

## CHAPTER III EXPERIMENTAL

### 3.1 Material

Styrene (99%), hexadecyltrimethylammonium bromide (C<sub>16</sub>TAB, 98%) and sodium hydroxide pellets (99%) were purchased from Fluka (Milwaukee,WI). The water insoluble initiator, 2,2'-azobis-2-methylpropionitrile (AIBN, 98%) was purchased from Aldrich Chemicals Company (Milwaukee,WI). The substrate, Aerosil® OX50, a non porous fumed silica, was obtained from Degussa Huls Company (city state country) with a reported BET surface area and average primary particle size of 35-65 m<sup>2</sup>/g and 40 nm, respectively. Tetrahydrofuran (THF) (HPLC grade) was obtained from Lab-Scan Analytical Sciences (BKK, Thailand). All chemicals were used as received

### 3.2 Equipment

Instrument	Model
Total Organic Carbon Analyzer	TOC_5000A, Shimadzu
Particle Size Analyzer	MALVERN Mastersizer X Ver.2.15
Surface Area Analyzer	BET N <sub>2</sub> surface area Autosorb-1 Quantachrome
Fourier Transform Infrared	BRUKER EQUINOX55/S
Thermogravimetric Analysis	Dupont Instrument TGA 2950
UV-VIS Spectrophotometer	Perkin Elmer-Lamda 16
Atomic Force Microscope	Multimode- Nanoscope IIIa software

### 3.3 Methodology

#### 3.3.1 Adsorption Measurement

The adsorption of C<sub>16</sub>TAB on non porous silica was studied by placing 20 mL of known concentrations of C<sub>16</sub>TAB solutions on 0.5 g of silica in 24

mL vials and allowing them to equilibrate at 30 °C in a shaker bath for 24 hours. The feed solution was adjusted to pH 8 using 0.1 M sodium hydroxide solution. A pH of  $\approx 8$  was used to insure a negative surface charge and minimize the dissolution of silica. After equilibration, the supernatant was separated from the mixture by syringe filter. The adsorption of CTAB onto silica was measured by determining the feed and equilibrium surfactant concentrations using a Total Organic Carbon analyzer (TOC). The quantity of CTAB on silica was calculated by the concentration difference method as shown in the following equation.

$$\text{CTAB}_{\text{adsorp}} = \frac{([[\text{CTAB}]_I - [\text{CTAB}]_E] / 1000) \times V_{\text{sol}}}{W_{\text{silica}}}$$

Where

$$\begin{aligned} \text{CTAB}_{\text{adsorp}} &= \text{Adsorption of CTAB, } (\mu\text{mol/g}) \\ [\text{CTAB}]_I &= \text{Initial concentration of CTAB solution, } (\mu\text{M}) \\ [\text{CTAB}]_E &= \text{Equilibrium concentration of CTAB, } (\mu\text{M}) \\ V_{\text{sol}} &= \text{Volume of solution, (ml)} \\ W_{\text{silica}} &= \text{Weight of silica, (g)} \end{aligned}$$

The adsorption isotherm is a plot between adsorption of CTAB on silica ( $\mu\text{mol/g}$ ) and equilibrium concentration of CTAB solution ( $\mu\text{M}$ )

### 3.3.2 Adsolubilization Measurement

In order to determine the adsolubilization of styrene, feed solutions with known CTAB and styrene concentrations in pH 8 water were brought into contact with samples of 0.5 g of silica in 24 mL vials sealed with paraffin film. The system was kept at 30°C and allowed to equilibrate for 24 hours in a shaker bath. After equilibration, the supernatant was filtered using a syringe filter and the styrene concentration in the supernatant was measured using spectrophotometry at 280 nm. The amount of adsolubilized styrene was calculated from the concentration difference between the feed solution and the equilibrium concentration. Measurement of styrene adsolubilization was made at two adsorbed CTAB concentrations ( 20 and 100  $\mu\text{mol/g}$  ) using the following equation.

$$\text{Styrene}_{\text{adsorp}} = \frac{([[\text{Styrene}]_I - [\text{Styrene}]_E] / 1000) \times V_{\text{sol}}}{W_{\text{silica}}}$$

Where

$\text{Styrene}_{\text{adsorp}}$	=	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)

Adsolubilization isotherms plot the adsolubilized styrene versus the equilibrium styrene concentration.

### 3.3.3 Admicellar Polymerization

Ultra-thin polymer films on silica was prepared using the experimental matrix shown in Table 3.1

**Table 3.1** Experimental Matrix showing two levels of adsorbed CTAB, two levels of adsolubilized styrene, and 8 levels of initiator:styrene ratio

Adsorbed CTAB ( $\mu\text{mol/g}$ )	CTAB( $\mu\text{mol/g}$ ):adsolubilized styrene ( $\mu\text{mol/g}$ )	AIBN:Styrene (mole:mole)
20	20:10 (2:1)	1:1, 1:5, 1:7, 1:10, 1:15, 1:20, 1:25, 1:50
	20:40 (1:2)	1:1, 1:5, 1:7, 1:10, 1:15, 1:20, 1:25, 1:50
100	20:10 (2:1)	1:1, 1:5, 1:7, 1:10, 1:15, 1:20, 1:25, 1:50
	20:40 (1:2)	1:1, 1:5, 1:7, 1:10, 1:15, 1:20, 1:25, 1:50

The admicellar polymerization process was carried out following these steps:

1. CTAB solution was prepared with distilled water and the pH adjusted to 8. AIBN was dissolved in ethanol at a ratio of 40 ml of ethanol per gram of AIBN. AIBN concentrations were varied as shown in Table 3.1.

2. CTAB and AIBN solutions were mixed together and the solution brought up to 250 mL. The combined solution was then added to 15 g of silica in a flask and styrene added. The flask was sealed with paraffin film and foil.
3. The mixture was stirred overnight at 600 rpm and 30° C.
4. The polymerization was carried out by placing the reaction flask in a water bath at 70° C for 2 hours.
5. The reaction was terminated by placing the reaction flask in a water bath at 20° C.
6. The slurry was washed with distilled water until no foaming was observed.
7. The modified silica was then filtered, dried at 70° C for 24 hrs and pushed through a 120 mesh sieve.

#### 3.3.4 Polymer Extraction

10 grams of the modified silica was stirred with 150 ml THF overnight at ambient conditions and then washed with refluxing THF for 4 hours. The silica was filtered and rinsed with new THF. The filtrate was evaporated to reduce the volume. The polymer was precipitated by adding the concentrated filtrate into distilled water (250 mL). The extracted polymer was filtered and dried in a vacuum oven at 40 °C for 24 hours.

#### 3.3.5 Characterization

##### 3.3.5.1 *Fourier Transform Infrared Spectroscopy (FTIR)*

FTIR spectra of extracted polymer material, modified silicas, unmodified silicas and CTAB 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 directivity,  $D^*$ , of  $1 \times 10^9$  cmHz<sup>1/2</sup> w<sup>-1</sup> and scanned with a repetition of 32 scans. KBr pellet technique was applied in the preparation of samples.

##### 3.3.5.2 *Thermogravimetric Analysis (TGA)*

Extracted material, modified silica, unmodified silica and

CTAB were characterized using a TGA 5.1 DuPont Instrument model 2950. Samples (10-15 mg) were placed in the Pt pan. Thermogravimetric analyses of all samples were carried out from 25° C to 700° C at a heating rate of 10° C/min under nitrogen atmosphere.

#### 3.3.5.3 Gel Permeation Chromatography (GPC)

All of extracted material (polystyrene) samples were characterized by a Walters gel permeation chromatography model 150-CV. Tetrahydrofuran (HPLC grade) was used as a mobile phase at a flow rate of 1.0 ml/min. Polymer solutions were auto-injected with a volume of 100  $\mu$ L at temperature 30 °C. The column set used was a PLgel 10  $\mu$ L mixed B 2 columns (Church Stretton, UK). Polystyrene standards were used for calibration (Church Stretton, UK). The detector used was refractive index detector (RI)

#### 3.3.5.4 Atomic Force Microscopy (AFM)

The multimode atomic force microscope equipped with Nanoscope IIIa software from Digital instruments, Inc. (Santa Barbara, CA) was used. 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 (TESO-10) with a resonant frequency of approximately 266.7 kHz and length of 125  $\mu$ m were also obtained from Digital Instruments, Inc. The microscope was enclosed within a Plexiglas® box (14"x14"x30") that is continuously flushed with dry air (7 $\pm$ 2% relative humidity) at ambient temperature.

The topographic image of tapping mode image was interpreted by changing the oscillating amplitude of the tip during a tip tapped on the sample surface. The tip-sample interaction will affect the amplitude and the frequency of the tip. The interaction can be repulsive or attractive force. If the oscillating amplitude is set to be constant, when the tip touches the sample at different surfaces, the oscillating frequency will change and will result in frequency shifts caused by the different interacting force between the tip and the surface. The characteristics of the sample can be analyzed and characterized by these changes in

the frequency. The phase image can be used to interpret the stiffness of the sample surface. The softer part of the sample will be seen as a darker region, while the hard part will be seen brighter in contrast.

To identifying polymer at the valleys between the modified silica can be detected by imaging under lower and then higher forces. After capturing the images at the lower tapping force, the same surface is captured again with the higher force to deform or remove polymer film. The images between before and after changing the force to be higher are compared, the polymer film or the artifacts from the curvature at the valleys can be differentiated. If there is no difference between the two images, the darker region in the phase image represents the polymer film, but after higher force detection, the darker regions in the phase image disappear or changing, this means the darker region in the phase image may be caused by the artifacts from the curvature or adsorbed water (humidity), which will affect the phase image of the surface at the same way.