



CHAPTER III EXPERIMENTAL

3.1 Materials

Aerosil[®]OX50, a nonporous fumed silica, was obtained from Degussa Huls Company (Germany) with reported particle size of 40 nm. Styrene (99 %), hexadecyltrimethylammonium bromide (C₁₆TAB, 98 %) and sodium hydroxide pellets (99 %) were purchased from Fluka (Milwaukee, WI). The water-soluble initiator, VA-044 was purchased from Wako Pure Chemical Industries, Ltd, Japan. Tetrahydrofuran (THF, HPLC grade) was then obtained from Lab-Scan Analytical Sciences (BKK, Thailand). The RAFT agent cumyl dithiobenzoate (CDB) was supplied by the Department of Polymer Science, The University of Southern Mississippi, USA.

3.2 Equipment

Instrument	Model
TOC 5000	Shimadzu 5000
UV-VIS Lambda 10	Perkin Elmer
Thermogravimetric Analysis	Perkin Elmer (TGA 7)
Fourier Transform Infrared	BRUKER EQUINOX55/S
Gel Permeation Chromatography	Water Gel Permeation Chromatography model 150-CV
Atomic Force Microscopy	Digital Instruments Nanoscope IIIa

3.3 Adsorption Isotherm

A stock CTAB solution was adjusted to pH 8 by adding 0.1 M NaOH solution. Samples containing 0.5 gm of silica and 20 ml of CTAB solution were prepared in 24 ml vials and equilibrated in a shaker bath for 24 h at 30 °C. Syringe filtering was then used to separate the supernatant for analysis. The equilibrium CTAB concentration was determined by total organic carbon Analyzer (TOC 5000). A mass balance was then used to determine the amount of adsorbed CTAB.

The amount of CTAB adsorption on silica could calculate from initial and equilibrium CTAB concentration by the following equation.

$$CTAB_{adsorp} = \frac{\{[CTAB]_i - [CTAB]_E\}}{1000W_{silica}} V_{sol} \quad (3.1)$$

Where:

- CTAB_{adsorp} = Adsorption of CTAB (μmol/g)
- [CTAB]_i = Initial concentration of CTAB solution (μM)
- [CTAB]_E = Equilibrium concentration of CTAB solution (μM)
- V_{sol} = Volume of solution (ml)
- W_{silica} = Weight of silica (g)

3.4 Adsolubilization Measurement

The samples were prepared by varying styrene concentration at constant CTAB concentration. The styrene/CTAB solution and 0.5 g of silica were put in sealed 24 ml vials and placed in a shaker bath for 24 hours at 30 °C. The supernatant was then removed by syringe filter and the styrene concentration determined by UV-Vis spectrophotometer operated at 280 nm (Perkin Elmer Lambda 10) (Kitiyanan, 1996). The adsolubilization of styrene was calculated by simple mass balance between initial and equilibrium

concentration of styrene solution. The isotherm was plotted as adsolubilization of styrene on silica ($\mu\text{mol/g}$) and equilibrium concentration of styrene solution (μM).

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

Where:

- Styrene_{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)

3.5 Admicellar Polymerization

The following steps were followed in preparing the AP modified samples.

1. CTAB was dissolved in distilled water adjusted to pH 8 and AIBN was dissolved in ethanol at a ratio of 0.5 g of AIBN to 30 ml of ethanol. For VA-044 the ratio was 36 g of VA-044 to 100 g of water.
2. The solution mixture of CTAB and VA-044 was brought up to volume of 250 ml and poured into 15 g of silica in an Erlenmeyer flask
3. Styrene was then added and the flask sealed.
4. Stir the mixture for 24 hours to achieve equilibrium at room temperature.
5. Raise the temperature to 70 °C for two hour in the shaker bath to cause polymerization, terminate the polymerization process at 0 °C in an ice bath.

6. The sample was allowed to settle, the supernatant removed, and the sample washed repeatedly with distilled water until the water did not foam upon agitation.

7. The modified silica was then filtered, dried in the vacuum oven overnight and ground into powder through a 110 sieve.

3.6 Admicellar Polymerization Using RAFT Agent

1. AIBN was dissolved in ethanol at a ratio of 0.5 mg to 1 ml of ethanol to make a stock solution. A styrene/CDB stock solution was prepared by adding 36.9 mg of CDB to 5.44 g of styrene. VA-044 was dissolved in the water in the ratio of 36 g VA-044 to 100 g water

2. The CTAB solution 250 ml was added to 15 g of silica in a round bottom flask.

3. The styrene/CDB 0.0181 g and relative AIBN/ETOH solutions were then added into the mixture and the pH of the system adjusted to 7 by adding 0.1 NaOH solution. The flask was then sealed with paraffin film. For water soluble initiator, 0.081 g of VA-044 solution was added to the CTAB/silica mixture. 0.181 g of the styrene/CDB stock was then added and the pH adjusted to 7 by the addition of 0.1 NaOH solutions.

4. The mixture was stirred for 24 hours to achieve equilibrium at room temperature.

5. Polymerize the mixture at 70 °C for twenty-four hours in a water bath under nitrogen atmosphere and terminate the polymerization process in an ice bath.

6. The reaction mixture was washed by 10 times of 1000 ml of water to remove accessible surfactant.

7. The modified silica was filtered, dried overnight and ground into a fine powder with motor.

3.7 Conditions for Admicellar Polymerization

The CTAB feed concentration was chosen so that the equilibrium bulk concentration was approximately 80 % of CMC in order to prevent emulsion polymerization in the presence of micelles. This made the equilibrium adsorption $\approx 100\mu\text{mol/g}$ of silica.

3.7.1 Reaction Time

Reaction times of 1, 2, 4 and 6 hours were chosen to examine conversion of styrene. An initiator to monomer ratio of 1: 5 and monomer to CTAB loadings of 1:1, 1:2 and 2:1 (100:100, 100:200, 50:100) were examined.

3.7.2 Monomer Loading

The styrene feeds were set so that the adsorbed CTAB to adsolubilized styrene ratios were 1:2 and 2:1 (50:100 and 100:200 $\mu\text{moles/g}$).

3.7.3 Initiator Loading

Eight initiator to monomer ratios were studied for both water soluble (VA-044) and insoluble initiators (AIBN) at two hours reaction time for both monomer loading levels (1:2 and 2:1).

Table 3.1 Polymerization conditions for AIBN and VA-044 samples

adsorbed CTAB ($\mu\text{mol/g}$)	CTAB : adsolubilized styrene ($\mu\text{mol/g}$) : ($\mu\text{mol/g}$)	VA-044 : styrene mole : mole
100	100:50 (2:1)	1:1, 1:5, 1:7, 1:10, 1:15, 1:20, 1:25, 1:50
	100:200 (1:2)	1:1, 1:5, 1:7, 1:10, 1:15, 1:20, 1:25, 1:50

3.8 Polymerization condition for RAFT-AP

Table 3.2 Polymerization condition of CDB/AIBN via AP

adsorbed CTAB ($\mu\text{mol/g}$)	adsorbed CTAB : adsolubilized styrene ($\mu\text{mol/g} : \mu\text{mol/g}$)	RAFT : AIBN	Reaction time (h)
100	1:1	0.04:1	24
		1:1	
		5:1	

Table 3.3 Polymerization condition of CDB/VA-044 via AP

adsorbed CTAB ($\mu\text{mol/g}$)	adsorbed CTAB : adsolubilized styrene ($\mu\text{mol/g} : \mu\text{mol/g}$)	RAFT : VA-044	Reaction time (h)
100	1:1	0.02:1	24

3.9 Polymer Extraction

150 ml of THF solvent was added into 10 g of modified silica to extract the polystyrene formed on silica surface. After stirring for overnight and refluxing for additional 4h the sample was filtered and filtrate collected. The filtrate was allowed to evaporate until reduced to approximately $\frac{1}{2}$ of its original volume. It was then poured into 250 ml of distilled water. The precipitated polystyrene was collected by filtering and dried it in a vacuum oven overnight at 30 °C.

3.10 Characterization

3.10.1 Thermogravimetric Analysis

TGA analyses were performed on the modified silicas, extracted silicas, untreated silica, CTAB and extracted polystyrene using a Perkin Elmer (TGA 7). The samples were analyzed from 30 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

3.10.2 Fourier Transform Infrared Spectroscopy

FTIR spectra of modified and extracted materials were observed using a Vector 3.0 Bruker spectrophotometer with a resolution of 4cm^{-1} in the frequency range of 4000 to 400 cm^{-1} . A KBr pellet technique was used and the information collected by deuterated triglycinesulfate detector (DTGS) with a specific directivity, D^* , of $1 \times 10^9 \text{cmHz}^{1/2} \text{w}^{-1}$ and 32 scans.

3.10.3 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 μm 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.

3.10.4 Atomic force Microscopy

The multimode atomic force microscope equipped with Nanoscope IIIa software was employed in this study. Topographic, amplitude and phase images were captured simultaneously using tapping mode AFM. A-J type scanner with the maximum scan size of 125 μm was used. Silicon tips

with a resonance frequency of approximately 266.7 kHz and length of 125 μm were obtained from digital instrument, 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 %.

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.

In tapping mode, the tip is oscillating close to its resonant frequency. When the tip is brought close to the sample, the tip-sample interaction will influence the amplitude and frequency of the tapping. The interaction forces can be attractive or repulsive. If the oscillating amplitude is set at a constant value by the feedback loop, then the oscillating frequency may change and different surface will result in different frequency shifts due to different interacting forces between the tip and the surface. These changes in the frequency can be used to analyze the characteristics of the samples. That phase contrast depends on the driving frequency and imaging tapping force. Tapping force is related to "the ratio of engaged oscillating amplitude to the free air oscillating amplitude" or *setpoint ratio*. Different contrasts have been observed when imaging under region (attractive regime) or brighter region (repulsive regime) by changing the imaging tapping force or driving frequency. (See, 2001)

Amplitude-modulation force microscopy, usually known as tapping mode AFM is the most extensively used dynamic force microscopy method for nanometer-scale characterization and modification of surfaces in air and liquid

environments. The true atomic resolution images of inorganic surfaces have been obtained (Paulo, 2001).

The light regions in the topographic images, black regions in the phase images and the “patches” in amplitude images illustrate the presence of polystyrene on silica surface. All three types of images are needed in order to confidently identify the polystyrene on the silica surface.