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Gen Kojima[a]; Yoneho Tabata[a]
[a] Takasaki Radiation Research Establishment Japan Atomic Energy Research Institute, Takasaki, Japan

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Radiation-Induced Copolymerization of Tetrafluoroethylene and Propylene. I. Copolymerization in Bulk

GEN KOJIMA and YONEHO TABATA*

Takasaki Radiation Research Establishment
Japan Atomic Energy Research Institute
Takasaki, Japan

ABSTRACT

Radiation-induced bulk copolymerization of tetrafluoroethylene (TFE) and propylene was carried out under various conditions from the kinetic point of view. The reaction scheme is discussed and the following mechanism is inferred: 1) the initiation reaction is not influenced by either irradiation temperature or monomer composition when TFE is rich, 2) the rate determining step in the propagation reaction is the addition of the TFE monomer to the propagating radical with propylene unit at its chain end, and 3) the termination reaction is dominated by the recombination of these propagating radicals without a preference for cross-termination. The relation between the inherent viscosity and the number-average molecular weight of the copolymer was also determined.

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*Correspondence should be mailed to: Department of Nuclear Engineering, University of Tokyo, Tokyo, Japan.

INTRODUCTION

Radiation-induced homopolymerization of tetrafluoroethylene (TFE) [1-8] and the copolymerization of TFE with some α-olefins [9-20] have been reported previously.

Copolymers of TFE with ethylene and isobutylene are crystalline and difficult to dissolve in almost all solvents. TFE-propylene copolymer, on the other hand, is amorphous and can be dissolved in several organic solvents. Although the copolymerization of TFE with ethylene has a fairly high alternating nature, the copolymerization of TFE with propylene or isobutylene has a much more highly alternating one.

Kinetics and reaction scheme of both TFE homopolymerization and TFE-ethylene copolymerization have been extensively investigated by our group. We have been continuing our work on TFE-propylene copolymerization in both bulk and solution.

In this article the bulk copolymerization of TFE and propylene initiated by γ-rays from ^{60}Co sources is reported. TFE and propylene monomers have been copolymerized at various temperatures below room temperature in a dose rate range of 6.9×10^4 to 1×10^6 r/hr. Polymerization rate, molecular weight, and monomer composition in copolymers were measured to investigate the kinetics and mechanism of the copolymerization.

Very few relationships between inherent viscosity and molecular weight of fluorine-containing polymers have been reported because they usually have no solvents. TFE-propylene alternating copolymers, on the other hand, are soluble in some solvents so that the relationship between inherent viscosity and the number-average molecular weight can be determined.

EXPERIMENTAL

Materials

TFE monomer was prepared by the pyrolysis of chlorodifluoromethane. The monomers were purified by distillation at low temperatures up to over 99.9%.

Commercial propylene with a purity of more than 99.7% was used without purification. Major impurities were propane (0.25%) and ethane (0.05%).

Polymerization and Polymer Recovery

The necessary amounts of both monomers were introduced into Pyrex glass ampoules (25 cc) and stainless steel ampoules (20 cc) and deaired to 10^{-3} to 10^{-4} Torr by conventional method. Ampoules containing monomer mixture were irradiated by γ-rays from ^{60}Co sources of 9000 and 4800 Ci. The irradiation dose rate hereafter referred to is space dose rate. The irradiation temperature was controlled to within ±2°C.

The copolymer obtained was dissolved in tetrahydrofuran (THF) to get about 10 wt% solution and precipitated by methanol to remove the low molecular weight fraction. The precipitated copolymer was dried for 50 hr at 80°C under vacuum.

Measurements of Composition, Inherent Viscosity, and Number-Average Molecular Weight of Copolymer

Carbon, fluorine, and hydrogen content of the copolymers were measured by means of elemental analysis for the calculation of copolymer composition. Although the independent determination of each of these elements enabled the calculation of copolymer composition, carbon content gave the most reliable results.

Inherent viscosity of copolymer in THF solution at 30°C was measured with a Ubbelohde's viscometer. Huggins' constant (k') was also obtained from the viscosity measurement.

Number-average molecular weight of copolymer was obtained by the measurement of osmotic pressure of copolymer solution in THF at 30°C by means of an osmometer (502 type made by Hewlett-Packard Co.).

RESULTS

Polymerization Rate and Inherent Viscosity of Copolymer

Time-conversion curves in the copolymerization at various temperatures are shown in Fig. 1.

Polymerization is not preceded by an induction period. The yield increases linearly with the irradiation time below 10 wt% conversion. Thus copolymerization is considered to proceed in a

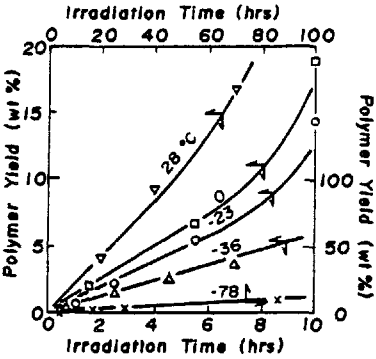

FIG. 1. Time-conversion curves of TFE-propylene copolymerization at various temperatures. Irradiation was carried out in a molar ratio (C_2F_4/C_3H_6) of 2 at a dose rate of 3 × 10^5 r/hr.

stationary state at low conversion. The polymerizations are accelerated at conversions above 10%.

The initial rate of polymerization is shown in Fig. 2 as a function of temperature. The rate increases rather rapidly as the temperature rises.

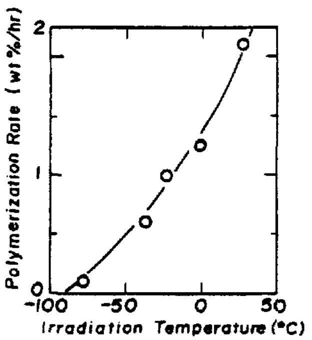

FIG. 2. Polymerization rate as a function of irradiation temperature. Irradiation was carried out in a molar ratio of 2 at a dose rate of 3 × 10^5 r/hr.

The yield was not increased when the ampoules were kept standing after irradiation. Thus it was confirmed that postpolymerization does not take place in this TFE-propylene system.

Inherent viscosities of copolymers obtained at low conversions from -78°C to room temperature are shown in Fig. 3. A maximum was observed at about -23°C. TFE content in copolymers, on the other hand, was constant at about 50 mole % throughout the temperature region.

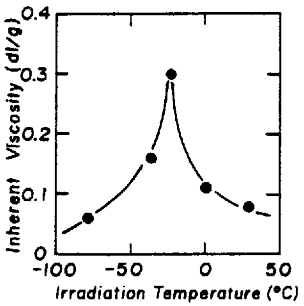

FIG. 3. Inherent viscosities of copolymer as a function of irradiation temperature. Irradiation was carried out in a molar ratio of 2 at a dose rate of 3×10^5 r/hr.

In Fig. 4 the polymerization rate and inherent viscosity of copolymer as a function of dose rate is shown. The polymerization rate and the inherent viscosity depend upon approximately the 0.5 and -0.3 power of the dose rate, respectively, in the monomer compositions. These results imply that bimolecular termination reaction is prevalent, at least when the monomer mixture is rich in TFE. Any noticeable change of TFE content in copolymer with dose rate was not observed.

Both polymerization rate and inherent viscosity of the copolymer at low conversion were strongly affected by the initial monomer composition, as shown in Fig. 5.

The polymerization rate increases rapidly with the concentration of TFE in the monomer mixture. It increases at a factor of about ten as the TFE concentration varies from 10 to 90 mole %. The inherent viscosity of the copolymer also increases remarkably as

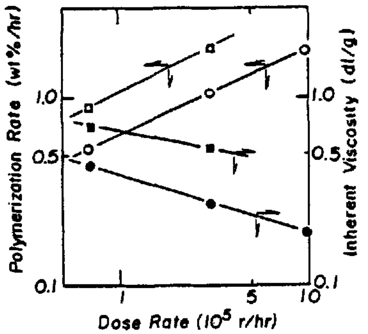

FIG. 4. Dose rate dependencies of polymerization rates and inherent viscosities. Irradiation was carried out at -23°C. Molar ratios: 2 (○ , ●) and 9 (□ , ■).

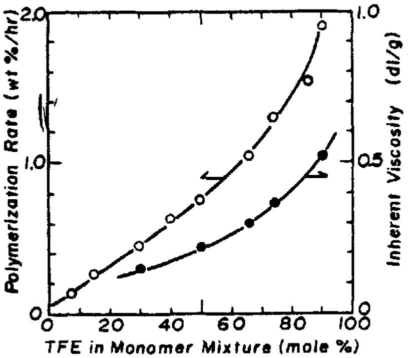

FIG. 5. Polymerization rate and inherent viscosity as a function of monomer composition. Irradiation was carried out at -23°C at a dose rate of 3 × 10^5 r/hr.

the initial monomer mixture becomes rich in TFE. The appearance of the copolymer changes from greasy to gummy as the inherent viscosity changes from 0.1 to 0.5 dl/g.

On the other hand, it was observed that copolymer composition changes very little with the concentration of TFE in the initial monomer mixture. The resultant composition curve is shown in Fig. 6. Monomer reactivity ratios of TFE and propylene at -23°C, obtained by the Fineman-Ross method, are 0.01 and 0.1, respectively. These values are much smaller than those calculated with Alfrey-Price's Q and e values [21].

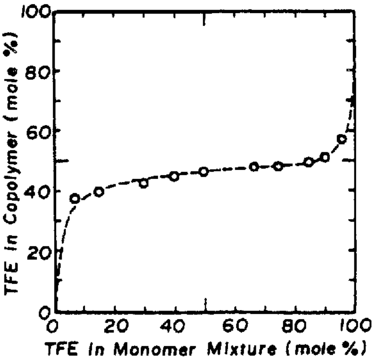

FIG. 6. Composition curve of TFE-propylene system. Irradiation was carried out at -23°C at a dose rate of 3 × 10^5 r/hr. ○ : Observed values. - - -: Calculated from $r_{C_3H_6} = 0.1$ and $r_{C_2F_4} = 0.01$.

The experimental results mentioned above were analyzed below the conversion of 10 wt%. However, at higher conversions the polymerization becomes rather complicated. With an initial molar ratio of TFE and propylene of 2, homopolymerization of TFE starts to take place at about 60 wt% (66 mole %) conversion, since almost equal moles of both monomers are consumed.

Changes of polymer yield, inherent viscosity, Huggins' constant, and gel formation as functions of irradiation time are shown in Fig. 7.

Polymer yield increases rather rapidly with the irradiation time. The inherent viscosity, on the other hand, increases remarkably and Huggins' constant increases in a similar fashion. It was observed that the THF-insoluble fraction, which is not the TFE homopolymer, is formed by an irradiation dose of over 6 × 10^6 R. These results suggest that the copolymer chain length increases and branched chains are formed. As a result, a three-dimensional network may be formed by further irradiation.

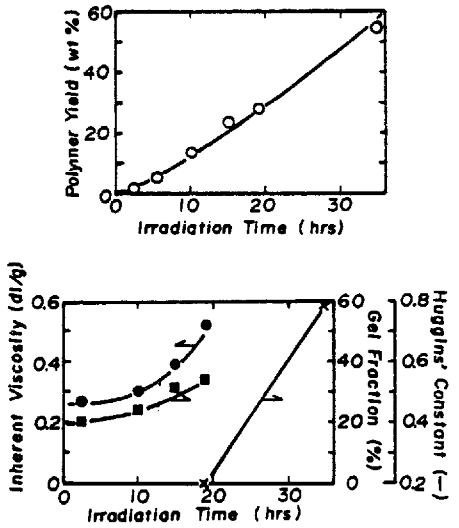

FIG. 7. Polymerization yield, inherent viscosity of copolymer, Huggins' constant, and gel formation as a function of irradiation time. Irradiation was carried out at $-23^\circ C$ at a dose rate of 3×10^5 r/hr. The molar ratio of C_2F_4/C_3H_6 was 2. (Top) Polymer yield. (Bottom) Inherent viscosity (●), Huggins' constant (■), and gel fraction (×).

In the course of copolymerization, as mentioned above, the monomer composition changes gradually and the precipitated polymers increase; therefore, the rate of copolymerization and the molecular weight of copolymers obtained at different irradiation doses should be influenced by these factors.

Molecular Weight of Copolymers

The copolymers obtained under any condition were colorless and transparent. X-ray diffraction curves of copolymers gave a broad rather than a sharp peak. Thermal analysis of the copolymers by means of DSC and DTA showed that they had no melting point but they did have a glass transition temperature below room temperature. These results indicate that the copolymers are completely amorphous.

It was made clear by NMR spectra that the copolymers have an alternating structure. Detailed experimental results will be published elsewhere in near future.

Many fluorine-containing polymers have few solvents, whereas these copolymers are soluble in several organic solvents such as THF, chloroform, and trichlorotrifluoroethane. They are swollen in several nonpolar solvents but are, however, neither insoluble nor swollen in polar solvents such as esters and alcohols.

The relationship between inherent viscosity and number-average molecular weight of the copolymers is shown in Fig. 8. It shows that the inherent viscosity of the copolymers is well expressed by the equation

$$[\eta] = 6.2 \times 10^{-5}\,\overline{M}_n^{\,0.84} \tag{1}$$

in which $[\eta]$ and $\overline{M}_n$ express the inherent viscosity (dl/g) and the number-average molecular weight, respectively. The TFE-propylene copolymer is so highly alternating and the polymers obtained under any conditions have such similar structures that the inherent viscosity of copolymers obtained at low conversions under various conditions can be related with number-average molecular weight by a single equation as shown above.

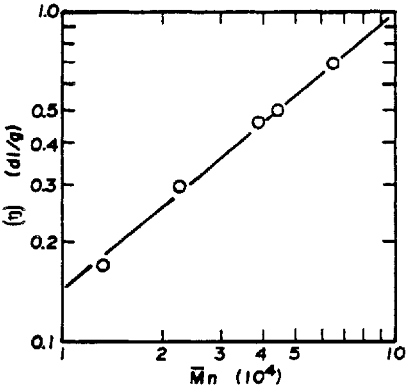

FIG. 8. Relation between inherent viscosity ($[\eta]$) and number-average molecular weight ($\overline{M}_n$). Content of C_2F_4 in copolymer: 48 to 56 mole %.

DISCUSSION

Elementary Reaction Steps

Elementary reaction steps in the bulk copolymerization of TFE and propylene are generally expressed as follows:

Initiation

$$M_1,\ M_2 \longrightarrow 2R\cdot \qquad R_i = \phi I \tag{2}$$

Propagation

$$R\cdot + M \longrightarrow RM\cdot \qquad R_{po} = k_{po}[R\cdot][M] \tag{3}$$

$$RM_n^{\cdot} + M \longrightarrow RM_{n+1}^{\cdot} \qquad R_{pr} = k_p[RM_n^{\cdot}][M] \tag{4}$$

$$\left[\begin{array}{llr}
RM_{n,1}^{\cdot} + M_1 \longrightarrow RM_{n+1,1}^{\cdot} & R_{11} = k_{11}[RM_{n,1}^{\cdot}][M_1] & (5)\\
RM_{n,1}^{\cdot} + M_2 \longrightarrow RM_{n+1,2}^{\cdot} & R_{12} = k_{12}[RM_{n,1}^{\cdot}][M_2] & (6)\\
RM_{n,2}^{\cdot} + M_2 \longrightarrow RM_{n+1,2}^{\cdot} & R_{22} = k_{22}[RM_{n,2}^{\cdot}][M_2] & (7)\\
RM_{n,2}^{\cdot} + M_1 \longrightarrow RM_{n+1,1}^{\cdot} & R_{21} = k_{21}[RM_{n,2}^{\cdot}][M_1] & (8)
\end{array}\right]$$

Chain transfer

$$RM_n^{\cdot} + M \longrightarrow P_n + R\cdot \qquad R_{tr} = k_{tr}[RM_n^{\cdot}][M] \tag{9}$$

Termination

$$RM_n^{\cdot} + RM_m^{\cdot} \longrightarrow P_{n+m} \text{ or } P_n + P_m \qquad R_t = k_t[RM_n^{\cdot}]^2 \tag{10}$$

In these expressions M_1, M_2, $RM_{n,1}\cdot$, $RM_{n,2}\cdot$, and R· denote propylene monomer, TFE monomer, propagating radical with propylene unit at its propagating chain end, that with TFE unit, and primary radical, respectively. R, k, and [ ] mean the corresponding rate (mole/liter hr), rate constant (liter/mole hr), and concentration (mole/liter), respectively. ϕ and I express the efficiency of producing primary radical (mole/liter r) and dose rate (r/hr).

General Features of the Copolymerization

Logarithmic plots of both over-all polymerization rate and number-average degree of polymerization against reciprocal absolute temperature are shown in Fig. 9. (Number-average degree of polymerization can be calculated from number-average molecular weight and copolymer composition.) Apparent activation energy of the copolymerization was calculated from the over-all polymerization rate to be 3200 cal/mole.

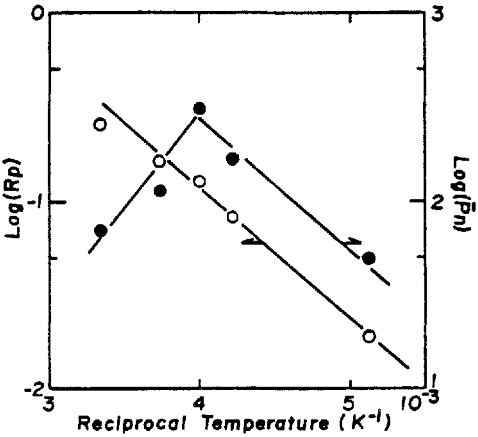

FIG. 9. Logarithmic rate (R_p) and degree ($\overline{P}_n$) of polymerization as a function of reciprocal temperature. Irradiation was carried out in a molar ratio of 2 at a dose rate of 3 × 10^5 r/hr. Polymerization rate is expressed in term of mole/liter hr.

Figure 10 shows that R_p and $\overline{P}_n$ are dependent on the 0.45 and -0.42 powers of the dose rate.

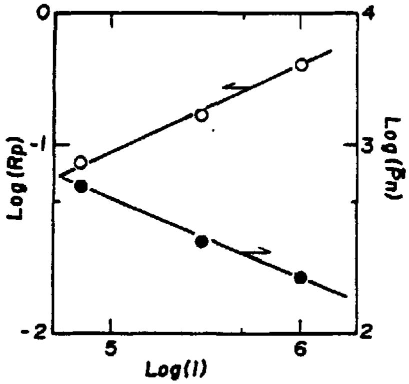

FIG. 10. Dependencies of rate (R_p) and degree ($\overline{P}_n$) of polymerization on dose rate (I). Irradiation was carried out at -23°C in a molar ratio of 2.

The apparent activation energy and the dependencies of both rate and degree of polymerization on dose rate support the idea that copolymerization proceeds by a radical mechanism.

Figure 9 shows that over-all polymerization rate (R_p) and degree of polymerization ($\overline{P}_n$) below -23°C can be expressed by the equations

$$R_p = 71 \exp(-3200/RT) \tag{11}$$

$$\overline{P}_n = 1.6 \times 10^5 \exp(-3200/RT) \tag{12}$$

in which R_p is expressed in mole/liter hr.

These equations indicate that a constant number of polymers, equal to 4.4×10^{-4} mole/liter hr, are produced at any temperature below -23°C at a dose rate of 3×10^5 r/hr.

The rapid decrease in the degree of polymerization and the resultant increase in the number of polymers above -23°C imply that chain transfer to propylene monomer takes place as in the case of propylene homopolymerization [22].

This copolymerization is considered to proceed in the stationary state since the monomers are consumed proportionally to the irradiation time.

In ordinary radical polymerizations, the degree of polymerization is expressed as a function of the polymerization rate as in equation

$$\frac{1}{P_n} = \frac{k_{tr}}{k_p} + \frac{2k_{td} + k_{tc}}{k_p{}^2[M]^2} R_p \tag{13}$$

where k_{td} and k_{tc} denote rate constants of termination by disproportionation and by recombination, respectively. This relation is also expected to be valid in the case of copolymerization.

Figure 11 shows that the relation between R_p and $1/\overline{P}_n$ can be fitted to Eq. (13). Moreover, Fig. 11 gives us the information that no chain transfer occurs at -23°C.

Consequently, we may accept that copolymerization proceeds without chain transfer in the temperature region below -23°C since the number of polymer is kept constant in that region as shown in Fig. 9.

Because of the level of the degree of polymerization, we may suppose that the termination reaction takes place mainly between the growing polymer radicals.

Initiation

The number of initiating radicals (ν, mole/liter hr) and that of polymers produced per hour (N, mole/liter hr) can be related by Eq. (14), when chain transfer does not occur;

$$\nu = \frac{2}{2 - x} N \tag{14}$$

where x denotes the relative rate constant of the recombination to the over-all termination reaction, i.e., $k_{tc}/(k_{td} + k_{tc})$.

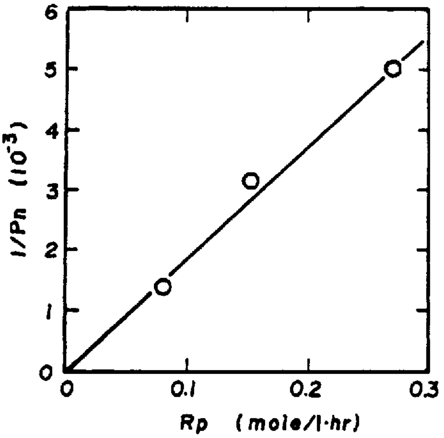

FIG. 11. Relation between rate of polymerization (R_p) and reciprocal degree of polymerization ($1/\bar{P}_n$). Irradiation was carried out at -23°C in a molar ratio of 2 at dose rates of 6.9×10^4, 3×10^5, and 9.7×10^5 r/hr, respectively.

Figure 10 shows that the number of polymers is almost proportional to the dose rate, which suggests that initiating radicals are formed proportionally to the dose rate.

Therefore, the rate of initiation can be expressed by

$$R_i = \nu/2 = \{1.47/(2 - x)\} 10^{-9} I \tag{15}$$

in which R_i is expressed in mole/liter hr. Thus ϕ is equal to $\{1.47/(2 - x)\} \times 10^{-9}$ (mole/liter r).

The G value for the yield of the initiating radical is roughly estimated by using both the value of R_i and the density of the reaction medium (~1 g/cc at -23°C when the molar ratio of TFE/propylene equals 2). Since the absorption energy in the reaction medium is nearly 100 erg/g (6.25×10^{13} eV/g) for the irradiation of 1 roentgen, Eq. (16) is derived:

$$G = \frac{100 \times 2N_0\phi}{6.25 \times 10^{13} \times 10^3} = \frac{2.8}{2 - x} \qquad (16)$$

in which N_0 is Avogadro's number. Thus the G value varies from 2.8 to 1.4, depending upon the contribution of either type of termination.

The constant number of polymers shown in Fig. 9 below -23°C means that initiating radicals are produced independently of irradiation temperature, which is to be expected in the case of radiation- or photoinduced polymerizations.

Moreover, the number of polymers produced per hour varies little with the change in monomer composition when TFE exceeds 50 mole % in the monomer mixture, as shown in Fig. 12. Consequently, the rate of initiation in the region is also independent of monomer composition.

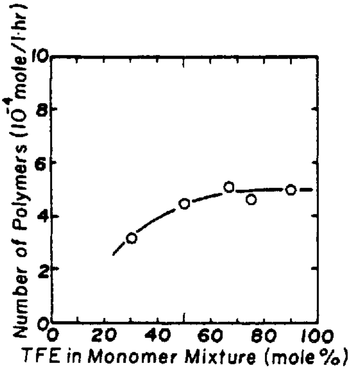

FIG. 12. Number of polymers produced per hour as a function of monomer composition. Irradiation was carried out at -23°C at a dose rate of 3×10^5 r/hr.

Therefore, in the discussions to follow about the bulk copolymerization of TFE and propylene in the stationary state, we assume no chain transfer and a constant rate of initiation in the temperature region below -23°C.

Propagation

The stationary state assumption of primary radicals ($R\cdot$) and propagating radicals ($RM_{n,1}\cdot$, $RM_{n,2}\cdot$ and the sum of these propagating radicals $RM_n\cdot$) leads to the equations

$$2\phi I = k_{po}[R\cdot][M] \tag{17}$$

$$k_{po}[R\cdot][M] = 2k_t[RM_n\cdot]^2 \tag{18}$$

$$\equiv 2\{k_{t11}[RM_{n,1}\cdot]^2 + k_{t12}[RM_{n,1}\cdot][RM_{n,2}\cdot] + k_{t22}[RM_{n,2}\cdot]^2\} \tag{19}$$

$$k_{12}[RM_{n,1}\cdot][M_2] = k_{21}[RM_{n,2}\cdot][M_1] \tag{20}$$

in which k_{t11}, k_{t22}, and k_{t12} denote the rate constants of termination reactions as shown by

$$RM_{n,1}\cdot + RM_{m,1}\cdot - P_{n+m} \text{ or } P_n + P_m \qquad R_{t11} = k_{t11}[RM_{n,1}\cdot]^2 \tag{21}$$

$$RM_{n,2}\cdot + RM_{m,2}\cdot - P_{n+m} \text{ or } P_n + P_m \qquad R_{t22} = k_{t22}[RM_{n,2}\cdot]^2 \tag{22}$$

$$RM_{n,1}\cdot + RM_{m,2}\cdot \rightarrow P_{n+m} \text{ or } P_n + P_m \qquad R_{t12} = k_{t12}[RM_{n,1}\cdot][RM_{n,2}\cdot]$$

Equations (17), (19), and (20) can be combined into

$$\phi I = \{k_{t11}[RM_{n,1}\cdot]^2 + k_{t12}[RM_{n,1}\cdot][RM_{n,2}\cdot] + k_{t22}[RM_{n,2}\cdot]^2\}$$

$$[RM_{n,2}\cdot] = \alpha[RM_{n,1}\cdot] \tag{25}$$

in which α is $k_{12}[M_2]/k_{21}[M_1]$.

By substituting Eq. (25) into (24), we obtain

$$\phi I = K_t[RM_{n,1}\cdot]^2 \tag{26}$$

in which K_t is $k_{t11} + k_{t12}\alpha + k_{t22}\alpha^2$.

Consequently, concentrations of both propagating radicals are expressed as

$$[RM_{n,1}\cdot] = \sqrt{\phi I/K_t} \tag{27}$$

$$[RM_{n,2}] = \alpha\sqrt{\phi I/K_t} \tag{28}$$

Thus the over-all polymerization rate can be written in the form of Eq. (29) since the majority of monomers are consumed in the propagating step.

$$R_p = \{k_{11}[M_1] + k_{12}[M_2] + k_{22}\alpha[M_2] + k_{21}\alpha[M_1]\}\sqrt{\phi I/K_t} \tag{29}$$

The values of $k_{22}/k_{21} = 0.01$ and $k_{11}/k_{12} = 0.1$ have been obtained from the copolymerization data; on the other hand, the fact that k_{11} is very small whereas k_{22} is very large has been shown from homopolymerization data for both monomers [9, 22]. Therefore the relation among the rate constants is $k_{11} \ll k_{12} \ll k_{21}$. Therefore the rate-determining step in the propagation of the alternating copolymerization of TFE-propylene is the addition of TFE monomer onto the propagating radical with the propylene unit at its chain end.

According to the relation between k_{12} and k_{21} above given, α should be smaller than unity provided $[M_2]/[M_1]$ would not be extremely large. On the other hand, it is known that k_{t22} is also very small [9].

Thus R_p can be expressed approximately by Eq. (30) when $[M_1]$ is not very large:

$$R_p = \frac{k_{12}[M_2]\ (2 + r_2[M_2]/[M_1])}{(k_{t11} + k_{t12}\alpha)^{1/2}}\sqrt{\phi I} \tag{30}$$

in which r_2 is the monomer reactivity ratio of TFE.

Termination

Let us examine Eq. (30) in the following two cases; (a) Cross-termination is predominant as the termination step, and (b) recombination of the propagating radicals having propylene units at their chain ends is predominant as the termination step.

In the former case, Eq. (30) leads to

$$R_p/[M_2] = \sqrt{\frac{k_{12}k_{21}}{k_{t12}}}\left(2\sqrt{\frac{[M_1]}{[M_2]}} + r_2\sqrt{\frac{[M_2]}{[M_1]}}\right)\sqrt{\phi I} \tag{31}$$

Equation (31) indicates that $R_p/[M_2]$ decreases with increasing $[M_2]$ and has a minimum at a monomer composition of $[M_2]/[M_1] = 2/r_2$. This is not supported by the experimental results shown in Fig. 14.

In the latter case, Eq. (30) leads to

$$R_p/[M_2] = \frac{k_{12}}{\sqrt{k_{t11}}}(2 + r_2[M_2]/[M_1])\sqrt{\phi I} \tag{32}$$

Equation (32) indicates that R_p increases proportionally to $[M_2]$ when $[M_2]/[M_1]$ is small and that $R_p/[M_2]$ increases proportionally to $[M_2]/[M_1]$ when the latter becomes large.

Figures 13 and 14 show that the experimental results agree quite well with Eq. (32).

Similarly, the degree of polymerization is expressed by Eq. (33) when termination is assumed to be caused by the reaction of $RM_{n,1}\cdot$:

$$\overline{P}_n/[M_2] = \frac{k_{12}}{\sqrt{k_{t11}}(2 - x)}(2 + r_2[M_2]/[M_1])\frac{1}{\sqrt{\phi I}} \tag{33}$$

Changes of $\overline{P}_n$ and $\overline{P}_n/[M_2]$ as functions of $[M_2]$ and $[M_2]/[M_1]$ are also plotted in Figs. 13 and 14, respectively. These results

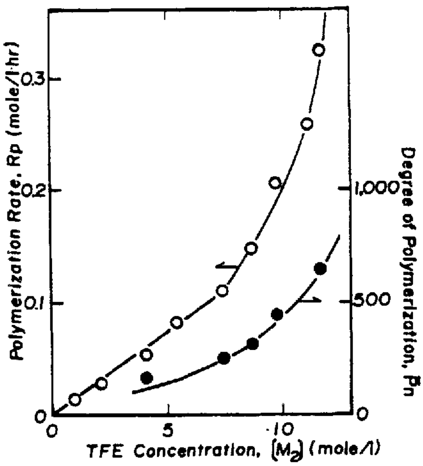

FIG. 13. Polymerization rate (R_p) and degree of polymerization ($\bar{P}_n$) as a function of C_2F_4 concentration in the monomer mixtures ([M_2]). Irradiation was carried out at -23°C at a dose rate of 3×10^5 r/hr.

show fairly good agreement with Eq. (33), although a slight deviation is found in the region where [M_2] is small.

Thus it may be concluded that the termination reaction takes place mainly via the recombination of $RM_{n,1}\cdot$ as shown in Eq. (21) and that cross-termination does not play any important role.

CONCLUSIONS

Copolymerization of TFE and propylene proceeds to give a highly alternating copolymer. The monomer reactivity ratios of TFE and propylene at -23°C were estimated to be 0.01 and 0.1, respectively.

The copolymerization reaction proceeds by a radical mechanism with an apparent activation energy of 3.2 kcal/mole in the temperature region from -78 to 28°C.

The yield of initiating radicals is independent of both irradiation

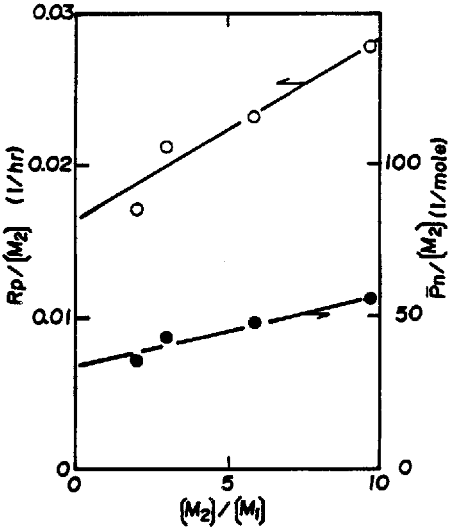

FIG. 14. Rate (R_p) and degree ($\bar{P}_n$) of polymerization as a function of $[M_2]/[M_1]$. Irradiation was carried out at -23°C at a dose rate of 3×10^5 r/hr.

temperature and monomer composition when TFE is rich. The rate of initiation is expressed by

$$R_i = \frac{1.5}{2 - x} \times 10^{-9} I$$

The G value of initiation is nearly $2.8/(2 - x)$.

The rate of propagation is controlled by the reaction step of the addition of TFE monomer to the propagating radical with a propylene chain end, so that rate and degree of polymerization are largely affected by the concentration of TFE.

Termination may be caused by the recombination of propagating radicals having propylene chain ends, and there is no evidence that cross-termination prevails.

Chain transfer does not play a significant role below -23°C. On the other hand, chain transfer increases rapidly at higher temperatures.

Thus the rate and degree of polymerization below -23°C can be expressed by

$$R_p = \frac{k_{12}}{\sqrt{k_{t11}}} (2 + r_2[M_2]/[M_1])[M_2] \sqrt{\phi I}$$

$$P_n = \frac{k_{12}}{\sqrt{k_{t11}}(2-x)} (2 + r_2[M_2]/[M_1])[M_2] (\sqrt{\phi I})^{-1}$$

On the other hand, correlation between inherent viscosity and number-average molecular weight is found to be expressed as

$$[\eta] = 6.2 \times 10^{-5} \overline{M}_n^{0.84}$$

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