

Synthesis and Characterization of Hydroquinone Based Benzoxazines and their Polymers Using Solventless System

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Abstract: This paper concentrates on synthesis and characterization of benzoxazine based on hydroquinone, aniline and formaldehyde using solventless system. Suitable reaction condition was determined. The structure of benzoxazine has characterized by Nuclear Magnetic Resonance (NMR), Infrared (IR). The thermal properties were determined by Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analyzer (TGA).

Key Words: Benzoxazine; Phenolic Resin; Synthesis; Characterization

Introduction

All chemicals were used without further purification. Typical reactions employed in forming the benzoxazine compounds based on Hydroquinone, formaldehyde and aniline are illustrated in (Scheme1).

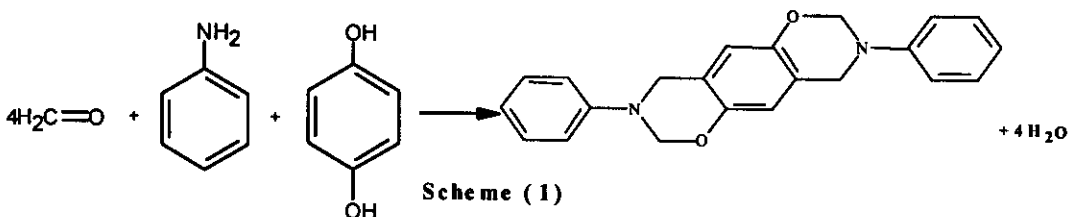
In this experiment, aniline-based benzoxazine was synthesized by using solventless system. Ishida and Hatsuo (1995) has defined solventless method as following:

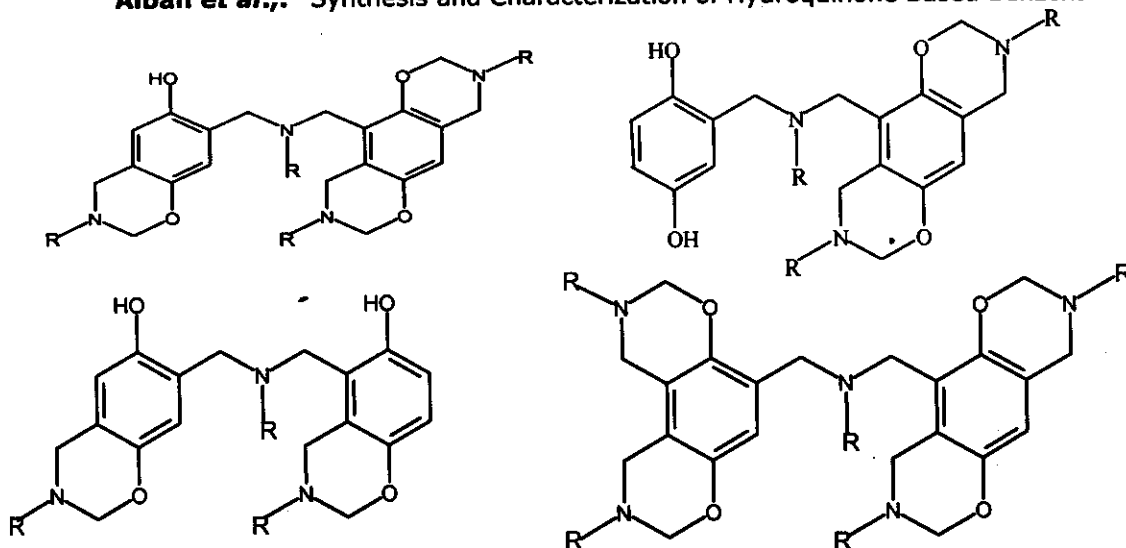
"A method for preparing a desired benzoxazine compound comprises preparing a substantially homogeneous reaction mixture that includes a phenolic compound, a primary amine, and an aldehyde, but no solvent other than for the solvency which the reactants may have for each other following its preparation, the reaction mixture is maintained at a temperature for a period sufficient to cause the reactants to combine chemically to form the desired compound."

Synthesis of Aniline Based Benzoxazine Using Solventless System: (9.7gm, 0.32mol) of Para-formaldehyde, (12gm, 0.1mol) of hydroquinone and (14gm, 0.15mol) of aniline are mixed together to 78°C to obtain a clear brownish homogeneous solution. The solution is then heated to 116°C for approximately 15 minutes, the desired benzoxazine as indicated in Scheme (1) obtained. Purification of the precursors was accomplished as following:

The fluid was dissolved in 200ml of ethyl ether to eliminate any un reacted formaldehyde or aniline and by repeatedly washing their ether solutions with 3N NaOH solution to eliminate any phenolic structures in the precursors and then the ether solution was washed several times with water and dried over sodium sulfate (Na₂SO₄) to obtain a fine white powder. Caution was taken to store the synthesis and purification products in a dry and cold environment (~ - 4°C) to ensure that no

reaction occurred prior to any experiment. The solventless process results in a reaction medium in which the reactive components comprise substantially 100 percent of the mixture, making it possible to carry out the reaction in minutes, rather than hours. The use of a non-solvent, heterogeneous reaction mixture rather than a homogeneous. Any of several methods may be used to carry out the solventless reaction; For example, in instances where the reactants, i. e., the aldehyde, the primary amine, and the phenolic compound are all solids, the solids may be physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants so as to produce the benzoxazine desired in the time required (Ishida, Hatsuo). Alternatively, as in the case where one or more of the reactants is a liquid, the reactants may simply be combined and heated to the point at which they all become liquid, either through melting, or by being dissolved in one or more of the liquid components present. The resulting mixture is then maintained at a temperature and for a period sufficient to bring about the desired reaction for the benzoxazine compound being synthesized. While no catalyst is required for the reaction leading to the product previously described, if desired, for instance in order to change the composition of the products formed in the reaction mixture, acid catalysts such as HCL, or basic catalysts, for instance, NaOH, may be employed. The composition and structures of precursor were analyzed by proton Nuclear Magnetic Resonance (NMR) spectroscopy in CDCl₃ as well as Infrared (IR), Differential Scanning Calorimeter (DSC) and ThermoGravimetric Analyzer (TGA). The Infrared (IR) spectrometer used was 435. The NMR spectrometer used was avarian 200 instrument operating at 200 MHz.





Deuterated Chloroform ($CDCl_3$) was used as a solvent and tetramethyl silane (TMS) was used as an internal standard. A Perkin-Elmer TAS-7 Differential Scanning Calorimeter (DSC) and ThermoGravimetric Analyzer (TGA) instruments were used to examine the thermal characteristics of the curing process and weight loss of the samples, respectively.

Determination of Reaction Conditions: The optimized temperature and reaction time in synthesize benzoxazine based on aniline using solventless system were found $116^\circ C$ and 15 minutes, respectively. It should be noted that increasing moles of aniline in synthesize aniline based on benzoxazine using solventless system has no significant difference on the viscosity, however increasing moles of hydroquinone provides viscous products and the viscosity of these products increases with increasing moles of hydroquinone.

Spectroscopy Analyses

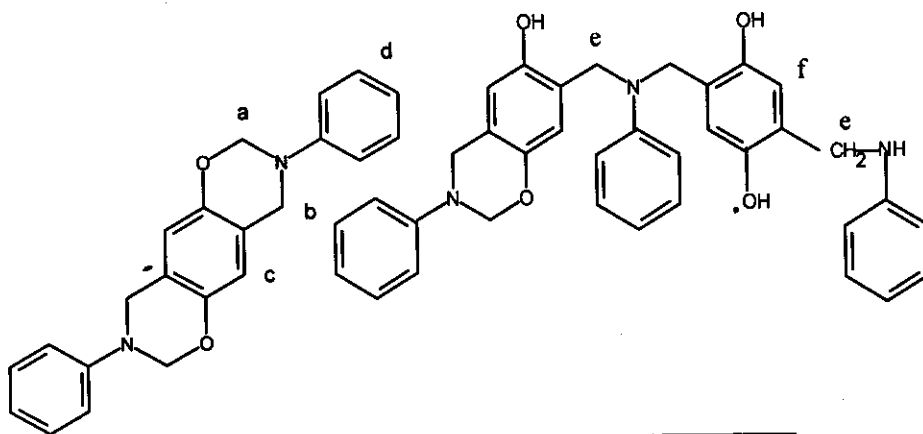
Infrared Spectroscopy (IR): The Mannich reaction illustrated above was found to represent almost complete conversion of the starting hydroquinone to its benzoxazine and derivatives (Ishida and Hatsuo, 1992). The precursors as synthesized include, in addition to the monomeric structures illustrated below; various amounts of dimers and higher oligomers in the composition which have a catalytic effect on the curing reaction; that is reduces the reaction induction time and increase the reaction rate (Ishida and Hatsuo, 1992). These dimers and higher themselves consisted of a series of different isomeric structures that shared the structural characteristics of possessing both benzoxazine rings and opened free phenolic groups (Dunkers and Ishida, 1995; Eckstein *et al.*, 1961). Listed next are some of the possible structures for the dimers of benzoxazines H-a. Because the number of possible structures in dimers and higher oligomers is so large, not to mention the possible existence of branched and cyclic structures, it would be very difficult to determine the composition of each and every component in the product by H-NMR alone. This symmetry makes all the vibrational modes active. Using the work of Ning and Ishida as a foundation, more detailed studies of benzoxazines as monomers for novel phenolic resins are being pursued from a molecular perspective; infrared spectroscopy is very effective in meeting these goals.

However, the vibrational spectra of these benzoxazines are very complicated (Dunkers and Ishida, 1995). There is very little information in the literature that can aid in the assignment of the vibrational spectra of these molecules (Sullivan *et al.*, 1957; Eckstein *et al.*, 1961). Unlike the benzene vibrations which are well characterized (Dunkers and Ishida, 1995). Many oxazine vibrations are heavily coupled to each other and to the benzene ring vibrations. The structures of 3, 4- dihydro-3-substituted 1, 3 benzoxazines were verified by IR spectrometer. Infrared spectrum of the synthesized benzoxazine compositions was collected from thin films coated onto KBr discs and is depicted in Fig. (1).

The symmetry of the benzoxazine molecule is C_1 since the nitrogen atom is out of the plane of the benzoxazine ring. Assignments will be made based on the bands that appear in region attributed to specific group frequencies. Only the C-O, O-C, C-N and N-C stretching should appear above 500 cm^{-1} . The antisymmetric C-N-C stretching modes can be found in the regions 1220 and 750 cm^{-1} , respectively in Fig. (1). It is quite common to find more than one band attributable to the C-N stretching vibrations in each region (Raymend *et al.*, 1981). The C-O-C antisymmetric and stretching modes appear in the regions of 1150 and 1130 cm^{-1} , respectively as seen in Fig. (1).

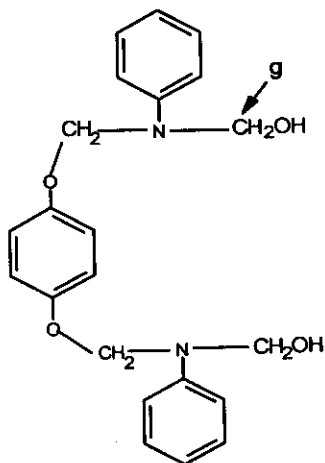
The Peaks at 1360, 1420 and 2850 cm^{-1} are unique to the methylene groups in the benzoxazine ring. The CH_2 twist at 1305 cm^{-1} is assigned to the CH_2 groups (Dunkers and Ishida, 1995). The Peak at 1480 cm^{-1} is attributable to the tetra-substituted benzoxazine mode in the ortho substituted (methylene-amine methylene bridge) phenolic structures formed by the reaction between the oxazine ring and the free ortho position of a phenol structure. The band at 680 cm^{-1} is assigned to the mono-substituted benzene ring. The band at 1600 cm^{-1} is assigned to the C=C in the benzene ring and the C-H band appears at 3020 cm^{-1} .

Nuclear Magnetic Resonance Spectroscopy (NMR): The structure of obtained benzoxazine is shown in Scheme (2). The 1H -NMR spectra of the purified benzoxazine product using solventless system is depicted in Fig. (2). The important peak assignments of aniline based benzoxazine using solventless system are displayed in Table (1).



Scheme (2) the structure of H-a monomer and dimer using solvent and solventless systems

The chemical shift at 4.5 p.p.m in [Fig (2), (e)] is attributable to CH₂ in Mannich bridge structures, [-CH₂-N-CH₂-] which refers to some structures of benzoxazine such as, dimers and higher oligomers, that found in the reaction mixture of aniline based benzoxazine products. The peak assigned at 5.3 p.p.m in [Fig (2), (g)] is attributable to CH₂ in the following structure, which may be found in the reaction mixture of aniline based benzoxazine products using solventless system.



The peaks found less than 3 p.p.m are assigned to traces of CH₃, used as solvent in purification of benzoxazine products. The assignments of each resonance are also made on the monomers and simplified dimers structures. The percentage of each component in the precursor mixture is difficult to determine by NMR alone since the detailed structures of the dimers and higher oligomers are not known. However, it is possible to determine the ratio between the number of methylene units in the benzoxazine ring [Fig (2), (a) and (b) with chemical shifts at 5.35 and 4.55 p.p.m respectively] and the number of the methylene units existing in the bridge structures [Fig (2), (e) with chemical shift at 4.5 p.p.m] by examining

their integrated intensities of the resonance peaks. For this synthesis which corresponds to 88% ring structures in the composition.

This number is indicative of the percentage of polymerizable structure, or ring content, in the whole composition without pointing out what kind of molecular structures these rings or bridge belong to. From these experiment, it seems that, while the majority of the composition after the synthesis is hydroquinone benzoxazine monomer, there are fractions of the composition with free phenolic hydroxyl structures existing in dimers and higher oligomers which were formed by subsequent reactions between the rings and the ortho position of hydroquinone hydroxyl groups. Furthermore, it also shows that these structures in the dimers and higher oligomers are capable of undergoing further reaction with formaldehyde and primary amine to form the oxazine ring again, in addition the presence the dimers and higher oligomers with free phenolic OH structures in the precursor is actually advantageous for initiating subsequent polymerization reactions.

Thermal Analysis

Differential Scanning Calorimeter (DSC): Experiments were always performed below 300°C to prevent any possible degradation reactions inside the chamber. The areas under the curves were quantified by drawing a straight-line extension of both sides of each exothermic. These calculations and the normalization procedures were performed by the d.s.c software. DSC results are displayed in Fig. (3). The summary of results obtained from isothermal experiments at scanning rate 10°C/min for benzoxazine monomers are summarized in Tables 2 and 3.

ThermoGravimetric Analyzer (TGA): The most widely used ThermoGravimetric Analyzer (TGA) method is based on continuous measurement of weight on a sensitive balance (called a thermobalance) as sample temperature is increased in air or in an inert atmosphere; this is referred to as nonisothermal TGA. Data are recorded as a thermogram of weight versus temperature. Weight loss may arise from evaporation of residual moisture or solvent, but at higher temperatures, it results from polymer decomposition.

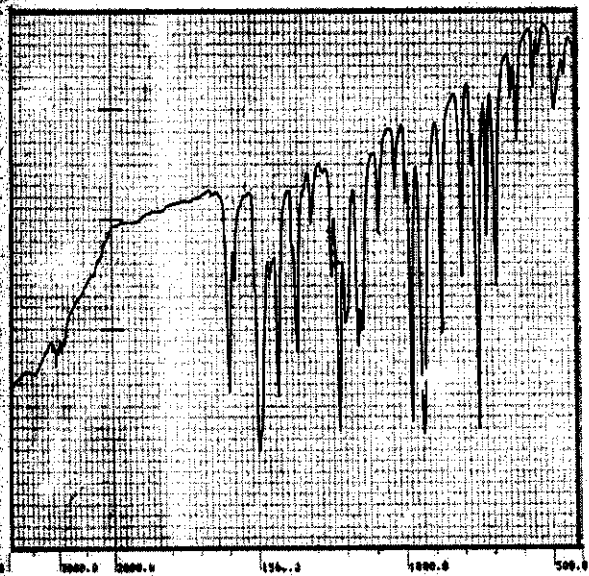


Fig. 1: Infrared of Aniline Based Benzoxazine Using Solventless

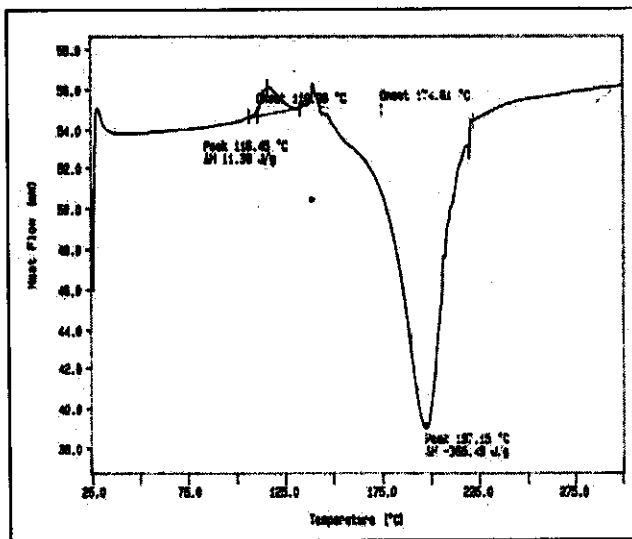


Fig. 3: DSC of Aniline Based Benzoxazine Using Solventless

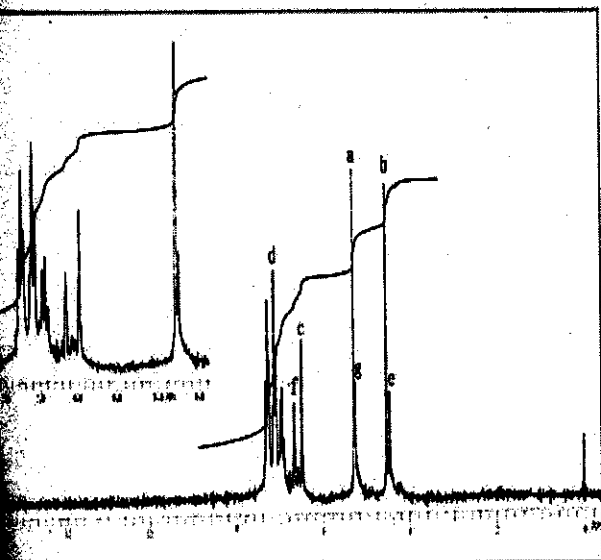


Fig. 2: ¹H NMR Spectra of Aniline-Based Benzoxazine Using Solventless

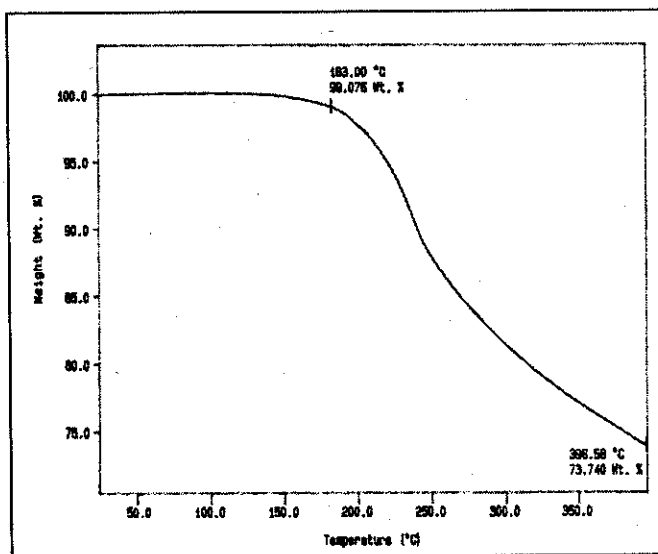


Fig.4: TGA of Aniline Based Benzoxazine Using Solventless

Table 1: ¹H Assignments of Aniline Based Benzoxazine using Solventless System

Assignments	a	b	c	d	e	f	g
¹ H (p.p.m)	5.33	4.55	6.5	6.9-7.15	4.5	6.7	5.3

Table 2: Summary of Results Obtained from Isothermal Experiments

Assignments	Endotherm Peak(°C)	Onset Endotherm(°C)	ΔH(Jg ⁻¹)
	116.45	110.99	11.38

Table 3: Crosslinking Temperatures Obtained from D.S.C Experiments

Assignments	Exotherm Peak(°C)	Onset Exotherm(°C)	ΔH(Jg ⁻¹)
	197.15	174.61	-355.49

Residual weight is frequently an accurate reflection of char formations of interest in flammability testing. TGA instruments allow thermograms to be recorded on microgram quantities of material (Malcamp, 1990). It should be noted that benzoxazine monomers have under gone to curing reactions at 125°C for 20 minutes. The TGA results are displayed in Fig. 4.

Calculation Bond Lengths of the Precursors

Composition: The calculations bond lengths of the oxazine ring of the monomer and open-ring structure of a dimer are depicted in tables 4 and 5 respectively.

Table 4: Calculated Bond Lengths of the Oxazine Ring of the Monomer

Amine	C-O	C-H	N-R
Aniline	1.394	1.083	1.415

The C-O and C-H are the bonds that break upon polymerization. R represents the amine. All bond lengths are in angstrom (Å°).

Table 5: Calculated Bond Lengths of the Open-Ring Structure of a Dimer

Amine	O-H	C-Ring	C-H	N-CH ₂	N-R
Aniline	0.950	1.538	1.102	1.484	1.416

The O-H, C-Ring, and the C-H are formed upon polymerization. N-CH₂ and N-R are from the Mannich Bridge. R represents the amine. All bond lengths are in angstrom (Å°)

Conclusion

Benzoxazines based on hydroquinone, formaldehyde and aniline was synthesized as phenolic resins via ring-opening polymerization. Suitable reaction condition was determined, aniline based benzoxazine was synthesized using solventless system. The components and their structures have been characterized by IR, NMR and X- the thermal analysis achieved using DSC and TGA instruments. The composition of aniline-based benzoxazine synthesized using solventless system consists mainly of monomer, dimer and higher oligomers with both benzoxazine ring and free phenol structures

References

Dunkers, J. and H.Ishida; 1995. *spectrochimica Acta*, Vol. 51A, No.5, P, 855.
 Eckstein, Z., P. Gluzinski, W. Hofman, Urabnski and J. Chem; 1961. Soc. 489.
 Ishida and Hatsuo; 1995. 2903 Weybridge Road, Shaker Heights, Ohio 44120(us) Wo 95/31447. 23.11-95.
 Ishida and Hatsuo; 1992. PCT /U.S 92/ 01886,
 Sullivan, D.G.O., P.W Sadler and J. Chem; 1957. Soc. 2917.
 Raymend, B. Seymour, Charles, E.Carraher and J. Polymer; 1981. Chemistry An introduction Page 34-36.
 Malcamp; 1990. Stevens. Polymer Chemistry Introduction, Second Edition. Page 171.