

CHAPTER III

EXPERIMENTAL

3.1 General Material Handling

Since the silatrane complexes are slightly moisture and air sensitive, all operations were done under N₂ atmosphere.

Fumed silicon dioxide (surface area of 320 m²/g, average particle size of 0.007 μm) was purchased from Aldrich Chemical Company. It was dried in oven at 90°C for 10 hr. Moreover, other SiO₂ or beach sand can also be used.

Ethylene glycol (EG, HOCH₂CH₂OH), purchased from Labscan, was used as reaction solvent. It was distilled by fractional distillation at 200°C under N₂ atmosphere. Triisopropanolamine [TIS, N(CH₂CHCH₃OH)₃] was obtained from Fluka Chemical Company, and dried in desiccator. Commercial grade triethylenetetramine [TETA, H₂N(CH₂CH₂NH)₃] supplied by Union Carbide Thailand Limited, was purified by vacuum distillation at 120°C (1 mmHg).

Anhydrous diethyl ether and dichloromethane, used as solvents for precipitation, were purchased from Baker Analytical Co. Dichloromethane was distilled over anhydrous calcium chloride under N₂ atmosphere. Anhydrous diethyl ether was dried by adding anhydrous calcium chloride, let stand for 24 hr with occasional shaking, and then filtered into another clean, dry bottle.

HPLC grade THF, used as solvent for molecular weight determination, was purchased from J.T. Baker Inc. and used as received. AR. grade methanol used for hydrolyzed silatrane complexes was purchased from Labscan and used as received to mixed with DI water (1:1). MgO solution used as hydrolysis solvent prepared by stirring 0.5 g in 1 liter of distilled demonized water and measuring pH = 11.3.

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

3.2 General Instrumental/Characterization Methods

3.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were obtained using a Bruker FTIR instrument with a resolution of 4 cm^{-1} . The powder samples were pressed to form pellets, by mixing 1.0 % of sample with 99 wt.% pure and dry crystalline potassium bromide, KBr, and followed by hydraulically pressing. The sample pellet was then placed in the chamber which was then purged with N_2 for 20 min to remove CO_2 atmosphere.

3.2.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

^{13}C - and ^1H -NMR spectra were obtained using a 500 MHz JEOL spectrometer at the Chemistry department, Faculty of science, Chulalongkorn University. A sample was dissolved in deuterated methanol and DMSO. Tetramethylsilane (TMS) was used as the internal reference proton and carbon NMR.

3.2.3 Gel Permeation Chromatography (GPC)

Gel permeation chromatograms were performed using Water GPC 600E instrument attached with UV and RI detectors (Water 486 and Water 410 respectively). The separating column was styra gel which can separate the molecular weight species of the range between 0 to 1,000, calibrated with standard narrow distribution polystyrene. THF was used as a solvent at ambient temperature. The sample solutions (concentration less than 0.3 % weight) were prepared by filtering through $0.45\ \mu\text{m}$ pore membrane filter.

3.2.4 Rheometric Measurement

The fluid rheometer utilizing cone and plate rheometer, model ARES, from Rheometric Scientific Inc., was used to determine $G'(\omega)$, $G''(\omega)$,

and $\eta^*(\omega)$ with multi-frequency mode from 0.1 to 1.6 rad/s using 10 g an transducer and with 20% strain input. The rheometrics fluids spectrometer using a 50 mm diameter cone with 0.04 radian angle. Temperature was controlled by a circulating fluid bath. For each time point, measurement of a set of 10 frequencies from 0.1 to 1.6 rad/s took approximately 10 sec.

3.2.5 Scanning Electron Microscope (SEM)

SEM digitized micrographs were obtained from a JEOL 5200-2AE (MP 15152001) scanning electron microscope with magnification range of 35-200,000. Micrographs of the sample surfaces were obtained using a voltage of 10 kV at 2,000 and 7,500 magnification. The samples were obtained after being pyrolyzed to 800°C and stuck to aluminium stubs. Before characterization, these stubs with samples were dried in vacuum oven at 70°C for 5 hr and then coated with gold by vapor deposition.

3.2.6 BET Surface Area Measurement

Autosorb-1 Gas Sorption System (Quantachrome Corporation) was used to determine the surface area of pyrolyzed polysilatrane by the Brunauer-Emmett-Teller method (BET). A gaseous mixture of nitrogen and helium combined using a gas mixer was allowed to flow through the system at a constant rate of 30 cc./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 2 hr before measurement. The surface area of the samples was obtained from five point adsorption isotherm at p/p_o ratio less than 0.3. The results were calculated based on the desorption surface area and the dried weight of the sample after analysis.

3.3 Methodology

This section is divided into three parts. The first part, which is the synthetic procedure for formation of silatrane complexes, was carried out at

various TETA concentrations, curing temperature, and curing time. The second part describes the sol-gel transition of the polysilatrane and the last part is the pyrolysis study.

3.3.1 *Synthesis of Silatrane Complexes*

From the previous work (Piboonchaisit P., 1996), the higher the level of TIS, the higher the amount of SiO₂ is dissolved. First, an excess of TIS was used while fixing the ratio of SiO₂ and TIS at 1:2.5, and the effect of vacuum distillation time was studied.

3.3.1.1 Variation of Vacuum Distillation Time

6.09 g (100 mmol) of fumed silicon dioxide (SiO₂), triisopropanolamine (TIS) 47.8 g (250 mmol), 100 ml of ethylene glycol (EG) and triethylene tetramine (TETA) 0.38 g (5% mmol of SiO₂) were placed into a 250 ml, 2-necked reaction flask. The reaction mixture was stirred until it became homogenous, and oil bath was then heated to 200°C. The reaction time was started after immersing the reaction flask into the oil bath. SiO₂ was dissolved slowly and the reaction temperature was set at the distillation point of EG while a continuous removing of by product, H₂O, to promote the forward reaction. During the course of a reaction, the same amount of fresh EG as distillate was added. The reaction was completed in 30 hr in the absence of TETA catalyst, as indicated by formation of a clear solution. In the reaction that used TETA as a catalyst the reaction mixture turns clear in only 3 hr. Most of the remaining EG was removed by vacuum distillation (1 mmHg) at 120°C with variation of time from 2-10 h.

3.3.1.2 Variation of Vacuum Distillation Temperature

Following the results from 3.3.1.1, the experiments were carried out by fixing the amount of SiO₂, TIS and TETA at 3.05 g (50 mmol), 9.61 g (50 mmol) and 0.38 g (5% mmol of SiO₂), respectively. The procedure was the same as described in 3.3.1.1, except that the temperature used for vacuum distillation (1 mmHg) to remove EG was varied from 110°-220°C.

0.1 g of the product obtained from each completed reaction was weighed for GPC characterization. After removal of remaining ethylene glycol, the viscous product was purified by precipitating with 10 % dichloromethane in diethyl ether. The white powder product was filtered off, and dried in a vacuum oven at 50°C. The final product was characterized by TGA, FTIR and NMR.

3.3.2 *Sol-Gel Transition Study of Polysilatrane*

The product after removal of residual ethylene glycol has the appearance of a hard plastic, and was used to study sol-gel transition without purification. The material was dissolved in the hydrolysis solvent systems (H₂O, H₂O/MeOH, and H₂O/MgO) at concentration of about 150 % w/v. The hydrolysis temperature was varied at 40°, 50° and 60°C. The solution was stirred until homogenous, prior to being transferred to the rheometer for rheological analysis. The solution needed to be preheated at the hydrolysis temperature in water bath until the solution has enough viscosity to remain on the plate of the rheometer. Then the viscous solution was quickly transferred to the rheometer with cone and plate attachment that was pre-heated to the hydrolysis temperature. The gelation time was calculated from the time when the solution was first heated in the water bath.

3.3.3 *Pyrolysis of Polysilatrane Gel*

The polysilatrane gel obtained from 3.3.2 was pyrolyzed in furnace at 10°C/min at various temperatures from 200° to 800°C. The pyrolysis conditions were also varied, and comparison was made between samples that were pyrolyzed starting from 500°C versus those pyrolyzed starting at room temperature. The pyrolysis products were then characterized by FTIR, BET and SEM.