

# Synthesis and Characterization of Novel Aromatic Ether Nitrile Monomer Containing Propenylphenoxy Groups and Properties of Its Copolymer with 4,4'-Bismaleimidodiphenylmethane

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**ABSTRACT:** A novel aromatic ether nitrile monomer containing propenyl groups, 2,6-di{2-[(*E*)-1-propenyl]phenoxy} benzonitrile (DPPB), was synthesized by the reaction of 2,6-dichlorobenzonitrile and 2-allylphenol using anhydrous potassium carbonate as the acid acceptor, *N*-methyl pyrrolidone as the dipolar aprotic solvent, and toluene as the dehydrating agent. The chemical structure of DPPB was characterized by FTIR and <sup>1</sup>H-NMR. The monomer was used to modify a popular commercial bismaleimide, 4,4'-bismaleimidodiphenylmethane (BMDPM), to improve the shear strength of the resin. The results showed that DPPB could effectively improve the shear strength of the BMDPM resin without decreasing the heat resistance of BMDPM. A better result was obtained when the composition of DPPB in the copolymer was 45 wt %. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1465–1472, 2002

**Key words:** 2,6-di{2-[(*E*)-1-propenyl]phenoxy} benzonitrile; bismaleimide; modification; heat resistant polymers

## INTRODUCTION

Bismaleimide (BMI) resins are one of the most important thermosetting polymers because of

their high thermal stability, nonvolatility, and low cost.<sup>1</sup> Some examples of applications include multilayer printed boards for large-scale computers, encapsulation resins and passivation layers for integrated circuit dies, advanced carbon fiber composites for the aerospace industry, and structural adhesives.<sup>2</sup> However, the brittleness of the neat resins is a major hazard in their applications. Therefore, a lot of investigations in the past 30 years have focused on improvement of the toughness of the resins. As a result, many additives have been found and studied well, which are

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able to enhance the toughness of the BMIs effectively, including poly(ether imide), poly(siloxane imide), allyl-terminated copolymers, reactive rubber, and so on.<sup>3–10</sup>

Poor shear strength is another disadvantage of the neat BMI resins.<sup>11</sup> However, a few reports focusing on overcoming the disadvantage could be found in the literature.<sup>11,12</sup> Furthermore, some studies were not practical because of using expensive additives or complex processing procedures.<sup>13</sup> In some cases, although some additives definitely increased the shear strength of the resins, the heat resistance of the cured resins was usually strongly decreased.<sup>11</sup> In order to find useful modifiers for increasing the shear strength of BMI, we attempted to add a class of additives or comonomers to BMI.<sup>12</sup> The results showed that the additives containing cyano groups and aromatic rings could greatly increase the shear strength of the resin without decreasing the heat resistance of the cured resin.<sup>12</sup>

For the purpose of further studying the properties of the additives containing cyano groups and aromatic rings, especially the properties of the additive-modified BMI resins, a novel monomer, 2,6-di{2-[(*E*)-1-propenyl]phenoxy} benzonitrile (DPPB), was prepared in our laboratory. In this article we report the synthesis of the monomer and the properties of its copolymer with 4,4-bismaleimidodiphenylmethane (BMDPM). Because of more reactive sites in the monomer, it is also expected that the monomer can be used not only as a modifier for BMI but also in other fields such as drugs, optical materials, and biochemical materials.

## EXPERIMENTAL

### Materials

2,6-Dichlorobenzonitrile (DCBN) was an industrial product and was purified by sublimation. 2-Allylphenol was prepared by the reported method<sup>14</sup> and purified by fractional distillation under a vacuum (bp 110–113°C at 0.092 MPa). IR (KCl,  $\text{cm}^{-1}$ ) 3482 (—OH); 997, 916 (allyl); 3075, 1637 (aryl ring); 2906, 2976 (—CH<sub>2</sub>—). ANAL. Calcd for C<sub>9</sub>H<sub>10</sub>O: C, 80.59%; H, 7.46%. Found: C, 80.89%; H, 7.55%. EIMS *m/z* (% relative intensity): 134 (M<sup>+</sup>, 70.99), 91 (100). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, chemical shifts are referenced to TMS,  $\delta$ ): 5.16 (=CH<sub>2</sub>—), 5.97 (—CH=), 3.39 (—CH<sub>2</sub>—), 6.78–7.14 (phenyl ring). BMDPM was also an industrial product and

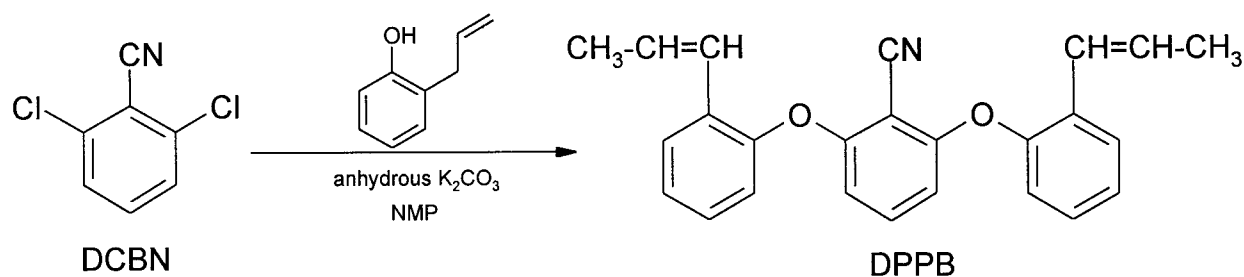
was recrystallized twice from toluene before use. Other materials were used as received, and analytical reagent grade solvents were used.

### Preparation of DPPB

*N*-methyl pyrrolidone (NMP, 250 mL), toluene (200 mL), DCBN (53.4 g, 0.31 mol), and 2-allylphenol (96.0 g, 0.72 mol, 16% excess to DCBN) were charged into a 1000-mL four-necked round-bottom flask fitted with a condenser, nitrogen inlet, Dean–Stark trap, thermometer, and mechanical stirrer. The mixture was stirred for 15 min under a purge of N<sub>2</sub>. Then anhydrous K<sub>2</sub>CO<sub>3</sub> (99.0 g, 0.72 mol) was charged to the flask and the reaction mixture heated to 120°C. After maintaining this temperature for 2 h, the temperature was raised to 150°C and the toluene was removed. Then the reaction mixture was heated to 170°C and kept at that temperature for 4 h. Finally, the temperature was raised to 190°C and maintained for 4 h. After cooling to room temperature, the reaction mixture was poured into 2 L of ice water. The precipitate was filtered and washed with a cold dilute sodium hydroxide solution (5 wt %) and water. The precipitate was dissolved in acetone, reprecipitated to remove unreacted 2-allylphenol and any trapped salts, filtered, and dried. After recrystallizations from a mixture of CH<sub>3</sub>OH and H<sub>2</sub>O (4:1, v/v), DPPB was obtained as white crystal needles (88.0 g, mp 164–166°C, 77% yield). ANAL. Calcd for C<sub>25</sub>H<sub>21</sub>NO<sub>2</sub>: C, 81.74%; H, 5.72%; N, 3.81%. Found: C, 82.02%; H, 5.74%; N, 3.74%.

### Blending, Copolymerization, and Preparation of Impact and Shear Specimens

The BMDPM and DPPB in certain compositions were first ground in a glass mortar and then thoroughly mixed using a vibrating mixer. The blend was sieved with a 180 mesh/cm<sup>2</sup> sieve. A fine solid powder of the blend (6.0 g) was then placed in a 5.8 × 0.86 × 0.62 cm aluminum mold, 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 turned completely 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 complete the cure. The shear specimens of the blend were obtained by using the following procedure: the fine solid powder of the above blend (5.0 g) was placed on a metal plate



**Figure 1** The procedure for synthesis of the novel monomer.

with a temperature controller. The temperature on the surface of the plate was maintained at  $160 \pm 2^\circ\text{C}$ . After melting and keeping at that temperature for 15 min, the prepolymer was quickly applied to two preheated (at  $160^\circ\text{C}$ )  $7.02 \times 2.02 \times 0.20$  cm aluminum slices; 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 usual manner and moved to an oven at  $160^\circ\text{C}$ . The temperature was maintained at  $160^\circ\text{C}$  for 6 h. Then the temperature was elevated and kept at  $180^\circ\text{C}$  for 4 h,  $200^\circ\text{C}$  for 2 h,  $220^\circ\text{C}$  for 5 h, and  $240^\circ\text{C}$  for 2 h. The specimens for testing the shear strength were thus obtained.

### Instrumentation

The melting point was measured by the capillary method and was uncorrected. The FTIR spectra were recorded on a Nicolet 20SDX-IR spectrophotometer using KCl pellets. Elemental analyses were carried out on a Calo Erba 1106 elemental analyzer. <sup>1</sup>H-NMR was carried out on a Bruker ACP-300 spectrometer (300 MHz) using CDCl<sub>3</sub> as a solvent and TMS as an internal standard. The curing behavior of the prepolymers of BMDPM with DPPB was studied using a Du Pont DSC2910 differential scanning calorimetry (DSC) instrument at a heating rate  $10^\circ\text{C}/\text{min}$  in nitrogen. The thermal stability of the cured resins was determined on a Du Pont TGA2950 thermogravimetric analysis (TGA) analyzer at a heating rate of  $10^\circ\text{C}/\text{min}$  in air. The shear tests were carried out using a tension tester according to China State Standard GB1450.1-83. The impact test was carried out using a Charpy tester according to China State Standard GB25711-81.

## RESULTS AND DISCUSSION

### Synthesis and Characterizations of DPPB

No report about the synthesis of DPPB was found in the literature. However, the procedure for

preparation of the analogue of the compound, 2,6-di(4-aminophenoxy) benzonitrile, was reported by several authors.<sup>15–18</sup> In summary, the analogue was prepared by reacting 2,6-difluorobenzonitrile with 4-aminophenol in a dipolar aprotic solvent in the presence of some inorganic bases. The procedure was not practical because of the complex pretreatment procedure for solvents and the use of the expensive raw material, 2,6-difluorobenzonitrile.<sup>15–18</sup> In this study we describe a convenient synthetic procedure using a cheaper raw material, DCBN. The solvent NMP was directly used without any pretreating procedure. The water, which was contained in the solvent and formed by the reaction of 2-allylphenol and K<sub>2</sub>CO<sub>3</sub>, was removed by the toluene–water azeotropic mixture. The procedure is shown in Figure 1.

We found in our work that the amount of oxygen in the reaction system was an important factor for preparation of DPPB. It was very necessary for oxygen to be absent from the reaction system, which was by means of continuously introducing pure N<sub>2</sub> to the reaction system. Contrarily, a dark red solution was formed in the initial stage of the reaction and the yield of DPPB was strongly decreased due to the formation of an oxide of 2-allylphenol. It was also important for increasing the yield of DPPB to maintain the reaction system at higher temperatures ( $170\text{--}190^\circ\text{C}$ ) for a longer reaction time ( $>6$  h).

Although some dipolar aprotic solvents such as *N,N*-dimethylacetamide or dimethylsulfoxide (DMSO) could be used in this work, preparation of DPPB needed more reaction time because of the low reactivity of DCBN at the boiling temperature of the solvents ( $<180^\circ\text{C}$ ). Therefore, NMP was preferred because of its higher boiling point.

It was very interesting that the rearrangement product of the allyl group was found. According to the initial design, we wished to obtain the monomer containing allyl groups by the synthetic procedure just mentioned. However, no signals as-

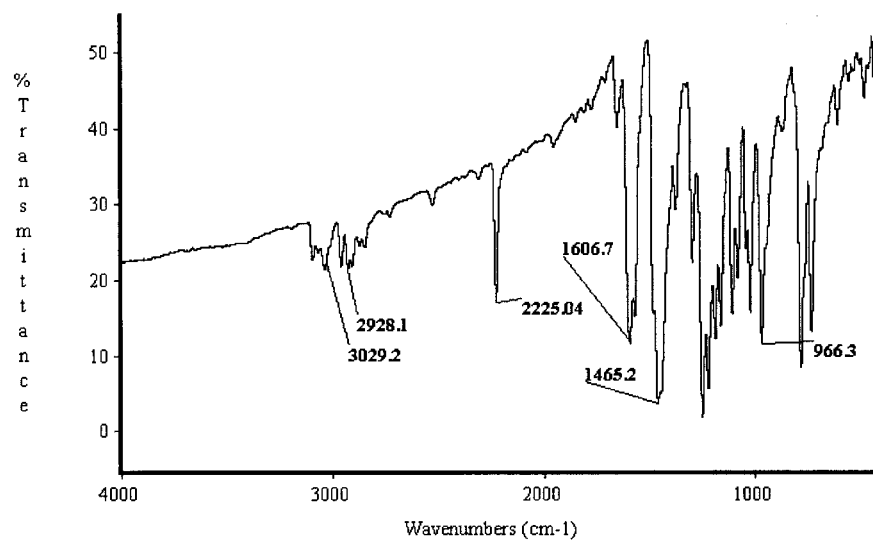


Figure 2 The FTIR spectrum of DPPB.

signed to allyl groups could be observed by FTIR and  $^1\text{H-NMR}$  spectra of the product shown in Figures 2 and 3. Indeed, the absorption bands at  $966\text{ cm}^{-1}$  assigned to  $-\text{CH}=\text{CH}-$  are found in

Figure 2, and a doublet at 1.67 ppm assigned to  $-\text{CH}_3$  is observed in Figure 3. These spectra mean that the product did not contain allyl groups but did contain propenyl groups with an

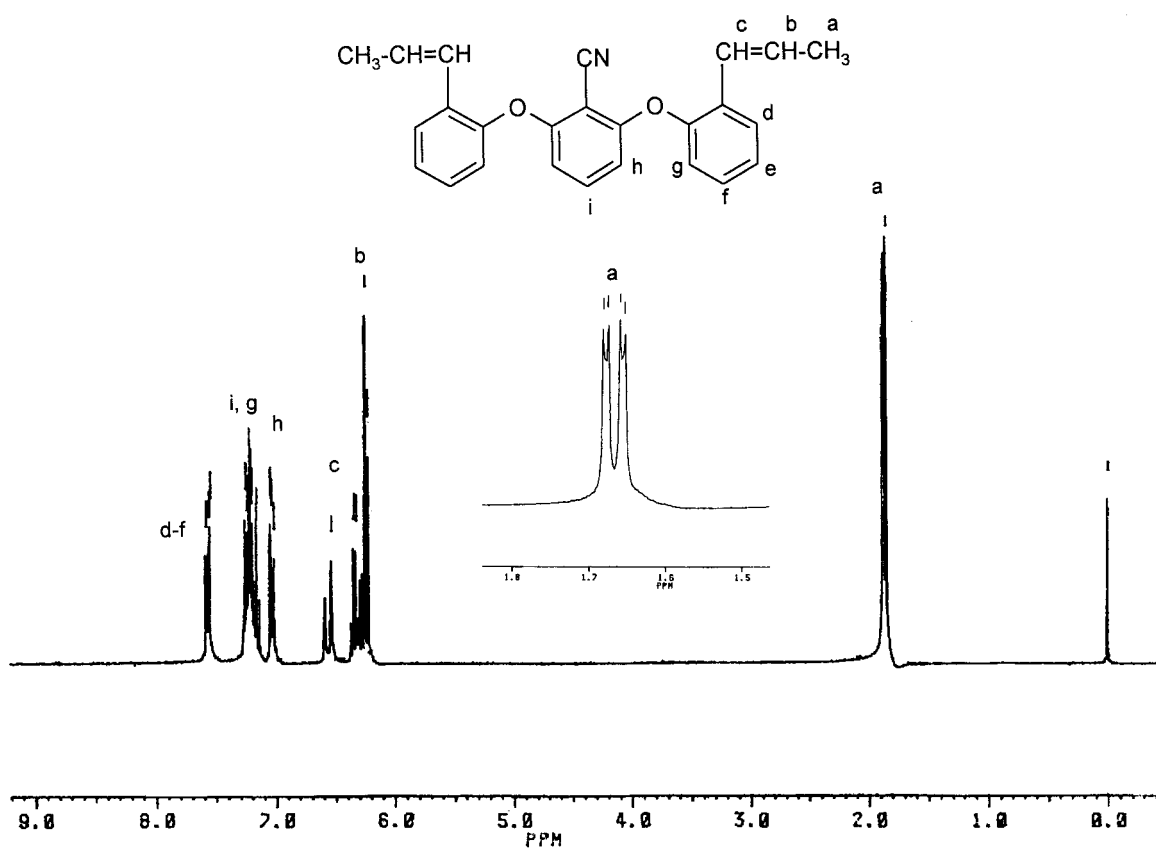


Figure 3 The  $^1\text{H-NMR}$  spectrum of DPPB (300 MHz).

**Table I FTIR Characteristics of DPPB**

Absorption ( $\text{cm}^{-1}$ )	Assignment
966, 3029	<i>trans</i> —CH=CHCH <sub>3</sub>
1606	Aromatic ring
1247, 1043	—C—O—C—
2225	—CN
2928	—CH <sub>3</sub>

E-configuration. The results also showed that the allyl could be rearranged to propenyl in the reaction system in the presence of a base at a higher temperature.<sup>19</sup>

It is worthy of being noted that the allyl compounds are only rearranged to propenyl at high temperature by a strong base, such as *t*-BuOK in DMSO, according to the report of Crivello and Conlon.<sup>19</sup> However, as compared with *t*-BuOK (potassium *tert*-butoxide), the K<sub>2</sub>CO<sub>3</sub> employed in our work is not strong base and it also leads the rearrangement of allyl. This means that the basicity of K<sub>2</sub>CO<sub>3</sub> in NMP at high temperature is similar to that of *t*-BuOK in DMSO.

The detailed spectrum data of DPPB are shown in Table I and Figure 3. By means of the data and the elemental analysis result (Experimental section), the chemical structure of the monomer is confirmed as being the same as proposed.

### Thermohomopolymerization of DPPB

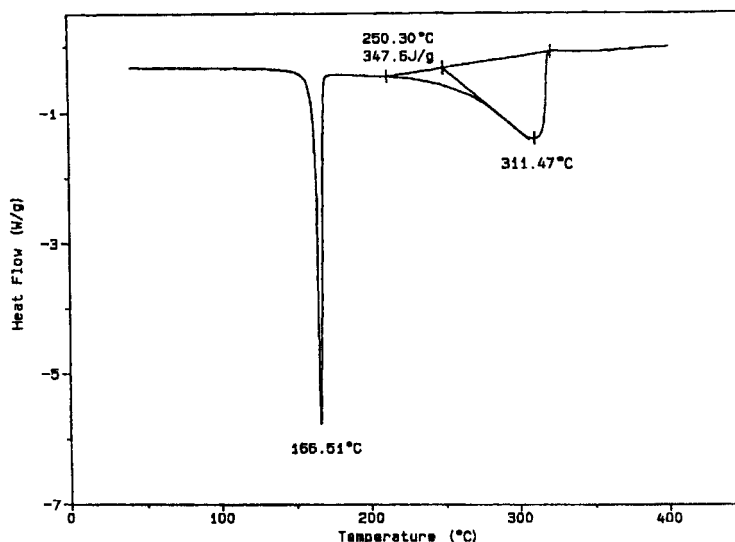
Figure 4 presents DSC traces of DPPB with heating. The endothermic peak at 166°C is attributed

to melting of DPPB. The lack of an exothermic peak from 166 to 400°C shows that thermohomopolymerization of DPPB is negative in that range of temperatures.

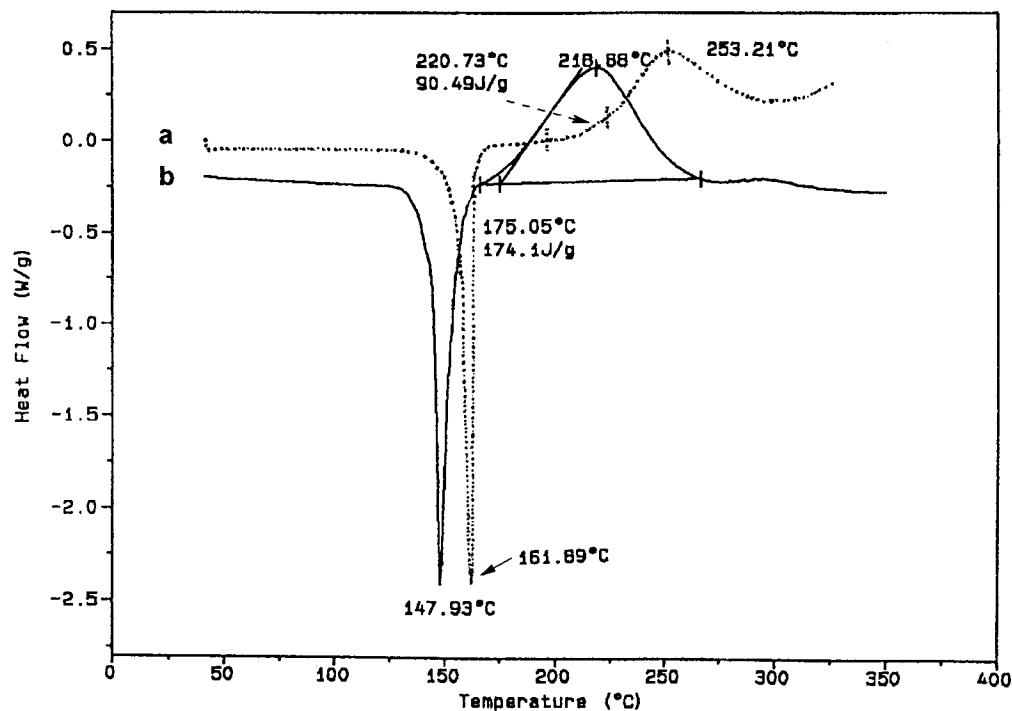
It is puzzling why an endothermic peak appears at 311°C in Figure 4. The answer can be given after observing the sample box in the DSC apparatus. No residue of the monomer sample in the box was observed after single scanning from 50 to 400°C indicated that the monomer was evaporated under the DSC trace condition. In other words, the endothermic peak appearing at 311°C is attributed to boiling of DPPB. An important datum for the monomer, heat of boiling ( $\Delta H_b$ ) can be obtained from the figure, the value of which is 347.5 J/g.

### Copolymerization Reaction of DPPB with BMDPM

In the DSC trace of BMDPM a sharp endotherm indicating melting is observed at 162°C (Fig. 5, spectrum a). Mixing of DPPB with BMDPM (45 wt %) results in a decrease in the melting transition (Fig. 5, spectrum b). This means that a DPPB/BMDPM comelting substance with a melting point of 148°C was formed. In the figure exothermic transitions of curing of BMDPM or DPPB/BMDPM are also observed in the temperature range of 175–300°C. The heat of the curing reaction ( $\Delta H$ ), the fusion temperature of BMDPM (or DPPB/BMDPM,  $T_m$ ), the onset temperature of the curing reaction ( $T_{\text{onset}}$ ), and the exothermic peak position ( $T_{\text{exo}}$ ) are determined from the DSC traces and are listed in Table II. An increase in



**Figure 4** The DSC traces of DPPB.



**Figure 5** The DSC traces of BMDPM (spectrum a) and the DPPB/BMDPM blend (45 wt %, spectrum b).

the  $\Delta H$  values and a decrease in the  $T_m$  is produced by adding DPPB to BMDPM.

Table III is the comparison of the gel time between BMDPM and the DPPB/BMDPM blend. The gel time was measured by the following procedure: a fine solid powder of the DPPB/BMDPM blend in a certain composition (1.0–2.0 g) was placed on an electrothermal metal plate with a temperature controller, which kept the testing temperature within  $\pm 2^\circ\text{C}$ . Then the liquid was stirred with a glass rod when the blend was melted. With the increase of time the viscosity of the liquid became high and a fibrillous string appeared when the rod drew the sticky liquid. When gelation of the sample occurred, none of the

fibrillous string could be observed. The gel time was defined as the period from putting the sample on the electrothermal metal plate to that when no fibrillous string could be observed. We found that adding DPPB to BMDPM greatly shortened the gel time of BMDPM. It also means that the reaction activity of DPPB with BMDPM is very high.

The relative thermal stability for the cured DPPB/BMDPM copolymer (45 wt % DPPB) is evaluated by thermogravimetry. The results are given in Figure 6 and Table IV. A high heat resistance index ( $T_i$ ) of  $229^\circ\text{C}$  indicates that the DPPB/BMDPM resin has a high level of thermooxidative stability.

**Table II** Comparison of Thermal Characteristics between BMDPM and DPPB/BMDPM Blend

	$T_m$ ( $^\circ\text{C}$ )	$T_{\text{onset}}$ ( $^\circ\text{C}$ )	$T_{\text{exo}}$ ( $^\circ\text{C}$ )	$\Delta H$ (J/g)
BMDPM	162	221	253	90.49
DPPB/BMDPM	148	175	219	174.1

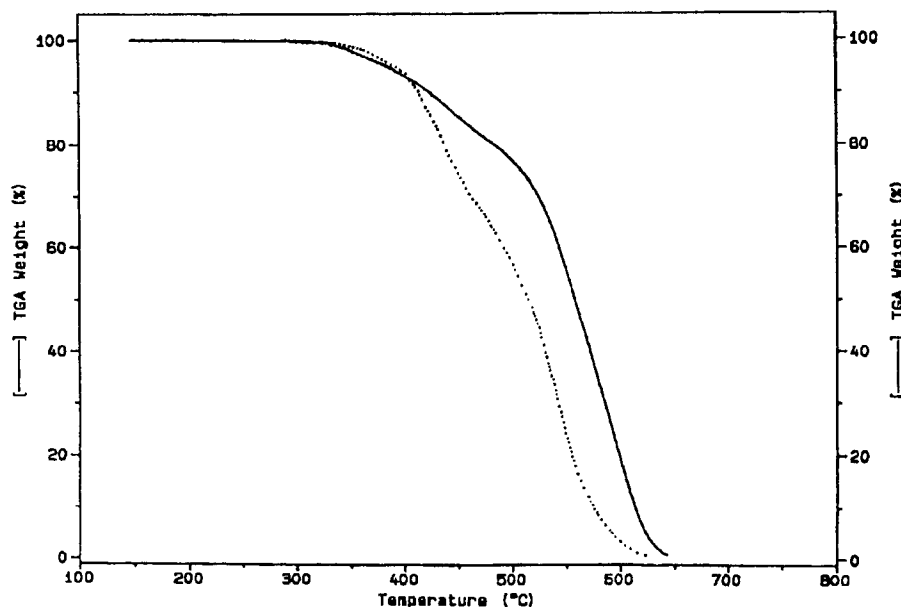
The composition of DPPB in the blend is 45 wt %.

**Table III** Gel Time of DPPB/BMDPM Blend (45 wt %)

Temp. ( $^\circ\text{C}$ )	Gel Time (min)	
	BMDPM	DPPB/BMDPM
160	—	13
180	117	6
220	4.5	0.7

The gel time was measured according to the method described in the text.





**Figure 6** The TGA curves of (···) BMDPM and (—) the DPPB/BMDPM cured resin (45 wt %).

#### Mechanical Properties of DPPB/BMDPM Resin

DPPB was expected to improve the shear properties of BMDPM. Figure 7 shows the shear strength dependence on the composition of DPPB/BMDPM copolymers by weight. The curve shows a maximum in shear strength when the composition of DPPB in the copolymer is 45 wt %. As compared with the neat BMDPM matrix, the copolymer matrix can attain 4.7 times the shear strength. In order to further investigate the properties of the DPPB/BMDPM copolymer, the impact strength of the copolymer in which the composition of DPPB is 45 wt % was measured. The results showed that the impact strength was 4.77 kJ/m<sup>2</sup>, which is 5.5 times that of neat BMDPM. The reason why introducing DPPB to BMDPM can improve the mechanical properties of the resin will be investigated in future work.

#### CONCLUSION

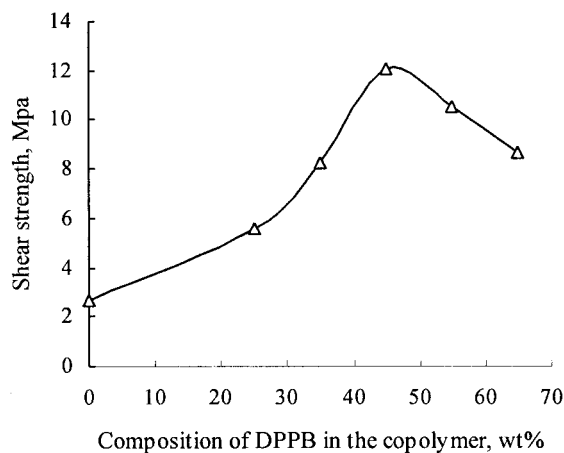
The following conclusions can be obtained based on this work:

1. The novel monomer DPPB was synthesized by the reaction of 2,6-dichlorobenzonitrile and 2-allylphenol in the presence of anhydrous K<sub>2</sub>CO<sub>3</sub> in NMP.
2. The DPPB/BMDPM copolymer (45 wt % DPPB) had a lower melting point and a lower peak exothermal temperature than those of neat BMDPM, and the cured copolymer had higher thermooxidative stability.
3. DPPB can effectively improve the shear strength and impact strength of BMDPM. Better results were obtained when the DPPB composition was 45 wt % in the DPPB/BMDPM blend.

**Table IV** TGA Data of DPPB/BMDPM Copolymer

	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
DPPB/BMDPM	384	424	453	524	558	443	555	229

The composition of DPPB in the copolymer is 45 wt %;  $T_5$ ,  $T_{10}$ ,  $T_{15}$ ,  $T_{30}$ , and  $T_{50}$ , the temperatures when the weight loss is 5, 10, 15, 30, and 50%, respectively;  $T_{\max 1}$  and  $T_{\max 2}$ , the decomposition peak temperatures;  $T_i$ , the heat resistant temperature index,  $T_i = 0.49[T_5 + 0.60(T_{30} - T_5)]$ .



**Figure 7** The shear strength versus the composition (wt %) of the DPPB/BMDPM blend.

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