



Highly cross-linked thermosetting resin of maleimidobenzoxazine functionalized with benzocyclobutene

Yuanrong Cheng, Tianke Qi, Yunxia Jin, Dunying Deng, Fei Xiao*

Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, PR China

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ABSTRACT

Maleimidobenzoxazine monomer functionalized with benzocyclobutene (BCB) and its cured resin has been successfully prepared. BCB-modified maleimidobenzoxazine monomer (HMI-AB) was synthesized by the reaction of 4-aminobenzocyclobutene (AMBCB), *p*-hydroxyphenylmaleimide (HMI) and paraformaldehyde in dioxane under reflux. Fourier transform infrared spectroscopy (FTIR), ¹H and ¹³C nuclear magnetic resonance spectroscopy (NMR) were used to characterize the structure of the monomer. The monomer HMI-AB possesses three kinds of polymerizable functional groups of BCB, maleimide and benzoxazine. The polymerization behavior of the monomer is studied by differential scanning calorimetry (DSC) and FTIR. DMA study demonstrates that the cured resin show high storage modulus and high *T_g* at ca. 350 °C. TGA study shows that the cured resin possess good thermal stability.

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1. Introduction

The preparation and study of benzoxazine (BOZ) resins has attracted much attention for the high flexibility in molecular design and excellent performance compared to traditional phenol resins [1–3]. In order to improve the performance for applications in rigorous environments, many approaches have been applied for the development of high-performance polybenzoxazine-based materials. The first strategy is to enhance the toughness or reinforce polybenzoxazines with other polymers [4–8] or inorganic additives [9–16]. The second strategy is to enhancing the thermal properties of polybenzoxazines through the introduction of other polymerizable functionalities into the BOZ structure via molecular engineering and tailoring of BOZ monomer. There has been considerable interest in functionalized polybenzoxazine to improve the thermal stability and thermomechanical performance to expand their end-use applications in harsh environments. Many polymerizable functionalities such as allyl [17], methacryloyl [18], maleimide [19–21], norbornane [21], acetylene [22,23], propargyl [24], epoxy [25], and nitrile group [26] have been introduced into BOZ monomers.

Maleimide-modified BOZ N-(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)-maleimide (HMI-AN) [19–21] has been prepared by using *p*-hydroxyphenylmaleimide (HMI) as a reactive phenol with aniline. It was demonstrated that the introduction of

maleimide enhances the thermal stability and *T_g*. Besides, polymerizable groups such as allyl [20], propargyl [20] and nitrile [27] have been introduced into maleimidobenzoxazine. The corresponding polymers with high crosslinking show improved thermal stability and higher *T_g*. The maleimidobenzoxazine monomer with nitrile functionality can be cross-linked by cyclotrimerization of nitrile catalyzed by Lewis acid.

Polymers functionalized with benzocyclobutene (BCB) have drawn much attention for their excellent thermal stability and dielectric performance [28–30]. BCB based polymers have been especially applied in integrated circuit packaging, MEMS packaging, etc. BCB ring can be converted to conjugated diene structure at proper temperature and undergoes radical polymerization or Diels–Alder reaction. In this paper, BCB ring as a polymerizable group was introduced in the maleimidobenzoxazine monomer to enhance the performance of BOZ resins. We originally synthesized monomer with multifunctional groups containing maleimide, BCB and BOZ. So the monomers can be cured at proper temperature to prepare highly cross-linked resins. These resins demonstrate improved heat resistance, thermal properties, and thermomechanical properties compared with the BOZ resins reported.

2. Experimental section

2.1. Materials

4-Bromobenzocyclobutene (BrBCB, 97%) was purchased from Chemtarget Technologies Co., Ltd. *p*-Hydroxyphenylmaleimide

* Corresponding author. Tel.: +86 21 65642110; fax: +86 21 65103056.

E-mail address: feixiao@fudan.edu.cn (F. Xiao).

(HMI), dioxane, dichloromethane, paraformaldehyde, anhydrous sodium sulfate and sodium carbonate were used as received. Aniline (AN) was purified by vacuum distillation. 4-Aminobenzocyclobutene (AMBCB) was prepared by aminating of BrBCB with ammonia–water according to the literature else [31]. HMI–AN was prepared according to the literature [21].

2.2. Characterization

^1H NMR and ^{13}C NMR spectra were recorded with a Bruker DMX–500 Spectrometer using CDCl_3 as solvent. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna–IR 550 II FTIR spectrophotometer operating at a resolution of 4 cm^{-1} . The samples for FTIR test were prepared by KBr pellet method. Thermal gravimetric analysis (TGA) was performed on a Shimadzu DTG–60H simultaneous DTA–TG apparatus with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Differential scanning calorimetry (DSC) was measured on a TA Q200 calorimeter. Dynamic mechanical analysis (DMA) was carried out on a TA Q800 instrument by the 3-point bending method at a heating rate of $3\text{ }^\circ\text{C min}^{-1}$ with the test frequency at 1 Hz.

2.3. Preparation of monomer

N-(3-(Benzocyclobutene-4-yl)-3,4-dihydro-2H-benzo[*e*] [1,3]oxazin-6-yl)-maleimide (HMI–AB). AMBCB (1.19 g, 10 mmol), paraformaldehyde (0.60 g, equal to 20 mmol formaldehyde), HMI (1.89 g 10 mmol) and dioxane (30 mL) was added in a 50 mL single necked round-bottomed flask equipped with a PTFE-coated magnetic stir bar and a reflux condenser. The solution was stirred and heated to reflux for 12 h, and the turbid solution became transparent with light yellow. After cooling down to room temperature, the solution was condensed on a rotary evaporator and the crude product was obtained. The crude product was then dissolved in 50 mL dichloromethane and washed with 20% Na_2CO_3 solution for 3 times and then with deionized water until neutral. The dichloromethane solution was separated and dried over anhydrous sodium sulfate for 12 h, and then filtered, concentrated and dried under vacuum to give 2.52 g HMI–AB in 76% yield. ^1H NMR (500 MHz, CDCl_3): 3.07 (s, 4H), 4.61(s, 2H), 5.33(s, 2H), 6.82(s, 2H), 6.84–7.27 (m, 6H).

2.4. Preparation of the thermosetting resin

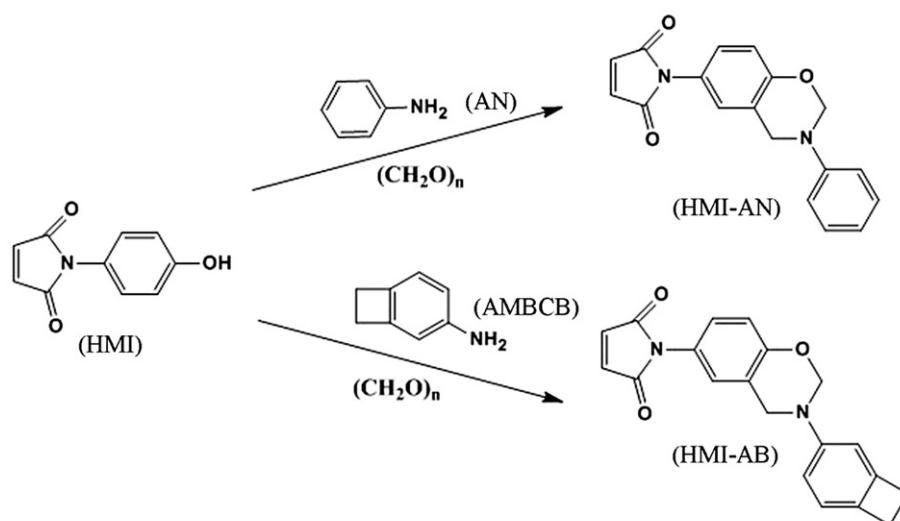
The prepared monomers existed as powders at room temperature were placed into glass–plate molds ($40\text{ mm} \times 20\text{ mm} \times 2\text{ mm}$). After degassing in a vacuum oven at $130\text{ }^\circ\text{C}$ for an hour with an approximate pressure at 0.01 MPa, the molds were then heated at $150\text{ }^\circ\text{C}$ for 2 h, then at 180, 200, 220, 240 and $260\text{ }^\circ\text{C}$ for 1 h, respectively. After cooled to room temperature, the thermosetting resins were polished as rectangular bars with a size of $30\text{ mm} \times 13\text{ mm} \times 2\text{ mm}$ for DMA test.

3. Results and discussion

3.1. Preparation and characterization of BCB–functionalized BOZ

The novel hybrid monomer HMI–AB was prepared by the reaction of HMI and paraformaldehyde with AMBCB as shown in Scheme 1. HMI–AN as control sample was prepared by HMI and paraformaldehyde with aniline for comparison. Both monomers are soluble in many common organic solvents such as acetone, chloroform, ethyl acetate, dioxane, tetrahydrofuran.

Fig. 1 shows the ^1H NMR spectra of HMI–AB and HMI–AN. As to HMI–AN, the characteristic protons of the oxazine ring appeared as two singlets at 4.66 and 5.37 ppm assigned to $\text{Ar}-\text{CH}_2-\text{N}-$ and $-\text{O}-\text{CH}_2-\text{N}-$, respectively. The singlet at 6.82 ppm was assigned to the protons of $-\text{CH}=\text{CH}-$ in the maleimide structure. The multiplets at 6.84–7.37 ppm were assigned to protons of the aromatic ring. As to HMI–AB, the characteristic protons of the oxazine ring appeared as two singlets at 4.61 and 5.33 ppm. The characteristic protons of maleimide structure appeared at 6.82 ppm, and the multiplets at 6.84–7.27 ppm were assigned to protons of the aromatic rings. The singlet at 3.07 ppm was attributed to the methylene protons of the four-membered ring of BCB. The ^1H NMR spectra established the structures of HMI–AN and HMI–AB. The structure of monomer HMI–AB was confirmed by ^{13}C NMR (shown in Fig. 2). The peak at 29.17 ppm was assigned to the methylene of the four-membered ring of BCB. The characteristic carbon resonances of the oxazine ring appeared at 51.22 ppm for $\text{Ar}-\text{C}^*\text{H}_2-\text{N}-$ and at 80.84 ppm for $\text{N}-\text{C}^*\text{H}_2-\text{O}-$, respectively. The strong resonance at 134.14 ppm corresponded to the olefinic carbons of maleimide, and 169.78 ppm was attributed to the carbonyl carbons of maleimide.



Scheme 1. Preparation of the maleimidobenzoxazine monomers from different aromatic amines.

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