



# Metal ion functional polybenzoxazine based on phenol and 2-aminopyridine



Tugba Orhan Lekesiz, Jale Hacıoğlu\*

Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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## ABSTRACT

A novel  $\text{Co}^{2+}$  ion functional benzoxazine monomer based on phenol and 2-aminopyridine was prepared, polymerized by step-wise curing and characterized via direct pyrolysis mass spectrometry in addition to classical spectrometry techniques. Curing of neat monomer yielded a highly cross-linked polymer as a consequence of competing and consecutive reactions involving the heterocyclic ring opening followed by attack of  $-\text{NCH}_2$  groups to ortho and para positions of phenol and pyridine rings and coupling of  $-\text{NCH}_2$  groups. On the other hand, the coordination of metal ion to nitrogen atoms of the pyridyl rings inhibited the attack of  $-\text{NCH}_2$  groups to ortho and para positions of pyridine rings and eventually decreased the extent of cross-linking.

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## 1. Introduction

Polybenzoxazines as a new class of polymeric resin possessing various advantageous that overcome the limitations of conventional phenolic and epoxy resins, have received significant attention both academically and industrially. They exhibit excellent properties such as a high thermal stability, high glass transition temperature, high modulus, low water absorption, low dielectric constant, and near-zero shrinkage upon curing [1–8]. Their facile and versatile syntheses from relatively abundant materials involving phenols, amines, their functional analogs and formaldehyde offer enormous design flexibility opportunity. Various benzoxazines bearing functional groups such as acetylene [9,10], nitrile [11–14], allyl [15], propargyl [16] or involving nanoparticles [17–20] were prepared to improve mechanical and thermal properties.

Few studies also appeared in the literature, concentrated on incorporation of transition metal ions into polybenzoxazine matrices not only to improve thermal properties but also to provide new potential applications in optics, catalysis, biosensors, microelectronics and magnetic data storage [21–22]. Low and Ishida discussed the incorporation of various transition metal salts and determined that the presence of transition metal salt increases char formation of polybenzoxazines independent of the amine and phenol structures. Actually, in their study coordination of metal ion

to host polymer was not aimed. Recently, Kawaguchi and his co-workers, in a detail study on synthesis and polymerization of a benzoxazine monomer bearing 4-pyridyl moiety on the nitrogen atom claimed efficient capturing of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  ions as a consequence of formation of insoluble colored precipitates [22]. However, characterization of the resulting metal ion coordinated polymer was not discussed.

In this study, synthesis of a novel type of polybenzoxazine coordinated to cobalt metal ion was achieved. Considering the possibilities of generation of various side products due to the higher reactivity of 4-aminopyridine and intramolecular hydrogen bonding with phenol groups, 2-aminopyridine was selected as the amine group for the synthesis of the benzoxazine monomer. For this purpose, firstly, the benzoxazine monomer bearing 2-pyridyl functional group was synthesized, purified and characterized. Then, the monomer was coordinated to  $\text{Co}^{2+}$  ions through the nitrogen atom on the pyridine ring. Finally, the effects of coordination to metal ion on structural and thermal characteristics of the polybenzoxazine generated by curing were investigated via direct pyrolysis mass spectrometry in addition to classical techniques such as TGA and DSC.

## 2. Experimental

### 2.1. Materials

Phenol (99.5%), paraformaldehyde, anhydrous cobalt(II) chloride, sodium hydroxide and chloroform were purchased from

\* Corresponding author.

E-mail address: [jale@metu.edu.tr](mailto:jale@metu.edu.tr) (J. Hacıoğlu).

Sigma Aldrich Co. 2-aminopyridine (99.5%) was supplied by Merck. All chemicals were used as received without further purification.

## 2.2. Synthesis of the neat and $\text{Co}^{2+}$ functional benzoxazine monomers

Benzoxazine monomer was prepared according to the literature methods [24]. The mixture of phenol (5 mmol), 2-aminopyridine (5 mmol), and paraformaldehyde (10 mmol) was stirred at 110 °C for 60 min. 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 several times with NaOH aqueous solution (3 mol/L) and deionized water, respectively. The chloroform solution was dried over anhydrous  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. The residue was fractionated by silica gel column chromatography using hexane/ethyl acetate mixture as an eluant to obtain crude benzoxazine as a yellow solid. Contrary to the general applications, purification of the monomer to separate any side product generated by the condensation reaction of formaldehyde with the aromatic units that would inhibit the coordination of metal ion, was highly crucial.

For the coordination of the metal ion, the purified benzoxazine monomer and  $\text{CoCl}_2$ , in 2:1, 1:1 and 1:2 mol ratios, were mixed in chloroform and refluxed for 6 h according to the literature methods [23]. Evaporation of the solvent yielded greenish yellow solid.

## 2.3. Synthesis of the neat and $\text{Co}^{2+}$ functional benzoxazine polymers

Polymerizations of the neat and  $\text{Co}^{2+}$  coordinated benzoxazine monomers were achieved by step-wise curing of the monomers at 170 and 200 °C for 60 min each and 210 °C for 120 min in an oven. The temperatures at which evaporation and/or degradation of monomer take place were determined by gradual heating of the monomer inside the mass spectrometer. The temperatures of the steps of the curing cycle were selected as few centigrades lower than these values. The curing of the monomers was also performed inside the mass spectrometer while recording mass spectra continuously.

## 2.4. Characterization

Proton NMR spectra were acquired with a Bruker AC250 (250.133 MHz) spectrometer using  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. The resonances at 4.88 and 5.61 ppm correspond to the methylene protons (C1 and C2) of Ar-CH<sub>2</sub>-N and O-CH<sub>2</sub>-N of the oxazine ring, respectively. The chemical shifts (ppm) at 6.72 (2H, H10 and H12), 6.90 (3H, H4, H5 and H6), 7.10 (1H, H4), 7.54 (1H, H11) and 8.24 (1H, H13) are assigned to the aromatic protons. The resonances at 46.24 and 75.25 ppm correspond to the methylene carbons (C1 and C2) of Ar-CH<sub>2</sub>-N and O-CH<sub>2</sub>-N of the oxazine ring, respectively. Other chemical shifts (ppm) are assigned to the resonances of the carbons: 108.0 (C10), 115.0 (C7), 117.22 (C12), 121.0 (C5, C3), 126.69 (C6), 127.78 (C4), 137.95 (C11), 148.21 (C13), 154.52 (C9), 157.58 (C8). Anal. calcd. for  $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}$ : C, 73.58; H, 5.66; N, 13.21; O, 7.67%. Found: C, 72.46; H, 5.85; N, 13.29%.

ATR-FT-IR analysis of the samples was performed by directly insertion of solid sample using Bruker Vertex 70 Spectrophotometer with 0.4  $\text{cm}^{-1}$  resolution.

SEM studies of the samples in powder form, fixed on an aluminum stub using carbon tape, were conducted using a scanning electron microscope Quanta 400 F Field Emission SEM instrument.

TGA and DSC analyses (TGA) 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 of the samples (0.010 mg) in flared quartz sample vials were performed on a Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 15–1500 Da coupled to a direct insertion probe. The samples were heated to 650 °C at a rate of 10 °C/min while recording 70 eV EI mass spectra, at a rate of 1 scan/s. The step-wise curing of the monomers and the pyrolysis of the polymers, if generated any, during the curing process were also utilized inside the mass spectrometer while recording the mass spectra continuously at a rate of 1 scan/s. All the analyses were repeated at least twice to ensure reproducibility.

Collision induced dissociation experiments were conducted using argon as the collision gas and 40, 30 and 20 eV EI ionization. The daughter spectra of the precursor ions were recorded at the temperatures at which the yield of the selected precursor ion was maximized. Interpretation of the pyrolysis mass spectra was achieved by analyses of the trends in single ion evolution profiles and precursor-ion spectra.

## 3. Results and discussion

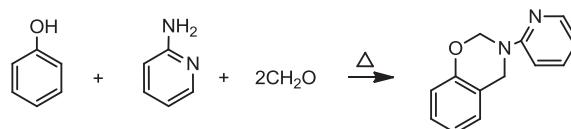
### 3.1. Synthesis of neat and $\text{Co}^{2+}$ functional benzoxazine based on aminopyridine and phenol

Benzoxazine monomer was synthesized from phenol, 2-aminopyridine and paraformaldehyde via solventless method (Scheme 1).

The proton NMR spectrum of the neat benzoxazine is presented in Fig. 1. The strong resonances at 4.88 and 5.61 ppm correspond to the methylene protons (C1 and C2) of Ar-CH<sub>2</sub>-N and O-CH<sub>2</sub>-N of the oxazine ring, respectively. The resonance signals (labeled 3 and 4) in the range of 6.90–7.54 ppm are typical region for the phenyl ring. In addition, the signals at around 6.71, 7.53 and 8.35 ppm (labeled 5, 6 and 7 respectively) are attributed to the protons of the pyridyl ring.

The FTIR spectrum of the benzoxazine monomer is shown in Fig. 2a. Typical absorption bands for the benzoxazine are observed at 1480, 1380, 1230, 1033 and 946  $\text{cm}^{-1}$ , corresponding to the disubstituted benzene rings, CH<sub>2</sub> wagging, Ar-O-C antisymmetric stretching, C-O-C symmetric stretching and vibration modes of cyclic substituted benzene rings, respectively. The absorptions at 1597, 1584 and 1564  $\text{cm}^{-1}$  are assigned to the C-H stretching vibrations and the ones at 1436 and 947  $\text{cm}^{-1}$  are associated to C=N and C-N stretching vibrations of the pyridine ring. Thus, the NMR and FTIR spectra for the monomer are in good agreement with the expected chemical structure.

The intensities of the peaks due to pyridine stretching and bending modes at 1597, 1436 and 947  $\text{cm}^{-1}$  are decreased relative to the absorption bands of phenyl ring in the FTIR spectra of  $\text{Co}^{2+}$  functional benzoxazines supporting the coordination of the metal ion to the electron-rich segment of the benzoxazine monomers, the nitrogen atom in the pyridine rings (Fig. 2b i and ii). The decrease becomes more significant as the  $\text{Co}^{2+}$ /monomer mole ratio



Scheme 1. Synthesis of benzoxazine monomer based on phenol and 2-aminopyridine.

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