



CHAPTER III EXPERIMENTAL

3.1 Materials

Aerosil[®]OX50, a nonporous silica, was obtained from Degussa Hüls Company with a reported BET surface area and average primary particle size of 35 - 65 m²/g and 40 nm, respectively. Hexadecyltrimethylammonium bromide (CTAB, 98%), styrene (99%), and sodium hydroxide pellets (99%) were purchased from Fluka. 2, 2'-Azobis-2-methylpropionitrile (AIBN, 98%), a water insoluble initiator, was obtained from Aldrich Chemicals Company. Tetrahydrofuran (THF) AR grade, and HPLC grade were obtained from Lab-Scan Analytical Sciences. All materials were used without further purification.

3.2 Equipment

Instrument	Model
Total Organic Carbon Analyzer	TOC 5000A, Shimadzu
UV-VIS spectrophotometer	Perkin Elmer-Lamda 16
Particle Size Analyzer	MALVERN Mastersizer X Ver. 2.15
Surface Area Analyzer	BET N ₂ surface area Autosorb-1 Quantachrome
Scanning Electron Microscope	JEOL JSM-5200
Fourier Transform Infrared	BRUKER EQUINOX55/S
Thermogravimetric Analysis	Dupont Instrument TGA 2950
Gel Permeation Chromatography	Waters 150-CV

3.3 Methodology

3.3.1 Adsorption Measurement

CTAB solutions of different known concentrations were prepared in distilled water and adjusted to pH 8 using 0.1 M NaOH solution. 20 ml of CTAB solutions were added to 0.5 g of silica in 24 ml vials. The mixtures were allowed to equilibrate at 30°C in a shaker bath for 24 hr. After equilibration, the supernatant was separated from the mixture by syringe filter. The adsorption of CTAB onto silica was studied by measuring the surfactant concentration before and after equilibration using a Total Organic Carbon analyzer (TOC). The adsorption of CTAB onto silica was determined by simple mass balance. The adsorption isotherm is a plot between adsorption of CTAB on silica ($\mu\text{mol/g}$) and equilibrium concentration of CTAB solution (μM).

3.3.1.1 Sample Calculation

The adsorption of CTAB onto silica was studied by measuring the surfactant concentration before and after equilibration using a Total Organic Carbon analyzer. (TOC) The difference between initial and equilibrium concentrations was used to calculate the quantity of CTAB adsorption using equation 3.1.

$$\text{CTAB}_{\text{adsorp}} = \frac{[(\text{[CTAB]}_I - \text{[CTAB]}_E)/1000] \times V_{\text{sol}}}{W_{\text{silica}}} \quad (3.1)$$

where:

$\text{CTAB}_{\text{adsorp}}$ = Adsorption of CTAB, ($\mu\text{mol/g}$)

$[\text{CTAB}]_I$ = Initial concentration of CTAB solution, (μM)

$[\text{CTAB}]_E$ = Equilibrium concentration of CTAB, (μM)

V_{sol} = Volume of solution, (ml)

W_{silica} = Weight of silica, (g)

3.3.2 Adsolubilization Measurement

Stock styrene-in-surfactant and surfactant solutions were used to prepare samples containing constant CTAB concentration but different styrene concentrations. The styrene/CTAB solutions were placed on 0.5 g of silica in 24 ml vials sealed with paraffin. The mixture was kept at 30°C and allowed to equilibrate for 24 hours in a shaker bath. The supernatant was filtered using a syringe filter and then measured the styrene concentration in supernatant by using UV-Vis spectrophotometer. An adsolubilization of styrene was calculated by simple mass balance. In this study, the adsolubilization measurements of styrene were detected in two different adsorbed CTAB concentrations (20 and 100 $\mu\text{mol/g}$) on silica surface. The adsolubilization isotherm is a plot between adsolubilization of styrene on silica ($\mu\text{mol/g}$) and equilibrium concentration of styrene solution (μM).

3.3.2.1 *Sample calculation*

The adsolubilization of styrene into CTAB bilayer on silica was studied by measuring the styrene concentration in the CTAB solution before and after equilibration by using UV detector at 280 nm (Ktiyanan *et al.*, 1996). Adsolubilization of styrene were calculated using equation 3.2.

$$\text{Styrene}_{\text{adsol}} = \frac{([[\text{Styrene}]_I - [\text{Styrene}]_E] / 1000) \times V_{\text{sol}}}{W_{\text{silica}}} \quad (3.2)$$

where:

$\text{Styrene}_{\text{adsol}}$ = Adsolubilization of styrene, ($\mu\text{mol/g}$)

$[\text{Styrene}]_I$ = Initial concentration of styrene solution, (μM)

$[\text{Styrene}]_E$ = Equilibrium concentration of styrene solution, (μM)

V_{sol} = Volume of solution, (ml)

W_{silica} = Weight of silica, (g)

3.3.3 Admicellar Polymerization

The preparation of ultra-thin film polymer on silica was conducted and the synthesis conditions are shown in Table 3.1.

Table 3.1 Admicellar polymerization condition

CTAB _{adsorp} ($\mu\text{mol/g}$)	CTAB _{adsorp} : Styrene _{adsol} ($\mu\text{mol/g}$) : ($\mu\text{mol/g}$)	Reaction time (h)
20	20 : 10 (1:0.5)	1, 2, 4, 6
	20 : 20 (1:1)	1, 2, 4, 6
	20 : 40 (1:2)	1, 2, 4, 6
100	100 : 50 (1:0.5)	1, 2, 4, 6
	100 : 100 (1:1)	1, 2, 4, 6
	100 : 200 (1:2)	1, 2, 4, 6

CTAB_{adsorp} = Adsorbed CTAB, ($\mu\text{mol/g}$)

Styrene_{adsol} = Adsolubilized Styrene, ($\mu\text{mol/g}$)

The admicellar polymerization process were carried out following these steps:

1. CTAB was dissolved in distilled water at pH 8 and AIBN was dissolved in ethanol. Amount of AIBN used were in the ratio of 1 mole AIBN: 5 mole of styrene.
2. CTAB and AIBN solutions were mixed together and the solution for a total volume of 250 ml. The solution was placed on 15 grams of silica in a flask and styrene monomer was added to the mixture. Then the flask was sealed with rubber stopper and paraffin film.
3. The mixture was stirred by a magnetic stirrer and left for 24 h at 30°C to equilibrate.
4. Polymerization was carried out by heating the reaction flask at 70°C for the required reaction times.
5. The reaction was terminated by placing the reaction flask in an ice bath.
6. The modified silica was washed by water until no “foaming” was observed.

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

3.3.4 Polymer Extraction

7 grams of the modified silica was stirred overnight in THF (150 mL) and then refluxed in the same THF (AR grade) for 4 h. The silica was filtered and rinsed with additional THF. The filtrate was evaporated to reduce the volume. The polystyrene was precipitated by adding the concentrated filtrate into distilled water (150 ml). The extracted polymer was separated and dried in a vacuum oven for 24 h at 40°C.

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⁻¹ in the frequency range from 4000 to 400 cm⁻¹. The samples were observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D^* , of 1×10^9 cmHz^{1/2}w⁻¹ and scanned with a repetition of 32 scans.

3.3.5.2 *Thermogravimetric analysis*

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 30°C to 700°C at heating rate of 10°C/min under nitrogen atmosphere.

3.3.5.3 *Gel permeation chromatography*

All of extracted polystyrene samples were characterized by a Waters gel permeation chromatography model 150-CV. Tetrahydrofuran (HPLC grade) was used as a mobile phase at 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 µl mixed B 2 columns. Polystyrene standards were used for calibration.

3.3.5.4 *Atomic force microscope*

The multimode atomic force microscope equipped with Nanoscope IIIa software from Digital Instruments, Inc. (Santa Barbara, CA). Topographic and phase images were capture simultaneously using tapping mode AFM. A J-type scanner with the maximum scan size of 125 μ m was used. Silicon tips with a resonant frequency of approximately 266.7 kHz and length of 125 μ m were obtained from Digital Instruments, Inc. The microscope was enclosed within a Plexiglas[®] 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%.