

CHAPTER II

EXPERIMENTAL INVESTIGATION

2.1 General Procedures

Because the product is susceptible to moisture and air, all reactions were performed in an inert, N₂, atmosphere with the careful exclusion of moisture and air. Solvents were dried by distillation using standard methods, and the glassware was oven dried prior to use.

Amorphous 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. Ethylene glycol (EG), used as solvent, was purchased from Farmitalia Carlo Erba (Barcelona) and distilled under N₂ atmosphere before use. Triethylenetetramine (TETA), base catalyst, was a gift from Union Carbide Thailand Limited and was purified by distillation under vacuum. Catechol and 4-*tert*-butylcatechol, used as received, were purchased from Fluka Chemika. Methanol and acetonitrile were distilled from magnesium metal activated with iodine and calcium hydride respectively. Both were then stored in oven-dried bottles with molecular sieves. They were purchased from J.T. Baker INC. (Phillipsburg, USA).

2.2 Analytical Characterization

2.2.1 Spectroscopic Characterization

Mass Spectroscopy (MS):

A Fison Instrument (VG Autospec-Ultima 707E) with VG data system was used to obtain the mass spectra. Samples were run directly without any matrix by the direct probe injection with the positive electron impact ionization technique (EI⁺ mode) under the ionization energy of 70 eV. Peaks were calibrated using perfluorokerosene (PFK) peaks as reference peaks. The m/e range was set from 40 to 1000.

Fourier Transform Infrared Spectroscopy (FTIR):

FTIR spectra were obtained on a FT-45A Bio-Rad spectrometer collected with 64 scans with a resolution of ± 4 cm⁻¹. Samples were ground with oven dried optical grade KBr (1:20) followed by hydraulical pressing into pellets. Pure KBr pellet was used as background. The chamber was purged with dry N₂ for at least 5 min before data collection.

Nuclear Magnetic Spectroscopy (NMR):

¹H-, ¹³C- and ²⁹Si-NMR were recorded at room temperature using a 500 MHz JEOL spectrometer at the Scientific and Instrumental Research Equipment Center, Chulalongkorn University. 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. ¹³C-NMR spectra were recorded at 9065 Hz using 4,000 scans, a pulse width of 4.75 sec, a pulse delay of 2.5 sec and a sweep width of 20,000 Hz. Deuterated dimethylsulfoxide (DMSO-d₆) and tetramethylsilane (TMS) were used as standard solvent and standard internal reference, respectively. ²⁹Si-NMR spectra were recorded on a 500 MHz using DMSO-d₆ as the solvent. The spectra were obtained using a

pulse width of 5.0 sec, a pulse delay of 5 μ sec, a sweep width of 16,000 Hz, 64 scans with a 10 sec delay time and 9,500 data point scans.

2.2.2 X-ray Diffraction

XRD patterns were obtained using a PN 3710 Philip Analytical Instrument at the Metallurgy and Materials Science Research Institute. Samples were 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 in the range of 5-80 degree 2θ at a scan speed of 0.6 degree 2θ min and 0.02 degree 2θ increments.

2.2.3 Thermal Analysis

Differential Scanning Calorimetry (DSC):

Thermograms were obtained by using a NETZSCH DSC 200 (Germany). Samples of 5-20 mg were packed in hermetical aluminum pans, and heated under N₂ flowing in the DSC chamber from room temperature to 450°C at a ramp rate of 10°C/min to determine sample transition temperatures.

Thermogravimetric Analysis (TGA):

Thermogravimetric analyser from NETZSCH TGA 200 to follow decomposition as a function of temperature and to find the percent ceramic yield. Samples of 10-20 mg were loaded in platinum pan and heated from room temperature to 950°C with a heating rate of 10°C/min. The experiments were carried out under N₂/O₂ atmosphere with flow rates of 15 ml/min, and the balance flow set at 40 ml/min.

2.3 Experiments

2.3.1 Synthesis of LC copolymer from silica, catechol (CAT) and 4-*tert*-butylcatechol (*t*-BUT)

The one-step synthesis was carried out in a 250 ml two-neck round bottom flask. Silica (MW = 60), 2.00 g (33 mmol), catechol (MW = 110), 4.356 g (39.6 mmol), 4-*t*-butylcatechol (MW = 166), 4.3824 g (26.4 mmol), and TETA (MW = 146), 4.868 g (100 mole% of Si) were mixed together, followed by 80 ml of distilled EG. The mixture was stirred at room temperature for 10 min to obtain a homogeneous solution. Subsequently, it was heated in the oil bath with a distillation set up to the boiling point of EG for 5 hours under N₂ atm. The temperature of oil bath was controlled at 215±5°C, and the vapor temperature in the distillation system was held at ~110°C. The by-product, water, formed in the reaction, with some distilled EG was removed off. The mixture was then gradually cooled down to room temperature at which the precipitate formed. Excess EG was removed out by vacuum distillation under about 10⁻² torr with the temperature of 110±5°C. The precipitate product was washed with dried methanol to remove the remaining EG, catechol and *t*-butylcatechol, followed by dried acetonitrile to remove the excess TETA under the atmosphere of N₂. The product was vacuum dried at 100°C for 20 minutes to obtain dried pale yellow powder, and packed in a sealed-vial under N₂. It was characterized by MS, FTIR, XRD, NMR and thermal analyses.

2.3.2 Variation of catechol and 4-*tert*-butylcatechol mole ratio

The same procedure as used in 2.3.1 was used here. The mole ratio of CAT and *t*-BUT was varied from 1.9:0.1 to 0.0:2.0 as 1 mole equivalent silica was used (6.966 g : 0.553 g to 0 g : 11.067 g of CAT : *t*-BUT, as 2 g (33

mmol) of silica was used). TETA was used as the catalyst in the amount of 4.867 g (100 mole%). EG, 80 ml, was added as the solvent. The reaction mixture was heated for 5 hours.

2.3.3 Variation of reaction time

The reaction time for each reaction done in section 2.3.2 was varied at 3, 4 or 5 h. 1-, 2-, 7-, and 9-hour reaction times were also used with the mole ratio 1.2:0.8 of CAT:*t*-BUT. TETA was used in the amount of 100 mole% silica. The procedure was the same as that mentioned in 2.3.1.

2.3.4 Variation of TETA

The mole percent TETA was varied between 16.67 and 100 mole % of silica used in the reaction with the mole ratio of CAT and *t*-BUT fixed at 1.2:0.8. The reaction mixture was heated under N₂ atm for 5 h. The procedure was the same as that mentioned in 2.3.1.