

Curing Behavior of 4,4'-Diamonodiphenyl Methane-Based Benzoxazine Oligomers/Bisoxazoline Copolymers and the Properties of Their Cured Resins

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ABSTRACT: 1,3-Phenylene bisoxazoline is synthesized and characterized. The optimal synthetic conditions for yield (92%) are as follows: reaction temperature = 115°C; ratio (mol) of ethanolamine to 1,3-dicyanobenzene = 2.5 : 1; ratio (mol) of zinc acetate to 1,3-dicyanobenzene = 0.055; reaction time = 6 h. 4,4'-diamonodiphenyl methane-based benzoxazine and its oligomers (Oligo-Da) are synthesized and characterized. The curing behavior and properties of the Oligo-Da/1,3-PBO copolymer resins are investigated. It was found that the cure induction time and cure time of the molten mixture from Oligo-Da/1,3-PBO could be reduced, compared with that from Oligo-Ba/1,3-PBO, especially above 175°C. The reason lies in that the bisphenol generated in ring opening of Ba has more steric hindrance than the phenol generated in ring opening of Da because of isopropyl group. Thus, the Mannich bridge structure in the Da poly-

mer is relatively much easier to form between the ortho positions of phenolic hydroxyl groups than that in the Ba polymer. Curing temperature of Oligo-Da/1,3-PBO could be lowered with triphenylphosphite as a catalyst. SEM results confirm that 1,3-PBO could toughen Oligo-Da system when the mol ratio of 1,3-PBO and Oligo-Da is ≤ 1 because of the formation of ether–amide bonds. However, a brittle fracture surface is observed because of too higher crosslinking density of the cured resin, when the mol ratio of 1,3-PBO and Oligo-Da is > 1 . The cured resin from Oligo-Da/1,3-PBO has superior heat resistance, electrical insulation, and water resistance than that from Oligo-Ba/1,3-PBO. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1359–1366, 2006

Key words: 4,4'-diamonodiphenyl methane; benzoxazine; 1,3-phenylene bisoxazoline; curing behavior

INTRODUCTION

Phenolic resins are preferred in a wide range of applications, from commodity and construction materials to aerospace industry. This recognition emerges from the fact that these resins have several desirable characteristics, such as superior mechanical strength, heat resistance, dimensional stability, and chemical resistance. However, these traditional phenolic resins have many shortcomings. For example, the resins were often cured using hexamethylenetetramine as a curing agent. Thus, many volatiles, such as water, ammonia compounds, *etc.*, are produced in the curing process. These volatiles sometimes reduce the properties of cured phenolic resins because of the formation of microvoid.

To solve these problems, the addition coreaction of novolac phenolic resin with phenylene bisoxazoline has been explored by Culbertson et al. to derive a new class of nonconventional phenolic thermosetting res-

in¹ This resin had low shrinkage, excellent toughness (G_{IC} is ~ 5 times greater than those of epoxy and BMI), high T_g , low flammability, and low smoke emission. Bisoxazoline has been used to chain extend and/or crosslink phenolic resin. There were no volatile by-products produced in the reaction of novolac phenolic resin and bisoxazoline, as shown in Figure 1.

Recently, Ishida and coworkers^{2–8} synthesized various types of benzoxazines and studied their cured kinetics and mechanical properties. Benzoxazine ring is found to be stable at low temperature, but a ring-opening reaction occurs at high temperature, when both the phenolic hydroxyl group and tertiary amine group are produced.⁹ Using the phenolic hydroxyl groups, benzoxazine has been successfully modified with epoxy,^{8,10–12} ATBN or CTBN,¹³ poly(imide-siloxane),¹⁴ polyurethane,¹⁵ and bisoxazoline.^{16,17} The polybenzoxazine modified with epoxy has a higher crosslink density and T_g than the polybenzoxazine homopolymer. The mechanical properties of polybenzoxazine were also improved.^{8,10–12} New type of addition coreaction of resin from benzoxazine with phenylene bisoxazoline was developed by Kimura et al.^{16,17} The cured resin prepared from bisphenol A-

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based benzoxazine-bisoxazoline copolymers has many advantages. For example, it has good flowability below 140°C; curing reaction proceeded above 180°C rapidly; and there are no volatiles produced in the curing process. Additionally, it has superior heat resistance, electrical insulation, water resistance, and mechanical properties than those of the cured resins from conventional bisphenol A-type novolac phenolic resin-bisoxazoline copolymers (or benzoxazine/epoxy copolymers). Recently, to improve the thermal stability and mechanical properties of polybenzoxazine, a series of benzoxazine resins based upon alky-substituted arylamine were synthesized by Ishida and Sanders.¹⁸ Aromatic diamine-based benzoxazine/epoxy copolymers also were developed by Yi Gu et al.¹⁹ because they have better heat resistance and electrical insulation than bisphenol A-based benzoxazine/epoxy copolymers. However, the investigation was not reported in detail.

Our object is to combine the advantages of aromatic diamine-based benzoxazine and benzoxazine/bisoxazoline copolymers, to achieve a higher thermal stability of cured resins and reduce the resin cure time, and lower the resin cure temperature according to the aromatic diamine-based benzoxazine and oligomers (Oligo-Da)/1,3-PBO copolymers. In addition, 1,3-PBO, which is a raw material to prepare benzoxazine/bisoxazoline copolymers, is more proper to be applied in commerce, if its price is lower.^{20,21} To get lower price 1,3-PBO, we also expect to obtain a good yield of 1,3-PBO using general chemical material and reagents by one-step reaction.

In this report, 4,4'-diaminodiphenyl methane-based benzoxazine and its oligomers (Oligo-Da) were synthesized. The curing behavior of the Oligo-Da-bisoxazoline copolymers and some properties of their cured resins were investigated by FTIR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), DMA, SEM, etc. The synthesis conditions of 1,3-PBO from ethanolamine and 1,3-dicyanobenzene by one-step reaction were also investigated.

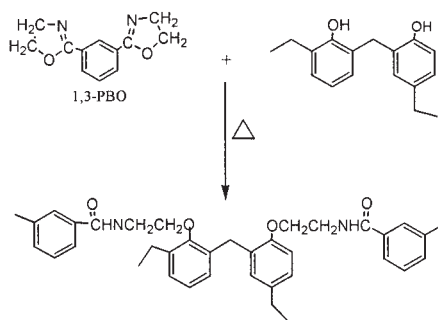


Figure 1 Polymerization of bisoxazoline-phenolic system.

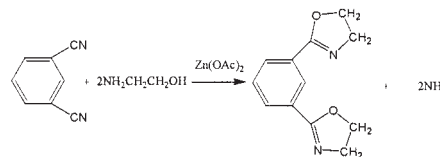


Figure 2 Synthesis of 1,3-PBO by one-step reaction.

EXPERIMENTAL

Materials

Ethanolamine, zinc acetate, 1,3-dicyanobenzene, ammonia, 4,4'-diaminodiphenyl methane, toluene, formaldehyde (37% in water), phenol, bisphenol A, aniline (99%), and ethanol were purchased from Shanghai Chemical Group, China. Triphenylphosphite (as a curing catalyst) was supplied by Shanghai First Reagent Company, China. All chemicals were of analytical reagent grade and were used without further purification.

Synthesis of 1,3-PBO

The synthesis of 1,3-PBO was carried out according to the method reported by Witte and Seeliger²² (Fig. 2). A mixture of ethanolamine, zinc acetate, and 100 mL toluene were added to a 500-mL three-necked round-bottomed flask (equipped with a temperature controller, overhead stirrer, and a reflux condenser). The mixture was heated at 86°C with stirring, until the water was separated and removed. The toluene was distilled out and a homogeneous solution was obtained. Then, the homogeneous solution was cooled to room temperature. 1,3-Dicyanobenzene was added to the homogeneous solution and heated for about 3–6 h at 100–130°C, until ammonia gas ceased to evolve. The resulting product was cooled to room temperature under nitrogen and then washed twice with a mixture of 500 mL ice water and 200 mL ammonia. Products were dried in vacuum at 50°C to a constant weight and then were recrystallized from ethanol. 1,3-PBO was obtained and the structures were analyzed by ¹H-NMR measurement. ¹H-NMR measurement was carried out on a Bruker spectrometer at 300 MHz. CDCl₃ was used as the solvent. Melting point measurement was carried out on an X-4 digital microscope melting point measurement Instrument (Beijing Guangdian Instruments Co., Ltd.).

Synthesis of 4,4'-diaminodiphenyl methane-based benzoxazine and its oligomers (oligo-Da)

Oligo-Da was synthesized according to the method reported by Ishida and coworkers³ (Fig. 3). The reaction was carried out using toluene as the solvent. The procedure is as follows: 0.1 mol 4,4'-diaminodiphenyl

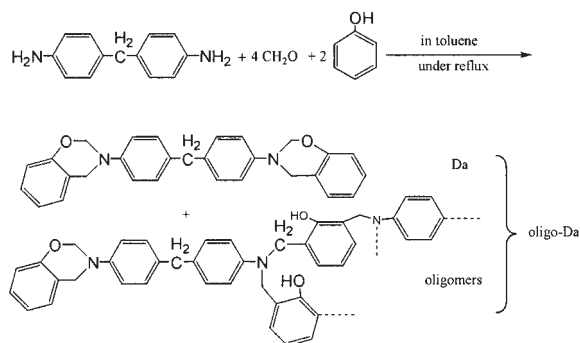


Figure 3 Synthesis of Oligo-Da.

methane in 20 mL toluene was added dropwise into 0.4 mol formaldehyde (37% in water) in 80 mL of toluene, keeping the temperature below 10°C in an ice bath. The mixture was stirred for 10 min. To the mixture, 0.2 mol phenol in 100 mL toluene was added, and the temperature was raised. The mixture solution was refluxed for 6 h and the water produced was separated and removed. Then, the solvent was distilled out and the product was obtained. The structures of Oligo-Da were analyzed by ¹H-NMR measurement. ¹H-NMR measurement was carried out on a Bruker spectrometer at 300 MHz. CDCl₃ was used as the solvent.

Bisphenol A-based benzoxazine-containing oligomers (Oligo-Ba) were also synthesized, using the same method.

Preparation of cured resin

Oligo-Da was heated to 90°C for about 0.5 h. Then, 1,3-PBO was added slowly to it by mechanical stirring, until a clear molten mixture was obtained. Cured resin from Oligo-Da/1,3-PBO were prepared with various mol ratios of 1,3-PBO, following the same procedure. These molten mixtures were variously step post cured at 170°C for 2 h, 190°C for 2 h, 200°C for 2 h, and 230°C for 2 h. Cured resin from Oligo-Ba/1,3-PBO was prepared, following the same method.

Characterization of curing using FTIR, DSC, and TGA

The structure of the cured resin was analyzed using an FTIR spectrometer. FTIR spectra were obtained on a PerkinElmer-2 spectrometer (KBr pellet). DSC was measured with a heating rate of 10°C/min under N₂ atmosphere on Perkin-Elmer DSC6 apparatus. Dynamic scans of the samples were recorded. TGA were performed on a DuPont 2000 Thermogravimetric Analyzer. Cured samples were weighed in the sample pan and then heated in the TGA furnace at a heating rate of 5°C/min. The resulting thermograms were recorded.

Properties of the cured resin from oligo-Da/1,3-PBO

To investigate the curing rate of the cured resin, gelation time was estimated using JIS K6910. A spatula was placed on the steel plate and was heated to the constant temperature. About 0.5 g of the sample was put on the steel plate and spreaded to a disc of ~3 cm in diameter, with the spatula. Then, the sample was kneaded by pressing it uniformly (approximately once per second), but with care to avoid spreading. The time until when the sample does not string to the spatula any more was measured. It was taken as the gelation time of the sample. Water absorption was estimated using JIS K7209. The disk test pieces (~50 mm in diameter and 3 mm thick) were weighed to the nearest 0.1 mg, and the mass was taken as *M*₁. Then, the test pieces were put in a container containing boiling water and cooled down by putting them in water kept at temperature of the testing room for 15 min. After taking the test pieces out of the water, they were weighed to the nearest 0.1 mg, and the mass was taken as *M*₂. Water absorption was calculated by the following equation

$$\text{Water absorption(\%)} = (M_2 - M_1)/M_1 \times 100$$

Electrical insulation was estimated by volume resistivity. Volume resistivity was measured by Guangzhou Semiconductor Material Research Institute, SDY-4 using JIS K6911. The disk test pieces (~50 mm in diameter and 3 mm thick) were charged with electricity (500 V), and after 1 min, volume resistance was measured. Volume resistivity was calculated by the following equation.

$$\rho_v = \pi d^2 / 4t \times R_v$$

where ρ_v is the volume resistivity; *d* is the outside diameter of the inner circle of the face electrode, *t* is the thickness of the test piece, and *R_v* is the volume resistance. Fracture surfaces of the cured resin were examined using scanning electron microscopy (Hitachi ISI-SX-40 SEM). Dynamic mechanical analysis was done using TA DMA2928. Specimens (0.5 × 10 × 40 mm³, depth × width × length) were tested in a single cantilever configuration. The thermal transitions were studied in the 35–270°C range at a heating rate of 2°C/min and at a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis of 1,3-PBO

The synthesis effect factors such as reaction temperature, ratio (mol) of ethanolamine to 1,3-dicyanobenzene, ratio (mol) of zinc acetate to 1,3-dicyanobenzene, and reaction time were investigated. The relation of

TABLE I
Relation of Yield and Reaction Effect Factors

Sample	A (°C)	B	C	D (h)	Yield (%)	Melting point (°C)
1	130	2:1	0.055	4	27	137–146
2	130	2.5:1	0.082	5	40	136–145
3	130	3:1	0.110	6	35	137–147
4	100	2:1	0.082	6	62	136–142
5	100	2.5:1	0.110	4	70	137–142
6	100	3:1	0.082	5	33	137–139
7	115	2:1	0.110	5	52	142–146
8	115	2.5:1	0.055	6	92	141–142
9	115	3:1	0.082	4	62	147–151

A: reaction temperature; B: ratio (mol) of ethanolamine to 1,3-dicyanobenzene; C: ratio (mol) of zinc acetate to 1,3-dicyanobenzene; D: reaction time.

yield and reaction effect factors is shown in Table I. The optimal conditions for yield (92%) are as follows: reaction temperature = 115°C; ratio (mol) of ethanolamine to 1,3-dicyanobenzene = 2.5 : 1; ratio (mol) of zinc acetate to 1,3-dicyanobenzene = 0.055; reaction time = 6 h.

¹H-NMR spectrum of 1,3-PBO is shown in Figure 3 and the structure of 1,3-PBO is confirmed: δ 8.42, 8.03–8.05, 7.41–7.46 (Ar—H); δ 4.39–4.45 (O—CH₂); δ 4.02–4.08 (N—CH₂) (Fig. 4).

Synthesis of oligo-Da

The synthesis of oligo-Da was carried out using toluene as the coboiling solvent. The water produced in the reaction was separated gradually, and the oligo-Da mixture yield was 88–95%. ¹H-NMR spectrum of oligo-Da is shown in Figure 5. The peaks b, c assigned to the methylene proton of benzoxazine ring were detected. The peak e assigned to the methylene proton attached to the tertiary amine group was also detected. It implies that the reaction product contains Da and oligomers because the tertiary amine groups were produced only while benzoxazine ring opened. Then, the ratio of benzoxazine ring and oligomers was cal-

culated by examining the ratio between the integrated intensities of the resonance peaks in ¹H-NMR. The ratio between the intensity of b, c peaks and the intensity of e peak was 8.9 : 1.1. This means that the ratio of benzoxazine ring and oligomers was 8.9 : 1.1. Thus, the presence of the phenolic hydroxyl groups mol ratio in oligo-Da mixture is about 11%. Oligo-Ba was synthesized and phenolic hydroxyl groups mol ratio in oligo-Ba mixture was calculated using the same method. The ratio of benzoxazine ring and oligomers was 3 : 1. The phenolic hydroxyl groups mol ratio was about 25%.

Curing reaction of oligo-Da with 1,3-PBO

To investigate the curing reaction of Oligo-Da with 1,3-PBO in detail, FTIR measurement was carried out. FTIR spectra of the compound before and after the curing reaction of Oligo-Da with 1,3-PBO are shown in Figure 6. As a result, the absorption at 947 cm⁻¹ assigned to trisubstituted benzene ring with benzoxazine ring attached disappeared. The absorption at 3410 cm⁻¹ assigned to the secondary amine group and

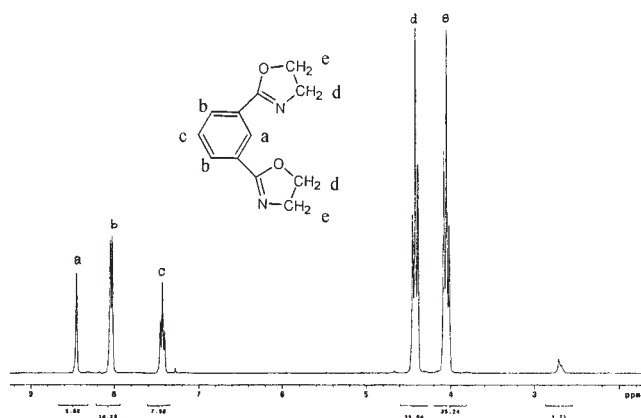


Figure 4 ¹H-NMR spectrum of 1,3-PBO.

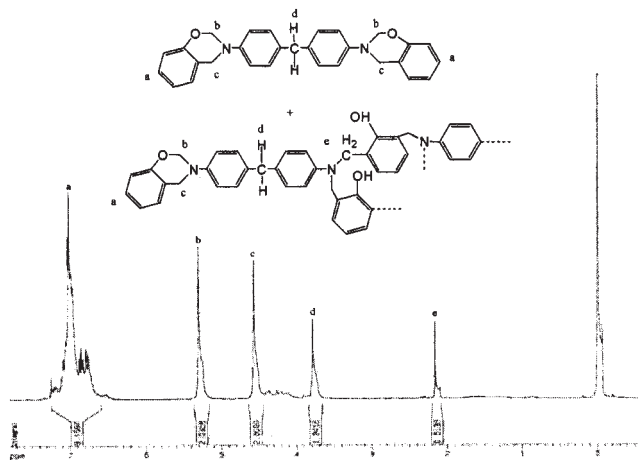


Figure 5 ¹H-NMR spectrum of oligo-Da.

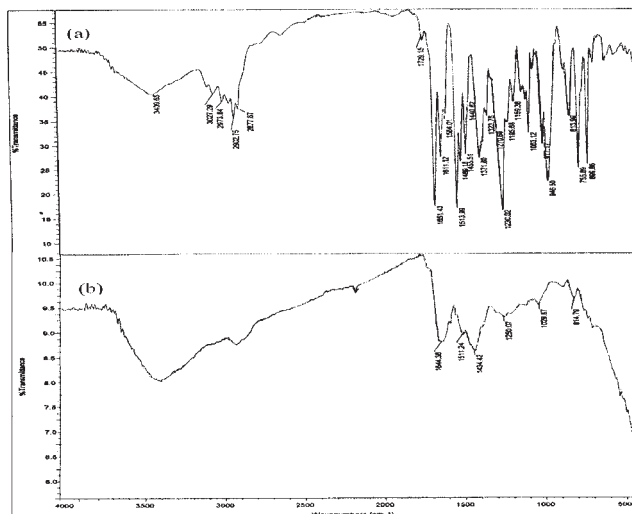


Figure 6 FTIR spectra of the compound before and after the curing reaction of oligo-Da with 1,3-PBO (mol ratio 1 : 1). (a) before curing reaction, (b) after curing reaction.

very small amount of phenolic hydroxyl group that could not react with oxazoline ring became more wider, and the absorption at 1644, 1434 cm^{-1} assigned to the amide group also appeared (Fig. 6). It was found out that benzoxazine ring had opened and the phenolic hydroxyl groups had generated and reacted with oxazoline ring, as shown in Figure 11.

DSC of cures of the Oligo-Ba and Oligo-Da, Oligo-Ba/1,3-PBO, and Oligo-Da/1,3-PBO (mol ratio 1 : 1) (with or without triphenylphosphite as catalyst) are shown in Figures 7–10. An exothermic peak derived from the curing reaction was observed in all the systems. However, the cure of Oligo-Da/1,3-PBO had a sharper slope and shifted to the lower peak temperature than that of Oligo-Ba/1,3-PBO (Fig. 8). It was found that curing of Oligo-Da/1,3-PBO proceeded more rapidly than that of Oligo-Ba/1,3-PBO. Thus, it is believed that the phenolic hydroxyl groups ratio in Oligo-Da is more than that in Oligo-Ba because the phenolic hydroxyl groups with free ortho positions in

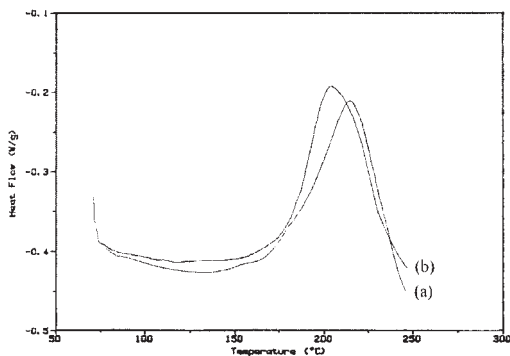


Figure 7 DSC of cures of (a) Oligo-Ba and (b) Oligo-Da.

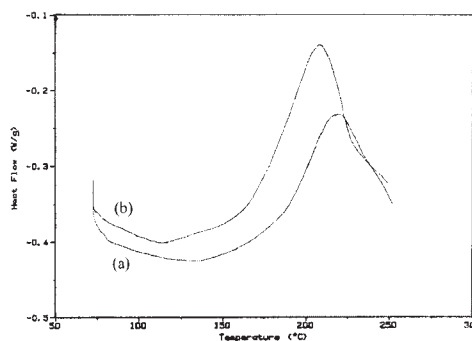


Figure 8 DSC of cures of (a) Oligo-Ba/1,3-PBO and (b) Oligo-Da/1,3-PBO (mol ratio 1 : 1).

the oligomers may have an accelerative effect on the curing reaction, reduce the cure induction time and cure time, and lower the cure temperature.^{2,6,9,15,16} Unexpectedly, the phenolic hydroxyl groups ratio in Oligo-Da (11%) before the curing reaction is less than that in Oligo-Ba (25%) before the curing reaction. Despite the explanation given earlier, it is believed that the bisphenol generated in ring opening of Ba has more steric hindrance than the phenol generated in ring opening of Da, because of the isopropyl group (Fig. 11). So, the Mannich bridge structure in the Da polymer is relatively much easier to form between the ortho positions of phenolic hydroxyl groups than that in the Ba polymer. Thus, in a same period, the curing reaction of Oligo-Da/1,3-PBO is quick than that of Oligo-Ba/1,3-PBO. DSC of cures of the Oligo-Da and Oligo-Ba supported this idea (Fig. 7).

To Oligo-Ba/1,3-PBO and Oligo-Da/1,3-PBO (mol ratio 1 : 1), DSC cure of the cure of mixture with triphenylphosphite as a catalyst had a shift to the lower temperature, compared with that without triphenylphosphite as a catalyst (Figs. 9 and 10). It was found that cure temperature could be lowered with triphenylphosphite as a catalyst.

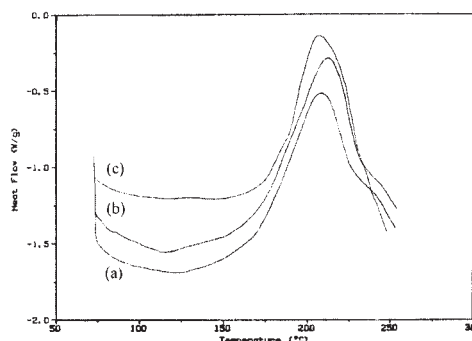


Figure 9 DSC of cures of the Oligo-Da and Oligo-Da/1,3-PBO (mol ratio 1 : 1). (a) Oligo-Da, (b) Oligo-Da/1,3-PBO (without triphenylphosphite), and (c) Oligo-Da/1,3-PBO (with triphenylphosphite).

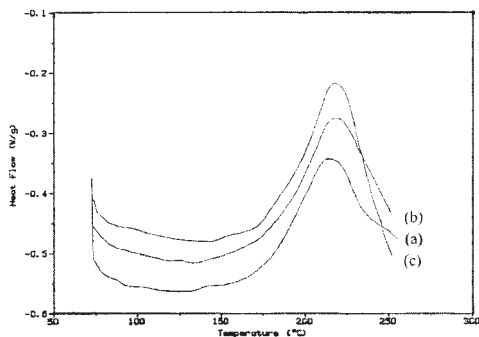


Figure 10 DSC of cures of the Oligo-Da and Oligo-Ba/1,3-PBO (mol ratio 1 : 1). (a) Oligo-Ba/1,3-PBO (with triphenylphosphite), (b) Oligo-Ba/1,3-PBO (without triphenylphosphite), and (c) Oligo-Ba.

Table II shows the gelation time of the molten mixture from Oligo-Ba/1,3-PBO and Oligo-Da/1,3-PBO (mol ratio 1 : 1). Both of the molten mixtures were thermally stable for a long time. It is because the ring-opening reaction of benzoxazine ring is difficult to occur under 120°C, and a majority of the phenolic hydroxyl groups contributed to the curing reaction are not produced, although there are a few phenolic hydroxyl groups that will react with oxazoline rapidly in the condition of high temperature (for example above 175°C).¹ However, the gelation time is shortened with the rise of curing temperature because benzoxazine ring opened and a great deal of phenolic hydroxyl groups are produced easily. Then, a great deal of phenolic hydroxyl groups react with oxazoline ring rapidly above 175°C.¹ The reaction rate of Oligo-Da/1,3-PBO molten mixture is faster than that of Oligo-

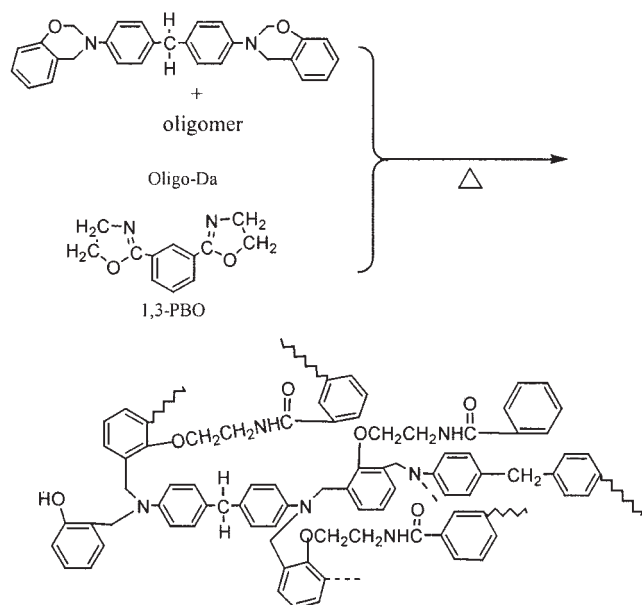


Figure 11 The curing reaction of Oligo-Da and 1,3-PBO.

TABLE II
Gelation Time of Oligo-Da/1,3-PBO and Oligo-Ba/1,3-PBO Mixture

Temperature (°C)	Gelation time (min)	
	Oligo-Da/1,3-PBO	Oligo-Ba/1,3-PBO
120	>60	>60
160	19	25
180	5.8	8
190	3.2	5
200	1.5	3
210	1	2
220	0.5	1

Ba/1,3-PBO molten mixture because the bisphenol generated in ring opening of Ba has more steric hindrance than the phenol generated in ring opening of Da because of isopropyl group, as stated earlier. The steric hindrance has an effect on the formation of Mannich bridge structure in polybenzoxazine. This result is identical with that of DSC. Both DSC and gelation time results indicate that the cure induction time and cure time of the molten mixture from Oligo-Da/1,3-PBO (mol ratio 1 : 1) could be reduced, compared with that from Oligo-Ba/1,3-PBO (mol ratio 1 : 1).

Properties of the cured resin

Figure 12 shows the TGA thermograms of the cured resin from Oligo-Ba and Oligo-Da, Oligo-Ba/1,3-PBO and Oligo-Da/1,3-PBO. From Figure 12, it can be seen that cured resin from Oligo-Da have better thermal stability than that from Oligo-Ba, and cured resin from Oligo-Da/1,3-PBO have better thermal stability than that from Oligo-Ba/1,3-PBO. The thermal stability of cured resin from Oligo-Da/1,3-PBO is the best in all. This is because the cured resin from Oligo-Da has a 4,4'-diamonodiphenyl methane (N—Ph—CH₂—Ph—N) rigid group between bridging points, but the cured resin from Oligo-Ba has a phenylamine (N—Ph) group between bridging points. The degree of the

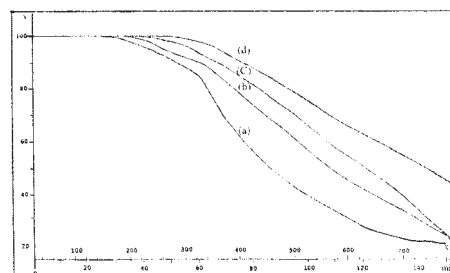


Figure 12 TGA thermograms of cured resins. (a) Oligo-Ba, (b) Oligo-Da, (c) Oligo-Ba/1,3-PBO, and (d) Oligo-Da/1,3-PBO.

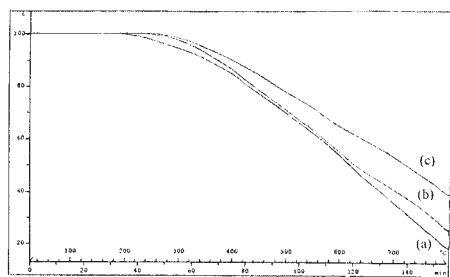


Figure 13 TGA thermograms of cured Oligo-Da/1,3-PBO resins. (a) 1,3-PBO : Oligo-Da = 0.5 : 1, (b) 1,3-PBO : Oligo-Da = 0.8 : 1, (c) 1,3-PBO : Oligo-Da = 1 : 1.

movement of the molecular chain was hindered¹⁸ by N—Ph—CH₂—Ph—N is greater than that by N—Ph. Figure 13 shows the effect of 1,3-PBO concentration on thermal stability. Because of the higher crosslinking density of the Oligo-Da/1,3-PBO, the thermal stability is increased. Hence, when 1,3-PBO concentration is higher, thermal stability is enhanced. Table III shows properties of the cured resin from Oligo-Da/1,3-PBO (mol ratio 1 : 1) or Oligo-Ba/1,3-PBO (mol ratio 1 : 1). The glass-transition temperature (T_g) of cured resin from Oligo-Da/1,3-PBO (mol ratio 1 : 1) is 243°C, which is higher than that from Oligo-Ba/1,3-PBO (mol ratio 1 : 1). The reason is explained by the same results of TGA. The volume resistivity of the cured resin from Oligo-Da/1,3-PBO is relatively higher than that from Oligo-Ba/1,3-PBO.

Water absorption after 2 h boiling of the cured resin from Oligo-Da/1,3-PBO is much lower than the cured resin from Oligo-Ba/1,3-PBO. Although the kinetics of the water absorption needs to be further investigated (this will be investigated and reported in future, in some other place), the possible reason may be explained as follows: in Oligo-Ba/1,3-PBO system, the hydroxyl group of the polybenzoxazine main will be consumed upon curing with oxazolines (this is confirmed by IR). This leaves the nitrogen atom of the Mannich (Ph—N) base to be isolated, leading to the cured polymer to be more hydrophilic than the phenolic OH and Mannich N to be hydrogen bonded²³ in a six-membered ring structure. Thus, water absorption after 2 h boiling of the cured resin from Oligo-Ba/1,3-PBO is relatively high. However, in Oligo-Da/1,3-PBO

system, although the nitrogen atoms of the Mannich base are isolated, the cured resin from Oligo-Da/1,3-PBO have a —Ph—CH₂—Ph— rigid and hydrophobic groups between two nitrogen atoms of the Mannich base. In other words, the nitrogen atoms of the Mannich base are connected by —Ph—CH₂—Ph— group. Therefore, the hydrophilicity of the nitrogen atoms of the Mannich base decreases to a great degree. Thus, water absorption after 2 h boiling of the cured resin from Oligo-Ba/1,3-PBO is much lower than that of the cured resin from Oligo-Da/1,3-PBO.

Figure 14 shows the SEM photographs of fractured surfaces of cured resin from different mol ratio Oligo-Da and 1,3-PBO. It is clear that 1,3-PBO could toughen Oligo-Da systems, when the mol ratio of 1,3-PBO and Oligo-Da is ≤ 1 because of the formation of ether-amide bonds.^{1,16,17} However, too higher crosslinking density of the cured resin indicates a remarkable brittle fracture surface, when the mol ratio of 1,3-PBO and Oligo-Da is > 1 .

CONCLUSIONS

1,3-PBO is synthesized by one-step reaction from 1,3-dicyanobenzene and ethanolamine. The optimize conditions for yield (92%) are as follows: reaction temperature = 115°C; ratio (mol) of ethanolamine to 1,3-dicyanobenzene = 2.5 : 1; ratio (mol) of zinc acetate to 1,3-dicyanobenzene = 0.055; reaction time = 6 h. The structures of 1,3-PBO are confirmed by ¹H-NMR. 4,4'-diaminodiphenyl methane-based benzoxazine and its oligomers (Oligo-Da) are synthesized and characterized. The curing behavior and some properties of the Oligo-Da/1,3-PBO copolymers resin are investigated. Both DSC and gelation time results indicate that the cure induction time and cure time of the molten mixture from Oligo-Da/1,3-PBO could be reduced, compared with that from Oligo-Ba/1,3-PBO, especially above 175°C. The reason lies in that bisphenol the generated in ring opening of Ba has more steric hindrance than the phenol generated in ring opening of Da because of isopropyl group. Thus, the Mannich bridge structure in the Da polymer is relatively much easier to form between the ortho positions of phenolic hydroxyl groups than that in the Ba polymer. Curing temperature of Oligo-Da/1,3-PBO could be lowered

TABLE III
Properties of the Cured Resin

Sample	T_g^a (°C)	Volume resistivity (Ω cm)		Water absorption ^b (wt %)
		Before boiling	After 2 h boiling	
Oligo-Da/1,3-PBO	243	1.6×10^{16}	5.3×10^{15}	0.08
Oligo-Ba/1,3-PBO	232	1.1×10^{16}	3.2×10^{15}	0.23

^a Peak temperature of tan δ from DMA.

^b After 2 h boiling.

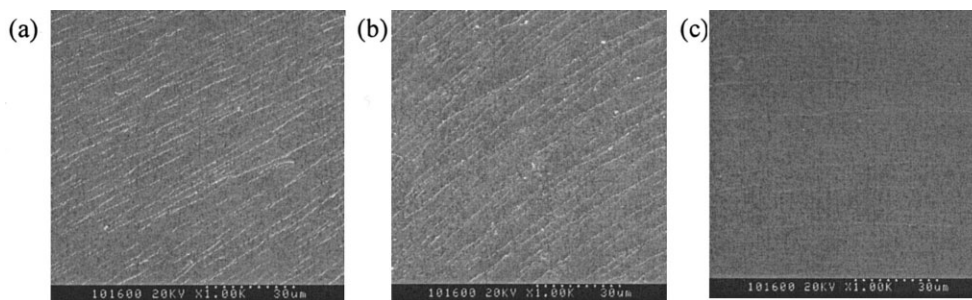


Figure 14 SEM photographs of fractured surfaces of cured resin from Oligo-Da/1,3-PBO. (a) Oligo-Da/1,3-PBO (mol ratio 1 : 0.67), (b) Oligo-Da/1,3-PBO (mol ratio 1 : 1), and (c) Oligo-Da/1,3-PBO (mol ratio 1 : 2).

with triphenylphosphite as a catalyst. SEM results confirm that 1,3-PBO could toughen Oligo-Da system when the mol ratio of 1,3-PBO and Oligo-Da is ≤ 1 because of the formation of ether–amide bonds.¹ However, a brittle fracture surface was observed because of too higher crosslinking density of the cured resin when the mol ratio of 1,3-PBO and Oligo-Da is >1 . The cured resin from Oligo-Da/1,3-PBO has superior heat resistance, electrical insulation, and water resistance than that from Oligo-Ba/1,3-PBO.

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