Kinetic Studies on the Radiation-Induced Solution Polymerization of Tetrafiuoroethyiene

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Solution Polymerization of Tetrafluoroethylene

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ABSTRACT

Kinetic studies on the radiation-induced polymerization
and postpolymerization of tetrafluoroethylene were car-
ried out using chlorofluorohydrocarbons as the solvents.
The mechanism of the radiochemical formation of radicals
and the kinetics of the radical decay during in-source and
postpolymerization are discussed. The remarkable post-
polymerization is explained by the unusually slow rate of
the bimolecular chain termination. The mechanism of
chain transfer reactions is also discussed.

INTRODUCTION

Several papers on the radiation-induced polymerization of tetrafluoroethylene have been published in the last decade [1-4]. From these investigations it was found that tetrafluoroethylene can be polymerized by radiation with a considerably high rate, and a remarkable postpolymerization, which is considered to be a rare case, takes place. Several kinetic studies indicate that tetrafluoroethylene polymerizes via radical mechanism and its remarkable postpolymerization seems to be due to the slow recombination rate of growing radicals. However, little information is available as to the role of solvents and the mechanism of the postpolymerization.

Kinetic studies on the initiation, propagation, and termination processes of the polymerization have been made using chlorofluorohydrocarbons as the solvents. The effects of the solvents on radical formation, the rate of propagation, and the chain termination are discussed. The kinetics of the radical decay is also discussed.

EXPERIMENTAL

Materials

Monomer. Tetrafluoroethylene (C_2F_4) was prepared by pyrolyzing chlorodifluoromethane in a platinum-lined tubular reactor at 700-800°C. After the product mixture was washed with water to remove a by-product of hydrogen chloride, C_2F_4 monomer was distilled by using a low-temperature distillation column. A purity higher than 99.9% was confirmed by gas chromatographical analysis of the C_2F_4 obtained.

Solvents. Commercial trichlorotrifluoroethane $(CClF_2CCl_2F$, R-113), dichlorodifluoromethane $(CCl_2F_2$, R-12), and chlorodifluoromethane $(CHClF_2$, R-22) were used as solvents without any purification.

Procedures

The polymerizations were carried out by using a 50-ml and a 1.8-liter stainless steel autoclave. The autoclaves were degassed

by two freeze-thaw cycles under pumping, after the monomer solu-
tions are introduced. In-source polymerizations were done by
γ-rays from a ^{60}Co source at various temperatures. Postpolymer-
izations were conducted in a temperature range between -30 and
-10°C. The reaction temperature was controlled by circulating
coolant from a refrigerator through the jacket of the autoclave.
The temperature in the autoclave was maintained within ±1.0°C.
The unreacted monomer and the solvent were distilled out after
the polymerization. then the polymer was placed in an electrical
oven maintained at 120°C for longer than 10 hr to remove the
small amount of solvent absorbed by the polymer. The polymer
yield was determined gravimetrically.

The dried polymer was then crushed to a fine powder of less
than 30 μ in order to measure the physical and mechanical
properties. Polytetrafluoroethylene can not be dissolved in
most solvents. so that the molecular weight of the polymer can
not be determined by solution viscosity measurement. However,
it is known that the density of the fabricated polymer is related
to the molecular weight [5]. Both the fabrication of the specimen
and the measurement of the density were carried out according to
JIS-K-6891.

The measurement of the tensile strength was also done under
JIS conditions.

The radical concentrations in the polymerization systems
were also measured. Diphenylpicrylhydrazyl (DPPH), which
can exhibit the polymerization completely, was used as the radical
scavenger. The radical concentrations were determined from the
amounts of DPPH consumed. The concentration can be measured
by an electrophotometer using a red filter (655 mμ).

RESULTS AND DISCUSSION

Initiation Step

Recent studies on the radiation-initiated polymerization of
tetrafluoroethylene have indicated that the solution polymerization
proceeds at a higher rate than the bulk polymerization, and the
sensitizing effect may be explained by an increase in the initiation
and propagation reactions due to the presence of the solvent [2].
Furthermore. it is known that the rate of the solution polymeri-
zation is affected by the kind of solvent used. and perfluoro-
chlorohydrocarbon gives a higher rate and a polymer of higher

molecular weight than can be obtained by using other solvents [4].

In order to clarify the role of the solvent in the initiation reaction of the polymerization, the radiochemical yields of free radical (G_R) in the C_2F_4-solvent systems were measured by using the DPPH method, and the results are given in Fig. 1. In the presence of perfluorochlorohydrocarbon, e.g., R-113 and R-12, a sensitization for the radical formation was observed. In contrast, R-22, which has a hydrogen atom in its molecule, showed a protective effect.
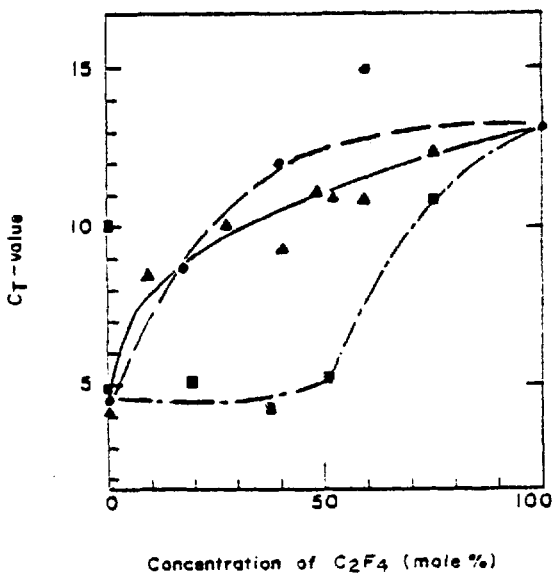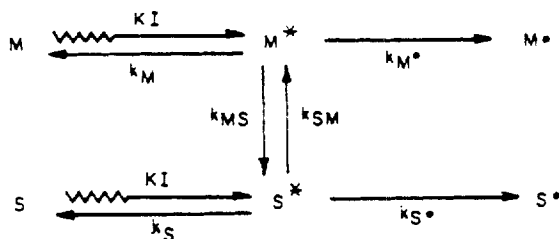

Concentration of C_2F_4 (mole %)

FIG. 1. G-values of free radical production in mixtures of C_2F_4 with various chlorofluorocarbons. (▲) $C_2Cl_3F_3-C_2F_4$. (●) $CCl_2F_2-C_2F_4$. (■) $CHClF_2-C_2F_4$.

. These effects of the perfluorochlorohydrocarbons on G_R can be explained by the energy transfer mechanism. Energy transfer processes are schematically summerized as [6]

where M and S represent a monomer and a solvent, respectively, and S^* and M^* are excited species produced by the absorption of radiation energies. S· and M· represent a solvent and a monomer radical. K is a constant which only depends on the unit of the dose rate I.

Provided the stationary state treatment can be applied with respect to the excited species S^* and M^*, and further by introducing the following constants ϕ_M, ϕ_S, x_M, and x_S,

$$c_M = kM \cdot / (kM + kM \cdot), \qquad \phi_S = kS \cdot / (kS + kS \cdot)$$

$$X_M = kMS / (kM + kM \cdot), \qquad x_S = kSM / (kS + kS \cdot) \qquad (1)$$

the concentrations of radicals in the solvent-monomer mixture can be expressed as

$$[R \cdot] = KI\phi_M \frac{m + (x_M / x_S)(\phi_S / \phi_M)}{m - (x_M / x_S)} \qquad (2)$$

where m is the ratio of the concentration of the monomer to that of the solvent $(m = M/S, M + S = 1.0)$.

x_M and x_S represent the probabilities of transfer of excitation energy from monomer to solvent and from solvent to monomer, respectively. ϕ_M and ϕ_S are equivalent to the rate constant of

free radical production in pure monomer and solvent, respectively.
The ratio $x_{M'} x_S$ can be calculated from Eq. (2) by using the experi-
mental values of G_R in Fig. 1, and the results are given in Table 1.

TABLE 1. Energy Transfer Rate in
Perfluorochlorohydrocarbon-Monomer
Binary Mixture

Solvent	$x_{M'} x_S$	S, M
R-113	0.26	0.3
R-12[a]	0.20	0.3

[a]In the range of concentration of C_2F_4
between 0 and 50 mole %.

The lines for both R-113 and R-12 in Fig. 1 represent the
theoretical relationship based on Eq. (2) calculated with the
values of Table 1. The good agreement between the theoretical
lines and experimental data supports the idea that the energy
transfer reactions are involved in the radical formation in this
binary mixture. It is also shown from Table 1 that the energy
transfer from solvent to monomer predominates in the system
since the ratio $x_{M'} x_S$ is smaller than unity. It is not yet explained
as to why R-22 shows a protective effect, but it may be due its
effect on radical formation.

Therefore, the increase in the rate of polymerization by the
use of perfluorochlorohydrocarbon may be attributed to the sen-
sitization of the solvent for radical formation. However, the low
rate of bulk postpolymerization may be caused by other mechanisms.

All the radicals responsible for the postpolymerization should be
supplied by irradiation during the in-source polymerization, since
the thermal polymerization of C_2F_4 can be neglected at low
temperatures.

Figure 2 shows the radical concentrations as a function of the
molar ratio of monomer to solvent immediately after preirradiation
measured by the DPPH method in the case of the solution polymeri-
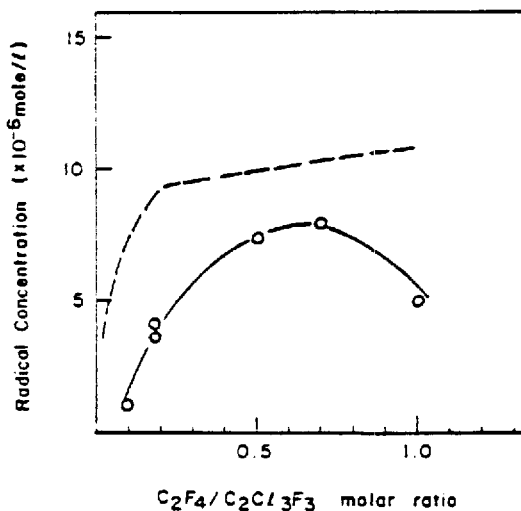zation in R-113. The radical concentration calculated from G_R of

FIG. 2. The radical concentrations immediately after pre-irradiation as a function of $C_2F_4/C_2Cl_3F_3$ molar ratio. The dotted line is calculated from a G-value of Fig. 1. Irradiation: 2×10^4 R hr $\times$ 2.5 min at $-30°C$.

Fig. 1 is represented by the dotted line which corresponds to the concentration, if it is assumed that the radicals formed do not decay. Figure 3 shows the effect of irradiation time on the radical concentration as in Fig. 2.

It is apparent from Figs. 2 and 3 that bimolecular chain termination or radical decay occurs during in-source polymerization, since the radical concentrations measured are exclusively lower than the calculated ones. Moreover.it is interesting that the concentration of the radical that survives preirradiation depends on the C_2F_4/R-113 mole ratio and has a maximum value at a C_2F_4/R-113 mole ratio of 0.5 to 0.7. The effect of solvent on the concentration of the surviving polymer radicals is difficult to explain clearly. However, in the higher solvent concentration region, the polymers would have low molecular weights, large mobility and the viscosity of the system would be expected to be low, so that the greater decay of radicals would be due to the large probability of collision of polymer radicals.

The relationship between C_2F_4/R-113 mole ratio and radical concentration can be derived from the postpolymerization rate.
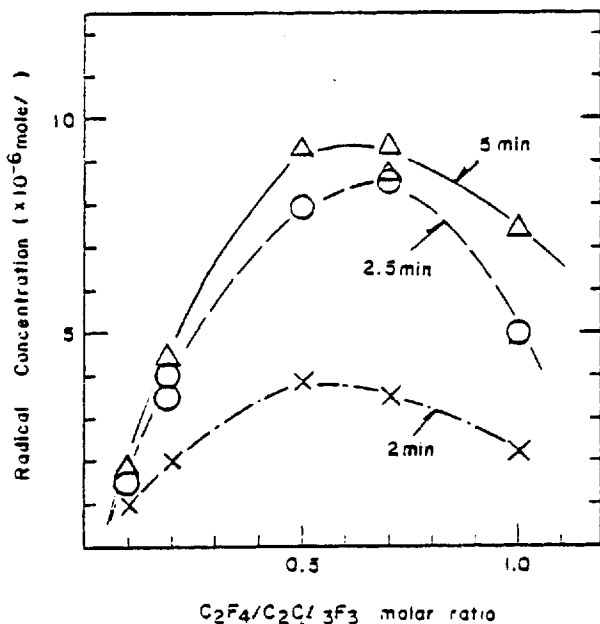
FIG. 3. The effect of irradiation time on the radical concen-
tration immediately after preirradiation as a function of the molar
ratio of monomer to solvent. Dose rate: 2×10^4 R/hr. Irradiation
temperature: -30°C.

The rate of postpolymerization at an early stage can be written as

$$R_p = k_p[M][P\cdot] \tag{3}$$

where k_p is the propagation rate constant and $[M]$ is the concentra-
tion of the monomer. The concentration of the growing polymer
radical $[P\cdot]$ is only related to the in-source polymerization condi-
tions and is proportional to the dose or irradiation time t_R when
the dose or the dose rate is relatively small.

$$[P\cdot] = K't_R \tag{4}$$

Combining Eqs. (3) and (4) gives

$$k_p K' = R_p / [M] \cdot t_R \tag{5}$$

In this equation, K' is only dependent on monomer concentration if the dose rate is constant, and also it is apparent from Eq. (4) that K' is proportional to the concentration of the radical surviving pre-irradiation. The results are given in Table 2.

TABLE 2. Comparison of Radical Concentration Derived from Post-polymerization Rate at Various C_2F_4, R-113 Ratios

C_2F_4, R-113 mole ratio	t_R (min)	R_p (mole/liter hr)	$k_p K$ (min/hr)
1.0	2.2	0.375	0.029
0.7	1.9	0.331	0.043
0.5	2.1	0.200	0.030

At a C_2F_4, R-113 mole ratio of 0.7, the value of $R_p K$ is a maximum. Since postpolymerization was conducted at the same temperature, k_p is constant so that K is a maximum at a C_2F_4/R-113 mole ratio of 0.7. These results are in agreement with those of Figs. 2 and 3. The effect of the solvent on the concentration of the surviving growing radical may be partly explained by the low rate of bulk postpolymerization.

Propagation Step

The overall activation energy for the postpolymerization rate in the initial stage may be equivalent to that of the propagation reaction since the postpolymerization rate is expressed by Eq. (3).

Figure 4 shows examples of the time-conversion relation in postpolymerization. The activation energy for the postpolymerization rate in R-113 solution was calculated to be 11.7 kcal/mole, which is slightly larger than the 10.3 kcal/mole for bulk postpolymerization observed by Oshima et al. [1].
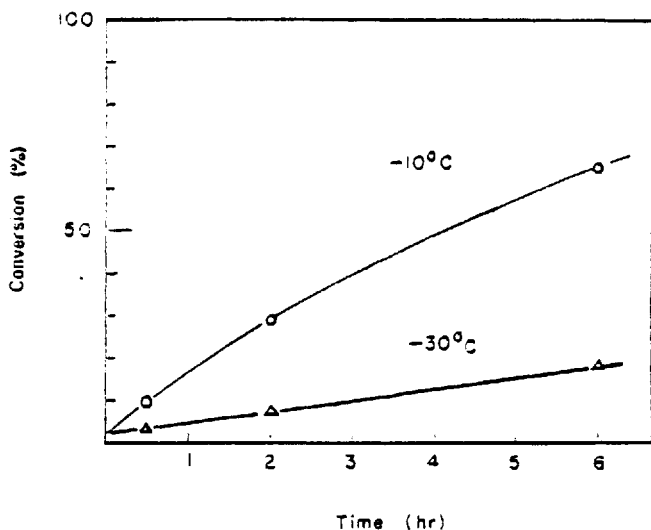
FIG. 4. Temperature dependence on the rate of postpolymeri-
zation. $C_2F_4/C_2Cl_3F_3$ molar ratio: 1.0. In-source polymerization:
2×10^4 R, hr $\times$ 3 min at $-30°C$.

The slightly larger activation energy may be due to the protective
effect of the solvent on the growing polymer end.

From these results, together with those of the preceding section,
the propagation rate constant k_p can be calculated as 3.6×10^{10}

$\exp(-11700/RT)$ (liter, mole sec). The relatively large k_p may
explain the high postpolymerization rate.

Termination Step

In the solution polymerization of C_2F_4 the resultant polymer
precipitates from the solvents since the polymer can not be dis-
solved in the solvents. Therefore the growing radicals may be
occluded in the polymers formed and then bimolecular chain
termination would be considerably suppressed. The remarkable
after-effect seems to be due to this fact. However, as was men-
tioned previously, the radical decay by chain termination occurs
to some extent in the early stage of polymerization in which the
viscosity of the system is relatively low.

The rate of bimolecular chain termination, that is, the rate of radical decay, is formulated by

$$-d[P\cdot]/dt = k_t[P\cdot]^2 \qquad (6)$$

where k_t is the rate constant for the termination. Integrating Eq. (6):

$$-1/[P\cdot]_0 + 1/[P\cdot]_t = k_t t \qquad (7)$$

where $[P\cdot]_0$ and $[P\cdot]_t$ represent the initial radical concentration and the concentration after polymerization time t, respectively. Combining Eqs. (3) and (7):

$$1/R_{Pt} - 1/R_{P0} = (k_t/k_p[M])t \qquad (8)$$

where R_{P0} and R_{Pt} are the polymerization rate at t = 0 and t = t, respectively.

From Eq. (8) the reciprocal of the rate R_{Pt} is proportional to polymerization time t, if the concentration of the monomer remains constant throughout the postpolymerization. The reciprocal of the experimental rate of the postpolymerization vs reaction time at constant monomer concentration is plotted in Fig. 5.

Monomer is supplied to the polymerization vessel to maintain the reaction pressure in the course of polymerization, and the concentration of the monomer can be kept constant because the solubility of the polymer in both monomer and solvent is negligibly small. The good linear relationship in Fig. 5 suggests the presence of bimolecular termination in the postpolymerization. From the gradient of the line which corresponds to the value of $k_t/k_p[M]$, k_t was calculated to be 1.8×10 liter/mole sec at 0°C. This k_t is extremely low compared with those of the other monomers (see Table 3). The remarkable after-effect can be explained by this low rate of termination and the negligibly small decay of the polymer radical.

In postpolymerization in which there is no supply of radical and negligible decay of the growing radicals, it is assumed that
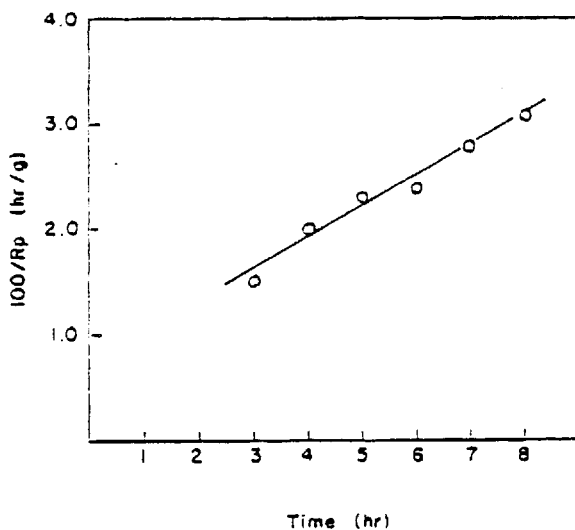
Time (hr)

FIG. 5. Postpolymerization rate as a function of the duration of polymerization. $C_2F_4/C_2Cl_3F_3$ molar ratio: 0.5, which was kept constant during postpolymerization. In-source polymerization: 2×10^4 R/hr × 2.0 min at -30°C. Postpolymerization temperature: 0°C.

TABLE 3. Comparison of k_t of C_2F_4 Solution Polymerization with Those of Other Homopolymerizations

Monomer	Temperature (°C)	k_t (liter/mole sec)
Styrene	25	3.6×10^8
MMA	25	1.0×10^7
MA	26.5	3.55×10^8
VC	25	1.0×10^8
C_2F_4	0	1.8×10

the chain transfer reaction can be neglected. The molecular weight
of polymer can be described as

$$\overline{P} = \int R_p \, dt / [P \cdot]_0 \tag{9}$$

$\int R_p \, dt$ $(= \int -dM/dt \, dt = \int -dM)$ is the polymer yield, so that the
molecular weight does not depend on the kind of solvent but only
on the polymer yield and the initial concentration of the polymer
radical $[P \cdot]_0$ (which depends on the preirradiation dose). However,
the molecular weight depends on the kind of solvent, as previously
mentioned. Therefore, the assumption of neglecting chain transfer
processes may be inapplicable to the polymerization. If the chain
transfer reactions are predominant in chain termination, the
molecular weight of polymer is expressed by

$$\overline{P} = \int R_p \, dt / \left\{ \int R_{tr} \, dt + [P \cdot]_0 \right\} \tag{10}$$

where R_{tr} $(= k_{tr}[P \cdot][S])$ is the rate of the chain transfer reaction.
The fact that the decay of radicals is negligibly small and the
resultant polymers are not dissolved in the solvent means that
$[P \cdot]$ and $[S]$ are constant, so that $\int R_{tr} \, dt$ is proportional to the
polymerization time, and the molecular weight $\overline{P}$ would vary
slightly with polymer yield or reaction time. The density and
tensile strength of the fabricated polymer, both of which depend
on the molecular weight of polytetrafluoroethylene, do not change
with the polymer yield (see Fig. 6). Figure 7 illustrates the rapid
decay of radicals in the absence of monomer at higher temperatures.
These experiments were carried out as follows. Unreacted mono-
mers were removed after 2 hr of postpolymerization in R-113, and
thereafter the decay of radical was detected by using the DPPH
method. These results support the idea that the chain transfer
reaction is most important in chain termination.

   Kagiya et al. proposed an evaluation method for the activation
energy of the radical substitution reactions based on the quantum
chemistry [7]. By using their proposed formula (Eq. 11), the
activation energies of the chain transfer of the polymer radical
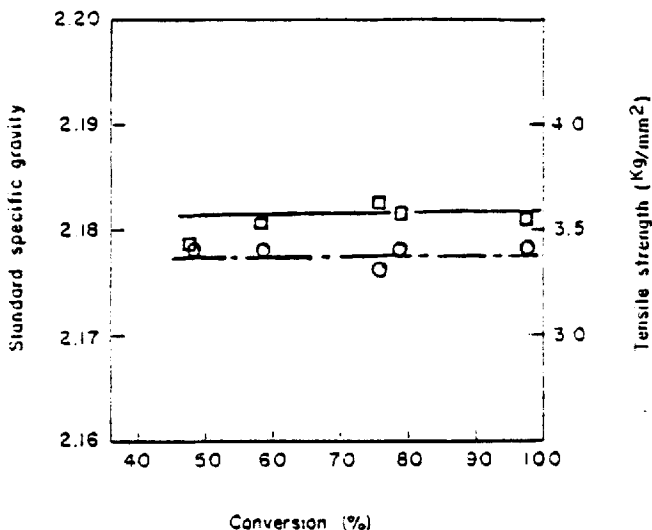to solvent were evaluated. The results are given in Table 4.

FIG. 6. Standard specific gravity and mechanical strength of the fabricated polymer as a function of the extent of postpolymerization. (□) Standard specific gravity. (○) Tensile strength.

$$E_a = \frac{D_i \left\{ (1 - 2\alpha)D_f + \alpha^2 D_i \right\}^3}{(D_f - \alpha^2 D_i)^2}$$

$$\alpha = \exp(0.0190Q) \tag{11}$$

D_i and D_f are the bond dissociation energies of the initial and the final bonds, respectively, and Q is the heat of reaction. The bond dissociation energies of various solvents evaluated by the method of Errede [8] are shown in Fig. 8. The relative rate constants k_{tr}, were calculated and are given in Table 4, based on the assumption that the pre-exponential factors are not altered in the same solvent. The real activation energies would be greater than those of Table 4 because the solvation effect of solvent on polymer radical is disregarded in our consideration.

The results of Table 4 indicate that the chain transfer reaction may be an abstraction of the fluorine atom by a radical.
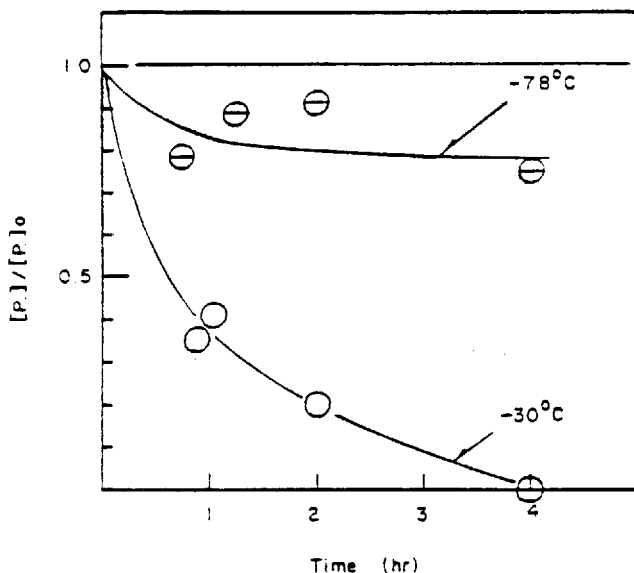
FIG. 7. Temperature dependence on the radical decay after irradiation in the absence of the monomer.

CONCLUSION

The radiation-induced solution polymerization and the post-polymerization of tetrafluoroethylene experiments mentioned above lead to the following conclusions:

(1) In the radiochemical formation of radicals, perfluorochloro-hydrocarbons exhibit a sensitizing effect which can be explained by the energy transfer mechanism. On the other hand, R-22 shows a protecting effect. The difference in the rate of polymerization between the different solvents may be attributed to these effects.

(2) The polymer radicals decay during the in-source polymerization, and the decay rate depends on the monomer concentrations.

(3) The remarkable postpolymerization is due to the unusually slow rate of bimolecular termination of the growing radicals.

(4) The solvent effect on the molecular weight of polymers can be explained by the chain transfer to solvent.

TABLE 4. The Activation Energies of Chain Transfer Reactions Evaluated by Eq. (11)

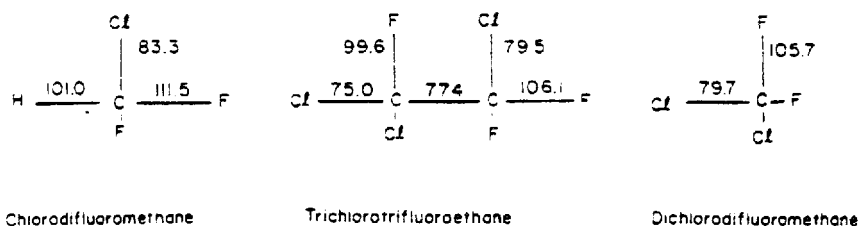| Chain transfer reactions	E_a (kcal/mole)	$k_{tr'}$
$CF_2 + H{-}CClF_2 \longrightarrow CF_2H + \cdot CClF_2$	10.9	1.0
$CF_2 + Cl{-}CHF_2 \longrightarrow CF_2Cl + \cdot CHF_2$	5.7	1.4×10^{-1}
$CF_2 + F{-}CHClF \longrightarrow CF_3 + \cdot CHClF$	4.7	9.0×10^{-1}
$CF_2 + Cl{-}CClFCClF_2 \longrightarrow CF_2Cl + \cdot CClFCClF_2$	20.9	1.0
$CF_2 + Cl{-}CF_2CCl_2F \longrightarrow CF_2Cl + \cdot CF_2CCl_2F$	18.9	5.7×10
$CF_2 + F{-}CClFCCl_2F \longrightarrow CF_3 + \cdot CFClCCl_2F$	14.6	4.2×10^{5}
$CF_2 + F{-}CCl_2CClF_2 \longrightarrow CF_3 + \cdot CCl_2CClF_2$	4.3	1.2×10^{13}
$CF_2 + Cl{-}CClF_2 \longrightarrow CF_2Cl + \cdot CClF_2$	6.9	1.0
$CF_2 + F{-}CCl_2F \longrightarrow CF_3 + \cdot CCl_2F$	6.4	2.5

FIG. 8. Bond dissociation energies (in kcal/mole) of various chlorofluorohydrocarbons.

ACKNOWLEDGMENT

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