

A Convenient Procedure for Preparation of a Novel Allylphenoxytriazine Monomer and the Properties of Its Copolymer with Bismaleimide (BMI)

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ABSTRACT: A novel allylphenoxytriazine monomer, 2,4-di (2-allylphenoxy)-6-*N,N*-dimethylamino-1,3,5-triazine (DAPDMT) was prepared in one-pot by reacting cyanuric chloride with 2-allylphenol at first, and then by directly treating the adduct with *N,N*-dimethylamine without separation. The monomer was used to modify a popular commercial bismaleimide (BMI) resin, 4,4'-bismaleimidodiphenyl methane (BMDPM), and the results showed that the monomer could effectively improve mechanical properties

of BMDPM resin without greatly decreasing heat resistance of the resin. The better results were obtained when the molar ratio of DAPDMT/BMDPM was 1 : 4. Because of more reactive sites in the monomer, the potential uses of the monomer were predicted. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2279–2284, 2002

Key words: polyimides; modification; additives

INTRODUCTION

The allyltriazine monomers, such as triallyl cyanurate and 2,4-diallyloxy-6-phenoxy-1,3,5-triazine, have been well studied^{1–3} and widely used as modifiers for several commercial plastics.^{4,5} Some examples of applications include improving strength of polyethylene (PE) or polypropylene (PP) and increasing heat resistance of unsaturated polyester resins.^{4,5} In recent years they have received attention in aerospace/aeronautics, electronic, and insulating materials industry because of their excellent modifying results for some thermo-setting polymers.^{6–9} However, only a few reports about the allylphenoxy triazine monomers have been found.^{7–9} It is known that the monomers (or oligomers) could be used as precursors for synthesis of the epoxy resins with excellent properties⁹ and as a modifier^{7,8} for bismaleimides (BMIs), a kind of high-performance resin. Because of more reactive sites in the monomers, it is also expected that they not only can be used in polymers, but also can be used in the other fields such as in drugs, optical, and biochemical materials.

In previous works^{10,11} we reported the syntheses of two new allylphenoxytriazine monomers, triallylphenoxytriazine (TAPT) and 2,4-di (2-allylphenoxy)-6-(2-naphthylloxy)-1,3,5-triazine (DAPNPT), and the properties of their copolymers with a popular commercial BMI, 4, 4'-bismaleimidodiphenylmethane (BMDPM). To obtain a new kind of the triazine modifiers and study their properties, a novel monomer, 2,4-di (2-allylphenoxy)-6-*N,N*-dimethylamino-1,3,5-triazine (DAPDMT) was prepared in our laboratory. In this article, we reported the synthesis of the monomer and the properties of its copolymer with BMDPM. Finally, the potential applications of the monomer in other fields were also predicted.

EXPERIMENTAL

Materials

Cyanuric chloride was an industrial product 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 method¹² and purified by fractional distillation under vacuum, b.p. 110–113°C/0.092 MPa. IR (KCl), cm⁻¹, 3482 (—OH), 997, 916 (allyl), 3075, 1637 (aryl ring), 2906, 2976 (—CH₂—). Anal. Calcd for C₉H₁₀O: 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 (CDCl₃, chemical shifts are referenced to TMS), δ (ppm): 5.16 (=CH₂—), 5.97 (—CH=), 3.39 (—CH₂—), 6.78–7.14 (phenyl ring). BMDPM was also an indus-

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trial product, and was recrystallized twice from toluene before use. Other materials were used as received. AR grade solvents were used.

Instrumentation

The 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 CD_3COCD_3 (or CDCl_3) as solvent and TMS as the internal standard. MS were obtained using a VG 7070 Analyzer. Elemental analyses were carried out on a Calo Erba 1106 Elemental Analyzer. Curing behaviors of DAPDMT/BMDPM resins were studied using a Du Pont DSC 2100 Differential Scanning Calorimeter at a heating rate $10^\circ\text{C}/\text{min}$ in nitrogen. Thermal stability of the cured resins was determined on a Du Pont 2100 Thermogravimetric Analyzer at a heating rate $10^\circ\text{C}/\text{min}$ in air.

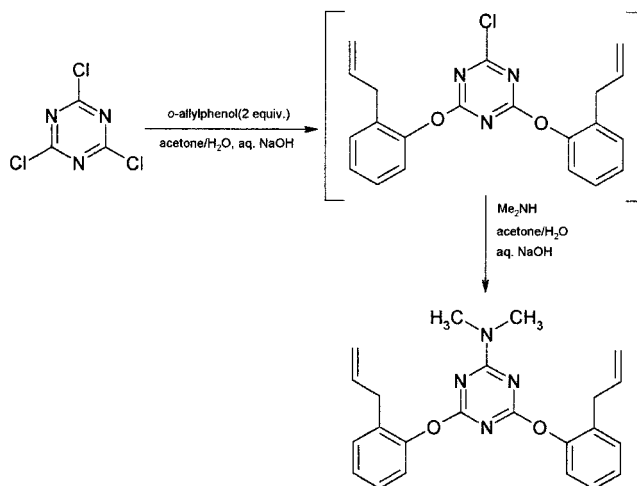
The impact test was carried out using a Charpy tester according to China State Standard GB25711-81. The shear test was carried out using a Tension tester according to China State Standard GB1450.1-83.

Synthesis of DAPDMT

To stirred cyanuric chloride (18.45 g, 0.1 mol), dissolved in acetone (200 mL), was added dropwise in a solution of 2-allylphenol (26.67g, 0.20 mol) and NaOH (8.00 g, 0.20 mol) in H_2O (100 mL) saturated by N_2 at $0\text{--}5^\circ\text{C}$. The reaction mixture was stirred vigorously for 1 h at $0\text{--}5^\circ\text{C}$, for 2 h at $15\text{--}20^\circ\text{C}$, and maintained for 1 h at $25\text{--}30^\circ\text{C}$. Then, 33% aqueous Me_2NH (15.00 g, 0.10 mol) was added dropwise to the mixture at such a rate that the reaction temperature did not exceed 30°C . Having added all the amine solution, the reaction was allowed to continue for 2 h at $35\text{--}40^\circ\text{C}$ and then cooled to 0°C . A white crystalline solid was filtered, washed with cold water then with MeOH, and finally was recrystallized from EtOH. DAPDMT was obtained as white crystalline needles in a yield of 76%, m.p. $91\text{--}92^\circ\text{C}$. Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{O}_2\text{N}_4$: C, 71.19 %; H, 6.16 %; N, 14.46 %. Found: C, 71.13 %; H, 6.19 %; N, 14.40 %.

Preparation of the impact and shear specimens

Mixture of BMDPM and DAPDMT in a 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. The fine solid powder of blend (6.0 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°C . The temperature was maintained for 30 min so that a transparent melting liquid was obtained. After 6 h, the liquid



Scheme 1 The procedure for preparation of DAPDMT.

mixture had turned completely to a solid consistency. 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 complete cure. The impact specimens of the blends were thus obtained. 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 $160 \pm 2^\circ\text{C}$. After melting, the blend was applied quickly to two preheated (at 160°C) aluminum slices (the dimension of both the slices was $7.02 \times 2.02 \times 0.20$ cm, and the applied area of the prepolymer was 2.02×2.02 cm). The applied area of aluminum slices were quickly overlapped according to general procedure and moved to an oven at 160°C . The temperature was maintained at 160°C for 6h. 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.

RESULTS AND DISCUSSION

Synthesis and characterization of DAPDMT

Until now, no report about the synthesis of DAPDMT has been found in the literature. Generally, the analogs of the monomer, 2-alkyloxy (or alkylamino)-4,6-diallyloxy-1,3,5-triazine, are synthesized by a two-step procedure.^{1,2} Thus, first, the intermediates, 2-alkyloxy (phenoxy or *N*-alkylamino)-4,6-dichloro-1,3,5-triazine are prepared by the reaction of cyanuric chloride and alcohols or alkylamines. Then, the intermediates, rigorously purified, are treated with a large amount of allyl alcohol to obtain the final products. The procedure is not convenient. It is especially difficult to prepare the pure intermediates in large scales suitable for synthesis of the final products because the intermediates are easily hydrolyzed.^{1,2}

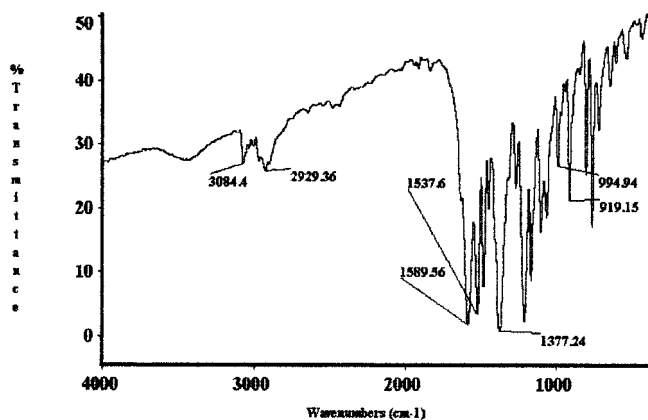
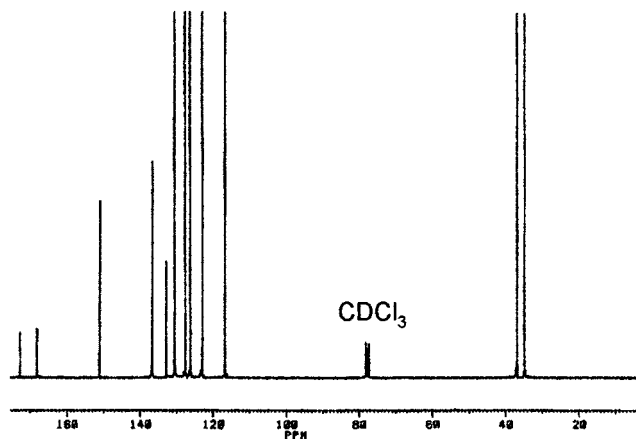


Figure 1 FTIR spectrum of DAPDMT.

In this article we describe a convenient one-pot way to prepare DAPDMT. The procedure is shown in Scheme 1.

The route is available for preparation of DAPDMT in large scales. The intermediate, 2-chloro-4,6-di (2-allylphenoxy)-1,3,5-triazine without separation from the reaction system is directly treated with *N,N*-dimethylamine, and the final product could be isolated as white crystalline solid from the reaction system when the reaction completed.

The chemical structure of the monomer was characterized by FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$. Figure 1 is the FTIR spectrum of DAPDMT. Characteristic absorption peaks appeared at 1589 and 1377 cm^{-1} due to the resonances of C—N in the triazine ring. The absorption bands at 2971 and 2929 cm^{-1} are assigned to $-\text{CH}_3$. Characteristic absorptions at 3075, 995, and 919 cm^{-1} are assigned to allyl groups. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of DAPDMT in Figures 2 and 3 confirm further the structure proposed. In Figure 2,

Figure 3 $^{13}\text{C-NMR}$ spectrum of DAPDMT.

aromatic ring protons of DAPDMT are observed as multiples at 7.10–7.28 ppm. The protons of allylic carbon give a doublet at 3.30 ppm. The multiples at 5.04 and 5.88 ppm indicate protons of $\text{CH}_2=$ and $=\text{CH}-$ groups, respectively. A singlet appearing at 2.96 is assigned $-\text{N}-\text{CH}_3$. $^{13}\text{C-NMR}$ spectrum of DAPDMT in Figure 3 shows 12 different carbon signals, as expected. The corresponding data are given in the following (δ , ppm): 122.9, 136.6, and 34.8 ($-\text{CH}_2\text{CH}=\text{CH}_2$); 150.9, 116.7, 127.5, 126.2, 130.5, and 132.8 (phenyl rings); 167.9 and 172.6 (triazine ring); 36.9 ($-\text{N}-\text{CH}_3$).

Mechanical properties of DAPDMT-modified BMDPM resins

DAPDMT was expected to improve mechanical properties of BMDPM. Table I shows the impact strength and shear strength depending on the composition of

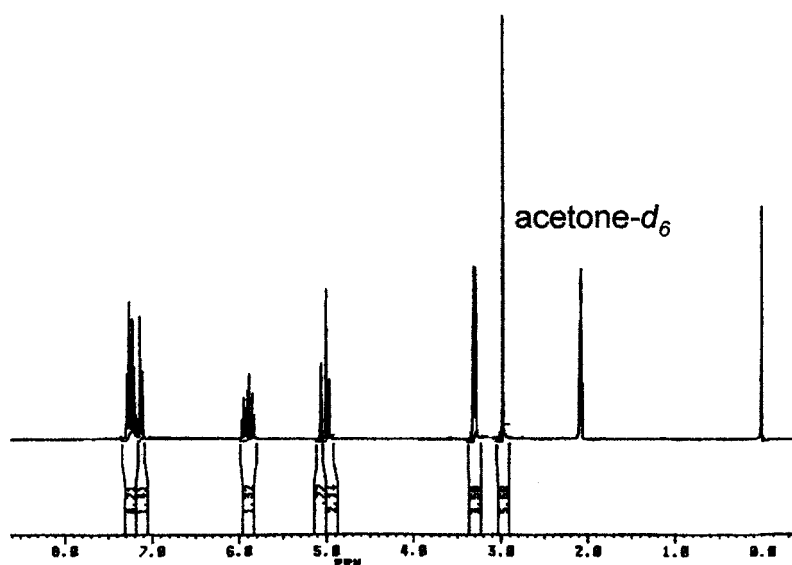
Figure 2 $^1\text{H-NMR}$ spectrum of DAPDMT.

TABLE I
The Mechanical Properties of the BMDPM/DAPDMT Copolymer

| Polymers | Impact strength (KJ/M ²) | Shear strength (MPa) |
|----------------------|--------------------------------------|----------------------|
| n (DAPDMT)/n (BMDPM) | | |
| 0 | 0.86 | 2.65 |
| 1/2 | 3.25 | 6.21 |
| 1/4 | 6.25 | 8.35 |
| 1/6 | 4.23 | 5.87 |

DAPDMT/BMDPM copolymers by molar ratio. It is found that there is higher impact strength and shear strength when the molar ratio of DAPDMT/BMDPM in the matrix is 1 : 4. Compared with the neat BMDPM matrix, the DAPDMT/BMDPM copolymer matrix can attain 7.3 times the impact strength and 3.2 times the shear strength, respectively. However, the impact strength and the shear strength decrease when the molar ratio of DAPDMT/BMDPM in the copolymer are not 1 : 4. The results indicated a variety of crosslinking densities of the cured DAPDMT/BMDPM resins. It was well known that introducing allyl additives to BMI resin via "ene/Diels-Alder" reaction¹³ 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. Hence, in this work, when the molar ratio of DAPDMT/BMDPM was 1 : 4, the crosslinking density of the cured resin would be lower and the toughness of the resin was increased. However, when the molar ratio between DAPDMT and BMDPM was lower (or more) than 1 : 4, the crosslinking density of the resin would be in-

TABLE II
Comparison of Thermal Characteristics between BMDPM and BMDPM/DAPDMT*

| Compounds | T_m (°C) | Onset temperature (T_1 , °C) | T_{exo} (°C) | ΔH (J/g) |
|--------------|------------|---------------------------------|----------------|------------------|
| BMDPM | 162 | 221 | 253 | 90.49 |
| BMDPM/DAPDMT | 153 | 230 | 253 | 223.5 |

* The molar ratio of BMDPM/DAPDMT was 4:1.

creased. As a result, the toughness of the resin was decreased.

Thermal analysis of the copolymers between BMDPM and DAPDMT

Curing reaction of the DAPDMT/BMDPM blend

In DSC trace of BMDPM a sharp endothermic peak indicating melting is observed at 162°C (Fig. 4A). However, an endothermic peak is observed at 153°C (Fig. 4B) for the DAPDMT/BMDPM blend (1 : 4, molar ratio). It means that a comelting substance with a melting point of 153°C is formed in the DAPDMT/BMDPM blend. It is found that exothermic transitions of curing of BMDPM or DAPDMT/BMDPM copolymer are also observed in the temperature range of 200–300°C in Figure 4. Heat of curing reaction (ΔH), fusion temperatures of BMDPM and DAPDMT/BMDPM copolymer (T_m), onset temperature of curing reaction (T_1), and exothermal peak position (T_{exo}) are determined from DSC traces and listed in Table II. It is seen that adding DAPDMT to BMDPM causes a decrease in fusion temperature and an increase in ΔH values.

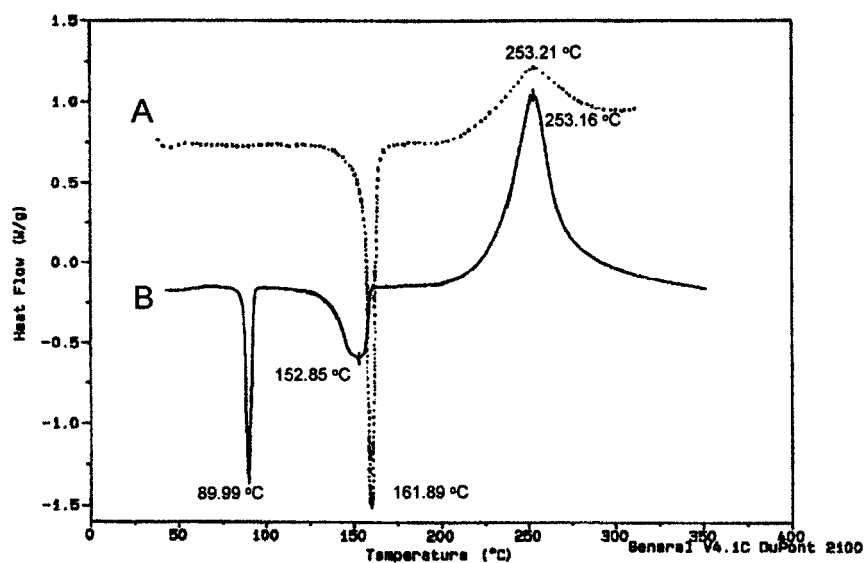


Figure 4 DSC traces of BMDPM (A) and the BMDPM/DAPDMT blend (4 : 1, molar ratio; B).

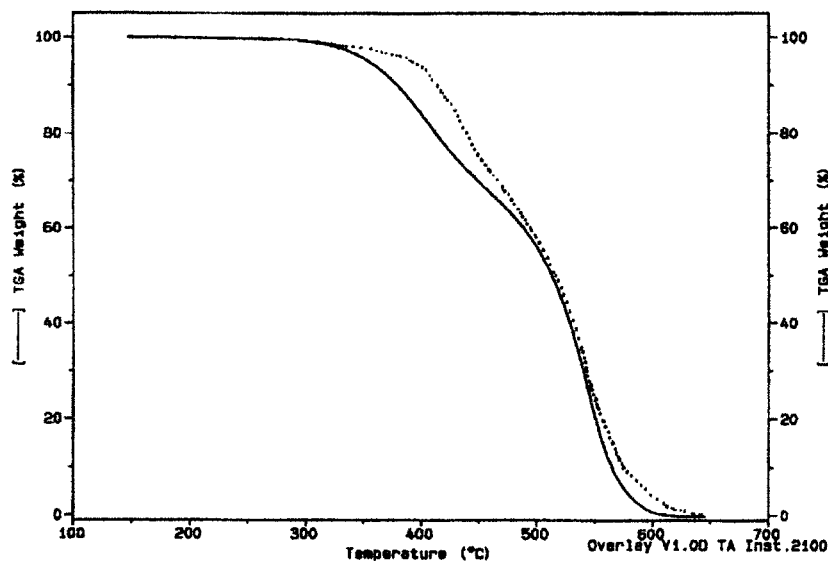


Figure 5 TGA curves of DMDPM (· · ·) and the BMDPM/DAPDMT copolymer (4 : 1, molar ratio, —).

Thermal oxidative stability of the cured DAPDMT/BMDPM copolymer

Relative thermal stability for cured the DAPDMT/BMDPM copolymer (1 : 4, molar ratio) is evaluated by thermogravimetry. The results are given in Figure 5 and Table III, respectively. A higher heat resistant index¹⁴ (T_c), 205°C, indicates that DAPDMT-modified BMDPM resin has a high level of thermal oxidative stability.

Some potential applications of DAPDMT in the other fields

Although this work shows that DAPDMT does not homopolymerize on heating, it does not include the cases of the presence of some catalysts. Therefore, it could be predicted that the homopolymer could be formed through the cation (or anion) homopolymerizing reaction. As a result, the new materials containing triazine rings, which may have excellent electric and optical properties, will be produced. Furthermore, DAPDMT could be copolymerized with some other monomers containing vinyl groups such as acrylate, propylene, ethylene, and so on. The copolymers may have excellent properties.

It is also important that the derivatives of DAPDMT could be synthesized through various reactions due to more active positions in the monomer. Therefore, with exception of the possible usage, DAPDMT may have potential applications in drugs, pesticides, and fine chemicals.

CONCLUSION

1. A novel functional triazine monomer, 2, 4-di (2-allylphenoxy)-6-*N,N*-dimethylamino-1,3,5-triazine (DAPDMT) was prepared in a one-pot reaction.
2. DAPDMT was used to modify 4,4'-bismaleimidodiphenyl methane (BMDPM), and the modified resin has good mechanical properties and high thermal oxidative stability. The better results were obtained when the molar ratio between DAPDMT and BMDPM is 1 : 4.

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TABLE III
The TGA Data of BMDPM/DAPDMT Copolymer^a

| Compounds | The weight loss temperature (°C) | | | | | | | |
|--------------|----------------------------------|----------|----------|----------|----------|--------------|--------------|-------|
| | T_5 | T_{10} | T_{15} | T_{30} | T_{50} | $T_{\max 1}$ | $T_{\max 2}$ | T_c |
| BMDPM | 395 | 415 | 428 | 465 | 516 | 432 | 542 | 214 |
| DAPDMT/BMDPM | 361 | 385 | 402 | 457 | 517 | 414 | 540 | 205 |

^a The molar ratio of BMDPM/DAPDMT was 4:1. T_5 , T_{10} , T_{15} , T_{30} , and T_{50} were the temperature when weight loss was 5, 10, 15, 30, and 50%, respectively. $T_{\max 1}$ and $T_{\max 2}$ was decomposition peak temperature. T_c was heat-resistant temperature index¹⁴ calculated according to $T_c = 0.49[T_5 + 0.60(T_{30} - T_5)]$.

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