Novel Bismaleimide with Naphthalene and Aryl Ether Linkages

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ABSTRACT: A novel bismaleimide (BMI), bis(4-maleimidophenoxy-3,5-dimethylphenyl)naphthylmethane, containing a pendant naphthalene and aryl ether linkage, was synthesized from bis(4-hydroxy-3,5-dimethylphenyl)naphthylmethane through multistep reactions. The BMI was characterized by Fourier transform infrared spectroscopy, elemental analysis, and mass spectroscopy. Owing to the pendant naphthalene group and aryl ether linkage in the backbone, the BMI possessed an excellent balance of properties; solubility, processability, and thermal stability. The BMI was cured with 4,4'-diaminodiphenylmethane at various mole ratios, and their thermal properties were investigated by differential scanning calorimetry and thermogravimetric analysis. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 833–839, 1999

Key words: pendant naphthalene unit; aryl ether linkage; processing window; end caps

INTRODUCTION

Bismaleimides are an important class of additiontype polyimides and are well known for their excellent processability and balance of thermal, electrical, and mechanical properties. They are employed as resins in advanced composites and in electronics such as multilayered printed circuit boards. They have been evaluated as potential replacements for epoxy resins where high temperature performance 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 investigations are concerned with bismaleimides containing naphthalene structure. Varma et al.¹ and Hoyt et al.² have reported on ester bismaleimide monomers with 2,6-naphthalene moiety and 1,5diamino naphthalene-based bismaleimide, respectively.

In our previous study,³ we synthesized bis(4-maleimido-3,5-dimethyl)naphthylmethane (BMDN), which contained a pendant naphthalene group. BMDN exhibited better T_g , moisture resistance, lower coefficient of thermal expansion (α), and better thermal stability than that of the epoxy system. However, the BMDN bismaleimide monomer had a high melting point and its thermal curing reaction occurred immediately after fusion. The narrow processing window of such resins is a concern unless solution processing is employed. Besides BMDN being high melting, it is barely soluble in common organic solvents for electrical laminate application. In order to improve the processing properties, Pres-

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ton et al.⁴ and Chisholm et al.⁵ have reported on bismaleimide (BMI) monomers with pendant maleimide groups and "reactive diluents" to overcome the problem. In addition, Goldfarb et al.⁶ published structure–property relationships of bismaleimides containing oxyalkylene linkages and reactive flexible oligomers, as chain extenders for BMIs, to decrease the crosslink density of the cured BMI resins.^{7–9} In this study, the synthesis of a novel bismaleimide containing the pendant naphthalene unit and aryl ether linkage is attempted. The new BMI is expected to possess the processability and solubility while maintaining the high thermal properties of the cured polymer.

EXPERIMENTAL

Materials

2,6-Dimethylphenol (Acros), 2,6-dimethylaniline (Acros), 1-naphthaldehyde (Acros), p-chloronitrobenzene (TCI), ferric chloride hexahydrate (Ishizu), hydrazine monohydrate (Katayama), maleic anhydride (Janssen), sodium acetate (Nacalai tesque, extra pure reagent), acetic anhydride (Janssen), p-toluenesulfonic acid monohv-4,4'-diaminodiphenylmethane (Ferak). drate (DDM; Janssen), were all used as received. N,N'dimethylformamide (DMF) was dried by fractional distillation from calcium hydride and stored over 4 Å molecular sieves. All other solvents were obtained from various commercial sources and used without further purification. Bis(4-hydroxy-3,5-dimethylphenyl)naphthylmethane (BHDN) and bis(4-maleimido-3,5dimethylphenyl)naphthylmethane (BMDN) were synthesized according to methods reported³; mp 156–157°C and 312–314°C, respectively.

Measurements

Fourier transform infrared spectra were recorded on a Nicolet Magna-520 spectrometer with KBr pellets. Mass spectrometric analyses were performed on a VG 70-250s GC/MS spectrometer with Heraeus CHN-Rapid elemental analyses. Differential scanning calorimeter (Perkin-Elmer DSC-7) measurements were made at a scanning 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 m/m in length being used at a heating rate of 10°C/min. The thermal expansion increased with temperature and the α values were calculated from the slope. In addition, the storage modulus E' was studied when the sample was subjected to temperature scan mode with a threepoint bending system at a programmed heating rate of 10°C/min from ambient to 320°C at a frequency of 1 Hz. Thermogravimetric analyses were performed on a Perkin Elmer TGA-7 thermal analyzer using a heating rate of 20°C/min in N₂ at a purge pressure of 25 psi within the temperature range of 30 to 700°C. The specimens [20 m/m (D) \times 1 m/m (T)] were subjected to vacuum pretreatment of 1 torr at 120°C for 4 h to eliminate absorbed water. Melting points were obtained on a polarizing microscope (Laboratory Devices MEL-TEMP.II).

Preparation of Bis(4-aminophenoxy-3,5dimethylphenyl) naphthylmethane (BAPDN)

Into a reactor equipped with a stirrer, a reflux condenser and a nitrogen inlet were charged 26

mL of DMF, 19.86 g (0.052 mol) of BHDN, 16.70 g (0.106 mol) of *p*-chloronitrobenzene, and 8.56 g (0.062 mol) of potassium carbonate. The reaction mixture was refluxed at $158-160^{\circ}$ C for 10 h under a nitrogen atmosphere. After completion of the reaction, the reaction mixture was poured into cold water to yield dinitro compound, and was collected by filtration. The solid was washed with methanol, filtered and dried under vacuum.

To 16.85 g (0.027 mol) of the dinitro compound in 54 g of 2-methoxyethanol was added 0.6 g of charcoal and 0.064 g of ferric chloride hexahydrate. Over a period of 1 h, 70 g of 80% hydrazine monohydrate was added to the above mixture at 100°C and then maintained at that temperature for 11 h. After the removal of active carbon, 100 mL water was added to the hot solution. Upon cooling, the white precipitate was collected, washed well with water, and then dried *in vacuo*. The yield of BAPDN (13.8 g, 91%), mp 214– 215°C; IR(KBr)cm⁻¹: 3402,1622 (NH str.), 788 (α -nap.), 1219 (C–O–C); analysis calculated for C₃₉H₃₆N₂O₂: C, 82.98; H, 6.38; N, 4.96% found: C, 82.54; H, 6.50; N, 4.92%.

Preparation of Bis(4-maleimidophenoxy-3,5dimethylphenyl) naphthylmethane (BMPDN)

A three-necked flask equipped with an addition funnel and a nitrogen inlet was charged with a solution of maleic anhydride 8.64 g (0.088 mol) in acetone (26 mL). Under a nitrogen atmosphere, BAPDN 22.56 g (0.04 mol) in acetone (97 mL) was added dropwise to the above mixture. A slightly exothermic reaction and product precipitation were observed and the reaction mixture was allowed to stir at room temperature for 7 h and then at $52-54^{\circ}$ C for an additional 2 h. The yellow precipitate was collected, washed with fresh toluene to remove excess maleic anhydride, and then dried in a vacuum to obtain bismaleamic acid.

To a 250 mL round-bottomed flask was added 22.8 g (0.03 mol) of bismaleamic acid and 92 mL of DMF. The solution was heated to $60-62^{\circ}$ C with stirring. Acetic anhydride (18 mL) and 1.62 g of sodium acetate (300 mL and 27 g, respectively per mol of water condensed)¹⁰ were added to the preheated solution. The temperature of the reaction mixture was raised to $68-70^{\circ}$ C and then allowed to stir at that temperature for 8 h. The reaction mixture was poured into cold water to yield BMPDN (18.68 g, 86%), mp 148–150°C; IR (KBr) cm⁻¹: 1780, 1717 (imide ring), 1378, 1143 (C–N–C), 1225 (C–O C), 689 (maleimide ring), 784(α -



nap.); mass spectrum FAB intensity (%): 724 (30, M^+); analysis calculated for $C_{47}H_{36}N_2O_6$: C, 77.90; H, 4.97; N, 3.87% found: C, 77.17; H, 5.14; N, 3.84%.

Moisture Absorption¹¹

Samples [20 m/m (D) \times 1 m/m (T)] of each cured resin disk were exposed to water 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, the samples were wiped to remove surface water and weighed immediately. The results of these tests were recorded for each resin system.

RESULTS AND DISCUSSION

Monomer Synthesis

Scheme 1 shows the synthetic routes to BADN, BHDN, and BMDN. The BMPDN was prepared according to the chemical reactions outlined in Scheme 2. Typically, the BMDN and BMPDN



Figure 1 DSC scans for bismaleimide monomers.

were prepared via a two-step (i.e., bismaleamic acid formation and imidization) method. The formation of the bismaleamic acid is a fast and exothermic reaction, and the imidization can be carried out thermally or chemically. In this study, the synthesis of a bismaleimide involves chemical imidization, using acetic anhydride in the presence of a catalytic amount of sodium acetate at a specific temperature.¹² The typical infrared spectra of bismaleimide and the corresponding bismaleamic acid exhibited several distinctive differences. The bismaleimide showed a strong absorption at 1714-1717 cm⁻¹, 689-691 cm⁻¹, and weak absorption at $1775-1780 \text{ cm}^{-1}$, assigned to asymmetric and symmetric C=O stretching vibration of imide ring ,respectively. It also lacked the absorptions at 2800-3200 cm⁻¹ associated with the carboxylic OH stretching vibration and 1536-1547 cm⁻¹ for the NH stretching of the amide group. Consequently, imidization could be monitored by means of these absorptions. In addition, BMPDN has a characteristic peak at 1225 cm⁻¹ due to the ether linkage¹³ in the backbone.

Thermal Behavior

The thermal behavior of the bismaleimide was investigated by DSC, as shown in Figure 1. Curing reactions of three bismaleimides [BMPM, (4,4'-bismaleimidophenylmethane), BMDN, and BMPDN] can be safely completed below 400°C. without decomposition during curing. The subsequent heating after quenching from 350°C showed no traces of an exotherm. The DSC 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. The low fusion temperature of BMPDN provides a substantial temperature gap between melting (T_m) and the onset of polymerization (T_i) . This can be ascribed to the likelihood that a small quantity of impurity can have a marked effect on the rate of polymerization¹⁴ and also to the incorporation of phenoxy groups into the structure of BMDN leading to a lowering of T_m and an increase in $\Delta T (= T_i$ $-T_m$). The thermal behavior of the bismaleimides is given in Table I. In general, the melting points tend to become higher with increasing molecular weight because of the increase in cohesive energy between molecules.¹⁵ However, as shown in Table I, the BMPDN contradicts this general rule. This is probably the result of flexible groups (such as ether linkages) between phenyl units of the long-chain BMI monomer, which interfere with close packing between molecules leading to a decrease in T_m (150°C). Unfortunately, it was not possible to measure ΔH_m and ΔH_p for the sample BMDN because, with this material, the melting endotherm and the polymerization exotherm were not resolved.

The solubilities of bismaleimides in various solvents were investigated and results are summarized in Table II. All bismaleimides were readily

BMI Code	M_w (g/mol)	T_m (°C)	T_i (°C)	$\begin{array}{c} \Delta H_m \\ (\text{KJ/mol}) \end{array}$	$\begin{array}{c} \Delta {S_m} \\ \text{(J/mol K)} \end{array}$	ΔH_p (KJ/mol)
$\mathbf{BMPM}^{\mathbf{b}}$	358	160	178	31.3	70.4	35.2
BMDN	540	315	317	_	—	_
BMPDN	724	150	226	4.8	11.3	49.1

Table I Thermal Behavior Data of Bismaleimides^a

^a $T_m = \Delta H_m / \Delta S_m$. ΔH_p : heat of polymerization. $\Delta T = T_i - T_m$ (cure window).

^b Adapted from ref. 11.

BMI Code	Acetone	MIBK	THF	Solvent Methyl- Cellusolve	Dioxane	DMF	NMP
BMPM BMDN BMPDN	 +	 +	 +	 +	 +h	++ ++ ++	++ ++

Table II Solubility of Bismaleimides^a

^a (++) Soluble at room temperature, (--) insoluble, (+-) partially soluble at room temperature, and (+h) soluble on heating.

soluble in polar aprotic solvent. However, in common organic solvents BMPM was insoluble, and BMDN exhibited somewhat limited solubility, while BMPDN was soluble even at room temperature. Although the molecular structures of BMDN and BMPDN were almost equivalent, the solubility and the thermal properties were quite different. Therefore, the molecular volumes of both bismaleimides were investigated. The molecular volume of BMDN 8.35×10^{-22} cm³/molecule) was lower than that of BMPDN $(11.4 \times 10^{-22} \text{ cm}^3/$ molecule), which indicated that the molecules of BMDN packed more densely than did BMPDN. BMPDN has a relatively longer distance between the two maleimido end caps (containing flexible and pendant group^{16,17}) than does BMDN. The ratio of molecular volume for the two bismaleimides (r = 0.73) is almost the same as the length ratio (r' = 0.71) of each substituent group, $-C_6H_4(COCH)_2$ (d = 85 nm) and $-C_6H_4OC_6H_4$ -(COCH)₂ (d = 120 nm).¹³ BMPDN had a larger molecular space which led to an increase in solubility.

Chain extension between two crosslink sites is a way to improve the toughness of a polymer. Figure 2(a) summarizes the preparation of a BMI resin extended with a diamine. Stoichiometric mixing of bismaleimide with a diamine led to the formation of linear polymer¹⁸⁻²⁰ (including prepolymer I and polyaspartimide). Usually BMI was employed in excess to obtain chain extension (Michael addition reaction) and to crosslink: a prepolymer with mainly maleimide terminations is formed first and then cured upon heating, to temperatures around 200°C or higher, to form the polymer.²¹⁻²⁴ However, when chain extension of BMI was done with much lower diamine mole ratios (such as 3/1), the nonstoichiometric reaction Figure 2(b) could occur²⁵ (including prepolymer II and III). The polymerization and crosslinking reaction of bismaleimides, as exemplified by BMI/diamine, have been shown to be quite complex. The reaction can yield combinations of chain extension, branching, and crosslinking depending on the cure path and cure state. Since the Michael addition reaction occurs at a lower temperature, the predominant reaction is chain extension between the amine and double bond of BMI, with negligible reaction between the BMI monomers.²⁶ For the BMI/diamine, if excess BMI was employed, the structure of these compositions 2/1 [in Figure 2(a), n = 1] and 3/1 [in Figure 2(b), main product is II] were almost identical. The quick



(a). If m=n +1, m/n is stoichiometric reaction



(b). If m/n is nonstoichiometric reaction



Figure 2 The preparation of bismaleimide resins extended with diamine. (a) Stoichiometric reaction (mole ratio: 1.2/1, 1.5/1, 2/1). (b) Nonstoichiometric reaction (mole ratio: 3/1).



 Some free BMI molecules are yet to be reacted and bound to the network
Some BMI remain free and homopolymerization can occurs

Figure 3 Schematic drawing of the final network structure showing the products of the BMI/DDM mix system after heating.

dissolution in DMSO of the heated (around 200°C) BMI/DDM suggested that the reactions of secondary amino groups of chain-extended resins with the residual double bonds of bismaleimide²⁵ and homopolymerization were probably negligible (also, the respective DSC analysis clearly revealed that no polymerization takes place below 200°C). From the above discussion, the resulting structure of the prepolymers after heat-induced reactions, along with the possible products and/or unreacted species, are depicted in Figure 3.

Thermal Properties and Thermal Stability of Polymer

The thermal stabilities of these resins were compared by the temperature of decomposition (T_d) , temperature of maximum rate of weight loss $(T_{\rm max})$, and percent char yield at 700°C and are summarized in Table III. All these cured resins were stable up to 410°C and the char yields at 700°C were all around 41%. In general, higher T_g , T_d , and char yield were obtained with higher BMI/DDM ratio, which may be attributed to the higher crosslink density, and the higher bond dissociation energy of the cured bismaleimide polymer matrix.

Other Physical Properties of Polymer

Some physical properties of cured products are shown in Table IV. The coefficient of thermal

Table III Thermal Properties of Polymers

Polymer Code	$\begin{array}{c} T_g \\ (^{\circ}\mathrm{C}) \end{array}$	T _d ^c 2 (°C)	T _{max} ^d (°C)	Char Yield 700°C (%)
BMDN/DDMª				
1/1	292	416	520	41
1.2/1	298	424	522	42
BMPDN/DDM ^b				
1/1	236	413	457	39
1.2/1	251	421	469	41
1.5/1	253	424	473	41
2/1	262	436	477	44
3/1	264	441	477	44

^a Cure: 200°C (2 h) + 270°C (4 h) + 300°C (1.5 h).

^b Cure: 190°C (2 h) + 250°C (4 h) + 260°C (1.5 h).

^c T_d : Onset temperature for decomposition.

^d $T_{max}^{"}$: The temperature of maximum rate of weight loss.

expansion (α) was taken from the glassy state below T_{g} . The high cross-link densities (increasing BMI concentration in BMDN/DDM has increased the elastic modulus at rubber state, as shown in Fig. 4) from low molecular weight oligomers limit the segmental motions of the cured material and thus reduce the free volume. Hence, the α values of cured products decrease with the decrease in oligomer molecular weights, while density and water absorption increased with the increase in BMI/DDM ratio. This was attributed to strong intermolecular dipole–dipole interaction between the imide groups.

CONCLUSIONS

A novel bismaleimide containing a pendant naphthalene and aryl ether linkage has provided an

Table IV	Influence	of Molar	Ratio	on	Various
Properties	s in BMI/D	DM ^a			

ρ	MA	α
(g/cc)	(%)	$(10^{-5}/°C)$
1.243	0.479	5.06
1.255	0.554	4.15
1.193	0.878	5.56
1.207	1.014	4.64
1.224	1.044	4.45
1.237	1.109	4.39
1.245	1.222	4.32
	ho (g/cc) 1.243 1.255 1.193 1.207 1.224 1.237 1.245	$\begin{array}{c c} \rho & MA \\ (g/cc) & (\%) \\ \hline \\ 1.243 & 0.479 \\ 1.255 & 0.554 \\ \hline \\ 1.193 & 0.878 \\ 1.207 & 1.014 \\ 1.224 & 1.044 \\ 1.237 & 1.109 \\ 1.245 & 1.222 \\ \hline \end{array}$

^a ρ : Bulk density of polymer. MA: Moisture absorption. α : Coefficient of thermal expansion.



Figure 4 DMA results for the BMI/DDM at various mole ratios.

excellent balance of properties in processability, solubility, and thermal stability, which meet the essential requirements for electrical laminate application. By careful selection of bismaleimide to amine ratio, the crosslink density, thermal stability, and physical properties of the resulted polymers can be controlled.

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REFERENCES

1. Varma, I. K.; Fohlen, G. M.; Parker, J. A. J Polym Sci Part A Polym Chem 1982, 20, 283.

- Hoyt, A. E.; Benicewicz, B. C.; Hung, S. J Polym Prepr 1989, 30(2), 536.
- Wang, C. S.; Leu, T. S.; Hsu, K. R. Polymer 1998, 39(13), 2921.
- Preston, P. N.; et al. Macromolecules 1994, 27, 1147.
- 5. Chisholm, M. S.; et al. Polymer 1992, 33, 838.
- 6. Goldfarb, I. J.; et al. Polymer 1993, 34, 813.
- 7. Morgan, R. J.; et al. Polymer 1993, 34, 835.
- 8. Wilkinson, S. P.; et al. Polymer 1993, 34, 870.
- 9. Takeda, S.; et al. J Appl Polym Sci 1988, 35, 1341.
- Mikroyannidis, J. A. J Polym Sci Part A Polym Chem 1989, 27, 3465.
- Wang, C. S.; Hwang, H. J. J Polym Sci Part A Polym Chem 1996, 34, 1493.
- Stenzenberger, H. D. In Polyimides; Wilson, D. et al., Eds.; Blackie: Glasgow/London,1990; p 79.
- 13. Nagai, A.; et al. J Appl Polym Sci 1990, 41, 2241.
- Barton, J. M.; Hamerton, I.; Rose, J. B.; Warner, D. Polymer 1991, 32, 358.
- Hsiao, S. H.; Chang, C. F. J Polym Res 1996, 3(1), 31.
- Varma, I. K.; Fohlen, G.; Parker, J. A. U.S. Patent 4,276,344, 1981.
- 17. Heisey, C.; et al. ACS PMSE 1992, 67, 28.
- 18. Rakoutz, M.; Balme, M. Polym J 1987, 19(1), 173.
- Mikroyannidis, J. A. et al. J Polym Sci Part A Polym Chem 1991, 29, 411.
- 20. Wang, C. S.; Hwang, H. J. Polymer 1996, 37, 499.
- Enoki, T.; Takeda, T.; Ishiik, K. J Thermosetting Plastics Jpn 1993, 14, 131.
- High Performance Polymers; Hergenrother, P. M., Ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1994; p170.
- 23. Pan, P. J.; et al. J Appl Polym Sci 1992, 45, 103.
- Principles of Polymerization; Odian, G., Ed.; Wiley: New York, 1993; p 160.
- Varma, I. K.; et al. Angew Makromol Chem 1987, 153, 15.
- Leung, C. L.; et al. ACS Polym Mater Sci Eng 1985, 52, 134.