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Polymer Degradation and Stability 93 (2008) 739−744

Polymer Degradation and Stability

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Synthesis and thermal properties of the thermosetting resin based on cyano functionalized benzoxazine

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Received 11 July 2007; received in revised form 26 September 2007; accepted 6 October 2007
Available online 12 October 2007

Abstract

A novel thermosetting resin based on cyano functionalized benzoxazine (BZCN) has been synthesized from 2,6-bis(4-diaminobenzoxy)benzonitrile phenol and formaldehyde by solution reaction. The structure of the monomer is supported by FTIR, ^{1}H NMR and ^{13}C NMR spectra, which have exhibited that the reactive benzoxazine rings and cyano group exist in the molecular structure of BZCN. The curing reactions of BZCN are monitored by the disappearance of the nitrile peak and the tri-substituted benzene ring that is attached with oxazine ring peak at 2231 and 930 cm^{-1}, respectively. The complete cured materials could achieve char yields up to 70% at 800 °C in nitrogen atmosphere, above 64% at 600 °C in air (20% oxygen) environments and the glass transition temperature up to 250 °C. The thermally activated curing polymerization reaction of BZCN follows multiple polymerization mechanisms via the ring-opening polymerization of oxazine rings and the triazine ring-formation of cyano groups, which contribute to the stability of the polymer.

Keywords: Thermosetting resins; Thermally activated polymerization; Thermal properties; Cyano functionalized benzoxazine

1. Introduction

In recent years, the development of the benzoxazine-based family of phenolic resins has attracted significant attention. Various phenols and primary amines have been used to synthesize benzoxazine resins [1−4]. As a result of the ring-opening polymerization [5−7], polybenzoxazine overcomes many shortcomings associated with traditional phenolic resins such as releasing condensation by-products and using strong acids as catalysts, while retaining good thermal properties and flame retardancy of phenolic resins [8−12]. Also like epoxides and polyimide, polybenzoxazine has excellent mechanical properties and molecular design flexibility. Polybenzoxaines undergo near-zero volumetric changes or expansion upon curing processing of benzoxaine resins [13]. To further improve the thermal stability of polybenzoxazine, a cyano group was introduced into the benzoxazine monomer. The cyano groups can polymerize and improve the nitrogen content of polybenzoxazine [2,14−17], which improves the flame retardancy of the polymers.

Recently, Chaisuwan and Ishida [17] synthesized two types of functional benzoxazine with nitrile functionalities to improve thermal properties. This functional polybenzoxazine has good processibility and thermal stability for applications to advanced composites. In our previous work, we have synthesized the bisphthalonitrile−benzoxazine monomer and its polymer. This polymer has also good processibility, thermal and thermo-oxidative stability, flame retardancy and mechanical properties [18].

In this paper, we report a novel benzoxazine monomer with cyano functionality which was synthesized via 2,6-bis(4-diaminobenzoxy)benzonitrile, phenol and formaldehyde in solution. The structure and thermal properties of the monomer, oligomer and polymer were studied. The main purpose of the research is to develop high thermo-oxidative benzoxazine

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doi:10.1016/j.polymdegradstab.2007.10.002

monomers and resins that lead to high performance polymers and composites.

2. Experimental

2.1. Materials

Phenol, *N*-methyl-2-pyrrolidone (>99%), potassium carbonate (99%) were obtained from TianJin BODI chemicals. 4-Aminophenol (CP) was obtained from Sinopharm Chemical Reagent Co. Ltd. 2,6-Dichlorobenzonitrile was purchased from Yangzhou Tianchen chemicals Co. Ltd of Jiangsu. Acetone (AR, 99%), toluene (AR) and formaldehyde solution (AR, 37%) were obtained from Chongqing Fine Chemical Research Institute. All the solvents used were certified as A.C.S grade and were used without further purification.

2.2. Measurements

The FTIR spectra of monomer and resins were recorded on Shimadzu FTIR8400S Fourier Transform Infrared spectrometer in KBr pellets at 4000–400 cm^{-1} in air (20% oxygen) environments. ^1H NMR and ^{13}C NMR spectra were obtained using a Bruker AV400 nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 400 MHz and the corresponding carbon frequency using $CDCl_3$ as solvent. The thermal curing behavior of monomer was measured by TA Instruments Modulated DSC-Q100 with a heating rate of 20 °C/min and a nitrogen flow rate of 50 ml/min. The thermal decomposition of polymer was determined by TA instruments Q50 thermogravimetric analyzer with a heating rate of 20 °C/min under nitrogen or air (20% oxygen) environments. The rheological behavior of curing process was performed by TA Instruments Rheometer AR-G2 with a heating rate of 10 °C/min and at 10 Hz in air (20% oxygen) environments.

2.3. Synthesis

2.3.1. Synthesis of 2,6-bis(4-diaminobenzoxy)benzonitrile

4-Aminophenol, 2,6-dichlorobenzonitrile and potassium carbonate with a mole ratio of 2:1:1.05 and a certain amount of the solution of *N*-methyl-2-pyrrolidone and toluene were taken in a 500 ml three neck round bottom flask equipped with a mechanical stirrer and refluxing condenser. The reaction mixture was refluxed at 140–160 °C for 4–5 h. Then the crude product was washed with dilute NaOH (1 mol/l) solution and de-ionized water. The precipitate was collected and dried at 80 °C under a vacuum chamber for 12 h. The purified product is a lilac power (yield 86%, Fig. 1) and the melting point is 185 °C. Typical IR data: 3466 cm^{-1} ($-NH_2$), 2231 cm^{-1} (−CN), 1253 cm^{-1} (stretch, C−O−C), 830 cm^{-1} (1,4-substitution of benzene ring).

2.3.2. Synthesis of the benzoxazine containing cyano groups (BZCN)

In a 500 ml three neck round bottom flask equipped with a mechanical stirrer and refluxing condenser, 2,6-bis(4-diaminobenzoxy)benzonitrile, phenol and formaldehyde with a mole ratio 1:2:4 were taken and then toluene was added. The reaction mixture was refluxed at 90 °C for 2 h and at 110 °C for 3 h. Then the product was dissolved in acetone and washed with 1 N NaOH solution and de-ionized water. The precipitate was collected and dried at 80 °C in vacuum. The purified product benzoxazine containing cyano groups (BZCN) was obtained, shown in Fig. 1. The obtained product was a carmine powder with melting point 120 °C, the typical IR characteristic data: 2231 cm^{-1} (−CN), 930 cm^{-1} [15,19] (tri-substituted benzene ring attached with oxazine ring), 1222, 1027 cm^{-1} (stretch, C−O−C) [15,19], 1164, 836 cm^{-1} (stretch C−N−C) [15], 1447 cm^{-1} (CH_2 antisymmetric stretch) [19]; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.648 ($N-CH_2-Ar$), 5.356 ($N-CH_2-O$). ^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm): 50.80 ($Ar-CH_2-N$), 79.55 ($N-CH_2-O$), 115.46 ($Ar-C{\equiv}N$).

2.3.3. Preparation of prepolymer and polymer

The prepolymer and polymer were prepared by thermally activated polymerization of monomer in air-circulation oven. The polymerization procedures of the prepolymer and polymer are described in Table 1.

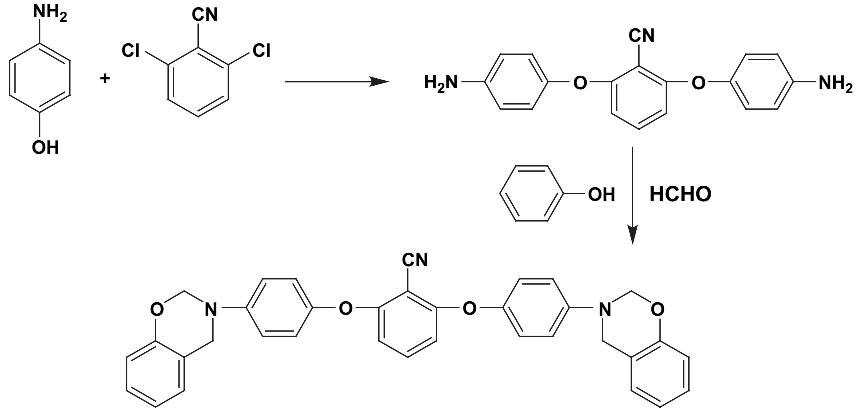

Fig. 1. The synthesis of 2,6-bis(4-diaminobenzoxy)benzonitrile and benzoxazine containing cyano groups (BZCN).

Table 1
The curing schedule of the prepolymer and polymer

Samples	Time and temperature
a	120 °C and 5 h
b	120 °C and 5 h; 160 °C and 3 h
c	120 °C and 5 h; 160 °C and 3 h; 220 °C and 3 h
d	120 °C and 5 h; 160 °C and 3 h; 220 °C and 3 h; 240 °C and 3 h
e	120 °C and 5 h; 160 °C and 3 h; 220 °C and 3 h; 240 °C and 3 h; 260 °C and 2 h
f	120 °C and 5 h; 160 °C and 3 h; 220 °C and 3 h; 240 °C and 3 h; 260 °C and 6 h

3. Results and discussion

3.1. Characterization of the structure of BZCN

The structure of BZCN as shown in Fig. 1 is verified by ^{1}H NMR and ^{13}C NMR spectroscopies and the corresponding spectra are shown in Figs. 2 and 3. In ^{1}H NMR, resonances appearing at 4.648 and 5.356 ppm are assigned to the methylene protons in the oxazine ring of BZCN [15]. The prominent resonance at 6.385–7.333 ppm in the aromatic frequency corresponds to the hydrogen in the benzene ring. Furthermore, the structure of BZCN is confirmed by using ^{13}C NMR and the corresponding chemical shifts are shown in Fig. 3. Along with the well agreement between the calculated by ChemDraw Ultra 8.0 and observed data of the experimental analysis for the purified sample.

The resonance appearing at 4.988 ppm is assigned to the methylene protons in the Mannich Bridge of the dimer. The ratio of the integral area of the methylene protons in the oxazine ring and in the Mannich Bridge of dimer is 10.54. Thus, the ratio of the ring-forming structure was calculated to be as high as 91.3%. It shows that the targeted compound obtained is quite pure [13], which contributed to the further ring-opening polymerization for obtaining polybenzoxazine.

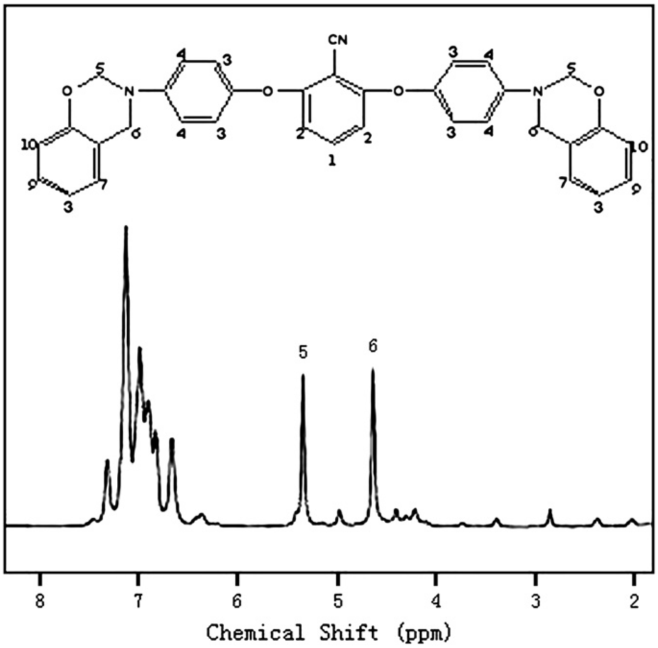

Fig. 2. ^{1}H NMR spectra of BZCN in $CDCl_3$.

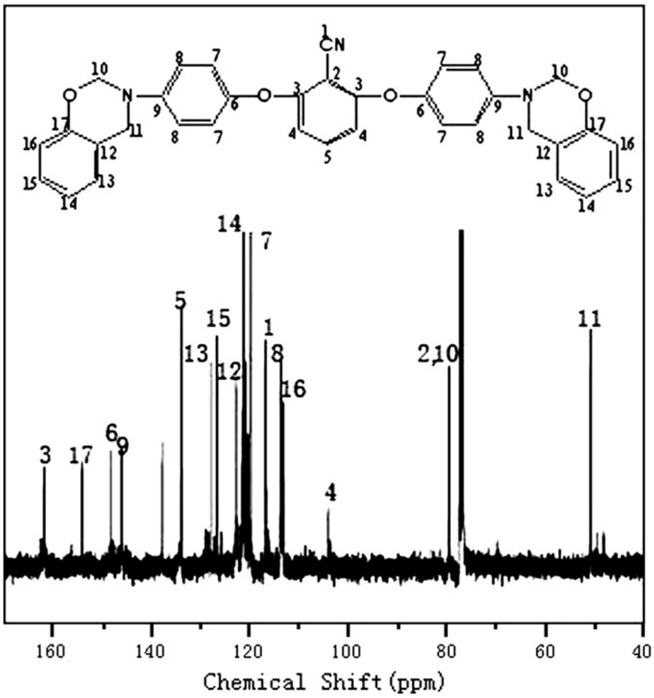

Fig. 3. ^{13}C NMR spectra of BZCN.

The appearance of –CN at 2231 cm^{-1} and tri-substituted benzene ring attached with oxazine ring at 930 cm^{-1} can be observed. The characteristic band of antisymmetric C–O–C stretch appears at 1227 cm^{-1} for the compound studied, while the band at 1028 cm^{-1} is assigned to the symmetric stretch. These results show that a novel benzoxazine containing cyano groups can be synthesized by this technique [9].

Figs. 4 and 5 show the FTIR spectra of prepolymer and polymer obtained by the polymerization procedure described

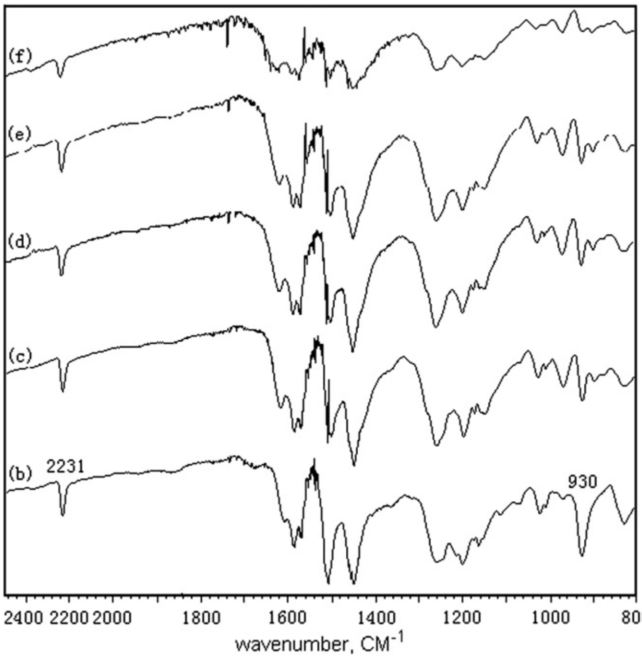

Fig. 4. FTIR spectra of the monomer and prepolymers, from 2500–800 cm^{-1}.

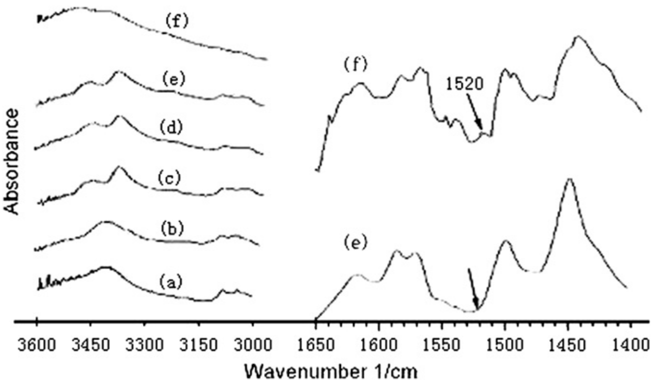

Fig. 5. FTIR spectra of the monomer and prepolymers, from 3600–3000 cm^{-1} and 1650–1400 cm^{-1}.

in the previous section. The peaks at 930, 2231 and 1520 cm^{-1} show changes in intensity as a function of cured temperature. There is no change of the characteristic peaks after polymerized at 120 °C for 5 h in oven (Figs. 4 and 5b). The intensity of the peak at 930 cm^{-1} attributed to tri-substituted benzene ring that is attached with oxazine ring decreases, and the intensity of the peak of −OH at 3370 cm^{-1} enhances with the increase of temperature and time. These apparent changes are observed at 160 °C for 3 h, shown in Figs. 4 and 5c, which contribute to the indication of oxazine ring-opening. The absorption intensity of the peak at 3370 cm^{-1} enhances gradually and the absorption intensity of the peak at 930 cm^{-1} decreases along with the increase of temperature and time, suggesting the increase of the extent of the ring-opening of the monomers (Figs. 4 and 5c–f). The absorption intensity of the peak at 2231 cm^{-1} decreases obviously (Fig. 5e,f) and a new characteristic peak at 1520 cm^{-1} was observed (Fig. 5e,f), indicating the formation of triazine ring [20]. These thermally activated reaction characteristics show that polymerization could have happened. As per these results, the curing polymerization reaction of BZCN follows multiple polymerization mechanisms via the ring-opening of oxazine rings and the triazine ring-formation of cyano groups, shown in Fig. 6.

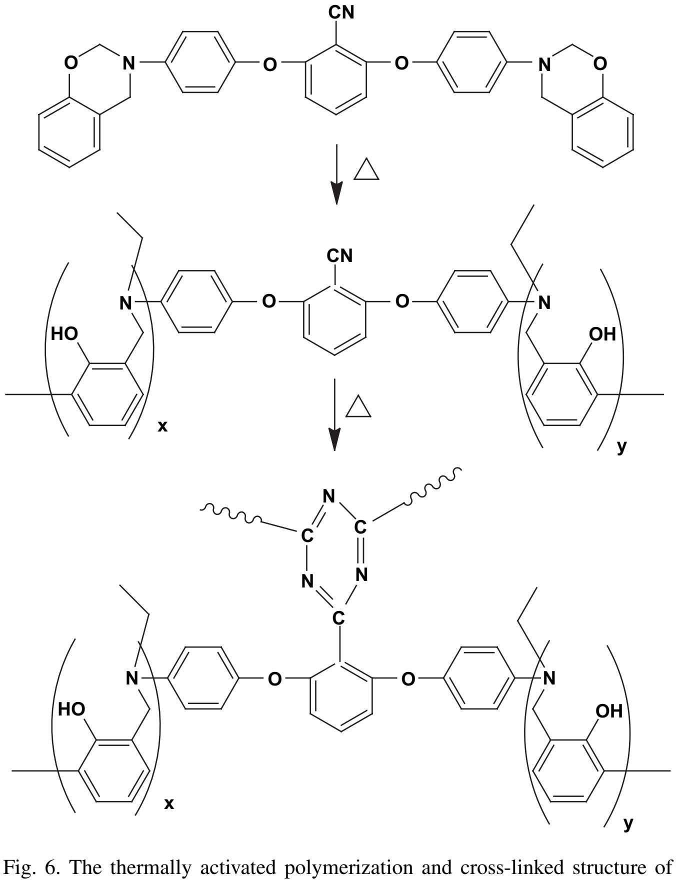

Fig. 6. The thermally activated polymerization and cross-linked structure of BZCN.

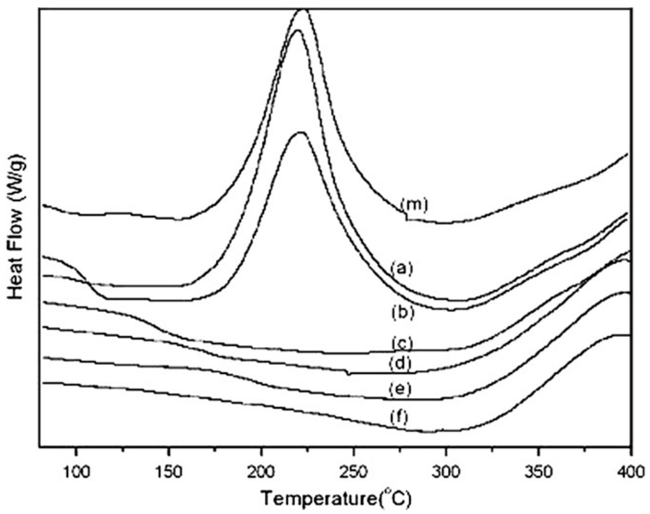

Fig. 7. DSC spectra of BZCN and prepolymers.

3.2. DSC and TGA analyses

The thermally activated polymerization reactions of BZCN were studied by DSC and the thermal decompositions of the prepolymer and polymer were examined by TGA, as shown in Figs. 7–9. The main results of DSC and TGA

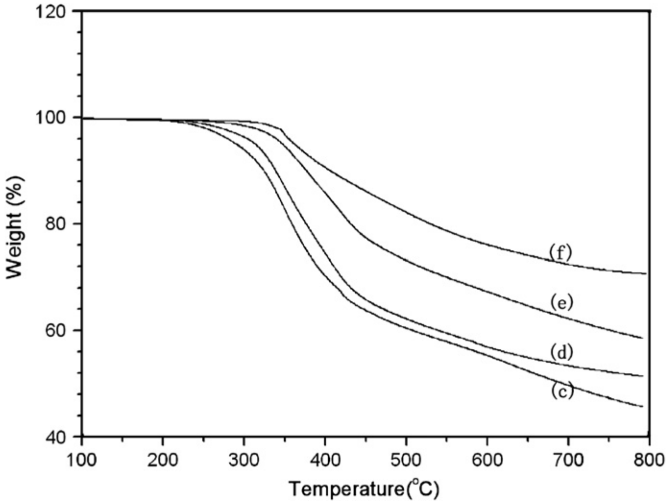

Fig. 8. TGA curves of prepolymers.

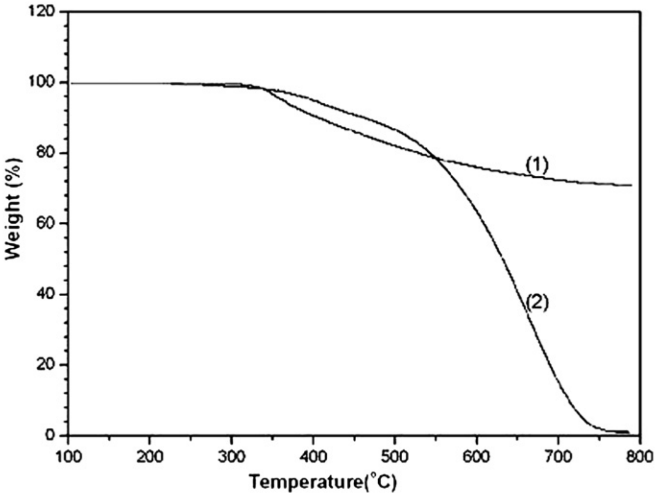

Fig. 9. TGA curves of polymer (1) in nitrogen; (2) in air.

determinations are summarized in Table 2. BZCN shows polymerization exotherms (T_{top}) at 220 °C. The peak width from 139 °C to 296 °C, is attributed to the wide processing temperature window (T_{window}). From the DSC results of Fig. 7b and c, we can find that the exotherm peak has an obvious decrease, even disappears with the increase of pre-cured temperature and time, the heating flow of complete polymerization gradually reaches zero, while the heating flow of monomer is 182.83 J/g. This is in accord with the change of the peak absorption at 3370 cm^{-1}. The T_gs of the prepolymer and polymer increase with the extent of polymerization, as shown in Fig. 7 and Table 2. The T_g of the prepolymer polymerized at 220 °C for 3 h has an improvement of 30% over that of the prepolymer polymerized at 160 °C for 3 h. And the T_g of the polymer polymerized at 260 °C for 6 h has a significant improvement of 29.5% over that of the prepolymer polymerized at 260 °C for 2 h. As per these results, the higher T_g is mainly attributed to the formation of the triazine ring and the increase of the cured extent of the polymer, while the curing of benzoxazine resin at 260 °C leads to structure rearrangement for the formation of thermally stable network structures. Therefore, we can control the cured extent using glass transition temperature by curing temperature or time. The T_g of the wholly cured polymer at 260 °C for 6 h up to 250 °C. These results correspond very well to FTIR data and the schematic structures of Fig. 6.

Table 2
The thermal properties of monomer and resins

Sample	ΔH_{curing} (J/g)	T_g (°C)	T_{top} (°C)	T_{window} (°C)	T_i (°C)	$T_{5\%}$ (°C)	Char yield (%)
Monomer	182.83	–	220	139–296	–	–	–
a	167.4	96	219	152–300	272	288	42
b	126.8	106	220	160–302	275	298	43
c	0.3581	140	276	255–271	288	290	46
d	–	170	–	–	307	312	51
e	–	193	–	–	332	347	59
f	–	250	–	–	341	364	70.7

–: No result.

TGA curves of the polymer are shown in Figs. 8 and 9, and the typical results are listed in Table 2. According to these results, the thermal properties of the prepolymer and polymer depend on curing temperature and time. The polymer exhibits thermal stability up to 364 °C, the initial decomposition temperature (T_i) is 341 °C, the temperature at weight loss of 10% is up to 407 °C in nitrogen atmosphere, and the char yield at 800 °C is 70.7% under nitrogen. Also the polymer has a good thermo-oxidative stability with the initial decomposition temperature (T_i) up to 321 °C and the char yield at 600 °C up to 64.4% in air (20% oxygen) environments.

3.3. The rheological behavior

Fig. 10 shows the relationship between rheological behaviors and temperature under curing process of thermally activated polymerization. It shows that BZCN has lower viscosity and wide processing temperature window under 200 °C. The storage modulus (G') increases quickly from 202 °C to 210 °C, it is observed that the monomer has been transferred from viscosity flow state to solid state and at the same time G'' also increased. Based on TA instrument rheological software, the cross-point of G' and G'' is observed at 210 °C, which means that the resin underwent gelation transition. The delta curve exhibits one sharp peak at 202 °C. As per these results, it means that the benzoxazine monomer containing cyano groups could be polymerized via oxazine ring-opening polymerization mechanisms which are consistent with the DSC results. This rheological character of BZCN exhibits good processibility and thermally activated polymerization. This rheological behavior is very useful to the process and application.

4. Conclusion

The thermosetting resin based on cyano functionalized benzoxazine (BZCN) has been successfully synthesized from

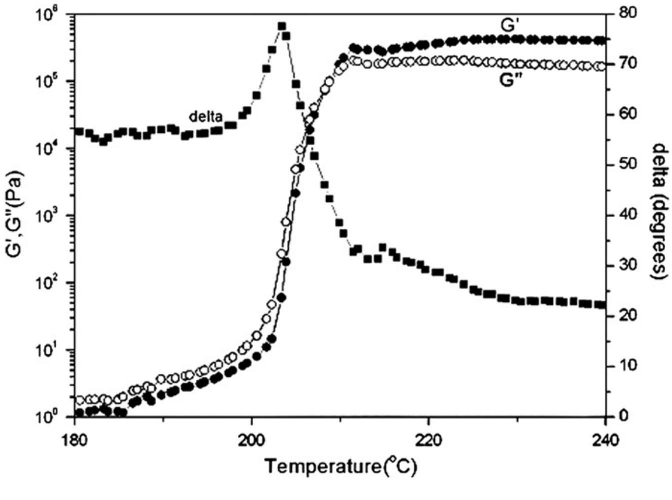

Fig. 10. The rheological behaviors of the benzoxazine monomer under thermal polymerization.

2,6-bis(4-diaminobenzoxy)benzonitrile, phenol and formaldehyde by solution reaction. The structure of the monomer was supported by FTIR, ^{1}H NMR, and ^{13}C NMR spectra, which have shown that reactive benzoxazine rings and cyano groups exist in the molecular structure of BZCN. The thermally activated polymerization of BZCN and thermal properties of polymers are monitored by FTIR, DSC and thermogravimetric analyzer (TGA) at different temperatures and times. The incorporation of the cyano functionality into benzoxazine results in increase of glass transition temperature and char yields. The T_g of the complete cured polymer is about 250 °C. The char yield is up to 70.7% at 800 °C in nitrogen and up to 64.4% at 600 °C in air (20% oxygen) environments. These performances are the basement of the future processes and application for development of heat-resistant and high performance composites.

Acknowledgement

This project was sponsored by ''Excellent Talents Program'' of University of Electronic Science and Technology of China.

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