Novel fluorinated poly(aryl ether)s derived from 1,2-bis(4-(4-fluorobenzoyl)phenoxy)-hexafluorocyclobutane

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ARTICLE INFO

ABSTRACT

Two novel poly(aryl ether)s were prepared from 1,2-bis(4-(4-fluorobenzoyl)-phenoxy)-hexafluorocyclobutane and aromatic bisphenols by the aromatic nucleophilic substitution reaction in a polar aprotic solvent. These polymers have good thermal stability up to 341 °C with 10% weight loss in inert atmosphere and good solubility in common organic solvents such as THF, DMAc, DMF and DMSO.

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1. Introduction

Poly(aryl ether)s are a class of high performance materials known for their excellent combination of chemical, physical and mechanical properties. This class of advanced material is currently receiving considerable attention for potential application in the aerospace, optics, electronics and other high technology fields. However, it is difficult for conventional poly(aryl ether)s to be used as thin films and coating materials because of their poor solubility. In addition, their poor solubility makes the polymerization condition difficult. Therefore, a great deal of effort has been focused on the preparation of soluble poly(aryl ether)s [1–4]. Fluorinated poly(aryl ether)s, specially perfluorocyclobutane (PFCB)-containing poly(aryl ether)s have been explored [5–7] for a variety of applications, such as high performance structure coating, interlayer dielectrics, circuit board laminas, dielectric wave guides and optical cladding layer [8], because the PFCB aromatic ether polymers, combining the stability of fluorocarbon segments and the engineering thermoplastic nature of polyaryl ethers, exhibit good solubility, excellent processability and optical transparency, high temperature performance and low dielectric constants [9–11].

Therefore, a novel aromatic monomer containing a perfluorocyclobutane group, 1,2-bis(4-(4-fluorobenzoyl)phenoxy)-hexafluorocyclobutane 6, was designed and synthesized in our laboratory, and two novel fluorinated poly(aryl ether)s were prepared by polycondensation of 6 with aromatic diphenols. The solubility of the resulting poly(aryl ether)s in several common organic solvents was tested. The polycondensation process, corresponding composition and structure, as well as physical and thermal properties of the polymers were investigated.

2. Experimental

2.1. Materials

Ether (Et₂O) was freshly distilled under nitrogen over sodium. Acetonitrile (MeCN), DMAc and fluorobenzene were distilled over CaH₂. DMF was stirred over MgSO₄ overnight at room temperature, and then vacuum distilled. Zinc granular was treated with 5% aqueous hydrochloric acid for several minutes, and then washed with water, ethanol and ether successively, and dried in vacuum. 4,4′-Dihydroxybenzophenone (DHBP) was recrystallized from acetone. Resorcinol was sublimed before use. Other reagent and materials were used as received.

2.2. Analysis

^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (162 MHz) spectra were recorded on a Bruker AM 400 spectrometer system.

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Chloroform-d and dimethyl sulphoxide-d_6 were used as the solvent 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, respectively. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. MS spectra were recorded on a Finnigan MAT-8430 instrument with electron-impact ionization at 70 eV. 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 DMF as eluent with a 1.0 ml/min flow rate. The system was calibrated with polystyrene standards. Dynamic thermo-gravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 system on powder samples at a heating rate of 10 °C/min in N$_2$. The wide-angle X-ray diffraction (WXRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu Kα1 radiation, operated at 40 kV and 300 mA. The solubility was determined by immersing 0.1 g polymer in various solvents (1.0 g) at 25 °C with magnetic stirring.

2.3. Synthesis and characterization of the fluorinated monomer

2.3.1. Synthesis of 1,2-bis(4-bromophenoxy)-perfluorocyclobutane 2
Compound **2** was prepared using published procedures [5–7]. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.44–7.50 (m, 4H), 7.05 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H). ^{19}F NMR (CDCl$_3$, 376 MHz, ppm): δ −126.7, −128.0, −128.6, −129.5, −130.1, −130.2, −130.8, −131.3 and −131.4.

2.3.2. Synthesis of 1,2-bis(4-formylphenoxy)-hexafluorocyclobutane 3
Compound **3** was prepared using published procedures [12]. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.16 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 7.6 Hz, 2H), 7.82–7.86 (m, 4H), 9.89 (s, 1H), 9.91 (s, 1H). ^{19}F NMR (CDCl$_3$, 376 MHz, ppm): −132.1, −131.7, −130.2, −129.6, −128.9, −128.3, −127.7, −127.56 and −126.9.

2.3.3. Synthesis of 4,4'-((1,2,3,3,4,4-hexafluorocyclobutane-1,2-diyl)bis(oxy))-dibenzoic acid 4
To a 250 ml three-neck round-bottom flask equipped with a thermometer, a sealed mechanical stirrer, and a pressure-equalizing dropping funnel were charged a mixture of compound **3** (2.870 g and 7.10 mmol), pyridine (60 ml) and a solution of sodium carbonate (0.318 g and 3.00 mmol) in water (20 ml). The reaction mixture was cooled to 5 °C, and a solution of KMnO$_4$ (2.467 g and 15.62 mmol) in water (60 ml) was added dropwise. After complete addition the reaction was maintained at 5 °C with vigorous stirring for 4 h. Then the mixture was stirred at 40 °C for 12 h. The precipitated MnO$_2$ was filtered off and the filtrate was concentrated to about 50 ml under reduced pressure. The solution was acidified with dilute hydrochloric acid, and the product was filtered and washed with water and dried to afford 2.860 g (92%) of **4** as a white solid. ^{1}H NMR (DMSO, 400 MHz, ppm): δ 7.30 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 8.01–8.06 (m, 4H), 13.10 (s, 1H), 13.16 (s, 1H). ^{19}F NMR (DMSO, 376 MHz, ppm): δ −130.9, −130.3, −130.1, −129.7, −129.6, −128.9, −128.0, −127.4 and −126.9.

2.3.4. Synthesis of 1,2-bis(4-(4-fluorobenzoyl)phenoxy)-hexafluorocyclobutane 6
In a flame dried three-neck round-bottom flask compound **4** (1.95 g and 4.47 mmol) and thionyl chloride (20 ml) were charged. The reaction mixture was stirred at 75 °C for 3 h. The reaction

mixture was then warmed to 90 °C to remove excess thionyl chloride. After removal of the trace quantities of thionyl chloride in vacuum, compound **5** was obtained and used directly for the next step without further purification. Fluorobenzene (20 ml) was then added to dissolve the mixture of compound **5** and anhydrous aluminium trichloride (2.39 g and 17.88 mmol). The reaction mixture was stirred at 90 °C for 12 h. Water was added to quench the reaction and then ether was added. The organic layers were washed with water, dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether:ethyl acetate = 85:15) to afford 1.06 g (42%) of compound **6** as a white solid. ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.30 (t, J = 8.8 Hz, 4H), 7.37 (d, J = 8.8 Hz, 4H), 7.72–7.76 (m, 4H), 7.83 (d, J = 8.8 Hz, 4H). ^{19}F NMR (CDCl$_3$, 376 MHz, ppm): δ −121.1, −120.5, −115.8, −115.2 and −105.6. ^{13}C NMR (DMSO, 100 MHz, ppm): δ 118.4, 118.6, 120.5, 135.0, 135.3, 135.4, 136.2, 136.6, 157.2, 166.3, 168.8 and 195.8. IR (KBr, cm^{-1}): ν 3080, 1662, 1600, 1505, 1417, 1377, 1279, 1232, 1156, 1041, 1001, 929, 854, 764, 678 and 596. MS(EI): m/z 554, 459, 312, 199, 188, 123 and 95.

2.4. Polymerization

A typical example for polymer **P1** is given as follows [13]. To a 100 ml three-neck round-bottom flask equipped with a stirrer, a Dean–Stark trap and condenser, and a nitrogen inlet were added compound **6** (0.592 g and 1.0 mmol) and 4,4'-dihydroxybenzophenone (0.214 g and 1.0 mmol). Then DMAc (15 ml), toluene (12 ml) and potassium carbonate (0.290 g, 2.1 mmol) were charged to the reaction flask. Under an atmosphere of nitrogen, the solution was heated to reflux (140 °C) to dehydrate the system. The reaction mixture was kept refluxing until the presence of water was no longer observed in the Dean–Stark trap. This usually took between 6 and 8 h. Upon dehydration, the polymerization was carried out at 180 °C for approximately 12 h, and the reaction was terminated about the point where the viscosity increased dramatically. When the reaction mixture became too viscous, DMAc (2–3 ml) was added. The reaction mixture was diluted with about an equimolar volume of DMAc and filtered to remove the inorganic salts. The polymer solution was then coagulated in approximately 10× volume of a 4/1 (v/v) mixture of methanol/water, washed with methanol, water, then dried in a vacuum oven for 24 h. Polymer **P2** was obtained in a similar way as to polymer **P1**.

P1: 72.3% yield; ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.75 (m, 12H), 7.15 (m, 12H). ^{19}F NMR (CDCl$_3$, 376 MHz, ppm): δ −105, −110, −115, −117, −120 and −121. IR (KBr, cm^{-1}): 3060, 1653, 1590, 1497, 1241, 928, 857, 766, 677 and 502.

P2: 83% yield; ^{1}H NMR (CDCl$_3$, 400 MHz, ppm): δ 7.75 (m, 8H), 7.41 (s, 1H), 7.15 (m, 8H), 6.96 (m, 3H). ^{19}F NMR (CDCl$_3$, 376 MHz, ppm): δ −105, −110, −115, −117, −120 and −121. IR (KBr, cm^{-1}): 3066, 1597, 1480, 1227, 929, 855, 767, 680 and 593.

3. Results and discussion

3.1. Synthesis and characterization of 1,2-bis(4-(4-fluorobenzoyl)phenoxy)-hexafluorocyclobutane 6

The synthesis of compound **6** was outlined in Scheme 1. Compound **2** was prepared from 4-bromophenol using published procedures [5–7]. Treatment of **3** with t-BuLi followed by addition of DMF gave known aldehyde **3** [12]. Oxidation of **3** with KMnO$_4$ in water and pyridine gave **4** in quantitative yield. Then, 4,4'-((1,2,3,3,4,4-hexafluorocyclobutane-1,2-diyl)bis(oxy))-dibenzoic acid **4** was converted into corresponding chloride **5** with thionyl chloride. As compound **5** is readily hydrolyzed to acid in air, it was prepared and immediately used without further isolation and
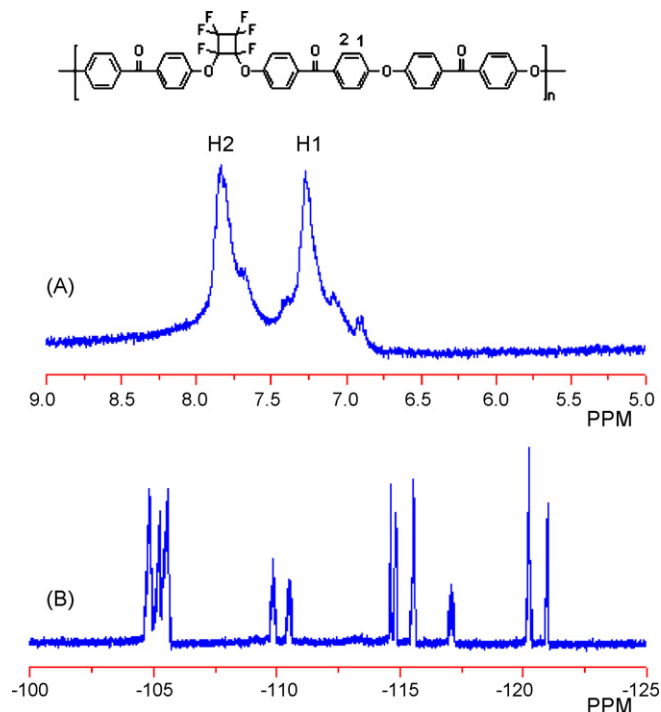
Scheme 1. Synthesis of 1,2-bis(4-(4-fluorobenzoyl)phenoxy)-hexafluorocyclobutane **6**.

purification [14]. The next step involved a Friedel–Crafts acylation reaction between **5** and fluorobenzene. Typically, anhydrous aluminium trichloride (4.0 equiv.) was used as a catalyst and fluorobenzene (10.0 equiv.) was used as a reactant and solvent. The crude product was purified by flash column chromatography, and then recrystallized twice to afford polymer grade monomer **6** in 42% yield. It is noteworthy that hexafluorocyclobutyl fluorine signals in ^{19}F NMR (between −115 and −121 ppm) of compound **6** appear downfield than that of compounds **2**, **3** and **4** (between −126 and −132 ppm). This result showed that 4-fluorobenzyl group has more electron-withdrawing character than that of bromo and formyl groups.

3.2. Synthesis of poly(aryl ether)s

The polymerization of the aromatic difluoride **6** with aromatic bisphenols (resorcinol and DHBP) was carried out in DMAc/toluene solvent mixture in the presence of anhydrous potassium carbonate

as shown in Scheme 2. The reaction temperature was maintained at 140 °C and water (formed during phenoxide formation) was removed by azeotropic distillation with toluene. The reaction was allowed to continue at this temperature for 6–8 h with vigorous stirring. Upon completion of bisphenoxides formation and dehydration (6–8 h), the reaction temperature was raised to 180 °C to effect the nucleophilic displacement. High molar mass polymers were obtained within 12 h as judged by the dramatic increase of the viscosity of the reaction medium. At completion of the reaction, the hot reaction mixture was poured into a mixture of methanol and water. The polymer that coagulated was filtered and washed with methanol, and then washed several times with hot water to remove any inorganic impurities, dried in a vacuum at 110 °C for 24 h.

The molecular weights of the fluorinated poly(aryl ether)s determined by GPC in DMF using polystyrene as standard are in the range of 10253–13494 for Mn and of 11277–14519 for Mw with the Mw/Mn values of 1.08–1.10 (Table 1). This indicated that the

Scheme 2. Synthesis of fluorinated poly(aryl ether)s.

Table 1
GPC analysis of the fluorinated poly(aryl ether)s

Polymer	Mn	Mw	Mw/Mn
P1	13,494	14,519	1.08
P2	10,253	11,277	1.10

GPC in DMF vs. polystyrene at 35 °C.

Table 2
Solubility of the fluorinated poly(aryl ether)s[a]

Polymer	DMF	NMP	DMAc	DMSO	CHCl₃	THF	30% HCl	30% NaOH	Conc. H₂SO₄
P1	++	++	++	++	++	++	−−	−−	+−
P2	++	++	++	++	++	++	−−	−−	+−

[a] ++: Soluble at room temperature in 2 h; +−: soluble at room temperature in 12 h; −−: insoluble at refluxing.

Fig. 1. FT-IR spectra of the fluorinated poly(aryl ether)s.

medium molecular weight polymers were formed. The Mn and Mw of polymer **P1-2** were not high, which might be due to the low reactivity of the monomer **6**. The chemical structures of poly(aryl ether)s were characterized by FT-IR, ^{1}H NMR, and ^{19}F NMR. All of the poly(aryl ether)s showed characteristic absorption bands at 1227–1241 cm^{-1} and 1653–1655 cm^{-1} due to aryl ether linkages and C=O, respectively, and a strong sharp band near 928 cm^{-1} is

diagnostic for the presence of hexafluorocyclobutyl group. This easily resolved absorption has proven to be a useful analytical tool since this region in the IR is rarely occupied by other functionalities [3] (Fig. 1). In addition, the hexafluorocyclobutyl groups in polymer **P1** were characterized further by ^{19}F NMR (Fig. 2), in which fluorine signals of these groups were presents from −109 to −121 ppm. The signals at −105 ppm could be attributable to the terminal fluorine group of polymer. The ^{19}F NMR chemical shifts of polymer **P1** was similar to that of monomer **6**. As polymer **P1** was obtained by the coagulation from polymer solution followed by wash with methanol, there was no unreacted monomer **6** in polymer **P1**.

3.3. Solubility of poly(aryl ether)s

Table 2 shows the solubility of the fluorinated poly(aryl ether)s determined quantitatively by dissolving 0.1 g of solid polymer in 1.0 g of organic solvents. It can be seen that the perfluorocyclobutyl-containing fluorinated poly(aryl ether)s possessed good solubility in common organic solvents, such as NMP, DMAc, DMSO, DMF, THF and chloroform. The good solubility could be resulted from the presence of PFCB group and aryl ether linkages [15].

The WAXD patterns of the fluorinated poly(aryl ether)s are shown in Fig. 3. They showed that both the polymers were amorphous. No crystalline or semi-crystalline phase was detected. This might be interpreted by the presence of perfluorocyclobutyl groups, which decreased the intra- and inter-polymer chain interactions, resulting in loose polymer chain packaging and aggregates. The amorphous phase endows some special features to poly(aryl ether)s, such as good solubility in solvents.

3.4. Thermal properties of poly(aryl ether)s

Thermal properties of the fluorinated polymers were evaluated by means of thermo-gravimetric analysis (TGA). The results are
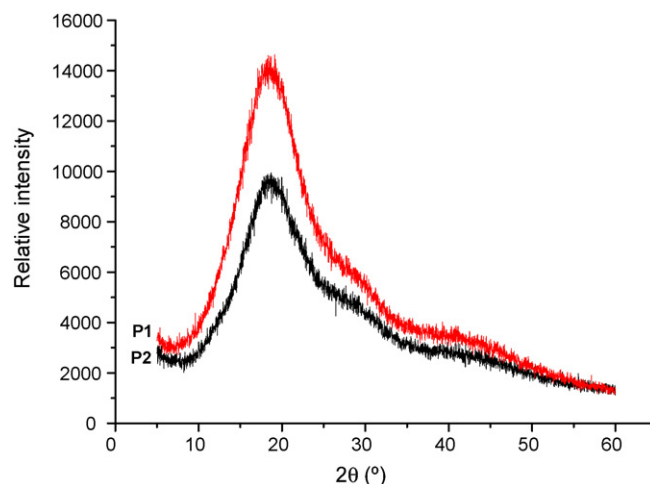

Fig. 2. ^{1}H NMR (**A**) and ^{19}F NMR (**B**) spectra of **P1**.

Fig. 3. Wide-angle X-ray diffraction patterns of the poly(aryl ether)s.

Table 3
Thermal properties of the fluorinated poly(aryl ether)s

Polymer	T_f (°C)[a]	T_s (°C)[a]	R_w (%)[b]
P1	285	341	51.5
P2	279	324	33.1

[a] Measured at 10 °C/min in N_2; T_f: 5% weight loss at the first stage; T_s: 10% weight loss at the second stage.
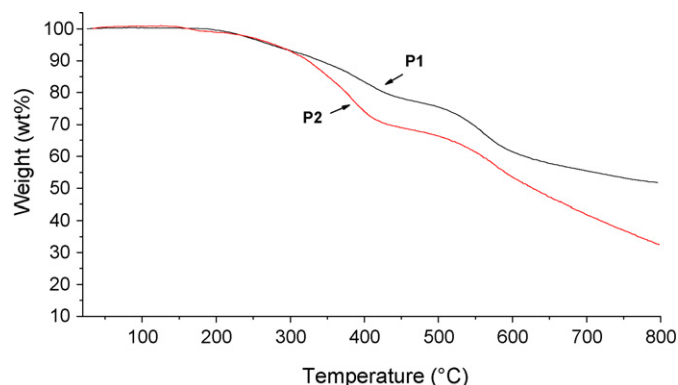[b] Residual weight retention at 800 °C.

Fig. 4. TGA cures of the poly(aryl ether)s in nitrogen.

listed in Table 3. Fig. 4 shows TGA curves of the fluorinated poly(aryl ether)s. The weight loss at 300 °C in TGA cures could be due to the decomposition of the oligomers at a lower temperature or the reaction between the terminal hydroxyl and terminal fluorine group at a relative high temperature. The temperatures corresponding to the second weight-loss stage were determined in the range of 500–550 °C in nitrogen, at which the main polymers were decomposed. In addition, the char yields of the fluorinated poly(aryl ether)s at 800 °C under nitrogen are 33.1–51.5%. The high residue at 800 °C is attributed to the presence of carbonyls of the polymers' backbone and fluorine [16]. The results of thermal analysis demonstrate that the resulting poly(aryl ether)s should have good thermal stability.

4. Conclusion

A novel fluorinated monomer, 1,2-bis(4-(4-fluorobenzoyl)-phenoxy)-hexafluorocyclobutane **6** was prepared by the Friedel–Crafts acylation reaction between **5** and fluorobenzene. The aromatic nucleophilic substitution reaction between 1,2-bis(4-(4-fluorobenzoyl)phenoxy)-hexafluorocyclobutane and aromatic bisphenols provides novel poly(aryl ether)s containing the PFCB group. The aryl ether linkages and PFCB group serve to increase the solubility of polymers. Meanwhile, the resulting polymers possessed good thermal stability and reasonable molecular weight.

Acknowledgments

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