



Chapter III

Experimental

3.1 General Information

3.1.1 Instruments

- Infrared Spectrophotometer; Perkin Elmer-781, U.S.A.
- Fourier Transform ^1H NMR Spectrometer; Jeol FX 90 Q, Japan.
- Mass Spectrometer; Jeol DX-300, Japan.
- High Performance Liquid Chromatography; Shimadzu LC-3A, Japan.
- Elemental Analyzer; Perkin Elmer, Model Perkin Elmer 240 analyzer.
- Melting Point; BUCHI 510, Germany.
- Gas Liquid Chromatography; Shimadzu GC-9A, Japan.
- Vacuum Oven (Isotemp); Fisher Model 281, U.S.A.
- Refrigerated Bath; RB-12
- High Vacuum Pump; Javac-JD60, Australia
- Differential Thermal Analyzer; Shimadzu Thermal Analysis Instrument DT-30, Japan.

3.1.2 Chemicals and Solvents

2-Phenylethyl bromide	FLUKA AG, purum
Carbon disulfide	MERCK
Anhydrous zinc chloride	FLUKA AG, purum
Paraformaldehyde	MERCK
Conc. sulfuric acid	MERCK
Conc. hydrochloric acid	MERCK
Anhydrous sodium sulfate	FLUKA AG, purum
Sodium carbonate	FLUKA AG, purum
Petroleum ether (bp. 40-60 °C)	MERCK
Sodium metal	
Tert- butyl alcohol	FLUKA AG, PURISS
Potassium tert.-butoxide	FLUKA AG, PURUM
P-tert.-Butylcatechol	FLUKA AG, PURUM
Diethyl ether	BDH
Azobis(isobutyronitrile) (AIBN)	
Benzene	MERCK
Methanol	MERCK
Toluene	MERCK
Dimethylsulfoxide (DMSO)	FLUKA AG, PURISS
P-dioxane	BDH
Acetone	MERCK
Ethanol	
Methylene chloride	MERCK
Benzyl triethyl ammonium chloride	FLUKA AG, PURUM
Trimethyl sulfonium iodide	FLUKA AG
Sodium hydroxide	MERCK
Chloroform	MERCK

Benzyl alcohol	MERCK
N-propanol	MERCK
Potassium iodide	BDH
Bromophenol blue Indicator	
Potassium bromide	BDH
Styrene monomer	FLUKA AG
Silicone oil	
Dry ice	
Nitrogen gas	
Anion exchange resin, DOWEX SBR-P	



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

3.2 Purification of Solvents and Chemicals

3.2.1 Azobis(isobutyronitrile)

AIBN was dissolved in anhydrous methanol and heated below 60 °C, then filtered. The filtrate was allowed to cool in the refrigerator and the white crystals recovered. After two more recrystallizations, the crystals were dried under reduced pressure in a desiccator at room temperature for 2 days. The purified initiator was stored in a dark room to avoid photoinitiation.

3.2.2 Benzene

Benzene was dried over calcium chloride for 1 week, then it was distilled at 80 °C.

3.2.3 Anhydrous methanol

Methanol was dried over Lindas type 4A molecular sieve for 2 days. It was fractionally distilled before use.

3.2.4 Styrene monomer

Styrene monomer was washed with aq. 5% NaOH to remove inhibitor then with water. It was dried for several hours with $MgSO_4$ and stored over Lindas type 5A molecular sieve. It was fractionally distilled before use.

3.2.5 Other solvents

Petroleum ether, tert-butyl alcohol, diethyl ether, toluene, dimethyl sulfoxide, acetone, ethanol, methylene chloride, chloroform, benzyl alcohol, and n-propanol were distilled before use.

3.3 Experimentals

3.3.1 Synthesis of p-Chloromethylstyrene [36]

3.3.1.1 Chloromethylation of 2-Phenylethyl bromide

A 111g (0.6 mole) of 2-phenylethyl bromide was dissolved in 50 ml of carbon disulfide in a 500 ml three-necked round-bottomed flask equipped with a stirrer, gas inlet tube, and a reflux condenser. Anhydrous zinc chloride as a catalyst (12.5 g) and paraformaldehyde (15 g) were added to the flask in three separate portions during the course of reaction. Hydrogen chloride was bubbled into the reaction mixture with rapid stirring for 20 hrs. at 35 - 40°C (Figure 3.1). After the reaction, the lower phase of the reaction mixture was dissolved in water. The organic phase was washed with water, dilute sodium carbonate, and again with water. After being dried with anhydrous sodium sulfate, the carbon disulfide was distilled from the product, and the unreacted 2-phenylethyl bromide was recovered by distillation at a pressure of about 10 torr.

The product, a mixture of ortho- and para-(2-bromoethyl) benzyl chloride was obtained by distillation, bp. 90-94°C at 2 torr. The mixture was dissolved in 100 ml of petroleum ether and

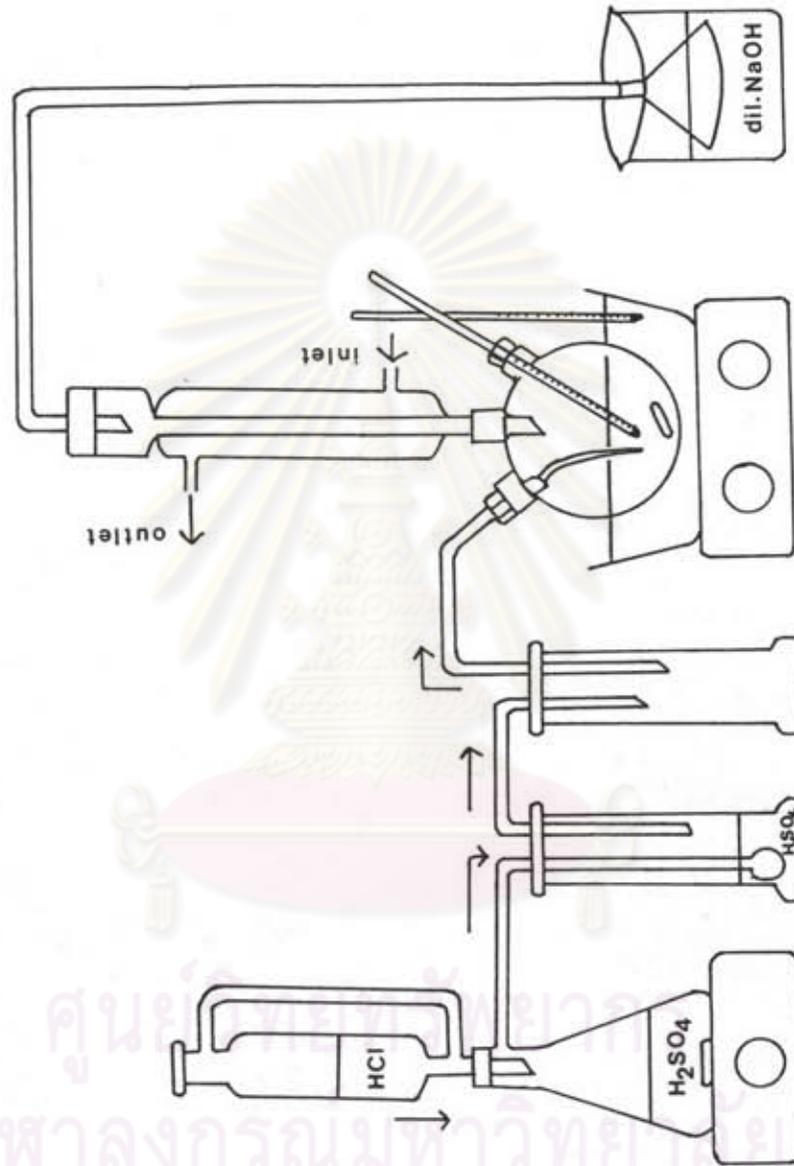


Fig.3.1 The apparatus for chloromethylation of 2-phenylethyl bromide

the solution was chilled overnight in a refrigerator. The remaining liquid was decanted, and solid obtained was recrystallized 4 times from 200 ml of petroleum ether. The yield was 48%, mp 50-51°C. (literature [36]: 51%, mp 48-50°C)

IR (KBr): ν (cm^{-1}), 3040, 2970, 1930, 1810, 1695, 1270, 1220, 850, 690-600, and 630.

^1H NMR (CDCl_3) : δ (ppm), 3.15 (t, J = 6.6, 2H)

3.55 (t, J = 7.1, 2H)

4.57 (s, 2H)

7.24 (d, J = 8.1, 2H)

7.38 (d, J = 8.4, 2H)

^{13}C NMR (CDCl_3) : δ (ppm), 32.67, 38.84, 45.94, 128.72, 128.94, 136.03, and 139.07

Mass spectrum : (m/e), 232 (M^+), 197, 153, 139, and 117 (base peak).

3.3.1.2 Dehydrobromination of p-(2-Bromoethyl)benzyl chloride to p-Chloromethylstyrene.

A 9.2 g (0.4 mole) portion of sodium metal was carefully added to 350 ml of tert-butyl alcohol at 50°C. After all the metal reacted, the solution was cooled to room temperature, and 93.4 g (0.4 mole) of p-(2-bromoethyl) benzyl chloride was added to a solution. The mixture was stirred at 35°C for 2 hrs. Then the reaction mixture was poured into 3 liters of water and extracted with ether. The extract was dried with anhydrous sodium sulfate. The ether was removed under reduced pressure and the residue was distilled in the presence of p-tert-butylcatechol (or cuprous chloride) as an inhibitor to give 47.3g (77.8%) of p-chloromethylstyrene bp 92°C at 2 torr.

IR(KBr): ν (cm^{-1}), 3090, 1920, 1830, 1630, 1515, 1450, 1410,
1270, 915, 830, 690

$^1\text{H NMR}$ (CDCl_3): δ (ppm), 7.34 (s, 4H)
6.70 (d.d, $J_{cb} = 17.6$, $J_{ca} = 10.8$, 1H)
5.73 (d.d, $J_{cb} = 17.6$, 1H)
5.25 (d.d, $J_{ca} = 10.98$, 1H)
4.54 (s, 2H)

3.3.2 Synthesis of Poly(p-chloromethylstyrene) and Its Copolymers with Styrene Monomer

3.3.2.1 Homopolymerization of p-Chloromethylstyrene

28.3 g of p-chloromethylstyrene was dissolved in 60 g of benzene in a three-necked round bottomed flask. 0.09 g of AIBN, an initiator, was then added. The solution was purged with nitrogen gas for 30 min, then polymerization was carried out under nitrogen atmosphere at 60°C for 7 hrs, with stirring rate of 75 rpm. After the reaction, the solution was poured into a large amount of methanol to precipitate the polymer. The resulting polymer was then purified by recrystallization of its benzene solution with excess methanol 3 times. The obtained product had \bar{M}_w 180,050 and, T_g 116.44°C .

IR (film): ν (cm^{-1}), 3040, 2940, 1920, 1800, 1610, 1515, 1450,
1430, 1270, 830, 840, 680

$^1\text{H NMR}$ (CDCl_3): δ (ppm), 7.08, 6.50, 4.53, 1.56, 1.43

Elemental analysis found: C=71.18%, H=6.24%, Cl=22.48%

3.3.2.2 Copolymerization of p-Chloromethylstyrene with Styrene Monomer.

The certain amount of p-chloromethylstyrene and styrene was dissolved in benzene in a three-necked round bottomed flask, and AIBN was added. The solution was purged with nitrogen gas for 30 minutes, then the polymerization was carried out under nitrogen atmosphere at 60 °C for 7 hrs, with stirring rate of 75 rpm. The amount of both concentrate monomers was varied as shown in Table 3.1. After the reaction, the solution was poured into a large amount of absolute methanol to precipitate the polymer. The resulting polymers were then purified by redissolving in benzene and reprecipitation from absolute methanol at least 3 times.

Table 3.1 Polymerization data for p-chloromethylstyrene and styrene

Copolymer (batch)	* CMST (mole)	** STY (mole)	Benzene (solvent) (g)	Weight of product (g)
a	0.022	0.29	68	4.401
b	0.064	0.256	73	5.293
c	0.13	0.19	80	6.120
d	0.11	0.05	44	4.336
e	0.14	0.02	50	5.278

* p - Chloromethylstyrene monomer

** Styrene monomer

The products were white powder obtained with T_g , \bar{M}_w , and elemental analysis as exhibited in Table 3.2

Table 3.2 Some physical properties and elemental analysis of poly(p-chloromethylstyrene-co-styrene)

Copolymer (batch)	\bar{M}_w	T_g (°C)	Elemental analysis		
			C (%)	H (%)	Cl (%)
a	50,120	110.50	89.26	7.38	3.21
b	99,650	110.64	84.09	7.40	8.52
c	110,200	112.24	79.46	6.62	14.00
d	119,855	112.93	74.04	6.57	19.38
e	177,675	113.37	73.19	6.39	21.32

The IR and NMR spectra of all the products were recorded. They were similar to each other and showed significant signals as follows:

IR (film) : ν (cm^{-1}), 3040, 2940, 1920, 1800, 1610, 1515, 1425, 1450, 1270, 830 - 840, 680.

^1H NMR (CDCl_3) : δ (ppm), 7.05, 6.50, 4.50, 1.54, and 1.42.

3.3.3 Carboxylation of Poly(p-chloromethylstyrene) and their Copolymers, Poly(p-chloromethylstyrene-co-styrene)

3.3.3.1 Carboxylation of Poly(p-chloromethylstyrene)

A 6.0 g of poly(p-chloromethylstyrene) was stirred in 120 ml of dimethylsulfoxide with 2.54 g. of sodium bicarbonate at 155 °C for 6 hrs. The resin was then collected on a glass filter, washed with dimethylsulfoxide, hot water, and a 2:1 mixture of dioxane and water, then rinsed with dioxane, acetone, ethanol, methylene chloride, and benzene. The cream - coloured product.

was obtained after drying at 100°C under vacuum. The yield was 44.8 %. The chlorine content in the product was determined by modified Volhard method. It was found to have the chlorine content of 0.0155 mmole/1g.polymer.

3.3.3.2 Carboxylation of Poly(p-chloromethylstyrene-co-styrene)

Carboxylation of copolymers was carried out by the same manner as mentioned in section 3.4.3.1. The quantities of reactant polymers and reagents had shown in Table 3.3.

Table 3.3 Experimental data for carboxylation of poly(p-chloromethylstyrene-co-styrene)

Copolymer (batch)	* $\text{P}-\text{CH}_2-\text{Cl}$ (g)	NaHCO_3 (g)	DMSO (ml)	% yield
a	3.6	1.76	100	77.78
b	2.5	1.2	70	54.80
c	5.0	2.1	120	78.60
d	5.0	2.3	120	76.00
e	3.6	1.8	100	68.33

* poly(p-chloromethylstyrene-co-styrene)

The IR spectra of all the products were recorded. They were similar to each other and showed significant signals as following:

IR (KBr) : ν (cm^{-1}) 3020, 2980, 2900, 1910, 1800, 1705, 1610, 1580, 1515 and 825.

The chloride content in the products were investigated by the same method as mentioned in section 3.4.3.1. It was found to have the chlorine contents of 0.0098, 0.0139, 0.0144, 0.0145, and 0.0140 mmole/1g.polymer for batch a, b, c, d, and e, respectively.

3.3.4 Epoxidation of Poly(p-carboxaldehydestyrene) and their Copolymers, Poly(p-carboxaldehydestyrene-co-styrene)

3.3.4.1 Epoxidation of Poly(p-carboxaldehydestyrene)

In an ice bath, 45 ml of an aqueous solution of sodium hydroxide was slowly added into 90 ml of dichloromethane solution containing 2.5 g of poly(p-carboxaldehydestyrene), 0.7 g of benzyltriethyl ammonium chloride and 2.02 g trimethyl sulfonium chloride*. After the complete addition, the solution mixture was brought to room temperature and continued stirring for 12 hours. The polymer was then collected and washed with water, methanol and ether. After drying at 70 °C under reduced pressure, the product showed : \bar{M}_w 157,903 , T_g 141.2 °C , epoxidation content 2.6864 mmole/1g.polymer. For the method to determine the epoxidation content, please see section 3.6.1.3.

* preparation from trimethylsulfonium iodide (see section 3.7).

3.3.4.2 Epoxidation of Poly(p-carboxaldehyde-styrene-co-styrene)

Epoxidation of poly(p-chloromethylstyrene-co-styrene) was carried out by the same condition as for homopolymer. The quantities of reactant polymers and reagents used in epoxidation were varied as shown in Table 3.4. IR spectra of each product were recorded which were similar to each other.

IR (KBr: ν) (cm^{-1}), 3020, 2920, 2850, 1940, 1800, 1600, 1510, 1450, 1270, 1050, 880

Table 3.4 Experimental data for epoxidation of poly(p-carboxaldehydestyrene-co-styrene)

Copolymer (batch)	* $\text{P}-\text{CHO}$ (g)	$(\text{CH}_3)_3\text{SCl}^+\text{Cl}^-$ (g)	$\phi-\text{CH}_2(\text{C}_2\text{H}_5)_3\text{NH}_4^+\text{Cl}^-$ (g)	CH_2Cl_2 (ml)	50% NaOH (ml)
a	2.5	2.030	0.7	90	45
b	1.2	0.990	0.3	40	20
c	3.5	3.155	0.9	140	70
d	3.5	3.155	0.9	140	70
e	2.3	1.972	0.6	90	45

T_g , \bar{M}_w and epoxidation content of products were determined and the results were exhibited in Table 3.5

Table 3.5 Some results of poly(p-epoxystyrene-co-styrene)

Copolymer (batch)	\bar{M}_w (approximately)	T_g ($^{\circ}\text{C}$)	Epoxidation content. (% conversion)
a	43,955	108.5	80.55
b	87,393	125.5	80.10
c	96,645	138.3	68.20
d	105,112	142.5	50.10
e	155,820	142.6	44.57

3.4 Test for some properties of a resist

3.4.1 Spin Coating

10% w/v solution of a desired resist was dropped on Indium tin oxide wafer which fixedly held on a bowl of spin coater. A speed of wafer rotating was 7000 rpm for 30 seconds. After the spin time was complete, the thickness coated wafer was around 10000 \AA . It was sent to softbake at the temperature of 70 $^{\circ}\text{C}$ in the oven, for 3 hours.

3.4.2 Irradiation

After complete softbaking, the coated wafer was connected under a mask, then it was irradiated under UV light, wavelength of 365 nm, 2-5 mJ/cm^2 , for 2-3 seconds.

3.4.3 Development

After complete irradiation, placing the irradiated substrate in a bath of made-up solution under the trade name "OMR Negative Developer" and agitating it gently in order to move away the dissolving resist was performed.

3.5 Characterization of Monomers and Polymers.

3.5.1 Infrared (IR) Measurement.

Infrared (IR) spectra of monomers and polymers were recorded by using Perkin - Elmer Infrared Spectrophotometer model 780. The liquid monomers were recorded as neat samples by using NaCl cell. The polymers powder were examined by using KBr method, while some polymers could be cast as films, then directly examined.

3.5.2 Nuclear Magnetic Resonance (NMR) Measurement

The ^1H NMR and ^{13}C NMR spectra of monomers and polymers were taken by using Fourier Transform NMR spectrometer, Jeol, model JNX-FX 90 Q. The samples were dissolved in CDCl_3 or any suitable solvents to make the solution of 5 % concentration.

3.5.3 Differential Thermal Analysis (DTA)

DTA thermograms of polymers were obtained over the temperature range of 40 - 400 °C with heating rate of 10 °C/min,

the N_2 (g) flow rate of 30 ml/min and the sensitivity of 10 V were selected. The weight of specimens used was mg. The reliable glass transition (T_g) of polymers were obtained.

3.5.4 High Performance Liquid Chromatography (HPLC)

Calibration curve of Standard polymers, molecular weight range 580 - 2,250,000, was obtained by using HPLC, Shimadzu LC - 3A. With the following condition ;

Column : Linear ultrastyrigel (GPC)
 Mobile phase : Toluene
 Detector : Reflective Index Detector (RID)
 Temperature : Room temp
 Flow rate : 1 ml / min
 Pressure : 42 kg / cm²
 Attenuation : 2 mV / full scale
 Injection volume : 50 uL

Standard polymers and samples were dissolved in toluene as 0.05 % w/v solution. The suitable average molecular weight was obtained.

3.5.5 Gas Liquid Chromatography (GC)

The purity of p-(2-bromoethyl)benzyl chloride was examined, it was pure or not by using Gas Liquid Chromatography, Shimadzu GC-9A. Sample was dissolved in carbon disulfide as 10 % w/v solution. A chromatogram was obtained, under the following condition;

Column : Chromatopac C - R3A (capillary)
 Column temp. : 180 °C
 Injection temp. : 275 °C
 Flow rate : 40 ml/min

3.6 Analysis of Polymer Composition

3.6.1 Determination of Chloride in Polymers

To determine a chloride content of polymer could be carried out in two ways. i.e, modified Volhard method and elemental analysis.

3.6.1.1 Chloride Analysis by a Modified Volhard Method

Around 200 mg of the chloromethylated polymer was accurately weighed in a test tube and heated with pyridine (3ml) for 2 hrs. at 100 °C. Contents were quantitatively transferred into a 125 ml Erlenmeyer flask with 50 % acetic acid (30 ml) and concentrated nitric acid (5 ml) was then added. The mixture was stirred for 30 minutes. Ferric alum indicator (3 drops) and standard AgNO_3 solution (20 ml, 0.05 N) were then added with stirring. The side of Erlenmeyer flask was washed with minimal amount of distilled water, and toluene (10 ml) was added. The solution was titrated with standard NH_4SCN solution. The solution became a permanent tinge of red - brown at the end point.

3.6.1.2 Determination of Chloride by Elemental Analysis

The element content of polymer in the sample could be examined by using Elemental Analyzer, Perkin Elmer 240 using the following condition; combustion temp. 950 °C, reduction temp. 650 °C, helium pressure 18.5 psi. and oxygen pressure 17.5 psi. The suitable elemental percentage contents were obtained.

3.6.2 Determination of Epoxide Content by Modified Iodometric Method

Around 1 g of sample was weighed into Erlenmeyer flask, and 25 ml of benzyl alcohol together with 25 ml of n-propanol were added. Then 10 drops of bromophenol blue as an indicator and 3 g of KI in 5 g of water were performed. The solution was stirred to make it well mixing. Titration was carried out with 1N HCl, the blue solution became yellow at the end point.

3.7 Preparation of Trimethylsulfonium Chloride by Ion Exchange

To prepare a well-packed column (diameter of 3 cm, length of 60 cm), a supply of an ion exchange resin of narrow size (50-100 mesh), DOWEX SBR-P (size of 50-100 mesh, 60 g), was desirable.

5.0 g of trimethylsulfonium iodide was dissolved in 5 ml distilled water, then the solution was gently poured into a well-packed column. The solution was allowed to elute from the column at the rate of about 2 ml per minute. After complete anion exchange, the obtained solution was dried under reduced pressure evaporation.