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Keniuchi Ishigure^a; Yoneho Tabata^a; Keichi Oshima^a

^a Department Nuclear Engineering, Faculty of Engineering University of Tokyo, Tokyo, Japan

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Radiation-Induced Copolymerization of Chlorotrifluoroethylene with Olefins

KENKICHI ISHIGURE, YONEHO TABATA, and KEICHI OSHIMA

*Department Nuclear Engineering
Faculty of Engineering
University of Tokyo
Tokyo, Japan*

SUMMARY

The copolymerizations of chlorotrifluoroethylene with propylene and isobutylene were carried out at $0 \sim -78^{\circ}\text{C}$ by γ -ray irradiation. It was found that alternating copolymers are obtained over a wide range of monomer composition for both systems. The alternating copolymer of chlorotrifluoroethylene with isobutylene was found to be highly crystalline, but the copolymer of chlorotrifluoroethylene with propylene was found to be amorphous. The copolymerizations were considered to proceed via a radical mechanism, but in the case of the isobutylene-chlorotrifluoroethylene system a cationic polymerization also takes place simultaneously at -78°C .

INTRODUCTION

In previous papers it has been reported by the authors that tetrafluoroethylene copolymerizes easily with olefins, such as ethylene [1], propylene [2], and isobutylene [3]. It has been found that the copolymers obtained alternate over a wide range of the monomer compositions, and that tetrafluoroethylene-ethylene and tetrafluoroethylene-isobutylene copolymers, especially, are highly crystalline. In the present paper,

copolymerizations of chlorotrifluoroethylene with propylene and isobutylene are reported. A part of this work was reported in a previous paper [4]. Chlorotrifluoroethylene is expected to show the same copolymerization behavior as tetrafluoroethylene, since their reactivities are very similar.

It was reported recently by M. Ragazzine et al. [5] that chlorotrifluoroethylene copolymerizes easily with ethylene when initiated by trialkylboron over a wide range of temperatures to give highly crystalline and alternating copolymers. It was pointed out by Manno [6] that the radiation-induced copolymerization of chlorotrifluoroethylene with ethylene is a quite interesting reaction from the practical point of view.

EXPERIMENTAL

Chlorotrifluoroethylene was synthesized by dechlorination of 1,1,2-trichlorotrifluoroethylene with zinc dust in ethanol, and commercial propylene and isobutylene were used after distillation. Polymerizations were carried out in glass ampoules or stainless steel vessels by means of γ -ray irradiation from a Co-60 source. The copolymer composition was determined by elemental analysis of chlorine. Viscosity was measured at 25°C using tetrachloroethylene as the solvent. Nuclear magnetic resonance spectra were measured at 100°C. Model C-60H and Model 4H-100 spectrometers (Japan Electron Optics) were employed for the measurements at 60 and 100 MHz, respectively.

RESULTS

Copolymerization of Chlorotrifluoroethylene with Propylene

In Fig. 1 the time conversion curves of copolymerization in comparison with the homopolymerization of chlorotrifluoroethylene are shown. The conversion is linear with irradiation dose at the initial stage of copolymerization. Copolymerization is not preceded by an induction period. The copolymer obtained at -78°C is soluble in the monomer mixture, and the copolymerization therefore proceeds in the homogeneous phase. The copolymers formed at higher temperatures, on the other hand, are only swelled in the monomer mixtures and the systems are heterogeneous. This difference may be due to the difference in molecular weights of the copolymers obtained.

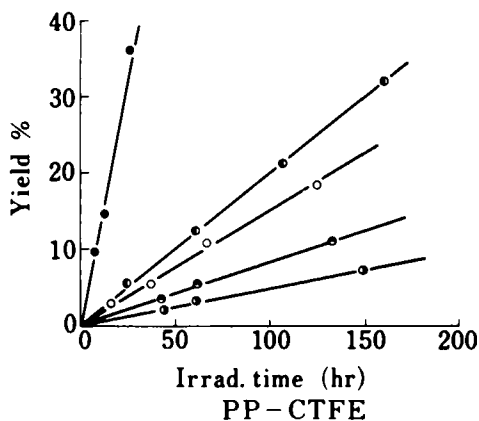


Fig. 1. Time conversion curves for propylene-chlorotrifluoroethylene system. Dose rate; 1.1×10^5 rad/hr. \bullet : chlorotrifluoroethylene, 100 mole %, -78°C . \circ : chlorotrifluoroethylene, 78 mole %, -78°C . \circ : chlorotrifluoroethylene, 47 mole %, -78°C . \ominus : chlorotrifluoroethylene, 29 mole %, -78°C . \bullet : chlorotrifluoroethylene, 78 mole %, -35°C .

There is a maximum of the copolymerization rate at about 90 mole % of chlorotrifluoroethylene in the monomer mixture, and the copolymerization rates are higher than the homopolymerization rate of chlorotrifluoroethylene over almost all the monomer compositions. The copolymer is soluble in a few solvents, such as carbon tetrachloride or perchloroethylene. Intrinsic viscosity measurements are shown in Fig. 2. The molecular weight of the copolymer decreases with increasing concentration of propylene in the monomer mixture. It should be remembered that the copolymerization rate decreases in the same fashion with increasing concentration of propylene.

It is evident from the copolymer composition curve at -35°C that alternating copolymer is obtained over a wide range of monomer compositions. Monomer reactivity ratios were calculated as $r_1(\text{PP}) = 0.24$ and $r_2(\text{CTFE}) = 0.01$ at -78°C and as $r_1 = 0.06$ and $r_2 = 0.00$ at -35°C .

Copolymerization of Chlorotrifluoroethylene with Isobutylene

The monomer composition dependency of the copolymerization rate is given in Fig. 3. The curves at -35 and 0°C are similar to each other in shape; the rate decreases with increasing isobutylene concentration in the

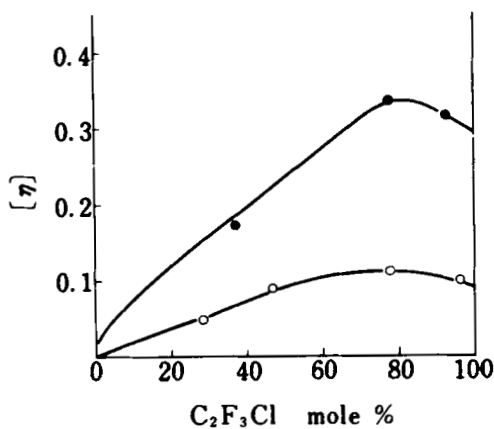


Fig. 2. Intrinsic viscosity of copolymers obtained from various monomer composition. ●: copolymers obtained at $-35^\circ C$. ○: copolymers obtained at $-78^\circ C$.

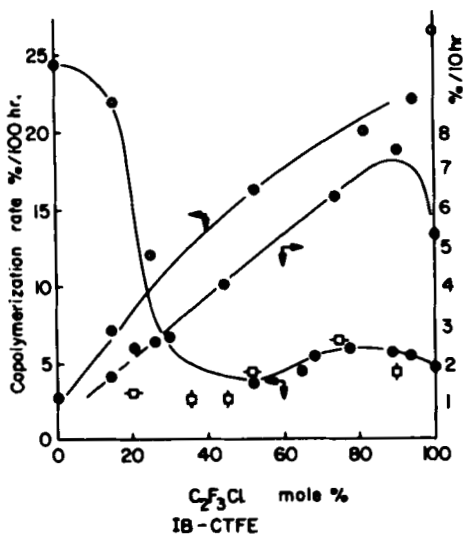


Fig. 3. Monomer composition dependency of copolymerization rate for isobutylene-chlorotrifluoroethylene system. Dose rate; 1.1×10^5 rad/hr. ●: $-78^\circ C$. ◐: $-35^\circ C$. ◑: $0^\circ C$. □: containing 2 wt % methanol.

◑: containing 2 wt % ammonia.

monomer mixture. The trend is, however, different at -78°C in comparison with foregoing cases. The rate increases enormously at the higher concentrations of isobutylene in the monomer mixtures. Since it is well known that isobutylene polymerizes easily at low temperature via a cationic mechanism, it is inferred that the remarkable increase of the rate at the high isobutylene concentration results from cationic polymerization proceeding simultaneously. To make sure about this point, additives, such as methanol or ammonia, known well as cation scavengers, were added to the system. These additives reduced the rate at the high concentration of isobutylene in the monomer mixture at -78°C as shown in the Fig. 3, while they had little effect on the rate at low isobutylene concentration. It is therefore concluded that two types of polymerizations take place simultaneously at -78°C ; one is a radical copolymerization and the other is a cationic polymerization. The polymers formed in this system are not soluble in the monomer mixture, and the system is heterogeneous.

The copolymer composition curve was shown in a previous paper [4]. Alternating copolymer is obtained over a wide range of the monomer concentration at 0°C . The chlorotrifluoroethylene contents are extraordinarily low in the polymers obtained at -78°C . The monomer reactivity ratios were determined as $r_1(\text{IB}) = 0.04$ and $r_2(\text{CTFE}) = 0.00$ at 0°C and as $r_1 = 0.06$ and $r_2 = 0.00$ at -35°C . It was difficult to determine the reactivity ratios at -78°C owing to the presence of the homopolymerization of isobutylene.

The isobutylene-chlorotrifluoroethylene copolymers obtained at 0 and -35°C were found to be highly crystalline by x-ray diffraction measurement of the copolymers. The x-ray diffraction pattern of the copolymer was quite different from that of polychlorotrifluoroethylene. The melting point of the copolymer was about 150°C and was not so high as that of isobutylene-tetrafluoroethylene copolymers, which were $220\sim 230^{\circ}\text{C}$. The polymer obtained at -78°C , on the other hand, was sticky and appeared to be amorphous.

From conversion curves for the copolymerizations of ethylene, propylene, and isobutylene with chlorotrifluoroethylene, it was made clear that the copolymerization rate is highest in the ethylene-chlorotrifluoroethylene system and lowest in the isobutylene-chlorotrifluoroethylene system. The copolymerization rate in bulk decreases with increasing carbon number of olefin as the comonomer, and this trend was also observed in the copolymerization of tetrafluoroethylene with olefins.

It is evident from the results mentioned above that two types of polymerization take place simultaneously at -78°C . One is a radical copolymerization and the other is a cationic polymerization. It is difficult to conclude

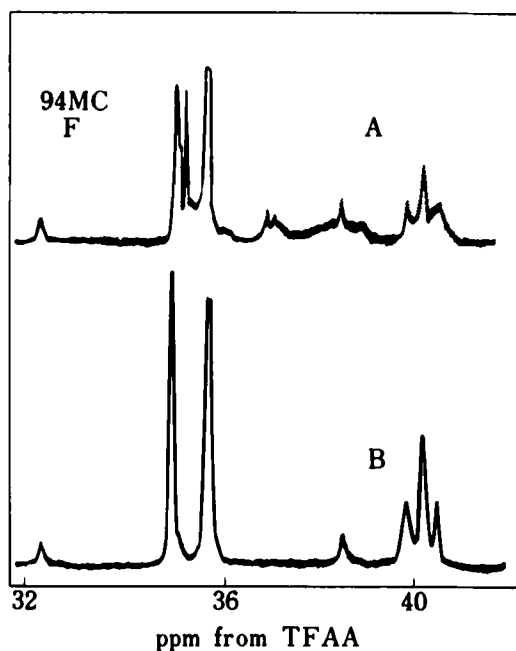


Fig. 4. NMR spectra of copolymers. Fluorine resonance, 94 MHz. A: crude polymer obtained at -78° . B: assumed alternating copolymer obtained at 0° C.

whether the cationic polymerization is homopolymerization of isobutylene or copolymerization of isobutylene with chlorotrifluoroethylene. To obtain more information about this point, the structures of the polymers were investigated by means of high resolution NMR. Proton spectra of the copolymers were compared with the spectrum of polyisobutylene. As reported previously [8], the proton spectrum of the alternating copolymer, especially the methylene resonance ranging from 6.8 to 8.2 ppm (τ value), is too complicated to be explained. In the spectrum of a crude polymer obtained at -78° C, there appeared extra resonances besides the peaks that are expected from the superposition of the spectrum of the alternating copolymer with that of polyisobutylene. The 94 MHz fluorine spectra are given in Fig. 4. The fluorine spectrum of alternating copolymer seems to be rather simple; CF_2 resonance splits to an AB-type quartet centered at about 35.5 ppm from trifluoroacetic acid, and CFCl resonance appears to be a triplet through the coupling to vicinal protons. The fluorine spectrum

(A) of the crude polymer obtained at -78°C , however, is different from that (B) of the alternating copolymer. A sharp peak appears between the central two peaks of the CF_2 resonances, and smaller peaks appear from 37 to 39 ppm, though they are not well resolved. These changes in the spectrum seem to suggest that a cationic copolymerization of isobutylene with chlorotrifluoroethylene takes place at -78°C simultaneously.

DISCUSSION

The monomer composition dependency of the copolymerization rate in the propylene-chlorotrifluoroethylene system is quite similar to that of the isobutylene-chlorotrifluoroethylene system. The rate decreases with increasing concentration of olefins as the comonomers. As already discussed in the copolymerization of tetrafluoroethylene with isobutylene [3], the degradative chain transfer of growing radical to monomer olefin may be the main reason for the remarkable decrease in the rate at the higher concentrations of olefin in the monomer mixture. This seems to be supported by the decrease in molecular weight of the copolymer obtained from the monomer mixture with higher concentrations of olefins.

In Table 1 the monomer reactivity ratios are summarized in comparison with those calculated from the Q and e values shown in Table 2. Since the alternative tendency in these copolymerizations is considered to be mainly due to the large difference in polarity factors between olefins and fluoro-monomers, both r_1 and r_2 should decrease with increasing number of carbons of olefin in the present copolymerization systems. Experimental values appear to be consistent with this order, but are a little smaller than expected from the calculation, especially for the ethylene-chlorotrifluoroethylene system. The abnormality in the calculated values (the large deviation from the other two olefins) for the propylene-chlorotrifluoroethylene system results from an unusually small value of Q for propylene. It should be noted that the system of propylene and chlorotrifluoroethylene is homogeneous at -78°C but not at -35°C . A large temperature dependence of the reactivity ratios in the propylene-chlorotrifluoroethylene system may be due to the heterogeneity of the system. The heterogeneity might lead to the tendency of the copolymers obtained to be likely to be more alternative than, expected from the difference in the polarity factors in the monomer pairs.

It is quite interesting to consider the structure of the isobutylene-chlorotrifluoroethylene copolymer. There are two possibilities for the

Table 1. Monomer Reactivity Ratios

Systems		Experimental values			Calculated values
		-78°C	-35°C	0°C	
Ethylene [5]	r_1^a	0.07	0.116 ^b	0.17	0.54
	r_2	0.001	0.004	0.009	0.10
Propylene	r_1	0.24	0.06	—	0.02
	r_2	0.01	0.00	—	0.35
Isobutylene	r_1	—	0.06	0.04	0.16
	r_2	—	0.01	0.00	0.02

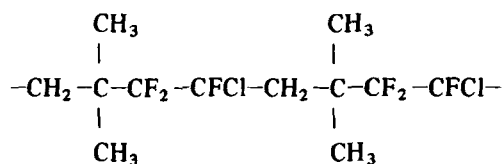
^a r_1 and r_2 are the reactivity ratios of olefin and chlorotrifluoroethylene, respectively.

^b: -40°C.

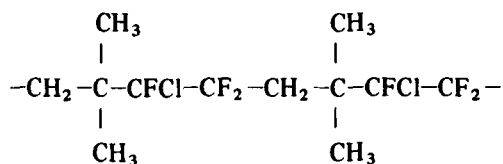
Table 2. Q and e Values of Relevant Monomers [7]

	Ethylene	Propylene	Isobutylene	Chlorotrifluoroethylene
Q	0.015	0.002	0.033	0.020
e	-0.20	-0.78	-0.98	1.48

structure, assuming the usual "head to tail" addition of isobutylene units. As reported in the previous paper [8], the alternating copolymer obtained by a radical process has the structure of Type I and not of Type II, which means that a propagating radical attacks a chlorotrifluoroethylene monomer on the carbon atom with two fluorine atoms as substituents. In the case of cationic copolymerization, which is suggested to take place at -78°C, it is rather difficult to conclude which structure the copolymer has. The NMR spectra of the polymer obtained at -78°C appear to be so poor in resolution that no decisive conclusion can be deduced. However, it is of great interest to consider which carbon atom of chlorotrifluoroethylene monomer is attacked by an active species of a growing chain, because all the hydrogen atoms are substituted in this monomer. It was reported that "frontier electron density," which can be calculated using the simple LCAO MO method, may give an idea about the opening mode of the monomer



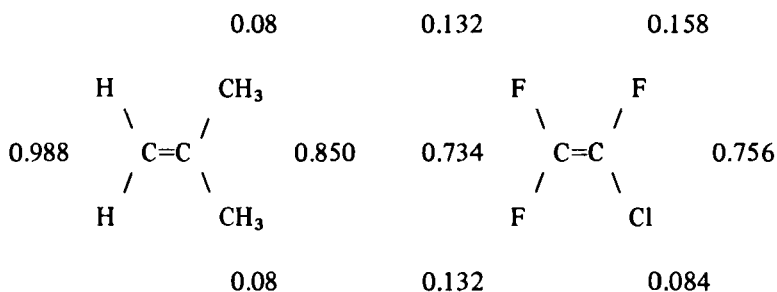
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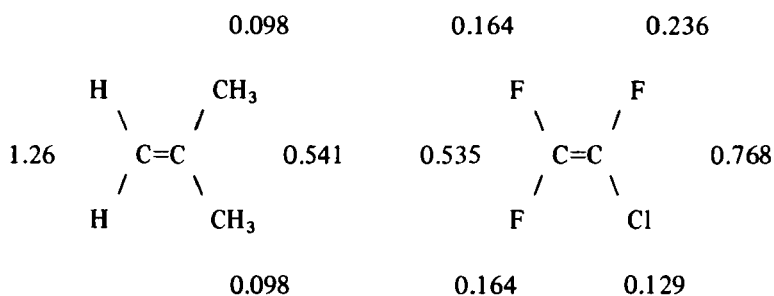
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double bond [9]. The calculation of frontier electron densities was made for isobutylene and chlorotrifluoroethylene in the cases of radical and cationic polymerizations. The results are shown together with the parameters used.

The attack of a reagent takes place on an atom where the frontier electron density is highest. It is evident that a propagating species attacks an isobutylene monomer on the CH_2 carbon atom in both radical and cationic polymerizations, since the frontier electron density is the highest there in both cases. This theoretical expectation agrees well with the chemical sense that is accepted in general. The situation, however, is a little different in the case of chlorotrifluoroethylene. The frontier electron density is the highest on the CFCl carbon for both radical and cationic polymerizations, but the difference of the electron density is very small between the CFCl and the CF_2 carbon atoms for the former case. Therefore, the reaction may be possible on both carbon atoms in a radical process as far as the frontier electron density is concerned. The experimental results, on the other hand, show that the attack of active species takes place only on the CF_2 carbon atom in radical polymerization, and probably this disagreement is explained by steric hindrance. The attack of a propagating radical may be possible only on the CF_2 carbon atom because of bulky chlorine substituent. The calculated frontier electron density does not seem to be inconsistent with Structure II in cationic polymerization.



Radical polymerization



Cationic polymerization

Substituent	a	b	1
-CH ₃	3.0	-0.1	1.0
-F	2.1	0.2	1.25
-Cl	1.8	0.18	0.8

a: Assuming α_X as a Coulomb integral on the substituent X, $\alpha_X = \alpha + a\beta$.

b: Assuming α_{adj} as a Coulomb integral on the carbon atom adjacent to X, $\alpha_{adj} = \alpha + b\beta$.

1: Assuming β_{C-X} as a resonance integral between C and X, $\beta_{C-X} = 1\beta$.

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