

Synthesis and Properties of Aromatic Polyamides Based on Non-, Methyl-, and Phenyl-Substituted 4,4'-Bis(1,4-phenylenedioxy)dibenzoic Acids

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SYNOPSIS

4,4'-(1,4-Phenylenedioxy)dibenzoic acid (**3**), 4,4'-(2,5-tolylenedioxy)dibenzoic acid (*Me-3*), and 4,4'-(2,5-biphenylenedioxy)dibenzoic acid (*Ph-3*) were prepared by the nucleophilic substitution reaction of *p*-fluorobenzonitrile with hydroquinone, methylhydroquinone, and phenylhydroquinone, respectively, followed by alkaline hydrolysis. Several aromatic polyamides having inherent viscosities of 0.66–1.34 dL/g were directly prepared by a Yamazaki phosphorylation polyamidation technique from dicarboxylic acids **3**, *Me-3*, and *Ph-3*, respectively, with aromatic diamines using triphenyl phosphite and pyridine as condensing agents. The solubility of methyl- or phenyl-substituted polyamides was remarkably enhanced when compared to that of nonsubstituted analogues. Most of the substituted polyamides revealed an amorphous nature and were readily soluble in a variety of organic solvents including *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide, dimethyl sulfoxide, and *m*-cresol. Transparent, flexible, and tough films of these polymers could be cast from the DMAc or NMP solutions. These films had tensile strength of 60–100 MPa, elongation to break of 6–11%, and tensile modulus of 1.68–2.25 GPa. The glass transition temperatures (T_g) of most polyamides could be determined by differential scanning calorimetry (DSC) and were in the range of 200–232°C. Thermogravimetric analyses established that these polymers were fairly stable up to 450°C, and the 10% weight loss temperatures were recorded in the range of 458–535°C in nitrogen and 468–528°C in air atmosphere. In general, the phenyl-substituted polyamides exhibited relatively higher T_g , thermal stability, and solubility. © 1996 John Wiley & Sons, Inc.

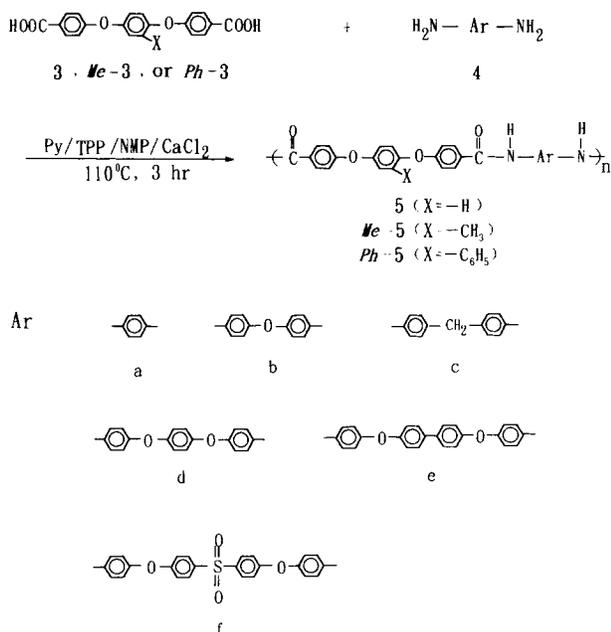
Keywords: aromatic polyamides • ether-dicarboxylic acids

INTRODUCTION

In a separate article,¹ 4,4'-(1,4-phenylenedioxy)-dibenzoic acid **3** was successfully obtained by the nucleophilic substitution reaction of *p*-fluorobenzonitrile with the potassium phenolate of hydroquinone and subsequent hydrolysis of the intermediate dinitrile. Following the Yamazaki phosphorylation polyamidation method,² high molecular weight polyamides were directly polycondensated from this ether-dicarboxylic acid with aromatic di-

amines. Through this kind of molecular design, ether linkages were incorporated into the aramid (aromatic polyamide) main-chain, and it was expected to improve the processability of the aramids such as enhanced solubility in organic solvents. However, the polyamides obtained from more rigid or symmetric diamines such as *p*-phenylenediamine, 4,4'-bis(4-aminophenoxy)biphenyl, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, and 1,4-bis(4-aminophenoxy)benzene revealed a high degree of crystallinity possibly due to better packing of polymer chain, thus, leading to very low solubility. One of the successful approaches to improve the processability of aramids is the introduction of bulky pendant group into the polymer backbone. For ex-

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Scheme 2.

in solubility, crystallinity, and thermal properties, was also investigated.

EXPERIMENTAL

Materials

Hydroquinone (**1**) (from Janssen), methylhydroquinone (or toluhydroquinone) (*Me-1*) (from TCI), and phenylhydroquinone (or 2,5-biphenol) (*Ph-1*) (from TCI) were used as received. *p*-Fluorobenzonitrile (from TCI) was also used without previous purification.

4,4'-Bis(4-aminophenoxy)biphenyl (**4e**) and bis[4-(4-aminophenoxy)phenyl]sulfone (**4f**) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenols and *p*-chloronitrobenzene in the presence of a base such as K_2CO_3 , giving the bis(*p*-nitrophenoxy) compounds, and subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. *p*-Phenylenediamine (**4a**, from TCI) was purified by vacuum distillation. The other reagent-grade aromatic diamines such as 4,4'-oxydianiline (**4b**, from TCI), 4,4'-diaminodiphenylmethane (**4c**, from TCI), 1,4-bis(4-aminophenoxy)benzene (**4d**, from TCI) were used without purification. Commercially obtained anhydrous calcium chloride were dried under vacuum at 180°C for 10 h. *N*-methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure

over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (from TCI) was purified by distillation under reduced pressure.

Syntheses of Bis(ether nitrile)s

According to the synthetic procedure of 4,4'-(1,4-phenylenedioxy)dibenzonitrile (**2**) described in another separate work,¹ 4,4'-(2,5-tolylenedioxy)dibenzonitrile (*Me-2*) and 4,4'-(2,5-phenylenedioxy)dibenzonitrile (*Ph-2*), were synthesized via the aromatic nucleophilic substitution reaction of *p*-fluorobenzonitrile with the potassium bisphenolates of methylhydroquinone and phenylhydroquinone. Their yield, melting points, elemental analyses, and spectral data are listed as follows.

Me-2: yield 91.5%, mp 162–163°C. IR (KBr): 2228 cm^{-1} ($C\equiv N$ str.), 1487–1603 cm^{-1} (arom. $C=C$ str.), 1241 cm^{-1} ($C-O-C$ str.). ¹H-NMR ($CDCl_3$):

Table I. Inherent Viscosities, Average Molecular Weights, and Film Quality of Polyamides

Polymer ^a	η_{inh}^b (dL/g)	$\bar{M}_p^c \times 10^{-4}$	Film Quality ^e
5a	0.52	— ^d	— ^f
5b	0.76	—	—
5c	0.73	—	—
5d	0.81	—	—
5e	—	—	—
5f	0.98	—	Flexible
<i>Me-5a</i>	0.66	—	—
<i>Me-5b</i>	0.96	4.9	Flexible
<i>Me-5c</i>	0.73	5.5	Flexible
<i>Me-5d</i>	0.80	5.5	Flexible
<i>Me-5e</i>	0.77	—	Brittle
<i>Me-5f</i>	0.67	5.8	Flexible
<i>Ph-5a</i>	0.90	—	Flexible
<i>Ph-5b</i>	1.34	9.6	Flexible
<i>Ph-5c</i>	1.29	8.6	Flexible
<i>Ph-5d</i>	1.30	8.4	Flexible
<i>Ph-5e</i>	0.78	7.0	Flexible
<i>Ph-5f</i>	0.99	7.3	Flexible

^a Polymerization was carried out with 1.25 mmol of each monomer, 2.50 mmol of TPP, 1 mL of pyridine, and 0.4 g of $CaCl_2$ in 2–5 mL of NMP at 105°C for 3 h.

^b Measured at 0.5 g/dL in DMAc containing 5 wt % LiCl dissolved, at 30°C.

^c Number-average molecular weights correspond to the peaks of the GPC curves, with DMF + 0.01 mol/L LiBr as the eluent and polystyrene as the standard.

^d Insoluble in the eluent of GPC measurements.

^e Films were cast by slow evaporation of polymer solutions in DMAc.

^f Insoluble in DMAc.

Table II. Solubility of Polyamides^a

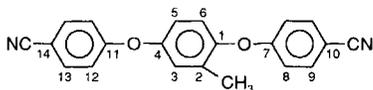
Polymer	Solvents ^b					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
5a	-	-	-	-	-	-
5b	-	-	-	-	-	-
5c	+	-	-	-	-	-
5d	-	-	-	-	-	-
5e	-	-	-	-	-	-
5f	+	+	-	-	-	-
<i>Me-5a</i>	-	-	-	-	-	-
<i>Me-5b</i>	+	+	+	+	+h	-
<i>Me-5c</i>	+	-	-	-	-	-
<i>Me-5d</i>	+	+	+	+	+h	-
<i>Me-5e</i>	+	-	-	-	-	-
<i>Me-5f</i>	+	+	+	+	+	-
<i>Ph-5a</i>	+	+	+h	+	-	-
<i>Ph-5b</i>	+	+	+	+	+s	-
<i>Ph-5c</i>	+	+	+	+	+h	-
<i>Ph-5d</i>	+	+	+	+	+h	-
<i>Ph-5e</i>	+	+	+	+	+	-
<i>Ph-5f</i>	+	+	+	+	+h	-

^a +: soluble, -: insoluble, +h: soluble on heating, +s: swelling on heating.

^b NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

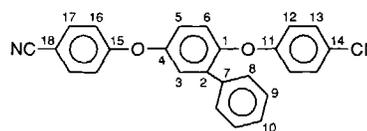
δ 7.66 (q, 4H), 7.09 (t, 3H), 6.98 (d, 4H), 2.17 ppm (s, 3H). ¹³C-NMR (CDCl₃): δ 161.37 (C₁, C₄), 151.77 (C₁₁), 149.14 (C₇), 134.16 (C₉, C₁₃), 132.68 (C₂), 123.32 (C₆), 122.55 (C₅), 119.26 (C₃), 118.63 (C≡N), 117.89 (C₁₂), 116.71 (C₈), 105.71 (C₁₄), 105.27 (C₁₀), 16.08 ppm (—CH₃).

ANAL. Calcd for C₂₁H₁₄N₂O₂ (326.35): C, 77.29%; H, 4.32%; N, 8.58%. Found: C, 77.04%; H, 4.49%; N, 8.45%.



Ph-2: yield 85.8%, mp 191–192°C. IR (KBr): 2224 cm⁻¹ (C≡N str.), 1405–1603 cm⁻¹ (arom. C=C str.), 1241 cm⁻¹ (C—O—C str.). ¹H-NMR (CDCl₃): δ 7.65 (d, 2H), 7.52 (d, 2H), 7.43 (d, 1H), 7.32 (q, 5H), 7.21 (s, 1H), 7.11 (d, 1H), 7.09 (d, 2H), 6.88 ppm (d, 2H). ¹³C-NMR (CDCl₃): δ 161.40 (C₄), 161.25 (C₁), 152.24 (C₁₁), 148.03 (C₁₅), 136.66 (C₇), 135.83 (C₂), 134.26 (C₁₃), 134.0 (C₁₇), 128.74 (C₉), 128.41 (C₈), 128.10 (C₁₀), 123.49 (C₃), 122.98 (C₅), 120.60 (C₆), 118.69 (C≡N), 118.00 (C₁₂), 117.09 (C₁₆), 106.32 (C₁₄), 105.60 ppm (C₁₈).

ANAL. Calcd for C₂₆H₁₆N₂O₂ (388.42): C, 80.40%; H, 4.15%; N, 7.21%. Found: C, 80.22%; H, 4.40%; N, 7.34%.

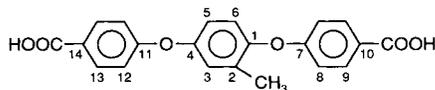


Syntheses of Bis(ether carboxylic acid)s

According to the synthetic procedure of ether-diacid **3** described elsewhere,¹ the bis(ether carboxylic acid)s *Me-3* and *Ph-3* were obtained by the alkaline hydrolysis of the corresponding bis(ether nitrile)s *Me-2* and *Ph-2*.

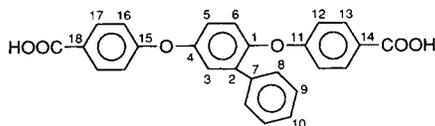
Me-3: yield 91.5%, mp 302–304°C. IR (KBr): 2560–3100 cm⁻¹ (O—H str.), 1682 cm⁻¹ (C=O str.), 1431–1605 cm⁻¹ (arom. C=C str.), 1234 cm⁻¹ (C—O—C str.). ¹H-NMR (CDCl₃): δ 7.95 (t, 4H), 7.0–7.15 (m, arom. protons, 7H), 2.11 ppm (s, 3H). ¹³C-NMR (CDCl₃): δ 166.80 (C=O), 161.35 (C₁), 161.19 (C₄), 151.94 (C₁₁), 149.14 (C₇), 132.20 (C₂), 131.76 (C₉), 131.71 (C₁₃), 125.23 (C₁₄), 124.74 (C₁₀), 122.99 (C₅), 122.56 (C₆), 119.14 (C₃), 117.13 (C₁₂), 115.80 (C₈) ppm (—CH₃).

ANAL. Calcd for $C_{21}H_{16}O_6$ (364.35): C, 69.23%; H, 4.43%. Found: C, 69.21%; H, 4.30%.



Ph-3: yield 80.9%, mp 261–263°C. IR (KBr): 2400–3200 cm^{-1} (O—H str.), 1686 cm^{-1} (C=O str.), 1424–1503 cm^{-1} (arom. C=C str.), 1226 cm^{-1} (C—O—C str.). $^1\text{H-NMR}$ (CDCl_3): δ 8.0 (d, 2H), 7.89 (d, 2H), 7.17–7.51 (arom. protons, 10H), 6.96 ppm (d, 2H). $^{13}\text{C-NMR}$ (CDCl_3): δ 166.65 (C=O), 161.26 (C_4), 160.84 (C_1), 152.21 (C_{11}), 147.69 (C_{15}), 135.94 (C_7), 135.40 (C_2), 131.66 (C_{13}), 131.47 (C_{17}), 128.66 (C_9), 128.27 (C_8), 127.76 (C_{10}), 125.36 (C_{14}), 124.67 (C_{18}), 123.48 (C_3), 122.13 (C_5), 120.55 (C_6), 117.30 (C_{12}), 116.18 ppm (C_{16}).

ANAL. Calcd for $C_{26}H_{18}O_6$ (426.42): C, 73.23%; H, 4.25%. Found: C, 72.87%; H, 4.38%.



Polymer Synthesis

A typical polymerization procedure is as follows. A mixture of 0.5330 g (1.25 mmol) of 4,4'-(2,5-biphenylenedioxy)dibenzoic acid **Ph-3**, 0.2476 g (1.25 mmol) of 4,4'-diaminodiphenylmethane (**4c**), 0.3 g of calcium chloride, 0.9 mL of triphenyl phosphite (TPP), 0.8 mL of pyridine, and 2.5 mL of NMP was heated with stirring at 105°C for 3 h. As the polycondensation proceeded, the reaction mixture became viscous. The resultant polymer solution was trickled into 300 mL of methanol giving rise to a stringy precipitate which was washed thoroughly with methanol and hot water, collected by filtration and dried. The yield was quantitative, the inherent viscosity of the polymer in DMAc containing 5 wt % LiCl was 1.29 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

Measurements

The inherent viscosities were determined by using a Cannon–Fenske dilution viscometer thermostated at 30°C. Molecular weights of polyamides were determined by gel permeation chromatography (GPC) on a Shimadzu LC-6A apparatus, using Tosoh TSK-GEL columns, DMF with 0.01 M LiBr as eluent, a

pumping rate of 1 mL/min, and a refractive index detector. The system was calibrated with polystyrene standards (Tosoh, Japan). Infrared (IR) analysis was performed using a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were conducted with a Perkin-Elmer C,H,N 2400 elemental analyzer. The 400-MHz $^1\text{H-NMR}$ spectra were recorded at 30°C on a Jeol EX-400 NMR spectrometer using tetramethylsilane (TMS) as an internal reference. The 100-MHz $^{13}\text{C-NMR}$ spectra were recorded with the same FT NMR spectrometer with deuteriochloroform (CDCl_3) or per-deuterodimethyl sulfoxide ($\text{DMSO-}d_6$) as an internal reference. Glass transition temperatures, taken as the midpoint of the change in slope of baseline, were measured on a DuPont DSC 1090 instrument with a heating rate of 20°C/min. Thermogravimetry (TG) on the polymer films was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. About 9–11 mg of the polymer was heated in flowing nitrogen or air (50 cm^3 min) at a heating rate of 20°C/min. The measurements were taken after an initial 250°C/5 min drying step. The wide-angle x-ray diffraction measurements were recorded at room temperature (ca. 25°C) on powder or film specimens of about 0.1 mm

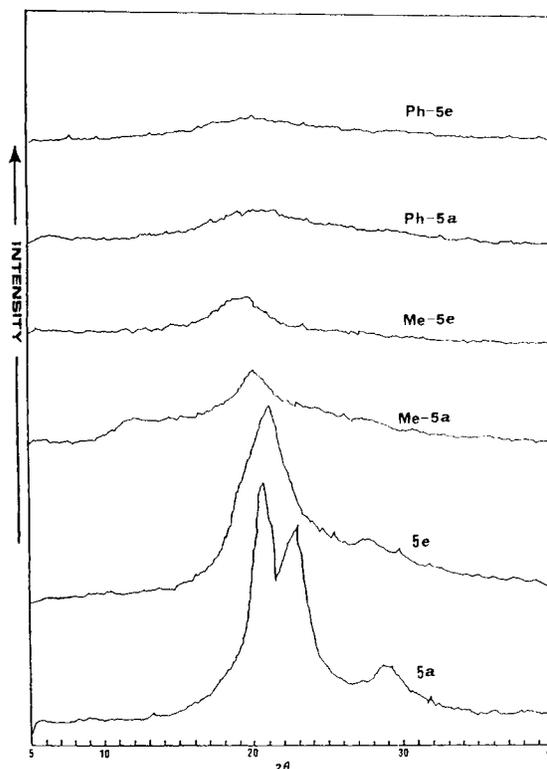


Figure 4. Wide-angle x-ray diffractograms of some representative polyamides.

Table III. Tensile Properties of Polyamide Films

Polymer	Strength at Yield (MPa)	Strength at Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
5a	— ^a	—	—	—
5b	—	—	—	—
5c	—	—	—	—
5d	—	—	—	—
5e	—	—	—	—
5f	64	56	37	1.69
<i>Me-5a</i>	—	—	—	—
<i>Me-5b</i>	—	86	6	2.18
<i>Me-5c</i>	—	76	6	2.07
<i>Me-5d</i>	—	98	7	2.35
<i>Me-5e</i>	—	—	—	—
<i>Me-5f</i>	—	66	6	1.68
<i>Ph-5a</i>	94	100	8	2.60
<i>Ph-5b</i>	85	81	9	2.25
<i>Ph-5c</i>	93	84	11	2.05
<i>Ph-5d</i>	82	81	9	2.08
<i>Ph-5e</i>	—	81	8	1.94
<i>Ph-5f</i>	74	79	10	1.83

^a Measurable specimens were not obtained.

thick with a Rigaku Geiger Flex D-Max III x-ray diffractometer, using Ni-filtered CuK α radiation (operating at 40 kV and 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. Tensile properties of the polymer films were determined from stress-strain curves obtained by an Instron universal tester Model 1130 with a load cell of 5 kg. A gauge of 2 cm and an elongation rate of 5 cm/min were used for this study. The measurements were conducted at room temperature using solution-cast film specimens of 0.5 cm wide, 6 cm long, and about 0.1 mm thick, and an average of at least five individual determinations was employed.

RESULTS AND DISCUSSION

Monomer Synthesis

4,4'-(1,4-Phenylenedioxy)dibenzoic acid (**3**), 4,4'-(2,5-tolylenedioxy)dibenzoic acid (*Me-3*), and 4,4'-(2,5-biphenylenedioxy)dibenzoic acid (*Ph-3*) were prepared by the nucleophilic substitution reaction of the corresponding hydroquinones with *p*-fluorobenzonitrile followed by alkaline hydrolysis. The synthetic procedure is outlined in Scheme 1. The structures of intermediate dinitriles and dicarboxylic acids were confirmed through IR, ¹H- and ¹³C-NMR spectro-

scopy, and elemental analysis. In particular, the IR and ¹³C-NMR spectra gave the most powerful evidence.

Figure 1 shows the FTIR spectra of dinitrile *Ph-2* and diacid *Ph-3*. When *Ph-2* was hydrolyzed into *Ph-3*, the sharp absorption near 2228 cm⁻¹ of C \equiv N group in *Ph-2* disappeared, and characteristic absorptions peculiar to carboxyl group occurred at about 1682 and 2500–3300 cm⁻¹. The ¹³C-NMR spectra of dinitrile *Ph-2* and diacid *Ph-3* are given in Figure 2 and Figure 3, respectively. The most obvious features of the spectra are the shifts of the resonance signals for the carbons of C \equiv N groups and their adjacent carbons C₁₄ and C₁₈. The C₁₄ and C₁₈ of *Ph-2* are shielded by the anisotropic field induced by the π electrons of C \equiv N, and hence C₁₄ and C₁₈ resonate at higher field than the other aromatic carbons. After the cyano group was converted into carboxyl group, the original resonances around 118.6 ppm due to the cyano carbons vanished, the resonances of carbonyl carbons appeared around 166.6 ppm, and the resonance peaks of C₁₄ and C₁₈ moved to lower field (from 106.3 to 125.4 ppm, from 105.6 to 124.7 ppm, respectively) due to the lack of anisotropic shielding.

Polymer Synthesis

Three series of aromatic polyamides **5a–f**, *Me-5a–f*, and *Ph-5a–f*, were directly prepared by a Ya-

mazaki phosphorylation polyamidation technique from dicarboxylic acids **3**, *Me-3*, and *Ph-3*, respectively, and aromatic diamines **4a–f** using triphenyl phosphite and pyridine as condensing agents (Scheme 2). Except for those of **5a–e** and *Me-5a*, all other reaction solutions were homogeneously transparent throughout the reaction. About 1 h after the reaction proceeded, the reaction solutions became highly viscous indicating the formation of high molecular weight polymers. The results of these polycondensation reactions are summarized in Table I. Their inherent viscosities ranged from 0.52 to 1.34 dL/g. The solubility of the methyl- and phenyl-substituted polyamides was remarkably enhanced due to the introduction of pendant groups. Almost all *Me-5* and *Ph-5* serial polyamides were soluble in the DMAc or NMP and afforded flexible and tough films by means of solution-casting. Almost all of them were also soluble in the eluent of GPC measurements, DMF containing 0.01 mol/L of LiBr, to permit molecular weight determination. The GPC curves indicated that the number-average molecular weights of these polyamides were in the range of 49,000–96,000 relative to polystyrene standard.

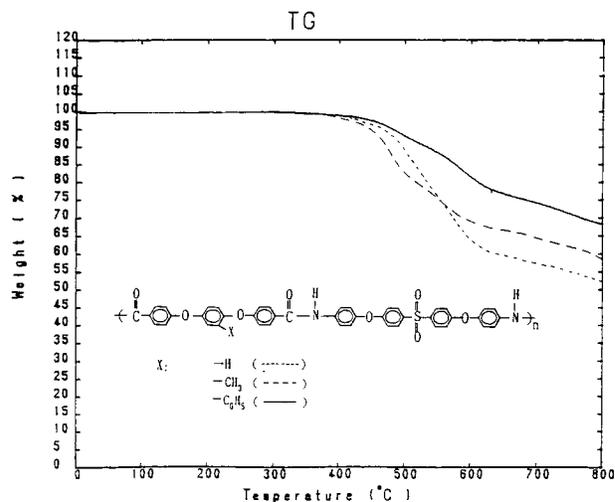


Figure 5. The TG curves of polyamides **5f**, *Me-5f*, and *Ph-5f*, with a heating rate of 20°C/min in nitrogen.

Properties of Polymers

The solubility of polyamides was studied qualitatively. The results are presented in Table II. Due to the introduction of pendant methyl or phenyl groups on the aromatic ring, the solubility of **5** series poly-

Table IV. Thermal Properties of Polyamides

Polymer	T_g^a (°C)	T_d^b (°C)		Char Residual ^c (wt %)
		In N ₂	In Air	
5a	—	489	461	55.7
5b	—	490	468	62.3
5c	216	453	470	61.3
5d	—	501	479	57.0
5e	—	503	492	65.9
5f	220 (356) ^d	495	494	53.0
<i>Me-5a</i>	—	474	476	58.0
<i>Me-5b</i>	—	468	477	64.1
<i>Me-5c</i>	—	475	489	65.5
<i>Me-5d</i>	200	458	473	65.8
<i>Me-5e</i>	220	468	478	66.1
<i>Me-5f</i>	217	472	468	59.4
<i>Ph-5a</i>	—	511	491	67.4
<i>Ph-5b</i>	219	513	501	64.1
<i>Ph-5c</i>	218	509	518	66.5
<i>Ph-5d</i>	209	522	500	63.7
<i>Ph-5e</i>	232	517	502	58.4
<i>Ph-5f</i>	231	535	528	68.2

^a From the second heating traces of DSC measurements conducted at a heating rate of 20°C/min in N₂.

^b Decomposition temperature at which 10% weight loss was recorded with thermogravimetry at a heating rate of 20°C/min.

^c Char residual at 800°C in nitrogen.

^d The endotherm peak temperature observed on the first heating DSC trace.

amides was apparently enhanced, in particular to polar aprotic solvents such as NMP, DMAc, DMF, and DMSO. Almost all polyamides of **5** series were insoluble in all the solvents tested. Among the *Me-5* series polyamides, those obtained from flexible ether group-containing or polar sulfonyl group-containing diamines such as **4b**, **4d**, and **4f**, were soluble in NMP, DMAc, DMF, DMSO, or *m*-cresol; however, those derived from more rigid diamines such as **4a**, **4c**, and **4e** showed poor solubility. Furthermore, the bulky pendant phenyl group-bearing *Ph-5* series polyamides showed obviously enhanced solubility, and they were readily soluble in polar solvents such as NMP, DMAc, DMF, and DMSO at room temperature and, most of them, even soluble in hot *m*-cresol.

Typical x-ray diffractograms of some polyamides are shown in Figure 4. The hydroquinone-based polyamides **5a** and **5e** revealed highly crystalline patterns. For methylhydroquinone-based polyamides *Me-5a* and *Me-5e*, the intensity of reflection peaks around $2\theta = 20^\circ$ was remarkably decreased. Polyamides *Ph-5a* and *Ph-5e* based on phenylhydroquinone exhibited amorphous diffraction patterns. The results of solubility and x-ray diffraction measurements clearly indicate that the presence of methyl or phenyl substituent on the 1,4-dioxyphenylene unit interferes with the close packing of polyamide chains, thus, leading to a decreased crystallinity and an increased solubility. This may be attributed to the fact that the pendant groups reduce the backbone symmetry and regularity and interrupt intermolecular hydrogen bonding.

Most polyamides containing methylhydroquinone or phenylhydroquinone moiety could be cast into flexible films by slow evaporation of their polymer solutions in DMAc or NMP. The tensile properties of these flexible polyamide films are included in Table III. These films had tensile strength of 66–100 MPa, elongation to break of 6–11%, and tensile modulus of 1.68–2.25 GPa. Among the hydroquinone-based polyamides **5a–f**, only **5f** could be cast into a flexible film and its tensile property is also listed in Table III. The polymer film showed a clear yield point on the stress-strain curve, and its elongation at break reached up to 37%. This implies that polymer **5f** behaves as a semi-crystalline and tough material. However, polyamides *Me-5f* and *Ph-5f*, analogues of **5f**, showed a lower elongation at break on the tensile test. This can be explained by their amorphous nature due to the presence of pendant groups. Most *Ph-5* series polyamides necked on tensile test, whereas their elongations to break were not high and ranged from 8 to 11%.

The thermal properties of the polyamides were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal behavior data of these polyamides are listed in Table IV. Rapid cooling from elevated temperatures of approximately 400°C to room temperature to form more amorphous materials, and thus, some polyamides displayed distinct glass transitions on subsequent heating DSC traces. These polyamides had T_g s in the range of 200–232°C. However, some polyamides like **5a,b,d,e**, *Me-5a,b,d,e*, and *Ph-5a* show no discernable glass transition in their DSC traces, probably due to their rigid structure or high degree of crystallinity. The *Ph-5* series polyamides revealed relatively higher T_g s. It is reasonable because of the presence of bulky pendant phenyl group leading to the steric hindrance of segment movement.

Thermogravimetric traces indicated that the introduction of pendant groups did not lead to significant loss in thermal stability. These polyamides were stable up to 450°C in both air and nitrogen. Due to higher aromaticity, the *Phs-5* series polyamides revealed higher initial decomposition temperatures (T_d) than the other two series. Typical TG curves are shown in Figure 5. The 10% weight loss temperatures of these three polyamide series, **5**, *Me-5*, and *Ph-5*, were recorded respectively in the range of 453–503, 458–475, and 509–535°C in nitrogen and 461–494, 468–489, and 491–528°C in air. All the polyamides have left more than 50 wt % char residue at 800°C in nitrogen. In general, the polyamides of *Me-5* series began to degrade at slightly lower temperatures than the corresponding ones of the other two series due to the presence of less stable methyl group. However, they degraded at a lower initial degradation rate in air, possibly attributed to the occurrence of crosslinking reactions of benzyl radical and the oxidation of methyl groups. As shown in Table IV, most *Me-5* series polyamides have higher T_d s in air than in nitrogen.

CONCLUSION

We have obtained three bis(ether carboxylic acid)s, 4,4'-(1,4-phenylenedioxy)dibenzoic acid (**3**), 4,4'-(2,5-tolylenedioxy)dibenzoic acid (*Me-3*), and 4,4'-(2,5-biphenylenedioxy)dibenzoic acid (*Ph-3*), in high yield and high purity from the nucleophilic aromatic fluoro-displacement of *p*-fluorobenzonitrile with the corresponding hydroquinones and subsequent alkaline hydrolysis of the intermediate dinitriles. The structures of diacids **3**, *Me-3*, and *Ph-3*

were evidenced by elemental analysis and IR, ¹H-NMR, and ¹³C-NMR spectroscopy.

The solution direct polycondensation of diacids *Me-3* and *Ph-3* with aromatic diamines, using triphenyl phosphite and pyridine as condensing agents, to generate high molecular weight polyamides was successful. The polyamides obtained had inherent viscosities above 0.66 dL/g and up to 1.34 dL/g in DMAc-5 wt % LiCl. However, an unsatisfactory result was obtained in cases of diacid **3** with rigid or short-chain aromatic diamines.

The polyamides (*Me-5* and *Ph-5*) derived from diacids *Me-3* and *Ph-3* revealed higher solubility than those derived from diacid **3**. Almost all the *Me-5* and *Ph-5* serial polyamides were amorphous and readily soluble in polar solvents like DMAc and NMP and afforded flexible and tough films by means of solvent casting. The polymer films exhibited good tensile properties. These polyamides had *T_g*s in the range of 200–232°C recorded by DSC, and the *Ph-5* series polymers revealed relatively higher *T_g*s due to the higher aromaticity and/or the steric hindrance effect caused by the pendant phenyl group. Thermogravimetry confirmed the thermal and thermooxidative stability of the polyamides, showing 10% weight loss temperatures higher than 460°C and a char yield of greater than 53% at 800°C under nitrogen.

High solubility indicates that the methyl- or phenyl-substituted polyamides *Me-5* and *Ph-5* are readily processable from solution even at high molecular weight. Thus, the improved processability of these polyamides, combined with the retention of a good thermal resistance, makes these polymers an attractive soluble high-performance material.

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