CHAPTER III
EXPERIMENTAL

3.1 Materials

Hi-Sil®255, an amorphous precipitated silica, was obtained from PPG-Siam Co., Ltd. and had a N_2 BET surface area of 170 ± 15 m^2/ g. Hexadecyltrimethyl ammonium bromide (CTAB) 98%, Styrene 99% and Isoprene 98% were purchased from Fluka 2, 2' -Azobisisobutyronitrile (AIBN), a water insoluble initiator, was obtained from Aldrich Chemicals Company with 98% purity. Sodium hydroxide pellets with 99 % purity were obtained from BDH Laboratory Supplies. Tetrahydrofuran (THF) was obtained from Lab-Scan Analytical Sciences. All materials were used without further purification.

3.2 Experimental Setup

The continuous reactor system consisted of a stirred feed tank, a stirred reactor and a product tank. The feed tank was made of stainless steel having 17-liter capacity with a lid and internal baffles. The reactor vessel was a one-liter borosilicate glass bottle with a screw cap. The product tank was a stainless steel tank. Mixtures in the reactor and feed tanks were well mixed with a magnetic bar and mechanical stirrer, respectively. Reactor temperature was maintained at constant 70 ± 2°C by using a circulating heater and water bath. The fluid flow rates were controlled by using a Masterflex Digital console drive peristaltic pump with easy-load model 7518-60 head. The reactor system is shown in Figure 3.1.

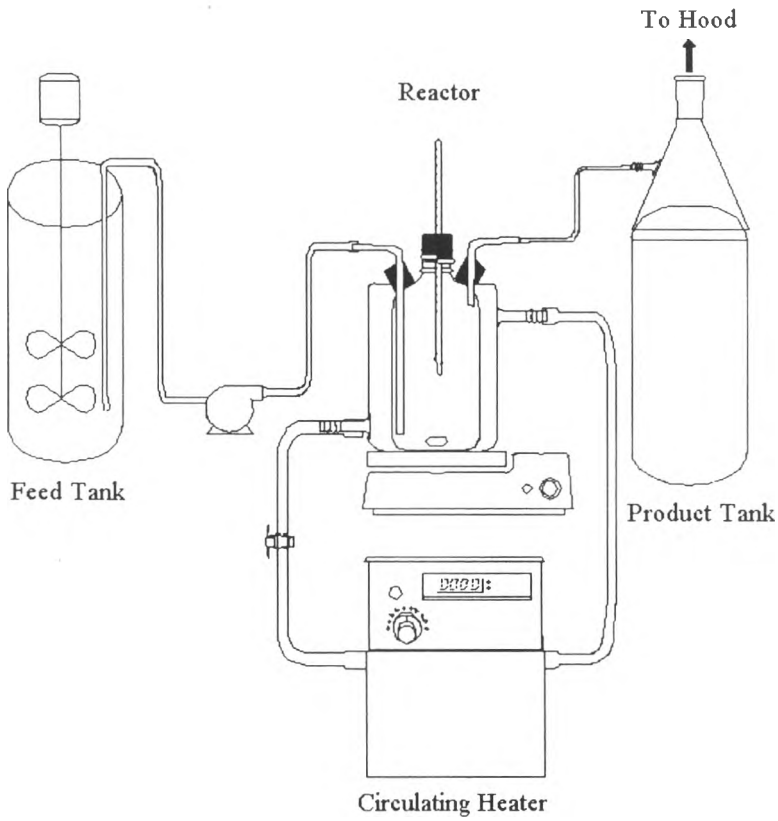

Figure 3.1 The continuous admicellar polymerization system.

3.3 Experimental Procedures

3.3.1 Adsorption Isotherm of CTAB onto Silica Hi-Sil®255

Adsorption experiments were conducted in capped 24-ml vials. Two-gram samples of silica were mixed with 20 ml of CTAB solution at different concentrations and a constant pH of 8. The samples were allowed to equilibrate at 30°C for 24 hours and then centrifuged at 2000 rpm for 10 minutes. The supernatant was taken to analyze the CTAB concentration. The CTAB adsorption was calculated by the concentration difference method. Then the adsorption data was used to plot the adsorption isotherm. From the adsorption isotherm, the critical micelle concentration (CMC) of CTAB on Hi-

Sil®255 could be determined. It is very crucial to keep CTAB concentration below CMC in order to avoid micelle formation.

3.3.2 Surface Modification Procedure

The amorphous precipitated silica was modified using combinations of styrene and isoprene co-monomers at a 1:3 molar ratio. The amounts of the co-monomers fed into the feed tank were 5, 20 and 30 grams per kilogram of silica. The polymerization times were 30, 45 and 60 minutes, which are denoted by S, M and L, respectively.

The silica surface modification procedure consisted of: (1) weighing one kg of silica, (2) adding 200 grams CTAB to 12.5 liters of deionized water and stirring until the surfactant completely dissolved, (3) adjusting the pH of the surfactant solution to 8 using sodium hydroxide solution, (4) adding the silica to the surfactant solution in the feed tank, (5) dissolving 1.65 grams of AIBN and 1:3 molar ratio of styrene and isoprene co-monomer into 99.7% ethanol at the ratio of 30 ml per 0.5 gram of AIBN and then adding this mixture to the feed tank, and (6) allowing the system to equilibrate with constant stirring for 24 hours, forming the feed stock.

The reactor was heated to 70°C in a water bath heated by a circulating heater. By adjusting the pump flow rate, the reaction was allowed to proceed for various resident times. The reaction effluent, collected in the product tank, was allowed to settle and the supernatant was decanted. The modified silica was washed by counter current washing for five days with daily stirring or until the wash water no longer foamed on agitation. The silica was then dried at 110°C for 24 hours and reground into a powder through a 120-mesh sieve.

3.3.3 Analysis and Measurement Method

The CTAB concentration was determined by using a Total organic Carbon Analyzer (TOC). The original and modified silicas were characterized by the techniques listed in Table 3.1. Polymer extraction was performed by boiling seven grams of the modified silica in tetrahydrofuran (THF) for 4 hours. The slurry was cooled to room temperature, filtered, and rinsed with hot THF. The polymer was precipitated by adding the filtrate to water. Extracted polymer was analyzed by a Fourier Transform Infrared (FTIR) spectroscopy. Imaging of silica aggregates was performed by Scanning Electron Microscope (SEM). Thermogravimetric Analysis (TGA) was used to determine the amount of co-polymer formed on the silicas. Additionally, the nitrogen BET surface area and mean agglomerate particle size were also determined.

Table 3.1 Silica test methods.

Parameter	Technique/ Instrument
CTAB concentration	Total Organic Carbon Analyzer (TOC_5000A, Shimadzu)
Specific surface area	BET N_2 surface area Autosorb-1 Quantachrome
Particle size	MALNERN Mastersizer X Ver. 2.15
Surface morphology	Scanning Electron Microscope (SEM) JEOL JSM-5200
Functional groups	Fourier Transform Infrared Spectroscopy (FTIR) BRUKER EQUINOX55/S
Amount of polymer formed	Thermogravimetric Analysis (TGA) Du Pont Instrument TGA 2950