



Effects of curing on structure and thermal characteristics of polybenzoxazine based on *p*-nitroaniline



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ABSTRACT

Among the polybenzoxazines, nitroaniline based benzoxazine polymers are not popular for which the polymerization process overlaps with the beginning of the thermal degradation. Phenol and *p*-nitroaniline based benzoxazine monomer was synthesized and polymerized by applying different temperatures and curing periods systematically to investigate the effect of curing program on polymerization mechanisms via direct pyrolysis mass spectrometry, DP-MS technique. In order to get a better insight on the process, low energy DP-MS analysis was also performed and the results showed that the polymerization of nitroaniline based benzoxazine mainly proceed via attack of NCH₂ groups to the phenol ring, contrary to the opposing reaction pathways suggested for benzoxazine based on aniline and the radicals generated by elimination of nitroaniline during curing and/or pyrolysis combined to form unsaturated linkages, resulting a very high char yield.

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1. Introduction

Traditional phenolic resins are widely used in electronics, aerospace and other industries due to their good heat resistance, low flammability, electrical insulation and dimensional stability [1–4]. Among these attractive properties, they have a number of shortcomings such as brittleness, necessity of use of acid or base catalysts and generation of by-products during curing causing some environmental problems [5,6]. Polybenzoxazines are a class of thermosetting phenolic resins that are connected by a Mannich bridge (–CH₂–N(R)–CH₂–) instead of methylene (–CH₂–) bridge associated with the traditional phenolics. Polybenzoxazines have been developed to overcome the shortcomings of traditional phenolic resins such as releasing condensation by-products and using acid or base catalysts for polymerization [7,8]. They provide additional characteristics that are not found in traditional phenolics such as; excellent dimensional stability, low water absorption and stable dielectric properties [7,9–16].

The oxazine ring opens into a phenolic structure linked by a Mannich base upon curing and polymerization mainly proceeds via attack of NCH₂ groups to phenol ring. However, polymerization by

different reaction pathways was also proposed [10,17,18]. In general, the thermal polymerization of benzoxazine monomers was achieved at around temperatures corresponding to the exothermic ring opening polymerization peak in the differential scanning calorimetry, DSC, curve. In most cases, a multi-step curing program was selected by trial and error method without any scientific reasoning. On the other hand, the polymerization process often overlaps with the beginning of the degradation because of the high temperatures required [6,19–21]. It has been found that series of polybenzoxazines based on aniline and various phenolic derivatives, the onset of the thermal cleavage of Mannich base, occurs at approximately 260 °C almost independent of the variation of amines and phenolic derivatives. However, the char yield ranged from 30 to 70% depending on the amine or phenolic derivative used in the synthesis of the benzoxazine monomer.

It may be thought that certain polymerization routes may be predominant under certain curing conditions. As thermal degradation mechanism depends on the structure of the polymer, investigation of thermal characteristics, especially thermal degradation products and mechanism of polybenzoxazines prepared by different curing programs, should also supply valuable information for polymerization mechanism. Eventually, polymerization pathways and degree of crosslinking can be controlled to prepare polybenzoxazines with desired properties.

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Consequently, the aim of this work is to investigate the effects of curing program used for polymerization of benzoxazine monomer based on nitroaniline, for which the polymerization process overlaps with the beginning of the thermal degradation due to the highly electron withdrawing character of nitro group, on polymerization and thermal degradation mechanisms via direct pyrolysis mass spectrometry, DP-MS technique.

2. Experimental

2.1. Materials

Phenol (99.5%), paraformaldehyde, sodium hydroxide and chloroform were purchased from Sigma Aldrich Co. 4-nitroaniline (99.5%) was supplied by Merck. All chemicals were used as received without further purification.

2.2. Synthesis of 3-(4-nitrophenyl)-3,4-dihydro-2H-1,3-benzoxazine monomer

Benzoxazine monomer was prepared according to the literature methods from phenol, 4-nitroaniline and paraformaldehyde via solventless method as shown in Scheme 1 [5].

The viscous liquid obtained by stirring the mixture of phenol (5 mmol), 4-nitroaniline (5 mmol) and paraformaldehyde (10 mmol) at 140 °C for 60 min, was cooled to about 50 °C and about 30 mL chloroform was gradually added. Then, the solution was poured into a separatory funnel, washed several times with NaOH aqueous solution (3 mol/L) and deionized water, respectively and then dried over anhydrous MgSO₄. After the removal of the solvent under reduced pressure, the residue was fractionated by silica gel column chromatography using hexane/ethyl acetate mixture as an eluent to obtain crude benzoxazine as a yellow-orange solid and characterized by FTIR, NMR and MS techniques (Supplementary materials).

The resonances at 4.75 and 5.42 ppm correspond to the methylene protons (C1 and C2) of Ar-CH₂-N and O-CH₂-N of the oxazine ring, respectively. The chemical shifts (ppm) at 6.88 (2H, C6 and C7), 6.96 (1H, C5), 7.06 (2H, C10 and C14), 7.08 (1H, C4), and 8.15 (2H, C11 and C13) are assigned to the aromatic protons. The resonances at 49.49 and 77.02 ppm correspond to the methylene carbons (C1 and C2) of Ar-CH₂-N and O-CH₂-N of the oxazine ring, respectively. The chemical shifts (ppm) are assigned to the resonances of the carbons: 115.08 (C7), 117.31 (C10, C14), 120.07 (C5), 121.62 (C3), 125.84 (C11, C13), 126.76 (C4), 128.36 (C6), 140.48 (C12), 152.94 (C9), 154.05 (C8). Anal. calcd. for C₁₄H₁₂N₂O₃: C, 65.62; H, 4.72; N, 10.93; O, 18.73%. Found: C, 65.43; H, 4.60; N, 10.99; O, 18.98%.

2.2.1. Synthesis of 4-aminoaniline based benzoxazine polymer

The polymerization of 4-aminoaniline based benzoxazine monomer was attempted by applying several curing programs involving systematic changes in the temperature, period and number of steps of the curing, in order to determine the

optimum curing program. In the light of literature findings and our previous experience, the period of curing was decreased as the temperature of the process was increased. The products obtained were first analyzed by DSC technique to determine whether the polymerization was completed or not. Abbreviations used for the products are given according to the DSC results and the temperature and the period applied during the curing process; if DSC data indicated incomplete polymerization, then the samples are symbolized by letter M, if complete polymerization was achieved according to DSC data, then the samples are symbolized by P. The curing temperatures are denoted by letters a, b and c for 160, 180 and 200 °C respectively, and the periods of curing in hours are also stated in the symbols. The curing programs applied and the abbreviations used for the products are summarized in Table 1.

2.2.2. Characterization

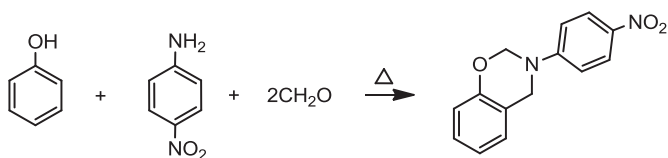
Proton NMR spectra were acquired with a Bruker AC250 (250.133 MHz) spectrometer using CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. ATR-FT-IR analyses of the samples were performed by directly insertion of solid sample using Bruker Vertex 70 Spectrophotometer with 0.4 cm⁻¹ resolution. 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. All the analyses were repeated at least twice to ensure reproducibility. In order to minimize dissociation of thermal degradation products during ionization, the pyrolysis analyses were also utilized at electron energies of 20 eV. As expected, reproducibility decreased noticeably. In addition, the ion yields are diminished drastically and few product peaks can be detected in the 20 eV pyrolysis mass spectra. Thus, only limited information can be obtained. Thus, 20 eV pyrolysis mass spectra were only used to identify the fragments generated during thermal degradation process.

Table 1

The temperature (°C) and period (h) of each step of the curing process and the abbreviations used for the products.

One step curing				
T°C	hour	Abbreviation for the product		
160	1,2... 8	Ma1, Ma2...Ma8		
	10	Pa10		
	12	Pa12		
180	3	Pb3		
	6	Pb6		
200	1	Pc1		
	2	Pc2		
Two step curing				
First step		Second step		Abbreviation for the product
T°C	hour	T°C	hour	
160	3	200	1	Pa3c1
			2	Pa3c2
180	3	200	1	Pb3c1
			2	Pb3c2
			3	Pb3c3
6	1	Pb6c1		



Scheme 1. Synthesis of benzoxazine monomer based on 4-nitroaniline and phenol.

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