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ORIGINAL PAPER

Studies on the isomeric effect of nitrile functionality on the polymerization and thermal properties of *ortho*-norbornene-based benzoxazine resins

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Abstract
Three norbornene-functional mono-benzoxazines with attached nitrile group at the *para*-, *meta*-, and *ortho*-position with respect to the nitrogen atom in the oxazine ring, respectively, have been synthesized to investigate the isomeric effect of nitrile group on the polymerization and thermal properties of resulting polybenzoxazines. The chemical structures of newly obtained benzoxazine monomers are investigated by ^{1}H and ^{13}C NMR spectroscopy and FT-IR spectroscopy. Besides, the polymerization behaviors including oxazine ring, nitrile group as well as norbornene functionality in each benzoxazine are studied by differential scanning calorimetry (DSC) and in situ FT-IR. In addition, the thermal properties of corresponding polybenzoxazines are investigated by TGA. The nitrile group at *ortho*-position in benzoxazine has been found to be easier activated to polymerize compared with other two isomers. Moreover, the resulting polybenzoxazine derived from *ortho*-nitrile containing benzoxazine also shows the best thermal stability with a T_{d5} of 371 °C, and a char yield of 56%.

Keywords Benzoxazine · Norbornene · Nitrile · Isomeric effect

Introduction

Benzoxazine is a type of newly developed high performance thermosetting resin, which can be synthesized from various phenols, amines, and formaldehyde via Mannich reaction [1–6]. Its polymeric product, polybenzoxazine, is generally obtained through the polymerization of benzoxazine by heating with/without catalysts/initiations. Polybenzoxazine has a lot of outstanding properties, such as high glass transition temperature [7], low dielectric constant [8, 9], good thermal stability and excellent mechanical performance [10–15]. The above attractive performance makes it good potential candidate for applications in aerospace [16], automotive [17], electronic industries [18] and other high performance areas. In addition, the rich molecular design flexibility of benzoxazine results in a variety of new benzoxazine structures with different functionalities, such as alkynyl [19, 20], nitrile [21], maleimide [21–23] and norbornene [15, 24–26]. The incorporation of above groups also allows synthesizing different benzoxazines to tailor the desired properties.

In recent years, researchers have developed several benzoxazine resins with norbornene functionality [14, 15, 24–26]. The additional cross-linked networks generated from the cross-linking reaction via the carbon-carbon double bond in the end-cap of norbornene leads the high performance of norbornene-based benzoxazines [27–29]. Zhang and coworker [15] prepared a type of benzoxazine monomer containing both norbornene and acetylene functionalities, which showed extremely low temperature terpolymerization behaviors including the polymerization procedures of the oxazine ring, acetylene and norbornene functionalities. In addition, benzoxzines with nitrile group have received a lot of attentions due to their excellent flame retardancy and outstanding thermal stability [30, 31]. Unfortunately, it has been well-known that the nitrile group is hard to be polymerized completely even after long-duration thermal treatments at elevated temperature (as high as ~350 °C) [32–35]. Some fundamental studies have been carried out to examine the effects on the polymerization and properties of nitrile-containing thermosetting resins [30, 36, 37]. Besides, there are also a lot of researchers concentrating on the isomeric effect of benzoxazines [38–40].

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Inspired by all of the above findings, we report a study on the isomeric effect of nitrile on the polymerization and properties of norbornene functional benzoxazines. In the current study, a series of *ortho*-norbornene-functional benzoxazine monomers containing nitrile group at the *para*-, *meta*-, *ortho*-position with respect to the nitrogen atom in the oxazine ring, respectively, have been successfully synthesized and the thermal properties have been investigated. As a result, the nitrile group in the *ortho*-benzoxazine isomer shows the least unpolymerized residual after our designed polymerization procedures. Additionally, the resulting polybenzoxazine derived from *ortho*-nitrile containing benzoxazine also shows the highest thermal stability. Therefore, changing position of nitrile to "*ortho*" in aminobenzonitrile is an effective strategy to lower the polymerization temperature of nitrile-containing benzoxazines and improve the thermal stability of the resulting polybenzoxazines.

Experimental

Materials

Endo-5-norbornene-2,3-dicarboxylic anhydride, o-aminophenol (99%) and paraformaldehyde (99%) were purchased from Sinopharm Chemical reagent Co. Ltd. Sigma-Aldrich. 2-Aminobenzonitrile, 3-aminobenzonitrile and 4-aminobenzonitrile (98%) were purchased from Rhawn. Sodium hydroxide (NaOH), acetic acid and xylenes was purchased from Shanghai First Chemical Co., Shanghai, China. (3aS,4R,7S,7aS)-2-(2-Hydroxyphenyl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene-1,3(2H)-dione (*o*HPNI) was synthesized following the reported methods [14].

Instrumentation

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained from a Bruker AVANCE II 400 NMR spectrometer using $CDCl_3$ as solvent. The average number of transients for ^{1}H NMR testing was 64, while that for ^{13}C NMR testing was 1024.

Elemental analyses of newly synthesized benzoxazine monomers were conducted on an Elementar Vario EL-III analyzer.

Fourier transform infrared (FT-IR) spectra were performed at room temperature at the range of 4000–500 cm^{-1} using the Nicolet AVATAR360 FT-IR spectrometer.

In situ Fourier transform infrared (in situ FT-IR) spectra were performed at 140, 160, 180, 200, 220, 240, 260, 280 and 300 °C at the range of 4000–500 cm^{-1} using the Nicolet AVATAR360 FT-IR spectrometer.

Differential scanning calorimetry (DSC) was conducted by using NETZSCH DSC model 204f1. For each sample, a heating rate of 10 °C/min with a nitrogen flow rate set as 60 mL/min was applied during the DSC measurement.

Thermogravimetric analyses (TGA) were carried out on a NETZSCH STA449-C Thermogravimetric Analyzer with a 40 mL/min flow rate in a N_2 atmosphere, and a heating rate of 10 °C/min from room temperature (RT) to 800 °C was performed during the TGA testing.

Synthesis of *o*HPNI-*o*an

In a 250 mL round-flask were added 2-aminobenzonitrile (1.18 g, 0.01 mol), *o*HPNI (2.55 g, 0.01 mol), paraformaldehyde (0.61 g, 0.02 mol), and 50 mL of xylenes. The reaction mixtures were stirred under reflux condition for as long as 18 h. After the reaction was completed, the chemical mixture was cooled to room temperature and washed with 30% aqueous NaOH solution for three times followed by twice with water. Finally, light pink crystals were obtained by removing the solvent through evaporation (yield ca. 85%). ^{1}H NMR (400 MHz, $CDCl_3$), ppm: δ = 1.64 (dt, 1H), 1.79 (dt, 1H), 3.44 (dd, 2H), 3.49 (m, 2H), 4.58 (d, 2H, Ar-CH_2-N), 5.28 (d, 2H, O-CH_2-N-), 6.25 (m, 2H), 6.79–7.25 (Ar, 7H). IR spectra (KBr), cm^{-1}: 2219 (C ≡ N, stretching), 1771, 1709 (imide I), 1386 (imide II), 1239 (C-O-C stretching), 941 (oxazine ring corresponding mode), 700 (C-H out-of-plane). Anal. Calcd for $C_{24}H_{19}N_3O_3$: C, 72.53; H, 4.82; N, 10.57. Found: C, 72.60%; H, 4.78%; N, 10.62%.

Synthesis of *o*HPNI-*m*an

The *o*HPNI-*m*an was synthesized using the same procedure as *o*HPNI-*o*an, and orange crystals were obtained (yield ca. 90%). ^{1}H NMR (400 MHz, $CDCl_3$), ppm: δ = 1.63 (dt, 1H), 1.81 (dt, 1H), 3.45 (dd, 2H), 3.51 (m, 2H), 4.66 (d, 2H, Ar-CH_2-N), 5.32 (d, 2H, O-CH_2-N-), 6.27 (t, 2H), 6.81–7.41 (Ar, 7H). IR spectra (KBr), cm^{-1}: 2229 (C ≡ N, stretching), 1770, 1713 (imide I), 1371 (imide II), 1239 (C-O-C stretching), 940 (oxazine ring corresponding mode), 693 (C-H out-of-plane). Anal. Calcd for $C_{24}H_{19}N_3O_3$: C, 72.53; H, 4.82; N, 10.57. Found: C, 72.41%; H, 4.76%; N, 10.61%.

Synthesis of *o*HPNI-*p*an

The *o*HPNI-*p*an was also synthesized according to the above mentioned method as *o*HPNI-*o*an, and yellow crystals were obtained (yield ca. 86%). ^{1}H NMR (400 MHz, $CDCl_3$), ppm: δ = 1.65 (dt, 1H), 1.80 (dt, 1H), 3.45 (dd, 2H), 3.50 (m, 2H), 4.70 (d, 2H, Ar-CH_2-N), 5.35 (d, 2H, O-CH_2-N-), 6.28 (t, 2H), 6.64–7.57 (Ar, 7H). IR spectra (KBr), cm^{-1}: 2217 (C ≡ N, stretching), 1774, 1713 (imide I), 1383 (imide II), 1240 (C-O-C stretching), 946 (oxazine ring corresponding mode), 700 (C-H out-of-plane). Anal. Calcd for $C_{24}H_{19}N_3O_3$: C, 72.53; H, 4.82; N, 10.57. Found: C, 72.62%; H, 4.88%; N, 10.53%.

Thermally activated polymerization of benzoxazine resins

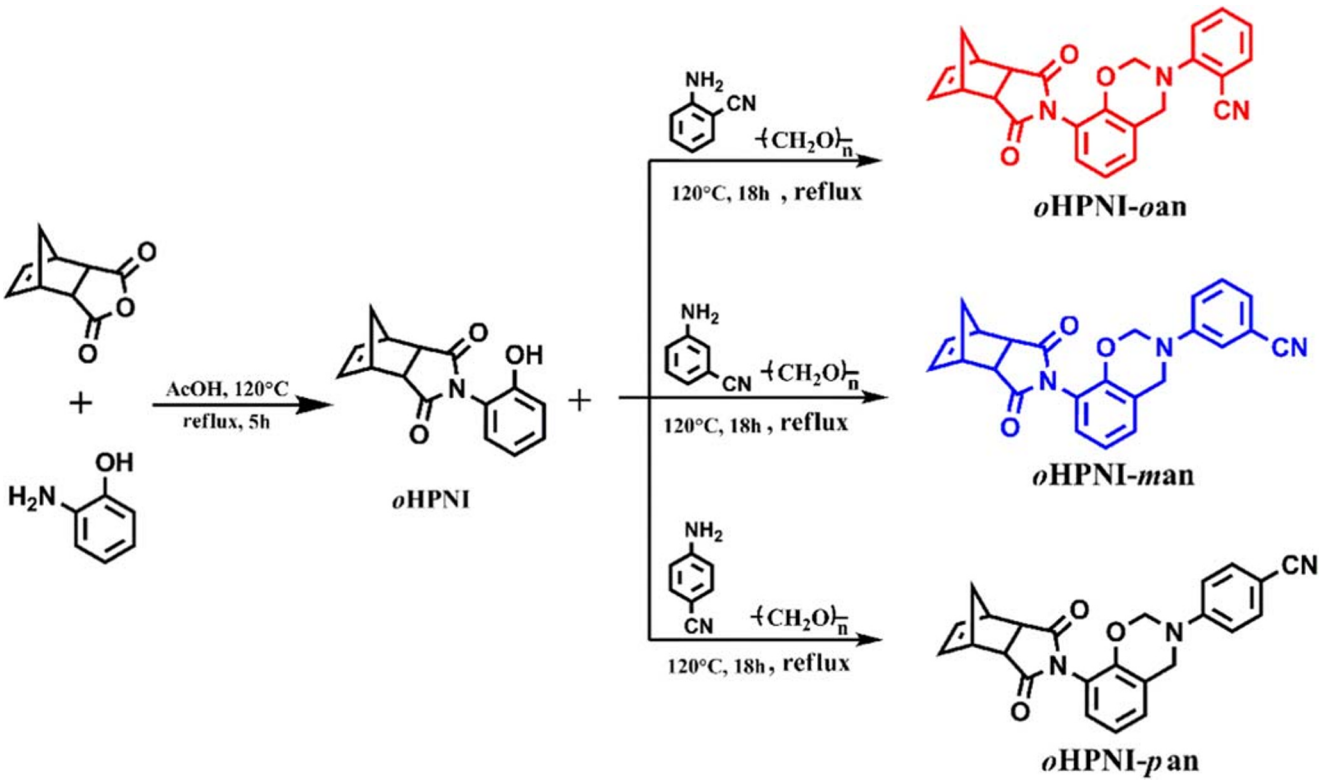
Polymerization of *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an to obtain poly (*o*HPNI-*o*an), poly(*o*HPNI-*m*an) and poly(*o*HPNI-*p*an), respectively, was carried out using a stepwise method. Each benzoxazine monomer was polymerized at various temperatures in the air-circulation oven. The temperature profile was as follows: 180 °C/1 h, 200 °C/1 h, 220 °C/1 h, 240 °C/1 h, 260 °C/1 h and 280 °C/1 h.

Results and discussion

Synthesis of benzoxazine monomers

A series of *ortho*-norbornene-functional benzoxazine isomers with attached nitrile group at the *para*-, *meta*-, *ortho*-position with respect to the nitrogen atom in the oxazine ring, respectively, have been successfully synthesized starting from the raw materials of *o*HPNI, aminobenzonitrile, and paraformaldehyde as shown in Scheme 1. Prior to this study, the approaches to obtain benzoxazines containing only norbornene [14, 21, 24–26] or nitrile [31] have already been investigated. However, no report has studied the benzoxazines with norbornene and nitrile groups in the same benzoxazine molecule. Herein, benzoxazine structures with *ortho*−/*meta*−/*para*-nitrile functionality have been achieved to investigate the effect of positional isomerism of nitrile group on the polymerization of benzoxazines and thermal properties of the resulting polybenzoxazines.

The structures of benzoxazine monomers were confirmed by ^{1}H and ^{13}C NMR and FT-IR spectroscopy. The positions of the characteristic protons and carbons are indicated using different letters as shown in Fig. 1(a). As can be seen in Fig. 1(b), the typical resonances of oxazine ring, Ar-CH_2-N- and -O-CH_2-N- for *o*HPNI-*o*an are observed at around 4.58 and 5.28 ppm, respectively, and those for *o*HPNI-*m*an and *o*HPNI-*p*an are located at around 4.66 and 5.32 ppm, and 4.70 and 5.35 ppm, respectively [29]. It should be noticed that the oxazing characteristic signals seem to be doublet rather than singlet, which is due to the atropisomerization formed in *ortho*-imide functional benzoxazines [41]. Besides, the protons related to the unsaturated double bond of norbornene appear at 6.28 ppm for all of these benzoxazines. Additionally, the existence of oxazine ring can also be confirmed by ^{13}C NMR spectra in Fig. 1(c). The typical resonances of Ar-*C*H_2-N- and -O-*C*H_2-N for *ortho*-nitrile based benzoxazines present at 52.35 and 80.34 ppm, and both typical resonances for *meta*- and *para*-nitrile based ones are located at 52.35 and 78.76 ppm, and 52.35 and 77.68 ppm [29]. Moreover, the typical signals for the carbons in –C ≡ N group for *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an appear at 107.05, 113.26 and 103.48 ppm, respectively [31].



Scheme 1 Synthesis of *ortho*-norbornene-based benzoxazines containing nitrile group through a two-step strategy

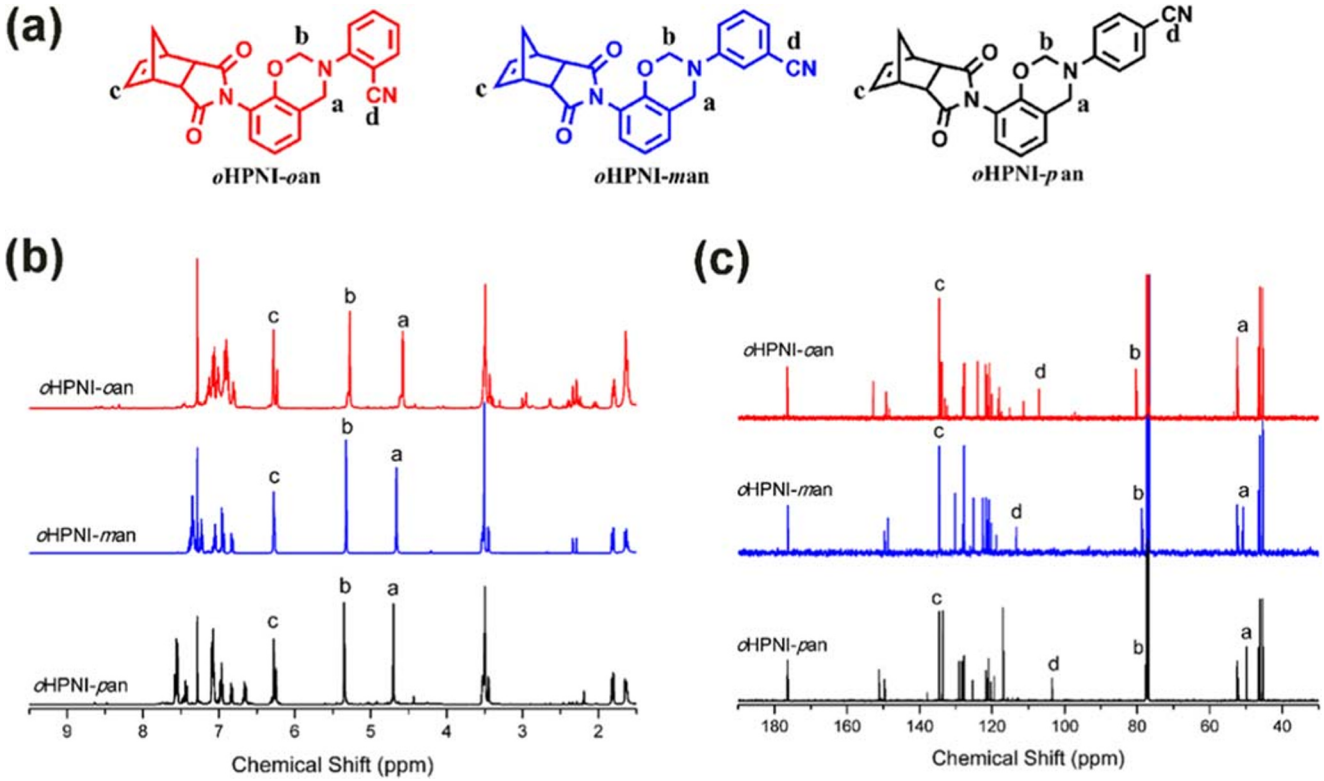


Fig. 1 (**a**) ^{1}H and ^{13}C assignments for benzoxazine monomers. (**b**) ^{1}H NMR spectra of *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an. (**c**) ^{13}C NMR spectra of *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an

Furthermore, the characteristic carbon resonances of carbon-carbon double bond in norbornene for *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an can be observed at 134.62, 134.65 and 134.63 ppm, respectively [15].

FT-IR analysis was further adopted to confirm the structures of newly obtained benzoxazines. As can be seen in Fig. 2, the bands at 941 and 1239 cm^{-1} in *o*HPNI-*o*an can be observed, which are assigned to be the oxazine ring related mode and C-O-C asymmetric stretching mode, respectively.

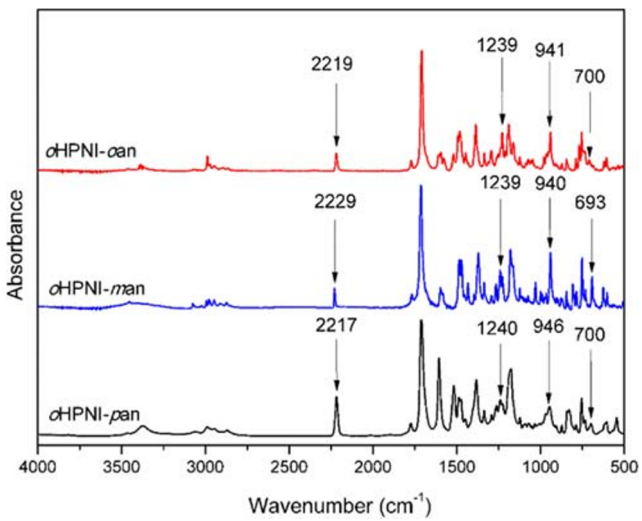


Fig. 2 FT-IR spectra of benzoxazine monomers

Those characteristic bands for *o*HPNI-*m*an and *o*HPNI-*p*an are located at 940 and 1239 cm^{-1}, and 946 and 1240 cm^{-1}, respectively [42, 43]. Besides, the norbornene corresponding bands are centered at 700, 693 and 700 cm^{-1} for *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an, respectively [44]. Moreover, the typical band of nitrile group appears at 2219 cm^{-1} for *o*HPNI-*o*an, and *o*HPNI-*m*an and *o*HPNI-*p*an shows the characteristic bands at 2229 cm^{-1} and 2217 cm^{-1}, respectively [45]. The above results from NMR and FT-IR analyses are effective evidence to ensure the successful preparation of the target benzoxazine monomers.

Polymerization behaviors of *ortho*-norbornene functional benzoxazine monomers containing nitrile group

The polymerization behaviors of benzoxazines containing both norbornene and nitrile groups were investigated by DSC and in situ FT-IR. As shown in Fig. 3, the endothermic peaks for *o*HPNI-*o*an and *o*HPNI-*m*an can be observed at 212 and 224 °C, which is corresponding to the melting transition of resins. Besides, the existence of the melting peaks for both monomers also indicates the existence of crystal form in their final products. However, no melting peak can be observed for *o*HPNI-*p*an. It is possible that the melting behavior of *o*HPNI-*p*an was completely overlapped by its exothermic peak, thus

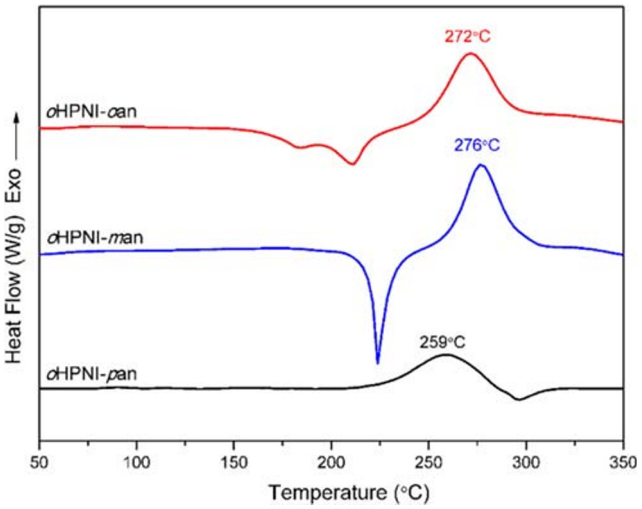


Fig. 3 DSC thermograms of benzoxazine monomers

only a broad exothermic peak with a lower peak temperature (259 °C) can be observed. In addition, *o*HPNI-*p*an exhibits an endothermic peak at around 290 °C. This usual endotherm is caused by the initial degradation stage as indicated by the followed TGA results. Moreover, it should be mentioned that three polymerization procedures could be involved in the exothermic peaks, including ring-opening polymerization of oxazine ring, norbornene and nitrile groups. Although the previous studies have indicated the electron-withdrawing characteristic of the nitrile group leads to an increased polymerization temperature of oxazine ring [46], the polymerization mechanisms for benzoxazine-norbornene-nitrile system has never been investigated.

Hence in situ FT-IR analysis was further carried out to explore the structural changing of these benzoxazine isomers during thermally activated polymerization. As shown in Fig. 4, it can be observed that the bands at around 940 cm^{-1} and 1240 cm^{-1} related to the oxazine ring modes and C-O-C asymmetric stretching modes for these benzoxazines decrease starting from 240 °C and completely disappear at 260 °C [43]. Besides, the typical bonds of nitrile at about 2220 cm^{-1} also gradually decrease with increasing the temperature, which indicates the polymerization of nitrile group can also take place along with the ring-opening polymerization process of oxazine rings. Notably, the decreasing of nitrile-related bonds are found to be with different quantities, which are 59%, 47% and 51% *o*HPNI-*o*an, *o*HPNI-*m*an and *o*HPNI-*p*an, respectively. The corresponding conversion of each benzoxazine can be detected through the intensity variation of nitrile with respect to the internal reference, such as the unchanged bonds relating to imide functionality. In addition, norbornene characteristic bands of these three benzoxazines also disappear progressively, and completely disappear after the final thermal treatment at 280 °C. On the basis of our previous report about the polymerization between norbornene and nitrile group, we

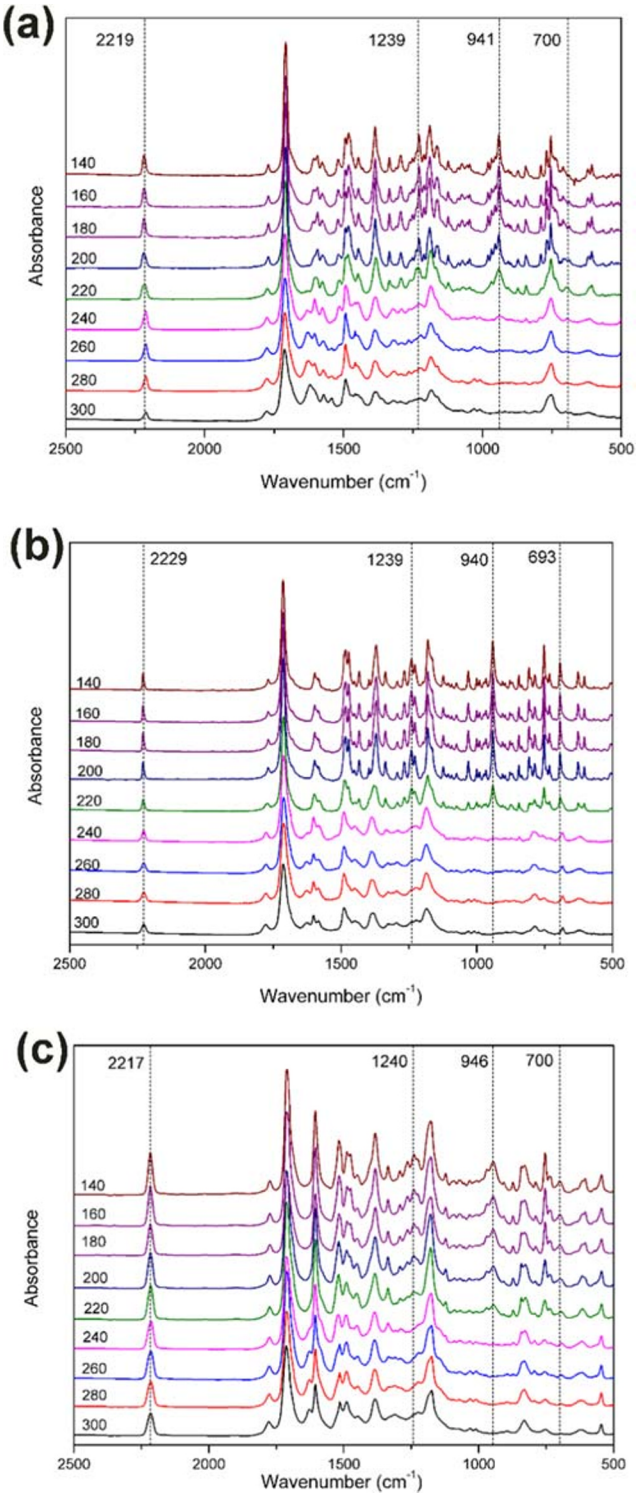
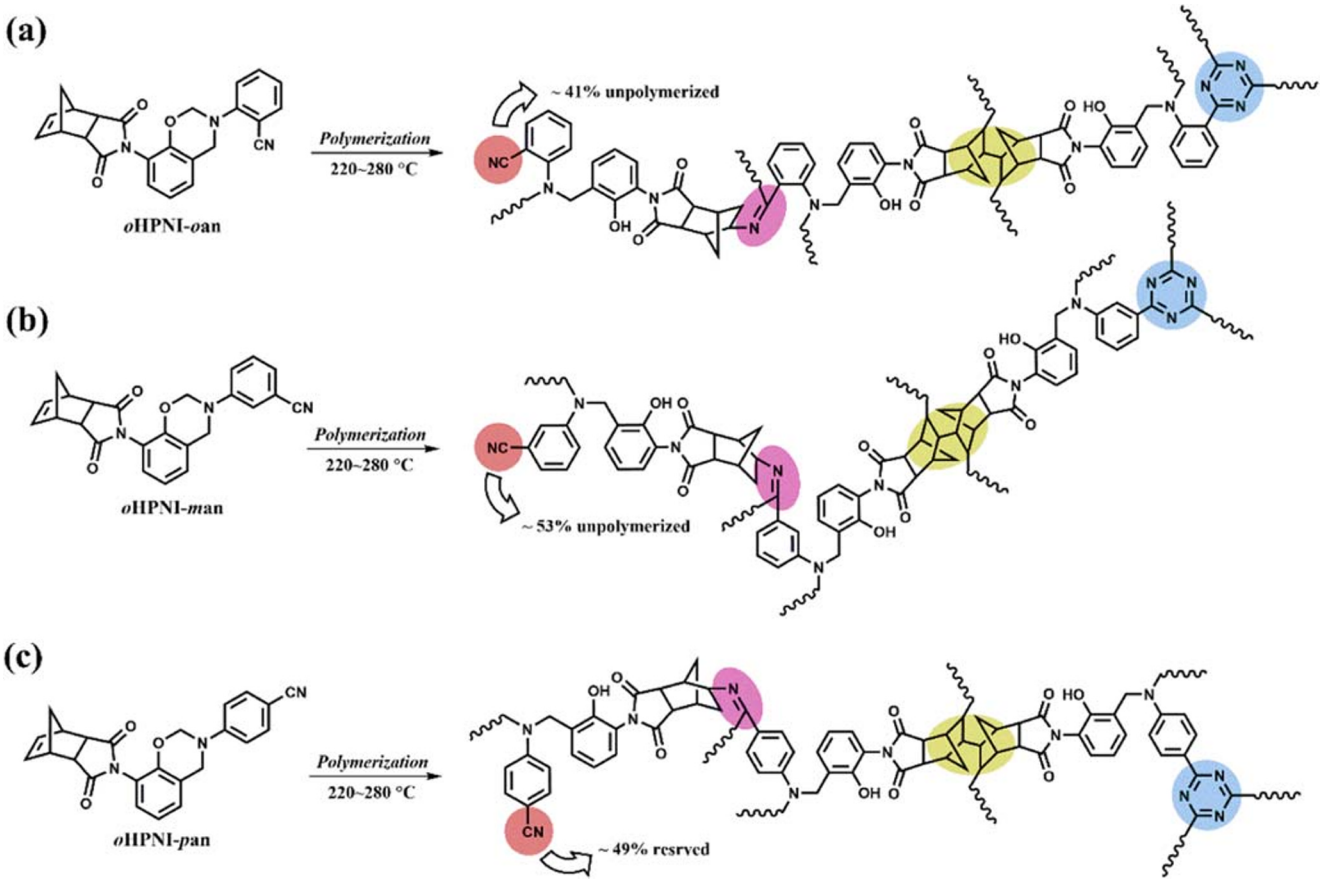


Fig. 4 In situ FT-IR of *o*HPNI-*o*an(**a**), *o*HPNI-*m*an(**b**) and *o*HPNI-*p*an(**c**)

can assume a similar cross-linking reaction could also be taken place in these benzoxazines [30]. Therefore, the proposed thermally activated curing behaviors of these three benzoxazines containing norbornene and nitrile groups are described as shown in Scheme 2.



Scheme 2 Proposed thermally activated polymerization behaviors of *o*HPNI-*o*an (**a**), *o*HPNI-*m*an (**b**) and *o*HPNI-*p*an (**c**)

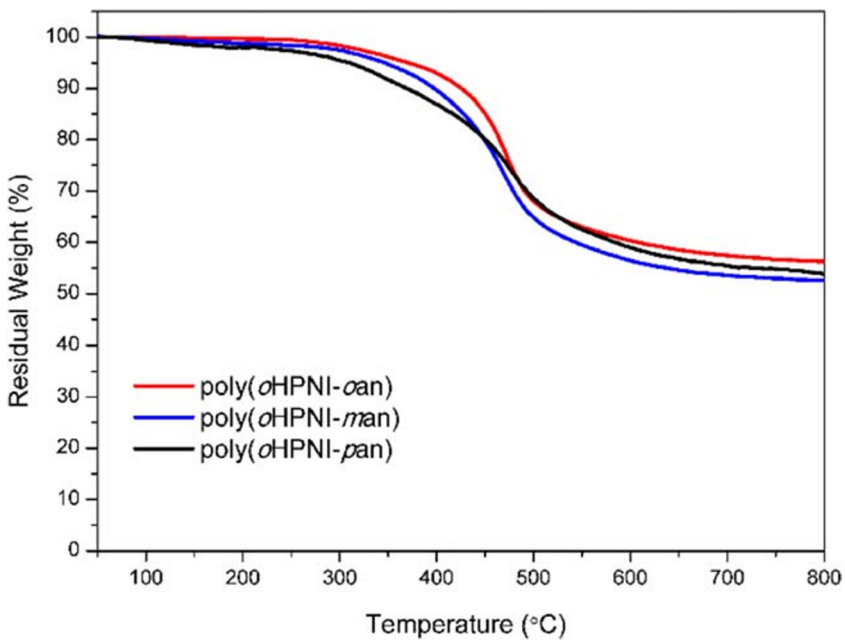


Fig. 5 Thermogravimetric analysis of poly(*o*HPNI-*o*an), poly(*o*HPNI-*m*an) and poly(*o*HPNI-*p*an)

Table 1 Thermal properties of polybenzoxazines

Sample	T_{d5} (°C)	T_{d10} (°C)	Yc (wt.%)
poly(*o*HPNI-*o*an)	371	426	56
poly(*o*HPNI-*m*an)	344	397	53
poly(*o*HPNI-*p*an)	309	370	54

Thermal stability of benzoxazine-norbornen-nitrile based thermosets

The thermogravimetric analysis (TGA) under N_2 was carried out to investigate the thermal stability of polybenzoxazines, and the weight loss curves from room temperature to 800 °C at a heating rate of 10 °C/min are shown in Fig. 5. It can be seen in Fig. 5 that the values of 5% weight loss temperatures (abbreviated as T_{d5}) are 371 °C, 344 °C and 309 °C for the polybenzoxazines derived from ortho-, meta-, para-nitrile based benzoxazines, respectively. Besides, the temperatures of 10% weight loss (abbreviated as T_{d10}) are found to be 426 °C, 397 °C and 370 °C for poly(*o*HPNI-*o*an), poly(*o*HPNI-*m*an) and poly(*o*HPNI-*p*an), respectively. In addition, poly(*o*HPNI-*o*an) shows the highest char yield value (Y_c) of 56% at 800 °C, while poly(*o*HPNI-*m*an) and poly(*o*HPNI-*p*an) exhibits relative lower Yc as 53% and 54%, respectively. The data from TGA results are summarized in Table 1. Moreover, the derivative weight-loss curves of polybenzoxazines were also obtained as shown in Fig. 6. The broadening of the derivative peak at around 350 °C for poly(*o*HPNI-*p*an) results in the lowest T_{d5} and T_{d10} values amongst these polybenzoxazine. Furthermore, the broadening of the main derivative peaks at around 480 °C determines a slow rate of decomposition over a wide temperature range, which can be beneficial from the excellent flammability point of view.

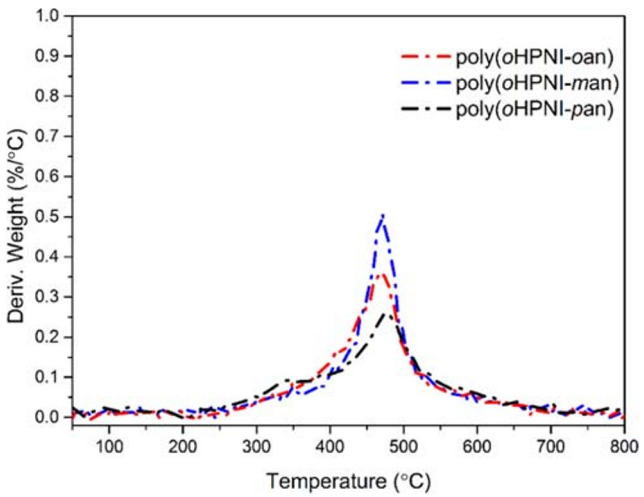


Fig. 6 DTG of poly(*o*HPNI-*o*an), poly(*o*HPNI-*m*an) and poly(*o*HPNI-*p*an)

Conclusions

A series of benzoxazine monomers bearing both norbornene and nitrile groups were designed and successfully synthesized in this study. Particularly, the nitrile group was incorporated to the *para*-, *meta*- and *ortho*-position with respect to the nitrogen atom in the oxazine ring, respectively. The nitrile functionality was found to be much easier to activated as it is attached at *ortho*-position in benzoxazine. In addition, the cross-linked networks derived from the polymerization of *ortho*-benzoxazine isomer showed highest thermal stability than the ones based on *meta*- and *para*-isomers. The current study suggests great potential for designing highly thermally stable polymers based on benzoxazine-norbornene-nitrile thermosetting resins.

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