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Synthesis of a novel benzoxazine containing benzoxazole structure

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Abstract

A high-purity benzoxazine (Boz-BOA) containing benzoxazole structure was successfully synthesized by three-step synthetic method using 2-(4-aminophenyl)-1*H*-benzoxazole-5-amine (BOA) and *ortho*-hydroxybenzaldehyde. The structure of Boz-BOA was confirmed by FTIR and ¹H NMR spectra. The DSC was utilized to probe the curing behavior of Boz-BOA and exhibited a narrow melting peak and curing exothermic peak.

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Keywords: Benzoxazine; Benzoxazole; Synthesis; Characterization

Recently, a novel class of thermosetting resins called polybenzoxazines (PBZs) has received much attention due to their fascinating properties, such as high modulus, high glass transition temperature (T_g), low water absorption [1], low surface energy [2], near-zero volumetric shrinkage [3,4] and no volatile release upon curing [5]. Although PBZs are expected for applications in harsh conditions due to good properties, the thermal properties were still not good enough. A lot of works were struggling to improve PBZs' thermal stability. An effective method for the thermal stability enhancement is the preparation of specially designed novel monomers containing other polymerizable groups such as propargyl ether [6], allyl [7] and nitrile [8]. This way successfully improved their glass transition temperature (T_g) and decomposition temperature due to the increasing crosslink densities of PBZs. However, the materials contain special groups, such as propargyl ether [6], were usually prepared difficultly.

According to Low's study [9], aniline fragments were volatilized during the decomposition of PBZs firstly. Therefore, the introduction of aniline segments to cross-linking networks is an effective way to improve PBZs' thermal stability. Benzoxazines based on diamine exhibited good thermal properties because aniline segments were introduced to cross-linking networks by their own spacers [10]. However, high-purity diamine-based benzoxazines were synthesized difficultly by traditional method due to the byproducts during reaction and the poor solubility of diamine. Moreover, the byproducts, such as methylol group and triazas, in diamine-based benzoxazines were synthesized by traditional method would release volatile upon curing and impair the thermal properties of PBZs [11,12].

In general, the more rigid of a polymer chain is, the higher T_g value is. So an effective way for increasing T_g is the introduction of rigid structures to polymer. This work concentrates on the synthesis of a high-purity aromatic

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Scheme 1. Synthesis of Boz-BOA: (a) DMAC, 50 °C; (b) NaBH₄, ethanol; (c) 1,4-dioxine and DMF, 85 °C.

diamine-based benzoxazine containing benzoxazole structure (Boz-BOA). By incorporating benzoxazole structure as a rigid structure into the benzoxazine, we expected to form a polybenzoxazine with better thermal stability. High-purity Boz-BOA was synthesized successfully using 2-(4-aminophenyl)-1*H*-benzoxazole-5-amine (BOA) and *ortho*-hydroxybenzaldehyde.

1. Experimental

Ortho-hydroxybenzaldehyde (24.4 g, 0.2 mol), BOA (24.4 g, 0.1 mol) and *N*,*N*-dimethylacetamide (DMAc) (120 mL) were introduced into a 250 mL three-neck flask under a nitrogen atmosphere. The mixture was stirred at 50 °C for 4 h. After the mixture cooling to room temperature, the precipitate was filtered and dried in a vacuum oven at 150 °C for 2 h. Brick red powder (42.4 g, 98% yield) with a melting of 267 °C (DSC) and a melting enthalpy of 108 J/ g. FTIR (KBr): 1616 cm⁻¹ (C=N stretch), 3404 cm⁻¹ (OH stretch).

Boz-1 (21.7 g, 0.05 mol) and ethanol (120 mL) were introduced into a 250 mL three-neck flask with a nitrogen inlet and a magnetic stirrer. 5.7 g (0.15 mol) of sodium borohydride (NaBH₄) was added portions while the mixture was stirred. After 12 h, the mixture was poured into de-ionized water (500 mL) and the precipitate was filtered and dried in a vacuum oven at 105 °C for 2 h. 21.6 g (99% yield) of chrysoidine powder with a melting peak of 208 °C (DSC) was obtained. ¹H NMR (400 MHz, DMSO- d_6): δ 4.22 (d, 2H, -NH-CH₂-Ar–), 4.27 (d, 2H, -NH-CH₂-Ar–), 5.89 (t, 2H, Ar–NH-CH₂–), 6.03 (t, 2H, Ar–NH-CH₂–), 9.57 (d, 2H, -Ar–OH), 6.61–7.81 (15H, Aromatic *H*). FTIR (KBr): 1272 cm⁻¹ (C–N stretch), 1522 cm⁻¹ (N–H bending), 3409 cm⁻¹ (N–H stretch), 3200–3500 cm⁻¹ (OH stretch).

Boz-2 (16.4 g, 0.04 mol), paraformaldehyde (2.64 g, 0.088 mol), 1,4-dioxine (100 mL) and *N*,*N*-dimethylformamide (DMF) (10 mL) were introduced into a 250 mL three-neck flask. The mixture was stirred at 85 °C for 8 h. After the mixture was cooled to room temperature, the precipitate was filtered and dried in a vacuum oven at 140 °C for 2 h. 15.6 g (86% yield) of saffron powder with a melting of 204–206 °C (micro-melting point apparatus) and a curing peak temperature of 267 °C was obtained. ¹H NMR (400 MHz, DMSO-*d*₆): δ 4.69 (s, 2H, –N–CH₂–Ar–), 4.78 (s, 2H, –N– CH₂–Ar–), 5.48 (s, 2H, –N–CH₂–O–), 5.55 (s, 2H, –N–CH₂–O–), 6.71–8.01 (15H, Aromatic *H*). FTIR (KBr): 927 and 943 cm⁻¹ (oxazine), 1034 cm⁻¹ (Ar–O–C symmetric stretch), 1225 cm⁻¹ (Ar–O–C asymmetric stretch), 1373 cm⁻¹ (C–N stretch).

2. Results and discussion

Because of the poor solubility of BOA and the formation of gelation between BOA and paraformaldehyde, highpurity Boz-BOA was not synthesized by traditional method. In this work, both of them were well solved and highpurity Boz-BOA was successfully synthesized by three-step synthetic method (Scheme 1). In the first step, Boz-1 was synthesized by *ortho*-hydroxybenzaldehyde and BOA. The ¹H NMR spectra of Boz-1 was not showed because Boz-1 could dissolve in neither CHCl₃ nor DMSO well.



Fig. 1. ¹H NMR spectra (DMSO- d_6) of Boz-2 (a) and Boz-BOA (b).



Fig. 2. DSC curve for Boz-BOA at the heating rate of 10 $^\circ\text{C/min}$ in N_2.

In the second step, the imine linkage of Boz-1 was reduced by NaBH₄ at room temperature, while the benzoxazole structure should be preserved. The ¹H NMR spectra of Boz-2 and the assignment were showed in Fig. 1, the signals at 5.89 and 6.03 ppm assigned to Ar–NH–CH₂– which confirmed the reduction imine linkage. Additionally, the benzoxazole structure was preserved successfully, because there were no other signals in its ¹H NMR spectra.

In the third step, *N*,*N*-dimethylformamide (DMF) was added to 1,4-dioxine as a cosolvent because of the partial solubility of Boz-2 in 1,4-dioxine. Interestingly, the resonances of the oxazine ring appeared with two groups of singlets at 5.48 and 4.69 ppm, 5.55 and 4.78 ppm due to its asymmetry structure which assigned to $-O-CH_2-N-$ and Ar-CH₂-N-, respectively. Besides, two characteristics absorptions at 927 and 943 cm⁻¹ were observed in IR, also confirming the asymmetry structure. No signals at around 4.0 ppm resulting from the ring opening of benzoxazines was appeared [13], revealing the high-purity of Boz-BOA. Furthermore, the melting point of Boz-BOA was in the range of 204–206 °C obtained from micro-melting point apparatus, which illuminated the high-purity.

Fig. 2 shows the DSC curve of Boz-BOA. The melting point of Boz-BOA was 208 °C, while the exothermic curing peak temperature was 267 °C and the exothermic enthalpy was 338 J/g. The residual phenolic OH and methylol group that remained in benzoxazine on account of the difficulty of the purity broaden the exothermic curing peak. However, in this case, the exothermic curing peak exhibited narrow windows, demonstrating the high-purity of Boz-BOA [14,15]. As the result, Boz-BOA has been achieved successfully and further detailed study on Boz-BOA will be reported later.

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References

- [1] H. Ishida, D.J. Allen, J. Polym. Sci. B: Polym. Phys. 34 (1996) 1019.
- [2] C. Wang, Y. Wang, P. Tung, F. Chang, et al. Langmuir 22 (2006) 8289.
- [3] H. Ishida, H.Y. Low, Macromolecules 30 (1997) 1099.
- [4] X. Liu, Y. Gu, J. Appl. Polym. Sci. 84 (2002) 1107.
- [5] X. Ning, H. Ishida, J. Polym. Sci. A: Polym. Chem. 32 (1994) 1121.
- [6] T. Agag, T. Takeichi, Macromolecules 34 (2001) 7257.
- [7] T. Agag, T. Takeichi, Macromolecules 36 (2003) 6010.
- [8] Z. Brunovska, R. Lyon, H. Ishida, Thermochim. Acta 195 (2000) 257.
- [9] H.Y. Low, H. Ishida, Polymer 40 (1999) 4365.
- [10] H. Xiang, H. Ling, J. Wang, et al. Polym. Compos. 26 (2005) 563.

- [11] Z. Brunovska, J.P. Liu, H. Ishida, Macromol. Chem. Phys. 200 (1999) 1745.
- [12] C.H. Lin, S.L. Chang, C.W. Hsieh, et al. Polymer 49 (2008) 1220.
- [13] D.J. Allen, H. Ishida, Polymer 48 (2007) 6763.
- [14] P. Velez-Herrera, K. Doyama, H. Abe, et al. Macromolecules 41 (2008) 9704.
- [15] C. Chang, C. Lin, H. Lin, et al. Eur. Polym. J. (2009) 680.