

Polymerization of maleimides containing s-triazine rings in presence of aromatic di- or tri-amines

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SUMMARY

New thermosetting resins were prepared by crosslinking of 2,4,6-tris[4-(maleimido)phenoxy]-s-triazine (TM) or 2,4-bis[4-(maleimido)phenoxy]-6-diethoxyphosphinyl-s-triazine (BM) in presence of various aromatic di- or tri-amines. The maleimide-amine adducts initiated thermal polymerization at lower temperature than did the corresponding neat maleimides. The thermal stability of cured resins was evaluated by thermogravimetric analysis. The cured resins derived from the maleimide-amine adducts were less thermally stable than those of the corresponding neat maleimides. The initial decomposition temperature of the polymers obtained from the maleimide-amine adducts was not remarkably influenced by the chemical structure of the aromatic amine utilized.

INTRODUCTION

In recent years, the class of addition-type polyimides has been investigated extensively. Bismaleimides are of particular interest because of their easy availability, low price, excellent processing characteristics, outstanding thermal stability, and low flammability at elevated temperatures in the finally cured state. The application of these polymers for structural composites in combination with high modulus fibers is somewhat limited due to their brittleness. Stoichiometric mixing of bismaleimide with a diamine leads to the formation of linear polyaspartimides with poor thermal stability (1). These resins, however, afforded by casting coherent and flexible films. Thus by a careful selection of bismaleimide to amine ratio, it is possible to control the crosslink density and to retain the outstanding thermal stability of these polymers. The polymerization of several bismaleimides in presence of diamines has been described in the literature (2-4).

Certain new phosphorylated or nonphosphorylated maleimide systems containing s-triazine rings were synthesized recently (5). The present investigation deals with the crosslinking of these polymer precursors in presence of some aromatic di- or tri-amines. The maleimide-amine adducts were prepared utilizing a relatively small concentration of amine in order their cured resins to combine an improved flexibility with a satisfactory thermal stability.

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EXPERIMENTAL

Reagents and Solvents

The synthesis and characterization of 2,4,6-tris[4-(maleimido)phenoxy]-s-triazine (TM) or 2,4-bis[4-(maleimido)phenoxy]-6-diethoxyphosphinyl-s-triazine (BM) has been described elsewhere (5). p-Phenylenediamine (Aldrich) was sublimed at about 110°C under vacuum (2-3 mm). 4-Aminophenyl ether and 4,4'-diaminodiphenylsulfone (Merck) were purified by recrystallization from acetonitrile and methanol, respectively. N,N-Dimethylformamide (DMF) (Aldrich) was dried by refluxing and fractionally distilled from calcium hydride.

Measurements

Infrared (IR) spectra were recorded on a Perkin-Elmer 710B spectrometer with KBr pellets. 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 N₂ atmosphere at a flow rate of 60 cm³/min. TGA measurements were made at a heating rate of 20°C/min in N₂ or air at a flow rate of 60 cm³/min.

Preparation of the Maleimide-Amine Adducts

The trismaleimide-amine adducts were prepared by dissolving a mixture of TM and amine in DMF and subsequent heating at 60°C for 2 h. Trismaleimide and diamine were mixed in a mol ratio 1:0.5 for preparing the TM-P, TM-E, and TM-S adducts (see Scheme 1). In the case of TM-C adduct, trismaleimide was mixed with triamine in a mol ratio 1:0.3. The trismaleimide-amine adducts were isolated by removal of the solvent at about 60°C under reduced pressure.

The same procedure was also used for preparing the bismaleimide-amine adducts. Bismaleimide and diamine were mixed in a mol ratio 1:0.3 for the preparation of BM-P, BM-E, and BM-S adducts. The BM-C adduct was prepared by mixing bismaleimide with triamine in a mol ratio 1:0.1.

Curing of the Maleimide-Amine Adducts

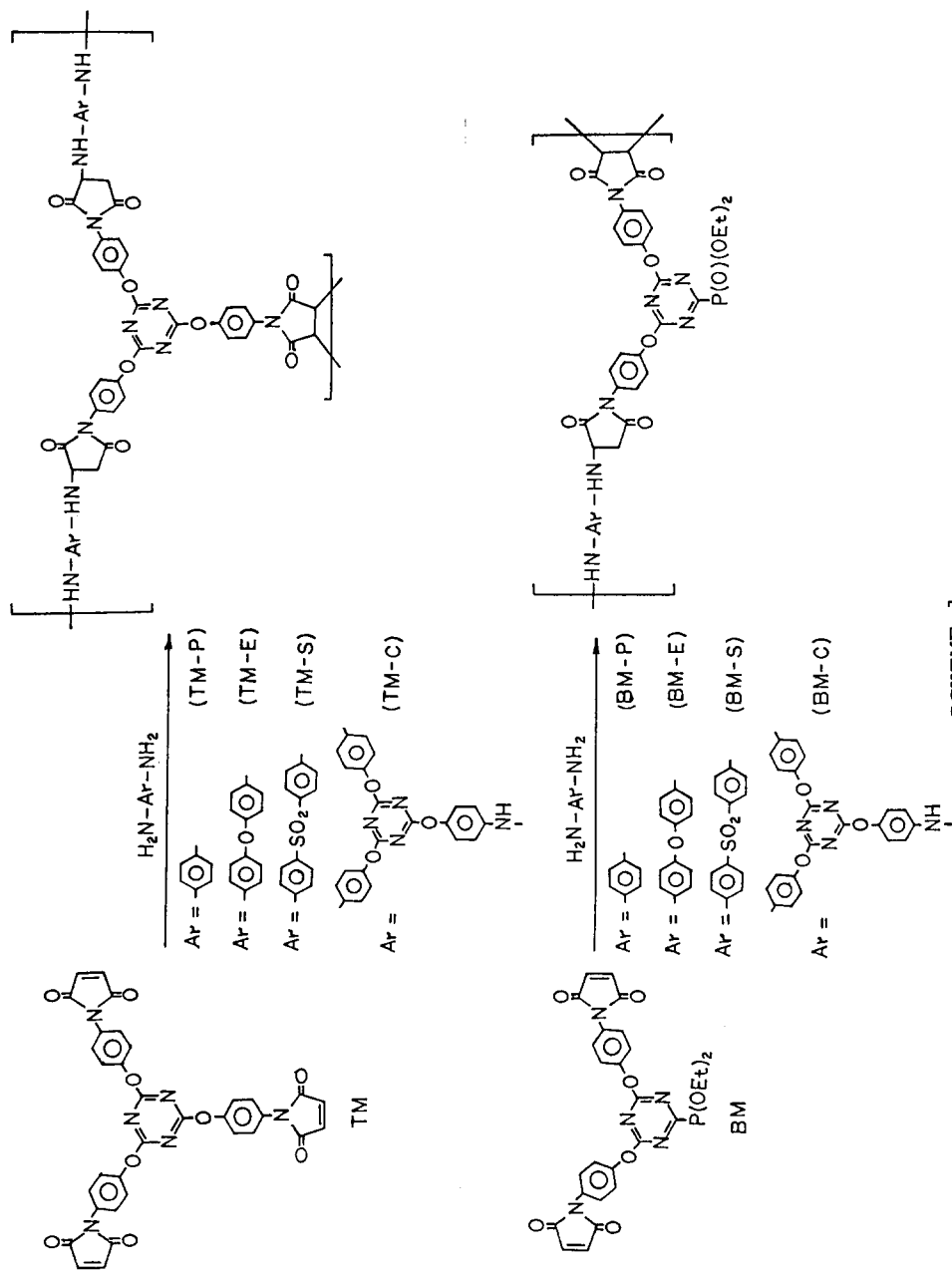
Powdered maleimide-amine adducts were separately placed in a shallow aluminium dishes and heated into an air oven at 160°C for 15 min and subsequently at 220°C for 1 h.

For comparative purposes, the cured resins of neat maleimides TM and BM were prepared by heating at 220°C for 2 h and then at 240°C for 40 min.

RESULTS AND DISCUSSION

Scheme 1 outlines the polymerization reactions of TM and BM in presence of certain aromatic di- or tri-amines. Throughout the text these polymers are referred to by the letter designations shown in parentheses.

The olefinic bond of maleimides is highly electron deficient due to the two flanking imide carbonyl groups. As a consequence maleimides are highly reactive and capable of undergoing nucleophilic attack by amines (Michael addition reaction). In



SCHEME 1

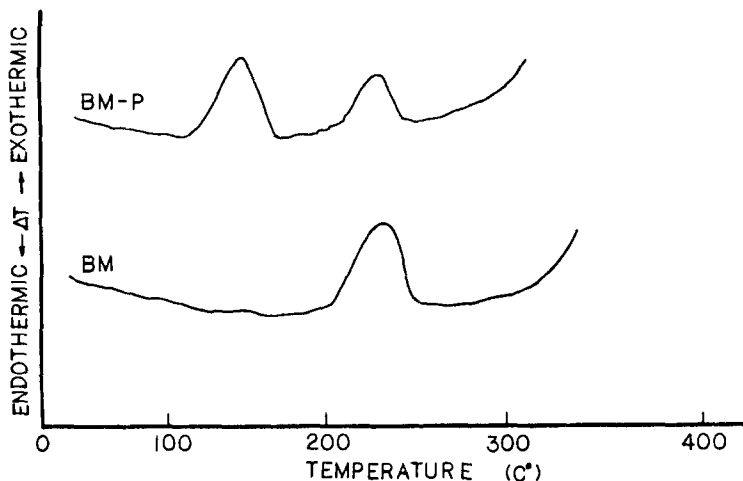


Figure 1. DTA scans of BM-P adduct as well as of neat BM in N_2 atmosphere.

the present case, a part of the maleimide system remained unreacted due to the nonstoichiometric amounts of maleimide and amine which were mixed. Upon heating these mixtures afforded cured resins having a complex chemical structure as was outlined in Scheme 1. Polymerization proceeded both by crosslinking through the maleimide olefinic bonds as well as by a Michael addition reaction between maleimide and amine. The extent of these polymerization reactions was depended upon the reactants ratio utilized.

The curing behaviour of the maleimide-amine adducts was investigated by DTA in N_2 atmosphere. Figure 1 presents typical DTA scans of BM-P adduct as well as of neat BM. The DTA thermograms of all maleimide-amine adducts showed two separated exotherms assigned to their polymerization reactions. In contrast, neat polymer precursors BM and TM exhibited only one exotherm associated with their thermal polymerization. The temperature of initiation of polymerization (T_i) and the temperature of termination of polymerization (T_t) were determined from the DTA traces and are listed in Table 1. These temperatures were obtained by extrapolating the front and back side of the exotherm to the base line. The observed bimodal character in the DTA scans should be due to different curing temperatures of the maleimide-amine adduct and the remaining unreacted maleimide. The first exotherm observed at a temperature range of 122-190°C was attributed to the curing of the maleimide-amine adduct. The second exotherm appeared at 202-282°C was assigned to the crosslinking through the maleimide olefinic bonds. Note that in neat TM and BM an exotherm associated with the polymerization reaction was observed above 210°C.

From Table 1 it can be seen that curing of TM-S and BM-S adducts occurred at comparatively higher temperatures. The lower nucleophilicity of 4,4-diaminodiphenylsulfone due to the presence of the electron-withdrawing sulfonyl group should be

TABLE 1
DTA Data of Maleimide-Amine Adducts and Neat Maleimides

Sample	1st Exotherm		2nd Exotherm	
	$T_i^a, ^\circ\text{C}$	$T_t^b, ^\circ\text{C}$	$T_i, ^\circ\text{C}$	$T_t, ^\circ\text{C}$
TM			228	264
TM-P	133	172	215	258
TM-E	140	178	221	265
TM-S	164	190	242	282
TM-C	138	171	212	247
BM			202	246
BM-P	122	161	207	244
BM-E	139	171	205	250
BM-S	152	185	243	261
BM-C	136	166	210	248

^aTemperature of initiation of polymerization.

^bTemperature of termination of polymerization.

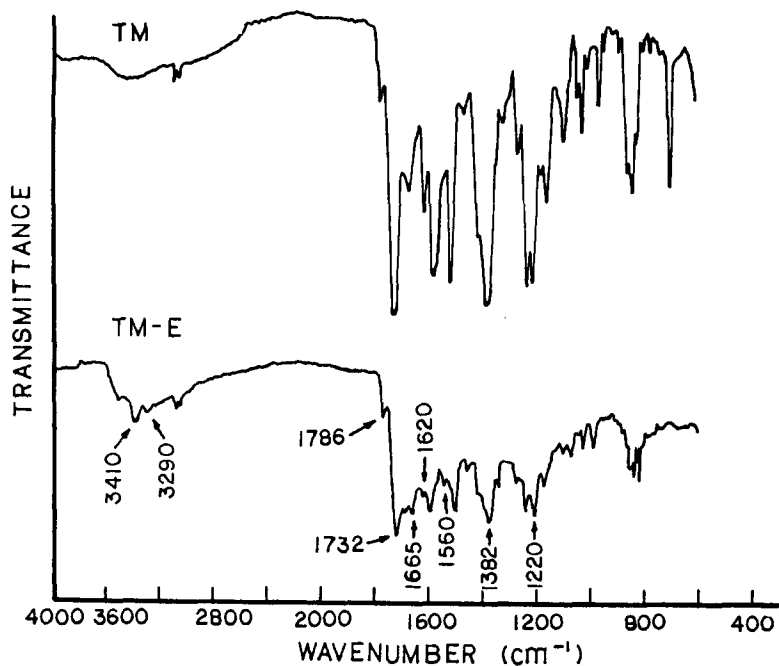


Figure 2. IR spectra of TM-E adduct and TM.

responsible for this behaviour.

Figure 2 presents the IR spectra of polymer precursors TM and TM-E adduct. Both spectra showed characteristic absorptions of imide structure (1786 , 1732 , 1382 cm^{-1}), C=N (1665 cm^{-1}), C=C (1620 cm^{-1}), and ether bond (1220 cm^{-1}). The TM-E adduct exhibited additional absorption bands at 3420 - 3360 cm^{-1} (NH stretching) and 1560 cm^{-1} (NH deformation) along with a broadening. Note that all BM-amine adducts showed absorptions around 1245 cm^{-1} (P=O) and 1070 - 1040 cm^{-1} (P-O-C). Finally, TM-S and BM-S adducts showed absorptions at 1165 and 1310 cm^{-1} assigned to the sulfonyl group.

The thermal and thermo-oxidative stability of cured resins was evaluated by dynamic TGA under anaerobic or aerobic conditions. Figure 3 shows typical TGA thermograms in N_2 . The relative thermal stability of cured resins could be assessed by comparing the initial decomposition temperature (IDT) obtained by extrapolation, the maximum polymer decomposition temperature (PDT_{max}), and the char yield (Y_C) at 800°C in N_2 and air. The results are listed in Table 2. It can be seen that the polymers obtained from maleimide-amine adducts were less thermally stable than those of the corresponding neat maleimides because of the thermally sensitive-NH-linkages. In addition, all polymers derived from the phosphorylated bismaleimide (BM) showed a lower thermal stability than did the corresponding polymers of trismaleimide (TM) due to the relatively easy thermal dissociation of the diethoxyphosphinyl groups. In contrast, the former polymers afforded higher char yield especially under aerobic conditions. Char formation is important to the prediction of flammability. A linear relationship between the oxygen index and the char residue on pyrolysis for halogen-free polymer has

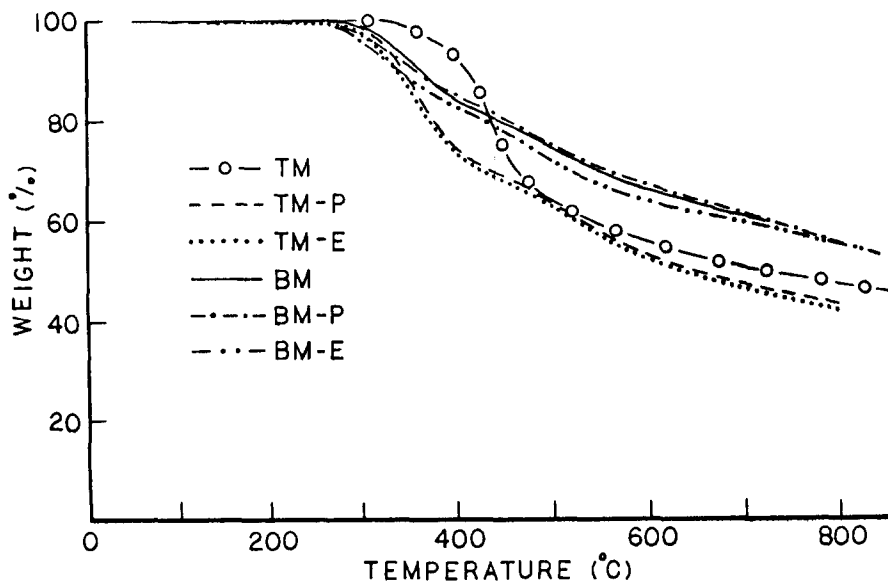


Figure 3. Typical TGA thermograms of polymers in N_2 atmosphere.

TABLE 2.
TGA Data of Polymers

Polymer	In N ₂			In Air		
	IDT ^a , °C	PDT ^b _{max} , °C	Y _C ^c , %	IDT, °C	PDT _{max} , °C	Y _C , %
TM	363	459	49	361	433	3
TM-P	321	379	44	310	395	4
TM-E	312	372	42	312	400	2
TM-S	320	375	41	315	404	3
TM-C	313	383	43	313	402	2
BM	326	376	58	324	378	22
BM-P	304	365	57	303	352	38
BM-E	300	351	56	300	345	34
BM-S	308	365	59	301	343	34
BM-C	302	368	55	303	340	36

^aInitial decomposition temperature.

^bMaximum polymer decomposition temperature.

^cChar yield at 800°C.

been proposed (6). Char yield was essentially unaffected upon polymerization of TM and BM in presence of aromatic amines. The IDT in N_2 or air of the polymers obtained from the maleimide-amine adducts was not remarkably influenced by the chemical structure of the aromatic di- or tri-amine utilized. The IDT in air was slightly lower than that in N_2 . This supports that decomposition was not seriously affected by the presence of oxygen.

CONCLUSIONS

A novel class of thermosetting resins usable as matrix resins for composites were prepared by polymerization of TM or BM in presence of various aromatic di- or tri-amines. This modification aimed to improve the flexibility of cured resins and to retain their heat-resistance. The maleimide-amine adducts initiated thermal polymerization at lower temperatures than did the corresponding neat maleimides. In the maleimide-amine adducts, the chemical structure of the amine utilized influenced the polymerization temperature. Higher curing temperatures were observed when aromatic diamines having a relatively low nucleophilicity were used. All polymers derived from the maleimide-amine adducts were less heat-resistant than those of the corresponding neat maleimides because of the thermally sensitive -NH- linkages. Incorporation of phosphorus in these resins reduced their initial decomposition temperature and increased their char yield. The chemical structure of aromatic amine did not affect significantly the initial decomposition temperature of cured resins.

ACKNOWLEDGEMENTS

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