Polyamides and Polyimides Prepared from Diaminomaleonitrile and Their Cross-Linking to Thermally Stable Resins

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SYNOPSIS

Unsaturated cyano-substituted polyamide and polyimides were prepared from the reactions of diaminomaleonitrile with terephthaloyl dichloride and tetracarboxylic dianhydrides such as pyromellitic dianhydride and benzophenone tetracarboxylic dianhydride. The polymers were characterized by inherent viscosity measurements, by FTIR and ^{1}H-NMR spectroscopy, as well as by DTA and TGA. They were soluble in polar aprotic solvents and certain strong inorganic and organic acids. Upon curing at 300°C for 70 h, cross-linked polymers were obtained that were stable up to 397–426°C in N_2 or air and afforded anaerobic char yield of 56–61% at 800°C. Their glass transition temperatures as determined by the thermal mechanical analysis (TMA) method were 210–249°C. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Diiminosuccinonitrile[1,2] (DISN) has been formed from the addition of hydrogen cyanide to cyanogen and it is known to undergo self-condensation to afford a tetramer: diaminomaleonitrile[3] (DAMN). The latter can be alternatively prepared by reduction of DISN. A number of polyfunctional heterocyclic dinitriles and diamines, which are new condensation polymer building blocks, have been synthesized utilizing both DISN and DAMN as starting materials. The dinitrile are easily converted to the corresponding dicarboxylic acids. Both the dicarboxylic acids and diamines form heat-resistant polymers with high softening and glass transition temperatures. Two such series of polymers, polyamides from 1,2,5-thiadizole-3,4-dicarbonyl chloride[4] as well as polyamides from 1- and 2-methyl-1,2,3-triazole-4,5-dicarbonyl chloride,[5] have already been described. However, no polymers have been directly prepared from DAMN.

The present investigation is a continuation of our previous publications on the production of new cyano-substituted polyamides and polyimides.[6-13] It deals with the synthesis and characterization of a new series of cross-linkable unsaturated cyano-substituted polyamides and polyimides derived from DAMN. Upon heat-curing, they afford thermally stable cross-linked polymers without the evolution of volatile byproducts. They would be utilized as matrix resins for high-temperature composites.

EXPERIMENTAL

Characterization Methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer with KBr pellets. ^{1}H-NMR 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. DTA and TGA were performed on a DuPont 990 thermal analyzer system. DTA measurements were made using a high-temperature (1200°C) cell at a heating rate of 20°C/min in N_2 atmosphere at a flow rate of 60 cm³/min and with a ΔT sensitivity of 1°C/in. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N_2 or air at a flow rate of 60

cm^3/min. Thermal studies were also carried out in static air with a heating rate of 5°C/min using the thermal mechanical analyzer (TMA) Model 943 attached to a DuPont 2000 thermal analyzer. The inherent viscosities of polyamides were determined for solutions of 0.5 g/100 mL in N,N-dimethylformamide (DMF) at 30°C using an Ubbelohde suspended level viscometer. The wide X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

To determine the equilibrium water absorption, powder samples of polymers were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator where 65% relative humidity (rh) was maintained by means of an oversaturated aqueous solution of NaNO$_2$ at 20°C and were periodically weighed.

Reagents and Solvents

Diaminomaleonitrile (DAMN) and terephthaloyl dichloride were recrystallized from ethanol 95% and n-hexane, respectively. Pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. N,N-Dimethylformamide (DMF) was dried by refluxing and fractionally distilled from CaH$_2$. All reagents and solvents were obtained from Aldrich.

Preparation of Polymers

Polyamide PA

A flask was charged with a mixture of DAMN (1.2972 g, 12.0 mmol), DMF (25 mL), and triethylamine (2.4286 g, 24.0 mmol). Terephthaloyl dichloride (2.4362 g, 12.0 mmol) dissolved in DMF (20 mL) was added dropwise at 0°C under N$_2$. An exothermic reaction was observed and the mixture was subsequently stirred at room temperature in a stream of N$_2$ for 4 h. Then, it was poured into water to precipitate a brown solid that was filtered off, washed with water, and dried to afford polyamide PA (2.00 g, 70%, inherent viscosity 0.35 dL/g in DMF).

Polyimides PIP and PIB

PMDA (1.3087 g, 6.0 mmol) was added portionwise under N$_2$ to a stirred solution of DAMN (0.6486 g, 6.0 mmol) in DMF (20 mL) at 0°C. An exothermic reaction took place and the solution became viscous. Stirring of the mixture was continued at room temperature for 3 h in a stream of N$_2$. The intermediate

polyamic acid was isolated by pouring an aliquot of the reaction solution into water. Upon standing for approximately 8 h, it precipitated as a yellow-brown solid. Cyclodehydration of polyamic acid to the corresponding imide was accomplished by refluxing the remaining solution for about 10 h. Then, it was poured into water. The dark brown solid obtained was filtered off, washed with water, and dried to afford polyimide PIP (1.45 g, overall yield 83%, inherent viscosity 0.56 dL/g).

Polyimide PIB was similarly prepared as a brown solid in 90% yield (2.13 g) by reacting DAMN (0.6486 g, 6.0 mmol) with BTDA (1.9334 g, 6.0 mmol). It had an inherent viscosity of 0.48 dL/g in DMF.

Curing of Polymers

The isolated polymers PA, PIP, and PIB were each placed separately in an aluminum dish and curing was accomplished by heating in static air at 300°C for 70 h.

RESULTS AND DISCUSSION

Unsaturated cyano-substituted polymers were prepared according to the chemical reactions of Scheme 1. More particularly, the reaction of DAMN with terephthaloyl dichloride in the presence of triethylamine afforded polyamide PA. In addition, polyimides PIP and PIB were synthesized by reacting DAMN with PMDA and BTDA, respectively, and subsequent thermal cyclodehydration of the intermediate polyamic acids. The presence of the electron-withdrawing cyano segments next to the amino groups are expected to reduce the nucleophilicity of the latter. However, the reactions occurred at low temperature and the polymers were obtained in satisfactory yields (70–90%).

The polymers were characterized by inherent viscosity (η_{inh}) measurements, FTIR and ^{1}H-NMR spectroscopy, and DTA and TGA as well as by studying their solubility and water absorption behavior. The η_{inh} ranged from 0.35 to 0.56 dL/g, thus indicating a relatively low degree of polymerization. The polyimides displayed higher η_{inh} values than did the polyamide.

Figures 1 and 2 present the FTIR spectra of polyamide PA and polyimide PIP. PA showed characteristic absorption bands at 2978 (N—H stretching); 2210 (C≡N); 1690 (C=O); 1636 (olefinic bond); 1512 (N—H deformation); and 1286 cm^{-1} (C—N stretching and N—H bending). PIP dis-
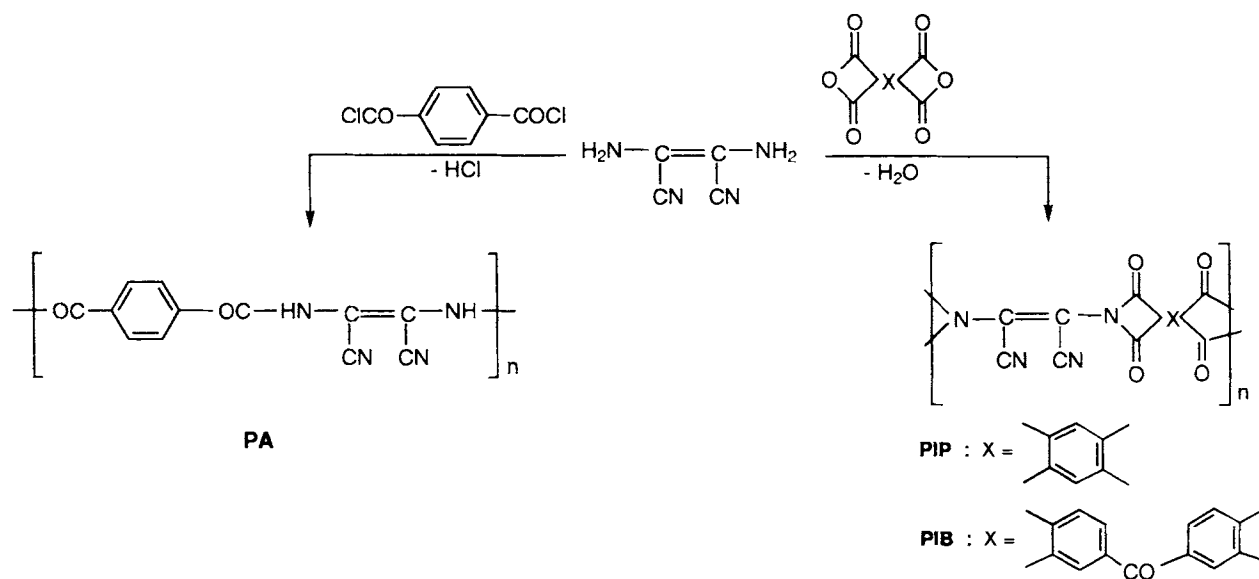
Scheme 1

played absorptions at 2214 (C≡N); 1638 (olefinic bond); 1784, 1732 (imide-I); 1370 (imide-II); 1098 (imide-III); and 726 cm^{-1} (imide-IV). The imide-I band was attributed to the stretching vibrations of the two carbonyls, whereas the imide-II, -III, and -IV bands were assigned to axial, transverse, and out-of-plane vibrations of the cyclic imide structure, respectively.

Figure 1 presents also typical ^{1}H-NMR spectrum of polyamide **PA** in DMSO-d_6 solution. It showed
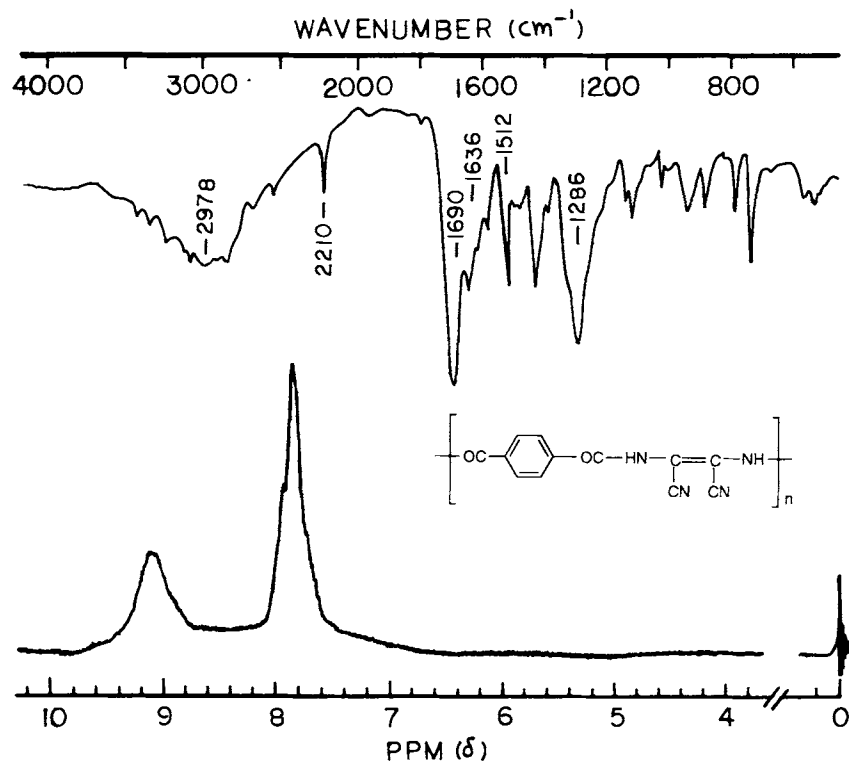
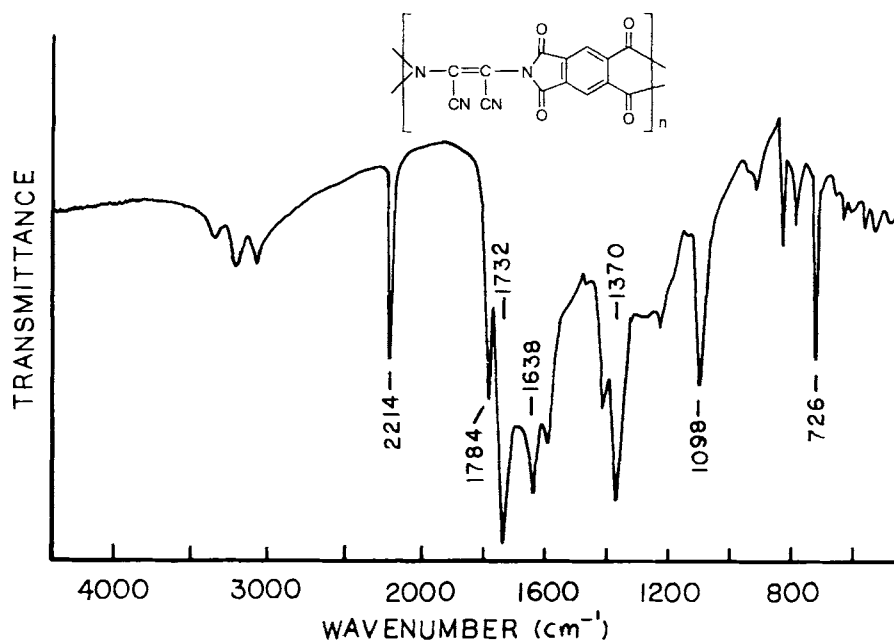**Figure 1**   FTIR and ^{1}H-NMR spectrum of **PA.**

Figure 2 FTIR spectrum of **PIP**.

a broad peak at 9.08 δ (NH) and a multiple peak at 7.87 δ (aromatic protons).

Table I summarizes the solubility behavior of the synthesized polymers. Polyamide **PA** was soluble at ambient temperature in polar aprotic solvents (DMF, NMP), whereas polyimides **PIP** and **PIB** were dissolved in these solvents upon heating. All polymers were readily soluble at room temperature in certain strong inorganic and organic acids (H_2SO_4 98%, CCl_3COOH) and completely insoluble in acetonitrile and 1,4-dioxane.

Figure 3 presents the wide X-ray diffractions for powder specimens of polymers. Polyamide **PA** showed crystalline peaks at 2θ = 18.2, 25.9, and 28.3°, whereas polyimides **PIP** and **PIB** displayed an amorphous pattern.

The equilibrium water absorption of polyamide **PA** was determined. The mol of the absorbed water per amide equivalent weight was 0.12, which cor-

responds to a moisture absorption of 1.81% after an exposed time of 48 h.

Figure 4 presents the TGA and DTA traces in N_2 of polymers. **PA** was stable up to approximately 200°C and lost roughly about 60% of its weight in one step. **PIP** and **PIB** started to lose weight around 170°C and their thermal degradation took place in more than one step. The DTA traces of **PIP, PIB,** and **PA** displayed broad endotherms at 207, 221, and 345°C, respectively, associated with their softening and partial thermal degradation as well. The softening of polymers at these temperatures was confirmed upon gradual heating into a capillary tube.

The polymers were cross-linked through their olefinic bonds as well as through the cyano groups by heating at 300°C in static air. The initial decomposition temperature (IDT) and the char yield (Y_c) at 800°C in N_2 of the resulting resins were considerably affected upon the curing duration. The results

Table I   Solubilities of Polymers[a]

Sample	Solvents[b]						
	DMF	NMP	H_2SO_4 98%	CCl_3COOH	CH_3CN	1,4-Dioxane	Cyclohexanone
PA	++	++	++	++	−	−	+
PIP	+	+	++	++	−	−	−
PIB	+	+	++	++	−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; −, insoluble.
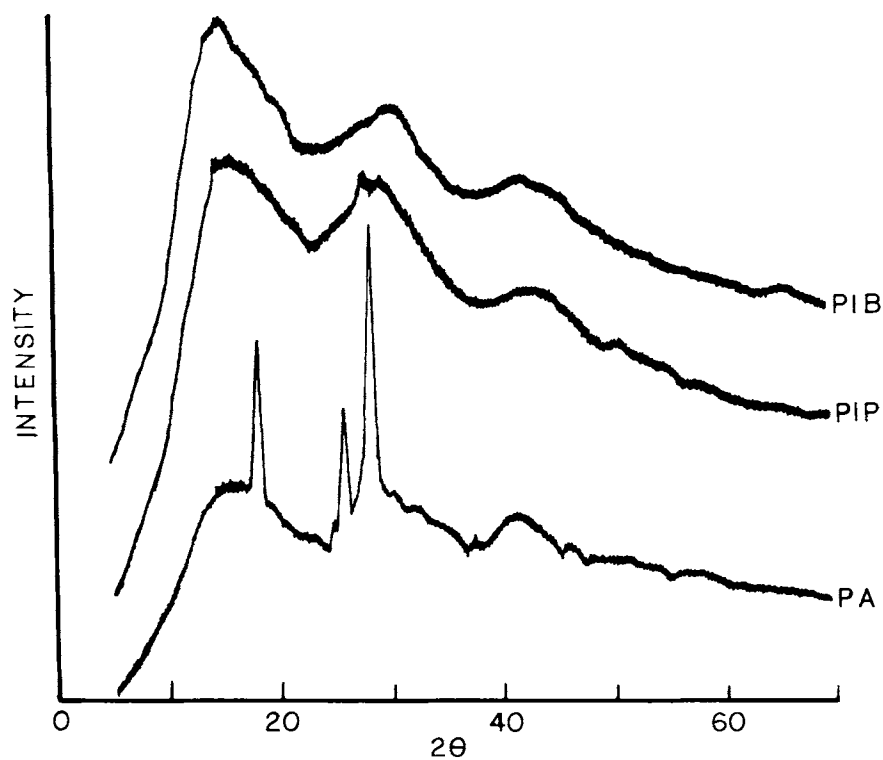[b] DMF, *N,N-dimethylformamide;* NMP, *N*-methylpyrrolidone.

Figure 3 X-ray diffraction patterns of polymers **PA**, **PIP**, and **PIB**.

are shown in Figure 5 for a typical polymer **PIP**. The IDT and Y_c were increased with increasing the curing time up to 70 h and they remained unchanged beyond this time. Therefore, the time of 70 h was the optimum for curing at 300°C.

The cured polymers obtained from **PA, PIP,** and **PIB** by curing at 300°C for 70 h are referred to by the designations **PA′, PIP′,** and **PIB′**, respectively. Figure 6 shows their TGA thermograms in N_2 and air. The IDT, the polymer decomposition temper-
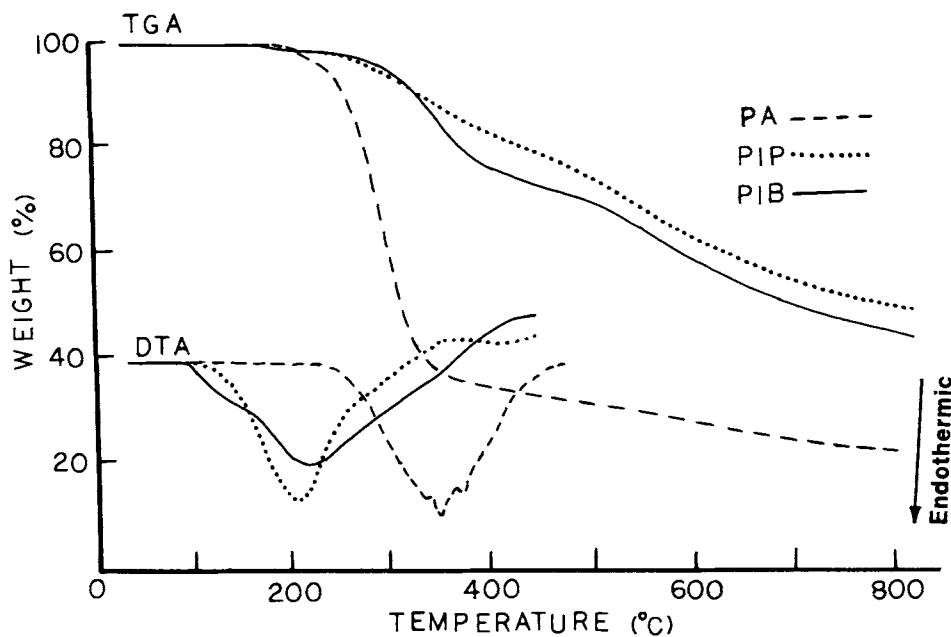

Figure 4 TGA and DTA traces of polymers **PA, PIP,** and **PIB**. Conditions: N_2 flow 60 cm³/min; heating rate 20°C/min.
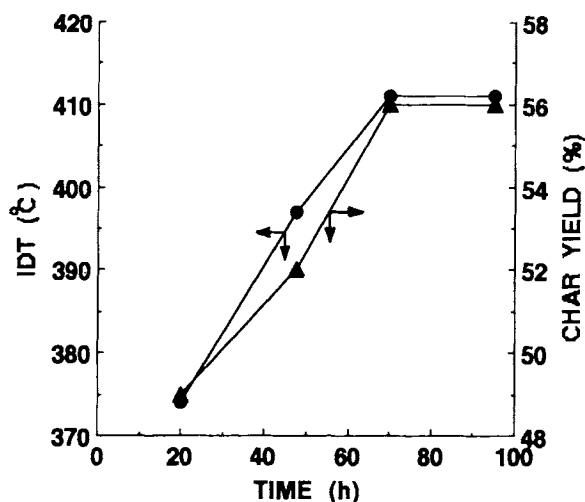
Figure 5 IDT and Y_c at 800°C in N_2 of polymer **PIP** as a function of the curing time at 300°C.

ature (PDT), and the maximum polymer decomposition temperature (PDT$_{max}$) both in N_2 and air are listed in Table II. IDT and 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. Comparing the TGA traces in N_2 of the cured polymers with those of the corresponding uncured samples (Figs. 6 and 4), the remarkably higher thermal stability of the former owing to their network structure is obvious. Specifi-

cally, the cured polymers were stable up to 397–426°C in N_2 and air and afforded an anaerobic char yield of 56–61% at 800°C. The cured polymers of the present investigation compared with other analogous resins obtained from cyano-substituted polyamides and polyimides of our previous publications[6-13] showed somewhat higher IDT values, but their anaerobic char yields at 800°C were slightly lower.

The cured polymers were obtained as dark brown solids and were completely insoluble in solvents for the uncured samples. Their FTIR spectra were broader than those of the corresponding uncured samples and showed a significant reduction of the absorption band around 2200 cm^{-1} assigned to the cyano groups. It is believed that they were consumed through the trimerization reaction forming melamine and isomelamine rings.[14-16] Finally, the glass transition temperatures (T_g's) as determined by the thermal mechanical analysis (TMA) method for the cured polymers **PA'**, **PIP'**, and **PIB'** were 232, 210, and 249°C, respectively (Fig. 7).

CONCLUSIONS

1. Unsaturated cyano-substituted polyamides and polyimides were prepared utilizing diaminomaleonitrile as the starting material.
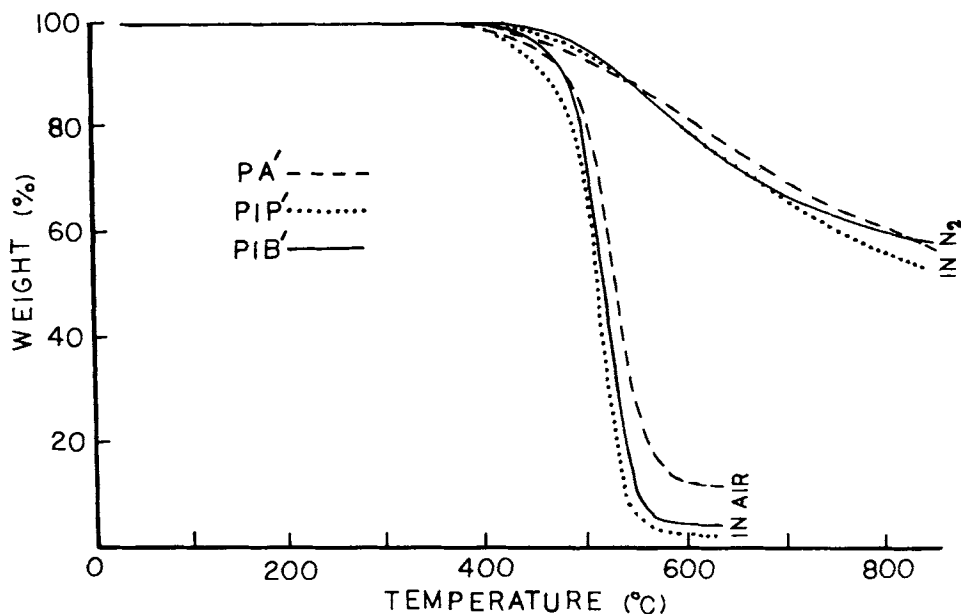2. They were soluble in polar aprotic solvents and certain strong inorganic and organic acids.

Figure 6 TGA thermograms of cured polymers **PA'**, **PIP'**, and **PIB'** in N_2 and air. Conditions: gas flow 60 cm^3/min; heating rate 20°C/min.

Table II   Thermal Stabilities of Cured Polymers

Sample	N₂				Air		
	IDT[a] (°C)	PDT[b] (°C)	PDT$_{max}$[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT$_{max}$ (°C)
PA′	408	545	582	61	397	482	523
PIP′	411	531	552	56	405	460	508
PIB′	426	537	571	61	419	482	512

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

3. The X-ray diffractions of polymers revealed that the polyimides had amorphous patterns, whereas the polyamide displayed some crystalline peaks.
4. The polymers were cross-linked upon curing at 300°C for 70 h. The cured polymers were stable up to 397–426°C in N₂ and air and afforded an anaerobic char yield of 56–61% at 800°C. Their glass transition temperatures were 210–249°C.
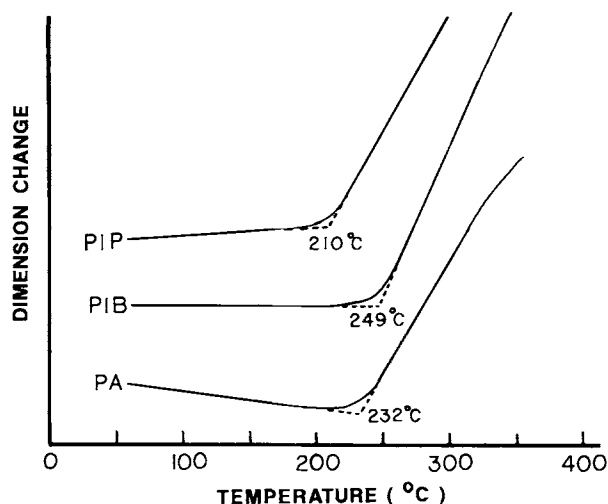

Figure 7 TMA curves of cured polymers **PA′**, **PIP′**, and **PIB′** in static air. Conditions: heating rate 5°C/min.

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