

# Synthesis and Characterization of Triallylphenoxytriazine and the Properties of Its Copolymer with Bismaleimide

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**ABSTRACT:** A new modifier for bismaleimide (BMI), 2,4,6-tris(2-allylphenoxy)-1,3,5-triazine (TAPT), with higher yield was prepared by a phase-transfer catalyzing (PTC) procedure through the reaction of cyanuric chloride with 2-allylphenol in the presence of aq. NaOH using tetrabutyl ammonium bromide in chloroform. The thermo-homopolymerization behavior of TAPT was investigated by differential scanning calorimetry (DSC), and the results showed that TAPT does not polymerize on heating. The copolymerization reaction of TAPT and 4,4'-(bismaleimidophenyl) methane (BMDPM) was also studied, and the results showed that TAPT can effectively improve mechanical properties of BMDPM. The better results were obtained when the TAPT composition was in the range 30–40 wt %. The glass fabric reinforced TAPT/BMDPM matrix composite with excellent mechanical and electric properties could be prepared by processing the resin (30 wt % TAPT) in dimethylformamide (DMF)/toluene (1:1, v/v) solution. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1248–1257, 2001

**Key words:** 2,4,6-tris(2-allylphenoxy)-1,3,5-triazine (TAPT); phase-transfer catalyst; bismaleimide (BMI); heat resistance materials; glass fabric reinforced matrix composite

## INTRODUCTION

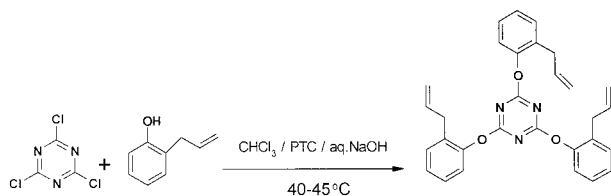
Bismaleimide (BMI) resins are one of the most important thermosetting polymers and have received attention in aerospace and aeronautics because of their high thermal stability, nonvolatility, and low cost.<sup>1</sup> However, their usage as matrix resins for advanced composites is limited because of their inherent brittleness. Although a lot of methods for improving the toughness of the resins have been studied in the past 30 years,<sup>1–5</sup> the majority of them were unsatisfactory. The reason is that the methods assuredly increased the toughness of the resins, but heat resistance of the cured resins was usually decreased.<sup>1</sup> In some cases, some modifiers, such as rubber and some thermoplastic polymers, could strongly decrease the heat resistance.<sup>1,2</sup>

From the point of view of molecular design, introducing flexible linkage or chains into BMI can effectively improve the toughness of the resins.<sup>1,6</sup> On the other hand, introducing aromatic heterocyclic groups into the resins can prevent strongly decreasing heat resistance of the cured resins.<sup>1</sup> It was well known that allyl groups were “tough” and s-triazine rings were “heat resistant”.<sup>1</sup> Hence, theoretically, the co-reaction between BMI resins and the modifiers containing allyl groups and s-triazine rings could give good toughness and thermal stability to the cured resins.

The aim of our work is to investigate the properties of the copolymers between the modifiers containing allyl groups and s-triazine rings and a popular BMI, 4,4'-(bismaleimidophenyl) methane (BMDPM). In this paper, we describe the preparation of a new modifier, triallylphenoxytriazine (TAPT), and the properties of its copolymer with BMDPM. To study the properties of the TAPT/

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**Figure 1** the procedure for preparation of TAPT.

BMDPM resin, glass-fabric-reinforced composites based on the resin were also prepared. Furthermore, the mechanical properties of the composite at room temperature and high temperature (at 180 and 200 °C) and the electric properties at room temperature were also tested.

## EXPERIMENTAL

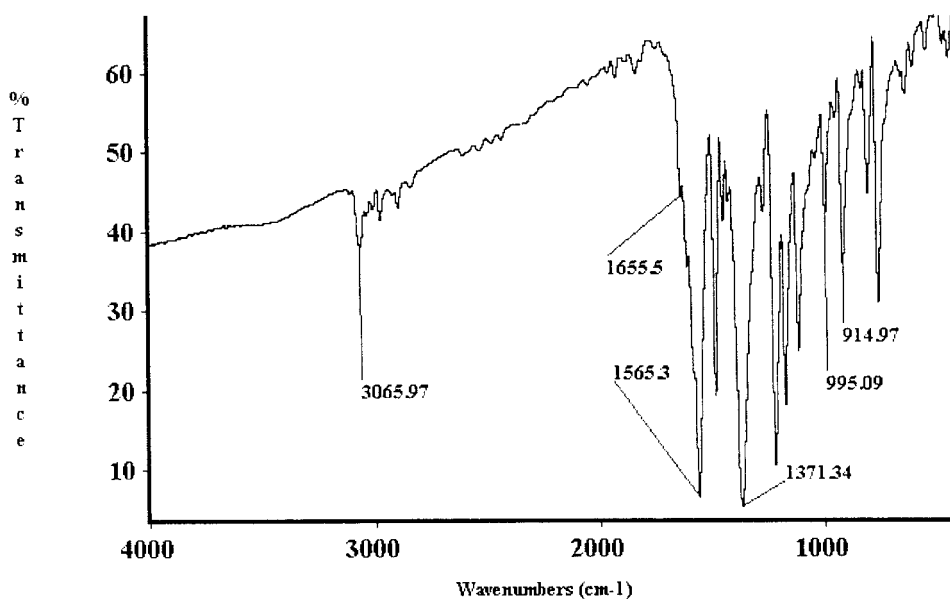
### Materials

Cyanuric chloride was provided by the Chenguang Institute of Chemical Industry, the Ministry of Chemical Industry of China, and was purified by distillation at first and then by recrystallizations from petroleum ether (60–90 °C; mp, 145–147 °C). 2-Allylphenol was prepared by the reported method<sup>7</sup> and purified by fractional distillation under vacuum (bp, 110–113 °C/0.092 Mpa). BMDPM was an industrial product and was recrystallized twice from toluene before use. Other materials were used as received. AR grade solvents were used.

## Synthesis

### Preparation of TAPT

Cyanuric chloride (18.45 g, 0.1 mol), tetrabutyl ammonium bromide (0.53 g), and chloroform (200 mL) were added to a 500-mL three-necked round-bottomed flask, fitted with a condenser, nitrogen inlet, a thermometer, and a mechanical stirrer. After a transparent solution was obtained, a solution of 2-allylphenol (46.90 g, 0.35 mol, 17% excess to cyanuric chloride) and NaOH (14.00 g, 0.35 mol) in doubly distilled water (50 mL) saturated with N<sub>2</sub> was quickly added to the flask at 15–20 °C (see Figure 1). The reaction mixture was stirred vigorously under purge of N<sub>2</sub> for 0.5 h at the same temperature and then at 25–30 °C for 2 h and at 40–45 °C for 1 h. After cooling to room temperature, the reaction mixture was transferred to a separated funnel and water was removed. The chloroform layer containing TAPT was isolated, washed with cold dilute sodium hydroxide solution (5 wt %) and then water, and dried with anhydrous MgSO<sub>4</sub>. The solvent was evaporated under residue pressure. The crude product was obtained as a pale-yellow oil, which slowly solidified at room temperature. After recrystallization twice from a solvent mixture of methanol and acetone (5:1, v/v), TAPT was obtained as white crystal needles; 40.0 g, mp 110–111 °C, yield 84%. Elemental analysis: Calcd. for C<sub>30</sub>H<sub>27</sub>N<sub>3</sub>O<sub>3</sub>: C 75.45%; H 5.70%; N 8.80%. Found: C 75.17%; H 5.66 %; N 8.81%. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR), <sup>13</sup>C-NMR, and



**Figure 2** FTIR spectrum of TAPT.

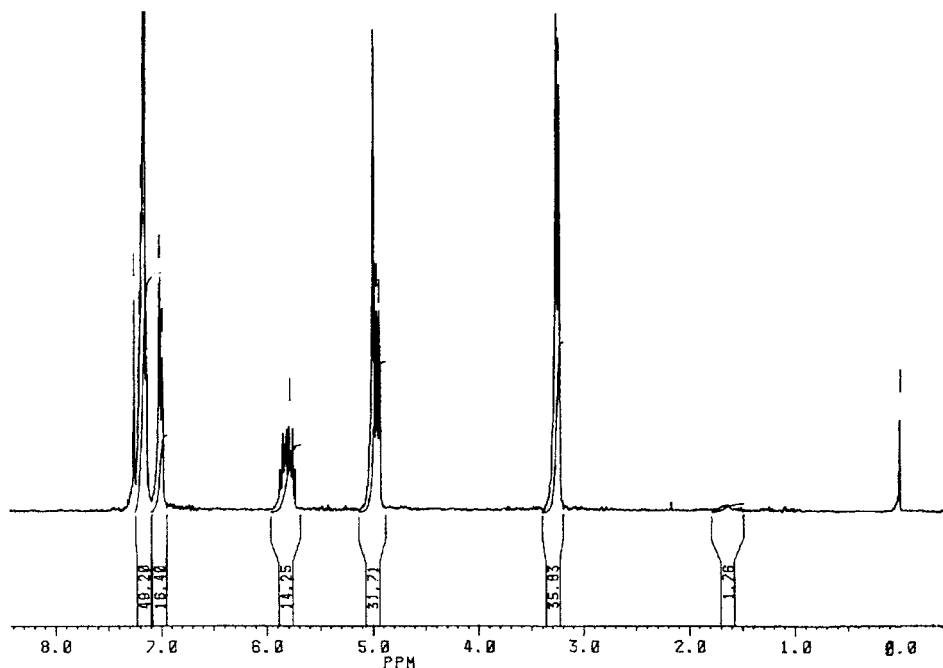


Figure 3  $^1\text{H-NMR}$  spectrum of TAPT.

Fourier transform infrared (FTIR) spectra of the product are given in Figures 2, 3, and 4, respectively.

***Blending, Copolymerization, and Preparation of the Impact, Shear, and Flexural Specimens***

BMDPM and TAPT in certain composition was first ground in a glass mortar and then thor-

oughly mixed with a vibrating mixer. The blend was sieved with a 180 mesh  $\text{cm}^{-2}$  sieve. Fine solid powder of blend (6 g) was then placed in an aluminum mold with dimensions of  $5.8 \times 0.86 \times 0.62$  cm, which was placed in an oven at  $160^\circ\text{C}$ . The temperature was maintained for 30 min so that a transparent melting liquid was obtained. After 6 h, the liquid mixture had turned completely

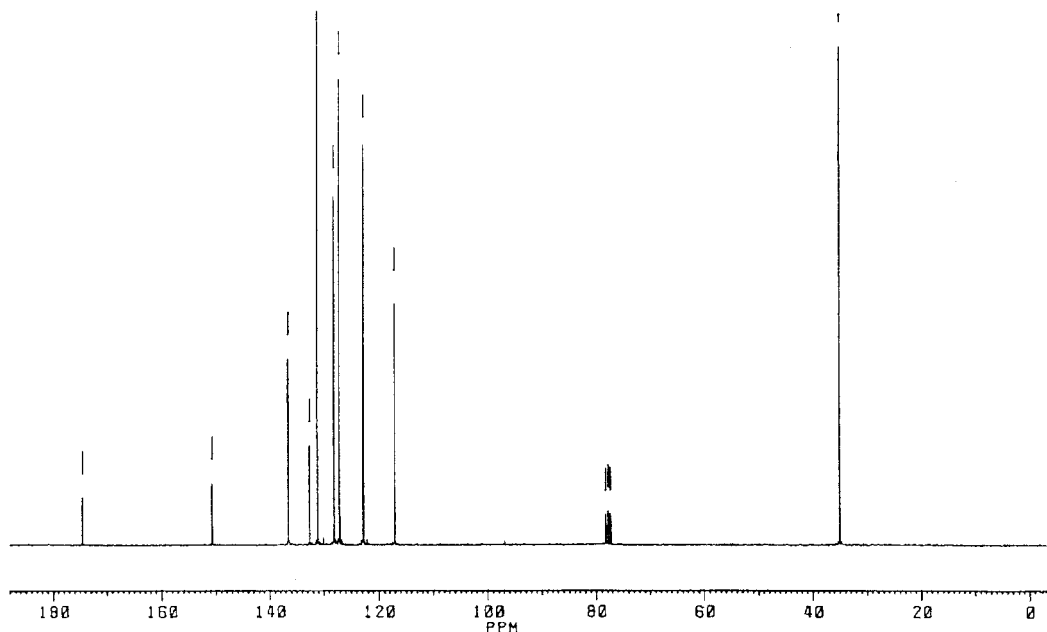


Figure 4  $^{13}\text{C-NMR}$  spectrum of TAPT.

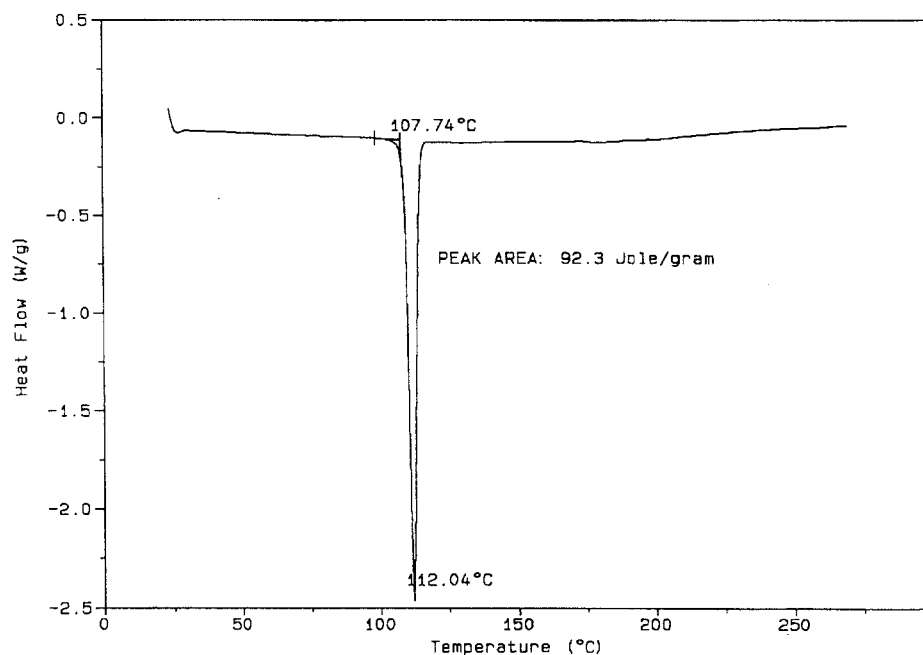


Figure 5 DSC trace of TAPT.

solid. The temperature was then elevated and kept at 180 °C for 8 h, 200 °C for 2 h, 220 °C for 5 h, and 240 °C for 2 h to completely cure the

material. The impact and flexural specimens of the blends were thus obtained. The shear specimens of the blend were obtained by the following

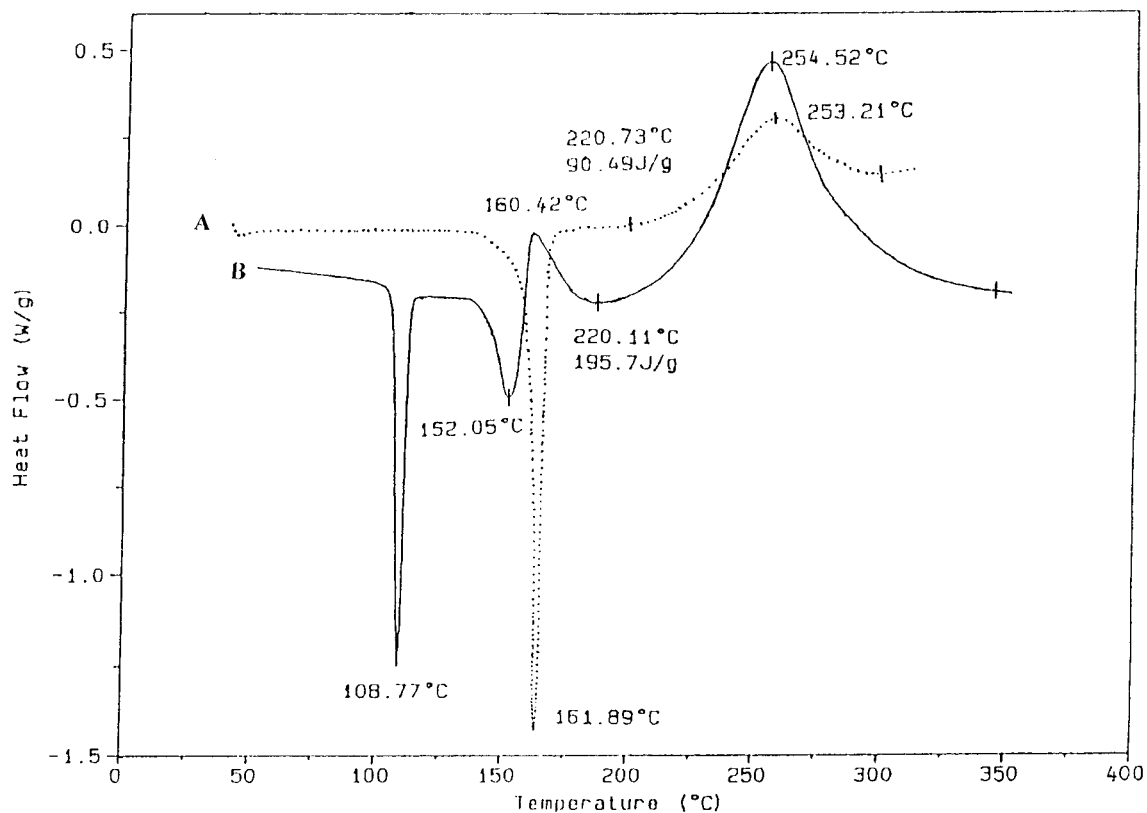


Figure 6 DSC traces of (A) BMDPM and (B) TAPT/BMDPM copolymer.

procedure: the fine solid powder of the blend just mentioned was placed on a metal plate that had been heated to 160 °C. After melting, the blend was applied quickly to two heated aluminum plates (the dimension of both the plates was  $7.02 \times 2.02 \times 0.20$  cm, and the applied area of the blend was  $2.02 \times 2.02$  cm). The applied areas of aluminum plates were quickly overlapped and moved to an oven. The heat procedure was the same as that of the impact and flexural specimens. A slight difference was that the aluminum was heated under a pressure of  $1 \text{ kg/cm}^{-2}$ .

### Laminate Fabrication

Alkali-free glass fabric treated by KH550 (an organic silicon coupling agent), weighting  $600 \text{ g/m}^2$ , was provided by Dongfang Insulating Material Factory (Sichuan), China, and was used for the prepreg preparation. The resin for laminate fabrication was obtained by refluxing TAPT/BMDPM (30 wt %) blend in dimethylformamide (DMF)/toluene (1:1, v/v) solution after 3–4 h. This homogeneous solution, containing 40–50% (w/v) adduct, was used directly for immersing the glass fabric.

### Instrumentation

Melting point was measured by the capillary method and uncorrected. FTIR spectra were recorded on a Nicolet 20SDX-IR spectrophotometer using KCl pellets.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  were carried out on a Bruker ACP-300 spectrometer (300 MHz), using  $\text{CD}_3\text{COCD}_3$  (or  $\text{CDCl}_3$ ) as solvent and tetramethylsilane (TMS) as internal standard. Curing behaviors of TAPT/BMDPM resins were studied with a Du Pont DSC2910 differential scanning calorimeter at a heating rate of  $10 \text{ }^\circ\text{C/min}$  in nitrogen. Thermal stability of the cured resins was determined on a Du Pont TGA2950 thermogravimetric analyzer at a heating rate of  $10 \text{ }^\circ\text{C/min}$  in nitrogen or in air. Dynamic mechanical analysis of the cured resins was carried out on a Du Pont DMA983 tester at a vibration frequency of 10 Hz and at a heating rate of  $5 \text{ }^\circ\text{C/min}$  in nitrogen. The dimension of the specimens of the cured resins for DMA analysis was  $5 \times 0.2 \times 0.05$  cm.

The impact test was carried out using a Charpy tester according to China State Standard GB25711-81. The flexural and shear tests were carried out using a Tension Tester according to China State Standard GB1042-79 and 1450.1-83, respectively.

The flexural strength of glass-fabric-reinforced composites was measured on a Shimadzu AG-10A

**Table I Comparison of Thermal Characteristics between BMDPM and BMDPM/TAPT**

Compound	$T_m$ (°C)	Onset Temperature (°C)	$T_{\text{exo}}$ (°C)	$\Delta H$ (J/g)
BMDPM	162	221	253	90.49
BMDPM/TAPT	152	220	255	195.7

Tester according to China State Standard GB1449-83 by using a span-to-depth ratio of 4:1. All samples had a dimension of 2.0 cm (width)  $\times$  0.2 cm (thickness), and a crosshead speed of 2 mm/min was used. The electric properties of the composites were carried on a ZC-36 Tester under the dryness condition with a test frequency of 50 Hz.

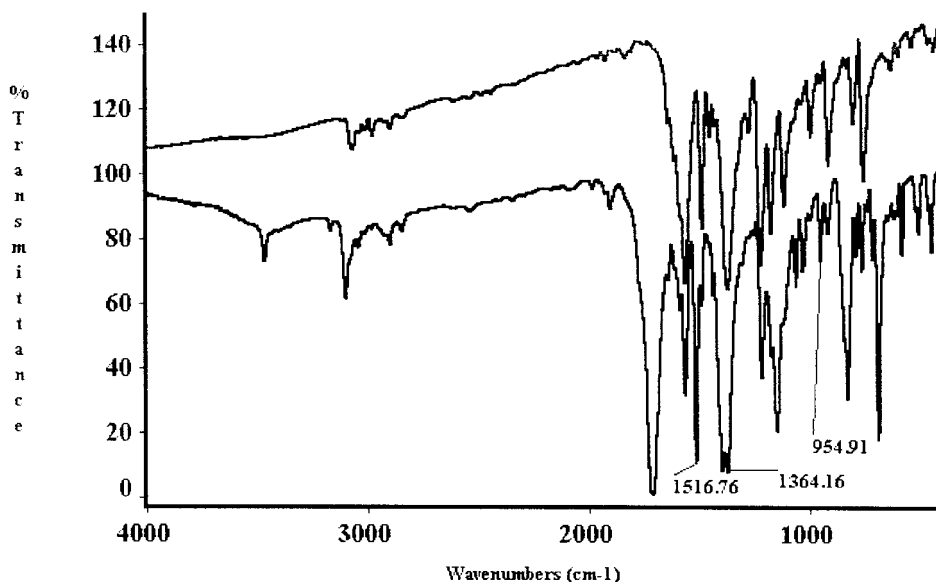
## RESULTS AND DISCUSSION

### Syntheses and Characterization of TAPT

Two procedures for preparation of TAPT have been described in two Japanese patents.<sup>8,9</sup> One is a water-free route; for example, TAPT is prepared by reacting 2-allylphenol with cyanuric chloride in acetone using an organic amine such as triethylamine or pyridine as acid acceptor. Another is a popular procedure that was first reported by Dudley and his colleagues.<sup>10</sup> In the procedure, a mixture of acetone and water (1:1, v/v) is used as solvent and aq. NaOH is used as acid acceptor. In this paper we describe a new way to prepare TAPT. The procedure is shown in Figure 1.

In this procedure,  $\text{CHCl}_3$  and a quaternary ammonium were used as solvent and phase transfer catalyst (PTC), respectively. We attempted to synthesize TAPT by the two routes just mentioned, but the yield of TAPT was lower than that in chloroform/phase-transfer catalysis (PTC) system. It has also been observed that a lower yield of TAPT was obtained by vigorously stirring for a long period of time when chloroform/water was used as the reaction medium in the absence of PTC. This result indicates that PTC could be useful in the transfer of reactants between phases.<sup>11</sup>

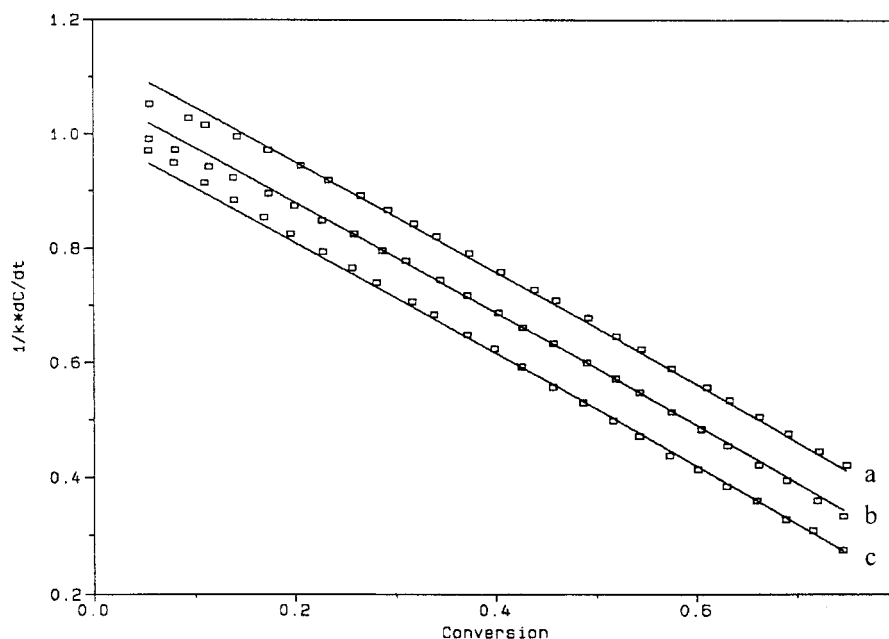
The crude TAPT obtained by removing chloroform was very easy to be purified by recrystallization using a mixture of methanol and acetone (5:1, v/v) or methanol and chloroform (5:1, v/v). The purified compound was white crystal needles that can be dissolved in acetone, chloroform, and chloromethane.



**Figure 7** FTIR spectra of TAPT (top) and TAPT/BMDPM copolymer (bottom).

The chemical structure of TAPT was characterized by FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopy. Figure 2 is the FTIR spectrum of TAPT. Characteristic absorption peaks appear at  $1565$  and  $1371\text{ cm}^{-1}$  due to the resonances of C—N in the triazine ring, and characteristic absorptions at  $1221$ ,  $1175$ , and  $1117\text{ cm}^{-1}$  are assigned to —C—O—C— stretching. The absorption bands at  $2975$  and  $1655\text{ cm}^{-1}$  are assigned to —CH<sub>2</sub>— and aromatic ring backbone stretching, respectively.

Characteristic absorptions at  $3066$ ,  $995$ , and  $915\text{ cm}^{-1}$  are assigned to allyl groups.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of TAPT in Figures 3 and 4 further confirm the structure proposed. The  $^1\text{H-NMR}$  spectrum of TAPT in Figure 2 shows five different proton signals, as expected. Aromatic ring protons of TAPT are observed as multiples at  $6.98$  and  $7.16\text{ ppm}$ , respectively. The protons of allylic carbon give a doublet at  $3.23\text{ ppm}$ . The multiples at  $4.96$  and  $5.75\text{ ppm}$  indicate protons of



**Figure 8** Relationship between  $1/k(dc/dt)$  and  $(1 - c)$  at (a)  $195$ , (b)  $205$ , and (c)  $215\text{ }^\circ\text{C}$ .

**Table II Kinetic Parameters of BMDPM/TAPT Resin in Nitrogen**

Activation Energy (KJ/mol)	Reaction Order	Log Z (min <sup>-1</sup> )
51.8 ± 0.88	0.944 ± 0.0096	4.27 ± 0.096

CH<sub>2</sub>= and =CH— groups, respectively. The <sup>13</sup>C-NMR spectrum of TAPT in Figure 3 shows 10 different carbon signals, as expected. The corresponding data are as follows: 34.7 (—CH<sub>2</sub>—CH=CH<sub>2</sub>), 114.7 (aromatic ring, —C-6), 115.6 (—CH<sub>2</sub>—CH=CH<sub>2</sub>), 123.7 (aromatic ring, —C-4), 127.1 (aromatic ring, —C-5), 127.4 (aromatic ring, —C-3), 130.4 (aromatic ring, —C-2), 134.1 (—CH<sub>2</sub>—CH=CH<sub>2</sub>), 149.8 (aromatic ring, —C-1), 160.5 (triazine ring, —C-2, 4, 6).

#### Thermo-homopolymerization Reaction of TAPT

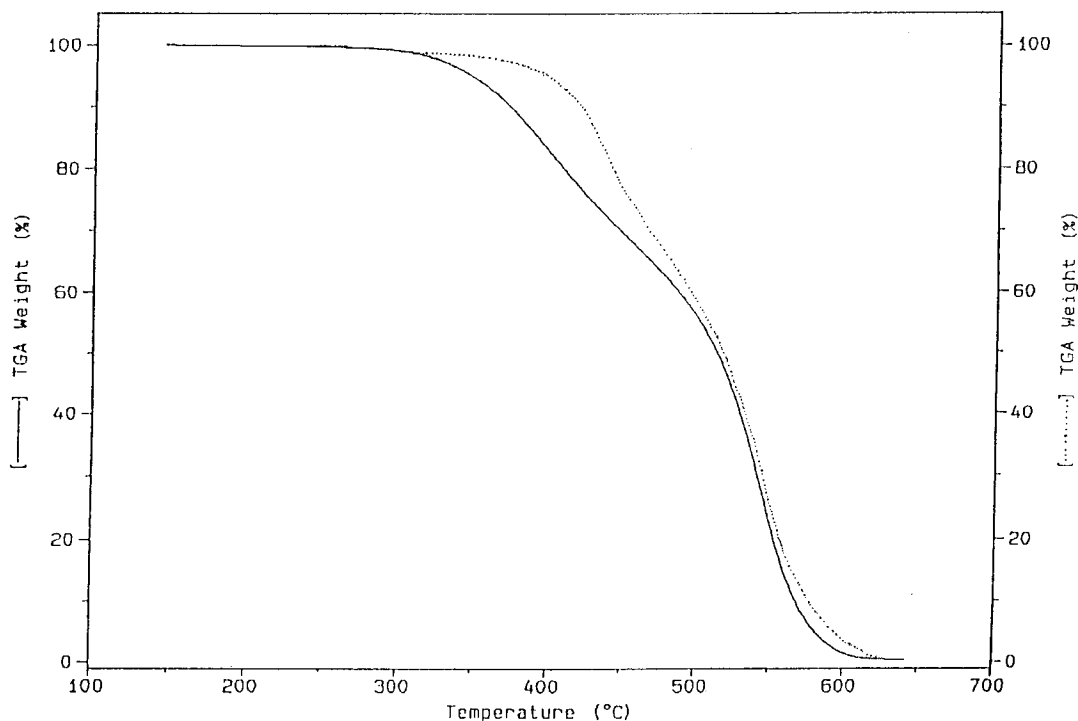
DSC traces of TAPT on heating are shown in Figure 5. The endothermic peak at 113 °C is attributed to melting of TAPT. No exothermic peak from 113 to 250 °C indicates that thermo-homopolymerization of TAPT is negative in the temperature range studied.

#### Copolymerization Reaction of TAPT with BMDPM

In the DSC trace of BMDPM, a sharp endotherm indicating melting is observed at 162 °C (Figure 6A). Mixing of TAPT with BMDPM (30 wt %) results in a decrease in melting transition (Figure 6B) and an exothermic peak at 160 °C associated with the “ene/Diels–Alder” reaction between the BMDPM double bond and the vinylic double bond of TAPT. Exothermic transitions of curing of BMDPM or TAPT/BMDPM are also observed in Figure 6 in the temperature range 190–300 °C. Heat of curing reaction ( $\Delta H$ ), fusion temperature of BMDPM (or TAPT/BMDPM), onset temperature of curing reaction ( $T_1$ ), and exothermal peak position ( $T_{\text{exo}}$ ) are determined from DSC traces and listed in Table I. An increase in  $\Delta H$  values and a decrease in  $T_m$  temperature is noted following addition of TAPT to BMDPM.

The copolymerization reaction of TAPT with BMDPM (30 wt % TAPT) is also elucidated by the FTIR spectra. The spectrum of the uncured TAPT/BMDPM copolymer is shown in Figure 7. The absorptions at 995 and 915 cm<sup>-1</sup> for allylic groups in TAPT decrease significantly.

The activation energy for curing reaction of TAPT/BMDPM resin is determined according to dynamic method using the Borchardt–Daniels



**Figure 9** TGA data of BMDPM (dotted line) and TAPT/BMDPM copolymer (30 wt% TAPT; solid line).

**Table III** TGA Data of TAPT/BMDPM Copolymer<sup>a</sup>

Compound	The Weight Loss Temperature (°C)							
	$T_5$	$T_{10}$	$T_{15}$	$T_{30}$	$T_{50}$	$T_{\max 1}$	$T_{\max 2}$	$T_i$
BMDPM	395	415	428	465	516	432	542	214
TAPT/BMDPM	347	372	392	447	513	401	543	199

<sup>a</sup>  $T_5$ ,  $T_{10}$ ,  $T_{15}$ ,  $T_{30}$ , and  $T_{50}$  were the temperatures when weight loss was 5, 10, 15, 30, and 50%, respectively;  $T_{\max 1}$  and  $T_{\max 2}$  were the decomposition peak temperatures;  $T_i$  was the heat-resistant temperature index;  $T_i = 0.49[T_5 + 0.60(T_{30} - T_5)]$ .

DSC kinetics program,<sup>12</sup> which permits the calculation of activation energy ( $E$ ), pre-exponential factor ( $Z$ ), and order of reaction ( $n$ ) from single DSC scan of a reaction exotherm. The method assumes that the reaction follows  $n$ th-order kinetics; that is,

$$\frac{dc}{dt} = K_{(T)}(1 - c)^n \quad (1)$$

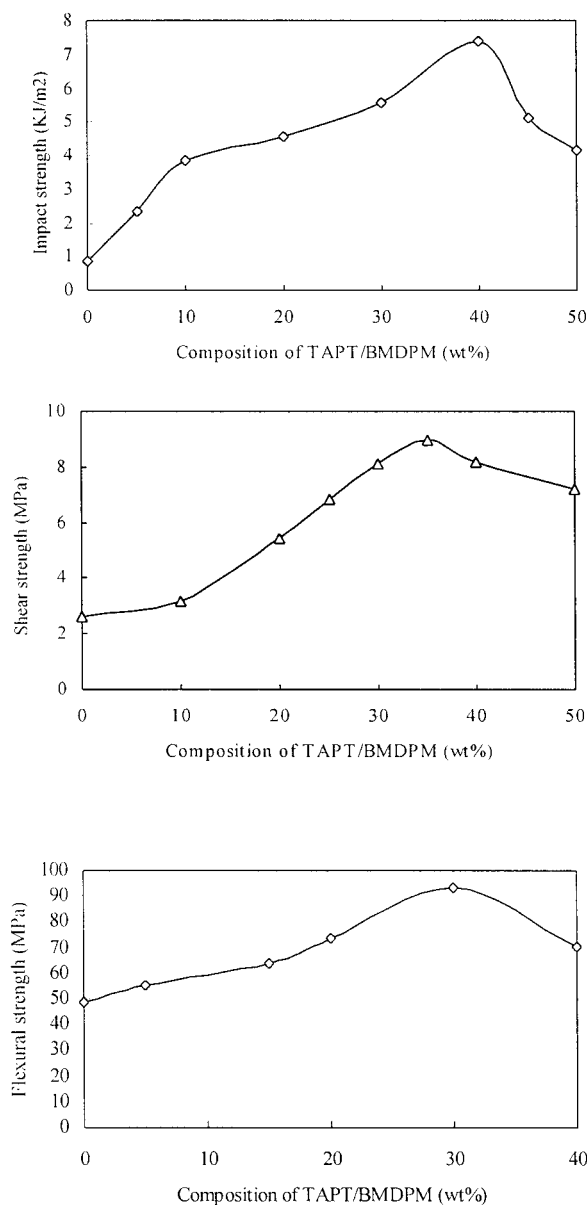
where  $c$  is the fractional conversion (dimensionless),  $K_{(T)}$  is the specific rate constant at temperature  $T$  ( $s^{-1}$ ), and  $n$  is the reaction order (dimensionless). The method also assumes that the temperature dependence of reaction rate follows the Arrhenius expression.

Typical plots of  $1/K_{(T)} * (dc/dt)$  versus  $(1 - c)$  are given in Figure 8. The results are given in Table II.

Relative thermal stability for cured the TAPT/BMDPM copolymer (30 wt % TAPT) is evaluated by thermogravimetry. The results are given in Figure 9 and Table III. A high heat resistant index ( $T_i$ ), 199 °C, indicates that TAPT/BMDPM resin has a high level of thermooxidative stability.

### Mechanical Properties of TAPT/BMDPM Resin

TAPT was expected to improve mechanical properties of BMDPM. The impact strength, flexural strength, and shear strength depending on the composition of TAPT/BMDPM copolymers by weight are shown in Figure 10. The three curves show the maximum in impact strength, shear strength, and flexural strength when the compositions of TAPT in the copolymer are 40, 35, and 30 wt %, respectively. Compared with the neat BMDPM matrix, the copolymer matrix can attain 8.6 times the impact strength, 3.4 times the shear strength, and 1.9 times the flexural strength. Meanwhile, all copolymers show higher impact strength, shear strength, and flexural strength. It is worthy of noting that the impact strength,



**Figure 10** Mechanical properties versus composition (wt %) of TAPT/BMDPM blend: impact strength versus composition (top); shear strength versus composition (middle); and flexural strength versus composition (bottom).



**Table IV DMA Results of TAPT/BMDPM Copolymer**

Composition of BMDPM/TAPT Copolymer in Weight	Glass Transition Temperature (°C)
80/20	314, 383
70/30	322, 359
60/40	210

shear strength, and flexural strength decrease dramatically when the compositions of TAPT exceed 40, 35, and 30 wt %, respectively. Thus, introducing TAPT to BMDPM can give the matrix good mechanical properties, and such mechanical behavior is related to the network structure of the cured resins.

The DMA results in the range 50–400 °C for TAPT/BMDPM copolymers at various weight compositions are shown in Table IV. All copolymers of TAPT/BMDPM show glass transition temperatures in the range 210–390 °C, and these glass transition temperatures decrease with increasing of the TAPT compositions. It is interesting that the TAPT/BMDPM cured resin has only one glass transition temperature when TAPT loading is 40 %, and has two glass transition temperatures when TAPT composition is 30 and 20%. The results indicate a variety of morphology of the phases in the TAPT/BMDPM cured resin from homogenous to phase separation. This variety should be caused by forming two components in the matrix. One component is the copolymer formed by “ene-Diels–Alder” reaction of TAPT with BMDPM and another is the homopolymer of BMDPM. Because of different chemical components between the copolymers and the homopolymer, two phases with different structure and size are formed in the matrix. With variety of the composition of TAPT, the difference of the size of the phases increases or decreases. Consequently,

compatibility between the two phases aggravates or improves. When the composition of TAPT is in the 30–40 % range, a more compatible network is formed, which contains more “ene-Diels–Alder” reaction products. Hence, the degree of the phase separation decreases. With the increasing of tough “ene-Diels–Alder” reaction products, the mechanical properties of TAPT/BMDPM cured resin are strongly improved.

### The Properties of Laminate Fabrication

Mechanical and electric properties of glass-fabric-reinforced TAPT/BMDPM matrix (30 wt % TAPT) were determined (Table V). The results show that the composites have excellent properties.

## CONCLUSION

The following conclusions can be drawn on the basis of this work:

1. 2,4,6-tris(2-Allylphenoxy)-1,3,5-triazine (TAPT) with a yield of 84% was prepared by a new phase-transfer catalyzing method.
2. TAPT/BMDPM copolymer (30 wt %) has lower curing activation energy, and the cured resin has higher thermooxidative stability.
3. TAPT can effectively improve mechanical properties of 4,4'-(bismaleimidophenyl) methane (BMDPM). The better results were obtained when the TAPT composition was in the range 30–40 wt %.
4. The glass-fabric-reinforced TAPT/BMDPM matrix composite with excellent mechanical and electric properties could be prepared by processing the resin (30 wt%TAPT) in DMF/toluene (1:1, v/v) solution.

**Table V Physical Properties of Glass-Fabric-Reinforced TAPT/BMDPM Matrix Composite<sup>a</sup>**

Flexural Strength (MPa)			Water Adsorb. (% , 20°C, 100 h)	$R_S$ ( $\Omega \times 10^{12}$ )	$R_V$ ( $\Omega \cdot m \times 10^{13}$ )	Dc	Df
25°C	180°C	200°C					
580	431	412	0.127	2.9	1.2	4.76	0.0085

<sup>a</sup>  $R_S$  and  $R_V$  is surface and volume resistivity of the composite at 25°C, respectively; Dc and Df is dielectric constant and dissipation factor of the composite at 25°C under 1 MHz, respectively.

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