

CHAPTER II

EXPERIMENTAL PART

2.1 Materials

Since the tetra-coordinated spirosilicate monomers are very sensitive to either moisture or air, all operations were performed under nitrogen atmosphere, nitrogen gas, N₂, in glove box and also all glassware used was dried in an oven at 100°C overnight. All reactions were also run under nitrogen with magnetically stirring.

Fumed silicon dioxide, SiO₂, (surface area of 320 m²/g and the average particle size of 0.007 μm) was purchased from Aldrich Chemical Company and fused silicon dioxide or HI-SIL 927 silica, SiO₂, (surface area of 182 m²/g, by BET) was donated by PPG Siam Silica Co., Ltd. They were dried in an oven at 110°C overnight and then stored in desiccator under nitrogen gas before used as raw material.

Ethylene glycol (HOCH₂CH₂OH, EG, or C2), boiling point 196-198°C, purchased from Lab-Scan Analytical Science and Baker Analyzed Reagent, was used as both reactant and solvent. It was distilled in a fractional distillation set at 200°C under nitrogen gas and stored under nitrogen gas prior to use.

3-amino-1,2-propanediol {HOCH₂CH(CH₂NH₂)OH, C3}, boiling point 264°-265°C/739mmHg, and 2-amino-2-methyl-1,3-propanediol {HOCH₂C(CH₃)(NH₂)CH₂OH, C4}, boiling point 151°C/10mmHg, were purchased from Aldrich Chemical Company. They were used as received and were stored under nitrogen gas in desiccator.

Commercial grade triethylenetetramine { $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, TETA}, boiling point $266^\circ\text{-}267^\circ\text{C}$, was purchased from FACAI PolyTech Co., Ltd. and was distilled in a simple distillation under vacuum (0.1mmHg) at 120°C . It was used as a base catalyst, and solvent and also stored under nitrogen gas.

Potassium hydroxide {KOH} was purchased from Baker Analyzed Reagent, it was used as catalyst and as received.

Acetonitrile { CH_3CN }, boiling point $81^\circ\text{-}82^\circ\text{C}$, and methanol { CH_3OH }, boiling point 64.7°C , were used as precipitating agents. They were purchased from Lab-Scan Analytical Science and Baker Analyzed Reagent and 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.

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

2.2 Equipment

2.2.1 Mass Spectroscopy (MS)

Mass spectra (MS) 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 initiator and cesium iodine (CsI) was used as a reference.

2.2.2 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, N₂. Sample weights were typically from 5 to 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 with ramp rate 10°C/min was from room temperature (27°C) to 750°C, while DSC measurements were conducted from -15°C to 400°C at the heating rate of 10°C/min and the flow rate of nitrogen gas was 40 ml/min.

2.2.3 Nuclear Magnetic Spectroscopy (NMR)

¹H-NMR and ¹³C-NMR were performed on a Bruker 200 MHz spectrometer at the Chemistry Department, Faculty of Science, Chulalongkorn University and a 500 MHz JEOL spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University.

Both spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-d₆) used as solvent and reference for chemical shift measurements. 32 Scans were run for proton, while ¹³C samples were pulsed for more than 650 Scans. ²⁹Si-NMR spectra were obtained using a 500 MHz JEOL spectrometer. Deuterated dimethyl sulfoxide (DMSO-d₆) was used as solvent and tetramethylsilane (TMS) was used as reference for chemical shift measurements. The samples were pulsed for 4 hours.

2.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were performed using a Bruker instrument with a resolution of 4cm⁻¹. The samples were mixed with pure and dried crystal potassium bromine, KBr, at an approximate sample:KBr ratio of 1:20 and ground to thoroughly mix. The samples were transferred to the sample holder and then quickly placed in the chamber, which was purged with

nitrogen, by constant flow rate, to remove CO₂ before initiating data acquisition.

2.3 General Procedures

2.3.1 Synthesis of glycolato spirosilicate or bis(ethane-1,2-diylldioxy) silane. $Si(OCH_2CH_2O)_2$, tetra-coordinated spiro-silicate, directly from silica, SiO₂, and ethylene glycol

To obtain optimum conditions for the bis(ethane-1,2-diylldioxy) silane, Si(OCH₂CH₂O)₂, four variations in the reactions were studied.

2.3.1.1 *Effect of TETA concentration on the synthesis of bis (ethane-1,2-diylldioxy)silane*

A mixture of 12.5mmol (0.75g) silica (surface area of 320 cm²/g or 182 cm²/g), 15 mL of ethylene glycol, and 12.5 mmol (1.83g) TETA was placed into a 50 mL two-neck round bottomed flask equipped with a simple distillation set. The mixture was heated to the boiling point of ethylene glycol under nitrogen with constant magnetically stirring, to distill ethylene glycol and water formed as by-product during the reaction. During the course of reaction, an equal amount of dried and fresh ethylene glycol was added when approximately the same amount came off, and the distillation was continued until the mixture turned clear, meaning that it was completed. The mixture was then allowed to cool down to room temperature and then precipitated by adding trace amount of dried methanol, CH₃OH, in dried acetonitrile, CH₃CN, and kept in refrigerator over night. The precipitate was then filtered, washed several times with dried acetonitrile to remove excess TETA and EG, and dried in a desiccator using vacuum pump, 0.1mmHg, at room temperature overnight to remove methanol and acetonitrile.

This procedure was repeated at different TETA concentration of 25%(0.458g, 3.13mmol), 50% (0.915g, 6.25mmol), 75% (1.373g, 9.38mmol), 100% (1.83g, 12.5mmol), 125% (2.29g, 15.63mmol), 150% (2.75g, 18.75mmol), and 200% (3.66g, 25mmol), mmol equivalent to silica.

2.3.1.2 Effect of KOH concentration on the synthesis of bis(ethane-1,2-diylldioxy)silane

According to A, synthesis of bis(ethane-1,2-diylldioxy) silane was carried out by adding silica, SiO₂, 12.5 mmol (0.75g), 15 mL of ethylene glycol, 125%, 15.63 mmol (2.288g) of TETA, and 2-10% mmol equivalent of KOH to silica into a 50 mL two-neck round bottomed flask equipped with a simple distillation set. The reaction mixture was heated at 200°C to distill EG and water, by-product produced during the reaction, with mechanically stirring. An equal amount of dried and fresh ethylene glycol was added when approximately the same amount came off. The distillation was continued until the mixture turned cleared, meaning that it was finished. The mixture was then allowed to cool down, precipitated by adding trace amount of dried CH₃OH in dried CH₃CN, and kept in refrigerator overnight. The precipitate was then filtered, washed several times with dried acetonitrile and dried in desiccator under vacuum pump at room temperature overnight.

2.3.1.3 Effect of ethylene glycol (EG) concentration on the synthesis of bis(ethane-1,2-diylldioxy)silane

Referring to the variations of TETA and KOH concentration, bis(ethane-1,2-diylldioxy) silane was synthesized by mixing silica 12.5 mmol (0.75g), 15 mL of ethylene glycol, 125%, 15.63 mmol (2.29g) TETA, and 2-10% mmol equivalent of KOH to silica into a 50 mL two-neck round bottomed flask equipped with a simple distillation set. The reaction mixture was heated at 200°C to distill EG and water, by-product, with mechanically stirring. An equal amount of dried and fresh ethylene

glycol was added when approximately the same amount came off. The distillation was continued until the mixture turned cleared, meaning that it was finished. The mixture was then allowed to cool down, precipitated by adding trace amount of dried CH_3OH in dried CH_3CN , kept in refrigerator overnight, filtered, washed several times by dried acetonitrile and then dried in a desiccator under vacuum overnight.

This step was repeated at different amount of EG: 5, 7.5, 10, 15, 20 mL.

2.3.1.4 Effect of reaction time on the synthesis of bis(ethane-1,2-diylldioxy)silane

2.3.1.4.1 Without potassium hydroxide (KOH)

Bis(ethane-1,2-diylldioxy)silane was synthesized by mixing silica 12.5 mmol (0.75g), 15 mL of ethylene glycol, and 15.63 mmol (2.29g) TETA, into a 50 mL two-neck round bottomed flask. The synthesis procedure was the same as above. The reaction time was varied from 8 to 24 hours.

2.3.1.4.2 With potassium hydroxide (KOH)

Bis(ethane-1,2-diylldioxy)silane was synthesized by mixing silica 12.5 mmol (0.75g), 15 mL of ethylene glycol, 15.63 mmol (2.288g) TETA, and 2-10% mmol equivalent of KOH to silica into a 50 mL two-neck round bottomed flask. The same procedure was repeated. The reaction time to synthesize bis(ethane-1,2-diylldioxy)silane with KOH was varied from 4-12 hours.

2.3.2 Synthesis of ethylene glycol derivatives, six-membered spirosilicate, bis(2-amino-2-methyl propane-1,3-diylldioxy) silane, tetra-coordinated spirosilicate, directly from silica and 2-amino-2-methyl-1,3-propanediol

To obtain the best conditions for the synthesis of bis(2-amino-2-methylpropane-1,3-diylldioxy)silane, $Si\{OCH_2C(CH_3)(NH_2)CH_2O\}$, five variations in the reactions were studied.

2.3.2.1 Effect of reaction temperature on synthesis of bis(2-amino-2-methylpropane-1,3-diylldioxy)silane

Because the boiling point of 2-amino-2-methyl-1,3-propanediol is 151°C/10mmHg, we need to run the reaction under vacuum, 0.1mmHg, at temperature starting from 140°C to 165°C. A mixture of 6.67 mmol (0.4g) fumed SiO₂ (surface area of 320 cm²/g); 10 mL TETA; and 13.34 mmol (1.4g) 2-amino-2-methyl-1,3-propanediol was placed into a 50 mL two-neck round-bottomed flask. The mixture was heated at the above temperature under vacuum, 0.1mm/Hg, with constant magnetically stirring to distill off 2-amino-2-methyl-1,3-propanediol, TETA, and water formed as by product. The solutions were allowed to cool down to room temperature, purified by adding trace amount of dried CH₃OH in dried CH₃CN, and kept in refrigerator overnight. The precipitate was then filtered, washed several times with dried acetonitrile to remove TETA and C4 and dried in desiccator under vacuum, 0.1mmHg, at room temperature overnight.

2.3.2.2 Effect of 2-amino-2-methyl-1,3-propanediol, C4, concentration on the synthesis of bis(2-amino-2-methylpropane-1,3-diylldioxy) silane

A mixture of 6.67 mmol (0.4g) fumed SiO₂ (surface area of 320 cm²/g), 10 mL of TETA, and 13.34 mmol (1.4g) 2-amino-2-methyl-1,3-propanediol was placed into a 50 mL two-neck round-bottomed flask. The mixture was heated at 160°C under vacuum, 0.1mm/Hg, with constant magnetically stirring to distill off 2-amino-2-methyl-1,3-propanediol, TETA, and water formed as by product. The mixture was allowed to cool down, purified by adding trace amount of dried CH₃OH in dried CH₃CN, then kept in refrigerator over night. The precipitate was then

filtered, washed with dried acetonitrile several times and dried in desiccator under vacuum, 0.1mmHg, at room temperature overnight.

This process was repeated at different 2-amino-2-methyl-1,3-propanediol concentrations: 13.34 mmol (1.4g), 20.01 mmol (2.1g), 26.68 mmol (2.8g), 40.02 mmol (4.2g), and 53.36 mmol (5.6g).

2.3.2.3 Effect of TETA concentration on the synthesis of bis(2-amino-2-methylpropane-1,3-diylldioxy) silane

A mixture of 6.67mmol (0.4g) fumed SiO₂ (surface area of 320 cm²/g); 10 mL of TETA; and 40.00mmol (4.2g) 2-amino-2-methyl-1,3-propanediol was placed into a 50mL two-neck round-bottomed flask and heated at 160°C under vacuum, 0.1mm/Hg. The product was purified by adding trace amount of dried CH₃OH in dried CH₃CN, filtered, washed with dried acetonitrile several times and dried in desiccator under vacuum, 0.1mmHg, at room temperature overnight.

This procedure was repeated with different amounts of TETA: none, 5, 10, 12, and 15 mL.

2.3.2.4 Effect of KOH concentration on the synthesis of bis(2-amino-2-methylpropane-1,3-diylldioxy)silane

A mixture of 6.67mmol (0.4g) fumed SiO₂ (surface area of 320 cm²/g), 10 mL of TETA, 40.02 mmol (4.2g) C4, and 2-10% of KOH was placed in a 50 mL two-neck round-bottomed flask and heated at 160°C under vacuum, 0.1mm/Hg. The solution mixture was purified by adding trace amount of dried CH₃OH in dried CH₃CN, filtered, washed with dried acetonitrile several times and dried in desiccator at 0.1mmHg at room temperature overnight.

2.3.2.5 *Effect of reaction time on the synthesis of bis(2-amino-2-methylpropane-1,3-diylldioxy)silane*

2.3.2.5.1 *Without potassium hydroxide (KOH)*

A mixture of 6.67mmol (0.4g) fumed SiO₂ (surface area of 320 cm²/g), 10 mL of TETA, and 40.02 mmol (4.2g) 2-amino-2-methyl-1,3-propanediol was placed in a 50 mL two-neck round-bottomed flask and heated at 160°C under vacuum, 0.1mm/Hg to distill off C₄, TETA, and water formed during the reaction as by-product at 14 hr, 18 hr, 20 hr, 24 hr, 28 hr, 34 hr, and 48 hr. The product was purified by adding trace amount of dried CH₃OH in dried CH₃CN, filtered, washed with dried acetonitrile several times and dried in desiccator under vacuum at room temperature overnight.

2.3.2.5.2 *With potassium hydroxide (KOH)*

The same procedure as the one without KOH was repeated, but the reaction time was varied from 6, 10, 14, to 18 hours.

2.3.3 Synthesis of ethylene glycol derivatives five-membered spiro-silicate, bis(3-amino propane-1,2-diylldioxy)silane, Si {OCH₂C(CH₃)(NH₂)O}₂, tetra-coordinated spiro-silicate, directly from silica and 3-amino-1,2-propanediol

To obtain the best conditions for the synthesis of bis(3-aminopropane-1,2-diylldioxy)silane, Si{OCH₂CH(CH₂NH₂)O}₂, five variations in the reactions were studied.

2.3.3.1 *Effect of reaction temperature on the synthesis bis(3-aminopropane-1,2-diylldioxy)silane*

Referring to the boiling point of 3-amino-1,2-propanediol, 264°-265°C/739mmHg and the condition to synthesize bis(2-amino-2-methyl-1,3-diylldioxy)silane, we also need to run the reaction under vacuum, 0.1mmHg, at temperature of 150°C and 160°C. A mixture of 5

mmol (0.3g) fumed SiO₂ (surface area of 320 cm²/g); 5 mL TETA; and 20 mmol (1.82g) of 3-amino-1,2-propanediol is placed into a 50 mL two-neck round-bottomed flask. The mixture was heated at the above temperature with constant magnetically stirring to distill off TETA and water, as by product.

2.3.3.2 Effect of 3-amino-1,2-propanediol concentration on the synthesis bis(3-aminopropane-1,2-diylldioxy)silane

A mixture of 5 mmol (0.3g) fumed SiO₂, 5 mL of TETA; and 10 mmol (0.91g) 3-amino-1,2-propanediol was placed into a 50 mL two-neck round-bottomed flask. The mixture was heated to 160°C to distill off 3-amino-1,2-propanediol, TETA, and water, as by product. The solution mixture was cooled down, purified the product by adding trace amount of dried CH₃OH in dried CH₃CN, and kept in refrigerator overnight. The precipitate was then filtered, washed several times with dried acetonitrile to remove TETA and C3 and dried in desiccator under vacuum, 0.1mmHg, at room temperature overnight.

This procedure was repeated with different 3-amino-1,2-propanediol concentrations: 10 mmol (0.91g), 20 mmol (1.82g), 30 mmol (2.73g), and 40 mmol (3.64g).

2.3.3.3 Effect of TETA concentration on the synthesis of bis(3-aminopropane-1,2-diylldioxy)silane

5 mmol (0.3g) fumed SiO₂, 5 mL of TETA, and 30 mmol (2.73g) 3-amino-1,2-propanediol was added into a 50 mL two-neck round-bottomed flask. The mixture was heated under vacuum at 0.1mmHg, 160°C to distill off C3, TETA, and water, as by product. The solution mixture was cooled down, the product was purified with trace amount of dried CH₃OH in dried CH₃CN, and afterward kept in refrigerator overnight. The precipitate was filtered, washed several times with dried acetonitrile and dried in desiccator under vacuum at room temperature overnight.

This step was repeated with different TETA concentrations: none, 5, 7, and 10 mL.

2.3.3.4 Effect of KOH concentration on the synthesis of bis(3-aminopropane-1,2-diylldioxy)silane

5 mmol (0.3g) Fumed SiO₂, 5 mL of TETA, 30 mmol (2.73g) 3-amino-1,2-propanediol, and 2-10% of KOH was added into a 50 mL two-neck round-bottomed flask. The mixture was heated under vacuum at 0.1mm/Hg, 160⁰C. The solution mixture was cooled down, purified with a trace amount of dried CH₃OH in dried CH₃CN, and then kept in refrigerator overnight. The product was filtered, washed several times with dried acetonitrile and dried in desiccator under vacuum, 0.1mmHg, at room temperature overnight.

2.3.3.5 Effect of reaction time on the synthesis of bis(3-amino-propane-1,2-diylldioxy)silane

2.3.3.5.1 Without potassium hydroxide (KOH)

A mixture of 5 mmol (0.3g) fumed SiO₂, 5 mL of TETA, and 30 mmol (2.73g) C3 was placed in a 50 mL two-neck round-bottomed flask. The mixture was heated to 160⁰C to distill off C3, TETA, and water, as by product at 10, 12, 14, 18, and 20 hours. The product mixture was purified with a trace amount of dried CH₃OH in dried CH₃CN, filtered, washed with dried acetonitrile several times and dried in desiccator under vacuum, 0.1mmHg, at room temperature overnight.

2.3.3.5.2 With potassium hydroxide (KOH)

The same procedure as the one without KOH was repeated, but the reaction time was varied from 6, 10, 12, to 14 hours.