

Synthesis, Characterization, and Curing of Unsaturated Polyamides Derived from 2,6-Di(4-Carboxystyryl)Pyridine and 2,6-Bis(4-Carboxybenzylidene) Cyclohexanone

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SYNOPSIS

Two new series of heat-curable polyamides were prepared utilizing the unsaturated dicarboxylic acids 2,6-di(4-carboxystyryl)pyridine (DCSP) and 2,6-bis(4-carboxybenzylidene)cyclohexanone (BCBC) as starting materials. They were prepared from the condensation of 4-carboxybenzaldehyde with a half molar amount of 2,6-dimethylpyridine or cyclohexanone, respectively. The dicarboxylic acids reacted with various aromatic diamines, utilizing triphenyl phosphite and pyridine as condensing agents, to yield polyamides. In addition, two model diamides were prepared by condensing the dicarboxylic acids with aniline. Characterization of starting materials, polyamides, and model compounds was accomplished by IR and $^1\text{H-NMR}$ spectroscopy. The curing behavior of polyamides was investigated by DTA. Upon heat-curing, the unsaturated polyamides were crosslinked through their olefinic bonds to afford insoluble, heat-resistant resins. The thermal stability of the resins was evaluated by TGA and isothermal gravimetric analysis (IGA). The cured resins were stable up to 310–322°C in N_2 or air and afforded anaerobic char yield of 57–69% at 800°C.

INTRODUCTION

Polyamides and particularly wholly aromatic polyamides (aramids) are of great technical interest because they possess useful properties, such as high thermostability, low flammability, and excellent mechanical properties.^{1–3} Processability of most aramids, however, is extremely difficult because of their high softening temperatures and insolubility in most organic solvents. It is possible to synthesize a polymer precursor with lower softening temperature and higher solubility, which, upon subsequent curing, affords a crosslinked thermostable structure.

Polyamides containing suitable double bonds can afford useful materials with many technological applications.^{4–6} They can be crosslinked through their double bonds without the evolution of any gaseous product.

The present investigation deals with the synthesis, characterization, and curing of two new series of unsaturated heat-curable polyamides. The first series of polyamides bearing styrylpyridine segments was based on DCSP, which was synthesized by condensing 2,6-dimethylpyridine with 4-carboxybenzaldehyde. It is well known that poly(styrylpyridine) (PSP), derived from the polycondensation of 2,4,6-trimethylpyridine or 2,6-dimethylpyridine with 1,4-benzenedicarbaldehyde, are highly thermostable thermosetting resins with easy processability, which can be used as matrix resins for composites.⁷ Recently, various polymers, such as polyamides, polyimides, polyesters, polyurethanes, and epoxy resins containing styrylpyridine segments, have been synthesized.^{8–11} The polyamides derived from DCSP are expected to combine the attractive properties of the PSP resins. More particularly, they are expected to possess good thermal stability and antiflammability properties, high char yield in nonoxidative atmosphere, easy processability, which make them able to give rise to composite materials having a good

mechanical behavior, especially at high temperatures.

The second series of polyamides was based on BCBC, which was synthesized from the acid catalyzed condensation of cyclohexanone with 4-carboxybenzaldehyde. Recently, the synthesis of certain arylidene polymers has been reported.¹²⁻¹⁴ In addition, a new class of unsaturated polyamides and polyimides obtained from 2,6-bis(3-aminobenzylidene)cyclohexanone has been synthesized in our laboratory.¹⁵ The polyamides obtained from BCBC are also expected to display, after heat-curing, outstanding thermal stability and high anaerobic char yield. They can be used as matrix resins for composites.

EXPERIMENTAL

Instrumentation

Melting points were determined on an electrothermal melting point apparatus IA6304 and were uncorrected. IR spectra were recorded on a Perkin-Elmer 710B spectrometer with KBr pellets. ¹H-NMR spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ) are given in p.p.m. with tetramethylsilane as an internal standard. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 mL in H₂SO₄ 98% or DMF at 30°C using an Ubbelohde suspended level viscometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Du Pont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in N₂ atmosphere at a flow rate of 60 cm³/min. Dynamic TGA measurements were made at a heating rate of 20°C/min.

Reagents and Solvents

2,6-Dimethylpyridine, cyclohexanone, and aniline were purified by distillation. 4-Carboxybenzaldehyde was recrystallized from ethanol 95%. 4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylether and 4,4'-diaminodiphenylsulphone were recrystallized from benzene, acetonitrile, and methanol, respectively. 1,4-Phenylenediamine was sublimated at about 110°C under vacuum (2-3 mm). Triphenyl phosphite was purified by vacuum distillation. 1-Methyl-2-pyrrolidone (NMP) and pyridine were dried by distillation under reduced pressure over calcium hydride. Acetic anhydride, 1,4-dioxane, and lithium chloride were used as supplied.

Preparation of Dicarboxylic Acids

2,6-Di(4-carboxystyryl)Pyridine (DCSP)

A flask, equipped with magnetic stirrer and condenser, was charged with a mixture of 4-carboxybenzaldehyde (7.5065 g, 50.0 mmol), 2,6-dimethylpyridine (2.6790 g, 25.0 mmol), and acetic anhydride (30 mL). The mixture was refluxed under N₂ for 35 h. A solid product separated during the heating period. The mixture was subsequently poured into water and was stirred for about 6 h to hydrolyze excess acetic anhydride. The whitish solid was filtered off, was washed thoroughly with water, and was dried to afford DCSP (5.80 g, yield 62%, mp > 300°C). It was recrystallized from a mixture of DMF/water (vol. ratio 1 : 1). IR (KBr) cm⁻¹: 3100-2820 (OH stretching and pyridine CH stretching); 1708 (C=O); 1620 (C=C and C=N); 1440, 1305 (C-O stretching and OH deformation); 980 (OH deformation); 805, 740 (2,6-disubstituted pyridine). ¹H-NMR (DMSO-*d*₆) δ : 8.15-7.20 (*m*, aromatic, pyridine ring, and olefinic).

2,6-Bis(4-Carboxybenzylidene)Cyclohexanone (BCBC)

A flask, equipped with magnetic stirrer and gas trap, was charged with a mixture of 4-carboxybenzaldehyde (6.1909 g, 40.0 mmol), cyclohexanone (1.9630 g, 20.0 mmol), and 1,4-dioxane (80 mL). The mixture was heated at about 50°C. Dry hydrogen chloride was bubbled through the stirred mixture as a catalyst. An exothermic reaction was observed and the temperature of the mixture was maintained at around 70°C. A yellow solid separated after 2 h of stirring. It was filtered off, was washed thoroughly with water, and was dried to afford BCBC (6.25 g, yield 86%, mp > 300°C). A purified sample was obtained by recrystallization from DMF. IR (KBr) cm⁻¹: 3110-2830 (OH stretching and cyclohexanone CH stretching); 1710-1690 (carboxylic C=O and cyclohexanone C=O); 1620 (C=C); 1443, 1303 (C-O stretching and OH deformation); 1430 (cyclohexanone CH deformation); 947 (OH deformation). ¹H-NMR (DMSO-*d*₆) δ : 8.18-7.60 (*m*, 8H aromatic and 2H olefinic): 2.83 (*m*, 6H, cyclohexanone ring).

Preparation of Polyamides

Polyamide 1a

A mixture of DCSP (1.8569 g, 5.0 mmol), 4,4'-diaminodiphenylmethane (0.9914 g, 5.0 mmol), triphenyl phosphite (3.1029 g, 10.0 mmol), pyridine

(3 mL), lithium chloride (1.5 g), and NMP (15 mL) was heated at 100°C for 6 h under N₂. The viscous reaction mixture was poured into water. The light brown solid obtained was filtered off, was washed with water, and then was extracted with refluxing acetone and was dried to afford 1a (Scheme 1) (2.59 g, yield 97%). Inherent viscosity in H₂SO₄ 98% was 0.23 dL/g.

Polyamide 1b

Polyamide 1b was similarly prepared as a light brown solid in 95% yield (2.54 g) from a mixture of DCSP (1.8569 g, 5.0 mmol), 4,4'-diaminodiphenylether (1.0012 g, 5.0 mmol), triphenyl phosphite (3.1029 g, 10.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL). Inherent viscosity in DMF was 0.21 dL/g.

Polyamide 1c

Polyamide 1c was similarly prepared as a light brown solid in 92% yield (2.69 g) from a mixture of DCSP (1.8569 g, 5.0 mmol), 4,4'-diaminodiphenylsulphone (1.2416 g, 5.0 mmol), triphenyl phosphite (3.1029 g, 10.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL). Inherent viscosity in DMF was 0.18 dL/g.

Polyamide 1d

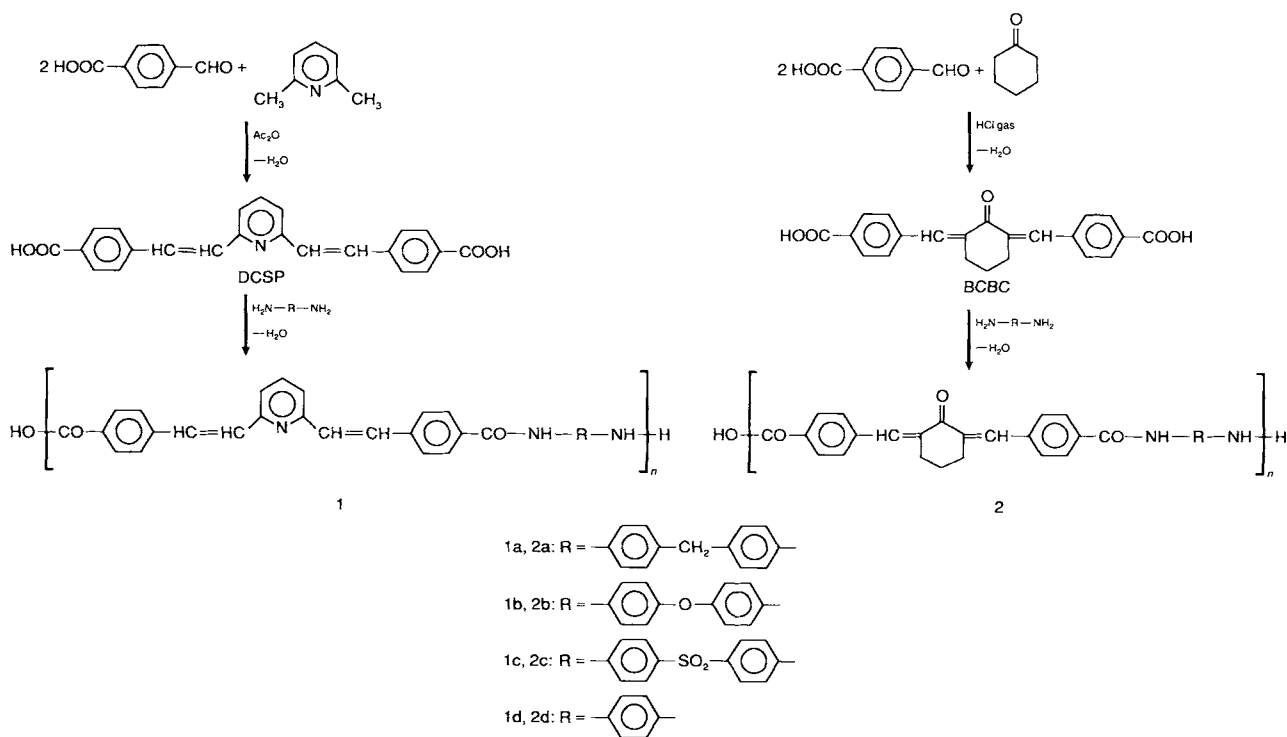
Polyamide 1d was similarly prepared as a light brown solid in 96% yield (2.13 g) from a mixture of DCSP (1.8569 g, 5.0 mmol), 1,4-phenylenediamine (0.5407 g, 5.0 mmol), triphenyl phosphite (3.1029 g, 10.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL). Inherent viscosity in H₂SO₄ 98% was 0.20 dL/g.

Polyamide 2a

A mixture of BCBC (1.4495 g, 4.0 mmol), 4,4'-diaminodiphenylmethane (0.7931 g, 4.0 mmol), triphenyl phosphite (2.5590 g, 8.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL) was heated at 100°C for 6 h under N₂. The viscous reaction mixture was then poured into water to precipitate polyamide 1a as a light brown solid. It was chopped up in a home blender, was washed with water, was extracted with refluxing acetone, and was dried to afford 2a (2.01 g, yield 96%). Inherent viscosity in H₂SO₄ 98% was 0.16 gL/g.

Polyamide 2b

Polyamide 2b was similarly prepared as a light brown solid in 95% yield (2.00 g) from a mixture of BCBC



Scheme 1

(1.4495 g, 4.0 mmol), 4,4'-diaminodiphenylether (0.8010 g, 4.0 mmol), triphenyl phosphite (2.5590 g, 8.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL). Inherent viscosity in H₂SO₄ 98% was 0.18 dL/g.

Polyamide 2c

Polyamide 2c was similarly prepared as a light brown solid in 93% yield (2.14 g) from a mixture of BCBC (1.4495 g, 4.0 mmol), 4,4'-diaminodiphenylsulphone (0.9932 g, 4.0 mmol), triphenyl phosphite (2.5590 g, 8.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL). Inherent viscosity in H₂SO₄ 98% was 0.15 dL/g.

Polyamide 2d

Polyamide 2d was similarly prepared as a light brown solid in 97% yield (1.69 g) from a mixture of BCBC (1.4495 g, 4.0 mmol), 1,4-phenylenediamine (0.4326 g, 4.0 mmol), triphenyl phosphite (2.5590 g, 4.0 mmol), pyridine (3 mL), lithium chloride (1.5 g), and NMP (15 mL). Inherent viscosity in H₂SO₄ 98% was 0.19 dL/g.

Preparation of Model Diamides

Diamide SDA

A mixture of DCSP (1.1142 g, 3.0 mmol), aniline (0.5587 g, 6.0 mmol), triphenyl phosphite (1.8617 g, 6.0 mmol), pyridine (3 mL), and NMP (10 mL) was heated at 100°C for 6 h under N₂. The mixture was subsequently poured into ice water. The light brown solid obtained was filtered off, was washed with water, and was dried to afford SDA (1.53 g, yield 98%). A purified sample with mp 285–288°C was obtained by recrystallization from a mixture of DMF/water (vol. ratio 1 : 2). IR (KBr) cm⁻¹: 3320 (NH stretching); 1665 (C=O); 1618 (C=C and C=N); 1557 (NH deformation); 1510, 1463 (aromatic and pyridine ring); 1280 (C—N stretching and NH bending); 980 (trans HC=CH). ¹H-NMR (DMSO-*d*₆) δ: 8.20 (*bs*, 2H, NHCO); 7.98 (*m*, 4H, aromatic ortho to carbonyl); 7.70–6.80 (*m*, 14H other aromatic, 3H pyridine ring, and 4H olefinic).

Diamide CDA

A mixture of BCBC (1.0871 g, 3.0 mmol), aniline (0.5587 g, 6.0 mmol), triphenyl phosphite (1.8617 g, 6.0 mmol), pyridine (3 mL), and NMP (10 mL) was heated at 100°C for 6 h under N₂. Then it was poured into ice water and the light brown semisolid,

thus obtained, was isolated by decantation. It was washed with water and was dried to afford CDA (1.48 g, yield 96%). A purified sample with mp 69–72°C was obtained by recrystallization from a mixture of DMF/water (vol. ratio 1 : 1). IR (KBr) cm⁻¹: 3300 (NH stretching); 2960 (cyclohexanone CH stretching); 1710–1650 (amide C=O and cyclohexanone C=O); 1612 (C=C); 1550 (NH deformation); 1500 (aromatic); 1450 (aromatic and cyclohexanone CH deformation); 1270 (C—N stretching and NH bending); 760 (C=CH). ¹H-NMR (DMSO-*d*₆) δ: 8.16 (*bs*, 2H, NHCO); 7.87 (*m*, 4H, aromatic ortho to carbonyl); 7.64–7.20 (*m*, 14H other aromatic and 2H olefinic); 2.78 (*m*, 6H, cyclohexanone ring).

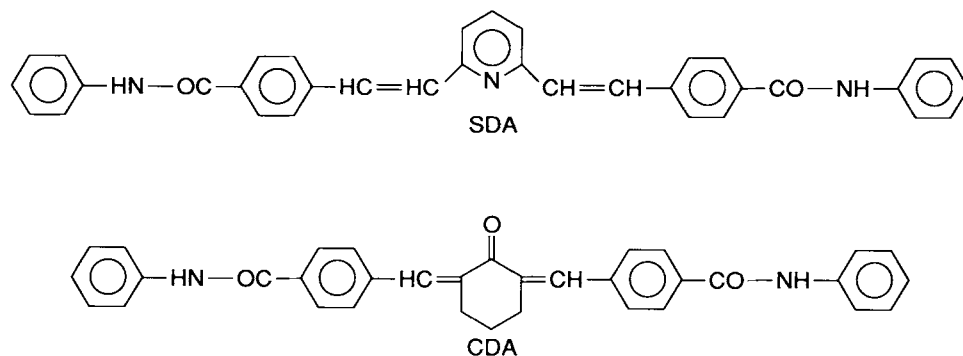
Curing Procedure of Polyamides 1a–1d and 2a–2d

Polyamides 1a–1d were cured by heating into a circulated air oven at 240°C for 22 h. Curing of polyamides 2a–2d was similarly accomplished by heating at 265°C for 30 h.

RESULTS AND DISCUSSION

The unsaturated dicarboxylic acids DCSP and BCBC were used as starting materials for preparing two new series of heat-curable polyamides. Scheme 1 outlines the synthesis of these dicarboxylic acids as well as of polyamides. More particularly, DCSP was prepared by condensing 2,6-dimethylpyridine with a double molar amount of 4-carboxybenzaldehyde in the presence of acetic anhydride. The reaction conditions were similar to those utilized for the preparation of poly(styrylpyridine).¹⁶ BCBC was prepared from the condensation of cyclohexanone with a double molar amount of 4-carboxybenzaldehyde in the presence of dry hydrogen chloride as catalyst. The reaction was strongly exothermic and was carried out in 1,4-dioxane. When ethanol was used as reaction medium, the desired dicarboxylic acid was not obtained, probably due to the formation of the corresponding ethyl diester. A literature survey revealed that both DCSP and BCBC have not been synthesized previously.

DCSP and BCBC were condensed directly through the phosphorylation reaction with various aromatic diamines to afford polyamides 1 and 2, respectively (Scheme 1). The reactions were carried out in a mixture of NMP and pyridine in the pres-



Scheme 2

ence of triphenyl phosphite and lithium chloride at 100°C. All polyamides were isolated as light brown solids in nearly quantitative yields. The inherent viscosities of the polyamides were 0.15–0.23 dL/g. It is well known that the polycondensation reactions occur via an acyloxy *N*-phosphonium salt followed by aminolysis.¹⁷

The present investigation was extended to include the synthesis of two model diamides SDA and CDA (Scheme 2). They were synthesized from the reactions of aniline with DCSP and BCBC, respectively. These model compounds were prepared under

the experimental conditions used for preparing the polyamides.

The structures of starting materials, DCSP and BCBC, were confirmed by IR and ¹H-NMR spectroscopy. Figures 1 and 2 present the IR and ¹H-NMR spectra of these dicarboxylic acids and their assignments are given in the Experimental section. Dicarboxylic acid, DCSP, could have the pyridinium salt structure because its molecule contained both the pyridine and carboxylic moieties. The solubility behavior of DCSP conformed to the pyridinium salt structure. Thus, although this compound was in-

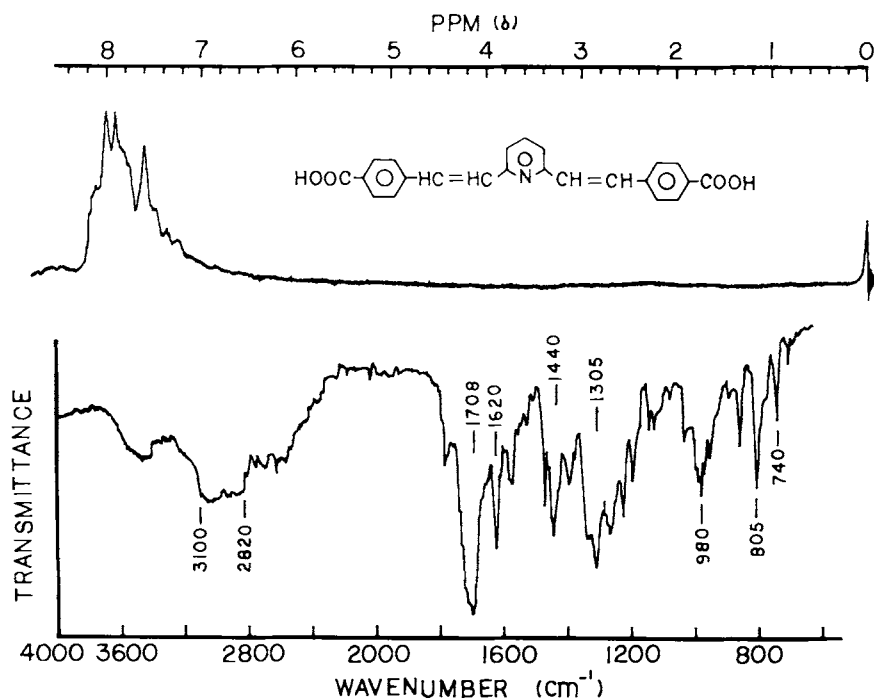


Figure 1 IR and ¹H-NMR spectrum in DMSO-*d*₆ solution of DCSP.

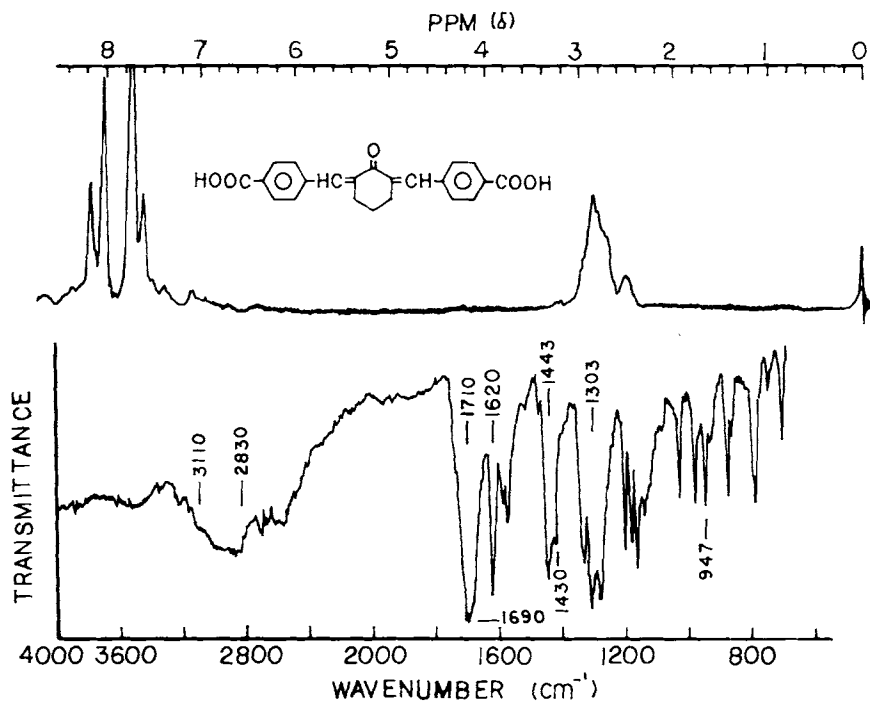


Figure 2 IR and ^1H -NMR spectrum in $\text{DMSO}-d_6$ solution of BCBC.

soluble in less efficient solvents, such as chloroform or acetone, it dissolved completely at room temperature in these media upon adding a few drops of triethylamine and it reprecipitated from these solutions by adding some drops of hydrochloric acid. The ^1H -NMR spectra, both of DCSP and BCBC in

$\text{DMSO}-d_6$ solutions, did not show a peak at the downfield region associated with the carboxylic protons.

Polyamides were characterized by IR and ^1H -NMR spectroscopy. Characterization of model compounds was also accomplished by these spectro-

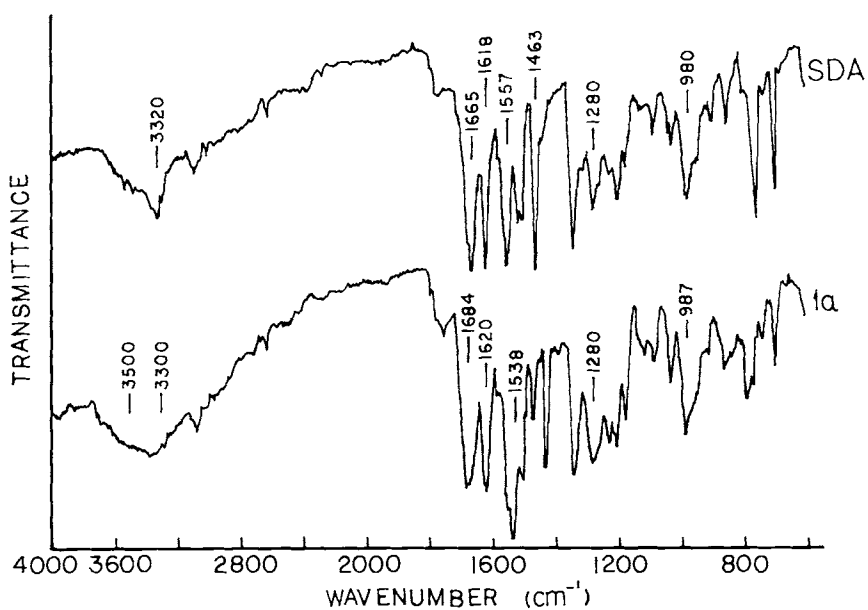


Figure 3 IR spectra of polyamide 1a (bottom) as well as the corresponding model diamide SDA (top).

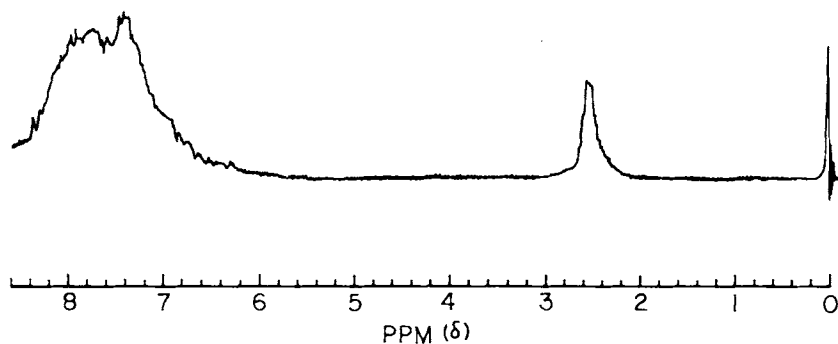


Figure 4 $^1\text{H-NMR}$ spectrum in $\text{DMSO-}d_6$ solution of polyamide 1a.

scopic methods (see the Experimental section). The spectral data of model compounds were in agreement with those of polyamides. As an example, Figure 3 presents the IR spectra of polyamide 1a as well as the corresponding model diamide SDA. All polyamides displayed characteristic absorption bands around 3500–3300 (NH stretching), 1680 (C=O), 1540 (NH deformation), and 1280 cm^{-1} (C-N stretching and NH bending). The polyamides' absorption, near 1620 cm^{-1} , was attributed to the C=C bond. Polyamides 2a–2d showed a broadening of the absorption band associated with carbonyl due to the cyclohexanone carbonyl, which absorbed around 1720 cm^{-1} .

Figure 4 shows a typical $^1\text{H-NMR}$ spectrum of polyamide 1a. It displayed a broad multiplet peak

at 8.35–6.68 δ (NHCO , aromatic, olefinic, and pyridine ring protons) and a broad singlet at 2.53 δ (methylene protons).

These polyamides were soluble in polar aprotic solvents, such as DMF, N,N -dimethylacetamide, N -methylpyrrolidinone, DMSO, as well as in CCl_3COOH and concentrated H_2SO_4 .

The unsaturated polyamides, 1a–1d, were cross-linked through their olefinic bonds by curing at 240°C for 22 h to afford resins, which are referred to by the designations 1a'–1d', respectively. Similarly, the network polymers, obtained from polyamides 2a–2d upon curing at 265°C for 30 h, are referred to by the designations 2a'–2d', respectively.

Curing behavior of polyamides, before and after heat-curing, was investigated by DTA. Figure 5 pre-

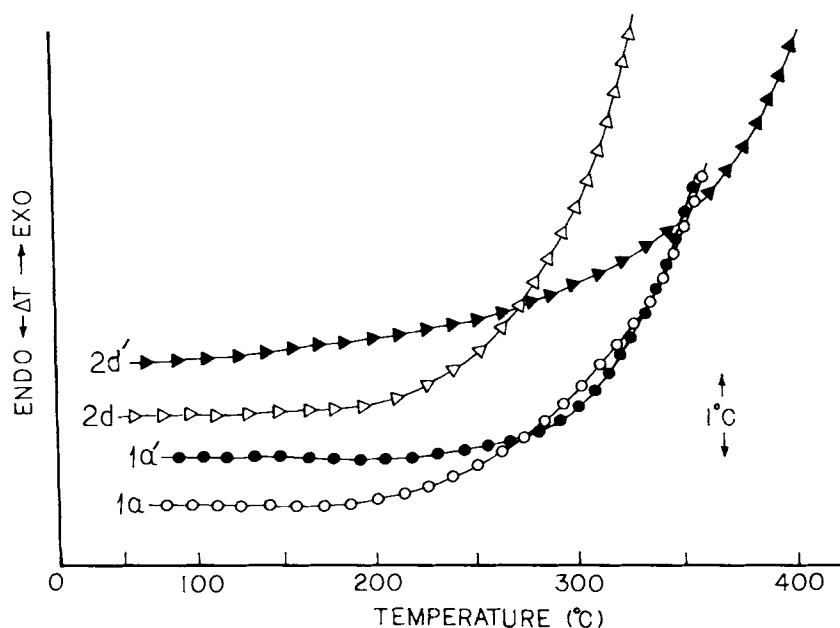


Figure 5 DTA traces of polyamides 1a and 2d, as well as the corresponding cured samples 1a' and 2d'. Conditions: N_2 flow 60 cm^3/min ; heating rate 20°C/min.

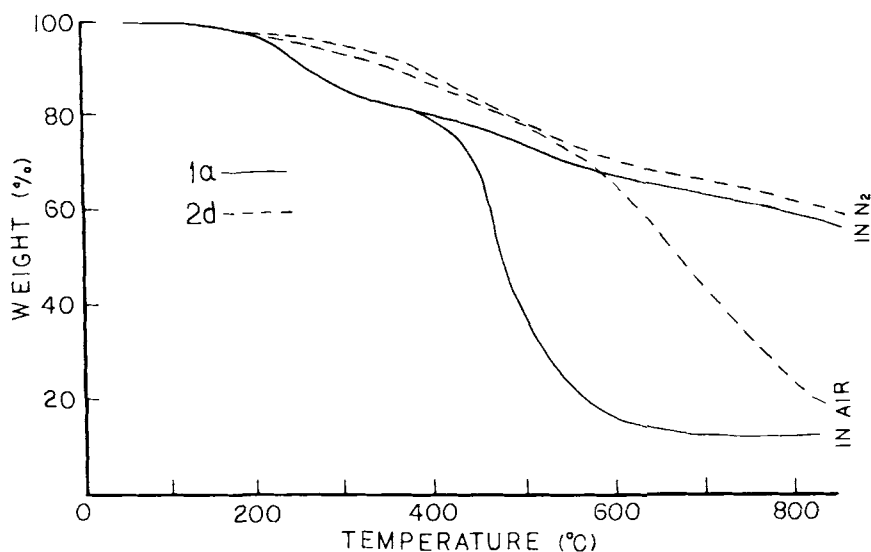


Figure 6 TGA thermograms of polyamides 1a and 2d in N_2 and air. Conditions: Gas flow $60 \text{ cm}^3/\text{min}$; heating rate $20^\circ\text{C}/\text{min}$.

sents typical DTA traces in N_2 of polyamides 1a and 2d, as well as the corresponding cured samples 1a' and 2d'. The uncured polyamides, 1a and 2d, displayed broad exotherms above 190°C , whereas the cured samples, 1a' and 2d', showed exotherms beyond 300°C . The exotherms of the uncured samples could be attributed to their crosslinking through the olefinic bonds, as well as to a gradual thermal degradation occurring above 190°C , which was con-

firmed from their TGA traces (Fig. 6). The exotherms of the cured samples beyond 300°C were associated with their thermal degradation. Analogous behavior has been observed with the unsaturated polyamides derived from 2,6-bis(3-aminobenzylidene)cyclohexanone.¹⁵

Thermal behavior of polyamides, 1a-1d, bearing styrylpyridine segments is expected to be similar to that of PSP resins. Hsu et al.¹⁸ have studied the

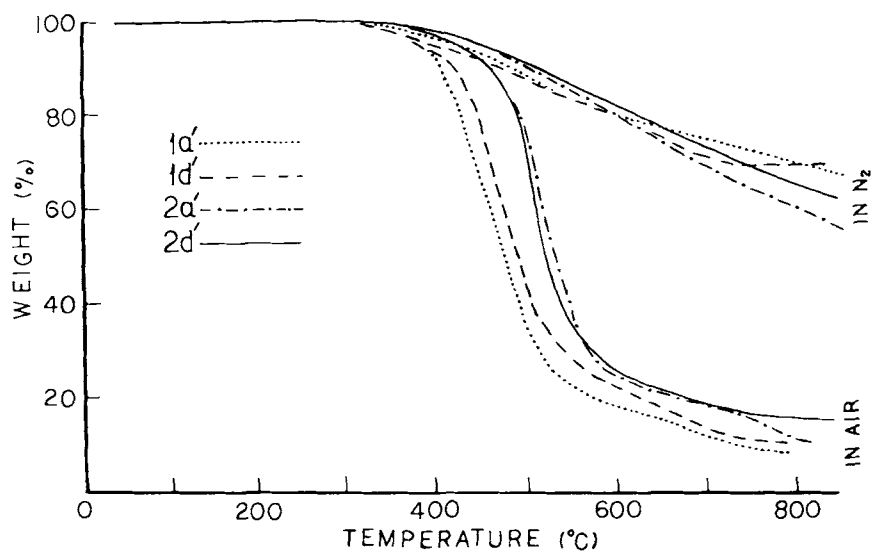


Figure 7 TGA thermograms of cured polyamides 1a', 1d', 2a', 2d' in N_2 and air. Conditions: Gas flow $60 \text{ cm}^3/\text{min}$; heating rate $20^\circ\text{C}/\text{min}$.

thermal behavior of model compounds, such as 4-styrylpyridine and 2,6-distyrylpyridine, in the range of 250–300°C. They have reported the formation of fused aromatic compounds arising from a Diels–Alder type reaction. In addition, Clavreul et al.¹⁹ have studied the thermal behavior of the styrylpyridines alone or in the presence of their precursors. They have showed addition of a methyl group of the substituted pyridine to the C=C double bond of a styrylpyridine derivative and, because of the possible reversion, could be followed by elimination of the same or a different methylpyridine.

All cured polyamides were insoluble even in CCl_3COOH and concentrated H_2SO_4 . The IR spectra of the cured polyamides were more broad than those of the corresponding uncured samples showing a reduction of the absorption at 1620 cm^{-1} assigned to the C=C double bond. Note that cured polyamides were remarkably more thermally stable than the corresponding uncured samples, due to their crosslinked structure.

Thermal stabilities of cured polyamides were evaluated by TGA and isothermal gravimetric analysis (IGA). Figure 7 presents typical TGA traces of cured polyamides 1a', 1d', 2a', 2d' in N_2 and air atmospheres. The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDT_{max}), both in N_2 and air, as well as the anaerobic char yield (Y_c) at 800°C, are listed in Table I. PDT corresponds to the temperature at which a weight loss of 10% was recorded. PDT_{max}

corresponds to the temperature at which the maximum rate of weight loss occurred.

Typical TGA thermograms of uncured polyamides 1a and 2d in N_2 and air are shown in Figure 6. All uncured polyamides started to lose weight at about 150°C and their thermal degradation occurred in multiple steps. Their IDT, PDT, PDT_{max} , and Y_c values were remarkably lower than those of the corresponding cured samples, due to the network structure of the latter.

Cured polyamides were stable up to 310–322°C in N_2 or air. They afforded anaerobic char yield of 57–69% at 800°C. Their thermal stabilities were not influenced significantly by the structure of the aromatic diamine utilized for the synthesis. However, polyamides 1c' and 2c', derived from 4,4'-diaminodiphenylsulphone, were less thermally stable, showing lower IDT value in most cases. Polyamides 2a'–2d', containing cyclohexanone rings, seemed to be more heat-resistant than the corresponding polyamides 1a'–1d' bearing styrylpyridine segments, since they showed higher IDT.

By examining the IDT, the relative order of thermal stability of polyamides 2a'–2d' with respect to the diamine utilized for preparation, was

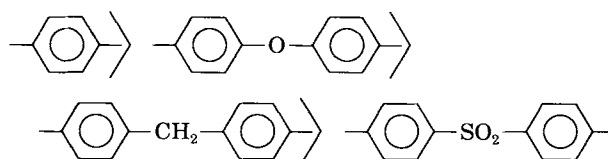


Table I Thermal Stabilities of Cured Polyamides

Sample	N_2				Air		
	IDT ^a (°C)	PDT ^b (°C)	$\text{PDT}_{\text{max}}^{\text{c}}$ (°C)	Y_c^{d} (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)
1a'	311	480	512	68	310	406	471
1b'	313	489	508	69	313	435	478
1c'	310	465	498	62	310	432	512
1d'	311	467	508	67	310	421	471
2a'	317	498	653	59	316	456	508
2b'	319	500	664	62	317	457	535
2c'	316	479	508	57	315	454	498
2d'	322	502	657	64	321	458	499

^a Initial decomposition temperature.

^b Polymer decomposition temperature.

^c Maximum polymer decomposition temperature.

^d Char yield at 800°C.

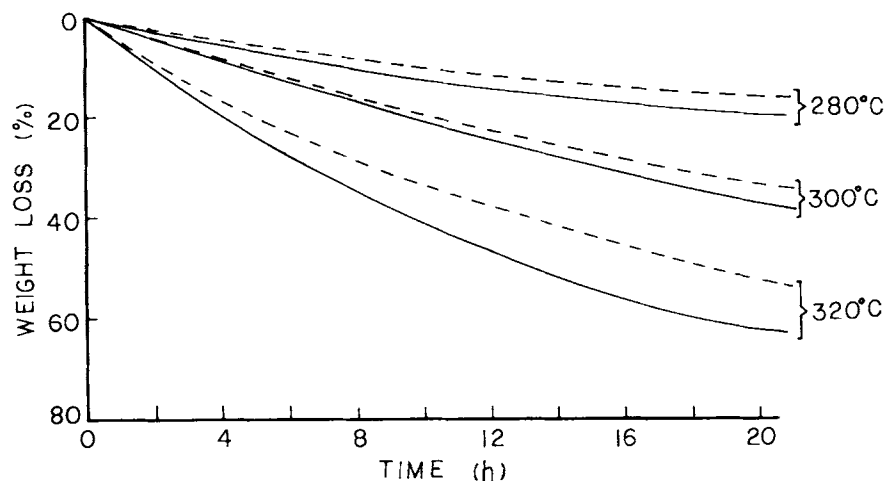


Figure 8 IGA traces of cured polyamides 1b' (—) and 2d' (----) in static air at 280, 300, and 320°C.

However, this order of thermal stability was not followed in the case of polyamides 1a'–1d'.

Thermal stabilities of two typical cured polyamides, 1b' and 2d', were ascertained also by IGA. Figure 8 presents their IGA traces at 280, 300, and 320°C. After isothermal aging at these temperatures for 20 h, polyamide 1b' displayed a weight loss of 19.8, 37.3, and 62.3%, respectively. Similarly, polyamide 2d' showed a weight loss of 16.0, 33.3, and 52.7%, respectively. It is seen that polyamide 2d' was more thermostable than polyamide 1b'. Both polymers were severely degraded above 300°C under these conditions.

Both series of the synthesized unsaturated polyamides can be used as matrix resins for composites. They are new, tractable polyamides that can be subsequently crosslinked upon curing through their olefinic bonds without the evolution of volatile by-products to yield heat-resistant resins.

CONCLUSIONS

1. The unsaturated dicarboxylic acids, DCSP and BCBC, were prepared by condensing 4-carboxybenzaldehyde with 2,6-dimethylpyridine or cyclohexanone, respectively. They reacted with various aromatic diamines, utilizing the phosphorylation method, to afford heat-curable polyamides.
2. The spectral data of polyamides were in agreement with those of the corresponding model diamides, SDA and CDA, prepared

from the condensation of aniline with DCSP and BCBC, respectively.

3. Polyamides were soluble in polar aprotic solvents, but became insoluble upon heat-curing due to crosslinking through their olefinic bonds.
4. The cured polyamides showed high thermal stability, being stable up to 310–322°C and affording an anaerobic char yield of 57–69% at 800°C. They can be used as matrix resins for composites.

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