Preparation and Properties of Aromatic Polyamides from 1,4-Bis(*p*-carboxyphenoxy)naphthyl and Aromatic Diamines

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ABSTRACT: A new aromatic dicarboxylic acid, 1,4-bis(*p*-carboxyphenoxy)naphthyl (**3**), was synthesized by the reaction of *p*-fluorobenzonitrile with 1,4-naphthalenediol, followed by hydrolysis. Aromatic polyamides having inherent viscosities of 1.27–2.22 dL/g were prepared by the triphenyl phosphite activated polycondensation of diacid **3** with various aromatic diamines. Most of the resulting polymers showed an amorphous nature and were readily soluble in a variety of organic solvents including *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), and *m*-cresol. Transparent, tough, and flexible films of these polymers could be cast from the DMAc or NMP solutions. The cast films had tensile strengths ranging from 64–104 MPa, elongations-at-break from 6 to 10%, and initial moduli from 1.52 to 2.14 GPa. These polyamides had glass transition temperatures in the range of 195 to 240°C. Almost all polymers were thermally stable up to 400°C, with 10% weight loss being recorded above 480°C in air and nitrogen atmospheres. © 1997 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem **35:** 2273–2280, 1997

Keywords: 1,4-bis(*p*-carboxyphenoxy)naphthyl; aromatic polyamides; solubility

INTRODUCTION

Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.[1] However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms due to high melting or to high glass transition temperatures and their limited solubility in organic solvents.[2] Therefore, a great deal of effort has been expended to try to improve the processing characteristics of the relatively intractable polymers. One of the successful approaches to increase solubility and processability of aromatic polyamides without sacrificing their high thermal stability is the introduction of bulky pendent group into the polymer backbone. Some organic-soluble aromatic polyamides have been demonstrated by using highly pendent phenylated aromatic groups such as tetraphenylthiophene,[3,4] tetraphenylfuran,[5] and tetraphenylethylene[6] into the polyamide backbone. We also have already reported the synthesis of new organic-soluble aromatic polyamides and polyimides having high glass transition temperatures by the incorporation of biphenyl-2,2′-diyl or 1,1-binaphthyl-2,2′-diyl units having kinked, cranked, and twisted noncoplanar structures into the polymer main chain backbone.[7–9] Recently, in continuation of these studies, we are interested in the potential usefulness of a 1,4-naphthyl structure as being simultaneously a bulky and symmetrical unit in the polymer main chain. To obtain more insight into the effect of flexible ether linkages

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on properties of aromatic polyamides, 1,4-bis(*p*-carboxyphenoxy)naphthyl was synthesized as a monomer in the present study. The novel aromatic polyamides were prepared by direct polycondensation of the diacid with various aromatic diamines. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers were also investigated.

EXPERIMENTAL

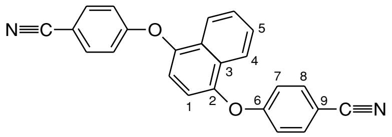
Materials

p-Phenylenediamine (**4a**) and benzidine (**4c**) were purified by sublimation. *m*-Phenylenediamine (**4b**) was vacuum-distilled before use. The other reagent-grade aromatic diamines such as 4,4′-oxydianiline (**4d**), 3,4′-oxydianiline (**4e**), 4,4′-methylenedianiline (**4f**), 1,4-bis(*p*-aminophenoxy)benzene (**4g**), and α,α'-bis(*p*-aminophenyl)-1,4-diisopropylbenzene (**4h**) were used as received. According to a reported method,[10] 4,4′-bis(*p*-aminophenoxy)biphenyl (**4i**), 2,2-bis[*p*-(*p*-aminophenoxy)phenyl]propane (**4j**), 1,1-bis[*p*-(*p*-aminophenoxy)phenyl]-1-phenylethane (**4k**), 2,2-bis[*p*-(*p*-aminophenoxy)phenyl]hexafluoropropane (**4l**), bis[*p*-(*p*-aminophenoxy)phenyl] sulfone (**4m**), and α,α'-bis[*p*-(*p*-aminophenoxy)-1,4-diisopropyl]benzene (**4n**) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenols and *p*-chloronitrobenzene in the presence of potassium carbonate, giving the dinitro compounds, which were subsequently reduced using hydrazine as the reducing agent and palladium as the catalyst. *N*-methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride. Anhydrous calcium chloride was dried in a vacuum oven at 180°C for 10 h.

Monomer Synthesis

1,4-Bis(p-Cyanophenoxy)naphthyl (2)

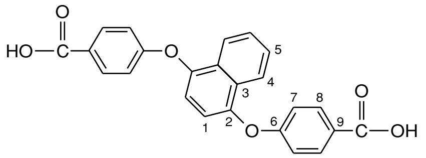
1,4-Bis(*p*-cyanophenoxy)naphthyl (**2**) was prepared by the nucleophilic fluorodisplacement of *p*-fluorobenzonitrile with 1,4-naphthalenediol (**1**). In a three-neck flask equipped with a nitrogen inlet, a Dean–Stark trap and a condenser were placed 16.02 g (100 mmol) of (**1**) and 27.64 g (200 mmol) of potassium carbonate with 100 mL of toluene and 200 mL of NMP. The mixture was heated with stirring at 140°C for 6 h under nitrogen to facilitate dehydration. After the toluene had been removed, the mixture was cooled and then 24.22 g (200 mmol) of *p*-fluorobenzonitrile was added. The reaction was carried out at 170°C for 10 h, and then the reaction mixture was allowed to cool and was poured into 3 L of cool water. The product was filtered and recrystallized from acetonitrile to afford 21.75 g (60% yield) of white needles, mp 197–198°C (by DSC). The IR spectrum (KBr) exhibited absorptions (C≡N) at 2228 cm^{-1} and (C—O—C) at 1108 and 1236 cm^{-1}. ANAL. Calcd for $C_{24}H_{14}N_2O_2$ (362.38): C, 79.54%; H, 3.89%; N, 7.73%. Found: C, 79.26%; H, 4.08%; N, 7.61%. EIMS: *m/z* (%) 362 (M^+, 100), 260 (22), 204 (15). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 106.114 (C-9), 116.008 (C-1), 117.380 (C-7), 118.642 (C≡N), 122.153 (C-5), 127.585 (C-4), 128.133 (C-3), 134.132 (C-8), 147.756 (C-6), 161.966 ppm (C-2). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.01 ($[AB]_2$ quartet, naphthyl, 2H), 7.62 (d, phenylene, 4H), 7.55 [$(AB)_2$ quartet, naphthyl, 2H], 7.13 (s, naphthyl, 2H), 7.06 ppm (d, phenylene, 4H).



1,4-Bis(p-Carboxyphenoxy)naphthyl (3)

1,4-Bis(*p*-carboxyphenoxy)naphthyl (**3**) was synthesized by the hydrolysis of dinitrile compound **2.** The procedure was modified from the method of Heath and Wirth.[11] A mixture of 45.0 g of potassium hydroxide and 20.0 g of dinitrile compound (**2**) in 250 mL of ethanol and 250 mL of distilled water was stirred at ca. 100°C under a nitrogen atmosphere until no further ammonia was generated. The solution was cooled, and the pH value was adjusted by hydrochloric acid to near 3. The white precipitate formed was collected by filtration and dried under vacuum. The yield was 100% white powder without further purification, mp 354–355°C (by DSC). The IR spectrum (KBr) exhibited an absorption at 1680 cm^{-1} (C=O). ANAL. Calcd for $C_{24}H_{16}O_6$ (400.39): C, 71.99%; H, 4.02%. Found: C, 71.91%; H, 3.99%. EMIS: *m/z* (%) 400 (M^+, 100), 279 (15), 65 (34); ^{13}C-NMR (100 MHz, DMSO-d_6): δ = 116.419 (C-1), 116.694 (C-7), 121.961 (C-5), 125.307 (C-9), 127.557, 127.630 (C-3, C-4), 131.799 (C-8), 147.436 (C-6), 161.792 (C-2), 166.766 ppm (COOH). ^{1}H-NMR

(400 MHz, DMSO-d_6): δ = 8.01 [(AB)$_2$ quartet, naphthyl, 2H], 7.99 (d, phenylene, 4H), 7.63 [(AB)$_2$ quartet, naphthyl, 2H], 7.28 (s, naphthyl, 2H), 7.13 ppm (d, phenylene, 4H).



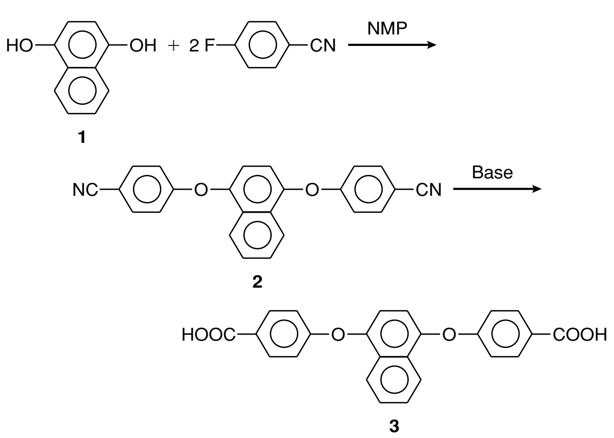
Polymerization

Polyamide 5d from 3 and 4d by Direct Polycondensation Method

A typical example of polycondensation is as follows: A mixture of 0.25 g (1.25 mmol) of diamine **4d,** 0.50 g (1.25 mmol) of diacid **3,** 0.5 g of calcium chloride, 5 mL of NMP, 1 mL of pyridine, and 0.9 mL of triphenyl phosphite was heated at 100°C for 3 h. The reaction mixture was trickled into 300 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried at 100°C under vacuum. The yield was quantitative. The inherent viscosity of the polymer was 2.22 dL/g, measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30°C. Other polymers were synthesized similarly.

Measurements

Infrared spectra were recorded on a Jasco FT/IR-700 Fourier transform infrared spectrometer. Elemental analysis were run in a Perkin–Elmer model 2400 C, H, N, analyzer. ^{1}H- and ^{13}C-NMR spectra were measured on a Jeol EX-400 Fourier transform nuclear magnetic resonance spectrometer. The X-ray crystallographic data were collected on a CAD-4 diffractometer. Mass spectrometry (MS) spectra were obtained by using a Joel JMS-D300 mass spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using a Cannon–Fenske viscosimeter. Thermogravimetric analysis was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku thermal analysis station TAS-100. Measurements were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20°C/min. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis



Scheme 1.

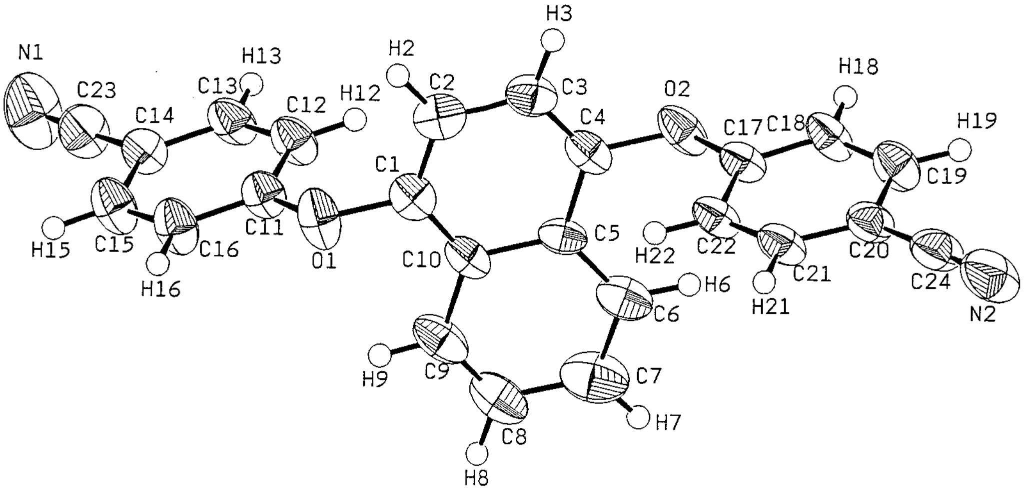


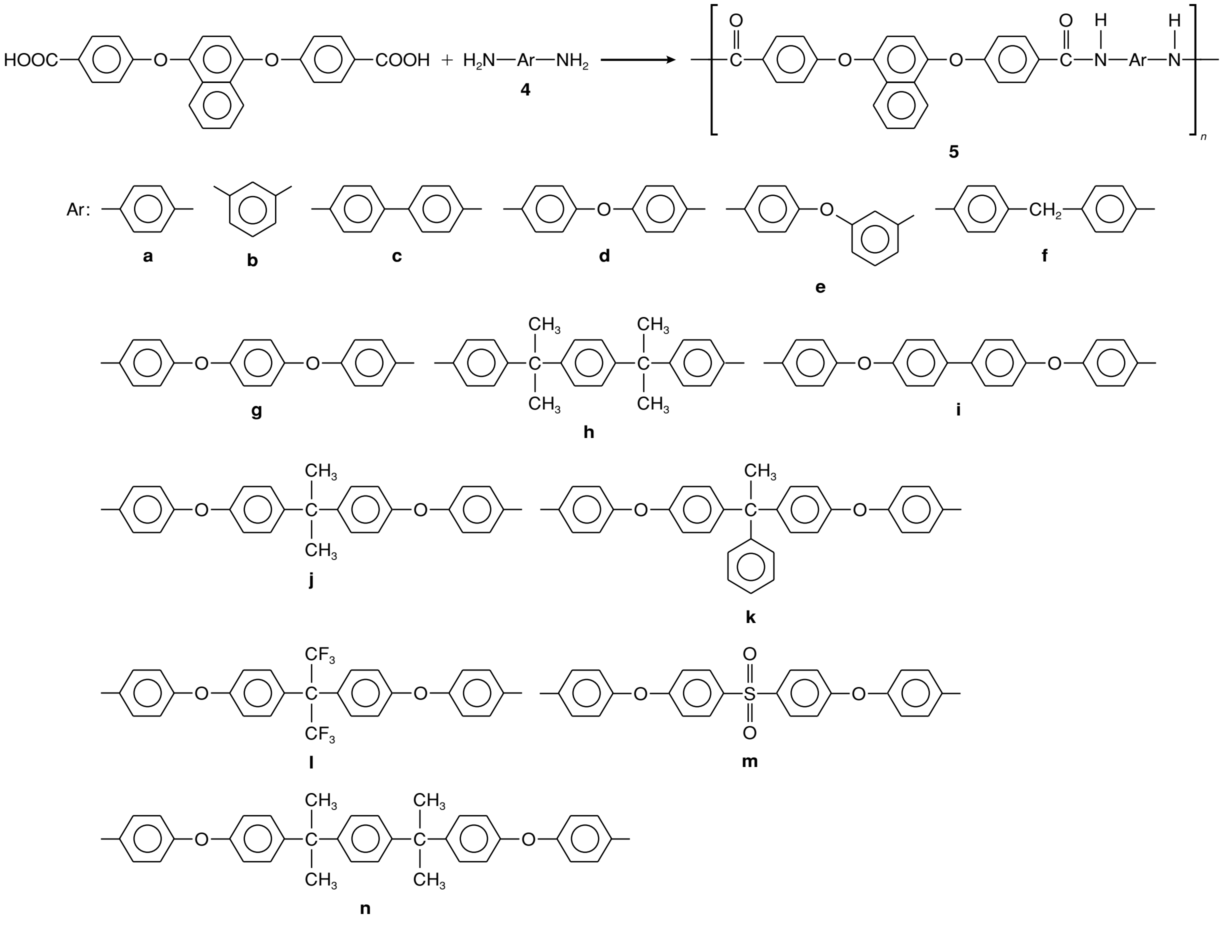
Figure 1. Molecular structure of dinitrile **2.**

controller in flowing nitrogen (30 cm^3/min) at a heating rate of 20°C/min. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered CuK_α 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 Universal Tester Model 1130 with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge of 2 cm and a drawing speed of 5 cm/min were used for this study. Measurements were performed at room temperature (ca. 20°C) with film specimens that were approximately 0.5 cm wide, 6 cm long, and about 0.1 mm thick; an average of at least five individual determinations was obtained.

RESULTS AND DISCUSSION

Monomer Synthesis

A new polymer-forming dicarboxylic acid, 1,4-bis(*p*-carboxyphenoxy)naphthyl (**3**), and its intermediate compound, 1,4-bis(*p*-cyanophenoxy)-naphthyl (**2**), were successfully synthesized from 1,4-naphthylenediol and *p*-fluorobenzonitrile as starting materials by the nucleophilic fluorodisplacement reaction followed by hydrolysis according to the synthetic route shown in Scheme 1. The chemical structures of all synthesized compounds were confirmed by means of elemental analysis, the characteristic peaks in the NMR spectra, and the characteristic absorption bands in the IR spectroscopic techniques. Concerning the synthesis of diacid (**3**), the disappearance of characteristic cyano stretching bands at around 2228 cm^{-1} in the IR spectra revealed completion of the hydrolysis of dicyano compound **2.** The elemental analyses of all of these compounds were also in good agreement with the calculated values for the proposed structures. According to the basis of the shielding effect of carbon, the positions of chemical shifts for carbons were readily assigned from ^{13}C-NMR experiments of compound **2** and **3.** The ^{13}C-NMR spectra of **2** exhibited exactly 10



Scheme 2.

Table I. Preparation of Polyamides[a]

Polymer Code	η_{inh}[b] (dL/g)
5a	1.40
5b	1.34
5c	1.68
5d	2.22 (2.06)[c]
5e	1.42
5f	1.40
5g	1.52
5h	1.28
5i	1.30
5j	1.86
5k	1.32
5l	1.58
5m	1.27
5n	1.70

[a] Polymerization was carried out with 1.25 mmol of each monomer, 0.9 mL of triphenyl phosphite, 1 mL of pyridine, and 0.5 g of $CaCl_2$ in 5 mL of NMP at 110°C for 3 h.

[b] Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30°C.

[c] Measured in concentrated sulfuric acid.

peaks due to symmetry and were consistent with the calculated values, while spectra of **3** showed only 9 peaks owing to overlapping of some peaks. The structure of **2** was also confirmed by X-ray diffraction analysis. X-ray crystal data for **2** were acquired from a colorless single crystal obtained by slow crystallization of an acetonitrile solution of **2.** The structure of **2** exhibits symmetrical and bulky molecular characteristics (Fig. 1). The structure coincides with that deduced from the spectroscopic data.

Polymer Synthesis

The direct polycondensation of aromatic diamines with dicarboxylic acids using a mixture of triphenyl phosphite and pyridine as condensing agents is a convenient method for the preparation of polyamides on a laboratory scale.[12] A series of new 1,4-naphthyl containing high-molecular-weight aromatic polyamides (**5a–n**) were prepared from the diacid (**3**) and various aromatic diamines (**4a–n**) by the direct polycondensation reaction (Scheme 2). The reaction conditions and the results are summarized in Table I. Polymers **5a–n** were successfully obtained in almost quantitative yields with inherent viscosities of 1.27–2.22 dL/g. The solubility of the polymers affected the inherent viscosity of the resulting polymers significantly. In general, the molecular weight of the polymers obtained from the phosphorylation reaction is highly dependent on the reactant concentration. Higher molecular weights for these polymers could be obtained by using a higher initial reactant concentration and by adding a proper amount of supplemental NMP into the viscous re-

Table II. Solubility Behavior of Polyamides[a]

Polymer	Solvent[b]					
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF
5a	−	−	−	−	−	−
5b	+	+	+	+	+	−
5c	−	−	−	−	−	−
5d	+	±	±	±	+	−
5e	+	+	+	+	+	−
5f	+	+	+	+	−	−
5g	+	±	−	−	+	−
5h	+	+	±	+	−	s
5i	+	+	−	−	+	−
5j	+	+	±	±	+	s
5k	+	+	s	s	+	+h
5l	+	+	+	+	+	+
5m	+	+	s	s	+	+
5n	+	+	+h	+h	+	s

[a] Solublity: +: soluble at room temperature; +h: soluble on heating; ±: partially soluble; s: swelling; −: insoluble even on heating.

[b] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; THF: tetrahydrofuran.

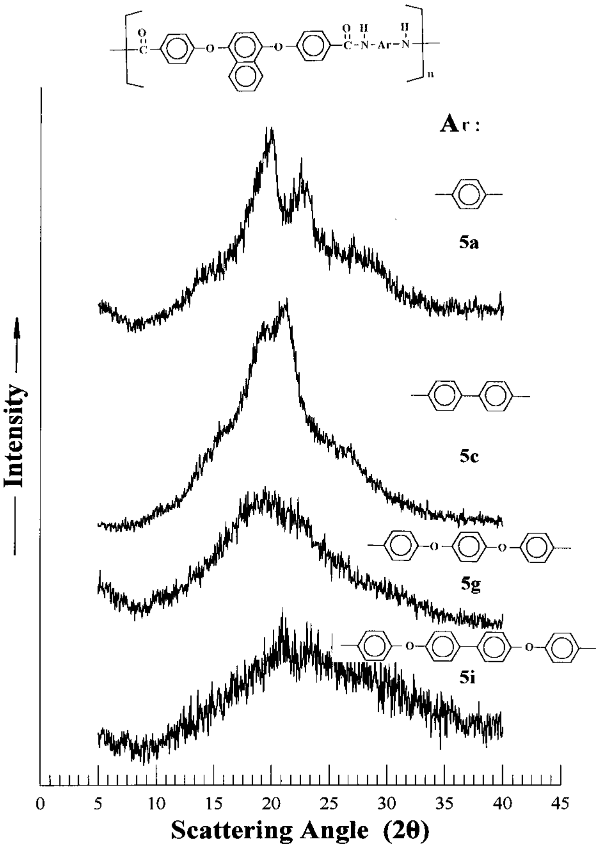


Figure 2. Wide-angle X-ray diffraction patterns of polyamides.

action solution before the formation of a swollen gel. All the molecular weights of these polymers are sufficiently high to permit the casting of tough and flexible films. The formation of aromatic polyamides was confirmed by means of IR spectroscopy. The FTIR spectra of the polymers exhibited characteristic amide absorption bands at 3300–3340 and 1650–1670 cm^{-1}.

Polymer Characterization

The solubility behavior of these aromatic polyamides was qualitatively tested in various solvents, and those results are summarized in Table II. All of the polyamides except polymers **5a** and **5c** were highly soluble in polar solvents such as *N,N*-dimethylacetamide (DMAc) and NMP. Some of the polymers were also soluble in dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *m*-cresol, and even in less polar THF. Polymers **5a** and **5c** had poor solubility due to having symmetrical and rigid *p*-phenylene or biphenylene diamine moieties. X-ray diffraction results, as discussed below, revealed that polymers **5a** and **5c** had a higher crystallization tendency than that of the other polyamides. The solubility behavior was consistent with the results of X-ray diffraction studies. Thus, the solubility of aromatic polyamides was significantly improved by the introduction of the bulky and symmetrical 1,4-naphthyl unit into the polymer backbone.

As-prepared powders and films were structurally characterized by X-ray diffraction studies (Fig. 2), which revealed that polyamides **5a** and **5c** had a fair degree of crystallinity, whereas all of the other polymers were completely amorphous. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, which is in agreement with the general rule that the solubility decreases with increasing crystallinity, and this could be attributed to the introduction of the bulky 1,4-naphthyl unit along the polymer backbone.

The mechanical properties of the solution cast films of the polyamides from the DMAc solutions are given in Table III. The tensile strengths, elongations at break, and tensile moduli of these polymer films were in the range of 65 to 104 MPa, 6–10%, and 1.54–2.14 GPa, respectively.

The thermal behavior of the polymers was evaluated by means of DSC and thermogravimetric analysis (TGA). Figure 3 shows typical DSC and TGA curves of a representative polymer **5d,** and the thermal behavior data of all the polymers are given in Table IV. Quenching from elevated temperatures to room temperature yields more amorphous samples so that the glass transition temperatures (T_g) of these polyamides, except for **5a** and **5c,** could be easily measured in the DSC charts of the second heating trace, and observed in the range of 195 to 240°C, depending on the structure of diamine moiety, and decreased with decreasing rigidity and symmetry of the polymer backbone (Table IV). The thermal stability of the polyamides **5a–n** was studied by TGA. Typical TGA curves in air and nitrogen atmospheres of representative polymer **5d** are shown in Figure 3. The temperatures of 10% weight loss in nitrogen and air atmospheres were determined from original thermograms and tabulated in Table IV. In general, all the polymers exhibited good thermal stability with no significant weight loss up to temperatures of approximately 400°C in air and nitrogen atmospheres, and the temperatures at 10% weight loss were above 480°C on the TGA curves. The amount of carbonized residue (char yield) of the polyamides in a nitrogen atmo-

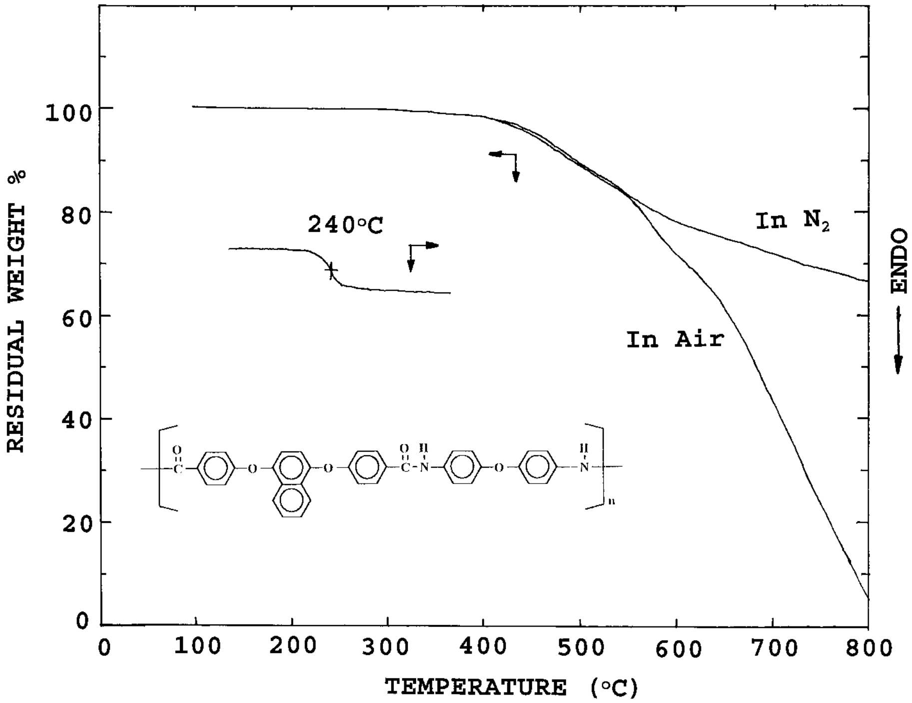


Figure 3. TG and DSC thermograms of polyamide **5d.** Heating rate = 20°C/min.

sphere was in the range of 50 to 70% weight even at 800°C.

CONCLUSIONS

New soluble aromatic polyamides containing a 1,4-naphthyl unit were successfully synthesized by the direct polycondensation of 1,4-bis(*p*-carboxyphenoxy)naphthyl and various aromatic diamines using triphenyl phosphite and pyridine as condensing agents. These polyamides having

Table III. Tensile Properties of Polyamide Films[a]

Polymer	Tensile Strength (MPa)	Elongation-at-Break %	Initial Modulus (GPa)
5b	84	10	1.91
5e	82	8	1.72
5f	64	8	1.38
5g	86	8	1.90
5h	83	9	1.61
5i	73	7	1.64
5j	104	9	2.14
5k	70	7	1.64
5l	71	8	1.52
5m	74	8	1.66
5n	65	6	1.54

[a] Polymer films were prepared by slow evaporation of their DMAc solutions at 90°C for 12 h, followed by vacuum dried at 100°C for 6 h.

Table IV. Thermal Properties of Polyamides

Polymer	T_g[a] (°C)	$T_{10\%}$[c] (°C) In Air	$T_{10\%}$[c] (°C) In Nitrogen	Char Yield[d] (%)
5a	–[b]	469	475	64.3
5b	204	429	409	53.5
5c	–	484	504	60.3
5d	240	489	495	66.6
5e	233	491	502	65.6
5f	220	478	485	69.2
5g	220	488	499	65.2
5h	195	438	438	47.6
5i	213	507	514	70.4
5j	213	507	506	57.3
5k	227	496	497	61.9
5l	216	499	510	58.9
5m	220	490	500	59.2
5n	213	495	495	58.1

[a] From the second heating traces of DSC measurements conducted at a heating rate of 20°C/min in nitrogen.
[b] No discernible transitions was observed.
[c] Temperature at which 10% weight loss was recorded by thermogravimetry conducted at a heating rate of 20°C/min.
[d] Residual weight % at 800°C in nitrogen.

high molecular weight (inherent viscosities to 2.22 dL/g) were obtained. The introduction of bulky and symmetrical 1,4-naphthyl unit containing ether linkages into the polyamide backbone showed excellent solubility in various organic solvents, good thermal stability, and could be cast to transparent, tough, and flexible films. Thus, these aromatic polyamides are considered to be promising soluble high-temperature polymeric materials.

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