Allylamine-Adducted Bismaleimide Resins. I. The Curing Reactions

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SYNOPSIS

A variety of allylamine-adducted bismaleimide (A-BMI) resins were prepared by reacting bismaleimide (BMI), such as 4,4′-bismaleimidodiphenylmethane (BDM) and 4,4′-bismaleimidodiphenylether (BDE), with various molar ratio of allylamine through the Michael addition. The prepared A-BMI resins are a partial crystalline or completely amorphous solid, depending on the amount of adducted allylamine. Two types of curing reactions for the A-BMI resins were detected by differential scanning calormetry and verified by the mass spectroscopies of cured resins: one is the homopolymerization of A-BMI resins through opening of the double bonds in the maleimide groups; the other is the reactions between allyl groups and benzene rings, taking place mainly when most of the double bonds in maleimide groups of the A-BMI resins have been opened by allylamines. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Bismaleimide (BMI) resins have been increasingly used as a matrix resin for composites because they have a higher service temperature than epoxies and are easier to process than other polyimides. The major components of all the current BMI grades consist of the methylene dianiline (MDA) derivative, 4,4′-bismaleimidodiphenylmethane (BDM).[1] However, to upgrade the BDM resins for composite applications, two processing problems remain to be overcome. One is that the gelation time of a typical hot melt BDM mixture with *O,O′*-diallylbisphenol A toughener at 160°C is about 100 min.[2] BDM is a crystalline solid with a melting temperature of 155–156°C, close to the cure temperature; it often incurs early cure during the preparation of a hot melt resin system. The other problem is that BDM has a tendency to recrystallize from the mixture during ageing.[3] Thus, the hot melt type BDM resin systems often show inconsistent properties from batch to batch.

In this regard, we initiated a project several years ago to modify BMI resins, aiming to reduce their crystallinity and processing temperature. A series of allylamine-adducted BMI (A-BMI) resins, such as allylamine-adducted BDM (A-BDM) and allylamine-adducted 4,4′-bismaleimidodiphenylether (A-BDE) were synthesized by reacting BMI with various molar ratios of allylamine through Michael additions. In the first part of this study, the curing properties of A-BDM and A-BDE were investigated and it was found that two types of curing reactions took place: the homopolymerization of A-BMI resins through opening of the residual double bonds; the reactions between allyl groups and benzene rings.

EXPERIMENTAL

Sample Preparation

BDM and BDE were prepared from maleic anhydride and 4,4′-diaminodiphenylmethane and from maleic anhydride and 4,4′-diaminodiphenylether, respectively, by the method described in the literature[4–8] with some modifications. In general, a solution of diamine (1 mol) in acetone was added dropwise into the flask that was already charged with a solution of maleic anhydride (2 mol) in acetone. The addition was completed after about 2 h at ice bath temperature under a nitrogen atmosphere, and

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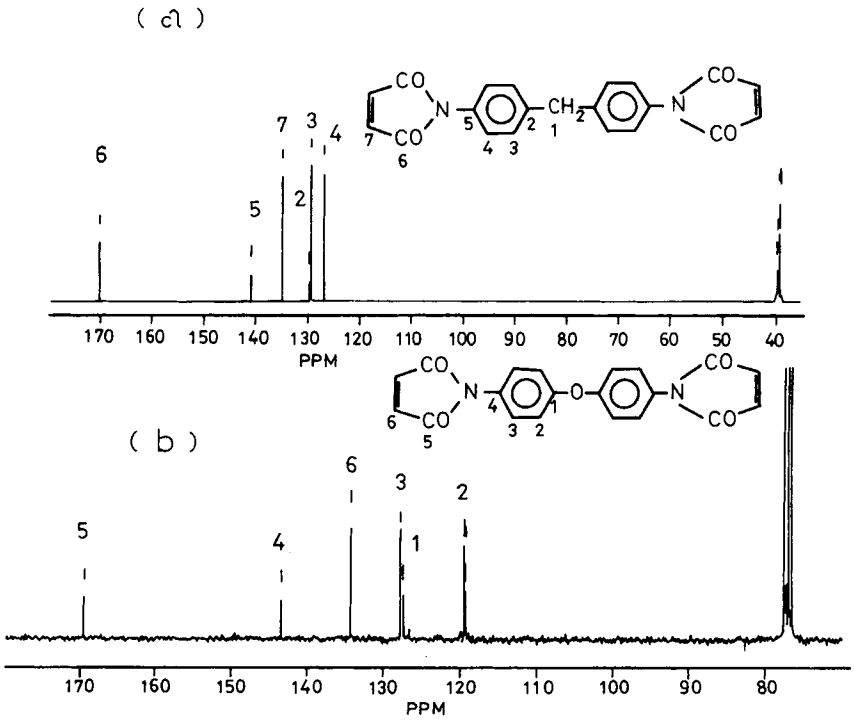


Figure 1 ^{13}C-NMR spectra of the prepared (a) BDM and (b) BDE.

then the flask was stirred overnight at room temperature. Afterward, the yielded insoluble amic acid was filtrated, washed with acetone, and dried under vacuum. Cyclization of the amic acid (0.5 mol) was carried out in an acetone solution containing acetic anhydride (1 mol), triethylamine (0.3 mol), and nickel(II) acetate tetrahydrate (0.03 mol) at room temperature under a nitrogen atmosphere for about 50 h until BMI precipitated. The precipitate was then collected and washed with a sodium bicarbonate solution until free from acetic acid. The product was finally recrystallized from $CHCl_3$/MeOH (1 : 1 by volume) solution.

Allylamine-adducted BMIs were prepared by the following method. Various amounts of the allylamine solution in chloroform were added dropwise into the flask that was already charged with BMI (0.2 mol) slurry in chloroform (BMI was difficult to dissolve in chloroform), and the reaction was carried out for about 5 h at 40°C under nitrogen atmosphere until BMI was completely dissolved and clear solution was obtained. The solution was washed with distilled water and then the solid products were obtained by removing the chloroform under vacuum at 90°C.

The A-BMIs were cured in hot press for 2 h at 180°C and 5 h at 220°C both under 1.38×10^7 Pa pressure.

Analytical Techniques

Infrared spectra of the samples were recorded on a Hitachi 270-30 model IR with KBr pellets. Their ^{13}C-nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AM-300WB model NMR

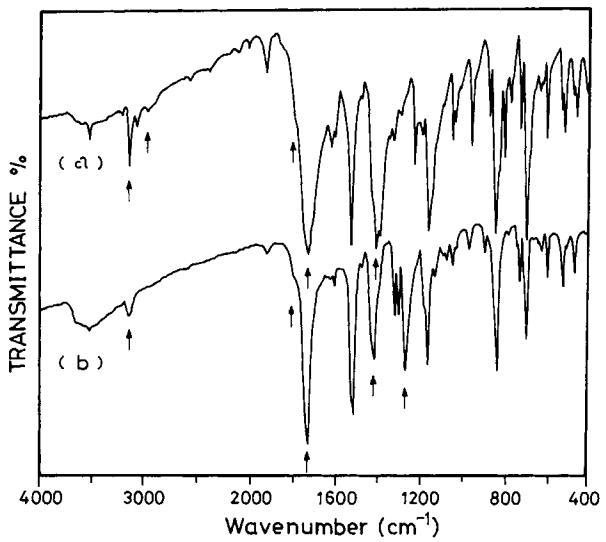


Figure 2 IR spectra of the prepared (a) BDM and (b) BDE.

spectrometer with dimethyl sulfoxide-d_6 (DMSO-d_6) as a solvent and internal standard. The phase transition and curing exotherm of BDM and BDE with and without modification by allylamine were measured by differential scanning calorimetry (DSC) performed in a Du Pont 9900-910 model DSC. Tests were run at a heating rate of 10°C/min. Thermogravimetric analysis of the samples was conducted in a Perkin–Elmer TGA-2 model thermogravimetric analyzer by heating from 50 to 800°C at a heating rate of 10°C/min. The mass spectra of A-BDM and A-BDE and their cured resins were recorded on a Finnigan Mat TSQ-46C model mass spectrometer.

RESULTS AND DISCUSSION

Characterization of A-BMI

The prepared BDM and BDE were characterized by ^{13}C-NMR and IR spectroscopies and by comparison of their melting points. The ^{13}C-NMR spectra are shown in Figure 1, provided with the assignments of each carbons in the molecules referring to Kumar et al.[9] For the IR spectra of BMI, the characterization peaks are 3140 cm^{-1} (ν =C—H maleimide), 1780 cm^{-1} (ν C=O out of phase), 1720 cm^{-1} (ν C=O in phase), and 1410 cm^{-1} (ν C—N—C),[10] all appeared in the IR spectra of prepared BDM and BDE as shown in Figure 2. However, the difference between BDM and BDE can be seen from the peaks at 2920 cm^{-1} (ν —CH_2—) for BDM and at 1250 cm^{-1} (ν —O—) for BDE.

By reaction of allylamine in various molar ratios with BDM, the intensity of the peak contributed by the double bonds in the maleimide groups decreased rapidly with increasing the amount of allylamine (Fig. 3). (The molar percentage is calculated by dividing the moles of allylamine by the moles of BDM.) The reaction of 150 mol % allylamine with BDM had almost opened all the double bonds. However, the intensity of the peak at 920 cm^{-1} contributed by the allyl groups was gradually increased with increasing the amount of allylamine. On the other hand, the peak at 3330 cm^{-1} contributed by the secondary amine groups in the reacted allylamines did not appear until the amount of allylamine was more than 10 mol %.

In general, five compounds shown below may possibly be yielded as allylamine was reacted with BDM or BDE.

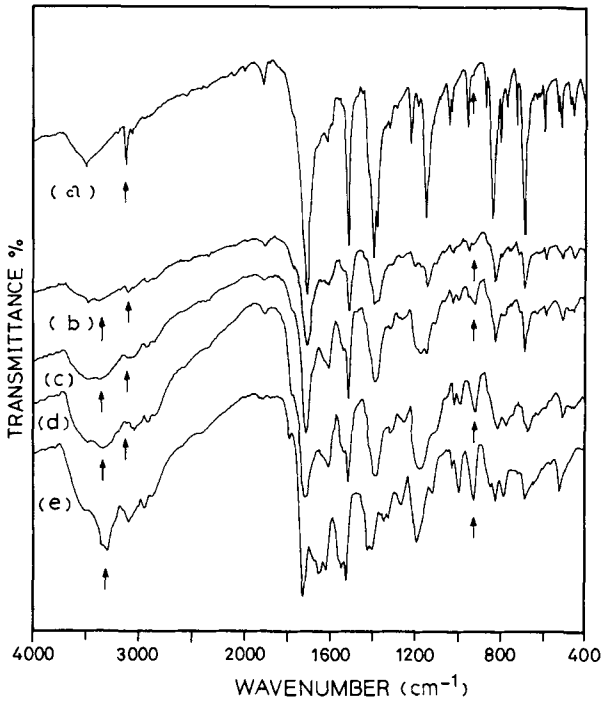
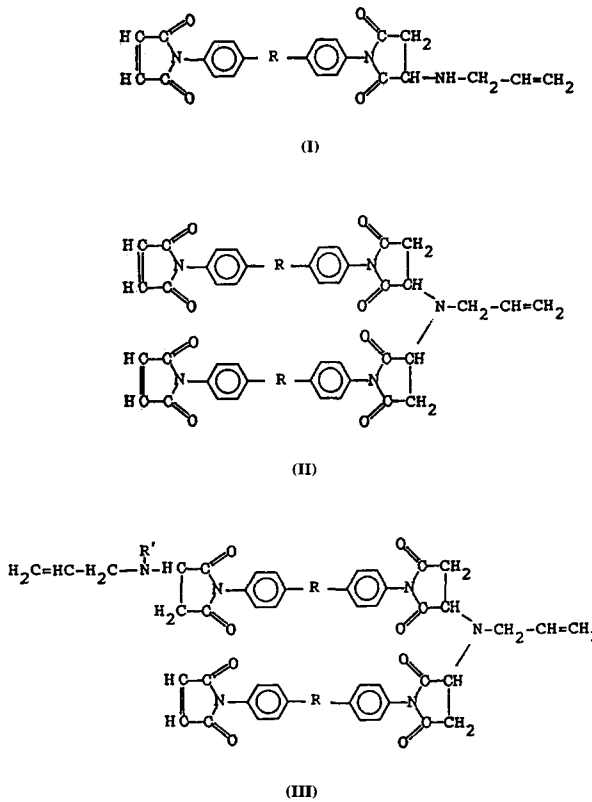
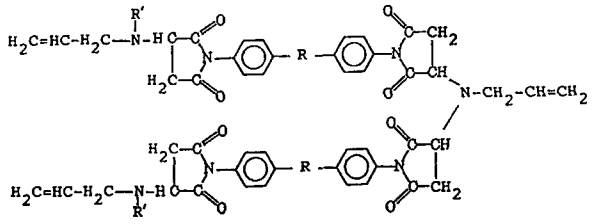
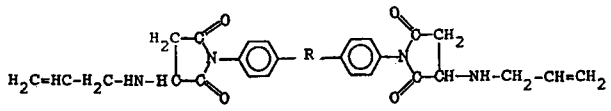


Figure 3 IR spectra of (a) 10% A-BDM, (b) 50% A-BDM, (c) 100% A-BDM, (d) 150% A-BDM, and (e) 200% A-BDM.





(IV)



(V)

where R = CH_2 for A-BDM or 0 for A-BDE; R' = H or reacted BMI.

The concentration of compounds I–V in the yielded A-BMI is dependent on the amount of allylamine reacting with BDM or BDE. However, they were difficult to separate from each other by gel permeation chromatography owing to the similar size and structure among the compounds II, III, and IV. However, it is presumable that the major component of the A-BDM resin prepared by reacting BDM with 10 mol % allylamine or less is compound II because the peak contributed by the secondary amine groups did not appear and that contributed by the double bonds in the maleimide groups significantly reduced its intensity. As the molar ratio of allylamine was increased from 10 to 150 mol %, the intensity of the latter peak decreased rapidly while that of the peaks contributed by the second amine groups and allyl groups gradually increased, implying that compounds II, III, and IV should be yielded in sequence along with the increase of molar ratio of allylamine. As the amount of allylamine was more than 150 mol %, compounds IV and V in the yielded A-BDM should be dominated in view of the fact that no double bonds were left. On the other hand, the change in IR data of A-BDE as a function of molar ratio of allylamine to be reacted is similar to that for A-BDM, indicating that their yielded components are similar.

Figure 4 shows the mass spectrum of 200% A-BDM prepared by reacting BDM with 200 mol % allylamine. The mass spectra of BMIs and their derivatives have been extensively studied.[9,11,12] Accordingly, a peak at m/e 41 and a basic peak at 56 are explained by the cleavage of the allylamine groups to the $[CH_2—CH=CH_2]^+$ and $[NH_2—CH_2—CH=CH_2]^+$ fragments, respectively. It is believed that $[CH_2—CH=CH_2]^+$ fragments were obtained mostly from the fragments of allylamine groups with both amine hydrogen groups reacted in the compound IV, whereas $[NH_2—CH_2—CH=$

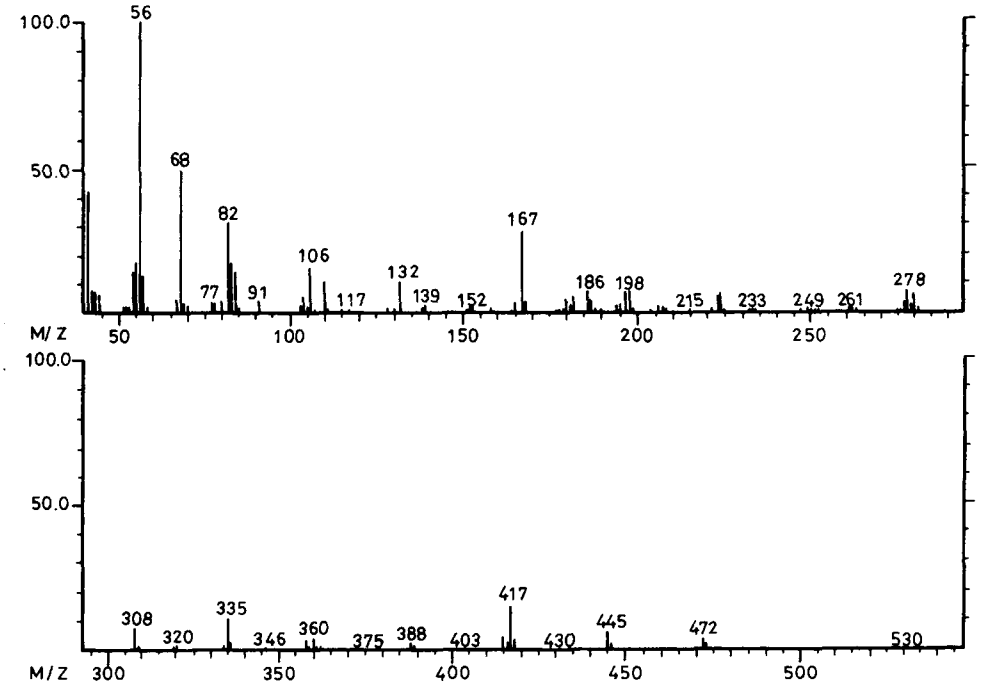


Figure 4 Mass spectrum of 200% A-BDM.

$CH_2]^+$ fragments were mostly from those with a single amine hydrogen group reacted in compounds IV and V. In that case, the ratio of allylamine groups with both amine hydrogen groups reacted to those with a single amine hydrogen group reacted in the 200% A-BDM would be 43%, determined from its mass spectrum. By the same token, the ratio for the 200% A-BDE prepared by reacting BDE with 200 mol % allylamine would be 30%.

Curing Properties of A-BMI

The heat of fusion for BDM is 93 J/g with a melting point at 155°C, measured by the DSC spectrum shown in Figure 5. As 10 mol % allylamine was reacted with BDM, the yielded 10% A-BDM had the heat of fusion dropped to 18.8 J/g as shown in Figure 6. (The scale of vertical axis, i.e., the heat flow, in Fig. 6 is triple times the scale in Fig. 5.) Moreover, its curing reaction takes place rapidly as soon as it melts, much faster and at a lower temperature than that of pure BDM, indicating that a small amount of the yielded compound II greatly interfered with the crystallization of BDM and accelerated the curing reaction. The accelerating effects of compound II might be because the C=O in the maleimide groups withdraws an electron so that the allyl group becomes more positive charged and accelerates the homopolymerization of BDM monomers. The homopolymerization of BDM monomers during cure of the 10% A-BDM was verified by the mass spectrum of its cured resin that shows a basic peak at m/e 358 as seen in Figure 7(a), equal to the mass of BDM monomers, and obviously contributed by the cleavage of polymerized BDM to its monomer units.

As 50 mol % allylamine was reacted with BDM,

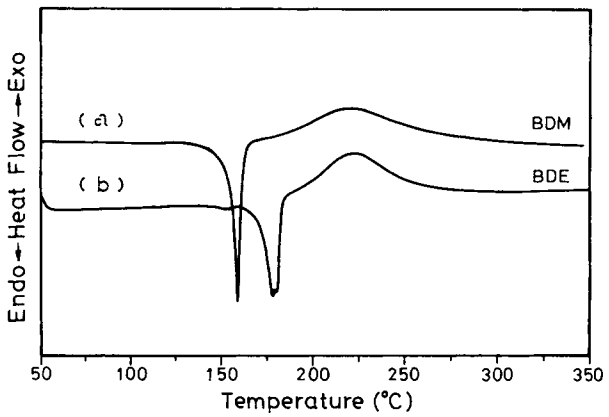


Figure 5 DSC spectra of the prepared (a) BDM and (b) BDE.

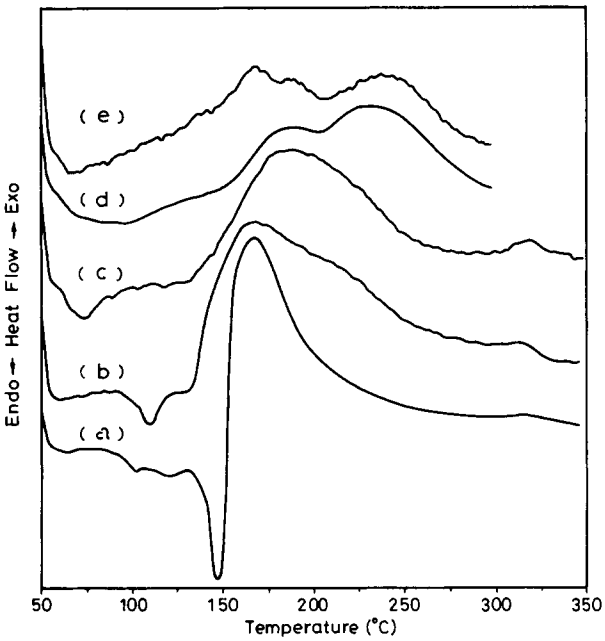


Figure 6 DSC spectra of (a) 10% A-BDM, (b) 50% A-BDM, (c) 100% A-BDM, (d) 150% A-BDM, and (e) 200% A-BDM.

the yielded 50% A-BDM has a melting point of 111°C and heat of fusion further dropped to 6.3 J/g as seen in Figure 6. The curing exotherm peak temperature at 164°C is still similar to that of 10% A-BDM but the peak becomes broad, indicating that more curing reactions than just homopolymerization took place. As 100 mol % allylamine was reacted with BDM, the yielded 100% A-BDM also had a broad curing peak but with the peak temperature shifted to 187°C. Apparently, the major type of curing reaction was different from the homopolymerization, for the amount of double bonds in maleimide groups is too small to conduct the homopolymerization. When the amount of allylamine that reacted with BDM was higher than 100 mol %, the DSC spectra of the yielded A-BDM had an additional peak at about 250°C (Fig. 6). The additional peak resulted from the degradation instead of the curing reaction, verified by the loss of weight at 250°C in the TGA thermogram of 150% A-BDM prepared by reacting BDM with 150 mol % allylamine (Fig. 8). The mass spectrum of cured 200% A-BDM shows a basic peak at m/e 44 as seen in Figure 7(b), indicating that allylamine groups are prone to cleavage. Thus, the degradation at 250°C is believed to result from the cleavage of allylamine groups.

Furthermore, a significant observation on the mass spectrum of cured 200% A-BDM is its fragmentation to m/e 106, 132, 182, 208, 198, 224, 280,

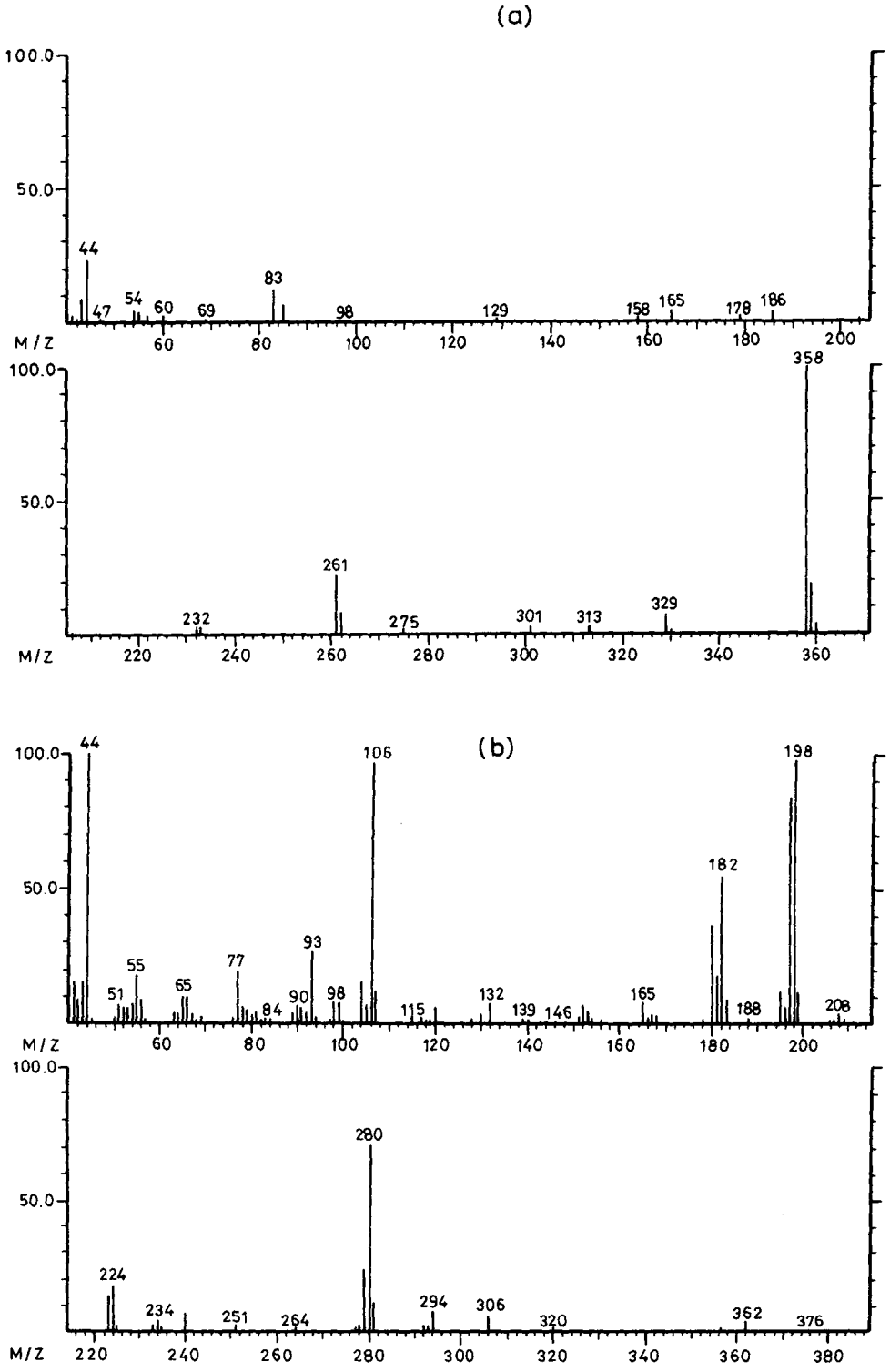


Figure 7 Mass spectra of cured (a) 10% A-BDM and (b) 200% A-BDM.

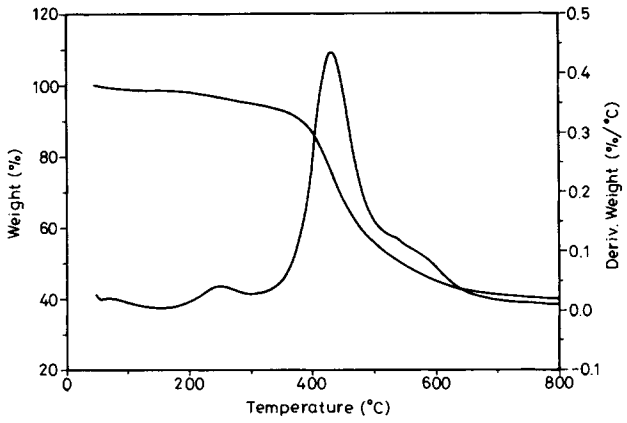
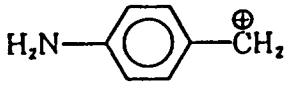
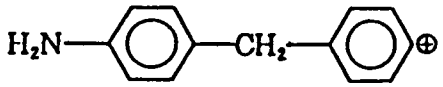


Figure 8 TGA thermogram of 150% A-BDM.

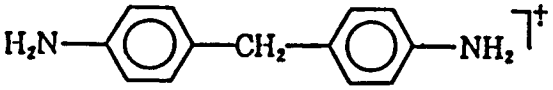
and 306. According to the mass spectra of BDM derivatives reported by Kumar et al.,[9] the peaks at *m/e* 106, 182, 198, and 280 are contributed by the cleavage of BDM groups to the following fragments I, II, III, and IV, respectively,



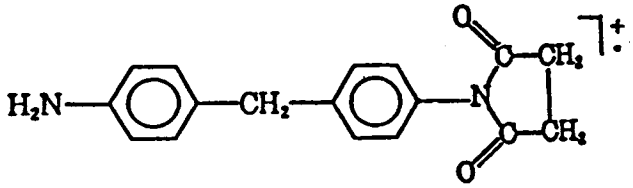
Fragment I, *m/e* 106



Fragment II, *m/e* 182

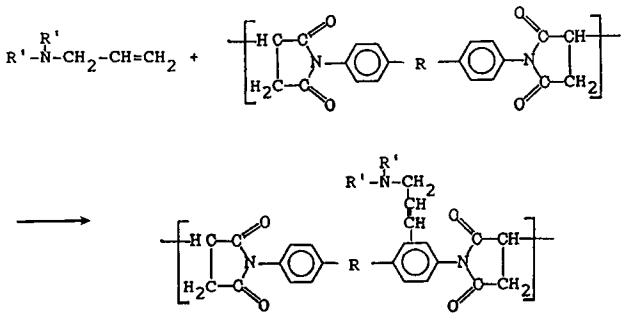


Fragment III, *m/e* 198



Fragment IV, *m/e* 280

Interestingly, the peaks at *m/e* 132, 208, 224, and 306 have 26 units more than those contributed by the fragments I–IV, respectively, indicating that some of the BDM units had been attached by $-C_2H_2-$ groups during the curing reaction. Because the 200% A-BDM has no double bonds in the maleimide groups for the curing reaction, the possible reactions between allylamine groups and BDM units is by electrophilic aromatic substitution. The reaction is suggested as follows,



where R = CH_2 for BDM unit or O for BDE unit; R′ = cleavaged portion of allylamine groups.

The allylamine groups are prone to cleavage at temperatures higher than 200°C. Therefore, it is speculated that the cleavaged allylamine groups are electrophilic and capable of undergoing the electrophilic aromatic substitution. The curing exotherm

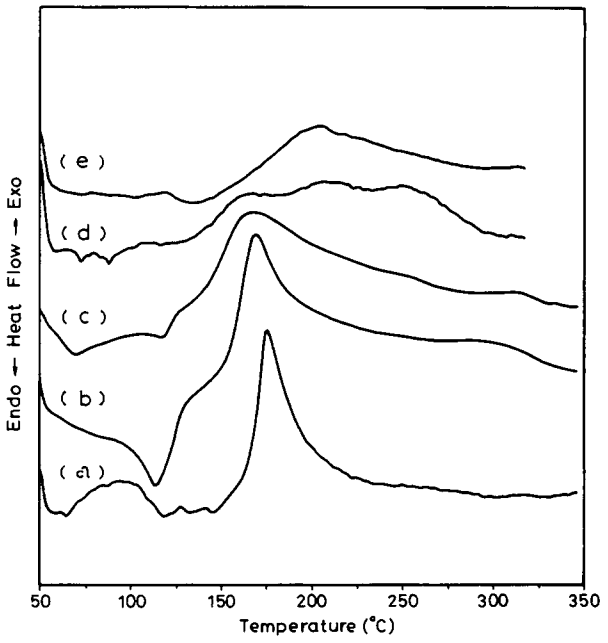


Figure 9 DSC spectra of (a) 10% A-BDE, (b) 50% A-BDE, (c) 100% A-BDE, (d) 150% A-BDE, and (e) 200% A-BDE.

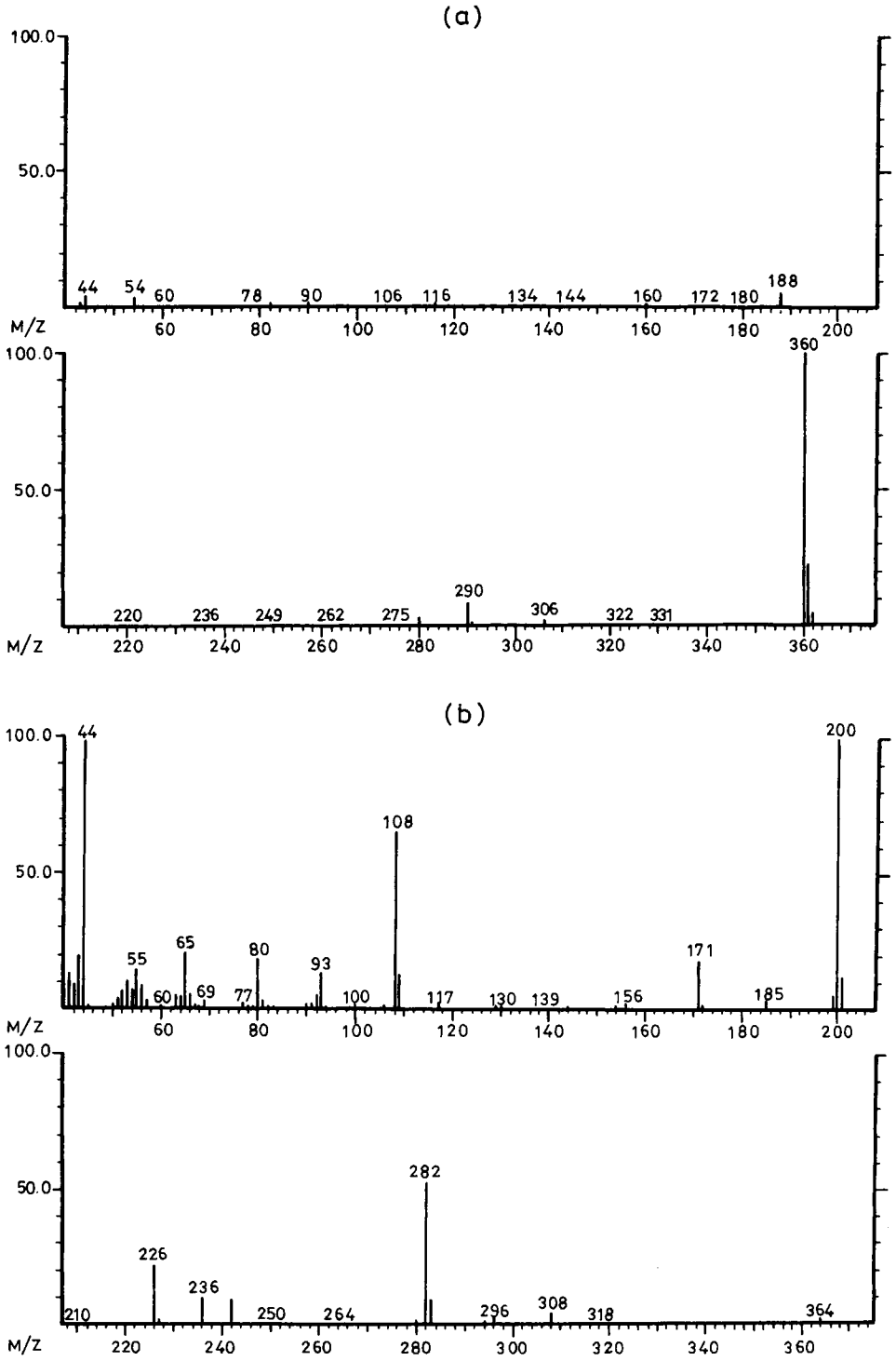


Figure 10 Mass spectra of cured (a) 10% A-BDE and (b) 200% A-BDE.

of A-BDM has only two peaks; one of them at around 165°C is contributed by the homopolymerization through the opening of double bonds in the maleimide groups; the other curing peak at around 200°C overlapped with the degradation peak of curing A-BDM resin. We believe that the electrophilic aromatic substitution proceeded during the simultaneous reactions between degradation and curing.

Unfortunately, due to the complicated curing system, no further experimental evidence except mass spectra of cured A-BDM was obtained.

On the other hand, BDE monomers have a melting point at 177°C with the heat of fusion 82 J/g, measured from the DSC spectrum shown in Figure 5. As 10 mol % allylamine was reacted with BDE, the yielded 10% A-BDE is an amorphous solid with a sharp curing exothermal peak at 176°C (Fig. 9). The mass spectrum of cured 10% A-BDE shows a basic peak at m/e 360 [Fig. 10(a)], which is equal to the mass of BDE monomer. Apparently, the peak is contributed by the cleavage of polymerized BDE to BDE monomer units. Similar to the 10% A-BDM, the compound II yielded by the reaction of BDE with allylamine has interfered with the crystallization of BDE and accelerated its homopolymerization.

As BDE was reacted with 50 mol % allylamine, the yielded 50% A-BDE has a broad fusion peak at 114°C and a curing exotherm peak broader than that of 10% A-BDE but at the similar peak temperature as seen in Figure 9. The broad fusion peak is believed to be contributed by the melting of compound II, for it is the dominant component in 50% A-BDE. By the same token, the small fusion peak at 111°C in the DSC spectrum of 50% A-BDM (Fig. 6) should also be contributed by the melting of compound II and irrelevant to the fusion of BDM.

As 100 mol % allylamine was reacted with BDE, some of the compound II was reacted to compounds III and IV so that the intensity of the fusion peak was significantly reduced (Fig. 9). In addition, the curing exotherm peak becomes much broader than that of the A-BDE adducted with less allylamine but has the similar peak temperature. As BDE was reacted with 150 mol % allylamine, the yielded 150% A-BDE has an additional broad curing exotherm peak appearing at around 200°C, overlapped with the degradation peak at 250°C. As the amount of allylamine reacted with BDE was increased to 200 mol %, the original homopolymerization peak disappeared, and the curing peak merged with the degradation peak into one peak at around 200°C. Similar to the A-BDM, the degradation resulted from the cleavage of allylamine groups as indicated by the mass spectra of A-BDE resins. Simultaneous reactions between the degradation and cure imply that the cleavaged allylamine groups contributed to the curing reactions.

The mass spectrum of cured 200% A-BDE shows a basic peak at m/e 44 and several significant peaks at m/e 108, 200, 226, 282, and 308 [Fig. 10(b)]. The basic peak at m/e 44 is contributed by the cleavage of allylamine groups. Similar to the mass spectrum of cured 200% A-BDM, the peaks at m/e 108, 200, and 282 are contributed by the corresponding fragments I, III, and IV with the $-CH_2-$ group replaced by the $-O-$ group. The peaks at m/e 226 and 308 have 26 m/e more than those contributed by the corresponding fragments III and IV, respectively, indicating that some of the BDE units were attached by the $-C_2H_2-$ group. Similar to the A-BDM, we believe that the attachment resulted from the reactions of cleavaged allylamine groups and BDE groups by electrophilic aromatic substitution as shown in eq. (1). In that case, the electrophilic aromatic substitution contributes to the major curing reaction at around 200°C. On the other hand, the discrepancy in mass spectra between cured 200% A-BDE and cured 200% A-BDM, such as missing of the peaks contributed by the corresponding fragment II and by the corresponding fragment I attached by the $-C_2H_2-$ group for the cured 200% A-BDE, is because the bonding energy of some chemical bonds is changed as the $-CH_2-$ group in the BDM unit is replaced by the $-O-$ group.

Similar to the A-BDM, A-BDE has two types of curing reactions: one is the homopolymerization of BDE accelerated by compound II taking place at about 170°C; the other is the reaction between allyl groups and benzene rings taking place at about 200°C. It was found in the second part of the study that the networks formed by two different curing reactions are immiscible and the properties of cured A-BDM and A-BDE are highly dependent on the amount of allylamine used for adduction.[13]

CONCLUSIONS

The crystallization and curing reactions of A-BMI, such as A-BDM and A-BDE, were found to be greatly affected by the amount of allylamine to adduct BMI through the Michael addition. As 10 mol % allylamine was used to prepare the A-BMI, the crystallization of BMI in 10% A-BMI was interfered with or prohibited by the yielded compound II, which was also found to accelerate the homopolymerization through the opening of residual double bonds in maleimide groups. As the amount of allylamine to react with BMI was increased, the amount of residual double bonds decreased so that the homopolymerization became impossible. In that case, curing reactions of the A-BMI resins were dominated by the reactions between allyl groups and benzene rings taking place at a temperature near the cleavage temperature of allylamine groups.

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