Radiation-Induced Polymerization of Ethylene in Pilot Plant. IV. Kinetic Analysis

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Synopsis

The kinetics of the radiation-induced polymerization of ethylene in a flow system using *tert*-butyl alcohol aqueous solution as a medium were studied. The polymerization was carried out in a large-scale pilot plant with a 50-liter central source-type reactor at various mean residence times and dose rates under constant pressure of 300 kg/cm^2, temperature of 30°C, and ethylene molar fraction of ca. 0.4. The reaction mixture in the reactor was back-mixed flow from the residual polymer concentration in the reactor. The results of the polymerization were analyzed by kinetic treatment based on a reaction mechanism with both first- and second-order terminations for the propagating radical. The apparent rate constants, except for that of second-order termination (k_{t2}), were consistent with those determined by small-scale batch experiments. The k_{t2} is 20 to 40 times larger than that in the batch experiments. The k_{t2} increases with decrease in mean residence time and with agitation, probably because of mobility of the propagating radical.

INTRODUCTION

Radiation-induced polymerization of ethylene in a pilot plant has been carried out at the Takasaki Radiation Chemistry Research Establishment. In the previous papers,[1-3] we reported a summary of the process development and pilot-scale experimental results of ethylene polymerization in bulk, wet-wall, and heavy-phase recycling processes. In the large-scale pilot plant with a central source-type wet-wall reactor of 50-liter capacity, the continuous discharge of the polymer slurry and production of fine powder polyethylene were successfully performed.[3]

On the other hand, a small-scale batch experiment of ethylene polymerization in *tert*-butyl alcohol containing 5 vol % water has been carried out for the kinetic analysis of the polymerization.[4-6] The experiment showed that the dose rate exponents for polymerization rate, polymer molecular weight, and number of polymer chain were 0.8, −0.1, and 0.9, respectively, in the dose rate range of 3.7 × 10^4 to 1.6 × 10^5 rads/hr. These results were well explained with kinetics of the polymerization containing both first- and second-order terminations for the concentrations of propagating radical. The effects of pressure and amount of medium on the polymerization were investigated and discussed from the kinetic point of view.[5,6]

In this paper the results of the large-scale pilot plant operation were analyzed in relation to the kinetics of the small-scale batch experiments.
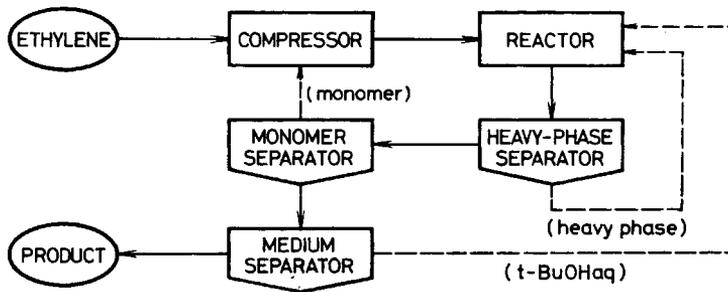
Fig. 1. Block diagram of pilot plant for ethylene polymerization in flow system.

EXPERIMENTAL

Figure 1 shows a block diagram of the pilot plant. Ethylene and *tert*-butyl alcohol aqueous solution (t-BuOHaq) were charged to the reactor, where the polymerization took place by gamma-ray irradiation, and transferred to the separator. The heavy phase in equilibrium with the reaction mixture (light phase) was recycled from the separator to the reactor for preventing polymer deposit. The reaction mixture was reduced in pressure and separated into polymer slurry and unreacted ethylene. The polymer suspended in diluted t-BuOHaq was washed with water and dried to a fine powder polyethylene.

Details of the apparatus and procedure of the large-scale pilot plant were described before.[3]

RESULTS AND DISCUSSION

Flow Pattern in the Reactor

Residence time distribution of the reaction mixture in the reactor is necessary for the kinetic analysis of the polymerization. If the produced polymer flows together with the reaction mixture, the residence time distribution is calculated from the time course of the polymer concentration at the reactor outlet after irradiation is stopped.

Figure 2 is a schematic flow diagram of the reaction mixture, where F and C are the flow rate of the reaction mixture and the polymer concentration, respectively; subscripts 1, 2, and 3 indicate inlet of the reactor and inlet and outlet of the high-pressure separator, respectively; and V_r and V_s are the volumes of the reaction mixture in the reactor and separator, respectively. Since the recycling heavy phase (shaded parts in Fig. 2) contains no reaction mixture, the following equations are given:

$$F_1 = F_2 = F_3 = F$$

$$C_1 = 0$$

$$\theta_r = V_r/F, \qquad \theta_s = V_s/F$$

where θ_r and θ_s are the mean residence times of the reaction mixture in the reactor and separator, respectively.

If the reaction mixture is back-mixed flow in both reactor and separator, the relative polymer concentration at outlet of the separator, $C_r(t)$, is given theoretically by the following equation as a function of time:
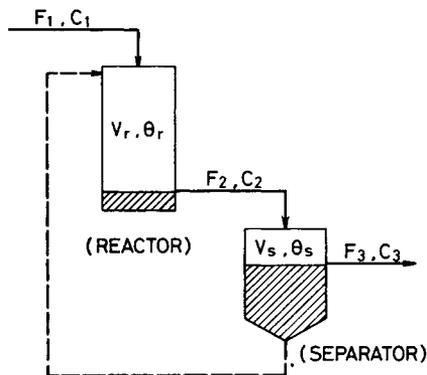
Fig. 2. Schematic flow diagram of reaction mixture in reactor and high-pressure separator. Shaded parts indicate heavy phase.

$$C_r(t) = C_3(t)/C_3(0) = [\theta_r/(\theta_r - \theta_s)] \exp(-t/\theta_r) - [\theta_s/(\theta_r - \theta_s)] \exp(-t/\theta_s)$$

where t is the time after irradiation is stopped.

Figure 3 shows an example of the relative polymer concentration at the outlet of the high-pressure separator. The results agree with the calculated curve by assuming back-mixed flow in both reactor and separator.

Kinetic Consideration of the Polymerization

The elementary steps of the polymerization proposed in the previous paper[4] are

Initiation

$$M \rightarrow R_1^{\cdot} \tag{1a}$$

$$B \rightarrow R_1^{\cdot} \tag{1b}$$

$$W \rightarrow R_1^{\cdot} \tag{1c}$$
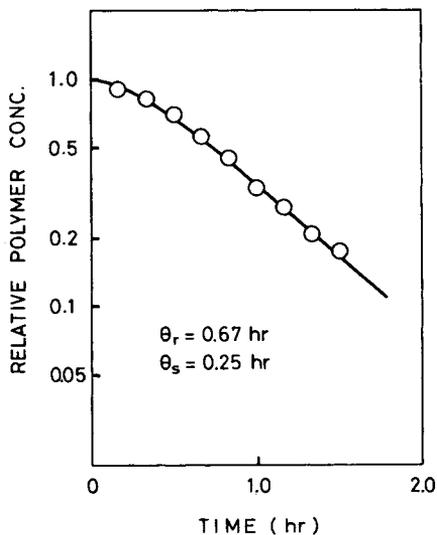
Fig. 3. Change of polymer concentration at outlet of high-pressure separator with time after irradiation is stopped in run 41, where θ_r and θ_s are 0.67 and 0.25 hr, respectively.[3] Solid line is calculated by assuming back-mixed flow in both reactor and separator.

$$R_i = (k_{im}[\mathrm{M}] + k_{ib}[\mathrm{B}] + k_{iw}[\mathrm{W}])I = GI \tag{2}$$

Propagation

$$\mathrm{R}_n{}^{\cdot} + \mathrm{M} \rightarrow \mathrm{R}_{n+1}{}^{\cdot} \tag{3}$$

$$R_p = k_p[\mathrm{R}{\cdot}][\mathrm{M}] = K_p[\mathrm{R}{\cdot}] \tag{4}$$

Transfer

$$\mathrm{R}_n{}^{\cdot} + \mathrm{Y} \rightarrow \mathrm{P}_n + \mathrm{R}_1{}^{\cdot} \tag{5}$$
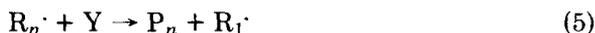
$$R_{tr} = k_{tr}[\mathrm{R}{\cdot}][\mathrm{Y}] = K_{tr}[\mathrm{R}{\cdot}] \tag{6}$$

First-Order Termination

$$\mathrm{R}_n{}^{\cdot} + \mathrm{Z} \rightarrow \mathrm{P}_n \tag{7}$$

$$R_{t1} = k_{t1}[\mathrm{R}{\cdot}][\mathrm{Z}] = K_{t1}[\mathrm{R}{\cdot}] \tag{8}$$

Second-Order Termination

$$\mathrm{R}_m{}^{\cdot} + \mathrm{R}_n{}^{\cdot} \rightarrow \mathrm{P}_{m+n} \tag{9}$$
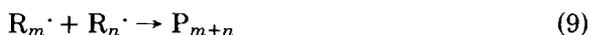
$$R_{t2} = k_{t2}[\mathrm{R}{\cdot}]^2 \tag{10}$$

where M, B, and W denote ethylene, *tert*-butyl alcohol, and water, respectively; $\mathrm{R}_n{}^{\cdot}$ is the propagating radical composed of n monomers; Y is the substance to which the activity of the propagating radical is transferred; Z is the substance by which the propagating radical is deactivated; P_n is dead polymer composed of n monomers; R_i, R_p, R_{tr}, R_{t1}, and R_{t2} are the rates of initiation, propagation, transfer, first-order termination, and second-order termination, respectively; k_{im}, k_{ib}, k_{iw}, k_p, k_{tr}, k_{t1}, and k_{t2} are rate constants; G, K_p, K_{tr}, and K_{t1} are apparent rate constants; and I is the dose rate.

The polymerization is initiated by radicals from ethylene, *tert*-butyl alcohol, and water with gamma-ray irradiation. The propagation proceeds with the addition of monomer to the radicals. First-order termination is brought about mainly by radical occlusion in the polymer, and second-order termination by mutual recombination of the radicals.

As the reaction mixture in the reactor is back-mixed flow, the kinetic analysis in the flow system can be carried out on the basis of the above reaction mechanism.

The material balances of the reactor with respect to the concentrations of the propagating radical [R·], the polymer M_p, and the polymer chain N_p are resulted in

$$\frac{d[\mathrm{R}{\cdot}]}{dt} = GI - K_{t1}[\mathrm{R}{\cdot}] - k_{t2}[\mathrm{R}{\cdot}]^2 - ([\mathrm{R}{\cdot}]/\theta) \tag{11}$$

$$\frac{dM_p}{dt} = K_p[\mathrm{R}{\cdot}] - (M_p/\theta) \tag{12}$$

$$\frac{dN_p}{dt} = GI + K_{tr}[\mathrm{R}{\cdot}] - \tfrac{1}{2}k_{t2}[\mathrm{R}{\cdot}]^2 - (N_p/\theta) \tag{13}$$

where θ is the mean residence time of the reaction mixture in the reactor. By assuming steady state of the operation, we have

$$[R\cdot] = \{[(K_{t1} + 1/\theta)^2 + 4k_{t2}GI]^{1/2} - (K_{t1} + 1/\theta)\}/2k_{t2} \tag{14}$$

$$R_p = M_p/\theta = K_p[R\cdot] \tag{15}$$

$$N_p/\theta = GI + K_{tr}[R\cdot] - (k_{t2}[R\cdot]^2/2) \tag{16}$$

where R_p is the rate of polymerization at steady state of the operation.

From eqs. (14), (15), and (16), we obtain

$$N_p/R_p = a(I/R_p) + b \tag{17}$$

where

$$a = G\theta/2 \tag{18}$$

$$b = \frac{2K_{tr} + K_{t1}}{2K_p}\,\theta + \frac{1}{2K_p} \tag{19}$$

The results of pilot-plant operation at steady state are summarized in Table I together with the reaction conditions. Plots of N_p/R_p versus I/R_p at various mean residence times give straight lines, as shown in Figure 4. As we know from eq. (17), the slope and the intercept of the line give a and b. The slope a is plotted against mean residence time in Figure 5, which gives a straight line through the origin as expected from eq. (18). From the slope of the straight line, G is 2.5×10^{-9} mole/l.-rad. A plot of b versus mean residence time also gives a straight line as in Figure 6. The slope and intercept of the line give $(2K_{tr} + K_{t1})/2K_p = 4.6 \times 10^{-5}$ and $\tfrac{1}{2}K_p = 5.0 \times 10^{-5}$ hr, respectively.

The rate constant by small-scale batch experiment[4] indicates that a substantial transfer reaction does not take place. Assuming $K_{tr} = 0$, we obtain $K_p = 1.0 \times 10^4$ hr^{-1} and $K_{t1} = 0.9$ hr^{-1}.

From eqs. (14) and (15), we also obtain the following relation:

$$R_p = c(I/R_p) - d \tag{20}$$

where

$$c = K_p{}^2G/k_{t2} \tag{21}$$

$$d = (K_p/k_{t2})(1/\theta) + (K_pK_{t1}/k_{t2}) \tag{22}$$

TABLE I
Results of Pilot Plant Operation[a]

Mean residence time, hr	Dose rate $\times 10^{-5}$, rad/hr	Ethylene molar fraction	Rate of polymerization, mole/l. hr	Molecular weight $\times 10^{-4}$	Concn. of polymer chains $\times 10^4$, mole/l.
0.36	0.45	0.37	0.168	5.5	0.308
0.36	1.0	0.39	0.282	5.0	0.569
0.36	1.7	0.35	0.346	3.5	0.998
0.76	0.45	0.41	0.200	7.0	0.608
0.74	1.0	0.41	0.357	6.5	1.14
0.72	1.7	0.40	0.432	4.5	1.94
1.05	0.45	0.37	0.271	8.9	0.897
1.09	1.0	0.37	0.396	7.3	1.66
1.07	1.7	0.39	0.554	5.3	3.13

[a] Reaction conditions: pressure, 300 kg/cm^2; temperature, 30°C.
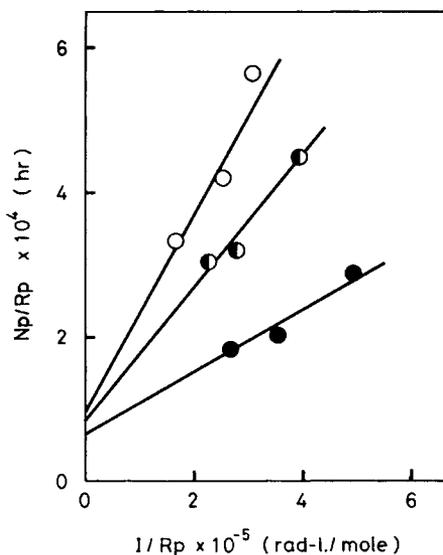
Fig. 4. Plot of N_p/R_p vs. I/R_p at various mean residence times: [●] 0.36 hr; [◐] 0.72–0.76 hr; [○] 1.05–1.09 hr. Reaction conditions: pressure, 300 kg/cm²; temperature; 30°C; ethylene molar fraction, ca. 0.4.

Equation (20) indicates that a plot of R_p against I/R_p gives a straight line the slope of which is constant, independent of the mean residence time. As shown in Figure 7, however, the slope of the line decreases with decrease in the mean residence time. This seems to be caused by the increase of the rate of second-order termination. The rate constant of second-order termination, k_{t2}, apparently increases with decrease in the mean residence time.

From K_p and G, the apparent rate constant of second-order termination k_{t2} is in the range of 1.1×10^5 to 2.5×10^5 l./mole-hr under the reaction conditions shown in Table I.
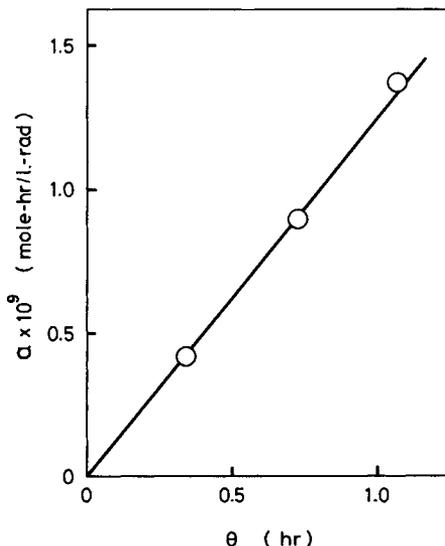
Fig. 5. Plot of a vs. θ.
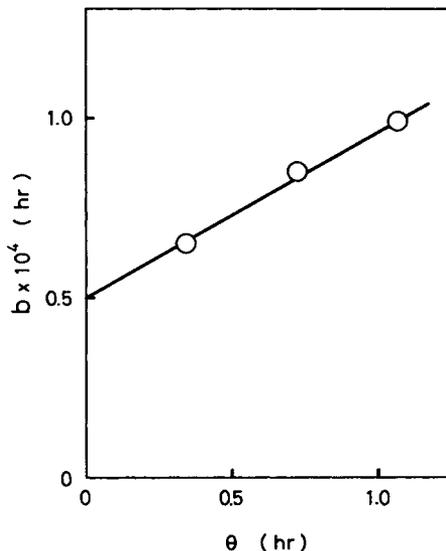
Fig. 6. Plot of b vs. θ.

In this heterogeneous reaction system, it is concluded that the polymerization proceeds through the propagating chain in two different physical states, a loose state and a rigid one, where the mobility of the propagating chain is different.[7] In the loose state, the propagating chain is more mobile and second-order termination is predominant.

The increase in k_{t2} with decrease in mean residence time is explained by the fact that the fraction of the propagating chain in the loose state is increased. The explanation is consistent with the small-scale batch experiment[8] where low molecular weight fraction of polymer increases at shorter reaction time.
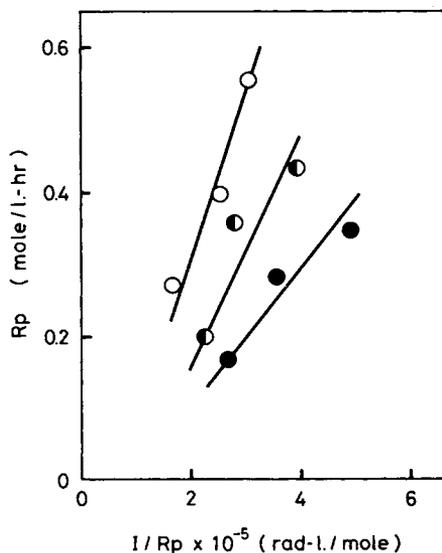
Fig. 7. Plot of R_p vs. I/R_p at various mean residence times. Reaction conditions and symbols are the same as in Fig. 4.
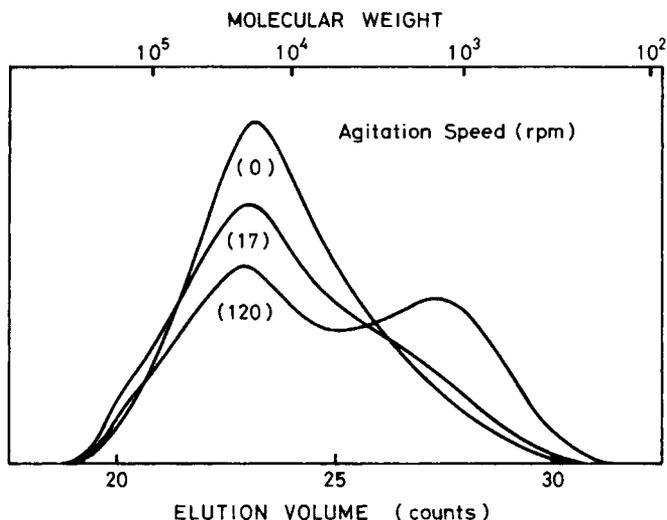
Fig. 8. Effect of agitation on molecular weight distribution of polymer formed by batch polymerization of ethylene in *tert*-butyl alcohol containing of 7 vol % water. Reaction conditions: pressure, 300 kg/cm^2; temperature, 25°C; dose rate, 1.3 × 10^5 rads/hr; amount of *tert*-butyl alcohol aqueous solution, 70 ml in 100 ml reactor; reaction time, 2 hr; agitation blade, propeller.

In batch experiments without agitation at 300 kg/cm^2, G is 2.2 × 10^{-9} mole/l. rad, K_p is 5.6 × 10^3 hr^{-1}, K_{t1} is 1.22 hr^{-1}, and k_{t2} is 6.4 × 10^3 l./mole hr.[9] The apparent rate constants of elementary reactions obtained in the flow system are consistent with the above constants, except for large k_{t2}. The k_{t2} of 5 × 10^4 l./mole hr at longer residence time is larger than that in the batch system. This may be due to the effect of agitation in the flow system.

As shown in Figure 8, the unimodal molecular weight distribution of the polymer changes to the bimodal distribution when agitation is applied. The peak at higher molecular weight is decreased with agitation, while the peak at lower molecular weight is increased. This result can be attributed to the increased mobility of the polymer radical with agitation. The larger k_{t2} is mainly due to both agitation and the short mean residence time. The slightly higher value of K_p than that in the batch experiment may be due to the increase in the monomer diffusion rate by agitation.

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