

Radiation-Induced Seeded Copolymerization of Tetrafluoroethylene with Propylene. II. Kinetic Analysis

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Synopsis

The radiation-induced seeded copolymerization of tetrafluoroethylene with propylene was kinetically analyzed by assuming that growing radical in polymer particle is deactivated by degradative chain transfer to propylene and/or by recombination with newly entered radical which grows for a while before recombination. Apparent rate constant of initiation is 2.6×10^{-9} mole/liter rad independent of the monomer composition in polymer particles. Apparent rate constant of propagation lies in the range of 10^5 hr⁻¹ increasing with tetrafluoroethylene fraction. Change in apparent rate constant of chain transfer with propylene fraction suggests that first-order termination by radical occlusion or radical escape to aqueous phase may occur simultaneously with the degradative chain transfer. Average number of radical in a particle is found to increase with dose rate and levelled off at the value of 0.9. The higher value above 0.5 is explained by Trommsdorff effect. The dose rate exponent of average number of radical changes from 1 to 0 with increasing dose rate. This change is consistent with the dose rate effect on the polymerization rate under the constant number of polymer particles.

INTRODUCTION

In emulsion polymerization, number of polymer particles and monomer concentration play an important role in determining polymerization rate and polymer molecular weight. For an example, the rate of polymerization is proportional to the number of polymer particles and the monomer concentration for styrene.¹ Accordingly, in case of seeded polymerization under the constant monomer concentration, the polymerization rate must be independent of dose rate corresponding to radical initiator concentration. In the seeded copolymerization of tetrafluoroethylene with propylene by radiation, however, the rate of polymerization is proportional to the 0.5–0.9 power of the dose rate depending on both dose rate and monomer composition in polymer particles.² This is explained by considering that first-order termination by degradative chain transfer of propagating radical to propylene becomes predominant with increasing propylene fraction in the particles and decreasing the dose rate. In this copolymerization, the number of polymer particles as well as the dose rate are important factors to determine an interval of radical entrance from aqueous phase to the particle.

Quantative understanding of kinetics and mechanism of the reaction is difficult in this emulsion copolymerization started from emulsifier-water system because the number of polymer particles cannot be determined clearly due to the indistinct picture of the particles in electron microscopy.

In this paper, the results of seeded copolymerization² is kinetically analyzed by considering the mechanism containing both first-order termination by degradative chain transfer to propylene and second-order termination by mutual recombination for the propagating radicals.

EXPERIMENTAL

Apparatus and Procedure

The copolymerization was carried out in a 5 liter autoclave by semibatch operation at a controlled pressure of 25 kg/cm², a temperature of 40°C, and an agitation speed of 500 rpm. Details were described in the previous paper.²

Molecular Weight Distribution

Molecular weight distribution was measured by using a high-speed liquid chromatograph (Waters Associates Model ALC 201) with a four-column series of nominal pore sizes 10³, 10⁴, 10⁵, 10⁶ Å of μ -Styragel. The measurement was carried out at a room temperature with tetrahydrofuran as a solvent at a flow rate of 1.0 ml/min. The gel permeation chromatography (GPC) calibration curve was obtained with standard polystyrene.

RESULTS AND DISCUSSION

Molecular Weight Distribution

Figure 1 shows molecular weight distributions of polymer produced by radiation-induced seeded copolymerization of tetrafluoroethylene with propylene

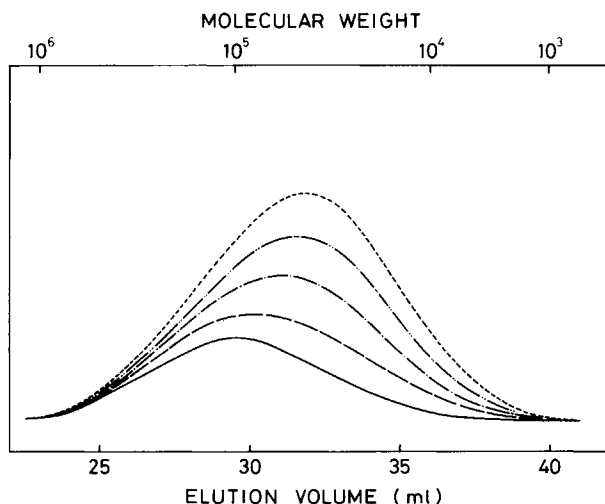


Fig. 1. Molecular weight distributions of polymers formed at various reaction times (hr): (—) 0 (seed polymer); (---) 3; (-·-·) 6; (····) 9; (- - - -) 12. Reaction conditions: pressure, 25 kg/cm²; temperature, 40°C; dose rate, 8.8×10^4 rad/h; propylene mole% in polymer particles, 71.4%; agitation speed, 500 rpm. Peak area of the distribution is proportional to polymer concentration in latex.

at various reaction times. Under the reaction conditions of lower dose rate and higher propylene fraction of monomer mixture in polymer particles, the fraction of lower molecular weight increases and molecular weight at the peak shifts from 1×10^5 to 4×10^4 with the reaction time. The distribution curves in Figure 1 are normalized in such a way that the area is proportional to the polymer concentration in latex. A distribution curve of newly produced polymer in a certain range of reaction time can be then calculated from the difference of two distribution curves in Figure 1.

Figure 2 shows distribution curves calculated as well as the curve of seed polymer. The calculated distribution curves at various reaction time ranges are almost same in peak molecular weight (about 4×10^4) and in the shape ($\overline{M}_w/\overline{M}_n = 2-3$). This fact suggests that the polymerization proceeds almost steadily through the whole reaction time when the reaction conditions are kept constant.

Mechanism and Kinetics

For the seeded copolymerization by radiation, following characteristics are made clear under the experimental conditions. Rate of polymerization increases with increasing the dose rate and decreasing propylene fraction in the particles. Molecular weight of the polymer increases with decreasing propylene fraction. The molecular weight is almost independent of the dose rate at higher propylene fraction, and decreases with the dose rate at lower propylene fraction. Monomer concentration and composition in polymer particles are nearly constant during the polymerization.

From these facts, we propose the elementary reactions (1) to (8), with following assumptions: (a) growing radical in a particle is deactivated by degradative chain transfer to propylene and by recombination with newly entered radical which grows for a while before recombination; (b) allyl radical formed by chain transfer

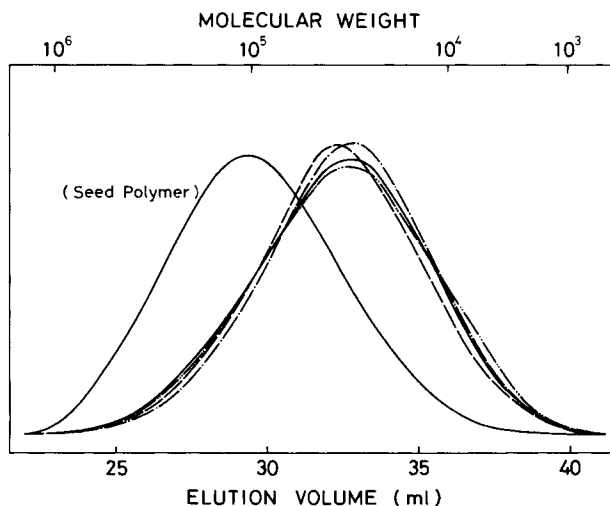
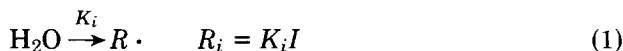


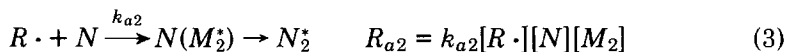
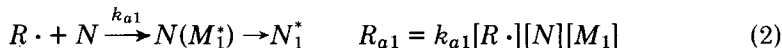
Fig. 2. Calculated distribution curves of polymers formed at various reaction periods (h): (—) 0-3; (---) 3-6; (-·-·) 6-9; (-·-·-·) 9-12. Reaction conditions are the same as in Figure 1. Peak areas are normalized.

reaction cannot reinitiate the polymerization; (c) rates of polymerization and radical recombination in aqueous phase are negligibly small; (d) propagation rate is independent of propagating chain length.

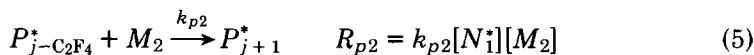
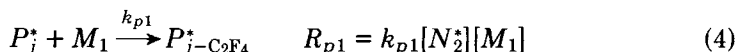
Elementary reactions and reaction rates are given in eqs. (1) to (8):
initiation:



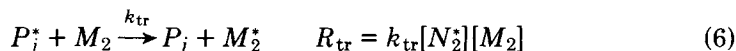
activation of particles:



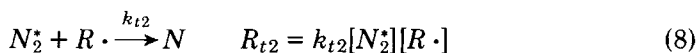
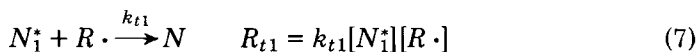
propagation in particles:



chain transfer to propylene:



deactivation of particles:



where $R \cdot$ is an initiating radical formed in aqueous phase by radiation, I is the dose rate, N is a nonactive polymer particle, and N_1^* and N_2^* are active polymer particles containing a growing tetrafluoroethylene radical and a growing propylene radical, respectively. $N(M_1^*)$ and $N(M_2^*)$ denote polymer particles containing a tetrafluoroethylene monomer radical and a propylene monomer radical, respectively. P_j^* and $P_{j-C_2F_4}^*$ are growing propylene and tetrafluoroethylene radicals composed of j units of $(-C_2F_4-C_3H_6-)$. M_1 and M_2 are tetrafluoroethylene and propylene monomers, respectively. P_j is a dead polymer and M_2^* is a stable allyl radical. R_i , R_a , R_p , R_{tr} , R_t and K_i , k_a , k_p , k_{tr} , k_t are rates and rate constants of initiation, activation of particles, propagation in particles, chain transfer to propylene, and deactivation of particles, respectively.

The differential equations can be formulated for the respective active species using the elementary steps shown above.

Radical concentration in the aqueous phase $[R \cdot]$:

$$\begin{aligned} \frac{d[R \cdot]}{dt} &= K_i I - (k_{a1}[M_1] + k_{a2}[M_2])[R \cdot][N] - (k_{t1}[N_1^*] + k_{t2}[N_2^*])[R \cdot] \\ &= K_i I - K_a [R \cdot][N] - K_t [R \cdot][N^*] \quad (9) \end{aligned}$$

where

$$K_a = k_{a1}[M_1] + k_{a2}[M_2] \quad (10)$$

$$K_t = (1 - \alpha)k_{t1} + \alpha k_{t2} \quad (11)$$

$$\alpha = [N_2^*]/[N^*] \quad (12)$$

$$[N^*] = [N_1^*] + [N_2^*] \quad (13)$$

Number of active polymer particles containing a growing tetrafluoroethylene and a growing propylene radical $[N_1^*]$ and $[N_2^*]$:

$$\frac{d[N_1^*]}{dt} = k_{a1}[R \cdot][N][M_1] + k_{p1}[N_2^*][M_1] - k_{p2}[N_1^*][M_2] - k_{t1}[R \cdot][N_1^*] \quad (14)$$

$$\begin{aligned} \frac{d[N_2^*]}{dt} = & k_{a2}[R \cdot][N][M_2] + k_{p2}[N_1^*][M_2] \\ & - k_{p1}[N_2^*][M_1] - k_{tr}[N_2^*][M_2] - k_{t2}[N_2^*][R \cdot] \end{aligned} \quad (15)$$

As far as the consumption of the initiating radicals, K_t is equal to K_a , eq. (9) becomes

$$\frac{d[R \cdot]}{dt} = K_i I - K_a [R \cdot][N_T] \quad (16)$$

where

$$[N_T] = [N] + [N^*] \quad (17)$$

By assuming a steady state of the reaction, eqs. (18) and (19) are obtained

$$[R \cdot] = K_i I / K_a [N_T] \quad (18)$$

$$[N^*] = \{K_a [R \cdot] / (K_a [R \cdot] + K_t [R \cdot] + K_{tr})\} [N_T] \quad (19)$$

where

$$K_{tr} = \alpha k_{tr}[M_2] \quad (20)$$

As the copolymerization of tetrafluoroethylene with propylene is alternative in the wide monomer composition³ and the copolymers with high molecular weight are obtained, the propagation rates R_{p1} and R_{p2} must be approximately equal

$$k_{p1}[N_2^*][M_1] = k_{p2}[N_1^*][M_2] \quad (21)$$

From eqs. (12) and (21), we get

$$\alpha = \frac{[N_2^*]}{[N^*]} = \frac{k_{p2}[M_2]}{k_{p1}[M_1] + k_{p2}[M_2]} \quad (22)$$

Equation (22) indicates that α depends only on the monomer composition in polymer particles.

Following rate equations are given for the polymerized monomer M_p and the number of polymer chains N_p :

$$\begin{aligned} \frac{d[M_p]}{dt} = & k_{p1}[N_2^*][M_1] + k_{p2}[N_1^*][M_2] \\ = & \{\alpha k_{p1}[M_1] + (1 - \alpha)k_{p2}[M_2]\} [N^*] \end{aligned}$$

$$= \frac{2k_{p1}[M_1]k_{p2}[M_2]}{k_{p1}[M_1] + k_{p2}[M_2]} [N^*] = K_p [N^*] \quad (23)$$

$$\frac{d[N_p]}{dt} = K_a [R \cdot] [N] = K_a [R \cdot] ([N_T] - [N^*]) \quad (24)$$

where

$$K_p = \frac{2k_{p1}[M_1]k_{p2}[M_2]}{k_{p1}[M_1] + k_{p2}[M_2]} \quad (25)$$

The rate of polymerization R_p and the number-average degree of polymerization \bar{P} at steady state are shown in eqs. (26) and (27), respectively,

$$R_p = \frac{d[M_p]}{dt} = K_p [N^*] \quad (26)$$

$$\bar{P} = \left(\frac{d[M_p]}{dt} \right) / \left(\frac{d[N_p]}{dt} \right) \quad (27)$$

Combining eqs. (18), (19), and (26), a relation between rate of polymerization and dose rate is given by

$$\frac{[N_T]}{R_p} = \frac{1}{K_p} + \frac{K_t}{K_p K_a} + \frac{K_{tr}}{K_p K_i} \left(\frac{[N_T]}{I} \right) \quad (28)$$

Relation between degree of polymerization and dose rate is also given in eq. (29) from eqs. (18), (19), (23), (24), and (27):

$$\frac{1}{\bar{P}} = \frac{K_i K_t}{K_p K_a} \left(\frac{I}{[N_T]} \right) + \frac{K_{tr}}{K_p} \quad (29)$$

Plots of $[N_T]/R_p$ vs. $[N_T]/I$ at various monomer compositions in polymer particles give straight lines as shown in Figure 3; the slope of the straight line and the intercept of the extrapolated line are equal to $K_{tr}/K_p K_i$ and $(1/K_p + K_t/K_p K_a)$ from the relationship in eq. (28). Plots of $1/\bar{P}$ against $I/[N_T]$ at various monomer compositions are also given by straight lines as in Figure 4. As we know from eq. (29), the slope and the intercept of the straight line give $K_i K_t/K_p K_a$ and K_{tr}/K_p at each monomer composition in the particles. The values K_i , K_p , K_{tr} , and K_t/K_a at various monomer compositions can be determined from the slopes and the intercepts of the lines using the polymerization results shown in Table I, and the results are summarized in Table II.

Figure 5 shows that apparent rate constant of initiation K_i is nearly constant independent of the monomer composition in the particles. The value of 2.6×10^{-9} mole/liter rad is consistent in the order of magnitude with that calculated from G value for radical formation from water (5.5).⁴ The decrease in K_i at higher propylene fraction may be due to the formation of propylene radical in aqueous phase by increasing propylene solubility in water.

As shown in Figure 6, apparent rate constant of propagation K_p is in the order of 10^5 hr⁻¹ and is proportional to the tetrafluoroethylene concentration which is calculated from dissolved amounts of tetrafluoroethylene and propylene in the particles by assuming their critical molar volumes and polymer density of 1.46 g/cm³. The proportionality shows that $k_{p1}[M_1]$ is negligibly small compared with $k_{p2}[M_2]$ in eq. (25) and α is nearly equal to 1 in eq. (22) under the experimental range.

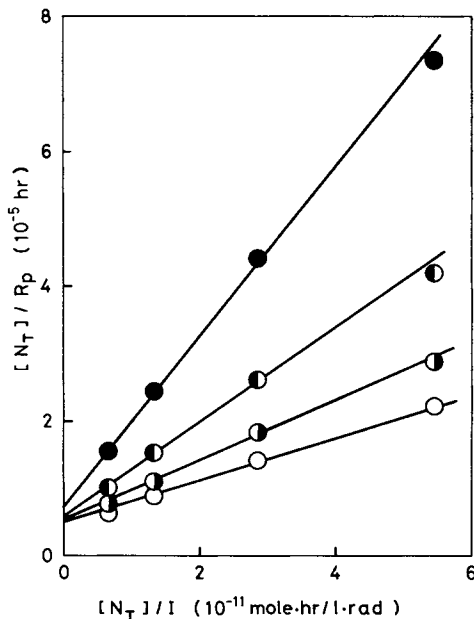


Fig. 3. $[N_T]/R_p$ vs. $[N_T]/I$ at various propylene mole % in polymer particles: (○) 10%; (◐) 30%; (◑) 50%; (●) 70%. Other reaction conditions: pressure, 25 kg/cm²; temperature, 40°C; agitation speed, 500 rpm.

Apparent rate constant of chain transfer to propylene K_{tr} is expected to increase in proportion to the propylene concentration as shown in eq. (20). In fact, K_{tr} increases with propylene concentration as shown in Figure 7. However, the line does not pass through origin. This deviation from eq. (20) suggests that

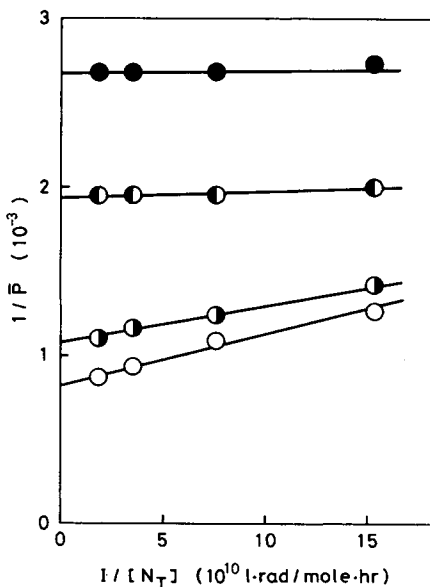


Fig. 4. $1/\bar{P}$ vs. $I/[N_T]$ at various propylene mole% in polymer particles. Symbols and reaction conditions are the same as in Figure 3.

TABLE I
 Data Used in this Kinetic Analysis^a

Dose rate (rad/h)	Polymerization rate [mol/liter h]						Degree of polymerization (10^2)			
	Mole ratio in particles (C_2F_4/C_3H_6)						Mole ratio in particles (C_2F_4/C_3H_6)			
	90/10	70/30	50/50	30/70	90/10	50/50	70/30	50/50	90/10	30/70
4.6×10^4	0.113	0.087	0.060	0.034	11.7	9.1	5.1	5.1	3.7	3.7
8.8×10^4	0.179	0.137	0.096	0.056	10.7	8.6	5.1	5.1	3.7	3.7
1.9×10^5	0.292	0.229	0.165	0.103	9.1	8.1	5.1	5.1	3.7	3.7
3.8×10^5	0.419	0.333	0.247	0.162	8.0	7.0	5.0	5.0	3.6	3.6

^a Details are described in previous paper. Polymerization rate and degree of polymerization are calculated by assuming $(C_2F_4-C_3H_6)$ as monomer unit.

TABLE II
Results of Kinetic Analysis

Mole ratio in particles (C ₂ F ₄ /C ₃ H ₆)	$\frac{1}{K_p} + \frac{K_t}{K_p K_a}$ (h) ($\times 10^{-6}$)	$\frac{K_{tr}}{K_p K_i}$ (L rad/mol)	$\frac{K_{tr}}{K_p}$ (-)	$\frac{K_i K_t}{K_p K_a}$ (mol h/L rad)	K_i (mol/L rad) ($\times 10^{-9}$)	K_p (h ⁻¹) ($\times 10^5$)	K_{tr} (h ⁻¹) ($\times 10^2$)	$\frac{K_t}{K_a}$ (-)
90/10	5.0	3.1×10^5	8.3×10^{-4}	2.7×10^{-15}	2.7	2.5	2.0	0.25
70/30	5.5	4.3×10^5	1.1×10^{-3}	2.2×10^{-15}	2.6	2.2	2.4	0.19
50/50	6.0	7.1×10^5	1.9×10^{-3}	4.0×10^{-16}	2.6	1.7	3.2	0.02
30/70	7.5	1.2×10^6	2.7×10^{-3}	2.0×10^{-16}	2.3	1.3	3.8	0.01

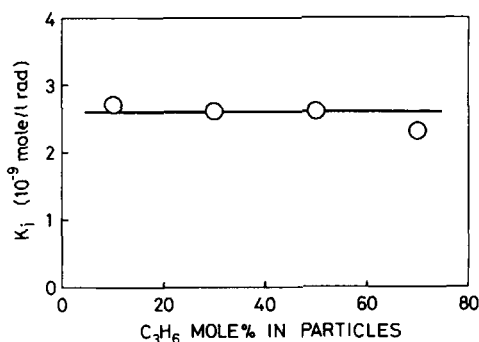


Fig. 5. Apparent rate constant of initiation K_i vs. propylene mole % in polymer particles.

first-order termination by radical occlusion or radical escape to aqueous phase may occur simultaneously with the degradative chain transfer.

The ratio of apparent rate constants for deactivation and activation of particles K_t/K_a increases with tetrafluoroethylene fraction as in Table II. The increase in K_t/K_a must be due to the change in K_t , because K_a is assumed to be scarcely affected by monomer composition. The change in K_t is explained by assuming that k_{t1} is extremely larger than k_{t2} , that is, growing tetrafluoroethylene radical is more active than growing propylene radical even in termination reaction by

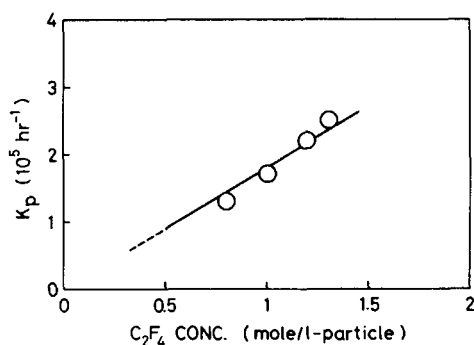


Fig. 6. Apparent rate constant of propagation K_p vs. tetrafluoroethylene concentration in polymer particles.

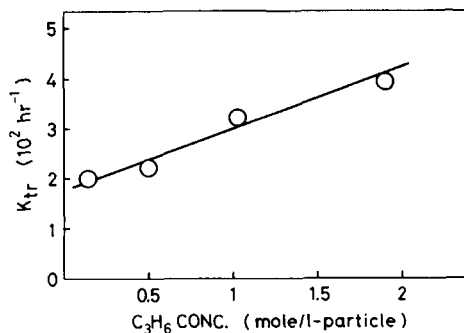


Fig. 7. Apparent rate constant of chain transfer to propylene K_{tr} vs. propylene concentration in polymer particles.

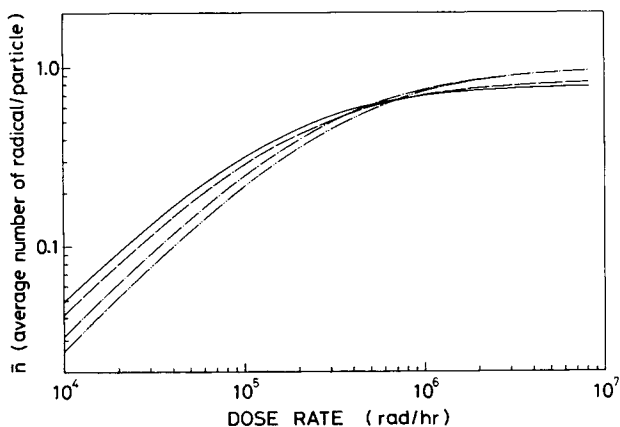


Fig. 8. Average number of radical in a particle versus dose rate at various propylene mole % in polymer particles: (—) 10%; (--) 30%; (-·-·) 50%; (- - -) 70%.

recombination. In case that a propagating radical recombines immediately with newly entered radical from aqueous phase, K_t is equal to K_a . Smaller K_t/K_a than 1 suggests that recombination of radicals takes place after newly entered radical grows for a while probably because of poor polymer mobility.

Figure 8 shows log-log plots of dose rate and average number of radicals in each particle (\bar{n}) at various monomer compositions. The \bar{n} increases in proportion to the dose rate at lower dose rate region and levels off at higher dose rate. The dose rate exponent of \bar{n} , which is correspond to that of polymerization rate under constant number of polymer particles, changes from 1 to 0 with increasing dose rate. In the experimental dose rate range, it lies in the range of 0.85 to 0.3 being consistent with the experimental result.² The increase of \bar{n} at lower dose rate is explained by the fact that the propagating radical is deactivated before a new radical enters from aqueous phase. Higher \bar{n} than 0.5 at higher dose rate region is explained by Trommsdorff effect,⁵ that is, a polymer particle contains two radicals, propagating polymer radical and newly entered radical, for a while probably because of poor polymer mobility at poor monomer concentration.

In summary, seeded copolymerization of tetrafluoroethylene with propylene by radiation could be kinetically treated based on the mechanism taking account both first-order and second-order terminations, and apparent rate constants of initiation, propagation, and chain transfer were determined. The average number of radical in a particle is found to increase in proportion to the dose rate at lower dose rate region and to level off at about 0.9 with increasing dose rate. The higher value above 0.5 at higher dose rate is explained by Trommsdorff effect. Dose rate exponent of the average number of radical is found to change from 1 to 0 with dose rate. The change is consistent with dose rate effect on polymerization rate under constant number of polymer particles.

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