

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemicals

##### 3.1.1 Monomers

Styrene (STY) ( $C_8H_8$ )

Siam Resin & Chemical Co., Ltd. Thailand.

Colorless liquid, b.p. 145-146°C, m.p. -31°C,

f.p. 31°C,  $M = 104.15 \text{ g/mol}$ ,  $D = 906.7 \text{ kg/m}^3$ .

Methyl Methacrylate (MMA) ( $C_5H_8O_2$ )

Siam Resin & Chemical Co., Ltd. Thailand.

Colorless liquid, b.p. 99°C, m.p. -50°C,

f.p. 10°C,  $M = 100.12 \text{ g/mol}$ ,  $D = 942 \text{ kg/m}^3$ .

##### 3.1.2 Initiator

2,2'-Azo-bis-isobutyronitrile (AIBN) ( $C_8H_{12}N_4$ )

Siam Resin & Chemical Co., Ltd. Thailand.

White needle-like crystal, Assay 98% min., m.p. 100-103°C,

Iron 0.0005% max., Chlorides 0.003% max.,  $M = 164.22 \text{ g/mol}$ .

##### 3.1.3 Matrix Polymer

Poly(N-Vinyl Pyrrolidone) (PVP K-30)  $-(C_5H_9NO)_n-$

Fluka, analytical grade.

White powder,  $M_w = 40,000$

#### 3.1.4 Solvents

Ethanol ( $C_2H_5OH$ )

BDH Chemical Ltd., UK, commercial grade,

Colorless, b.p.  $78.32^\circ C$ , f.p.  $-117.3^\circ C$ ,

$M = 46.07$  g/mol,  $D = 781.5$  kg/m<sup>3</sup>.

Methanol ( $CH_3OH$ )

BDH Chemical Ltd., UK, commercial grade,

Colorless, b.p.  $64.65^\circ C$ , f.p.  $-97^\circ C$ ,

$M = 32.04$  g/mol,  $D = 791$  kg/m<sup>3</sup>.

Chloroform ( $CHCl_3$ )

Carlo Erba, HPLC grade,

Colorless, b.p.  $61.2^\circ C$ ,  $M = 119.38$  g/mol.

#### 3.1.5 Other Chemicals

Sodium hydroxide ( $NaOH$ )

EKA Noble, analytical grade,

White pellets,  $M = 40$  g/mol.

Sodium chloride ( $NaCl$ )

E. Merck, reagent grade,

White scales,  $M = 58.44$  g/mol.

Calcium oxide ( $CaO$ )

Fluka, laboratory grade,

White marble,  $M = 56.08$  g/mol.

Magnesium sulfate ( $\text{MgSO}_4$ )

E. Merk, analytical grade,

White scales,  $M = 120.37 \text{ g/mol}$ .

Hydroquinone (HQ)

E. Merk, analytical grade,

White powder, b.p.  $286^\circ\text{C}$ , m.p.  $171; 172^\circ\text{C}$ .

Polystyrene standards

Shodex standard S-66.0

White powder

( $M_w = 3,160,000; 156,000; 28,500; 2,950$ ).

### 3.2 Equipment and Glassware

Gel Permeation Chromatography (GPC)

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

K-806 M Column (Showa Denko Co., Ltd.).

Scanning Electron Microscopy (SEM)

JEOL JSM-T220A.

Nuclear Magnetic Resonance Spectroscopy (NMR)

AC-F200, 200 MHz, Bruker Spectrospin.

Differential Scanning Calorimeter (DSC)

NETZSCH DSC 200, Switzerland.

Fourier-Transform Infrared Spectroscopy (FTIR)

PERKIN ELMER Spectrometer 1760 x U.S.A.

Elemental Analysis (EA)

PERKIN ELMER PE 2400 Series II: option CHN, U.S.A.

Centrifuge Type CR 5 B2

Hitachi, MAX speed 5000 rpm, Japan.

Four-necked round bottom flask

Round bottom flask

Semicircular anchor-type blade

Mechanical stirrer

Nitrogen gas inlet tube

Water bath

Heating mantle

Other general laboratory glassware and equipment.

### 3.3 Procedure

#### 3.3.1 Purification of Chemicals

##### 3.3.1.1 Styrene and Methyl Methacrylate Monomers

The monomer was purified by washing with aqueous sodium hydroxide solutions in a separatory funnel to remove an inhibitor. The mixture was mixed by shaking and opening the stopper frequently to release the pressure. The organic phase and aqueous phase were left to enable complete separation and the red aqueous solution was then removed. The same procedure was repeated until the aqueous solution remained colorless. Aqueous sodium chloride was added to the monomer and was mixed thoroughly again. The above procedure was repeated for 2-3 times. The

monomer was then washed 3 times with deionized water to remove sodium hydroxide, and was subsequently dried over magnesium sulfate. Finally, it was distilled under reduced pressure, then stored in a dark brown bottle in a refrigerator before use.

#### 3.3.1.2 Initiator

2,2'-Azo-bis-isobutyronitrile was recrystallised from methanol, collected by filtering on a glass filter, dried in air, then stored in a refrigerator before use. It was kept in a reduced pressure desiccator for 1/2 h before use as a polymerizing initiator.

#### 3.3.1.3 Matrix Polymer

Poly(N-vinyl pyrrolidone) (PVP K-30) with average molecular weights of 40,000, analytical grade from Fluka, was used as a matrix polymer without further purification.

#### 3.3.1.4 Solvents

Ethanol and Methanol were purified by fractional distillation at an atmospheric pressure prior to use. Calcium oxide was added to ethanol in the distillation flask to dehydrate the retained moisture. The calcium oxide was later removed.

### **3.4 Synthesis of Poly(Styrene-co-Methyl Methacrylate)**

#### 3.4.1 Dispersion Copolymerization of Styrene and Methyl Methacrylate with 2,2'-Azo-bis-isobutyronitrile

A 1000 cm<sup>3</sup> four-necked round bottom flask equipped with a mechanical stirrer, a semicircular anchor-type blade, a reflux condenser, a thermometer and a

nitrogen gas inlet tubing was charged with poly(N-vinyl pyrrolidone), and a solvent mixture of ethanol and water, then the nitrogen gas was purged slowly into the reaction mixture. The solution was heated in a water bath to a reaction temperature of 62°C with a constant stirring rate for 1 h. The monomer mixture of styrene and methyl methacrylate, AIBN initiator were added through a glass funnel to the matrix polymer solution which is soluble in the mix solvent. After all mixture had been added, the temperature of the reaction mixture was constantly maintained at 60°C, while stirring at a constant speed with a slow purging of nitrogen gas for 10 h. The polymerization was subsequently stopped by adding a hydroquinone/methanol solution to the reaction mixture sample and the reaction flask was cooled in an ice bath to room temperature and the reaction mass was transferred to a 1000 cm<sup>3</sup> beaker and diluted with methanol. It was mixed thoroughly at room temperature. The polymeric beads were isolated by centrifuging the reaction mixture, and decanting the supernatant. The beads were cleaned with methanol by a repeatedly sedimentational redispersion process until the supernatant was clear, then they were dried at room temperature for 24 h. Finally, the product was placed in an oven at 70°C for 24 h to remove the residual methanol.

#### 3.4.2 The Effect of Matrix Polymer (Poly(N-Vinyl Pyrrolidone)) Concentration

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using matrix polymer concentrations given in Table 3.1

Table 3.1 Various Matrix Polymer Concentrations for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	P1	P2	P3	P4	P5	P6
PVP (wt%)	0	2	6	8	10	12

\*EtOH/H<sub>2</sub>O = 70/30, reaction temperature = 60°C, agitation rate = 290 rpm, reaction time = 10 h.

### 3.4.3 The Effect of Ethanol-to-Water Ratios

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using the solvent mixture ratios of ethanol and water given in Table 3.2 and 3.3.

Table 3.2 Various Solvent Mixture Ratios of Ethanol and Water for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	S1	S2	S3	S4	S5	S6
EtOH:H <sub>2</sub> O (wt%)	100:0	90:10	80:20	70:30	60:40	0:100

\*PVP 8 wt%, reaction temperature = 70°C, agitation rate = 290 rpm, reaction time = 8 h.

Table 3.3 Various Solvent Mixture Ratios of Ethanol and Water for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	S7	S8	S9	S10
EtOH:H <sub>2</sub> O (wt%)	90:10	80:20	70:30	60:40

\*PVP 8 wt%, reaction temperature = 60°C, agitation rate = 290 rpm, reaction time = 10 h.

#### 3.4.4 The Effect of the Reaction Temperature

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using reaction temperatures given in Table 3.4.

Table 3.4 Various Reaction Temperatures for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	RT1	RT2	RT3	RT4
Temp (°C)	50	60	70	80

\*PVP 8 wt%, EtOH/H<sub>2</sub>O = 70/30, agitation rate = 290 rpm, reaction time = 10 h.

#### 3.4.5 The Effect of the Agitation Rate

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using agitation rates given in Table 3.5.

Table 3.5 Various Agitation Rates for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	A1	A2	A3	A4
Agitation rate (rpm)	80	150	200	290

\*PVP 8 wt%, EtOH/H<sub>2</sub>O = 70/30, reaction temperature = 60°C, reaction time = 10 h.

#### 3.4.6 The Effect of the Reaction Time

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using reaction times given in Table 3.6.



Table 3.6 Various Reaction Times for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	T1	T2	T3	T4
Time (h)	6	8	10	15

\*PVP 8 wt%, EtOH/H<sub>2</sub>O = 70/30, reaction temperature = 60°C, agitation rate = 290 rpm.

#### 3.4.7 The Effect of the Feed Ratio of Styrene/Methyl Methacrylate

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using styrene feeds given in Table 3.7.

Table 3.7 Various Styrene Feeds for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	F1	F2	F3	F4	F5
Styrene (mole%)	0	25	50	75	100

\*PVP 6 wt%, EtOH/H<sub>2</sub>O = 70/30, reaction temperature = 60°C, reaction time = 8 h.

#### 3.4.8 Determination of the Conversion

Dispersion copolymerization of styrene and methyl methacrylate was repeated by removing the reaction mixture from the reactor at the desired various reaction times shown in Table 3.8. The polymeric beads were isolated from the reaction mixture and determined gravimetrically. The conversion was calculated as given below

$$\% \text{ conversion} = \frac{\text{weight of the copolymer}}{\text{weight of the initial monomer}} \times 100 \quad (3.1)$$

Table 3.8 Various Reaction Times for Dispersion Polymerization of Styrene and Methyl Methacrylate\*

No.	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
Time (h)	0.33	0.47	0.6	0.73	1	2	4	6	8	10

\*PVP 6 wt%, EtOH/H<sub>2</sub>O = 70/30, reaction temperature = 70°C, agitation rate 290 rpm.

From above the reaction times, the reaction products were determined gravimetrically as conversion of the reaction.

#### 3.4.9 Investigation of the Particle Growth

Dispersion copolymerization of styrene and methyl methacrylate was repeated by using the reaction times given in Table 3.9. In each reaction time, the reaction mixture was removed from the reactor and the copolymer beads were then isolated. The average size and size distributions of the copolymer beads were evaluated through the micrographs taken from a scanning electron microscope.

Table 3.9 Various Reaction Times for Dispersion Copolymerization of Styrene and Methyl Methacrylate\*

No.	PF1	PF2	PF3	PF4	PF5	PF6	PF7	PF8
Time (h)	0.6	0.73	1	2	4	6	8	10

\*PVP 6 wt%, EtOH/H<sub>2</sub>O = 70/30, reaction temperature = 70°C, agitation rate = 290 rpm.

### 3.5 Copolymer Characterization

#### 3.5.1 Determination of the Functional Groups of the Copolymer and Copolymer Composition

The FT-IR absorbance spectrum of each sample of poly(styrene-*co*-methyl methacrylate) was measured by the KBr pellet method and compared with those of the standard polystyrene and PVP K-30. The spectra are recorded by means of a high resolution option in the wave number range from 400 to 4000  $\text{cm}^{-1}$  on an FTIR spectrophotometer.

The copolymer composition was calculated by using  $^1\text{H-NMR}$  Spectrophotometry with  $\text{CDCl}_3$  as a solvent. The spectra are recorded with a high resolution option at a temperature of  $36.5^\circ\text{C}$ .  $^{13}\text{C-NMR}$  is performed with solutions of the sample in deuterated chloroform to determine the carbonyl group. The percentages of carbon, hydrogen and nitrogen were measured by using an EA technique by a rapid combustion method. In this method, gas chromatographically separated species of the copolymers by a frontal analysis were quantitatively detected by a thermal conductivity detector.

#### 3.5.2 Determination of Poly(Styrene-*co*-Methyl Methacrylate) Particle Size and Size Distribution

The particle size and size distribution of poly(styrene-*co*-methyl methacrylate) were measured by taking electron micrographs of the particles on an SEM.

The dried polymer particles were coated with a thin layer of gold in vacuum. In each sample, 400 particles on the electron micrograph were measured to calculate the particle size, particle size distribution (PSD), the coefficient of variation (CV), and standard deviation (SD) of the particles.

### 3.5.3 Determination of the Average Molecular Weights of Poly(Styrene-co-Methyl Methacrylate)

The average molecular weights of poly(styrene-co-methyl methacrylate) were measured by using a GPC (LC-10AD, CTO-10AC, C-R7A plus (SHIMADZU) with a refractive-index detector (RID-6A) and an ultraviolet-visible detector (SPD-10AV) under the following conditions: a pair of Showa Denko columns (K-806 M; 300 mm x 8 mm I.D; packing with styrene-divinylbenzene gels having the number of theoretical plates 17,000), chloroform eluent of a flow rate of 0.017 cm<sup>3</sup>/s, and the working temperature at 25°C. The calibration curves of GPC analysis were obtained by using a narrow molecular weight distribution polystyrene standards (Shodex standard S-66.0 with molecular weights of 3,160,000, 156,000, 28,500, 2,950, respectively). Polystyrene standards 0.04% each in chloroform (HPLC grade) were prepared and the injection volume, 70 µl, of each standard was injected. For each poly (styrene-co-methyl methacrylate), 0.04% solution of dried sample was prepared in chloroform (HPLC grade). The solutions were then filtered using a 0.45 µm membrane filter, 70 µl of the filtered polymer solution was then injected into the GPC for analysis.

#### 3.5.4 Determination of the Thermal Properties of Poly(Styrene-*co*-Methyl Methacrylate)

The thermal properties of poly(styrene-*co*-methyl methacrylate) were measured by DSC operating at 25°C in a N<sub>2</sub> atmosphere of the NETZSCH DSC 200. A measuring method of dynamic heat flux, heating rate at 5°C/min, and temperature between 25°C to 500°C are used to determine the glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and decomposition temperature ( $T_d$ ).