N-Cyano-substituted homopolyamide and copolyamides

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Certain biscyanamides were synthesized by reacting aromatic diamines with cyanogen bromide. They were used as starting materials for preparing a new series of *N*-cyano-substituted homopolyamide and copolyamides. Homopolyamide was prepared from the reaction of terephthaloyl dichloride with 4,4'-biscyanamidediphenylmethane. Various copolyamides were prepared by reacting terephthaloyl dichloride with a mixture of an aromatic diamine and the corresponding biscyanamide. The polycondensations were carried out in solution at low temperature in the presence of acid acceptor. In addition, a model compound was synthesized from the reaction of 4,4'-biscyanamidediphenylmethane with a double molar amount of benzoyl chloride. The polyamides were characterized by *FT*i.r. and ^{1}H n.m.r. spectroscopy as well as by inherent viscosity measurements. The modified polyamides showed higher solubility in common solvents than the corresponding unsubstituted polyamide. Crosslinked polymers were obtained by curing the *N*-cyano-substituted polyamides. Their thermal stability was correlated with the curing conditions as well as the concentration of cyano groups. The cured modified polyamides were stable up to 317–370°C in N_2 or air and afforded anaerobic char yield of 45–58% at 800°C.

(Keywords: *N*-cyano-substituted polyamides; modified polyamides; crosslinked polymers; thermally stable polymers; biscyanamides)

INTRODUCTION

The preparation of high-performance polymers that have high decomposition and glass transition temperatures is of interest. Wholly aromatic polyamides possess many attractive characteristics such as excellent mechanical properties and thermal stability. However, they possess poor processability due to their limited solubility and high glass transition or melt temperatures. The incorporation of *N*-alkyl or aryl substituents along the polymer backbone has been reported as an approach to enchance their solubility and reduce glass transition temperatures[1–5].

The present investigation is concerned with the synthesis and heat-curing of a new series of *N*-cyano-substituted homopolyamide and copolyamides. They were prepared by the low-temperature solution polycondensation of terephthaloyl dichloride with certain *N*-cyano-substituted diamines in the presence of an acid acceptor. The modified polyamides are expected to display good solubility characteristics. In addition, on curing they are expected to afford heat-resistant network polymers without the evolution of volatile by-products, which is a desirable feature in any curing process. The concentration of cyano groups in copolyamides can be varied by altering the molar ratio of the reagents and therefore the crosslinking density of cured resins can be adjusted. The *N*-cyano-substituted polyamides can be used as matrix resins for composites since they are expected to be tractable precursors of heat-resistant resins.

Compounds of the general structure NCHN–Ar–NHCN, where Ar = aryl, are known as biscyanamides. Upon curing, they afford melamine or isomelamine rings by a cycloaddition reaction. On the basis of this reaction, certain heat-resistant polymers have been prepared. The curing behaviour of biscyanamides has been correlated with their chemical structures[6–10]. Most biscyanamides are polymerized without melting due to their high reactivity. In addition, some heat-resistant polymers have been prepared from the reactions of aromatic biscyanamides with bismaleimides[11].

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus (IA6304) and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 16PC *FT*i.r. spectrometer with KBr pellets. ^{1}H 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. D.t.a. and 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 in N_2 atmosphere at a flow rate of 60 cm^3 min^{-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 of polymers were determined for solutions of 0.5 g per 100 ml in concentrated H_2SO_4 at 30°C using an Ubbelohde

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suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyser.

Reagents and solvents

4,4'-Diaminodiphenylmethane and 4,4'-diaminodiphenylether were recrystallized from toluene and acetonitrile respectively. 1,4-Phenylenediamine was sublimed under reduced pressure (2–3 mm). Terephthaloyl dichloride was recrystallized from n-hexane. Benzoyl chloride was purified by distillation. *N,N*-Dimethylformamide (DMF) was dried by distillation under reduced pressure over calcium hydride. Cyanogen bromide and triethylamine were used as supplied.

*Preparation of biscyanamides **1a**, **1b** and **1c*** (Scheme 1)

Biscyanamides **1a**, **1b** and **1c** were prepared according to the following general procedure. A flask was charged with a solution of cyanogen bromide (98.0 mmol) in water (50 ml) which was cooled at 0°C. DMF (50 ml) and sodium bicarbonate (76.2 mmol) were added to the solution. Aromatic diamine (32.6 mmol) dissolved in DMF (50 ml) was subsequently added dropwise at 0–10°C for 2 h. Stirring of the mixture at this temperature was continued for a further 2 h. The insoluble material was removed by filtration and the filtrate was added to cold water (500 ml). The solid precipitated was filtered off, washed with water and dried in a vacuum oven at about 30°C. It was recrystallized from a mixture of 2-methoxy-ethanol/water (1:1 v/v). The products **1a**, **1b** and **1c** were obtained in 93–95% yield and did not show a melting temperature upon gradual heating to 300°C. They were characterized as follows.

4,4'-Biscyanamidediphenylmethane (***1a***). Analysis: Calculated for $C_{15}H_{12}N_4$: C, 72.56%; H, 4.87%; N, 22.67%. Found: C, 71.96%; H, 4.92%; N, 22.53%.
I.r. (KBr) cm^{-1}: 3500–3000 (N–H strecthing); 2240 (C≡N); 1618 (N–H deformation); 1518 (aromatic); 1258 (C–N stretching).
^1H n.m.r. (DMSO-d_6) δ: 9.68 (s, 2H, NHCN); 7.26–6.80 (m, 8H, aromatic); 3.71 (s, 2H, CH_2).

4,4'-Biscyanamidediphenylether (***1b***). Analysis: Calculated for $C_{14}H_{10}N_4O$: C, 67.20%; H, 4.00%; N, 22.40%. Found: C, 66.40%; H, 4.31%; N, 22.10%.
I.r. (KBr) cm^{-1}: 3500–3000 (N–H stretching); 2240 (C≡N); 1620 (N–H deformation); 1510–1500 (aromatic); 1235 (C–N stretching).
^1H n.m.r. (DMSO-d_6) δ: 9.70 (s, 2H, NHCN); 7.20–6.70 (m, 8H, aromatic).

1,4-Phenylenebiscyanamide (***1c***). Analysis: Calculated for $C_8H_6N_4$: C, 60.74%; H, 3.82%; N, 35.42%. Found: C, 60.10%; H, 4.02%; N, 35.12%.
I.r. (KBr) cm^{-1}: 3500–3000 (N–H stretching); 2240 (C≡N); 1640 (N–H deformation); 1500–1515 (aromatic); 1250 (C–N stretching).
^1H n.m.r. (DMSO-d_6) δ: 9.65 (s, 2H, NHCN); 7.25–6.80 (m, 4H, aromatic).

Preparation of homopolyamides and copolyamides (Scheme 2)

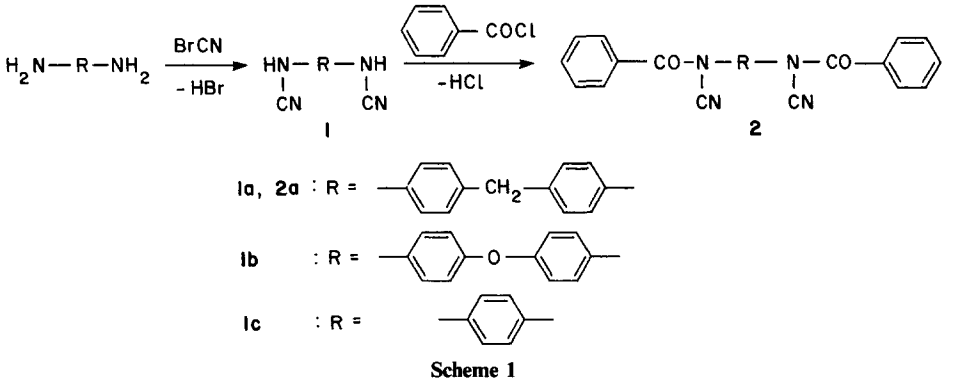
A flask equipped with dropping funnel and magnetic stirrer was charged with a solution of biscyanamide **1a**, **1b** or **1c** (x mol) and an aromatic diamine 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether or 1,4-phenylenediamine (y mol) in DMF. Triethylamine [$2(x + y)$ mol] was added to the solution. Terephthaloyl dichloride ($x + y$ mol) dissolved in DMF was added dropwise to the stirred solution at 0°C under N_2. The mixture was subsequently stirred at ambient temperature for 3 h in a stream of N_2. It was poured into water and the solid precipitated was filtered off, washed with water and dried. The weights of reagents, the reaction yields and the inherent viscosities of the products are summarized in *Table 1*.

Curing of homopolyamides and copolyamides

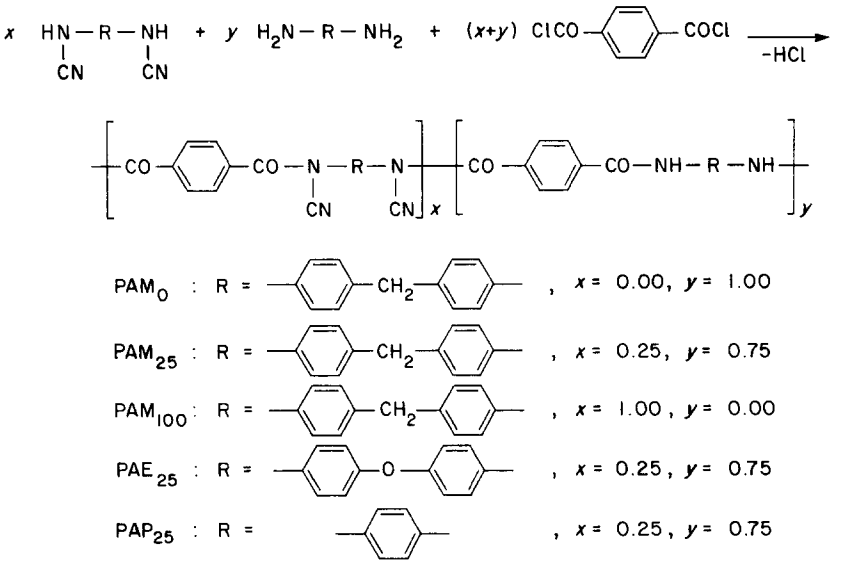
The isolated homopolyamides and copolyamides were placed in an aluminium dish and curing was accomplished by heating in an oven at 240°C for 40 h.

*Preparation of model compound **2a*** (Scheme 1)

A flask was charged with a solution of **1a** (1.0000 g, 5.0 mmol) in DMF (30 ml). Triethylamine (1.012 g, 10.0 mmol) was added to the solution. Benzoyl chloride (1.4057 g, 10.0 mmol) was added dropwise to the solution at 0°C under N_2. Next the mixture was stirred at ambient temperature for 3 h in a stream of N_2. It was poured into ice–water and the solid obtained was filtered off, washed with water and dried to afford **2a** (1.80 g, yield 88%). A purified sample obtained by recrystallization from a mixture of DMF/water (1:2 v/v) had m.p. 160–165°C.
Analysis: Calculated for $C_{29}H_{20}N_4O_2$: C, 76.30%; H, 4.41%; N, 12.27%. Found: C, 75.71%; H, 4.72%; N, 12.15%.



Scheme 1



Scheme 2

Table 1 Quantities of reagents, reaction yields and inherent viscosities of polyamides

Polyamide	Quantities of reagents (g (mmol))			Yield (%)	η_{inh}[a] (dl g^{-1})
	Biscyanamide	Aromatic diamine	Terephthaloyl dichloride		
PAM_0		2.5000 (12.6)	2.5583 (12.6)	89	0.16
PAM_{25}	0.3972 (1.6)	0.9517 (4.8)	1.2993 (6.4)	96	0.17
PAM_{100}	0.6000 (2.4)		0.4906 (2.4)	91	0.12
PAE_{25}	0.5255 (2.1)	1.2615 (6.3)	1.7052 (8.4)	94	0.16
PAP_{25}	0.3320 (2.1)	0.6812 (6.3)	1.7052 (8.4)	95	0.16

[a]Inherent viscosities in 98% H_2SO_4 (0.5 g dl^{-1}) at 30°C

RESULTS AND DISCUSSION

Biscyanamides **1a**, **1b** and **1c** (*Scheme 1*) were synthesized by reacting various aromatic diamines with cyanogen bromide in the presence of sodium bicarbonate following published procedures[10–12]. The reactions were carried out in a mixture of DMF/water. It was found that the yields were increased with increasing concentration of DMF in the reaction medium. The yields were 93–95% utilizing a mixture of DMF/water with volume ratio 2:1. Biscyanamides were characterized by elemental analyses as well as *FT*i.r. and ^{1}H n.m.r. spectroscopy (see Experimental).

Scheme 2 outlines the preparation of homopolyamides and copolyamides. More particularly, homopolyamides PAM_0 and PAM_{100} were prepared from the reactions of terephthaloyl dichloride with 4,4′-diaminodiphenylmethane and **1a**, respectively. Homopolyamide PAM_0 was synthesized for comparative purposes. In addition, random copolyamides PAM_{25}, PAE_{25} and PAP_{25} were prepared by reacting terephthaloyl dichloride with a mixture consisting of an aromatic diamine and the corresponding biscyanamide in a molar ratio of 3:1. The cured polyamides obtained from this molar ratio of diamines showed the highest thermal stability, as discussed below. The reactions took place in DMF solution utilizing triethylamine as acid acceptor.

To obtain fundamental information about the structure of modified polyamides, the model compound **2a** was synthesized from the reaction of **1a** with a double molar amount of benzoyl chloride in the presence of triethylamine (*Scheme 1*).

The substituted polyamides showed a low degree of polymerization since their inherent viscosities ranged from 0.12 to 0.17 dl g^{-1} (*Table 1*). The η_{inh} value of reference polyamide PAM_0, prepared under the same experimental conditions, was 0.16 dl g^{-1}. Thus the *N*-substitution of polyamides did not influence remarkably their degree of polymerization.

Polyamides and model compound were characterized by *FT*i.r. and ^{1}H n.m.r. spectroscopy. *Figure 1* presents the *FT*i.r. spectra of model compound **2a** and homopolyamide PAM_{100}. It is seen that these spectra are in agreement. Homopolyamide PAM_{100} displayed characteristic absorptions at 2240 (C≡N); 1795, 1696

(C=O); 1617, 1513 (aromatic) and 1280 cm^{-1} (C–N). The broad absorption band at 3600–2800 cm^{-1} was assigned to the terminal NH and COOH groups as well as to the methylene groups. Note that the carbonyl of secondary polyamides displayed only an absorption at 1650 cm^{-1}.

The ^1H n.m.r. spectra of **2a** and PAM_{100} were also in agreement (*Figure 2*). More particularly, PAM_{100} showed multiplet peaks at 8.06–7.90 (4H, *ortho* to C=O); 7.40–6.80 (8H, other aromatic) and 3.85 δ (CH_2). Model compound **2a** displayed multiplet peaks at 8.16–7.63 (4H, *ortho* to C=O); 7.50–6.70 (14H, other aromatic) and 3.90 (2H, CH_2).

The *N*-cyano-substituted polyamides showed significantly higher solubility in common organic solvents than did the unsubstituted polyamide PAM_0. Their solubility was increased with increasing concentration of cyano groups. *Table 2* presents the solubility behaviour of PAM_{100} and PAM_0. The modified homopolyamide PAM_{100} was readily soluble in polar aprotic solvents (DMF, *N*-methylpyrrolidone) and concentrated H_2SO_4. It also dissolved upon heating in CCl_3COOH and partially in *m*-cresol and cyclohexanone. In contrast, PAM_0 dissolved only in warm H_2SO_4 (98%). The higher solubility of modified homopolyamide and copolyamides was assigned to the disruption of the chain packing caused by the pendant cyano groups which contributed to their amorphous nature[5]. In addition, the intermolecular hydrogen bonding between the NH and C=O groups disappeared or was reduced. It has been reported that some *N*-alkyl- or aryl-substituted polyamides present higher solubility than the corresponding unsubstituted ones[1–5].

The *N*-cyano-substituted polyamides afforded heat-resistant network structures by crosslinking through their cyano groups upon curing at 240°C for various periods (20, 40 and 60 h). The initial decomposition temperature (IDT) of cured resins was significantly influenced by the curing time. *Figure 3* presents the IDT of various

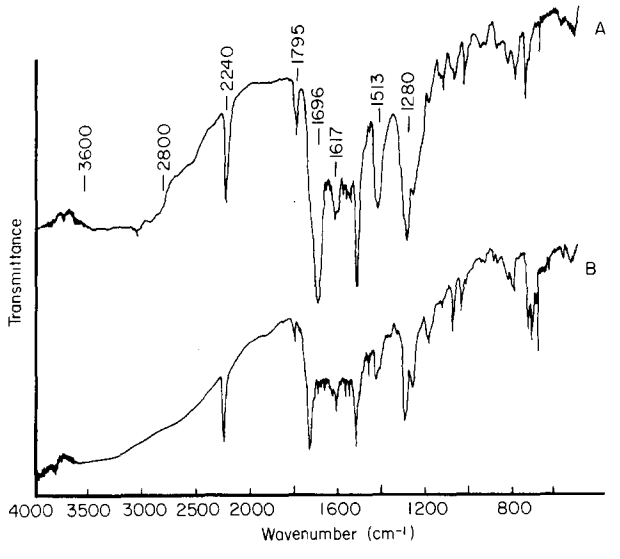


Figure 1 *FT*i.r. spectra of polyamide PAM_{100} (A) and model compound **2a** (B)

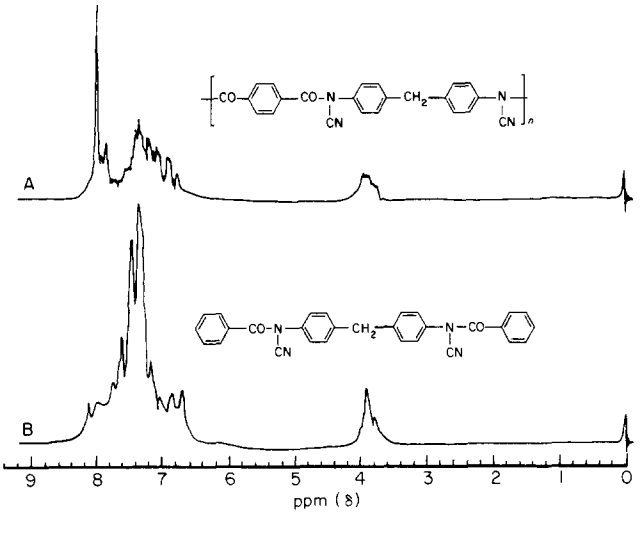


Figure 2 ^1H n.m.r. spectra of polyamide PAM_{100} (A) and model compound **2a** (B)

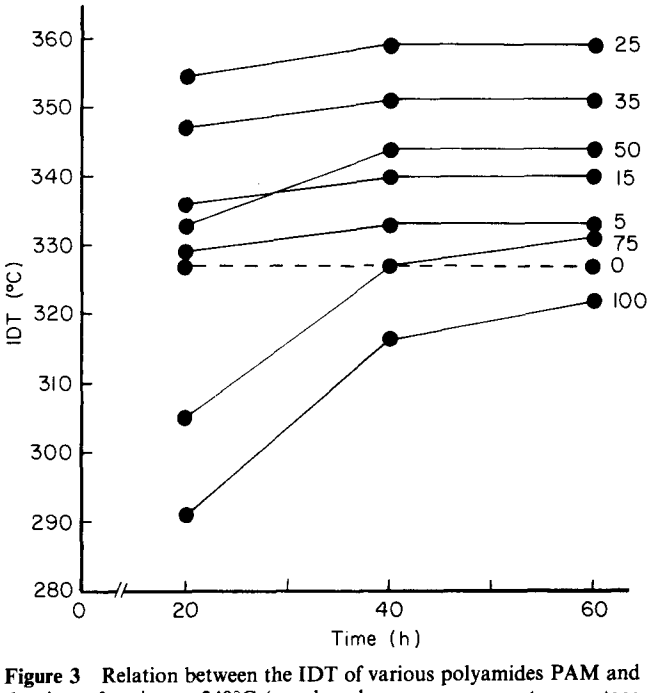


Figure 3 Relation between the IDT of various polyamides PAM and the time of curing at 240°C (numbers by curves represent percentage substitution of **1a** in PAM)

Table 2 Solubilities of polyamides[a]

Sample	Solvents[b]								
	DMF	NMP	CH_3CN	MEK	1,4-Dioxane	*m*-Cresol	CH	H_2SO_4 (98%)	CCl_3COOH
PAM_{100}	++	++	–	–	–	+–	+–	++	+
PAM_0	–	–	–	–	–	–	–	+	–

[a]Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +–, partially soluble or swollen; –, insoluble
[b]DMF, *N*,*N*-dimethylformamide; NMP, N-methylpyrrolidone; MEK, methyl ethyl ketone; CH, cyclohexanone

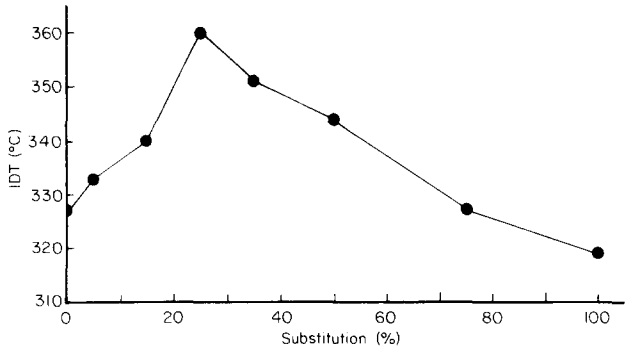


Figure 4 Relation between the IDT of cured (at 240°C for 40 h) polyamides PAM′ and the percentage substitution of 4,4′-biscyanamidediphenylmethane (**1a**)

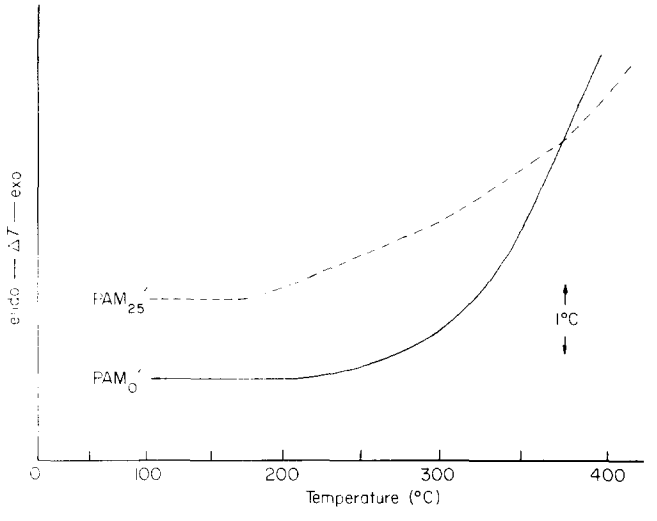


Figure 5 D.t.a. traces of cured polyamides $PAM_{0'}$ and $PAM_{25'}$. Conditions: N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

N-cyano-substituted polyamides as a function of curing time. To investigate the curing conditions in a systematic way, various homo- or copolyamides were prepared by reacting **1a** and 4,4′-diaminodiphenylmethane with terephthaloyl dichloride according to the general procedure (see Experimental). The percentage substitution of **1a** in these polyamides was 0, 5, 15, 25, 35, 50, 75 and 100%. It is seen from *Figure 3* that the IDT of polyamides was remarkably increased with increasing the curing time from 20 to 40 h. Beyond this time, the IDT of polyamides remained unchanged or was slightly increased. The optimum curing time for a heat-curing at 240°C was therefore 40 h. The IDT was not affected by the curing time in the case of reference polyamide PAM_0 (0% substitution of **1a** in polyamide).

The IDT of cured (at 240°C for 40 h) polyamides PAM was considerably influenced by the percentage substitution of **1a** in these polyamides (*Figure 4*). It can be seen that the IDT was increased with increasing the percentage substitution of **1a** in polyamides up to 25%. Since the IDT was reduced beyond this value, 25% substitution of **1a** in PAM was the optimum.

The resins obtained upon curing at 240°C for 40 h from polyamides PAM_0, PAM_{25}, PAM_{100}, PAE_{25} and PAP_{25} are referred to by the designations $PAM_{0'}$, $PAM_{25'}$, $PAM_{100'}$, $PAE_{25'}$ and $PAP_{25'}$, respectively. The curing behaviour of polyamides was investigated by d.t.a. *Figure 5* presents the d.t.a. traces of $PAM_{0'}$ and $PAM_{25'}$ in N_2. The IDT of these polyamides in N_2 determined by t.g.a. were 327 and 359°C, respectively. The large exotherms of polyamides above these temperatures were associated with their thermal degradation. It is seen that $PAM_{25'}$ showed a well distinguished broad exotherm beyond 200°C, attributable to crosslinking reactions through the remaining cyano groups. The presence of the latter was confirmed from the *FT*i.r. spectrum of $PAM_{25'}$ (*Figure 6*) which displayed residual absorption at 2240 cm^{-1}. Finally, it can be seen from *Figure 5* that a transition associated with the glass transition (T_g) of cured polyamides could not be detected from their d.t.a. traces.

Thermal stabilities of cured polyamides were evaluated by t.g.a. and isothermal gravimetric analysis (i.g.a.). *Figure 7* presents the t.g.a. traces of $PAM_{0'}$, $PAP_{25'}$ and $PAM_{100'}$ in N_2 and air atmospheres. Some t.g.a. data for all cured samples are listed in *Table 3*. More particularly, the IDT, the polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDT_{max}) both in N_2 and air as well as the char yield (Y_c) at 800°C in N_2 are summarized in *Table 3*. PDT was determined for a temperature at which 10% weight loss was observed. PDT_{max}

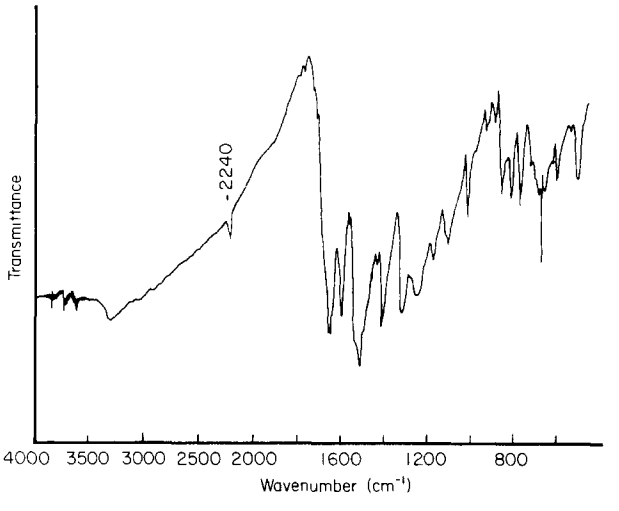


Figure 6 *FT*i.r. spectrum of cured polyamide $PAM_{25'}$

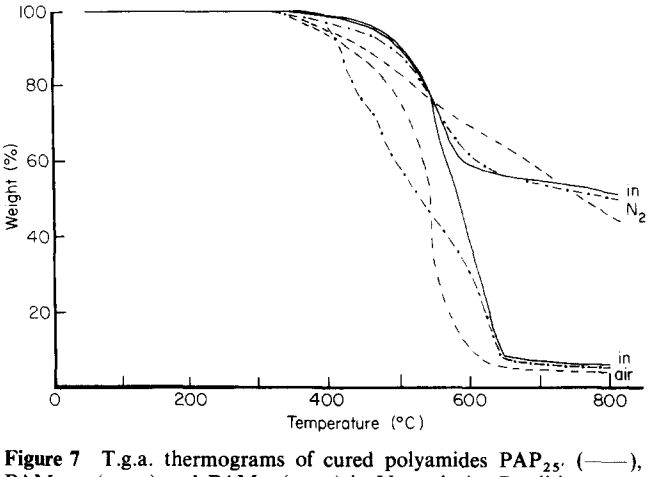


Figure 7 T.g.a. thermograms of cured polyamides $PAP_{25'}$ (——), $PAM_{100'}$ (– – –) and $PAM_{0'}$ (–·–·) in N_2 and air. Conditions: gas flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

Table 3 Thermal stabilities of cured polyamides

Sample	N_2				Air		
	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)
$PAM_{0'}$	327	501	551	51	321	422	460
$PAM_{25'}$	359	482	500	58	353	476	517
$PAM_{100'}$	318	454	541	45	317	433	545
$PAE_{25'}$	347	486	523	54	342	474	533
$PAP_{25'}$	370	501	574	52	363	503	556

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

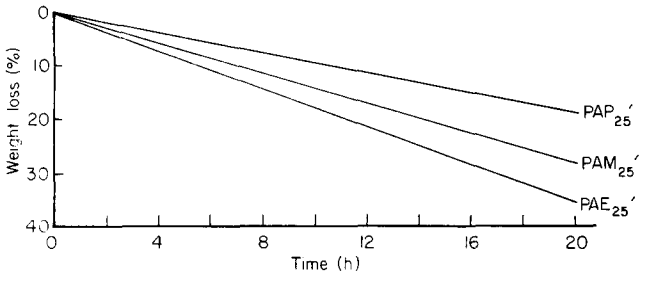


Figure 8 I.g.a. traces in static air of cured polyamides $PAP_{25'}$, $PAM_{25'}$ and $PAE_{25'}$ at 340°C

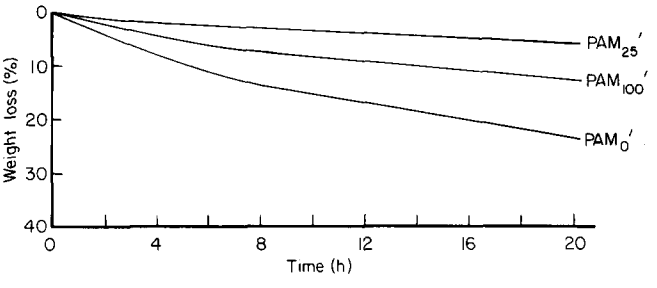


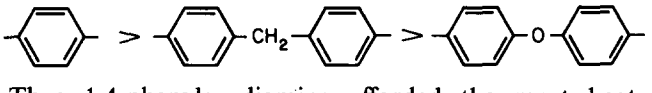
Figure 9 I.g.a. traces in static air of cured polyamides $PAM_{25'}$, $PAM_{100'}$ and $PAM_{0'}$ at 300°C

corresponds to the maximum rate of weight loss.

The cured modified polyamides were stable up to 317–370°C in N_2 or air and afforded anaerobic char yield of 45–58% at 800°C. Taking the IDT as the criterion of thermal stability, the relative order of thermal stability was as follows:

$$PAP_{25'} > PAM_{25'} > PAE_{25'} > PAM_{0'} > PAM_{100'}$$

It is obvious from *Figure 4* that the modified copolyamides PAM′ containing up to 75% substitution of **1a** were more thermally stable than reference polyamide $PAM_{0'}$. Copolyamide $PAM_{25'}$ showed the highest thermal stability as compared to other PAM′ copolyamides. Upon comparing copolyamides $PAP_{25'}$, $PAM_{25'}$ and $PAE_{25'}$ the relative order of thermal stability, with respect to the diamine utilized for their preparation was:



Thus 1,4-phenylenediamine afforded the most heat-resistant copolyamide because of its rigid structure.

The above order of thermal stability was confirmed from the i.g.a. traces of $PAP_{25'}$, $PAM_{25'}$ and $PAE_{25'}$ at 340°C in static air (*Figure 8*). After 20 h isothermal ageing they displayed weight losses of 20.0, 29.0 and 36.0%, respectively.

Figure 9 presents the i.g.a. traces of $PAM_{25'}$, $PAM_{100'}$ and $PAM_{0'}$ at 300°C in static air. They showed weight losses of 6.0, 12.5 and 23.0%, respectively, after 20 h isothermal ageing. In this case, $PAM_{100'}$ showed lower weight loss than $PAM_{0'}$ because it underwent additional crosslinking during isothermal ageing.

It should be emphasized that the cured modified homopolyamide and copolyamides exhibited remarkably higher heat resistance than the cured resins obtained from various biscyanamides[10].

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