

Structural Modification of Polyisophthalamides by Incorporating Dimethylaminoazobenzene Pendent Groups

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ABSTRACT: Certain structurally modified polyisophthalamides with bulky azo pendent groups were prepared from the polycondensation of 5-(4'-dimethylaminoazobenzene) isophthaloyl chloride with various aromatic diamines. The corresponding unmodified polyisophthalamides were also synthesized to compare their properties. The modified polyisophthalamides showed higher solubility in certain solvents, such as 1,4-dioxane, *m*-cresol, cyclohexanone, and CCl₃COOH, than the parent polyamides. The hydrophilicity of the modified polyisophthalamides was estimated by water absorption measurements, and it was found to be significantly higher than that of the corresponding unmodified counterparts. The modified polyisophthalamides were crosslinked upon heat curing, and they were stable up to 340–374°C in N₂ or air and afforded anaerobic char yields of 68–72% at 800°C. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 921–930, 1997

Key words: modified polyisophthalamides; thermally stable polymers; azo pendent groups; polyamides; synthesis; diazotization; 5-aminoisophthalic acid; *N,N*-dimethylaniline

INTRODUCTION

The structural modification of known high-performance polymers is a process of growing importance. Thus, the introduction of voluminous pendent substituents along the polymer main chain is an approach to improve the processability of aromatic polymers widely used in recent years.^{1–5} A dense packing of the polymer chains is prevented by the presence of bulky groups, and such a modification brings improvements in the solubility in organic solvents.

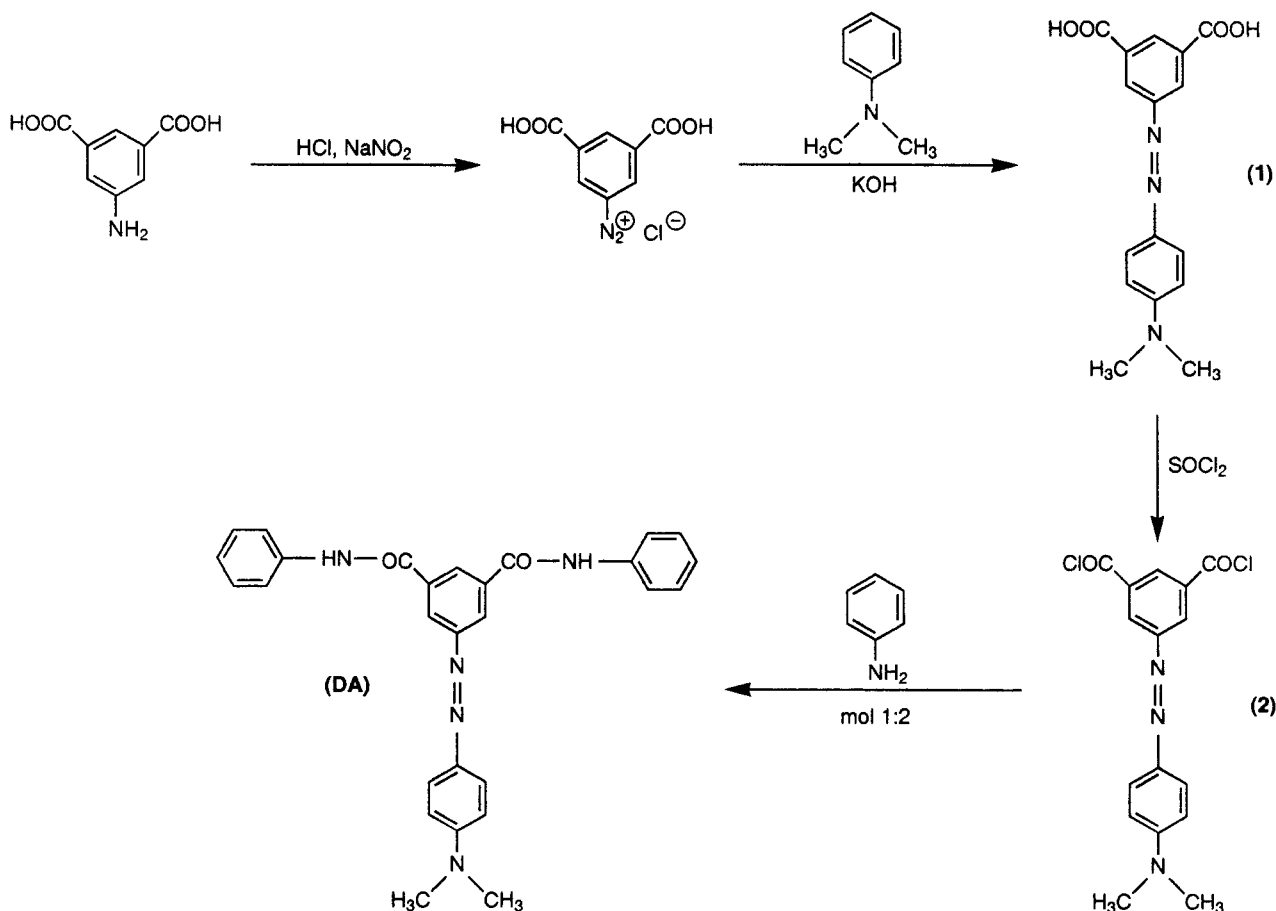
Aromatic polyamides, particularly polyisophthalamides and polyterephthalamides, are recognized as polymers of superior thermal stability and good mechanical properties. They are widely

used as mainly high temperature fibers. Numerous modifications of polyisophthalamides, which are polymers of great interest, have already been reported.^{6–14} Furthermore, in previous articles we reported the synthesis and characterization of polyisophthalamides containing bulky groups on the 5 position of the isophthaloyl moiety. More particularly, polyisophthalamides with *N*-benzylidene¹⁵ or phthalimide¹⁶ pendent groups have been prepared. They displayed an improved thermal stability and enhanced solubility in comparison to the parent structures.

The present work deals with the synthesis and characterization of a new series of modified polyisophthalamides prepared by the solution polycondensation method of 5-(4'-dimethylaminoazobenzene)isophthaloyl chloride with various aromatic diamines. The incorporation of voluminous azo pendent groups along the polymer backbone was expected to affect their properties.

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Scheme 1 Preparation of compound 2 and model diamide DA.

EXPERIMENTAL

Characterization Methods

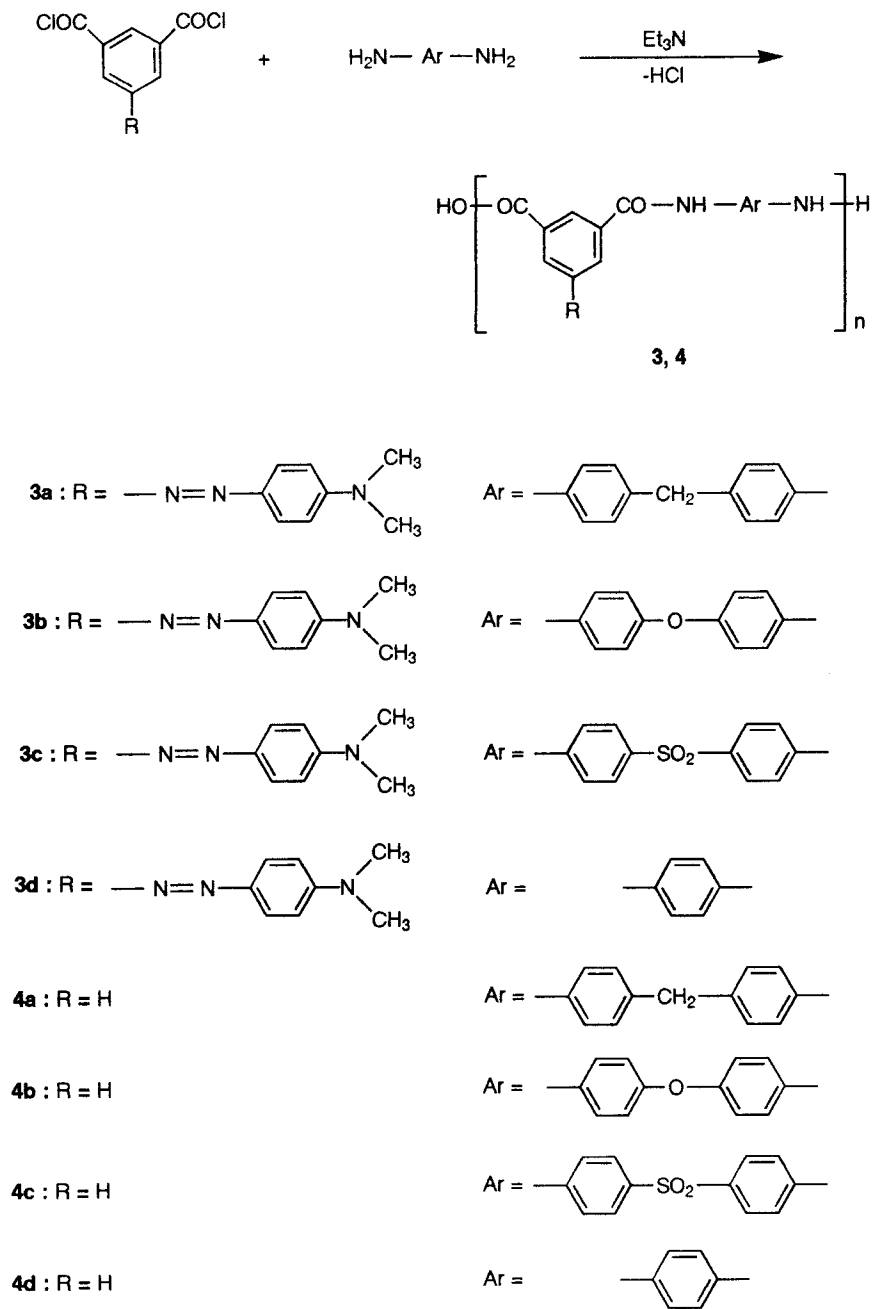
Melting temperatures were determined on an electrothermal melting point apparatus (IA6304) and are uncorrected. UV-visible (UV-vis) spectra were obtained on a Pharmacia LKB-Biochrom 4060 UV-vis spectrophotometer. FTIR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer with KBr pellets. $^1\text{H-NMR}$ 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. Dynamic thermal analyses (DTA) and thermogravimetric analyses (TGA) were performed on a DuPont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in an N_2 atmosphere at a flow rate of 60 cm^3/min . Dynamic TGA measurements were made at a heating rate

of 20°C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min . The inherent viscosities of the polymers were determined for solutions of 0.5 g/100 mL in *N,N*-dimethylacetamide (DMAc) or in H_2SO_4 98% at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. The wide angle X-ray diffraction patterns were obtained for powder specimens on an 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 was maintained by means of an oversaturated aqueous solution of NaNO_2 at 20°C. The samples were periodically weighed.

Reagents and Solvents

5-Aminoisophthalic acid was recrystallized from a mixture of DMF/water (v/v ratio 3 : 1). 4,4'-



Scheme 2 Preparation of polyamides **3a–3d** and **4a–4d**.

Diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, and 4,4'-diaminodiphenylsulfone were recrystallized from toluene, acetonitrile, and methanol, respectively. 1,4-Phenylenediamine was sublimed under reduced pressure. DMAc was dried by refluxing and fractionally distilled from CaH_2 . Isophthaloyl chloride was recrystallized from *n*-hexane. Aniline and *N,N*-dimethylaniline were purified by distillation.

Preparation of Starting Material

5-(4'-Dimethylaminoazobenzene)isophthaloyl Chloride (2)

5-Aminoisophthalic acid (7.5754 g, 41.8 mmol) was dissolved in dilute hydrochloric acid (30 mL concentrated HCl in 200 mL water). (See Scheme 1.) Diazotization was accomplished by adding a solution of sodium nitrite (3.2330 g, 46.0 mmol)

Table I Inherent Viscosities and Solubility Behavior of Polyamides

Sample	η_{inh} (dL/g)	Solvents							
		DMF	NMP	DMSO	1,4-Dioxane	<i>m</i> -Cresol	CH	H ₂ SO ₄ 98%	CCl ₃ COOH
3a	0.39 ^a	++	++	++	+	++	++	++	++
3b	0.37 ^a	++	++	++	+	++	++	++	++
3c	0.38 ^a	++	++	++	+	++	++	++	++
3d	0.38 ^a	++	++	++	+	++	++	++	+
4a	0.66 ^a	++	++	++	–	–	–	++	+
4b	0.65 ^a	++	++	++	–	–	–	++	+
4c	0.72 ^a	++	++	++	–	+	–	++	+
4d	0.65 ^b	–	–	–	–	–	–	+	–

Solubility: (++) soluble at room temperature; (+) soluble in hot; (–) insoluble. DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulfoxide; CH, cyclohexanone.

^a Inherent viscosity in *N,N*-dimethylacetamide (0.5 g/100 mL) at 30°C.

^b Inherent viscosity in concentrated H₂SO₄ (0.5 g/100 mL) at 30°C.

in water (20 ml) at 0°C with stirring. *N,N*-Dimethylaniline (5.0675 g, 41.8 mmol) dissolved in an aqueous solution of potassium hydroxide (4.4497 g, 79.5 mmol) was added dropwise to the stirred solution. Stirring of the mixture was continued for 3 h. The red solid precipitate was filtered off, washed with water and then with acetone, and dried to afford 5-(4'-dimethylaminoazobenzene)isophthalic acid (**1**) (8.38 g, yield 64%, mp 235–238°C).

ANAL. Calcd for C₁₆H₁₅N₃O₄: C, 61.32%; H, 4.83%; N, 13.42%. Found: C, 60.42%; H, 4.92%; N, 12.91%. UV-vis (DMF) nm: 426 (–N=N–, $\eta \rightarrow \pi^*$). IR (KBr) cm⁻¹: 3424–2688 (O–H stretching); 1701 (C=O); 1607 (aromatic); 1403, 1314 (C–O stretching and O–H deformation); 1366 (C–N stretching of tertiary amine).

A mixture of **1** (7.0000 g, 22.3 mmol), acetonitrile (30 mL), thionyl chloride (15 mL), and a catalytic amount of DMF was refluxed for 1 h. Excess thionyl chloride and volatile components were subsequently stripped off by distillation under reduced pressure, and the dark red solid obtained was washed with ether and dried to afford **2** (6.73 g, yield 86%). A purified sample obtained by recrystallization from DMAc–acetone (v/v, 1 : 4) had a mp of 158–162°C.

ANAL. Calcd for C₁₆H₁₃N₃O₂Cl₂: C, 55.01%; H, 3.75%; N, 12.04%. Found: C, 54.40%; H, 3.76%; N, 11.73%. UV-vis (DMF) nm: 428 (–N=N–, $\eta \rightarrow \pi^*$). IR (KBr) cm⁻¹: 1720 (C=O); 1544 (aromatic); 1387 (C–N

stretching of tertiary amine). ¹H-NMR (DMSO-*d*₆) δ : 8.33–8.00 (*m*, 3H, aromatic of isophthalic acid segment); 7.80–7.10 (*m*, 4H, other aromatic); 3.88–3.44 (*m*, 6H, CH₃).

Preparation of Model Diamide DA

A flask was charged with a mixture of aniline (0.5289 g, 5.7 mmol), DMAc (5 mL), and triethylamine (0.5748 g, 5.7 mmol) (Scheme 1). Compound **2** (1.0000 g, 2.84 mmol) dissolved in DMF (5 mL) was added dropwise to the stirred solution at 0°C under N₂. Stirring of the mixture was continued for 5 h at ambient temperature under N₂ and then it was poured into water. The red solid was filtered off, washed with water, and dried to afford **DA** (1.20 g, yield 91%). A purified sample of **DA** with mp 253–256°C was obtained by recrystallization from a mixture of DMF–water (v/v, 1 : 1).

ANAL. Calcd for C₂₈H₂₅N₅O₂: C, 72.54%; H, 5.44%; N, 15.12%. Found: C, 71.97%; H, 5.43%; N, 14.88%. UV-vis (DMF) nm: 430 (–N=N–, $\eta \rightarrow \pi^*$). IR (KBr) cm⁻¹: 3340 (N–H stretching); 1664 (C=O); 1602 (aromatic); 1539 (N–H deformation); 1387 (C–N stretching of tertiary amine); 1329 (C–N stretching and N–H bending). ¹H-NMR (DMSO-*d*₆) δ : 9.20 (*b*, 2H, NHCO); 8.40–7.60 (*m*, 17H, aromatic); 4.26–4.10 (*m*, 6H, CH₃).

Preparation of Polyamides 3a–3d and 4a–4d

A typical procedure for the preparation of polyamide **3a** is given (Scheme 2). A flask was charged

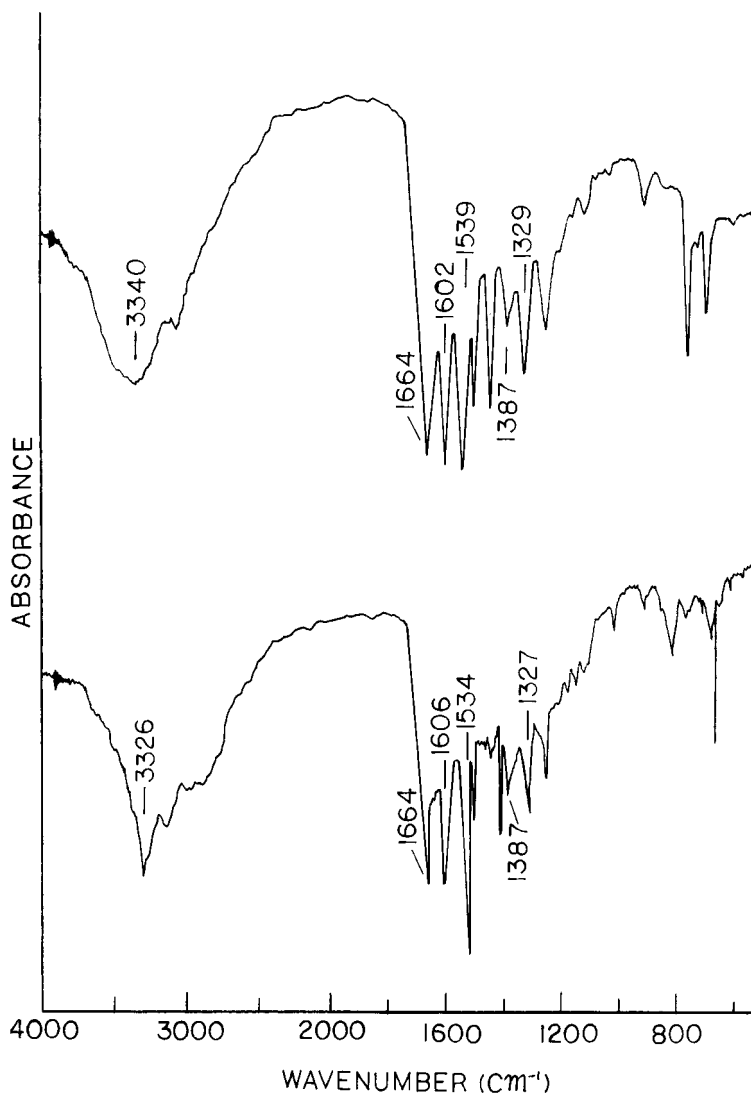


Figure 1 FTIR spectra of model diamide **DA** (top) and polyamide **3a** (bottom).

with a mixture of 4,4'-diaminodiphenylmethane (0.6761 g, 3.4 mmol), DMAc (8 mL), and triethylamine (0.6761 g, 6.8 mmol). Compound **2** (1.2000 g, 3.4 mmol) dissolved in DMAc (10 mL) was added dropwise to the stirred solution at 0°C under N₂. The mixture was subsequently stirred at ambient temperature for 5 h under N₂, and then it was poured over crushed ice. The reddish solid obtained was filtered off, washed with water, and dried to afford **3a** (1.54 g, yield 94%).

Curing of Polyamides

The isolated polyamides were each placed in an aluminum dish and curing was accomplished by heating in an oven at 270°C for 4 h in static air.

RESULTS AND DISCUSSION

5-(4'-Dimethylaminoazobenzene)isophthaloyl chloride (**2**) was used as the starting material for the preparation of a novel class of modified polyisophthalamides. Scheme 1 outlines the synthesis of compound **2** as well as of model diamide **DA**. More particularly, the diazonium salt of 5-aminoisophthalic was coupled with *N,N*-dimethylaniline to afford **1**. The latter was converted to the corresponding acid chloride **2** by reacting with thionyl chloride. The reaction of **2** with a double molar amount of aniline in the presence of triethylamine yielded model diamide **DA**.

Scheme 2 shows the preparation of modified and unmodified polyisophthalamides by reacting

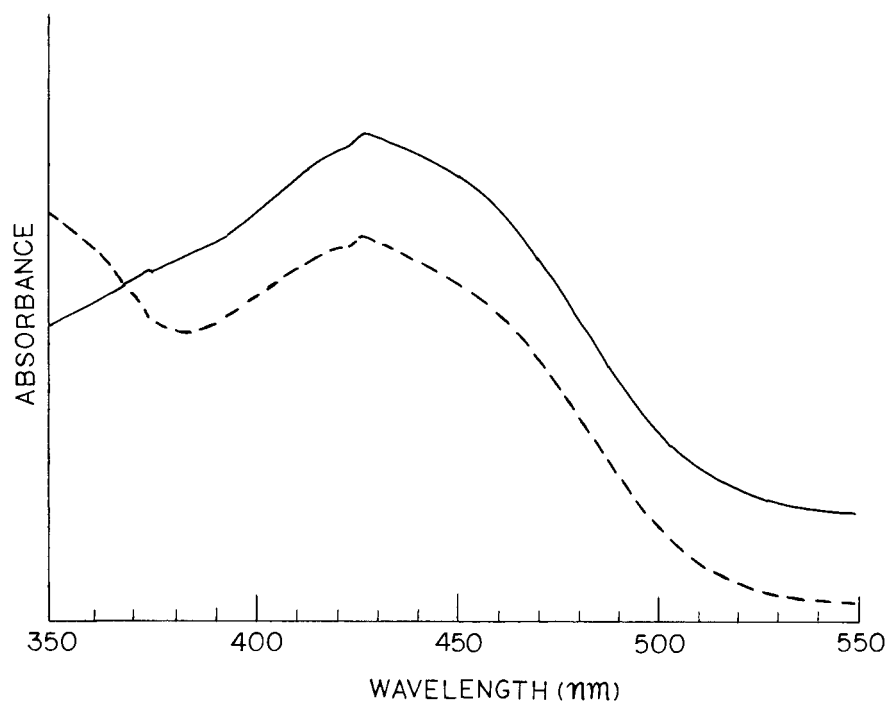


Figure 2 UV-visible spectra of compounds (—) 1 and (---) 2 in DMF solution.

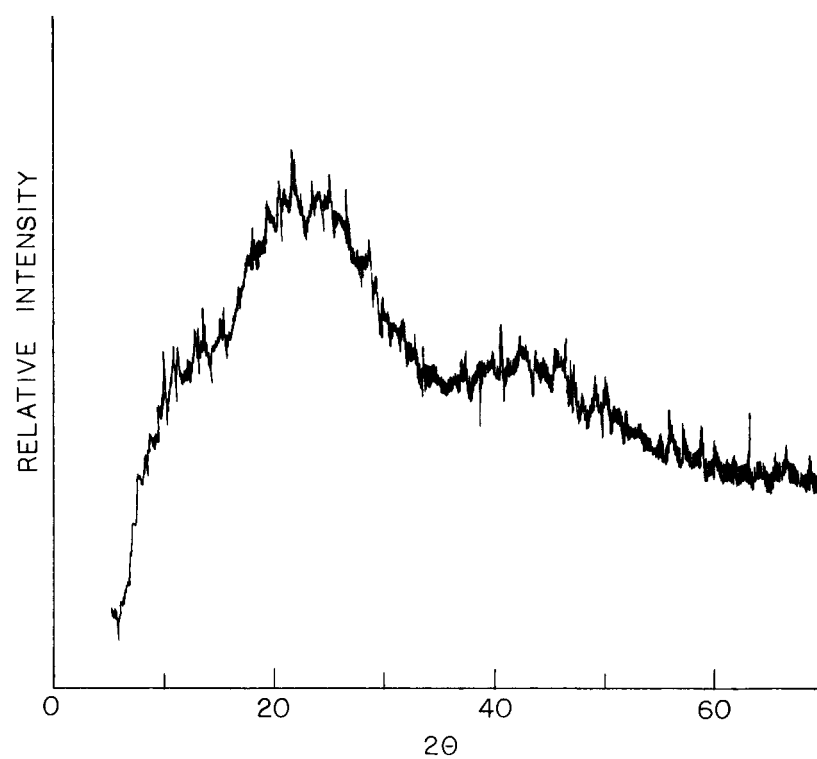


Figure 3 X-ray diffractogram of polyamide 3c.

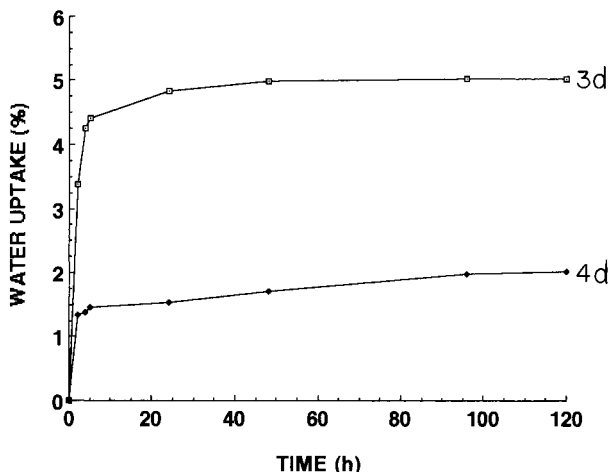


Figure 4 Water absorption (%) versus time for polyamides **3d** and **4d**.

various aromatic diamines with **2** or isophthaloyl chloride, respectively. The polyamides were synthesized by the low temperature solution polycondensation method utilizing triethylamine as the acid acceptor.

The inherent viscosities of modified polyisophthalamides ranged from 0.37 to 0.39 dL/g and were lower than those of the unmodified polyamides prepared under the same experimental conditions (Table I).

Compounds **1**, **2**, and **DA** were characterized

by elemental analyses as well as UV-vis, FTIR and $^1\text{H-NMR}$ spectroscopy (see Experimental). The $^1\text{H-NMR}$ spectrum of **1** was not recorded, because it was insoluble even in polar aprotic solvents. Figure 1 presents the FTIR spectra of **DA** and polyamide **3a**, which were in agreement. Specifically, both compounds displayed absorptions associated with the amide structure around 3335 (N—H stretching), 1664 (C=O), 1536 (N—H deformation), and 1328 cm^{-1} (C—N stretching and N—H bending). In addition, they showed absorptions at about 1604 (aromatic) and 1387 cm^{-1} (C—N stretching of tertiary amine). It is well known^{17,18} that the —N=N— absorption of aromatic azo compounds is very difficult to identify with IR spectroscopy, because it is not only weak but is also overlapped by other aromatic bands near 1500 cm^{-1} . Therefore, the azo bond was verified by UV-vis spectroscopy, because it displays a characteristic absorption in the region of 400–450 nm. Figure 2 presents the UV-vis spectra of compounds **1** and **2** obtained in DMF solution.

The $^1\text{H-NMR}$ spectrum of modified polyisophthalamide **3a** in $\text{DMSO-}d_6$ solution displayed peaks at 10.64 (NHCO), 8.56–8.51 (aromatic ortho to C=O), 8.00–6.91 (other aromatic), 3.66 (CH_2), and 3.00 δ (CH_3).

The X-ray diffraction profiles of modified polyisophthalamides revealed their generally amorphous nature. Figure 3 presents a typical X-ray

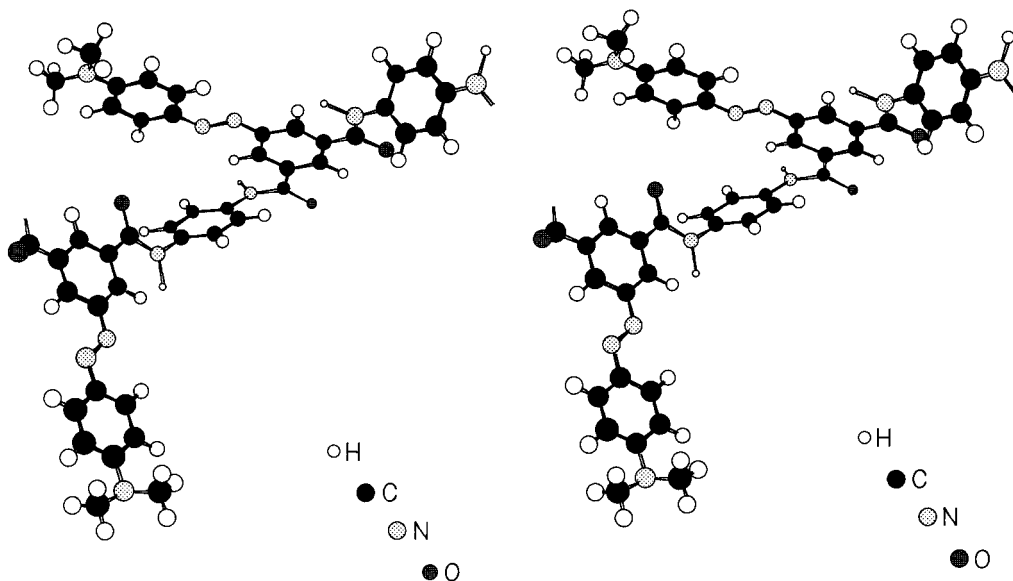


Figure 5 Stereoscopic view for two repeat molecule units of polyamide **3d** (ChemDraw 3D Plus Σ , Cambridge Scientific Inc.).

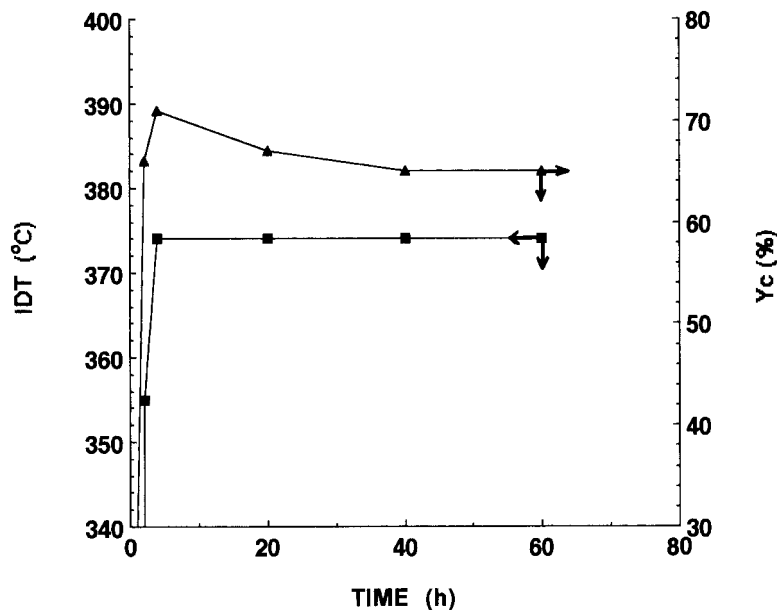


Figure 6 IDT and Y_c in N_2 at $800^\circ C$ of polyamide **3c** as a function of the time for curing at $270^\circ C$.

diffractogram for a powder specimen of polyisophthalamide **3c**. It displayed weak diffraction peaks that indicate the presence of a small fraction of crystalline or mesomorphic material.

The solubility behavior of modified polyisophthalamides was studied and compared to that

of the corresponding unmodified ones (Table I). The attachment of the pendent dimethylaminoazobenzene groups along the polymer backbone remarkably increased the solubility in certain solvents. More particularly, the modified polyisophthalamides were dissolved upon heating in

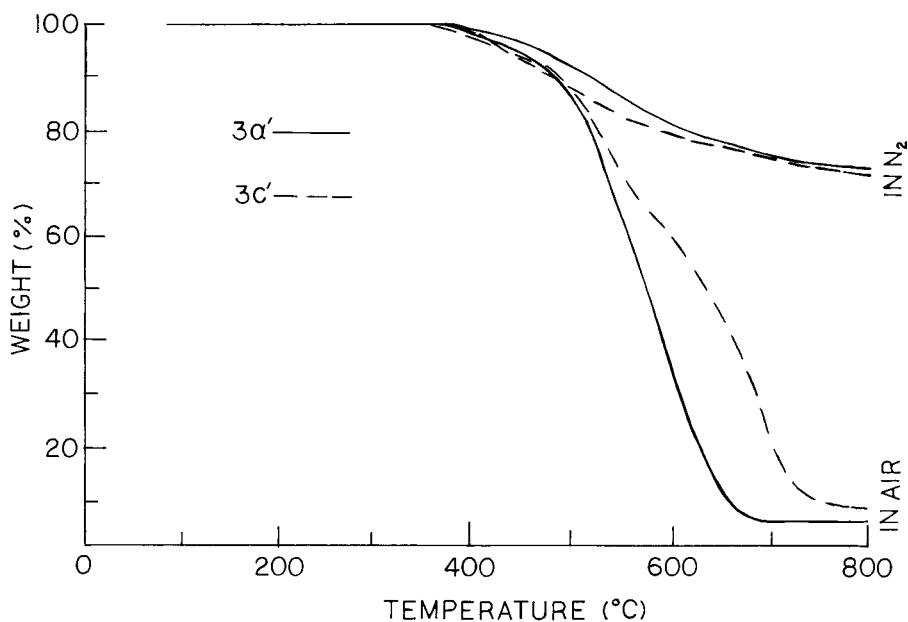


Figure 7 TGA thermograms of cured polyamides **3a'** and **3c'** in N_2 and air. Conditions: gas flow $60\text{ cm}^3/\text{min}$, heating rate $20^\circ C/\text{min}$.

Table II Thermal Stabilities of Cured Polyamides

Sample	N ₂				Air		
	IDT (°C)	PDT (°C)	PDT _{max} (°C)	Y _c (%)	IDT (°C)	PDT (°C)	PDT _{max} (°C)
3a'	374	512	552	72	359	471	523
3b'	370	498	517	71	347	489	522
3c'	372	474	518	71	351	486	537
3d'	365	482	541	68	340	422	460
4a'	336	498	482	70	325	467	519
4b'	310	407	422	69	300	437	442
4c'	355	508	441	67	344	478	541
4d'	329	498	484	66	317	456	486

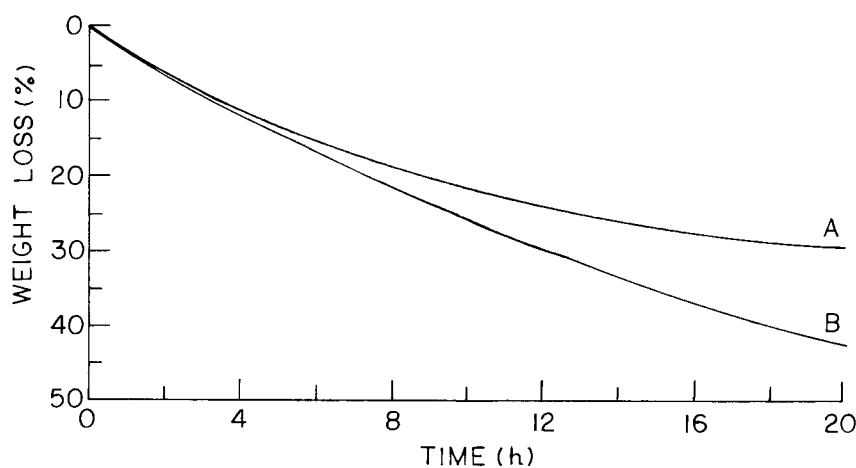
IDT, initial decomposition temperature; PDT, polymer decomposition temperature; PDT_{max}, maximum polymer decomposition temperature; Y_c, char yield at 800°C.

1,4-dioxane and at room temperature in *m*-cresol and cyclohexanone whereas the corresponding unmodified ones were insoluble in these solvents. Polyamide **4c** was only dissolved in hot *m*-cresol. The modified polyisophthalamides were also more soluble in CCl₃COOH than the parent polyamides. However, modified and unmodified polymers displayed a comparable solubility in more efficient solvents such as DMF, NMP, DMSO, and H₂SO₄ 98%.

It is well established⁸ that the introduction of bulky substituents along a polyamide main chain inhibits crystallization, a result that is in line with the enhanced solubility and higher hydrophilicity. The isothermal moisture absorption for a typical pair of polyamides (**3d** and **4d**) is shown in Figure 4. The moles of the absorbed water per

amide equivalent weight were 0.44 and 0.13, respectively, after a time exposure of 96 h. Modified polyisophthalamide **3d** showed a remarkably higher hydrophilicity than **4d**. Figure 5 presents the stereoscopic view for two repeat molecule units of **3d** indicating the increased degree of disorder. Obviously, the incorporation of the dimethylaminoazobenzene pendent groups along the polyisophthalamide backbone increased the water accessibility through the polymer chains.

The DTA traces of the modified polymers did not show endotherms associated with their softening. Crosslinked polymers were obtained upon heat curing the synthesized polymers at 270°C in static air. The cured polymers were obtained as dark brown solids and were completely insoluble in solvents for the untreated samples. To find the

**Figure 8** IGA traces at 300°C in static air of cured polyamides (a) **3a'** and (b) **4a'**.

optimum curing time, polyisophthalamide **3c** was heated at 270°C for various periods and the initial decomposition temperature (IDT) as well as the char yield (Y_c) at 800°C in N_2 of the obtained network polymer were determined by TGA (Fig. 6). The IDT and Y_c were increased up to 4 h, and then they were reduced or remained unchanged beyond this time. Therefore, the optimum curing time at 270°C was 4 h. The unmodified polyisophthalamides were also cured under the same experimental conditions for comparing their thermal properties.

The cured polymers obtained from polyamides **3a–3d** and **4a–4d** by curing at 270°C for 4 h are referred to by the designations **3a'–3d'** and **4a'–4d'**, respectively. Their thermal stability was evaluated by dynamic TGA and isothermal gravimetric analysis (IGA). Figure 7 presents typical TGA curves in N_2 and air for the cured polymers **3a'** and **3c'**. The IDT, the polymer decomposition temperature (PDT), and the maximum polymer decomposition temperature (PDT_{max}) in N_2 and air, and the Y_c at 800°C for all cured polymers are summarized in Table II. The IDT and the PDT were determined for a 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.

Taking the IDT as criterion of thermal stability, the modified polyisophthalamides showed higher thermal stability than the corresponding unmodified ones. Specifically, even though all polyamides displayed comparable Y_c in N_2 , their structural modification increased the IDT values by 22–60°C in N_2 and 7–47°C in air.

The higher thermal stability of the cured modified polyisophthalamides was also confirmed by IGA. Figure 8 presents the IGA traces in static air at 300°C for the pair of cured polymers **3a'** and **4d'**. They exhibited weight losses of 29.0 and 42.5%, respectively, after 20 h isothermal aging.

CONCLUSIONS

1. A novel class of modified polyisophthalamides bearing bulky azo pendent groups were prepared from the polycondensation of 5-(4'-dimethylaminoazobenzene)isophthaloyl chloride with various aromatic diamines.

2. The synthesized modified polyisophthalamides were amorphous and showed an enhanced solubility in common organic solvents and higher hydrophilicity than the unmodified polyisophthalamides.
3. Crosslinked polymers were obtained upon curing at 270°C for 4 h. They were stable up to 340–374°C in N_2 or air and afforded anaerobic char yields of 68–72% at 800°C.

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