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Aromatic polyamides and polyimides with benzimidazole or benzoxazinone pendent groups prepared from 5-(2-benzimidazole)- or 5-(2-benzoxazinone)-1,3-phenylenediamine

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New aromatic polyamides and polyimides containing benzimidazole or benzoxazinone pendent groups were prepared from 5-(2-benzimidazole)- or 5-(2-benzoxazinone)-1,3-phenylenediamine. They were characterized by inherent viscosity and water absorption measurements, Fourier transform infra-red, ^{1}H nuclear magnetic resonance, X-ray, thermomechanical, thermogravimetric and isothermal gravimetric analyses. Their properties were compared with those of the parent polymers derived from 1,3-phenylenediamine. The modified polymers displayed better solubility than the unmodified ones and dissolved in polar aprotic solvents and certain inorganic and organic acids. The polyamides bearing benzimidazole or benzoxazinone pendent groups exhibited higher or lower, respectively, hydrophilicity than the reference polyamide. All modified polymers were amorphous and showed lower glass transition temperatures and thermal stability than the corresponding unmodified ones. Some of them softened in the region of 133–205°C. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyamides; polyimides; modification)

INTRODUCTION

Aromatic polyamides and polyimides are both of commercial importance and academic interest[1]. They exhibit high thermal stability and excellent mechanical properties. However, they are difficult materials to process because of their high glass transition and softening temperatures as well as their insolubility in most organic solvents. Attempts to improve the processability of these polymers have been made through the introduction of flexible bondings in the polymer backbone and voluminous pendent groups to the main chain. In regard to the latter point of view, many polymers such as polyterephthalamides[2], polyterephthalates[3], polyimides[4] and other polyheterocycles[5] have been prepared from monomers containing bulky pendent groups. In addition, certain aromatic polyamides with benzoxazole[6] or benzothiazole[7] side groups have been synthesized.

In previous work, we have reported the synthesis of aromatic polyamides and polyimides with benzoxazole or benzothiazole[8], *N*-benzylidene[9], phthalimide[10], furamido[11], ester[12], amide[13] and ether[14] pendent groups.

The present investigation deals with the synthesis and characterization of a new series of modified polyamides and polyimides with benzimidazole or benzoxazinone side groups. The benzimidazole structure exhibits unusual chemical resistance to acid, basic and oxidizing reagents[15]. In addition, both these heterocyclic structures are thermally stable.

EXPERIMENTAL

Instrumentation

Melting temperatures were determined on a Thomas-Hoover electrothermal melting point apparatus (model IA6304) and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 16PC Fourier transform infra-red (*FT*i.r.) spectrometer with KBr pellets. ^{1}H nuclear magnetic resonance (n.m.r.) spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in parts per million 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 system. Ground polymer samples of about 10 mg each were examined by t.g.a. and isothermal gravimetric analysis (i.g.a.) and the weight loss comparisons were made between comparable specimens. 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 TMA 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 approximately 2 mm thickness prepared by pressing polymer powder for 3 min under 5 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 X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

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

Reagents and solvents

3,5-Dinitrobenzoyl chloride and terephthaloyl chloride were recrystallized from n-hexane. 1,2-Phenylenediamine and 2-aminobenzoic acid were recrystallized from ethyl acetate and distilled water, respectively. Pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Triethylamine was purified by distillation. DMAc was dried by refluxing over CaH_2, and fractionally distilled from CaH_2. Hydrazine hydrate and 84% polyphosphoric acid (PPA) were used as supplied.

Preparation of starting materials

5-(2-Benzimidazole)-1,3-phenylenediamine (**3**$_a$). A flask equipped with a dropping funnel and magnetic stirrer was charged with a solution of 1,2-phenylenediamine (6.4884 g, 60.0 mmol) and triethylamine (6.0714 g, 60.0 mmol) in DMAc (80 ml). 3,5-Dinitrobenzoyl chloride (13.8336 g, 60.0 mmol) dissolved in DMAc (30 ml) was added dropwise to the stirred solution at 0°C under N_2. The mixture was subsequently heated at 60°C overnight in a stream of N_2. It was poured into ice water and the pale brown solid precipitate was filtered off, washed with water and dried to afford **1**$_a$ (14.93 g, yield 82%). A purified sample obtained by recrystallization from a mixture of 1,4-dioxane/water (2:1 v/v) had m.p. 296–299°C.

Anal. calcd for $C_{13}H_{10}N_4O_5$: C, 51.64%; H, 3.34%; N, 18.54%. Found: C, 51.47%; H, 3.38%; N, 18.62%.

I.r. (KBr, cm^{-1}): 3432–3228 (N–H stretching); 1656 (C=O); 1630, 1570 (N–H deformation); 1542, 1344 (NO_2); 1604, 1460 (aromatic).

^1H n.m.r. (dimethylsulfoxide DMSO-d_6) δ: 9.10–8.80 (br, 1H, NHCO; 3H aromatic of 3,5-dinitrobenzoic acid ring); 7.43–6.70 (m, 4H, other aromatic); 4.36 (br, 2H, NH_2).

A flask equipped with a mechanical stirrer was charged with a mixture of **1**$_a$ (12.4100 g, 41.1 mmol) and 84% PPA (120 g). It was heated at 180°C for 15 h. Fresh P_2O_5 (~ 10 g) was added to the mixture to compensate for the water of condensation. The reaction temperature was increased to 220°C and held at this temperature for 30 h. Next the mixture was cooled to room temperature and precipitated in water. The brown solid obtained was filtered off, washed thoroughly with water, then with dilute $NaHCO_3$ and finally with water, and dried to afford **2**$_a$ (8.90 g, yield 76%). It was recrystallized from a mixture of dimethylformamide/water (1:2 v/v) and did not show a m.p. upon heating up to 300°C.

Anal. calcd for $C_{13}H_8N_4O_4$: C, 54.92%; H, 2.84%; N, 19.72%. Found: C, 54.86%; H, 2.80%; N, 19.78%.

I.r. (KBr, cm^{-1}): 3334 (N–H stretching); 1618 (C=N); 1533 (N–H deformation); 1540, 1348 (NO_2); 1594, 1462 (aromatic).

^1H n.m.r. (DMSO-d_6) δ: 8.75–8.58 (m, 3H, aromatic of 3,5-dinitrobenzoic acid ring); 7.67–7.23 (m, 4H, aromatic of benzimidazole segment). The NH proton was unobserved.

A flask equipped with a dropping funnel and magnetic stirrer was charged with a mixture of **2**$_a$ (3.2300 g, 11.4 mmol), ethanol 95% (80 ml) and a catalytic amount of 10% palladium on activated carbon. Hydrazine hydrate (16 ml) diluted with ethanol 95% (20 ml) was added dropwise to the stirred mixture at about 60°C and then it was refluxed overnight. During this period, most of the solid gradually dissolved. The mixture was filtered and the solid obtained consisted of catalyst and unreacted **2**$_a$. The latter could be introduced to a new hydrogenation. The filtrate was concentrated under vacuum to remove approximately two-thirds of the solvent. The residue was diluted with water and the brown solid obtained was filtered off, washed with water and dried to afford **3**$_a$ (1.25 g, yield 49%). It was recrystallized from a mixture of DMF/water (1:2 v/v) and had m.p. 153–156°C.

Anal. calcd for $C_{13}H_{12}N_4$: C, 69.61%; H, 5.40%; N, 24.99%. Found: C, 69.03%; H, 5.46%; N, 25.12%.

I.r. (KBr, cm^{-1}): 3332–3210 (N–H stretching); 1618 (C=N); 1608 (N–H deformation); 1594, 1484 (aromatic); 1276 (C–N stretching).

^1H n.m.r. (DMSO-d_6) δ: 7.63–7.22 (m, 4H, aromatic of benzimidazole segment); 6.60 (m, 2H, aromatic of 4 and 6 positions of 1,3-phenylenediamine ring); 5.87 (m, 1H, aromatic of 2 position of 1,3-phenylenediamine ring); 4.83 (br, 4H, NH_2). The NH proton was unobserved.

5-(2-Benzoxazinone)-1,3-phenylenediamine (**3**$_b$). Compound **1**$_b$ was prepared as a yellow-brown solid in 80% yield by reacting 2-aminobenzoic acid with 3,5-dinitrobenzoyl chloride in the presence of triethylamine according to the procedure described for **1**$_a$. The product was isolated by pouring the reaction mixture into water in which a small amount of sodium chloride had dissolved. It was recrystallized from acetonitrile (m.p. 233–236°C).

Anal. calcd for $C_{14}H_9N_3O_7$: C, 50.75%; H, 2.74%; N, 12.69%. Found: C, 50.13%; H, 2.81%; N, 12.52%.

I.r. (KBr, cm^{-1}): 3380–3270 (N–H and O–H stretching); 1705 (carboxylic C=O); 1686 (amide C=O); 1542, 1346 (NO_2); 1470 (aromatic).

^1H n.m.r. (DMSO-d_6) δ: 8.76 (m, 1H COOH, 1H NHCO); 8.60–8.51 (m, 3H, aromatic of 3,5-dinitrobenzoic acid ring); 7.20–6.53 (m, 4H, other aromatic).

Compound **2**$_b$ was prepared as a light brown solid in 87% yield from the cyclodehydration of **1**$_b$ in PPA. More particularly, cyclodehydration was accomplished by heating a mixture of **1**$_b$ with 84% PPA at 150°C for 30 h. It was recrystallized from acetonitrile (m.p. 225–228°C).

Anal. calcd for $C_{14}H_7N_3O_6$: C, 53.67%; H, 2.25%; N, 13.42%. Found: C, 53.50%; H, 2.31%; N, 13.48%.

I.r. (KBr, cm^{-1}): 1778 (C=O); 1626 (C=N); 1542, 1346 (NO_2); 1604, 1474 (aromatic).

^{1}H n.m.r. (DMSO-d_6) δ: 8.68–8.53 (m, 3H, aromatic of 3,5-dinitrobenzoic acid ring); 7.60–7.21 (m, 4H, aromatic of benzoxazinone segment).

A hydrogenation flask was charged with a mixture of $\mathbf{2_b}$ (2.3200 g, 7.4 mmol), 1,4-dioxane (30 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 for 5 h. The catalyst was removed by filtration and the filtrate was poured into water. The yellow-brown solid precipitate was filtered off, washed with water and dried to afford $\mathbf{3_b}$ (1.73 g, yield 92%). It was recrystallized from a mixture of 1,4-dioxane/water (1:2 v/v) and had m.p. 182–185°C.

Anal. calcd for $C_{14}H_{11}N_3O_2$: C, 66.38%; H, 4.38%; N, 16.60%. Found: C, 65.98%; H, 4.41%; N, 16.51%.

I.r. (KBr, cm^{-1}): 3492–3314 (N–H stretching); 1762 (C=O); 1606 (C=N); 1590 (N–H deformation); 1600, 1474 (aromatic); 1266 (C–N stretching).

^{1}H n.m.r. (DMSO-d_6) δ: 7.60–7.20 (m, 4H, aromatic of benzoxazinone segment); 6.21 (m, 2H, aromatic of 4 and 6 positions of 1,3-phenylenediamine ring); 5.84 (m, 1H, aromatic of 2 position of 1,3-phenylenediamine ring); 4.20 (br, 4H, NH_2).

Preparation of polyamides

Polyamides $\mathbf{PA_a}$ *and* $\mathbf{PA_b}$. A flask equipped with a dropping funnel and a magnetic stirrer was charged with a solution of $\mathbf{3_a}$ (0.6051 g, 2.7 mmol) and triethylamine (0.5464 g, 5.4 mmol) in DMAc (15 ml) containing 5 wt% LiCl. Terephthaloyl chloride (0.5482 g, 2.7 mmol) dissolved in DMAc (10 ml) was added dropwise to the stirred solution at 0°C under N_2. Stirring of the mixture was continued at ambient temperature for 4 h in a stream of N_2. It was poured into water and the brown solid precipitate was filtered off, washed with water and dried in a vacuum oven at about 150°C to afford $\mathbf{PA_a}$ (0.93 g, yield 97%, n_{inh} 0.46 dl g^{-1} in DMAc).

Anal. calcd for $(C_{21}H_{14}N_4O_2)_n$: C, 71.18%; H, 3.98%; N, 15.81%. Found: C, 70.95%; H, 3.87%; N, 15.93%.

$\mathbf{PA_b}$ was similarly prepared as a yellow-brown solid in 95% yield by reacting $\mathbf{3_b}$ with terephthaloyl chloride in the presence of triethylamine (n_{inh} 0.42 dl g^{-1} in DMAC).

Anal. calcd for $(C_{22}H_{13}N_3O_4)_n$: C, 68.93%; H, 3.42%; N, 10.96%. Found: C, 68.50%; H, 3.47%; N, 10.87%.

Polyimides $\mathbf{PIP_a}$, $\mathbf{PIP_b}$ *and* $\mathbf{PIB_a}$, $\mathbf{PIB_b}$. PMDA (0.5453 g, 2.5 mmol) was added to the stirred solution of $\mathbf{3_a}$ (0.5603 g, 2.5 mmol) in DMAc (20 ml) at 0°C. Stirring of the viscous solution was continued at ambient 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 90°C overnight. It was subsequently poured into water and the brown solid obtained was filtered off, washed thoroughly with water and dried in a vacuum oven at approximately 150°C to afford $\mathbf{PIP_a}$ (0.97 g, yield 96%, n_{inh} 0.58 dl g^{-1} in DMAc).

Anal. calcd for $(C_{23}H_{10}N_4O_4)_n$: C, 67.98%; H, 2.48%; N, 13.79%. Found: C, 67.83%; H, 2.53%; N, 13.65%.

$\mathbf{PIP_b}$ was similarly prepared as a brown solid in 93% yield by reacting $\mathbf{3_b}$ with PDMA (n_{inh} 0.52 dl g^{-1} in DMAc).

Anal. calcd for $(C_{24}H_9N_3O_6)_n$: C, 66.21%; H, 2.08%; N, 9.65%. Found: C, 65.98%; H, 2.14%; N, 9.58%.

$\mathbf{PIB_a}$ was similarly prepared as a brown solid in 94% yield from the reaction of $\mathbf{3_a}$ with BTDA (n_{inh} 0.55 dl g^{-1} in DMAc).

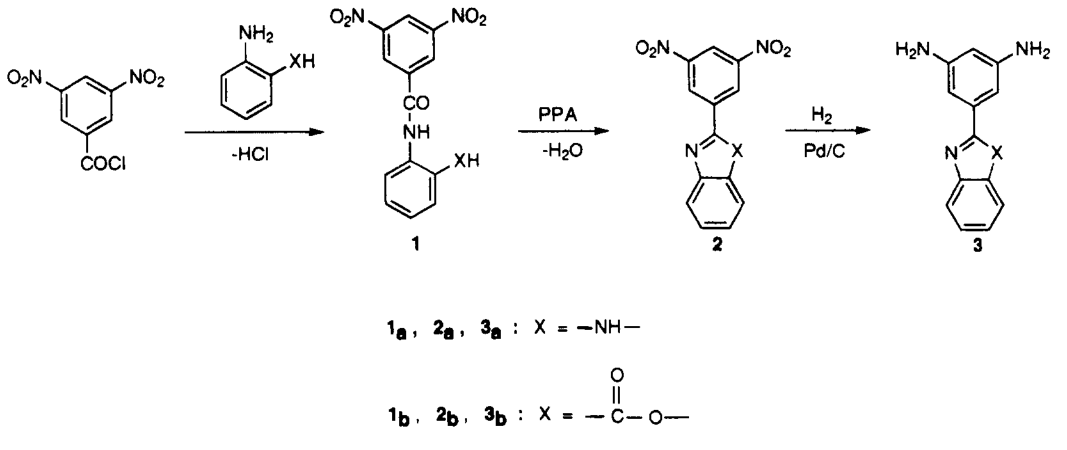
Anal. calcd for $(C_{30}H_{14}N_4O_5)_n$: C, 70.59%; H, 2.76%; N, 10.98%. Found: C, 70.12%; H, 2.84%; N, 10.86%.

$\mathbf{PIB_b}$ was similarly prepared as a brown solid in 96% yield by reacting $\mathbf{3_b}$ with BTDA (n_{inh} 0.50 dl g^{-1} in DMAc).

Anal. calcd for $(C_{31}H_{13}N_3O_7)_n$: C, 69.02%; H, 2.43%; N, 7.79%. Found: C, 68.85%; H, 2.47%; N, 7.66%.

RESULTS AND DISCUSSION

Scheme 1 shows the synthetic route for two new diamines bearing pendent benzimidazole or benzoxazinone segments. Specifically, 3,5-dinitrobenzoyl chloride reacted with 1,2-phenylenediamine or 2-aminobenzoic acid to yield compounds $\mathbf{1_a}$ and $\mathbf{1_b}$, respectively. The reactions took place in DMAc utilizing triethylamine as acid acceptor. The cyclcodehydration of compounds $\mathbf{1_a}$ and $\mathbf{1_b}$ to benzimidazole and benzoxazinone derivative occurred in PPA by heating. Compound $\mathbf{1_a}$ was cyclodehydrated with greater difficulty than $\mathbf{1_b}$, since heating in PPA up to 220°C was applied and fresh P_2O_5 was added to the reaction mixture to compensate for the water evolved. The catalytic hydrogenation of



Scheme 1

compounds 2_a and 2_b to the corresponding diamines 3_a and 3_b was accomplished by means of hydrazine hydrate or on a Parr apparatus, respectively. In the case of 2_b, prolonged hydrogenation should be avoided, because a catalytic reduction of the carbonyl group was possible.

The steric effects for the synthesized new diamines 3_a and 3_b are favourable, although the voluminous pendent groups could influence their reactivities toward dicarboxylic acids due to steric hindrance. The optimized geometries, as calculated by means of CSC Chem 3D PlusΣ Molecular Modeling System, showed that the steric hindrance exerted by the bulky pendent substituents on the reactive amino groups is negligible. The rings of 1,3-phenylenediamine and of benzimidazole or benzoxazinone seem to possess almost planar conformation. Note that 5-(2-benzoxazole) or 5-(2-benzothiazole) isophthaloyl chlorides[6,7] as well as 5-(2-benzoxazole)- or 5-(2-benzothiazole)-1,3-phenylenediamine[8] utilized as starting materials for the preparation of aromatic polyamides behaved in a similar manner.

All monomers were characterized by elemental analyses as well as i.r. and ^{1}H n.m.r. spectroscopy. *Figure 1* presents the *FT*i.r. spectra of 1_a, 2_a and 3_a. Compound 2_a lacked the absorption of 1_a at 1656 cm^{-1} assigned to the carbonyl, which suggests that cyclization to form the benzimidazole ring was complete. Notably, the C=N characteristic absorption band appeared at 1618 cm^{-1} in 2_a. In addition, compound 3_a lacked the strong absorptions of 1_a and 2_a near 1540 and 1344 cm^{-1} associated with the nitro groups, which supports their complete reduction.

A novel class of modified polyamides and polyimides was prepared, as shown in *Scheme 2*. More particularly, diamines **3** were polycondensed with terephthaloyl chloride in DMAc solution at low temperature to afford polyamides **PA**. In addition, modified polyimides **PIP** and **PIB** were prepared from the reactions of **3** with PMDA or BTDA, respectively. Their intermediate poly(amic acids) were cyclodehydrated by heating in the presence of acetic anhydride and sodium acetate.

The properties of the modified polymers were compared with those of the corresponding unmodified ones. The latter were prepared under the same experimental conditions utilizing 1,3-phenylenediamine instead of **3**. *Table 1* presents their chemical structures, the n_{inh} values and designations.

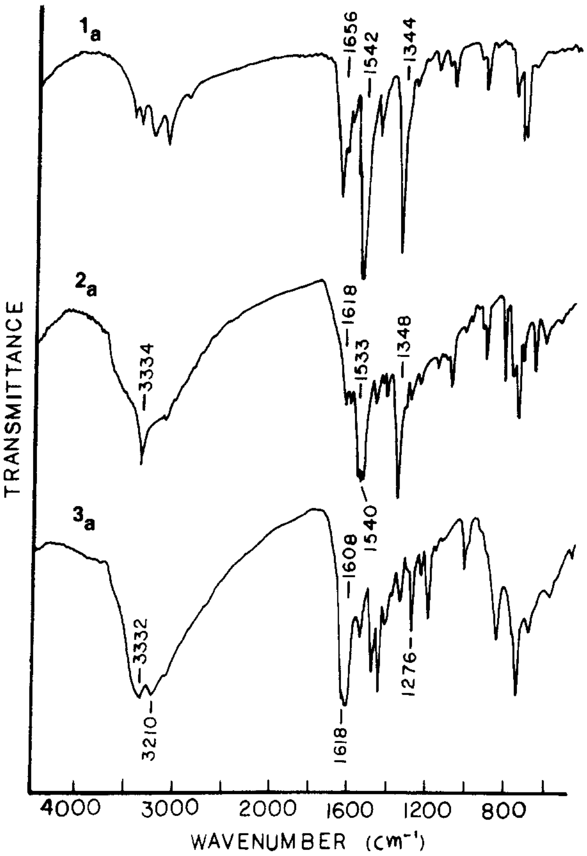
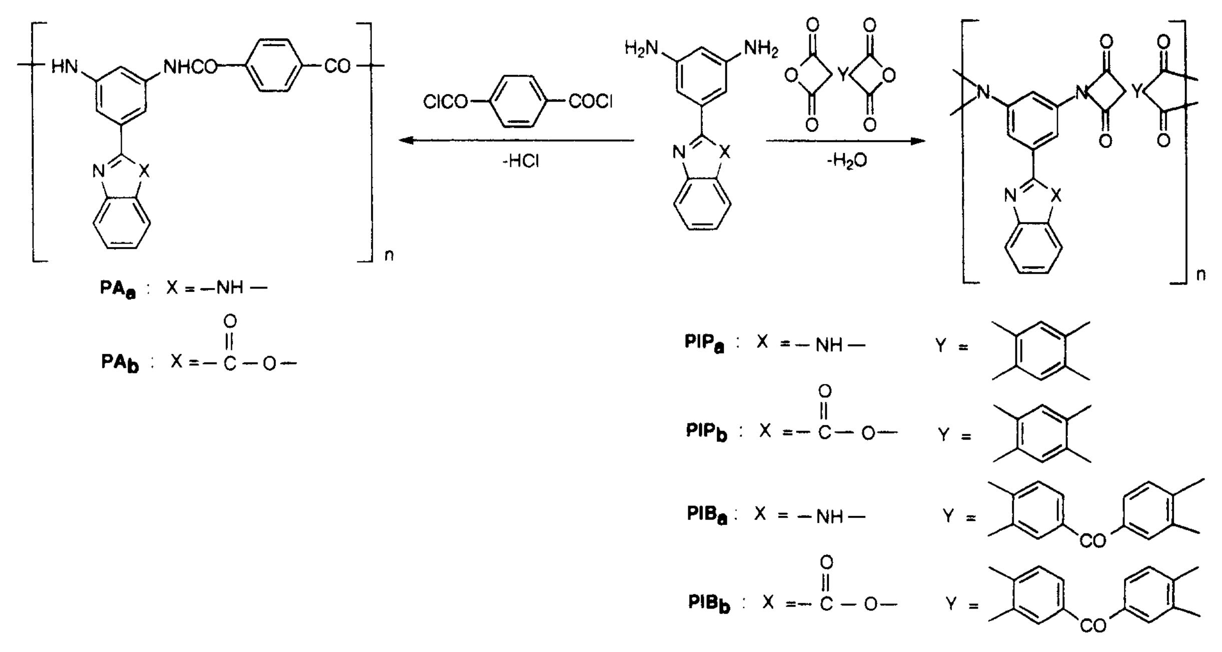


Figure 1 *FT*i.r. spectra of compounds 1_a, 2_a and 3_a

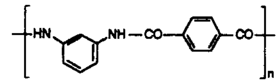
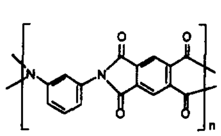
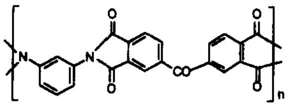
The modified polymers were obtained in nearly quantitative yields (93–97%) and their n_{inh} values ranged from 0.42 to 0.58 dl g^{-1}. They were characterized by i.r., ^{1}H n.m.r., X-ray, t.m.a., t.g.a. and i.g.a.

The i.r. spectra of polymers confirmed the proposed



Scheme 2

Table 1 Structures and designations of unmodified polymers

Structure	Designation
	**PA**[a]
	**PIP**[b]
	**PIB**[b]

[a] Polyamide **PA** was prepared in DMAc solution containing 5 wt% LiCl. It had inherent viscosity (η_{inh}) 0.51 dl g^{-1} in DMF

[b] The η_{inh} of polyimides **PIP** and **PIB** could not be determined owing to the limited solubility of these polyimides in polar aprotic solvents. The η_{inh} of the intermediate polyamic acids were determined by taking an aliquot from their solutions in DMF and diluting before making the measurements. The polyamic acids of polyimides **PIP** and **PIB** had η_{inh} 0.53 and 0.48 dl g^{-1}, respectively

structures. Specifically, polyamide **PA$_a$** showed absorption bands at 3226 (N–H stretching), 1658 (C=O), 1616 (C=N), 1548 (N–H deformation), 1464 (aromatic) and 1278 cm^{-1} (C–N stretching and N–H bending). Polyimides **PIP$_a$** and **PIB$_a$** displayed characteristic absorption bands at 1780, 1726 or 1724, 1344 or 1354 and 748 or 716 cm^{-1} assigned to the imide structure. Polymers **PA$_b$**, **PIP$_b$** and **PIB$_b$** showed an additional absorption band around 1768 cm^{-1} associated with the carbonyl group of the benzoxazinone moieties.

The ^{1}H n.m.r. spectrum of a typical polyamide **PA$_b$** in DMSO-d$_6$ solution showed a broad band at 9.05–8.90 (NHCO) and multiplets at 7.80–7.70 (aromatic of terephthalic acid segments) and 7.58–7.20 δ (aromatic of benzoxazinone segments).

The modified polymers displayed an enhanced solubility in common solvents owing to the presence of the bulky pendent groups, which did not allow a dense chain packing. *Table 2* presents the solubilities of modified polymers **PA$_a$**, **PA$_b$**, **PIP$_a$** and **PIP$_b$** as well as of the corresponding unmodified counterparts. Polyamides **PA$_a$** and **PA$_b$** were soluble at room temperature in polar aprotic solvents (DMF, NMP, DMSO) and H_2SO_4. In contrast, **PA** dissolved in hot polar aprotic solvents and at ambient temperature only in H_2SO_4. Polyimides **PIP$_a$** and **PIP$_b$** were soluble upon heating or even at room temperature in polar aprotic solvents, whereas **PIP** dissolved partially in polar aprotic solvents and completely only in hot H_2SO_4. The polymers bearing benzoxazinone pendent groups displayed better solubility than those containing benzimidazole side groups.

An attempt was made for structural characterization by the X-ray method of modified polymers. *Figure 2* presents typical X-ray diffractograms for powder specimens of polymers **PA$_a$**, **PIP$_a$** and **PIB$_a$**. They had the same pattern and displayed very weak diffraction peaks which supports their generally amorphous character.

The water absorption of polyamides was measured to estimate their hydrophilicity. It is well known[16] that the moisture absorption is proportional to the concentration of amide groups in polymer. *Figure 3* presents the isothermal water absorption for polyamides **PA$_a$**, **PA$_b$** and **PA** as a function of the time exposed. They showed

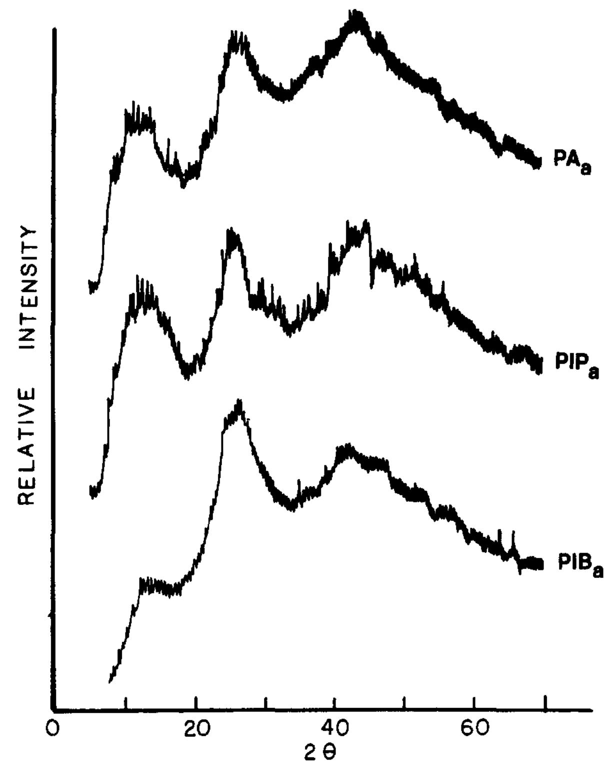


Figure 2 Wide-angle X-ray scattering curves for polymers **PA$_a$**, **PIP$_a$** and **PIB$_a$**

Table 2 Solubilities[a] of polymers

	Solvents[b]								
Sample	DMF	NMP	DMSO	H_2SO_4	CCl_3COOH	*m*-Cresol	1,4-Dioxane	CH_3CN	CH
PA$_a$	++	++	++	++	+	+−	+−	+−	+−
PA$_b$	++	++	++	++	++	+	+	+−	+
PA	+	+	+	++	+	−	−	−	−
PIP$_a$	+	+	+	++	+	−	−	−	−
PIP$_b$	++	++	++	++	++	+−	+−	+−	+
PIP	+−	+−	+−	+	+−	−	−	−	−

[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

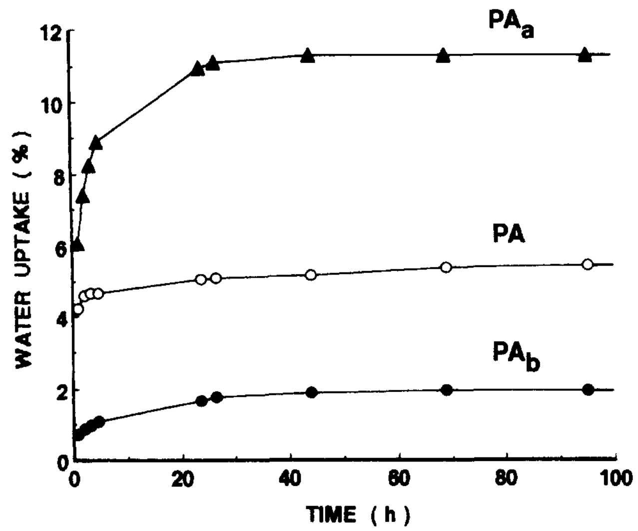


Figure 3 Water absorption (%) *versus* time for polyamides **PA$_a$**, **PA$_b$** and **PA**

water uptake of 11.28, 1.96 and 5.48%, respectively, after 100 h exposure time. These values correspond to moles of absorbed water per amide equivalent weight 1.11, 0.21 and 0.36. Therefore, the hydrophilicity of polyamides followed the trend **PA$_a$** > **PA** > **PA$_b$**. The modified polyamides were expected to exhibit an improved hydrophilicity, because the bulky pendent groups disrupted the chain packing and hence increased the water accessibility. However, **PA$_b$** showed lower hydrophilicity than **PA**, probably due to inter- and intramolecular hydrogen bonds between the amide and the benzoxazinone carbonyl, which compete with the amide–water hydrogen bonds. This feature conforms with certain literature data[17,18].

The thermomechanical characterization of polymers was accomplished by the t.m.a. method utilizing a suitably loaded penetration probe. The glass transition (T_g) and softening (T_s) temperatures of modified and unmodified polymers were determined from the onset temperatures of these transitions and are listed in *Table 3*. Polyimide **PIP** did not show any transition up to 300°C. Polymers **PA$_a$**, **PA**, **PIP$_a$**, **PIB$_a$** and **PIB** displayed only a glass transition and did not soften upon heating up to approximately 300°C. The T_s values determined by the t.m.a. method were in agreement with those obtained in a conventional melting point apparatus. The modified polymers showed significantly lower T_g values than the parent counterparts. All the polymers bearing benzoxazinone pendent groups softened in the range of 133–205°C and displayed lower T_g values than the corresponding polymers with benzimidazole side groups.

The thermal stability of polymers was evaluated by t.g.a. and i.g.a. *Figure 4* presents typical t.g.a. thermograms of polymers **PA$_a$**, **PIP$_a$** and **PIB$_a$** in N_2 and air. The initial decomposition temperature (*IDT*), the polymer decomposition temperature (*PDT*), the maximum polymer decomposition temperature (PDT_{max}) in

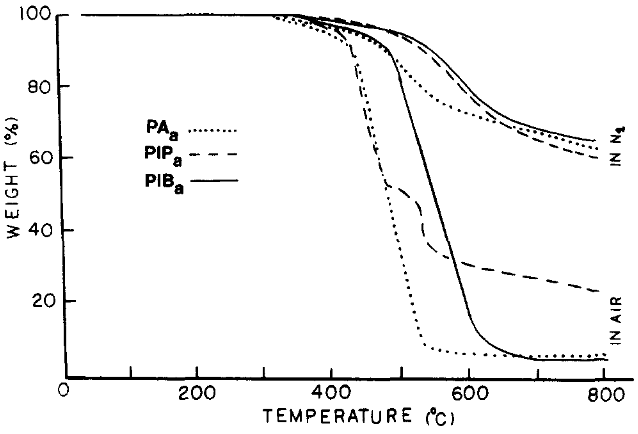


Figure 4 T.g.a. thermograms of polymers **PA$_a$**, **PIP$_a$** and **PIB$_a$** in N_2 and air. Conditions: gas flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

Table 3 T.g.a. and t.m.a. date for polymers

	T.g.a.								
	N_2				Air			T.m.a.	
Sample	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)	T_g[e] (°C)	T_s[f] (°C)
PA$_a$	336	490	527	64	325	437	460	185	–
PA$_b$	310	365	389	57	305	361	381	103	140
PA	344	463	528	56	341	433	471	238	–
PIP$_a$	360	545	600	62	352	437	456	180	–
PIP$_b$	355	437	430	59	344	411	448	130	205
PIP	367	501	551	57	366	489	527	–	–
PIB$_a$	363	556	608	67	355	493	525	197	–
PIB$_b$	331	433	400	61	327	419	450	95	133
PIB	374	533	589	56	370	474	501	247	–

[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

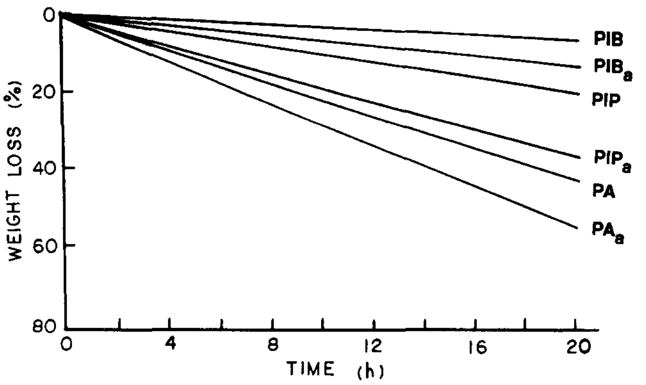


Figure 5 I.g.a. traces in static air at 320°C of polymers **PA$_a$**, **PA**, **PIP$_a$**, **PIP**, **PIB$_a$** and **PIB**

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 temperatures at which 0.5 and 10% weight loss were observed, respectively. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

Taking the *IDT* as the criterion of thermal stability, it is seen that the modified polymers were somewhat less thermally stable than the corresponding unmodified ones. However, they afforded slightly higher Y_c at 800°C. More particularly, the modified polymers were stable up to 305–363°C in N_2 or air and afforded Y_c of 57–67% at 800°C in N_2. Upon comparing the chemical structures of the pendent groups, it is seen that benzimidazole showed better thermal stability than benzoxazinone. It has been reported that the incorporation of benzoxazole or benzothiazole side groups along the polyamide and polyimide backbone improved their thermal stability[6–8].

The lower thermal stability of modified polymers in comparison to that of the corresponding unmodified was verified by i.g.a. *Figure 5* presents typical i.g.a. traces for polymers **PA$_a$**, **PA**, **PIP$_a$**, **PIP**, **PIB$_a$** and **PIB** at 320°C in static air. After 20 h isothermal ageing, they displayed weight losses of 54.2, 42.0, 36.2, 19.0, 12.5 and 5.8%, respectively. The remaining weights determined from the i.g.a. traces were in the following order: **PIB** > **PIB$_a$** > **PIP** > **PIP$_a$** > **PA** > **PA$_a$**.

CONCLUSIONS

A new class of modified polyamides and polyimides having benzimidazole or benzoxazinone pendent groups were synthesized. The modified polymers were amorphous and displayed lower glass transition temperatures and thermal stability but enhanced solubility in common organic solvents than the corresponding parent polymers.

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