

CHAPTER II

EXPERIMENTAL SECTION

2.1 General Material Handling

All reactions were carried out under N₂ atmosphere with the careful exclusion of extraneous moisture and air since the copolymer is slightly sensitive to moisture. The glassware used for these experiments was oven dried. All solvents were dried prior to use and were stored in bottles over molecular sieves. The starting materials (fumed silica powder, ethylene glycol, triethylenetetramine) were obtained from commercial sources.

Amorphous, precipitated silicon dioxide (SiO₂), with a multipoint BET surface area of 182 m²/g, was donated by PPG Siam Silica Co., Ltd. and used as received. It was stored in a dry environment prior to use to prevent moisture adsorption. Ethylene glycol (EG), used as solvent in the reaction, was distilled before used by fractional distillations at 200 °C. It was purchased from Farmitalia Carlo Erba (Barcelona). Triethylenetetramine (TETA) was used as a base catalyst. It was obtained from Union Carbide Thailand Limited and distilled under vacuum prior to use. Catechol was purchased from Fulka Chemika and hydroquinone was obtained from Riedel-deHaen. Both starting materials were used as received. Methanol and acetonitrile were purchased from J.T. Baker Inc.(Phillipsburg, USA) and purified by standard techniques. Methanol was distilled from magnesium metal activated with iodine. Acetonitrile was distilled from calcium hydride.

The glassware was cleaned by soaking in an NaOH/i-PrOH cleaning solution bath, followed by rinsing with water and acetone, respectively, and finally dried in oven at 125 °C-150 °C prior to use.

2.2 Instrumentation / Characterization

2.2.1 Spectroscopic Characterization

Fourier Transform Infrared Spectroscopy (FT-IR) : FT-IR spectra were recorded on a Bio-Rad FT-45A fourier transform infrared spectrometer with a resolution of $+4\text{ cm}^{-1}$. Sample was prepared using using random cutting of crystalline and optical grade KBr commercially available from Carlo Erba Reagent. The KBr was pressed hydraulically into pellet and quickly taken to the FT-IR sample chamber. The sample chamber was flushed for 10 minutes with dry N_2 to remove CO_2 before initiating data acquisition. The KBr spectra background was collected with a minimum of 64 scans. After obtaining the background spectra, the sample is then mixed with dried KBr at an approximate ratio of 1: 20 sample:KBr, using the same KBr sample used in the background spectrum. The solid mixture was ground and transferred to the sample holder using the same procedure as mentioned above.

Nuclear Magnetic Spectroscopy (NMR) : ^1H -NMR and ^{13}C -NMR spectra were obtained using a 500 MHz JEOL spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University and a Bruker 200 MHz at Chemistry Department, Faculty of Science, Chulalongkorn University. Both of spectra were recorded at room temperature in deuterated dimethyl sulfoxide (DMSO-d_6). ^1H -NMR spectra were recorded at the frequency of 10,000 Hz using 16 scans, a pulse width and a pulse delay of 5.5

sec and 30 sec., respectively and a sweep width of 16,000 Hz. ^{13}C -NMR spectra were recorded at the frequency of 9056 Hz using 4,000 scans, a pulse delay of 2.5 sec, a pulse width of 4.75 sec and sweep width of 20,000 Hz. Tetramethylsilane (TMS) was used as the internal reference for chemical shift measurements in both cases.

^{29}Si -NMR spectra were recorded on a 500 MHz JEOL spectrometer. Sample was dissolved in DMSO- d_6 . The solution was run using a pulse width of 5.0 sec, a pulse delay 5 μsec , a sweep width of 16,000 Hz, 64 scans with a 10 sec delay time and 9,500 data point scans.

Mass Spectroscopy (MS) : Mass spectra were obtained on a Fison Instrument (VG Autospec-ultima 707E) with VG data system. The direct probe injection was used in the electron impact ionization technique under ionization energy of 70 eV (EI^+ mode). Perfluorokerosene (PFK) was used as a standard for peak calibration. The sample could run directly without any matrix. The range studied was set from m/e 40 to 1,000.

2.2.2 Thermal Analysis

Differential Scanning Calorimeter (DSC) : DSC was carried out under flowing N_2 at rate of 15 ml/min using a Netzch DSC 200 (Germany). Sample sizes, typically 5-20 mg, was placed into aluminum pan. The pan was crimped to improve thermal contact between the sample and container. Sample was first heated from 28 to 220 $^\circ\text{C}$ and then cooled down to 28 $^\circ\text{C}$. The sample was then reheated from 28 to 450 $^\circ\text{C}$. Scanning experiment was conducted at a heating rate of 10 $^\circ\text{C}/\text{min}$ to determine the melting temperature (T_m) and/or the crystallization temperature (T_c).

Thermogravimetric Analysis (TGA) : TGA thermograms were determined using thermogravimetric analyzer from Netzsch instrument to obtain decomposition temperature (T_d) and percent ceramic yield. 10-20 mg sample sizes were loaded in Pt pan and heated under N_2 / O_2 using a flow rate of 15 ml/min. The balance flow meter was set at 40 ml/min. Heating rate of $10^\circ C/min$ from 28 to $950^\circ C$ was used.

2.2.3 X-Ray Diffraction

XRD patterns were run by the Metallurgy and Materials Science Research Institute using a PW 3710 Philip Analytical Instrument. The sample was ground and packed in a glass specimen holder. It was placed in the goniometer using $Cu(K\alpha)$ small radiator and operating at 40 kV and 30 MA. Scans were measured in the range of 5-80 degree 2θ at a scan speed of 0.6 degree 2θ min in 0.0 degree 2θ increments.

2.3 Experiments

The experimental section is separated into two parts. The first part describes the one step synthesis of an inorganic copolymer of silica, catechol and hydroquinone. The other describes the variations in mol ratio of catechol : hydroquinone, reaction time, and TETA concentration explored in efforts to optimize the best condition for obtained product.

2.3.1 One step synthesis LC copolymer of silica, catechol, and hydroquinone

Silica, 2.00 g (33 mmol), was weight out, mixed with catechol, 6.239 g (56.1 mmol), hydroquinone, 1.101 g (9.9 mmol), and TETA, 4.868 g (100 mol % Si) in a 250 ml two-neck reaction flask. Distilled ethylene glycol was added to bring total volume of solution to 80 ml. The solution mixture was magnetically stirred at room temperature for 10 min until it became homogeneous. It is then heated to the boiling point of ethylene glycol using oil-bath for 5 h. under N₂ atmosphere. The temperature of the oil bath is controlled at 220±5 °C, while the vapor temperature in distillation system was still at 110±5 °C under nitrogen atmosphere. The water formed, in the reaction, was distilled off. After 5 h. of heating, the mixture is slowly cooled down to room temperature and solid product will be precipitated out by itself. The remaining ethylene glycol was removed by vacuum distillation (10⁻² torr) which controlled the oil bath temperature at 100±5 °C until almost solid product was left in the flask. To remove ethylene glycol and TETA in the product, the product was then washed with dried methanol followed by acetonitrile until the filtrate is colorless . The pale-yellow solid obtained was dried at ambient temperature, followed by vacuum drying at 150 °C for 20 min. to obtain dried copolymer. Typical yield is 5.7 g or 61.38 %. The product dissolves partially in methanol, however dissolves easily in hot ethylene glycol and DMSO. The pale-yellow solid will become brown, on exposure to air and/or moisture. The product was characterized by FT-IR, NMR, MS spectroscopy, DSC, TGA, and X-ray diffraction.

2.3.2 Variation of catechol : hydroquinone mole ratio

The experiments presented below were to determine the optimum mole ratio of catechol and hydroquinone which gives the best copolymer characteristics. A typical reaction involved mixing silica (2.00 g, 33 mmol), catechol and hydroquinone in a two-neck reaction flask. The amounts of catechol and hydroquinone were varied as shown in Table 2.1 :

Table 2.1 Mole ratio variation of catechol : hydroquinone

Sample	Number of mole	
	Catechol	Hydroquinone
H0	2.0	0.0
H1	1.9	0.1
H2	1.8	0.2
H3	1.7	0.3
H4	1.6	0.4
H5	1.5	0.5
H6	1.4	0.6
H7	1.3	0.7
H8	1.2	0.8
H9	1.1	0.9
H10	1.0	1.0

For example, to prepare sample H1, 1.9 and 0.1 moles of catechol and hydroquinone respectively, were reacted with 1 mole of SiO_2 was used. If 33 mmol of SiO_2 was used, catechol 6.973 g ($1.9 \times 33 \text{ mmol} = 62.7 \text{ mmol}$), and hydroquinone, 0.367 g ($0.1 \times 33 \text{ mmol} = 3.3 \text{ mmol}$) were weighed out for sample H1. TETA, 4.868 g (100 mol % Si) and sufficient EG were added so that the final volume was 80 ml. This solution was stirred at room

temperature until it became homogeneous with silica and then heated. Distillation was done slowly to expel by-product water that formed and minimize the volume of ethylene glycol lost from the reaction mixture. After 5 h. of distillation, the solution was cooled to room temperature at which time solid slowly precipitated. Excess EG was removed by vacuum and the solid was then washed with dried methanol and acetonitrile. The solid was dried by suction under N_2 atmosphere for 3 h., and weighed. The product was stored in a sealed-vial under N_2 .

2.3.3 Reaction time variation

This part is to investigate the optimum reaction time for producing the copolymer. A typical reaction involved mixing silica, 2.00 g (33 mmol), catechol, 6.973 g (56.1 mmol), hydroquinone, 0.367 g (9.9 mmol), and TETA 4.868 g (100 mol % Si). EG was added so that the final volume was 80 ml. This reaction mixture was stirred and heated to distill for various distillation time (0 to 5 hours). At the end of each reaction time, the solution was cooled to room temperature precipitating product. Vacuum distillation was used to remove EG and the solid product was washed with dried methanol and acetonitrile. Finally, the product was suctioned under N_2 for 3 h. until the product dried.

Reaction times of 3, 4, and 5 h were used with the same mole ratios used for sample H0 to H8.

2.3.4 Variation of TETA concentration

A typical reaction involved mixing silica, 2.00 g (33 mmol), catechol, 6.973 g (56.1 mmol), and hydroquinone, 1.101 g (9.9 mmol) with various amounts of TETA (0 to 100 % mol) followed by addition of EG to a total volume of 80 ml. The reaction procedures were then repeated as above.