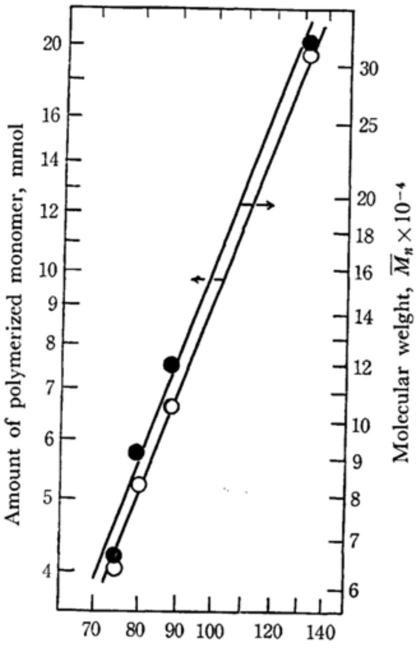

Fig. 6. Amount of polymerized monomer and polymer molecular weight *vs.* ethylene fugacity. (Reaction conditions are the same as for Fig. 2.)

monomers, which is proportional to the *n*th power of the monomer fugacity. The rate of propagation is thus given by Eq. (20) instead of Eq. (15):

$$R_p = k_p[\mathrm{RM}\cdot]f_{\mathrm{M}}{}^n = 2fk_dk_pI_0f_{\mathrm{M}}{}^nt \qquad (20)$$

By integrating (20) with t and by substituting Eq. (20) for R_p in Eq. (17), Eqs. (21) and (22) are obtained:

$$M_p = 2fk_dk_pI_0f_{\mathrm{M}}{}^nt^2 \qquad (21)$$

$$\overline{DP}_n = 1/2\cdot k_pf_{\mathrm{M}}{}^nt \qquad (22)$$

The fact that the observed exponent, n, is 2.5, as is shown in Eqs. (18) and (19), suggests that the propagation proceeds by the addition of associated monomers which consist of 2—3 units.

Effect of Reaction Temperature. The experimental results are listed in Table 2. The time-yield and time-molecular weight curves for the polymerizations at various reaction temperatures from 40 to 100°C are shown in Figs. 7 and 8 respectively. Figure 7 shows that the rate of polymerization is markedly accelerated with time at 30 and 40°C, but the acceleration becomes less remarkable with a rise in temperature. Figure 8 shows that the molecular weight of the polymer increases linearly with the time in the polymerization at 30—40°C, and when the temperature rises, the plots deviate from proportionality. These corresponding facts may indicate that the rate of chain termination increases with a rise in the temperature.

TABLE 2. EFFECTS OF REACTION TEMPERATURE ON THE POLYMER YIELD AND MOLECULAR WEIGHT

Reaction temp. °C	Amount of AIBN mmol	Reaction time hr	Polymer yield g	Molecular weight $\overline{M}_n \times 10^{-4}$
30	0.700	4.0	0.14	15.9
		8.0	0.49	33.5
		14.0	1.47	57.0
55	0.140	1.0	0.14	13.7
		2.0	0.37	20.3
		3.7	0.85	27.5
65	0.140	1.0	0.32	6.1
		2.0	0.75	10.1
		4.0	1.92	13.6
100	0.140	1.0	2.44	1.2
		2.0	2.45	1.3
		4.0	2.44	1.1

Ethylene pressure, 400 kg/cm²; volume of reaction vessel, 100 m*l*

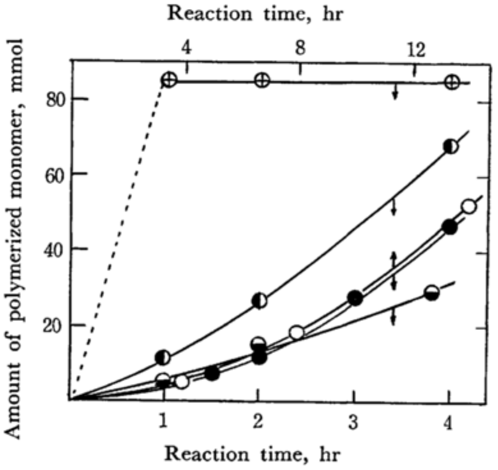

Fig. 7. Relation between amount of polymerized monomer and reaction time at various reaction temperatures.
(Reaction conditions : pressure 400 kg/cm² ;
○: 30°C, AIBN 0.70 mmol,
●: 40°C, AIBN 0.98 mmol,
◒: 55°C, AIBN 0.14 mmol,
◐: 65°C, AIBN 0.14 mmol,
⊕: 100°C, AIBN 0.14 mmol)

The dependence of the polymer yield and the molecular weight on the amount of the initiator in the polymerization at the higher temperatures of 100 and 140°C is shown in Fig. 9 and Table 3. It is well known that the exponents of the initiator of the polymerization rate and the molecular weight are 0.5 and −0.5 in polymerization with a rapid second-order termination, and 1.0 and 0 in polymerization with a rapid first-order termination with respect to the radicals.

From the slope of the lines in Fig. 9, the exponents of this polymerization are found to be 0.8

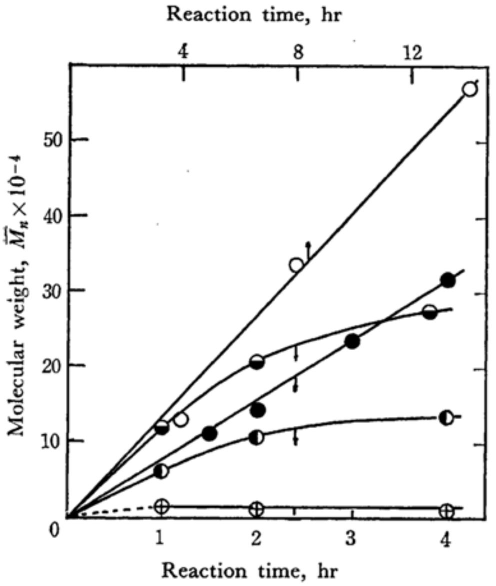

Fig. 8. Relation between polymer molecular weight and reaction time at various reaction temperatures. (Reaction conditions and notes are the same as for Fig. 7.)

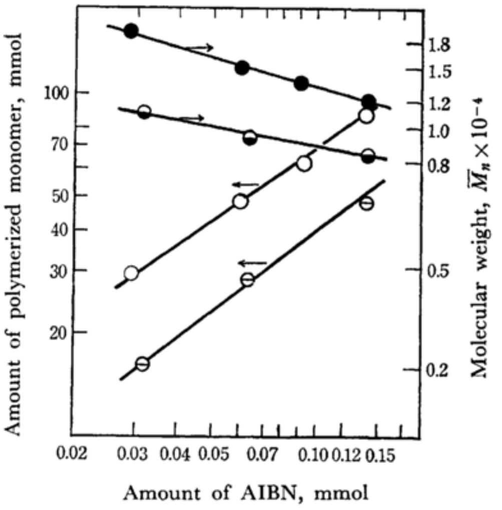

Fig. 9. Logarithmic plot of amount of polymerized monomer and polymer molecular weight *vs.* amount of initiator at higher temperatures.
(Reaction conditions: pressure, 400 kg/cm^2; time, 1.0 hr; temperatures, ○, ●: 100°C, ⊖, ◒: 140°C)

and −0.2, respectively, for the polymer yield and the molecular weight at a constant time. These high exponents indicate that the contribution of the first-order termination is larger than that of the second-order termination.

Considering the first-order termination and transfer reactions, and using the empirical rate equation of the propagation (Eq. (20)), Eqs. (23) and (24) are derived for the polymer yield and the molecular weight; these equations can be used to evaluate the rates of termination and transfer reactions.[20]

TABLE 3. EFFECTS OF AMOUNT OF AIBN ON THE POLYMER YIELD AND MOLECULAR WEIGHT IN the POLYMERIZATION AT HIGHER TEMPERATURES

Reaction temp. °C	Amount of AIBN mmol	Polymer yield g	Molecular weight $\overline{M}_n \times 10^{-4}$
100	0.029	0.81	1.9
	0.061	1.34	1.5
	0.092	1.76	1.2
	0.140	2.44	1.2
140	0.032	0.46	1.1
	0.064	0.79	0.95
	0.140	1.34	0.85

Ethylene pressure, 400 kg/cm^2; reaction time, 1.0 hr; volume of reaction vessel, 100 m*l*

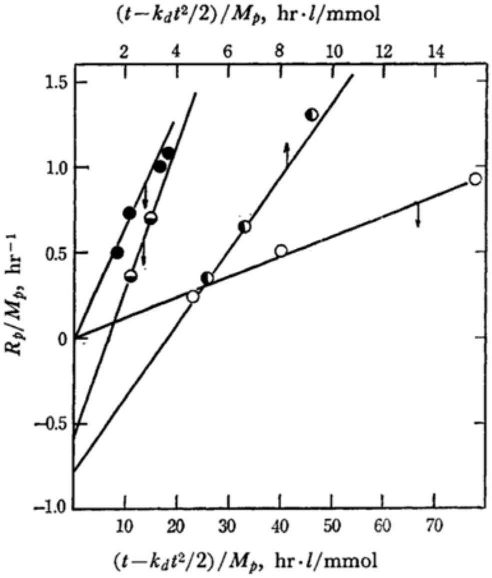

Fig. 10. R_p/M_p *vs.* $(t-k_dt^2/2)/M_p$ at the various reaction temperatures.
(Reaction conditions and notes are the same as for Fig. 7.)

$$R_p/M_p = 2fk_dI_0f_M{}^{2.5}(1/M_p)(t-k_dt^2/2) - k_t[Z] \tag{23}$$

$$1/\overline{DP}_n = 2fk_dI_0(1/M_p)(t-k_dt^2/2) + k_{tr}[Y]/k_pf_M{}^{2.5} \tag{24}$$

where Z is the substance by which the radical is deactivated, Y is the subtance with which the radical is transferred, and the ethylene fugacity exponent used is experimentally determined as

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

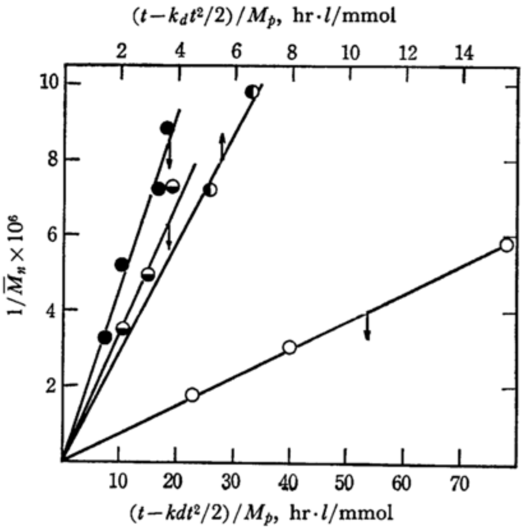

Fig. 11. $1/\overline{M}_n$ *vs.* $(t-k_dt^2/2)/M_p$ at the various reaction temperatures.
(Reaction conditions and notes are the same as for Fig. 7.)

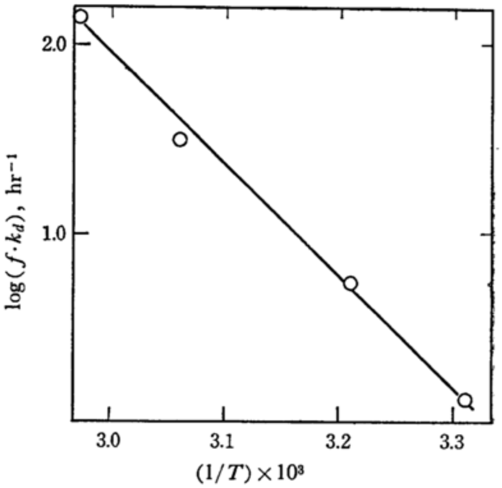

Fig. 12. Effect of temperature on the initiation rate constant, fk_d.

has been described above. The decomposition rate constant of AIBN, k_d, has been reported to be nearly constant, independent of the reaction media.[14-17] In the calculation of Eqs. (18) and (19), therefore, the value of k_d which was determined by Tobolsky[21] in benzene at various temperatures from 37 to 100°C was used. The plot of R_p/M_p against $(t-k_dt^2/2)/M_p$ according to Eq. (18) is shown in Fig. 10. The intercept on the axis of R_p/M_p gives the rate of termination (k_t[Z]). The rate of termination is thus shown to be approximately zero at 30 and 40°C and to increase with a rise in the temperature.

Figure 11 shows the plot of $1/\overline{M}_n$ against $(t-k_dt^2/2)M_p$ according to Eq. (19). Straight lines through the point of origin are obtained, their slopes corresponding to the rate of initiation. The correlation between the initiation rate and the temperature is shown in Fig. 12 as an Arrehenius plot. The activation energy of the initiation reaction is obtained as *ca.* 27 kcal/mol. The order of magnitude of the value is close to that of the decomposition of AIBN, *i. e.*, 30.8 kcal/mol.[14]

The fact that the lines in Fig. 11 pass through the point of origin indicates that the rate of the transfer reaction is approximately zero at temperatures from 30 to 65°C.

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[21] J. P. Van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).