

## High glass transition temperature bismaleimide-triazine resins based on soluble amorphous bismaleimide monomer

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**ABSTRACT:** A novel bismaleimide (DOPO-BMI) with unsymmetrical chemical structure and DOPO pendant group has been prepared. The particular molecular structure makes DOPO-BMI show an intrinsic amorphous state with a  $T_g$  about 135°C and excellent solubility in most organic solvents, which is beneficial to the processability of bismaleimide composite materials. A series of bismaleimide-triazine (BT) resins have been prepared based on DOPO-BMI and 2,2-bis(4-cyanatophenyl)propane at various weight ratios. The prepared BT resins show outstanding solubility in organic solvent and low viscosity about 10–671 mPa s at 180°C. The cured BT resins exhibit high glass transition temperature ( $T_g$ ) over 316°C. As the weight ratio of DOPO-BMI increases to 80% (BT80), the  $T_g$  can rise to 369°C ( $\tan \delta$ ). The cured BT resins also show good thermal stability with the 5% weight loss temperature over 400°C under both nitrogen and air atmosphere. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42882.

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### INTRODUCTION

Bismaleimide/cyanate ester composite resins, known as bismaleimide-triazine (BT) resins,<sup>1</sup> have been extensively applied in high-density flip-chip substrates<sup>2–5</sup> because of their outstanding properties such as high glass transition temperature (190–290°C), low water absorption (0.2–2.5 wt %), good dimensional stability, and low dielectric constant (2.4–3.5).<sup>6,7</sup> However, the binary bismaleimide and cyanate ester composite resins show poor processability. The commonly used bismaleimides such as *N,N'*-(4,4'-diphenylmethane)bismaleimide can just dissolve in strong polar organic solvents such as dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidone (NMP). Besides, the common BT resins have narrow processing window due to the small temperature difference between the melting point and the initial curing temperature of bismaleimides.

Lots of works have been done to improve the processability of BT resins.<sup>8–10</sup> Expanding agent or co-cured materials such as 2,2'-diallylbisphenol A are frequently used to modify BT resins.<sup>11–13</sup> The allyl group could react with the double bond of bismaleimide by Ene/Diels–Alder reaction<sup>14,15</sup> and the phenolic hydroxyl group could promote the polymerization of the cyanate ester,<sup>16,17</sup> which make the prepolymer of BT resins dissolve in acetone or keep as viscous fluids at room temperature. However, this approach may decrease the  $T_g$  of the cured BT resins

because the allylic compounds usually form soft groups which are unstable to heat. The modified BT resins usually show low  $T_g < 300^\circ\text{C}$ .

Another strategy is to prepare novel bismaleimide monomers with good processability and excellent thermal properties. Based on the structure–property relationship, the unsymmetrical molecular structure and bulky pendant group are helpful for improving the solubility of the molecules.<sup>18–21</sup> Chen *et al.* reported a series of bismaleimides with a bulky phthalide group or unsymmetrical structure, which are soluble in organic solvents such as acetone, dichloromethane, and tetrahydrofuran.<sup>22,23</sup>

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) has usually been used to improve the thermal performance and flame retardancy of materials.<sup>24,25</sup> In this article, DOPO as the bulky pendant group was introduced into bismaleimide with unsymmetrical structure to improve the processability of bismaleimide monomer and bismaleimide composite. The prepared bismaleimide monomer DOPO-BMI shows an intrinsic amorphous state with a  $T_g$  about 135°C and could dissolve in most low boiling point solvents such as acetone. A series of binary BT resins are prepared based on DOPO-BMI and 2,2-bis(4-cyanatophenyl)propane by the melting blending method. The prepared BT resins show outstanding solubility in the solvents for prepreg and low viscosity about 10–1000 mPa s at 180°C,

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while the cured BT resins show high glass transition temperature over 316°C, and good thermal stability both under nitrogen and air atmosphere.

## EXPERIMENTAL

### Materials

2,2-Bis(4-cyanatophenyl)propane (known as bisphenol A dicyanate ester, BADCy) was purchased from Shanghai Huifeng Trade Co., Ltd. The unsymmetrical diamine (DOPO-NH<sub>2</sub>) was prepared according to the method reported.<sup>26</sup> Maleic anhydride, *p*-toluenesulfonic acid (*p*-TSA), and other organic solvents were used as received without further purification.

### Synthesis of 1-(4'-Maleimido)phenyl-1-[4'-(4''-maleimido)phenoxy]phenyl-1-[(9,10-dihydro-9-oxa-10-phosphaphenanthrene)-10-yl]ethane (DOPO-BMI)

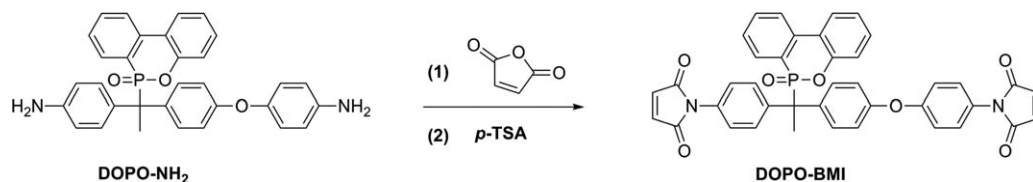
DOPO-NH<sub>2</sub> (5.18 g, 0.01 mol), maleic anhydride (1.96 g, 0.02 mol) and mixed solvent (toluene/DMF = 2.0/1.0, 100.0 mL) were added into a 250.0-mL round-bottomed flask equipped with a Dean-Stark apparatus. The mixture was stirred at room temperature for 3.0 h under nitrogen atmosphere. Then *p*-TSA (0.38 g, 2.0 mmol) was added and the solution was refluxed for 8.0 h. The mixture was cooled to room temperature and poured into ice water with fierce stirring to obtain light yellow powder. After purification with column chromatography (ethyl acetate/petroleum ether = 1.0/1.0), 6.1 g target product was obtained in 90.0% yield. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, δ): 8.20–6.80 (m, 20H, Ar H), 7.20 (s, 2H; CH=CH (b or b')), 7.19 (s, 2H; CH=CH (b' or b)), 1.76 and 1.72 (d, 3H; C-CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ): 170.49 and 170.33 (C=O), 135.21 and 135.18 (CH=CH), 110–160 (aromatic), 54.05 and 53.33 (C-CH<sub>3</sub>), 24.63 (C-CH<sub>3</sub>); <sup>31</sup>P-NMR (202 MHz, DMSO-*d*<sub>6</sub>, δ): 35.69 (O-P=O); IR (KBr): ν = 1714 (s; ν<sub>s</sub>(C=O)), 1780 (w; ν<sub>as</sub>(C=O)), 1396 (m; ν<sub>s</sub>(N-C=O)), 1143 (m; ν<sub>s</sub>(C-N-C)), 690 cm<sup>-1</sup> (m; ν<sub>s</sub>(C-H)).

### Preparation of DOPO-BMI/BADCy Composite Resins

BT20 was prepared via mixing DOPO-BMI and BADCy in 20 : 80 by weight. The mixture was stirred fiercely at 140°C for about 40 min to obtain a homogeneous brown resin. After degassed under vacuum at 180°C for 1 h, the sample was cured at 230°C for 2 h, 260°C for 2 h, 280°C for 2 h, and 300°C for 8 h in an oven. BT40, BT60, and BT80 samples were prepared by the same method with DOPO-BMI weight ratio at 40%, 60%, and 80%, respectively.

### Characterizations

Fourier-transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 6700 spectrometer by KBr pellet method. In all cases, 32 scans at a resolution of 4 cm<sup>-1</sup> were used to record the spectra ranging from 400 to 4000 cm<sup>-1</sup>. Nuclear magnetic resonances were performed on a Bruker DMX500 with dimethyl sulfoxide-*d*<sub>6</sub> (DMSO-*d*<sub>6</sub>) as solvent.



Scheme 1. Synthetic route of DOPO-BMI.

Table I. Solubility of DOPO-BMI and DOPO-BMI-Based BT Resins in Various Solvents

Solvents	DOPO-				
	BMI	BT20	BT40	BT60	BT80
Dichloromethane	O <sup>a</sup>	O	O	O	O
Tetrahydrofuran	O	O	O	O	O
Ethyl acetate	O	O	O	O	O
Chloroform	O	O	O	O	O
1,4-Dioxane	O	O	O	O	O
Acetone	O	O	O	O	O
<i>N,N</i> -Dimethylformamide	O	O	O	O	O
Dimethylsulphoxide	O	O	O	O	O
<i>N</i> -Methyl-2-pyrrolidinone	O	O	O	O	O
Toluene	Δ <sup>b</sup>	Δ	Δ	Δ	Δ
Ethanol	X <sup>c</sup>	X	X	X	X

<sup>a</sup>“O” soluble (≥100 mg mL<sup>-1</sup>).

<sup>b</sup>“Δ” soluble under heating at 50°C.

<sup>c</sup>“X” insoluble.

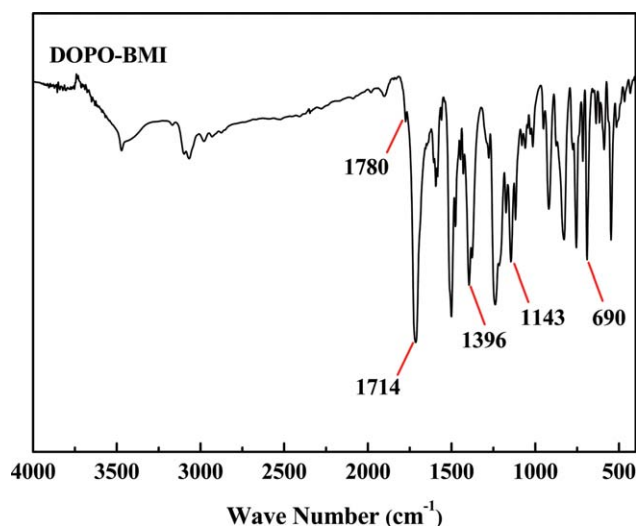
The solubility of DOPO-BMI monomer and DOPO-BMI-based BT resins were tested as follows. The sample (100 mg) was mixed with a solvent (1 mL) by shaking for 1 min. The solvent is considered soluble if the mixture is transparent, marked as “Δ” or “O” in Table I. Otherwise, the solvent is considered insoluble, marked as “X” in Table I. The viscosity of prepared BT resins were carried out on a Thermofisher HAAKE MARS III rotary rheometer with a shear rate at 5 s<sup>-1</sup> and a heating rate at 5°C min<sup>-1</sup> in the temperature range of 130–180°C.

Differential scanning calorimetry (DSC) was performed on a TA Q200 calorimeter under a nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>. X-ray diffraction (XRD) was carried out on a Rigaku-D/max-rB advanced X-ray diffractometer. Dynamic mechanical analysis (DMA) was carried out on a TA Q800 analyzer in three-point bending method at a heating rate of 3°C min<sup>-1</sup> with a frequency of 1 Hz. Thermal gravimetric analysis (TGA) was recorded with a Shimadzu DTG60 simultaneous DTA-TG apparatus at a heating rate of 10°C min<sup>-1</sup> under air and nitrogen atmosphere, respectively. Flexural properties of samples were measured at ambient temperature with a three-point bending mode using an MTS CMT6104.

## RESULTS AND DISCUSSION

### Preparation of DOPO-BMI Monomer

For better solubility and higher glass transition temperature, DOPO as the bulky pendant group was introduced into the bis-maleimide monomer with unsymmetrical chemical structure.



**Figure 1.** FTIR of DOPO-BMI. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

DOPO-NH<sub>2</sub> and maleic anhydride were first reacted at room temperature to produce a maleamic acid intermediate. Next, *p*-TSA was used to initiate the cyclodehydration of the maleamic acid to form the imide ring of bismaleimide (Scheme 1).

The chemical structure of DOPO-BMI was confirmed by a combination of FTIR and NMR. In the FTIR spectrum of DOPO-BMI (Figure 1), the characteristic absorption of the maleimide =C—H vibration occurs at 690 cm<sup>-1</sup>. The strong absorption at 1714 cm<sup>-1</sup> and the weak absorption at 1780 cm<sup>-1</sup> belong to the typical symmetric and asymmetric stretching vibration of C=O in the cyclic maleimide ring. The absorption at 1396 cm<sup>-1</sup> and 1143 cm<sup>-1</sup> is assigned to N—C=O and C—N—C stretching of the imide ring, respectively.<sup>27</sup>

The NMR spectra of DOPO-BMI are shown in Figure 2. The chemical shifts of the aromatic protons range from 6.50 to 8.50 ppm. The singlets at 7.20 and 7.19 ppm belong to protons of the different maleimide ring. The peaks at 1.76 and 1.72 ppm are assigned to protons of the methyl. The peaks at 170.49 and 170.33 ppm are assigned to C=O, and the peaks at 135.21 and 135.18 ppm are assigned to CH=CH of imide ring. The other 24 peaks in the range of 110–160 ppm belong to the aromatic carbons. The attribution for these carbons was supplied in the Supporting information (Figure S1). The chemical shifts of C—CH<sub>3</sub> appear at 54.05 and 53.33 ppm. The peak at 24.63 ppm is assigned to C—CH<sub>3</sub>. It is worth pointing out that the methyl proton and the quaternary carbon of C—CH<sub>3</sub> show unusual double peaks, which were also reported by Lin.<sup>26</sup> There is only one single peak at 35.69 ppm in <sup>31</sup>P NMR, in accord with the phosphorus structure in DOPO-BMI. All the results are in good agreement with the proposed structure of DOPO-BMI as shown in Scheme 1.

#### Solubility and Morphology of DOPO-BMI Monomer

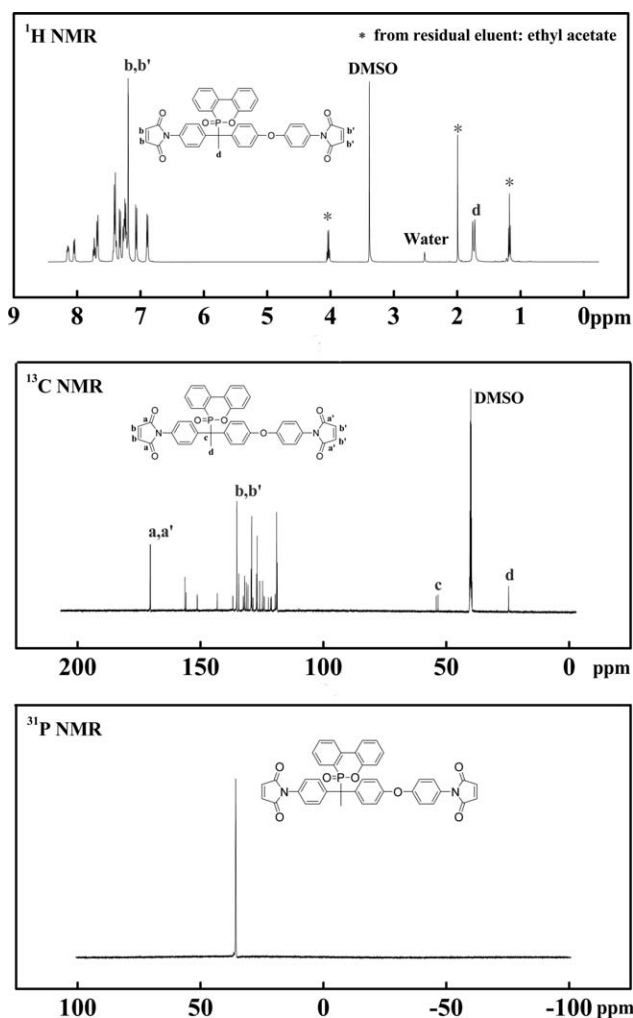
The good solubility of the resins in low-boiling-point solvent is necessary for the molding process of composite materials. For example, in the lamination process and filament winding process, the resins should be dissolved in a suitable solvent for the subse-

quent impregnation of the reinforced materials. In this work, the unsymmetrical structure and the DOPO pendant group reduce the molecular symmetry of DOPO-BMI, thus reduce the crystallinity and improve the solubility of bismaleimide monomer in the low-boiling-point solvents, such as acetone, ethyl acetate, and tetrahydrofuran. For example, DOPO-BMI can easily dissolve in acetone in high concentrations (>100 mg mL<sup>-1</sup>). The solubility results are summarized in Table I.

DOPO-BMI shows a glass transition at about 135°C in the DSC curve (Figure 3) without obviously melting exothermic peak. This phenomenon was usually found in some amorphous molecular materials that readily form stable amorphous glasses above room temperature.<sup>28</sup> The amorphous state of DOPO-BMI monomer is also confirmed by the XRD pattern that shows only one wide weak diffraction (Supporting Information, Figure S2).

#### Processability and Cure Behavior of DOPO-BMI-Based BT Resins

DOPO-BMI monomer was blended with 2,2-bis(4-cyanatophenyl)propane (BADCy) at 140°C, with the aiming at preparing high-*T*<sub>g</sub> BT resins with well processability. In addition to the



**Figure 2.** NMR spectra of DOPO-BMI.

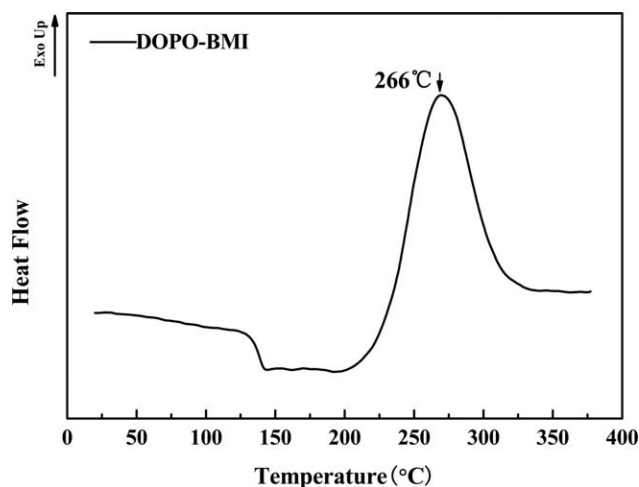


Figure 3. DSC curve of DOPO-BMI.

outstanding solubility in most organic solvents (as shown in Table I), the prepared BT resins show low molten viscosity (Figure 4). The viscosity of BT resins increased as the content of DOPO-BMI increased. BT20 and BT 40 exhibited low viscosity  $<63$  mPa s at 130–180°C. The molten viscosity of BT60 and BT80 at 180°C was 61 and 671 mPa s, respectively. The BT resins also showed the normal viscosity temperature dependence.

DSC curves of DOPO-BMI-based BT resins are shown in Figure 5. The curing of BT resins begins around 200°C and ends at about 330°C. Only one exothermic peak for the cure of BT resin is observed, which suggests the overlap of the curing exothermic peaks of DOPO-BMI and BADCy or the co-curing of DOPO-BMI and BADCy.

For better understanding the cure behavior of BT resins based on DOPO-BMI and BADCy, the cure procedures of the representative BT60 were tracked with FTIR as shown in Figure 6. After BT60 was kept at 140°C for 2 h, the absorptions at 2270 and 2237  $\text{cm}^{-1}$  assigned to the cyanate group of BADCy<sup>29</sup> were

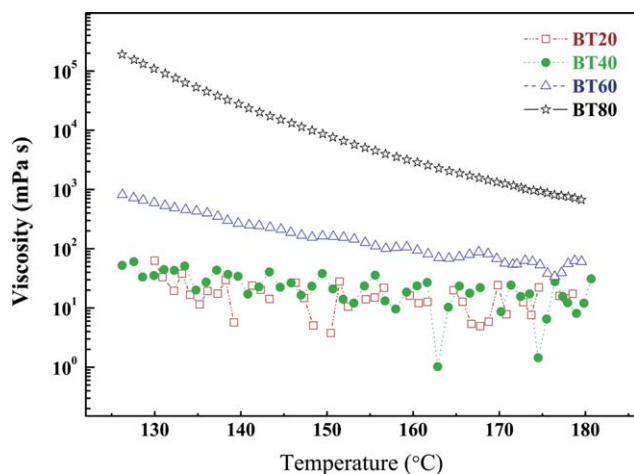


Figure 4. Viscosity of BT resins in the range of 130–180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

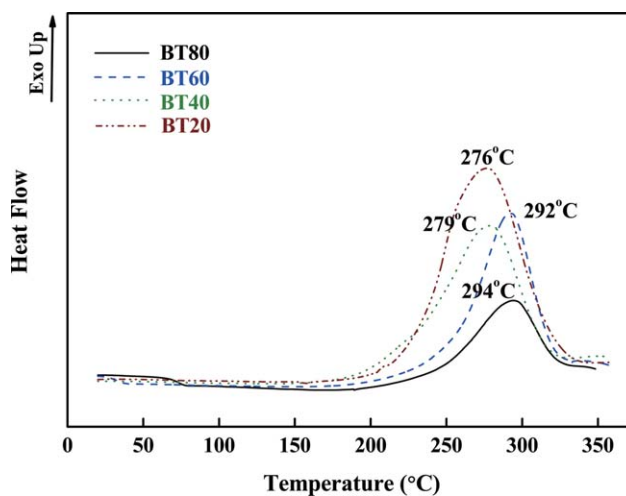


Figure 5. Curing profiles of BT resins with different weight ratio of DOPO-BMI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

not weakened, which meant that little curing reaction occurred at this stage. The two absorptions weakened as the temperature raised and finally disappeared after BT60 was cured at 260°C for 2 h, while the absorption at 1560  $\text{cm}^{-1}$  assigned to the absorption of triazine appeared and strengthened.<sup>30</sup> It suggested that BADCy self-polymerized and gave a triazine structure (I). Absorption at 690  $\text{cm}^{-1}$  belonged to carbon–carbon double bond of maleimide<sup>31</sup> weakened as the cure temperature rose, which implied that the homopolymerization of DOPO-BMI (II) or the co-curing of DOPO-BMI and BADCy occurred at high temperatures. According to the research of Lin<sup>30</sup>, the characteristic absorption at 1365  $\text{cm}^{-1}$  may be presumably attributed to the pyrimidine structures (III) and the pyridine structures (IV) which are formed via the co-reaction of bismaleimide and cyanate resin. As shown in Figure 6, the absorption at 1365  $\text{cm}^{-1}$  appeared and strengthened as the curing temperature raised, indicating that the co-curing reaction between DOPO-BMI and

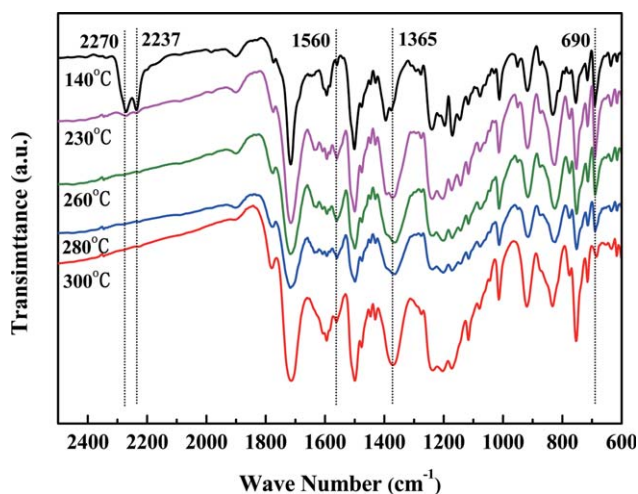
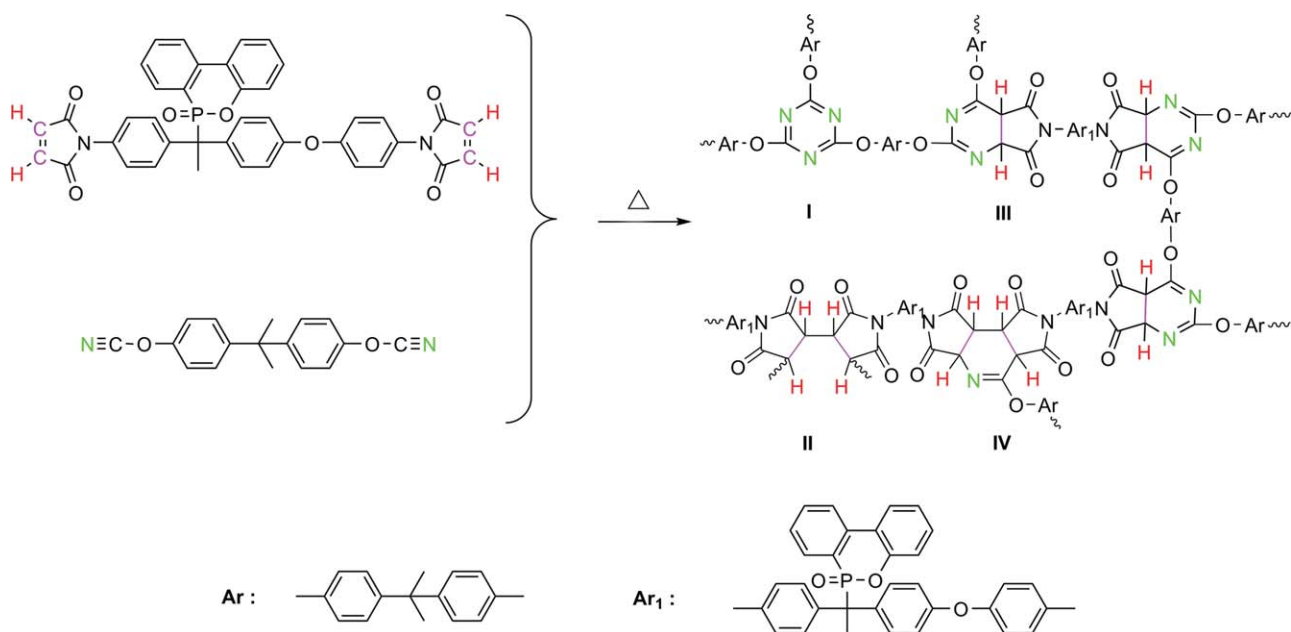


Figure 6. FTIR spectra of BT60 at different cure stages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





**Scheme 2.** Possible co-reaction of DOPO-BMI and BADCy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

BADCy occurred at high temperature. Hence, three kinds of polymerization may exist: (i) self-polymerization of BADCy, (ii) homopolymerization of DOPO-BMI, (iii) co-curing between DOPO-BMI and BADCy, as shown in Scheme 2.<sup>30,32</sup>

### Mechanical Property of Cured BT Resins

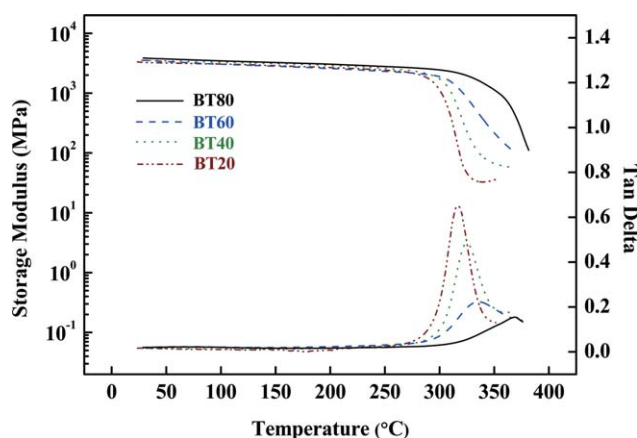
The glass transition temperature ( $T_g$ ) is an important parameter to evaluate the heat resistance of the polymer. The storage modulus could suggest the stiffness of the cured resins. And dynamic mechanical analysis (DMA) is the best way to carry out the two parameters. The maximal peak temperature of tan delta is identified as the  $T_g$ . The DMA curves of the cured BT resins are shown in Figure 7, and the detailed data are listed in Table II.

The storage moduli ( $E'$ ) of the cured BT resins are larger than 3.0 GPa at room temperature. The modulus increases to

3.8 GPa as the weight ratio of DOPO-BMI raises to 80%. The high storage modulus is primarily contributed by bismaleimide DOPO-BMI with lots of rigid groups, such as benzene and biphenyl, which can enhance the stiffness of the polymer.

According to the  $\tan \delta$  curves, all the cured BT resins show high glass transition temperature above 316°C as the result of the high cross-linking density and lots of the rigid groups, which can restrict the mobility of chain segments, reduce the free volume, and increase the glass transition temperature. The  $T_g$  increases with the content of DOPO-BMI increase and the BT80 has the maximum  $T_g$  about 369°C ( $\tan \delta$ ).

The flexural strength and flexural modulus were measured to evaluate the mechanical properties of the cured BT resins by three-point bending technique. The cured BT resins show high flexural modulus around 3.0–4.5 GPa and well flexural strength about 110–160 MPa. The detailed results are included in Table III.



**Figure 7.** DMA curves of the cured BT resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

### Thermal Stability of Cured BT Resins

The thermal stability of the polymer is usually evaluated by comparing the initial decomposition temperature (5% weight loss temperature) and char yield at 600°C ( $Y_{600}$ ) under nitrogen and air atmosphere, respectively. So the thermal stability of the cured BT resins was characterized by thermogravimetric analysis. TGA curves are shown in Figure 8 and the data are collected in Table II.

The 5% weight loss temperatures ( $T_5$ ) of the cured BT resins are all above 400°C in nitrogen [Figure 8(a)], which suggests that the cured BT resins have good thermal stability. The initial decomposition temperatures of the cured BT resins decrease slightly as the content of DOPO-BMI increases, which may be assigned to the weak carbon–phosphorous bond (the bond energy of carbon–phosphorous bond is only about 513.4 kJ mol<sup>-1</sup>) of DOPO-BMI. Qian also suggested that the phosphaphenanthrene group was

**Table II.** Thermal and Mechanical Properties of the Cured BT Resins

Sample	$E'$ (GPa) <sup>a</sup>	$T_g$ (°C) tan $\delta$	N <sub>2</sub>				Air			
			$T_5^b$ (°C)	$T_{10}^c$ (°C)	$Y_{600}^d$ (%)	$Y_{700}^e$ (%)	$T_5^b$ (°C)	$T_{10}^c$ (°C)	$Y_{600}^d$ (%)	$Y_{700}^e$ (%)
BT20	3.3 ± 0.1	316	416	421	47	44	415	420	30	1.8
BT40	3.5 ± 0.1	325	404	412	48	46	403	411	52	31
BT60	3.6 ± 0.2	335	400	408	53	51	400	408	57	45
BT80	3.8 ± 0.1	369	400	407	56	54	402	409	60	50

<sup>a</sup>Storage modulus at 30°C.<sup>b</sup>5% weight loss temperature.<sup>c</sup>10% weight loss temperature.<sup>d</sup>Char yield at 600°C.<sup>e</sup>Char yield at 700°C.

eliminated first at high temperature.<sup>34</sup> Besides, the cured BT resins show high char yield at 600°C in the range of 47–56% in nitrogen, which is primarily attributed to the large amount of the rigid structure such as benzene and biphenyl.

According to the curves in Figure 8(b), the 5% and 10% weight loss temperatures of the cured BT resins in air are approximate to that in nitrogen, which means that the cured BT resins also have outstanding thermal stability under air atmosphere.

The char yields of the cured BT resins at 600 and 700°C increase as the weight ratio of DOPO-BMI increases. The  $Y_{600}$  (52–60%) in air is a little higher than that (48–56%) in nitrogen when the weight ratio of DOPO-BMI is over 20%. This may be attributed to the fact that oxygen-rich atmosphere is beneficial for PO-free radicals and *o*-phenylphenoxy-free radicals turning into the phosphorus-rich residues<sup>34</sup> and a proportion of heat is absorbed during this process. Besides, the formed outer phosphorus-rich residues can inhibit the heat shift into the inner segments and

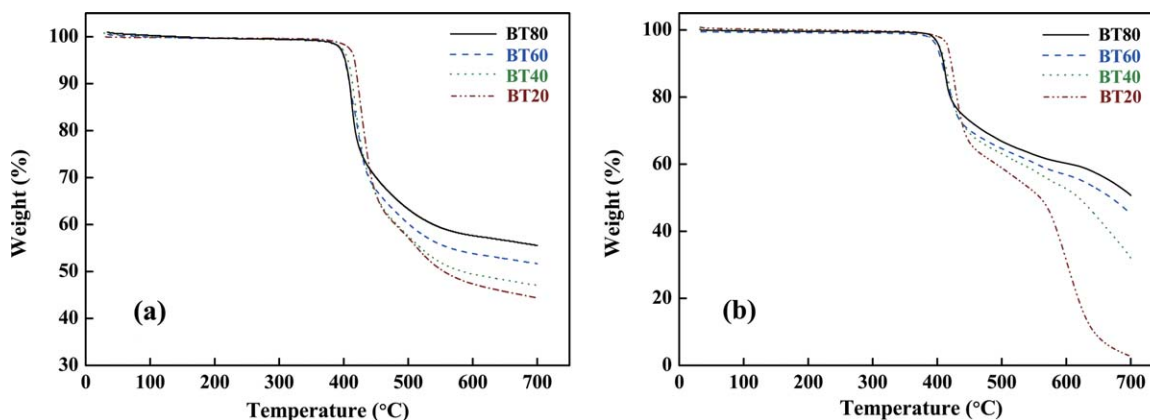
slow down the decomposition of the polymer. However, the oxygen is also good for the combustion of materials at high temperature. This is the possible reason for that the char yields at 700°C of the cured BT resins under air atmosphere (1.8–50%) are lower than that (44–54%) under nitrogen atmosphere.

## CONCLUSIONS

DOPO as the pendant group was introduced into bismaleimide (DOPO-BMI) with unsymmetrical chemical structure. DOPO-BMI monomer shows an intrinsic amorphous state with a glass transition at about 135°C. The amorphous DOPO-BMI monomer and the BT resins exhibit excellent solubility in the commonly used low boiling point solvents, such as acetone, ethyl acetate, and tetrahydrofuran. Besides, the BT resins show low viscosity about 10–671 mPa s at 180°C. DMA shows that the cured BT resins have high stiffness with the storage modulus ranged from 3.3 to 3.8 GPa at room temperature and high glass transition temperature ranged from 316 to 369°C (tan  $\delta$ ). In addition, the cured BT resins show outstanding thermal stability with initial decomposition temperature above 400°C both under nitrogen and air atmosphere. The char yields at 600°C increased from 47% to 56% in nitrogen as the weight ratio of DOPO-BMI increased from 20% to 80%. The advantages of good solubility, low molten viscosity, high glass transition temperature,

**Table III.** Flexural Properties of Cured BT Resins

	BT20	BT40	BT60	BT80
Flexural modulus (GPa)	3.3	3.7	4.1	4.3
Flexural strength (MPa)	135	159	146	118



**Figure 8.** TGA curves of the cured BT resins: (a) nitrogen; (b) air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and excellent thermal stability make the DOPO-BMI-based BT resins a promising candidate for application in the microelectronic packaging and aerospace industry.

#### ACKNOWLEDGMENTS

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