Unsaturated polyamides with pendent cyano groups derived from 1,4-bis(2-cyano-2-carboxyvinyl)benzene

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Various homopolyamides and copolyamides bearing olefinic bonds and pendent cyano groups were prepared by reacting aromatic diamines with the acid chloride of 1,4-bis(2-cyano-2-carboxyvinyl)benzene. In addition, the latter reacted with aniline to afford a model diamide. The monomers were characterized by infra-red and ^{1}H nuclear magnetic resonance spectroscopy, as well as by elemental analyses. Characterization of polyamides was accomplished by infra-red spectroscopy, differential thermal analysis, thermogravimetric analysis, isothermal gravimetric analysis and inherent-viscosity measurements. The synthesized homopolyamides were soluble in polar aprotic solvents and certain strong inorganic and organic acids. Upon thermal curing, crosslinked polymers were obtained. The thermal stabilities of cured resins were correlated with the curing conditions and their composition. They were stable up to 391–407°C in N_2 or air and afforded anaerobic char yield of 64–70% at 800°C.

(Keywords: cyano-substituted polyamides; thermal stability; crosslinking)

INTRODUCTION

Aromatic polyamides (aramids) are well accepted as highly thermally stable materials[1,2]. Some of them are available for use as flame-resistant fibres, high-strength and high-modulus fibres as well as high-performance plastics[3]. A number of studies have been made on the synthesis and thermal characterization of aromatic polyamides[4–7]. However, they are difficult to process, owing to their limited solubility in organic solvents and their high melting or softening temperatures. Many attempts have been made to increase the solubility of polyamides by introducing bulky and unsymmetrical groups into the polymer backbone.

The present investigation deals with the synthesis, characterization and curing of certain tractable homopolyamides and copolyamides bearing olefinic bonds and pendent cyano groups. They are expected to possess an improved processability owing to their solubility in common organic solvents as well as their lower melting or softening temperatures. Upon thermal curing, they are expected to afford heat-resistant network polymers without the evolution of volatile by-products.

The present work is a continuation of our studies on the preparation of new cyano-substituted polyamides. In earlier papers we reported the synthesis of certain polyamides containing enaminonitrile segments[8,9] as well as some *N*-cyano-substituted homopolyamides and copolyamides[10]. Recently, we synthesized a new series of unsaturated heat-curable polyamides bearing cyano pendent groups derived from 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene[11].

The polyamides described in the present investigation were based on the reactions of various aromatic diamines with 1,4-bis(2-cyano-2-carboxyvinyl)benzene. The latter was synthesized by reacting 1,4-benzenedicarboxaldehyde with cyanoacetic acid. A literature survey revealed that certain monomers were synthesized from the Knoevenagel condensation between ω-hydroxyalkoxy-substituted benzaldehydes and methyl cyanoacetate[12]. The monomers were homo- or copolymerized at high temperature (160°C) in the presence of dibutyltin diacetate to afford polyesters containing a highly dipolar repeat unit[12].

In addition, curable, thermally stable poly(enamino-nitriles) were synthesized from a vinylic nucleophilic substitution polymerization of certain bis(1-chloro-2,2-dicyanovinyl) aromatic monomers with 4,4′-diamino-diphenyl ether[13]. They formed poly(4-aminoquinoline) repeat units by an intramolecular cyclization reaction occurring above 300°C.

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electro-thermal melting-point apparatus IA6304 and are uncorrected. I.r. spectra were recorded on a Perkin–Elmer 710B spectrometer with KBr pellets. ^{1}H n.m.r. spectra were obtained in deuterated dimethylsulfoxide (DMSO-d_6) 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 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 0.5°C/inch ($\sim$0.2°C cm^{-1}). Dynamic t.g.a. measurements were made at a heating

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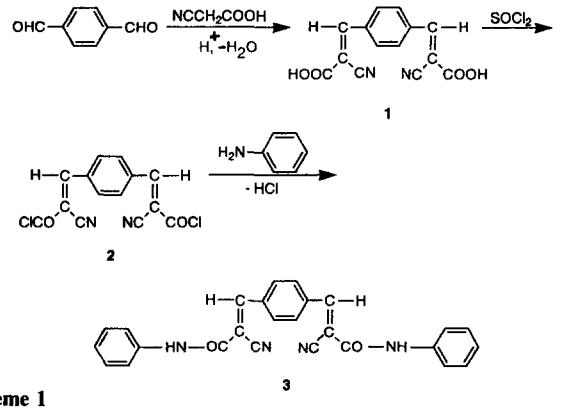


Scheme 1

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 98% H_2SO_4 or *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 a Philips PW-1830 X-ray 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 (r.h.) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20°C, and were periodically weighed.

Reagents and solvents

1-4-Benzenedicarboxaldehyde and terephthaloyl dichloride were recrystallized from distilled water and n-hexane, respectively. Aniline, triethylamine and thionyl chloride were purified by distillation. 4,4′-Diaminodiphenylmethane, 4,4′-diaminodiphenyl ether and 4,4′-diaminodiphenylsulfone were recrystallized from toluene, acetonitrile and methanol, respectively. 1,4-Phenylenediamine was sublimed at about 110°C under vacuum (2–3 mmHg). *N,N*-Dimethylformamide (DMF) was dried by distillation under reduced pressure over calcium hydride. Cyanoacetic acid, glacial acetic acid and acetonitrile were used as supplied.

Preparation of starting materials (Scheme 1)

1,4-Bis(2-cyano-2-carboxyvinyl)benzene (*1*). A flask equipped with magnetic stirrer and condenser was charged with a mixture of 1,4-benzenedicarboxaldehyde (4.0239 g, 30 mmol), cyanoacetic acid (3.8282 g, 90 mmol), acetonitrile (40 ml) and glacial acetic acid (2 ml). The mixture was stirred and refluxed for 30 h. It was subsequently cooled in an ice bath for 1 h. The whitish solid obtained was filtered off, washed thoroughly with water and dried to afford **1** in 80% yield (6.44 g). It was recrystallized from DMF (m.p. 280–283°C, decomposition).

I.r. (KBr) cm^{-1}: 3050–2810 (O–H stretching); 2245 (C≡N); 1690 (C=O); 1603 (C=C); 1570 (aromatic); 1430, 1280 (C–O stretching and O–H deformation).

^{1}H n.m.r. (DMSO-d_6) δ: 11.40 (b, 2H, COOH); 8.08–7.92 (m, 4H aromatic and 2H olefinic).

Analysis: calculated for $C_{14}H_8N_2O_4$, C 62.69%, H 3.00%, N 10.45%; found, C 61.74%, H 3.08%, N 10.32%.

1,4-Bis(2-cyano-2-carboxyvinyl)benzene acid chloride (*2*). A flask equipped with magnetic stirrer, condenser and gas trap was charged with a mixture of **1** (2.8000 g, 10.4 mmol), acetonitrile (15 ml), thionyl chloride (8 ml) and a few drops of DMF. The mixture was stirred and gradually heated at 80°C for 1.5 h to obtain a homogeneous solution. Acetonitrile and volatile components were stripped off by distillation under reduced pressure. The light brown solid was washed with ether, filtered and dried to afford **2** in 82% yield (2.60 g). A purified sample obtained by recrystallization from a mixture of acetone/ether (volume ratio 1:2) had m.p. > 300°C.

I.r. (KBr) cm^{-1}: 3070, 1564, 1437 (aromatic); 2250 (C≡N); 1740 (C=O); 1614 (C=C).

^{1}H n.m.r. (DMSO-d_6) δ: 8.13–7.93 (m, 4H, aromatic and 2H olefinic).

Analysis: calculated for $C_{14}H_6Cl_2N_2O_2$, C 55.11%, H 1.98%, N 9.18%; found, C 54.83%, H 2.05%, N 9.13%.

Preparation of model diamide 3 (Scheme 1)

A flask was charged with a solution of aniline (0.9686 g, 10.4 mmol) in DMF. Compound *2* (1.5860 g, 5.2 mmol) dissolved in DMF was added dropwise to the solution at 0°C under N_2. Triethylamine (1.0524 g, 10.4 mmol) was subsequently added to the solution at 0°C. The mixture was stirred at ambient temperature for 4 h in a stream of N_2. It was poured into ice–water and the pale yellow solid obtained was filtered off, washed with water and dried to afford **3** in 64% yield (1.39 g). It was recrystallized from a mixture of DMF/water (volume ratio 2:1) and had m.p. 253–256°C.

I.r. (KBr) cm^{-1}: 3275 (N–H stretching); 3070, 1507, 1460 (aromatic); 2240 (C≡N); 1667 (C=O); 1607 (C=C); 1546 (N–H deformation); 1263 (C–N stretching and N–H bending).

^{1}H n.m.r. (DMSO-d_6) δ: 10.46 (b, 2H, NHCO); 8.10–6.80 (m, 14H aromatic and 2H olefinic).

Analysis: calculated for $C_{26}H_{18}N_4O_2$, C 74.63%, H 4.34%, N 13.39%; found, C 73.25%, H 4.26%, N 13.47%.

Preparation of polyamides (Scheme 2)

As a typical example, the preparation of polyamide M_{100} is given. A flask equipped with magnetic stirrer was charged with a solution of 4,4′-diaminodiphenylmethane (0.5948 g, 3 mmol) in DMF (8 ml). Compound **2** (0.9150 g, 3 mmol) dissolved in DMF (8 ml) was added dropwise to the stirred solution at 0°C under N_2. Triethylamine (0.6071 g, 6 mmol) was subsequently added to the solution at 0°C. Stirring of the mixture was continued at ambient temperature in a stream of N_2 for 4 h. It was poured into water to precipitate M_{100} as a light brown solid. It was filtered off, washed with water and dried (1.21 g, 94%).

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

Curing procedure of polyamides

The isolated polyamides were cured by heating in an oven at 320°C for 50 h.

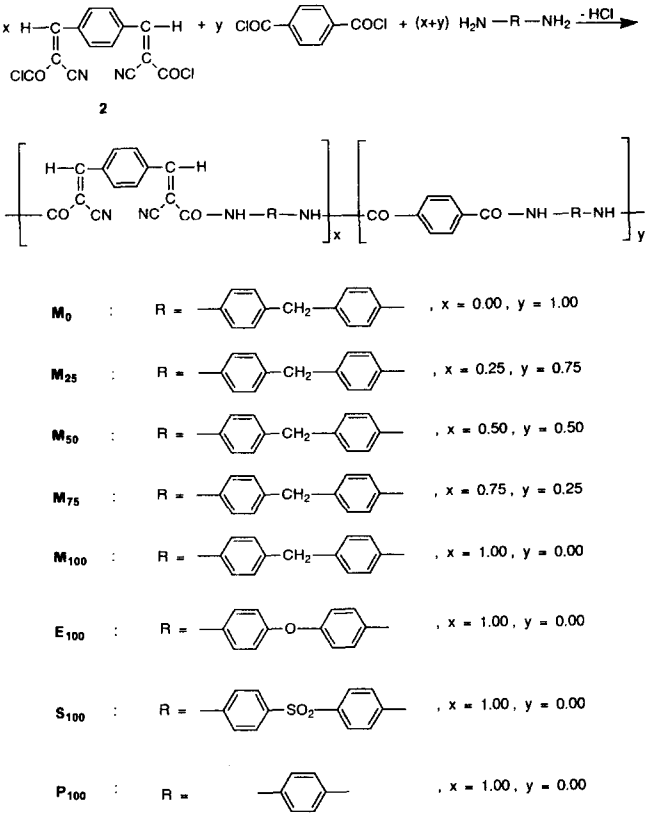
RESULTS AND DISCUSSION

Scheme 1 outlines the preparation of starting materials and model compound. More particularly, 1,4-benzene-

Table 1 Reaction yields and inherent viscosities of polyamides

Sample	M_0	M_{25}	M_{50}	M_{75}	M_{100}	E_{100}	S_{100}	P_{100}
Yield (%)	89	93	94	96	94	94	95	93
η_{inh} (dl g^{-1})	0.23[a]	0.21[b]	0.18[b]	0.15[b]	0.12[b]	0.14[b]	0.12[b]	0.13[b]

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



Scheme 2

dicarboxaldehyde reacted with cyanoacetic acid in acetonitrile in the presence of glacial acetic acid to afford the dicarboxylic acid **1**. Excess cyanoacetic acid was used to improve the reaction yield and the crystallized product was washed with water to dissolve the unreacted cyanoacetic acid. The addition of a catalytic amount of piperidine afforded a product that contained the piperidine segment probably as a salt owing to the presence of the carboxylic moieties. The dicarboxylic acid **1** reacted with thionyl chloride utilizing DMF as catalyst to yield the corresponding acid chloride **2**. The latter reacted with aniline in the presence of triethylamine to afford the model diamide **3**.

Homopolyamides and random copolyamides were prepared according to the reactions of *Scheme 2*. More particularly, homopolyamides M_{100}, E_{100}, S_{100} and P_{100} were prepared from the reactions of **2** with an equimolar amount of 4,4′-diaminodiphenylmethane, 4,4′-diaminodiphenyl ether, 4,4′-diaminodiphenylsulfone or 1,4-phenylenediamine, respectively. Copolyamides M_{25}, M_{50} and M_{75} were prepared by reacting a mixture of **2** and terephthaloyl dichloride with 4,4′-diaminodiphenylmethane. In addition, homopolyamide M_0 was prepared from the reaction of terephthaloyl dichloride with 4,4′-diaminodiphenylmethane for comparative purposes.

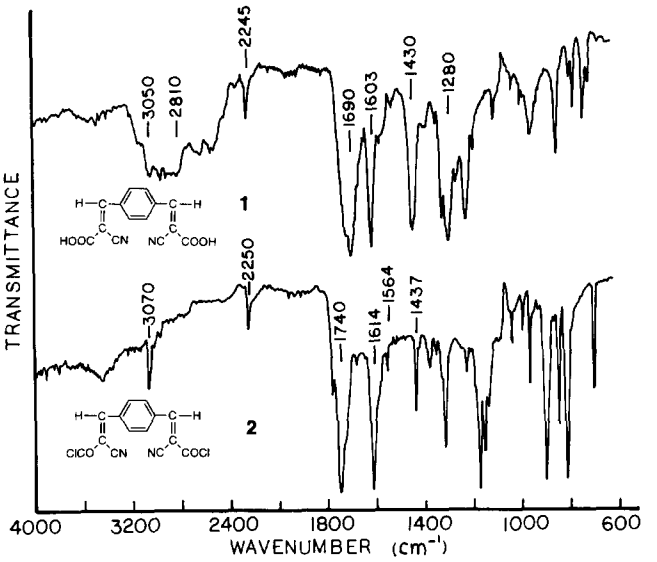


Figure 1 I.r. spectra of dicarboxylic acid **1** (top) and the corresponding acid chloride **2** (bottom)

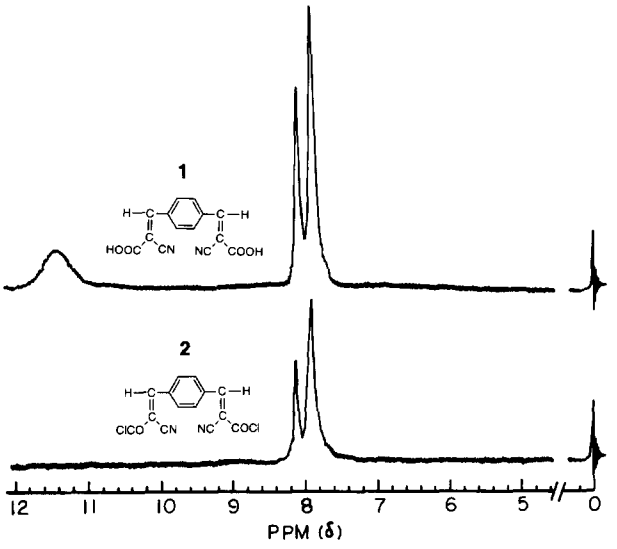


Figure 2 ^{1}H n.m.r. spectra of dicarboxylic acid **1** (top) and the corresponding acid chloride **2** (bottom) in DMSO-d_6 solution

All polyamides were prepared in DMF solution at low temperature utilizing triethylamine as an acid acceptor.

The starting materials and model compound were characterized by i.r. and ^{1}H n.m.r. spectroscopy as well as by elemental analyses (see 'Experimental'). *Figures 1* and *2* present the i.r. and ^{1}H n.m.r. spectra of both the dicarboxylic acid **1** and the corresponding acid chloride **2**. Compound **1** showed a broad i.r. absorption at 3050–2810 cm^{-1} associated with the carboxylic OH stretching vibrations, whereas compound **2** lacked this

absorption band. In addition, the ^1H n.m.r. spectrum of **1** showed a broad peak at $\delta = 11.40$ ppm assigned to COOH that was exchangeable with D_2O.

Figure 3 presents the i.r. spectra of model diamide **3** as well as a typical homopolyamide P_{100}. It can be seen that they were in agreement. Both spectra displayed characteristic absorption bands around 3300 (N–H stretching), 3070, 1500, 1460 (aromatic), 2230 (C≡N), 1670 (C=O), 1610 (C=C), 1530 (N–H deformation and C–N stretching) and 1260 cm^{-1} (C–N stretching and N–H bending). Copolyamides also showed the same characteristic absorptions but the intensity of the C≡N absorption band depended upon the concentration of the cyano groups.

The cyano-substituted polyamides displayed considerably higher solubility in organic solvents than did the reference polyamide M_0. Their solubility was increased with increasing concentration of cyano groups. *Table 2* presents the solubility behaviours of M_{100} and M_0. Homopolyamide M_{100} was soluble at ambient temperature in polar aprotic solvents (DMF, NMP, DMSO) and certain strong inorganic and organic acids (98% H_2SO_4, CCl_3COOH). It was also partially soluble in cyclohexanone upon heating. In contrast, M_0 dissolved at ambient temperature only in 98% H_2SO_4 and upon heating in NMP and CCl_3COOH. The pendent cyano groups of polyamides disrupted their chain packing, thereby making solvation easier.

The inherent viscosities (η_{inh}) of the cyano-substituted polyamides ranged from 0.12 to 0.21 dl g^{-1} (*Table 1*), thus suggesting a relatively low degree of polymerization. Note that the η_{inh} values decreased with increasing concentration of dicarboxylic acid **1**.

Figure 4 presents the d.t.a. traces of homopolyamides M_{100}, E_{100}, S_{100} and P_{100} before and after thermal curing. It is seen that M_{100} and S_{100} displayed large endotherms at 189 and 233°C, respectively, assigned to their softening. These softening temperatures were confirmed by gradual heating of the homopolyamides in a capillary tube. Homopolyamides E_{100} and P_{100} did not display endotherms associated with their softening. A transition of E_{100} at 194°C could be attributed to glass transition (T_g).

The wide-angle X-ray diffractograms of two typical homopolyamides P_{100} and S_{100} were obtained. P_{100} showed crystalline peaks at $2\theta = 19.2$ and 25.4°, whereas S_{100} showed an amorphous pattern.

Figure 5 shows the isothermal moisture absorption for homopolyamides M_0 and M_{100}. The moles of absorbed water per amide equivalent weight were 0.33 and 0.18, respectively, after an exposure time of 100 h. Generally, moisture absorption is proportional to the frequency of amide groups[14]. The decrease did not correspond quantitatively to the higher amide equivalent weight of M_{100}, but it was greater than expected.

The cyano-substituted homopolyamides and copolyamides afforded thermally stable network structures upon curing at 300°C. The initial decomposition temperature

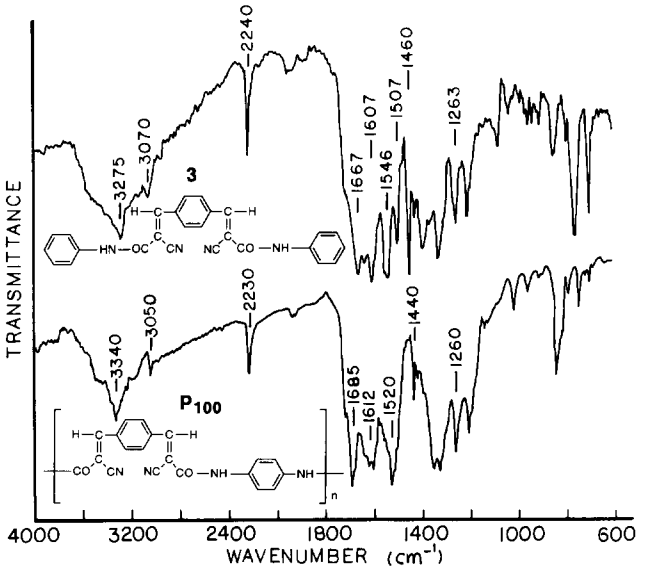


Figure 3 I.r. spectra of model diamide **3** (top) and homopolyamide P_{100} (bottom)

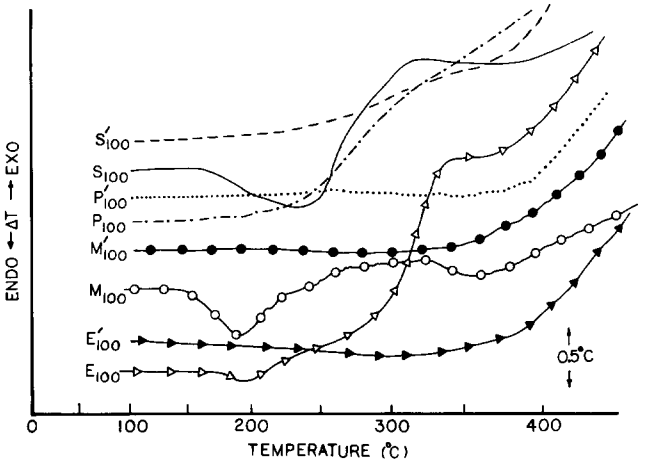


Figure 4 D.t.a. traces of homopolyamides M_{100}, E_{100}, S_{100} and P_{100} as well as the corresponding cured (at 320°C for 50 h) samples M'_{100}, E'_{100}, S'_{100} and P'_{100}. Conditions: N_2 flow, 60 cm^3 min^{-1}; heating rate, 20°C min^{-1}

Table 2 Solubilities of polyamides[a]

Sample	Solvents						
	DMF[b]	NMP[c]	DMSO[d]	*m*-Cresol	CH[e]	H_2SO_4 (98%)	CCl_3COOH
M_{100}	++	++	++	−	+−	++	++
M_0	−	+	−	−	−	++	+

[a] Solubility: (++) soluble at room temperature; (+) soluble in hot solvent; (+−) partially soluble or swollen; (−) insoluble
[b] DMF = *N*,*N*-dimethylformamide
[c] NMP = *N*-methylpyrrolidone
[d] DMSO = dimethylsulfoxide
[e] CH = cyclohexanone

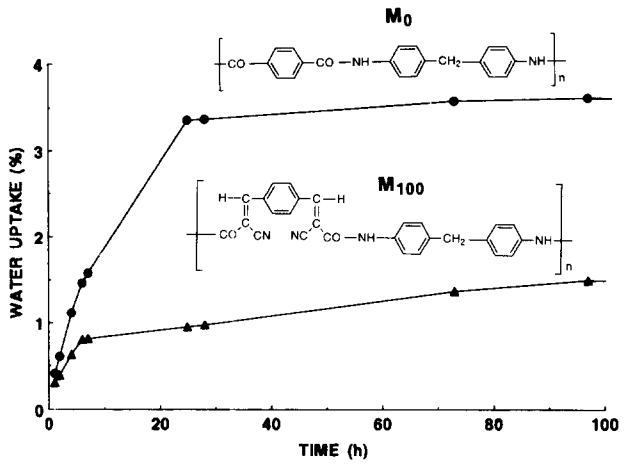


Figure 5 Water absorption (%) *versus* time for homopolyamides M_0 and M_{100}

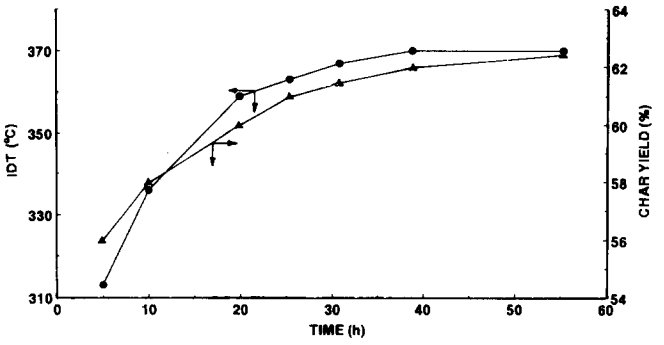


Figure 6 *IDT* and char yield at 800°C in N_2 of homopolyamide S_{100} *versus* the curing time at 300°C

(*IDT*) and the char yield (Y_c) at 800°C in N_2 of cured resins were significantly affected by the curing time. *Figure 6* presents the *IDT* and Y_c of a typical homopolyamide S_{100} as functions of the curing time at 300°C. They increased with increasing curing time up to about 50 h and remained almost unchanged beyond this time. The optimum time was, therefore, 50 h for the curing temperature of 300°C.

The influence of the percentage substitution of dicarboxylic acid **1** in various polyamides M on their *IDT* and Y_c was investigated. The percentage substitution of **1** in these polyamides was 0, 25, 50, 75 and 100% (*Scheme 2*). The *IDT* and Y_c at 800°C in N_2 of the cured (at 300°C for 50 h) polyamides were dependent upon their composition (*Figure 7*). It is seen that the *IDT* and Y_c increased with increasing percentage substitution of **1** in polyamides up to 25% and they were reduced beyond this value. Therefore, the composition of copolyamide M_{25} was the optimum from the aspect of thermal stability. An analogous behaviour has been observed in *N*-cyano-substituted polyamides[10].

Curing of polyamides at temperatures higher than 300°C increased their *IDT* value in addition. The cured resins obtained from homopolyamides M_{100}, E_{100}, S_{100} and P_{100} at 320°C for 50 h are referred to by the designations M'_{100}, E'_{100}, S'_{100} and P'_{100}, respectively. Some t.g.a. data for these cured resins 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 in air as well as the Y_c at 800°C in N_2 are summarized in *Table 3*. *IDT* and *PDT* were determined for a temperature at which 1 and 10% weight loss was observed, respectively. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

Figure 8 presents the t.g.a. traces in N_2 of cured resins. They were stable up to 391–407°C in N_2 or air and afforded anaerobic Y_c of 64–70% at 800°C. It is seen that the chemical structure of the aromatic diamines utilized

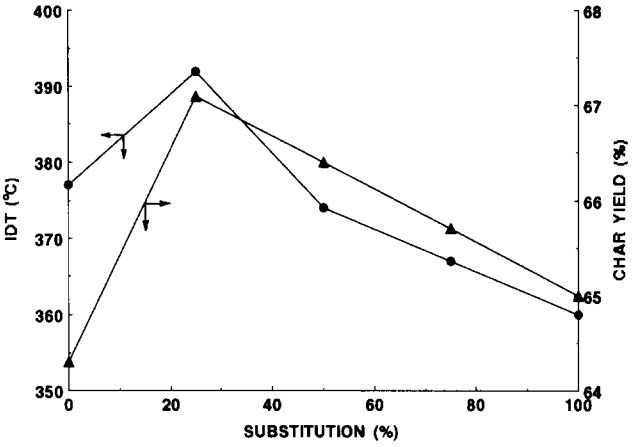


Figure 7 *IDT* and char yield at 800°C in N_2 of cured (at 320°C for 50 h) polyamides M *versus* the percentage substitution of dicarboxylic acid **1** in them

Table 3 Thermal stabilities of cured resins

Sample	N_2				Air		
	IDT[a] (°C)	*PDT*[b] (°C)	PDT_{max}[c] (°C)	Y_c[d] (%)	*IDT* (°C)	*PDT* (°C)	PDT_{max} (°C)
M'_{100}	400	541	554	64	393	487	570
E'_{100}	407	552	556	64	398	489	571
S'_{100}	404	537	552	63	391	478	517
P'_{100}	395	560	563	70	392	496	560

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

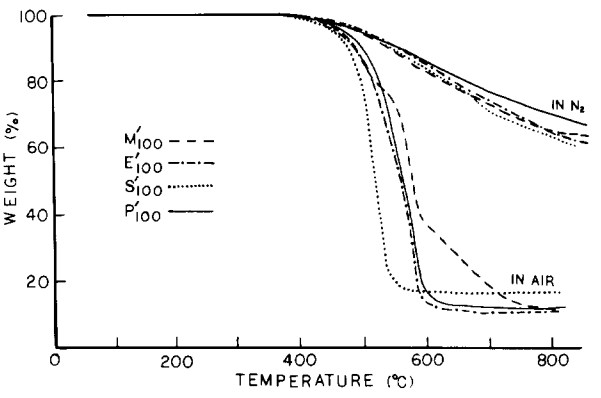


Figure 8 T.g.a. thermograms of cured (at 320°C for 50 h) homopolyamides M'_{100}, E'_{100}, S'_{100} and P'_{100} in N_2 and air. Conditions: gas flow, 60 cm^3 min^{-1}; heating rate, 20°C min^{-1}

for the preparation of polyamides did not influence their thermal stability remarkably.

The thermal stability of a typical cured resin P'_{100} was ascertained by isothermal gravimetric analysis (i.g.a.). After 20 h isothermal ageing in static air at 320, 330 and 340°C, P'_{100} displayed weight losses of 23.3, 41.3 and 62.7%, respectively.

The d.t.a. traces of cured resins did not show transitions associated with the T_g (*Figure 4*). They displayed large exotherms above 350°C assigned to thermal degradation.

Evidence for the network structure of cured resins was obtained from their i.r. spectra. They were very broad and showed a considerable reduction of the absorption band around 2230 cm^{-1} assigned to the cyano groups. It is reasonable to accept that the cyano groups were consumed through the trimerization reaction. In addition, the cured resins were completely insoluble even in polar aprotic solvents and 98% H_2SO_4.

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