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Effects of Alkyl Halides on the γ-Ray Induced Polymerization of Ethylene in Liquid Carbon Dioxide

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The ^{60}Co γ-ray induced polymerization of ethylene in a liquid carbon dioxide solvent was carried out under a pressure of 400 kg/cm^2 at 30°C in the presence of such alkyl halides as CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, C_2H_5Br, C_2H_5I, $C_2H_4Cl_2$, $C_2H_2Cl_4$, C_2Cl_6, C_2F_6, C_2F_5Cl, $C_2F_4Cl_2$, $C_2H_3Cl_3$, and $C_2F_2Cl_4$, and their effects on the polymerization rate and the molecular weight of the polymer formed were investigated. Both the rate and the molecular weight were increased by adding $C_2F_4Cl_2$, C_2F_5Cl, and C_2F_6. A study of the radiolysis of these three fluorocarbons by mass spectrometric analysis showed that bond scissions of these substances took place mainly at the C–C bond. When other halogen compounds besides the three fluorocarbons were added to the reaction mixture, the rate and the molecular weight were decreased and C–X (X: halogen) bond scission was predominant in those substances. On the basis of these results, the role of the additives in the polymerization was discussed in relation to their radiolysis reactions.

In previous papers,[1-3] liquid carbon dioxide was found to be a useful solvent for the γ-ray induced polymerization of ethylene. It was shown from a kinetic study of the polymerization that the rate of initiation increased with an increase in the concentration of the carbon dioxide solvent. The role of the solvent in the initiation has been ascribed to the fact that the absorption step of radiation energy depends on the electron density of the reaction mixture. Further, the radiolysis products of the solvent were found to have some effects on the termination reaction of the polymerization.

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In consideration to their high electron density and high chemical reactivity, alkyl halides are expected to have various radiation-induced effects on the polymerization. In this paper, the effects of various alkyl halides on the polymerization of ethylene in liquid carbon dioxide will be investigated, and the role of the additives will be discussed in relation to their radiolysis reactions.

Experimental

The reaction vessel was a stainless-steel autoclave with a capacity of 100 *ml*. The ethylene used was 99.9% pure (free of CO and H_2S) and contained less than 5 ppm of O_2. The carbon dioxide was 99.99% pure; its major impurities were H_2O (37 ppm), CH_4 (20 ppm), and O_2 (2 ppm). The alkyl halides were all reagent-grade and were refined in a usual way. Both liquid carbon dioxide and alkyl halide were first charged into the vessel (liquid CO_2, 20 g; alkyl halide, 5 g). Ethylene was then fed in to about 400 kg/cm^2 at 30°C. The density of the reaction system could thus be kept almost constant in all experiments. The reaction temperature was controlled within ± 0.5°C by using an automatic controller during the course of the reaction. The irradiation of ^{60}Co γ-rays was carried out for 3 hr at a dose rate of 2.5×10^4 rad/hr. The amount of polymer formed was determined by direct weighing. The number-average molecular weight of the polymer thus formed was obtained from the intrinsic viscosity measurements using Tung's formula.[4] Infrared absorption spectra were recorded for film samples in the range of 4000—400 cm^{-1}. Mass spectra for several kinds of alkyl halides were taken on a Hitachi mass spectrometer, Model RMU-6, under a pressure of 10^{-3} mmHg.

Results and Discussion

Polymerization in the Presence of Various Alkyl Halides. The polymer yield and the number-average molecular weight of the polymer formed in the presence of various alkyl halides are summarized in Table 1. The number of moles of the polymer chain, defind as the ratio of the polymer yield to the molecular weight, $M_p/\bar{M}_n$, is also listed in the last column of the table. The polymer yield and the polymer's molecular weight were found to decrease in many cases when alkyl halides were added to the reaction mixture. However, when some fluorocarbons, such as C_2F_6, C_2F_5Cl and CF_2ClCF_2Cl, were added, both the rate and the molecular weight increased. In the series of polymerizations in the presence of C_2H_5Cl, C_2H_5Br, or C_2H_5I, ethyl chloride or bromide gave about the same yields and molecular weights, though they were much lower than those without additives. On the other hand, ethyl iodide gave an extremely low yield. Polychlorinated hydrocarbons, such as CH_2Cl_2, $CHCl_3$, CCl_4, CH_2ClCH_2Cl, $CHCl_2$-$CHCl_2$, and C_2Cl_6, did not show any change in the yield. On the other hand, the molecular weight decreased markedly with an increase in the number of chlorine atoms in the molecule of the additives. This relation between the molecular weight and the number of chlorine atoms was also observed with the use of fluorocarbons.

Table 1. Effects of alkyl halides on polymer yield, molecular weight and number of moles of polymer chain

Alkyl halide	Polymer yiled M_p, g	Molecular weight $\bar{M}_n\times10^{-4}$	Number of moles of polymer chain $N_p\times10^4$ mol/*l*
——	0.816	13.9	0.59
CH_2Cl_2	0.472	3.8	1.42
$CHCl_3$	0.260	<1	—
CCl_4	0.435	<1	—
C_2H_5Cl	0.473	2.16	2.20
C_2H_5Br	0.512	3.1	1.65
C_2H_5I	0.013	—	—
CH_2ClCH_2Cl	0.522	1.8	2.91
$CHCl_2CHCl_2$	0.289	<1	—
C_2Cl_6	0.420	0.1	42
C_2F_6	0.860	19.4	0.44
C_2F_5Cl	1.063	15.1	0.70
CF_2ClCF_2Cl	1.229	13.2	0.93
$CFCl_2CF_2Cl$	0.458	3.35	1.38
$CFCl_2CFCl_2$	0.359	0.85	4.70

Reaction conditions: pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; time, 3 hr; carbon dioxide, 20 g; alkyl halide, 5 g; reactor volume, 100 *ml*.

On the other hand, the infrared spectrum of a low-molecular-weight polymer obtained in the presence of $CHCl_3$ showed the characteristic C–Cl bands at 583 cm^{-1} (C–Cl axial), 695 cm^{-1} (C–Cl stertching), and 777 cm^{-1} (C–Cl stretching in CCl_3),

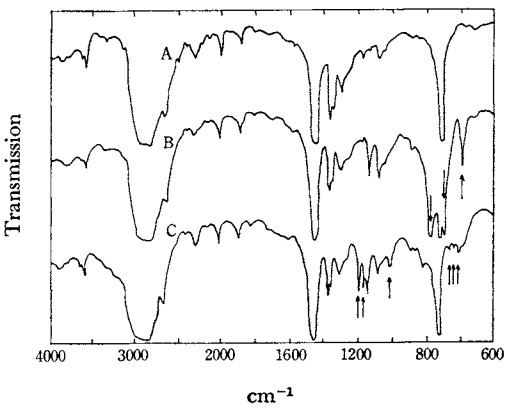

Fig. 1. Infrared spectra of polymers formed in various alkyl halides: (A) free; (B) $CHCl_3$; (C) $CFCl_2CFCl_2$. Reaction pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; time, 3 hr; carbon dioxide, 20 g; alkyl halide, 5 g.

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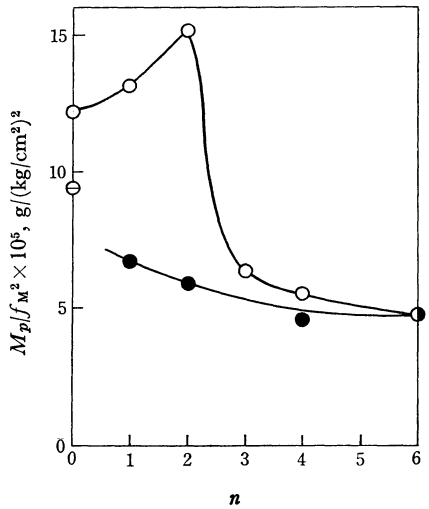

Fig. 2. The amount of polymer formed *vs.* the number of chlorine substitution of halogenated ethane derivatives: (⊖) free; (●) $C_2H_{6-n}Cl_n$; (○) $C_2F_{6-n}Cl_n$. Reaction pressure, 400 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; time, 3 hr; carbon dioxide, 20 g; halogenated ethane derivative, 5 g.

as is given in Fig. 1. In the case of $CFCl_2CFCl_2$, both C–Cl stretching bands (603, 633, 658 cm^{-1}) and C–F stretching bands (1000, 1156, 1190 cm^{-1}) were observed. The role of the additives and their radiolysis products in the polymerization and the step of their introduction into the polymer chain will be discussed below.

Polymerization in the Presence of Halogenated Ethane Derivatives. Using the results listed in Table 1, the polymer yields are plotted in Fig. 2 against the number of the chlorine substitution for two series of halogenated ethane derivatives, *i.e.*, $C_2H_{6-n}Cl_n$ and $C_2F_{6-n}Cl_n$, where n stands for the number of the chlorine substitution.

The fugacity of ethylene of the reaction system is inevitably changed depending on the nature of the additives. Several authors have previously reported that the polymerization rate and the polymer molecular weight are proportional to the square of ethylene fugacity.[2] Hence, the polymer yields in Fig. 2 are divided by the square of ethylene fugacity to normalize them to a unit of fugacity.

It can be seen that the yield under a unit of fugacity is much smaller in the presence of chlorinated hydrocarbons than that of the blank experiment without additives, and that it decreases gradually with the increase in the number of the chlorine substitution. On the other hand, in the case of fluorcarbons, it increases with the number of the chlorine substitution and passes through a maximum at $n=2$; thereafter it decreases with an increase in the number of the substitution. Thus, CF_2ClCF_2Cl gives a maximum yield which is about 1.5 times as large as that of the blank experiment. However, in the cases of $CF_2ClCFCl_2$ and $CFCl_2CFCl_2$ the yield becomes almost the same as that of the corresponding chlorinated hydrocarbons.

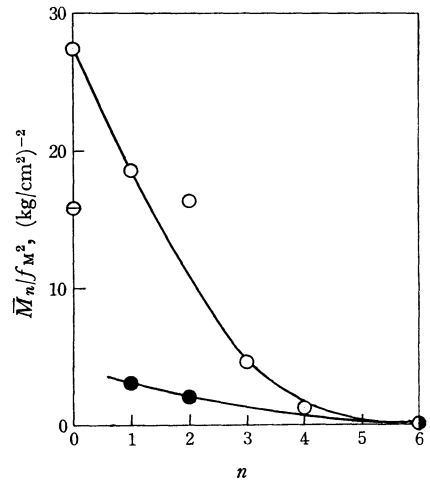

Fig. 3. Molecular weight *vs.* the number of chlorine substitution of halogenated ethane derivatives. Reaction conditions and notes are the same as Fig. 2.

Figure 3 shows the relation between the molecular weight of the polymer (normalized to a unit of ethylene fugacity) and the number of the chlorine substitution. In the series of chlorinated ethanes, the molecular weight under a unit of fugacity is markedly reduced by additives and decreases with the number of the chlorine. The decrease in the molecular weight with the chlorine content is also observed in the case of fluorocarbons. However, in the latter case, the molecular weight is larger than that in the case of no additives in the lower region of the chlorine substitution (less than $n=2$).

Futher, in Fig. 4, the number of moles of the

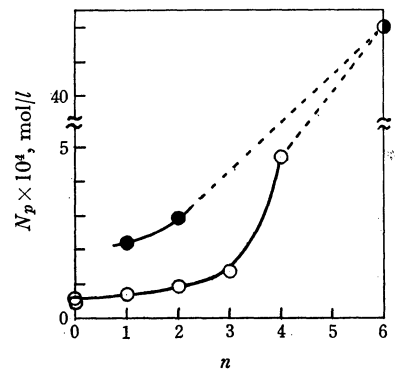

Fig. 4. Number of polymer chains *vs.* the number of chlorine substitution of halogenated ethane derivatives.
Reaction conditions and notes are the same as Fig. 2.

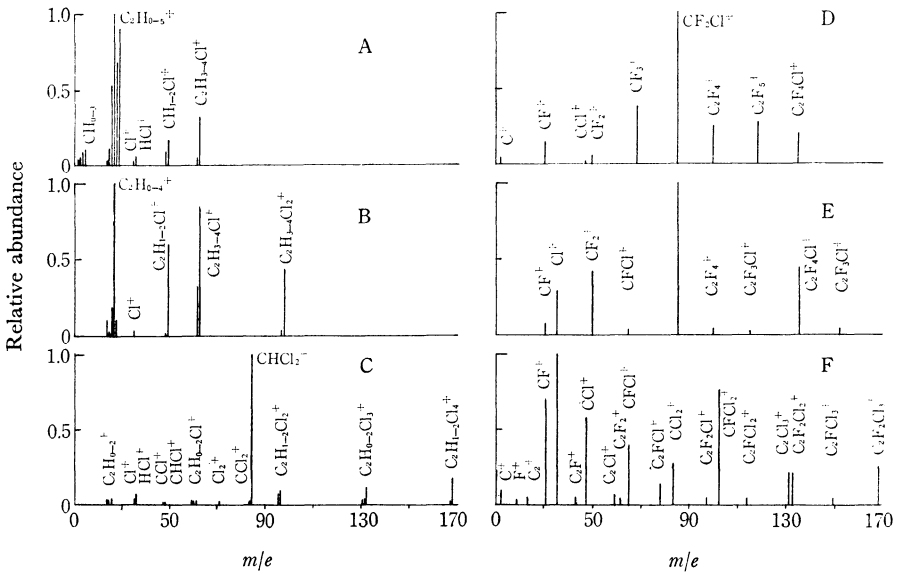

Fig. 5. Mass spectra of halogenated ethane derivatives: (A) C_2H_5Cl; (B) CH_2ClCH_2Cl; (2) $CHCl_2CHCl_2$; (D) C_2F_5Cl; (E) CF_2ClCF_2Cl; (F) $CFCl_2CFCl_2$.

polymer chain is also plotted against the number of chlorine substitution. The number of the polymer chain is shown to increase with the chlorine substitution in both hydro- and fluorocarbons.

From the results presented above, the increase in the polymer yield in the order of $C_2F_6 < C_2F_5Cl < CF_2ClCF_2Cl$, which is reported in Fig. 2, may be ascribed to the increase in the rate of initiation. The promoting effects of these fluorocarbons on the propagation reaction should also be considered in terms of the following results, obtained in the presence of C_2F_6. Thus, as is shown in Figs. 2 and 3, both the yield and the molecular weight increase upon the addition of C_2F_6. On the other hand, the number of the polymer chain is shown in Fig. 4 to be almost the same as that of the blank experiment. In contrast to the cases of C_2F_6, C_2F_5Cl, and CF_2ClCF_2Cl, the yield and the molecular weight are depressed by the addition of other fluorocarbons, such as $CF_2ClCFCl_2$ and $CFCl_2CFCl_2$, and all the chlorinated hydrocarbons employed. This means that these additives contribute mainly to promoting the termination reaction. Further, the decrease in the moleculr weight and the increase in the number of the polymer chain with the chlorine substitution suggest that the chlorine atom in these compounds plays an important role in the chain-transfer reaction.

Thus, from the point of view of their characteristic roles, the halogenated ethanes may be classified into two different groups. One group, such as C_2F_6, C_2F_5Cl, and CF_2ClCF_2Cl, promotes the polymerization, while the other group, such as $CF_2ClCFCl_2$, $CFCl_2CFCl_2$, C_2H_5Cl, CH_2ClCH_2Cl, $CHCl_2CHCl_2$ and C_2Cl_6, retards it.

Free Radicals from the Radiolysis of the Additives and Their Role in the Polymerization. In Fig. 5, the relative abundance of the ions detected by the mass spectrometer is plotted against the *m/e* for several halogenated ethane derivatives. The large relative abundance of the $C_2H_{0-5}^+$ ions in C_2H_5Cl and that of the $C_2H_{0-4}^+$, and $C_2H_{3-4}^+$ ions in CH_2ClCH_2Cl indicates that the bond cleavage by radiation occurs mainly at C–Cl and C–H in these compounds. On the other hand, C_2F_5Cl and CF_2ClCF_2Cl are shown to cleave mainly at the C–C bond, since CF_2Cl^+ and CF_3^+ in C_2F_5Cl, and CF_2Cl^+ in CF_2ClCF_2Cl, are observed to be predominant in their spectra. Moreover, the figure shows that the cleavage in highly-chlorinated ethane derivatives occurs at the C–C and C–Cl bonds about equally.

These mass spectrometric data suggest that such radicals as $CF_3\cdot$ and $CF_2Cl\cdot$ are mainly produced by the C–C bond dissociations of C_2F_5Cl and CF_2ClCF_2Cl, which promote the polymerization. Further, several kinds of hydrocarbon radicals, chlorine atoms, and highly-chlorinated radicals, such as $CHCl_2\cdot$ and $CFCl_2\cdot$, are produced by the use of C_2H_5Cl, CH_2ClCH_2Cl, $CHCl_2CHCl_2$, and $CFCl_2CFCl_2$, which retard the polymerization.

From this information on the effect of halogenated compounds on the polymerization and on the structure of their radiolysis products, it might be said that CF_3 or CF_2Cl radicals act as initiators of the polymerization. However, hydrocarbon radicals, chlorine atoms, or highly-chlorinated radicals act mostly in the termination rather than in the initiation reaction of the polymerization.

In view of the fact that the rate of cross combina-

tion is faster than that of the combination of the radical with the same structure, a cross termination reaction between the growing chain radical and the radical generated from the added halogen compounds is considered to be important. The relative fraction of the cross termination can be expressed in terms of the rate constants, $k_{AR}/(k_{AA}k_{RR})^{0.5}$, for the following reactions:

$$A\cdot + A\cdot \rightarrow A_2 \qquad k_{AA} \qquad (1)$$
$$R\cdot + R\cdot \rightarrow R_2 \qquad k_{RR} \qquad (2)$$
$$A\cdot + R\cdot \rightarrow AR \qquad k_{AR} \qquad (3)$$

where A· represents a halogen-containing radical, and R·, a growing radical.

Many data have recently been accumulated on the cross combination reactions of low-molecular-weight alkyl radicals with or without halogen atoms.[5-9] The values of $k_{AR}/(k_{AA}k_{RR})^{0.5}$ for $R=CH_3$ and C_2H_5 do not differ from each other; both lie between 1.5—2.6. Hence, the difference in the effects of the additives on the ethylene polymerization may be ascribed to the difference in the reactivities of the radicals formed by the radiolysis to the ethylene monomer rather than that to the growing radicals.

The relative reactivity of CF_3, CH_3, and CCl_3 radicals to the ethylene monomer can be evaluated in terms of their activation energies, E_a, in the following addition reactions:

$$CF_3\cdot + CH_2{=}CH_2 \rightarrow CF_3{-}CH_2CH_2\cdot \qquad E_{aCF_3} \qquad (4)$$
$$CH_3\cdot + CH_2{=}CH_2 \rightarrow CH_3{-}CH_2CH_2\cdot \qquad E_{aCH_3} \qquad (5)$$
$$CCl_3\cdot + CH_2{=}CH_2 \rightarrow CCl_3{-}CH_2CH_2\cdot \qquad E_{aCCl_3} \qquad (6)$$

Recently, a two-constant approximate formula (7) was proposed for the evaluation of the activation energy of the radical substitution reaction in the gaseous phase:[10]

$$E_a = D_i - \alpha D_f(1+\beta D_i) \qquad (7)$$

In this formula, D_i is the dissociation energy of the initial system, and D_f, that in the final system, while α and β are constants. In estimating the activation energies of the above addition reactions, (4), (5), and (6), D_i corresponds to D_π, the π-dissociation energy of ethylene. Hence,

$$E_a = D_\pi - \gamma D_f \qquad (8)$$

where γ is equal to $\alpha(1+\beta D_\pi)$. Since the D_π is constant in the reactions (4), (5), and (6), Eq. (8) shows that the activation energy depends solely upon the dissociation energy of the bond formed in the final system, D_f, and that it decreases with an increase in D_f. The C–C bond dissociation energies for CF_3–CH_3 and CH_3–CH_3 are 90[11]—117[12] and 83[13] kcal respectively, while that for CCl_3–CH_3 is estimated by thermodynamic calculation to be 77.7 kcal.[14,15] Since the order of the C–C bond dissociation energies for CF_3–CH_2CH_2·, CH_3–CH_2CH_2·, and CCl_3–HC_2CH_2· is the same as that for the corresponding compounds, such as CF_3–CH_3, CH_3–CH_3, and CCl_3–CH_3, the order of the activation energies of the reactions (4), (5), and (6) may be considered to be: $E_{aCF_3} < E_{aCH_3} < E_{aCCl_3}$.

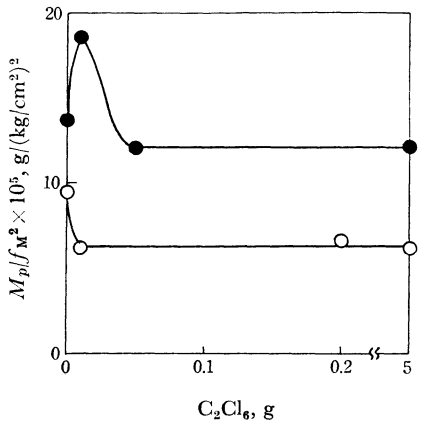

Fig. 6. The amount of polymer formed *vs.* the amount of C_2Cl_6 added. Reaction pressure, 400 kg/cm²; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; time, 3 hr; carbon dioxide, 20 g; C_2F_6, 5 g; C_2F_4, (○) free, (●) 1 mol% to C_2H_4.

Figure 6 shows the results of the polymerization carried out in the presence of the mixture of C_2Cl_6 and C_2F_6. In the polymerization in the C_2F_6 solvent, the polymer yield under a unit of ethylene fugacity is markedly depressed by the addition of a very small amount of C_2Cl_6. Moreover, when a small amount of C_2F_4 (1 mol% to C_2H_4) was added to the mixed solvent of C_2Cl_6 and C_2F_6, the yield increases in the low-concentration range of C_2Cl_6, but declines to a constant value as the amount of C_2Cl_6 increases. The decrease in the yield, however, is shown to become less pronounced than in the case without C_2F_4. These facts suggest that the chlorine-

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containing radicals produced by the radiolysis of C_2Cl_6, which will act as a terminating agent of the growing radicals, are effectively scavenged by C_2F_4, and that they are changed into highly-fluorinated radicals which contribute mainly to the initiation reaction. The decrease in the polymer yield at high concentrations of C_2Cl_6 may be ascribed to the reaction between the growing radicals and the radicals from C_2Cl_6, which are not scavenged by C_2F_4.