

Thermally Activated Polymerization Behavior of Bisphenol-S/Methylamine-Based Benzoxazine

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ABSTRACT: A bifunctional benzoxazine monomer, 6,6'-bis(3-methyl-3,4-dihydro-2H-benzo[e][1,3]oxaziny) sulfone (BS-m), was synthesized from bisphenol-S, methylamine, and formaldehyde via a solution method. The chemical structure of BS-m was characterized with ¹H and ¹³C-nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and elemental analysis. The ring-opening polymerization reaction of BS-m monomer was studied by FTIR, ¹³C solid-state NMR, and differential scanning calorimetry. With the polymerization reaction proceeding, the intensities of the FTIR absorption peaks of CH₂, C—O—C, and C—N—C of the oxazine ring decreased gradually, and some of these absorption peaks disappeared. The shapes and intensities of the

absorption peaks associated with benzene ring, sulfone group, and aromatic C—S bond changed in various ways. The changes in the solid-state ¹³C-NMR pattern, including chemical shifts, intensity of resonances, and line-width, were observed from the spectra of BS-m and the corresponding polybenzoxazine. The melting process of BS-m overlapped with the beginning of the ring-opening polymerization reaction. The polymerization kinetic parameters were evaluated for nonisothermal and isothermal polymerization of BS-m. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 813–822, 2012

Key words: benzoxazine; bisphenol-S; ring-opening polymerization; kinetics; differential scanning calorimetry

INTRODUCTION

Benzoxazines are oxygen and nitrogen-containing heterocyclic compounds obtained from phenol, formaldehyde, and amine. Monofunctional benzoxazine was first synthesized by Holly and Cope,¹ and then the benzoxazine chemistry was studied.^{2,3} After bisphenol-A type bifunctional benzoxazine was synthesized,⁴ the thermally activated ring-opening polymerization reaction of benzoxazines was also studied, and the excellent properties of polybenzoxazines were recognized, including good thermal and mechanical properties, low water absorption, and superior electrical properties. Since then, the studies on benzoxazines have attracted much attention, and various benzoxazines have been synthesized from different phenols and amines.^{5–12} At the same time, the polymerization reaction and properties related to benzoxazine materials have been widely studied.^{12–30} In addition, the application of benzoxazines is developed in various fields of high performance materials, such as electronics and aerospace indus-

tries, and benzoxazines are used as a potential matrix.

Bifunctional benzoxazines can be synthesized from bisphenols with monoamines or phenols with diamines. However, limited by the poor solubility of the starting compounds (bisphenols and aromatic diamines) and benzoxazine products, the synthesis reactions of the benzoxazines not all proceed easily. Among the bifunctional benzoxazines, the bisphenol-A-based bifunctional benzoxazines are easily prepared, while the benzoxazines based on sulfone (SO₂)-containing bisphenols or aromatic diamines are relatively difficult to be synthesized.^{10–12} In addition, the synthesis reaction of benzoxazines is affected by the electron effect from electron-withdrawing or electron-donating groups in the molecules of starting materials. When an electron-withdrawing group is attached to the aromatic ring of a bisphenol, the synthesis reaction of benzoxazine will become difficult.³¹ SO₂ moiety is a strong electron-withdrawing group with high rigidity and can be introduced into benzoxazine via bisphenol-S or 4,4'-diaminodiphenyl sulfone to provide some desired properties.^{10–12,32} However, it was reported that starting material and partially ring-opened product were observed in the synthesized product by ¹³C-nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy,³² respectively.

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Of course, the structure, morphology, and properties of polybenzoxazines are governed by the benzoxazine monomer molecular structure, but the polymerization reaction condition is also an important factor affected the morphology and properties of polybenzoxazines. In addition, the polymerization behavior of benzoxazines depends on their chemical structures and the reaction conditions. Although many reports involved the study on the polymerization of benzoxazines, the polymerization behavior of benzoxazine based on bisphenol-S and methylamine has not been reported in detail.

In this study, 6,6'-bis(3-methyl-3,4-dihydro-2H-benzo[e]^{1,3}oxazinyl) sulfone (abbreviated as BS-m) was synthesized from bisphenol-S, methylamine, and formaldehyde via a solution method, and characterized by ¹H and ¹³C-NMR spectroscopy, FTIR, and elemental analysis. The ring-opening polymerization of BS-m monomer was studied by FTIR, ¹³C solid-state NMR, and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

Bisphenol-S (4,4'-dihydroxydiphenyl sulfone) (99%), was purchased from Shanghai Chemical Reagent Co. (China). Formaldehyde solution (37% in water), methylamine solution (33% in ethanol), dioxane, and chloroform were obtained from Tianjin Chemical Reagent Co. (China). All chemicals were used as received.

Synthesis of 6,6'-bis(3-methyl-3,4-dihydro-2H-benzo[e][1,3]oxazinyl) sulfone

To a 100-mL three-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, 3.765 g methylamine, 6.493 g formaldehyde, and 20 mL dioxane were added. The mixture was stirred for 1 h in an ice bath before adding the solution of 5.005 g bisphenol-S in 15 mL dioxane. Then, the mixture was heated and allowed to reflux for 8 h at 92°C. Subsequently, the solvent was removed by distillation under reduced pressure, and the residue was dissolved in about 20 mL chloroform. The chloroform solution was washed several times with 3 mol/L NaOH aqueous solution and deionized water, respectively. Thereafter, the chloroform was removed by distillation under reduced pressure. The product was dried at 70°C in a vacuum oven for 12 h, then at 100°C in an air circulated oven for 3 h, and finally a pale yellow powder was obtained.

Preparation of polybenzoxazine

BS-m was isothermally polymerized at 190°C in an air circulated oven for 4 h to form into polybenzoxazine (PBS-m).

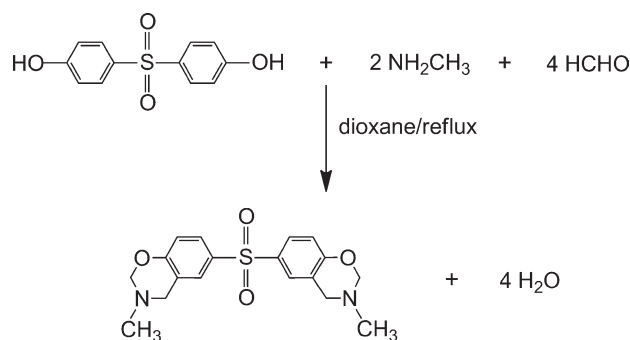
Measurements

Both ¹H and ¹³C-NMR spectra were recorded by a Bruker Avance III 600 NMR spectrometer at a proton frequency of 600 MHz and the corresponding carbon frequency. Dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) was used as a solvent and tetramethylsilane (TMS) as an internal standard. Solid-state NMR experiments were carried out at room temperature (25°C) on a Bruker Avance III 400 NMR spectrometer operating at a ¹³C resonance frequency of 100.568 MHz. Samples were analyzed under cross-polarization/magic-angle spinning (CP/MAS) conditions using 4-mm zirconia rotors at a spinning frequency of 5 kHz. A 90° pulse width of 4 ms was used, and the CP Hartmann-Hahn contact time was set at 3.0 ms. The chemical shifts of ¹³C spectra were externally referenced to the carbon signal of solid adamantane (38.48 ppm relative to TMS).

FTIR spectra were obtained with a Nicolet 380 FTIR spectrometer at a resolution of 4 cm⁻¹. BS-m sample was finely ground with KBr powder and pressed into a disk, and then the disk was placed in an isothermal oven under air atmosphere. During the polymerization reaction process, the disk was repeatedly removed at a regular time interval and scanned with the FTIR spectrometer.

The quantitative analyses of C, H, N, O, and S were carried out on an Exeter Analytical CE-440 elemental analyzer.

The nonisothermal and isothermal polymerization reactions of BS-m monomer were monitored with a Shimadzu DSC-41 differential scanning calorimeter operating in a nitrogen atmosphere. The DSC instrument was calibrated with high purity indium. α -Al₂O₃ was used as the reference material. In nonisothermal analyses, BS-m samples weighted about 5.6 mg were scanned at different heating rates of 5, 7.5, 10, 12.5, and 15°C/min, respectively. In addition, BS-m samples weighted about 5 mg were first heated to 150, 160, 165, and 170°C in DSC at a heating rate of 10°C/min, respectively, and then the samples were quickly removed and cooled down to room temperature. Thereafter, the samples were reheated at the same heating rate to 300°C, respectively. Isothermal analyses were performed at temperatures of 176, 181, 186, 191, and 196°C, respectively. The amount of BS-m samples was about 11 mg. Before loading sample, the furnace was first heated up to a desired temperature and kept for a certain period of time. When the system reached an equilibrium state, the sample cell was quickly set on the calorimetric detector plate. The reaction was considered complete when the rate curve leveled off to a baseline. After each isothermal run, the sample was rapidly cooled to 10°C and then reheated at 10°C/min to 280°C to determine the residual heat of reaction, ΔH_r .



Scheme 1 Chemical reaction of BS-m monomer synthesis.

Therefore, the total heat evolved during the polymerization reaction is $\Delta H_0 = \Delta H_i + \Delta H_r$. Besides, the glass transition temperature (T_g) of the PBS-m was determined by DSC at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

Synthesis and characterization

BS-m was synthesized from bisphenol-S, methylamine, and formaldehyde via a solution method.¹² The product purification procedure was different from what the published literature described.³² The synthesis reaction mechanism is shown in Scheme 1. The chemical structure of BS-m was confirmed by ¹H and ¹³C-NMR, FTIR, and elemental analysis.

The ¹H-NMR (DMSO-*d*₆) spectrum of BS-m is shown in Figure 1. The presence of benzoxazine-ring structure was confirmed by the resonances appearing at 3.98 ppm due to the methylene protons of Ar-CH₂-N and 4.86 ppm due to O-CH₂-N of the oxazine ring, respectively. The resonance of methyl protons of N-CH₃ was observed at 2.46 ppm (6H, H1). In addition, the signals at 6.89 and 6.91 ppm (2H and H5), 7.63, and 7.64 ppm (4H, H8, and H6) are assigned to the aromatic protons. The intensity ratio by the six protons (H1, H2, H3, H5, H6, and H8) was determined roughly to be 3 : 2 : 2 : 1 : 1 : 1, which is well coincident with the theoretical protons ratio based on the chemical structure.

The ¹³C-NMR (DMSO-*d*₆) spectrum of BS-m is shown in Figure 2. The resonances appeared at 51.17 and 84.81 ppm are assigned to the methylene carbons (C2 and C3) of Ar-CH₂-N and O-CH₂-N of the oxazine ring, respectively. The methyl carbon (C1) of N-CH₃ was observed at 39.53 ppm. Other chemical shifts (ppm) are assigned to the aromatic carbon resonances: 117.24 (C5), 121.63 (C9), 127.47 (C6), 127.84 (C8), 133.39 (C7), and 158.17 (C4).

The ¹H and ¹³C-NMR spectra of BS-m are consistent with the proposed structure, and no start material is observed.

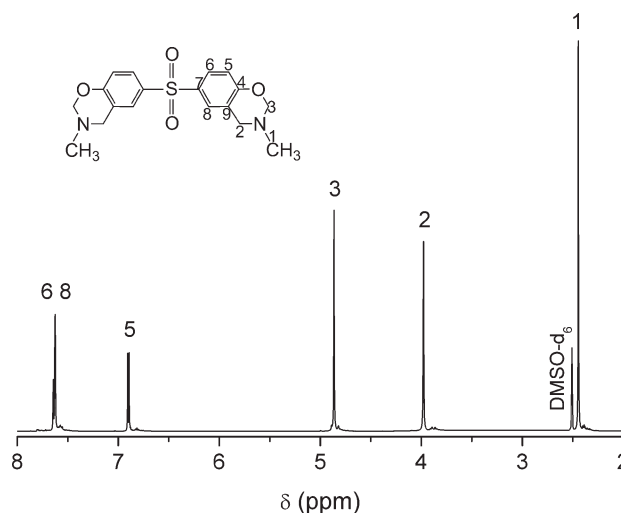


Figure 1 ¹H-NMR spectrum of BS-m monomer.

Elemental analysis of BS-m shows that the experimental results (C, 59.88%; H, 5.65%; N, 7.73%; O, 17.81%; S, 8.92%) are in reasonable agreement with the calculated values (C, 60.00%; H, 5.56%; N, 7.78%; O, 17.78%; S, 8.89%).

The FTIR spectrum of BS-m is shown in Figure 3(A). The characteristic absorptions at 1116 and 1187 cm⁻¹ are assigned to the asymmetric stretching vibrations of C-N-C, while the absorption peaks at 839 and 856 cm⁻¹ correspond to the symmetric stretching vibrations of C-N-C.³³ The symmetric and asymmetric stretching vibrations of C-O-C are observed at 1050 and 1236 cm⁻¹,³³ respectively. The absorptions at 1444, 1484, 1573, and 1600 cm⁻¹ are associated with the aromatic C=C stretching vibrations of the benzene ring. The C-H out-of-plane bending of the benzene ring can be found at 747, 821, 898, 913, 925, and 974 cm⁻¹. Besides, the aromatic C-H stretching vibration of the benzene ring

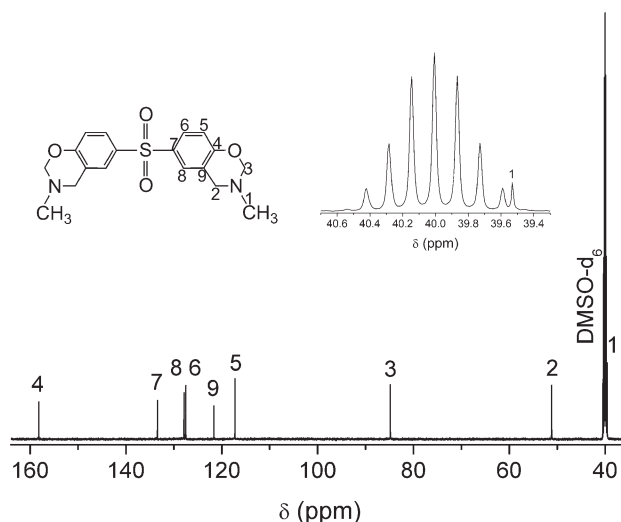


Figure 2 ¹³C-NMR spectrum of BS-m monomer.

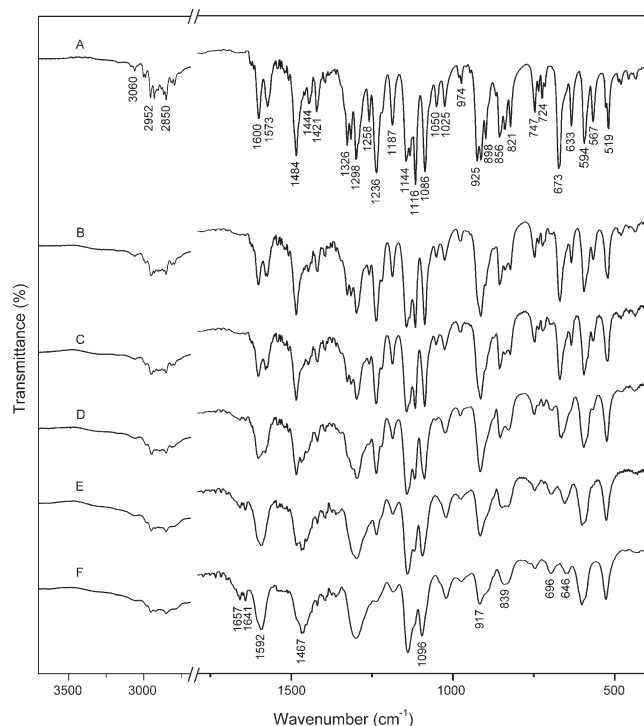


Figure 3 FTIR spectra of (A) BS-m monomer, and polymerized at 170°C in air for: (B) 10 min, (C) 30 min, (D) 60 min, (E) 120 min, and (F) 360 min.

appeared at 3060 cm^{-1} , and the C—H symmetric and asymmetric stretching vibrations of CH_2 in the oxazine ring are at 2850 and 2930 cm^{-1} , respectively. The C—H symmetric stretching vibrations of CH_3 appear at 2882 and 2905 cm^{-1} , and the C—H asymmetric stretching vibrations of CH_3 occur at 2955 and 2989 cm^{-1} . The absorption peaks at bands of 724, 1258, 1326, and 1421 cm^{-1} are due to the rocking, twisting, wagging, and scissoring vibrations of CH_2 in the oxazine ring, respectively. In addition, the peaks at 1025, 1132, and 1144 cm^{-1} are assigned to the symmetric stretching vibrations of SO_2 group, while the peaks at 1298 and 1314 cm^{-1} are ascribed to the asymmetric stretching vibrations of SO_2 group. The bands at 567 and 633 cm^{-1} are attributed to the scissoring vibrations of SO_2 group, and the peaks at 519 and 594 cm^{-1} belong to the in-plane bending vibrations of SO_2 . The bands at 673, 735, and 1086 cm^{-1} originate to the aromatic C—S stretching vibrations. The FTIR spectrum of BS-m is consistent with the proposed structure and no ring-opening product is observed.

Structure changes in the ring-opening polymerization reaction

The FTIR spectra of BS-m polymerized at 170°C for different times in air are shown in Figure 3(B–F). It can be seen that the absorption intensities associated with CH_2 , C—O—C, and C—N—C of the oxazine

ring decreased with the ring-opening reaction proceeding, such as the peaks at 1421, 1326, 1236, 1187, 1116, 1050, 856, and 839 cm^{-1} . Correspondingly, owing to the ring-opening polymerization, trisubstituted benzene ring turned into tetra-substituted benzene ring, and the absorption intensities associated with benzene ring changed, especially at bands of 1600, 1573, 1484, 974, 925, 913, 898, 821, and 747 cm^{-1} . The two absorption peaks at 1600 and 1573 cm^{-1} gradually disappeared and came into a new absorption peak at band of 1592 cm^{-1} , while the absorption peak at 1484 cm^{-1} gradually decreased. Meanwhile, the peak at the band of 1467 cm^{-1} became obvious, and the absorption is assigned to the in plane C=C stretching of the tetra-substituted benzene ring occurred in the polybenzoxazine. Moreover, the two absorption peaks at 925 and 913 cm^{-1} quickly disappeared and became into a new absorption peak at the band of 917 cm^{-1} at the beginning of the reaction, and, thereafter, its intensity gradually decreased with the reaction proceeding. The weak absorption at about 3350 cm^{-1} is ascribed to the stretching of —OH group formed in the reaction. As can be seen, the shapes and intensities of the absorption peaks associated with SO_2 and aromatic C—S at 1314, 1298, 1144, 1132, 1086, 735, 673, 633, 594, 567, and 519 cm^{-1} changed with the ring-opening polymerizing, and some absorptions disappeared in the reaction, such as peaks at 673, 633, and 567 cm^{-1} . In addition, the new bands appeared at 1641 and 1657 cm^{-1} are assigned to the absorption of Schiff base formed in the polymerization.^{34–36} The changes in FTIR spectra show the structure variations in the ring opening polymerization reaction and confirm the formation of the corresponding PBS-m.

Based on the variation of the FTIR spectra, some absorption intensities were normalized, and their relative conversions (α) at various isothermal polymerization temperatures were determined by the Beer–Lambert law from their normalized changes as follows^{36–38}:

$$\alpha = 1 - \frac{(A_i/A_r)_{T,t}}{(A_i/A_r)_{T,t=0}} \quad (1)$$

where T is the polymerization temperature, t is the polymerization time, $(A_i/A_r)_{T,t}$, and $(A_i/A_r)_{T,t=0}$ are the ratios of integrated intensity of a specified band to the integrated intensity of the internal standard band at the time t and at the starting time, respectively. The band at 1025 cm^{-1} was used as an internal standard to normalize the absorption intensities of the reactive groups, for the intensity of the absorption at 1025 cm^{-1} remained almost unchanged in the polymerization. The conversions of different

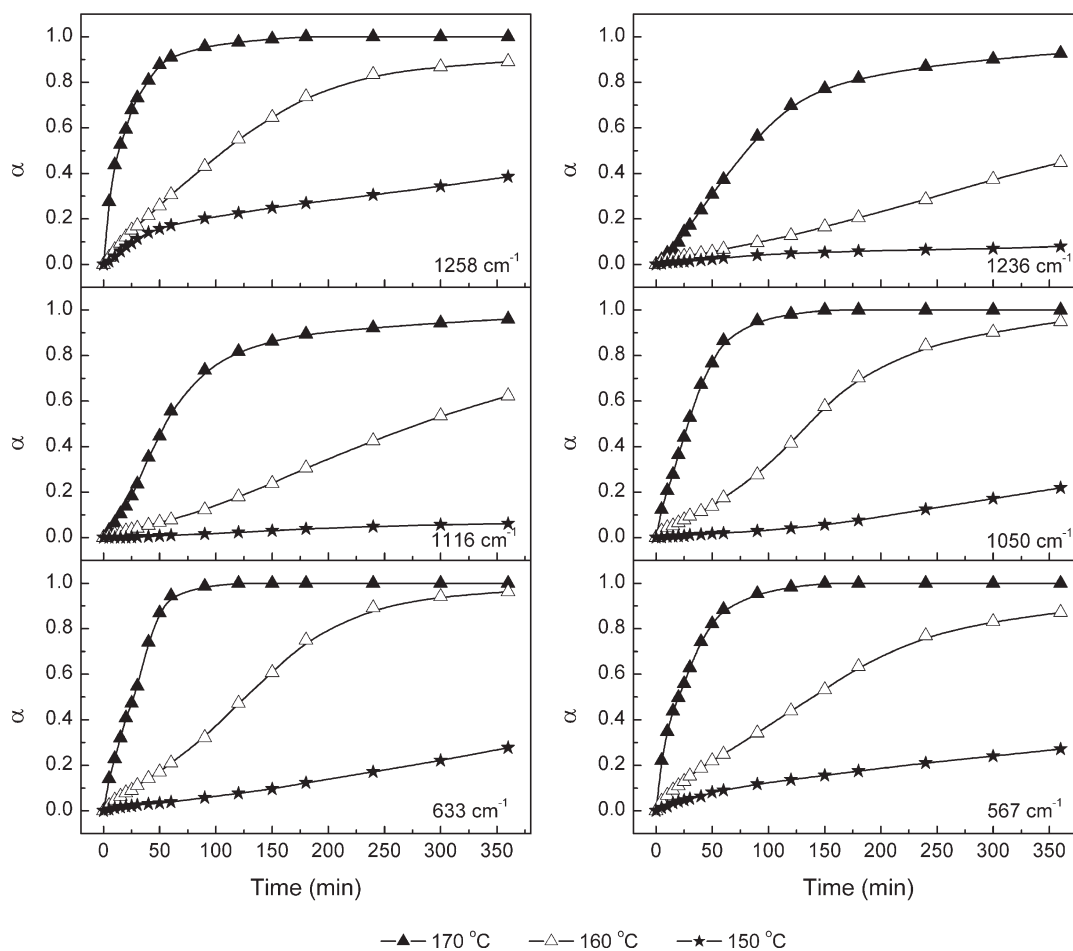


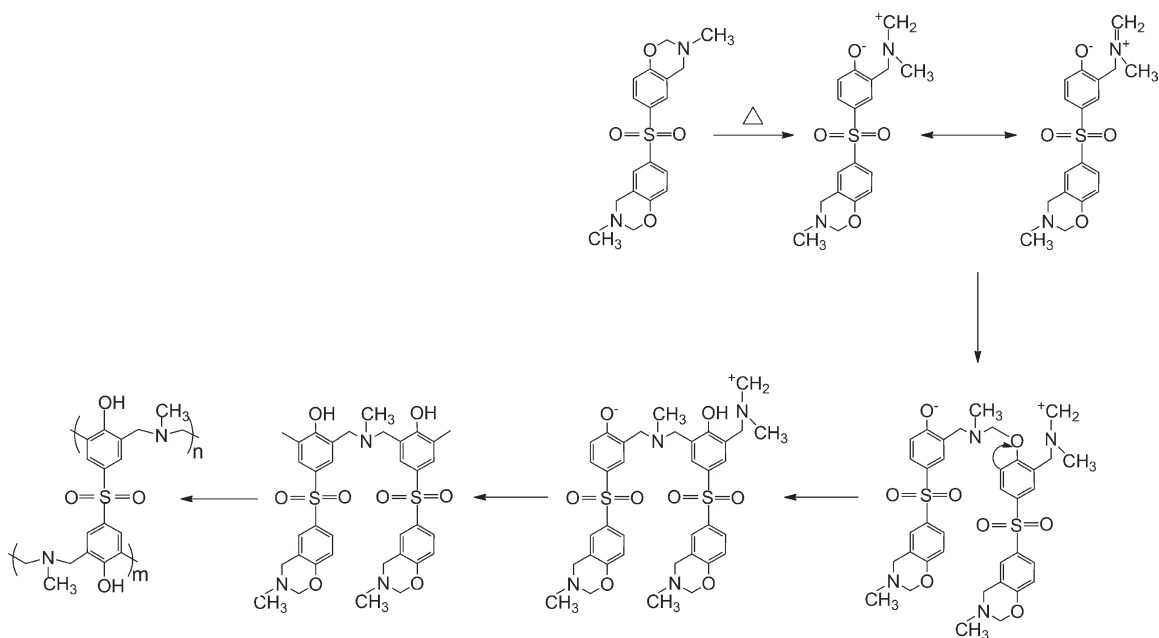
Figure 4 Plots of conversion versus reaction time for various absorption bands at different temperatures in air.

absorption bands were calculated according to eq. (1), and some plots of conversion against reaction time are shown in Figure 4. As can be seen, the effect from temperature change on the variation of conversion is significant for various absorption bands. For a specified band, a higher conversion was gained at a higher reaction temperature in the same reaction time. In addition, the reaction rates were different for various bands at the same reaction temperature, indicating the complexity of the polymerization.

The thermally activated polymerization of benzoxazine is generally thought to be a cationic ring-opening reaction.^{13,25,26,39} As shown in Scheme 2, with the temperature rising, the heterolytic cleavage of the C—O bond in the oxazine ring in BS-m results in the formation of an oxygen anion and a carbocation or an iminium ion, and the carbocation and the iminium ion are in equilibrium.³⁹ So, the ring-opening reaction is initiated. Then, the carbocation in one BS-m molecule attacks the oxygen anion in another BS-m molecule, and a new C—O bond is formed. Thereafter, the oxygen atom harvests the ortho

hydrogen on the benzene ring to form into a phenol hydroxyl, and the —CH₂—NR—CH₂— bridges the benzene ring on the *ortho*-position to form into a Mannich bridge structure. As a result, PBS-m is formed with a crosslink network in this way, and the T_g of the PBS-m is 213°C.

In addition, the solid-state CP/MAS ¹³C-NMR spectra of BS-m and the corresponding PBS-m are shown in Figure 5. As can be seen, the chemical shifts of BS-m monomer are very close to the observed chemical shifts in DMSO-*d*₆ solution-state NMR spectrum in Figure 2. Corresponding to the assignments in Figure 2, the peaks appeared at 51.30 and 86.12 ppm are the resonances of methylene carbons (C2 and C3) of Ar—CH₂—N and O—CH₂—N of the oxazine ring, respectively. The resonance of methyl carbon (C1) of N—CH₃ is a doublet with one peak at 37.57 and one at 39.28 ppm. Other chemical shifts (ppm) are the aromatic carbon resonances: 117.74 and 118.47 (C5), 120.48 and 122.20 (C9), 127.08 and 128.55 (C6), 130.48 (C8), 134.86 (C7), and 158.51(C4). Moreover, the calculated chemical shifts for the structure of PBS-m show good agreement



Scheme 2 Mechanism for thermally activated ring-opening polymerization of BS-m.

with the observed chemical shifts of C1, C2, C3, and C4 in PBS-m, while a strong overlapping resonance of aromatic carbons (C5, C6, C7, C8, and C9) is observed at 129.34 ppm. Meanwhile, the resonances at 61.62 and 84.88 ppm are assigned to the C2 and C3 of the unopened oxazine rings in PBS-m, respectively. In addition, some chemical shifts exclusive to BS-m are observed intensity decreased and line-width broadened in the PBS-m spectrum due to the crosslink of the molecular chains, whereas the chemical shift of 16.60 ppm native to PBS-m is not observed in the BS-m spectrum. The changes in the solid-state ^{13}C -NMR pattern from benzoxazine to the corresponding polybenzoxazine are similar to those observed for the bisphenol-A type benzoxazines.³⁹

Ring-opening polymerization kinetics

The ring-opening polymerization kinetic analysis was performed by monitoring the heat release behavior in the reaction and both nonisothermal and isothermal DSC modes were used to characterize the polymerization process.

In nonisothermal DSC mode, a multiple-heating-rate method was used to evaluate the polymerization reaction kinetic parameters by measuring the exothermic peak temperatures (T_p s) at several heating rates. The nonisothermal DSC curves for BS-m polymerization at different heating rates are shown in Figure 6. An endothermic peak appeared at about 165°C, followed by an exothermic reaction process. The exothermic peaks correspond to the polymerization reaction of BS-m, and the reaction kinetic parameters were determined by Kissinger and

Flynn–Wall–Ozawa methods based on the difference in the exothermic peak temperatures of the DSC curves.^{40–42}

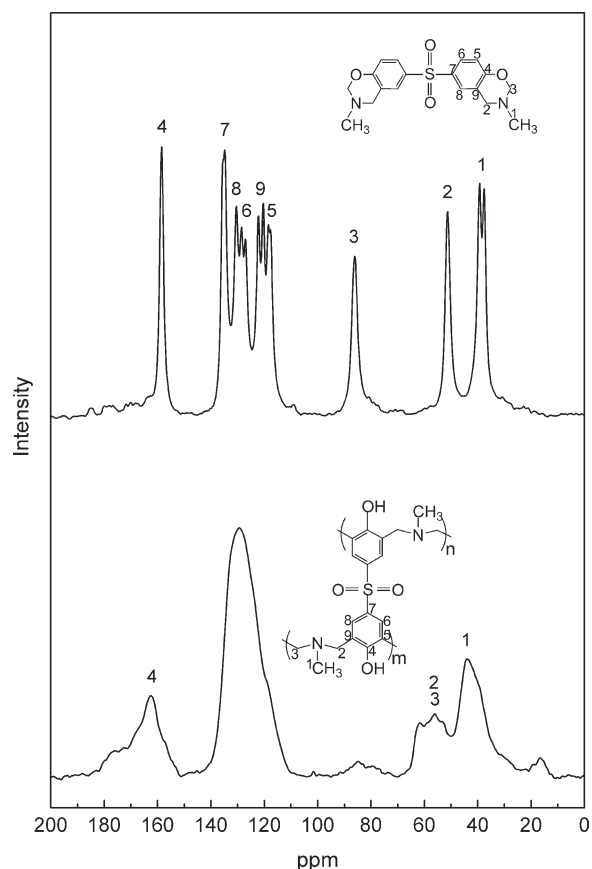


Figure 5 ^{13}C solid state NMR spectra of BS-m monomer and the corresponding polybenzoxazine.

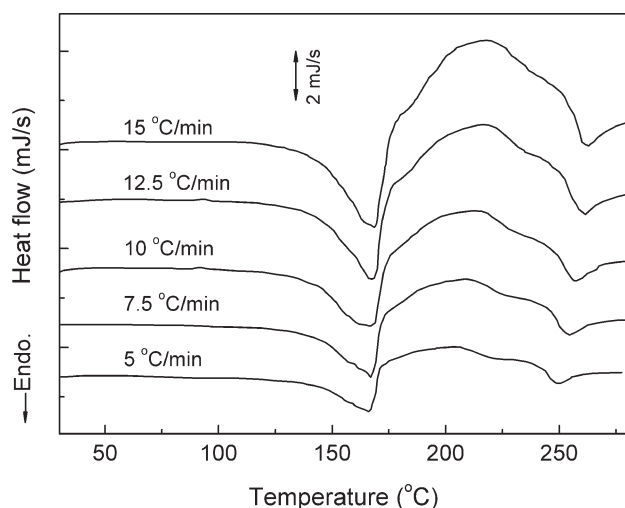


Figure 6 DSC curves of BS-m at different heating rates.

Kissinger's technique assumes that the maximum reaction rate occurs at peak temperatures, where $d^2\alpha/dt^2 = 0$, and it can be expressed as

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_p} \quad (2)$$

where β is the linear heating rate, A is the pre-exponential factor, E is the activation energy, and R is the universal gas constant. Therefore, a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ gives the values of E and A .

Flynn-Wall-Ozawa method assumes that the degree of conversion at peak temperatures for different heating rates is constant, and it can be expressed as

$$\ln \beta = -1.052 \frac{E}{RT} + C \quad (3)$$

where C is a constant, T is the isoconversion temperature, and the other parameters are the same as described previously. E can be obtained from the slope of the plot of $\ln \beta$ versus $1/T_p$.

According to eqs. (2) and (3), the polymerization kinetic parameters were calculated, and the results are listed in Table I. It can be seen that the activation energy values obtained by the two methods are very close.

Here, it should be noted that the endothermic peaks in the nonisothermal DSC curves correspond to the melting process of BS-m. Meanwhile, the polymerization reaction begins along with the melting process, which can be traced from the variation of FTIR spectra within the melting temperature range. In addition, this reaction behavior can be elucidated by DSC. BS-m samples were first heated to a certain medium temperature in DSC, quickly cooled down

to a room temperature, and then reheated to some desired temperatures. The first heated and reheated DSC curves are shown in Figure 7. As can be seen, a small exothermic peak appears before the melting endothermic process in the second DSC curves for BS-m samples first heated to 150, 160, and 165°C, which may be the result of the decrease in the number of the BS-m monomer molecules. When BS-m samples are first heated to 150, 160, and 165°C, some BS-m molecules may polymerize into BS-m oligomers, and the number of the BS-m monomer molecules decreases. Therefore, when these samples are reheated, the polymerization exothermic process dominates the reaction in the beginning, then the melting endothermic process, and finally the polymerization again. For BS-m sample first heated to 170°C, no endothermic peak can be seen in the reheated DSC curve, which may be due to all the BS-m monomers molecules have formed into oligomers. With the end temperature rising in the first heating process, the polymerization exothermic peak shifts to higher temperature and the heat released decreases in the reheated DSC curve.

In general, it is assumed that the heat evolution recorded by DSC is proportional to the extent of consumption of the reactive groups. Therefore, in isothermal DSC mode, the extent of reaction (α) and the reaction rate ($d\alpha/dt$) can be determined as follows:

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \quad (4)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_0} \times \frac{dH}{dt} \quad (5)$$

where ΔH_t is the reaction heat within the time t , dH/dt is the flow rate of heat, and ΔH_0 is the total reaction heat, which is the maximum heat value determined among all the isothermal and nonisothermal polymerization reactions.

The isothermal DSC curves for BS-m polymerization at different temperatures are shown in Figure 8. The total exothermic reaction heat for BS-m polymerization is 179.0 J/g. Naturally, some

TABLE I
Peak Temperatures and Kinetic Parameter Values
Obtained from Nonisothermal DSC Curves

Heating rate (°C/min)	T_p (°C)	Kissinger		Flynn-Wall-Ozawa E (kJ/mol)
		E (kJ/mol)	A (s ⁻¹)	
5	203.0	129.3	5.3×10^{13}	130.6
7.5	208.5			
10	213.0			
12.5	216.5			
15	218.0			

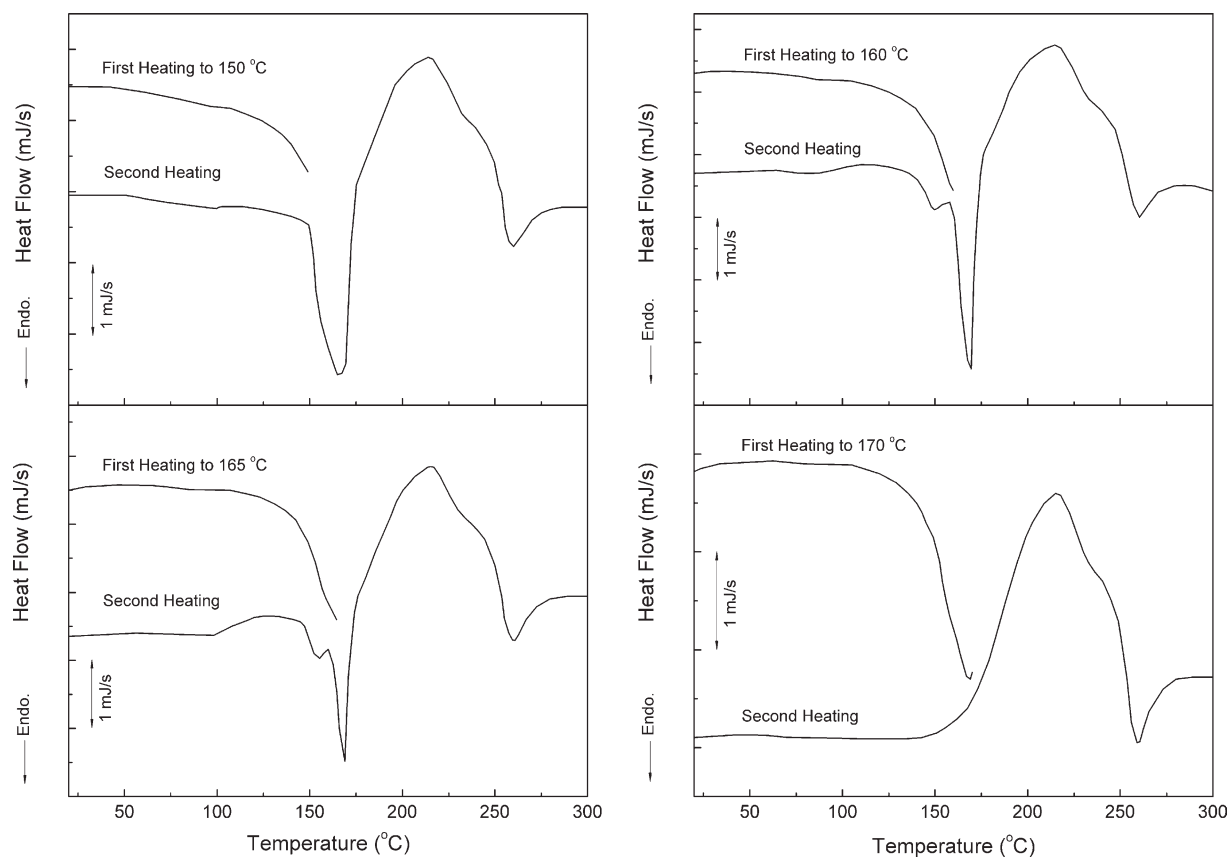


Figure 7 The first heated and reheated DSC curves of BS-m at a heating rate of 10°C/min.

polymerization heat cannot be determined, for the beginning of the polymerization reaction of BS-m overlaps with the melting process. Therefore, the isothermal polymerization kinetics of BS-m that can be studied only involves the reaction process after the melting process. According to eqs. (4) and (5), α and $d\alpha/dt$ were calculated, and the

plots of α versus t , $d\alpha/dt$ versus α at different temperatures are shown in Figures 9 and 10, respectively.

Generally, the reaction kinetic models for thermo-setting resins fall into two main types, n th-order and autocatalytic. The difference of the two models is in the different conversion values at which the

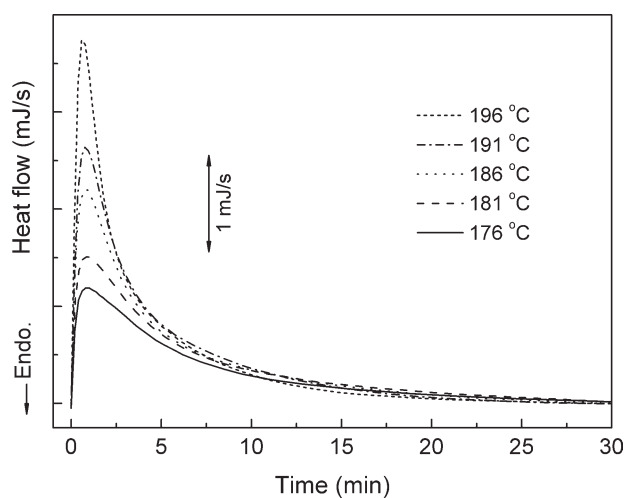


Figure 8 DSC curves of BS-m at different temperatures.

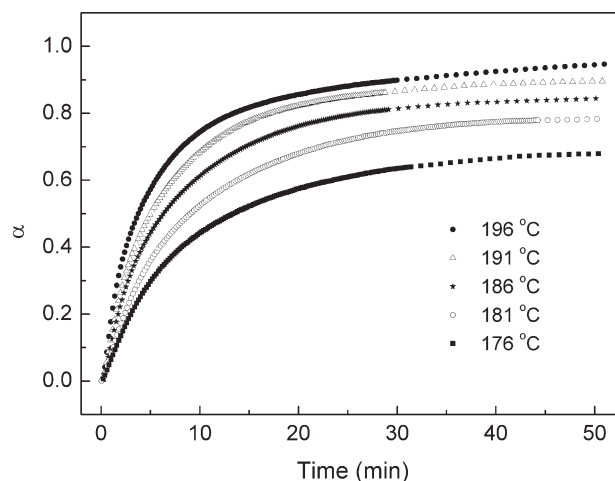


Figure 9 Plots of conversion versus reaction time at different temperatures.

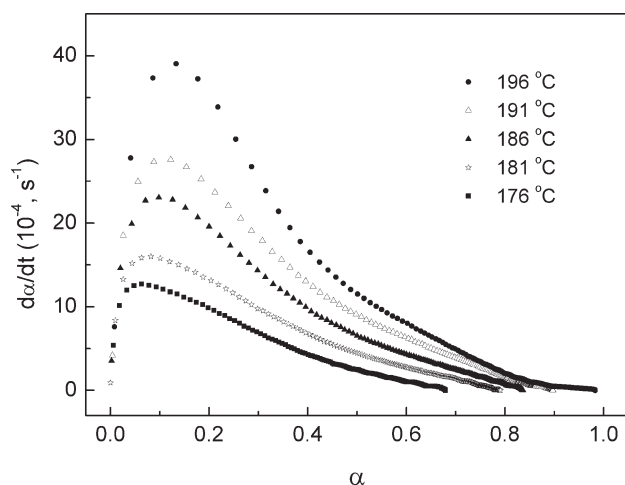


Figure 10 Plots of reaction rate versus conversion at different temperatures.

maximum rate of reaction occurs: zero conversion or a finite conversion value.

Autocatalytic characteristics are shown for the reaction rate varied with conversion in Figure 10, and so the reaction rate can be described by the following autocatalytic kinetic equation⁴³:

$$\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n \quad (6)$$

where m and n are the reaction orders, k is the rate constant at temperature T , following Arrhenius eq. (7):

TABLE II
Kinetic Parameter Values Obtained from Isothermal DSC Curves

Temperature (°C)	k ($10^{-3}, s^{-1}$)	m	n	E ($kJ mol^{-1}$)	A (s^{-1})
176	2.90	0.22	3.16	123.8	6.98×10^{11}
181	3.95	0.27	2.82		
186	5.90	0.28	2.71		
191	7.90	0.34	2.59		
196	12.00	0.37	2.66		

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (7)$$

where all parameters have usual Arrhenius significance.

Based on the experimental data, kinetic parameters, k , m , and n , were obtained by fitting the experimental data to eq. (6) with nonlinear regression. Then, according to Arrhenius equation, E and A were calculated via least squares linear regression. The results are listed in Table II, and the comparisons of the experimental data with the kinetic model are shown in Figure 11. The isothermal reaction activation energy value is close to the results obtained in the nonisothermal mode.

CONCLUSIONS

Bisphenol-S and methylamine-based benzoxazine monomer were synthesized via a solution method.

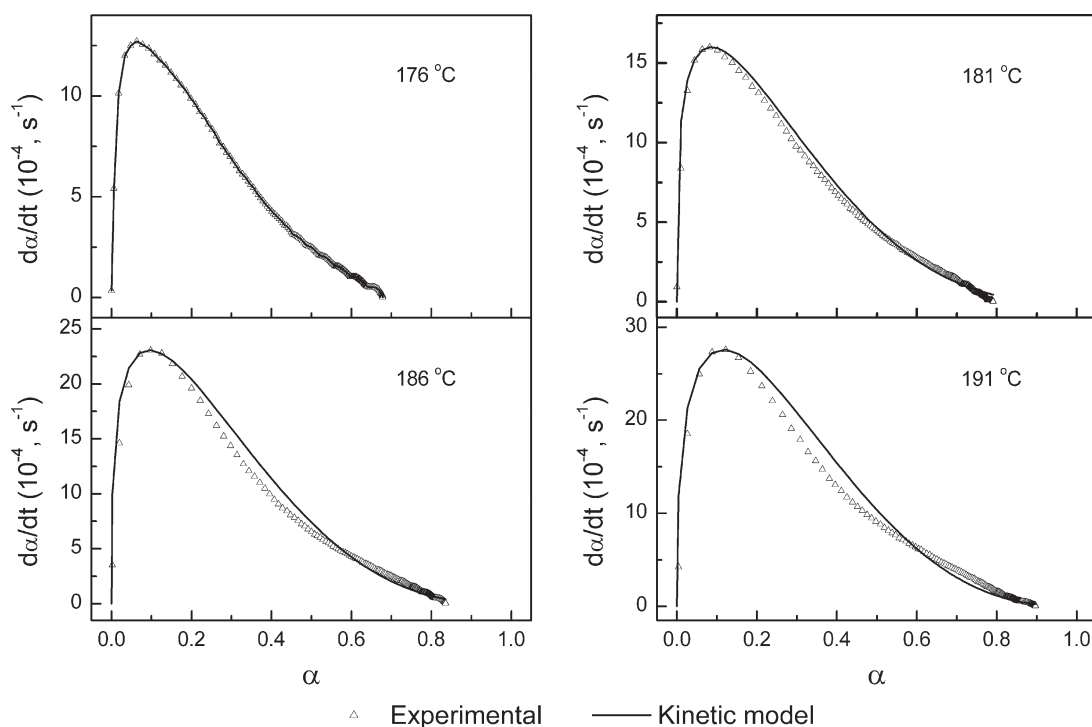


Figure 11 Comparisons of the experimental results with the kinetic model data.

With the polymerization reaction proceeding, the intensities of the FTIR absorption peaks of CH₂, C—O—C, and C—N—C of the oxazine ring decreased gradually, and some of these absorption peaks disappeared. The shapes and intensities of the absorption peaks associated with benzene ring, SO₂ group, and aromatic C—S bond changed in various ways. The changes in the solid-state ¹³C-NMR pattern, including chemical shifts, intensity of resonances, and line-width were observed from the spectra of the benzoxazine monomer and the corresponding polybenzoxazine. The melting process of BS-m overlapped with the beginning of the ring-opening polymerization reaction. The polymerization kinetic parameters were evaluated for nonisothermal and isothermal polymerization of BS-m.

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