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HIGH-TEMPERATURE RESINS OBTAINED FROM BISMALEAMIC ACIDS OF β,β'-DICHLOROTEREPHTHALYL DIMALONITRILE

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ABSTRACT

A novel class of bismaleamic acids was synthesized from the reactions of β,β'-dichloroterephthalyl dimalonitrile with a double molar amount of the monomaleamic acid derived from an aromatic diamine utilizing triethylamine as an acid acceptor. Both monomaleamic and bismaleamic acids were characterized by IR and ^{1}H-NMR spectroscopy as well as elemental analyses. Bismaleamic acids were soluble in various organic solvents. Upon curing at 300°C for 15 h, they yielded insoluble network polymers by dehydration to the corresponding bismaleimides and subsequent crosslinking through their olefinic bonds. It was shown by IR spectroscopy that curing of bismaleamic acids rearranged, at least in part, the enamino nitrile units to 4-aminoquinoline. The cured resins were characterized by DTA and TGA. They showed excellent thermal stability because they were stable up to 355–389°C in N_2 and air and afforded an anaerobic char yield of 57–66% at 800°C. In addition, the thermal stability of a typical cured resin was evaluated by isothermal gravimetric analysis.

INTRODUCTION

The development of heat-resistant high-performance polymers in the past two decades has drawn the attention of many polymer scientists all over the world [1–5]. In general, heat-resistant polymers should possess excellent thermooxidative stability at higher temperature (>300°C) for a long period of time. In addition to that, several other important properties, including good chemical stability against acid and base, high strength and high modulus, and acceptable solubility in common organic polar solvents, are also expected from them.

Aromatic bismaleimides and their intermediate bismaleamic acids have been among the most successful polymer precursors for thermostable resins [6]. The bismaleimides can be self-polymerized through their reactive maleic double bonds to give highly crosslinked polyimides [7]. In addition, nucleophilic difunctional reagents can add to the maleic double bonds to yield linear, high-molecular-weight polyimides [8, 9].

Work in this laboratory has been concentrated on the development of new heat- and fire-resistant resins derived from maleimides or their substituted derivatives [10–22]. Most of them were obtained from chain-extended bismaleimides, biscitraconimides, or bisnadimides. Their cured resins are expected to have improved properties and to possess a reduced brittleness compared to those derived from ordinary bismaleimides.

The present investigation deals with the synthesis, characterization, and polymerization of new heat-resistant resins obtained from bismaleamic acids of β,β'-dichloroterephthalyl dimalonitrile (DTD). Upon curing, these bismaleamic acids were dehydrated to the corresponding bismaleimides and then crosslinked through their olefinic bonds. In addition, curing at relatively high temperatures could possibly rearrange the enamino nitrile units into 4-aminoquinoline.

A literature survey revealed that DTD has been used as the starting material for preparing thermally stable poly(enamino nitrile) [23–25]. More particularly, DTD was reacted with an equimolar amount of 4,4′-diaminodiphenyl ether while utilizing 4-(dimethylamino)pyridine as an acid acceptor. The poly(enamino nitrile) thus obtained exhibited excellent thermal stability which was attributed to the formation of substituted quinoline rings [23–25].

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}H-NMR spectra were obtained by using a Varian T-60A spectrometer at 60 MHz. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as the internal standard. DTA and TGA were performed on a Du Pont 990 thermal analyzer system. DTA measurements were made by using a high temperature (1200°C) cell in an N_2 atmosphere at a flow rate of 60 cm^3/min. 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. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer.

Reagents and Solvents

Terephthaloyl dichloride was recrystallized from *n*-hexane. Malonitrile was distilled under reduced pressure (92–94°C/8 mm). 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). Maleic anhydride was recrystallized from acetic anhydride. *N,N*-Dimethylformamide (DMF) was dried by refluxing and fractionally distilled from calcium hydride. Phosphorus oxychloride, chloroform, triethylamine, and benzyltrimethylammonium chloride were used as supplied. All reagents and solvents were from Aldrich.

Preparation of Starting Material

β,β'-Dichloroterephthalyl Dimalonitrile (DTD)

Terephthaloyl dichloride (2.8423 g, 14.0 mmol) and malonitrile (1.8497 g, 28.0 mmol) were mixed with chloroform (70 mL). To the vigorously stirred mixture a solution of benzyltriethylammonium chloride (1.50 g, 6.58 mmol) in 6 *N* NaOH (60 mL) was added dropwise at 0°C. Stirring of the mixture at this temperature was continued for 3 h. The precipitated solid was filtered off, washed with isopropanol, and dried to afford the intermediate disodium bisenolate (DSB) (3.40 g, 79%, mp > 350°C). It was recrystallized from distilled water.

IR (KBr) cm^{-1}: 3650–3410 (ONa); 2240 (C≡N); 1600, 1570, 1430 (aromatic); 1407 (alkene disubstituted *gem*).

^{1}H-NMR (D_2O) δ: 7.63 (s, aromatic).

A flask was charged with a mixture of DSB (2.80 g, 9.14 mmol) and phosphorus oxychloride (15 mL). It was refluxed for 1 h. Phosphorus oxychloride and volatile components were stripped off by distillation under reduced pressure. The residue was washed with ether and dried to afford DTD (2.68 g, 98%, mp 177–179°C).

IR (KBr) cm^{-1}: 2250 (C≡N); 1623, 1564, 1428 (aromatic); 1417 (alkene disubstituted *gem*); 664 (C—Cl).

^{1}H-NMR ($CDCl_3$) δ: 7.93 (s, aromatic).

Preparation of Maleamic Acids

Maleamic Acid 1a

A flask equipped with magnetic stirrer and dropping funnel was charged with a solution of 4,4'-diaminodiphenylmethane (1.1896 g, 6.0 mmol) in acetone (10 mL). To the stirred solution, maleic anhydride (0.5884 g, 6.0 mmol) dissolved in acetone (8 mL) was added dropwise at 0°C under N_2. An exothermic reaction was observed. Stirring of the mixture was continued at ambient temperature for 3 h in a stream of N_2. The precipitated pale brown solid was filtered off, washed with acetone, and dried to afford 1a (1.00 g, yield 56%). A purified sample having a melting temperature of 176–180°C was obtained by recrystallization from a mixture of DMF/water (volume ratio 1:5).

Analysis. Calculated for $C_{17}H_{16}N_2O_3$: C, 68.91; H, 5.44; N, 9.45%. Found: C, 69.04; H, 5.47; N, 9.39%.

IR (KBr) cm^{-1}: 3500–3040 (NH_2, NH, and OH); 2925 (CH_2); 1724 (carboxylic C=O); 1626 (amide C=O); 1570 (NH deformation); 1403 (OH deformation); 1324 (C—N).

^{1}H-NMR (DMSO-d_6) δ: 10.63 (bs, 1H, COOH); 8.62–8.23 (m, 1H NHCO and 2H NH_2); 7.67–6.35 (m, 8H aromatic and 2H olefinic); 3.73–3.62 (m, 2H, CH_2).

Maleamic Acid 1b

Maleamic acid 1b was similarly prepared as a pale brown solid in 42% yield (0.75 g) by reacting 4,4′-diaminodiphenylether (1.2014 g, 6.0 mmol) with maleic anhydride (0.5884 g, 6.0 mmol) in acetone. It had a melting temperature of 207–210°C after recrystallization from a mixture of DMF/water (volume ratio 1:3).

Analysis. Calculated for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39%. Found: C, 64.87; H, 4.54; N, 9.22%.

IR (KBr) cm^{-1}: 3350–2960 (NH_2, NH, and OH); 1700 (carboxylic C=O); 1625 (amide C=O); 1563 (NH deformation); 1405 (OH deformation); 1320 (C—N); 1238 (aromatic ether).

^{1}H-NMR (DMSO-d_6) δ: 10.43 (bs, 1H, COOH); 8.50–8.15 (m, 1H NHCO and 2H NH_2); 7.75–6.20 (m, 8H aromatic and 2H olefinic).

Maleamic Acid 1c

Maleamic acid 1c was similarly prepared as a light yellow solid in 51% yield (1.06 g) by reacting 4,4′-diaminodiphenylsulfone (1.4899 g, 6.0 mmol) with maleic anhydride (0.5884 g, 6.0 mmol) in acetone. It was recrystallized from a mixture of DMF/water (volume ratio 1:6) to afford a purified sample with a melting temperature of 187–190°C.

Analysis. Calculated for $C_{16}H_{14}N_2O_5S$: C, 55.48; H, 4.07; N, 8.09%. Found: C, 55.97; H, 4.12; N, 7.93%.

IR (KBr) cm^{-1}: 3490–3050 (NH_2, NH, and OH); 1706 (carboxylic C=O); 1627 (amide C=O); 1575 (NH deformation); 1395 (OH deformation); 1318 (C—N); 1140 (SO_2).

^{1}H-NMR (DMSO-d_6) δ: 10.78 (bs, 1H, COOH); 8.69–8.30 (m, 1H NHCO and 2H NH_2); 7.57–7.43 (m, 4H aromatic ortho to SO_2); 6.60–6.41 (m, 4H other aromatic and 2H olefinic).

Maleamic Acid 1d

Maleamic acid 1d was similarly prepared as an orange solid in 73% yield (1.05 g) by reacting 1,4-phenylenediamine (0.7570 g, 7.0 mmol) with maleic anhydride (0.6864 g, 7.0 mmol) in acetone. A purified sample having a melting temperature of 175–178°C was obtained by recrystallization from a mixture of DMF/water (volume ratio 1:7).

Analysis. Calculated for $C_{10}H_{10}N_2O_3$: C, 58.25; H, 4.89; N, 13.59%. Found: C, 59.07; H, 4.96; N, 13.37%.

IR (KBr) cm^{-1}: 3560–3010 (NH_2, NH, and OH); 1695 (carboxylic C=O); 1620 (amide C=O); 1573 (NH deformation); 1503 (aromatic); 1400 (OH deformation); 1320 (C—N).

^{1}H-NMR (DMSO-d_6) δ: 10.60 (bs, 1H, COOH); 8.40 (bs, 1H NHCO and 2H NH_2); 7.75–6.23 (m, 4H aromatic and 2H olefinic).

Preparation of Bismaleamic Acids

Bismaleamic Acid 2a

A flask equipped with a magnetic stirrer was charged with a solution of maleamic acid 1a (3.5560 g, 12.0 mmol) in DMF (20 mL). DTD (1.7947 g, 6.0 mmol) and triethylamine (2.4286 g, 24.0 mmol) were added to the solution and the mixture was heated at 75°C overnight. It was subsequently poured into ice water containing hydrogen chloride. The light brown solid was filtered off, washed thoroughly with water, and dried to afford 2a (3.80 g, yield 77%). A purified sample obtained by recrystallization from a mixture of DMF/water (volume ratio 2:1) had a melting temperature of 162–175°C.

Analysis. Calculated for $C_{48}H_{34}N_8O_6$: C, 70.41; H, 4.19; N, 13.69%. Found: C, 69.12; H, 4.26; N, 13.75%.

Bismaleamic Acid 2b

Bismaleamic acid 2b was similarly prepared as a light brown solid in 68% yield (2.24 g) from the reaction of maleamic acid 1b (2.3864 g, 8.0 mmol) with DTD (1.1964 g, 4.0 mmol) in the presence of triethylamine (1.6190 g, 16.0 mmol) utilizing DMF as the reaction solvent. It was recrystallized from a mixture of DMF/water (volume ratio 1:1), and it did not show any clear melting temperature.

Analysis. Calculated for $C_{46}H_{30}N_8O_8$: C, 67.15; H, 3.68; N, 13.62%. Found: C, 66.57; H, 3.82; N, 13.96%.

Bismaleamic Acid 2c

Bismaleamic acid 2c was similarly prepared as a brown solid in 71% yield (2.60 g) from the reaction of maleamic acid 1c (2.7710 g, 8.0 mmol) with DTD (1.1964 g, 4.0 mmol) in the presence of triethylamine (1.6190 g, 16.0 mmol) utilizing DMF as the reaction solvent. A purified sample obtained by recrystallization from a mixture of DMF/water (volume ratio 1:1) had a melting temperature of 165–173°C.

Analysis. Calculated for $C_{46}H_{30}N_8O_{10}S_2$: C, 60.12; H, 3.29; N, 12.19%. Found: C, 59.20; H, 3.37; N, 12.31%.

Bismaleamic Acid 2d

Bismaleamic acid 2d was similarly prepared as a brown solid in 63% yield (3.22 g) from the reaction of maleamic acid 1d (3.2993 g, 16.0 mmol) with DTD (2.3929 g, 8.0 mmol) in the presence of triethylamine (3.2381 g, 32.0 mmol) utilizing DMF as the reaction solvent. It was recrystallized from a mixture of DMF/water (volume ratio 1:1), and it did not show any clear melting temperature.

Analysis. Calculated for $C_{34}H_{22}N_8O_6$: C, 63.95; H, 3.47; N, 17.55%. Found: C, 62.13; H, 3.58; N, 17.74%.

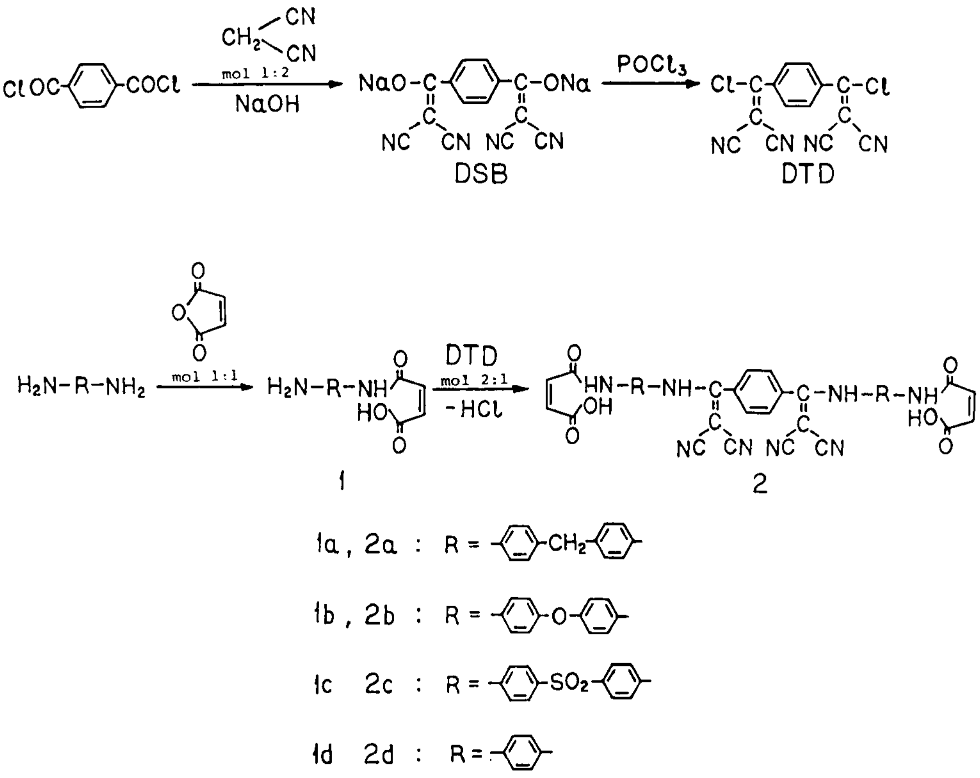
General Procedure for Curing Bismaleamic Acids

The bismaleamic acid isolated was heated in a shallow dish placed into a circulating air oven at 300°C for 15 h to afford a crosslinked polymer.

RESULTS AND DISCUSSION

Scheme 1 outlines the preparation of DTD and monomaleamic acids 1a–1d, which were used as starting materials, as well as of bismaleamic acids 2a–2d. The synthesis of DTD was based on the known chemistry of monofunctional compounds [26, 27]. More particularly, malonitrile was condensed with a half molar amount of terephthaloyl dichloride in the presence of sodium hydroxide in a two-phase system [23–25]. The resulting disodium bisenolate (DSB) reacted with phosphorus oxychloride to afford DTD.

Monomaleamic acids 1a–1d derived from an aromatic diamine (4,4′-diaminodiphenylmethane, 4,4′-diaminodiphenylether, 4,4′-diaminodiphenylsulfone, or 1,4-phenylenediamine) were prepared by adding maleic anhydride portionwise to a stirred solution of equimolar amounts of diamine in acetone [12, 15]. Under these conditions, the corresponding bismaleamic acids were not formed to a detectable



SCHEME 1.

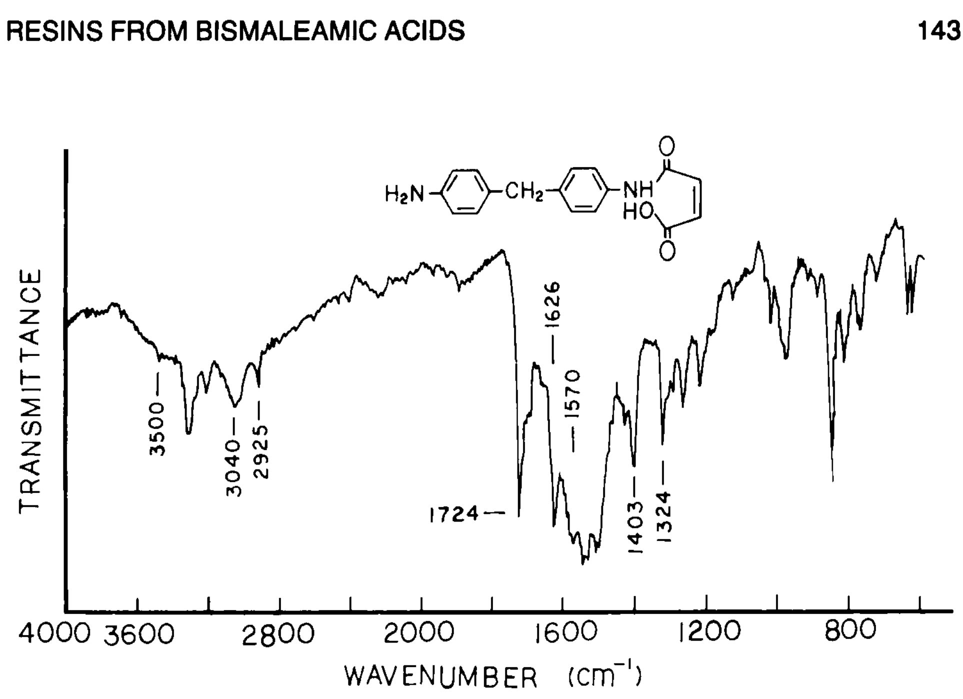


FIG. 1. IR spectrum of monomaleamic acid 1a.

extent. The isolated monomaleamic acids were characterized by IR and ^{1}H-NMR spectroscopy as well as by elemental analyses (see Experimental Section). Figures 1 and 2 present typical IR and ^{1}H-NMR spectra of monomaleamic acid 1a.

Monomaleamic acids 1a-1d reacted with a half molar amount of DTD in DMF to yield bismaleamic acids 2a-2d by vinylic nucleophilic substitution [28].

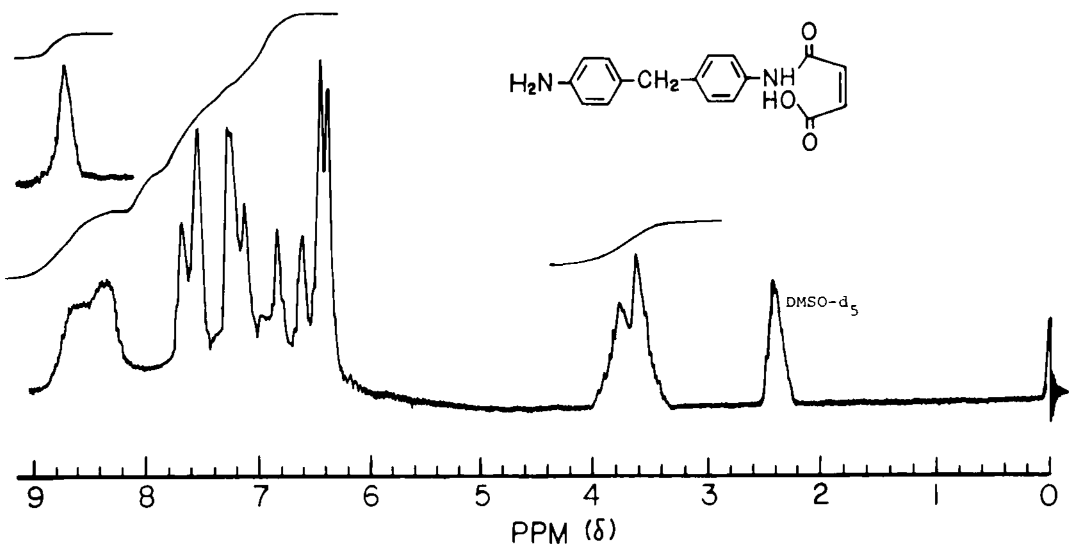


FIG. 2. ^{1}H-NMR spectrum of monomaleamic acid 1a in DMSO-d_6 solution.

The reaction was carried out by heating at 75°C for 15 h. Triethylamine was used as the acid acceptor. A double molar amount of triethylamine with respect to that of monomaleamic acid was added to the reaction solution due to their salt formation. Bismaleamic acids were isolated by precipitation into water containing hydrochloric acid. The yield of bismaleamic acids ranged from 63 to 77%. Upon gradual heating, certain bismaleamic acids did not display a clear melting temperature because of their cyclodehydration to bismaleimides and subsequent crosslinking.

The structures of bismaleamic acids were confirmed by elemental analyses (see Experimental Section) as well as by IR and ^{1}H-NMR spectroscopy (Table 1). Figure 3 presents a typical IR spectrum of bismaleamic acid 2b. All bismaleamic acids showed a strong and broad absorption band about 3600–3200 cm^{-1} associated with the NH and carboxylic OH stretching vibrations. The C≡N groups exhibited a strong and sharp absorption near 2240 cm^{-1}. A broadening of the carbonyl absorption was observed in some cases due to a partial overlapping of the carboxylic and amide carbonyls which absorbed around 1720 and 1670 cm^{-1}, respectively. The absorption at about 1560 cm^{-1} was assigned to the NH deformation of the secondary amide and amine. Aromatic ring stretching vibrations were observed near 1600 and 1500 cm^{-1}. The absorption near 1600 cm^{-1} was also attributed to C=C stretching vibrations. Finally, the absorption at about 1410 cm^{-1} was assigned to alkene (disubstituted *gem*).

Figure 4 presents a typical ^{1}H-NMR spectrum of bismaleamic acid 2b. All bismaleamic acids showed a broad signal at about 10.50 δ assigned to the carboxylic as well as enamine proton ($NH{=}C(CN)_2$). They also exhibited a multiplet around 7.90–6.30 δ associated with the NHCO, aromatic, and olefinic protons.

Table 2 presents the solubility of bismaleamic acids in various organic media. All bismaleamic acids displayed comparable solubility behaviors. It is seen that they were readily soluble even in less efficient solvents such as tetrahydrofuran and methyl ethyl ketone. This is important from a technological point of view for composite fabrication.

Upon curing at 300°C for 15 h, the isolated bismaleamic acids became dark brown solids and were insoluble for the untreated samples. The resins obtained from bismaleamic acids 2a–2d by curing (at 300°C for 15 h) are referred to by the designations 2a′–2d′, respectively. Figure 3 presents typical IR spectra both of 2b and 2b′. An attempt was made to elucidate the structure of the cured resin by comparing these spectra. Although the IR spectrum of cured resin was broader than that of the uncured sample, it showed certain distinguishable differences. More particularly, 2b′ displayed a significant decrease in the C≡N band at 2235 cm^{-1}. In addition, the absorption at 1720 cm^{-1} associated with the carboxylic carbonyl disappeared in 2b′ and a new absorption at 1746 cm^{-1} assigned to the imide carbonyl was observed. These spectral features are in agreement with the chemical reactions of Scheme 2 which are believed to occur during curing of 2b. Upon heat curing, thermal cyclodehydration of bismaleamic acid to the corresponding bismaleimide took place initially. The latter afforded a network polymer by thermally induced crosslinking through the maleimide olefinic bonds. In addition, a rearrangement, at least to a measure, of the enamino nitrile segment to 4-aminoquinoline occurred at higher temperatures. This behavior conforms to the literature data [23, 24, 29]. In the present case, the rearrangement could not be monitored by studying the IR absorption band at 3560–3210 cm^{-1} of 2b (Fig. 1) because the NH and COOH absorption overlaid that of the resulting amino group.

TABLE 1. IR and ^{1}H-NMR Spectral Data of Bismaleamic Acids

	IR	^{1}H-NMR
Compound	Wavenumber in cm^{-1}	Chemical shifts (δ in ppm)[a]
2a	3600–3060 (NH and carboxylic OH); 2930 (CH_2); 2240 ($C\equiv N$); 1723 (carboxylic $C=O$); 1646 (amide $C=O$); 1607 ($C=C$ and aromatic); 1557 (NH deformation); 1505 (aromatic); 1410 (alkene disubstituted *gem*)	10.47 (b, 2H COOH, and 2H $NHC=C$); 7.90–6.40 (m, 2H NHCO, 20H aromatic, and 4H olefinic); 3.77 (s, 4H, CH_2)
2b	3560–3210 (NH and carboxylic OH); 2235 ($C\equiv N$); 1720 (carboxylic $C=O$); 1675 (amide $C=O$); 1608 ($C=C$ and aromatic); 1553 (NH deformation); 1503 (aromatic); 1240 (aromatic ether); 1408 (alkene disubstituted *gem*)	10.67 (b, 2H COOH, and 2H $NHC=C$); 7.80–6.30 (m, 2H NHCO, 20H aromatic, and 4H olefinic)
2c	3570–3290 (NH and carboxylic OH); 2240 ($C\equiv N$); 1723 (carboxylic $C=O$); 1642 (amide $C=O$); 1603 ($C=C$ and aromatic); 1557 (NH deformation); 1508 (aromatic); 1407 (alkene disubstituted *gem*); 1338, 1160 (SO_2)	10.45 (b, 2H COOH, and 2H $NHC=C$); 7.90–6.38 (m, 2H NHCO, 20H aromatic, and 4H olefinic)
2d	3570–3255 (NH and carboxylic OH); 2248 ($C\equiv N$); 1723 (carboxylic $C=O$); 1640 (amide $C=O$); 1610 ($C=C$ and aromatic); 1570 (NH deformation); 1523 (aromatic); 1410 (alkene disubstituted *gem*)	10.46 (b, 2H COOH, and 2H $NHC=C$); 7.83–6.37 (m, 2H NHCO, 12H aromatic, and 4H olefinic)

[a] In DMSO-d_6 solution (b = broad; m = multiplet; s = singlet).

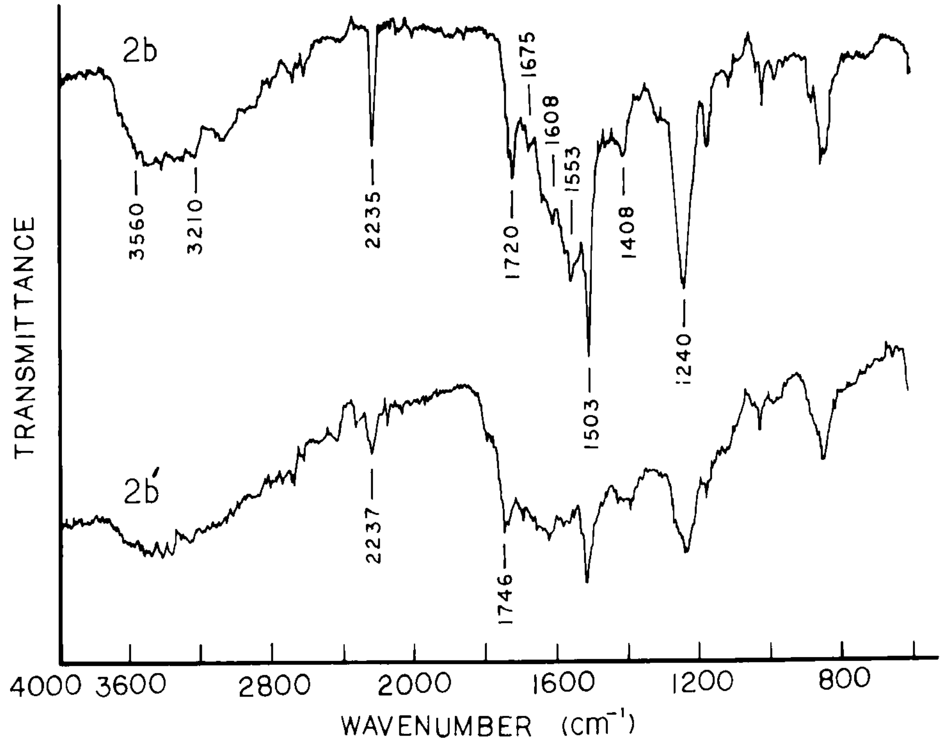


FIG. 3. IR spectra of bismaleamic acid 2b (top) and the corresponding cured resin 2b′ (bottom).

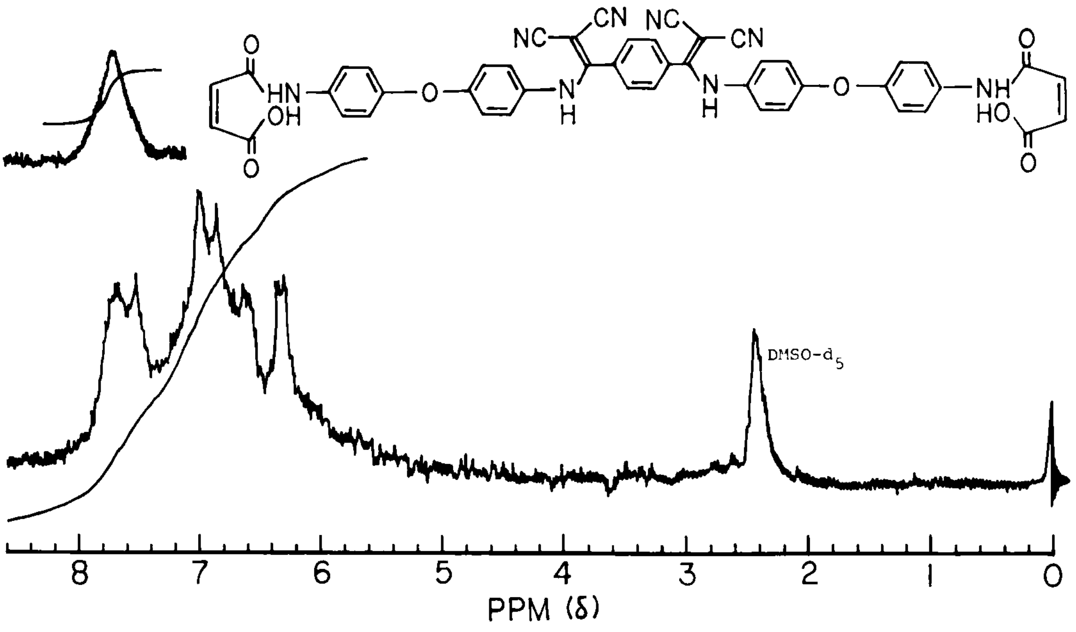


FIG. 4. ^{1}H-NMR spectrum of bismaleamic acid 2b in DMSO-d_6 solution.

TABLE 2. Solubility Behavior of Bismaleamic Acids[a]

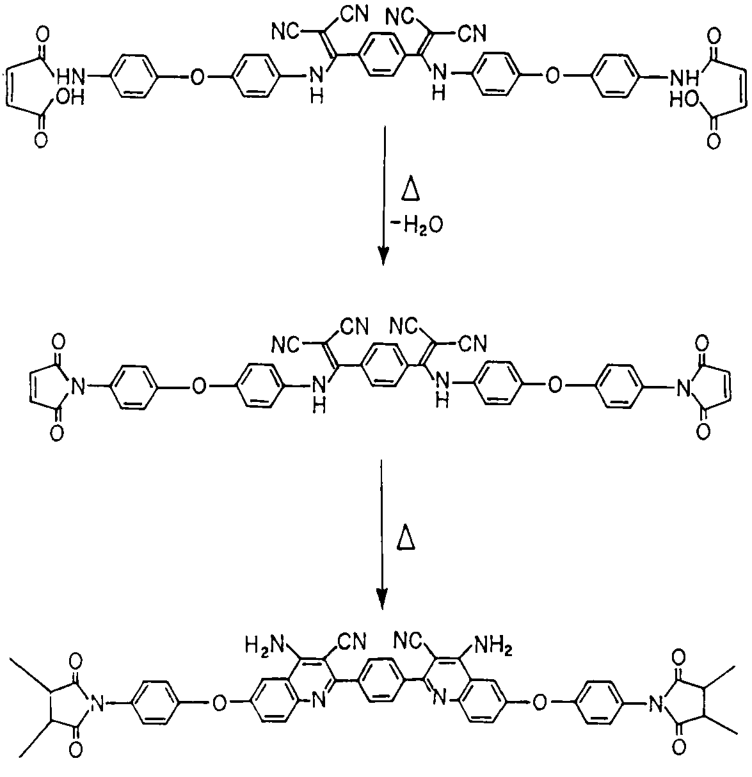
Medium	Solubility	Medium	Solubility
DMSO	+ +	Tetrahydrofuran	+ +
DMF	+ +	Methyl ethyl ketone	+ +
1,4-Dioxane	+ +	Acetone	+
Methanol	±	Chloroform	−
Ethanol	±	Toluene	−

[a]Solubility: (+ +) soluble at room temperature, (+) soluble on heating, (±) partially soluble on heating, (−) insoluble.

Figure 5 presents the TGA thermograms in N_2 of bismaleamic acids 2a-2d. It is seen that they showed an initial weight loss starting in the region of 127-142°C due to their cyclodehydration to the corresponding bismaleimides. After the first step of weight loss, the TGA curves leveled off, and the next onset of decomposition occurred at approximately 330°C.

Figure 6 shows the DTA traces in N_2 of polymers 2a′-2d′. They displayed large and broad exotherms beyond 350°C associated with their thermal degradation.

Thermal stabilities of cured resins were evaluated by TGA as well as by iso-



SCHEME 2.

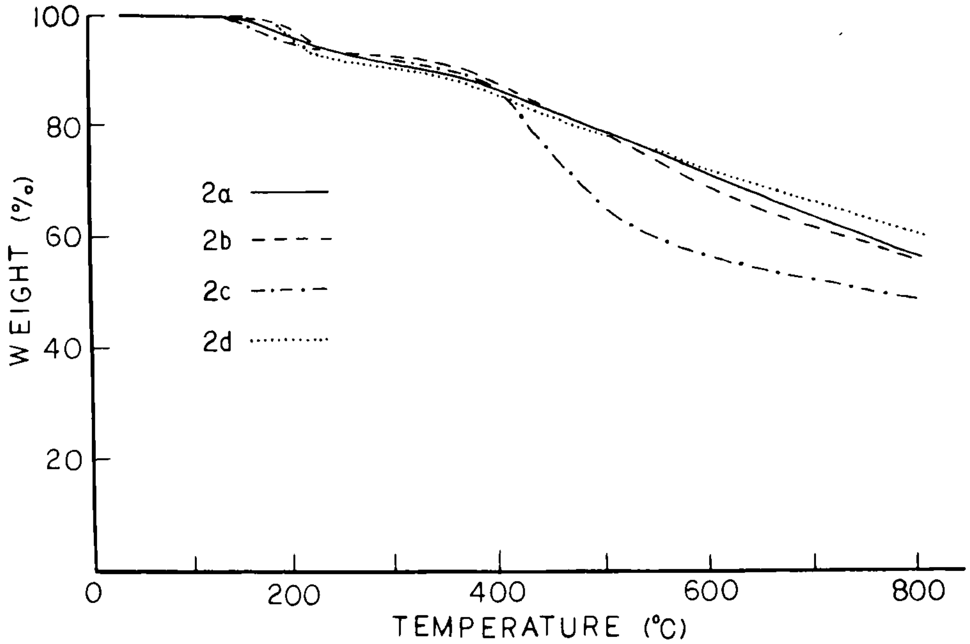


FIG. 5. TGA thermograms of bismaleamic acids 2a–2d. Conditions: N_2 flow, 60 cm^3/min; heating rate, 20°C/min.

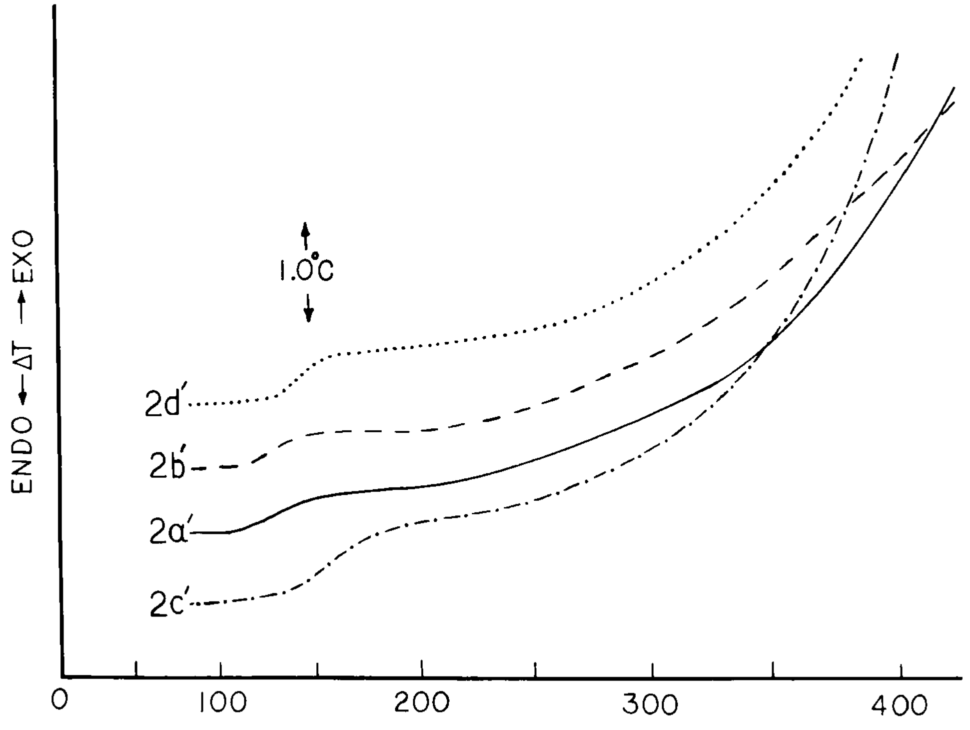


FIG. 6. DTA traces of cured resins 2a′–2d′. Conditions: N_2 flow, 60 cm^3/min; heating rate, 20°C/min.

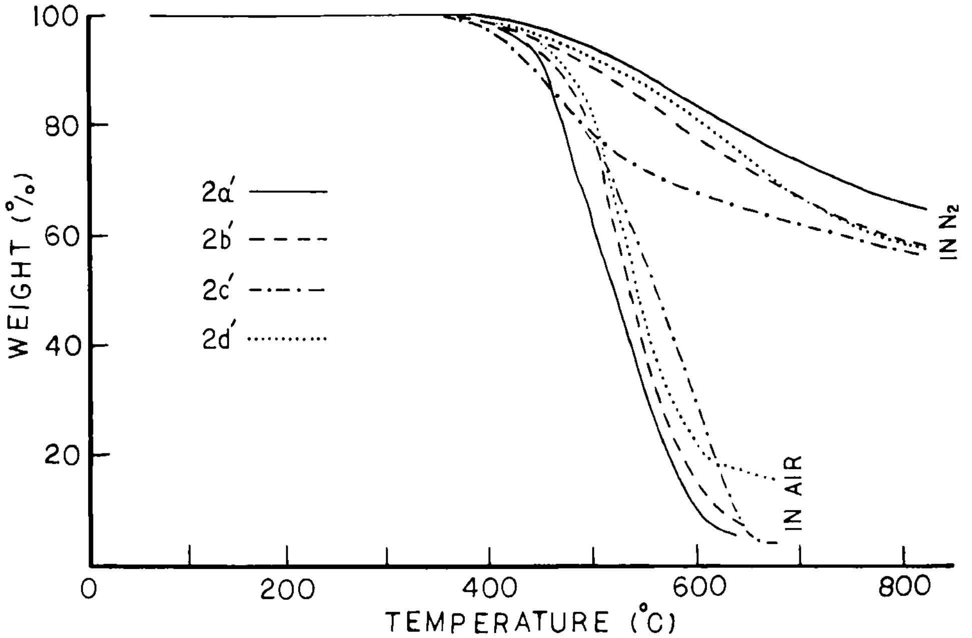


FIG. 7. TGA thermograms of cured resins 2a′-2d′ in N_2 and air. Conditions: Gas flow, 60 cm^3/min; heating rate, 20°C/min.

thermal gravimetric analysis (IGA). Figure 7 presents their TGA traces 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 3. PDT was determined by the intersection of the tangent to the steepest portion of the TGA curve with its strain line before polymer degradation. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred.

Thermal stabilities of the uncured bismaleamic acids were also evaluated for comparative purposes (Table 3). Presumably a limited curing of the uncured samples occurred during the course of the TGA experiment. Under the TGA experimental conditions utilized (heating rate 20°C/min), this curing was insignificant in comparison to that attained during heat treatment of bismaleamic acids at 300°C for 15 h.

The cured resins were dramatically more thermostable than the corresponding uncured samples because of their crosslinked structure and the rearrangement to the 4-aminoquinoline segment. They did not show a weight loss up to 355-389°C in N_2 or air, and they had an anaerobic char yield of 57-66% at 800°C. Their relative thermal stabilities could be judged on the basis of their IDT values. Cured resins 2a′, 2b′, and 2d′ showed comparable thermal stabilities. Resin 2c′ derived from 4,4′-diaminodiphenylsulfone was the least thermostable polymer obtained and afforded the lowest char yield. The IDT in air was somewhat lower than that in N_2. The ratio $(IDT)_{air}/(IDT)_{N_2}$ ranged from 0.99 to 0.96. All resins were almost completely pyrolyzed beyond 600°C in air.

TABLE 3. TGA Data of Cured Resins as Well as of the Corresponding Uncured Samples

	In N_2				In air		
Sample	IDT,[a] °C	PDT,[b] °C	PDT_{max},[c] °C	Y_c,[d] (%)	IDT, °C	PDT, °C	PDT_{max}, °C
2a′	389 (138)[e]	456 (227)	545 (411)	66 (57)	374 (131)	441 (221)	498 (478)
2b′	385 (134)	450 (278)	589 (419)	60 (56)	370 (130)	430 (264)	467 (460)
2c′	359 (127)	400 (252)	478 (430)	57 (49)	355 (123)	460 (241)	527 (492)
2d′	385 (142)	474 (194)	627 (441)	59 (60)	376 (138)	478 (186)	508 (486)

[a] Initial decomposition temperature.

[b] Polymer decomposition temperature.

[c] Maximum polymer decomposition temperature.

[d] Char yield at 800°C.

[e] Numbers in parentheses indicate the values of the corresponding uncured samples.

Figure 8 presents the IGA traces of cured resin 2a′ in static air at 260, 280, 300, 320, and 340°C. After 20 h of isothermal aging at these temperatures, resin 2a′ displayed weight losses of 2.8, 7.1, 16.1, 28.2, and 49.0%, respectively. The results showed that an increased degradation occurred above 300°C under these conditions.

Thermal stability of the cured resins was comparable to that of poly(enamino nitrile) [23-25]. The synthesized bismaleamic acids could be used as matrix resins for composites because they showed remarkable properties (such as solubility of the polymer precursors in common solvents and excellent thermal stability of the cured resins).

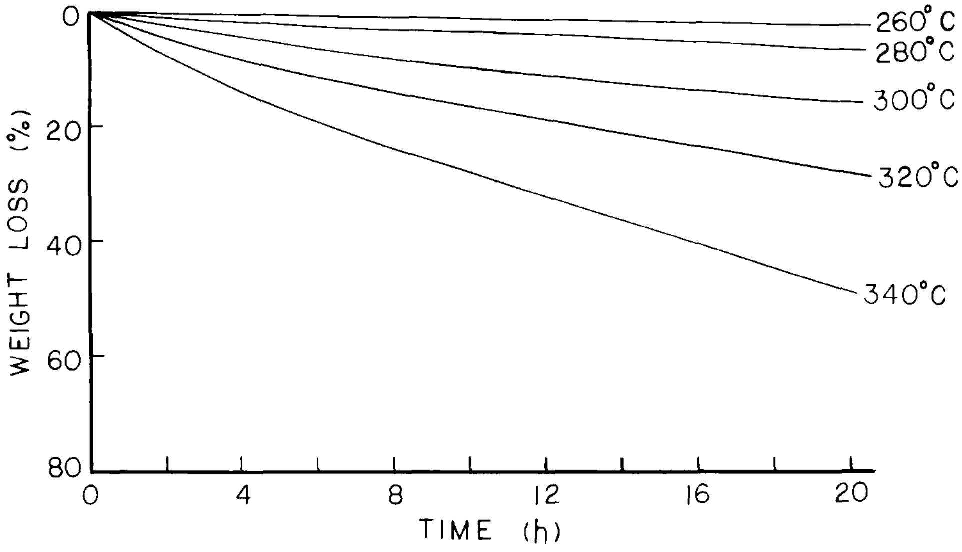


FIG. 8. IGA traces of cured resin 2a′ in static air at 260, 280, 300, 320, and 340°C.

CONCLUSIONS

1. Terephthaloyl dichloride was condensed with a double molar amount of malonitrile in the presence of NaOH to yield the disodium bisenolate (DSB). The reaction of DSB with phosphorus oxychloride afforded the corresponding dichloride (DTD). The latter reacted with the monomaleamic acids 1a–1d derived from an aromatic diamine to yield a novel series of bismaleamic acids 2a–2d bearing enamino nitrile units.
2. Bismaleamic acids 2a–2d behave as polymer precursors. Upon heat curing they first cyclodehydrate to the corresponding bismaleimides. The latter were subsequently crosslinked through the maleimide olefinic bonds.
3. Curing of bismaleamic acids at about 300°C affords insoluble heat-resistant resins by rearrangement of the enamino nitrile unit to 4-aminoquinoline.
4. The cured resins show excellent thermal stability because they are stable up to 355–389°C in N_2 and air, and they have an anaeorobic char yield of 57–66% at 800°C.
5. Bismaleamic acids are attractive polymer precursors because they combine useful properties such as solubility of monomers in various organic solvents and excellent thermal stability of the cured resins. They can be used as matrix resins for high-temperature composites.

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