Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Fluorine Chemistry 124 (2003) 183–188

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

A novel perfluoromonomer: perfluoro-2,3-dihydro-1,4-benzodioxin

Weihong Liu[a,1], Yasuhiro Koike[b,c], Yoshi Okamoto[a,*]

[a]Six Metrotech Center, Polymer Research Institute, Polytechnic University, Brooklyn, NY 11201, USA
[b]Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan
[c]ERATO, Koike Photonics Polymer Project, K2 Town Campus 144-8 Ogura, Saiwai-ku, Kawasaki 212-0054, Japan

Received 4 June 2003; received in revised form 6 August 2003; accepted 7 August 2003

Abstract

A novel perfluoromonomer, perfluoro-2,3-dihydro-1,4-benzodioxin (FDB), was synthesized. The homopolymerization and copolymerizations of FDB were investigated. The structure and physical properties of those polymers were characterized.

Keywords: Perfluoromonomer; Fluorinated polymer; Radical polymerization; Perfluoro-2,3-dihydro-1,4-benzodioxin

1. Introduction

Fluorinated polymers have become of increasing interest in the development of advanced materials having high thermal and oxidative stabilities, chemical resistance, superior electrical insulating ability and superior optical properties [1,2]. Unlike their hydrocarbon analogues, most fluorinated vinyl monomers such as perfluorostyrene, perfluoroacrylic esters and other trifluorovinyl compounds are scarcely polymerized under normal free radical conditions except tetrafluoroethylene and chlorotrifluoroethylene [1,3]. Therefore, designing and synthesizing new perfluoromonomers is still a main topic in fluorine and polymer chemistry. Until now, only few classes of perfluoromonomers could be radically homopolymerized under normal conditions. Typical examples are perfluoro-dioxoles [2,4], perfluoro-dihydrodioxins [5,6] and perfluoro-dienes [2]. Their common characteristic is that their polymer structure contains rings. The monomers containing a ring exhibited unusual reactivity probably due to the presence of ring strain. With those monomers, amorphous perfluoropolymers were developed to exhibit extraordinary properties [2]. Regarding the class of monomers of perfluoro-dihydrodioxins, the polymerization reactivity was extensively investigated by Krespan and Dixon [5,6]. Recently, a partially fluorinated monomer, 2,3-difluoro-1,4-benzodioxin has been reported to be homopolymerized to yield a high polymer [7]. This encourages us to synthesize a novel perfluoromonomer, perfluoro-2,3-dihydro-1,4-benzodioxin (FDB), to investigate on its polymerization reactivity. Hence, the homopolymerization and copolymerizations were studied using styrene (St) as a comonomer. The polymer structure was characterized by ^{1}H, ^{19}F, ^{13}C NMR and FTIR spectroscopy. The physical properties of the polymers were also characterized. This monomer may be applied to enhance the copolymer properties as a comonomer. The copolymerization of FDB with St produces polymers though the homopolymerization only affords oligomers.

2. Experimental

2.1. Materials

Styrene (Aldrich) and perfluorobenzene (SynQuest Fluorochemical Lab. Inc.) were distilled before use. Chlorine gas, SbF_3, $SbCl_5$ and other reagents were commercially obtained from Aldrich and used as received. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

2.2. Monomer synthesis

2.2.1. Synthesis of 2,2,3,3-tetrahydro-5,6,7,8-tetrafluoro-1,4-benzodioxin (a)

This compound was prepared from hexafluorobenzene and ethylene glycol according to a literature method [8]. The

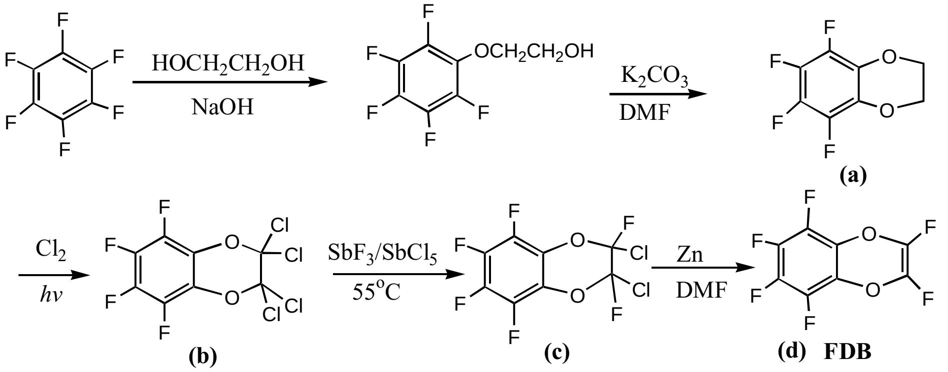
---

[*] Corresponding author. Fax: +1-718-260-3508.

E-mail addresses: whliu888@hotmail.com (W. Liu), yokamoto@poly.edu (Y. Okamoto).

[1] Tel.: +1-718-260-3965; fax: +1-718-260-3125.

0022-1139/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2003.08.003



Scheme 1. Monomer synthesis.

procedure is described in Scheme 1. Yield, 40%. mp: 79–80 °C. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.36 (s, 4H). ^{19}F NMR ($CDCl_3$) δ (ppm): −165.04 (s, 2F on aromatic ring); −169.74 (s, 2F on aromatic ring).

2.2.2. Synthesis of 2,2,3,3-tetrachloro-5,6,7,8-tetrafluoro-1,4-benzodioxin (b)

2,2,3,3-Tetrahydro-5,6,7,8-tetrafluoro-1,4-benzodioxin (a) was photochlorinated under a GE Sun-Lamp at about 120 °C with chlorine gas. The reaction was monitored by proton NMR and stopped when the proton peaks disappeared on the NMR spectrum. The product (b) was purified by distillation. Yield, 82%. bp: 62–64 °C (0.50 mmHg) ^{1}H NMR ($CDCl_3$) δ (ppm): none. ^{19}F NMR ($CDCl_3$) δ (ppm): −159.27 (s, 2F on aromatic ring); −160.73 (s, 2F on aromatic ring). GC/MS: *m*/*e* 346 (M^+) with expected fragmentation pattern.

2.2.3. Synthesis of 2,3-difluoro-2,3-dichloro-5,6,7,8-tetrafluoro-1,4-benzodioxin (c)

A suspension of 11.9 g (66.0 mmol) of SbF_3 in 11.5 g (33.0 mmol) of 2,2,3,3-tetrachloro-5,6,7,8-tetrafluoro-1,4-benzodioxin was stirred at 55 °C for 10 h with addition of 0.4 ml $SbCl_5$. The volatile product transferred under vacuum was washed with a saturated aqueous $NaHCO_3$ solution, and purified by distillation. Yield, 85%. bp: 40–42 °C (2.0 mmHg). The product is a mixture of stereoisomers. ^{1}H NMR ($CDCl_3$) δ (ppm): none. ^{19}F NMR ($CDCl_3$) δ (ppm): −78.52 (s, CFClO of major isomer); –81.66 (s, CFClO of minor isomer); −159.02 (s, 2F on aromatic ring); −160.52 (s, 2F on aromatic ring). GC/MS: *m*/*e* 312 (M^+) with expected fragmentation pattern.

2.2.4. Synthesis of FDB (d)

A mixture of 30.0 g (0.096 mol) of 2,3-difluoro-2,3-dichloro-5,6,7,8-tetrafluoro-1,4-benzodioxin (c), 100 ml of dry DMF, 12.0 g (0.18 mol) of zinc dust, and 1.0 ml of 1,2-dibromoethane was stirred at 120 °C for 10 h under argon atmosphere. The mixture was then poured into a large amount of water. The aqueous layer was extracted with diethyl ether. The combined organic layer was washed with water and dried over Na_2SO_4. After removal of ether, the crude product was distilled to give 13.0 g (56%) of FDB. bp: 65–67 °C (30.0 mmHg). ^{1}H NMR ($CDCl_3$) δ (ppm): no proton. ^{19}F NMR ($CDCl_3$) δ (ppm): −140.51 (s, 2F, CF=); −159.28 (s, 2F on aromatic ring); −161.25 (s, 2F on aromatic ring). GC/MS: *m*/*e* 242 (M^+) with expected fragmentation pattern.

2.3. Polymerization

2.3.1. Homopolymerization

Polymerization was carried out under an argon atmosphere in a glass tube equipped with a three-way stopcock. FDB (1.5 g, 6.2 mmol) and perfluorobenzoyl peroxide (F-BNO) (19 mg, 0.045 mmol) were charged in the glass tube, which was then degassed and refilled with argon in three vacuum freeze-thaw cycles. The tube was sealed and heated at 80 °C for 24 h. The product was precipitated into methanol, isolated with a centrifuge and dried under vacuum at 50 °C.

2.3.2. Copolymerization

Similar to the homopolymerization, FDB, St and AIBN were charged in the glass tube, which was then degassed and refilled with argon in three vacuum freeze-thaw cycles. The tube was sealed and heated at 60 °C. The products were precipitated in methanol, isolated with a centrifuge and dried under vacuum at 50 °C.

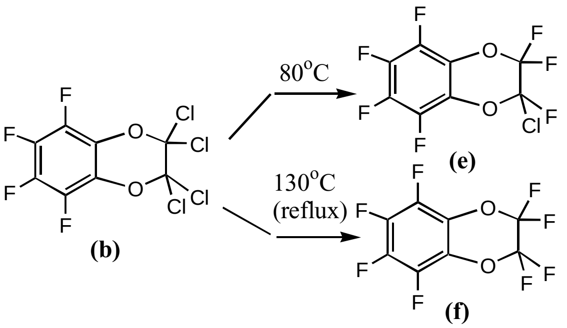
2.4. Measurements

The ^{1}H, ^{19}F and ^{13}C NMR spectra were obtained using a Bruker ACF 300 spectrometer (300 MHz for ^{1}H and 282 MHz for ^{19}F and 75 MHz for ^{13}C measurement). FTIR spectra were obtained with a Perkin-Elmer FTIR-1600 spectrometer. GC–mass analysis was accomplished on HP 5890 Gas Chromatograph and HP 5970B Mass Spectrograph. Size exclusion chromatographic (SEC) analysis was accomplished on a system with a Waters 510 pump in line with TSK gel HMXL and H5000 columns and dual detectors of a Waters 440UV absorbance detector and a Waters R401 differential refractometer, in which chloroform was eluted with a flow rate of 1.0 ml/min at 30 °C. The molecular weight of the polymers was calibrated with standard PS. The differential scanning calorimetry (DSC) measurement was performed on a DSC 2920 module in conjunction with the TA Instrument 5100 system at a heating rate of 10 °C/min under a nitrogen atmosphere. The midpoint of the heat capacity transition was taken as glass transition temperature (T_g). The refractive index of the film was obtained with a Metricon Model 2010 prism coupler.

3. Results and discussion

3.1. Monomer synthesis

Monomer was synthesized according to Scheme 1. All the melting point and the boiling points reported here are uncorrected. In the step of fluorination with SbF_3, we noted that temperature affects the reactions. The reaction kept at 55 °C for 10 h afforded the main products with two chlorines replaced by fluorine. The reactions at 80 and 130 °C were found three chlorines and all chlorines to be replaced, respectively (Scheme 2). A perfluoro-compound, perfluoro-2,2,3,3-tetrahydro-1,4-benzodioxin (f), was easily obtained with a high yield at elevated temperature, which was confirmed by ^{19}F NMR and GC/MS analysis [yield, 65%. bp: 113–115 °C. ^{19}F NMR ($CDCl_3$) δ (ppm): −92.64 (s, 4F, $-OCF_2CF_2O-$); −158.82 (s, 2F on aromatic ring); −160.32 (s, 2F on aromatic ring). GC/MS: *m/e* 280 (M^+) with expected fragmentation pattern].



Scheme 2. Fluorination with SbF_3 at elevated temperatures.

The last step in the synthesis of monomer was dehalogenation of 2,3-difluoro-2,3-dichloro-5,6,7,8-tetrafluoro-1,4-benzodioxin (c) with activated zinc in DMF. The method adopted here is similar to that for the preparation of other perfluoro-dihydrodioxins [5].

3.2. Homopolymerization

The homopolymerization of FDB was carried out using perfluoro-benzyl peroxide as an initiator at 80 °C. Contrary to the result of 2,3-difluoro-1,4-benzodioxin which gave high polymers [7], the homopolymerization of FDB afforded only an oligomer based on SEC analysis as shown in Table 1. The degree of polymerization (DP) was estimated to be 10. Attempts to homopolymerize this monomer via emulsion polymerization techniques using sodium dodecylbenzenesulfonate as an emulsifier and ammonium persulfate as an initiator failed. The low polymerization reactivity may be mainly related to the steric effects of the *ortho*-fluoro substituents of the perfluorinated monomer. Krespan and Dixon have reported that perfluoro-2,3-dihydro-2,3-dimethyl-1,4-dioxin and 2,3-dichloro-5,6-difluoro-1,4-dioxin gave oligomers, whereas perfluoro-2,3-dihydro-1,4-dioxin and perfluoro-2-methyl-2,3-dihydro-1,4-dioxin gave high polymers under similar polymerization conditions [5,6]. They explained this as follows: the initial step of the polymerization, i.e. the addition of carbon-based free radicals to the 2,3-dihydro-1,4-dioxin monomer, is a favourable reaction; the rate of propagation, i.e. the addition of the resulting radical to another monomer, appeared to be governed by steric constraints. The polymerization reactivity is low for those monomers containing a bulky group attached to the ring.

The ^{19}F NMR of the oligomer was shown in Fig. 1A. The peak from −154.0 to −166.0 ppm was assigned to the fluorines on the side group of aromatic ring and the perfluorobenzoyl group at the end. The broad peak from −108.0 to −144.0 ppm was assigned to the main-chain fluorines. FTIR spectrum of the oligomer was shown in Fig. 2A. The bands at 1492, 1516 and 1531 cm^{-1} were assigned to

Table 1
Radical homopolymerization and copolymerization of FDB[a]

Run	Feed ratio, St/FDB (mol/mol)	Temperature (°C)	Time (h)	Yield (%)[b]	Copolymer composition[c], St/FDB (mol/mol)	$M_n \times 10^{-4}$ [d]	M_w/M_n[d]	T_g (°C)
1	0/1	80	24	24	0/100	0.25	1.68	–
2	1/1	60	48	57	75/25	0.90	1.62	137
3	4/1	60	48	63	89/11	1.28	2.16	109, 134
4	1/0	60	24	94	100/0	2.30	2.79	103

[a] Conditions: bulk, [initiator] = 2.0 mol% to vinyl groups; initiator: run 1, F-BNO; runs 2–4, AIBN.
[b] Methanol-insoluble part.
[c] Determined by ^{13}C NMR.
[d] Determined by SEC with PS standard.

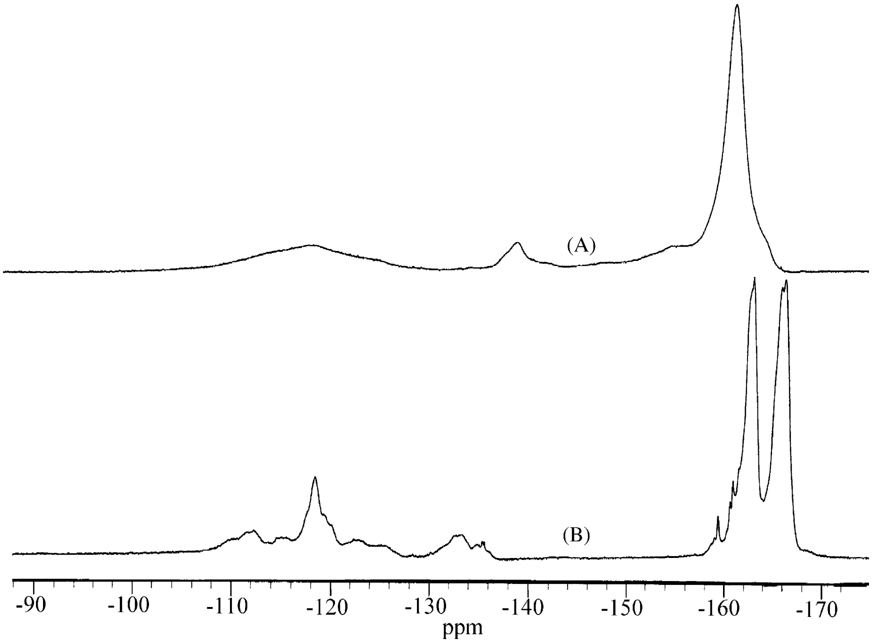


Fig. 1. ^{19}F NMR spectra of the oligomer of FDB (run 1 in Table 1) (A) and the copolymer of St and FDB (run 2 in Table 1) (B).

the skeletal C=C stretching of the fluorinated aromatic ring. The bands at 1025, 1132, and 1170 cm^{-1} were assigned to CF stretching. No obvious band was found in the range of 1700–1800 cm^{-1}, indicating that ring opening did not occur during the homopolymerization.

3.3. Copolymerization with St

It has been reported that the copolymerizations of perfluoro-2-methyl-2,3-dihydro-1,4-dioxin with tetrafluoroethylene, ethylene and vinyl acetate proceeded readily at 25–55 °C [6]. The easy incorporation of 5–20 wt.% of perfluoro-2-methyl-2,3-dihydro-1,4-dioxin into the solid copolymers was ascribed to the receptivity to attack by a spectrum of radical types [6]. Here we performed the copolymerization of FDB with St using AIBN as an initiator. It was noted that the copolymerization in bulk also proceeded readily at 60 °C. A gel-like product was obtained during polymerization. After dissolving it in chloroform and precipitating it in a large amount of methanol, a white solid product was obtained. The molecular weight and yield of the copolymers are lower than those of the homopolymer of St as shown in Table 1. This may occur because the FDB has a favourable reception for the growing St species and the new formed FDB radical species has a lower growing ability compared with St radical species.

The copolymer structure was characterized by ^{19}F, ^{1}H and ^{13}C and FTIR spectroscopy. As shown in Fig. 1B, the ^{19}F spectrum of copolymer of FDB and St is quite different from that of homopolymer. The peak at about –164.0 ppm was split into two peaks which was ascribed to the fluorines on the side group. The peaks from 108.0 to 138.0 ppm ascribed

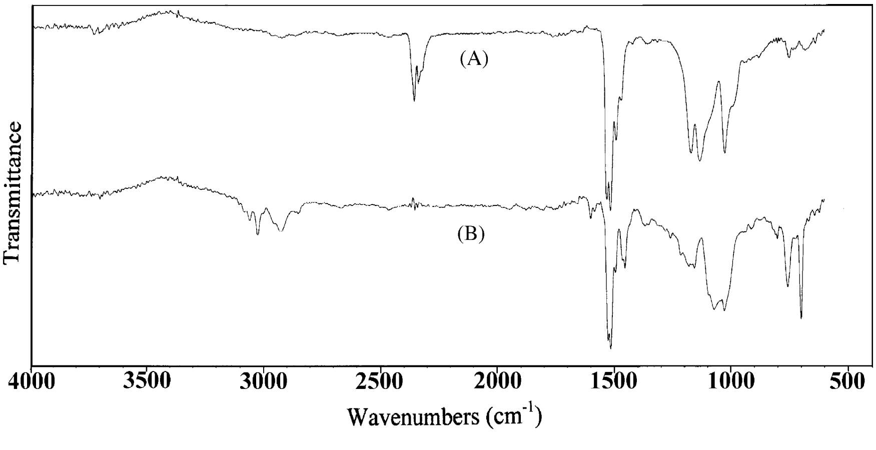


Fig. 2. FTIR spectra of the oligomer of FDB (run 1 in Table 1) (A) and the copolymer of St and FDB (run 2 in Table 1) (B).

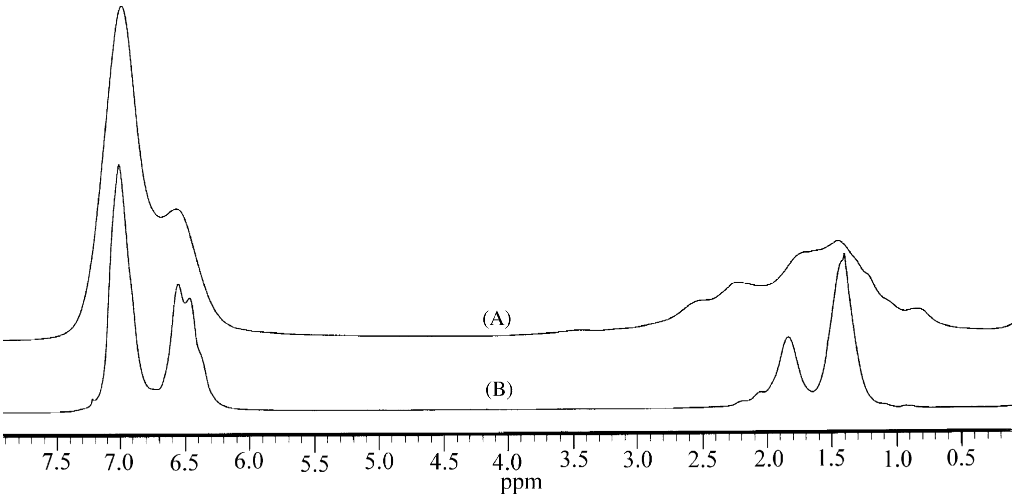


Fig. 3. ^{1}H NMR spectra of the copolymer of St and FDB (run 2 in Table 1) (A) and the homopolymer of St (run 4 in Table 1) (B).

to the fluorines in the main-chain appear a sharp peak at −118.0 ppm. This may suggest that the product has a copolymer structure.

FTIR spectrum of the copolymer was shown in Fig. 2B. The presence of the aromatic ring =C–H stretching at 3027 and 3060 cm^{-1} and the aliphatic CH and CH$_2$ stretching bands at 2843 and 2924 cm^{-1} illustrates that the copolymer contains St unit. The skeletal C=C stretching vibrations of the aromatic ring in the St unit and FDB unit overlapped in the range of 1450–1610 cm^{-1}. The typical CF stretching vibration at 1027 cm^{-1} was also observed in the copolymer. The absence of carbonyl absorption in the range of 1700–1800 cm^{-1} indicated that ring opening did not occur during the copolymerization.

Furthermore, the ^{1}H NMR spectra of the copolymer and PS are also quite different from each other. As shown in Fig. 3, the main-chain proton peak becomes broader compared with PS. The two obvious peaks at 2.2 and 2.5 ppm observed may be due to the St units adjacent to the FDB unit. The fluorinated units have an electronic drawing power and make the adjacent proton chemical shift downfield in NMR spectrum.

In order to calculate the copolymer composition, the ^{13}C NMR spectrum was recorded in chloroform-*d* at 50 °C and the central peak of chloroform (77.0 ppm) was used as an internal reference. As shown in Fig. 4, by comparison the NMR spectra of the copolymer and the homopolymer of St, the peaks at 32–47 ppm were assigned to the main-chain carbon in the St units, whereas the peaks at 104–112 ppm were assigned to the main-chain carbon in the FDB units. By comparing the peak area of the peaks at 104–112 ppm and 32–47 ppm, we can easily obtain the copolymer compositions which are given in Table 1. Due to the copolymerization, the NMR spectrum in the range of the main-chain carbon of the St units obviously changed. The ^{13}C NMR spectra further illustrates that the product is a real copolymer, not a mixture of the two homopolymers.

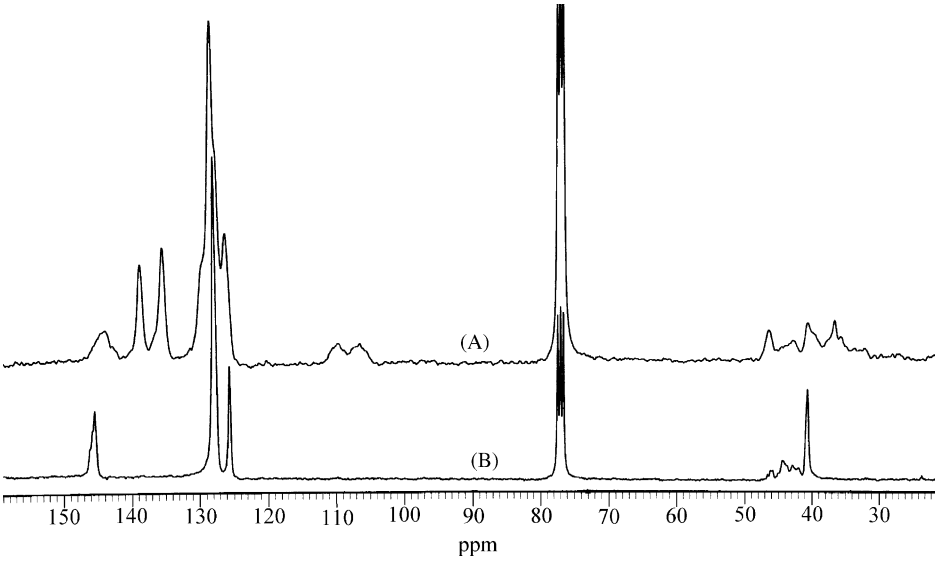


Fig. 4. ^{13}C NMR spectra of the copolymer of St and FDB (run 2 in Table 1) (A) and the homopolymer of St (run 4 in Table 1) (B).

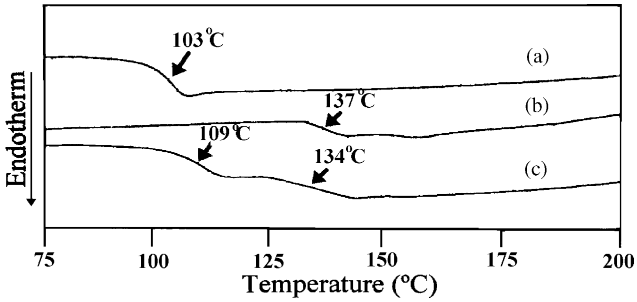


Fig. 5. DSC curves of the homopolymer of St (a), the copolymers of St and FDB (run 2 in Table 1) (b) and (run 3 in Table 1) (c).

3.4. Physical properties

Glass transition temperature is an important physical property to evaluate an amorphous polymer. Fig. 5 shows the DSC curves of polystyrene and copolymers. The copolymer of FDB and St (St/FDB = 75/25 mol/mol; run 2 in Table 1) was determined to have a T_g of 137 °C, whereas the homopolymer of St obtained at 60 °C (run 4 in Table 1) exhibits a T_g at 103 °C. Thus, the T_g of the copolymer was improved 34 °C by incorporation of 25 mol% of FDB. In the case of using a large amount of St, the copolymer (run 3 in Table 1) exhibits two obvious glass transitions at 109 and 134 °C. The first glass transition is close to that of the homopolymer of St, and the second glass transition is close to that of the copolymer with 25 mol% of FDB (run 2 in Table 1). This may suggest that there is a large fraction of polystyrene block in the copolymer produced.

The thin film of the homo-oligomer (run 1 in Table 1), PS and the copolymer of FDB and St (St/FDB = 75/25 mol/mol; run 2 in Table 1) were readily obtained by casting on aluminum foil from their chloroform solutions. The refractive index was measured by using the films. The refractive indices of the film of the homo-oligomer at the wavelengths of 632.8 and 1544 nm were 1.4721 and 1.4659, respectively. The refractive indices of the film of PS at the wavelengths of 632.8 and 1544 nm were 1.5843 and 1.5658, respectively. Furthermore, the refractive indices of the copolymer of FDB and St (St/FDB = 75/25 mol/mol; run 2 in Table 1) were measured at 632.8 and 1544 nm to be 1.5339 and 1.5152, respectively. The lower refractive index of the copolymer was related to the presence of fluorinated units.

4. Conclusion

A novel perfluoromonomer, perfluoro-2,3-dihydro-1,4-benzodioxin, was synthesized. The polymerization reactivity of this monomer is quite low and only an oligomer was obtained via homopolymerization. The copolymerization of FDB with styrene was readily performed using a radical initiator to afford a copolymer with a higher glass transition temperature. This monomer may be applied to enhance the copolymer properties through the copolymerization as a comonomer.

Acknowledgements

This work was supported in part by the Japan Science and Technology Corporation through the Grant for ERATO-Photonic Polymer.

References

[1] (a) L.A. Wall (Ed.), Fluoropolymers, vol. XXV, Wiely, New York, 1972;
(b) A.F. Feiring, in: R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry Principles and Commercial Applications, Plenum Press, New York, 1994, Chapter 15, p. 339;
(c) D.P. Carlson, W. Schmiegel, Ullmann's Encyclopedia of Industrial Chemistry, vol. A11, VCH Publishers, New York, 1988, p. 393.

[2] (a) B.E. Smart, A.E. Feiring, C.G. Krespan, Z.Y. Yang, M.H. Hung, P.R. Resnick, W.R. Dolbier Jr., X.X. Rong, Macromol. Symp. 98 (1995) 753–767;
(b) M.H. Hung, P.R. Resnick, B.E. Smart, W.H. Buck, Fluorinated plastics, amorphous, in: J.C. Salamone (Ed.), Polymeric Materials Encyclopedia, CRC Press, Boca Raton, 1996, pp. 2466–2476.

[3] S.V. Gangal, Tetrafluoroethylene polymers, in: H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges (Eds.), Encyclopedia of Polymer Science and Engineering, vol. 16, Wiley/Interscience, New York, 1989, pp. 577–642.

[4] M.H. Hung, Macromolecules 26 (1993) 5829–5834.

[5] C.G. Krespan, D.A. Dixon, J. Org. Chem. 56 (1991) 3915–3923.

[6] C.G. Krespan, D.A. Dixon, Perhalodioxins and perhalodihydrodioxins, in: G.A. Olah, R.D. Chambers, G.K.S. Prakash (Eds.), Synthetic Fluorine Chemistry, Wiley, New York, 1992, pp. 313–327.

[7] T. Masahiro, K. Akihiro, I. Masanori, Jpn Kokai Tokkyo Koho, JP 08-012668, 1996.

[8] J. Burdon, V.A. Damodaran, J.C. Tatlow, J. Chem. Soc. (1964) 763–765.