Synthesis of novel poly(hydroxyether terephthalate) via polyaddition of 2,5-difluoroterephthalic acid with aromatic bis(epoxide)s

Xiao-Song Huang [a], Feng-Ling Qing [a,b,*]

[a] College of Chemistry, Chemical Engineering and Biotechnology, and State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, 2999 North Renmin Lu, Shanghai 201620, China

[b] Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Lu, Shanghai 200032, China

ABSTRACT

A novel and more reliable synthetic route to 2,5-difluoroterephthalic acid was developed. A series of new poly(hydroxyether terephthalate) were prepared by the polyaddition of 2,5-difluoroterephthalic acid with various aromatic bis(epoxide)s catalyzed by tetrabutyl ammonium bromide.

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1. Introduction

Poly(hydroxyether esters) (PHEEs) are a class of novel thermoplastics derived from the reaction between bis(epoxide)s and diacids [1,2]. These polymers are of industry interest since they can combine excellent mechanical properties with processability and barrier properties [3]. Besides, this class of materials displays the typical biodegradability [4,5], which makes the materials a class of interesting candidates for environmentally benign materials. Due to the potential applications, the investigations on these polymers have begun to appear [6–11].

From the structural view of point, the properties of PHEE are quite dependent on the type of both bis(epoxide)s and diacids used. In the previous studies, the PHEEs were prepared via diglycidyl ether of bisphenol A with aliphatic diacids or terephthalic acid [12–16]. It is known that hydrogen bond can have a significant effect on the thermal properties, crystallization behavior, mechanical properties, and so on of polymers [17]. In this paper, we describe the synthesis of novel fluorine-containing poly(hydroxyether teraphthalate) using 2,5-difluoroterephthaic acid (DFTA) and various aromatic bis(epoxide)s. It is our interest to see whether the fluorine atoms can provide the additional hydrogen bond interaction between polymer chains and how the various aromatic groups have effect on the T_g of the polymers. The synthesized PHETs were characterized and their properties including thermal and solubility were also discussed herein.

2. Results and discussion

2.1. Synthesis of 2,5-difluoroterephthalic acid (DFTA) 4

The synthesis of 2,5-difluoroterephthalic acid (DFTA) has been reported in the early literatures. Lee et al. [18] described the preparation of DFTA through cyanation of 1,4-dibromo-2,5-difluorobenzene followed by acidic hydrolysis. Unfortunately, we repeated his work only to get the product in very poor yield. Cassidy and Reddy [19] documented the synthesis of DFTA starting from 2,5-difluorotoluene. However, the overall yield of this method is also not satisfactory. Thus, new synthetic route to DFTA has to be developed in an attempt to improve the overall yield.

Our synthetic sequence of 2,5-difluoroterephthalic acid was outlined in Scheme 1. 2,5-Dimethyl-1,4-benzenediamine was firstly converted to 2,5-dimethyl-1, 4-benzenebis(diazonium) tetrafluoroborate 1 in 90% yield via Balz-Schiemann reaction. The second step involved the dry pyrolysis of diazo salt 1 to give 2,5-difluo-p-xylene 2. Attempts to prepare compound 4 by direct oxidation of 2 with potassium permanganate failed. Finally,

* Corresponding author at: Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Science, 354 Fenglin Lu, Shanghai 200032, China. Tel.: +86 21 54925187; fax: +86 21 64166128.
E-mail address: flq@mail.sioc.ac.cn (F.-L. Qing).
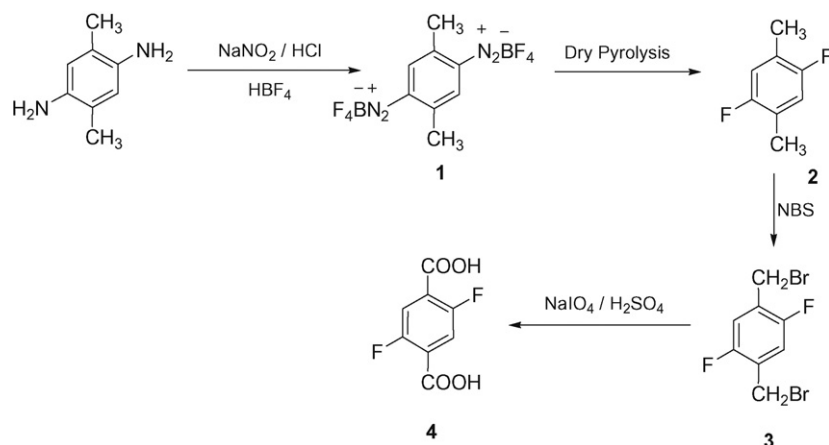
Scheme 1. Synthesis of 2,5-difluoroterephthalic acid **4**.

benzylic bromination of **2** with NBS followed by oxidation with 1.0 equiv. of sodium periodate in the presence of 2% H_2SO_4 gave DFTA **4**. To our delight, the overall yield of 2,5-difluoroterephthalic acid as high as 50% was obtained.

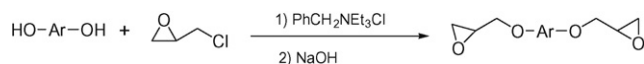## 2.2. Synthesis of aromatic bis(epoxide)s 5–10

The aromatic bis(epoxide)s **5–10** (Table 1) were prepared by a standard procedure [20,21] in which the appropriate bisphenol was treated with an excess of epichlorohydrin in the presence of benzyltriethylammonium chloride (Scheme 2). Initially, the phenolic functionalities react with the epichlorohydrin to yield chlorohydrin and epoxide intermediate species over 12 h at 80 °C. Conversion to the epoxide functionalities is completed by treatment with excess sodium hydroxide at 80 °C over 1 h. The yields of the bis(epoxide)s ranged from 15% to 60% (Table 1).

2.3. Polymer synthesis

The polyaddition of DFTA with aromatic bis(epoxide)s **5–10** in the presence of tetrabutylammonium bromide (TBAB) was carried out in dioxane at 80 °C for 40 h (Scheme 3). The corresponding polymers **11a–f** were obtained in 65–83% yields. In all of these cases, the reaction mixture was consistently homogeneous, with products remaining in the solution. The chemical structures of polymers **11a–f** were characterized by FT-IR, ^{1}H NMR and ^{19}F NMR spectroscopy. Shown in Fig. 1 is the FT-IR spectrum of **11a**. The absorption band at 3500–3400 cm^{-1} was ascribed to the stretching vibrations of hydroxyl group which reflect the wide distribution of hydrogen-bonded hydroxyl stretching frequencies. The peak at 1731 cm^{-1} was attributable to the symmetrical carbonyl stretching vibrations. The C-F multiple stretching absorptions were also detected in the range of 1300–1100 cm^{-1}. From the ^{1}H NMR spectrum

Table 1
Characterization data for aromatic bis(epoxide)s

Compound	Aromatic bis(epoxide)s	mp (°C)	Yield (%)
5		75.1–76.0	50
6		Oil	47
7		129.3–130.8	60
8		116.9–117.4	40
9		Oil	25
10		174.2–174.5	15

Scheme 2. Synthesis of aromatic bis(epoxide)s 5–10.
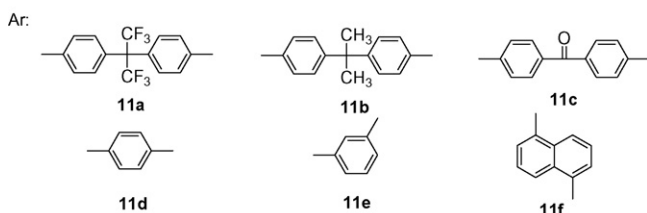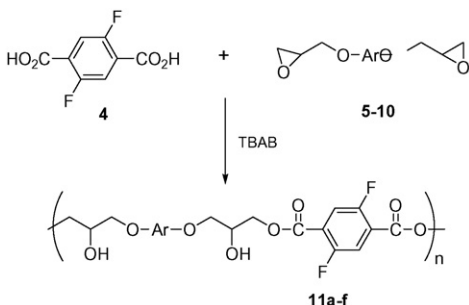
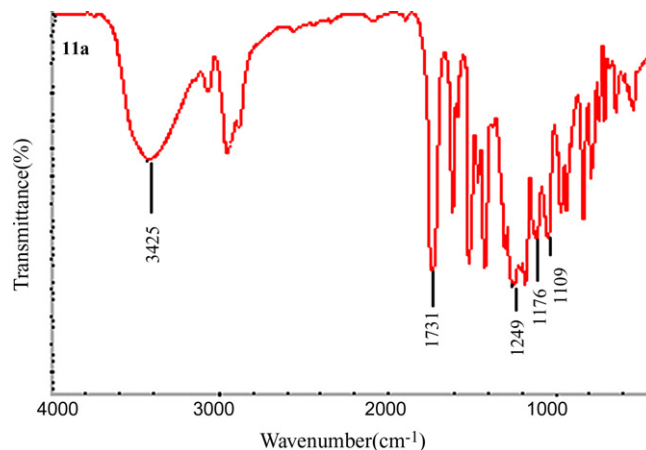Scheme 3. Synthesis of poly(hydroxyether terephthalate)s.

Fig. 1. FT-IR spectrum of 11a.

fluorines of trifluoromethyl groups and aromatic ring appeared at −63.56 ppm (s, F_a, 6F) and −115.30 ppm (s, F_b, 2F) respectively. The molecular weights of the fluorinated polymers determined by GPC in THF or DMF using polystyrene as standard are in the range of 32,600–49,100 for Mn and 44,400–62,800 for Mw with the Mw/Mn values of 1.28–1.60 (Table 2).

2.4. Hydrogen-bond interactions

To investigate whether the fluorine atoms can provide the additional intermolecular hydrogen bond interactions in the fluorine-containing poly(hydroxyether terephthalate)s, polymer 11g was synthesized from the polyaddition from terephthalic acid (TA) and with bis(epoxide) 6 under the same reaction conditions

(Fig. 2A) of 11a, it can be seen that protons in aromatic ring appeared at 7.79 ppm (t, H_6, 2H), 7.29 ppm (d, H_5, 4H), 7.03 ppm (d, H_4, 4H); signals of 4.59–4.49 ppm (m, H_1, 4H), 4.41–4.37 ppm (m, H_2, 2H), 4.26–4.18 ppm (m, H_3, 4H) belonged to protons in the aliphatic chain. In ^{19}F NMR spectrum (Fig. 2B), signals of
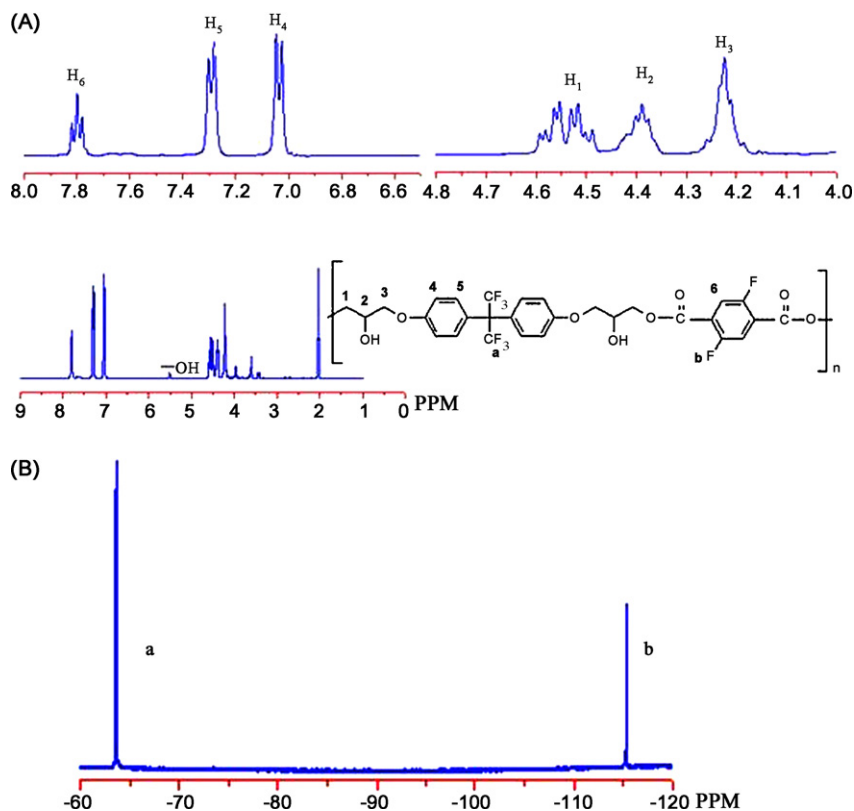

Fig. 2. ^1H NMR (A) and ^{19}F NMR (B) spectra of 11a.

Table 2
Yield and GPC results of polymers **11a–f**

Polymer	Yield	Mn ($\times 10^{-4}$)	Mw ($\times 10^{-4}$)	Mw/Mn
11a[a]	75	3.26	4.60	1.41
11b[a]	71	3.41	5.46	1.60
11c[b]	83	4.91	6.28	1.28
11d[a]	65	3.54	5.51	1.55
11e[a]	73	4.42	5.58	1.26
11f[a]	70	3.32	4.44	1.33

[a] GPC in THF vs. polystyrene at 35 °C.
[b] GPC in DMF vs. polystyrene at 35 °C.

Table 3
Solubility of polymers **11a–f**[a]

Polymer	Solvent							
	DMSO	DMF	MeOH	Dioxane	THF	CHCl₃	Acetone	Toluene
11a	++	++	+	++	++	+	++	+
11b	++	++	+	++	++	+	++	+
11c	++	++	+	++	−	−	−	−
11d	++	++	+	++	++	+	++	+
11e	++	++	+	++	++	+	++	+
11f	++	++	+	++	++	+	++	+

[a] ++, soluble at room temperature; +, partially soluble or swelling; −, insoluble.

for preparation of polymer **11b**. The molecular weight of polymer **11g** is 10,700 for Mn and 13,300 for Mw. The investigation of the hydrogen bond interactions was carried out by comparison the hydroxyl stretching vibration range of 3700–3000 cm^{-1} in FT-IR spectra of polymers **11b** and **11g** (Fig. 3). The broad bands reflect the wide distribution of hydrogen-bonded hydroxyl stretching frequencies. The shoulder bands centered at 3570 cm^{-1} are
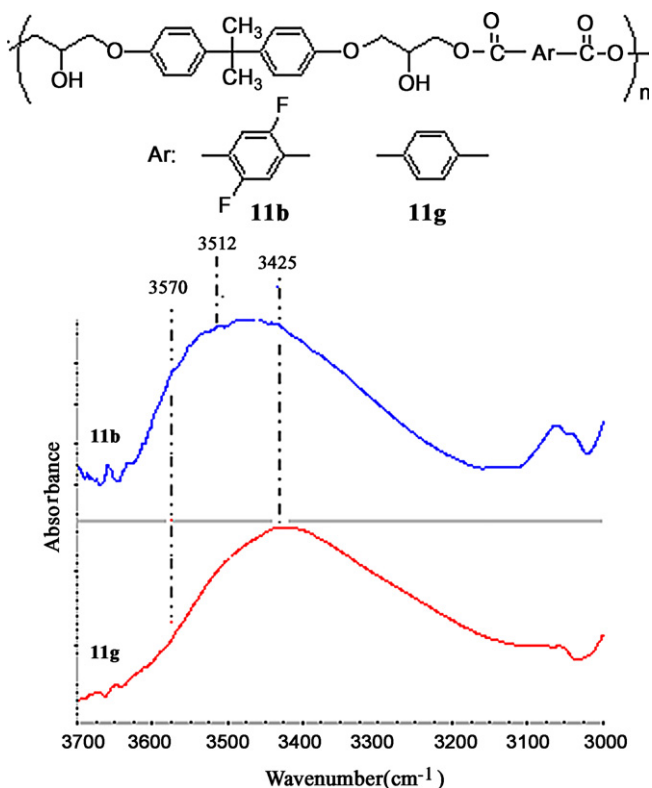
Fig. 3. Comparison of FT-IR spectra in the region of 3700–3000 cm^{-1} for **11b** and **11g**.

Table 4
Thermal properties of polymers **11a–f**

Polymer	T_g (°C)[a]	T_d (°C)[a]	$T_{5\%}$ (°C)[b]	$T_{10\%}$ (°C)[b]	R_w (%)[c]
11a	91	357	299	327	22
11b	66	347	217	323	9
11c	55	355	334	351	21
11d	74	349	305	326	16
11e	69	330	242	292	14
11f	135	348	321	335	18

[a] DSC and TGA at 10 °C/min in N₂.
[b] Temperatures at 5% and 10% weight loss.
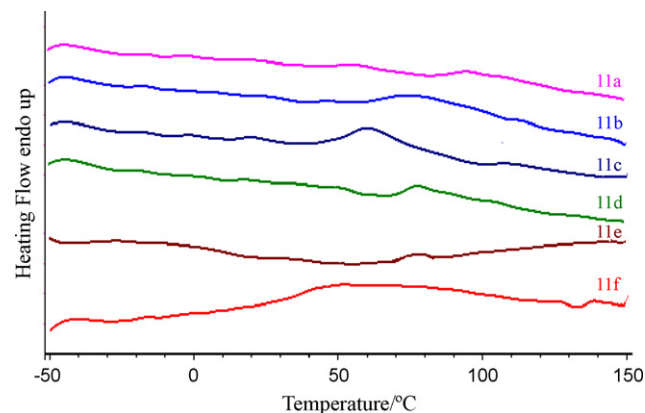[c] Residual weight retention at 500 °C.

ascribed to the free hydroxyls [22]. It was noted that a new band at a higher frequency (∼3512 cm^{-1}) is discernable. This showed that there was the formation of the weaker hydrogen bond –OH···–F interactions in **11b**.

2.5. Solubility

The solubility of the resulting polymers **11a–f** in a number of solvents was examined. As summarized in Table 3, all the polymers were soluble in DMSO, DMF and dioxane while partially soluble or swelling in methanol. However, polymer **11c** was insoluble in THF, chloroform, acetone and toluene. The results indicated that the obtained PHETs exhibited good solubility.

2.6. Thermal properties of polymers

Thermal properties of polymers **11a–f** were evaluated by means of differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA). The results are listed in Table 4. DSC was used to determine the glass transition temperatures of polymers. All the samples were first heated up to 150 °C and held for 5 min to remove thermal history, followed by quenching to −70 °C. A heating rate of 10 °C/min in nitrogen was used at all cases. The DSC curves of **11a–f** are presented in Fig. 4. It can be seen that all the polymers are amorphous thermoplastics with glass transition temperatures (T_g) of 55–135 °C. As expected, **11f** derived from the relatively rigid naphthyl unit exhibited the highest T_g (135 °C). The T_g of PHET decreases as the Ar portion of the polymer backbone becomes more flexible. The T_g of **11a** (91 °C) was higher than that of **11b** (66 °C), this might be attributed to the bulky trifluoromethyl moieties. The TGA curves of polymers **11a–f** under nitrogen atmosphere are given in Fig. 5. The polymers exhibited temperatures corresponding to 5% weight loss ranging from 217 to 334 °C and 10% weight loss ranging from 292 to 351 °C under nitrogen. The initial thermal decomposition temperatures (T_d) were

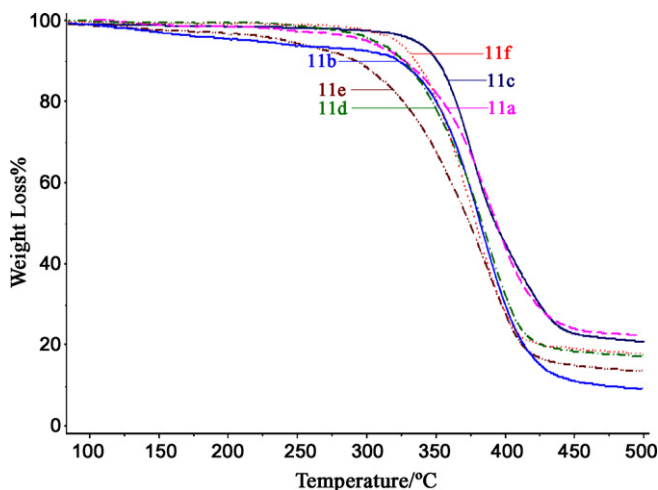**Fig. 4.** DSC curves of polymers **11a–f** in nitrogen.

Fig. 5. TGA curves of polymers **11a–f** in nitrogen.

determined in the range of 330–357 °C in nitrogen for all polymers tested. Meanwhile, the residual weight retention at 500 °C was also summarized in Table 4. It showed that the residual weight of **11a** at 500 °C under nitrogen was 22%, much higher than that of **11b** (9%), which indicated that the thermal stability can be improved by the introduction of trifluoromethyl moieties.

3. Conclusion

A novel and more reliable synthetic route to 2,5-difluoroterephthalic acid (DFTA) was developed. The polyaddition of DFTA with various aromatic bis(epoxide)s to produce a series of poly(hydroxyether terephthalate)s (PHET) in good yields. The introduction of DFTA may contribute to the formation of additional hydrogen bond interactions in PHET. The glass transition temperatures of PHET are also dependent on the aromatic unit (Ar) used.

4. Experimental

4.1. Materials

Dioxane was freshly distilled under nitrogen over sodium. 2,5-Dimethyl-1,4-benzenediamine was obtained from Zhejiang Dragon Chemical Co., Ltd. Hexafluorobisphenol A was obtained from Zigong Longxiang Chemical Co., Ltd and purified by sublimation. Bisphenol A was obtained from Sinopharm Chemical Reagent Co., Ltd and recrystallized from toluene. 4,4′-Dihydroxybenzophenone was obtained from Shanghai Dere Finechem Co., Ltd and recrystallized from acetone. 1,5-Dihydroxynaphthalene was obtained from Fluka. Other reagents or materials were used as received.

4.2. Measurements

Melting point ranges were determined on a WRS-2A capillary melting point apparatus (uncorrected). Elemental analysis was carried out on a Carlo-Erba1106 system. The FT-IR measurements were conducted on a Nicolet 380 FT-IR spectrophotometer at room temperature. To obtain the FT-IR spectra, the thin films of plain PHET were cast onto KBr windows from 2 wt.% DMF solution. The films obtained were further dried in vacuo at 60 °C for 72 h to remove residual solvent. All of casting films used in the study were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. The FT-IR spectra were recorded with 32 scans at a

resolution of 2 cm^{-1} for signal accumulation. Gas chromatography/mass spectrometry (GC/MS) was recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. ^{1}H NMR (400 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker AM 400 spectrometer system. Chloroform-d, acetone-d$_6$ and dimethyl sulphoxide-d$_6$ were used as the solvents and chemical shifts reported were internally referenced to Me$_4$Si (0 ppm) and CFCl$_3$ (0 ppm) for ^{1}H and ^{19}F nuclei. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual-wavelength absorbance detector and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 mm × 300 mm). GPC measurements were carried out at 35 °C using THF or DMF as an eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 204 F1 system under nitrogen calibrated with indium and zinc standards. All the samples were first heated up to 150 °C and held for 5 min to remove thermal history, followed by quenching to −70 °C. A heating rate of 10 °C/min was used at all cases. Dynamic thermogravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 system on powder samples at a heating rate of 10 °C/min under nitrogen atmosphere from 25 to 500 °C.

4.3. Synthesis of 2,5-dimethyl-1,4-benzenebis(diazonium) tetrafluoroborate 1

2,5-Dimethyl-1,4-benzenediamine (27.2 g, 0.20 mol) was dissolved in 110 mL of 37% hydrochloric acid to form a slurry. With energetic stirring, one-third of the slurry was first added to 38% fluoroboric acid (219.2 g, 160 mL, 0.95 mol) at or below −10 °C. Sodium nitrite (30.36 g, 0.44 mol) in 50 mL of water was slowly added to the suspension. Entire amount of the slurry may be added by the time half of the nitrite has been added. After addition of the nitrite solution, the mixture was allowed to stir for 45 min with continued cooling. The resultant precipitate was suction filtered and washed with cold water (200 mL), cold ethanol (200 mL) and finally cold ether (300 mL). The obtained beige solid was dried under high vacuum overnight to give 60.05 g of **1** (90%) with mp 149–151 °C. This material was used directly for the next step without further purification.

4.4. Synthesis of 2,5-difluo-p-xylene 2

Compound **1** (57.30 g, 0.17 mol) was placed in a 500-mL round-bottom flask connected with two cold traps and a gas absorption bottle. With low-speed stirring, the flask was carefully heated in an oil bath at 80 °C until the gas evolution began. A small amount of sea sand may be added to avoid vigorous decomposition. The temperature of the oil bath was gradually increased to 120 °C to complete the decomposition. Finally, the black residue was then distilled in steam and extracted with diethyl ether. The organic layer was washed with 5% sodium bicarbonate and then dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was recrystallized from hexane. White crystals of compound **2** (17.50 g, 72%) were obtained with mp 39.0–40.2 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.80 (t, J = 8 Hz, 2H), 2.21 (s, 6H). ^{19}F NMR (376 MHz, CDCl$_3$): δ −124.6 (t, J = 7.52 Hz, 2F).

4.5. Synthesis of 1,4-bis(bromomethyl)-2,5-difluorobenzene 3

Following the general procedure of Greenwood et al. [17], compound **2** (8.55 g, 60 mmol) was dissolved in 100 mL of carbon

tetrachloride in a 250-mL round-bottom flask equipped with a condenser. *N*-Bromosuccinimide (22.43 g, 126 mmol) was added along with 0.02 g of benzoyl peroxide as an initiator. Under nitrogen atmosphere, the mixture was heated under reflux with two 275 W sunlamp placed 5 cm from the reaction flask for 4.5 h, and the resulting suspension was suction filtered to remove succinimide byproduct. The solvent was then removed from the filtrate under reduced pressure, and the crude product was recrystallized from ethanol to give 15.35 g (85%) of white needle-like crystals as compound **3** with mp 110–112 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.13 (t, J = 7.6 Hz, 2H), 4.44 (s, 4H). ^{19}F NMR (376 MHz, CDCl$_3$): δ −121.6 (t, J = 7.52 Hz, 2F). MS (EI): m/z 300 (M$^+$).

4.6. Synthesis of 2,5-difluoroterephthalic acid (DFTA) 4

To a mixture of compound **3** (7.50 g, 25 mmol), sodium periodate (5.35 g, 25 mmol) was added 50 mL of 2% H$_2$SO$_4$. The reaction mixture was heated at 95 °C for 24 h. It was subsequently cooled to room temperature, stoppered and placed in a freezer for several hours. The cold mixture was filtered and the precipitate was washed with water. The solids were recrystallized from acetic acid to give 4.04 g (80%) of compound **4** as white crystals with mp 316–319 °C. IR (ν_{max}, cm^{-1}, KBr): 3427–2512, 1691, 1184. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 13.86 (s, COOH), 7.71 (t, J = 8.0 Hz, 2H). ^{19}F NMR (376 MHz, CDCl$_3$): δ −115.81 (t, J = 7.5 Hz, 2F). MS (EI): m/z 202 (M$^+$). Anal. Calcd. for C$_8$H$_4$O$_4$F$_2$: C, 47.52%, H, 1.98%. Found: C, 47.80%, H, 2.04%.

4.7. General procedure for preparation of bis(epoxide)s 5–10

Under argon atmosphere, the bisphenol (15 mmol), benzyl-triethylammonium chloride (0.02 g, 0.09 mmol), and epichlorohydrin (30 mL, 35.4 g, 0.38 mol) were heated at 80 °C over 12 h. After that, a solution of 50% aqueous sodium hydroxide (3.6 g, 45 mmol NaOH) was added dropwise to the vigorously stirred solution over 1 h. On completion of addition, the mixture was allowed to stir at this temperature for 4 h. The reaction mixture was then cooled and poured into methylene chloride (200 mL) and washed with water (4 × 100 mL). The organic layer was separated, dried over magnesium sulfate and filtered to yield a clear filtrate. The solvent was removed under reduced pressure to yield crude **5–10** as either an oil or a solid. Bis(epoxide)s **5**, **6** and **9** were purified via chromatography on silica gel using ethyl acetate/petroleum ether (1/5, v/v) as the eluent. Bis(epoxide)s **7**, **8** and **10** were purified by twice recrystallizations from ethanol.

Compound **5**: IR (ν_{max}, cm^{-1}, KBr): 1612, 1260, 1245, 1176, 967. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35–7.30 (m, 4H), 6.95–6.92 (m, 4H), 4.28 (dd, J = 11.2, 2.8 Hz, 2H), 4.02 (dd, J = 11.2, 5.6 Hz, 2H), 3.41–3.39 (m, 2H), 2.96 (t, J = 4.8 Hz, 2H), 2.80 (t, J = 4.8 Hz, 2H).

Compound **6**: IR (ν_{max}, cm^{-1}, KBr): 1609, 1245, 1035, 1184, 913. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15–7.11 (m, 4H), 6.84–6.80 (m, 4H), 4.17 (dd, J = 10.8, 3.2 Hz, 2H), 3.95 (dd, J = 10.8, 5.6 Hz, 2H), 3.34–3.32 (m, 2H), 2.89 (t, J = 4.4 Hz, 2H), 2.74 (t, J = 4.4 Hz, 2H), 1.63 (s, 6H).

Compound **7**: IR (ν_{max}, cm^{-1}, KBr): 1641 (C=O), 1602, 1252, 1026, 910. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.79–7.75 (m, 4H), 7.02–6.96 (m, 4H), 4.34–4.30 (dd, J = 10.8, 3.2 Hz, 2H), 4.02 (dd, J = 11.2, 5.6 Hz, 2H), 3.40–3.37 (m, 2H), 2.93 (t, J = 4.4 Hz, 2H), 2.78 (t, J = 4.4 Hz, 2H).

Compound **8**: IR (ν_{max}, cm^{-1}, KBr): 1630, 1498, 1344, 1109, 910. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.85 (s, 4H), 4.16 (dd, J = 10.8, 3.2 Hz, 2H), 3.91 (dd, J = 10.8, 5.6 Hz, 2H), 3.34–3.31 (m, 2H), 2.89 (t, J = 4.8 Hz, 2H), 2.73 (t, J = 4.8 Hz, 2H).

Compound **9**: IR (ν_{max}, cm^{-1}, KBr): 1598, 1490, 1288, 1082, 908. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.19–7.14 (m, 1H), 6.54–6.50 (m, 3H), 4.19 (dd, J = 11.2, 3.2 Hz, 2H), 3.91 (dd, J = 11.2, 5.6 Hz, 2H), 3.4–3.31 (m, 2H), 2.88 (t, J = 4.8 Hz, 2H), 2.73 (t, J = 4.8 Hz, 2H).

Compound **10**: IR (ν_{max}, cm^{-1}, KBr): 1593, 1405, 1267, 1043, 918. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.77 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 8.0 Hz, 2H), 7.02 (d, J = 7.6 Hz, 2H), 4.50 (dd, J = 11.6, 2.8 Hz, 2H), 4.03 (dd, J = 11.6, 6.4 Hz, 2H), 3.49–3.46 (m, 2H), 2.91 (t, J = 4.8 Hz, 2H), 2.82 (t, J = 4.8 Hz, 2H).

4.8. General procedure for the synthesis of poly(hydroxyether terephthalate)s 11a–f

Poly(hydroxyether terephthalate)s were prepared by the polyaddition of 2,5-difluoroterephthalic acid **4** with various aromatic bis(epoxide)s **5–10** under a nitrogen atmosphere. The following procedure is for the preparation of **11a** and is a representative for the preparation of the rest of the polymers. Compound **4** (0.202 g, 1 mmol), **5** (0.448 g, 1 mmol) and TBAB (0.02 g, 0.06 mmol) were dissolved in 2.5 mL of dioxane in a polymerization tube. The reaction was carried out at 80 °C for 40 h. After cooling to the room temperature, the mixture was poured into ethanol/hexane (1/5, v/v, 100 mL) to precipitate a polymer. It was re-precipitated three times from THF into ethanol/hexane (1/1) and dried in vacuo at 60 °C for 48 h.

Polymer **11a**: IR (ν_{max}, cm^{-1}, KBr): 1727, 1611, 1513, 1421, 1249, 1176, 1109, 1042. ^{1}H NMR (400 MHz, acetone-d$_6$): δ 7.79 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.4 Hz, 4H), 7.03 (d, J = 8.8 Hz, 4H), 4.59–4.49 (m, 4H), 4.41–4.37 (m, 2H), 4.26–4.18 (m, 4H). ^{19}F NMR (376 MHz, acetone-d$_6$): δ −63.56 (s, 6F), −115.30 (s, 2F).

Polymer **11b**: IR (ν_{max}, cm^{-1}, KBr): 1728, 1606, 1507, 1420, 1256, 1181, 1099,1040,1038. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.81 (t, J = 7.6 Hz, 2H), 7.07 (d, J = 8.2 Hz, 4H), 6.83 (d, J = 8.4 Hz, 4H), 4.41–4.35 (m, 4H), 4.26–4.13 (m, 2H), 4.05–3.95 (m, 4H), 1.55 (s, 6H). ^{19}F NMR (376 MHz, DMSO-d$_6$): δ −115.27 (s, 2F).

Polymer **11c**: IR (ν_{max}, cm^{-1}, KBr): 1724, 1600, 1504, 1421, 1245, 1171, 1108, 1033. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.89 (t, J = 7.6 Hz, 2H), 7.81 (d, J = 6 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H), 4.47–4.33 (m, 4H), 4.25–4.18 (m, 2H), 4.18–4.07 (m, 4H). ^{19}F NMR (376 MHz, DMSO-d$_6$): δ −115.25(s, 2F).

Polymer **11d**: IR (ν_{max}, cm^{-1}, KBr): 1728, 1589, 1506, 1420, 1257, 1181, 1099, 1043. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.87 (t, J = 7.6 Hz, 2H), 6.88 (s, 4H), 4.45–4.29 (m, 4H), 4.25–4.08 (m, 2H), 3.97–3.91 (m, 4H). ^{19}F NMR (376 MHz, DMSO-d$_6$): δ −115.30(s, 2F).

Polymer **11e**: IR (ν_{max}, cm^{-1}, KBr): 1727, 1596, 1493, 1420, 1257, 1180, 1098, 1047. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.86(t, J = 7.6 Hz, 2H), 7.16 (s, 1H), 6.55–6.52 (m, 3H), 4.47–4.29 (m, 4H), 4.25–4.09 (m, 2H), 4.10–3.92 (s, 4H). ^{19}F NMR (376 MHz, DMSO-d$_6$): δ −115.26 (s, 2F).

Polymer **11f**: IR (ν_{max}, cm^{-1}, KBr): 1726, 1595, 1506, 1418, 1261, 1179, 1082. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 7.85–7.76 (m, 4H), 7.35 (d, J = 6.8 Hz, 2H), 6.98 (s, 2H), 4.55–4.45 (m, 4H), 4.34–4.22 (m, 2H), 4.19–4.02 (s, 4H). ^{19}F NMR (376 MHz, DMSO-d$_6$): δ −115.27 (s, 2F).

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