Polyisophthalamides with pendent phthalimide groups

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Certain structurally different polyisophthalamides containing pendent phthalimide groups were synthesized from 5-(phthalimide)isophthalic acid and aromatic diamines by the phosphorylation method. Their chemical, physical and thermal properties were determined and compared with those of the corresponding unsubstituted polyisophthalamides. The polymers were characterized by *FT*i.r., ^{1}H n.m.r., thermogravimetric analysis, isothermal gravimetric analysis and inherent viscosity measurements. The modified polyisophthalamides showed enhanced solubilities in some solvents, such as 1,4-dioxane, *m*-cresol and trichloroacetic acid, in comparison to the unmodified analogues. In addition, the incorporation of the pendent phthalimide groups in the polyisophthalamide backbone increased remarkably the thermal stability of the polymer. The modified polyamides were stable up to 317–351°C in N_2 or air and afforded anaerobic char yields of 55–66% at 800°C. Water absorption and X-ray measurements were also performed.

(Keywords: aromatic polyamides; modified polyisophthalamides; thermally stable polymers)

INTRODUCTION

Aromatic polyamides are widely used as high temperature resistant polymers and have received the attention of many research workers[1]. Numerous polyamides containing various substituents on the aromatic rings have been synthesized.

Polyisophthalamides are among the most interesting aromatic polyamides. Their chemical structures have been modified by introducing nitro[2,3], iminobenzoyl[4], oxybenzoyl[5], phenoxy[6] and *N*-benzylidene[7] groups as substituents on position 5 of the isophthalic segment. In addition, polyisophthalamides with pendent imide groups have been prepared from 4,4′-diaminodiphenyl ether and imide diacid chlorides by solution polycondensation[8]. 5-(Phthalimide)isophthaloyl dichloride has been included among the imide-diacid chlorides of this paper, but detailed results concerning the synthesis and characterization of monomer and polymer have not been reported.

The present investigation deals with the synthesis and characterization of modified polyisophthalamides prepared by the phosphorylation polycondensation method using 5-(phthalimide)isophthalic acid and various aromatic diamines. Furthermore, their physical and thermal characteristics were compared with those of the unsubstituted polyisophthalamides.

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. *FT*i.r. spectra were recorded on a Perkin–Elmer 16PC spectrometer with KBr pellets. ^{1}H n.m.r. spectra were recorded using a Varian T-60A spectrometer at 60 MHz. Chemical shifts are given in parts per million (ppm) with tetramethylsilane as the internal standard. Differential thermal analysis (d.t.a.) and thermogravimetric analysis (t.g.a.) were performed on a DuPont 990 thermal analyser system. D.t.a. measurements were made using a high temperature (1200°C) cell at a heating rate of 20°C min^{-1} in an N_2 atmosphere at a flow rate of 60 cm^3 min^{-1} and with a ΔT sensitivity of 0.4°C cm^{-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}. The inherent viscosities (η_{inh}) of the polymers were determined for solutions of 0.5 g in 100 cm^3 of either *N,N*-dimethylformamide (DMF) or concentrated H_2SO_4 at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett–Packard 185 analyser. The wide-angle X-ray diffractions were obtained for powder specimens on a Philips PW-1830 diffractometer.

To determine the equilibrium water absorptions, polymer samples were preconditioned 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. The samples were weighted periodically.

Reagents and solvents

5-Aminoisophthalic acid was recrystallized from a DMF/water mixture (3/1 v/v). 4,4′-Diaminodiphenyl sulfone, 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenyl ether were recrystallized from methanol, toluene and acetonitrile, respectively. 1,4-Phenylenediamine and phthalic anhydride were sublimed under reduced pressure. DMF was refluxed and fractionally distilled over CaH_2. Triphenyl phosphite and pyridine were purified by distillation.

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Preparation of 5-(phthalimide)isophthalic acid 2

Phthalic anhydride (3.2696 g, 22.09 mmol) was stepwise added to a stirred solution of 5-aminoisophthalic acid (4.0000 g, 22.09 mmol) in DMF (30 cm^3) at ambient temperature. The mixture was subsequently heated at 60°C overnight under N_2. The intermediate phthalamic acid **1** was isolated as a whitish solid by pouring an aliquot of the reaction solution into water. A purified sample of **1** obtained by recrystallization from DMF/water (1/2 v/v) had a melting point (m.p.) of over 340°C.

Analysis: Calculated for $C_{16}H_{11}NO_7$: C, 58.35%; H, 3.37%; N, 4.26%. Found: C, 57.71%; H, 3.38%; N, 4.08%.

I.r. (KBr, cm^{-1}): 3285–2460 (N–H and O–H stretch); 1727 (carboxylic C=O); 1701 (amide C=O); 1602 (aromatic); 1575 (N–H deformation); 1439, 1413 (C–O stretch); 1350 (C–N stretch and N–H bend).

^1H n.m.r. (dimethyl sulfoxide-d_6, ppm): 10.50 (br, 3H, carboxylic); 9.03 (br, 1H, NHCO); 8.36–8.10 (m, 3H, aromatic H of isophthalic ring); 8.00–7.20 (m, 4H, other aromatics).

Acetic anhydride (10 cm^3) and freshly fused sodium acetate (0.2 g) were added to the remaining solution and the mixture was heated at 100°C overnight under N_2. The mixture was then poured into water, stirred at room temperature for 5 h and the resultant light yellow solid was filtered off, washed with water and dried to afford **2** (5.91 g, overall yield 86%). Crude **2** was recrystallized from DMF (m.p. >340°C).

Analysis: Calculated for $C_{16}H_9NO_6$: C, 61.73%; H, 2.92%; N, 4.50%. Found: C, 61.12%; H, 2.94%; N, 4.29%.

I.r. (KBr, cm^{-1}): 3068–2510 (O–H stretch); 1785, 1717 (imide C=O); 1717 (carboxylic C=O); 1607 (aromatic); 1429, 1413 (C–O stretch); 1120 (imide structure).

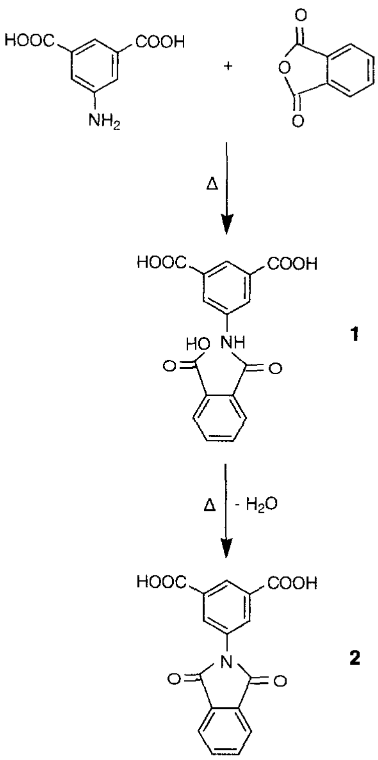
^1H n.m.r. (dimethyl sulfoxide-d_6, ppm): 10.03 (br, 2H, carboxylic); 8.30–8.10 (m, 3H, aromatic H of isophthalic ring); 7.66–7.45 (m, 4H, other aromatics).

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

A typical phosphorylation polycondensation for the preparation of polyamide **3a** is given. A flask was charged with a mixture of compound **2** (0.7000 g, 2.24 mmol), 4,4′-diaminodiphenylmethane (0.4450 g, 2.24 mmol), triphenyl phosphite (1.3953 g, 4.49 mmol), pyridine (2 cm^3), lithium chloride (0.5 g) and DMF (20 cm^3). This mixture was stirred and heated at 100°C under N_2 overnight. The viscous solution was subsequently poured over crushed ice. The resultant brown solid was filtered off, washed with water and dried in a vacuum oven at about 150°C to afford polyamide **3a** (1.04 g, yield 98%).

RESULTS AND DISCUSSION

The reactions in *Scheme 1* show the method applied for the synthesis of 5-(phthalimide)isophthalic acid **2**. More particularly, the reaction of 5-aminoisophthalic acid with phthalic anhydride afforded the phthalamic acid **1**. DMF was used as the reaction solvent because 5-aminoisophthalic acid dissolves only in polar aprotic solvents. The reaction required heating because of the low nucleophilicity of 5-aminoisophthalic acid. Compound **1** was cyclodehydrated to the corresponding phthalimide **2** by means of acetic anhydride and a catalytic amount of sodium acetate.



Scheme 1

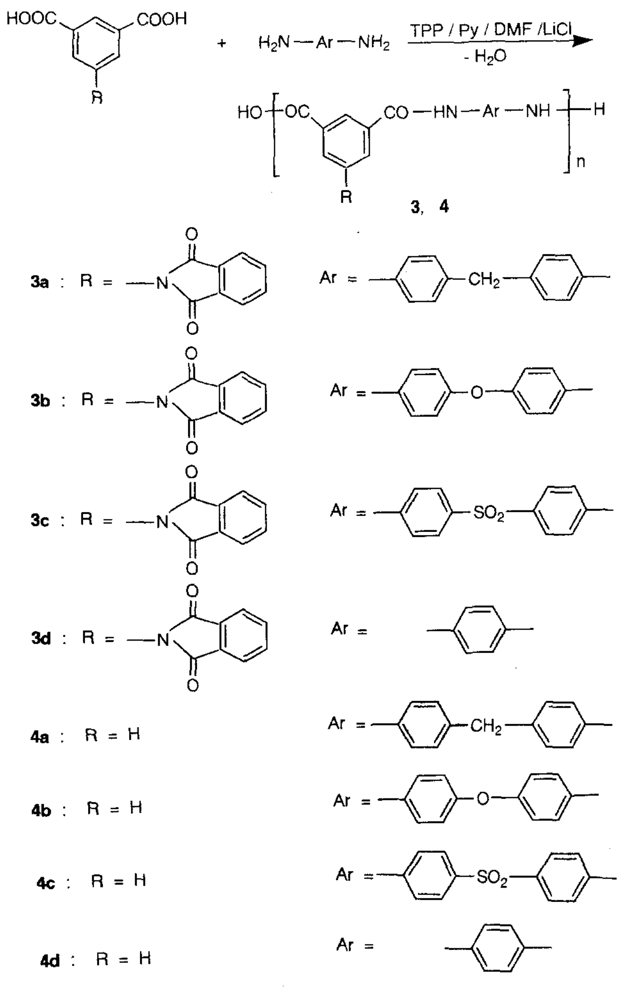
Modified polyisophthalamides and the corresponding unmodified polyisophthalamides were synthesized from the reactions of aromatic diamines with compound **2** or isophthalic acid, respectively (*Scheme 2*). The polycondensation was carried out in DMF solution by the phosphorylation method[9,10], utilizing triphenyl phosphite and pyridine as the condensing agents.

Monomers **1** and **2** were characterized by elemental analyses as well as by *FT*i.r. and ^1H n.m.r. spectroscopy. *Figure 1* presents the *FT*i.r. spectra of compounds **1** and **2**. The imidization reaction could be monitored by *FT*i.r. spectroscopy because the spectra of **1** and **2** show certain differences. Specifically, compound **2** lacks the absorption at 1575 cm^{-1} (N–H deformation) and displays new absorption bands at 1785 and 1120 cm^{-1} (imide structure). Both compounds display absorptions at around 3200–2800 (carboxylic O–H) and 1710 cm^{-1} (carboxylic C=O).

The ^1H n.m.r. spectrum of compound **2** (*Figure 2*) shows peaks at 10.03 (COOH), 8.30–8.10 (aromatic H of isophthalic ring) and 7.66–7.45 ppm (other aromatics). The carboxylic acid protons were exchangeable with D_2O.

Figure 3 presents the d.t.a. traces of compounds **1** and **2**. The endotherm at 206°C for phthalamic acid was assigned to the thermally induced cyclodehydration to the corresponding phthalimide because compound **2** lacks this endotherm. Note that both compounds did not show melting up to 340°C upon gradual heating in a capillary tube. Thermal cyclodehydration of **1** to **2** was complete because both spectra display an endotherm at 416°C followed by a large exotherm attributable to melting and degradation.

Characterization of the polyamides was accomplished by *FT*i.r., ^1H n.m.r. and inherent viscosity measurements. *Figure 4* presents typical *FT*i.r. spectra of **3a** and **4a**. Modified polyisophthalamide **3a** shows characteristic absorptions for the imide structure at 1785, 1727, 1387,



Scheme 2

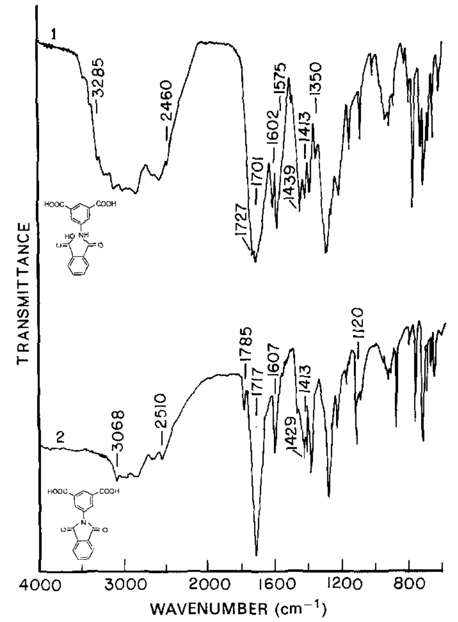


Figure 1 *FT*i.r. spectra of compounds **1** and **2**

1115 and 717 cm^{-1} owing to the presence of pendent phthalimide groups. These peaks are not present in the spectrum of unmodified polyisophthalamide **4a**. In addition, **3a** displays absorptions at 3350–3200 (N–H stretch), 1654 (amide C=O), 1602 (aromatic) and 1513 cm^{-1} (N–H stretch).

The ^{1}H n.m.r. spectrum of polyisophthalamide **3a** in dimethyl sulfoxide-d_6 solution (*Figure 5*) shows peaks at 10.73 (NHCO), 8.66–8.31 (aromatic H ortho to C=O), 8.00–7.10 (other aromatics) and 4.50 ppm (CH_2).

One aim of the present investigation was to increase the solubility of the modified polyisophthalamides by introducing the bulky pendent phthalimide groups. The solubilities of the modified and unmodified polyisophthalamides are summarized in *Table 1*. The former display enhanced solubilities in 1,4-dioxane, *m*-cresol and

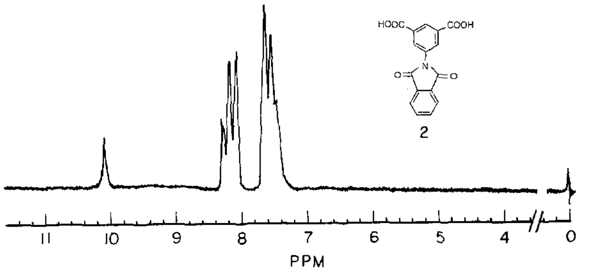


Figure 2 ^{1}H n.m.r. spectrum of compound **2** in dimethyl sulfoxide-d_6 solution

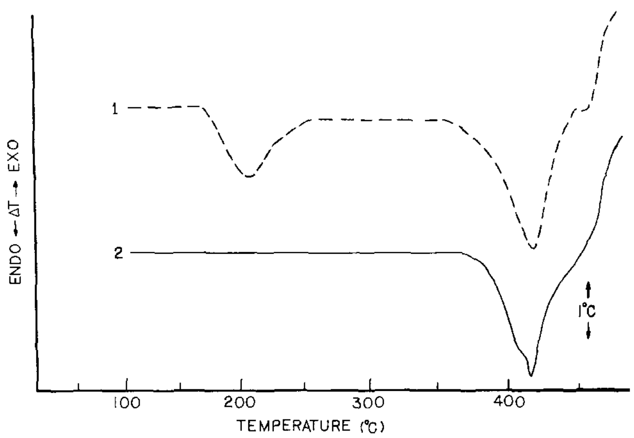


Figure 3 D.t.a. traces of compounds **1** and **2** in N_2 (N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1})

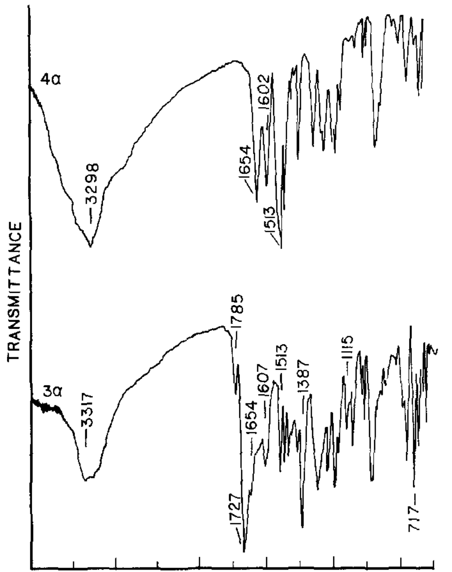


Figure 4 *FT*i.r. spectra of polyamides **3a** and **4a**

trichloroacetic acid. The solubilities of the modified polyisophthalamides in DMF and H_2SO_4 (98%) are comparable to those of the unmodified polyisophthalamides in these solvents.

The inherent viscosities of the modified polyisophthalamides ranged from 23 to 26 $cm^3\,g^{-1}$ (*Table 1*). No considerable differences in the η_{inh} values of the modified and unmodified polyisophthalamides were observed.

Figure 6 presents a typical wide-angle X-ray diffraction pattern for a powder specimen of polyisophthalamide **3c** indicative of an amorphous structure.

The isothermal moisture absorptions for the polyamides **3d** and **4d** are shown in *Figure 7*. The numbers of moles of absorbed water per amide equivalent weight were 0.44 and 0.10, respectively. The equilibrium water absorption was much higher for the modified polyisophthalamide than for the unmodified analogue. This behaviour could be attributed to the introduction of the bulky side groups in that the degree of disorder will be affected with an increase in the accessibility of the polymer to water, a result in agreement with the enhanced solubility[4]. Moreover, the phthalimide carbonyls could form hydrogen bonds with the water molecules.

The thermal stabilities of the modified and unmodified polyisophthalamides were evaluated by t.g.a. and isothermal gravimetric analysis (i.g.a.). *Figure 8* presents typical t.g.a. traces for the polymers **3a**, **3b**, **4a** and **4b** in N_2 and air. The initial decomposition temperatures (*IDT*), the polymer decomposition temperatures (*PDT*) and the maximum polymer decomposition temperatures (PDT_{max}) both in N_2 and air as well as the anaerobic char yields (Y_c) at 800°C for all the polymers studied are listed in *Table 2*. The *IDT* and *PDT* were determined by the temperatures at which 0.5 and 10% weight loss were observed, respectively. PDT_{max} corresponds to the

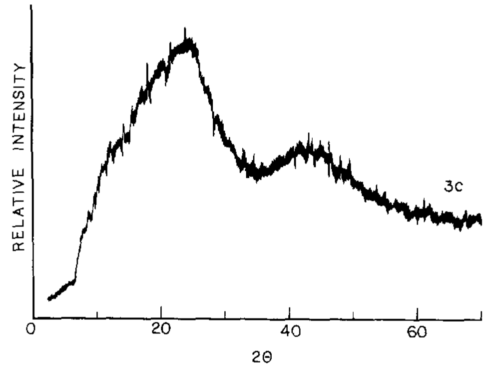


Figure 6 X-ray diffraction pattern of polyamide **3c**

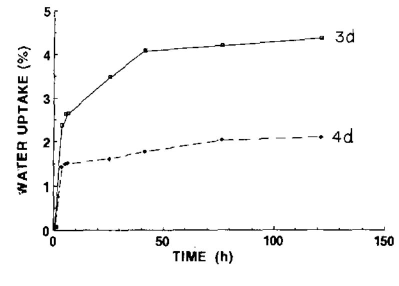


Figure 7 Water absorption (%) *versus* time for polyamides **3d** and **4d**

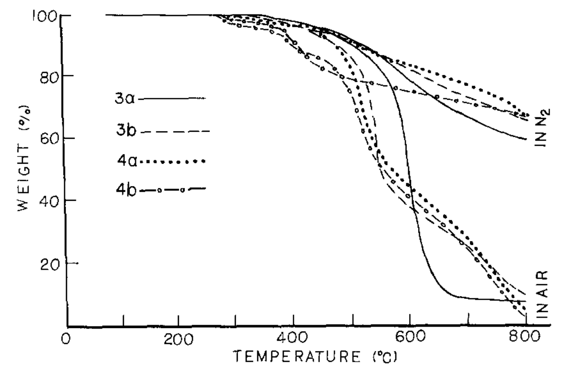


Figure 8 T.g.a. thermograms of polyamides **3a**, **3b**, **4a** and **4b** in N_2 and air (gas flow 60 $cm^3\,min^{-1}$; heating rate 20°C min^{-1})

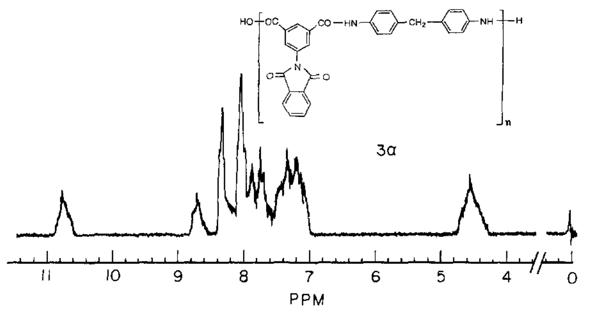


Figure 5 ^1H n.m.r. spectrum of polyamide **3a** in dimethyl sulfoxide-d_6 solution

Table 1 Inherent viscosities and solubilities of the polyamides

Sample	η_{inh} ($cm^3\,g^{-1}$)	Solubility[a] DMF	1,4-Dioxane	*m*-Cresol	H_2SO_4 (98%)	CCl_3COOH
3a	26[b]	++	+	++	++	++
3b	24[b]	++	+	++	++	++
3c	24[b]	++	+	++	++	++
3d	25[b]	++	+−	++	++	++
4a	25[b]	++	−	−	++	+
4b	24[b]	++	−	−	++	+
4c	23[b]	++	−	+	++	+
4d	25[c]	−	−	−	+	−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot; +−, partially soluble or swollen; −, insoluble
[b] 0.5 g in 100 cm^3 of DMF
[c] 0.5 g in 100 cm^3 of concentrated H_2SO_4

Table 2 Thermal stabilities of the polyamides

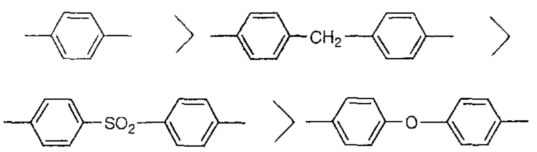
	N_2				Air		
Sample	*IDT*[a] (°C)	*PDT*[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	*IDT* (°C)	*PDT* (°C)	PDT_{max} (°C)
3a	347	519	552	60	343	503	571
3b	319	516	519	66	317	478	537
3c	321	508	537	60	320	501	560
3d	351	517	571	55	350	517	589
4a	286	471	475	67	272	460	501
4b	272	407	415	67	260	460	523
4c	276	501	440	61	283	463	498
4d	296	490	510	61	294	452	503

[a] Initial decomposition temperature
[b] Polymer decomposition temperature
[c] Maximum polymer decomposition temperature
[d] Anaerobic char yield at 800°C

temperature at which the maximum rate of weight loss occurred.

The modified polyamides showed much better thermal characteristics than the corresponding unmodified polyamides. However, all the polyamides studied displayed comparable Y_c in N_2. The incorporation of the phthalimide side groups increased the *IDT* by about 55°C. Thus the *IDT* in N_2 for polyamides **3a** and **4a** were 347 and 286°C, respectively. It has been reported that the attachment of pendent iminobenzoyl[4] or phenoxy[6] groups to the polyisophthalamide backbone decreases the thermal stability of the polymer. In the present case the stiff phthalimide segments could be responsible for the significantly higher thermal stability of the modified polyisophthalamides.

Taking the *IDT* as the criterion of thermal stability, the relative order of thermal stability with respect to the aromatic diamine utilized for the polymer preparation was



The thermal stabilities of polyamides **3a** and **4a** were ascertained by i.g.a. *Figure 9* presents the i.g.a. traces in static air for **3a** at 260, 300 and 320°C and for **4a** at 260°C. After 20 h of isothermal ageing the weight losses were 6.5, 15.0, 24.2 and 14.1%, respectively. These results confirm the remarkably high thermal stability of the modified polyisophthalamides.

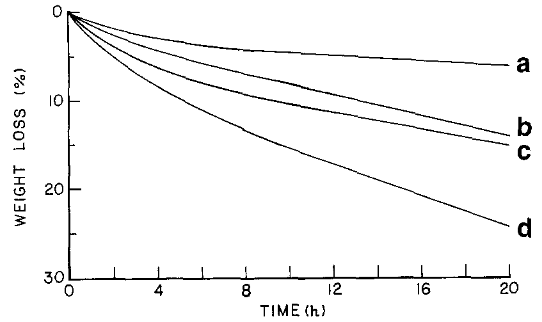


Figure 9 I.g.a. traces in static air: (a) **3a** at 260°C; (b) **4a** at 260°C; (c) **3a** at 300°C; (d) **3a** at 320°C

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