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Journal Name

ARTICLE

Vinyl benzoxazine: a novel heterobifunctional monomer can undergo both free radical polymerization and cationic ring-opening polymerization

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Abstract: A novel heterobifunctional monomer, namely (6-ethenyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (VBOZO)), which contain both vinyl group and benzoxazine group, was successfully prepared by normal Wittig method from aldehyde-containing benzoxazine precursor of 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine-6-carbaldehyde. VBOZO underwent free radical polymerization initiated by azodiisobutyronitrile (AIBN) and obtained a homopolymer P(VBOZO) with number-average molecular weight about 5050 g mol⁻¹. Meanwhile the benzoxazine group keeps unchanged in copolymer and can undergo cationic polymerization at high temperature to form crosslinked polymers. The benzoxazine-containing linear P(VBOZO) has T_g about 125 °C and show much better thermal stability than that of polystyrene. The peak temperature assigned to cationic ring-opening polymerization of P(VBOZO) centered at 263.0 °C. The VBOZO also copolymerized with styrene under free radical condition to get copolymer P(VBOZO-co-St). The polymerization character of VBOZO is very similar to styrene and the copolymer composition is very close to feed ratio of monomers. All copolymers show high thermal stability and the char yields at 800 °C are over 20%.

Keywords: Vinyl benzoxazine, free radical polymerization, polybenzoxazine, cationic ring-opening polymerization, copolymerization, styrene

Introduction

Polybenzoxazine has attracted much attention due to its excellent mechanical and thermal properties with good handling capability for material processing and composite manufacturing¹⁻¹⁰. Benzoxazine monomers can be obtained in large batch by simple Mannich reaction and then polymerized through the thermal cationic ring-opening of oxazine ring without any initiator or catalyst. Their immensely rich molecular design flexibility allows designing and preparing various molecular structures with desired properties. Moreover, they release no reaction byproducts during the ring-opening polymerization reactions. Furthermore, no volatiles are released upon polymerization, and nearly zero shrinkage is achieved for its ring-opening polymerization nature. These fascinating characteristics make polybenzoxazine a promising candidate in various applications such as electronics, aerospace, composites, coatings, and

adhesives.¹¹⁻¹⁵

From the practical standpoint, polybenzoxazine still suffer from some disadvantages and these limitations will restrict its wide applications in high-Tech fields. Usually benzoxazine monomers are powder-like organics and film-forming ability cannot meet the requirements for most applications. Additionally, the polybenzoxazines are brittle as a consequence of rigidity molecular structure and high crosslink density of polybenzoxazine. So, several strategies have been developed to overcome the associated shortcomings of benzoxazine resins, such as (i) preparation of modified monomers with additional polymerizable group,^{12, 16} (ii) synthesis of novel polymeric benzoxazine precursors,¹¹ and (iii) blending with high performance polymers or fillers and fibers^{13, 15}. The most direct route to increase molecular weight and impact resistance of polybenzoxazine is the synthesis of well-defined high molecular weight polymeric precursors by incorporating benzoxazine units either as side chain or as chain-end or in main chain^{11, 12}.

To obtain a well-defined polymer, it is very important to choose both a right polymerization technology and right monomer. Chain growth polymerization, including free radical, ionic, ring-opening and coordination reaction, is the most powerful method to obtain commercial polymers. How to get a well-defined polymeric benzoxazine precursor with high molecular weight depends mainly on the right choice of monomer.

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Bifunctional monomer is referred to the monomer which possess two polymerizable group¹⁷⁻²⁸. If the two polymerizable groups have identical reactivity (homobifunctional monomer), they are used mainly to prepare crosslinked polymers in one step for lack of group selectivity. On the contrary, as the monomer has two kinds of polymerizable groups (heterobifunctional monomer) which are a low copolymerizing combination and have large differences in reactivity, a noncrosslinked soluble polymer whose main chain is formed by a higher reactive functional group will be obtained with suspending pendants of the remaining lower reactive group. Furthermore, the remaining functional group on the side chain in every repeating unit does not lose reactivity and will be allowed to undergo polymer reaction under the more fitting condition. These functional polymers can be used for self-crosslinkable materials.

In fact, some modified benzoxazines which possess second polymerizable groups have the potential to be used as bifunctional monomers to prepare well-defined polymeric benzoxazine precursors. Among them double-band-related benzoxazines show resistless charms to researchers. For this type of benzoxazine can first undergo chain polymerization to obtain well-defined linear polymer with dense benzoxazine pendent groups. Though allyl-containing benzoxazine monomers²⁹⁻³⁷ have been widely studied, almost no research declared that linear polymeric benzoxazine precursor was prepared by these monomers by chain growth polymerization technology. Maleimide group³⁸⁻⁴⁰ was introduced into benzoxazine and serve as another polymerizable group. It was found that the bifunctional monomer showed a two stage process of thermal polymerization. Fusible polymaleimides with a T_g of around 100°C could be obtained by thermally polymerizing at 130°C. Further polymerizing the polymaleimides at 240°C resulted in a completely cured resin showing a T_g of 204°C. But the structure details of the fusible polymaleimides were not given in that paper. The free radical copolymerization character of this monomer with styrene was also studied²⁵. The first well-defined linear polymeric benzoxazine precursor through free radical polymerization was reported by Yagci's group⁴¹. A heterobifunctional monomer (BEM) possessing both methacrylate and benzoxazine functionalities was synthesized and characterized. BEM was then copolymerized with styrene by free radical polymerization using AIBN as initiator. It was found that free radical copolymerization of this monomer is a convenient pathway that allows easy synthesis for polymeric precursor with side-chain benzoxazines which can be cured thermally. But they didn't supply any details about BEM homopolymer. To further extend the study, Yagci and Ishida⁴¹ developed a new methacryloyl-benzoxazine-containing monomer and study its photopolymerization behavior as well as thermal polymerization. As the free radical initiator, benzoyl peroxide (BPO), was added into the monomer at 70°C, it was found that even under such mild condition the decomposition of monomer is still happening, it appears that the monomer is relatively sensitive to heat, and at least some part of the molecule will undergo decomposition before its

polymerization. It is demonstrated that photopolymerization^{42,43} is feasible to anchor the acrylate in the monomer in spite of the difficulty experienced with free radical polymerization with and without an initiator. Norbornene functional benzoxazine was also reported to prepare highly crosslinked polybenzoxazines⁴⁴.

In this article, we propose a new heterobifunctional benzoxazine, namely vinyl benzoxazine, which can be used as universal monomer to prepare the linear polymeric precursor with side-chain benzoxazine group. The typical character of this styrene-like monomer is the second polymerizable double bond directly connects to benzoxazine structure without linking spacers. Both homo- and copolymerization characters of this monomer were studied.

Experimental

Reagents and solvents

p-hydroxybenzaldehyde (Alfa, 98%, recrystallized from water), aniline (Alfa, 99+%), azodiisobutyronitrile (Sinopharm, 95%), styrene (Alfa, 99%, purification according to standard method), Potassium tert-butoxide (Alfa, 97%), Methyltriphenylphosphonium Bromide (98+%), formaldehyde (Sinopharm, 37%), THF (Sinopharm, 99%), Dichloromethane (Sinopharm, 99%), petroleum ether (Sinopharm, 60-90°C), Ethyl acetate (Sinopharm, 98%), toluene (Sinopharm, 98%).

3-phenyl-3,4-dihydro-2H-1,3-benzoxazine-6-carbaldehyde (ABOZO)

ABOZO was prepared according to reported method with some modifications^{45,46}. Into a 500 mL three-necked flask with stirrer, aqueous formaldehyde solution (32 g, 0.4 mol) and toluene (60 mL) was added at room temperature. The mixture was cooled down to 5°C by ice water under stirring and then a cooled mixture of aniline (18.6 g, 0.2 mol) and toluene (20 mL) was dropped into flask under rapid stirring and kept the temperature below 5°C. After 30 min's stirring at this temperature, p-hydroxybenzaldehyde (24.4 g, 0.2 mol) in toluene (60 mL) was added into flask under stirring. And then the temperature was brought back to ambient temperature automatically without heating and kept under room temperature for one hour with continuous stirring. Then heating was applied and the temperature was gradually raised to 95°C and stirred at this temperature for 5 hr. Part of the solvent was removed from the reaction mixture under reduced pressure and chloroform was added to dissolve the residues. The resulting solution was washed with 0.5 mol·L⁻¹ NaOH aqueous solution and water for three times to remove the impurities and unreacted reagents. After that, the solvent was evaporated by a rotary evaporator. Thereafter, the crude, yellow product was recrystallized from toluene for three times to afford a white crystal powder (ABOZO) (mp 98–99°C, yield 68%). ¹H NMR (CDCl₃, TMS, ppm): 9.79 (1H, CHO), 7.60 (1H, Ar-H), 7.54 (1H, Ar-H), 7.25 (2H, Ar-H), 7.09 (2H, Ar-H), 6.94 (1H, Ar-H), 6.89 (1H, Ar-H), 5.41 (2H, CH₂), 4.64 (2H, CH₂).

6-ethenyl-3-phenyl-3,4-dihydro-2H-1,3-benzoxazine(VBOZO)

The standard Wittig method was adopted to prepare VBOZO. Under Argon atmosphere, Methyltriphenylphosphonium Bromide (10.072g) was added into 100mL two-neck flask containing 40mL dried THF, then Potassium tert-butoxide(5.62g) was added into flask under stirring. Rapidly the colorless solution turned to bright yellow and the stirring was continued for 1hr. ABOZO (4.78g , 20mmol) in THF(20mL) was dropped into flask under stirring and kept the temperature below 25°C. After finishing addition, the reaction proceeded at room temperature for 5.5hr. Then water was added to stop the reaction. The THF and water was removed by rotary evaporator and the residues was extracted with CH₂Cl₂(70ml×2) .The organic phase was washed with water thoroughly and dried with anhydrous Na₂SO₄. After evaporation away solvent, a viscous liquid left. The VBOZO was obtained by chromatograph (eluent: petroleum ether/ ethyl acetate, 6/1) as white powder. Yield 33%, mp 42°C-44°C. Elemental analysis: Find C, 81.43; H, 6.49; N, 5.77, calculated based on C₁₆H₁₅NO: C, 80.98; H, 6.37; N, 5.90.

Polymerization of VBOZO

VBOZO 710mg (3mmol), AIBN 14.2mg and toluene 5mL was mixed in polymerization tube. The reaction mixture was treated under three-time freeze-in-thaw and the tube was sealed under Argon. And then the tube was heated up and stirred at 60 °C for 24 hr under argon atmosphere. After the reaction mixture was cooled to room temperature, the reaction solution was dropped into large amount of methanol and the resulting precipitate was filtered and collected to afford the crude product as light yellow color. Purification was done by dissolving-precipitating method for three times in toluene(or DMF)-methanol couple. Finally 0.20g white powder was obtained and the yield was 28%.

For copolymerization with styrene, the same procedure was used except the different amount of styrene was added and the molar ratio of VBOZO to styrene was varied.

Characterization

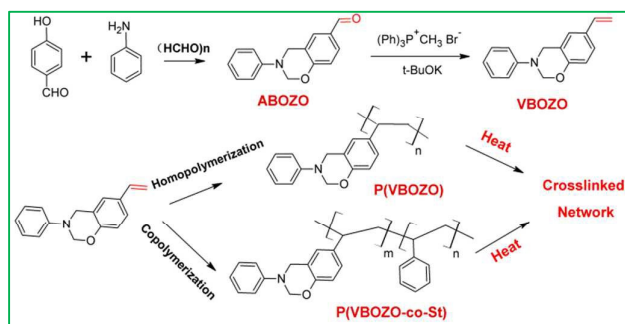
The structures of the compounds were verified by proton (¹H) and carbon (¹³C) nuclear magnetic resonance spectroscopy (NMR) using Bruker AV400 NMR spectrometer at proton frequency of 400 MHz at room temperature. Fourier transform infrared (FTIR) spectra were recorded with a Bruker Vertex 70 FTIR spectrometer. Solid samples were prepared as KBr pellets and liquid samples were prepared by casting onto KBr windows, recorded at room temperature in the region of 4000-400 cm⁻¹ with a resolution of 4 cm⁻¹. The thermal stability was investigated by thermogravimetric analysis (TGA) performed on TG/DTA6300 instruments thermogravimetric analyzer. Nitrogen was used as a purge gas for all testing. A heating rate of 20 °C·min⁻¹ with a flow rate of 100 mL·min⁻¹ was used for all tests. Differential scanning calorimetry (DSC) was undertaken using TA Instruments Q20 running TA Q Series Advantage software on samples placed in hermetically sealed aluminum pans. Experiments were conducted at a heating rate of 5°C·min⁻¹ from -20 to 300 °C under flowing nitrogen (20 mL·min⁻¹). Elemental analysis was performed on Elementar Vario Micro cube elemental analyzer. The molecular weight of

polymer was determined by gel permeation chromatography (GPC) in THF using polystyrene as standards. The flow rate of THF was maintained as 1mL/min. The chromatograms were recorded using Waters 510 pump and Waters 410 differential RI detector. Mass spectrometry (MS) was undertaken using Bruker Daltonics microTOF II electrospray ionization high resolution mass spectrometry, the quality range was 50-20000 of m/z.

Results and discussion

Synthesis and characterization of VBOZO

The new heterobifunctional monomer, VBOZO, was first prepared in our group and its synthetic routes were shown in Scheme 1. First



Scheme 1 Synthesis route of VBOZO and its free radical polymerization and curing reaction

ABOZO was obtained according to Gu's method⁴⁶ with good yield. The aldehyde group was transferred to double bond by universal Wittig method. Though VBOZO has low melting point (42°C-44°C) and always appeared as viscous liquid, crystal can be obtained readily after short time storing. High pure VBOZO suitable for polymerization obtained by chromatograph and its chemical structure was characterized by different methods.

IR spectrum of VBOZO is shown in Fig.1. The peak at 1627 cm⁻¹ is attributed to vinyl group connecting to benzene ring, it means that the aldehyde groups have successfully changed into double bond. Peak located at 1600 cm⁻¹ is typical benzene ring absorption. The bands at 1489 cm⁻¹, 1235 cm⁻¹, 1028 cm⁻¹ and 944 cm⁻¹ are assigned to the characteristic modes related to the benzoxazine ring. These peaks certify the presence of that both vinyl and benzoxazine unit.

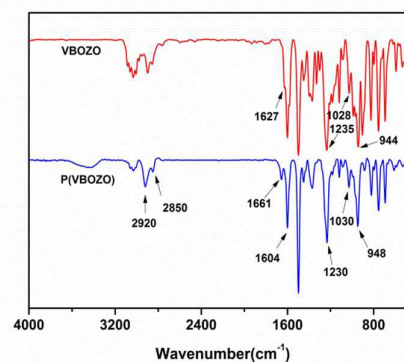


Figure 1 FT-IR spectra of VBOZO and P(VBOZO)

The ^1H NMR spectrum of VBOZO is shown in Fig.2. A set of peaks appear in the range of 6.69-7.25ppm comes from all benzene ring. The chemical shifts for double bond protons locate at 6.61ppm ($=\text{CH}-\text{Ph}$) and 5.64ppm, 5.11ppm($\text{CH}_2=\text{C}-$). The benzoxazine ring is characterized with resonance peaks at 4.66 ppm ($\text{Ar}-\text{CH}_2-\text{N}$) and 5.45 ppm ($\text{O}-\text{CH}_2-\text{N}$). Comparing with reported results, these peaks shifted to high ppm due to its enlarged conjugated structure. Meanwhile, the integrated peak area ratio of these protons is consistent with theoretic value based on chemical structure of VBOZO.

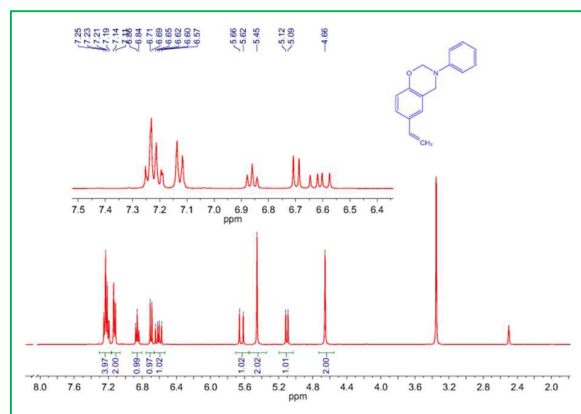


Figure 2 ^1H NMR spectrum of VBOZO (solvent: $\text{DMSO}-d_6$)

^{13}C NMR spectrum of VBOZO is shown in Fig.3. Peaks assigning to benzene ring and double bond appear at 154.12ppm, 148.06ppm, 136.05ppm, 130.48ppm, 129.28ppm, 128.56ppm, 127.12ppm, 125.68ppm, 124.44ppm, 121.58ppm, 120.61ppm, 118.41ppm, 116.76ppm, 111.70ppm. The typical benzoxazine ring protons appear at 79.62ppm ($\text{O}-\text{CH}_2-\text{N}$ -) and 50.45ppm ($\text{Ar}-\text{CH}_2-\text{N}$ -).

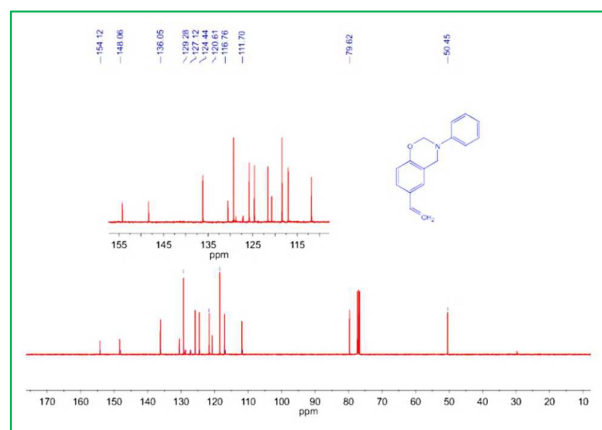


Figure 3 ^{13}C NMR spectrum of VBOZO (solvent: CDCl_3)

The thermal properties of VBOZO were studied by DSC and results are indicated in Fig.4. From DSC curve, the sharp endotherm peak located 42.7°C assigns to melting point of VBOZO, the value is consist very well with that from melting point detector. A small exothermic process around 120-170°C is due to thermal initiated

free radical homopolymerization of VBOZ. For most free radical monomer shows thermal polymerization character at relatively high temperature. The ring-opening polymerization of benzoxazine occurs in the temperature range of 200°C-250°C, the exothermal peak locates at 219.35°C.

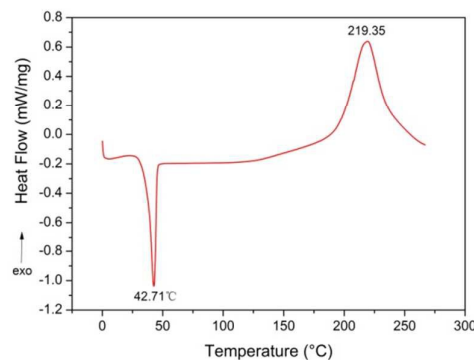


Figure 4 DSC curve of VBOZO

Polymerization of VBOZO initiated using AIBN and characterization of corresponding polymer

As expected, the newly designed heterobifunctional monomer VBOZO can be initiated by AIBN, a typical free radical initiator under normal polymerization condition. After polymerization and purification, a white powder was obtained and the sample was used for structure analysis. After polymerization, the typical double bond absorption (peak appearing at 1627 cm^{-1}) disappears completely (Fig.1), a set of new peaks locating at 2920 cm^{-1} and 2850 cm^{-1} due to polymer chain appears, it means that the monomer have been transferred into polymer under polymerization condition. More important, the characteristic absorption for benzoxazine unit, such as peaks at 1230 cm^{-1} , 1030 cm^{-1} , 948 cm^{-1} , still remains. The result shows that under free radical polymerization condition, the benzoxazine unit is stable enough and doesn't undergo thermal initiated ring-opening polymerization.

^1H NMR of P(VBOZO) is shown in Fig.5. Comparing with ^1H NMR spectrum of VBOZO (Fig.2), the peaks assigned to double bond (6.61ppm, 5.64ppm, 5.11ppm) completely disappear, and new wide peaks locate in the range of 0.75ppm-2.25ppm is found which is attributed to main chain polyethylene protons. This change indicates that double bond have undergone polymerization. The peaks between 6.0ppm-7.5ppm are due to benzene protons. After free radical polymerization, the typical benzoxazine peaks locating at 5.28ppm ($\text{O}-\text{CH}_2-\text{N}$ -), 4.31ppm ($\text{Ar}-\text{CH}_2-\text{N}$ -) still exist. It also certifies that the benzoxazine groups keep unchanged during free radical polymerization.

The molecular weight of P(VBOZO) was measured by GPC method, number-average molecular weight (M_n) and weight-average molecular weight (M_w) are 5050 g mol^{-1} and 9360 g mol^{-1} , and the polydispersity index (PDI) is 1.85. The molecular weight of P(VBOZO) is relatively low at present, the possible reason is the high steric hindrance of benzoxazine unit in monomer.

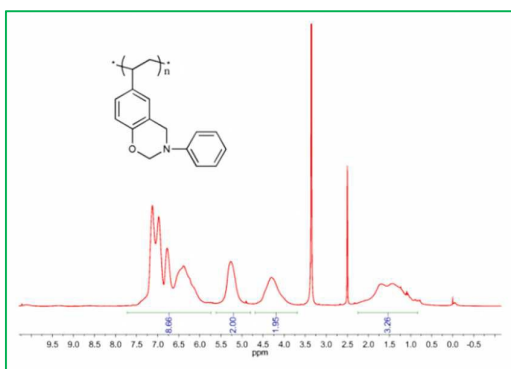


Figure 5 ^1H NMR spectrum of P(VBOZO) (solvent: DMSO- d_6)

The thermal property of P(VBOZO) was studied by DSC and TGA. From DSC result (Fig.6), we find the T_g of P(VBOZO) is about 125°C , higher than that of polystyrene. The high T_g results in large spatial volume of benzoxazine group and it needs more free volume to rotate around the main chain. A sharp exothermal peak attributed to ring-opening polymerization of benzoxazine appears in the temperature range of $230\text{--}290^\circ\text{C}$, the peak temperature is nearly 263°C and possesses polymerization enthalpy 198 Jg^{-1} . Comparing with the monomer, the peak temperature increased dramatically for its rigid nature of the benzoxazine-containing polymer.

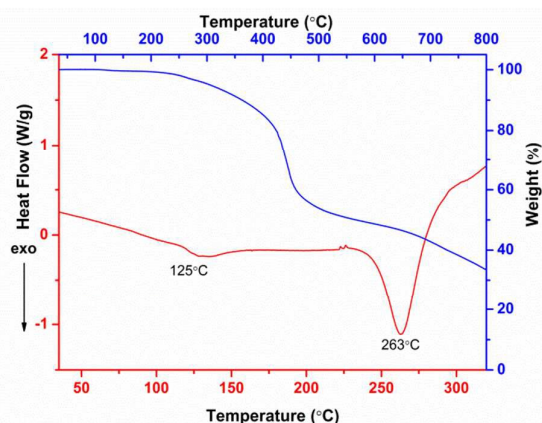


Figure 6 DSC and TGA curves of P(VBOZO)

The thermal stability of P(VBOZO) is also shown in Fig.6. No weight loss is observed under 250°C . The 5% and 10% weight loss temperature of P(VBOZO) are as high as 306°C and 363°C , respectively. High thermal stability is very important for benzoxazine-containing thermoplastic resin. For this type polymer has the potential to be processed as traditional thermoplastic resin and then applies post-curing procedure to obtain high performance crosslinking materials. The char yield (CR) of P(VBOZO) at 800°C is as high as 35%, much bigger than that of polystyrene. It is well known that at such high temperature the char yield of polystyrene is near zero and the normal limited oxygen index is about 18%^{47,48}. The high thermal stability of P(VBOZO) comes from the fact that the benzoxazine unit in P(VBOZO) will undergo ring-opening polymerization at high temperature and

result in a crosslinked polymer (Scheme 1)^{1, 11-15}. So this research provides a brand new route to prepare high thermal stability thermoplastic with potential curing group in main chain.

To better understand the curing processes of P(VBOZO), the curing kinetics of P(VBOZO) was investigated by using non-isothermal differential scanning calorimetry (DSC) at different heating rates (Fig. 7)⁴⁹⁻⁵². It can be observed that the exothermic peak shifts to higher temperature with higher heating rate. Kissinger, Ozawa, and Flynn–Wall–Ozawa methods were used to determine the kinetic parameters and built the kinetic models. The activation energy of P(VBOZO) is 145.0 kJ mol^{-1} (Kissinger method), 146.2 kJ mol^{-1} (Ozawa method), 144.5 kJ mol^{-1} (Flynn–Wall–Ozawa method), respectively. Similar to traditional bisphenol-A based benzoxazine resin, the P(VBOZO) also shows self-catalyzed character.

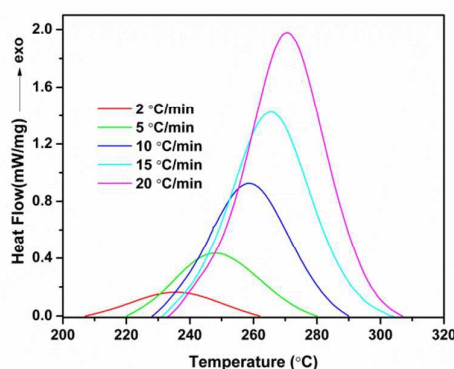


Figure 7 DSC thermograms of P(VBOZO) at different heating rates

Copolymerization with styrene and properties of copolymers

The copolymers of VBOZO with styrene also were prepared by free radical polymerization and the data is listed in Table 1. The molecular weight of copolymer is a little higher than that of P(VBOZO) homopolymer. The possible reason is that the steric hindrance resulting from VBOZO is reduced by styrene. From IR spectra of these copolymers, the typical absorption peaks for benzoxazine appear at 1230 cm^{-1} , 1030 cm^{-1} and 950 cm^{-1} . The composition of copolymer is calculated from their ^1H NMR spectra and the results are collected in Table 1. The data shows that composition of copolymer is very close to feed ration of monomers, it means the VBOZO and styrene have similar polymerization character.

Table 1 Free Radical Polymerization of VBOZ with St in Toluene

| Polymer/ Feed ratio | Conversion (%) ^a | Composition (NMR) | M_n^b | M_w/M_n^b |
|------------------------|--------------------------------|----------------------|---------|-------------|
| P(VBOZ) | 28 | 100 | 5050 | 1.85 |
| P(VBOZO/St) 2:1 | 49 | 69.4/30.6 | 8950 | 1.48 |
| P(VBOZO/St) 1:1 | 42 | 52.2/47.8 | 6600 | 1.73 |
| P(VBOZO/St) 1:2 | 37 | 35.2/64.8 | 7600 | 1.35 |

^a Determined by weight.

^b Determined by GPC measurements.

The thermal ring-opening polymerization character of copolymers was studied by DSC. From DSC curves, we can figure out the peak temperatures for benzoxazine polymerization of three copolymers are 263°C, 254°C and 272°C, respectively.

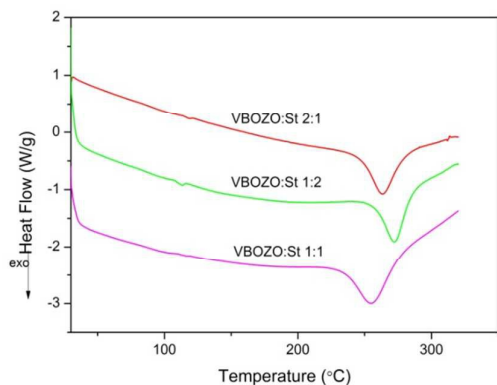


Figure 8 DSC thermograms of P(VBOZO-co-St)

The thermal stability of three copolymers was evaluated by TGA (Fig.9) and the data are listed in Table 2. Both the 5% and 10% weight loss temperature of copolymers are higher than that of polystyrene. The most important, exceeding 400°C, the thermal stability of copolymer is much better than that of polystyrene. At 500°C, the polystyrene nearly decomposes completely and the char yield is 0.95%. But all copolymers show high thermal stability and char yields at 800°C are over 20%. So introducing benzoxazine groups into thermoplastic polymer can effectively increase the thermal stability and fire retardant. We can further image that if we pre-treated the copolymers at suitable temperature range and make the benzoxazine group undergo ring-opening polymerization thoroughly, the final crosslinked polymer will show much better thermal stability.

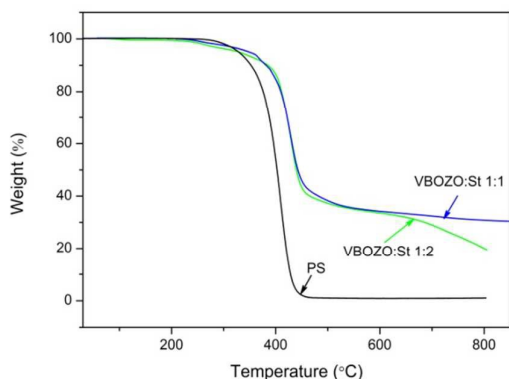


Figure 9 TGA thermograms of P(VBOZO-co-St) and PS

Table 2 Thermal properties of P(VBOZO-co-St) and PS .

| Polymer | $T_{5\%}^a$ (°C) | $T_{10\%}^b$ (°C) | Y_{C800}^c (%) |
|--------------------|------------------|-------------------|------------------|
| P(VBOZO-co-St) 1:1 | 349 | 382 | 30.7 |
| P(VBOZO-co-St) 1:2 | 330 | 385 | 20.1 |
| PS | 329 | 353 | 0.95 |

^a The 5% weight loss temperature in a nitrogen atmosphere.

^b The 10% weight loss temperature in a nitrogen atmosphere.

^c Char yield at 800 °C in a nitrogen atmosphere.

Conclusions

Heterobifunctional monomers combine different polymerization technology together and can act as ideal starting materials for preparation of well-defined polymer precursors. Benzoxazines possesses high polymerization temperature during cationic ring-opening polymerization and show excellent thermal stability under normal free radical polymerization conditions. Introducing vinyl group into benzoxazine structure is a direct route to prepare novel benzoxazine-containing heterobifunctional monomer. In this research, a novel heterobifunctional monomer, VBOZO, which contain both vinyl group and benzoxazine group, was successfully prepared by Wittig reaction. VBOZO can be initiated by AIBN to obtain a well-defined homopolymer P(VBOZO) with pendent benzoxazine groups. The M_n of P(VBOZO) is about 5050g/mol. The benzoxazine-containing linear P(VBOZO) has T_g about 125°C and shows much better thermal stability than that of polystyrene. The peak temperature being assigned to cationic ring-opening polymerization of P(VBOZO) locates at 263.0°C. The VBOZO also copolymerized with styrene under free radical condition to get copolymer P(VBOZO-co-St). The polymerization character of VBOZO is very similar to styrene and the copolymer composition is very close to feed ratio of monomers. All copolymers show high thermal stability and the char yields at 800°C are over 20%.

Acknowledgements

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Graphical Abstract

Vinyl benzoxazine: a novel heterobifunctional monomer can undergo both free radical polymerization and cationic ring-opening polymerization

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