

# Investigation on the Properties of a Three-Component Copolymer Consisting of Tris(Allylphenoxy) Triazine Monomer and a Diamine-Chain-Extension Bismaleimide

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**ABSTRACT:** A new type of modified bismaleimide resin was obtained by copolymerization between tris(allylphenoxy)triazine monomer (TAPT) and an aromatic diamine-chain-extension bismaleimide [e.g., 4,4'-diaminodiphenylmethane (DADPM)-chain-extension 4,4'-bismaleimidodiphenylmethane (BMDPM)]. The new three-component-polymer system had good processibility and mechanical properties. Better re-

sults were obtained when the weight ratio of TAPT to the DADPM-chain-extension BMDPM resin was 30%. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 475–480, 2004

**Key words:** polyimides; thermoset resins; addition polyimides; composite matrix resins.

## INTRODUCTION

As an important class of materials with higher ratio of properties to price, bismaleimide (BMI) resins have received much attention in many industrial fields.<sup>1</sup> For example, they are used in multi-layer-printed boards for large-scale computers, as encapsulation resins and passivation layer for integrated circuit (IC) dies, as advanced carbon fiber composites for aerospace industry, and so on.<sup>1,2</sup> The disadvantages of the neat resins are their inherent brittleness. To obtain resins with good properties, usually, the neat resins should be modified. Therefore, many investigations focus on improvement of toughness of the resins in the past 30 years.<sup>3–13</sup> As a result, many methods were well studied and a lot of modifiers are found, in which aromatic diamines are more practical and effective. The toughness of BMI can be improved by so-called chain-extension procedure via Michael addition reaction between aromatic diamines and double bonds of BMI.<sup>1,4,10</sup>

Among the diamine-chain-extension BMI resins, 4,4'-diaminodiphenylmethane (DADPM)/4,4'-bismaleimidodiphenylmethane (BMDPM) system has been industrialized.<sup>1,4</sup> However, its poor processibility, such as poor solubility in common organic solvents and high melting viscosity, should be improved.<sup>10</sup> For this purpose, Varma and coworkers introduced triallyl cyanurate (TAC) to the diamine-chain-extension BMI resins and obtained a new three-component resin with good processibility and mechanical properties.<sup>10</sup> However, the heat resistance of the cured resins strongly decreased.<sup>10</sup>

To prepare new BMI resins with good processibility, mechanical properties, and heat resistance, an attempt to synthesize a new modified BMI resin was carried out in our laboratory. The results showed that the copolymer system derived from tris(allylphenoxy)triazine (TAPT) and an aromatic diamine-chain-extension BMI resin (e.g., 4, 4'-diaminodiphenylmethane-chain-extension-4, 4'-bismaleimidodiphenylmethane) met the requirement mentioned above. The new three-component copolymer is soluble in organic solvents and has lower melting viscosity. Moreover, its mechanical properties and thermooxidative stability are good. Herein, we report the results.

## EXPERIMENTAL

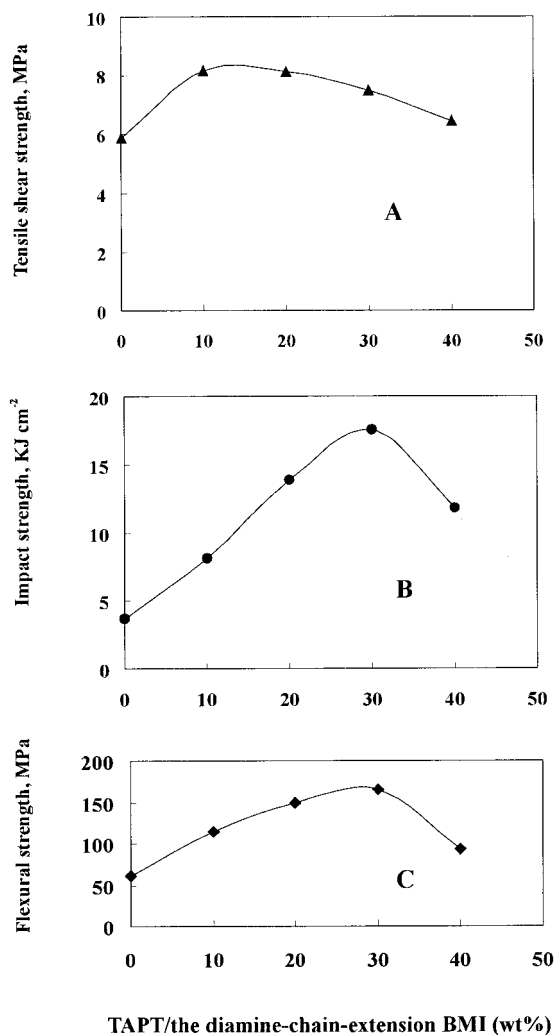
### Materials

TAPT monomer was synthesized according to the reported method.<sup>14</sup> DADPM was an industrial product

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**Figure 1** Relationship between mechanical properties of the three-component copolymer and the weight ratio of TAPT/DADPM-BMDPM. (A, impact strength versus the ratio; B, tensile shear strength versus the ratio; C, flexural strength versus the ratio).

and purified by distillation under vacuum. BMDPM was also an industrial product and was recrystallized twice from toluene before use. Other materials were used as received. Analytical reagent grade solvents were used. All solvents were purchased from Aldrich (Milwaukee, WI).

#### Instrumentation and test methods

Melting viscosity of the resins was measured by using a Rotatory viscometer NDJ-I with the third rotator. Curing behaviors of the resins were studied by using a DuPont DSC 2100 differential scanning calorimeter at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in nitrogen. Thermooxidative stability of the cured resins was determined with a DuPont 2100 thermogravimetric analyzer at a heating rate of  $10^{\circ}\text{C min}^{-1}$  by using com-

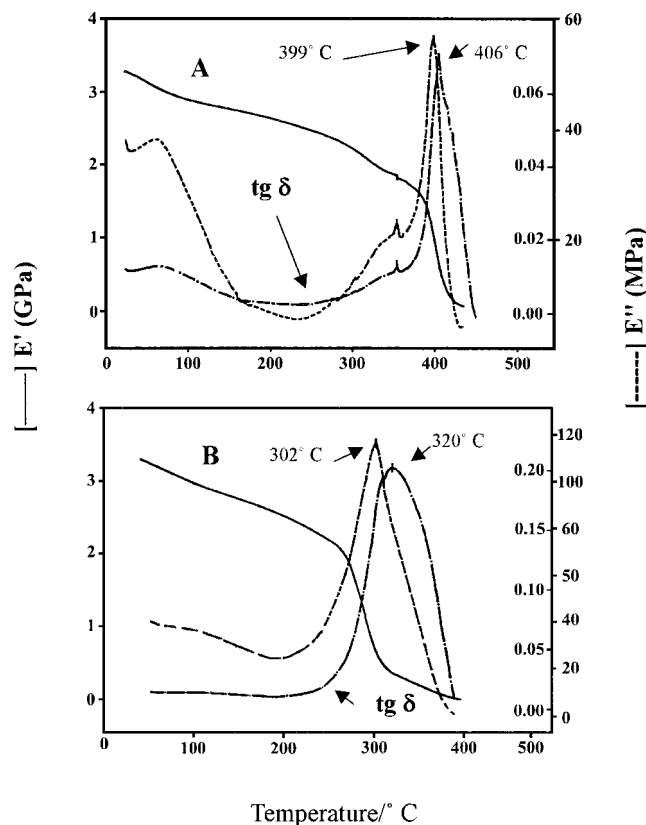
pressed air as carrier gas. Dynamic mechanical analysis of the cured resins was carried out on a DuPont DMA 983 tester by using a vibration frequency of 1.0 Hz at a heating rate  $5^{\circ}\text{C min}^{-1}$  in nitrogen.

Impact testing was carried out by using a Charpy tester according to China State Standard GB 25711-81. Flexural and shear tests were measured with a tension tester according to China State Standard GB 1042-79 and GB 1450.1-83, respectively.

#### Preparation and curing of the three-component copolymers

##### Preparation of DADPM-chain-extension BMDPM resin

BMDPM and DADPM were mixed with a molar ratio of 3.7:1.0 in a mixture solvent of methyl isobutyl ketone (MIBK) and dichloromethane (2:1, v/v) at room temperature. Refluxing the mixture for 4 h gave a homogenous solution. After evaporation of the solvents under vacuum, the chain-extension resin was obtained as a red-brown solid.



**Figure 2** DMA curves of the DADPM-chain extension BMDPM resin (A) and the three-component copolymer (B) [ $n(\text{BMDPM})/n(\text{DADPM}) = 3.7$ ; TAPT/DADPM-BMDPM = 30 wt %].

**TABLE I**  
**Comparison of Solubility and Melting Viscosity Between the DADPM-Chain-Extension BMDPM Resin and the Three-Component Copolymer<sup>a</sup>**

Polymer	Solubility <sup>b</sup>							Melting viscosity (cp)
	Acetone	MIBK <sup>c</sup>	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	DMAC <sup>d</sup>	DMSO <sup>e</sup>	NMP <sup>f</sup>	
A	+/-	+/-	+/-	±	+	+	+	550
B	±	+	±	+	+	+	+	370

<sup>a</sup> A and B are the DADPM-chain-extension BMDPM resin and the three component copolymer, respectively.

<sup>b</sup> +, dissoluble; ±, dissoluble at heating; +/-, partially dissoluble at heating.

<sup>c</sup> Methyl isobutyl ketone (MIBK).

<sup>d</sup> *N,N*-dimethylacetamide (DMAC).

<sup>e</sup> Dimethylsulfoxide (DMSO).

<sup>f</sup> *N*-methyl pyrrolidone (NMP).

### Preparation of the three-component copolymers

TAPT and the DADPM-chain-extension BMDPM resin in certain compositions were mixed in dimethylacetamide (DMAC) at room temperature. After heating the mixture at ~120°C for 1 h, the solution was poured into ice water. The solid was collected by

filtration, washed with water, and dried under vacuum at 50°C. The three-component copolymers were thus obtained as a yellow-red solid.

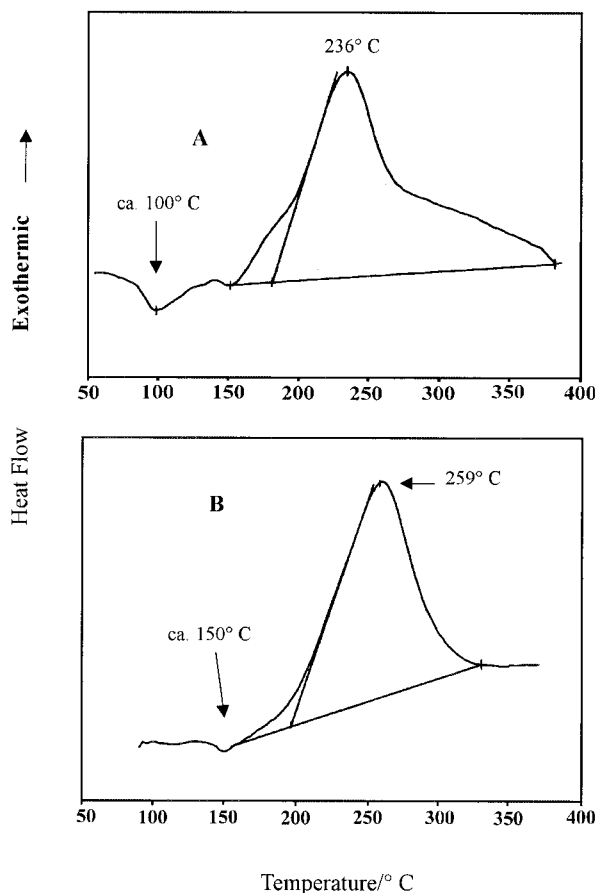
### Curing of the three-component copolymers

The three-component copolymers were ground in a glass mortar and a fine solid powder was introduced into an aluminum dish in an oven at 160°C. The dish was kept at the set temperature for 6 h. Then, the temperature was elevated and kept at 180°C for 4 h, 200°C for 2 h, 220°C for 5 h, and 240°C for 5 h.

Analogously, cured DADPM-chain-extension BMDPM resin was obtained by using the same procedure.

### Preparation of impact, flexural, and shear specimens

The three-component copolymers were first ground in a glass mortar and then sieved with a 180-mesh-cm<sup>-2</sup> sieve. Fine solid powder of blend (6.0 g) was then placed in an aluminum mold with dimensions of 5.8 × 0.86 × 0.62 cm, which was placed in an oven at 160°C. The temperature was maintained for 30 min so that a transparent melting liquid was obtained. After 6 h, the liquid mixture had completely turned solid. The temperature was then elevated and kept at 180°C



**Figure 3** DSC traces of DADPM-chain-extension BMDPM resin (A) and the three-component copolymer (B) [ $n(\text{BMDPM})/n(\text{DADPM}) = 3.7$ ; TAPT/DADPM-BMDPM = 30 wt %].

**TABLE II**  
**Comparison of Thermal Characteristics Between the DADPM-Chain-Extension BMDPM Resin and the Three-Component Copolymer<sup>a</sup>**

Polymers	Onset temperature		$\Delta H$ (J/g)
	( $T_1$ , °C)	$T_{\text{exo}}$ (°C)	
A	221	253	90.49
B	230	253	223.5

<sup>a</sup> A and B are the DADPM-chain-extension BMDPM resin and the three-component copolymer, respectively. The weight ratio of TAPT/ the DADPM-chain-extension BMDPM resin was 30%.

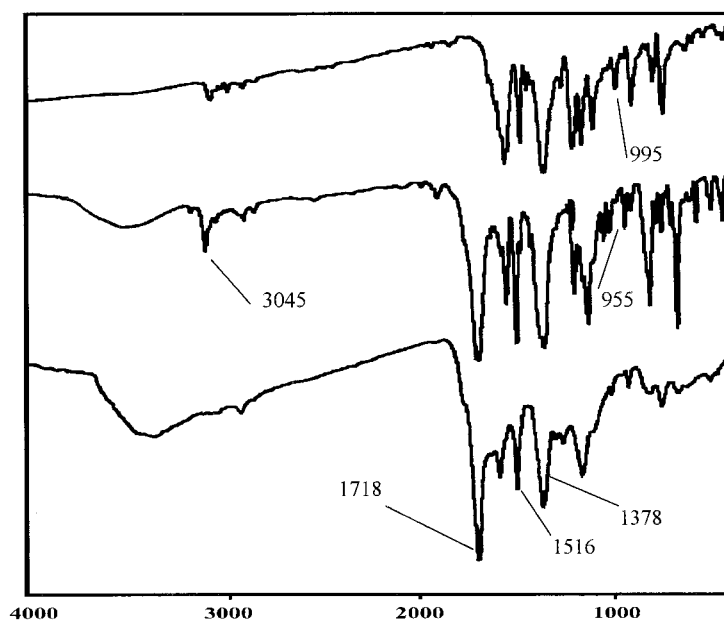


Figure 4 IR spectra of TAPT (top) and the three-component copolymer (middle, uncured; bottom, cured).

for 8 h, 200°C for 2 h, 220°C for 5 h, and 240°C for 2 h to complete the cure. The impact and flexural specimens of the copolymers were thus obtained. The tensile shear specimens of the blend were obtained by using the following procedure: the fine solid powder of the copolymers mentioned above (5.0 g) was placed on a metal plate with a temperature controller. The temperature on the surface of the plate was maintained at  $160 \pm 2^\circ\text{C}$ . After melting and being stirred at that temperature for 5 min, the prepolymer was applied quickly to two preheated (at  $160^\circ\text{C}$ ) aluminum slices (the dimension of both the slices was  $7.02 \times 2.02 \times 0.20$  cm, and the area for applying the prepolymer on each slice was  $2.02 \times 2.02$  cm). The aluminum slices were quickly overlapped according to the general manner and moved to an oven at  $160^\circ\text{C}$  and maintained for 6 h. Then, the temperature was elevated and kept at  $180^\circ\text{C}$  for 8 h,  $200^\circ\text{C}$  for 2 h,  $220^\circ\text{C}$  for 5 h, and  $240^\circ\text{C}$  for 2 h. Thus, the specimens for testing shear strength were obtained.

## RESULTS AND DISCUSSION

### Mechanical properties of the three-component copolymers

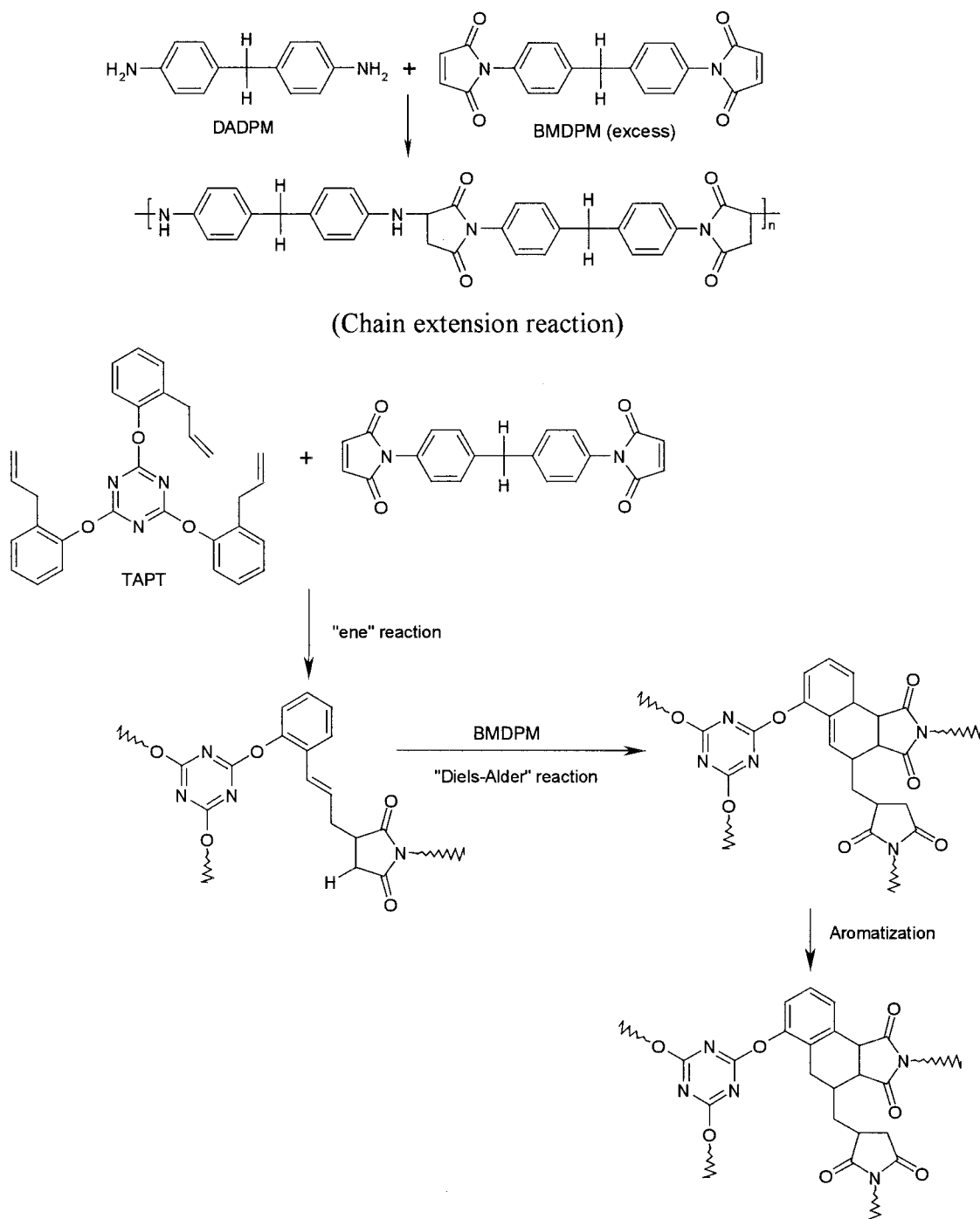
It was known<sup>6</sup> that DADPM-chain-extension BMDPM resin has good properties when the molar ratio between DADPM and BMDPM is 1 : 3.7. In the present work, we used the same molar ratio to prepare the TAPT/DADPM-chain-extension BMDPM resin (e.g., the three-component copolymer). Figure 1 gives the changes of the mechanical properties of the three-component copolymers with the changes of the

weight ratio of TAPT to the DADPM-chain-extension BMDPM resin. The three curves show the maximum in impact strength, flexural strength, and tensile shear strength, when the weight ratio of TAPT to the DADPM-chain-extension BMDPM resin is 30, 30, and 10%, respectively. Compared with the DADPM-chain-extension BMDPM matrix, the three-component copolymer attains impact strength of 4.8 times, flexural strength of 2.7 times, and tensile shear strength of 1.4 times, respectively. However, the impact strength, tensile shear strength, and flexural strength decrease dramatically when the ratio exceeds 30, 30, and 10 wt %, respectively.

Figure 2 shows DMA curves of the three-component copolymer and the DADPM-chain-extension BMDPM resin in the range of temperature of  $50\text{--}400^\circ\text{C}$ . The two cured resins show glass transition temperatures in the range of  $301\text{--}399^\circ\text{C}$ . The glass transition temperature of the cured three-component copolymer is lower than that of the cured DADPM-chain-extension BMDPM resin, suggesting lower crosslinking density in the cured three-component copolymer. Consequently, the mechanical properties of the DADPM-chain-extension BMDPM resin are improved by adding TAPT.

### Processibility of the three-component copolymers

Solubility and melting viscosity of the three-component copolymer are listed in Table I. It is seen that the three-component copolymer is soluble in common organic solvents and has lower melting viscosity, indicating its good processibility.



**Scheme 1** The copolymerization reaction of TAPT with the diamine-chain-extension BMI.<sup>4</sup>

### Thermal analysis of the copolymer

Figure 3 gives DSC traces of the three-component copolymer and the DADPM-chain-extension BMDPM resin. As shown in Figure 3, two endothermic peaks indicating the melting point of the resins are observed at  $\sim 100^\circ\text{C}$  [Fig. 3(A)] and  $\sim 150^\circ\text{C}$  [Fig. 3(B)], respectively. The exothermic transitions of curing of DADPM-chain-extension BMDPM resin and the three-component copolymer are also observed in the range

of  $200\text{--}300^\circ\text{C}$ . Heat of curing reaction ( $\Delta H$ ), onset temperature of curing reaction ( $T_1$ ), and exothermal peak position ( $T_{\text{exo}}$ ) are determined from the DSC traces and are listed in Table II. As depicted in Table II, adding TAPT to the DADPM-chain-extension BMDPM resin causes a decrease in  $\Delta H$  values and an increase in exothermal peak position ( $T_{\text{exo}}$ ).

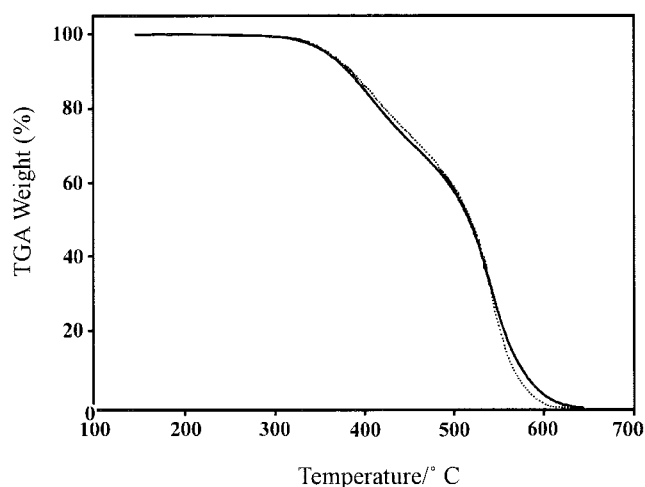
The copolymerization products between TAPT and the DADPM-chain-extension BMDPM resin was also



elucidated by IR spectra. Figure 4 shows the IR spectra of TAPT and the three-component copolymer (uncured and completely cured resin). Characteristic absorption peaks appear at 1516 and 1378  $\text{cm}^{-1}$  because of the resonance of C—N in triazine rings. The absorption bands at 1718  $\text{cm}^{-1}$  are assigned to carbonyl groups in BMI. The absorption peak at 995  $\text{cm}^{-1}$  associated with allylic groups of TAPT disappears and a new peak at 956  $\text{cm}^{-1}$  assigned to the vinyl groups in the uncured three-component copolymer, suggesting occurrence of -ene reaction between allylic groups of TAPT and the double bonds of BMDPM. However, in the completely cured three-component copolymer, the peak at 956  $\text{cm}^{-1}$  was not observed, exhibiting formation of crosslinking networks produced by the reaction of the -ene adducts with BMDPM via Diels–Alder and aromatization reaction, as shown in Scheme 1.<sup>1,4,10</sup>

#### Thermooxidative stability of the cured three-component copolymer

Usually, relative thermooxidative stability of thermosetting resins was evaluated by the results of TGA of the resins in air because the majority of the resins was used in the atmosphere.<sup>4,10</sup> Figure 5 gives TGA curves of the three-component copolymer and the DADPM-chain-extension BMDPM resin. The data are listed in Table III. For thermosetting resins, the heat-resistant index in air,  $T_i$ , is an important parameter to evaluate thermooxidative stability of the resins.<sup>4,6</sup> Compared with the  $T_i$  of the DADPM-chain-extension BMDPM resin (207°C), the three-



**Figure 5** TGA curves of the three-component copolymer (···) and in the DADPM-chain-extension BMDPM (—) resin [ $n(\text{BMDPM})/n(\text{DADPM}) = 3.7$ ; TAPT/DADPM-BMDPM = 30 wt %].

**TABLE III**  
TGA Data of the DADPM-Chain-Extension BMDPM Resin and the Three-Component Copolymer<sup>a</sup>

Polymer <sup>b</sup>	Weight loss temperature (°C)					
	$T_5$	$T_{10}$	$T_{15}$	$T_{30}$	$T_{50}$	$T_i^c$
A	360	387	407	467	516	208
B	355	380	396	450	513	202

<sup>a</sup> In air, heating rate is 10°C  $\text{min}^{-1}$ . The weight ratio of TAPT/DADPM-chain-extension BMDPM resin was 30 wt %.

<sup>b</sup> A and B are the DADPM-chain-extension BMDPM resin and the three component copolymer, respectively.

<sup>c</sup>  $T_i$  is heat-resistant temperature index.  $T_i = 0.49[T_5 + 0.60(T_{30} - T_5)]$ .

component copolymer has a  $T_i$  of 201°C (cf. Table III), exhibiting that adding TAPT to the DADPM-chain-extension BMDPM resin did not greatly cause a decrease to the heat resistance of the resin.

#### CONCLUSION

A new type of modified BMI resin was obtained by copolymerization between TAPT monomer and the DADPM-chain-extension BMDPM. The new three-component copolymer had good processibility and mechanical properties and thermooxidative stability. Better results were obtained when the weight ratio of TAPT to the DADPM-chain-extension BMDPM resin was 30 wt %.

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