

CHAPTER III

EXPERIMENTAL

3.1 Materials

Fused silicon dioxide or HI-SIL 927 silica (SiO_2), with a surface area of $168 \text{ m}^2/\text{g}$, by BET, was donated by PPG Siam Silica Co., Ltd.

Fumed silicon dioxide with a surface area $320 \text{ m}^2/\text{g}$ was purchased from Aldrich Chemical Company. Both Fused and Fumed silicon dioxide were dried in oven at 100°C for 10 h.

2-amino-2-methyl-1,3-propanediol ($\text{HOCH}_2\text{C}(\text{CH}_3)(\text{NH}_2)\text{CH}_2\text{OH}$) was purchased from Aldrich Chemical Company, used without purification and kept under nitrogen atmosphere.

Ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$), purchased from Labscan, was used as a reaction solvent. It was distilled by fractional distillation at 200°C under N_2 atmosphere. Triethylenetetramine [TETA, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_2\text{NH})_3$] was purchased from Facai Polytech Co., Ltd., used as received and as a catalytic base. It was purified by vacuum distillation at 120°C (0.1 mmHg).

Potassium hydroxide (KOH) was purchased from Baker Analyzed Reagent, It was used as received as catalyst.

Methanol (CH_3OH) and acetonitrile (CH_3CN) were purchased from Baker Analyzed Reagent and Lab-scan Analytical Science. They were used as precipitating agents and purified by fractional distillation under nitrogen gas over magnesium activated with iodine and calcium hydride, respectively. Both were stored over molecular sieves.

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

Hydrochloric acid solution (HCl) and ammonium hydroxide solution (NH₄OH) were diluted with deionized water at various concentrations. They were used as an electrolyte.

3.2 Equipment

3.2.1 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were obtained on a Vector 3.0 Bruker Spectrometer with 32 scans at a resolution of 4 cm⁻¹. A frequency range of 4000-400 cm⁻¹ was observed using a deuterated triglycinesulfate detector (DTGS) with specific detectivity of $D^* = 1 \times 10^9 \text{ cm} \times \text{Hz}^{1/2} \times \text{W}^{-1}$. The powder samples were pressed to form pellets by mixing with pure and dry crystalline potassium bromide, KBr.

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H and ¹³C-NMR spectra were obtained on a 200 MHz JEOL spectrometer at the Chemistry Department, Faculty of Science, Chulalongkorn University at room temperature. While ²⁹Si-NMR spectra were obtained on 500 MHz JEOL spectrometer at the Scientific and Instrument Research Equipment Centre, Chulalongkorn University. Deuterated dimethyl sulfoxide (DMSO-d₆) was used as a solvent. Tetramethylsilane (TMS) was used as the reference.

3.2.3 Thermogravimetric Analysis (TGA)

TGA measurement data were obtained on a Du Pont instrument, Du Pont TGA 2950, using a platinum pan, using samples of 12-15 weight. The temperature program was started from room temperature to 750°C, with a heating rate of 10°C/min and nitrogen flow rate of 25 mL/min.

3.2.4 Scanning Electron Microscope (SEM)

SEM digitized micrographs were obtained from a JEOL 5200-2AE (MP 15152001) scanning electron microscope with magnification range of 35-20,000X. Micrographs of the sample surfaces were obtained using a voltage 25 kV at 5000 and 7500 magnification. The pyrolyzed samples were stuck to aluminium stubs. Before characterization, these stubs with samples were dried in vacuum oven at 60°C and kept in silica gel-container before coated with gold by vapor deposition.

3.2.5 BET Surface Area Measurement

Surface area of pyrolyzed product was determined by Autosorb-1 Gas sorption system (Quantachrome Corporation) with the Brunauer-Emmett-Teller method (BET). A gaseous mixture of nitrogen and helium was allowed to flow through the system at a constant rate of 30 ml/min. The nitrogen gas was injected with a one milliliter syringe to calibrate the analyzer for each gas composition and also used as the adsorbate at liquid nitrogen temperature. Each sample was degassed at 300°C for 3 h before measurement. The surface area of the samples was obtained from five point adsorption. The results were calculated based on the desorption surface area and the dried weight of the sample after analysis.

3.2.6 Wide Angle X-Ray Diffractometer (WXR)

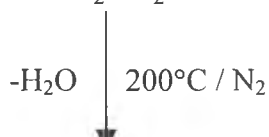
WXR used in this study was D/MAX 2000 series of Rigaku X-ray Diffractometer system. X-ray of Cu k-30 mA was used as a source. The k-beta filter was used to eliminate interference peak. Divergence slit and scattering slit at 1 degree together with 0.3 mm of receiving slit were set. The experiment was performed in the range of 5-90 degree with scan speed 5 deg/min and 0.02 degree for scan step.

3.2 Methodology

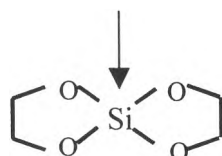
3.3.1 Synthesis Method

3.3.1.1 *Synthesis of Tetra-Coordinated Spirosilicate, C2 from Silica and Ethylene Glycol*

The reaction mixture was prepared according to Sun (2000) in a round bottom flask at room temperature. Powder of fused silica (6g, 0.1mol) was dissolved in excess of ethylene glycol (20 ml), resulting in clear solution. Afterwards triethylenetetramine (18.24g, 0.12mol) was quickly added. The reaction was carried out under nitrogen atmosphere at the boiling point of ethylene glycol. The mixture was heated to distill off EG and by-product water, see figure 3.1. The mixture turned yellow clear in 24 h and was then allowed to stand at room temperature to cool down. The solution was precipitated by using 10% of distilled methanol in 90% of distilled acetonitrile. The white powder product was stored in a silica gel container due to the moisture absorption property.



Purification



Tetra-coordinated spiro silicates :C2

Figure 3.1 Schematic of the C2 monomer synthesis.

3.3.1.2 Synthesis of Aminospirosilicate, C4 from Silica and 2-Amino-2-methyl-1,3-propanediol

The product of aminospirosilicate, C4 (Sun, 2000) was prepared in a round bottom flask at room temperature with a mixture of 0.033 mol (2 g) fumed silica, 50 mL of TETA, 0.2 mol (21 g) 2-amino-2-methyl-1,3 propanediol, and 7 mol percent of KOH equivalent to silica. The reaction was carried out at 160°C under vacuum, 0.1 mmHg, for 14 h, see figure 3.2, to obtain TETA and water as by-product. The mixture was then allowed to cool down, precipitated by using 10% of distilled methanol in 90% of distilled acetonitrile. The white powder product was kept in silica gel container due to the moisture absorption property.

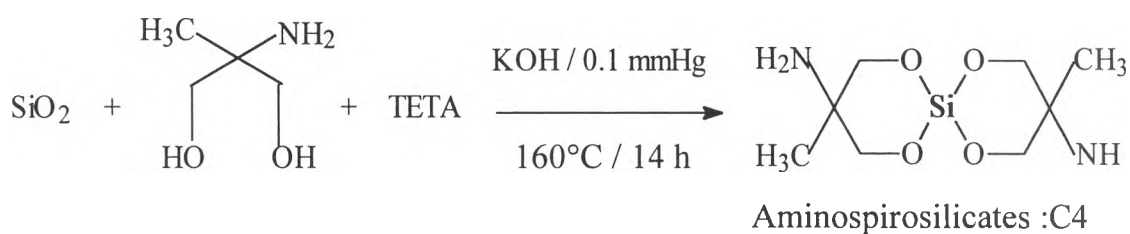


Figure 3.2 Schematic of the C4 monomer synthesis.

3.3.2 Determination of Curing Conditions

3.3.2.1 Synthesis of Polymer C2

To determine the suitable condition of polymer C2, time and temperature were investigated to obtain crosslinked polymer by further heating the reaction mixture under vacuum, 0.1 mmHg. As the distillation was continued, the clear solution became more viscous.

The curing temperature was varied from 110°, 120°, and 130°C by fixing curing time at 3 h and 5 h. The product was then precipitated as described for monomer. The suitable condition temperature was the point that the highest ceramic yield obtained, using TGA measurement.

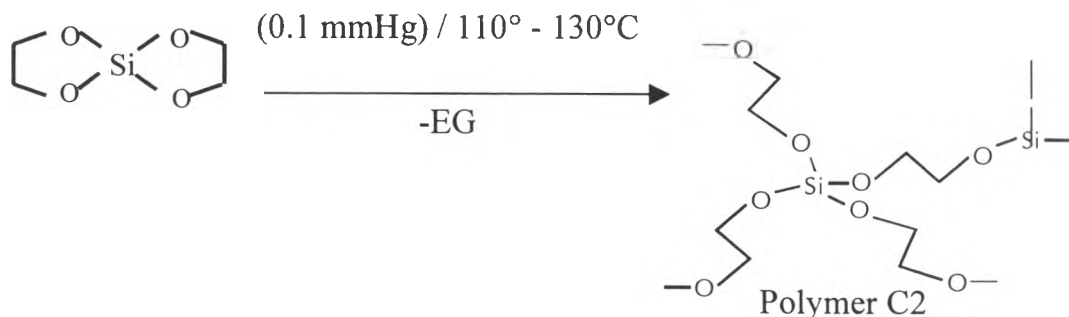


Figure 3.3 Schematic of the C2 polymer synthesis.

3.3.2.2 Synthesis of Polymer C4

To determine the suitable condition of polymer C4, time and temperature were investigated to obtain crosslinked polymer by further heating the reaction mixture under vacuum, 0.1 mmHg. As the distillation was continued, the clear solution became more viscous.

The curing temperature was varied from 170° and 180°C by fixing curing time at 5 h and 10 h. The product was then precipitated as described for monomer. The suitable condition temperature was the point that the highest ceramic yield obtained, using TGA measurement.

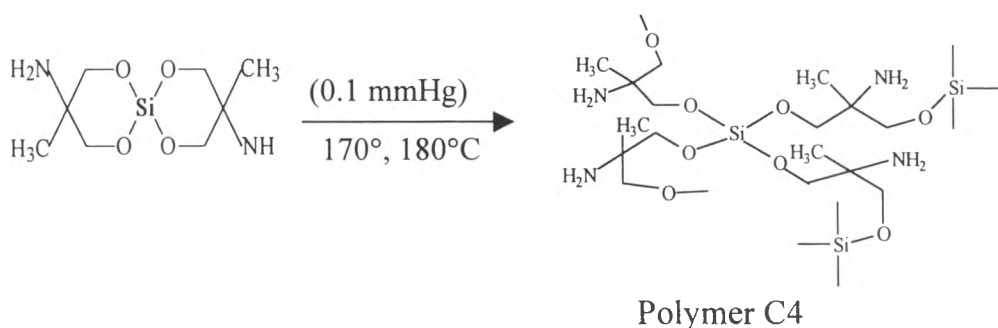


Figure 3.4 Schematic of the C4 polymer synthesis.

3.3.3 Sol-gel Transition Study

Hydrolysis of the products from 3.3.1 and 3.3.2 was carried out by addition of either HCl or NH₄OH solution at various concentrations. The mixture was prepared directly in 7 in. crucible at room temperature, resulting in a formed-gel product, afterwards the gel was aged at room temperature. To study the sol-gel transition, at each hour the aliquots of mixture are deducted and dried using high vacuum (0.1 mmHg) to remove solvent. The hydrolysis reaction was also carried out at 40° and 60°C.

3.3.4 Pyrolysis of Hydrolyzed Product

The hydrolyzed gel obtained from 3.3.3 was pyrolyzed in a furnace at a heating rate of 10°C/min to 750°C and temperature maintained at 750°C, for 7 h. The pyrolyzed products were then characterized by TGA, FTIR, BET, SEM and WXR. D.

3.3.5 Density Measurement

The volumetric property of the monomer C2, the stable hydrolyzed product from 3.3.3, was determined using a 25 mL pycnometer (for powder form product) and distilled isooctane as media. The measurement was performed at 25°C. The purified product in the bottle was weighed in the range of 0.5-1.0 g. The media was added until covering the product. Then the bottle was sonicated and incubated at 25°C for 2 h before adding the media to the marked point. The same procedure was made with fused silica for comparison.