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Synthesis and characterization of a novel functional monomer containing two allylphenoxy groups and one *S*-triazine ring and the properties of its copolymer with 4,4′-bismaleimidodiphenylmethane (BMDPM)

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Abstract

A novel modifier for bismaleimide (BMI), 2,4-di (2-allylphenoxy)-6-(2-naphthyloxy)-1,3,5-triazine (DAPNPT) with higher yield was prepared in one-pot by reacting cyanuric chloride with 2-allylphenol at first, and then by directly treating the adduct with 2-naphthol without separation. The chemical structure of the monomer was characterized by FTIR, mass spectrum, ^{1}H NMR and ^{13}C NMR. By means of differential scanning calorimeter, the thermo-homopolymerization behavior of DAPNPT was investigated and the results showed that DAPNPT did not polymerize at a range of temperatures from 50 to 250°C. The properties of the DAPNPT-modified 4,4′-bismaleimidodiphenylmethane (BMDPM) resins were also studied. The results showed that DAPNPT could effectively improve mechanical properties of BMDPM resin without greatly decreasing heat resistance of the resin. Better results were obtained when the molar ratio of DAPNPT/BMDPM was 1:2. © 2001 Published by Elsevier Science Ltd.

Keywords: 2,4-Di (2-allylphenoxy)-6-(2-naphthyloxy)-1,3,5-triazine (DAPNPT); Triazine derivatives; Monomers

1. Introduction

Among the addition type polyimides, bismaleimides (BMIs) were more important because of their high thermal stability, nonvolatility and low cost [1]. Some examples of applications include multilayer-printed boards for large-scale computers, encapsulation resin and passivation layer for IC dies, advanced carbon fiber composites for aerospace industry, and structural adhesives [1,2]. However, directly using the neat resins as matrix resins for advanced composites was limited due to their inherent brittleness. Although a lot of methods for improving the toughness of the resins have been studied in the past thirty years, including polyetherimide, polysiloxaneimide, allyl-termined copolymers, reactive rubber, and so on [3–13], the majority of them were unsatisfactory [4]. The reason was that the methods assuredly increased the toughness of the resins, but heat resistance of the cured resins was usually decreased [1]. In some cases, some modifiers, such as rubber and some thermoplastic polymers, could strongly decrease the heat resistance [1,4].

According to the principles of molecular design, introducing flexible linkage or chains into BMI can effectively improve the toughness of the resin [7]. On the other hand, introducing aromatic heterocyclic groups into the resin can prevent strongly decreasing heat resistance of the cured resin [1]. It was well known that allyl group was 'tough' [1,10,12–15] and *S*-triazine rings were 'heat resistant' [16,17]. 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 was to investigate the properties of the copolymers between the modifiers containing allyl groups and *S*-triazine rings and a popular commercial BMI, 4,4′-bismaleimidodiphenylmethane (BMDPM). In our previous work, we reported the preparation of triallylphenoxytriazine (TAPT) and the properties of its copolymer with BMDPM [18]. In order to obtain new kind of allylphenoxy triazine modifiers and study their properties, especially the properties of their copolymers with BMI, a novel

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monomer, 2,4-di (2-allylphenoxy)-6-(2-naphthyloxy)-1,3,5-triazine (DAPNPT) was synthesized in our laboratory. In this paper, we report the synthesis of the monomer and the properties of its copolymer with BMDPM. Because of more reactive positions in the monomer, it is expected that the monomer not only can be used as a modifier for BMI, but also can be used in the other fields such as in drugs, optical and biochemical materials.

2. Experimental

2.1. Materials

Cyanuric chloride was provided by Chenguang Institute of Chemical Industry, the Ministry of Chemical Industry of China, and was purified by distillation at first and by recrystallizations then from petroleum ether (60–90°C), m.p. 145–147°C. 2-Allylphenol was prepared by the reported method [19] and purified by fractional distillation under vacuum, b.p. 110–113°C/0.092 MPa. IR (cm^{-1}) (KCl), 3482 (–OH), 997, 916 (allyl), 3075, 1637 (aryl ring), 2906, 2976 ($-CH_2-$). Anal. calcd for $C_9H_{10}O$: C 80.59%; H 7.46%. Found: C 80.89%; H 7.55%. MS (EI), *m/z* (relative intensity, %): 134 (M^+, 70.99), 91 (100). ^1H NMR ($CDCl_3$, chemical shifts were referenced to TMS), δ (ppm): 5.16 ($=CH_2-$), 5.97 ($-CH=$), 3.39 ($-CH_2-$), 6.78–7.14 (phenyl ring). BMDPM was an industrial product, and was recrystallized twice from toluene before use. Other materials were used as received. AR grade solvents were used.

2.2. Preparation of DAPNPT

To stirred cyanuric chloride (18.45 g, 0.1 mol), dissolved in acetone (200 ml), was added dropwise a solution of 2-allylphenol (26.67 g, 0.20 mol) and NaOH (8.00 g, 0.20 mol) in H_2O (100 ml) saturated by N_2 at 0–5°C. The reaction mixture was stirred vigorously for 1 h at 0–5°C and for 2 h at 15–20°C. At these stages the Fujiwara test[1] [20] for dichlorotriazine was positive. The temperature was allowed to increase to 25°C and maintained for 1 h at 25–30°C. When the test was negative, a solution of 2-naphthol (14.4 g, 0.1 mol) and NaOH (4.00 g, 0.1 mol) in H_2O (100 ml) saturated by N_2 was added dropwise to the mixture for 1 h. After the reaction mixture was stirred for 2 h at 35–40°C, the temperature was decreased to 0–5°C. A sticky pale yellow solid was filtered, washed with cold water, then with ethyl alcohol and finally recrystallized twice from a solution of isopropyl alcohol and acetone (3:1, v/v). DAPNPT was obtained as white cubic crystals in a yield of 70%, m.p. 142.5–143°C. Anal. calcd for $C_{31}H_{25}N_3O_3$: C 76.39%; H 5.13%; N 8.62%. Found: C 76.33%; H 5.18%; N 8.56%.

2.3. Blending, copolymerization, and preparation of the impact and shear specimens

Mixture of BMDPM and DAPNPT in certain composition was first ground in a glass mortar, and then thoroughly mixed using a vibrating mixer. The blend was sieved with a 180 mesh cm^{-2} sieve. Fine solid powder of blend (6.0 g) was then placed in an aluminum mould with dimensions of 5.8 cm × 0.86 cm × 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 blend had turned completely solid. The temperature was then elevated and kept at 180°C for 5 h, 200°C for 2 h, 220°C for 5 h and at 240°C for 2 h to completely get cured. The impact specimens of the blends were obtained thus. The shear specimens of the blend were obtained by using following procedure: the fine solid powder of the blend mentioned above was placed on a metal plate with temperature controller. The temperature on the surface of the plate was maintained at 160 ± 2°C. After melting, the blend was applied quickly to two preheated (at 160°C) aluminum slices (the dimension of both the slices was 7.02 cm × 2.02 cm × 0.20 cm, and the applied area of the prepolymer was 2.02 cm × 2.02 cm). The applied area of aluminum slices were quickly overlapped and moved to an oven at 160°C. The temperature was maintained at 160°C for 6 h (in the period a pressure of 0.1 kg cm^{-2} was brought to bear on the applied area of the aluminum slices). Then the temperature was elevated and kept at 180°C for 5 h, 200°C for 2 h, 220°C for 5 h and at 240°C for 2 h. Thus, the specimens for testing shear strength were obtained.

2.4. Instrumentation

Melting point was measured by capillary method and uncorrected. FTIR spectra were recorded on a Nicolet 20SDX-IR spectrophotometer using KCl pellets. ^1H NMR and ^{13}C NMR were carried out on a Bruker ACP-300 Spectrometer (300 MHz), using CD_3COCD_3 (or $CDCl_3$) as solvent and TMS as internal standard. Curing behaviors of DAPNPT/BMDPM resins were studied using a Dupont DSC2910 differential scanning calorimeter at a heating rate 10°C min^{-1} in nitrogen. Thermal stability of the cured resins was determined on a Dupont TGA2950 thermogravimetric analyzer at a heating rate 10°C min^{-1} in air. Dynamic mechanical analysis of the cured resins was carried out on a Dupont DMA983 tester at a heating rate of 5°C min^{-1} in nitrogen. The dimension of the specimens of the cured resins for DMA analysis was 5 cm × 0.2 cm × 0.05 cm.

The impact test was carried out using a Charpy tester according to China State Standard GB25711-81. The shear

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[1] Fujiwara test for dichlorotriazine: an aqueous solution of pyridine was spotted onto a filter paper, followed by a 2 M solution of NaOH, and the reaction mixture was spotted onto the alkaline pyridine. In the presence of dichlorotriazine, a yellow color appears.

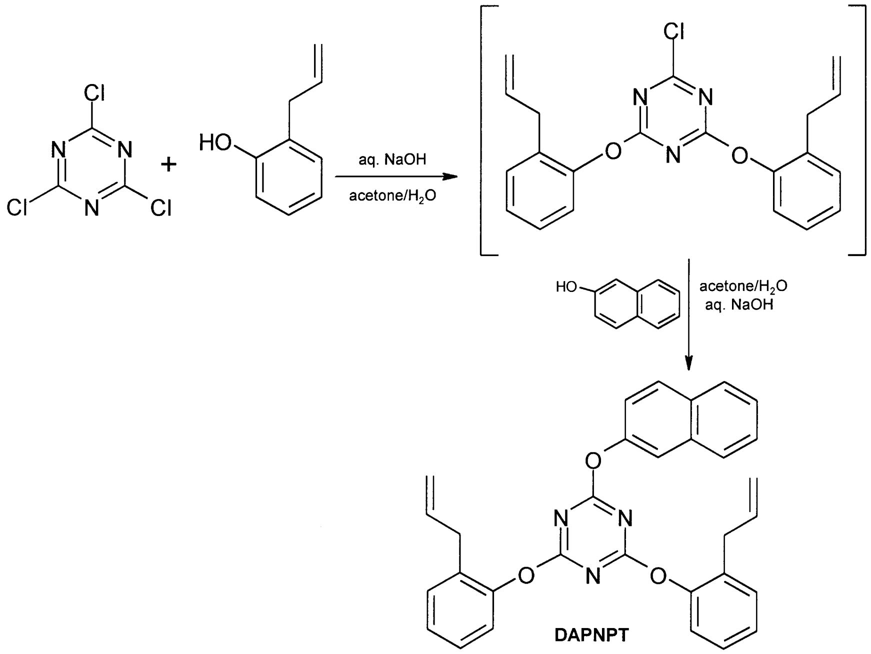

Fig. 1. The procedure for preparation of DAPNPT in this paper.

test was carried out using a Tension tester according to China State Standard GB 1450.1-83.

3. Results and discussion

3.1. Synthesis and characterization of DAPNPT

Until now, no report about the synthesis of DAPNPT has been found. Generally, the analogues of the monomer, 2-alkyloxy (or alkylamino)-4, 6-diallyloxy-1,3,5-triazine, were synthesized by a two-step procedure [21–23]. Thus, firstly, the intermediates, 2-alkyloxy (phenoxy or *N*-alkylamino)-4,6-dichloro-1,3,5-triazine were prepared by the reaction of cyanuric chloride and alcohols or alkylamines. Then, the intermediates, rigorously purified, were treated with a large amount of allyl alcohol to obtain the final products. The two-step procedure was not convenient because of the complicated route for purification of the crude intermediates [21–23]. In many cases, it was difficult to prepare the pure intermediates suitable for syntheses of the final products after recrystallizing twice the crude intermediates because the intermediates were easy to hydrolyze [21,22].

In this paper, we report a convenient one-pot method to synthesize DAPNPT. The procedure is shown in Fig. 1.

The route was suitable for preparation of DAPNPT in large scales. The intermediate, 2-chloro-4,6-di (2-allylphenoxy)-1,3,5-triazine without separation from the reaction system was directly treated with 2-naphthol, and the final product could be isolated as white yellow solid from the reaction system when the reaction was completed.

However, it must be pointed out that two factors, the molar ratio between cyanuric chloride and 2-allylphenol and the amount of dichlorotriazine in the reaction system, were more important for preparation of the monomer. It was very necessary to keep the molar ratio between cyanuric chloride and 2-allylphenol at 1:2 and use Fujiwara test [20] for dichlorotriazine. Contrarily, side products could be formed in the reaction system. The reason was that either the excess of cyanuric chloride (or 2-allylphenol) or the remaining dichlorotriazine in the reaction system could cause the formation of complex by-products, which greatly affect the yield and purification route of the final monomer.

The chemical structure of DAPNPT was characterized by FTIR, ^{1}H NMR, ^{13}C NMR and mass spectrum. Fig. 2 is an FTIR spectrum of DAPNPT. Characteristic absorption peaks appear at 1560 and 1357 cm^{-1} due to the resonance

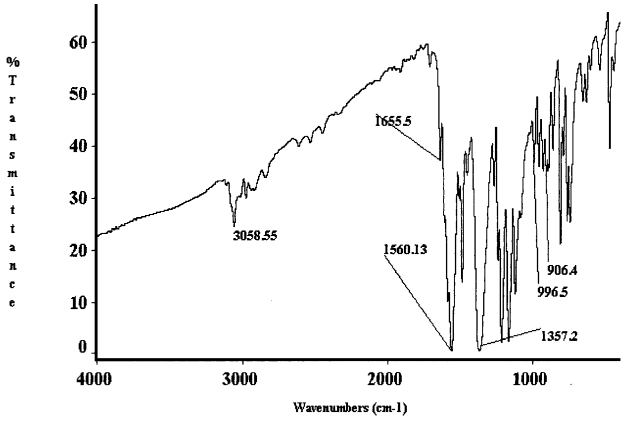

Fig. 2. FTIR spectrum of DAPNPT.

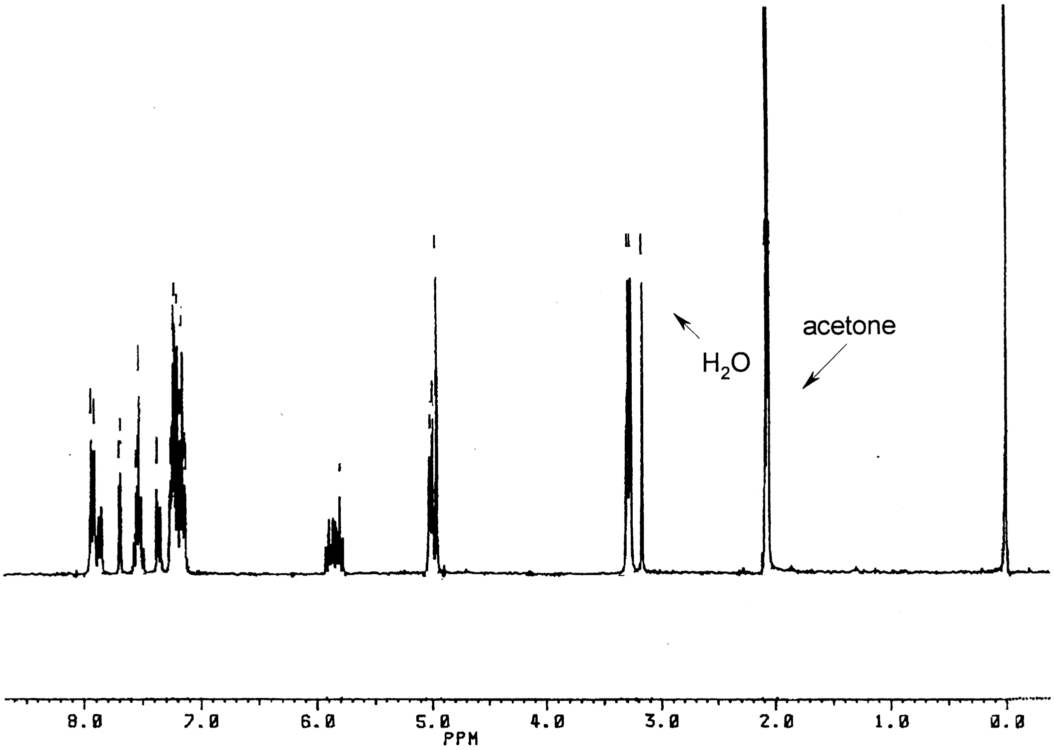

Fig. 3. ^{1}H NMR spectrum of DAPNPT (300 MHz, 25°C, in acetone-d_6).

of C–N in triazine ring. The absorption bands at 995 and 906 cm^{-1} were assigned to allyl groups. Characteristic absorption peaks appear at 3056 and 1639 cm^{-1} due to the resonance of aromatic rings. ^{1}H NMR and ^{13}C NMR spectra of DAPNPT in Figs. 3 and 4 confirm further the structure proposed. ^{1}H NMR spectrum of DAPNPT in Fig. 3 shows eight groups of different proton signals. Among the signals, five groups were contributed to the phenyl rings and the

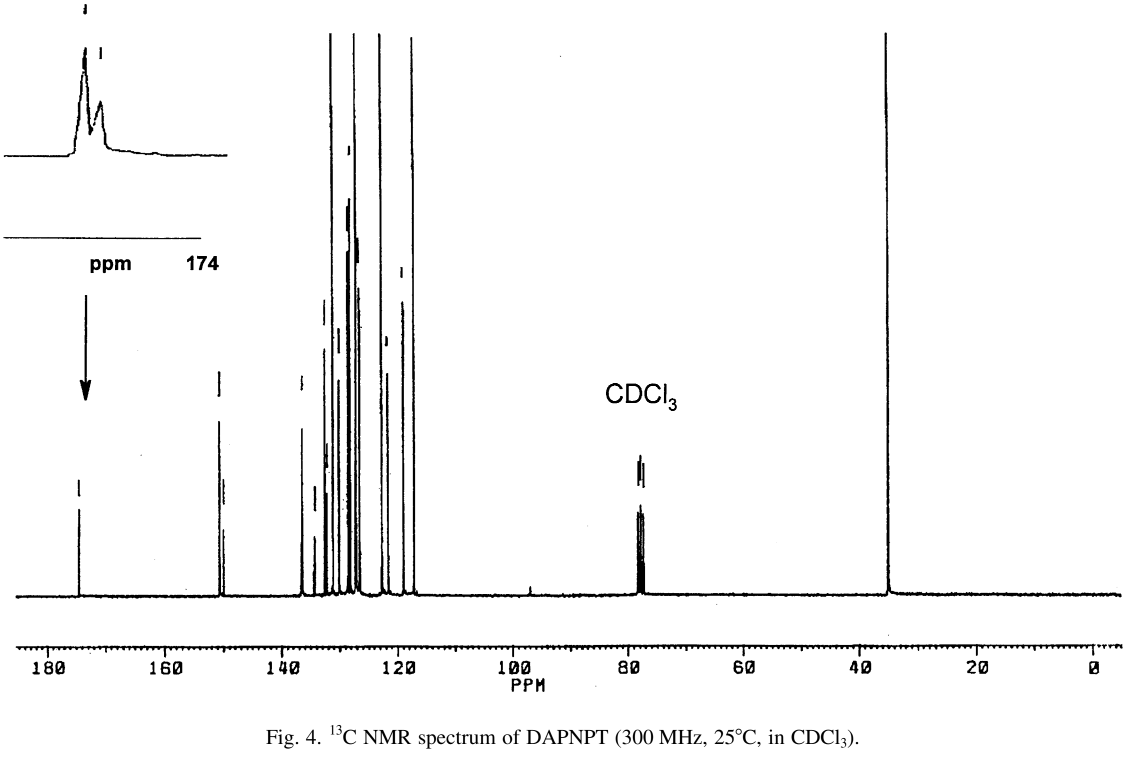

Fig. 4. ^{13}C NMR spectrum of DAPNPT (300 MHz, 25°C, in $CDCl_3$).

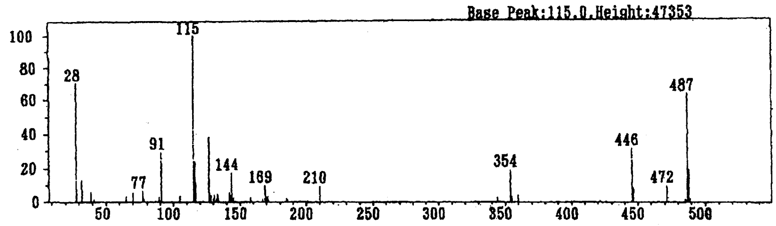

Fig. 5. Mass spectrum of DAPNPT (70 eV, without heating).

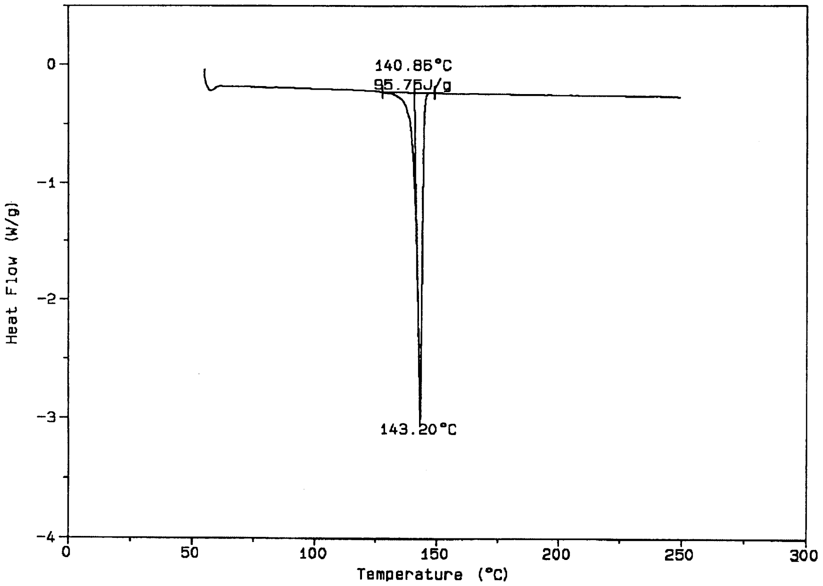

Fig. 6. DSC traces of DAPNPT.

naphthyl ring in DAPNPT. The corresponding range of chemical shifts for the phenyl rings and the naphthyl ring were 7.12–7.37 and 7.37–7.93 ppm, respectively. Three groups of the proton signals contributed to the allyl group are also observed in Fig. 3. The protons of $-CH_2-$ in allyl group gave a doublet at 3.26 ppm. The multiples at 4.98 and 5.80 ppm indicate protons of $CH_2=$ and $=CH-$ groups, respectively. ^{13}C NMR spectrum of DAPNPT in Fig. 4 shows 21 different carbon signals as expected. The corresponding data (ppm) are given in the following: 34.9 ($-\mathit{C}H_2CH{=}CH_2$); 116.9 (phenyl rings, $-\mathit{C}$-6); 118.9 (naphthyl ring, $-\mathit{C}$-3); 121.5 (naphthyl ring, $-\mathit{C}$-4); 122.6 ($-CH_2CH{=}\mathit{C}H_2$); 126.4 (phenyl rings: $-\mathit{C}$-4); 126.9 (naphthyl ring, $-\mathit{C}$-7); 127.1 (naphthyl ring, $-\mathit{C}$-6); 127.9 (phenyl rings, $-\mathit{C}$-5); 128.3 (naphthyl ring, $-\mathit{C}$-5); 128.4 (naphthyl ring, $-\mathit{C}$-8); 129.9 (naphthyl ring, $-\mathit{C}$-9); 130.9 (phenyl rings, $-\mathit{C}$-3); 132.1 (naphthyl ring, $-\mathit{C}$-10); 132.4 (phenyl rings, $-\mathit{C}$-2); 134.2 (naphthyl ring, $-\mathit{C}$-2); 136.3 ($-CH_2\mathit{C}H{=}CH_2$); 149.8 (naphthyl ring, $-\mathit{C}$-1); 150.5 (phenyl rings, $-\mathit{C}$-1); 174.3 (triazine ring: $-\mathit{C}$-6); 174.4 (triazine ring, $-\mathit{C}$-2, 4). Mass spectrum of DAPNPT in Fig. 5 gives a molecular ion peak of 487 (M^+), which also means that the chemical structure of DAPNPT was the same as that proposed.

3.2. Thermo-homopolymerization reaction of DAPNPT

Fig. 6 is DSC traces of DAPNPT on heating. The endothermic peak at 143°C was attributed to melting of DAPNPT. No exothermic peak from 143 to 250°C showed that thermo-homopolymerization of DAPNPT was negative in this range of temperatures.

3.3. Copolymerization reaction of DAPNPT with BMDPM

In DSC trace of BMDPM a sharp endothermic peak indicating melting was observed at 162°C (Fig. 7(A)). However, an endothermic peak was observed at 134°C (Fig. 7(B)) for the DAPNPT/BMDPM blend (1:2 molar ratio). It

Table 1
Comparison of thermal characteristics between neat BMDPM and BMDPM/DAPNPT copolymer

	T_m (°C)	Onset temperature (°C)	T_{exo} (°C)	ΔH (J g^{-1})
BMDPM	162	221	253	90.49
DAPNPT/BMDPM (1:2 molar ratio)	134	226	266	242.2

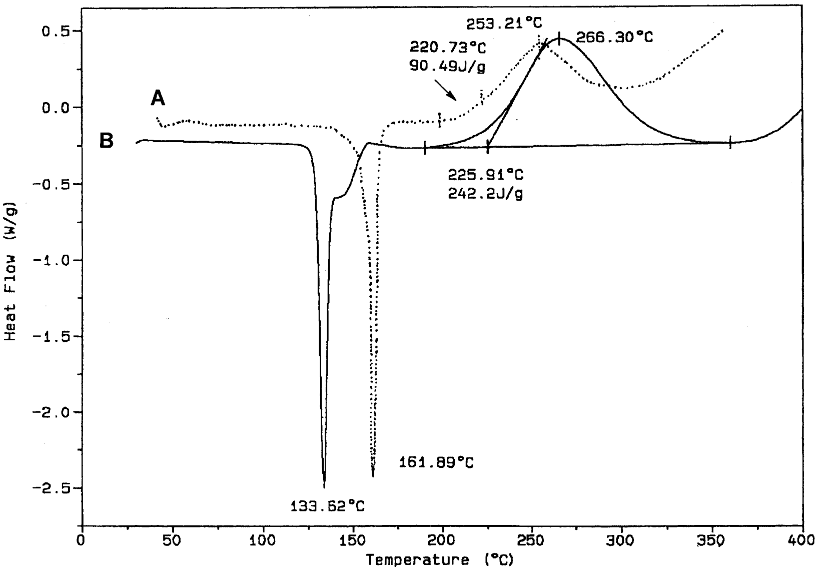

Fig. 7. DSC traces of BMDPM (A) and the DAPNPT/BMDPM blend (B).

means that a DAPNPT/BMDPM co-melting substance with a melting point of 134°C was formed. In this figure exothermic transitions of curing of BMDPM or DAPNPT/BMDPM copolymer were also observed in the temperature range of 200–300°C. Heat of curing reaction (ΔH), fusion temperatures of BMDPM and DAPNPT/BMDPM copolymer (T_m), onset temperature of curing reaction, and exothermal peak position (T_{exo}) were determined from DSC traces and are listed in Table 1. It was seen that adding DAPNPT to BMDPM caused an increase in ΔH values and a decrease in fusion temperature (T_m).

Relative thermal stability for the cured DAPNPT/BMDPM copolymer (1:2 molar ratio) was evaluated by thermogravity. The results are given in Fig. 8 and Table 2, respectively. A higher heat resistant index (T_i), 206°C (see Table 2), indicated that DAPNPT-modified BMDPM resin had a high level of thermo-oxidative stability.

3.4. Mechanical properties of DAPNPT-modified BMDPM resin

DAPNPT was expected to improve mechanical properties

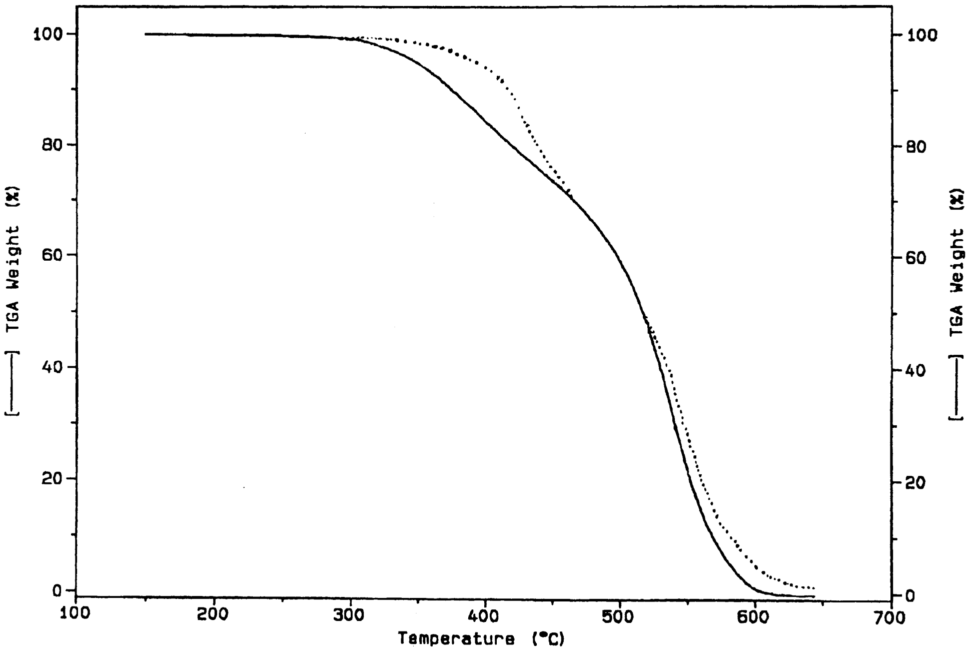

Fig. 8. TGA curves of the cured BMDPM (…) and DAPNPT/BMDPM (—) resin.

Table 2
The TGA data of the cured BMDPM/DAPNPT resin in air (T_5, T_{10}, T_{15}, T_{30} and T_{50} are the temperatures when weight loss was 5, 10, 15, 30 and 50%, respectively. $T_{\max1}$ and $T_{\max2}$ are decomposition peak temperatures. T_i is the heat-resistant temperature index calculated according to $T_i = 0.49[T_5 + 0.69(T_{30} - T_5)]$) (see Ref. [6])

	Weight loss temperature (°C)							
	T_5	T_{10}	T_{15}	T_{30}	T_{50}	$T_{\max1}$	$T_{\max2}$	T_i
BMDPM	395	415	428	465	516	432	542	214
BMDPM/DAPNPT (2:1 molar ratio)	350	377	398	466	517	390	538	206

of BMDPM. Table 3 shows the impact strength and shear strength depending on the composition of DAPNPT/BMDPM copolymers by molar ratio. It was found that there was higher impact strength and shear strength, when the molar ratio of DAPNPT/BMDPM in the matrix was 1:2. As compared with the neat BMDPM matrix, the copolymer matrix can attain 9.9 times the impact strength and 3.1 times the shear strength, respectively. However, it was worth noting that the impact strength and the shear strength dramatically decreased when the molar ratio of DAPNPT/BMDPM in the copolymer exceeded 1:2. It means that DAPNPT can effectively improve the mechanical properties of BMDPM and such mechanical behavior could be related to the network structure of the cured resins.

Fig. 9 shows the DMA curves in the range of 50–400°C for BMDPM/DAPNPT copolymers at various molar ratios. It was found that all copolymers of BMDPM/DAPNPT showed glass transition temperatures in the range of the temperature from 280 to 390°C, and these glass transition temperatures decreased with increasing the DAPNPT compositions. It was interesting that the cured DAPNPT/BMDPM resin had lower glass transition temperature when the molar ratio between DAPNPT and BMDPM was 1:2, and had higher glass transition temperatures when the ratio was 1:4 and 1:6, respectively. The results indicated a variety of crosslinking densities of the cured DAPNPT/BMDPM resins. It was well known that introducing allyl additives to BMI resin via 'ene/Diels–Alder' reaction could decrease the crosslinking densities of the cured BMI matrix. Because of the decrease in crosslinking density of the cured BMI resin, the toughening of the resin could be attained. It means that allyl compound acted as an extender for BMI. Therefore, the results shown in Table 3 could be clarified by means of analyzing Fig. 9. When the molar ratio of DAPNPT/BMDPM was 1:2, the cured resin had lower glass transition temperature. It meant that the crosslinking density of the cured resin was lower and the toughness of the

Table 3
Comparison of mechanical properties between neat BMPDM and the BMDPM/DAPNPT copolymers

Polymers	Impact strength (kJ M^{-2})	Shear strength (MPa)
BDPM homopolymer	0.86	2.65
n(BMDPM)/n(DAPNPT) copolymers		
2.0	8.51	8.29
4.0	4.45	7.28
6.0	3.26	6.67

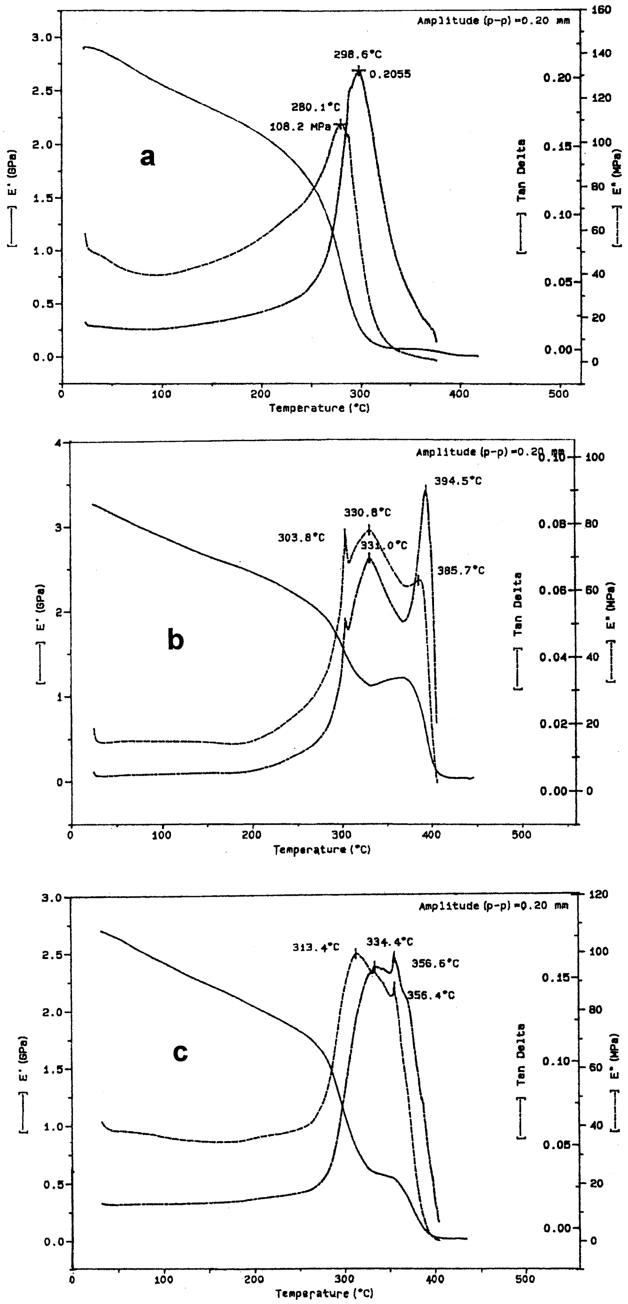

Fig. 9. DMA curves of the BMDPM/DAPNPT copolymers [n(BMDPM)/n(DAPNPT) = 2 (a); 4 (b); 6 (c)].

resin was increased. However, when the molar ratio between DAPNPT and BMDPM exceeded 1:2, the glass transition temperature of the cured resin increased. It means that the crosslinking density of the resin increased with decreasing the DAPNPT compositions. As a result, the toughness of the resin was decreased.

4. Conclusion

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

1. A novel monomer, 2,4-di (2-allylphenoxy)-6-(2-naphthyloxy)-1,3,5-triazine (DAPNPT) was prepared in one-pot reaction and the chemical structure was characterized by FTIR, mass spectrum, ^{1}H NMR and ^{13}C NMR.
2. DAPNPT/4,4′-bismaleimidodiphenylmethane (BMDPM) copolymer (1:2 molar ratio) had lower melting temperature than that of neat BMDPM resin and the cured copolymer had high thermo-oxidative stability.
3. DAPNPT can effectively improve mechanical properties of BMDPM. The better results were obtained when the molar ratio between DAPNPT and BMDPM was 1:2.

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