



# A well-defined poly(vinyl benzoxazine) obtained by selective free radical polymerization of vinyl group in bifunctional benzoxazine monomer

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## ABSTRACT

**Abstract:** A heterobifunctional monomer, namely, 3-(4-ethenylphenyl)-3,4-dihydro-2H-1,3-benzoxazine (VBOZN), which contains both vinyl group and benzoxazine group, was successfully prepared by three-step method with high purity and satisfactory yield. The chemical structure of VBOZN was identified by NMR, FTIR and elemental analysis. VBOZN selectively underwent free radical polymerization initiated by azodiisobutyronitrile to obtain homopolymer P(VBOZN) with  $M_n$  4960 and  $M_w$  11700. The benzoxazine-containing linear P(VBOZN) has  $T_g$  about 112 °C and shows better thermal stability than that of polystyrene. The P(VBOZN) was cured by heating without any catalyst and the peak temperature assigned to cationic ring-opening polymerization of P(VBOZN) centered at 244 °C. The molecular weight of P(VBOZN) could be improved dramatically by copolymerization of VBOZO with N-phenylmaleimide. Both homopolymer and copolymers show high stability and theoretical limiting oxygen index are near 30. P(VBOZN) and copolymers are not only new kinds of well-defined multifunction polymers with the potential of postpolymerization and/or chemical modification, they are also novel intrinsic fire retarded polymers.

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## 1. Introduction

Well-defined multifunctional polymers bearing reactive functionalities are an intriguing class of starting materials as building blocks for the construction of smart materials and advanced macromolecular architectures [1–4]. However, direct introduction of functional moieties onto existing polymer chain can be difficult and often requires elaborated protective-group chemistry. Many efforts have been paid to chase down more effective and convenient method to solve this problem and it has been proved [5,6] that direct polymerization of suitable functional monomers is an atom efficient route.

Bifunctional monomer refers to molecular which contains two polymerizable groups. But if the two groups show same reactivity (namely homobifunctional monomer), such as divinyl benzene, ethylene glycol bis(meth)acrylates and so on, they will react

simultaneously during polymerization and result in crosslinking polymer instead of linear functional polymer [7]. So homobifunctional monomers are not a right choice for preparation of soluble multifunctional polymers. On the contrary, when the two groups shows different reactivity or different polymerization mechanism (namely hetero-bifunctional monomer), one group can be selectively converted to obtain a linear polymer and the remaining group as pendent reactive site for further postpolymerization or chemical modification. Obviously this is the better choice for preparation of well-defined multifunctional polymers. But the success of this method is highly dependent on the selectivity of the two polymerizable groups and the stability of second group during first group polymerization. Therefore, design and synthesis of heterobifunctional monomers which bearing two different functional moieties in one molecular that do not interfere with each other during the polymerization process, i.e., are orthogonal in their polymerization behaviour, is highly attractive. To date, a few heterobifunctional monomers have been reported in the literature [1–3,7–17].

Though heterobifunctional monomers offer an ideal route to

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prepare well-defined multifunctional polymer, but in most cases post-polymerization (and/or post chemical modification) of second polymerizable group still need additional initiator, crosslinking agent, UV irradiation [2,7–10,14] and this procedure always need vast amount of solvent to aid the mixing of functional polymers and additives.

It is well-known that catalyst (or initiator)-free thermal polymerization is a very convenient and somewhat green method to prepare polymers. Benzoxazine resins possess such virtue and recently polybenzoxazine attracted many attentions from both academic and industrial area [18–22]. Benzoxazines undergo catalyst-free thermal initiated cationic ring-opening polymerization at relatively high temperature (>200 °C). Though benzoxazine-containing precursor polymers have been reported [23–28], but well-defined benzoxazine-containing polymer is still a challenge [19,20].

In this paper, a high pure benzoxazine-based hetero-bifunctional monomer, 3-(4-ethenylphenyl)-3,4-dihydro-2H-1,3-benzoxazine (VBOZN), which contains both vinyl and benzoxazine group, was prepared through three-step Schiff base route. The VBOZN was well characterized by NMR, MS and elemental analysis. A well-defined P(VBOZN) was prepared by free radical polymerization being initiated by AIBN. P(VBOZN) shows high thermal stability and undergo crosslinking reaction over 200 °C. Copolymerization of VBOZN with N-phenylmaleimide was also studied.

## 2. Experimental

### 2.1. Reagents and solvents

4-vinylaniline (95%), were obtained from TCI (shanghai) development Co., LTD. Salicylaldehyde, paraformaldehyde, *p*-methoxyphenol, NaBH<sub>4</sub>, N-phenylmaleimide and azobisisobutyronitrile (AIBN) were purchased from Alfa Aesar. All solvent, such as THF, Dichloromethane, petroleum ether, Ethyl acetate, toluene, were purchased from Sinopharm Chemical Reagent Co., Ltd.

#### 2.1.1. 2-((E)-[(4-ethenylphenyl)imino]methyl) phenol (SB)

The Schiff base was prepared according to reported method with some modifications [29]. *p*-Aminostyrene (2.38 g, 20.0 mmol) and *p*-methoxyphenol (0.1 g) in 40 mL ethanol was added into a three-neck flask equipped with magnetic stirrer, cooling condenser and argon inlet and outlet. Then salicylaldehyde (2.44 g, 20.0 mmol) was dropped into the flask under stirring and kept the mixture below 30 °C during addition. After stirring at this temperature for 4 h, the temperature was raised to 60 °C by gentle heating and kept at this temperature for 0.5 h. Then the mixture was cooled to room temperature and the Schiff base was precipitated as yellow crystals. The precipitate was filtered off, washed with ethanol and dried under vacuum at 30 °C. 3.95 g product was obtained. m.p. 83–85 °C. <sup>1</sup>H NMR (400 MHz, DMSO) δ: 13.11 (1H, s, =CH=N-), 9.00 (1H, s, -OH), 6.96–7.68 (4H, m, Ar-H), 6.78 (1H, m, =CH-), 5.88 (1H, d, *J* = 8 Hz, CH<sub>2</sub> = ), 5.29 (1H, d, *J* = 8 Hz, CH<sub>2</sub> = ). <sup>13</sup>C NMR (100 MHz, DMSO) δ: 163.53, 160.80, 147.90, 136.43, 136.41, 133.75, 133.03, 127.70, 122.15, 119.81, 119.62, 117.07, 114.88. Anal. calcd for C<sub>15</sub>H<sub>13</sub>NO: C 80.68, H 5.87, N 6.27; found: C 80.48, H 5.95, N 6.30. The SB can be directly used for next reaction without any further purification.

#### 2.1.2. 2-[(4-ethenylphenyl)amino]methyl phenol (R-SB)

R-SB was prepared as reported method [30]. A solution of A (1.79 g, 8 mmol) in ethanol (20 mL) was added into three-neck flask and kept the temperature below 5 °C by ice-water bath, and NaBH<sub>4</sub> (0.16 g, 4 mmol) was added into flask in small portions while

stirring. The reaction process was monitored by TLC. When the reduction was complete (about 2 h), 20 mL of water was added, and the resulting product was extracted with methylene chloride (20 × 3 mL), washed with water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated to dryness, giving 1.69 g of white powder, m.p. 111–114 °C. <sup>1</sup>H NMR (400 MHz, DMSO) δ: 9.51 (1H, s, -OH), 6.53–7.17 (4H, m, Ar-H), 6.51 (1H, s, -CH = ), 5.46 (1H, d, *J* = 8, -CH<sub>2</sub> = ), 4.90 (1H, d, *J* = 8, -CH<sub>2</sub> = ). 6.17 (1H, t, *J* = 6, -N-H), 4.21–4.19 (1H, d, *J* = 8, -CH<sub>2</sub>-N). <sup>13</sup>C NMR (100 MHz, DMSO) δ: 155.45, 149.29, 137.29, 128.65, 127.96, 127.52, 126.04, 125.46, 119.22, 112.47, 108.78, 41.55. Anal. calcd for C<sub>15</sub>H<sub>15</sub>NO: C 79.97, H 6.71, N 6.22; found: C 80.15, H 6.75, N 6.23.

#### 2.1.3. 3-(4-ethenylphenyl)-3,4-dihydro-2H-1,3-benzoxazine (VBOZN)

A solution of R-SB (1.69 g, 7 mmol), paraformaldehyde (0.242 g, 8.05 mmol) and *p*-methoxyphenol (0.030 g) in 15 mL of 1,4-dioxane was added into three-neck flask and stirred at 100 °C for 4.5 h under argon atmosphere. Then the solution was evaporated under reduced pressure to remove the organic solvent, the resulting solid was dissolved in 50 mL CH<sub>2</sub>Cl<sub>2</sub>, and washed with diluted solution of sodium hydroxide (1%, wt%). The organic layer was collected, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated to dryness to obtain a viscous light yellow liquid. The VBOZN was obtained by chromatograph (eluent: petroleum ether/ethyl acetate, 10/1) as light yellow powder. 0.88 g of VBOZN was obtained and was stored in refrigerator. M.p.: 52–53 °C. IR (KBr) ν: 1624, 1604, 1514, 1334, 1222, 1032, 929 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, DMSO) δ: 6.71–7.35 (4H, m, Ar-H), 6.61 (1H, t, =CH-), 5.64 (1H, d, *J* = 8 Hz, -CH<sub>2</sub> = ), 5.08 (1H, d, *J* = 8 Hz, -CH<sub>2</sub> = ). 4.66 (2H, s, Ar-CH<sub>2</sub>-N), 5.45 (2H, s, O-CH<sub>2</sub>-N); <sup>13</sup>C NMR (100 MHz, DMSO) δ: 154.36, 147.92, 136.57, 129.99, 128.14, 127.67, 127.49, 121.75, 120.93, 117.54, 116.69, 112.03, 49.24, 78.82. Anal. calcd for C<sub>16</sub>H<sub>15</sub>NO: C 80.98, H 6.37, N 5.90; found: C 81.09, H 6.39, N 5.91.

### 2.2. Free radical polymerization of VBOZN and its copolymerization

VBOZN 0.57 g (2.4 mmol), AIBN 11.4 mg and toluene 4 mL was mixed in polymerization tube. The reaction mixture was treated under three-time freeze-in-thaw before the tube was sealed under Argon. And then the tube was heated up and stirred at 60 °C for 24 h 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 powder. Purification was done by dissolving-precipitating method for three times in toluene-methanol couple. After vacuum dry 0.22 g white powder was obtained and the yield was 39%.

For copolymerization of VBOZN with N-phenyl maleimide, the same procedure was used.

### 2.3. Characterization

The structures of the compounds were verified by proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) 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<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. 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<sup>-1</sup> with a flow rate of 100 mL·min<sup>-1</sup> was used for

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