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Oligomer preparation from hexane by radical polyaddition with bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate†

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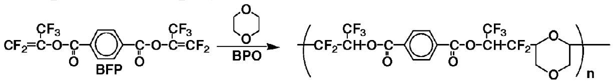
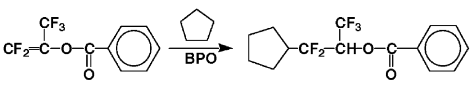
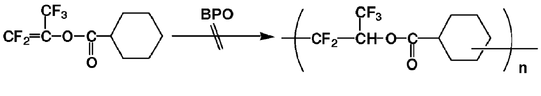
Polymer preparation from hexane as a starting material by radical polyaddition with bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [CF_2=$C(CF_3)OCOC_6H_4COO$–$C(CF_3)$=CF_2] was investigated to afford polymers bearing a molecular weight of as high as 5.5 × 10^3, and the polyaddition mechanism including 1,5-radical shift mechanism was proposed.

In previous work[1] it has been demonstrated that the *F*-enol benzoate, 2-benzoxypentafluoropropene [CF_2=$C(CF_3)OCO$–C_6H_5] (BPFP),[2] serves as a good and selective acceptor towards nucleophilic radicals generated from cyclic ethers, alcohols, and the tin hydride to afford the addition products which are potentially useful for the preparations of a variety of functionalized organofluorine compounds. The reaction was developed for the preparation of polymer from bis(α-trifluoromethyl-β,β-difluorovinyl) terephthalate [CF_2=$C(CF_3)O$–$COC_6H_4COOC(CF_3)$=CF_2] (BFP) with 1,4-dioxane which was incorporated into the polymer main chain (eqn. (1)).[3] This led to the preparation of polymers bearing diethyl ether, 1,2-dimethoxyethane, triethylamine or glutaraldehyde moieties in the polymer main chain derived from BFP with corresponding compounds.[4] The results have pointed out that polymers could be synthesized from bisperfluoroisopropenyl esters with these compounds which have never been supposed to be incorporated into polymer main chains.


(1)

The radicals derived from cyclic hydrocarbons such as cylcopentane, cyclohexane and cycloheptane were also found to achieve the addition reaction onto BPFP.[5] The radical addition might then be applicable to a variety of compounds which possess carbon–hydrogen bonds. It was, however, unsuccessful to prepare polymer from α-trifluoromethyl-β,β-difluorovinyl cyclohexanecarboxylate [CF_2=$C(CF_3)OCOC_6H_{11}$] by self-polyaddition (eqns. (2) and (3)).


(2)


(3)

This paper is concerned with the preparation of polymers from BFP with hexane which is a typical aliphatic hydrocarbon. In order to investigate the polyaddition reaction conditions, the radical addition of BPFP with hexane was carried out at 80 °C initiated by benzoyl peroxide (BPO) for 1, 3, and 5 days reaction times at a feed of BPFP to hexane of 1.0 to 10. The conversions of BPFP measured by GC were 61.2%, 66.1% and 63.1%, respectively. The reaction was found to be almost completed within 1 day. The reaction scarcely took place in the lower feed amount of hexane. The products were purified by treating the reaction system with a silica gel column (eluent, hexane : chloroform = 9 : 1) in order to remove benzoic acid formed by decomposition of BPO, and by separating with size exclusion chromatography (SEC). The results of GC analyses showed that two major products were obtained. The results of mass spectra by chemical ionization method showed the low-boiling material should be 1 : 1 addition product of BPFP with hexane since the molecular ion peak was observed at m/z = 338, and the high-boiling material 2 : 1 addition product since the molecular ion peak was at m/z = 590. The structure of 2 : 1 addition product was determined by NMR measurements. The absorption at 5.9 ppm in ^{1}H NMR was assignable to the proton of –CF_2–**CH**(CF_3)– and the peaks around 8 ppm are assigned to phenyl protons. The absorptions of the hexane moiety appeared from 0.7 to 2.6 ppm. These suggest that the compound is the reaction product of BPFP with hexane. Assignment of the carbons of methyl, methylene and methine were determined by the help of the distortionless enhancement by polarization transfer (DEPT) NMR measurement. The absorptions of trifluoromethyl and difluoromethylene fluorines were measured at around 70 ppm and from −100 to −120 ppm, respectively. The ratio of methyl, methylene and methine of the hexane moiety in the addition compound was about 1 : 1 : 1 which was calculated from the areas of the corresponding ^{1}H NMR peaks.

More detailed analysis on the di-addition product of BPFP with hexane was carried out by the J-resolved NMR measurement. The result is shown in Fig. 1. The methyl group whose absorptions are measured from 0.8 to 1.0 ppm is concluded to be adjacent to the methylene group since the splitting of the peaks is three, and the other methyl group assigned to the peaks from 1.0 to 1.2 ppm is

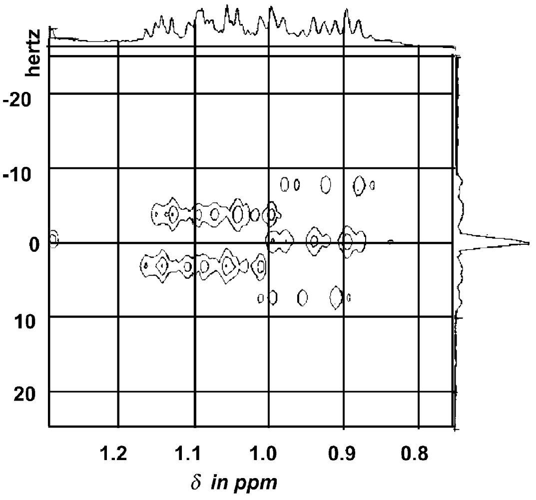


Fig. 1 J-resolved 1D NMR spectrum of 2 : 1 addition product of BPFP with hexane.

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† Electronic supplementary information (ESI) available: Experimental details. See http://www.rsc.org/suppdata/cc/b4/b406116k/

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Table 1 Polyaddition of BFP with hexane

Hexane/ mmol	BPO = /mmol	Time/ days	Yield[b] (%)	$Mn \times 10^3$	Mw/Mn
5	2	7	5		
10	2	7	19		
25	2	7	24	3.2	1.8
50	1	5	14	5.5	1.4
50	2	5	39	3.8	1.9
50	2	7	31		
50	1	7	13	4.3	1.3
50	2	21	39	3.7	1.9
100	2	7	6		

[a] BFP: 5.0 mmol; temp.: 80 °C. [b] After reprecipitation with CH_3OH.

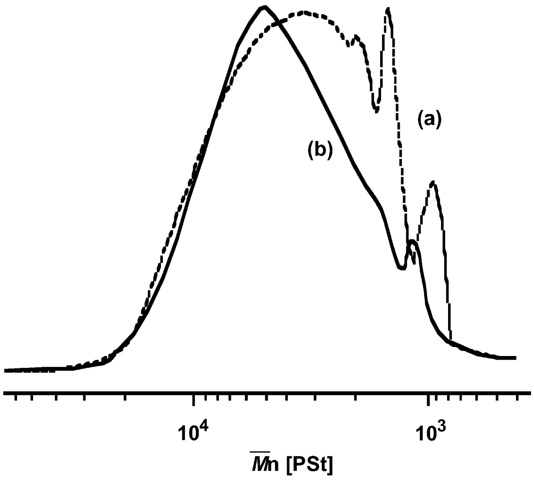
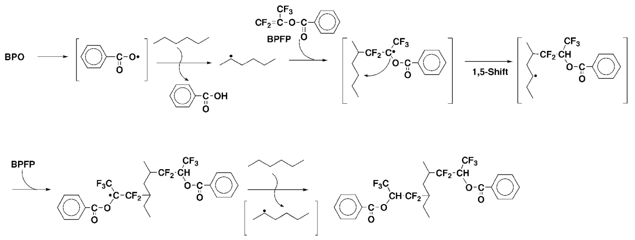


Fig. 2 SEC of polyaddition product of BFP with hexane; (a) before reprecipitation, (b) after reprecipitation with methanol.



Scheme 1 Postulated addition reaction mechanism of BPFP with hexane.

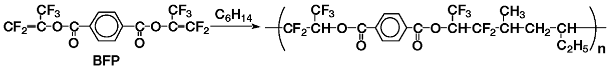
adjacent to the methine group since the splitting is two. The conclusion of the structural analyses of the product is shown in Scheme 1. The product might be yielded by the addition of the radical derived from the hydrogen-abstraction at the 2-position of hexane to the α-carbon of BPFP followed by the 1,5-radical shift. The hydrogen-abstraction from methylene carbon is reported to be much easier compared to that from methyl carbon.[6]

Polyaddition of perfluoroisopropenyl esters with hexane was investigated since polyaddition of α-trifluoromethyl-β,β-difluorovinyl cyclohexanecarboxylate was unsuccessful though the radical additions of BPFP with hydrocarbons such as cyclopentane, cyclohexane and cycloheptane took place, as has been described above.[5] The results of polyaddition of BFP with hexane are summarized in Table 1. Polymers of molecular weights of several thousands are yielded under the reaction conditions examined here, as expected based on the results of the model reaction mentioned above. The yields, however, are low in the case of lower feed ratio of hexane, and higher concentrations of BPO in feed are necessary to obtain enough yields of polymers. The molecular weights of polymers produced increase with increases in the amount of hexane charged to the reaction system.

The typical SEC of the product of BFP with hexane is shown in Fig. 2. The molecular weight distribution of the sample before reprecipitation is multimodal. The polyaddition may then take place with side reactions besides the reaction depicted in Scheme 1. The higher molecular weight polymer can be separated by reprecipitation with methanol, as shown by the solid line in Fig. 2 which shows the unimodal molecular weight distribution.

The results of the polyaddition reactions showed that the gel formation besides soluble polymer production took place in the reaction systems of heptane and octane. Hexane works, therefore, bifunctionally, and heptane and octane perform as bifunctional and multifunctional compounds.

The structure of the polymer was determined by NMR measurement. The peak around 6.0 ppm in ^1H NMR was assignable to the methine proton of the BFP moiety in the polymer chain and the absorptions at about 8.0 ppm were assigned to phenyl protons. The peaks assignable to the hexane moiety appeared from 0.5 to 2.5 ppm. The polyaddition reaction is concluded to take place at methylene carbons of hexane since the absorptions around 1.0 ppm were assigned to methyl protons and the peak at 2.1 ppm was assignable to methine protons of the hexane moiety in the polymer main chain determined on the basis of the results of the model reaction of BPFP with hexane as described previously. The results of ^{19}F NMR and ^{13}C NMR supported the conclusion. Therefore, the reaction is depicted as in eqn. (4).



(4)

One of the reasons why the preparation of polymer from $CF_2{=}C(CF_3)OCOC_6H_{11}$ failed is probably because of low concentration of the cyclohexyl group compared to that of the perfluoroisopropenyl group in combination with its restricted structure of cyclohexyl group compared to aliphatic hydrocarbons which might disturb the radical shift.

The 5% weight-loss temperature of the polymer derived from BFP with hexane was about 279 °C measured by thermogravimetric analysis.

This might be the first example which gives the clear evidence that an aliphatic hydrocarbon like hexane could be a starting material to preparation of a polymer in one step reaction and could perform as a bifunctional compound. Though aliphatic hydrocarbons used to be named as sort of "paraffin" compounds which means "hardly reactive", these results suggest that aliphatic hydrocarbons might possibly be the starting materials for organic syntheses and polymer preparation.

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Notes and references

1 T. Narita, T. Hagiwara, H. Hamana, K. Tomooka, Y.-Z. Liu and T. Nakai, *Tetrahedron Lett.*, 1995, **36**, 6091.
2 (*a*) C.-P. Qian and T. Nakai, *Tetrahedron Lett.*, 1988, **29**, 4119; (*b*) C.-P. Qian, T. Nakai, D. A. Dixon and B. E. Smart, *J. Am. Chem. Soc.*, 1990, **112**, 4602.
3 (*a*) T. Narita, T. Hagiwara, H. Hamana, K. Enomoto, Y. Yoshida and Y. Inagaki, *Macromol., Rapid Commun.*, 1998, **19**, 485; (*b*) H. Fujiwara, M. Iwasaki, T. Narita and H. Hamana, *J. Fluorine Chem.*, in press
4 (*a*) T. Narita, T. Hagiwara and H. Hamana, *Macromol. Chem. Phys.*, 2000, **201**, 220; (*b*) T. Narita, H. Hamana, M. Takeshita and H. Nakagawa, *J. Fluorine Chem.*, 2002, **117**, 67; (*c*) T. Narita, H. Hamana, M. Takeshita, K. Nishizawa and K. Kitamura, *J. Fluorine Chem.*, 2002, **117**, 55.
5 T. Narita, T. Hagiwara, H. Hamana, K. Kitamura, Y. Inagaki and Y. Yoshida, *J. Fluorine Chem.*, 1999, **97**, 263.
6 J. Fossey, D. Lefort, and J. Sorba, *Free Radicals in Organic Chemistry*, J. Wiley & Sons, New York, 1995, p. 213.