Synthesis of a Novel Benzoxazine Precursor Containing Phenol Hydroxyl Groups and Its Polymer

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ABSTRACT: A novel benzoxazine precursor containing phenol hydroxyl groups was synthesized from bisphenol A, 4,4′-diaminodiphenyl methane, and formaldehyde with a molar ratio of 2:1:4. The benzoxazine precursor was characterized with Fourier transform infrared, proton nuclear magnetic resonance, and size exclusion chromatography. The curing reaction was monitored by the gel time, differential scanning calorimetry, and Fourier transform infrared. The obtained polybenzoxazine showed high thermal stability and a high glass-transition temperature. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2219–2223, 2008

Key words: ring-opening polymerization; synthesis; thermal properties

INTRODUCTION

As a new type of phenolic resin, polybenzoxazine (PBZ) has attracted much attention because of its excellent properties, such as zero release of volatiles[1] and nearly zero shrinkage or volumetric expansion upon curing,[2] and thermal and mechanical properties similar to those of polybismaleimides.[3–5]

Various types of benzoxazine precursors (BZ precursors) have been synthesized from a phenolic derivative, a primary amine, and formaldehyde. Initially, monofunctional BZ precursors were synthesized from monofunctional phenols, monofunctional amines, and formaldehyde. These monofunctional BZ precursors could not form polymers with high molecular weights.[6] Lately, difunctional BZ precursors have been synthesized from difunctional phenols (or monofunctional phenols), monofunctional amines (or difunctional amines), and formaldehyde. Crosslinking polymers have been formed by the ring-opening polymerization of benzoxazine rings.[7–12] Recently, benzoxazine oligomers have been synthesized from difunctional phenols, difunctional amines, and formaldehyde. Liu and coworkers[13–15] and Takeichi et al.[16] reported the synthesis of PBZ precursors with a high molecular weight containing a phenol end group and an amine end group from bisphenol A, 4,4′-diaminodiphenyl methane (DDM; or ethylene diamine or hexamethylene diamine), and formaldehyde in a molar ratio of 1 : 1 : 4 (Scheme 1).

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We used a 2 : 1 : 4 molar ratio of the difunctional phenol, difunctional amine, and formaldehyde and designed a novel BZ precursor containing phenol hydroxyl groups (Scheme 2). This precursor could be cured at a lower temperature because of the large number of phenol hydroxyl groups.

EXPERIMENTAL

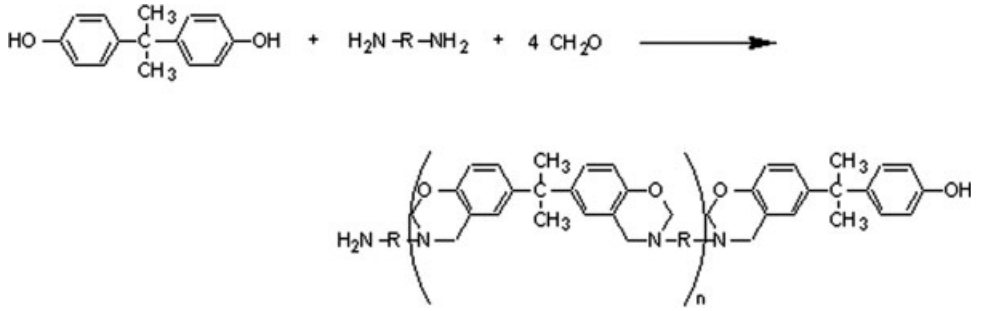
Materials

DDM was purified by recrystallization from ethanol. Other regents, including formaldehyde (37 wt % in water), bisphenol A, 1,4-dioxane, and triethylamine, were purchased from Shanghai Chemistry Reagent Co. (Shanghai, China) and used as received.

Synthesis of the BZ precursors

To a 250-mL, three-necked flask, 23.1 mL (0.3 mol) of an aqueous formaldehyde solution, 14.9 g (0.075 mol) of DDM, 0.7 g of triethylamine, and 75 mL of dioxane were added at 30°C. After 34.2 g (0.15 mol) of bisphenol A was added, the temperature was raised to refluxing for 1–5 h. Upon cooling, the reaction mixture was poured into an excess amount of cold ethanol. The precipitates were dissolved in 250 mL of dichloromethane and washed several times with distilled water. Evaporating the dichloromethane *in vacuo* resulted in a yellowish power.

Proton nuclear magnetic resonance (^{1}H-NMR; $CDCl_3$, 300 MHz, δ): 1.50–1.59 [—C(CH_3)$_2$—], 3.77 (Ar—CH_2—Ar), 4.49 (Ar—CH_2—N), 5.25 (—O—CH_2—NR—), 6.60–7.20 ppm (Ar—H). Fourier transform infrared (FTIR; KBr, ν): 945 (benzene ring



Scheme 1 Synthetic route to PBZ precursors with a high molecular weight.

to which an oxazine ring was attached), 1045 (C—O—C symmetric stretching), 1231 (C—O—C asymmetric stretching), 1365 (C—N stretching), 1513 (trisubstituted benzene ring), 3337 cm^{-1} (phenolic hydroxyl groups).

Thermal curing of the BZ precursors

The BZ precursors were heated in a stainless rectangular mold with a stepwise cure in an air-circulating oven. The step profile was as follows: 100°C for 2 h, 140°C for 2 h, 180°C for 2 h, and 200°C for 2 h.

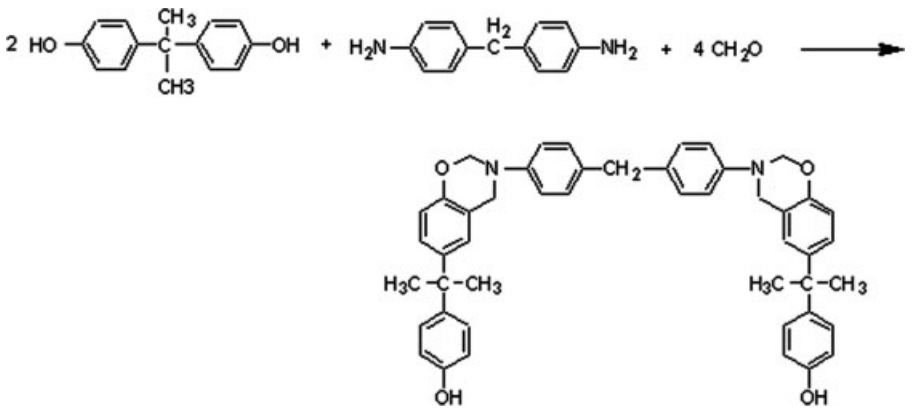
Measurements

FTIR spectra were recorded on a Thermo Nicolet Avatar 370 FTIR spectrometer (Madison, WI). Samples were prepared as KBr pellets. ^{1}H-NMR spectra were recorded on a Bruker Avance 300 instrument (Newport, VA). Deuterated chloroform was used as the solvent, and tetramethylsilane was used as the internal standard. Size exclusion chromatography measurements were carried out in tetrahydrofuran (1 mL/min) at 40°C with a Waters 515 liquid chromatograph (Milford, MA) equipped with three Styragel columns (HR-3, HR-4, and HR-6) and a refractive-index detector. Differential scanning calorimetry (DSC) thermograms were recorded with a Mettler–Toledo DSC822e instrument (Zurich, Switzerland) at a heating rate of 10°C/min under an N_2 atmosphere. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 (New Castle, DE) at a heating rate of 10°C/min under a nitrogen atmosphere. The gas flow rate was 100 mL/min. Dynamic mechanical analysis (DMA) was performed on a Netzsch DMA 242 instrument (Bavaria, Germany), a specimen with dimensions of approximately 16 × 6 × 3 mm^3 was tested in the single cantilever mode with a frequency of 1 Hz, and the sample was heated at a rate of 3°C/min from room temperature to 250°C. The viscosity of the precursor solution was measured with a Brookfield DV-II+PRO viscometer (Middleboro, MA) at a concentration of 0.35 g dmL-1 in dichloromethane at room temperature. An RV 3 spindle was selected, and the speed was 100 rpm.

RESULTS AND DISCUSSION

Characterization of the BZ precursor

Figure 1 shows the ^{1}H-NMR spectrum of the BZ precursor. The resonances at 5.24 and 4.48 ppm correspond to the methylene protons of —O—CH_2—N= and Ar—CH_2—N= in the benzoxazine ring, respectively. The peaks at 1.50–1.63 ppm were assigned to methyl protons of —$C(CH_3)_2$—. The benzoxazine ring content in the BZ precursor could be deter-



Scheme 2 Synthetic route to the BZ precursor.

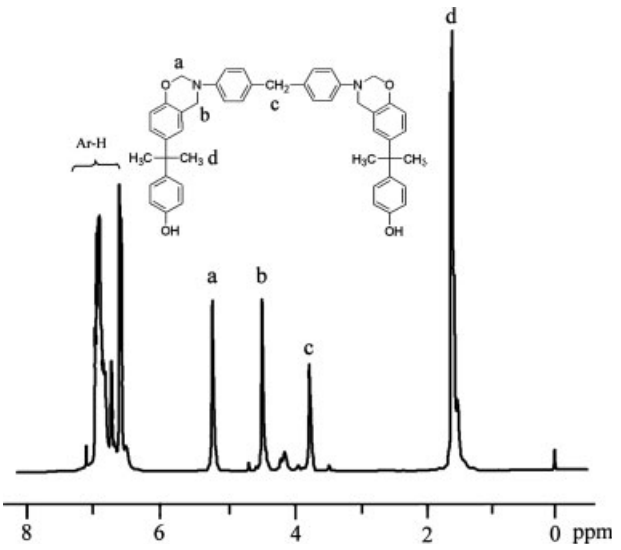


Figure 1 ^{1}H-NMR spectrum of the BZ precursor.

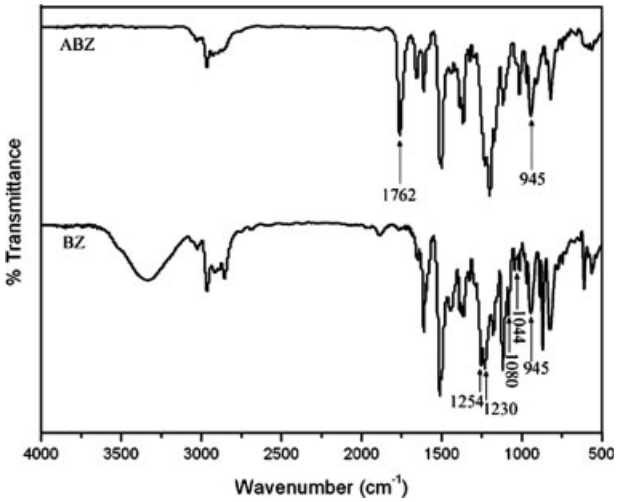


Figure 2 FTIR spectra of the BZ precursor and acetylated benzoxazine (ABZ).

mined from ^{1}H-NMR spectra with the following equation:

$$\text{Ring content } (\%) = 3I/I' \times 100$$

where I is the integrated intensity of the methylene units of Ar—CH_2—N= in the oxazine ring and I' is the integrated intensity of the methyl protons of —$C(CH_3)_2$—. The ring content thus determined for BZ2 was 82.4%.

The hydroxyl functionality was determined via the acetylation method. The acetylation reaction was carried out with acetic anhydride in the presence of excess pyridine at room temperature for 1 h. FTIR analysis confirmed complete acetylation because the absorption band of the phenolic hydroxyl groups disappeared completely (see Fig. 2). The hydroxyl functionality could be calculated from the ^{1}H-NMR spectrum with the following equation:

$$\text{Hydroxyl functionality} = 4A/A'$$

where A is the integrated intensity of the acetyl groups and A' is the integrated intensity of the methyl protons of —$C(CH_3)_2$—. The average hydroxyl functionality was 2.5.

Figure 2 shows the FTIR spectrum of the BZ precursor. Characteristic absorption bands at 945 cm^{-1} due to the benzene ring to which an oxazine ring was attached and at 1230 and 1044 cm^{-1} due to the asymmetric and symmetric stretching of C—O—C in the oxazine ring were observed.[17] In addition, bands at 1254 and 1080 cm^{-1} due to the asymmetric and symmetric stretching of C—O—C for the phenolic end groups were also observed, suggesting the presence of phenolic hydroxyl groups in the BZ precursor. The ^{1}H-NMR and FTIR data supported the idea that benzoxazines ringed with phenolic hydroxyl groups were synthesized successfully.

Effects of the refluxing time on the compositions of the BZ precursors

To investigate the effect of the refluxing time on the compositions of the BZ precursors, we took samples at different times. The samples taken at 1, 2, 3, 4, and 5 h were labeled BZ1, BZ2, BZ3, BZ4, and BZ5,

TABLE I
Effects of the Refluxing Time on the Precursor Compositions

Refluxing time (h)	Precursor	Monomer content (wt %)[a]	Ring content (%)[b]	Hydroxyl functionality[b]	Viscosity (mPa s)[c]
1	BZ1	55.2	88.7	2.2	72
2	BZ2	50.9	82.4	2.5	76
3	BZ3	38.2	72.8	3.1	86

[a] Calculated by the division of the area under the monomer peak by the whole area of the size exclusion chromatograph.
[b] Calculated from ^{1}H-NMR.
[c] At a concentration of 0.35 g/dL in dichloromethane at room temperature.

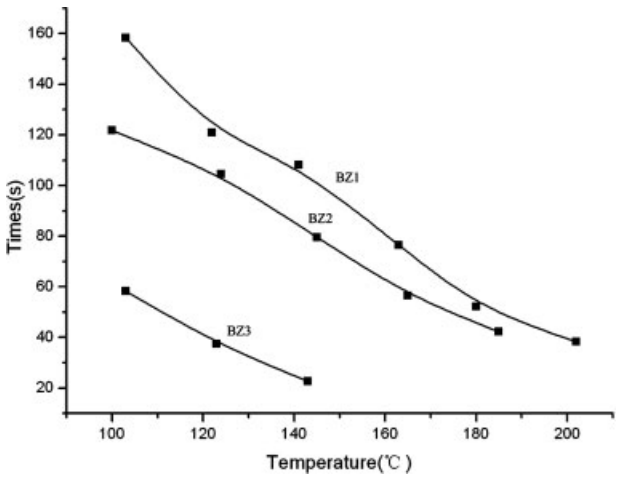


Figure 3 Gel times of the BZ precursors at different temperatures.

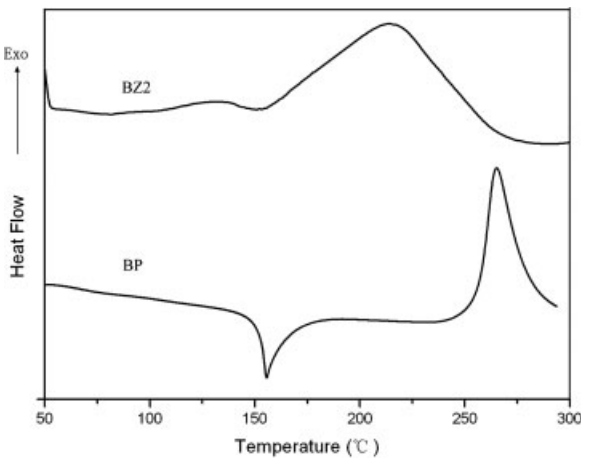


Figure 4 DSC thermograms for the curing of BZ2 and BP.

respectively. We found that the refluxing time remarkably affected the structures of the products. The BZ1–BZ3 precursors were all soluble in tetrahydrofuran and chloroform. The BZ4 precursor was partly soluble in tetrahydrofuran and chloroform with a small amount of swollen gel. The BZ5 precursor was a firm, crosslinked gel.

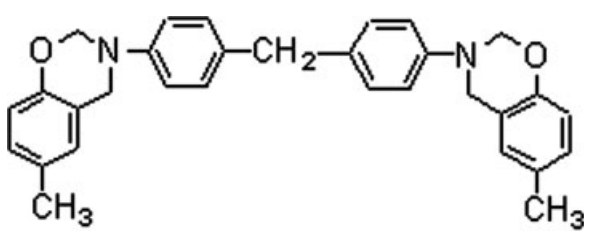
The effects of the refluxing time on the precursor compositions are summarized in Table I. As the refluxing time increased, the contents of the monomer and benzoxazine ring decreased, whereas the hydroxyl functionality and viscosity of the precursors increased. This happened because the phenol hydroxyl groups could initiate the ring-opening polymerization of the benzoxazine ring. With the refluxing time prolonged, ring-opening polymerization continuously occurred and formed hydroxyl groups, and the molecular weights of the precursors also increased.

Polymerization of the BZ precursors

Figure 3 shows the gel times of the BZ1–BZ3 precursors at different temperatures. The gel times of the precursors became shorter with the temperature rising. Moreover, at the same temperature, the precursors obtained at longer refluxing times showed shorter gel times (BZ3). This occurred because the precursors obtained at longer refluxing times contained a large number of hydroxyl groups. Therefore, the curing reaction rate of the precursors could be accelerated, and the gel time became shorter.

The thermal curing reactions of BZ2 and DDM-based benzoxazine monomer BP (Scheme 3) were studied with DSC (see Fig. 4). The exothermic peak of the ring-opening polymerization for BZ2 was centered at 215°C, and the onset exothermic temperature was 153°C, which was much lower than that of the BP monomer. Its onset exothermic temperature was 241°C. In comparison with BP, BZ2 had free phenolic hydroxyl groups that could catalyze the crosslinking reaction so that it occurred at a low temperature.

The thermal curing reaction was also monitored with FTIR (see Fig. 5). As the temperature increased, the absorption band at 1503 cm^{-1} due to the trisubstituted benzene ring and the band at 1326 cm^{-1} due to CH_2 wagging decreased. On the other hand, a



Scheme 3 Benzoxazine monomer BP.

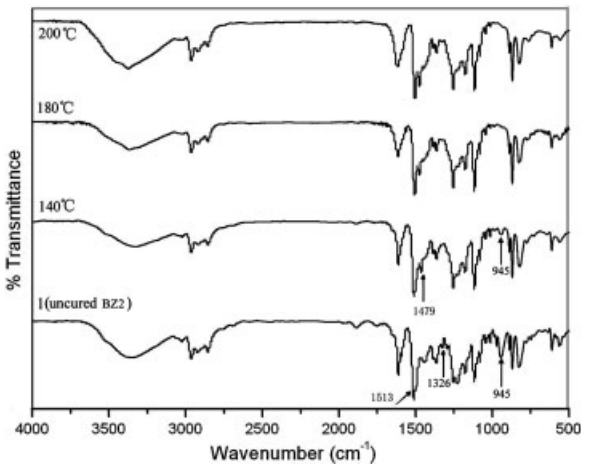


Figure 5 FTIR spectra of uncured BZ2 and BZ2 after each curing stage.

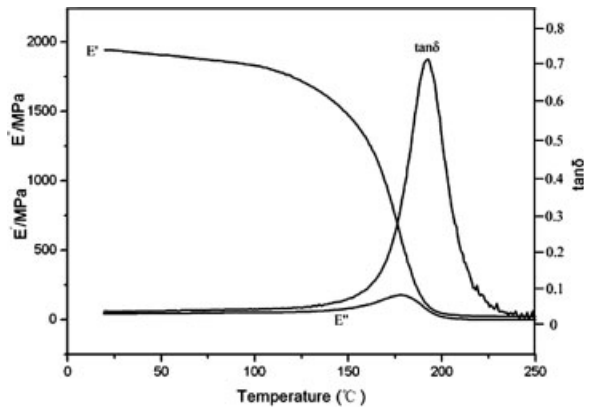


Figure 6 DMA spectra of PBZ (E' is the storage modulus, and E'' is the loss modulus).

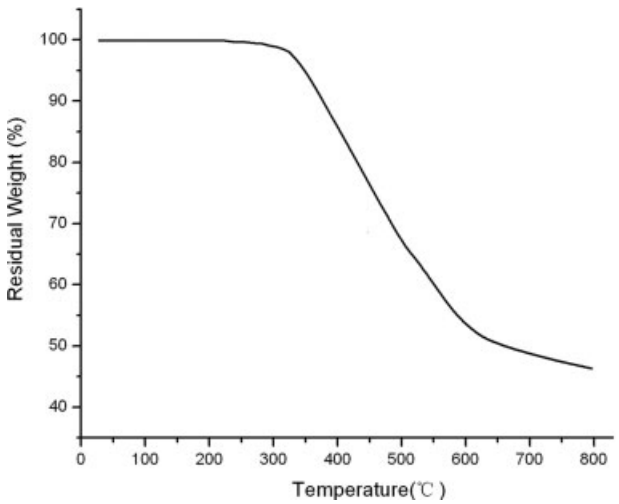


Figure 7 TGA thermogram of PBZ.

new absorption band at 1479 cm^{-1} due to the tetrasubstituted benzene ring appeared, suggesting that the ring-opening polymerization of BZ precursors occurred and formed PBZs. When the sample was postcured at 200°C for 2 h, the intensities of the characteristic absorption bands at 1503 and 1479 cm^{-1} were unchanged, and this indicated that the ring-opening polymerization was completely performed at 180°C.

Thermal properties of the PBZ resin

Figures 6 and 7 show the DMA and TGA thermograms of PBZ. PBZ showed a high glass-transition temperature (T_g). T_g was 179°C from the maximum of the loss modulus and 192°C from the maximum of the tan δ peak. The PBZ resin was a highly thermally stable polymer, with 5 and 10% weight loss temperatures of 346 and 375°C, respectively. In addition, the ultimate char yield of PBZ was up to 44% at 800°C under N_2.

CONCLUSIONS

BZ precursors containing phenol hydroxyl groups were successfully synthesized from bisphenol A, DDM, and formaldehyde in a 2:1:4 ratio. With different refluxing times, the precursor compositions, including the monomer content, benzoxazine ring content, and hydroxyl functionality, could be controlled. The precursors could be cured at a lower temperature. The obtained PBZ exhibited good thermal stability, and its T_g was 179°C from the maximum of the loss modulus and 192°C from the maximum of the tan δ peak.

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