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Yoneho Tabata[a]; Wataru Ito[b]; Keichi Oshima[a]; Jiro Takaci[c]
[a] Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan [b] Industrial Research Institute, Tokyo, Japan [c] Central Research Institute Asahi Glass Co., Ltd., Tokyo, Japan

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Radiation-Induced Polymerization of Tetrafluoroethylene in Solution

YONEHO TABATA

Department of Nuclear Engineering
University of Tokyo
Tokyo, Japan

WATARU ITO

Industrial Research Institute
Tokyo, Japan

KEICHI OSHIMA

Department of Nuclear Engineering
University of Tokyo
Tokyo, Japan

and

JIRO TAKAGI

Central Research Institute
Asahi Glass Co., Ltd.
Tokyo, Japan

SUMMARY

Polymerization of tetrafluoroethylene in monochlorodifluoromethane was carried out at low temperatures with γ-rays from a ^{60}Co source. An activation energy of 4.3 kcal/mole was obtained for the in-source polymerization, and this is higher than that of bulk polymerization, 2.7 kcal/mole. It was found that a remarkable postpolymerization takes place even if the reaction system is in liquid state. A kinetic treatment for the postpolymerization is described.

INTRODUCTION

Radiation-induced polymerization of tetrafluoroethylene in monochlorodifluoromethane R-22 was carried out. It was observed that the postpolymerization takes place very rapidly as does the in-source polymerization of the monomer [1-7].

The effects of solvent and temperature on polymerization have been investigated.

EXPERIMENTAL

Monomers were charged in a 100-ml stainless-steel reactor vessel at low temperatures. After the vessel was deaerated by pumping at -196°C, the monomers were irradiated in the liquid phase. The reaction system was stirred during irradiation and the temperature was automatically controlled during polymerization.

RESULTS AND DISCUSSION

The temperature and pressure inside the autoclave were measured during irradiation, and the results are shown in Fig. 1. As shown in Fig. 1, sharp rises in temperature and pressure inside the reactor were observed in the bulk polymerization at 2.8 hr of irradiation whereas the pressure and temperature were practically constant for the entire solution polymerization period. This shows that solution polymerization can be controlled and carried out in safety, even if the reaction vessel is large compared with our ampoule experiments.

Conversion curves at various temperatures for the in-source polymerization are shown in Fig. 2. The rate of polymerization increases with the polymerization temperature up to -10°C; however, the rate decreases sharply above -10°C. This indicates that the ceiling temperature of polymerization is around -10°C.

Plots of conversion as a function of the square of irradiation time, t^2, are shown in Fig. 3 for conversions below 70%. The results indicate a linear relationship may exist between conversion and t^2. This suggests that the polymer radicals grow independently without termination reaction or with few terminations below about 70% conversion.

Arrhenius plots are given in Fig. 4 for solution polymerization compared with bulk polymerization. An activation energy of 4.3 kcal/mole was

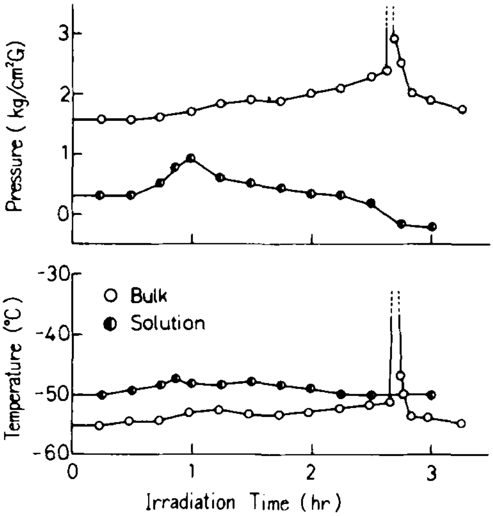

Fig. 1. Pressure and temperature in the reactor as a function of irradiation time for bulk and solution polymerizations. Dose rate: 5 X 10^4 r/hr. Molar ratio of solvent to monomer (S/M); 3 for the solution polymerization.

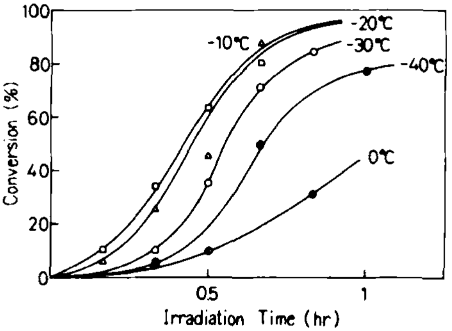

Fig. 2. Effect of temperature on the conversion curves in the solution polymerization of tetrafluoroethylene. Dose rate: 1.5 X 10^4 r/hr. Molar ratio S/M: 2.

obtained from the plot for the solution polymerization, and 2.7 kcal/mole for bulk polymerization. One reason for the higher activation energy value in solution polymerization may be the larger temperature dependence of the initiation reaction of fragment radicals from the solvent than of

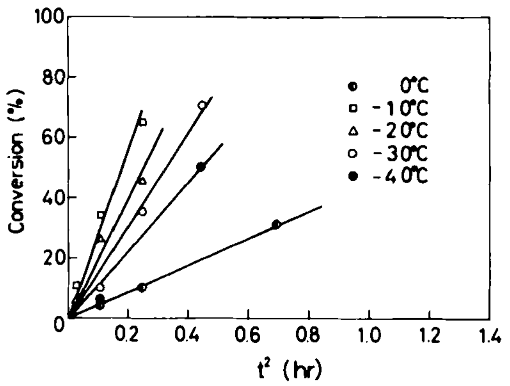

Fig. 3. Conversions as a function of t^2 at various temperatures for the solution polymerization.

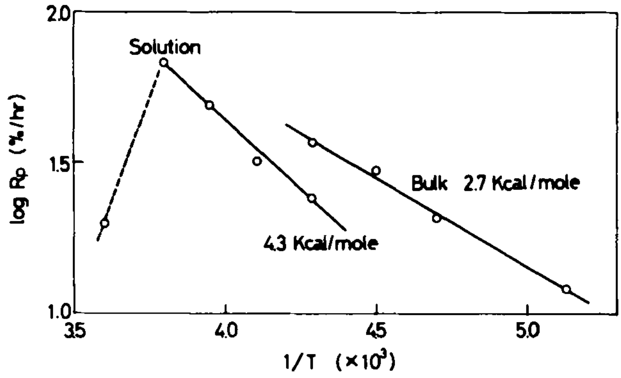

Fig. 4. Arrhenius plot of the bulk and solution polymerizations.

monomer radicals. The results also indicate that the solution polymerization proceeds at higher rates in the higher temperature region than does the bulk polymerization.

Conversion curves in the solution polymerization at various concentrations of monomers are shown in Fig. 5.

The rates of polymerization are plotted in Fig. 6 as a function of the monomer concentration.

The sensitizing effect of the solvent on polymerization may be explained by an increase in the initiation and propagation reactions due to the presence of the solvent.

Fragments from the solvent were clearly shown to be in the polymers through activation analysis; therefore, an additional initiation reaction takes

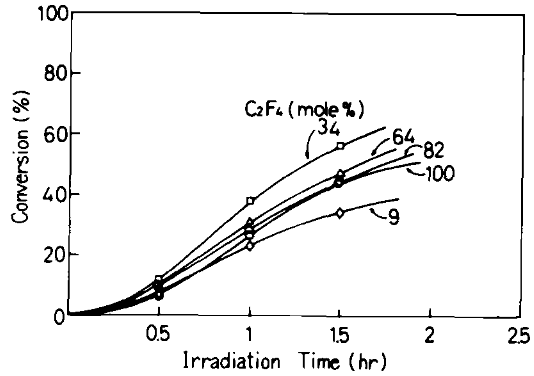

Fig. 5. Relations between conversion and irradiation time at various molar concentrations of tetrafluoroethylene in the solvent.

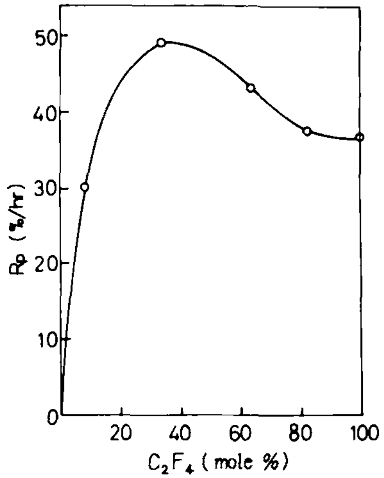

Fig. 6. Rate of polymerization as a function of molar concentration of tetrafluoroethylene in the solvent.

place in the solution polymerization. On the other hand, the propagation reaction may be enhanced by the presence of solvent. Diffusion of monomers in the reaction system may be different between the bulk and solution polymerization systems. The diffusion of monomers into the polymer precipitates may be easier in the presence of solvent than in nonsolvent system because the polymer precipitate is swelled by the solvent. This may also be one of the reasons for the promoting effect by the solvent.

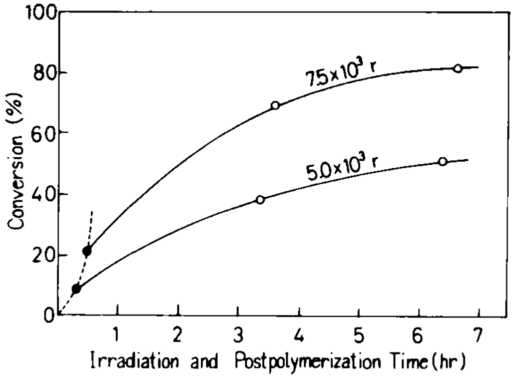

Fig. 7. Postpolymerizations at -40°C for two different preirradiation doses of 5.0 X 10^3 and 7.5 X 10^3 r. Molar ratio S/M: 2.

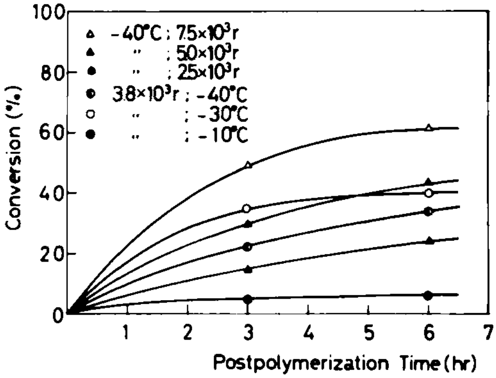

Fig. 8. Conversions as a function of postpolymerization time at various conditions.

It was observed that a remarkable postpolymerization takes place in the irradiated monomers in the presence of R-22 solvent. One of the results is shown in Fig. 7. After irradiation at -40°C for 20 and 30 min at a dose rate of 1.5 X 10^4 r/hr, postpolymerization was carried out at the same temperature. The molar ratio of the solvent to the monomer was 2.

It is interesting to note that postpolymerization takes place very rapidly even if the system is in the liquid phase.

According to Fig. 7, the postpolymerization rate is roughly proportional to the preirradiation dose. This means that the short-chain polymer radicals which were produced by preirradiation grow independently after irradiation. This is also shown in Fig. 8.

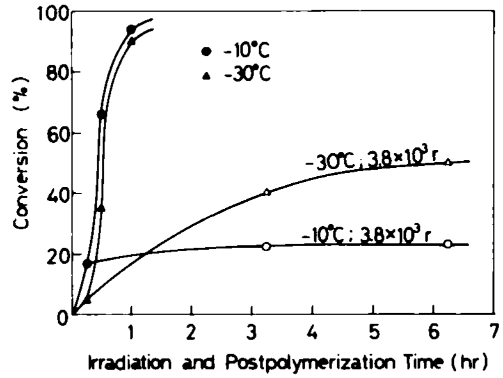

Fig. 9. Conversion curves in postpolymerization at two different polymerization temperatures: -10 and -30°C. Preirradiation was made at each corresponding temperature in a dose rate of 1.5 X 10^4 r/hr. Molar ratio S/M: 2.

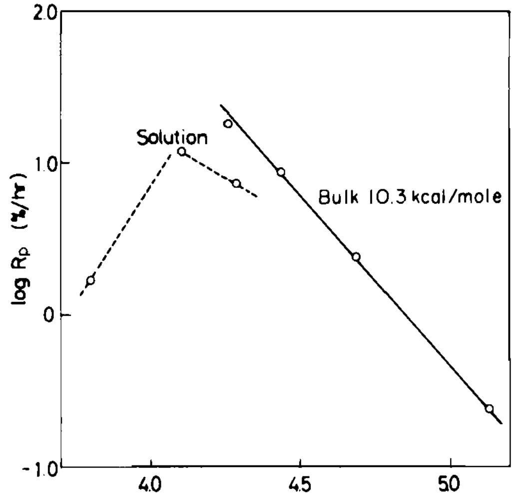

Fig. 10. Arrhenius plots of the postpolymerizations in bulk and in solution.

A bimolecular termination process becomes important for higher concentrations of polymer radicals in a later stage of postpolymerization.

The temperature dependence of postpolymerization is shown in Fig. 9. It is evident from Fig. 9 that the in-source polymerization is extremely

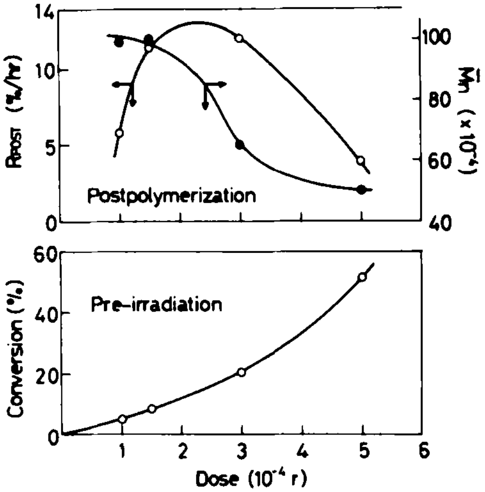

Fig. 11. Rate of postpolymerization and number-average molecular weight as a function of preirradiation dose.

rapid. The rate is faster at -10°C than at -30°C, whereas the postpolymerization is relatively slow and the rate at -10°C is much less than that at -30°C. This suggests that the propagation reactions are extremely different in in-source and postpolymerizations. It is interesting that the ceiling temperature in postpolymerization is shifted to a lower value in comparison with that in in-source polymerization.

Arrhenius plots of postpolymerizations in bulk and in solution are shown in Fig. 10.

The effect of the preirradiation dose on postpolymerization was examined. The initial rate of postpolymerization and the number-average molecular weight as a function of irradiation dose are shown in Fig. 11. The number-average molecular weight was obtained by measuring the density of the polymers.

Polymers from both the in-source polymerization and from the preceding postpolymerization were included in the density measurements. The postpolymerization was carried out at -40°C. The in-source polymerization for the preceding postpolymerization was carried out at -60°C at a dose rate of 3×10^4 r/hr with equimolar mixtures of the monomer and the solvent. The result is also shown in Fig. 11.

The kinetics of the postpolymerization can be described as follows:

			Rate
Propagation	$P_n\cdot + M \longrightarrow$	$P_{n+1}\cdot$	$k_p[P\cdot][M]$
Termination	$P_n\cdot + P_m\cdot \longrightarrow$	P_{n+m} or $P_n + P_m$	$k_t[P\cdot]^2$

Therefore, the rate of polymerization R_p is expressed by

$$R_p = -\frac{d[M]}{dt} = k_p[P\cdot][M] = \frac{k_p[M][P\cdot]_0}{1 + k_t[P\cdot]_0 t}$$

where

$$[P\cdot]_0 = k_i t_i I = k_i D \quad (D = It_i)$$

$$[M] = [M]_0 - kt_i = [M]_0 - k\frac{D^2}{I^2}$$

for the initial stage of postpolymerization. Then,

$$R_p = \frac{k_p k_i D[M]_0 - k\frac{D^2}{I^2}}{1 + k_i k_t D t}$$

where P is polymer, P• is its radical, M monomer, k_p propagation rate constant, k_t termination rate constant, k_i rate constant of the formation of monomer radicals, I dose rate, D irradiation dose, $[P\cdot]_0$ the initial concentration of polymer radicals, and $[M]_0$ the initial concentration of monomers.

For the initial stage of postpolymerization, the rate of postpolymerization can be described as

$$R_p = k_i k_p D[M]_0 - \frac{kD^2}{I^2} \quad (t \to 0)$$

Differentiating R_p with respect to irradiation dose D,

$$\frac{\partial R_p}{\partial D} = k_i k_p [M]_0 - 3\frac{k_i}{I^2} D^2$$

Therefore, R_p takes a maximum at $D = I([M]_0/3k)$ under the condition of $\partial R_p/\partial D = 0$. This is clearly shown qualitatively in Fig. 11.

The conversion of monomers, C, can be obtained by integrating the rate of polymerization with respect to polymerization time

$$C = \frac{1}{[M]_0 - K\frac{D^2}{I^2}} \int_0^t R_p\, dt = \log(1 + k_i k_t D t)$$

Number-average molecular weight $\bar{M}_n$ is proportional to $\sqrt{C/[P\cdot]}$ in the initial stage of polymerization

$$\bar{M}_n \propto \frac{1}{k_i D} \log(1 + k_i k_t D t)$$

Under the condition $\partial \bar{M}_n/\partial D = 0$, D approaches zero. This means that the molecular weight becomes larger with decreasing preirradiation doses.

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