Macromolecules

Steric Hindrance Control Synthesis of Primary Amine-Containing Benzoxazines and Properties of the Resulting Poly(benzoxazine imide) Thermosetting Films

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Supporting Information

ABSTRACT: Primary amine-containing benzoxazines **3** and **6** were prepared from an unsymmetrical diamine **1**, in which the amine group ortho to diethyl substituents, the hindered amine, is not reactive toward aldehyde at room temperature. Based on **6**, three poly(benzoxazine imide) (PBzI) thermosets were prepared by low-temperature polymerization, followed by thermal treatment. Experimental data show that incorporating thermosetting benzoxazine into a polyimide increased the T_{gy} tensile modulus, dimensional stability, flame retardancy, and contact angle without sacrificing too much in thermal stability.



INTRODUCTION

Main-chain-type polybenzoxazines are an active concept in the recent development of benzoxazines. They can be prepared by Mannich-type polycondensation of diamine, bisphenol, and formaldehyde.¹⁻⁵ Other than the Mannich-type polycondensation, the main-chain-type polybenzoxazines can be prepared using other approaches. Endo et al. prepared main-chain type polybenzoxazines based on the click reactions of a bifunctional alkynyl compound with a benzoxazine core and a bisazide counterpart.⁶ Through highly efficient click polycondensation, the benzoxazine ring was successfully introduced into the polymer main chain without any side reaction. Yagci et al. prepared a benzoxazine-containing diol from the condensation of bisphenol A, formaldehyde, and 2-(2-aminoethoxy)ethanol.⁷ High molecular weight polyetheresters containing benzoxazine were then prepared by the polycondensation of diacid chloride and the diol. After curing the polyetheresters, thermosets with good thermal stability and toughness induced by the soft etherester can be obtained. The synthetic approach opens new pathways for preparing curable thermoplastic elastomers. Mainchain-type polybenzoxazines based on the hydrosilylation reaction of a diallyllic benzoxazine with 1,1,3,3-tetramethyldisiloxane in the presence of a Pt catalyst were developed by the same group.⁸ With this approach, it is possible to prepare benzoxazine-containing polysiloxanes without affecting the benzoxazine moieties. Yagci et al. also prepared main-chaintype polybenzoxazine via the Sonogashira coupling reaction between diiodobisbenzoxazine and diacetylene bisether or diacetylene bisbenzoxazine.9 Polybenzoxazines with two different cross-linkable groups in the main chain can be obtained using this approach. After curing, thermosets with thermal stability comparable to classical polybenzoxazines can be achieved. Liu et al. prepared a main-chain-type polybenzoxazine through the Diels–Alder reaction of a bisfuranic benzoxazine with bismaleimide.¹⁰ During thermal curing, a retro-Diels–Alder reaction occurred, and simultaneous curing of benzoxazine and maleimide led to a cross-linked polybenzoxazine with a T_g value of 242 °C. Ishida et al. prepared main-chain-type polybenzoxazines by oxidative coupling of propargyl benzoxazines and ethynyl benzoxazines.¹¹ Thermosets with a char yield as high as 72% can be achieved using this approach.

Since difunctional benzoxazine is prepared from the condensation of bisphenol/amine/formaldehyde or diamine/phenol/ formaldehyde, it is difficult to precisely prepare benzoxazine with residual amino groups. Recently, Ishida et al. prepared benzoxazine with primary amine using protection and deprotection procedures.¹² For example, they reduced the tetrachlorophthalimide (TCP)-protected *p*-nitroaniline, carried out the benzoxazine synthesis, and then deprotected the TCP-protected benzoxazine using hydrazine hydrate at 20 °C. They also used TCP-protected aminophenol to prepare TCP-protected benzoxazine and deprotected the benzoxazine using hydrazine hydrate. In addition, they used trifluoroacetic anhydride (TFA)-protected *p*-aminophenol to prepare TFAprotected benzoxazines and deprotected the benzoxazine using sodium boron hydride. The primary amine-containing benzox-

Received:August 22, 2013Revised:October 20, 2013Published:November 4, 2013

azine was applied to prepared poly(benzoxazine amide).¹³ By combining the thermoplastic nature of polyamide and thermosetting nature of the polybenzoxazine, they created thermoplastic/thermoset crossover molecules that offer processability, ductility, film formability, chemical resistance, and dimensional stability.

The literature on the hybrid of polyimide and polybenzoxazine has rarely been reported.^{14,15} Takeichi et al. prepared polyimide and polybenzoxazine alloys.¹⁴ The polymer alloy films from polyimide/benzoxazine are considered to form semi-IPN consisting of a linear polyimide and polybenzoxazine network, in which two components are well miscible as confirmed by transparency and one single T_g . They found that the T_g values remarkably increased with the content of polyimide. Polybenzoxazine enhanced the modulus of polyimide, while polyimide improved the toughness of polybenzoxazine. Takeichi et al. also prepared alloys of polybenzoxazine/poly(siloxane imide) with or without OH groups.¹⁵ The hydroxyl poly(siloxane imide) system formed cross-linked polymer with one T_g while the poly(siloxane imide) system imide) system showed phase separation and displayed two T_g . To the best of our knowledge, no poly(benzoxazine imide) (PBzI) has been reported.

Loustalot et al.¹⁶ studied the copolymerization of bismaleimide and aromatic diamine with/without dialkyl group ortho to the amino group. They found the reaction onset temperature of bismaleimide and aromatic diamine increased with the increase of steric hindrance created by the alky group. Duffy et al.^{17,18} studied the effect of steric hindrance on the reaction of siliconcontaining aliphatic amines with phenylglycidyl ether and found that steric hindrance produced a great change in the reaction rate. In our previous work, ¹⁹ we prepared a series of polyimides based on two unsymmetrical diamines: 1-(4-aminophenyl)-1-(3,5dimethyl-4-aminophenyl)-1-(6-oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)ethane (1') and 1-(4-aminophenyl)-1-(3,5diethyl-4-aminophenyl)-1-(6-oxido-6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-yl)ethane (1). In the preliminary experiment, we took advantage of the concept of steric hindrance to precisely prepare primary amine-containing benzoxazine by the condensation of diamine (1' or 1)/phenol/formaldehyde with a molar ratio of 1:1:2. We found that a high-purity primary aminecontaining benzoxazine could be prepared from the condensation of 1/phenol/formaldehyde but failed using the condensation of 1'/phenol/formaldehyde. This result suggests the steric hindrance induced by the diethyl groups in 1 is large enough to prevent the reaction of hindered amino groups with aldehyde. On the basis of this result, we prepared primary amine-containing benzoxazines 3 and 6 from the unsymmetric diamine 1, in which the hindered amino group is stable toward aldehyde. According to our previous work,¹⁹ the hindered amino groups are reactive toward anhydride, so we prepared three PBzIs based on 6 and three dianhydrides. After thermal treatment, PBzI thermosets can be obtained. The detailed synthetic strategy and the effect of oxazine on the mechanical, flame-retardant, dimensional, contact angle, and thermal properties of polyimides were discussed.

EXPERIMENTAL SECTION

Materials. Unsymmetric diamines 1 and 1' were prepared according to our previous work.¹⁹ *s*-Trioxane (from Acros), 2-hydroxybenzalde-hyde (from Showa), paraformaldehyde (from TCI), and sodium borohydride (NaBH₄, from Acros) were used as received. 5,5'-Methylenebis(2-hydroxybenzaldehyde) (4) was prepared from 2-hydroxybenzodehyde and *s*-trioxane in the presence of sulfuric acid.²⁰ 4,4'-Diaminodiphenyl ether (ODA, from Chriskev) was

recrystallized from methanol. Phthalic anhydride (from Showa), 3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA, from Acros), 4,4'-oxydiphthalic anhydride (ODPA, from Chriskev), and 4,4'-bisphenol A dianhydride (BPADA, from Chriskev) were recrystallized from acetic anhydride. *N*,*N*-Dimethylacetamide (DMAc, from TEDIA) was purified by distillation under reduced pressure over calcium hydride (from Acros) and stored over molecular sieves. The other solvents used were commercial products (HPLC grade) and were used without any further purification.

Characterization. NMR measurements were performed using a Varian Inova 600 NMR in DMSO- d_{6i} and the chemical shift was calibrated by setting the chemical shift of DMSO- d_6 as 2.49 ppm. IR spectra were obtained in the standard wavenumber range of 400-4000 cm⁻ using a PerkinElmer RX1 infrared spectrophotometer. Differential scanning calorimetry (DSC) was performed using a PerkinElmer DSC 7 in a nitrogen atmosphere at a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed with a PerkinElmer Pyris1 at a heating rate of 20 °C/min in a nitrogen or air atmosphere. Dynamic mechanical analysis (DMA) was performed with a PerkinElmer Pyris Diamond DMA with a sample size of $5.0 \times 1.0 \times 0.002$ cm. The storage modulus E' and tan δ were determined as the sample was subjected to a temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1 Hz. The test was performed using a tension mode with an amplitude of 25 μ m. Thermomechanical analysis (TMA) was performed by an SII TMA/SS6100 at a heating rate of 5 °C/min. The coefficient of thermal expansion (CTE) was measured in the range from 50 to 200 °C. Flame retardancy of polyimides was performed by a UL-94VTM vertical thin test. In that test, an 8 in. \times 2 in. sample was wrapped around a 1/2 in. mandrel and then taped on one end. The mandrel was removed, leaving a cone-shaped sample that was relatively rigid. The two flame applications were 3 s instead of 10 s. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition was noted if polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample, and the self-extinguishing time (t_2) and dripping characteristics were recorded. If t_1 plus t_2 was less than 10 s without any dripping or the dripping does not ignite the cotton, the polymer was considered to be a VTM-0 material. If t_1 plus t_2 was in the range of 10-30 s without any dripping or the dripping does not ignite the cotton, the polymer was considered to be a VTM-1. The contact angle of the polymer sample was measured at 25 °C using a FTA100B contact angle goniometer interfaced with image-capture software by injecting a 5 μ L liquid drop. To obtain reliable contact data, at least three droplets were dispensed in different regions of the same piece of film, and at least two pieces of film were used to obtain reliable contact angle data. Thus, at least six contact angles were averaged for each type of film. The tensile testing was performed by EZ-SX with sample dimensions of 20 mm \times 5 mm \times 50 μ m at 25 °C.

Synthesis of 2. 1 (5.0 g, 0.010 mol), 2-hydroxybenzaldehyde (1.3919 g, 0.011 mol), and DMAc (50 mL) were introduced into a 250 mL glass flask equipped with a condenser, a hydrogen balloon, and a magnetic stirrer. The mixture was reacted at 25 °C for 12 h. NaBH₄ (0.6272 g, 0.017 mol) was added. The reaction mixture was further stirred at room temperature for 12 h. The mixture was then poured into water. The precipitate was filtered and dried in a vacuum oven at 105 °C. A yellow powder (4.8 g, 80% yield) with a melting point of 199 °C (DSC) and melting enthalpy of 81.7 J/g was obtained. ¹H NMR $(DMSO-d_6), \delta = 0.99 (6H, H^2), 1.55 (3H, H^{20}), 2.31 (4H, H^3), 4.17$ (2H, H²⁵), 4.41 (2H, NH₂), 5.96 (1H, NH), 6.41 (2H, H²³), 6.77 (1H, H²⁸), 6.81 (2H, H⁵), 6.83 (1H, H³⁰), 7.01 (2H, H²²), 7.06 (2H, H⁸, H²⁹), 7.10 (2H, H¹⁰, H¹⁴), 7.18 (1H, H²⁷), 7.27 (1H, H¹⁵), 7.31 (1H, H⁹), 7.63 (1H, H¹⁶), 7.88 (1H, H¹¹), 8.00 (1H, H¹⁷), 9.48 (1H, OH). FTIR (KBr): 1191 cm⁻¹ (C–N stretch), 3223 cm⁻¹ (OH stretch), 3394 cm⁻¹ (NH stretch).

Synthesis of 3. 2 (5.0 g, 0.008 mol), paraformaldehyde (0.2806 g, 0.009 mol), and chloroform (30 mL) were introduced into a 100 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. The mixture was reacted at 60 °C for 12 h. The mixture was then poured into *n*-hexane. The precipitate was filtered and dried in a vacuum oven at 60 °C. A white powder (3.6 g, 70% yield) with a melting point of

184 °C (DSC) and an exothermic peak temperature of 245 °C and exothermic enthalpy of 57.8 J/g was obtained. ¹H NMR (DMSO-*d*₆), $\delta = 0.94$ (6H, H²), 1.66 (3H, H²⁰), 2.26 (4H, H³), 4.42 (2H, NH₂), 4.61 (2H, H²⁵), 5.40 (2H, H³²), 6.74 (2H, H⁵), 6.78 (1H, H³⁰), 6.89 (1H, H²⁸), 6.93 (2H, H²³), 6.95 (1H, H¹⁰), 7.00 (1H, H⁸), 7.12 (2H, H²⁷, H²⁹), 7.18 (2H, H²²), 7.23 (3H, H⁹, H¹⁴, H¹⁵), 7.61 (1H, H¹⁶), 7.76 (1H, H¹¹), 7.95 (1H, H¹⁷). ¹³C NMR (DMSO-*d*₆), $\delta = 13.10$ (C²), 23.82 (C³), 24.41 (C²⁰), 48.72 (C²⁵), 52.01 (C¹⁹), 78.17 (C³²), 115.98 (C²³), 116.22 (C³⁰), 118.70 (C⁸), 120.40 (C²⁸), 120.71 (C¹²), 121.33 (C¹³), 122.54 (C¹⁸), 123.11 (C¹⁷), 123.45 (C¹⁰), 125.04 (C¹¹), 125.68 (C²⁶), 130.13 (C²²), 130.24 (C¹⁵), 131.72 (C¹⁴), 131.77 (C⁶), 133.06 (C¹⁶), 136.13 (C²¹), 141.35 (C¹), 146.25 (C²⁴), 150.78 (C⁷), 153.97 (C³¹). FTIR (KBr): 970 cm⁻¹ (N–C–O stretch), 1034 cm⁻¹ (Ar–O–C symmetric stretch), 1297 cm⁻¹ (Ar–O–C asymmetric stretch), 1370 cm⁻¹ (C–N stretch), 3351, 3448 cm⁻¹ (N–H stretch).



Synthesis of 5. 1 (5.0 g, 0.010 mol), 4 (1.3276 g, 0.005 mol), and DMAc (50 mL) were introduced into a 250 mL glass flask equipped with a condenser, a hydrogen balloon, and a magnetic stirrer. The mixture was reacted at 25 °C for 12 h. NaBH₄ (0.4312 g, 0.011 mol) was added. The reaction mixture was further stirred at room temperature for 12 h. The mixture was then poured into water. The precipitate was filtered and dried in a vacuum oven at 105 °C. A yellow powder (4.6 g, 75% yield) was obtained. ¹H NMR (DMSO-*d*₆), δ = 0.99 (12H, H²), 1.55 (6H, H²⁰), 2.31 (8H, H³), 3.70 (2H, H³²), 4.17 (4H, H²⁵), 4.41 (4H, NH₂), 5.90 (2H, NH), 6.41–8.00 (34H, Ar–H), 9.30 (2H, OH). FTIR (KBr): 1198 cm⁻¹ (C–N stretch), 3223 cm⁻¹ (OH stretch), 3384 cm⁻¹ (NH stretch).



Synthesis of 6. 5 (5.0 g, 0.004 mol), paraformaldehyde (0.2777 g, 0.009 mol), and chloroform (30 mL) were introduced into a 100 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. The mixture was reacted at 60 $^{\circ}$ C for 12 h. The mixture was then



poured into *n*-hexane. The precipitate was filtered and dried in a vacuum oven at 60 °C. A white powder 3.4 g (70% yield) with a melting point of 120 °C (DSC), an exothermic peak temperature of 255 °C, and exothermic enthalpy of 147 J/g was obtained. ¹H NMR (DMSO-*d₆*), $\delta = 0.94$ (12H, H²), 1.63 (6H, H²⁰), 2.26 (8H, H³), 3.77 (2H, H³³), 4.42 (4H, NH₂), 4.52 (4H, H²⁵), 5.33 (4H, H³²), 6.69 (2H, H³⁰), 6.74 (4H, H⁵), 6.88 (4H, H²³), 6.91 (2H, H¹⁰), 6.97 (6H, H⁸, H²⁷, H²⁹), 7.13 (4H, H²²), 7.19 (6H, H⁹, H¹⁴, H¹⁵), 7.58 (2H, H¹⁶), 7.73 (2H, H¹¹), 7.93 (2H, H¹⁷). ¹³C NMR (DMSO-*d₆*), $\delta = 13.12$ (C²), 23.82 (C³), 14.38 (C²⁰), 18.85 (C²⁵), 52.01 (C¹⁹), 77.96 (C³²), 115.86 (C²³), 116.16 (C³⁰), 118.71 (C⁸), 120.69 (C¹¹), 125.69 (C²⁶), 126.00 (C⁵), 127.02 (C²⁷), 127.61 (C⁹), 127.84 (C²⁹), 128.62 (C⁴), 130.15 (C²²), 130.21 (C¹⁵), 131.51 (C¹⁴), 131.73 (C⁶), 133.03 (C¹⁶), 136.56 (C²⁸), 136.14 (C²¹), 141.34 (C¹), 146.26 (C²⁴), 150.76 (C⁷), 152.16 (C³¹). FTIR (KBr): 950 cm⁻¹ (N-C-O stretch), 1044 cm⁻¹ (Ar-O-C symmetric stretch), 1368 and 3474 cm⁻¹ (N-H stretch).

Synthesis of 7. 3 (1.0 g, 1.66 mmol) and DMAc (2.68 g) were introduced into a 100 mL glass flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer. After 3 had dissolved completely, pathalic anhydride (0.2466 g, 1.66 mmol) was added. The reaction was carried out at 3-5 °C for 4 h. The mixture was then poured into water. The precipitate was filtered and dried in a vacuum oven at 60 °C. A light yellow powder 0.99 g (80% yield) was obtained.

Preparation of PBzIs. Experimental data show that poly-(benzoxazine amic acid) based on **6** and dianhydrides (BTDA, ODPA, and BPADA) are viscous, but the film became brittle after thermal treatment, probably due to too high a cross-linking density. Therefore, **6**/ODA/dianhydride with a molar ratio of 0.1-0.3:0.9-0.7:1was applied to prepare PBzI. The synthesis of PBzI was exemplified by the synthesis of **O-3** (the composition of polymer code is listed in Table 1) from the condensation of **6**, ODA, and ODPA. To a 100 mL three-neck round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet, **6** (0.30 g, 0.25 mmol), ODA (0.1155 g, 0.58 mmol), and DMAc (2.68 g) were added. After the monomers had dissolved completely, ODPA (0.2557 g, 0.82 mmol) was added. The reaction was carried out at 3-5 °C for 12 h to obtain the **O-3** precursor. Then, the viscous poly(amic acid) solution of **O-3** precursor was cast on glass by an automatic film applicator and dried overnight at 60 °C, 100 °C (1 h),

Table 1. Sample ID, Composition, and Mechanical Properties of PBzI Thermosets

sample ID	anhydride	6:ODA	film quality	tensile strength (MPa)	elongation at break (%)	initial modulus (GPa)
O-0	ODPA	0:1	flexible	118	8	1.7
0-1	ODPA	1:9	flexible	111	5	2.6
O-2	ODPA	2:8	flexible	110	4	3.2
0-3	ODPA	3:7	flexible	103	3	3.9
BT-0	BTDA	0:1	flexible	111	8	1.7
BT-1	BTDA	1:9	flexible	112	7	2.2
BT-2	BTDA	2:8	flexible	110	4	2.4
BT-3	BTDA	3:7	flexible	105	3	3.3
BPA-0	BPADA	0:1	flexible	85	9	1.4
BPA-1	BPADA	1:9	flexible	93	6	1.9
BPA-2	BPADA	2:8	flexible	104	6	2.2
BPA-3	BPADA	3:7	flexible	113	5	2.7

Scheme 1. Synthesis of Benzoxazines 3' and 6' via Traditional One-Pot Mannich Condensation



Scheme 2. Synthesis of 3 by a Two-Pot Procedure



Figure 1. ¹H NMR spectrum of 3 in DMSO- d_6 .

200 $^{\circ}C$ (1 h), and 300 $^{\circ}C$ (1 h), respectively. The other PBzIs were similarly prepared.

RESULTS AND DISCUSSION

Synthesis of 3' and 6' by a One-Pot Procedure. Benzoxazine 3' was initially synthesized by a traditional one-pot Mannich condensation of 1, phenol, and formaldehyde (Scheme 1). Table S1 lists the effect of reaction conditions on the synthesis of **3**'. Run 1–run 8 failed to prepare **3**' with reasonable purity. Benzoxazine **3**' prepared in run 9 displayed the best purity, as its ¹H NMR spectrum shown in Figure S1. On the basis of the reaction condition in run 9, we prepared **6**' by the traditional Mannich condensation of **1**, bisphenol A, and formaldehyde. Figure S2 shows the ¹H NMR of **6**' prepared by the reaction condition in run 9, Table S1. Benzoxazine **6**' with some impurity was formed but could not meet the requirement for polycondensation.

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Scheme 3. Synthesis of 6 Prepared by the Two-Pot Procedure



Figure 2. ¹H NMR spectra of **6** in DMSO- d_6 .

Synthesis of 3 by a Two-Pot Procedure. In order to prepare 3 with high purity, we prepared 3 using a two-pot procedure (Scheme 2).²¹ In the first pot, 1 reacted with 2-hydroxybenzaldehyde, yielding an intermediate with imine linkage. Sodium borohydride was then employed to reduce the imine linkage, yielding 2. In the second pot, paraformaldehyde was added to the chloroform solution of 2 to induce ring closure condensation. Figure S3 shows the ¹H NMR spectra of 1 and 2. From the spectrum of 2, the signal of amino (4.41 ppm) ortho to the diethyl groups was well preserved, suggesting the stability of hindered amino toward aldehyde. The signals of phenolic OH (9.48), CH₂NH (4.17), and CH₂NH (5.96) support the reaction of 2-hydroxylbenzaldehyde with the unhindered amino group.

Figure 1 shows the ¹H NMR spectrum of 3. The characteristic peaks of benzoxazine, $O-CH_2-N$ (5.40) and $Ph-CH_2-N$ (4.61) were clearly observed. Figures S4–S6 show the ¹³C, ¹H–¹H COSY, and HETERCOR of 3, further supporting the structure of 3.

Synthesis of 6 by a Two-Pot Procedure. Benzoxazine 6 was prepared by a two-pot procedure similar to 3 except the 2-hydroxylbenzaldehyde was replaced by 4 (Scheme 3). Figure S7 shows the ¹H NMR spectrum of 5. The signal of hindered amino at 4.41 ppm was well preserved while the signals of phenolic OH (9.48), CH₂NH (4.17), and CH₂NH (5.90) support the reaction of unhindered amino with 4. Figure 2 shows the ¹H NMR spectrum of 6. The characteristic peaks of benzoxazine, O-CH₂-N

Scheme 4. Synthesis and Thermal Treatment of 7





Figure 3. DSC of thermograms of 3 and 7.



Figure 4. DSC of thermograms of 6, O-3, and O-2 precursors.

(5.33) and Ph–CH₂–N (4.52) were clearly observed, supporting the structure of **6**. Figures S8–S10 show the ¹³C, ¹H–¹H COSY, and HETERCOR of **6**, further supporting the structure of **6**.

Synthesis and Thermal Treatment of 7. Model reaction between phthalic anhydride and 3 was performed to obtain 7

(Scheme 4). Figure S11 shows the ¹H NMR spectra of 3 and 7. To avoid ring-opening of benzoxazine, 7 was not completely dry, so solvent peaks were observed in Figure S11. The disappearance of the amino signal (4.4 ppm) and appearance of an amide signal (9.2 ppm) support the reaction of amino and anhydride.

Scheme 5. Synthesis of PBzI Thermosets





Figure 5. Photos of O-series PBzI thermosetting films.

The characteristic peaks (4.6 and 5.4 ppm) of benzoxazine remained while methylene (4.2 ppm) signal resulting from the ring-opening of benzoxazine was found. It is known that acid catalyzed the ring-opening of benzoxazine,²² so 7 with a partial ring-opened structure was obtained. Figure S12 show the ¹H NMR spectra of 7 after accumulative thermal treatment at each temperature for 1 h. The characteristic peaks of benzoxazine at 4.6 and 5.4 ppm reduced gradually after 140 °C and disappeared completely after 180 °C. The signals marked as (a)–(c) were signals from ring-opened benzoxazine structure.²³ The solubility of 7 after 260 °C thermal treatment was poor, so its NMR spectrum was not reliable. The cross-linking and the hydrogen bonding resulting from the phenolic structure might be

responsible for the poor solubility. IR spectra were applied to monitor the imidization of amic acid to imide. Figure S13 shows IR spectra of 7 after accumulative thermal treatment at each temperature for 20 min. The carbonyl absorption at 1651 cm⁻¹ and a broad carboxylic acid absorption at around 3387 cm⁻¹ at room temperature support the structure of amic acid. The absorption disappeared gradually after thermal treatment. New characteristic absorptions of imide at 1780 and 1718 cm⁻¹ and 1376 cm⁻¹ for C–N–C appear at temperatures higher than 140 °C, indicating that the imidization of amic acid starts at this temperature.

DSC Thermograms of Benzoxazines. Figure 3 shows DSC thermograms of 3 and 7. Benzoxazine 3 displays an exothermic



peak at 245 °C, and the corresponding exothermic enthalpy is 150 J/g. Benzoxazine 7 shows an exothermic peak with an enthalpy of 45 J/g. The smaller enthalpy is probably due to the existence of partial ring-opened structure, as supported by the signal of ring-opened structure in Figure S11.

Figure 4 shows DSC thermograms of 6, O-3, and O-2 precursors after vacuum drying at 60 °C for 12 h. 6 exhibits an exothermic peak with an enthalpy of 69 J/g. To observe the exotherms of O-3 and O-2 precursors in the DSC scan, O-3 and O-2 precursors were not dried at temperature higher than 60 °C. The broad endothermic peak of O-3 and O-2 precursors at 100–180 °C is due to the evaporation of solvent. An exothermic peak with enthalpy of 28 and 19 J/g was observed for O-3 and O-2 precursors, respectively. Based on model reaction, it is known that O-3 and O-2 precursors contained a partial ring-opened structure, which explains the smaller the exothermic enthalpy of O-3 and O-2 precursors than 6.



Figure 7. DMA thermograms of PBzI thermosetting films.

Synthesis of PBzI. The preparation of PBzI was performed by reacting 6/ODA/dianhydride with a molar ratio of 0.1-0.3:0.9-0.7:1 by a two-step procedure (Scheme 5 and Table 1). The mixture was reacted at 3-5 °C to form poly(benzoxazine amic acid), followed by a thermal treatment. As suggested by the model reaction of 7, ring-opening of benzoxazine and thermal imidization of amic acid occurred after thermal treatment, leading to PBzI thermosets.

Properties of PBzI Thermosetting Films. *Film Quality and Mechanical Properties.* Figure 5 shows the photos of Oseries PBzI thermosetting films. The others are shown in Figures S14 and S15. As shown in the figures, all the PBzI thermosets are flexible and bendable. Figure 6 shows the stress-strain curves of

Table 2. Thermal Properties of PBzI Thermosets

		$T_{g}(^{\circ}C)$		
sample ID	DMA ^a	DSC^{b}	TMA ^c	CTE $(ppm/^{\circ}C)^d$
O-0	301	294	280	43
O-1	320	310	298	46
O-2	348	325	305	32
O-3	349	325	306	24
BT-0	292	279	269	47
BT-1	316	300	291	48
BT-2	340	316	302	45
BT-3	349	329	304	41
BPA-0	233	218	214	59
BPA-1	255	236	233	54
BPA-2	285	262	257	53
BPA-3	305	284	273	48

^{*a*}Measured by DMA at heating rate of 5 °C/min; T_g was determined from the peak temperature of the tan δ curve. ^{*b*}From the second DSC heating scan at a heating rate of 20 °C/min. ^{*c*}Measured by TMA at a heating rate of 5 °C/min. ^{*d*}Coefficient of thermal expansion are recorded from 50 to 200 °C.

Table 3. Thermal Stability Data of PBzI Thermosetting Films

	T_{d5}^{a} (°C)		$T_{d10}^{\ \ b}$	(°C)	
sample	N_2	air	N ₂	air	char yield ^c (%)
O-0	546	588	588	627	59
0-1	460	512	523	605	57
O-2	449	477	490	542	59
0-3	449	459	487	515	58
BT-0	557	580	590	617	59
BT-1	477	485	536	571	58
BT-2	464	488	505	566	60
BT-3	445	474	480	542	57
BPA-0	536	526	555	554	48
BPA-1	503	503	538	553	51
BPA-2	470	476	510	517	51
BPA-3	460	460	492	504	52

^aTemperature corresponding to 5% weight loss by thermogravimetry at a heating rate of 20 °C/min. ^bTemperature corresponding to 10% weight loss by thermogravimetry at a heating rate of 20 °C/min. ^cResidual weight % at 800 °C.

PBzI thermosetting films, and the data of mechanical properties are listed in Table 1. Incorporating curable benzoxazine reduced the elongation at break but increased the initial modulus. For example, elongation at break reduced from 8% for **BT-0** to 3% for **BT-3**. The tensile strength of the O and BT series was reduced gradually with the content of **6**, while that of the BPA series was increased gradually with the content of **6**. Incorporating **6** not only can reduce intermolecular interaction because of the bulky structure of biphenylene phosphinate but also can increase rigidity due to the cross-linking effect. It is thought that the factor of reducing intermolecular interaction dominates in the O and BT series since ODPA and BTDA are rigid dianhydrides. In contrast, the factor of cross-linking dominates in the BPA series since BPADA is a flexible dianhydride.

Thermal Properties. The dynamic and thermal mechanical properties of PBzI thermosets were evaluated by DMA and TMA, respectively. Figure 7 shows the DMA thermograms of PBIz thermosetting films, and the data are summarized in Table 2. The T_g value obtained from the peak temperature of tan δ increased with the content of **6** (Table 2). For example, the T_g



Figure 8. TMA curves of PBzI thermosetting films.

value increased from 233 °C for **BPA-0** to 305 °C for **BPA-3**. In addition, the height of tan δ decreased with the content of **6**, demonstrating the power of cross-linking in enhancing the rigidity. The same trend was observed in DSC measurement, as listed in Table 2. Figure 8 shows TMA curves of PBIz thermosetting films. T_g values measured by TMA had the same trend with those measure by DMA. The coefficient of thermal expansion (CTE) decreased with the content of **6** (Table 2), demonstrating the advantage of cross-linking in dimensional stability. For example, CTE was reduced from 43 ppm/°C for



Figure 9. TGA thermograms of PBzI thermosetting films in a N_2 atmosphere.

O-0 to 24 ppm/°C for **O-3**. The value of 24 ppm/°C is relatively low for a polymer without biaxial orientation.

Thermal Stability and Flame Retardancy. TGA thermograms of PBzI thermosets in a N₂ atmosphere and air atmosphere are shown in Figure 9 and Figure S16, respectively. The 5 wt % degradation temperatures decrease with the content of **6**. However, the lowest 5 wt % degradation temperature is still as high as 445 °C in a nitrogen atmosphere and 460 °C in air atmosphere (Table 3). The data demonstrate the moderate-to-high

Table 4. UL-94 VTM Data of PBzI Thermosets

sample	P (wt %)	1st burning time (s)	2nd burning time (s)	dripping	UL-94 grade
O-0	0	4.5	2.0	no	VTM-0
0-1	1.08	1.4	0.5	no	VTM-0
O-2	1.83	0.8	0.4	no	VTM-0
O-3	2.39	0.7	0.2	no	VTM-0
BT-0	0	4.3	1.7	no	VTM-0
BT-1	1.05	1.6	0.8	no	VTM-0
BT-2	1.80	1.0	0.6	no	VTM-0
BT-3	2.35	0.8	0.3	no	VTM-0
BPA-0	0	4.8	2.2	no	VTM-0
BPA-1	0.79	2.0	1.2	no	VTM-0
BPA-2	1.40	1.2	0.8	no	VTM-0
BPA-3	1.88	0.8	0.3	no	VTM-0

BT-0 BT-1 Contact angle=45.12° Contact angle=51.26°





Figure 10. Contact angle of BT-series PBzI thermosetting films.

thermal stability of PBzI thermosets. As to the flame retardancy, according to the UL-94VTM vertical thin test, the $t_1 + t_2$ of PBzI thermosets is much smaller than that of neat polyimide and is less than 4 s for all PBzI thermosetting films (Table 4), so they belong to the VTM-0 grade. The phosphorus element is thought to be responsible for the enhanced flame retardancy.

Contact Angle. Figure 10 shows the contact angle of water for BT-series PBzI thermosets. The photos of other PBzI thermosets are shown in Figures S17 and 18. The contact angle increases slightly with the content of **6**. Polybenzoxazine has been reported as a material with a high contact angle, $^{24-26}$ which explains the increase of contact angle with the content of **6**. In addition, the hydrophobic diethyl group might be responsible for the increased contact angle.

CONCLUSIONS

We have successfully prepared a primary amine-containing benzoxazine **6** from an unsymmetrical diamine **1**, in which the hindered amino group is stable toward aldehyde at room temperature. The advantage of this steric hindrance control synthesis is that no protection and deprotection procedures are required. Three series of PBzI thermosetting films based on **6**/ODA/ dianhydride were prepared since the hindered amino group is reactive toward anhydride. Incorporating thermosetting benzoxazine increased the T_{gy} dimensional stability, flame retardancy,

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and contact angle while maintaining moderate-to-high thermal stability and mechanical properties.

ASSOCIATED CONTENT

Supporting Information

Table S1 and Figures S1–S18. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the National Science Council of the Republic of China for financial support.

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