Synthesis and Properties of Aromatic Polyamides Based on 4,4'-(2,7-Naphthalenedioxy)dibenzoic Acid

SHENG-HUEI HSIAO, CHIN-PING YANG, KUAN-YU CHU

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., 3rd Sec., Taipei, Taiwan, Republic of China

ABSTRACT: 4,4'-(2,7-Naphthalenedioxy)dibenzoic acid, a new aromatic dicarboxylic acid monomer, was prepared starting from 2,7-dihydroxynaphthalene and *p*-fluorobenzonitrile in three steps. Using triphenyl phosphite (TPP) and pyridine as condensing agents, a series of novel aromatic polyamides were synthesized by the direct polycondensation of the diacid monomer and aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride. The resulting polyamides had inherent viscosities ranging from 0.48 to 0.67 dL/g. Most of these polyamides were readily soluble in polar solvents, such as NMP and *N,N*-dimethylacetamide (DMAc). Transparent, flexible, and tough films were cast from their DMAc solutions. They had tensile strengths of 65–70 MPa, elongations to break of 5–7%, and initial moduli of 1.4–1.6 GPa. Most of these polymers proved to be amorphous, with glass transition temperatures in the range between 143–227°C. Thermogravimetric analysis (TG) showed that all the polyamides were stable up to 450°C in both air and nitrogen atmospheres. © 1997 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem **35:** 1469–1478, 1997
Keywords: 4,4'-(2,7-naphthalenedioxy)dibenzoic acid; polyamides

INTRODUCTION

Wholly aromatic polyamides (aramids) are thermally stable polymers with an attractive combination of chemical, physical, and mechanical properties.[1] However, in many cases they are insoluble and do not melt below their decomposition temperature. Therefore, processing in melt or solution is impossible. Thus, considerable research has been carried out aimed at developing aramids that have better processability while retaining their outstanding thermal and mechanical properties.

Introduction of flexibilizing groups[2–5] as well as bulky groups[6–12] in the polymer backbone results in soluble or thermoplastic polyamides. The introduction of ether linkages is known to improve the processability of rigid polymers. It has been generally recognized that aryl ether kinks inserted in aromatic main chains provide them a significantly lower energy of internal rotation, thus, leading to higher solubility and moldability while lowering the T_g. On the other hand, the incorporation of rigid moieties, such as naphthalene rings, into the polymer chain generally leads to an enhanced thermal stability with respect to the benzene ring.[13] The goal of increased solubility together with retained high thermal stability or high T_g has been achieved in preparing polyamides containing both naphthalene rings and flexible groups like ether.[14–19]

An alternative way to achieve the above-mentioned objectives is to use the diacid monomers, which have both naphthalene ring and ether linkage such as 4,4'-(2,7-naphthalenedioxy)dibenzoic acid (**3**). The present article describes the synthesis of this novel diacid (**3**), and the synthe-

sis and basic characterization of polyamides based on diacid **3** and various aromatic diamines.

EXPERIMENTAL

Materials

2,7-Dihydroxynaphthalene (**1**) (Janssen; now Acros) and *p*-fluorobenzonitrile (TCI) were used without previous purification. *p*-Phenylenediamine (**4a**) was purified by sublimation. *m*-Phenylenediamine (**4b**) was vacuum distilled prior to use. According to a reported method,[20,21] 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**4h**) (m.p. 123–124°C), bis[4-(4-aminophenoxy)phenyl] sulfone (**4i**) (m.p. 185–187°C), 1,1-bis-[4-(4-aminophenoxy)phenyl]-1-phenylethane (**4j**) (m.p. 72°C), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**4k**) (m.p. 162–163°C), and bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**4l**) (m.p. 187–189°C) were prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursors 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. The other aromatic diamines were used without previous purification. Commercially available calcium chloride ($CaCl_2$) was 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. Triphenyl phosphite (TPP; Fluka) was used as received.

Monomer Synthesis

4,4'-(2,7-Naphthalenedioxy)dibenzonitrile (2)

In a 300-mL flask, 16.3 g (0.102 mol) of 2,7-dihydroxynaphthalene (**1**) and 28.5 g (0.206 mol) of K_2CO_3 were suspended in a mixture of 60 mL of DMF and 70 mL of toluene, and the suspension was heated at reflux temperature using a Dean–Stark trap to remove the water azeotropically. After complete removal of water, the residual toluene was distilled off. Then, the reaction mixture was cooled to about 60°C, and *p*-fluorobenzonitrile (25.0 g; 0.206 mol) was added and heating was continued at 150°C for 6 h. On cooling, the reaction mixture was poured into 700 mL of water, and the precipitated purple solid was collected by filtration, washed thoroughly with water, and

dried. The yield of the product was 35.3 g (96%). The crude product was purified by recrystallization from 600 mL of ethanol to afford **2** as purple needles. The yield of the purified product was 31.7 g (86%); m.p. 138–140°C. The IR spectrum (KBr) exhibited absorptions at 2220 (C≡N) and 1250 cm^{-1} (C—O). ^{1}H-NMR (CDCl$_3$): δ 7.91 (d, 2H, H$_e$), 7.62 (d, 4H, H$_a$), 7.37 (s, 2H, H$_c$), 7.22 (d, 2H, H$_d$), 7.07 ppm (d, 4H, H$_b$). ^{13}C-NMR (CDCl$_3$): δ 161.17 (C^7), 153.67 (C^4), 135.31 (C^5), 134.23 (C^2), 130.47 (C^9), 128.35 (C^8), 119.79 (C^6), 118.67 (cyano carbon), 118.43 (C^3), 115.85 (C^{10}), 106.40 ppm (C^1).
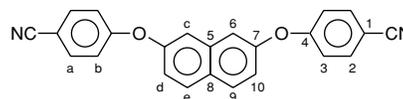
ANAL. Calcd for $C_{24}H_{14}N_2O_2$ (362.39): C, 79.54%; H, 3.89%; N, 7.73%. Found: C, 79.30%; H, 3.84%; N, 7.58%.

4,4'-(2,7-Naphthalenedioxy)dibenzoic Acid (3)

In a 1000-mL flask, a suspension of dinitrile **2** (30.5 g; 0.084 mol) in a mixed ethanol/water (500 mL/500 mL) solution containing dissolved 94.5 g (1.68 mol) of KOH was boiled under reflux. Reflux was continued for about 2 weeks until the evolution of ammonia had ceased. The suspension seemed never to turn into a clear solution. Thus, the reaction was stopped, and the reaction mixture was divided into two portions by filtration. The hot filtrate was allowed to cool and acidified by conc. HCl to pH = 2–3. The gray precipitated product from the filtrate of another portion was filtered off, washed with water, and dried *in vacuo,* to give 11.5 g of diacid **3.** The filtered solid product was suspended in 800 mL of water and the suspension was also acidified by conc. HCl to pH = 2–3. Another 28.8 g of product was obtained from this portion. Thus, the total yield is 100%. The product obtained from the latter portion was found to be of higher purity and, hence, was used for the characterization and polymer synthesis. Its m.p. was 328°C (DSC). IR (KBr): 2600–3500 (O—H), 1670 (C=O), 1400–1600 (arom. C=C), 1250 cm^{-1} (C—O). ^{1}H-NMR (DMSO-d$_6$): δ 8.10 (d, 2H, H$_e$), 8.00 (d, 4H, H$_a$), 7.59 (s, 2H, H$_c$), 7.31 (d, 2H, H$_d$), 7.14 ppm (d, 4H, H$_b$). ^{13}C-NMR (DMSO-d$_6$): δ 166.64 (carbonyl carbon), 160.68 (C^7), 153.97 (C^4), 135.29 (C^5), 131.82 (C^2), 130.57 (C^9), 127.67 (C^8), 125.87 (C^1), 119.49 (C^6), 117.85 (C^3), 115.16 ppm (C^{10}).
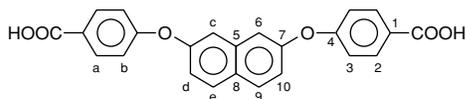
ANAL. Calcd for $C_{24}H_{16}O_6$ (400.39): C, 71.99%; H, 4.02%. Found: C, 68.71%; H, 3.84%.

Polymer Synthesis

A typical polymerization procedure is described as follows. A mixture of 0.5005 g (1.25 mmol) of 4,4′-(2,7-naphthalenedioxy)dibenzoic acid (**3**), 0.1352 g (1.25 mmol) of *m*-phenylenediamine (**4b**), 0.3 g of $CaCl_2$, 0.9 mL of TPP, 0.8 mL of pyridine, and 1.5 mL of NMP was heated with stirring at 110°C for 3 h. As polycondensation proceeded, the solution became viscous gradually. The resulting viscous polymer solution was trickled into 300 mL of methanol with stirring, giving a fibrous white precipitate that was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was quantitative and the inherent viscosity of the polymer (**5b**) in DMAc + 5 wt % LiCl was 0.48 dL/g. IR (KBr): 3310 (N—H), 1655 (C=O), 1260 cm^{-1} (C—O).

All other polymers were prepared by a similar procedure.

Preparation of Polyamide Films

A solution of polymer was made by dissolving about 0.8 g of the polymer in 8 mL of hot DMAc or NMP to afford an approximate 10 wt % solution. The clear solution was poured into a 9-cm diameter glass culture dish, which was placed in a 80°C oven overnight to remove the solvent. The semidried polyamide film was stripped off from the glass surface and further dried *in vacuo* at 100°C for 6 h. The obtained films had about 0.1 mm in thickness and were utilized for x-ray diffraction and tensile tests.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. ^{1}H- and ^{13}C-NMR spectra were measured on a JEOL EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-d$_6$) as an external reference, working at 400 and 100 MHz, respectively. Elemental analyses were run in a Perkin–Elmer Model 2400 C, H, N analyzer. The inherent viscosities of the polymers were determined at 30°C for solutions having the concentration of 0.5 g polymer/100 mL DMAc-5 wt % LiCl, using a Cannon–Fenske viscometer. A DuPont DSC 1090 instrument was used to determine the thermal transitions. Heating rate was 20°C/min. Glass transition temperatures (T_gs) were read at the middle of the slope in the baseline shift, and were taken from the second heating trace after quenching. Thermogravimetry (TG) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20°C/min. Wide-angle x-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 x-ray diffractometer, using Ni-filtered CuK$_\alpha$ radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5-40°$. An Instron universal tester Model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the samples. A gauge of 2 cm and a strain rate of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.1 mm thick), and an average of at least five individual determinations was used.
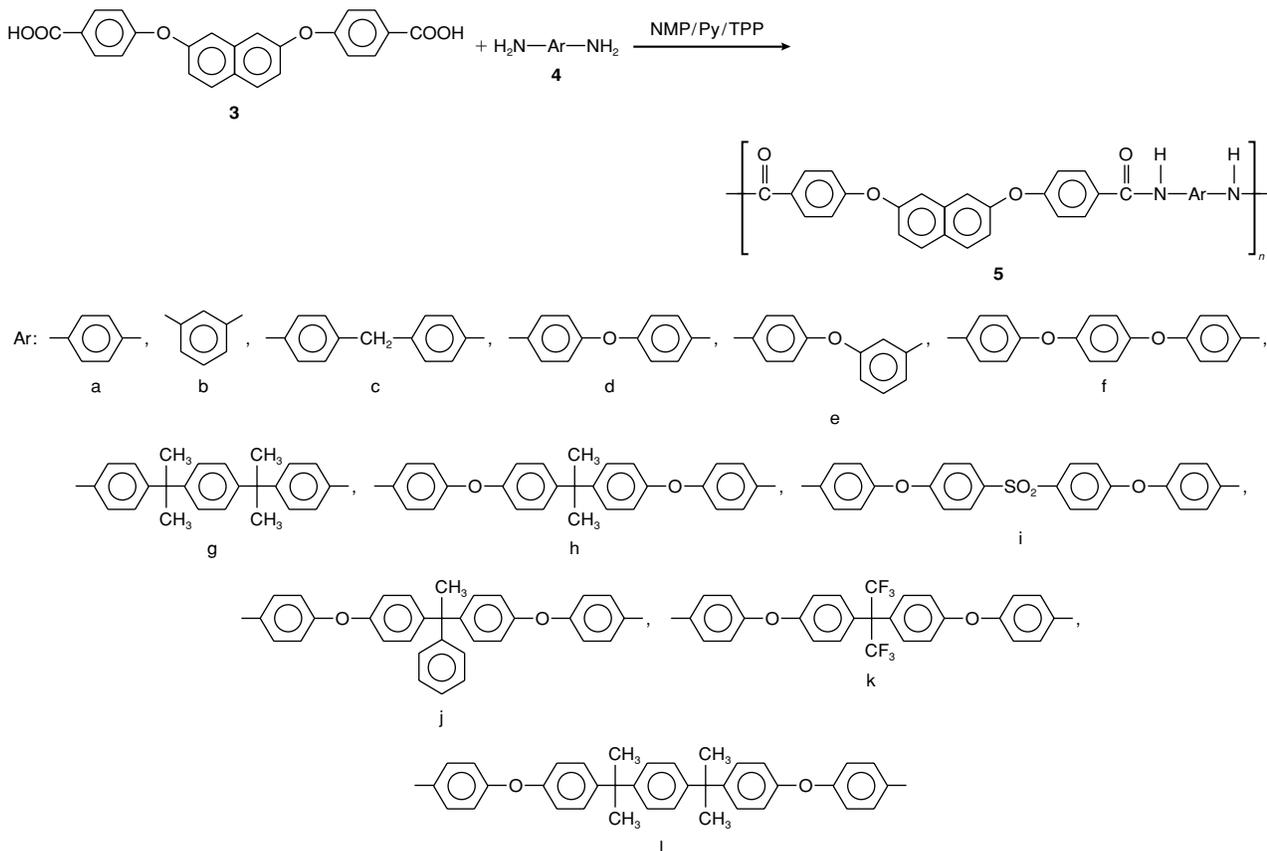
RESULTS AND DISCUSSION

Monomer Synthesis

The naphthalene unit containing bis(ether carboxylic acid) **3** was prepared using a two-stage
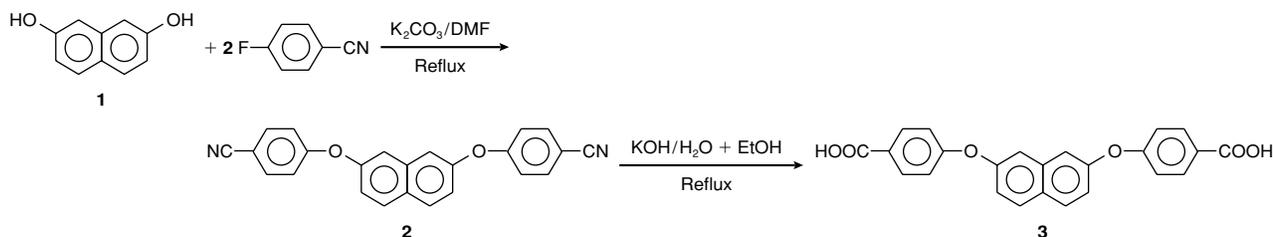
Scheme 1.

Scheme 2.

procedure from 2,7-dihydroxynaphthalene (**1**) and *p*-fluorobenzonitrile shown in Scheme 1.

First, bis(ether nitrile) **2** was prepared by the nucleophilic fluorodisplacement reaction of diol **1** and two equivalents of *p*-fluorobenzonitrile in DMF in the presence of K$_2$CO$_3$. Then, the intermediate dinitrile **2** was readily converted into diacid **3** by alkaline hydrolysis in excellent yields. The structures of dinitrile **2** and diacid **3** were confirmed by FT–IR and NMR spectroscopy. Figures 1–3 reproduce the FT–IR, ^{1}H-NMR, and ^{13}C-NMR spectra of the intermediate dinitrile **2** and the diacid monomer **3**. All the spectra data are consistent with their structures. Although the elemental analysis showed that the found value of carbon of diacid **3** was lower than the calculated one by about 3%, the purity of diacid **3** was still high enough for the preparation of high-molecular-weight polymers.

Polymer Synthesis

Several polyamides (**5a–l**) were prepared by a Yamazaki–Higashi[22] phosphorylation polyami-

dation technique that involved the direct polycondensation of diacid **3** and diamines **4a–l** using TPP and pyridine as condensing agents in NMP containing CaCl$_2$ at 110°C for 3 h (Scheme 2). By using the reaction conditions listed in Table I, all of the reaction solutions were homogeneously transparent throughout the reaction and became highly viscous. As shown in Table I, the inherent viscosities of these polyamides stay in the range of 0.48–0.67 dL/g. However, if the purity of diacid monomer can be further increased, polymers with even higher viscosities should be obtained. Except for polyamide **5a** derived from *p*-phenylenediamine (**4a**), the other polyamides were soluble in DMAc and afforded free-standing films by means of solution casting. However, the films obtained from polyamides **5c, 5d, 5f,** and **5i** embrittled upon creasing, which may be due to a high level of crystallinity of these polyamides.

The structure of the polyamides can be verified by IR spectroscopy, and a typical FT–IR spectrum of representative polyamide **5b** is shown in Figure 4. The characteristic absorptions of amide group were observed near 3310 cm^{-1} (N—H str.) and
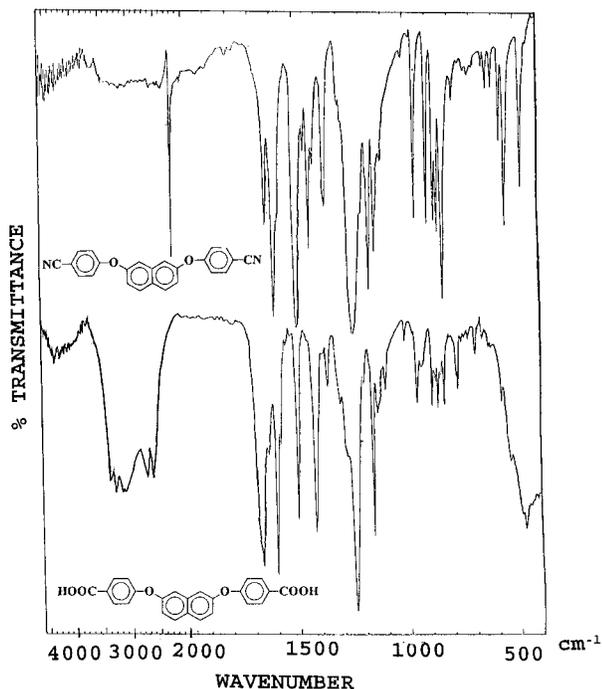
Figure 1. IR spectra of 4,4′-(2,7-naphthalenedioxy)-dibenzonitrile (**2**) and 4,4′-(2,7-naphthalenedioxy)dibenzoic acid (**3**).

1655 cm^{-1} (C=O str.), and that of aryl ether stretching appeared around 1260 cm^{-1}.

Properties of Polymers

The solubility of polyamides was studied qualitatively, and the results are summarized in Table II. The solubility behavior of these polyamides is partially governed by the of diamine moieties. The polyamides **5a, 5d, 5f,** and **5i** showed less solubility, and they were only soluble in DMAc or NMP. This can be attributed to high level of crystallinity developed in these polymers, as evidenced by their x-ray diffraction patterns shown in Figure 5. Incorporation of *meta*-catenated phenylene unit into the polymer backbone, for example, polyamides **5b** and **5e,** interrupted the chain packing, thus leading to an enhanced solubility. The polyamides obtained from flexibilizing group-linked "multiring" diamines such as **4g–h** and **4j–l** dissolved readily in NMP, DMAc, DMF, and DMSO at room temperature and even in less polar solvents like *m*-cresol and THF. This is reasonable because not only the chain flexibility is increased by the flexibilizing linkages, but also the density of amide groups, which can form intramolecular hydrogen bonding is decreased due to the incorporation of long chain diamine residue. Comparing the solubility behavior between polymers **5 f** and **5g,** it is found that the isopropylidene group is more effective in improving the solubility than the ether group. This may be explained by the fact that the former not only flexibilizes the polymer chain but interferes with the close packing of polymer chains.

As mentioned in Table I, all the polyamides except for **5a, 5c, 5d, 5f,** and **5i** could be cast into flexible and tough films. These flexible films revealed an amorphous pattern like that of polyamide **5b** shown in Figure 5. These films were
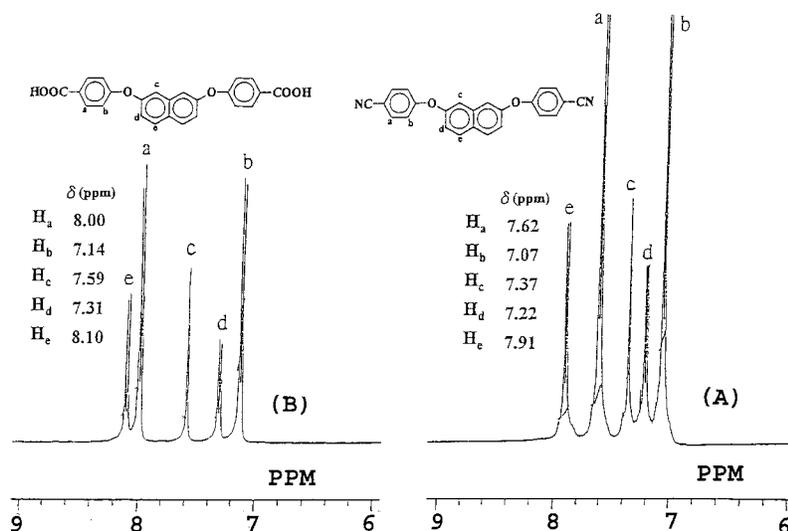

Figure 2. ^{1}H-NMR spectra of (A) 4,4′-(2,7-naphthalenedioxy)dibenzonitrile (**2**) in CDCl$_3$ and (B) 4,4′-(2,7-naphthalenedioxy)dibenzoic acid (**3**) in DMSO-d$_6$.

Figure 3. ^{13}C-NMR spectra of (A) 4,4′-(2,7-naphthalenedioxy)dibenzonitrile (**2**) in CDCl$_3$ and (B) 4,4′-(2,7-naphthalenedioxy)dibenzoic acid (**3**) in DMSO-d$_6$.
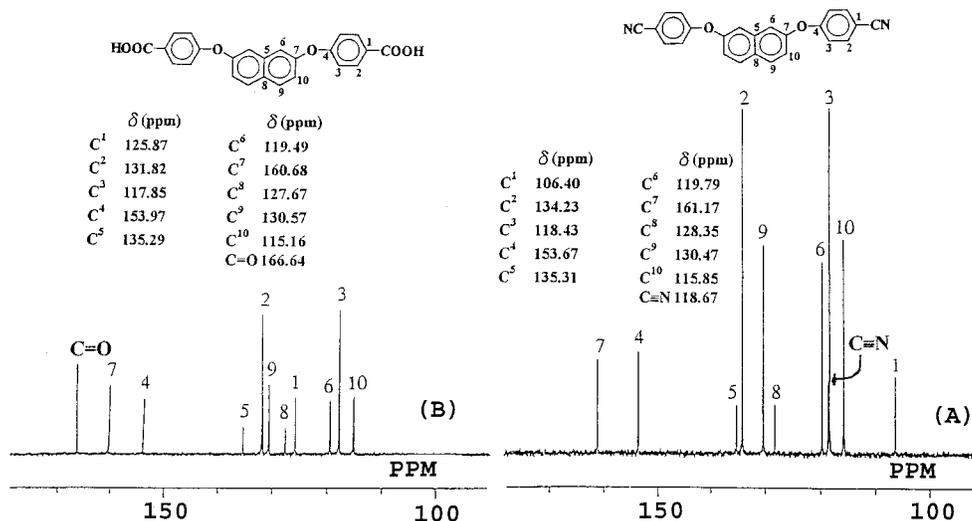
subjected to tensile test, and the results are presented in Table III. All specimens did not neck during the tensile test. They exhibited tensile properties of a similar level, irrespective of the diamine component. The tensile strength, elongation to break, and initial modulus of these films were in the ranges of 65–70 MPa, 5–7%, and 1.4–1.6 GPa, respectively.

Thermal properties of all the polyamides were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The representative TG curves of polyamide **5a** measured in air

Table I. Synthesis Conditions, Inherent Viscosities, and Film Quality of Polyamides

| Polymer Code | Amount of Reagent Used[a] | | | η_{inh}[c] (dL/g) | Film Quality[d] |
	NMP (mL)	Pyridine (mL)	CaCl$_2$ (g)		
5a	3 + 2[b]	1	0.4	0.61	—[e]
5b	1.5	0.8	0.3	0.48	Flexible
5c	2.5	1	0.4	0.50	Slightly brittle
5d	3	1	0.3	0.67	Brittle
5e	1	0.8	0.4	0.53	Flexible
5f	2 + 5	0.8	0.4	0.60	Brittle
5g	2	0.8	0.4	0.61	Flexible
5h	2 + 1	0.8	0.3	0.60	Flexible
5i	2 + 1	0.8	0.3	0.56	Brittle
5j	2	0.8	0.3	0.52	Flexible
5k	2	0.8	0.3	0.50	Flexible
5l	2	0.8	0.4	0.56	Flexible

[a] Amount of each diacid and diamine monomer = 1.25 mmol; TPP = 0.9 mL (2.5 mmol); reaction temperature = 110°C; reaction time = 3 h.
[b] "3 + 2" means that an initial amount of 3 mL NMP was used and an additional 2 mL of NMP were added when the reaction solution appeared turbid.
[c] Measured in DMAc containing 5 wt % LiCl on 0.5 g/dL at 30°C by a Connon–Fenske viscometer.
[d] Films were cast by solw evaporation of polymer solutions in DMAc.
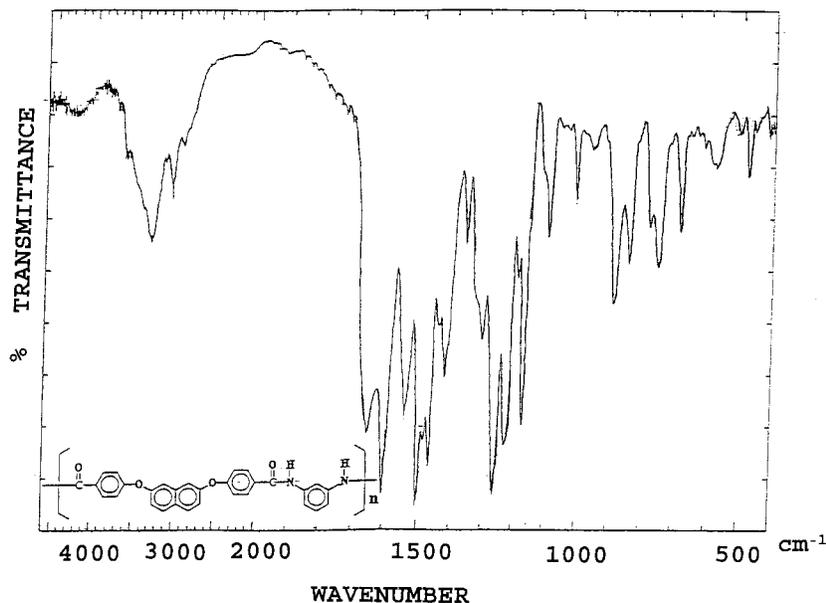[e] Insoluble in DMAc.

Figure 4. The IR spectrum of polyamide **5a**.

and in nitrogen are illustrated in Figure 6. **5a** showed no significant weight loss below 450°C in air or nitrogen, and 68.5 wt % residue remained when heated to 800°C in nitrogen. Included in Table IV are the 10% weight loss temperatures of these polyamides, which were in the range of 495–525°C in air and 484–527°C in nitrogen. The higher 10% weight loss temperatures of some of the polymers, such as **5g, 5h,** and **5l,** in air than in nitrogen may be attributed to oxidation and/ or oxidative crosslinking of the aliphatic groups. Among these polymers, polyamide **5g** revealed the relatively lower decomposition temperature and the lowest char yield (53.7%). This can possibly be ascribed to the highest density of the aliphatic segment in the repeating unit of polymer chain.

Table II. Solubility Behavior of Polyamides[a]

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

[a] Solubility: +, soluble at room temperature; +**h**, on heating; −, insoluble.
[b] NMP: *N*-Methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. All the polymers were soluble in DMAc + 5 wt % LiCl.
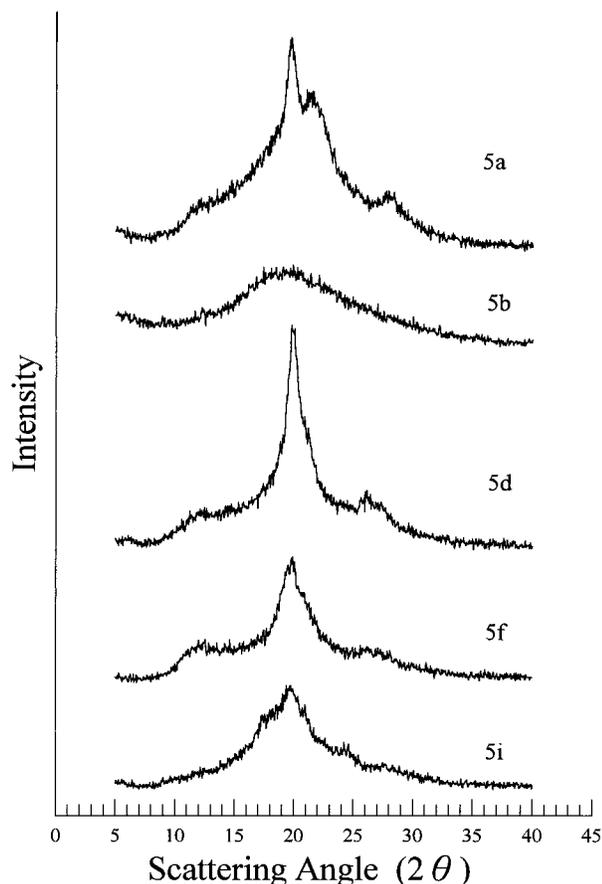
Figure 5. Wide-angle x-ray diffractograms of polyamides **5a, 5b, 5d, 5f,** and **5i**.

Except for the crystalline polyamides **5a, 5c,** and **5d,** all the other polymers showed distinct baseline shifts on their DSC heating traces. Glass transition temperatures (T_gs), defined by the midpoint of baseline shift, of the new polymers stay in the range of 143–227°C. Some of the poly-

Table III. Tensile Properties of Polyamide FIlms[a]

Polymer Code	Strength at Break Point (MPa)	Elongation at Break Point (%)	Initial Modulus (GPa)
5b	68	5	1.4
5e	69	6	1.6
5g	70	7	1.4
5h	66	6	1.4
5j	65	6	1.4
5k	67	7	1.4
5l	70	7	1.5

[a] Films were cast from slow evaporation of the polymer solutions in DMAc.
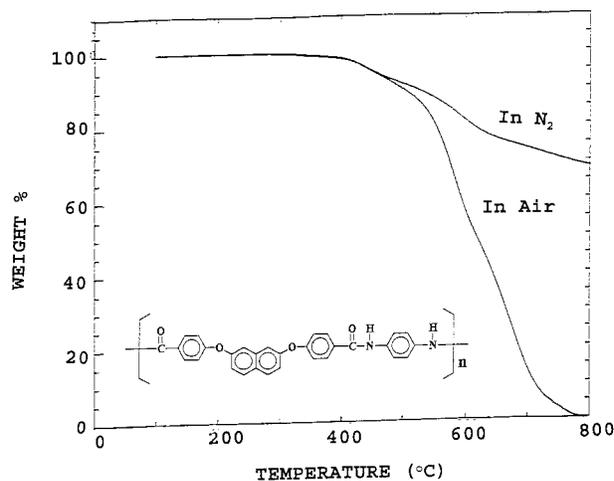

Figure 6. TG curves of polyamide **5a** at a heating rate of 20°/min.

amides showed a medium broad endotherm in their first DSC heating traces. However, in most cases rapid cooling and reheating showed a strong T_g and disappearance of the melting transition, and thus, may represent low crystallization rate. A typical diagram is shown in Figure 7. The polyamide **5i** exhibited the highest T_g, 227°C, probably associated with an enhanced intermolecular attraction caused by the presence of polar sulfonyl groups and semicrystalline characteristic. All the other polyamides had T_g below 200°C. The lower T_g accompanied with these polyamides is apparently due to the introduction of ether linkages into
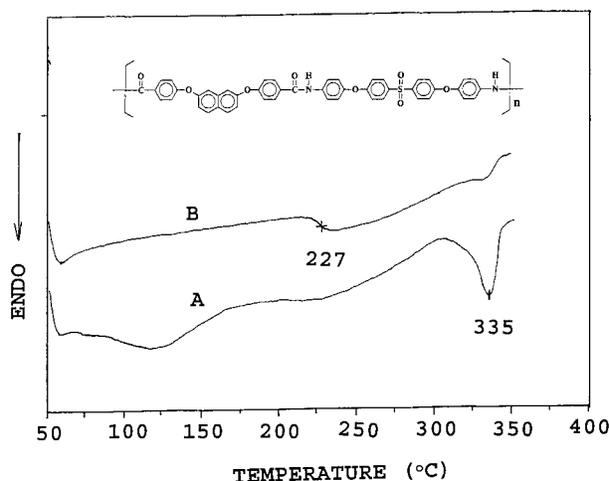

Figure 7. DSC curves of polyamide **5i** at a heating rate of 20°/min; (A) first heating, (B) second heating.

Table IV. Thermal Properties of Polyamides

Polymer Code	$T_g{}^a$ (°C)	Decomposition Temperature[d] (°C)		Char Yield[e] (%)
		In N_2	In Air	
5a	—[b]	520	499	68.5
5b	168	504	512	66.1
5c	— (350)[c]	524	519	70.5
5d	—	519	503	66.0
5e	164	510	520	58.4
5f	191 (224)	506	503	60.1
5g	155	484	495	53.7
5h	143	514	522	61.6
5i	227 (335)	527	505	62.1
5j	177	523	525	66.0
5k	163	524	524	59.0
5l	166	516	519	55.2

[a] The samples were heated to 350°C with a heating rate of 20°C/min and rapidly cooled to room temperature. The midpoint of baseline shift on the subsequent second DSC heating trace was defined as T_g.

[b] No discernible transitions was observed.

[c] Values in the parentheses were the peak temperatures of endotherms observed on the first DSC heating traces.

[d] Temperature at which 10% weight loss were recorded by thermogravimetry at a heating rate of 20°C/min.

[e] Residual wt % at 800°C in nitrogen.

the polymer backbones. Furthermore, it is interesting to note that the large window between T_g and the decomposition temperature makes these polymers attractive for practical processing.

CONCLUSIONS

A new dicarboxylic acid monomer containing both naphthalene ring and ether group, 4,4′-(2,7-naphthalenedioxy)dibenzoic acid, was prepared in high yield starting from the fluorodisplacement reaction of 2,7-dihydroxynaphthalene and *p*-fluorobenzonitrile in the presence of potassium carbonate. A series of new aromatic polyamides were directly synthesized from this diacid monomer with various aromatic diamines by means of triphenyl phosphite and pyridine. The molecular weights of the polyamides are sufficiently high to permit casting of flexible and tough films. Most of the polymers are amorphous and exhibit T_gs in the range of 143–227°C. All the polyamides were stable up to 450°C in both air and nitrogen atmospheres. High solubility and a large window between T_g and decomposition temperature indicate that these polyamides are easily processed from solution or melt.

REFERENCES AND NOTES

1. P. E. Cassidy, *Thermally Stable Polymers,* Dekker, New York, 1980.
2. C. Chiriac and J. K. Stille, *Macromolecules,* **10,** 712 (1977).
3. J. Adduci, L. L. Chapoy, G. Jonsson, J. Kops, and B. M. Shinde, *J. Appl. Polym. Sci.,* **28,** 2069 (1983).
4. S. B. Idage, B. B. Idage, B. M. Shinde, and S. P. Vernekar, *J. Polym. Sci., Polym. Chem. Ed.,* **27,** 583 (1989).
5. N. Avella, G. Maglio, R. Palumbo, F. Russo, and M. C. Vignola, *Makromol. Chem., Rapid Commun.,* **14,** 545 (1993).
6. Y. Imai, N. N. Malder, and M. Kakimoto, *J. Polym. Sci., Polym. Chem. Ed.,* **22,** 2189 (1985).
7. M.-L. Xie, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **29,** 55 (1991).
8. M. Yoneyama, K. D. A. Kuruppu, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **26,** 2917 (1988).
9. H.-J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **28,** 3293 (1990).

10. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **29,** 767 (1991).

11. Y. Oishi, H. Takado, M. Yoneyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **28,** 1763 (1990).

12. M. Yamashita, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **31,** 1513 (1993).

13. G.-S. Liou, M. Maruyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.,* **31,** 2499 (1993).

14. C.-P. Yang and W.-T. Chen, *Makromol. Chem.,* **193,** 2323 (1991).

15. C.-P. Yang and W.-T. Chen, *Makromol. Chem.,* **194,** 1595 (1993).

16. C.-P. Yang and W.-T. Chen, *Makromol. Chem.,* **193,** 2323 (1992).

17. C.-P. Yang, S.-H. Hsiao, and C.-C. Jang, *J. Polym. Sci., Part A: Polym. Chem.,* **33,** 1095 (1995).

18. C.-P. Yang and J.-H. Lin, *J. Polym. Sci., Part A: Polym. Chem.,* **34,** 341 (1996).

19. F. A. Bottino, G. D. Pasquale, N. Leonardi, and A. Pollicino, *J. Polym. Sci., Part A: Polym. Chem.,* **34,** 1305 (1996).

20. K. Suematsu, *Macromolecules,* **18,** 2083 (1985).

21. S.-H. Hsiao, C.-P. Yang, and J.-C. Fan, *Macromol. Chem. Phys.,* **196,** 3041 (1995).

22. N. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci., Polym. Chem. Ed.,* **13,** 1373 (1975).