

Synthesis of a Novel Series of Propargyloxyphenyl Maleimides and Their Characterization as Thermal-Resistance Resins

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Received 11 September 2008; accepted 25 July 2009

DOI 10.1002/app.31174

Published online 2 November 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Novel thermosetting monomers possessing both maleimide and propargyl groups were first designed and synthesized. The monomers included *N*-(2-propargyloxyphenyl) maleimide (2-PPM), *N*-(3-propargyloxyphenyl) maleimide (3-PPM), and *N*-(4-propargyloxyphenyl) maleimide (4-PPM), and their structures were confirmed with Fourier transform infrared (FTIR) spectroscopy, ¹H-NMR, and elemental analysis. The cure behaviors of these monomers were characterized with differential scanning calorimetry and FTIR spectroscopy, and the results indicated that the monomers had a broader processing window than normal bismaleimide (BMI) resins. The

thermal properties of the cured monomers were characterized with thermogravimetric analysis and dynamic mechanical analysis. The 5% mass loss temperatures of the cured monomers were high (ca. 400°C), and the glass-transition temperatures of cured 2-PPM, 3-PPM, and 4-PPM were 386, 373, and 387°C, respectively, which were much higher than those of typical commercial blended BMI resins. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3103–3109, 2010

Key words: addition polymerization; monomers; thermal properties

INTRODUCTION

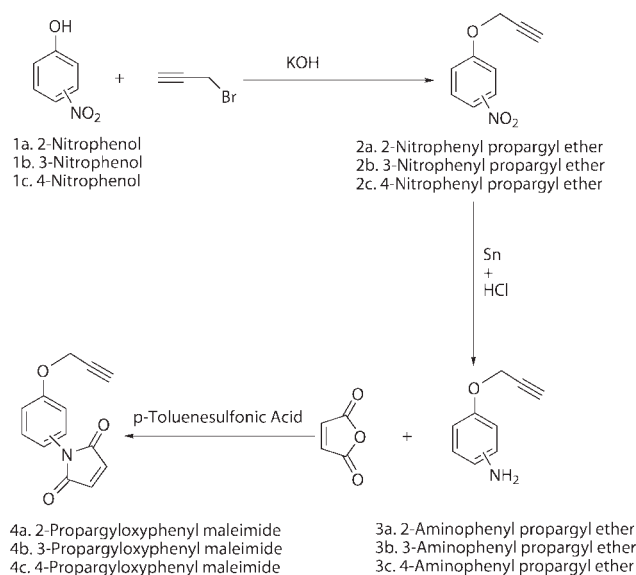
Thermosetting bismaleimide (BMI) resins are used as matrices for advanced composites in aerospace and electronics industries. They possess excellent thermal and oxidative stability, flame-retardation properties, and a low propensity for moisture absorption. However, BMI resins are brittle as a result of the aromatic nature and high crosslink density of the network.¹

To overcome the brittleness, many toughened resins have been blended with BMI resins, such as cyanate ester, aromatic diamines, and polysiloxanes.^{2–4} In particular, when allyl derivatives of phenols are blended with BMI resins, the brittleness of BMI resins is substantially reduced, and their high heat resistance is still retained. In the literature, series of allylic derivatives of phenols have been used to toughen BMI resins, such as 2,2'-diallyl bisphenol A, 2,2'-diallyl bisphenol F, and allyl phenolic resin,^{5–9} and this has led to the commercialization of new resin systems based on BMI chemistry. XU292, a blend resin of 2,2'-diallyl bisphenol A with 4,4'-bismaleimido diphenyl methane, was developed by Ciba-Geigy Co. and

has better toughness and higher heat resistance.¹⁰ Recently, propargyl derivatives of phenols have been developed as high-performance resins, and they possess good thermal stability and moisture resistance.^{11,12} Bispropargyl ether bisphenol A has been investigated in blends with BMI resins by our group, and a highly thermally stable resin system has been obtained; this indicates that propargyl ether phenol is also a good modifier like allyl ether phenols for toughening BMI resins.¹³

However, some adverse properties of blended BMI resins should be noted. First, most BMI resins are crystalline solids with a melting point close to the initial curing temperature of the blended resins. Partial curing often occurs during the preparation of a hot melt resin system, and this makes it difficult to control the viscosity of the final resin. Second, most BMI resins exhibit poor solubility in common solvents and other resins, and this restricts the content of BMI resins in blended systems. The shelf life of blended resins is also limited because BMI tends to recrystallize from blended systems. In addition, blends often show inconsistent properties from batch to batch because of their preparation from BMI and other modifier resins by a hot melt-blending reaction. Novel resins with well-defined structures, possessing both maleimide and other reactive groups such as allyl or propargyl groups in one molecular unit, are expected to overcome the aforementioned disadvantages.

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Scheme 1 Synthesis of the novel monomers 2-PPM, 3-PPM, and 4-PPM.

In this study, a novel kind of thermosetting monomer bearing both maleimide and propargyl groups was synthesized. The monomers included *N*-(2-propargyloxyphenyl) maleimide (2-PPM), *N*-(3-propargyloxyphenyl) maleimide (3-PPM), and *N*-(4-propargyloxyphenyl) maleimide (4-PPM), which have not been reported in the literature until now; the synthetic routes are shown in Scheme 1. Furthermore, their cure behavior and thermal properties were also studied in detail.

EXPERIMENTAL

Materials and instruments

2-Nitrophenol, 3-nitrophenol, and 4-nitrophenol (analytical reagent; Beijing Chemical Regent Corp., Beijing, China), maleic anhydride (analytical reagent; Beijing Chemical Regent), potassium hydroxide (analytical reagent; Beijing Chemical Regent), stannum powder (chemically pure; Hubei Tianmen Regent Corp., China), and *p*-toluenesulfonic acid (analytical reagent; Beijing Yili Chemical Regent Corp., Beijing, China) were used as received. Propargyl bromide (chemically pure; Yang Nong Chemical Corp., China) was distilled before use. Other reagents were used without further purification.

Fourier transform infrared (FTIR) spectra were obtained with a Bruker Tensor 27 (Germany). $^1\text{H-NMR}$ spectra were recorded on a Bruker DMX-300 (300 MHz) with hexadeuterated dimethyl sulfoxide as the solvent. The cure characteristics of the resins were studied by differential scanning calorimetry (DSC) with a Mettler Thermal Analysis DSC-822e (Switzerland) at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Thermogravimetric analysis

(TGA) was performed with a Netzsch STA 409PC (Germany) at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Dynamic mechanical analysis (DMA) was carried out on a Netzsch DMA242 under a nitrogen atmosphere at a heating rate of $3^\circ\text{C}/\text{min}$, and the test frequency was 1 Hz.

Preparation of nitrophenyl propargyl ether (2a, 2b, and 2c in Scheme 1)

2-Nitrophenyl propargyl ether, 3-nitrophenyl propargyl ether, and 4-nitrophenyl propargyl ether were prepared with the same method; the synthesis of 2-nitrophenyl propargyl ether is presented as an example. In a 250-mL flask, 13.9 g (0.1 mol) of 2-nitrophenol and 5.6 g (0.1 mol) of potassium hydroxide were dissolved in 100 mL of ethanol, and then 14.28 g of propargyl bromide (0.12 mol) was added dropwise under agitation at room temperature. The reaction mixture was refluxed for 4 h. The solution was filtered to remove KBr, and then the solvent was evaporated by vacuum distillation to yield a white powder. The crude product was purified by recrystallization in ethanol to obtain white acicular crystals. The products were characterized with $^1\text{H-NMR}$ and FTIR spectroscopy.

2-Nitrophenyl propargyl ether

$^1\text{H-NMR}$ [*d*-hexadeuterated dimethyl sulfoxide (*d*-DMSO, δ): 7.90–7.18 (m, 4H, aromatics), 5.02 (s, 2H, $-\text{CH}_2-$), 3.69 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3255 (v, $\equiv\text{C}-\text{H}$), 2129 (v, C \equiv C), 1606, 1500, 1448 (v, aromatic), 1516, 1350 (v, $-\text{NO}_2$), 1248 (v, Ar–O–C), 750 (δ , $=\text{C}-\text{H}$ of *o*-phenyl).

3-Nitrophenyl propargyl ether

$^1\text{H-NMR}$ (*d*-DMSO, δ): 7.87–7.23 (m, 4H, aromatics), 4.98 (s, 2H, $-\text{CH}_2-$), 3.65 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3285 (v, $\equiv\text{C}-\text{H}$), 2128 (v, C \equiv C), 1582, 1498, 1451 (v, aromatic), 1524, 1351 (v, $-\text{NO}_2$), 1246 (v, Ar–O–C), 814 (δ , $=\text{C}-\text{H}$ of *m*-phenyl).

4-Nitrophenyl propargyl ether

$^1\text{H-NMR}$ (*d*-DMSO, δ): 8.27, 7.24 (d, 4H, aromatics), 5.03 (s, 2H, $-\text{CH}_2-$), 3.72 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3260 (v, $\equiv\text{C}-\text{H}$), 2126 (v, C \equiv C), 1590, 1498, 1452 (v, aromatic), 1512, 1333 (v, $-\text{NO}_2$), 1251 (v, Ar–O–C), 847 (δ , $=\text{C}-\text{H}$ of *p*-phenyl).

Preparation of aminophenyl propargyl ether (3a, 3b, and 3c in Scheme 1)

2-Aminophenyl propargyl ether, 3-aminophenyl propargyl ether, and 4-aminophenyl propargyl ether were synthesized by the reduction of corresponding

nitrophenyl propargyl ether. The preparation of 2-aminophenyl propargyl ether is presented as an example. 2-Nitrophenyl propargyl ether (17.7 g, 0.1 mol) and 23.7 g (0.2 mol) of stannum powder were placed in a 250-mL flask. After 50 mL of concentrated hydrochloric acid was added dropwise, the mixture was refluxed for 1 h. The solution was neutralized with aqueous sodium hydroxide and extracted with dichloromethane three times. The dichloromethane was removed under reduced pressure, and the residue was distilled to yield a colorless, oily liquid. The boiling point at the pressure of 40 mmHg of 2-aminophenyl propargyl ether, 3-aminophenyl propargyl ether, and 4-aminophenyl propargyl ether was 82, 90, and 126°C, respectively. The products were characterized with ¹H-NMR and FTIR spectra.

2-Aminophenyl propargyl ether

¹H-NMR (*d*-DMSO, δ): 6.95–6.52 (m, 4H, aromatics), 4.75 (s, 2H, $-\text{CH}_2-$), 4.69 (s, 2H, $-\text{NH}_2$), 3.69 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3458, 3372 (v, $-\text{NH}_2$), 3288 (v, $\equiv\text{C}-\text{H}$), 2122 (v, $\text{C}\equiv\text{C}$), 1616, 1503, 1458 (v, aromatic), 1278 (v, $\text{Ar}-\text{O}-\text{C}$), 744 (δ , $=\text{C}-\text{H}$ of *o*-phenyl).

3-Aminophenyl propargyl ether

¹H-NMR (*d*-DMSO, δ): 6.93–6.19 (m, 4H, aromatics), 5.06 (s, 2H, $-\text{CH}_2-$), 4.65 (s, 2H, $-\text{NH}_2$), 3.51 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3446, 3371 (v, $-\text{NH}_2$), 3283 (v, $\equiv\text{C}-\text{H}$), 2121 (v, $\text{C}\equiv\text{C}$), 1602, 1495, 1452 (v, aromatic), 1289 (v, $\text{Ar}-\text{O}-\text{C}$), 765 (δ , $=\text{C}-\text{H}$ of *m*-phenyl).

4-Aminophenyl propargyl ether

¹H-NMR (*d*-DMSO, δ): 6.95, 6.53 (d, 4H, aromatics), 4.76 (s, 2H, $-\text{CH}_2-$), 4.61 (s, 2H, $-\text{NH}_2$), 3.53 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3434, 3360 (v, $-\text{NH}_2$), 3287 (v, $\equiv\text{C}-\text{H}$), 2119 (v, $\text{C}\equiv\text{C}$), 1625, 1509, 1453 (v, aromatic), 1264 (v, $\text{Ar}-\text{O}-\text{C}$), 744 (δ , $=\text{C}-\text{H}$ of *o*-phenyl).

Preparation of the propargyloxyphenyl maleimide monomers (4a, 4b, and 4c in Scheme 1)

2-PPM, 3-PPM, and 4-PPM were synthesized by the reaction of the corresponding aminophenyl propargyl ether with maleic anhydride in a mixed solution of dimethylformamide and toluene. The synthesis of 2-PPM is described as an example. 2-Aminophenyl propargyl ether (14.7 g, 0.1 mol) was dissolved in 80 mL of toluene and 20 mL of dimethylformamide, and the solution was placed in a 250-mL flask. The solution was stirred, and 11.8 g (0.12 mol) of maleic

anhydride was added; the mixture was reacted at room temperature for 2 h. After 1.9 g (0.01 mol) of *p*-toluenesulfonic acid was added, the solution was refluxed for 4 h. The mixture was poured into 500 mL of ice water, and a yellow precipitate was obtained. After filtration, the precipitate was recrystallized in ethanol to get yellow crystals; the yield was about 90%. The products were characterized with ¹H-NMR, FTIR spectroscopy, and elemental analysis.

2-PPM

¹H-NMR (*d*-DMSO, δ): 7.44–7.06 (m, aromatics), 7.17 (s, 2H, maleimide), 4.77 (s, 2H, $-\text{CH}_2-$), 3.54 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3250 (v, $\equiv\text{C}-\text{H}$), 2119 (v, $\text{C}\equiv\text{C}$), 1598, 1506, 1461 (v, aromatic), 1248 (v, $\text{Ar}-\text{O}-\text{C}$), 1160 (v, $\text{C}-\text{N}-\text{C}$ of maleimide), 754 (δ , $=\text{C}-\text{H}$ of *o*-phenyl), 692 (δ , $=\text{C}-\text{H}$ of maleimide). ANAL. Calcd: C, 68.72%; H, 3.96%; N, 6.17%. Found: C, 68.76%; H, 3.98%; N, 6.19%.

3-PPM

¹H-NMR (*d*-DMSO, δ): 7.44–76.96 (m, aromatics), 7.18 (s, 2H, maleimide), 4.90 (s, 2H, $-\text{CH}_2-$), 3.60 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3277 (v, $\equiv\text{C}-\text{H}$), 2115 (v, $\text{C}\equiv\text{C}$), 1602, 1495, 1460 (v, aromatic), 1247 (v, $\text{Ar}-\text{O}-\text{C}$), 1157 (v, $\text{C}-\text{N}-\text{C}$ of maleimide), 775 (δ , $=\text{C}-\text{H}$ of *m*-phenyl), 698 (δ , $=\text{C}-\text{H}$ of maleimide). ANAL. Calcd: C, 68.72%; H, 3.96%; N, 6.17%. Found: C, 68.20%; H, 4.01%; N, 6.23%.

4-PPM

¹H-NMR (*d*-DMSO, δ): 7.30, 7.13 (d, aromatics), 7.02 (s, 2H, maleimide), 4.85 (s, 2H, $-\text{CH}_2-$), 3.60 (s, 1H, $\equiv\text{C}-\text{H}$). FTIR (KBr): 3266 (v, $\equiv\text{C}-\text{H}$), 2131 (v, $\text{C}\equiv\text{C}$), 1600, 1509, 1448 (v, aromatic), 1237 (v, $\text{Ar}-\text{O}-\text{C}$), 1155 (v, $\text{C}-\text{N}-\text{C}$ of maleimide), 839 (δ , $=\text{C}-\text{H}$ of *p*-phenyl), 688 (δ , $=\text{C}-\text{H}$ of maleimide). ANAL. Calcd: C, 68.72%; H, 3.96%; N, 6.17%. Found: C, 68.39%; H, 4.02%; N, 6.21%.

Thermal curing of the novel monomers

The cure behavior of 2-PPM, 3-PPM, and 4-PPM was characterized with DSC and FTIR spectroscopy. The monomers were cured to obtain cured resins with the following procedure: 170°C for 2 h, 200°C for 2 h, and 250°C for 2 h. The thermal stability of the cured resins was evaluated with TGA, and their dynamic mechanical properties were characterized with DMA.

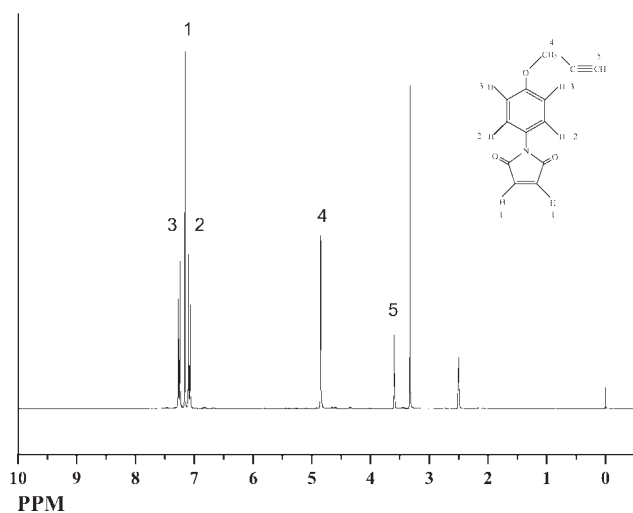


Figure 1 $^1\text{H-NMR}$ spectrum of the 4-PPM monomer.

RESULTS AND DISCUSSION

Synthesis of 2-PPM, 3-PPM, and 4-PPM

The monomers could not be prepared directly with aminophenol because of the similar reactive properties of the amine and hydroxyl groups. In this study, 2-PPM, 3-PPM, and 4-PPM were synthesized via three steps: first, nitrophenol was reacted with propargyl bromide to form nitrophenyl propargyl ether;¹⁴ second, nitrophenyl propargyl ether was reduced to aminophenyl propargyl ether;¹⁵ and lastly, aminophenyl propargyl ether was reacted with maleic anhydride to form corresponding propargyloxyphenyl maleimide monomers.¹⁶ The intermediate products were confirmed with $^1\text{H-NMR}$ and FTIR spectroscopy. The final products, 2-PPM, 3-PPM, and 4-PPM, were characterized with $^1\text{H-NMR}$, FTIR spectroscopy, and elemental analysis. For example, the $^1\text{H-NMR}$ spectrum of 4-PPM is shown in Figure 1, and the FTIR spectrum of 4-PPM

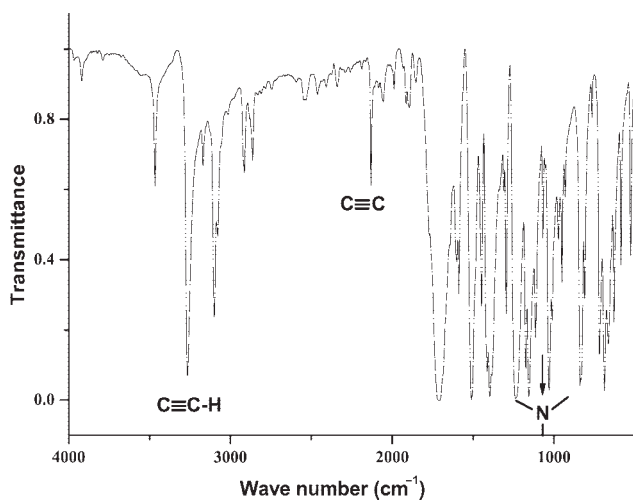


Figure 2 FTIR spectrum of the 4-PPM monomer.

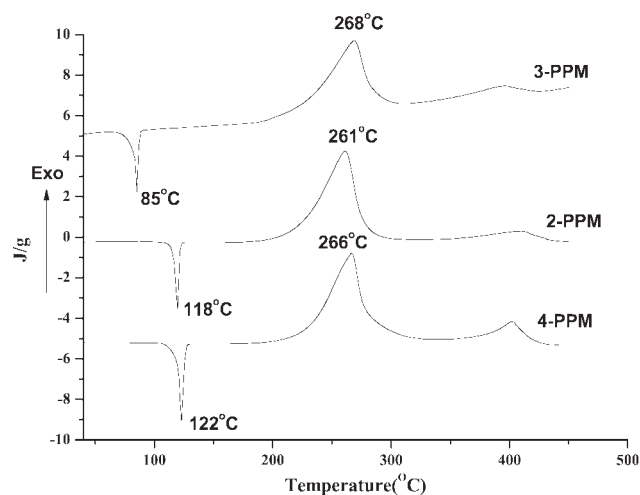


Figure 3 DSC profile of the monomers.

is shown in Figure 2. In the $^1\text{H-NMR}$ spectrum of 4-PPM, the doublet situated in the range of 7.13–7.30 ppm was associated with aromatic protons, whereas the singlet appearing at 7.02 ppm was assigned to maleimide protons. The peak signal that appears at 4.85 ppm was attributed to $-\text{CH}_2-$ of the propargyl group, whereas the singlet at 3.60 ppm was assigned to the $-\text{C}\equiv\text{CH}$ proton of the propargyl group. Also, FTIR spectra showed peaks at 3266 and 2131 cm^{-1} attributable to $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$ of the propargyl group. The peak at 1155 cm^{-1} was attributed to C-N-C of the maleimide group. The peaks at 1600, 1509, and 1448 cm^{-1} were relevant for the aromatic rings. The analysis results identified the structures of the products. The monomers were dissolved readily in common organic solvents such as ethanol, acetone, and tetrahydrofuran.

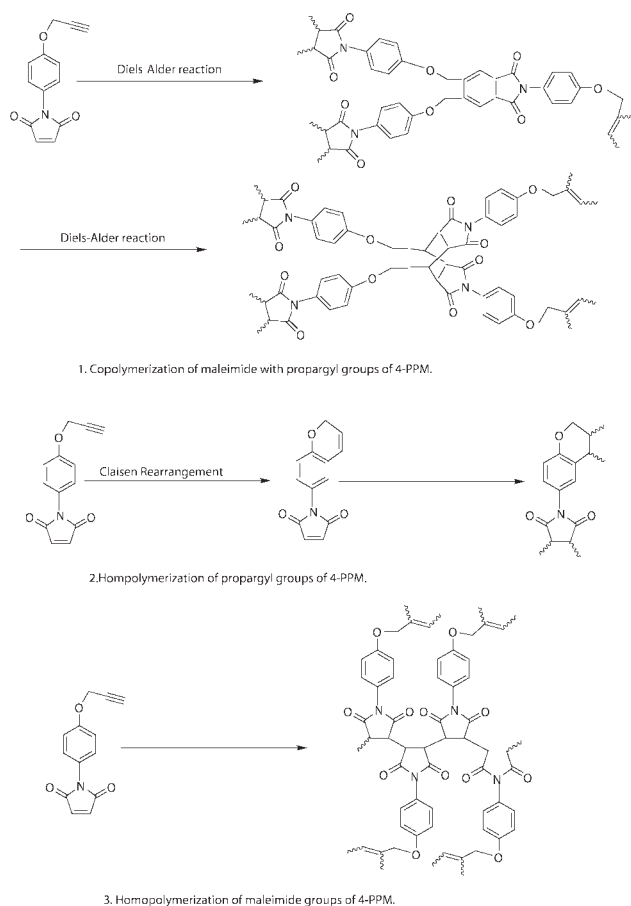
Curing behavior of the monomers

In this section, DSC was applied to evaluate the cure behavior and determine the cure kinetic parameters of the monomers. Figure 3 shows the DSC curves of 2-PPM, 3-PPM, and 4-PPM, and the analysis data are compiled in Table I.

All the thermograms showed one endotherm and one exotherm. The endotherms were attributed to the melting transitions of the monomers. To the best

TABLE I
DSC Data and Calculated Kinetic Parameters for 2-PPM, 3-PPM, and 4-PPM

	Melting temperature (°C)	Onset cure temperature (°C)	Peak cure temperature (°C)
2-PPM	118	222	261
3-PPM	85	221	268
4-PPM	122	229	266



Scheme 2 Possible curing reactions of 4-PPM in the curing process.

of our knowledge, most BMI resins have high melting points that are very close to their cure temperatures, and this indicates that they will start to polymerize and crosslink as soon as they melt. For example, the melting point of a typical BMI resin, 4,4'-bismaleimido diphenyl methane, is as high as 155–156°C, which is very close to its onset cure temperature.¹⁷ In other words, 4,4'-bismaleimido diphenyl methane exhibits a narrow process window, which is defined as the temperature between the melting point and the onset cure temperature. However, the melting points of 3-PPM, 2-PPM, and 4-PPM were about 85, 118, and 122°C, respectively; they were much lower than their cure temperatures (the onset cure temperatures of the three monomers were ca. 220°C). This meant that the monomers possessed a broad process window. Therefore, because of their low melting points, the novel monomers exhibited better processability than BMI resins.

In addition, the exotherms were attributed to the curing reactions of the monomers. For the three monomers, the onset cure temperatures were in a similar range of 220–230°C, and the peak cure temperatures also changed little between 261 and 269°C; this indicated the same cure behavior for these

TABLE II
Kinetic Parameters for 2-PPM, 3-PPM, and 4-PPM
Calculated with the C–R Equation

	n	E_a (kJ/mol)	A
2-PPM	1	165.3	1.24×10^{13}
3-PPM	1	140.0	2.05×10^{10}
4-PPM	1	181.6	3.15×10^{14}

monomers. Because of the strong electron-withdrawing property, the maleimide group could react with the electron-donating propargyl group via addition reactions. The literature includes a report that acetylene compounds can copolymerize with maleimide groups via Diels–Alder reactions.¹ With 4-PPM as an example, possible curing reactions of the monomers are proposed in Scheme 2.

Furthermore, the cure kinetics was also studied on the basis of the DSC curves. There are many methodologies used to calculate the kinetic parameters. In this work, the Coats–Redfern (C–R) equation was chosen to obtain the cure kinetic parameters for the monomers.^{18,19}

The C–R equation can be written as follows:

$$\ln\{g(\alpha)/T^2\} = \ln\{AR/\Phi E(1 - 2RT/E)\} - E/RT$$

where $g(\alpha)$ (the integral conversion function), $= [1 - (1 - \alpha)^{1-n}]/(1 - n)$ [for $n = 1$, $g(\alpha) = -\ln(1 - \alpha)$]; Φ is the heating rate of DSC; R is the universal gas constant; n is the reaction order; A is the Arrhenius frequency factor; E is the apparent activation energy; T is the absolute temperature; and α , estimated from the fractional enthalpy of the reaction, is the fractional conversion at temperature T . Kinetic plots

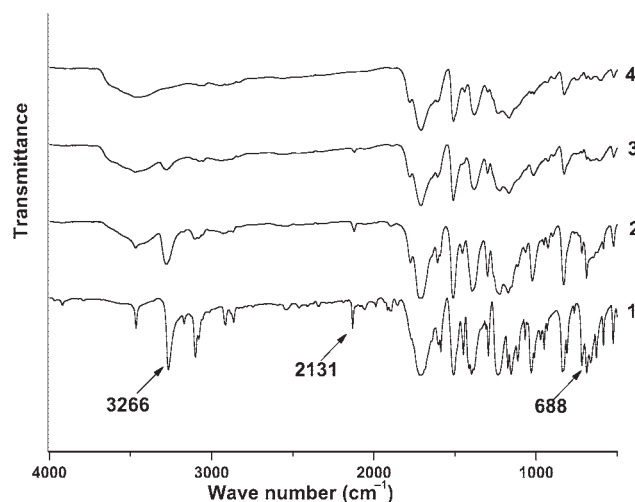


Figure 4 FTIR spectra for 4-PPM after each curing stage: (1) uncured, (2) cured at 170°C for 2 h, (3) cured at 170°C for 2 h plus 200°C for 2 h, and (4) cured at 170°C for 2 h plus 200°C for 2 h plus 250°C for 2 h.

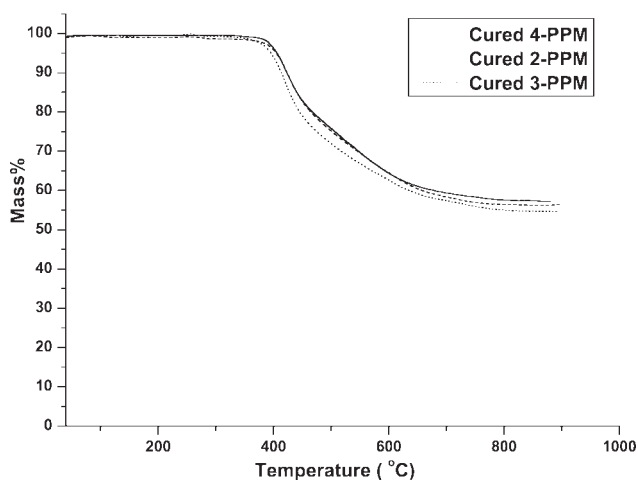


Figure 5 TGA profiles for the cured maleimide monomers.

were made with different n values according to the C-R equation, and the one that best fit furnished the value of n . The calculated kinetic parameters are compiled in Table II.

It was shown that the curing reactions followed mostly first-order kinetics. The cure apparent activation energy (E_a) values were in the range of 150–200 kJ/mol.

FTIR spectra were used to follow the cure process. With 4-PPM used as an example, the FTIR spectra revealed that it cured during different temperature stages, as shown in Figure 4. According to the analysis of the FTIR spectra in the Experimental section, the absorptions at 3266 and 2131 cm^{-1} were assigned to $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$, respectively. The absorption at 688 cm^{-1} was assigned to $=\text{C}-\text{H}$ of the maleimide group. Figure 4 shows that the three absorptions mentioned previously all decreased with the cure temperature increasing. Furthermore, the decreasing extents of the absorptions that belonged to the maleimide and propargyl groups were almost the same, and this indicated that the consumption rates of the two groups might be close in curing reactions. After 4-PPM cured at 250°C, the absorption of the two groups disappeared, and this revealed that it was cured completely by this cure procedure.

Thermal analysis of the cured resins

The monomers were cured at 170°C for 2 h, 200°C for 2 h, and 250°C for 6 h to obtain brown and compact cured resins. The thermal stability of the cured resins was characterized with TGA, and the profiles are shown in Figure 5. The three cured resins exhibited similar degradation curves. The 5% mass loss temperatures of cured 2-PPM, 3-PPM, and 4-PPM were as high as 405, 395, and 405°C, respectively,

and this indicated that the cured resins possessed excellent thermal stability. Also, the char yields at 900°C for cured 2-PPM, 3-PPM, and 4-PPM were 56.5, 54.6, and 57.1%; they were much higher than those of cured blend BMI resins.^{5,13} The high char yields suggest that it is possible to use these monomers as matrices for ablative materials. In addition,

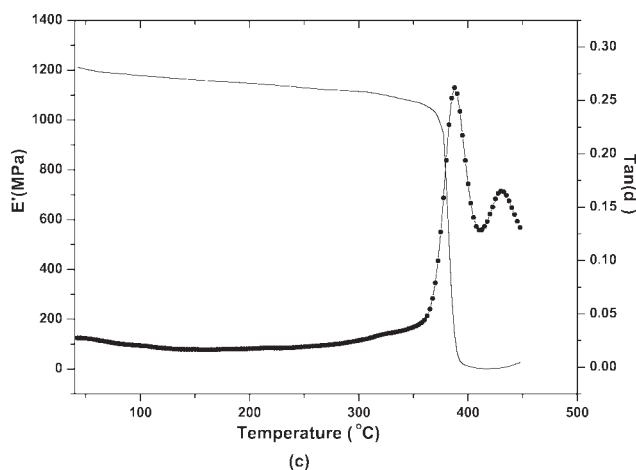
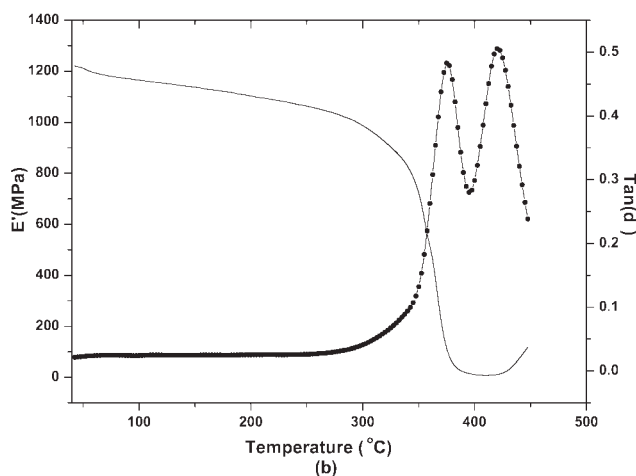
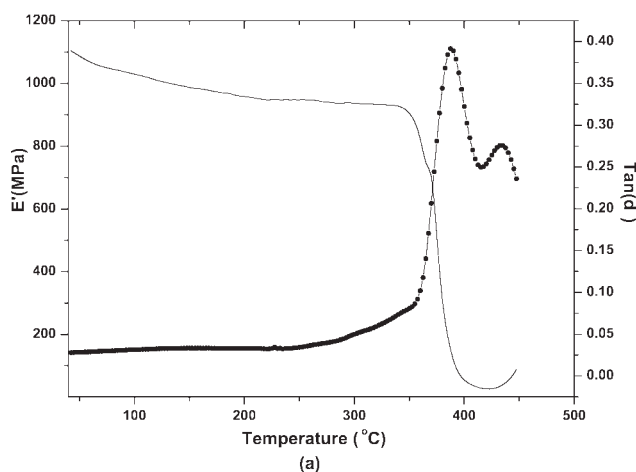


Figure 6 DMA profiles for the cured maleimide monomers: (a) cured 2-PPM, (b) cured 3-PPM, and (c) cured 4-PPM [tan (d) = loss factor].

TABLE III
 T_g Values of Some Commercial Blend BMI Resins

Resin system	XU 292	QY-8911-2	Narmco 5270	Narco 5250-4
T_g (°C)	273	286	287	295

from the TGA data, it could also be observed that cured 2-PPM and cured 4-PPM presented slightly better thermal stability than cured 3-PPM.

DMA is an efficient tool for measuring the dynamic mechanical properties of cured resins. The storage modulus (E') and the loss factor ($\tan \delta$) for cured 2-PPM, 3-PPM, and 4-PPM are shown as functions of temperature in Figure 6. The retention rates of E' at 350°C for cured 2-PPM and 4-PPM were 92 and 89%; that is, they were much higher than that of cured 3-PPM (59%). In addition, all curves of $\tan \delta$ versus temperature showed two peaks. The first peak was attributed to the glass transition of the cured resins, and the glass-transition temperature (T_g) was defined as the peak temperature; the second peak was attributed to the degradation of the cured resins. It was noteworthy that the three cured resins exhibited high T_g values. The T_g values of cured 2-PPM and 4-PPM were as high as 386 and 387°C, respectively; that is, they were a little higher than T_g of cured 3-PPM (373°C). Furthermore, Table III shows the T_g values of some typical commercial blend BMI resins;⁹ the T_g values of the cured products for the three monomers were much higher than those of the typical commercial BMI resins.

CONCLUSIONS

Novel thermosetting monomers bearing both maleimide and propargyl groups were successfully synthesized. The DSC study showed that the monomers exhibited a broader process window than common BMI resins because of their lower melting tempera-

tures, and the three monomers presented almost the same cure behaviors. The TGA results indicated that the cured resins presented excellent thermal stability because their 5% mass loss temperatures were high (ca. 400°C), and their char residue at 900°C was also higher than 50%. The DMA study suggested that the T_g values of the cured resins were between 373 and 387°C; that is, they were much higher than those of typical blended BMI resins. Because of the excellent process and thermal properties, these novel thermosetting monomers could be candidates for high-performance composite matrices.

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