

# Syntheses and Thermal Properties of Ether-Containing Bismaleimides and Their Cured Resins

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**Abstract:** Aromatic bismaleimides (BMIs) were prepared by the condensation of maleic anhydride with multiring diamines containing ether bridges. The thermal behavior of the bismaleimides was investigated by differential scanning calorimetry (DSC). Thermogravimetric analysis (TGA) and thermomechanical analysis (TMA) were utilized to characterize the thermal properties of the cured resins. The effect of the structures of bismaleimides on their thermal behavior and the thermal properties of the cured resins is discussed. Increasing molecular weight between reactive endgroups lowered melting points of BMIs, leading to a large temperature range between their melting point and the initial polymerization temperature. The introduction of ether bonds together with other flexible partners to bismaleimide resins decreased the glass transition temperatures or softening temperatures and the brittleness of the cured bismaleimide resins without extreme loss of their thermal stability. The cured bismaleimides were stable up to 450°C in both air and nitrogen.

**Keywords:** Bismaleimides, Thermal properties.

## Introduction

Polyimides, which are well known as high temperature-resistant polymers, may be categorized into two different groups: condensation-type and addition-type resins. Condensation-type polyimides exhibit excellent high temperature thermal and mechanical properties, but have unattractive processing characteristics in composite and adhesive applications. Addition-type polyimide resins are produced from bisimides bearing reactive end cappers. One of the most important types of bisimides is the bismaleimides (BMI) [1]. They are suitable for use in a wide range of composite materials since they contain unsaturated double bonds that can thermally polymerize without the evolution of volatiles that cause voids. The BMI resins can be processed in a manner similar to epoxies, while they exhibit higher glass transition temperatures than epoxies. Major applications for BMI structural composites are in military aircraft and in aircraft engines.

4,4'-Bismaleimidodiphenylmethane, based on 4,4'-diaminodiphenylmethane, is the most widely used building block for BMI resin because the precursor diamine is readily available at low cost. However, 4,4'-bismaleimidodiphenylmethane has a

relatively high melting point and a relatively low polymerization temperature and therefore does not flow easily in the uncured state. Moreover, the cured product is extremely brittle because of the highly crosslinked structure. For this BMI to be useful as a matrix resin for high-performance structural composite materials, a great deal of work has been performed to achieve greater fracture toughness in the BMI resin. One popular approach is to use diamines, dithiols, allylphenols such as *o,o'*-diallyl bisphenol A, or reactive flexible oligomers as chain extenders for BMIs to decrease the crosslinking density of the cured BMI resins [2-10]. However, introducing such tougheners usually causes a lowering of the thermo-oxidative stability of the cured products.

In order to enhance the toughness of BMI resins while maintaining favorable properties at elevated temperatures, much effort has been given to the development of long-chain aromatic diamines [11-13]. It has been demonstrated that the introduction of phenoxy units to the BMI structure decreased the brittleness of the cured resins significant without reduction in their heat-resistant properties [11]. In this study, some long-chain BMIs are synthesized from four- or five-ring aromatic diamines containing -O-, as well as  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{C}(\text{CF}_3)_2-$ , or

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–C(C<sub>6</sub>H<sub>5</sub>)(CH<sub>3</sub>)– bridging groups. For the purpose of comparative study, some BMIs from one to three-ring aromatic diamines without –O– linkage are also synthesized. The effect of the structures of these BMIs on their thermal behavior and the thermal properties of the cured resins will be discussed.

## Experimental

### 1. Materials

*m*-Phenylenediamine (Janssen), 4,4'-diaminodiphenylmethane (TCI),  $\alpha,\alpha'$ -bis(4-aminophenyl)-1,4-diisopropylbenzene (Mitsui Petrochemical Ind.; MPI),  $\alpha,\alpha'$ -bis(4-aminophenyl)-1,3-diisopropylbenzene (MPI) were used as received. According to a procedure described in [14], the other diamines, such as 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane,  $\alpha,\alpha'$ -bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene, and  $\alpha,\alpha'$ -bis[4-(4-aminophenoxy)phenyl]-1,3-diisopropylbenzene were prepared by the aromatic nucleophilic substitution reaction of *p*-chloronitrobenzene (TCI) with the corresponding bisphenols such as 2,2-bis(4-hydroxyphenyl)propane (Wako), 1,1-bis(4-hydroxyphenyl)-1-phenylethane (MPI), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (Kriskev),  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,4-diisopropylbenzene (MPI), and  $\alpha,\alpha'$ -bis(4-hydroxyphenyl)-1,3-diisopropylbenzene (MPI) in the presence of a base such as K<sub>2</sub>CO<sub>3</sub>, giving the bis(*p*-nitrophenoxy) compounds, followed by subsequent reduction of the dinitro compounds using hydrazine as the reducing agent and palladium as the catalyst. Maleic anhydride (Fluka), acetic anhydride (Fluka), and triethylamine (Fluka) were used without purification.

### 2. Synthesis of bismaleimides

Nine bismaleimides, including *m*-phenylenebismaleimide (BMI-1), 4,4'-bismaleimidodiphenylmethane (BMI-2),  $\alpha,\alpha'$ -bis(4-maleimidophenyl)-1,4-diisopropylbenzene (BMI-3),  $\alpha,\alpha'$ -bis(4-maleimidophenyl)-1,3-diisopropylbenzene (BMI-4), 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane (BMI-5), 1,1-bis[4-(4-maleimidophenoxy)phenyl]-1-phenylethane (BMI-6), 2,2-bis[4-(4-maleimidophenoxy)phenyl]hexafluoropropane (BMI-7),  $\alpha,\alpha'$ -bis[4-(4-maleimidophenoxy)phenyl]-1,4-diisopropylbenzene (BMI-8), and  $\alpha,\alpha'$ -bis[4-(4-maleimidophenoxy)phenyl]-1,3-diisopropylbenzene (BMI-9), were prepared from the corresponding diamines and maleic anhydride via a two-stage procedure that included a ring-opening addition reaction to give *N,N*-bismaleamic acids, followed by chemi-

cal cyclodehydration to bismaleimides. A detailed synthetic procedure for BMI-6 is described as follows. A 500-mL four-necked flask was charged with maleic anhydride 15.57 g (0.159 mol) and acetone (100 mL). A solution of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane 37.4 g (0.072 mol) in acetone 100 mL was added into the flask and stirred for 6 hrs at room temperature. The resulting *N,N*-bismaleamic acid precipitated out and suspended in the reaction medium. The intermediate amic acid was separated by filtration, washed with acetone to remove remaining maleic anhydride, and dried. A 500 mL three-necked flask was charged with dried *N,N*-bismaleamic acid 50 g (0.075 mol), sodium acetate 2 g, and triethylamine 5 mL. Acetic anhydride 40 mL was added dropwise into the mixture over a period of 40 minutes. After complete addition, the reaction mixture was heated at reflux temperature. The suspension turned into a clear solution after about 1 hr. Reflux was continued for an additional 2 hrs, and the solution was then poured into cold water. The precipitate was collected and washed with sodium bicarbonate solution until it was free from acetic acid, then finally washed with water and dried in vacuo, giving 45 g (0.0663 mol, 92.1 % yield) of the product; m.p. 131 °C.

Anal. Calcd for C<sub>40</sub>H<sub>28</sub>O<sub>6</sub>N<sub>2</sub> (632.67): C, 75.94%; H, 4.46 %; N, 4.43%. Found: C, 73.96%; H, 4.69%; N, 4.11%.

### 3. Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were performed using a Perkin-Elmer C, H, N 2400 elemental analyzer. <sup>1</sup>H NMR spectra were determined at 30 °C on a Jeol-JNM-PMX 60 NMR spectrometer with tetramethylsilane (TMS) as an internal reference. The DSC traces were measured on a Sinku Riko TA-7000 thermal analysis controller at a heating rate of 20 °C/min in flowing nitrogen (30 cm<sup>3</sup>/min). Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm<sup>3</sup>/min) at a heating rate of 20 °C/min. The measurements were taken after an initial 250 °C/5 min drying step. Thermomechanical analysis (TMA) was conducted with a Rigaku TMA 8140 at a heating rate of 10 °C/min in nitrogen.

## Results and Discussion

### 1. Monomer synthesis

The bismaleimides (BMIs) were prepared from

the corresponding diamines and maleic anhydride according to a two-stage method described by White et al. [15]. As shown in Scheme 1, the BMIs-1 to 9 were prepared by the ring-opening addition reactions of various diamines with maleic anhydride in acetone, giving the *N,N*-bismaleamic acids, followed by catalytic cyclodehydration with acetic anhydride, sodium acetate, and triethylamine. The structures of these BMI monomers were confirmed through IR, <sup>1</sup>H NMR spectroscopy, and elemental analysis. The formation of BMI could be readily confirmed by the disappearance of the AB doublets corresponding to the olefinic protons of bismaleamic acid and the resonance of amide and carboxyl protons, as well as the appearance of the singlet due to the olefinic protons of maleimide ring.

## 2. Thermal behavior of bismaleimides

The thermal behavior of all the bismaleimides was investigated by differential scanning calorimetry (DSC). The DSC curve of a typical bismaleimide is shown in Figure 1. Endothermic behavior due to fusion of the solid state is observed in the lowest temperature region. The melting point ( $T_m$ ) is defined as the peak temperature of the endotherms. Next, thermal polymerization of double bonds occurs exothermally. The polymerization initial tem-

peratures ( $T_i$ ) is the onset temperature of the exothermic peak. The polymerization reaction converges via the the polymerization peak temperature ( $T_p$ ), where the reaction rate reaches its maximum. The thermal behavior data of all the bismaleimides are 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. However, as shown in Table I, these bismaleimides (with the exception of BMI-3 and BMI-8) contradict this general rule. This is prob-

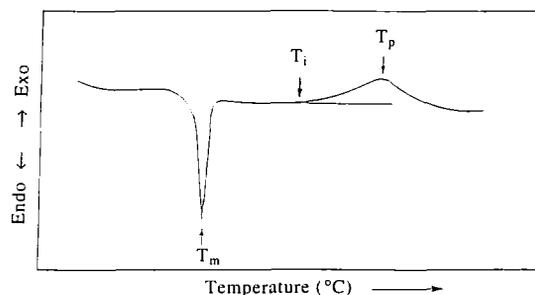


Figure 1. DSC curve of typical bismaleimide.  $T_m$ , melting point;  $T_i$ , polymerization initial temperature; and  $T_p$ , polymerization peak temperature.

Table I. Thermal behavior data of bismaleimides.

Bismaleimide code (M.W.)	$T_m^{(a)}$ (°C)	$\Delta h_f^{(b)}$ (J/g)	$T_i^{(c)}$ (°C)	$\Delta T^{(d)}$ (°C)	$T_{p1}^{(e)}$ (°C)	$\Delta h_p^{(f)}$ (J/g)	$T_{p2}^{(g)}$ (°C)
BMI-1 (268.2)	205	81.1	243	38	253	263.7	-
BMI-2 (358.4)	161	85.2	205	44	227	94.6	-
BMI-3 (504.6)	-	-	235	-	242	64.6	-
BMI-4 (504.6)	135	54.7	245	110	287	89.6	-
BMI-5 (570.6)	85	-	216	131	287	359.5	-
BMI-6 (632.7)	131	5.2	240	109	289	411.5	-
BMI-7 (678.5)	90	-	230	140	315	200.6	-
BMI-8 (688.8)	212	154.8	230	18	265	355.6	308
BMI-9 (688.8)	90	19.2	210	120	243	453.2	273

(a)  $T_m$ , melting point.

(b)  $\Delta h_f$ , specific heat of fusion.

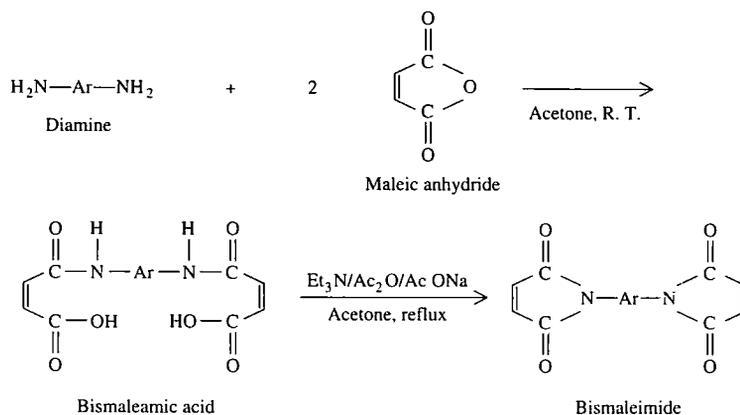
(c)  $T_i$ , polymerization initial temperature.

(d)  $\Delta T$ ,  $T_i - T_m$ .

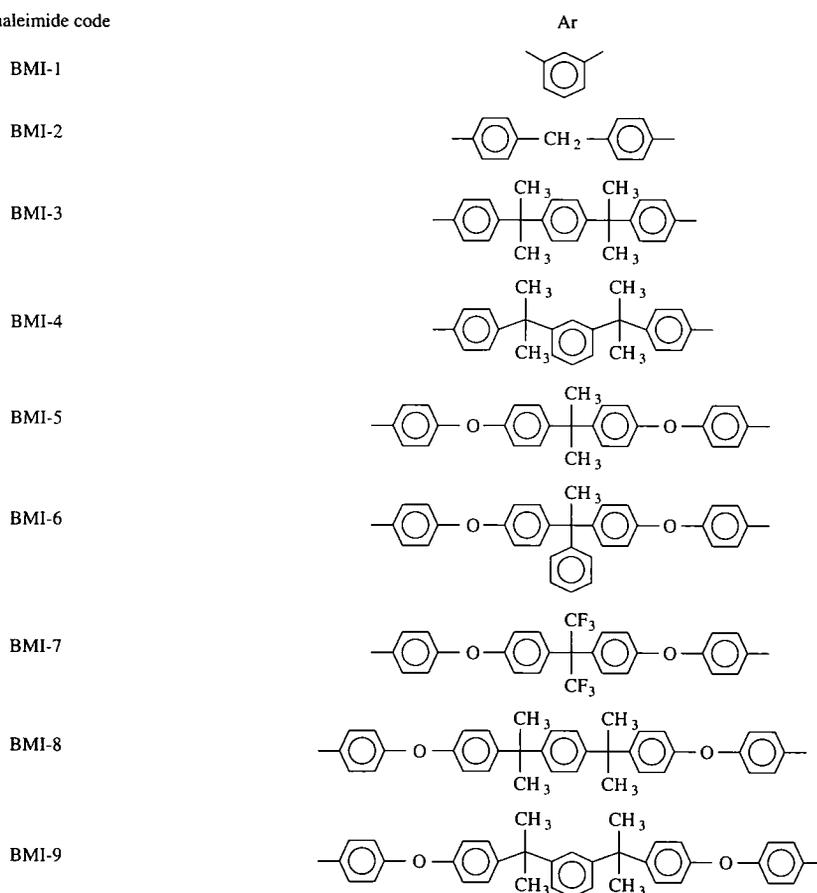
(e)  $T_{p1}$ , first polymerization peak temperature.

(f)  $\Delta h_p$ , specific heat of polymerization.

(g)  $T_{p2}$ , second polymerization peak temperature.



Bismaleimide code



Scheme 1. Preparation of various bismaleimides.

ably the result of flexible linkages (such as ether and isopropylidene linkages) and bulky groups (such as hexafluoroisopropylidene and phenylethylidene groups) between phenyl units of the long-chain BMI

monomer, which interfere with close packing between molecules leading to a decrease in  $T_m$ . Moreover, the existence of an *m*-phenylene unit should be another factor causing a  $T_m$  decrease, such as in

the cases of BMI-4 and BMI-9. It is interesting to note that the DSC trace of BMI-3 showed no melting endotherm. This can be ascribed to the close proximity of  $T_m$  and  $T_i$ , which probably caused an overlap of the endotherm and the exotherm. The bismaleimide BMI-8, an analogue to BMI-3 but bearing two more phenoxy groups, also displayed a higher  $T_m$  (212 °C) and higher heat of fusion ( $\Delta H_f$ ) than other BMIs. This means that the symmetrical 1,4-phenylenediisopropylidene segment give BMI-3 and BMI-8 a high packing density in the crystalline state.

The polymerization initial temperatures of these bismaleimides are in the small range of 205-245 °C. This indicated that the reactivity of double bonds of BMI was not significantly affected by the chain length and the structure of diamine component. Since the long-chain diamine-based BMIs have lower melting points, they have a large processing temperature range between their melting points and polymerization initial temperatures, at which the material has good fluidity for moldability. Therefore, these ether-containing bismaleimides (with the exception of BMI-8) have enhanced moldability. The influence of flexible linkages on the moldability of BMI can be clearly seen from Figure 2. The range between  $T_m$  and  $T_i$  ( $\Delta T$ ) is enlarged to 110 °C (BMI-4) from 38 °C by the insertion of two phenyleneisopropylidene units into the structure of BMI-1. Further insertion leads to a  $T_i$  lowering and a  $\Delta T$  increase (see BMI-9). Figure 3 compares the DSC heating traces of isomeric BMI-8 and BMI-9. The para isomer BMI-8 provides the higher melting transition and the smaller processing temperature range; the *meta* isomer BMI-9 has a lower melting point but shows a larger processing temperature range. Moreover, it is notable that BMI-8 and BMI-9 show two exothermic peaks in their DSC traces. This is probably due to the presence of a long and flexible segment between cure sites, which provides the suitable mobility of the cured network in an early stage. As the resins are treated at a higher temperature, the mobility of residual reactive sites increases, and the curing reactions start again to yield resins with more cured structure. Such a curing process must proceed until resins with fully crosslinked structure are obtained.

### 3. Thermal properties of cured bismaleimide resins

All the bismaleimides were cured at 250 °C in air for 10 hrs. The thermal properties of the cured resins were evaluated by thermogravimetry (TG) and thermomechanical analysis (TMA), and the results are presented in Table II. The TG curves of a typi-

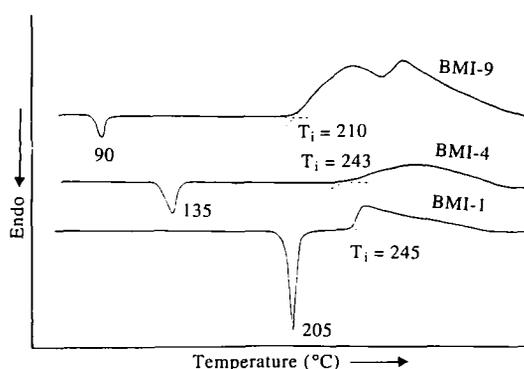


Figure 2. DSC traces of BMI-1, BMI-4, and BMI-9 with a heating rate of 20 °C/min in nitrogen.

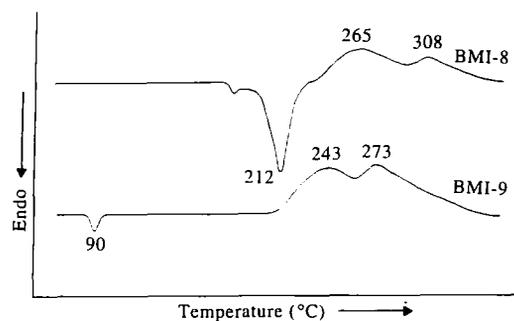


Figure 3. DSC curves for BMI-8 and BMI-9 with a heating rate of 20 °C/min in nitrogen.

cal cured BMI-8 resin are shown in Figure 4. This cured BMI resin did not show obvious decomposition before 450 °C in air or nitrogen. This means that increasing the molecular weight between cure sites in the BMI molecule in order to decrease the crosslinking density of the cured resin does not cause a significant reduction in thermal stability. All other BMI resins showed a similar decomposition behavior to that of BMI-8 resin. The 10% weight loss temperatures of these cured bismaleimides were recorded respectively in the range of 461-497 °C in air and 460-500 °C in nitrogen. All the bismaleimide resins left more than 25 wt% char residue at 800 °C in nitrogen. The glass transition temperatures ( $T_g$ s) of the cured bismaleimide resins were measured by TMA using a penetration method. The influence of the incorporation of flexible segments on the  $T_g$  is indicated in Figure 5. The cured resins of BMI-8 and BMI-9 possessed relatively lower  $T_g$ s. This may be due to a relatively long distance between cured sites of these BMI molecules. The cured resin of BMI-6 also had a relatively lower  $T_g$ , probably attributed to the presence of an asymmetric and bulky

**Table II.** Thermal properties of cured bismaleimide resins<sup>(a)</sup>.

Cured Resin	T <sub>g</sub> <sup>(b)</sup> (°C)	T <sub>d</sub> <sup>(c)</sup> (°C)		Char residual <sup>(d)</sup> in wt%
		in N <sub>2</sub>	in Air	
BMI-1	479	500	497	46.5
BMI-2	409	473	487	48.2
BMI-3	—	460	461	33.8
BMI-4	428	463	475	32.0
BMI-5	435	475	477	43.7
BMI-6	283	465	470	38.2
BMI-7	445	475	485	25.2
BMI-8	235	481	486	36.8
BMI-9	239	456	472	41.0

(a) Cured at 250 °C for 10 hrs.

(b) Glass transition temperature determined by TMA, using a penetration method.

(c) Decomposition temperature at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min.

(d) Char residual at 800 °C in nitrogen.

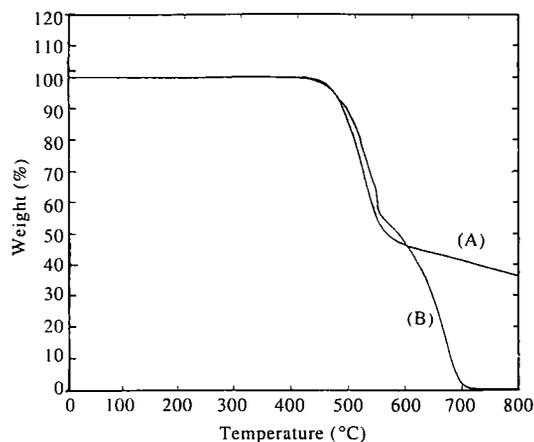
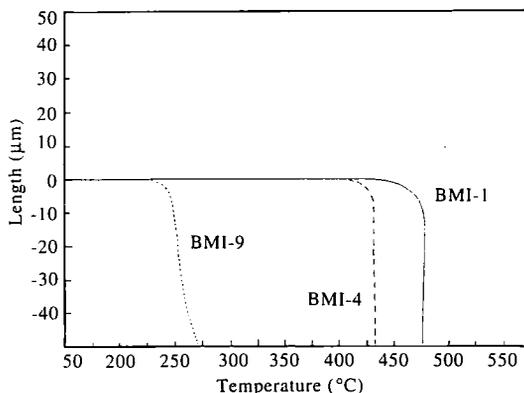
triphenylethane unit. Thus, the toughness and moldability of BMI resins might be improved by increasing the molecular weight between endgroups in the BMI molecules by the incorporation of phenoxy and other flexible groups, which decreased the crosslinking density of the cured resins without great reductions in their thermal resistance.

## Conclusion

The nine bismaleimides (BMIs) were prepared in high yield by the ring-opening addition reactions of the corresponding diamines with maleic anhydride, giving the *N,N*-bismaleamic acids, followed by catalytic cyclodehydration with acetic anhydride. The long-chain diamine-based BMIs have a large processing temperature range between their melting points and polymerization initial temperatures, at which the material has good fluidity for moldability. Increasing the molecular weight between cure sites in the BMI molecule in order to decrease the crosslinking density of the cured resin does not cause a significant reduction in thermal stability. These cured BMI resins were stable up to 450 °C in both air and nitrogen atmospheres. Therefore, these ether-containing bismaleimides are expected to be high temperature-resistant polymers with good processability.

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**Figure 4.** TG curves for the cured resin of BMI-8 with a heating rate of 20 °C/min in nitrogen (A) and in air (B).**Figure 5.** TMA curves of the BMI resins of BMI-1, BMI-4, and BMI-9 cured at 250 °C for 10 hrs.

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