Polyterephthalamides with Naphthoxy-Pendent Groups

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ABSTRACT: A series of new aromatic polyamides having pendent naphthoxy groups were synthesized by the triphenyl phosphite-activated polycondensation of (2-naphthoxy)terephthalic acid (NOTPA) with various aromatic diamines in a medium consisting of N-methyl-2-pyrrolidone (NMP), pyridine, and calcium chloride. The diacid monomer NOTPA was prepared from the nitro displacement of dimethyl 2-nitroterephthalate with the potassium naphthoxide of β-naphthol, followed by base-induced ester hydrolysis. All the resulting polymers were noncrystalline and readily soluble in aprotic polar solvents such as NMP and N,N-dimethylacetamide. Almost all the polymers could be solution-cast to tough, creasable amorphous films with good mechanical properties, the values of tensile strengths ranging from 90 to 124 MPa with initial moduli ranging from 1.72 to 2.51 GPa. Except for two examples, all the other polyamides displayed discernible glass transitions between 189 and 248 °C in the differential scanning calorimetric traces. These polyamides showed insignificant decomposition below 400 °C in nitrogen or air. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 1781–1789, 2002

Keywords: aromatic polyamides; (2-naphthoxy)terephthalic acid; bulky pendent group; solubility; thermal properties; high performance polymers; high temperature materials; polyamides

INTRODUCTION

Aromatic polyamides are an important class of high-performance polymers that offer excellent physical and chemical properties, thermal and oxidative stability, flame resistance, and superior mechanical properties. Wholly aromatic polyamides such as poly(1,4-phenyleneterephthalamide) and poly(1,4-benzamide) are well accepted as heat-resistant materials with a high mechanical strength, easily forming lyotropic solutions.1–3 Fibers obtained from anisotropic solutions of these materials have been used in applications where high thermal stability and mechanical strength are required. For example, Kevlar aramid fiber products have been used in industrial applications since their introduction in the 1970s by Du Pont.4 They have been evaluated extensively in various industries and reported in the literature. However, infusibility and limited solubility in organic solvents are the characteristic properties of wholly aromatic polyamides that make them generally difficult or too expensive to process, thus restricting their applications.

Because the aforementioned problems restrict the further applications of aromatic polyamides, considerable effort has been made to improve their properties by structural modification.5–11 The attachment of bulky pendent groups on the aromatic units may provide a significant increase in both the glass-transition temperature ($T_g$) and the solubility of aromatic polyamides.9–15 Thus, the $T_g$ is raised by the restriction of segmental
mobility brought about by the incorporation of bulky groups, whereas solubility is improved by decreasing the packing density and crystallinity. This structural modification minimizes the trade-off between processability and the positive/useful properties of aromatic polyamides.

Polyesters from terephthalic acid and hydroquinone or 4,4'-biphenol are highly crystalline and possess theoretical melting points that are so high that thermal decomposition prevents any processing from the melt. It has been demonstrated that polyesters from aryloxyterephthalic acids or arylthioterephthalic acids with hydroquinone or its derivatives are semicrystalline engineering plastics with a broad nematic phase above their melting points.16–19 Similarly, polyterephthalamides from terephthalic acid and short-chain, symmetric aromatic diamines are highly crystalline, insoluble materials that decompose above 450 °C without melting. In connection with our interest in preparing easily processable high-performance polymers, this work investigates the synthesis and basic characterization of polyterephthalamides with pendent naphthoxy groups. The thermally stable and flexible naphthoxy group is expected to provide desired properties to the substituted polymers.

**EXPERIMENTAL**

**Materials**

β-Naphthol, potassium tert-butoxide, triphenyl phosphate, and dimethyl 2-nitroterephthalate (all from TCI) were used without further purification. Commercially obtained anhydrous calcium chloride was dried under vacuum at 150 °C for 6 h. N-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over a 4Å molecular sieve. p-Phenyleneedianime (2a, from TCI) and m-phenyleneedianime (2b, from TCI) were purified by vacuum distillation prior to use. 2,2-Bis[4-(4-aminophenoxy)phenyl] ether (2h) (mp: 128–129 °C) was prepared by the aromatic nucleophilic substitution reaction of 4,4'-oxydiphenol and p-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction of the intermediate bis(p-nitrophenoxy) compound using hydrazine monohydrate as the reducing reagent and Pd/C as the catalyst.20 All other diamines such as 4,4'-oxydianiline (2c, from TCI), 4,4'-methyleneedianilne (2d, from TCI), 2,2-bis(4-aminophenyl)hexafluoropropane (2e, from Al-drich), 1,4-bis(4-aminophenoxy)benzene (2f, from TCI), 4,4'-bis(4-aminophenoxy)biphenyl (2g, from TCI), 2,2-bis[4-(4-aminophenoxy)phenyl]propene (2i, from TCI), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (2j, from TCI), and 9,9-bis(4-aminophenyl)fluorene (2k, from TCI) were used without further purification.

**Monomer Synthesis**

**Dimethyl (2-Naphthoxy)terephthalate (NODMT)**

Potassium tert-butoxide (44.88 g; 0.40 mol) was added to a stirred solution of 57.66 g (0.40 mol) of β-naphthol in 150 mL of dry toluene and 400 mL of N,N-dimethylformamide (DMF) under nitrogen atmosphere. The reaction mixture was heated, and about 200 mL of solvent were removed by distillation. After cooling to room temperature, dimethyl 2-nitroterephthalate (95.86 g; 0.40 mol) was added, and the reaction mixture was heated to 100 °C for 10 h. After cooling, the solution was concentrated in a rotary evaporator and poured into ice water. Following several extractions with ethyl acetate, the combined extracts were washed with saturated NaCl solution and then dried over anhydrous sodium sulphate. The ethyl acetate solution was concentrated in a rotary evaporator, and the product was recrystallized from methanol affording 56.6 g (40% yield) of powders; mp: 67–69 °C (lit.17 78–80 °C).

IR (KBr): 1726, 1707 (C=O stretch), 1290, 1226 cm−1 (C—O stretch). 1H NMR (CDCl3, δ, ppm): 3.83 (s, 3H, —CH3), 3.87 (s, 3H, —CH3), 7.23–8.00 (m, 10H, ArH). 13C NMR (CDCl3, δ, ppm): 166.98 (C=O), 157.28, 156.17, 135.83, 135.18, 132.80, 131.20, 131.06, 128.64, 128.09, 128.02, 127.50, 125.74, 125.22, 122.52, 120.21, 114.39 (114.39–157.28, aromatic carbons), 52.43 (methyl carbons). ELEM. ANAL. Calcd. for C20H16O5 (336.4): C, 71.42%; H, 4.79%. Found: C, 71.60%; H, 4.58%.

**(2-Naphthoxy)tere phthalic Acid (NOTPA; 1)**

To a stirred solution of 40 g of potassium hydroxide in a mixture of water (100 mL) and ethanol (200 mL) was added 10 g of NODMT. The reaction mixture was heated at reflux overnight. After cooling to room temperature, the reaction mixture was acidified to pH 2–3 by concentrated HCl to yield a precipitate, which was collected on a filter and washed thoroughly with water. Recrystallization from ethanol/water (3:1) yielded 8.6 g (94%) of diacid NOTPA; mp: 294–298 °C (lit.17 above 310 °C accompanied by decomposition).
IR (KBr): 2500–3500 (O–H stretch), 1694 (C=O stretch), 1292, 1246 cm⁻¹ (C–O stretch).

1H NMR [dimethyl sulfoxide (DMSO)-d₆, δ, ppm]: 7.25–7.98 (m, 10H, ArH). 13C NMR (DMSO-d₆, δ, ppm): 168.45, 168.41 (C=O), 157.18, 156.95, 137.19, 135.60, 133.32, 131.56, 131.46, 129.71, 129.19, 128.56, 128.20, 126.33, 126.03, 122.95, 120.90, 114.55 (aromatic carbons). ELEM. ANAL. Calcd. for C₁₈H₁₂O₅ (308.3): C, 70.13%; H, 3.92%. Found: C, 70.15%; H, 3.68%.

Polymerization

A typical example of polycondensation follows. A mixture of 0.216 g (2.0 mmol) of diamine 2b, 0.617 g (2.0 mmol) of diacid NOTPA, 0.40 g of calcium chloride, 6 mL of NMP, 1.5 mL of pyridine, and 1.2 mL of triphenyl phosphite was heated at 100 °C for 3 h. The obtained polymer solution was poured slowly into 300 mL of methanol. The stringy, fiberlike polymer precipitate was washed thoroughly with methanol and hot water, collected by filtration, and dried at 100 °C under vacuum. The yield was 0.81 g (99%). The inherent viscosity of polymer 3b was 0.60 dL/g, measured at a concentration of 0.5 g/dL in N,N-dimethylacetamide (DMAc) containing 5 wt % LiCl at 30 °C.

IR (film): 3340 (N–O), 1680 cm⁻¹ (C=O). 1H NMR (DMSO-d₆, δ, ppm): 10.38 (s, 1H, amide), 10.57 (s, 1H, amide), 7.26–8.24 (m, 14H, ArH). ELEM. ANAL. Calcd. for (C₂₄H₁₆N₂O₅)ₙ: C, 75.78%; H, 4.24%; N, 7.36%. Found: C, 74.55%; H, 4.28%; N, 7.35%.

Other polyamides were synthesized analogously.

Measurements

Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. Elemental analyses were run in a PerkinElmer model 2400 CHN analyzer. 1H and 13C NMR spectra were measured on a JEOL EX-400 spectrometer with CDCl₃ or DMSO-d₆ as the solvent and tetramethylsilane as the internal reference. Inherent viscosities of all polymers were determined at 0.5 g/dL concentration in DMAc 5 wt % LiCl using a Cannon-Fenske viscometer at 30 °C. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Measurements were performed with 3–5-mg samples heated in flowing nitrogen or air (30 cm³/min) at a heating rate of 20 °C/min. Differential scanning calorimetric (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC in flowing nitrogen (20 cm³/min) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 at a scan rate of 10 °C/min with a penetration probe of 1.0 mm in diameter under an applied constant load of 10 mN. Wide-angle X-ray diffractograms (WAXDs) were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer with Ni-filtered Cu Kα radiation (40 kV, 15 mA), and the scanning rate was 2°/min. Measurements were performed with film specimens of about 0.1 mm in thickness. An Instron
Figure 1. $^1$H NMR (a) and $^{13}$C NMR (b) spectra of NOTPA in DMSO-$d_6$. 
Universal Tester model 1130 with a load cell of 5 kg and a gauge length of 2 cm was used to examine the stress-strain behavior of the samples at a crosshead speed of 5 mm/min. Measurements were performed at room temperature (ca. 20 °C) with film specimens (0.5 cm wide, 6 cm long, and ca. 0.1 mm thick), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

The aromatic diacid monomer, NOTPA (1), used for the preparation of new polyamides was prepared in a similar way as that reported in the literature. Scheme 1 outlines the synthetic route for NOTPA. The nitro group of dimethyl 2-nitroterephthalate was subjected to a nucleophilic substitution with potassium naphthoxide prepared in situ from β-naphthol with potassium tert-butoxide, followed by saponification of the resulting dimethyl ester NODMT. IR, NMR, and elemental analysis were used to identify the structures of all intermediates and monomers. The IR spectrum of diester NODMT showed characteristic absorption bands at 1726 and 1707 cm⁻¹ (C=O stretching). After the saponification and acidification to NOTPA, the carbonyl absorptions shifted to lower frequency at around 1694 cm⁻¹ together with the appearance of broad absorption bands around 2500–3500 cm⁻¹ (H-
bonded O—H stretching). Figure 1 displays the 1H NMR and 13C NMR spectra of NOTPA. All the spectroscopic data obtained agreed with the expected structures. Quantitative conversion of the diester to the dicarboxylic acid monomer was confirmed by the disappearance of the resonance peaks for the methyl protons at 3.83 and 3.87 ppm in the 1H NMR spectrum and for the methyl carbons at 52.43 ppm in the 13C NMR spectrum.

**Polymer Synthesis**

A series of new aromatic polyamides 3a–k containing naphthoxy-pendent p-phenylene units were prepared from NOTPA (1) and various aromatic diamines 2a–k by the direct polycondensation reaction using triphenyl phosphate and pyridine as condensing agents (Scheme 2).21 These polymers were obtained in almost quantitative yield with inherent viscosities of 0.58–2.00 dL/g, as shown in Table 1. All the molecular weights of these polymers are sufficiently high to permit casting tough and flexible films.

The formation of polyamides was confirmed by IR and 1H NMR spectroscopy. The IR spectra of the polymers exhibited characteristic absorptions of the amide group at around 3300 cm⁻¹ (N—H stretching) and 1680 cm⁻¹ (C=O stretching). Figure 2 illustrates typical 1H NMR spectra for polyamides 3b and 3c. The amide protons were observed between 10.38 and 10.57 ppm, appearing likely as a doublet pattern. This can be attributed to the fact that one of the amide groups is ortho to the naphthoxy group, and the other is meta.

**Properties of Polymers**

Table 1 summarizes the qualitative solubility of the polyamides in various solvents. Most polymers were soluble in aprotic polar solvents such as DMAC, NMP, and DMP and even in less-polar solvents like m-cresol. Polyamers 3i and 3j obtained from long-chain, flexible diamines were also readily soluble in tetrahydrofuran. However, polymer 3a with rigid and symmetrical p-phenylene unit along the polymer backbone. Good solubility makes these polymers potential candidates for practical applications in spin-coating and casting processes.

All polyamides except for 3a could be solution cast into transparent, flexible, and tough films. These films were subjected to tensile testing, and the results are also summarized in Table 1. These films had tensile strengths of 90–124 MPa, elongation to break of 4–19%, and initial moduli of

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**Table 1. Inherent Viscosities, Solubility, and Tensile Properties of the Polyamides**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>ηinh</th>
<th>NMP</th>
<th>DMAC</th>
<th>DMF</th>
<th>DMSO</th>
<th>m-Cresol</th>
<th>THF</th>
<th>Solubilityb</th>
<th>Tensile Properties of the Polymer Filmsc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(dL/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tensile Strength</td>
</tr>
<tr>
<td>3a</td>
<td>2.00</td>
<td>δ</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>103</td>
</tr>
<tr>
<td>3b</td>
<td>0.60</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>124</td>
</tr>
<tr>
<td>3c</td>
<td>1.27</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>113</td>
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<td>3d</td>
<td>1.40</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<td>–</td>
<td>–</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>115</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>+</td>
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<td>–</td>
<td>101</td>
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<td>3h</td>
<td>0.65</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>94</td>
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<tr>
<td>3i</td>
<td>1.23</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>94</td>
</tr>
<tr>
<td>3j</td>
<td>1.34</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>–</td>
<td>+</td>
<td>90</td>
</tr>
</tbody>
</table>

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a Determined in DMAC containing 5 wt% LiCl at 30 °C, at a concentration of 0.5 g/dL.
b The qualitative solubility was tested with 10-mg samples in 1 mL of solvent; + = soluble at room temperature, +h = completely soluble on heating at 100 °C, δ = partially soluble on heating, and − = insoluble even on heating.
c Films were cast by the slow evaporation of polymer solutions in DMAC. The cast films were then dried in vacuo at 160 °C for 6 h prior to the tensile test.
1.72–2.51 GPa. Some of the polymers yielded during tensile testing and had moderate elongation to break, indicative of high toughness.

The crystallinity of the prepared polyamides was measured by WAXD studies. All the NOTPA-based polymers showed an essentially amorphous character, confirmed by the WAXD patterns depicted in Figure 3. Thus, the amorphous nature of these polymers was in line with their enhanced solubility, which agrees with the general rule that the solubility increases with decreasing crystallinity. When comparing the WAXD patterns of polymers 3f and 3h with their counterparts without the naphthoxy substituent (data from a prevous study), the amorphous nature of the polymers was further confirmed.

![Figure 2. 1H NMR spectra: (a) polyamide 3b and (b) polyamide 3c in DMSO-d<sub>6</sub>.](image1)

Figure 2. 1H NMR spectra: (a) polyamide 3b and (b) polyamide 3c in DMSO-d<sub>6</sub>.

![Figure 3. WAXD patterns of some naphthoxy-pendent polyamides and two analogous polyamides without the pendent group.](image2)

Figure 3. WAXD patterns of some naphthoxy-pendent polyamides and two analogous polyamides without the pendent group.
vious publication\textsuperscript{20}), one can see an obvious effect of the introduction of the pendent naphthoxy group on decreasing the crystallinity of these polyamides. Apparently, the bulky side groups increased the disorder in the repeating unit and the chain packing.

The thermal stability of the polyamides was analyzed by TGA. Typical TGA curves in both air and nitrogen atmospheres of a representative polyamide 3a are shown in Figure 4. The onset decomposition temperatures and the temperatures at a 10\% weight loss in nitrogen and air atmospheres were determined from original thermograms and are listed in Table 2. In general, all the polymers exhibited high thermal stability with no significant weight loss up to temperatures of approximately 400 °C both in nitrogen or air. The amount of carbonized residue (char yield) of polyamides in nitrogen atmosphere was in the range of 43–66\% weight even at 800 °C.

DSC and TMA were used to evaluate the thermal transitions of these polyamides. The influence of residual solvent or the absorbed moisture and history of thermal annealing is sometimes observed in the first heating scans of DSC and TMA. The polyamide samples were heated at 250 °C for 30 min prior to the DSC and TMA scans. DSC observed no $T_g$ value for polyamides 3a and 3k, probably because of structural rigidity. DSC could easily determine the $T_g$ values of the other polyamides. They were in the range of 189–248 °C, decreasing with decreasing rigidity and symmetry of the polymer backbone. The series of polyamides showed lower $T_g$'s possibly because of the increased polymer free volume caused by the naphthoxy-pendent group. All polymers indicated no clear melting endotherms from $T_g$ to 400 °C on the DSC thermograms. This result supports the amorphous nature of these polyamides. The softening temperatures ($T_s$) (may be referred to as apparent $T_g$) of the polymer film samples were

![Figure 4. TGA thermograms of polyamide 3a with a heating rate of 20 °C/min.](image)

**Table 2.** Thermal Properties of the Polyamides

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)\textsuperscript{b}</th>
<th>$T_s$ (°C)\textsuperscript{c}</th>
<th>$T_d$ at Onset (°C)\textsuperscript{d}</th>
<th>$T_d$ at 10% (°C)\textsuperscript{d}</th>
<th>Char Yield (wt %)\textsuperscript{e}</th>
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</thead>
<tbody>
<tr>
<td>3a</td>
<td>—\textsuperscript{f}</td>
<td>—\textsuperscript{f}</td>
<td>448</td>
<td>444</td>
<td>470</td>
</tr>
<tr>
<td>3b</td>
<td>214</td>
<td>210</td>
<td>430</td>
<td>407</td>
<td>448</td>
</tr>
<tr>
<td>3c</td>
<td>216</td>
<td>215</td>
<td>428</td>
<td>430</td>
<td>460</td>
</tr>
<tr>
<td>3d</td>
<td>215</td>
<td>215</td>
<td>432</td>
<td>430</td>
<td>473</td>
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<tr>
<td>3e</td>
<td>248</td>
<td>250</td>
<td>434</td>
<td>422</td>
<td>449</td>
</tr>
<tr>
<td>3f</td>
<td>206</td>
<td>206</td>
<td>412</td>
<td>427</td>
<td>445</td>
</tr>
<tr>
<td>3g</td>
<td>207</td>
<td>210</td>
<td>420</td>
<td>408</td>
<td>460</td>
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<tr>
<td>3h</td>
<td>189</td>
<td>186</td>
<td>397</td>
<td>399</td>
<td>507</td>
</tr>
<tr>
<td>3i</td>
<td>203</td>
<td>202</td>
<td>411</td>
<td>400</td>
<td>518</td>
</tr>
<tr>
<td>3j</td>
<td>213</td>
<td>212</td>
<td>427</td>
<td>420</td>
<td>502</td>
</tr>
<tr>
<td>3k</td>
<td>—\textsuperscript{f}</td>
<td>266</td>
<td>420</td>
<td>413</td>
<td>462</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The samples were heated at 250 °C for 30 min prior to all the thermal analyses.

\textsuperscript{b} Glass-transition temperature, taken as the midpoint temperature of the baseline shift on the DSC heating trace at a scan rate of 20 °C/min.

\textsuperscript{c} Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace at a heating rate 10 °C/min.

\textsuperscript{d} Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas-flow rate of 30 cm\textsuperscript{3}/min.

\textsuperscript{e} Residual weight percentage at 800 °C.

\textsuperscript{f} No discernible transition.
determined by the TMA method using a loaded penetration probe. They were obtained from the onset temperature of the probe displacement on the TMA trace. In all cases, the $T_s$ values obtained by TMA are comparable to the $T_g$ values measured by the DSC experiments (Table 2). There is a large window between $T_g$ or $T_s$ and the decomposition temperature of each polymer, which could be advantageous in the processing of these polymers by the thermoforming technique.

CONCLUSIONS

A series of new high molecular weight aromatic polyamides based on the diacid, (2-naphthoxy)terephthalic acid, were successfully prepared by direct polycondensation with various aromatic diamines using triphenyl phosphite and pyridine as condensing agents. All polyamides were amorphous. The introduction of the bulky pendent naphthoxy group into the polymer backbone leads to significantly improved solubility of the polymer in various organic solvents. Most of these polymers exhibited a desired combination of properties requiring high-performance materials that include excellent mechanical properties, high thermal stability, and excellent solubility in organic solvents for fabrication.

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REFERENCES AND NOTES