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Radical Copolymerization of a Highly Fluorinated Cyclic Olefin Octafluorocyclopentene with Alkyl Vinyl Ethers

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Summary

Fluoropolymers are potential candidates for use in the fields of specific coating and lithography. Their versatility could be enhanced by increasing their glass transition temperature, T_g. In order to achieve this, the copolymerization of a highly fluorinated cyclic monomer, octafluoro-cyclopentene (OFCPE), with three kinds of alkyl vinyl ethers was investigated with a radical initiator in bulk. It was found that OFCPE and cyclohexyl vinyl ether (CHVE) copolymerized successfully, and the weight average molecular weight and T_g of the copolymer reached values of 12,000 and 124.9°C, respectively. Copolymer composition was close to a OFCPE:CHVE unit ratio = 0.5:0.5. The monomer reactivity ratios estimated by the Yamada-Itahashi-Otsu nonlinear least-squares procedure were found to be $r_{1,\mathrm{OFCPE}} = 0.005 \pm 0.020$ and $r_{2,\mathrm{CHVE}} = 0.154 \pm 0.017$.

Introduction

Fluoropolymers are highly versatile and have various applications because of their excellent properties. Such properties include their ability to repel and lubricate, their chemical and thermal inertness, and their low values of refractive index, dielectric constant, and absorbance of UV light [1]. Fluoropolymer's properties allow potentially fruitful applications in their use as specific coatings and in the electronics and opto-electronics fields [2,3]. These potential applications are largely as a result of the fluorine content, which has allowed the development of fluorinated polymer backbones used in areas requiring good optical transparency, photosensitivity, solubility in aqueous base, and etch resistance [4]. One limitation, however, on the applications of fluoropolymers is their low glass transition temperature T_g as compared with their hydrogen homologous polymers. If a higher value of T_g could be achieved, then this would extend the range of their potential application. One way of obtaining a higher value of T_g is to modify the structure by incorporating cyclic perfluoroolefin into the main chain. The problem is that they are hard to polymerize due to the electron poorness. However, better results can be obtained in copolymerization with electron-rich monomers such as vinyl ethers, which are also poorly reactive under radical conditions [5].

One such combination previously reported on was the copolymerization of a cyclic perfluoroolefin, octafluorocyclopentene (OFCPE), with ethyl vinyl ether (EVE). We found that OFCPE and EVE copolymerized almost alternatively to form copolymers with an improved maximum T_g at 80°C [6]. Though this T_g value compares favorably with T_g at -43°C for poly(EVE) [7], even higher T_g values are required for most of the practical applications. In this study, we selected three kinds of comonomers, tert-butyl vinyl ether, methyl isopropenyl ether, and cyclohexyl vinyl ether, which were homopolymerized by cationic initiators giving higher T_g values (67-88°C) than that of poly(EVE) [7-9]. It was expected that copolymers of OFCPE with the comonomers would show higher T_g values than that of poly(OFCPE-*co*-EVE). Additionally, the reactivity ratios of OFCPE and CHVE on the copolymerization were calculated.

Experimental

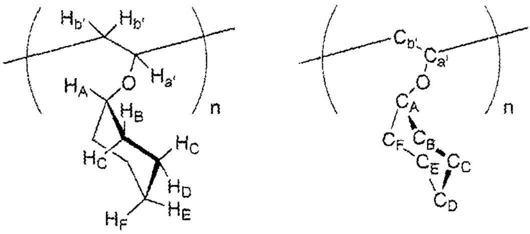
Materials

Octafluorocyclopentene (OFCPE from Central Glass Co., Ltd.), tert-butyl vinyl ether (tBVE from Sigma-Aldrich Fine Chemicals), methyl isopropenyl ether (MIPE from Tokyo Kasei Kogyo Co., Ltd.) and cyclohexyl vinyl ether (CHVE from BASF Corporation) were purified by distillation in a nitrogen atmosphere and kept below 10°C in a refrigerator until just before use. Initiator, 2,2'-azobis-isobutyronitrile (AIBN), was purchased from Kishida Corp. and used without any purification. Other chemicals were used as received.

Polymerization

To carry out the polymerization, glass tubes with butyl rubber stoppers and screw tops were used as reaction vessels. First, AIBN and alkyl vinyl ether were weighed and charged in the tube under a dry-nitrogen atmosphere. The tube was then capped with the stopper and screw top, before being charged with OFCPE using an airtight syringe. Polymerization was carried out in a water bath under prescribed conditions by stirring with reciprocal shaking at 80 strokes min^{-1}. After the polymerization, the tube was removed and the polymer was precipitated with excess methanol. The precipitate was filtrated and dried under reduced pressure for 24 h at ambient temperature. This isolated polymer was then weighed to calculate the yield and then analyzed by ^{1}H and ^{13}C NMR, Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and elemental analysis.

The ^{1}H and ^{13}C NMR chemical shifts of CHVE homopolymer (Scheme 1) have not been reported. The chemical shifts determined in this work were as follows: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 ($H_{a'}$), 1.5-1.7 ($H_{b'}$), 3.29 (H_A), 1.88 (H_B), 1.22 (H_C), 1.72 (H_D), 1.53 (H_E), and 1.1-1.2 (H_F) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 71.443 ($C_{a'}$), 42.424 ($C_{b'}$), 75.099 (C_A), 33.457 ($C_{B,F}$), 24.497 ($C_{C,E}$), and 25.870 (C_D) ppm.



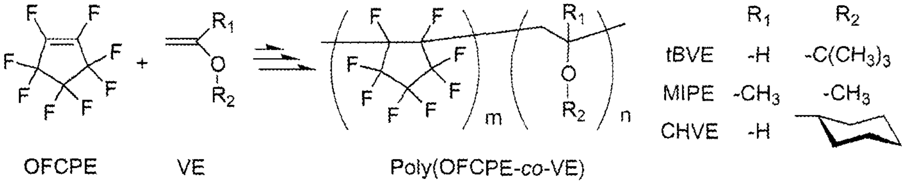
Scheme 1. Poly(CHVE)

Characterization

^{1}H and ^{13}C NMR measurements were made on a Varian 400 VLX spectrometer operated at 400 and 100 MHz. Chlorobenzene was used as an internal standard for calculation of the copolymer composition, $CDCl_3$ as a solvent, and tetramethylsilane as a standard indicating 0 ppm. FTIR spectra were recorded from KBr pellets on a Nicolet Avatar 360 FTIR spectrometer. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) using a TOSOH HLC-8220 GPC system, equipped with refractive index (RI) and ultra violet (UV) detectors, under the following conditions: TSK-GEL Super HM-H linear type column and THF (HPLC grade) eluent at a flow rate of 0.6 mL min^{-1} at 40°C. The calibration curves for GPC analysis were obtained using polystyrene standards with a low polydispersity (*Mn* 5.0 x 10^{2} - 1.11 x 10^{6}, TOSOH Corporation). Thermal analysis was conducted repeatedly with a SEIKO Instrumental Inc. EXSTAR 6000 differential scanning calorimeter (DSC) in aluminum pans (5 mmϕ) at a 10°C min^{-1} heating rate. Elemental analysis of carbon and hydrogen content was made on a Yanaco CHN-corder MT-5, and fluorine content was analyzed using a Yanaco SX-elements microanalyzer YS-10.

Results and discussion

In the previous report [6], we showed that little homopolymerization of octafluorocyclopentene (OFCPE) occurred using free radical initiators. However, the radical copolymerization of OFCPE with ethyl vinyl ether (EVE) proceeded smoothly giving polymeric products (Mw > 15,000, T_g 80°C) with a reasonable yield (>45%). The homopolymers prepared by cationic polymerization of tert-butyl vinyl ether (tBVE), methyl isopropenyl ether (MIPE), and cyclohexyl vinyl ether (CHVE) showed relatively high glass transition points, T_g, of 88, 81, and 67°C, respectively, compared with other poly(n-alkyl vinyl ether)s [7-9]. Though the radical copolymerization of tBVE and CHVE with hexafluoroisopropyl methacrylate and α-fluoroacrylate was reported as providing high molecular weight copolymers [5], the copolymers showed relatively low T_g values ranging from 73-82°C. In this study, the copolymerization of OFCPE with tBVE, MIPE, and CHVE was carried out with a radical initiator, 2,2'-azobis-isobutyronitrile (AIBN) in bulk (Scheme 2). The analytical results of the products are listed in Tables 1 and 2 with the copolymer compositions calculated from the elemental analysis data and ^{1}H-NMR spectra.



Scheme 2. Copolymerization of OFCPE and vinyl ethers

Table 1. Copolymerization of OFCPE and vinyl ethers in bulk[a].

entry	Vinyl Ether	Feed	Conditions	Copolymers			Molar fraction in copolymer	DSC
	(VE)	OFCPE / VE (molar ratio)	(h / °C)	Total Yield (%)	*Mn*	*Mw*	OFCPE / VE (unit ratio)	Tg (°C)
1-1	tBVE	3 / 7	7 / 70	0.30	2,400	2,900	0.29 / 0.71	nd[b]
1-2	tBVE	5 / 5	7 / 70	0.97	2,000	2,500	0.42 / 0.58	92.6
1-3	tBVE	7 / 3	7 / 70	1.07	1,900	2,300	0.43 / 0.57	101.1
1-4	tBVE	5 / 5	72 / 55	10.46	1,900	2,600	0.46 / 0.54	103.2
1-5	MIPE	5 / 5	9 / 70	1.13	2,500	3,000	0.45 / 0.55	111.3
1-6	MIPE	6.25 / 3.75	9 / 70	0.67	2,200	2,700	0.46 / 0.51	111.9

[a] Initiator: AIBN, 0.5 mol%. [b] not detected.

Table 2. Copolymerization of OFCPE and CHVE in bulk[a].

entry	Feed	Copolymers			Molar fraction in copolymer	Unit Yield	
	OFCPE / CHVE (molar ratio)	Total Yield (%)	*Mn*	*Mw*	OFCPE / CHVE (unit ratio)	OFCPE (%)	CHVE (%)
ref.	0/10	5.0	2,500	3,200	0 / 1	-	5.0
2-1	3/7	50.6	7,000	11,500	0.41 / 0.59	65.0	40.2
2-2	4/6	45.4	7,400	12,000	0.45 / 0.55	49.6	40.7
2-3	5/5	35.6	7,600	12,000	0.47 / 0.53	33.9	38.5
2-4	6/4	25.6	7,500	11,700	0.48 / 0.52	21.8	35.1
2-5	7/3	16.2	7,300	11,000	0.51 / 0.49	13.0	28.9

[a] Conditions: AIBN, 0.5 mol%; at 70°C for 7 h.

Copolymerization of OFCPE with tBVE and MIPE

The copolymerization of OFCPE with tBVE proceeded slowly giving low molecular weight products with T_g values higher than 100°C in cases where the molar composition was close to 0.5:0.5 (Table 1). Although increasing the reaction time led to a higher yield, the molecular weight and T_g value hardly increased. Considering the results of Castelvetro et al. [5], who reported a lowering molecular weight caused by the α-methyl group of methacrylate in the copolymerization with tBVE, this result can be attributed to steric hindrance between the tert-butyl group and OFCPE unit in the main chain. The copolymerization with MIPE also produced a higher T_g copolymer (111.9°C), with, however, a low yield and low molecular weight similar to those of poly(OFCPE-*co*-tBVE) (Table 1). A longer reaction time did not lead to any increase in yield. This is considered to be due to the degradative chain transfer by the isopropenyl group of MIPE. The copolymerization at lower temperature (tBVE 45°C, MIPE 60°C) increased the T_g value (tBVE 114.2°C, MIPE 115.8°C) and molecular weight (tBVE: Mw=3,500, MIPE: Mw=3,200), but the yield was not improved significantly despite a longer reaction time of up to 336 h.

Copolymerization of OFCPE with CHVE

The copolymerization of OFCPE and CHVE was carried out while varying the monomer feed ratio in the range of [OFCPE]:[CHVE] = 3:7-7:3, for 7 h at 70°C in bulk (Table 2). Despite the low yield of CHVE homopolymer (entry ref. in Table 2), a maximum yield value of 50.6% of the copolymer was obtained at [OFCPE]:[CHVE] = 3:7 (entry 2-1), and decreased in parallel with the decrease in the CHVE feed ratio. The OFCPE unit content in the copolymer changed slightly within only a narrow range of 0.41-0.51, suggesting that the copolymerization proceeded alternatively in the case of an excessive feed of OFCPE. Interestingly, although the yield of CHVE-unit changed in the narrow range of 29-41%, the yield of OFCPE-unit decreased from 65 to 13% as the OFCPE feed ratio was increased. This suggests that the copolymerization proceeded like a pseudo 1^{st}-order reaction, dependent on [CHVE]. This means that a rate-determining step of the copolymerization would be a reaction between an OFCPE end-radical and CHVE monomer. All the GPC spectra of the copolymers, which were monitored by RI and UV detectors, exhibited a similar unimodal profile in the range of log(MW) = 3.2-4.5. Maximum values of average molecular weights were Mn 7,600 and Mw 12,000 at the feed ratio, [OFCPE]:[CHVE] = 5:5. These results are slightly lower than those of poly(OFCPE-*co*-EVE), but higher than those of the copolymers with tBVE and MIPE. This is due to there being less steric hindrance between the cyclohexyl group and the OFCPE-unit compared to the tert-butyl group and OFCPE-unit.

Hard and transparent films were formed from the copolymers using a convenient solvent-casting method. The T_g of the copolymers was measured on a DSC. Each DSC spectrum on a 2nd-scan of the copolymer showed a single transition point (Figure 1). The T_g value increased with increase in the OFCPE-unit content giving a maximum value of 124.9°C at OFCPE:CHVE = 0.51:0.49 unit ratio of the copolymer (entry 2-5 in Table 2). This T_g value is higher than those of other copolymers with tBVE and MIPE, as a result of having a higher molecular weight of poly(OFCPE-*co*-CHVE) compared to those of the other copolymers.

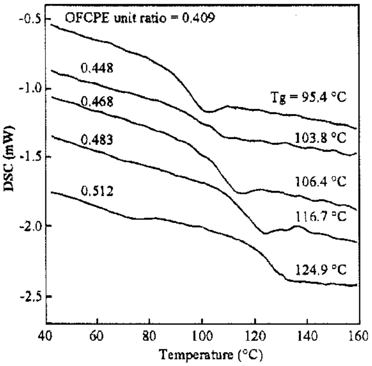


Figure 1. DSC thermograms of poly-(OFCPE-co-CHVE). Samples: entry 2-1–2-5.

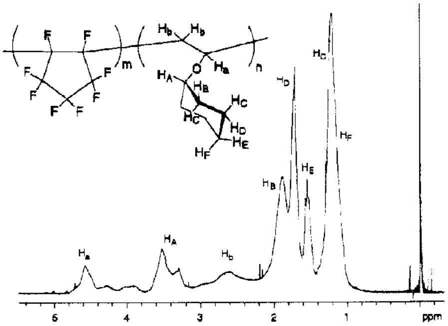


Figure 2. ^{1}H NMR spectrum of poly (OFCPE-*co*-CHVE). Sample: entry 2-3

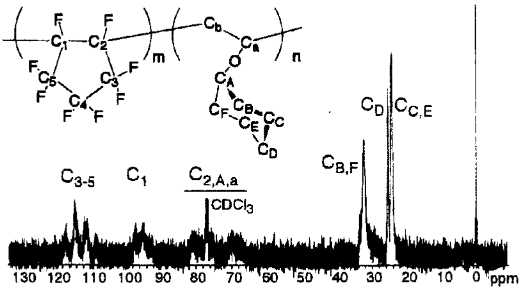


Figure 3. ^{13}C NMR spectra of poly-(OFCPE-*co*-CHVE). Sample: entry 2-3.

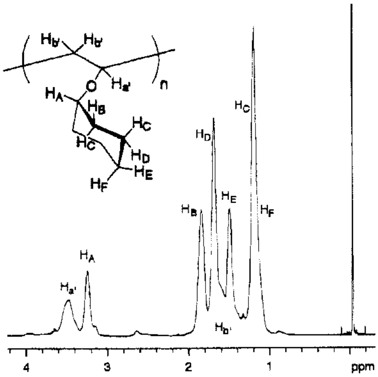


Figure 4. ^{1}H NMR spectrum of poly-(CHVE). Sample: entry ref.

The ^{1}H and ^{13}C NMR spectra of a typical product (entry 2-3 in Table 2) are shown in Figures 2 and 3, the main peaks being assigned to the corresponding hydrogen and carbon atoms from ^{1}H and ^{13}C NMR (COSY) spectrum analyses. In the ^{1}H NMR spectrum, a broad peak at δ 4.6 ppm is assigned to the hydrogen atom **H$_a$** on **C$_a$** of CHVE-unit adjacent to OFCPE-unit. In the ^{13}C NMR spectrum, multiplet peaks at δ 90-100 and 110-120 ppm were assigned to the carbon atoms of OFCPE-unit, as reported previously [6]. FTIR spectrum of the product showed absorption peaks of ν_{C-F} and ν_{C-O-C} at 1200 and 1100 cm^{-1}, respectively. These results also indicate that the product is a copolymer of OFCPE and CHVE.

In the ^{1}H NMR spectrum of the copolymer, some minor broad peaks were also observed in the range of δ 3.8-4.4 ppm, which can be also assigned to the $\mathbf{H_a}$. Figure 4 shows the ^{1}H NMR spectrum of CHVE homopolymer, where the peak assigned to $\mathbf{H_{a'}}$ was observed only at δ 3.52 ppm. The peak of $\mathbf{H_A}$ on $\mathbf{C_A}$ in cyclohexyl group of the copolymer was also observed plurally at about 3.3 and 3.5 ppm (Figure 2), compared to a single peak at 3.29 ppm of $\mathbf{H_A}$ in the CHVE homopolymer (Figure 4). Thus, the multiple peaks of $\mathbf{H_a}$ and $\mathbf{H_A}$ in the copolymer suggest that there is a distribution in sequence length of CHVE-unit in the copolymer. These minor peaks gradually diminished with increase in the OFCPE-unit content in the copolymers, indicating a shift to more alternative structures of OFCPE and CHVE-units.

Monomer Reactivity Ratios for OFCPE and CHVE

Monomer reactivity ratios for OFCPE (M_1) and CHVE (M_2) were derived from the copolymer composition data in Table 2, using the Yamada-Itahashi-Otsu nonlinear least-squares (NLLS) procedure with consideration of the weight of experimental data [6,10]. A graphical solution of the Lewis-Mayo integrated equation (LM) was used for the initial values of the calculation [11], giving initial values of $\boldsymbol{r}_{1,\mathrm{OFCPE,LM}} = 0.017 \pm 0.003$ and $\boldsymbol{r}_{2,\mathrm{CHVE,LM}} = 0.157 \pm 0.003$.

The initial values of $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ were repeatedly corrected by equations (1) and (2) until they settled at the optimum values. When the NLLS procedure gave less than zero, $\boldsymbol{r}_1$=0.000001 was used as the initial value for the further calculations.

$$\Delta \boldsymbol{r}_1 = \frac{\sum\left(F_{r1i}F_i^{\,0}/L_i\right)\sum\left(F_{r2i}^{\;2}/L_i\right)-\sum\left(F_{r2i}F_i^{\,0}/L_i\right)\sum\left(F_{r1i}F_{r2i}/L_i\right)}{\sum\left(F_{r1i}^{\;2}/L_i\right)\sum\left(F_{r2i}^{\;2}/L_i\right)-\left[\sum\left(F_{r1i}F_{r2i}/L_i\right)\right]^2} \qquad (1)$$

$$\Delta \boldsymbol{r}_2 = \frac{\sum\left(F_{r2i}F_i^{\,0}/L_i\right)\sum\left(F_{r1i}^{\;2}/L_i\right)-\sum\left(F_{r1i}F_i^{\,0}/L_i\right)\sum\left(F_{r1i}F_{r2i}/L_i\right)}{\sum\left(F_{r1i}^{\;2}/L_i\right)\sum\left(F_{r2i}^{\;2}/L_i\right)-\left[\sum\left(F_{r1i}F_{r2i}/L_i\right)\right]^2} \qquad (2)$$

where $\boldsymbol{F}(\boldsymbol{x}_i,\boldsymbol{y}_i,\boldsymbol{z}_i;\boldsymbol{r}_1,\boldsymbol{r}_2)=0$, according to the general procedure of Wentworth [12], $\boldsymbol{x}_i$, $\boldsymbol{y}_i$, and $\boldsymbol{z}_i$ are the OFCPE mol fractions in feed and copolymer, and conversion (mole/mole) obtained in the ith experiment, respectively. And, $\boldsymbol{F}_{r1i}=(\partial \boldsymbol{F}/\partial \boldsymbol{r}_1)_i$, $\boldsymbol{F}_{r2i}=(\partial \boldsymbol{F}/\partial \boldsymbol{r}_2)_i$, $\boldsymbol{F}_i^{\,0}(\boldsymbol{x}_i,\boldsymbol{y}_i,\boldsymbol{z}_i;\boldsymbol{r}_1^{\,0},\boldsymbol{r}_2^{\,0})=0$, and $\boldsymbol{L}_i=(\boldsymbol{F}_{xi}^{\,2}/\boldsymbol{W}_{xi})+(\boldsymbol{F}_{yi}^{\,2}/\boldsymbol{W}_{yi})+(\boldsymbol{F}_{zi}^{\,2}/\boldsymbol{W}_{zi})$, where $\boldsymbol{F}_{xi}=(\partial \boldsymbol{F}/\partial \boldsymbol{x})_i$, $\boldsymbol{F}_{yi}=(\partial \boldsymbol{F}/\partial \boldsymbol{y})_i$, $\boldsymbol{F}_{zi}=(\partial \boldsymbol{F}/\partial \boldsymbol{z})_i$, and $\boldsymbol{W}_{xi}$, $\boldsymbol{W}_{yi}$, and $\boldsymbol{W}_{zi}$ denote the weights of $\boldsymbol{x}_i$, $\boldsymbol{y}_i$, and $\boldsymbol{z}_i$, respectively. Consequently, after repeating the calculations ten times, the monomer reactivity ratios: $\boldsymbol{r}_{1,\mathrm{OFCPE,NLLS}}$ and $\boldsymbol{r}_{2,\mathrm{CHVE,NLLS}}$ were determined as follows;

$$\boldsymbol{r}_{1,\mathrm{OFCPE,NLLS}} = 0.005 \pm 0.020,\quad \boldsymbol{r}_{2,\mathrm{CHVE,NLLS}} = 0.154 \pm 0.017$$

Both ratios are small values, especially $\boldsymbol{r}_{1,\mathrm{OFCPE,NLLS}}$, which is very close to zero. The value is reasonable, because OFCPE never homopolymerizes. Since the $\boldsymbol{r}_1\boldsymbol{r}_2$ value is also nearly zero, it is easy to infer that copolymerization propagates alternatively in the case of excessive feed of OFCPE.

Conclusions

The copolymerization of a highly fluorinated cyclic monomer, OFCPE, and alkyl vinyl ethers, tBVE, MIPE, and CHVE, was examined with a free radical initiator, AIBN, in bulk. Despite the poor homopolymerizability of each monomer, the copolymerization took place and produced the corresponding copolymers, which had a glass transition temperature higher than 100°C. In particular, the copolymerization of OFCPE with CHVE gave a copolymer showing a T_g value as high as 124.9°C and molecular weight reached up to 12,000. Copolymer composition calculated from elemental analysis data and ^{1}H NMR spectra was close to the OFCPE:CHVE unit ratio = 0.5:0.5. The monomer reactivity ratios were estimated by the Yamada-Itahashi-Otsu nonlinear least-squares procedure as $r_{1,\mathrm{OFCPE}} = 0.005 \pm 0.020$ and $r_{2,\mathrm{CHVE}} = 0.154 \pm 0.017$. The reactivity ratios clearly suggest that the copolymerization proceeded alternatively in the case of an excessive feed of OFCPE.

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