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Radiation-Induced Copolymerization of Tetrafluoroethylene and Propylene. 2. Copolymerization in Solution

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ABSTRACT

Copolymerization of tetrafluoroethylene and propylene in chlorofluorohydrocarbon solvents was carried out below room temperature with γ-rays from a ^{60}Co source. A remarkable rate-accerelating effect was observed in these solution systems, although the activation energies and the compositions of copolymers were almost the same as those in bulk system. The most effective solvent was found to be trichlorotrifluoroethane.

Kinetic results of the copolymerization in trichlorotrifluoroethane solution system revealed the role of solvent to be complicated, with the possibility of affecting almost all reaction steps of the polymerization.

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INTRODUCTION

Radiation-induced copolymerization of tetrafluoroethylene (TFE) and propylene in bulk was reported in a previous paper [1]. TFE homopolymerization and TFE-ethylene copolymerization, on the other hand, are known to be accelerated by chlorofluorohydrocarbon solvents [2-4].

TFE-propylene copolymerization proceeds rapidly in chlorofluorohydrocarbon solution systems. The role of the solvent is discussed from the kinetic results.

EXPERIMENTAL

Materials used, method of polymerization, and measurements of polymer properties are similar to those described in a previous paper [1].

RESULTS AND DISCUSSIONS

Copolymerizations were carried out in trichlorotrifluoroethane (R-113), trichlorofluoromethane (R-11), dichlorodifluoromethane (R-12), dichlorotetrafluoroethane (R-114), and monochlorodifluoromethane (R-22) at various temperatures below room temperature.

Copolymerizations in R-113 and R-11 proceed homogeneously due to the high solubility of the copolymer in these solvents, while copolymerizations in other solvents proceed heterogeneously.

Typical time-conversion curves for both homogeneous and hetrogeneous copolymerization reactions are shown in Figs. 1 and 2, respectively. Monomer conversions at various temperatures for both cases increase linearly as the reaction time increases. This result suggests that copolymerization proceeds in the stationary state for both systems and that gelation is not so dominant as to cause the Trommsdorf effect.

Polymerization rates as a function of temperature obtained from the slopes of each curve in Figs. 1 and 2 and other data are shown in Fig. 3 compared with those of bulk copolymerization. Rates in any solvent and in bulk increase rather rapidly as the temperature rises. The most effective rate-accelerating solvent is R-113.

In Fig. 4 are shown the Arrhenius plots for solution and bulk polymerization. Apparent activation energies are almost the same for all cases, including bulk polymerization (3200 cal/mole).

The compositions of copolymers obtained in solution and bulk

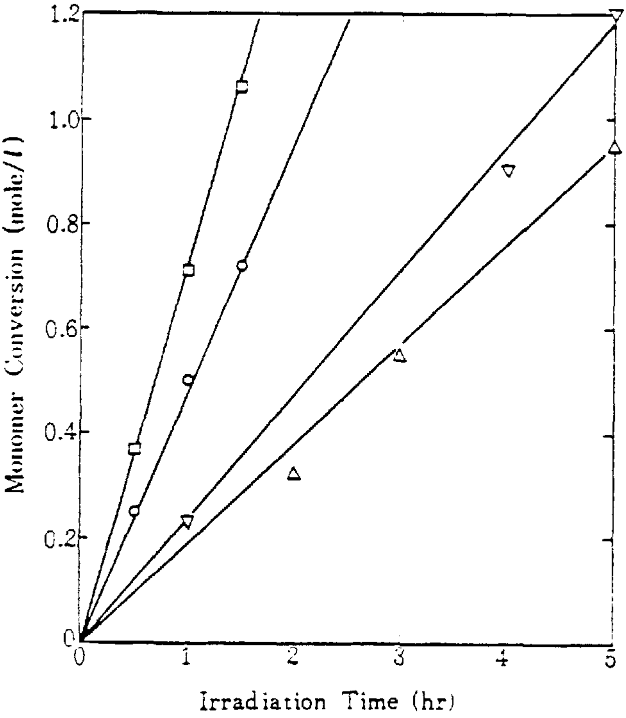

FIG. 1. Time-convertion curves in R-113 solution polymerization. Irradiation was carried out with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, at a dose rate of 3 × 10^5 r/hr, and at 25 (□), 0 (○), -23 (▽), and -36°C (△).

systems are the same so the solvents do not affect the monomer reactivity ratios.

These facts suggest that solution polymerization proceeds essentially by the same scheme as does polymerization in bulk.

The molecular weights of copolymers obtained, on the other hand, vary with temperature as shown in Fig. 5. A maximum molecular weight is observed in any solution system, just as is the case in bulk. The maximum molecular weight values at a radiation dose rate of 3 × 10^5 r/hr in solution systems are almost the same (12,000-14,000) and are observed at a polymerization temperature of 0° C for all solvents examined, whereas the molecular weight observed in bulk polymerization is 23,000 at -23° C.

Polymerization rate and molecular weight of copolymer change as the monomer concentration in the reaction medium is varied, as

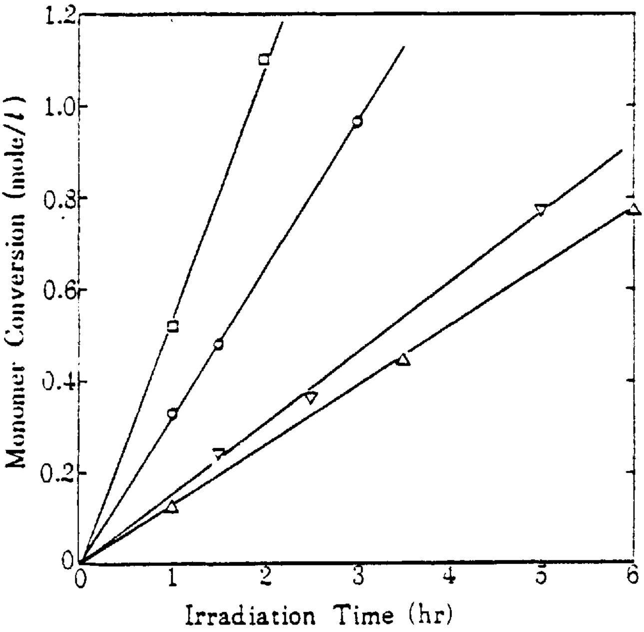

FIG. 2. Time-conversion curves in R-12 solution polymerization. Irradiation was carried out with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, at a dose rate of 3×10^5 r/hr, and at 25 (□), 0 (○), -23 (▽), and -36°C (△).

shown in Fig. 6. Both polymerization rate and molecular weight increase with monomer concentration and have a maximum value at the vicinity of 80% of monomer concentration (molar ratio of monomers/solvent = 4).

The higher molecular weight of copolymer obtained at 0°C in solution system compared to the bulk system suggests that these solvents affect not only the initiating step but also the propagation or the termination step in the polymerization, although these seem to contradict the activation energy and the copolymer composition results mentioned above.

Time-conversion curves at various dose rates for the R-113 solution system at 0°C are shown in Fig. 7. Monomer conversion increases linearly at any dose rate.

Dose rate dependencies of polymerization rate and molecular weight are shown in Fig. 8. The polymerization rate is proportional

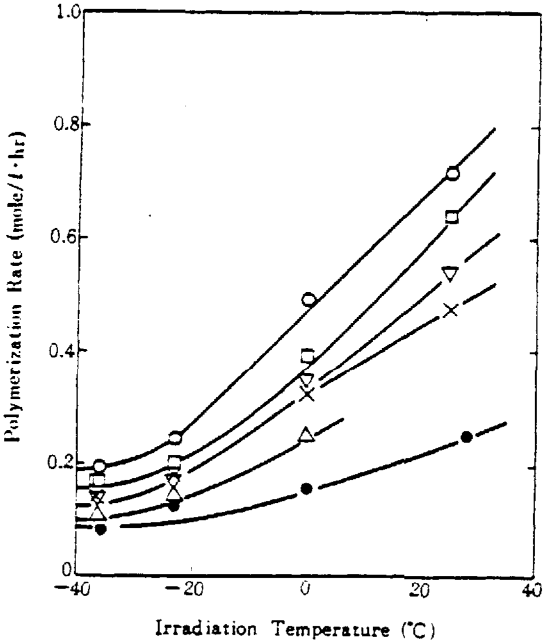

FIG. 3. Polymerization rates as a function of irradiation temperature. Irradiation was carried out with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, and at a dose rate of 3×10^5 r/hr. ○: R-113. □: R-11. ▽: R-12. ×: R-114. △: R-22. ●: Bulk.

to the 0.65 power and molecular weight is proportional to the -0.16 power of the dose rate at 0° C. These dependencies differ from those in bulk polymerization where the dependencies are 0.45 and -0.42, respectively.

Thus some contribution of the chain transfer reaction is suggested to exist in the case of the solution system.

The degree of polymerization can be calculated as reported in a previous paper [1]. Figure 9 shows the relation between the degree of polymerization and the polymerization rate at various dose rates. The reciprocal degree of polymerization ($\bar{P}_n$) and the polymerization rate (R_p) can be related, as in the bulk system, by

$$\frac{1}{\bar{P}_n} = \frac{k_{tr}([M] + [S])}{k_p[M]} + \frac{2k_{td} + k_{tc}}{k_p^2[M]^2} R_p$$

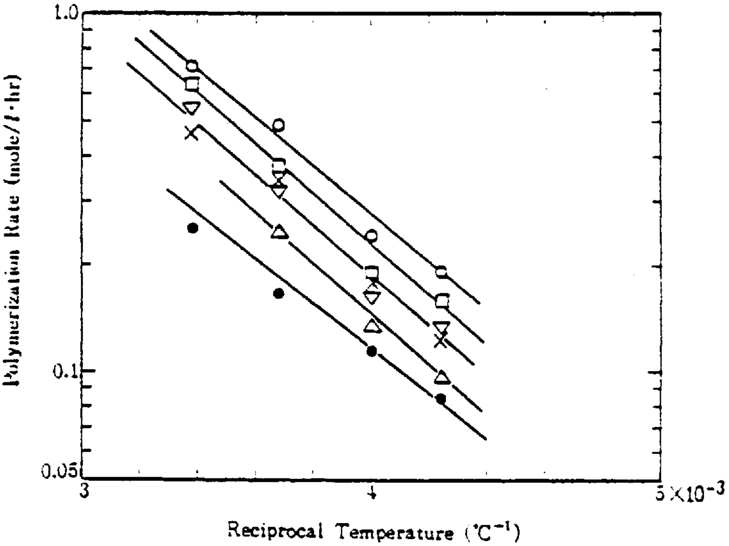

FIG. 4. Arrhenius plots for C_2F_4-C_3H_6 copolymerization. Irradiation was carried out with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, and at a dose rate of 3 × 10^5 r/hr. ○: R-113. □: R-11. ▽: R-12. ×: R-114. △: R-22. ●: Bulk.

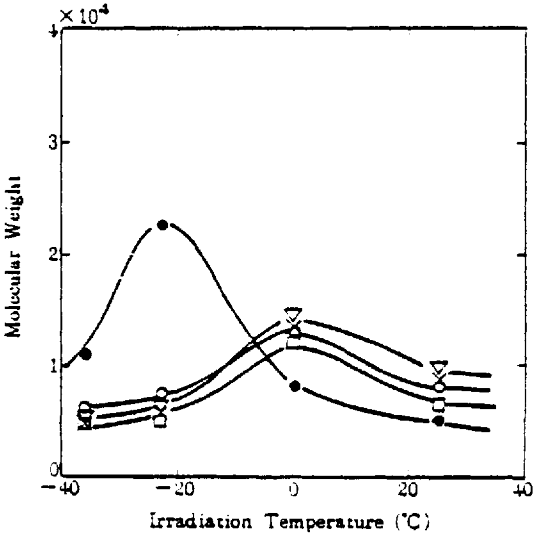

FIG. 5. Molecular weight of copolymers as a function of irradiation temperature. Irradiation was carried out with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, and at a dose rate of 3 × 10^5 r/hr. ○: R-113. □: R-11. ▽: R-12. ×: R-114. ●: Bulk.

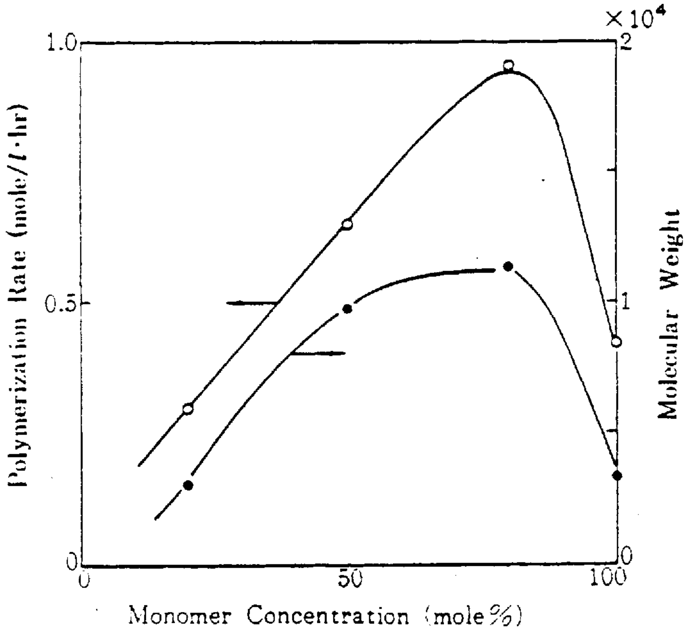

FIG. 6. Polymerization rate and molecular weight as functions of monomer concentration in the initial reaction mixture. Irradiation was carried out in R-113 with a C_2F_4/C_3H_6 molar ratio of 2, at 0°C, and at a dose rate of 3×10^5 r/hr. ○ : Polymerization rate. ● : Molecular weight.

where [M], [S], k_p, k_{tr}, k_{td}, and k_{tc} denote the concentration of monomers and solvent; and the rate constants of propagation, chain transfer, termination by disproportionation, and termination by recombination, respectively.

Figure 9 shows clearly that the above equation also fits in this solution system. The ratio of rate constant of chain transfer to propagation obtained is 10^{-3} for equimolar monomer solvent mixtures.

The copolymers obtained were found to include chlorine in their chains as fragments from chlorinated solvents. Table 1 lists the chlorine contents of the copolymers, the number-average molecular weights, the average number of chlorine atoms contained in each polymer molecule, and the irradiation dose rate. (Chlorine content was measured by radioactivation analysis.) The average number of chlorine atoms in a copolymer molecule is nearly three, corresponding to one molecule of R-113. This suggests that each polymer molecule

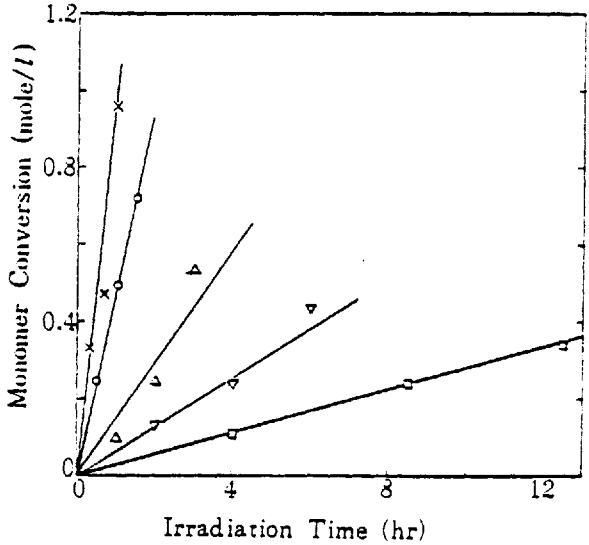

FIG. 7. Time-conversion curves at different dose rates. Irradiation was carried out at 0°C with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1 and at dose rates of 1×10^6 (×), 3×10^5 (○), 7×10^4 (△), 2×10^4 (▽), and 4.4×10^3 (□) r/hr, respectively.

TABLE 1. Chlorine Contents in Copolymers[a]

Dose rate (r/hr)	Cl content (ppm)	Molecular weight	Number of Cl per copolymer
9.7×10^5	7100	1.0×10^4	2.0
3.0×10^5	5640	1.5×10^4	2.5
6.9×10^4	3680	2.6×10^4	2.8

[a] Solvent: R-113.

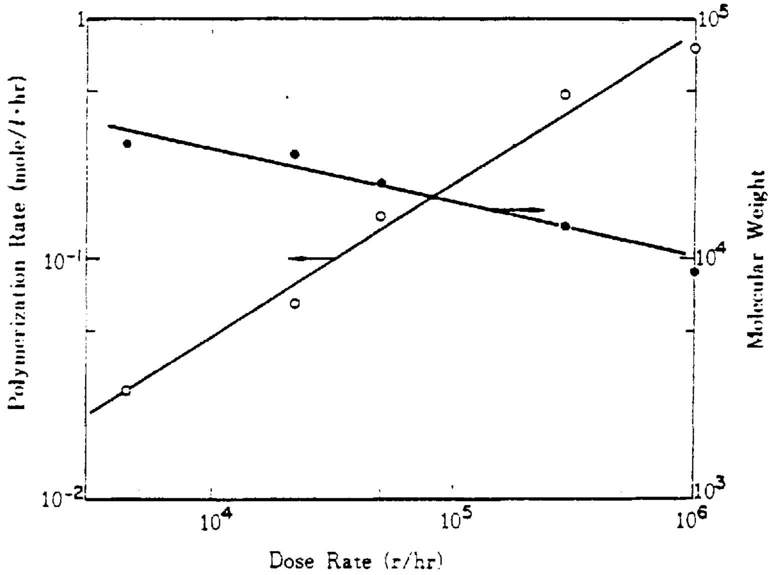

FIG. 8. Dependencies of polymerization rate and molecular weight of copolymers on the irradiation dose rate in R-113 solution copolymerization. Irradiation was carried out with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, and at 0° C.

contains chlorine atoms at its chain ends, and that fragments of the solvent initiate polymerization and chain transfer occurs mainly in the solvent.

CONCLUSION

Copolymerizations of tetrafluoroethylene and propylene are accelerated with chlorofluorohydrocarbon solvents. Trichlorotrifluoroethane (R-113) is the most effective rate-accelerator among those solvents.

The dose rate dependencies of polymerization rate and molecular weight in R-113 solution polymerization are 0.65 and -0.16, respectively. These dose rate dependencies and the chlorine content in copolymers suggest the existence of chain transfer to the solvent. The ratio of chain transfer constant to propagation constant is 1×10^{-3}

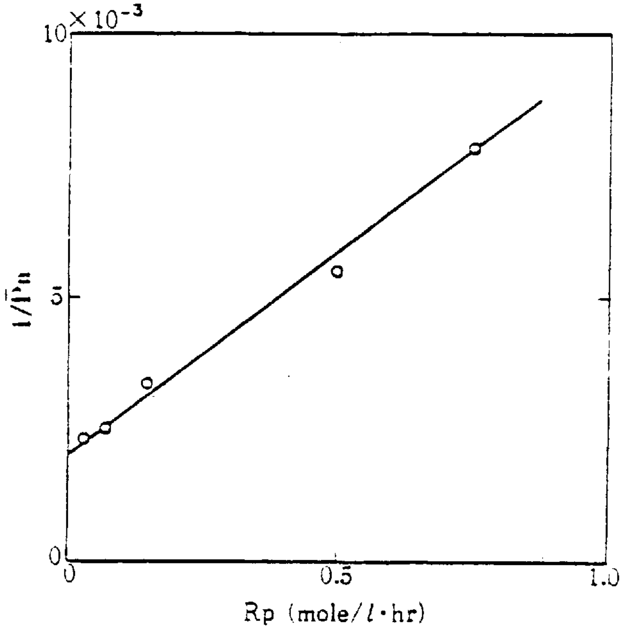

FIG. 9. Relation between the reciprocal degree of polymerization ($1/\bar{P}_n$) and the polymerization rate (R_p) in R-113 solution copolymerization. Irradiation was carried out at 0°C with a C_2F_4/C_3H_6 molar ratio of 2, monomers/solvent molar ratio of 1, and at various dose rates.

R-113 is considered to affect the various steps in the copolymerization such as initiation and propagation as well as chain transfer. The activation energy (3200 cal/mole) and the reactivity ratio of monomers do not differ from those in bulk copolymerization.

REFERENCES

[1] G. Kojima and Y. Tabata, J. Macromol. Sci.—Chem., A-6(3), 417 (1972).

[2] Y. Tabata, W. Ito, K. Oshima, and J. Takagi, J. Macromol. Sci.—Chem., A-4(4), 815 (1970).

[3] M. Hisasue, H. Ukihashi and Y. Tabata, Soc. Polym. Sci. Japan, 19th Symp. Macromol., Kyoto, 1970.

[4] M. Yamabe, H. Miyake, H. Ukihashi and Y. Tabata, Soc. Polym. Sci. Japan, 19th Symp. Macromol., Kyoto, 1970.

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