

# High Temperature Laminating Resins Based on Maleimido End-Capped Pyromellitimide

JOHN A. MIKROYANNIDIS\* and ANASTASIOS P. MELISSARIS, *Chemical Technology Laboratory, Department of Chemistry, University of Patras, Patras 260 01, Greece*

## Synopsis

A novel class of bismaleimides, biscitraconimides, and bisdichloromaleimides chain-extended by pyromellitimide was prepared and characterized by infrared and proton nuclear magnetic resonance spectroscopy. These polymer precursors were prepared by reacting maleic/citraconic/dichloromaleic anhydride (1 mol) with an equimolar amount of a diamine and subsequently with pyromellitic dianhydride (0.5 mol). The tetraamic acid formed was cyclodehydrated by chemical or thermal means. The curing behavior of polymer precursors was investigated by differential thermal analysis. Bismaleimide was thermally polymerized at a relatively higher temperature than the corresponding biscitraconimide and at lower temperature than bisdichloromaleimide. The curing temperature of monomers fluctuated between 209 and 318°C. Dynamic thermogravimetric analysis of the cured aromatic resins showed that they were approximately stable up to 370°C both in nitrogen and air. Their char yield was 53–63% at 800°C under anaerobic conditions. The relative thermal stability of the cured resins, with respect to the diamine utilized for imidization, was of the order *p*-phenylenediamine > 4-aminophenyl ether > 4,4'-diaminodiphenylmethane > 4,4'-diaminodiphenylsulfone > hexamethylenediamine. In addition, the thermal and thermooxidative stability of polymers was ascertained by isothermal gravimetric analysis.

## INTRODUCTION

Considerable interest exists in the use of high-strength lightweight composites which are replacing metals in many engineering applications. The polymer used as a binder in these composites is most commonly an epoxy, although several other resins such as phenolic, novolac, poly(ether sulfone), polyphenylsulfone, polyester, and bismaleimides have also been used for certain applications. Bismaleimides<sup>1-13</sup> are thermally polymerized to rigid polymers which can be used as matrix resins. However, these were found to be inherently brittle because of the extensive crosslinking that occurs during polymerization.

In an effort to overcome this problem, Kovacic<sup>14</sup> reported the reaction of amine-capped liquid elastomeric prepolymers with bismaleimides to afford polymers. However, they did not exhibit the required degree of heat resistance. Kumar et al.<sup>15</sup> prepared linear low-molecular-weight preimidized precursors which can be thermally polymerized. These precursors were synthesized by an addition reaction of bismaleimide (1 mol) with an aromatic diamine (2 mol). Recently, Varma et al.<sup>16</sup> investigated the polymerization of several bismaleimides in the presence of aromatic diamines. The resins ob-

\* Address for correspondence: Navmahias Ellis 48-52, Patras 26441, Greece.

tained exhibited better mechanical properties but could not be considered heat resistant because of the thermally sensitive —NH— linkages.

In connection with our interest in development of new high-temperature composite matrix resins with improved flexibility,<sup>17</sup> we carried out the synthesis and characterization of several bismaleimides containing a pyromellitimide structure between the two polymerizable maleimido groups. The cured resins obtained from these polymer precursors should be less brittle compared with those of regular bismaleimides because of the extended polymer chain. In addition, the incorporation of a pyromellitimide unit between the maleimido groups should not reduce the extraordinary heat resistance of these polymers due to the inherent thermal and oxidative stability of the pyromellitimide structure. However, the structural modification of the regular bismaleimides by a pyromellitimide should not be superior than that attained by a imidized benzophenone tetracarboxylic dianhydride<sup>17</sup> from the aspect of resin flexibility due to the higher rigidity of the former.

### EXPERIMENTAL

Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrophotometer with KBr pellets. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were obtained using a Varian T-60A spectrometer at 60 MHz. Chemical shifts ( $\delta$ ) 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 thermal analyzer system. DTA measurements were made using a high temperature (1200°C) cell in an N<sub>2</sub> atmosphere at a flow rate of 60 cm<sup>3</sup>/min. TGA measurements were made at a heating rate of 20°C/min in atmospheres of N<sub>2</sub> or air at a flow rate of 60 cm<sup>3</sup>/min.

### Reagents and Solvents

Pyromellitic dianhydride (PMDA) and maleic anhydride (Merck) were purified by recrystallization from acetic anhydride. Citraconic anhydride (Aldrich) was distilled under reduced pressure (bp 100°C/15 mm). Dichloromaleic anhydride (Aldrich) was recrystallized from *n*-hexane. *p*-Phenylenediamine (Aldrich) was sublimed at about 110°C under vacuum (2–3 mm). 4-Aminophenyl ether, 4,4'-diaminodiphenylmethane, and 4,4'-aminodiphenylsulfone (Aldrich) were purified by recrystallization from acetonitrile, benzene, and methanol, respectively. Hexamethylenediamine (Merck) was used as supplied. *N,N*-dimethylacetamide (DMAc) (Aldrich) and dimethyl sulfoxide (DMSO) (Merck) were refluxed in the presence of calcium hydride and then distilled under reduced pressure.

### Synthesis of Polymer Precursors

To a vigorously stirred solution of diamine in DMAc under nitrogen atmosphere, an equimolar amount of maleic anhydride dissolved in DMAc was added dropwise at ambient temperature. The solution was stirred for about 4 h under nitrogen atmosphere. A half-molar amount of PDMA dissolved in DMAc was added dropwise to the stirred solution and stirring was

continued for another 5 h in a stream of nitrogen. One-half of the solvent was removed from an aliquot of the reaction solution under reduced pressure, and the residue was poured into water. The solid thus obtained was filtered, washed with water, and dried to afford the tetraamic acid for characterization. To the remaining solution, acetic anhydride, and sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) were added in order to cyclodehydrate the tetraamic acid by chemical means. The reaction mixture was heated at 90°C for 3 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 repeatedly with a dilute solution of sodium bicarbonate, then with water, and finally dried at about 60°C overnight.

DMSO instead of DMAc was used as reaction solvent for all stages only for preparing bismaleimide 7. Yields of monomers thus prepared were 65–93%.

### Polymer Preparation

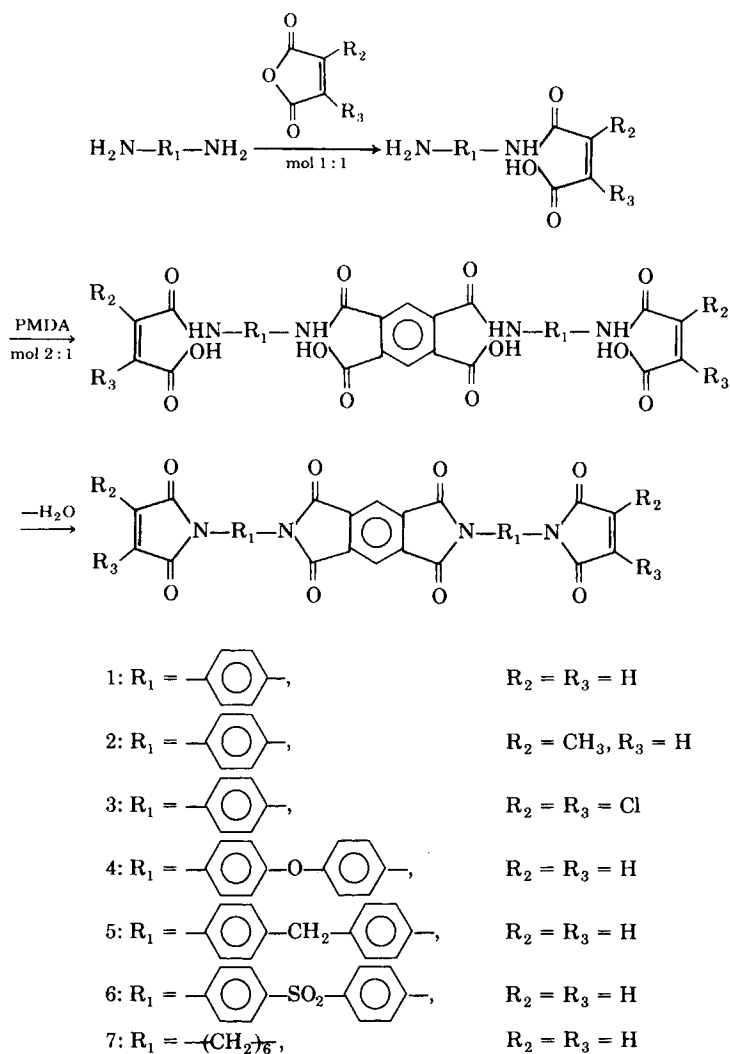
A solution of tetraamic acid in DMAc was heated in a shallow dish placed into a circulated air oven at 160°C for 30 min in order to evaporate the solvent. The temperature of the oven was next quickly raised to 230°C for 2 h and then at 280°C for 40 min. The polymer was alternatively prepared by heating the isolated bismaleimide at 230°C for 2 h and then at 280°C for 40 min.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of Monomers

A series of novel bismaleimides or their substituted derivatives as bis-citraconimides and bisdichloromaleimides was prepared according to the reaction sequences shown in Scheme I

The reaction of diamine with an equimolar amount of maleic or citraconic or dichloromaleic anhydride afforded almost exclusively the monomaleamic acid or its substituted derivative of diamine. The corresponding bismaleamic acid of diamine was not formed to a detectable amount when the anhydride was added portionwise to the stirred solution of diamine.<sup>17</sup> The reaction proceeded readily at ambient temperature and was slightly exothermic. The temperature range of 20–50°C was found to be suitable. The preferred temperature range was 20–30°C. The tetraamic acid was prepared subsequently by reacting with PMDA *in situ*. This reaction was not exothermic and seemed to be slower than that of the first stage. Such behavior should be attributed to the lower basicity of the monomaleamic acid of diamine compared with that of diamine. Additional hours of stirring at room temperature ensured the completion of reaction. The order of addition might be inverse at the second reaction. However, the anhydride was preferred to added gradually to the amine solution. These reactions took place utilizing DMAc as solvent. Other aprotic solvents such as DMSO, *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidinone (NMP) could be also used. In the case of bismaleimide 7, DMSO was used as reaction solvent because the monomaleamic acid of hexamethylenediamine was insoluble in DMAc. The reagent concentrations



Scheme I.

might be varied in such a way that the concentration of the tetraamic acid produced was between 20 and 30%.

The tetraamic acids did not precipitate in a satisfactory yield by pouring a part of the reaction solution into water or other nonsolvents. Therefore, about one-half of the solvent was removed from an aliquot of the reaction solution under reduced pressure and the residue was poured into water. The yellow solids thus obtained were found to be the required tetraamic acids. Their characterization by IR and  $^1\text{H-NMR}$  spectroscopy is discussed below.

The tetraamic acids were cyclodehydrated *in situ* to the corresponding imides by chemical or thermal means. The chemical cyclodehydration was performed with acetic anhydride and sodium acetate. Pyridine might also be used instead of sodium acetate. The chemical cyclodehydration could not be completed at ambient temperature. Therefore, the reaction mixture was

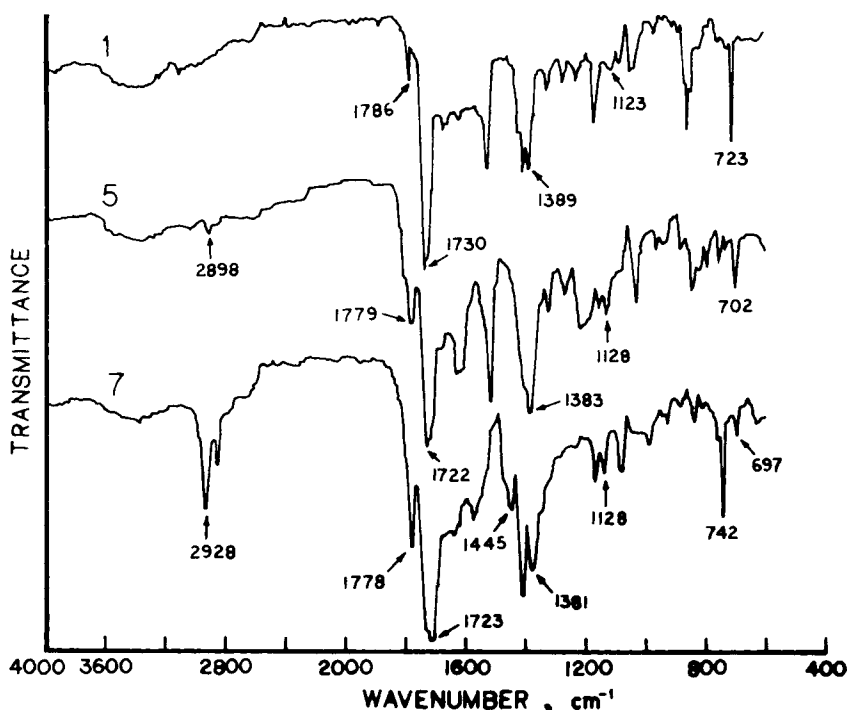


Fig. 1. IR spectra of monomers 1 (top), 5 (middle) and 7 (bottom).

heated at 90°C for a sufficient time (~ 3 h). This method may be considered as a combination of chemical and thermal imidization. To accelerate cyclodehydration, a 50% excess of acetic anhydride was added to the tetraamic acid solution. The thermal imidization method was the most efficient and convenient. This method included refluxing of the tetraamic acid solution in DMAc for about 2.5 h. The cyclodehydration occurred was followed by <sup>1</sup>H-NMR spectral measurements. Particularly, refluxing of the tetraamic acid solution was continued until the peaks at 10.70–10.50  $\delta$  associated with the carboxylic protons disappeared completely. The solution thus obtained after imidization could be used for composite fabrication.<sup>12</sup>

The IR spectra of the amic acids isolated showed absorption bands at 3278–3255, 3062–3040, 1558–1548, and 1280–1275  $\text{cm}^{-1}$  assigned to the amic

TABLE I  
Important IR-Spectral Absorptions of Monomers ( $\text{cm}^{-1}$ )

Sample	Imide structure	Olefinic bond	Aromatic ring	Other structures
1	1786, 1730, 1389, 1123, 723	1605	1531, 1593, 1495	
2	1787, 1724, 1388, 1119, 703	1611	1522, 1596, 1498	2915, 1439 (C—CH <sub>3</sub> )
3	1783, 1726, 1387, 1120	1622	1518, 1596, 1497	726 (C—Cl)
4	1782, 1729, 1378, 1121, 692, 704	1610	1520, 1598, 1494	1253 (aromatic ether)
5	1779, 1722, 1383, 1128, 702	1604	1517, 1589, 1493	2898, 1440 (Ph—CH <sub>2</sub> —Ph)
6	1785, 1732, 1377, 1122, 708	1620	1508, 1592, 1488	1341, 1165 (—SO <sub>2</sub> —)
7	1778, 1723, 1381, 1128, 697	1623	1522, 1580, 1484	2928, 1445, 742 [—(CH <sub>2</sub> ) <sub>6</sub> —]

TABLE II  
<sup>1</sup>H-NMR Spectral Data of Tetraamic Acids

Tetraamic acid	Chemical shifts ( $\delta^a$ , ppm) and assignments
1	10.65 (b, 4H, —COOH); 8.30–7.80 (bm, <sup>c</sup> 4H, —CONH— and 2H aromatic of PDMA ring); 7.50 (m, 8H, aromatic ortho to —NH); 6.70 (m, 4H, olefinic)
2	10.50 (bs, <sup>d</sup> 4H, —COOH); 8.40 (b, 4H, —CONH—); 8.10–7.40 (m, 2H, aromatic of PMDA ring and 8H, aromatic ortho to —NH—); 6.10 (m, 2H, olefinic); 2.20 (s, 6H, —CH <sub>3</sub> )
3	10.60 (b, 4H, —COOH); 8.40 (b, 4H, —CONH—); 8.00–7.50 (m, 2H, aromatic of PMDA ring and 8H, aromatic ortho to —NH—)
4	10.70 (b, 4H, —COOH); 8.70 (b, 4H, —CONH—); 8.30 (s, 2H, aromatic of PMDA ring); 7.60 (m, 8H, aromatic ortho to —NH—); 7.00 (m, 8H, aromatic ortho to —O—); 6.45 (m, 4H, olefinic)
5	10.60 (b, 4H, —COOH); 8.50 (b, 4H, —CONH—); 8.20–7.60, (m, 2H, aromatic of PMDA ring and 8H, aromatic ortho to —NH—); 6.95 (m, 8H, aromatic ortho to —CH <sub>2</sub> —); 6.50 (m, 4H, olefinic); 3.60 (s, 4H, —CH <sub>2</sub> —)
6	10.70 (b, 4H, —COOH); 8.50 (b, 4H, —CONH—); 8.30–7.80 (m, 2H, aromatic of PMDA ring and 8H, aromatic ortho to —SO <sub>2</sub> —); 7.40 (m, 8H, aromatic ortho to —NH—); 6.50 (m, 4H, olefinic)
7	10.55 (b, 4H, —COOH); 7.90 (s, 2H, aromatic of PMDA ring); 7.00–6.20 (bm, 4H, —CONH— and 4H, olefinic); 3.10 (m, 8H, —NHCH <sub>2</sub> —); 1.60–1.20 (m, 16H, —NHCH <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> —)

<sup>a</sup>In DMSO-*d*<sub>6</sub> solution.

<sup>b</sup>Broad.

<sup>c</sup>Broad multiplet.

<sup>d</sup>Broad singlet.

acid structure. Typical IR spectra of bismaleimides 1, 4, and 7 for the synthesis of which *p*-phenylenediamine, 4,4'-diaminodiphenylmethane, and hexamethylenediamine were utilized, respectively, are shown in Figure 1. The important IR band assignments for all the polymer precursors synthesized are listed in Table I. All spectra showed the absence of the bands characteristic of the amic structure; instead, new strong absorption bands at 1787–1778 and 1732–1718 cm<sup>-1</sup> (imide-I), 1389–1377 cm<sup>-1</sup> (imide-II), 1128–1119 cm<sup>-1</sup> (imide-III), and 708–697 cm<sup>-1</sup> (imide-IV) were observed, indicating the completion of imidization reaction. These observations demonstrated that the progress of imidization could be followed also by IR spectroscopy. The imide-I band is attributed to the stretching vibrations of two carbonyls that are weakly coupled. Imides-II, -III, and -IV bands have been assigned to axial, transverse, and out-of-plane vibrations of cyclic imide structure. The weak band at about 1680 cm<sup>-1</sup> observed in the IR spectra of some monomers indicated a small formation of the corresponding isoimide structure.

The structure of the tetraamic acids isolated was assigned not only with IR but also with <sup>1</sup>H-NMR spectroscopy. The <sup>1</sup>H-NMR spectral data for all tetraamic acids are summarized in Table II. The inequality of the carboxylic protons resulting from the reaction of maleic or citraconic anhydride with diamine and those arising from the reaction of pyromellitic dianhydride with diamine along with the presence of possible isomers contributed to the broad appearance of their peaks. The —NH—CO— protons of monomer 7 reso-

nated at about 7.00  $\delta$  whereas those of the other monomers resonated at 8.70–8.30  $\delta$ . This differentiation of the chemical shifts of the —NH—CO— protons is encountered in secondary aliphatic and aromatic amides. The aromatic protons of the PMDA ring resonated at a relatively downfield value (8.30–7.80  $\delta$ ) compared with that of the other aromatic protons. Such behavior is attributed to the deshielding of these protons due to the presence of the strong electron-withdrawing carbonyl groups.<sup>18</sup> In the case of tetraamic acid 6, the aromatic protons ortho to SO<sub>2</sub> resonated at about 7.80  $\delta$  for the same reason. From Table II it can be seen that the olefinic protons of biscitraconimide 2 showed a relatively upfield value compared with that of the olefinic protons of bismaleimide 1 due to the presence of the electron-donating methyl group.

### Curing Behavior of Monomers

The polymer precursors did not show any sharp melting point in a capillary tube because they were crosslinked upon gradual heating. To investigate the curing behavior, DTA thermograms were recorded in nitrogen. Broad exothermic peaks were observed in the temperature range of 209–318°C. These exotherms are believed to be due to thermally induced polymerization reactions because the DTA thermograms of the cured resins did not show exotherms in the same temperature range. The temperature of the first energy release  $T_i$  (start of polymerization), the exothermic peak position  $T_{exo}$ , and the temperature of termination of polymerization  $T_f$  were determined from the DTA traces and are listed in Table III. It can be seen that the temperature of exothermic peak position was affected by the presence of substituents in the olefinic bond. Thus the  $T_{exo}$  of biscitraconimide 2 was 21°C lower than that of the corresponding bismaleimide 1. In contrast, the  $T_{exo}$  of bisdichloromaleimide 3 was 10°C higher than that of bismaleimide 1. The  $T_i$  and  $T_f$  showed the same trend. It can be seen that bismaleimides 4, 5, and 6 are polymerized at relatively higher temperatures compared with that of bismaleimide 1. Thus, the exotherm was shifted to higher temperatures as the concentration of the olefinic bonds in the monomers was reduced. Consequently, the modification of bismaleimides by chain extension may improve the flexibility of their cured resins, but the modified bismaleimides require higher temperatures to be polymerized through the olefinic bonds.

Cured resins were obtained either by heating the monomer isolated or from the tetraamic acid solution by evaporation of the solvent and subsequent imidization and polymerization. The polymers obtained by applying these methods on the same compound exhibited almost identical thermal characteristics. Note that the isolation of bismaleimides or their substituted derivatives was performed for the purpose of structure characterization and investigation of the curing behavior. To fabricate composites, one can cyclodehydrate the tetraamic acid by refluxing its solution in DMAc or other aprotic solvent and then prepare laminates by coating graphite cloth or glass fabric with this solution.<sup>12</sup>

Curing of monomers 1–7 according to the procedure described in the Experimental section afforded the respective crosslinked resins 1'–7'. Throughout the text these resins are referred to by their notations.

TABLE III  
 DTA Results of Various Monomers

Sample	$T_i$ (°C) <sup>a</sup>	$T_{exo}$ (°C) <sup>b</sup>	$T_f$ (°C) <sup>c</sup>
1	223	268	290
2	209	247	262
3	256	278	296
4	238	273	307
5	261	292	309
6	266	297	318
7	237	256	273

<sup>a</sup>Temperature of starting of polymerization.

<sup>b</sup>Temperature of exothermic peak position.

<sup>c</sup>Temperature of termination of polymerization.

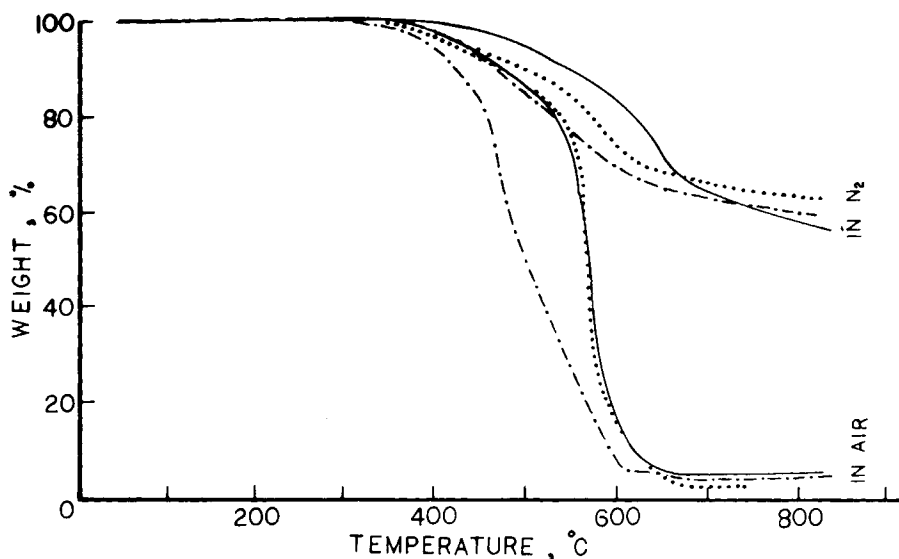


Fig. 2. TGA thermograms of polymers 1' (—), 2' (---), and 3' (···) in  $N_2$  and air atmosphere.

### Evaluation of Thermal and Thermo-Oxidative Stability of Cured Resins

Thermal stability of cured resins was evaluated by TGA and isothermal gravimetric analysis (IGA). Typical TGA thermograms in nitrogen and air are shown in Figures 2 and 3. The initial decomposition temperature (IDT) obtained by extrapolation, the maximum polymer decomposition temperature ( $PDT_{max}$ ) both in  $N_2$  and air as well as the temperature of complete pyrolysis (TCP) and the char yield ( $Y_c$ ) at 800°C under anaerobic conditions are listed in Table IV. TCP was determined by the intersection of the tangent to the steepest portion of the TGA curve with its strain-line part after the polymer degradation. From the TGA curves it can be seen that all polymers, with the exception of 7', were approximately stable up to 370°C, even in air. Beyond that temperature, however, they started losing weight. Polymer 2', obtained



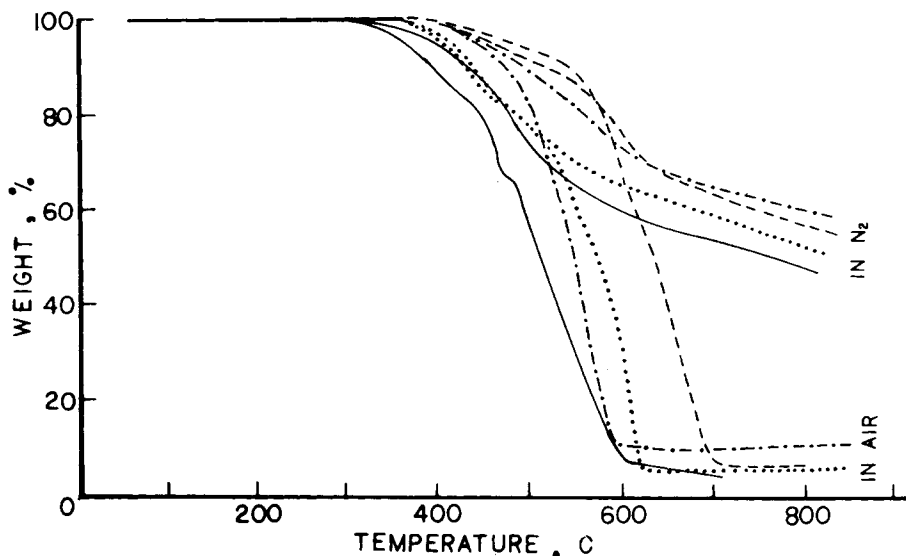
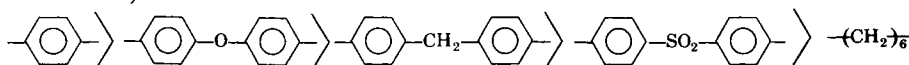


Fig. 3. TGA thermograms of polymers 4' (---), 5' (-·-·-), 6' (·····), and 7' (—) in  $N_2$  and air atmosphere.

by curing biscitraconimide, started thermal degradation at  $367^\circ\text{C}$  in air but was stable up to  $389^\circ\text{C}$  under anaerobic conditions. Polymer 7' containing aliphatic segments started losing weight at about  $364^\circ\text{C}$  in  $N_2$  and  $352^\circ\text{C}$  in air.

Based on the IDT and the  $\text{PDT}_{\text{max}}$  in  $N_2$  it can be seen from Table IV that polymer 3' was more thermally stable than 2' and less than 1'. Thus, the substitution of maleic double bond with a methyl or chloro group reduced thermal stability of cured resin. Interestingly, Table IV points out that the IDT in air of resin 3' was lower by  $25^\circ\text{C}$  than that of resin 1' whereas its  $\text{PDT}_{\text{max}}$  in air was somewhat higher. Consequently, the chloro substitution of maleic double bond did not remarkably influence the thermooxidative stability of cured resin. In addition, resin 3' afforded higher char yield under anaerobic conditions than that of 1'.

By examining the IDT,  $\text{PDT}_{\text{max}}$ , and the general form of the TGA curves, the relative order of thermal stability, with respect the diamine utilized for imidization, was



Polymer 1' containing linkages of *p*-phenylenediamine was stiffer than other polymers due to the absence of flexible bridging groups such as  $\text{—O—}$ ,  $\text{—CH}_2\text{—}$ ,  $\text{—SO}_2\text{—}$ . It is well known<sup>19</sup> that maximum thermal stability in polymers is usually obtained when thermally unreactive ring structures contribute a major portion of the polymer composition. The phenyl ring in the backbone of the chain is not only relatively thermally unreactive but also increases the rigidity. Stiffer chains resist thermally induced vibrations and therefore a higher temperature is required for their degradation. For all these reasons the most rigid polymer 1' was also the most thermally stable com-

TABLE IV  
 TGA Results of Various Polymers

Polymer	N <sub>2</sub>				Air			
	IDT (°C) <sup>a</sup>	PDT <sub>max</sub> (°C) <sup>b</sup>	TCP (°C) <sup>c</sup>	Y <sub>c</sub> (%) <sup>d</sup>	IDT (°C)	PDT <sub>max</sub> (°C)	Weight loss (%) <sup>e</sup>	IDT <sub>air</sub> /IDT <sub>N<sub>2</sub></sub>
1'	410	640	672	58	392	568	17.3	0.96
2'	389	577	611	59	367	478		0.94
3'	385	597	626	63	371	572		0.96
4'	407	605	637	58	404	594	24.5	0.99
5'	386	594	648	56	382	574	16.6	0.99
6'	379	550	578	53	368	556	27.5	0.97
7'	364	502	530	56	352	517	35.3	0.97

<sup>a</sup>Initial decomposition temperature.

<sup>b</sup>Maximum polymer decomposition temperature.

<sup>c</sup>Temperature of complete pyrolysis.

<sup>d</sup>Char yield at 800°C.

<sup>e</sup>Isothermal weight loss at 390°C after 50 min.

pared with the other polymers synthesized. It is important to note that the thermooxidative stability of resin 4' was significantly higher than that of 1'. Thus, the IDT and PDT<sub>max</sub> of resin 4' in air were raised by 12 and 26°C, respectively, from those of resin 1'. The lower thermal and thermooxidative stability of resin 7' was attributed to the thermally sensitive aliphatic hexamethylene bridge incorporated in the polymer backbone. Figure 3 shows that its thermooxidative degradation took place in more than one step, indicating overlapping reactions. Pyrolysis of the aliphatic segments is believed to occur initially.

All cured resins gave under anaerobic conditions char yields 63–53%, indicating that char yield was not seriously affected by the structure of the diamine utilized for imidization. However, all resins formed a small char residue beyond 600°C in air.

From Table IV it can be seen that the ratio of the initial decomposition temperature in air to that in nitrogen (IDT<sub>air</sub>/IDT<sub>N<sub>2</sub></sub>) varied from 0.99 to 0.94. This suggests that the onset of bond cleavage was basically thermal in nature and not influenced to any great extent by the presence of oxygen.

In addition, the cured resins were examined by IGA at 390°C in air. The percentage weight loss of several cured resins under these conditions after 50 min is listed in Table IV. It can be seen that resin 5' showed the lowest weight loss. Resin 7' containing aliphatic segments exhibited the highest weight loss obtained. Some of the IGA results are not in agreement with the dynamic TGA data. It has been reported that there is a rough correlation between dynamic TGA and IGA under certain conditions.<sup>20</sup> However, it is not unusual to uncover thermal stability differences by IGA that were not apparent by TGA.<sup>21,22</sup> Figure 4 presents the IGA traces of resin 1' in nitrogen at 380, 430, 550, and 600°C as well as in air at 390, 450, and 500°C. A weight loss of 15.2, 29.9, and 91.1% occurred in air after 30 min at 390, 450, and 500°C, respectively. This supports that a roughly increased thermooxidative degradation of this resin took place above 450°C.

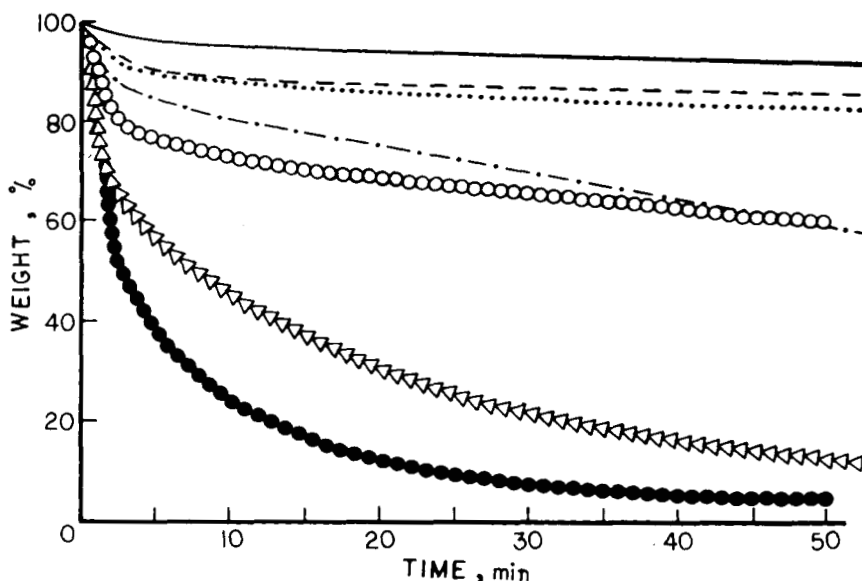


Fig. 4. IGA traces of polymer 1' in  $N_2$  at 380 (—), 430 (---), 550 (○) and 600°C (◁) as well as in air at 390 (···), 450 (---), and 500°C (●).

## CONCLUSIONS

Heat-resistant polymers were obtained by curing at 230–280°C several new bismaleimides, biscitraconimides, and bisdichloromaleimides. All polymers, with exception of those containing aliphatic segments, were thermally stable up to 370°C in nitrogen or air. The maximum rate of weight loss occurred at 475–640 and 478–594°C in nitrogen and air, respectively. The char yield at 800°C under anaerobic conditions was 53–63%. The cured resin containing hexamethylene moieties was the less thermally stable polymer obtained.

A grant from the Greek Ministry of Industry, Energy and Technology (General Secretariat of Research and Technology) is gratefully acknowledged.

## References

1. N. E. Scale, U.S. Pat. 2,444,536 (1948).
2. F. Grundschober and J. Sambeth, U.S. Pat. 3,380,964 (1969).
3. F. Grundschober, U.S. Pat. 3,533,966 (1970).
4. A. Bergain, A. Combet, and P. Grosjean, U.S. Pat. 3,562,223 (1971).
5. A. Bergain, A. Combet, and P. Grosjean, U.S. Pat. 3,562,223 (1971).
6. M. A. J. Mallet, *Mod. Plast.*, **78**(Jun.), (1973).
7. H. D. Stenzenberger, *Appl. Polym. Symp.*, **22**, 77 (1973).
8. I. Masanobu, Y. Masato, K. Masaaki, and Y. Satoshi, Japan Kokai 741,8199 (1974).
9. D. O. Hummel, K. U. Heinen, H. Stenzenberger, and H. Siesler, *J. Appl. Polym. Sci.*, **18**, 2015 (1974).
10. G. T. Kwiatkowski, L. M. Robenson, G. L. Brode, and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 961 (1975).
11. H. D. Stenzenberger, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **31**, 91 (1977).
12. I. K. Varma, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 283 (1982).

13. J. A. Mikroyannidis, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1717 (1984).
14. P. Kovacic, U.S. Pat. 2,818,405 (1957).
15. D. Kumar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 245 (1983).
16. I. K. Varma, A. K. Gupta, Sangita, and D. S. Varma, *J. Appl. Polym. Sci.*, **28**, 191 (1983).
17. A. P. Melissaris and J. A. Mikroyannidis, *J. Polym. Sci., Polym. Chem. Ed.*, to appear.
18. F. A. Bovey, *Nuclear Resonance Spectroscopy*, Academic, New York, 1969, p. 58.
19. Y. P. Khanna and E. M. Pearce, *J. Appl. Polym. Sci.*, **27**, 2053 (1982).
20. G. F. L. Ehlers, "Structure Stability Relationships of Polymers Based on Thermogravimetric Analysis Data, Part I," AFML-TR-74-177, 1974.
21. C. Arnold, Jr., *J. Polym. Sci., Macromol. Rev.*, **14**, 265 (1979).
22. G. L. Hagnauer and B. R. LaLiberte, *J. Appl. Polym. Sci.*, **20**, 3073 (1976).

Received November 17, 1986

Accepted May 28, 1987