



Effects of aromatic diboronic acid on thermal characteristics of polybenzoxazines based on phenol and aniline

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ABSTRACT

In this work, polybenzoxazines based on phenol and aniline were prepared by curing as-synthesized and purified monomers in the presence of aromatic diboronic acid, BDBA. Condensation reactions between BOH groups of diboronic acid and phenolic OH groups of benzoxazine took place during curing only when unreacted phenol, or low mass oligomers were present in the medium. Generation of fragments involving B-O-C groups and significant improvement in thermal characteristics were detected upon curing the as-synthesized monomer in the presence of even 5 wt % BDBA. On the other hand, enhancement in thermal characteristics was not detected for the polybenzoxazine prepared by curing the purified monomer, when the wt % of BDBA was lower than 15%.

1. Introduction

During last decades, the studies on modification of polybenzoxazines as an attractive alternative to epoxies and traditional phenolic resins have been increased almost exponentially not only for defense and aerospace but also for electronic industrial and technological applications. The features of these polymers such as no requirement for harsh catalysts, high thermal stability, excellent electrical properties and molecular design flexibility and low melt viscosity make this class of polymers a promising candidate for high performance composites [1–8]. Several benzoxazine monomers either in solution or in melt state can easily be prepared from reactions of various types of amines, phenolic derivatives and formaldehyde [9–14]. Therefore, the molecular design flexibility of benzoxazines eases that certain desired properties synthesis. The polybenzoxazines are obtained by step-wise curing of the monomers via mainly thermally activated ring-opening reaction to form a Mannich base bridge. However, some limitations on their use in practical applications exist as the monomers are usually powder and processing into thin films is rather difficult. Additionally, the formed polymers are brittle as a consequence of the short molecular weight of the network structure. Another problem is the high curing temperatures. In order to overcome the problems related with polybenzoxazine and improve thermal and mechanical properties, polybenzoxazine composites involving transition metals, graphite, montmorillonites, and carbon nanotubes were prepared [15–27].

Few studies focused on polybenzoxazine composites involving

boron compounds also appeared in the literature [28–35]. Nanocomposites of polybenzoxazines based on bisphenol A and aniline involving boron carbide with improved mechanical and thermal properties were prepared [31]. Recently, poly(bisphenol A borate) with excellent thermal resistance and high char yield was synthesized by using bisphenol A and boric acid [32]. In another study, polybenzoxazines prepared using benzoxazine precursors bearing carborane moiety were synthesized. It has been determined that incorporation of carborane moiety endowed the benzoxazine resins with excellent thermal and thermo-oxidative stabilities [33]. Recently, polybenzoxazines modified with phenyl boronic acid, PBA, were prepared and characterized. It has been determined that the incorporation of PBA not only accelerated the ring-opening polymerization of benzoxazine monomer, leading to the lower curing temperature but also increased thermal stability and char yield of the polybenzoxazine significantly [34].

It can be thought that the use of benzene diboronic acid, BDBA, instead of phenyl boronic acid should improve thermal characteristics further. Thus, our main objective was to prepare composites of polybenzoxazines based on phenol and aniline by curing the monomer in the presence of aromatic diboronic acid. However, preliminary results indicated no significant improvement in thermal characteristics of the polybenzoxazine prepared even in the presence of 15 wt% BDBA, although generation of boraxine net-work was detected. In the light of our previous experience, we decided to use instead of purified benzoxazine monomer, as-synthesized monomer involving dimer and low

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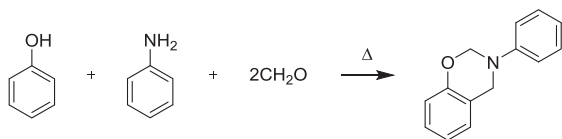
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Scheme 1. Synthesis of benzoxazine monomer based on aniline and phenol.

mass oligomers as by-products. In this work we discuss the influence of aromatic diboronic acid on polybenzoxazines prepared curing as-synthesized and purified monomers in the presence of various amounts of BDBA.

2. Experimental

2.1. Materials

Phenol (99.5%), paraformaldehyde, sodium hydroxide and chloroform were purchased from Sigma Aldrich Co. Aniline, hexane, ethyl acetate, MgSO_4 were supplied by Merck. All chemicals were used as received without further purification.

2.2. Synthesis of benzoxazine monomer (aBz and pBz) and polymers (PaBz and PpBz)

Benzoxazine monomer was synthesized according to the literature method from phenol, aniline and paraformaldehyde via solventless method as shown in Scheme 1 [2]. The mixture of phenol (5 mmol), aniline (5 mmol), and paraformaldehyde (10 mmol) was stirred at 110 °C for 1–1.5 h. Subsequently, the viscous liquid was cooled to about 50 °C, and about 30 mL chloroform was gradually introduced into the flask. Then, the chloroform solution was poured into a separatory funnel and washed three times with NaOH aqueous solution (3 mol/L) and deionized water, respectively. The chloroform solution was dried over anhydrous MgSO_4 and the solvent was removed under reduced pressure. The light orange residue was named as as-synthesized benzoxazine monomer, aBz. The residue was fractionation of crude monomer by silica gel column chromatography using hexane/ethyl acetate mixture as an eluent yielded pure benzoxazine monomer pBz as a yellow solid.

Benzoxazine monomers based on phenol and aniline cured at 150, 175 and 200 °C for 1 h each in vented oven. Reddish brown colored as-synthesized polymer (PaBz) and pure polymer (PpBz) were obtained.

The resonances at 4.64 and 5.60 ppm correspond to the methylene protons (H1 and H2) of Ar-CH₂-N and O-CH₂-N of the oxazine ring, respectively. The chemical shifts (ppm) at 6.79 (1H, H12), 6.82 (1H, H6), 6.88 (1H, H7), 6.90 (1H, H5) 7.02 (2H, H10 and H14), 7.12 (1H, H4), and 7.26 (2H, H11 and H13) are assigned to the aromatic protons. The crude monomer has broader peaks in the proton NMR spectrum. The resonances at 50.45 and 79.51 ppm correspond to the methylene carbons (C1 and C2) of Ar-CH₂-N and O-CH₂-N of the oxazine ring, respectively. Other chemical shifts (ppm) are assigned to the resonances of the carbons: 117.08 (C7), 118.31 (C10, C14), 120.85 (C5), 120.95 (C12), 121.48 (C3), 126.78 (C6), 127.91 (C4), 129.36 (C11, C13), 148.45 (C9), 154.45 (C8).

2.3. Preparation of polybenzoxazine/BDBA composites (PaBz/BDBA and PpBz/BDBA)

For the preparation of polybenzoxazine composites involving 5 or 20 wt% BDBA, firstly, BDBA was dispersed in 3 mL of N-methylpyrrolidone (NMP) and refluxed at 80 °C for 1–2 h. Then crude or pure benzoxazine monomer is dispersed in the solution. The blends were casted on glass plate. After drying at 80 °C for 2 h under vacuum, the films were cured step-wise at 150, 175 and 200 °C for 1 h each in vented oven. The polybenzoxazine/BDBA (PaBz/BDBA and PpBz/BDBA)

composites obtained were transparent reddish-brown colored.

2.4. Characterization

Proton NMR spectra were acquired with a Bruker AC250 (250.133 MHz) spectrometer using CDCl_3 as the solvent and tetramethylsilane (TMS) as the internal standard. ATR-FT-IR analysis of the samples was performed by directly insertion of solid sample using Bruker Vertex 70 Spectrophotometer with 0.4 cm^{-1} resolution. TGA and DSC analyses were performed on a Perkin Elmer Instrument STA6000 under nitrogen atmosphere at a flow rate of 20 mL/min and a heating rate of 10 °C/min. Direct pyrolysis mass spectrometry, DP-MS, analyses were performed by a triple quadrupole Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 10–1500 Da coupled to a direct insertion probe. During the pyrolysis, the temperature was increased to 50 °C at a rate of 5 °C/min, then, was raised to 650 °C with a rate of 10 °C/min and kept at 650 °C for 5 additional minutes. 0.01 mg samples were pyrolyzed in the flared quartz sample vials while recording 70 eV EI mass spectra at a mass scan rate of 1 scan/s. The analyses were repeated several times to assess reproducibility. Each time, almost exactly the same trends were detected.

3. Results and discussions

Although, the NMR and FTIR spectra of both as-synthesized and purified monomers were almost identical, mass spectrum of as-synthesized benzoxazine monomer showed a weak dimer peak ($m/z = 422$ Da) and peaks at 316 Da due to loss of $\text{CH}_2\text{NHC}_6\text{H}_5$ from dimer and indicating presence of dimer and most probably low mass oligomers as by-products (Fig. 1). On the other hand, the mass spectrum of purified monomer is in accordance with expected fragmentation pattern for benzoxazine monomer based on phenol and aniline, showing

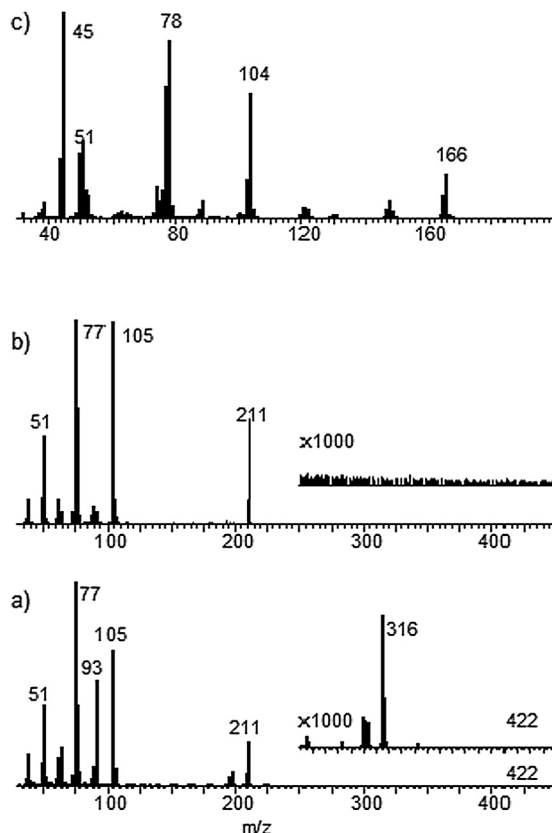


Fig. 1. Mass spectra of (a) as-synthesized (b) purified benzoxazine monomer based on phenol and aniline.

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