Chapter IV

Results and Discussions

4.1 Synthesis of N -Phenylmaleimide

In this work, the route for synthesis N-phenylmaleimide composed of two steps, synthesis of maleanilic acid and conversion of maleanilic acid to N-phenylmaleimide as following:

4.1.1 <u>Synthesis of Maleanilic Acid</u>

In this step, maleanilic acid was prepared by reaction of aniline and maleic anhydride by using diethyl ether as a solvent.
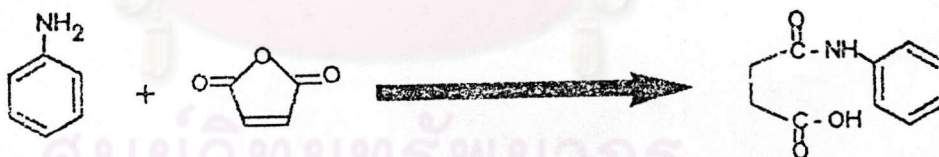
After completing the reaction, 95.6 % yield of a fine cream-colored powder was obtained. The melting point of this product was 202.5-205.0°C (literature[41] : 201-202°C, 97-98 % yield)

IR(KBr) spectrum of maleanilic acid was shown in Figure 4.1.It was clearly shown the O-H stretching of carboxylic group appeared at ν 3200-2400 cm^{-1} with C=O stretching at ν 1720cm^{-1}

which indicated the presence of amide group in the molecule.
The other absorption bands in Figure 4.1 were interpreted as
detailed in Table 4.1.

Table 4.1 The assignment for the IR spectrum of maleanilic
acid.

Wavenumber $\nu(cm^{-1})$	Assignment
3200-2400	O-H str. of carboxylic group
3272	N-H str.
3210	N-H str.
3072	C-H str. of aromatic
1880	overtone region of aromatic ring
1700	C=O str.
1624	C=C str. of aromatic ring
1534	N-H bending
1447	C-N str.
850	} C-H out of plane bending
757	of aromatic ring
689	
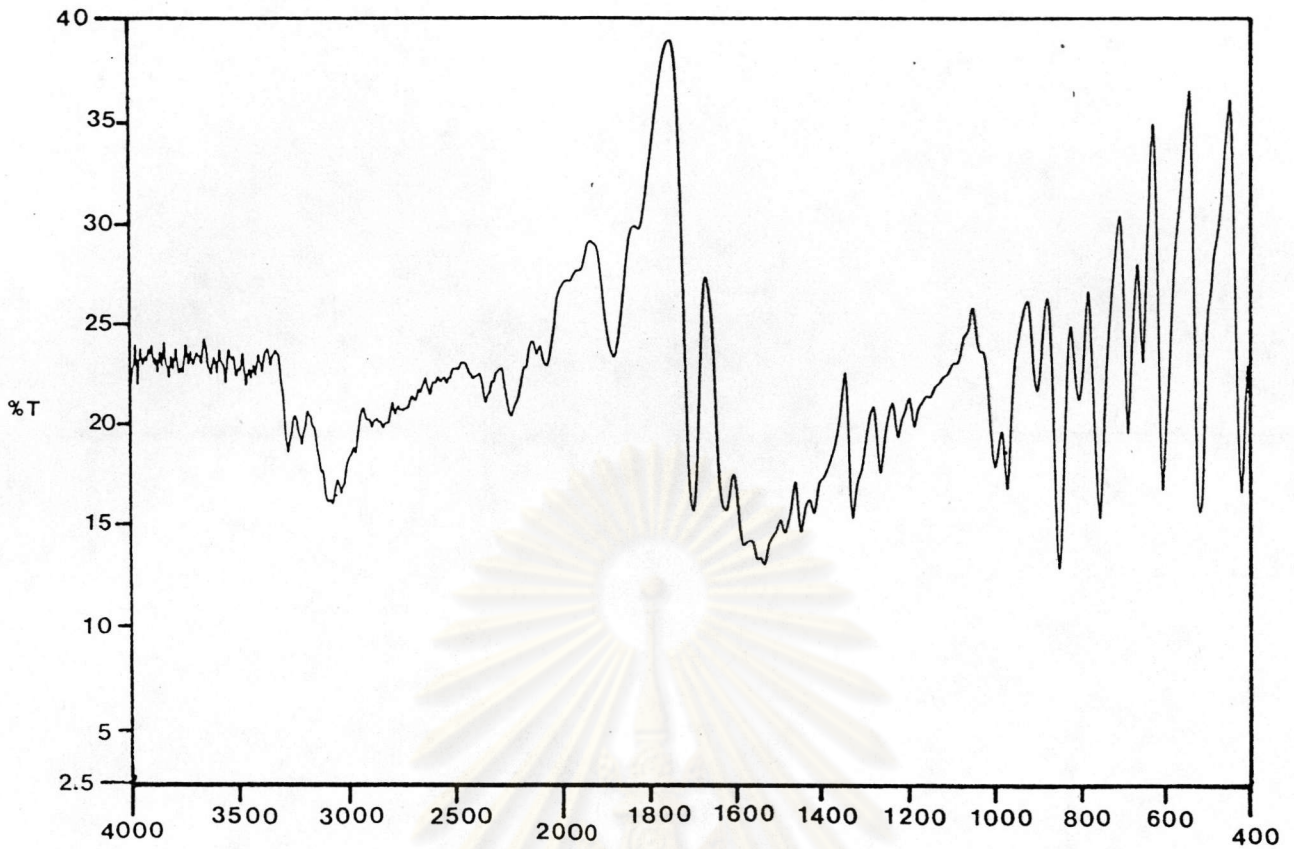
Figure 4.1 IR (KBr) spectrum of maleanilic acid.

4.1.2 Conversion of Maleanilic acid to N-Phenylmaleimide

The resulting maleanilic acid in the last step without purification was treated with acetic anhydride and sodium acetate for 30 minutes at 100 °C.
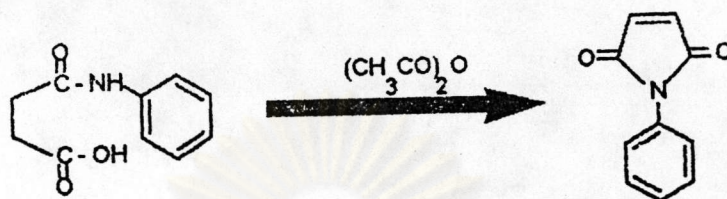
When the reaction finished, N-Phenylmaleimide was separated. After the third recrystallization in cyclohexane, the canary-yellow needles were obtained with 77.5 % yield and m.p. 89.0-90.0 °C. Therefore, the yield of overall reaction for synthesis of N-phenylmaleimide was 74.86 %.

From the experiment, it was found that the purity of acetic anhydride was essential. The less purity of acetic anhydride was, the less product would be obtained.

The obtained N-phenylmaleimide could be characterized by spectroscopic technique. Its IR (KBr) spectrum in Figure 4.2 exhibited the absorption bands at ν 3163, 3093, 1596, 150 and 1456cm^{-1} which indicated that aromatic ring was in the molecule and there were absorption bands of amide group at ν 1711 cm^{-1}, C=O stretching, and ν 1395 cm^{-1}, C-N stretching. The other absorption bands were assigned as detailed in Table 4.2.

Due to the symmetry of N-phenylmaleimide molecule, its
^{1}H NMR spectrum (Figure 4.3) exhibited two signals at δ 6.81
and 7.43 ppm. The first was attributed to the two imide protons
(   ) and the later was dued to the five phenyl protons.

The mass spectrum (Figure 4.4) of the synthesized N-phe-
nylmaleimide showed the molecular ion (M$^+$) at m/e 174.1 which
was the base peak too. Other fragmentations were shown at m/e
146.1 and 129.1. The first peak was due to the fragmentation
of CO radical from the molecular ion. The latter was derived
from the fragmentation of OH radical after the fragmentation of
the CO radical. The mass fragmentation pattern was proposed in
Scheme 4.1.
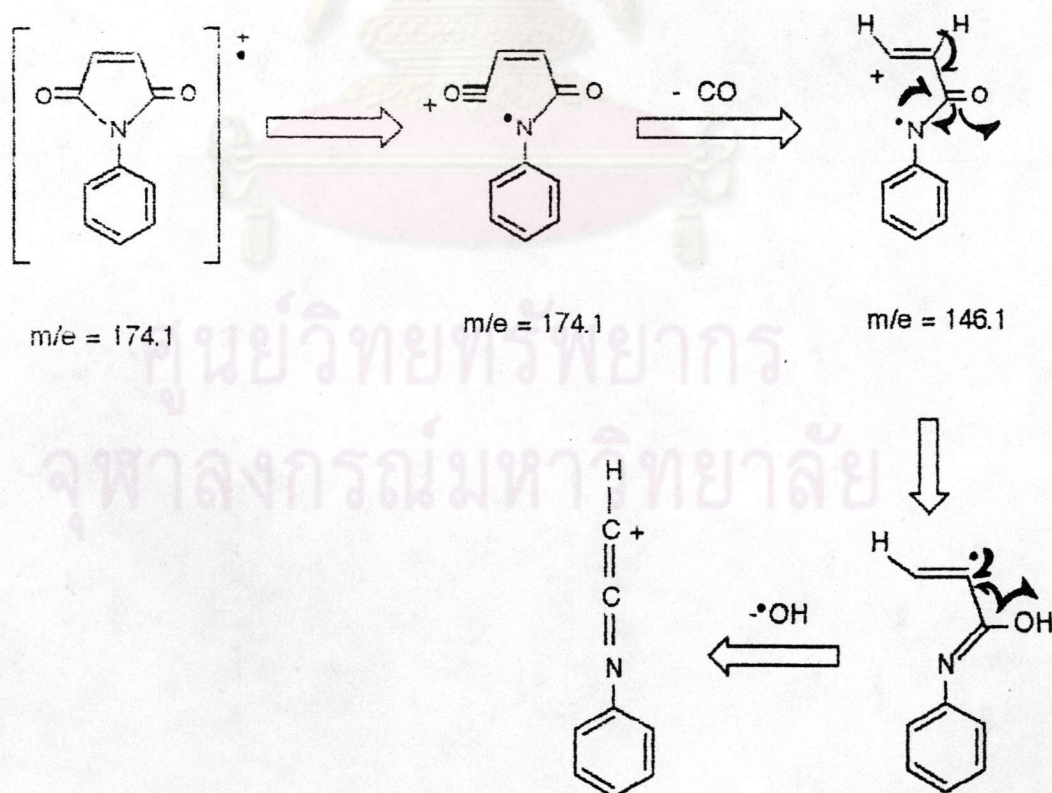
Scheme 4.1

The spectroscopic data (IR NMR and Mass) and a physical property confirmed that the obtained product was N-phenylmaleimide.

Table 4.2 The assignment for the IR spectrum of N-phenylmaleimide

Wavenumber ν (cm^{-1})	Assignment
3163	N-H str.
3093	C-H str. of aromatic
1896	overtone region of aromatic
1879	ring
1711	C=O str.
1596	
1508	C=C str. of aromatic ring
1456	
832	
757	C-H out of plane bending
697	of aromatic ring

Figure 4.2 IR (KBr) spectrum of N-phenylmaleimide.

Chemical Shift (δ)
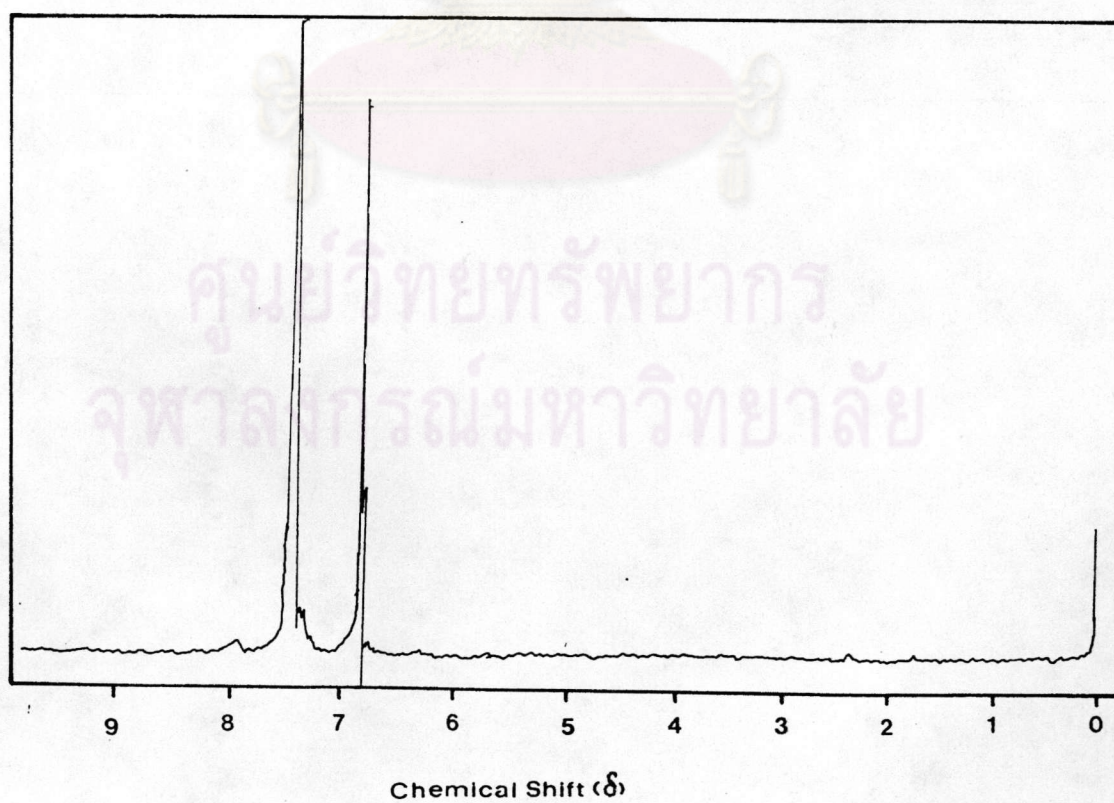
Figure 4.3 The ^{1}H NMR spectrum of N-phenylmaleimide in $CDCl_3$
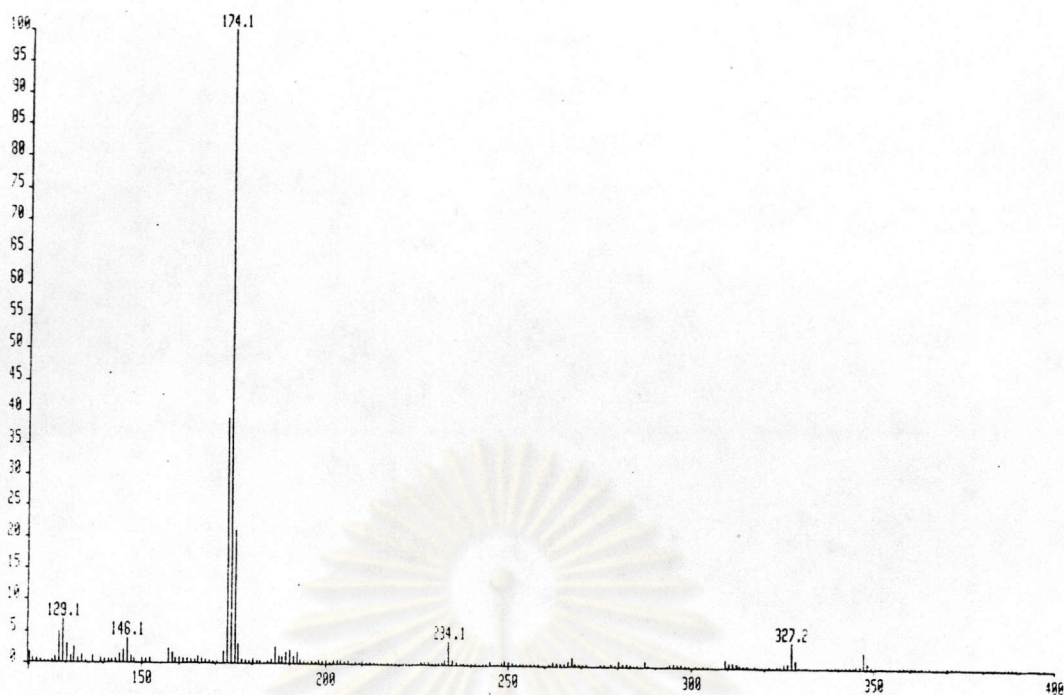
Figure 4.4 The mass spectrum of N-phenyl maleimide.

4.2 Synthesis of *p*-Chloromethylstyrene

In this research work, the method of Kondo et al [36] was used to synthesize *p*-chloromethylstyrene. This method consisted of two steps of reactions, chloromethylation of 2-phenylethyl bromide and dehydrobromination of *p*-(2-bromoethyl)-benzyl chloride. The detail of each steps was described as following :

4.2.1 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.
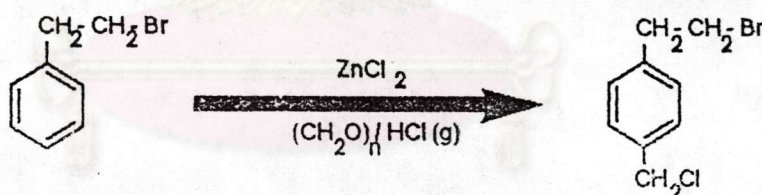

Though it was reported that chloromethyl methyl ether was often employed in the chloromethylation of aromatic compound, this reagent now is known to be highly carcinogenic compound. Therefore, it was not used in this work.

The white needle crystal with 49 % yield was obtained after the fourth recrystalization, while 50% yield was obtained after second recrystallization in method of Kondo et al.

From the observation in several repeating experiments, it was found that the factors effected the yield of the product could be concluded as following. First, the purity of starting material, 2-phenylethyl bromide, must be high. Less products will be obtained if the starting material was slightly brown. The purities of paraformaldehyde and anhydrous $ZnCl_2$ were also neccessary. It was found that the % yield of product decreased if one of them retained moisture. Especially, its reactivity was reduced by moisture.

The proposed mechanism of chloromethylation of 2-phenylethyl bromide was shown in Scheme 4.2 [43, 44].
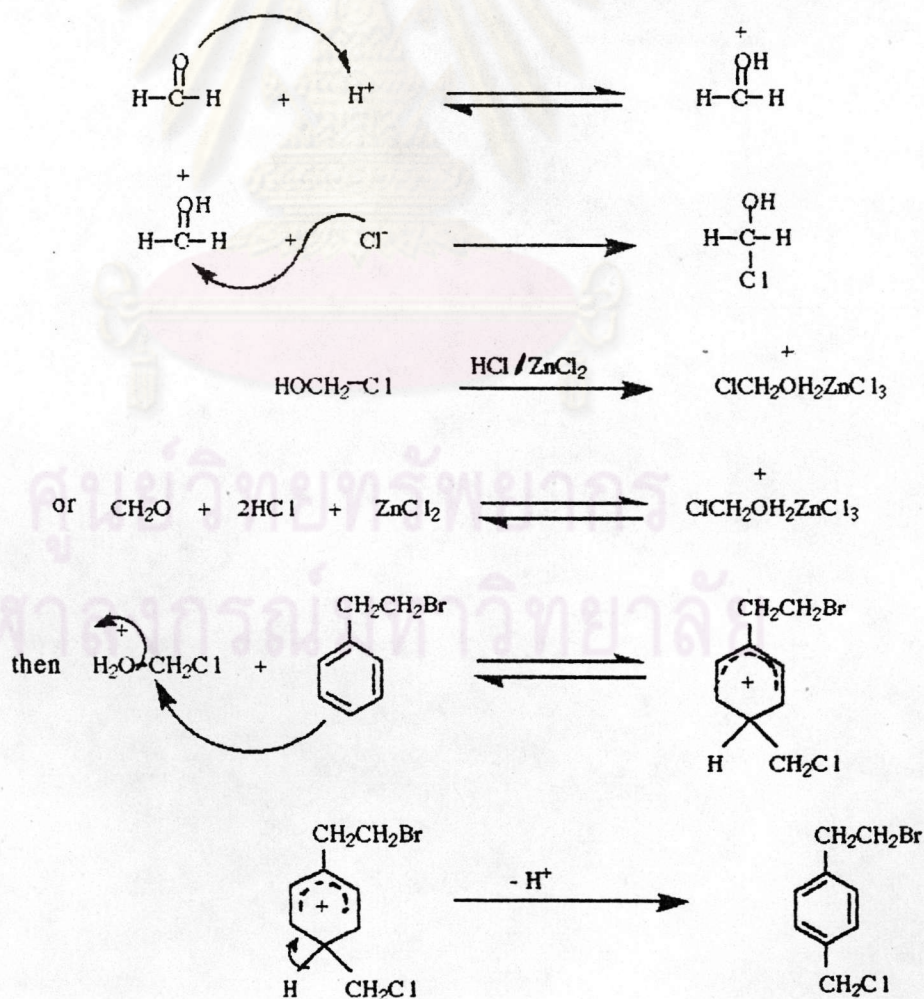
Scheme 4.2

Actually, *o*-(2-bromoethyl)benzyl chloride was formed as a by product, but it could easily be separated by recrystalliza- tion from petroleum ether (b.p. 40-60 °C). It was reported that around 3.5 % of *o*-(2-bromoethyl)benzyl chloride remained after the fourth recrystallization [49].

IR (KBr) spectrum of *p*-(2-bromoethyl)benzyl chloride was shown in Figure 4.4. It was obviously observed C-Cl bending appearance 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 concurrent with the absence of such absorption bands in the IR spectrum of *p*-phenylethyl bromide (Figure 4.5). The other absorption bands in Figure 4.4 were interpreted as detailed in Table 4.3.

Table 4.3 The assignment for the IR spectrum of

p-(2-bromoethyl)benzyl chloride

Wavenumber ν (cm^{-1})	Assignment
3040	C-H str. of aromatic
2970	C-H str. of aliphatic
1930	overtone region of aromatic
1810	ring
1695	
1270	C-Cl bending
1220	C-Br bending
850	C-H out of plane bending of aromatic ring
680-660	C-Cl str.
630	C-Br str.

Furthermore, the ^{1}H NMR spectrum (Figure 4.7) of this product also showed two doublets in the aromatic region at δ 7.24 and 7.38 ppm which were the characteristic of *para*-substitution of aromatic compound. The other signals were assigned as detailed in Table 4.4.
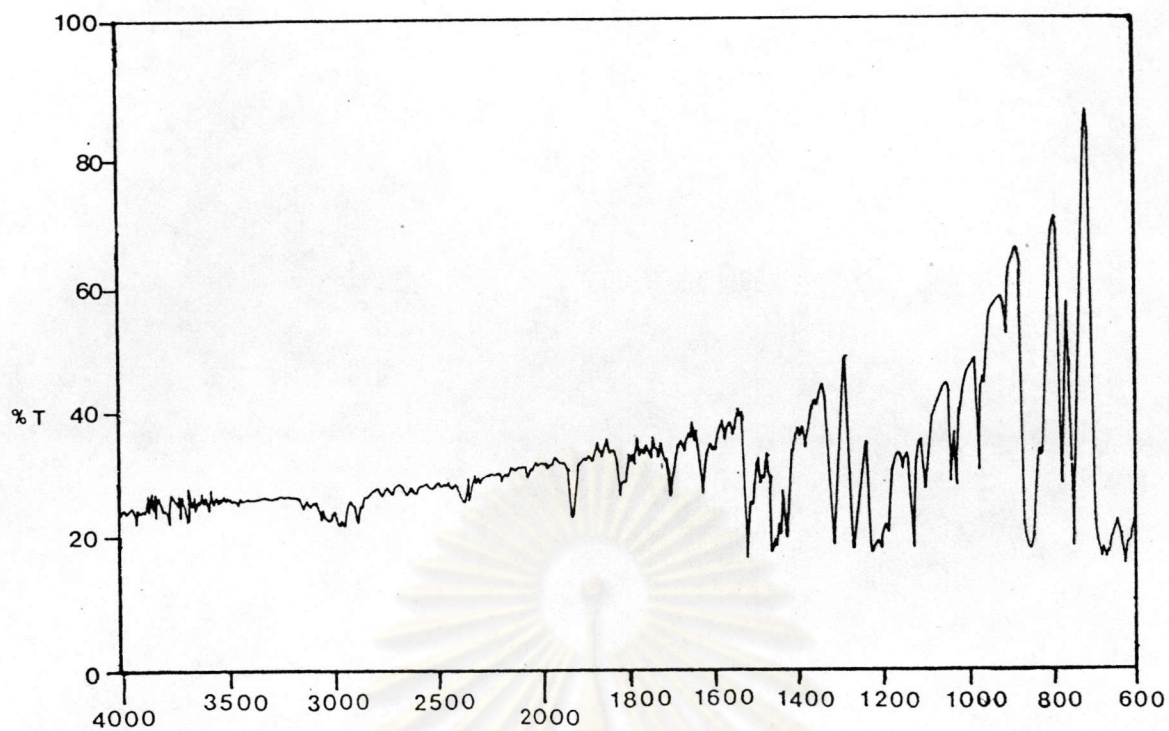
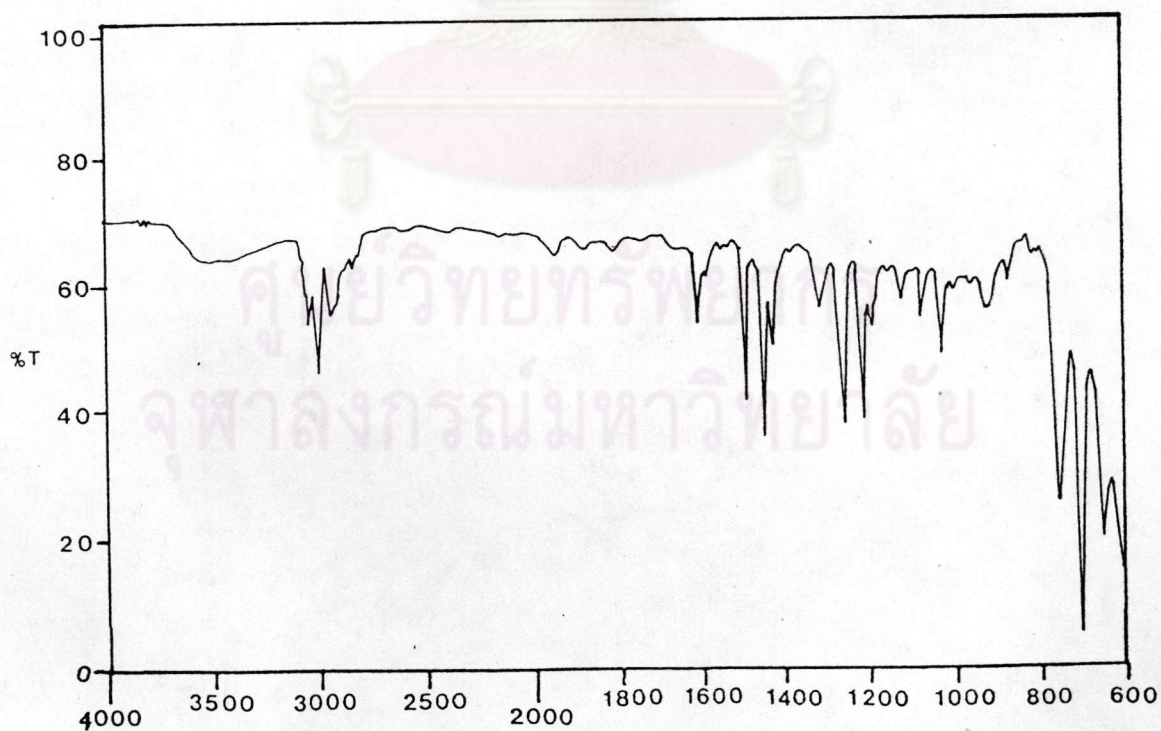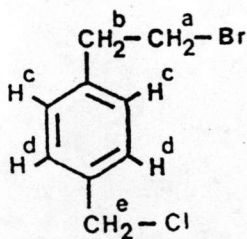Figure 4.5 IR (KBr) spectrum of *p*-(2-bromoethyl)benzyl chloride.

Figure 4.6 IR (NaCl) spectrum of 2-phenylethyl bromide.

p-(2-bromoethyl)benzyl chloride

Table 4.4 The assignment for the ^{1}H NMR spectrum of
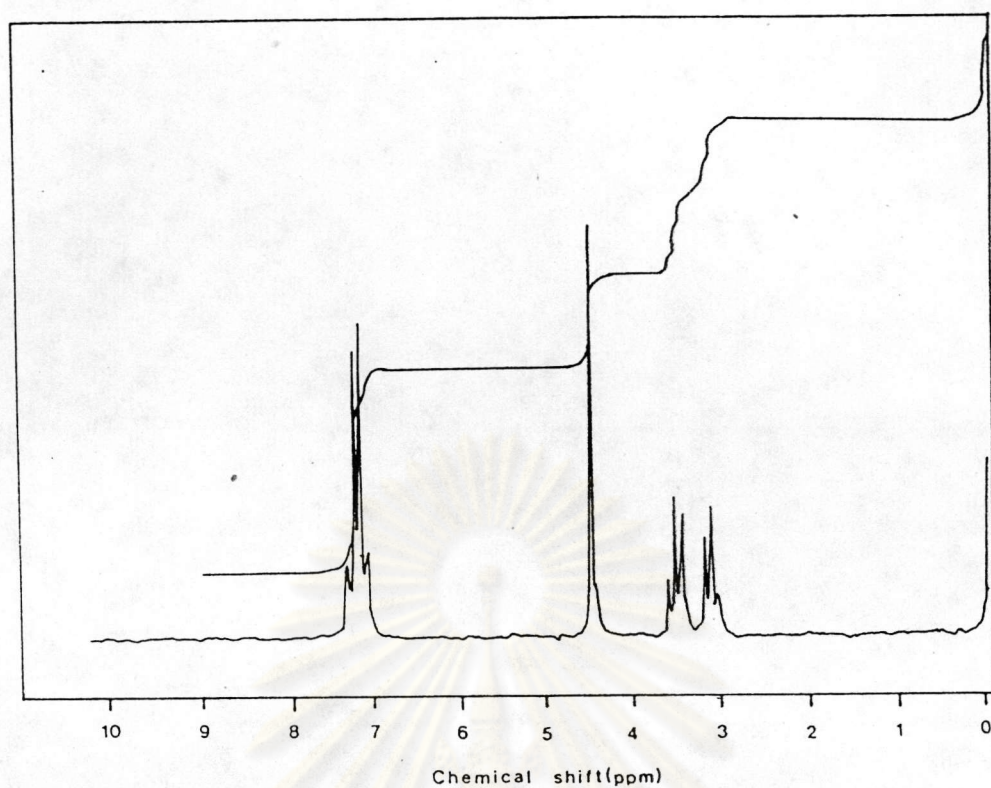*p*-(2-bromoethyl)benzyl chloride

Chemical Shift δ (ppm)	Peak Type	Assignment
7.39	d, 2H (J=8.36Hz)	H^d, aromatic ring
7.22	d, 2H (J=8.05Hz)	H^c, aromatic ring
4.55	s, 2H	$-CH_2-Cl$
3.57	t, 2H (J=7.10Hz)	$-CH_2-Br$
3.16	t, 2H (J=6.60Hz)	$-CH_2-$

Since chlorine was more electronegative than bromine, two protons at the ortho-position to chloromethyl group (H^d) were more strongly deshielding than the other two protons close to 2-bromoethyl group (H^c). Therefore, a doublet at δ 7.38 ppm was assigned to H^d protons, the other at 7.22 ppm was assigned to H^c protons.
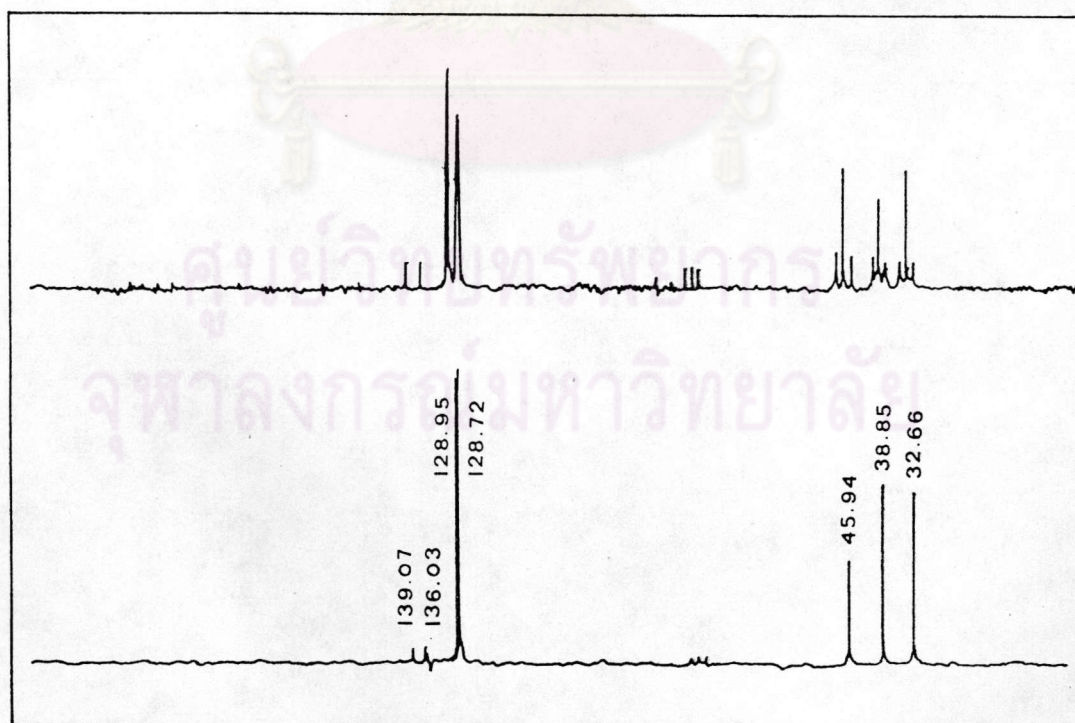
In addition, the ^{13}C NMR spectrum (Figure 4.8) indicated the important carbon signal of chloromethyl group was at δ 45.94 ppm. The other signals at δ 32.67, 38.84 ppm were the signals of -^{b}CH$_2$- and -^{a}CH$_2$-Br, respectively and the signals in the range of 128.72-139.07 ppm corresponded to the aromatic carbons, characteristic of para-substituted aromatic compound (Table 4.5). Consequently, the ^{13}C NMR spectrum confirmed the structure of *p*-(2-bromoethyl)benzyl chloride.

Table 4.5 The assignment for the ^{13}C NMR spectrum of
p-(2-bromoethyl)benzyl chloride

| Chemical Shift δ (ppm)	Assignment
32.66	-^{b}CH$_2$-
38.85	-^{a}CH$_2$-
45.94	-^{g}CH$_2$-
128.72	-^{d}CH= (aromatic ring)
128.95	-^{e}CH= (aromatic ring)
136.03	-^{c}C= (aromatic ring)
139.07	-^{f}C= (aromatic ring)

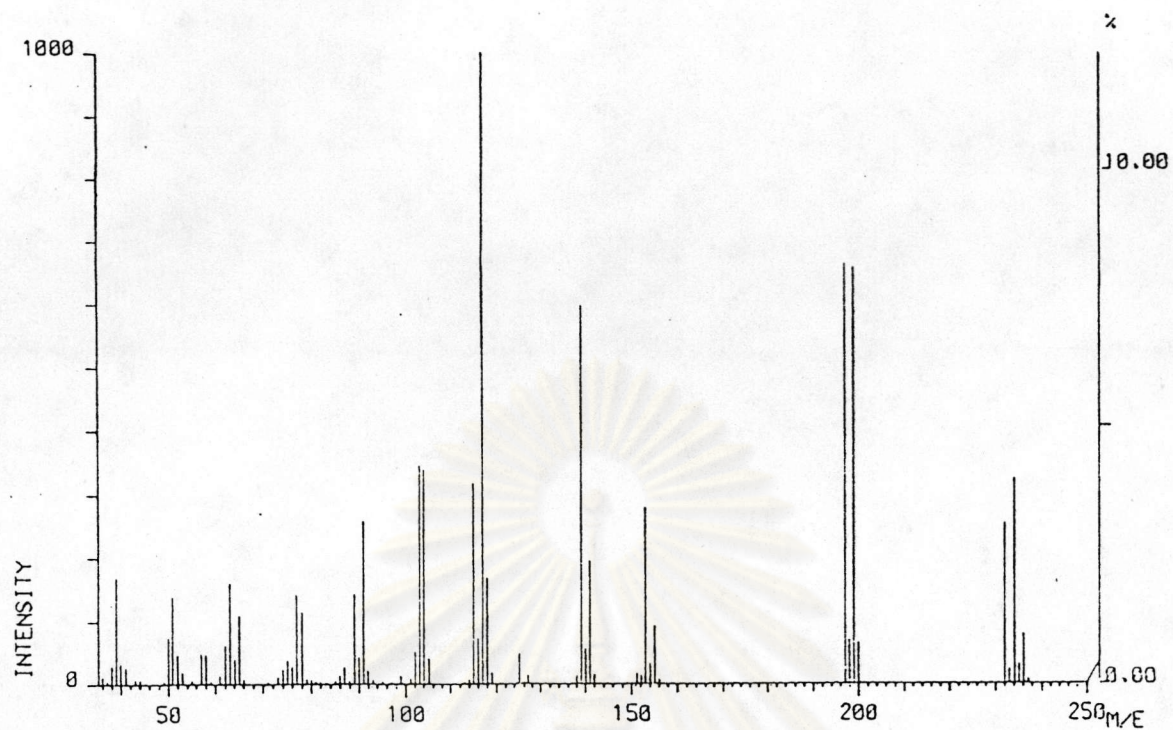Figure 4.7 The ^{1}H NMR spectrum of p-(2-bromoethyl)benzyl chloride in CDCl$_3$

Figure 4.8 The ^{13}C NMR spectrum of p-(2-bromoethyl)benzyl chloride. in CDCl$_3$.

The mass spectrum (Figure 4.9) of this compound had the molecular ion (M$^+$) at m/e 232 and the base peak at 117 which was the fragmentation from molecular ion by the loss of Cl atom and HBr. Other fragmentations were observed 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$_2$CH$_2$Br 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$_2$Br radical to give a -CH$_2$Cl substituted tropylium ion. The mass fragmentation pattern was summarized in Scheme 4.3.
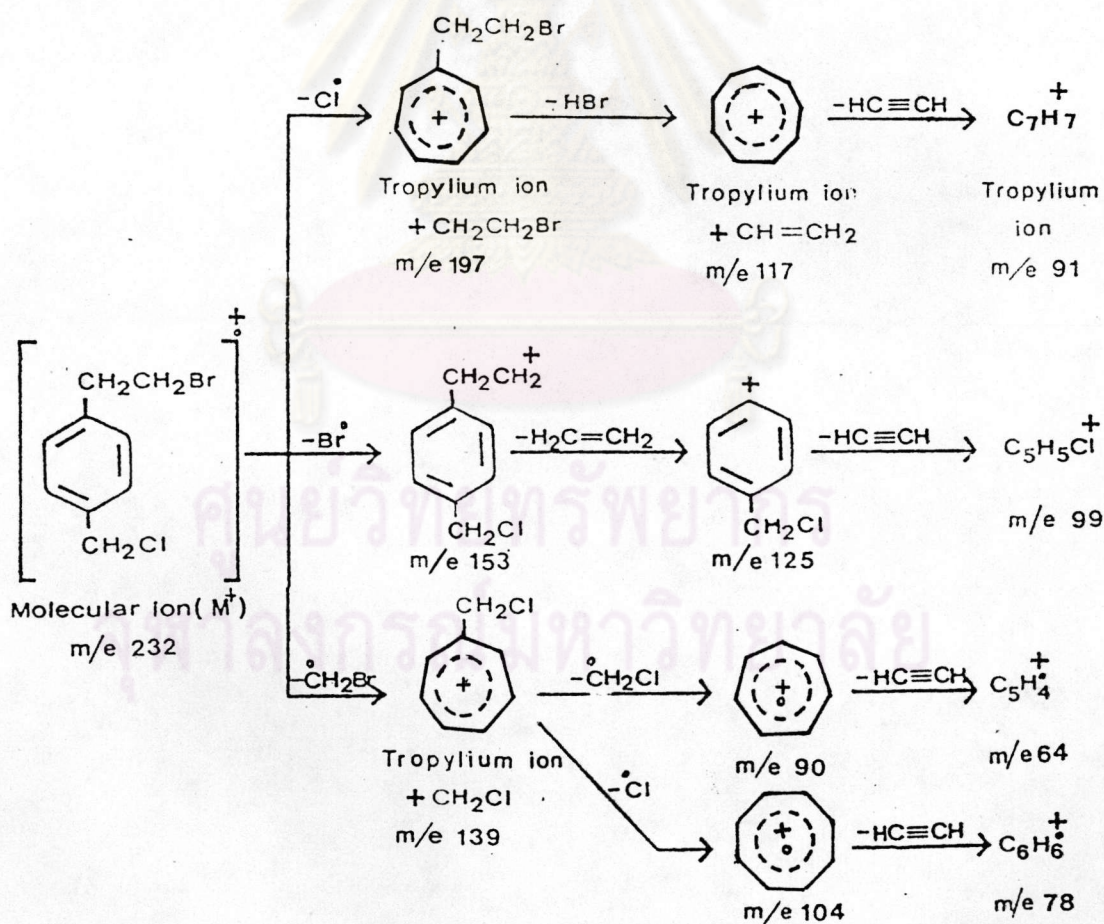
Scheme 4.3

Figure 4.9 The mass spectrum of *p*-(2-bromoethyl)benzyl chloride.

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

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

Dehydrobromination of *p*-(2-bromoethyl)benzyl chloride was carried out with potassium *tert*-butoxide and *tert*-butanol at 35 °C for 2 hours. After completing reaction, *p*-chloromethylstyrene was obtained with b.p. 90-94 °C at 2 mmHg. and 75.62 % yield. Therefore, the yield of overall reaction from chloromethylation to dehydrobromination was 37.05 %. The obtained product was colorless with strong pungent odor.
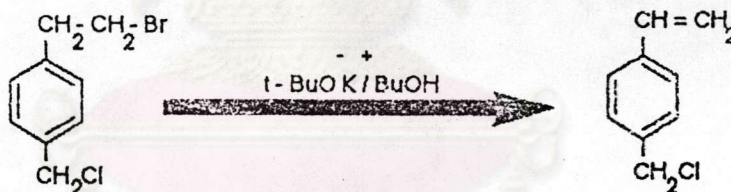
It was found that the side reaction, the formation of ether compound, was usually occurred by reaction of *p*-chloromethylstyrene and potassium *tert*-butoxide.
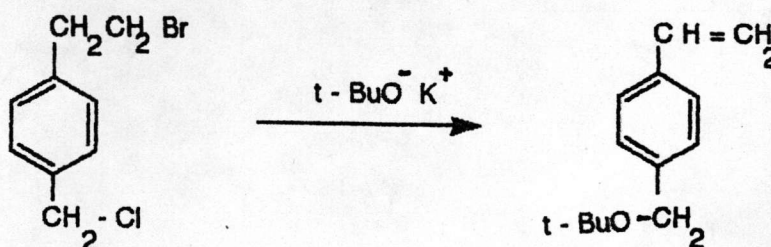
Therefore, potassium *tert*-butoxide should be carefully added in equivalent amount to that of *p*-(2-bromoethyl)benzyl chloride. To avoid the accompanying of ether compound distillation of *p*-chloromethylstyrene was performed in the temperature range of 90-94 °C at 2 mmHg. It must be distilled as soon as posible to prevent polymerization of this monomer.

Characterization of this product was performed by spectroscopic technique. Its IR (NaCl) spectrum was shown in Figure 4.10. The absorption bands at ν 3118, 1920, 1829, 1615, 1508, 1450 and 830 cm^{-1} indicated the pressence of the aromatic ring in the molecule. The appearance of the absorption bands at ν 1412 and 916 cm^{-1} concomitant with the absence of the absorption band at ν 1222 cm^{-1} denoted that dehydrobromination was occurred. The other absorption bands were interpreted in detail in Table 4.6.

Table 4.6 The assignment for the IR spectrum of
p-chloromethylstyrene.

Wavenumber ν (cm^{-1})	Assignment
3118	C-H str. of aromatic
2970	C-H str. of aliphatic
1920	overtone region of aromatic
1829	ring
1625	
1508	C=C str. of aromatic ring
1450	
1412	=CH$_2$ in plane bending of alkene
1270	C-Cl bending
1220	C-Br bending
915	=CH$_2$ out of plane bending of alkene
830	C-H out of plane bending of aromatic ring
690	C-Cl str.

Furthermore, the ^{1}H NMR spectrum of p-chloromethylsty-
rene, Figure 4.11, also showed the signals at δ 6.70, 5.75, and
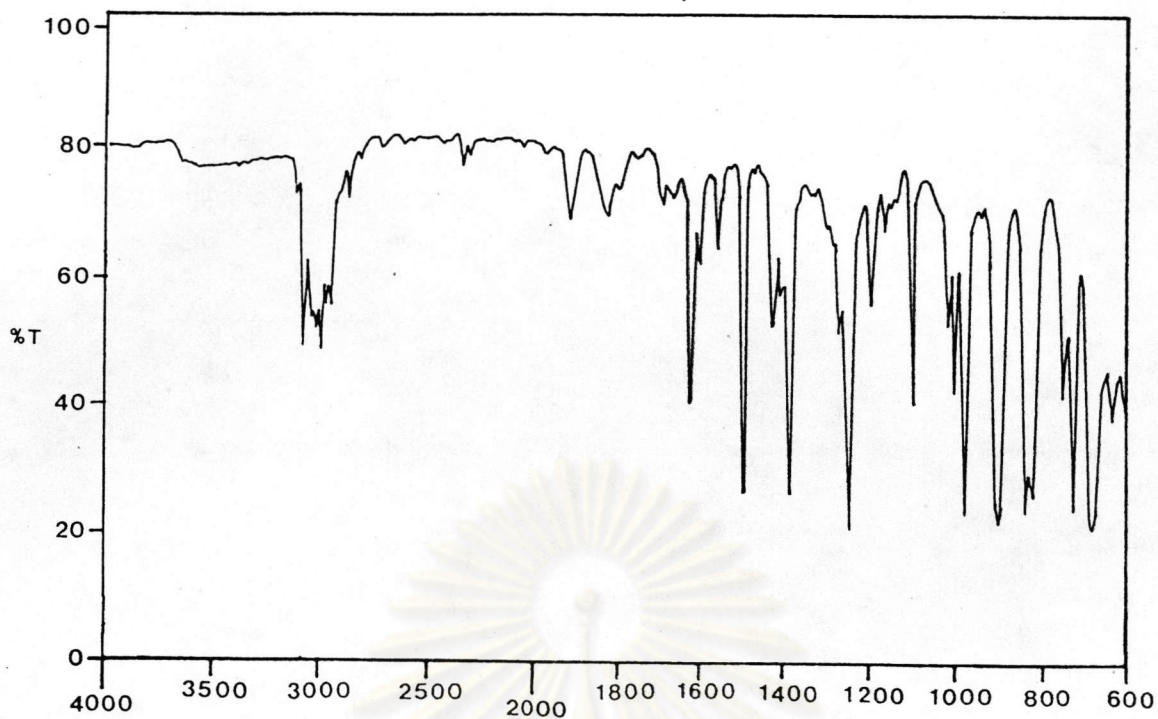5.25 ppm which one due to the olefinic protons (Table 4.7).

Figure 4.10 IR (NaCl) spectrum of *p*-chloromethylstyrene.

Chemical shift(ppm)
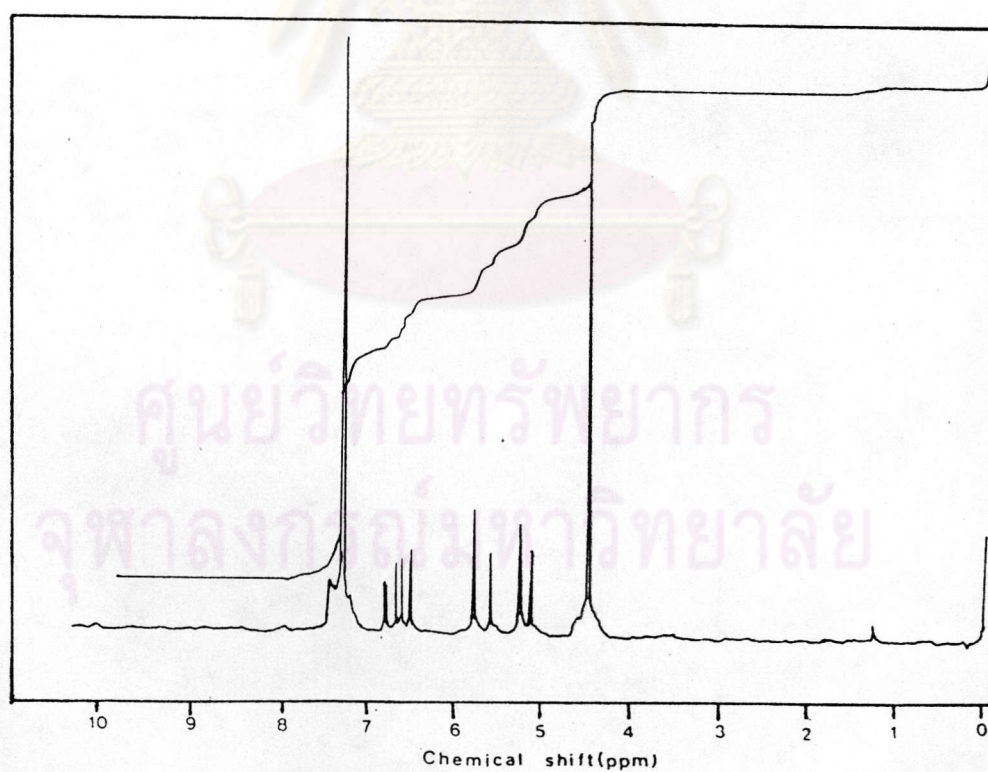
Figure 4.11 The ^{1}H NMR spectrum of *p*-chloromethylstyrene in CDCl$_3$.
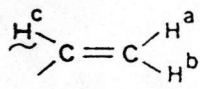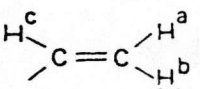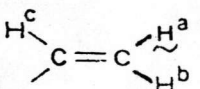
This confirmed that there was a structure of olefinic group (C=C) in the molecule. A doublet of doublets at δ 6.71 ppm corresponded to the H^c proton. It was strongly deshielded by aromatic ring and coupled with H^b proton (J_{cb}=17.6 Hz) and with H^a proton (J_{ca} = 10.8 Hz). Moreover, a doublet of doublets at δ 5.73 ppm was belong to H^b protons which were coupled with 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 H^a proton was coupled with H^c proton (J_{ca} = 10.98 Hz) and with the H^b proton (J_{ab} = 2 Hz).
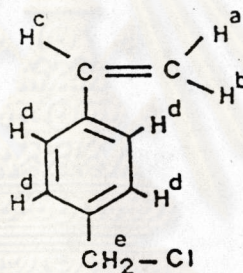
p-Chloromethylstyrene

Table 4.7 The assignment for the ^{1}H NMR spectrum of

p-chloromethylstyrene

Chemical Shift δ (ppm)	Peak Type	Assignment
7.34	br. s, 4H	aromatic protons
6.70	dd, 1H (J_{cb}=17.6) (J_{ca}=10.8)	H^cC=CH^a/H^b
5.73	dd, 1H (J_{cb}=17.6) (J_{ab}=2)	H^cC=CH^a/H^b
5.25	dd, 1H (J_{ca}=10.98) (J_{ab}=2)	H^cC=CH^a/H^b
4.54	s, 2H	$-CH_2-Cl$

4.3 Copolymerization

4.3.1 Copolymerization of *p*-Chloromethylstyrene and Styrene

p-Chloromethylstyrene and styrene were copolymerized in benzene using AIBN as initiator. After reaction, the solution was more viscous.
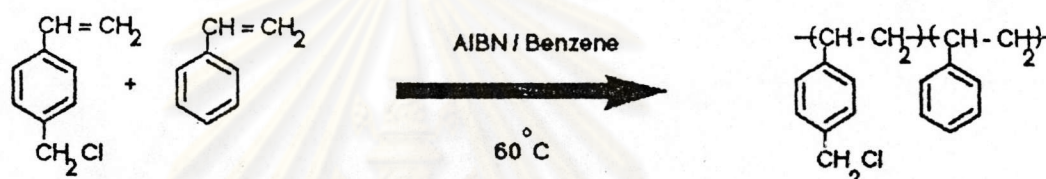
The white powder was obtained with 55.81 % yield after the third recrystallization. It had T_g 94.75 $^\circ$C and Mw 32,995. From elemental analysis, it contained C 77.28 %, H 6.76 %, and Cl 14.23 % which was agreed with the calculated value from the repeating unit of this copolymer, C 79.58 %, H 6.63 %, and Cl 13.79 %.

The IR (KBr) spectrum of this compound was shown in Figure 4.15a. The absorption bands at ν 1410 and 915 cm^{-1} disappeared while the absorption band at ν 1449cm^{-1} appeared. Thus, it indicated that the olefinic group of the monomer became the aliphatic moiety in the polymer. The -CH$_2$-Cl bending (wagging) and C-Cl stretching remained at ν 1265 and 625 cm^{-1}. 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)

Wavenumber ν (cm^{-1})	Assignment
3055	C-H str. of aromatic
3024	
2921	C-H str. of aliphatic
2848	
1908	overtone region of aromatic
1798	ring
1701	
1603	
1492	C=C str. of aromatic ring
1449	
1420	C-H bending of aliphatic
1265	-CH$_2$-Cl bending (wagging)
830-760	C-H out of plane
697	bending of aromatic ring
700	C-Cl str.

Besides, the ^{1}H NMR spectrum of this compound was also confirmed that *p*-chloromethylstyrene were copolymerized to form poly(*p*-chloromethylstyrene-co-styrene). This was shown by two broad singlets at δ 1.56 and 1.43 ppm, which were the chemical

shifts of ($-CH-CH_2-$) and ($-CH-CH_2-$) respectively, while there was no any signal in the olefinic region (Figure 4.12). The other signals were assigned as detailed in Table 4.9.

<u>Table</u> 4.9 The assignment for the ^{1}H NMR spectrum of poly(p-chloromethylstyrene-co-styrene)

Chemical Shift δ (ppm)	Assignment
7.05	H, of aromatic
6.50	
4.50	$-CH_2-Cl$
1.54	($-CH-CH_2-$)
1.41	($-CH-CH_2-$)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย
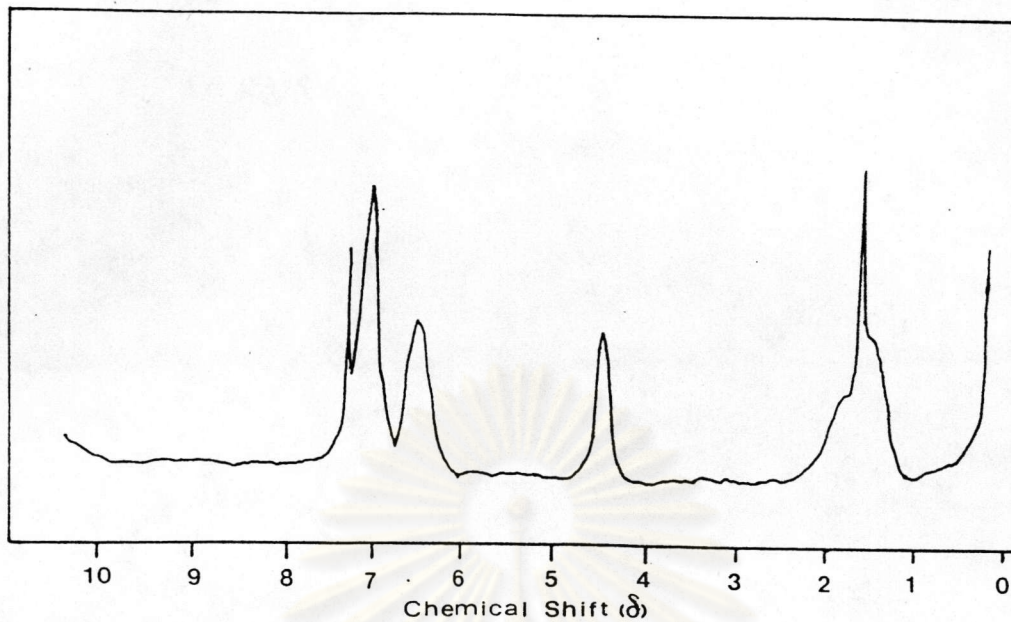
Figure 4.12 The ^{1}H NMR spectrum of poly(p-chloromethylstyrene
-co-styrene) in CDCl$_3$.

4.3.2 Copolymerization of *p*-Chloromethylstyrene, Styrene and N-Phenylmaleimide

Bacause of a low glass transition temperature (T_g) of poly(*p*-chloromethylstyrene-co-styrene), N-Phenylmaleimide had been interested to use as a third monomer in polymerization process. Copolymerization of *p*-chloromethylstyre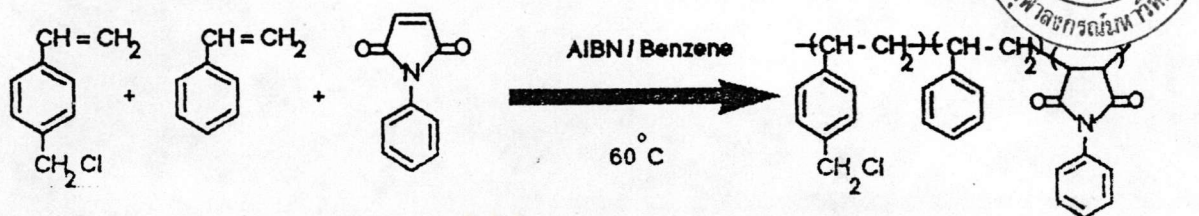ne, styrene and N-phenylmaleimide was carried out by using the same method for copolymerization of *p*-chloromethylstyrene and styrene. The % mole of *p*-chloromethylstyrene was kept constant at 50 %, while % mole of N-phenylmaleimide was varied as follows ; 5 %, 10 %, 25 % and 50 %, for batch b, c, d, and e, respectively, and % mole of styrene was the rest of mole of *p*-chloromethylstyrene and N-phenylmaleimide. The resulting products were then converted to the final products, poly(*p*-epoxystyrene-co-styrene-co-N-phenylmaleimide which will be described later.

The IR (KBr) spectra of these compounds were shown in Figure 4.13. They were similar to each other except the intensity of the absorption bands at ν 1700 and 1421 cm^{-1} which are due to C=O stretching and C-N stretching of amide group, respectively. It was found that the more N-phenylmaleimide was in the polymer chain, the higher intensity of absorption bands

at ν 1700 and 1421 cm^{-1}, relative to the absorption band of -CH$_2$-Cl bending at ν 1267 cm^{-1}, was observed. The other absorption bands were assigned as detailed in Table 4.10.

Table 4.10 The assignment for the IR spectrum of poly (p-chloromethylstyrene-co-styrene-co-N-phenyl-maleimide)

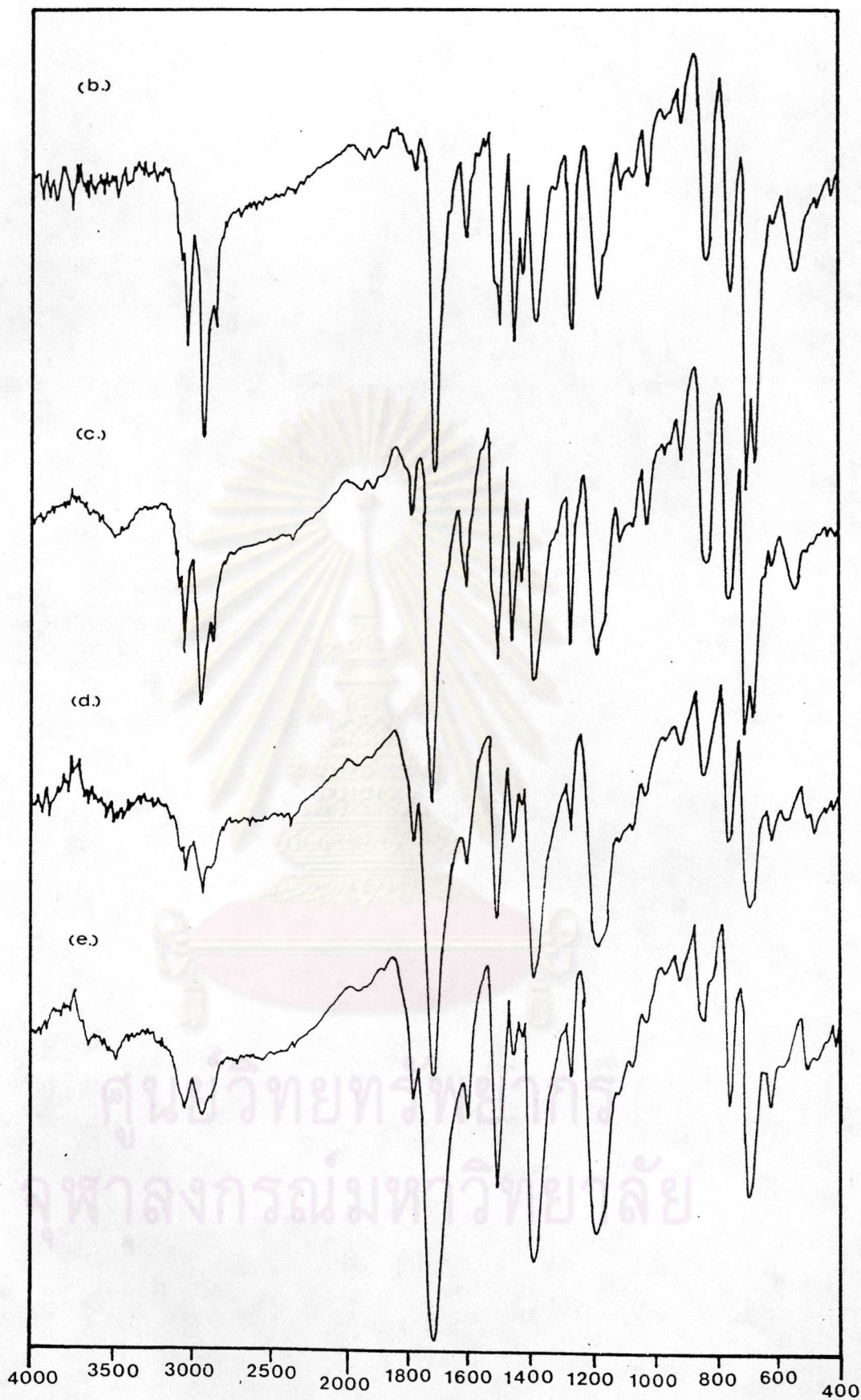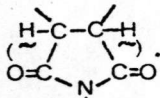| Wavenumber ν (cm^{-1})	Assignment
3025	C-H str. of aromatic
2919	C-H str. of aliphatic
2849	
1945	overtone region of aromatic
1775	ring
1710	C=O str. of amide
1610	
1495	C=C str. of aromatic ring
1449	
1421	C-N str.
1378	C-H bending of aliphatic
1270	-CH$_2$-Cl bending (wagging)
910	C-H out of plane
832	bending of aromatic ring
700	C-Cl str.

Figure 4.13 IR (KBr) spectrum of poly(*p*-chloromethylstyrene-co-styrene-co-N-phenylmaleimide).
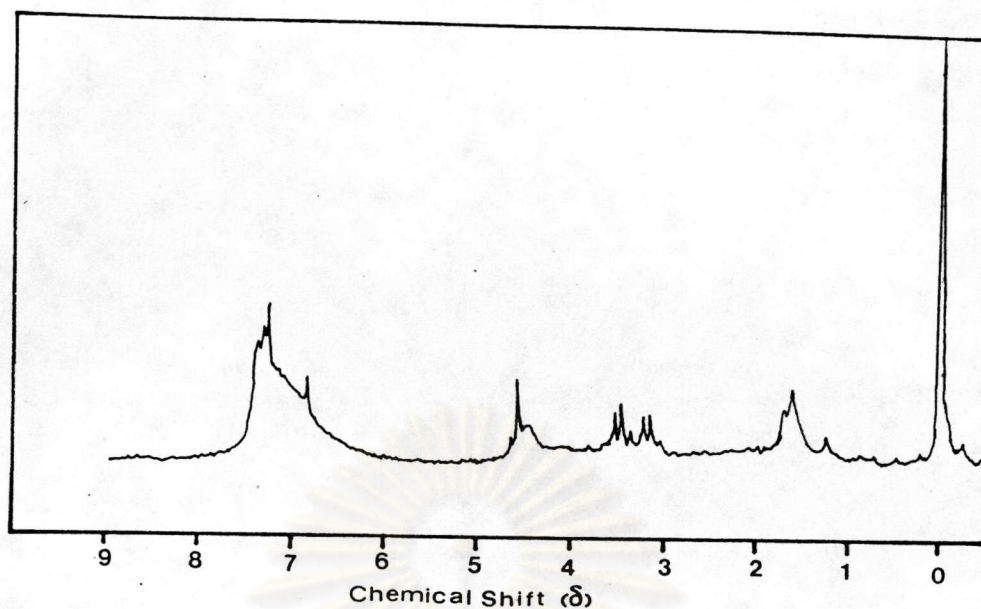
Figure 4.14 The ^{1}H NMR spectrum of poly(p-chloromethylstyrene -co-styrene-co-N-phenylmaleimide) in $CDCl_3$.

The typical ^{1}H NMR spectrum of poly(p-chloromethylsty-rene-co-styrene-co-N-phenylmlaleimide) was shown in Figure 4.14. The more intense was the signal at δ 3.08-3.17 ppm were attributed to the protons of imide ring ( ). The other signals at δ 6.60-7.05,1.54 and 1.42 ppm were due to aromatic,($-CH-CH_2-$) and ($-CH-CH_2-$) protons respectively. Consequently, the ^{1}H NMR spectroscopy confirmed the structure of poly(p-chloromethyl-styrene-co-styrene-co-N-phenylmaleimide).

Other anlysis of poly(P-chloromethylstyrene-co-styrene) and poly(P-chloromethylstyrene-co-styrene-co-N-phenylmaleimide), such as elemental analysis, weight average molecular weight, and glass transition temperature, were shown in Table 4.11, 4.12, and 4.13. The amount of nitrogen content was determined by elemental analysis. It was found that the nitrogen content increased significantly when the % mole of N-phenylmaleimide in the feed increased. But the difference of nitrogen content between the calculated and determined value from the elemental analysis increased when the % mole of N-phenylmaleimide in the feed increased, it might be due to the bulkiness of N-phenyl-maleimide induced hard propagation between copolymer radicals and N-phenylmaleimide monomers.

From the obtained molecular weight of resulting copoly-mers, it was seen that the more N-phenylmaleimide in the feed was,the higher molecular weight of copolymers was obtained. It might be resulted from the bulkiness of N-phenylmaleimide induced slow termination between polymer radicals [45]. From

the literature, the suitable molecular weight of polymers were mostly in the range of 50,000-200,000. But from the experiment, the molecular weight of the resulting polymers were almost in this range. In fact, a high molecular weight negative resist needed a lower dose of incident light to cause crosslinking. In the contrast of resolution, the solution of a high molecular weight negative resist was too viscous to make a thin film, then resolution of resist was not good. Therefore, the synthesis of polymer with a suitable molecular weight was necessary.

For the molecular weight distribution, as the matter of the fact that the contrast of a resist is high with corresponding narrowness in molecular weight distribution [46]. Unfortunately, the resulting polymers from the experiment had molecular weight distribution rather broad since it was difficult to control copolymers to obtain nearly monodisperse due to the different reactivities of the three monomers used.

The glass transition temperature(T_g) : The glass transition temperature of poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene-costyrene-co-N-phenylmaleimide) were 94.75, 101.49, 102.51, 135.69, 181.40°C for batch a,b,c,d,and e, respectively. Glass transition temperature of the photoresist showed significant role in irradiation step of photolithography. The high glass transition temperature would have a good thermal stability and did not change its shape with high temperature during exposure. Image profiles that are stable to 200°C are desirable for several processes used in semiconductor manu-

facturing[42]. On the contrast, the low glass transition tempe-
rature polymer deformed easily and the resolution was low too.

Although glass transition temperature of resulting
polymers did not reach 200 °C, they increased with the
increasing of N-phenylmaleimide unit in the polymer chain. This
might be due to an imide ring restricting the rotation of its
C-C bonds in the polymer chain [45].

Table 4.11 Polymerization data of poly(p-chloromethylsty-
rene-co-styrene) and poly(p-chloromethylstyrene
-co-styrene-co-N-phenylmaleimide)

Copolymer (batch)	Composition of Monomers in Feed (% mole)			% Yield
	CMST*	ST**	NPhMI***	
a	50	50	0	56.02
b	50	45	5	53.17
c	50	40	10	52.96
d	50	25	25	44.56
e	50	0	50	44.86

* p-Chloromethylstyrene monomer

** Styrene monomer

*** N-Phenylmaleimide monomer

Table 4.12 The elemental analysis of poly(*p*-chloromethyl-
styrene-co-styrene) and poly(*p*-chloromethyl-
styrene-co-styrene-co-N-phenylmaleimide)

Copolymer (batch)	Elemental Analysis							
	C(%)		H(%)		N(%)		Cl(%)	
	Calced	Found	Calced	Found	Calced	Found	Calced	Found
a	79.58	77.28	6.63	6.76	0	0.31	13.79	16.05
b	78.34	77.64	6.45	6.59	0.53	1.19	13.47	14.46
c	77.20	76.58	6.29	6.45	1.03	1.79	13.12	12.94
d	73.91	72.22	6.09	5.47	2.39	2.71	12.14	10.37
e	69.83	62.97	5.21	4.63	4.28	3.77	10.90	10.10

* Calculated from repeating unit

Table 4.13 The analysis of molecular weight and glass transition temperature (T_g) of poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide)

Copolymer (batch)	Mn[*]	Mw[**]	MWD[***]	T_g(°C)
a	12,971	32,994	2,5543	94.75
b	12,921	49,326	3.1875	101.41
c	15,242	87,324	5.7294	102.51
d	32,639	143,302	4.3905	135.96
e	35,968	148,590	4.1312	181.40

   * Number average molecular weight

 ** Weight average molecular weight

 *** Molecular weight distribution

Table 4.14 Determination of chlorine in polymers by modified Volhard method

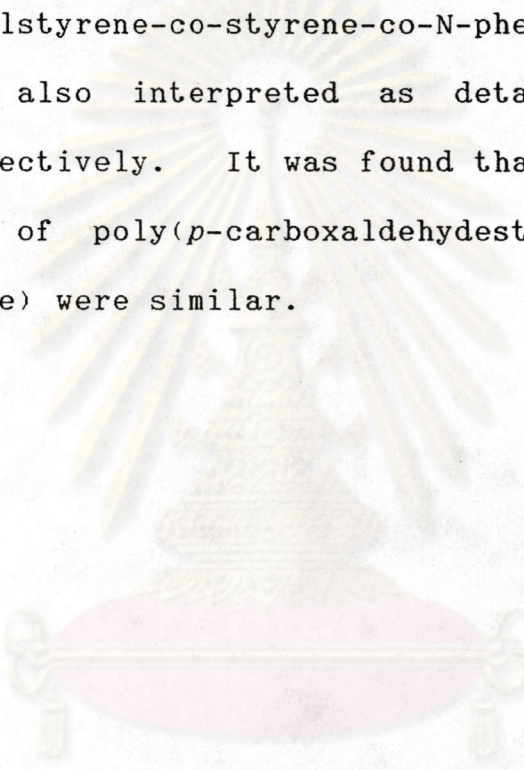| Copolymer (batch)	The amount of chlorine (mmole/1g polymer)	
	Calculated	Found
a	3.9037	4.0097
b	3.7948	3.8906
c	3.6985	3.7057
d	3.4356	3.3502
e	3.0794	3.2046

4.4 Carboxylation of poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide.
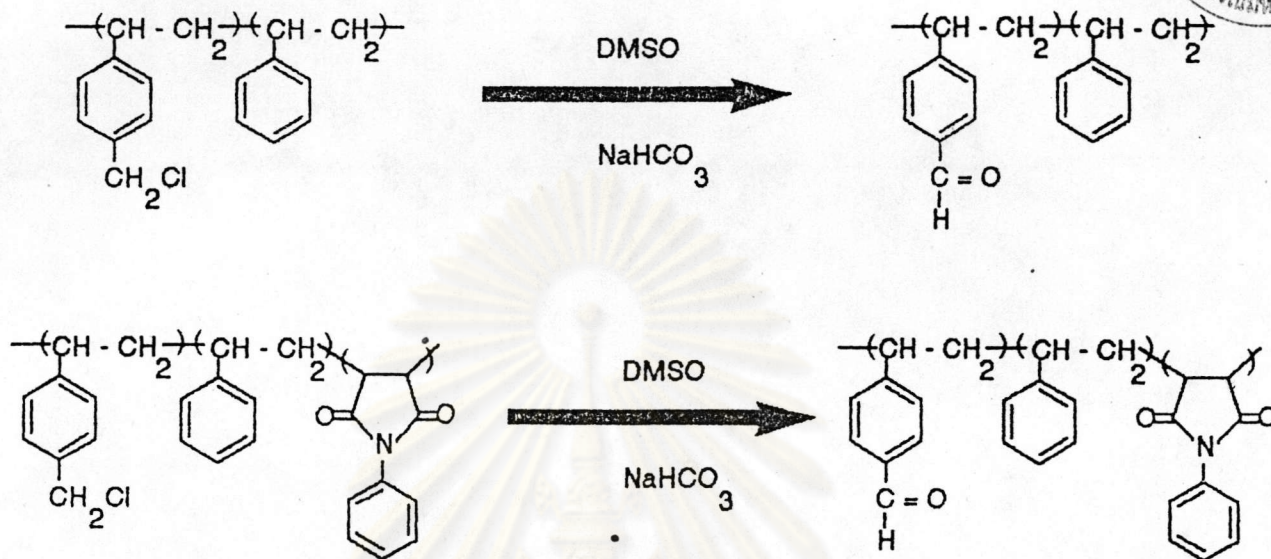
Carboxylation of poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide) were carried out by using dimethylsulfoxide and sodium bicarbonate at 155 °C, for 6 hrs. After the completing of reaction, the products were separated and purified by washing with several solvents, then dried under reduce pressure. The cream-colored polymers obtained. It was expected that chloromethyl groups were converted to carboxaldehyde groups which could be detected by IR spectroscopy (Figure 4.15b, 4.16b).

From the IR spectras of all the products, they indicated that poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide) were oxidized by dimethylsulfoxide and sodium bicarbonate. The resulting

products were aldehydic resins which showed an aldehydic C-H stretching absorption at ν 2,724 cm^{-1} and increased the intensity of carbonyl absorption bands at ν 1,700 cm^{-1}. While the absorption bands of C-Cl bending (wagging) at ν 1,212 cm^{-1} and C-Cl stretching at ν 700cm^{-1} of starting polymers disappeared (see Figure 4.15 and 4.16). The other absorption bands of poly (p-carboxaldehyde-styrene-co-styrene), Figure 4.15 b, and poly (p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide), Figure 4.16b , were also interpreted as detailed in Table 4.14 and 4.15, respectively. It was found that the IR spectras of all products of poly(p-carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide) were similar.

Table 4.14 The assignment for the IR spectrum of
poly(*p*-carboxaldehydestyrene-co-styrene)

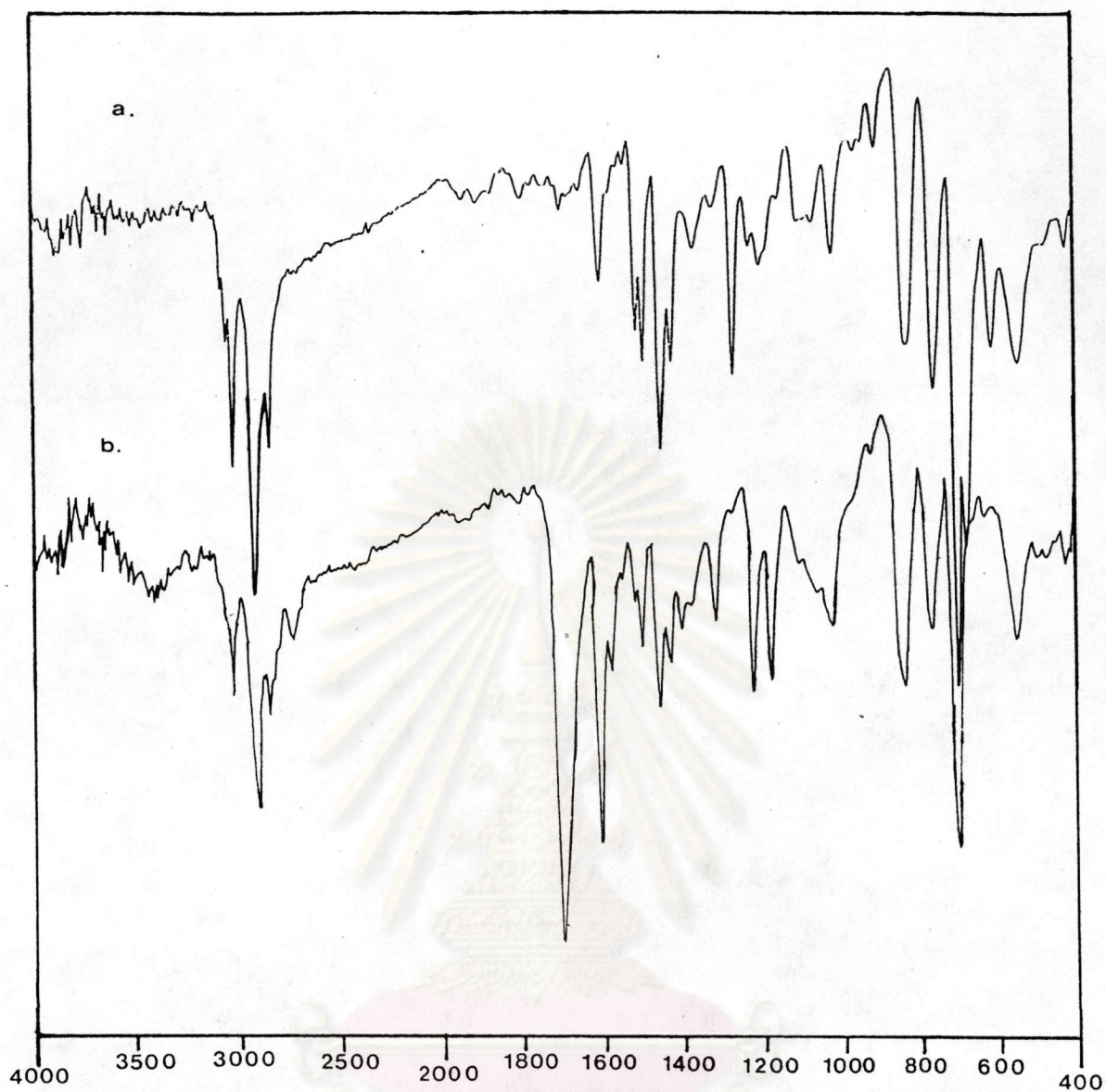| Wavenumber ν (cm^{-1})	Assignment
3024	C-H str. of aromatic
2916	C-H str. of aliphatic
2850	
2729	C-H str. of aldehyde
1700	C=O str.
1603	
1493	C=C str. of aromatic ring
1451	
1270	-CH$_2$-Cl bending (wagging)
828	C-H out of plane bending of aromatic ring
700	C-Cl str.

Figure 4.15 IR (KBr) spectrum of

(a.) poly(p-chloromethylstyrene-co-styrene)

(b.) poly(p-carboxaldehydestyrene-co-styrene).

Table 4.15 The assignment for the IR spectrum of
poly(p-carboxaldehydestryrene-co-styrene-
co-N-phenylmaleimide)

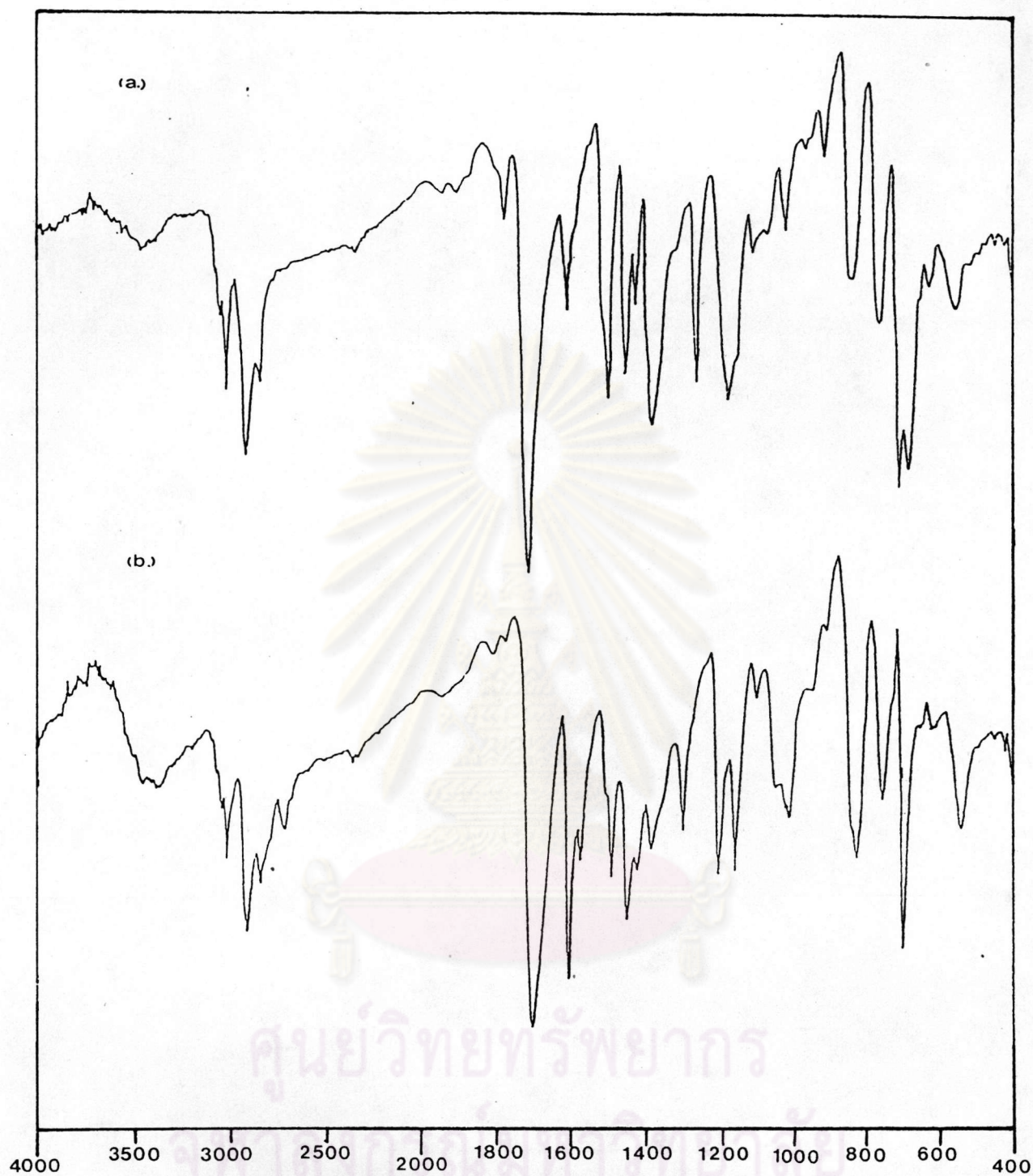| Wavenumber ν (cm^{-1})	Assignment
3024	C-H str. of aromatic
2917	C-H str. of aliphatic
2848	
2724	C-H str. of aldehyde group
1702	C=O str. of amide
1603	
1493	C=C str. of aromatic ring
1450	
1386	C-N str.
829	C-H out of plane bending of aromatic ring
700	C-Cl str.

Figure 4.16 IR (KBr) spectrum of

(a.) poly(*p*-chloromethylstyrene-co-styrene-co-
N-phenylmaleimide)

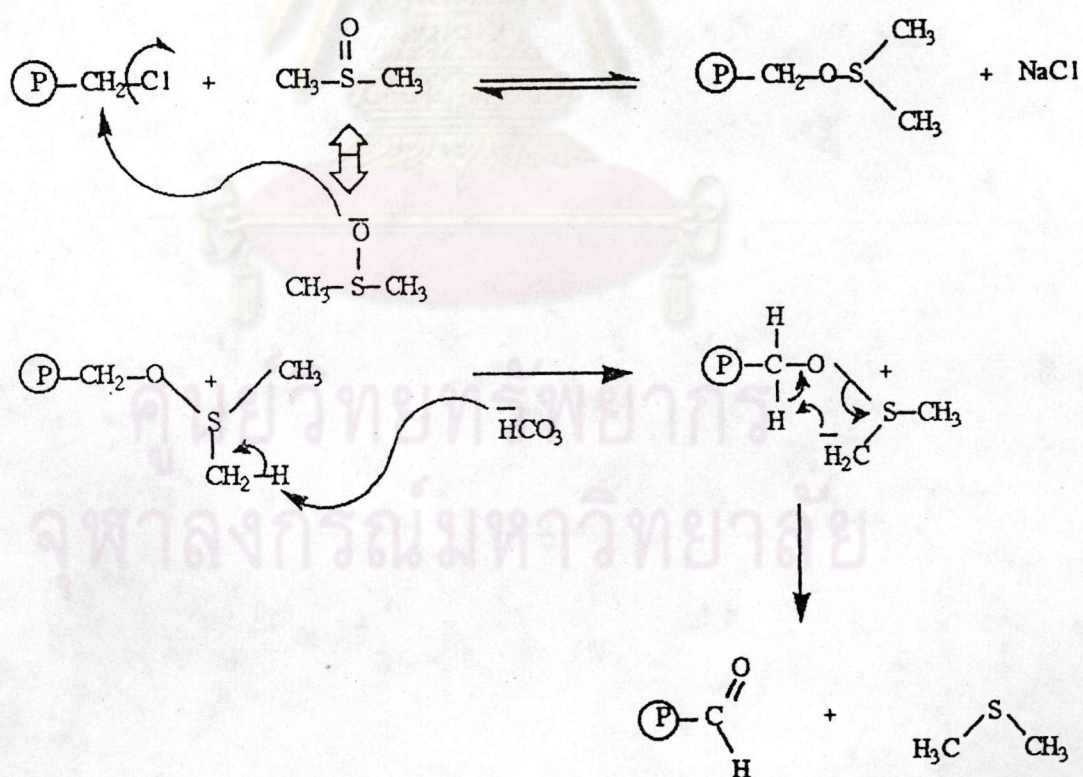(b.) poly(*p*-carboxaldehydestyrene-co-styrene-co-
N-phenylmaleimide).

The mechanism was proposed as shown in Scheme 4.4 [50].

Let   . and
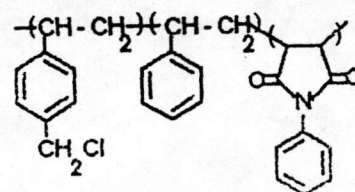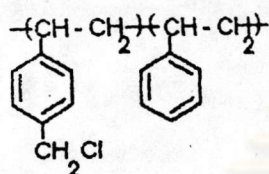
are presented by   P -CH$_2$-Cl

Scheme 4.4

Besides, all products were determined for chloride content by modified Volhard method. The result was shown in Table 4.16. It was found that the amount of chloride was left only little.

Table 4.16 The determination of chloride content in poly (*p*-carboxaldehydestyrene-co-styrene) and poly (*p*-carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide.

Copolymer (batch)	NPhMI (%mole)	Chloride content (mmole/1g.polymer)		% Conversion
		Before*	After**	
a	0	4.0097	0.0874	97.81
b	5	3.8906	0.0642	98.35
c	10	3.7057	0.0736	98.06
d	25	3.3502	0.4526	86.49
e	50	3.2046	0.4317	86.53

* Before carboxylation of polymers

** After carboxylation of polymers

4.5 Epoxidation of Poly(*p*-carboxaldehydestyrene-co-styrene) and Poly(*p*-carboxaldehydestyrene-co-styrene-co-N-phenyl-maleimide.

A large number of functional polymers have been prepared by chemical modification of polystyrene under classical conditions; more recently, phase transfer catalysis has been used in modification of polystyrene in three phase systems. The reactions involved mainly nucleophilic displacements on chloromethylated polystyrene resins, additions to carboxaldehyde substituted polystyrene, or reaction of polystyrene derivatives having reactive nucleophilic pendant groups with various electrophiles. These reactions under phase transfer catalysis have been now extented to the modification of chloromethylated polystyrene and it has generally been found that the phase transfer catalyzed reactions afford better results than those carried out under classical conditions both in term of polymer purity and in term of functional yields.

The polymer with oxirane pendant groups could be prepared by using different procedures such as using the simple epoxidation of polymer having vinyl pendant groups with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane, a reaction which gave satisfactory results but required that the starting polymer 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 time caused the presence of carbonyl group in the polymer chain

suggesting that opening of the epoxide ring had ocurred.

The better method, which was selected to use in this work, for preparation of polymers with oxirane pendant groups, poly(p-epoxystyrene-co-styrene) and poly(p-epoxystyrene-co-styrene-co-N-phenylmaleimide), involved the reaction of poly(p-carboxaldehydestyrene-co-styrene) or poly(p-carboxaldehydestyrene-co-styrene-co-N-phenylmaleimide) with trimethylsulfonium chloride in a presence of a phase transfer catalyst [51].

The sulfonium ylid reaction gave poor results when attempted with trimethyl sulfonium iodide under phase transfer conditions; this result was not totally unexpected as iodides are often considered undesirable for phase transfer reaction due to excessive solubility in organic medium. The same reaction carried out under classical conditions using potassium *tert*-butoxide in DMSO or *n*-butyllithium in THF also gave poor results [51].

The reaction with trimethyl sulfonium chloride and 50 % aqueous sodium hydroxide in the presence of benzyltriethyl ammonium chloride gave excellent results.
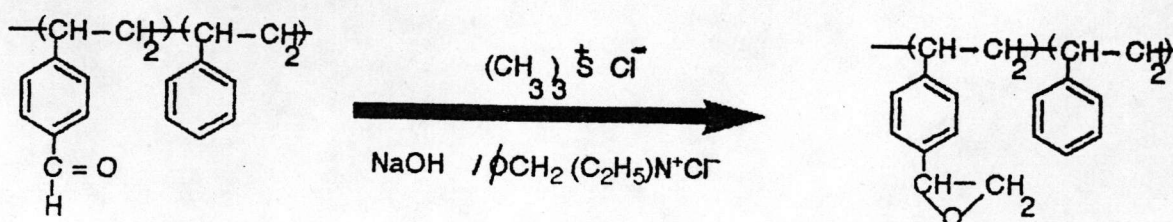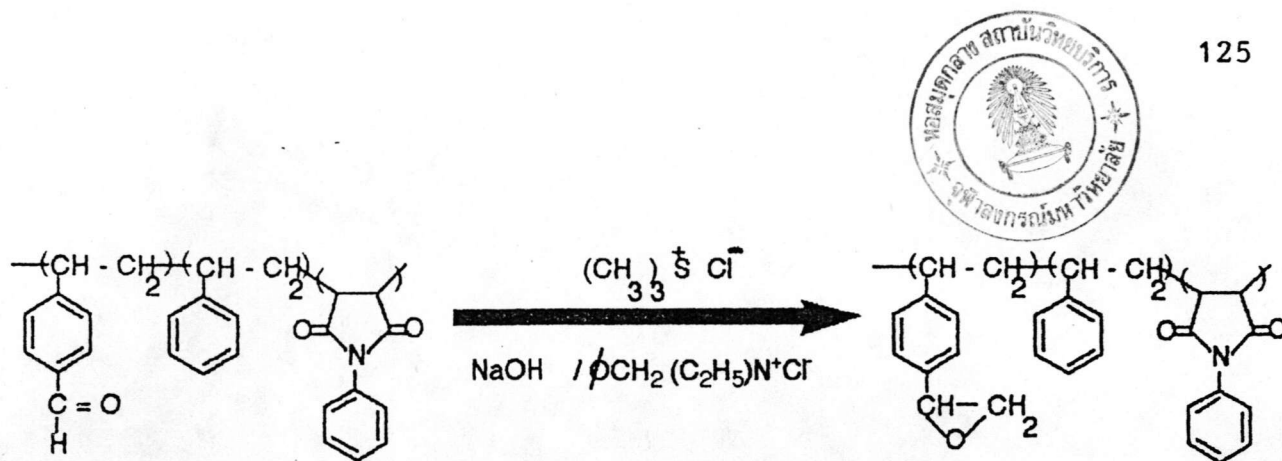
However, trimethylsulfonium chloride was not available. It was thus obtained via ion exchange of trimethylsulfonium iodide through anion exchange resin, DOWEX SBR-P. It was then used as aqueous solvent of trimethylsulfonium chloride.

From the IR spectras of poly(*p*-epoxystyrene-co-styrene) and poly(*p*-epoxystyrene-co-styrene-co-N-phenylmaleimide), Figure 4.17 and 4.18 b, they were observed that there was increasing in intensity of two -C-O symmetric stretching bands and -C-O asymmetric stretching band of epoxide groups at ν=1255, 839 and 759 cm^{-1}. It indicated that the carboxaldehyde groups converted to epoxide groups. The other absorption bands of poly(*p*-epoxystyrene-co-styrene) and poly(*p*-epoxystyrene-co-styrene-co-N-phenylmaleimide) were interpreted as detailed in Table 4.17 and 4.18, respectively.

Table 4.17 The assignment for the IR spectrum of
poly(*p*-epoxystryrene-co-styrene)

Wavenumber ν (cm^{-1})	Assignment
3024	C-H str. of aromatic
2920	C-H str. of aliphatic
1602	⎫
1509	⎬ C=C str. of aromatic ring
1453	⎭
1248	⎫ C-O sym. str. of epoxide gr.
881	⎭
757	C-O asym. str. of epoxide gr.
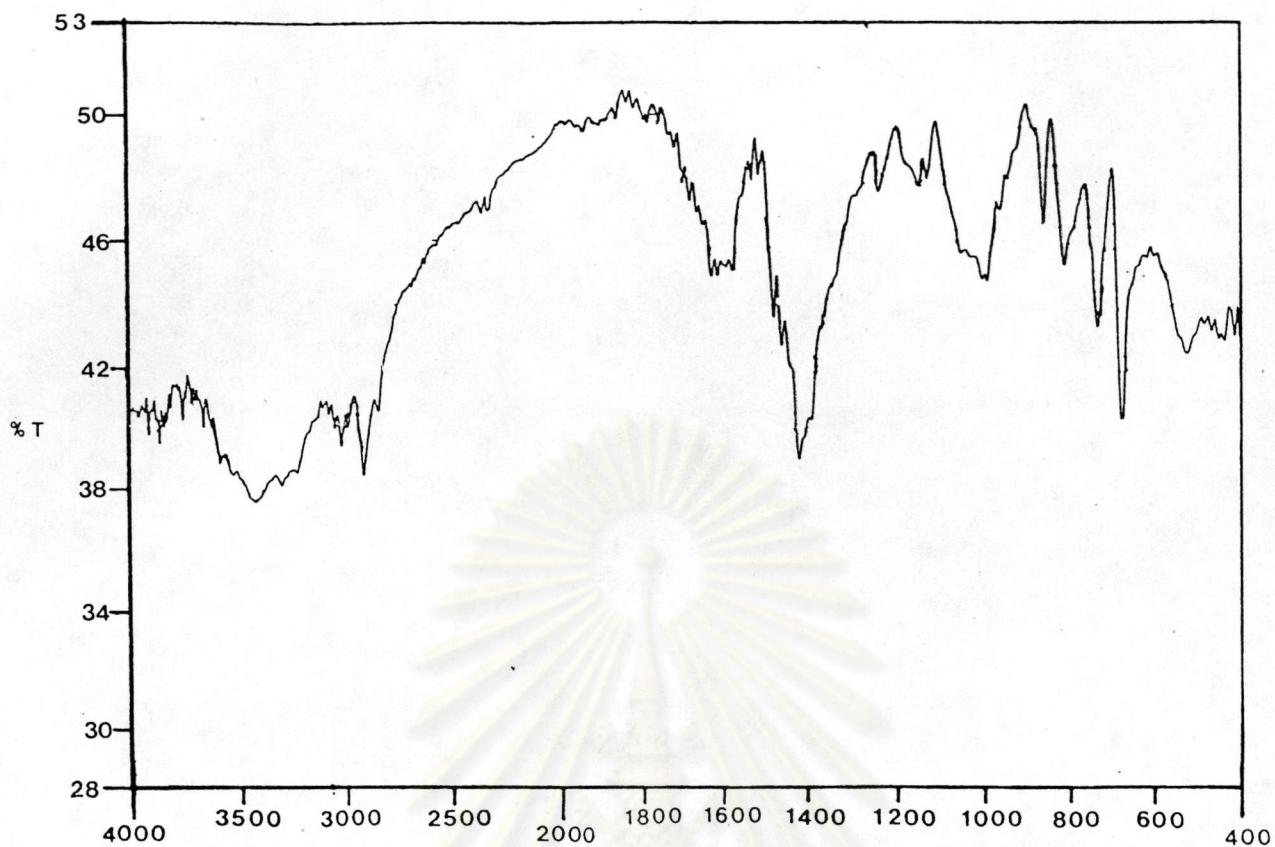
Figure 4.17 IR (KBr) spectrum of poly(*p*-epoxystyrene-co-styrene).

Table 4.18 The assignment for the IR spectrum of poly
(*p*-epoxystryrene-co-styrene-co-N-phenylma-
leimide)

Wavenumber ν (cm^{-1})	Assignment
3043	C-H str. of aromatic
2930	C-H str. of aliphatic
1706	C=O str.
1595	⎫
1496	⎬ C=C str. of aromatic ring
1444	⎭
1393	C-N str.
1255	⎫ C-O sym. str. of epoxide gr.
839	⎬
759	C-O asym. str. of epoxide gr.

The proposed mechanism of epoxidation reaction using trimethylsulfonium chloride and phase transfer catalyst was shown in scheme 4.5 [45].
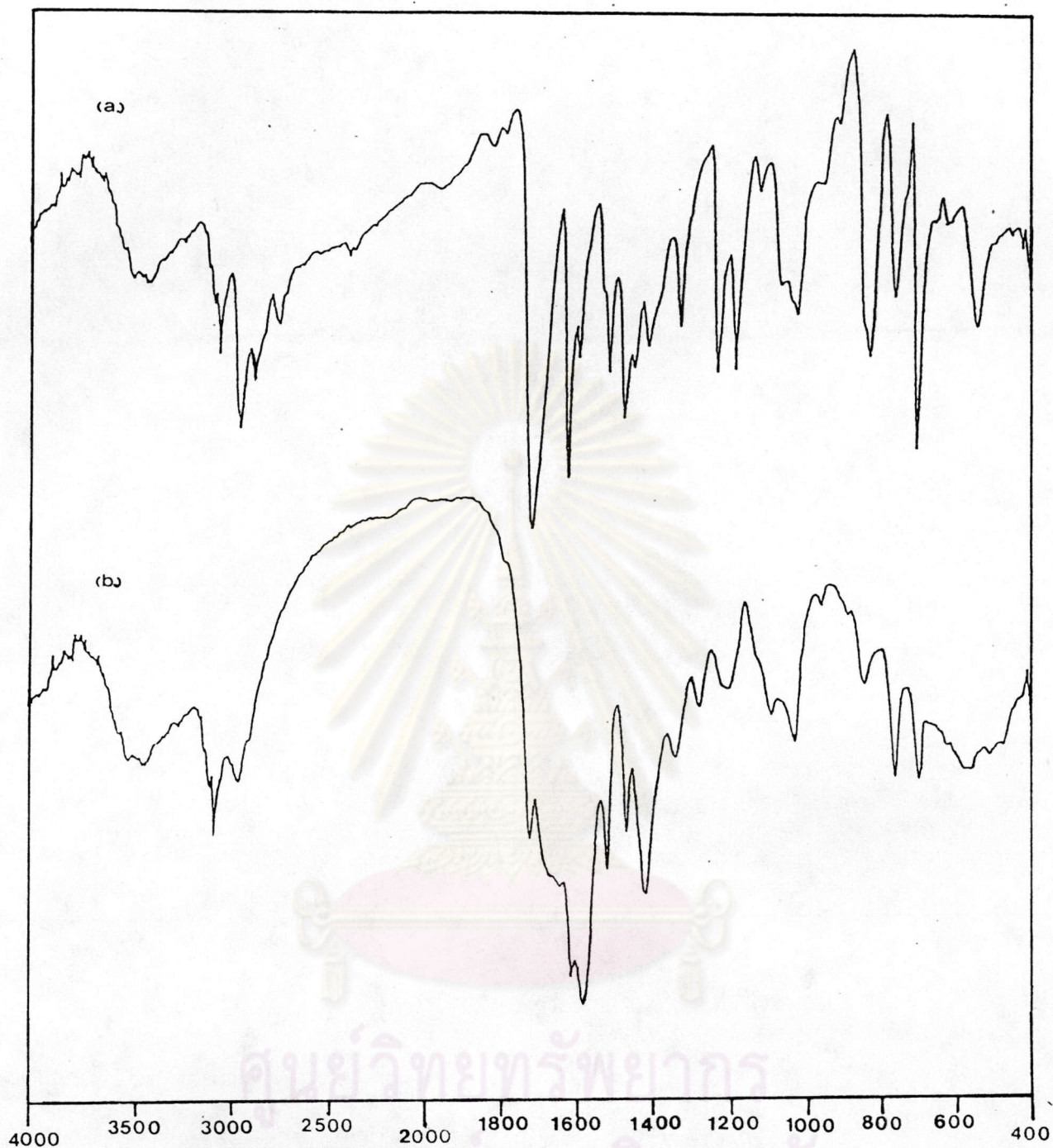
<u>Figure</u> 4.18 IR (KBr) spectrum of

(a.) poly(*p*-carboxaldehydestyrene-co-styrene-co-
N-phenylmaleimide)

(b.) poly(*p*-epoxystyrene-co-styrene-co-
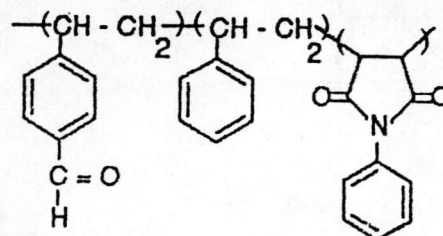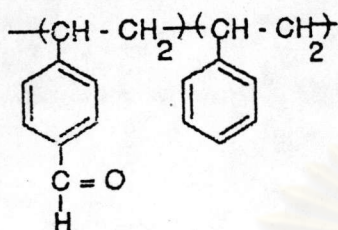N-phenylmaleimide).

Let a phase transfer catalyst ; $\phi CH_2(C_2H_5)N^+Cl^- = Q^+Cl^-$

P.B. : Phase boundary

O.P. : Organic phase

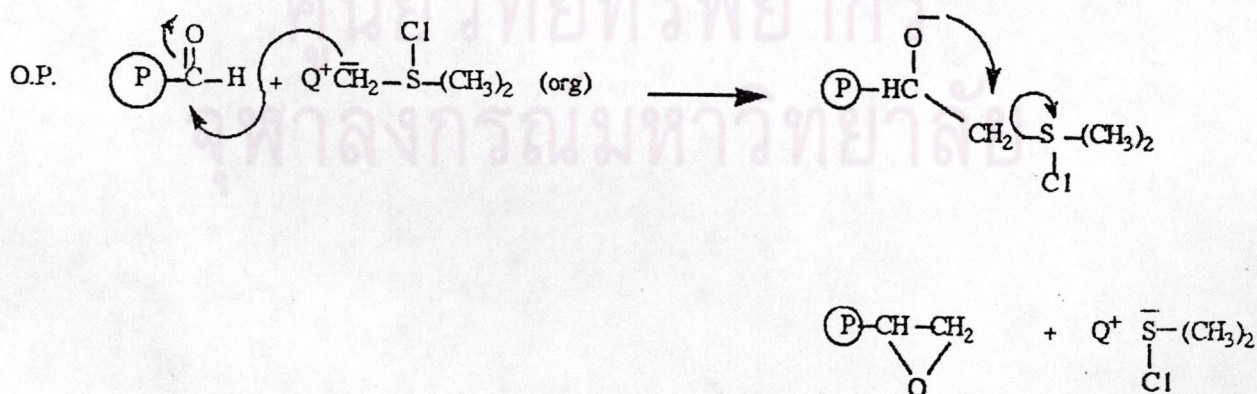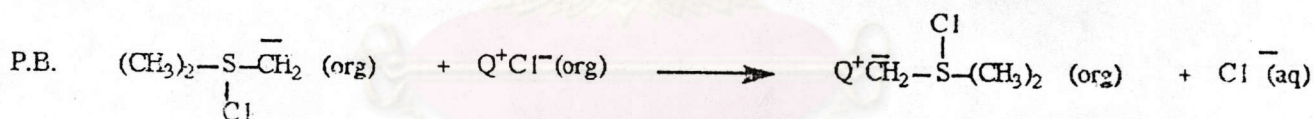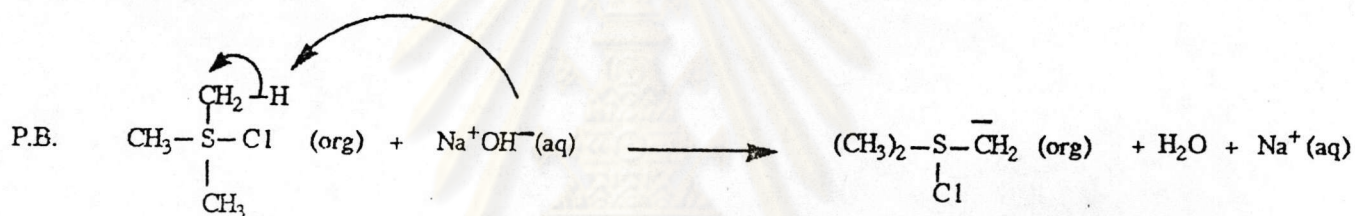Let   and

are presented by : P —CH
(with O above CH)

Scheme 4.5

Table 4.19 The analysis data for determination of epoxide content.

Copolymer (batch)	Carboxaldahyde Content* (mmole/1g. polymer)	Epoxide Content (mmole/1g. polymer)	% Conversion
a	3.9223	3.0547	77.95
b	3.8246	3.0095	78.65
c	3.7221	2.8053	75.37
d	2.8976	1.7099	59.01
e.	2.7729	1.4824	53.46

* The amount of carboxaldehyde groups before epoxidation which calculated from the disappearence of chloride in the carboxylation step.

Therefore, the finish products still have chloromethyl groups and carboxaldehyde groups incorporated with epoxide groups in the same polymer chain. But these materials could be used for photolithography application as photoresist [43]. The amount of functional groups content in the resulting polymer was summaried in Table 4.20.

Table 4.20 The analysis data for functional group contents in poly(P-epoxystyrene-co-styrene) and poly (p-epoxystyrene-co-styrene-co-N-phenylmaleimide).

Copolymer (batch)	NPhMI (%mole)	Functional Group Contents(mmole/1g. polymer)		
		Chloromethyl Group	Carboxaldehyde Group	Epoxide Group
a	0	0.0847	0.8694	3.0574
b	5	0.0642	0.8169	3.0095
c	10	0.0736	0.9168	2.8053
d	25	0.4526	1.1877	1.7099
e	50	0.4317	1.2905	1.4824

In case of glass transition temperature, Table 4.21, it was observed that glass transition was relatively little increased from the glass transition temperature of poly(p-chloromethylstyrene-co-styrene) and poly(p-chloromethylstyrene-co-styrene-co-N-phenylmaleimide).

Table 4.21 The glass transition temperature of poly
(*p*-epoxystyrene-co-styrene) and poly(*p*-epoxy-
styrene-co-styrene-co-N-phenylmaleimide).

Copolymer (batch)	NPhMI (% mole)	T_g (°C)
a	0	102.7
b	5	111.8
c	10	127.3
d	25	148.5
e	50	195.7