

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Aerosil<sup>®</sup> OX50, a nonporous fumed silica was obtained from Degussa Hüls Company (Germany) with a reported BET surface area of 35-65 m<sup>2</sup>/g and 40 nm particle size. Styrene (99%), isoprene (99%), hexadecyltrimethylammonium bromide (C<sub>16</sub>TAB, 98%) and sodium hydroxide pellets (99%) were purchased from Fluka (Milwaukee, WI). 2,2'-Azobis-2-methylpropionitrile (AIBN, 98%), a water-insoluble initiator, was obtained from Aldrich Chemicals Company, Inc. (Milwaukee, WI). Tetrahydrofuran (THF) AR grade, and HPLC grade were then purchased from Lab-Scan Analytical Sciences (BKK, Thailand). All materials were used without further purification.

### 3.2 Equipment

**Table 3.1** The instruments and models which used in thesis work

Instrument	Model
TOC 5000	Shimadzu 5000
UV-VIS Lambda 10	Perkin Elmer
Thermogravimetric Analysis	Perkin Elmer (TGA2950)
Fourier Transform Infrared	Nicolet model Nexus 670
Gel Permeation Chromatography	Water Gel Permeation Chromatography model 150-CV
Atomic Force Microscopy	Digital Instruments Nanoscope IIIa

### 3.3 Methodology

#### 3.3.1 Adsorption measurement

CTAB solutions were made in distilled water which was adjusted to pH8 using 0.1 M NaOH solutions. Then, 20 ml of different known CTAB concentration solutions were placed on 0.5 g of silica in 24-ml vials. The solution mixture was allowed to equilibrate at 30 °C for 24 hours in a shaker-water bath. The supernatant was then collected using a syringe filter. The adsorption of CTAB onto silica was studied by measuring the surfactant concentration before and after the adsorption process in CTAB solution using a Total Organic Carbon analyzer (TOC\_5000A, Shimadzu). The difference between initial and equilibrium concentration was used for calculate the quantity of adsorbed surfactant following this equation.

$$CTAB_{adsorp} = \frac{([CTAB]_I - [CTAB]_E) \times V_{sol}}{W_{silica}}$$

Where

- CTAB<sub>adsorp</sub> = Adsorption of CTAB, (μmol/g)
- [CTAB]<sub>I</sub> = Initial concentration of CTAB solution, (μmolar)
- [CTAB]<sub>E</sub> = Equilibrium concentration of CTAB, (μmolar)
- V<sub>sol</sub> = Volume of solution, (ml)
- W<sub>silica</sub> = Weight of silica, (g)

The adsorption isotherm was a plot between adsorption of CTAB on silica (μmol/g) and concentration of CTAB solution (μmolar).

#### 3.3.2 Adsolubilization Measurement

A known amount of styrene and isoprene monomers were dissolved in CTAB solution at pH 8 and stir overnight. These were then mixed in known ratios to produce mixtures that have constant surfactant concentration but variable comonomer concentrations. The solutions were added to 0.5 g of silica in 24-ml vials sealed with paraffin film. The mixture was kept at 30°C and left for

equilibration for 24 hours in a shaker-water bath. After equilibration, the vials were centrifuged and the supernatant was removed by syringe filter. The bulk styrene concentration was then measured by UV-Vis spectrophotometer detection at 280 nm and isoprene concentration was measured by headspace GC. Once the equilibrium concentrations were determined, the adsolubilization of styrene and isoprene into CTAB bilayer on silica was calculated through a simple mass balance. In this study, the adsolubilization measurements of styrene and isoprene were detected in two different adsorbed CTAB concentration level (20  $\mu\text{mol/g}$  and 100  $\mu\text{mol/g}$ ) on silica surface. The adsolubilization isotherm was a plot between adsolubilized of styrene and isoprene on silica ( $\mu\text{mol/g}$ ) and equilibrium concentration of styrene and isoprene solution ( $\mu\text{M}$ ).

### 3.3.3 Admicellar Polymerization

The preparation of ultra-thin polymer films on silica was conducted by admicellar polymerization. Two levels of adsorption and three levels of adsolubilization (at ratios of styrene:isoprene 1:3, 1:1, and 3:1) was studied. The admicellar polymerization process was carried out following these steps

- 1) CTAB was added to deionized water which was adjusted to pH 8 by using sodium hydroxide solution, and stirred until dissolved. The mole ratio of AIBN and comonomer was kept constant at 1:25.

- 2) CTAB and AIBN solutions were mixed together and the solution was adjusted into 250 ml by deionized water. The mixed solution was added to 15 g of silica in the flask. Styrene and isoprene monomers in various ratios were added to the mixture in the flask. Then the flask was sealed with rubber stopper and paraffin film.

- 3) The mixture, with magnetic bar stirring 500 rpm, was left at 30°C for 24 hr for equilibration.

- 4) The polymerization was carried out by heating the reaction flask in a water bath at 70°C for 4 hr.

- 5) The polymerization reaction was terminated by placing the reaction flask on an ice bath.

6) The modified silica was washed by distilled water until no foaming observed.

7) The modified silica was filtered, dried at 70°C for 12 hr and sieved by a 120-mesh sieve.

### 3.3.4 Polymer Extraction

The modified silica was stirred overnight and then refluxed in THF (AR grade) at 65°C for 4 hr using the ratio of modified silica 7 g : THF 150 ml. The slurry was filtered and rinsed with THF again. The filtrate was evaporated to reduce the volume. The polymer was precipitated by adding the concentration filtrate into methanol. The extracted polymer was filtered and dried in vacuum oven at 40°C for 24 hr.

### 3.3.5 Characterization

#### 3.3.5.1 *Fourier Transform Infrared Spectroscopy*

FTIR spectra of the extracted material were obtained from a Vector 3.0 Bruker Spectrophotometer with a resolution of 4 cm<sup>-1</sup> in the frequency range from 4000 to 400 cm<sup>-1</sup>. The samples were observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D\*, of 1x10<sup>9</sup>cm\* Hz<sup>1/2</sup>\*w<sup>-1</sup>.

#### 3.3.5.2 *Thermogravimetric Analysis*

Modified silica, extracted silica, pure silica, CTAB and extracted material were analyzed by a TGA 5.1 Dupont Instrument model 2950. All samples were carried out from 30°C to 700°C at a heating rate of 10°C/min under nitrogen atmosphere.

#### 3.3.5.3 *Gel Permeation Chromatography*

All of the extracted copolymer samples were characterized by Water Gel Permeation Chromatography model 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 µm at temperature 30°C. The column set used was PLgel 10 µl mixed B 2 columns (Church Stretton, UK). Polystyrene standards were used for calibration.

#### *3.3.5.4 Atomic Force Microscopy*

Samples were examined by a multimode atomic force microscope with Nanoscope IIIa software from Digital Instruments, Inc. (Santa Barbara, CA). Topographic and phase images were captured simultaneously using tapping mode AFM. A J-type scanner with the maximum scan size of 125 $\mu$ m was used. Silicon tips with a resonant frequency of approximately 266.7 kHz and length of 125  $\mu$ m were obtained from Digital Instruments, Inc. The microscope was enclosed within a Plexiglas<sup>®</sup> box (14" x 14" x 30"). Dry air (7 $\pm$ 2% relative humidity) was pumped into the container. All tapping mode images were captured at room temperature and in air with a relative humidity less than 25%.