Cyano-substituted polyamides derived from 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene and their heat-curing to thermally stable resins

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4-Carboxybenzaldehyde was condensed with cyanoacetic acid to afford 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene (**1**). Homopolyamides were prepared from the polycondensation of **1** with aromatic diamines utilizing triphenyl phosphite and pyridine as condensing agents. In addition, various copolyamides were prepared by reacting a mixture consisting of **1** and terephthalic acid with an aromatic diamine. The synthesized polyamides contained olefinic bonds and pendent cyano groups. The homopolyamides showed higher solubility in common solvents than did the reference polyamide prepared from terephthalic acid and an aromatic diamine. Their differential thermal analysis traces revealed that they softened between 200°C and 300°C. Upon curing at 300°C for 70 h, they yielded heat-resistant crosslinked polymers. The thermal stabilities of the cured polymers were correlated with the curing conditions and their composition. They displayed higher thermal stability than the reference polyamide and were stable up to 372–405°C in N_2. Furthermore, they are noteworthy for their high char yield at 800°C, namely, 68–78% in N_2 and 58–69% in air.

(Keywords: cyano-substituted polyamides; modified polyamides; thermally stable polymers)

INTRODUCTION

High performance materials for technological applications require the use of easily processable thermally stable polymers with high glass transition temperatures. There are a large number of aromatic polyamides available for investigation, but they are poorly soluble in most organic solvents and have high melting temperatures[1,2].

The present investigation deals with a new series of unsaturated heat-curable aromatic homopolyamides and copolyamides bearing cyano pendent groups. They were derived from 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene synthesized by an acid catalysed condensation of 4-carboxybenzaldehyde with cyanoacetic acid. The main objective of this study was the synthesis of new easily processable aromatic polyamides with relatively low melting temperatures which are readily soluble in polar aprotic solvents and certain acids. In addition, by heat-curing these polyamides afford thermally stable crosslinked polymers without the evolution of volatile by-products through their olefinic bonds and cyano groups. The synthesized polyamides could be used therefore as matrix resins for high temperature composites.

Recently, new cyano-substituted polyamides have been prepared and crosslinked in the Chemical Technology Laboratory at the University of Patras. In particular, the synthesis of polyamides containing enamino nitrile moieties[3,4] and N-cyano substituted polyamides[5] as well as unsaturated polyamides with pendent cyano groups derived from 1,4-bis(2-cyano-2-carboxyvinyl)benzene[6] has been reported.

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 Fourier transform infra-red (*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. 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 N_2 atmosphere at a flow rate of 60 cm^3 min^{-1} and with a ΔT sensitivity of 1°C in^{-1} ($\sim$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 of polyamides were determined for solutions of 0.5 g/100 ml in *N*,*N*-dimethylformamide (DMF) 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 patterns were obtained for powder specimens on an X-ray PW-1830 Philips diffractometer.

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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, and were periodically weighted.

Reagents and solvents

4-Carboxybenzaldehyde was recrystallized from acetonitrile. 4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylsulfone were recrystallized from toluene, acetonitrile and methanol, respectively. DMF was dried by distillation under reduced pressure over calcium hydride. 1,4-Dioxane was purified by distillation. Cyanoacetic acid, terephthalic acid, glacial acetic acid, triphenyl phosphite and pyridine were used as supplied.

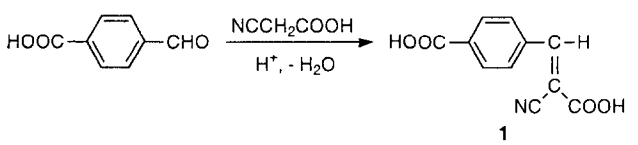
Preparation of starting material (Scheme 1)

1-Carboxy-4-(2-cyano-2-carboxyvinyl)benzene (*1*). A flask equipped with magnetic stirrer and condenser was charged with a mixture of 4-carboxybenzaldehyde (12.0104 g, 80.0 mmol), cyanoacetic acid (10.2084 g, 120.0 mmol), 1,4-dioxane (150 ml) and glacial acetic acid (5 ml). The mixture was stirred and refluxed for 70 h. It was subsequently concentrated by distillation under reduced pressure and the residue was poured into ice–water. The whitish solid obtained was filtered off, washed with water and dried to afford **1** (13.72 g, 79%). It was purified by recrystallization from DMF (m.p. 272–274°C, decomposition).

I.r. (KBr) cm^{-1}: 3100–2550 (O–H stretching); 2260 (C≡N); 1725–1690 (C=O); 1623 (C=C); 1440, 1300 (C–O stretching and O–H deformation).

^1H n.m.r. (DMSO-d_6) δ: 11.57 (b, 2H, COOH); 8.15–7.87 (m, 4H aromatic and 1H olefinic).

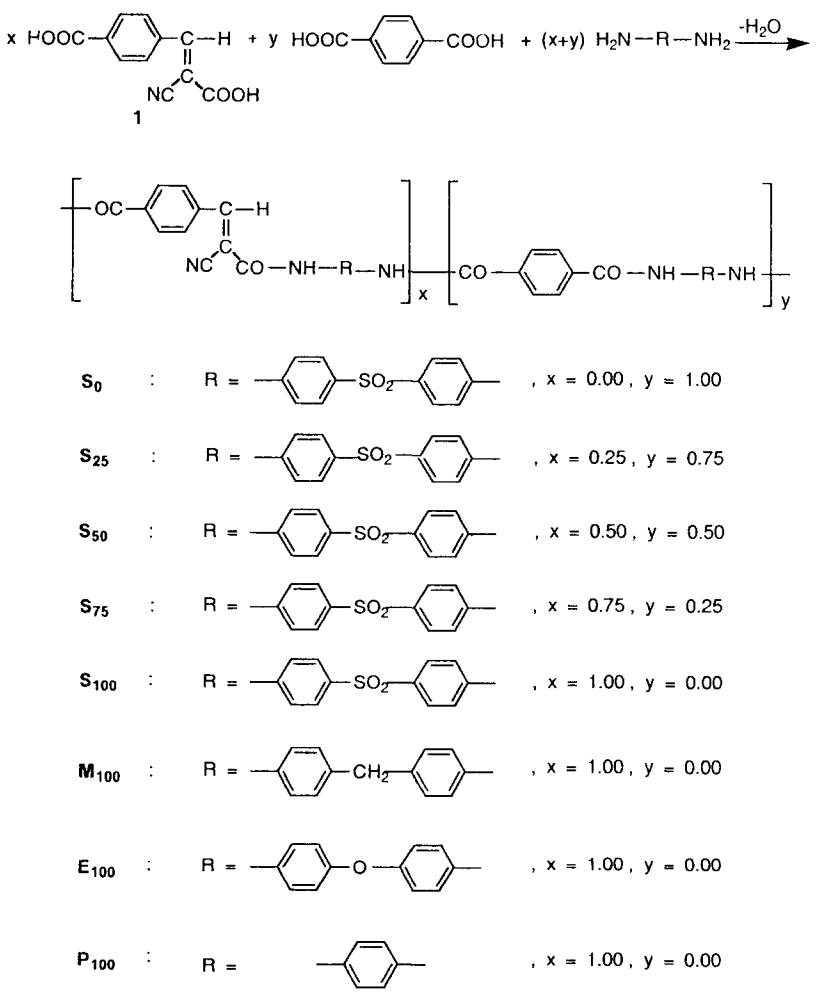
Analysis: calculated for $C_{11}H_7NO_4$: C, 60.83%; H, 3.25%; N, 6.45%. Found: C, 59.42%; H, 3.28%; N, 6.39%.



Scheme 1

Preparation of polyamides (Scheme 2)

As a typical example, the preparation of polyamide S_{100} is given: a flask equipped with magnetic stirrer and condenser was charged with a solution of **1** (1.3032 g, 6.0 mmol) and 4,4'-diaminodiphenylsulfone (1.4899 g, 6.0 mmol) in DMF (20 ml). Triphenyl phosphite (3.7235 g, 12.0 mmol), pyridine (1 ml) and lithium chloride (0.5000 g) were added to the solution. The mixture was stirred and heated at 100°C for 5 h under N_2. It was subsequently poured into water and the light yellow solid obtained was filtered off, washed with water, extracted



Scheme 2

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

Polyamide	Quantities of reactants [g(mmol)]			Yield (%)	η_{inh}[a] (dl g^{-1})
	Compound 1	Terephthalic acid	Aromatic diamine		
S_0		1.3290 (8.0)	1.9865 (8.0)	97	0.14
S_{25}	0.4344 (2.0)	0.9968 (6.0)	1.9865 (8.0)	94	0.13
S_{50}	0.8688 (4.0)	0.6645 (4.0)	1.9865 (8.0)	95	0.12
S_{75}	1.3032 (6.0)	0.3323 (2.0)	1.9865 (8.0)	93	0.12
S_{100}	1.3032 (6.0)		1.4899 (6.0)	96	0.11
M_{100}	1.5204 (7.0)		1.3879 (7.0)	95	0.12
E_{100}	1.3032 (6.0)		1.2014 (6.0)	92	0.14
P_{100}	1.3032 (6.0)		0.6488 (6.0)	94	0.13

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

with refluxing acetone in a Soxhlet for 12 h and dried to afford S_{100} (2.47 g, 96%).

The weights of reactants, the reaction yields and the inherent viscosities of all homopolyamides and copolyamides thus prepared are listed in *Table 1*.

Curing of polyamides

The isolated polyamides were placed in an aluminium dish and curing was accomplished by heating in an oven at 300°C for 70 h.

RESULTS AND DISCUSSION

1-Carboxy-4-(2-cyano-2-carboxyvinyl)benzene (**1**) was utilized as starting material for the preparation of new unsaturated homopolyamides and copolyamides bearing pendent cyano groups. Compound **1** was synthesized from the condensation of 4-carboxybenzaldehyde with cyanoacetic acid in the presence of glacial acetic acid (*Scheme 1*). The reaction was carried out in refluxing 1,4-dioxane and excess cyanoacetic acid was used to improve the reaction yield. The latter was satisfactory (79%) and therefore the addition of a catalyst was not necessary. Note that piperidine has been used as catalyst in analogous reactions[7]. A literature survey revealed that compound **1** has not been previously synthesized.

Scheme 2 outlines the preparation of homopolyamides and random copolyamides. More particularly, homopolyamides S_{100}, M_{100}, E_{100} and P_{100} were prepared from the reactions of **1** with 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether and 1,4-phenylenediamine, respectively. Copolyamides S_{25}, S_{50} and S_{75} were prepared by reacting a mixture consisting of **1** and terephthalic acid with 4,4'-diaminodiphenylsulfone. In addition, a reference homopolyamide S_0 was prepared from the reaction of terephthalic acid with 4,4'-diaminodiphenylsulfone. All polyamides were prepared by the phosphorylation method utilizing triphenyl phosphite and pyridine as condensing agents. They were prepared in nearly quantitative yields and their inherent viscosities ranged from 0.11 to 0.14 dl g^{-1} (*Table 1*).

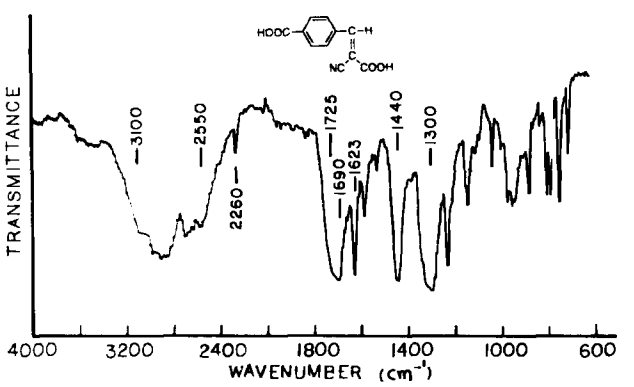


Figure 1 *FT*i.r. spectrum of compound **1**

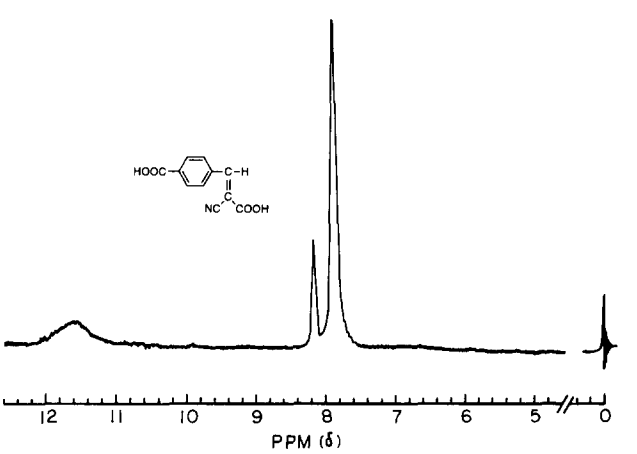


Figure 2 ^{1}H n.m.r. spectrum of compound **1** in DMSO-d_6 solution

Compound **1** was characterized by elemental analysis as well as i.r. and ^{1}H n.m.r. spectroscopy (see Experimental). *Figures 1* and *2* show the *FT*i.r. and ^{1}H

n.m.r. spectra of **1**. A strong and broad i.r. absorption band appeared at 1725–1690 cm^{-1} assigned to the C=O vibrations. In addition, the C≡N group showed a characteristic i.r. absorption at 2260 cm^{-1}. The ^1H n.m.r. spectrum of **1** displayed a broad peak at 11.57 δ assigned to the carboxylic protons which were exchangeable with D_2O.

In the *FT*i.r. identification of the synthesized polyamides (*Figure 3*) some typical absorptions were assigned around 3400–3000 (N–H stretching); 2240 (C≡N); 1700 (C=O); 1600 (C=C); 1530 (N–H deformation and C–N stretching); 1485 (aromatic) and 1320 cm^{-1} (C–N stretching and N–H bending).

One of the aims of this work was to evaluate the effect of the incorporation of the pendent cyano groups on the solubility of aromatic polyamides. For this reason, a comparative study of the solubilities in common organic solvents was done. *Table 2* presents the solubility behaviour of homopolyamides S_{100} and S_0. It is seen that the modified polyamide showed higher solubility in typical organic solvents than did the reference polyamide. More particularly, S_{100} was readily soluble in polar aprotic solvents such as DMF, dimethylsulfoxide (DMSO), *N*-methyl pyrrolidone (NMP) as well as in concentrated H_2SO_4 and CCl_3COOH. Polyamide S_0 was soluble at room temperature only in H_2SO_4 (98%) and upon heating in DMF, DMSO, NMP and CCl_3COOH. Copolyamides S_{25}, S_{50} and S_{75} displayed lower solubility in organic solvents than homopolyamide S_{100}. The pendent cyano groups of the modified polyamides did not allow a dense packing of the chains thus increasing their solubility.

The thermal behaviour of polyamides was investigated by d.t.a. *Figure 4* shows the d.t.a. traces of homopolyamides S_{100}, M_{100}, E_{100} and P_{100}. They exhibited broad endotherms between 200°C and 300°C attributable to their softening. Upon gradual heating in a capillary tube in a melting point apparatus, they also softened at this temperature region. The endotherms were followed by an exotherm associated with their crosslinking reactions and partial thermal degradation.

Figure 5 shows the wide-angle X-ray diffractograms of three typical homopolyamides (S_{100}, M_{100} and E_{100}), which confirmed their amorphous pattern.

The isothermal moisture absorption of homopolyamides S_0 and S_{100} is given in *Figure 6*. The number of moles of absorbed water per amide equivalent weight was 0.42 and 0.45, respectively, after exposure for 150 h. It is well

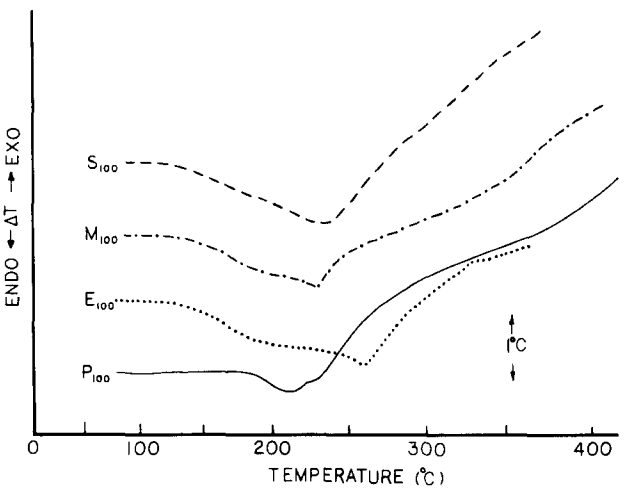


Figure 4 D.t.a. traces of polyamides S_{100}, M_{100}, E_{100} and P_{100}. Conditions: N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

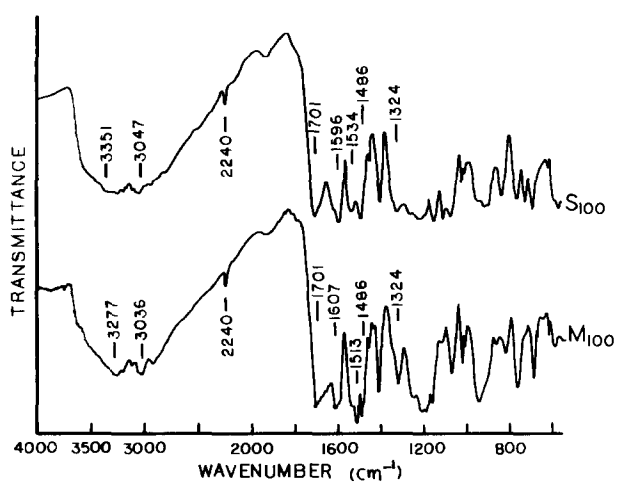


Figure 3 *FT*i.r. spectra of polyamides S_{100} and M_{100}

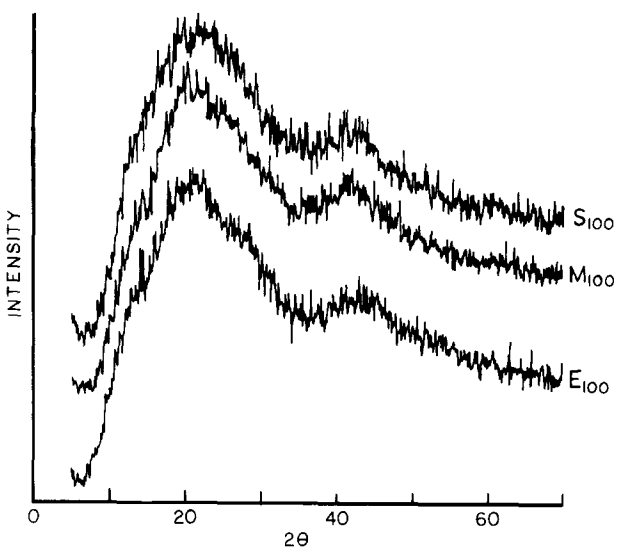


Figure 5 X-ray diffraction patterns of polyamides S_{100}, M_{100} and E_{100}

Table 2 Solubilities of polyamides[a]

Sample	Solvents[b]								
	DMF	NMP	DMSO	*m*-Cresol	CH	H_2SO_4 98%	CCl_3COOH	CH_3CN	1,4-Dioxane
S_{100}	++	++	++	–	–	++	++	–	–
S_0	+	+	+	–	–	++	+	–	–

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

known that the moisture absorption is proportional to the frequency of amide groups[8]. In the present case, the moisture absorption of the modified polyamide S_{100} was slightly higher than expected.

Heat-resistant crosslinked polymers were obtained from modified polyamides through their cyano groups as well as the olefinic bonds upon heating at 300°C. To optimize the curing conditions, a typical polyamide (M_{100}) was heated at 300°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 crosslinked polymer were determined by t.g.a. The results are shown in *Figure 7*. It is seen that both the IDT and Y_c increased with increasing curing time up to ~70 h and were reduced beyond this time. The time of 70 h was therefore the optimum for heat-curing at 300°C.

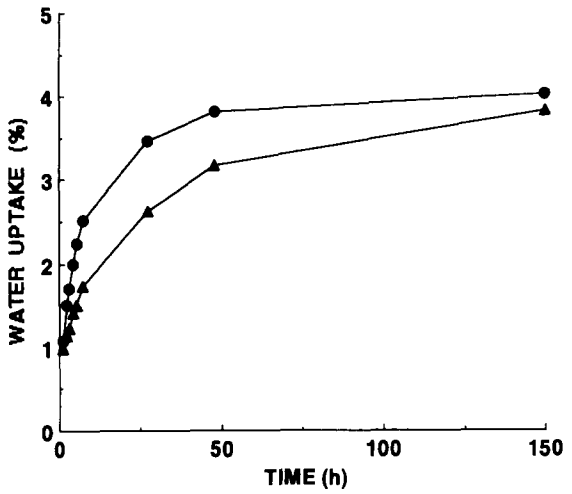


Figure 6 Water absorption (%) *versus* time for polyamides S_0 (●) and S_{100} (▲)

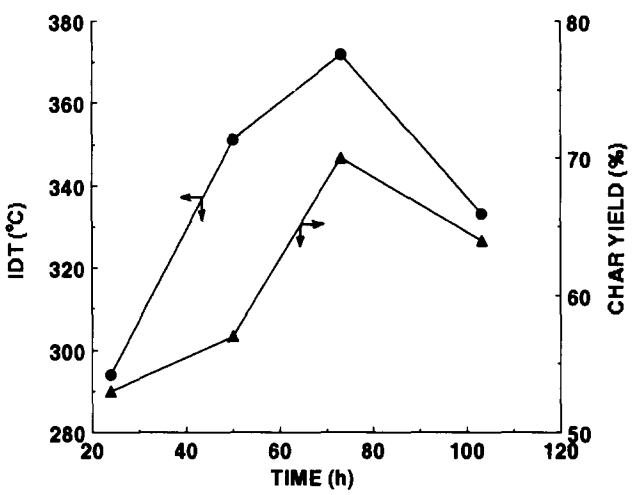


Figure 7 IDT and Y_c at 800°C in N_2 of polyamide M_{100} *versus* the curing time at 300°C

The crosslinked polymers obtained upon curing at 300°C for 70 h from polyamides S_0, S_{25}, S_{50}, S_{75}, S_{100}, M_{100}, E_{100} and P_{100} are referred to by the designations S'_0, S'_{25}, S'_{50}, S'_{75}, S'_{100}, M'_{100}, E'_{100} and P'_{100}, respectively. Their thermal stability was evaluated by t.g.a. in N_2 and air. The IDT, the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}) and the Y_c at 800°C both in N_2 and air for all cured polymers are listed in *Table 3*. The IDT and PDT were determined for a temperature at which 1 and 10% weight loss was observed, respectively. The PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

Figure 8 presents the t.g.a. traces of cured polyamides S'_{100}, M'_{100}, E'_{100} and P'_{100} in N_2 and air. Since their IDT and Y_c did not differ significantly, their thermal stability was not affected remarkably by the aromatic

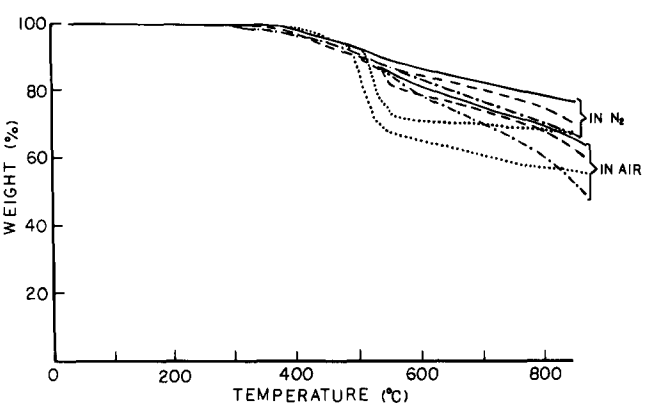


Figure 8 T.g.a. traces of cured polyamides S'_{100} (– – –), M'_{100} (–·–), E'_{100} (···) and P'_{100} (——) in N_2 and air. Conditions: gas flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

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)	Y_c (%)
S'_0	372	527	501	67	370	489	523	31
S'_{25}	405	567	463	77	385	490	485	67
S'_{50}	377	497	411	74	373	467	411	64
S'_{75}	375	498	419	74	370	478	415	64
S'_{100}	374	512	426	74	370	503	537	66
M'_{100}	372	519	444	70	370	508	541	59
E'_{100}	377	508	523	68	375	523	508	58
P'_{100}	378	537	441	78	374	517	523	69

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

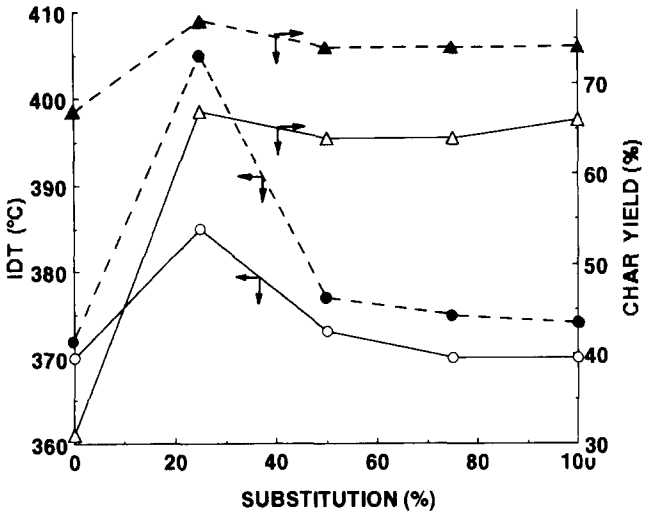


Figure 9 IDT and Y_c at 800°C in N_2 (---) and air (——) of cured polyamides S′ *versus* the percentage substitution of compound **1** in them

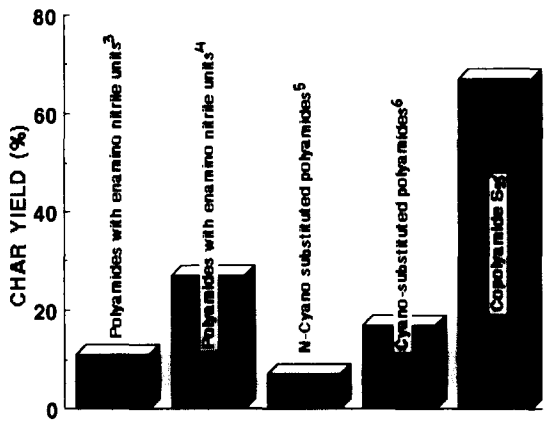


Figure 10 Comparison of the char yield at 800°C in air of cured copolyamide S'_{25} with that of other similar types of cured polyamides

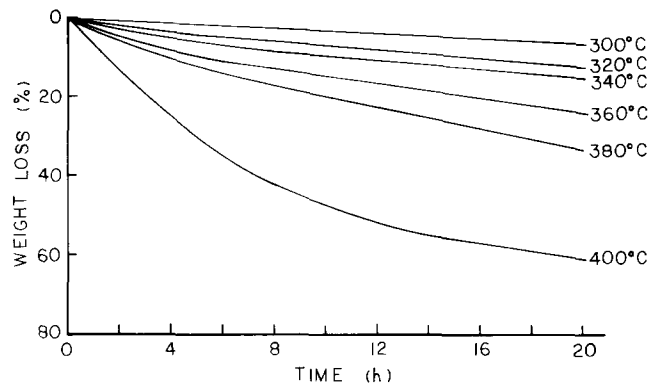


Figure 11 I.g.a. traces in static air of cured polyamide P'_{100} at 300, 320, 340, 360, 380 and 400°C

diamine used in the preparation. In contrast, both the IDT and Y_c at 800°C in N_2 and air of cured polyamides S'_0, S'_{25}, S'_{50}, S'_{75} and S'_{100} were influenced by the percentage substitution of **1** in them (*Figure 9*). It can be seen that the IDT and Y_c were increased with increasing percentage substitution of **1** in polyamides up to 25% and were reduced beyond this value. Consequently, S'_{25} was the most thermally stable polymer obtained being

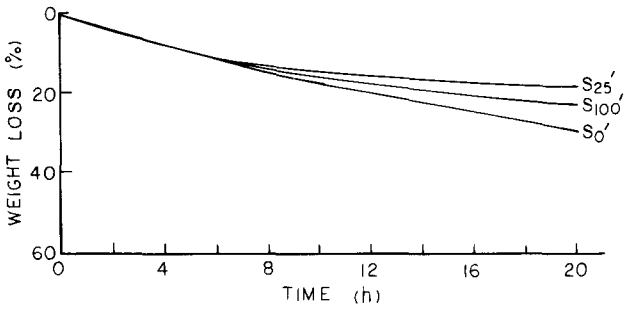


Figure 12 I.g.a. traces in static air at 320°C of cured polyamides S'_0, S'_{25} and S'_{100}

stable up to 405°C and affording a Y_c of 77% at 800°C in N_2.

It is interesting to note that these thermosetting polymers displayed significantly higher Y_c values at 800°C in N_2 and particularly in air than did the reference polymer (*Table 3*). In particular, S'_0 had a Y_c of 31% at 800°C in air whereas S'_{25}, S'_{50}, S'_{75} and S'_{100} had Y_c values of 64–67% under the same conditions. Similarly, the other cured polyamides M'_{100}, E'_{100} and P'_{100} showed Y_c values of 58–69% at 800°C in air. This behaviour reveals that in the case of the cyano-substituted polyamides the decomposition process was different leading to higher Y_c values. *Figure 10* shows comparative Y_c values at 800°C in air of cured copolyamide S'_{25} with other cured cyano-substituted polyamides prepared in the Chemical Technology Laboratory, University of Patras. From these results the superiority of S'_{25} in Y_c formation among the compared polyamides is apparent.

Figure 11 presents the isothermal gravimetric analysis (i.g.a.) traces of a typical cured polyamide P'_{100} at 300, 320, 340, 360, 380 and 400°C in static air. After 20 h isothermal ageing, it displayed weight losses of 6.3, 12.3, 14.9, 23.7, 32.7 and 60.3%, respectively. The results revealed that an increased degradation of the polyamide occurred above 380°C under these conditions.

In addition, the relative thermal stability of three cured polyamides (S'_0, S'_{25} and S'_{100}) was evaluated by i.g.a. (*Figure 12*). They showed weight losses of 28.7, 17.5 and 22.0%, respectively, after 20 h isothermal ageing at 320°C in static air. The results confirmed that the relative order of thermal stability was as follows: $S'_{25} > S'_{100} > S'_0$.

An attempt was made to elucidate the structure of cured polyamides by i.r. spectroscopy. Their *FT*i.r. spectra were broad and showed a remarkable reduction of the absorption band near 2240 cm^{-1} assigned to C≡N groups. In addition, the cured polyamides became completely insoluble in solvents for the uncured samples. All these features gave evidence for the network structure of cured polyamides.

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