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The robustness of thermoset of main-chain type polybenzoxazine precursor prepared through a strategy of A-A and B-B polycondensation

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A polybenzoxazine precursor, P(BF-bapp)-1, was prepared through a strategy of A-A and B-B polycondensation. The A-A monomer is 5,5'-methylenebis(2-hydroxybenzaldehyde), and the B-B monomer is 2,2-bis [4-(4-aminophenoxy)phenyl] propane (BAPP). The inherent viscosity (at 0.5 g/dL in NMP) of P(BF-bapp)-1 is as high as 0.34 dL/g, which is higher than that (0.23 dL/g) of a structurally similar polybenzoxazine precursor, P(BF-bapp)-2, that was prepared through traditional Mannich condensation of BAPP/bisphenol F/paraformaldehyde. A third structurally similar polybenzoxazine precursor, P(BF-bapp)-3, with an inherent viscosity of 0.09 dL/g, and a phenol and BAPP-based benzoxazine monomer, P-bapp, were prepared for properties comparison. After thermal curing of the benzoxazines, we found that a benzoxazine thermoset based on a high molecular weight precursor has advantages in higher T_g , higher char yield, lower refractive index (low dielectric constant according to Maxwell's equation), and better mechanical properties. The results demonstrate the robustness of a polybenzoxazine precursor prepared through a strategy of A-A and B-B polycondensation, which has never been reported in the benzoxazine field.

Introduction

Monomer type benzoxazines are generally prepared by Mannich condensation of bisphenol/mono amine/formaldehyde, and can be polymerized to thermosets by means of thermally activated ring-opening polymerization.¹⁻⁶ Benzoxazine thermosets exhibit many advantages, such as good thermal properties^{4, 7-11}, low surface energy¹²⁻¹⁴ and good dielectric properties^{10, 15-17}. However, benzoxazine thermosets based on monomer type benzoxazines have some shortcomings such as poor film quality. To obtain flexible polybenzoxazines with superior thermal properties and mechanical properties, main-chain type polybenzoxazine precursors have been developed.^{18, 19} For example, Endo *et al.*²⁰ Yagci *et al.*²¹⁻²³ Liu *et al.*²⁴, Ishida *et al.*²⁵, and Takeichi *et al.*²⁶ prepared main-chain type polybenzoxazine precursors using strategies other than Mannich condensation. Takeichi *et al.*²⁷⁻²⁹ Yagci *et al.*³⁰, and Ishida *et al.*³¹ prepared main-chain type polybenzoxazine precursors via Mannich condensation. The thermosets based on main-chain type polybenzoxazine precursors exhibited better thermal properties than thermosets based on monomer type benzoxazines. However, preparing a main-chain type polybenzoxazine precursor through Mannich condensation of diamine, bisphenol and paraformaldehyde led to polybenzoxazine precursor with moderate-to-low molecular weight (MW) due to side reactions.^{13, 27-31} Therefore, to prepare polybenzoxazine precursor with moderate-to-high MW, a strategy other than Mannich condensation should be applied. In this work, we prepared a polybenzoxazine precursor, P(BF-bapp)-1, with a moderate-to-high MW, through an A-A and B-B type polycondensation. The A-A monomer is 5,5'-methylenebis(2-hydroxybenzaldehyde), and the B-B monomer is 2,2-bis [4-(4-aminophenoxy)phenyl] propane (BAPP). To demonstrate the robustness of

P(BF-bapp)-1 and systematically discuss the effect of the MW of benzoxazine on the properties of a benzoxazine thermoset, we also prepared another three structurally similar benzoxazines with different MW. The second polybenzoxazine precursor, P(BF-bapp)-2, with a moderate MW, was prepared through a traditional Mannich condensation of BAPP, bisphenol F, and paraformaldehyde using toluene/ethanol as a solvent. The third polybenzoxazine precursor, P(BF-bapp)-3, with a moderate-to-low MW, was prepared from the Mannich condensation of BAPP, bisphenol F, phenol, and paraformaldehyde, in which phenol was used as a chain terminator. The fourth benzoxazine, a monomer type benzoxazine, P-bapp, was prepared from the Mannich condensation of BAPP, phenol, and formaldehyde. Through study of these four structurally similar benzoxazines, we demonstrate the benefit of a polybenzoxazine precursor prepared through a strategy of A-A and B-B polycondensation in thermal, mechanical, and dielectric properties of the resulting benzoxazine thermoset.

Experimental

Materials. 2,2-bis[4-(4-aminophenoxy)phenyl]propane (BAPP) was purchased from Chriskev. 2-Hydroxybenzaldehyde and phenol were purchased from Showa. s-Trioxane and sodium borohydride (NaBH₄) were purchased from Acros. Paraformaldehyde and bisphenol F were purchased from TCI. N,N-Dimethylacetamide (DMAc) was purchased from Tedia and 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. Differential scanning calorimetry (DSC) scans were obtained using a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 10 °C/min. NMR measurements were performed using a Varian Inova 400 NMR in CDCl₃ or DMSO-*d*₆, and the chemical shift was calibrated by setting the chemical shift of CDCl₃ (DMSO-*d*₆) as 7.24 (2.49) ppm. Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris1 at a heating rate of 20 °C/min in an atmosphere of nitrogen or air. Thermomechanical analysis (TMA) was performed by an SII TMA/SS6100 at a heating rate of 5 °C/min. The coefficient of thermal expansion (CTE) in the

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

temperature range of 50–150 °C was recorded from the second-run data. Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer Pyris Diamond DMA with a sample size of 5.0 cm x 1.0 cm x 0.2 cm. The storage modulus E' and $\tan \delta$ were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1 Hz. The test was performed by a tension mode with an amplitude of 25 μm . Tensile testing was performed by EZ-SX with sample dimensions of 20 mm x 5 mm x 50 μm at 25 °C. The refractive index (n) at various wavelengths was obtained by an Ellipsometry GES-5E. The dielectric constant (ϵ) was calculated from the Maxwell's equation with $\epsilon = 1.1n^2$, in which n is the refractive index at 633 nm. Size exclusion chromatography (SEC) was carried out on a Perkin-Elmer series 200a using tetrahydrofuran as the eluent at 40 °C with a flow rate of 1.0 mL/min. Size exclusion chromatography (SEC) was also carried out on a Hitachi LaChrom Elite using N-methylpyrrolidinone (NMP) as the eluent at 60 °C with a flow rate of 0.6 mL/min. The data were calibrated with polystyrene standards. The inherent viscosities were determined at 0.5 g dL⁻¹ concentration in N-methylpyrrolidinone (NMP) using a Prema B801-2 viscometer at 30 °C.

Synthesis of 5,5'-methylenebis(2-hydroxybenzaldehyde) (1).³² s-Trioxane 10.0 g (0.111 mol), 2-hydroxybenzaldehyde 89.46 g (0.732 mol), acetic acid 100 g, and sulfuric acid 3.09 g were introduced into a 250-mL glass flask equipped with a nitrogen inlet and a magnetic stirrer. The mixture was reacted at 85 °C for 22 h. After the reaction solution was cooled to room temperature, the precipitate was filtered, dissolved in methanol, and poured into water. The precipitate was filtrated and then dried in a vacuum oven at 70 °C.

Synthesis of P(BF-bapp)-1. P(BF-bapp)-1 was prepared by a three-step, two-pot procedure. In the first pot, 5,5'-methylenebis(2-hydroxybenzaldehyde) 5.0 g (0.020 mole), BAPP 8.01 g (0.02 mole), and dry DMAc 42 mL were introduced into a round-bottom 100 mL glass flask equipped with a nitrogen inlet, and a magnetic stirrer (Scheme 1). The reaction mixture was stirred at room temperature for 24 h. After that, the viscous solution was diluted with DMAc 10 mL, and NaBH₄ 1.77 g (0.048 mole) was added into the solution. The reaction mixture was further stirred at room temperature for 24 h. The solution was then poured into water. The fiber-like precipitate was filtered and dried in a vacuum oven at 60 °C. A white precipitate of 8.67 g (70% yield) was obtained. The sample ID of the product is named pre-P(BF-bapp)-1. In the second pot, pre-P(BF-bapp)-1 1.0 g (0.002 mole), paraformaldehyde 0.11 g (0.004 mole), and chloroform 30 mL were introduced into a round-bottom 100 mL glass flask equipped with a nitrogen inlet, a condenser and a magnetic stirrer. The reaction mixture was stirred at reflux temperature for 12 h. After that, the mixture was poured into hexane. The precipitate was filtered and dried in a vacuum oven at 60 °C. A light yellow powder of P(BF-bapp)-1 0.88 g (85% yield) was obtained.

Synthesis of P(BF-bapp)-2. BAPP 1.0 g (0.002 mole), bisphenol F 0.49 g (0.002 mole), paraformaldehyde 0.29 g (0.010 mole), and 9 mL of a mixed solvent of toluene/ethanol (2/1, v/v) were introduced into a round-bottom 100 mL glass flask equipped with a nitrogen inlet, a condenser and a magnetic stirrer (Scheme 2). The reaction mixture was stirred at 80 °C for 15 h. After that, the mixture was poured into methanol. The precipitate was filtered and dried in a vacuum oven at 60 °C. A light yellow powder 1.28 g (80% yield) was obtained.

Synthesis of P(BF-bapp)-3. BAPP 3.0 g (0.007 mole), bisphenol F 1.02 g (0.005 mole), phenol 0.41 g (0.004 mole), paraformaldehyde 0.88 g (0.029 mole), and 30 mL of a mixed solvent of toluene/ethanol (2/1, v/v) were introduced into a round-bottom 100 mL glass flask equipped with a nitrogen inlet, a condenser and a magnetic stirrer (Scheme 2). The reaction mixture was stirred at 80 °C for 15 h. After that, the mixture was poured into hexane. The precipitate was filtered and dried in a vacuum oven at 60 °C. A light yellow powder 3.92 g (82% yield) was obtained.

Synthesis of P-bapp. BAPP 1.0 g (0.002 mole), phenol 0.46 g (0.005 mole), paraformaldehyde 0.29 g (0.010 mole), and 15 mL of a mixed solvent of toluene/ethanol (2/1, v/v) were introduced into a round-bottom 100 mL glass flask equipped with a nitrogen inlet, a condenser and a magnetic stirrer (Scheme 2). The reaction mixture was stirred at

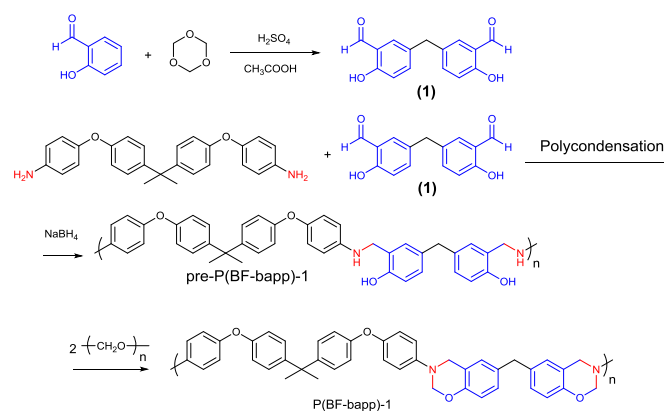
80 °C for 24 h. After that, the mixture was dried by evaporation of the solvent under vacuum. A light yellow powder 1.5 g (95% yield) was obtained.

Curing of polybenzoxazine precursors. Polybenzoxazine precursors, P(BF-bapp)-1, P(BF-bapp)-2, and P(BF-bapp)-3, were dissolved in NMP, with a concentration of 10 wt%, 25 wt%, and 30 wt%, respectively. The solution was then cast onto glass by an automatic film applicator. The resulting films were transparent and colorless. They were dried at 80 °C overnight and cured at 120, 160, 200, 240 °C for 1h each in an air-circulating oven. After that, brown transparent films (about 60 μm) were obtained by soaking the coated glass in water. The sample ID of the cured polybenzoxazine films are named C-P(BF-bapp)-1, C-P(BF-bapp)-2, and C-P(BF-bapp)-3, respectively. The letter C in the sample ID corresponds to the word cured.

Curing of P-bapp. P-bapp was melted, stirred and transferred to an aluminum mold and then cured at 180, 200, 220, 240 °C for 2 h each in an air-circulating oven. Thereafter, sample was allowed to cool slowly to room temperature to prevent cracking. The sample ID of the cured P-bapp is named C-P-bapp.

Results and Discussion

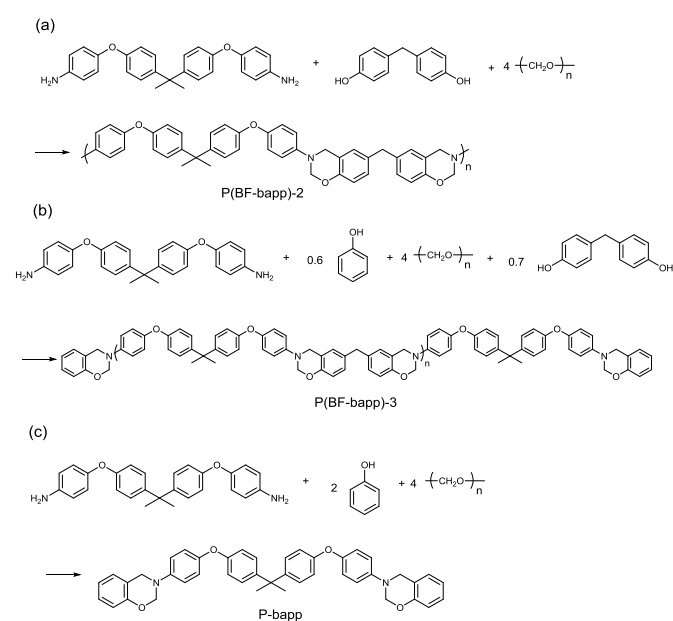
Synthesis of benzoxazines. To prepare a polybenzoxazine precursor with a high MW, we applied a strategy other than Mannich condensation. The benzoxazine, P(BF-bapp)-1, was prepared by a A-A and B-B type, three-step polycondensation procedure (Scheme 1). The starting material, 5,5'-methylenebis(2-hydroxybenzaldehyde) (**1**) was prepared from 2-hydroxybenzaldehyde and s-trioxane in the presence of sulfuric acid according to a reported procedure.³² In the first step, a polymer with imine linkages was produced by the polycondensation of BAPP and (**1**). Sodium borohydride was then employed to reduce the imine linkage in the second step, yielding pre-P(BF-bapp)-1. The structure of pre-P(BF-bapp)-1 was confirmed by a ¹H-NMR spectrum (Figure S1). In the third step, paraformaldehyde was added to induce the ring closure of pre-P(BF-bapp)-1, yielding P(BF-bapp)-1. To demonstrate the robustness of P(BF-bapp)-1 and systematically discuss the effect of the MW of benzoxazine on the properties of the resulting thermoset, we prepared another three structurally similar benzoxazines. The second benzoxazine, P(BF-bapp)-2, was prepared from the Mannich condensation of BAPP, bisphenol F, and paraformaldehyde (Scheme 2). Gelation occurred for this synthesis in a homo-solvent such as chloroform, dioxane, and toluene (Table S1). However, the gelation phenomenon could be significant improved using toluene/ethanol as a reaction solvent, as suggested in our previous work¹³. The third benzoxazine, P(BF-bapp)-3 was prepared from the Mannich condensation of BAPP, bisphenol F, phenol, and paraformaldehyde (Scheme 2), in which phenol was used as a chain terminator, suggested by Ishida et al.³³. The fourth benzoxazine, P-bapp, was prepared from Mannich condensation of BAPP, phenol, and paraformaldehyde (Scheme 2).



Scheme 1. Synthesis of (**1**) and P(BF-bapp)-1.

Table 1. The ratios of crosslinking sites to benzoxazine units for the benzoxazines.

Sample	Structure	Ratio of reactive sites to benzoxazine
P(BF-bapp)-1		6/2 = 3
P(BF-bapp)-2		(6n+8)/(2n+2)
P(BF-bapp)-3		8/2 = 4



Scheme 2. Synthesis of three benzoxazines for comparison.

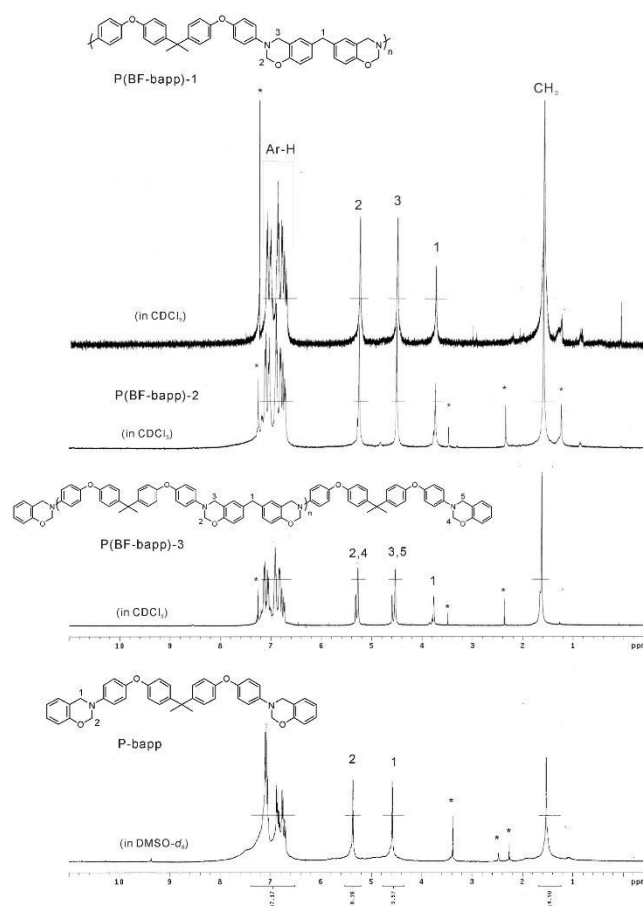
Table 2. The inherent viscosity and SEC data of P(BF-bapp)-1, P(BF-bapp)-2, and P(BF-bapp)-3.

Sample	viscosity (dL/g) ^a	M _w /M _n (in THF)	M _w /M _n (in NMP)
P(BF-bapp)-1	0.34	-/ ^b	1.7 × 10 ⁵ /4.2 × 10 ⁴
P(BF-bapp)-2	0.23	7.9 × 10 ⁴ /1.9 × 10 ⁴	1.1 × 10 ⁵ /2.0 × 10 ⁴
P(BF-bapp)-3	0.07	7.0 × 10 ³ /2.7 × 10 ³	9.3 × 10 ³ /4.4 × 10 ³

^a Inherent viscosity, measured at 0.5 g/dL in NMP at 30 °C.^b Insoluble in THF.

Figure 1 shows the ¹H-NMR spectra of the four benzoxazines. The characteristic peaks of oxazine at 4.5 and 5.3 were clearly observed for P(BF-bapp)-1 and P(BF-bapp)-2. The characteristic peaks of oxazine at 4.6 and 5.4 were also clearly observed for P-bapp. For P(BF-bapp)-3, the characteristic peaks of oxazine were split due to the different environment of benzoxazine in the repeating unit and terminal units. Table 2 shows the inherent viscosity (at 0.5 g/dL in NMP) of P(BF-bapp)-1, P(BF-bapp)-2, and P(BF-bapp)-3. The value is 0.34, 0.23, and 0.07 dL/g, respectively. No inherent viscosity data is available for P-bapp since it is only a monomer. SEC data were measured in THF. The number-average molecular weight (M_n) of P(BF-bapp)-2 and P(BF-bapp)-3 is 19000 and 2700 g/mol, respectively. The weight-average molecular

weight (M_w) of P(BF-bapp)-2 and P(BF-bapp)-3 is 79000 and 7000 g/mol, respectively. However, no SEC data of P(BF-bapp)-1 is available since it is insoluble in THF for SEC measurement. Therefore, SEC analysis were also performed in NMP, and the data were listed in Table 2. P(BF-bapp)-1 shows the highest M_n (4.2 × 10⁴) and M_w (1.7 × 10⁵). Through the viscosity and SEC data, the order of MW of the benzoxazines is P(BF-bapp)-1 > P(BF-bapp)-2 > P(BF-bapp)-3 > P-bapp.

Figure 1. ¹H-NMR spectra of the benzoxazines.

DSC analysis. Figure 2 shows the DSC thermograms of the benzoxazines. The exothermic data such as peak temperature and enthalpy are listed in Figure

2. P(BF-bapp)-1, with the highest MW, display the highest exothermic peak temperature. Tsai et al. studied DSC thermograms of polyacrylonitrile precursors with different MWs.³⁴ They found that the polyacrylonitrile precursor with the highest MW displayed the highest onset exothermic temperature and peak temperature. The higher MW hinders the mobility of polymer chain to access each other is thought to be the reason for higher ring-opening polymerization temperature of P(BF-bapp)-1. Figure 2 also shows the order of exothermic enthalpy is P-bapp > P(BF-bapp)-3 > P(BF-bapp)-2 \approx P(BF-bapp)-1. According to previous researches on ring-opening polymerization mechanism of benzoxazine,^{1, 4, 35} the free ortho and para positions to the O or N of oxazine were reactive sites. The reactive sites of each benzoxazine are marked as red arrows in Table 1. The ratio of reactive sites to benzoxazine is 4 for P-bapp, $(6n+8)/(2n+2)$ for P(BF-bapp)-3, and 3 for both P(BF-bapp)-1 and P(BF-bapp)-2. The value of $(6n+8)/(2n+2)$ is 3.09 if $n=10$, and is 3.03 if $n=30$. Therefore, the order of the ratio of reactive sites to benzoxazine is P-bapp > P(BF-bapp)-3 > P(BF-bapp)-2 \approx P(BF-bapp)-1. The trend is consistent with that of exothermic enthalpy.

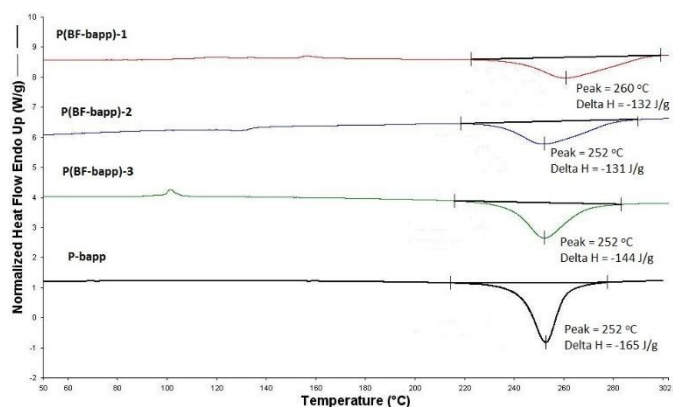


Figure 2. DSC thermograms of the benzoxazines.

Thermal properties. Figure S2 shows photos of C-P(BF-bapp)-1 and C-P(BF-bapp)-2. All the cured films are void-free and bendable. Figure 3 shows the DMA thermograms of the benzoxazine thermosets. The T_g values determined from the peak of $\tan(\delta)$ for C-P(BF-bapp)-1, C-P(BF-bapp)-2, C-P(BF-bapp)-3, and C-P-bapp are 305, 302, 284, and 194 °C, respectively. Figure 4 shows the TMA thermograms of the benzoxazine thermosets. The T_g values taken from the onset temperature of TMA thermograms are 256, 258, 244, and 173 °C, respectively. TMA and DMA data show that the T_g value of a benzoxazine thermoset increased initially with the MW of its precursor, but reach a plateau at a higher MW. The trend for the T_g and MW is similar to thermoplastic polymers,³⁶⁻³⁸ but has never been reported for benzoxazine thermosets. The coefficients of thermal expansion (CTE) in the temperature range of 50-150 °C are 50, 51, 51, and 77 ppm/°C, respectively. C-P-bapp, which has the lowest T_g , shows the highest CTE. However, no difference in CTE value was observed for other benzoxazine thermosets. Figure 5 shows the TGA thermograms of the benzoxazine thermosets. The 5 wt% decomposition temperatures ($T_{d5\%}$) in a nitrogen atmosphere for C-P(BF-bapp)-1, C-P(BF-bapp)-2, C-P(BF-bapp)-3, and C-P-bapp are 422, 429, 424, and 424 °C, respectively. The char yields at 800 °C in a nitrogen atmosphere are 60, 57, 52, and 41 %, respectively. The thermal stability of benzoxazine thermosets is independent of the MW of its precursor. However, the char yield at 800 °C increased with the MW of its precursor. According to Takechi's research²⁷, the extension of network increases the crosslinking density in the thermoset, leading to the enhancement in the char yield.

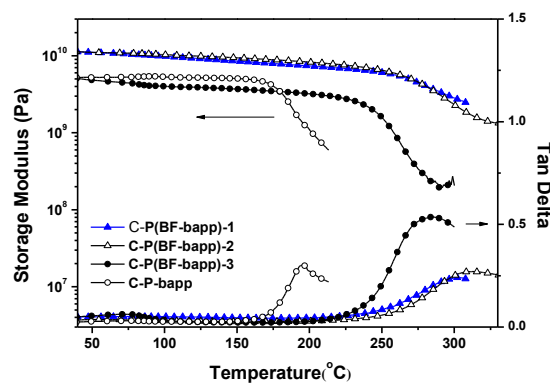


Figure 3. DMA thermograms of the benzoxazine thermosets.

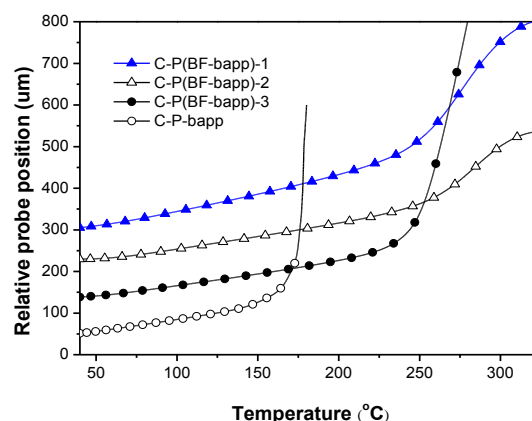


Figure 4. TMA thermograms of the benzoxazine thermosets.

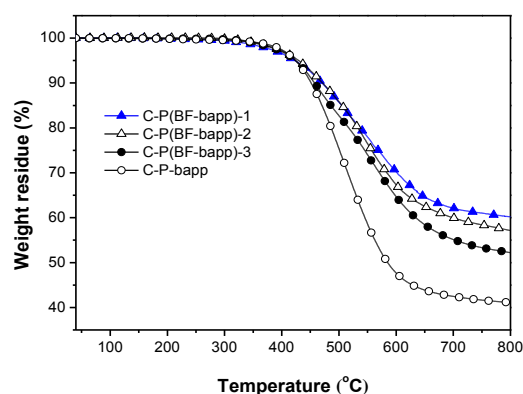


Figure 5. TGA thermograms of the benzoxazine thermosets in N_2 atmosphere.

Mechanical properties. Figure 6 shows the stress-strain curves of C-P(BF-bapp)-1, C-P(BF-bapp)-2, and C-P(BF-bapp)-3. Note that the self-supporting film of C-P-bapp is too brittle, so no stress-strain curve was presented. The tensile strengths (elongation at break) for C-P(BF-bapp)-1, C-P(BF-bapp)-2, and C-P(BF-bapp)-3 are 75 MPa (3.1%), 57 MPa (1.9%), and 29 MPa (1.3%), respectively. Both tensile strengths of the benzoxazine thermoset increased with the MW of its precursor, demonstrating an advantage of a higher precursor's MW in mechanical properties. The trend for tensile strengths and

MW is similar to thermoplastic polymers.³⁹⁻⁴¹ However, a typically yield behavior was not observed due to the brittleness of thermosets.

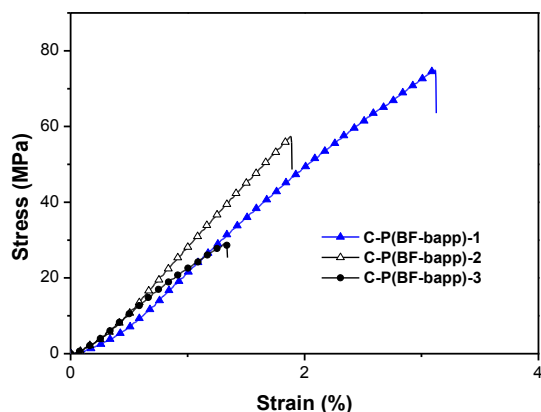


Figure 6. Stress-strain curves of C-P(BF-bapp)-1, C-P(BF-bapp)-2, and C-P(BF-bapp)-3.

Refractive index and dielectric constant. Figure 7 shows the refractive index of C-P(BF-bapp)-1, C-P(BF-bapp)-2 and C-P(BF-bapp)-3 at various wavelengths. Note that the self-supporting film of C-P-bapp cannot be achieved, so no refractive index-wavelength curve was presented. The refractive indexes for C-P(BF-bapp)-1, C-P(BF-bapp)-2 and C-P(BF-bapp)-3 at 633 nm are 1.692, 1.709, and 1.712, respectively. The dielectric constant calculated by the Maxwell's equation $\epsilon = 1.1n^2$, in which n is the refractive index at 633 nm, are 3.14, 3.22, and 3.25, respectively. The dielectric constant of the benzoxazine thermoset decreased with the MW of its precursor. The refractive index data demonstrate the advantage of higher precursor's MW in dielectric properties.

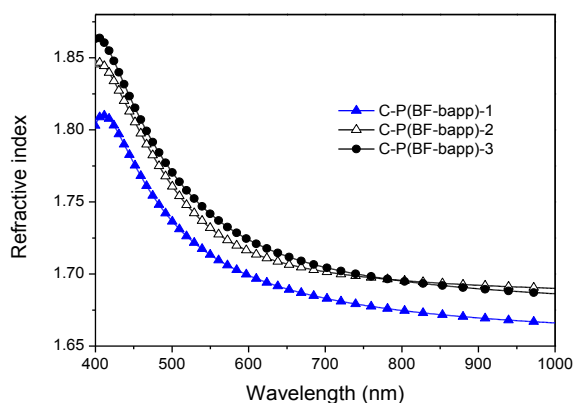


Figure 7. The refractive index of benzoxazine thermosets at various wavelengths.

Takeichi et al. reported the enhancement in the thermal stability of the thermoset of polybenzoxazine precursor can be attributed to the increase in the crosslinking density due to the extension of the network.²⁷ Based on the concept, we proposed an illustration of the crosslink network from benzoxazines with different MWs in Figure 8. Generally, small building blocks have more freedom than the large building blocks to pack the network structure, resulting in a network structure that is not as regular as that built from large building block. This explains the higher T_g and better mechanical properties of benzoxazine thermosets from higher MW benzoxazines. In addition, less regular packing of benzoxazine thermoset from low MW benzoxazine leads to more phenolic OH that is not intermolecular hydrogen-bonded, and thus increases the polarity of benzoxazine thermosets. This

probably explains the fact that the dielectric constant of a benzoxazine thermoset decreased with the MW of its precursor.

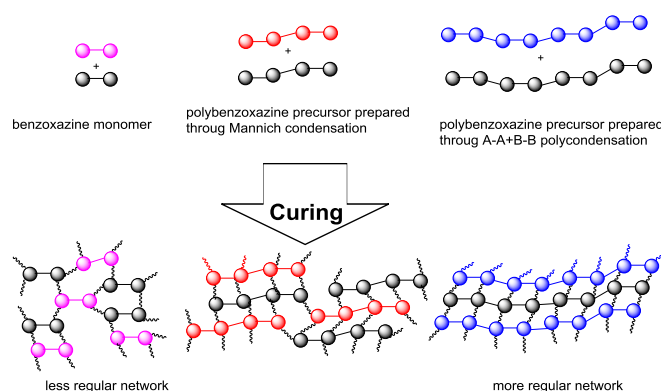


Figure 8. Illustration of crosslink network from benzoxazines with different MWs.

Conclusions

We report a strategy to prepare a polybenzoxazine precursor, P(BF-bapp)-1, by an A-A and B-B type polycondensation. The P(BF-bapp)-1 exhibits much higher MW than the structurally similar polybenzoxazine precursor, P(BF-bapp)-2, which was prepared by a traditional Mannich condensation. To demonstrate the robustness of P(BF-bapp)-1 and systematically discuss the effect of the MW of benzoxazine on the properties of the resulting thermoset, we also prepared other benzoxazines, P(BF-bapp)-3 and P-bapp. TMA and DMA data show that the T_g of the benzoxazine thermoset initially increased with the MW of its precursor, but reached a plateau at higher MW (Figures 3-4). TGA data show that the thermal stability of benzoxazine thermosets is independent of the MW of its precursor. However, the char yield increased with the MW of its precursor (Figure 5). The tensile strength and elongation at break of benzoxazine thermosets increased with the MW of its precursor (Figure 6). The refractive index of the benzoxazine thermoset decreased with the MW of its precursor (Figure 7). The experimental data show that a benzoxazine thermoset based on a high MW precursor has advantages in higher T_g , higher char yield, lower refractive index (lower dielectric constant according to Maxwell's equation), and better mechanical properties. Through this study, we demonstrate the benefit of a polybenzoxazine precursor prepared through a strategy of A-A and B-B polycondensation in thermal, mechanical, and dielectric properties of the resulting benzoxazine thermoset.

Acknowledgements

The authors thank the Ministry of Science and Technology of Taiwan for financial support.

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Graphical Abstract

The robustness of thermoset of main-chain type polybenzoxazine precursor prepared through a strategy of A-A and B-B polycondensationMeng Wei Wang,^a Ru Jong Jeng,^{a*} Ching Hsuan Lin^{b*}

A polybenzoxazine precursor was prepared through a strategy of A-A and B-B polycondensation.

The precursor exhibits much higher molecular weight than those prepared by traditional Mannich condensation.

After curing, the resulting thermoset shows robustness in thermal, mechanical, and dielectric properties.

