

Syntheses and Properties of Aromatic Polyamides Derived from 4,4'-Oxydibenzoic Acid and Aromatic Diamines

Sheng-Huei Hsiao* and Chou-Huan Yu

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Rd., Sec. 3, Taipei 104, Taiwan, Republic of China

Abstract: A series of aromatic polyamides were synthesized by direct polycondensation of 4,4'-oxydibenzoic acid with various aromatic diamines in *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride, using triphenyl phosphite and pyridine as condensing agents. The resultant polyamides had inherent viscosities of 0.21-1.48 dL/g. Most of the polymers were organo-soluble and could be solution-cast into flexible and strong films. The glass transition temperatures (T_g s) of most polyamides could be determined with the help of differential scanning calorimetry (DSC) traces, which were recorded in the range of 170-275 °C. Thermogravimetric data of these polymers indicated that most of the polyamides showed no significant weight loss before 450 °C in either air or nitrogen atmospheres.

Keywords: Aromatic polyamides, 4,4'-Oxydibenzoic acid.

Introduction

Wholly aromatic polyamides have been noted for their high thermal and chemical resistance as well as high strength and high modulus as fibers [1, 2]. However, they are usually difficult to process due to their high glass-transition or melting temperatures and limited solubility. Several modifications of the chemical structure have been used in order to lower the transition temperatures and to improve the solubility of aromatic polyamides. It is well known that the insertion of appropriate flexibilizing groups into the polymer backbone [3-6] and the incorporation of thermally stable bulky pendant groups [7-14] may enhance the processability of aromatic polyamides without significantly sacrificing their outstanding thermal and mechanical properties.

It is well known that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperatures and crystalline melting temperatures, as well as significant improvements in solubility and other processing characteristics of the polymers without greatly sacrificing thermal stability. This kind of structural modification was usually realized by the insertion of arylene ether seg-

ments into the diamine monomer. The approach of synthesizing the bis(*p*-aminophenoxy) compounds by a nucleophilic substitution of a bisphenol and *p*-chloronitrobenzene, followed by reduction of the resulting dinitro compounds, is very popular in the literature [15-20].

4,4'-Oxydibenzoic acid is a currently commercially available dicarboxylic acid monomer containing an aryl ether linkage. Recently, this diacid has been usually used as a monomer in combination with the diamines to screen novel polyamides. However, systematic study on the polyamides based on 4,4'-oxydibenzoic acid has not yet been made. The present study deals with the synthesis of serial aromatic polyamides from 4,4'-oxydibenzoic acid and various aromatic diamines by using the Yamazaki-Higashi [21] phosphorylation polyamidation technique. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers have been investigated.

Experimental

1. Materials

4,4'-Oxydibenzoic acid (1) was used as received from TCI. Reagent-grade aromatic diamines such as *m*-phenylenediamine (2a, from Janssen), 2,4-

*To whom all correspondence should be addressed.

diaminotoluene (**2b**, from TCI), 4,4'-diaminodiphenyl ether (**2c**, from TCI), 3,4'-diaminodiphenyl ether (**2d**, from Mitsui Petrochemical Ind.), 4,4'-diaminodiphenylmethane (**2e**, from TCI), 1,4-bis(*p*-aminophenoxy)benzene (**2f**, from TCI), α,α' -bis(4-aminophenyl)-1,4-diisopropylbenzene (**2h**, from Mitsui Petrochemical Ind.), and α,α' -bis(4-aminophenyl)-1,3-diisopropylbenzene (**2i**, from Mitsui Petrochemical Ind.) were used without purification. According to a reported method [22], the other aromatic diamines such as 1,2-bis(aminophenoxy)benzene (**2g**), 4,4'-bis(4-aminophenoxy)biphenyl (**2j**), 2,2'-bis(4-aminophenoxy)biphenyl (**2k**), 3,3',5,5'-tetramethyl-4,4'-bis(4-aminophenoxy)biphenyl (**2l**), 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (**2o**), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**2n**), bis[4-(4-aminophenoxy)phenyl] sulfone (**2p**), α,α' -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**2q**), and α,α' -bis[4-(4-aminophenoxy)phenyl]-1,3-diisopropylbenzene (**2r**) were prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene and the corresponding bisphenols in the presence of potassium carbonate, with subsequent reduction of the intermediate dinitro compounds using hydrazine (H₂N-NH₂) as the reducing agent and palladium as the catalyst. Commercially obtained anhydrous calcium chloride (CaCl₂) (Wako) was dried under vacuum at 180 °C for 10 hrs. N-Methyl-2-pyrrolidone (NMP) (TCI), triphenyl phosphite (TPP) (Wako), and pyridine (Wako) were used without purification.

2. Synthesis of polyamides

A typical example of preparation of **3b** is as follows: A mixture of 0.6456 g (2.5 mmol) of 4,4'-oxydibenzoic acid (**1**), 0.3054 g (2.5 mmol) of 2,4-diaminotoluene (**2b**), 0.4 g of calcium chloride, 1.6 mL of triphenyl phosphite (TPP), 1.25 mL of pyridine, and 5 mL of NMP was heated with stirring at 110 °C for 3 hrs. The viscous polymer solution obtained was trickled into 400 mL of methanol, giving a fibrous precipitate that was washed thoroughly with methanol and hot water, collected by filtration, and dried. The yield was 99%, the inherent viscosity of the polymer was 0.97 dL/g as measured in DMAc containing 5 wt% LiCl at a concentration of 0.5 g/dL at 30 °C.

All other polyamides were synthesized by an analogous procedure.

3. 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. The clear solution was poured into a $\psi = 9$ cm glass culture dish, which was placed in a 80 °C oven over-

night to remove most of the solvent. The semi-dried polyamide film was stripped from the glass surface and further dried *in vacuo* at 120 °C for 6 hrs. The obtained films had about 0.1 mm thickness and were utilized for X-ray diffraction and tensile tests.

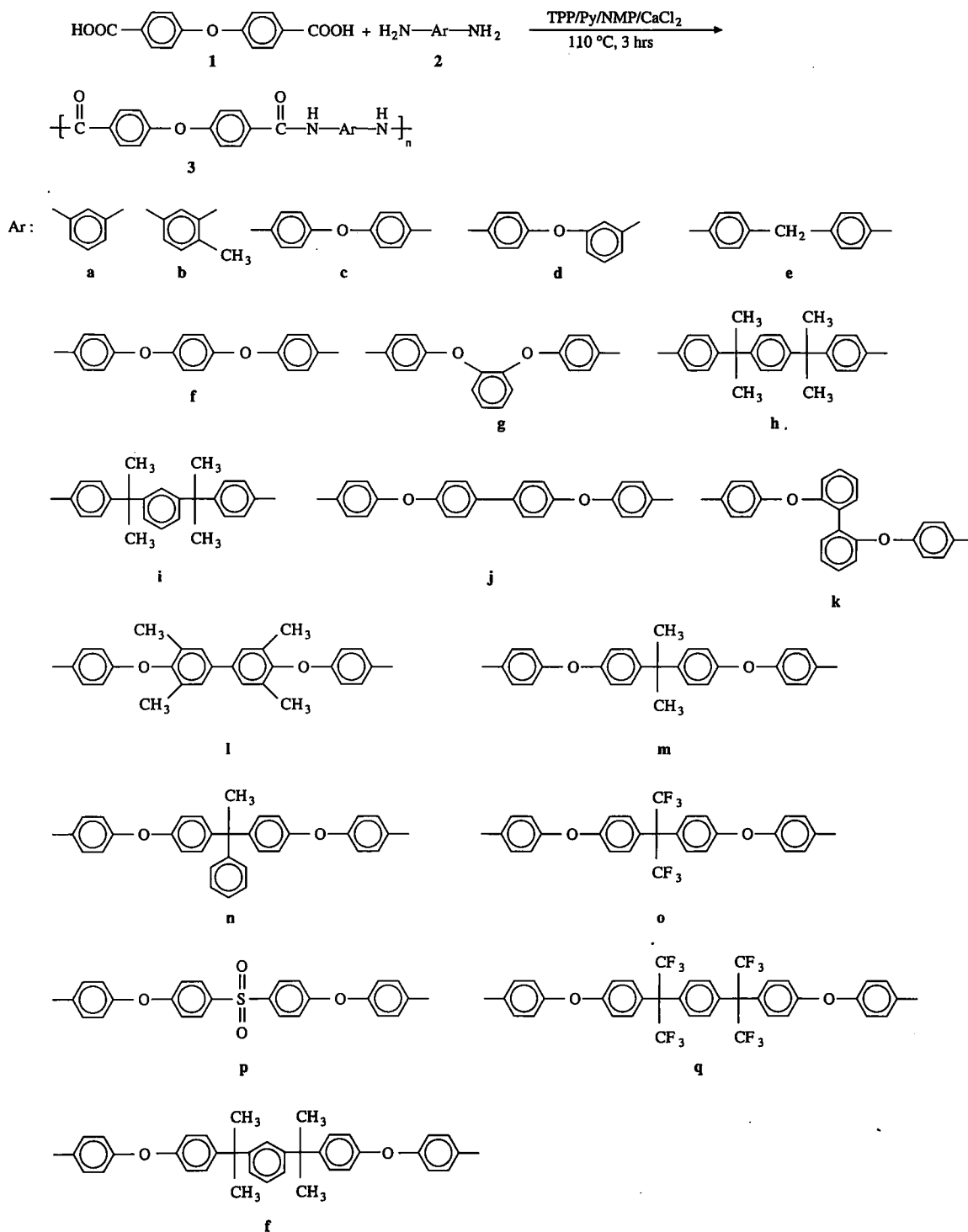
4. Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined by means of gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Shimadzu LC-6A apparatus (column: Tosoh TSK-GEL; eluent: DMF containing 0.01 mol/L of lithium bromide). The inherent viscosities were measured with a Cannon-Fenske viscometer thermostated at 30 °C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions. The heating rate was 20 °C/min. Glass transition temperatures (T_g s) were read at the middle of the change in the heat capacity, and were taken from the second heating scan after quick cooling. Thermomechanical analysis (TMA) was conducted with a Rigaku TMA 8140 at a heating rate of 10 °C/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 cm³/min) at a heating rate of 20 °C/min. Wide-angle x-ray diffractograms were obtained on a Rigaku Geiger Flex D-Max IIIa, using Ni-filtered CuK α radiation (40 KV, 15 mA). The scanning rate was 2 °C/min over a range of $2\theta = 5-40^\circ$. An Instron universal tester Model 1130 with a load cell of 5 Kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a crosshead speed 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). An average of at least five individual determinations was used.

Results and Discussion

1. Polymer synthesis

As outlined in Scheme 1, aromatic polyamides **3a-r** were prepared by a direct polycondensation technique from 4,4'-oxydibenzoic acid and various aromatic diamines in the NMP solution containing calcium chloride using triphenyl phosphite (TPP) and pyridine as condensing agents. The polycondensation reaction was carried out at 110 °C for 3 hrs. In



Scheme 1. Synthesis of polyamides from 4,4'-oxydibenzoic acid and various diamines.

the cases of preparation of polymers **3c**, **3f**, and **3j**, precipitation occurred after the polymerization had

preceded for about 30 min, and the precipitates could not be dissolved by adding additional solvents.

These heterogeneous reactions could not produce high molecular weight polymers. The inherent viscosities of the resulting polymers were only between 0.21 and 0.26 dL/g. All other reaction solutions were homogeneously transparent throughout the reaction and the obtained polymers had inherent viscosities ranging from 0.66 to 1.48 dL/g. Polyamides **3c**, **3e**, **3f**, **3j**, and **3k** were not sufficiently soluble in the eluent to allow the molecular weight to be determined by GPC. As shown in Table I, the weight-average molecular weights (M_w) of the soluble polymers were in the range of 57000-156000, and the polydispersity index (M_w/M_n) ranged from 1.53 to 2.69. Except for polyamides **3c**, **3f**, and **3j**, all other polyamides were soluble in DMAc and could be cast into free-standing films. Among these films, those of **3e** and **3k** cracked upon creasing, and the others were flexible and tough. The molecular structures of these polyamides were confirmed through IR spectroscopy, and a typical FT-IR spectrum of polyamide **3a** was shown in Figure 1. Some characteristic absorptions can be observed in this IR spectrum, such as N-H stretching near 3300 cm^{-1} , carbonyl stretching near 1650 cm^{-1} and aryl ether stretching near 1260 cm^{-1} .

2. Properties of polymers

2.1 Solubility

The solubility of polyamides was studied quali-

Table I. Inherent viscosities, average molecular weights, polydispersities, and film quality of polyamides.

Polymer code	$\eta_{inh}^{(a)}$ (dL/g)	$M_n^{(b)}$ ($\times 10^{-4}$)	$M_w^{(b)}$ ($\times 10^{-4}$)	M_w/M_n	Film ^(c) quality
3a	1.27	4.7	12.7	2.69	Flexible
3b	0.97	4.5	10.3	2.29	Flexible
3c	0.26	(d)	(d)	—	(e)
3d	1.06	5.6	10.6	1.88	Flexible
3e	0.92	(d)	(d)	—	Brittle
3f	0.22	(d)	(d)	—	(e)
3g	0.66	3.6	8.8	2.46	Flexible
3h	1.01	5.2	12.1	2.32	Flexible
3i	0.66	3.7	5.7	1.53	Flexible
3j	0.21	(d)	(d)	—	(e)
3k	1.04	(d)	(d)	—	Brittle
3l	1.48	5.4	10.2	1.88	Flexible
3m	1.13	5.3	11.2	2.11	Flexible
3n	0.82	4.6	10.0	2.17	Flexible
3o	1.06	6.4	14.5	2.28	Flexible
3p	0.70	5.6	11.1	1.99	Flexible
3q	0.75	4.7	11.4	2.41	Flexible
3r	0.83	6.4	15.0	2.35	Flexible

(a) Measured in DMAc-5 wt% LiCl on 0.5 g/dL at 30 °C.

(b) Determined by GPC on the standard polystyrene calibration with DMF containing 0.01 mol% LiBr as the eluent.

(c) Films were solution-cast from polymer solution in DMAc.

(d) Insoluble in the eluent of GPC measurement.

(e) Insoluble in DMAc.

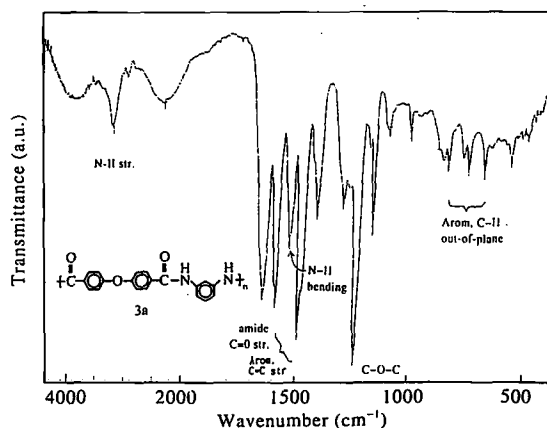


Figure 1. The IR spectrum of polyamide **3a**.

tatively, and the results are presented in Table II. The solubility of these polyamides was related to the diamine moieties. Except for **3c**, **3f**, and **3j**, almost all the polyamides showed excellent solubility in polar aprotic solvents such as NMP, DMAc, DMF, and DMSO, and some of them were also soluble in less polar solvents such as *m*-cresol and THF. The reason for the low solubility of the polyamides **3c**, **3f**, and **3j** might be related to their high crystallinity. The introduction of a methyl group on the aromatic rings, insertion of flexible (such as

Table II. Solubility behavior of polyamides^(a).

Polymer	solvent ^(b)					
	DMAc	NMP	DMF	DMSO	<i>m</i> -cresol	THF
3a	++	++	++	--	--	--
3b	++	++	++	++	+-	--
3c	--	--	--	--	--	--
3d	++	++	++	++	--	--
3e	++	++	--	--	--	--
3f	--	+-	--	--	--	--
3g	++	++	++	++	++	--
3h	++	++	++	++	++	--
3i	++	++	++	++	++	++
3j	--	--	--	--	--	--
3k	++	++	--	---	--	--
3l	++	++	++	+-	++	--
3m	++	++	++	+-	++	--
3n	++	++	++	++	+-	++
3o	++	++	++	++	++	++
3p	++	++	++	++	++	--
3q	++	++	++	--	++	++
3r	++	++	++	++	++	++

(a) ++: soluble at room temperature, + -: partial soluble or swollen, --: insoluble even on heating.

(b) DMAc: *N,N*-dimethylacetamide; NMP: *N*-methyl-2-pyrrolidone; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. All the polyamides were insoluble in acetone, chloroform, methanol, and ethanol.

isopropylidene) or polar groups (such as sulfone) between aromatic rings, or incorporation of bulky groups (such as phenyl and trifluoromethyl) or asymmetric aromatic rings (such as *m*-phenylene and *o*-phenylene) in the polymer main chains significantly enhanced the solubility of polyamides. All the polyamides were insoluble in common solvents such as acetone, chloroform, methanol, and ethanol.

2.2 Crystallinity

The crystallinity of these polymers was evaluated by X-ray diffraction measurements. Polyamides **3c**, **3f**, and **3j** were measured in powder form, and the other polyamides as films. Typical X-ray diffractograms of some representative polyamides are illustrated in Figure 2. Polyamides **3c**, **3f**, and **3j** revealed crystalline diffraction patterns. The film of polyamide **3k** also showed a crystalline pattern. However, although the cast film of polymer **3e** was brittle, it did not show an obvious crystalline pattern. Furthermore, the other polyamides exhibited amorphous

diffraction patterns like that of polyamide **3i** as shown in Figure 2.

2.3 Tensile properties

Most of the polyamides could be cast into good-quality and creasable films by slow evaporation of their polymer solutions in DMAc. The tensile properties of these flexible polyamide films are listed in Table III. Some polymer films like **3b**, **3d**, **3l**, **3m**, and **3o** behaved as ductile materials. They showed yield points on their stress-strain curves and moderate elongation at break point. Other films showed no yield points and lower elongation before breaking, indicative of a strong and hard nature.

2.4 Thermal properties

The thermal stability of these polyamides was determined by thermogravimetry (TG). Typical TG thermograms in both air and nitrogen atmospheres of a representative polyamide **3a** are shown in Figure 3. The 10% weight loss temperatures in air and in nitrogen, and the char residue wt% at 800 °C in nitrogen of all these polyamides are summarized in Table IV. For most polyamides, the 10% weight loss temperatures of the polyamides were above 450 °C, and the char yields at 800 °C in nitrogen were higher than 50%. In general, the introduction of alkyl groups into the polymer backbone decreased the decomposition temperature.

The polyamides were rapidly cooled from elevated temperatures at approximately 350 °C to room temperature to form predominantly amorphous samples, and thus, distinct glass transitions generally could be observed on the subsequent heating DSC traces. Glass transition temperatures (T_g) of these polyamides were read at the middle of baseline shift of the second DSC heating traces. Typical DSC curves for polymer **3a** are illustrated in Figure

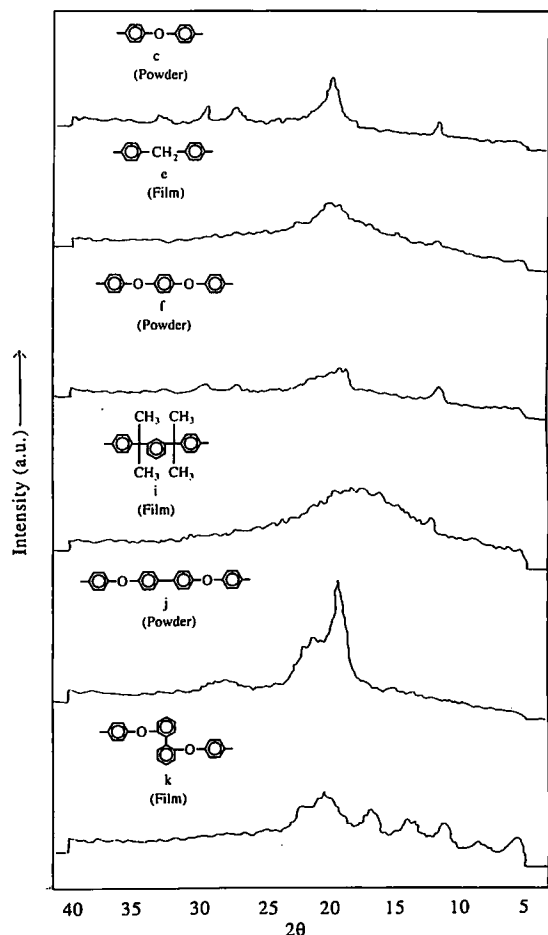


Figure 2. Wide-angle X-ray diffraction patterns of polyamides.

Table III. Tensile properties of polyamide films.

Polymer	Yield strength (MPa)	Strength to break (MPa)	Elongation to break (%)	Tensile modulus (GPa)
3a	—	88	11	1.77
3b	87	83	13	1.58
3d	66	75	29	1.68
3g	—	82	8	1.75
3h	—	74	11	1.52
3l	79	77	36	1.39
3m	76	68	18	1.45
3n	—	80	11	1.48
3o	74	67	24	1.45
3p	—	67	9	1.47
3q	—	69	11	1.43
3r	—	68	10	1.42

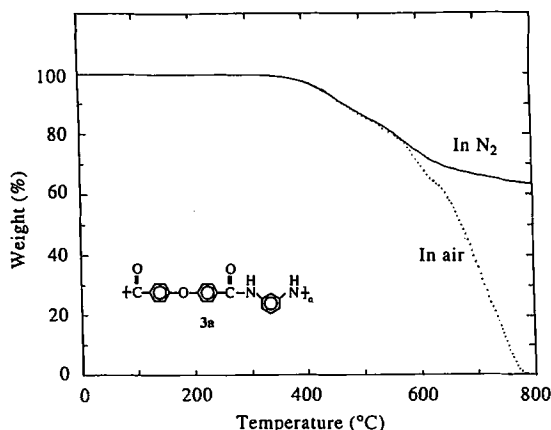


Figure 3. TG thermograms for polyamide 3a, with a heating rate of 20 °C/min.

Table IV. Thermal behavior data of polyamides.

Polymer	$T_s^{(a)}$ (°C)	$T_g^{(b)}$ (°C)	Decomposition temperature ^(c)		Residue at 800 °C in N ₂ (wt%)
			in N ₂ (°C)	in air (°C)	
3a	151	250	467	474	64.0
3b	165	250	452	458	55.5
3c	—	231	515	493	59.8
3d	132	234	496	499	61.9
3e	—	255	483	495	65.3
3f	—	216	490	495	65.3
3g	127	206	491	488	60.8
3h	161	242	446	448	49.3
3i	108	170	463	467	50.4
3j	—	240	513	507	45.0
3k	—	223	489	490	50.0
3l	174	275	496	491	65.3
3m	148	219	493	488	58.6
3n	157	226	502	493	62.3
3o	154	232	516	514	53.0
3p	158	245	508	504	55.0
3q	160	211	483	492	55.6
3r	100	173	491	493	51.7

(a) Softening temperature was recorded by TMA at heating rate of 10 °C/min.

(b) From the second heating traces of DSC measurement conducted with a heating rate of 20 °C/min in nitrogen.

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

4. The T_g data of these polymers were also listed in Table IV. With the exception of 3i and 3r, the T_g s of other polyamides were all above 206 °C and up to 275 °C. The T_g values of these polyamides depended on the diamine moiety. The insertion of rigid biphenylene unit or polar sulfonyl group (such as in 3j and 3p) helps to increase T_g , while the introduction of *o*- or *m*-phenylene unit or flexible aliphatic linkages causes a T_g lowering. Bipheny-

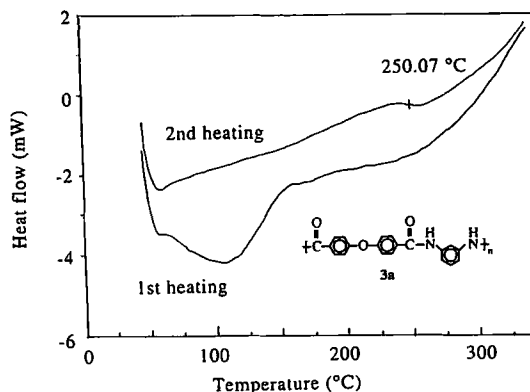


Figure 4. DSC traces of polyamide 3a at a heating rate of 20 °C/min in nitrogen.

lene-units containing polyamides 3j and 3l have T_g at 240 (3j) and 275 °C (3l). The only difference in these two structures are methyl groups in ortho-position to both ether linkages. The higher T_g is attributed to the hindrance of rotation at these bonds, resulting in an increased chain stiffness. Polymers 3n ($T_g = 226$ °C) and 3o ($T_g = 232$ °C) showed a higher T_g than polymer 3m ($T_g = 219$ °C) due to the presence of bulky pendant phenyl and trifluoromethyl groups leading to the steric hindrance of segment movement.

The softening temperatures (T_s) of these polyamides were measured by thermomechanical analysis (TMA), and the T_s values of the polyamides that could be cast into flexible films are listed in Table IV. A typical TMA trace is shown in Figure 5. The softening temperatures of these polymers stayed in the 100-174 °C range. Polyamides 3i and 3r had lower softening temperatures due to the presence of flexible *m*-diisopropylbenzene units in the backbones. The softening temperature (which may be considered as the apparent T_g) of polymer films measured by TMA showed a similar decreasing tendency to that of the T_g measured by DSC, although the values were much lower than the T_g 's. This difference may be explained by the fact that these ether-containing polyamides exhibit a high degree of plasticity near T_g .

Conclusions

A series of aromatic polyamides based on 4,4'-oxydibenzoic acid and various aromatic diamines were prepared by the direct polycondensation technique using triphenyl phosphite and pyridine as condensing agents. The molecular weights of the obtained polymers depended upon the diamine na-

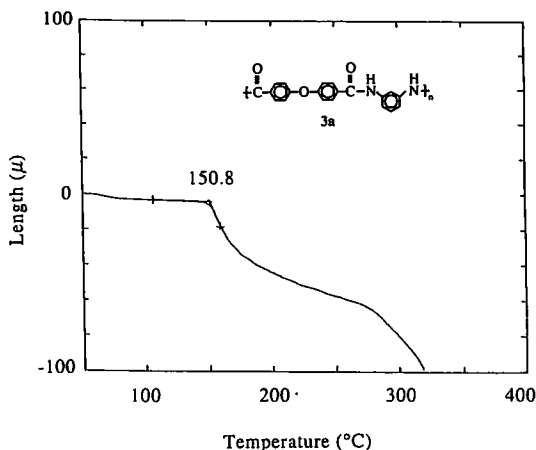


Figure 5. The TMA curve for polyamide 3a at a heating rate of 10 °C/min in nitrogen.

ture and the solubility of polymer in the reaction medium. Depending on the diamines used, these polyamides may be made with high degree of crystallinity or with an amorphous nature. Most of the polyamides exhibited a desired combination of properties that included high solubility, good tensile properties, excellent thermal stability, and large window between the decomposition temperature and T_g .

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