

# Heat-Resistant Polyimides and Polyamides Prepared from 2,7-Diamino-9-Dicyanomethylene-Fluorene

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## SYNOPSIS

9-Fluorenone was nitrated with fuming nitric acid to yield 2,7-dinitro-fluorenone (1). It was condensed with malononitrile in the presence of glacial acetic acid and a catalytic amount of piperidine to afford 2,7-dinitro-9-dicyanomethylene-fluorene (2). It was catalytically hydrogenated to the corresponding diamine (3). The latter was used as starting material for the preparation of new polyimides and polyamides bearing dicyanomethylene units. In addition, a bismaleimide was synthesized from the reaction of 3 with maleic anhydride and subsequent cyclodehydration of the intermediate bismaleamic acid. The FT-IR spectra of polymers were in agreement with those of the synthesized model compounds. The polymers and bismaleimide yielded crosslinked resins upon curing at 300°C for 40 h in the presence of a catalytic amount of 4,4'-diaminodiphenylmethane. They were stable up to 355–430°C in N<sub>2</sub> or air and afforded anaerobic char yield of 52–57% at 800°C. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Aromatic polyamides and polyimides are known to be remarkably stable polymers.<sup>1</sup> One of the problems in high-temperature polymers is their poor processability caused by low solubility in organic solvents and high melting or softening temperatures. Because of the interest that they have generated, considerable effort has been made in the last few years to modify their chemical structure to change their properties with regard to a specific application or to a particular property.

In early articles, we previously reported on the synthesis, characterization, and curing of polyamides containing enamino nitrile units<sup>2,3</sup> and N-cyano substituted polyamides<sup>4</sup> as well as unsaturated polyamides with pendant cyano groups derived from 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene<sup>5</sup> and 1,4-bis(2-cyano-2-carboxyvinyl)benzene.<sup>6</sup> In addition, we have reported the synthesis of cyano-substituted polyester, polyurethanes, and epoxy resin derived from 2,6-bis(4-hydroxybenzylidene)-1-di-

cyanomethylene-cyclohexane,<sup>7</sup> 1-(2,2-dicyanovinyl)-3,4-dihydroxybenzene,<sup>8</sup> and polyamides and polyimides derived from 2,6-bis(3-aminobenzylidene)-1-dicyanomethylene-cyclohexane.<sup>9</sup>

As a continuation of these studies, this article describes the synthesis and crosslinking of new polyimides and polyamides bearing pendant dicyanomethylene segments. They are expected to present an enhanced solubility in polar aprotic solvents due to the presence of the bulky pendant moieties. In addition, they afford through their cyano groups heat-resistant crosslinked resins by heat-curing without the evolution of volatile by-products. These resins could be used as matrix resins for high-temperature composites.

## EXPERIMENTAL

### Characterization Methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. FT-IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. <sup>1</sup>H-NMR spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts ( $\delta$

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values) are given in parts per million with tetramethylsilane as an internal standard. TGA was performed on a DuPont 990 thermal analyzer system, and dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N<sub>2</sub> or air at a flow rate of 60 cm<sup>3</sup>/min. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 mL in N,N-dimethylformamide at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. The wide X-ray diffractions were obtained for powder specimens on a X-ray PW-1840 Philips 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 was maintained by means of an oversaturated aqueous solution of NaNO<sub>2</sub> at 20°C, and were periodically weighted.

### Reagents and Solvents

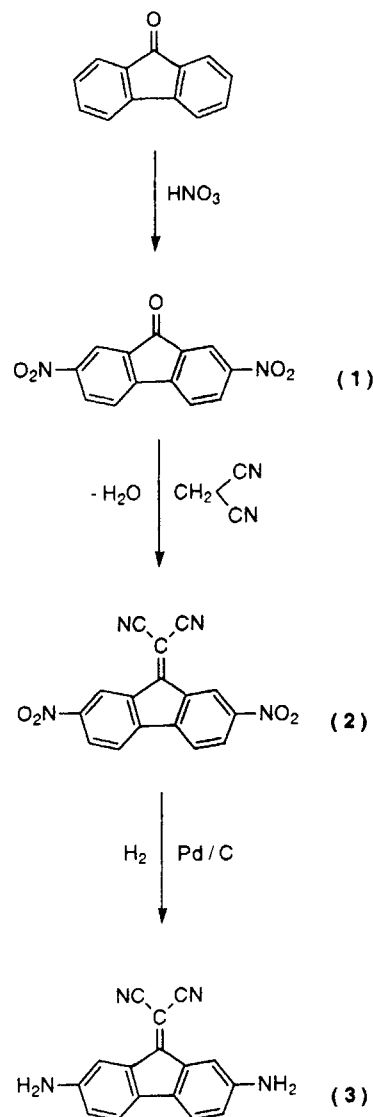
Maleic anhydride, benzophenone tetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and phthalic anhydride were recrystallized from acetic anhydride. Terephthaloyl dichloride was recrystallized from n-hexane. Triethylamine, acetonitrile, and benzoyl chloride were purified by distillation. N,N-dimethylformamide (DMF) was dried by distillation under reduced pressure over calcium hydride. The 9-fluorenone, malononitrile, piperidine, glacial acetic acid, acetic anhydride, and fuming nitric acid were used as supplied.

### Preparation of Starting Material

#### 2,7-Diamino-9-Dicyanomethylene-Fluorene (3) (Scheme 1)

A flask equipped with a condenser and a magnetic stirrer was charged with granular 9-fluorenone (6.0000 g, 33.29 mmol) and cooled in an ice bath. Fuming nitric acid with a density of 1.52 g/cm<sup>3</sup> (30 mL) was added to the flask at 0°C. It was subsequently heated at 95–100°C and the content was refluxed for about 3 h to obtain a clear solution with a reddish-brown color. Upon cooling at ambient temperature, 2,7-dinitrofluorenone (1) was crystallized as a yellow solid. It was filtered off, washed with water, and dried (8.34 g, 92%). A purified sample was obtained by recrystallization from glacial acetic acid (mp 291–294°C, lit.<sup>10</sup> 292–294°C).

ANAL: calcd for: C<sub>13</sub>H<sub>6</sub>N<sub>2</sub>O<sub>5</sub>: C, 57.79%; H,



2.24%; N, 10.37%. Found: C, 57.16%; H, 2.26%; N, 10.21%. IR (KBr) cm<sup>-1</sup>: 1.732 (C=O); 1.607 (aromatic); 1.523, and 1.350 (NO<sub>2</sub>) <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>) δ: 8.38–8.13 (m, 4H, aromatic ortho to NO<sub>2</sub>); 7.41 (m, 2H, other aromatic).

A flask was charged with a solution of 2,7-dinitrofluorenone (1) (8.0000 g, 29.38 mmol) and malononitrile (3.8828 g, 58.77 mmol) in acetonitrile (50 mL). Glacial acetic acid (10 mL) and a catalytic amount of piperidine (c. 2 mL) were added to the stirred solution and the mixture was refluxed for 3 h. It was subsequently concentrated by distillation under reduced pressure and the residue was poured into ice-water. The dark brown solid obtained was filtered off, washed with water, and dried to afford

2,7-dinitro-9-dicyanomethylene-fluorene (2) in 97% yield (9.12 g). It was recrystallized from a mixture of DMF/ethanol 95% (vol ratio 1 : 1) to yield a purified sample with mp 305–307°C.

ANAL: calcd for  $C_{16}H_6N_4O_4$ : C, 60.38%; H, 1.90%; N, 17.61%. Found: C, 59.86%; H, 1.92%; N, 17.54%. IR (KBr)  $cm^{-1}$ : 2,230 (C≡N); 1,617 (exocyclic C=C); 1,586 (aromatic); 1,523 and 1,345 ( $NO_2$ ).  $^1H$ -NMR (DMSO- $d_6$ )  $\delta$ : 8.43–7.96 (m, 4H, aromatic ortho to  $NO_2$ ); 7.40–7.25 (m, 2H, other aromatic).

A hydrogenation flask was charged with a mixture of 2,7-dinitro-9-dicyanomethylene-fluorene (2) (8.5000 g, 26.54 mmol), DMF (50 mL), and a catalytic amount of 10% palladium on activated carbon. The hydrogenation was carried out on a Parr apparatus under a pressure of about 3 atm at ambient temperature until no more hydrogen was taken up (c. 6 h). The catalyst was removed by filtration and the filtrate was poured into water. The brown solid was filtered off, washed with water, and dried to afford 2,7-diamino-9-dicyanomethylene-fluorene (3) in 95% yield (6.60 g). It was recrystallized from a mixture of DMF/water (vol ratio 1 : 1) (mp > 340°C).

ANAL: calcd for  $C_{16}H_{10}N_4$ : C, 74.42%; H, 3.90%; N, 21.70%. Found: C, 73.92%; H, 3.94%; N, 21.51%. IR (KBr)  $cm^{-1}$ : 3,340 (N—H stretching); 2,199 (C≡N); 1,654 (exocyclic C=C); 1,617, (N—H deformation); 1,476 (aromatic).  $^1H$ -NMR (DMSO- $d_6$ )  $\delta$ : 7.37–6.62 (m, 6H, aromatic); 4.94 (b, 4H,  $NH_2$ ).

## Preparation of Model Compounds (Scheme 2)

### Model Diimide 4

A flask was charged with a solution of 3 (1.0000 g, 3.84 mmol) in DMF (10 mL). Phthalic anhydride

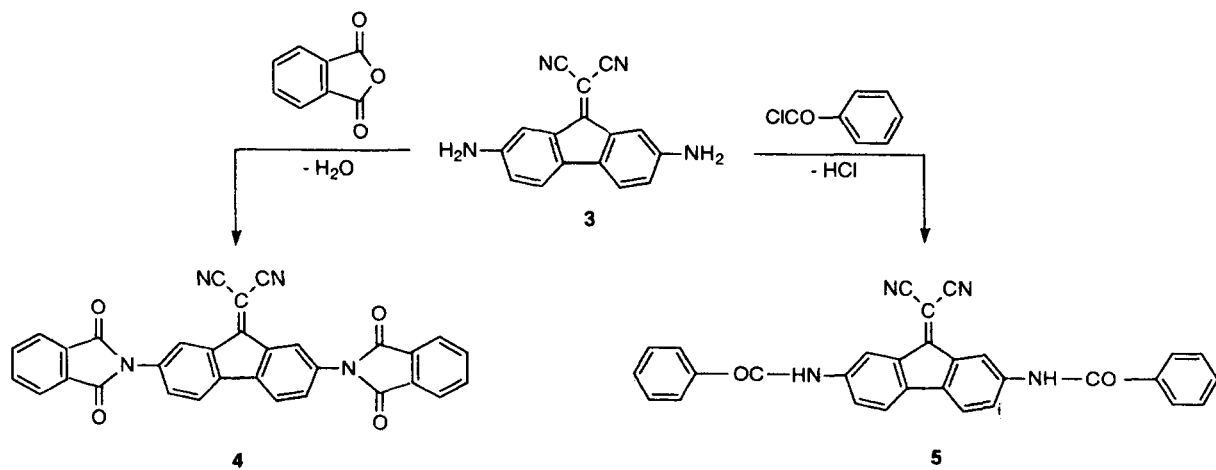
(1.1374 g, 7.68 mmol) was added to the stirred solution at 0°C. The mixture was stirred at ambient temperature for 3 h under  $N_2$ . Acetic anhydride (4 mL) and fused sodium acetate (0.1 g) were added to the mixture, and it was heated at 90°C overnight. It was poured into water and stirred at room temperature for 5 h. The brown solid obtained was filtered off, washed with water, and dried to afford 4 (1.79 g, 90%). It was recrystallized from a mixture of DMF/water (vol ratio 1 : 1) and had mp 230–235°C.

ANAL: calcd for  $C_{32}H_{14}N_4O_4$ : C, 74.13%; H, 2.72%; N, 10.81%. Found: C, 73.71%; H, 2.74%; N, 10.65%. IR (KBr)  $cm^{-1}$ : 2,199 (C≡N); 1,780 and 1,722 (imide C=O); 1,659 (exocyclic C=C); 1,476 (aromatic); 1,376 and 1,083 and 717 (imide structure).  $^1H$ -NMR (DMSO- $d_6$ )  $\delta$ : 8.08–7.95 (m, 8H, aromatic of imide segments); 7.41–6.81 (m, 6H, other aromatic).

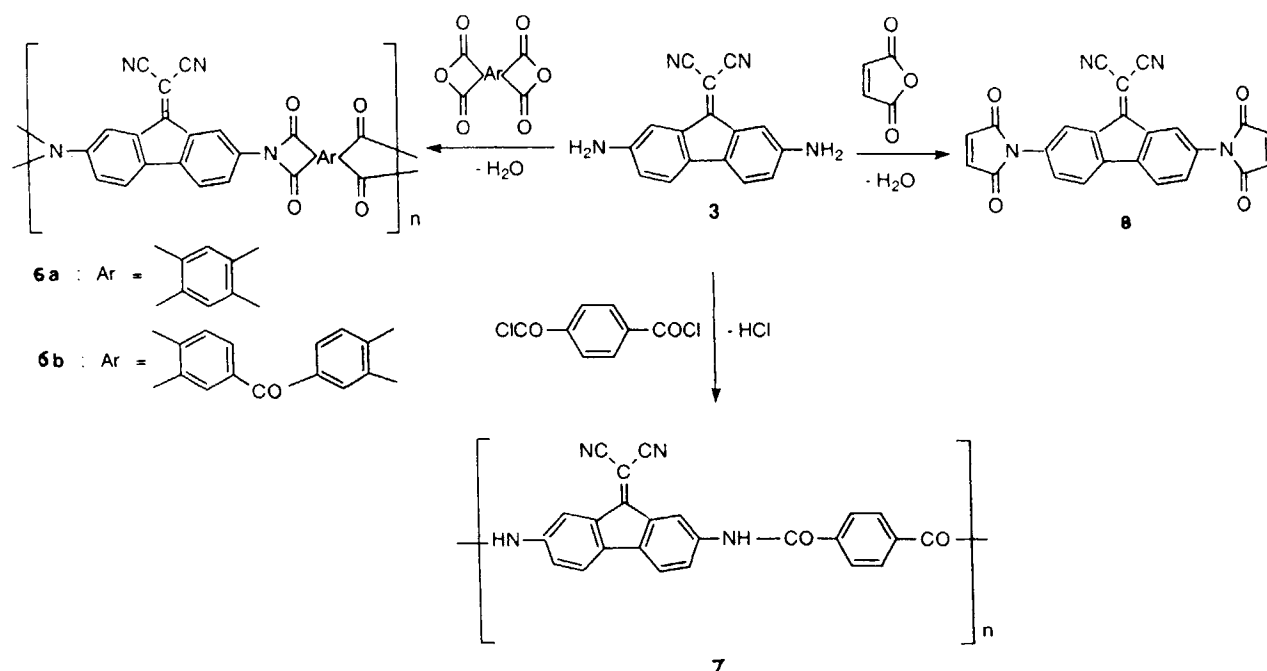
### Model Diamide 5

A flask was charged with a solution of 3 (1.0000 g, 3.84 mmol) in DMF (10 mL). Benzoyl chloride (1.0804 g, 7.68 mmol) diluted with DMF (5 mL) and then triethylamine (0.7772 g, 7.68 mmol) were added portionwise to the stirred solution at 0°C. Stirring of the mixture was continued at room temperature for 3 h under  $N_2$ . It was subsequently poured into water, and the brown solid obtained was filtered off, washed with water, and dried to afford 5 (1.65 g, 92%). A purified sample obtained by recrystallization from a mixture of DMF/water (vol ratio 1 : 2) had mp 210–215°C.

ANAL: calcd for  $C_{30}H_{18}N_4O_2$ : C, 77.26%; H, 3.89%; N, 12.01%. Found: C, 76.78%; H, 3.93%; N, 11.86%. IR (KBr)  $cm^{-1}$ : 3,340 (N—H stretching);



Scheme 2



Scheme 3

2,199 (C≡N); 1,640 (C=O); 1,602 (exocyclic C=C); 1,539 (N—H deformation); 1,471 (aromatic); 1,308 (amide structure). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ: 10.4 (b, 2H, NHCO); 8.01 (m, 4H, aromatic next to C=O); 7.66–6.86 (m, 12H, other aromatic).

#### Preparation of Polymers and Polymer Precursor (Scheme 3)

##### Polyimides 6a and 6b

PMDA (0.9759 g, 3.84 mmol) dissolved in DMF (10 mL) was added dropwise to a stirred solution of 3 (1.0000 g, 3.84 mmol) in DMF at 0°C. Then the mixture was stirred for 3 h under N<sub>2</sub>. Acetic anhydride (5 mL) and fused sodium acetate (0.1 g) were added to the mixture. It was heated at 90°C overnight, and then it was poured into water and stirred at room temperature for 5 h. The brown solid was filtered off, washed with water, and dried to afford polyimide 6a as a brown solid (1.73 g, 94%).

Polyimide 6b was similarly prepared as a brown solid in 95% yield (1.99 g) by reacting 3 (1.0000 g, 3.84 mmol) with BTDA (1.2374 g, 3.84 mmol).

##### Polyamide 7

A flask was charged with a solution of 3 (1.0000 g, 3.84 mmol) in DMF (10 mL). Granular terephthaloyl

dichloride (0.7796 g, 3.84 mmol) and then triethylamine (0.7772 g, 7.68 mmol) were added portionwise to the stirred solution at 0°C. The mixture was stirred at room temperature for 3 h under N<sub>2</sub>. It was subsequently poured into water and the brown solid obtained was filtered off, washed with water, and dried to afford 7 (1.44 g, 96%).

##### Bismaleimide 8

Maleic anhydride (0.7531 g, 7.68 mmol) was added portionwise to a stirred solution of 3 (1.0000 g, 3.84 mmol) in DMF (10 mL) at 0°C. The solution was stirred at ambient temperature for 3 h under N<sub>2</sub>. Acetic anhydride (4 mL) and fused sodium acetate (0.1 g) were added to the solution and it was heated at 90°C overnight. Next, it was poured into water and stirred at room temperature for 5 h. The brown solid obtained was filtered off, washed with water, and dried to afford 8 (1.48 g, 92%). It was recrystallized from a mixture of DMF/water (vol ratio 1 : 2) (mp > 340°C).

ANAL: calcd for C<sub>24</sub>H<sub>10</sub>N<sub>4</sub>O<sub>4</sub>: C, 68.90%; H, 2.41%; N, 13.39%. Found: C, 68.32%; H, 2.46%; N, 13.09%. IR (KBr) cm<sup>-1</sup>: 2,199 (C≡N); 1,774 and 1,717 (imide C=O); 1,654–1,638 (exocyclic and olefinic C=C); 1,471 (aromatic); 1,376 (imide structure). <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>) δ: 7.40–6.75 (m, 6H, aromatic); 6.45–6.36 (m, 4H, olefinic).

### Curing of Polymers and Polymer Precursor

The isolated polymers 6a, 6b, and 7 were mixed with 4,4'-diaminodiphenylmethane (5% by weight) in an aluminum dish, and curing was accomplished by heating the mixture in an oven at 300°C for 40 h.

Bismaleimide 8 was cured at 300°C for 20 h. Then it was powdered and mixed with 4,4'-diaminodiphenylmethane (5% by weight), and the mixture was postcured at 300°C for a further 20 h.

### RESULTS AND DISCUSSION

2,7-Diamino-9-dicyanomethylene-fluorene (3) was utilized as starting material for preparing new polyimides and polyamides bearing pendant dicyano-

methylene units. Scheme 1 outlines the synthesis of 3. In particular, 9-fluorenone was nitrated with fuming nitric acid according to a published method<sup>10</sup> to yield 2,7-dinitrofluorenone (1). It is well-known from the literature that the nitration of 9-fluorenone utilizing fuming nitric acid and concentrated sulfuric acid affords trinitro or tetranitro derivatives.<sup>11,12</sup> Compound 1 was condensed with malononitrile to yield 2,7-dinitro-9-dicyanomethylene-fluorene (2). The reaction was carried out in acetonitrile in the presence of glacial acetic acid and a catalytic amount of piperidine.<sup>13</sup> The water produced should be removed from the reaction mixture to improve the reaction yield. Hydrogenation of 2 to the corresponding diamine 3 was accomplished in DMF using palladium on activated carbon as catalyst. Com-

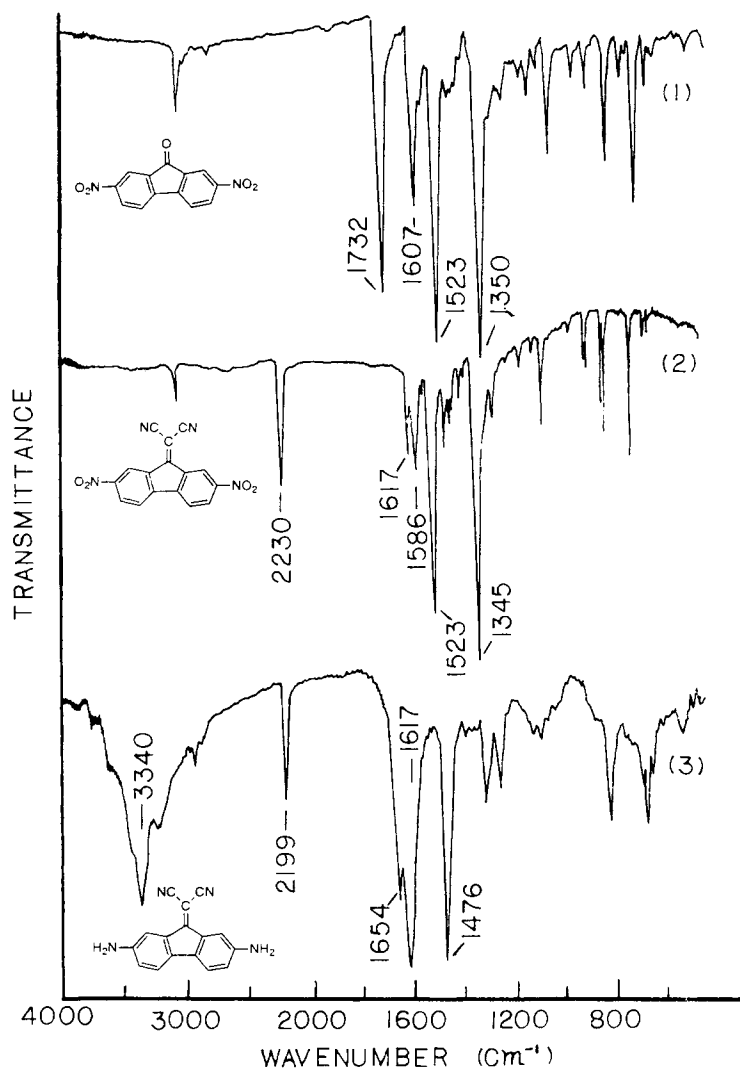


Figure 1 FT-IR spectra of compounds 1, 2, and 3.

pound 3 has been alternatively prepared with Sn and HCl.<sup>13</sup>

Model compounds were synthesized for comparative purposes. In particular, model diimide 4 and diamide 5 were prepared from the reactions of 3 with phthalic anhydride and benzoyl chloride, respectively (Scheme 2). They were prepared under the same experimental conditions used for preparing the respective polymers.

Scheme 3 presents the preparation of polymers as well as polymer precursor. Polyimides 6a and 6b were prepared by reacting 3 with PMDA and BTDA, respectively. The intermediate polyamic acids were cyclodehydrated to the corresponding polyimides using acetic anhydride and fused sodium acetate as catalyst. Bismaleimide 8 was similarly synthesized from the reaction of 3 with maleic anhydride. Polyamide 7 was prepared by reacting 3 with terephthaloyl dichloride in the presence of triethylamine as acid acceptor.

The monomers were characterized by elemental analyses as well as FT-IR and <sup>1</sup>H-NMR spectroscopy. Figure 1 presents the FT-IR spectra of compounds 1, 2, and 3. Certain distinctive differences could arise upon comparing the spectra. In particular, compound 1 showed absorption bands at 1,732 (C=O) and 1,523 and 1,350 cm<sup>-1</sup> (NO<sub>2</sub>). Compound 2 displayed absorptions at 2,230 (C≡N);

1,523 and 1,345 cm<sup>-1</sup> (NO<sub>2</sub>) whereas lacks the absorption assigned to the carbonyl group. Diamine 3 exhibited absorption bands at 3,340 (N—H stretching); 2,199 (C≡N); and 1,617 (N—H deformation) whereas lacks the absorptions associated with the nitro groups.

The FT-IR spectra of model compounds were in agreement with those of the corresponding polymers. Figure 2 presents the FT-IR spectra of model diimide 4 and polyimide 6a. Both compounds showed characteristic absorptions at 1,780 and 1,722 (imide I); 1,376 or 1,361 (imide II); 1,083 or 1,099 (imide III); and 717 or 727 cm<sup>-1</sup> (imide IV). The imide I band was attributed to the stretching vibrations of two carbonyls that are weakly coupled. The imide II, III, and IV bands were assigned to axial, transverse, and out-of-plane vibrations of cyclic imide structure. Bismaleimide 8 also displayed the absorptions of the imide structure.

Figure 3 presents the FT-IR spectra of model diamide 5 and polyamide 7. They showed characteristic absorption bands around 3,340 (N—H stretching); 1,650 (C=O) and 1,539 cm<sup>-1</sup> (N—H deformation). Note that all polymers displayed an absorption near 2,200 cm<sup>-1</sup> assigned to the cyano groups.

The wide X-ray diffractions for powder specimens were obtained for the synthesized polymers. Figure

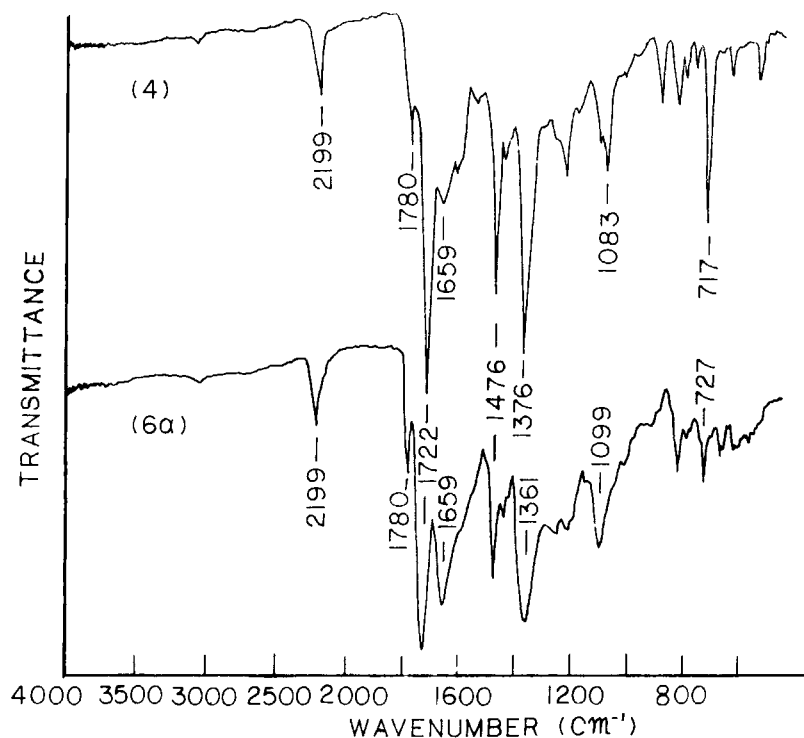


Figure 2 FT-IR spectra of model diimide 4 and polyimide 6a.

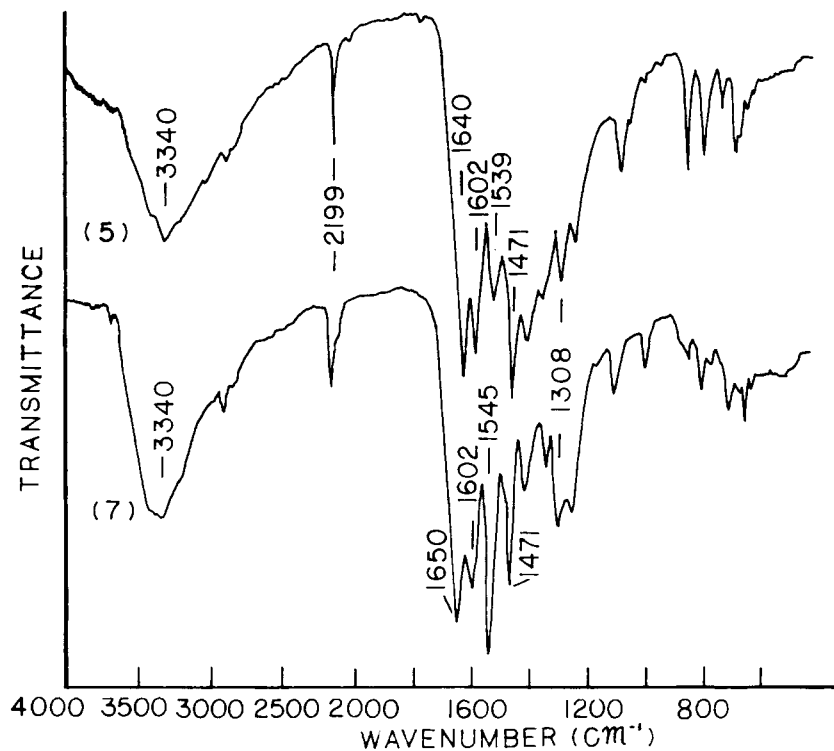


Figure 3 FT-IR spectra of model diamide 5 and polyamide 7.

4 presents typical X-ray diffractograms of polyimide 6b and polyamide 7 which showed amorphous pattern.

The equilibrium water absorption of two representative polymers was determined. Figure 5 pre-

sents the isothermal moisture absorption (%) versus the time exposed for polyimide 6b and polyamide 7. The latter showed higher moisture absorption due to the presence of the NHCO groups.<sup>14</sup>

Since polyimides 6a and 6b were insoluble in polar

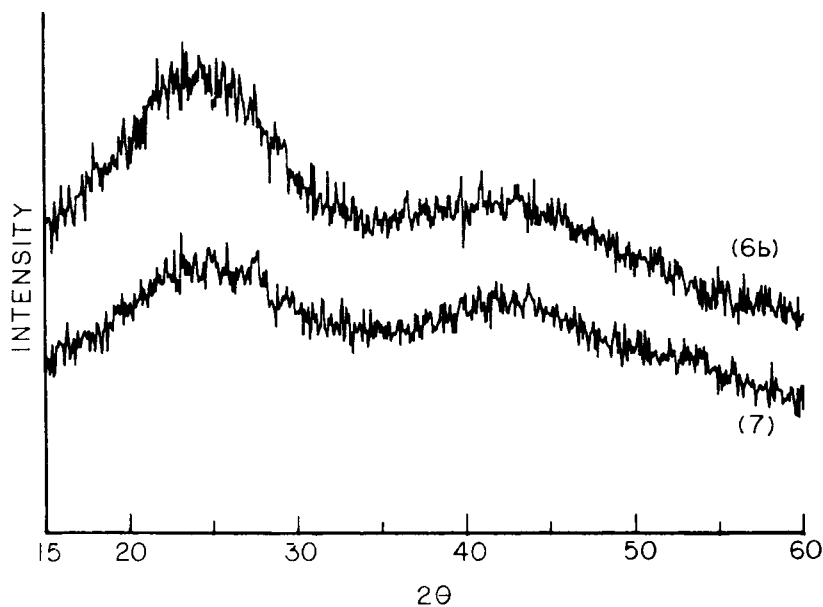


Figure 4 X-ray diffraction patterns of polyimide 6b and polyamide 7.

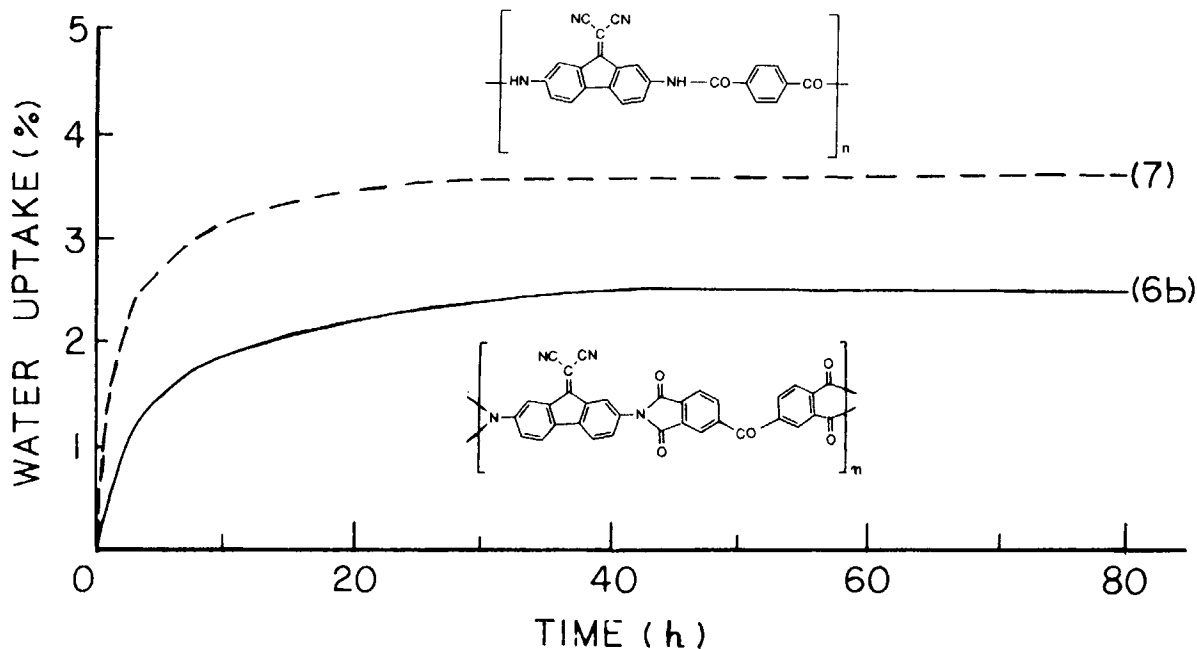


Figure 5 Water absorption (%) vs. time for polyimide 6b and polyamide 7.

aprotic solvents, the inherent viscosities ( $n_{inh}$ ) of the corresponding polyamic acids in DMF solution were determined. They were 0.17 and 0.18 dL/g respectively. The  $n_{inh}$  of polyamide 7 in DMF solution was 0.17 dL/g.

Upon heat-curing, the synthesized polymers and bismaleimide afforded crosslinked resins through their cyano groups as well as the olefinic bonds. To optimize the curing conditions with respect to the thermal stability of the obtained resin, a typical

polymer 7 was heated under various conditions (temperature and time) in the presence or absence of a catalytic amount of 4,4'-diaminodiphenylmethane (DDM). The initial decomposition temperature (IDT) and the char yield ( $Y_c$ ) at 800°C in  $N_2$  of the resulting resins were determined and correlated with the curing conditions (Fig. 6). Since the highest IDT and  $Y_c$  were obtained upon heating at 300°C for 40 h in the presence of DDM (5% by weight), these curing conditions were the optimum.

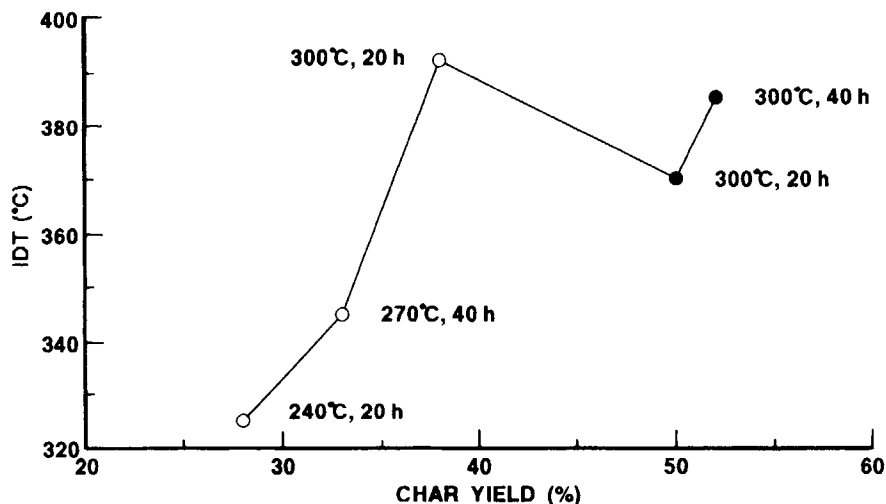
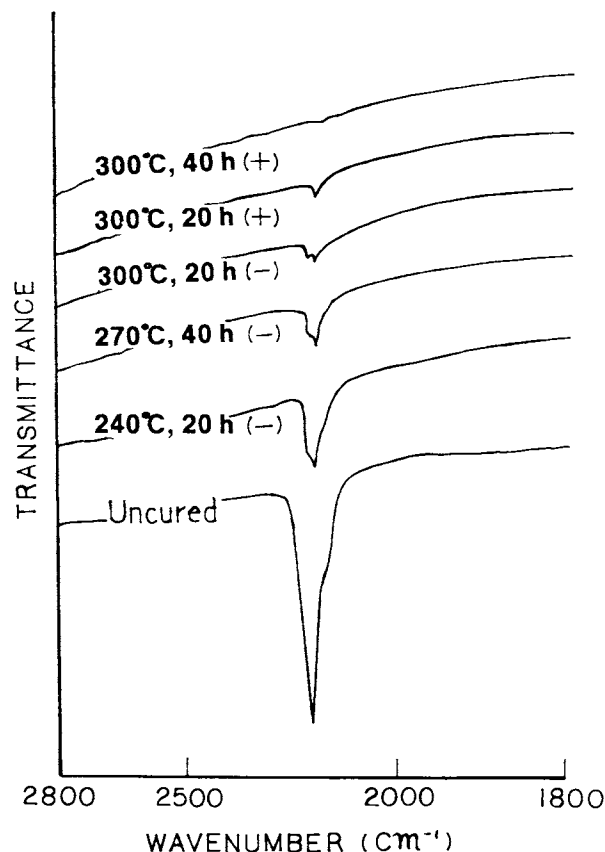


Figure 6 IDT and  $Y_c$  at 800°C in  $N_2$  of polyamide 7 as a function of the curing conditions in the presence (●) or absence (○) of DDM.





**Figure 7** FT-IR spectra of polyamide 7 under various curing conditions in the presence (+) or absence (-) of DDM. All spectra were magnified by the same factor.

Generally, it is well-known that the addition of an aromatic diamine to a cyano-substituted polymer precursor during its heat-curing improves its thermal stability.<sup>15</sup>

Evidence for the network structure of the cured resins was obtained from their FT-IR spectra. They showed a remarkable reduction of the absorption

band around  $2,200\text{ cm}^{-1}$  associated with the cyano groups (Fig. 7). In addition, they became completely insoluble even in concentrated  $\text{H}_2\text{SO}_4$ .

The resins obtained from polymers 6a, 6b, and 7, as well as from bismaleimide 8 by curing at  $300^\circ\text{C}$  for 40 h in the presence of DDM, are referred to by the designations 6a', 6b', 7', and 8', respectively. In the case of bismaleimide 8, DDM was not added at the beginning of heat-curing (see Experimental section) to avoid a Michael-type addition of the aromatic diamine to bismaleimide.

The thermal stabilities of cured resins were evaluated by TGA and isothermal gravimetric analysis (IGA). The IDT, the polymer decomposition temperature (PDT), and the maximum polymer decomposition temperature ( $\text{PDT}_{\text{max}}$ ) both in  $\text{N}_2$  and air, as well as the anaerobic  $Y_c$  at  $800^\circ\text{C}$  for all cured resins, are listed in Table I. The IDT and PDT were determined for a temperature at which 0.5 and 10% weight loss was observed, respectively.  $\text{PDT}_{\text{max}}$  corresponds to the temperature at which the maximum rate of weight loss occurred. Figure 8 presents the TGA traces of cured resins 6b' and 7' in  $\text{N}_2$  and air.

The cured resins were stable up to  $355\text{--}430^\circ\text{C}$  in  $\text{N}_2$  or air, and afforded anaerobic  $Y_c$  of 52–57% at  $800^\circ\text{C}$ . The IDT in air was slightly lower than that in  $\text{N}_2$ .

The relative order of thermal stability of cured resins was ascertained by IGA. Figure 9 presents the IGA traces in static air of 6a' (at  $340^\circ\text{C}$ ), 6b' (at 320, 340, and  $360^\circ\text{C}$ ), 7' (at  $320^\circ\text{C}$ ), and 8' (at  $320^\circ\text{C}$ ). Upon comparing the IGA traces, the relative order of thermal stability was as follows:  $6b' > 6a' > 7' > 8'$ .

It is seen that the remaining weight followed the trend of the IDT determined by dynamic TGA. The TGA and IGA results revealed that polyimides were significantly more thermally stable than polyamide.

**Table I** Thermal Stabilities of Cured Polymers

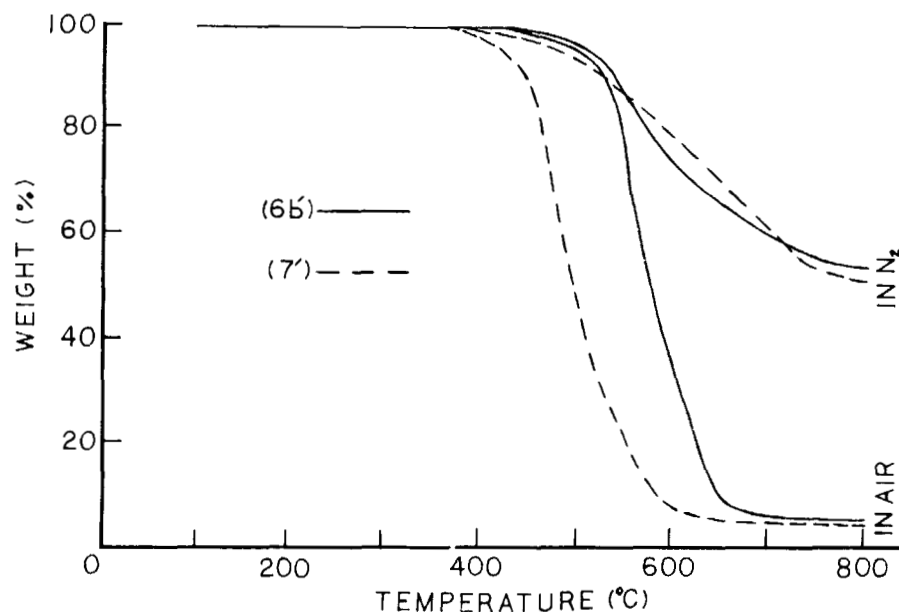
Sample	$\text{N}_2$				Air		
	IDT <sup>a</sup> ( $^\circ\text{C}$ )	PDT <sup>b</sup> ( $^\circ\text{C}$ )	$\text{PDT}_{\text{max}}^{\text{c}}$ ( $^\circ\text{C}$ )	$Y_c^{\text{d}}$ (%)	IDT ( $^\circ\text{C}$ )	PDT ( $^\circ\text{C}$ )	$\text{PDT}_{\text{max}}$ ( $^\circ\text{C}$ )
6a'	415	533	574	57	407	512	533
6b'	430	531	553	55	415	527	552
7'	381	533	535	52	363	450	500
8'	374	523	530	55	355	419	460

<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  $800^\circ\text{C}$ .



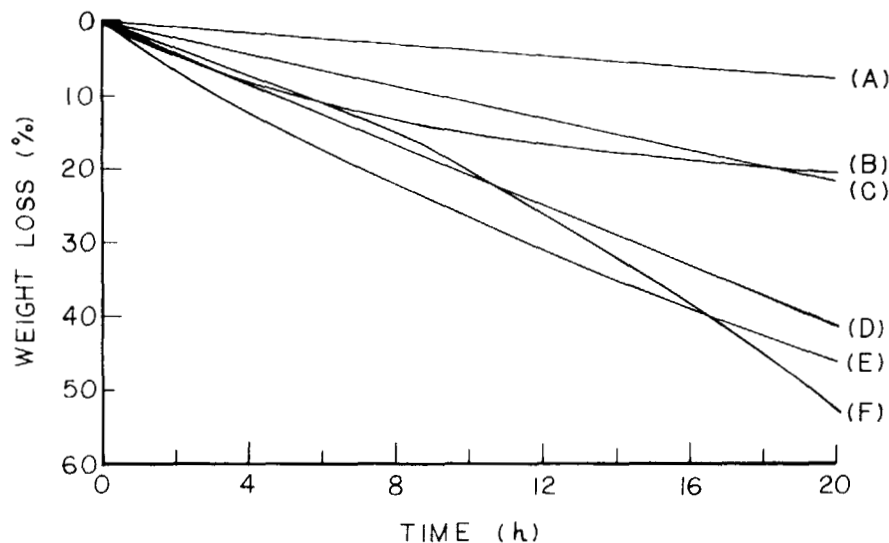
**Figure 8** TGA thermograms of cured polyimide 6b' and polyamide 7' in  $N_2$  and air. Conditions: gas flow,  $60 \text{ cm}^3/\text{min}$ ; heating rate,  $20^\circ\text{C}/\text{min}$ .

Cured polyamide 7' displayed lower IDT in  $N_2$  and air, as well as anaerobic  $Y_c$  at  $800^\circ\text{C}$ , compared with other analogue cyano-substituted polyamides cured under comparable conditions, which were prepared from 1-carboxy-4-(2-cyano-2-carboxyvinyl)benzene<sup>5</sup> and 1,4-bis(2-cyano-2-carboxyvinyl)benzene.<sup>6</sup> However, the cured polymers of the present investigation showed higher IDT in  $N_2$  and air and slightly lower anaerobic  $Y_c$  at  $800^\circ\text{C}$  than

did the cured polyamide and polyimides which were synthesized from 2,6-bis(3-aminobenzylidene)-1-dicyanomethylene-cyclohexane.<sup>7</sup>

## CONCLUSIONS

1. 2,7-Diamino-9-dicyanomethylene-fluorene (3) was used as starting material for the



**Figure 9** IGA traces in static air of cured polymers 6a' at  $340^\circ\text{C}$  (D); 6b' at  $320^\circ\text{C}$  (A),  $340^\circ\text{C}$  (C), and  $360^\circ\text{C}$  (F); 7' at  $320^\circ\text{C}$  (E); and 8' at  $320^\circ\text{C}$  (B).

preparation of a novel class of cyano-substituted polyimides and polyamides.

2. The polyamide was soluble in polar aprotic solvents, whereas polyimides were insoluble in them. The synthesized polymers displayed amorphous X-ray patterns.
3. Polyamide and polyimides, as well as bis-maleimide, yielded crosslinked resins upon curing at 300°C for 40 h in the presence of a catalytic amount of 4,4'-diaminodiphenylmethane. They were stable up to 355–430°C in N<sub>2</sub> or air, and afforded anaerobic char yield of 52–57% at 800°C.

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