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Novel fluorinated polymer from 18-crown-6 by radical polyaddition

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Abstract

Radical polyaddition of bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [$CF_2{=}C(CF_3)OCOC_6H_4COOC(CF_3){=}CF_2$] (BFP) with 18-crown-6 to produce fluorinated polymer bearing crown ether moiety in main chain is described. Prior to polyaddition, the model reaction of 2-benzoxypentafluoropropene [$CF_2{=}C(CF_3)OCOC_6H_5$] (BPFP) with 18-crown-6 was investigated to afford suitable reactions condition for polyaddition. The polyaddition of BFP with 18-crown-6 yielded a soluble polymer bearing $M_n = 5.5 \times 10^4$ with unimodal molecular weight distribution after purification by reprecipitation with cold ethanol.

Keywords: Bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate; Crown ether; Fluoropolymer; Polyaddition; Radical polymerization

1. Introduction

Numerous fluorinated vinyl monomers are hardly polymerized with radical initiators whereas tetrafluoroethylene and chlorotrifluoroethylene polymers are readily produced under free radical conditions [1]. Trifluorovinyl and α-trifluoromethylvinyl compounds have scarcely been polymerized with radical and anionic initiators although hydrocarbon analogues are readily polymerized under conventional polymerization conditions [1]. The radical polymerization of 2-benzoxypentafluoropropene [$CF_2{=}C(CF_3)OCOC_6H_5$] (BPFP) was examined using α,α′-azobisisobutyronitrile or benzoyl peroxide (BPO) as a radical initiator under various conditions, with the aim of synthesizing the perfluorinated polymer followed by hydrolysis of ester to produce perfluorinated poly(vinyl alcohol) derivative, of interest as a new material, but failed. During the investigation of the radical polymerization reactivity of BPFP, the addition reaction of BPFP with tetrahydrofuran (THF) was found to produce a 1:1 adduct of the vinyl groups with THF in high yields in the presence of BPO at 60 °C in THF as a solvent [2]. To develop the radical addition reaction of perfluoroisopropenyl esters with cyclic ethers, radical polyadditions of bifunctional bis(α-trifluoromethyl-β,β-difluorovinyl) dicarboxylates [$CF_2{=}C(CF_3)OCO{-}R{-}COOC(CF_3){=}CF_2$] with compounds possessing carbon–hydrogen bonds, such as 1,4-dioxane (Eq. (1)) [3], diethyl ether [4], 1,2-dimethoxyethane [4], dimethyldiethoxysilane [5], diformylalkane [6] and triethylamine [7] have previously been reported to yield the corresponding polymer bearing a molecular weight of as high as 10^4. To grow up the addition reaction, the present paper is concerned with the production of the polymers from a bifunctional perfluoroisopropenyl ester, bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [$CF_2{=}C(CF_3)OCOC_6H_4COOC(CF_3){=}CF_2$] (BFP), with 18-crown-6. No report on polymer syntheses directly from crown ether itself as a starting material has been available. It should be exciting if a soluble polymer is obtained from crown ether which has 24 hydrogens to be attacked in the radical polyaddition.

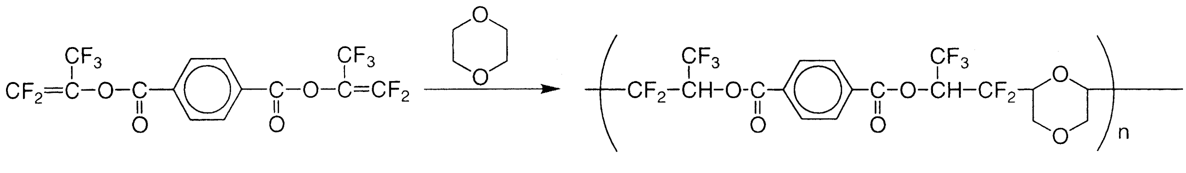

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Table 1
Radical reaction of BPFP with 18-Crown-6[a]

Run	BPO (mmol)	Temperature (°C)	Time (day)	Conversion (%)[b]
1	0.1	60	1	51
2	0.1	60	3	63
3	0.1	80	1	50
4	0.1	80	3	62
5	0.2	60	1	40
6	0.2	60	3	86
7	0.2	80	1	45
8	0.2	80	3	92

[a] BPFP: 1.0 mmol; 18-crown-6: 10.0 mmol.

[b] Conversion of BPFP measured by GC.

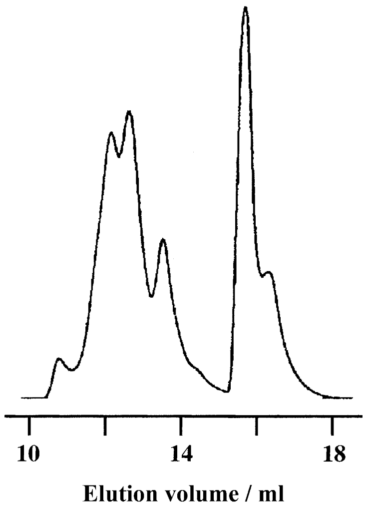


Fig. 1. Liquid chromatogram of the reaction of BPFP with 18-crown-6 (run 6 in Table 1).

2. Results and discussion

2.1. Addition reaction

Prior to polyaddition, the radical addition of 18-crown-6 with monofunctional BPFP was examined as a model reaction in order to clarify the radical addition reactivity of 18-crown-6. The results are summarized in Table 1. The reaction was found to take place in homogenous phase since the melting point of 18-crown-6 is about 40 °C. The BPFP concentrations decrease under all experimental conditions. The conversions of BPFP measured by GC are increased with larger amount of BPO added, longer reaction time and under higher reaction temperature.

The result of liquid chromatography (LC) measurement is shown in Fig. 1. The LC indicates that 1:1–4:1 addition products of BPFP with crown ether are yielded. The isomers of these addition products might also be produced. The determination of the structures of the reaction products was impossible since the trial to separate these products by preparatory liquid chromatography was hardly successful. This suggests that the crown ether might be multifunctional compound in the reaction system. The results of the model reaction point out that the polyaddition of BFP with the crown ether might be possible if reaction conditions are properly arranged since the radical addition reactivity of the crown ether is found to be high enough to prepare polymers.

2.2. Polyaddition reaction

The polyaddition of BFP with 18-crown-6 was investigated though the results of the model reaction of BPFP with 18-crown-6 suggest that the polyaddition might be possible if reaction conditions are properly arranged. The results are summarized in Table 2. The yields of products are generally increased with increasing the amount of 18-crown-6 added into the reaction system. The gelation takes place at lower concentration of 18-crown-6 in feed, as has been expected. The soluble polymers, on the other hand, are yielded at higher feed ratio of 18-crown-6 to BFP. The effect of reaction temperature is limited in spite of higher yields

Table 2
Polyaddition BFP with 18-Crown-6[a]

Run	18-Crown-6 (mmol)	Temperature (°C)	Time (h)	Yield (%)	M_n ($\times 10^4$)[b]	M_w/M_n
1	10	60	12	8	4.2	2.67
2	10	60	24	Gel	–	–
3	10	80	12	Gel	–	–
4	10	80	24	Gel	–	–
5	20	60	24	25	3.6	2.38
6	20	60	72	54	5.5	1.98
7	20	80	24	28	4.2	2.14
8	20	80	72	62	5.4	2.54
9	30	60	24	32	3.9	2.47
10	30	60	72	61	4.5	2.32
11	30	80	24	29	3.6	1.87
12	30	80	72	60	4.9	2.44

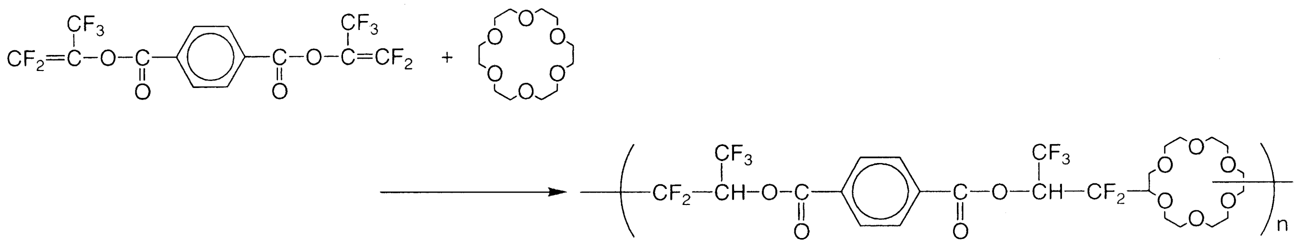
[a] BFP: 1.0 mmol; initiator: BPO 0.2 mmol.

[b] Estimated by GPC in THF eluent based on polystyrene standards after reprecipitation.

obtained at 80 °C in the model reaction system. Polymers possessing molecular weights of more than thirty thousands are obtained.

The result of GPC of the reaction system, as shown in Fig. 2a, indicates multimodal molecular weight distribution and many kinds of polymers are concluded to be produced. The polymer can be fractionated by reprecipitation in cold ethanol and the GPC of the polymer shows unimodal molecular weight distribution, as shown in Fig. 2b.

The results of NMR measurements of the product are shown in Fig. 3. The results of the assignment of each absorption are depicted in each figure. The product is concluded to be consisted of BFP to 18-crown-6 to be about 1:1 since the ^{1}H NMR integral intensity ratio of the peaks *a*, *b* and *c* is 1.98:4.0:21.3 (theoretical 2:4:22). The structure of the polymer is hardly determined since 18-crown-6 possesses 24 hydrogens which are probable to be attacked by radical. The reaction might take place via Eq. (2).



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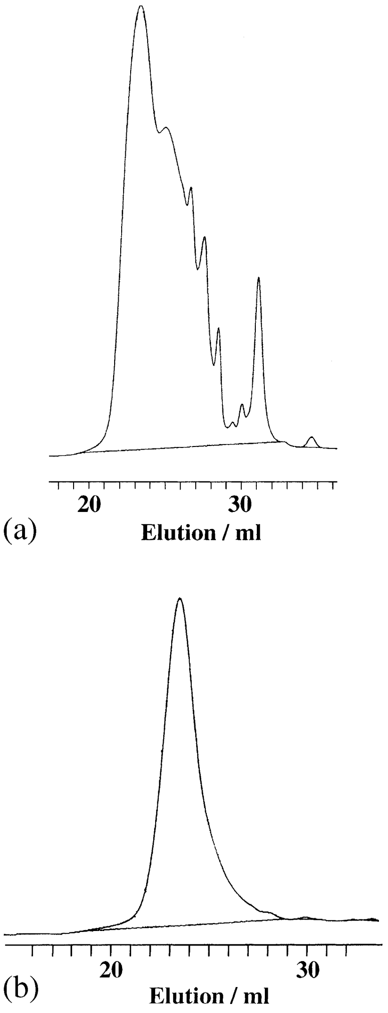

Fig. 2. SEC of reaction system of BFP with 18-crown-6 (a) (run 8 in Table 2) and the polymer after reprecipitation of THF solution into cold ethanol (b).

The result of thermogravimetric analysis is shown in Fig. 4. The 5% weight-loss temperature of the polymer is about 320 °C, which is the similar value to that of the polymer derived from BFP with 1,4-dioxane.

3. Experimental part

All experiments related to polymerization were carried out under a purified nitrogen atmosphere in order to preclude oxygen and moisture.

3.1. Reagents

BFP was synthesized by applying the synthetic method of BPFP reported by Nakai et al. [8] from terephthaloyl chloride with 1,1,1,3,3,3-hexafluoropropan-2-ol by the addition of hexane solution of butyllithium. Commercial butyllithium in hexane solution was used after determination of the concentration by alkalimetry. Terephthaloyl chloride was used as received. 1,1,1,3,3,3-Hexafluoropropan-2-ol (Central Glass Co.) was dried by refluxing over calcium hydride and distilled under reduced pressure of nitrogen atmosphere. 18-Crown-6 was recrystallized with acetonitrile. BPO was purified by pouring the chloroform solution of BPO into methanol at 0 °C.

3.2. Polyaddition reaction

Polyaddition of BFP with 18-crown-6 was carried out by adding BFP, 18-crown-6 and BPO to the round-bottomed flask. After a definite time, the polymer was isolated by precipitation from 98% ethanol, and then dried thoroughly below 80 °C in vacuo. The structure of the resulting reaction product was confirmed by ^{1}H, ^{13}C and ^{19}F NMR.

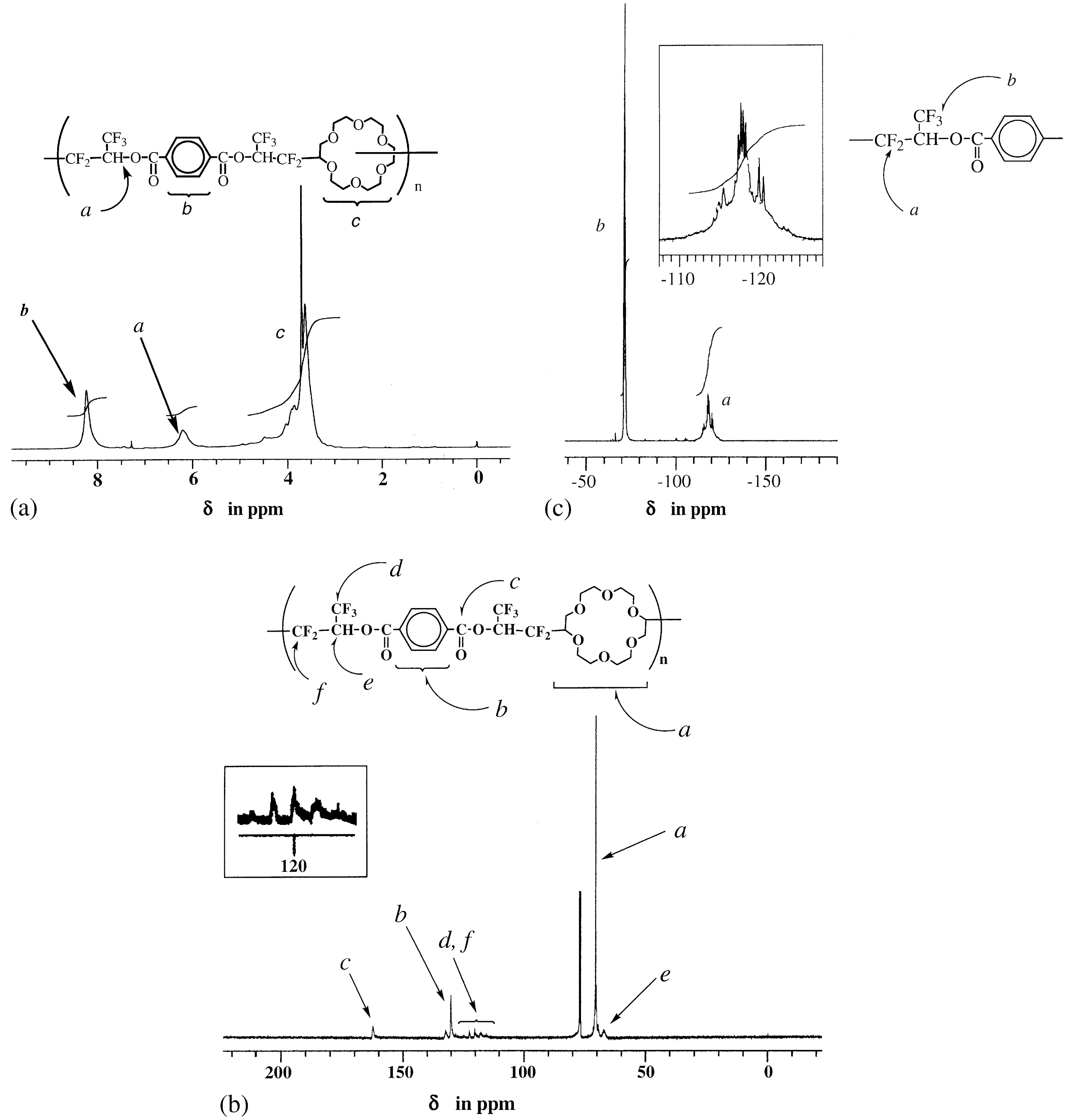

Fig. 3. ^{1}H (a), ^{13}C (b) and ^{19}F NMR (c) of reaction product of BFP with 18-crown-6.

3.3. Measurements

NMR spectra were recorded on a JEOL JNM-ECP500 FT-NMR spectrometer using deuterated chloroform as a solvent. ^{19}F NMR spectra were measured under proton decoupling conditions using deuterated chloroform as a solvent. Chemical shift of ^{19}F NMR was determined based on absolute magnetic field intensity. Liquid chromatography (LC) was carried out with LC-908JAI (Japan Analytical Ind.) with Gel H1 & H2 column series using chloroform as an eluent at room temperature (flow rate 3.8 ml min^{-1}). SEC was measured with a TOSOH HLC-802A apparatus at 38 °C with TSK gel GMH$_{XL}$-GMH$_{XL}$ and Shodex KF-802 column series using THF as an eluent (flow rate 1.0 ml min^{-1}). The molecular weight measured by SEC was calculated from the calibration curve for standardized polystyrene. Thermogravimetric analysis was carried out with a TGA 51 thermogravimeter with Thermal Analyst

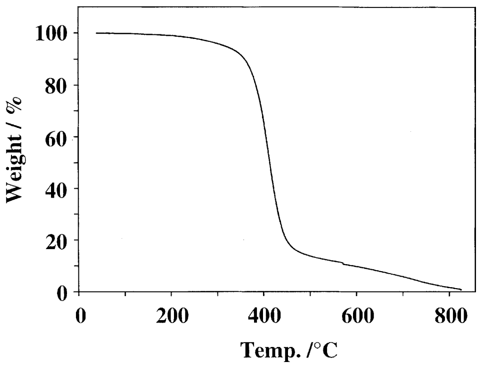

Fig. 4. Thermogravimetric analysis of the polymer derived from BFP with 18-crown-6.

2000 (TA Instruments) under nitrogen atmosphere with a heating rate of 10 °C $\min^{-1}$.

4. Conclusion

Radical polyaddition of BFP with 18-crown-6 was investigated to afford soluble polymers bearing molecular weights as high as 5.5×10^4 with unimodal molecular weight distribution after fractional reprecipitation with cold ethanol, although 18-crown-6 possesses as high as 24 hydrogens which are probable to be attacked by radical. This might be the first example crown ether is incorporated into polymer main chain by one step reaction.

Acknowledgements

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