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Radiation-Induced Copolymerization of Fluorine-Containing Monomers*

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SUMMARY

Radiation-induced copolymerizations of various monomers, including perfluoro-olefines with CF_2O and of α-olefines with monochlorotrifluoroethylene, have been studied. It was found that CF_2O can be copolymerized randomly via radical process, with most of monomers examined and that alternating copolymers can be obtained from the copolymerization of α-olefines with monochlorotrifluoroethylene. The structural study of these copolymers was carried out by infrared, X-ray diffraction and NMR measurements. The structure of isobutylene-monochlorotrifluoroethylene copolymer was determined precisely through proton and fluorine resonances.

INTRODUCTION

Several papers on radiation-induced copolymerization of various monomers with tetrafluoroethylene have been reported from our laboratory [1]. The study of copolymerization is now extended to a combination of monomers and the polymerization conditions. In this paper, radiation-induced copolymerizations of various monomers with perfluoro-formaldehyde and of α-olefines with chloro-trifluoroethylene are reported.

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EXPERIMENTAL

Perfluoro-formaldehyde (CF_2O) was prepared by the radiation-induced oxidation of tetrafluoroethylene. The monomer was purified by distillation at low temperatures.

Chlorotrifluoroethylene (CTFE) was synthesized by a catalytic dechlorination of 1,1,2-trichlorotrifluroethane in ethanol solvent at 70°C in the presence of Zn.

The other monomers were purified by distillation. Elementary analysis of copolymers was made for H, F, and C.

The infrared spectra, X-ray diffractions, and NMR spectra of the copolymers were measured.

RESULTS AND DISCUSSION

The results of the copolymerization of various monomers with CF_2O are shown in Table 1. Although CF_2O is difficult to homopolymerize under the influence of radiation, small amounts of polymers can be obtained by high-dose irradiation. The infrared spectra of the monomer and homopolymer are shown in Fig. 1.

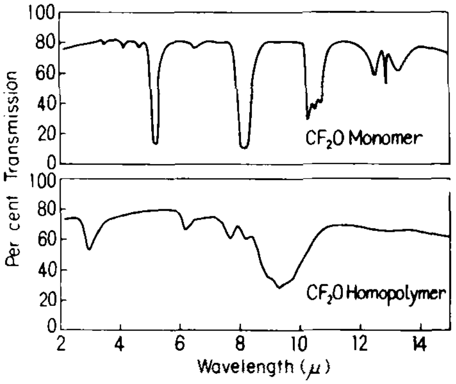

Fig. 1. Infrared spectra of CF_2O monomer and its homopolymer.

The structure of the homopolymer may be very similar to that of polyformaldehyde, and it is written as $-CF_2-O-CF_2-O-CF_2-O-$.

The infrared spectra of copolymers of CF_2O-perfluoroolefines and of CF_2O-α-olefines are shown in Figs. 2 and 3, respectively.

Table 1. Copolymerization of CF_2O with Various Monomers[a]

				Character of copolymer			
Comonomers	Molar concentration of monomer	Irradiation time (hr)	Conversion (wt%)	Appearance	CF_2O concentration in copolymer (mole %)	mp (°C)	dp (°C)
$CF_2=CF_2$	92.5	14	12.8	Solid	5.1	318	509
$CF_2=CF-CF_3$	50	109	21.8	Grease	–	–	–
$CF_2=CFCl$		40	67.5	Solid	26.3	140	222
$CH_2=CH_2$		39	35.5	Grease	8.9	–	–
$CH_2=CH-CH_3$	46	65	22.5	Oil	–	–	–
$CH_2=C(CH_3)_2$	50	44	17.2	Oil	–	–	–
$CH_2=CHCN$	43	89	60	Solid	2.3	–	–

[a] Solvent: R-113. Dose rate: 2.5×10^5 r/hr. Polymerization temperature: 25°C. Concentration of monomers: 40 mole % in the solvent.

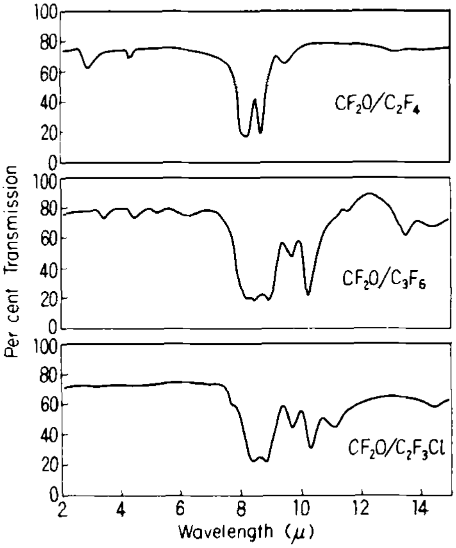

Fig. 2. Infrared spectra of copolymers.

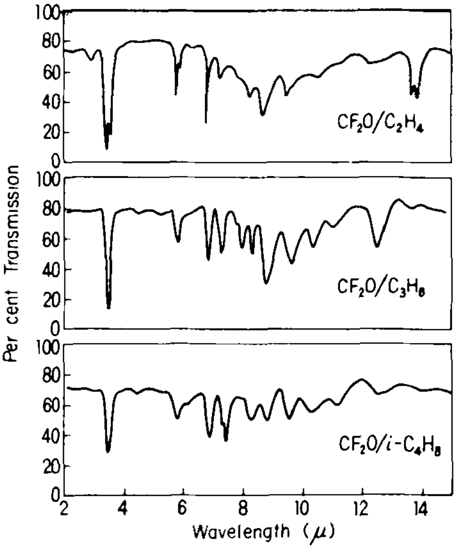

Fig. 3. Infrared spectra of copolymers.

Copolymerization of ethylene with CF_2O has been studied more precisely and the results are indicated in Table 2 and Fig. 4.

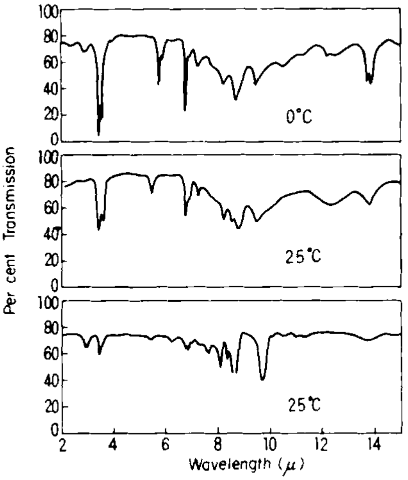

Fig. 4. Infrared spectra of CF_2O–C_2H_4 copolymers polymerized at various conditions.

It is obvious from the data that the copolymerization of CF_2O with various monomers is taking place under the influence of ionizing radiation. It is clear from the infrared spectra that CF_2O monomers are randomly distributed in the copolymer because the spectra of the copolymers are quite different from those of the homopolymers.

In most cases the polymerization of formaldehyde proceeds via an ionic mechanism. However, the electronic structure of perfluoroformaldehyde is quite different from the usual formaldehydes due to the strong electron affinity of fluorine atoms of the monomer. In our copolymerization case, the reaction may proceed via radical mechanism.

In the case of copolymerization of CF_2O with ethylene, the structure of the copolymer depends profoundly on the polymerization temperature and the concentration of one component in the monomer mixtures.

The infrared spectra changes continuously depending on the polymerization conditions, as shown in Fig. 4.

The relation between rate of copolymerization and concentration of CF_2O in the monomer mixture is shown in Fig. 5 at O and 25°C.

Table 2. Copolymerization of CF_2O with C_2H_4[a]

CF_2O concentration in the monomers (mole %)	Monomer concentration in R-113 solvent (mole %)	Polymerization temperature (°C)	Irradiation time (hr)	Conversion (wt%)	Character of copolymers: Appearance	Character of copolymers: CF_2O concentration in copolymers (mole %)	Character of copolymers: Molecular weight
50	38	25	39	35.5	Grease	8.9	440
20	"	"	22	48.1	Grease	–	500
30	100 (bulk)	"	112	8.7	Solid	3.4	1000
70	67	0	42	5.2	Grease	–	–
50	"	"	32	6.9	Wax	5.5	–
40	"	"	35	11.1	Wax	9.7	–
30	"	"	30	11.0	Solid	10.2	–
20	"	"	32	16.6	Solid	2.1	–

[a] Solvent: R-113. Dose rate: 2.5×10^5 r/hr.

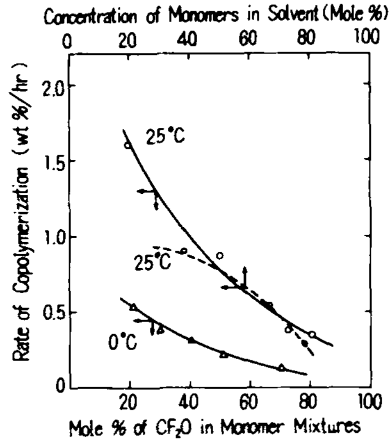

Fig. 5. Rate of copolymerization as a function of molar concentration of CF_2O in the monomer mixtures of CF_2O–C_2H_4 and of the concentration of monomers in solvent R-113.

The rate of copolymerization decreases sharply with the concentration of CF_2O in the monomer mixtures. On the other hand, the rate decreases slowly with the concentration of monomers in the solvent.

For the copolymerization of CTFE with propylene, the relations between the rate of copolymerization and the concentration of CTFE in monomer mixtures are shown at -35 and -78°C in Fig. 6. A maximum in the rate of copolymerization was observed at a concentration of about 90 mole % CTFE in the monomer mixture.

Experimental results on the copolymerization of isobutylene (IB) with CTFE are shown for different temperatures in Fig. 7. As is obvious from the figure, the copolymerization at -78°C is very different from those at O and -35°C. For the polymerization at -78°C, the effects of methanol and ammonia are noteworthy in the higher concentration region of IB. The polymerization in this region is strongly inhibited by the additives, suggesting an ionic polymerization mechanism at -78°C.

Rate of copolymerization is compared among three different olefines in Fig. 8. It is evident from Fig. 8 that the rate of copolymerization is in a order ethylene > propylene > isobutylene. Composition curves in the PP-CTFE system are shown in Fig. 9 at -35 and -78°C, respectively.

Monomer reactivity ratios were determined from Fig. 9 as follows:

$r_1 = 0.06, r_2 = 0.00, -35°\text{C}$
$r_1 = 0.24, r_2 = 0.01, -78°\text{C}$

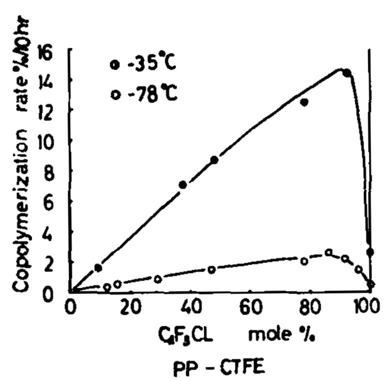

Fig. 6. Rate of copolymerization as a function of molar concentration of C_2F_3Cl in the copolymerization of propylene-C_2F_3Cl.

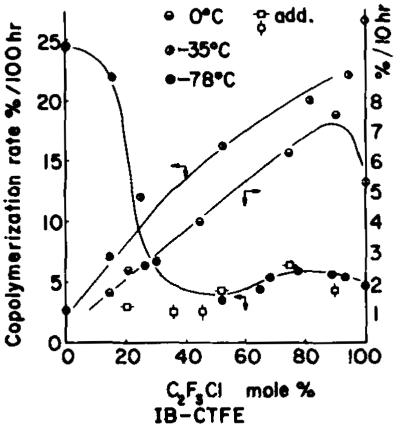

Fig. 7. Rate of copolymerization as a function of molar concentration of C_2F_3Cl in the copolymerization of isobutylene-C_2F_3Cl. (–□–) CH_3OH. (ф) NH_3.

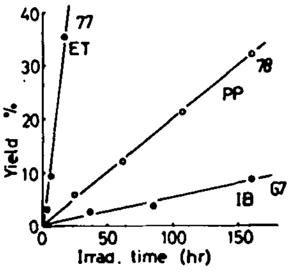

Fig. 8. Relations between yield (%) and irradiation time for copolymerizations of ethylene (ET), propylene (PP), and isobutylene (IB).

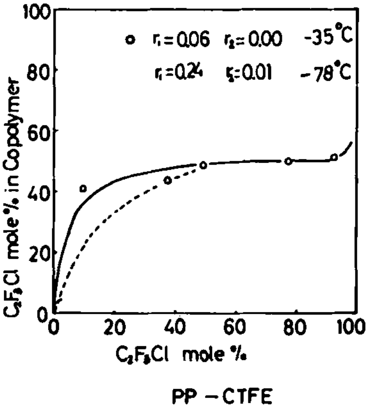

Fig. 9. Composition curve in the copolymerization of propylene (PP)-chlorotrifluoroethylene (CTFE)

In a wide range of monomer concentration of one component, an alternating copolymer can be obtained.

The composition curves in the IB-CTFE system are shown in Fig. 10. The copolymerization composition curve at -78°C is extremely different from that at 0°C. A very regular alternating copolymer is obtained at 0°C for a very wide range of monomer concentrations, and the monomer reactivity ratio is calculated to be $r_1 = 0.04$, $r_2 = 0.00$. X-ray diffraction curves of the copolymers and the homopolymer of CTFE are indicated in Fig. 11.

The copolymer is highly crystalline, and the crystallinity depends on the polymerization condition. The amorphous peak was observed at $2\theta = 10°C$ and the content of amorphous part is much higher in copolymer A than in

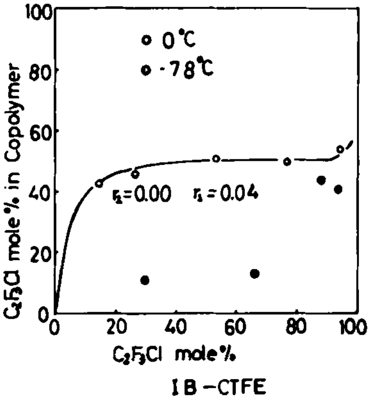

Fig. 10. Composition curves of the copolymerization of isobutylene (IB)-chlorotrifluoroethylene (CTFE).

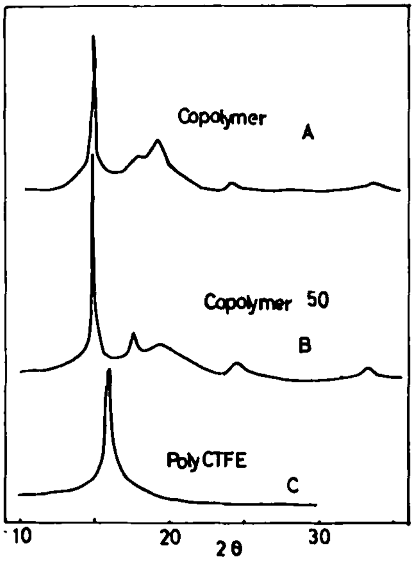

Fig. 11. X-ray diffraction curves of IB-CTFE copolymers and CTFE-polymer.

copolymer B. These results strongly suggest that the copolymer has a very regular structure and may be an alternating form. This is to be expected from the monomer reactivity ratio.

To determine the structure of copolymer more precisely, the NMR spectra

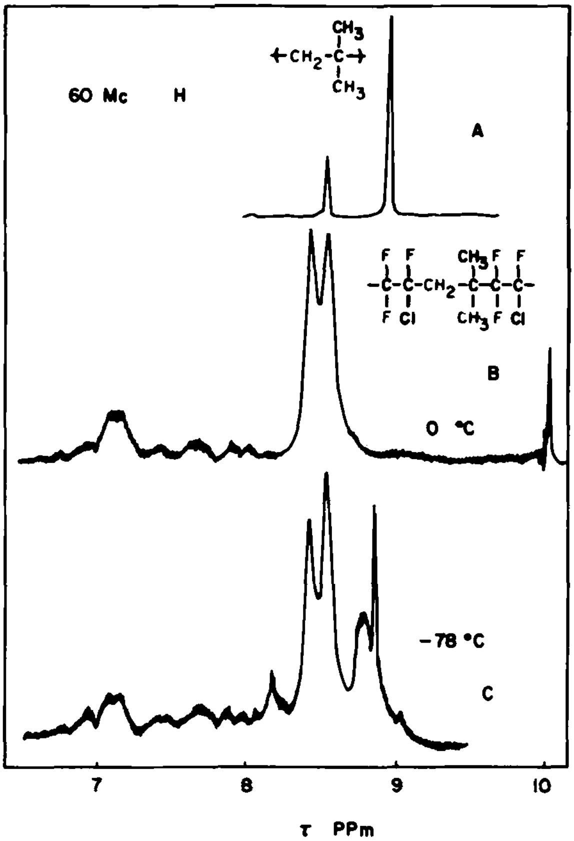

Fig. 12. Proton NMR spectra of polyisobutylene and IB-CTFE copolymers. Measurement was carried out in C_2Cl_4 at 100°C.

of hydrogen in the copolymers were measured. The spectra of polyisobutylene and the copolymers are shown in Fig. 12.

The 60 MHz proton spectrum of the copolymer is shown in Fig. 12. It is known [2] that polyisobutylene shows methyl and methylene resonances at 8.85 and 8.52 τ. The doublet centered at 8.44 τ and the weak shoulders at 8.60 ~ 8.85 τ are assigned to methyl groups, and the complex resonances at 6.85 ~ 8.02 τ are attributed to methylene groups. The doublet, the components of which at 8.36 and 8.52 τ are of equal intensity, is due to the regular alternating structure, and the other shoulders at 8.60 ~ 8.85 τ are due to the nonregular structures.

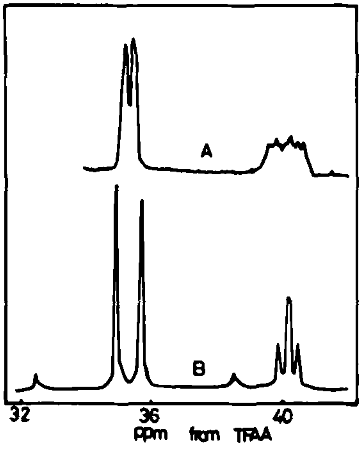

Fig. 13. Fluorine NMR spectra of IB-CTFE copolymer polymerized at 0°C. (A) 56 Mc, (B) 94 Mc. Measurement was carried out in C_2Cl_4 at 100°C.

In Fig. 13 the fluorine NMR spectra of the copolymer measured at 56 and 94 MHz are shown. A comparatively sharp doublet and an unresolved broad singlet are found at higher fields of 35.5 and 40 ppm, from trifluoroacetic acid (TFA) as an internal standard, respectively, in the 56 MHz spectrum.

The spearation between the two peaks of the doublet at the lower field is about 0.3 ppm (17 cps), and the relative intensity ratio of the doublet to the broad singlet is approximately 2:1. Thus, the doublet is assigned to the $-CF_2-$ group in the $-CF_2-CFCl-$ unit of the copolymer and the singlet at the higher field to the $-CFCl-$ group.

The spectrum at 94 MHz is obviously somewhat different from that at 56 MHz. New two weak peaks, the intensities of which are approximately equal, appear at 32.4 and 38.6 ppm in the 94 MHz spectrum and the separation between the components of the doublet at 35.5 ppm increases to 0.54 ppm (51 cps) in the spectrum. The peak at 40 ppm assigned to the $-CFCl-$ unit splits to a triplet, the equally spaced components of which have relative intensities in the ratio 1:2:1. The splitting of the $-CFCl-$ resonance is due to coupling of the fluorine atom with two equivalent 1/2 spin nuclei, and the coupling constant was estimated to be 28 cps. It is known that the coupling in the $-CF_2-$ group may be due to the asymmetric carbon atom at its nearest neighbor; on the other hand, the effect of the third neighboring asymmetric center may be negligible.

An observation of this kind seems to be rare in polymeric systems, though it has been often observed in low molecular weight compounds.

It may be concluded from the analysis of these experimental results that the polymers obtained at 0°C will have sterospecific structures. The details will be published elsewhere in near future.

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