

CHAPTER III EXPERIMENTAL

3.1 Materials

Rice husk was kindly supplied by Pornjalearn Rice Mill Industry, Ratchaburi, Thailand. Hi-Sil[®] 255, a commercial porous silica, was supplied by PPG-Siam Co., Ltd. (Rayong, Thailand) with a reported specific surface area of $170 \pm 15 \text{ m}^2/\text{g}$. Polystyrene resin (STYRON[™] 656 D) was supplied by DOW Chemical Co., Ltd (Thailand). Hexadecyltrimethylammonium bromide (CTAB, 98%) and styrene (99%) were purchased from Fluka. 2, 2'Azobis-2-methypropionitrile (AIBN, 98%), a water insoluble initiator, were obtained from Aldrich Chemicals Company. Hydrochloric acid (37%), sulfuric acid (96%), and sodium hydroxide (anhydrous pellets) were purchased from Carlo Erba Reagenti (Thailand). Tetrahydrofuran (THF) AR grade was purchased from Lab-Scan Analytical Sciences. All chemicals were used without further purification.

3.2 Methodology

3.2.1 Preparation of Silica from Rice Husk

3.2.1.1 *Rice Husk Preparation*

Rice husk was initially screened to remove dirt and other contaminants. It was then ball milled to reduce the average particle size to pass through a 212 μm standard sieve.

3.2.1.2 *Silica Preparation*

The rice husk powder was modified using several different chemical methods. Acid leaching (HCl and H₂SO₄) with known acid concentrations was performed by refluxing at 105°C/3 h in a ratio of 40 g rice husk to 400 mL of acid solution. After leaching, the rice husk was thoroughly washed with distilled

water until neutral, and then oven dried in air at 110°C overnight. The treated rice husk was calcined in an electric muffle furnace (CARBOLITE, CSF 12/13) at 600° or 800°C at a heating rate of 10°C/min and held at temperature for 6 h.

3.2.1.3 *Silica Characterization*

Silica content was determined using wavelength dispersion x-ray fluorescence (WD-XRF, Philips PW 1400). Wide-angle x-ray diffraction (WAXD) was also used to determine powder diffraction patterns (XRDs) of all samples (D/Max-2000). A JEOL JSM-5200 scanning electron microscope (SEM) was also used to observe the microstructure of the samples. The specific surface areas were measured using the Brunauer-Emmett-Teller (BET) method with an adsorptometer (Autosorb-1 Quantachrome). Particle size distributions were also examined using a particle size analyzer (MALVERN Mastersizer X Ver. 2.15).

3.2.2 Surface Modification via Admicellar Polymerization

3.2.2.1 *Adsorption Isotherm of CTAB onto Silica*

Adsorption experiments were conducted in capped 24-ml vials. 0.5 g of silica was mixed with 20 mL of CTAB solution at different concentrations and at a constant pH 8. The samples were allowed to equilibrate at 30°C for 48 h and then centrifuged at 1000 rpm for 10 min. The supernatant was taken and analyzed for CTAB concentration. The adsorption of CTAB onto silica was studied by measuring the surfactant concentration before and after equilibration using a Total Organic Carbon Analyzer (TOC 5000A, Shimadzu). The quantity of adsorbed CTAB on silica was calculated by the concentration difference method. The adsorption isotherm was plotted between the amount of CTAB adsorbed on silica ($\mu\text{mol/g}$) and equilibrium concentration of CTAB solution (μM).

3.2.2.2 *Admicellar Polymerization*

Two different kinds of amorphous silica were used in this study. One was the commercial porous silica (Hi-Sil[®] 255) and the other was the

silica obtained from rice husk. The typical procedure for preparation of ultra-thin polymer films on both silicas via admicellar polymerization process is described in the following. CTAB was dissolved in distilled water at pH 8. pH of the solution was adjusted by using 0.1 M sodium hydroxide solution and the solution was stirred until the surfactant was completely dissolved. AIBN was dissolved in ethanol. The amount of AIBN used was in the ratio of 1 mole of AIBN to 1 mole of styrene monomer. The amount of CTAB used was in the ratio of 1 mole of CTAB to 2 mole of styrene monomer. CTAB and AIBN solutions were mixed together and the volume adjusted to 250 mL. The solution was added to 20 g of silica in a flask and styrene monomer was then added to the mixture. The flask was sealed with rubber stopper, paraffin film and foil. The mixture was allowed to equilibrate at 30°C in a shaker bath for 48 h. The equilibrated samples were placed at 70°C for 2 h to allow the polymerization to take place. The polymerization was terminated by cooling to 20°C. The supernatant was then decanted and the solid (modified silica) was washed using distilled water until the wash water was no longer “foamed”. The washed silica was filtered out, dried for 12 h at 70°C and kept in a desiccator.

3.2.2.3 *Extraction and Characterization of Polymer*

Polymer extraction was performed by stirring 10 g of the modified silica in tetrahydrofuran (THF) overnight and the mixture was then refluxed at 65°C for 4 h. The slurry was cooled to room temperature, filtered, and rinsed with hot THF. The extracted polymer was dried in a vacuum oven at 40°C overnight.

The extracted polymer was characterized by a Fourier transform infrared spectrometer (FTIR) (BRUKER EQUINOX55/S). The silica aggregates were also observed by using a scanning electron microscope (SEM) (JEOL JS M-5200). Thermogravimetric analysis (TGA) (Dupont Instrument TGA-2950) was used to determine the amount of polymer formed on the modified silica surface. The samples were heated from 30° to 700°C at 10°C/min under nitrogen. BET surface areas were also measured using a Autosorb-1 Quantachrome. Additionally, the molecular weight of the extracted polymer was characterized using gel permeation chromatography (GPC) (Waters 150-CV). Tetrahydrofuran (HPLC grade) was used as a mobile phase at a flow rate 1.0 ml/min. Polymer solutions were

auto-injected with a volume of 100 μL at temperature 30°C. The column set used was a PLgel 10 μm mixed B 2 columns. Polystyrene standards were used for calibration. Refractive index detector was used as the detector.