CHAPTER III
EXPERIMENTAL

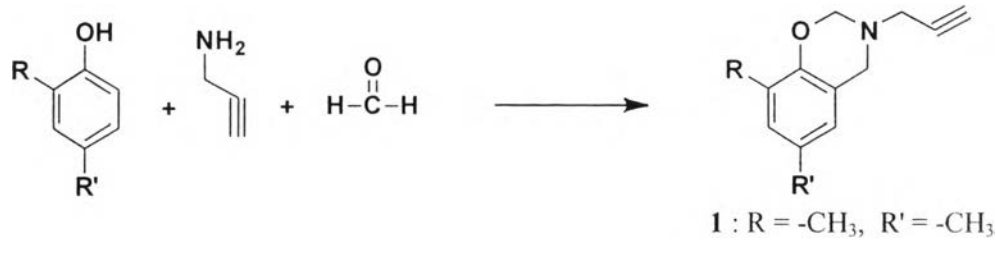
3.1 Materials

2,4-dimethyl phenol, propargylamine, adipoyl dichloride, Terephthaloyl dichloride and deuterated-chloroform ($CDCl_3$) were purchased from Aldrich, Germany. Formaldehyde solution was purchased from Ajax Chemical, Australia. Sodium hydroxide, sodium sulfate anhydrous, dioxane, diethyl ether, chloroform, dichloromethane, isopropanol and tetrahydrofuran (THF) were a product of RCI Labscan, Thailand. All chemicals were used as received.

3.2 Experimental

3.2.1 Preparation of Benzoxazine Monomer

Benzoxazine monomer was prepared by adding propagylamine (1.92 g, 0.03 mol) into formaldehyde solution (6.70 mL, 0.09 mol) in dioxane (20 mL). Then, 2,4-dimethyl phenol (3.66 g, 0.03 mol) was added to the solution, and refluxed at 110°C for 6 hours (Scheme 3.1). The reaction was followed by thin layer chromatography (TLC) and FT-IR spectroscopy (FT-IR). The solution obtained was dissolved in diethyl ether, and washed with 0.1 M sodium hydroxide (NaOH) and distillated water several times. The solution was dried over by anhydrous sodium sulfate, and the solvent was removed to obtain crude product (**1**).

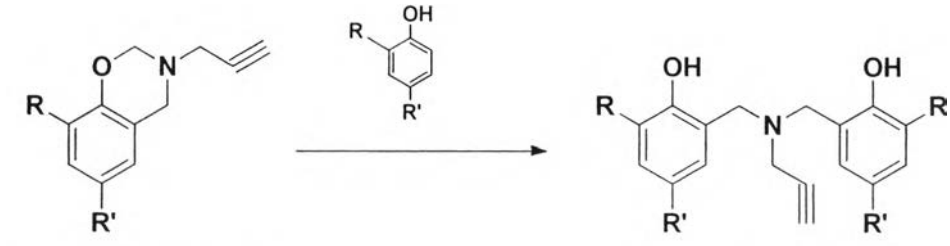


1 : R = -CH_3, R' = -CH_3

Scheme 3.1

3.2.2 Preparation of Benzoxazine Dimer

Benzoxazine dimer was prepared via ring-opening reaction of the benzoxazine monomer and phenol derivatives by adding 2,4-dimethyl phenol into **1**, and stirred at 110°C until viscous material was obtained (Scheme 3.2). The reaction was followed by TLC and FT-IR. The crude product was recrystallized in isopropanol to obtain crystal product of **2**.

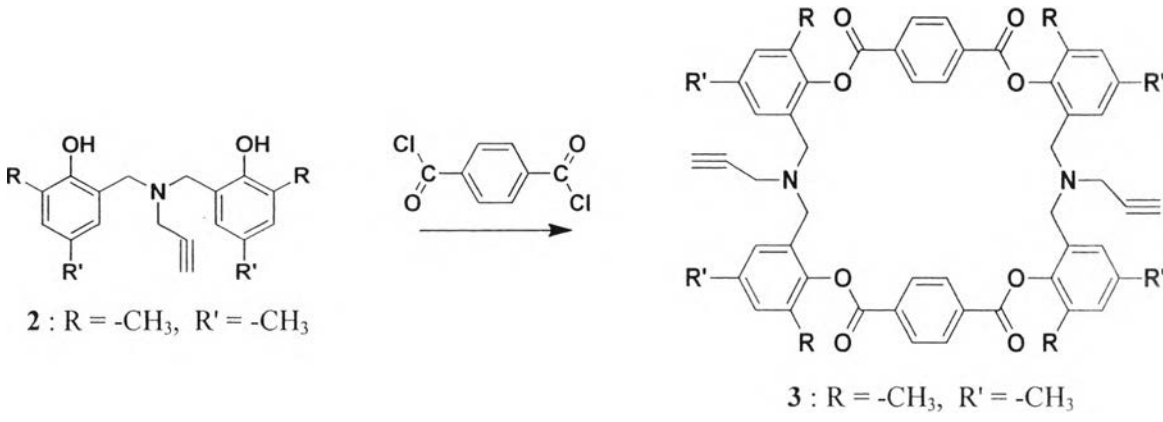


1 : R = -CH_3, R' = -CH_3 **2** : R = -CH_3, R' = -CH_3

Scheme 3.2

3.2.3 Preparation of Macrocyclic Ester: Heterogeneous Reaction

Macrocyclic compound was obtained by esterification of benzoxazine dimer and diacid chloride as shown in Scheme 3.3. **2** (1.62 g, 5 mmol) and an aqueous solution of NaOH (0.80 g, 10 mmol in 50 mL water) were dissolved in dichloromethane (100 mL). A solution of terephthaloyl dichloride (1.02 g, 5 mmol) in tetrahydrofuran (50 mL) was added dropwise and stirred at room temperature for 24 hrs. The solution obtained was collected, and washed with distilled water, followed by drying over anhydrous sodium sulfate. The solvent was removed to and the crude product was recrystallized to obtain **3**.



2 : R = -CH_3, R' = -CH_3

3 : R = -CH_3, R' = -CH_3

Scheme 3.3

3.2.4 Preparation of Macrocyclic Ester: Homogeneous Reaction

Terephthaloyl dichloride (101.5mg, 0.5mmol) was dissolved in THF (100 mL). A solution of **2** (161.7 mg, 0.5 mmol) and NaOH (80 mg, 2 mmol) in THF (50 mL) was added dropwisely and stirred at room temperature for 7 days. The reaction was followed by TLC. The solution obtained was collected, and washed with distilled water, followed by drying over anhydrous sodium sulfate. The solvent was removed to obtain crude product. The crude product was further purified by column chromatography.

3.2.5 Preparation of Macrocyclic Ester: Interfacial Polycondensation

A 0.15 M solution of **2** in water in the presence of various catalysts (i.e. NaOH, K_2CO_3 and Et_3N) and a 0.15 M solution of terephthaloyl dichloride in dichloromethane in separate syringes were added dropwisely into the mixture of dichloromethane (35 mL), water (10 mL) and hexadecyltrimethylammonium bromide, and stirred at room temperature for 7 days. The solution obtained was washed with distilled water several times and evaporated to dryness. The product obtained was further purified by column chromatography. In case of adipoyl dichloride, similar procedures were proceeded.

3.3 Characterizations

Compound **1** – **3** were confirmed by a Bruker Fourier transform infrared (FTIR) spectrometer in the range 4000 - 650 cm^{-1} at a resolution of 2 cm^{-1}, a Bruker Avance nuclear magnetic resonance (NMR) spectrometer (Germany) operating at Larmor frequencies of 500.13 MHz which used $CDCl_3$ as a solvent, and a Bruker Daltonic Micro-TOF mass spectrometer (ESI-TOF) in positive ion mode.