

## CHAPTER III EXPERIMENTAL

### 3.1 Material

All chemicals were obtained commercially and used as received. Aerosil<sup>®</sup>OX50, a nonporous fumed silica was obtained from Degussa Huls Company (Frankfurt, Germany) with a reported BET surface area of 35-65 m<sup>2</sup>/g and 40 nm particle size. Polyethoxylated octyl phenol (Triton X-100) was obtained from Union Carbide Co. with a purity of 100%. Styrene (99%) was purchased from Fluka (Milwaukee, WI). Tetrahydrofuran (HPLC grade), Tetrahydrofuran (A.R. grade), and Methanol (A.R. grade) were purchased from Lab-Scan Analytical Sciences (BKK, Thailand).

### 3.2 Equipment

Instrument	Model
UV-2950 Spectrophotometer	Shimazu Co.
Thermogravimetric Analysis	Dupont Instrument (TGA 2950)
Specular Reflection FTIR	Nexus 670 Nicolet Spectrophotometer
Gel Permeation Chromatography	Waters Gel Permeation Chromatography model 150-CV
Atomic Force Microscopy	Digital Instruments Nanoscope IIIa

### 3.3 Adsorption Measurement

Surfactant adsorption isotherm was measured by mixing a concentrated surfactant solution with measured amounts of purified water to provide a series of surfactant solutions of varying concentration. These solutions were added to 24 ml glass vials each containing 0.5 g of silica and sealed with screw caps. The vials were allowed to equilibrate at 30 °C for 1 day. The solids were then separated by syringe filter and the supernatant surfactant concentration analyzed using an UV-2950 Spectrophotometer (Shimadzu Co.) at 275 nm. Surfactant adsorption was calculated by the change in concentration method.

$$\text{Triton X-100}_{\text{adsorbed}} = \frac{[\text{Triton X-100}]_I - [\text{Triton X-100}]_E * V_{\text{sol}}}{1000 W_{\text{silica}}}$$

- where
- $\text{Triton X-100}_{\text{adsorb}}$  = Adsorption of Triton X-100, ( $\mu$  mol/g)
  - $[\text{Triton X-100}]_I$  = Initial concentration of Triton X-100, ( $\mu$ M)
  - $[\text{Triton X-100}]_E$  = Equilibrium concentration of Triton X-100, ( $\mu$ M)
  - $V_{\text{sol}}$  = Volume of solution, (ml)
  - $W_{\text{silica}}$  = Weight of silica, (g)

The adsorption isotherm is plotted between adsorption of Triton X-100 on silica ( $\mu$ mol/g) and equilibrium concentration of Triton X-100 solution ( $\mu$ M).

### 3.4 Adsolubilization Measurement

Adsolubilization isotherms were measured by placing 0.5 g silica in 24 ml vials with a solution that varying quantities of styrene. The surfactant concentration was chosen to ensure that the system equilibrated below the CMC assuming that the adsolubilization did not significantly affect adsorption. In this study, the adsolubilization measurements of styrene were detected in two different adsorbed Triton X-100 concentrations (50 and 100  $\mu$ mol/g) on silica surface.

The samples were allowed to equilibrate as in the adsorption studies and then separate the supernatant for analysis. The styrene concentration was determined by a UV detector operating at 246 nm. A mass balance was used to calculate the amount of adsolubilized styrene

$$\text{Styrene}_{\text{adsol}} = \frac{[\text{Styrene}]_I - [\text{Styrene}]_E * V_{\text{sol}}}{1000 W_{\text{silica}}}$$

where

- $\text{Styrene}_{\text{adsol}}$  = Adsolubilization of styrene, ( $\mu\text{mol/g}$ )
- $[\text{Styrene}]_I$  = Initial concentration of styrene solution, ( $\mu\text{M}$ )
- $[\text{Styrene}]_E$  = Equilibrium concentration of styrene solution, ( $\mu\text{M}$ )
- $V_{\text{sol}}$  = Volume of solution, (ml)
- $W_{\text{silica}}$  = Weight of silica, (g)

The adsolubilization isotherm is plotted between adsolubilized of styrene on silica ( $\mu\text{mol/g}$ ) and equilibrium concentration of styrene solution ( $\mu\text{M}$ )

### 3.5 Admicellar Polymerization

The surfactant feed concentration was chosen in order to prevent emulsion polymerization in the presence of micelles so that the equilibrium bulk concentration was approximately 80% and 40% of CMC representing adsorption levels of approximately  $100\mu\text{mol/g}$  and  $50\mu\text{mol/g}$  of silica. The Triton X-100 to monomer concentration ratios were varied from 2:1, 1:1, 1:2, 1:3, 1:4, 1:5 and 1:6. The amount of AIBN used was in the ratio of 1 mole AIBN: 15 mol of styrene. The volumes of ethanol were about 40 times the amount of initiator using for dissolve the initiator. The adsorption experiments were carried out by placing equilibrated samples containing water, surfactant, ethanol, styrene, silica, and AIBN solution into a shaker bath where they were left at  $30\text{ }^\circ\text{C}$  for 24 hr. The polymerizations were carried out by heating the reaction flask at  $70^\circ\text{C}$  for 2 h. The reaction is terminated by placing the reaction flask in an ice bath.

The modified silica is washed by water until no foaming was observed upon agitation. The modified silica is filtered, dried for 12 hr. at 70 °C and ground into a fine powder with mortar.

### **3.6 Polymer Extraction**

Ten to twelve grams of modified silica were stirred overnight with 150 ml of THF. The slurry was then refluxed for a further 4 hours in the same THF and filtered. The volume of the filtrate was reduced by evaporation to 5 ml. The filtrate was then added to 50 ml. of methanol the extracted polymer was filtered and dried in a vacuum oven at 40°C for 24 h.

### **3.7 Characterization Techniques**

#### 3.7.1 Fourier Transform Infrared Spectroscopy

FTIR spectra of the modified silica, unmodified silica, and extracted material were acquired by Specular Reflection FTIR on Nexus 670 Nicolet Spectrophotometer.

#### 3.7.2 Thermogravimetric Analysis

Modified silica, extracted silica, pure silica, Triton X-100 and extracted polystyrene were analyzed by TGA 7 Perkin Elmer instrument. All samples were carried out from 30°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

#### 3.7.3 Gel Permeation Chromatography

All extracted polystyrene samples were characterized by Waters Gel Permeation Chromatography model 150-CV. Tetrahydrofuran (HPLC) grade was used as the 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 Pl-gel 10 µl mixed B 2 columns (Church Stretton, UK). Polystyrene standards were used for calibration.

### 3.7.4 Atomic Force Microscopy

Atomic Force Microscopy is a versatile tool for investigation various properties of a substrate surface down to atomic level. AFM consists of a piezoelectric drive, an optical head and a feedback controller. The piezoelectric drive allows the displacement of the sample in X, Y and Z positions in atomic resolution.

As the tip cantilever is moved towards the sample's surface, the cantilever will deflect. The movements of the cantilever are detected by the changes in the photodiode output, which is sent to an electronic feedback controller where the signal is interpreted. The controller then alters the potential needed to maintain the vertical location of the cantilever. This feedback controller works to maintain a constant force on the cantilever. Any changes in potentials will be monitored and the signal converted to a topographic image.

The atomic force microscope, a multimode Nanoscope IIIa AFM, was purchased from Digital Instruments Inc.(Santa Barbara, CA). Topographic and phase images were captured simultaneously using tapping mode AFM. All imaging was done by using 125- $\mu\text{m}$  silicon tips obtained from Digital Instruments, Inc. A set-point ratio (ratio of the engaged oscillation amplitude to the free air oscillation amplitude) between 0.5 and 0.7 was used for all topographic and phase images unless otherwise stated. With this set-point ratio, darker regions will represent the softer polystyrene film, whereas brighter regions will represent the harder silica substrate.

The thickness of the polystyrene films was analyzed by using the Nanoscope IIIa software version 4.23r23 (Digital Instruments). The microscope was enclosed within a Plexiglas<sup>®</sup> box (14 x 14 x 30 in.). Dry air ( $7 \pm 2\%$  relative humidity) was pumped into the container. The relative humidity inside the container was monitored by a humidity probe obtained from Cole-Parmer Instrument Co. (Vernon Hills, IL). All tapping mode images were captured at room temperature and in air with a relative humidity < 25%.