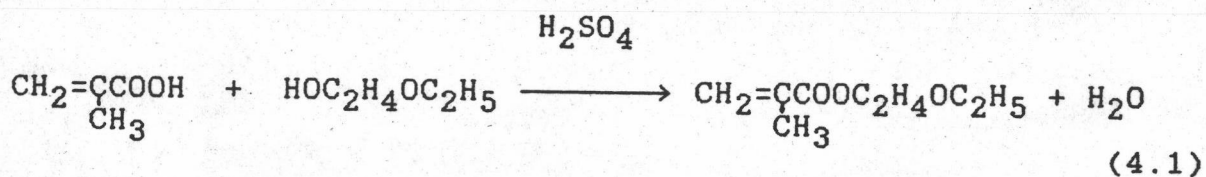# CHAPTER IV

RESULTS AND DISCUSSION

1) Preparation of a monomer

1.1) Preparation of 2-ethoxyethyl methacrylate

The method involved a condensation reaction between methacrylic acid and 2-ethoxyethanol in refluxing benzene under acidic conditions (concd. H_2SO_4) in the presence of phenothiazene and 2,6-di-tert-butyl-p-cresol as inhibitors.

$$CH_2=\underset{CH_3}{C}COOH \ + \ HOC_2H_4OC_2H_5 \ \xrightarrow{H_2SO_4} \ CH_2=\underset{CH_3}{C}COOC_2H_4OC_2H_5 \ + \ H_2O$$

$$(4.1)$$

The by-product, water, was removed as a binary azeotrope with benzene during the 12 h refluxing period. After benzene was removed, the residue was washed with sodium bicarbonate and then with water. The organic extract was dried over anhydrous magnesium sulfate and distilled under reduced pressure to give a colorless product (75% yield). ^{1}H NMR (CDCl$_3$) and IR (neat) spectra are shown in Fig.2 and 3.

2) Preparation of polymers

2.1) Preparation of chloromethylated polysulfone:POLYMER 1
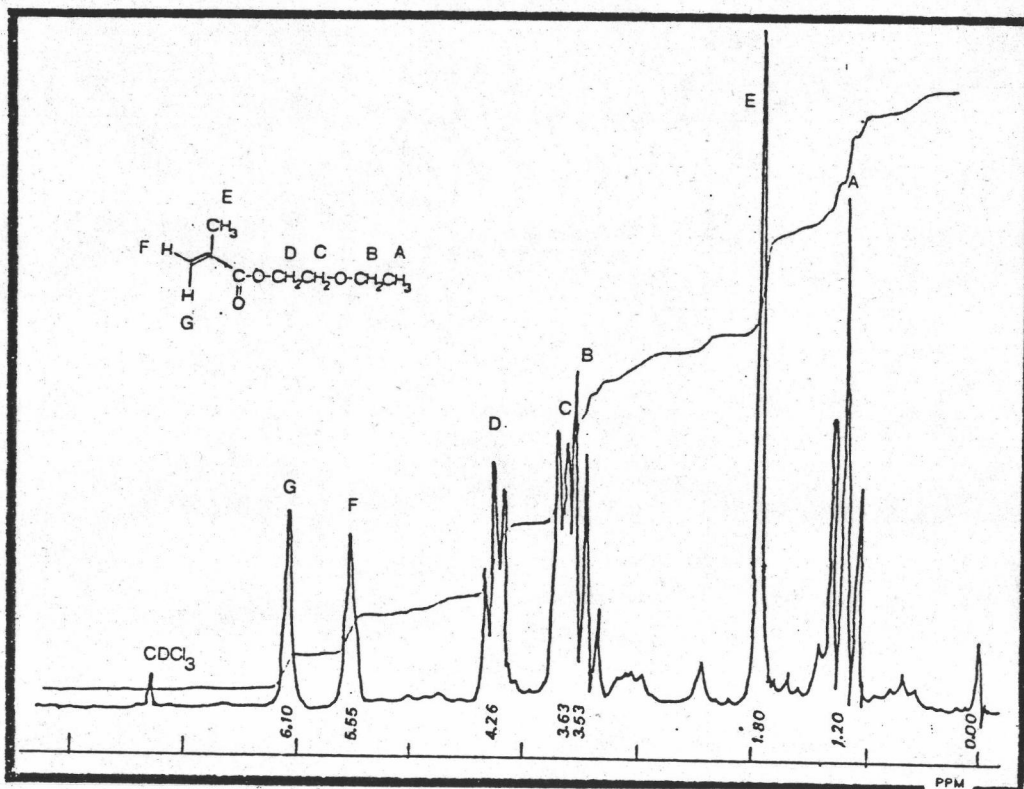
Polysulfones are a family of engineering thermoplastics

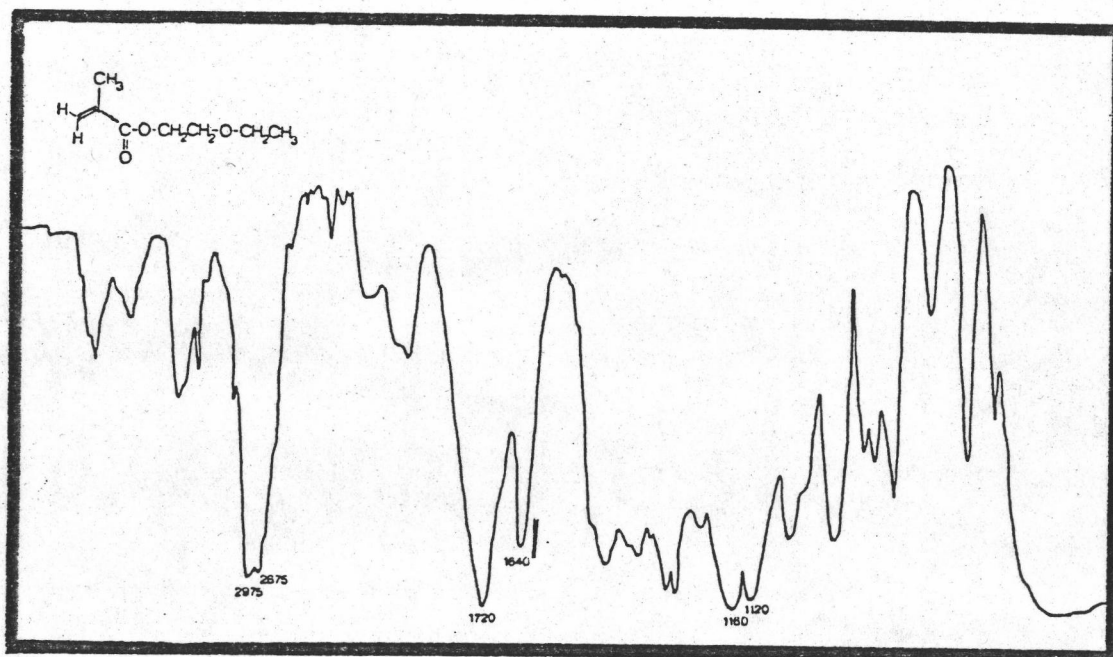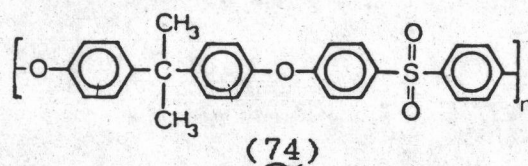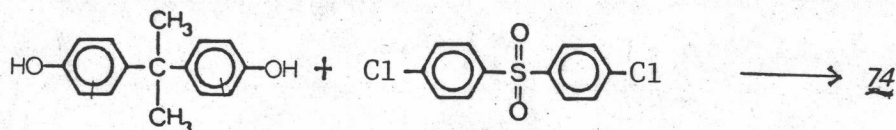Fig.2 ^{1}H NMR(CDCl$_3$) spectrum of 2-ethoxyethyl methacrylate

Fig.3 IR (neat) spectrum of 2-ethoxyethyl methacrylate

with excellent high-temperature properties. In 1965 Union Carbide introduced Udel polysulfone (<u>74</u>) in the US.

$$\left[O - \bigcirc - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \bigcirc - O - \bigcirc - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - \bigcirc \right]_n$$

(<u>74</u>)

$\overline{M}_w = 30,000$, d= 1.24 , $T_g = 190^{\circ}C$, $n_D^{20} = 1.633$

The udel polysulfone can be prepared by reacting 4,4-dichlorodiphenylsulfone with an alkali salt of bisphenol A in highly polar solvents, such as dimethylsulfoxide or sulfolane.

$$HO - \bigcirc - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \bigcirc - OH \; + \; Cl - \bigcirc - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - \bigcirc - Cl \; \longrightarrow \; \underline{74}$$

(4.2)

In this research, Udel (Union Carbide) Polysulfone was used as starting material. To modify this polymer, chloromethylation has been proved to be one of the most versatile and reliable routes to functionalized polysulfones. The chloromethylation process of polysulfone can be divided into three steps.

(i) Preparation of acetyl chloride

Synthesis of acetyl chloride involved the reaction of anhydrous sodium acetate and phosphorus oxychloride at room temperature.

$$3CH_3COONa \; + \; POCl_3 \; \longrightarrow \; 3CH_3COCl \; + \; Na_3PO_4 \qquad (4.3)$$
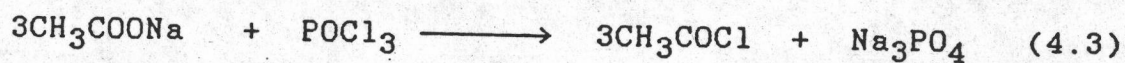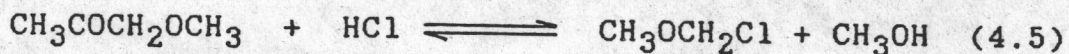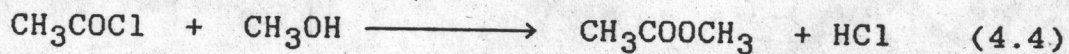
The two components were mixed in a round-bottom flask and the reaction mixture was allowed to stand for 12 h. After double distillation, the colorless product(bp. 51-52°C) was obtained in 38.1% yield.

It is important that all the apparatus must be perfectly dry, since acetyl chloride is decomposed by water. The set-up should be assembled in the hood.

(ii) Preparation of chloromethyl methyl ether-methyl acetate mixture

This preparation [67] involved the addition of acetyl chloride to a slight excess of anhydrous dimethoxymethane containing a catalytic amount(~ 6 mol%) of methanol at room temperature. Methanol triggers a series of reactions commencing with formation of hydrogen chloride (reaction 4.4), and hydrogen chloride reacts with dimethoxymethane to form chloromethyl methyl ether and methanol in an equilibrium process (reaction 4.5). The equilibrium is displaced to the right by reentry of methanol into reaction 4.4.

$$CH_3COCl \ + \ CH_3OH \longrightarrow CH_3COOCH_3 \ + \ HCl \qquad (4.4)$$
$$CH_3COCH_2OCH_3 \ + \ HCl \rightleftharpoons CH_3OCH_2Cl \ + \ CH_3OH \quad (4.5)$$

After 36 hours a near-quantitative conversion to an equimolar mixture of chloromethyl methyl ether and methyl acetate is obtained. The concentration of an NMR assay of this solution
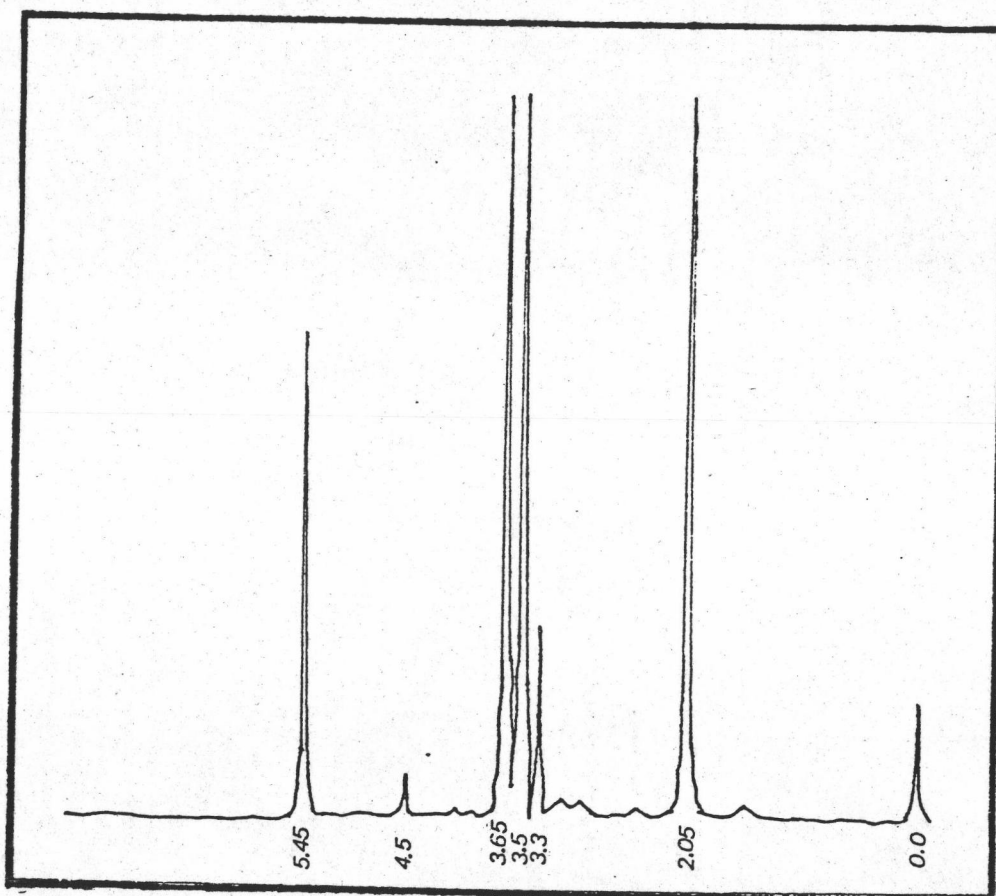
is 6.14 M (see Fig. 4 and Appendix A).
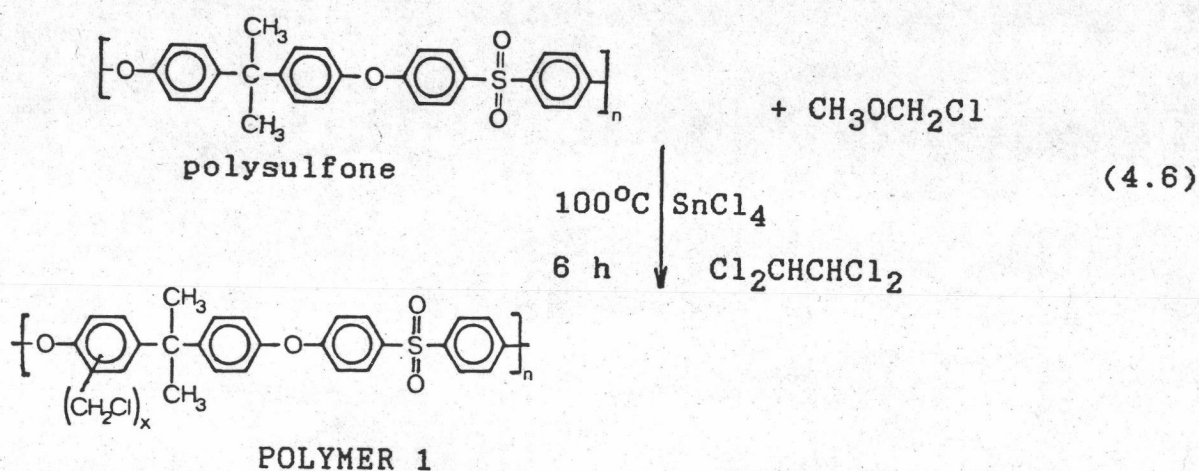

Fig.4 ^{1}H NMR(CDCl$_3$) spectrum of chloromethyl methyl
ether-methyl acetate mixture

Chloromethyl methyl ether is a suspected mild carcinogen.
For this reason, the preparation should be carried out in an
efficient hood.

(iii) Chloromethylation of polysulfone

The procedure of Sittatrakul [23] was used without modification. The mixture of polysulfone resin in sym-tetrachloroethane, chloromethyl methyl ether solution and a catalytic amount of stannic chloride was stirred at 100°C for 6 h before the catalyst was deactivated by methanol. This reaction can be represented as in equation (4.6).

$$\left[\ O-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\!\!\bigcirc\!\!-O-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\!\!\bigcirc\ \right]_n + CH_3OCH_2Cl$$

polysulfone

$$100°C \left|\ SnCl_4 \right.$$
$$6\ h \downarrow\ Cl_2CHCHCl_2$$

(4.6)

$$\left[\ O-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\!\!\bigcirc\!\!-O-\!\!\bigcirc\!\!-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\!\!\bigcirc\ \right]_n$$
$$(CH_2Cl)_x$$

POLYMER 1

The POLYMER 1 was recovered and purified as process described in the experimental section. The objective of washing the polymer product with dioxane solution is to eliminate stannic chloride as mentioned by Sittatrakul [23]. ^{1}H NMR(CDCl$_3$), and IR(film) spectra are shown in Fig.5 and 6. From elemental analysis data, the degree of substitution (DS) is 1.62 (see Appendix B).

2.2) Preparation of poly(vinylbenzyl chloride):POLYMER 2

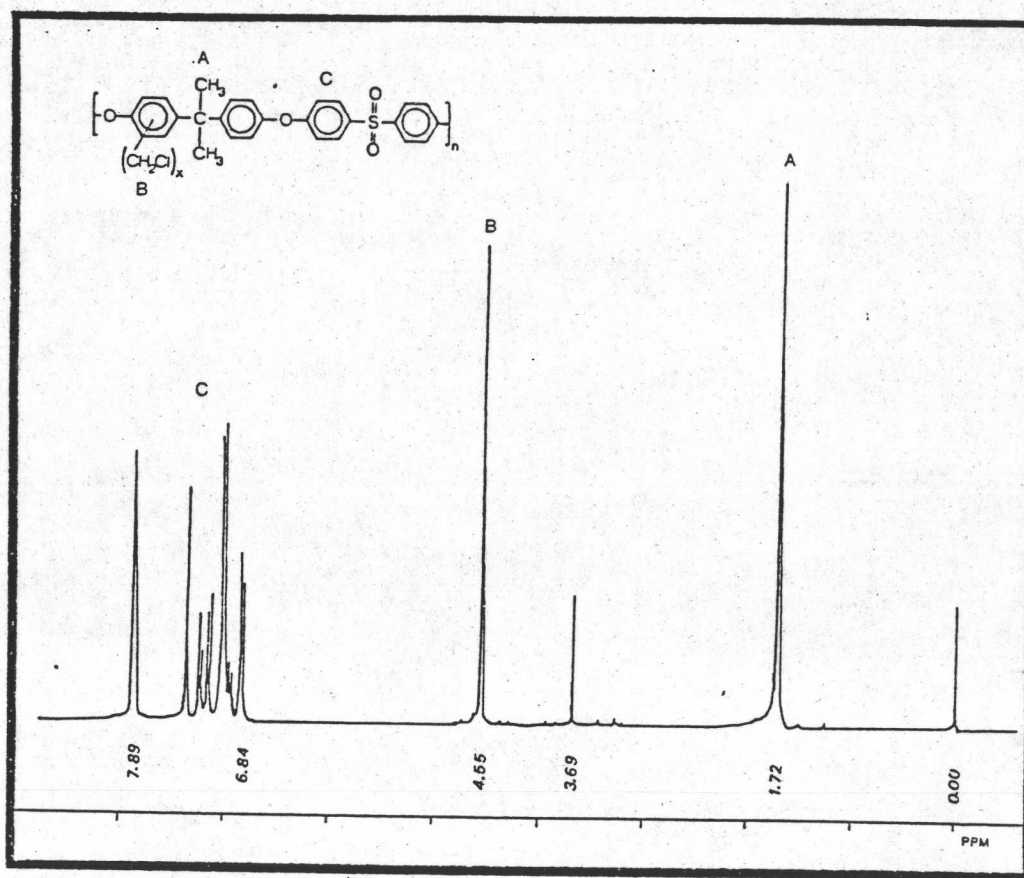The poly(vinylbenzyl choride);POLYMER 2 was prepared in 66.7% yield by radical polymerization of the purified vinyl-

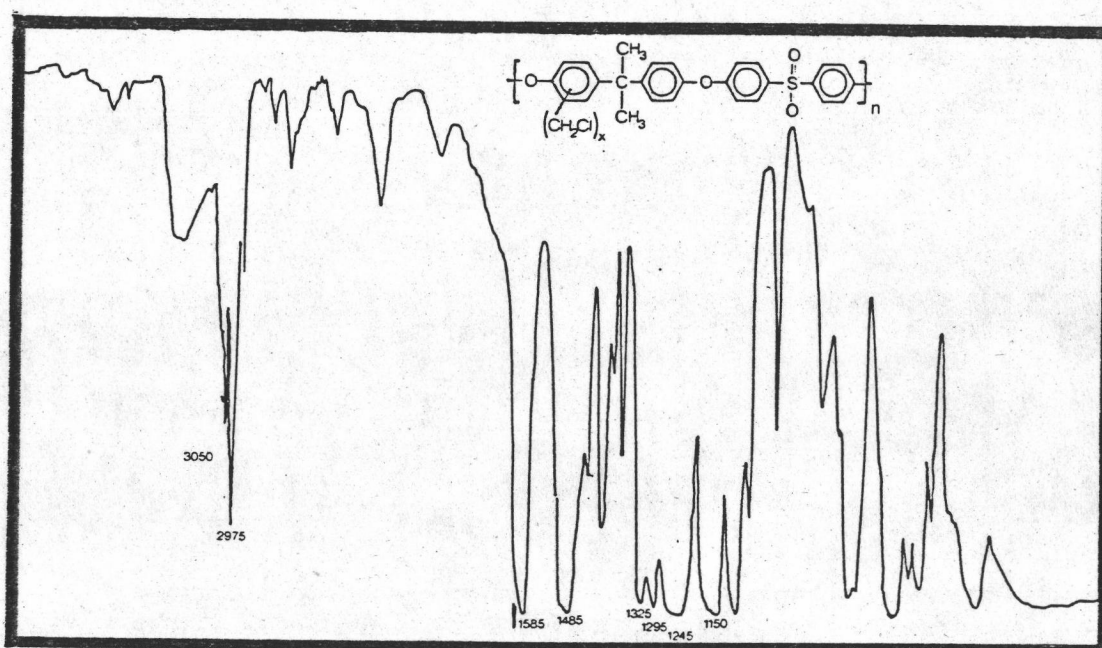Fig.5 ^{1}H NMR(CDCl$_3$) spectrum of chloromethylated polysulfone (POLYMER 1)
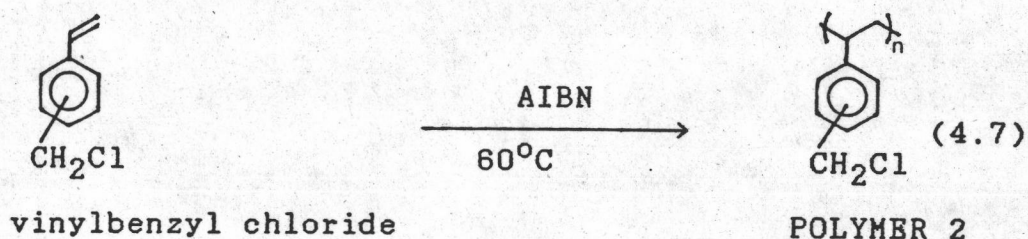

Fig.6 IR (film) spectrum of chloromethylated polysulfone (POLYMER 1)

benzyl chloride (mixture of 60% meta and 40% para) using AIBN as
an initiator at 60°C for 3 h. The polymerization reaction
can be represented as in equation (4.7).

$$\text{vinylbenzyl chloride} \xrightarrow[60°C]{AIBN} \text{POLYMER 2} \quad (4.7)$$

^{1}H NMR(CDCl$_3$) and IR(film) spectra are shown in Fig. 7
and 8 respectively. The chlorine content (by elemental
analysis) in POLYMER 2 is 23.71% (calcd 23.23%, see Appendix C).

2.3) Preparation of poly(vinylbenzyl chloride-co-2-ethoxy-
ethyl methacrylate):POLYMER 3

The poly (vinylbenzyl chloride-co-2-ethoxyethyl
methacrylate);POLYMER 3 was prepared in 49.2% yield by radical
copolymerization of vinylbenzyl chloride (mixture of 60% meta and
40% para) and 2-ethoxyethyl methacrylate using AIBN as an
initiator at 60°C for 3 h. This reaction can be represented
as in equation (4.8).

vinylbenzyl 2-ethoxyethyl
chloride methacrylate
POLYMER 3

(4.8)
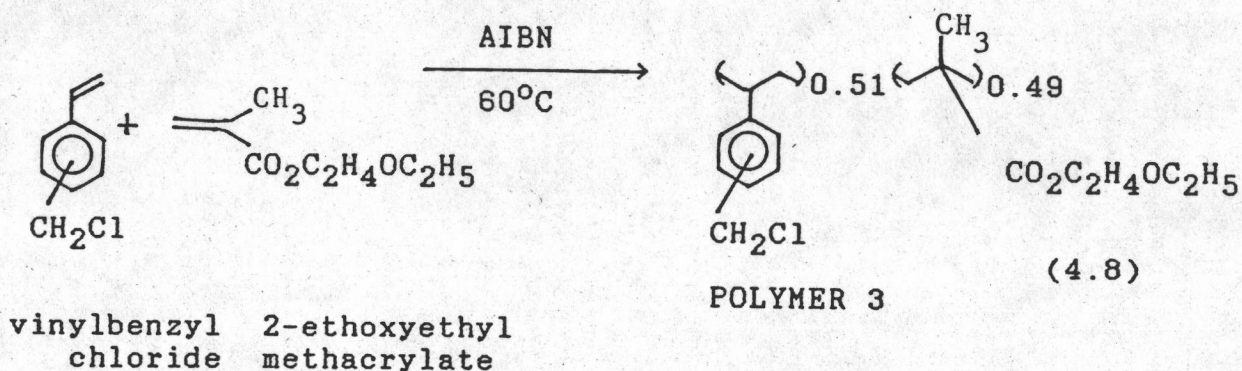
^{1}H NMR(CDCl$_3$) and IR(film) spectra are shown in Fig.9 and 10 respectively. The chlorine content (by elemental analysis) in POLYMER 3 for $(C_9H_9Cl)_{0.51}(C_8H_{14}O_3)_{0.49}$ is 11.61% (calculated 11.41%; see Appendix D).

3) Preparation of cesium ferrocenecarboxylate (CFC)

The procedure for preparation of cesium ferrocenecar- boxylate was developed by Sittatrakul [23]. The principle of this procedure is "like dissolves like". Since ferrocenecar- boxylic acid is slightly low in polarity, it can be dissolved in low polar solvent such as tetrahydrofuran. However, one can observe the increase in polarity when the ferrocenecarboxylic group is changed to cesium ferrocenecarboxylate salt. The cesium ferrocenecarboxylate salt did not dissolve in tetrahy- drofuran as a result of its high polarity. Using this simple principle, cesium ferrocenecarboxylate can be easily prepared.
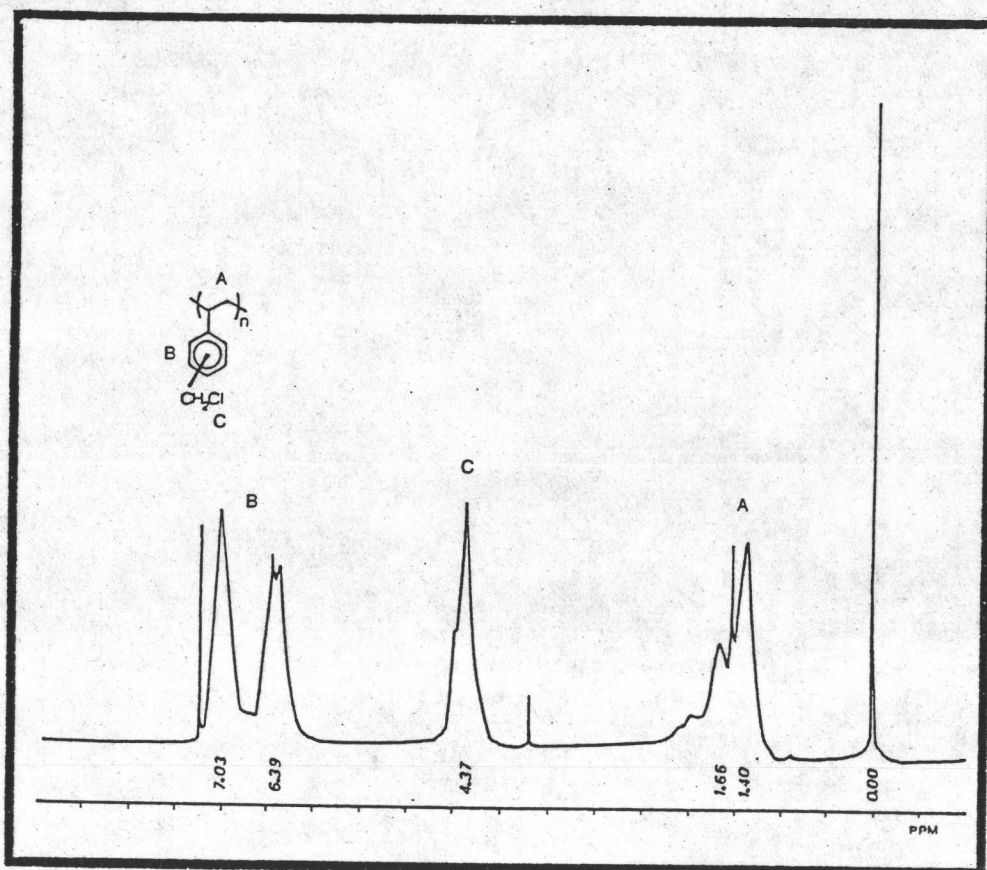
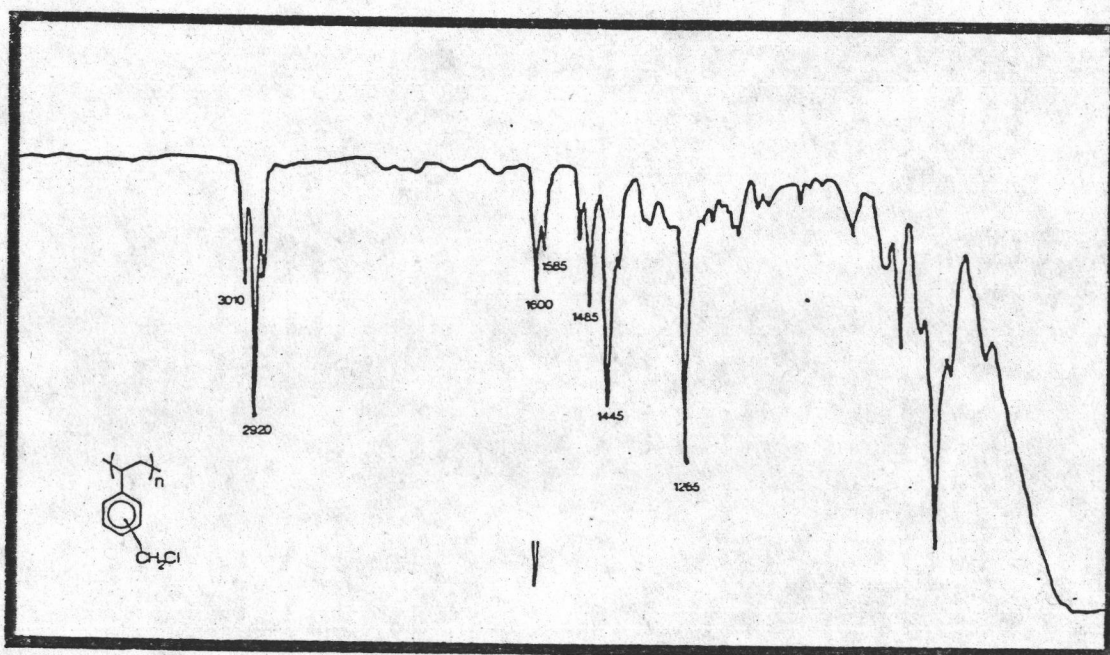Fig.7 ^{1}H NMR(CDCl$_3$) spectrum of poly(vinylbenzyl chloride)
(POLYMER 2)

Fig.8   IR (film) spectrum of poly(vinylbenzyl chloride)
(POLYMER 2)

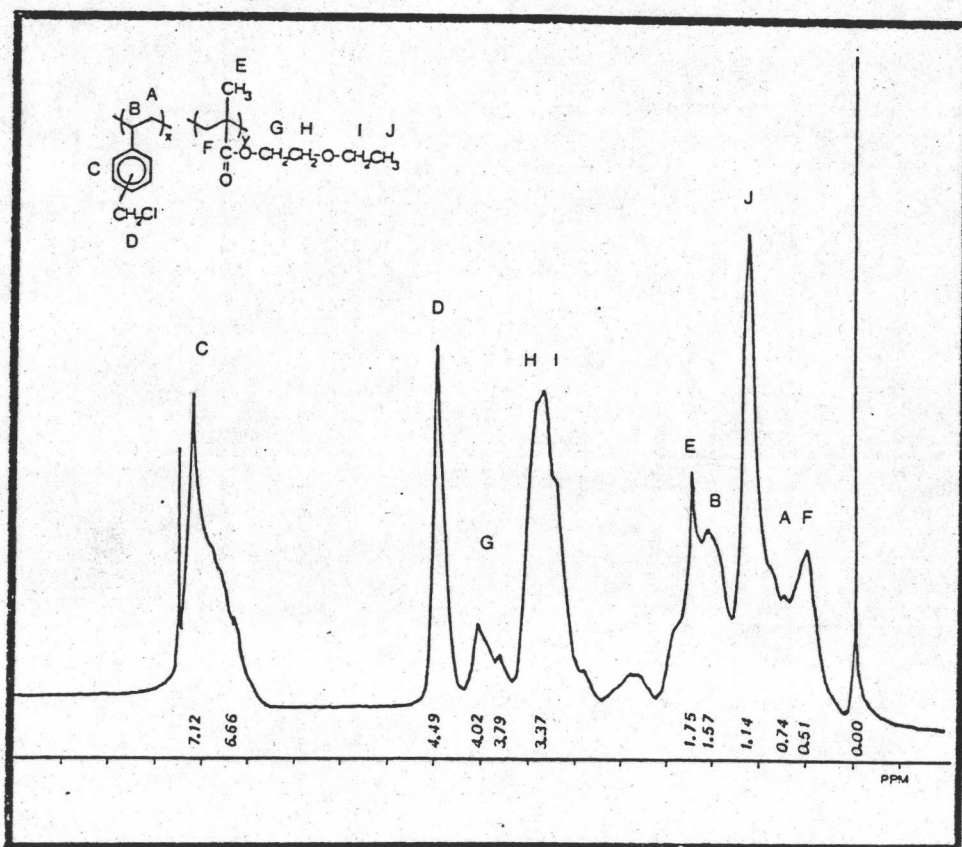Fig.9 ^{1}H NMR(CDCl$_3$) spectrum of poly(vinylbenzyl chloride
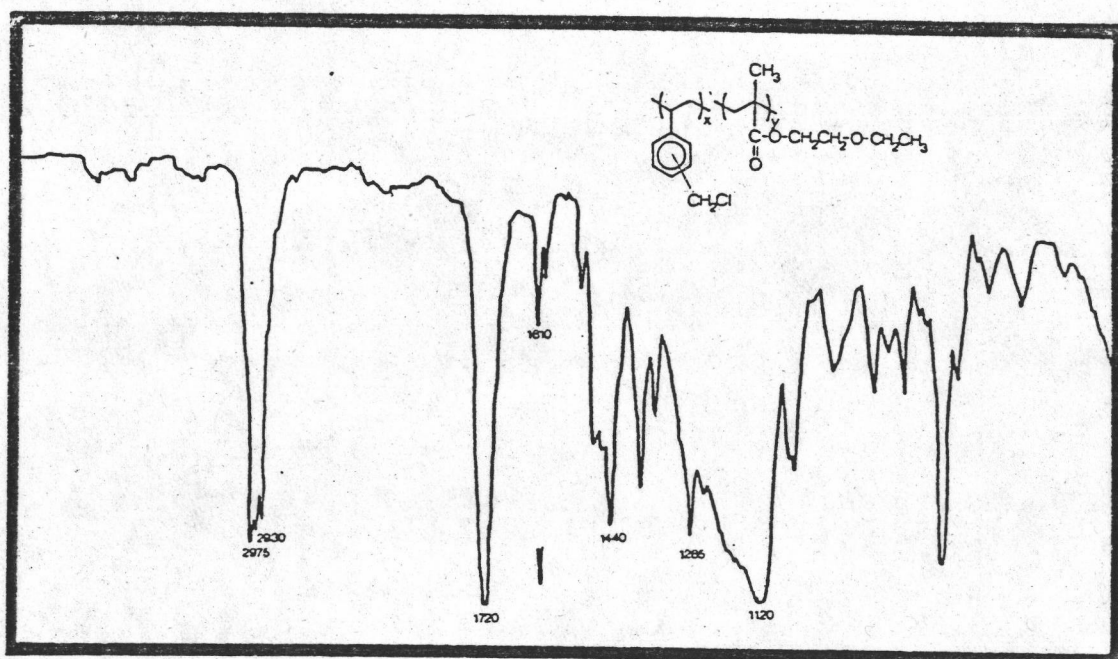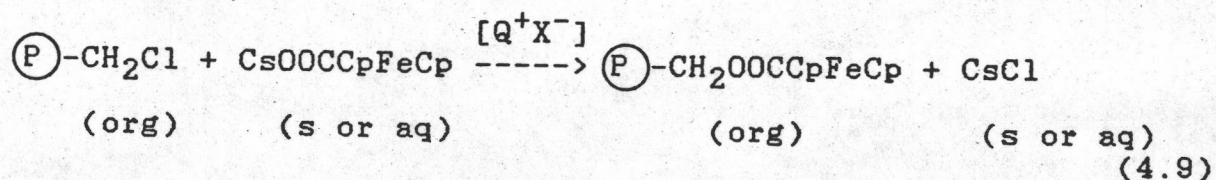-co-2-ethoxyethyl methacrylate) (POLYMER 3)

Fig.10   IR (film) spectrum poly(vinylbenzyl chloride-co-
2-ethoxyethyl methacrylate) (POLYMER 3)

4) Esterification reactions of chloromethylated polymers with cesium ferrocenecarboxylate under phase-transfer catalyst condition

The nucleophilic displacement of chloride in the polymer by cesium ferrocenecarboxylate is promoted by a phase transfer catalyst either in a liquid-liquid or solid-liquid two phase reaction. The catalyst can transfer an anion of the reagent in the form of an ion pair across the interface to react with the substrate dissolved in organic solvent at high rate. In general, the catalysts mostly used can be onium salts or complexing agents which can mask and solubilize alkali metal ions.

In this investigation, the esterification reaction of chloromethylated polymers with cesium ferrocenecarboxylate (CFC) was studied under phase-transfer catalysis (PTC) conditions. The overall reaction can be shown by equation (4.9).

$$\text{P}-CH_2Cl + CsOOCCpFeCp \xrightarrow{[Q^+X^-]} \text{P}-CH_2OOCCpFeCp + CsCl$$

(org)   (s or aq)   (org)   (s or aq)

(4.9)

Where aq and org denote the aqueous and organic phase respectively, Q^+ is the catalyst cation, $[Q^+X^-]$ is an ion pair of the phase-transfer catalyst, and $\text{P}-CH_2Cl$ is the chloromethylated polymer.

As proposed by Starks [20], all phase-transfer catalyzed reactions involved at least two steps: (1) transfer of one reagent from its "normal" phase into the second phase (an extraction or anion-transfer step); and (2) reaction of the transferred reagent with the nontransferred reagent.

Thus, the overall reaction can be broken down according to the PTC postulate into an extraction step, in equation (4.10) and the chemical reaction in equation (4.11).

$$[Q^+X^-]_{org} + CpFeCpCOO^-_{aq} \rightleftharpoons [Q^+CpFeCpCOO^-]_{org} + X^-_{aq} \qquad (4.10)$$

$$[Q^+CpFeCpCOO^-]_{org} + \text{(P)}-CH_2Cl_{org} \longrightarrow [Q^+Cl^-]_{org} + \text{(P)}-CH_2OOCCpFeCp_{org}$$
$$(4.11)$$
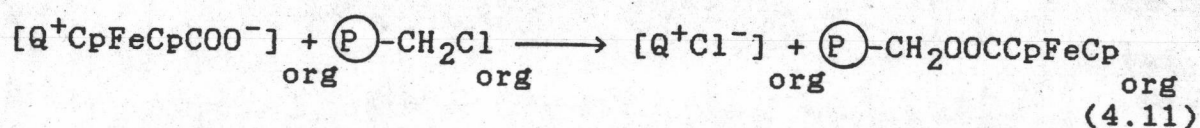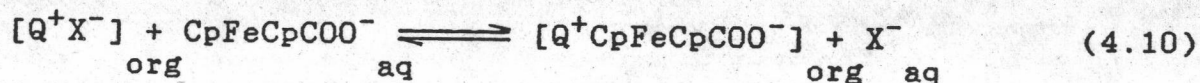
The anion, $CpFeCpCOO^-$, is extracted by the onium salt cation Q^+ to form an ion pair, $[Q^+CpFeCpCOO^-]$, in the organic phase, and undergoes a fast displacement with $\text{(P)}-CH_2Cl$ to give a product, $\text{(P)}-CH_2OOCCpFeCp$. The new salt $[Q^+Cl^-]$ then returns to the aqueous phase, where Q^+ picks up a new $CpFeCpCOO^-$ ion for the next cycle.

The ferrocenecarboxymethylated polymer products from the esterification reaction were collected by the procedure described in the experimental part. ^{1}H NMR and IR spectra of the products from the general procedure 1-4 are shown in Fig.11-16.

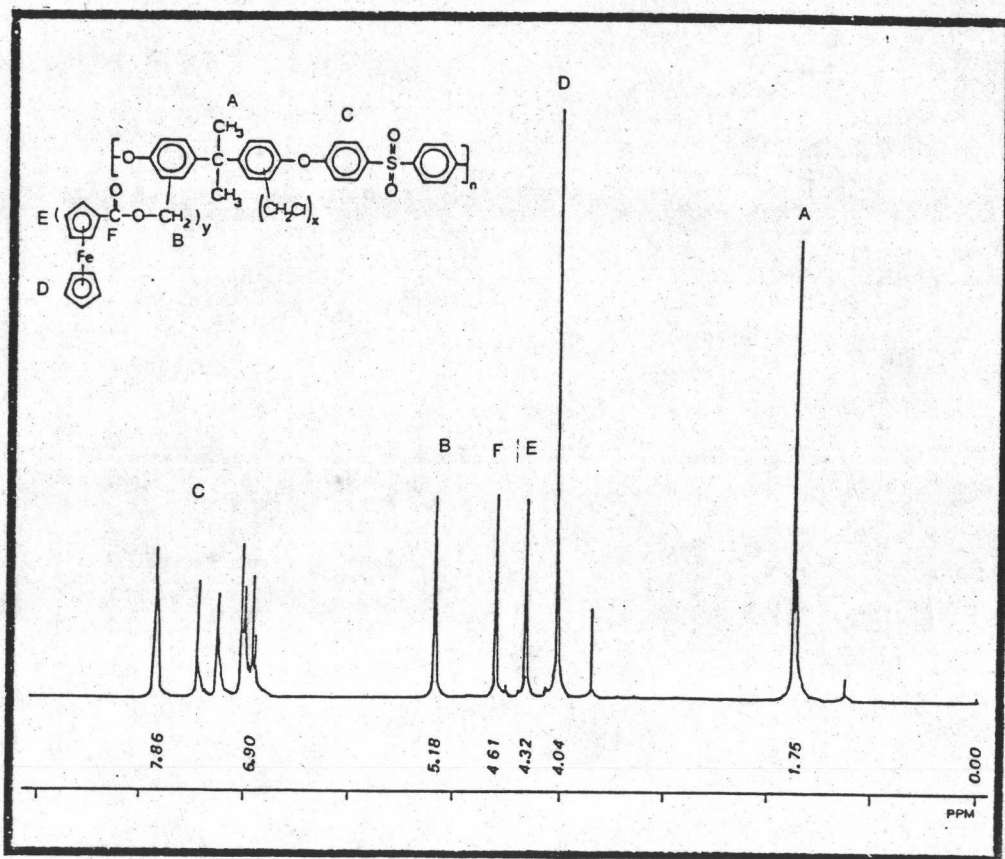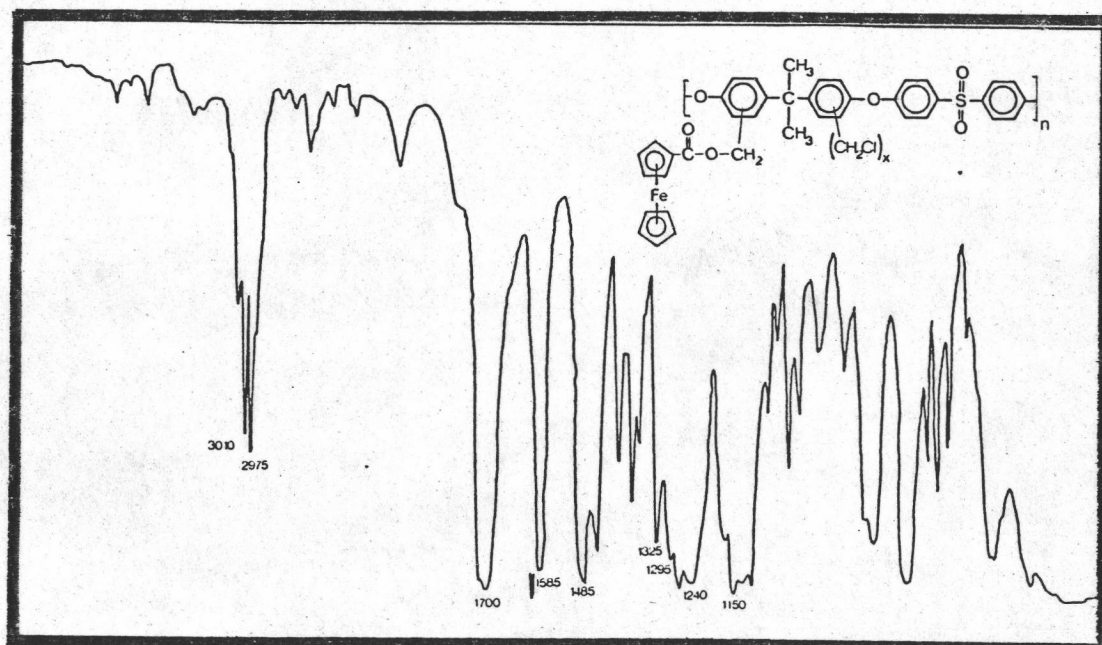Fig.11 ^{1}H NMR(CDCl$_3$) spectrum of the ester product of POLYMER 1
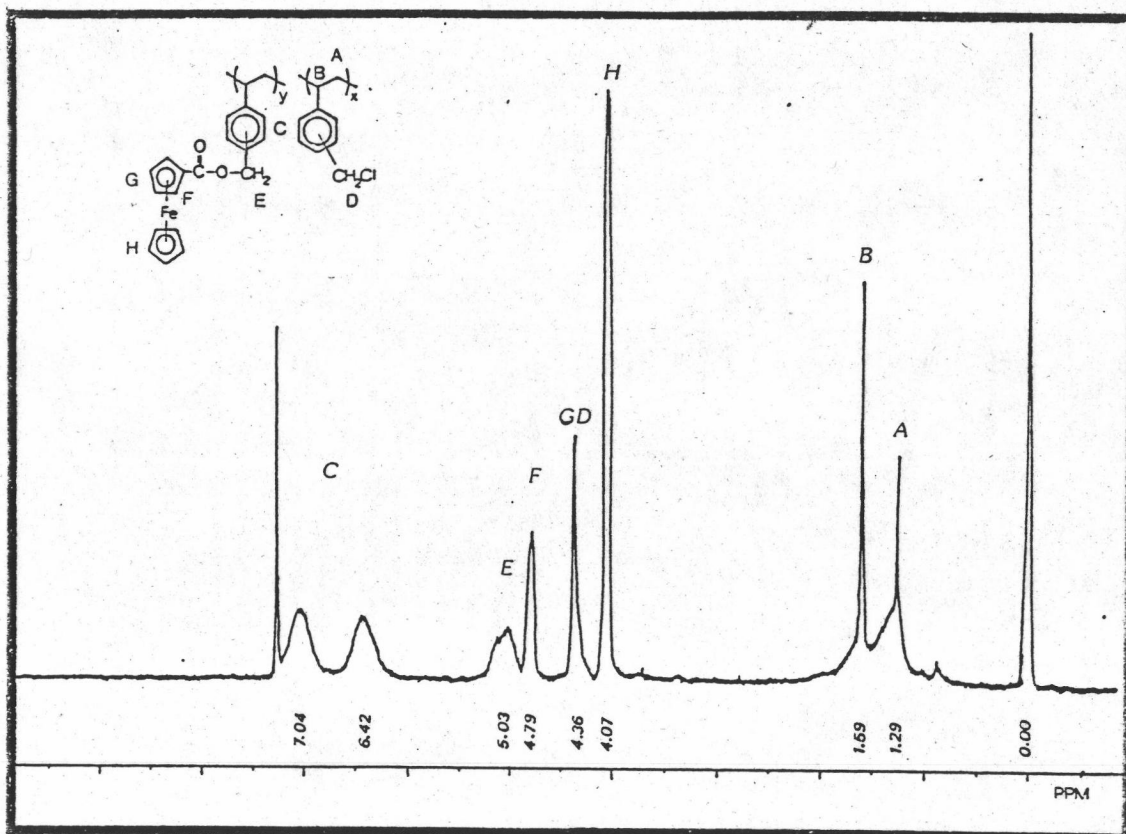

Fig.12 IR (film) spectrum of the ester product of POLYMER 1

Fig.13　^{1}H NMR(CDCl$_3$) spectrum of the ester product of POLYMER 2

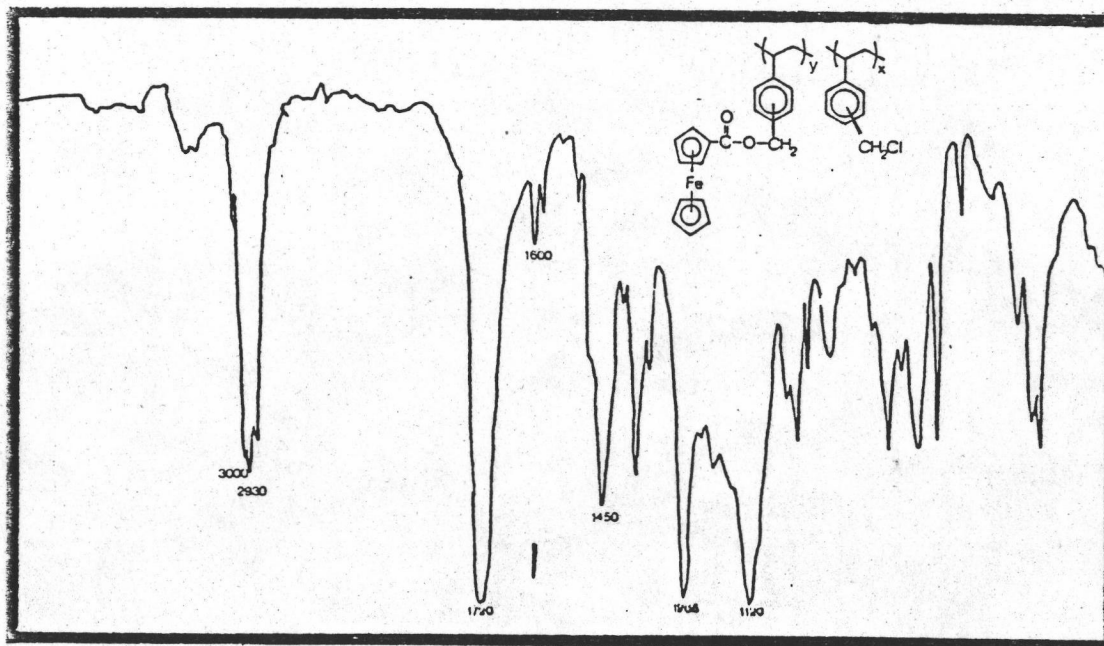Fig.14　IR (film) spectrum of the ester product of POLYMER 2
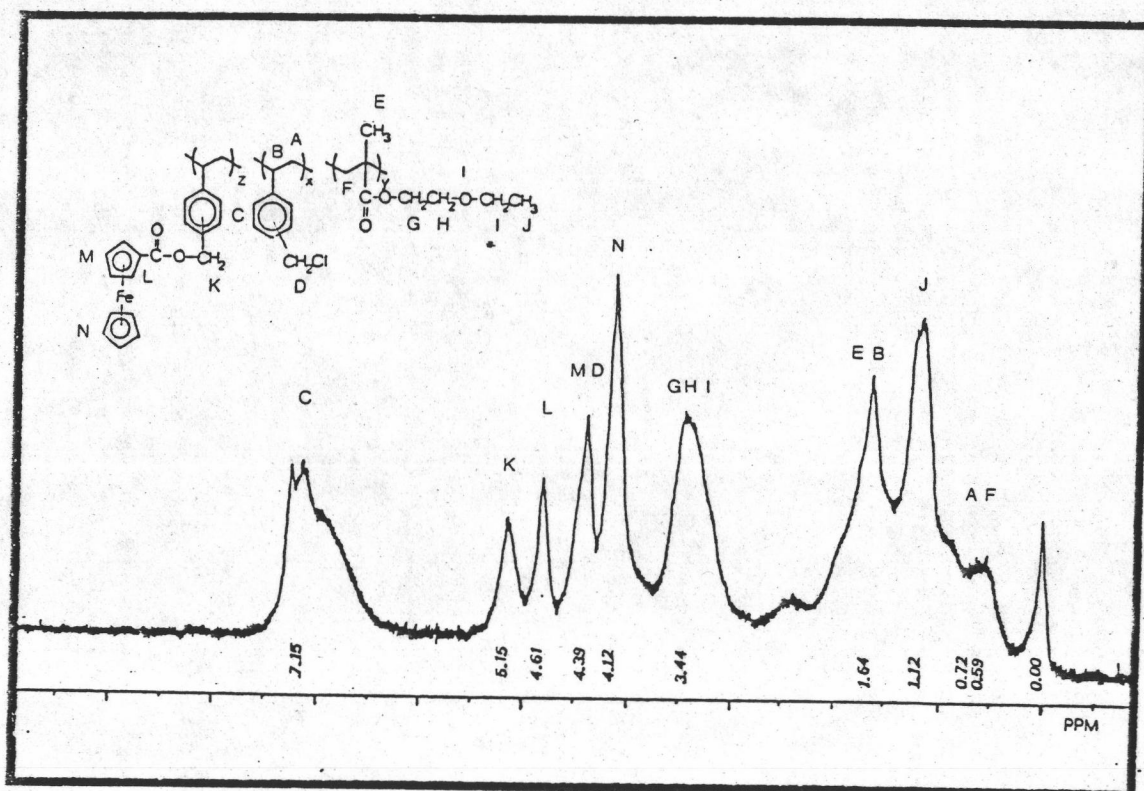
Fig.15 ^{1}H NMR(CDCl$_3$) spectrum of the ester product
of POLYMER 3
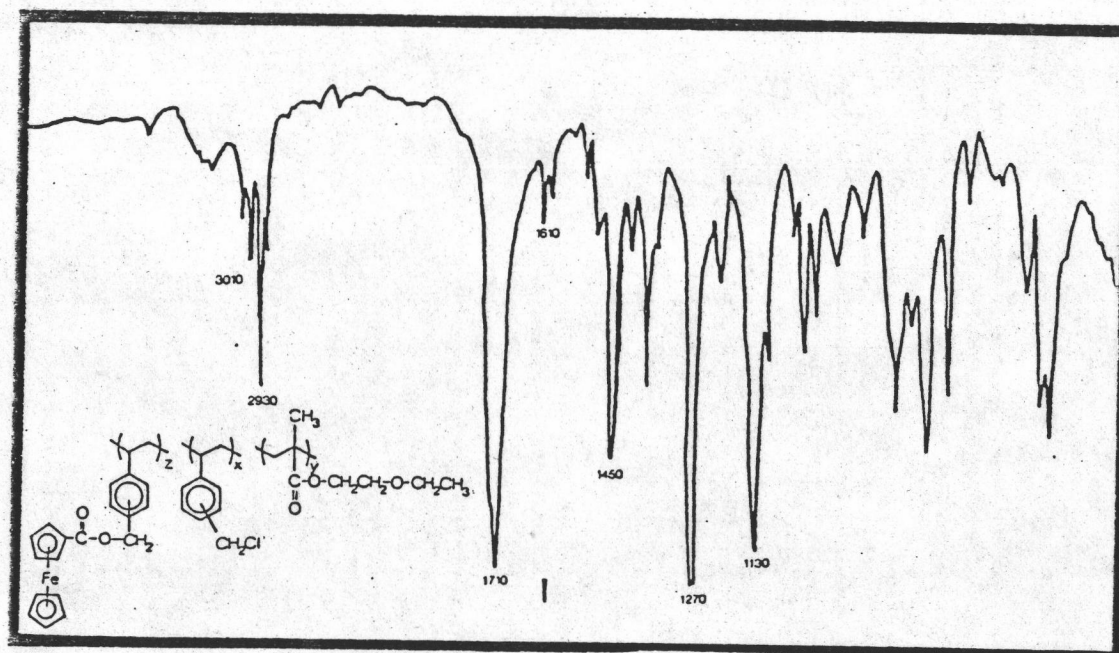
Fig.16 IR (film) spectrum of the ester product
of POLYMER 3

In studying the effect of the reaction parameters, general procedures were used and the following reaction parameters were investigated.

4.1) the reaction temperature

4.2) the mole ratio of $CFC/-CH_2Cl$ in POLYMER 1

4.3) the amount of PTC

4.4) stirring rate

4.5) solvent

4.6) type of PTC

4.7) the reaction system

4.8) the polymer structure

4.1) Effect of the reaction temperature

The conditions and results of reaction between POLYMER 1 and CFC are summarized in Table 8. The effect of temperature on the degree of esterification is clearly shown in Fig.17 plotting between the degree of esterification and reaction time. From Figure 17, the degree of esterification increased as the reaction temperature and the reaction time increased. The rate of reaction can be considered as the slope of each curve. In the first 10 h, the slope of the high reaction temperature was higher than that of the lower reaction temperature. As reaction time increased, the slope decreased slowly and was nearly constant at about 40 h. The degree of esterification reaction

TABLE 8   Effect of temperature on esterification reaction of POLYMER 1 with cesium ferrocenecarboxylate in a liquid-liquid two-phase system*

no	temp.	time (h)	degree of esterification
1	30	5	22
2	30	10	27
3	30	20	44
4	30	40	58
5	45	5	37
6	45	10	55
7	45	20	69
8	45	40	86
9	60	2	56
10	60	5	68
11	60	10	82
12	60	20	92
13	60	40	99
14	60	60	98

* The esterification reaction of POLYMER 1 with CFC in the presence of TBAC as a PTC catalyst was carried out in a $CHCl_3-H_2O$(5 mL/0.5 mL) two phase system with a stirring rate of ca. 200 rpm. The CH_2Cl/CFC/TBAC molar ratio used was 1/1.5/1.
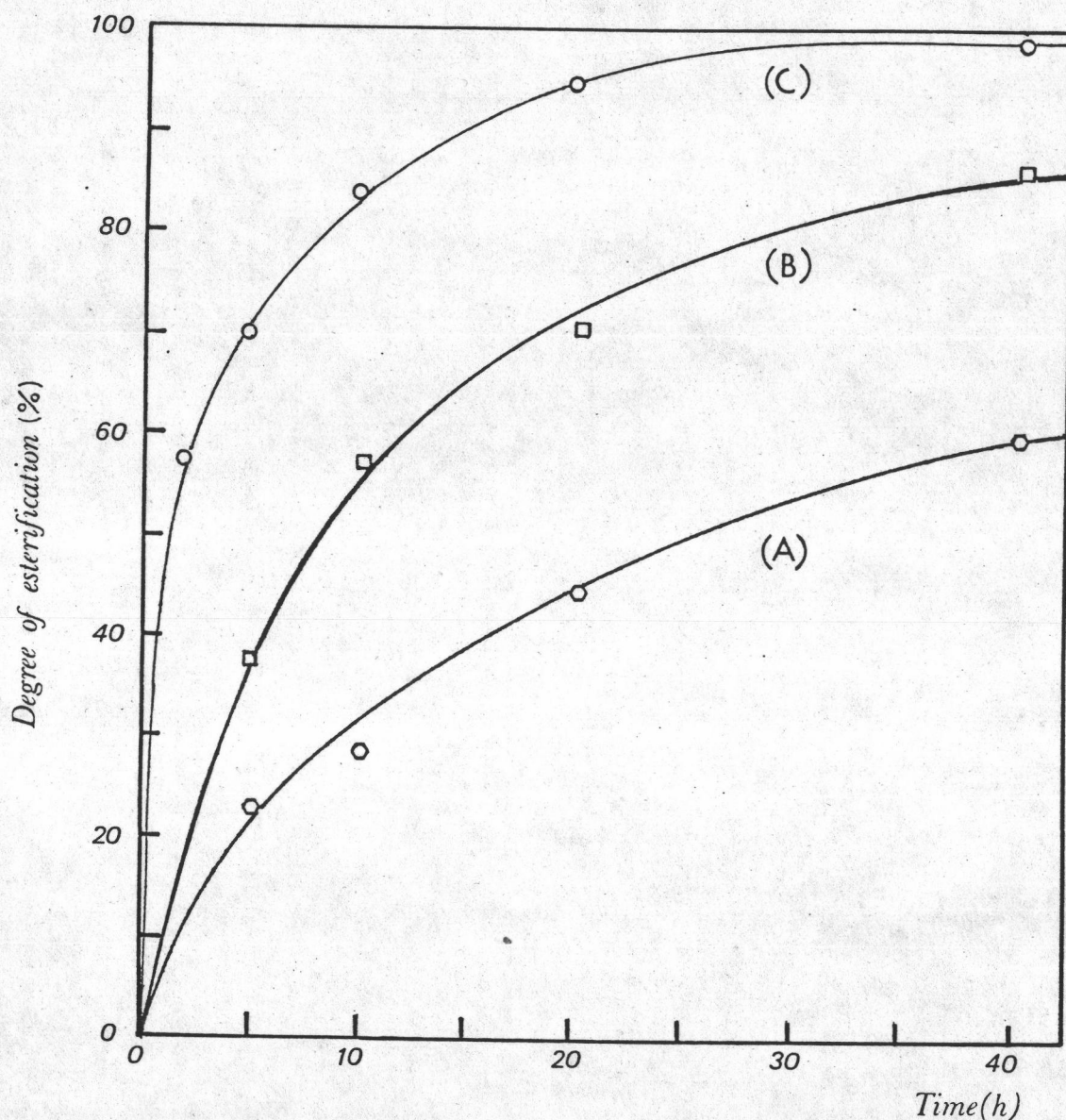
Fig.*17* . Effect of temperature on esterification reaction of
polymer 1 with CFC in a liquid-liquid two-phase system
using TBAC as a PTC. The reaction of polymer 1 (0.3
mmol) in chloroform(5mL) with an aqueous solution of
CFC(0.45 mmol in distilled water(0.5 mL)) in the
presence of TBAC(0.3 mmol) was carried out at :

(A) 30°C; (B) 45°C; (C) 60°C

at 60°C, 45°C and 30°C are 99%, 86% and 58% respectively(nos. 13, 8, 4).

The results suggest that the reaction temperatures influence the degree of esterification both in the reaction rate and in the maximum degree of esterification obtained. When the reaction temperature increases, the reaction rate increases rapidly in the first 10 h. The increasing becomes slows down as the reaction time increases and is constant at about 40 h.

From these results we can conclude that the optimum reaction temperature and reaction time for the esterification reaction between POLYMER 1 and CFC in the liquid-liquid two-phase system using TBAC as a PTC are 60°C and 40 h respectively.

4.2) Effect of the mole ratio of CFC/-CH$_2$Cl in POLYMER 1

The reaction conditions and the results of reaction between POLYMER 1 and CFC are summarized in Table 9 and Figure 18. Figure 18 shows that the degree of esterification increased as a result of an increase both in the mole ratio of CFC/-CH$_2$Cl in POLYMER 1 and in the reaction time. The changes in the slope of curves are similar to that in the effect of reaction temperature. The degree of esterification at 40 h for the reaction using the mole ratio of CFC/-CH$_2$Cl in POLYMER 1; 1/1, 1.5/1 and 2/1 are 74%, 99% and 96%, respectively

TABLE 9 Effect of substrate/reagent ratios on esterification reaction of POLYMER 1 with cesium ferrocenecarboxylate in a liquid-liquid two-phase system[*]

no	ratio $-CH_2Cl/CFC/TBAC$	time (h)	degree of esterification
15	1/1/1	5	54
16	1/1/1	10	65
17	1/1/1	20	75
18	1/1/1	40	74
19	1/1.5/1	2	56
20	1/1.5/1	5	68
21	1/1.5/1	10	82
22	1/1.5/1	20	92
23	1/1.5/1	40	99
24	1/1.5/1	60	98
25	1/2/1	5	85
26	1/2/1	10	94
27	1/2/1	20	98
28	1/2/1	40	86

[*]The esterification reaction of POLYMER 1 with CFC in the presence of TBAC as a PTC catalyst was carried out in a $CHCl_3-H_2O$(5 mL/0.5 mL) two phase system at 60°C with a stirring rate of ca. 200 rpm.

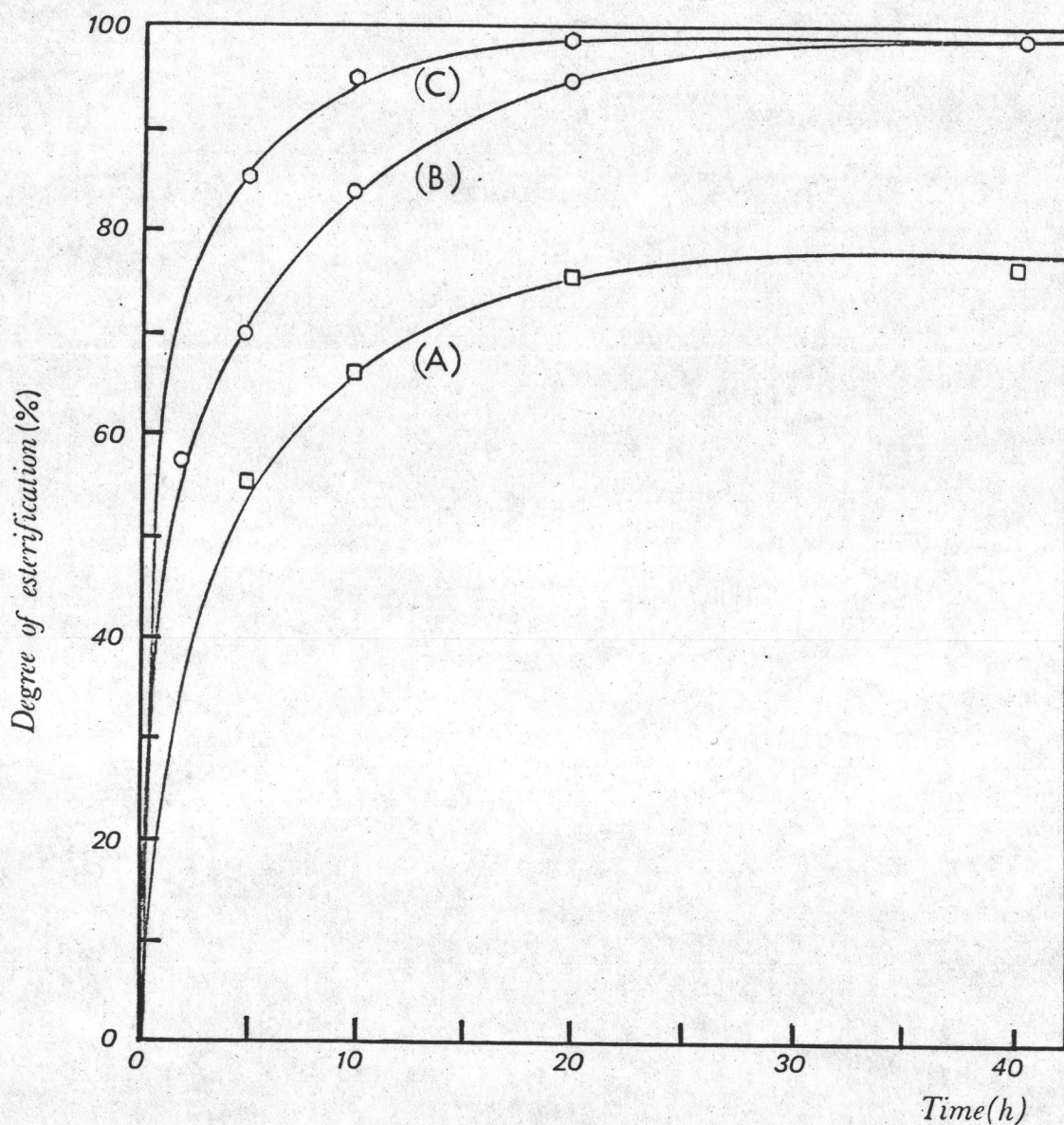Fig.*18* . Effect of the mole ratio of CFC/-CH$_2$Cl in **POLYMER** 1 on
esterification reaction of polymer 1 with CFC in a
liquid-liquid two-phase system using TBAC as a PTC. The
reaction of polymer 1 (0.3 mmol) in chloroform(5mL)
with an aqueous solution of CFC in the presence of TBAC
(0.3 mmol) was carried out at 60°C and the
CFC/-CH$_2$Cl/TBAC molar ratios were :
(A)1/1/1; (B)1.5/1/1; (C) 2/1/1

(nos.18,23,28).

The results suggest that the degree of esterification is influenced by the mole ratio of CFC/-CH$_2$Cl in POLYMER 1. When the CFC/-CH$_2$Cl mole ratio was increased, the reaction rate in the first 10 h was increased very rapidly. However, the approximately constant degree of esterification was obtained after 20 h for the mole ratio of 2/1 ($\sim$ 98%) and 40 h for the mole ratio of 1.5/1 ($\sim$ 99%).

Increasing in the mole ratio of CFC/-CH$_2$Cl in POLYMER 1 caused the increase in the concentration of CpFeCpCOO$^-$ anion and thus shifted the equilibrium to the side of the ester product. A similar result was reported by Starks [20]. From Figure 18, when the mole ratio of CFC/-CH$_2$Cl was 1/1 the maximum degree of esterification was only 78%. This seems to indicate that some of CFC undergoes thermal decomposition to give dark-gray material.

From these results, we can conclude that the optimum mole ratio of CFC/-CH$_2$Cl in POLYMER 1 should be 1.5/1 and the reaction time is 40 h. This mole ratio can save the amount of CFC used whereas the high degree of esterification still obtain in the proper time.

4.3) Effect of the amount of PTC

In this study, the amount of PTC was varied while the amounts of -CH$_2$Cl in POLYMER 1 and CFC were kept constant.

TABLE 10 Effect of the amount of PTC on esterification
reaction of POLYMER 1 with cesium ferrocenecarboxylate in a
liquid-liquid two-phase system[*]

no	ratio -CH$_2$Cl/CFC/TBAC	time (h)	degree of esterification
29	1/1.5/0.1	5	27
30	1/1.5/0.1	10	47
31	1/1.5/0.1	20	77
32	1/1.5/0.1	40	85
33	1/1.5/0.1	60	92
34	1/1.5/0.5	5	57
35	1/1.5/0.5	10	70
36	1/1.5/0.5	20	89
37	1/1.5/0.5	40	90
38	1/1.5/1	2	56
39	1/1.5/1	5	68
40	1/1.5/1	10	82
41	1/1.5/1	20	92
42	1/1.5/1	40	99
43	1/1.5/1	60	98
44	1/1.5/1.5	40	82

TABLE 10 (continued)

no	ratio -CH$_2$Cl/CFC/TBAC	time (h)	degree of esterification
45	1/1.5/2	5	61
46	1/1.5/2	10	69
47	1/1.5/2	20	73
48	1/1.5/2	40	78
49	1/1.5/4	40	75

*The esterification reaction of POLYMER 1 with CFC in the presence of TBAC as a PTC catalyst was carried out in a CHCl$_3$-H$_2$O(5 mL/0.5 mL) two phase system at 80°C with a stirring rate of ca. 200 rpm.
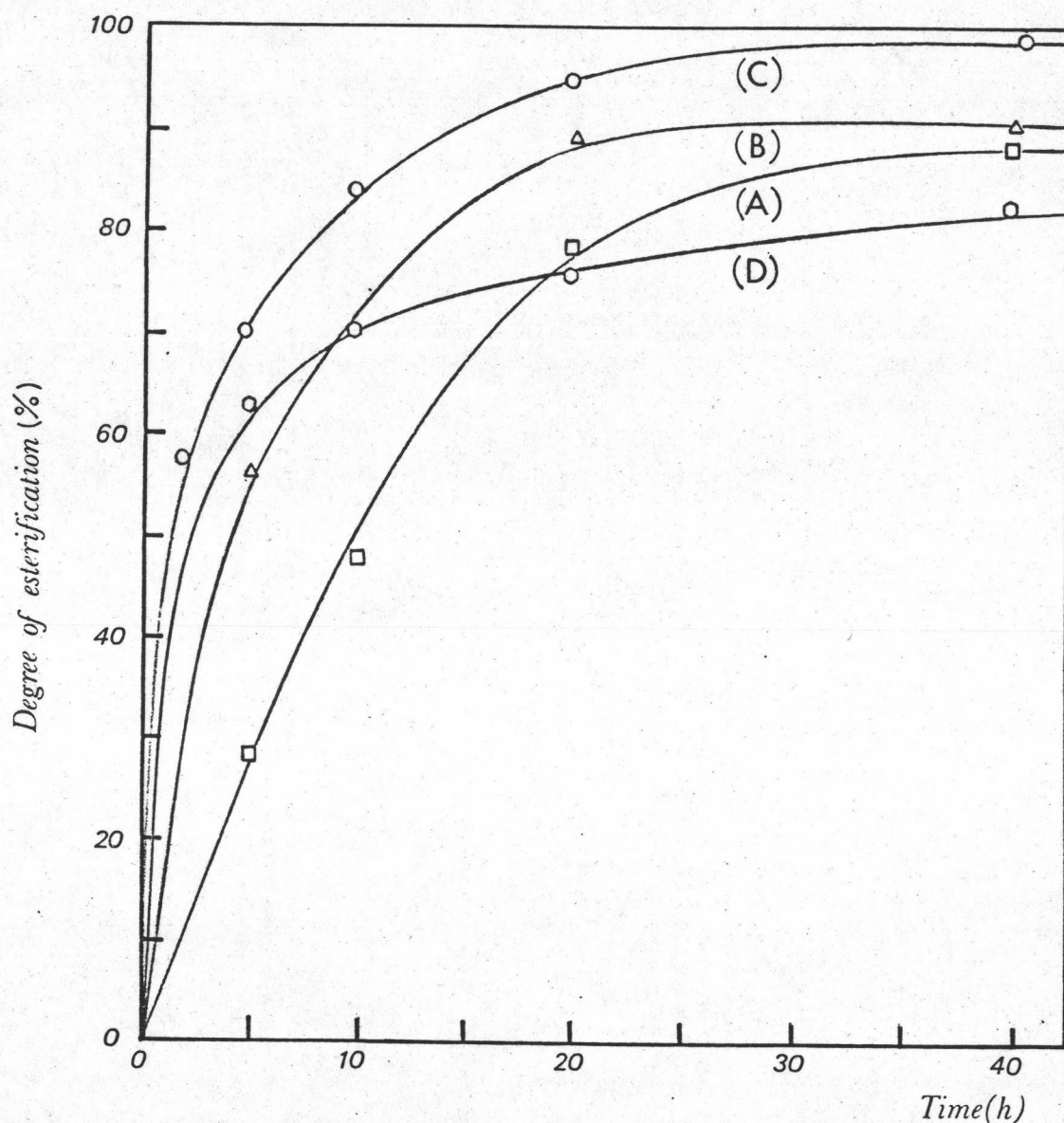
Fig.*19*. Effect of the amount of TBAC on esterification reaction of polymer 1 with CFC in a liquid-liquid two-phase system using TBAC as a PTC. The reaction of polymer 1 in chloroform with an aqueous solution of CFC in the presence of TBAC was carried out at 60°C and the CFC/-CH$_2$Cl/TBAC molar ratios were :

(A)1.5/1/0.1; (B)1.5/1/0.5; (C)1.5/1/1; (D)1.5/1/2

Fig.20. Relation between the degree of esterification and the amount of TBAC in a liquid-liquid two-phase system. The reaction of polymer 1 (0.3 mmol) in chloroform (5mL) with an aqueous solution of CFC (0.45 mmol in distilled water (0.5 mL)) in the presence of TBAC (0.3 mmol) was carried out at 60°C for 40 h.

The reaction conditions and results are summarized in Table 10 and Figure 19.

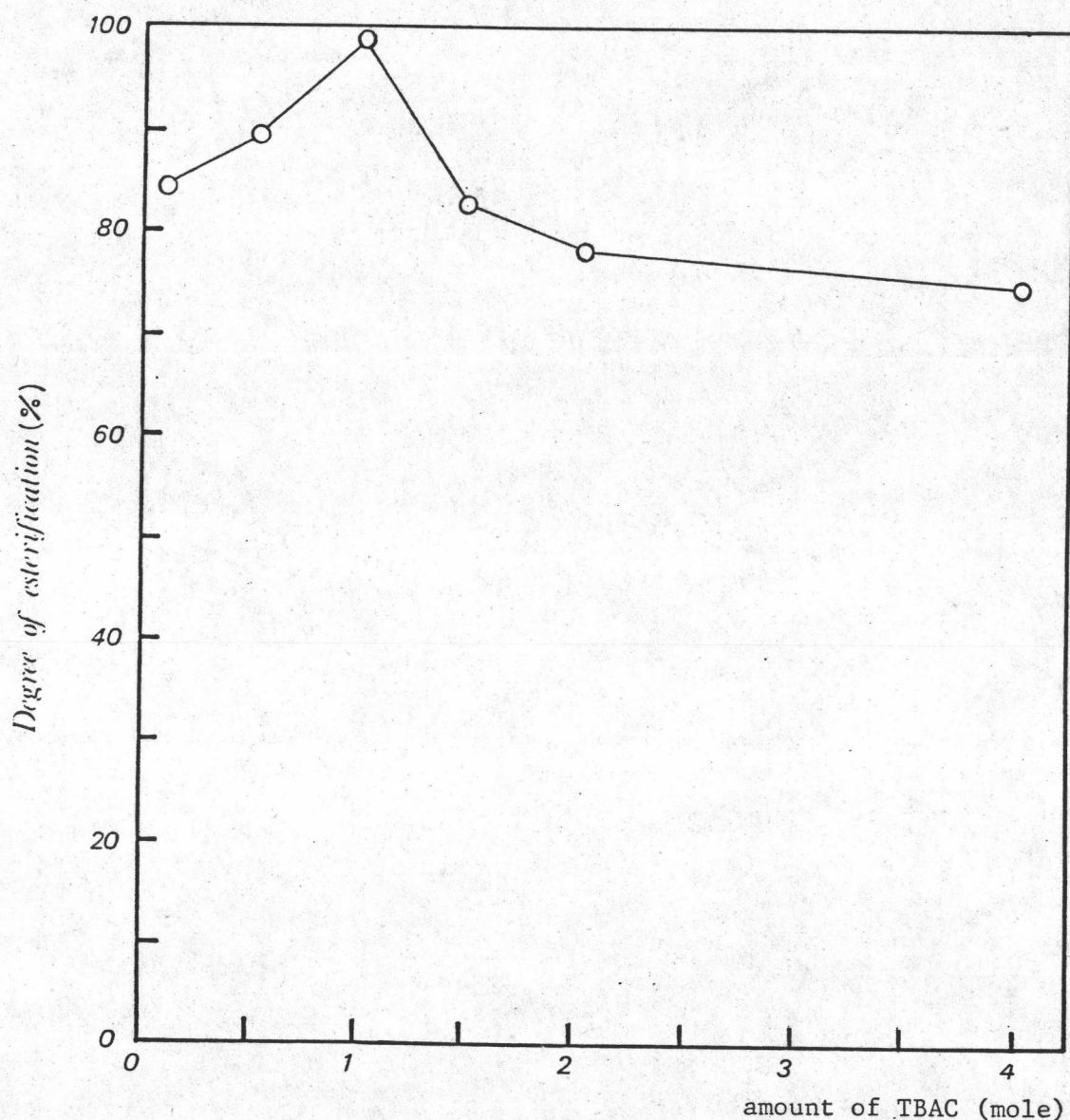From Figure 19 it is apparent that the degree of esterification increased as the number of moles of TBAC and the reaction time increased (curve A,B and C). The slope of the curves in the first 10 h increased and was approximately zero after 40 h. The degrees of esterification were 85%, 90% and 99% when the number of moles of TBAC used are 0.1, 0.5 and 1, respectively (nos.32, 37, 42). However, the degree of esterification decreased when the number of moles of TBAC used was higher than 1 (nos. 44,48, and 49).

The relation between the degree of esterification at 40 h and the number of moles of TBAC used is shown in Fig.20. It is seen that the degree of esterification reached the maximum when the molar ratio of $CFC/-CH_2Cl/TBAC$ was 1.5/1/1 and decreased when the molar ratios were lower or higher than 1.5/1/1. These results can be understood by the examination of the chemical reactions in equations (4.10) and (4.11). When the mole ratio of TBAC increases, the concentration of $[Q^+CpFeCpCOO^-]$ in the organic phase increases and thereby the rate of the reaction (4.11) increases. However, when the mole ratio of TBAC is greater than 1 , the concentration of the chemical species is too high in the organic phase. The organic phase seems to be overclouded with the bulky molecules of the polymer and catalyst and therefore the rate of exchanging of anions between $CpFeCpCOO^-$

(large anion) and Cl⁻ (small anion) (eq.4.10) is decreased.
This behavior is the cause of lowering in the rate of reaction
4.11.

4.4) Effect of stirring rate

The effect of stirring rate on the degree of esterifi-
cation was also investigated.   The reaction conditions and the
results are reported in Table 11 and Fig.21.   Figure 21 shows
that the degree of esterification increased as the stirring rate
increased and it seemed to reach a maximum limit at about 200 rpm
both in the solid-liquid and liquid-liquid two-phase systems.
However, the degree of esterification obtained from the solid-
liquid two phase system was lower than that of the liquid-liquid
two phase system (93% vs 99%).   We could not apply the
stirring speed higher than 200 rpm since it causes the splashing
of the reaction mixture.

4.5) Effect of solvent

The effect of solvent on the degree of esterification
of POLYMER 1 was investigated in three systems.   These were the
solid-liquid two phase system, the liquid-liquid two phase
system and a homogeneous system.   The reaction conditions and
results are summarized in Table 12

The results indicate that chloroform ($\mathcal{E}$=4.81[20]) is the
ideal solvent for the esterification reactions of POLYMER 1 with

TABLE 11 Effect of stirring rate on esterification reaction of POLYMER 1 with cesium ferrocenecarboxylate in a two-phase system*

no	stirring rate (rpm)	reaction two-phase system	degree of esterification
50	0	solid-liquid	69
51	50	solid-liquid	81
52	100	solid-liquid	86
53	200	solid-liquid	93
54	0	liquid-liquid	79
55	50	liquid-liquid	88
56	100	liquid-liquid	90
57	200	liquid-liquid	99

*The esterification reaction of POLYMER 1 with CFC in the presence of TBAC as a PTC catalyst was carried out in a $CHCl_3-H_2O$(5 mL/0.5 mL) or in a $CHCl_3$ (solid-liquid) two phase system at $60^{\circ}C$ with varying stirring rates for 40 h. The $CH_2Cl/CFC/PTC$ molar ratio used was 1/1.5/1.
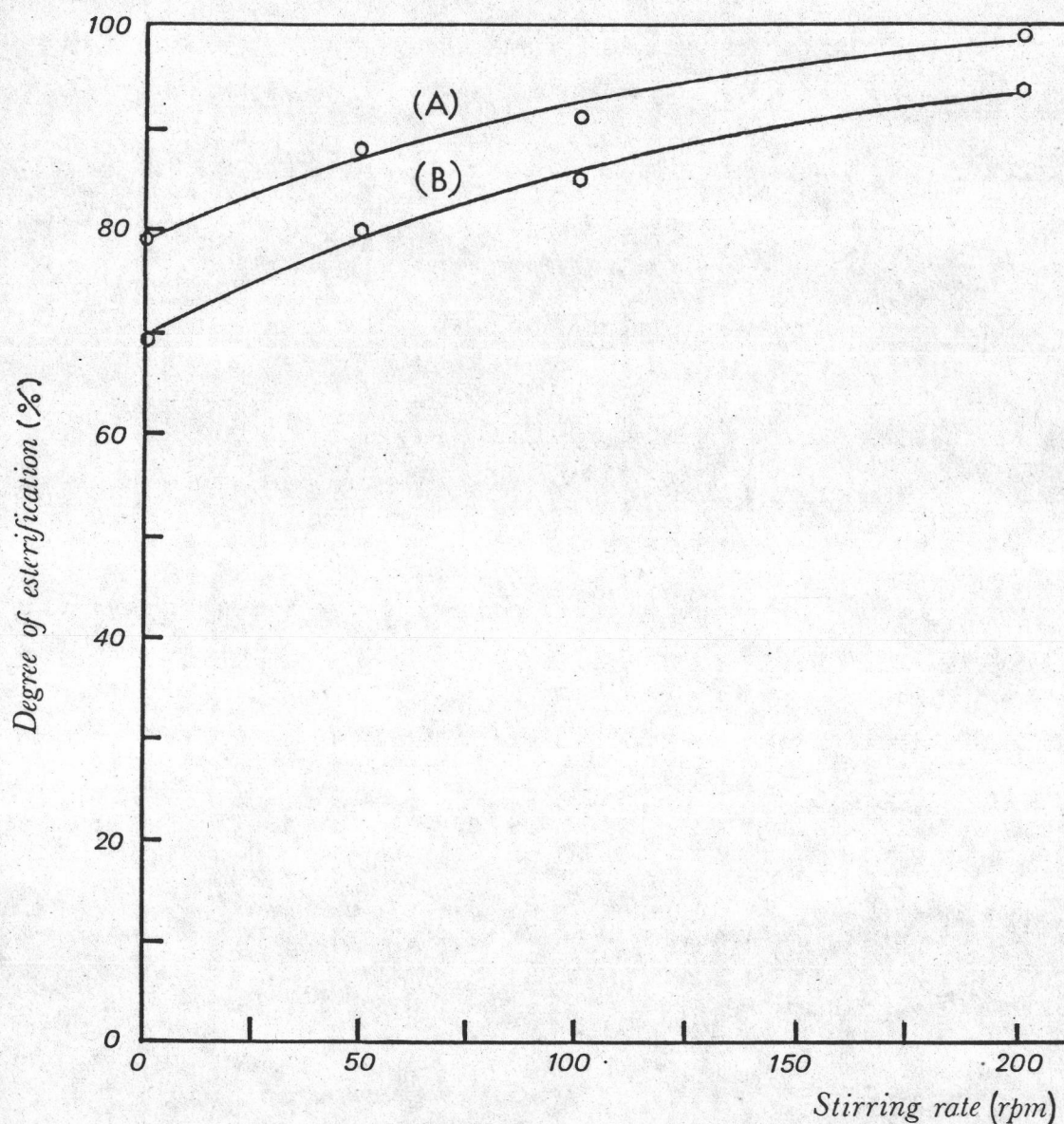
Fig. 21. Effect of stirring rate on esterification of polymer 1
with CFC in a liquid-liquid and solid-liquid two-phase
systems using TBAC as a PTC.The reaction of polymer 1
(0.3 mmol) in chloroform(5mL) with CFC(0.45 mmol) or
an aqueous solution of CFC (0.45 mmol in distilled
water(0.5 mL)) in the presence of TBAC(0.3 mmol) was
carried out at 60°C for 40 h.

(A) liqiud-liquid; (B) solid-liquid

TABLE 12 Effect of solvent on the degree of esterification reaction of POLYMER 1 with cesium ferrocenecarboxylate in a two-phase system[*]

| no	solvent[**]	bp. (°C)	dielectric constant	reaction system	degree of esterification
58	chloroform	61.2	4.81 (20)	solid-liquid	93
59	THF[a]	65.4	7.58 (25)	solid-liquid	86
60	sym-tetra chloroethane	142-146	8.20 (20)	solid-liquid	dark material
61	2-nitro toluene	225	27.40 (20)	solid-liquid	crossed linked polymer
62	DMF	153	36.71 (25)	solid-liquid	crossed linked polymer
63	DMSO	190	46.60 (25)	homogeneous	crossed linked polymer
64	chloroform	61.2	4.81 (20)	liquid-liquid	99
65	THF	65.4	7.58 (25)	liquid-liquid	polymer did not dissolve
66	sym-tetra chloroethane	142-146	8.20 (20)	liquid-liquid	19
67	sym-tetra chloroethane	142-146	8.20 (20)	liquid-liquid	10[b]
68	2-nitro toluene	225	27.40 (20)	liquid-liquid	86
69	DMF	153	36.71 (25)	liquid-liquid	polymer did not dissolve

[a]The product was a partially crosslinked polymer.

[b]TBAS was used as a PTC.

[*]The esterification reaction of POLYMER 1 with CFC in the presence of TBAC as a PTC catalyst was carried out in a liquid-liqu (organic solvent-H_2O =5 mL/0.5 mL)or in a solid-liquid two phase systems at 60°C with a stirring rate of ca.200 rpm for 40 h. The CH_2Cl/CFC/TBAC molar ratio used was 1/1.5/1.
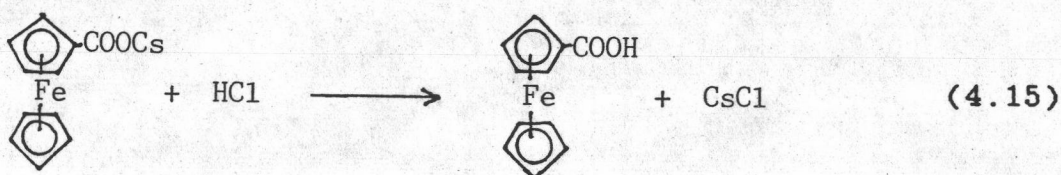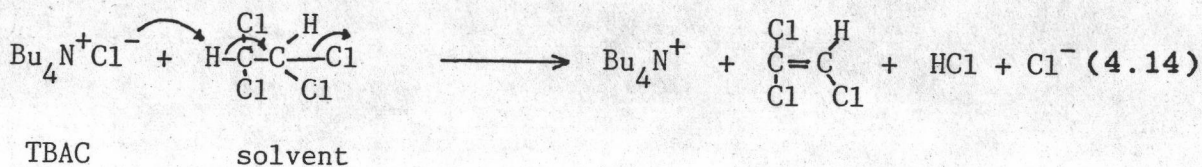
CFC in both liquid-liquid and solid-liquid two phase systems.
No cross-linked polymers were observed in these two systems.
However, when the reaction is carried out in the solvent systems
with higher dielectric constants (nos.61, 62, 63 and 69). The
crosslinked polymers were obtained. In a polar solvent system
the solvent promotes a partial dissociation of the CH_2-Cl bond
in the polymer molecules. This process not only increases the
ease of nucleophilic displacement of the chloride by cesium fer-
rocenecarboxylate (eq.4.12) but also promotes the displacement of
chloride by an aromatic nucleus (eq.4.13).

$$(4.12)$$

$$(4.13)$$
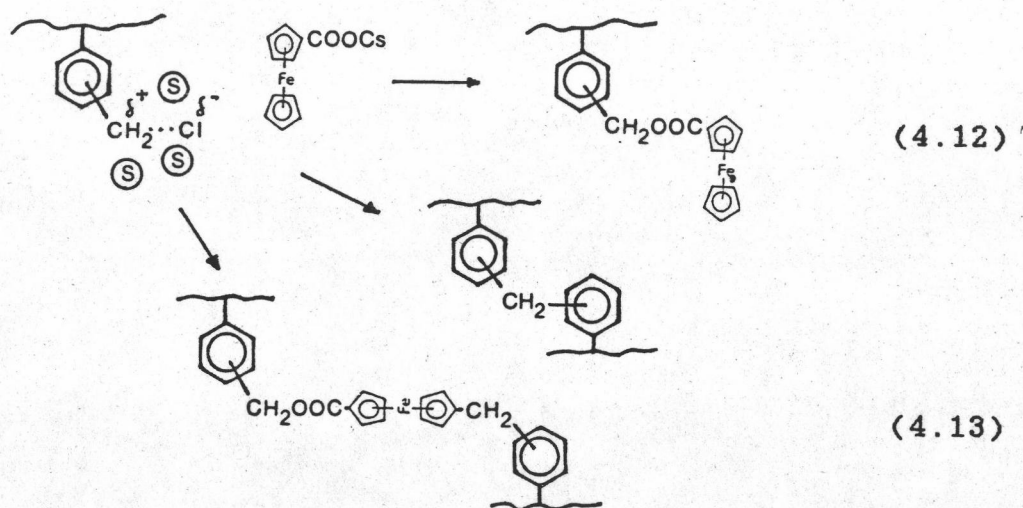
The chemical reaction in eq.4.13 could be an intramole-
cular or intermolecular cross-linking which results in the gel
formation.

When 1,1,2,2 -tetrachloroethane (ϵ = 8.20) was used as

a solvent in the liquid-liquid two phase system, the degree of esterification was very low (10 - 19%). This was probably due to the cationic exchange reaction between CFC and hydrogen chloride generated from the catalytic degradation of the solvent by the catalyst. These reactions are shown in equations (4.14) and (4.15).

$$Bu_4N^+Cl^- + H\overset{Cl}{\underset{Cl}{-}}\overset{H}{\underset{Cl}{C}}Cl \longrightarrow Bu_4N^+ + \overset{Cl}{\underset{Cl}{C}}=\overset{H}{\underset{Cl}{C}} + HCl + Cl^- \quad (4.14)$$

TBAC   solvent

$$\text{(ferrocene)}COOCs + HCl \longrightarrow \text{(ferrocene)}COOH + CsCl \quad (4.15)$$

Hydrogen chloride may react with ferrocenecarboxylic acid by protonation at the iron as shown in equation 4.16.

$$\text{(ferrocene)}COOH + HCl \dashrightarrow Cl^-Fe^+\text{-}H\,\text{(COOH)} \quad (4.16)$$
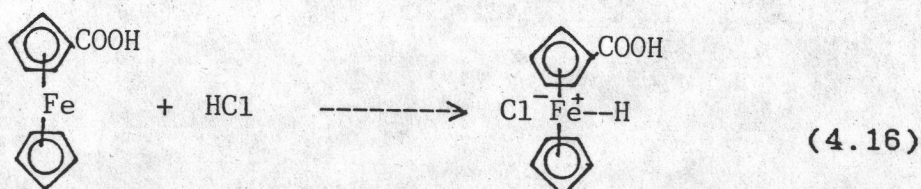
This would result in the dark-gray product that was observed after the reaction had proceeded for 9 h, and low degree of esterification would be expected.

4.6) Effect of type of PTC

The effect of type of PTC on the esterification reaction of POLYMER 1 with CFC in two-phase systems were summarized in Table 13. When symmetric tetrabutylammonium salts are used as catalysts (e.g. TBAC, TBAB, TBAI and TBAS) in both solid-liquid and liquid-liquid two-phase systems. It was found that the degree of esterification of the polymer was influenced by the paired anion of the ammonium salt, and Cl^- was more effective than Br^-, I^- and HSO_4^-.

The relation between the degree of esterification in the reaction of polymer 1 with CFC at $60^{\circ}C$ for 40 h and the paired ion of tetrabutylammonium is shown in Fig.22. It seems that the catalyst activity depends upon the ability of the catalyst to transfer between the two phases. As noted by Starks [20], there are two principal characteristics of the anion that most influence its ability to transfer the catalyst cation. First, the more the anion is hydrated, the more it will be in an aqueous phase. Second, the more lipophilic character of anion added to the total lipophilic of the cation-anion pair, the more the catalyst partitioning into the organic phase. Based on this principle, TBAB and TBAI are more readily partitioned into an organic phase than TBAC, while TBAS is extremely hydrophilic so it always remains in an aqueous phase. So TBAC is a good catalyst compared to TBAB, TBAI and TBAS.

TABLE 13 Effect of PTC on esterification reaction of POLYMER 1 with cesium ferrocenecarboxylate in a two-phase system[*]

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no	PTC	reaction two-phase system	degree of esterification
70	TBAC	solid-liquid	93
71	TBAB	solid-liquid	80
72	TBAI	solid-liquid	77
73	TBAS	solid-liquid	45
74	TBPC	solid-liquid	82
75	DCHC	solid-liquid	76
76	TBAC	liquid-liquid	99
77	TBAB	liquid-liquid	87
78	TBAI	liquid-liquid	85
79	TBAS	liquid-liquid	45
80	TBPC	liquid-liquid	93
81	DCHC	liquid-liquid	79

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[*]The esterification reaction of POLYMER 1 with CFC in the presence of a PTC catalyst was carried out in a $CHCl_3$-H_2O(5 mL/0.5 mL) or in a pure $CHCl_3$ two phase (solid-liquid) systems at 60°C with a stirring rate of ca. 200 rpm for 40 h. The CH_2Cl/CFC/PTC molar ratio used was 1/1.5/1.
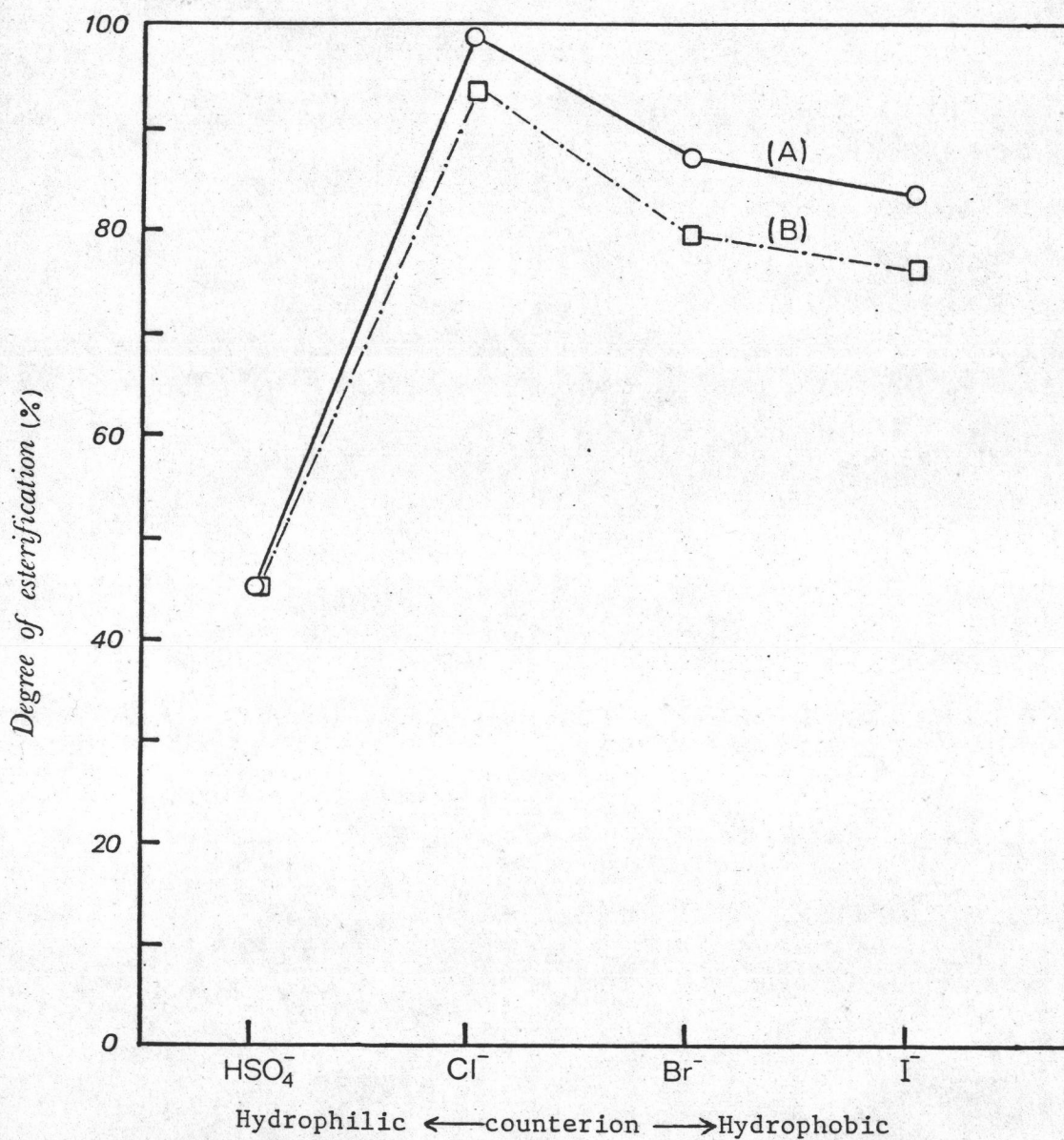
Fig.22. Relation between the degree of esterification and the paired ion of tetrabutylammonium in the liquid-liquid and the solid-liquid two-phase systems. The reaction of polymer 1 (0.3 mmol) in chloroform(5mL) with CFC (0.45 mmol) or an aqueous solution of CFC (0.45 mmol in distilled water (0.5 mL)) in the presence of Bu_4NX (0.3 mmol) was carried out at $60^{\circ}C$ for 40 h.

(A) liqiud-liquid; (B) solid-liquid

As shown in Table 13, TBPB, which is a quaternary phosphonium salt, shows a relatively lower catalytic activity than TBAC both in the solid-liquid and liquid-liquid two-phase systems. However, the catalytic activity of DCHC is much lower than that of TBAC or TBPC.

In order to understand why the catalytic activity of DCHC is much lower than that of TBAC, the molecular structure of DCHC [20] along with its estimated cavity and the ionic diameter of a cesium ion [19] must be considered.
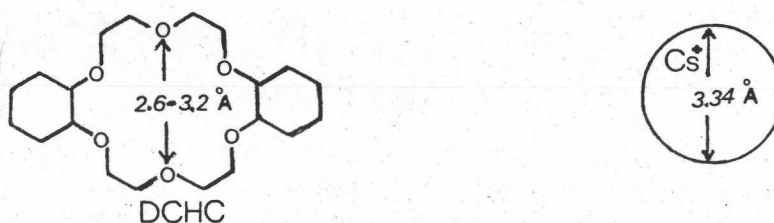
Since the size of the cesium ion is too large to fit into the cavity of DCHC, the DCHC-cesium complex is not so stable and the efficiency of this complex to carry a ferrocenecarboxylate anion into the organic phase is rather low. Therefore, the degree of esterification of POLYMER 1 in this case is much lower than in the case of using TBAC as a catalyst.

The results in Table 13 not only suggest that the distribution of the catalyst cations between organic and aqueous phases depends on the organic structure of the cation, but also on the nature of the anion associated with the cation. Application of the HSAB concept to the esterification reaction of POLYMER 1 leads to the conclusion that the hard acid (quaternary

ammonium salt) is more effective with the hard base, $CpFeCpCOO^-$.
Consequently, the order of the catalytic activity is as
follows: TBAC > TBPC > TBAB > TBAI > DCHC > TBAS.

4.7) Effect of the reaction system

The results from this study show that the degree of
esterification obtained from the liquid-liquid two-phase system
is normally higher than that from the solid-liquid two-phase
system. One of the reasons for this seems to be the difference
in interfacial area available for the anion exchange reaction.
In the liquid-liquid two-phase system, the interfacial area of
small droplets of an aqueous phase dispersing in the organic
phase is higher than the interfacial area of the solid reagent
in the solid-liquid two phase system. Another reason is the
thermal decomposition of CFC reagent in the solid-liquid two
-phase system is higher than that in the liquid-liquid system.
Whereas the solid CFC in the solid-liquid two-phase system tends
to receive heat directly from an oil bath and decomposes more
readily, an aqueous CFC dispersing in the organic phase
receives heat from the solvent.

In conclusion the results suggest that the esterifica-
tion reaction of POLYMER 1 with CFC using PTC as a catalyst in
the liquid-liquid two-phase system is superior to the reaction
in the solid-liquid two-phase system.

94

4.8) Effect of the polymer structure

The conditions and results of the reaction between
POLYMER 1-3 and CFC are summarized in Tables 14 through 16.
Tables 14 and 15 show the effect of the polymer structure on the
esterification reaction at 30°C and 60°C respectively. These
results are also illustrated in Fig.23 and 24. The figures
indicate that the degree of esterification increased in the
following order: POLYMER 1 > POLYMER 2 > POLYMER 3.

The data of Table 16 show that the degree of esterifica-
tion in the liquid-liquid two-phase systems was higher than or
equal to that in the solid-liquid two-phase system. The diffe-
rence in the degree of esterification in the liquid-liquid two-
phase system of the three polymers at 30°C and 60°C is clearly
shown in Fig 23 and 24. These results indicate that POLYMER 1
has a higher reactivity than those of POLYMER 2 and 3.
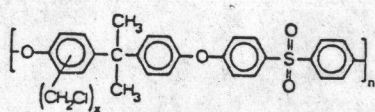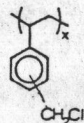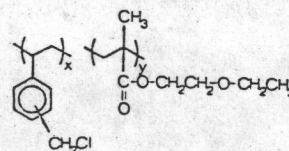
POLYMER 1   POLYMER 2   POLYMER 3

By considering the structures of POLYMER 1 and POLYMER 2,
it is clearly that POLYMER 1 should have more steric hindrance in
structure than those of POLYMER 2. This is due to the further

TABLE 14 Effect of polymer structure on esterification reaction of POLYMER 1-3 with cesium ferrocenecarboxylate in a liquid-liquid two-phase system at 30°C*

no	polymer structure	time (h)	degree of esterification
82	POLYMER 1	5	22
83	POLYMER 1	10	27
84	POLYMER 1	20	44
85	POLYMER 1	40	58
86	POLYMER 2	5	10
87	POLYMER 2	10	12
88	POLYMER 2	20	24
89	POLYMER 2	40	33
90	POLYMER 3	5	3
91	POLYMER 3	10	5
92	POLYMER 3	20	8
93	POLYMER 3	40	16

*The esterification reaction of POLYMER 1-3 with CFC in the presence of TBAC as a PTC catalyst was carried out in a $CHCl_3-H_2O$(5 mL/0.5 mL) two phase system with a stirring rate of ca. 200 rpm. The CH_2Cl/CFC/TBAC molar ratio used was 1/1.5/1.

POLYMER 1 : chloromethylated polysulfone

POLYMER 2 : poly(vinylbenzyl chloride)
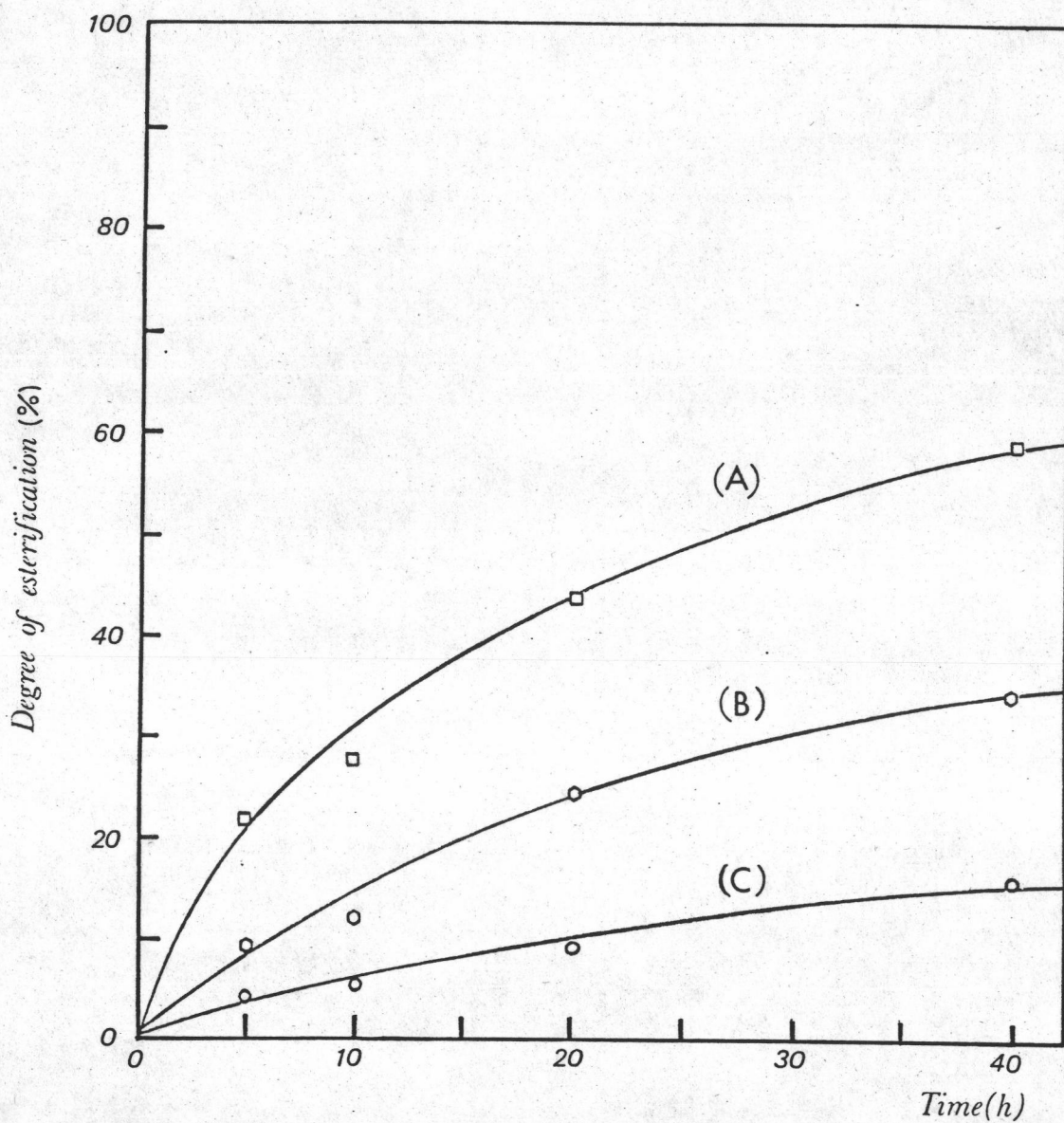
POLYMER 3 : poly(VBC-co-2-EEMA)

Fig. *23.* Effect of the polymer structure on esterification
reaction in a liquid-liquid two-phase system using TBAC
as a PTC. The reaction of polymer in chloroform with
an aqueous solution of CFC in the presence of TBAC was
carried out at $30^{\circ}C$ and the $CFC/-CH_2Cl/TBAC$ molar
ratio was 1.5/1/1

(A)polymer 1; (B)polymer 2; (C)polymer 3

TABLE 15 Effect of polymer structure on esterification
reaction of POLYMER 1-3 with cesium ferrocenecarboxylate in a
liquid-liquid two-phase system at 60°C*

no	polymer structure	time (h)	degree of esterification
94	POLYMER 1	2	56
95	POLYMER 1	5	68
96	POLYMER 1	10	82
97	POLYMER 1	20	92
98	POLYMER 1	40	99
99	POLYMER 2	2	25
100	POLYMER 2	5	38
101	POLYMER 2	10	54
102	POLYMER 2	20	64
103	POLYMER 2	40	80
104	POLYMER 3	2	13
105	POLYMER 3	5	24
106	POLYMER 3	10	30
107	POLYMER 3	20	53
108	POLYMER 3	40	70

*The esterification reaction of POLYMER 1-3 with CFC
in the presence of TBAC as a PTC catalyst was carried out in a
$CHCl_3-H_2O$(5 mL/0.5 mL) two phase system with a stirring rate of
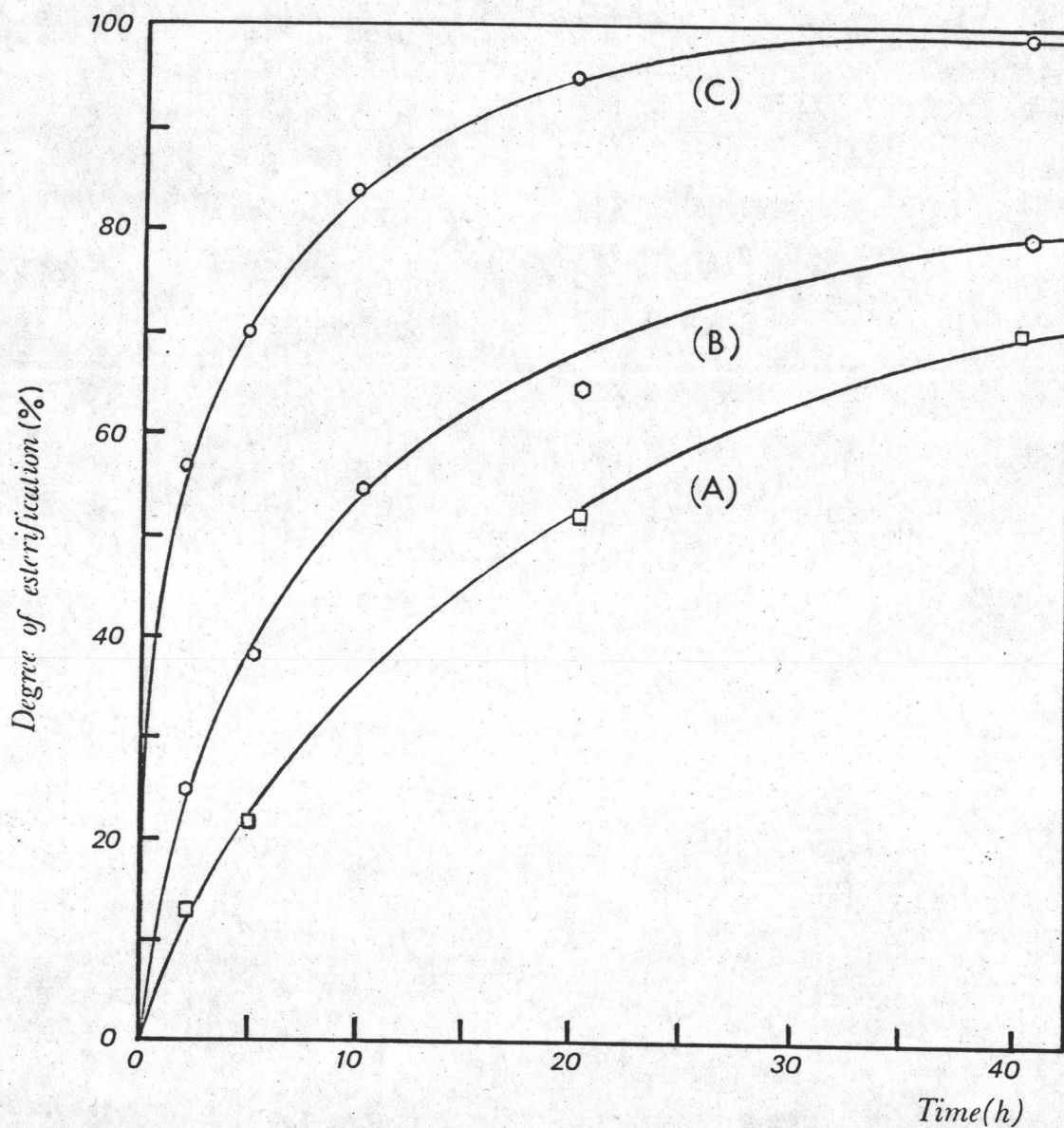ca. 200 rpm. The $-CH_2Cl$/CFC/TBAC molar ratio used was 1/1.5/1.

Fig.24. Effect of the polymer structure on esterification reaction in a liquid-liquid two-phase system using TBAC as a PTC. The reaction of polymer in chloroform with an aqueous solution of CFC in the presence of TBAC was carried out at 60°C and the CFC/-CH$_2$Cl/TBAC molar ratio was 1.5/1/1

(A)polymer 1; (B)polymer 2; (C)polymer 3

TABLE 16   Effect of polymer structure on esterification
reaction of the chloromethylated polymer with cesium
ferrocenecarboxylate in a two-phase system[*]

no	polymer structure	reaction two-phase system	degree of esterification
109	POLYMER 1	solid-liquid	93
110	POLYMER 2	solid-liquid	80
111	POLYMER 3	solid-liquid	71
112	POLYMER 1	liquid-liquid	99
113	POLYMER 2	liquid-liquid	80
114	POLYMER 3	liquid-liquid	70
115	POLYMER 2	liquid-liquid[a]	33
116	POLYMER 3	liquid-liquid[a]	16
117	POLYMER 2	liquid-liquid[b]	7
118	POLYMER 3	liquid-liquid[b]	3

[*]The esterification reaction of POLYMER 1-3 with CFC in the
presence of TBAC as a PTC catalyst was carried out in a $CHCl_3$-
H_2O(5 mL/0.5 mL) or in a pure $CHCl_3$ two-phase (solid-liquid)
system at 60°C with a stirring rate of ca. 200 rpm for 40 h.
The CH_2Cl/CFC/PTC molar ratio used was 1/1.5/1.

[a]The reaction temperature was 30°C.

[b]The reaction temperature was 30°C and toluene was used as
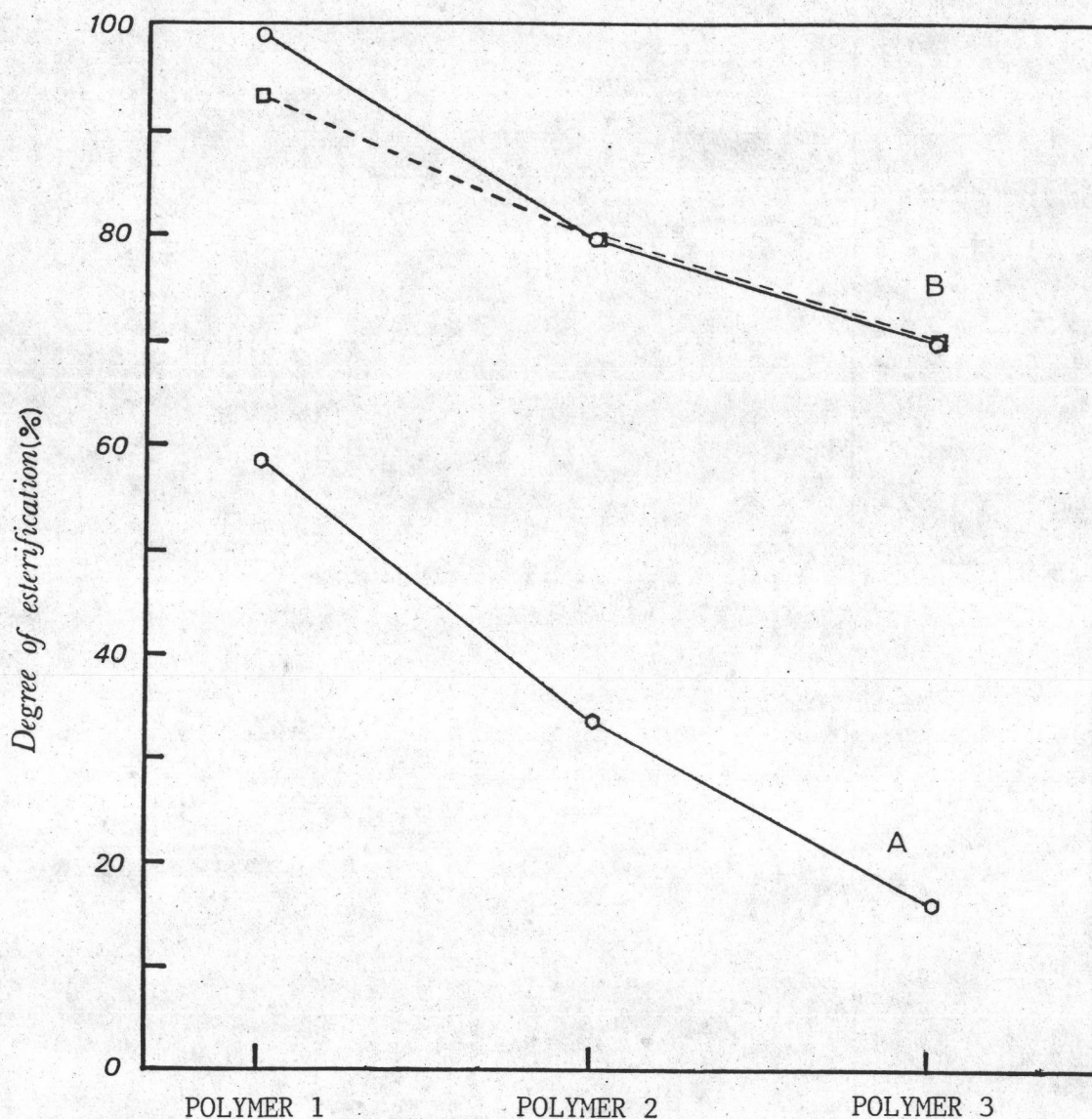   solvent.

Fig.25. Relation between the degree of esterification and
the polymer structure in the solid-liquid and the
liquid-liquid two-phase systems using TBAC as a PTC.
The reaction of polymer in chloroform with CFC or an
aqueous solution of CFC in the presence of TBAC was
carried out at (A) $30^{o}C$; (B) $60^{o}C$ for 40 h.
The $CFC/-CH_2Cl/TBAC$ molar ratio used is 1.5/1/1.

————liqiud-liquid; ————solid-liquid

position of the chloromethyl group in POLYMER 2 from the polymer backbone than that in POLYMER 1. However, the results also show that POLYMER 2 has a lower reactivity than POLYMER 1. The reason for these results is the effect of polymer coiling. POLYMER 1 has a more rigid-backbone (T_g= 164°C) which makes its chloromethyl group more exposed to the reagent and it is therefore more readily attacked by the reagent than the chloromethyl groups of POLYMER 2 (T_g= 66°C).

In case of the reactivity of POLYMER 2 (T_g=66°C) and 3 (T_g=28°C), the steric effect and coiling effect are the the major factors in their chloromethyl groups being attacked by the reagent. The coiling effect occurs in POLYMER 3 more than in POLYMER 2 and the bulky side groups of POLYMER 3 also provide steric hindrance to their chloromethyl groups from being attacked by the reagent, and therefore these polymers have lower reactivity than POLYMER 2.

5) Determination of iron in the ferrocenecarboxymethylated polymers

The method for iron determination developed by Rosenberg and Riber [68] was used with some modifications.

5.1) Preparing a calibration curve for iron determination
The procedure for preparing a calibration curve is

described in the experimental part. In the standard solution, hydrogen peroxide and dilute nitric acid are used to oxidize ferrous ion to ferric ion according to equation (4.17).

$$2Fe^{2+} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{3+} + 2H_2O \qquad (4.17)$$
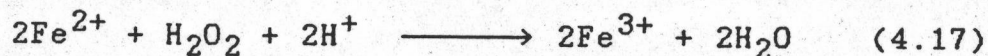
Furthermore, strong nitric acid can prevent the hydrolysis of ferric ion as in equation (4.18).

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ \qquad (4.18)$$
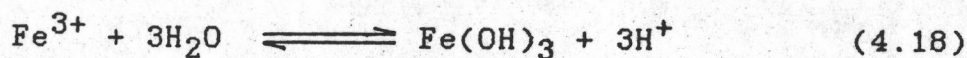
Ferric ion will form a characteristic blood-red complex with excess thiocyanate as in equation (4.19).

$$Fe^{3+} + 6SCN^- \longrightarrow Fe(SCN)_6^{3-} \qquad (4.19)$$

$$\text{excess} \qquad\qquad \text{blood-red solution}$$
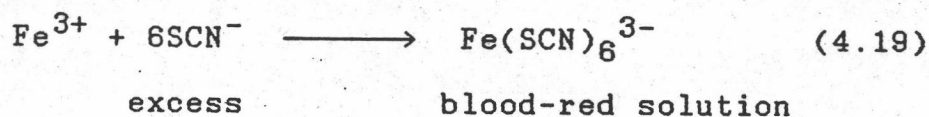
The optical densities of the blood-red solution were measured at 480 nm in 1 cm cell in a UV-spectrophotometer. Table 17 shows the optical densities of the complex obtained by using 1 to 5-mL aliquots of the standard solution. A plot of optical density against concentration resulted in a straight line as shown in Fig. 26.

TABLE 17   The absorption data for the determination of iron

mL of the standard solution (corresponds to the concentration of Fe^{3+} x 1.75×10^{-5}M)	Absorbance at 480 nm
1.0	0.155
2.0	0.314
3.0	0.464
4.0	0.617
5.0	0.785

The percent confidence by the least-square method is 0.999.

5.2) Determination of iron

The procedure used for determination of iron was described in the experimental part.   The ferrocene polymer was digested with concentrated nitric acid and hydrogen peroxide in a Kjedahl flask until a clear colorless solution was obtained. The digestion time depends on the nature of polymer.   It was found that the digestion time for POLYMER 1 was 24 h while the digestion time for POLYMER 2 and 3 was 36 h.

The percent iron and conversion of the esterification product were calculated from equations (4.20) and (4.21), respectively.
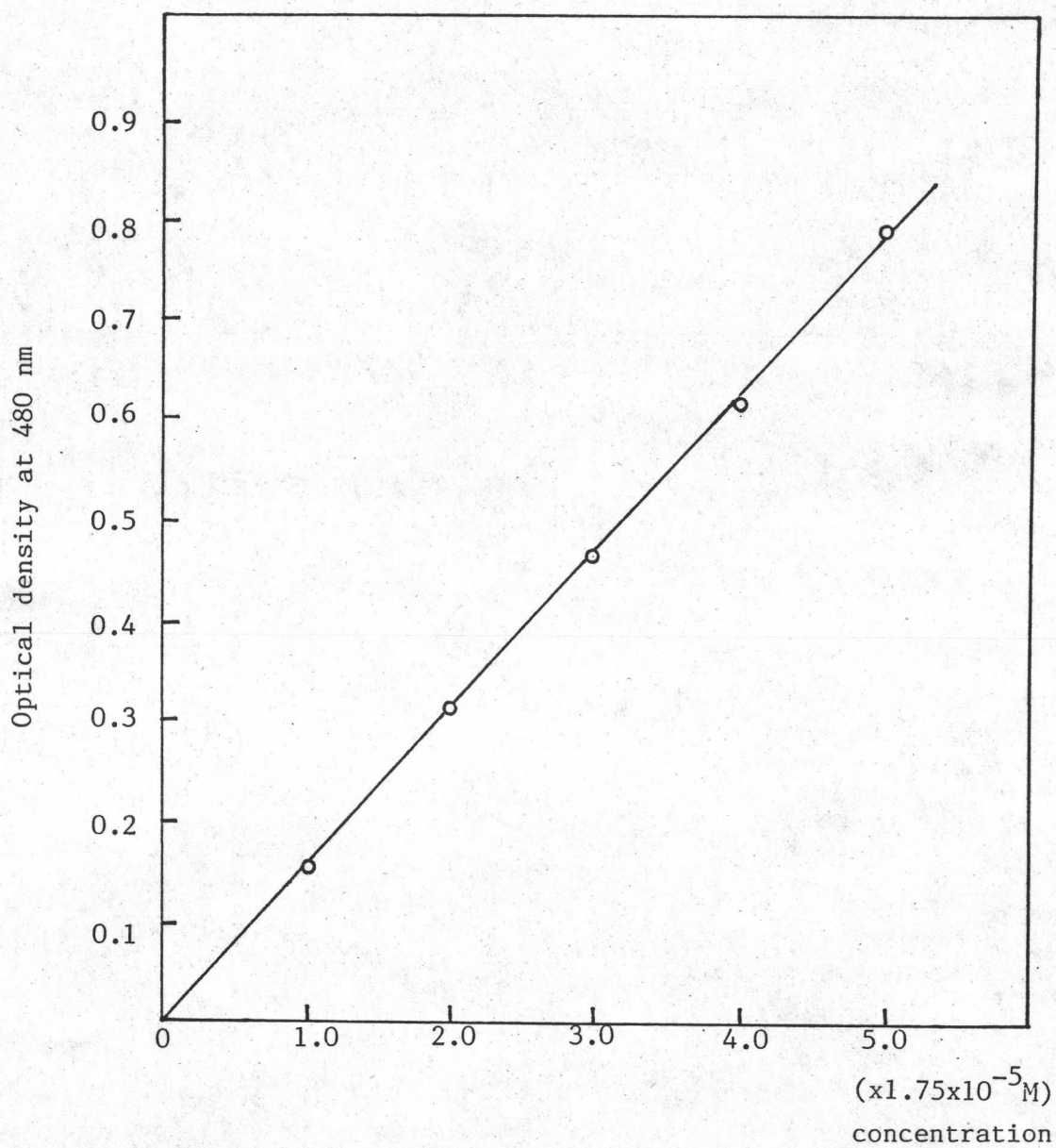
Fig. 26 Plot of optical density against concentration of iron.

$$\%Fe = \frac{50 \times 50 \times 55.847 \times 100 \times C}{10 \times 1000 \times W} \qquad (4.20)$$

C: the concentration of Fe obtained from

the calibration curve

W: the weight of used polymer

$$\%\text{Conversion} = \frac{\%Fe\ \underline{(experimental)} \times 100}{\%Fe\ (theoretical)}$$

$$(4.21)$$

The calculation of %Fe (theoretical; based on %Cl of chloromethylated polymer) and an example for iron determination are shown in Appendix E. The %Fe (theoretical) in POLYMERS 1, 2 and 3 are 10.77, 16.13 and 11.21, respectively.

6) Determination of the viscosity of polymers

Polymer solutions at various concentrations were prepared by dissolving a known amount of polymer in chloroform and then filtering the solution. The flow times of these polymer solutions and of a solvent were measured in the Ostwald viscometer at 25°C. The results of these measurements are shown in Tables 18 through 20.

The specific viscosity (η_{sp}) of the polymer solution is obtained by using equation (4.22):

$$\eta_{sp} = \frac{t - t_o}{t_o} \qquad (4.22)$$

(where t and t_o are the flow times of polymer solution and of pure solvent respectively).

The reduced specific viscosity (η_{red}) is the specific viscosity per unit concentration as in equation (4.23):

$$\eta_{red} = \eta_{sp}/c \qquad (4.23)$$

(where c is the concentration of the polymer solution).

The intrinsic viscosity [η] is the reduced specific viscosity at infinite dilution and is defined as present in equation (4.24).

$$[\eta] = \lim_{c \to 0} \eta_{sp}/c \qquad (4.24)$$

In practice, as in this experiment, the intrinsic viscosity of a polymer solution is obtained by extrapolating the plot of $_{sp}$ against c to zero concentration as shown in Fig.27, 28 and 29. The intrinsic viscosities [η] at 25°C of POLYMER 1, 2 and 3 obtained by this method are 0.54, 0.51 and 0.83 dL/g, respectively.

TABLE 18 The determination of the viscosity of POLYMER 1

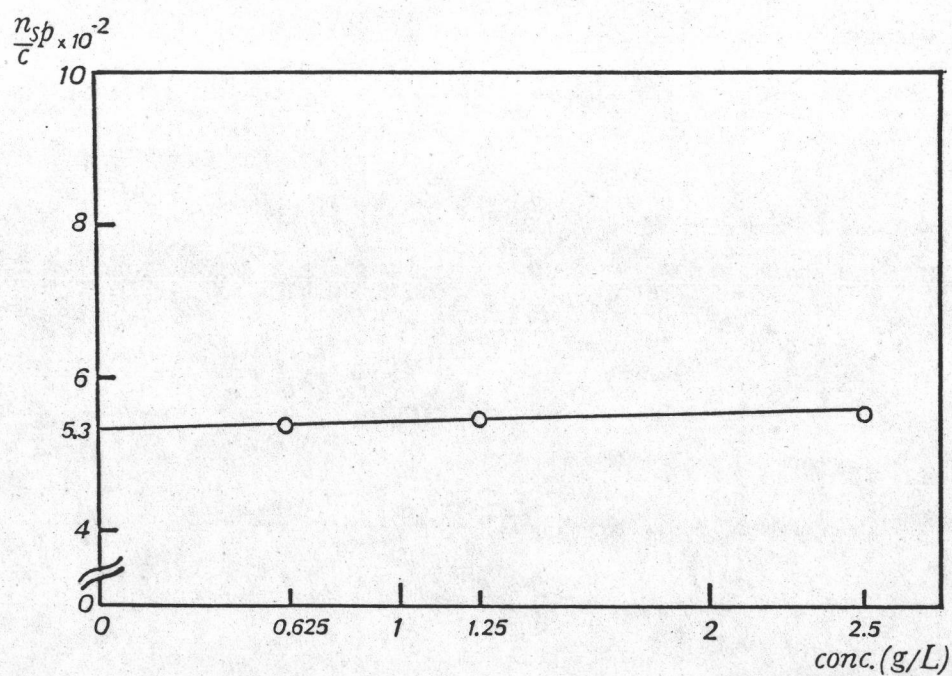|	flow time of chloroform	concentration (g/L) of polymer in chloroform			
Polymer 1	181.2	0.625	1.25	2.50	5.00
avr.flow time (sec) ,t		187.2	193.6	206.0	228.6
η_{sp} $\frac{(t-t_o)}{t_o}$		.033	.0684	.137	.267
$\frac{\eta_{sp}}{c}$		.0529	.0547	.0548	.0524

Fig.27. Plot of η_{sp}/c against concentration of POLYMER 1 solution

TABLE 19 The determination of the viscosity of POLYMER 2

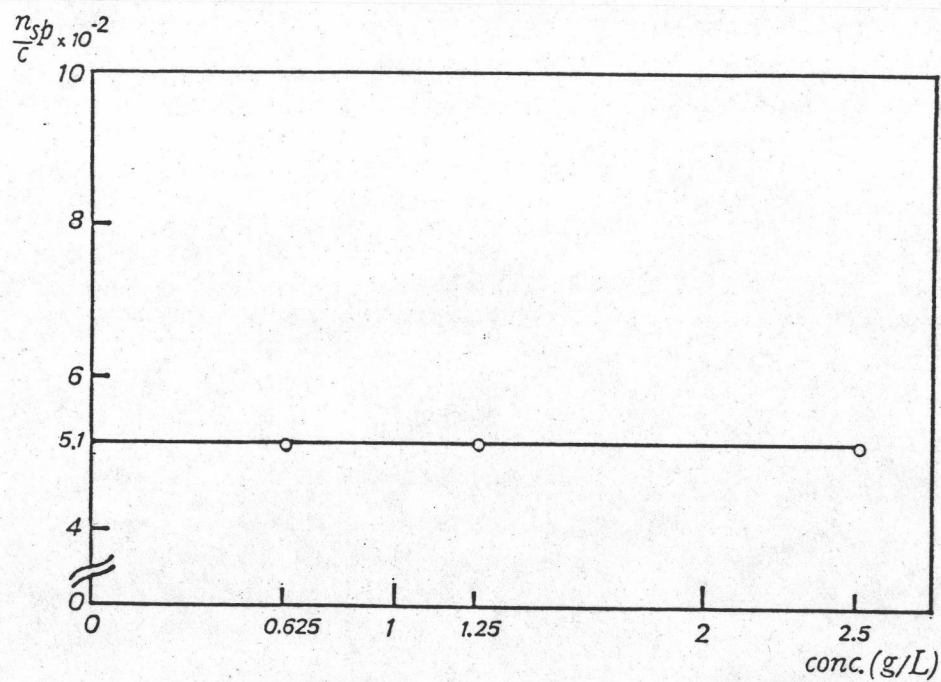|	flow time of chloroform	concentration (g/L) of polymer in chloroform			
Polymer 2	181.3	0.625	1.25	2.50	5.00
avr.flow time (sec) ,t		187.2	192.9	204.0	227.6
$\eta_{sp} \frac{(t-t_o)}{t_o}$		.032	.064	.125	.254
$\frac{\eta_{sp}}{c}$		.0512	.0512	.0500	.0510

Fig.28. Plot of η_{sp}/c against concentration of
POLYMER 2 solution

TABLE 20   The determination of the viscosity of POLYMER 3

	flow time of chloroform	concentration (g/L) of polymer in chloroform			
Polymer 3	181.3	0.625	1.25	2.50	5.00
avr. flow time (sec) , t		190.9	201.5	224.6	271.3
η_{sp} $\frac{(t-t_o)}{t_o}$		.053	.1116	.239	.4962
$\frac{\eta_{sp}}{c}$		.0844	.0893	.0954	.0992
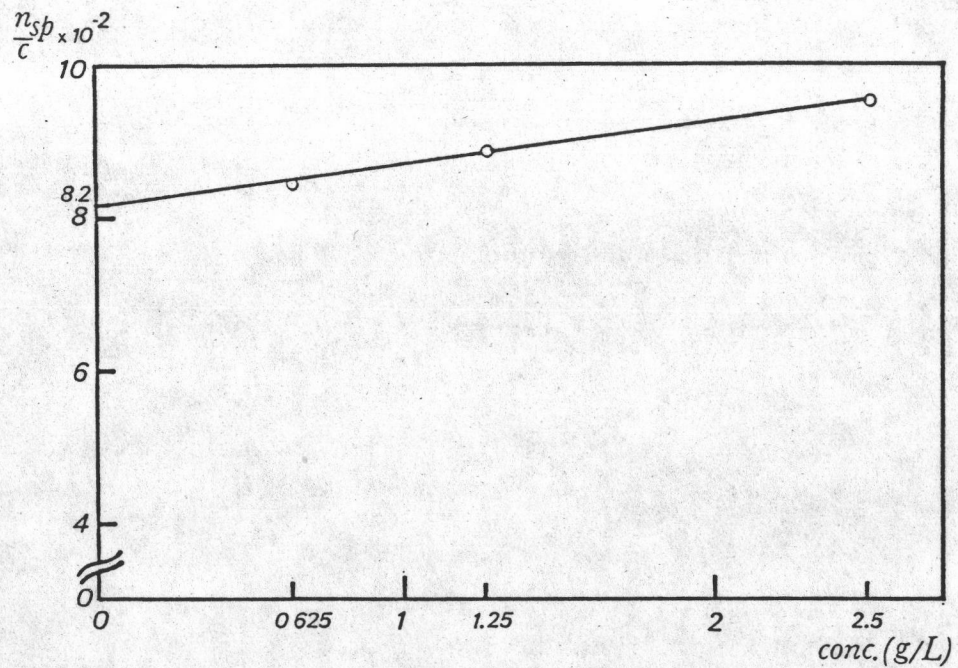
Fig.29. Plot of η_{sp}/c against concentration of
POLYMER 3 solution