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Synthesis and Properties of Highly Cross-Linked Thermosetting Resins of Benzocyclobutene-Functionalized Benzoxazine

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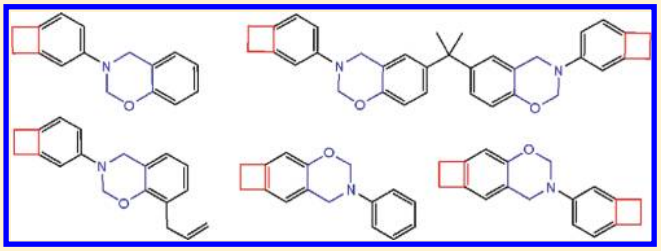
Supporting Information

ABSTRACT: Benzocyclobutene- (BCB-) functionalized benzoxazine (BOZ) monomers and resins have been successfully prepared. BCB-functionalized BOZ monomers were synthesized by the reaction of 4-aminobenzocyclobutene (AMBCB), phenol and paraformaldehyde or by the reaction of 4-hydroxylbenzocyclobutene (OHBCB), arylamine, and paraformaldehyde in toluene under reflux. Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR) are used to characterize the structure of the monomers. The monomers possess two kinds of ring-opening polymerizable functional groups of BCB and BOZ. So the monomers can be cured at proper temperature to prepare highly cross-linked resins. The polymerization behavior of the monomers is studied by differential scanning calorimetry (DSC) and FTIR. DMA study demonstrates that these polymers show high storage moduli which can be maintained in a wide temperature range up to 300 °C and high T_g at ca. 350 °C. The TGA study shows that the cured resins possess good thermal stability.



INTRODUCTION

Benzoxazine (BOZ), a novel series of six-membered heterocyclic ring monomers that contains oxygen and nitrogen, has got many people's attention.[1−3] It can be prepared by dehydration condensation reaction of primary amines, phenols and aldehydes under certain conditions. The benzoxazine ring is stable at room temperature for a long period and undergoes ring-opening polymerization to generate a nitrogen-containing phenolic resin similar to PF resins at proper temperature. The low viscosity of the BOZ monomers facilitates for process of manufacture. The polymerization of benzoxazine does not generate any volatiles and near zero shrinkage occurs during the period of polymerization of the monomers. The benzoxazine resins also possess many good properties, such as good flame retardancy, good chemical resistance, low water absorption, excellent mechanical properties and good electrical properties, etc. BOZ can be widely used as heat-resistant materials, composite materials, electronic packaging materials and others.

Traditional BOZ also suffers some shortcomings such as relatively low thermal stability, high curing temperature and brittleness, etc.[1] Modification or molecular engineering of BOZ monomer is necessary to overcome these problems. In order to improve the thermal stability and performance of BOZ resins, bifunctional precursors were utilized or polymerizable functional groups were introduced. BOZ prepared by bisphenol compounds such as bisphenol A,[2] 4,4′-dihydroxy benzophenone,[4] and 1,5-naphthalenediol[5] has showed improved thermal mechanical property than the ordinary epoxy resins. Allyl-,[6] acetylene-,[7] maleimide-,[8−10] and norbornene-based[10] precursors can also be employed to prepare BOZ. Polymerization of these monomers with multi-functional groups can be cross-linked to improve the heat resistance, toughness and processability properties. Agag et al. has synthesized a series of allyl containing BOZ, for which the cured polymer shows glass transition temperature up to 322 °C. Liu et al.[8] synthesized a phthalocyanine containing maleimide of BOZ monomer, which has good processing (low melting point of 52−55 °C and good solubility in common solvents), and good heat resistance for the cured monomers (glass transition temperature of 204 °C, 10% weight loss temperature of 366 °C). Yagci et al. reported a new monomer possessing both benzoxazine and coumarin rings.[11] The monomer underwent dimerization via the 2 + 2 cycloaddition reaction to form cyclobutane rings upon photolysis around 300 nm. However, thermogravimetric analysis showed unfavorable thermal stability ($T_{5\%}$ at 303.7 °C) of the cured bifunctional benzoxazine monomer, which was caused by the poor thermal stability of the cyclobutane rings.

Meanwhile, benzocyclobutene (BCB) based polymer materials have drawn much attention for their outstanding properties (such as high thermal stability, low dielectric constant and dielectric loss, good flatness and mechanical properties).[12−16] They were especially applied in the field of electrical and electronic packaging. BCB ring can be converted to conjugated diene structure under proper temperature and undergoes radical polymerization or Diels−Alder reaction. Such polymers have excellent electrical performance and have been applied in integrated circuit packaging, MEMS packaging, etc.

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In this paper, BCB ring as polymerizable group was introduced in the BOZ monomers to realize the performance enhancement of BOZ resins. We originally synthesized monomers with multifunctional groups containing BCB and BOZ. The monomers possess two kinds of ring-opening polymerizable functional groups of BCB and BOZ. So the monomers can be cured at proper temperature to prepared highly cross-linked resins. These resins may demonstrate improved heat resistance, thermal properties, and thermal mechanical properties compared to the BOZ resin reported.

EXPERIMENTAL SECTION

Materials. 4-Bromobenzocyclobutene (BrBCB, 97%) and 4-hydroxylbenzocycolbutene (OHBCB) were purchased from Chem-target Technologies Co., Ltd. Phenol, bisphenol A (BPA), 2-allylphenol, toluene, dichloromethane, paraformaldehyde, anhydrous sodium sulfate, and sodium hydroxide all were used as received. Aniline was purified by vacuum distillation. 4-Aminobenzocyclobutene (AMBCB) was prepared by aminating of 4BrBCB with ammonia–water according to the literature else.[17] 6,6′-(Propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[*e*][1,3]oxazine) (B-a) was synthesized via a solvent-free method.[18]

Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker DMX-500 Spectrometer using $CDCl_3$ as solvent. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-IR 550 II FTIR spectrophotometer operating at a resolution of 4 cm^{-1}. Thermal gravimetric analysis (TGA) was performed on a Shimadzu DTG-60H simultaneous DTA–TG apparatus with a heating rate of 10 °C·min^{-1} in nitrogen atmosphere. Differential scanning calorimetry (DSC) was measured on a TA Q200 calorimeter. Dynamic mechanical analysis (DMA) was carried out on TA Q800 instrument by the 3-point bending method at a heating rate of 3 °C·min^{-1} with the test frequency at 1 Hz.

Preparation of Monomers. *3-(Benzocyclobutene-4-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazine (P–AB).* AMBCB (1.19 g, 10 mmol), paraformaldehyde (0.60 g, equal to 20 mmol formaldehyde), phenol (0.94 g 10 mmol) and toluene (20 mL) was added in a 50 mL single necked round-bottomed flask equipped with a PTFE-coated magnetic stir bar and a reflux condenser. The solution was stirred and heated to reflux for 5 h, and the turbid solution became transparent with light yellow. After cooling down to room temperate, the solution was condensed on a rotary evaporator and the crude product was obtained. The crude product was then dissolved in 50 mL dichloromethane and washed with 20% NaOH solution for 3 times and then with deionized water until neutral. The dichloromethane solution was separated and dried over anhydrous sodium sulfate for 12 h, and then filtered, concentrated and dried under vacuum to give 2.01 g P–AB in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$): 3.07 (s, 4H), 4.57 (s, 2H), 5.30 (s, 2H), 6.78–7.10 (m, 7H).

6,6′-(Propane-2,2-diyl)bis[3-(benzocyclobutene-4-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazine] (B–AB). The preparation method is similar to that of P–AB except that phenol (0.94 g 10 mmol) was substituted by BPA (1.14 g, 5 mmol). 2.10 g of the product was obtained in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): 1.57 (s, 6H), 3.09 (s, 8H), 4.53 (s, 4H), 5.28 (s, 4H), 6.68–6.95 (m, 12H).

8-Allyl-3-(benzocyclobutene-4-yl)-3,4-dihydro-2H-benzo[e][1,3]-oxazine (ALP–AB). The preparation method is similar to that of P–AB except that phenol (0.94 g, 10 mmol) was substituted by 2-allylphenol (1.34 g, 10 mmol). 2.22 g of the product was obtained in 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): 3.07(s, 4H), 3.33 (d, 2H), 4.55 (s, 2H), 5.03 (m, 2H), 5.30 (s, 2H), 5.97 (m, 1H), 6.79–6.96 (m, 6H).

6,7-(Ethane-1,2-diyl)-3-phenyl-3,4-dihydro-2H-benzo[e][1,3]-oxazine (HB–A). OHBCB (2.40 g, 20 mmol), paraformaldehyde (1.20 g, equal to 40 mmol of formaldehyde), aniline (1.86 g, 20 mmol), and toluene (20 mL) was added in a 50 mL single necked round-bottomed flask equipped with a PTFE-coated magnetic stir bar and a reflux condenser. The solution was stirred and heated to reflux for 5 h, and the turbid solution became transparent with light yellow. After cooling down to room temperate, the solution was condensed on a rotary evaporator and the crude product was obtained. The crude product was then dissolved in 50 mL dichloromethane and washed with 20% NaOH solution for 3 times and then with deionized water until neutral. The dichloromethane solution was separated and dried over anhydrous sodium sulfate for 12 h, and then filtered, concentrated and dried under vacuum to give 4.20 g of HB–A in 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$): 3.07 (s, 4H), 4.57 (s, 2H), 5.30 (s, 2H), 6.78–7.10 (m, 7H).

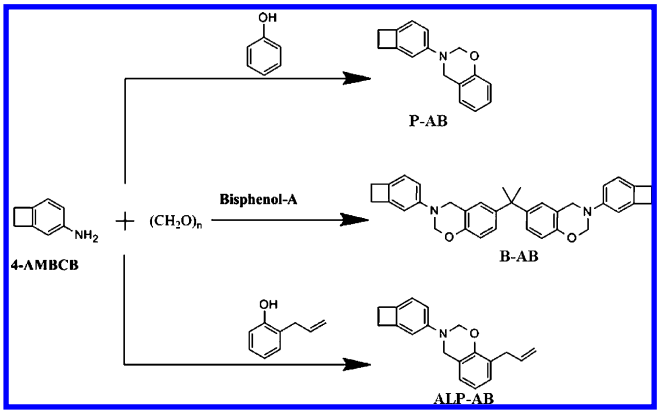
3-(Benzocyclobutene-4-yl)-3,4-dihydro-2H-benzo[e][1,3]oxazine (HB–AB). The preparation method is similar to that of HB–A except that aniline was substituted by AMBCB. 4.80 g of the product was obtained in 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$): 3.08 (s, 8H), 4.55 (s, 2H), 5.26 (s, 2H), 6.52–6.96 (m, 5H).

Preparation of Thermosetting Resins. The prepared monomers existed as powders or semifluid at room temperature were placed into glass-plate molds (40 mm × 20 mm × 2 mm). After degassing in a vacuum oven at 130 °C for an hour with an approximate pressure at 0.01 MPa, the molds were then heated at 150 °C for 2 h, then at 180, 200, 220, 240, and 260 °C for 1 h, respectively. After cooled to room temperature, the thermosetting resins were polished as rectangular bars with a size of 30 mm × 13 mm × 2 mm for DMA test.

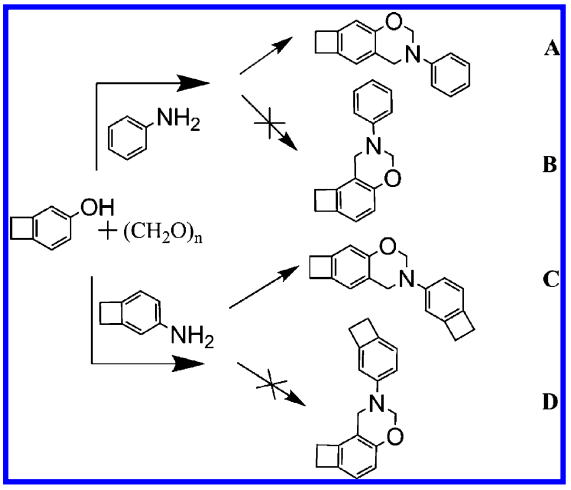
RESULTS AND DISCUSSION

1. Preparation and Characterization of BCB-Functionalized BOZ. The synthesis of BCB-functionalized BOZ

Scheme 1. Preparation of AMBCB-Based Benzoxazine Monomers



Scheme 2. Preparation of OHBCB-Based Benzoxazine Monomers



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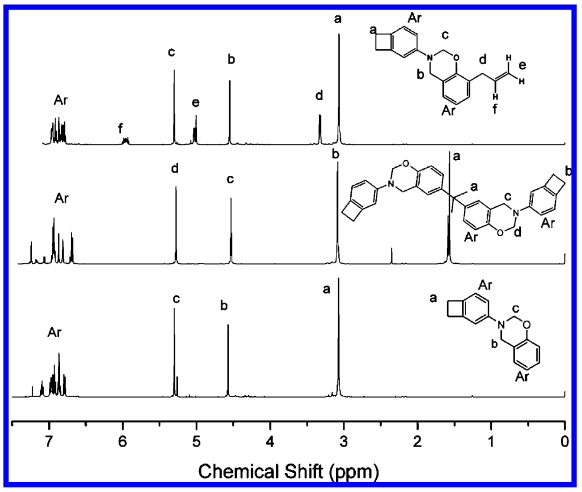

Figure 1. ^{1}H NMR spectrum of AMBCB-prepared BOZ monomers.

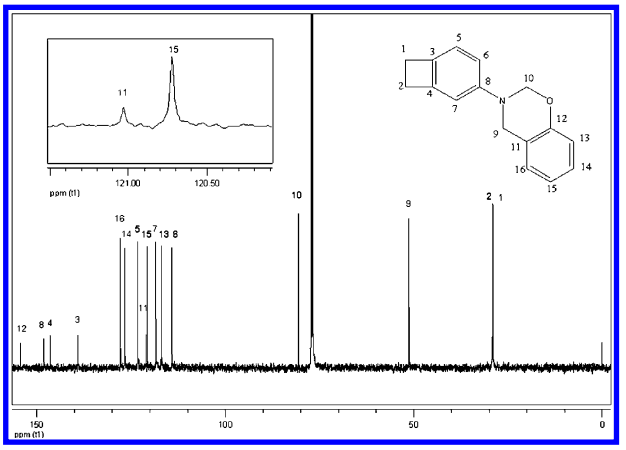

Figure 2. ^{13}C NMR spectrum of P−AB.

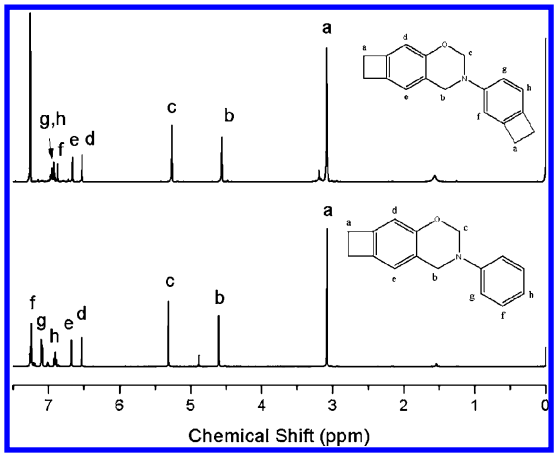

Figure 3. ^{1}H NMR spectrum of OHBCB-prepared BOZ monomers.

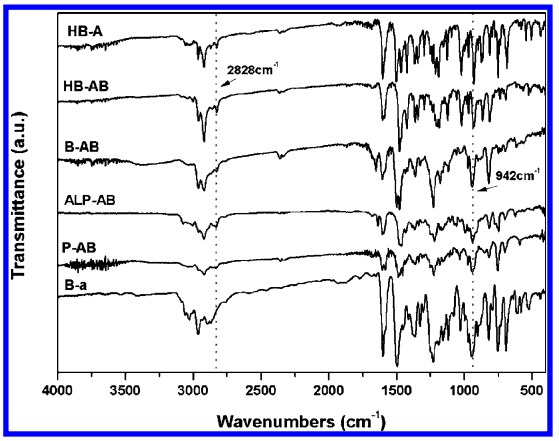

Figure 4. FTIR spectra of BCB-functionalized benzoxazine monomers.

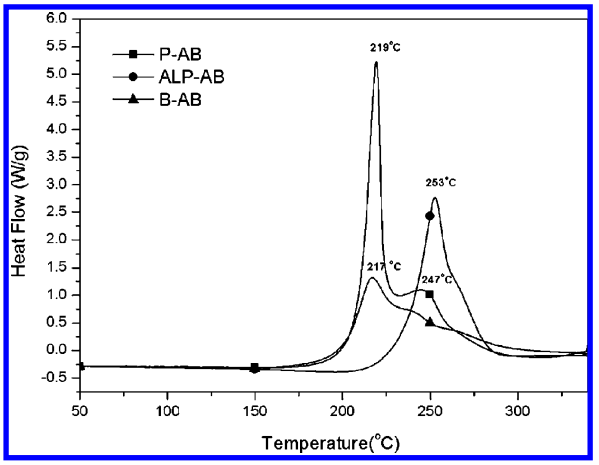

Figure 5. DSC curves of AMBCB-based benzoxazine monomers.

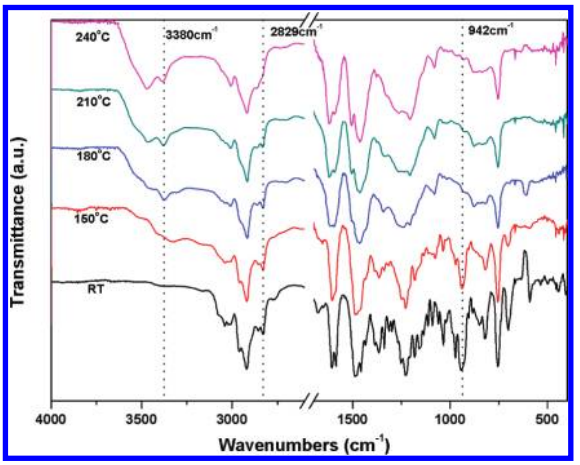

Figure 6. Vibrational analysis of the polymerization of oxazine ring and BCB ring in P−AB at different cure stages.

monomers were based on two routes. The first route is based on the reaction of AMBCB and paraformaldehyde with different phenols such as phenol, bisphenol A, and 2-allylphenol, and the scheme is shown in Scheme 1. The second route is based on the reaction of OHBCB and paraformaldehyde with different aromatic amines such as aniline and AMBCB, as shown in Scheme 2.

The chemical structure of the prepared BCB-functional BOZs was characterized by ^{1}H NMR. The ^{1}H NMR spectra shown in Figure 1 established the structures of BCB-functional BOZs prepared by AMBCB. As to P−AB, 3.07(s, 4H) is attributed to the methylene protons of the four-membered ring of BCB. The aromatic protons appeared as multiplet at 6.78−7.10 ppm. Here, 4.57 (s, 2H), and 5.30 (s, 2H) are attributed to −Ar−CH_2−N− and −N−CH_2−O−, respectively, which prove the formation of benzoxazine ring. As to B−AB, the peaks at 1.57 ppm attributed to the $C(CH_3)_2$ with other peaks similar to that of P−AB. Besides, the ^{1}H NMR spectrum of ALP−AB is

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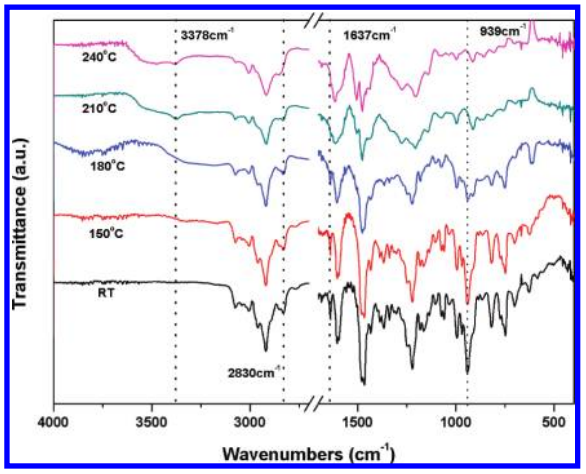

Figure 7. Vibrational analysis of the polymerization of oxazine ring and BCB ring in ALP−AB at different cure stages.

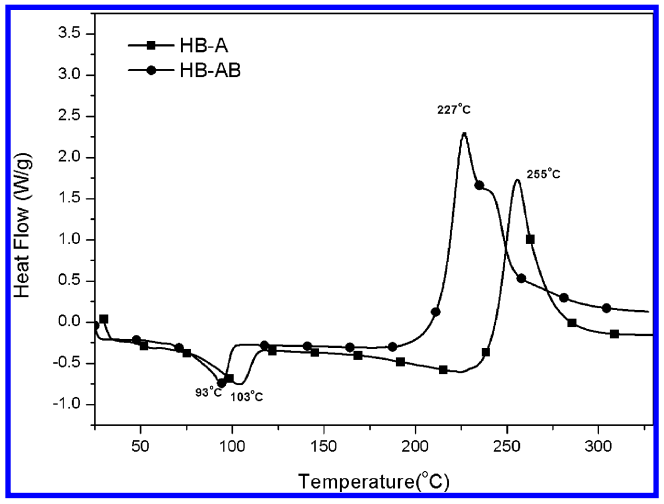

Figure 8. DSC curves of OHBCB-prepared monomers.

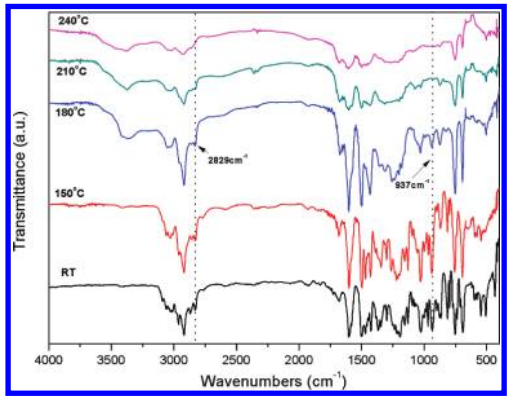

Figure 9. FTIR of HB−A at different curing stage.

shown in Figure 1. The two multiples at 5.03 and 5.97 ppm are typical for the protons of $=CH_2$ and $=CH-$ in the allyl group, respectively. The protons of $-CH_2-$ of the allyl group showed a doublet at 3.33 ppm. Other peaks are similar to that of P−AB. The analysis of ^1H NMR shows that we have prepared BCB-functional BOZs successfully. ^{13}C NMR also proved the structures of the BCB-functional BOZs.

Figure 2 shows the ^{13}C NMR spectra for P−AB. The peaks at 21.15 and 21.90 ppm are assigned to the $-CH_2-CH_2-$

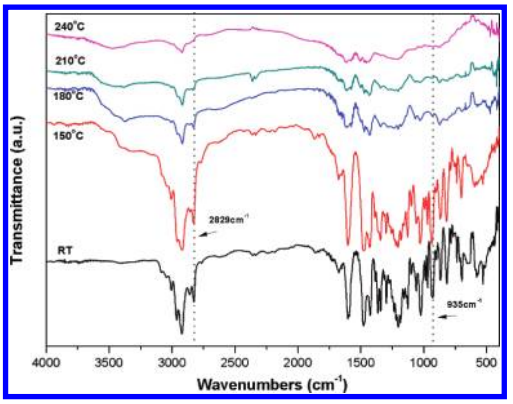

Figure 10. FTIR of HB−AB at different curing stage.

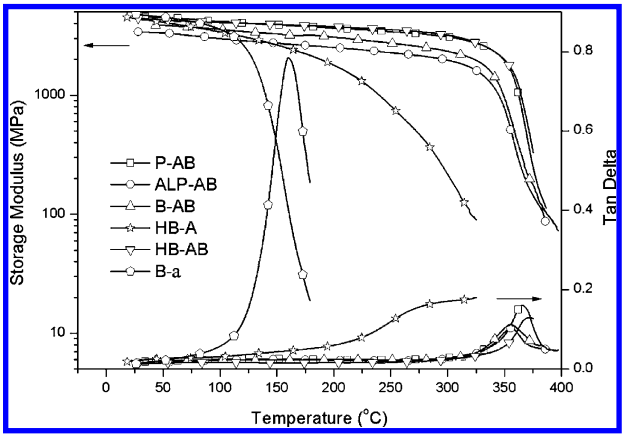

Figure 11. DMA curves of BCB-functionalized benzoxazine polymer compared with B-a resin.

carbons in the BCB moiety. The characteristic carbon resonances of the oxazine ring appear at 51.15 ppm for C−C*H_2−N− and at 80.64 ppm for N−C*H_2−O−, respectively, which support the formation of benzoxazine. Besides, all the peaks refer to the corresponding carbon in the monomer, which suggest the structure of P−AB. ^{13}C NMR spectra for other monomers were shown in Supporting Information.

As shown in Scheme 2, two structures may be generated as OHBCB was used for preparing the BCB functionalized BOZ. However, according to the ^1H NMR shown in Figure 3, we can determine that structure A is right and structure B is not generated. As to HB−A, 3.07 (s, 4H) was ascribed to the methylene protons of the four-membered ring of BCB. 4.57 (s, 2H) and 5.29 (s, 2H) was ascribed to the methylene protons of benzoxazine, which indicates that the formation of benzoxazine ring. The singlet peaks at 6.53 and 6.67 indicated that the two aromatic protons on the BCB ring are not adjacent, so we can confirm the structure of HB−A as structure A. The reason may be that the hindrance of BCB on the phenol influences the ring formation of BOZ. The ^1H NMR spectrum of HB−AB was also similar to that of HB−A, and we can confirm the structure of HB−AB as structure C. The ^{13}C NMR spectra of the monomers were shown in Supporting Information.

All the FTIR spectra of the monomers are shown in Figure 4. The characteristic absorptions of benzoxazine structure for the monomers were at 1230−1236 cm^{-1} (asymmetric stretching of C−O−C of BOZ ring for AMBCB prepared monomers), 1028−1036 cm^{-1} (symmetric stretching of C−O−C of benzoxazine ring), 1327−1340 cm^{-1} (CH_2 wagging), and

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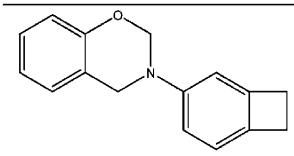
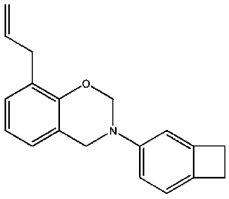
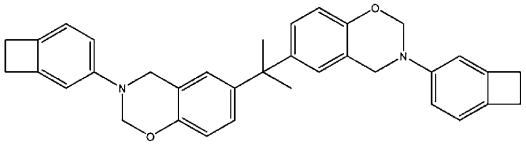
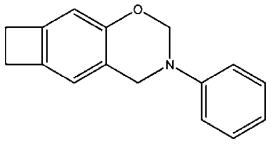
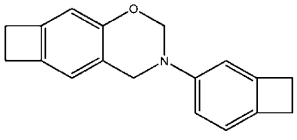
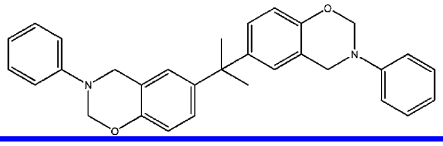
Table 1. Thermal Properties of Polybenzoxazines

Monomers	Initial storage modulus (GPa) at 40 °C	T_g(°C)	$T_{5\%}$(°C)	$T_{10\%}$(°C)	Char yield (%) at 600 °C
	4.50	366	396	408	51.9
	3.38	356	396	403	32.1
	3.88	356	378	388	44.1
	4.22	~300	348	367	45.1
	4.36	370	397	408	52.1
	4.6	160	308	343	35

1470−1600 cm^{-1} (benzene ring), which was in accordance with that of B-a. The characteristic band at 940−950 cm^{-1} due to the out-of-plane C−H vibration of the benzene ring to which the oxazine ring is attached is observed.[6] The characteristic peak for BCB at 1475 cm^{-1} was overlapped by trisubstituted benzene ring of BOZ. Another peak at 2832 cm^{-1} was assigned to the vibration of $-CH_2-$ in BCB.[19] As to ALP−AB, allyl group appeared at 3084 cm^{-1} (stretching of =C−H) and 1637 cm^{-1} (stretching of C=C).

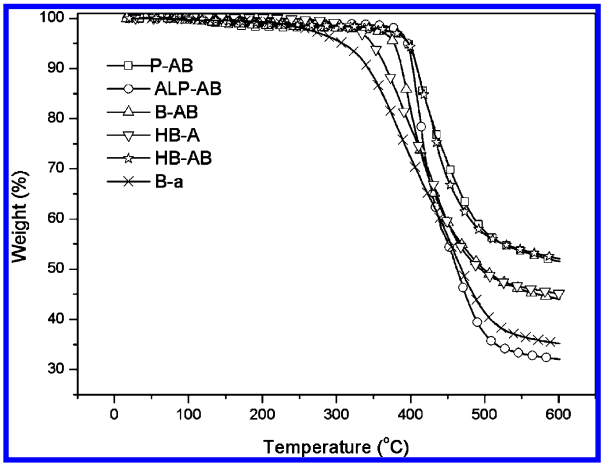


Figure 12. TGA curves of resins cured by BCB-functionalized benzoxazine compared with B-a resin.

2. Curing Behavior of BCB-Functional BOZ Monomer. The cure behavior of BCB-functional BOZ monomers was studied by DSC from room temperature to 350 °C at a ramping rate of 10 °C/min, and the DSC curves are list in Figure 5. For P−AB and B−AB, the initial exothermal temperature begins at 170 °C, and two exothermal peaks at 215−220 °C (primary) and 245 °C (secondary). For P−AB, the exotherm shows a maximum at 219 °C with a moderate peak at 247 °C and the total heat of polymerization is 641.2 J/g. For B−AB, the exotherm shows a maximum at 217 °C with a shoulder at 242 °C and the total heat of polymerization is 485.2 J/g. We think that the first sharp exothermal peak is ascribed to the ring-opening polymerization of BOZ and the second moderate peak is ascribed to the ring-opening polymerization of BCB. In other words, ring-opening reaction of BOZ ring is easier than that of BCB ring, which can be confirm by the following FTIR study. The initial exothermal temperature of ALP−AB is 210 °C and only an exothermal peak at 253 °C with a shoulder was found, and the total heat of polymerization is 457.7 J/g. This may be

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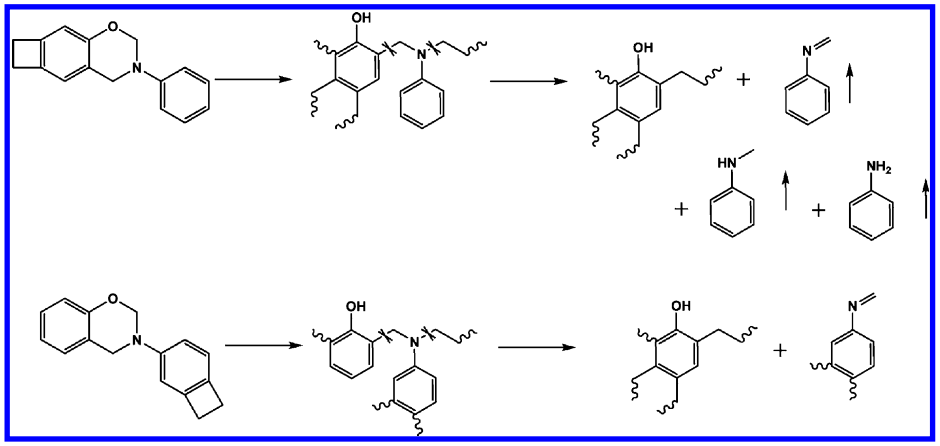
Scheme 3. Possible Thermal Curing and Degradation Mechanism of BCB-Functionalized Benzoxazine



that the allyl group on the phenyl ring is a steric hindrance for the formation of phenolic Mannich bridge structure via the ortho position, and the polymerization is forced to proceed through the less favorite para position.[20] The ring-opening temperature of BOZ enhanced to 250 °C, which overlap the ring-opening reaction of BCB.

The cure behavior of P−AB and ALP−AB was studied by FTIR. FTIR was tested after the samples were treated 1 h at 150, 180, 210, and 240 °C, respectively and the FTIR spectra are shown in Figure 6 and Figure 7. The appearance of absorption peak at 3380 cm^{-1} for the phenolic hydroxyl group after the curing indicates the ring-opening of benzoxazine. The characteristic absorption bands of benzoxazine structure at 932−942 cm^{-1} (vibrational mode of cyclic C−O−C), 1037 cm^{-1} (symmetric stretching of C−O−C), and 1348 cm^{-1} (CH_2 wagging) gradually decreased, and disappeared by the end of the 240 °C cure, suggesting the completion of ring-opening of benzoxazine to afford polybenzoxazine.

From Figure 6 for P−AB, 942 cm^{-1} for BOZ ring disappeared after the sample was treated at 180 °C for 1 h. The BCB ring at 2829 cm^{-1} disappeared after the sample was treated at 240 °C. For ALP−AB in Figure 7, 942 cm^{-1} for BOZ ring still exist after the sample was treated at 180 °C for 1 h. This indicates that the BOZ ring for ALP−AB shows less reaction action than that of P−AB, which caused by the hindrance of allyl on the BOZ ring in ALP−AB. This is in accordance with the judgment of DSC. The absorption peak for allyl group at 1637 cm^{-1} disappeared after treatment of 210 °C for 1 h, which indicated that allyl group may undergo radical polymerization or Diels−Alder reaction with BCB.

The cure behavior of HB−A prepared by OHBCB is quite different from that of P−AB and B−AB. Because the BCB ring and oxazine ring exits on the same benzene ring, the BCB ring may lead to the hindrance for the ring-opening reaction of oxazine, which may increase the temperature for the polymerization of BOZ. HB−A shows a single exothermic peak at 255 °C based on DSC test (shown in Figure 8). According to FTIR curves for different cure stage shown in Figure 9, after curing at 180 °C for an hour, 937 cm^{-1} for oxazine still exists apparently and 2829 cm^{-1} for BCB also exists. Finally after cured at 240 °C for an hour, 937 cm^{-1} for BOZ and 2829 cm^{-1} for BCB disappeared. Compared to HB−A, HB−AB exhibits an exothermic peak at 227 °C and a shoulder at 240 °C. From the FTIR curves for different cure stage in Figure 10, 937 cm^{-1} for oxazine became not obvious after curing at 180 °C for an hour, which indicates that oxazine ring is easier to open. This may be that the AMBCB make the ring- tension of oxazine increased and the thermal stability of oxazine decreased.

3. Property of Cured BCB−BOZ Resin. The DMA curves of cured BCB−BOZ resins are shown in Figure 11. As shown in Table 1, all the resins exhibit high storage modulus. The initial storage modulus of P−AB is as high as 4.5 GPa at 40 °C. The high initial storage modulus of the resins was caused by the high cross-linking of the monomers by dual ring-opening polymerization. Compared to traditional BOZ such as B-a, the cured BCB−BOZ resins except from HB−A resins can maintain high storage modulus in a wide temperature range up to 300 °C. Except from cured HB−A, the tan δ curves of the polymers exhibit that the resins shows low loss factor below 300 °C. Glass transformation by tan δ of the polymers is as high as 366 °C for P−AB. The high T_g was also attributed to the high cross-linking of the monomers. The cured HB−A shows a relative low glass transition temperature below 300 °C. This may be that the network of cured HB−A is thermal unstable and thermal degradation happened.

TGA curves (Figure 12) shows that the resins have good thermal stability as the temperature below 380 °C except from HB−A, and the 5% and 10% weight loss temperatures (T_5 and T_{10}) are list in Table 1. Compared with the traditional benzoxazine such as B-a, the incorporation of BCB rings improves the thermal stability of the polymers. Typically, the cured P−AB and HB−AB show T_5 at 396 and 397 °C, respectively. The cured HB−A shows relatively low T_5 at 348 °C. A possible thermal degradation mechanism of cured BCB-functionalized benzoxazine is listed in Scheme 3. As aniline is used for preparing HB−A, the Mannich bridge in the network tend to break up and arylamine such as aniline, *N*-methyleneaniline and *N*-methylaniline may be released.[21,22] However, as AMBCB is used for preparing benzoxazine, no small molecule is released as the Mannich bridge breaks in the network, which can prevent the resin from thermal degradation.

■ CONCLUSION

A series of novel benzoxazine monomers functionalized by BCB groups have been successfully prepared. ^1H NMR and ^{13}C NMR spectroscopes were used to confirm the structures of the monomers. The cure behavior of the monomers was tested by DSC and FTIR. Because of the high cross-linking density arisen from the dual ring-opening polymerization, the BCB-functionalized benzoxazine resins show high T_g at ca. 350 °C and high

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storage moduli which can be maintained in a wide temperature range up to 300 °C. The high thermal stability was confirmed by TGA with the highest 5% weight loss temperature above 390 °C, which is attributed to the incorporation of BCB ring of the monomers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{13}C NMR data for the monomers of B−AB, ALP−AB, HB−A, and HB−AB. 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.

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