Polymer Vol. 37 No. 15, pp. 3331–3337, 1996
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0032-3861/96/$15.00 + 0.00

Aromatic polyamides and polyimides bearing bulky ether pendent groups derived from 1-aryloxy-2,4-diaminobenzenes

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(Received 21 December 1995)

Two new diamines, 1-(1-naphthoxy)-2,4-diaminobenzene and 1-(biphenylyl-4-oxy)-2,4-diaminobenzene, were synthesized and used for the preparation of modified polyamides and polyimides bearing bulky ether groups. Their properties were compared with those of the corresponding unmodified polymers. Characterization of polymers was accomplished by inherent viscosity measurements, Fourier transform infra-red, ^{1}H nuclear magnetic resonance, X-ray, differential thermal and thermomechanical, thermogravimetric and isothermal gravimetric analyses. The modified polyamides and polyimides showed considerably higher solubility than analogous unsubstituted polymers and dissolved in polar aprotic solvents and certain inorganic and organic acids upon heating or even at room temperature in some cases. The incorporation of the ether groups along the polymer backbone decreased the glass transition temperatures, which ranged from 110 to 195°C. In addition, certain modified polymers softened at the region 190–273°C. The modified polymers were more thermally stable than the parent counterparts, being stable up to 350–404°C and affording char yields of 59–70% at 800°C in N_2. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyamides; polyimides; modification)

INTRODUCTION

Aromatic polyamides and polyimides have already been noted for their high temperature resistance and excellent mechanical properties[1]. They are also known as difficult processable materials due to their high glass transition (T_g) and softening (T_s) temperatures. The second problem arising for these polymers is their limited solubility in common organic solvents.

Since the above described problems restrict the further applications of the aromatic polyamides and polyimides, considerable effort has been made to improve their properties by structural modification. One of the approaches to increasing solubility and lowering T_g and T_s is the incorporation of bulky pendent groups along the polymer backbone. Many polymers such as polyterephthalamides[2], polyisophthalamides[3,4], polyterephthalates[5], polyimides[6] and other polyheterocycles[7] have been structurally modified by polymerization or copolymerization of monomers containing bulky pendent groups. In addition, polyamides with phenoxy[8,9] and phenylthio[9,10] groups have been reported.

Recently we have reported the synthesis of aromatic polyamides and polyimides with benzoxazole or benzothiazole[11], *N*-benzylidene[12], phthalimide[13], furamido[14], ester[15] and amide[16] pendent groups.

The present work deals with the synthesis and characterization of polyamides and polyimides with ether pendent groups. The well known thermally stable and flexible ether bond is expected to provide desired properties to the substituted polymers. Properties such as thermal stability, solubility, T_g and T_s attracted the main interest.

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. Fourier-transform infra-red (*FT* i.r.) spectra were recorded on a Perkin-Elmer 16PC *FT* i.r. spectrometer with KBr pellets. Nuclear magnetic resonance (^{1}H-n.m.r.) spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in ppm with tetramethylsilane as an internal standard. Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) were performed on a DuPont 990 thermal analyser. D.t.a. measurements were made using a high temperature (1200°C) cell at a heating rate of 20°C min^{-1} in N_2 atmosphere at a flow rate of 60 cm^3 min^{-1} and with a ΔT sensitivity of 0.5°C in^{-1}. Dynamic t.g.a. measurements were made at a heating rate of 20°C min^{-1} in atmospheres of N_2 or air at a flow rate of 60 cm^3 min^{-1}. Thermomechanical analysis (t.m.a.) was recorded on a DuPont 943 t.m.a. using a loaded penetration probe at a scan rate of 20°C min^{-1} in N_2 with a flow rate of 60 cm^3 min^{-1}. The t.m.a. experiments were conducted in duplicate. The t.m.a. specimens were pellets of 8 mm diameter and 2 mm

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thickness prepared by pressing powder of polymer for 3 min under 5–7 kpsi at ambient temperature. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 ml in *N,N*-dimethylacetamide (DMAc) at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyser. The wide angle X-ray diffraction (WAXD) patterns were obtained for powder specimens on a X-ray PW-1840 Philips diffractometer.

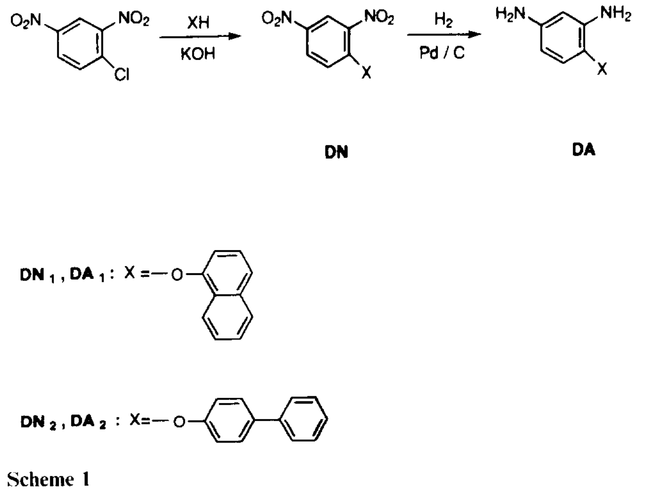
To determine the equilibrium water absorption, polymer samples were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator where 65% relative humidity (r.h.) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20°C, and were periodically weighed.

Reagents and solvents

1-Chloro-2,4-dinitrobenzene, 1-naphthol and biphenyl-4-ol were recrystallized from methanol, distilled water, and ethanol 50%, respectively. Terephthaloyl chloride was recrystallized from *n*-hexane. Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Triethylamine and dimethylacetamide (DMAc) were dried by distillation over KOH and CaH_2, respectively.

Preparation of starting materials (Scheme 1)

1-(1-Naphthoxy)-2,4-diaminobenzene (DA$_1$). 1-Chloro-2,4-dinitrobenzene (4.4561 g, 22.0 mmol) was added to a solution of 1-naphthol (3.7440 g, 26.0 mmol) and potassium hydroxide (1.4028 g, 25.0 mmol) in ethanol 95% (20 ml). The mixture was refluxed overnight. Next it was poured into water and stirred for about 30 min. The yellow solid precipitate was filtered off, washed with water and dried to afford DN$_1$ (6.69 g, 85%). It was purified by recrystallization from a mixture of CH_3CN/EtOH (1 : 1 v/v). M.p. 124–128°C. Anal. Calcd. for $C_{16}H_{10}N_2O_5$: C, 61.94%; H, 3.25%; N, 9.03%. Found: C, 61.72%; H, 3.29%; N, 10.08%. I.r. (KBr, cm^{-1}): 1608 (aromatic); 1534, 1346 (NO_2); 1480 (aromatic); 1388 (naphthyl ring); 1268 (C–O–C). ^1H n.m.r. (DMSO-d_6) δ: 8.47 (s, 1H, aromatic of position 3 of dinitrobenzene ring); 7.77–7.22 (m, 7H, aromatic of positions 5 and 6 of dinitrobenzene ring and of positions 4, 5, 6, 7 and 8 of naphthyl segment); 6.78–6.63 (m, 2H, aromatic of positions 2 and 3 of naphthyl segment).



Scheme 1

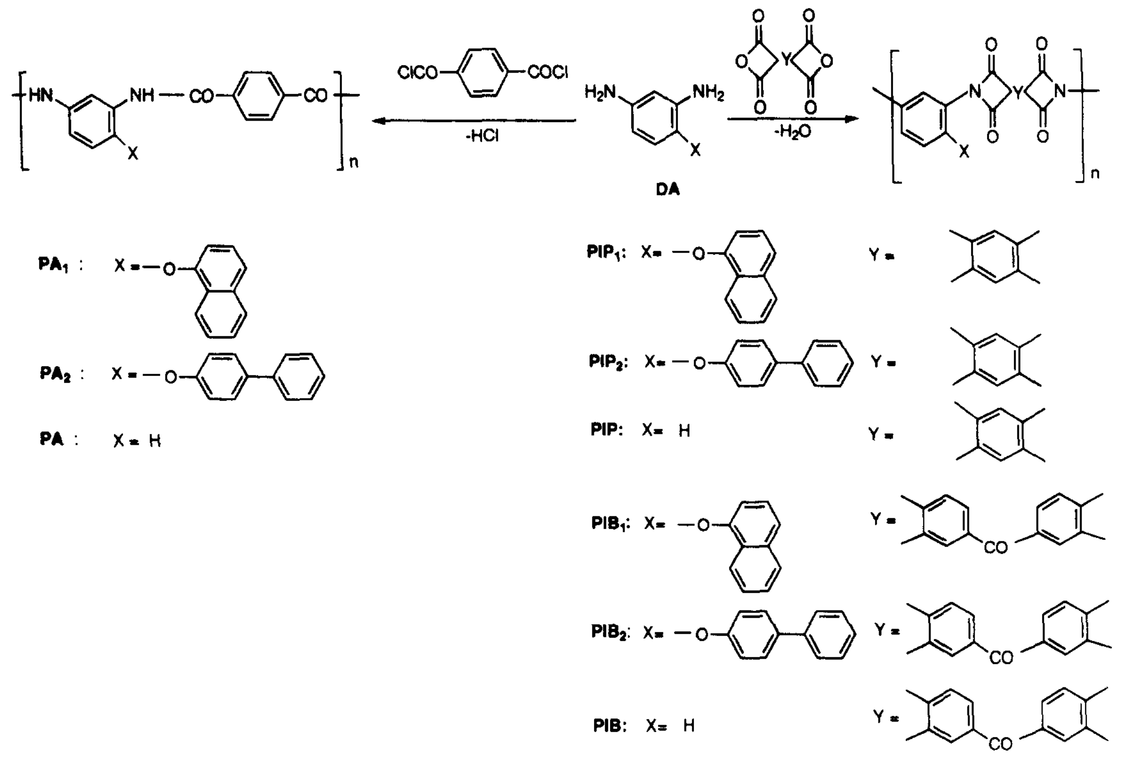
A hydrogenation flask was charged with a mixture of compound DN$_1$ (2.30 g, 7.4 mmol), ethanol 95% (15 ml) and a catalytic amount of 10% palladium on activated carbon. The hydrogenation was carried out on a Parr apparatus under a pressure of about 2 atm at ambient temperature until no more hydrogen was taken up (ca. 5 h). The solid gradually dissolved during hydrogenation. The catalyst was removed by filtration and the solution was concentrated in a rotary evaporator and poured into water. The brown solid precipitate was filtered off, washed with water and dried to afford DA$_1$ (1.75 g, 95%). A purified sample was obtained by recrystallization from a mixture of toluene/$CHCl_3$ (2 : 1 v/v). M.p. 76–79°C. Anal. Calcd. for $C_{16}H_{14}N_2O$: C, 76.78%; H, 5.64%; N, 11.19%. Found: C, 76.55%; H, 5.58%; N, 11.32%. I.r. (KBr, cm^{-1}): 3356–3220 (N–H stretching); 1620 (N–H deformation); 1596, 1506, 1460 (aromatic); 1392 (naphthyl ring); 1260 (C–N stretching); 1218 (C–O–C). ^1H n.m.r. (DMSO-d_6) δ: 7.80–7.27 (m, 7H, aromatic of naphthyl segment); 6.53–6.38 (m, 2H, aromatic of positions 5 and 6 of 1,3-phenylenediamine ring); 6.00 (s, 1H, aromatic of position 3 of 1,3-phenylenediamine ring); 4.47 (br, 4H, NH_2).

1-(Biphenylyl-4-oxy)-2,4-dinitrobenzene (DA$_2$). Compound DN$_2$ was obtained as a yellow solid in 62% yield (4.82 g) by reacting 1-chloro-2,4-dinitrobenzene (4.6589 g, 23.0 mmol) with a solution of biphenyl-4-ol (5.1000 g, 30.0 mmol) and potassium hydroxide (1.4028 g, 25.0 mmol) in ethanol 95% (20 ml) according to the procedure described for DN$_1$. It was recrystallized from a mixture of CH_3CN/MeOH (1 : 4 v/v). M.p. 112–115°C. Anal. Calcd. for $C_{18}H_{12}N_2O_5$: C, 64.29%; H, 3.60%; N, 8.33%. Found: C, 64.13%; H, 3.54%; N, 8.22%. I.r. (KBr, cm^{-1}): 1610 (aromatic); 1522, 1342 (NO_2); 1482 (aromatic); 1246 (C–O–C). ^1H n.m.r. (DMSO-d_6) δ: 8.57 (s, 1H, aromatic of position 3 of 1,3-dinitrobenzene ring); 8.03–6.90 (m, 11H, other aromatic).

Compound DN$_2$ was catalytically hydrogenated in ethanol 95% on a Parr apparatus according to the procedure described for DA$_1$. The catalyst was removed by filtering the hot reaction mixture, because the product precipitated at the end of hydrogenation. DA$_2$ was obtained as a brown solid in 94% yield (1.73 g) and it was recrystallized from a mixture of EtOH/water (2 : 1 v/v). M.p. 135–137°C. Anal. Calcd. for $C_{18}H_{16}N_2O$: C, 78.24%; H, 5.84%; N, 10.14%. Found: C, 77.97%; H, 5.75%; N, 10.26%. I.r. (KBr, cm^{-1}): 3422–3342 (N–H stretching); 1620 (N–H deformation and aromatic); 1510, 1484 (aromatic); 1220 (C–N stretching and C–O–C). ^1H n.m.r. (DMSO-d_6) δ: 7.60–7.25 (m, 5H, aromatic of positions 2′, 3′,4′, 5′ and 6′ of biphenyl segment); 6.93 (s, 2H, aromatic of positions 2 and 6 of biphenyl segment); 6.80 (s, 2H, aromatic of positions 3 and 5 of biphenyl segment); 6.72 (s, 1H, aromatic of position 6 of 1,3-phenylenediamine ring); 6.64 (s, 1H, aromatic of position 5 of 1,3-phenylenediamine ring); 6.07 (s, 1H, aromatic of position 3 of 1,3-phenylenediamine ring); 4.50 (br, 4H, NH_2).

Preparation of polymers (Scheme 2)

A typical procedure for the preparation of polyamide PA$_1$ is as follows: A flask equipped with magnetic stirrer was charged with a solution of DA$_1$ (0.8000 g, 3.2 mmol)



Scheme 2

and triethylamine (0.6476 g, 6.4 mmol) in DMAc (7 ml). Terephthaloyl chloride (0.6479 g, 3.2 mmol) dissolved in DMAc (5 ml) was added dropwise to stirred solution at −10°C under N_2. Stirring of the mixture was continued at room temperature in a stream of N_2 for 4 h. It was subsequently poured into water and the brown solid precipitate was filtered off, washed with water then with acetone and dried to afford PA_1.

A typical procedure for the preparation of polyimide PIP_1 is as follows: Granual PMDA (0.6540 g, 3.0 mmol) was added to a stirred solution of DA_1 (0.8280 g, 3.0 mmol) in DMAc (10 ml) at 0°C. The solution became viscous, and stirring was continued at room temperature for 3 h under N_2. Acetic anhydride (5 ml) and fused sodium acetate (0.2 g) were added to the solution and it was heated at 100°C overnight. It was subsequently poured into water and the brown solid obtained was filtered off, washed with water and dried to afford PIP_1.

The reaction yields, the inherent viscosities and the elemental analyses for all polyamides and polyimides are listed in *Table 1*.

RESULTS AND DISCUSSION

Scheme 1 outlines the synthetic route applied for the preparation of two new aromatic diamines bearing bulky pendent ether groups. Specifically, 1-chloro-2,4-dinitrobenzene reacted in ethanol 95% with the potassium naphthoxide prepared *in situ* from 1-naphthol and potassium hydroxide to afford DN_1. Since 1-naphthol has higher acidity than ethanol, a slight excess of 1-naphthol with respect to potassium hydroxide was used to avoid the formation of potassium ethoxide. The catalytic hydrogenation of DN_1 in ethanol 95% yielded DA_1. Diamine DA_2 was similarly synthesized utilizing biphenyl-4-ol instead of 1-naphthol.

Table 1 Yields, inherent viscosities and elemental analyses of polyamides and polyimides

Polymer	Yield (%)	η_{inh}[a] (dl g^{-1})	Empirical formula		Elemental analyses		
					C (%)	H (%)	N (%)
PA_1	97	1.28	$(C_{24}H_{16}N_2O_3)_n$	Calcd	75.78	4.24	7.36
				Found	75.55	4.18	7.27
PA_2	95	1.38	$(C_{26}H_{18}N_2O_3)_n$	Calcd	76.83	4.46	6.89
				Found	76.54	4.35	6.96
PIP_1	95	1.17	$(C_{26}H_{12}N_2O_5)_n$	Calcd	72.22	2.80	6.48
				Found	71.87	2.71	6.34
PIP_2	94	1.02	$(C_{28}H_{14}N_2O_5)_n$	Calcd	73.36	3.08	6.11
				Found	73.12	2.96	5.97
PIB_1	97	1.22	$(C_{33}H_{16}N_2O_6)_n$	Calcd	73.88	3.01	5.22
				Found	73.70	2.94	5.05
PIB_2	96	1.18	$(C_{35}H_{18}N_2O_6)_n$	Calcd	74.73	3.23	4.98
				Found	74.54	3.15	4.84

[a] Inherent viscosity in DMAc (0.5 g dl^{-1}) at 30°C

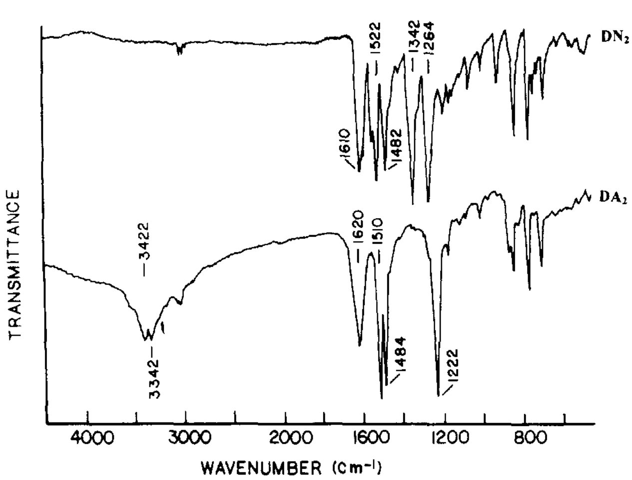


Figure 1 *FT* i.r. spectra of compounds DN_2 and DA_2

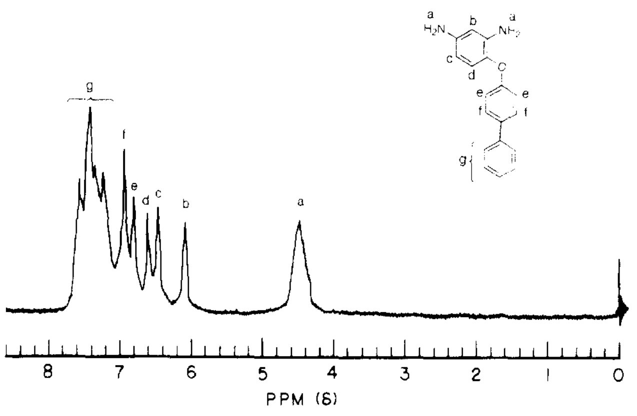


Figure 2 ^1H n.m.r. spectrum of compound DA_2 in DMSO-d_6 solution

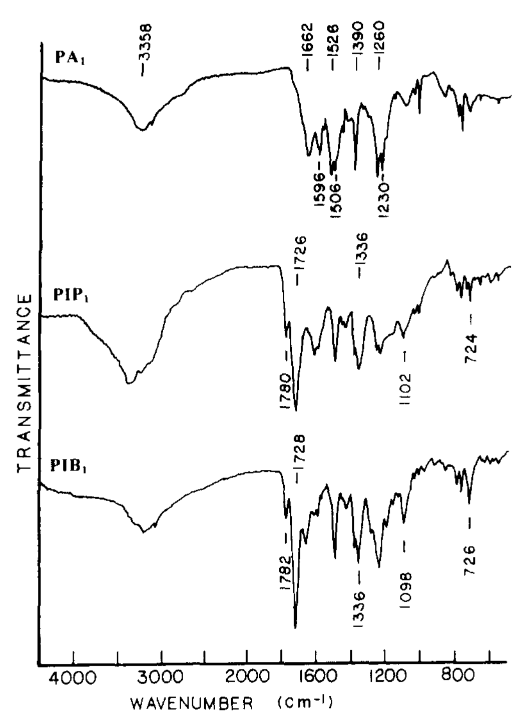


Figure 3 *FT* i.r. spectra of polyamide PA_1 as well as of polyimides PIP_1 and PIB_1

A new class of modified polyamides and polyimides were prepared utilizing diamines DA_1 and DA_2 as starting materials (*Scheme 2*). More particularly, these diamines reacted with terephthaloyl chloride by the solution polycondensation method to afford polyamides PA_1 and PA_2 respectively. In addition, the reactions of diamine DA_1 with PMDA and BTDA afforded polyimides PIP_1 and PIB_1 respectively. Similarly polyimides PIP_2 and PIB_2 were prepared by reacting DA_2 with these tetracarboxylic acid dianhydrides. Their intermediate poly(amic acid)s were cyclodehydrated by heating in the presence of acetic anhydride and sodium acetate.

The corresponding unmodified polymers were also synthesized to compare their physical and thermal properties with those of the modified ones. Particularly, polyamide PA (n_{inh} $1.32\,dl\,g^{-1}$ in DMAc) was prepared from 1,3-phenylenediamine and terephthaloyl chloride. Finally, polyimides PIP and PIB were synthesized from 1,3-phenylenediamine by reacting with PMDA and BTDA, respectively. Since polyimides PIP and PIB were partially soluble in polar aprotic solvents, the n_{inh} of their intermediate poly(amic acid)s were determined. They were 1.07 and $1.13\,dl\,g^{-1}$, respectively, in DMAc.

The monomers were characterized by elemental analyses as well as i.r. and ^1H n.m.r. spectroscopy. *Figure 1* presents typical *FT* i.r. spectra of compounds DN_2 and DA_2. Both compounds showed an absorption band around $1240\,cm^{-1}$ associated with an ether bond. Compound DN_2 displayed absorptions at 1522 and $1342\,cm^{-1}$ assigned to the nitro groups. The lack of these absorptions in DA_2 confirmed the complete hydrogenation of the nitro groups. DA_2 showed new absorption bands at 3422–3342 (N–H stretching) and $1620\,cm^{-1}$ (N–H deformation).

Figure 2 shows the ^1H n.m.r. spectrum of DA_2 in a DMSO-d_6 solution. It displayed multiplets at 7.60–6.80 (protons of biphenyl segment), 6.72, 6.64 and 6.07 (protons of positions 6, 5 and 3, respectively, of 1,3-phenylenediamine ring) as well as a broad at 4.50 ppm (NH_2). The protons of amino groups were exchangeable with D_2O.

The modified polymers were obtained in 94–97% yields and their n_{inh} values ranged from 1.38 to $1.02\,dl\,g^{-1}$. Their characterization was accomplished by i.r., ^1H n.m.r., X-ray, d.t.a., t.m.a., t.g.a. and isothermal gravimetric analysis (i.g.a.).

Figure 3 presents the *FT* i.r. spectra of polyamide PA_1 as well as of polyimides PIP_1 and PIB_1. PA_1 showed characteristic absorption bands at 3358 (N–H stretching); 1662 (C=O); 1596, 1506 (aromatic); 1526 (N–H deformation); 1390 (naphthyl ring); 1260 (C–N stretching and N–H bending) and $1230\,cm^{-1}$ (ether bond). PIP_1 and PIB_1 displayed absorptions associated with the imide structure. In the case of PIP_1, they appeared at 1780, 1726, 1336, 1102 and $724\,cm^{-1}$. The absorption at $1240\,cm^{-1}$ was assigned to the ether bonds.

Since all the polymers were soluble at room temperature or upon heating in polar aprotic solvents (see below), their ^1H n.m.r. spectra could be recorded. The ^1H n.m.r. spectra of the polymers were in agreement with the proposed structures. A typical ^1H n.m.r. spectrum of polyamide PA_2 in a DMSO-d_6 solution showed a singlet at 10.38 (NHCO), multiplets centered at 7.80 (aromatic of terephthalic acid segments) and multiplets

Table 2 Solubilities of polymers[a]

	Solvents[b]								
Polymer	DMF	NMP	DMSO	CCl_3COOH	H_2SO_4	1,4-Diozane	CH_3CN	CH	m-Cresol
PA_1	++	++	++	++	++	+	+−	+	+
PA	+	+	+	+	+	−	−	−	−
PIP_1	+	+	+	++	−	−	−	+−	−
PIP	+−	+−	+−	+−	+	−	−	−	−
PIB_1	++	++	++	++	−	+−	−	+−	+
PIB	+−	+−	+−	+−	+	−	−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +−, partially soluble; −, insoluble
[b] DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulfoxide; CH, cyclohexanone

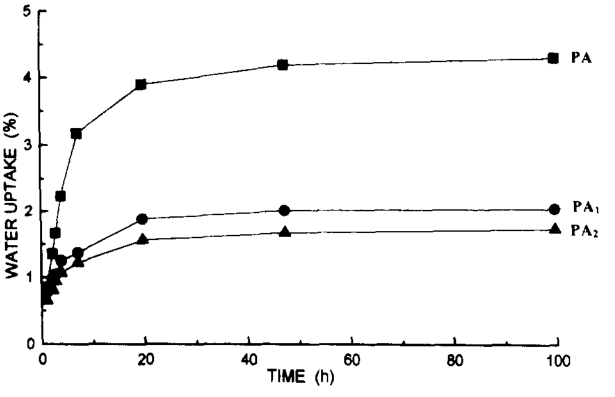


Figure 4 Water absorption (%) *versus* time for polyamides PA_1, PA_2 and PA

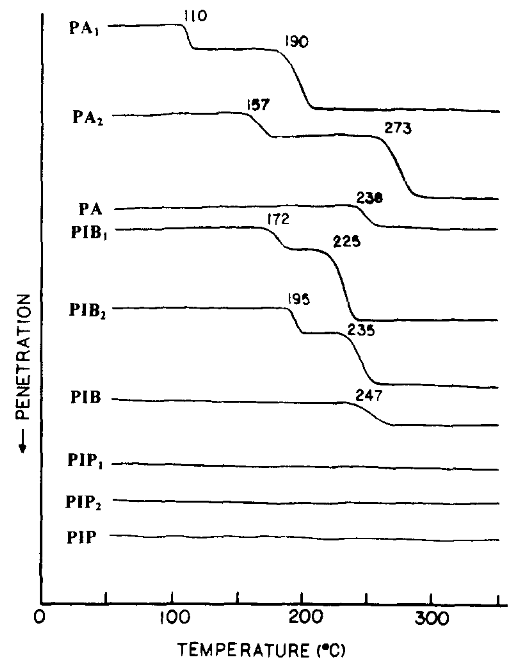


Figure 5 T.m.a. thermograms for both modified and unmodified polymers. Conditions: N_2 flow, 60 cm^3 min^{-1}; heating rate, 20°C min^{-1}

at 7.40–6.90 ppm (aromatic of 1,3-phenylenediamine rings and biphenyl moieties).

One of the main objectives of the present investigation was the improvement of the polymer solubility due to their bulky pendent groups. *Table 2* presents the solubilities of modified polymers PA_1, PIP_1 and PIB_1 as well as of the corresponding unmodified ones. It is seen that the structural modification of polymers enchanced their solubility. Specifically, PA_1 was soluble at room temperature in polar aprotic solvents (DMF, NMP, DMSO) and certain acids (H_2SO_4, CCl_3COOH) and upon heating in *m*-cresol, 1,4-dioxane and cyclohexanone. In contrast, PA dissolved only in hot polar aprotic solvents and acids. PIB_1 displayed better solubility in most solvents than PIP_1. Note that PIB_1 was readily soluble even at ambient temperature in polar aprotic solvents and certain acids. The modified polymers PA_2, PIP_2 and PIB_2 containing biphenylyl-4-oxy pendent groups showed comparable solubilities with the corresponding polymers bearing 1-naphthoxy segments.

The enhanced solubility of modified polymers was in line with their amorphous character which was confirmed from the WAXD. The voluminous ether pendent groups along the polymer backbone was responsible for this behaviour. The optimized geometry for two repeating units of the macromolecule of PA_1, as calculated by means of CSC ChemDraw PlusΣ Molecular Modelling System, revealed that the bulky side groups increased remarkably the disorder in the chain packing.

The hydrophilicity of polyamides was estimated by measuring their equilibrium water absorption as a function of the time exposed (*Figure 4*). Polyamides PA, PA_1 and PA_2 showed a water uptake of 4.30, 2.04 and 1.95%, respectively, after 100 h exposure time. The corresponding number of moles of absorbed water per amide equivalent weight for these polyamides was 0.90, 0.21 and 0.20. The number of equilibrium of water absorption was significantly lower for the modified polyamides PA_1 and PA_2 than for the unmodified one PA. This feature could be attributed to the inter- and intra-molecular hydrogen bonding between the amide and ether groups which competes with the amide–water hydrogen bonds. An analogous behaviour has been observed in polyisophthalamides with phenoxy pendent groups[8,10].

T_gs and T_ss of polymers were determined by the t.m.a. method, using a suitably loaded penetration probe. *Figure 5* shows the t.m.a. traces in N_2 for both modified and unmodified polymers. The T_g and T_s values were determined from the onset temperatures of transitions and are listed in *Table 3*. No transition was detected up to approximately 350°C for the polyimides PIP_1, PIP_2 and PIP derived from PMDA. In the case of PA and PIB, only T_g transition was obtained. It is seen that the modified polymers displayed lower T_g than the parent polymers, which conforms with literature data[8,9]. On

Table 3 T.g.a. and t.m.a. data

	T.g.a.								
	In N_2				In air			T.m.a.	
Polymer	*IDT*[a] (°C)	*PDT*[b] (°C)	PDT_{max}[c] (°C)	Yc[d] (%)	*IDT* (°C)	*PDT* (°C)	PDT_{max} (°C)	T_g[e] (°C)	T_s[f] (°C)
PA_1	350	457	517	62	340	456	533	110	190
PA_2	359	471	508	70	348	449	513	157	273
PA	347	450	505	45	333	417	498	238	
PIB_1	396	547	563	64	380	539	587	172	225
PIB_2	394	555	571	64	389	533	595	195	235
PIB	382	533	600	54	375	502	591	247	
PIP_1	398	530	557	60	389	548	554		
PIP_2	404	550	563	59	391	559	577		
PIP	392	521	547	55	373	506	577		

[a] Initial decomposition temperature
[b] Polymer decomposition temperature
[c] Maximum polymer decomposition temperature
[d] Char yield at 800°C
[e] Glass transition temperature
[f] Softening temperature

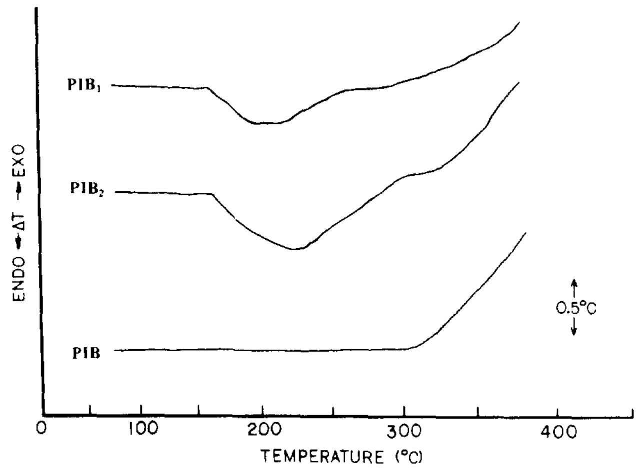


Figure 6 D.t.a. traces of polyimides PIB_1, PIB_2 and PIB. Conditions: N_2 flow, 60 cm^3 min^{-1}; heating rate, 20°C min^{-1}

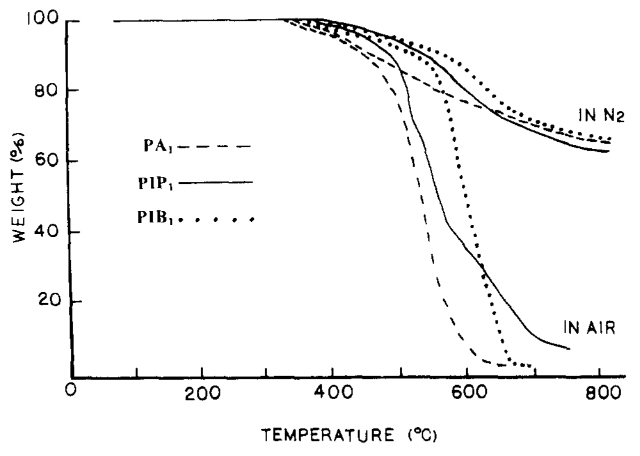


Figure 7 T.g.a. thermograms in N_2 and air of polyamide PA_1 and polyimides PIP_1 and PIB_1. Conditions: gas flow, 60 cm^3 min^{-1}; heating rate, 20°C min^{-1}

the other hand, the modified polyamides as well as the polyimides of BTDA showed a T_s in the region 190–273°C.

The thermal behaviour of polymers was also investigated by d.t.a. in N_2. *Figure 6* presents typical d.t.a. curves for polyimides PIB_1, PIB_2 and PIB. The modified polyimides exhibited a broad endotherm at 220–240°C associated with their softening. In contrast, the unmodified polyimide did not display any endotherm up to 300°C. The T_s values determined by d.t.a. were in agreement with those of t.m.a. The d.t.a. scans of polymers did not exhibit T_g transitions even when they repeated after heating at 270°C. The limited sensitivity of the utilized high temperature d.t.a. cell contributed to this feature.

The thermal stabilities of polymers was investigated using t.g.a. and i.g.a. *Figure 7* shows representative t.g.a. thermograms of polymers PA_1, PIP_1 and PIB_1. The initial decomposition temperature (*IDT*), the polymer decomposition temperature (*PDT*), the maximum polymer decomposition temperature (PDT_{max}) in both N_2 and air as well as the anaerobic char yield (Y_c) at 800°C for all polymers are summarized in *Table 3*. The *IDT* and *PDT* were determined for the temperature at which 0.5 and 10% weight loss was observed respectively. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

The modified polymers were more thermally stable than their unmodified counterparts, since their *IDT* and *PDT* in both N_2 and air as well as the anaerobic Y_c at 800°C were higher. Upon comparing the chemical structures of the pendent groups, it is seen that biphenylyl-4-oxy was more stable than 1-phenoxy.

The higher thermal stability of the modified polymers in comparison to that of the analogous unmodified was verified by i.g.a. *Figure 8* shows typical i.g.a. traces for the polymers PA_2, PA, PIP_2, PIP, PIB_2 and PIB at 310°C in static air. After 20 h isothermal ageing, they displayed weight losses of 23.6, 25.6, 15.0, 18.7, 9.6 and 17.1% respectively.

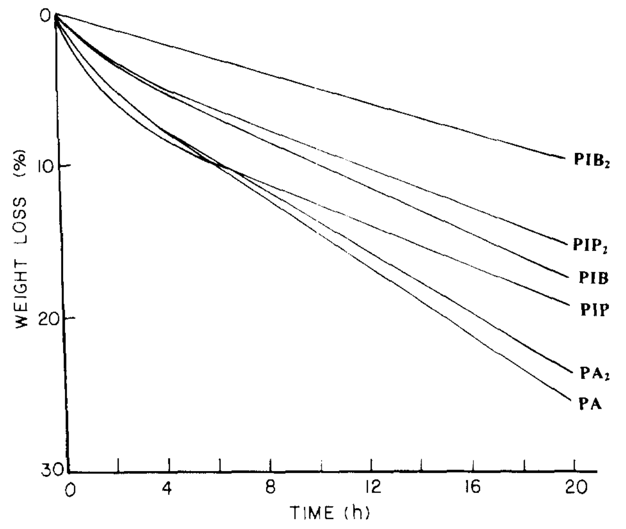


Figure 8 T.g.a. traces at 310°C in static air of polyamides PA_2, PA as well as of polyimides PIP_2, PIP and PIB_2, PIB

CONCLUSIONS

1. A series of modified polyamides and polyimides bearing naphthoxy and biphenylyloxy pendent groups were synthesized from two new aromatic diamines.
2. The modified polymers showed an enchanced solubility but lower hydrophilicity than the unmodified polymers.
3. The modification of polymers caused a decrease in T_g of 50–128°C. Certain modified polymers displayed T_ss in the range 190–273°C.
4. The modified polymers started to lose weight at 350–404°C in N_2 and were more thermally stable than the unmodified ones.

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