

Synthesis and Properties of Novel Aromatic Polyamides Derived from 2,2-Bis[4-(4-amino-2-fluorophenoxy)phenyl]hexafluoropropane and Aromatic Dicarboxylic Acids

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ABSTRACT: A series of polyamides were synthesized by the direct polycondensation of 2,2-bis[4-(4-amino-2-fluorophenoxy)phenyl]hexafluoropropane with various commercially available dicarboxylic acids such as terephthalic acid, isophthalic acid, 5-*t*-butyl isophthalic acid, and 2,6-naphthalene dicarboxylic acid. The synthesized polyamides were soluble in several organic solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide, dimethyl sulfoxide, tetrahydrofuran, and chloroform, and they exhibited inherent viscosities of 0.42–0.59 dL/g. The polyamides exhibited weight-average molecular weights of up to 26,000, which depended on the exact repeating unit structure. These polyamides showed good thermal stability up to 440°C for a 10%

weight loss in synthetic air. The polyamides synthesized from 5-*t*-butyl isophthalic acid and isophthalic acid exhibited glass-transition temperatures of 217 and 185°C, respectively (by differential scanning calorimetry) in nitrogen. The polyamides synthesized from terephthalic acid and 2,6-naphthalene dicarboxylic acid showed melting temperatures of 319 and 385°C, respectively. The polyamides films were pale yellow, with tensile strengths of up to 82 MPa, moduli of elasticity of up to 2.3 GPa, and elongations at break of up to 9%, which depended on the exact repeating unit structure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 691–696, 2003

Key words: polyamides; strength; thermal properties

INTRODUCTION

Aromatic polyamides (aramids) belong to a class of high-performance heat-resistant materials.^{1,2} For example, Kevlar and Nomex, made out of terephthalic acid and 1,4-phenylene diamine or 1,3-phenylene diamine, respectively, have ultrahigh strengths and high moduli. These polyamides exhibit a number of useful properties, such as high thermal stability, chemical resistance, and low flammability, and excellent mechanical properties as fibers.³ However, the poor solubility and high softening temperatures or melting temperatures (T_m 's) caused by their high crystallinity and the high stiffness of the polymer backbone lead to difficult processability for these aramids. Attempts to increase the solubility of aromatic polymers have been made through the incorporation of flexible links into the main chain^{4,5} or by the replacement of symmetrical aromatic rings by unsymmetrical ones;⁶ this leads to a decrease in the crystallinity. Another approach to increasing the solubility is the introduction of bulky pendant groups into the polymer backbone.⁷

Considerable attention has been devoted to the preparation of fluorine-containing condensation poly-

mers because of their unique properties and high performance.^{8,9} Several researchers^{10–12} reported that solubility is improved with the incorporation of hexafluoroisopropylidene groups between two rigid phenyl rings in the polymer backbone.¹³

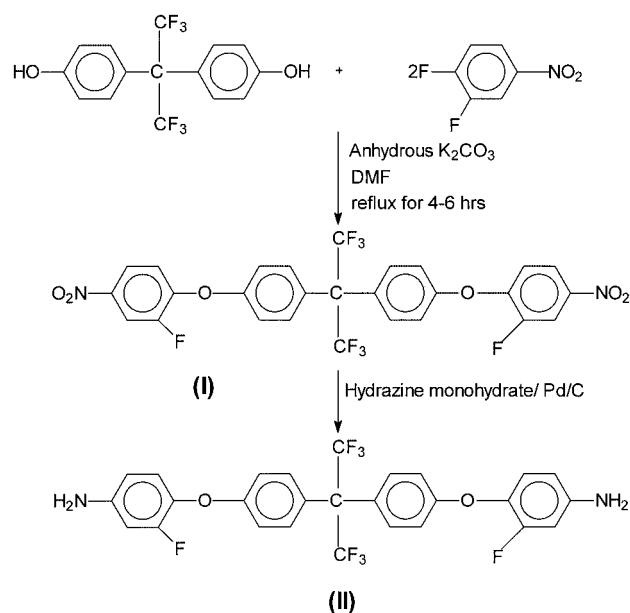
In this study, 2,2-bis[4-(4-amino-2-fluorophenoxy)phenyl]hexafluoropropane (II) was prepared by the reaction of 2,2-bis(4-hydroxy phenyl)hexafluoropropane with 3,4-difluoro nitrobenzene, which was followed by reduction. This diamino monomer was used to prepare a number of novel polyamides by its reaction with different diacids. A detailed characterization of the polyamides was performed, and the properties of the polymers were evaluated.

EXPERIMENTAL

General considerations

Elemental analysis (carbon, hydrogen, and nitrogen) was performed with a Heraeus Carlo Erba 1106 elemental analyzer. ¹H-NMR (400 MHz) and ¹³C-NMR (75 MHz) spectra were recorded on a Bruker ARX 400 instrument [0 ppm reference with tetramethylsilane (¹H-NMR and ¹³C-NMR)]. IR spectra were recorded with a Bruker IFS 55 spectrophotometer with KBr pellets. Gel permeation chromatography was obtained with a Waters instrument. Tetrahydrofuran (THF) was

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Scheme 1 Reaction scheme for the synthesis of the monomers.

used as an eluent; a Styragel HR-4 (WAT044226) column (the column temperature was maintained at 100°C) was employed. The molecular weight and polydispersity are reported versus monodisperse polystyrene standards. Differential scanning calorimetry (DSC) measurements were made on a TA Instruments DSC-2920 instrument at a heating/cooling rate of 20°C/min under nitrogen. The glass-transition temperature (T_g) was taken at the midpoint of the step transition in the second heating run. Thermogravimetry was measured on a TA Instruments model TGA-2950 thermogravimetric analyzer. A heating rate of 10°C/min was used for the determination of the decomposition temperature at a 5% weight loss under synthetic air. Isothermal gravimetry was performed at 400°C for 7 h in air on a TA 2950 instrument. The dynamic mechanical analysis (DMA) was performed on a Netzsch DMA-242 instrument in the tension mode on thin-film (80–100- μ m) samples at a heating rate of 2 K/min (1 and 10 Hz). The mechanical properties of the thin polymer films were evaluated at room temperature on a PL Thermal Sciences miniature materials tester under a strain rate of 5%/min.

Starting materials

All reagents were purchased from Lancaster, Acros, Aldrich, or Fluka Chemical Co. and used as received unless otherwise noted. *N*-Methylpyrrolidone (NMP; Fluka) and *N,N*-dimethylformamide (DMF; E. Merck, India) were purified through stirring with NaOH and were distilled twice from P₂O₅ under reduced pressure.

Synthesis of II

First step

Hexafluorobisphenol (19.80 g, 0.05 mol) in DMF (100 mL) was placed in a three-neck, round-bottom flask with a Dean-Stark trap, a magnetic stirring bar, and a nitrogen inlet. The solution was thoroughly deoxygenated with a stream of nitrogen. Anhydrous K₂CO₃ (0.1 mol) was added and followed by sufficient toluene (15–20 mL) to enable the solution to boil at 130–135°C. Under a stream of nitrogen, the mixture was brought to a boil and dewatered (1–1.5 h). After the mixture cooled at 60–70°C, 3,4-difluoro-1-nitrobenzene (19.08 g, 0.12 mol) was added, and the mixture was refluxed for 3–4 h. Subsequently, some toluene was distilled off, and mixture was poured into a stirred ice–water mixture (1.5 L). Stirring was continued for a few hours or overnight. The product (dinitro compound) was a yellow solid (yield = 95%).

Second step

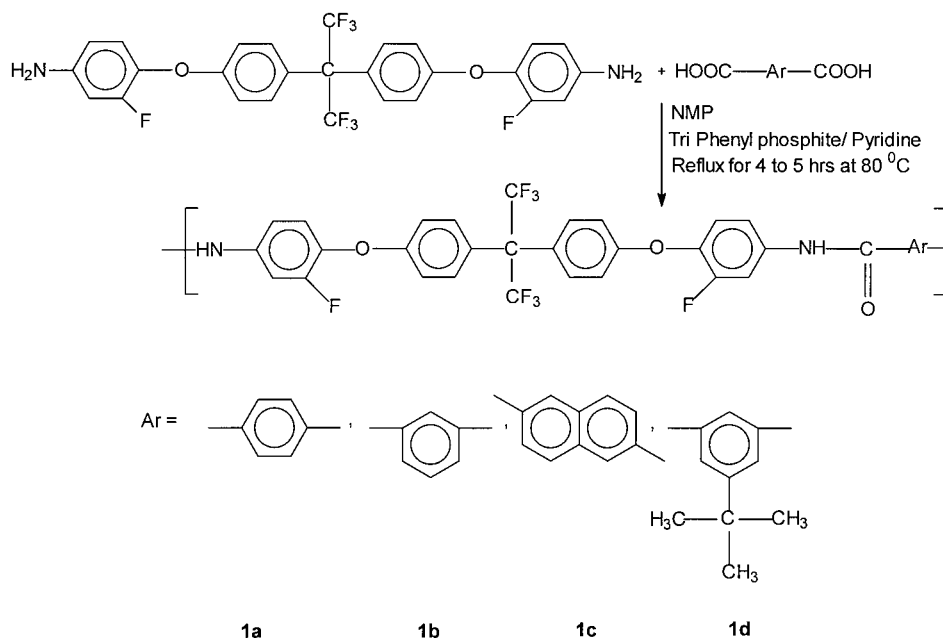
The dinitro compound (13.78 g), Pd/C (10%, 0.4 g), and EtOH (600 mL) were placed in a three-neck, round-bottom flask to which hydrazine monohydrate (35 mL) was added dropwise for 1 h at 85°C under nitrogen. When the addition was completed, the reaction was continued for another 24–26 h, after which the catalyst was filtered off from the hot, colorless solution of the diamines. The volume of the solution was reduced to 10% by rotary evaporation and recrystallized from ethyl alcohol (yield = 82%, mp = 154–156°C).

Dinitro compound

Yield: 89.5%. mp: 152°C. ELEM. ANAL. Calcd. for (C₂₇H₁₄O₆F₈N₂) (614.30 g/mol): C, 52.7%; H, 2.28%; N, 4.56%. Found: C, 52.34%; H, 2.21%; N, 4.49%. IR (KBr): 3092 (aromatic C—H), 1536, 1348 (NO₂), 1236 (C—O—C). ¹H-NMR [dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), δ , ppm]: 8.5 (2H, s), 8.4 (2H, d), 8.1 (2H, d), 7.1–7.5 (8H, d).

Diamino compound

Yield: 89.5%. mp: 152°C. ELEM. ANAL. Calcd. for (C₂₇H₁₈O₂F₈N₂) (554.30 g/mol): C, 58.48%; H, 3.24%; N, 5.05%. Found: C, 58.39%; H, 3.19%; N, 4.98%. IR (KBr): 3447, 3397 (NH₂), 3089 (aromatic C—H), 1206 (C—O—C). ¹H-NMR (DMSO-*d*₆, δ , ppm): 7.25 (4H, d, J = 8.2 Hz), 6.9 (2H, t, J = 8.2 Hz), 6.75 (4H, d, J = 8.2 Hz), 6.45 (2H, d, J = 8.2 Hz), 6.3 (2H, d, J = 8.2 Hz), 6.9 (4H, s, NH₂).



Scheme 2 Reaction scheme for the synthesis of the polyamides.

Polymerization

Fluorine-containing polyamides were prepared by the direct polymerization of diamine **II** with various aromatic diacids with triphenyl phosphite and pyridine in NMP. A mixture of the diamine (1.38 g, 2.5 mmol), diacid (25 mmol), calcium chloride (0.36 g), NMP (5 mL), pyridine (1.4 mL), and triphenyl phosphite (1.4 mL) was heated with stirring. The precipitated polymer was washed thoroughly with methanol and hot water and then dried at 100°C *in vacuo*. The yield was 96–97%.

1a

ELEM. ANAL. Calcd. for (C₃₅H₂₀O₄F₈N₂) (684.30 g/mol): C, 61.40%; H, 2.92%; N, 4.09%. Found: C, 61.23%; H, 2.88%; N, 3.96%. IR (KBr): 3357 (N—H), 1665 (C=O). ¹H-NMR (DMSO-*d*₆, δ, ppm): 10.50 (2H, s, —NH), 6.8–8.6 (18H, m).

1b

ELEM. ANAL. Calcd. for (C₃₅H₂₀O₄F₈N₂) (684.30 g/mol): C, 61.40%; H, 2.92%; N, 4.09%. Found: C,

61.23%; H, 2.88%; N, 3.96%. IR (KBr): 3354 (N—H), 1664 (C=O). ¹H-NMR (DMSO-*d*₆, δ, ppm): 10.58 (2H, s, —NH), 6.8–8.5 (18H, m).

1c

ELEM. ANAL. Calcd. for (C₃₉H₂₂O₄F₈N₂) (734 g/mol): C, 63.76%; H, 2.99%; N, 3.81%. Found: C, 63.61%; H, 2.91%; N, 3.79%. IR (KBr): 3353 (N—H), 1663 (C=O). ¹H-NMR (DMSO-*d*₆, δ, ppm): 10.92 (2H, s, —NH), 6.8–8.8 (20H, m).

1d

ELEM. ANAL. Calcd. for (C₃₉H₂₈O₄F₈N₂) (740 g/mol): C, 63.24%; H, 3.78%; N, 3.78%. Found: C, 62.94%; H, 3.70%; N, 3.65%. IR (KBr): 3357 (N—H), 1666 (C=O). ¹H-NMR (DMSO-*d*₆, δ, ppm): 10.47 (2H, s, —NH), 8.6–7.0 (17H, m), 1.31 (9H, s).

RESULTS AND DISCUSSION

Synthesis of the monomer

The synthetic route of **II** is shown in Scheme 1.

TABLE I
Inherent Viscosities (η_{inh}), Weight-Average Molecular Weights (M_w), and Film Qualities of the Polyamides

Polymer	Yield	η_{inh}	M_w	M_w/M_n	Film quality	Water absorption (%)
1a	96	0.423	26,000	1.4	Flexible	2.10
1b	95	0.465	22,320	1.3	Flexible	2.15
1c	98	0.422	21,450	1.6	Flexible	2.36
1d	96	0.591	28,990	1.8	Flexible	1.78

M_n = number-average molecular weight.

According to the reported method,¹⁴ a dinitro compound (**I**) was synthesized from condensation of 2,2-bis(4-hydroxyphenyl)hexafluoropropane with 3,4-difluoro nitrobenzene in the presence of K_2CO_3 with DMF as a solvent. The reduction of the dinitro compound to an amino compound can be carried out in several ways; the most common methods are catalytic hydrogenation (H_2/Pd) and treatment with an acid (HCl) and a metal or metal salts (e.g., iron, zinc, or $SnCl_2$) or hydrazine/ $Pd-C$ as a reducing agent. The latter is a convenient method in the laboratory and was used for the preparation of diamine **II** in this work. The structures of the intermediate dinitro compound **I** and diamine **II** were confirmed by Fourier transform infrared (FTIR), 1H -NMR, and elemental analysis; the results agree well with the proposed structures. Detailed analytical data are provided in the Experimental section.

Preparation of the polymers

Two synthetic methods are available for the preparation of a polymer of a moderate or larger molar mass: polycondensation at low temperatures ($<100^\circ C$) and direct polycondensation in solutions with phosphates, especially in the presence of metal salts.¹⁵ Most aramids are synthesized by solution polycondensation at low temperatures with aromatic diacid chloride and with an aromatic diamine in polar aprotic solvents. The direct polycondensation of aromatic diamines with aromatic dicarboxylic acids with triphenyl phosphite and pyridine as condensation agents is known to be a convenient method for preparing aromatic poly-

TABLE II
Thermal Properties of the Polyamides

Polymer	T_g ($^\circ C$)		T_m ($^\circ C$)	10% Weight-loss temperature ($^\circ C$)
	DSC	DMA		
1a	—	—	319	435
1b	185	168	—	440
1c	—	—	385	460
1d	217	185	—	432

amides.^{6,16,17} We used this method in our synthesis. The reaction scheme and the structures of the polymers are shown in Scheme 2.

The polyamides were obtained in almost quantitative yields (Table I) with inherent viscosities of 0.42–0.59 dL/g. The lower viscosity of these polyamides, compared with that of the polyamides synthesized from 2,2[4-(*p*-aminophenoxy)phenyl]propane,¹⁸ was due to the slight nucleophilicity of amine compound **II** induced by the strongly electron-withdrawing trifluoromethyl groups.^{10,19} The electronegativity of fluorine acted to diminish the basicity of the amines. The polymers obtained were analyzed by FTIR, 1H -NMR, and elemental analysis. The IR spectra showed characteristic amide absorptions at 3310 and 1660 cm^{-1} corresponding to amino and carbonyl groups, respectively. The 1H -NMR spectra showed a sharp singlet around 10.5 ppm corresponding to the amide proton. Detailed analytical data are provided in the Experimental section.

The water absorption of the polymers was calculated from the weight-gain values of the polymer films

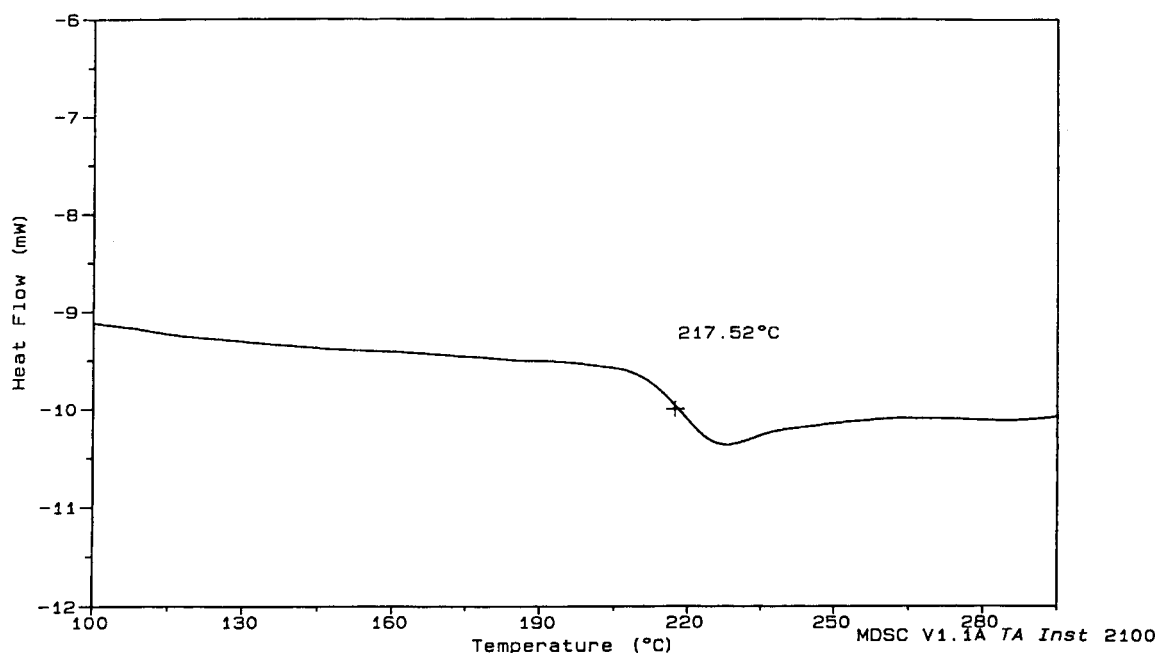


Figure 1 DSC plot of polyamide 1d.

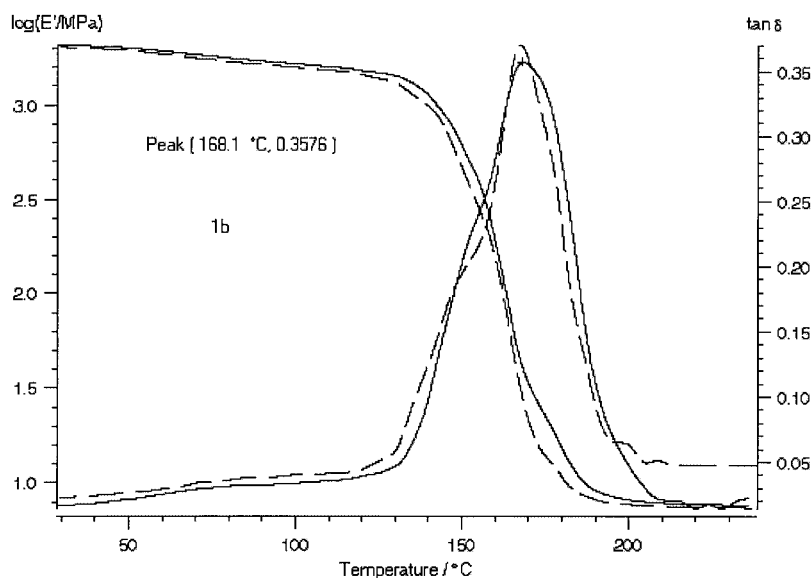


Figure 2 DMA plot of polyamide **1b**.

(with a Mettler balance of sensitivity of 10^{-6} g) after their immersion in double-distilled water for 72 h. The values are 1.36–2.36 wt % (Table I), which are comparable to those of many other semifluorinated polyamides.^{16,20}

Polymer properties

The solubility of the polyamides was tested in various solvents at room temperature. All the polyamides were soluble in polar aprotic solvents such as DMF, *N,N*-dimethylacetamide, NMP, DMSO, THF, pyridine, and chloroform. Their highly soluble nature was attributed to the introduction of hexafluoropropane groups into the polymer backbone.^{6,10,16} The pendant fluorine atom was also responsible for the enhanced solubility.

The thermal behavior and T_g 's of the polymers were evaluated by thermogravimetric analysis (TGA) and DSC, respectively. The values are summarized in Table II. The TGA curves of these polymers indicated that no loss of mass of the polymers occurred below 360°C. The lowest thermal stability of **1d** was due to the presence of an oxidizable *t*-butyl unit.

DSC measurements were conducted at a 20°C/min heating rate under a nitrogen atmosphere, and second heating scans were used to evaluate T_g . Polyamides **1b**

and **1d** showed T_g 's at 185 and 217°C, respectively. The representative DSC curve for polymer **1d** is shown in Figure 1. Polymer **1a** and **1c** showed melting peaks at 319 (melting energy = 21.7 J/g) and 385°C (melting energy = 20.6 J/g), respectively.

T_g 's of polymers **1b** and **1d** were also evaluated by DMA. The $\tan \delta$ peak values at 10 Hz for these polymers were 20–25°C lower than the DSC T_g values. A representative DMA plot for polymer **1b** is shown in Figure 2.

Transparent, tough, and flexible polymer films were obtained via casting from their DMF solutions. Table III summarizes the tensile properties of the polymers. They had tensile strengths of up to 85 MPa, initial moduli of 2.3 GPa, and elongations at break of up to 9%, which depended on the exact repeat unit structure.

CONCLUSIONS

New processable polyamides were prepared from **II** and aromatic dicarboxylic acids. The resulting polyamides had satisfactory thermal stability and mechanical properties (tensile strengths of up to 85 MPa and moduli of 2.3 GPa), as well as excellent solubility in different organic solvents. The polymers exhibited low water absorption (1.36–2.36 wt %). These materials

TABLE III
Mechanical Properties of the Polyamides

Polymer	Tensile strength (MPa)	Initial modulus (GPa)	Elongation at break (%)
1a	82	1.8	9
1b	65	2.1	6
1c	73	2.3	4
1d	71	1.6	7

may find applications as membranes for the selective separation of water from organic streams.¹⁸

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