Influence of Electronic Effects from Bridging Groups on Synthetic Reaction and Thermally Activated Polymerization of Bisphenol-Based Benzoxazines

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ABSTRACT: Six bis-benzoxazines based on bisphenols with different bridging groups, —$C(CH_3)_2$—, —CH_2—, —O—, —CO—, —SO_2—, and single bond, were synthesized in toluene. The influence of electronic effects from bridging groups on ring-forming reaction and thermal ring-opening polymerization were relatively discussed in detail. Their structures were characterized by high-performance liquid chromatography, Fourier transform infrared, ^{1}H NMR, differential scanning calorimetry, and elementary analysis. The quantum chemistry parameters of the bisphenols and bis-benzoxazines were calculated by molecular simulation. The results indicated that the electron-withdrawing groups inhibited the synthetic reaction by decreasing the charge density of α-Cs of bisphenols and increasing energy barriers of the synthetic reactions. However, the electron-withdrawing groups promoted the thermally activated polymerization, which resulted from their activation energy and curing temperature decrease by increasing the bond length and lowering the bond energy of C—O on oxazine rings. Besides, because of stronger electron-withdrawing sulfone group, there were more arylamine methylene Mannich bridge structure in the polybenzoxazine. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 1443–1452, 2011

KEYWORDS: barrier; benzoxazine; bridging group; electronic effect; molecular modeling; quantum chemistry

INTRODUCTION Polybenzoxazines, as an alternative to traditional phenolic resins, are widely used in the areas of electrical insulation, electrical encapsulation, aeronautical technology, and astronautical technology. They exhibit excellent heat resistance, mechanical properties, electric insulating properties, good dimension stability, low water absorption, and low dielectric constant.[1–6]

Benzoxazine is a novel thermosetting resin, which is easily derived from phenol, formaldehyde, and primary amine via a Mannich condensation and can be polymerized thermally or catalytically. It was first synthesized in solvent by Holly and Cope in 1944.[7] Later, Burke et al.[8–11] systemically studied the Mannich reaction and found that the reaction mechanism of the benzoxazine synthesis proceeded by two steps. The first step was adding amine to formaldehyde to form an *N*,*N*-dihydroxymethylamine. The second step was the *N*,*N*-dihydroxymethylamine reacting with ortho position of the phenol and the labile hydrogen of the phenolic hydroxyl group, respectively, to form the benzoxazine ring. Since 1990 in the world, Ishida and coworkers[12–18] have synthesized numerous benzoxazines based on different phenolic compounds as well as aromatic or aliphatic primary amines, and then discussed the properties of their correspondent polybenzoxazines. Ishida and Lin developed new synthetic routes of benzoxazines from the reactants such as 1,3,5-triphenylhexahydro-1,3,5-triazine or 2-hydroxybenzaldehyde.[19] At the same time, the thermally activated polymerization of benzoxazine precursors[20–23] and their catalytical polymerization from carboxylic acids, Lewis acids, imidazoles, and other kinds of compounds with labile hydrogen[24–26] were also investigated widely. The synthetic reaction and thermally activated polymerization behaviors of some monofunctional benzoxazines with different substituting groups were also studied.[27]

However, there were some insufficiencies in the previous researches. First, the systematic and comparative investigation of different monomers from the view of structural factors is needed. Then, the existed researches were mainly relied on experimental data and lack of detail analysis at molecular and electronic level. The relationship of ring-forming reaction and thermal ring-opening polymerization is rarely reported. Besides, monofunctional benzoxazines, as model compounds, are hard to produce casting samples to test their physical and mechanical properties, so that it is necessary to study the difunctional benzoxazines combinating synthetic reaction, thermally activated polymerization, structure, and property together.

To systemically investigate the influence of electronic effects from bridging groups of bisphenols on synthetic reaction,

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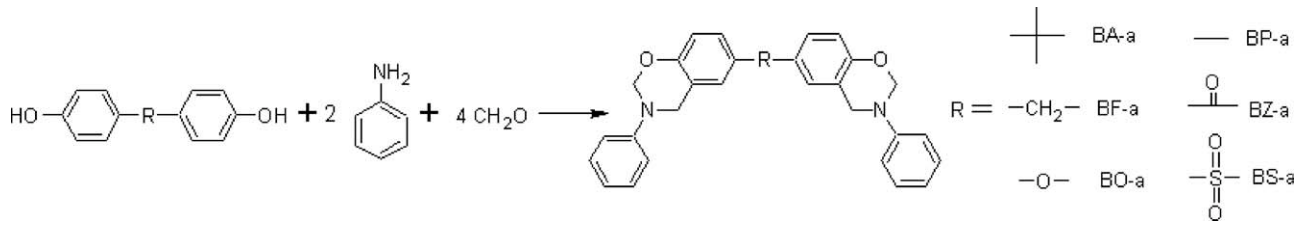


SCHEME 1 Synthesis of BX-as.

thermally activated polymerization and the properties of the polymers, six difunctional benzoxazines based on bisphenols with different bridging groups, —$C(CH_3)_2$— (BA-a), —CH_2— (BF-a), —O— (BO-a), —CO— (BZ-a), —SO_2— (BS-a), and single bond (BP-a), as the reference, were prepared via Scheme 1. The influence of electronic effects on synthetic reaction and thermally activated polymerization are systemically discussed by experimental data and molecular simulation analysis in this article, and the influence of electronic effects on the properties of polybenzoxazines will be reported later.

EXPERIMENTAL

Materials

The following chemicals: phenol, phosphoric acid (14.7 mol L^{-1}), aqueous formaldehyde solution (13.4 mol L^{-1}), aniline, toluene, sodium bicarbonate, sodium hydroxide, ethyl alcohol, and HPLC-grade THF were purchased from the Chengdu Kelong Chemical Reagents Corp. (China). The following bisphenols: 4,4′-dihydroxydiphenylpropane (BA), 4,4′-dihydroxydiphenylether (BO), 4,4′-dihydroxybenzophenone (BZ), 4,4′-Dihydroxydiphenylsulfon (BS), and 4,4′-dihydroxybiphenyl (BP) were bought from J&K scientific (China). All reagents were used as received.

Synthesis of 4,4′-Dihydroxydiphenylmethane (BF)

BF was synthesized by mixing phenol (0.3 mol, 28.2 g), phosphoric acid (0.2 mol, 23.0 g), and aqueous formaldehyde solution (0.1 mol, 8.1 g) and stirring at 45 °C for 4 h. The product was filtrated, and then washed with 1 N $NaHCO_3$ solution. A white crystal product was recrystallized from ethyl alcohol.

Yield: 23%. Melting point: 167 °C (DSC). ^{1}H NMR ($CDCl_3$, ppm): 3.68 (Ar—CH_2—Ar), 9.13 (—OH).

Synthesis of Benzoxazines

Method 1

Stoichiometric amounts of aniline (0.2 mol, 18.6 g), aqueous formaldehyde solution (0.4 mol, 32.5 g), and bisphenol (0.1 mol) were dissolved in toluene (50 mL) in a 250-mL three-necked flask. The mixture was stirred and refluxed at 80 °C for 5 h. Then, the product was washed with 1 N solution of sodium hydroxide and cooled overnight. The product was filtrated, washed with ethyl alcohol, and dried in vacuum drying oven. A white crystal was obtained finally.

TABLE 1 Yields and Melting Points of Boz-BXs

	Yield (%)	Melting Point (°C)
BA-a	86	123
BF-a	83	122
BO-a	75	122
BP-a	65	205/216
BZ-a	63	206
BS-a	47	183

BA-a. Yield: 86%. Melting point: 123 °C (DSC). Purity: 99% (HPLC). ^{1}H NMR ($CDCl_3$, ppm): 5.30 (N—CH_2—O), 4.55 (O—CH_2—Ar), 1.57 (—CH_3). FT-IR (cm^{-1}): 1231, 1028 (C—O—C), 952 (benzoxazine ring).

BF-a. Yield: 83%. Melting point: 122 °C (DSC). Purity: 99% (HPLC). ^{1}H NMR ($CDCl_3$, ppm): 5.35 (N—CH_2—O), 4.60 (O—CH_2—Ar), 3.79 (Ar—CH_2—Ar). FT-IR (cm^{-1}): 1227, 1027 (C—O—C), 948 (benzoxazine ring).

BO-a. Yield: 75%. Melting point: 122 °C (DSC). Purity: 99% (HPLC). ^{1}H NMR ($CDCl_3$, ppm): 5.35 (N—CH_2—O), 4.59 (O—CH_2—Ar). FT-IR (cm^{-1}): 1221, 1029 (C—O—C), 937 (benzoxazine ring).

Method 2

To a 250-mL three-necked flask toluene (50 mL) and stoichiometric amounts of aniline (0.2 mol, 18.6 g), aqueous formaldehyde solution (0.4 mol, 32.5 g) and bisphenols (0.1 mol) were charged. The mixture was stirred and refluxed for 5 h. Powders were precipitated gradually. The product was filtrated, washed with ethyl alcohol and dried in vacuum drying oven. A crystal product was obtained finally.

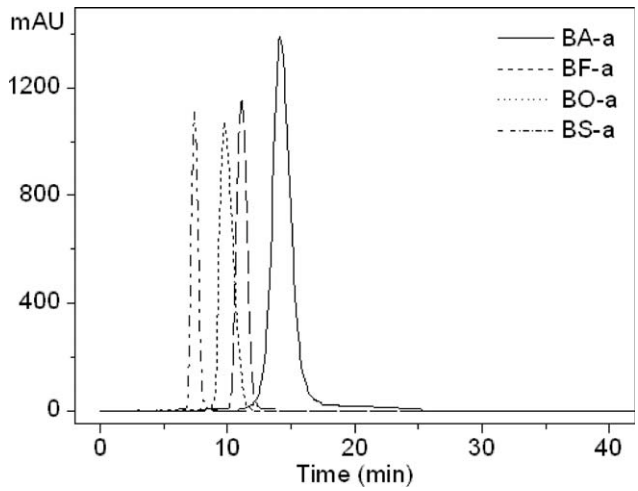


FIGURE 1 HPLC spectrum of BX-as.

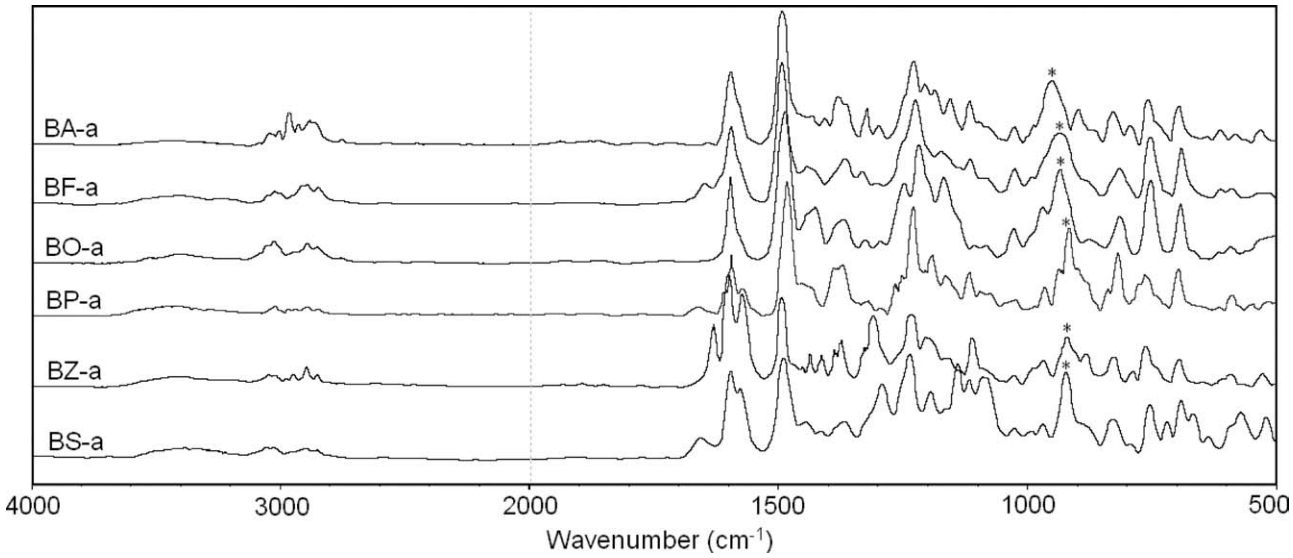


FIGURE 2 FT-IR spectra of BX-as.

BP-a. Yield: 65%. Melting point: 205/216 °C (DSC). ^{1}H NMR ($CDCl_3$, ppm): 5.39 (N—CH_2—O), 4.63 (O—CH_2—Ar). FT-IR (cm^{-1}): 1232, 1026 (C—O—C), 919 (benzoxazine ring).

BZ-a. Yield: 63%. Melting point: 206 °C (DSC). ^{1}H NMR ($CDCl_3$, ppm): 5.43 (N—CH_2—O), 4.67 (O—CH_2—Ar). FT-IR (cm^{-1}): 1206, 1029 (C—O—C), 917 (benzoxazine ring).

Method 3

Synthesis of BS-a. 1,4-Dioxane (50 mL) and 4,4′-Dihydroxydiphenylsulfon (BS, 0.1 mol, 25.0 g) were added into a 250-mL three-necked flask. The mixture was stirred at 70 °C until it became transparent. Then, aqueous formaldehyde solution (0.4 mol, 32.5 g) was added. Aniline (0.2 mol, 18.6 g) was charged by a drop funnel for 1 h. The mixture was stirred and refluxed for 4 h. Then, the mixture was washed with 1 N solution of sodium hydroxide, and cooled overnight. Faint yellow crystal was obtained.

Yield: 47%. Melting point: 183 °C (DSC). Purity: 99% (HPLC). ^{1}H NMR ($CDCl_3$, ppm): 5.45 (N—CH_2—O), 4.70 (O—CH_2—Ar). FT-IR (cm^{-1}): 1239, 1028 (C—O—C), 915 (benzoxazine ring).

Preparation of Polybenzoxazines

To remove entrapped air, the benzoxazine crystals were melted under vacuum for 10 min. The appropriate cure conditions were listed as follows: BA-a, BO-a, and BF-a: 140 °C/10 min (under vacuum), 180 °C/5 h. BZ-a and BP-a: 210 °C/10 min (under vacuum), 180 °C/5 h. BS-a: 190 °C/10 min (under vacuum), 180 °C/5 h. After melting and prepolymerizing under vacuum for 10 min, BZ-a, BP-a, and BS-a did not recrystallize and kept the states of fusant at 180 °C.

Computation

Molecular simulation was determined with the software Material Studio 4.0 (Accelrys, USA). Density functional theory method with local density approximation calculation was performed using the Dmol^3 program embedded in Material Studio 4.0 package. All transition state searches were conducted using the Dmol^3 program with the linear synchronous transit/quadratic synchronous transit method.

Characterizations and Measurements

FT-IR spectra were obtained with a Nicolet Magna 650 spectrometer at a resolution of 2 cm^{-1} using the KBr pellet technique. ^{1}H NMR spectroscopies were conducted on a Bruker TD-65536 NMR (400 MHz) in deuterated chloroform as solvent with tetramethylsilane as the internal reference. HPLC analyses were conducted with a HPLC system consisting of a Shimadzu-CBM20A equipped with a VP-ODS column (5 μm, 250 $\times$ 4.6 mm^2, Shimpack, Japan) set at 30 °C. THF/water (v/v = 1:1) was used as the eluant at a flowrate of 0.5 mL min^{-1}. The eluate was monitored at 254 nm. DSC was performed using a TA Instruments DSC Q20 at a variety heating

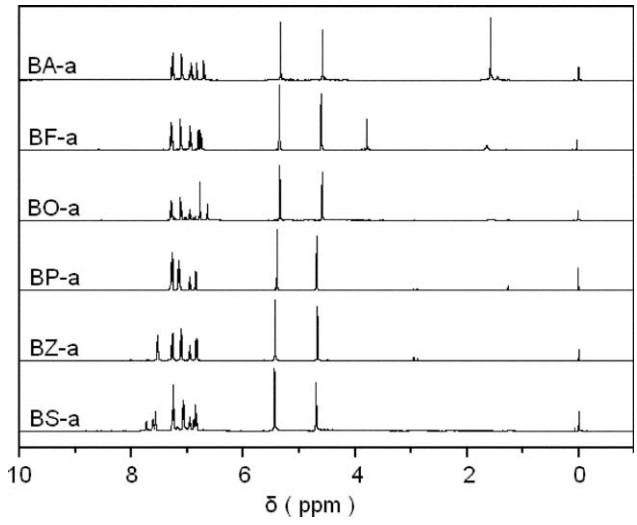
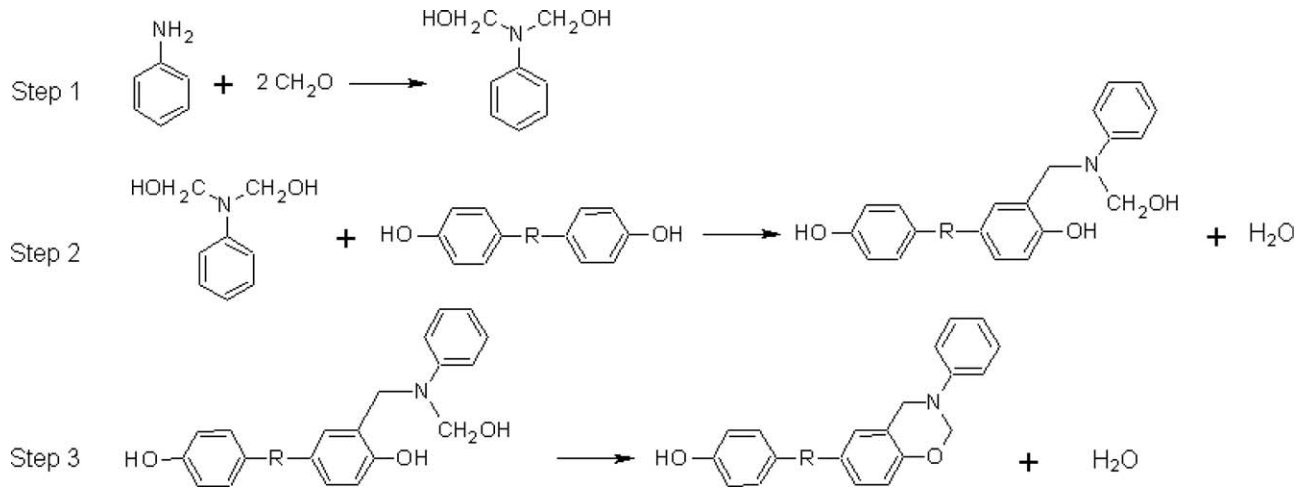


FIGURE 3 ^{1}H NMR spectra of BX-as.



SCHEME 2 Steps in the synthesis of the benzoxazine ring.

rates of 5, 10, 15, and 20 °C min^{-1} under nitrogen atmosphere. Elementary analysis was tested by a Elementar Vario Micro Organic Elemental Analyzer.

RESULTS AND DISCUSSION

All monomers were recrystallized to remove the by-products. Yields of the bisphenol-based benzoxazine monomers (BX-as) were listed in Table 1. The electronic effect of bridging groups in bisphenol influences the synthetic reaction. The yield gets higher with the increase of the electron-donating efficiency of bridging groups. BA-a exhibits the highest yield of 86%. On the contrary, with the increase of the electron-withdrawing character, the yield is decreased. BS-a with strong electron-withdrawing bridging group shows the lowest yield of 47%.

Melting points of BX-as obtained from differential scanning calorimetry (DSC) are also listed in Table 1. The bridging groups of BA-a, BF-a, and BO-a are flexible, so the melting points of three monomers are lower. The molecular structures of BP-a, BZ-a, and BZ-a are rigid, so their melting points are higher.

Figure 1 shows the high-performance liquid chromatography (HPLC) spectra of BA-a, BF-a, BO-a, and BS-a. As can be seen in the figure, there is only one peak in each plot and the integral area percentage of each peak is over 99%. The results indicated that each monomer is composed of only one main compound with high purity. The HPLC spectra of BP-a and BZ-a are not obtained because they are not dissolvable in eluant, tetrahydrofuran (THF).

The chemical structures of BX-as were confirmed by Fourier transform infrared (FT-IR) and ^{1}H NMR spectra. The FT-IR spectra (Fig. 2) show the typical absorption bands because of out-of-plane bending vibration of the benzoxazine rings at BA-a: 952 cm^{-1}, BF-a: 948 cm^{-1}, BO-a: 937 cm^{-1}, BP-a: 919 cm^{-1}, BZ-a: 917 cm^{-1}, and BS-a: 915 cm^{-1}, respectively. The bands moved to high wavenumber by the effects of electron-donating groups. The results indicated that electron-donating groups increased the energy of the bending vibration of the benzoxazine ring. In the ^{1}H NMR spectroscopies (Fig. 3), the characteristic resonances observed at BA-a: 5.30 ppm, BF-a: 5.35 ppm, BO-a: 5.35 ppm, BP-a: 5.39 ppm, BZ-a: 5.43 ppm, and BS-a: 5.45 ppm, respectively, are assigned to the structure of N—CH_2—O on benzoxazine rings. The typical

TABLE 2 Charge of α-C, Bond Length of O—H and Energy Barrier of Reaction Obtained from MS

	Charge of α-C	Bond Length of O—H (Å)	Energy Barrier of Reaction (kJ mol^{-1})	
			Step 2	Step 3
BA	−0.0735	0.9740	223.9	173.9
BF	−0.0721	0.9740	234.3	152.7
BO	−0.0686	0.9740	211.5	135.0
BP	−0.0715	0.9742	332.0	134.6
BZ	−0.0672	0.9749	364.1	100.0
BS	−0.0644	0.9749	418.9	118.5

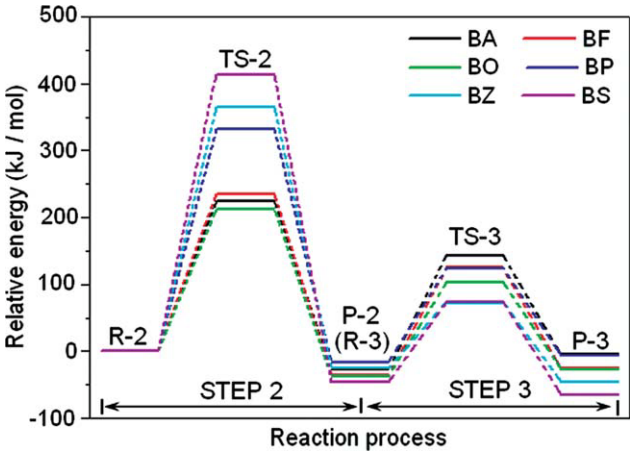


FIGURE 4 Calculated relative energies of synthetic reaction via Step 2 and Step 3.

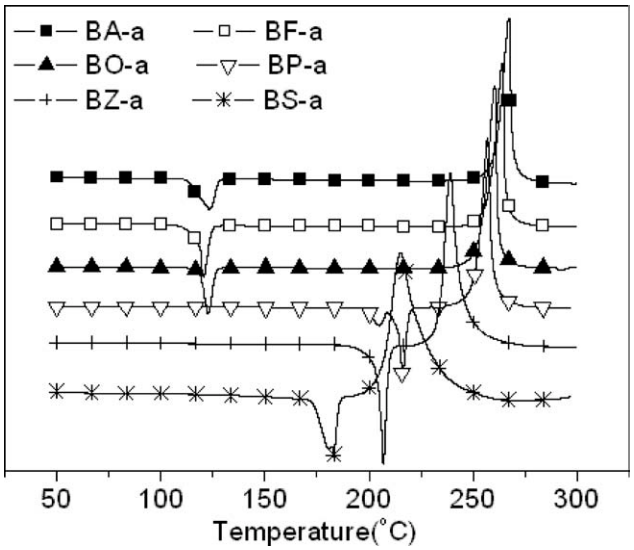


FIGURE 5 Nonisothermal DSC thermograms of BX-as.

resonances at BA-a: 4.55 ppm, BF-a: 4.60 ppm, BO-a: 4.59 ppm, BP-a: 4.63 ppm, BZ-a: 4.67 ppm, and BS-a: 4.70 ppm, respectively, are assigned to the structure of Ar—CH_2—N on benzoxazine rings. The resonances shifted to high field by the influence of electron-donating groups. The results of FT-IR and ^{1}H NMR indicated that the characteristics of oxizaine rings are changed because of the electronic effect of bridging groups, which may influence the ring-open reaction.

The reaction pathway of the Mannich condensation synthesizing benzoxazine in solution by traditional one-pot method is separated into three steps, which is illustrated in Scheme 2. It proceeds by adding aniline to formaldehyde to form *N*,*N*-dihydroxymethylamine, which then reacts with ortho position of the bisphenol and the phenolic hydroxyl group, respectively, to form the benzoxazine ring.[9] Therefore, the charge density of the α-C on ortho position of bisphenol and the ability of removing the labile hydrogen of the phenolic hydroxyl group become the main factors affecting the ring-forming reaction.

The net charges of α-Cs by Hirshfeld method and the O—H bond lengths of bisphenols calculated using the Dmol^3 program embedded in Material Studio 4.0 package are listed in Table 2. The bond lengths of O—H are slightly changed. The electron-donating groups increase the net charges of α-Cs, which enhance the activities of bisphenol to form oxazine

TABLE 3 Summary of the DSC Results

	T_{onset} (°C)	T_{peak} (°C)	T_{offset} (°C)	ΔH (kJ mol^{-1})
BA-a	261	267	270	144.0
BF-a	257	264	266	140.2
BO-a	254	260	263	144.8
BP-a	251	257	260	143.9
BZ-a	234	239	247	160.7
BS-a	206	215	228	157.3

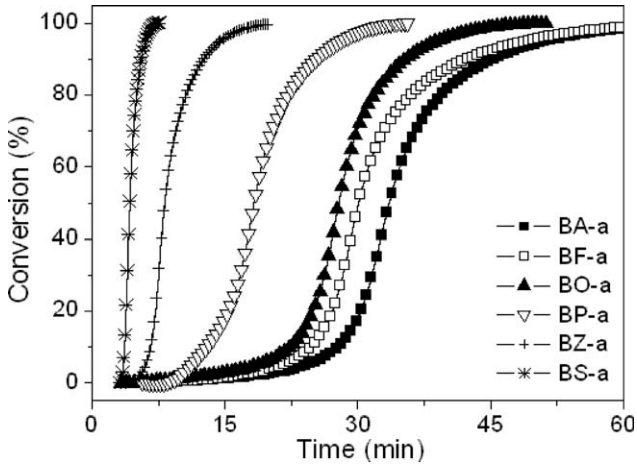


FIGURE 6 Conversion curves of BX-as at 210 °C.

rings. The electron-withdrawing groups are opposite. BA has the maximum net charge of α-C, −0.0735, which is higher than that of BS, −0.0644. It is in accordance with the phenomenon that yield of BA-a is 39% higher than that of BS-a.

The energies of reactants, transition states, and products were calculated by the transition state searches. The Step 1 in Scheme 2 of each system is the same. Therefore, only Steps 2 and 3 were calculated. The energies of the reactants of Step 2 (R−2) are considered as benchmarks, that is, calculate the energies of transition states and products using the formula 1:

$$E_{\text{relative}} = E_{\text{calculated}} - E_{\text{R}-2} \quad (1)$$

The calculated relative energies of synthetic reaction via Steps 2 and 3 are shown in Figure 4, and the calculated energy barrier of each step is listed in Table 2. When compared with BP system, the energy barriers of Step 2 of BA, BF, and BO systems with electron-donating groups are much

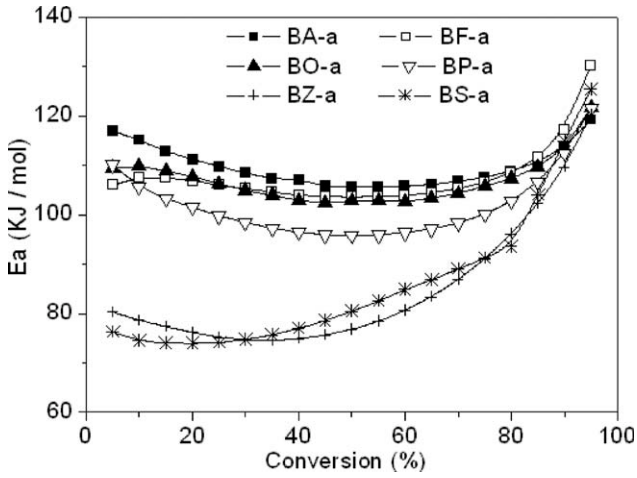
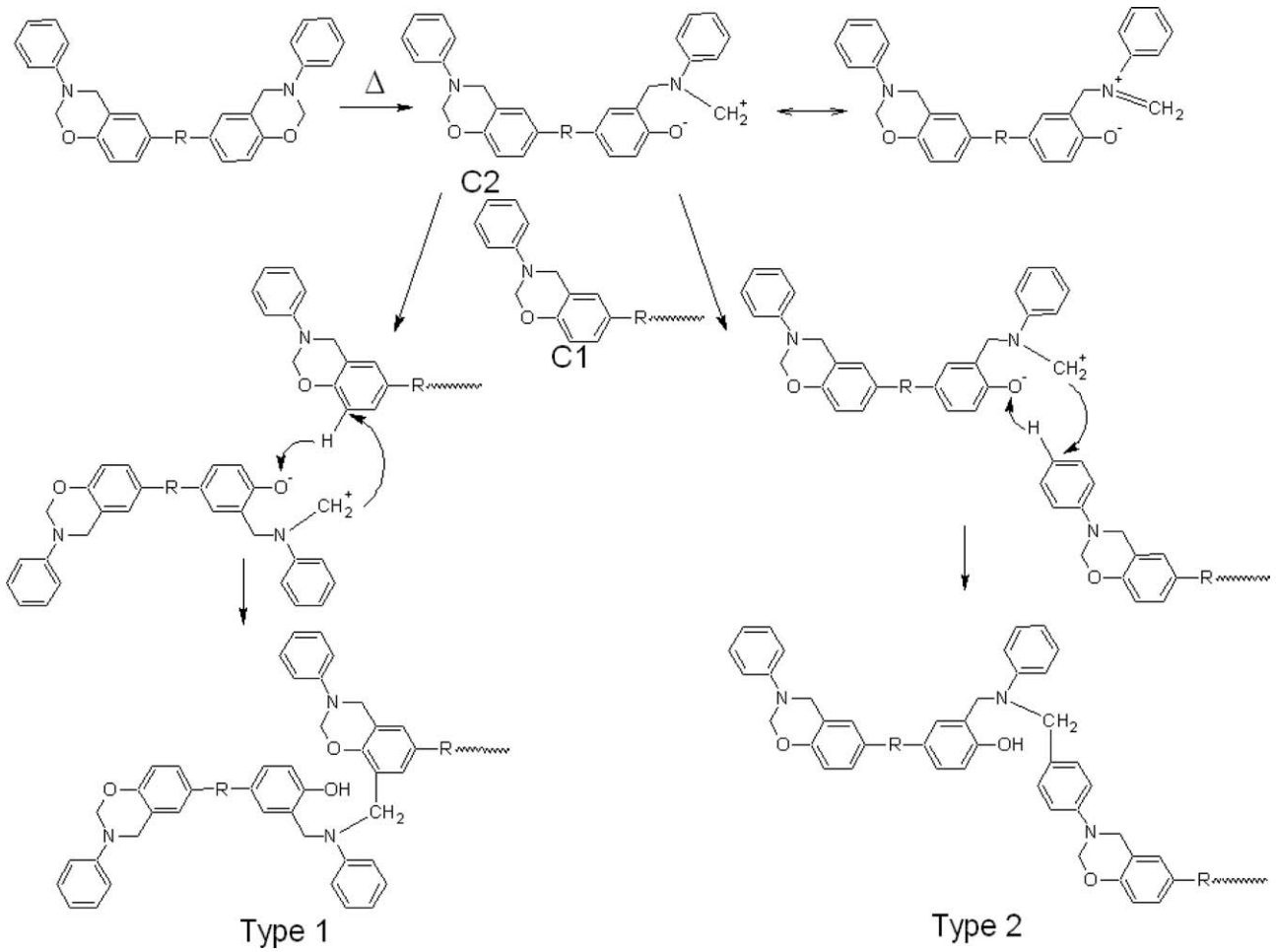


FIGURE 7 Relationship between activation energy and conversion of benzoxazines.

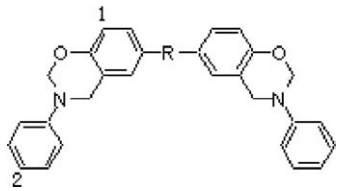


SCHEME 3 Thermal ring opening polymerization mechanism of benzoxazines.

lower, whereas those of BZ and BS systems with electron-withdrawing groups are much higher. The trend of Step 3 is opposite, but at a moderate range. Thus, Step 2 is the controlling approach of the synthetic reaction. Step 2 of BA system proceeded via the transition state TS-2 with an energy barrier of 223.9 kJ mol^{-1}. The energy barrier of Step 2 of BS system is 418.9 kJ mol^{-1}, nearly twice as much as that of the BA system. In this case, *N*,*N*-dihydroxymethylamine can condense to form oligomers without reacting with bisphenols. Thus, it was difficult to synthesize BS-a via the traditional one-pot method. We add aniline with a drop funnel to control the reaction of aniline with formaldehyde to make more BS participate in the ring-forming reaction. In a word, the electron-withdrawing groups can increase the energy barriers of the synthetic reactions and restrain the reactions.

All above is consistent with the result that electron-donating bridging groups of bisphenol are benefitial for synthesis of benzoxazine monomers. Electronic effects also have a great effect on the stability of oxizaine ring, which can be seen from the typical bands of benzoxazine rings in FT-IR and the characteristic resonances of protons on oxazine rings in ^1H NMR. Thus, the thermal open-ring polymerization may change.

TABLE 4 Bond Length of C—O and Charge of C1 and C2 Obtained from MS



	Bond Length of C—O (Å)	Charge Partitioning by Hirshfeld Method	
		C1	C2
BA-a	1.4303	−0.0666	−0.0644
BF-a	1.4308	−0.0653	−0.0634
BO-a	1.4311	−0.0618	−0.0608
BP-a	1.4310	−0.0651	−0.0635
BZ-a	1.4401	−0.0601	−0.0616
BS-a	1.4436	−0.0570	−0.0666

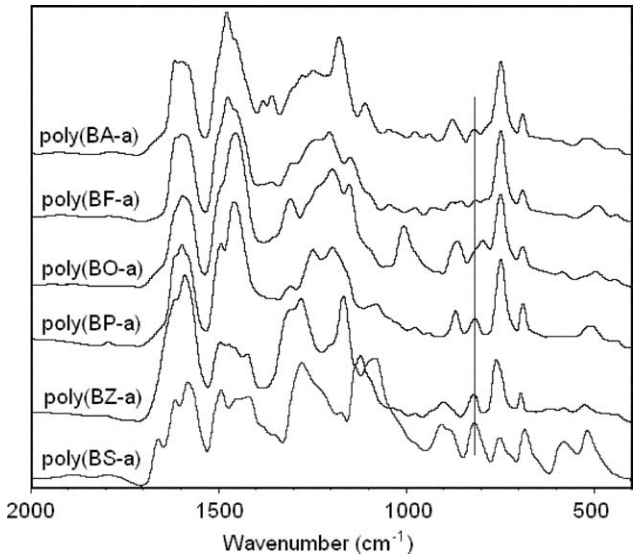


FIGURE 8 FT-IR spectrum of poly(BX-a)s.

Figure 5 shows the nonisothermal DSC thermograms (10 °C min^{-1}) of the benzoxazine monomers, and the summary of the results is listed in Table 3. BA-a shows an endothermic peak at 123 °C attached to melting and an exothermic peak at 267 °C because of thermally activated polymerization. When compared with BP-a, the exothermic peak temperatures of BA-a, BF-a, and BO-a with electron-donating groups are higher, whereas those of BZ-a and BS-a with electron-withdrawing groups are lower. The exothermic peak temperature of BS-a with strong electron-withdrawing group is at 215 °C, which is 52 °C lower than that of BA-a with strong electron-donating group. Besides, the exothermic enthalpies on curing of BZ-a and BS-a are ~160 kJ mol^{-1}, of which the other four monomers are close to 140 kJ mol^{-1}. The results indicated that the polymerization mechanisms of BZ-a and BS-a, affected by electron-withdrawing groups, may be different from the other four monomers.

To further study the polymerization behavior, isothermal DSC scanning of benzoxazine monomers at 210 °C was done, and the conversion versus time curve is shown in Figure 6. It was obvious that benzoxazines with electron-withdrawing groups reacted much faster than those with electron-donating groups. The conversion of BS-a reached to 90% only in 10 min, but the conversion of BA-a is below 20% even after reacting for 30 min.

The Ozawa method[28,29] is frequently used to evaluate dynamic DSC data to study reactions. This linear equation with the form $y = a + bx$ ($x = 1/T$), can be used to calculate

TABLE 5 Weight Loss of Benzoxazines During Thermal Polymerization[a]

	Weight Loss at 180 °C for 5 h (%)	Weight Loss at 200 °C for 2 h[b] (%)
BA-a	1.73	1.77
BF-a	1.89	1.96
BO-a	2.10	2.13
BP-a	2.26	2.34
BZ-a	2.35	2.42
BS-a	3.21	3.41

[a] Monomer of 2.5 g was heated in a weighing bottle under nitrogen atmosphere.
[b] The sample was tested after heated at 180 °C for 5 h.

the optimal kinetic parameter of E_α by multiple linear regression.

The general Ozawa's iso-conversion method:

$$\ln(\beta) = C - 1.052\frac{E_\alpha}{RT_\alpha}$$

where β is heating rate in K min^{-1}; E_α is activation energy of conversion at α in kJ mol^{-1}; and T_α is temperature of conversion at α in K.

The dependence of the apparent activation energies of both benzoxazine resins as a function of degree of curing determined by the general Ozawa's iso-conversion method is shown in Figure 7. For all monomers, the E_α values decrease at early stage of curing because of the catalysis of phenolic hydroxyl groups derived from polymerization. Then, the E_α values increase owing to the elevation of viscosity and crosslink density. The trend of BA-a we obtained is different from the regularity of BA-a reported before.[30] It is reported that the apparent activation energy at initial stage is less than 80 kJ mol^{-1} and the apparent activation energy increases with the conversion increasing. It is because that their sample is impure and the impurity can catalyze the reaction. Contrasted with BP-a, the E_α values of BA-a, BF-a, and BO-a are a little higher, and those of BZ-a and BS-a are obviously lower. Hence, the conversion of BS-A at 210 °C reaches high level in a short time. The results indicated that the electron-donating group restrained the polymerization, whereas the electron-withdrawing group facilitated it. In addition, the E_α values of BZ-a increases rapidly just at a conversion of 40% and those of BS-a rises fast even at a conversion of 30%. The E_α values of other four systems increase quickly at a conversion of 70%. The

SCHEME 4 Possible degradation pathway involved in the thermally activated polymerization of benzoxazine.

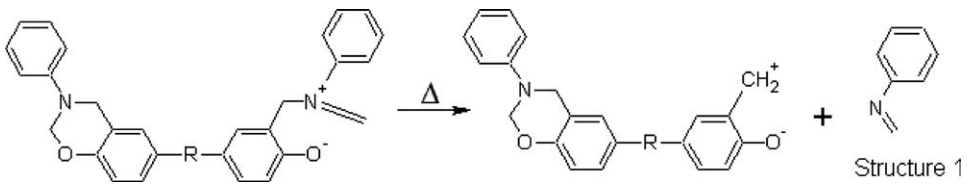


TABLE 6 Results from Elementary Analysis of Two Benzoxazines and Their Polymers

	N Content (%)		C Content (%)		H Content (%)	
	Theoretical Value	Measured Value	Theoretical Value	Measured Value	Theoretical Value	Measured Value
BA-a	6.06	6.04	80.52	80.50	6.49	6.46
Poly(BA-a)	5.83	5.79	79.14	79.11	6.08	6.22
BS-a	5.79	5.75	69.42	69.22	4.96	4.90
Poly(BS-a)	5.36	5.40	66.85	66.90	4.74	4.87

results revealed that polymerization of BZ-a and BS-a became diffusion controlling at initial stage of curing because of the different polymerization mechanism which had been discussed in detail below.

Scheme 3 shows the mechanism of thermally activated polymerization of benzoxazines.[20,31,32] The ring-opening initiation of benzoxazine results in the cleavage of C—O bond and the formation of a carbocation and an oxygen anion. Then, the active carbon atoms marked C1 and C2 suffer electrophilic attack from the carbocation and the protons transfer to the oxygen anions to form hydroxyl groups. Two types of cross-link structures signed Type 1 and Type 2 are formed. Thus, the stability of C—O bond and the activity of C1 and C2 are crucial to the thermally activated polymerization. Theoretically, electron-withdrawing group in benzoxazine monomers can decrease the charge density of oxygen on oxazine ring and destabilize C—O bond, which becomes easier to cleave and initiate polymerization. As a result, the bond length of C—O will increase. Electron-donating groups play an opposite role.

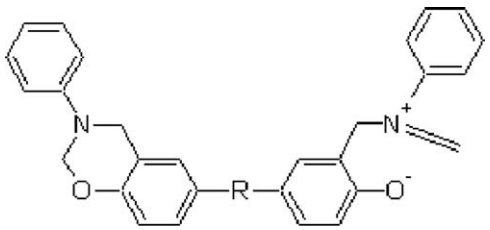
To analyze the influence of electronic effects on thermally activated polymerization quantitatively, bond lengths of C—Os and charge densities of C1 and C2 are calculated by Material Studio. The results are listed in Table 4. The electron-donating groups shorten the bond lengths of C—Os. However, the electron-withdrawing groups extend them. Theoretically, bond length is related to bond energy, that is, the longer the bond length is, the lower the bond energy is. Thus, the C—O bond of BA-a with the strongest electron-donating group is the most stable and the C—O bond of BS-a with the strongest electron-withdrawing group is the most unstable. This trend is in accordance with the results that BS-a with strong electron-withdrawing react faster and initial E_α values is much lower. When increasing the reactivity in the benzoxazine ring, the electron-withdrawing groups also lead to a decrease in the yield simply because of the fast oligomerization processes during the synthesis. As the oligomers were removed during the work up, the yield decreased. This also is the reason that the yield of BS-a is lower.

In the systems of BA-a, BF-a, BO-a, and BP-a, charges of C1 are higher than those of C2. But in the systems of BZ-a and BS-a, charges of C2 are higher. Especially in BS-a, charge of C2 (−0.0666) is evidently higher than that of C2 (−0.0570). Therefore, it is easier for benzoxazines with electron-withdrawing groups to form the Type 2 structure.

To prove the conclusion above, FT-IR of polybenzoxazines is conducted (Fig. 8). The typical absorption bands of benzoxazine rings at 917–952 cm^{-1} nearly disappear. The absorption bands at 690 and 750 cm^{-1} associated to monosubstituted benzene in poly(BZ-a) and poly(BS-a) are weaker than those of the other four polymers. In addition, the absorption bands of 1,4-substitued benzene at 820 cm^{-1} in poly(BZ-a) and poly(BS-a), especially the later one, are much stronger than those in the others. The results indicated that BZ-a and BS-a tended to form the Type 2 structure and the other four monomers inclined to generate the Type 1 structure.

It is reported that one of the defects of benzoxazine is the out-gassing issue during the polymerization process because of the dissociation of the zwitter-ionic intermediate accompanied by release of imine.[33] The volatile organic compounds cause foaming or formation of pore. The weight loss during

TABLE 7 C—N^+ Bond Length of the Zwitter-Ionic Intermediate Obtained from MS



	BA-a	BF-a	BO-a	BP-a	BZ-a	BS-a
Bond length of C—N^+ (Å)	1.4506	1.4454	1.4469	1.4522	1.4530	1.4837

polymerization influenced by electronic effect is also investigated in our work, and the results are listed in Table 5. The weight loss of BS-a is 3.21%, and the weight losses of benzoxazines with electron-donating groups are all close to 2%. It is reported that the weight loss at the same condition for the bisphenol A/aniline based monomer is 8.7%,[33] whereas the current result is 1.77%. This significant discrepancy must be because of their sample used, which is impure. During the thermally activated polymerization process of bisphenol-based benzoxazine, the possible degradation pathway is shown in Scheme 4. To confirm the structure of fugitive constituent, the contents of C, N, and H of BA-a, BS-a, and their polymers are measured by elementary analysis. We postulate that the releaser is structure 1 and calculate the theoretical values of the contents of C, H, and N of the cured resins using the formulas 2, 3, and 4:

$$C\% = a_C - b\frac{84}{105} \quad (2)$$

$$H\% = a_H - b\frac{7}{105} \quad (3)$$

$$N\% = a_N - b\frac{14}{105} \quad (4)$$

In the formulas, a_C, a_H, and a_N are the theoretical contents of C, H, and N of BX-a, respectively. And b is the weight loss of poly(BX-a) during the polymerization process.

As can be seen in the Table 6, the measured values are approximately similar to the theoretical values. Therefore, the fugitive constituent is structure 1.

We also calculated the C—N^+ bond lengths of the zwitterionic intermediates to determine the stability of the intermediates, and the results are listed in Table 7. The C—N^+ bond length of the BS-a intermediate is 1.4837 Å, much longer than those of the other intermediates. The results indicated that the C—N^+ bond length of the BS-a intermediate, influenced by the electron-withdrawing sulfone group, is the least stable and easily cleaved to release imine.

CONCLUSIONS

In this article, six bisphenol-based benzoxazines with different bridging groups were synthesized. The influence of electronic effects of the bridging groups on ring-forming reaction and thermally activated polymerization were investigated. Electron-withdrawing groups and electron-donating groups acted an opposite role both in the two reactions. Electron-withdrawing groups decreased the charge density of α-C of bisphenols, which increased the reaction energy barrier between —N—$(CH_2$—$OH)_2$ and α-C resulting in lower monomer yield. In the stage of thermally activated polymerization, electron-withdrawing groups weakened C—O bond of benzoxazine, which was availed for initiation of polymerization and lowered the energy barrier and cure temperature. Further, electronic effect changed the activity of ortho-C of benzoxazine rings and para-C of aniline, which altered the polymerization mechanism and the structures of the polymers. Owing to the effect of electron-withdrawing sulfone group, there were more arylamine methylene Mannich bridge type polybenzoxazine formed and more weight loss during polymerization produced in BS-a system.

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