

## CHAPTER III

## EXPERIMENTAL

## A) Apparatus and Instruments

Vacuum oven: TOWNSON & MERCER LTD. CROYDON, ENGLAND

Vacuum pump: EDWARDS HIGH VACUUM, CRAWLEY, ENGLAND

Liquid nitrogen dewars: TAYLOR-WHARTON, INDIANAPOLIS  
PLANT, USA

Viscosity Bath: GCA/PRECISION SCIENTIFIC, CHICAGO,  
ILLINOIS

Viscometer: CANNON A446, size 25,  $C_0 = 0.002090$  @40°

Eyela Cool Ace: TOKYO RIKAKIKAI CO., LTD.

Eyela Aspirator A-2S: TOKYO RIKAKIKAI CO., LTD.

IR-Spectrophotometer A-302: JASCO. JAPAN SPECTROSCOPIC  
CO., LTD.

UV-Spectrophotometer UV-240: SHIMADZU

$^1\text{H}$  NMR Spectrometer EM-360 60 MHz

$^1\text{H}$  NMR Spectrometer, Bruker WP-300 Fourier Transform

## B) Solvents, Reagents, Catalysts and Polymer

## 1) Solvents and Reagents

2-ethoxyethanol	FLUKA AG
benzene	MERCK
chloroform	MERCK

methanol	MERCK
dimethoxymethane	FLUKA AG, puriss
vinylbenzyl chloride	FLUKA AG, techn.
methacrylic acid (MA)	FLUKA AG, purum.
azobis(isobutyronitrile) (AIBN)	
1,1,2,2-tetrachloroethane	FLUKA AG, pract.
p-dioxane	BDH
tetrahydrofuran (THF)	FLUKA AG, purum.
N,N-dimethylformamide (DMF)	CarloErba, RPE
dimethylsulfoxide (DMSO)	BDH, LR
conc. nitric acid	MERCH
fuming nitric acid	MERCH
sodium bicarbonate	BDH, LR
sodium hydroxide	Eka Aktiebolag
stannic chloride	FLUKA AG, purum.
hydrochloric acid	Carlo Erba, RPE
ferrocenecarboxylic acid	ALDRICH
cesium hydroxide monohydrate	FLUKA AG, pract.
anhydrous sodium acetate	FLUKA AG, puriss.
phosphorus oxychloride	FLUKA AG, purum.
2,6-di- <u>tert</u> -butyl-p-cresol	FLUKA AG, purum.
phenothiazine	FLUKA AG, purum.
ferrous ammonium sulfate	FLUKA AG, puriss.
potassium thiocyanate	BDH, AR.
hydrogen peroxide, 30%	FLUKA AG, purum.
polysulfone resin	ALDRICH

2-nitrotoluene	FLUKA AG, purum.
toluene	FLUKA AG, purum.
benzophenone	FLUKA AG,
molecular sieve type 4A	FLUKA
magnesium turnings	BDH, LR
iodine resublimed	BDH, LR
potassium carbonate , anhydrous	FLUKA AG, purum.

## 2) Phase Trasfer Catalysts

tetrabutylammonium chloride	(TBAC)	FLUKA AG
tetrabutylphosphonium chloride	(TBPC)	FLUKA AG
dicyclohexyl 18-crown-6	(DCHC )	FLUKA AG
tetrabutylammonium hydrogen sulfate	(TBAS)	FLUKA AG
tetrabutylammonium bromide	(TBAB)	FLUKA AG
tetrabutylammonium iodide	(TBAI)	FLUKA AG

## C) Purification of Solvents and Chemicals

### 1) Solvents

#### 1.1) 1.1.2.2 Tetrachloroethane

This solvent was distilled (bp.142-146°C) and stored in the presence of molecular sieves (4A).

#### 1.2) Anhydrous methanol

Clean dried magnesium turnings(5g) and iodine (0.5g)

with 50-75 mL of absolute methanol were warmed in a flask until the iodine disappeared and all of the magnesium was converted to methoxide. Up to 1 L of methanol was added and, after refluxing for 2-3 h, it was distilled (bp. 64.5°C) and kept in the presence of molecular sieves (4A)

### 1.3) Dimethoxymethane

The chief impurity of dimethoxymethane is methanol, which can be removed by treatment with sodium wire, followed by fractional distillation from sodium wire (bp. 42.5°C). The solvent was kept dry by storing in contact with molecular sieves (4A).

### 1.4) N,N-dimethylformamide (DMF)

DMF decomposes slightly at its normal bp. to give small amounts of dimethylamine and carbon monoxide. The decomposition is catalyzed by acidic or basic material, so that even at room temperature DMF is appreciably decomposed if allowed to stand for several hours with solid KOH, NaOH or CaH<sub>2</sub>.

Use of Linda type 4A molecular sieves was selected, followed by distillation under reduced pressure (bp. 76°C/39 mmHg.).

### 1.5) Dimethylsulfoxide (DMSO)

The DMSO was dried by prolonged contact with Linda type 4A molecular sieves, then fractionally distilled under reduced pressure. (bp. 75.6°C/12 mmHg.)

1.6) Tetrahydrofuran (THF)

This solvent was refluxed with Na wire and benzophenone until the blue color was established; fractional distillation (bp. 65.5°C) followed.

1.7) Chloroform

The purification of chloroform involved washing it with distilled water to removed ethanol, drying with  $K_2CO_3$ , refluxing with  $P_2O_5$  and then distilling (bp. 61.2°C).

1.8) Benzene

The purification of benzene involved shaking first with conc.  $H_2SO_4$ , then with water, third with diluted NaOH, and again with water, followed by drying with anhydrous  $CaCl_2$  and Linda type 4A molecular sieves, and distillation.(bp. 80°C)

1.9) Concentrated nitric acid

High purity colourless nitric acid (approx.92%) was obtained by direct distillation of fuming nitric acid under reduced pressure (bp. 25-26°C/ 20 mmHg) and stored in a desiccator kept in a refrigerator.

1.10) p-Dioxane

This solvent was dried by contact with Na wire overnight, then fractionally distilled (bp. 101°C).

## 2) Monomers and radical initiator

### 2.1) Vinylbenzyl chloride (VBC)

The purification of VBC involved extracting VBC with 0.5% NaOH (to remove tert-butyl catechol and nitromethane) until a colorless extract was obtained. The extract was washed twice with water and dried overnight over anhydrous sodium sulfate in the presence of a small quantity of phenothiazine. Distillation of the monomer under reduced pressure yielded a colourless liquid (bp. 124-125°C/26 mmHg). The distillate was kept under N<sub>2</sub> atmosphere in the refrigerator and redistilled before use.

### 2.2) 2-Ethoxyethanol

2-Ethoxyethanol was purified by drying over anhydrous sodium sulfate, filtering and then fractional distillation (bp. 135°C).

### 2.3) Methacrylic acid (MA)

The purification of MA involved drying it overnight over anhydrous sodium sulfate in the presence of phenothiazine and 2,6-di-t-butyl-4-methylphenol as inhibitors, filtering it and then fractionally distilling it under reduced pressure to give a colorless liquid (bp. 83-84°C/20 mmHg). The distillate was stored under N<sub>2</sub> atmosphere in the refrigerator and redistilled before use.

## 2.4) Azobis(isobutyronitrile) (AIBN)

The purification of AIBN involved heating AIBN in methanol and then filtering. The filtrate was allowed to cool in the refrigerator and the white crystals recovered. After two more recrystallizations, the crystals were dried under the reduced pressure in a desiccator at room temperature for 2 days. The purified initiator was stored in a refrigerator in a bottle that was wrapped with aluminium foil to avoid photoinitiation.

### D) Preparation of Starting Materials

#### 1) Preparation of a monomer

##### 1.1) Preparation of 2-Ethoxyethyl Methacrylate

The procedure of Sittatrakul [23] was used with some modification. A 1-L round-bottom flask equipped with a Dean-Stark trap coupled to a water cooled condenser was charged with 84.4 mL (86.09g, 1.0 mol) of freshly purified methacrylic acid, 106.6 mL (99.13g, 1.1 mol) of purified 2-ethoxyethanol, 2.0g conc. sulfuric acid, 0.1g ( $4.5 \times 10^{-4}$  mol) of 2,6-di-tert-butyl-p-cresol, 0.1g ( $5.0 \times 10^{-4}$ ) of phenothiazine and 250 mL of purified benzene. The mixture was heated to reflux with an oil bath at 100°C for 12 h. The by-product, water, was removed during the refluxing period in a yield of about 18 mL. After cooling, the benzene solvent was removed by rotary evaporator. The residue was washed with

a 5% sodium bicarbonate solution until the wash was basic to litmus paper, then the residue was further washed with water. The organic extract was dried over anhydrous magnesium sulfate and distilled under reduced pressure to give 120 g of colorless product. (bp. 90°C/20 mmHg.).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.2 (t,  $J=7.0$  Hz, 3H, R-O- $\text{CH}_2\text{CH}_3$ ), 1.8 (s, 3H,  $\text{CH}_2\text{C}(\text{CH}_3)\text{-COO-R}$ ), 3.53 (q,  $J=7.0$  Hz, 2H, R-O- $\text{CH}_2\text{CH}_3$ ), 3.63 (t, 2H, R-O- $\text{CH}_2\text{CH}_2\text{-O-CH}_2\text{CH}_3$ ), 4.26 (t, 2H, R-O- $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ ), 5.55 (m, 1H,  $\text{H}-\text{C}(\text{CH}_3)=\text{COOR}$ ), 6.10 (m, 1H,  $\text{H}-\text{C}(\text{CH}_3)=\text{COOR}$ ). IR (neat): 2975, 2875(m,  $\nu\text{CH}_3$ ), 1720(s,  $\nu\text{C=O}$ ), 1640 (m,  $\nu\text{C=C}$ ), 1240, 1040(s,  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$ , C-O-C), 1160 and 1120  $\text{cm}^{-1}$ (s,b, C-O-C).

## 2) Preparation of polymers

### 2.1) Preparation of chloromethylated polysulfone: POLYMER 1

#### (i) Acetyl chloride

In a 500 mL round-bottom flask equipped with a reflux condenser was placed 260 g (3.17 mol) of anhydrous sodium acetate. The dropping funnel attached with a drying tube was charged with 156 mL (1.70 mol) of phosphorus oxychloride and the funnel was attached to the top of the condenser. The phosphorus oxychloride was allowed to run slowly onto sodium acetate with frequent shaking over a period of 30 min. The dropping funnel was removed and the drying tube was attached to the condenser. The reaction mixture was allowed to stand for 10-12 h, then it was distilled until



no more liquid came out. The distillate was redistilled to afford 94.9 g (38.1%) of a colorless liquid (bp. 52-53°C).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 2.7 (s,  $\text{CH}_3\text{COCl}$ ).

(ii) Preparation of Chloromethyl Methyl Ether-Methyl Acetate Mixture

The procedure of Amato et al [67] was used without modification. A 500 mL three necked round bottom flask equipped with thermometer, magnetic stirrer, and a rubber septum was charged with 110.2 mL (1.25 mol) molecular sieve-dried dimethoxymethane and 2.9 mL (0.07 mol) of anhydrous methanol. The solution was cooled to 0°C in an ice water bath. Then 86 mL (1.19 mol) of acetyl chloride was added by a syringe in three portions. During the addition the temperature rose from 0°C to 25°C. The reaction mixture was allowed to stir at room temperature for 36 h. The yield of the mixture is 184.0 mL.  $^1\text{H}$  NMR (reaction mixture): 3.5 (s,  $\text{ClCH}_2\text{OCH}_3$ ), 5.45 (s,  $\text{ClCH}_2\text{OCH}_3$ ), 4.5 (s,  $\text{CH}_3\text{OCH}_2\text{OCH}_3$  from unreacted  $\text{CH}_3\text{OCH}_2\text{OCH}_3$ ). The relative intensity of the peaks are consistent with a 6.1 M solution of chloromethyl methyl ether in methyl acetate.

(iii) Chloromethylation of Polysulfone

A 500 mL two-necked flask equipped with a water condenser, a magnetic stirrer, and a pressure equalizing dropping funnel, was charged with 146.6 mL (900 mmol) of chloro-

methyl methyl ether solution, 150 mL of 1,1,2,2 tetrachloroethane, and 0.52 mL (4.5 mmol) of stannic chloride. The mixture was stirred and heated to 100°C in an oil bath. While the solution was maintained at 100°C, a solution of 20.0 g (45 meq) of polysulfone in 252 mL of 1,1,2,2 tetrachloroethane was added slowly over a period of 15 min. The reaction mixture was stirred and maintained at 100°C for 6 h before the catalyst was deactivated by injecting 2 mL of methanol into the flask. Chloromethylated polysulfone was recovered by pouring the reaction mixture into a large excess of methanol with vigorous stirring. The polymer was filtered, washed with some methanol and dried in a vacuum desiccator for 24 h. The crude product was further purified by redissolving it in dioxane; the solution was then filtered and the filtrate was added dropwise in a large excess of methanol with vigorous stirring. The resin was then filtered and washed first with 40% aqueous dioxane, and then with 40% aqueous dioxane containing 10% conc. HCl, water, and methanol. After drying in a vacuum oven at 80°C for 48 h, it yielded 14.3 g of POLYMER 1 :  $[\eta] = 0.54$  dL/g in chloroform at 25°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.75 (s, methyl protons), 4.55 (s, Ar- $\text{CH}_2\text{Cl}$ ), 6.84-7.89 (Ar-H). IR (film): 3030 ( $\nu$  CH, aromatic), 2975 ( $\nu$  CH, aliphatic), 1580, 1485 ( $\nu$  C=C), 1325, 1295 ( $\nu$  O=S=O). Anal. Calcd. for  $(\text{C}_{28.6}\text{H}_{23.6}\text{O}_4\text{SCl}_{1.6})_n$  : C, 66.05; H, 4.57; S, 6.16; Cl, 10.91. Found: C, 66.06; H, 4.71; S, 5.82; Cl, 11.00.  $T_g = 164^\circ\text{C}$ .

## 2.2) Preparation of Poly(vinylbenzyl chloride):POLYMER 2

A 40 mL vacuum hydrolysis glass tube was charged with 10.0 mL (10.83 g, 70.9 mmol) of purified vinylbenzyl chloride, 0.105 g (0.63 mmol) of AIBN. The tube was equipped with an evacuation connector that was then connected to a three-way stopcock; the other two inlets of the stopcock were connected to a vacuum pump and a source of dry nitrogen. After the nitrogen gas was purged for about 5 min, the contents of the tube were frozen by immersing the tube in a liquid nitrogen bath; then the tube was evacuated and the monomer was thawed; then nitrogen was introduced, and the contents refrozen and reevacuated. The freeze-thaw degassing cycles were repeated three times before the tube was sealed under vacuum. The monomer was polymerized by heating the sealed tube in a preheated oil bath at 60°C for 3 h and by observing the bubbles of nitrogen generated from the decomposition of the initiator rise very slowly. The tube was removed from the oil bath and placed quickly in an ice water bath in order to stop the polymerization. The polymer was dissolved in chloroform and then added dropwise to a large excess of vigorously stirred methanol to precipitate the polymer. The product was collected by filtration and dried in a vacuum oven at 50°C for 24 h. The crude product was purified twice by redissolving it in chloroform, filtering it, and reprecipitating it in a large excess of methanol. After drying in a vacuum oven at 50°C for 24 h it afforded 7.0 g (66.7%) of

POLYMER 2.  $[\eta] = 0.51$  dL/g in chloroform at 25°C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.40-1.66 (bm, 3H,  $\text{OCHCH}_2$ ), 4.37 (bm, 2H,  $\text{Ar-CH}_2\text{Cl}$ ), 6.34-6.47 and 7.03-7.25 (two bm, 4H,  $\text{Ar-H}$ ). IR (film): 3010 (m,  $\nu\text{CH}$ , aromatic), 2920 (s,  $\nu\text{CH}$ , aliphatic), 1600, 1585, 1485, 1445 ( $\nu\text{C=C}$  phenyl), 1265 (s,  $\nu\text{CH}_2\text{Cl}$ ), 900, 830, 800, 710 (m, p substituted phenyl). Anal Calcd. for  $(\text{C}_9\text{H}_9\text{Cl})_n$ : C, 70.83; H, 5.94; Cl, 23.23. Found: C, 70.82; H, 5.95; Cl, 23.71.  $T_g = 66^\circ\text{C}$ .

2.3) Preparation of Poly(vinylbenzyl chloride-co-2-ethoxyethyl methacrylate):POLYMER 3

A 40 mL vacuum hydrolysis glass tube was charged with 8.0 mL (8.66 g, 56.6 mmol) of purified vinylbenzyl chloride, 12.6 mL (12.46 g, 78.7 mmol) of purified 2-ethoxyethyl methacrylate, and 0.211 g (1.28 mmol) of AIBN. After three freeze-thaw degassing cycles were completed, the tube was sealed under vacuum. The monomers were copolymerized by heating the sealed tube in a preheated oil bath at 60°C for 3 h and by observing the bubbles of nitrogen generated from the decomposition of the initiator rise very slowly. The tube was removed from the oil bath and placed immediately in an ice water bath in order to stop the polymerization. The polymer was dissolved in chloroform and then added dropwise to a large excess of vigorously stirred methanol to precipitate the polymer. The product was collected by filtration and dried in a vacuum oven at 50°C

for 24 h. The crude product was purified twice by redissolving it in chloroform, filtering it, and reprecipitating it in a large excess of methanol. After drying in a vacuum oven at 50°C for 24 h it afforded 10.4 g (49.2%) of POLYMER 3.  $[\eta] = 0.83$  dL/g in chloroform at 25°C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.14 (s, 3H,  $\text{RO-CH}_2\text{CH}_3$ ), 1.75(s, 3H,  $\text{RCH}_2\text{CR}''(\text{CH}_3)\text{COOR}'$ ), 3.37(4H,  $\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ ) 4.49(s, 2H,  $\text{Ar-CH}_2\text{Cl}$ ), 6.66-7.27(4H,  $\text{Ar-H}$ ). IR (film): 2975, 2875(m,  $\nu\text{CH}_3$ ), 1720(s,  $\nu\text{C=O}$ ), 1265(s,  $\nu\text{CH}_2\text{Cl}$ ), 1240, 1040 ( $-\text{C-O-C}-$ ). Anal Calcd. for  $(\text{C}_9\text{H}_9\text{Cl})_{0.51}(\text{C}_8\text{H}_{14}\text{O}_3)_{0.49}$ : C, 65.69; H, 7.46; Cl, 11.41. Found: C, 65.70; H, 7.32; Cl, 11.61.  $T_g = 28^\circ\text{C}$ .

### 3) Preparation of Cesium Ferrocenecarboxylate (CFC)

Into a 250-mL Erlenmeyer flask was placed ferrocenecarboxylic acid and a reagent grade tetrahydrofuran. The mixture was stirred under  $\text{N}_2$  atmosphere until all the ferrocenecarboxylic acid was dissolved. The solution was filtered and a saturated cesium hydroxide solution was added dropwise with vigorous stirring until a yellow-brown precipitate of cesium ferrocenecarboxylate was formed. The mixture was allowed to stir for 20-30 min more. The salt was collected by filtration under  $\text{N}_2$  atmosphere, then washed three times with THF and dried in a vacuum oven at room temperature for 3 days.

## E) Esterification Reaction of Chloromethylated Polymers with Cesium Ferrocenecarboxylate

### 1) General Procedure for the Esterification Reaction of POLYMER 1 with Cesium Ferrocenecarboxylate in a Liquid-Liquid Two-Phase System.

Into a 50-mL round-bottomed flask was placed 0.10g(0.3 meq) of POLYMER 1 dissolved in 5 mL of chloroform, 0.09g(0.3 mmol) of TBAC, and 0.16g(0.45 mmol) of cesium ferrocenecarboxylate dissolved in 0.5 mL of distilled water. The ratio of meqCl/CFC/TBAC is reported in Table 9-10. The flask was equipped with a water cooled condenser and heated with stirring at about 200 rpm under nitrogen in an oil bath at 60°C for 40 h. The contents of the flask were poured into a large excess of vigorously stirred methanol. The product was collected by filtration, washed twice with 15 mL of methanol, and dried in a vacuum oven at 40°C for 24 h. The crude product was purified twice by redissolving it in chloroform, filtering it, and reprecipitating it from a large excess of methanol. After drying in a vacuum oven at 40°C for 24 h, it afforded 0.12g(47.6%) of a purified yellow ester. The degree of esterification was found to be 99% (based on iron analysis).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$ 1.72 (s, methyl protons), 4.04, 4.32, 4.61 (proton on cyclopentadienyl rings), 5.18 (s, Ar- $\text{CH}_2\text{OOCR}$ ), 6.90-7.86 (Ar-H). IR (film): 3030 ( $\nu$  CH aromatic), 2975 ( $\nu$  CH aliphatic), 1580, 1485 ( $\nu$  C=C), 1325, 1295 ( $\nu$  O=S=O). Anal.

Calcd. for  $(C_{46}H_{37.9}O_{7.2}SCl_{0.01}Fe_{1.59})_n$ : C, 66.87; H, 4.62; Fe, 10.70. Found: C, 66.44 ; H, 4.73; Fe, 10.66.

## 2) General Procedure for the Esterification Reaction of POLYMER 1 with Cesium Ferrocenecarboxylate in a Solid-Liquid Two-Phase System.

Into a 50-mL round-bottom flask was placed 0.10g(0.3 meq) of POLYMER 1 dissolved in 5 mL of chloroform, 0.16g(0.45 mmol) of cesium ferrocenecarboxylate and 0.09g(0.3 mmol) of TBAC. The mole ratio of  $-CH_2Cl/CFC/TBAC$  is 1/1.5/1. The flask was equipped with a water cooled condenser and heated with stirring at about 200 rpm under nitrogen in an oil bath at 60°C for 40 h. The contents of the flask were poured into a large excess of vigorously stirred methanol. The product was collected by filtration, washed twice with 15 mL of methanol, and dried in a vacuum oven at 40°C for 24 h. The crude product was purified twice by redissolving it in chloroform, filtering it, and reprecipitating it from a large excess of methanol. After drying in a vacuum oven at 40°C for 24 h, it afforded 0.10g (38.9%) of a purified yellow ester. The degree of esterification was found to be 93% (based on iron analysis).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.72 (s, methyl protons), 4.04, 4.32, 4.61 (proton on cyclopentadienyl rings), 5.18 (s,  $Ar-CH_2OOCR$ ), 6.90-7.86 (Ar-H). IR (film): 3030 ( $\nu$ CH, aromatic), 2975 ( $\nu$ CH, aliphatic), 1580, 1485 ( $\nu$ C=C), 1325, 1295 ( $\nu$ O=S=O). Anal.

Calcd. for  $(C_{45}H_{37}O_7SCl_{0.1}Fe_{1.5})_n$ : C, 66.83; H, 4.61; Fe, 10.28.  
Found: C, 66.59; H, 5.18; Fe, 10.02.

**3) General Procedure for the Esterification Reaction of Poly(vinylbenzyl chloride): POLYMER 2 with Cesium Ferrocenecarboxylate in a Liquid-Liquid Two-Phase System.**

Into a 50-mL round-bottomed flask was placed 0.10g(0.66 meq) of POLYMER 2 dissolved in 5 mL of chloroform, 0.19g(0.66 mmol) of TBAC, and 0.36g(0.99 mmol) of cesium ferrocenecarboxylate dissolved in 0.5 mL of distilled water. The ratio of meqCl /CFC/TBAC used was 1/1.5/1. The flask was equipped with a water cooled condenser and heated with stirring at about 200 rpm under nitrogen in an oil bath at 60°C for 40 h. The contents of the flask were poured into a large excess of vigorously stirred methanol. The product was collected by filtration, washed twice with 15 mL of methanol, and dried in a vacuum oven at 50°C for 24 h. The crude product was purified twice by redissolving it in chloroform, filtering it, and reprecipitating it from a large excess of methanol. After drying in a vacuum oven at 50°C for 24 h, it afforded 0.15g(79.2%) of a purified brown ester. The degree of esterification was found to be 80% (based on iron analysis).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  1.29-1.59 (3H, ArCHCH<sub>2</sub>), 4.07, 4.36, 4.79 (proton on cyclopentadienyl rings), 4.36 (s, 2H, Ar-CH<sub>2</sub>Cl), 6.42 and 7.04 (4H, Ar-H). IR (film): 3000 (m,  $\nu$ CH, aromatic), 2930 (s,  $\nu$ CH, aliphatic), 1720 ( $\nu$ C=O),



1600, 1450 ( $\nu$ C=C phenyl), 1265 (s,  $\nu$ CH<sub>2</sub>Cl). Anal Calcd. for (C<sub>17.8</sub>H<sub>16.2</sub>O<sub>1.6</sub>Cl<sub>0.2</sub>Fe<sub>0.8</sub>)<sub>n</sub>: C, 69.39; H, 5.31; Fe, 14.53. Found: C, 68.87; H, 5.40; Fe, 12.90.

4) General Procedure for the Esterification Reaction of Poly(vinylbenzyl chloride-co-2-ethoxyethyl methacrylate): POLYMER 3 with Cesium Ferrocenecarboxylate in a Liquid-Liquid Two-Phase System.

Into a 50-mL round-bottomed flask was placed 0.10g(0.3 meq) of POLYMER 3 dissolved in 5 mL of chloroform, 0.10g(0.3 mmol) of TBAC, 0.18g(0.45 mmol) of cesium ferrocenecarboxylate dissolved in 0.5 mL of distilled water. The ratio of meqCl/CFC/TBAC used was 1/1.5/1. The flask was equipped with a water cooled condenser and heated with stirring at about 200 rpm under nitrogen in an oil bath at 60°C for 40 h. The contents of the flask were poured into a large excess of vigorously stirred methanol. The product was collected by filtration, washed twice with 15 mL of methanol, and dried in a vacuum oven at 50°C for 24 h. The crude product was purified twice by redissolving it in chloroform, filtering it, and reprecipitating it from a large excess of methanol. After drying in a vacuum oven at 50°C for 24 h, it afforded 0.06g(81.6%) of a purified brown ester. The degree of esterification was found to be 70% (based on iron analysis). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.12 (s, 3H, RO-CH<sub>2</sub>CH<sub>3</sub>), 1.64(s, 3H, RCH<sub>2</sub>CR'(CH<sub>3</sub>)COOR''), 3.44 (6H, R'OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>), 4.12, 4.39, 4.61

(proton on cyclopentadienyl rings), 4.39 (s, 2H, Ar-CH<sub>2</sub>Cl), 7.15(4H, Ar-H). IR (film): 3010(νCH<sub>3</sub>), 2930(s,νCH, aliphatic), 1710(νC=O), 1610, 1450(νC=C), 1270 (s,νCH<sub>2</sub>Cl), 1130(ν,C-O-C). Anal Calcd. for (C<sub>12.4</sub>H<sub>14.7</sub>O<sub>2.2</sub>Cl<sub>0.2</sub>Fe<sub>0.4</sub>)<sub>n</sub>: C, 66.53; H, 6.58; Fe, 8.88. Found: C, 66.22; H, 6.79; Fe, 8.84.

#### F) Determination of Iron in Ferrocenecarboxymethylated Polymers

The procedure of Rosenberg and Riber [68] was used with some modifications.

##### 1) Preparing a calibration curve for iron determination

Dried ferrous ammonium sulfate, 0.3511 g(0.89 mmol), was weighed and placed into a 1-L volumetric flask containing 10 mL dilute nitric acid(1:10%vol.), and 1 mL hydrogen peroxide solution (30%); distilled water was added to bring the volume up to 1 L. The standard solution contains 0.05 mg iron per mL. 1 to 5-mL aliquots of this standard solution were transferred to 50-mL volumetric flasks. To each volumetric flask was added 10 mL of distilled water, 5 mL diluted nitric acid, 3 drops hydrogen peroxide, and 10 mL of 10% potassium thiocyanate solution. Each solution was then brought up to 50 mL with distilled water. The optical densities of these solutions were measured with a spectrophotometer at 480 nm, using a 1-cm cell, and plotted against concentrations.

##### 2) Determination of iron

Into a 15-mL Kjeldahl flask was placed 3-8 mg of ferrocenecarboxylated polymer, two milliliters of concentrated nitric acid and three drops of hydrogen peroxide solution. A blank solution was prepared in another Kjeldahl flask. Both flasks were heated in an oil bath at about 90°C for 24 hours until a clear, colorless solution was obtained. Additional hydrogen peroxide solution was added to the cooled flask if necessary. After cooling, the contents from each flask were filtered and were transferred quantitatively into a 50-mL volumetric flask. Distilled water was added to bring the volume up to 50 mL. An aliquot of 10 mL solution was transferred to another 50-mL volumetric flask. To each volumetric flask was added 10 mL of distilled water, 2 mL of diluted nitric acid, 2 drops of hydrogen peroxide, and 10 mL of potassium thiocyanate solution. Each solution was then brought up to 50 mL with distilled water. The optical density of the sample solution was measured against the blank solution in a spectrophotometer at 480 nm, using a 1-cm cell. The iron content in polymer was obtained by comparing the measured optical density with the calibration curve.

#### G) General Procedure for the determination of the viscosity of polymer

50 mg of dried polymer were weighed into a 10-mL graduated flask on an analytical balance and dissolved in 5-6 mL purified chloroform. The solution was made up to the mark and

filtered through a sintered glass filter into a clean dry tube (solution 1: polymer concentration 5.00 g/L). 5 mL of this solution was pipetted into the Ostwald viscometer which was suspended vertically in a viscometer bath. After temperature equilibration, the time required for the solution to flow from mark M1 to mark M2 was measured. The average of three measurements was taken as the flow time ( $t$ ) of polymer solution. The flow time of solvent ( $t_0$ ) was determined in a similar manner. The other measurements at lower concentration were made by the dilution method. 5 mL of solution 1 were pipetted into a 10-mL volumetric flask and brought up to 10 mL with chloroform. The polymer solution was filtered as described above (solution 2: polymer concentration 2.50 g/L), then its flow time was measured. After the viscometer had been cleaned and dried, the measurements were repeated for polymer concentrations of 1.25 and 0.625 g/L obtained by successive dilution of solution 2. For each of the polymer solution studied, the specific viscosity ( $\eta_{sp}$ ) was calculated. To obtain  $[\eta]$  for the polymer, plot of  $\eta_{sp}/c$  versus  $c$  and linear extrapolation of the plot to  $c=0$  was performed.