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Novel poly(aryl ether)s containing benzimidazole pendants derived from 1,4-bis(2-benzimidazolyl)-2,5-difluorobenzene

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Abstract A new difluoride monomer bilaterally substituted with rigid benzimidazole groups was synthesized efficiently. A series of new poly(aryl ether)s (PAEs) containing benzimidazole pendants were prepared from the novel difluoride monomer with various commercially available aromatic bisphenols using nucleophilic aromatic substitution reaction. All the PAEs show high glass transition temperatures ($T_g > 205$ °C), excellent thermal stability ($T_d > 420$ °C), and good solubility in common organic solvents.

Introduction

Poly(aryl ether)s (PAEs) are well-recognized high-performance engineering thermoplastics due to their excellent physical properties such as high level of strength, high glass transition temperature, good electrical properties, thermo-oxidative stability, and chemical resistance [1–6]. PAEs containing heterocyclic rings have been extensively investigated in the past decades. Examples of these high-temperature heterocycle-containing polymers include poly(aryl ether-oxadiazoles) [7, 8], poly(ary1 ether-benzoxazoles) [9], poly(ary1 ether-benzothiazoles) [10], poly(ary1 ether-phenylquinoxalines) [11, 12], and poly(ary1 ether-benzimidazoles) [13–15]. The interest in these polymers is due to the heterocycle's tendency to enhance adhesive and mechanical properties as well as glass transition temperatures of the PAEs while retaining thermal stability and processability [16].

PAEs with benzimidazole pendant groups will be expected to be good candidates for high-performance thermoplastics [17, 18]. In the field of making poly(ary1 ether-benzimidazoles), researches are usually focused on the syntheses and properties of PAEs bearing benzimidazole groups in the backbone of polymers; however, the syntheses and properties of PAEs with pendant benzimidazole groups are little known. It implies that the relationship between the structure and the properties of PAEs containing benzimidazole pendants should be further investigated. In this article, we reported the syntheses of a new series of PAEs containing benzimidazole pendants. The synthesized PAEs were characterized and their properties including thermal stability, solubility, and morphology were also discussed herein.

Experimental section

Materials

2,5-Difluoroterephthalic acid (DFTA) was synthesized according to our previously reported method [19]. 1-Methyl-

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2-pyrrolidinone (NMP) was stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4 Å molecular sieves. 4,4′-Isopropylidenediphenol (bisphenol-A) and 4,4′-(Hexafluoroisopropylidene)diphenol (Bisphenol AF) were recrystallized from toluene. 4,4′-Dihydroxybenzophenone (DHBP) and 4,4′-dihydroxydiphenylsulfone (bisphenol-S) were recrystallized from acetone and ether/hexanes. *o*-Phenylenediamine was obtained from Sinopharm Chemical Reagent Co., Ltd. Other reagents or materials were used as-received.

Measurements

Elemental analysis was carried out on a Carlo-Erba1106 system. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. 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), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker AV 400 spectrometer system. 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, a Waters 2487 dual-wavelength absorbance detector, and a set of Waters Styragel columns (HR3, HR4, and HR5, 7.8 × 300 mm^2). GPC measurements were carried out at 35 °C using THF 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 100 °C and held for 5 min to remove thermal history, then quenching to −35 °C followed by heating to 300 °C. A heating rate of 10 °C/min was used at all cases. 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 under nitrogen atmosphere from 25 to 800 °C. The wide-angle X-ray diffraction (XRD) was conducted on a Rigaku D/max-2500 X-ray diffractometer with Cu/Kα1 radiation, operated at 40 kV and 300 mA.

Synthesis of 1,4-bis(2-benzimidazolyl)-2,5-difluorobenzene

DFTA (6.06 g, 30 mmol), *o*-phenylenediamine (6.48 g, 60 mmol), and polyphosphoric acid (PPA) (60 g) were added in a 100-mL three-necked flask. The flask was heated to 200 °C and stirred for 6 h under nitrogen. The reaction mixture was cooled to room temperature and poured into 600 g of ice/distilled water with stirring and neutralized slowly by 10 wt% of sodium bicarbonate ($NaHCO_3$) aqueous solution. Afterward, the precipitate was collected by filtration and washed with water. The crude product was decolorized with activated charcoal in *N*,*N*-dimethylformamide (DMF) (60 mL). After removing the charcoal, the DMF solution was concentrated to a volume of about 40 mL and chilled in a cooled environment. The resulting crystals were collected by filtration to give 9.34 g (90%) of 1,4-bis(2-benzimidazolyl)-2,5-difluorobenzene (BIDF) as pale yellow crystalline solid. M.p.(DSC): 351 °C. IR (KBr, cm^{-1}): 3054, 1621, 1586, 1548, 1471, 1399, 1341, 1229, 1158. ^{1}H NMR (DMSO-d_6, ppm): δ 12.80 (s, 2H), 8.24 (t, $J = 8.0$ Hz, 2H), 7.75 (d, $J = 8.0$ Hz, 2H), 7.63 (d, $J = 8.0$ Hz, 2H), 7.32–7.25 (m, 4H). ^{19}F NMR (DMSO-d_6, ppm): δ −118.7 (t, $J = 7.5$ Hz, 2F). ^{13}C NMR (DMSO-d_6, ppm): δ 112.1, 119.1, 120.3, 122.2, 123.3, 135.1, 142.9, 144.6, 154.0, 156.5. MS (EI): m/z 346 (M$^+$), 328, 255, 173, 91, 64. Anal. Calcd. for $C_{20}H_{12}F_2N_4$: C, 69.36, H, 3.49, N, 16.18. Found: C, 69.64, H, 3.54, N, 16.42.

General procedure for the syntheses of PAEs

The following procedure is for the preparation of polymer P-1 and is a representative for the preparation of the rest of the polymers. In a three-necked reaction flask equipped with a nitrogen inlet and Dean-stark trap fitted with a condenser and nitrogen outlet, 4,4′-(Hexafluoroisopropylidene)diphenol (0.84 g, 2.5 mmol) was dissolved in 30 mL of NMP, and then K_2CO_3 (0.69 g, 5 mmol) was added under nitrogen purge. Then 30 mL of toluene was added. The reaction mixture was heated to reflux (140 °C) and stirred at this temperature for 6–8 h to dehydrate the system. Upon dehydration, the mixture was cooled to 80 °C. BIDF monomer (0.865 g, 2.5 mmol) was added subsequently and stirred for 20 h at 180 °C. Then the reaction mixture was precipitated into 400 mL of water with 5% of acetic acid. The precipitate was filtered and reprecipitated from THF into methanol, which was filtered, washed, and dried in vacuum at 110 °C for 24 h.

Polymer P-1: 85% yield; IR (KBr, cm^{-1}): 3064, 1615, 1518, 1473, 1251, 1199, 1171, 965. ^{1}H NMR (DMSO-d_6, ppm): δ 12.80 (s, 2H), 8.24 (t, $J = 8.0$ Hz, 2H), 7.76–7.69 (m, 4H), 7.65–7.60 (m, 4H), 7.37–7.25 (m, 8H). ^{19}F NMR (DMSO-d_6, ppm): δ −63.27 (s, 6F).

Polymer P-2: 82% yield; IR (KBr, cm^{-1}): 3060, 2965, 1613, 1548, 1486, 1378, 1270, 1105, 849. ^{1}H NMR (DMSO-d_6, ppm): δ 12.61 (s, 2H), 8.24 (t, $J = 8.0$ Hz, 2H), 7.75–7.57 (m, 4H), 7.49–7.35 (m, 4H), 7.27–7.21 (m, 8H), 1.69 (s, 6H).

Polymer P-3: 90% yield; IR (KBr, cm^{-1}): 3054, 1645, 1598, 1470, 1374, 1312, 1270, 922. ^{1}H NMR (DMSO-d_6, ppm): δ 12.63 (s, 2H), 8.24 (t, $J = 8.0$ Hz, 2H), 7.87–7.72 (m, 4H), 7.68–7.59 (m, 4H), 7.37–7.24 (m, 8H).

Polymer P-4: 91% yield; IR (KBr, cm^{-1}): 3058, 1581, 1490, 1445, 1378, 1283, 1148, 839. ^1H NMR (DMSO-d_6, ppm): δ 12.81 (s, 2H), 8.25 (t, $J = 8.0$ Hz, 2H), 7.85–7.69 (m, 4H), 7.42–7.38 (m, 4H), 7.17–7.11 (m, 8H).

Results and discussion

Synthesis of BIDF

The synthetic route of a new aromatic difluoride monomer BIDF was outlined in Scheme 1. The precursor DFTA was prepared through multistep reaction starting from 2,5-dimethyl-1,4-benzenediamine according to our previously reported method [19]. Monomer BIDF was synthesized by PPA catalyzed condensation reaction between *o*-phenylenediamine and DFTA in high yield (90%).

The composition and structure of BIDF was confirmed by MS, FT-IR, ^1H NMR, ^{19}F NMR, ^{13}C NMR, and elemental analysis. In the IR spectra of DFTA and BIDF, the C–F stretching absorptions were detected in the range of 1300 to 1100 cm^{-1} (Fig. 1). For BIDF, the hetero-ring stretching associated with the imidazole ring can be clearly identified by the strong C=N absorption band at 1621 cm^{-1} and the characteristic absorption band for carbonyl group at 1691 cm^{-1} was disappeared, which indicated that DFTA was converted into BIDF completely. From the ^1H NMR spectrum (Fig. 2a) of BIDF, it can be seen that protons in imidazole ring appeared at 12.80 ppm (s, H_a, 2H); signal of 8.24 ppm (t, H_b, $J = 8.0$ Hz, 2H) belonged to protons in difluorobenzene ring; signals of 7.75 ppm (d, H_c, $J = 8.0$ Hz, 2H), 7.63 ppm (d, H_d, $J = 8.0$ Hz, 2H), and 7.32–7.25 ppm (m, H_e, 4H) belonged to the protons in benzimidazole ring. ^{19}F NMR spectrum provided a triplet peak at −118.7 ppm (t, $J = 7.5$ Hz, 2F) for BIDF (Fig. 2b). ^{13}C NMR spectrum also showed all of the ten different carbon atoms expected for the monomer's structure (Fig. 2c). The elemental analysis results of BIDF were matched with the theoretical values which further confirmed the successful synthesis of the high-purity monomer.

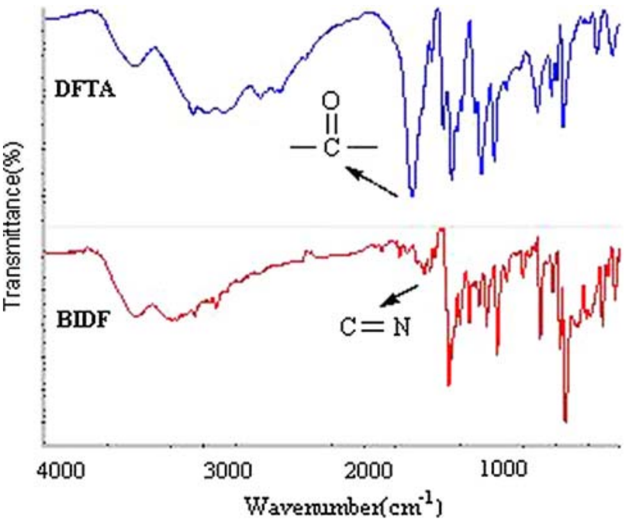
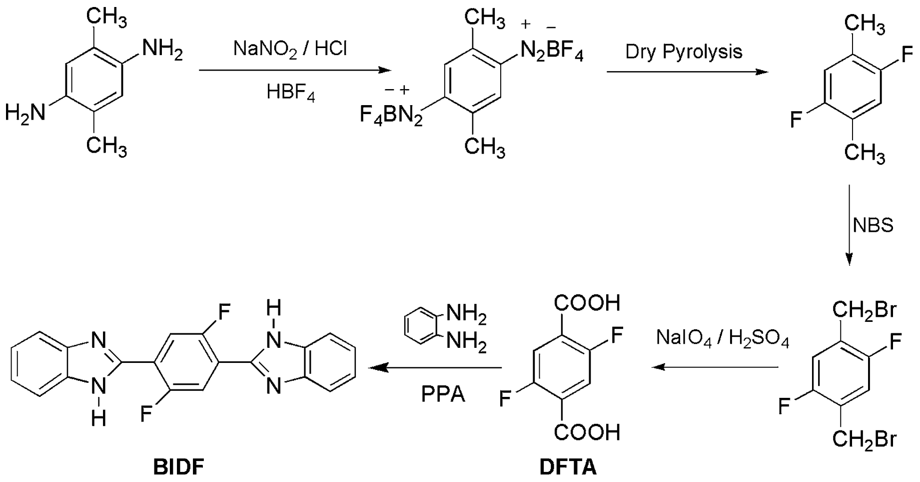


Fig. 1 FT-IR spectra of DFTA and BIDF

Polymer synthesis

PAEs containing benzimidazole pendants were achieved by the aromatic nucleophilic substitution reaction of BIDF with various commercially available aromatic bisphenols in the presence of excess potassium carbonate in NMP (Scheme 2). The reaction temperature was firstly maintained at 140 °C for 6–8 h to remove water by azeotropic distillation with toluene. Upon completion of bisphenoxides formation and dehydration, monomer BIDF was then added and the reaction temperature was raised to 180 °C to accomplish the nucleophilic displacement. The resulting

Scheme 1 Synthesis of BIDF



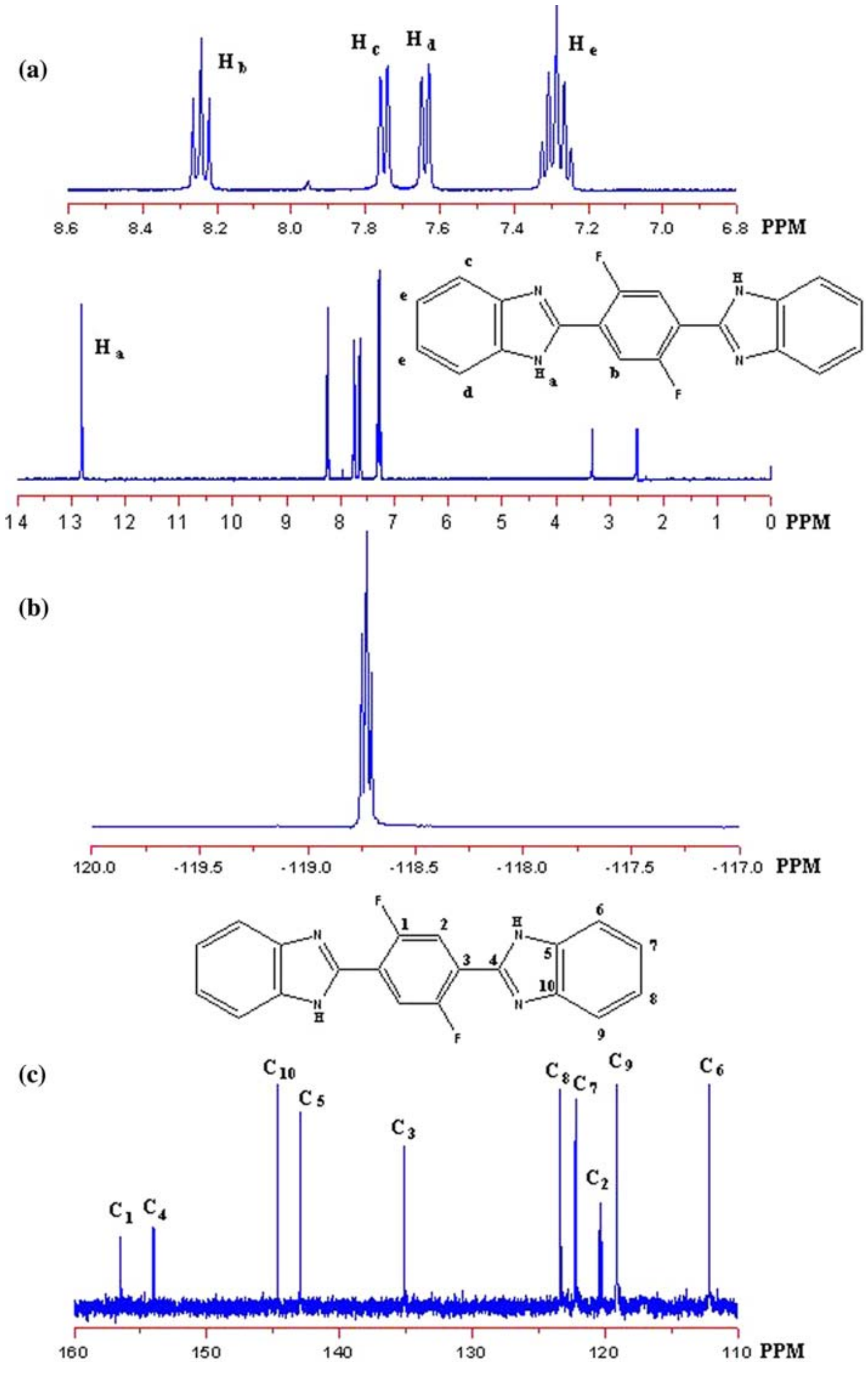
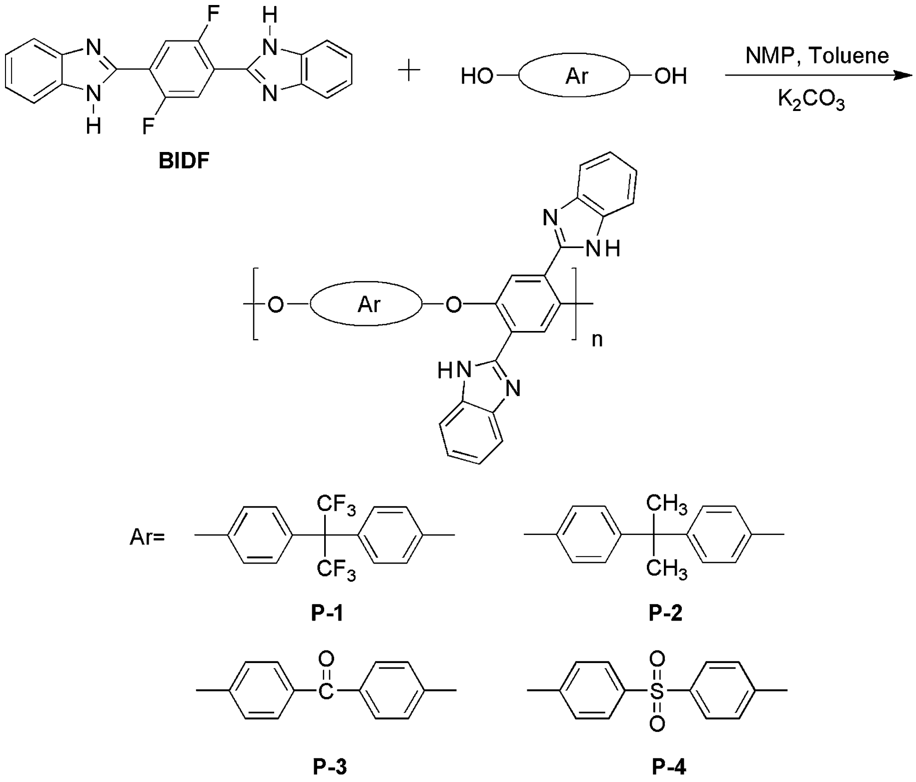


Fig. 2 **a** ^{1}H NMR, **b** ^{19}F NMR, and **c** ^{13}C NMR spectra of BIDF

viscous solution was poured into a mixture of acetic acid and water, and then the polymer was reprecipitated from THF into methanol. The polymer was collected by filtration, washed with methanol, and dried in vacuum at 110 °C for 24 h. All the polymers were light yellow solids.

The chemical structures of PAEs were confirmed by FT-IR, ^{1}H NMR, and ^{19}F NMR spectroscopies. All the polymers showed characteristic absorption band at 1230–1247 cm^{-1} due to aryl ether linkages in IR spectra (Fig. 3). In addition, the C–F multiple stretching absorptions in P-1 were detected in the range of 1300 to 1100 cm^{-1}; P-2 had characteristic absorption band at 2965 cm^{-1} due to the methyl group; P-3 possessed the characteristic absorption band at 1645 cm^{-1} due to the carbonyl group; the band at 1148 cm^{-1} was assigned to the sulfone linkage of P-4 (Fig. 3). From the ^{1}H NMR spectrum (Fig. 4a) of P-1, it

Scheme 2 Synthesis of PAEs containing benzimidazole pendants



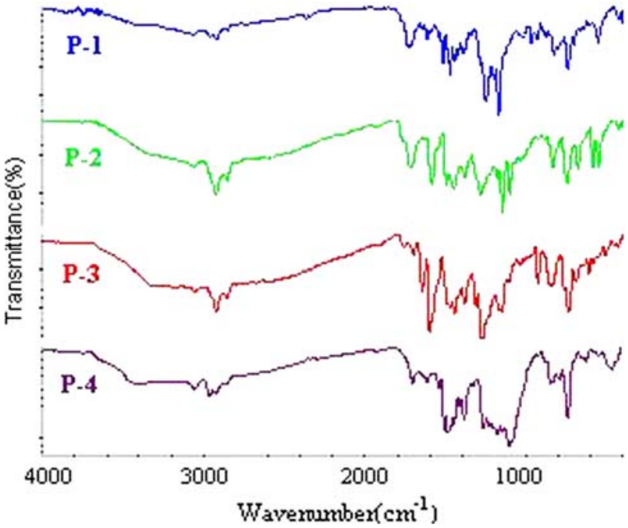


Fig. 3 FT-IR spectra of PAEs containing benzimidazole pendants

can be seen that signal of N–H in imidazole ring appeared at 12.80 ppm (s, H_a, 2H), and signals of aromatic protons appeared at 8.24 (t, H_b, 2H), 7.76–7.69 (m, $H_{c,d}$, 4H), 7.65–7.60 (m, H_e, 4H), 7.37–7.25 (m, $H_{f,g}$, 8H). ^{19}F NMR spectrum presented a signal of fluorine for trifluoromethyl group at −63.27 ppm (s, 6F) (Fig. 4b).

The inherent viscosities of PAEs were in the range of 0.21 to 0.52 dL/g while the molecular weights of the polymers determined by GPC in THF using polystyrene as standard were in the range of 13,400 to 23,800 for M_n and of 29,500 to 45,200 for M_w with the M_w/M_n values of 1.8 to 2.2 (Table 1). These results indicated a low to medium molecular weight polymer formation, which may be ascribed to the steric hindrance effect in the nucleophilic substitution reaction resulting from the bulky benzimidazole groups in BIDF monomer.

Solubility and WAXD test of PAEs

The solubilities of the polymers were examined in various organic solvents with a concentration of 8 to 10 wt%. As summarized in Table 2, all the PAEs containing benzimidazole pendants showed good solubilities in common organic solvents such as DMSO, DMF, DMAc, NMP, and THF at room temperature and they were also soluble in $CHCl_3$ upon heating. The improved solubilities of PAEs may due to the introduction of bulky benzimidazole pendants which could decrease the crystallinity of solid polymers as can be evidenced by WAXD.

Figure 5 shows the WAXD curves of the PAEs. From the figure, their diffraction patterns were broad and no real sharp peaks were observed. This demonstrates that the structures of the PAEs are amorphous in nature. The decrease in the crystallinity led to easier permeation of solvent, which in turn improved the solubilities of the PAEs.

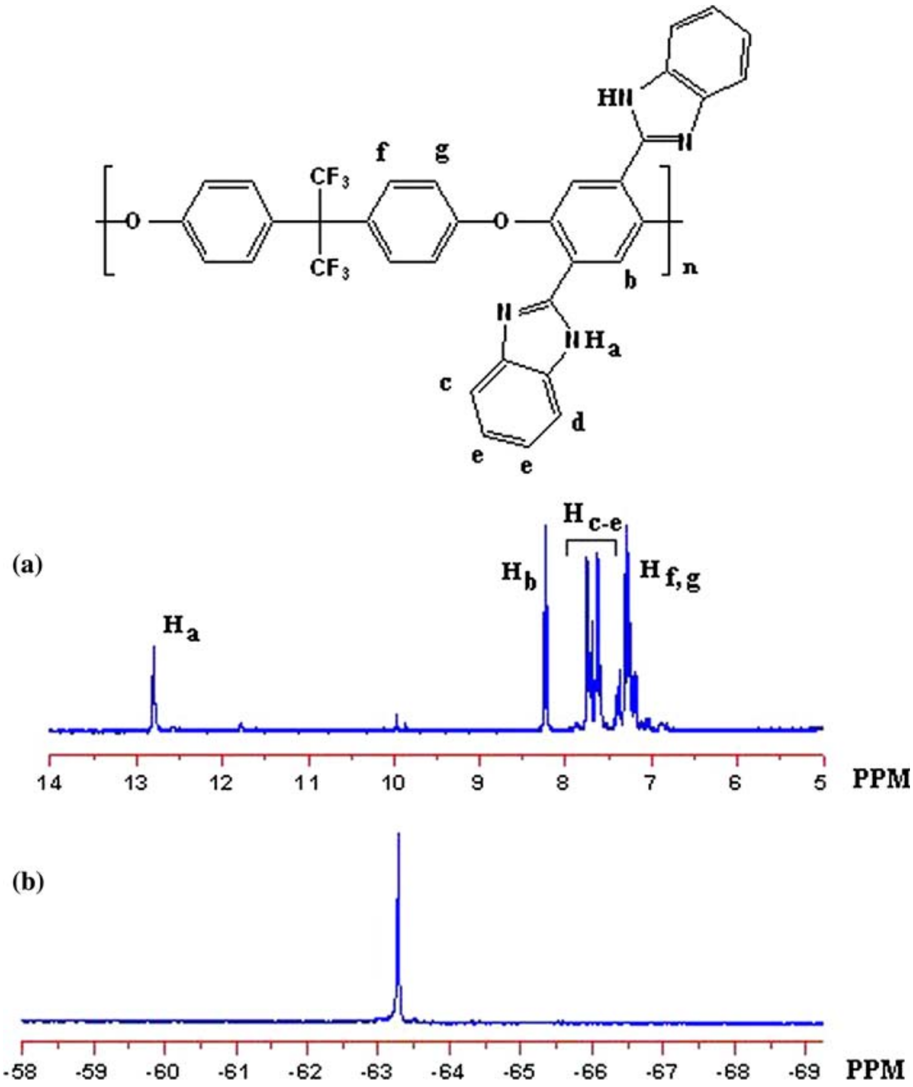


Fig. 4 ^{1}H NMR (**a**) and ^{19}F NMR (**b**) spectra of P-1

Table 1 GPC results of PAEs containing benzimidazole pendants

Polymer	η_{inh} (dL/g)[a]	M_n^b	M_w^b	M_w/M_n^b
P-1	0.25	14,900	31,200	2.1
P-2	0.21	13,400	29,500	2.2
P-3	0.47	23,200	41,700	1.8
P-4	0.52	23,800	45,200	1.9

[a] η_{inh} at 5 wt% of PAEs in NMP at 25 °C

[b] GPC in THF versus polystyrene at 35 °C

Thermal properties of PAEs

Thermal properties of PAEs were evaluated by means of DSC and TGA and the results are listed in Table 3. All the polymers exhibited no crystallization or melting transition and considerably higher T_g values than the similar PAEs containing benzoyl pendants [20] in DSC measurements. This is attributed to the more rigid structures of these polymers because of the presence of a benzimidazole unit. The comparison of the DSC curves of the PAEs series was shown in Fig. 6. The T_g ranged from 205 to 227 °C. As expected, P-2 derived from the flexible bisphenol-A exhibited lower T_g (205 °C) than that of P-3 (215 °C) or P-4 (219 °C) which derived from the relatively more rigid DHBP or bisphenol-S. P-1 showed the highest T_g (227 °C) among this series of polymers, this might be attributed to the existence of bulky trifluoromethyl moieties which inhibit free rotation of the polymer backbone to a greater extent.

The TGA curves of polymers under nitrogen atmosphere were given in Fig. 7. A slight weight loss before 400 °C in TGA curves could be detected due to trace quantities of high boiling solvent such as NMP in PAEs or the instability of the instrument which result in the fluctuation of the

Table 2 Solubility of polymers PAEs containing benzimidazole pendants

Polymer	Solvent[a]							
	DMSO	DMF	DMAc	NMP	THF	$CHCl_3$	Acetone	Toluene
P-1	++	++	++	++	++	+	−	−
P-2	++	++	++	++	++	+	−	−
P-3	++	++	++	++	++	+	−	−
P-4	++	++	++	++	++	+	−	−

[a] ++ = soluble at room temperature, + = soluble upon heating, − = insoluble on refluxing

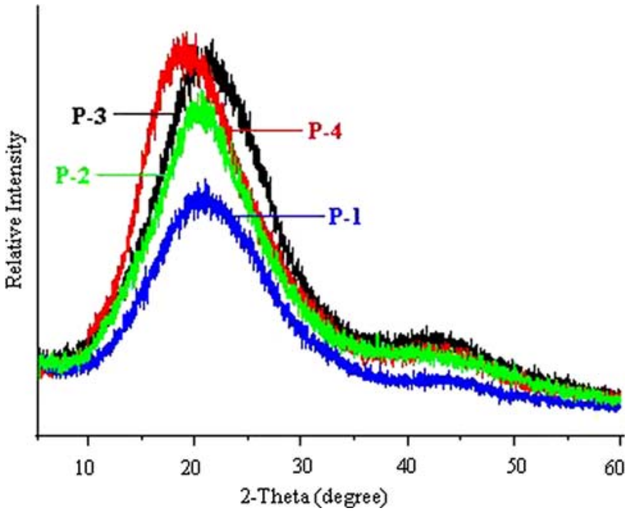


Fig. 5 Wide-angle XRD patterns of PAEs

Table 3 Thermal properties of PAEs containing benzimidazole pendants

Polymer	T_g^a (°C)	T_5^a (°C)	T_{10}^a (°C)	Char yield[b] (%)
P-1	227	458	462	30.7
P-2	205	449	454	28.0
P-3	215	467	470	21.5
P-4	219	471	479	26.9

[a] Measured at 10 °C/min in N_2; T_5, T_{10}: the decomposition temperatures at 5 and 10% weight loss

[b] Char yield at 800 °C

baseline. The temperatures corresponding to 5 and 10% weight loss were determined in the range of 449 to 471 °C and 454 to 479 °C, respectively (Table 2) for polymers. P-2 had the lowest T_5 (449 °C) and T_{10} (454 °C) due to the presence of more flexible isopropyl unit in the polymer backbone which can reduce the rigidity and stability of polymer chains. In addition, the char yields of the PAEs at 800 °C under nitrogen are 21.5–30.7%. These results of thermal analysis demonstrated that the resulting PAEs could hold excellent thermal stabilities, which would be facilitated to their applications.

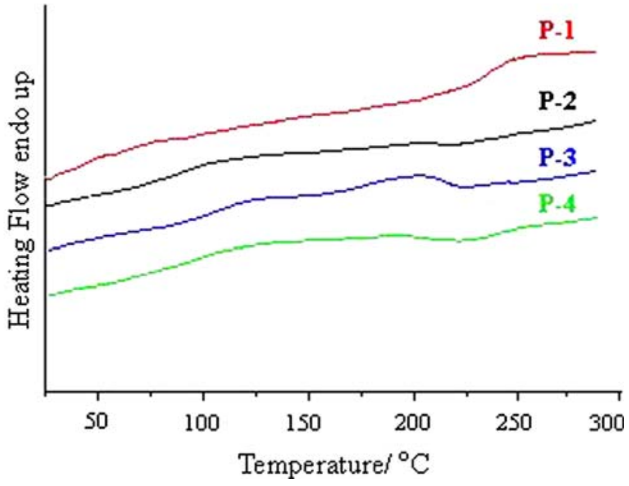


Fig. 6 DSC curves of PAEs under nitrogen

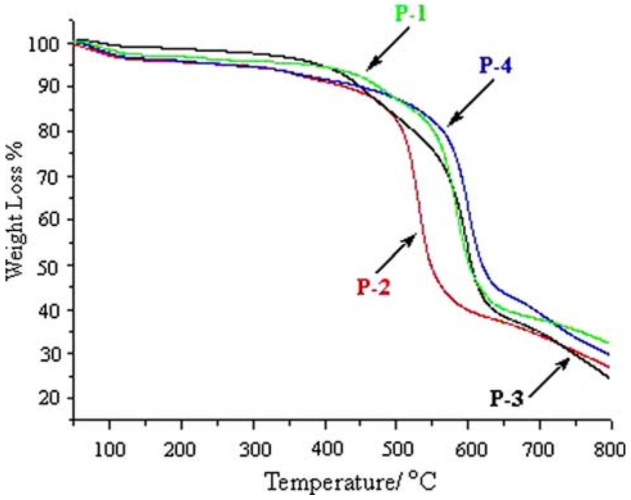


Fig. 7 TGA curves of PAEs under nitrogen

Conclusion

A novel difluoride monomer, BIDF, was prepared, characterized, and subsequently reacted with various aromatic bisphenols to prepare a series of PAEs containing benzimidazole pendants. The prepared polymers showed excellent thermal stability and very high glass transition temperatures which are comparable to those of PAE analogues.

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References

1. Hergenrother PM, Connell JW (1994) Adv Polym Sci 117:67
2. Dutta PK, Banerjee S, Maiti S (1996) In: Cheremisinoff NP (ed) Handbook of engineering polymeric materials. Marcel Dekker, New York
3. Banerjee S, Maier G, Burger M (1999) Macromolecules 32:4279
4. Qi Y, Ding J, Day M, Jiang J, Callender CL (2005) Chem Mater 17:676
5. Chikashige Y, Chikyu Y, Miyatake K (2005) Macromolecules 38:7121
6. Banerjee S, Maier G (1999) Chem Mater 11:2179
7. Heddck JL (1991) Polym Bull 25:543
8. Lu JP, Miyatake K, Hlil AR, Hay AS (2001) Macromolecules 34:5860
9. Hilborn JG, Labadie JW, Hedrick JL (1990) Macromolecules 23:2854
10. Maier G, Hecht R (1995) Macromolecules 28:7558
11. Connell JW, Hereenrother PM (1989) Polym Mater Sci Eng 60:527
12. Hedrick JL, Labadie JW (1988) Macromolecules 21:1883
13. Foster RT, Marvel CS (1965) J Polym Sci Part A Polym Chem 3:417
14. Chen CC, Wang LF, Wang JJ, Hsu TC (2002) J Mater Sci 37:4109. doi:10.1023/A:1020079617880
15. Kim TH, Kim SK, Lim TW, Lee JC (2008) J Membr Sci 323:362
16. Hamciuc C, Hamciuc E, Bruma M, Klapper M, Pakula T, Demeter A (2001) Polymer 42:5955
17. Wright JB (1951) Chem Rev 48:397
18. Addision AW, Rao TN, Wahlgren CG (1983) J Heterocycl Chem 20:1481
19. Huang XS, Qing FL (2008) J Fluorine Chem 129:1076
20. Person D, Cassidy PE, Fitch JW (1996) React Funct Polym 30:229