

Synthesis and properties of aromatic polyamides based on 4,4'-(1,5-naphthalenedioxy)dibenzoic acid

Sheng-Huei Hsiao*, Kuan-Yu Chu

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, 3rd Section, Taipei, Taiwan, Republic of China

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SUMMARY:

4,4'-(1,5-Naphthalenedioxy)dibenzoic acid (**3**), a novel aromatic dicarboxylic acid monomer, was prepared by nucleophilic substitution reaction of 1,5-dihydroxynaphthalene and *p*-fluorobenzonitrile in *N,N*-dimethylformamide (DMF) in the presence of potassium carbonate and subsequent alkaline hydrolysis of the intermediate dinitrile, 4,4'-(1,5-naphthalenedioxy)dibenzonitrile. Using triphenyl phosphite (TPP) and pyridine as condensing agents, a series of novel aromatic polyamides were synthesized by direct polycondensation of diacid **3** and twelve aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride. The resulting polyamides had inherent viscosities above 1,14 and up to 4,45 dL/g. Most of these polyamides are readily soluble in polar solvents, such as NMP, DMF, and *N,N*-dimethylacetamide (DMAc). Transparent, flexible, and tough films could be cast from their DMAc or NMP solutions. Most of these polymers were amorphous in nature, as indicated by their wide-angle X-ray diffractograms. Thermogravimetric analysis (TG) showed that all the polyamides were stable up to 450°C in both air and nitrogen atmosphere. Most of them revealed a distinct glass transition on the differential scanning calorimetry (DSC) traces in the range of 183–259°C.

Introduction

Wholly aromatic polyamides, such as poly(*p*-phenyleneterephthalamide), poly(*m*-phenyleneisophthalamide), and poly(*p*-benzamide), exhibit a number of useful properties such as thermal stability, chemical resistance, and low flammability together with excellent mechanical properties in the form of fibers^{1,2}. However, their application range is restricted owing to poor processability, both by solution and melt methods, caused by the poor solubility in most organic solvents and by high softening or melting temperatures. The need for engineering plastics overcoming these problems recently increased.

One approach to increase the solubility of aromatic polyamides is the introduction of flexible^{3–6} and/or bulky^{7–14} groups into the polymer chain. It has been generally recognized that aromatic ether links inserted in aromatic main chains provide them with a significantly lower energy of internal rotation, thus leading to higher solubility and modability while lowering the T_g . On the other hand, incorporation of rigid moieties, such as naphthalene rings, into the polymer chain generally leads to an enhanced thermal stability with respect to the benzene ring¹⁵. The goal of increased solubility, together with retained high thermal stability or high T_g , could be achieved by preparing polyamides containing both naphthalene rings and flexible groups like ether.

It has been proven that the insertion of naphthalenedioxy units into the polymer backbone could afford soluble aromatic polyamides with high T_g ¹⁶⁻²⁰. For example, several organosoluble polyamides could be obtained from the combination of 4,4'-(1,5-naphthalenedioxy)dianiline with various aromatic dicarboxylic acids¹⁷. This article describes an alternative route to prepare this kind of polyamides which bear both naphthalene rings and ether groups in the main chain, i.e., 4,4'-(1,5-naphthalenedioxy)dibenzonitrile was first synthesized by aromatic nucleophilic substitution reaction between *p*-fluorobenzonitrile and 1,5-dihydroxynaphthalene; this intermediate dinitrile was then hydrolyzed to 4,4'-(1,5-naphthalenedioxy)dibenzoic acid; finally, a series of novel naphthalenedioxy units-containing polyamides were produced from this diacid and various aromatic diamines by the Yamazaki-Higashi phosphorylation polyamidation technique²¹. The structure of resulting polyamides, having both crank shaft-like 1,5-disubstituted naphthalene unit and ether group in the repeating unit, is expected to provide balanced properties of high thermal stability and good processability. The effects of the diamine structure on the polymerization reactions and on the properties of the resulting polyamides will also be investigated.

Experimental part

Materials

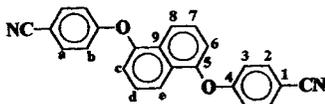
1,5-Dihydroxynaphthalene (**1**) (Janssen Chimica) and *p*-fluorobenzonitrile (TCI) were used without previous purification. *p*-Phenylenediamine (**4a**) was purified by sublimation. *m*-Phenylenediamine (**4b**) was vacuum-distilled prior to use. According to a reported method²², 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**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 *α,α*-bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**4l**) (m.p. 187–189 °C) were prepared by the 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. The other aromatic diamines were used without previous purification. Calcium chloride (CaCl₂) 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.

4,4'-(1,5-Naphthalenedioxy)dibenzonitrile (**2**)

In a 300-mL flask, 16.3 g (0.102 mol) of 1,5-dihydroxynaphthalene (**1**) and 28.5 g (0.204 mol) of K₂CO₃ 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 gray solid was collected by filtration and washed with water. The yield of the product was 32.1 g (87%). The crude product was purified by recrystallization from 2:1 volume mix-

ture of chloroform and methanol to afford **2** as a gray crystalline needles. The yield of the purified product was 28,0 g (76%); m. p. 222–224 °C.

The IR spectrum (KBr) exhibited absorptions at 2230 (C≡N) and 1250 cm⁻¹ (C—O).
¹H NMR (CDCl₃): δ = 7,89 (d, 2H, H_c), 7,63 (d, 4H, H_a), 7,48 (t, 2H, H_d), 7,18 (s, 2H, H_c), 7,06 ppm (d, 4H, H_b).
¹³C NMR (CDCl₃): δ = 161,75 (C⁵), 150,88 (C⁴), 134,26 (C²), 128,61 (C⁹), 126,54 (C⁸), 118,99 (C⁷), 118,64 (cyano carbon), 117,80 (C³), 116,90 (C⁶), 106,22 ppm (C¹).



C ₂₄ H ₁₄ N ₂ O ₂ (362,39)	Calc.	C 79,54	H 3,89	N 7,73
	Found	C 79,48	H 3,80	N 7,67

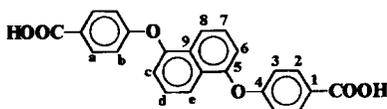
4,4'-(1,5-Naphthalenedioxy)dibenzoic acid (**3**)

In a 1000-mL flask, a suspension of dinitrile **2** (28,0 g; 0,077 mol) in an ethanol/water mixture (400 mL/400 mL) containing dissolved 54,2 g (1,569 mol) of KOH was boiled under reflux. The suspension turned into a clear solution after about 3 days. Reflux was continued for about one day until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any possible insoluble impurities. The hot filtrate was allowed to cool and acidified by conc. HCl to pH ≈ 3. The gray precipitated product was filtered off, washed with water, and dried *in vacuo*, to give 29,2 g of diacid **3**. Yield 95%; m. p. 337 °C (DSC).

IR (KBr): 2400–3200 (O—H), 1690 (C=O), 1400–1600 (arom. C=C), 1250 cm⁻¹ (C—O).

¹H NMR (DMSO-*d*₆): δ = 7,99 (d, 4H, H_a), 7,88 (d, 2H, H_c), 7,58 (t, 2H, H_d), 7,28 (d, 2H, H_c), 7,12 ppm (d, 4H, H_b).

¹³C NMR (DMSO-*d*₆): δ = 166,66 (carbonyl carbon), 161,26 (C⁵), 151,00 (C⁴), 131,75 (C²), 127,98 (C⁹), 126,90 (C⁸), 125,46 (C¹), 118,12 (C⁷), 117,01 (C³), 116,53 ppm (C⁶).



C ₂₄ H ₁₆ O ₆ (400,39)	Calc.	C 71,99	H 4,02
	Found	C 71,93	H 4,00

Polymer synthesis

A typical polymerization procedure is as follows: a mixture of 0,5005 g (1,25 mmol) of 4,4'-(1,5-naphthalenedioxy)dibenzoic acid (**3**), 0,1352 g (1,25 mmol) of *m*-phenylenediamine (**4b**), 0,4 g of CaCl₂, 0,9 mL of TPP, 1,5 mL of pyridine, and 6 mL of NMP was heated with stirring at 110 °C for 3 h. As polycondensation proceeded, the solution became viscous gradually. The resulting highly viscous polymer solution was trickled into 300 mL of methanol with stirring, giving a fibrous pale-brown 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 1,64 dL/g.

IR (film): 3445 (N—H), 1655 (C=O), 1400–1600 (arom. C=C), 1250 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 semi-dried 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 ready for X-ray diffraction measurements and tensile tests.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. ^1H 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 were measured with a Cannon-Fenske viscometer thermostated at 30°C. The DSC traces were measured on a DuPont 910 differential scanning calorimeter coupled to a DuPont 1090 thermal analyzer at a heating rate of 20°C/min in flowing air (50 cm^3/min). 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_α radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5\text{--}40^\circ$. 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 reaction from 1,5-dihydroxynaphthalene (**1**) and *p*-fluorobenzonitrile (*Scheme 1*). First, bis(ether nitrile) **2** was prepared by nucleophilic fluorodisplacement reaction of diol **1** and two equivalents of *p*-fluorobenzonitrile in DMF in the presence of K_2CO_3 . The yield was high, with 76% after recrystallization. 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 elemental analysis, FTIR, and NMR spectroscopy. The purity of diacid **3** was high enough for the preparation of high-molecular-weight polymers.

Fig. 1 shows the FTIR spectra of dinitrile **2** and diacid **3**. When the cyano group was converted into the carboxyl group, the characteristic absorption peak of cyano

Scheme 1:

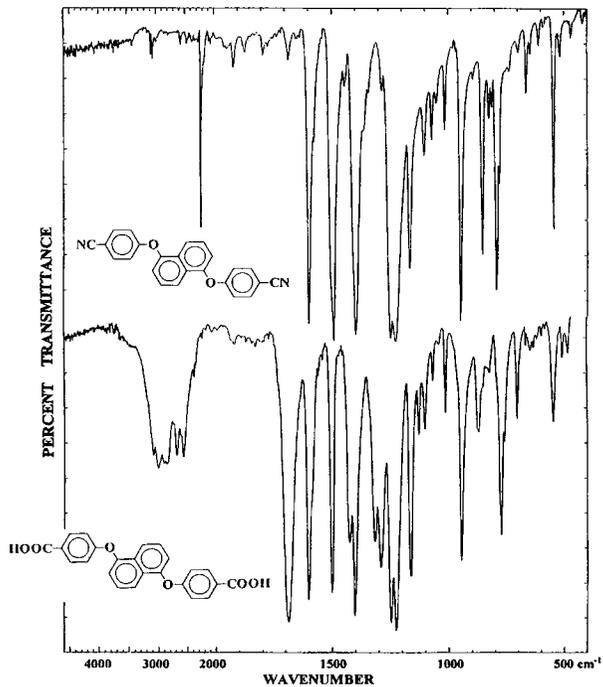
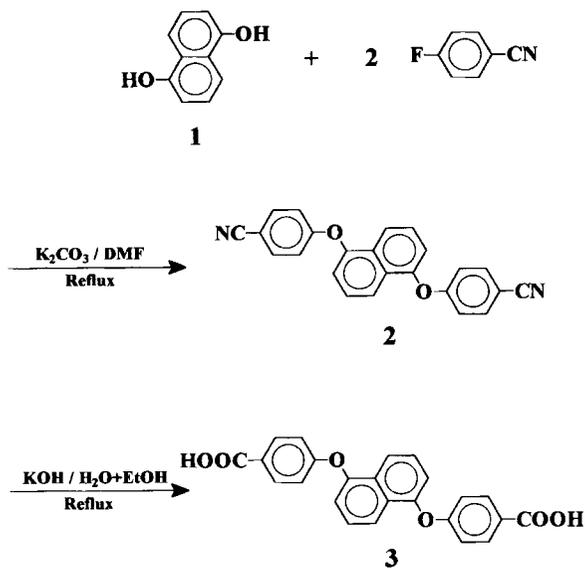


Fig. 1. Infrared spectra of 4,4'-(1,5-naphthalenedioxy)dibenzonitrile (**2**) and 4,4'-(1,5-naphthalenedioxy)dibenzoic acid (**3**)

group near 2230 cm^{-1} disappeared, and the carbonyl stretching absorption at about 1690 cm^{-1} and the broad absorption band of hydroxy group in the region from 2400 to 3200 cm^{-1} appeared.

The comparative ^{13}C NMR spectra of dinitrile **2** and diacid **3** are shown in Fig. 2, and each carbon atom shows an obviously assignable resonance peak. After the dinitrile was hydrolyzed into the diacid, the original resonance signal at $118,64\text{ ppm}$ due to cyano carbon vanished, and the resonance signal of the carbonyl carbon appeared at $166,66\text{ ppm}$. In the spectrum of dinitrile **2**, the C^1 resonated at higher field ($106,22\text{ ppm}$) than the other aromatic carbons due to the anisotropic shielding effect induced by the cyano group. After the cyano group was converted into the carboxyl group, the resonance peak of C^1 of the original dinitrile moved to lower field ($125,46\text{ ppm}$) because of the lack of anisotropic shielding. The other resonance peaks are in good agreement with the proposed structures of compounds **2** and **3**.

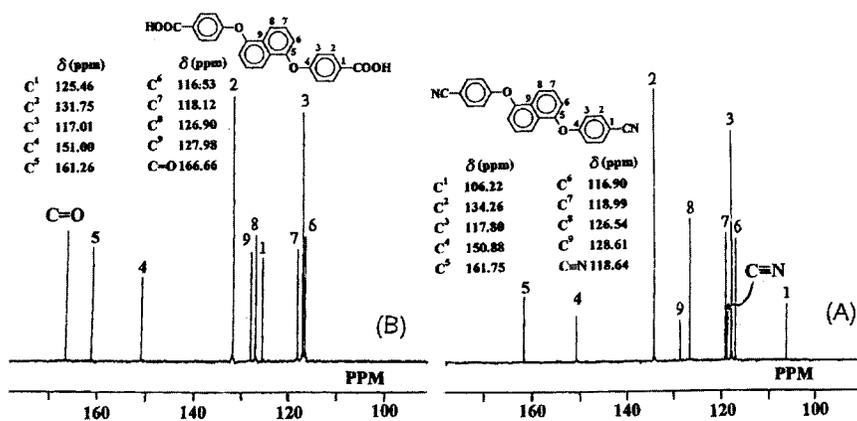


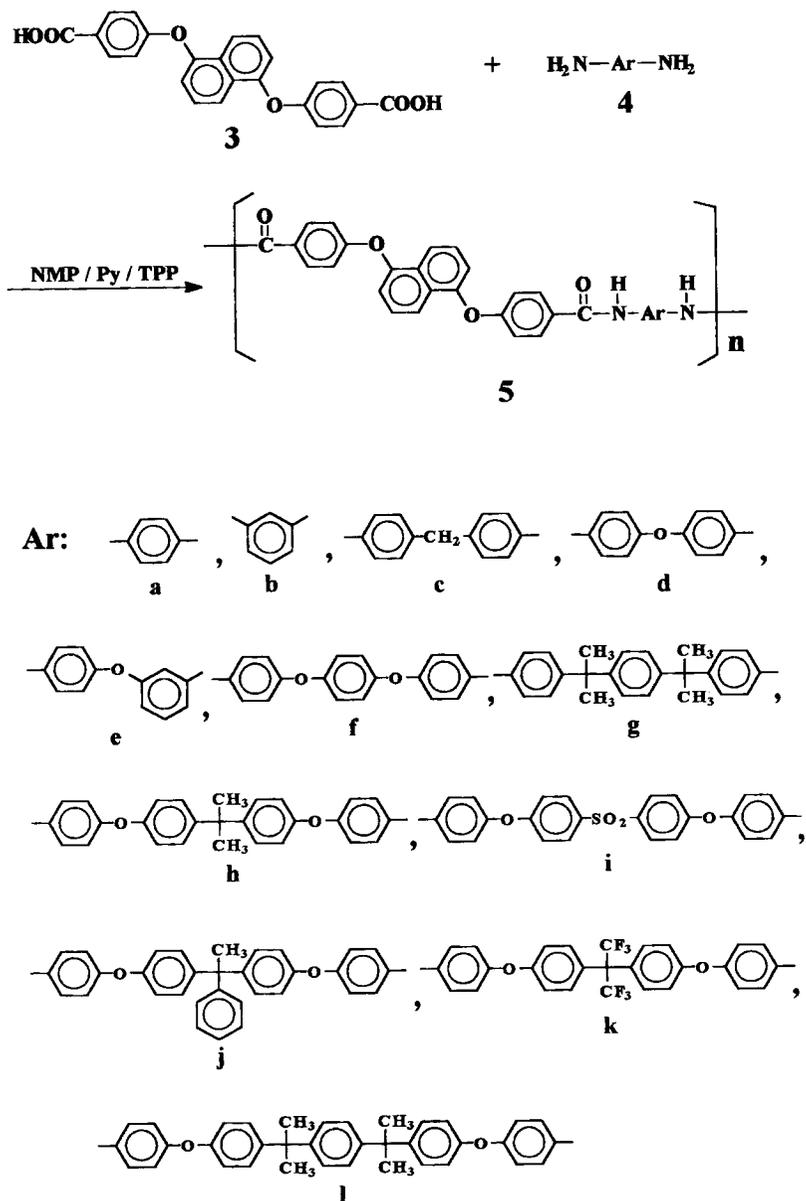
Fig. 2. ^{13}C NMR spectra of (A) 4,4'-(1,5-naphthalenedioxy)dibenzonitrile (**2**) in CDCl_3 and (B) 4,4'-(1,5-naphthalenedioxy)dibenzoic acid (**3**) in $\text{DMSO}-d_6$

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 solvent²³. 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-Higashi phosphorylation polyamidation method²²) has been known to be another convenient method for the preparation of polyamides on a laboratory scale. This method was popularly used on screening new polyamides²⁴⁻²⁶ and also successfully employed in the synthesis of poly(amide-imide)s²⁷⁻³³ based on imide ring-preformed dicarboxylic acids. This technique avoids using moisture-sensitive acid chlorides and is very convenient and efficient. Therefore, this technique was utilized to prepare the new series of polyamides studied in this article.

Serial polyamides **5a–l** were directly polycondensated from 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 Tab. 1, all of

Scheme 2:



Tab. 1. Synthesis conditions, inherent viscosities, and film quality of polyamides based on 4,4'-(1,5-naphthalenedioxy)dibenzoic acid

Polymer code	Amount of reagent used ^{a)}			$\eta_{inh}^{b)}$ dL/g	Film quality ^{c)}
	NMP in mL	Pyridine in mL	CaCl ₂ in g		
5a	10	2,5	0,6	1,72	— ^{d)}
5b	6	1,5	0,4	1,64	Flexible
5c	8	2	0,5	2,03	Flexible
5d	10	2,5	0,6	1,50	Flexible
	4 + 10 ^{e)}	1	0,5	4,45 ^{f)}	— ^{d)}
	6 + 6	1,5	0,7	2,51	Flexible
	10	2	0,6	2,15	Flexible
5e	6	1,5	0,4	2,09	Flexible
5f	8 + 5	2	0,5	2,62	Flexible
5g	8	2	0,5	1,42	Flexible
5h	8 + 2	2	0,5	2,07	Flexible
5i	8	2	0,5	1,14	Flexible
5j	8	2	0,5	1,20	Flexible
5k	8	2	0,5	1,34	Flexible
5l	10	2,5	0,5	1,35	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) Measured in DMAc containing 5 wt.-% LiCl in 0,5 g/dL at 30 °C by a Cannon-Fenske viscometer.

c) Films were cast by slow evaporation of polymer solutions in DMAc, except for that of **5f** cast from NMP.

d) Insoluble in either DMAc or NMP.

e) "4 + 10" means that an initial amount of 4 mL NMP was used, and an additional 10 mL of NMP was added when the reaction solution was too viscous to stir.

f) The polymer gelled during the reaction and could not be redissolved by further addition of NMP.

the reaction solutions were homogeneously transparent throughout the reaction and became highly viscous, indicating the formation of high molecular weights. As shown in Tab. 1, the inherent viscosities of these polyamides obtained were above 1,14 dL/g and up to 4,45 dL/g. Using a higher initial reactant concentration led to a higher viscosity (e. g., in the cases of polyamides **5c** and **5d**). However, using a too high initial concentration usually resulted in an intractable swollen gel. Except for polyamide **5a** derived from *p*-phenylenediamine (**4a**), the other polyamides were soluble in the DMAc or NMP and afforded flexible and tough films by means of solution-casting.

The structures of these polyamides can be ascertained by IR spectroscopy. The characteristic absorptions of amide group were observed near 3445 cm⁻¹ (N—H str.) and 1665 cm⁻¹ (C=O str.), and that of aryl ether stretching appeared near 1250 cm⁻¹.

Properties of polymers

The solubility of polyamides was studied qualitatively, and the results are summarized in Tab. 2. In fact, due to the presence of 1,5-naphthalenedioxy moiety, most of the polyamides exhibited high solubility in polar aprotic solvents such as DMF, DMSO, DMAc, and NMP. The solubility behavior of these polyamides is partially governed by the residue of diamines. The polyamide **5a** derived from rigid *p*-phenylenediamine was insoluble in all the solvents tested. This can be attributed to the fact that it is highly crystalline, as evidenced by its X-ray diffraction pattern shown

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

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

a) Solubility: +, soluble at room temperature; +h, soluble at high temperature; and –, insoluble.

b) DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; THF: tetrahydrofuran. All the polymers were soluble in DMAc +5 wt.-% LiCl.

in Fig. 3. Incorporation of *meta*-catenated phenylene unit into the polymer backbone, e. g., in polyamides **5b** and **5e**, increased the flexibility of polymer chain, thus leading to an enhanced solubility. The polyamides obtained from flexibilizing group-linked “multiring” diamines such as **4g–l** dissolved 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 use of long chain diamines. Comparing the solubility behavior between polymers **5f** 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.

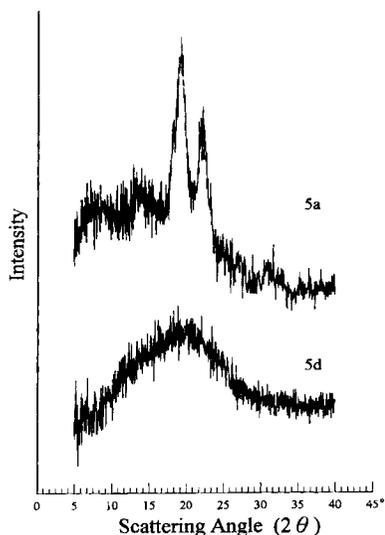


Fig. 3. Wide-angle X-ray diffractograms of polyamides **5a** and **5d**

Tab. 3. Tensile properties of polyamide films^{a)}

Polymer code	Strength at yield point in MPa	Strength at break point in MPa	Elongation at break point in %	Initial modulus in GPa
5b	83	72	26	2,3
5c	76	81	37	2,1
5d	107	95	14	2,2
5e	84	74	32	2,2
5g	79	77	38	1,9
5h	87	88	53	2,0
5i	77	68	26	2,1
5j	83	71	19	2,2
5k	73	73	37	1,9
5l	85	73	34	1,8

^{a)} Films were cast by slow evaporation of the polymer solutions in DMAc.

As mentioned in Tab. 1, all the polyamides except for **5a** could be cast into flexible and tough films. These flexible films showed an amorphous nature as indicated by their X-ray diffraction patterns, which all revealed an amorphous halo like that of polyamide **5d** shown in Fig. 3. These films were subjected to tensile test, and the results are presented in Tab. 3. They showed excellent tensile properties, with yield strengths of 73–107 MPa, tensile strengths of 68–95 MPa, elongations to break of 14–53%, and initial moduli of 1,8–2,3 GPa. All the specimens yielded under tension and revealed moderate elongations at break point, indicative of high toughness.

Tab. 4. Thermal properties of polyamides

Polymer code	$T_g^{a)}$ °C	Decomposition temperature ^{b)} in °C		Char yield ^{c)} in wt.-%
		in N ₂	in air	
5a	–	516	478	67,0
5b	234	514	504	68,8
5c	237	502	494	68,0
5d	230	525	502	68,7
5e	227	529	521	70,2
5f	225	510	494	63,8
5g	259	487	499	59,1
5h	212	516	520	58,5
5i	238	522	514	60,6
5j	214	517	511	63,5
5k	220	525	511	57,2
5l	183	517	515	61,3

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) Temperature at which 10% weight loss was recorded by thermogravimetry at a heating rate of 20°C/min.

c) Residual weight % at 800°C in nitrogen.

Thermal properties of all the polyamides were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). All the polyamides showed similar TG curves with no significant weight loss below 450°C in air or nitrogen, but with more than 57 wt.-% residue remaining when heated to 800°C in nitrogen. As shown in Tab. 4, the 10% weight loss temperatures of these polyamides were recorded in the range of 478–521°C in air and 487–529°C in nitrogen. Except for the crystalline polyamide **5a**, all the other polymers showed distinct baseline shifts in their DSC heating traces. Glass transition temperatures (T_g 's), defined by the midpoint of baseline shift, of the new polymers appear in the range of 183–259°C. Polyamide **5l** has the lowest T_g , 183°C, which is due to the highest amount of flexible bridges, isopropylidene and ether groups, per repeating unit of the macromolecule. All other polyamides exhibit T_g 's higher than 212°C. The large window between T_g and the decomposition temperature makes these polymers attractive for practical processing.

Conclusions

A new diacid monomer containing both naphthalene ring and ether group, 4,4'-(1,5-naphthalenedioxy)dibenzoic acid, was prepared in high yield and high purity starting from the fluorodisplacement of *p*-fluorobenzonitrile with 1,5-dihydroxynaphthalene in the presence of potassium carbonate. High molecular weight aro-

matic polyamides could be directly synthesized from this diacid monomer and various aromatic diamines. The molecular weights of these polyamides are sufficiently high to permit casting flexible and tough films. Except for the polyamide derived from *p*-phenylenediamine, all other polyamides are amorphous in nature and reveal excellent solubility in a variety of organic solvents. All the polyamides were stable up to 450 °C in both air and nitrogen atmospheres. These polyamides had T_g 's in the range of 183–259 °C. High solubility and large window between T_g and the decomposition temperature indicate that the polyamides are readily processable from solution or melt 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 high-performance polymeric material.

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