

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Chemical, Equipment, and Glassware

##### 3.1.1 Chemicals

###### 3.1.1.1 Monomers

Styrene(St),  $C_6H_5CH:CH_2 = 104.15$ ,  
Wako Pure Chemical Industries Co., Ltd.

Methyl methacrylate(MMA),  
 $CH_2:CCH_3COOCH_3=100.12$   
Wako Pure Chemical Industries Co., Ltd.

###### 3.1.1.2 Matrix Polymer

Poly(methyl vinyl ether)(PMVE) 50% in methanol,  
 $(CH_3OCH:CH_2)_n$ ,  $\bar{M}_w=46,000$ ,  $\bar{M}_n=16,000$   
Tokyo Chemical Industry Co., Ltd.

###### 3.1.1.3 Initiator

$\alpha, \alpha'$ -Azobis-iso-butyronitrile(AIBN),  
 $NC(CH_3)_2CN:NC(CH_3)_2CN = 164.22$   
Wako Pure Chemical Industries Co., Ltd.

###### 3.1.1.4 Solvents

Ethanol 99%,  $CH_3CH_2OH=46.07$   
Japan Ethanol Industry.  
Methanol,  $CH_3OH=32.04$ ,  
Wako Pure Chemical Industries Co., Ltd.

Hexane,  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3=86.18$ ,  
Wako Pure Chemical Industries Co., Ltd.  
Chloroform,  $\text{CHCl}_3=119.38$ ,  
Wako Pure Chemical Industries Co., Ltd.

### 3.1.1.5 Other Chemicals

Magnesium sulfate( $\text{MgSO}_4$ ),  
Calcium oxide( $\text{CaO}$ ),  
Drynap(Na min 8 wt.%, Pb 90 wt.%),  
Hydroquinone( $\text{C}_6\text{H}_4(\text{OH})_2$ ),  
Sodium hydroxide( $\text{NaOH}$ ),  
Conc. sulfuric acid( $\text{H}_2\text{SO}_4$ ).  
All were from Wako Chemical Industries Co., Ltd.

## 3.1.2 Equipment and Glassware

### 3.1.2.1 Equipment

Gel Permeation Chromatography (GPC)  
Shimadzu (CTO-10A)  
Scanning Electron Microscopy (SEM) Hitachi (S430)  
Elemental Analysis (EA) Perkin-Elmer (2400II, 240C)  
Differential Scanning Calorimeter (DSC)  
Seiko (DSC200-SSC5000)  
X-ray Photoelectron Spectroscopy (XPS)  
VG (ESCALAB Mk II), 260 watts  
Nuclear Magnetic Resonance Spectroscopy (NMR)  
JEOL (JNM-GX270), 270 MHz  
Fourier-Transform Infrared Spectroscopy (FT-IR)  
JEOL (JIR-RFX3001)  
Thermal Gravimetry/Differential Thermal Analysis  
(TG/DTA) Seiko (TG/DTA200-SSC5000)

### 3.1.2.2 Glassware

Two-necked flask, 200 ml	1	unit
Spiral condenser	1	unit
Calcium chloride tube	1	unit
Nitrogen gas tube	1	unit
Centrifugal tube, 100 ml	4	units
Glass filter holder, dia 47 mm	1	unit

## 3.2 Procedure

### 3.2.1 Preparation

#### 3.2.1.1 Purification of St and MMA Monomers

a) Removal of the inhibitor: The inhibitor was removed by washing the 200 ml of the monomer with 10% aqueous NaOH. Roughly equal parts of the basic solution and the monomer were placed in a separatory funnel and mixed by tumbling. The heavier aqueous phase was then drained off. The procedure was repeated once or twice until the aqueous phase remained clear. The monomer was then washed with distilled water until the litmus paper showed that all the base had been removed.

b) Drying of the cleaned monomer: 20 g of  $MgSO_4$ , a drying agent, was added to the above monomer and left the solution overnight.

c) Distillation of the monomer: 0.2 g of hydroquinone was added to the dried monomer and the monomer was distilled under the  $N_2$  atmosphere at 20 mmHg for St(b.p. 45-46°C) and 100 mmHg for MMA(b.p. 40-41°C)

### 3.2.1.2 Preparation of the Solvents, Matrix Polymer and Initiator

#### a) ethanol

1 l of ethanol (b.p. 78°C) was refluxed with 250 g of the freshly ignited CaO for 6 hr. It was left overnight and was then distilled with precaution to exclude the retained moisture.

#### b) n-hexane

1 l of n-hexane (b.p. 69°C) was washed with 500 ml of conc. H<sub>2</sub>SO<sub>4</sub> for 4-5 times, followed by washing with the distilled water until all the acid had been removed. The solvent was washed with 500 ml of 10% aqueous NaOH for 4-5 times. It was then washed with the distilled water until all the base had also been removed. It was refluxed overnight with 30 g of drynap (Na min. 8 wt%, Pb 90 wt%) and was distilled with precaution to exclude the retained moisture.

#### c) the matrix polymer

PMVE available from the manufactory is in the solution of methanol, so methanol should be eliminated first. The retaining methanol solvent can be removed from the PMVE matrix polymer by keeping in a reduced pressure desiccator at 10-20 mmHg for 2 days and it was then dried in a vacuum oven for 1 night.

#### d) AIBN initiator

A saturated solution of AIBN in methanol was refrigerated in a refrigerator without disturbance. The crystals of the AIBN were collected on a fritted-glass filter.

## 3.2.2 Synthesis of Poly(styrene-co-methyl methacrylate)

### 3.2.2.1 Solution Copolymerization

1) 5 g of the mixed monomers at various St/MMA feed ratios as shown in Table 3.1 was added into 30 g of the mixed solvent(ethanol:n-

hexane=80:20 by wt%) in the presence of 0.05 g AIBN initiator. It was refluxed for 18 hr at 55°C in an oil bath (oil bath temperature was 60°C) under the N<sub>2</sub> atmosphere. As the reaction progressed, the polymers were then precipitated.

Table 3.1 Feed ratio of St/MMA (mole %) in solution copolymerization (mixed solvent: 80 wt% EtOH)

No.	1s	2s	3s	4s	5s	6s	7s
% St	0	25	38	50	62	75	100

2) 100-150 ml of methanol was added to terminate the reaction, rinsed with methanol and the solid was then collected by filtering with a membrane filter having a pore size of 0.2  $\mu\text{m}$ .

3) The copolymer was dried in a vacuum oven at 50°C for 10-12 hr.

### 3.2.2.2 Bulk Copolymerization

1) 0.0125 g of AIBN together with 25 g of the monomers at various St/MMA feed ratios as shown in Table 3.2 was stirred under the N<sub>2</sub> atmosphere at 55°C in the oil bath (oil bath temperature was 60°C) for 18 hr.

Table 3.2 Feed ratio of St/MMA (mole %) in bulk copolymerization (mixed solvent: 80 wt% EtOH)

No.	1b	2b	3b	4b	5b	6b	7b
% St	0	25	38	50	62	75	100

2) After the reaction had been finished, 80-100 ml of chloroform was added to the viscous mass in order to reduce the product viscosity. Then the product was reprecipitated in 700 ml of methanol.

3) The precipitated product was collected by filtering on a glass filter and rinsed with methanol. It was then dried by the same method of the solution copolymerization.

### 3.2.2.3 Dispersion Copolymerization

1) 3 g of PMVE as matrix polymer was dissolved along with 5 g of St-MMA monomer mixture, then it was added into 30.0 g of the mixed solvent containing 0.05 g of AIBN initiator. The concentrations of the mixed monomer and mixed solvent were shown in Tables 3.3 and 3.4.

Table 3.3 Feed ratio of St/MMA (mole %) in dispersion copolymerization (mixed solvent: 80 wt% EtOH)

No.	1ds	2ds	3ds	4ds	5ds	6ds	7ds
%St	0	25	38	50	62	75	100

Table 3.4 Mixed solvent ratio of ethanol: n-hexane(weight %) (monomer feed content: 25 mole% styrene)

No.	1de	2de	3de	4de	5de	6de	7de
%EtOH	0	20	35	50	65	80	100

Dispersion polymerization was carried out in a 200-ml, two-necked flask, equipped with a spiral condenser.

2) The reaction flask was immersed in a constant-temperature oil bath at 60°C (reaction temperature was 55°C), refluxed under the N<sub>2</sub> atmosphere for 18 hr. As the reaction progressed, the polymers were then precipitated.

3) 100-150 ml of methanol was added to terminate the reaction, then the solid was washed repeatedly with methanol by a decantation method using a centrifugal separator.

4) The solid was collected by filtering with a membrane filter having a pore size of 0.2 μm.

5) The solid was dried by the same method of the solution copolymerization.

### 3.2.2.4 Effect of the Dispersion Copolymerization Temperature

The copolymerization reaction was repeated by varying the temperatures of the reaction mixture as shown in Table 3.5 for 75 mole% styrene feed and 80 wt% ethanol of the mixed solvent.

Table 3.5 The constant reaction mixture temperature (monomer feed content: 75 mole% St, mixed solvent content: 80 wt% EtOH)

No.	1dt	2dt	3dt	4dt
Reaction temp (°C)	40	50	64	73

Note: The temperatures of the oil bath were 40, 50, 70 and 80°C, respectively.

## 3.3 Characterization

### 3.3.1 Determination of Average-molecular Weights

The GPC solution was prepared by dissolving 2 mg of the polymer into 2 ml of tetrahydrofuran (THF), the solution was agitated and then filtered with a 1  $\mu\text{m}$  microfilter.

Average molecular weights were calculated by using a GPC (Shimadzu CTO-10A) operating at 40°C with the columns in the THF solvent. The columns, which have the theoretical plates more than 10,000 were packed with poly(styrene-co-divinylbenzene). The flow rate was regulated at 1.0 ml/min. Both the UV and RI detectors were used.

### 3.3.2 Determination of the Polymer Particle Size

The particle size was measured by using an SEM(model S430; Hitachi). Specimens were prepared by placing the purified polymer powder on a aluminium

stub which was mounted with the double-faced adhesive tape, then it was coated under vacuum with a thin layer of gold. On an average, the diameters of 100 random polymer particles on the SEM micrograph were measured by either the method of multiplication of the measured particle size and the magnification power in each sample; or the direct size measurement of each particle on the micrograph in comparison with the scale of length shown by the microscopic magnification. The latter is more frequently used. The standard deviation of the mean was also calculated.

### 3.3.3 Determination of $T_g$ and $T_d$ of the Polymer

Measurements of  $T_g$  and  $T_d$  were made by using a DSC (DSC 200; SEIKO) and TG/TDA (TG/DTA 200; SEIKO). Ca. 10 mg of the sample was placed in the aluminium pan that was put on the sensor at room temperature along with an empty pan to assist output balance. Then they were rapidly heated at a rate of 10°C/min to the required temperatures (400°C of DSC and 500°C of TG/DTA).

### 3.3.4 Determination of Copolymer Composition

The FT-IR, model JIR-RFX 3001 was used to characterize the functional groups of the copolymer by the KBr pellet method.

The NMR, model JNM-GX270 of Jeol and the EA, model 2400II-240C of Perkin-Elmer were used to measure and calculate the copolymer composition. Detailed methods of the measurements were described in Appendixes C and D.

### 3.3.5 Determination of Surface Properties

The surface properties of the copolymers were determined by using a XPS (VG (ESCALAB Mk II), 260 watts). Samples were prepared by mounting the polymer powder on the sample holders of 10 nm in diameter. The photoelectrons were collected from a central area of 4\*7 mm<sup>2</sup> at 5-8\* 10<sup>-10</sup> Torr.