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Syntheses and properties of aromatic polyamides and polyimides based on 3,3-bis[4-(4-aminophenoxy)phenyl]-phthalimidine

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3,3-Bis[4-(4-aminophenoxy)phenyl]phthalimidine (**2**) was used as the monomer with various aromatic dicarboxylic acids and tetracarboxylic dianhydrides to synthesize polyamides and polyimides, respectively. The diamine **2** was derived by a nucleophilic substitution of 3,3-bis(4-hydroxyphenyl)phthalimidine with *p*-chloronitrobenzene in the presence of K_2CO_3 and then reduced by hydrazine and catalyst. Polyamides (**4a–g**) having inherent viscosities of 0.94–2.08 $dl\,g^{-1}$ were prepared by direct polycondensation of the diamine **2** with various aromatic diacids using triphenyl phosphite and pyridine as condensing agents. All the aromatic polyamides were amorphous and readily soluble in various polar solvents such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide, dimethylsulfoxide and *N*-methyl-2-pyrrolidone (NMP). Transparent and flexible films of these polymers could be cast from the DMAc solutions. These aromatic polyamides had glass transition temperatures in the range of 307–338°C and 10% weight loss occurred up to 460°C. The polyimides were synthesized from diamine **2** and various aromatic dianhydrides via a two-stage procedure that included ring-opening polyaddition in DMAc to give poly(amic acid)s, followed by thermal or chemical conversion to polyimides. Most of the aromatic polyimides obtained by chemical cyclization were found to be soluble in NMP, *m*-cresol and *o*-chlorophenol. These polyimides showed almost no weight loss up to 500°C in air or nitrogen atmosphere.

(Keywords: phthalimidines; polyamides; polyimides)

INTRODUCTION

High-performance plastic materials are currently receiving considerable attention for their potential applications in various industries. In particular, aromatic polyamides (aramids) and polyimides are known to have excellent high-temperature resistance, mechanical strength and superior electrical/insulating properties[1]. Unless carefully designed, however, aromatic polymers of the class have high melting or softening temperatures and insoluble nature in most organic solvents, which make these systems difficult to process. Therefore, much effort has been spent on preparing tractable aromatic polymers by changing the chemical nature of the macrochain to some degree while maintaining its desired properties. It has been observed that the presence of an oxygen atom between two benzene nuclei in the repeating units of the polymer increases the processability with little reduction in thermal stability[2,3]. On the other hand, a polymer chain having a cyclic side cardo group (for example, a fluorene, a phthalide, or a phthalimidine group) generally possesses a favourable combination of properties such as good thermo-oxidative stability, relatively high glass transition temperature and good mechanical properties. Review articles concerning the chemistry and physical properties of such macromolecules have been published[4,5]. Recently, we have successfully synthesized and characterized soluble aromatic polyamides and polyimides derived from arylene ether-containing cardo diamines such as 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene[6], 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide[7] and *N*-phenyl-3,3-bis[4-(4-aminophenoxy)phenyl]phthalimidine[8]. Concurrent with our effort, a different structure of polymers bearing amide-aryl ether phthalimidine and imide-aryl ether phthalimidine units were under investigation.

EXPERIMENTAL

Reagents and solvents

3,3-Bis(4-hydroxyphenyl)phthalimidine was prepared by stirring phenolphthalein (from Wako) and a large excess of concentrated NH_4OH at room temperature for 14 day. It was treated with charcoal and recrystallized from methanol; m.p. 279–280°C (lit.[9] 281–282°C). Hydrazine monohydrate (from Wako) and *p*-chloronitrobenzene (from TCI) were used as received. Reagent-grade aromatic dicarboxylic acids such as terephthalic acid (from Fluka), isophthalic acid (from Fluka), 5-t-butyl isophthalic acid (from Amoco Chemical Co.),

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2,6-naphthalenedicarboxylic acid (from TCI), 4,4′-biphenyldicarboxylic acid (from TCI), 4,4′-sulfonyldibenzoic acid (from New Japan Chemical Co.) and 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (from Chriskev) were used without further purification. Pyromellitic dianhydride (PMDA; from TCI), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA; from Chriskev), 4,4′-oxydiphthalic anhydride (ODPA; from Chriskev), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA; from TCI) and 4,4′-sulfonyldiphthalic anhydride (SDPA; from New Japan Chemical Co.) were recrystallized from acetic anhydride before use. Commercially obtained calcium chloride (from Wako) was dried under vacuum at 180°C for 10 h. *N,N*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *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 (from TCI) was purified by vacuum distillation.

*Synthesis of 3,3-bis[4-(4-nitrophenoxy)phenyl]-phthalimidine (**1**)*

A mixture of 63.5 g (0.2 mol) of 3,3-bis(4-hydroxyphenyl)phthalimidine, 72.5 g (0.46 mol) of *p*-chloronitrobenzene, 69.1 g (0.5 mol) anhydrous potassium carbonate and 200 ml of dry DMF was heated at 160°C for 8 h and cooled. The mixture was then poured into 500 ml of ethanol/water (1:1 v/v). The precipitate was collected by filtration and recrystallized from glacial acetic acid to afford 100.7 g (90%) of yellow crystals; m.p. 241–243°C.

Analysis: calculated for $C_{32}H_{21}N_3O_7$, C 68.69%, H 3.78%, N 7.51%; found, C 68.57%, H 3.93%, N 7.40%.

I.r. (KBr) (cm^{-1}): 1489, 1336 (NO_2); 1251 (C–O–C).

^1H n.m.r. (DMSO-d_6) δ (ppm): 9.84 (s, 1H, N–H); 8.25 (d, 4H, Ar–NO_2); 7.55–7.76 (m, 4H, phthalimidine aromatic); 7.40 (d, 4H, Ar–O); 7.20 (d, 4H, Ar–O); 7.14 (d, 4H, Ar–NO_2).

^{13}C n.m.r. (DMSO-d_6) δ (ppm): 168.56, 162.67, 154.02, 149.76, 142.66, 140.18, 132.59, 131.23, 129.33, 129.00, 126.42, 125.02, 123.68, 120.44, 117.88, 69.62.

*Synthesis of 3,3-bis[4-(4-aminophenoxy)phenyl]-phthalimidine (**2**)*

The obtained dinitro compound **1** (50 g, 0.089 mol), 0.27 g of 10% Pd/C and 180 ml of ethanol were introduced into a three-necked flask to which 90 ml of hydrazine monohydrate were added dropwise over a period of 1 h at 85°C. After the addition was complete, the reaction was continued at the reflux temperature for another 4 h. The mixture was filtered to remove Pd/C and concentrated under reduced pressure. The concentrate was subsequently added to water to precipitate a solid, which was collected by filtration and dried to afford 3,3-bis[4-(4-aminophenoxy)phenyl]phthalimidine (39.6 g, 89% yield) as a white solid; m.p. 129–130°C (lit.[10] 130–131°C).

Analysis: calculated for $C_{32}H_{25}N_3O_3$, C 76.94%, H 5.04%, N 8.41%; found, C 75.93%, H 5.04%, N 8.50%.

I.r. (KBr) (cm^{-1}): 3354 (N–H); 1238 (C–O–C).

^1H n.m.r. (DMSO-d_6) δ (ppm): 9.63 (s, 1H, N–H); 7.60–7.68 (m, 4H, phthalimidine aromatic); 7.17 (d, 4H, Ar–O); 6.79 (d, 4H, Ar–O); 6.74 (d, 4H, Ar–NH_2); 6.57 (d, 4H, Ar–NH_2); 4.97 (S, 4H, amino).

^{13}C n.m.r. (DMSO-d_6) δ (ppm): 168.28, 158.30, 150.23, 145.61, 145.21, 136.48, 132.04, 130.98, 128.33, 124.65, 123.24, 120.99, 116.02, 114.88, 69.31.

*Polyamide **4b** from **2** and **3b***

A mixture of 0.6245 g (1.25 mmol) of **2**, 0.2077 g (1.25 mmol) of isophthalic acid (**3b**), 0.2 g of calcium chloride and 0.8 ml of triphenyl phosphite in 1.6 ml of pyridine and 3 ml of NMP was heated with stirring at 100°C for 3 h under nitrogen. The reaction mixture was trickled into 250 ml of methanol, giving rise to a stringy precipitate, which was washed thoroughly with methanol and hot water, collected by filtration and dried. The yield was quantitative. The inherent viscosity of the polymer in DMAc was 1.55 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} at 30°C.

I.r. (film) (cm^{-1}): 3288 (N–H); 1690 (C=O); 1230 (C–O–C).

Other polyamides were synthesized by analogous procedures.

*Polyimide **7-Ha** from **2** and **5a** by thermal conversion method**

To a stirred solution of 0.500 g (1 mmol) of **2** in 6.9 ml of *N,N*-dimethylacetamide (DMAc), 0.2183 g (1 mmol) of PMDA was added in three portions under a nitrogen atmosphere at room temperature for 2 h after the complete addition of the dianhydride. The inherent viscosity of the poly(amic acid) in DMAc was 1.37 dl g^{-1}, measured at a concentration of 0.5 g dl^{-1} at 30°C.

I.r. (film) (cm^{-1}): 3300 (O–H and N–H); 1663 (C=O).

The poly(amic acid) solution thus obtained was cast onto a glass plate and the solvent was removed at 80°C in an air oven for 1 h. The semi-dried film was further dried and imidized by sequential heating at 120°C for 10 min, 150°C for 10 min, 180°C for 10 min and 250°C for 30 min.

I.r. (film) (cm^{-1}): 1777, 1719 (C=O); 1379 (C–N).

*Polyimide **7-Cb** from **2** and **5b** by chemical conversion method**

To a stirred solution of 0.5 g (1 mmol) of diamine **2** in 7.6 ml of DMAc, 0.2945 g (1 mmol) of BPDA was added in three portions under a nitrogen atmosphere at room temperature. The polymerization solution was stirred at room temperature for 2 h after the complete addition of the dianhydride. A solution of acetic anhydride (3 ml), pyridine (1.5 ml) and DMAc (3 ml) was added slowly to the obtained poly(amic acid) at ambient temperature and the resulting solution was held at 80°C for 2 h. The reaction mixture was poured into methanol and the solid collected by filtration, washed with methanol and then hot water and dried *in vacuo*. The inherent viscosity of the chemically imidized polyimide in NMP with a 0.5 g dl^{-1} concentration at 30°C was 1.14 dl g^{-1}.

I.r. (film) (cm^{-1}): 1775, 1719 (C=O); 1379 (C–N).

Characterization methods

Elemental analyses were run in a Perkin-Elmer model 2400 CHN analyser. I.r. spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infra-red spectrometer. ^{13}C n.m.r. spectra were measured at 30°C on a JEOL

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* Polyimides obtained by the chemical cyclodehydration method are designated with a C while those obtained by the thermal means are designated with an H

EX-400 n.m.r. spectrometer. The inherent viscosities were measured with a Cannon-Fenske viscosimeter thermostated at 30°C. A 1% solution (w/v) was taken as measure of solubility. The d.s.c. traces were measured on a Sinku Riko 7000 differential scanning calorimeter coupled to a Basic Component TA 7000 thermal analyser at the rate of 20°C min^{-1} in flowing nitrogen (30 cm^3 min^{-1}). Thermogravimetric analyses (t.g.a.) were conducted with a Rigaku Thermoflex TG 810 coupled to a Rigaku TAS-100. Experiments were carried out on 10 ± 2 mg samples heated in flowing nitrogen (50 cm^3 min^{-1}) at a heating rate of 20°C min^{-1}. The wide-angle X-ray measurements were performed at room temperature (about 25°C) with film specimens about 0.1 mm thick on a Rigaku Geiger Flex D-Max IIIa X-ray diffractometer, using Ni-filtered Cu Kα radiation (40 kV, 15 mA). The scanning rate was 2° min^{-1}. An Instron Universal Tester model 1130 with a load cell of 5 kg was used to study the stress–strain behaviour of the samples. A gauge of 2 cm and a strain rate of 5 cm min^{-1} were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long and about 0.1 mm thick), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

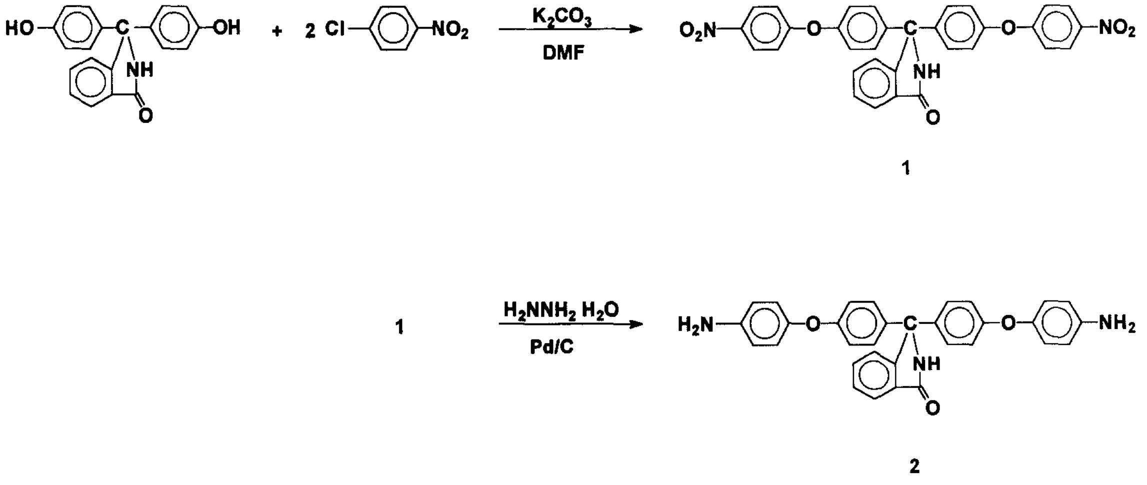
Monomer synthesis

The synthesis of the diamine containing a preformed phthalimidine group and aryl ether linkages, 3,3-bis[4-(4-aminophenoxy)phenyl]phthalimidine (**2**), was achieved by condensation of *p*-chloronitrobenzene with 3,3-bis(4-hydroxyphenyl)phthalimidine, which was prepared by the reaction of phenolphthalein and concentrated aqueous ammonia, giving 3,3-bis[4-(4-nitrophenoxy)-phenyl]phthalimidine (**1**), followed by catalytic reduction (*Scheme 1*). The dinitro compound **1** was synthesized by the modification of the procedure of Kuenzel *et al.*[10] from 3,3-bis(4-hydroxyphenyl)phthalimidine and *p*-chloronitrobenzene in the presence of potassium carbonate dissolved in dry DMF by refluxing for 8 h to give quantitative yield. Reduction of the dinitro compound to an amino compound can be carried out in a number of ways; for example, the most frequently used methods employ catalytic hydrogenation (H_2/Pd), or treatment of the nitro compound with acid (HCl) and metal or metal salt (such as iron, zinc, tin or $SnCl_2$), or hydrazine–Pd/C as reducing agent. The latter is quite a convenient method in laboratory and is available for the preparation of diamine **2** in the present work. Although the recrystallization of crude diamine **2** was difficult owing to the asymmetry of the phthalimidine side group, the characters of poor solubility for product **2** and good solubility for excess hydrazine in water gave diamine **2** with high purity and yield when its concentrated mixture was added to water to precipitate the solid. The structures of intermediate dinitro compound and diamine were confirmed by means of elemental analysis, and i.r., ^{1}H and ^{13}C n.m.r. spectroscopic techniques. The ^{13}C n.m.r. spectrum of dinitro compound **1** exhibited exactly 16 peaks consistent with the calculated values, while the diamine **2** showed only 15 peaks owing to overlapping of one peak (see 'Experimental' section).

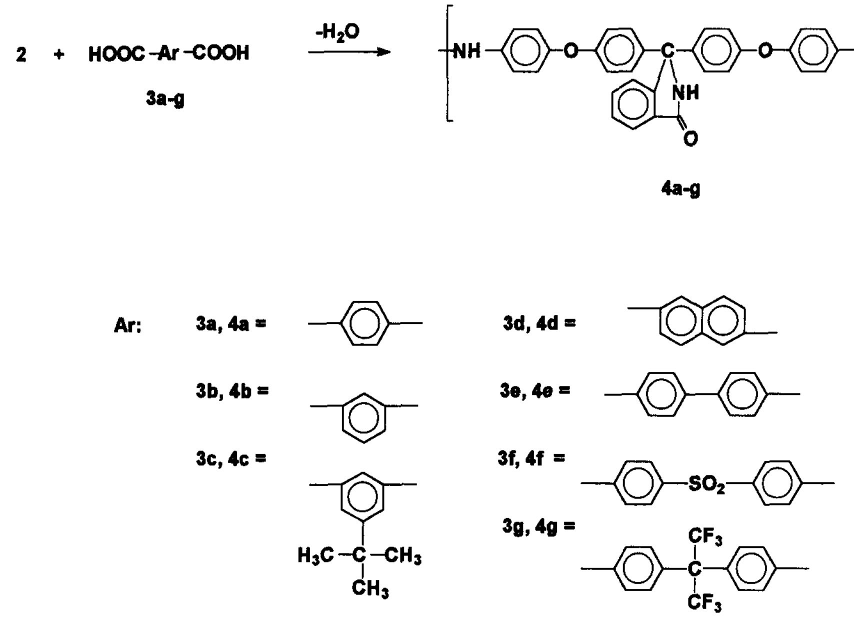
Preparation of polyamides and polyimides

The direct polycondensation of aromatic diamines with dicarboxylic acids using triphenyl phosphite and pyridine as condensing agents is a convenient method for the preparation of aromatic polyamides on a laboratory scale[11,12]. This method was applied here to prepare the phthalimidine-containing polyamides **4a–g** from diamine **2** and structurally differential aromatic dicarboxylic acids **3a–g** (*Scheme 2*).

Many factors influence polyamide preparation via the phosphorylation reaction. After numerous experiments in which solvent, reactant concentration, temperature, added amount of metal salts, etc., were varied, the conditions listed in *Table 1* have been found to be optimal. In the conditions used, all the reactions proceeded readily in a homogeneous state. In some cases, an additional volume of NMP was added to the reaction mixture to reduce the viscosity of the polymer solution and to provide for smooth stirring. *Table 1* summarizes the results of polycondensation. All polyamides were obtained in nearly quantitative yields and their inherent viscosities ranged from 0.94 to 2.08 dl g^{-1}. The inherent viscosities of the resultant polymers were affected by both the reactivity and the chemical structure of the diacids. The more satisfactory result obtained from terephthalic acid (**3a**) may be due to its high reactivity and rigid moiety.



Scheme 1



Scheme 2

Table 1 Preparation of polyamides from diamine **2** and various aromatic diacids[a]

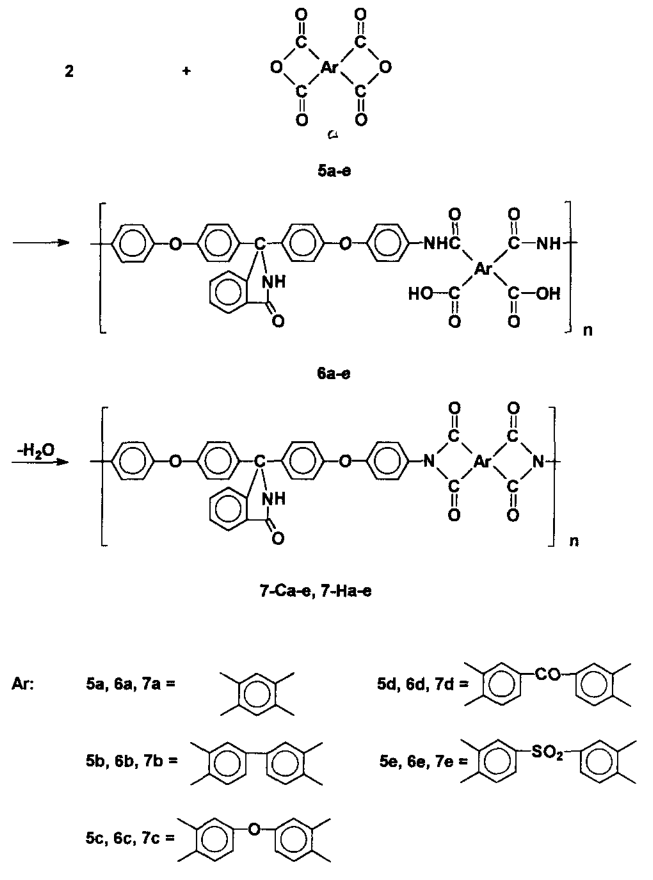
Polymer	Initial amount of NMP (ml)	Additional amount of NMP (ml)	Polymer Yield (%)	Polymer η_{inh}[b] (dl g^{-1})
4a	4	20	99	2.08
4b	3	0	99	1.55
4c	3	0	99	0.94
4d	4	4	99	1.78
4e	4	0	99	1.39
4f	3	2	99	1.46
4g	4	0	99	1.23

[a] Polymerization was carried out with 1.25 mmol of each monomer, 0.8 ml of triphenyl phosphite, 1.6 ml of pyridine and 0.2 g of calcium chloride in NMP at 100°C for 3 h

[b] Measured at a concentration of 0.5 g dl^{-1} in DMAc at 30°C

The elemental analyses of the polyamides are listed in *Table 2*. In most cases the carbon values were found to be lower than the calculated ones for the proposed structures. This may be attributed to the hygroscopic characteristics of the amide group. The moisture uptake for polyamides **4a–g** was in the range of 1.59–3.50% at room temperature (ca. 23°C) and normal pressure in our laboratory. The corrected values were in good agreement with the calculated ones after deducting the amount of moisture uptake.

Polyimides were synthesized conveniently by the two-step polycondensation of a dianhydride and a diamine in an aprotic solvent such as DMAc[13–15]. In the preparation of poly(amic acid)s from aromatic dianhydrides and diamines in a polar solvent, the process of monomer addition also plays an important role for successful polymerization[16,17]. The aromatic polyimides as shown in *Scheme 3* were synthesized by the two-step polymerization method using phthalimidine-containing diamine **2** and aromatic tetracarboxylic dianhydrides, which involved the ring-opening polyaddition and subsequent cyclodehydration.



Scheme 3

Table 3 summarizes the results of viscosity measurements of poly(amic acid)s prepared from diamine **2** in dry DMAc and aromatic dianhydrides, which were added in three portions at room temperature. The inherent viscosities of the resulting poly(amic acid)s were in the range of 0.73–1.37 dl g^{-1}. The flexible and transparent polyimide films obtained by the thermal treatments had poor solubility in organic solvents.

Table 2 Elemental analysis of polyamides

Polymer	Formula (molecular weight)		Elemental analysis (%) C	H	N	Moisture uptake (%)[a]
4a	$(C_{40}H_{27}N_3O_5)_n$	Calcd	76.30	4.32	6.67	
	$(629.67)_n$	Found	76.04	4.65	5.80	2.92
		Corr.[b]	78.26	4.51	5.97	
4b	$(C_{40}H_{27}N_3O_5)_n$	Calcd	76.30	4.32	6.67	
	$(629.67)_n$	Found	76.06	4.65	5.79	2.89
		Corr.[b]	78.26	4.52	5.96	
4c	$(C_{44}H_{35}N_3O_5)_n$	Calcd	77.06	5.14	6.13	
	$(685.78)_n$	Found	76.13	5.24	5.31	3.50
		Corr.[b]	78.79	5.06	5.50	
4d	$(C_{44}N_{29}N_3O_5)_n$	Calcd	77.75	4.30	6.18	
	$(679.73)_n$	Found	77.27	4.55	5.38	2.79
		Corr.[b]	79.43	4.42	5.53	
4e	$(C_{46}H_{31}N_3O_5)_n$	Calcd	78.28	4.43	5.95	
	$(705.77)_n$	Found	77.63	4.75	5.22	2.86
		Corr.[b]	79.85	4.61	5.37	
4f	$(C_{46}H_{31}N_3O_7S)_n$	Calcd	71.77	4.06	5.46	
	$(769.84)_n$	Found	72.11	4.37	4.83	2.36
		Corr.[b]	73.81	4.27	4.94	
4g	$(C_{49}H_{31}N_3O_5F_6)_n$	Calcd	68.77	3.65	4.91	
	$(855.79)_n$	Found	69.77	3.97	4.42	1.59
		Corr.[b]	70.88	3.91	4.49	

[a] Moisture uptake (%) = $[(W - W_0)/W_0] \times 100\%$, where W = weight of polymer sample after standing at room temperature, and W_0 = weight of polymer sample after drying in vacuum at 100°C for 10 h

[b] Corrected value = found value × (100% + moisture uptake %) for C and N
Corrected value = found value × (100% − moisture uptake %) for H

Table 3 Synthesis of polyimides

Poly(amic acid)[a] Code	η_{inh}[b] (dl g^{-1})	Polyimide[c] Code	η_{inh}[d] (dl g^{-1})
6a	1.37	**7-Ca**	1.25
6b	1.20	**7-Cb**	1.14
6c	0.78	**7-Cc**	0.70
6d	0.73	**7-Cd**	0.45
6e	1.02	**7-Ce**	0.89

[a] Polymerization was carried out with 1 mmol of each monomer at room temperature for 2 h

[b] Measured at 0.5 g dl^{-1} in DMAc at 30°C

[c] Polyimides **7-Ca–e** were obtained by using chemical cyclodehydration method

[d] Measured at 0.5 g dl^{-1} in NMP at 30°C

Alternatively, chemical treatment of poly(amic acid)s with a mixture of acetic anhydride and pyridine is also effective in obtaining polyimides[18]. By this procedure the polyimides had a good solubility in NMP with inherent viscosities of 0.45–1.25 dl g^{-1}. The elemental analysis values of these polyimides as shown in *Table 4* were generally in good agreement with their respective structures.

Table 4 Elemental analysis of polyimides

Polymer[a]	Formula (molecular weight)		Elemental analysis (%) C	H	N
7-Ca	$(C_{42}H_{23}N_3O_7)_n$	Calcd	74.00	3.40	6.16
	$(681.66)_n$	Found	74.73	3.79	5.50
7-Cb	$(C_{48}H_{27}N_3O_7)_n$	Calcd	76.08	3.59	5.55
	$(757.76)_n$	Found	76.82	3.77	5.01
7-Cc	$(C_{48}H_{27}N_3O_8)_n$	Calcd	74.51	3.52	5.43
	$(849.86)_n$	Found	75.58	3.76	4.89
7-Cd	$(C_{49}H_{27}N_3O_8)_n$	Calcd	74.90	3.46	5.35
	$(785.77)_n$	Found	75.34	3.65	4.83
7-Ce	$(C_{48}H_{27}N_3O_9S)_n$	Calcd	70.15	3.31	5.11
	$(821.83)_n$	Found	70.92	3.58	4.62
7-Ha	$(C_{42}H_{23}N_3O_7)_n$	Calcd	74.00	3.40	6.16
	$(681.66)_n$	Found	74.73	3.79	5.50
7-Hb	$(C_{48}H_{27}N_3O_7)_n$	Calcd	76.08	3.59	5.55
	$(757.76)_n$	Found	76.82	3.77	5.01
7-Hc	$(C_{48}H_{27}N_3O_8)_n$	Calcd	74.51	3.52	5.43
	$(849.86)_n$	Found	75.58	3.76	4.89
7-Hd	$(C_{49}H_{27}N_3O_8)_n$	Calcd	74.90	3.46	5.35
	$(785.77)_n$	Found	75.34	3.65	4.83
7-He	$(C_{48}H_{27}N_3O_9S)_n$	Calcd	70.15	3.31	5.11
	$(821.83)_n$	Found	70.92	3.58	4.62

[a] Polyimides **7-Ca–e** and **7-Ha–e** were prepared through chemical and thermal cyclodehydration, respectively

Properties of polyamides

The solubility of polymers **4a–g** was tested in various solvents at room temperature, and the results are summarized in *Table 5*. Almost all of the polyamides were readily soluble in polar solvents such as DMAc, DMF, NMP and DMSO, and even in pyridine, *o*-chlorophenol and *m*-cresol. Their high-solubility nature is attributed to the introduction of bulky phthalimidine and aryl ether units along the polymer backbone. Moreover, polyamides **4f** and **4g** are found to have

Table 5 Solubility of polyamides[a]

Solvent	Polymer 4a	4b	4c	4d	4e	4f	4g
Dimethylacetamide	+	+	+	+	+	+	+
Dimethylformamide	+	+	+	+	+	+	+
Dimethylsulfoxide	+	+	+	+	+	+	+
N-Methyl-2-pyrrolidone	+	+	+	+	+	+	+
Pyridine	+	+	+	+	+	+	+
m-Cresol	+	+	+	+	+	+	+
Tetrahydrofuran	–	–	–	–	–	+	+

[a] (+) Soluble at room temperature, (–) insoluble

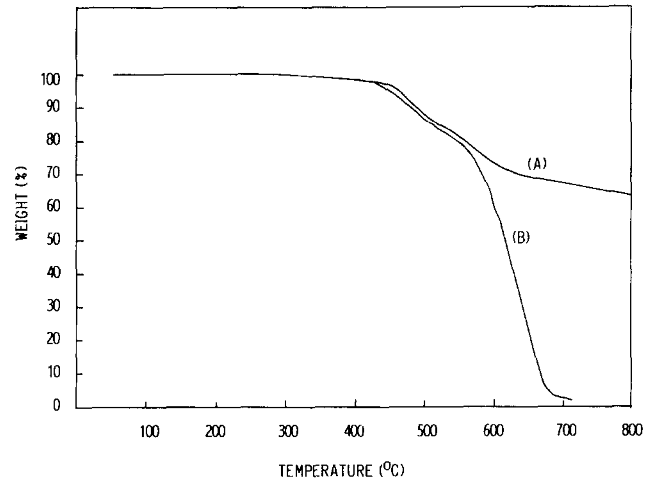


Figure 1 T.g.a. curves for aromatic polyamide **4a** at a heating rate of 20°C min^{-1} in (A) nitrogen and (B) air

higher solubility in tetrahydrofuran compared with other polyamides of similar structure, which may be due to the presence of sulfonyl and hexafluoroisopropylidene moieties, but all the polymers were entirely insoluble in chloroform, benzene and methanol. The X-ray diffraction studies of the polymers show that all the polyamides exhibit an amorphous pattern. In general most of the cardo polymers are amorphous, primarily because of the bulky pendent structure.

The thermal behaviour of these polymers was evaluated by means of t.g.a. and d.s.c. The t.g.a. curves for these polymers, typical ones of which are shown in *Figure 1*, indicated that all of the polyamides did not lose weight below 450°C in nitrogen. The 10% decomposition temperatures both in air and in nitrogen atmosphere and the char yield at 800°C in nitrogen are summarized in *Table 6*. In nitrogen or an air atmosphere, the 10% weight-loss temperatures are about 476–516°C or 464–484°C, respectively. The amount of carbonized residue of polyamides in nitrogen atmosphere was more than 60 wt% even at 800°C. The polyamides bearing phthalimidine cardo groups (**4a–g**) were more thermally stable in comparison with the similar structure of polyamides with phthalide cardo groups[7]. This difference is probably due to the structural differences between cardo groups, in that the cyclic amide group has better thermal resistance than the cyclic ester group.

The glass transition temperatures (T_g) of polyamides **4a–g** were 307–338°C, determined by d.s.c., and decreased with decreasing rigidity and symmetry of the polymer backbone. The higher T_g values of polymers **4f** and **4g** can probably be attributed to the increase of intermolecular forces by the sulfonyl and hexafluoroisopropylidene groups.

Tough and flexible films of the soluble polyamides could be obtained by casting from their DMAc solutions. *Table 7* lists the tensile properties of the polyamide films. The films had tensile strength of 68–78 MPa, elongation at break of 7–31% and tensile modulus of 1.53–1.89 GPa.

Properties of polyimides

The solubility of the polyimides seems to depend on the route of cyclodehydration of the poly(amic acid)s to polyimides. The solubility of polyimides **7-Ha–e** and **7-Ca–e** prepared by thermal and chemical conversion procedures, respectively, was studied qualitatively and the results are listed in *Table 8*. Except for **7-Ca**, most of the resultant polyimides made by chemical cyclodehydration were soluble in organic solvents such as DMAc, NMP and *o*-chlorophenol. When the chemically imidized polyimides were heated at 250°C for another 30 min in an air oven to achieve complete imidization, their solubility did not change and was the same as for the corresponding polyimides **7-Ca–e**. However, polymers **7-Ha–e** prepared by thermal cyclodehydration had limited solubility. This result was the same as for the corresponding polyimides prepared by thermal cyclodehydration starting from 9,9-bis[4-(4-aminophenoxy)phenyl]fluorene[6], 3,3-bis[4-(4-aminophenoxy)-phenyl]phthalide[7] and *N*-phenyl-3,3-bis[4-(4-aminophenoxy)phenyl]phthalimidine[8] with various aromatic dianhydrides, which had poorer solubility than those

Table 6 Thermal behaviour data of polyamides

Polymer	D.s.c. T_g[a] (°C)	T.g.a. Decomposition temperature[b] (°C) In air	In nitrogen	Residue (wt%) at 800°C
4a	323	480	489	64
4b	307	464	483	62
4c	317	478	483	60
4d	331	483	516	66
4e	338	484	500	67
4f	326	480	476	61
4g	318	483	494	65

[a] From the second heating traces of d.s.c. measurements conducted with a heating rate of 20°C min^{-1} in nitrogen

[b] Temperature at which a 10% weight loss was recorded by t.g.a. at a heating rate of 20°C min^{-1}

Table 7 Tensile properties of polyamide films

Polymer[a]	Strength at yield (MPa)	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
4a	–	73	13	1.89
4b	–	75	7	1.53
4c	–	75	13	1.66
4d	–	74	13	1.72
4e	–	78	13	1.71
4f	–	76	11	1.65
4g	74	68	31	1.55

[a] Films were cast from polymer solutions of DMAc

Table 8 Solubility of polyimides[a] in various solvents[b]

Polymer	DMAc	DMF	DMSO	NMP	*m*-Cresol	*o*-Chlorophenol	Py	Conc. H_2SO_4
7-Ca	– –	– –	– –	+ +	+ –	+ +	– –	+ +
7-Ha	– –	– –	– –	– –	– –	+ +	– –	+ +
7-Cb	+ +	+ –	+ –	+ +	+ +	+ +	+ +	+ +
7-Hb	– –	– –	– –	– –	– –	– –	– –	+ +
7-Cc	+ +	+ +	+ +	+ +	– –	+ +	+ +	+ +
7-Hc	– –	– –	– –	– –	– –	– –	– –	+ +
7-Cd	+ +	+ –	– –	+ +	+ +	+ +	+ +	+ +
7-Hd	– –	– –	– –	– –	– –	– –	– –	+ +
7-Ce	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
7-He	+ +	+ +	– –	+ +	– –	+ +	– –	+ +

[a] Solubility (+ +) soluble at room temperature, (+ –) partially soluble or swollen, (– –) insoluble

[b] DMAc = *N*, *N*-dimethylacetamide; DMF = *N*, *N*-dimethylformamide; DMSO = dimethylsulfoxide; NMP = *N*-methyl-2-pyrrolidone; Py = pyridine

Table 9 Thermal behaviour data of polyimides

	D.s.c.	T.g.a.		
	T_g[a]	Decomposition temperature[b] (°C)		
Polymer	(°C)	In air	In nitrogen	Residue (wt%) at 800°C
7-Ha	347	541	544	58
7-Hb	305	557	555	62
7-Hc	288	541	542	58
7-Hd	286	554	551	59
7-He	297	515	519	49

[a] From the second heating traces of d.s.c. measurements conducted with a heating rate of 20°C min^{-1} in nitrogen

[b] Temperature at which a 10% weight loss was recorded by t.g.a. at a heating rate of 20°C min^{-1}

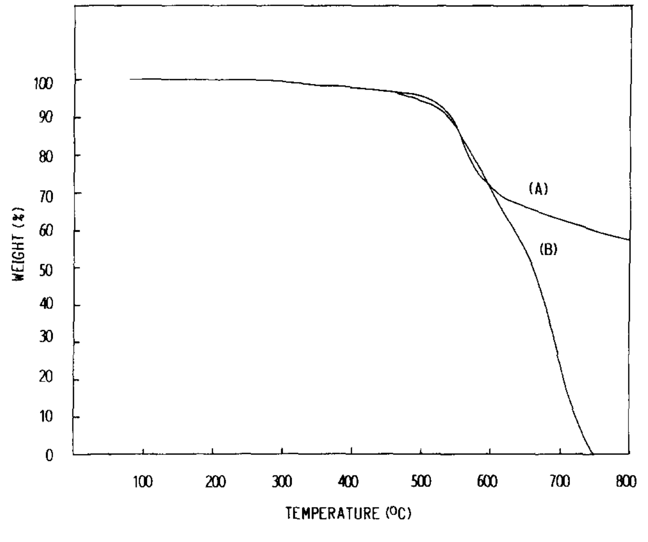


Figure 2 T.g.a. curves for polyimide **7-Ha** at a heating rate of 20°C min^{-1} (A) nitrogen and (B) air

from the chemical cyclodehydration method. The difference in solubility for the thermally and chemically converted polyimides containing the bis(phenoxy)-phthalimidine unit is attributed to the extent of molecular aggregation of thermally imidized polyimides during the cyclodehydration of corresponding poly(amic acid)s. All of the polyimides **7-Ha–e** were practically amorphous as evidenced by the X-ray diffraction studies.

Table 10 Tensile properties of polyimide films prepared by thermal conversion method

Polymer	Strength at break (MPa)	Elongation to break (%)	Initial modulus (GPa)
7-Ha	106	7	2.49
7-Hb	110	9	2.41
7-Hc	107	8	2.13
7-Hd	105	10	2.17
7-He	93	4	2.31

The thermal properties of the polyimides prepared by thermal cyclodehydration are summarized in *Table 9*. Representative thermograms are shown in *Figure 2*. All the polyimides showed a similar pattern of decomposition with no significant weight loss below 500°C under air or nitrogen. The char yields of these polyimides at 800°C in nitrogen were up to 62%. The tetracarboxylic dianhydrides had a significant influence on the thermal and thermo-oxidative stability of the polyimides. Based on the 10% weight-loss temperatures in nitrogen, the following relative order of thermal stability was observed: **7-Hb** > **7-Hd** > **7-Ha** > **7-Hc** > **7-He**. The SDPA-derived polyimide **7-He** having sulfonyl connecting group had the lowest decomposition temperature and aerobic char yield. The polyimides had glass transition temperatures in the 286–347°C range. This order was quite comparable to the decreasing order of stiffness and polarity of the polymer backbones.

Table 10 summarizes the tensile properties of the aromatic polyimide films prepared by the thermal conversion method. The films had tensile strength of 93–110 MPa, elongation at break of 4–10% and tensile modulus of 2.13–2.49 GPa.

CONCLUSIONS

The introduction of aryl ether phthalimidine segments into aromatic polymer backbones resulted in aromatic polyamides and polyimides with good thermal stability as well as excellent solubility in organic solvents. Thus, the present aromatic polymers are considered as new candidates for processable high-performance polymeric materials.

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