

# Soluble aromatic polyamides bearing asymmetrical diaryl ether groups

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## Abstract

A series of novel aromatic polyamides containing asymmetrical diaryl ether structure were synthesized by the phosphorylation polyamidation of 5-(4-aminophenoxy)-1-naphthylamine with various dicarboxylic acids. The polymers were obtained in high yields and moderately high inherent viscosities (0.74–1.36 dl/g). Except for one example, all the polyamides were amorphous and readily soluble in many organic solvents and could afford flexible and tough films via solution casting. The cast films exhibited good mechanical properties with tensile strengths of 90–128 MPa, elongations at break of 9–64%, and initial moduli of 2.08–3.08 GPa. Glass-transition temperatures ranged from 222 to 288 °C by DSC. Thermal stabilities by TGA for the polymer series ranged from 462 to 517 °C in air at the point of 10% weight loss. These polyamides displayed a lower crystallinity and better solubility and film-forming capability than the corresponding analogues derived from symmetrical 1,5-diaminonaphthalene and 1,5-bis(4-aminophenoxy)naphthalene.

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*Keywords:* Aromatic polyamides; Asymmetric ether-diamine; High-performance polymers

## 1. Introduction

Wholly aromatic polyamides (aramids) have been well known for their high mechanical properties, good chemical resistance, and excellent thermal stability [1–3]. However, it is difficult for aramids to be used as thin films and coatings because they have low solubility in almost all available solvents except for concentrated sulfuric acid. To obtain different properties and for different applications, various structural changes have been introduced in the aramid backbone [4–15]. The incorporation of ether groups or other flexibilizing linkages into the main chain generally leads to a significant improvement in the solubility and/or thermo-plasticity of aramids. It has been recognized that the incorporation of aryl-ether linkages generally imparts an enhanced solubility, processability, and toughness of the polymers without substantial diminution of thermal properties.

1,5-Diaminonaphthalene (1,5-DAN) has a symmetric and rigid molecular structure, and we found that its derived aramids generally exhibit low solubility and high melting and softening temperature, together with a highly brittle nature. In a previous publication [16], 1,5-bis(4-aminophenoxy)naphthalene (1,5-BAPON) has been synthesized and used to prepare aramids with 1,5-bis(phenoxy)naphthalene in the backbone. However, most of aramids derived from rigid dicarboxylic acids showed a limited solubility because of high level of crystallinity. It was demonstrated that aramids containing ether linkages as well as asymmetrical groups are significantly more flexible and more soluble than conventional aramids [17–20]. As part of our continuing efforts in developing tractable high-performance polymers containing naphthalene units, the present study describes the synthesis of a new ether-diamine, 5-(4-aminophenoxy)-1-naphthylamine, and its derived aramids. Since the new monomer is molecularly asymmetric, the resulting aramids should possess three possible diads randomly distributed in the main chain that may lead to a better solubility than the 1,5-DAN and 1,5-BAPON based aramids and retain other positive properties such as high thermal stability.

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## 2. Experimental

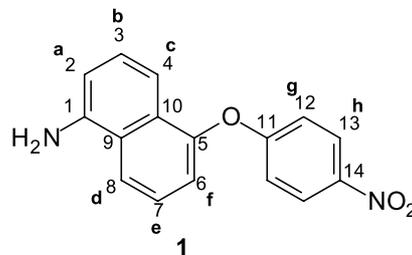
### 2.1. Reagents and solvents

5-Amino-1-naphthol (TCI), 1,5-diaminonaphthalene (TCI), 4-chloronitrobenzene (Acros), potassium carbonate ( $K_2CO_3$ ) (Fluka), 10% palladium on charcoal (Pd/C) (Fluka), hydrazine monohydrate (Acros), and the aromatic dicarboxylic acids including terephthalic acid (**3a**) (TCI), isophthalic acid (**3b**) (TCI), 4,4'-biphenyldicarboxylic acid (**3c**) (TCI), 4,4'-dicarboxydiphenyl ether (**3d**) (TCI), 4,4'-sulfonyldibenzoic acid (**3e**) (New Japan Chemical Co.), 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**3f**) (TCI), 1,4-naphthalenedicarboxylic acid (**3g**) (Wako), and 2,6-naphthalenedicarboxylic acid (**3h**) (TCI) were used as received. *N*-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) (Fluka) was purified by distillation under reduced pressure. Commercially obtained anhydrous calcium chloride ( $CaCl_2$ ) was dried under vacuum at 180 °C for 8 h prior to use.

### 2.2. Synthesis of 5-(4-nitrophenoxy)-1-naphthylamine (**1**)

In a 250 ml flask, 5-amino-1-naphthol (10.03 g, 0.063 mol), 4-chloronitrobenzene (10 g, 0.063 mol) were dissolved in 100 ml of *N,N*-dimethylformamide (DMF). Then, potassium carbonate (8.7 g, 0.063 mol) was added and the reaction solution was heated at reflux temperature for 10 h. After cooling, the mixture was poured into 400 ml of saturated aqueous sodium chloride solution. The precipitated brown solid was washed repeatedly with water and dried to a dark brown product [16.4 g, 93%; mp = 115–117 °C (onset to the peak top temperature) according to differential scanning calorimetry (DSC) at a scan rate of 5 °C/min, lit. [21] 116–117 °C].

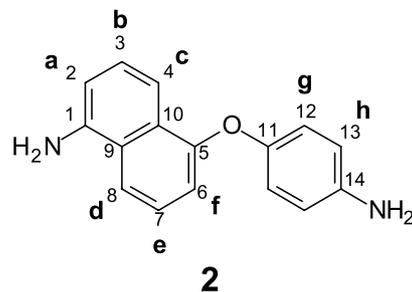
Elem. anal. Calcd for  $C_{16}H_{12}N_2O_3$  (280.28): C, 68.57%; H, 4.32%; N, 9.99%. Found: C, 68.95%; H, 4.12%; N, 9.96%. IR (KBr): 1512, 1342 ( $-NO_2$ ), 1250  $cm^{-1}$  (C–O).  $^1H$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 8.15 (d,  $J=8.6$  Hz, 2H,  $H_b$ ), 7.90 (d,  $J=8.3$  Hz, 1H,  $H_d$ ), 7.42 (t,  $J=7.7$  Hz, 1H,  $H_c$ ), 7.22 (d+t,  $J=7.6$  Hz, 2H,  $H_b$ ,  $H_c$ ), 7.15 (d,  $J=7.1$  Hz, 1H,  $H_f$ ), 6.99 (d,  $J=8.6$  Hz, 2H,  $H_g$ ), 6.81 (d,  $J=7.4$  Hz, 1H,  $H_a$ ), 4.99 (2H,  $-NH_2$ ).  $^{13}C$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 164.1 ( $C^{11}$ ), 150.2 ( $C^5$ ), 143.9 ( $C^1$ ), 142.2 ( $C^{14}$ ), 127.7 ( $C^{10}$ ), 127.4 ( $C^3$ ), 125.9 ( $C^{13}$ ), 125.0 ( $C^9$ ), 123.9 ( $C^7$ ), 119.7 ( $C^8$ ), 116.7 ( $C^4$ ), 116.4 ( $C^{12}$ ), 110.5 ( $C^2$ ), 109.7 ( $C^6$ ).



### 2.3. Synthesis of 5-(4-aminophenoxy)-1-naphthylamine (**2**)

A mixture of compound **1** (16 g, 0.057 mol), 10% Pd/C (0.2 g), hydrazine monohydrate (10 ml), and ethanol (200 ml) was heated at reflux temperature for about 4 h. The reaction solution was filtered while hot to remove Pd/C, and the filtrate was poured into a saturated aqueous sodium chloride solution to give a light-brown precipitate that was isolated by filtration, thoroughly washed by distilled water, and dried in vacuo (10.2 g, 71%; mp = 109–110 °C according to DSC at 5 °C/min).

Elem. anal. Calcd for  $C_{16}H_{14}N_2O$  (250.30): C, 76.78%; H, 5.64%; N, 11.19%. Found: C, 76.22%; H, 5.68%; N, 11.24%. IR (KBr): 3460, 3379 ( $-NH_2$ ), 1234  $cm^{-1}$  (C–O).  $^1H$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 7.66 (d,  $J=8.4$  Hz, 1H,  $H_d$ ), 7.53 (d,  $J=8.4$  Hz, 1H,  $H_c$ ), 7.25 (t,  $J=7.8$  Hz, 1H,  $H_c$ ), 7.22 (t,  $J=7.7$  Hz, 1H,  $H_b$ ), 6.84 (d,  $J=8.7$  Hz, 2H,  $H_g$ ), 6.79 (d,  $J=7.3$  Hz, 1H,  $H_a$ ), 6.70 (d,  $J=7.6$  Hz, 1H,  $H_f$ ), 6.66 (d,  $J=8.7$  Hz, 2H,  $H_b$ ), 4.57 (2H,  $-NH_2$ ), 3.15 (2H,  $-NH_2$ ).  $^{13}C$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 155.0 ( $C^5$ ), 148.2 ( $C^{11}$ ), 143.5 ( $C^1$ ), 142.9 ( $C^{14}$ ), 127.0 ( $C^{10}$ ), 126.1 ( $C^3$ ), 124.6 ( $C^9$ ), 124.1 ( $C^7$ ), 120.6 ( $C^{12}$ ), 115.9 ( $C^{13}$ ), 115.3 ( $C^4$ ), 111.5 ( $C^8$ ), 110.5 ( $C^2$ ), 109.7 ( $C^6$ ).



### 2.4. Polymer synthesis

The phosphorylation polycondensation method was used to prepare the polyamides. A typical example for the preparation of polyamide **4a** is given. A flask was charged with 0.5006 g (2.00 mmol) of diamine **2**, 0.3323 g (2.00 mmol) of diacid **3a**, 0.1 g of  $CaCl_2$ , 2 ml of TPP, 0.8 ml pyridine, and 3.5 ml of NMP. This mixture was heated with stirring at 120 °C for 3 h. As polycondensation proceeded, the solution gradually became viscous. Then, the

viscous polymer solution was poured slowly into 300 ml of stirred methanol. The resulting fibrous precipitate was filtered off, washed thoroughly with methanol and hot water, and dried. The yield is almost quantitative. The inherent viscosity of polymer **4a** was 1.36 dl/g, as measured at a concentration of 0.5 dl/g in *N,N*-dimethylacetamide (DMAc) containing 5 wt% LiCl at 30 °C. Elem. Anal. Calcd for  $(C_{24}H_{16}N_2O_3)_n$  (380.40) $_n$ : C, 75.78%; H, 4.24%; N, 7.36%. Found: C, 74.65%; H, 4.40%; N, 7.28%.

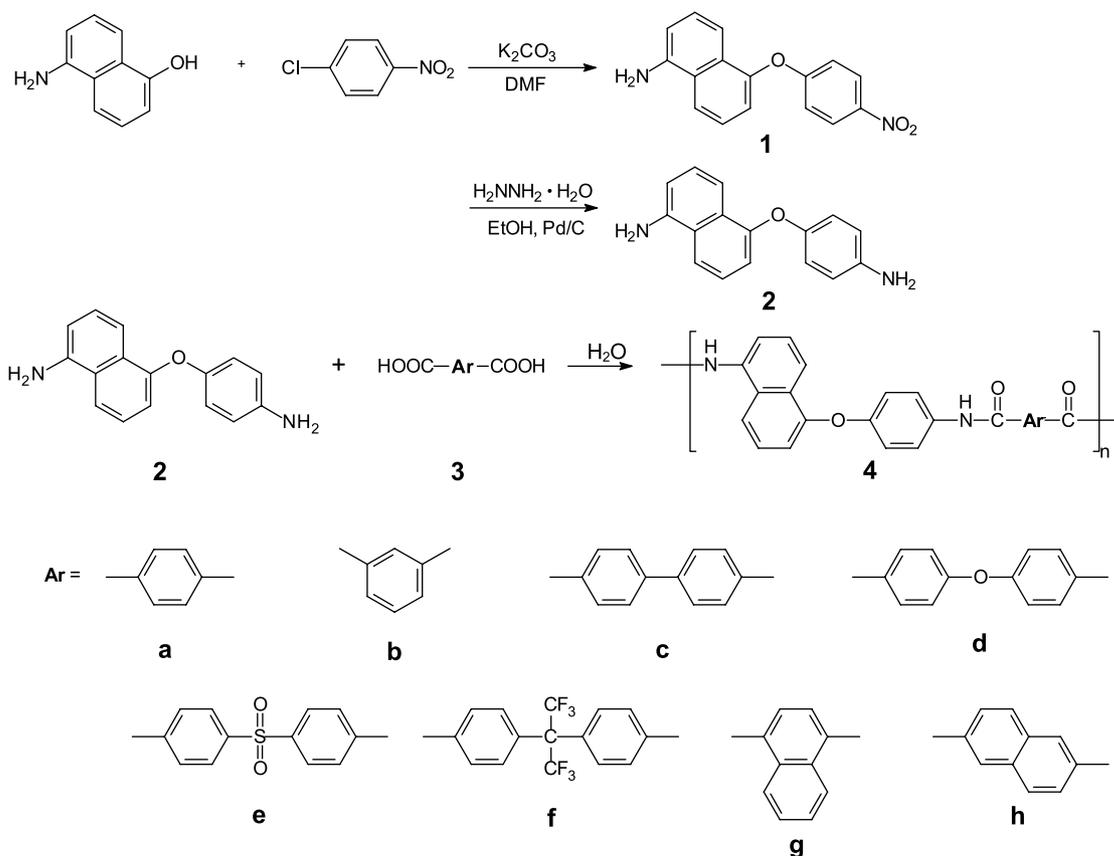
### 2.5. Film preparation

A solution of polymer was made by the dissolution of about 0.7 g of the polyamide in 8 ml of hot DMAc to afford an approximately 10 wt% solution. The clear solution was poured into 8-cm diameter glass culture dish, which was placed in a 90 °C oven for 12 h for evaporation of the solvent. The semidried polyamide film was released from the glass substrate by soaking in water and further dried in vacuum at 160 °C for 6 h. The obtained films were about 0.09 mm thick and used for tensile tests, solubility tests, X-ray diffraction measurements, and thermal analyses.

### 2.6. Instruments and characterization methods

Infrared spectra were recorded on a Horiba FT-720 Fourier transform infrared (FTIR) spectrometer. Elemental

analysis was made on a Heraeus Vario EL-III CHN analyzer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker AV-500 FT NMR spectrometer. The inherent viscosities of the polyamides were determined with a Cannon–Fenske viscometer at 30 °C. A universal tester LLOYD LRX with a load cell of 5 kg was used to study the stress–strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long and about 0.09 mm thick), and an average of at least three replicates was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer (operating at 40 kV and 30 mA) with graphite-monochromatized Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The scanning rate was  $2^\circ \text{ min}^{-1}$  over a range of  $2\theta = 10\text{--}40^\circ$ . Thermogravimetric analysis (TGA) was conducted with a Perkin–Elmer Pyris 1 TGA. Experiments were carried out on approximately 4–8 mg of samples in flowing nitrogen (flow rate =  $30 \text{ cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. Glass-transition temperatures ( $T_g$ ) were read at the middle of the transition in the heat capacity. Thermomechanical analysis (TMA) was conducted with a Perkin–Elmer TMA 7 instrument. The TMA experiments were conducted from



Scheme 1. Synthesis of diamine **2** and polyamides **4a-h**.

50 to 400 °C at a scanning rate of 10 °C/min using a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures ( $T_s$ ) were taken as the onset temperature of probe displacement on the TMA traces.

### 3. Results and discussion

#### 3.1. Monomer synthesis

The main diamine monomer, 5-(4-aminophenoxy)-1-naphthylamine (**2**), was synthesized with a two-step procedure outlined in Scheme 1. The first step was a nucleophilic etherification of 4-chloronitrobenzene with the potassium phenolate of 5-amino-1-naphthol, producing the intermediate nitro-amino compound **1**. In the second step, the intermediate compound **1** was reduced to ether-diamine **2** with hydrazine monohydrate and Pd/C catalyst in refluxing ethanol. The structures of compounds **1** and **2** were confirmed by elemental analyses as well as FTIR and NMR spectroscopy.

#### 3.2. Polymer synthesis

According to the phosphorylation technique described by Yamazaki and co-workers [22], a series of aromatic polyamides **4a–h** were synthesized from the ether-diamine **2** with various aromatic dicarboxylic acids **3a–h** (Scheme 1). The parentheses in the formula of **4** indicate that the asymmetric ether-diamine moieties may appear in the polymer chain as shown or in the reverse orientation. These polyamides should have three possible diads in their polymer chains, as shown in Fig. 1. The polyamidation was carried out via solution polycondensation using TPP and pyridine as condensing agents in the NMP solution containing dissolved  $\text{CaCl}_2$ . All the polycondensation reactions proceeded readily in a homogenous solution,

except for polyamide **4c**, which precipitated from the reaction medium when the reaction solution became viscous. As shown in Table 1, the obtained polyamides **4a–h** had a moderate to high inherent viscosity in the 0.74–1.36 dl/g range. Except for **4c**, all the **4** series polyamides could be solution-cast into flexible and tough films, indicative of high-molecular-weight polymers. For comparison, a referenced series of polyamides **5a–h** were also prepared from 1,5-DAN and diacids **3a–h** by the same method used for the **4** series polymers. During the synthesis of **5** series polymers, all the polyamides except **5f** precipitated from the reaction media because of insolubility. Almost all the **5** series polyamides were insoluble in any available organic solvent; thus, no attempts were made to cast them into films. Thus, the incorporation of asymmetrical diaryl ether structure obviously enhances the solubility and film formability of polyamides. In addition, the reported data [16] of some structurally related **6** series polyamides based on 1,5-BAPON are also listed in Table 1 for a comparative purpose.

Structural features of these polyamides were confirmed with FTIR and NMR spectroscopy. They exhibited characteristic absorptions of the amide group around 3300 (N–H stretching) and 1650  $\text{cm}^{-1}$  (C=O stretching). The strong absorption of aryl ether group appeared in the region of 1200–1250  $\text{cm}^{-1}$ . Fig. 2 shows a typical set of FTIR and  $^1\text{H}$  NMR spectra for polyamide **4a**. As can be seen, the spectra are in good agreement with the proposed structure. The resonance peaks appearing in the region of 10.49–10.71 ppm in the  $^1\text{H}$  NMR spectrum also support the formation of amide linkages.

#### 3.3. Properties of polyamides

The solubility behavior of polyamides **4a–h** was tested quantitatively and the results are listed in Table 1. All the newly synthesized polyamides, except for **4c**, showed excellent solubility in aprotic polar solvents, such as

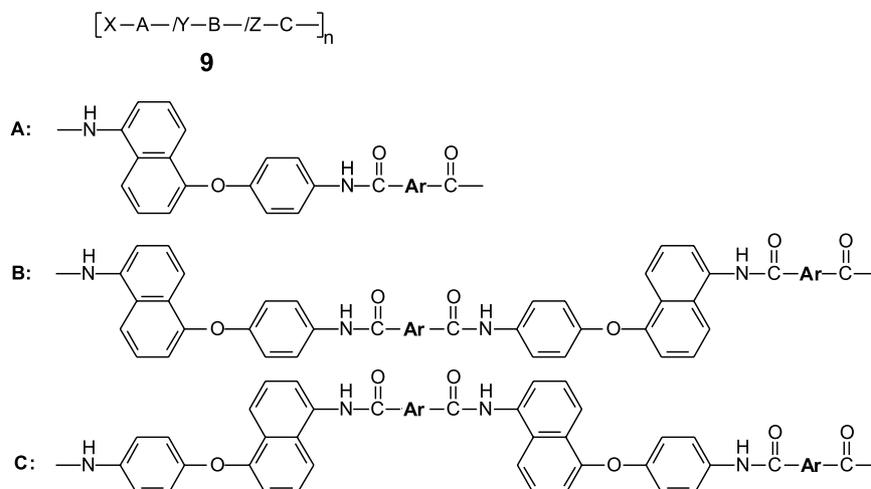


Fig. 1. Three possible segments in the polymer chains of **4a–h**.

Table 1  
Inherent viscosity, film properties, and solubility behavior of polyamides

Polymer code	$\eta_{inh}$ (dl/g) <sup>a</sup>	Film quality <sup>b</sup>	Solubility <sup>c</sup>					
			NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
4a	1.36	Flexible	+	+	+	+	–	–
4b	0.91	Flexible	+	+	+	+	+h	–
4c	1.25	Brittle	+	–	–	–	–	–
4d	1.21	Flexible	+	+	+	+	+h	–
4e	0.74	Flexible	+	+	+	+	+h	–
4f	0.78	Flexible	+	+	+	+	+h	+h
4g	0.91	Flexible	+	+	+	+	+h	–
4h	1.21	Flexible	+	+	+	+	–	–
5a <sup>d</sup>	0.59	– <sup>e</sup>	–	–	–	–	–	–
5b	0.62	–	–	–	–	–	–	–
5c	0.45 <sup>f</sup>	–	–	–	–	–	–	–
5d	0.86	Brittle	+h	–	–	–	–	–
5e	0.73	Brittle	+h	–	–	–	–	–
5f	0.54	Flexible	+	+	+	+	–	–
5g	0.27 <sup>f</sup>	–	–	–	–	–	–	–
5h	0.43 <sup>f</sup>	–	–	–	–	–	–	–
6a <sup>g</sup>	0.88 <sup>f</sup>	–	–	–	–	–	–	–
6b	1.14	Flexible	+	+	+	+	+	+
6c	0.81 <sup>f</sup>	–	–	–	–	–	–	–
6e	1.06	Flexible	+	+	+	+	+h	+h
6f	0.81	Flexible	+	+	+	+	+	+
6h	0.96 <sup>f</sup>	–	–	–	–	–	–	–

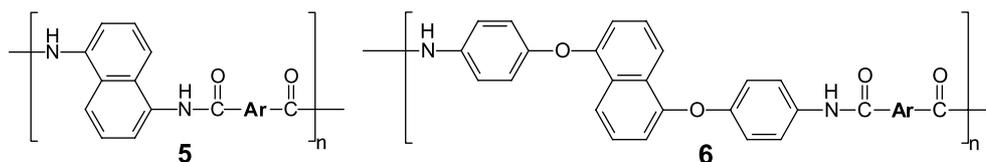
+, soluble at room temperature; +h, soluble on heating; –, insoluble; NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

<sup>a</sup> Inherent viscosity of the polyamides measured at a concentration of 0.5 g/dl in DMAc containing 5 wt% LiCl at 30 °C.

<sup>b</sup> Films were cast by the slow evaporation of polymer solution in DMAc or NMP.

<sup>c</sup> Qualitative solubility was tested with 10 mg of a sample in 1 ml of the stirred solvent.

<sup>d</sup> Referenced polyamides derived from 1,5-diaminonaphthalene and 1,5-bis(4-aminophenoxy)naphthalene:



<sup>e</sup> Insoluble in any available organic solvents.

<sup>f</sup> Measured at a concentration of 0.5 g/dl in concentrated H<sub>2</sub>SO<sub>4</sub> at 30 °C.

<sup>g</sup> The data of the 6 series shown here are those reported in literature (see Ref. [16])

NMP, DMAc, DMF and DMSO. As shown in Table 1, the asymmetric diamine-based polyamides 4a to 4h revealed an apparently enhanced solubility as compared to their corresponding counterparts of the 5 and 6 series. This can

be attributable to the random sequences within the polymer chain caused by the asymmetric ether-diamine components. Therefore, the excellent solubility makes these polyamides potential candidates for practical applications in spin-on and casting processes.

The WAXD patterns of polyamides 4a–h and 5a–h are shown in Fig. 3. The results indicate that all the 4 series polyamides except 4c are amorphous in nature. Thus, the amorphous nature of most 4 series polyamides also reflected in their excellent solubility and good film-forming ability. In contrast, the symmetric diamine based polyamides derived from rigid diacids, such as 5a, 5c, 5g, and 5h (and 6a, 6c, 6h, see Ref. [16]), showed semicrystalline patterns. Thus, the introduction of asymmetric ether-diamine moieties decreases the chain-to-chain interactions such as hydrogen bonding between amide groups, which interrupts the close

Table 2  
Thin film tensile properties of polyamides

Polymer code	Strength at break (MPa)	Elongation at break (%)	Initial modulus (GPa)
4a	109	9	2.58
4b	114	12	2.08
4d	100	64	2.15
4e	90	13	2.12
4f	95	12	2.32
4g	120	12	2.68
4h	128	12	3.08

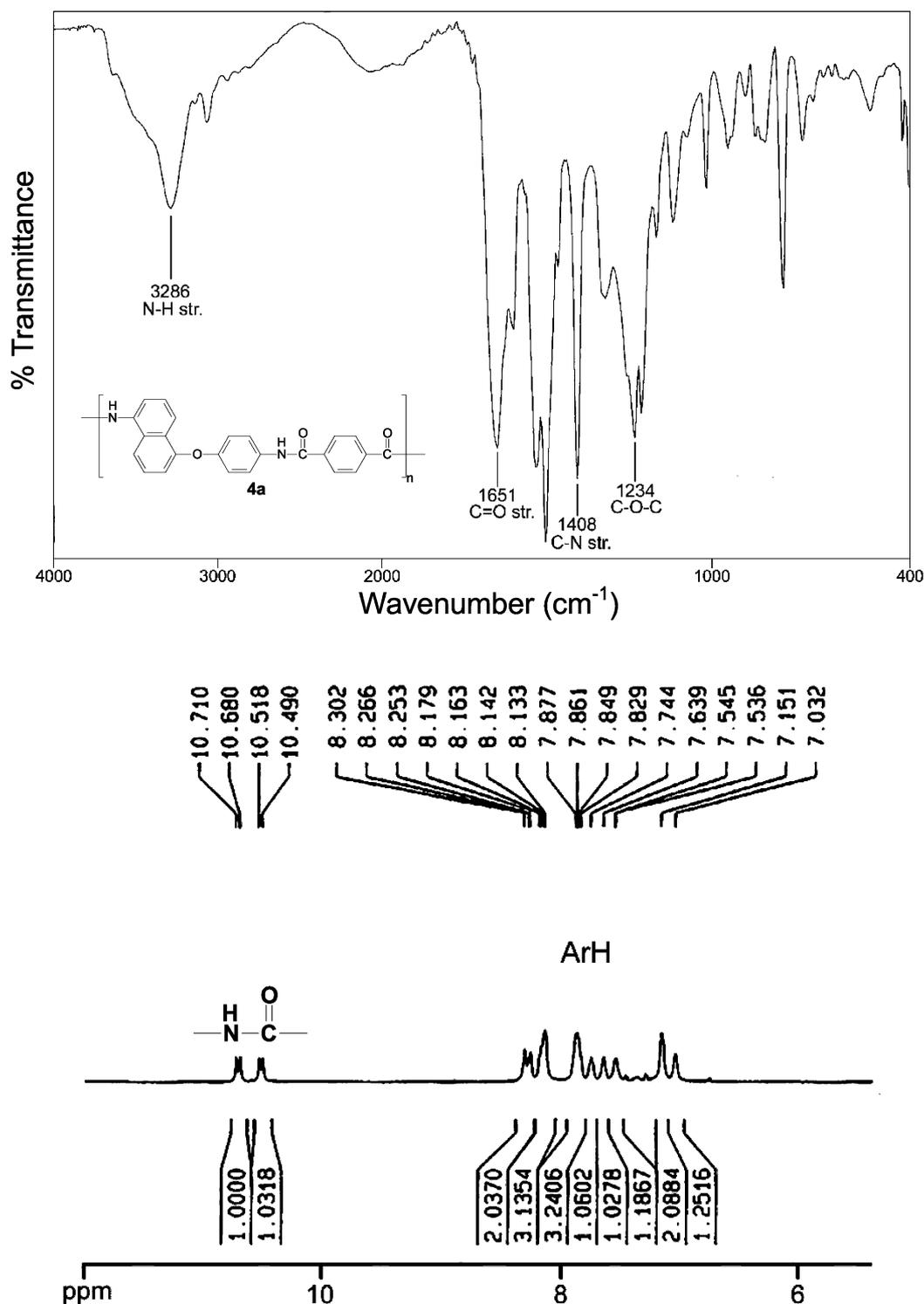


Fig. 2. IR (film) and <sup>1</sup>H NMR (in DMSO-*d*<sub>6</sub>) spectra of polyamide 4a.

packing of polymer chains, thereby leading to an enhancement in solubility and a decrease in crystallinity.

All the polyamides except 4c could be processed into good-quality and flexible films. These films were subjected to tensile tests and their tensile properties are summarized in Table 2. They showed good mechanical properties with strengths at break of 90–128 MPa, elongations at break of

9–64%, and tensile moduli of 2.08–3.08 GPa. Most of them necked during tensile test and showed a moderate extension to break, indicating strong and ductile materials.

The thermal properties of the polymers evaluated by DSC, TMA, and TGA are summarized in Table 3. To avoid the effects of the absorbed moisture and residual solvent in the film samples, we heated the samples at 300 °C for 1 h

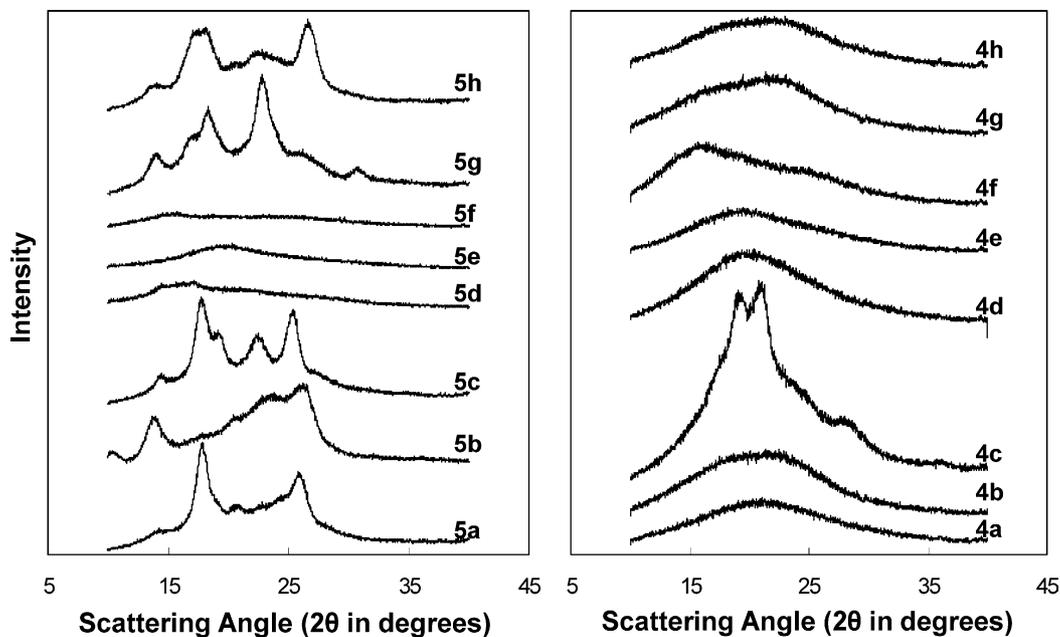


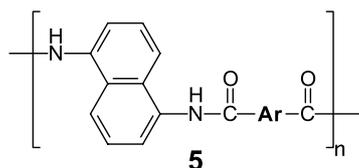
Fig. 3. WAXD patterns of polyamides 4a–h and 5a–h.

Table 3  
Thermal properties of polyamides

Polymer code <sup>a</sup>	$T_g^b$ (°C)	$T_s^c$ (°C)	$T_d$ (°C) <sup>d</sup> at 5% wt loss		$T_d$ (°C) <sup>d</sup> at 10% wt loss		Char yield <sup>e</sup> (%)
			In air	In N <sub>2</sub>	In air	In N <sub>2</sub>	
4a	264	250	424	425	479	483	72
4b	222	222	394	401	462	454	70
4c	288	N.D. <sup>f</sup>	470	490	500	531	70
4d	245	238	439	446	497	501	70
4e	280	279	437	441	480	483	68
4f	270	265	455	456	510	528	63
4g	244	243	418	425	477	470	72
4h	265	251	511	440	517	448	75
5a	– <sup>g</sup>	N.D. <sup>f</sup>	403	447	453	483	62
5b	283	N.D.	401	480	469	533	69
5c	–	N.D.	440	449	481	499	69
5d	286	N.D.	428	458	465	517	65
5e	–	N.D.	441	458	475	501	60
5f	310	278	447	447	502	510	61
5g	–	N.D.	429	453	457	486	68
5h	–	N.D.	435	474	477	509	68

All the polyamide samples were heated at 300 °C for 1 h prior to DSC, TMA, and TGA experiments.

<sup>a</sup> General structures of the referenced polyamides 5a–h:



<sup>b</sup> The midpoint temperature of heat capacity jump on the DSC heating trace (from 50 to 400 °C at 20 °C/min) was defined as  $T_g$ .

<sup>c</sup> Softening temperature, taken as the onset temperature of the probe displacement on the TMA trace at a scan rate of 10 °C/min.

<sup>d</sup> Decomposition temperature, recorded via TGA at a heating rate of 20 °C/min and a gas flow rate of 30 cm<sup>3</sup>/min.

<sup>e</sup> Residual weight percentages at 800 °C under nitrogen flow.

<sup>f</sup> Not detected (no available specimens).

<sup>g</sup> No discernible transitions.

prior to all thermal analyses. The glass-transition temperatures ( $T_g$ s) of polyamides **4a–h** were recorded between 222 and 288 °C by DSC. The lowest  $T_g$  of 222 °C was observed for polyamide **4b** derived from isophthalic acid (**3b**). The highest  $T_g$  value (288 °C) of polyamide **4c** may be due to its semicrystalline nature or the structural rigidity caused by the biphenylene unit. For comparison, the  $T_g$  values of the corresponding **5** series polyamides are also reported in Table 3. Most of the **5** series polyamides did not show obvious  $T_g$ s because of their rigid main chains or high crystallinity as evidenced by WAXD patterns. Besides, as can be seen from Table 3, polyamides **4b**, **4d**, and **4f** exhibited lower  $T_g$ s than the corresponding analogs of **5** series. This result is very reasonable and can be attributed to the fact that the introduction of the ether linkage provides a polymer chain with a decreased rotational barrier and the asymmetrical structure disturbs the dense packing between polymer chains.

The  $T_s$  values of these polymer films were also measured with TMA by the penetration method. They were obtained from the onset temperature of the probe displacement on the TMA trace. The TMA curves for the **4** series polyamides (except **4c**) are reproduced in Fig. 4. The  $T_s$  values of these polymers were observed in the range of 222–279 °C. In most cases, the  $T_s$  values obtained by TMA are comparable to the  $T_g$  values measured by the DSC experiments.

The thermal and thermo-oxidative stability of these polyamides were measured by TGA. The representative TGA curves of polyamides **4f** and **5f** are shown in Fig. 5. The temperatures of 5 and 10% weight loss in nitrogen and

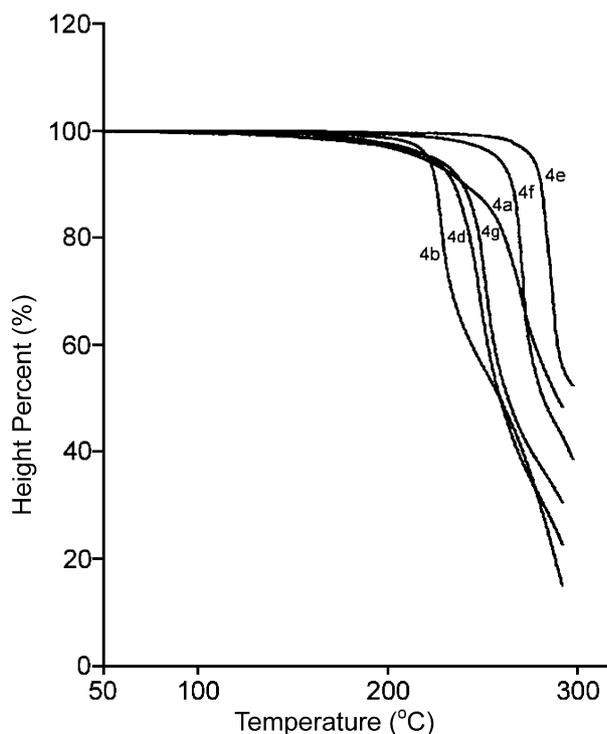


Fig. 4. TMA curves of the **4** series polyamides (except **4c**) at a heating rate of 10 °C/min.

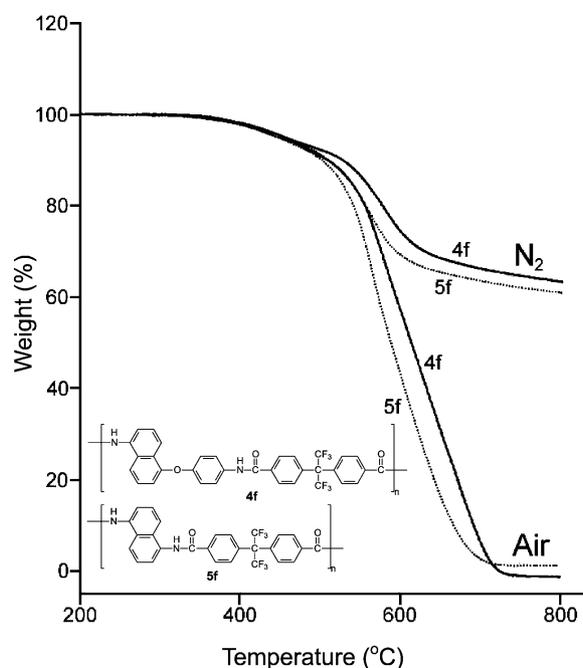


Fig. 5. TGA curves of polyamides **4f** and **5f** with a heating rate of 20 °C/min.

air atmospheres determined from the original TGA thermograms are included in Table 3. All polymers exhibited good thermal stabilities with the decomposition temperature ( $T_d$ 's) at 5% weight loss above 400 °C in both nitrogen and air atmospheres. The anaerobic char yield at 800 °C for all polymers was in the range of 63–75 wt%. Thus, the introduction of flexible ether links and molecular asymmetry did not deteriorate their thermal stability significantly.

#### 4. Conclusions

A novel asymmetrical ether-diamine, 5-(4-aminophenoxy)-1-naphthylamine (**2**), was synthesized in high purity from 5-amino-1-naphthol and 4-chloronitrobenzene via a two-step high-yielding procedure. A series of novel aromatic polyamides with high molecular weights have been successfully obtained by the Yamazaki–Higashi phosphorylation polyamidation of the ether-diamine with various aromatic dicarboxylic acids. Except for that obtained from the rigid 4,4'-biphenyldicarboxylic acid, the obtained polyamides were noncrystalline, displayed good solubility, and afforded flexible and tough films. In comparison with analogous polyamides based on the symmetric diamines such as 1,5-DAN and 1,5-BAPON, these polyamides showed apparently decreased crystallinity, enhanced solubility and film-formability, and still retained good thermal stability. Thus, the series polyamides can be considered as promising processable high-performance polymeric materials.

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