CHAPTER 3

EXPERIMENTAL

3.1 Chemicals

3.1.1 Monomers

Styrene monomer (St) was supplied by Ethernal Resin Co., Ltd.(Thailand). It was purified by removing the added inhibitor before use. It was washed twice with 10% aqueous sodium hydroxide in a seperating funnel. The aqueous phase was drained off, and the monomer phase was washed with distilled-deionized water until pH 7 was obtained. Then anhydrous sodium sulfate (100 g/l) was added to adsorb the remained amount of water in the monomer phase. Finally, the dried monomer was passed through an activated aluminum oxide column. The purified styrene was stored in a brown capped bottle under nitrogen atmosphere and kept in a refrigerator at –5°C.

n-Butyl acrylate (BuA) and 2-ethylhexyl acrylate (2-EHA) monomers were supplied by Union Carbide Thailand Co., Ltd. They were purified before use using the same cleaning procedure as styrene.

3.1.2 Initiator

2,2'-Azobisisobutyronitrile (AIBN) was provided by Siam Resin & Chemical Co., Ltd. It was purified prior use by recrystallization in methanol. The purified AIBN was collected in a bottle sealed with aluminum foil to protect the radiation from sun light and then stored in a refrigerator at –5°C.

3.1.3 Dispersant

Poly(*N*-vinylpyrrolidone) (PVP) was obtained from ISP Technology, Inc. They were used as received. In this study, three types of PVP were used: PVP K-15, PVP K-30 and PVP K-90. Their viscosity-average molecular weights are 10,000, 40,000 and 360,000, respectively.

3.1.4 Solvents

Ethanol and Methanol, commercial grade from Rungsup Chemical Co. Ltd., were distilled by fractional distillation at the normal atmosphere before use. Particularly, for ethanol, calcium oxide was added to dehydrate the retained moisture prior distillation.

3.1.5 Other Chemicals

Other chemicals of analytical grade, shown below were used as obtained from suppliers.

Sodium hydroxide (NaOH) : Merck

Sodium sulfate anhydrous (Na_2SO_4) : Merck

Calcium oxide (CaO) : Fluka

Chloroform HPLC grade ($CHCl_3$) : Carlo Erba

3.2 Glassware and Equipment

Four-necked round bottle flask, reflux condenser, thermometer, nitrogen gas tube, mechanical stirrer, water bath, cooling circulator, centrifugal tube, balance, desiccator, oven, and other general laboratory glassware and equipment.

3.3 Apparatus

Gel permeation chromotrography (GPC)

LC-AZ AD, CTO-10AC, C-R7A plus (Shimadzu)

Scanning electron microscopy (SEM)

Jeol, JSM-6400

Fourier transform infared spectroscopy (FTIR)

Perkin Elmer 1760 X

Nuclear magnetic resonance (NMR)

Jeol JNM-500 FT NMR spectrometer

Differential scanning calorimeter (DSC)

DSC 7 Perkin Elmer

3.4 Polymerization Procedure

3.4.1 Synthesis of Styrene and *n*-Butyl Acrylate Copolymer

Dispersion polymerization reactions were carried out in a 500 cm^3 round-bottom flask equipped with a Teflon paddle stirrer, a reflux condenser and a thermometer. The procedure used to prepare copolymer particles was as follows. PVP (1.6 g) and 70 g of the mixed solvent were introduced into the reaction flask. The clear solution was heated to 70°C, stirred at a rate of 100 rpm and nitrogen gas was bubbled through the solution for deoxygenation. After 1 hr, 0.1 g of AIBN dissolved in 10 g of monomer mixture was poured into the reaction flask. The homogeneous mixture became cloudy after a few minutes. The reaction was then allowed to polymerize for 8 hr under a constant rate of agitation. A slow steam of nitrogen gas was maintained during the polymerization. At a given time, the reaction was terminated by cooling to the room temperature. Methanol (100 cm^3) was added

to the reaction mixture, and mixed thoroughly. The polymer particles were isolated from the mixture by centrifugation at a rate of 3000 rpm for 30 min. The supernatant was decanted and the remaining polymer was washed with methanol and centrifuged again. This process was repeated three times or more until the supernatant was clear. Finally, the product was dried at room temperature.

In order to investigate the effect of important parameters on dispersion polymerization, a series of experiment was performed by varying variables as shown in Table 3.1

Table 3.1. The reaction parameters investigated in dispersion polymerization

Parameter	Standard recipe	Variable condition
Styrene:*n*-Butyl acrylate (mol%)	80:20	80:20, 85:15, 90:10, 95:5, 100:0
Dispersant type	PVP K-30	PVP K-15, 30, 90
Dispersant concentration (wt%)	2	1, 2, 4, 8, 12
Ethanol:Water (wt%)	90:10	70:30, 80:20, 90:10, 100:0
Agitation rate (rpm)	100	50, 100, 200, 300
Reaction time (hr)	8	0.5, 1, 2, 4, 6, 8, 10
Reaction temperature (°C)	70	65, 70, 75, 80
Crosslinking agent (wt%)	-	0.25, 0.50, 1, 2, 10

3.4.2 Synthesis of Styrene and 2-Ethylhexyl Acrylate Copolymer

In this section, we further study the copolymerization of St and 2-EHA to investigate the effect of different side chains of the acrylate monomer on the characteristics of the resulting copolymer.

The polymerization technique was performed similarly with those of the copolymerizations of St and BuA, following the standard recipe shown in Table 3.1. The variables and conditions were the mole ratio between St and 2-EHA at 95/5, 90/10, 85/15, and 80/20 respectively. The resulting copolymers were analyzed and compared with the copolymers obtained in Section 3.4.1.

3.5 Characterization

3.5.1 Structural Characterization

Fourier-transform infared spectrophotometer (FTIR) was used to characterize the functional groups of the copolymers. The copolymer sample was ground with the dried KBr powder, and compressed into a disc. The KBr disc was subjected to analyze on an IR spectrophotometer.

Copolymer composition was done by ^{1}H-NMR technique in $CDCl_3$ at room temperature using JNM-A500 specrometer. The copolymer composition was determined from the ratio of intensities of the characteristic protons of St, BuA, and 2-EHA (Details were described in Appendix A).

3.5.2 Particle Characterization

The particle size and size distributions of copolymer particles were measured using a scanning electron microscopy (SEM). Prior to measurement, the samples were prepared by placing a drop of diluted particles in methanol onto a cover glass glued on an SEM aluminum stub, evaporating the solvent to dryness and coating with a thin layer of gold.

The number average diameter ($\bar{d}_n$) and weight average diameter ($\bar{d}_w$) were calculated from the following equations.

$$\bar{d}_n = \frac{\sum_{i=1}^{N} d_i}{N} \tag{3.1}$$

$$\bar{d}_w = \frac{\sum_{i=1}^{N} d_i^4}{\sum_{i=1}^{N} d_i^3} \tag{3.2}$$

where d_i is the diameter of particle i. At least 200-300 particles per sample (N) were counted for calculations. The polydispersity index (PDI) and the coefficient of variation (CV) are defined as:

$$\text{PDI} = \frac{\bar{d}_w}{\bar{d}_n} \tag{3.3}$$

$$\text{CV} = \frac{\left(\frac{\sum_{i=1}^{N} (d_i - \bar{d}_n)^2}{N-1} \right)^{1/2}}{\bar{d}_n} \times 100 \tag{3.4}$$

3.5.3 Determination of Average Molecular Weights and Molecular Weight Distribution

The molecular weight analysis was determined by gel permeation chromatography (GPC). The measurements were made using a ultraviolet-visible detector, and a pair of Showa Denko columns (Shodex GPC K-806 M; 300 mm x 8 mm I. D.; packing with styrene-divinylbenzene gel having a number of theoretical plates of 17,000) at 25°C. The HPLC grade chloroform was used as a eluent at a flow rate of 0.017 $cm^3 s^{-1}$.

The GPC samples were prepared by dissolving the dried polymer sample in chloroform, then injecting the polymer solution of 0.07 cm^3 into GPC for analysis. The molecular weights of the polymer were obtained by calculation from calibration line using polystyrene standard sample supplied by Showa Denko (S-66.0).

3.5.4 Determination of the Thermal Property

Thermal behavior of polymer was examined by Differential Scanning Calorimeter (DSC) to obtain the glass transition temperature. The sample, 10-20 mg, was put into the aluminum pan. The measurements were carried out over a temperature range of 20 to 120°C with a heating rate of 10°C min^{-1}, under the nitrogen atmosphere.