

## Chapter III

### Experimental



### 3.1 General Information

#### 3.1.1 Instruments

- Infrared Spectrophotometer ; Perkin Elmer - 1430, USA.
- FT NMR Spectrometer ; Bruker ACF-200
- Mass Spectrometer ; Jeol DX-300, Japan
- Gel Permeable Chromatograph ; Waters 600e, USA.
- Differential Scanning Calorimeter ; Du Pont Instruments DSC 910s, USA.
- Elemental Analyzer ; Perkin Elmer, Model Perkin-Elmer 240 Analyzer, USA.
- Gas Liquid Chromatograph ; Shimadzu Model GC-14A, Japan
- Mechanical Stirrer ; JANKE & KUNKEL Model IKA - Labortechnik RE 16
- Vacuum Oven (Isotemp) ; Fisher Model 281, USA.
- Refrigerated Bath ; RB-12
- High Vacuum Pump ; Jovac - JD60, Australia.
- Rotary Evaporator ; Heidolph Model VV 2000

3.1.2 Chemicals and Solvents

- 2-Phenylethyl bromide	Aldrich
- Anhydrous zinc chloride	Fluka AG, purum
- Paraformaldehyde	Merck
- Carbon disulfide	Merck
- Conc. sulfuric acid	J.T. Baker
- Conc. hydrochloric acid	Mallinkrodt
- Anhydrous sodium sulfate	Carlo Erba
- Sodium carbonate	FluKa AG, purum
- Petroleum ether (b.p. range 35-60°C)	J.T. Baker
- Potassium <i>tert</i> -butoxide	FluKa AG, purum
- <i>Tert</i> -butyl alcohol	Carlo Erba
- Diethyl ether	J.T. Baker
- Cyclohexane	Carlo Erba
- Azobis(isobutyronitrile) (AIBN)	Nacalai Tesque
- Benzene	J.T. Baker
- Toluene	J.T. Baker
- Methanol	Merck
- Dimethylsulfoxide (DMSO)	Carlo Erba
- 1,4-Dioxane	Carlo Erba
- Acetone	Merck
- Ethanol	Carlo Erba
- Methylene chloride	Carlo Erba
- Benzyltriethylammonium chloride	Fluka AG, purum
- Trimethylsulfonium iodide	Fluka AG
- Sodium hydroxide	J.T. Baker

- Chloroform	Merck
- Benzyl alcohol	Carlo Erba
- <i>n</i> -Propyl alcohol	Merck
- Potassium iodide	BDH
- Bromophenol blue indicator	M&B
- Potassium bromide	BDH
- Styrene monomer	Fluka AG.
- Cuprous chloride	M&B
- Aniline	Riedel - de Haen
- Sodium hydrogencarbonate	Merck
- Sodium acetate anhydrous	Fluka AG, purum
- Maleic anhydride	Fluka AG, purum
- Acetic anhydride	
- Silicone oil	
- Anion exchange resin, DOWEX SBR-P	
- Dry ice	
- Nitrogen gas	

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## 3.2 Purification of Solvents and Chemicals

### 3.2.1 Styrene monomer

Styrene monomer was washed with 5 % NaOH solution to remove inhibitor and then with water. It was dried for several hours with  $\text{MgSO}_4$  and stored over Lindas type 5 A molecular sieves. It was fractionally distilled before use.

### 3.2.1 Acetic anhydride

Acetic anhydride was purified by azeotropic distillation with toluene. The acetic acid - toluene azeotrope boiled at  $100.6^\circ\text{C}$ . After a removal of the remaining toluene, the acetic anhydride was distilled at  $137.8 - 138.0^\circ\text{C}$ .

### 3.2.3 Azobis (isobutyronitrile) (AIBN)

AIBN was dissolved in anhydrous methanol and heated below  $60^\circ\text{C}$ , then filtered. The filtrate was allowed to cool in the refrigerator and the white crystals were recovered. After two recrystallizations, the crystals were dried over reduced pressure in a desiccator at room temperature for two days. The purified initiator was stored in the dark room to avoid photoinitiation.

#### 3.2.4 Benzene

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

#### 3.2.5 Anhydrous methanol

Methanol was dried over Linda type 4 A molecular sieves for two days. It was distilled before use.

#### 3.2.6 Aniline

Aniline was dried with KOH and distilled at reduced pressure (b.p. 65 °C/8 mm.Hg). A treatment with stannous chloride removed sulfur-containing impurities.

#### 3.2.7 Other solvents

Acetone, ethanol, methylene chloride, chloroform, benzyl alcohol, *n*-propyl alcohol, ether, dimethyl sulfoxide, 1,4-dioxane, cyclohexane, petroleum ether and *tert*-butyl alcohol were distilled before use.

### 3.3 Synthesis

#### 3.3.1 Synthesis of N-phenylmaleimide [48]

##### 3.3.1.1 Synthesis of maleanilic acid

Into a 1 l. three necked flask equipped with a stirrer, a reflux condenser and a dropping funnel were placed 39.2 g. (0.4 mole) of maleic anhydride and 500 ml. of diethyl ether. The stirrer was started and after all the maleic anhydride was dissolved, a solution of 36.4 ml. (37.2 g., 0.4 mole) of aniline in 40 ml. of ether was added. The resulting thick suspension was stirred at room temperature for 1 hour and was then cool to 15-20 °C in an ice bath to yield the desired products. The product was filtered by suction filtration. It was a fine, cream-colored powder, m.p. 202.5-205 °C. It was used in the next step without purification. The yield was 72.66 g. (95.6 %).

IR (KBr):  $\nu(\text{cm}^{-1})$ : 3200 - 2500, 3272, 3210, 3072, 1700, 1634, 1534, 1447, and 850

##### 3.3.1.2 Conversion of maleanilic acid to N-phenylmaleimide.

Into a 500 ml. Erlenmayer flask were placed 150 ml. of acetic anhydride and 14.6 g. of anhydrous sodium acetate. The maleanilic acid (71.0 g.) was added, and the resulting suspension swirled and heated on a water bath for 30 minutes.

The reaction mixture was cooled until slightly warmer than room temperature and poured into 300 ml. of ice water. The precipitated product was recovered by suction filtration, washed three times with 150 ml. portions of cold water and with 150 ml. of petroleum ether (b.p. 30-60 °C), and dried. The yield of crude N-phenylmaleimide was 50.10 g. (77.5 %), m.p. 89.0-90.5 °C. A recrystallization from cyclohexane gave canary-yellow needles, m.p. 89.0-90.0 °C.

IR (KBr):  $\nu(\text{cm}^{-1})$ , 3040, 1979, 1896, 1711, 1596, 1508, 1456, 1395, and 832

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta(\text{ppm})$ : 6.81 (s, 2H)  
7.43 (s, 5H)

Mass spectrum : (m/e) : 174.1( $\text{M}^+$ , base peak), 146.1 and 129.1

### 3.3.2 Synthesis of p-chloromethylstyrene [43]

#### 3.3.2.1 Chloromethylation of 2-phenylethyl bromide

111 g (0.6 mole) of 2-phenylethyl bromide was dissolved in 50 ml. of carbon disulfide in a 500 ml. three-necked round bottom flask equipped with a stirrer, gas inlet tube and a flux 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 the reaction. Hydrogen chloride was bubbled into the reaction mixture

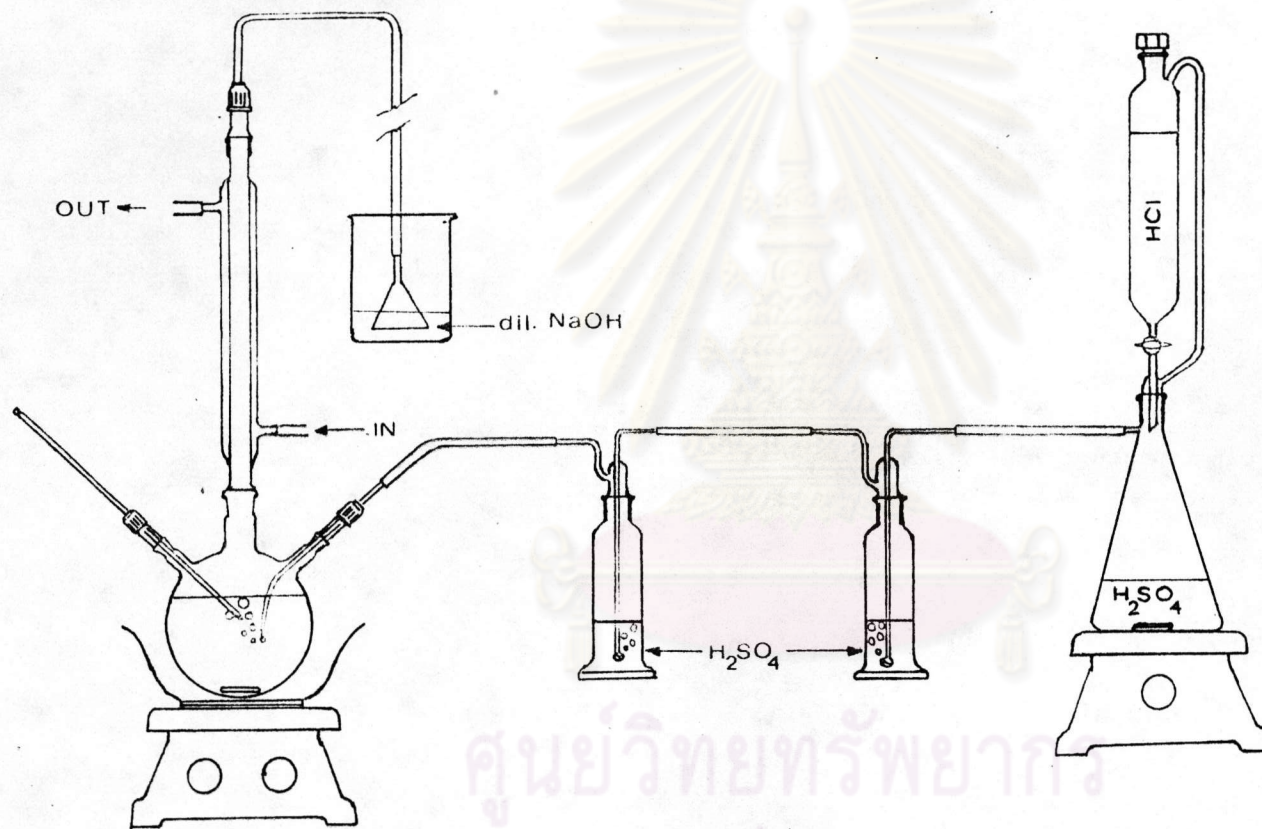


Figure 3.1 The apparatus for chloromethylation of 2-bromophenylethyl bromide.



with rapid stirring for 20 hrs. at 35 - 40 °C (Figure 3.1). After the reaction completed, the lower phase of the reaction mixture was dissolved in water. The organic phase was washed with water, dilute sodium carbonate solution, and again with water. After being dried with anhydrous sodium sulfate, carbon disulfide was removed from the product by distillation and the unreacted 2-phenylethyl bromide was recovered by distillation at the pressure of about 10 torr.

The product, a mixture of *ortho*- and *para*-(2-bromoethyl) benzyl chloride was obtained by distillation, b.p. 90-94 °C at 2 torr. The mixture was dissolved in 100 ml of petroleum ether and the solution was chilled overnight in a refrigerator. The remaining liquid was decanted and the solid obtained was recrystallized 4 times in 200 ml of petroleum ether. The yield was 49%, m.p. 50-51 °C. (literature [43]: 51%, m.p. 48-50 °C)

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

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (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)

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$  (ppm), 32.67, 38.84, 45.94, 128.72, 128.94,  
136.03, and 139.07

Mass spectrum : (m/e), 232( $\text{M}^+$ ), 197, 153, 139, and 117 (base peak)

### 3.3.2.2 Dehydrobromination of *p*-(2-bromoethyl) benzyl chloride to *p*-chloromethylstyrene.

A 33.6 g. (0.3 mole) of potassium *tert*-butoxide was dissolved in 150 ml of *tert*-butyl alcohol at 50 °C. After all potassium *tert*-butoxide dissolved, the solution was cooled to room temperature and 68.65 g. (0.3 mole) of *p*-(2-bromoethyl) benzyl chloride was added to the 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 cuprous chloride as an inhibitor to give 34.6 g. (75.62 % yield) of *p*-chloromethylstyrene, b.p. 92 °C at 2 torr.

IR(KBr) :  $\nu$  ( $\text{cm}^{-1}$ ), 3090, 1920, 1830, 1630, 1515, 1450, 1410,  
1270, 915, 830, and 690

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$  (ppm), 4.54 (s, 2H)  
5.25 (dd,  $J_{ca} = 10.98$ , 1H)  
5.73 (dd,  $J_{cb} = 17.6$ , 1H)  
6.70 (dd,  $J_{cb} = 17.6$ ,  $J_{ca} = 10.8$ , 1H)  
7.34 (s, 4H)

3.3.3. Synthesis of poly (*p*-chloromethylstyrene-co-styrene) and poly(*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide).



3.3.3.1 Copolymerization of *p*-chloromethylstyrene and styrene.

11.6 g. of *p*-chloromethyl styrene and 8.0 g. of styrene were dissolved in 35 ml. of benzene in a three-necked round bottom flask and 0.3 g. of AIBN was added. The solution was purged with nitrogen gas for 30 minutes. The polymerization was carried out under nitrogen atmosphere at 60 °C for 7 hrs. with stirring rate of 75 rpm. After the reaction, the solution completed was poured into a large amount of methanol to precipitate the polymer. The resulting polymers were then purified by recrystallization from its benzene solution with 3-folds excess of methanol. The obtained product, 10.94 g., had Mw 32,995 and Tg 94.75 °C.

IR(film) ;  $\nu(\text{cm}^{-1})$ , 3040, 2940, 1920, 1800, 1610, 1515, 1450,  
1450, 1270, 880-840, and 680

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ) :  $\delta$ (ppm.), 7.05, 6.50, 4.50, 1.54, and 1.42

Elemental analysis calcd : % C = 79.58, % H = 6.63, % N = 0.00

% Cl = 13.79

found : % C = 77.28, % H = 6.76, % N = 0.31

% Cl = 16.05

3.3.3.2. Copolymerization of *p*-chloromethylstyrene, styrene and N-phenylmaleimide.

Certain amount of *p*-chloromethylstyrene, styrene and N-phenylmaleimide were dissolved in benzene in a three-necked round bottom 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 styrene and N-phenylmaleimide were varied as shown in Table 3.1. After the reaction completed, the solution was poured into a large amount of absolute methanol to precipitate the aimed polymer. The resulting polymer were then purified by redissolving in benzene and reprecipitating from absolute methanol, at least 3 times.

Table 3.1 Polymerization data for *p*-chloromethylstyrene, styrene and N-phenylmaleimide.

Copolymer (batch)	AIBN		CMST*		ST**		NPhMI***		Weight of product (g)
	g.	%mole	g.	%mole	g.	%mole	g.	%mole	
b	0.30	1.2	11.60	49.4	7.13	44.5	1.32	4.9	10.66
c	0.30	1.2	11.60	49.4	6.34	39.5	2.64	9.9	10.90
d	0.30	1.2	11.60	49.4	3.97	24.8	6.58	24.6	9.89
e	0.30	1.2	11.65	49.5	0	0	13.2	49.3	11.13

\* *p*-chloromethylstyrene monomer

\*\* styrene monomer

\*\*\* N-phenylmaleimide monomer

The products were determined for  $M_w$ ,  $T_g$  and elemental analysis as exhibited in Table 3.2

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

Copolymer (batch)	$M_w$	$T_g$ ( $^{\circ}C$ )	Elemental analysis			
			C(%)	H(%)	N(%)	Cl(%)
b	49,326	101.49	77.64	6.59	1.19	14.46
c	87,324	102.51	76.58	6.45	1.78	12.94
d	143,302	135.69	72.22	5.47	2.71	10.37
e	148,590	181.40	62.97	4.63	3.77	10.10

The IR and  $^1H$  NMR spectra of all the products were recorded. They were similar to each other and showed significant signals as follows :

IR (KBr) :  $\nu$ ( $cm^{-1}$ ), 3055, 3024, 2919, 2848, 1710, 1599, 1494,  
1450, 1378, 1265, 1181, 825, 755, and 700

3.3.4 Carboxylation of poly(*p*-chloromethylstyrene-co-styrene) and poly(*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide).

3.3.4.1 Carboxylation of poly(*p*-chloromethylstyrene-co-styrene).

A 6.00 g. of poly(*p*-chloromethylstyrene-co-styrene) was stirred in 145 ml. of dimethylsulfoxide with 3.00 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 2:1 mixture of 1,4-dioxane and water then subsequently rinsed with 1,4-dioxane, acetone, ethanol, methylene chloride and benzene. The resulting product was dried under vacuum. The yield was 72.2 %. The chloride content in the resulting product was determined by modified Volhard method. It was found to have a chlorine content of 0.0874 mole/ 1g. polymer.

IR (KBr) :  $\nu(\text{cm}^{-1})$ , 3020, 2980, 2900, 1910, 1800, 1705, 1610, 1580, 1515, and 825

3.3.4.2 Carboxylation of poly(*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide).

A carboxylation of poly(*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide) was carried out by the same manner as mentioned in section 3.3.4.1. The quantities of the reactant polymers and reagents are shown in Table 3.3.

Table 3.3 Experimental data for carboxylation of poly (*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide).

Copolymer (batch)	* $\text{P}-\text{CH}_2\text{Cl}$ (g.)	$\text{NaHCO}_3$ (g.)	DMSO (mL.)	% yield
b	6.00	3.00	145	44.4
c	6.00	3.00	145	49.8
d	6.00	3.00	145	48.3
e	6.00	3.00	145	42.4

\* $\text{P}-\text{CH}_2\text{Cl}$  : poly(*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide)

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

IR (KBr) :  $\nu(\text{cm}^{-1})$ , 3054, 3024, 2915, 2848, 2724, 1701, 1603, 1493, 1450, 1387, 1211, 1168, 1015, 826, 759, and 700

The chloride content in the resulting polymers were investigated by the same method as mentioned in section 3.5.1.1. It was found to have chloride contents of 0.0642, 0.0736, 0.4526

and 0.4317 mmole/ 1g. polymer for batch b, c, d and e , respectively.

3.3.5 Epoxidation of poly(*p*-carboxaldehydestyrene-co-styrene) and poly(*p*-carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide)

3.3.5.1 Epoxidation of poly(*p*-carboxaldehydestyrene-co-styrene)

In the ice bath, 20 ml. of 50% sodium hydroxide was slowly added into 50 ml. of methylene chloride solution containing 1.01 g. of poly(*p*-carboxaldehydestyrene-co-styrene), 0.25 g. of benzyltriethyl ammonium chloride and 0.83 g. of trimethylsulfonium chloride\*. After the complete addition, the solution mixture was brought to room temperature and continued stirring for 12 hrs. The resulting polymer was then collected and washed with water, methanol and ether. After drying at 70 °C under reduced pressure, the product showed :  $T_g$  102.7 °C and epoxide content 3.0574 mmole/ 1g. polymer. The method for determining the epoxide content could be seen in section 3.5.2.

IR (KBr) :  $\nu(\text{cm}^{-1})$ , 3020, 2920, 2850, 1940, 1800, 1600, 1510, 1450, 1270, 1050, and 880

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\* Trimethylsulfonium chloride was prepared from trimethylsulfonium iodide (see section 3.6)



3.3.5.2 Epoxidation of poly(*p*-carboxaldehyde-styrene-co-styrene-co-N-phenylmaleimide).

Epoxidation of poly(*p*-carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide) was carried out by the same method as mentioned in section 3.3.5.1. The amounts of the reactant polymers and reagents are shown in Table 3.4. IR spectra of all products were recorded and were similar to each other.

IR (KBr) :  $\nu(\text{cm}^{-1})$ , 3069, 2930, 1706, 1595, 1563, 1496, 1444, 1393, 1314, 1078, 1020, 839, 759, and 696

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

Copolymer (batch)	* $\text{P}-\text{CO}-\text{H}$ (g.)	$(\text{CH}_3)_3\text{S}^+\text{Cl}^-$ (g.)	$\phi-\text{CH}_2(\text{C}_2\text{H}_5)_3\text{N}^+\text{Cl}^-$ (g.)	$\text{CH}_2\text{Cl}_2$ (ml.)	50%NaOH (ml.)
b	1.01	0.83	0.25	50.0	20.0
c	1.57	1.30	0.39	78.5	31.5
d	1.13	0.94	0.28	56.5	22.5
e	1.16	0.94	0.29	58.0	23.0

\*  $\text{P}-\text{CO}-\text{H}$  : poly(*p*-carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide)

$T_g$  and epoxide contents of the products were determined and the results are exhibited in Table 3.5.

Table 3.5 Some resulting  $T_g$  and epoxide contents of poly-(*p*-epoxystyrene-co-styrene-co-N-phenylmaleimide).

Copolymer (batch)	$T_g$ (°C)	Epoxide content (mmole/1 g.polymer)
b	111.8	3.0095
c	127.3	2.8053
d	148.5	1.7099
e	195.7	1.4824

### 3.4 Characterization of the monomers and the polymers.

#### 3.4.1 Infrared spectrum measurement

Infrared spectra of the monomers and the polymers were recorded by using Perkin - Elmer Infrared Spectrophotometer model 1430. The liquid monomers were recorded as neat samples by using NaCl cell. The polymer powders were examined as KBr pellet.

### 3.4.2 Nuclear magnetic resonance spectrum (NMR) measurement

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the monomers and the polymers were taken on Fourier Transform NMR Spectrometer, Model Bruker ACF-200. The samples were dissolved in  $\text{CDCl}_3$  or suitable solvents to make the solutions of 5% concentration.

### 3.4.3 Differential Scanning Calorimetry (DSC)

DSC thermograms of the polymers were obtained over a range of 30-450  $^{\circ}\text{C}$  with heating rate of 20  $^{\circ}\text{C}/\text{min.}$ , the  $\text{N}_2$  gas flow rate of 30 mL./min. and the sensitivity of 1 V was selected. The weight of the specimens used was milligrams. The reliable glass transition temperature ( $T_g$ ) of the polymers were obtained from the chromatograms.

### 3.4.4 Gel Permeation Chromatography (GPC)

A calibration curve of standard polymer (polystyrene), molecular weight range 2,980 - 8,420,000 was obtained by using GPC, Waters 600E with the following conditions;

Column : Linear Ultrastyrigel

Mobile Phase : Tetrahydrofuran (THF)

Detector : Reflexive Index Detector Model Water 410

Temperature : 45  $^{\circ}\text{C}$

Flow Rate : 1 mL./min.

Pressure : 168 Bar.

Attenuation : 1 V/full scale

Injection Volume : 100  $\mu$ L.

The standard polymers and sample solutions were prepared by dissolving in THF to have 0.15% w/v concentration. The suitable average molecular weights were obtained from the chromatograms.

### 3.5 Analysis of Polymers Composition

#### 3.5.1 Determination of chloride in the polymers.

The chloride content of the polymer could be determined by two methods i.e., modified Volhard and elemental analysis.

##### 3.5.1.1 Chloride analysis by a modified Volhard method.

200 mg. of the chloromethylated polymer was accurately weighed in a test tube and heated with pyridine (3 ml.) for 2 hrs. at 100 °C. The 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  $\text{AgNO}_3$  solution (20 ml., 0.05 M) were then added with stirring. The side of the erlenmeyer flask was washed with minimum amount of distilled water and 10 ml. of toluene was added. The solution was titrated with standard

$\text{NH}_4\text{SCN}$  solution. The solution became a permanent tinge of red-brown as an end point of the titration.

#### 3.5.1.2 Determination of chloride by elemental analysis.

The chloride contents of the polymer in the sample could be examined by using Elemental Analyzer, Perkin-Elmer 240 using helium pressure 18.5 psi., oxygen pressure 17.5 psi., combustion temperature of  $925^\circ\text{C}$  and reduction temperature of  $640^\circ\text{C}$ .

#### 3.5.2 Determination of epoxide content by modified iodometric method.

Around 1 g of sample was weighed in an erlenmayer flask, and 25 ml. of benzyl alcohol together with 25 ml. of n-propanol were added. 10 drops of bromophenol blues as an indicator and 3 g. of KI in 5 g. of water were placed into the flask. The solution was stirred. Titration was carried out with 0.1M HCl solution until the blue solution became yellow.

#### 3.6 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 used.

5.0 g. of trimethylsulfonium iodide was dissolved in 5 ml. distilled water, then the solution was gently introduced onto the well-packed column. The solution was allowed to elute from the column at the rate of about 2 ml./min.. The eluted solution was evaporated to dryness under reduced pressure.



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