Heat-Resistant Adhesive Resins Derived from Bismaleimides and Bisnadimides Containing Amide Linkages

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Synopsis

A novel class of bismaleimides and bisnadimides containing amide linkages in their backbones were synthesized and characterized. The synthesis of these polymer precursors was carried out by reacting a diamine containing amide linkages with maleic/nadic anhydride. They were alternatively prepared by reacting the monomaleamic/monoadiamic acid of an aromatic diamine (1 mol) with terephthaloyl chloride (0.5 mol) and subsequent cyclodehydration. The latter new preparation method circumvented the hydrogeneration necessary in the first method of synthesis. The monomers were characterized by infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. Differential thermal analysis (DTA) of monomers showed that bisnadimide and bismethylnadimide were polymerized at lower temperatures than the corresponding bismaleimide. Thermogravimetric analysis (TGA) in nitrogen and air atmosphere revealed that all polymers were stable up to 321–363°C. Their char yield at 800°C under anaerobic conditions was 49–67%.

INTRODUCTION

A variety of matrix resins for composite materials have been developed, in particular of epoxy and polyimide type. Bismaleimides and bisnadimides derived from the reaction of maleic and nadic anhydride with diamines are important polymer precursors for preparation of processible and void-free heat-resistant polyimides having potential application as matrix resins. Several maleimide-[1-3] and nadimide-capped[4-6] prepolymers have been commercially developed for high temperature-resistant laminates. However, a serious disadvantage of these resins was their inherent brittleness because of high crosslinking. Therefore, there is a need for a polyimide binder that can be used as matrix for fiber-reinforced composites that possess an improved flexibility, retain favorable properties, and have thermal and thermooxidative stability.

In an effort to develop matrix resins with improved flexibility, several bismaleimides chain-extended by means of tetracarboxylic acid dianhydrides have been prepared recently.[7,8] In continuation of this attempt, we report here the synthesis of some bismaleimides and bisnadimides, the chain of which was extended by incorporating amide structures between the two maleimide and nadimide rings. Since the wholly aromatic amides have been proved to acquire a relatively high degree of heat-resistance, these extended polymer

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precursors should yield high temperature-resistant laminating resins by thermal polymerization. On the other hand, several modified bisnadimides were prepared because the strained bicyclic ring system undergoes thermal polymerization at relatively low temperatures.

A literature survey revealed that several bismaleimides containing amide linkages have been synthesized and polymerized recently. They have been prepared by reacting an aromatic diamine with 4-nitrobenzoylchloride and subsequent hydrogenation and reaction with maleic anhydride.[9] In addition, bismaleimide resins obtained from N,N'-m-phenylenebis(m-aminobenzamide) and maleic or methylmaleic anhydride have been synthesized and characterized.[10] It should be noted that the commercially available Technochemie M-751 resin is based on the poly(amide–maleimide) resin concept.[11]

EXPERIMENTAL

Instrumentation

Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrophotometer with KBr pellets. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained using a Varian T-60A spectrometer at 60 MHz with DMSO-d_6 as solvent. Chemical shifts (δ) are given in parts per million with tetramethylsilane as an internal standard.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a DuPont 990 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in N_2 atmosphere at a flow rate of 60 cm^3/min. 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.

Melting points were determined on an Electrothermal melting point apparatus IA6304 and are uncorrected.

Reagents and Solvents

Maleic anhydride (Merck) and 5-norbornene-2,3-dicarboxylic anhydride (nadic anhydride) (Merck) were purified by recrystallization from acetic anhydride and chloroform, respectively. Terephthaloyl chloride (Aldrich) was recrystallized from n-heptane before use. p-Phenylenediamine (Aldrich) was sublimed at about 110°C under vacuum (2–3 mm). 4,4'-Diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, and 4-aminophenyl ether (Aldrich) were purified by recrystallization from benzene, methanol, and acetonitrile, respectively. Methyl-5-norbornene-2,3-dicarboxylic anhydride (methyl nadic anhydride), 4-nitroaniline, and 4-nitrobenzoylchloride (Aldrich) were used as supplied. N,N-dimethylacetamide (DMAc) (Aldrich) was dried by refluxing and fractionally distilled from calcium hydride.

Preparation of Polymer Precursors

Preparation of Bismaleimide 1

4-Nitroaniline (3.7295 g, 27.0 mmol), DMAc (60 mL), and pyridine (1.9750 g, 25.0 mmol) were placed in a three-necked flask equipped with a magnetic

stirrer and a nitrogen inlet. To the stirred solution granular 4-nitroben-zoylchloride (4.6392 g, 25.0 mmol) was added portionwise. A yellow solid precipitated after 10 min. Stirring of the reaction mixture under nitrogen atmosphere at room temperature was continued for about 4 h. The reaction mixture was poured into water. The solid obtained was filtered, washed with a dilute solution of hydrochloric acid, then with water, and dried to yield 4,4'-dinitrobenzanilide[12] (3.95 g, 55%). This was purified by recrystallizations from glacial acetic acid. The sample obtained had mp 266–268°C (lit. 264°C).

Recrystallized 4,4'-dinitrobenzanilide (3.4755 g 12.1 mmol), absolute ethanol (40 mL), and a small quantity of catalyst, 10% palladium on carbon, were introduced in the hydrogenation flask of a Parr apparatus. The hydrogenation was carried out under a pressure of 3.5 atm at room temperature until no more hydrogen was taken up (~ 3 h). The initially heterogeneous reaction mixture became a homogeneous solution at the end of hydrogenation. After filtration of the catalyst and removal of the volatile components in a rotary evaporator the required 4,4'-diaminobenzanilide[12] was obtained as a brown solid (2.10 g, 76%). Recrystallizations from water afforded a purified sample with mp 202–204°C (lit. 204°C).

Granular maleic anhydride (2.3534 g, 24.0 mmol) was added portionwise to a stirred solution of recrystallized 4,4'-diaminobenzanilide (2.7270 g, 12.0 mmol) in DMAc (35 mL) under nitrogen atmosphere. The mixture was stirred at room temperature for 4 h. Bismaleamic acid was isolated as a pale yellow solid by pouring an aliquot of the reaction solution over crushed ice. Cyclodehydration was accomplished by adding acetic anhydride and fused sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) to the reaction solution and heating at 90°C for 2.5 h. The reaction mixture was poured over crushed ice to yield bismaleimide 1 as a brown solid. This was filtered, washed with a dilute solution of NaHCO$_3$, next with water, and dried (3.96 g, 78%).

Preparation of Bismaleimide 2 by Reacting
N,N'-Bis(4-aminophenyl)terephthalamide with Maleic Anhydride

4-Nitroaniline (3.5914 g, 26.0 mmol), DMAc (20 mL), and pyridine (1.8960 g, 24.0 mmol) were placed in a three-necked flask equipped with a magnetic stirrer, a dropping funnel, and a nitrogen inlet. Terephthaloyl chloride (2.4362 g, 12.0 mmol) dissolved in 12 mL of DMAc was added dropwise to the stirred solution. A yellow solid precipitated after a short period of time. The reaction mixture was stirred under nitrogen atmosphere at room temperature for about 4 h and subsequently poured into water. The solid obtained was filtrated, washed with a dilute solution of hydrochloric acid, next with a solution of Na$_2$CO$_3$, then with water, and dried to afford N,N'-bis(4-nitrophenyl)terephthalamide[13,14] (2.58 g, 53%) having mp 291–293°C (lit.[13] 295°C). It was purified by recrystallization from DMF-MeOH (2:1 vol/vol).

Recrystallized N,N'-bis(4-nitrophenyl)terephthalamide (4.1447 g, 10.2 mmol), DMAc (40 mL), and a small quantity of catalyst, 10% palladium on carbon, were introduced in a hydrogenation flask of a Parr apparatus. The hydrogenation was carried out under a pressure of 3.5 atm at room temperature and was completed after about 4 h. The compound was gradually dissolved in DMAc

during the progress of hydrogenation. The catalyst was removed by filtration and the filtrate was poured into water. The solid thus obtained was filtered, washed with water, then with acetone, and dried to yield N,N'-bis(4-amino-phenyl)terephthalamide[14] (2.46 g, 70%, mp 275–277°C). It was purified by recrystallization from DMF–MeOH (1 : 1 vol/vol).

To a stirred solution of recrystallized N,N'-bis(4-aminophenyl)terephthal-amide (3.5677 g, 10.3 mmol) in 25 mL of DMAc maleic anhydride (2.0396 g, 20.8 mmol) dissolved in 8 mL of DMAc was added portionwise under nitrogen atmosphere at room temperature. Stirring of the reaction solution was contin-ued for 4 h. Bismaleamic acid was isolated by pouring an aliquot of the reaction solution over crushed ice. It precipitated also upon stirring the reaction mixture for a long time ($\sim$ 48 h). Cyclodehydration was carried out by adding acetic anhydride and sodium acetate (300 mL and 27 g, respec-tively, per mol of water condensed) to the reaction solution and heating at 90°C for 2.5 h. The reaction mixture was poured into water. The solid obtained was filtered, washed with a dilute solution of $NaHCO_3$, then with water, and dried to yield bismaleimide 2 (3.85 g, 74%).

General Method for the Preparation of Polymer Precursors 2–7

Maleic or nadic or methylnadic anhydride (1 mol) dissolved in DMAc was added dropwise to a vigorously stirred solution of equimolar amount of diamine in DMAc under nitrogen atmosphere at ambient temperature. The solution was stirred for about 4 h under nitrogen atmosphere. Terephthaloyl chloride (0.5 mol) dissolved in DMAc was added dropwise to the stirred solution under nitrogen atmosphere at room temperature. Stirring was contin-ued in a stream of nitrogen for additional 3 h. In the case of bismaleimide 4, the reaction solution was heated at 65°C for 3 h. An aliquot of the reaction solution was poured into water in order to isolate the diamic acid formed. The pale yellow solid thus obtained was filtered, washed with water, and dried. To the remaining solution acetic anhydride and sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) were added to cyclodehydrate the diamic acid. The reaction mixture was heated at 90°C for 2.5 h. During this period the color of the mixture became dark brown. The polymer precursor was isolated by pouring the mixture over crushed ice. The brown solid thus obtained was filtered, washed with a dilute solution of $NaHCO_3$, then with water, and finally dried. The yields of monomers thus prepared varied from 73 to 90%.

General Method for Polymer Preparation

The polymer was obtained by heating the monomer isolated at 220°C for 2 h and subsequently at 260°C for 30–40 min. Polymer was alternatively prepared from diamic acid solution according to the following procedure: A solution of diamic acid in DMAc was heated in a shallow dish placed in a circulated air oven at 160°C for 30 min to evaporate the solvent. The temperature of the oven was subsequently raised to 220°C for 2 h and then to 260°C for 30–40 min.
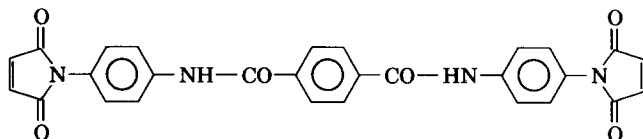
RESULTS AND DISCUSSION
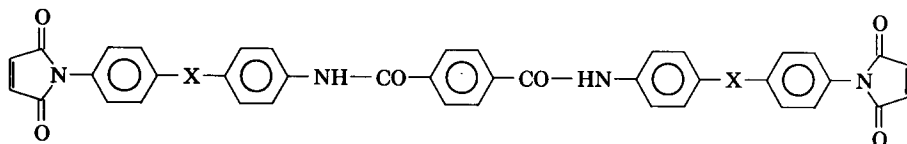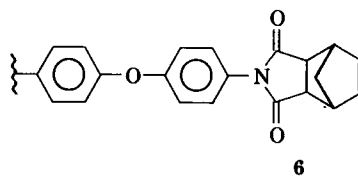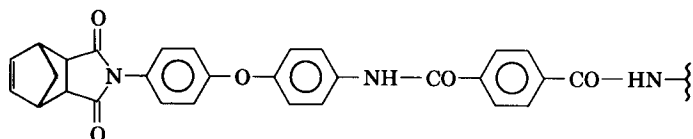
Polymer Precursors Synthesis

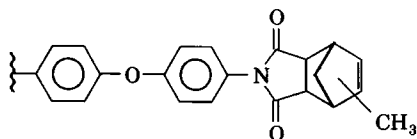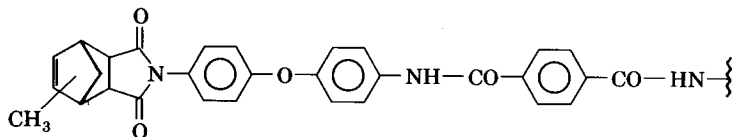The following bismaleimides and bisnadimides chain extended by amide structures were prepared and characterized:
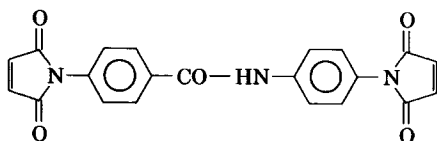
1

2

3: X = —CH$_2$—

4: X = —SO$_2$—

5: X = —O—

6

7

The structure of the above polymer precursors was selected in such a manner that their cured resins combine improved flexibility with a relatively high thermal and thermooxidative stability. The cured resins obtained from these polymer precursors are expected to be less brittle than those of the ordinary bismaleimides and bisnadimides because larger polymer segments would be available for internal motion. In addition, the presence of the flexible —NH—CO— linkages as well as of the flexible bridging groups such as —O—, —CH$_2$—, —SO$_2$— in the polymer backbone should reduce the brittleness of the cured resins. From observing the structure of the bismaleimides synthesized it is seen that the length of the bridge between the two maleimide groups varied by incorporating one or two amide linkages or by changing the structure of the diamine utilized for their preparation. On the other hand, the extended chain consisted of a wholly aromatic amide structure in order to make the cured resins sufficiently heat-resistant.

Bismaleimides 1 and 2 were synthesized according to the reaction sequence outlined in Scheme I. From this scheme it can be seen that the synthesis of bismaleimides 1 and 2 was based on the reactions of 4,4'-diaminobenzanilide[12] and N,N'-bis(4-aminophenyl)terephthalamide,[14] respectively, with maleic anhydride. These diamines were prepared by reacting 4-nitrobenzoylchloride or terephthaloyl chloride with 4-nitroaniline and subsequent reduction of the dinitro-intermediate. Reduction was accomplished by catalytic hydrogenation.
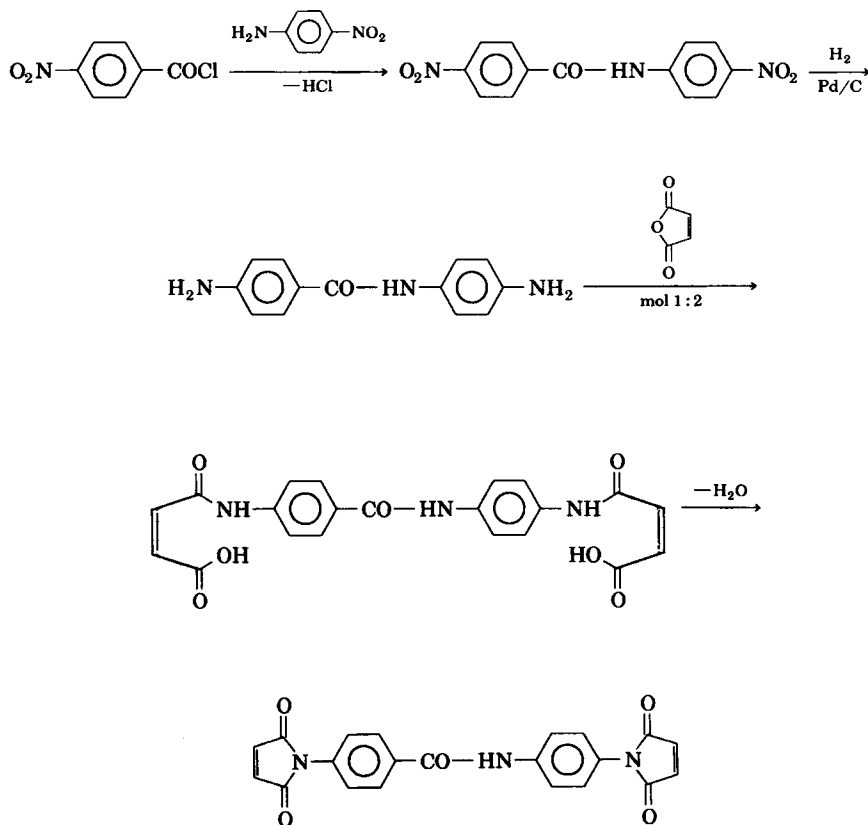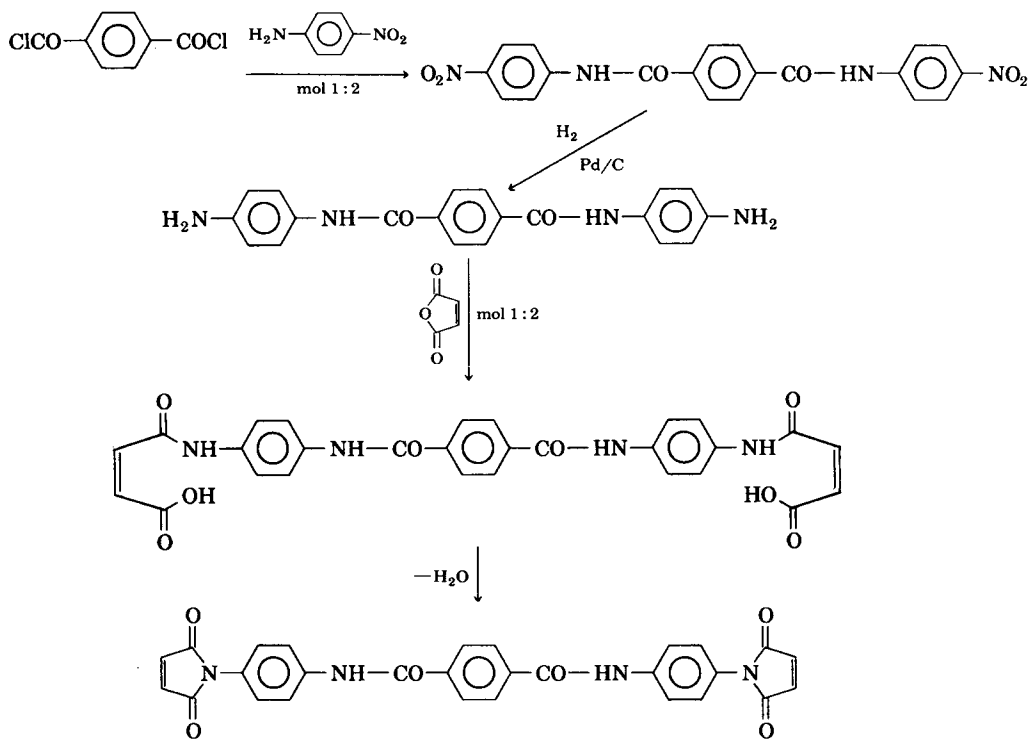
Scheme I

A new preparation method was developed for polymer precursors 2–7. This method could not be applied for preparing bismaleimide 1. As an example, the reaction sequence of Scheme II outlines this method for preparing bismaleimides 2–5:

Scheme II
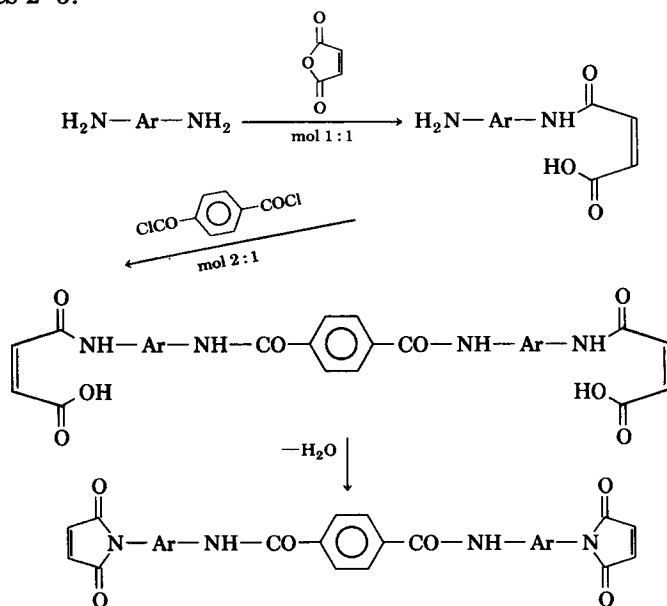
According to this method, the monomaleamic acid of a diamine was prepared at the first stage by adding a solution of maleic anhydride to a stirred solution of diamine at ambient temperature in an exact mol ratio 1 : 1. DMAc was used as reaction solvent, although several other polar aprotic solvents such as N,N-dimethylformamide (DMF) and N-methylpyrrolidinone (NMP) could be also used. The bismaleamic acid of diamine was not produced to a detectable amount under these conditions.[7]

At the second stage of this method, the monomaleamic acid of diamine reacted *in situ* with terephthaloyl chloride in mol ratio 2 : 1. The addition of an acid acceptor such as pyridine to the reaction mixture was not considered necessary. Polar aprotic solvents such as DMAc and NMP were employed as the reaction medium and acid acceptor.[15] It is well known that various amides have been prepared from analogous reactions utilizing DMAc as solvent without adding an acid acceptor.[16] It is reasonable to accept that at this stage terephthaloyl chloride preferred to react with the amino and not with the carboxylic group of the monomaleamic acid derived from diamine. The first reaction was spontaneous and more favored than the second one.

Cyclodehydration, the last stage of the preparation method, was carried out by thermal or chemical means. After thermal cyclodehydration, the product remained soluble in DMAc and its solution could be used for composite fabrication.

Scheme II outlines the method utilized for the preparation of bismaleimides 2–5. This method was also used for preparing bisnadimide 6 and bismethylnadimide 7. Evidently, this method is applicable for preparing all other monomers the chain of which can be extended by amidization of any aromatic or aliphatic dicarboxylic acid.

Bismaleimide 2 was prepared both by the synthetic route outlined in Scheme I and by that of Scheme II. Examination by IR and ^{1}H-NMR spectroscopy not only of these bismaleimides but also of the respective bismaleamic acids obtained from both methods showed that they were entirely identical.

It should be noted that the new preparation method outlined by Scheme II is very simple because it proceeded without isolation of the intermediate products. In addition, this method is time-saving and inexpensive since it avoids the hydrogenation necessary in the ordinary route of synthesis.[9,10] Furthermore, this method afforded pure products in relatively high yields (73–90%).

Polymer Precursors Characterization

From the literature[17,18] it is known that the IR spectra of polyamic acids, intermediate products for preparing polyimides, show absorption bands around 3280, 3070, 1560, and 1270 cm^{-1}. On the other hand, secondary amides absorb also in these regions. Particularly, the latter exhibit absorption bands at 3320–3070 (bonded NH stretching vibrations), 1550–1510 cm^{-1} (amide II), and near 1270 cm^{-1} (amide III). Figure 1 presents the IR spectra of bismaleimide 2 and the corresponding bismaleamic acid. Both spectra showed absorption bands in the aforementioned spectrum regions. However, bismaleimide exhibited several characteristic absorptions assigned to the imide structure at 1788 (imide I), 1170 (imide III), and 705 cm^{-1} (imide IV). In
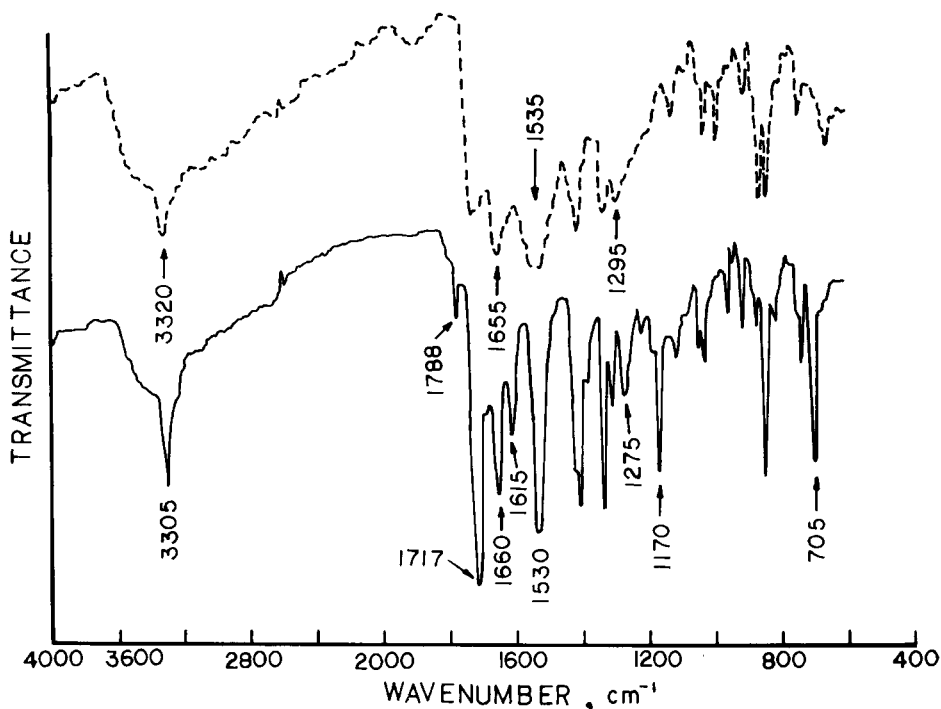
Fig. 1. IR spectra of bismaleimide 2 (———) and the corresponding bismaleamic acid (---).

addition, bismaleimide lacked the broad absorption at 3000–2500 cm^{-1} associated with the carboxylic OH stretching vibration. Consequently, the imidization could be monitored by IR spectroscopy on the basis of the characteristic absorptions at 1788, 1170, and 705 cm^{-1} and the elimination of the broad absorption at 3000–2500 cm^{-1}. The strongest absorption band in the IR spectrum of bismaleimide 2 at 1717 cm^{-1} was attributed to the imide carbonyl. The amide carbonyl absorbed at 1660 cm^{-1}. The strong absorption at 1530 cm^{-1} was assigned to a combination of NH deformation and C—N stretching vibrations. Finally, the sharp absorption band at 1615 cm^{-1} was attributed to the C=C stretching vibration. The important IR absorptions of all monomers synthesized are listed in Table I.

TABLE I
Characteristic IR-Spectral Absorptions of Monomers

Sample	KBr (cm^{-1})			
	Amide structure	Imide structure	Aromatic ring	Olefinic bond
1	3450–3210, 1670, 1527	1788, 1722	1590, 1515	1605
2	3355–3220, 1660, 1530	1788, 1717	1612, 1525	1615
3	3380–3205, 1660, 1528	1780, 1718	1588, 1515	1605
4	3370–3230, 1673, 1530	1790, 1720	1597, 1500	1618
5	3360–3210, 1665, 1540	1775, 1723	1598, 1510	1610
6	3425–3235, 1667, 1542	1778, 1725	1602, 1518	1612
7	3390–3217, 1662, 1538	1785, 1723	1588, 1517	1615

TABLE II
^{1}H-NMR Spectral Data of Diamic Acids

Diamic acid	Chemical shifts (δ^a ppm) and assignments
1	10.60(b,[b] 2H, —COOH), 9.60–9.20 (bs,[c] 3H, —CONH—), 8.15 (m,[d] 2H, aromatic ortho to —CO—), 7.70–7.25 (m, 6H, aromatic ortho to —NH—), 6.50 (m, 4H, olefinic)
2	10.70 (b, 2H, —COOH), 9.20–8.90 (b, 4H, —CONH—), 8.25 (s, 4H, aromatic of terephthalic ring), 7.70–7.30 (m, 8H, aromatic ortho to —NH—), 6.50 (m, 4H, olefinic)
3	10.60 (b, 2H, —COOH), 8.90 (b, 4H, —CONH—), 8.05 (s, 4H, aromatic of terephthalic ring), 7.40 (m, 8H, aromatic ortho to —NH—), 6.90 (m, 8H, aromatic ortho to —CH$_2$—), 6.45 (m, 4H, olefinic)
4	10.80 (bs, 2H, —COOH), 8.80–8.40 (b, 4H, —CONH—), 8.20–7.80 (m, 4H, aromatic of terephthalic ring and 8H, aromatic ortho to —SO$_2$—), 7.60–7.20 (m, 8H, aromatic ortho to —NH—), 6.40 (m, 4H, olefinic)
5	10.50 (b, 2H, —COOH), 8.60 (b, 4H, —CONH—), 8.10 (s, 4H, aromatic of terephthalic ring), 7.45 (m, 8H, aromatic ortho to —NH—), 7.10–6.50 (m, 8H, aromatic ortho to —O— and 4 H, olefinic)
6	10.45 (b, 2H, —COOH), 9.10–8.80 (b, 4H, —CONH—), 8.20 (s, 4H, aromatic of terephthalic ring), 7.50–7.20 (m, 8H, aromatic ortho to —NH—), 6.90 (m, 8H, aromatic ortho to —O—), 6.20 (m, 4H, olefinic), 3.50–3.10 (m, 8H, aliphatic of nadimide ring), 2.10 and 1.50 (s, 4H, methylene of nadimide bridge)
7	10.40 (b, 2H, —COOH), 9.10 (b, 4H, —CONH—), 8.15 (s, 4H, aromatic of terephthalic ring), 7.30 (m, 8H, aromatic ortho to —NH—), 6.80 (m, 8H, aromatic ortho to —O—), 5.90 (bm,[e] 4H, olefinic), 3.40–2.80 (m, 6H, aliphatic of nadimide ring), 2.00–1.20 (bm, 4H, methylene of nadimide bridge and 6H, methyl)

^{a} In DMSO-d$_6$ solution.
^{b} Broad.
^{c} Broad singlet.
^{d} Multiplet.
^{e} Broad multiplet.

Interpretable NMR spectra of the isolated bismaleimides or bisnadimides could not be recorded because of their insolubility even in polar aprotic solvents. However, intermediate diamic acids showed a relatively high solubility and therefore their ^{1}H-NMR spectra were recorded from DMSO-d$_6$ solution. The results are tabulated in Table II. The carboxylic and amide —NH— protons appeared at 10.80–10.40 and 9.60–8.40 δ, respectively, and were exchangeable with D$_2$O. From Table II it can be seen that the aromatic protons ortho to amide carbonyl exhibited a downfield shift compared to that of the other aromatic protons. This behavior was attributed to the deshielding effect of the strong electron-withdrawing carbonyl group.[19] In bismaleamic acid 4, the aromatic protons ortho to the —SO$_2$— group behaved in a similar manner. On the other hand, all diamic acids showed a peak around 6.50 δ associated with the olefinic protons, which clearly indicated the presence of maleimide or nadimide or methylnadimide group.

Curing Behavior of Polymer Precursors

The monomers synthesized did not show any definite melting point when heated in a capillary tube. A crosslinked network structure was obtained by heating the polymer precursors at 200–330°C. To investigate the curing
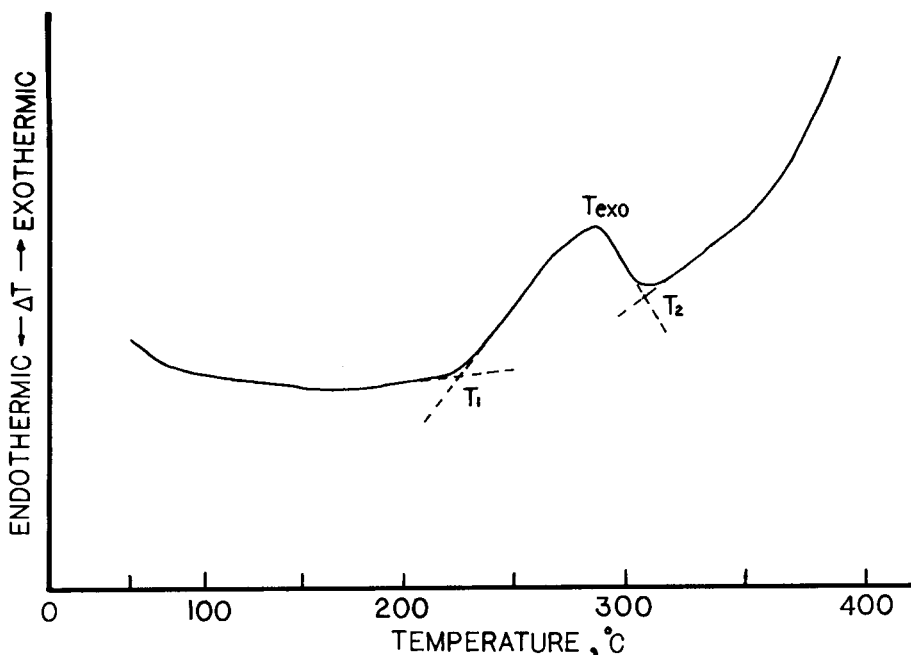
Fig. 2.   DTA trace of bismaleimide 3 in N_2 atmosphere.

behavior, thermal scans of monomers were performed using DTA in nitrogen atmosphere. Figure 2 presents typical DTA thermogram of bismaleimide 3. The first exotherm is believed to be due to thermally induced polymerization reaction. The large exotherm which follows is due to pyrolysis of the cured bisimide.

To compare the curing behavior of monomers, several thermal characteristics were determined from their DTA traces. Particularly, the onset temperature (T_1) for the polymerization reaction, the exothermic peak temperature (T_{exo}), and the temperature for completion of polymerization (T_2) were determined. The T_1 and T_2 were obtained by extrapolating the front side and the back side of the exothermic peak, respectively, to the base line (Fig. 2). The results are listed in Table III. The relative reactivity of monomers may be judged on the basis of T_{exo} values. It is seen that bismaleimide 1 containing the shortest bridge between the two polymerizable maleimide groups showed the lowest curing temperature. Thus, the polymerization of monomers was shifted to higher temperatures when the concentration of olefinic bonds was reduced. Comparison of the T_{exo} of bismaleimides 3, 4, and 5 showed that monomer 4 derived from 4,4'-diaminodiphenylsulfone was polymerized at a relatively high temperature. It may, therefore, be concluded that the presence of electron-withdrawing groups such as $-SO_2-$ in the monomer chain increased the curing temperature and reduced the reactivity of the maleimide olefinic bonds. This behavior confirms literature data.[9] On the other hand, comparison of the T_{exo} values of monomers 5, 6, and 7 revealed that the relative reactivity of the olefinic bonds decreased in the following order:

bismethylnadimide > bisnadimide > bismaleimide

TABLE III
Curing Temperatures of Monomers

Sample	T_1^a (°C)	T_{exo}^b (°C)	T_2^c (°C)
1	197	225	249
2	215	236	261
3	224	286	308
4	235	303	331
5	221	290	324
6	237	262	288
7	206	227	234

[a] Onset temperature of polymerization.
[b] Exothermic peak temperature.
[c] Temperature of completion of polymerization.

Bisnadimide was more readily polymerized than the corresponding bis-maleimide because the strained bicyclic ring system underwent thermal polymerization at relatively low temperatures. In the case of bismethylnadimide, the presence of the electron-donating methyl group increased, moreover, the reactivity of the olefinic bond.[20]

On the basis of the DTA results, cured resins were obtained from the diamic acid solution by evaporation of the solvent and subsequent cyclodehydration and polymerization. The cured resins obtained from monomers 1–7 are referred to by the designations 1'-7', respectively.

Thermal Properties of Polymers

The thermal and thermooxidative stability of the cured resins was ascertained by dynamic thermogravimetric analysis in nitrogen and air atmosphere. Figure 3 shows primary TGA thermograms of the cured resins in nitrogen. The temperature of initial weight loss (TIWL), the maximum polymer decomposition temperature (PDT_{max}) both in N_2 and air atmospheres as well as the temperature of complete pyrolysis (TCP) and the char yield (Y_c) at 800°C in anaerobic conditions were determined from the TGA traces and are listed in Table IV. In some cases, the TGA curve exhibited two degradation steps, and therefore two values of PDT_{max} were determined. It can be seen that the aforementioned characteristics of the cured resins did not differ remarkably by changing the chemical structure of the polymer precursors. This suggests that the pyrolysis of polymers proceeded mainly by scission of the $-NH-CO-$ segments and was not affected significantly by the chemical structure of the aromatic diamine utilized for monomer preparation.

It is seen that polymer 1' was thermally more stable than polymer 2' because its monomer contained only one amide linkage. In addition, all polymers obtained from bismaleimides, with exception of 4', afforded almost the same char yield (56–67%) under anaerobic conditions. Polymers 6' and 7' derived from bisnadimide and bismethylnadimide, respectively, were less thermally stable than those obtained from bismaleimides and afforded lower char yield in N_2. It is well known that cyclopentadiene or methylcyclopentadiene are evolved by retrograde Diels–Alder reaction when nadimides or
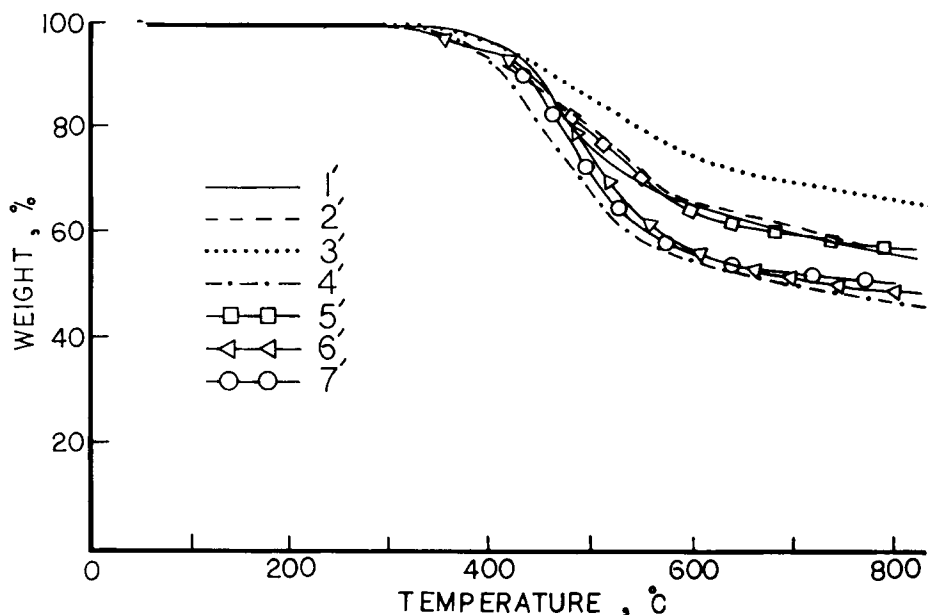
Fig. 3. TGA thermograms of polymers in N_2 atmosphere: (—) 1′; (---) 2′; ($\cdots$) 3′; (-·-) 4′; (-□-) 5′; (-◁-) 6′; (-○-) 7′.

TABLE IV
Thermal and Thermooxidative Stability of Polymers

	In N_2				In air		
Polymer	TIWL[a] (°C)	PDT$_{max}$[b] (°C)	TCP[c] (°C)	Y_c[d] (%)	TIWL (°C)	PDT$_{max}$ (°C)	$\dfrac{\text{TIWL}_{air}}{\text{TIWL}_{N_2}}$
1′	363	487	546	56	357	494, 577	0.98
2′	344	462, 565	590	56	341	575	0.99
3′	337	480, 562	610	67	338	539	1.00
4′	334	456	550	50	333	485	1.00
5′	345	465, 553	608	57	340	550	0.99
6′	322	504	578	49	324	522	1.01
7′	321	487	556	50	324	493	1.01

[a] Temperature of initial weight loss.
[b] Maximum polymer decomposition temperature.
[c] Temperature of complete pyrolysis.
[d] Char yield at 800°C.

methylnadimides are heated at about 300–400°C, but most of them are captured by copolymerization.[21]

The ratio of the temperature of initial weight loss in air to that in nitrogen atmosphere ($\text{TIWL}_{air}/\text{TIWL}_{N_2}$) varied from 0.98 to 1.01. This supports that decomposition was not seriously affected by the presence of oxygen. Interestingly, Table IV points out that in most cases the PDT$_{max}$ in air was higher than that in N_2. However, all cured resins were pyrolyzed almost completely when heated beyond 600–700°C in air.
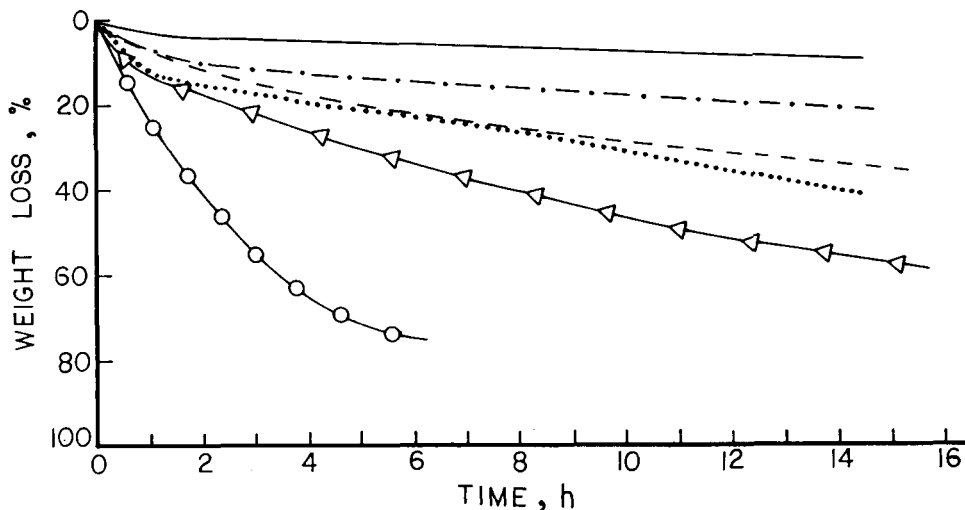
Fig. 4.   IGA traces of polymer 1' in N_2 at 310 (—), 360 (— · —) and 400°C (· · ·) as well as in air at 300 (— — —), 330 (-◁-), and 370°C (-○-).

The thermal and thermooxidative stability of polymer 1' was, furthermore, evaluated by isothermal gravimetric analysis (IGA). Figure 4 presents the IGA traces of this polymer in nitrogen at 310, 360, and 410°C as well as in air at 300, 330, and 370°C. A weight loss 9.21 and 21.05% was observed by isothermal aging of this polymer in N_2 for 14 h at 310 and 360°C, respectively.

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