

CHAPTER III

EXPERIMENTAL

3.1 Materials

Fumed silica, 3-amino-1,2-propanediol, 2-amino-2-methyl-1,3-propanediol were purchased from Aldrich Chemical Co., Inc. (USA), used without purification and kept under nitrogen atmosphere.

Triethylenetetramine (TETA) was also purchased from Facai Polytech Co., Ltd., and purified by distillation under vacuum at 120°C. It was used as a base catalyst and solvent.

Potassium hydroxide (KOH) was purchased from J.T. Baker Company Co., Ltd., and sodium hydroxide (NaOH) was purchased from EKA Chemicals Company Co., Ltd., used as catalyst and as received.

Acetonitrile and methanol were purchased from Labscan Asia Company Co., Ltd., and J.T. Baker Company Co., Ltd., and were purified by fractional distillation under nitrogen gas over calcium hydride and magnesium activated with iodine, respectively. Both were stored over molecular sieves under nitrogen gas and were used as precipitation agents.

Cyclohexanone was purchased from Ajax Laboratory Chemical Company Co., Ltd., and was purified by fractional distillation under nitrogen gas over calcium hydride. It was stored over molecular sieves under nitrogen gas and was used as protecting agent. Hydrochloric acid solution (36%wt) was purchased from Ajax Laboratory Chemical Company Co., Ltd., and used as acid catalyst in ketal formation and as received.

Phenol was purchased from Ajax Laboratory Chemical Company Co., Ltd., and used as received. Formaldehyde solution (37%wt) and paraformaldehyde were purchased from Merck Company Co., Ltd., and used as received. They were used as starting materials for benzoxazine synthesis.

1,4-Dioxane was purchased from Ajax Laboratory Chemical Company Co., Ltd. It was purified by distillation over calcium hydride and kept in sealed container.

Diethyl ether was purchased from J.T. Baker Company Co., Ltd., and it was stored over magnesium sulfate.

UHP grade nitrogen gas with 99.99% purity was purchased from Thai Industrial Gases Public Company Limited (TIG).

3.2 Equipment

3.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained by using a VECTOR 3.0 BRUKER spectrometer with 32 scans at a resolution of 2 cm^{-1} . A frequency range of $4000\text{-}400\text{ cm}^{-1}$ was observed using a deuterated triglycinesulfate detector (DTGS) with specific detectivity of D^* , of $1 \times 10^9\text{ cm} \times \text{Hz}^{1/2} \times \text{W}^{-1}$. Both neat techniques on ZnSe plate and KBr pellet were used.

3.2.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H -NMR and ^{13}C -NMR spectra were performed on a Bruker 500 MHz spectrometer at room temperature. The samples were pulsed at 500 MHz for proton and 200 MHz for carbon NMR with a spin rate of 21 rpm. A relaxation delay time was 1 sec with a sweep width of 3105 Hz or about 15 ppm, using a pulse of 45 μsec . Deuterated dimethyl sulfoxide (DMSO-d_6), deuterated chloroform, and deuterated methanol were used as solvents. 16 scans were run for proton NMR while carbon NMR samples were pulsed for more than 2 hours or more than 400 scans. Tetramethylsilane (TMS) was used as the reference for chemical shift measurements in both proton and carbon NMR.

^{29}Si -NMR spectra were obtained using a 500 MHz JEOL spectrometer. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent and tetramethylsilane (TMS) was used as the reference for chemical shift measurements. The samples were pulsed for 4 hours.

3.2.3 Thermal Analysis (TA)

Thermograms were conducted using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) mode. They were carried out on a Netzsch instrument, DSC 200 cell and TA 209 cell, respectively, with TASC 414/3 controller in nitrogen gas, N_2 . Sample weights were typically from 5-10 mg. For TGA measurements, the purge flow rate of nitrogen was set at 60 ml/min and 40 ml/min for the balance. The temperature analysis range in the TGA using a ramp rate of $10^\circ\text{C}/\text{min}$ was from 30°C to 750°C , while DSC measurements were conducted from -15° to 400°C at the heating rate of $10^\circ\text{C}/\text{min}$. The flow rate of nitrogen was 40 ml/min.

3.2.4 Mass Spectroscopy (MS)

Mass spectra were obtained using a VG Autospec model 7070E from Fison Instruments with VG data system. Samples were run in the positive fast atomic bombardment (FAB-MS^+) mode using glycerol as the matrix. Cesium gun was used as an initiator and cesium iodine (CsI) was used as a reference.

3.3 Methodology

3.3.1 Protecting Hydroxyl Groups of 3-Amino-1,2-propanediol (C3)

To obtain the optimum conditions for synthesis of ketal C3, 2 variations in the reaction were studied.

3.3.1.1 Effect of Reaction Time and Temperature on the Synthesis of Ketal C3

A mixture of 0.02 mmol (1.8222g) 3-amino-1,2-propanediol, 0.02 mmol (1.963g) cyclohexanone and 5% by vol of 1 M HCl was placed into a 50 mL two-neck round bottomed flask equipped with a simple distillation set. The mixture was heated to the temperature 100° and 110°C under nitrogen atmosphere to distill off water produced during the reaction. The reaction time was varied from 0-6 hours.

3.3.2 Synthesis of Benzoxazine from Formaldehyde, Phenol and Ketal C3

A mixture of 0.01 mmol (1.7126g) of ketal C3 and 0.023 mmol (1.86g) of formaldehyde solution was placed into 50 mL two-neck round bottomed flask equipped with a simple distillation set. The reaction mixture was left at 20°C for 2 hours. 0.01 mmol (0.9411g) phenol was then added, and the reaction was heated to 110°C for 2 hours.

3.3.3 Protecting Hydroxyl Groups of 2-Amino-2-methyl-1,3-Propanediol (C4)

To obtain optimum conditions for synthesis of ketal C4, 2 variations in the reaction were studied.

3.3.3.1 Effect of Reaction Time and Temperature on the Ketal C4 Synthesis

A mixture of 0.02 mmol (2.10g) 2-amino-2-methyl-1,3-propanediol, 0.02 mmol (1.963g) cyclohexanone and 5% by vol of 1 M HCl was placed into a 50 mL two-neck round bottomed flask equipped with a simple distillation set. The mixture was heated to the temperature 100° and

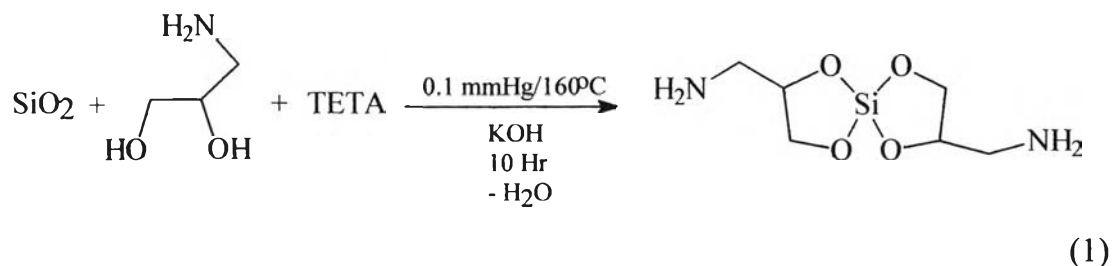
110°C under nitrogen atmosphere to distill off water produced during the reaction. The reaction time was varied from 0-5 hours.

3.3.4 Synthesis of Benzoxazine from Formaldehyde, Phenol and Ketal C4

A mixture of 0.01 mmol (1.8515g) of ketal C4 and 0.023 mmol (1.86g) of formaldehyde solution was placed into 50 mL two-neck round bottomed flask equipped with a simple distillation set. The reaction mixture was left at 20°C for 2 hours. 0.01 mmol (0.9411g) phenol was then added, and the reaction was heated to 110°C for 2 hours.

3.3.5 Synthesis of Spirosilicate C3 from Silica and 3-Amino-1,2-propanediol

The aminospirosilicate product (C3) synthesis followed Sun's method from fumed silica and 3-amino-1,2-propanediol, using triethylenetetramine (TETA) as both solvent and catalyst, KOH as co-catalyst under vacuum (1 torr) at 160°C for 10 hours. The product was precipitated by using trace amount of methanol in acetonitrile, and kept under nitrogen atmosphere for further use as a starting material in the step of benzoxazine derivative synthesis. Chemical reaction is shown in equation (1).



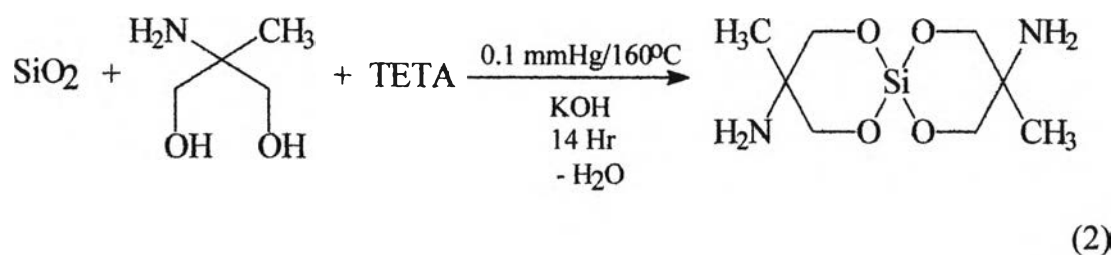
3.3.6 Synthesis of Spirosilicate C3/benzoxazine Comonomer

A mixture of 0.01 mmol (2.06g) spirosilicate C3, 0.043 mmol (1.29g) paraformaldehyde was placed into a 50 mL two-neck round bottomed

flask equipped with a simple distillation set under nitrogen atmosphere. The mixture was heated at 80°C for half an hour. Then 0.02 mmol (1.882g) phenol was added and the reaction mixture was heated to 110°C for half an hour.

3.3.7 Synthesis of Spirosilicate C4 from Silica and 2-Amino-2-methyl-1,3-propanediol

The aminospirosilicate product (C4) was synthesized followed Sun's method from fumed silica and 2-amino-2-methyl-1,3-propanediol, using triethylenetetramine (TETA) as both catalyst and solvent and small amount of potassium hydroxide as a co-catalyst. The reaction was done under vacuum (1 torr) at 160°C for 14 hours. The product was precipitated by using trace amount of methanol in acetonitrile. It was then kept under nitrogen atmosphere to use as a starting material in the step of benzoxazine derivative synthesis. Product structure is shown below.



3.3.8 Synthesis of Spirosilicate C4/benzoxazine Comonomer

A mixture of 0.01 mmol (2.34g) spirosilicate C4, 0.043 mmol (1.29g) paraformaldehyde was placed into a 50 mL two-neck round bottomed flask equipped with a simple distillation set under nitrogen atmosphere. The mixture was heated at 80°C for 3 hours. Then 0.02 mmol (1.882g) phenol was added and the reaction mixture was heated to 110°C for 3 hours.