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Unsaturated polyamides prepared from 3-amino- or 4-carboxycinnamic acid and their heat curing to thermally stable resins

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Unsaturated homopolyamide was prepared from 3-aminocinnamic acid (ACA) by the phosphorylation polycondensation method. In addition, various copolyamides were prepared from ACA and 4-aminobenzoic acid. Furthermore, an unsaturated homopolyamide was synthesized from 4-carboxycinnamic acid and 4,4′-diaminodiphenylmethane. The physical, chemical and thermal properties of the polyamides were correlated with those of the corresponding reference polyamides. The unsaturated polyamides showed an enhanced solubility in polar aprotic solvents and certain strong inorganic and organic acids compared to the reference polyamides. The X-ray diffractograms of polyamides showed some degree of crystallinity. Differential thermal analysis studies revealed melting of polyamides in the region of 237–292°C. The crosslinked polymers obtained from unsaturated polyamides by curing at 260°C for 20 h were remarkably more thermally stable than the reference polymers, being stable up to 310–366°C in N_2 or air, and afforded a char yield at 800°C of 66–80% in N_2 and 25–71% in air.

(Keywords: unsaturated polyamides; thermally stable resins; cinnamic acids)

INTRODUCTION

Aromatic polyamides (aramides) are some of the most thermally stable polymers[1]. However, their applications are restricted by their poor processability due to limited solubility in common organic solvents and high melting or softening temperatures. Therefore, it is of interest to prepare tractable polyamides with an improved processability that on subsequent treatment afford insoluble heat-resistant resins.

A literature survey revealed that certain unsaturated polyamides derived from fumaric acid have been prepared[2–6]. Unsaturated polyamides and particularly polyamides bearing olefinic bonds possess attractive properties and are used as fibres[7,8], membranes for reverse osmosis[9] and resins[10]. In addition, some polyamides bearing olefinic bonds have recently been prepared and crosslinked in our laboratory[11–14].

The present investigation deals with the synthesis and characterization of a new series of unsaturated polyamides prepared from inexpensive and easily synthesized starting materials. The incorporation of olefinic bonds with *trans* configuration in the polyamide backbone is expected to improve their solubility and consequently their processability. Furthermore, by heat curing they afford thermally stable crosslinked polymers through their olefinic bonds without evolving volatile by-products. The cured polymers are potential candidates as matrix resins for high-temperature composites.

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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 FT-IR 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. Thin-layer chromatography (t.l.c.) was performed on Merck silica gel 60 F_{254} films (0.2 mm) precoated on aluminium foil. Spots were visualized by u.v. light at 254 nm and ninhydrin in the case of 3-aminocinnamic acid (ACA). Dynamic thermal analyses (d.t.a.) and thermogravimetric analyses (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/100 ml in 98% H_2SO_4 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-1840 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% r.h. (relative humidity) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20°C and were periodically weighed.

Reagents and solvents

3-Nitrobenzaldehyde and 4-aminobenzoic acid (ABA) were recrystallized from water. 4-Carboxybenzaldehyde, 4,4′-diaminodiphenylmethane and malonic acid were recrystallized from acetonitrile, toluene and 1,4-dioxane, respectively. *N,N*-Dimethylformamide (DMF) was dried by refluxing and fractionally distilled from CaH_2. Ethanol (95%), triphenyl phosphite and pyridine were purified by distillation. Hydrazine hydrate was used as supplied. All reagents and solvents were obtained from Aldrich.

Preparation of starting materials

3-Aminocinnamic acid (ACA) (Scheme 1). A mixture of 3-nitrobenzaldehyde (9.0000 g, 59.55 mmol), malonic acid (6.1966 g, 59.55 mmol), 95% ethanol (30 ml) and pyridine (1.4143 g, 17.85 mmol) was refluxed for 24 h. It was subsequently cooled at 0°C; the white solid precipitated was filtered off, washed with water and dried to afford 3-nitrocinnamic acid (7.96 g; 72% yield). A purified sample obtained by recrystallization from 95% ethanol had m.p. 196–199°C (literature values 193–194°C (refs. 15, 18) and 204°C (ref. 16)). R_f ($CHCl_3$/MeOH 9/1) = 0.72.

Analysis calculated for $C_9H_7NO_4$: C, 56.54%; H, 3.69%; N, 7.33%. Found: C, 56.14%; H, 3.68%; N, 7.19%. I.r. (KBr) (cm^{-1}): 3092–2610 (O–H stretching); 1698 (C=O); 1636 (olefinic bond); 1576 (aromatic); 1524, 1358 (NO_2); 1418, 1280 (C–O stretching and O–H deformation); 980 (*trans* olefinic bond).

^1H n.m.r. (DMSO-d_6) δ (ppm): 8.37 (s, 1H, aromatic of position 2); 8.00–6.73 (m, 3H, other aromatic, and 2H, olefinic). The carboxylic proton was unobserved.

A flask equipped with a dropping funnel and magnetic stirrer was charged with a mixture of 3-nitrocinnamic acid (6.0000 g, 31.38 mmol), 95% ethanol (20 ml) and a catalytic amount of 10% palladium on activated carbon. It was refluxed and hydrazine hydrate (2 ml) diluted with 95% ethanol (5 ml) was added dropwise to the stirred solution. The mixture was refluxed for 10 min in total and it was subsequently filtered. The filtrate was cooled at 0°C and the whitish solid crystallized was filtered off, washed with water and dried to afford ACA (3.44 g; 68% yield). It was recrystallized from 95% ethanol (m.p. 177–180°C; literature values 183°C (ref. 16) and 181°C (ref. 17)). R_f ($CHCl_3$/MeOH 9/1) = 0.16.

Analysis calculated for $C_9H_9NO_2$: C, 67.06%; H, 9.07%; N, 8.69%. Found: C, 66.65%; H, 9.08%; N, 8.44%.

I.r. (KBr) (cm^{-1}): 3334 (N–H stretching); 3162–2630 (O–H stretching); 1668 (C=O); 1632 (olefinic bond); 1554, 954 (N–H deformation); 1532 (aromatic); 1396, 1288 (C–O stretching and O–H deformation); 986 (*trans* olefinic bond).

^1H n.m.r. (DMSO-d_6) δ (ppm): 8.43 (s, 1H, aromatic of position 2); 8.16–6.83 (m, 3H, other aromatic, and 2H, olefinic); 5.66 (b, 2H, NH_2). The carboxylic proton was unobserved.

4-Carboxycinnamic acid (CCA) (Scheme 2). A mixture of 4-carboxybenzaldehyde (4.0000 g, 26.64 mmol), malonic acid (5.5400 g, 53.28 mmol), 1,4-dioxane (30 ml) and a catalytic amount of piperidine was refluxed for 20 h. It was subsequently cooled at 0°C; the brownish solid precipitated was filtered off, washed with water and dried to afford CCA (4.15 g; 81% yield). It was recrystallized from DMF (m.p. > 300°C).

Analysis calculated for $C_{10}H_8O_4$: C, 62.49%; H, 4.20%. Found: C, 62.12%; H, 4.19%.

I.r. (KBr) (cm^{-1}): 2972–2542 (O–H stretching); 1690 (C=O); 1630 (olefinic bond); 1568 (aromatic); 1424, 1286 (C–O stretching and O–H deformation); 960 (*trans* olefinic bond).

^1H n.m.r. (DMSO-d_6) δ (ppm): 10.50 (b, 2H, COOH); 8.03–6.64 (m, 4H, aromatic, and 2H, olefinic).

General procedure for preparation of homopolyamides and copolyamides PA (Scheme 1)

A flask was charged with a mixture of ACA (x mol), ABA (y mol), DMF (15 ml), triphenyl phosphite ($x + y$ mol), pyridine (3 ml) and lithium chloride (0.30 g). It was stirred and heated at 100°C for 5 h under N_2. The mixture was subsequently poured over crushed ice and the brownish solid precipitated was filtered off, washed with water and then extracted with refluxing acetone and dried. The weights of reagents, the reaction yields and the inherent viscosities of the products are summarized in *Table 1*.

Preparation of polyamide PAC (Scheme 2)

A mixture of CCA (2.0000 g, 10.40 mmol), 4,4′-diaminodiphenylmethane (2.0632 g, 10.40 mmol), DMF (15 ml), triphenyl phosphite (6.4528 g, 20.80 mmol), pyridine (2 ml) and lithium chloride (0.30 g) was stirred and heated at 100°C for 5 h under N_2. It was subsequently poured over crushed ice and the brownish solid precipitated was filtered off, washed with water, extracted with refluxing acetone and dried to afford PAC (3.64 g; 99% yield; $\eta_{inh} = 0.35$ dl g^{-1} in 98% H_2SO_4).

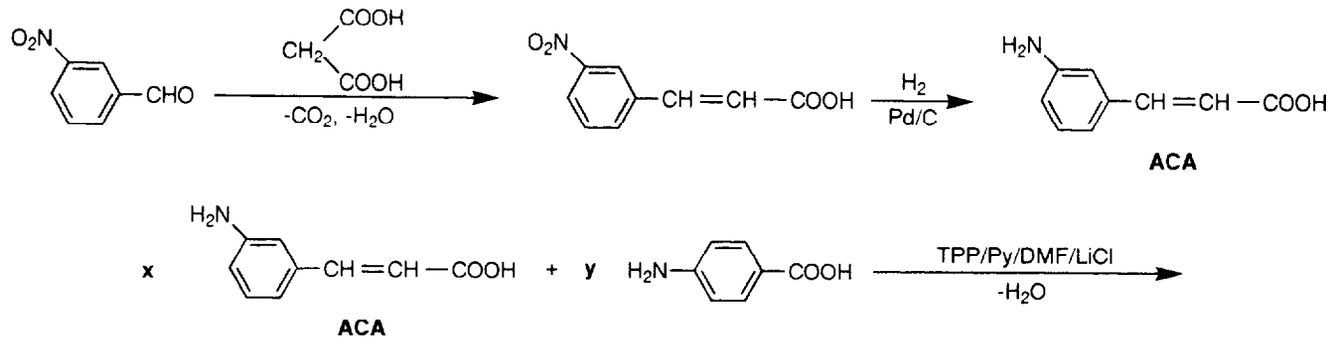
RESULTS AND DISCUSSION

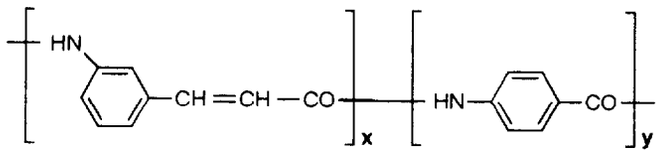
3-Nitrocinnamic acid was synthesized from the condensation of 3-nitrobenzaldehyde with malonic acid in the presence of pyridine[18] (*Scheme 1*). It is well known that 3-nitrocinnamic acid has been alternatively prepared by the Perkin reaction from 3-nitrobenzaldehyde, acetic anhydride and sodium acetate[19]. It was reduced to 3-aminocinnamic acid (ACA) by catalytic hydrogenation in ethanol utilizing hydrazine hydrate. Prolonged hydrogenation should be avoided, because the olefinic bond

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

Sample	Quantities of reagents (g (mmol)) ACA[a]	ABA[b]	Yield (%)	η_{inh}[c] (dl g^{-1})
PA_0		1.4988 (10.93)	97	0.32
PA_{25}	0.3997 (2.48)	1.0202 (7.44)	98	0.38
PA_{50}	0.4996 (3.10)	0.4251 (3.10)	98	0.39
PA_{75}	0.6993 (4.32)	0.1974 (1.44)	97	0.41
PA_{100}	1.1991 (7.44)		97	0.36

[a] ACA: 3-aminocinnamic acid
[b] ABA: 4-aminobenzoic acid
[c] Inherent viscosities in 98% H_2SO_4 (0.5 g dl^{-1}) at 30°C





PA_0 : x= 0.00, y= 1.00

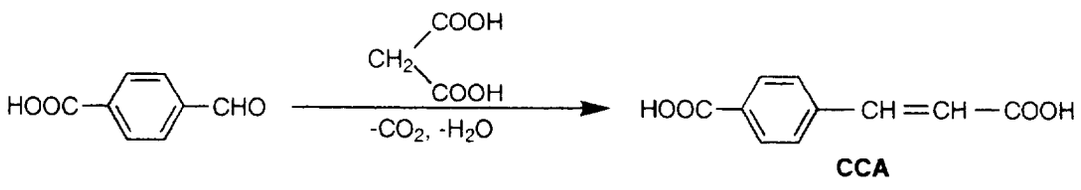
PA_{25}: x= 0.25, y= 0.75

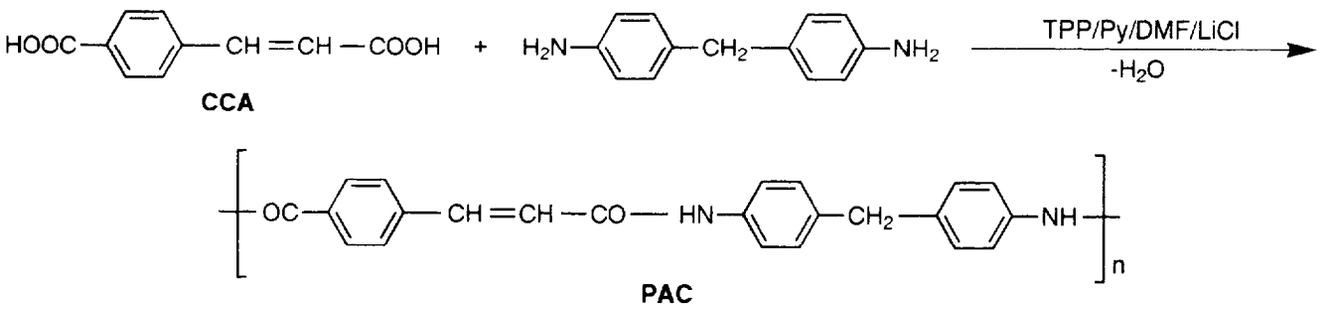
PA_{50}: x= 0.50, y= 0.50

PA_{75}: x= 0.75, y= 0.25

PA_{100}: x= 1.00, y= 0.00

Scheme 1





Scheme 2

could also be hydrogenated. The compound 3-$(NH_2)C_6H_4CH_2CH_2COOH$, which has a remarkably lower melting point (lit.[16] 95°C), was obtained under the same experimental conditions by extending the hydrogenation time above 40 min.

Various homopolyamides and copolyamides were prepared by the phosphorylation polycondensation method[20,21] according to the chemical reaction of *Scheme 1*. More particularly, ACA and 4-aminobenzoic acid (ABA) were homopolymerized and copolymerized under various molar ratios.

In addition, 4-carboxycinnamic acid (CCA) was synthesized from the condensation of 4-carboxybenzaldehyde with malonic acid in 1,4-dioxane in the presence of glacial acetic acid and piperidine (*Scheme 2*). Homopolyamide PAC was prepared from the reaction of CCA with 4,4′-diaminodiphenylmethane (DDM) utilizing triphenyl phosphite and pyridine as condensing agents. Furthermore, a reference polyamide PAR (η_{inh} = 0.36 dl g^{-1} in 98% H_2SO_4) derived from terephthalic acid and DDM was prepared under the same experimental conditions for comparative purposes.

All polyamides were obtained in nearly quantitative yields and their inherent viscosities (η_{inh}) in 98% H_2SO_4 were 0.32–0.41 dl g^{-1}.

Figure 1 presents the *FT*i.r. spectra of PA_{25} and PA_{100}. Homopolyamide PA_{100} showed characteristic absorption bands at 3340 (N–H stretching), 1652 (C=O), 1612 (olefinic bond), 1528 (N–H deformation), 1188 (C–N stretching and N–H bending) and 972 cm^{-1} (*trans* olefinic bond). Copolyamide PA_{25} displayed absorptions at 3342 (N–H stretching), 1702 (C=O), 1654 (C=O next to olefinic bond), 1606 (N–H deformation and olefinic bond), 1214 (C–N stretching and N–H bending) and 974 cm^{-1} (*trans* olefinic bond). The carbonyl of homopolyamide PAC absorbed at 1650 cm^{-1} whereas the other bands assigned to the amide structure appeared as in PA_{100}.

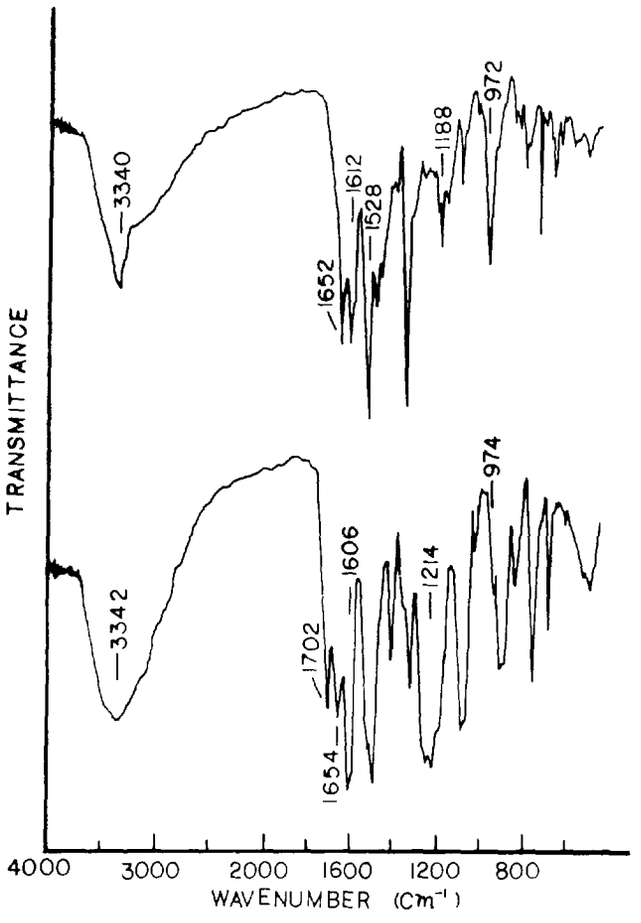


Figure 1 *FT*i.r. spectra of PA_{100} (top) and PA_{25} (bottom)

The ^1H n.m.r. spectra of polyamides PA_{25}–PA_{100} in DMSO-d_6 solution showed multiplets centred near $\delta = 8.51$–8.17 ppm (NHCO and aromatic protons *ortho* to carbonyl) and 8.02–6.92 ppm (other aromatic and olefinic protons).

It was shown that the introduction of the olefinic bonds along the polymer backbone improved their solubility in common organic solvents. *Table 2* presents the solubility behaviour of PA_0, PA_{25} and PA_{100}. Homopolyamide PA_{100} dissolved at ambient temperature in polar aprotic solvents (DMF, NMP, DMSO), 1,4-dioxane and certain inorganic and organic acids. In contrast, PA_0 was soluble only in DMSO, 98% H_2SO_4 and CCl_3COOH upon heating. Compared to the reference polyamide PAR, the unsaturated polyamide PAC also displayed a slightly higher solubility in common organic solvents.

Figure 2 presents the X-ray diffractograms for the synthesized polyamides. They generally showed some degree of crystallinity. The unsaturated polyamides PA_{25}, PA_{50}, PA_{100} and PAC, compared to the saturated polyamide PA_0, displayed an additional peak near $2\theta = 30°$, which could be associated to the presence of the olefinic bonds.

The isothermal moisture absorption for the pairs of polyamides PA_0 and PA_{25} as well as PAR and PAC was studied. A saturation in moisture absorption of polyamides was observed after a time exposed of 72 h. The amount of absorbed water per amide equivalent weight was 0.16, 0.58, 0.33 and 0.46 mol, respectively. The results revealed the significantly higher hydrophilicity of the unsaturated polyamides in comparison to that of the corresponding reference ones. The disorder in the chain packing caused by the incorporation of the *trans* configuration of ACA or CCA in unsaturated polyamides could be responsible for this feature. The degree of disorder increased the accessibility of water, a result that is in agreement with a better solubility.

Upon gradual heating into a capillary tube, the synthesized polyamides showed melting in the range of 237–292°C. *Figure 3* presents a typical d.t.a. trace in N_2 of copolyamide PA_{50}. It displayed an endotherm at 292°C (onset temperature 281°C) ascribable to its melting, which was interrupted by an exotherm assigned to crosslinking reactions through the olefinic bonds as well as to partial thermal degradation. The corresponding cured (at 260°C for 20 h) sample PA'_{50} did not exhibit a transition in this temperature region. The exotherm of PA'_{50} above 325°C was attributed to its thermal degradation.

The unsaturated polyamides were thermally crosslinked through their olefinic bonds to afford heat-resistant

Table 2 Solubilities of polyamides[a]

Sample	Solvents						
	DMF[b]	NMP[c]	DMSO[d]	CH_3CN	1,4-Dioxane	H_2SO_4 (98%)	CCl_3COOH
PA_0	–	–	+	–	–	+	+
PA_{25}	+	+	++	–	++	++	++
PA_{100}	++	++	++	–	++	++	++

[a] Solubility: (++) soluble at room temperature; (+) soluble in hot solvent; (–) insoluble
[b] DMF = *N*,*N*-dimethylformamide
[c] NMP = *N*-methylpyrrolidinone
[d] DMSO = dimethylsulfoxide

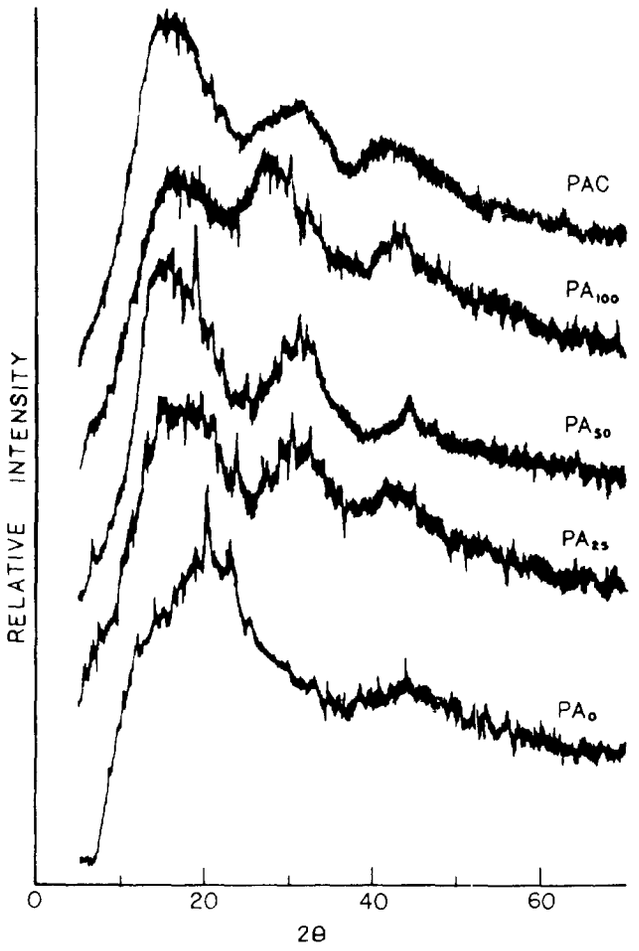


Figure 2 X-ray diffractograms of PA_0, PA_{25}, PA_{50}, PA_{100} and PAC

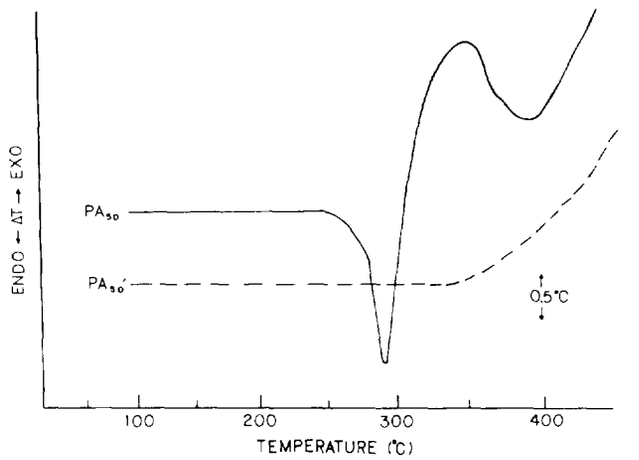


Figure 3 D.t.a. traces in N_2 of PA_{50} and the corresponding cured (260°C for 20 h) sample PA'_{50}. Conditions: N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

resins that could be used as matrix resins for high-temperature composites. The reference polyamides PA_0 and PAR were also cured under the same conditions for comparative purposes. The crosslinked polymers obtained from polyamides PA, PAC and PAR by curing at 260°C for 20 h are referred to by the designations PA', PAC' and PAR' respectively. The cured polymers obtained as dark brown solids were no longer soluble in solvents for the untreated polyamides. Their thermal stability was ascertained by dynamic t.g.a. and isothermal gravimetric analysis (i.g.a.). *Figure 4* presents typical t.g.a. curves in N_2 and air for cured polyamides PA'_{75} and PAC'. The initial decomposition temperature (*IDT*), the polymer decomposition temperature (*PDT*), the maximum polymer decomposition temperature (PDT_{max}) and the char yield (Y_c) at 800°C in both N_2 and air for all cured polyamides are summarized in *Table 3*. 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.

The cured polymers obtained from unsaturated polyamides were stable up to 310–336°C in N_2 or air and afforded char yield at 800°C of 66–80% in N_2 and 25–71% in air. The relative thermal stability of cured polymers could be assessed on the basis of the *IDT* and Y_c values in both N_2 and air. It is seen that the cured polymers derived from the unsaturated polyamides were significantly more thermally stable than the corresponding reference polymers owing to their network structure. In addition, the *IDT* and Y_c of the various PA' polymers were remarkably influenced by their composition. Specifically, both *IDT* and Y_c at 800°C in N_2 were increased on increasing the percentage substitution of ACA in polyamides up to 75% and they were reduced beyond this value (*Figure 5*).

The relative thermal stability of cured polyamides was also evaluated from their i.g.a. traces (*Figure 6*). The cured polyamides PA'_{75}, PA'_{50}, PA'_{25}, PA'_{100}, PAC' and PAR' showed weight losses of 10.4, 15.5, 16.5, 17.5, 23.8 and 58.6%, respectively, after 20 h isothermal ageing at 310°C in static air. It is obvious that the remaining weight of polyamides followed the trend of their Y_c at 800°C in air.

From *Table 3* it is seen that the cured polymers PA' derived from the unsaturated polyamides afforded Y_c at 800°C in air of 25–71% *versus* 14% for the corresponding reference polymer PA'_0. Obviously, the introduction of ACA into the polymer backbone changed its thermal degradation process to afford higher char yields.

CONCLUSIONS

3-Aminocinnamic acid (ACA) and 4-carboxycinnamic acid (CCA) were used as starting materials for the preparation of new unsaturated polyamides. They

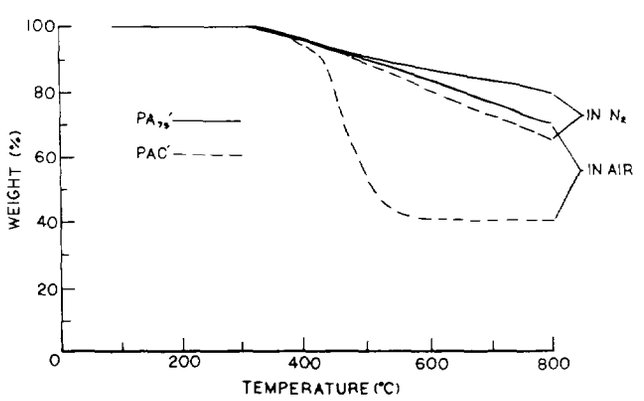


Figure 4 T.g.a. thermograms of cured polymers PA'_{75} and PAC' in N_2 and air. Conditions: gas flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

Table 3 Thermal stabilities of cured polymers

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 (%)
PA'_0	267	351	363	58	262	347	452	14
PA'_{25}	313	374	345	67	310	441	467	40
PA'_{50}	325	571	463	78	317	541	560	66
PA'_{75}	336	523	460	80	325	508	529	71
PA'_{100}	314	448	355	70	310	460	563	25
PAC'	333	493	538	66	325	441	452	40
PAR'	310	460	508	54	308	411	441	5

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

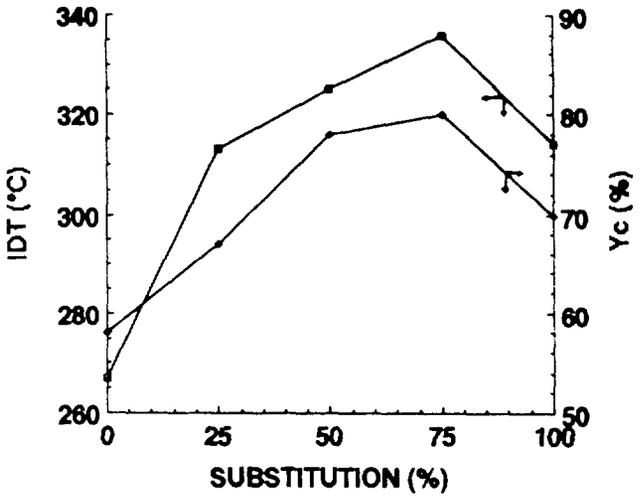


Figure 5 *IDT* and Y_c at 800°C in N_2 for cured polyamides PA' *versus* the percentage substitution of ACA in them

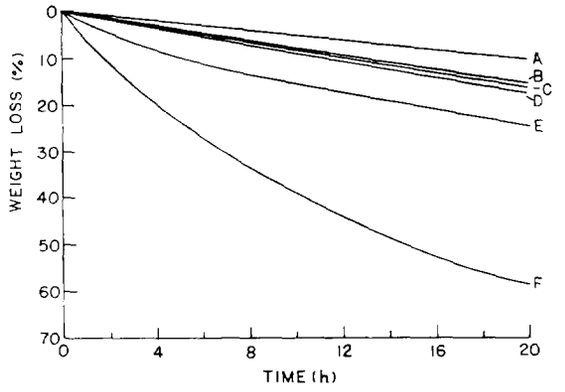


Figure 6 I.g.a. traces at 310°C in static air of cured polymers PA'_{75} (A), PA'_{50} (B), PA'_{25} (C), PA'_{100} (D), PAC' (E) and PAR' (F)

showed an enhanced solubility in polar aprotic solvents and certain strong inorganic and organic acids compared to the reference polyamides. The X-ray diffractograms of polyamides showed some degree of crystallinity and their d.t.a. traces revealed melting in the region of 237–292°C. Crosslinked polymers were obtained by heat curing. They were significantly more thermally stable than the reference ones.

REFERENCES

1 Cassidy, P. E. 'Thermally Stable Polymers', Dekker, New York, 1980
2 Balasubramanian, M., Nanjan, M. J. and Santappa, M. *Makromol. Chem.* 1981, **182**, 853; *J. Appl. Polym. Sci.* 1982, **27**, 1423
3 Jayaprakash, D., Ravikumar, L. and Nanjan, M. J. *Makromol. Chem., Rapid. Commun.* 1981, **2**, 611
4 Sachindrapal, P., Ramasamy, S. and Nanjan, M. J. *Polym. Bull.* 1981, **5**, 417
5 Sachindrapal, P. and Nanjan, M. J. *J. Polym. Sci., Polym. Chem. Edn.* 1983, **21**, 2301
6 Sachindrapal, P. and Nanjan, M. J. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 3705
7 Pletcher, T. C. and Morgan, P. W. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 643
8 Morgan, P. W. US Patent 3810528, 1974 (to E. I. du Pont de Nemours and Co.)
9 Credali, L., Parrini, P., Leonelli, E. and Choille, A. *Chim. Ind. (Milan)* 1974, **56**, 19; *Chem. Abstr.* 1974, **81**, 38271z; Proc. 4th Int. Symp. Fresh Water Sea, 1973, p. 95; *Chem. Abstr.* 1974, **81**, 64784p
10 Nakao, K. and Mito, M. Jap. Patent 75160343, 1975 (to Osaka Prefecture); *Chem. Abstr.* 1976, **84**, 136872
11 Mikroyannidis, J. A. *Eur. Polym. J.* 1992, **28**, 439
12 Mikroyannidis, J. A. *J. Appl. Polym. Sci.* 1992, **46**, 1001
13 Mikroyannidis, J. A. *Eur. Polym. J.* 1989, **25**, 557
14 Mikroyannidis, J. A. *J. Appl. Polym. Sci.* 1993, **48**, 1749
15 Kuskov, V. K. and Lomonosov, M. V. *Dokl. Akad. Nauk SSSR* 1956, **110**, 223
16 Tsatsas, G., Vassiliadou, N. and Choulis, N. *Bull. Soc. Chim. Fr.* 1964, **10**, 2612
17 Boyer, J. H. and Alul, H. *J. Am. Chem. Soc.* 1959, **81**, 2136
18 Wiley, R. H. and Smith, N. R. 'Organic Syntheses', Coll. Vol. 4, Wiley, New York, 1963, p. 731
19 Thayer, F. K. 'Organic Syntheses', Coll. Vol. 1, Wiley, New York, 1955, p. 398
20 Yamazaki, N., Higashi, F. and Kawabata, J. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 2149
21 Yamazaki, N., Matsumoto, M. and Higashi, F. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 1373