Synthesis and Properties of Novel Soluble Polyamides Having Ether Linkages and Laterally Attached *p*-Terphenyl Units

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ABSTRACT: A new ether-bridged aromatic dicarboxylic acid, 2′,5′-bis(4-carboxyphenoxy)-*p*-terphenyl (**3**), was synthesized by the aromatic fluoro-displacement reaction of *p*-fluorobenzonitrile with 2′,5′-dihydroxy-*p*-terphenyl in the presence of potassium carbonate, followed by alkaline hydrolysis. A set of new aromatic polyamides containing ether and laterally attached *p*-terphenyl units was synthesized by the direct phosphorylation polycondensation of diacid **3** with various aromatic diamines. The polymers were produced with high yields and moderately high inherent viscosities (0.44−0.79 dL/g). The polyamides derived from **3** and rigid diamines, such as *p*-phenylenediamine and benzidine, and a structurally analogous diamine, 2′,5′-bis(4-aminophenoxy)-*p*-terphenyl, were semicrystalline and insoluble in organic solvents. The other polyamides were amorphous and organosoluble and could afford flexible and tough films via solution casting. These films exhibited good mechanical properties, with tensile strengths of 91–108 MPa, elongations to break of 6−17%, and initial moduli of 1.95–2.43 GPa. These polyamides showed glass-transition temperatures between 193 and 252 °C. Most of the polymers did not show significant weight loss before 450 °C, as revealed by thermogravimetric analysis in nitrogen or in air. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 4056−4062, 2004
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INTRODUCTION

Rigid-rod aromatic polyamides (aramids), such as poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide), have been well known for their high-temperature resistance and excellent mechanical strength.[1,2] Fibers obtained from anisotropic solutions of these materials have been used in applications in which high thermal stability and mechanical strength are required.[3] However, infusibility and limited solubility in organic solvents are the characteristic properties of aramids that restrict synthesis and applications, especially of high-molecular-weight materials. Therefore, many efforts have been made to design the chemical structure of the rigid aromatic backbone to obtain aramids that are processable by conventional techniques.[4−16] Insertion of ether linkages lowers the segmental rotational barrier and increases the degree of conformational freedom, thus decreasing the glass-transition temperature (T_g). On the other hand, attachment of lateral bulky groups may impart an increase in T_g by

restricting segment mobility, while providing enhanced solubility because of decreased packing and crystallinity. Combining these two structural modifications minimizes the trade-off between improved processability and the desired properties of aramids. These modifications generally lead to soluble and amorphous polymers. In general, amorphous polyamides have a lower softening temperature and improved solubility compared to crystalline analogues; thus, they may open up their application in the areas of films, gas separation membranes, coatings, engineering plastics, polymer blends, and composites.

It has been demonstrated that polyamides based on *tert*-butylhydroquinone- and di-*tert*-butylhydroquinone-based diamines and dicarboxylic acids have enhanced solubility and acceptable thermal properties.[10–14] The improved solubility was attributed in part to the presence of bulky *tert*-butyl groups, which interrupt close chain packing and thus decrease chain–chain interactions. However, the thermal stability of the polyamides deteriorated slightly because of the less stable aliphatic segments. Therefore, we decided to replace the *tert*-butyl group by a thermally stable phenyl unit along the polyamide backbone. This article reports the present study's synthesis of a new aromatic dicarboxylic acid monomer containing flexible ether linkages and bulky, pendant phenyl groups and its polycondensation to polyamides with a set of aromatic diamines. Also discussed are the basic properties of these new polyamides, such as their solubility, film-forming capability, crystallinity, and mechanical and thermal characteristics.

EXPERIMENTAL

Materials

2,5-Diphenyl-*p*-benzoquinone, potassium carbonate (K_2CO_3) (Fluka), *p*-fluorobenzonitrile (Acros), *p*-chloronitrobenzene [Tokyo Chemical Industry (TCI)], 10% palladium on charcoal (Pd/C; Fluka), and hydrazine monohydrate (Acros) were used as received. *N*-Methyl-2-pyrrolidone (NMP) and pyridine (Py) were dried on distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves in a sealed bottle. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. 2′,5′-Dihydroxy-*p*-terphenyl (or 2,5-diphenylhydroquinone) (**1**) was obtained from the reduction of 2,5-diphenyl-*p*-benzoquinone according to a reported method.[17] *p*-Phenylenediamine (**4a**) (TCI) and benzidine (**4c**) (TCI) were purified by vacuum sublimation. *m*-Phenylendiamine (**4b**) was purified by vacuum distillation. 4,4′-Diaminodiphenyl ether (**4d**) (TCI), 1,4-bis(4-aminophenoxy)benzene (**4e**) (TCI) and 1,3-bis(4-aminophenoxy)benzene (**4f**) (TCI) were used as received. As reported in previous articles,[18–20] 4,4′-bis(4-aminophenoxy)biphenyl (**4g**) (mp = 198–199 °C), bis[4-(4-aminophenoxy)-phenyl] ether (**4h**) (mp = 128–129 °C), and 2′,5′-bis(4-aminophenoxy)-*p*-terphenyl (**4i**) (mp = 250–251 °C) were prepared by aromatic nucleophilic substitution reactions of the corresponding bisphenol precursors and *p*-chloronitrobenzene in the presence of potassium carbonate and the subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compounds using hydrazine monohydrate as the reducing reagent and Pd/C as the catalyst.

Monomer Synthesis

2′,5′-Bis(4-cyanophenoxy)-p-terphenyl (2)

In a 1-L round-bottomed flask equipped with a stirring bar and a condenser, a mixture of 25 g of 2,5-diphenyl-*p*-benzoquinone and 12 g of Zn powder in 500 mL of acetic acid was refluxed for 5 h. The resulting transparent, pale yellow solution was filtered while hot, and 1 L of water was then added into the filtrate. The resulting precipitate was filtered, collected, and dried as a light yellow solid [21.6 g, 86%; mp = 223–225 °C, according to differential scanning calorimetry (DSC) at a scan rate of 2 °C/min]. In a 300-mL round-bottomed flask, the obtained 2,5-dihydroxy-*p*-terphenyl (**1**) (13.1 g, 0.05 mol) and anhydrous potassium carbonate (13.8 g, 0.1 mol) were suspended in a mixture of 150 mL of dry DMF and 30 mL of toluene. Then, the mixture was refluxed at 140 °C using a Dean–Stark trap to remove small amount of water azeotropically. After most of the toluene was distilled, *p*-fluorobenzonitrile (12.5 g, 0.1 mol) was added to the mixture, and heating was continued at reflux for 10 h. The resulting solution was allowed to cool to room temperature and was then poured into 600 mL of methanol/water (1:1 by volume) to give white precipitates. After being washed repeatedly with water, the product was collected by filtration and then recrystallized from a mixture of DMF/methanol to afford 17.3 g (yield 75%) of pure 2′,5′-bis(4-cyanophenoxy)-*p*-terphenyl as white needles (mp = 289–290 °C, by DSC at 2 °C/min). IR (KBr): 2225 (C≡N), 1230,

1172 cm^{-1} (C—O—C). ANAL. Calcd for C$_{32}$H$_{20}$N$_2$O$_2$ (464.52): C, 82.74%; H, 4.34%; N, 6.03%. Found: C, 82.74%; H, 4.43%; N, 6.46%.

2′,5′-Bis(4-carboxyphenoxy)-p-terphenyl (3)

A suspension of the intermediate dinitrile **2** (12.0 g, 0.026 mol) in a mixture of water (250 mL) and ethanol (250 mL) containing dissolved potassium hydroxide (14.5 g, 0.26 mol) was heated at reflux temperature for 3 weeks until ammonia evolution ceased. The resulting solution was filtered hot to remove the insoluble solids, cooled, and acidified to pH 2–3 by concentrated HCl when a white solid precipitated. The solid was filtered off, washed thoroughly with water, and dried to yield 10.1 g (78%) of diacid **3**. The crude product was purified by crystallization from acetic acid as off-white fine needles (mp = 315–316 °C, by DSC at 2 °C/min). IR (KBr): 2500–3500 (O—H), 1682 (C=O), 1223, 1163 cm^{-1} (C—O—C). ^{1}H NMR (DMSO-d_6, δ, ppm): 7.88 (d, J = 6.9 Hz, 4H), 7.53 (d, J = 7.2 Hz, 4H), 7.37 (t, J = 7.7 Hz, 4H), 7.32 (s, 2H) 7.30 (t, J = 7.3 Hz, 2H), 7.04 (d, J = 6.9 Hz, 4H). ^{13}C NMR (DMSO-d_6, δ, ppm): 166.56, 161.10, 148.33, 135.49, 134.33, 131.50, 128.64, 128.32, 127.84, 124.76, 123.84, 116.36. ANAL. Calcd for C$_{32}$H$_{22}$O$_6$ (502.52): C, 76.48%; H, 4.41%. Found: C, 76.28%; H, 4.34%.

General Procedure for Preparation of Polyamides

A typical example of the preparation of polyamide **5d** follows. A flask was charged with 0.503 g (1 mmol) of diacid **3**, 0.445 g (1 mmol) of 4,4′-oxydianiline (**4d**), 0.2 g of CaCl$_2$, 0.8 mL of TPP, 0.8 mL of pyridine, and 2 mL of NMP. This mixture was heated with stirring at 120 °C for 3 h. As polycondensation proceeded, the solution gradually became viscous. Then the viscous polymer solution was poured slowly into stirred methanol. The resultant white fibrous solid was filtered off, washed thoroughly with methanol and hot water, and dried. The inherent viscosity of the polymer (**5d**) was 0.62 dL/g, as measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30 °C. IR (film): 3303 (N—H), 1652 (C=O), and 1218 cm^{-1} (C—O).
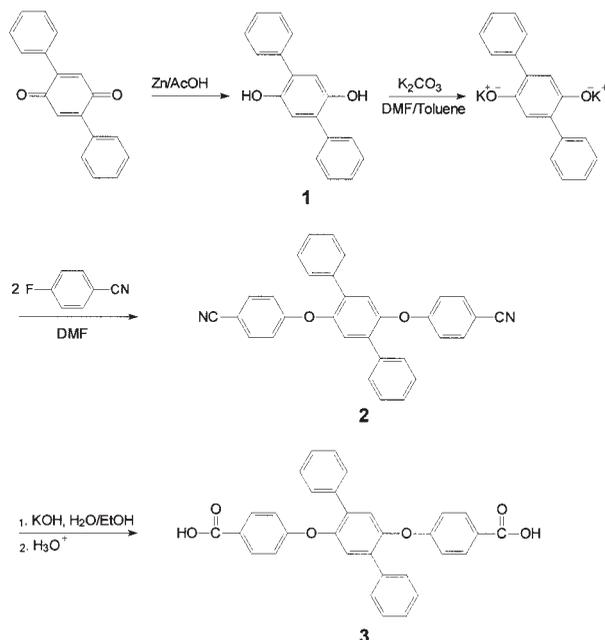
Film Preparation

A solution of polymer was made by dissolving about 0.8 g of the polyamide in 8 mL of hot DMAc to afford an approximately 10 wt % solution. The clear solution was poured into a 9-cm diameter glass culture dish that was placed in a 90 °C oven overnight for removal of the solvent. The semidried polyamide film was stripped off from the glass substrate and further dried in a vacuum oven at about 160 °C for 6 h. The obtained films were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analyses.

Characterization

Elemental analyses were made with a Heraeus Vario-III elemental analyzer. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 500-MHz FT-NMR spectrometer with DMSO-d_6 as the solvent and tetramethylsilane as the internal reference. The inherent viscosities of the polyamides were measured with a Cannon-Fenske viscometer at 30 °C. An Instron universal tester model 4400R with a load cell of 5 kg was used to study the stress–strain behavior of the polyamide film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long), and an average of at least three replicas was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a graphite monochromator, using nickel-filtered Cu Kα radiation (λ = 1.5418 Å, operating at 40 kV and 20 mA). The scanning rate was 3°/min over a 2θ range of 5–45°. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on samples of approximately 3–5 mg in flowing nitrogen or air (flow rate of 40 cm^3/min) at a heating rate of 10 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. Glass-transition temperatures (T_g) were read at the middle of the transition in the heat capacity. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted in the temperature range of 40–300 °C at a scan rate of 10 °C/min using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. The softening temperatures (T_s) were taken as the onset temperatures of probe displacement on the TMA traces.

Scheme 1.   Synthesis of diacid **3**.

RESULTS AND DISCUSSION

Monomer Synthesis

Beginning with 2,5-diphenyl-*p*-benzoquinone the preparation of 2′,5′-Bis(4-carboxyphenoxy)-*p*-terphenyl (**3**) was done in three main steps, as shown in Scheme 1. In the first step 2′,5′-dihydroxy-*p*-terphenyl (**1**) was obtained in good yield from the reduction of 2,5-diphenyl-*p*-benzoquinone by means of zinc powder in boiling acetic acid.[17] The second step was an aromatic nucleophilic fluoro-displacement reaction of *p*-fluorobenzonitrile with potassium phenolate of diol **1**, producing 2′,5′-bis(4-cyanophenoxy)-*p*-terphenyl (**2**). Finally, the dinitrile intermediate was readily converted by alkaline hydrolysis into dicarboxylic acid **3** of high purity and in high yield. IR, NMR, and elemental analyses confirmed the structures of the intermediate dinitrile and the diacid monomer. The IR spectrum of dinitrile compound **2** showed a characteristic sharp absorption band corresponding to —C≡N stretching at 2225 cm^{-1} that disappeared after hydrolysis. The dicarboxylic acid **3** displayed strong absorption bands of —COOH at 2500–3500 (—O—H stretching) and 1680 cm^{-1} (C=O stretching). Figure 1 illustrates the ^{1}H NMR and ^{13}C NMR spectra of dicarboxylic acid **3**. The assignments of each carbon and proton also are given in Figure 1. However, the protons of the

carboxylic acid groups were not observed, probably because of the fast exchange of these protons with a trace amount of moisture associated with the solvent. These spectra were in good agreement with the expected molecular structures.

Polymer Synthesis

Aromatic polyamides **5a–i** were synthesized using the Yamazaki–Higashi[21] phosphorylation polyamidation procedure from dicarboxylic acid **3** and diamines **4a–i** (Scheme 2). All the polycondensations proceeded readily in homogeneous and transparent solutions, except for polyamides **4a**, **4c**, and **4i**, which precipitated from the reaction medium when the system became viscous. As shown in Table 1, inherent viscosities of these polyamides ranged from 0.45 to 0.79 dL/g in DMAc–5 wt % LiCl. With the exception of **4a**, **4c**, and **4i**, the polyamides could be solution-cast into strong and flexible films, indicating high-molecular-weight polymers. Structural features of these polyamides were confirmed by FTIR spectroscopy. They exhibited characteristic absorptions of the
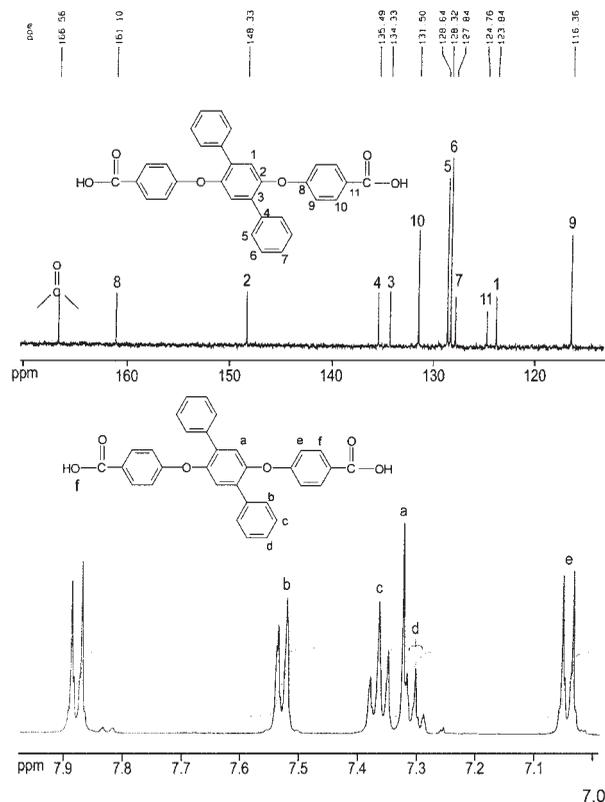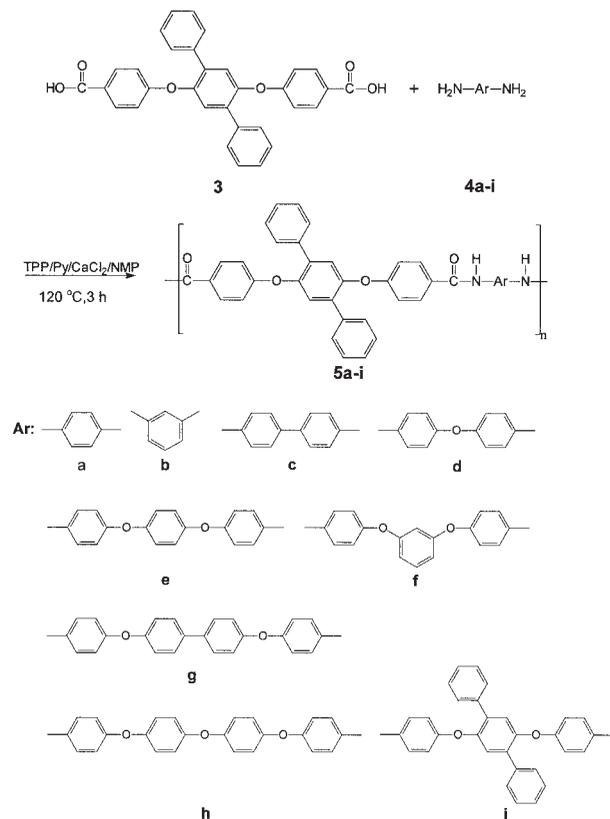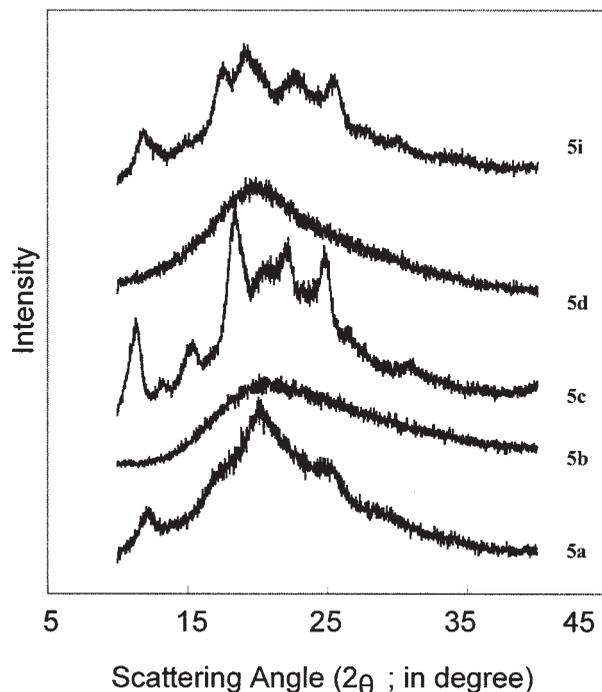

Figure 1. ^{1}H NMR and ^{13}C NMR spectra of diacid **3** in DMSO-d_6.

Scheme 2.   Synthesis of polyamides.

Figure 2.   WAXD patterns of polyamides.

amide group around 3300 cm^{-1} (N—H stretching) and 1650 cm^{-1} (C=O stretching). Strong absorption of aryl ether stretching appeared in the region of 1200–1250 cm^{-1}.

Polymer Properties

The WAXD patterns of some polyamides are illustrated in Figure 2. The polyamides derived from rigid diamines such as **5a** and **5c** showed some diffraction signals of medium to high intensity assignable to a semicrystalline polymer. Because of molecular regularity, polyamide **5i** also devel-

Table 1.   Inherent Viscosities and Solubility Behavior of Polyamides[a]

Polymer	η_{inh} (dL/g)[b]	Solvent[c]					
		NMP	DMAc	DMF	DMSO	m-Cresol	THF
5a	0.54	−	−	−	−	−	−
5b	0.45	+	+	+	+	−	+
5c	0.70	−	−	−	−	−	−
5d	0.62	+	+	+	+h	+	−
5e	0.79	+	+	+	−	−	−
5f	0.60	+	+	+	+	+	−
5g	0.67	+	+	+h	−	−	−
5h	0.45	+	+	+	+	+	+
5i	0.46	−	−	−	−	−	−

[a] Qualitative solubility was tested with 10 mg of sample in 1 mL of solvent. Symbols: +, soluble at room temperature; +h, soluble on heating at 100 °C; −, insoluble even on heating.
[b] Measured in DMAc-5 wt % LiCl at a concentration of 0.5 g/dL at 30 °C.
[c] NMP = N-methyl-2-pyrrolidone; DMAc = N,N-dimethylacetamide; DMF = N,N-dimethylformamide; DMSO = dimethyl sulfoxide; THF = tetrahydrofuran.

Table 2. Tensile Properties of Polyamide Films[a]

Polymer	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
5d	108	9	2.23
5e	101	17	1.97
5f	103	8	2.05
5g	99	17	1.95
5h	91	6	2.43

[a] Films were cast from slow evaporation of polymer solutions in *N,N*-dimethylacetamide. The cast films were dried under vacuum at 160 °C for 6 h prior to the tensile test.

oped a three-dimensional crystalline order, as observed by its WAXD pattern. This is consistent with that reported by Espeso et. al.[14] for the polyamides derived from 1,4-bis(4-carboxyphenoxy)-2,5-di-*tert*-butylbenzene and 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene. The other polyamides showed amorphous patterns similar to those of **5b** and **5d**.

The solubility behavior of all polyamides was qualitatively tested in some typical organic solvents, and the results are also reported in Table 1. The poor solubility of **5a**, **5c**, and **5i** can be attributed to their semicrystalline nature, as shown by X-ray diffractometry. All the amorphous polyamides showed excellent solubility in aprotic dipolar solvents, such as NMP, DMAc, DMF, and DMSO. Therefore, their excellent solubility makes these polymers potential candidates for practical applications in spin-on and casting processes.

Table 2 presents the tensile properties of the films of **5d**–**h** prepared via solution casting. They showed tensile strengths in the range of 91–108 MPa, elongations at break of 6–17%, and initial moduli of 1.95–2.43 GPa. The films of polyamides **5e** and **5g** necked during the tensile test and showed a moderate extension to break, indicating strong and ductile materials.

The thermal properties of the polymers determined by DSC, TMA, and TGA are summarized in Table 3. To avoid the effects of the moisture absorbed by the samples and the residual solvent in the film samples, the samples sealed in an aluminum pan were heated in the DSC sample holder at a heating rate of 20 °C/min up to 400 °C and then quenched at a programmed cooling rate of −200 °C/min to 40 °C. This quenching procedure led to predominantly amorphous samples in most cases of these polyamides. Reheating pro-

duced neat DSC thermograms in a second run from 40 to 400 °C, and within this range, a clear heat-capacity jump attributable to the glass transition could be observed in every polyamide except **5c**. DSC measurement showed that all polyamides except **5c** had T_g values between 193 and 252 °C, following the decreasing order of chain flexibility. The lowest T_g, 193 °C, was observed for polyamide **5h**, which was derived from the flexible multiring diamine **4h**. Polyamide **5f** also was found to have a relatively lower T_g of 197 °C, a result of the flexible *m*-phenylenedioxy linkages. No discernible T_g for polymer **5c** was observed by DSC, probably because of this polymer's high level of crystallinity, as shown by the WAXD pattern. The T_s values of the flexible film samples were also determined by the TMA method with a loaded penetration probe, and they were observed in the range 193–233 °C. The T_s values measured by TMA experiments were generally comparable to the T_g values observed by DSC.

The thermal and thermooxidative stabilities of these polyamides were evaluated in both nitrogen and air atmospheres using 10% weight loss values for comparison. Figure 3 shows the TGA thermograms of polyamide **5d**. The decomposition temperatures (T_d's) at 10% weight loss for these

Table 3. Thermal Properties of Polyamides

Polymer	T_g(°C)[a]	T_s(°C)[b]	T_d(°C)[c] In N$_2$	T_d(°C)[c] In Air	Char Yield (%)[d]
5a	252	—[f]	524	507	67
5b	224	230	519	533	66
5c	—[e]	—	524	524	67
5d	229	233	534	515	65
5e	207	207	538	518	63
5f	197	198	530	543	60
5g	223	219	549	550	65
5h	193	193	517	518	57
5i	226	—	526	526	63

[a] Midpoint temperature of baseline shift on the second DSC heating trace at a heating rate of 20 °C/min after quenching from 400 °C in nitrogen.
[b] Softening temperature measured by TMA using a penetration method and a heating rate of 10 °C/min. The film samples were heated at 250 °C for 30 min prior to the TMA experiment.
[c] Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 10 °C/min.
[d] Residual weight (%) at 800 °C at a scan rate of 10 °C/min in nitrogen.
[e] No discernible transition.
[f] No variable specimens.
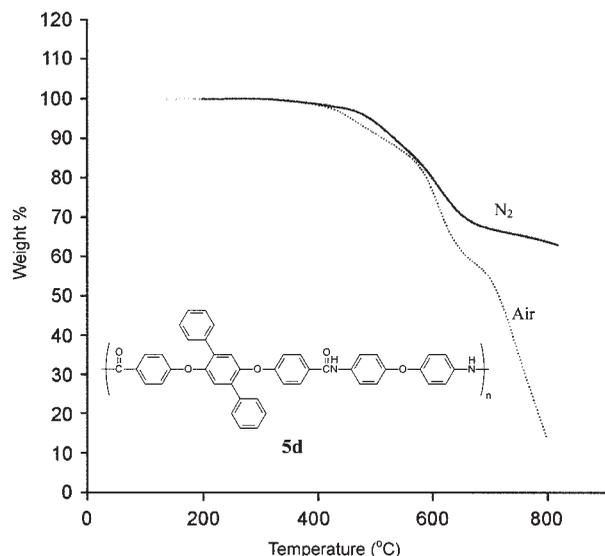
Figure 3. TGA thermograms of polyamide **5d**, at a heating rate of 10 °C/min.

polyamides were recorded as being in the range of 519–549 °C in nitrogen and 500–550 °C in air, which are higher temperatures than those reported for polyamides with *tert*-butyl groups.[10–14] This is reasonable because the present polyamides lack the less stable aliphatic units.

CONCLUSIONS

A novel diacid monomer, 2′,5′-bis(4-carboxyphenoxy)-*p*-terphenyl (**3**), was synthesized successfully from readily available reagents. A series of novel aromatic polyamides with ether and laterally attached *p*-terphenyl groups were synthesized from the polycondensation reactions of diacid **3** with various aromatic diamines by using triphenyl phosphite and pyridine as condensing agents. Except for those obtained from *p*-phenylenediamine, benzidine, and 2′,5′-bis(4-aminophenoxy)-*p*-terphenyl, the obtained polyamides were noncrystalline, displayed good solubility, and produced flexible and tough films. This combination of properties qualifies them as potential high-performance polymeric materials.

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