# Chapter IV

Results and Discussions

4.1 Synthesis of p-Chloromethylstyrene

In this research work, p-chloromethylstyrene was synthesized using the method of Kondo et al [36]. This involved two steps of reactions, chloromethylation of 2-phenylethyl bromide and dehydrobromination of p-(2-bromoethyl)benzyl chloride as following.

4.1.1 Chloromethylation of 2-Phenylethyl bromide

Therefore, the chloromethylation of 2-phenylethyl bromide was performed by reaction with hydrogen chloride gas and paraformaldehyde in the presence of anhydrous $ZnCl_2$ as a catalyst.
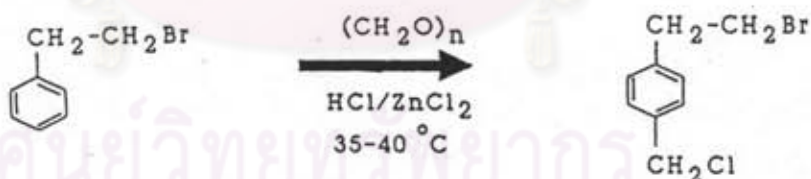

Though it was reported that chloromethyl methyl ether was often employed in the chloromethylation of aromatic compound, this reagent now is known to be highly carcinogenic. Therefore, it was not used in this study.

48% yield of white crystal product was obtained after the fourth recrystallization, while 51% was obtained after the second recrystallization in the method by Kondo et al.

From several repetitions of these experiments, the
factors effected the yield of the product could be concluded.
First, the starting material, 2-phenylethyl bromide, must be of
high purity. Less product will be obtained if the starting
material was slightly brown. The purity of paraformaldehyde and
anhydrous $ZnCl_2$ was also necessary. It was found that the yield
of the product decreased if either of them retained moisture.
Especially, in the case of anhydrous $ZnCl_2$ which was a catalyst,
moisture reduced its reactivity.

The proposed mechanism of this reaction was shown in
Scheme 4.1 [37, 38].
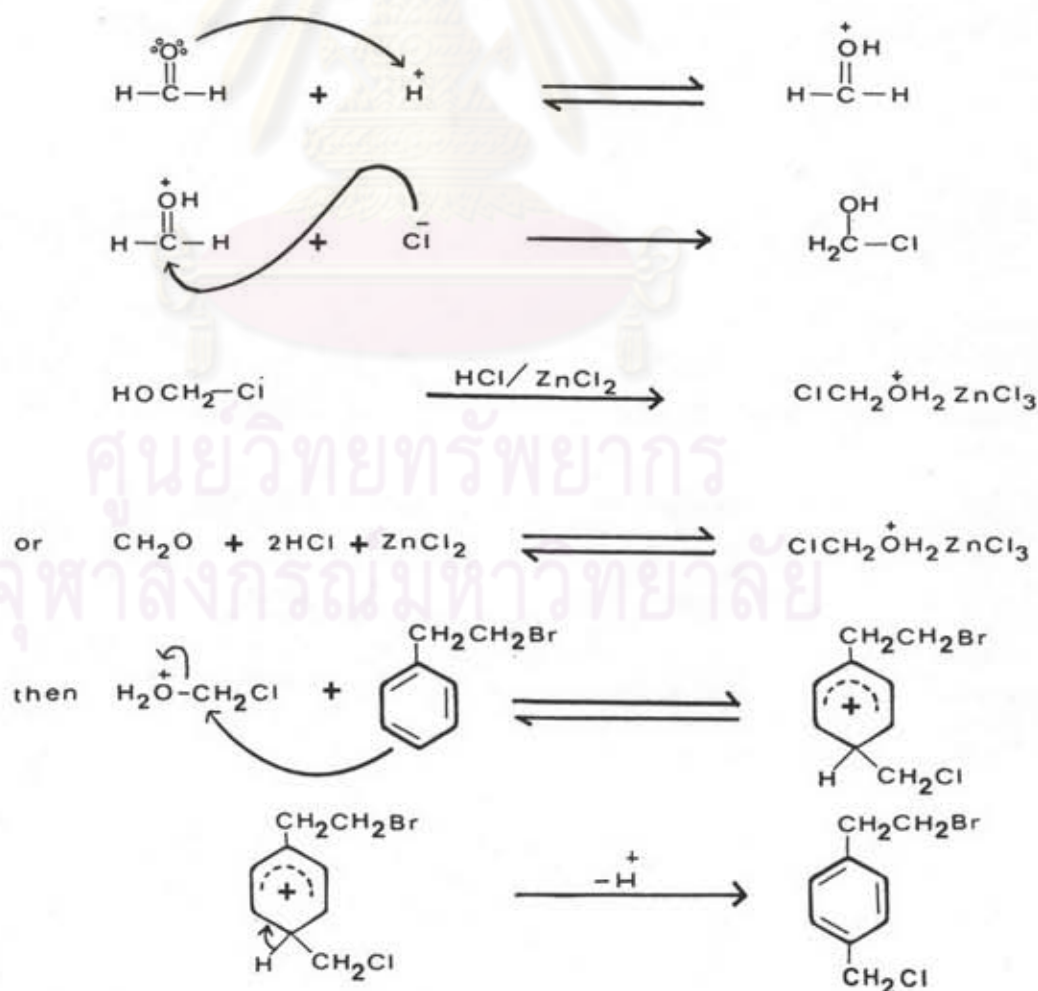
Scheme 4.1

Actually, o-(2-bromoethyl)benzyl chloride was formed as by product,but it could easily be separated by a few consecutive recrystallization from petroleum ether (bp 40-60°C). After fourth recrystallization, only little amount of o-(2-bromoethyl)benzyl chloride (3.5%) remained as shown in the gas chromatogram at the retention time 8.8 minutes (Figures 4.1).
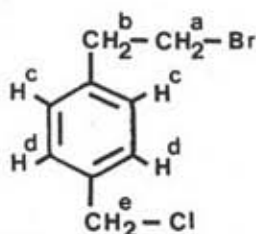
IR(KBr) spectrum of p-(2-bromoethyl)benzyl chloride was exhibited in Figure 4.2. It was clearly shown that C-Cl bending appeared at ν 1270 cm^{-1} and C-Cl stretching at ν 660 cm^{-1} which indicated the appearance of the chloromethyl group in the molecule comparing to the absence of such absorption bands in the IR spectrum of 2-phenylethyl bromide (Figure 4.3). The other absorption bands in Figure 4.2 were interpreted in details in Table 4.1.

Table 4.1 The assignment for the IR spectrum of p-(2-bromoethyl)
benzyl chloride.

Absorption frequency $\nu\,(cm^{-1})$	Assignment
3040	C–H str. aromatic
2970	C–H str. aliphatic
1930	overtone region
1810	of aromatic ring
1695	
1270	C-Cl bending ($-CH_2-Cl$)
1220	C-Br bending ($-CH_2-Br$)
850	= C-H out of plane bending (p-disubstituted aromatic)
680–660	C-Cl str.
630	C-Br str.

Furthermore, the ^{1}H NMR spectrum (Figure 4.4) of this product also showed two doublets in the aromatic region at δ 7.24 and 7.38 ppm which was the characteristic of para-substitution of the aromatic compound. The other signals were assigned in details in Table 4.2

p-(2-bromoethyl)benzyl chloride

Table 4.2   The assignment for the ^{1}H NMR spectrum of
              p-(2-bromoethyl)benzyl chloride.

Chemical shift δ (ppm)	Intensity	Assignment
7.38	d, 2H (8.36 Hz)	H^d, aromatic ring
7.24	d, 2H (8.1 Hz)	H^c, aromatic ring
4.57	s, 2H	$-CH_2-Cl$
3.55	t, 2H (J=7.1 Hz)	$-CH_2-Br$
3.16	t, 2H (J=6.6 Hz)	$-CH_2-$

Since chlorine was more electronegative than bromine, two
protons at the ortho-positions to chlorine (H^d) were more
strongly deshielded than the other two protons close to bromine
(H^c). Therefore, a doublet at δ 7.38 ppm was assigned to H^d
protons, the other at δ 7.24 ppm was assigned to H^c protons.

In addition, the ^{13}C NMR spectrum (Figure 4.5) indicated
the important carbon signal of chloromethyl group(-CH$_2$Cl) was at
δ 45.94 ppm. The other signals at 32.67, 38.84 ppm were the
signals of -^{b}CH$_2$- and -^{a}CH$_2$-Br, respectively and at
δ128.72-139.07 ppm corresponded to aromatic carbons. The spectrum
also showed that there were seven chemically distinct types of
carbons, the rest of four signals were of aromatic ring,
characteristic of para-disubsituted aromatic compound.

Consequently, the ^{13}C NMR spectrum confirmed the structure of p-(2-bromoethyl)benzyl chloride.

Table 4.3   The assignment for the ^{13}C NMR spectrum of p-(2-bromoethyl)benzyl chloride.

Chemical shift δ (ppm)	Assignment
32.67	$-^{b}CH_2-$
38.84	$-^{a}CH_2-Br$
45.94	$-^{g}CH_2-Cl$
128.72	$-^{d}CH=$ (aromatic ring)
128.94	$-^{e}CH=$ (aromatic ring)
136.03	$-^{c}C=$ (aromatic ring)
139.07	$-^{f}C=$ (aromatic ring)

The Mass spectrum (Figure 4.6) of this compound showed a molecular ion (M^{+}) at m/e 232 and the base peak at m/e 117 which was the fragmentation from molecular ion by the loss of Cl atom and HBr. Other fragmentations were shown at m/e 197, 153, and

139. The peak at m/e 197 represented the loss of Cl radical from M^+ to yield a CH_2CH_2Br substituted tropylium ion. The loss of Br radical from M^+ was observed at m/e 153. Another fragmentation from M^+ was the peak at m/e 139 which derived from the loss of CH_2Br radical to give a CH_2Cl substituted tropylium ion. The mass fragmentation pattern was summarized in Scheme 4.2.
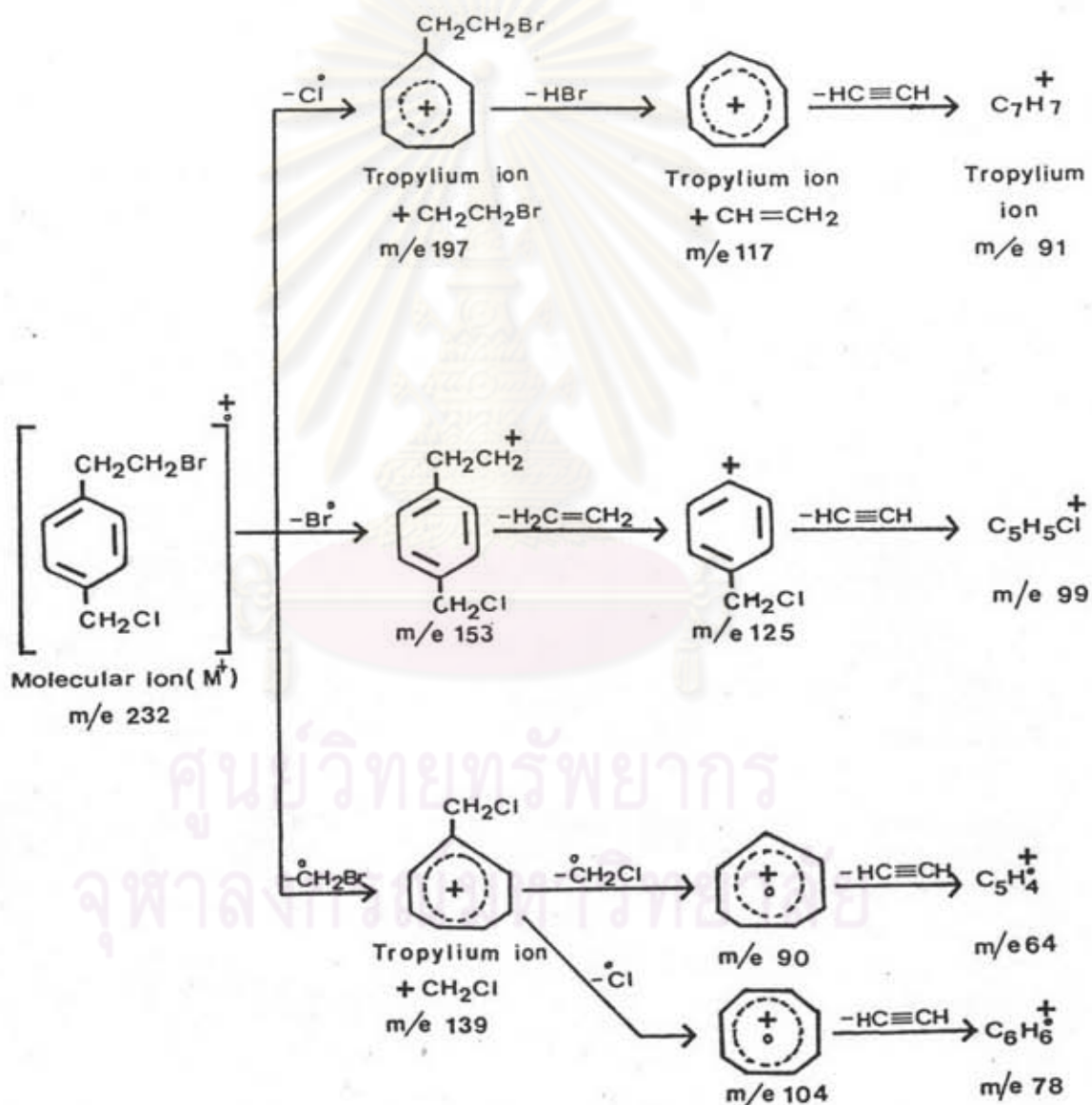
Scheme 4.2

From all of the data, some physical properties and spectroscopic technique (IR, NMR, Mass) confirmed that it was p-(2-bromoethyl)benzyl chloride.

A. After 1st recrystalization

6.983 min.

8.792 (10.8%)

R_t	peak area
6.983	55980
8.792	6046

B. After 2nd recrystalization

6.918 min.

8.725 (8.6%)

R_t	peak area
6.918	45850
8.725	3941

C. After 3rd recrystalization

6.998 min.

8.852 (5%)

R_t	peak area
6.998	55504
8.852	2775

D. After 4th recrystalization

6.972 minutes

8.813 (3.5%) minutes

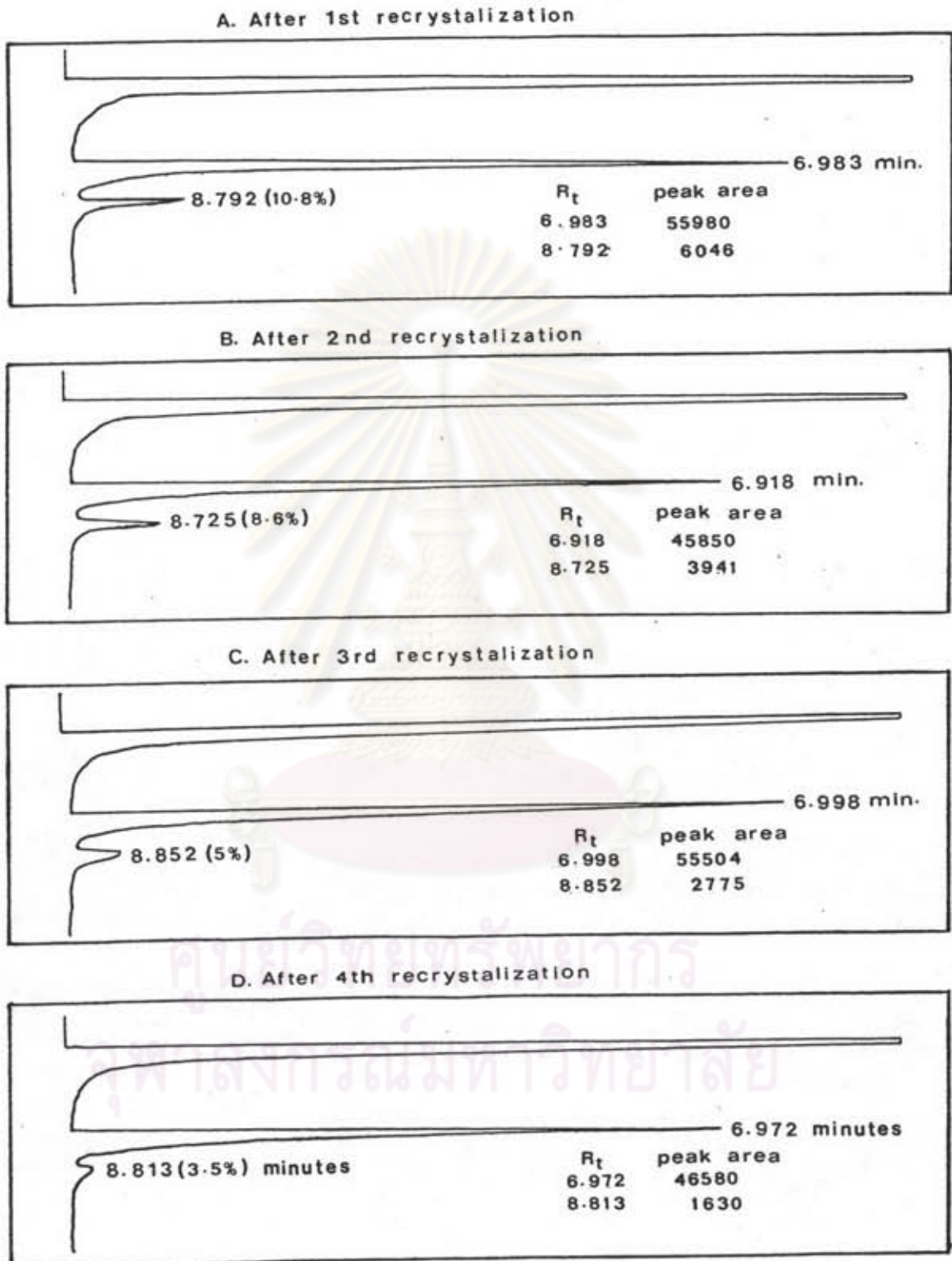| R_t	peak area
6.972	46580
8.813	1630

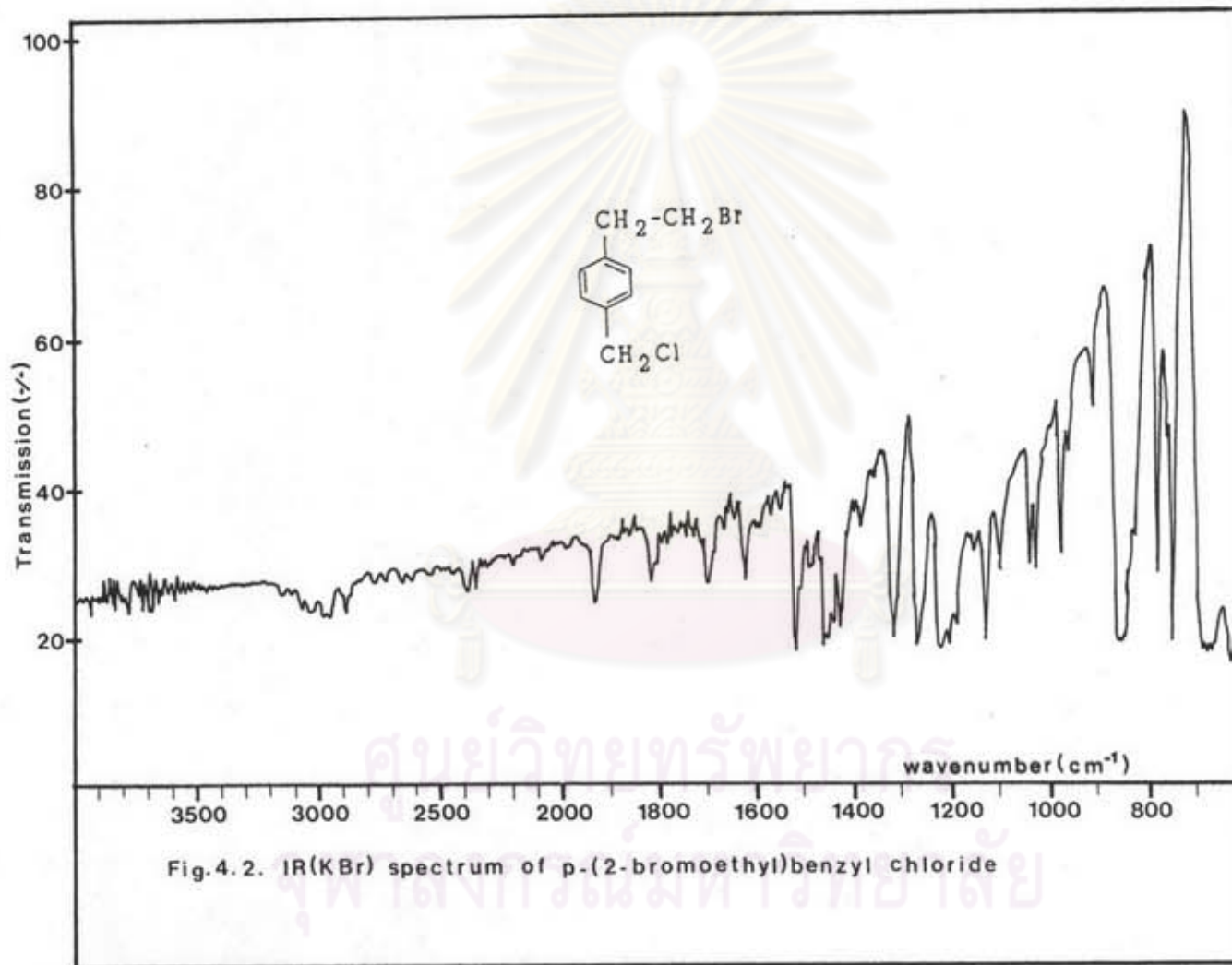Fig.4.1. Chromatogram of p-(2-bromoethyl)benzyl chloride after recrystalization

Fig.4.2. IR(KBr) spectrum of p-(2-bromoethyl)benzyl chloride

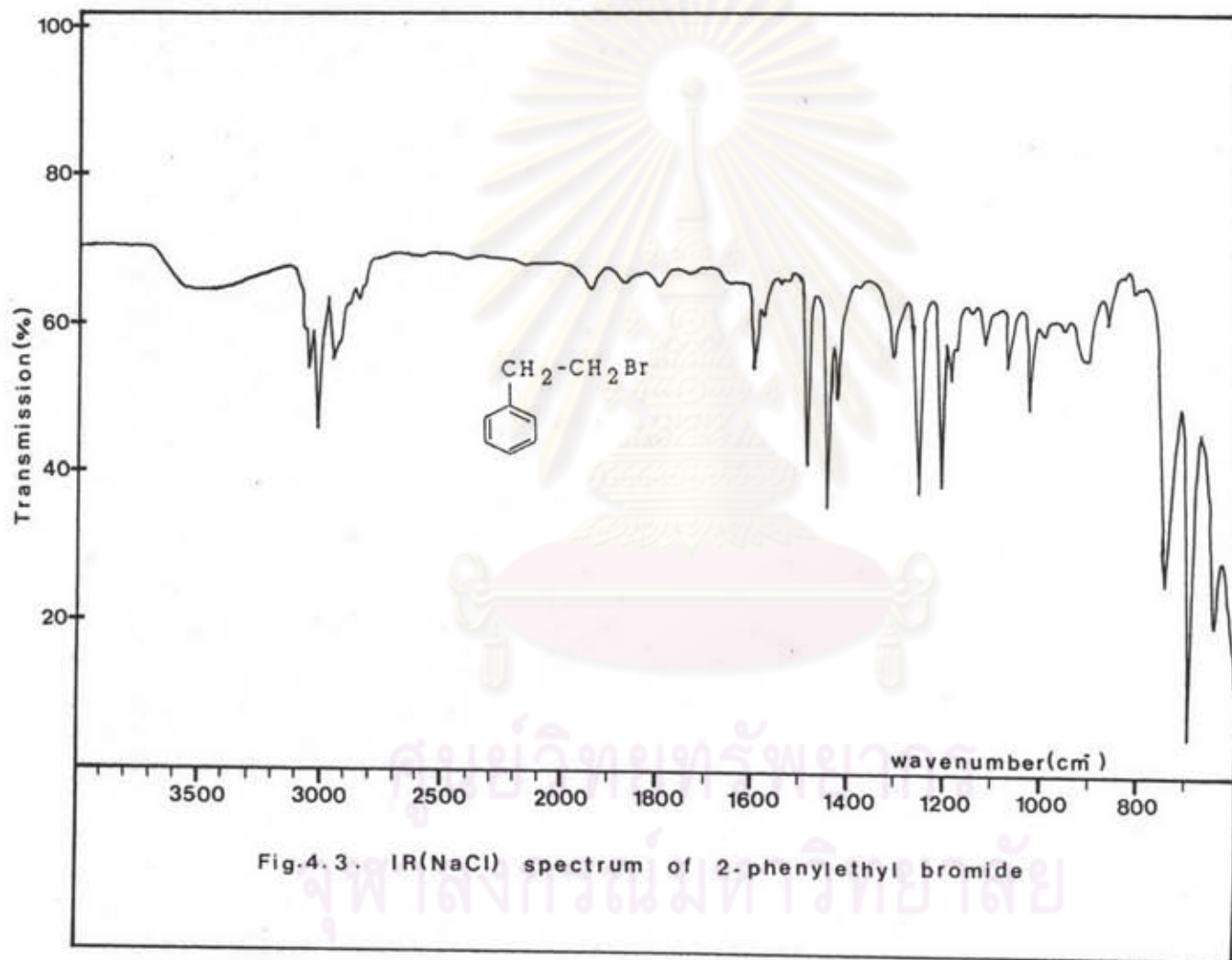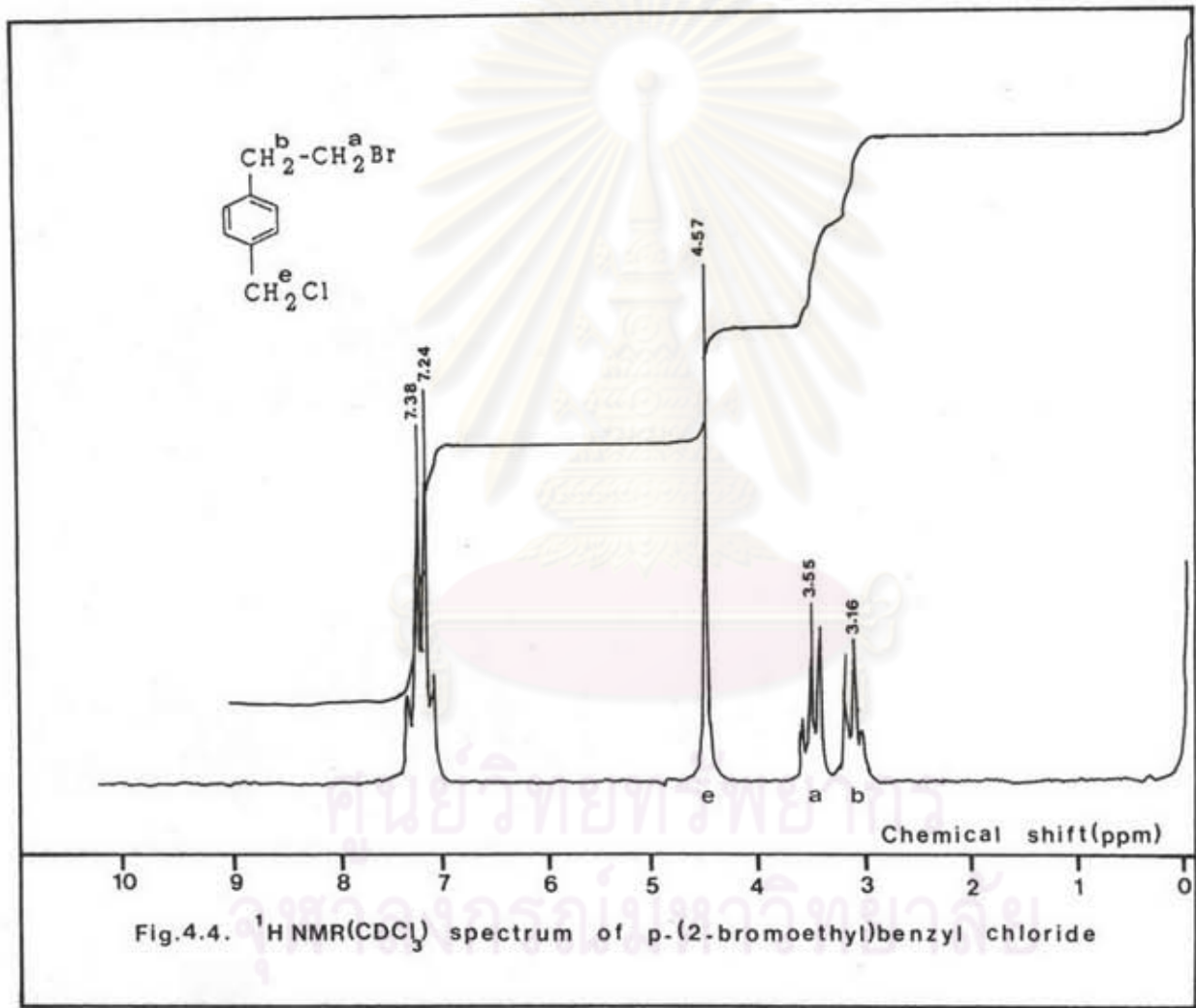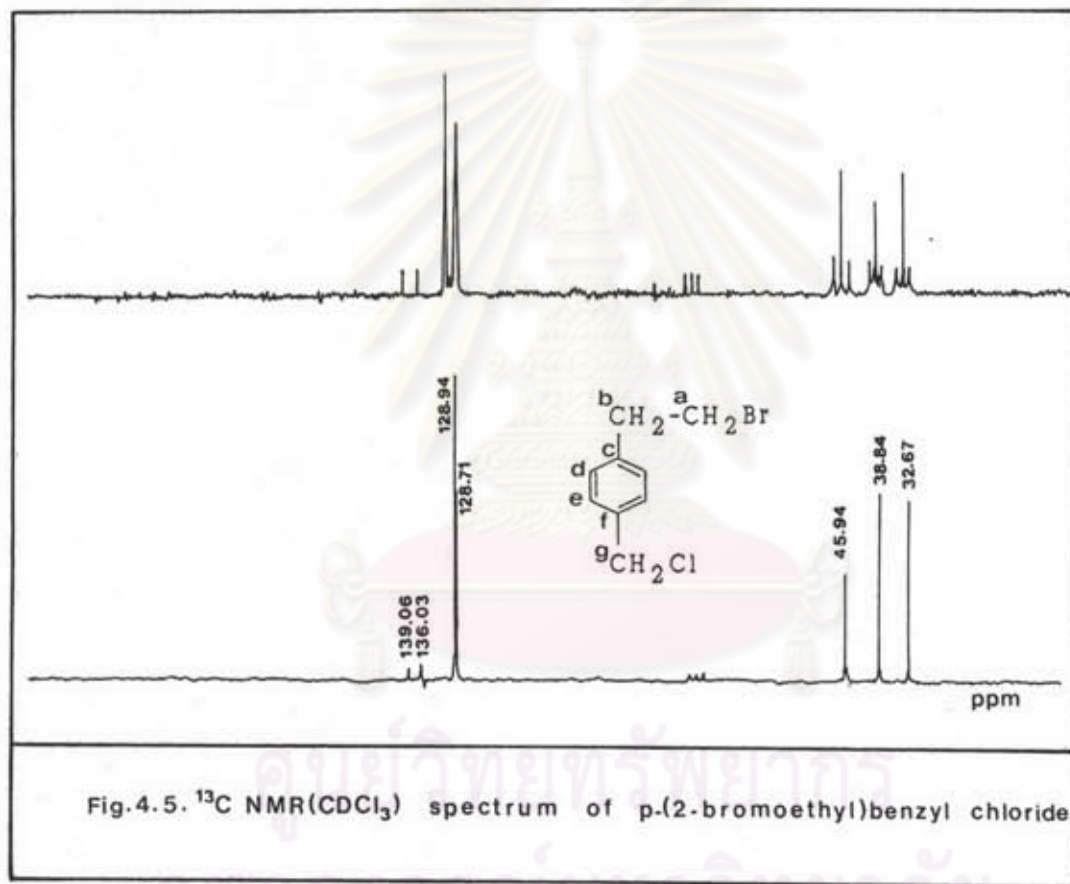Fig. 4.3. IR(NaCl) spectrum of 2-phenylethyl bromide

Fig.4.4. ^{1}H NMR(CDCl$_3$) spectrum of p-(2-bromoethyl)benzyl chloride

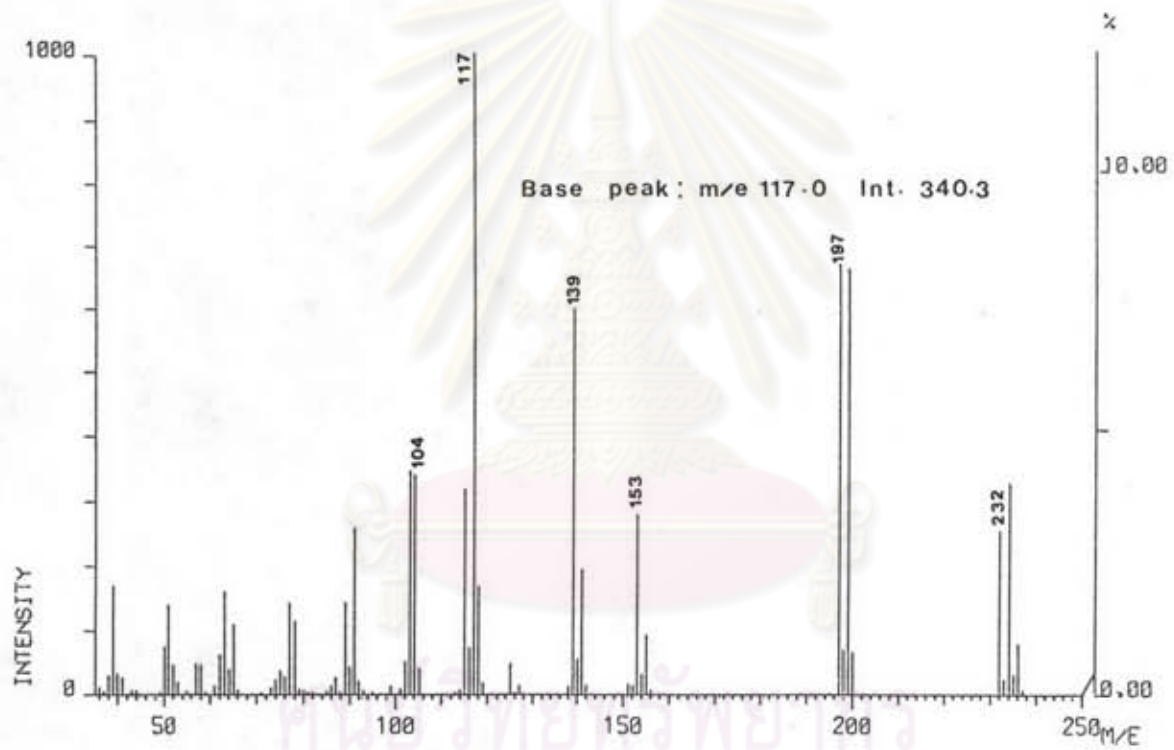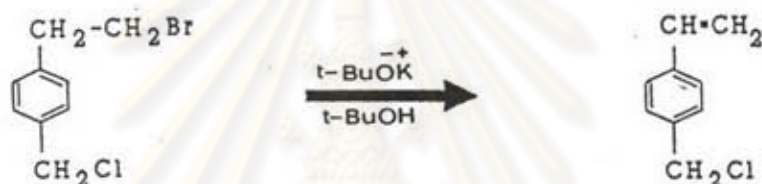Fig. 4.5. ^{13}C NMR(CDCl$_3$) spectrum of p-(2-bromoethyl)benzyl chloride

Fig.4.6. Mass spectrum of p-(2-bromoethyl)benzyl chloride

4.1.2 Dehydrobromination of p-(2-bromoethyl)benzyl chloride to p-chloromethylstyrene

After completing the dehydrobromination of p-(2-bromoethyl)benzyl chloride with potassium tert-butoxide at 35 °C for 2 hrs, p-chloromethylstyrene was obtained with bp 90-94 °C at 2 mmHg and 65% yield. Therefore, the yield of overall reactions from chloromethylation to dehydrobromination was 31.5%.   It was colorless with strong pungent.

It should be noted here that during the dehydrobromination, the formation of ether compound was sometimes occured by the reaction of p-chloromethylstyrene and potassium tert-butoxide.
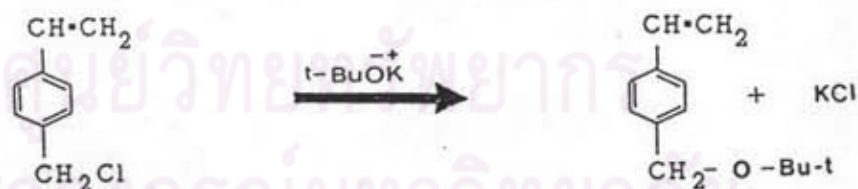
So the amount of potassium tert-butoxide should be carefully added in equivalent amount to that of p-(2-bromoethyl) benzyl chloride, and, while purification of the product under reduced pressure distillation was not performed over the temperature 90-94 °C at 2 mmHg. To avoid the ether compound came together with p-chloromethylstyrene. p-Chloromethylstyrene was so much reactive. To avoid polymerization of this monomer, it must be distilled right after its formation.

The product could be characterized by spectroscopic technique. IR (NaCl) spectrum was shown in Figure 4.7. The absorption bands at ν 3120, 1920, 1830, 1615-1450 and 830 cm^{-1} clearly indicated that there was aromatic ring in the molecule. The presence of the absorption bands at ν 1410 and 915 cm^{-1} concurrent with the absence of the absorption band at ν 1220 cm^{-1} denoted that dehydrobromination was occurred. The IR spectrum of this compound agreed with that of p-chloromethylstyrene reported by Arschady et al [39].

Table 4.4 The assignment for the IR spectrum of p-chloromethylstyrene

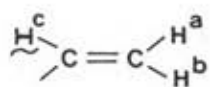| Absorption frequency ν (cm^{-1})	Assignment
3120	C-H str. aromatic
3090	-CH$_2$- asym. str.
2970	-CH$_2$- sym. str.
1920	overtone region
1830	of aromatic ring
1630, 1515, 1450	C=C str. aromatic
1410	= CH$_2$ in plane bending of alkene
1270	C-Cl bending (CH$_2$-Cl)
915	= CH$_2$ out of plane bending of alkene
830	= C-H out of plane bending of aromatic (para-disubstituted aromatic)
690	C-Cl str.
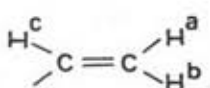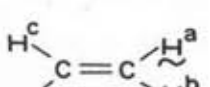
Moreover, the ^{1}H NMR spectrum of p-chloromethylstyrene also showed the signals at δ 6.70, 5.73 and 5.25 ppm which corresponded to the olefinic protons(Table 4.5). A doublet of doublets at δ 6.70 ppm was due to proton H^c. It was strongly deshielded by aromatic ring and coupled with proton H^b (J_{cb} = 17.6 Hz) and with proton H^a (J_{ca} = 10.8 Hz). Likewise, a doublet of doublets at δ 5.73 ppm was due to protons H^b which were coupled with the H^c proton (J_{cb} = 17.6 Hz) and the H^a proton (J_{ab} = 2 Hz). A doublet of doublets at δ 5.25 ppm was due to proton H^a which was coupled with H^c proton (J_{ca} = 10.98 Hz) and with the H^b proton (J_{ab} = 2 Hz).

Consequently, the ^{1}H NMR spectrum (Figure 4.8) of this compound confirmed that there was a structure of olefinic group ($\rangle$C=C$\langle$) in the molecule. Moreover, the pattern of its ^{1}H NMR spectrum absolutely agreed with that of the one reported by Kondo et al [36].
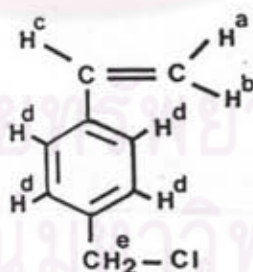
p-chloromethylstyrene

Table 4.5   The assignment for the ^{1}H NMR spectrum of p-chloromethylstyrene.

Chemical shift δ (ppm)	Intensity	Assignment
7.34	br. s, 4H	aromatic protons
6.70	d.d, 1H(J_{cb} = 17.6) (J_{ca} = 10.8)	H^c—C=C—H^a, H^b
5.73	d.d, 1H(J_{cb} = 17.6) (J_{ab} = 2)	H^c—C=C—H^a, H^b
5.25	d.d, 1H(J_{ca} = 10.98) (J_{ab} = 2)	H^c—C=C—H^a, H^b
4.54	s, 2H	$-CH_2-Cl$

Fig. 4.7. IR(NaCl) spectrum of p-chloromethylstyrene monomer
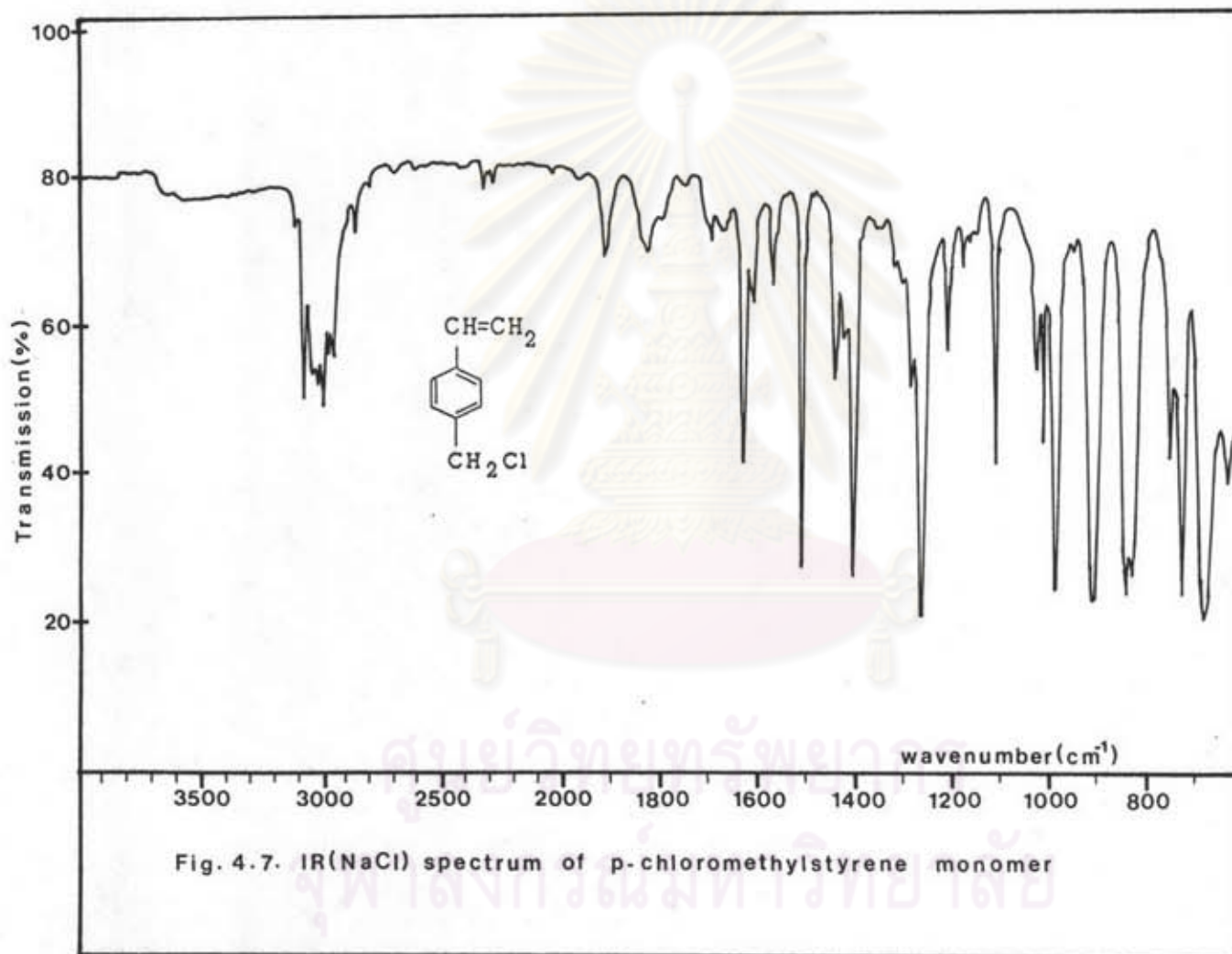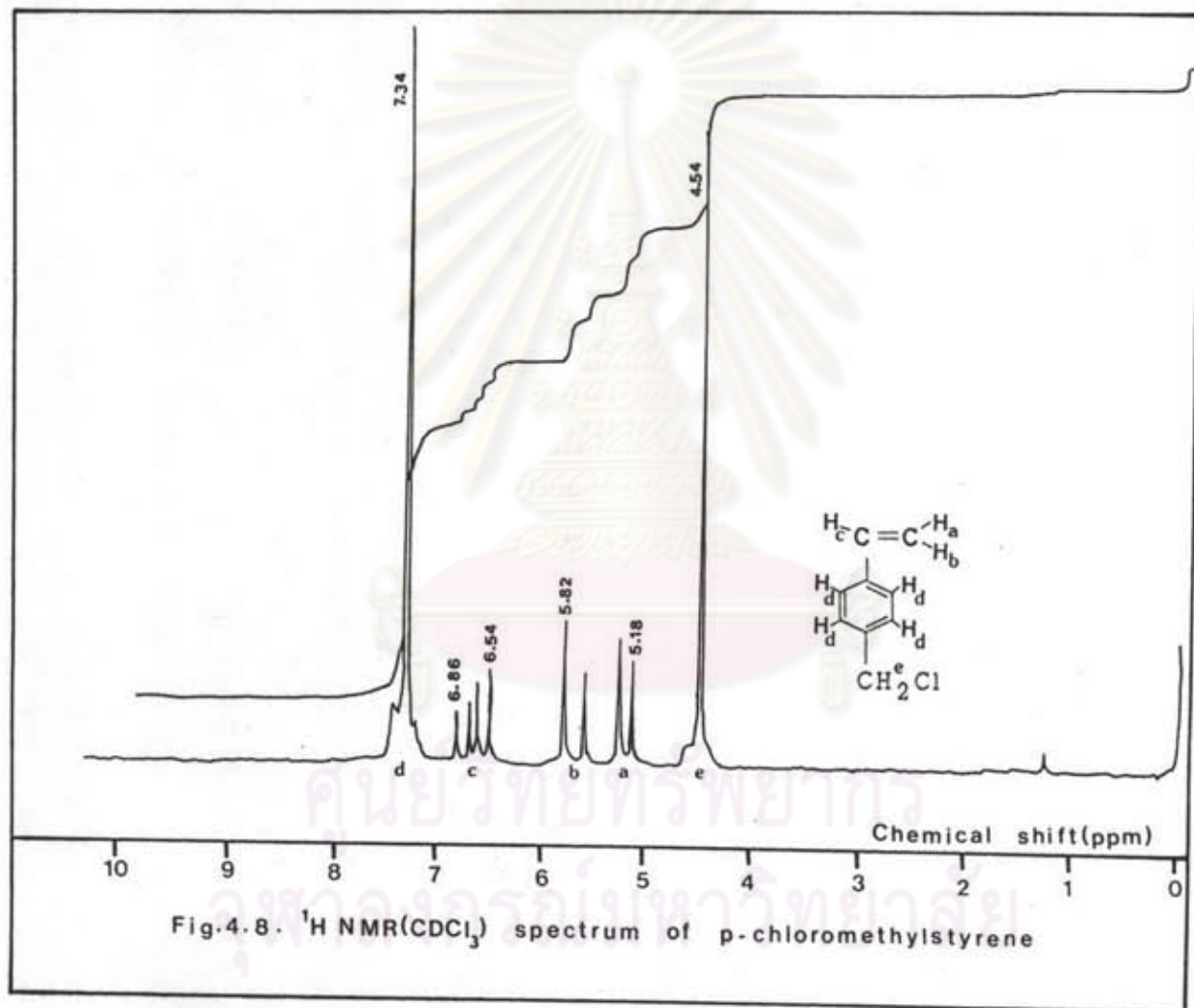
Fig. 4.8. ^{1}H NMR(CDCl$_3$) spectrum of p-chloromethylstyrene

4.2 Polymerization

4.2.1 Homopolymerization of p—chloromethylstyrene

p—Chloromethylstyrene was homopolymerized in benzene. After the reaction, the solution was more viscous.

The white powder was obtained with 44.8% yield after the third reprecipitation. It had T_g 116.44 $^\circ$C and $\overline{M}_p$ 180,050. From elemental analysis, it contained C 71.18%, H 6.24% and Cl 22.48% which was similar to the calculated value for the repeating unit, C 70.83%, H 5.94%, Cl 23.23%.

The IR (film) spectrum of this compound was shown in Figure 4.9. The absorption bands at ν 1410 and 915 cm^{-1} disappeared while the absorption band at 1440 cm^{-1} concurrently appeared. Thus, it indicated that the olefinic group of the monomer became the aliphatic moiety in the polymer. The -CH$_2$-Cl bending and C-Cl stretching remained at ν 1270 and 680 cm^{-1}, respectively. The other absorption bands were assigned as detailed in Table 4.6.

Table 4.6   The assignment for the IR spectrum of
            poly(p-chloromethylstyrene)

Absorption frequency ν (cm^{-1})	Assignment
3040	-C-H str. of aromatic
2940	-C-H str. of aliphatic
1920	overtone region
1800	of aromatic ring
1610	
1515	C=C str. of aromatic ring
1450	
1440	-C-H bending (aliphatic)
1270	-C-Cl bending (-CH$_2$-Cl)
830-840	-C-H out of plane bending of aromatic ring (para)
680	-C-Cl str.

Besides, the ^{1}H NMR spectrum of this compound was also confirmed that p-chloromethylstyrene monomer was homopolymerized to poly(p-chloromethylstyrene).This was shown by two broad singlets at δ 1.56 and 1.43 ppm while there was not any signal in the olefinic region (Figure 4.10). The other signals were assigned as detailed in Table 4.7.

Table 4.7   The assignment for the ^{1}H NMR spectrum of poly(p-chloromethylstyrene)

Chemical shift δ (ppm)	Assignment
7.08	H, aromatic
6.50	H, aromatic
4.53	$-CH_2-Cl$
1.56	$(-\overset{\overset{H}{\mid}}{C}-CH_2-)$
1.43	$(-\overset{\mid}{CH}-CH_2-)$

Fig.4.9. IR(film) spectrum of poly(p-chloromethylstyrene)

Fig. 4.10. ^{1}H NMR(CDCl$_3$) spectrum of poly(p-chloromethylstyrene)
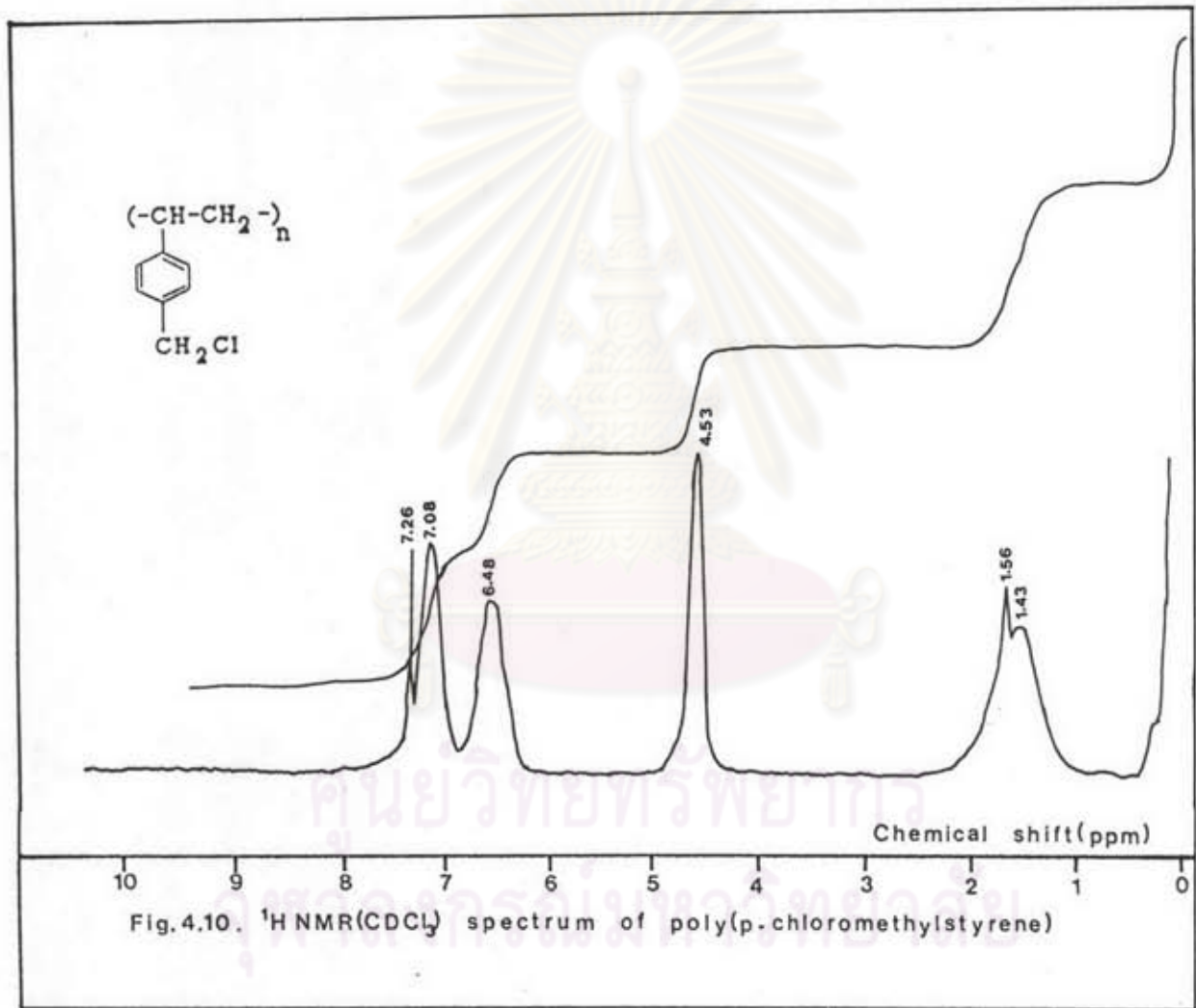
4.2.2 Copolymerization of p-Chloromethylstyrene and Styrene Monomer.

Though polystyrene was reported to be of high contrast, but it had low sensitivity [40]. So copolymerization of p-chloromethyl -styrene and styrene was carried out by using the same method for polymerization of p-chloromethylstyrene. The composition ratios of the two monomers($F_1:F_2$) were varied as follows; a) 0.10 : 0.90, b) 0.25 : 0.75, c) 0.50 : 0.50, d) 0.75 : 0.25 and e) 0.90 : 0.10. Poly(p-chloromethylstyrene-co-styrene) obtained was then converted into the final product, poly(p-epoxystyrene-co-styrene) which is described later.

The IR spectra of these compounds were shown in Figure 4.11. They were similar to that of poly(p-chloromethylstyrene), except the intensity of the absorption band at ν 1270 cm^{-1} was found that the more p-chloromethylstyrene moiety was in the chain, the higher intensity of absorption band at ν 1270 cm^{-1} was observed. The other absorption bands were assigned as detailed in Table 4.8.

Table 4.8   The assignment for the IR spectrum of
             poly(p-chloromethylstyrene-co-styrene).
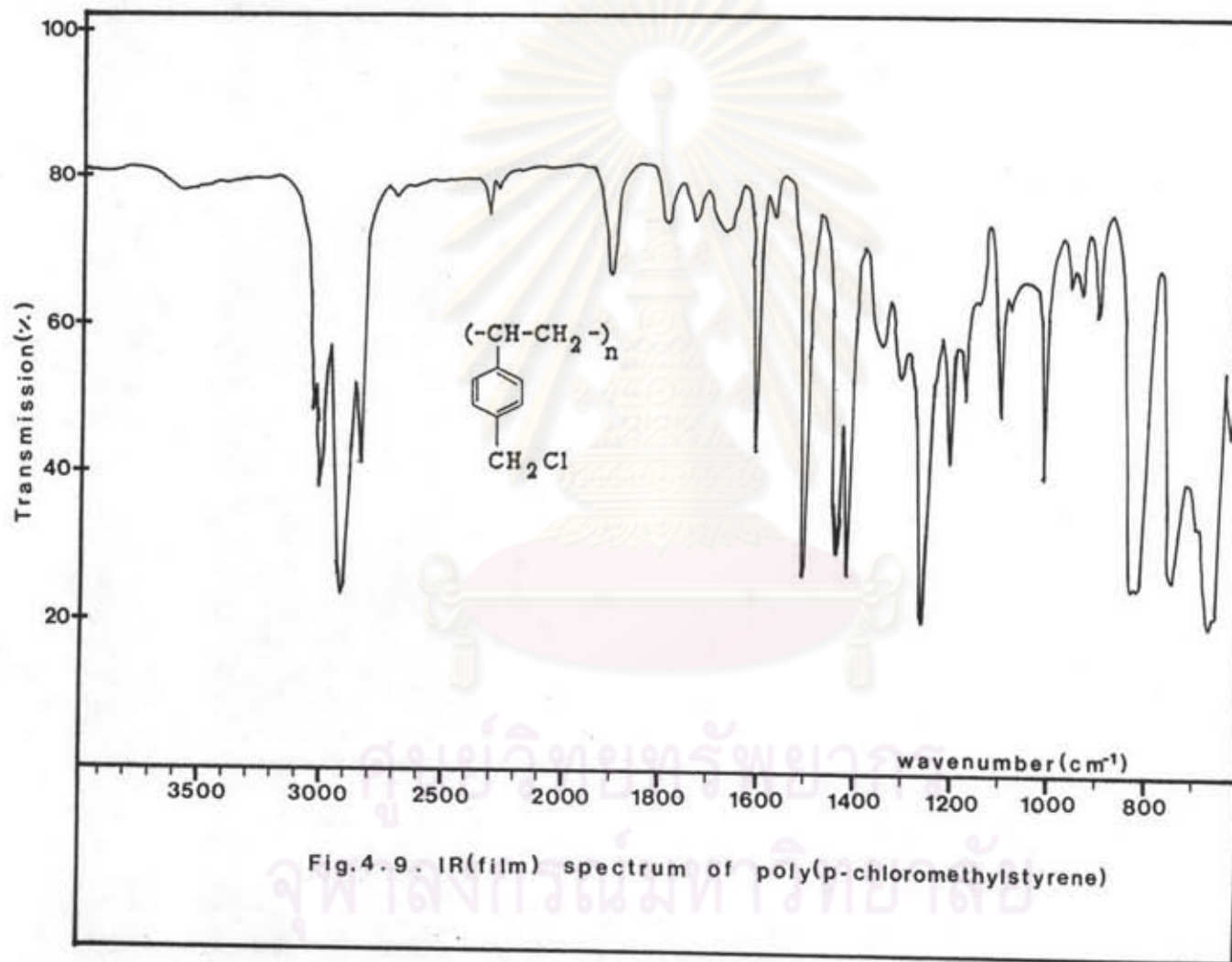
Absorption frequency ν (cm^{-1})	Assignment
3040	C-H str. aromatic
2940	C-H str. aliphatic
1920	overtone region
1800	of aromatic ring
1610	
1515	C=C str. aromatic
1450	ring
1425	C-H bending aliphatic
1270	CH$_2$-Cl bending
830-840	C-H out of plane bending (aromatic)
680	C-Cl str.

Likewise, the ^{1}H NMR spectra of these compounds were similar to that of poly(p-chloromethylstyrene). It was also found that the more the composition of p-chloromethylstyrene used, the more intense was the signal at δ 4.50 ppm. The other signals at δ 6.50-7.05 ppm(aromatic protons)[*], δ 1.54 ppm(-CH-CH$_2$-)[*] and at δ 1.42 ppm (-CH-CH$_2$-)[*] were observed (Figure 4.12).Consequently, the ^{1}H NMR spectra confirmed the structure of poly(p-chloromethylstyrene-co-styrene).

[*] from both styrene and p-chloromethylstyrene

$$+CH-CH_2+_n+CH-CH_2+_m$$

$$CH_2-Cl$$
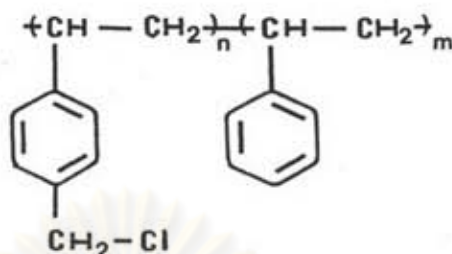
Poly(p-chloromethylstyrene-co-styrene)

Other analyses of both homopolymer and copolymers were shown in Table 4.9, 4.10, 4.11 and 4.12, respectively. The amount of chlorine was determined by both the elemental analysis and the modified Volhard method. It was found that the chlorine content increased significantly with an increase in the mole fraction of p-chloromethylstyrene in the feed. This corresponds with the reactivity ratio of p-chloromethylstyrene and styrene which were reported to be 1.32 and 0.72, respectively [36]. p-Chloromethylstyrene monomer was, therefore, more reactive than styrene monomer. The calculated elemental analysis of starting polymers were close to the found elemental analysis. Furthermore, the mole fraction of p-chloromethylstyrene (F_1) and styrene (F_2) in polymer chains from calculation and elemental analysis were close too.

Molecular weight : from the literature search, the suitable molecular weight of polymers were mostly in the range of 50,000-200,000. Fortunately, all the resulted polymers could also be synthesized with the molecular weights ranging from 50,000-200,000. In fact, a negative resist having high molecular weight needed a lower incident dose of light to cause

crosslinking. It indicated that this negative resist had high sensitivity. With high molecular weight, the solution was too viscous to make thin film, then resolution of a resist was not good. Therefore, the synthesis of polymer with suitable molecular weight was necessary.

Molecular weight distribution : as the matter of fact, the contrast of a resist is high with corresponding narrowness in molecular weight distribution [39]. Unfortunately, from the experiments the resulting polymers had molecular weight distribution rather broad since it was difficult to control copolymer to obtain nearly monodisperse due to the difference in monomer reactivities.

The glass transition temperature (T_g) : poly (p-chloromethylstyrene) and poly(p-chloromethylstyrene-co-styrene) had their T_g 110.5, 110.64, 112.24, 112.93, 113.37 and 116.44 $^\circ$C for batch a, b, c, d, e and f, respectively (Figure 4.13). They were rather high. The advantage of having high glass transition temperature is such that the polymer will not deform easily under stress, and the exposed and developed film will not change its shape with temperature therefore the film is suitable for high resolution application. On the contrary, the polymers, which had low T_g, deformed easily and the resolution was low too.

Table 4.9 Polymerization data of poly(p-chloromethylstyrene-co-styrene)

Copolymer (batch)	F_1	F_2	f_1	f_2	mole of CMSTY[*]	mole of STY[*]	% yield
a	0.10	0.90	0.07	0.93	0.022 (3.4g)	0.290 (30.2g)	13.10
b	0.25	0.75	0.20	0.80	0.064 (9.8g)	0.256 (26.7g)	14.50
c	0.50	0.50	0.42	0.58	0.130 (20 g)	0.190 (20 g)	15.30
d	0.75	0.25	0.69	0.31	0.110 (16.7g)	0.050 (5.2 g)	19.80
e	0.90	0.10	0.87	0.13	0.140 (21.3g)	0.020 (2.8 g)	21.86
f (homo)	–	–	–	–	0.200 (28.3g)	–	44.80

[*] obtained from calculation (please see Appendix I)

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Table 4.10 The Analysis of molecular weight and glass transition temperature (T_g) of polymers[*].

Copolymer (batch)	$\overline{Mp}$	[**]$\overline{Mw}$	[**]MWD	T_g	Composition ratios			
					from calculation		from elemental analysis	
					CMSTY (F_1)	STY (F_2)	CMSTY (F_1)	STY (F_2)
a	50,120	50,036	2.07	110.50	0.10	0.90	0.10	0.90
b	99,650	103,540	3.90	110.64	0.25	0.75	0.28	0.72
c	110,200	111,700	3.72	112.24	0.50	0.50	0.51	0.49
d	119,855	120,920	3.14	112.93	0.75	0.25	0.77	0.23
e	177,675	180,057	2.19	113.37	0.90	0.10	0.89	0.11
f (homo)	180,050	184,708	2.01	116.44	–	–	–	–

*   Poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene)

**   Analized by LABORATOIRE DE CHIMIE MACROMOLECULAIRE

Note : $\overline{Mp}$ = peak average molecular weight

      MWD   = molecular weight distribution

Table 4.11 The elemental analysis of poly(p-chloromethylstyrene)
and poly(p-chloromethylstyrene-co-styrene)

Copolymer (batch)	Elemental Analysis					
	C (%)		H (%)		Cl (%)	
	Caled.	found	Caled.	found	Caled.	found
a	89.26	89.26	7.49	7.83	3.25	3.21
b	85.22	84.09	7.15	7.40	7.63	8.52
c	79.52	79.46	6.67	6.62	13.81	14.00
d	74.80	74.04	6.28	6.57	18.92	19.38
e	72.34	73.19	6.07	6.39	21.59	21.32
f (homo)	70.83	71.18	5.94	6.24	23.23	22.48

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Table 4.12   Determination of chlorine in polymers by
              modified Volhard method

Copolymer (batch)	The amount of chlorine (mmole / 1g. polymer)	
	Calculated	Found
a	0.9155	0.8264
b	2.1493	2.2532
c	3.8901	3.9010
d	5.3296	5.3239
e	6.0817	6.0012
f (homo)	6.5437	6.3110

Fig. 4.11 IR spectra of poly(p-chloromethylstyrene—co—styrene) with different monomer ratio, of p-chloromethylstyrene and styrene a), b), c), d) and e)

Fig. 4.12 ^{1}H NMR spectra of poly (p–chloromethylstyrene–co–styrene) with different monomer ratio of p–chloromethylstyrene and styrene a), b), c), d) and e)
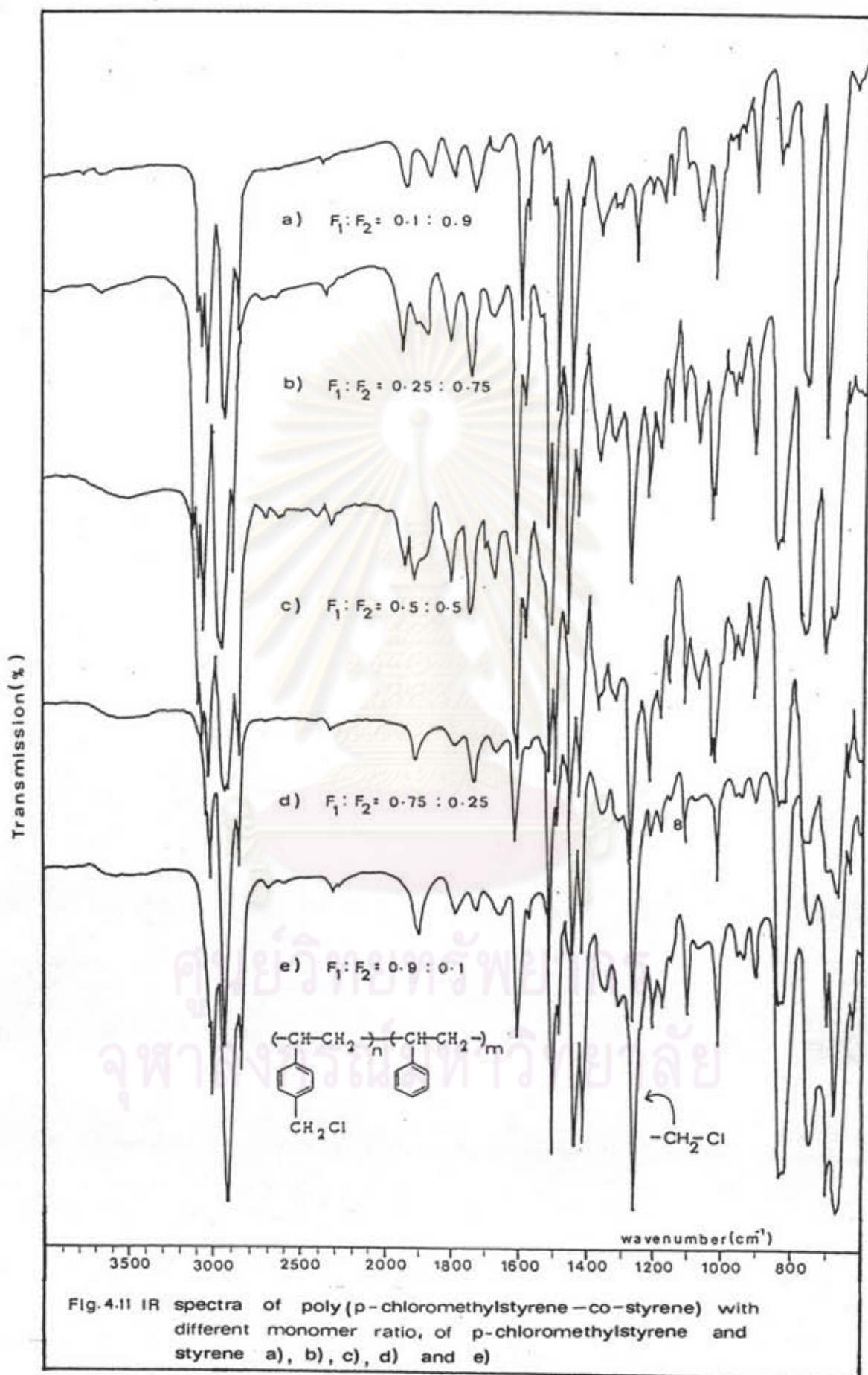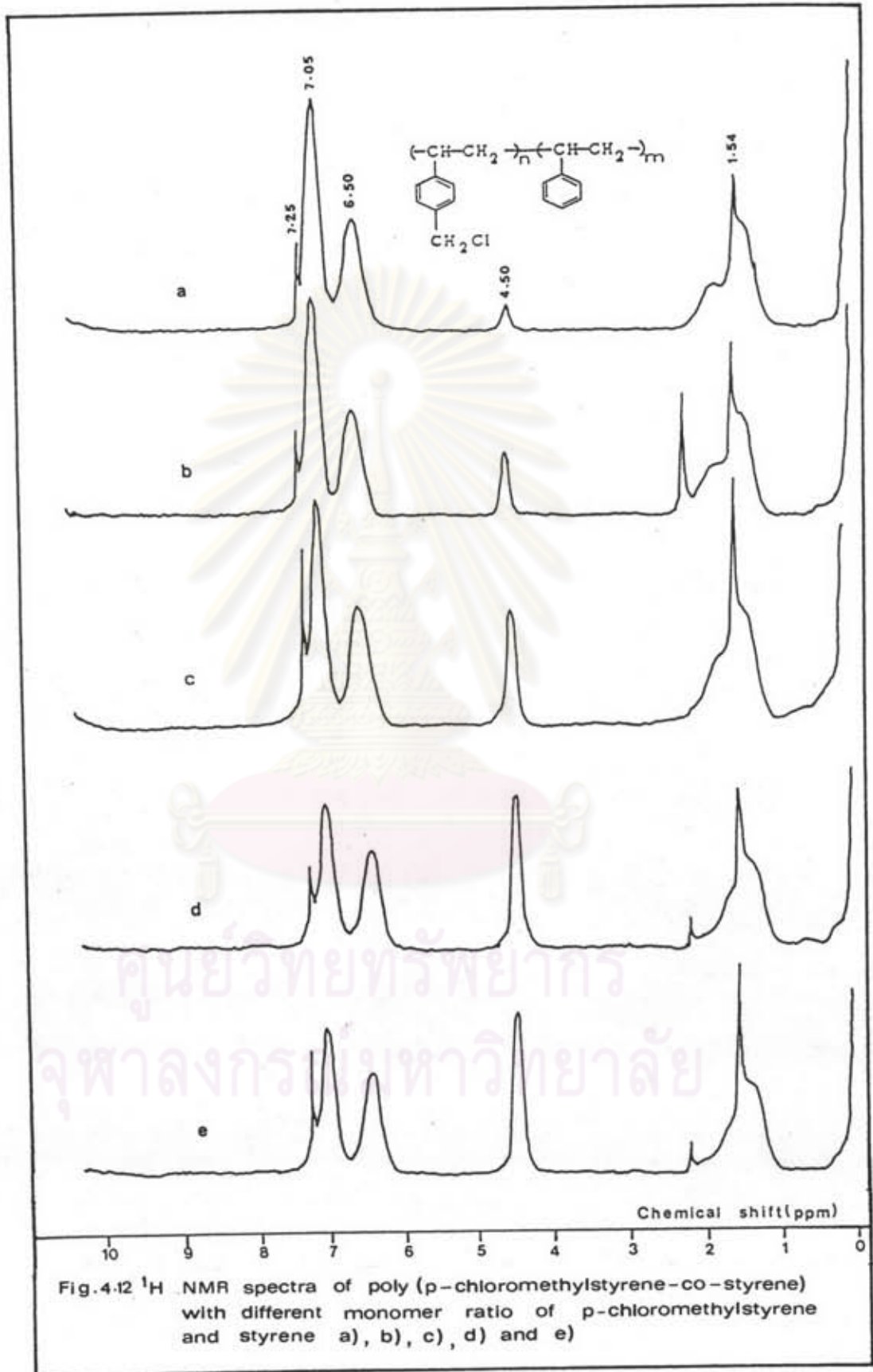
Fig. 4-13 DTA thermograms of poly(p-chloromethylstyrene-co-styrene): a, b, c, d
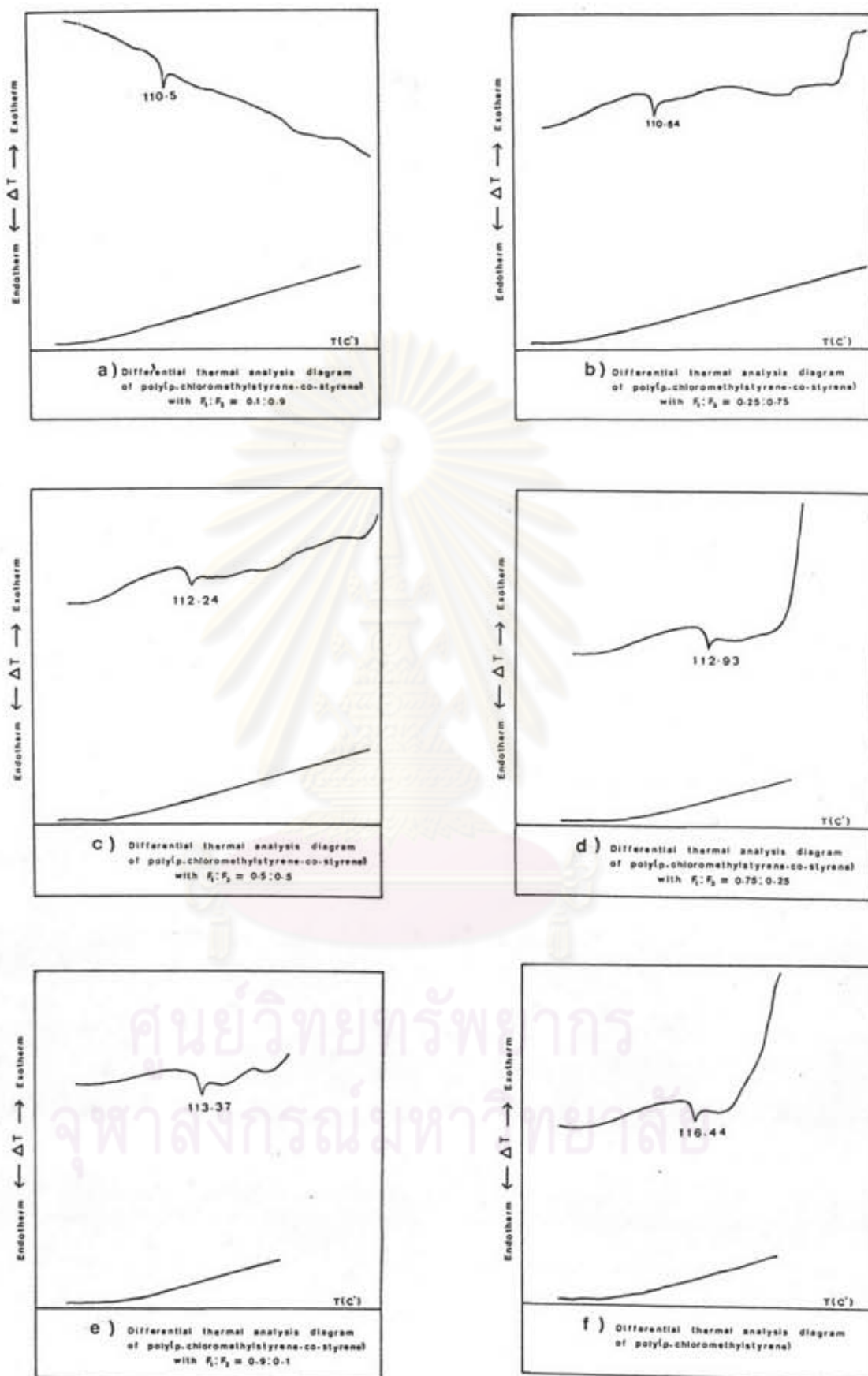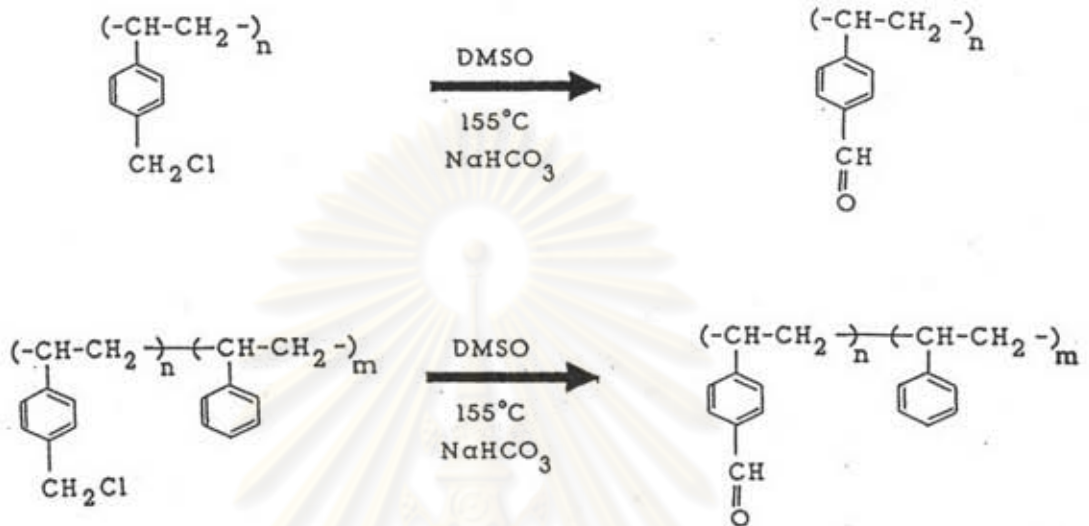
and e   and poly(p-chloromethylstyrene): f .

4.3   Carboxylation   of   Poly(p-chloromethylstyrene)   and
        Poly(p-chloromethylstyrene-co-styrene)

Carboxylation of poly(p-chloromethylstyrene) and poly
(p-chloromethylstyrene-co-styrene) were carried out by using
dimethylsulfoxide and sodium bicarbonate at 155 °C, for 6 hrs.
The products were purified by washing with several solvents, then
dried under reduced pressure.   The cream-colored products were
obtained and it was expected that the chloromethyl groups was
converted to the carboxaldehyde groups. They could be detected
by the IR spectra (Figure 4.14-4.15).

From the IR spectra of all products, it indicated that
the oxidation of poly(p-chloromethylstyrene) and their copolymers
with dimethylsulfoxide gave aldehydric resins which showed an
intense carbonyl absorption bands at ν 1700 cm^{-1} and aldehydric
C-H stretching absorption at ν 2720 cm^{-1}. While the absorption
bands of C-Cl bending at ν 1270 cm^{-1} and C-Cl stretching at ν 680
cm^{-1} of starting polymers disappeared.   The other absorption bands

were also interpreted in detail in Table 4.14. These values are in good agreement with those recorded by Ayres and Mann [41].

It was also found that the IR spectra of all products were similar, except the intensity of the carbonyl group at the absorption band of ν 1700 cm^{-1}.

Table 4.13 The assignment for the IR spectra of poly(p-carboxaldehydestyrene) and their copolymers.

Absorption frequency ν (cm^{-1})	Assignment
3020	C-H str. aromatic
2980	C-H str. aliphatic
2900	
2720	C-H str. aldehyde
1910	overtone region
1800	of aromatic ring
1700	C=O str.
1610	
1500	C=C str. aromatic
1455	
825	C-H out of plane bending (aromatic ring)

The mechanism was proposed as shown in Scheme 4.3 [42]:

Let $(-CH-CH_2-)_n$ and $(-CH-CH_2-)_n(-CH-CH_2-)_m$

CH_2Cl CH_2Cl

are represented by (P)-CH$_2$-Cl

$$\text{(P)}-CH_2-Cl + H_3C-\overset{\overset{O}{\|}}{S}-CH_3 \rightleftharpoons \text{(P)}-CH_2-O-\overset{+}{\underset{CH_3}{S}}-CH_3$$

$$H_3C-\overset{\bar{O}}{\underset{+}{S}}-CH_3$$

+ NaCl

$$\text{(P)}-CH_2-O-\overset{+}{S}\overset{CH_3}{\underset{CH_2-H}{|}} \xrightarrow{\quad\bar{H}CO_3\quad} \text{(P)}-\overset{H}{\underset{H}{C}}-O\overset{S}{\underset{H_2C}{\underset{+}{}}}-CH_3$$

$$\downarrow$$

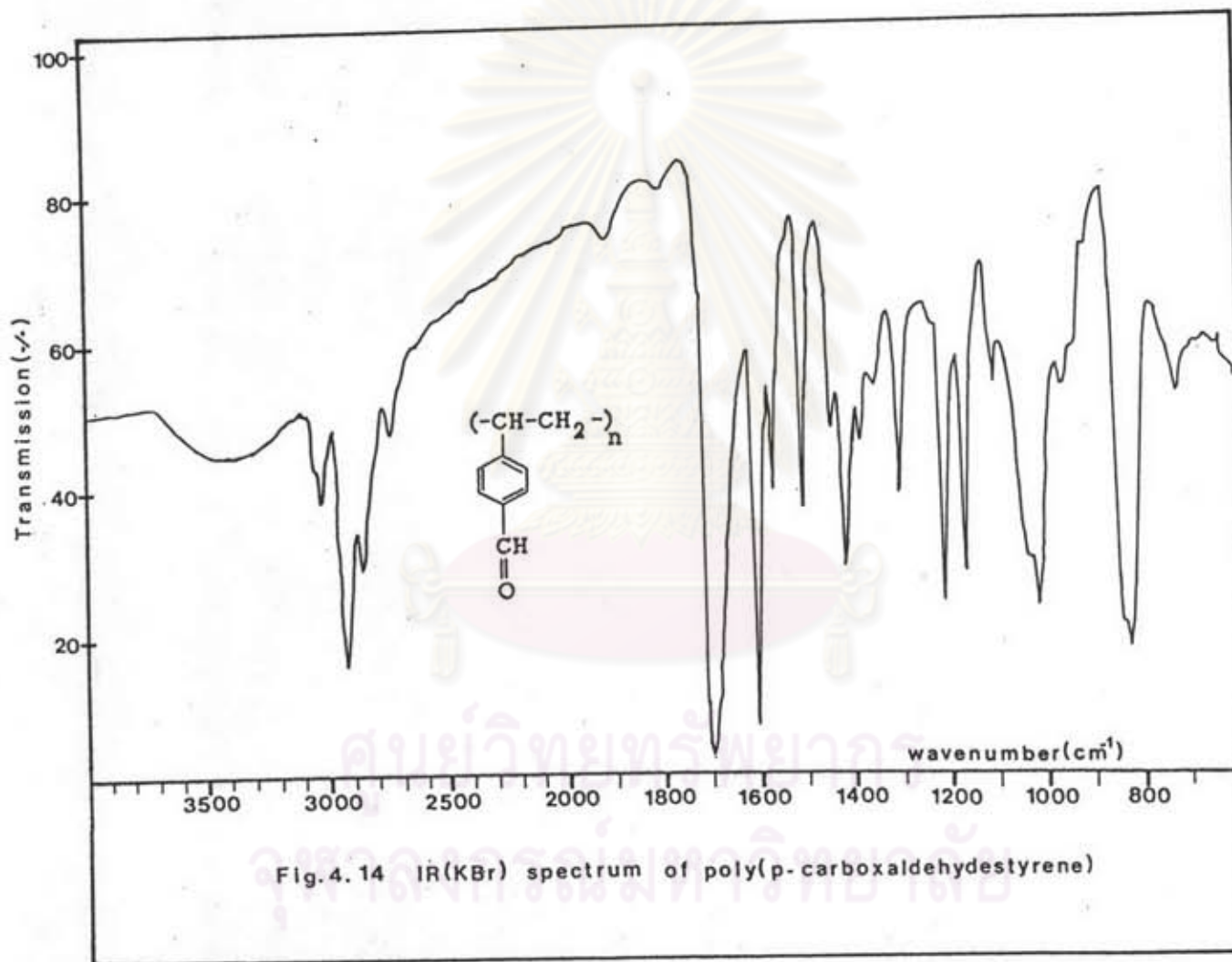$$\text{(P)}-\overset{\overset{O}{\|}}{C}-H + H_3C-S-CH_3$$
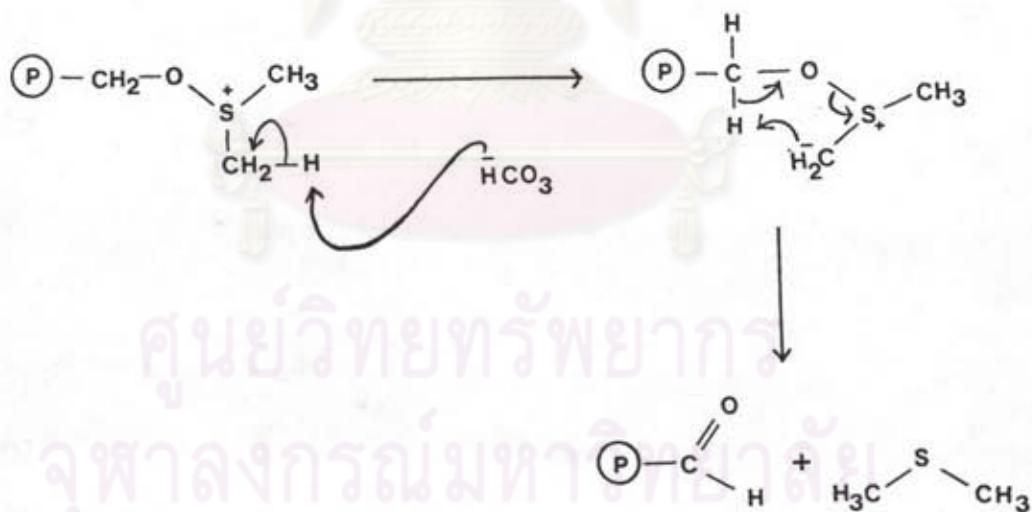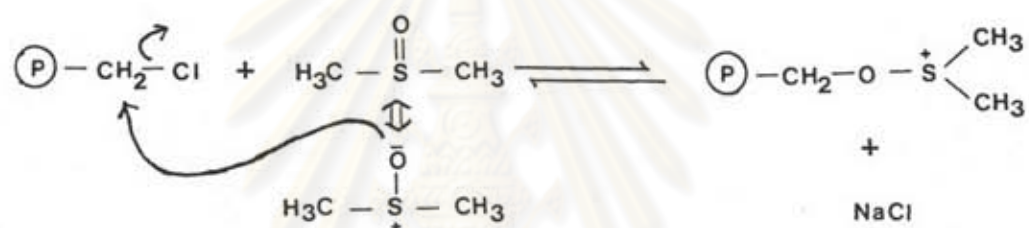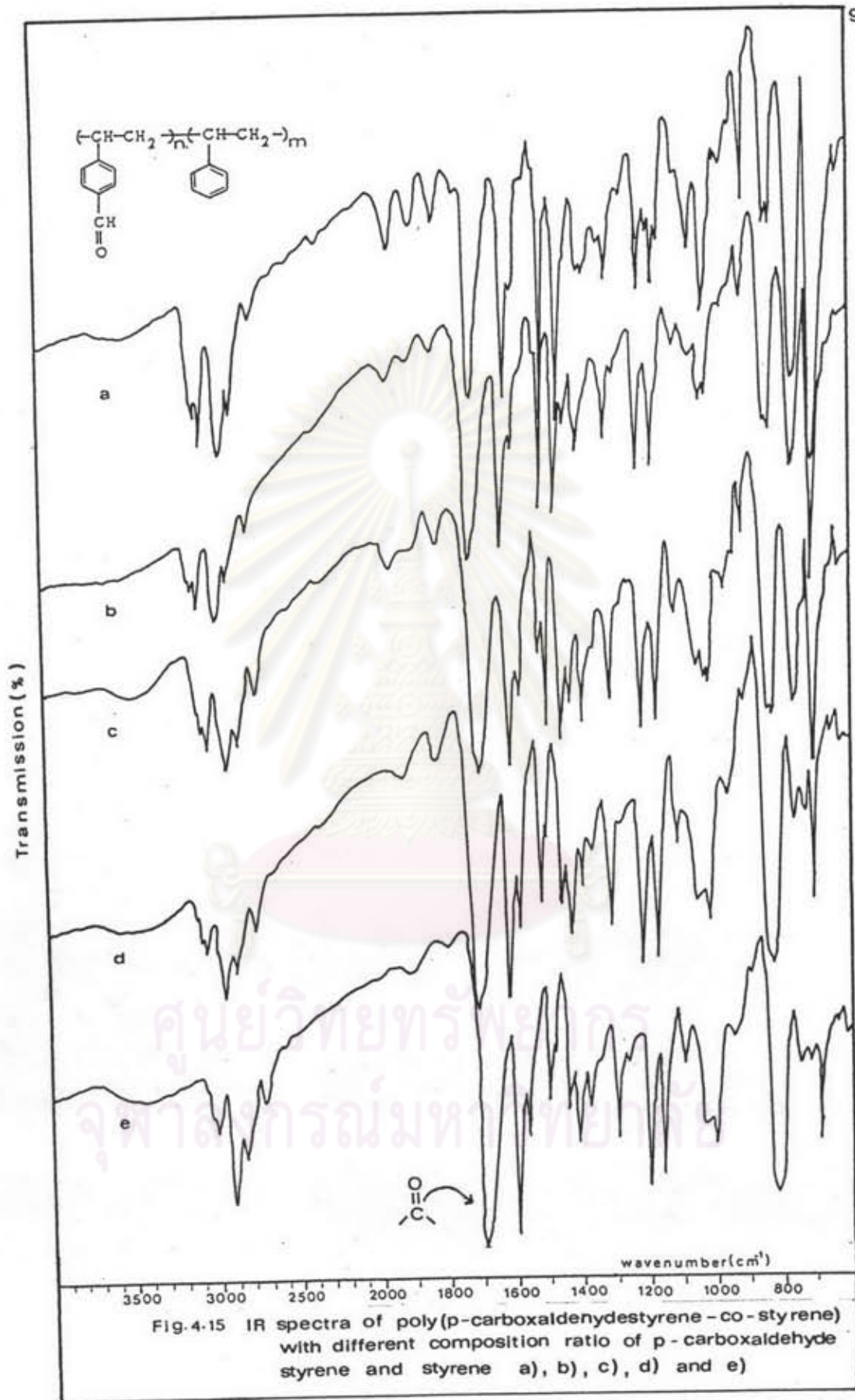
Scheme 4.3

Furthermore, all products were checked for the presence of chlorine by the modified Volhard method. The result was shown in Table 4.13. It was found that the amount of chlorine was left merely little, consequently, it could not be observed in the IR spectra. Although the chloromethyl groups could not completely change into the carboxaldehyde groups, but poly (p-chloromethylstyrene) and their copolymers could also be used as negative resists [43].

Table 4.14   Determination of the chlorine content of poly (p-carboxaldehydestyrene) and their copolymers.

Copolymer (Batch)	The amount of chlorine	
	mmole/1 g. polymer	*Percent/1g. polymer
a	0.0098	1.18
b	0.0139	0.62
c	0.0144	0.37
d	0.0145	0.27
e	0.0140	0.23
f (homo)	0.0155	0.25

* The calculation was relative to the starting polymer.

Fig. 4.14 IR(KBr) spectrum of poly(p-carboxaldehydestyrene)

Fig. 4·15 IR spectra of poly(p-carboxaldenydestyrene–co–styrene) with different composition ratio of p-carboxaldehyde styrene and styrene a), b), c), d) and e)

4.4   Epoxidations of Poly(p-carboxaldehydestyrene) and their Copolymers, Poly(p-carboxaldehydestyrene-co-styrene)

Poly(p-epoxystyrene) could be prepared by two different procedures as follows. The first approach made use of the simple epoxidation of poly(p-vinylstyrene) with m-chlorobenzoic acid (MCPBA) in dichloromethane. This reaction gave satisfactory results but required that poly(p-vinylstyrene) be available. The epoxidation reaction was found to be very sensitive to reaction conditions and somewhat prone to side reactions. For example the use of long reaction times caused the appearance of a carbonyl absorption band in the infrared spectrum of poly(p-epoxystyrene) suggesting that opening of the epoxide ring had occurred.

The better method which was used in this research work to prepare poly(p-epoxystyrene) and their copolymers was the reaction of poly(p-carboxaldehydestyrene) and their copolymers with trimethylsulfonium chloride in the presence of a phase transfer catalyst.

Though the sulfonium ylid reaction could also lead to poly (p-epoxystyrene) but it gave poor results when attemtped with trimethylsulfonium iodide under phase transfer condition ; this result was not totally unexpected as iodides are often considered undesirable for transfer reactions due to their excessive solubility in organic medium. The same reaction carried out under classical conditions using potassium t-butoxide in DMSO or n-butyllithium in THF also gave poor results [44].

The reaction with trimethylsulfonium chloride and 50% aqueous sodium hydroxide in the presence of benzyltriethyl

ammonium chloride, as phase transfer catalyst, gave excellent results.
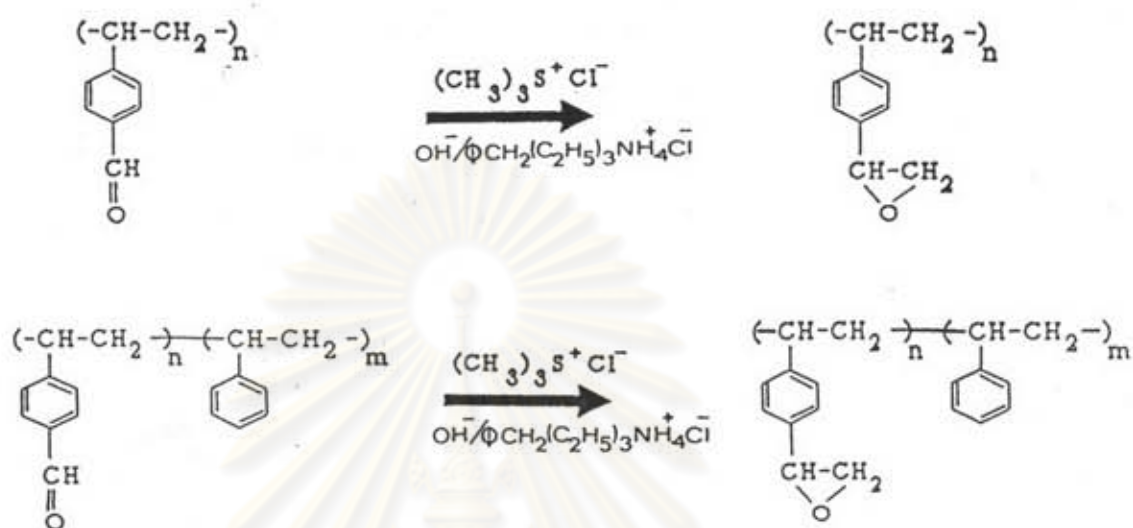
However, trimethylsulfonium chloride was not available. It was thus obtained via ion exchange of trimethylsulfonium iodide through anion exchange resin, DOWEX SBR-P. It was then used as aqueous solvent of trimethylsulfonium chloride.

To find out the suitable time used for the conversion of the carboxaldehyde group into the epoxide group, it was found that all batches had similar result: the carbonyl absorption band at ν 1700 cm^{-1} and C-H stretching of the aldehydric group at ν 2720 cm^{-1} decreased significantly with the reaction time. The reaction was followed by IR spectroscopy, monitoring at ν 1700 and 2720 cm^{-1}. It was found that the intensity of the absorption band at ν 1700 and 2720 cm^{-1} decreased while the appearance of epoxide stretching bands of -C-O symmetric stretching and -O-C asymmetric stretching at ν 1270 and 880 cm^{-1}, respectively. This indicated that the aldehydric group was converted to the epoxide group. However, after 15 hours of reaction, it seemed that not much more conversion had occurred. This could be observed in the

IR spectra of Figure 4.16, and the amount of epoxidation was determined by modified Iodometric method (Table 4.15). Therefore, the epoxidation of poly (p-carboxaldehydestyrene-co-styrene) and poly (p-carboxaldehydestyrene) were carried out for 15 hours. The result were obtained in the same manner as the previous ones.

The IR spectra of all products were shown in Figure 4.18 and 4.19. Not only the absorption band of aldehydric group but also the other absorption bands were assigned as detailed in Table 4.16. Actually, aldehydric functional groups should disappeared completely, but from the experiment the aldehydric group still appeared in the spectrum. It indicated that the conversion of this reaction was not complete (100%) as expected because of the steric hindrance of side aldehydric groups; the more the side groups present, the more difficult the epoxide groups form completely. The other possibility was the opening of the epoxide ring to become the carbonyl group which also showed the absorption band at γ 1700 cm^{-1}.

Table 4.15   Epoxide formation data with time

Copolymer (batch)	Epoxidation content (mmole/1g.polymer)			
	at 10 hours.	at 15 hours.	at 20 hours.	IR spectra showed in Figure
a	1.073	1.432	1.440	A
b	1.025	1.710	1.799	B
c	1.234	2.267	2.387	4.16
d	1.410	2.620	2.703	D
e	1.056	2.640	2.694	E
f (homo)	1.097	2.646	2.690	F

Note: - Calculation was shown in Appendix I

       - Fig. A, B, D, E and F were shown in Appendix II

Table 4.16 The assignment for the IR spectrum of poly(p-epoxystyrene) and their copolymers.

Absorption frequency ν (cm^{-1})	Assignment
3020	C-H str. aromatic
2920	C-H str. aliphatic
2720	C-H str.aldehydric gr.
1940	overtone region of
1800	aromatic ring
1700	C=O str.
1600	
1510	C=C str. aromatic
1450	
1270	C-O- sym. str.
1050	
880	C-O- asym. str.

The amount of conversion of chloromethyl group to epoxide group was exhibited in Table 4.17. The percent conversions were 80.55, 80.10, 68.20, 50.10, 44.57 and 42.5% for batch a, b, c, d, e and f, respectively. The suitable composition ratio of copolymers was batch c since it was the most compromising between epoxidation contents and time used (Figure 4.17b). In fact, epoxidation contents should increase respectively from batch a to f, and from the experiments the tendency of their epoxidation contents also correspondingly increased. In contrast, percent conversion of chloromethyl group to epoxide group decreased, it was expected that it was due to the difficulty in epoxidation

step, the steric effect of aldehydric group as discussed earlier. The other possibility was that some crosslinkings had occurred with the effect of light and/or time used. So T_g of polymers were rather high too (Table 4.18).

The molecular weight of poly(p-epoxystyrene) and poly(p-epoxystyrene-co-styrene) could not be determined directly by gel permeation chromatography because they did not dissolve in tetrahydrofuran or toluene which was used as mobile phase. However, their molecular weights correspond with those of poly(p-chloromethylstyrene) and poly (p-chloromethylstyrene-co-styrene) by assuming that the chloromethyl groups changed completely to the epoxide groups. For example, the higher the amounts of epoxide groups were, the higher the molecular weights of polymers would be.

Table 4.17 Determination of epoxidation content.

Copolymer (Batch)	Epoxidation Content	
	(mmole/1g.polymer)	% Conversion
a	0.6657	80.55
b	1.8048	80.10
c	2.6602	68.20
d	2.6673	50.10
e	2.6750	44.57
f (homo)	2.6864	42.50

Table 4.18   Glass   transition   temperature   of   poly
(p-epoxystyrene) and poly(p-epoxystyrene-co-styrene)

Copolymer (Batch)	* T_g ($^{\circ}$C)
a	108.5
b	125.5
c	138.3
d	142.5
e	142.6
f (homo)	141.2

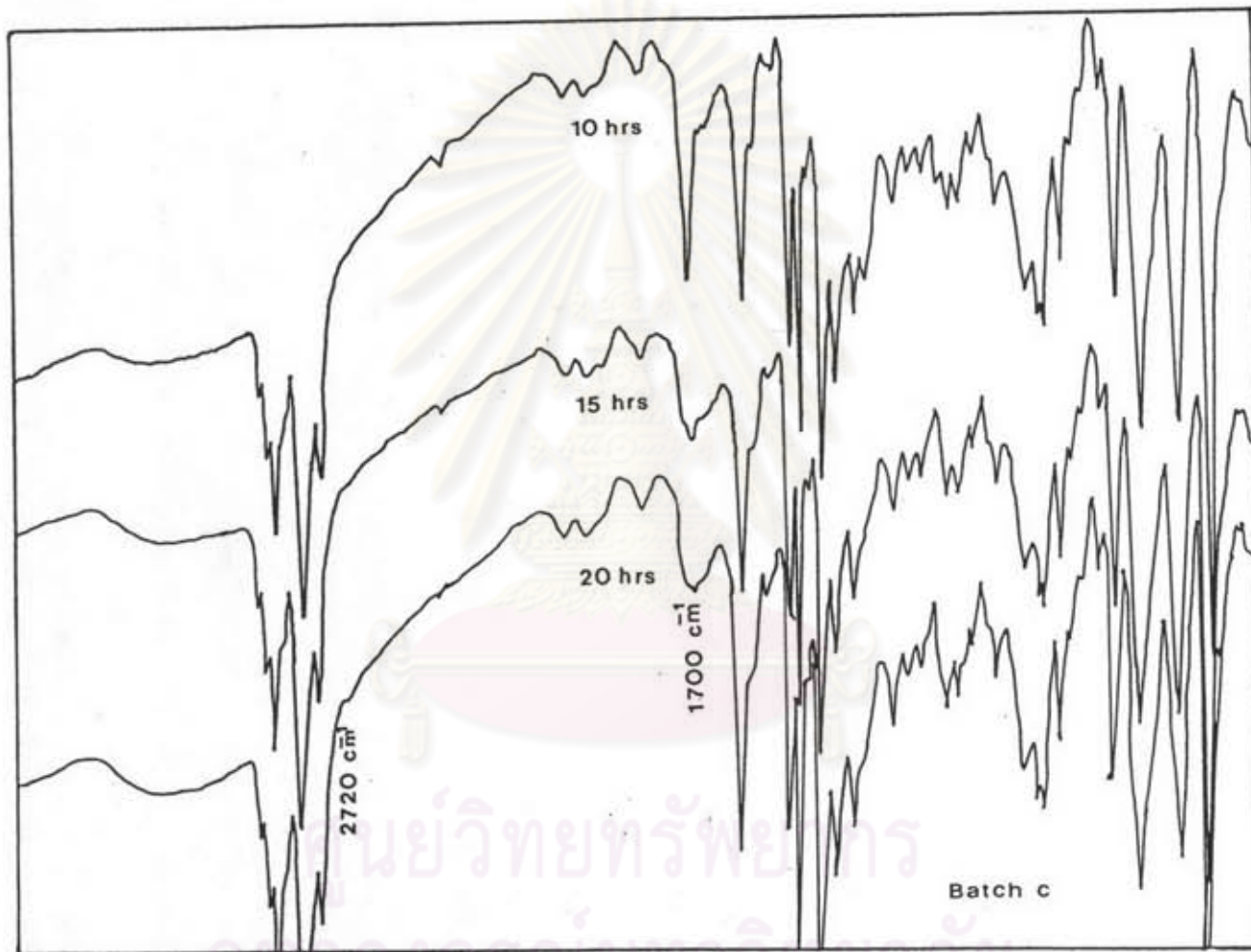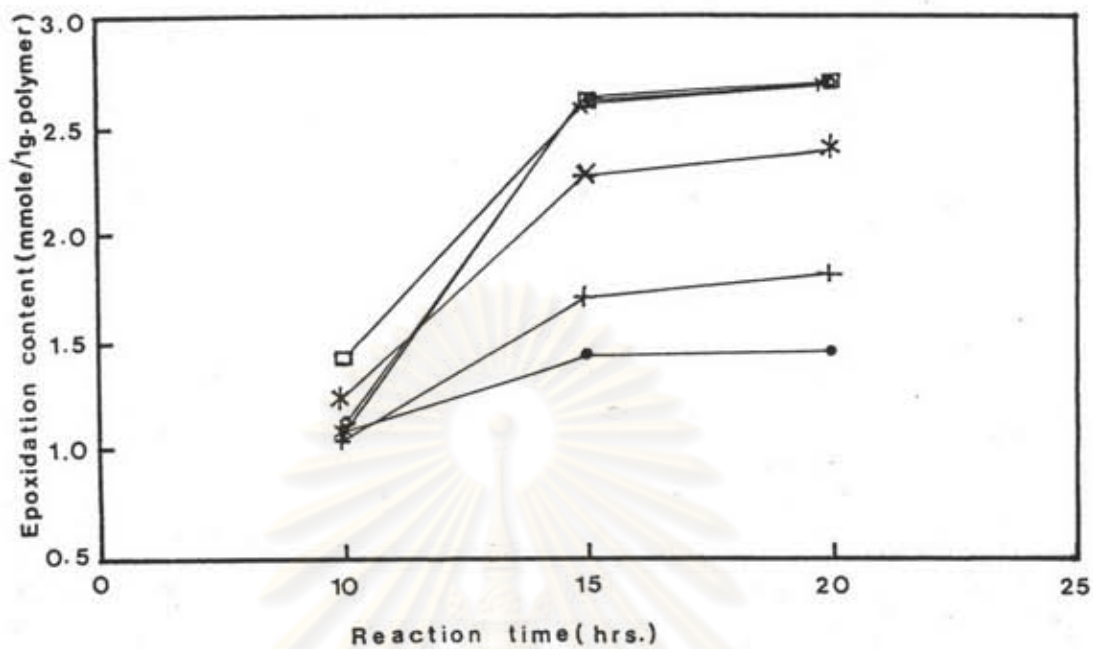*   DTA thermograms were exhibited in Figure 4.20.
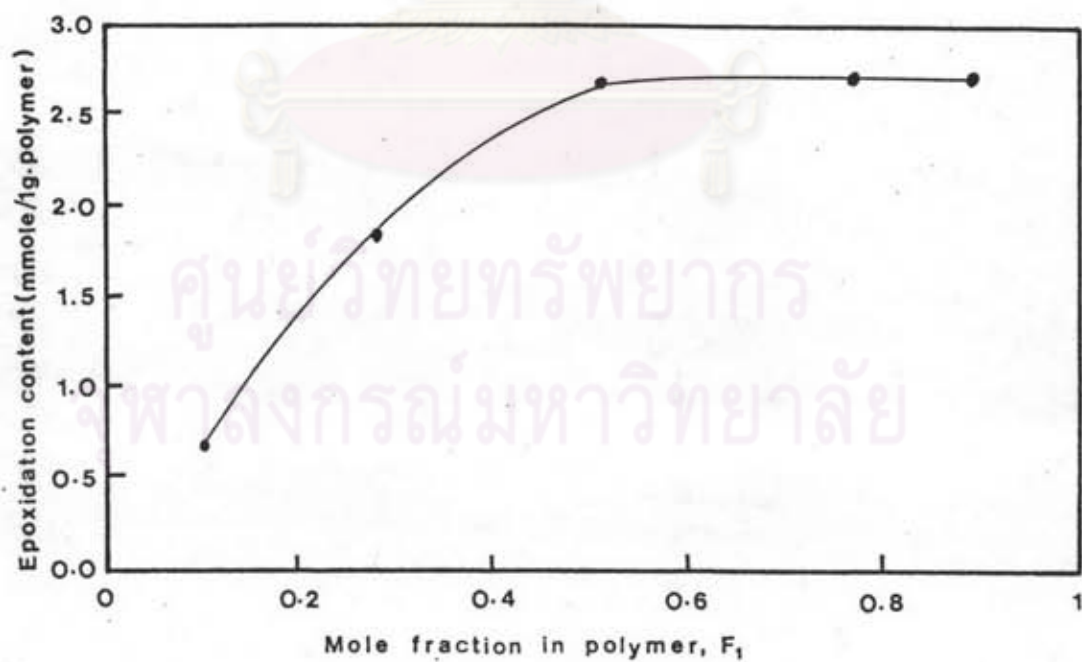
Fig. 4.16 Comparison of IR spectra : conversion of formyl gr. into epoxide gr.

at various times 10, 15 and 20 hours.

A: Graph of epoxidation content vs reaction time

B: Graph of epoxidation content vs mole fraction in polymer

Fig. 4.17 Graphs of epoxidation data: A and B

Fig. 4·18   IR(KBr) spectrum of poly(p-epoxystyrene)

Fig. 4.19 IR spectra of poly(p—epoxystyrene—co—styrene) with different composition ratio of p—epoxystyrene and styrene a), b), c), d) and e)
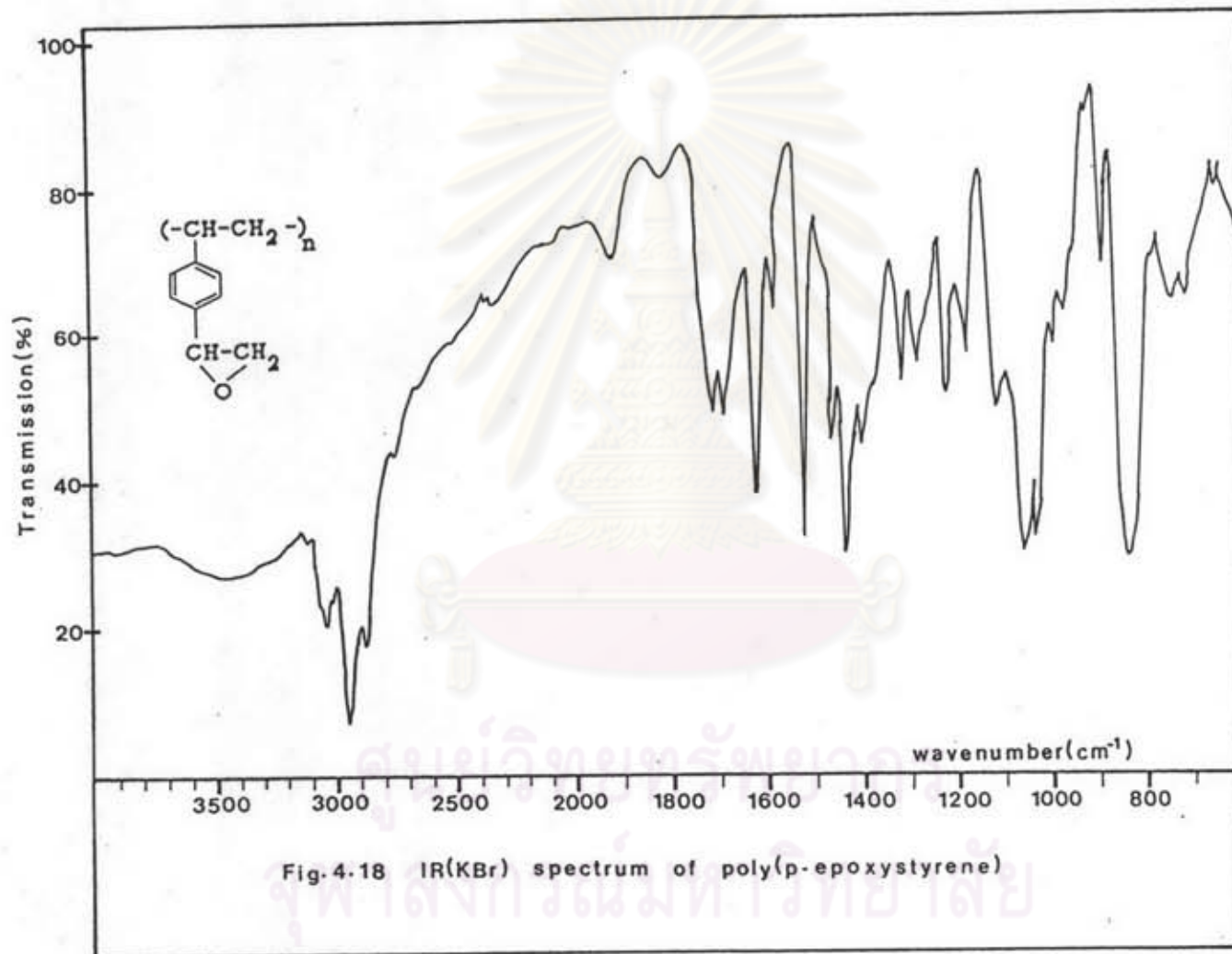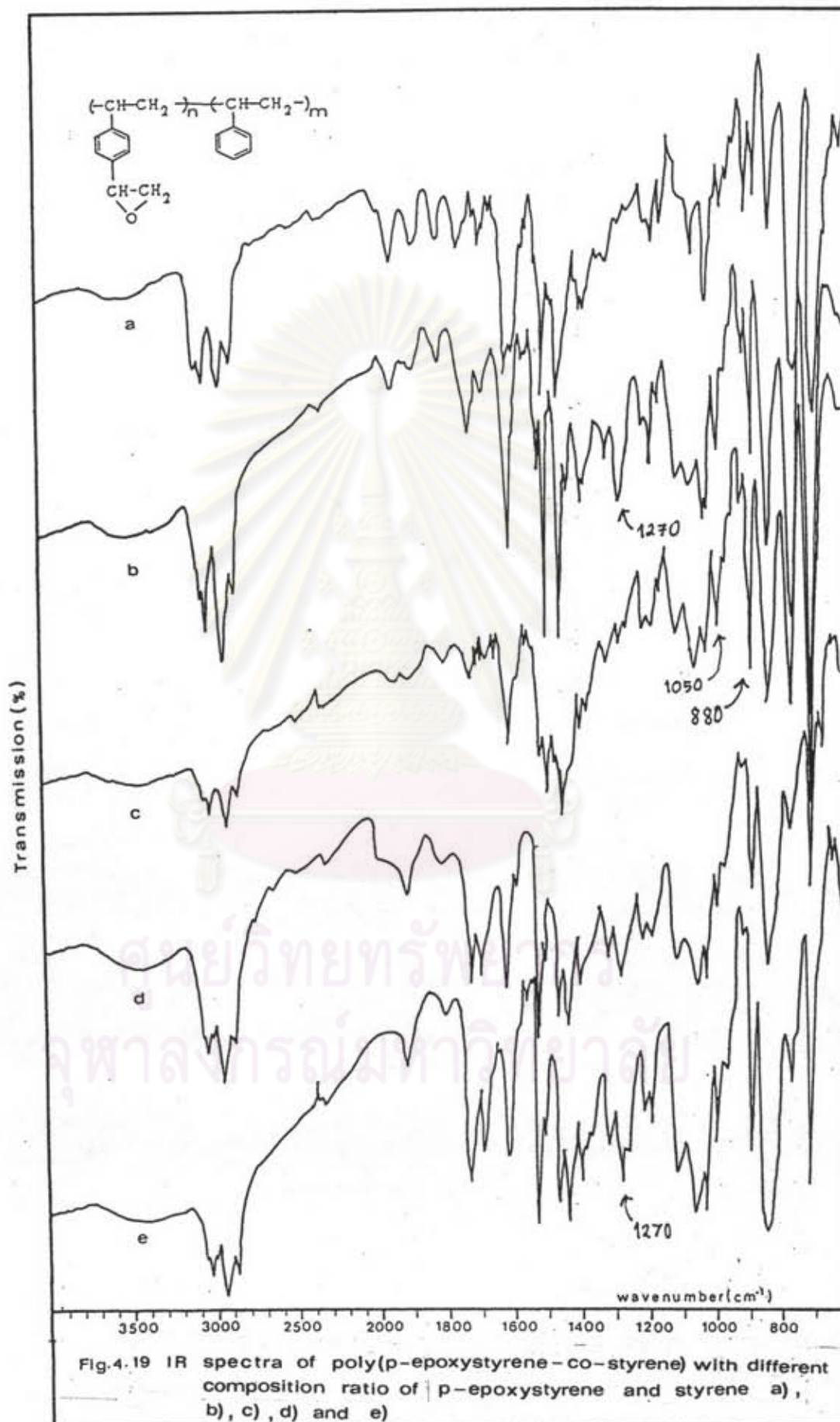
Fig.4.20 DTA thermograms of poly(p-epoxystrene-co-styrene): a,b,c,d

and e , and poly(p-epoxystyrene): f.

From all the data, it indicated that epoxidation could occur from the reaction using phase transfer catalyst. The mechanism was proposed in Scheme 4.4[45].
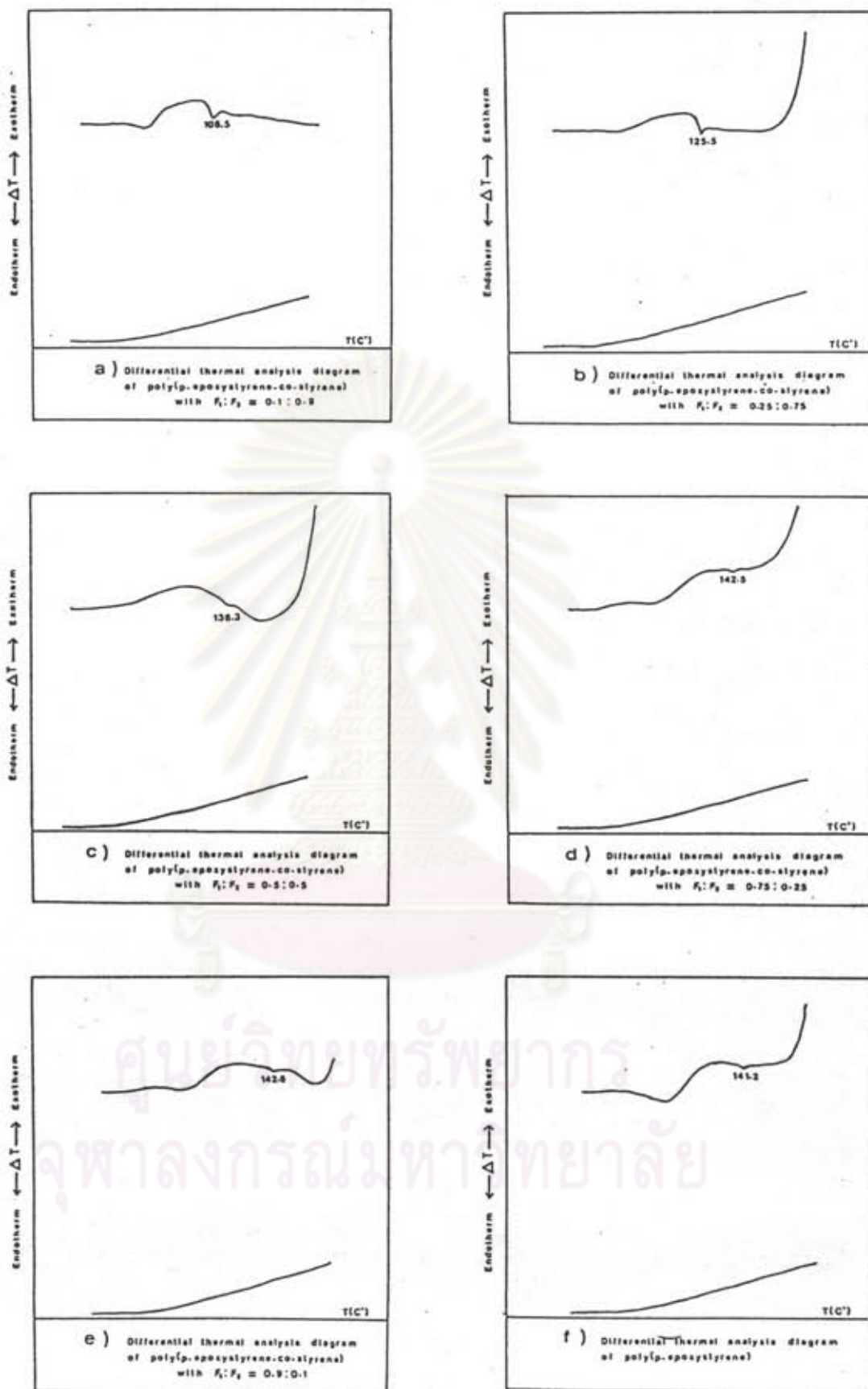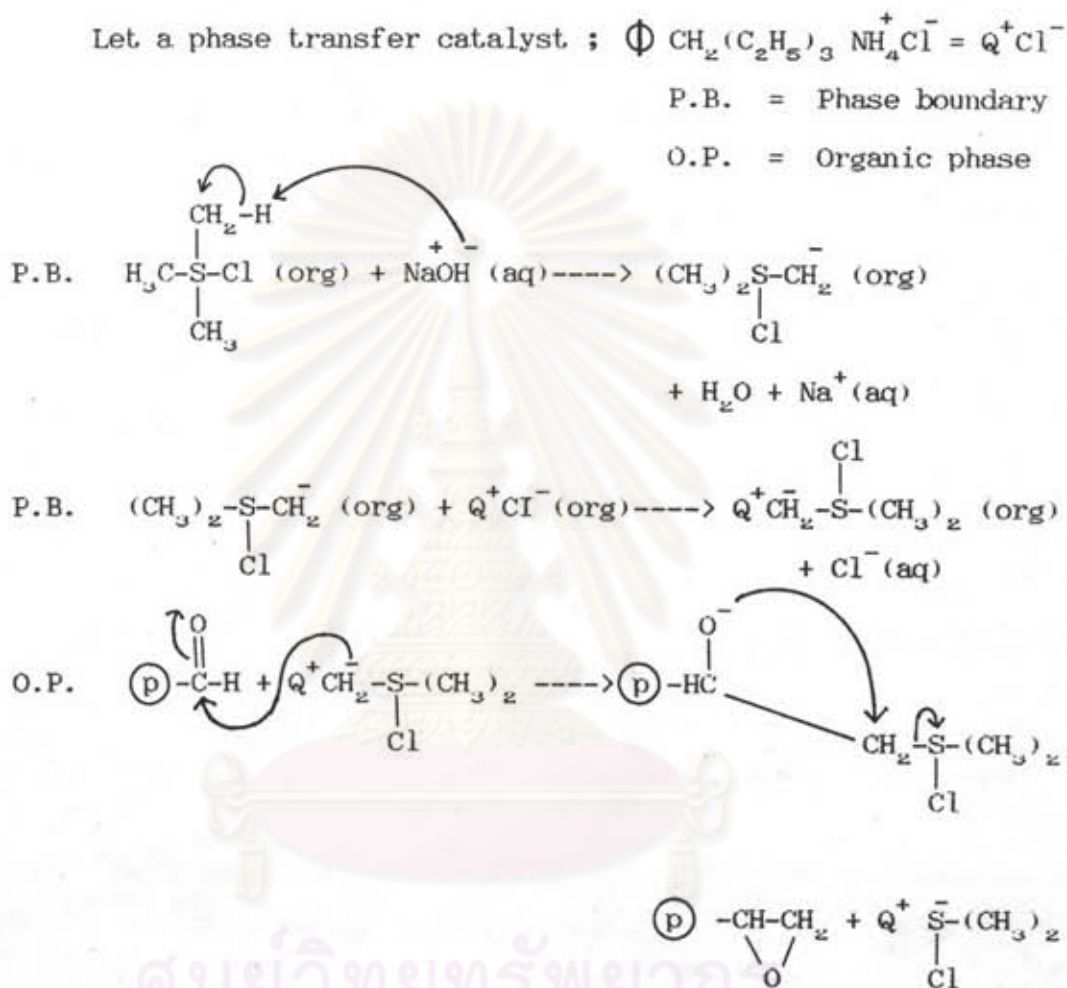
Let a phase transfer catalyst ; ϕ $CH_2(C_2H_5)_3$ $\overset{+}{N}H_4\overset{-}{Cl}$ = Q^+Cl^-

P.B. = Phase boundary

O.P. = Organic phase

P.B. $H_3C-\overset{+}{\underset{CH_3}{\overset{CH_2-H}{S}}}-\overset{-}{Cl}$ (org) + NaOH (aq) ----> $(CH_3)_2-\overset{-}{\underset{Cl}{S}}-\overset{-}{CH_2}$ (org)

        + H_2O + Na^+ (aq)

P.B. $(CH_3)_2-\overset{-}{\underset{Cl}{S}}-\overset{-}{CH_2}$ (org) + Q^+Cl^- (org) ----> $Q^+\overset{-}{CH_2}-\overset{Cl}{\underset{}{S}}-(CH_3)_2$ (org)

        + Cl^- (aq)

O.P. $\textcircled{p}-\overset{O}{\overset{||}{C}}-H$ + $Q^+\overset{-}{CH_2}-\underset{Cl}{S}-(CH_3)_2$ ----> $\textcircled{p}-HC\overset{O^-}{\diagup}$ $CH_2-\underset{Cl}{S}-(CH_3)_2$

        $\textcircled{p}-CH-CH_2$ + Q^+ $\overset{-}{\underset{Cl}{S}}-(CH_3)_2$
              $\diagdown O \diagup$

Scheme 4.4

So poly(p-epoxystyrene) and their copolymers were obtained, but the epoxide ring seemed to open easily because of the structural strain. From the experiment, epoxidation could not be carried out completely due to possible steric hindrance of the side carbonyl groups. Considering the T_g of polymers, they were rather high because some crosslinking had occurred during the reaction.

Therefore, epoxidation of batch c was carried out again. In order to prevent crosslinking, the reaction was performed under the same condition, except it was cooled at the temperature of around 15 $^{\circ}$C all the time. This gave the product with T_g 115° C, the epoxidation content was 2.790 mmole per 1g. polymer and the conversion of chloromethyl group (3.892 mmole per 1g. polymer) to epoxide group was 71.69%. The result was obviously better than the previous one. The IR spectra were also shown in figure 4.21.

The other objective of this research work, besides the attempt to synthesize poly(p-epoxystyrene) and poly (p-epoxystyrene-co-styrene), is to find the right composition of the epoxide moiety in the polymer which leads to the good negative photoresist. To achieve this objective the analysis of these copolymers comparing to poly(p-epoxystyrene) in terms of microlithographic characters must be done. Unfortunately, no such equipment is available in Thailand. However, all of these compounds were sent to analyze at the macromolecule laboratory, Montpellier Universite, France, the results were unsatisfactory probably due to their crosslinking either during the synthesis or delivery.

Furthermore, one of the copolymers (batch c) was subjected to the testing in the lithographic process comparing to the commercial one. Unfortunately, the light source used was UV which was not suitable for the negative photoresist containing p-epoxystyrene.

Fig. 4.21 The IR spectra of a) poly(p-chloromethylstyrene-co-styrene)
b) poly(p-carboxaldehydestyrene-co-styrene) and
c) poly(p-epoxystyrene-co-styrene)