

CHAPTER III EXPERIMENTAL

3.1 Materials

Styrene (99%), hexadecyltrimethylammonium tosilate (C₁₆TAT) were purchased from Fluka and Sigma respectively. 2, 2'-Azobis-2-methylpropionitrile (AIBN, 98%), a water-insoluble initiator, was obtained from Aldrich Chemicals Company. Methanol AR grade, Tetrahydrofuran (THF) AR grade, and HPLC grade were purchased from Lab-Scan Analytical Sciences (BKK, Thailand). All materials were used without further purification.

Table 3.1 List of instruments and models used in this work

Instrument	Model
Drop Shape Analysis System	Kruss (DSA-10Mk2)
Conductometer	Suntex and a Mettler Toledo conductivity cell (cell constant = 0.97)
Fourier Transform Infrared	Nicolet model Nexus 670
Thermogravimetric Analysis	Perkin Elmer (TGA 7)
Differential Scanning Calorimeter	Perkin Elmer (DSC 7)
X-ray diffraction	Rigaku (model Dmax 2002)
Gel Permeation Chromatography	Waters Gel Permeation Chromatography (SHIMADZU class VP)
Transmission electron microscopy	Jeol (JEM-1230)

3.2 Micellar Formation

Stock CTAT solutions of known weight was prepared in distilled water. Different concentrations of CTAT solution were made by pipetting different volumes of stock solution into volumetric flasks. Then 20 ml of the different known concentration CTAT solutions were placed in 24-ml vials. The solution was allowed

to equilibrate at 30 °C for 24 h in shaker-water bath. After that, the surface tension and conductivity of CTAT solutions were investigated by a contact angle tester and a conductometer respectively. Surface tension versus log of concentration and conductivity versus concentration were plotted. The CMC value is the break point of the curve.

3.3 Emulsion Polymerization

Stock solutions of styrene in surfactant were used to prepare samples containing constant CTAT concentration in various conditions as shown below.

Table 1.1 Emulsion polymerization conditions

CTAT (wt.%)	Styrene: AIBN (mole:mole)	Styrene loading (mole CTAT:mole Styrene)	Temperature (°C)
5	1:15, 1:30, 1:50	Low level (6:1)	70
	1:15, 1:30, 1:50	Medium level (3:1)	70
	1:15, 1:30, 1:50	High level (1.6:1)	70
10	1:15, 1:30, 1:50	Low level (6:1)	70
	1:15, 1:30, 1:50	Medium level (3:1)	70
	1:15, 1:30, 1:50	High level (1.6:1)	70
20	1:15, 1:30, 1:50	Low level (6:1)	70
	1:15, 1:30, 1:50	Medium level (3:1)	70
	1:15, 1:30, 1:50	High level (1.6:1)	50, 60, 70

The polymerization processes were carried out following these steps:

- i. CTAT was dissolved in distilled water. CTAT solution was allowed to equilibrate at 30 °C in shaker bath for 24 h.
- ii. Styrene monomer was added to the solution. Then the flask was sealed with rubber stopper and paraffin film. The mixtures

were shaken in a shaker bath and left for 24 h at 30 °C to equilibrate.

iii. AIBN was dissolved in ethanol. The amount of AIBN was varied. AIBN solution was added to the mixture. Then the flask was sealed with rubber stopper and paraffin film.

iv. Polymerization was carried out by heating the reaction flask in water bath at 70°C for 10 h.

v. The reaction was terminated by placing the reaction flask in an ice bath.

vi. The polymer was isolated by precipitation with methanol and washed with distilled water until no foaming was observed.

3.4 Characterization

3.4.1 Fourier Transform Infrared Spectroscopy

FTIR spectra of the extracted material were obtained from a Nexus 670 Nicolet 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 $\text{cm}^2 \cdot \text{Hz}^{1/2} \cdot \text{W}^{-1}$.

3.4.2 Thermal Stability

CTAT and polystyrene were analyzed by a TG-DTA Pyris Diamond (Perkin Elmer). All samples were carried out from 30 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere. And the thermograms of DSC were obtained with a Perkin-Elmer DSC-VII calorimeter. The instrument was calibrated with Indium standards. All thermograms were obtained with heating and cooling rates of 10 °C/min from 30 °C to 200 °C for CTAT and 30 °C to 300 °C for polystyrene.

3.4.3 X-ray Diffraction

All polystyrene samples were analyzed by X-ray diffraction (Rigaku, model Dmax 2002) with Ni-filtered $\text{CuK}\alpha$ radiation operated at 40 kV and 30 mA with scan speed 5.00 deg/min from the range of 5.00 to 50.00 deg.

3.4.4 Gel Permeation Chromatography

Obtained polymer samples were characterized by Waters Gel Permeation Chromatography (SHIMADZU class VP). Tetrahydrofuran (HPLC grade) was used as a mobile phase at flow rate 8.0 ml/min. Polymer solutions were manual by injected with a volume of 100 μ m at temperature 40°C. The column used was Styragel[Ⓟ] HT4 7.8x300 mm column. Polystyrene standards were used for calibration.

3.4.5 Transmission Electron Microscopy

The microstructures of the polymerized samples were obtained in a Jeol (JEM-1230) transmission electron microscope, operating at a acceleration voltage of 100 kV. Samples were diluted 6 times in an acidic solution of uranyl acetate (2 wt% at pH 4.2) and a small drop of the solution was placed on a carbon coated copper grid and dried at room temperature.