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γ-Rays radiation-induced homopolymerization of trifluorovinyl heptafluoropropyl ether

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Abstract

The polymerization of trifluorovinyl heptafluoropropyl ether ($CF_2{=}CF{-}O{-}C_3F_7$) (FVPE) was investigated by γ-rays irradiation to afford high-molecular weight polymer of FVPE.

Keywords: Fluoropolymers; γ-Rays; Trifluorovinyl heptafluoropropyl ether; Radical polymerization

1. Introduction

The polymerization reactivity of polyfluorinated vinyl monomers is extremely low except few compounds such as tetrafluoroethylene, chlorotrifluoroethylene [1,2] and hexafluoro-1,3-butadiene [3]. Copolymerization with other vinyl compounds has, then, been examined and many reports on alternating copolymers of polyfluorinated vinyl monomers with nonfluorinated ones have been published [1]. Trifluorovinyl heptafluoropropyl ether ($CF_2{=}CF{-}O{-}C_3F_7$) (FVPE) is in the similar situation. Homopolymer of FVPE has never yielded under usual polymerization conditions and alternating copolymers with several nonfluorinated vinyl monomers have been reported. The study has started on the investigation of producing alternating copolymer of FVPE with hexafluoroacetone under radical condition. All attempts finished in vain as far as yielding alternating copolymer was concerned. In the course of the study the γ-ray radiation-induced reaction of FVPE with hexafluoroacetone showed the decrease of FVPE monomer in the reaction systems to yield highly viscous oil. This paper concerns about the γ-ray radiation-induced homopolymerization of FVPE. No recent study on the radiation-induced homopolymerization of perfluorovinyl compounds has been reported [4].

2. Results and discussion

No copolymerization of FVPE with hexafluoroacetone was found to take place under radical and anionic polymerization conditions. The trace amount of products were analyzed to give the indication that the reaction of FVPE took place. The results suggested that the homopolymers of FVPE might, therefore, be obtained under suitable reaction conditions. The irradiation of FVPE with γ-rays from ^{60}Co was then examined. The continuous formation of radicals is well-known to take place by γ-rays irradiation on organic compounds. The reaction conditions and the results of polymerization are summarized in Table 1. The conversion of FVPE is found to be increased with increase of irradiation dose and yields of the products are also elevated. The product which was highly viscous liquid like pine resin was insoluble in usual organic solvents and partly soluble in hexafluorobenzene. The structural analyses were then restricted. The 5% weight-loss temperature (T_{d5}) which might be proportional to molecular weight of polymers was measured to give the results that the elevation of T_{d5} of the polymer yielded up to 1000 kGy was confirmed. The results suggest that

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Table 1
Radiation-induced polymerization of FVPE[a]

Dose (kGy)	Conversion[b] (%)	Yield (%)	T_{d5}[c] (°C)
10	2.4	2.1	–
30	50.9	4.2	–
100	–	12.0	–
160	55.9	16.5	–
250	66.1	23.1	144
500	96.2	40.6	169
1000	96.6	49.2	165
2000	–	72.9	156
3000	–	81.7	144
7400	–	80.2	130

[a] At room temperature; dose rate: 10 kGy/h.
[b] FVPE conversion measured by GC.
[c] T_{d5} of poly(FVPE) measured by TGA.

the increase of molecular weight of the polymers would presumably take place. Higher dose of irradiation over 1000 kGy showed the results of decreasing T_{d5}, which suggest low-molecular weight product formation or degradation of yielded polymers.

Measurement of viscosity of the hexafluorobenzene-soluble product yielded at 2000 kGy irradiation showed as high as $[\eta] = 0.47$. Homopolymer of FVPE was concluded to be produced under irradiation of γ-rays.

Fig. 1 shows the result of ^{13}C NMR measurement of hexafluorobenzene-soluble part of the product. Peaks around 130 and 148 ppm assignable to vinyl carbons of FVPE are disappeared in the spectrum of the product. The result suggests that the reaction of vinyl groups would take place. Results of diffusion reflection infrared spectral measurements of poly (FVPE) and the copolymer of poly(tetrafluoroethylene-*co*-FVPE) are shown in Fig. 2. The signal around 1750 cm^{-1} assignable to trifluorovinyl group of FVPE is disappeared in the spectrum of polymer. Peak at 933 cm^{-1} would be assigned to OC_3F_7 group as compared to that of poly(tetrafluoroethylene-*co*-FVPE). The peak around 3400 cm^{-1} may be assignable to carboxyl group which would be produced by the radical migration to yield acid fluoride during the polymerization followed by hydrolysis while ceasing the polymerization. The analyses of the product confirms the homopolymerization of FVPE.

3. Experimental

All experiments related to polymerization are carried out under purified nitrogen atmosphere in order to preclude oxygen

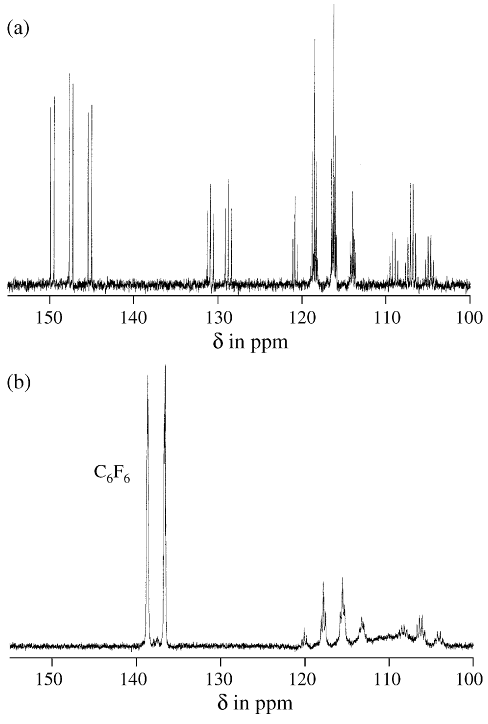

Fig. 1. ^{13}C NMR of (a) FVPE and (b) reaction product.

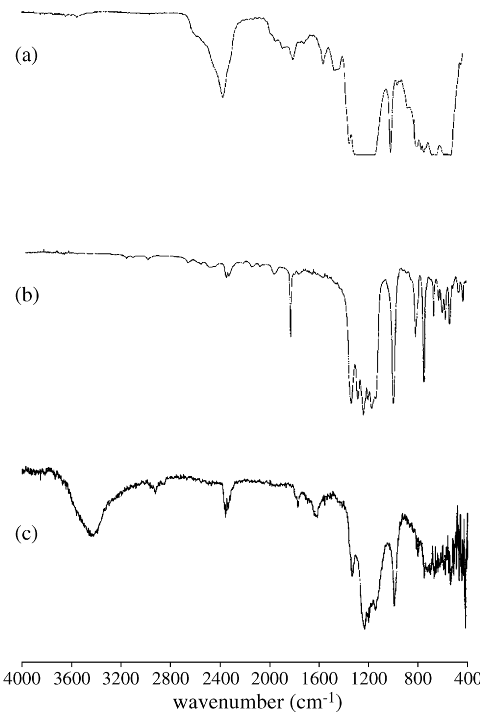

Fig. 2. IR of (a) poly(tetrafluoroethylene-*co*-FVPE), (b) FVPE, and (c) product by 2000 kGy irradiation.

and moisture. FVPE presented by courtesy of UNIMATEC Co was used after distillation. Polymerization was carried out by adding FVPE in a sealed glass ampoule which was carefully flame dried and irradiation with γ-rays from ^{60}Co source in Takasaki Advanced Radiation Research Institute, Japan Atomic Energy Agency at the dose rate of $10\,\mathrm{kGy\,h^{-1}}$ at room temperature under reduced pressure. Poly(tetrafluoroethylene-*co*-FVPE) was presented by DUPONT·MITSUI Fluorochemicals Co. The 5% weight-loss temperature (T_{d5}) was determined by thermogravimetric analysis (TGA). TGA was carried out with a TGA 51 thermogravimeter with a Thermal Analyst 2000 (TA Instruments) under nitrogen atmosphere with a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$. Measurement of vapour phase chromatography (GC) was carried out with a Hewlett-Packard 6890 with a DB-1, wide-bore fused silica capillary column ($15\,\mathrm{m} \times 0.53\,\mathrm{mm}$, film thickness: 1.5 μm, J&W) equipped with flame ionization detection. The column temperature was programmed from 100 to 300 °C at $20\,^{\circ}\mathrm{C\,min^{-1}}$. NMR spectrum was recorded on a JEOL JNM-ECP500 Fourier transform NMR spectrometer at 125 MHz for ^{13}C {[^{1}H (5 ppm) and ^{19}F (−85 ppm)]} in hexafluorobenzene as a solvent.

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