Synthesis and Thermal Properties of Bismaleimides with *Ortho*-Linked Aromatic Units

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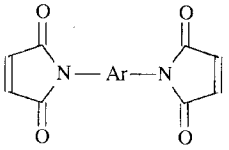
Abstract: Three bismaleimides (BMIs) each having an *ortho*-linked aromatic unit were prepared by condensation of maleic anhydride with 1,2-bis(4-aminophenoxy)benzene (**1a**), 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**1b**), or 2,3-bis(4-aminophenoxy)naphthalene (**1c**). The molecular structures of these BMIs were confirmed by elemental, IR, and NMR analyses. The thermal behavior of the BMIs was evaluated by differential scanning calorimetry (DSC), and the thermal properties of the thermally cured BMI resins were determined by dynamic thermogravimetric analysis (TGA) and thermomechanical analysis (TMA). The effects of structure of the BMIs on the curing behavior of the BMIs and on the properties of the cured resins were investigated. The BMI of **1a** had a relatively high melting point (256 °C) and immediately polymerized after having been melted. The **1b**- and **1c**-based BMIs with a bulkier molecular structure exhibited lower melting points (136 and 171 °C), facilitating the use of these BMIs in the molten state. The cured BMI resins did not show significant decomposition below 450 °C in air or nitrogen and did not soften below 400 °C.

Keywords: Bismaleimide, BMI, *Ortho*-linked bis(ether amine), Thermal property.

Introduction

Bismaleimides (BMIs) are a leading class of thermosetting or addition polyimides. Their excellent processability and balance of thermal and mechanical properties have made them extremely popular in advanced composites and electronics [1]. BMI resins offer a performance temperature range between epoxies and polyimides. The main reason for the intense interest in BMI system is their ability to be fabricated using epoxy-like conditions and without the evolution of void-forming volatiles, while they exhibit higher performance temperatures (up to 230 °C) and better hot/wet properties than epoxies. The major applications for BMI structural composites are in aero-engines and military aircraft. Glass fiber/BMI composites are also used in printed circuit boards.



BMIs

BMIs are produced from the condensation reaction of a diamine and maleic anhydride. Monomeric BMIs are relatively easy to make with a wide variety of structural variations available for property modification. Such fine tuning has been necessary in order to produce materials with good processing characteristics and acceptable properties. Almost every aromatic diamine can be converted into the corresponding BMI. The most widely used BMI-building block, however, is 4,4'-bismaleimidodiphenylmethane (4,4'MDA-BMI) because the precursor diamine, 4,4'-methylenedianiline (4,4'-MDA), is readily available at low cost. The reactivity of the double bond is due to the electron-withdrawing power of the two adjacent carbonyl groups. As a result, BMIs readily polymerize without the presence of a catalyst. Moreover, nucleophiles such as amines [2-6] or mercaptans [7] readily add across

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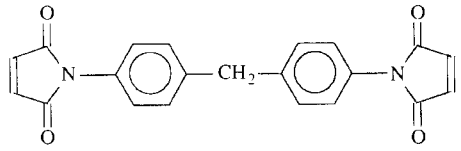
the activated double bond in the well-known Michael addition reaction.



4,4'MDA-BMI

One major drawback associated with many thermosetting networks is their inherent brittleness. The cured BMI resins are generally brittle due to their high crosslink density. A peculiar phenomenon that may be a result of the inherently brittle nature of BMI resins is their susceptibility to microcracking. For BMIs to be useful as matrix resins for high-performance structural composite materials, the fracture toughness must be improved without too much sacrifice of other important mechanical properties such as high-temperature flexural strength. To improve toughness, the BMI can be modified by the addition of additives or tougheners such as diamines [2-6], dithiols [7], diallyl bisphenols [8], allylamine [9], and reactive elastomers [10]. However, introducing such tougheners usually causes a lowering of the glass transition temperature and/or the thermal degradation temperature of the cured products.

Another approach employed to increase the toughness of BMI resins is the use of a BMI that has flexible ether groups and a long phenoxy chain within the monomer structure [11-16]. This BMI monomer has a high molecular weight, which makes it possible to reduce the crosslinking density of the cured products. Consequently, this BMI monomer by itself is expected to be suitable for making thermally stable composite materials because the cured product has good mechanical properties. However, the melting temperature (T_m) of BMI monomers tends to increase with increasing molecular weight because the cohesive energy between molecules in the crystal state is large. The increased T_m introduces a short gel time or short potlife of melt, because there is a decreased difference between the T_m and the onset temperature of the curing reaction. Thus, it seemed appropriate to examine possible alternative monomers for the preparation of ether-containing BMIs. The present study deals with the preparation and curing of some new BMIs containing ether linkages and *ortho*-linked aromatic units. It was expected that intermolecular interactions in the crystal state would be weakened and, thus, the T_ms of the BMIs would be lowered due to the incorporation of the less symmetric *ortho*-linked group in the BMI structure. Thus, the prepared BMIs were expected to have improved handling and processing characteristics and to yield cured resins with increased flexibility or reduced brittleness.

Experimental

1. Materials

According to a well-developed synthetic procedure [17,18], 1,2-bis(4-aminophenoxy)benzene (**1a**, mp 137~138 °C), 1,2-bis(4-aminophenoxy)-4-tert-butylbenzene (**1b**, mp 129~131 °C), and 2,3-bis(4-aminophenoxy)naphthalene (**1c**, mp 176~177 °C) were prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene with the bisphenolate ions of the corresponding aromatic diols such as catechol, 4-*tert*-butylcatechol, and 2,3-dihydroxynaphthalene, followed by palladium-catalyzed hydrazine reduction of the intermediate dinitro compounds. The other reagents such as acetic anhydride (Fluka) and triethylamine (Fluka) were used without further purification. The bismaleimide 4,4'MDA-BMI (from TCI) was also used as received.

2. Synthesis of bismaleimides

The bismaleimides containing an *ortho*-linked aromatic unit were prepared from corresponding diamines and maleic anhydride by a reported method [3,7,11]. A typical procedure for the preparation of 4-*tert*-butyl-1,2-bis(maleimidophenoxy)benzene (BMI **3b**) is described as follows.

2.1 4-*tert*-Butyl-1,2-bis(4-maleimidophenoxy) benzene (BMI **3b**)

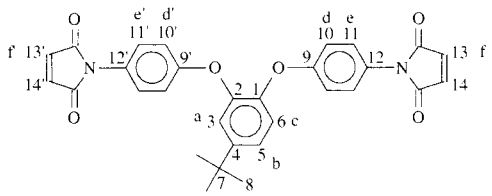
A 300-mL round-bottomed flask was charged with 4.6 g (0.046 mol + 0.1 g) of maleic anhydride, 8 g (0.023 mol) of 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**1b**), and 50 mL of dry acetone. Rapid formation of a yellow precipitate of the bisamic acid (**2b**) occurred on mixing the reactants together, and the slurry was stirred for an additional 6 h to complete the reaction. To the reaction flask were then added 0.5 g of sodium acetate and 2 mL of triethylamine, and the mixture was heated slowly to reflux. By means of an addition funnel 20 mL of acetic anhydride was added dropwise into the refluxing reaction mixture over a period of about 40 min, and heating was continued for an additional 4 h. The product (**3b**) was precipitated by pouring it into cold water and was then collected by filtration and washed thoroughly with water. After drying, the yield of the product was 10.6 g (91%), mp. 136 °C.

IR (KBr): 3120 (aromatic C–H str.), 2968 (aliphatic C–H str.), 1717 (C=O str.), 1398 (C–N str.), 1120, and 716 cm^{-1} (imide ring deformation).

^1H NMR (400 MHz in DMSO-d_6): δ 7.35 (d, H_b, 1H), 7.32 (overlapped AB doublets, H_a + H_e +

$H_{e'}$, 5H), 7.15 (d, H_c, 1H), 7.17 (two overlapped AB doublets, H_f + $H_{f'}$, 4H), 6.77 (two overlapped AB doublets, H_d + $H_{d'}$, 4H), and 1.27 ppm (s, $-CH_3$, 9H).

^{13}C NMR (100 MHz, in DMSO-d_6): δ 169.69, 169.66 (C=O), 156.53, 156.17 (C^9, $C^{9'}$), 148.69 (C^4), 145.27 (C^2), 144.40 (C^1), 134.33 (C^{13}, $C^{13'}$), 128.16 (C^{11}, $C^{11'}$), 125.92, 125.61 (C^{12}, $C^{12'}$), 122.74 (C^6), 121.35 (C^3), 119.57 (C^5), 116.89, 116.16 (C^{10}, $C^{10'}$), 34.24 (C^7), and 30.94 ppm (C^8).



Anal. Calcd for $C_{30}H_{24}N_2O_6$ (508.53): C, 70.86%; H, 4.76%; N, 5.51%. Found: C, 69.65%; H, 4.76%; N, 5.40%.

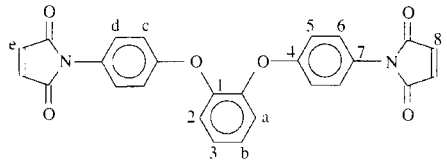
2.2 1,2-Bis(4-maleimidophenoxy)benzene (BMI **3a**)

BMI **3a** was prepared from 1,2-bis(4-aminophenoxy)benzene (**1a**) and maleic anhydride by an analogous procedure with 95% yield; mp. 255~256 °C.

IR (KBr): 3100 (aromatic C–H str.), 1713 (C=O str.), 1400 (C–N str.), 1228 (C–O–C str.), 1151, 717 cm^{-1} (imide ring deformation).

^{1}H NMR (400 MHz in DMSO-d_6): δ 7.27 (overlapped AB doublets, H_a + H_b + H_d, 6H), 7.10 (s, H_e, 4H), and 6.98 ppm (d, H_c, 4H).

^{13}C NMR (100 MHz, in DMSO-d_6): δ 169.42 (C=O), 156.16 (C^4), 146.56 (C^1), 127.86 (C^6), 125.94 (C^8), 122.01 (C^3), and 116.09 ppm (C^5).



Anal. Calcd for $C_{26}H_{16}N_2O_6$ (452.42): C, 69.02%; H, 3.56%; N, 6.19%. Found: C, 68.40%; H, 3.55%; N, 6.04%.

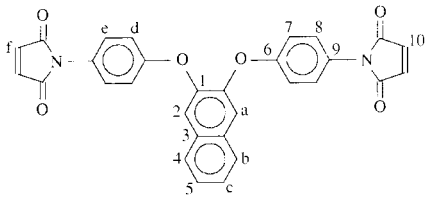
2.3 2,3-Bis(4-maleimidophenoxy)naphthalene (BMI **3c**)

The product was prepared from 2,3-bis(4-aminophenoxy)naphthalene (**1c**) and maleic anhydride by a similar procedure; yield 95%; mp. 169~170 °C.

IR (KBr): 3100 (aromatic C–H str.), 1713 (C=O str.), 1400 (C–N str.), 1228 (C–O–C str.), 1151, and 717 cm^{-1} (imide ring deformation).

^{1}H NMR (400 MHz in DMSO-d_6): δ 7.91 (d, H_b, 2H), 7.72 (s, H_a, 2H), 7.48 (d, H_c, 2H), 7.34 (d, H_d, 4H), 7.17 (s, H_f, 4H), and 7.12 ppm (d, H_e, 4H).

^{13}C NMR (100 MHz, in DMSO-d_6): δ 169.68 (C=O), 155.43 (C^6), 146.28 (C^1), 134.36 (C^{10}), 130.60 (C^3), 128.28 (C^8), 126.66 (C^4), 126.35 (C^5), 125.69 (C^9), 117.41 (C^2), and 117.19 ppm (C^7).



Anal. Calcd for $C_{30}H_{18}N_2O_6$ (502.48): C, 71.71%; H, 3.61%; N, 5.57%. Found: C, 70.04%; H, 3.61%; N, 5.57%.

3. Measurements

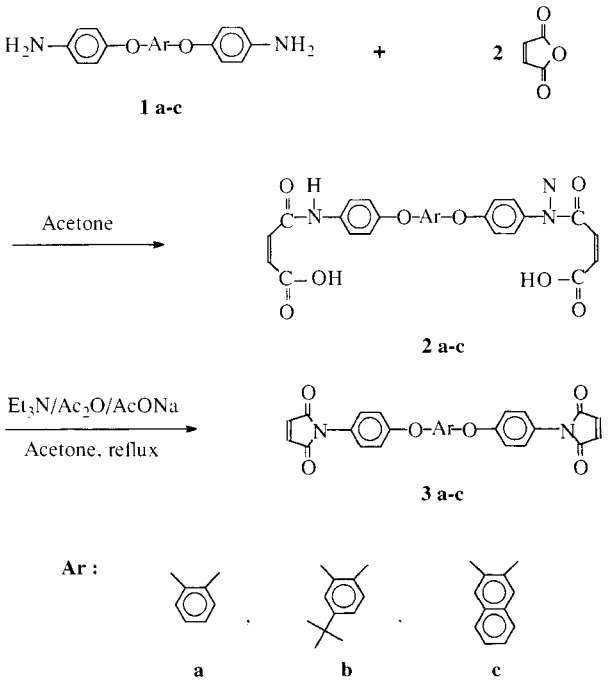
IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. NMR spectra were obtained on a Jeol EX-400 spectrometer. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC 7 coupled to a Thermal Analysis Controller TAC 7/DX. The heating rate was 10 °C/min. Thermogravimetric analysis (TGA) was conducted with a TA Instrument TGA 2050. Experiments were carried out on approximately 10 mg of samples in flowing nitrogen or air (flow rate 100 cm^3/min) at a heating rate of 20 °C/min. Thermomechanical analysis (TMA) was conducted with a Perkin-Elmer TMA 7 at a heating rate of 10 °C/min. Experiments were carried out using a penetration probe under a constant load of 30 mN. Softening temperatures (T_s) were read at the onset temperature of probe displacement.

Results and Discussion

1. Synthesis of bismaleimides

The bismaleimides BMI **3a-c** were synthesized from the corresponding diamines and maleic anhydride (Scheme 1) by a standard synthetic procedure for *N,N'*-arylene bismaleimide which involves the chemical dehydration of *N,N'*-bismaleamic acid with acetic anhydride, with sodium acetate as a catalyst. The yield is usually higher than 90%. IR, NMR, and elemental analyses confirmed the structures of these BMI monomers.

Figures 1~3 illustrate the comparative IR, ^{1}H NMR, and ^{13}C NMR spectra of bismaleamic acid **2b**



Scheme 1. Synthesis of *ortho*-linked bis(ether maleimide)s.

and its corresponding BMI **3b**. As shown in Figure 1, all BMIs show characteristic absorptions peculiar to the imide ring near 1720 (carbonyl stretching), 1400 (C–N stretching), 1120 and 720 cm^{-1} (imide ring deformation). The formation of BMI also could be readily confirmed by the disappearance of the AB doublets (6.61 and 6.30 ppm) corresponding to the olefinic protons of bismaleamic acid and the resonance (10.89 ppm) of amide and carboxyl protons, as well as the appearance of the singlet (at 7.17 ppm) due to the olefinic protons of the maleimide ring (Figure 2). Moreover, as shown in Figure 3, the formation of BMI also could be confirmed by the convergence of the resonance peaks of the carbonyl carbons and the olefinic carbons. Figures 4 and 5 present the ^{1}H- and ^{13}C-NMR spectra of BMIs **3a** and **3c**, respectively. Assignments of each carbon atom and proton are also given in the figures. These spectroscopic data are in good agreement with the molecular structures of **3a** and **3c**.

2. Thermal behavior of bismaleimides

The thermal behavior of BMIs **3a-c** was evaluated by differential scanning calorimetry (DSC), and their DSC curves are illustrated in Figure 6. The melting and cure data determined via DSC for the BMIs **3a-c** and 4,4'MDA-BMI as a reference are complied in Table I. The melting point (T_m) is defined as the peak temperatures of the melting endotherms, and the polymerization initial temperature (T_i) is defined as the onset temperature of the

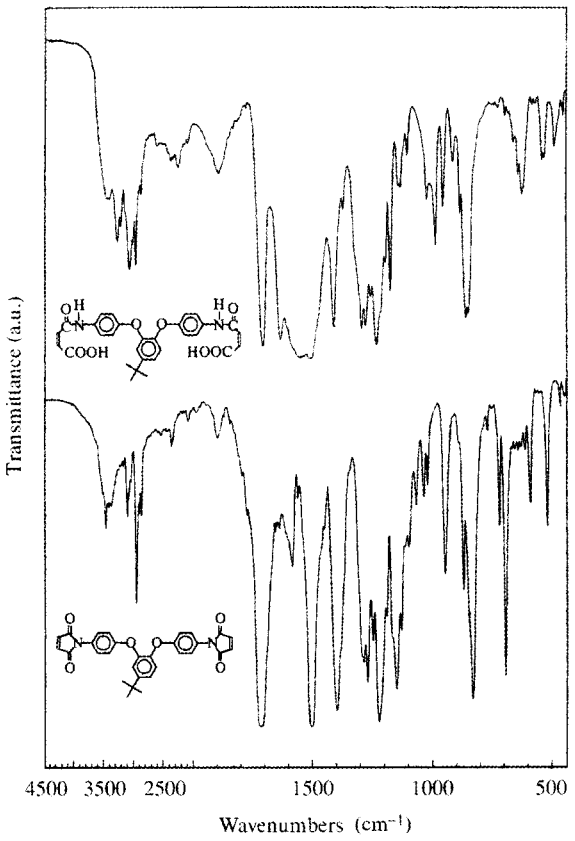


Figure 1. IR spectra of bismaleamic acid **2b** and bismaleimide **3b**.

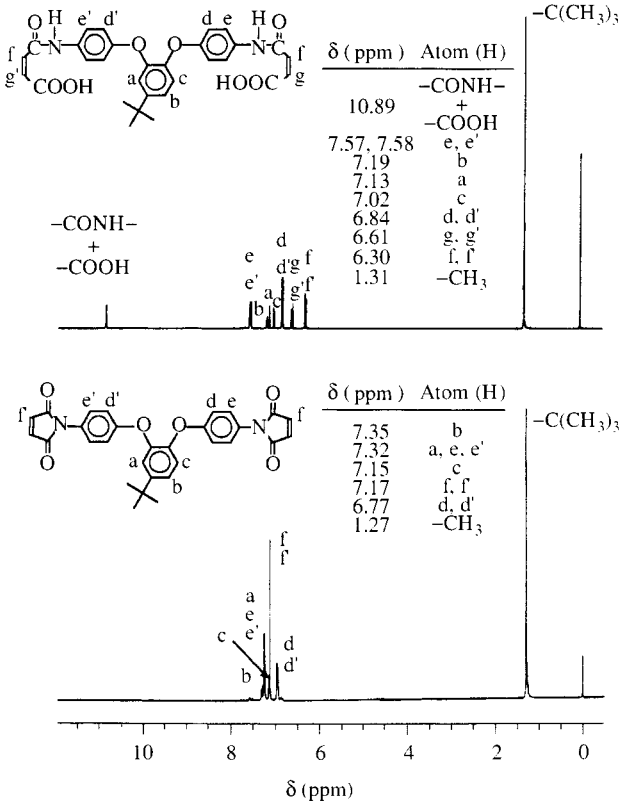


Figure 2. ^{1}H NMR spectra of bismaleamic acid **2b** and bismaleimide **3b** in DMSO-d_6.

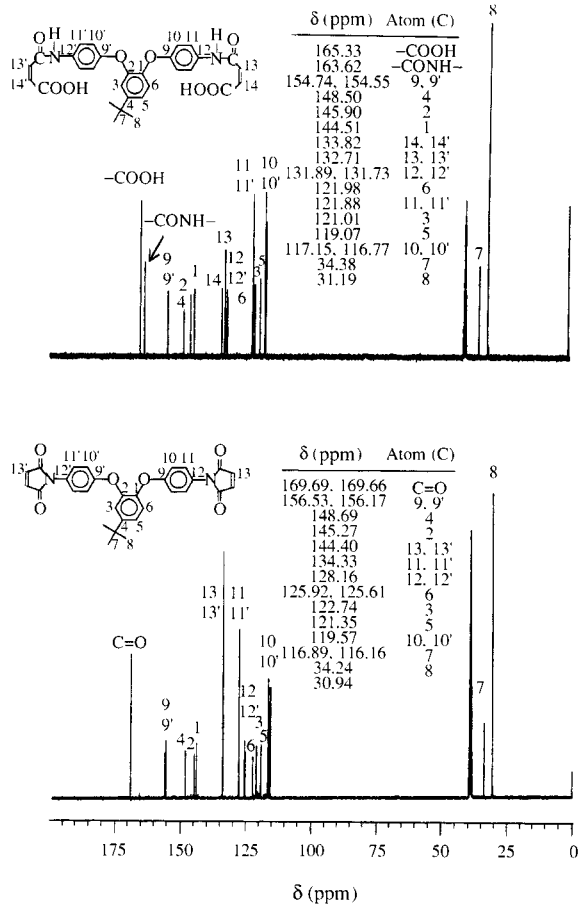


Figure 3. ^{13}C NMR spectra of bismaleamic acid **2b** and bismaleimide **3b** in DMSO-d_6.

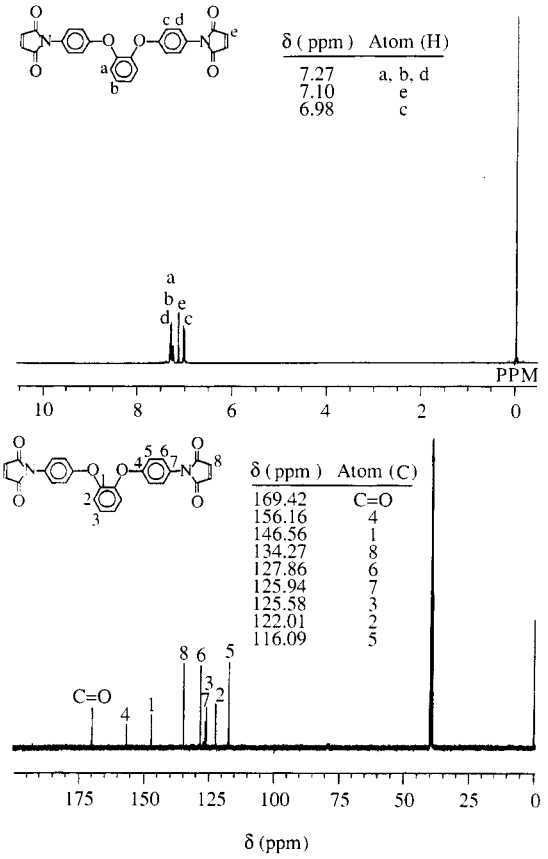


Figure 4. ^{1}H NMR and ^{13}C NMR spectra of bismaleamic acid **3a** in DMSO-d_6.

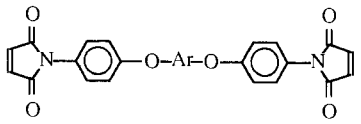
curing exotherms. Programmed DSC-scans revealed that endothermal transitions due to the melting of BMIs **3a** to **3c** occurred at 256, 136, and 171 °C, respectively. The high melting point for BMI **3a** is surprising. Introducing pendant bulky groups lowers the melting point of BMI. In general, the melting points tend to increase with increasing molecular weight because of the increase in cohesive energy between molecules. However, as shown in Table I, BMIs **3b** and **3c** contradict this general rule. This is considered to be due to a low packing density of molecules in the crystal state and weak intermolecular interaction for the bulky BMI **3b** and **3c**. Incorporating a *tert*-butyl or 2,3-naphthalenediyl group lowers the heat of fusion calculated from the endothermic peak area. It is suggested that the bulky BMIs have a crystal structure with low molecular density because the intermolecular interaction is relatively weak.

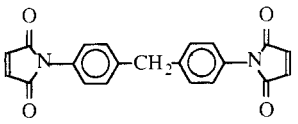
A very interesting property of a BMI is its ability to undergo a radical type, temperature-induced homopolymerization. The polymerization data for these BMIs are also given in Table I. BMI **3a** had a very short gel time and immediately polymerized after having been melted, because it had a relatively high melting point. The molten BMIs **3b** and **3c** started to polymerize at around 207 and 224 °C, respectively, which are higher than that of 4,4'MDA-BMI (184 °C) due to higher molecular weights. Since the bulky BMIs **3b** and **3c** have lower melting points, they have a larger processing temperature range between their melting points and polymerization initial temperatures, at which the materials have good fluidity for moldability. This result indicates that the BMIs **3b** and **3c** with the bulky pendant groups afford better process management of the molten state. The molar heat of polymerization is the enthalpy change from the double bond to the single bond. The molar heats of polymerization of BMIs **3a-c** are in the range of 47.1~52.8 KJ/mol, similar to that of 4,4'MDA-BMI.

3. Properties of the cured bismaleimide resins

All the bismaleimides were cured by the following heating program: 100 °C/30 min, 200 °C/30 min, and 300 °C/3 h with a programming rate of 20 °C/min under nitrogen atmosphere. The cured resin of 4,4'MDA-BMI is extremely rigid and brittle be-

Table I. Thermal behavior data of bismaleimides and their cured resins.





Monomer	Ar	M_w	DSC								TGA			TMA
			Melting[a]			Polymerization[b]					T_{10}[c] (°C)		Char yield[d] (%)	Ts[e] (°C)
			T_m (°C)	Δh_f (J/g)	ΔH_f (KJ/mol)	T_i (°C)	T_p (°C)	ΔT (°C)	Δh_p (J/g)	ΔH_p (KJ/mol)	in N_2	in air		
BMI **3a**		452.42	256	92.6	41.9	257	259	1	108.3	49.0	478	476	49.2	440
BMI **3b**		508.53	136	47.6	24.2	207	293	71	103.8	52.8	476	476	44.1	409
BMI **3c**		502.48	171	20.0	10.0	224	307	53	93.8	47.1	486	486	54.2	444
4,4'MDA-BMI		358.35	158	113.3	40.6	184	206	26	153.8	55.1	473	487	48.2	478

(a) M_w, molecular weight; T_m, melting point; Δh_f, specific heat of fusion; ΔH_f, molar heat of fusion.
(b) T_i, polymerization initial temperature; T_p, polymerization peak temperature; ΔT, T_i-T_m; Δh_p, specific heat of polymerization; ΔH_p, molar heat of polymerization.
(c) Temperature at which 10% weight loss of the cured resins was recorded by TGA at a heating rate of 20 °C/min. The resins were cured at 100 °C/30 min, 200 °C/30 min, and 300 °C/3 h.
(d) Residual wt% when heated to 800 °C in nitrogen.
(e) Softening temperature; onset temperature of the penetration probe displacement by TMA at a heating rate of 10 °C/min.

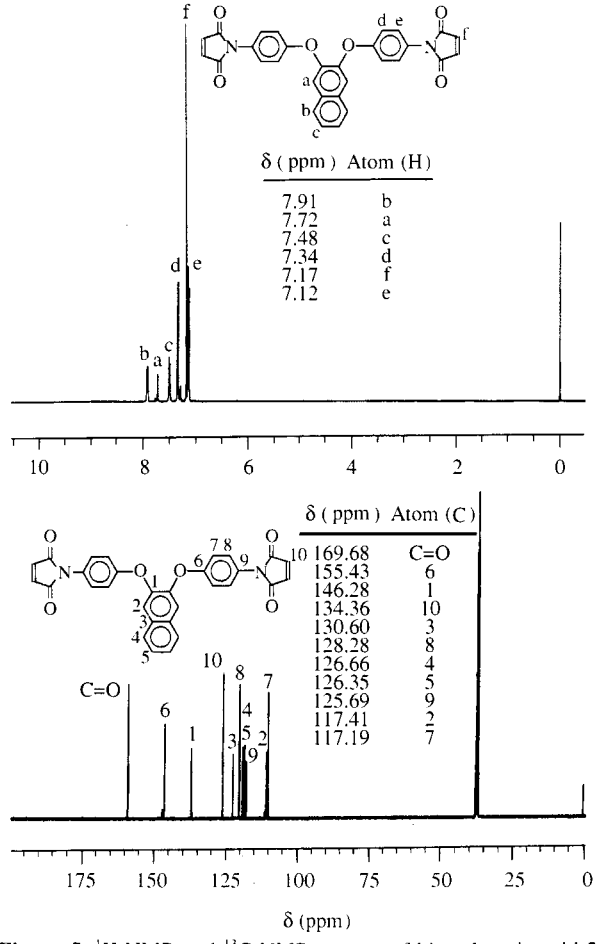


Figure 5. ^1H NMR and ^{13}C NMR spectra of bismaleamic acid **3c** in DMSO-d_6.

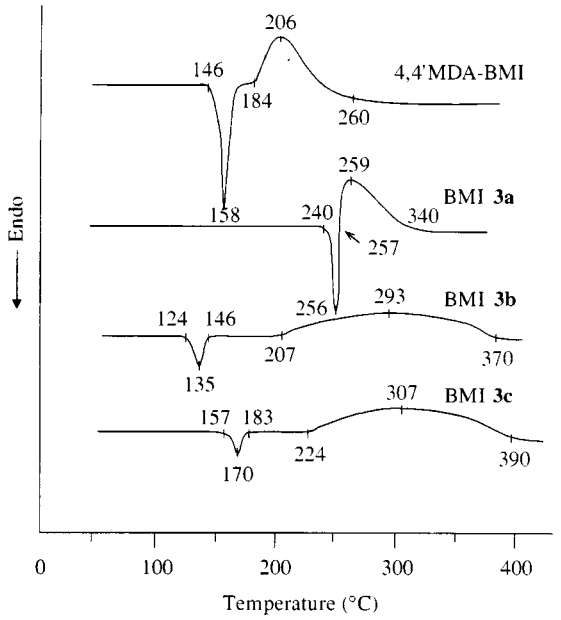


Figure 6. DSC curves of BMIs **3a-c** and 4,4'MDA-BMI with a heating rate of 10 °C/min in nitrogen.

cause of its high crosslink density; however, all the cured resins of BMIs **3a-c** are very tough. These results suggest that the introduction of ether linkages and the *ortho*-linked aromatic unit into the BMI molecules increased the strength and flexibility of the cured resins.

The thermal properties of the cured resins were

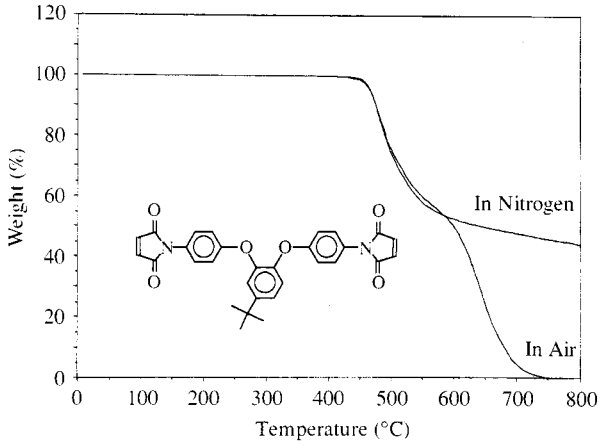


Figure 7. TGA curves for the cured resin of BMI **3b** with a heating rate of 20 °C/min.

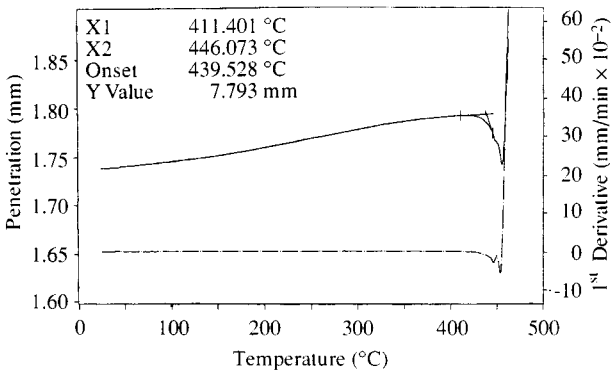


Figure 8. The TMA thermogram of the cured product of BMI **3a** with a heating rate of 10 °C/min.

evaluated by dynamic thermogravimetric analysis (TGA) and thermomechanical analysis (TMA), and the results are also summarized in Table I. The TG thermograms of a typical cured BMI **3b** are shown in Figure 7. This cured BMI resin did not show obvious decomposition below 450 °C in air or nitrogen. This means that increasing the molecular weight between cured sites in the BMI molecule in order to decrease the crosslinking density of the cured resin or introducing the *ortho*-linkage does not cause a significant reduction in thermal stability. The other BMI resins showed a similar decomposition behavior to that of BMI **3b**. Ten percentage weight loss temperatures of BMIs were recorded in the range of 476~497 °C in air and 476~500 °C in nitrogen. All the BMI resins left more than 44% char residue at 800 °C in nitrogen.

The softening temperatures (T_s) of the cured BMI resins were measured by the TMA method using a loaded penetration probe and were obtained from the onset temperatures of probe penetration. Figure 8 presents a typical TMA trace for the representative cured resin of BMI **3a**. None of the cured BMI softened below 400 °C. The cured BMIs **3a**, **3b**, and **3c** softened at around 440, 409, and 444 °C, respectively, and expanded dramatically above 450 °C. After the heat treatment during the TMA experiment, the appearance of these cured BMI resins turned from transparent and golden to darkened and foamed. The formation of the polymer foams is believed to be related to the early degradation of less stable aliphatic segments. The decrease in T_s for the cured resin of BMI **3b** might be due to the plasticizing effect of the pendent bulky *tert*-butyl group. On the whole, the cured resins containing *ortho*-linked aromatic units showed lower T_s values than those with the more commonly used 4,4'MDA-BMI owing to their more flexible molecular structures.

Conclusions

Three bismaleimides and their derivative polybismaleimide networks were synthesized from three *ortho*-linked bis(ether amine)s, i.e., 1,2-bis(4-aminophenoxy)benzene, 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene, and 2,3-bis(4-aminophenoxy)-naphthalene, for a comparison of their properties. Preliminary thermal analysis results implied that the bismaleimides with a bulkier molecular structure had lower melting points, facilitating the use of these monomers in the molten state. The cured bismaleimide resins were thermally stable up to 450 °C in both air and nitrogen atmospheres. Thus, the *ortho*-linked ether-containing bismaleimides may be useful as monomers for addition-type polyimides with better processing characteristics.

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