

Synthesis and Characterization of Cyano-Substituted Maleamic Acids and Maleimides and Their Polymerization to Thermally Stable Laminating Resins

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SYNOPSIS

A novel class of cyano-substituted maleimides were prepared and polymerized. Particularly, 4-aminobenzonitrile reacted with maleic or nadic anhydride to yield the amic acid, which was then cyclodehydrated to the corresponding maleimide or nadimide. In addition, the monomaleamic acids prepared from an aromatic diamine reacted with 4-cyanobenzaldehyde to afford maleamic acids that were cyclodehydrated to maleimides. All maleimides and nadimide as well as their intermediate amic acids were characterized by IR and $^1\text{H-NMR}$ spectroscopy. The curing behavior of polymer precursors was investigated by DTA. Upon curing at 240°C for 15 h, network polymers were obtained both by cross-linking through the maleimido olefinic bonds and the trimerization reaction of the cyano groups. They were stable up to $330\text{--}310^\circ\text{C}$ in N_2 or air and afforded anaerobic char yield of 60–40% at 800°C . © 1993 John Wiley & Sons, Inc.

INTRODUCTION

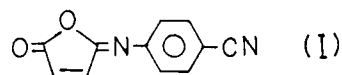
Maleimides are promising prepolymers usable as matrix resins for high-performance composites.¹ They possess high thermal stability along with good processability.

Cyano-disubstituted aromatic compounds are well-known polymer precursors that undergo a cyclotrimerization reaction to form heterocyclic rings.^{2–7} Their polycyclotrimerization reactions afford heat-resistant three-dimensional structures.

The present investigation deals with the synthesis, characterization, and polymerization of new cyano-substituted maleimides as well as their intermediate maleamic acids. They are expected to combine the attractive properties of maleimides and nitriles. In addition, their polymerization reactions are of interest, since they contain two reactive species, i.e., the maleimido and cyano groups. Upon heat curing, the synthesized cyano-substituted maleimides yield thermally stable cross-linked resins without the evolution of volatile byproducts.

The preparation of 4-(*N*-maleimido)benzonitrile

by rearranging the corresponding isoimide (I) in the presence of a hydroxy compound and a tertiary amine has been described in a German patent by Ciba-Geigy⁸:



In a recent publication of the Hitachi Research Laboratory, the thermal behavior and reactivities of the prepolymers prepared from aromatic biscyanamides and a bismaleimide have been studied.⁹

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 710B spectrometer with KBr pellets. $^1\text{H-NMR}$ 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 in N₂ atmosphere at a flow rate of 60 cm³/min. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N₂ or air at a flow rate of 60 cm³/min.

Reagents and Solvents

4-Aminobenzonitrile and 4-cyanobenzaldehyde were recrystallized from a mixture of ether/*n*-hexane in volume ratios 2 : 1 and 1 : 2, respectively. Maleic and nadic anhydride were recrystallized from acetic anhydride and chloroform, respectively. 4,4'-Diaminodiphenylether and 4,4'-diaminodiphenylsulfone were recrystallized from acetonitrile. 4,4'-Diaminodiphenylmethane was recrystallized from toluene. 1,4-Phenylenediamine was sublimed under reduced pressure (2–3 mm). *N,N*-Dimethylformamide (DMF) was dried by refluxing over and fractionally distilling from CaH₂. Analytical-grade acetone was used as supplied.

Preparation of Polymer Precursors 2 and 3

4-(*N*-Maleimido)benzonitrile (2)

Granular maleic anhydride (1.1767 g, 12 mmol) was added portionwise to a stirred solution of 4-aminobenzonitrile (1.4177 g, 12 mmol) in acetone (20 mL) at 0°C under N₂. The mixture was subsequently stirred at ambient temperature in a stream of N₂ for 3 h. The whitish solid precipitated was filtered off, washed with ether, and dried to afford maleamic acid **1** (2.32 g, 89%). A purified sample obtained by recrystallization from acetonitrile had an mp of 191–194°C.

IR (KBr) cm⁻¹: 3330–3040 (NH and carboxylic OH stretching); 2253 (C≡N); 1727 (carboxylic C=O); 1640 (amide C=O); 1610 (C=C); 1560 (NH deformation); 1422, 1338 (C—O stretching).

¹H-NMR (DMSO-*d*₆) δ: 10.63 (b, 2H, COOH and NHCO); 7.58 (bs, 4H, aromatic); 6.17 (s, 2H, olefinic).

A mixture of maleamic acid **1** (1.40 g, 6 mmol), acetone (15 mL), acetic anhydride (4 mL), and fused sodium acetate (0.10 g) was refluxed for 5 h. It was subsequently poured into ice water and stirred at room temperature to hydrolyze excess acetic anhydride. The whitish solid obtained was filtered off, washed with dilute sodium bicarbonate, then with water and dried to afford **2** (1.04 g, 82%). A purified

sample obtained by recrystallization from a mixture of ether/*n*-heptane had an mp of 136–138°C.

IR (KBr) cm⁻¹: 2260 (C≡N); 1786, 1727, 1390, 1160, 700 (imide structure); 1620 (C=C); 1602, 1430 (aromatic).

¹H-NMR (CDCl₃) δ: 7.76 (d, 4H, aromatic); 7.03 (s, 2H, olefinic).

4-(*N*-nadimido)benzonitrile (4)

4-Aminobenzonitrile (1.4177 g, 12 mmol) reacted similarly with nadic anhydride (1.9699 g, 12 mmol) in acetone (20 mL) to yield nadiamic acid **3** as a whitish solid in 65% yield (2.20 g). It was isolated by pouring the reaction solution into ice water. A purified sample obtained by recrystallization from a mixture of acetonitrile/water (vol. ratio 1 : 2) had an mp of 134–137°C.

IR (KBr) cm⁻¹: 3360–3100 (NH and carboxylic OH stretching); 1260 (C≡N); 1725 (carboxylic C=O); 1630 (amide C=O); 1608 (C=C); 1560 (NH deformation); 1427, 1339 (C—O stretching).

¹H-NMR (DMSO-*d*₆) δ: 11.72 (b, 1H, COOH); 10.27 (s, 1H, NHCO); 7.67 (s, 4H, aromatic); 6.10 (bs, 2H, olefinic); 3.27 (m, 4H, aliphatic of nadimide ring); 2.15 and 1.23 (m, 2H, methylene of nadimide bridge).

Cyclodehydration of **3** to **4** was carried out by refluxing for 5 h a mixture of nadiamic acid **3** (1.78 g, 6 mmol), acetone (15 mL), acetic anhydride (5 mL), and fused sodium acetate (0.10 g). The reaction solution was poured into ice water and **4** was obtained as a white solid in 90% yield (1.50 g). It was recrystallized from a mixture of tetrahydrofuran/*n*-heptane (vol. ratio 1 : 1) and had an mp of 169–172°C.

IR (KBr) cm⁻¹: 2250 (C≡N); 1782, 1720, 1387, 1182, 713 (imide structure); 1618 (C=C); 1426 (aromatic).

¹H-NMR (CDCl₃) δ: 7.94–7.40 (m, 4H, aromatic); 6.37 (s, 2H, olefinic); 3.50 (s, 4H, aliphatic of nadimide ring); 2.11 and 1.63 (m, 2H, methylene of nadimide bridge).

Preparation of Maleamic Acids 6a–6d

Maleamic Acid 6a

A flask equipped with magnetic stirrer and dropping funnel was charged with a solution of 4,4'-diaminodiphenylether (1.0012 g, 5 mmol) in DMF (10 mL). To the stirred solution, maleic anhydride (0.4903 g, 5 mmol) dissolved in DMF (10 mL) was added dropwise at 0°C under N₂. Stirring of the mixture was continued at ambient temperature for

3 h in a stream of N₂ to yield a solution of maleamic acid **5a**.

4-Cyanobenzaldehyde (0.6557 g, 5 mmol) was added to the solution of **5a** in DMF and the mixture was heated at 60°C for 10 h. It was subsequently poured into ice water and the yellow-brown solid obtained was filtered off, washed with water, and dried to yield **6a** in 88% overall yield (1.80 g). A purified sample obtained by recrystallization from dimethylsulfoxide had an mp of 108–112°C.

Maleamic Acid **6b**

A solution of maleamic acid **5b** in DMF was similarly prepared by reacting 4,4'-diaminodiphenylmethane (0.9914 g, 5 mmol) with maleic anhydride (0.4903 g, 5 mmol). It reacted subsequently with 4-cyanobenzaldehyde (0.6557 g, 5 mmol) to afford **6b** as a yellow-brown solid in 91% yield (1.86 g). It was recrystallized from a mixture of dimethylsulfoxide/water (vol. ratio 2 : 1) and had an mp of 154–157°C.

Maleamic Acid **6c**

A solution of maleamic acid **5c** in DMF was similarly prepared from the reaction of 4,4'-diaminodiphenylsulfone (1.2416 g, 5 mmol) with maleic anhydride (0.4903 g, 5 mmol). It reacted subsequently with 4-cyanobenzaldehyde (0.6557 g, 5 mmol) to afford **6c** as a pale yellow solid in 81% yield (1.87 g). It was recrystallized from a mixture of dimethylsulfoxide/water (vol. ratio 1 : 1) and had an mp of 168–172°C.

Maleamic Acid **6d**

A solution of maleamic acid **5d** in DMF was similarly prepared by reacting 1,4-phenylenediamine (0.5407 g, 5 mmol) with maleic anhydride (0.4903 g, 5 mmol). It reacted then with 4-cyanobenzaldehyde (0.6557 g, 5 mmol) to afford **6d** as a yellow solid in 83% yield (1.33 g). It was recrystallized from dimethylsulfoxide and had an mp of 226–228°C.

General Procedure for Preparation of Maleimides **7a–7d**

A flask was charged with a mixture of the isolated maleamic acid **6a–6d** (ca. 1 g), acetic anhydride (5 mL), and fused sodium acetate (0.2 g). The reaction solution was stirred and heated at 70°C for 12 h. It was subsequently poured into ice water and stirred to hydrolyze excess acetic anhydride. The brown solid obtained was filtered off, washed with dilute sodium bicarbonate, then with water, and dried in

a vacuum oven at about 50°C to afford maleimides **7a–7d** in nearly quantitative yield. They did not show a clear melting temperature upon gradual heating in a capillary tube.

Cross-linking of Polymer Precursors

The isolated maleimides **2**, **7a–7d**, and nadimide **4** or their intermediate amic acids **1**, **6a–6d**, and **3** were heated in a shallow dish placed into an oven at 240°C for 15 h to yield cross-linked polymers.

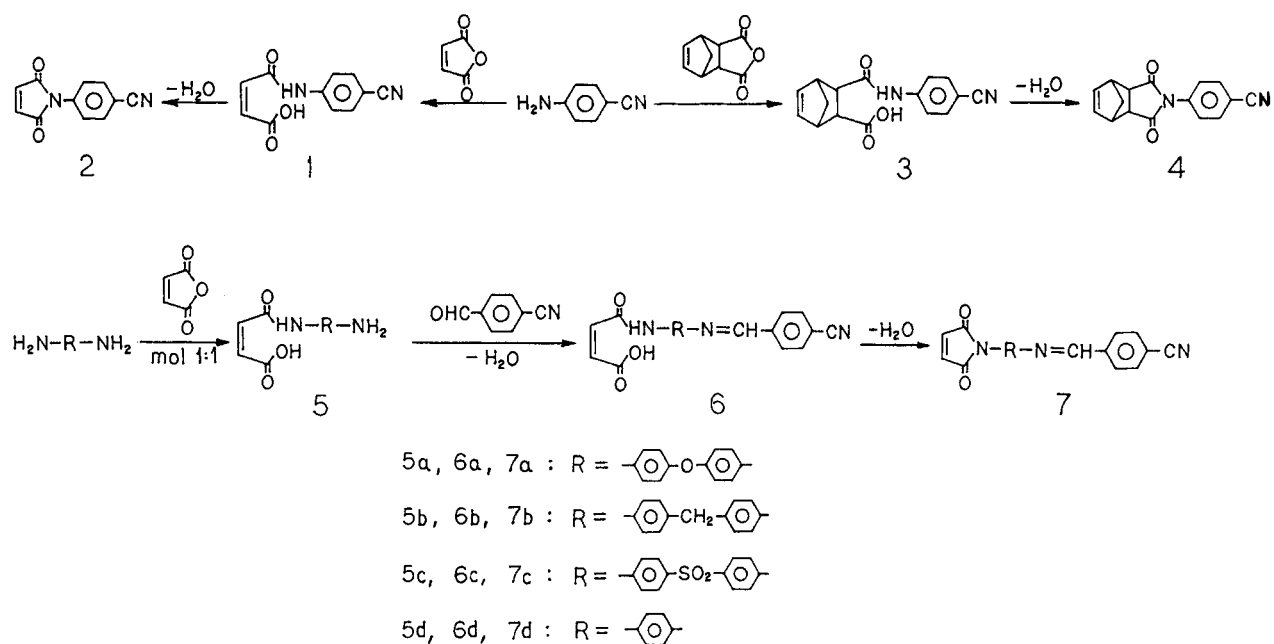
RESULTS AND DISCUSSION

Scheme 1 outlines the preparation of the cyano-substituted maleimides and their intermediate maleamic acids. More particularly, 4-aminobenzonitrile reacted with an equimolar amount of maleic anhydride in acetone to afford maleamic acid **1**. The latter was cyclodehydrated to maleimide **2** by acetic anhydride and sodium acetate. 4-Aminobenzonitrile reacted similarly with nadic anhydride to nadiamic acid **3**, which was cyclodehydrated to nadimide **4**.

In addition, a new series of cyano-substituted maleamic acids **6a–6d** bearing azomethine linkages as well as the corresponding maleimides **7a–7d** were synthesized. Particularly, monomaleamic acids **5a–5d** derived from an aromatic diamine were prepared by adding portionwise maleic anhydride to a stirred solution of an equimolar amount of diamine in DMF.^{10–12} Under these conditions, the corresponding bismaleamic acids were not formed to a detectable extent. The characterization of monomaleamic acids **5a–5d** has been described.¹² They reacted subsequently in DMF with 4-cyanobenzaldehyde to maleamic acids **6a–6d**. Their isolation was accomplished by pouring the reaction solution into a non-solvent. Maleamic acids were cyclodehydrated to maleimides **7a–7d** utilizing acetic anhydride as condensing agent.

The polymer precursors **2** and **4** as well as their amic acids **1** and **3** were characterized by IR and ¹H-NMR spectroscopy (see Experimental section). Figures 1–3 present typical IR and ¹H-NMR spectra of **1** and **2**. These spectra displayed certain distinct differences that could be used as the basis for monitoring the imidization reaction by IR and ¹H-NMR spectroscopy.

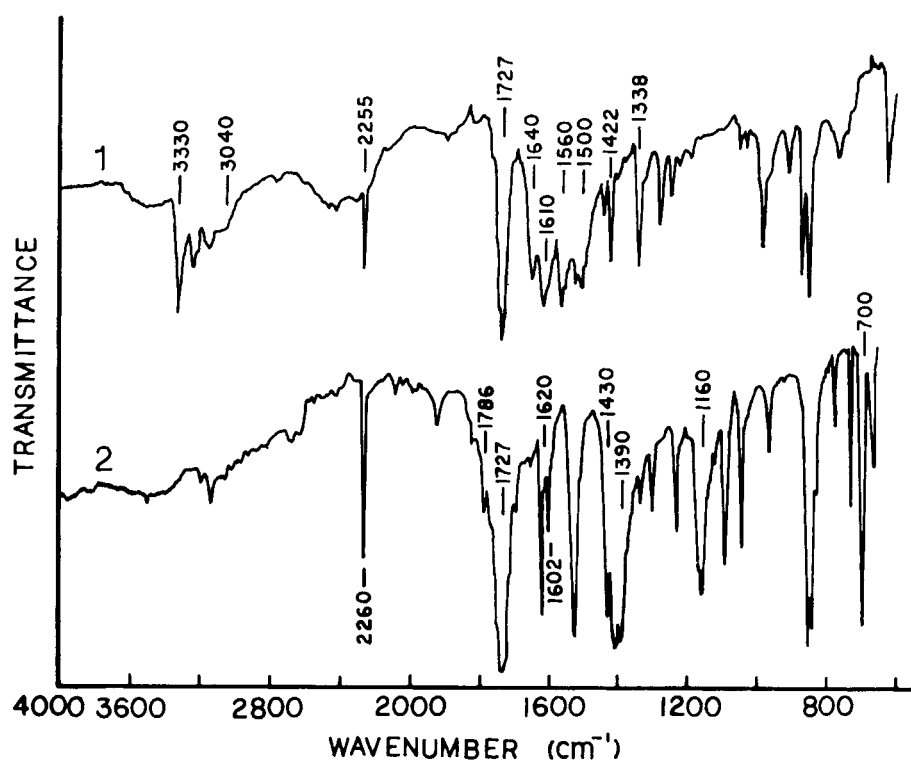
Characterization of maleamic acids **6a–6d** and maleimides **7a–7d** was accomplished also by IR and ¹H-NMR spectroscopy. Figure 4 presents typical IR and ¹H-NMR spectra of maleamic acid **6a**. It displayed characteristic IR absorptions at 3550–3310



Scheme 1

(NH and carboxylic OH stretching); 2250 (C≡N); 1723 (carboxylic C=O); 1638 (amide C=O); 1603 (C=C and C=N); 1560 (NH deformation); 1504 (aromatic); 1420 (carboxylic C—O stretching) and

1245 cm⁻¹ (aromatic ether). The ¹H-NMR spectrum of **6a** showed peaks at 8.53 (COOH and NHCO); 7.81–6.78 (CH=N and aromatic), and 6.23 δ (olefinic).

Figure 1 IR spectra of maleamic acid **1** and the corresponding maleimide **2**.

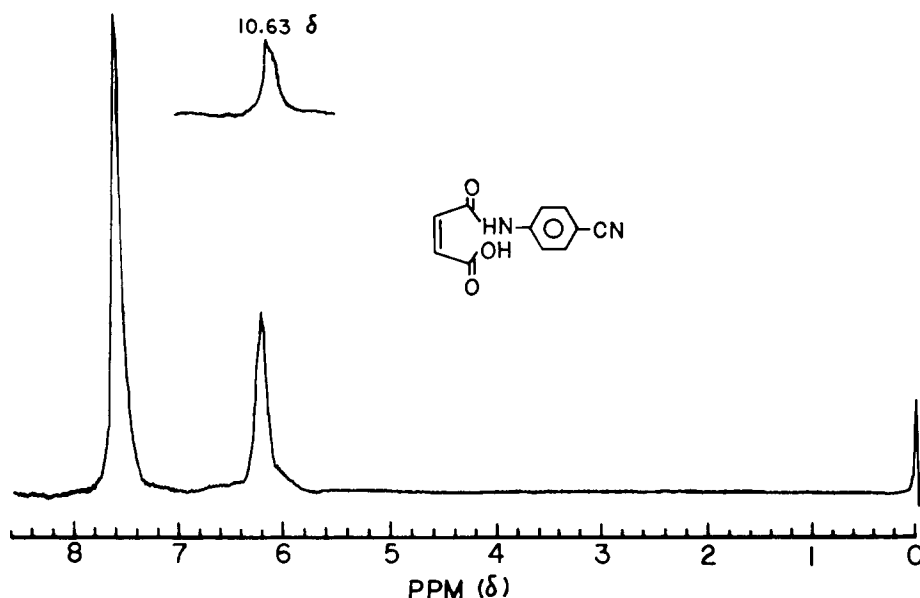


Figure 2 $^1\text{H-NMR}$ spectrum of maleamic acid **1** in $\text{DMSO-}d_6$ solution.

Figure 5 presents the IR and $^1\text{H-NMR}$ spectra of a representative maleimide **7b**. It displayed IR absorption bands at 2250 ($\text{C}\equiv\text{N}$); 1770, 1717, 1397, 1153, and 710 (imide structure); and 1607 ($\text{C}=\text{C}$ and $\text{C}=\text{N}$) and 1517 cm^{-1} (aromatic). The $^1\text{H-NMR}$ spectrum of **7b** showed bands at 7.63–7.10 ($\text{CH}=\text{N}$ and aromatic); 6.88 (olefinic), and 3.92 δ (CH_2).

DTA thermograms were recorded for all the cyano-substituted maleimides and nadimide. Figure 6

presents typical DTA traces of **2**, **4**, and **7b** in N_2 . Maleimide **2** and nadimide **4** exhibited endotherms with onset temperatures 137 and 170°C, respectively, corresponding quite well to their melting points. These endotherms were followed by a broad exotherm attributable to cross-linking reactions. Nadimide **4** showed an endothermic transition between 300 and 350°C that could be attributed to the following retrograde Diels–Alder reaction and loss of cyclopentadiene:

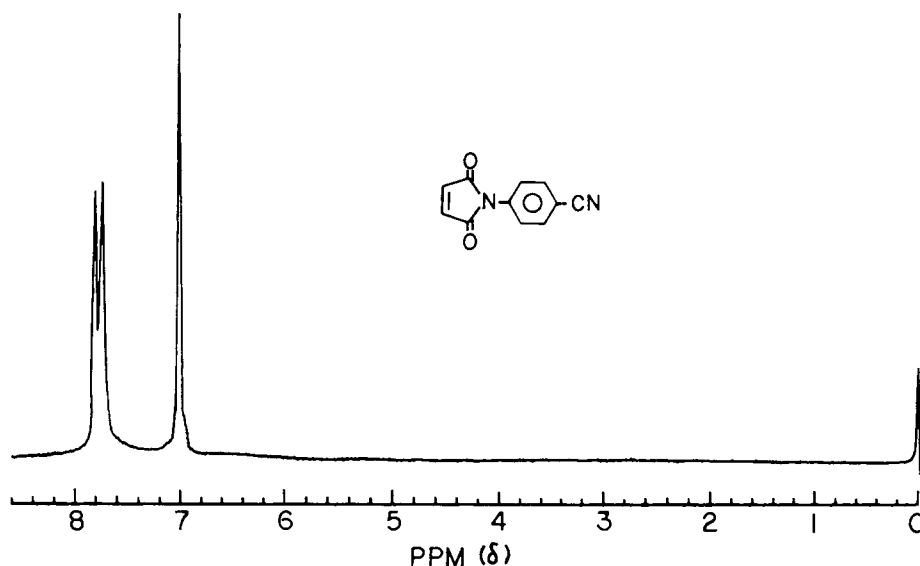


Figure 3 $^1\text{H-NMR}$ spectrum of maleimide **2** in CDCl_3 solution.

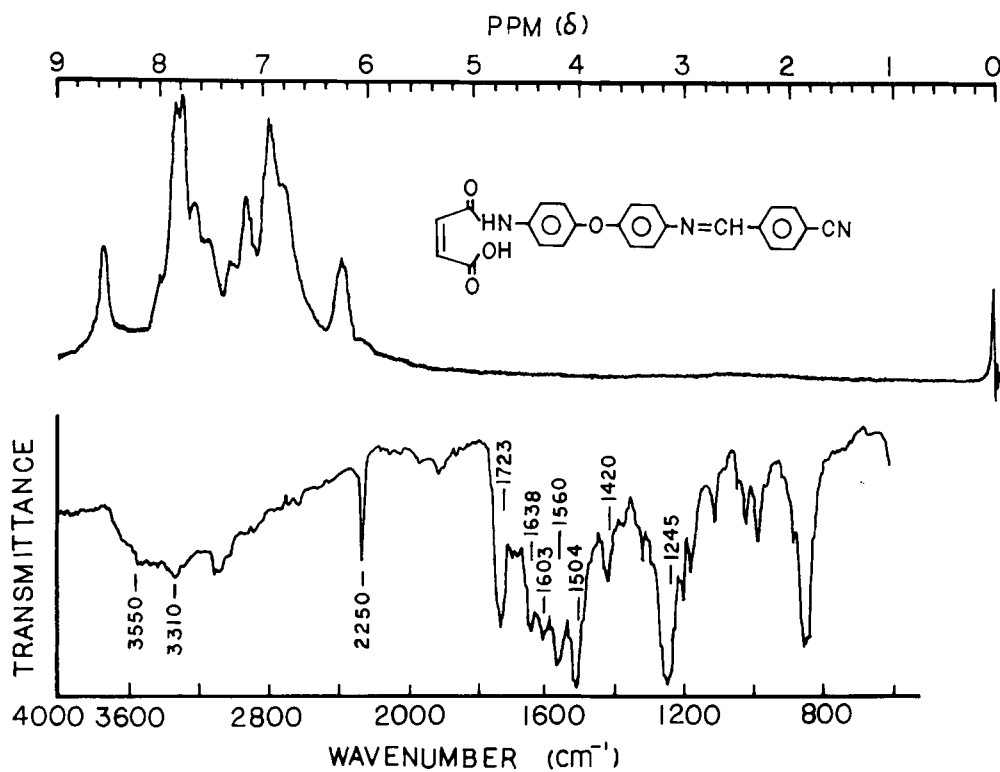


Figure 4 $^1\text{H-NMR}$ spectrum in $\text{DMSO-}d_6$ solution as well as IR spectrum of maleamic acid **6a**.

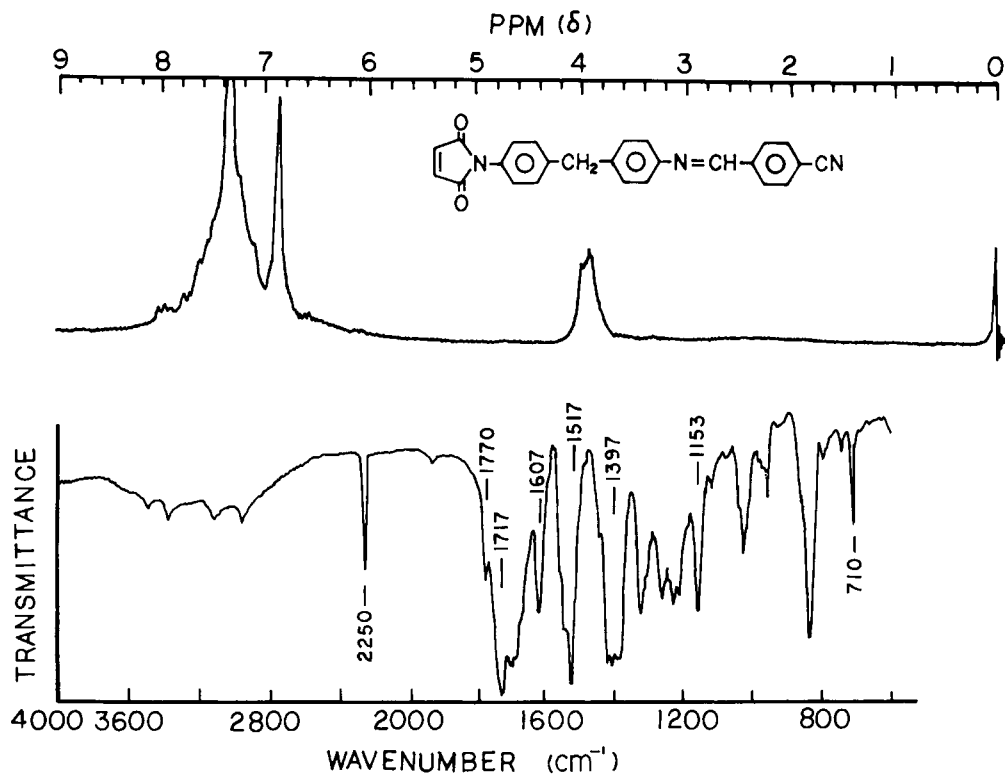


Figure 5 $^1\text{H-NMR}$ spectrum in $\text{DMSO-}d_6$ solution as well as IR spectrum of maleimide **7b**.

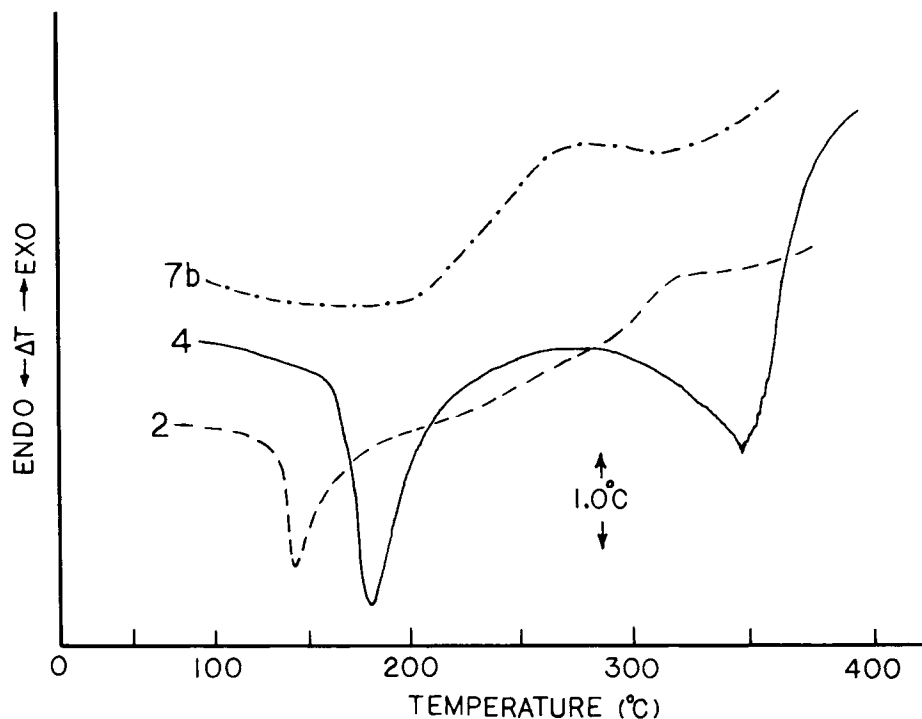
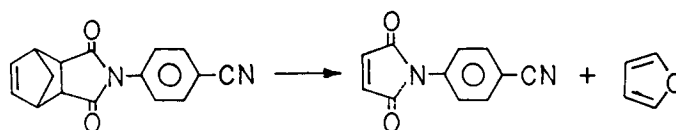


Figure 6 DTA traces of maleimides **2**, **7b**, and nadimide **4**. Conditions: N_2 flow $60\text{ cm}^3/\text{min}$; heating rate $20^\circ\text{C}/\text{min}$.

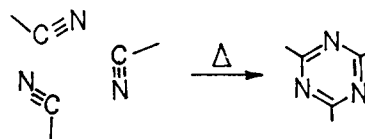


This behavior conforms to the literature data.^{13,14} Maleimide **7b** did not show a melting temperature, probably due to the formation of crossbonds upon gradual heating. The exotherm above 195°C of **7b** was assigned to cross-linking because the corresponding cured sample did not display an exothermic transition at this temperature region.

The cross-linked polymers obtained from polymer precursors **2**, **4**, and **7a–7d** by curing at 240°C for 15 h are referred to by the designations **2'**, **4'**, and **7a'–7d'**, respectively. They were alternatively prepared from the corresponding amic acids **1**, **3**, and **6a–6d** by curing (at 240°C for 15 h) and showed identical thermal properties with the former.

The chemical structure of cross-linked polymers should be complex because they resulted from monomers bearing two reactive segments, i.e., the maleimido (or nadimido) and cyano groups. They were insoluble even in polar aprotic solvents and therefore interpretable NMR spectra could not be recorded. An attempt was made to elucidate their chemical structure utilizing IR spectroscopy. Figure

7 presents a typical IR spectrum of polymer **2'**. Upon comparing this spectrum with that of parent monomer **2** (Fig. 1), a significant reduction of the absorption at 2260 cm^{-1} associated with the $\text{C}\equiv\text{N}$ group was observed. It is suggested, therefore, that the cyano groups are consumed in the trimerization reaction:



The absorption band of **2'** at 1610 cm^{-1} was assigned to the $\text{C}=\text{N}$ bonds of melamine although the aromatic rings absorb also at this spectrum region. Note that the IR spectra of all cured polymers displayed the residual absorption band of the $\text{C}\equiv\text{N}$ group. This supports that the trimerization reaction was slow and it was not completed under the curing con-

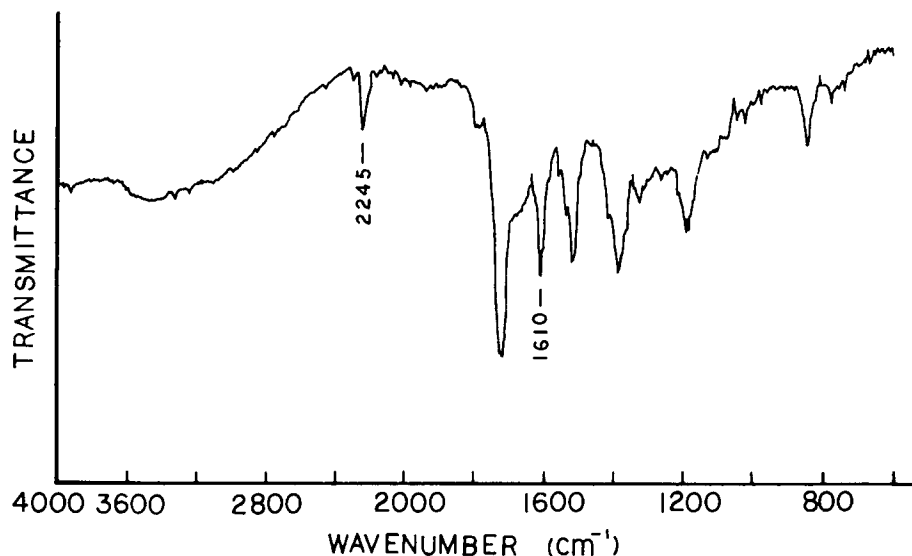
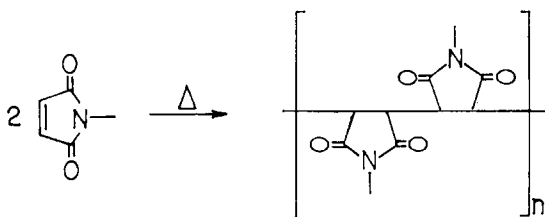


Figure 7 IR spectrum of polymer 2'.

ditions utilized. Another heat-induced reaction that took place with the maleimido groups of **2** was self-addition:



Thus, upon curing of **2**, a network polymer was obtained both through the trimerization reaction of the cyano groups and the cross-linking of the maleimido olefinic bonds. The other synthesized ma-

leimides and nadimides are expected to behave in a similar manner.

The extent of cross-linking of cured polymers was evaluated by extraction them with DMF at room temperature. Percent soluble fraction was calculated as

$$\% \text{ soluble fraction} = \frac{100 \cdot (\text{initial wt of material} - \text{wt of insoluble material})}{\text{initial wt of material}}$$

The results of the % extractable quantity in DMF for various cured (at 240°C for 15 h) polymers are summarized in Table I. It is seen that polymers **2'** and **4'** obtained from maleimide and nadimide, respectively, as well as polymer **7c'** showed appreciable

Table I Thermal Stabilities of Polymers

Polymer	% Extractable in DMF	N ₂				Air		
		IDT ^a (°C)	PDT ^b (°C)	PDT _{max} ^c (°C)	Y _c ^d (%)	IDT (°C)	PDT (°C)	PDT _{max} (°C)
2'	84	310	348	392	40	310	348	385
4'	97	313	381	419	40	313	380	419
7a'	46	329	411	397	57	329	433	385
7b'	22	325	381	385	57	323	415	385
7c'	93	318	404	407	53	317	412	406
7d'	42	330	411	408	60	328	415	404

^a Initial decomposition temperature.

^b Polymer decomposition temperature.

^c Maximum polymer decomposition temperature.

^d Char yield at 800°C.

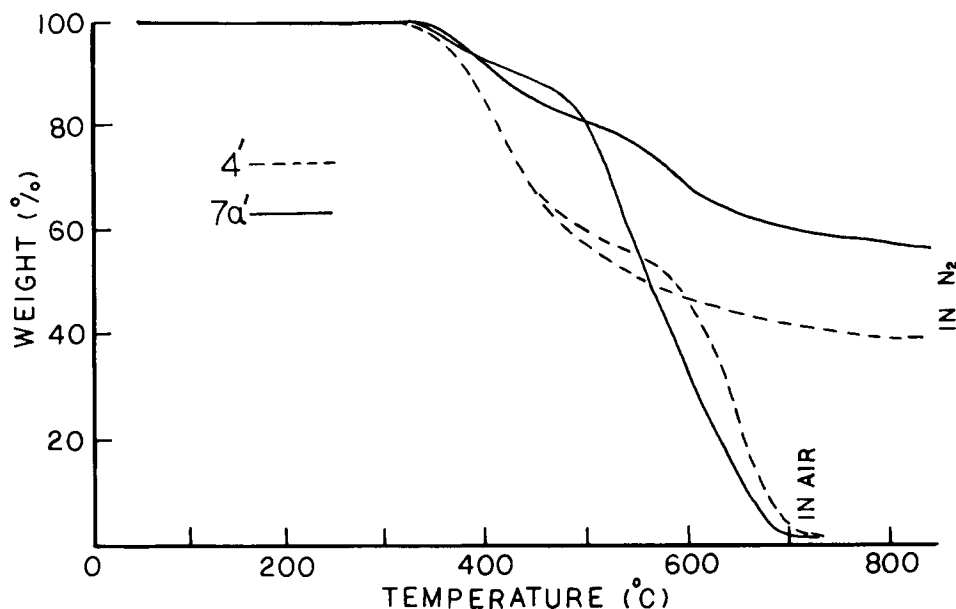


Figure 8 TGA traces of polymers **4'** and **7a'** in N_2 and air. Conditions: gas flow $60 \text{ cm}^3/\text{min}$; heating rate $20^\circ\text{C}/\text{min}$.

amounts of low molecular weight material. In contrast, polymers **7a'**, **7b'**, and **7d'** displayed higher molecular weight material.

Thermal stabilities of cured polymers were ascertained by TGA and isothermal gravimetric analysis (IGA). Figure 8 presents typical TGA traces of **4'** and **7a'** 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 was determined for a weight loss of 10%. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

Taking the IDT as the criterion of thermal stability, polymers **7a'**–**7d'** were more thermally stable than were **2'** and **4'**. Thus, the chain extension of monomers by incorporating various aromatic diamines with the azomethine bond improved the heat resistance of their polymers. In the case of **7a'**–**7d'**, an additional cross-linking could take place through the azomethine bond upon curing.¹⁵ Furthermore, these polymers afforded higher char yield in N_2 than did **2'** and **4'**. The ratio $IDT_{\text{Air}}/IDT_{N_2}$ ranged from 0.99 to 1.00, thus suggesting that thermal degradation of polymers was not affected remarkably by the presence of oxygen.

Thermal stability of a representative polymer **7a'** was evaluated also by IGA. Figure 9 presents the

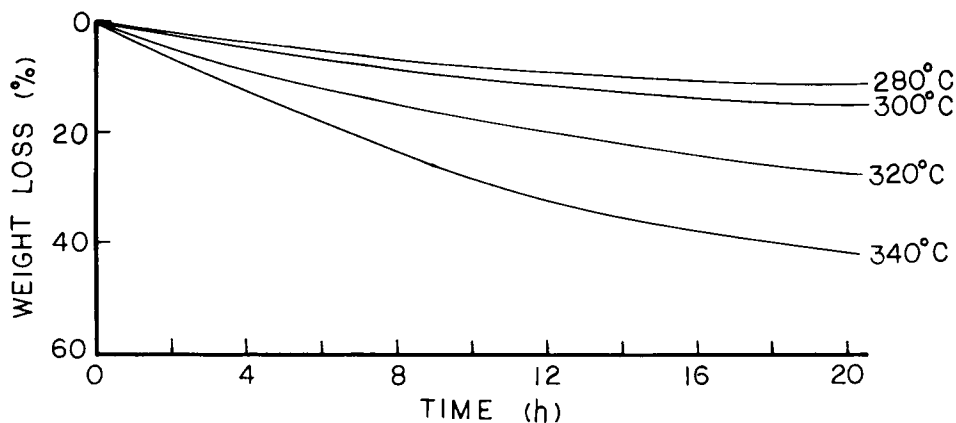


Figure 9 IGA traces of polymer **7a'** in static air at 280, 300, 320, and 340°C .

IGA traces of **7a'** in static air at 280, 300, 320, and 340°C. After 20 h isothermal aging at these temperatures, polymer **7a'** displayed a weight loss of 11.3, 15.0, 27.3, and 41.5%, respectively.

It should be pointed out that thermal stability of the synthesized polymers was inferior to that of resins obtained from bismaleimides. Thus, a series of bismaleimides bearing azomethine linkages afforded by curing (at 230°C for 2 h and then at 270°C for 30 min) resins that were stable up to 345–377°C in N₂ or air.¹⁵ The incomplete trimerization reaction of the C≡N groups, despite the long and strong curing conditions applied, should be responsible for this behavior.

The synthesized cyano-substituted maleimides or their intermediate amic acids could be used as matrix resins for composites.

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