

CHAPTER II

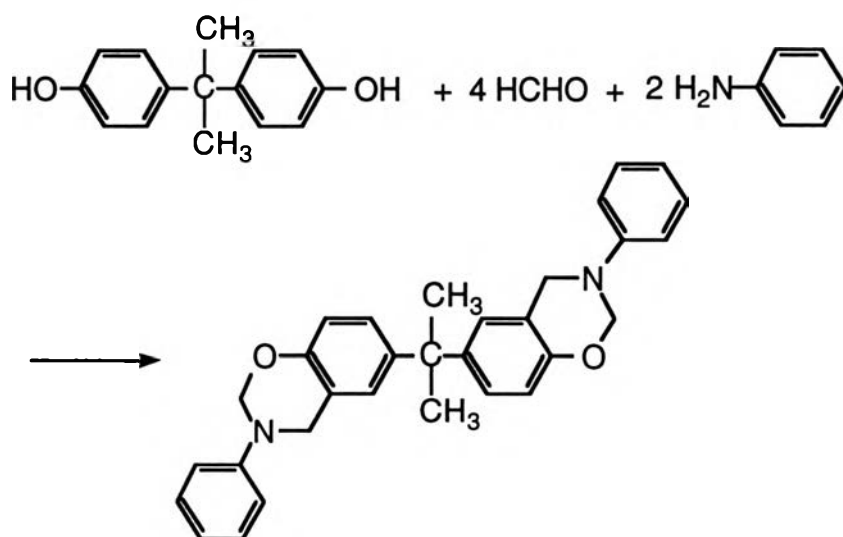
EXPERIMENTAL PART

2.1 Materials

Bisphenol-A and sodium sulfate were supplied by Aldrich. Formaldehyde aqueous solution (37%) was obtained from J.T. Baker Co. Aniline, 1,4-dioxane and diethylether were purchased from Ajex Chemical. Sodium hydroxide was purchased from Merk. All chemicals were used without further purification.

2.2 Monomer Synthesis

The benzoxazine based on bisphenol-A and aniline was synthesized according to the following scheme :



An aqueous solution of 0.4 mol formaldehyde and 80 ml dioxane were mixed in a 500 ml three-necked flask equipped with thermometer, condenser and dropping funnel, and was cooled by an ice bath. To this, 0.2 mol aniline in 20 ml dioxane was added slowly. The temperature of the solution in the flask was kept below 10 °C during the addition of aniline. The mixture was stirred magnetically for 10 min before adding a solution of 0.1 mol bisphenol-A in 10 ml dioxane. The temperature was then raised, and the mixture solution was allowed to reflux for 6 hours. The solvent, dioxane, was then removed by rotary evaporation, and the remaining viscous fluid was dissolved in 200 ml diethyl ether for purification.

In order to obtain pure benzoxazine monomer, the ether solution was repeatedly washed with 3N NaOH solution in a separatory funnel to minimize phenolic structures in the precursor. After washing with 3N NaOH, the purified ether solution was washed several times with distilled water to further eliminate any unreacted formaldehyde or aniline. The solution was then dried over sodium sulfate. A solid compound at room temperature was obtained by evaporating the ether. The purified material thus obtained will be abbreviated as B-a throughout the following text. The abbreviation B-a refers to two of its original components: bisphenol-A and aniline.

2.3 Curing Procedure

Samples containing approximately 2 grams of purified benzoxazine monomer were degassed in aluminum pans in a vacuum oven at 100 °C for 6 hours and then cooled to room temperature. The degassed material was cured isothermally at 155, 165, 175, and 185 °C for 30 min, 40 min, and 1 to 10 hours in the oven.

2.4 Characterization

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The purified material was examined by Fourier transform infrared spectrophotometer (FTIR) (Bio-Rad Model 5A) with a fixed resolution of 4 cm^{-1} . A frequency range of $4000\text{-}400\text{ cm}^{-1}$ was observed using a deuterated triglycinesulfate (DTGS) detector with a specific detectivity, D^* , of $1 \times 10^9\text{ cm.Hz}^{1/2}.\text{W}^{-1}$. The benzoxazine sample was mixed with KBr powder and pressed into a pellet for examination.

2.4.2 Size Exclusion Chromatography (SEC)

After checking the structure of purified B-a, the purity of this purified benzoxazine was further examined by size exclusion chromatograph (SEC) (Waters 486 instrument) equipped with a Styrogel column of molecular weight ranging from 50 - 100,000 at a flow rate of 1 ml/min with an ultraviolet absorption detector fixed at 254 nm.

2.4.3 Differential Scanning Calorimetry (DSC)

The thermal properties of the benzoxazine samples were studied by a modulated differential scanning calorimeter (DSC) (TA Instrument model 2920) purged with nitrogen gas at a rate of 40 ml/min. Approximately 5-10 mg of the B-a sample was placed in a high pressure aluminum pan. Experiments were run from $30\text{ }^\circ\text{C}$ to $310\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

2.5 Density Measurement

The volumetric expansion of cured samples were studied by density measurement according to ASTM D792 (Method A). By comparing the density of the monomer with that of the polymer, the shrinkage or expansion of the B-a material can be determined. Only bubble-free samples were used for these measurements. The temperature of the water bath was kept constant at 24 ± 1 °C for all water displacement density measurements. Seven samples for each condition were used and the average value was reported.