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Kinetics of the γ-Ray Induced Polymerization of Ethylene in 1,2-Dichlorotetrafluoroethane

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The γ-ray induced polymerization of ethylene in bulk or in solution in the presence of 26.9—67.3 g of 1,2-dichlorotetrafluoroethane (R-114) was carried out in a 100-m*l* reactor under a pressure of 210—400 kg/cm^2 and at 30°C, with a dose rate of 1×10^4—9×10^4 rad/hr. The rate of the polymerization and the molecular weight of the polymer formed increased with the reaction time and the pressure. The rate also increased upon the addition of an appropriate amount of R-114. On the other hand, the molecular weight decreased with an increase in the amount of R-114. The dose-rate exponents of the rate and the molecular weight were found to be 0.8 and -0.2 respectively. These results were analyzed kinetically, and the rates and the rate constants of the initiation, propagation, transfer, and termination reactions were evaluated. Further, the roles of R-114 in the polymerization were discussed.

Polychloromethanes are known as effective radical sources for the initiation reaction of the radiation-induced polymerization of some vinyl monomers, such as styrene and methyl methacrylate.[1] The polymerizations of these monomers are promoted by the presence of such compounds. In the case of ethylene, on the contrary, both the rate of the polymerization and the molecular weight of the polymer formed are markedly depressed. In ethylene polymerization it has been found to be effective to add some fluorinated or chlorofluorinated ethanes, such as hexafluoroethane, chloropentafluoroethane, or 1,2-dichlorotetrafluoroethane.[2] Promotion by chlorofluorinated hydrocarbons is also found in the copolymerization of ethylene with tetrafluoroethylene.[3]

The purposes of this paper are to elucidate the effects of the reaction conditions on the polymerization of ethylene in the presence of 1,2-dichlorotetrafluoroethane (R-114), and to discuss the roles of R-114 in the initiation, propagation, transfer, and termination reactions from the viewpoint of kinetics.

Experimental

The reaction vessel used was a stainless-steel autoclave with a capacity of 100 m*l*. The ethylene monomer was 99.9% pure (free from CO and H$_2$S), containing less than 3 ppm of O$_2$. Reagent-grade R-114 was purified by distillation before use. After the reaction vessel had been evacuated, a definite amount of R-114 was charged in. Ethylene was then fed in at 30°C. By using a specially-designed autoclave with a quartz window, the mixture of the monomer and the solvent was observed to be existing in a homogeneous liquid phase, with no separation in the reaction vessel.[3] Polymerization runs were carried out in bulk or in solution in the presence of 26.9—67.3 g of R-114 under a pressure of 210—400 kg/cm^2 and at a temperature of 30°C, with dose rate of 1×10^4—9×10^4 rad/hr. During the reaction, the temperature was maintained constant within ±1°C by using an automatic controller; the pressure remained essentially constant since the monomer conversion to the polymer was kept less than 10% in all runs (in most cases, less than 5%).

The polymer yield was determined by the direct weighing of the polymer formed after it had been dried to a constant weight in a vacuum oven at room temperature. The number-average molecular weight of the polymer was obtained from osmotic pressure measurements of solutions of the polymer in tetralin at 110°C using a Hewlett-Packard osmometer, Model 502.

Results and Discussion

Effects of Reaction Conditions

Effects of R-114 and Reaction Pressure. The experimental results are summarized in Table 1.

TABLE 1. EXPERIMENTAL RESULTS OF THE POLYMERIZATION IN BULK AND IN THE PRESENCE OF R-114[a)]

Reaction pressure kg/cm^2	Amount of R-114 g	Reaction time hr	Polymer yield mol/*l*[b)]	Molecular weight $\times10^{-4}$
400	0	0.33	0.091	10.7
		0.50	0.201	15.1
		0.75	0.387	21.3
		1.00	0.770	31.6
400	26.9	0.25	0.094	4.12
		0.33	0.166	5.39
		0.50	0.320	6.18
		0.67	0.509	7.10
400	67.3	0.33	0.119	2.73
		0.50	0.232	3.22
		0.67	0.325	3.45
		1.00	0.609	3.93
		1.33	0.830	3.98
310	29.6	0.50	0.166	3.30
		0.67	0.289	3.72
		1.00	0.523	4.51
310	57.4	0.50	0.152	2.14
		0.67	0.210	2.08
		1.00	0.364	2.45
		1.50	0.674	2.79
210	29.6	0.50	0.121	2.57
		0.67	0.173	2.61
		1.00	0.319	2.93
		1.42	0.471	3.18

a) Reaction conditions: temperature, 30°C; dose rate, 9.2 $\times10^4$ rad/hr; reactor volume, 100 m*l*.

b) Polymerized monomer.

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1) A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience Publishers, New York, (1962).

2) M. Hagiwara, H. Okamoto, and T. Kagiya, This Bulletin, **43**, 172 (1970).

3) M. Hagiwara, T. Miura, and T. Kagiya, *ibid.*, **42**, 3380 (1969).

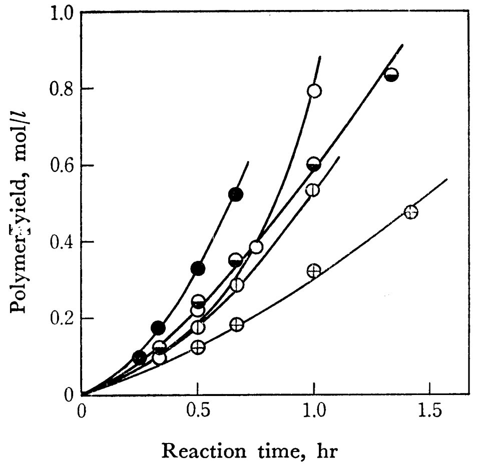

Fig. 1. Polymer yield *vs.* reaction time.
Reaction conditions: Temperature, 30°C; dose rate, 9.2×10^4 rad/hr; reactor volume, 100 m*l*; pressure (kg/cm^2) and amount of R-114 (g), (○) 400, 0; (●) 400, 26.9; (◒) 400, 67.3; (⦶) 310, 29.6; (⊕) 210, 29.6.

Figure 1 shows the relation between the polymer yield and the reaction time. It is clear that the rate of the polymerization increases with the time, since the time-yield relation gives an upward concave curve in all the polymerizations. A maximum rate was obtained when the amount of R-114 was varied in the range from zero to 67.3 g. The rate increased markedly with the reaction pressure, and was found to be proportional to 1.6 power of the pressure.

As can be seen in Fig. 2, the molecular weight also increases with the time, while it decreases with increase in the amount of R-114 and with the decrease in the pressure.

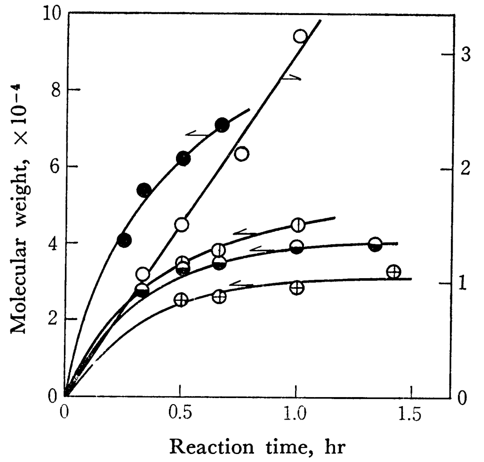

Fig. 2. Molecular weight *vs.* reaction time.
Reaction conditions are the same as in Fig. 1.

The observed increase in the rate and the molecular weight with the reaction time suggests that a stationary state with respect to the concentration of growing radicals is not realized in the polymerization. The time exponents of the polymer yield were found to be 1.9, 1.5, and 1.3 when the amounts of R-114 were 0, 26.9, and 67.3 g respectively at the pressure of 400 kg/cm^2. The fact that the time exponent of the polymer yield is close to 2.0 without a solvent suggests that the rate of termination is negligibly small in the bulk polymerization.4) On the other hand, since the time exponent decreases towards unity as the amount of R-114 increases, the termination rate becomes large in the solution polymerization, which approaches a stationary state with an increase in the amount of R-114.5)

The number of moles of the polymer chain, N_p (defined as the ratio of the polymer yield to the number-average molecular weight) given in Fig. 3 increases with the amount of R-114, and it is almost independent of the reaction pressure. The plots of N_p *vs.* the reaction time give an upward concave curve, while a straight line is obtained in the bulk polymerization. These facts suggest that the rate of transfer is small in the bulk polymerization, and that it increases with the amount of R-114.

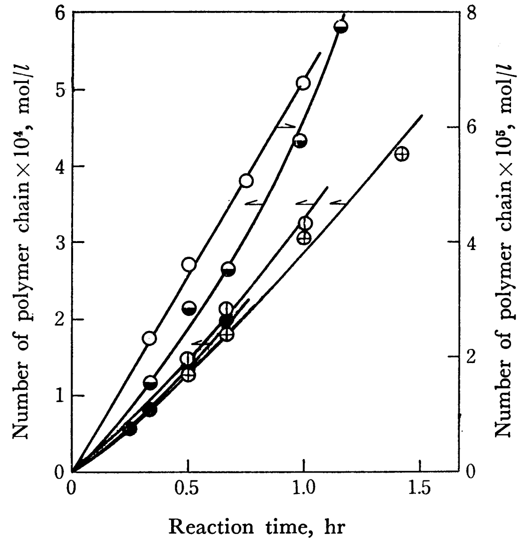

Fig. 3. Number of polymer chain *vs.* reaction time.
Reaction conditions are the same as in Fig. 1.

Effect of Dose Rate. The results are given in Table 2. Dose-rate exponents are determined from Fig. 4 to be 0.8 for the rate of the polymerization and

TABLE 2. EFFECT OF DOSE RATE ON POLYMER YIELD AND MOLECULAR WEIGHT$^{a)}$

Dose rate ×10^4 rad/hr	Polymer yield mol/l$^{b)}$	Molecular weight ×10^{-4}
0.9	0.089	5.15
2.5	0.171	5.00
5.1	0.307	4.50
9.2	0.609	3.93

a) Reaction conditions; temperature, 30°C; pressure, 400 kg/cm^2; amount of R-114, 67.3 g; time, 1 hr; reactor volume, 100 m*l*.

b) Polymerized monomer.

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4) S. Machi, M. Hagiwara, M. Gotoda, and T. Kagiya, This Bulletin, **39**, 2696 (1966).

5) M. Hagiwara, H. Mitsui, S. Machi, and T. Kagiya, *J. Polym. Sci.*, *A-1*, **6**, 609 (1968).

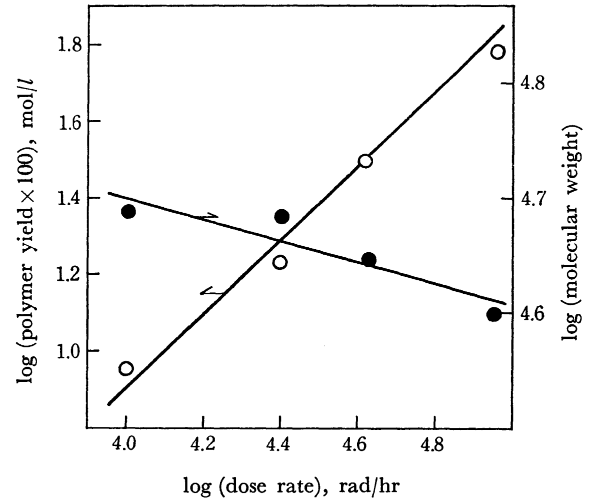

Fig. 4. Effect of dose rase on polymer yield and molecular weight.
Reaction conditions: pressure, 400 kg/cm²; temperature, 30°C, amount of R-114, 67.3 g; time, 1.0 hr; reactor volume 100 m*l*.

—0.2 for the molecular weight respectively. From this and the fact that R-114 is a precipitant of the polyethylene produced, it can be said that the termination by a mutual combination of growing radicals is not important in this polymerization.

Kinetical Consideration

Proposed Scheme of the Polymerization. On the basis of the experimental results presented above, the reaction scheme shown in Eqs. (1)—(6) can be proposed for this polymerization.

Initiation:

$$\mathrm{M,\ or\ S} \rightsquigarrow \mathrm{R_1\cdot} \qquad R_i = k_i f([\mathrm{M}], [\mathrm{S}])I \quad (1)$$

Propagation:

$$\mathrm{M} \rightleftarrows \mathrm{M^*}$$

$$\mathrm{M^*} + \mathrm{M} \overset{K_e}{\rightleftarrows} \mathrm{M_2^*} \qquad f_{\mathrm{M_2^*}} = K_e f_{\mathrm{M}}^2 \quad (2)$$

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$$\mathrm{R}_n\cdot + \mathrm{M_2^*} \rightarrow \mathrm{R}_{n+1}\cdot + \mathrm{M^*} \qquad R_p = k_p[\mathrm{R}_n\cdot]f_{\mathrm{M_2^*}} = k_pK_e[\mathrm{R}_n\cdot]f_{\mathrm{M}}^2 \quad (3)$$

Transfer:

$$\mathrm{R}_n\cdot + \mathrm{XY} \rightarrow \mathrm{R}_n\mathrm{X} + \mathrm{Y}\cdot \qquad R_{tr} = k_{tr}[\mathrm{XY}][\mathrm{R}_n\cdot] \quad (4)$$

Termination:

$$\mathrm{S} \rightsquigarrow \mathrm{S}\cdot \qquad R_{\mathrm{S}} = k_{\mathrm{S}}[\mathrm{S}]I \quad (5)$$

$$\mathrm{R}_n\cdot + \mathrm{S}\cdot \rightarrow \mathrm{R}_n\mathrm{S} \qquad R_t = k_t[\mathrm{S}\cdot]]\mathrm{R}_n\cdot] \quad (6)$$

where M and S represent the ethylene monomer and R-114 respectively; M* is an excited ethylene monomer, and M_2^*, an excited ethylene dimer; f_{M} and $f_{\mathrm{M_2^*}}$ are the fugacities of the substances indicated; $\mathrm{R_1}\cdot$ is an initiating radical, and $\mathrm{R}_n\cdot$, an active polymer chain composed of *n* monomers; XY is the substance to which the activity of $\mathrm{R}_n\cdot$ is transferred, and S·, the primary radical formed by the radiolysis of R-114 which causes the termination; R_i, R_p, R_{tr}, R_t, and R_{S} are the rates of initiation, propagation, transfer, termination, and formation of S· respectively, and *k*'s, the rate constants of these reactions; K_e is an equilibrium constant; [M], [S], [S·], and [XY], are the concentrations of M, S, S·, and XY respectively, and $f([\mathrm{M}],[\mathrm{S}])$, a function of [M] and [S]; where $[\mathrm{R}_n\cdot]$ is the concentration of active polymer chains ($= \sum_{\infty}^{n=1} \mathrm{R}_n\cdot$), and *I* is the dose rate.

In the above scheme, the initiating radicals are produced from both ethylene and R-114 under γ-ray irradiation. Although we can not entirely exclude the possibility that the initial stage of their formation is influenced by the presence of the hologenated solvent, which may act as a powerful electron scavenger, here it is assumed to be negligibly small. The formation of the excited ethylene dimer and its addition to a growing radical (reactions (2) and (3) are introduced with due consideration of the results of the bulk polymerization.[6,7] Further, the termination is assumed to be a combination of a growing radical with a primary radical from R-114 (reaction (6)).

Rate of Polymerization. For the reasons described above, the kinetics of the non-stationary state should be applied to this polymerization.[8] The overall rate of the polymerization, *R*, is expressed as:

$$R \risingdotseq R_p = k_pK_ef_{\mathrm{M}}^2[\mathrm{R}_n\cdot] \quad (7)$$

where $[\mathrm{R}_n\cdot]$ is given by:

$$[\mathrm{R}_n\cdot] = \int_0^t R_i\mathrm{d}t - \int_0^t R_t\mathrm{d}t \quad (8)$$

Since the polymerization was stopped at a low conversion, [M], [S] and f_{M} are considered to be essentially constant during the reaction. Further, if a steady state is assumed with respect to the concentration of the primary radical, [S·], Eq. (9) is obtained from Eqs. (1), (6), and (8):

$$[\mathrm{R}_n\cdot] = R_it - (k_t[\mathrm{S}\cdot]/k_pK_ef_{\mathrm{M}}^2)M_p \quad (9)$$

M_p is the amount of polymer formed, being approximately equal to $\int_0^t R_p\mathrm{d}t$. Hence, the combination of Eqs. (3) and (9) leads to:

$$R_p = k_pK_ef_{\mathrm{M}}^2R_it - k_t[\mathrm{S}\cdot]M_p \quad (10)$$

$$M_p\Big/\int_0^t M_p\mathrm{d}t = (1/2)k_pK_ef_{\mathrm{M}}^2R_i\left(t^2\Big/\int_0^t M_p\mathrm{d}t\right) - k_t[\mathrm{S}\cdot] \quad (11)$$

According to Eq. (11), the plots of $M_p\Big/\int_0^t M_p\mathrm{d}t$ *vs.* $t^2\Big/\int_0^t M_p\mathrm{d}t$ should make a straight line if the proposed scheme is valid. The numerical values of these two terms are obtained from the data in Table 1, while the plots are given in Fig. 5. The intercept of the straight lines obtained gives $k_t[\mathrm{S}\cdot]$, and the slope, $(1/2)k_pK_ef_{\mathrm{M}}^2R_i$.

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6) S. Machi, M. Hagiwara, M. Gotoda, and T. Kagiya, *J. Polym. Sci., A-1*, **4**, 1517 (1966).

7) M. Hagiwara, H. Okamoto, and T. Kagiya, *ibid., A-1*, **8**, 3303 (1970).

8) T. Kagiya, M. Izu, S. Machi, and K. Fukui, This Bulletin, **40**, 1049 (1967).

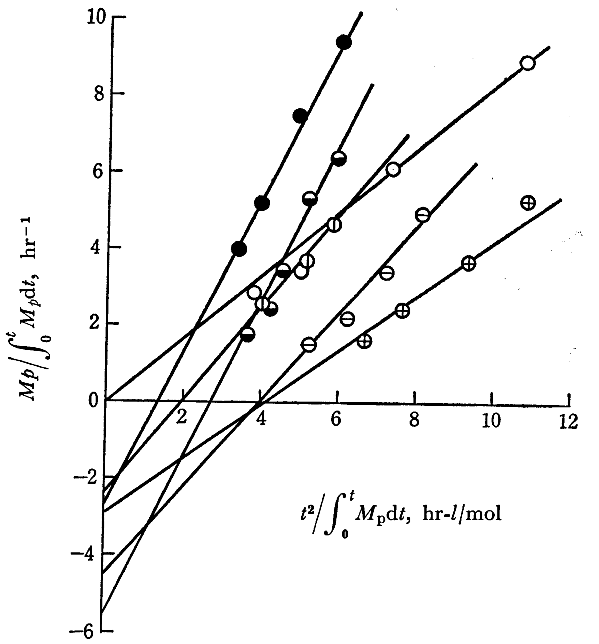

Fig. 5. $M_p/\int_0^t M_p dt$ vs. $t^2/\int_0^t M_p dt$.

Reaction conditions: pressure and amount of R-114, (⊖) 310 kg/cm², 57.4 g. Others are the same as in Fig. 1.

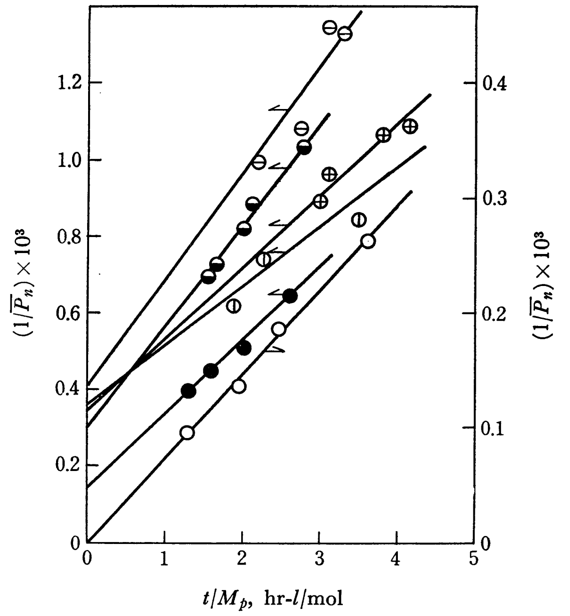

Fig. 6. $1/\bar{P}_n$ vs. t/M_p.

Reaction conditions are the same as in Fig. 5.

Degree of Polymerization. For the polymerization with no termination caused by the combination of growing radicals, the number-average degree of polymerization, $\bar{P}_n$, is given by Eq. (12):

$$\bar{P}_n = \int_0^t R_p dt \Big/ \left(\int_0^t R_i dt + \int_0^t R_{tr} dt\right) \quad (12)$$

Hence, the reciprocal degree of polymerization, $1/\bar{P}_n$, is given as:

$$1/\bar{P}_n = R_i(t/M_p) + k_{tr}[XY]/k_pK_ef_M^2 \quad (13)$$

In Eq. (13), [XY] can be assumed to be constant throughout the reaction. Figure 6 shows that the plots of $1/\bar{P}_n$ vs. t/M_p give a linear relation for every one of the polymerization runs. The slope of the lines is the overall rate of initiation, R_i, and the intercept on the ordinate is $k_{tr}[XY]/k_pK_ef_M^2$. After all, the numerical values of R_i, k_pK_e, $k_{tr}[XY]$, and $k_t[S\cdot]$ can be determined by the use of Eqs. (11) and (13). The results are summarized in Table 3.

Initiation Reaction. Since, as is shown in Table 3, the overall rate of initiation, R_i, increases markedly with the addition of R-114, it is clear that R-114 acts as an effective promotor for the initiation reaction. If the energy transfer between ethylene and R-114 does not occur, the overall rate of initiation can be represented as follows:

$$R_i = R_{iM} + R_{iS} = k_{iM}[M]I + k_{iS}[S]I$$
$$= (k_{iM}[M] + k_{iS}[S])I \quad (14)$$

where R_{iM} and R_{iS} are the rates of initiation from ethylene and R-114 respectively. Hence, R_{iS} can be evaluated with the use of R_{iM}, which is itself determined by the bulk polymerization. Although Fig. 7 shows some scatter, it can be seen that a linear relation exists between R_{iS} and the concentration of R-114. This indicates the validity of Eq. (14), and also the absence of energy transfer between ethylene and and R-114.

Table 3. Calculated rates and rate constants[a)]

Reaction pressure kg/cm²	Amount of R-114 g	Concentration mol/l		Fugacity[b)] kg/cm²		Rate and rate constant			
		C_2H_4	R-114	C_2H_4	R-114	$R_i\times10^4$ mol/l-hr	k_pK_e hr^{-1} $\times$(kg/cm²)$^{-2}$	k_{tr}[XY] hr^{-1}	k_t[S·] hr^{-1}
400	0	16.7	0	123.6	0	0.72	1.45	0	0
400	26.9	13.8	1.58	108.6	2.77	1.95	1.72	2.63	2.60
400	67.3	9.46	3.95	89.0	6.50	2.80	2.07	4.93	5.55
310	29.6	12.2	1.73	89.1	1.83	2.10	1.45	2.76	2.50
310	57.4	10.3	3.35	69.5	3.65	2.53	1.70	3.84	4.60
210	29.6	11.5	1.73	65.1	1.19	1.83	1.55	2.37	2.90

a) Reaction conditions: temperature, 30°C; dose rate, 9.2×10⁴ rad/hr; reactor volume, 100 ml.
b) Calculated by using the equation of state proposed by O. Redlich and J. N. S. Kwong, (Ref. 9).

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9) W. C. Edmister, "Applied Hydrocarbon Thermodynamics," Gulf Publishing Co., Houston (1961).

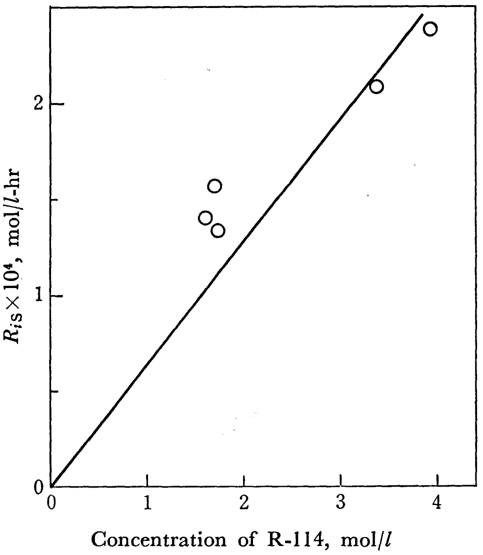


Fig. 7. Rate of initiation from R-114, R_{iS}, *vs.* concentration of R-114.
Reaction conditions: pressure, 210—400 kg/cm^2; temperature, 30°C; dose rate, 9.2×10^4 rad/hr; reactor volume, 100 ml.

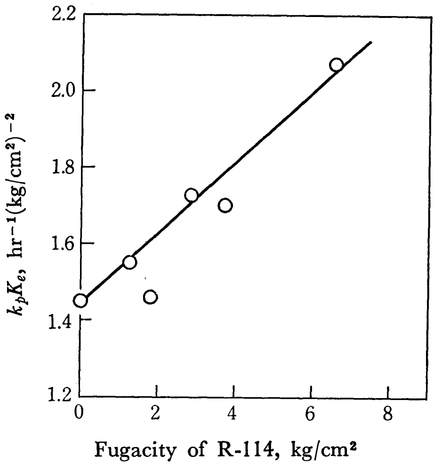


Fig. 8. Apparent rate constant of propagation, k_pK_e, *vs.* fugacity of R-114.
Reaction conditions are the same as in Fig. 7.

Propagation Reaction. The apparent rate constant of propagation, k_pK_e, is shown in Table 3 to increase with the amount of R-114. In Fig. 8 a linear relation is obtained between k_pK_e and the fugacity of R-114, $f_{\text{R-114}}$. This indicates that R-114 acts as promotor of the propagation reaction. The promotive effect of R-114 on the propagation reaction is also suggested by the studies of the copolymerization of ethylene with tetrafluoroethylene.[3] The mechanism of the promotion is not yet clear in detail, however, probably, strongly electronegative fluorine atoms in R-114 molecule have some effect on the reactivity of the growing radical in a solvated state. If that is the case, the linear relation between k_pK_e and $f_{\text{R-114}}$ in Fig. 8 can be interpreted as follows.

Equation (15) shows that some of the growing radicals exist in a solvated state:

$$R_n\cdot + S \overset{K_S}{\rightleftarrows} R_n\cdots S \tag{15}$$

$$[R_n\cdots S] = K_S[R_n\cdot]f_{\text{R-114}} \tag{16}$$

If the propagation reaction in R-114 consists of the addition of M_2^* to the growing radicals in a free state:

$$R_n\cdot + M_2^* \xrightarrow{k_{pf}} R_{n+1}\cdot + M^* \tag{17}$$

and to those in a solvated state:

$$R_n\cdots S + M_2^* \xrightarrow{k_{pS}} R_{n+1}\cdot + M^* + S \tag{18}$$

the rate of the propagation, R_p, can be written as Eq. (19):

$$R_p = \frac{(k_{pf}K_e + k_{pS}K_eK_Sf_{\text{R-114}})[R_n\cdot]f_{\text{M}}^2}{1+K_Sf_{\text{R-114}}} \tag{19}$$

Therefore, k_pK_e can be derived from a comparison with Eqs. (3) and (19) as follows:

$$k_pK_e = \frac{(k_{pf}K_e + k_{pS}K_eK_Sf_{\text{R-114}})}{1+K_Sf_{\text{R-114}}}$$

Further, if $f_{\text{R-114}}K_S$ is very small compared with unity, the above equation can be rewritten approximately as:

$$k_pK_e \fallingdotseq k_{pf}K_e + k_{pS}K_eK_Sf_{\text{R-114}} \tag{20}$$

which satisfies the linear relation in Fig. 8.

Transfer Reaction. As has been stated before, the transfer reaction is absent in the bulk polymerization, but it increases with the addition of R-114. Figure 9 shows that a straight line is obtained when k_{tr}[XY] is plotted against the concentration of R-114, [S], rather than against its fugacity, $f_{\text{R-114}}$. This may indicate that radiation energy takes part in the transfer reaction. Since the transfer has been found in a previous work to increase with an increase in the number of the chlorine atoms of a halogenated hydrocarbon solvent,[2] the reaction may be the abstraction of Cl from an excited R-114 molecule by the growing radical:

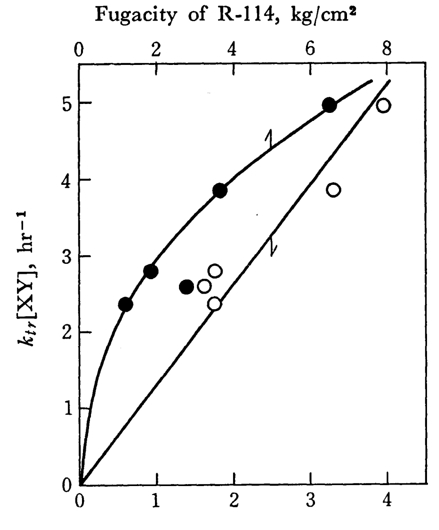


Fig. 9. Apparent rate constant of transfer, k_{tr}[XY], *vs.* concentration of R-114, and fugacity of R-114.
Reaction conditions are the same as in Fig. 7.

$$R_n\cdot + ClCF_2CF_2Cl^* \rightarrow R_nCl + CF_2CF_2Cl \tag{21}$$

The existence of a linear relation between k_{tr}[XY] and the concentration of R-114 supports the above conclusion that there is no energy transfer between ethylene and R-114.

Termination Reaction. As can be seen in Table 3, the apparent rate constant of termination, k_t[S·], increases with the addition of R-114. Figure 10 shows that k_t[S·] is nearly proportional to the concentration of R-114.

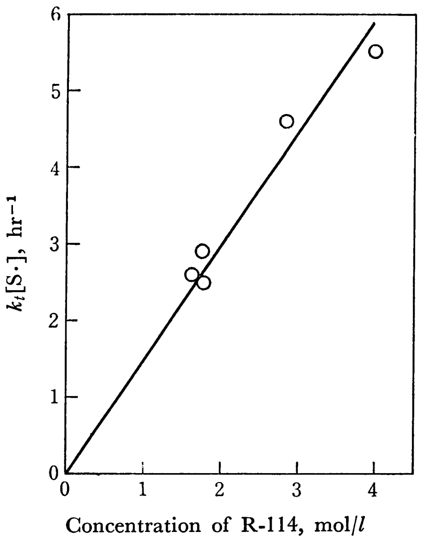
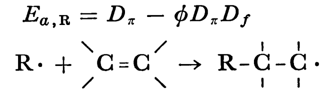


Fig. 10. Apparent rate constant of termination, k_t[S·], *vs.* concentration of R-114.
Reaction conditions are the same as in Fig. 7.

In this polymerization, as has been described above, the radicals formed from R-114 act both as initiators and as terminators. The mass spectrum of R-114 suggests that the radicals from R-114 are mainly CF_2Cl, plus smaller amounts of C_2F_4Cl and Cl.[2] Highly reactive radicals may contribute to the initiation more than those with less reactivity.

Recently, a semi-empirical Eq. (22) was proposed for use in estimating the activation energy of a radical-addition reaction to vinyl monomers (Eq. (23)):[10]

$$E_{a,\mathrm{R}} = D_\pi - \phi D_\pi D_f \qquad (22)$$



$$\mathrm{R}\cdot + \mathrm{C{=}C} \rightarrow \mathrm{R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}}\cdot \qquad (23)$$

In Eq. (22), D_π is a π-bond dissociation energy of the monomer, D_f is that of the δ-bond formed in the reaction, and ϕ is a constant. Since D_π is constant in this polymerization, it is clear that the activation energy needed to form an initiating radical depends solely on D_f, and that it decreases with an increase in D_f. This means that the radical, R·, will make a greater contribution to the initiation reaction if it can form a strong R-C bond in the reaction with ethylene.

TABLE 4. DISSOCIATION ENERGY OF THE BOND, $R{-}CH_3$

R	$D_{\mathrm{R-CH_3}}$ kcal/mol	$\Delta H_{f,\mathrm{R}}$ kcal/mol
F	108[12]	
CF_3	90,[13] 117[14]	
CH_2Cl	84.3[a]	27.7[b]
CH_3	83.2[a]	31.5
C_2H_5	81.4[a]	25.1
$CHCl_2$	80.1[a]	20.9[b]
Cl	78.7[a]	28.5
CCl_3	77.7[2], 78.4[a]	16.2[b]

a) Calculated from, $D_{\mathrm{R-CH_3}} = \Delta H_{f,\mathrm{R}} + \Delta H_{f,\mathrm{CH_3}} - \Delta H_{f,\mathrm{R-CH_3}}$ where, ΔH_f = standard heat of formation.
b) Estimated from the values of bond dissociation energy listed in Table 9 (p 24) of Ref. 11.

Table 4 gives the dissociation energy of the bonds between several R·'s and the CH_3 radical. If R· is the fluorine atom or a fluorine-containing radical, the bond with CH_3 is stronger than that of such hydrocarbon radicals as CH_3 or C_2H_5. Substitution by the chlorine atom, on the contrary, generally weakens the bond, although one mono-substituted radical, CH_2Cl, exceptionally forms a strong bond. From these facts, it seems reasonable to speculate that the strength of the R-C bond may be in the order of:

$$CF_2Cl,\ C_2F_4Cl,\ CF_3 > CH_2Cl,\ CH_3 > CHCl_2 > Cl,\ CCl_3$$

Hence, the order of the activation energy may be given as:

$$E_{a,\mathrm{CF_2Cl}},\ E_{a,\mathrm{C_2F_4Cl}} \ll E_{a,\mathrm{Cl}}$$

Thus, R-114 can probably contribute to the initiation through reactions (24) and (25):

$$CF_2Cl + CH_2{=}CH_2 \rightarrow CF_2Cl{-}CH_2{-}CH_2 \qquad (24)$$

$$C_2F_4Cl + CH_2{=}CH_2 \rightarrow C_2F_4Cl{-}CH_2{-}CH_2 \qquad (25)$$

and to the termination through reaction (26):

$$R_n\cdot + Cl \rightarrow R_nCl \qquad (26)$$

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[10] T. Kagiya and Y. Sumida, *Polymer J.*, **1**, 137 (1970).

[11] N. N. Semenov, "Some Problems in Chemical Kinetics and Reactivity (English translation)," Princeton Univ. Press, Princeton, (1958).

[12] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[13] J. B. Farmer, I. H. S. Henderson, F. P. Lossing and D. G. H. Marsden, *J. Chem. Phys.*, **24**, 348 (1956).

[14] V. H. Dibeler, R. M. Reese, and F. L. Mohler, *ibid.*, **20**, 761 (1952).