

# Polyamides Containing Olefinic Bonds

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## SYNOPSIS

The reaction of 2,5-dimethylpiperazine with a double molar amount of maleic anhydride afforded a new unsaturated dicarboxylic acid that was characterized by IR and <sup>1</sup>H-NMR spectroscopy. It was condensed with various aromatic diamines by the phosphorylation method to yield polyamides bearing olefinic bonds. They were readily soluble in polar aprotic solvents and certain acids. The DTA traces of polyamides showed exotherms above 250°C attributable to their cross-linking through the olefinic bonds and a partial thermal degradation. Evidence for the cross-linking of polyamides attained during their heat-curing was obtained from the IR spectra of the uncured and cured samples. Thermal stabilities of cured (at 300°C for 15 h) polyamides were evaluated by TGA and isothermal gravimetric analysis. They were stable up to 321–336°C in N<sub>2</sub> or air and afforded an anaerobic char yield of 61–71% at 800°C. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Polyamides are recognized as polymers with many technological applications. However, most of aromatic polyamides are rigid materials of low solubility, high melting temperature, and, therefore, poor processability. The preparation of soluble and tractable polyamides that upon subsequent curing afford thermally stable network resins is of interest.

The unsaturated polyamides and particularly polyamides bearing olefinic bonds possess attractive properties and are used as fibers,<sup>1,2</sup> membranes for reverse osmosis,<sup>3</sup> and resins.<sup>4</sup> Upon heat-curing, they are cross-linked through their double bonds without the evolution of volatile byproducts to yield heat-resistant resins.

The present investigation deals with a new class of unsaturated polyamides. A dicarboxylic acid bearing olefinic bonds was used as starting material for preparing these polyamides. It was synthesized from the reaction of 2,5-dimethylpiperazine with maleic anhydride in a molar ratio of 1 : 2. The preparation of polyamides was accomplished with or without the isolation of dicarboxylic acid. The un-

saturated polyamides yielded by curing thermally stable cross-linked polymers.

Certain unsaturated heat-curable polyamides derived from 2,6-bis(3-aminobenzylidene)cyclohexanone have been synthesized in our laboratory.<sup>5</sup> In addition, we have synthesized unsaturated polyamides from 2,6-bis(4-carboxybenzylidene)cyclohexanone,<sup>6</sup> 2,6-di(4-carboxystyryl)pyridine,<sup>6</sup> and 2,6-di(3-aminostyryl)pyridine.<sup>7</sup> The polyamides obtained from two latter compounds contained styrylpyridine segments. Finally, some aromatic unsaturated polyamides based on fumaric acid have been synthesized.<sup>8–12</sup>

## EXPERIMENTAL

### Instrumentation

Melting points were determined on an electrothermal melting-point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 710B spectrometer with KBr pellets. <sup>1</sup>H-NMR spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts ( $\delta$ ) are given in ppm with tetramethylsilane as an internal standard. The inherent viscosities of polyamides were determined for solutions of 0.5 g/100 mL in H<sub>2</sub>SO<sub>4</sub> 98% or *N,N*-dimethylformamide (DMF) at 30°C

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using an Ubbelohde suspended level viscometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a DuPont 990 thermal analyzer system. DTA measurements were made using a high-temperature (1200°C) cell in N<sub>2</sub> atmosphere at a flow rate of 60 cm<sup>3</sup>/min. Dynamic TGA measurements were made at a heating rate of 20°C/min.

### Reagents and Solvents

2,5-Dimethylpiperazine (a mixture of *cis* and *trans* isomers) was recrystallized from acetonitrile. Maleic anhydride was recrystallized from acetic anhydride. 4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylether, and 4,4'-diaminodiphenylsulfone were recrystallized from benzene, acetonitrile, and methanol, respectively. 1,4-Phenylenediamine was sublimed at about 110°C under vacuum (2–3 mm). Triphenyl phosphite (TPP), pyridine (Py), and triethylamine were purified by distillation. *N,N*-Dimethylformamide (DMF) and 1-methyl-2-pyrrolidone (NMP) were dried by distillation under reduced pressure over calcium hydride.

### Preparation of Starting Material DCA

A flask equipped with magnetic stirrer and dropping funnel was charged with a mixture of 2,5-dimethylpiperazine (3.4257 g, 30.0 mmol) and acetonitrile (80 mL). The mixture was stirred and heated at about 50°C to obtain a solution that was subsequently cooled at room temperature. Maleic anhydride (5.8836 g, 60.0 mmol) dissolved in acetonitrile (30 mL) was added dropwise to the vigorously stirred solution at ambient temperature under N<sub>2</sub>. An exothermic reaction was observed and stirring of the mixture at ambient temperature was continued for 2 h in a stream of N<sub>2</sub>. The precipitated solid was filtered off, washed with acetone, and dried to afford DCA as a white solid in 70% yield (6.50 g). A purified sample was obtained by recrystallization from 60% ethanol.

### Preparation of Polyamides

As a typical example, the preparation of polyamide **1a** utilizing two methods is given.

#### **Method A: Polycondensation of Isolated DCA with Diamine**

A flask equipped with magnetic stirrer and condenser was charged with a mixture of DCA (0.9309

g, 3.0 mmol), 4,4'-diaminodiphenylmethane (0.5948 g, 3.0 mmol), triphenyl phosphite (1.8617 g, 6.0 mmol), pyridine (3 mL), lithium chloride (1.0 g), and NMP (15 mL). The mixture was stirred and heated at 100°C for 3 h under N<sub>2</sub>. The viscous reaction mixture was poured into water and stirred at room temperature for 1 h. Polyamide **1a** was obtained as a light brown solid that was filtered off. It was chopped up in a home blender, washed with water, extracted with refluxing acetone, and dried (1.16 g, yield 82%).

#### **Method B: Polycondensation of Nonisolated DCA with Diamine**

A flask equipped with a magnetic stirrer was charged with a solution of 2,5-dimethylpiperazine (0.5709 g, 5.0 mmol) in DMF (25 mL). Maleic anhydride (0.9806 g, 10.0 mmol) was added portionwise to the stirred solution at ambient temperature under N<sub>2</sub>. An exothermic reaction was observed and the mixture was stirred at room temperature in a stream of N<sub>2</sub> for 2 h.

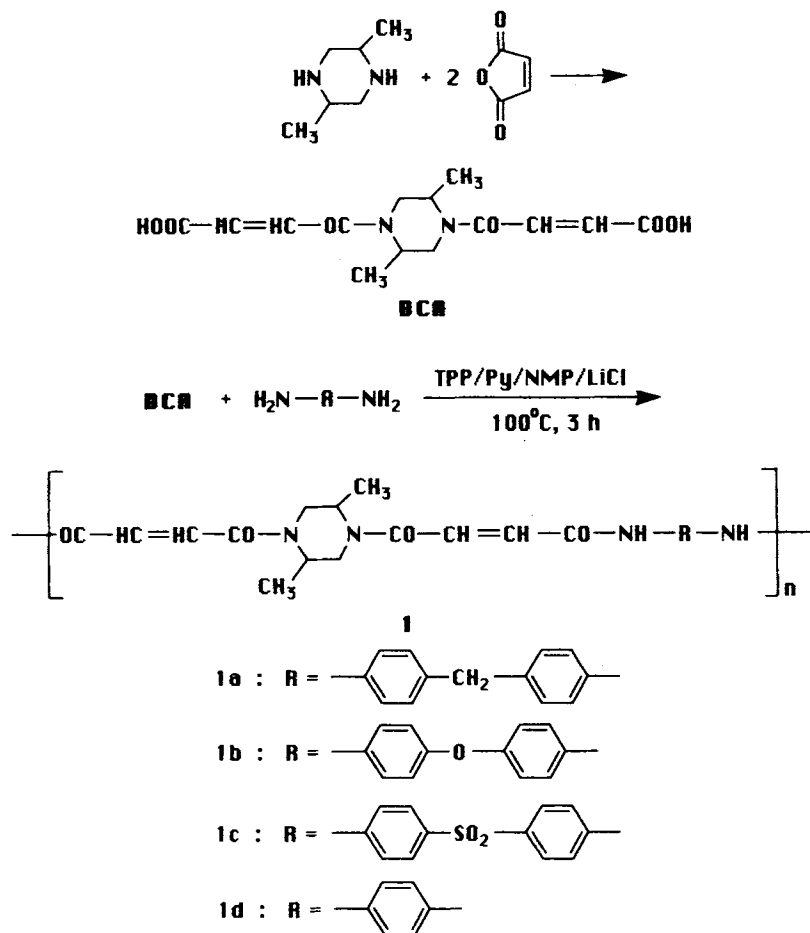
4,4'-Diaminodiphenylmethane (0.9914 g, 5.0 mmol), triphenyl phosphite (3.1029 g, 10.0 mmol), pyridine (4 mL), and lithium chloride (1.5 g) were added to the solution. The mixture was heated at 100°C for 3 h under N<sub>2</sub> and it was subsequently poured into water. Polyamide **1a** was isolated and purified as in method A (2.13 g, yield 90%).

### Curing Procedure of Polyamides

The isolated polyamides **1a–d** were cured by heating into an oven at 300°C for 15 h. Upon curing, the color of polyamides became dark brown.

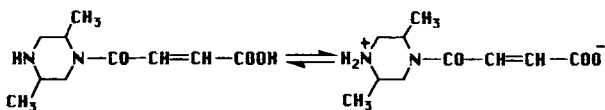
## RESULTS AND DISCUSSION

Scheme 1 outlines the preparation of DCA as well as the unsaturated polyamides **1a–d**. More particularly, DCA was synthesized by reacting 2,5-dimethylpiperazine with a double molar amount of maleic anhydride. The reaction was strongly exothermic and was carried out at ambient temperature in acetonitrile or DMF. It proceeded by a nucleophilic attack of the nitrogen to the carbonyl carbon followed by a proton transfer that stabilized the adduct. The methyl substituents of 2,5-dimethylpiperazine next to nitrogens enhanced significantly the nucleophilicity–basicity of the latter.<sup>13</sup> After the addition of the first maleic anhydride molecule to 2,5-



Scheme 1

dimethylpiperazine, the following dipolar ion structure could arise:



It is reasonable to accept, therefore, that the addition of the second molecule of maleic anhydride to the adduct was slower than the first one.

A literature survey revealed that DCA has not previously been synthesized. It was characterized by IR and  $^1\text{H-NMR}$  spectroscopy (Fig. 1). The IR spectrum of DCA showed characteristic absorption bands at 3150–2900 (O—H stretching); 1723 (N—C—H); 1630 (carboxylic C=O); 1607 (CH=CH and aromatic); and 1463 and 1410 (C—O and O—H deformation). The  $^1\text{H-NMR}$  spectrum of DCA in  $\text{D}_2\text{O}$  solution displayed multiplet peaks at 7.00–6.30 (4H, olefinic), 4.15–3.27 (6H, piperazine ring), and 1.35  $\delta$  (6H,  $\text{CH}_3$ ). The carboxylic protons of DCA showed a broad peak at

9.08  $\delta$  in the  $^1\text{H-NMR}$  spectrum of this compound in  $\text{DMSO-}d_6$  solution. They were exchangeable with  $\text{D}_2\text{O}$ .

DCA was used as starting material for preparing unsaturated polyamides **1a–d** (Scheme 1). They were prepared from the reactions of DCA with various aromatic diamines by the phosphorylation method.<sup>14–16</sup>

The polyamides showed a relatively low degree of polymerization since their inherent viscosities ranged from 0.26 to 0.30 dL/g (Table I). It is known<sup>17</sup> that the polycondensation method affords polyamides of low or moderate molecular weight. Higher molecular weight polyamides could be obtained from the dichloride of DCA. However, the synthesis of the latter by reacting DCA with thionyl chloride was not undertaken because the evolved hydrogen chloride could be added to the olefinic bonds under the strong experimental conditions.

Polyamides **1a–d** were alternatively prepared by polycondensation of nonisolated DCA with diamines (see Experimental section). More particularly, 2,5-

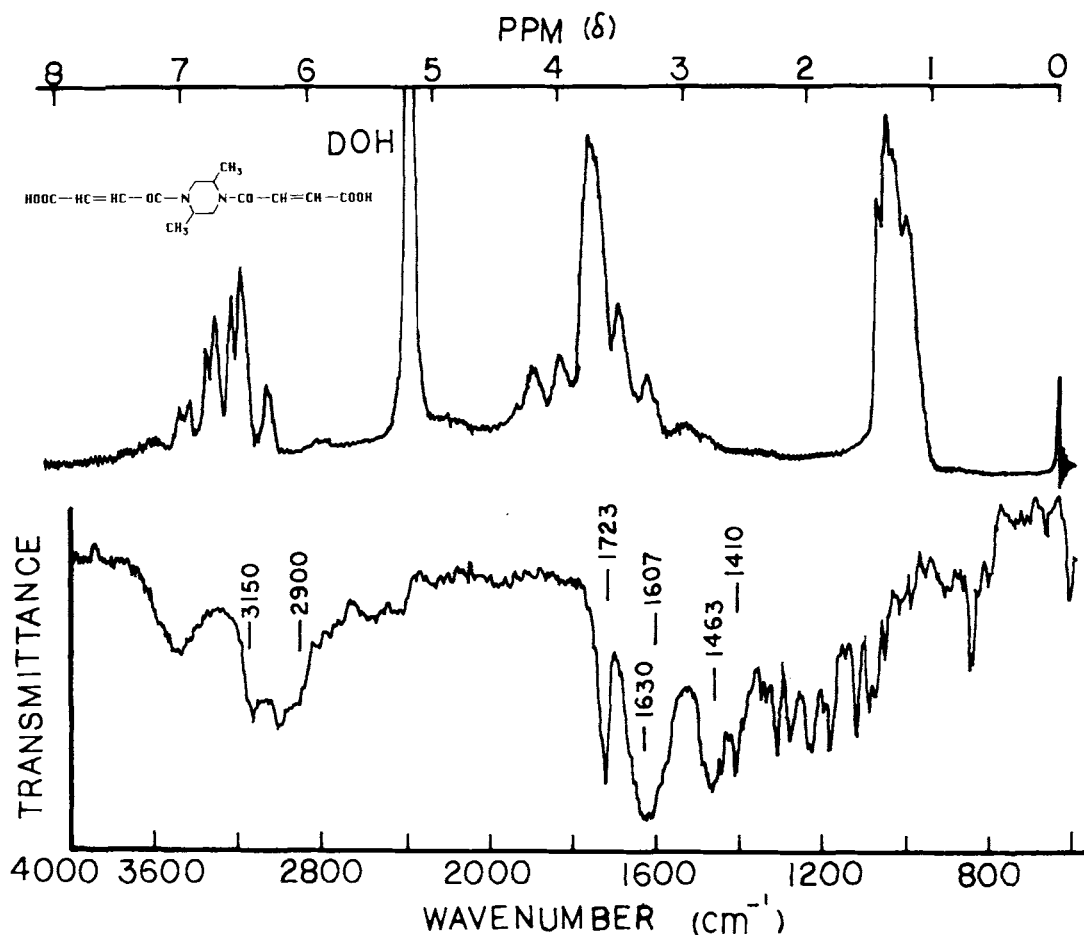


Figure 1 IR and  $^1\text{H}$ -NMR spectrum in  $\text{D}_2\text{O}$  solution of DCA.

dimethylpiperazine reacted with a double molar amount of maleic anhydride and the solution of DCA thus prepared reacted subsequently with diamines. The polyamides obtained by this method showed

slightly lower inherent viscosities and almost identical physical, chemical, and thermal properties as compared with those prepared from isolated DCA.

In addition, a reference polyamide bearing olefinic

Table I Thermal Stabilities of Cured Resins and Inherent Viscosities of the Uncured Samples

Sample	$n_{inh}$ (dL/g)	$\text{N}_2$				Air		
		IDT <sup>a</sup> (°C)	PDT <sup>b</sup> (°C)	PDT <sub>max</sub> <sup>c</sup> (°C)	$Y_c$ <sup>d</sup> (%)	IDT (°C)	PDT (°C)	PDT <sub>max</sub> (°C)
1a'	0.28 <sup>e</sup>	330	471	433	71	325	452	519
1b'	0.26 <sup>e</sup>	325	508	560	61	321	467	530
1c'	0.30 <sup>e</sup>	329	478	519	62	325	437	471
1d'	0.27 <sup>e</sup>	336	493	517	66	333	452	498
2'	0.35 <sup>f</sup>	359	503	533	42	355	448	470

<sup>a</sup> Initial decomposition temperature.

<sup>b</sup> Polymer decomposition temperature.

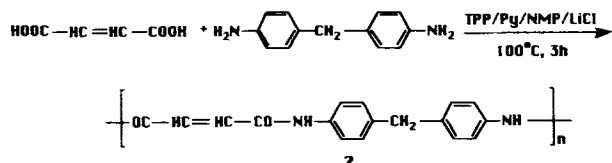
<sup>c</sup> Maximum polymer decomposition temperature.

<sup>d</sup> Char yield at 800°C.

<sup>e</sup> 0.5 g/100 mL in  $N,N$ -dimethylformamide.

<sup>f</sup> 0.5 g/100 mL in  $\text{H}_2\text{SO}_4$  98%.

bonds was synthesized for comparative purposes. Particularly, polyamide **2** was synthesized from the polycondensation of fumaric acid with 4,4'-diaminodiphenylmethane utilizing triphenyl phosphite and pyridine as condensing agents:



Polyamides **1a-d** were readily soluble in polar aprotic solvents such as DMF, NMP, DMSO, and *N,N*-dimethylacetamide as well as in certain acids such as H<sub>2</sub>SO<sub>4</sub> 98% and trichloroacetic acid. They dissolved by moderate heating in *m*-cresol and were insoluble completely in methyl ethyl ketone, acetonitrile, and 1,4-dioxane. Note that the reference polyamide **2** showed remarkably lower solubility since it did not dissolve in polar aprotic solvents and was soluble in warm H<sub>2</sub>SO<sub>4</sub> 98%.

Figure 2 presents a typical IR spectrum of polyamide **1a**. It showed characteristic absorptions at 3270 (N—H stretching); 3070–2910 (CH<sub>2</sub> and CH<sub>3</sub>); 1720 (N—C=O); 1610 (amide C=O,

CH=CH, and aromatic); 1517 (N—H deformation and C—N stretching); and 1306 and 1260 (C—N stretching and N—H bending).

Figure 3 presents the IR spectra of polyamide **1c** as well as the corresponding cured sample **1c'**. Polyamide **1c** displayed the characteristic absorptions of **1a** and, in addition, a strong absorption band at 1140 cm<sup>-1</sup> associated with the SO<sub>2</sub> group.

Curing behavior of polyamides before and after heat-treatment was investigated by DTA. It is believed that the unsaturated polyamides were cross-linked through their olefinic bonds upon curing. The resins obtained by curing polyamides **1a-d** and **2** at 300°C for 15 h are referred to by the designations **1a'-d'** and **2'**, respectively.

Figure 4 presents the DTA traces of polyamides **1b-d** as well as the corresponding cured samples **1b'-d'** in static air. It is seen that both the uncured and cured samples displayed exotherms beyond 250 and 320°C, respectively. The exotherms of the uncured samples above 250°C could be attributed to thermal cross-linking through their olefinic bonds as well as to a partial degradation that was confirmed by TGA. The exotherms of the cured samples were associated exclusively with their pyrolysis.

The cured polyamides became insoluble in sol-

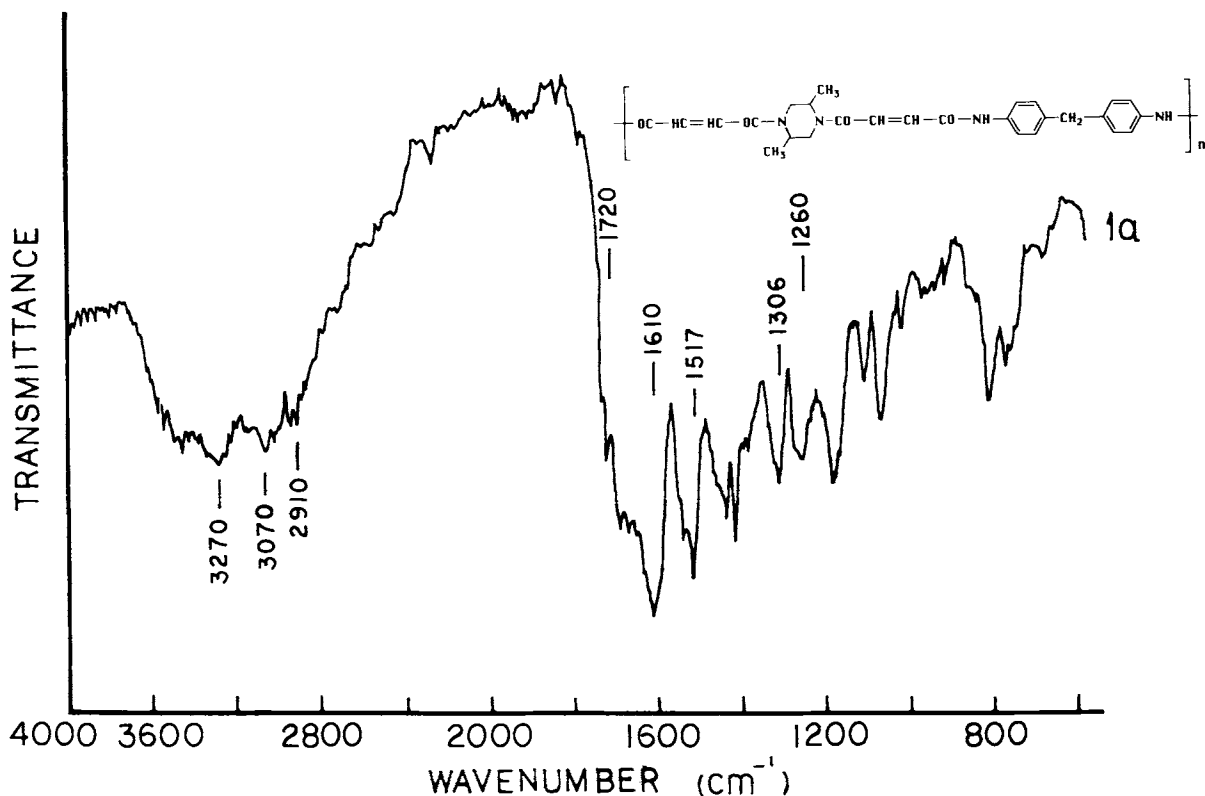


Figure 2 IR spectrum of polyamide **1a**.

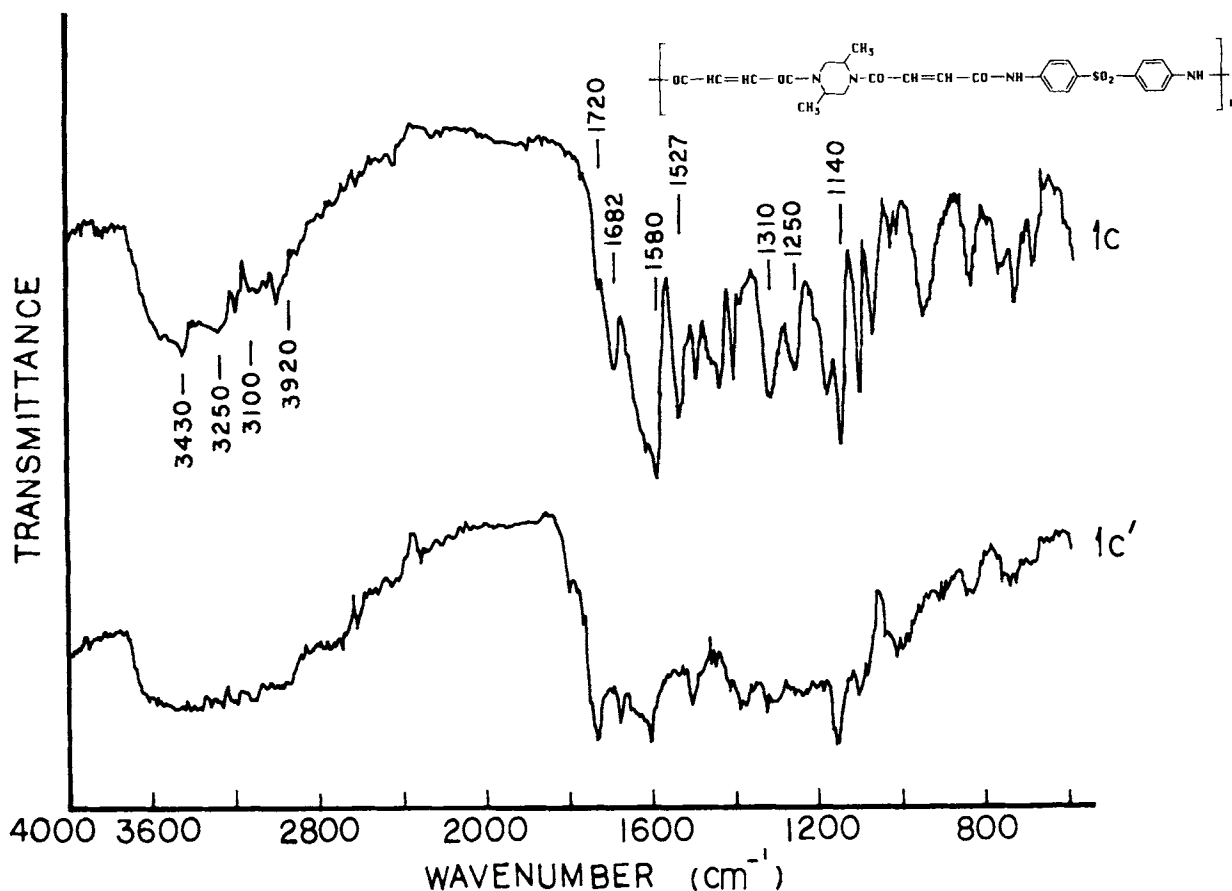


Figure 3 IR spectrum of polyamide 1c (top) as well as the corresponding cured sample 1c' (bottom).

vents for the uncured samples due to their network structure. Evidence for their cross-linking attained during heat-treatment was obtained from IR spectroscopy. Upon comparing the IR spectra of 1c and 1c' (Fig. 3), certain differentiations can result. More particularly, the IR spectrum of cured sample 1c' became broader and showed a significant decrease of the absorption band around  $1600\text{ cm}^{-1}$  assigned to the olefinic bonds. The amide carbonyl and the aromatic structure absorbed also near  $1600\text{ cm}^{-1}$ , and, therefore, this band could not disappear completely. Note that all cured resins were remarkably more heat-resistant than were the corresponding uncured samples due to the cross-linked structure of the former. This behavior conforms with our previous data.<sup>5,6</sup>

Thermal stabilities of cured polyamides were evaluated by TGA and isothermal gravimetric analysis (IGA). Figure 5 presents typical TGA thermograms of cured polyamides 1a' and 1d' in  $\text{N}_2$  and air atmospheres. The initial decomposition temperature (IDT), the polymer decomposition tempera-

ture (PDT), and the maximum polymer decomposition temperature ( $\text{PDT}_{\text{max}}$ ) both in  $\text{N}_2$  and air as well as the anaerobic char yield ( $Y_c$ ) at  $800^\circ\text{C}$  for all cured samples are listed in Table I. PDT was determined for a temperature at which a weight loss of 10% was recorded.  $\text{PDT}_{\text{max}}$  corresponds to the temperature at which the maximum rate of weight loss occurred.

The cured polyamides 1a'–d' were stable up to  $321\text{--}336^\circ\text{C}$  in  $\text{N}_2$  or air and afforded an anaerobic char yield of 61–71% at  $800^\circ\text{C}$ . The cured reference polyamide 2' did not show a weight loss up to  $355\text{--}359^\circ\text{C}$  and afforded an anaerobic char yield of 42% at  $800^\circ\text{C}$ . Thus, the introduction of 2,5-dimethylpiperazine rings in the polymer backbone reduced the IDT and increased considerably the  $Y_c$  values. The chemical structure of the diamine utilized for preparing polymers did not influence significantly the IDT of cured polyamides. However, polyamide 1d' prepared from 1,4-phenylenediamine displayed the highest IDT due to the more rigid structure.

The investigation was extended to include the

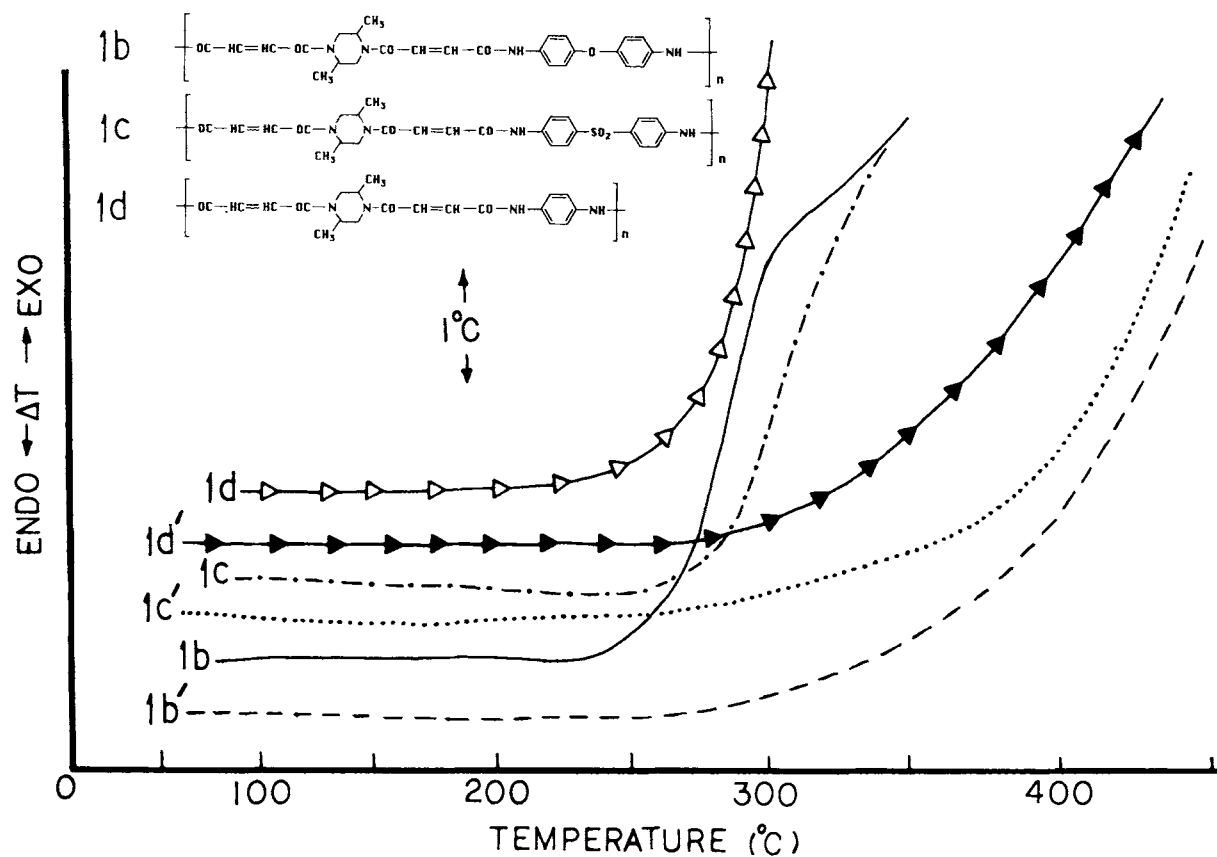


Figure 4 DTA traces of polyamides 1b, 1c, and 1d as well as the corresponding cured samples 1b', 1c', and 1d' in static air. Conditions: heating rate 20°C/min.

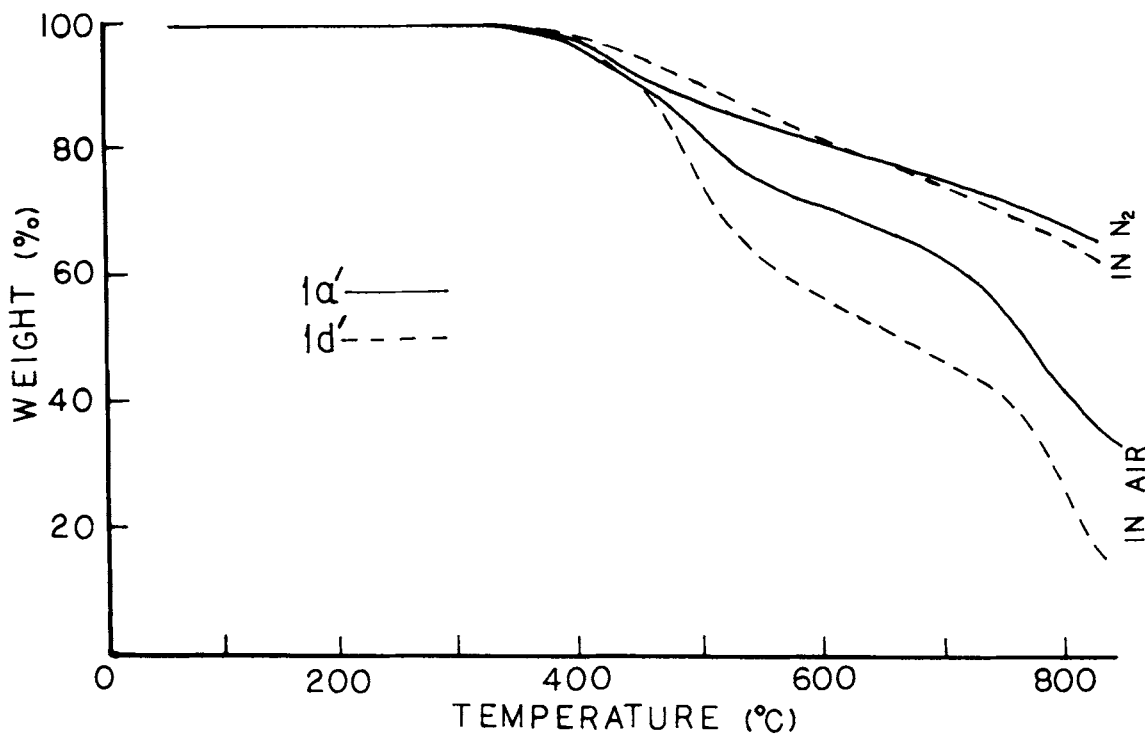


Figure 5 TGA thermograms of cured polyamides 1a' and 1d' in N<sub>2</sub> and air. Conditions: gas flow 60 cm<sup>3</sup>/min; heating rate 20°C/min.

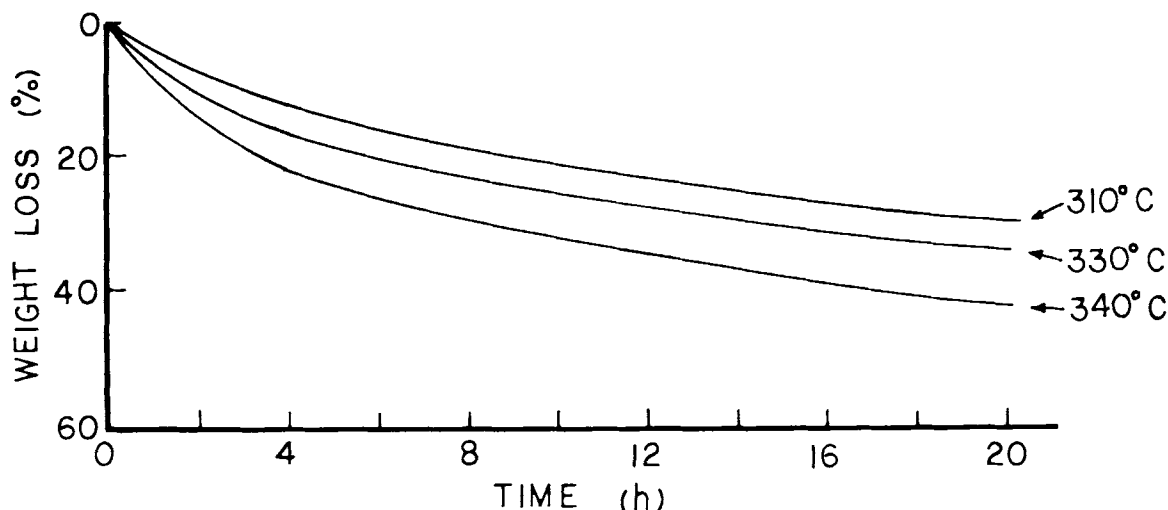


Figure 6 IGA traces in static air of cured polyamide 1a' at 310, 330, 340°C.

evaluation of thermal stability of a typical cured polyamide by IGA. Figure 6 presents the IGA traces in static air of 1a' at 310, 330, and 340°C. After 20 h isothermal aging at these temperatures, polyamide 1a' showed weight losses of 29.3, 33.3, and 42.0%, respectively.

## CONCLUSIONS

1. Unsaturated polyamides were prepared from a dicarboxylic acid obtained from the reaction of 2,5-dimethylpiperazine with a double molar amount of maleic anhydride. Polycondensation by the phosphorylation method was applied with or without isolating the dicarboxylic acid.
2. The polyamides were soluble in DMF, NMP, and other polar aprotic solvents as well as in concentrated  $H_2SO_4$  and  $CCl_3COOH$ .
3. Upon heat-curing, they were cross-linked through their olefinic bonds to yield insoluble thermally stable resins.

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