

Synthesis and properties of aromatic polyamides based on 4,4'-[1,4(1,3 or 1,2)-phenylenedioxy]dibenzoic acid

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SUMMARY:

Three isomeric bis(ether carboxylic acids), 4,4'-[1,2(1,3 or 1,4)-phenylenedioxy]dibenzoic acid (*o*-, *m*-, or *p*-3) were prepared by nucleophilic substitution reaction of the potassium phenolate of catechol, resorcinol, and hydroquinone, respectively, with *p*-fluorobenzonitrile, giving the corresponding bis(ether nitrile)s, followed by alkaline hydrolysis. Three series of isomeric polyamides were synthesized by direct polycondensation of the bis(ether carboxylic acid)s with various aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved metal salts such as CaCl₂ or LiCl using triphenyl phosphite and pyridine as condensing agents. The resultant polyamides had inherent viscosities of 0,52–1,63 dL/g. Most of the polymers were soluble in polar aprotic solvents such as *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), NMP, and dimethyl sulfoxide. The catechol-based polyamides revealed markedly higher solubility than those based on hydroquinone or resorcinol. Transparent, flexible and tough films could be cast from the DMAc or NMP solutions of most of the polyamides. All the casting films were characterized by tensile tests. The glass transition temperatures (T_g 's) of most polyamides could be determined with the help of differential scanning calorimetry (DSC) traces, which were recorded in the range of 183–232 °C. In general, the polyamides based on catechol had T_g 's comparable with the ones of the hydroquinone-based polyamides and higher T_g 's than the corresponding resorcinol-based ones. Thermogravimetric analysis data of these polymers indicated that all the polyamides were stable up to 400 °C in both air and nitrogen atmospheres.

Introduction

Wholly aromatic polyamides (aramids) are an important class of high-performance heat-resistant materials¹⁾. Commercially known Kevlar [poly(*p*-phenyleneterephthalamide)] and Nomex [poly(*m*-phenyleneisophthalamide)] are composed of phenylene units linked via an amide group and exhibit high crystallinity. Thus, they find use as ultrahigh-strength/high-modulus fibers. These polyamides exhibit a number of excellent properties such as high thermal stability, chemical resistance, low flammability, and excellent mechanical properties as fibers. Fabrication of aramids, however, is generally difficult because of their high melting or softening temperatures and limited solubility in most organic solvents. Thus, the applications of these aramids are fettered. Recently, new processable engineering plastics possessing moderately high glass transition temperatures and good solubility in organic solvents have been required for practical use, and a number of soluble high-temperature aramids have been reported^{2–6)}.

One of the useful approaches to improve the processability without extreme loss of their thermal stability is the introduction of flexible groups such as aryl ether, aryl

sulfide, isopropyl group, or sulfone group into the polymer chain⁷⁻¹¹). It has been generally recognized that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperatures and crystalline melting temperatures, as well as significant improvements in solubility and other process characteristics of the polymers without greatly sacrificing thermal stability. This kind of aramid structural modification was usually realized by the insertion of arylene ether segments into the diamine monomer. The approach to synthesize the bis(*p*-aminophenoxy) compound by a nucleophilic substitution of a bisphenol with *p*-chloronitrobenzene, followed by reduction of the resulting dinitro compound, is very popular in the literature¹²⁻¹⁸).

Recently, it has been demonstrated^{11,29}) that aromatic bis(ether-carboxylic acid)s could be readily synthesized through the nucleophilic displacement of *p*-fluorobenzonitrile with bisphenoxide ions followed by hydrolysis. The present investigation follows this synthetic route to prepare three isomeric ether-containing diacid monomers, 4,4'-[1,2(1,3 and 1,4)-phenylenedioxy]dibenzoic acids, starting from hydroquinone, resorcinol, and catechol, respectively. Several novel aramids on the basis of these diacids and aromatic diamines will be prepared and characterized by solubility, tensile properties, crystallinity, and thermal properties. The polymers were prepared by a phosphorylation polyamidation route, reported by Yamazaki et al.¹⁹), by means of triphenyl phosphite and pyridine. This route has been proved to be a very useful laboratory method and has been popularly used in the preparation of polyamides²⁰⁻²²) and poly(amide-imide)s²³⁻²⁷) directly from diamines with aromatic or aliphatic dicarboxylic acids and imide-bearing dicarboxylic acids.

Experimental part

Materials

All the isomeric benzenediols, catechol (*o*-1), resorcinol (*m*-1), and hydroquinone (*p*-1), were used as received from Janssen Chemical Ind. *p*-Fluorobenzonitrile (from TCI) was also used without previous purification.

According to a reported method²⁸) 4,4'-bis(4-aminophenoxy)biphenyl (**4g**), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**4h**), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**4i**), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**4j**), bis[4-(4-aminophenoxy)phenyl] sulfone [**4k**], and α, α' -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**4l**) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenols and *p*-chloronitrobenzene in the presence of potassium carbonate, 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 *m*-phenylenediamine (**4b**, from Janssen), 4,4'-oxydianiline (**4c**, from TCI), 3,4'-oxydianiline (**4d**, from Mitsui Petrochemical Ind.), 4,4'-diaminodiphenylmethane (**4e**, from TCI) and 1,4-bis(4-aminophenoxy)benzene (**4f**, from TCI) were used without purification.

Commercially obtained anhydrous calcium chloride and lithium chloride were dried under vacuum at 180 °C for 10 h. *N*-Methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium

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

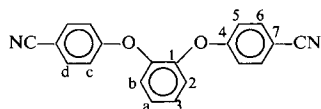
Syntheses of bis(ether nitrile)s 2

The bis(ether nitrile)s 2 were prepared by a nucleophilic fluoro-displacement of *p*-fluorobenzonitrile with the corresponding benzenediols 1 in the presence of a base, such as potassium carbonate, in a polar aprotic solvent like DMF. A typical preparative procedure for 4,4'-(1,2-phenylenedioxy)dibenzonitrile (*o*-2) is described as follows. In a 300-mL round-bottomed flask, K₂CO₃ (28,16 g; 0,2 mol) was suspended in a solution of catechol (11,2 g; 0,1017 mol) in 120 mL of a 1 : 1 volume mixture of DMF and toluene and heated at reflux temperature using a Dean-Stark trap to remove the water azeotropically. After toluene was removed completely, *p*-fluorobenzonitrile (25 g; 0,2064 mol) was added and heating was continued at 150 °C for 6 h. The reaction mixture was allowed to cool and poured into 600 mL of water. The product, which separated as a brown solid, was collected by filtration and dried. Yield: 31,67 g (99,7%). The crude product was recrystallized from methanol to afford colorless needles of 4,4'-(1,2-phenylenedioxy)dibenzonitrile (*o*-2) with a melting point of 116,5–118,0 °C in 82% (26 g) yield.

IR (KBr): 2226 (C≡N str.), 1454–1609 (arom. C=C str.), 1234 cm⁻¹ (C—O—C str.).

¹H NMR (CDCl₃): δ = 7,55 (d, H_d, 4H), 7,33 (d, H_a, 2H), 7,24 (d, H_b, 2H), 6,84 ppm (d, H_c, 4H).

¹³C NMR (CDCl₃): δ = 160,72 (C¹), 145,87 (C⁴), 134,00 (C⁶), 126,97 (C³), 123,28 (C²), 118,62 (C≡N), 116,95 (C⁵), 106,14 ppm (C⁷).



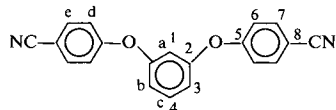
The other two bis(ether nitrile)s, 4,4'-(1,3-phenylenedioxy)dibenzonitrile (*m*-2), and 4,4'-(1,4-phenylenedioxy)dibenzonitrile (*p*-2) were synthesized in an analogous procedure.

Dinitrile *m*-2: Yield 81,5%; m. p. 122–123 °C.

IR (KBr): 2224 (C≡N str.), 1440–1591 (arom. C=C str.), 1234 cm⁻¹ (C—O—C str.).

¹H NMR (CDCl₃): δ = 7,63 (d, H_e, 4H), 7,43 (t, H_c, 1H), 7,06 (d, H_d, 4H), 6,92 (d, H_b, 2H), 6,78 ppm (s, H_a, 1H).

¹³C NMR (CDCl₃): δ = 160,72 (C²), 156,53 (C⁵), 134,25 (C⁷), 131,40 (C⁴), 118,56 (C⁶), 118,43 (C≡N), 116,33 (C³), 112,11 (C¹), 106,64 ppm (C⁸).

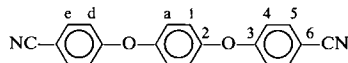


Dinitrile *p*-2: Yield 75,9%; m. p. 212–213 °C.

IR (KBr): 2226 (C≡N str.), 1417–1603 (arom. C=C str.), 1241 cm⁻¹ (C—O—C str.).

¹H NMR (CDCl₃): δ = 7,63 (d, H_e, 4H), 7,12 (s, H_a, 4H), 7,04 ppm (d, H_b, 4H).

¹³C NMR (CDCl₃): δ = 161,40 (C²), 151,69 (C³), 134,19 (C⁵), 122,01 (C¹), 118,62 (C≡N), 117,84 (C⁴), 106,19 ppm (C⁶).



$C_{20}H_{12}N_2O_2$ (312,33)	Calc.	C 76,91	H 3,87	N 8,97
<i>o</i> -2:	Found	C 76,81	H 3,87	N 8,97
<i>m</i> -2:	Found	C 76,63	H 4,01	N 8,81
<i>p</i> -2:	Found	C 76,63	H 3,93	N 8,76

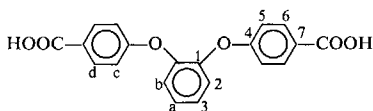
Syntheses of bis(ether carboxylic acid)s 3

The bis(ether carboxylic acid)s 3 were obtained by alkaline hydrolysis of the corresponding bis(ether nitrile)s 2. For example, a suspension of 4,4'-(1,2-phenylenedioxy)dibenzonitrile (*o*-2, 26 g; 0,083 mol) in 500 mL of a 1:1 volume mixture of water and ethanol containing 80 g (1,43 mol) of KOH was refluxed for 20 h. The resulting hot clear solution was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and was acidified by conc. HCl to pH = 3, and the white precipitate was filtered off, washed with water and dried in vacuo, to give 20,8 g (73% yield) of 4,4'-(1,2-phenylenedioxy)dibenzoic acid (*o*-3); m. p. 255–256 °C.

IR (KBr): 2500–3300 (O—H str.), 1684 (C=O str.), 1431–1609 (arom. C=C str.), 1272 cm^{-1} (C—O—C str.).

1H NMR (DMSO- d_6): δ = 7,90 (d, H_d , 4H), 7,35 (d, H_a , 2H), 7,31 (d, H_b , 2H), 6,91 ppm (d, H_c , 4H).

^{13}C NMR (DMSO- d_6): δ = 166,97 (C=O), 160,31 (C^1), 146,17 (C^4), 131,43 (C^5), 126,48 (C^3), 126,26 (C^7), 122,78 (C^2), 116,11 ppm (C^6).



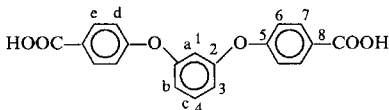
4,4'-(1,3-Phenylenedioxy)dibenzoic acid (*m*-3) and 4,4'-(1,4-phenylenedioxy)dibenzoic acid (*p*-3) were prepared in a similar method.

Dibenzoic acid *m*-3: Yield 73,7%; m. p. 299–301 °C.

IR (KBr): 2400–3300 (O—H str.), 1673 (C=O str.), 1427–1591 (arom. C=C str.), 1234 cm^{-1} (C—O—C str.).

1H NMR (DMSO- d_6): δ = 7,99 (d, H_c , 4H), 7,52 (t, H_c , 1H), 7,13 (d, H_d , 4H), 6,97 (d, H_b , 2H), 6,90 ppm (s, H_a , 1H).

^{13}C NMR (DMSO- d_6): δ = 166,71 (C=O), 160,37 (C^2), 156,76 (C^5), 131,73 (C^7), 131,62 (C^4), 125,66 (C^8), 117,60 (C^6), 115,46 (C^3), 111,20 ppm (C^1).

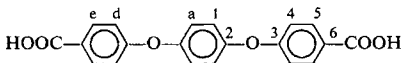


Dibenzoic acid *p*-3: Yield: 75,9%; m. p. 322–324 °C.

IR (KBr): 2400–3600 (O—H str.), 1684 (C=O str.), 1431–1603 (arom. C=C str.), 1230 cm^{-1} (C—O—C str.).

1H NMR (DMSO- d_6): δ = 8,00 (d, H_c , 4H), 7,24 (s, H_a , 4H), 7,10 ppm (d, H_b , 4H).

^{13}C NMR (DMSO- d_6): δ = 166,88 (C=O), 161,06 (C^2), 151,72 (C^3), 131,76 (C^5), 125,98 (C^6), 121,87 (C^4), 117,17 ppm (C^1).



$C_{20}H_{14}O_6$ (350,33)	Calc.	C 68,57	H 4,03
<i>o</i> -3:	Found	C 68,31	H 3,94
<i>m</i> -3:	Found	C 68,15	H 3,93
<i>p</i> -3:	Found	C 68,42	H 3,96

Polymer synthesis

A typical polymerization procedure is as follows. A mixture of 0,4379 g (1,25 mmol) of ether-diacid *o*-3, 0,2503 g (1,25 mmol) of 4,4'-oxydianiline (**4c**), 0,2 g of calcium chloride, 0,9 mL of triphenyl phosphite (TPP), 0,8 mL of pyridine, and 1 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 0,83 dL/g, measured at a concentration of 0,5 g/dL at 30 °C.

All other polyamides were synthesized by an analogous procedure as above.

Measurements

The inherent viscosities were measured with a Cannon-Fenske viscosimeter thermostated at 30 °C. Weight-average molecular weight (\bar{M}_w) and number-average molecular weight (\bar{M}_n) were determined by means of gel-permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0,01 mol/L of lithium bromide; flow rate: 1 mL/min; temperature: 40 °C; detector: a refractive index detector). IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were performed using a Perkin-Elmer C, H, N 2400 elemental analyzer. ¹H NMR and ¹³C NMR spectra were determined at 30 °C on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-*d*₆) as an external reference, working at 400 and 100 MHz, respectively. The DSC traces were measured on a Sinku Riko TA-7000 thermal analysis controller at the heating rate of 20 °C/min in flowing nitrogen (30 cm³/min). Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm³/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 scattering measurements were performed at room temperature (about 25 °C) with film specimens of about 0,1 mm thickness with a Rigaku Geiger Flex D-Max III_a X-ray diffractometer, using Ni-filtered Cu K_α radiation (operating at 40 kV and 15 mA). The scanning rate was 2°/min over a range of 2 θ = 5–40°. Tensile properties 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 performed at room temperature using solution-cast film specimens (0,5 cm wide, 6 cm long, and about 0,1 mm thick) and an average of at least five individual determinations was used.

Results and discussion

Monomer synthesis

The isomeric phenylenedioxydibenzoic acids *o*-, *m*-, and *p*-3 were prepared in high yields starting from the condensation of *p*-fluorobenzonitrile with catechol, resorcinol,

and hydroquinone, respectively, according to the synthetic route outlined in *Scheme 1*. According to the general procedure reported by Maglio¹¹⁾ and Liou²⁹⁾ et al., the bis(ether nitrile)s referred to as *o*-, *m*- and *p*-2 were prepared through the nucleophilic fluoro-displacement of *p*-fluorobenzonitrile with the bisphenoxide ion of the corre-

Scheme 1:

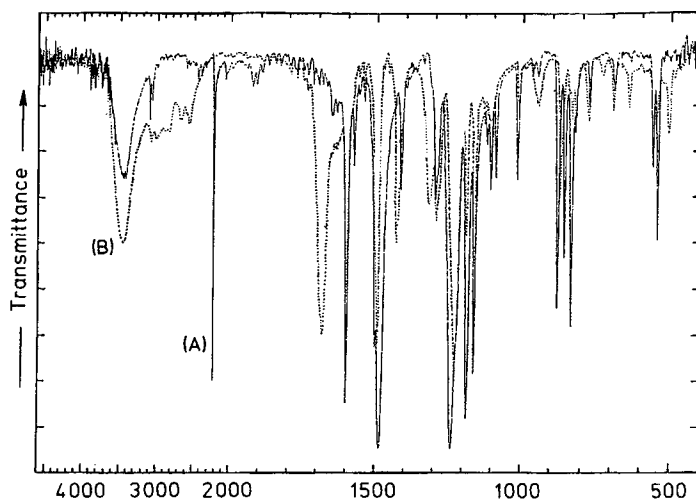
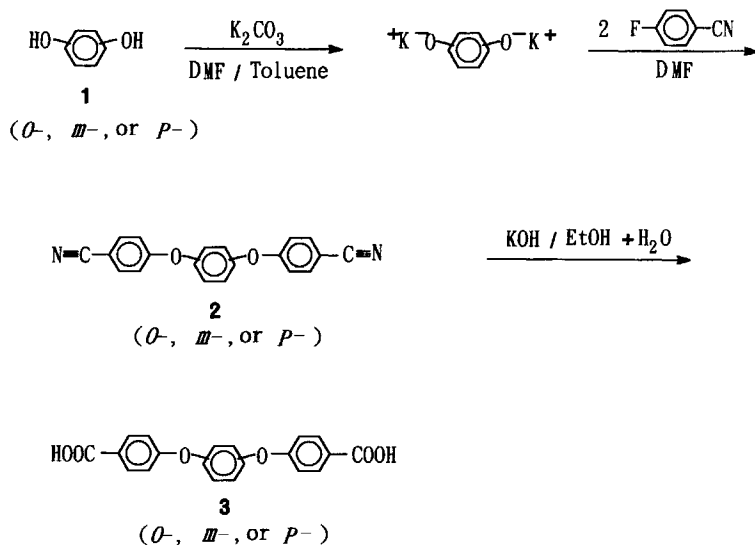


Fig. 1. IR spectra of (A) 4,4'-(1,4-phenylenedioxy)dibenzonitrile (*p*-2) and (B) 4,4'-(1,4-phenylenedioxy)dibenzoic acid (*p*-3)

sponding benzenediols (1). The yields of purified products were in the range of 76–82%. These bis(ether nitrile)s could then be readily converted into the corresponding bis(ether carboxylic acid)s by alkaline hydrolysis. The yield ranged from 73–80%, and the purity was high enough for the preparation of polymers with high molecular weights.

The structures of intermediate dibenzonitriles **2** and dibenzoic acids **3** were confirmed by elemental analysis and FTIR, ^1H NMR and ^{13}C NMR spectroscopy. The most important evidence could be seen from their IR and ^{13}C NMR spectra. Fig. 1 shows the FTIR spectra for 4,4'-(1,4-phenylenedioxy)dibenzonitrile (*p*-**2**) and 4,4'-(1,4-phenylenedioxy)dibenzoic acid (*p*-**3**). The $\text{C}\equiv\text{N}$ group in *p*-**2** gives a sharp absorption near 2260 cm^{-1} . When *p*-**2** was hydrolyzed into *p*-**3**, the characteristic band of $\text{C}\equiv\text{N}$ group disappeared, and the carbonyl stretching absorption occurred at

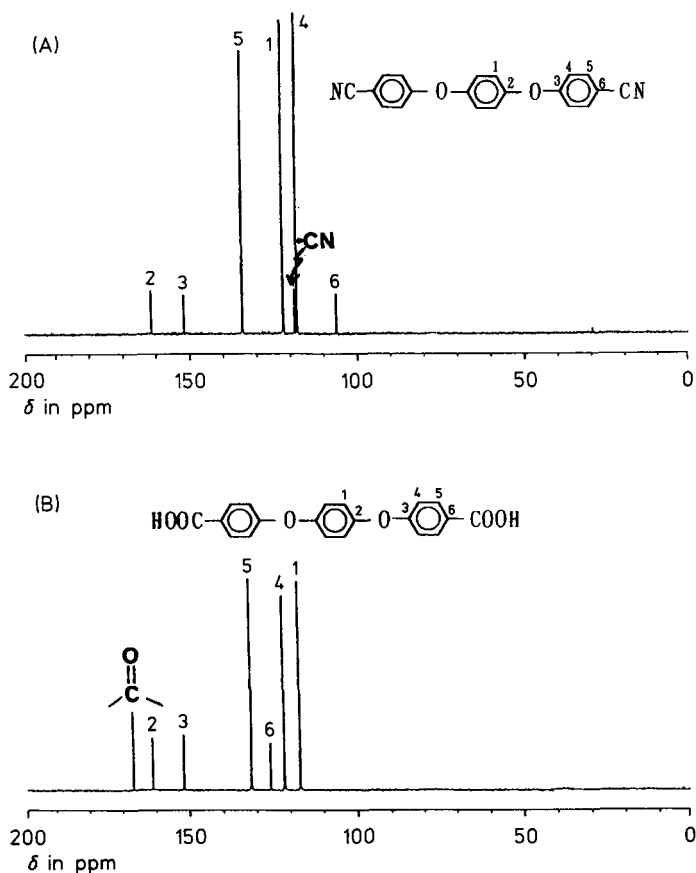


Fig. 2. ^{13}C NMR spectra of (A) 4,4'-(1,4-phenylenedioxy)dibenzonitrile (*p*-**2**) in CDCl_3 and (B) 4,4'-(1,4-phenylenedioxy)dibenzoic acid (*p*-**3**) in $\text{DMSO}-d_6$

about 1680 cm^{-1} and the broad O—H absorption appeared in the region from 2500 to 3500 cm^{-1} . The corresponding ^{13}C NMR spectra of dinitrile *p*-2 and diacid *p*-3 are shown in Fig. 2. The most obvious features of the spectra are the shifts of the resonance signals for the carbon of C≡N group and its adjacent carbon C⁶. The C⁶ of *p*-2 is shielded by the anisotropic field induced by the π electrons of C≡N, and hence C⁶ has resonance at higher field than the other aromatic carbons. After the cyano group was converted into a carboxyl group, the resonance peak of C⁶ moved to lower field (from 106,19 to 125,98 ppm) due to the lack of anisotropic shielding, the original signal at 118,24 ppm assigned to C≡N carbon disappeared, and the resonance of carbonyl carbon occurred at the farthest downfield (166,87 ppm).

The relevant data of IR, ^1H NMR, and ^{13}C NMR spectra of the resorcinol- and catechol-based dinitriles and diacids are summarized in the Experimental part. They are in good agreement with the expected structures.

Polymer synthesis

Aromatic polyamides were conventionally synthesized by low-temperature solution polycondensation of aromatic diacid chlorides with aromatic diamines in the presence of an acid acceptor in a polar aprotic solvent^{30–32}. In recent years, the direct polycondensation of aromatic dicarboxylic acids with aromatic diamines using triphenyl phosphite and pyridine as condensing agents (the so-called Yamazaki phosphorylation polyamidation method¹⁹) has been known to be another convenient method for the preparation of polyamides on a laboratory scale. In the present study, we followed this technique to prepare aromatic polyamides containing aryl ether groups by direct polycondensation of bis(ether carboxylic acid)s *o*-, *m*-, and *p*-3, respectively, with various aromatic diamines (Scheme 2).

The results of these polycondensation reactions are summarized in Tab. 1. The polyamides obtained from more rigid diamines such as *p*-phenylenediamine (**5a**) and 4,4'-bis(*p*-aminophenoxy)biphenyl (**5g**) with diacid *p*-3 or *m*-3 precipitated from the reaction media, due to the insolubility. In contrast, the polycondensation reaction between diacid *o*-3 and diamine **5a** or **5g** proceeded homogeneously throughout the reaction. This implies that incorporation of the *ortho*-linked phenylene unit enhances the solubility of polyamides. For all other cases, the resultant reaction solutions were homogeneously transparent and highly viscous. Tough, stringy precipitates were formed when the viscous polyamide solutions were trickled into stirring methanol. All the polymers were obtained in quantitative yields with inherent viscosities of 0,52–1,63 dL/g. The molecular weights of the polymers were determined by means of GPC using DMF containing 0,01 mol/L of lithium bromide as eluent and polystyrene for calibration. Owing to the lack of solubility, the molecular weights of some polymers were not determined. The \bar{M}_w values of the polyamides soluble in the eluent were recorded in the range of 72000 and 464000, and the polydispersity index \bar{M}_w/\bar{M}_n ranged from 1,53 to 3,44. The molecular weights of most polyamides are sufficiently high to permit casting flexible and tough films. However, some polyamides like *o*-5a, *m*-5a, f, g and *p*-5a, c, e–g were insoluble in organic solvents suitable for film casting, and some cast films such as those of *o*-5g, *m*-5c and *m*-5k were brittle. This may be

Tab. 1. Inherent viscosities and average molecular weights of polyamides

Polymer ^{a)}	$\eta_{inh}^{b)}$ dL/g	$10^{-4} \cdot \bar{M}_w^{c)}$	$10^{-4} \cdot \bar{M}_n^{c)}$	\bar{M}_w/\bar{M}_n	Film quality ^{d)}
<i>o</i> -5a	0,63	— ^{e)}	—	—	— ^{f)}
<i>o</i> -5b	0,61	31,7	10,1	3,17	Flexible
<i>o</i> -5c	0,83	13,0	5,9	2,22	Flexible
<i>o</i> -5d	0,85	—	—	—	Flexible
<i>o</i> -5e	0,71	—	—	—	Flexible
<i>o</i> -5f	0,85	22,3	7,1	3,16	Flexible
<i>o</i> -5g	1,08	—	—	—	Brittle
<i>o</i> -5h	0,85	20,8	7,0	2,96	Flexible
<i>o</i> -5i	0,90	14,3	7,6	1,88	Flexible
<i>o</i> -5j	1,02	19,0	9,9	1,92	Flexible
<i>o</i> -5k	1,05	23,2	10,9	2,12	Flexible
<i>o</i> -5l	1,00	18,6	8,7	2,14	Flexible
<i>m</i> -5a	1,01	—	—	—	—
<i>m</i> -5b	0,91	14,1	6,6	2,12	Flexible
<i>m</i> -5c	1,20	—	—	—	Brittle
<i>m</i> -5d	1,44	46,4	13,5	3,44	Flexible
<i>m</i> -5e	1,14	13,0	7,3	1,79	Flexible
<i>m</i> -5f	0,94	—	—	—	—
<i>m</i> -5g	0,68	—	—	—	—
<i>m</i> -5h	1,57	24,2	11,3	2,14	Flexible
<i>m</i> -5i	0,94	14,5	6,8	2,13	Flexible
<i>m</i> -5j	1,63	45,0	15,8	2,85	Flexible
<i>m</i> -5k	0,88	—	—	—	Brittle
<i>m</i> -5l	0,96	17,3	7,7	2,24	Flexible
<i>p</i> -5a	0,52	—	—	—	—
<i>p</i> -5b	0,69	7,2	4,6	1,57	Flexible
<i>p</i> -5c	0,76	—	—	—	—
<i>p</i> -5d	0,72	7,2	4,7	1,53	Flexible
<i>p</i> -5e	0,73	—	—	—	—
<i>p</i> -5f	0,81	—	—	—	—
<i>p</i> -5g	0,52	—	—	—	—
<i>p</i> -5h	0,75	8,9	5,5	1,63	Flexible
<i>p</i> -5i	0,76	10,7	6	1,79	Flexible
<i>p</i> -5j	0,72	10,5	6,5	1,61	Flexible
<i>p</i> -5k	0,98	—	—	—	Flexible
<i>p</i> -5l	0,96	12,1	6,6	1,84	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 CaCl₂ 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) Determined by GPC, with DMF + 0,01 mol/L LiBr as the eluent and polystyrene as the standard.

d) Films were cast by slow evaporation of polymer solutions in DMAc.

e) Insoluble in the eluent of GPC measurements.

f) Insoluble in DMAc.

Tab. 2. Solubility of polyamides^{a)}

Polymer	Solvents ^{b)}						
	NMP	DMAc	DMF	DMSO	sulfolane	<i>m</i> -cresol	THF
<i>o</i> -5a	–	–	–	–	–	–	–
<i>o</i> -5b	+	+	+	+	+h	+	–
<i>o</i> -5c	+	+	+	+	+h	+	–
<i>o</i> -5d	+	+	+	+	–	+	–
<i>o</i> -5e	+	+	+	+	+h	+	–
<i>o</i> -5f	+	+	+	+	–	+	–
<i>o</i> -5g	+	+	–	–	–	–	–
<i>o</i> -5h	+	+	+	+	–	+	+
<i>o</i> -5i	+	+	+	+	+h	+	+
<i>o</i> -5j	+	+	+	+	+	+	+
<i>o</i> -5k	+	+	+	+	+h	+	+
<i>o</i> -5l	+	+	+	+	+h	+	+
<i>m</i> -5a	–	–	–	–	–	–	–
<i>m</i> -5b	+	+	+	+	+h	+	+
<i>m</i> -5c	+	+h	–	–	–	–	–
<i>m</i> -5d	+	+	+	+	+h	+	+
<i>m</i> -5e	+	+	+	+	+	+	–
<i>m</i> -5f	+–	+–	–	–	–	–	–
<i>m</i> -5g	–	–	–	–	–	–	–
<i>m</i> -5h	+	+	+	+	+	+	+
<i>m</i> -5i	+	+	+	+	+h	+	+
<i>m</i> -5j	+	+	+	+	+h	+	+
<i>m</i> -5k	+	–	–	–	–	–	–
<i>m</i> -5l	+	+	+	+	+h	+	+
<i>p</i> -5a	–	–	–	–	–	–	–
<i>p</i> -5b	+	+	+	+	+h	+	+–
<i>p</i> -5c	–	–	–	–	–	–	–
<i>p</i> -5d	+	+	+h	+h	–	–	–
<i>p</i> -5e	+	–	–	–	–	–	–
<i>p</i> -5f	–	–	–	–	–	–	–
<i>p</i> -5g	–	–	–	–	–	–	–
<i>p</i> -5h	+	+	+	+	+h	+	+
<i>p</i> -5i	+	+	+	+	+h	+	+
<i>p</i> -5j	+	+	+	+	+h	+	+
<i>p</i> -5k	+	+	–	–	–	–	–
<i>p</i> -5l	+	+	+–	+–	+h	+	+

^{a)} +: soluble, –: insoluble, +–: partially soluble, +h: soluble on heating.

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

obtained from flexibilizing group-linked “multiring” diamines such as **4h**, **4i**, **4j** and **4l** dissolved even in less polar solvents like *m*-cresol and THF. Among these three series of isomeric polyamides, the *o*-5 series of *ortho* links showed markedly higher solubility

than the other two series. Except for *o*-5a and *o*-5g, containing a rigid diamine moiety, all other polyamides of *o*-5 series were readily soluble in polar aprotic solvents such as NMP, DMAc, DMF and DMSO and even in *m*-cresol. Among polyamides of the *m*-5 series, in addition to *m*-5a and *m*-5g, *m*-5c, *m*-5f, and *m*-5k showed decreased solubility compared to the corresponding isomeric polyamides of *o*-series. For the *p*-5 series polyamides, only those derived from *m*-phenylene-containing diamines such as 4b and 4d and "multiring" flexible diamines such as 4h, i, j, and k revealed higher solubility in the solvents tested.

The solubilities of these polyamides give some indication of the flexibility of the polymers as well as interactions between chains and with solvents. For the polymers investigated in this work, the least solubility shows up for those based on hydroquinone (*p*-5 series); this probably reflects the extended nature of the ether-dicarboxylic acid unit which can adopt a relatively planar configuration and probably allows relatively strong interchain interactions. The solubility of the resorcinol-based polymers (*m*-5 series) is slightly increased, possibly reflecting some loss of the extended nature of the chain. For catechol-based polymer (*o*-5 series), the solubility is significantly enhanced, probably attributable to the formation of bent structures due to the presence of *ortho* links, which will help to prevent the extended close packing of chains.

Typical X-ray diffractograms of some representative polyamides are illustrated in Fig. 3. The polyamides which embrittled upon film-casting or precipitated in the polycondensation reaction revealed crystalline patterns. The other polyamides exhibited amorphous diffraction patterns, and the amorphous nature corresponded to their excellent solubility and the formation of good-quality and creasable films during the film-forming process. The polyamides *p*-5a, c, e–g, derived from diacid *p*-3 and symmetric or rigid diamines 4a, c, e–g, showed crystalline patterns. Among the polyamides obtained from diacid *m*-3 with these diamines, only *m*-5e revealed a perceptibly reduced crystallinity, and the other polyamides still maintained a high level of crystallinity. In the *o*-series polyamides, only *o*-5g presented a crystalline diffraction pattern. Moreover, it should be noted that among the polyamides derived from sulfone-containing diamine 4k, only the cast film of *m*-5k was brittle, and it displayed a rougher X-ray diffraction pattern than the other two isomeric polyamides *p*-5k and *o*-5k. The reason was not investigated in detail; however, it should be associated with their chain packing density.

Most the polyamides could be cast into good-quality and creasable films by slow evaporation of their polymer solutions in DMAc or NMP. The tensile properties of these flexible polyamide films are included in Tab. 3. Most of these films showed no yield points on their stress-strain curves, and their elongation to break was not high. The tensile strength, elongation to break, and tensile modulus of the films were 21–91 MPa, 4–37%, and 1.07–2.53 GPa, respectively. Some polyamides of *p*-series such as *p*-5i, *p*-5j, and *p*-5k behaved as tough materials. They necked during tensile testing and had moderate elongation to break.

The thermal properties of all the polyamides were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The TG and DSC data of these polyamides are listed in Tab. 4. The polyamides were rapidly cooled from elevated temperatures at approximately 400 °C to room temperature to form predominantly

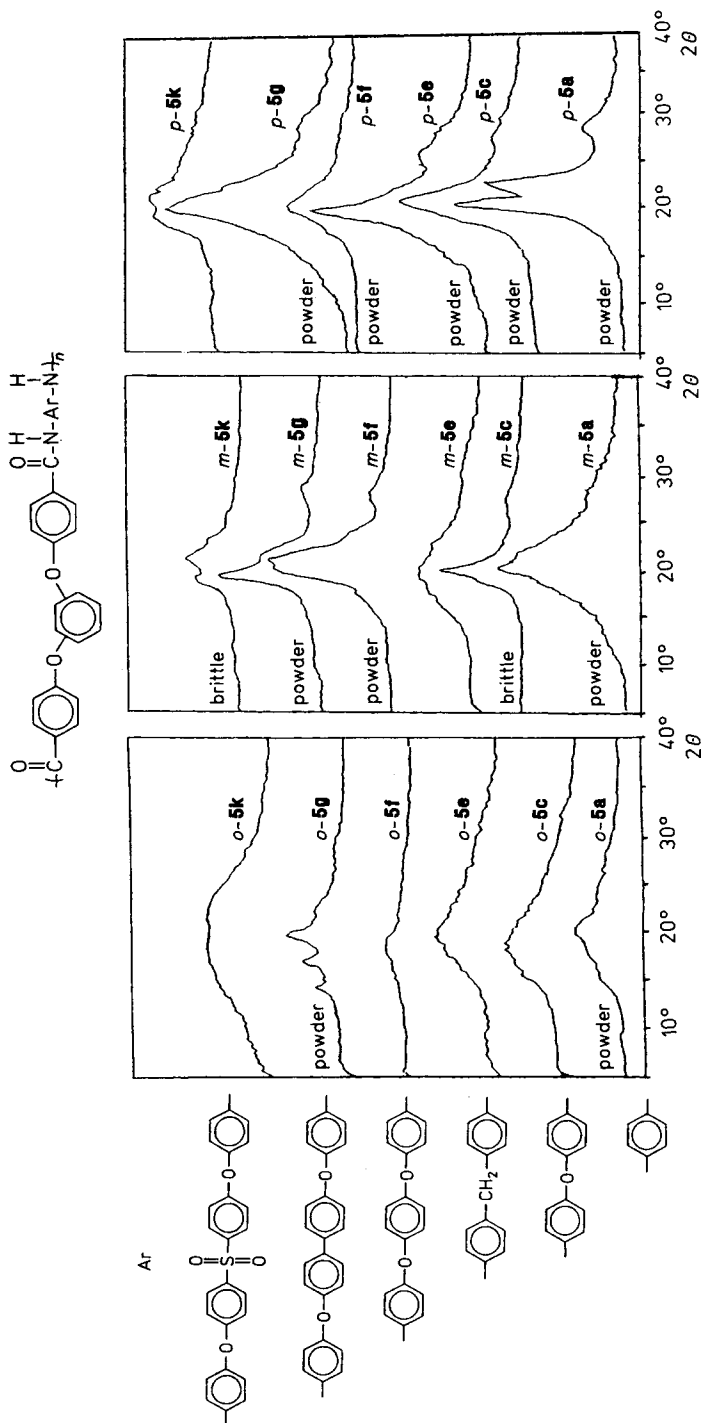


Fig. 3. Wide-angle X-ray diffractograms of polyamides

Tab. 3. Tensile properties of polyamide films

Polymer	Strength at yield in MPa	Strength at break in MPa	Elongation to break in %	Initial modulus in GPa
<i>o</i> -5a	— ^{a)}	—	—	—
<i>o</i> -5b	—	36	6	1,84
<i>o</i> -5c	—	—	6	2,53
<i>o</i> -5d	—	34	6	1,90
<i>o</i> -5e	—	80	10	1,73
<i>o</i> -5f	—	71	7	2,57
<i>o</i> -5g	—	—	—	—
<i>o</i> -5h	—	55	5	1,96
<i>o</i> -5i	61	48	6	1,96
<i>o</i> -5j	69	53	8	1,96
<i>o</i> -5k	64	56	9	1,82
<i>o</i> -5l	—	56	6	1,82
<i>m</i> -5a	—	—	—	—
<i>m</i> -5b	—	85	6	1,97
<i>m</i> -5c	—	—	—	—
<i>m</i> -5d	97	91	9	2,33
<i>m</i> -5e	—	21	10	2,33
<i>m</i> -5f	—	—	—	—
<i>m</i> -5g	—	—	—	—
<i>m</i> -5h	—	68	6	1,47
<i>m</i> -5i	—	87	6	1,93
<i>m</i> -5j	—	48	13	1,99
<i>m</i> -5k	—	—	—	—
<i>m</i> -5l	64	52	6	1,78
<i>p</i> -5a	—	—	—	—
<i>p</i> -5b	—	36	5	1,07
<i>p</i> -5c	—	—	—	—
<i>p</i> -5d	—	34	4	1,19
<i>p</i> -5e	—	—	—	—
<i>p</i> -5f	—	—	—	—
<i>p</i> -5g	—	—	—	—
<i>p</i> -5h	—	55	6	1,52
<i>p</i> -5i	61	48	25	1,63
<i>p</i> -5j	69	53	36	1,74
<i>p</i> -5k	64	56	37	1,69
<i>p</i> -5l	—	56	4	1,72

a) Serviceable specimens were not obtained.

amorphous samples, and thus, clear glass transitions generally could be observed on the subsequent heating DSC traces. These polyamides had T_g 's in the range of 183–232 °C. In general, the polyamides of the *ortho* series possessed T_g 's comparable to the ones of the corresponding *para* series, while the T_g 's of the *meta* series polyamides were lower. The T_g 's of *ortho*-phenylene-containing polyamides were

Tab. 4. Thermal properties of polyamides

Polymer	T_g ^{a)} °C	T_d ^{b)} /°C		Char residual ^{c)} in wt.-%
		in N ₂	in air	
<i>o</i> -5 a	—	488	464	52,2
<i>o</i> -5 b	219	478	487	51,6
<i>o</i> -5 c	218	503	481	59,1
<i>o</i> -5 d	205	493	495	58,9
<i>o</i> -5 e	211	502	499	65,9
<i>o</i> -5 f	214	499	485	56,2
<i>o</i> -5 g	232 (313) ^{d)}	529	485	63,7
<i>o</i> -5 h	210	502	513	57,5
<i>o</i> -5 i	208	504	509	56,2
<i>o</i> -5 j	211	515	506	59,4
<i>o</i> -5 k	231	513	506	52,8
<i>o</i> -5 l	184	506	513	51,2
<i>m</i> -5 a	—	490	479	65,1
<i>m</i> -5 b	208 (234)	486	500	61,8
<i>m</i> -5 c	219 (352)	488	492	60,2
<i>m</i> -5 d	198	498	506	62,4
<i>m</i> -5 e	192	430	477	46,3
<i>m</i> -5 f	208 (301)	485	469	52,9
<i>m</i> -5 g	210 (401)	516	528	43,7
<i>m</i> -5 h	183	449	483	44,9
<i>m</i> -5 i	193	502	512	55,2
<i>m</i> -5 j	208	514	504	53,5
<i>m</i> -5 k	209 (363)	471	482	52,2
<i>m</i> -5 l	184	509	523	50,9
<i>p</i> -5 a	—	489	461	55,7
<i>p</i> -5 b	—	394	429	41,5
<i>p</i> -5 c	—	490	468	62,3
<i>p</i> -5 d	207	447	466	53,8
<i>p</i> -5 e	216	441	470	61,3
<i>p</i> -5 f	—	501	479	57,0
<i>p</i> -5 g	—	503	492	65,9
<i>p</i> -5 h	193	496	505	54,6
<i>p</i> -5 i	204	504	509	60,4
<i>p</i> -5 j	211	515	496	57,1
<i>p</i> -5 k	220 (356)	495	494	53,0
<i>p</i> -5 l	195	503	519	48,3

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) Values in parentheses are the endotherm peak temperatures observed on the first heating DSC trace, with a heating rate of 20 °C/min.

considerably higher than expected. This may be due to a dipolar effect from the close proximity of the oxygen bridges and possible restriction of rotations about the ether linkages. The insertion of rigid biphenylene unit or polar sulfonyl group (such as in **5g** and **5k**) helps to increase T_g , while the introduction of *m*-phenylene unit or flexible aliphatic linkages causes a T_g lowering. However, the polyamides *o*-, *m*-, and *p*-**5a**, derived from *p*-phenylenediamine, and some other *p*-series polyamides like *p*-**5b**, **c**, **f**, **g**, did not show clear glass transitions on their DSC traces. Some crystalline polyamides exhibited endotherms in the first heating DSC traces. A typical DSC diagram is shown in Fig. 4. The first heating DSC trace of polymer *o*-**5g** showed a sharp endotherm peak at 313°C. Rapid cooling and reheating showed a strong T_g at 232°C and disappearance of the melting transition, pointing at a low crystallization rate. Although polymers *o*-**5a**, *m*-**5a**, *p*-**5a**, *p*-**5c**, *p*-**5e**, *p*-**5f**, and *p*-**5g** exhibited crystalline X-ray diffraction patterns, well-defined melting endotherms were not observed on the DSC traces before decomposition, possibly due to high melting points.

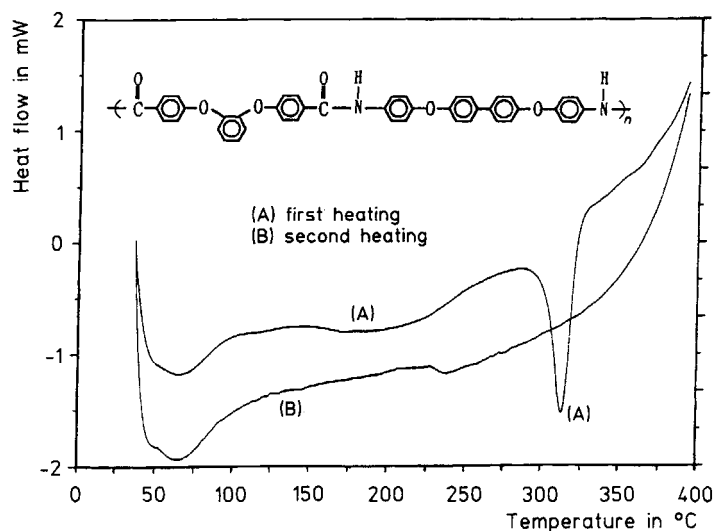


Fig. 4. DSC curves for polyamide *o*-**5g** (heating rate: 20°C/min)

As a representative example, the TG curves of polyamide *p*-**5f**, obtained from *p*-**3** and diamine **4f**, are shown in Fig. 5. All the other polyamides showed similar patterns of decomposition with no significant weight loss below 400°C in air or nitrogen, but with more than 50 wt.-% residue remaining when heated to 800°C in nitrogen. The 10% weight loss temperatures (T_{10}) of these three series of polyamides *o*-**5a-1**, *m*-**5a-1**, and *p*-**5a-1** were recorded respectively in the range of 464–513°C, 469–528°C and 429–519°C in air, and 478–529°C, 430–516°C and 394–515°C in nitrogen.

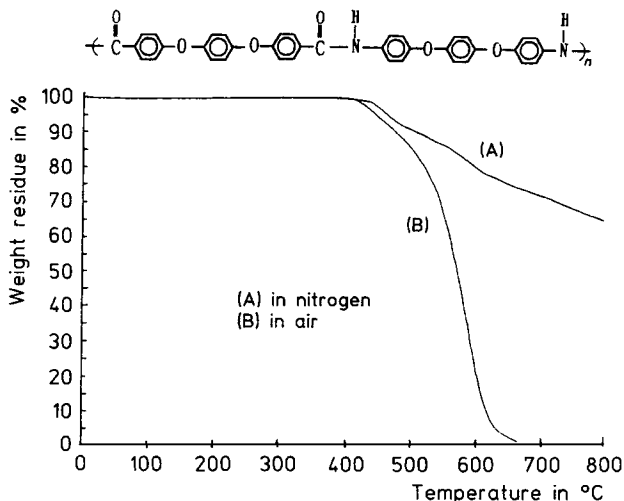


Fig. 5. TG curves of polyamide *p-5f* (heating rate: 20 °C/min)

Conclusions

Three isomeric phenylenedibenzoic acids, *o*-, *m*-, and *p*-3, were prepared in high yields and high purity starting from the condensation of *p*-fluorobenzonitrile with catechol, resorcinol, and hydroquinone, respectively. High molecular weight aromatic polyamides could be directly synthesized from bis(ether carboxylic acids) *o*-, *m*-, and *p*-3 and various aromatic diamines by means of the triphenyl phosphite/pyridine method. The molecular weights of most polyamides are sufficiently high to permit casting flexible and tough films. Due to the presence of phenoxy groups, most of the polyamides exhibited high solubility in amide-type solvents such as NMP, DMAc, and DMF. Among these three series of isomeric polyamides, the *o*-5 series with *ortho* links showed markedly higher solubility than the other two series. All the polyamides showed good thermal properties, i.e., high T_g and excellent thermal and thermooxidative stability. All the polyamides were stable up to 400 °C in both air and nitrogen. These polyamides had T_g 's in the range of 183–232 °C. In general, the polyamides of the *ortho* series possessed T_g 's comparable to the ones of the corresponding *para* series and higher T_g 's than the polyamides of the *meta* series.

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