

Soluble asymmetric bismaleimide with low molten viscosity and its high glass transition temperature polymer

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ABSTRACT: Three novel bismaleimide monomers (MBA-BMI, EBA-BMI, and PBA-BMI) with unsymmetrical backbone and different pendant groups were synthesized using asymmetric diamine and maleic anhydride as the precursors. The prepared bismaleimide monomers show good solubility in common organic solvents such as acetone and tetrahydrofuran. The EBA-BMI melt treated at 180 °C also shows low viscosity about 190–934 mPa s at the temperature range of 160–139 °C below its melting point (166 °C). In addition to the good processability, all three cured bismaleimides show high storage moduli at high temperatures (2.0 GPa at 400 °C), high glass transition temperatures over 400 °C, and good thermal stability with the 5% weight loss temperatures around 470 °C under nitrogen atmosphere. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43491.

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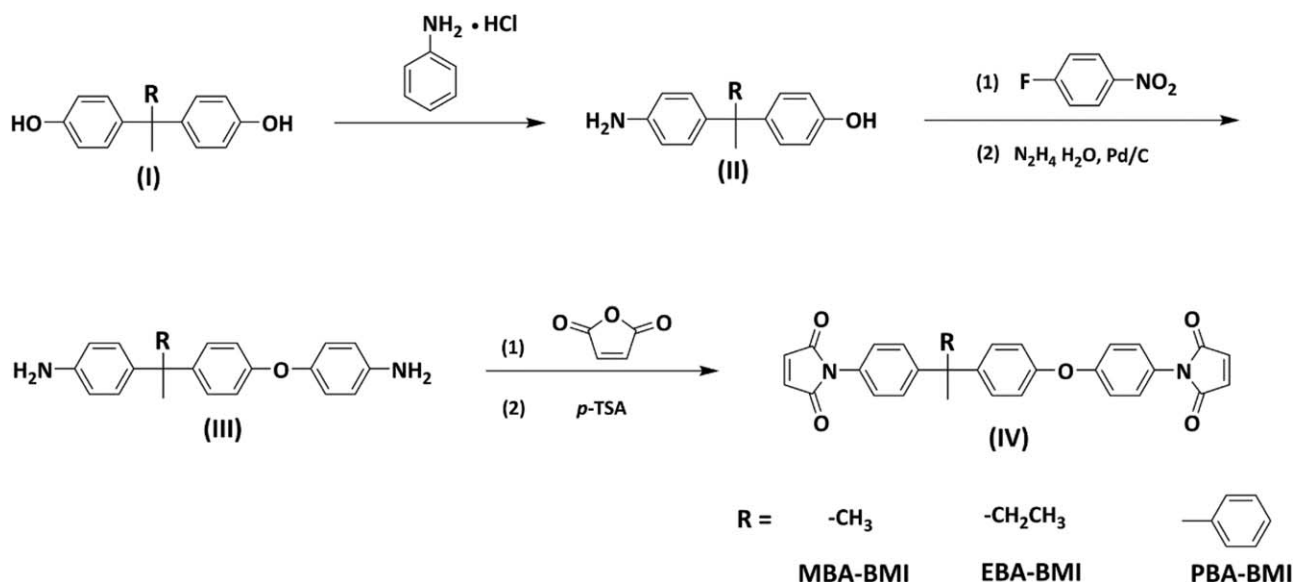
INTRODUCTION

Bismaleimide (BMI) is an attractive self-polymerized thermosetting resin for its outstanding thermal and oxidative stability (high service temperature over 230 °C),^{1,2} flame retardancy, low moisture absorption, good chemical, and corrosion resistance.³ Owing to the excellent properties, BMI has become an important high performance matrix resin, which is widely applied in microelectronics and aerospace industries, such as multilayer printed circuit boards, semiconductor packaging substrates^{4,5}; advanced composites, high temperature structure adhesives, and potting resins.⁶

The commonly used BMI monomers, such as N,N'-(4,4'-diphenylmethane)bismaleimide (DDM-BMI), have rigid and symmetric molecular structure, which result in some disadvantages of BMI such as high melting temperature, narrow processing temperature window, and poor solubility in the common organic solvents.^{7,8} To overcome these disadvantages and extend the application of BMI, great efforts have been made to improve the processability of BMI while maintaining its excellent thermal performance. One strategy is the copolymerization of BMI with expanding agents or other high performance resins such as diamine,⁹ allylic compound,¹⁰ cyanate ester,¹¹ epoxy resins,¹² and benzoxazine.¹³ Another effective strategy is the modification of BMI's chemical structure. A number of new chain-extended BMIs have been designed and synthesized, such as those containing amide,¹⁴ ester,¹⁵ naphthalene,¹⁶ phosphorus,¹⁷ silicon,¹⁸ 1,3,4-oxadiazole,¹⁹ biphenylene,²⁰ dicyclopentadiene or dipen-

tene,²¹ fluorenyl,^{22,23} parabanic,²⁴ allyl,²⁵ s-triazine,²⁶ phenylindane,²⁷ azobenzene,²⁸ epoxy backbone,²⁹ and metal complex.³⁰ Based on the structure–properties relationships, the unsymmetrical chemical structure can hinder the ordered packing or crystallization of the molecules, hence improve the solubility of the monomers. Recently, Chen synthesized three asymmetric bismaleimide monomers containing 1,3,4-oxadiazole group^{8,31} which are soluble in acetone and tetrahydrofuran. However, the melting points of the three BMI monomers are higher than 200 °C and close to the onset curing temperatures, which means the processing temperature window is very narrow for the molten resins.

Our previous work also revealed that the asymmetric bismaleimide monomer with DOPO pendant group showed very good solubility in common organic solvents such as acetone.³² The bismaleimide-triazine resins also showed low molten viscosity although the asymmetric bismaleimide is an amorphous solid with a T_g at 135 °C. To improve the processability of bismaleimide monomer, three novel asymmetric bismaleimide monomers with aryl ether and different pendant groups (Scheme 1) were designed and synthesized in this article. The prepared bismaleimide monomers show improved processability with good solubility in common organic solvents, low molten viscosity, and wide processing temperature window. Besides, the cured bismaleimides show attractive thermal stability, high storage modulus at high temperature, and high glass transition temperature.



Scheme 1. Synthetic route of the bismaleimide monomers.

EXPERIMENTAL

Materials

Bisphenol A and 4,4'-(1-phenylethylidene) biphenol were purchased from Aladdin Industrial. 2,2-Bis(4-hydroxyphenyl)butane was obtained from Jinan Fujing Chemical. Aniline hydrochloride, 4-fluoronitrobenzene, *p*-toluenesulfonic acid monohydrate (*p*-TSA), and palladium on carbon (5% Pd/C) were supplied by Energy Chemical. Hydrazine hydrate solution (50%), maleic anhydride, diatomite, anhydrous potassium carbonate, sodium hydroxide, hydrochloric acid (36–38%), and other solvents were obtained from Sinopharm Chemical Reagent. All the materials were used as received without further purification.

Monomer Synthesis

2-(4'-Aminophenyl)-2-(4'-hydroxyphenyl)propane (MBA) and 2-(4'-aminophenyl)-2-(4'-aminophenoxy)phenylpropane (MBA-NH₂) were synthesized according to the literature.³³ Bisphenol A (2.28 g, 0.01 mol) and aniline hydrochloride (3.40 g, 0.03 mol) were reacted at 180 °C in N₂ for 40 min to give MBA. Then, MBA (2.27 g, 0.01 mol) was reacted with 4-fluoronitrobenzene (1.41 g, 0.01 mol) in the presence of K₂CO₃ (1.38 g, 0.01 mol) to form the nitro intermediate which was reduced by hydrazine hydrate to give the asymmetric diamine MBA-NH₂.

2-(4'-Aminophenyl)-2-(4'-hydroxyphenyl)butane (EBA), 2-(4'-aminophenyl)-2-(4'-aminophenoxy)phenylbutane (EBA-NH₂), 1-(4'-aminophenyl)-1-(4'-hydroxyphenyl)-1-phenylethane (PBA), and 1-(4'-aminophenyl)-1-(4'-aminophenoxy)phenyl-1-phenylethane (PBA-NH₂) were synthesized in a similar way from 2,2-bis(4-hydroxyphenyl)butane and 4,4'-(1-phenylethylidene)biphenol, respectively. The NMR data of MBA, MBA-NH₂, EBA, EBA-NH₂, PBA, and PBA-NH₂ were summarized in Table I.

2-(4'-Maleimido)phenyl-2-[4'-(4''-maleimido)phenoxy]phenylpropane (MBA-BMI). MBA-NH₂ (3.18 g, 0.010 mol), maleic anhydride (1.96 g, 0.020 mol) and the mixed solvent (toluene/DMF = 2.0/1.0, 100 mL) were added into a 250 mL round bottom flask equipped with a Dean-Stark apparatus. The

mixture was reacted at room temperature for 3 h in nitrogen atmosphere. *p*-Toluenesulfonic acid monohydrate (*p*-TSA, 0.38 g, 2.0 mmol) was added and the reaction solution was refluxed for 8 h. After cooling and concentrating, the mixture was poured into a large amount of ice water with fierce stirring

Table I. NMR Data of the Bismaleimide Precursors

Sample	¹ H NMR (δ)	¹³ C NMR (δ)
MBA	9.09 (1 H, OH);	160–110 (aromatic);
	7.00–6.00 (8 H, aromatic);	41.2 (C-CH ₃);
	4.80 (2 H, NH ₂);	31.4 (C-CH ₃)
	1.50 (6 H, C-CH ₃)	
MBA-NH ₂	7.50–6.00 (12 H, aromatic);	160–110 (aromatic);
	4.907 and 4.908 (4 H, NH ₂);	41.4 (C-CH ₃);
	1.50 (6 H, C-CH ₃)	31.3 (C-CH ₃)
EBA	9.08 (1 H, OH);	110–160 (aromatic);
	7.00–6.00 (8 H, aromatic);	44.7 (C-CH ₃);
	4.80 (2 H, NH ₂);	34.2 (CH ₂ -CH ₃);
	1.93 (2 H, CH ₂ -CH ₃);	27.3 (C-CH ₃);
	1.41 (3 H, C-CH ₃)	9.7 (CH ₂ -CH ₃)
	0.63 (3 H, CH ₂ -CH ₃);	
EBA-NH ₂	7.50–6.00 (12 H, aromatic);	110–160 (aromatic);
	4.92 and 4.84 (4 H, NH ₂);	44.9 (C-CH ₃);
	1.98 (2 H, CH ₂ -CH ₃);	34.2 (CH ₂ -CH ₃);
	1.50 (3 H, C-CH ₃);	27.2 (C-CH ₃);
	0.64 (3 H, CH ₂ -CH ₃);	9.7 (CH ₂ -CH ₃)
PBA	9.25 (1 H, OH);	160–110 (aromatic);
	7.00–6.00 (13 H, aromatic);	51.00 (C-CH ₃);
	4.91 (2 H, NH ₂);	30.78 (C-CH ₃)
	2.00, (3 H, C-CH ₃)	
PBA-NH ₂	7.50–6.00 (17 H, aromatic);	160–110 (aromatic);
	4.93 (4 H, NH ₂);	51.2 (C-CH ₃);
	1.99 (3 H, C-CH ₃)	30.8 (C-CH ₃)

to get light yellow powder. The powder was purified by column chromatography (ethyl acetate/petroleum ether = 1.0/1.0) and the target product MBA-BMI (4.28 g) was obtained in 89.4% yield.

^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ): 7.50–6.80 (m, 12 H; Ar H), 7.164 (s, 2 H; $\text{CH}=\text{CH}$), 7.159 (s, 2 H; $\text{CH}=\text{CH}$), 1.67 (s, 6 H; C- CH_3); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, δ): 170.5 (C=O), 135.1 (CH=CH), 160–110 (aromatic), 42.6 (C- CH_3), 30.9 (C- CH_3); IR (KBr): $\nu = 1714$ [s; $\nu_s(\text{C}=\text{O})$], 1396 [m; $\nu_s(\text{N}-\text{C}=\text{O})$], 1143 [m; $\nu_s(\text{C}-\text{N}-\text{C})$], 690 cm^{-1} [m; $\nu_s(\text{C}=\text{H})$].

2-(4'-Maleimido)phenyl-2-[4'-(4''-maleimido)phenoxy]phenylbutane (EBA-BMI). EBA-BMI was synthesized in a similar way as MBA-BMI. EBA-NH₂ (3.32 g, 0.01 mol) was reacted with maleic anhydride (1.96 g, 0.02 mol) and then 0.38 g of *p*-TSA (2.0 mmol) was added. The mixture was refluxed with constant stirring for 8 h. After precipitation from the concentrated solution with water and purification by column chromatography (ethyl acetate/petroleum ether = 1.0/1.0), EBA-BMI was obtained in 70.0% yield (3.45 g).

^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ): 7.50–6.80 (m, 12 H; Ar H), 7.18 (s, 2 H; $\text{CH}=\text{CH}$), 7.17 (s, 2 H; $\text{CH}=\text{CH}$), 2.14 (q, 2 H; CH_2-CH_3), 1.60 (s, 3 H; C- CH_3), 0.72 (t, 3 H; CH_2-CH_3); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, δ): 170.5 (C=O), 135.1 (CH=CH), 160–110 (aromatic), 46.1 (C- CH_3), 33.9 (CH₂-CH₃), 26.9 (C- CH_3), 9.6 (CH₂-CH₃); IR (KBr): $\nu = 1714$ [s; $\nu_s(\text{C}=\text{O})$], 1396 [m; $\nu_s(\text{N}-\text{C}=\text{O})$], 1143 [m; $\nu_s(\text{C}-\text{N}-\text{C})$], 690 cm^{-1} [m; $\nu_s(\text{C}=\text{H})$].

1-(4'-Maleimido)phenyl-1-[4'-(4''-maleimido)phenoxy]phenyl-1-phenylethane (PBA-BMI). PBA-BMI was synthesized and purified by the same method as MBA-BMI from PBA-NH₂ (3.80 g, 0.010 mol), maleic anhydride (1.96 g, 0.02 mol) and *p*-TSA (0.38 g, 2.0 mmol). PBA-BMI was obtained as light yellow solid (4.37 g, 80.8%).

^1H NMR (500 MHz, $\text{DMSO-}d_6$, δ): 7.50–7.00 (m, 17 H; Ar H), 7.181 (s, 2 H; $\text{CH}=\text{CH}$), 7.177 (s, 2 H; $\text{CH}=\text{CH}$), 2.16 (s, 3 H; C- CH_3); ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, δ): 170.5 and 170.4 (C=O), 135.14 and 135.12 (CH=CH), 160–110 (aromatic), 52.1 (C- CH_3), 30.6 (C- CH_3); IR (KBr): $\nu = 1714$ [s; $\nu_s(\text{C}=\text{O})$], 1396 [m; $\nu_s(\text{N}-\text{C}=\text{O})$], 1143 [m; $\nu_s(\text{C}-\text{N}-\text{C})$], 690 cm^{-1} [m; $\nu_s(\text{C}=\text{H})$].

Preparation of Bismaleimide Polymers

MBA-BMI was melted at 200 °C and degassed under vacuum at 200 °C for 30 min. EBA-BMI was melted at 180 °C and then degassed under vacuum at 160 °C for 30 min. PBA-BMI was melted at 215 °C for 5 min and degassed under vacuum at 160 °C for 30 min. The molten samples were cured at 300 °C for 10 h and 350 °C for 3 h in an oven.

Characterization

Fourier transform infrared spectra (FT-IR) were carried out on a Nicolet 6700 spectrometer at a resolution of 4 cm^{-1} with KBr pellet. Nuclear magnetic resonances (NMR) were recorded on a Bruker DMX500 using dimethyl sulfoxide-*d*₆ ($\text{DMSO-}d_6$) as the solvent.

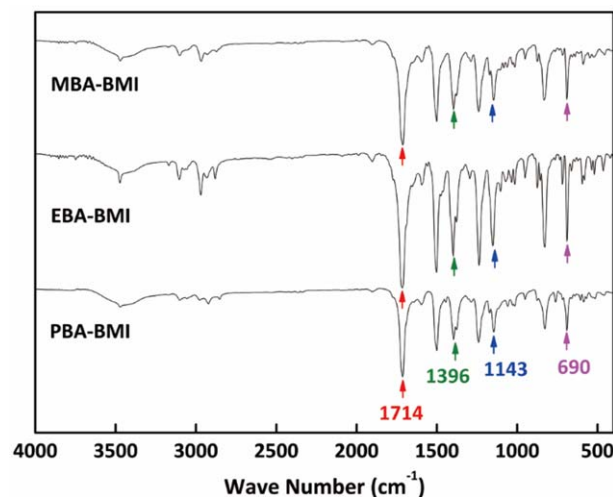


Figure 1. FTIR of the bismaleimide monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The solubility of bismaleimide monomers was tested as follows. The bismaleimide (30 mg) was mixed with a solvent (1 mL) by shaking for 1 min. The solvent is considered soluble if the mixture is transparent, marked as “+” or “+/ Δ ”. Otherwise, the solvent is considered insoluble, marked as “-”. The viscosity of the molten sample was performed on a HAAKE MARS III rotary rheometer with a shear rate of 5 s^{-1} .

Differential scanning calorimetry (DSC) was measured using a TA Q200 calorimeter under nitrogen atmosphere at a heating rate of 10 °C min^{-1} . Dynamic mechanical analysis (DMA) was carried out on a TA Q800 analyzer in three-point bending mode at a heating rate of 3 °C min^{-1} with a frequency of 1 Hz. Thermal gravimetric analysis (TGA) were performed with a Shimadzu DTG60 simultaneous DTA-TG apparatus at a heating rate of 10 °C min^{-1} under nitrogen atmosphere from ambient temperature to 800 °C.

RESULTS AND DISCUSSION

Synthesis of Bismaleimide Monomers

The preparation of asymmetric diamines (III) is the key process to obtain asymmetric bismaleimide monomers. The synthetic route was designed as shown in Scheme 1. First, the compounds (II) were synthesized from the bisphenol compounds (I) and aniline hydrochloride at 180 °C in N_2 for 40 min. Then, the compounds (II) were reacted with 4-fluoronitrobenzene in the presence of K_2CO_3 to form the nitro intermediates which were reduced by hydrazine hydrate to give the asymmetric diamines (III). The prepared asymmetric diamines (MBA-NH₂, EBA-NH₂, and PBA-NH₂) were characterized by NMR and the detailed data were summarized in Table I.

The prepared diamines (III) were reacted with maleic anhydride and *p*-TSA in a mixed solvent of toluene and DMF to give the bismaleimide monomers (IV). The chemical structures of the prepared bismaleimide monomers were confirmed by FTIR and NMR. Figure 1 shows the FTIR spectra of MBA-BMI, EBA-BMI, and PBA-BMI. All three bismaleimide monomers show a strong absorption at 1714 cm^{-1} belonging to the typical

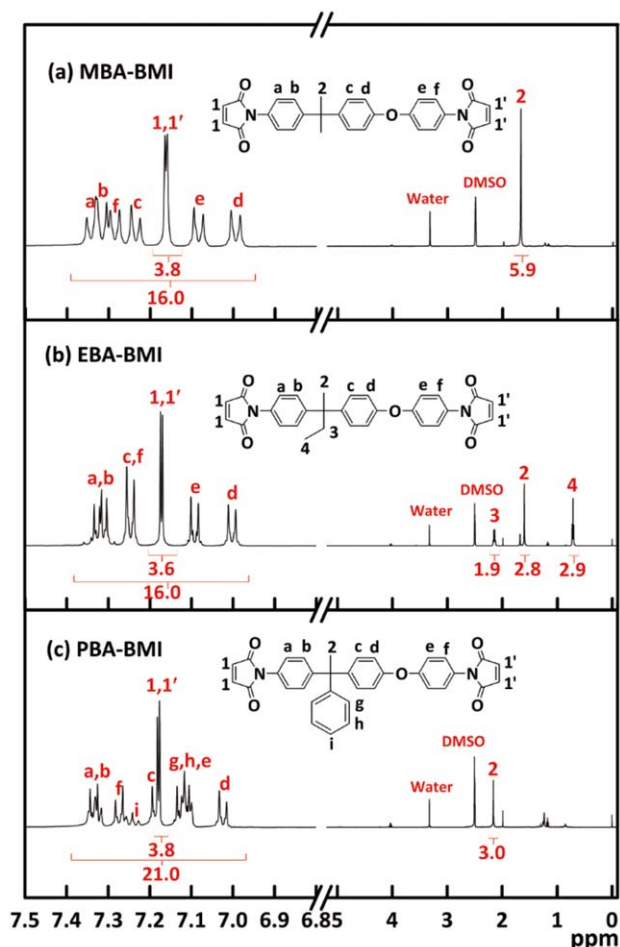


Figure 2. ^1H NMR of the bismaleimide monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

symmetric $\text{C}=\text{O}$ stretching vibration of cyclic maleimide ring. The moderate absorptions at 1396 and 1143 cm^{-1} are assigned to $\text{N}-\text{C}=\text{O}$ and $\text{C}-\text{N}-\text{C}$ stretching of the imide ring, respectively. The characteristic absorption of the maleimide $=\text{C}-\text{H}$ vibration is observed at 690 cm^{-1} .³⁴

^1H NMR of bismaleimide monomers are shown in Figure 2. For MBA-BMI, the olefinic protons of maleimide ring ($\text{CH}=\text{CH}$) occur at 7.164 and 7.159 ppm. The peaks from 7.50 to 6.50 ppm are assigned to the aromatic protons and the singlet at 1.67 ppm belongs to the methyl protons. The ^1H NMR spectra of EBA-BMI and PBA-BMI are similar to that of MBA-BMI as assigned in Figure 2(b,c). For EBA-BMI, the peaks at 7.18 and 7.17 ppm are assigned to the olefinic protons. The peaks at 2.14 ppm and 0.72 ppm are assigned to CH_2-CH_3 and CH_2-CH_3 , respectively. The singlet at 1.60 ppm belongs to the methyl protons of EBA-BMI. For PBA-BMI, the olefinic protons appear at 7.181 and 7.177 ppm. The aromatic protons occur in the range of 7.50 – 6.50 ppm and the singlet at 2.16 ppm is assigned to the methyl protons.

Solubility and Viscosity of Bismaleimide Monomers

The prepared asymmetric bismaleimides show good solubility in various solvents, such as acetone, tetrahydrofuran and 1,4-

Table II. Solubility of the Bismaleimide Monomers in Various Solvents

Solvents	MBA-BMI	EBA-BMI	PBA-BMI
Dichloromethane	+ ^a	+	+
Chloroform	+	+	+
Tetrahydrofuran	+	+	+
Ethyl acetate	+	+	+
1,4-Dioxane	+	+	+
Acetone	+	+	+
N,N-Dimethylformamide	+	+	+
Dimethylsulphoxide	+	+	+
N-Methyl-2-pyrrolidinone	+	+	+
Toluene	+/ Δ ^b	+/ Δ	+/ Δ
Ethanol	- ^c	-	-

^a "+" soluble ($\geq 30\text{ mg/mL}$).

^b "+/ Δ " soluble under heating at 50°C .

^c "-" insoluble.

dioxane. The data are summarized in Table II. MBA-BMI, EBA-BMI, and PBA-BMI can dissolve in common organic solvents with a concentration about 30 mg mL^{-1} , while the asymmetric bismaleimide containing 1,3,4-oxadiazole and DOPO group can dissolve in acetone with the concentration of 10 mg and 100 mg mL^{-1} , respectively.^{8,32} The good solubility is beneficial to the impregnation process and blending with other resins.

Figure 3 shows the DSC profiles of the bismaleimide monomers measured at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen. The endothermic melting peak of MBA-BMI appears at 188°C . The melting point of EBA-BMI is 166°C , lower than that of MBA-BMI. Compared to the methyl group, the ethyl pendant group is more helpful to increase the asymmetry and decrease the crystalline degree, which is beneficial to the low melting point of the monomer. PBA-BMI has the highest melting point at 206°C because of the rigid phenyl pendant group which can increase the steric hindrance and the rigidity of the molecular structure.

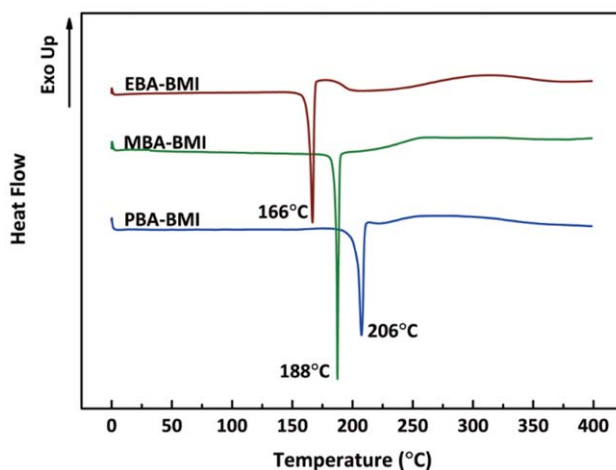


Figure 3. DSC thermograms of the bismaleimide monomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

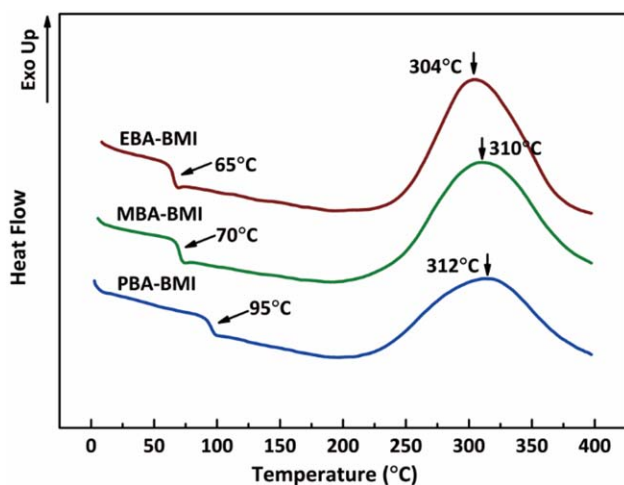


Figure 4. DSC profiles of the solidified bismaleimides after melt treated. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The broad curing exothermic peaks for EBA-BMI, MBA-BMI, and PBA-BMI are observed in Figure 3, which suggests curing of the bismaleimide monomer is moderate. Besides, the curing exothermal peaks of the bismaleimide monomers are observed at around 300 °C. Hence, high curing temperature and long curing time are necessary for the fully curing of the bismaleimide monomers.

Figure 4 shows the DSC curves of the solidified EBA-BMI, MBA-BMI and PBA-BMI after melt treated at 180, 200, and 215 °C for 5 min, respectively. The samples show different DSC behavior compared to that of the bismaleimide monomers in Figure 3. The melt-treated MBA-BMI, EBA-BMI, and PBA-BMI show glass transition stages at around 70, 65, and 95 °C, respectively and no obvious endothermic melting peaks are observed, which means a wide processing temperature window.

For investigating the processability of the asymmetric bismaleimide, EBA-BMI was melted at 180 °C and its viscosity–temperature relationship was carried out on a rheometer in the temperature range of 160–80 °C. As shown in Figure 5, EBA-BMI melt treated at 180 °C can keep a fluid state even at the temperature much lower than its melting point (166 °C). The viscosity of the molten EBA-BMI is increased from 190 to 4.92×10^6 mPa s as the temperature is reduced from 160 to 80 °C, which indicates a strong temperature dependency of the viscosity. In addition, the viscosity (190–934 mPa s) of EBA-BMI at 160–139 °C is lower than 1000 mPa s and meets the usage requirements of resin transfer molding process (RTM).

Curing Kinetics of the Melt Treated Bismaleimide Monomers

The curing kinetics of the melt treated EBA-BMI, MBA-BMI, and PBA-BMI were studied by non-isothermal DSC in combination with the Kissinger [eq. (1)] and Crane [eq. (2)] methods^{35,36}:

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \left(\frac{AR}{E_a} \right) - \frac{E_a}{RT_p} \quad (1)$$

$$\frac{d(\ln \beta)}{d \left(\frac{1}{T_p} \right)} = - \frac{E_a}{nR} \quad (2)$$

where β is the heating rate, T_p is the maximum temperature of the exothermic peak during the curing process, E_a is the apparent activation energy, A is the Arrhenius pre-exponential factor, and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

The key aspects of the non-isothermal DSC curves of the melt treated bismaleimide monomers with different heating rates of 5, 10, 15, and 20 °C min^{-1} , respectively, are summarized in Table III. With the increase of the heating rate, the maximum temperature of the exothermic peak (T_p) shifted to higher value for the thermal hysteresis.

The correspondence of $\ln \left(\frac{\beta}{T_p^2} \right)$ versus $1/T_p$ and $\ln \beta$ versus $1/T_p$ for melt treated bismaleimide monomers are presented in Figure 6 and the regression coefficients (R^2) are over 0.95. From the linear fitting to Kissinger equation, E_a and A are calculated, while n is obtained from the slope of the plot of $\ln \beta$ versus $1/T_p$ in combination with the Crane equation. The obtained E_a , A and n values are listed in Table III. The resulting activation energies for the melt treated EBA-BMI, MBA-BMI, and PBA-BMI are 104, 120, and 153 kJ mol^{-1} , respectively, which are compared well with the literature values.³⁷ The high E_a implies that the curing of the bismaleimide monomers needs more energy. The reaction orders (n) are 0.915, 0.925, and 0.940 for EBA-BMI, MBA-BMI, and PBA-BMI, respectively, which are equal to 1 approximately. It implies that the curing rate of the bismaleimide monomers mainly depends on the addition reaction of the imide double bond.

Thermal Performance of the Cured Bismaleimides

All the bismaleimide monomers were cured at 300 °C for 10 h and 350 °C for 3 h. The thermal behaviors of the bismaleimide polymers were examined by DSC. There are no obvious exothermic peaks on the DSC curves of the bismaleimide polymers up to 400 °C, which means the bismaleimide monomers are fully cured. This result is in agreement with the FTIR (Figure 7) of the cured bismaleimides. The characteristic absorption peaks of bismaleimide monomers at 690 cm^{-1} (=C-H vibration of maleimide) and 1143 cm^{-1} (C-N-C vibration of maleimide)

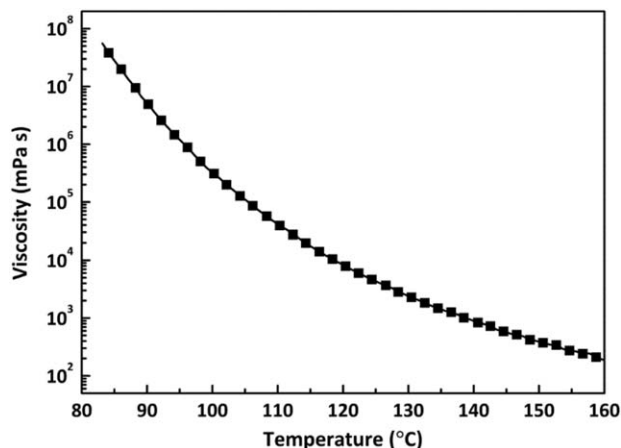


Figure 5. Viscosity of the molten EBA-BMI.

Table III. Nonisothermal DSC Data and Kinetic Parameters of the Melt Treated Bismaleimides

Sample	T_p (K)				E_a (KJ mol ⁻¹)	A	n
	5 °C min ⁻¹	10 °C min ⁻¹	15 °C min ⁻¹	20 °C min ⁻¹			
EBA-BMI	565	577	591	598	104	8.79×10^8	0.915
MBA-BMI	571	583	590	602	120	2.45×10^{10}	0.925
PBA-BMI	575	585	594	599	153	2.10×10^{13}	0.940

almost disappeared after EBA-BMI, MBA-BMI, and PBA-BMI were cured, which implies that the conversion of maleimide units to succinimide moieties is almost complete.⁷

The thermal stability of cured bismaleimides was evaluated by TGA (Figure 8). The initial decomposition temperature (5% weight loss temperature T_5) and char yield at 800 °C (Y_{800}) under nitrogen atmosphere are collected in Table IV.

The 5% weight loss temperatures (T_5) of cured bismaleimides are around 470 °C in nitrogen, which are similar to the T_5 of the other aryl ether-containing bismaleimides.³⁸ The high T_5 implies that the bismaleimide polymers have outstanding thermal stability and can serve at more harsh condition. According

to the work of Varma³⁹ and Fache,⁴⁰ the char formed on the surface of a burning polymer can serve as a heat shield to retard the further decomposition of the polymer. Thus, a high char yield is beneficial to the heat and flame resistance of polymer. All three cured bismaleimides show high char yield at 800 °C in nitrogen. The PBA-BMI has the highest char yield of 41.5%, and the char yield of the cured MBA-BMI and EBA-BMI are 39.8% and 39.2%, respectively. The possible reason is that PBA-BMI has one more phenyl group than MBA-BMI and EBA-BMI, and the aromatic groups are helpful for forming carbon residue.

The dynamic mechanical analysis (DMA) was used to characterize the glass transition temperature (T_g) and the storage modulus which are important parameters to evaluate the heat

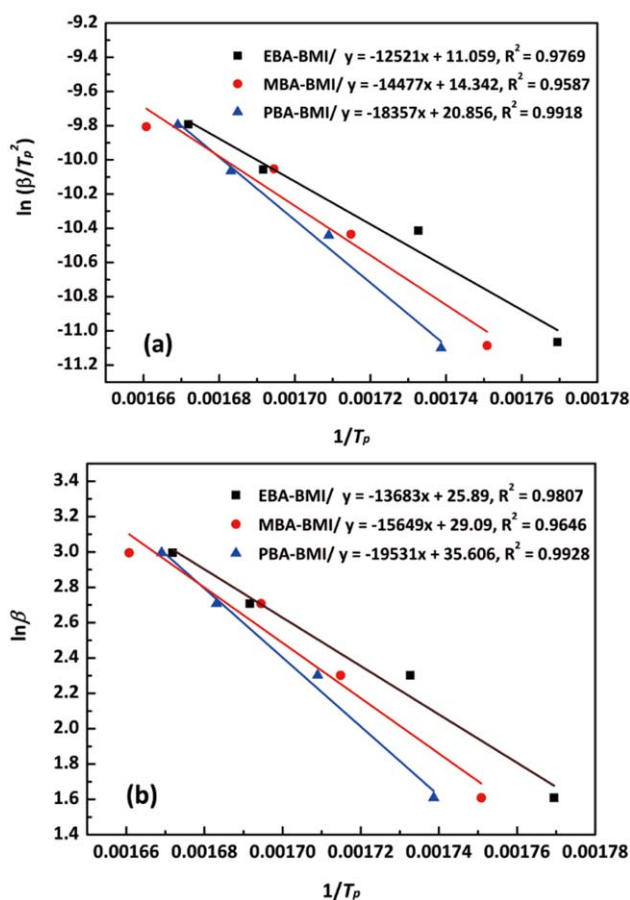


Figure 6. Kinetic plots of the melt treated bismaleimides: (a) Kissinger's equation; (b) Crane's equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

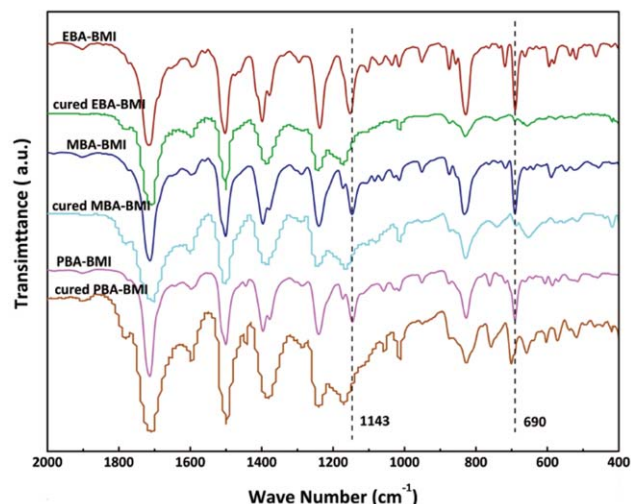


Figure 7. FTIR of the bismaleimides before and after curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Thermal and Mechanical Properties of the Cured Bismaleimides

Sample	Storage moduli (GPa)			T_5 (°C)	Y_{800} (%)
	30 °C	200 °C	400 °C		
EBA-BMI	3.3	2.5	2.0	468	39.2
MBA-BMI	3.5	2.8	2.2	471	39.8
PBA-BMI	3.6	2.6	2.0	466	41.5

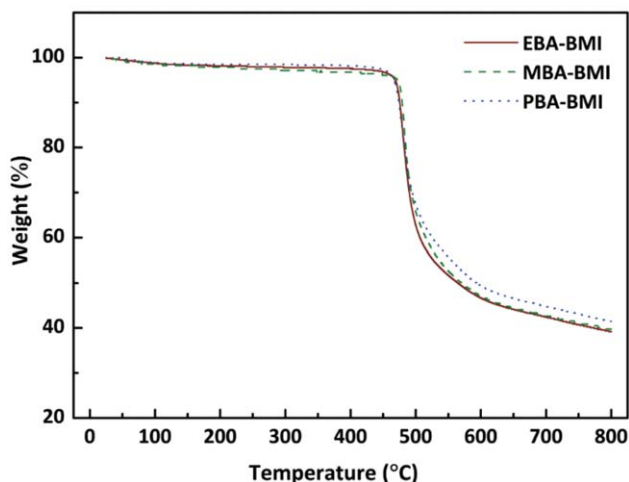


Figure 8. TGA of the cured bismaleimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resistance and the stiffness of the materials. The temperature-dependent storage modulus, loss modulus, and $\tan \delta$ of cured EBA-BMI, MBA-BMI, and PBA-BMI are shown in Figure 9. The characteristic data are collected in Table IV.

The cured EBA-BMI, MBA-BMI, and PBA-BMI show high storage moduli of 3.3, 3.5, and 3.6 GPa at ambient temperature, respectively. Besides, they can maintain high storage moduli of about 2.5–2.8 GPa at 200 °C and 2.0–2.2 GPa even at 400 °C, which means the cured bismaleimides have excellent stiffness in a wide temperature range. The loss moduli and $\tan \delta$ curves show no obvious relaxation peak and maximum between 30 and 400 °C. Thus, it is believed that the glass transition temperatures of cured EBA-BMI, MBA-BMI, and PBA-BMI are over 400 °C, which are close to the T_g (409 °C) of N,N'-(4,4'-diphenylmethane)bismaleimide.³⁸ The high storage modulus and high glass transition temperature may be primarily attributed to the rigid structure of multiphenyl groups and high cross-linking density which can hinder the mobility of chain segments at high temperature.

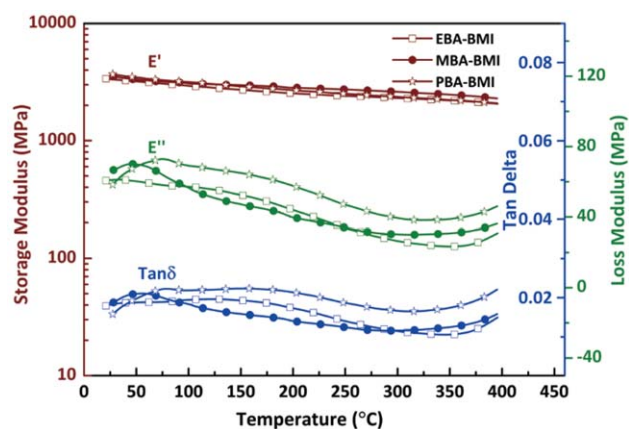


Figure 9. DMA curves of the cured bismaleimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

To improve the processability of bismaleimide without sacrificing the thermal properties, three novel bismaleimide molecules (MBA-BMI, EBA-BMI, and PBA-BMI) with unsymmetrical chemical structure and different pendant groups were designed and prepared. Results show that the unsymmetrical chemical structure is helpful in improving the solubility of the monomers in common organic solvents such as acetone. And the melt treated asymmetric bismaleimide monomers show wide processing temperature windows. Besides the good processability, the cured bismaleimides show outstanding thermal stability, high storage moduli, and high glass transition temperatures. The advantages of the good solubility, low molten viscosity, high temperature resistant, and outstanding thermal stability make the unsymmetrical bismaleimides promising candidates as matrix resins for the high-performance composites applied in the electronic and aerospace industries.

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