

# Radiation-Induced Seeded Copolymerization of Tetrafluoroethylene with Propylene. I. Effects of Agitation and Dose Rate

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## Synopsis

Seeded copolymerization of tetrafluoroethylene with propylene by radiation was studied by semibatch experiment at a constant pressure of 25 kg/cm<sup>2</sup>, a temperature of 40°C, and at various dose rates and monomer compositions in polymer particles. The polymerization rate and polymer molecular weight are in the ranges of 5.6–58.7 g/h·L-H<sub>2</sub>O and  $4.6 \times 10^4$ – $1.6 \times 10^5$ , respectively. The polymerization rate increases with agitation speed up to 300 rpm and slightly decreases above 500 rpm. The polymer molecular weight is the highest at 300 rpm. The polymerization rate and polymer molecular weight increase with tetrafluoroethylene fraction. At lower tetrafluoroethylene fraction, the polymerization rate is proportional to the 0.7–0.9 power of the dose rate and the polymer molecular weight is almost independent. The dose rate effects are explained by considering that first-order termination by degradative chain transfer to propylene is predominant at a lower tetrafluoroethylene fraction. Decrease in the dose rate dependence of the polymerization rate and increase in that of the polymer molecular weight with the tetrafluoroethylene fraction are due to the increase in second-order termination by recombination.

## INTRODUCTION

A series of investigations on radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene has been carried out in the Takasaki Radiation Chemistry Research Establishment.<sup>1–6</sup> In the emulsion copolymerization, high molecular weight, amorphous, rubberlike polymer with alternating structure was obtained. It was also reported that the rate of polymerization and the molecular weight of copolymer increase with the tetrafluoroethylene fraction in monomer mixture, and the rate of polymerization is proportional to the 0.3 power of the emulsifier concentration and the 0.7 power of the dose rate above the critical micelle concentration.<sup>4</sup>

The important factors governing the emulsion copolymerization are the number of polymer particles where polymerization takes place, and the monomer concentration and composition in the particles. In the copolymerization, monomer composition in polymer particles affects both the propagation and termination reactions, that is, the increase of the tetrafluoroethylene fraction brings about the increase of propagation rate and the decrease of first-order termination rate by depression of degradative chain transfer to propylene.

In this work, seeded copolymerization of tetrafluoroethylene with propylene by radiation was carried out in order to elucidate the effects of agitation and dose rate at constant number of polymer particles. We describe the agitation effects on the rate of polymerization and polymer molecular weight in connection with monomer concentration and composition in particles. The effects of dose rate at various monomer compositions were discussed on the basis of the reaction

mechanism containing both first-order and second-order terminations for the propagating radicals.

## EXPERIMENTAL

### Monomers

The tetrafluoroethylene (purity 99.9%) offered by the Asahi Glass Co. and research grade propylene (purity 99.7%) were used as received.

### Seed Latex

Seed latex of tetrafluoroethylene-propylene copolymer was prepared in a 30-L autoclave by radiation-induced emulsion polymerization. The polymerization was carried out at the controlled pressure of 30 kg/cm<sup>2</sup>, temperature of 40°C, dose rate of  $1.0 \times 10^5$  rad/h, monomer composition of about 75 mol % tetrafluoroethylene and 25 mol % propylene, agitation speed of 100 rpm, and emulsifier concentration of 10 g/L-H<sub>2</sub>O. The emulsifier used was ammonium perfluorooctanate (FC-143, purity 96%) obtained from 3M. Distilled water was used.

The polymer concentration in the seed latex was 39.0 g/L-H<sub>2</sub>O, and the number average molecular weight of polymer was  $10.5 \times 10^4$ .

### Apparatus and Procedure

The polymerization was carried out by a semibatch operation at a constant pressure of 25 kg/cm<sup>2</sup> and a temperature of 40°C. The flow sheet of the apparatus is shown in Figure 1.

The reaction vessel was a stainless steel autoclave (5 L) equipped with an agitator, a thermocouple well, a jacket for temperature control, and nozzles for monomer feed and sampling. The agitator with anchor type blade was mag-

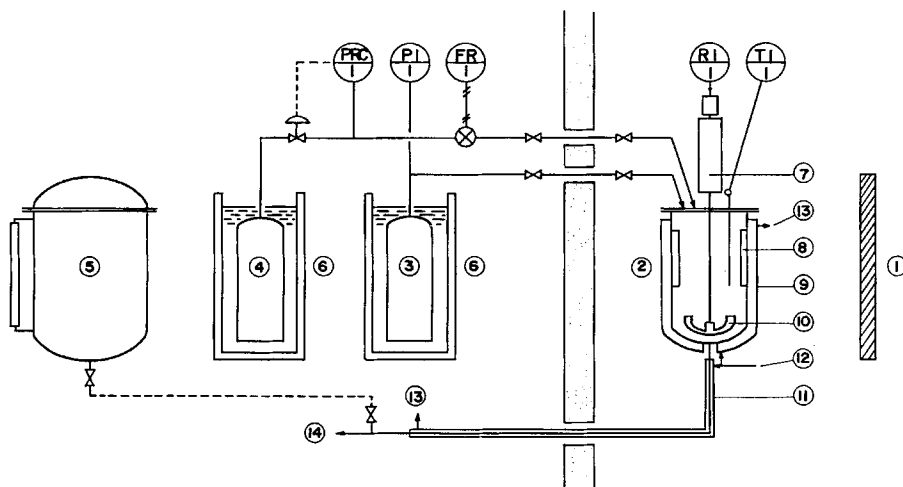


Fig 1. Flow sheet of the apparatus: (1) Co-60 radiation source; (2) reaction vessel; (3) monomer cylinder for initial charge; (4) monomer cylinder for makeup; (5) seed latex tank; (6) hot-water bath; (7) magnetically driven agitator; (8) baffle plates; (9) jacket for temperature control; (10) blade for agitation; (11) double tube; (12) hot-water inlet; (13) hot-water outlet; (14) latex sampling line.

netically driven with a variable speed motor. Four baffle plates were placed on the reactor wall for increasing turbulence.

After the reactor was swept out three times with nitrogen and evacuated, the seed latex of about 2 L was charged from a tank, and then the gaseous monomer mixture composed of tetrafluoroethylene and propylene was fed up to 25 kg/cm<sup>2</sup>. After a while, agitation was started. The pressure was adjusted by adding or purging of gaseous monomer at desired reaction temperature.

After the desired polymerization conditions were attained,  $\gamma$ -irradiation was started by placing a radiation source of Co-60 beside the reactor. During the polymerization, the reaction pressure was automatically controlled by adding makeup monomer through a pressure regulator. The reaction temperature was also controlled at 40°C by circulating hot water in the reactor jacket. As the composition of makeup monomer mixture was almost equal to the copolymer composition, the monomer composition in the reactor was kept constant during the polymerization.

### Measurement

Contents in the reactor were sampled in a free-piston tube at given time intervals during polymerization. The apparatus is shown in Figure 2.

The sampling line and the tube were maintained at the reaction temperature. The mixture of gaseous monomer and latex in the reactor was slowly transferred under the agitation to the tube by discharging water (C). The amount of the sample was determined from the volume of discharged water. After a few minutes, the mixture in the tube was separated into two phases; gaseous monomer and latex. While the pressure in the tube was kept constant by nitrogen (D), the latex was taken out to a separator through a valve (V-3). In the separator, the dissolved monomer was isolated from latex under atmospheric pressure. Monomer concentration in the polymer particles was calculated from the difference of total amount of the dissolved monomer in latex and that in water.

The compositions of gaseous monomer in the reactor and dissolved monomer in latex were measured with a gas chromatograph using helium as a carrier gas

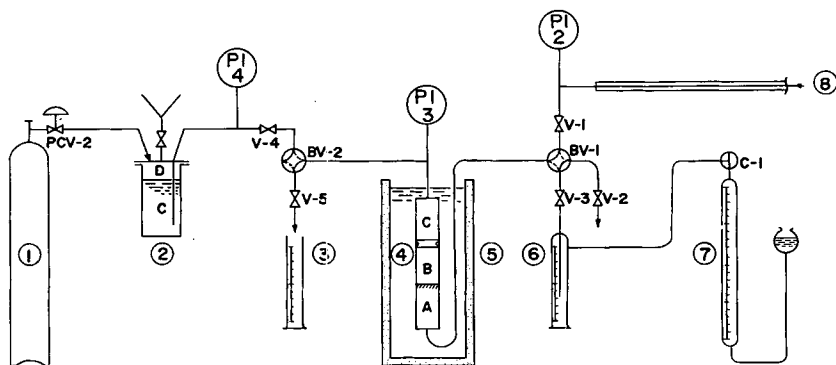


Fig. 2. Apparatus for sampling latex and measuring dissolved monomer: (1) nitrogen cylinder; (2) water reservoir; (3) water measuring cylinder; (4) free-piston tube; (5) hot water bath; (6) trap for separating gas and liquid; (7) gas burette; (8) latex sampling line from reactor. A, B, C, and D denote latex, gaseous monomer, water, and nitrogen gas, respectively.

and Porapak-Q (Water Associates) as a column-packing material.

Polymer concentration in latex was calculated from the difference of the total solid content and emulsifier content. The polymer concentration calculated by this method agreed with that measured after removal of the emulsifier by chemical treatment.<sup>1</sup>

The number-average molecular weight of the copolymer was determined by the following equation<sup>7</sup> from its intrinsic viscosity in tetrahydrofuran at 30°C:

$$[\eta] = 2.46 \times 10^{-4} \bar{M}_n^{0.70}$$

The number of polymer particles was determined from the particle diameter measured with electron microscope, JEM-7 of the Japan Electron Optics Laboratory Co., Ltd., after hardening the polymer particles by electron beam irradiation of 100 Mrad.<sup>4</sup>

## RESULTS AND DISCUSSION

### Copolymerization Mechanism

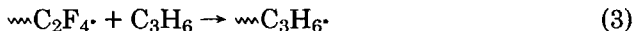
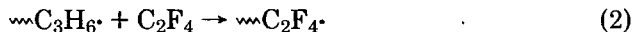
Following equations have been proposed as the overall reaction mechanism for the radiation-induced emulsion copolymerization of tetrafluoroethylene with propylene.<sup>3</sup>

*Initiation Step:*



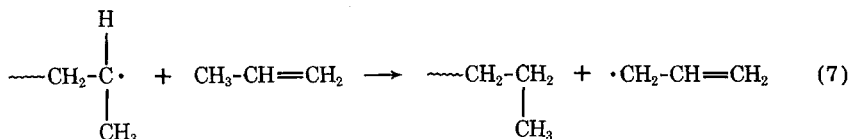
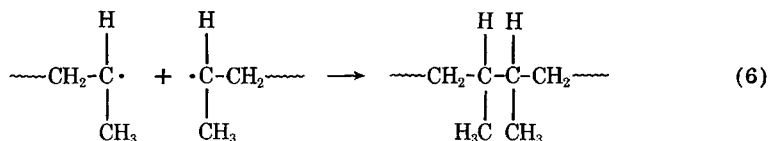
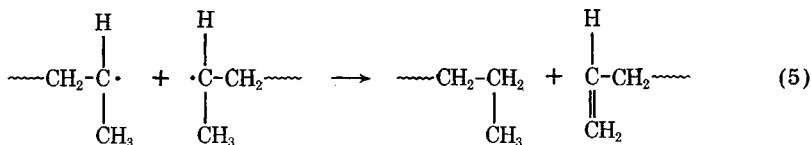
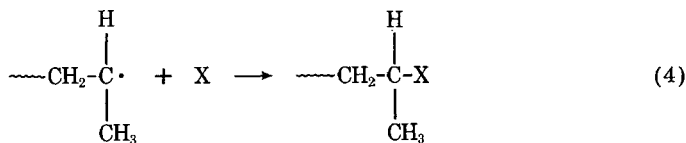
where  $M$  is monomers and  $X$  is OH or H radicals from radiolysis of water.

*Propagation Step:*



where eq. (2) is the rate determining step as the propagating propylene radical is more stable than the propagating tetrafluoroethylene radical.

*Termination Step:*



Reactions (4), (5), (6), and (7) are the recombination with initiating species, disproportionation of propagating radicals, mutual recombination of propagating radicals, and degradative chain transfer to propylene, respectively. Chain transfer to tetrafluoroethylene and emulsifier (FC-143) practically does not take place.

### Effect of Agitation Speed

In the copolymerization of tetrafluoroethylene with propylene, the alternating copolymer is produced in the wide range of monomer composition,<sup>1</sup> so that the consumption rate of tetrafluoroethylene is almost equal to that of propylene in the polymer particles. In case that the monomer diffusion to polymer particles is not sufficient, the monomer concentration and its composition in the particles must be changed proceeding with the polymerization. In this experiment, the polymerization reaction was carried out at lower pressure than the saturated vapor pressure of monomer mixture, so that the monomer droplets do not exist. Therefore, the monomer in gas phase is transferred to the particles by diffusion through the aqueous phase. From these reasons, the agitation speed plays an important role in determining the monomer concentration and its composition in polymer particles where the polymerization takes place.

Figure 3 shows changes of polymer concentration in latex with reaction time at various agitation speeds under the constant conditions of pressure, temperature, dose rate, and monomer composition in gas phase. The rate of polymerization increases with agitation speed up to 300 rpm, and slightly decreases above 500 rpm under the experimental range. The molecular weight is the highest at 300 rpm agitation speed, as shown in Figure 4. The molecular weight of the polymer formed at the agitation speed of 150 rpm is relatively high compared

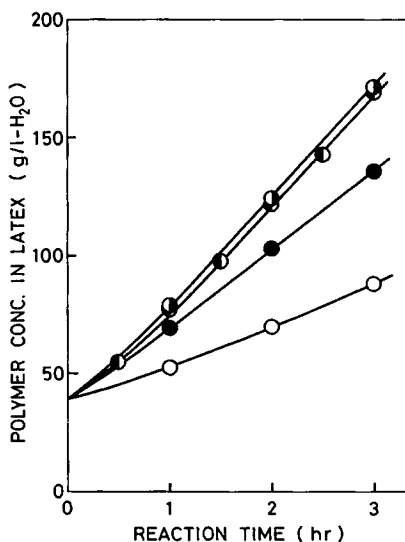


Fig. 3. Relations between polymer concentration in latex and reaction time at various agitation speeds: (○) 150 rpm; (◐) 300 rpm; (◑) 500 rpm; (●) 750 rpm. Other reaction conditions: pressure, 25 kg/cm<sup>2</sup>; temperature, 40°C; dose rate  $3.8 \times 10^5$  rad/h; propylene mol % in gas phase, about 20%.

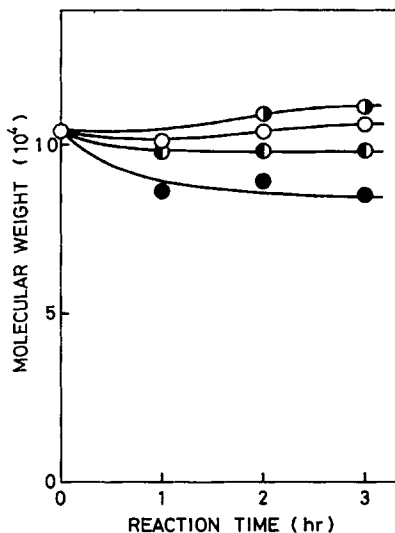


Fig. 4. Changes in polymer molecular weight with reaction time at various agitation speeds. Symbols and reaction conditions are the same as in Figure 3.

with those of polymers formed at 500 rpm and 750 rpm, though the polymerization rate is the lowest.

At the agitation speed of 150 rpm, monomer concentration in polymer particles is rapidly decreased with reaction time, as shown in Figure 5. In contrast to this change, the monomer concentrations at other agitation speeds are almost constant during the reaction, and these values are nearly three times larger than that of 150 rpm at the end of the reaction.

Figure 6 shows the changes of monomer composition in the particles with reaction time at various agitation speeds. At the agitation speed of 500 rpm and 750 rpm, the propylene fraction in the particles is almost constant and ap-

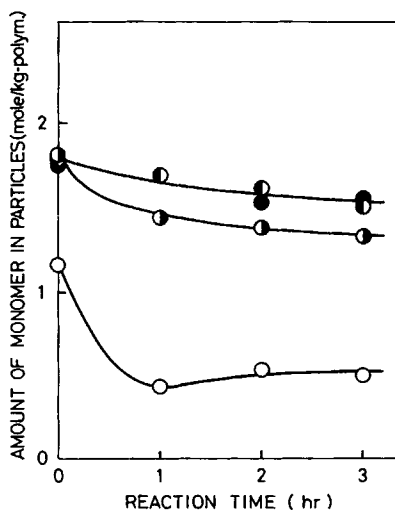


Fig. 5. Changes in amount of monomer in polymer particles with time at various agitation speeds. Symbols and reaction conditions are the same as in Figure 3.

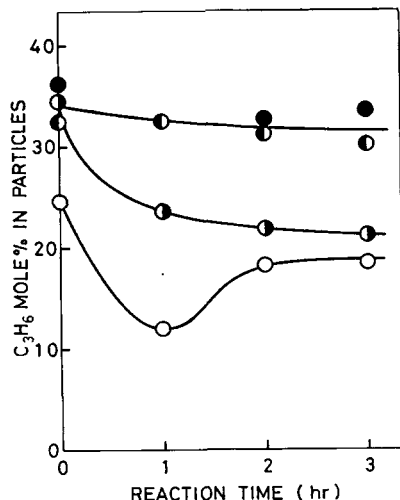


Fig. 6. Changes in monomer composition in polymer particles with time at various agitation speeds. Symbols and reaction conditions are the same as in Figure 3.

proximately equal to the value at equilibrium. At agitation speed lower than 500 rpm, the propylene fraction decreases with time. When the mole ratio of tetrafluoroethylene and propylene in gas phase is 80/20, that in the particles in equilibrium is 65/35, different from the consumption ratio of 50/50. Therefore, the fraction of propylene in the particles decreases when the rate of monomer diffusion to the particles is not adequate for the rate of copolymerization.

In the emulsion copolymerization of tetrafluoroethylene with propylene, the first-order termination by degradative chain transfer to propylene is assumed to occur together with the second-order termination by radical recombination.<sup>3</sup> Therefore, the decrease of the propylene fraction in polymer particles results in the increase of the polymerization rate and polymer molecular weight.

At the agitation speed of 150 rpm where the monomer diffusion is the rate determining step, higher molecular weight polymer is formed due to depression of the termination reaction probably because of the decrease in the propylene fraction. The highest polymerization rate and molecular weight at 300 rpm are due to the lower propylene fraction in polymer particles caused by deficient diffusion of monomer. At the agitation speed above 500 rpm, the monomer diffusion is enough to make the polymerization proceed at steady monomer concentration and composition. Both the rate of polymerization and polymer molecular weight at 750 rpm are lower than those at 500 rpm. This may be explained by the fact that the number of polymer particles decreases from  $1.5 \times 10^{15}$  to  $9 \times 10^{14}$  particles/mL- $H_2O$  by coagulation, which increases the second-order termination.

#### Effect of Monomer Composition in Polymer Particles

The copolymerizations were carried out at various monomer compositions and dose rates. Fluctuation of the monomer composition in gas phase directly affects both the concentration and composition of the monomer in polymer particles to disturb stationary polymerization reaction. However, in most of the experi-

ments, the monomer composition in gas phase could be well controlled during the operation, so that the copolymerization could proceed steadily, as shown in Figure 7, for example.

Polymer concentration in latex increases almost linearly with operation time. The rate of polymerization was calculated from the straight line under the stationary conditions. Polymer molecular weight decreases with time from that of seed polymer to steady value shown in Table I.

Figure 8 shows relations between the polymerization rate and mole fraction of tetrafluoroethylene in polymer particles at various dose rates. The polymerization rate increases in proportion to the tetrafluoroethylene fraction, and a slope of the line increases with the dose rate. The polymer molecular weight also increases with the fraction, as shown in Figure 9.

### Effect of Dose Rate

Figure 10 shows log-log plots of the polymerization rate and dose rate at various monomer compositions. The dose rate exponent of the polymerization rate is affected by the monomer composition and dose rate. At the region of the lower dose rate, the polymerization rate is proportional to the 0.9 power of the dose rate at the tetrafluoroethylene fraction of 30 mol %, and the exponent decreases to 0.7 at the fraction of 90 mol %. At the region of the higher dose rate, the exponent decreases from 0.7 to 0.5 with increasing the fraction from 30 to 90 mol %. The dose rate exponent also decreases with increasing dose rate.

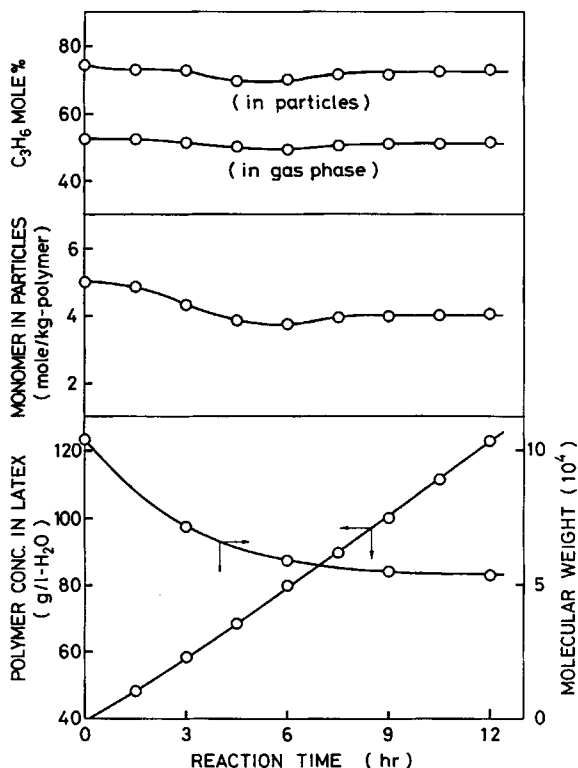


Fig. 7. Operational results in run 22. Reaction conditions are shown in Table I.



TABLE I  
Experimental Results<sup>a</sup>

Run no.	Dose rate (10 <sup>5</sup> rad/h)	Mole ratio in gas phase (C <sub>2</sub> F <sub>4</sub> /C <sub>3</sub> H <sub>6</sub> )	Mole ratio in particles (C <sub>2</sub> F <sub>4</sub> /C <sub>3</sub> H <sub>6</sub> )	Monomer concn in particles		Number of particles (10 <sup>15</sup> /mL-H <sub>2</sub> O)	Rate of polymerization (g/h-L-H <sub>2</sub> O)	Molecular weight of copolymer (10 <sup>4</sup> )
				(C <sub>2</sub> F <sub>4</sub> + C <sub>3</sub> H <sub>6</sub> ) [mol/kg-polymer]	(C <sub>2</sub> F <sub>4</sub> ) (C <sub>3</sub> H <sub>6</sub> )			
5	3.8	81.7/18.3	68.7/31.3	1.68	1.10	1.3	46.3	9.8
6	1.9	81.2/18.8	66.5/33.5	1.77	1.17	1.7	30.7	11.0
7	0.88	80.9/19.1	66.7/33.3	1.72	1.15	—	18.9	11.3
8	0.46	81.3/18.7	66.6/33.4	1.73	1.15	1.7	11.9	12.0
9	3.8	71.6/28.4	53.0/47.0	2.16	1.15	1.9	37.0	7.4
10	1.9	71.4/28.6	53.0/47.0	1.95	1.03	1.7	25.7	7.4
11	0.88	70.8/29.2	51.1/48.9	2.17	1.11	1.3	14.1	7.6
12	0.46	73.2/26.8	54.9/45.1	2.06	1.13	1.2	9.5	8.0
13	0.46	90.7/ 9.3	83.4/16.6	1.38	1.14	—	15.0	15.8
14	1.9	86.5/13.5	77.8/22.2	1.53	1.19	—	35.5	13.0
15	0.88	91.7/ 8.3	84.3/15.7	1.37	1.16	1.5	22.4	14.7
16	3.8	93.2/ 6.8	88.8/11.2	1.45	1.28	1.5	58.7	11.2
18	1.9	73.7/26.3	56.6/43.4	1.95	1.11	1.9	27.1	7.2
19	3.8	55.1/44.9	34.0/66.0	3.21	1.09	1.7	25.5	4.9
20	0.46	55.3/44.7	34.5/65.5	2.90	1.00	1.2	5.6	5.5
21	1.9	45.5/54.5	24.1/75.9	4.73	1.14	1.2	12.0	5.0
22	0.88	49.0/51.0	28.6/71.4	3.98	1.14	1.5	7.5	5.3

<sup>a</sup> Reaction conditions: pressure, 25 kg/cm<sup>2</sup>; temperature, 40°C; agitation speed, 500 rpm.

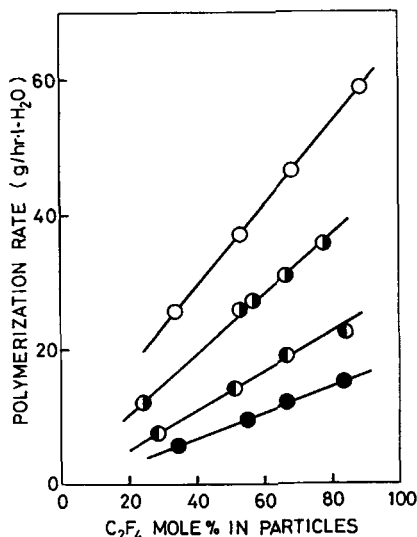


Fig. 8. Relations between polymerization rate and monomer composition in polymer particles at various dose rates: (○)  $3.8 \times 10^5$  rad/h; (◐)  $1.9 \times 10^5$  rad/h; (◑)  $8.8 \times 10^4$  rad/h; (●)  $4.6 \times 10^4$  rad/h. Other reaction conditions: pressure, 25 kg/cm<sup>2</sup>; temperature, 40°C; agitation speed, 500 rpm.

The relations between the polymer molecular weight and the dose rate are shown in Figure 11 for the various monomer compositions. The molecular weight is almost independent of the dose rate when the tetrafluoroethylene fraction is in the range of 30–50 mol %. At the higher fraction of tetrafluoroethylene, however, the molecular weight decreases slightly with the dose rate. The dose rate dependence of the molecular weight increases at the higher dose rate region.

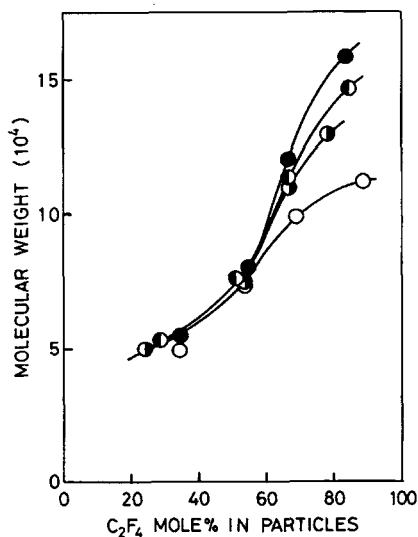


Fig. 9. Relations between polymer molecular weight and monomer composition in polymer particles at various dose rates. Symbols and reaction conditions are the same as in Figure 8.

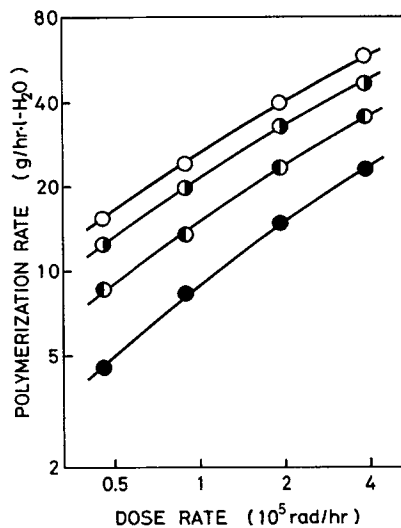


Fig. 10. Effects of dose rate on polymerization rate at various mole percents of tetrafluoroethylene in polymer particles: (○) 90%, (◐) 70%; (◑) 50%; (●) 30%. Other reaction conditions are the same as in Figure 8.

In the emulsion polymerization started from monomer and emulsifier aqueous solution, initiator and emulsifier concentrations determine the number of polymer particles. In case a propagating radical in a particle grows until a new radical enters from aqueous phase, the rate of polymerization depends on the number of polymer particles and the monomer concentration as in following equation<sup>8</sup>:

$$R_p = k_p [M] \frac{N}{2}$$

where  $R_p$  is the rate of polymerization,  $k_p$  is the rate constant,  $[M]$  is monomer

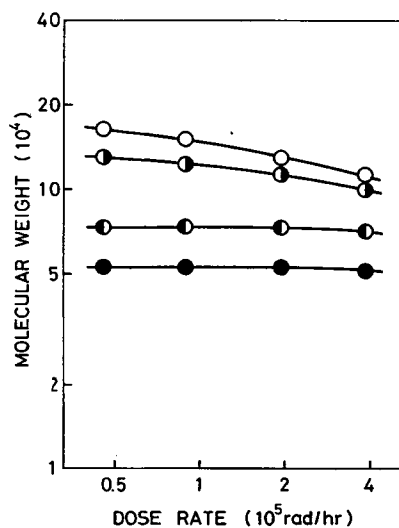


Fig. 11. Effects of dose rate on polymer molecular weight at various monomer compositions in polymer particles. Symbols and reaction conditions are the same as in Figure 10.

concentration, and  $N$  is the number of polymer particles. Under the constant monomer concentration, the rate of polymerization must be independent of the initiator concentration or dose rate in the seeded polymerization.

In the case of seeded copolymerization of tetrafluoroethylene with propylene by radiation, the polymerization rate is found to be proportional to the 0.5–0.9 power of the dose rate under experimental conditions. This fact shows that most of the propagating radicals in particles are deactivated before a new radical enters from aqueous phase. Higher dose rate dependence of the polymerization rate at a lower fraction of tetrafluoroethylene in particles is explained by considering that the first-order termination of the propagating chain is predominant due to the degradative chain transfer to propylene. The dose rate independence of the polymer molecular weight is consistent with above explanation.

With an increasing tetrafluoroethylene fraction in the particles, the lifetime of propagating chain becomes longer because of the depression of the degradative chain transfer. This is the main reason for the increases of the polymerization rate and polymer molecular weight with the tetrafluoroethylene fraction, as shown in Figures 8 and 9.

At the higher tetrafluoroethylene fraction, however, some of the propagating chains are deactivated by recombination with radical newly entered from aqueous phase. At the same monomer composition, the fraction of second-order termination by mutual recombination is also increased with the dose rate. It is explained by the above reasons that the dose rate dependence of the polymerization rate decreases with increasing the dose rate and the tetrafluoroethylene fraction in polymer particles. The increase in dose rate dependence of the polymer molecular weight at the higher dose rate and at the higher tetrafluoroethylene fraction is also explained by the increase of the second-order termination.

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