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Novel bismaleimide with naphthalene side group. 1. From 1-naphthaldehyde and 2,6-dimethylaniline

Chun-Shan Wang[a,*], **Tsu-Shang Leu**[a] **and Kuo-Run Hsu**[b]
[a]*Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701, ROC*
[b]*Department of Food Nutrition, China Junior College of Medical Technology, Tainan, Taiwan, ROC*
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Novel bismaleimide (BMI) and epoxy resin with naphthalene side group were synthesized from the intermediates bis(4-amino-3,5- dimethylphenyl)naphthylmethane (BADN) and bis(4-hydroxy-3,5- dimethylphenyl)naphthylmethane (BHDN) which were obtained from the reactions between 1-naphthaldehyde and 2,6-dimethylaniline or 2,6- dimethylphenol, respectively. The monomers were characterized by Fourier transform infrared spectroscopy, elemental analysis, mass spectrometry and potentiometery. Their corresponding bismaleimide bis(4-maleimido-3,5-dimethylphenyl)naphthylmethane (BMDN) and the diglycidyl ether of BHDN (DGEBN) were cured with 4,4′-diaminodiphenylmethane (DDM) at various mole ratio and their curing behaviors investigated by differential scanning calorimetry (d.s.c.) and (*FT*i.r.). Thermogravimetric analyses indicated that the cured systems of BMI and epoxy resins were stable up to 416–424 and 377–395°C, respectively, in nitrogen atmosphere, and the former afforded a relatively higher char yield than the latter. In addition, the cured bismaleimide possessed better T_g, moisture resistance, lower coefficient of thermal expansion (α) and dielectric constant (ϵ) than that of the epoxy system. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: naphthalene side group; moisture resistance; coefficient of thermal expansion)

INTRODUCTION

Polyimides[1–4] have remarkable high temperature resistance and good mechanical and electrical properties. However, condensation type polyimides usually suffer from processing problems due to their insolubility, infusibility and the evolution of volatiles during the ring formation. Epoxy resins[5] are widely used as matrix resins for structural composites because of their ease of handling and processability, however the limitation on the upper use temperature and poor hot/wet performance restrict their application.

Bismaleimides are an important class of addition type polyimides and well known for their excellent processability and balance of thermal, electrical and mechanical properties. They are employed as resins in advanced composities and electronics such as multilayered printed circuit (PC) boards. They have been evaluated as the potential replacement for epoxy resins where high temperature performances is required. Bismaleimides bridge the temperature performance gap between epoxy and polyimides. Epoxy resins usually cannot withstand the severe environment of surface mount technology (260°C, 30 s). The trend toward miniaturization, such as increasing circuit densities, high power chips, circuits with increased operating temperatures, along with more stringent insulation resistance requirements, have prompted investigation into bismaleimides for board fabrication. Nevertheless, few were concerned with bismaleimides containing naphthalene structure. Varma *et al.*[6] and Hoyt *et al.*[7] reported ester bismaleimide monomer with 2,6-naphthalene moiety and 1,5-diamino naphthalene-based bismaleimide, respectively.

The object of this study was to combine the special features of naphthalene structure (rigid, low moisture absorption and low coefficient of thermal expansion) with bismaleimide (high crosslink density, good thermal and electrical properties), in order to produce a new material with high T_g and adhesive strength, low moisture absorption, coefficient of thermal expansion and dielectric constant for multilayer circuit board and semiconductor encapsulation applications. The monomer will be copolymerized with DDM through the Michael addition and then crosslinked to produce a network polymer. Properties of the polymer will be compared with naphthalene-based epoxy resin to demonstrate its superiority.

EXPERIMENTAL

Materials

1-Naphthaldehyde (Acros), 2,6-dimethylaniline (Acros), 2,6- dimethylphenol (Acros), maleic anhydride (Janssen), sodium acetate (Nacalai tesque, extra pure reagent), acetic anhydride (Janssen), epichlorhydrin (Janssen), *p*-toluenesulfonic acid monohydrate (Ferak), triphenyl phosphine (Ferak), 4,4′-diaminodiphenylmethane (Janssen), were all used as received. *N,N*′-Dimethylformamide (DMF) was purified by distillation under reduced pressure over calcium hydride and stored over 4A molecular sieves. All other solvents were obtained from various commercial sources and used without further purification.

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[*] To whom correspondence should be addressed

Measurements

Melting points were obtained on a polarizing microscope (Laboratory Devices Mel-Temp. II). Fourier transform infrared (*FT*i.r.) spectra were recorded on a Nicolet Magna-520 or Bio-Rad FTS-165 spectrometer with KBr pellets. Mass spectrometric analyses were performed on a VG 70–250 s GC/MS spectrometer with a solid inlet. Elemental analyses were carried out with a Heraeus CHN-Rapid elemental analyzer.

Differential scanning calorimeter (Perkin-Elmer DSC-7) measurements were made at a scan rate of 20°C/min with 5–6-mg samples under nitrogen atmosphere and the glass transition temperature (T_g) values were taken as the change of the specific heat in the heat flow curves. The coefficient of thermal expansion (α) was measured with TMA mode of Perkin-Elmer DMA-7, a specimen 5 mm in length was used at a heating rate of 10°C/min. The thermal expansion increased with temperature and the α values were calculated from the slope. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 thermal analyzer using a heating rate of 20°C/min in N_2 at a purge pressure of 25 p.s.i., within the temperature range of 30–750°C. Dielectric constants (ϵ) were measured with a Du Pont-2970 dielectric analyzer at a frequency of 1 kHz and 30°C in a nitrogen atmosphere at a flow rate of 500 cm^3/min by the two parallel plate mode. The specimens (20 × 20 × 1 mm) were subjected to vacuum pretreatment of 1 Torr at 120°C for 4 h to eliminate absorbed water. Epoxy equivalent weight (EEW) of epoxy resin was determined by the $HClO_4$/potentiometric titration method.

The preparation of bis(4-amino-3,5-dimethylphenyl)naphthylmethane (BADN)

2,6-Dimethylaniline (48.47 g, 0.4 mol) was charged to a three-necked flask, equipped with a reflux condenser, and the contents were heated under nitrogen atmosphere to the reflux temperature. 1-Naphthaldehyde (15.62 g, 0.1 mol) dissolved in 3.3 ml (12 N) of hydrochloric acid was added dropwise over a period of 1.5 h. After the completion of addition the reaction mixture was maintained at reflux (*ca.* 120–124°C) for another 6 h. The reaction mixture was then cooled to 60°C, and 7.92 g of 20% aqueous solution of sodium hydroxide was added to the resulting suspension. The mixture was poured into methanol to precipitate a pale-white solid which was filtered, washed repeatedly with water, and dried to yield BADN (29.64 g, 78%), m.p. 217–218°C; IR(KBr) cm^{-1}: 3400, 1622 (NH str.), 801 (α-nap.); mass spectrum EI *m*/*e* intensity: 380 (100, M+); analysis calculated for $C_{27}H_{28}N_2$: C, 85.26; H, 7.37; N, 7.37%; found: C, 84.32; H, 7.19; N, 6.91%.

The preparation of bis(4-hydroxy-3,5-dimethylphenyl)naphthylmethane (BHDN)

Into a reactor equipped with a stirrer, a reflux condenser, a thermometer, a Dean-stark water separator and a nitrogen inlet, were charged 32.98 g (0.27 mol) of 2,6-dimethylphenol, 19.2 g (0.12 mol) of 1-naphthaldehyde, 2.34 g (0.012 mol) of *p*-toluenesulfonic acid monohydrate and 38 ml of toluene. The reaction mixture was refluxed at 132–134°C for 5 h under a nitrogen atmosphere. Water produced by the reaction was successively removed from the system by azeotrope with toluene. After completion of the reaction, the solution was cooled to 80°C, 5.2 g of 10% aqueous solution of sodium hydroxide was added to the resulting solution. The resulted solid was filtered and recrystallized from methanol/water (3:1, v/v) to produce light-brown crystals. The yield of BHDN (44.36 g, 97%), m.p. 156–157°C; IR(KBr) cm^{-1}: 3550, 1210 (OH str.), 784 (α-nap.); mass spectrum EI *m*/*e* intensity: 382 (100, M +); analysis calculated for $C_{27}H_{26}O_2$: C, 84.82; H, 6.81%; found: C, 84.40; H, 6.89%.

The preparation of bis(4-maleimido-3,5-dimethylphenyl)naphthylmethane (BMDN)

A three-necked flask equipped with an addition funnel and a nitrogen inlet was charged with a solution of maleic anhydride 10.59 g (0.108 mol) in THF (42 ml). Under a nitrogen atmosphere, BADN (18.62 g, 0.049 mol) in THF (149 ml) was added dropwise to the above mixture. A slightly exothermic reaction was observed and the reaction mixture was stirred at room temperature for 5 h and then at 52–54°C for an additional 2 h. The pale-gray precipitate was collected, washed with fresh THF to remove maleic anhydride, and then dried in a vacuum oven to obtain bismaleamic acid.

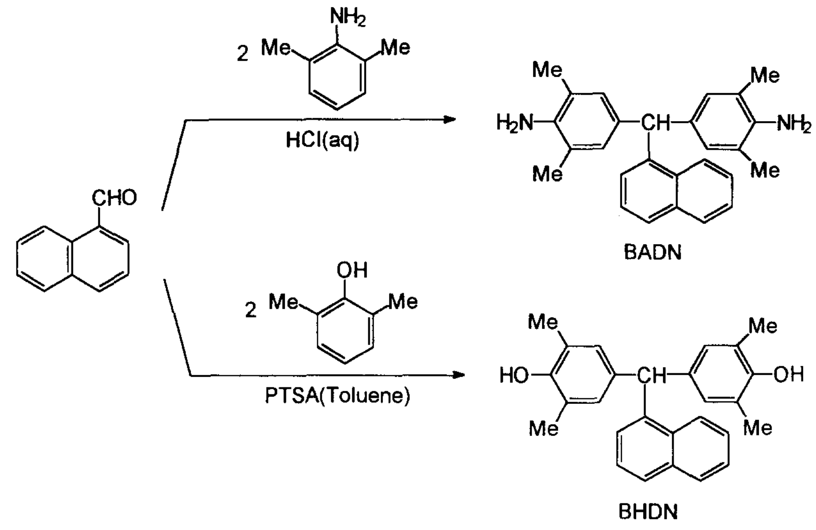
To a 250-ml round-bottomed flask was added 25.61 g (0.044 mol) of bismaleamic acid and 87 ml of DMF. The solution was heated to 64–66°C with stirring. Acetic anhydride (27 ml) and 2.45 g of sodium acetate (300 ml and 27 g, respectively, per mol of water condensed)[8], were added to the preheated solution. The temperature of the reaction mixture was raised to 85–87°C and then stirred at that temperature for 6 h. The reaction mixture was poured into cold water to yield BMDN as a yellow solid, which was filtered, washed with a dilute solution of sodium carbonate, water, and finally with methanol to yield BMDN (22.1 g, 93%), m.p. 312–314°C; IR(KBr) cm^{-1}: 1775, 1714 (imide ring), 1388, 1153 (C–N–C), 691 (maleimide ring), 785 (α-map.); mass spectrum FAB intensity (%): 540 (28, M+); analysis calculated for $C_{35}H_{28}N_2O_4$: C, 77.78; H, 5.19; N, 5.18%; found: C, 77.65; H, 5.36; N, 5.03%.

The preparation of diglycidyl ether of BHDN (DGEBN)

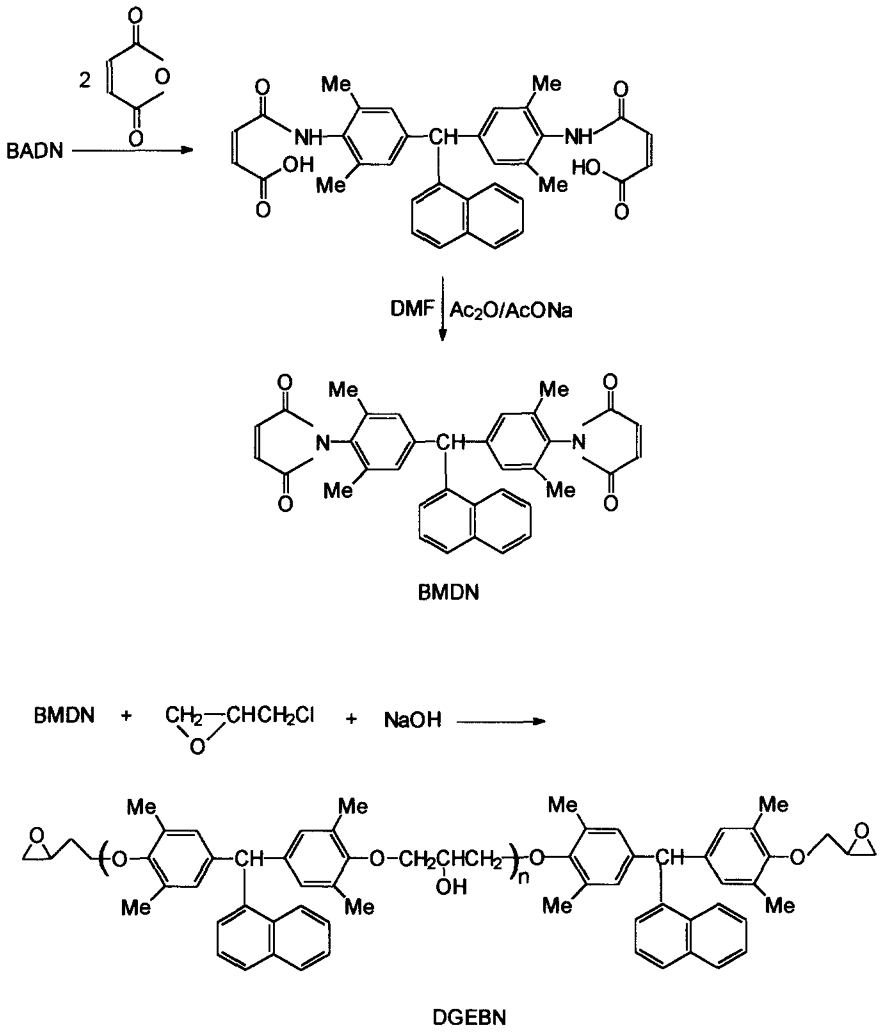
The epoxy resin (DGEBN) was synthesized by the modified procedure which has been reported by one of the authors[9]. To a 250-ml three-necked round-bottomed flask, equipped with a heating mantle, stirrer, thermometer, and reflux condenser, were charged 11.46 g (0.03 mol) of BHDN, 27.75 g (0.3 mol) of epichlorohydrin, and 18.03 g of isopropyl alcohol. The mixture was heated to 65°C and 12 g of 20% aqueous sodium hydroxide was added dropwise over a period of 45 min. After the completion of addition, the reaction mixture was maintained at 65°C for an additional 30 min. The organic phase was separated and further agitated with 4.8 g of 20% aqueous sodium hydroxide at 65°C for 30 min. The aqueous phase was separated from the organic phase and was discarded. The organic phase was washed several times with deionized water to remove the residual sodium chloride. The organic phase from water washes was placed on a rotary evaporator under a full vacuum at 150°C to remove the solvent completely. A yellow solid of DGEBN (13 g, 88%) was obtained, m.p. 66–67°C; epoxy equivalent weight (EEW): 254 (cal.: 247); mass spectrum FAB intensity (%): 494 (54, M+); analysis calculated for $C_{33}H_{34}O_4$: C, 80.16; H, 6.88%; found: C, 79.77; H, 6.97%.

Moisture absorption[10]

Samples (20 mm (*D*) × 1 mm (*T*)) of each cured resin disk were exposed to water for 48–58 h (until equilibrium saturation). The quantity of water absorbed as a result of these exposures was determined by weight differences before and after exposures. Before each weighing measurement,



Scheme 1



Scheme 2

the samples were wiped to remove surface water and weighed immediately. The results of these tests were plotted graphically for each resin system.

RESULT AND DISCUSSION

Monomer syntheses

Scheme 1 shows the synthetic routes to BADN and BHDN. The BMDN and DGEBN were prepared according to the chemical reactions outlined in *Scheme 2*. The BMDN was prepared via a two-step method, in which the bismaleamic acid was obtained by treating the diamine with maleic anhydride, followed by cyclization with acetic anhydride and sodium acetate. The typical infrared spectra of bismaleimide and the corresponding bismaleamic acid exhibited several distinctive differences. The bismaleimide

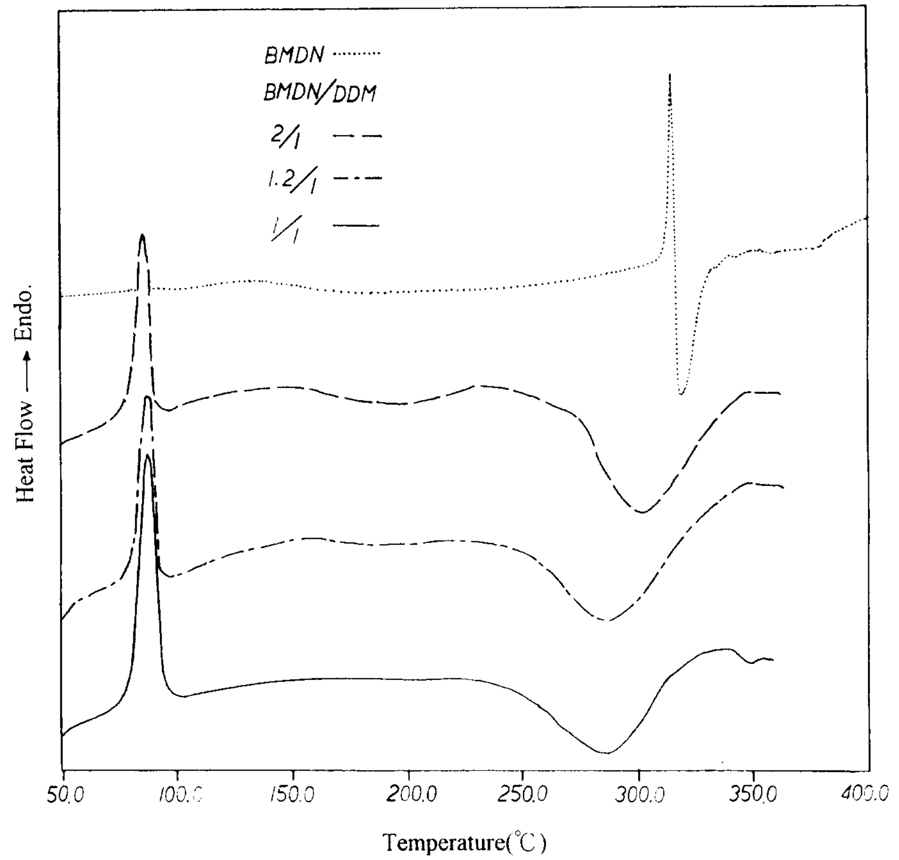


Figure 1 D.s.c. scans for BMI momomer and BMI-diamine adducts

Table 1 D.s.c. data of BMI/DDM, epoxide/DDM adducts and neat BMI

Sample	Formula	M_w	T_m (°C)	1st exotherm		2nd exotherm	
				T_i^a (°C)	$T_{exo.}^b$ (°C)	T_i^a (°C)	$T_{exo.}^b$ (°C)
BMDN	$C_{35}H_{28}N_2O_4$	540	315				320
DGEBN	$C_{33}H_{34}O_4$	494	67				
BMDN/DDM							
2/1				155	200	263	300
1.2/1				158	195	255	286
1/1[c]	$(C_{48}H_{42}N_2O_4)_n$	738				243	284
DGEBN/DDM							
2/1						158	204
1/1[d]	$(C_{46}H_{48}N_2O_4)_n$	692				155	200

[a,b] Onset and maximum temperatures for exotherm

[c,d] Linear polymers, their elemental analyses were in good agreement with the calculated values

showed a strong absorption at 1714, 691 cm^{-1} and weak absorption at 1775 cm^{-1}, assigned respectively to asymmetrical and symmetrical C=O stretching vibration of the imide ring, and lacked the absorption at 2800–3200 cm^{-1} associated with the carboxylic OH stretching vibration, and 1536 cm^{-1} for the NH stretching of the amide group. Consequently, imidization could be monitored by these absorptions. In the preparation DGEBN, an excess amount of epichlorohydrin (mole ratio 10:1) was used in order to minimise high molecular weight species. Hence, the typical product contained *ca.* 97% by weight of the monomeric DGEBN as shown in *Scheme 2*, where the degree of polymerization was nearly zero ($n \fallingdotseq 0$).

Thermal behavior and molecular structure

Figure 1 shows typical d.s.c. scans of BMI/DDM at various mole ratios along with a neat BMI. The d.s.c. scan of BMDN showed a sharp endothermic peak at 315°C, immediately followed by a narrow exothermic peak, almost overlapping the fusion endotherm with the polymerization exotherm. Barton *et al.*[11] reported a second exotherm (after polymerization) for pure bismaleimide, which he ascribed to the intramolecular reaction between maleimide groups (which did not require translational movement) and phenylene rings. However, no sign of a second exotherm was observed in our d.s.c. scan of neat BMDN. This may be attributed to the steric effect of two methyl substituents which inhibited the intramolecular reaction.

The synthesis of BMI/diamine adducts can be performed in solution or in the melt. Stoichiometric mixing of bismaleimide with a diamine led to the formation of a linear polymer (e.g. polyaspartimide)[12–15]. Usually BMI was employed in excess to obtain a polymer with some

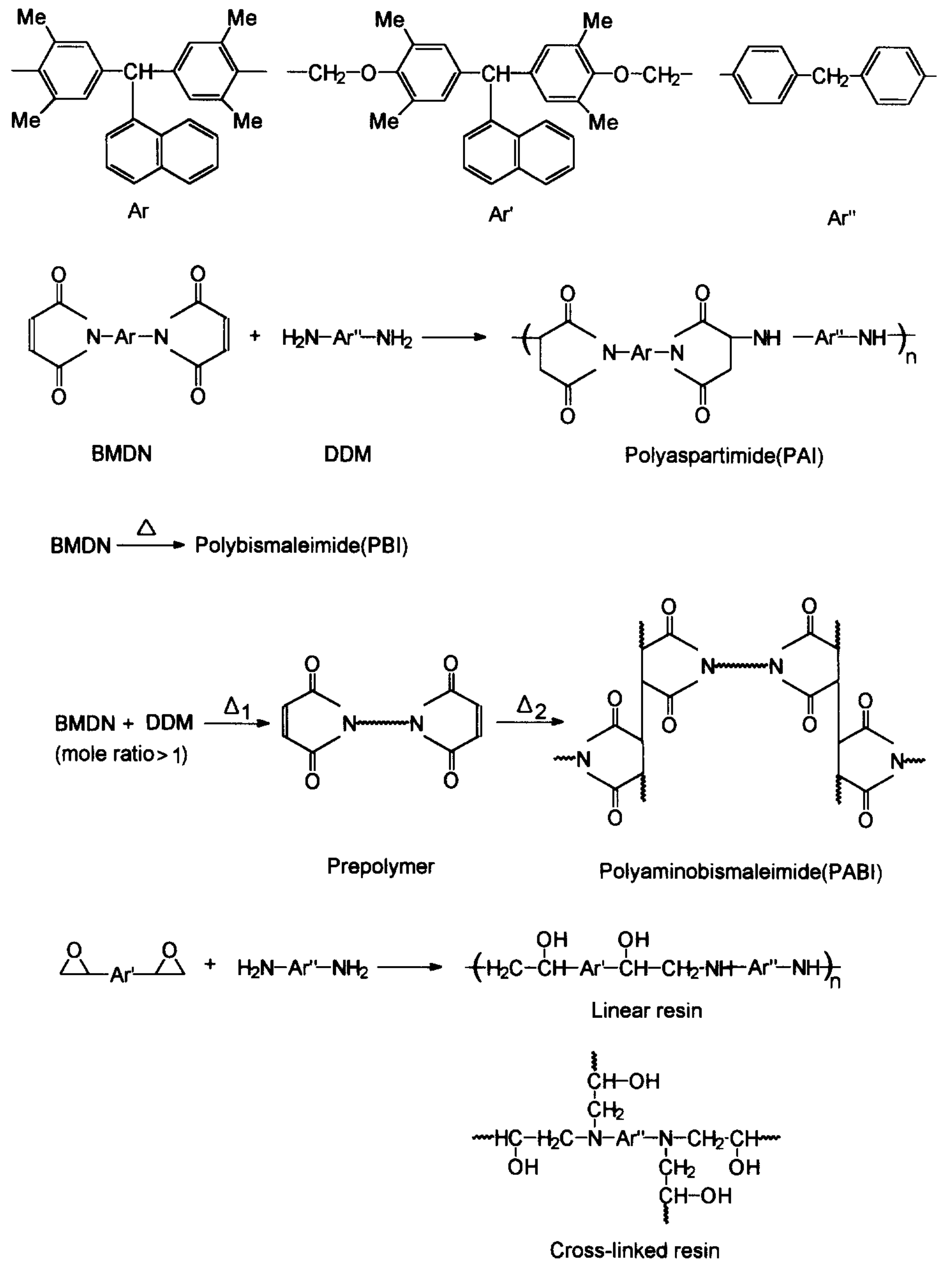


Figure 2 Polymer structure in the study

crosslinking and the network consisted of chain extension (Michael addition reaction) and crosslinking (e.g. polyaminobismaleimide)[16–19]. The curing characteristics are given in *Table 1*. For the BMDN/DDM system, if excess BMDN was employed, the d.s.c. scan of these compositions (2/1 and 1.2/1) exhibited two separate exothermic peaks. The first exothermic peak was attributed to the formation of the maleimide–amine adduct, a prepolymer with mainly terminal maleimide, while the second exothermic peak was assigned to the crosslinking through the maleimide double bonds, which occurred around 200°C or higher resulting in polyaminobismaleimides[20–22], as shown in *Figure 2*. The composition (1/1) exhibited only one exothermic peak indicating the diamine may have caused a chain extension reaction with bismaleimide immediately upon melt (m.p. 90°C). The polymerization exothermic peaks were broad (retard) and shifted to the lower temperature compared to that of the neat bismaleimide monomer, indicating that the nucleophilic addition of amines to the maleimide double bonds occurred readily and at a lower temperature than the neat exothermic temperature of BMI to form an oligomer with a maleimide double bond at the end which then further crosslinked to form polyaminobismaleimide.

The structures of polymers were confirmed by means of elemental analysis (E.A. for linear resins) and infrared spectroscopy (*FT*i.r.). The results of EA of these polymers were in good agreement with the calculated values for the proposed structures (see *Table 1*). *Figure 3* shows typical IR spectra of bismaleimide (BMDN), polybismaleimide (PBI), polyaspartimide (PAI), and polyaminobismaleimide (PABI) which exhibited several distinctive differences, The characteristic maleimide double bonds at 690 cm^{-1} had disappeared while the peak assigned to succinimide (C–N–C, 1190 cm^{-1})[23], had increased to a broad bond around this wavenumber. A reduction in maleimide (C–C–H, 3100 cm^{-1}) and an increase in saturated alicyclic (C–C–H, 2920 cm^{-1}) absorptions due to polymerization were observed. However, the absorption at 3100 cm^{-1} still

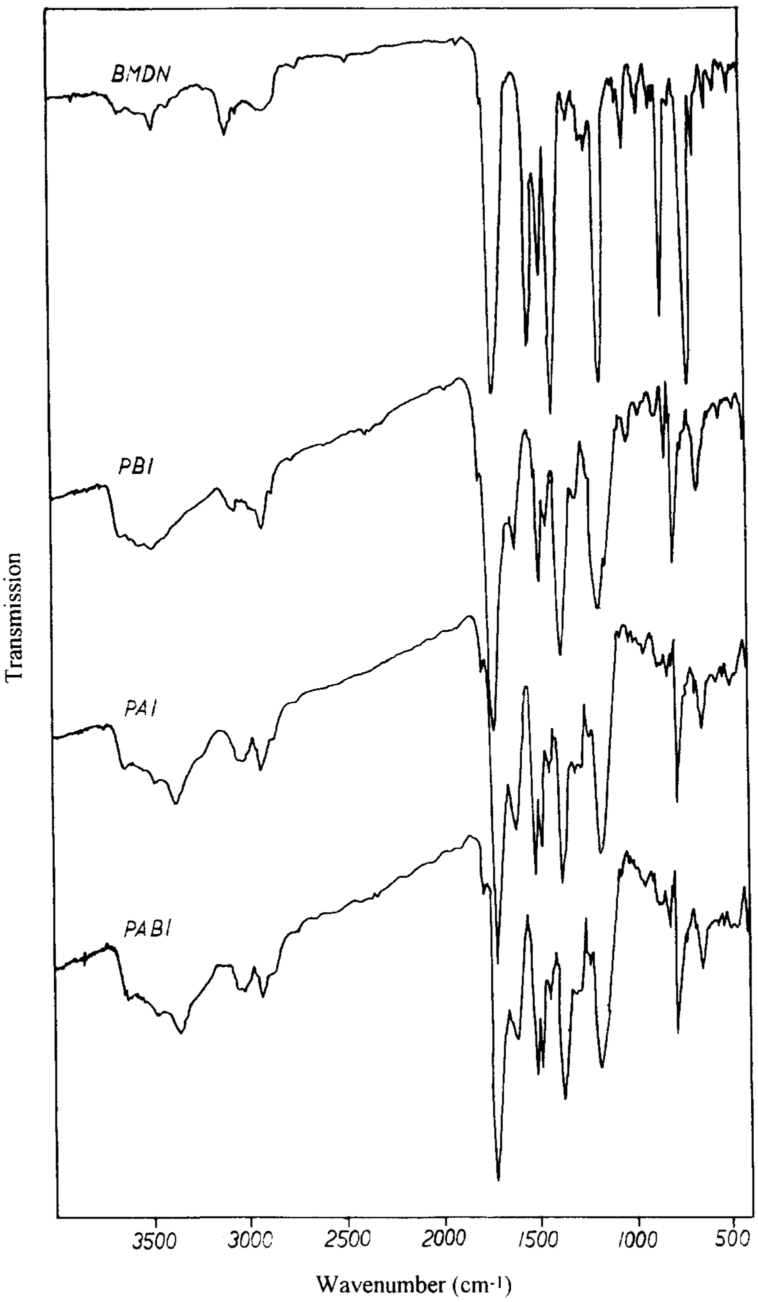


Figure 3 F.T.i.r. spectra of BMI monomer (BMDN), homopolymer (PBI) and BMI-diamine adducts (PAI,PABI)

remained for all polymers, indicating that some carbon–carbon double bonds have not completely reacted. The infrared spectra of PM and PABI were almost identical which may be attributed to the similar functional groups in both polymer matrices. A medium intensity band at 1640 cm^{-1}, which might be due to NH bending, and a new band at 3380 cm^{-1} for NH stretching confirmed the amino-addition reaction to the imide ring.

Thermal properties and thermal stability of polymer

Thermogravimetric analyses (t.g.a.) of the cured samples were carried out in a nitrogen atmosphere. The thermal stability of these resins were compared by the temperature of decomposition (T_d), temperature of maximum rate of weight loss (T_{max}), and percent char yield at 700°C; these are presented in *Table 2*. Glass transition temperature (T_g), thermal stability and anaerobic char yield of network polymers I and III were higher than their corresponding linear polymers II and IV. Epoxy resins, in general exhibited lower T_g, T_d, and char yield than bismaleimides which may be attributed to its lower crosslink density, and the lower bond dissociation energy than that of bismaleimides,

Other physical properties of polymer

Some physical properties of cured products are shown in *Table 3*. The coefficient of thermal expansion (α) was taken from the glassy state below T_g, and the α values of polymers I and III were lower than those of corresponding polymers II and IV. Network structure has a higher symmetry and lower polarity than that of linear polymers, and hence has lower dielectric constant values.

Absorbed moisture in a composite was found not only to plasticize the resin, causing a lowering of the T_g and in turn affecting mechanical response, but also to cause package cracking[24]. This crack (so-called popcorn phenomenon) is caused by evaporation and expansion of absorbed moisture

Table 2 Thermal properties of polymer

Polymer code		T_g (°C)	T_d (°C)	T_{max} (°C)	Char yield 700°C (%)
BMDN/DDM[a]					
I	1.2/1	298	424	522	42
II	1/1	292	416	520	41
DGEBN/DDM[b]					
III	2/1	212	395	421	21
IV	1/1	140	377	408	15

[a] Cure: 200°C/2 h + 270°C/4 h + 300°C/1.5 h

[b] Cure: 145°C/1 h + 200°C/2 h (Ph_3P cat.)

T_d, onset temperature for decomposition; T_{max}, the temperature of maximum rate of weight loss

Table 3 Physical properties of polymer

Polymer code		α (10^{-5}/°C)	ϵ	M.A. (%)
BMDN/DDM				
I	1.2/1	4.15	3.13	0.554
II	1/1	5.06	3.34	0.479
DGEBN/DDM				
III	2/1	6.94	4.22	0.796
IV	1/1	16.3	4.45	0.581

α, coefficient of thermal expansion; ϵ, dielectric constant; M.A., moisture absorption

in the package at the temperature of reflow soldering (215–260°C) during mounting semiconductors on printed circuit boards[25]. The moisture absorption results are given in *Table 3*. In general, bismaleimide absorbed less moisture than an epoxy system, while the naphthalene structure also greatly reduced the moisture absorption of the resultant polymers (common bisphenol A epoxy system absorbs *ca.* 3% moisture).

CONCLUSIONS

Polymerizations between bismaleimide and diamine were carried out with the bismaleimide in excess to produce maleimide end-capped telechelic oligomers. Heating at temperatures around 200°C or higher resulted in crosslinking the maleimide double bonds. The properties of the thermoset product could be varied by changing the structure, and the crosslink density. BMDN network has a higher glass transition temperature, thermal stability, lower coefficient of thermal expansion, dielectric constant and moisture absorption than that of the DGEBN system.

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