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Bis- or Tetra-Maleimides of Substituted s-Triazines Chain-Extended by Imide, Amide, and Urea Groups for Fire- and Heat-Resistant Applications

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Synopsis

Novel phosphorylated bismaleimides and nonphosphorylated tetramaleimides containing substituted s-triazine rings (chain-extended by imide, amide, or urea groups) were prepared and polymerized. These polymer precursors were prepared by reacting 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine or 2,4,6-tris(4-aminophenoxy)-s-triazine with maleic anhydride in combination with a bridging agent such as pyromellitic or benzophenone tetracarboxylic dianhydride, terephthaloyl chloride, and tolylene diisocyanate. The structure of polymer precursors was confirmed by infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy and their curing behavior was investigated by differential thermal analysis (DTA). The phosphorylated bismaleimides were thermally polymerized at a lower temperature than did the corresponding nonphosphorylated tetramaleimides. Dynamic thermogravimetric analysis (TGA) showed that the nonphosphorylated and phosphorylated cured resins were stable up to 320–370 and 312–327°C, respectively, in nitrogen or air atmosphere. In addition, the latter afforded a relatively higher char yield. The relative thermal and thermooxidative stability of polymers with regard to the chemical structure of the bridging group was of the order imide > amide > urea. Upon isothermal aging the phosphorylated polymers exhibited a lower weight loss than did the corresponding nonphosphorylated polymers.

INTRODUCTION

Several high temperature resistant polymers such as polyimides, polybenzimidazoles, and polyphenylquinoxalines have been synthesized and can be used for fabrication of high temperature, high performance composites. These polymers are cured by condensation reactions, liberating low molecular weight materials, thus forming voids when used for fabrication of composites. The polymer used as binder in these composites is most commonly an epoxy resin. However, the inherently flammable nature of the epoxy resins limits a wide application of such composites. More recently, the development of addition type prepolymers such as maleimide systems helped to overcome the aforementioned disadvantages. Unfortunately, most of the cured resins obtained from maleimides are brittle due to their high crosslink density.

The principal objective of this article was to develop new fire- and heat-resistant laminating resins with improved flexibility. They were obtained by thermal polymerization of several phosphorylated bismaleimides or nonphos-

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phorylated tetramaleimides. Ether linkages in the form of phenoxy groups were introduced in the s-triazine backbone. In addition, the chain of all monomers was extended by means of pyromellitic dianhydride, benzophenone tetracarboxylic dianhydride, terephthaloyl chloride, and tolylene diisocyanate. The presence of phenoxy groups along with the extended chain of monomers are expected to improve the flexibility of the cured resins. Furthermore, several of monomers contained phosphorus in the form of the diethoxyphosphinyl group attached directly to the s-triazine ring. The cured resins obtained from these monomers are expected to be fire-resistant.[1] The efficiency of the phosphorus moieties with respect their fire-retardancy is often dramatically increased in the presence of certain nitrogen compounds.[2,3]

Several phosphorylated or nonphosphorylated maleimide or nadimide systems derived from s-triazine have been synthesized and polymerized recently.[4] In addition, chain-extension of certain bismaleimides or bisnadimides has been accomplished by means of benzophenone tetracarboxylic dianhydride[5-8] pyromellitic dianhydride,[9] terephthaloyl chloride,[10] and diisocyanates.[7,11]

EXPERIMENTAL

Instrumentation

Infrared (IR) spectra were recorded on a Perkin–Elmer 710B spectrometer with KBr pellets. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were obtained using a Varian T-60A spectrometer at 60 MHz in DMSO-d_6 solution. 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 Du Pont 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.

Reagents and Solvents

2,4,6-Tris(4-aminophenoxy)-s-triazine was prepared by hydrogenation of the corresponding trinitro compound in DMF utilizing palladium on activated carbon as catalyst. The trinitro compound was synthesized from the reaction of cyanuric chloride with 4-$O_2NC_6H_4ONa$. The latter was prepared by reacting an aqueous solution of NaOH with an equimolar amount of 4-$O_2NC_6H_4OH$.[4] A somewhat different preparation method has been reported[12] for 2,4,6-tris(4-aminophenoxy)-s-triazine.

2,4-Bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine was similarly prepared by catalytic hydrogenation of the corresponding dinitro compound.[4] The latter was synthesized by reacting 2,4-dichloro-6-diethoxyphosphinyl-s-triazine with an aqueous solution of 4-$O_2NC_6H_4ONa$ prepared from equimolar amounts of 4-$O_2NC_6H_4OH$ and NaOH. Finally, 2,4-dichloro-6-diethoxyphosphinyl-s-triazine was synthesized by an Arbuzov type reaction between equimolar amounts of cyanuric chloride and triethyl phosphite.[4]

Maleic anhydride (Merck) and terephthaloyl chloride (Aldrich) were purified by recrystallizations from ether and n-heptane, respectively. Pyromellitic

dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) (Aldrich) were recrystallized from acetic anhydride. Tolylene diisocyanate (Merck) utilized a mixture of the 2,4- and 2,6-isomer of 65 and 35%, respectively, was distilled under reduced pressure (bp 126°C/11 mm). N,N-Dimethylformamide (DMF) (Aldrich) was refluxed in the presence of calcium hydride and then distilled under reduced pressure.

Preparation of Amic Acids

Amic Acid of 1, 2, 1', and 2'

A flask equipped with a nitrogen inlet, a dropping funnel, and a magnetic stirrer was charged with a solution of 2,4,6-tris(4-aminophenoxy)-s-triazine (3.2192 g, 8.0 mmol) in DMF (25 mL). To this vigorously stirred solution maleic anhydride (1.5690 g, 16.0 mmol) dissolved in DMF (8 mL) was added dropwise under nitrogen atmosphere. Stirring of the reaction mixture at ambient temperature was continued for 3 h. Granular PMDA (0.8725 g, 4.0 mmol) was subsequently added portionwise to the mixture. It was stirred at room temperature in a stream of nitrogen for additional 4 h to yield a solution of amic acid of 1.

In a likewise manner a solution of amic acid of 2 was prepared by reacting 2,4,6-tris(4-aminophenoxy)-s-triazine (4.0240 g, 10.0 mmol) with maleic anhydride (1.9612 g, 20.0 mmol) and BTDA (1.6111 g, 5.0 mmol).

According to this procedure, a solution of amic acid of 1' was prepared from the reaction of 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine (3.4511 g, 8.0 mmol) with maleic anhydride (0.7845 g, 8.0 mmol) and PMDA (0.8725 g, 4.0 mmol).

A solution of amic acid of 2' was similarly prepared by reacting 2,4-bis-(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine (4.3138 g, 10.0 mmol) with maleic anhydride (0.9806 g, 10.0 mmol) and BTDA (1.6112 g, 5.0 mmol).

Amic Acid of 3 and 3'

To a vigorously stirred solution of 2,4,6-tris(4-aminophenoxy)-s-triazine (3.2192 g, 8.0 mmol) in DMF (20 mL) maleic anhydride (1.5690 g, 16.0 mmol) dissolved in DMF (10 mL) was added dropwise at room temperature under nitrogen atmosphere. The mixture was stirred at room temperature for 3 h. Next, terephthaloyl chloride (0.8121 g, 4.0 mmol) dissolved in DMF (8 mL) was added portionwise to the mixture at ambient temperature. Stirring of the reaction mixture in a stream of nitrogen was continued for another 2.5 h to afford a solution of amic acid of 3.

A solution of amic acid of 3' was similarly prepared by reacting 2,4-bis-(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine (4.3138 g, 10.0 mmol) with maleic anhydride (0.9806 g, 10.0 mmol) and terephthaloyl chloride (1.0151 g, 5.0 mmol).

Amic Acid of 4 and 4'

Maleic anhydride (1.5690 g, 16.0 mmol) dissolved in DMF (8 mL) was added dropwise to a vigorously stirred solution of 2,4,6-tri(4-aminophenoxy)-s-tri-

azine (3.2192 g, 8.0 mmol) in DMF (20 mL) at room temperature under nitrogen atmosphere. After stirring of the mixture for 3 h, tolylene diisocyanate (0.6966 g, 4.0 mmol) diluted with DMF (5 mL) was added portionwise at room temperature. The mixture was subsequently heated at 85°C for 2 h in a stream of nitrogen to yield a solution of amic acid of 4.

The same procedure was used to prepare a solution of amic acid of 4' by reacting 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine (4.3138 g, 10.0 mmol) with maleic anhydride (0.9806 g, 10.0 mmol) and tolylene diisocyanate (0.8708 g, 5.0 mmol).

General Procedure for Isolation of Amic Acids and Polymer Precursors

The solution of amic acid in DMF was poured over crushed ice. The solid thus obtained was filtered and washed with water. It was dried at about 60°C overnight to afford the amic acid required for characterization.

To the remaining solution of amic acid in DMF acetic anhydride and fused sodium acetate (300 mL and 27 g, respectively, per mol of water condensed) were added in order to cyclodehydrate the amic acid. The mixture was heated at 90°C for 3.5 h. During this period the color of the reaction 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 sodium carbonate, then with water and dried at about 60°C overnight. The yields of the polymer precursors varied from 88 to 96%.

General Method for Preparation of Polymers

A solution of amic acid in DMF (ca. 8 mL) was heated in a shallow dish placed into a continuously circulated air oven maintained at 160°C for 30 min. At this stage the solvent was evaporated. The temperature of the oven was subsequently raised to 220°C and the curing was performed for 2 h. Postcuring was accomplished by heating at 245°C for 25 min.

RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer Precursors and Their Intermediate Amic Acids

The chain-extended tetramaleimides and bismaleimides were prepared from 2,4,6-tris(4-aminophenoxy)-s-triazine and 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine, respectively. These starting materials have been synthesized and characterized previously.[4]

The nonphosphorylated tetramaleimides 1, 2, 3, and 4 were prepared according to the reaction sequences outlined in Scheme I. The corresponding phosphorylated bismaleimides 1', 2', 3', and 4' were similarly prepared by the synthetic route presented in Scheme II. More particularly, the chain of monomers 1, 1', 2, and 2' was extended by imidized PMDA and BTDA. The chain of monomers 3 and 3' was extended by amidized terephthaloyl chloride. Finally, monomers 4 and 4' were extended by means of tolylene diisocyanate. The various chemical structures of these eight polymer precursors permit a systematic study not only between the phosphorylated and nonphosphorylated resins but also between the various bridging groups as well.
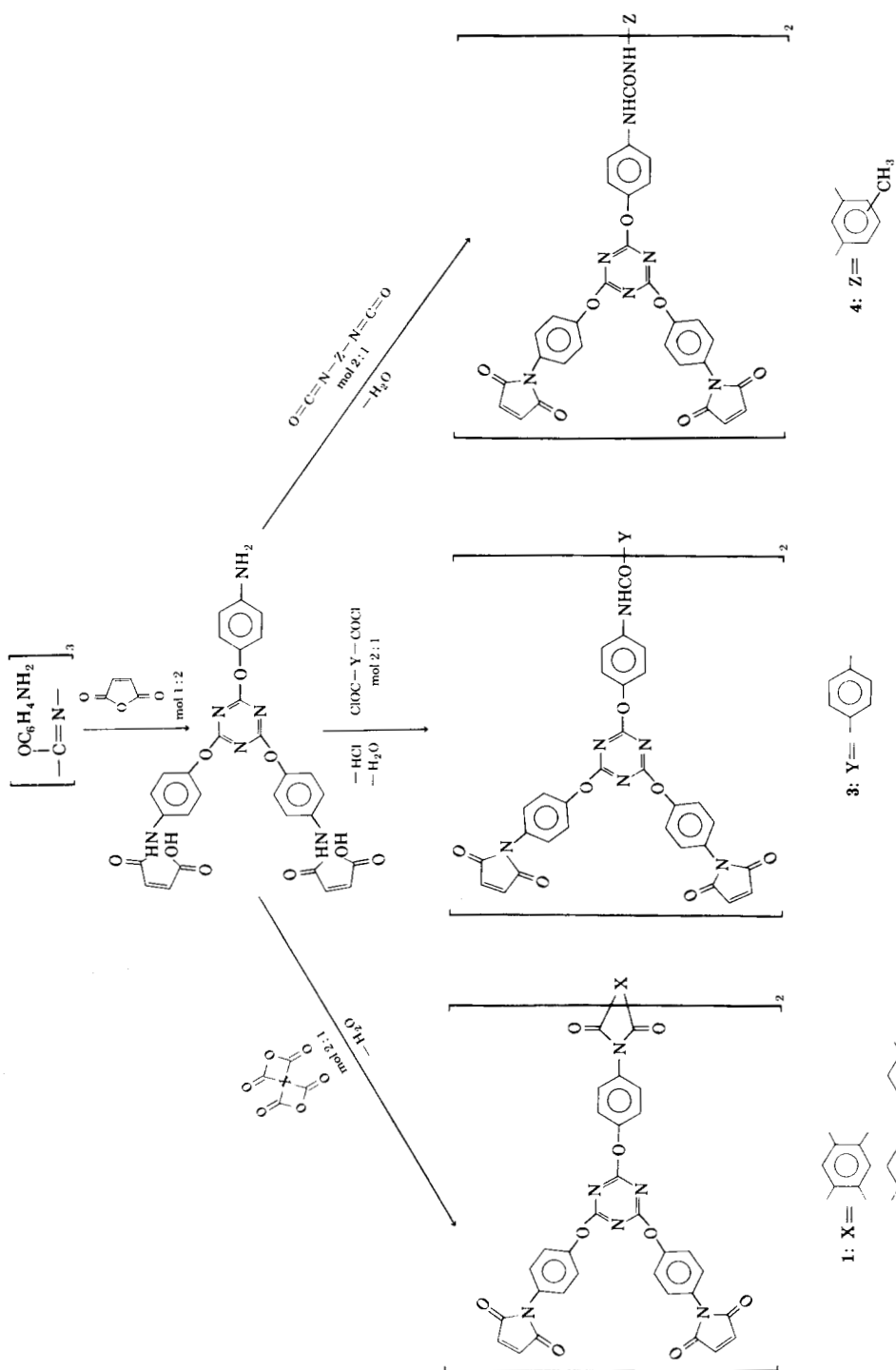
Scheme 1.

Scheme 2.

DMF was used as reaction solvent for preparing all monomers although several other polar aprotic solvents such as N,N-dimethylacetamide and N-methylpyrrolidinone could be also used. Unfortunately, other less efficient but more volatile solvents such as acetone, methylethylacetone, and tetrahydrofurane could not be utilized as reaction solvent due to the poor solubility of 2,4,6-tris(4-aminophenoxy)-s-triazine and 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine as well as of the intermediate amic acids formed. It is desirable to use volatile solvents due to the solvent retention in the prepregs when high-boiling polar solvents are utilized for fabricating composites.

The amic acids of **1** and **2** were prepared from the reaction of 2,4,6-tris(4-aminophenoxy)-s-triazine (1 mol) with maleic anhydride (2 mol) followed by the *in situ* reaction with PMDA or BTDA (0.5 mol). The amic acids of **1′** and **2′** were similarly prepared from the reaction of 2,4-bis(4-aminophenoxy)-6-diethoxyphosphinyl-s-triazine with equimolar amount of maleic anhydride and subsequent reaction with half-molar amount of PMDA or BTDA. These reactions proceeded readily at ambient temperature. The mixture was stirred for additional hours at room temperature to ensure completion of the reactions. At the second reaction the amine solution might also be added gradually to the tetracarboxylic dianhydride solution although the reverse order of addition was preferred.

The amic acids of **3** and **3′** were prepared by an analogous synthetic route utilizing terephthaloyl chloride as bridging agent. Thus, the bismaleamic acid resulting from the reaction of 2,4,6-tris(4-aminophenoxy)-s-triazine (1 mol) with maleic anhydride (2 mol) reacted subsequently *in situ* with terephthaloyl chloride (0.5 mol) in DMF at ambient temperature. At this stage terephthaloyl chloride preferred to react with the amino and not with the carboxylic group of bismaleamic acid.[10] No acid acceptor such as pyridine was added to the reaction mixture because DMF was employed as reaction medium and acid acceptor.[13,14]

The same method was applied for preparing the amic acids of **4** and **4′**. In this case, tolylene diisocyanate was used as bridging agent of the bismaleamic acid or the phosphorus-bearing monomaleamic acid arising from the first reaction. The isocyanate group preferred to react with the amino and not with the carboxylic group of the mono- or bis-maleamic acid due to the higher nucleophilicity of the former.[11] The urea forming reaction was catalyzed[15] by DMF, the reaction medium, which behaved as a weak base. The mixture was heated to complete this reaction. The progress of the reaction was followed by IR measurements of the reaction mixture. The reaction was completed when the absorption band at 2270 cm^{-1} associated with the isocyanate group disappeared.

After the reaction with the coupling agent all amic acids synthesized were isolated by pouring an aliquot of the reaction mixture into a nonsolvent. Their characterization by IR and ^{1}H-NMR spectroscopy is discussed below.

Cyclodehydration of the amic acids was accomplished by chemical means. For this purpose, acetic anhydride and fused sodium acetate were added to the amic acid solution in DMF and the mixture was heated to complete the imidization reaction. All polymer precursors were characterized by IR spectroscopy and their curing behavior was investigated by DTA.

TABLE I
IR Absorption Bands of Polymer Precursors

Sample	KBr (cm^{-1})
1	1782, 1720, 1375, 730 (imide structure); 3060, 1578, 1502 (aromatic); 1665 (C=N), 1605 (C=C); 1218 (ether bond).
1	1788, 1725, 1382, 725 (imide structure); 3040, 1575, 1503 (aromatic); 1658 (C=N); 1603 (C=C); 1222 (ether bond); 1245 (P=O); 1052–1023 (P—O—C).
2	1790, 1725, 1378, 728 (imide structure); 3055, 1582, 1506 (aromatic); 1657 (C=N); 1608 (C=C); 1220 (ether bond).
2'	1793, 1712, 1380, 700 (imide structure); 3035, 1580, 1500 (aromatic); 1647 (C=N); 1600 (C=C); 1217 (ether bond); 1240 (P=O); 1055–1020 (P—O—C).
3	1786, 1718, 1382, 698 (imide structure); 3045, 1583, 1503 (aromatic); 1646 (C=N); 1610 (C=C); 1216 (ether bond); 3380–3195 (NH stretching); 1558 (NH deformation); 1660 (amide carbonyl).
3'	1785, 1712, 1375, 698 (imide structure); 3050, 1605, 1503 (aromatic); 1645 (C=N); 1618 (C=C); 1222 (ether bond); 3420–3250 (NH stretching); 1552 (NH deformation); 1662 (amide carbonyl); 1242 (P=O); 1057–1022 (P—O—C).
4	1782, 1726, 1378, 700 (imide structure); 3030, 1580, 1502 (aromatic); 1660 (C=N); 1617 (C=C); 1222 (ether bond); 2940 (methyl); 3370–3240 (NH stretching); 1565 (NH deformation); 1678 (urea carbonyl).
4'	1783, 1718, 1385, 702 (imide structure); 3055, 1578, 1503 (aromatic); 1652 (C=N); 1610 (C=C); 1220 (ether bond); 2960 (methyl); 3460–3245 (NH stretching); 1542 (NH deformation); 1677 (urea carbonyl); 1243 (P=O); 1056–1022 (P—O—C).

All amic acids showed characteristic IR absorption bands around 3340, 1560, and 1270 cm^{-1}. The polymer precursors isolated exhibited several characteristic absorptions associated with the imide structure at 1790–1782, 1725–1717, 1382–1375, and 730–698 cm^{-1}. The most important absorptions and their assignments of all polymer precursors are listed in Table I. Figure 1 presents the IR spectra of tetramaleimide 4, the phosphorus-containing bismaleimide 4', as well as of the amic acid of 4'. Comparison of the IR spectra of 4 and 4' revealed that they differed mainly near 1030 cm^{-1} where the latter showed a strong absorption assigned to the P—O—C linkages. It is known[16] that the absorption of the P=O bond appears at 1350–1250 cm^{-1}. In the present case, the ether bond as well as the para-disubstituted aromatic rings showed also absorptions at this spectrum region. For this reason, the IR spectra of 4 and 4' did not differ remarkably at this spectrum region. On the other hand, the differences observed in the spectra of 4' and the corresponding amic acid could be used as basis for monitoring the imidization reaction by means of IR spectroscopy. More particularly, bismaleimide showed a strong absorption at 1718 cm^{-1} (imide carbonyl) and weak but sharp absorptions at 1780 and 700 cm^{-1} associated with the imide structure. In addition, it showed a less broad absorption at 3000–2500 cm^{-1} due to the elimination of the carboxylic OH stretching vibrations although the ureylene group absorbed also at this spectrum region.

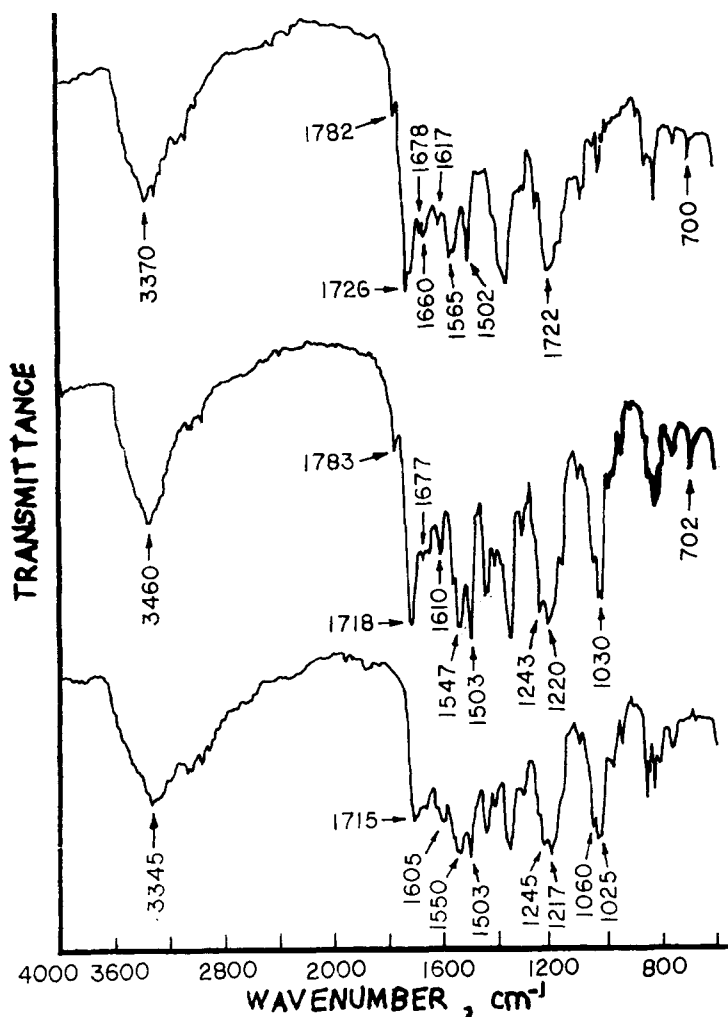Fig. 1.   IR spectra of tetramaleimide 4 (top), bismaleimide 4' (middle), and the amic acid of 4' (bottom).

The ^{1}H-NMR spectral data of all amic acids are tabulated in Table II. The carboxylic protons arising from the reaction of maleic anhydride with amine resonated at about the same region with those resulting from the reaction of PMDA or BTDA with amine. In addition, various isomers could emerge from these reactions. Therefore, the peak assigned to these protons appeared as a broad singlet in amic acids of 1, 1', 2, and 2'. From Table II it can be seen that the aromatic protons of PMDA, BTDA, and terephthaloyl chloride rings resonated at a relatively downfield value compared with that of the other aromatic protons. The deshielding effect of the electron-withdrawing carbonyl group was responsible for this behavior.[17] An eight-proton multiplet and a twelve-proton triplet appeared in amic acids of 1', 2', 3', and 4' substantiated the attachment of the diethoxyphosphinyl group to the s-triazine ring. Finally, it is seen that the —NHCO— protons resonated at a downfield value in comparison to that of the —NHCONH— protons.

Amic acid	Chemical shifts (δ,[a] ppm) and assignments
1	10.90 (bs,[b] 6H —COOH); 8.60–8.30 (bs, 6H, —NHCO—); 8.00–7.70 (m,[c] 2H, aromatic of PMDA ring and 12H, aromatic, ortho to —NH—); 7.40–7.00 (m, 12H, aromatic, ortho to —O—); 6.60 (m, 8H, olefinic).
1′	10.75 (bs, 4H, —COOH); 8.40 (bs, 4H, —NHCO—); 8.05–7.65 (m, 2H, aromatic of PMDA ring and 8H, aromatic, ortho to —NH—); 7.35–7.00 (m, 8H, aromatic, ortho to —O—); 6.45 (m, 4H, olefinic); 4.25 (m, 8H, —OC$\underline{H}_2$CH$_3$); 1.30 (t,[d] 12H, OCH$_2$C$\underline{H}_3$).
2	10.70 (bs, 4H, —COOH); 8.30–7.80 (m, 6H, —NHCO— and 6H, aromatic of BTDA rings); 7.60 (m, 12H, aromatic, ortho to —NH—); 7.20 (m, 12H, aromatic, ortho to —O—); 6.50 (m, 8H, olefinic).
2′	10.90 (bs, 4H, —COOH); 8.50 (bs, 4H, —NHCO—); 7.85–7.50 (m, 6H, aromatic of BTDA rings and 8H, aromatic, ortho to —NH—); 7.20 (m, 8H, aromatic, ortho to —O—); 6.55 (m, 4H, olefinic); 4.30 (m, 8H, —OC$\underline{H}_2$CH$_3$); 1.35 (t, 12H, —OCH$_2$C$\underline{H}_3$).
3	10.90 (s,[e] 4H, —COOH); 8.60–8.10 (m, 6H, —NHCO— and 4H, aromatic of terephthalic ring); 7.70 (m, 12H, aromatic ortho to —NH—); 7.40–7.00 (m, 12H, aromatic, ortho to —O—); 6.50 (m, 8H, olefinic).
3′	10.80 (s, 2H, —COOH); 8.50 (s, 4H, —NHCO—); 8.00 (m, 4H, aromatic of terephthalic ring); 7.60 (m, 8H, aromatic ortho to —NH—); 7.20 (m, 8H, aromatic ortho to —O—); 6.45 (m, 4H, olefinic); 4.30 (m, 8H, —C$\underline{H}_2$CH$_3$); 1.35 (t, 12H, —OCH$_2$C$\underline{H}_3$).
4	11.00 (s, 4H, —COOH); 8.40 (s, 4H, —NHCO—); 8.00–7.60 (m, 4H, —NHCONH— and 8H, aromatic ortho to —NHCO—); 7.45–7.10 (m, 19H, other aromatic); 6.60 (m, 8H, olefinic); 2.20 (s, 3H, —CH$_3$).
4′	10.90 (s, 2H, —COOH); 8.30 (s, 2H, —NHCO—); 7.95–7.65 (m, 4H, —NHCONH— and 4H, aromatic ortho to —NHCO—); 7.40–7.05 (m, 15H, other aromatic); 6.50 (m, 4H, olefinic); 4.20 (m, 8H, —OC$\underline{H}_2$CH$_3$); 2.25 (s, 3H, —CH$_3$); 1.30 (t, 12H, —OCH$_2$C$\underline{H}_3$.

[a] In DMSO-d_6 solution.
[b] Broad singlet.
[c] Multiplet.
[d] Triplet.
[e] Singlet.

Curing of Polymer Precursors and Thermal Stability of Cured Resins

All polymer precursors cured by addition-type reaction of the maleic olefinic bonds to afford crosslinked resins. The polymerization reaction was exothermic because the DTA thermograms of all monomers showed an exotherm at the temperature range of 196–276°C. Note that the completely cured resins did not show an exotherm at this temperature range. Figure 2 presents typical
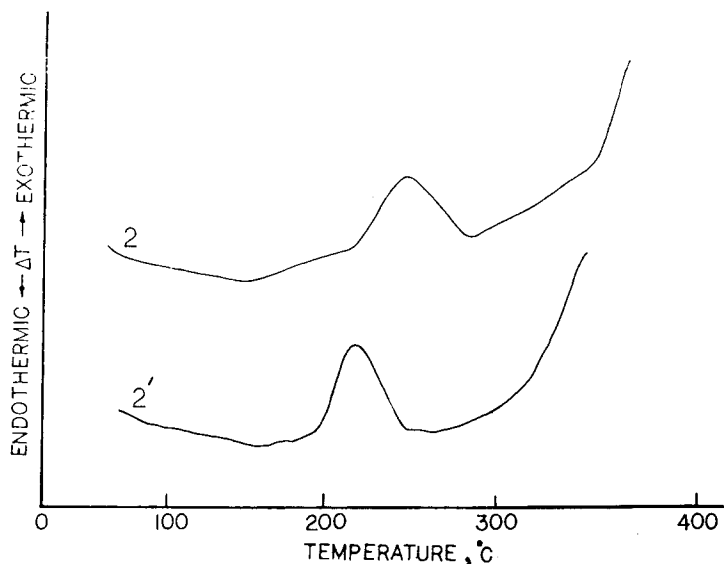
Fig. 2. DTA traces of tetramaleimide 2 and bismaleimide 2′ in N_2 atmosphere.

DTA traces of monomers 2 and 2′ in N_2 atmosphere. A large exotherm associated with the thermal degradation of resin followed the curing peak. The temperature of first energy release T_1 (start of polymerization), the exothermic peak temperature T_2, and the temperature of termination of polymerization T_3 were determined from the DTA traces and are presented for all samples in Table III. It can be seen that all phosphorylated monomers showed lower curing temperatures than the corresponding nonphosphorylated monomers. In addition, from Table III it can be seen that all phosphorus-containing monomers showed comparable curing temperatures. No remarkable differences were also observed between the curing temperatures of all non-

TABLE III
Curing Temperatures of Monomers and TGA Data of Polymers

Sample	Curing temperatures[a]			In N_2			In air			
	T_1 (°C)	T_2 (°C)	T_3 (°C)	IDT[b] (°C)	PDT^c_{max} (°C)	Y^d_c(800°C) (%)	IDT (°C)	PDT_{max} (°C)	Y_c(600°C) (%)	IDT_{air}/IDT_{N_2}
1	221	247	276	370	433	50	368	426	36	0.99
1′	196	212	237	327	376	64	323	370	55	0.99
2	215	250	274	347	420	54	336	412	16	0.97
2′	198	215	245	320	393	59	318	379	53	0.99
3	216	244	278	336	417	49	328	418	48	0.98
3′	213	235	263	317	368	64	316	367	64	0.99
4	226	248	269	323	413	50	320	380	35	0.99
4′	203	234	260	312	364	65	312	366	66	1.00

[a] Determined from the DTA traces of monomers.
[b] Initial decomposition temperature.
[c] Maximum polymer decomposition temperature.
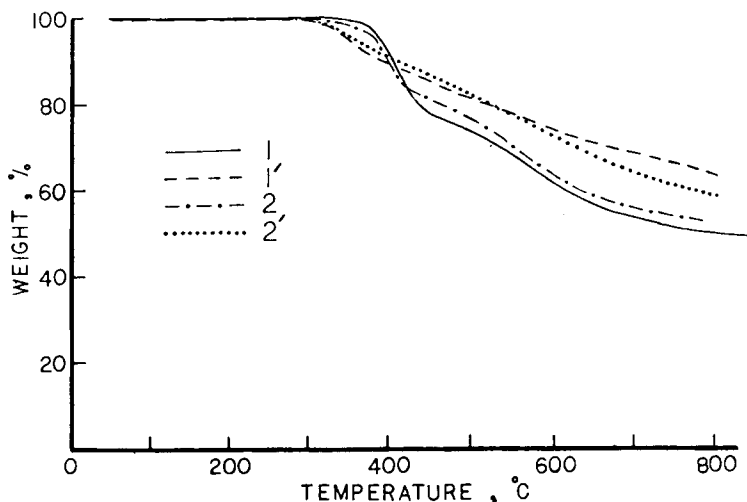[d] Char yield.

Fig. 3.   TGA thermograms of polymers 1, 1', 2, and 2' in N_2 atmosphere.

phosphorylated monomers. This behavior was attributed to the same chemical environment at the polymerizable maleimido groups which exists in each class of monomers. Apparently, the various chemical structures of the bridging group did not significantly influence the curing temperatures.

The thermal and thermooxidative stability of polymers was ascertained by dynamic TGA. Figures 3 and 4 show typical TGA thermograms of polymers in N_2 atmosphere. The initial decomposition temperature (IDT) obtained by extrapolation, the maximum polymer decomposition temperature (PDT_{max}) and the char yield (Y_c) at 800 or 600°C both in N_2 and air atmospheres are summarized in Table III. The results showed that the nonphosphorylated and phosphorylated polymers were stable up to 320–370 and 312–327°C, respectively, in N_2 or air atmosphere. The phosphorylated polymers exhibited a
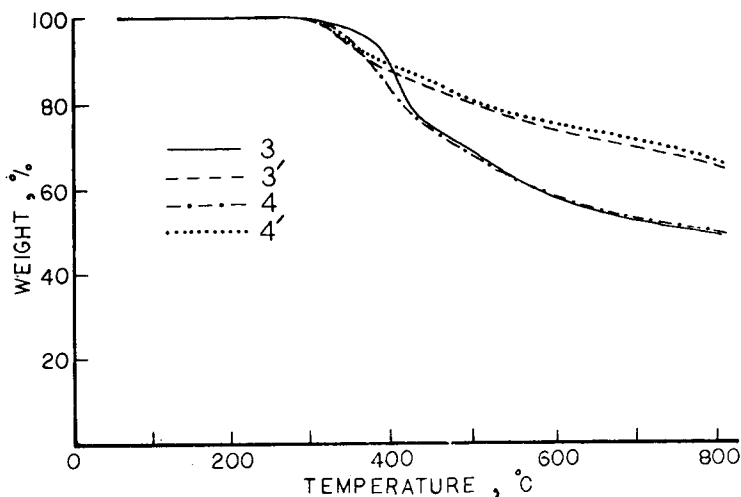

Fig. 4.   TGA thermograms of polymers 3, 3', 4, and 4' in N_2 atmosphere.
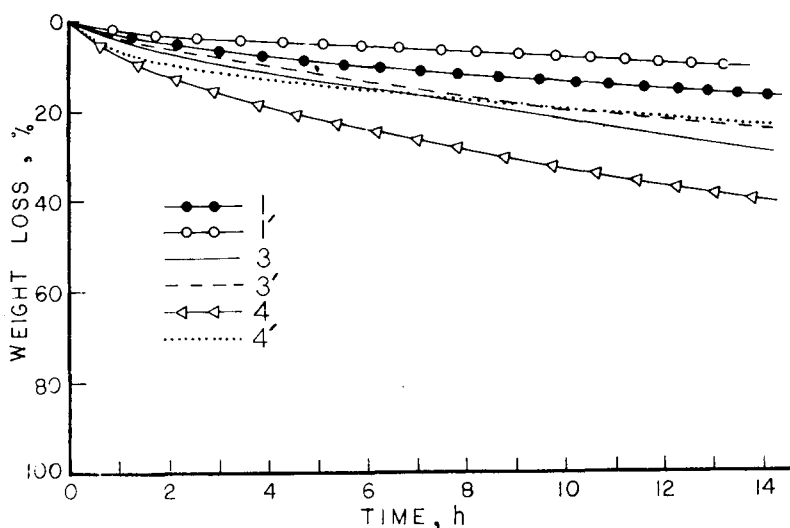
Fig. 5. IGA traces of polymers 1, 1', 3, 3', 4, and 4' at 300°C in air atmosphere (static).

significantly lower IDT and PDT_{max} than did the corresponding nonphosphorylated polymers due to the relatively easy thermal degradation of the phosphorus moieties. In contrast, all phosphorylated polymers afforded higher char yield than the corresponding nonphosphorylated polymers. It is well known[1] that phosphorus promotes char formation and reduces flammability. Comparison of the IDT and PDT_{max} both in N_2 and air atmospheres of the polymers 1 and 2 as well as of 1' and 2' showed that the polymers derived from PMDA were considerably more heat resistant than those of BTDA due to the stiffer structure of the former. From Table III it can be seen that the thermal and thermooxidative stability of the phosphorylated and nonphosphorylated polymers with regard to the chemical structure of the bridging group was of the following order: imide > amide > urea. Since the ratio IDT_{air}/IDT_{N_2} varied from 0.97 to 1.00 the onset of polymer degradation was thermal in nature and not oxidative. The nonphosphorylated polymers were almost completely pyrolyzed when heated beyond 600–700°C.

The thermooxidative stability of several typical polymers was also evaluated by isothermal gravimetric analyhsis (IGA). Figure 5 presents the IGA traces of polymers 1, 1', 3, 3', 4, and 4' at 300°C in air atmosphere (static) which showed a weight loss 16.2, 10.5, 27.7, 23.3, 38.5, and 22.3%, respectively, after 13 h. It can be seen that the phosphorylated polymers showed a lower weight loss than did the corresponding nonphosphorylated polymers because of their higher char yield.

CONCLUSION

It was demonstrated that a novel class of crosslinked heat-resistant polymers with relatively high anaerobic char yields (65–49% at 800°C) can be made by thermal-addition polymerization of several phosphorylated bismaleimides and nonphosphorylated tetramaleimides containing substituted s-triazine rings. The chain of monomers was extended by incorporating

various imide, amide and urea groups. These polymers can be especially useful for composites and adhesives.

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