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Effects of Solvent on the Copolymerization of Ethylene with Tetrafluoroethylene by Cobalt-60 Gamma Radiation

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The cobalt-60, γ-radiation induced copolymerization of ethylene with tetrafluoroethylene was carried out in the gas phase and in the liquid phase by using five solvents (liquefied carbon dioxide, carbon tetrachloride, ethylchloride, chloropentafluoroethane, and 1,2-dichloro-tetrafluoroethane) at a dose rate of 25000 rad/hr under a pressure of 300 kg/cm^2 at 30°C. A lower rate of the copolymerization and a copolymer of a lower molecular weight were obtained in liquid carbon dioxide and carbon tetrachloride than in the gas phase without a solvent. In ethyl chloride, the rate increased slightly, but the molecular weight decreased. On the other hand, both the rate and the molecular weight increased markedly in the fluorocarbon solvents. As a result of a detailed investigation of the copolymerization in 1,2-dichloro-tetrafluoroethane, a linear increase in the copolymerization rate and the copolymer molecular weight with the amount of solvent was noted, and there was no noticiable influence of the solvent on the copolymer composition. A kinetical discussion indicated that the addition reaction of tetrafluoroethylene to radicals produced by the influence of primary radiation on the reaction mixture is an important step in initiating the copolymerization. Also, the propagation reaction seemes to be strongly promoted by the fluorocarbon solvents.

The copolymer of ethylene with tetraflouroethylene made by γ-radiation at -78°C has been found to be a highly crystalline, random copolymer.[1] It has also been suggested that the copolymer is formed by a free radical-chain process.

In this work, the copolymerization of ethylene with tetraflouroethylene was carried out in the gas phase and in various solvents under a total pressure of 300 kg/cm^2 at 30°C by using cobalt-60 radiation, and the effects of solvents on the copolymerization were investigated. The variation in the structure of the copolymer formed with its composition was also reported.

Experimental

Materials. Tetrafluoroethylene synthesized by the debromination of 1,2-dibromo-tetrafluoroethane in the presence of a large excess of zinc dust and acetic acid was purified by freeze-thaw cycles using liquid nitrogen and pumping with a rotary vacuum pump, and was then stored in a stainless steel cylinder at -60°C. The ethylene was a polymerization-grade material from the Nisseki Kagaku Company; it was listed as 99.9% pure and showed typical analytical results of 5 ppm of oxygen and 10 ppm of acetylene. All the other materials were reagent grade and were used without further purification.

Copolymerization and Analysis. The copolymerization runs were carried out in a 100-m*l* stainless steel cylindrical vessel which had been evacuated before being filled with the reaction mixture. The transfer of tetrafluoroethylene and solvents (carbon dioxide, ethylchloride, chloro-pentafluoroethane, and 1,2-dichloro-tetrafluoroethane) from their steel storage cylinders was accomplished by cooling the reaction vessel with a dry ice-methanol bath. Ethylene was then fed in until the pressure reached 300 kg/cm^2 by means of an oilless-type compressor at a reaction temperature of 30°C. When carbon tetrachloride was used as the solvent, the reaction vessel was charged with a definite amount of carbon tetrachloride, and then the vessel was closed. Ethylene was then introduced until a pressure of 50 kg/cm^2 was reached and carefully bled out into the atmosphere to remove the dissolved air. This was repeated five times. During the reaction, the temperature was maintained constant within ± 1°C by using an automatic controller. The γ-radiation was from a cobalt-60 source, and the dose rate was 25000 rad/hr.

The copolymer yield was determined by direct weighing, while the number-average molecular weight of the copolymer was obtained from osmotic pressure measurements of solutions of the copolymer in tetralin at 130°C with the use of a Hewlett-Packard osmometer, Model 502. The molar ratio of ethylene-tetrafluoroethylene in the copolymer was evaluated by checking the carbon-hydrogen contents of the copolymer. X-Ray diffraction diagrams were obtained with a powder camera in a Rigaku Denki diffractometer, Model D-6C. Ni-filtered Cu$K\alpha$ radiation was used. The infrared absorption spectra were recorded for film samples by means of a Perkin Elmer spectrophotometer, Model-521, in the range of 400—2000 cm^{-1}. Differential thermal analyses were carried out by means of a Rigaku Denki thermal spectrometer, Model 4.

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[1] Y. Tabata, H. Shibano and H. Sobue, *J. Polymer Sci.*, *A*, **2**, 1977 (1964)

TABLE 1. COPOLYMERIZATION OF ETHYLENE WITH TETRAFLUOROETHYLENE IN VARIOUS SOLVENTS

Solvent	Amount of solvent g	Copolymer yield g	Molecular weight $\times 10^{-4}$	Molar fraction of C_2F_4 in copolymer mol%
None	0	0.26	3.6	12.6
Carbon dioxide	20	0.21	2.7	11.8
Carbon tetrachloride	60	0.09	0.098	13.0*
Ethylchloride	60	0.31	1.3	12.5
Chloropentafluoroethane	60	1.38	7.0	13.1
1, 2-Dichlorotetrafluoroethane	60	1.98	9.7	12.6

Reaction conditions: pressure, 300 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; reaction time, 1.0 hr; molar ratio of monomers, $C_2F_4/C_2H_4=1.0/99.0$; reactor volume, 100 m*l*.

* This was obtained by checking the fluorine content of the copolymer together with the contents of carbon and hydrogen.

Results and Discussion

Copolymerization in the Gas Phase and in Various Solvents. Table 1 summarizes the results of the copolymerization in the gas phase and in various solvents under a total pressure of 300 kg/cm^2 at 30°C. The solvents used in this work have been selected because of their different stabilities in reaction to ionizing radiation and because of the fact that they can be separated from the copolymer thus formed without difficulty. The addition of liquid carbon dioxide or carbon tetrachloride as a solvent was found to depress the polymerization rate and the molecular weight of the copolymer. In radiation polymerization in the presence of an added substance, it must be considered that the radiolysis products of the substance play an important role in the initiation and termination reactions. As has been reported in previous papers[2,3] pertaining to the γ-radiation-induced polymerization of ethylene in liquid carbon dioxide, growing chain radicals have been found to be terminated by oxygen produced by the radiolysis of carbon dioxide. Therefore, it is reasonable to conclude that the lower rates of copolymerization in these systems result from this type of contribution of solvents to termination reaction. The lowest molecular weight, obtained in a carbon tetrachloride solution, may be ascribed to a rapid transfer to the solvent.

In contrast to the above-mentioned results, the rate increases in ethylchloride, chloro-pentafluoroethane, and 1,2-dichloro-tetrafluoroethane. It should be noted especially that both the rate and the copolymer molecular weight increase markedly in the latter two fluorinated solvents. The results listed in the last column of Table 1 show that the molar ratio of tetrafluoroethylene to ehylene in the copolymer is little affected by the solvents used. The significance of these results will be discussed below from the viewpoint of kinetics.

Infrared Spectra of the Copolymers. The infrared spectra of the copolymers, together with the assignments of the absorption bands,[1] are shown in Fig. 1. The spectra of polyethylene and polytetrafluoroethylene are also given for ready comparison. It is obvious that the spectra of the copolymers are quite different from those of the two homopolymers. The bands at 1175, 1045, and 950 cm^{-1} which are characteristic of the copolymer become stronger with increase in the molar fraction of tetrafluoroethylene in the copolymer. This tendency is commonly observed in the spectra of the copolymers formed in other solvents.

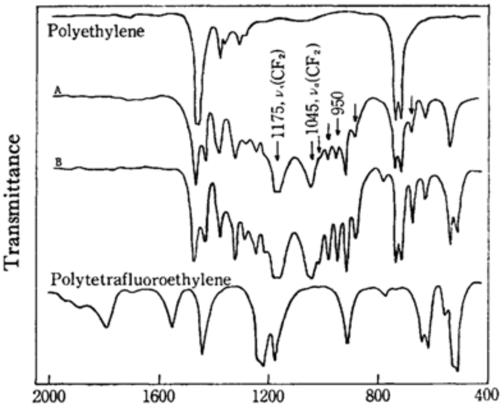

Fig. 1. Infrared spectra of copolymers. Molar fractions of tetrafluoroethylene in copolymers are (A) 3.9 and (B) 12.6 mol%.

X-Ray Diffraction Diagrams of the Copolymers. The X-ray diffraction diagrams of the copolymers, polyethylene, and polytetrafluoroethylene are given in Fig. 2. The diffraction peaks at $2\theta=20.9°$ and $2\theta=20.4°$ are observed, the strongest peaks for the copolymers of the molar fractions of tetrafluoroethylene in copolymers being 3.9 and 12.6% respectively. These peaks exist between

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[2] M. Hagiwara, H. Mitsui, S. Machi and T. Kagiya, *J. Polymer Sci., A-1*, **6**, 609 (1968).

[3] M. Hagiwara, H. Mitsui, S. Machi and T. Kagiya, *ibid., A-1*, **6**, 721 (1968).

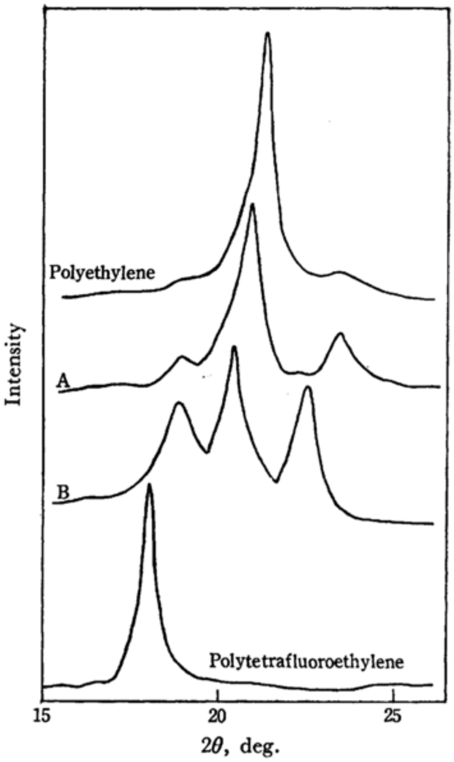

Fig. 2. X-ray diffraction diagrams of copolymers. The signs of each spectra are the same as shown in Fig. 1.

those of the two homopolymers, and their position varies continuously depending upon the molar ratio of the two monomers in the copolymer.

Thermograms of the Copolymers. Figure 3 shows the thermograms of the copolymers, together with those of polyethylene and polytetrafluoroethylene. It is obvious that the thermograms of the coplymers show no peaks obtained by the superposition of the thermograms of the two homopolymers, and that the crystalline melting temperature of the copolymer (134°C in Curve A and 187°C in Curve B) rises with the molar fraction of tetrafluoroethylene in the copolymer. In addition, a small endothermic peak at *ca.* 100°C was observed in the copolymer of which 12.6% was tetrafluoroethylene.

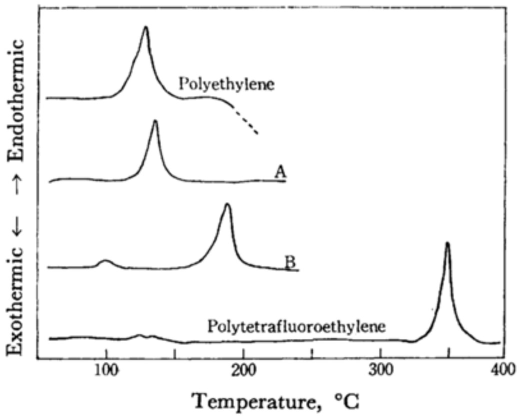

Fig. 3. Thermograms of copolymers for α-alumina in ambient air at heating rate of 5°C per minute. The signs of each curves are the same as shown in Fig. 1.

Polytetrafuoroethylene has been found to show several kinds of transitions at various temperatures. In the range studied in this work, two first-order transitions occurring in the crystalline region at relatively closely-spaced teaperatures around 90°C, and two second-order transitions in the amorphous region around 130°C, have been reported.4–6) In our thermograms of polytetrafluoroethylene, we observed, no peak at 90°C, but we did find small endothermic peaks near 130°C. Thus, although it has not been clearly shown, the small peak near 100°C in the copolymer is considered to correspond to the transitions around 130°C in polytetrafluoroethylene.

From these results of the infrared, X-ray diffraction, and from the differential thermal analyses, the alternative possibilities of the formation of a mixture of homopolymers and a block copolymer can be excluded.

Copolymerization in 1,2-Dichloro-tetrafluoroethane. The results given in Table 2 show the characteristic effects of 1,2-dichloro-tetrafluoroethane as a solvent on the copolymerization. We were able to observe the appearance of the reaction mixture throughout the copolymerization reaction by using a specially-designed stainless steel autoclave with a quartz window.7) When a sufficient amount of solvent was used (thirty grams of 1,2-dichlorotetrafluoroethane were found to be quite enough for a vessel with a capacity of 100 ml), it was observed that the mixture of the two monomers and the solvent exists in a homogeneous liquid phase, with no phase separation in the reaction vessel, and that copolymers formed separate continuously from the mixture as fine particles during the course of the reaction. Thus, in all the copolymerization runs carried out by the use of the solvent, the reaction takes place in the homogeneous-liquid-phase mixture of two monomers and the solvent used. On the other hand, the copolymerizationis a gas-phase reaction when no solvent is used.

In Fig. 4 the rate of copolymerization is plotted against the amount of solvent for three different concentrations of tetrafluoroethylene in the reaction mixture. In all cases, the rate is shown to increase linearly with the amount of solvent. Another

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4) Y. Araki, *J. Appl. Polymer Sci.*, **9**, 1515 (1965).
5) Y. Araki, *ibid.*, **9**, 3575 (1965).
6) Y. Araki, *ibid.*, **11**, 953 (1967).
7) S. Machi, M. Hagiwara and T. Kagiya, *J. Polymer Sci.*, *B-4*, 1019 (1966).

TABLE 2. COPOLYMERIZATION OF ETHYLENE WITH TETRAFLUOROETHLENE IN GAS PHASE AND IN 1,2-DICHLOROTETRAFLUOROETHANE

Run No.	Amount of solvent g	Concentration of monomers mol/l		Molar fraction of C_2F_4 in monomers mol%	Copolymer yield g	Molecular weight $\times 10^{-4}$	Molar fraction of C_2F_4 in copolymer mol%
		C_2H_4	C_2F_4				
1	0	17.50	0	0	0.23	20.88	0.0
2	0	16.89	0.173	1.02	0.26	3.61	12.6
3	0	17.17	0.230	1.32	0.35	4.00	13.8
4	30	15.18	0.149	0.98	1.13	5.81	13.0
5	60	11.07	0	0	0.21	5.14	0.0
6	60	11.18	0.022	0.20	0.49	5.64	3.9
7	60	12.50	0.062	0.49	0.85	6.10	8.8
8	60	12.57	0.132	1.04	1.98	9.70	12.6
9	60	12.71	0.188	1.46	2.85	12.84	16.2
10	80	11.04	0.113	1.01	2.10	11.32	12.5
11	120	6.43	0	0	0.27	4.20	0.0
12	120	6.61	0.036	0.53	1.29	8.25	10.3
13	120	6.71	0.074	1.08	3.15	16.20	13.3

Reaction condition: pressure, 300 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; reaction time, 1.0 hr; reactor volume, 100 ml.

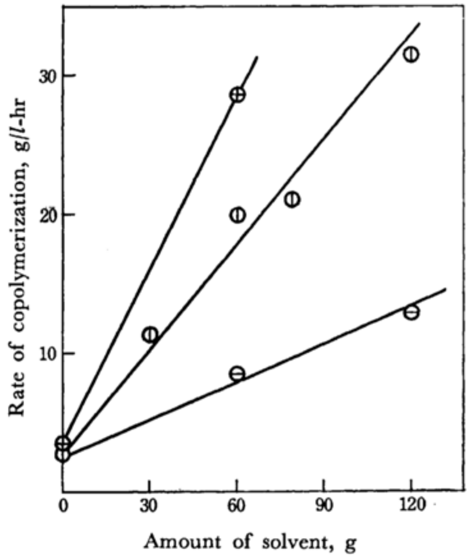

Fig. 4. Rate of copolymerization *vs.* amount of 1,2-dichloro-tetrafluoroethane. Reaction conditions: total pressure, 300 kg/cm^2; temperature, 30°C; dose rate, 2.5×10^4 rad/hr; reactor volume, 100 ml; concentrations of tetrafluoroethylene in monomers are about (⊖) 0.5, (⦶) 1.0 and (⊕) 1.5 mol%.

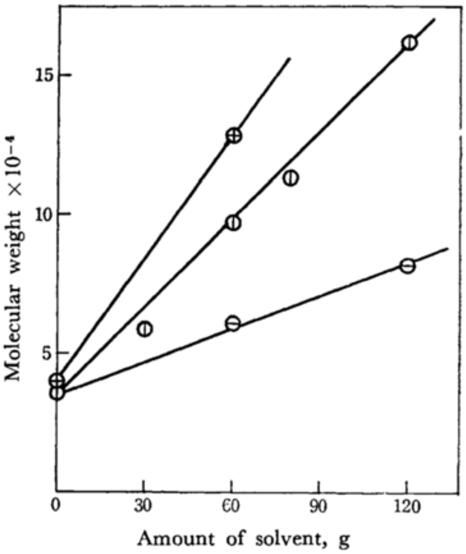

Fig. 5. Molecular weight of copolymers *vs.* amount of 1,2-dichlorotetrafluoroethane. Reaction conditions are the same as shown in Fig. 4.

characteristic phenomenon is the effect of the solvent on the molecular weight of the copolymer formed. As is shown in Fig. 5, our observation clearly demonstrates that the molecular weight increases linearly with the amount of solvent used. On the other hand, as can be seen in the last column of Table 2, the copolymer composition is not affected by the amount of solvent, but is determined exclusively by the molar ratio of the two monomers in the reaction mixture. The fraction of tetrafluoroethylene in the copolymer is much larger than that in the monomers.

By using Eq. (1) (given below), the rate of copolymer chain formation can be calculated; the results are plotted in Fig. 6 against the molar fraction of tetrafluoroethylene in monomers.

Rate of copolymer chain formation

$$=(M_p/t)(1/\bar{P}_n) \quad (\text{mol}/l\text{-hr}) \qquad (1)$$

M_p: copolymer yield (mol/l)

$\overline{P}_n$: total number of monomer units in one copolymer chain (–)

t: reaction time (hr)

A small amount of tetrafluoroethylene is shown to be quite effective in producing copolymer chains. In all cases when different amounts of a solvent are used, the rate increases with an increase in the fraction of tetrafluoroethylene. In the range where the molar fraction of tetrafluoroethylene is less than 1%, a higher rate is obtained when a larger amount of solvent is used. Three point on the ordinate show a significant contribution of the solvent to the polymer chain formation. In contrast to this, though a higer rate is obtained than in the case of no solvent at all, the rate comes not to be affected by the amount of solvent in the range above 1% of tetrafluoroethylene. From these observations, it can be concluded that 1,2-dichloro-tetrafluoroethane used as a solvent does not act as a transfer agent in the copolymerization, and that the addition reaction of tetrafluoroethylene to the radicals produced by the influence of radiation on the reaction mixture is important in initiating the copolymerization. Thus, the addition of tetrafluoroethylene to the primary radicals is considered to produce more reactive radicals, which can then effectively initiate the copolymerization with less activation energy. Further, the data in Fig. 6 show that, when a sufficient amount of a solvent is used, the rate of initiation is virtually independent of the amount of solvent at tetrafluoroethylene concentrations above 1%.

In connection with the discussions above, it is interesting to note that the copolymerization rate and the copolymer molecular weight increase linearly with the amount of solvent, as is reported in Figs. 4 and 5. These facts may indicate that the propagation reaction of the copolymerization is strongly promoted by the solvent. Further, the information on the copolymer composition given in Table 2, which shows no noticiable influence of the amount of solvent on the copolymer composition, leads to the conclusion that the enhancement in reactivity might occur at an active site of the propagating copolymer chain. The strongly electro-negative flourine atoms of the solvent might have some effect on the reactivity of the active site in a solvated state. A careful study of this aspect is being carried out and will be reported on later.

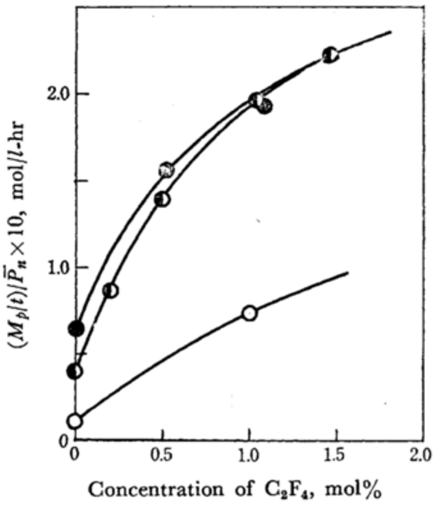

Fig. 6. Rate of copolymer chain formation, $(M_p/t)/\overline{P}_n$ *vs.* initial concentration of tetrafluoroethylene in monomers.
Amounts of solvent are (○) 0, (◐) 60 and (●) 120 g.