

## New Soluble Fluorinated Polyimides

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**Abstract:** The synthesis and properties of a class of soluble fluorine-containing aromatic polyimides are described. The polyimides show desirable features of materials for microelectronics applications.

**Keywords:** Soluble polyimides.

Aromatic polyimides have been widely used in aerospace, electrical and electronic applications due to their outstanding thermal stability, mechanical strength at elevated temperature and electrical properties<sup>1-3</sup>. However, polyimide materials are usually difficult to fabricate owing to their insolubility in most organic solvents and infusibility. Besides solubility, low moisture uptake of polyimide is also a major concern for microelectronics and optical applications. The present article describes the synthesis and characterization of a series of soluble, low moisture uptake polyimides derived from 1,4-bis (4-amino-2-trifluoromethylphenoxy)benzene and various aromatic tetracarboxylic dianhydrides.

### Experimental

#### *Measurements*

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Unity 200 spectrometer operating at 200 MHz in CDCl<sub>3</sub>, or DMSO-*d*<sub>6</sub>. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a Perkin-Elmer 7 series thermal analysis system in air at a heating rate of 10 °C/min.. FT-IR spectra were obtained with a Perkin-Elmer 782 Fourier transform spectrophotometer. Mass spectra were obtained on AEI MS-50 mass spectrometer. Tensile strength was obtained with 0.60 cm wide specimens in accordance with GB 1447-83 at rate of 5.0 mm min<sup>-1</sup>.

#### *Monomer Synthesis*

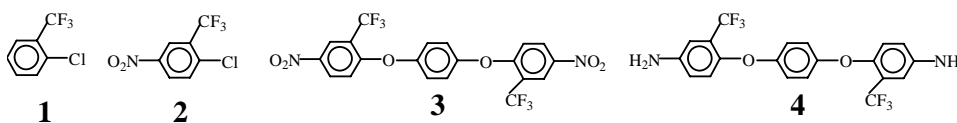
2-Chloro-5-nitro-trifluoromethylbenzene **2**<sup>4</sup>. A mixture of concentrated HNO<sub>3</sub>(45ml) and concentrated H<sub>2</sub>SO<sub>4</sub>(45ml) was added dropwise into a solution containing 54.2 g of 2-chloro-trifluoromethylbenzene **1** in 75 ml of concentrated H<sub>2</sub>SO<sub>4</sub> at 15°C. The crude product was purified by vacuum distillation at 103-104 °C/ 5-10

mmHg to afford 55.9g (84%) of 2-chloro-5-nitro-trifluoromethylbenzene **2**. IR (neat) 3113, 3044, 1944, 1255, 890, 843, 740  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  ppm. 8.56(s, 1H), 8.39(d, 2H), 7.76(d, 2H) Anal. Calcd for  $\text{C}_7\text{H}_3\text{ClF}_3\text{NO}_2$ : C, 37.25; H, 1.33; N, 6.21. Found: C, 37.16; H, 1.41; N, 6.11

1,4-bis(4-Nitro-2-trifluoromethylphenoxy)benzene **3**. A mixture of 250g (1.11mol) of **2**, 58.1g (0.53mol) of 1,4-hydroquinone, 111g (0.8mol) of anhydrous potassium carbonate and 423 mL of DMAc was stirred and heated to 130-135  $^\circ\text{C}$  under nitrogen for 24 hours. The mixture was poured into an excess amount of water. The precipitate was collected by filtration, washed with water. The product was recrystallized from 2-methoxyethanol to give gray needle-like crystals: 221.6g (86%); m. p. 216.7  $^\circ\text{C}$  (DSC in air); IR (KBr): 3445, 3119, 3088, 1621, 1598, 1532, 1480, 1335, 1287, 1252, 1049, 874, 840  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  ppm 8.52(dd, 2H), 8.44(d, 2H), 7.39 (s, 4H), 7.24 (d, 2H); MS (EI,  $m/z$ , % relative intensity): 488 ( $\text{M}^+$ , 100). Anal. Calcd for  $\text{C}_{20}\text{H}_{10}\text{F}_6\text{N}_2\text{O}_6$ : C, 49.18; H, 2.05; N, 5.74. Found: C, 48.98; H, 2.06; N, 5.85

1,4-bis(4-Amino-2-trifluoromethylphenoxy)benzene **4**. A mixture of 7.2 mL of concentrated HCl and 30 mL of 50% aqueous ethanol was added slowly to a mixture of 146.4 g (0.3 mol) of **3**, 100.6 g (1.8 mol) of reduced iron and 150 mL of 50% aqueous ethanol. The mixture was stirred under reflux for 2 hours, and to this mixture was then added slowly 8 mL of ammonium hydroxide solution. The mixture was filtered thermally and then removal of the solvent afforded a light-yellow solid, which was further purified by recrystallization from ethanol/water: 103 g (80%); m. p. 133.9  $^\circ\text{C}$  (DSC in air); IR (KBr): 3477, 3449, 3054, 1632, 1491, 1451, 1341, 1260, 1221, 1046, 871, 843, 828  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  6.94(d, 2H), 6.88(s, 4H), 6.80-6.84 (d, 2H), 6.40-6.76 (dd, 2H), 3.61 (s, 4H) ppm; MS (EI,  $m/z$ , % relative intensity) 428 ( $\text{M}^+$ , 100).  $^{13}\text{C NMR}$ ( $\text{CDCl}_3$ ):  $\delta$  153.8, 145.2, 143.8, 132, 126.2, 122.4, 121.8, 121.1, 121.0, 120.5, 119.0, 118.2, 115.5, 111.0 ppm. Anal. Calcd for  $\text{C}_{20}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_2$ : C, 56.07; H, 3.27; N, 6.54. Found: C, 56.27; H, 3.32; N, 6.58.

**Scheme 1.** Structures of Compound **1**, **2**, **3** and **4**

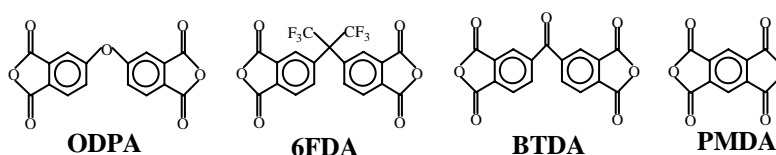


#### *Synthesis of Polyimide*

Polyimide **1**. Diamine **4** (2.8998g, 6.77mmol) was dissolved into 40 mL of NMP. To this was added ODP (2.1002g, 6.77mmol) and additional 3.8 mL of NMP. The solution was stirred at room temperature under argon for 24 hours to yield a viscous polyamic acid (PAA) solution. The polyamic acid was converted into polyimide using thermal imidization or chemical imidization method. For thermal imidization method, polyamic acid solution was cast onto a clean glass plate and thermally cured (80  $^\circ\text{C}/1\text{h}$ , 120  $^\circ\text{C}/1\text{h}$ , 180  $^\circ\text{C}/1\text{h}$ , 250  $^\circ\text{C}/4\text{h}$ , and 300  $^\circ\text{C}/3\text{h}$ ) to produce a fully imidized polyimide film. The chemical imidization was carried out by adding an equimolar mixture of acetic anhydride

and pyridine into the polyamic acid solution with mechanical stirring at ambient temperature for 2 h, and then heated at 60 °C for 4 h. The polyimide solution was poured into methanol. The precipitate was collected by filtration, washed thoroughly with methanol and dried at 80 °C in vacuum to give Polyimide **1**. IR (KBr) 1782, 1725, 1610, 1489, 1436, 1376, 1319, 1239, 1053, 962, 907, 825, 743 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.06(d, 2H), 7.85(s, 2H), 7.66(d, 2H), 7.63(d, 2H), 7.58(s, 2H), 7.25(s, 4H), 7.18(d, 2H) ppm; Anal. Calcd for C<sub>36</sub>H<sub>16</sub>F<sub>6</sub>N<sub>2</sub>O<sub>7</sub>: C, 61.53; H, 2.28; N, 3.99. Found: C, 61.22; H, 2.64; N, 4.05.

**Scheme 2.** Structures of the Aromatic Tetracarboxylic Dianhydrides



Polyimide **2** (6FDA/diamine **4**), Polyimide **3** (BTDA/diamine **4**) and Polyimide **4** (PMDA/diamine **4**) were prepared in the same method as Polyimide **1**.

## Results and Discussion

**Thermal Properties** The thermal properties of these polyimides are investigated by means of TGA and DSC. The decomposition temperature, the temperature at 5% weight loss and 10% weight loss are summarized in **Table 1**. Clearly, the differences in TGS can be attributed to the rigidity of the polymer chains.

**Table 1.** Thermal Properties of Polyimides

	Polyimide <b>1</b>	Polyimide <b>2</b>	Polyimide <b>3</b>	Polyimide <b>4</b>
T <sub>d</sub> (°C)	555	607	609	599
T <sub>5%</sub> (°C)	552	599	603	541
T <sub>10%</sub> (°C)	571	623	628	598
T <sub>g</sub> (°C)	255	229	244	292

**Mechanical and Electrical Properties** Thin films (6.35 x 127 mm) were tested for tensile properties in Instron instrument at 25 °C. The films had tensile strength of 83-137 MPa, elongation at break of 10-27%, and tensile modulus of 1.6-2.3 GPa. The electric properties of polyimide films were also measured. The surface resistance and volume resistance were at level of 10<sup>14-15</sup> Ω and 10<sup>15-16</sup> Ω·cm, respectively. The dielectric constant was at 2.8-2.9 at 1 kHz and the dissipation factor at 3-5 x 10<sup>-3</sup>.

**Solubility** All of the polyimides can be dissolved both in NMP and DMAc at a solid content of 0.5g/100ml even though the samples were thermally treated to 300 °C at such high temperature some of crosslinking in the polymer could occur.

**Moisture uptakes and Hydrolytic resistance** The moisture uptake of the polyimides was as low as 0.4-0.5 % except for Polyimide **3** which showed 0.71-0.82 % of moisture

absorption. This feature is very important for microelectronics applications such as passivation film and interlayer dielectrics in MCM-D.

### Conclusion

1,4-bis(4-Amino-2-trifluoromethylphenoxy)benzene has been synthesized from 1-trifluoromethyl-2-chlorobenzene and polymerized with dianhydrides to afford polyimides. The introduction of trifluoromethyl groups in the ether-bridged diamine component of polyimides results in dramatic changes in their properties, especially in the improvement of solubilities and lowering of the moisture uptakes. The polyimides showed excellent thermal stabilities, balanced mechanical properties, good electrical properties and excellent hygrothermal stabilities.

### Acknowledgment

Funding from the National Natural Science Foundation of China (NSAC) for Distinguished Young Scholars (Project No. 59925310 ) is gratefully acknowledged.

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Received 22 May 2000