

# Polyamides Based on Diamines Containing Aryloxy Groups: Structure-Property Relationships

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**Abstract:** Aromatic polyamides containing different numbers of p-oxyphenylene groups and different catenated positions in the benzene rings were prepared from terephthalic acid (TPA) and isophthalic acid (IPA) with various aryloxy-containing diamines by means of the phosphorylation polycondensation reaction. Most of the polyamides were moderately to highly crystalline, as indicated by X-ray diffraction and DSC measurements. Polyisophthalamides were readily soluble in polar amide-type solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc). Some non-crystalline polyamides could afford tough films by solution casting. Most polyisophthalamides revealed discernible glass transition on their DSC curves, and their  $T_g$  values were recorded in the range of 215-238 °C. No discernible glass transitions were observed for the polyamides of TPA by DSC. The thermal stability of these polymers did not show clear dependence on the structure of the diacid or the diamine. In addition, a series of polyamides having pendant groups was synthesized from the polycondensation of TPA and IPA with 1,4-bis(4-aminophenoxy)benzene and its derivatives with methyl, *tert*-butyl, or phenyl substituent on the central benzene ring. In most cases, the incorporation of pendant groups generally resulted in an enhanced solubility and a decreased  $T_g$  and crystallinity.

**Keywords:** Polyamides, Terephthalic acid, Isophthalic acid, Ether-diamines, Structure-property relationships.

## Introduction

Aromatic polyamides are an important class of high-performance polymers that offer excellent physical and chemical properties, thermal and oxidative stability, flame resistance, and superior mechanical and dielectric properties. Wholly aromatic polyamides such as poly(1,4-phenyleneterephthalamide) (PPT) and poly(1,4-benzamide) are well accepted as heat-resistant materials with a high mechanical strength, easily forming lyotropic solutions [1-3]. Fibers obtained from anisotropic solutions of these materials have been used in applications where high thermal stability and mechanical strength are required. For example, Kevlar aramid fiber products have been used in industrial applica-

tions since their introduction in 1972 by Du Pont Co [4]. They have been evaluated extensively in various industries and reported in the literature. However, infusibility and limited solubility in organic solvents are the characteristic properties of wholly aromatic polyamides that make them generally difficult or too expensive to process, thus restricting their applications.

During recent years, many efforts have been made with the aim of designing the chemical structure of the rigid aromatic backbone to obtain aromatic polyamides that are processable by conventional techniques [5-13]. The introduction of ether linkages and the distortion of molecular symmetry by *meta*- or *ortho*-catenated aromatic or heterocyclic units are known to enhance the processability

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of aromatic polyamides without a significant reduction in thermal stability [5-10]. Furthermore, the attachment of pendant groups on the aromatic units may provide a significant increase in both the glass-transition temperature ( $T_g$ ) and the solubility of aromatic polyamides [11-13]. Thus, the  $T_g$  is raised by the restriction of segmental mobility brought about by the incorporation of bulky groups, whereas solubility is improved by the decreasing of packing density and crystallinity. Combining these structural modifications minimizes the trade-off between processability and the positive/useful properties of aromatic polyamides.

In order to gain more insight into the "structure-property" relationships of aromatic polyamides, in this work two series of polyamides were prepared from terephthalic acid and isophthalic acid with some aromatic diamines composed of two to four phenylene units connected by ether linkages, in which the catenated position of the phenylene unit might be *ortho*, *meta*, or *para*-disubstituted. Moreover, in order to study the effects of pendant groups on the properties of polyamides, a series of polyamides based on 1,4-bis(4-aminophenoxy)benzene and its derivatives having pendant methyl, tert-butyl, and phenyl groups on the central phenylene ring were also synthesized. Some basic properties, such as solubility, film-formability, crystallinity, thermal properties, and "structure-property" relationships of the polyamides were investigated.

## Experimental

### 1. Materials

Commercially available terephthalic acid (TPA, from Hayashi), isophthalic acid (IPA, from Wako), 4,4'-oxydianiline (**1a**, from TCI), 3,4'-oxydianiline (**1b**, from Mitsui Petrochemical Ind.), 1,4-bis(4-aminophenoxy)benzene (**1c**, from TCI) and 1,3-bis(4-aminophenoxy)benzene (**1d**, from TCI) were used without further purification.

According to a well-developed method [14,15], 1,2-bis(4-aminophenoxy)benzene (**1e**) (mp. 137-138 °C), bis[4-(4-aminophenoxy)phenyl] ether (**1f**) (mp. 126-127 °C), 2,5-bis(4-aminophenoxy)toluene (Me-**1c**) (mp. 99-100 °C), 1,4-bis(4-aminophenoxy)-2-tert-butylbenzene [*t*-Bu-**1c**] (mp. 128-129 °C), and 2,5-bis(4-aminophenoxy)biphenyl (Ph-**1c**) (mp. 45-46 °C) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenols and *p*-chloronitrobenzene in the presence of potassium carbonate, giving the bis(*p*-nitrophenoxy) compounds, and by subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. A detailed syn-

thetic procedure for diamine **1f** is described subsequently. *N*-Methyl-2-pyrrolidone (NMP) and pyridine were dried with calcium hydride overnight and then distilled under reduced pressure. Triphenyl phosphite (TPP) was purified by distillation under reduced pressure. Commercially obtained anhydrous calcium chloride was dried under a vacuum at 180 °C for 8 hrs.

### 2. Synthesis of diamines

A typical procedure for preparing the ether-diamine with four benzene rings, bis[4-(4-aminophenoxy)phenyl] ether (**1f**), was as follows: A 300-mL round bottom glass flask was charged with 20.2 g (0.1 mol) of 4,4'-dihydroxydiphenyl ether, 31.6 g (0.2 mol + 0.1 g) of *p*-chloronitrobenzene, 27.6 g (0.2 mol) of potassium carbonate, and 100 mL of *N,N*-dimethylformamide (DMF). The mixture was heated with stirring at 140-150 °C for 10 hrs. After the reaction, the mixture was poured into 500 mL of water. The precipitated powder was filtered out, thoroughly washed with water, and dried to obtain 43 g (96% yield) of bis[4-(4-nitrophenoxy)phenyl] ether as a yellow powder; mp 146-148 °C. In the next step, a 500-mL round bottom flask was charged with 30 g (0.067 mol) of bis[4-(4-nitrophenoxy)phenyl] ether, 0.1 g of 10% Pd/C, 300 mL of ethanol, and 100 mL of tetrahydrofuran. The mixture was heated to reflux, and then 40 mL of hydrazine hydrate was added dropwise into the suspension solution over a period of 1 hr. After complete addition, the mixture was heated at reflux temperature for an additional 6 hrs. The hot solution was filtered to remove the Pd/C catalyst, and the product precipitated on cooling as shiny golden platelets. After standing overnight, the golden crystals were isolated by filtration, washed with water, and dried. The yield of bis[4-(4-aminophenoxy)phenyl] ether was 22 g (85% yield); mp 126-127 °C. IR (KBr): 3388, 3320 (N-H stretch), 1228  $\text{cm}^{-1}$  (C-O-C stretch).  $^1\text{H}$  NMR (400 MHz in DMSO- $d_6$ ):  $\delta$  6.94 (d, 4H, ArH), 6.87 (d, 4H, ArH), 6.76 (d, 4H, ArH), 6.62 (d, 4H, ArH), and 4.96 ppm (s, 4H, -NH $_2$ ).  $^{13}\text{C}$  NMR (100 MHz in DMSO- $d_6$ ): 155.92, 153.19, 147.65, 146.62, 121.55, 120.63, 119.09, and 115.93 ppm. Anal. Calcd for C $_{24}$ H $_{20}$ N $_2$ O $_3$  (384.43): C, 74.98%; H, 5.24%; and N, 7.28%. Found: C, 74.90%; H, 5.20%; and N, 7.19%.

The ether diamines **1e**, Me-**1c**, *t*-Bu-**1c**, and Ph-**1c** were synthesized by almost the same method as mentioned above.

### 3. Polymer synthesis

A typical synthetic procedure for polyamide m-**2f** is as follows. A mixture of 0.3322 g (2 mmol) of diacid IPA, 0.7688 g (2 mmol) of bis[4-(4-

aminophenoxy)phenyl] ether (**1f**), 0.4 g of calcium chloride, 4 mL of NMP, 1 mL of pyridine, and 1.6 mL of triphenyl phosphite (TPP) was heated with stirring at 120 °C for 3 hrs. As the polycondensation proceeded, the reaction mixture gradually became viscous and homogeneously transparent. The resultant polymer solution was poured slowly into 300 mL of methanol, giving rise to a fiber-like precipitate, which was washed thoroughly with methanol and hot water, collected by filtration and dried. The inherent viscosity of the polymer in DMAc containing 5 wt%-LiCl was 1.19 dL/g, measured at a concentration of 0.5 g/dL at 30 °C.

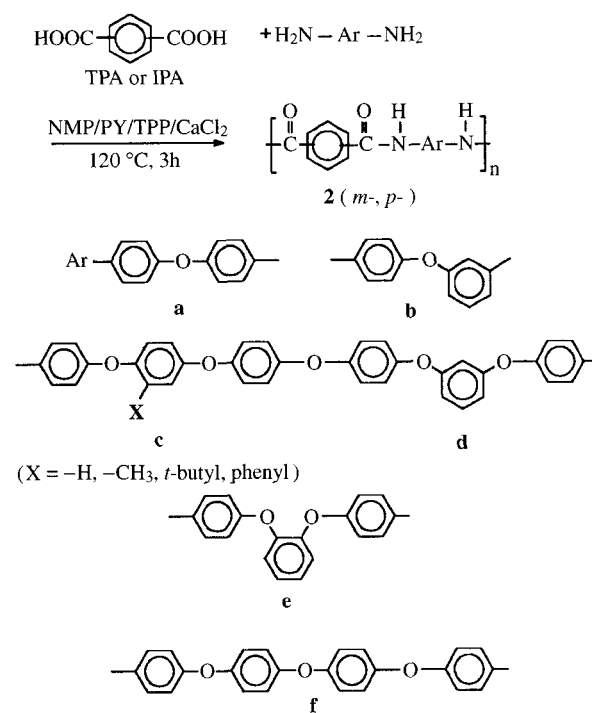
All other polyamides were synthesized by procedure analogous to that given above.

#### 4. Preparation of polyamide films

For the organo-soluble polyamides, a solution (approximately 5 wt%) was made by dissolving about 0.8 g of the polymer in 16 mL of hot DMAc. The solution was filtered into a 9-cm glass culture dish, which was placed in a 90 °C oven overnight to evaporate the solvent. The semi-dried polyamide film was stripped off from the glass substrate and further dried in a vacuum oven at 160 °C for 8 hrs. The obtained films were about 60 μm in thickness and were used for X-ray diffraction measurements, solubility tests, and thermal analysis. For the organo-insoluble polyamides, the powdery samples were also dried in vacuo at 160 °C for 8 hrs prior to being subjected to various tests.

#### 5. Measurements

All melting points of low molecular weight materials were determined on a MEL-TEMP II capillary melting point apparatus and were uncorrected. IR spectra were obtained on a Jasco FTIR-7000 Fourier transform spectrometer using the solution cast films. NMR spectra were obtained on a Jeol EX-400 spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer differential scanning calorimeter DSC 7 coupled to a Perkin-Elmer thermal analysis controller TAC7/DX at a scan rate of 20 °C/min in flowing nitrogen. Melting temperatures ( $T_m$ ) were read at the peak of melting endotherms on the first heating DSC traces before 500 °C. Glass transition temperatures ( $T_g$ ) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling from 400 °C. Thermogravimetric analysis (TGA) was conducted on a DuPont 951 Thermogravimetric Analyzer coupled to a DuPont 2000 Thermal Analyst. Experiments were performed with 9-11 mg of samples heated at a scan rate of 20 °C/min in flowing nitrogen (10 cm<sup>3</sup>/min). Thermomechanical analysis (TMA) was carried out



Scheme 1.

on a Perkin-Elmer TMA-7 using a loaded penetration probe with 1-mm diameter (static force: 10 mN). The samples were preheated at 250 °C for 30 min prior to the test. The TMA experiments were conducted from 40 to 300 °C at a scan rate of 20 °C/min. Softening temperatures ( $T_s$ ) were read at the onset temperatures of probe displacement on the TMA traces. Wide-angle X-ray diffraction (WAXD) patterns were recorded on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered copper  $K_\alpha$  radiation (40 KV, 20 mA,  $\lambda = 1.5418 \text{ \AA}$ ). The WAXD intensity was measured in the scattering angle ( $2\theta$ ) range of 5~45° at a scanning speed of 2°/min.

## Results and Discussion

### 1. Polymer synthesis

Aromatic polyamides are conventionally synthesized by low-temperature solution polycondensation of aromatic diacid chlorides with aromatic diamines in the presence of an acid acceptor in a polar aprotic solvent. In recent years, another method has proven to be a convenient and popular way to prepare high-molecular-weight polyamides based on the direct polycondensation of aromatic dicarboxylic acids with aromatic diamines in the presence of an aryl phosphite, an organic base such

**Table I.** Reaction conditions, inherent viscosities and film quality of polyamides.

Polymer code	Amounts of reagents used <sup>(a)</sup>			$\eta_{inh}^{(b)}$ (dL/g)	Remark <sup>(c)</sup>	Film quality <sup>(d)</sup>
	NMP (mL)	Pyridine (mL)	CaCl <sub>2</sub> (g)			
<i>p</i> -2a	10 + 2	2.5	1	1.82	P	— <sup>(f)</sup>
<i>p</i> -2b	6	1.5	0.6	1.42	P	Brittle
<i>p</i> -2c	10 + 8	2.5	1 + 0.5	2.09 <sup>(e)</sup>	P	—
<i>p</i> -Me-2c	8	2.0	0.8	1.07	H	—
<i>p</i> -( <i>t</i> -Bu)-2c	5	1.2	0.5	0.61	H	Flexible
<i>p</i> -Ph-2c	4	1.0	0.4	0.79	H	Flexible
<i>p</i> -2d	6	1.5	0.6	1.79 <sup>(e)</sup>	P	—
<i>p</i> -2e	5 + 1	1.25	0.5	1.41	H	—
<i>p</i> -2f	10 + 5	2.5	1 + 0.5	0.96	P	—
<i>m</i> -2a	4	1	0.4	0.89	H	Flexible
<i>m</i> -2b	3	1	0.3	0.61	H	Flexible
<i>m</i> -2c	4	1	0.4	1.58	H	Flexible
<i>m</i> -Me-2c	3	0.8	0.3	0.48	H	Flexible
<i>m</i> -( <i>t</i> -Bu)-2c	3	0.8	0.3	0.49	H	Flexible
<i>m</i> -Ph-2c	2.5	0.8	0.3	0.50	H	Flexible
<i>m</i> -2e	3	1	0.3	0.55	H	Brittle
<i>m</i> -2e	3	1	0.3	0.82	H	Brittle
<i>m</i> -2f	4	1	0.4	1.19	H	Flexible

(a) The polymerization was carried out at 120 °C for 3 hrs with 2 mmol each of diacid and diamine monomer, 2 mmol (about 1.6 mL) of triphenyl phosphite, and the amount of other reagents as indicated.

(b) Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt% LiCl unless otherwise indicated.

(c) H: homogeneously transparent throughout the reaction, P: precipitation occurred during the reaction.

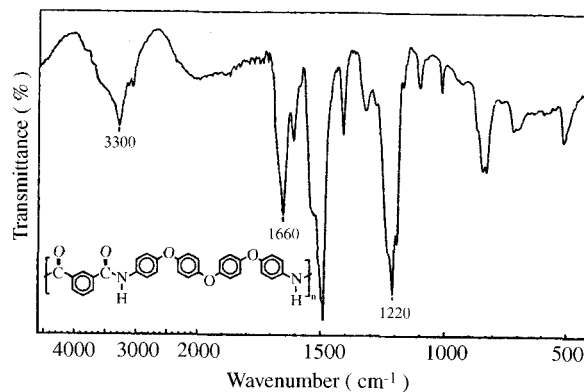
(d) Films were cast from slow evaporation of the polymer solutions in DMAc.

(e) Measured in concentrated sulfuric acid.

(f) Insoluble in any available organic solvent.

as pyridine, and a metal salt such as LiCl and CaCl<sub>2</sub> according to Yamazaki [16,17]. In the present study, we followed this technique to prepare aromatic polyamides by the direct polycondensation of IPA and TPA, respectively, with various ether-bridged aromatic diamines (Scheme 1).

The reaction conditions and results are summarized in Table I. The TPA and IPA-based polyamides had inherent viscosities in the range of 0.61-2.09 dL/g and 0.48-1.58 dL/g, respectively. With regard to the TPA polyamides, in some cases an early precipitation occurred during the polymerization due to the insolubility of the polymers, and adding more solvent and metal salt in order to carry out the reaction in a homogenous phase failed to produce a clear, viscous polymer solution. The polyamides *p*-(*t*-Bu)-2c and *p*-Ph-2c with bulky pendant groups were readily soluble in amide type solvents such as NMP and DMAc and could be solution-cast into flexible films from DMAc. Although *p*-2b could be dissolved in hot NMP or DMAc, solution casting yielded shrunken and embrittled films.

**Figure 1.** The IR spectrum of polyamide *m*-2f.

The other TPA-derived polyamides were insoluble in any available organic solvents; hence, no attempts were made to cast them into films. In contrast, in all cases of IPA polyamides, the polymerization proceeded homogeneously and transparently throughout the reaction. Almost all the IPA series polyamides exhibited good solubility in organic solvents and could be solution cast into flexible and tough films. It is worth noting that the cast films of polymers *m*-2d and 2e were brittle. This result may be attributed to their high level of crystallinity, as will be evidenced by the X-ray diffractography and DSC measurements presented later on. The key structural features of these polyamides were checked by IR spectroscopy. A typical IR spectrum for polyamide *m*-2f is illustrated in Figure 1. Some characteristic absorptions can be observed in the IR spectra, such as N-H stretching near 3300 cm<sup>-1</sup>, carbonyl stretching near 1660 cm<sup>-1</sup>, and aryl ether stretching near 1220 cm<sup>-1</sup>.

## 2. Polymer properties

### 2-1 Polyamides without pendant groups

The WAXD patterns of TPA and IPA polyamides are illustrated in Figures 2 and 3 respectively. The TPA polyamides showed a moderate to high level of crystallinity, possibly due to the high density of hydrogen bonding between polymer chains or good packing ability because of symmetry. The results of WAXD also revealed that the introduction of one to three *p*-oxyphenylene units into the repeat unit of PPT (e.g. *p*-2a, 2c, and 2f), and even the replacement of *p*-phenylene by *m*- or *o*-phenylene units (e.g. *p*-2d and 2e), could not change the crystalline nature of these polyamides. This may be attributed to the fact that these polyamides containing the rigid terephthalamide structure had strong intermolecular interactions. Molecular symmetry allows better packing, stronger inter-chain interactions and therefore lower solubility for the TPA

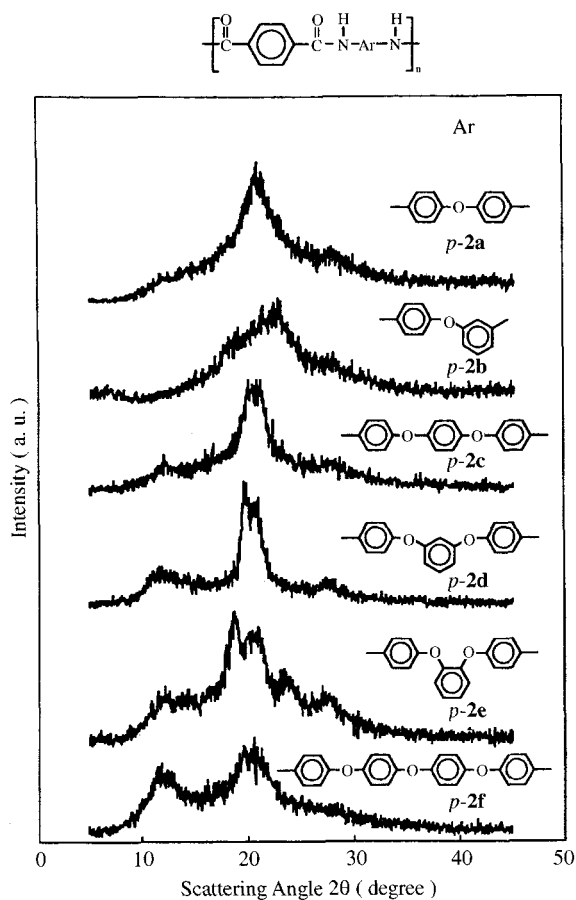


Figure 2. Wide angle X-ray diffraction patterns of polyterephthalamides *p*-2a-f.

polyamides. The incorporation of ether linkages could not seem to reduce the polymer crystallinity dramatically because it may increase the probability of the formation of hydrogen bonding. In some cases, changing the terephthalamide segment to isophthalamide reduced the polymer crystallinity. For example, as shown in Figure 3, the polyamides *m*-2d, 2b, and 2f showed amorphous diffraction patterns and they could afford flexible and tough films as described earlier. These results may be explained by the fact that the chains of these IPA polyamides exhibited a significant amount of nonlinearity, which prevents close packing of polymer chains. However, polyamides *m*-2c, 2d, and 2e revealed the WAXD patterns of modest to high level of crystallinity. The cast films of *m*-2d and *m*-2e embrittled upon creasing. The reason for this is not very clear; it may be related to good ordering of chain packing according to their chain configuration.

The solubility behavior of the polyamides was studied qualitatively in various solvents, and the results are listed in Table II. All the TPA polyamides

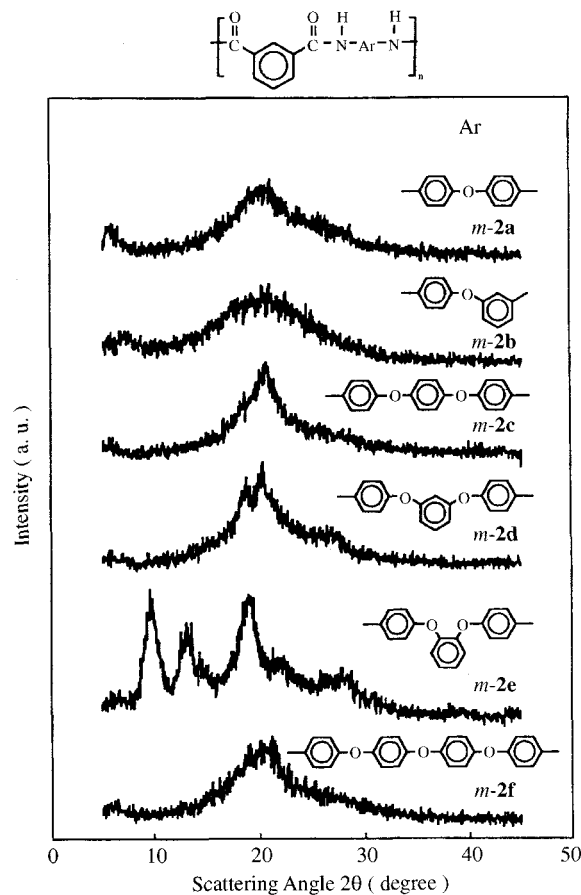


Figure 3. Wide angle X-ray diffraction patterns of polyterephthalamides *m*-2a-f.

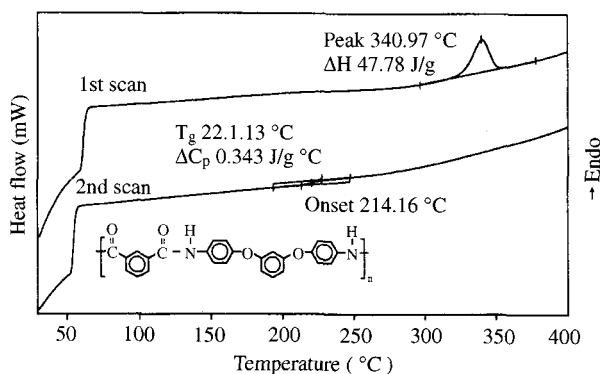
except *p*-2b and *p*-2e were insoluble in all the organic solvents tested. The solubility of *p*-2b and *p*-2e could be attributed to the less symmetric diamine structure. Poor solubility of most TPA-derived polyamides could be attributed to their moderate to high level of crystallinity as shown by the X-ray diffraction patterns. All of the *m*-series (IPA) polyamides showed a higher solubility than the *p*-series (TPA) polyamides, especially in NMP, DMAc, and DMSO. However, it should be pointed out that polyamides *m*-2d and *m*-2e revealed a lower solubility as compared to their isomeric polymer *m*-2c, indicating that polyamides *m*-2d and *m*-2e exhibited stronger intermolecular interactions, even though they had a non-para phenylene structure in the diamine moieties, possibly due to the origins of chain packing. It seems that the ordering of chain packing of *m*-2d and *m*-2e is higher than that of *m*-2c according to their chain configuration.

The thermal properties of the polyamides evaluated by DSC, TGA and TMA are summarized in Table III. Except for *m*-2b, *p*-2a and *p*-2c, all poly-

**Table II.** Solubility behavior of polyamides<sup>(a)</sup>.

Polymer code	Solvents <sup>(b)</sup>					
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
<i>p</i> -2a	-	-	-	-	-	-
<i>p</i> -2b	+h	+h	-	+h	-	-
<i>p</i> -2c	-	-	-	-	-	-
<i>p</i> -2d	-	-	-	-	-	-
<i>p</i> -2e	+	-	-	-	-	-
<i>p</i> -2f	-	-	-	-	-	-
<i>m</i> -2a	+	+	-	+	-	-
<i>m</i> -2b	+	+	+	+	+h-	-
<i>m</i> -2c	+	+	+	+	-	-
<i>m</i> -2d	+	-	-	-	-	-
<i>m</i> -2e	+	+h	-	+h	-	-
<i>m</i> -2f	+	+	-	+h	-	-

- (a) Qualitative solubility was determined using 10 mg of the polymer sample in 1 mL of solvent. +: soluble at room temperature; +h: soluble on heating at 100 °C; -: insoluble even on heating.  
 (b) DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; NMP: *N*-methyl-2-pyrrolidone.

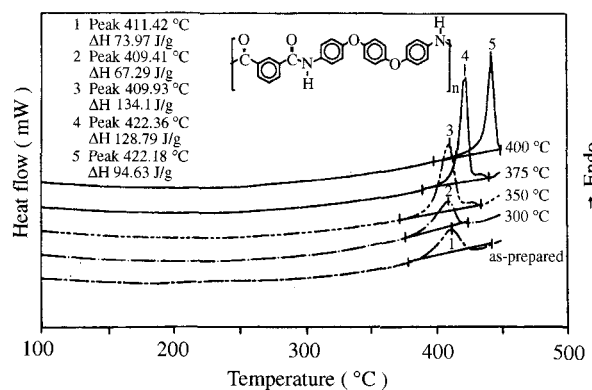
**Figure 4.** DSC curves of polyisophthalamide *m*-2d with a heating rate 20 °C/min in nitrogen.

mides showed melting endothermic peaks on the first heating DSC traces. All the polyamides from TPA showed higher melting temperatures than those from IPA, indicating stronger intermolecular interactions or better chain packing. In almost all cases, the melting endotherms disappeared on the second DSC heating traces after quenching the samples from elevated temperatures. No discernible glass transitions were observed for the TPA polyamides by DSC. In contrast, all IPA polyamides except *m*-2a showed clear glass transitions on their second DSC heating scans. Typical DSC curves for polyamide *m*-2d are shown in Figure 4. As shown in Table III, polyamides *m*-2b-f showed  $T_g$  values of between 215 and 238 °C, following the decreasing order of chain flexibility. The polymers that could be cast into free-standing films were also subjected to TMA

**Table III.** Thermal properties of polyamides.

Polymer code	$T_g^{(a)}$ (°C)	$T_m^{(b)}$ (°C)	$T_s^{(c)}$ (°C)	$T_d^{(d)}$ (°C)	Char yield <sup>(e)</sup> (wt%)
<i>p</i> -2a	— <sup>(f)</sup>	—	—	524	59
<i>p</i> -2b	—	408	257	500	68
<i>p</i> -2c	—	—	—	532	61
<i>p</i> -2d	—	443	—	500	61
<i>p</i> -2e	—	413	—	493	59
<i>p</i> -2f	—	450	—	491	60
<i>m</i> -2a	—	425	266	500	62
<i>m</i> -2b	238	—	237	502	68
<i>m</i> -2c	234	411	234	504	66
<i>m</i> -2d	221	341	210	496	64
<i>m</i> -2e	215	345	223	504	64
<i>m</i> -2f	217	348	217	513	63

- (a) Temperature at the midpoint of baseline shift on the second heating DSC traces after quenching from 400 °C. Heating rate: 20 °C/min.  
 (b) Peak temperature of melting endotherms on the first heating DSC traces before 500 °C.  
 (c) The onset temperature of the probe displacement on the TMA traces. A penetration probe of 1.0-mm diameter, an applied constant load of 10 mN, and a heating rate of 20 °C/min were used in the TMA experiments.  
 (d) Decomposition temperature at which a 10% weight loss was recorded by TGA conducted at a heating rate of 20 °C/min in nitrogen.  
 (e) Residual weight % at 800 °C in nitrogen.  
 (f) No discernible transitions were detected by DSC.

**Figure 5.** Comparisons of the DSC thermograms of sample *m*-2c and those after isothermal annealing at the indicated temperatures for 30 min.

experiments. Polyamide *p*-2b had a  $T_s$  of 257 °C and the *m*-2a-f series had  $T_s$  values in the range 210–266 °C. In most cases, the  $T_s$  values measured by TMA are comparable to the  $T_g$  values determined by DSC experiments. Moreover, melting peaks and resulting crystal structures in these polyamides subjected to various thermal treatments were also investigated using DSC and WAXD. For example, DSC thermograms were obtained for the samples prepared by heating sample *m*-2c at 20 °C/min to an-

**Table IV.** Effect of pendant substituents on the properties of polyamides.

Polymer code	Solubility <sup>(a)</sup>						Thermal properties				Char yield <sup>(f)</sup> (%)
	DMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	T <sub>g</sub> <sup>(b)</sup> (°C)	T <sub>m</sub> <sup>(c)</sup> (°C)	T <sub>s</sub> <sup>(d)</sup> (°C)	T <sub>d</sub> <sup>(e)</sup> (°C)	
<i>p</i> -2c	-	-	-	-	-	-	-(g)	-	-	524	59
<i>p</i> -Me-2c	-	-	-	-	-	-	-	445	-	467	64
<i>p</i> -( <i>t</i> -Bu)-2c	+	+h	-	+h	-	-	-	363	251	456	60
<i>p</i> -Ph-2c	+	+	+h	+	-	-	213	-	224	471	68
<i>m</i> -2c	+	+	+	+	-	-	234	411	234	504	66
<i>m</i> -Me-2c	+	+	+	+	+	-	198	-	210	462	67
<i>m</i> -( <i>t</i> -Bu)-2c	+	+	+	+	+	-	208	-	227	472	58
<i>m</i> -Ph-2c	+	+	+	+	+	+	189	-	192	496	67

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

(b) Temperature at the midpoint of baseline shift on the second heating DSC traces after quenching from 400 °C. Heating rate: 20 °C/min.

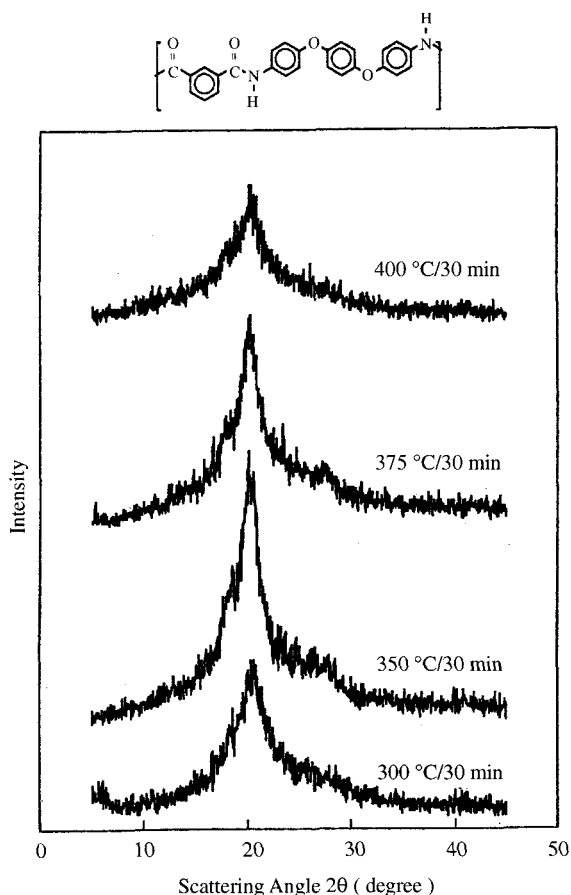
(c) Peak temperature of melting endotherms on the first heating DSC traces before 500 °C.

(d) Softening temperature measured by TMA (penetration method) at a heating rate of 20 °C/min.

(e) Decomposition temperature at which a 10% weight loss was recorded by TGA conducted at a heating rate of 20 °C/min in nitrogen.

(f) Residual weight % at 800 °C in nitrogen.

(g) No discernible transitions were detectable by DSC.



**Figure 6.** X-ray diffraction patterns of the polymer films of *m*-2c annealed at the indicated temperatures for 30 min.

nealing temperatures of 300, 350, 375 and 400 °C for 30 min, respectively, and subsequently cooling

the annealed sample to 30 °C with a programmed cooling rate of 20 °C/min. The corresponding DSC thermograms of these annealed samples, shown in Figure 5, illustrate that the melting peaks shifted to a higher temperature and became stronger and more sharp as the annealing temperature increased. X-ray diffraction patterns of these annealed samples are shown in Figure 6. The relative reflection intensity near 20 ° increased when a higher annealing temperature of 350 or 375 °C was applied. These observations can be interpreted by saying that original main lamellae of the crystal could be increasingly reorganized and/or thickened by the elevating annealing temperatures. However, annealing temperatures that are too high, such as 400 °C may destroy the lamellar structure of the crystal, thus leading to a decrease in crystallinity as indicated by a decreased melting enthalpy and reflection intensity.

Polymers *p*-2a-b and *m*-2a-b showed a similar TGA pattern with no weight loss up to 400 °C in nitrogen. Decomposition temperatures at 10% weight loss were recorded in the range of 491-532 °C for these polyamides, and 59-68% weight was retained even at 800 °C. These results indicate that the introduction of an ether group or a change of catenation position of the phenylene unit does not seem to result in a dramatic effect on thermal stability.

## 2-2 Polyamides with pendant groups

To evaluate the effect of pendant groups, polyamides were also prepared from modified monomers, methyl, *t*-butyl, and phenyl substituted **1c** following the same synthetic routes. The effects of pendant ring substituents on the solubility behavior and thermal properties of polyamides are summarized in

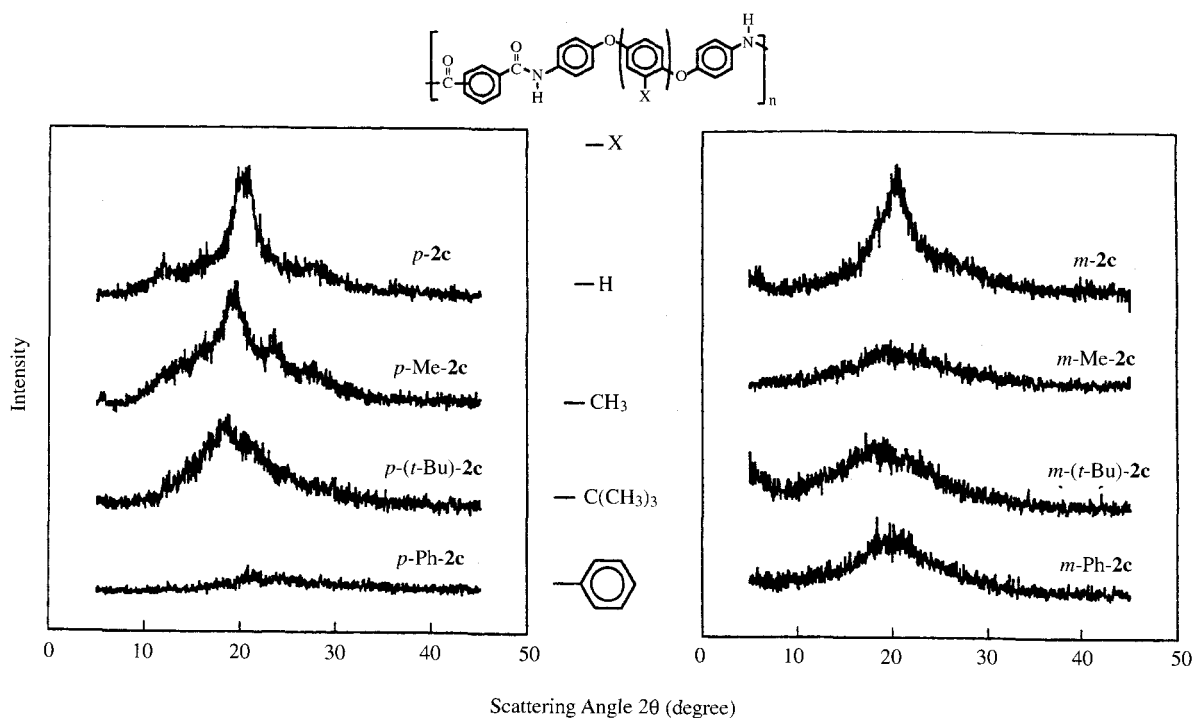


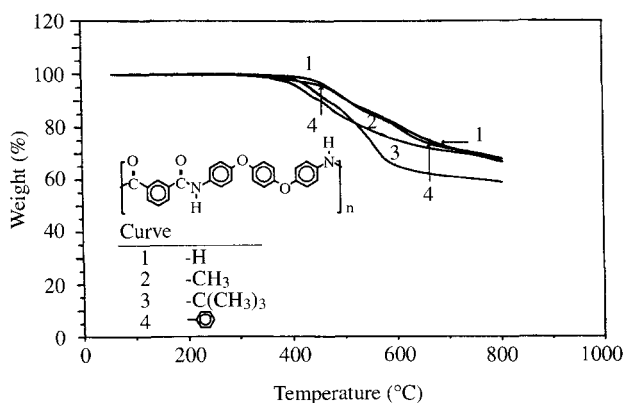
Figure 7. Effect of pendant substituents on the crystallinity of polyamides.

Table IV. The introduction of pendant groups into the polyamide backbone generally led to an improved solubility because of a decreased molecular order and intermolecular bonding. Polyamides *p-2c* and *p-Me-2c* were insoluble in organic solvents. However, *p-(t-Bu)-2c* and *p-Ph-2c* were soluble at room temperature in NMP and soluble in cold or hot DMAc and DMSO. Thus the presence of bulky pendant groups does help improve the solubility of polyamides. This could be explained by the reason cited above and was evidenced by WAXD. The effect of introducing pendant groups on the polymer crystallinity can be seen from Figure 7. Polymers *p-2c* and *p-Me-2c* showed moderately crystalline WAXD patterns, corresponding to their insoluble behavior in organic solvents. However, the attachment of *t*-butyl or phenyl groups causes a large decrease in crystallinity. Polyamides *p-(t-Bu)-2c* and *p-Ph-2c* were organosoluble and could be cast into transparent and tough films. In the *m*-series **2c** polyamides, all the polymers with pendant groups showed an amorphous WAXD pattern with a decreased packing density.

The thermal behavior data of the **2c** series of polyamides are also shown in Table IV. Although polymer *p-2c* exhibited a crystalline WAXD pattern, well-defined melting endotherms were not observed on the DSC trace before decomposition, possibly due to the high melting points. The incorporation of

pendant groups interrupted the hydrogen bonding and close packing of chains; hence, polymers *p-Me-2c* and *p-(t-Bu)-2c* showed a small and broad melting endotherm around 445 and 363 °C, respectively. Polyamide *p-Ph-2c* did not show any melting endotherms due to their amorphous nature. Due to high degree of crystallinity and/or rigidity of the polymer chain, no discernible  $T_g$ 's were observed for *p-2c*, *p-Me-2c* and *p-(t-Bu)-2c* by DSC. However, polyamide *p-Ph-2c* displayed a discernible  $T_g$  around 213 °C on its DSC thermogram. All the *m-2c* series polymers showed a strong  $T_g$  on their DSC curves, and the introduction of pendant groups resulted in a decrease in  $T_g$ . This may be due to the effects of chain separation, asymmetry, and irregularity caused by the side substituents. The  $T_s$  values of these polyamides were determined by TMA using a penetration method and were observed in the range 192-251 °C. The  $T_s$  values measured by TMA experiments are comparable to or slightly higher than the  $T_g$  values observed by DSC. A different thermal history and the distinctive nature of the testing methods may cause the difference. In the *m*-series, polyamides containing pendant groups *m-(t-Bu)-2c* showed the highest  $T_g$  and  $T_s$ . This might be result of increased rotational barriers and steric hindrance of segmental movement caused by the *t*-butyl groups. However, the introduction of a phenyl group could inhibit close chain packing and increase the poly-





**Figure 8.** TGA curves of polyamide *m-2c* and its analogues with different pendant groups, at a heating rate of 20 °C/min under nitrogen.

mer fractional free volume that increases polymer chain rotational and flexural mobility, thus leading to a slight decrease in  $T_g$  and  $T_s$ . The relatively lower  $T_g$ s and  $T_s$ s of the phenyl-substituted polymers may indicate that the effect of increased free volume prevails over the steric hindrance effect.

The thermal stability of the polyamides was evaluated by TGA. TGA curves of the *m-2c* series polyamides are shown in Figure 8. All the polyamides showed excellent thermal stability below 400 °C and retained more than 58% residue when heated to 800 °C in nitrogen. The introduction of aliphatic pendant groups, such as methyl and *t*-butyl groups, slightly lowering the initial decomposition temperature of polymers, and the effect of the phenyl group did not seem significant.

## Conclusions

A series of ether-containing polyamides was synthesized from terephthalic acid (TPA) and isophthalic acid (IPA) with aromatic ether diamines having different numbers of oxyphenylene units, different catenated positions on the phenylene ring, and different pendant groups. It was found that the polyamides based on IPA showed higher solubility than those derived from TPA. As evidenced by X-ray diffraction and DSC measurements, the TPA polyamides displayed a higher crystallinity than the corresponding IPA polyamides. Most IPA poly-

amides revealed a discernible glass transition on their DSC curves and their  $T_g$ s were in the range of 189–238 °C. However, DSC observed no  $T_g$  values for any TPA polyamides. For the polyamides without pendant groups, most of them showed a medium to strong melting endotherm on the DSC curves, and their thermal stability did not show clear dependence on the structure of the diacid or diamine. The incorporation of pendant groups on the polyamide backbones generally led to improved solubility and a substantial decrease in the level of crystallinity. The polyamides containing aliphatic groups, such as methyl or *t*-butyl groups, showed less thermal stability than the unsubstituted ones and those containing phenyl pendant groups.

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