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Radiation-Induced Polymerization of Tetrafluoroethylene*

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SUMMARY

Polymerization of tetrafluoroethylene was carried out in bulk at low temperatures by initiation with γ -rays from a ^{60}Co source. It was found that a remarkable postpolymerization takes place even in the liquid phase. Kinetic analysis has been made of the in-source and postpolymerizations. An activation energy of 2.7 kcal/mole was obtained for the in-source polymerization and 10.3 kcal/mole for the postpolymerization. The long lifetime of polymer radicals in the liquid phase at -78°C seems to be due to the slow recombination rate of the polymer radicals, based on the rodlike shape of the polymer radicals.

INTRODUCTION

Radiation-induced polymerization of tetrafluoroethylene has been studied under various conditions in our laboratory since 1959 and several papers on

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this subject have been published [1-3]. Several papers on the polymerization have been also published from other laboratories [5-12].

In this paper, radiation-induced polymerization of the monomer in liquid phase in bulk is reported. In-source and postpolymerizations are described.

EXPERIMENTAL

Monomers were introduced into a glass ampoule of 5 ml volume after purification of the monomers.

Oxygen was purged by evacuation at -196°C . The monomers were irradiated with γ -rays from a ^{60}Co source in the temperature region from -40 to -78°C .

Unreacted monomers were purged at -78°C after irradiation.

RESULTS AND DISCUSSION

Conversion as a function of irradiation time at various dose rates is shown in Fig. 1. It is obvious from the figure that polymerization takes

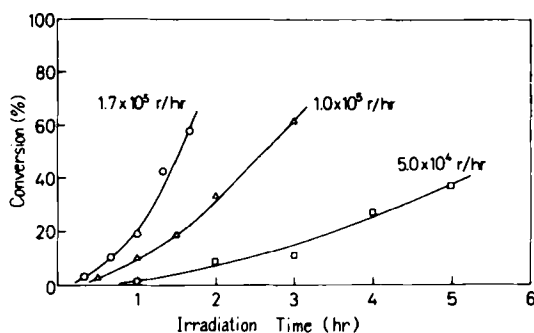


Fig. 1. Relations between conversion and irradiation time at various dose rates at -78°C .

place very rapidly at -78°C . An acceleration phenomenon was observed. From the conversion curves, it is difficult to know the exact dose rate dependency on the rate of polymerization. However, the dependency at constant conversion can be obtained.

The dose rate dependencies at 10 and 40% conversions are indicated in Fig. 2. The rate is proportional to the 0.8 power of dose rate at 10% conversion and to the 1.4 power at 40% conversion. The results indicate that

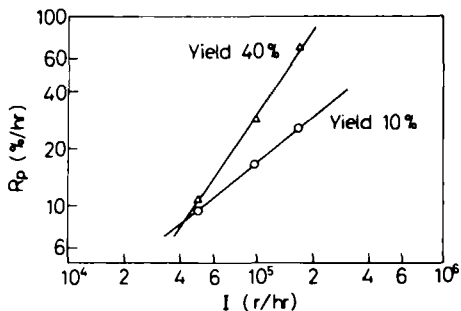


Fig. 2. Dose rate dependencies of the rates of polymerization at two different yields.

the dose rate dependency is a function of conversion and that a distinguishable gel effect exists in the polymerization.

The rate of polymerization R_p is described by

$$R_p = -\frac{d[M]}{dt} = \kappa_p [P\cdot] [M] \tag{1}$$

If the rate of the termination reaction is extremely low in comparison with the propagation rate, the rate of polymerization can be written as

$$R_p = \kappa_p f (\vartheta_M [M], \vartheta_S [S]) [M] I t \tag{2}$$

where κ_p is the propagation rate constant, $[P\cdot]$ is the concentration of growing radicals, $[M]$ is the monomer concentration f the number of radicals per unit irradiation dose produced in the system and a function of $\vartheta_M [M]$ and $\vartheta_S [S]$ (ϑ_M, ϑ_S are G-values of the radical formation from the monomer and solvent respectively), I is the intensity of radiation and, t is the irradiation time. The following relation is obtained by integrating Eq. (2):

$$C = \int_0^t R_p dt = -\int_0^C \frac{d[M]}{[M]} = \frac{1}{2} \kappa_p f (\vartheta_M [M], \vartheta_S [S]) [M] I t^2 \tag{3}$$

where C is the conversion. Equation (3) indicates that the conversion is

proportional to the square of the irradiation time, if the termination reaction is neglected.

The relation between conversion and t^2 is shown in Fig. 3. It is clear that a linear relationship exists between them, and this suggests that the in-source polymerization proceeds without any termination reaction in the initial stage of polymerization.

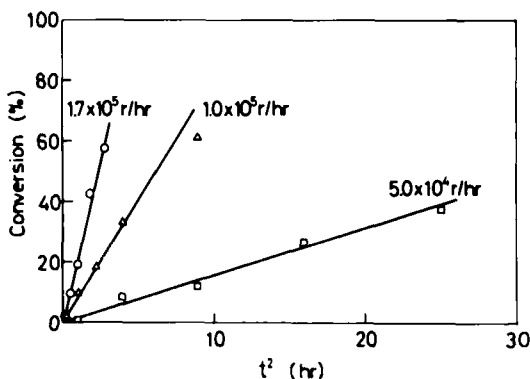


Fig. 3. Relationships between conversion and t^2 at various dose rates at -78°C .

The temperature dependency of polymerization was examined and the results are shown in Fig. 4.

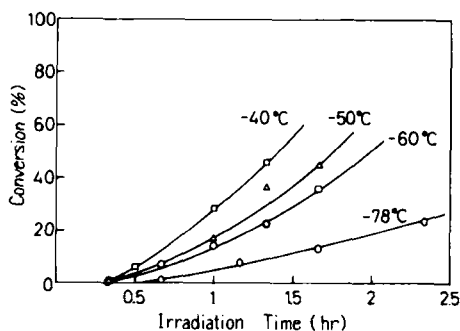


Fig. 4. Relations between conversion and irradiation time at various polymerization temperatures.

The rate increases appreciably with polymerization temperature in the region -78 to -40°C . An Arrhenius plot of the polymerization is shown in Fig. 5. An activation energy of 2.7 kcal/mole is obtained from the figure.

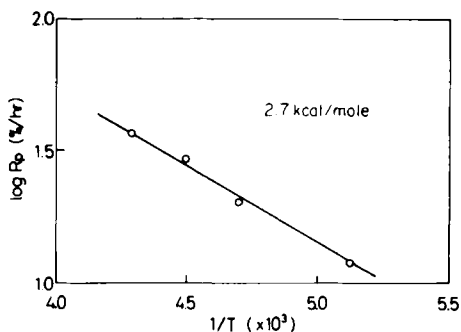


Fig. 5. Arrhenius plot of the polymerization of tetrafluoroethylene in bulk.

This agrees with the result reported previously [1]. The activation energy for propagation is rather low and this suggests the polymerization proceeds very easily even at low temperatures.

It was found that a remarkable postpolymerization takes place even in the polymerization system in the liquid phase. This seems to be a rare case which has been observed only under very specific conditions. An example is shown in Fig. 6.

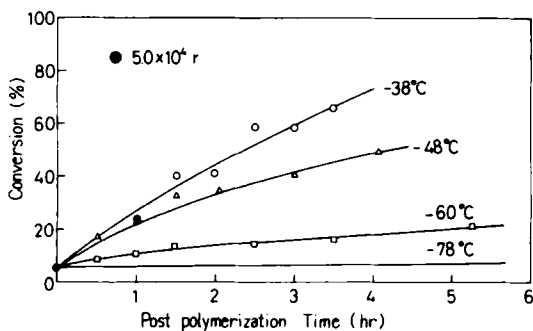


Fig. 6. Relations between conversion and polymerization time at various temperatures in the postpolymerization after 5.0×10^4 r irradiation at -78°C .

After preirradiation at a dose rate of 5.0×10^4 r at -78°C , the irradiated monomers, which include 5% polymers, were kept at various temperatures.

Postpolymerization does not proceed at -78°C for an appreciably long period, although rapid polymerization can be observed in the in-source polymerization. This indicates that the propagation reaction is profoundly enhanced by irradiation during polymerization. This has previously been observed in the solid-state polymerization of acrylamide and its derivatives. The activation energy in the postpolymerization, obtained from the Arrhenius plot in Fig. 7, is 10.3 kcal/mole. This is approximately 4 times that in the in-source polymerization.

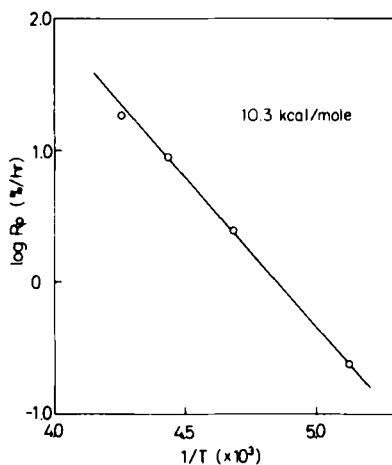
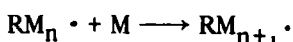


Fig. 7. Arrhenius plot of the postpolymerization of tetrafluoroethylene in bulk.

The effect of preirradiation on postpolymerization was also studied. Preirradiation was carried out at -78°C and postpolymerization at -38°C (Fig. 8). The rate of postpolymerization increases with the preirradiation dose. This is quite natural and suggests that polymer radicals grow independently without termination in the initial stage of polymerization.

The kinetics of postpolymerization can be described for the whole polymerization period as

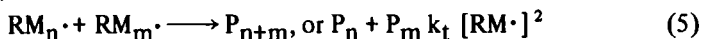
Chain propagation:



Rate

$$k_p [\text{RM}\cdot] [\text{M}] \quad (4)$$

Termination:



where k_p and k_t are rate constants of propagation and termination, respectively, and $[\text{RM}\cdot]$ and $[\text{M}]$ denote the concentrations of propagating radical and monomer, respectively.

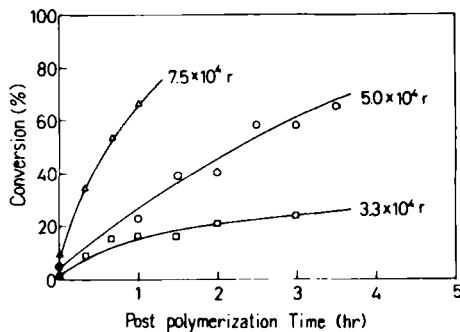


Fig. 8. Effect of preirradiation dose on the conversion curves in postpolymerization. The preirradiation was made for three different irradiation times of 40, 60, and 90 min at a dose rate of 5×10^4 r/hr at -78°C .

Decay of the growing radicals is assumed to be due to the termination reaction by coupling or disproportionation.

$$-\frac{d[\text{RM}\cdot]}{dt} = k_t [\text{RM}\cdot]^2 \quad (6)$$

By integrating Eq. (6), we can obtain the concentration of growing radicals.

$$[\text{RM}\cdot] = \frac{[\text{RM}\cdot]_0}{1 + k_t [\text{RM}\cdot]_0 t} \quad (7)$$

where $[\text{RM}\cdot]_0$ is the initial radical concentration. Then the rate of polymerization R_p can be described as

$$R_p = -\frac{d[\text{M}]}{dt} = k_p [\text{RM}\cdot] [\text{M}] = \frac{k_p [\text{M}] [\text{RM}\cdot]_0}{1 + k_t [\text{RM}\cdot]_0 t} \quad (8)$$

By integrating Eq. (8) again

$$\log \frac{[\text{M}]}{[\text{M}]_0} = \frac{k_p}{k_t} \log [1 + k_t [\text{RM}\cdot]_0 t] \quad (9)$$

where $[M]_0$ is the initial concentration of monomers. For $1 \ll k_t[RM\cdot]_0 t$

$$\log \frac{[M]_0}{[M]} = \left(\frac{k_p}{k_t} \right) \log k_t[RM\cdot]_0 + \left(\frac{k_p}{k_t} \right) \log t \quad (10)$$

$\log [M]_0/[M]$ is plotted as a function of $\log t$ and the relations are shown in Fig. 9.

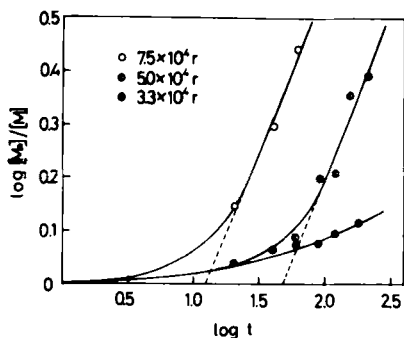


Fig. 9. Plots of logarithmic $[M_0]/[M]$ as a function of logarithmic polymerization time in the postpolymerizations at different preirradiation doses.

From the tangent of the plot for higher values of polymerization time t , the ratio of k_p/k_t is found to be 0.8 in the polymerization at -38°C . Similar plots were made for polymerizations at different temperatures and the results are shown in Fig. 10.

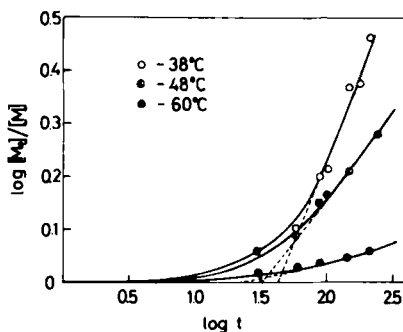


Fig. 10. Plots of logarithmic $[M_0]/[M]$ as a function of logarithmic polymerization time in the postpolymerizations at different temperatures. Preirradiation was carried out at -78°C for 1 hr at a dose rate of 5×10^4 r/hr.

The temperature dependence of k_p/k_t can be obtained from the data in Fig. 6.

The Arrhenius plot of k_p/k_t is shown in Fig. 11.

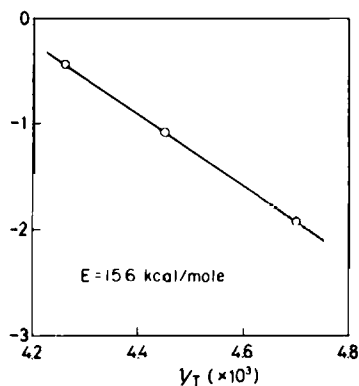


Fig. 11. Arrhenius plot of k_p/R_t in the postpolymerization.

The rate constant k_p and the ratio of k_p to k_t are written as

$$k_p = A e^{-E_p/RT} \quad (11)$$

$$k_p/k_t = B e^{-E/RT}$$

where $E = E_p - E_t$, and A and B are pre-exponential factors. From the Arrhenius plot of Fig. 9, E is estimated to be 15.6 kcal/mole.

The activation energy of polymerization was estimated from the Arrhenius plot of the initial rate of polymerization, as mentioned above, and this corresponds to the activation energy of propagation E_p . Therefore, the activation energy of termination E_t is found to be -5.3 kcal/mole.

In conclusion, the following points should be emphasized in connection with the radiation-induced liquid-state polymerization of tetrafluoroethylene.

- 1) Postpolymerization takes place very easily in the liquid phase.
- 2) There are large differences in activation energy between in-source and postpolymerizations, as in the case of solid-state polymerization. Propagation may be accelerated through vibrational excitation by subexcitation electrons during irradiation.
- 3) The initiating radicals are appreciably stable even in the liquid phase with a low-irradiation dose at temperatures around -78°C . This may be due

to a slow rate of termination because the propagating polymer radicals with short chain length are in a rodlike stiff conformation. The rate of coupling between the rodlike polymer radicals may be much less than the coupling between the dispersed polymer radicals, and radicals in the liquid phase have a long lifetime at -78°C . Postpolymerization is therefore possible by elevating the temperature of the irradiated monomers.

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