

CHAPTER II

EXPERIMENTAL INVESTIGATION

2.1 General Material Handling

Because the starting materials and the products are susceptible to moisture and air, all reactions were carried out under nitrogen atmosphere and products were stored in vials after purging with nitrogen gas. The glassware was oven dried prior to use.

Amorphous, precipitated silicon dioxide, with a multipoint BET surface area of 182 m²/g, was donated by PPG Siam Silica Co., Ltd. and used as received. Catechol and 4-tert-butylcatechol were purchased from Fluka Chemika, and hydroquinone was obtained from Riedel-deHaen. Ethylene glycol, was purchased from Farmitalia Carlo Erba (Barcelona), and distilled under nitrogen. Triethylenetetramine was donated by from Union Carbide Thailand Limited and purified by vacuum distillation. Methanol was purchased from J.T.Baker Inc. (Phillipsburg, USA), distilled from magnesium metal activated with iodine under nitrogen atmosphere, and then stored in dried bottles with molecular sieves 4A°.

2.2 Instrumentation/ Characterization

2.2.1 Spectroscopic Characterization

2.2.1.1 *Fourier Transform Infrared Spectroscopy (FTIR)*. FTIR spectra were recorded on a Bio-Rad FT-45A Fourier Transform Infrared Spectrometer with a resolution of 8 cm^{-1} . Analytical grade (KBr) from Fluka Chemika was pressed hydraulically into pellets, and used as a background spectrum. Samples were ground with oven dried KBr (1:20) followed by hydraulic pressing into pellets and quickly taken to the chamber. The pellet was flushed with dry nitrogen gas to remove carbon dioxide in the chamber before data acquisition. The functional groups of products were characterized.

2.2.1.2 *Nuclear Magnetic Resonance (NMR)*. ^1H -NMR and ^{13}C -NMR spectra were obtained at room temperature using 500 MHz JEOL spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University and ^1H -NMR spectra were recorded at a frequency of 10,000 Hz using 16 scans, a pulse width of 5.5 sec, a pulse delay of 30 sec and a sweep width of 16,000 Hz. ^{13}C -NMR spectra were recorded at 9065 Hz using 4,000scans, a pulse delay of 2.5 sec and a sweep width of 20,000 Hz. Deuterated dimethylsulfoxide (d_6 -DMSO) and tetramethylsilane (TMS) were used as solvent and standard internal reference, respectively.

2.2.1.3 *Mass Spectroscopy (MS)*. Direct probe injection was used for electron impact ionization (EI^+ mode) using an ionization energy of 70 eV. Perfluorotributylamine was used as a standard for peak calibration and the range studied was set from m/z 20 to 800. Mass spectra were recorded on a Finnigan MAT Incos 50 mass spectrometer instrument, at the Faculty of Science, Mahidol University.

2.2.2 Thermal Analysis

2.2.2.1 *Thermogravimetric Analysis (TGA)*. TGA profiles were recorded using a NETZSCH TGA 200 thermogravimetric analyzer to obtain decomposition of products as a function of temperature (T_d) and to measure the percent ceramic yield at 950°C. Samples were loaded in alumina pan, heated from room temperature to 950°C with a heating rate of 20°C/min., and carried out under N₂/O₂ atmosphere with a flow rate of 15 ml/min, the balance flow set at 40 ml/min.

2.2.2.2 *Differential Scanning Calorimetry (DSC)*. DSC profiles were obtained by using a NETZSCH DSC 200 (Germany). Samples were packed in hermetically sealed aluminum pans, and heated under flowing N₂ in the DSC chamber from ambient temperature to 450°C at a ramp rate of 10° C/min to determine sample transition temperatures.

2.2.3 X-ray Diffraction (XRD)

XRD spectra were obtained using a PN 3710 Philip Analytical Instrument at the Metallurgy and Materials Science Research Institute. Samples were ground and packed in a glass specimen holder, placed in the goniometer using Cu(K α) small radiator and operated at 40 kV and 30 MA. Scans were measured in the range of 5-80 degree 2 θ at a scan speed of 0.6 degree for 20 min and 0.02 degree 2 θ increments. The diffraction patterns determined the crystallinity of products.

2.3 Experimental

The experimental section is divided into two parts. The first part describes the one step synthesis of an organosilicon copolymer from SiO₂, catechol, hydroquinone, and 4-tert-butylcatechol by varying the mole ratio of comonomer, namely, hydroquinone, 4-tert-butylcatechol, and studying the effects of catalyst concentration (TETA) on the reaction. The other one described the chemical kinetic method to determine the order with respect to SiO₂ and the activation energy.

2.3.1 One step synthesis of an organosilicon copolymer from SiO₂, catechol, hydroquinone, and 4-tert-butylcatechol:

2.3.1.1 *Variation of hydroquinone: 4-tert-butylcatechol mole ratio.*

Table 2.1 Mole ratio variation of comonomers

Sample	Equivalent of mole ratio	
	Hydroquinone	4-tert-butylcatechol
HT05	0.0	0.5(2.7426 g, 16.5 mmol)
HT14	0.1(0.3634 g, 3.3 mmol)	0.4(2.1941 g, 13.2 mmol)
HT23	0.2(0.7267 g, 6.6 mmol)	0.3(1.6456 g, 9.9 mmol)
HT32	0.3(1.0901 g, 9.9 mmol)	0.2(1.0971 g, 6.6 mmol)
HT41	0.4(1.4535 g, 13.2 mmol)	0.1(0.5485 g, 3.3 mmol)
HT50	0.5(1.8168 g, 16.5 mmol)	0.0

Silicon dioxide (1.9830g, 33mmol), catechol (5.4504g, 49.5mmol), hydroquinone, and 4-tert-butylcatechol of each mole ratio, as shown in table 1 were stirred the at room temperature for 30 minutes in 80 ml of ethylene

glycol (EG), resulting in a yellow homogenous solution. TETA (100%mol of SiO₂, 4.8259 g, 33 mmol) was added before starting the condensation reaction by distillation at 210°C (oil bath). Removal of H₂O (byproduct) and any EG were continuously carried out during polymerization for 5 hours. The solution was then allowed to cool down to room temperature. The color of solution became darker from yellow to brown. Excess EG was removed out under vacuum (110°C/20mmHg). A viscous solution resulted on cooling to room temperature. The viscous liquid was precipitated and washed with dried MeOH. The product obtained was dried under N₂ at ambient temperature and placed in a sealed vial under pure N₂ gas. It was finally characterized by FTIR, TGA, DSC, XRD, NMR, and Mass spectroscopy.

2.3.1.2 Effect of TETA concentration on the reaction. The mole percent of TETA was varied at 10, 30, 50 % mole of SiO₂. The reaction procedure was then repeated as above.

2.3.2 Kinetic study:

2.3.2.1 Variation of reaction time. For the determination of the rate, experimental data give species concentration at various times during the reaction. However, the unreacted catechol, hydroquinone, and 4-tert-butylcatechol were difficult to measure because they were sensitive to moisture, air and decompose at high temperature. The unreacted SiO₂ can then be obtained to determine the order with respect to SiO₂ only.

The initial rate method measures the initial rate, r_0 , for the two different initial concentrations of SiO₂ (33mmol and 16.5 mmol in 80 ml of EG) while the other concentrations, reaction temperature, and pressure of N₂ gas were kept constant.

SiO₂ (33mmol or 16.5mmol), catechol (5.4504g, 49.5mmol), hydroquinone (0.7267 g, 6.6mmol), and 4-tert-butylcatechol (1.6456 g,

9.9mmol), were stirred at room temperature for 30 min in 80 ml of ethylene glycol (EG). The mixture gave a yellow homogenous solution. After adding TETA (100% mol of SiO₂, 4.8259 g, 33mmol) under N₂ atm., the reaction was started by distillation at 200°C using an oil bath. Removal of byproduct H₂O and any EG were continuously carried out during polymerization while the pressure of N₂ gas was kept constant for 0.5, 1.0, 1.5, 2.0 h. After the reaction was stopped, the mixture was cooled to room temperature to give a dark brown solution with unreacted SiO₂ at the bottom of the reaction flask. Ethylene glycol solvent was carefully collected by vacuum distillation at 130°C. Methanol was then added to wash all unreacted starting materials, but SiO₂, from viscous solid, followed by filtration under N₂ atmosphere, and washing with dried MeOH. The remaining unreacted SiO₂ was again washed with dried MeOH followed by furnace drying at 1000°C. SiO₂ was finally weighed at room temperature.

2.3.2.2 Variation of reaction temperature. Since the rate constant depends strongly on temperature, this relationship can be used to determine the activation energy. The reaction temperature were varied at 200°, 210°, and 220°C to give the rate constant of each temperature. The reaction procedures were repeated as above.