BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 2668—2675 (1967)

The Influence of Agitation on the Gas-phase Ethylene Polymerization Induced by γ-Rays

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(Received May 4, 1967)

The effect of agitation on the γ-ray induced polymerization of ethylene was studied in a gaseous system at a pressure of 400 kg/cm^2 and at a temperature of 30°C, with dose rates ranging from 9.0×10^2 to 3.8×10^5 rad/hr. Both the rate and the degree of polymerization decreased upon agitation to *ca.* 50% of those in the polymerization without agitation. The kinetical analysis of the experimental results has shown that this decrease in the rate and in the degree of polymerization is mainly due to a decrease in the absolute propagation rate. Further, it was found that agitation has no effect on initiation and transfer reactions. The termination was not effected by agitation under a high dose rate, but it was slightly promoted at lower dose rates.

Polyethylene in powder form has been found to be directly produced when ethylene of a high pressure is irradiated by γ-rays below the melting point of a polymer. We have, however, encountered two engineering problems in the development of the process:

1. Adequate temperature control in the reactor when considerable heat of reaction is released, and
2. Continuous removal of the polymer in powder form from the reactor.

As the first attempt to overcome these problems, an agitator was placed in the reactor to promote heat transfer and the mixing of the polymer with the gas.

The rate and the degree of polymerization have already been investigated[1-6] under various conditions without agitation in a small-scale reactor. The purpose of this paper is to evaluate the effects of agitation on the elementary reactions of polymerization, such as initiation, propagation, termination and transfer reactions, using a larger-scale laboratory apparatus.

Experimental

Polymerization in Large Laboratory Apparatus. Figure 1 is a schematic diagram of the system, showing the major pieces of equipment and the control instrumentation. All the vessels and pipe lines to be filled with high-pressure ethylene were made of stainless steel (SUS-27). The reaction vessel, one liter in capacity and 80.0 mm in internal diameter, had an external jacket for temperature controlling.

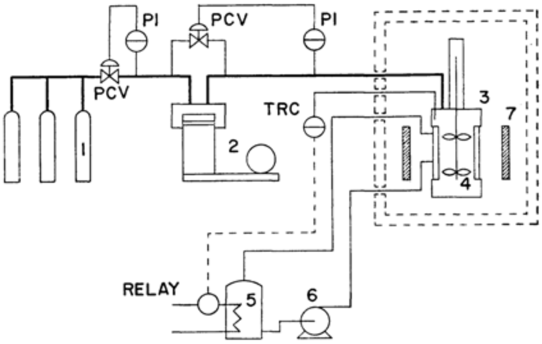

Fig. 1. Schematic diagram of experimental apparatus.
(1. ethylene reservoir, 2. compressor, 3. reactor, 4. agitator, 5. Dowtherm heater tank, 6. Dowtherm pump, 7. cobalt-60 source.)

A magnetically-driven, variable-speed (0—1000 rpm, measured by a tachometer) agitator of stainless steel was positioned vertically in the center of the reaction vessel. The two types of impellers, anchor type (A) and marine propeller (B), used in this study are shown in Fig. 2.

Before starting an experiment, the system was evacuated and swept out with ethylene four times. The ethylene monomer was then fed from a gas reservoir and compressed into the reactor to an operating pressure by the diaphragm compressor. The polymerization was carried out at a dose rate of 3.8×10^5 rad/hr under a pressure of 400 kg/cm^2 and at a temperature of 30°C. Two planar sources of cobalt-60, each consisting of 27000 curies, were placed parallel on two sides of the reactor.

The amount of the monomer polymerized was determined by directly weighing the polymer produced.

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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**, 3029 (1965).
4) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, This Bulletin, in press.
5) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, **A3**, 2931 (1965).
6) S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *ibid.*, in press.

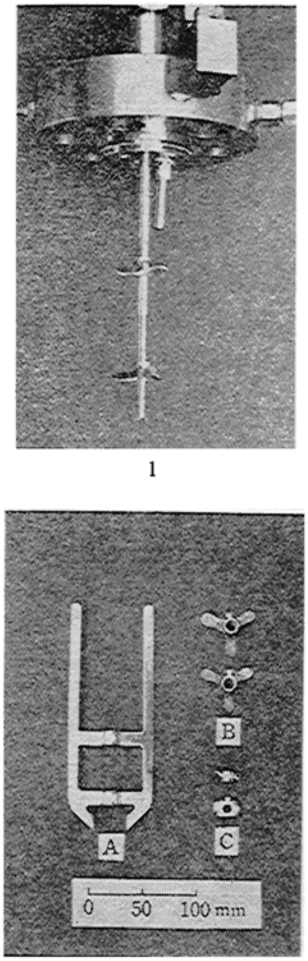

Fig. 2. Impellers.
(1. agitator shaft with magnets and marine propellers of large scale reactor, 2. A, anchor; B, marine propeller; C, propeller with two blades.)

The number-average degree of polymerization was calculated from the intrinsic viscosity using Tung's formula.[7]

Polymerization by Two-Stage Irradiation Method. In order to make a detailed investigation of the effects of agitation on the elementary reactions, the polymerization was carried out in two different stages.[5,6] The first irradiation was carried out at a dose rate of 2.5×10^4 rad/hr under a pressure of 400 kg/cm^2 and at 30°C. This was followed by the second irradiation, at the lower dose rate of 9.0×10^2 rad/hr and under various conditions.

The reaction vessel used was a staineless-steel autoclave with a 100-m*l* capacity. Agitation was carried out by rotating propellers with two blades (C) (shown in Fig. 2). The source of γ-rays was cobalt-60 (5000 curies) in a cylindrical case, outside which the reactor was placed.

Results

Polymer Yield and Degree of Polymerization. The results given in Tables 1 and 2 show the characteristic effects of agitation on the polymer yield and the degree of polymerization. As Table 1 shows, in the case of static runs the exothermic nature of the ethylene polymerization produced a great temperature rise, while in the agitated runs the reaction temperature was kept constant throughout the operation. In Fig. 3, the polymer yield is plotted against reaction time. It may be observed that the rate of polymerization increases

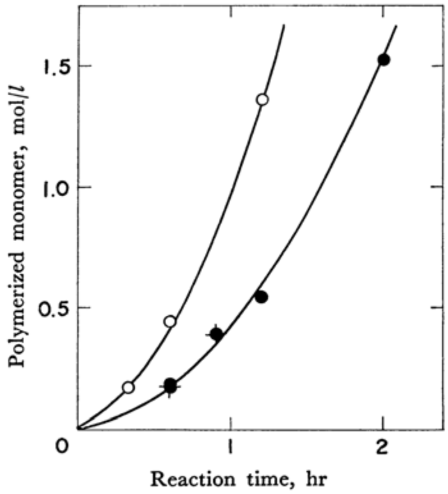

Fig. 3. Polymer yield *vs.* reaction time.

(Reaction conditions: pressure, 400 kg/cm^2; temperature, 30—45°C; dose rate, 3.8×10^5 rad/hr. Agitation: (○) no agitation, (●) 200 rpm, anchor, (-●-) 500 rpm, marine propeller.)

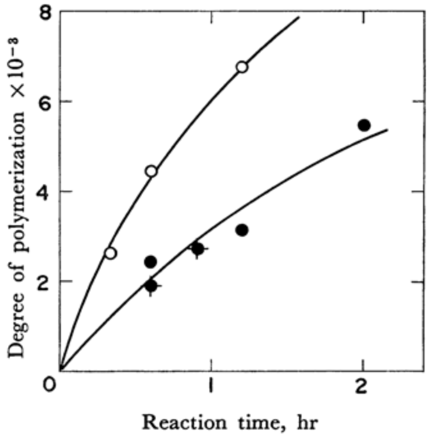

Fig. 4. Degree of polymerization *vs.* reaction time.

(Reaction conditions and notes are the same as Fig. 3.)

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[7] L. H. Tung, *ibid.*, **24**, 333 (1957).

Table 1. Effect of reaction time on polymer yield and degree of polymerization in the polymerization with and without agitation

Run No.	Reaction condition		Agitation		Polymer yield	Degree of polymerization
	Time hr	Temp. °C	Speed rpm	Type of impeller	g	$\times 10^{-3}$
1	0.33	30—34	0	—	4.8	2.61
2	0.6	30—45	0	—	12.4	4.65
3	0.6	30	200	anchor	5.2	2.43
4	0.6	30	500	marine propeller	4.7	1.89
5	0.9	30	500	marine propeller	11.0	2.72
6	1.2	30—45	0	—	38.1	6.79
7	1.2	30	200	anchor	15.3	3.14
8	2.0	30	200	anchor	42.9	5.46

Reaction pressure, 400 kg/cm^2; dose rate, 3.8×10^5 rad/hr; volume of reaction vessel, 1000 m*l*

Table 2. Effect of stirring speed on polymer yield and degree of polymerization

Run No.	Reaction condition		Stirring speed	Polymer yield	Degree of polymerization
	Time hr	Temp. °C	rpm	g	$\times 10^{-3}$
9	0.6	30	10	8.0	3.32
10	0.6	30	50	5.8	2.07
11	0.6	30	500	6.6	2.28
12	0.6	30	800	6.8	2.82

Reaction pressure, 400 kg/cm^2; dose rate, 3.8×10^5 rad/hr; type of agitator, anchor; volume of reaction vessel, 1000 m*l*

Table 3. Results of polymerization in one stage

Run No.	Reaction condition		Stirring speed	Polymer yield	Degree of polymerization
	Time hr	Dose rate rad/hr	rpm	g	$\times 10^{-3}$
13	4.0	9.0×10^2	0	0.490	18.9
14	4.0	9.0×10^2	500	0.165	6.78
15	0.50	2.5×10^4	0	0.140	5.14
16	0.75	2.5×10^4	0	0.381	9.45
17	1.0	2.5×10^4	0	0.740	9.50
18	1.5	2.5×10^4	0	1.554	17.5
19	0.75	2.5×10^4	500	0.163	4.03
20	1.5	2.5×10^4	500	0.482	6.18
21	2.0	2.5×10^4	500	0.912	8.93

Reaction pressure, 400 kg/cm^2; temperature, 30°C
Agitator, propeller with two blades; volume of reaction vessel, 100 m*l*

with the reaction time in both agitated and static systems, although the rate in the agitated system decreases to about 50% that in the static system.

The other characteristic effect of agitation is shown in Fig. 4, in which the degree of polymerization is plotted against the time. It can be seen that the agitation depresses the degree of polymerization to some extent, as has been observed with the polymer yield.

The decreases in polymer yield and in the degree of polymerization are shown as a function of the stirring speed in Fig. 5, where the coefficients of agitation for the polymer yield (ε_{M_p}) and for the degree of polymerization ($\varepsilon_{\bar{P}_n}$) are defined as follows:

$$\varepsilon_{M_p} = \frac{\text{Polymer yield in an agitated system}}{\text{Polymer yield in a static system}}$$

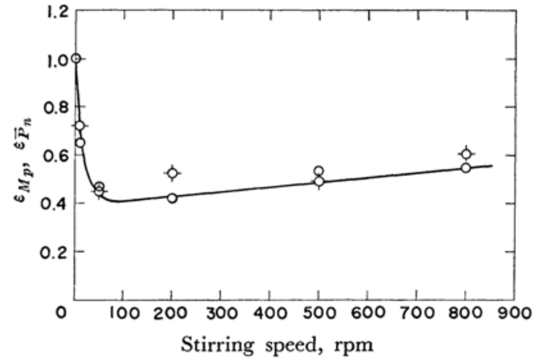

Fig. 5. ε_{M_p} and $\varepsilon_{\bar{P}_n}$ *vs.* stirring speed. (Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 3.8×10^5 rad/hr; agitation, anchor, (○) ε_{M_p}, (-⌽-) $\varepsilon_{\bar{P}_n}$.)

$$\varepsilon_{\bar{P}_n}=\frac{\begin{pmatrix}\text{Degree of polymerization of the}\\ \text{polymer formed in an agitated system}\end{pmatrix}}{\begin{pmatrix}\text{Degree of polymerization of the}\\ \text{polymer formed in a static system}\end{pmatrix}}$$

The agitation causes a sharp decrease in the minimum value in both ε_{M_p} and $\varepsilon_{\bar{P}_n}$ against the stirring speed, and they both slightly increase in the higher range of stirring speed. In addition, the decrease in the polymer yield is found to correspond to that in the degree of polymerization.

Polymerization in Two-stage Irradiation Method. In order to make a detailed investigation of the effects of agitation on the polymerization, ethylene was irradiated in two different stages. The results of the first irradiation are given in Table 3. The effects of agitation on the polymer yield and on the degree of polymerization are found to be similar to those in the large-scale experiments.

The results of the two-stage polymerization described above are given in Tables 4 and 5, where ΔM_p was calculated by this equation.

$$\Delta M_p = M_p - M_p' - M_p''$$

M_p: Total amount of monomer consumed in the polymerization of two stages

M_p': The amount of monomer consumed in the first stage

M_p'': The amount of monomer consumed for the propagation of the radicals produced in the second stage

Hence, the calculated ΔM_p value corresponds to the amount of monomer consumed during the second stage for the propagation of polymer radicals introduced in the first stage. When agitation is made either in the first or in the second stage, the overall propagation rate, *i. e.*, $\Delta M_p/t_{\mathrm{II}}$ (ΔM_p divided by the time of the second stage) markedly decreases, as Tables 4 and 5 show. The rate ($\Delta M_p/t_{\mathrm{II}}$) is reduced by agitation in the first irradiation (0.75 hr) to about 70% of that in the case without agitation in both stages (Table 4). As has been reported previously,[6] the rate is proportional to the time of the first stage (t_{I}) when there

TABLE 4. RESULTS OF TWO-STAGE POLYMERIZATION (1) EFFECT OF AGITATION IN THE FIRST STAGE

Run No.	First stage[a]		Second stage[b]		Total polymer yield	Monomer consumed for propagation
	Time	Stirring speed	Time	Stirring speed	M_p	ΔM_p
	hr	rpm	hr	rpm	g	g
22	0.75	0	2.0	0	0.962	0.458
23	0.75	500	2.0	0	0.606	0.320
24	1.5	500	2.0	0	1.080	0.477
25	2.0	500	2.0	0	1.562	0.527

a) Reaction conditions: Pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr
b) Reaction conditions: Pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 9.0×10^2 rad/hr
Agitator, propeller with two blades; volume of reaction vessel, 100 m*l*

TABLE 5. RESULTS OF TWO-STAGE POLYMERIZATION (2) EFFECT OF AGITATION IN THE SECOND STAGE

Run No.	First stage[a]		Second stage[b]		Total polymer yield	Monomer consumed for propagation
	Time	Stirring speed	Time	Stirring speed	M_p	ΔM_p
	hr	rpm	hr	rpm	g	g
22	0.75	0	2.0	0	0.962	0.458
26	0.75	0	2.0	500	0.671	0.249
27	0.75	0	4.0	500	1.053	0.507

a) Reaction conditions: Pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr
b) Reaction conditions: Pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 9.0×10^2 rad/hr
Agitator, propeller with two blades; volume of reaction vessel, 100 m*l*

is no agitation in either stage. On the contrary, the rate is found not to be proportional to t_I when there is agitation in the first stage. Further, Table 5 shows that, in the propagation without agitation in the first stage and with agitation in the second stage, the rate decreases to 55% of that in the case without agitation in both stages.

Discussion

It has previously been proposed by some of the present authors[2] that the γ-ray induced polymerization of ethylene proceeds by means of the reaction mechanism shown in Table 6. The polymerization is initiated by the interaction between ethylene monomer and γ-rays, and the excited dimer is assumed to add to a radical in the propagation step. Chain termination and transfer are found to be almost negligible at any normal temperature. However, first-order termination with respect to the growing polymer radical begins to occur around 60°C and increases with the temperature.[4] This first-order termination may conceivably be brought about by the reaction of a growing polymer radical with a radical fragment, which can make little contribution to the molecular weight of the high polymer.

Effect of Agitation on Termination Reaction. In order to determine the rate of termination, the following graphical method[8] was applied to the polymerization. The growing-polymer-radical concentration, $[\mathrm{R}\cdot]$ (*i. e.*, $\sum_{n=1}^{\infty}[R_n\cdot]$), at the time t is given as the difference between the total number of radicals produced and the number of radicals which vanish upon termination:

$$[\mathrm{R}\cdot] = \int_0^t R_i \mathrm{d}t - \int_0^t R_t \mathrm{d}t \tag{6}$$

Using Eqs. (1) and (4), and the relation, $M_p \approx \int_0^t R_p \mathrm{d}t$, Eq. (6) becomes:

$$[\mathrm{R}\cdot] = k_i \rho_M I t - \{k_t[\mathrm{Z}]/k_p K_e f_{\mathrm{M}}^2\} M_p \tag{7}$$

Where the concentration of radical fragments acting as terminating agents is assumed to be independent of the time.

TABLE 6. REACTION SCHEMES FOR THE γ-RAY-INDUCED POLYMERIZATION OF ETHYLENE AT NORMAL TEMPERATURE

		Rate	
Initiation	$\mathrm{M} \xrightarrow{k_i} \mathrm{R}_1\cdot$	$R_i = k_i \rho_{\mathrm{M}} I$	(1)
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)
Propagation	$\mathrm{R}_1\cdot + \mathrm{M}_2^* \xrightarrow{k_p} \mathrm{R}_3\cdot$		
	……………………	……………………	
	$\mathrm{R}_{n-2}\cdot + \mathrm{M}_2^* \xrightarrow{k_p} \mathrm{R}_n\cdot$	$R_p = k_p[\mathrm{R}\cdot] f_{\mathrm{M}_2^*}$	(3)
Termination	$\mathrm{R}_n\cdot + \mathrm{Z} \xrightarrow{k_t} P_n$	$R_t = k_t[\mathrm{R}\cdot][\mathrm{Z}]$	(4)
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)

M = ethylene monomer
M^* = excited ethylene
M_2^* = excited ethylene dimer
$\mathrm{R}_n\cdot$ = active polymer chain composed of n monomers
$[\mathrm{R}\cdot]$ = total concentration of all the active polymer chains
Y = substance to which the activity of $\mathrm{R}_n\cdot$ is transfered
$[\mathrm{Y}]$ = concentration of Y
Z = substance by which $\mathrm{R}_n\cdot$ is deactivated
$[\mathrm{Z}]$ = concentration of Z
P_n = dead polymer composed of n monomers
R_i, R_p, R_t and R_{tr} = rates of initiation, propagation termination and transfer reactions
k_i, k_p, k_t and k_{tr} = rate constants of initiation, propagation, termination and transfer reactions
M_p = total amount of monomer polymerized
$\overline{P}_n$ = number-average degree of polymerization
ρ_{M} = density of ethylene
f_{M} = fugacity of ethylene
$f_{\mathrm{M}_2^*}$ = fugacity of an excited ethylene dimer
I = dose rate
K_e = equilibrium constant

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[8] T. Kagiya, M. Izu, K. Fukui and S. Machi, presented at the 14th Polymer Symposium of the Society of Polymer Science, Japan, Kyoto, October, 1965.

By a combination of Eqs. (3) and (7) the rate of polymerization is given as:

$$\mathrm{d}M_p/\mathrm{d}t \simeq R_p = k_i k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 It - k_t[\mathrm{Z}]M_p \qquad (8)$$

Hence, both sides of Eq. (8) may be integrated with respect to the time and may be rearranged to give;

$$\left\{M_p \Big/ \int_0^t M_p \mathrm{d}t\right\} = \frac{1}{2} k_i k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 I \left\{t^2 \Big/ \int_0^t M_p \mathrm{d}t\right\} - k_t[\mathrm{Z}] \qquad (9)$$

According to Eq. (9), the plots of $\left\{M_p \Big/ \int_0^t M_p \mathrm{d}t\right\}$ *vs.* $\left\{t^2 \Big/ \int_0^t M_p \mathrm{d}t\right\}$ give a straight line and an apparent first-order termination rate constant can be obtained from the intercept on the ordinate.

As is shown in Fig. 6, for both static and agitated systems the best fits of most of the points to two straight lines were obtained with a value of the termination rate constant, $k_t[\mathrm{Z}]$ of 1.4 hr^{-1}. This indicates that the agitation has little effect on the termination under these conditions. The fact that the first order termination occurs even in a static system at normal temperatures, in contrast with the results reported previously,[2,3,6,7] may be due to the higher dose rate of γ-rays used. In order to determine the effect of the dose rate on the termination, small-scale experiments at a relatively lower dose rate were carried out. As Fig. 7 shows, no termination is observed in the static system, while the termination rate constant for the agitated system is obtained as 1.0 hr^{-1}. This difference in the effects of agitation on termination between the two cases of a high and a low dose rate may be ascribed to the difference in the concentration of radical fragments.

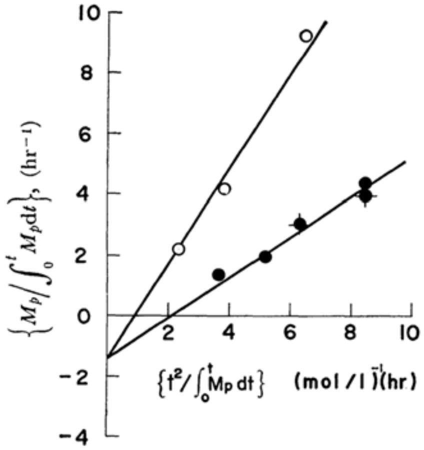

Fig. 6. $\left\{M_p \Big/ \int_0^t M_p \mathrm{d}t\right\}$ *vs.* $\left\{t^2 \Big/ \int_0^t M_p \mathrm{d}t\right\}$.

(Reaction conditions and notes are the same as Fig. 3.)

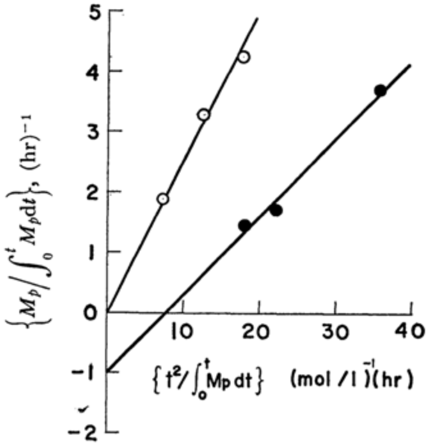

Fig. 7. $\left\{M_p \Big/ \int_0^t M_p \mathrm{d}t\right\}$ *vs.* $\left\{t^2 \Big/ \int_0^t M_p \mathrm{d}t\right\}$.

(Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr. Agitation: (○) no agitation, (●) 500 rpm, propeller with two blades.)

On the other hand, as has been described above, the overall propagation rate ($\Delta M_p/t_{\mathrm{II}}$) is also affected by agitation. The effect of agitation on the termination can be evaluated from the change in the overall propagation rate caused by the agitation in the first stage.

The polymer radical concentration, [R·], at the time t is derived from Eq. (6) as follows:

$$[\mathrm{R}\cdot] = \{k_i \rho_{\mathrm{M}} I / k_t[\mathrm{Z}]\}(1 - e^{-k_t[\mathrm{Z}]t}) \qquad (10)$$

Since ΔM_p is the quantity of the monomer consumed during the second stage for the propagation of polymer radicals introduced in the first stage, the overall propagation rate is given as:

$$\Delta M_p/t_{\mathrm{II}} = \{k_i k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 I / k_t[\mathrm{Z}]\}(1 - e^{-k_t[\mathrm{Z}]t_{\mathrm{I}}}) \qquad (11)$$

When termination in the first stage is negligibly small, *i. e.*, when $k_t[\mathrm{Z}]t_{\mathrm{I}} \ll 1$, Eq. (11) becomes:

$$\Delta M_p/t_{\mathrm{II}} = k_i k_p K_e \rho_{\mathrm{M}} f_{\mathrm{M}}^2 I t_{\mathrm{I}} \qquad (12)$$

indicating that the overall propagation rate is proportional to the irradiation time in the first stage, t_{I}; the relation of Eq. (12) has been shown in a previous paper[6] to be realized in a static system.

When the first-order termination reaction occurs in the first stage, the plots of $\Delta M_p/t_{\mathrm{II}}$ *vs.* $(1-e^{-k_t[\mathrm{Z}]t_{\mathrm{I}}})$ should give a straight line through the point of origin with an appropriate value of $k_t[\mathrm{Z}]$. For the experimental results listed in Table 4, various values of $k_t[\mathrm{Z}]$ have been tested by the trial-and-error method. The plots have been found to be on a straight line, as is shown in Fig. 8, when $k_t[\mathrm{Z}] = 1.0$ hr^{-1}; this is the same as has

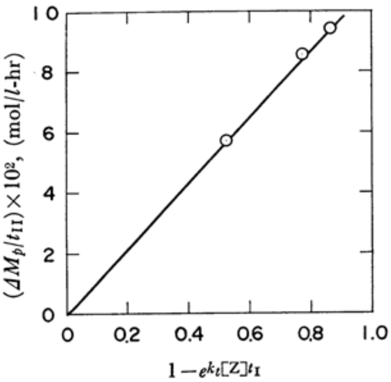

Fig. 8. $\Delta M_p/t_{II}$ vs. $1-e^{-k_t[Z]t_I}$.

(Reaction conditions: First Stage, pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; agitation, 500 rpm, propeller with two blades. Second Stage, pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 9.0×10^2 rad/hr; no agitation.)

been determined above. By using $k_t[Z]=1.0\ \text{hr}^{-1}$ and Eq. (10), it is shown that, in the irradiation of the first stage with agitation for 0.75 hr, about 30% of the polymer radicals produced are deactivated. The coincidence between the two value, experimental and theoretical, leads to the conclusion that the decrease in the overall propagation rate by the agitation in the first stage is due to the decrease in the number of polymer radicals which can survive the entire period of the first stage.

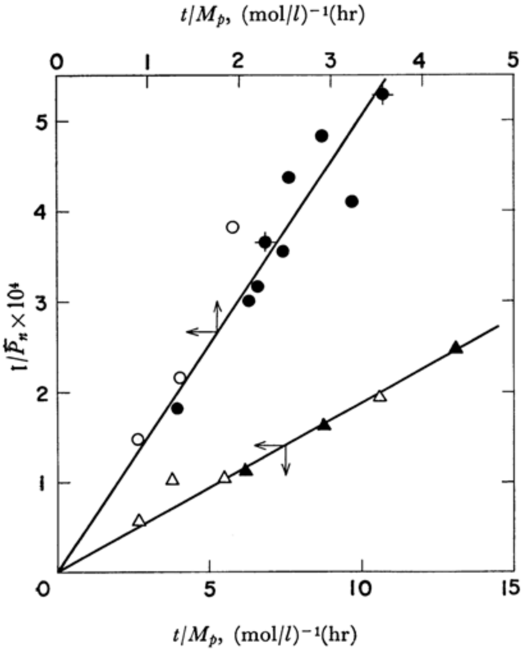

Fig. 9. $\overline{1}/P_n$ vs. t/M_p.

(Reaction conditions: Large Scale, pressure, 400 kg/cm^2; temperature, 30—45°C; dose rate, 3.8×10^5 rad/hr; (○) no agitation, (●) 200 rpm, anchor, (-●-) 500 rpm, marine propeller. Small Scale, pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; (△) no agitation, (▲) 500 rpm, propeller with two blades.)

Effect of Agitation on Initiation and Transfer Reaction. The reciprocal degree of polymerization is given by Eq. (13) for the polymerization without termination by the recombination of growing polymer radicals[2]:

$$1/\bar{P}_n = k_i\rho_M I\{t/M_p\} + k_{tr}[Y]/k_pK_ef_M^2 \qquad (13)$$

Consequently, when $1/\bar{p}_n$ is plotted against t/M_p, a straight line should be obtained. The slope of the line, corresponding to the coefficient of the first term on the right side, gives the rate of initiation, and the intercept which corresponds to the second term represents an additional creation of chain ends by transfer to the Y substance.

In Fig. 9, the results of two series of experiments are plotted by the procedure described above. It can be seen that the agitation has no effect on the initiation rates, which are determined from the slope of each line as 1.84×10^{-6} and 1.5×10^{-4} mol/l/hr for the polymerization on a small and on a large scale respectively. Furthermore, from the fact that both straight lines go through the point of origin, it can be said that the transfer reaction does not take place in the polymerization, irrespective of the agitation. Hence, no effect of agitation was observed on transfer reaction in either small- or large-scale systems.

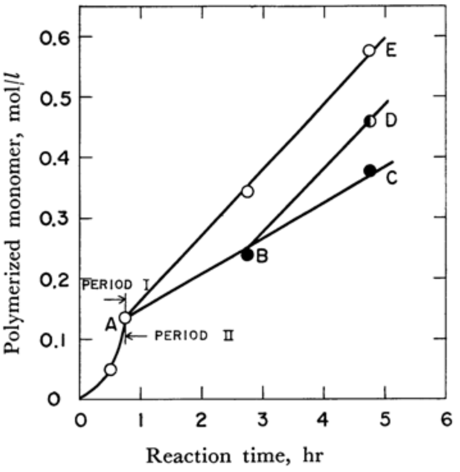

Fig. 10. Effect of agitation on overall propagation rate.

(Reaction conditions: First Stage, pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; no agitation. Second Stage, pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 9.0×10^2 rad/hr; (○) no agitation, (●) 500 rpm, propeller with two blades, (◐) 500 rpm, propeller with two blades (agitation was made during a half period of the second stage.).)

Effect of Agitation on Propagation Reaction. In order to evaluate the effect of agitation on the propagation reaction, several experiments were made by the two-stage irradiation method; the results are shown in Fig. 10. In the first stage for all experiments, ethylene was irradiated in a static system. For an experiment without agitation in the second stage, the polymer increase in this stage is given by a straight line, AE, and in the experiment given by the ABC line, the agitation was continued throughout the second stage. On the other hand, in the case of the ABD line, ethylene was irradiated in an agitated system during a half period of the second stage; *i. e.,* the agitation was stopped at B, and the polymerization was continued in a static system. It can be seen that the slope of the straight line, AE, is almost the same as that of BD. This indicates that the long-lived polymer radicals produced in the first stage are not deactivated by the agitation made in the AB period. It is also shown in Fig. 10 that the slope of the straight line (ABC) in a period with agitation is about a half of that (AE) in a period without agitation. Therefore, it can be said that the overall propagation rate is reduced by the agitation. The absolute propagation rates, *i. e.,* the overall propagation rate divided by the concentration of the long-lived polymer radicals produced in the first stage, have been calculated to be as shown in Table 7. The absolute propagation rate is found to be reduced by agitation to 55% of that in a static system. The mechanism of the retardation is not clear, but it may be ascribed to the fact that the agitation has some effect on the interaction between the gaseous monomer and the growing polymer radical. A careful study of this aspect is being carried out and will be reported on the next paper.

TABLE 7. EFFECT OF AGITATION ON THE ABSOLUTE PROPAGATION RATE

Stirring speed rpm	Absolute propagation rate mol/mol of radical/hr
0	5.70×10^3
500	3.12×10^3

Reaction pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 9.0×10^2 rad/hr
Agitator, propeller with two blades.

The authors wish to thank Mr. C. Hinaji and M. Y. Motoda for their helpful suggestions and the members of the project for their valuable discussions. They are also indebted to Mr. H. Nakajima for his assistance in performing the experimental work.