



The catalytic mechanism of benzoxazine to the polymerization of cyanate ester



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HIGHLIGHTS

- Two model compounds, PA and s-PA, were successfully synthesized and purified.
- There is no phenolic hydroxyl in the final ring-opened structures of s-PA.
- Compared with PA, s-PA also can catalyze the polymerization of BADCy.
- The main catalytic process is caused by the oxygen anion.
- The catalytic effect from the phenolic hydroxyl is a secondary factor.

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ABSTRACT

Two model compounds, 3-Phenyl-3,4-dihydro-2H-1,3-benzoxazine (PA) and 6,8-dimethyl-3-(2,4,6-trimethyl-phenyl)-3,4-dihydro-2H-1,3-benzoxazine (s-PA), were successfully synthesized and purified. Compared with PA, s-PA also catalyzed the polymerization of BADCy even though there was no phenolic hydroxyl in its final ring-opened structures. It was confirmed that the real mechanism of benzoxazine catalyzing the polymerization of cyanate ester is the nucleophilic addition reaction of the oxygen anion on ring-opened benzoxazine to the positively charged carbon atom on cyano group. The catalytic effect also contains the contribution from the phenolic hydroxyl, but it is a secondary factor.

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1. Introduction

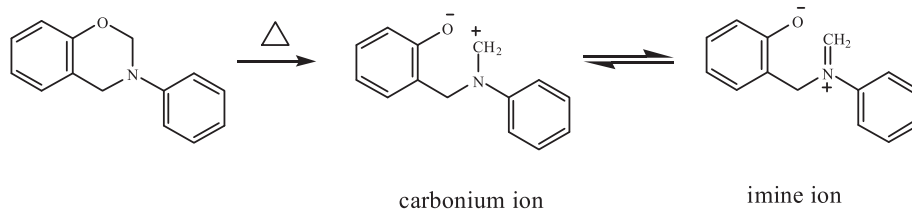
Polybenzoxazine (PBOZ) is a novel thermosetting resin [1]. Based on the research of the curing mechanism of benzoxazine [2–8], it has been known that benzoxazine successively undergoes the ring-opening reaction and electrophilic substitution reaction in the curing process. Firstly, the oxazine ring opens to form ion-pair isomers (Scheme 1). Then the carbonium ion is easy to attack the positions of higher charge density on the benzene ring or the oxygen anion. Therefore, benzoxazine with different structures finally

forms three crosslinked structures, containing phenolic Mannich bridge structure (Fig. 1, structure A), arylamine methylene bridge structure (Fig. 1, structure B) and aryether Mannich bridge structure (Fig. 1, structure C)

Currently, this resin family is seeking to combine its good flame retardance with the excellent thermal and dielectric properties of advanced cyanate ester resin. Studies on the co-curing process of benzoxazine-cyanate ester blending system have showed that the polymerization of cyanate ester can be proceeded at a much lower temperature [9]. According to the polymerization mechanism of cyanate ester, those compounds containing active hydrogen, like phenol, could be used as catalysts [10]. Therefore, it is generally considered the catalytic effect in the benzoxazine-cyanate ester system is from the generated phenolic hydroxyl after the ring-opening of benzoxazine [11,12]. The deduced catalytic mechanism

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Scheme 1. Thermal ring-opening reaction of benzoxazine.

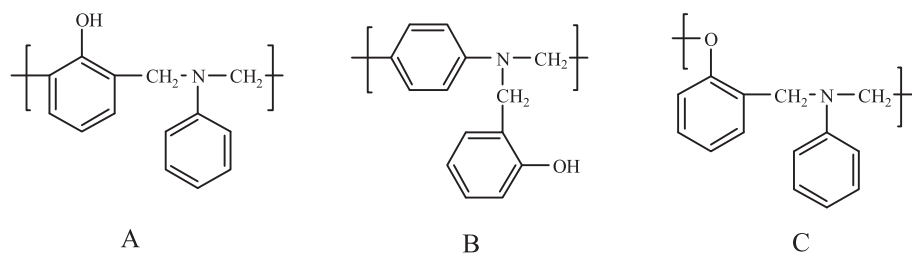


Fig. 1. Three structure types of polybenzoxazine.

is the active hydrogen attacks the nitrogen atom on cyano group, which is shown in [Scheme 2](#).

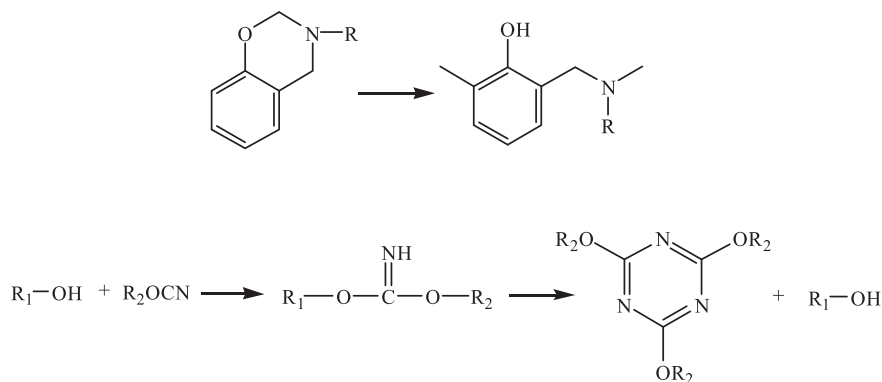
However, it has not been proved whether the catalysis of benzoxazine to cyanate ester can take effect before the formation of the phenolic hydroxyl? And the catalytic mechanism is yet unclear. It is necessary to take a more detailed study on the fundamental catalytic mechanism between benzoxazine and cyanate ester. In this work, two model compound, 6,8-dimethyl-3-(2,4,6-trimethyl-phenyl)-3,4-dihydro-2H-1,3-benzoxazine (s-PA) and 3-Phenyl-3,4-dihydro-2H-1,3-benzoxazine (PA), were synthesized. After the ring-opening reaction, the differences on the structures of PA and s-PA led to different crosslinked structures. On this basis, the catalytic mechanism of benzoxazine to the

polymerization of cyanate ester was investigated through the comparative study of s-PA and PA.

2. Experimental

2.1. Materials

The following chemicals: phenol, aqueous formaldehyde solution (34%), aniline, toluene, sodium hydroxide, ethyl alcohol, and 2,4-bimethyl phenol were purchased from the Chengdu Kelong Chemical Reagents Corp (China). 2,4,6-trimethyl aniline was purchased from Aladdin Chemistry Co. Ltd (China). Dicyanate of bisphenol A (BADCy) was provided by Wuqiao resin plant. All



Scheme 2. The polymerization of cyanate ester catalyzed by the phenolic hydroxyl generated from the ring-opened benzoxazine.

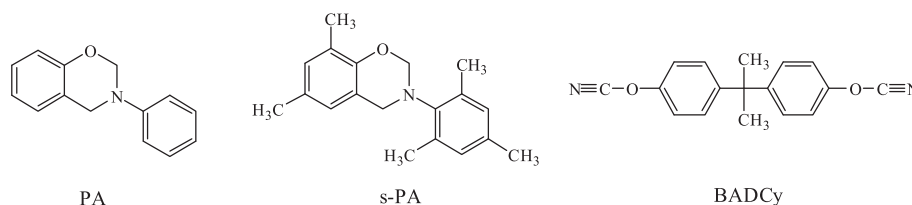


Fig. 2. The chemical structures of PA, s-PA and BADCy.

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