

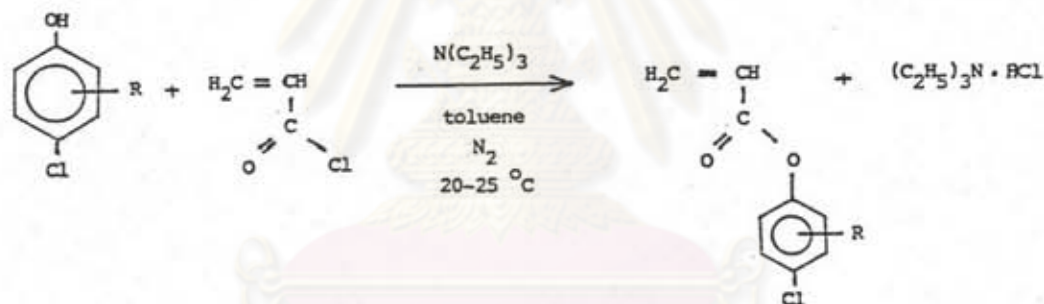
CHAPTER III

RESULTS AND DISCUSSION

3.1 The chlorophenyl acrylate monomers

3.1.1 Syntheses of the chlorophenyl acrylates

In this study, four chlorophenyl acrylates were synthesized by direct reaction of the corresponding chlorophenolic compounds and acryloyl chloride in dry toluene under the nitrogen



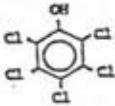
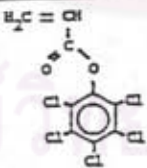
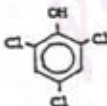
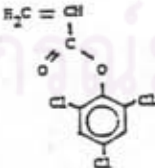
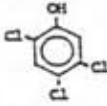
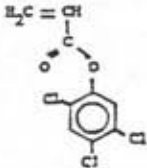
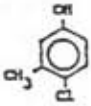
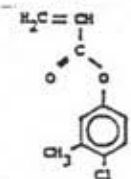
atmosphere and in the presence of freshly distilled triethylamine. During the reaction, the disappearance of the reactant and the formation of the product was monitored by thin layer chromatography. By this method, four chlorophenyl acrylate were obtained with high yield as shown in Table 3.1.

Pentachlorophenyl acrylate and 2,4,5-trichlorophenyl acrylate were white solid with melting points 78-79 °C and 63-64 °C, respectively. 4-Chloro-3-methylphenyl acrylate and 2,4,6-trichlorophenyl acrylate were colourless liquid. Both compounds have the

decomposition points at 120 °C, 10 mmHg. Attempts to purify these two compounds by vacuum distillation were unsatisfactory. Furthermore, the decomposition products were generated in the solution mixture as shown by tlc. They were thus purified by column chromatography using benzene as an eluent and silica gel as a packing material.

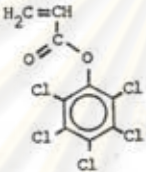
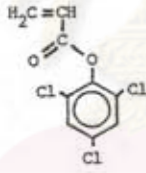
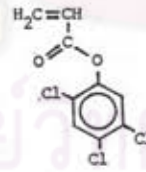
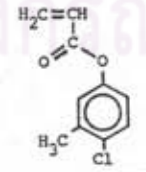
Thorough literature search reveals that 2,4,6-trichlorophenyl acrylate (2,4,6-TCPA), 2,4,5-trichlorophenyl acrylate (2,4,5-TCPA) and 4-chloro-3-methylphenyl acrylate (4-Cl-3-MPA), are novel acrylate compounds. In the case of pentachlorophenyl acrylate, it has been synthesized by the other research groups. Different melting points, 58 °C (28), 72 °C (27,29) and 82.5 °C (31), were however reported.

Table 3.1 The chlorophenyl acrylates

REACTANT	PRODUCT	YIELD (%)
	 Pentachlorophenyl acrylate (PCPA)	87
	 2,4,6-Trichlorophenyl acrylate (2,4,6-TCPA)	90
	 2,4,5-Trichlorophenyl acrylate (2,4,5-TCPA)	92
	 4-Chloro-3-methylphenyl acrylate (4-Cl-3-MPA)	85

All these products were clearly identified by infrared , proton nuclear magnetic resonance and mass spectroscopy. The observed elemental analysis values of these compounds agree very well with the calculated ones (Table 3.2).

Table 3.2 Elemental analysis of the chlorophenyl acrylates

The chlorophenyl acrylate		%C	%H
	found	33.89	0.87
	calculated	33.70	0.94
	% error	-0.19	0.07
	found	43.22	2.15
	calculated	42.94	1.99
	% error	-0.28	-0.16
	found	42.89	1.92
	calculated	42.94	1.99
	% error	0.05	0.07
	found	61.19	4.60
	calculated	61.07	4.58
	% error	-0.12	-0.02

3.1.2 Structural elucidation of the synthesized chlorophenyl acrylates

3.1.2.1 Pentachlorophenyl acrylate

The infrared spectrum of pentachlorophenyl acrylate and its assignment were shown in Figure 3.1 and Table 3.3, respectively. It should be noticed the absorption band at 1635 cm^{-1} which is assigned to C=C stretching. Normally, this band is a characteristic peak of monomer in free radical polymerization and will disappear when a polymer is formed.

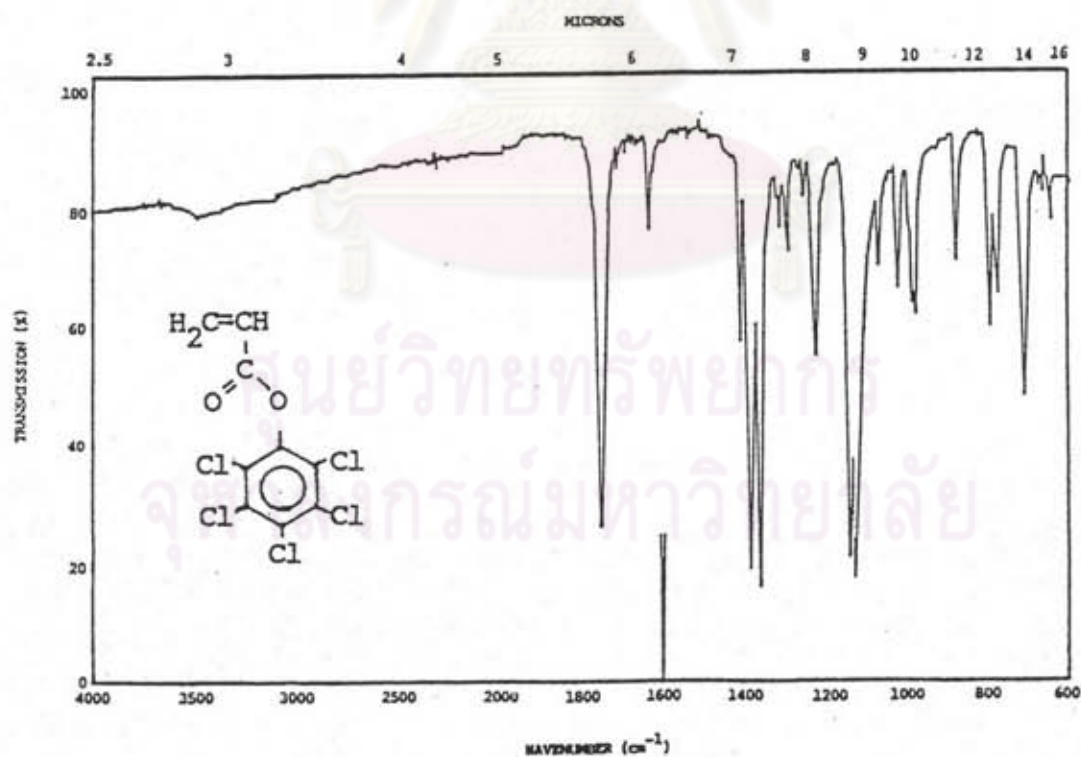


Figure 3.1 Infrared spectrum of pentachlorophenyl acrylate (KBr)

Table 3.3 Assignment of the various important bands in the infrared spectrum of pentachlorophenyl acrylate

Absorption bands (cm^{-1})	assignments
1760 (s)	C=O stretching vibration
1635 (m)	C=C stretching vibration
1410 (m), 1385 (s), 1360 (s)	C-H bending vibration , vinyl terminal
1140 (s), 1130 (s)	C-O-C stretching vibration
980 (m)	=C-H bending vibration
795 (m), 780 (m), 710 (m)	C-Cl stretching vibration

Its UV-Visible spectrum (Figure 3.2) shows the maximum absorption at 240 nm (ϵ 5300 $\text{mole}^{-1} \text{cm}^{-1}$) This confirms the presence of a benzene ring in pentachlorophenyl acrylate.

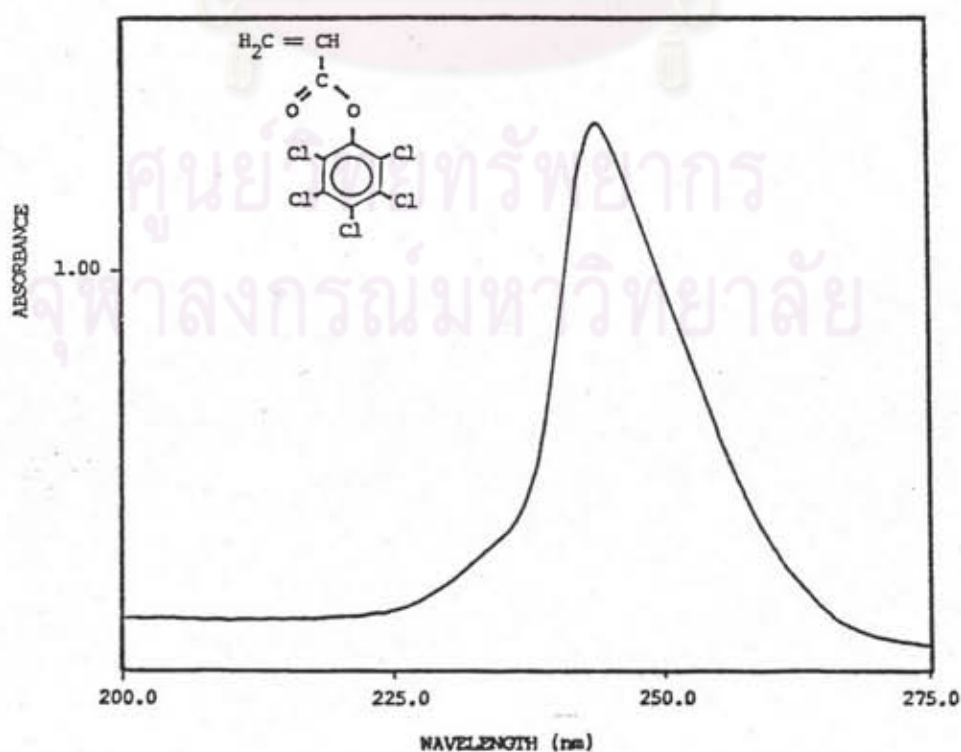
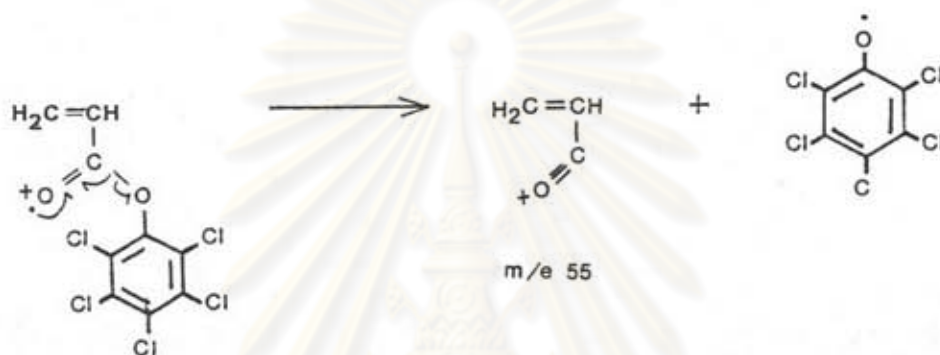


Figure 3.2 UV-Visible spectrum of pentachlorophenyl acrylate (CHCl_3)

The mass spectrum of this compound (Figure 3.3) exhibits the molecular ion at m/e 318. The ratio of $M^+ : M+2 : M+4 : M+6$ is 100.0 : 163.0 : 106.0 : 34.7 which is the characteristic of molecule contain 5 chlorine atoms. The base peak at m/e 55 is due to the vinylacylium ion resulted from the cleavage of C-O bond.



It also shows the other fragment ion at m/e 264 which corresponds to the phenolic moiety containing five chlorine atoms.

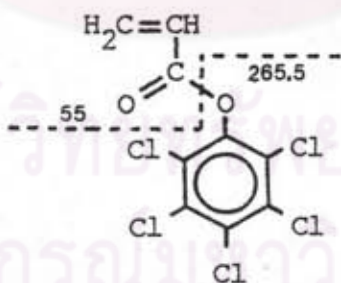
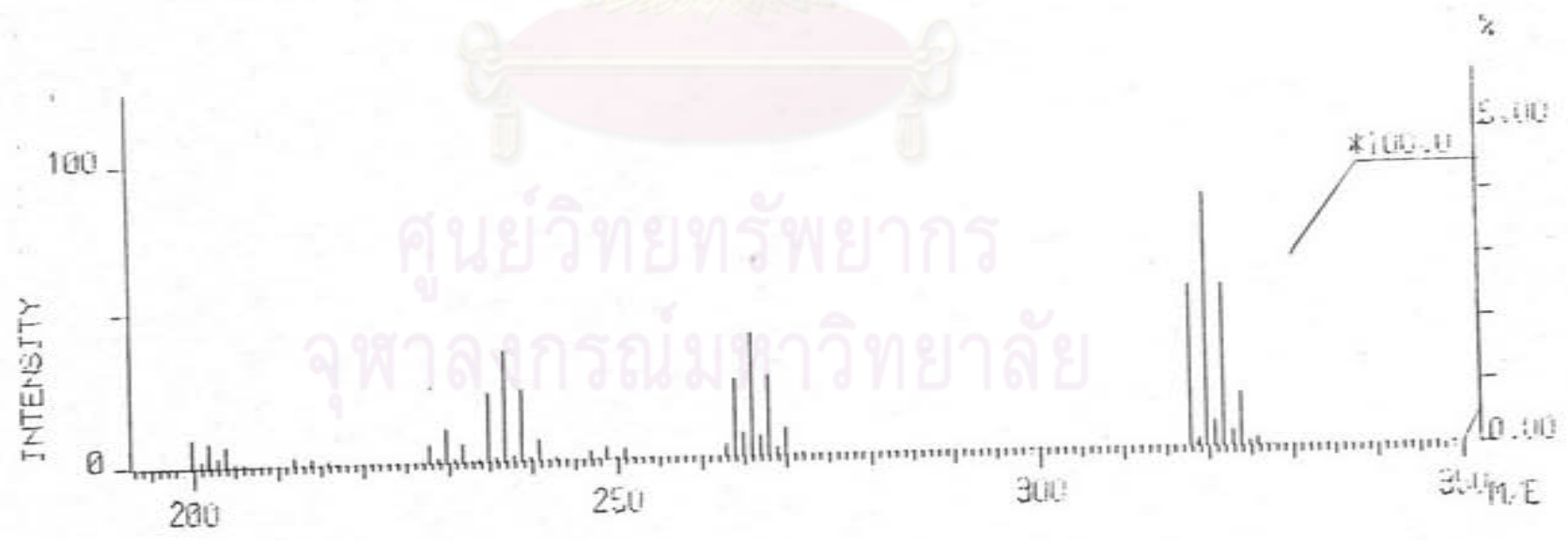
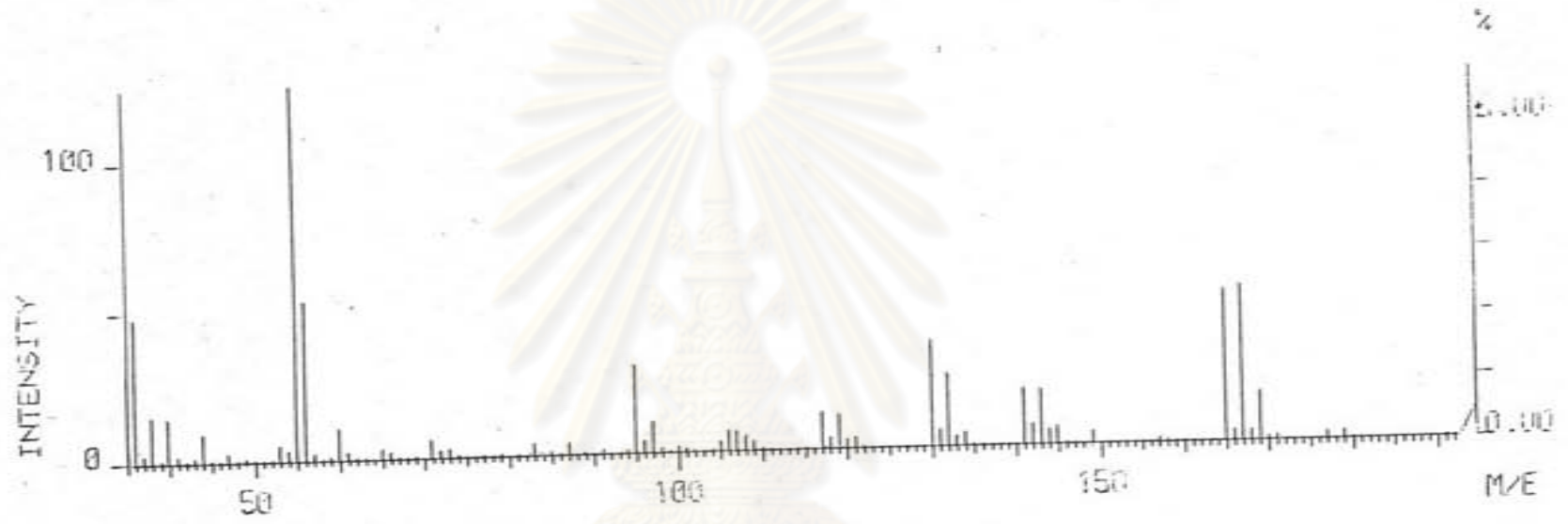


Figure 3.3 Mass spectrum of pentachlorophenyl acrylate



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย



Eventhough the NMR spectrum of pentachlorophenyl acrylate has been reported in the literatures (27, 28, 29), the clear interpretation of its spectrum is not mentioned. Thus it is worthwhile to deduce the structure of pentachlorophenyl acrylate by NMR spectroscopy here.

The NMR spectrum of pentachlorophenyl acrylate in deuteriochloroform shows the signals only in the range between δ 6.08–6.90 ppm (Figure 3.4). These signals are due to the vinylic

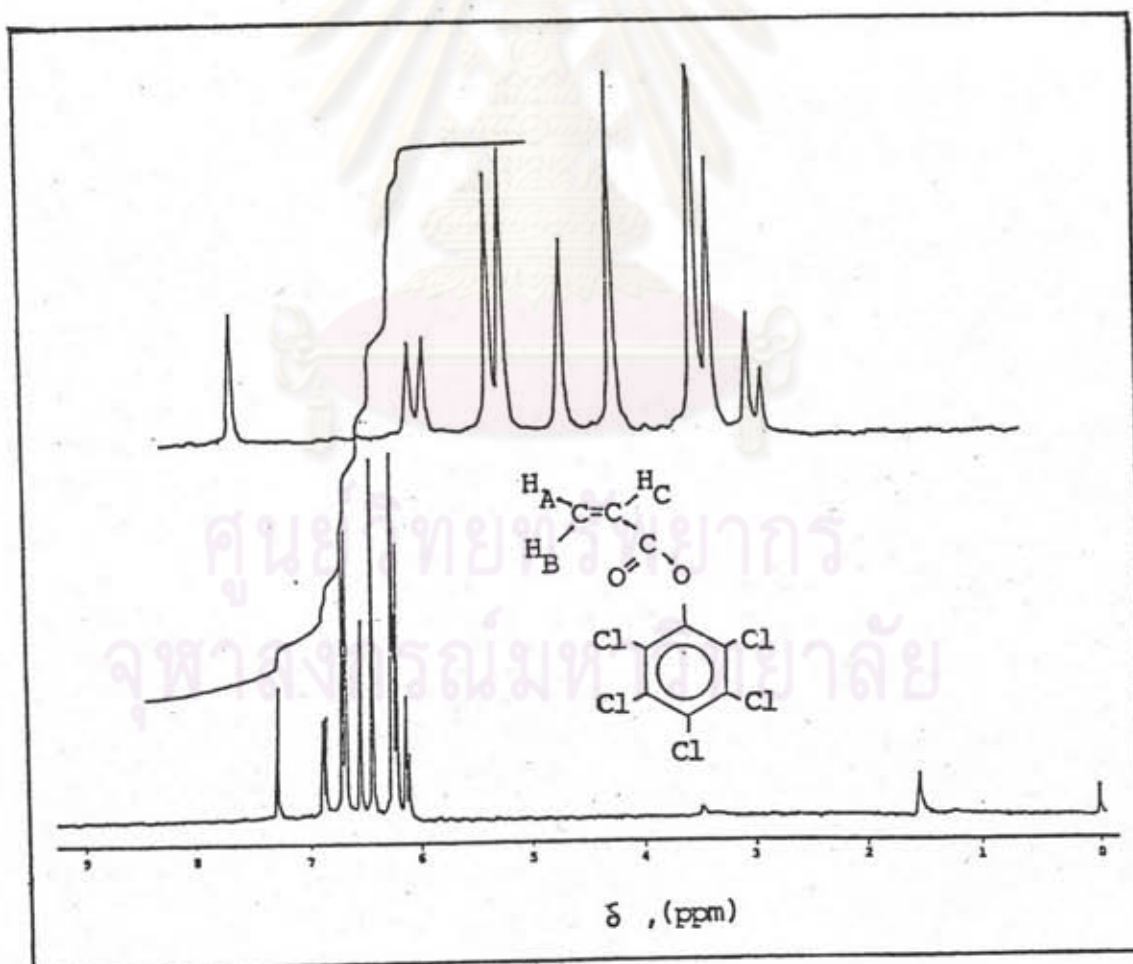
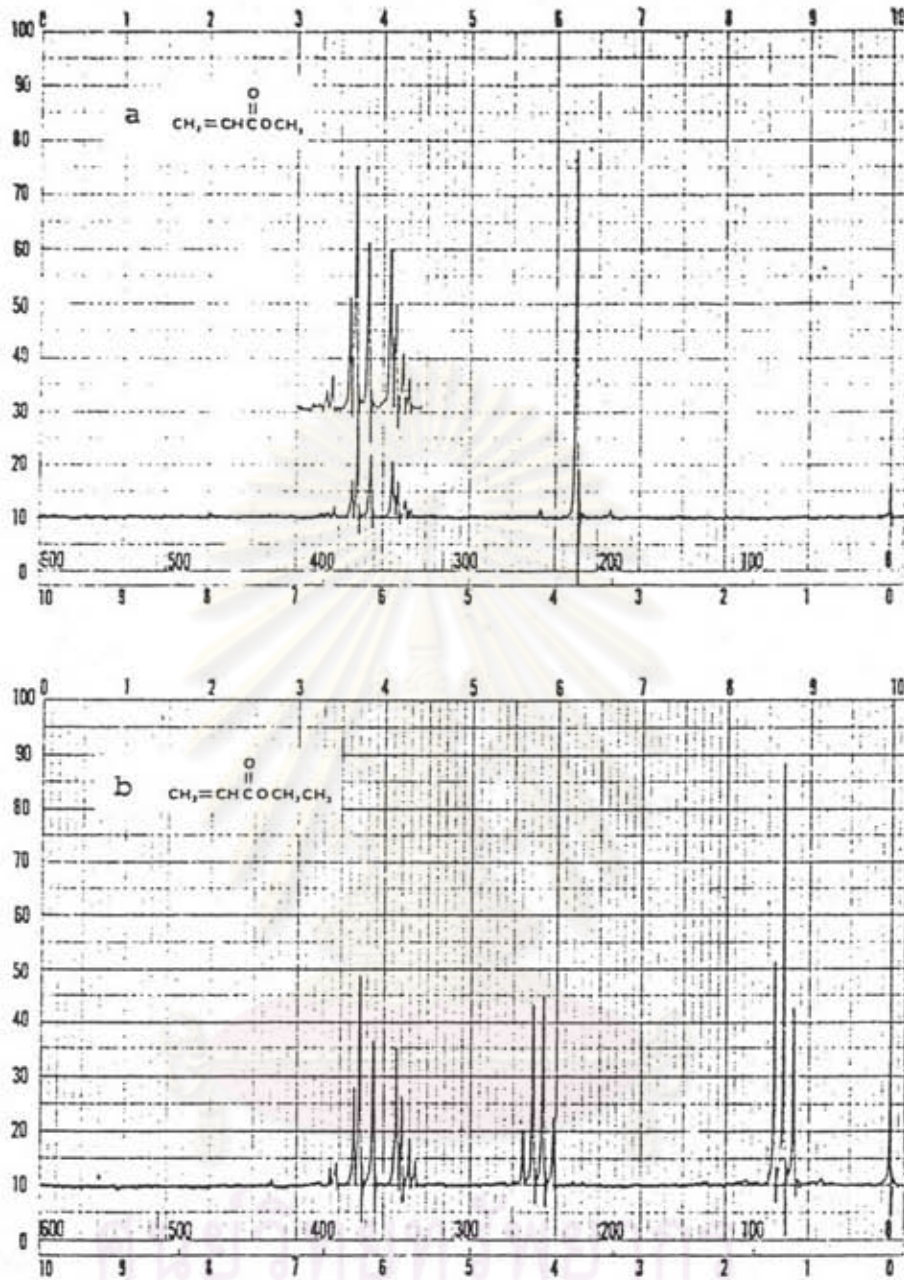


Figure 3.4 $^1\text{H-NMR}$ spectrum of pentachlorophenyl acrylate (CHCl_3)



* Figure 3.5 a $^1\text{H-NMR}$ spectrum of methyl acrylate

b $^1\text{H-NMR}$ spectrum of ethyl acrylate

* from the Aldrich NMR Catalog Vol.3, 1975

protons. A well defined pair of doublets at δ 6.10 and 6.21 ppm ($J = 3$ Hz) is assigned to the geminal proton trans to the chlorophenolic carboxyl group (H_A). The other well defined pair of doublets at δ 6.67 and 6.86 ppm ($J = 3$ Hz) corresponds to the other geminal proton cis to the chlorophenolic carboxyl group (H_B). The signal for the last vinylic proton (H_C), which is gem to the chlorophenolic carboxyl group, should also appear as a pair of doublets due to the coupling with H_A ($J_{AC} = 11$ Hz) and with H_B ($J_{BC} = 18$ Hz). Unfortunately, a part of each doublet falls at the same positions of the other two protons. Therefore only one of each doublet is observed in the spectrum, i.e. δ 6.41 and 6.53 ppm. This pattern is similar to those of acrylate compounds (Figure 3.5a and 3.5b).

Consequently, from the above spectral evidences the synthesized compound is confirmed a pentachlorophenyl acrylate.

3.1.2.2 2,4,6-Trichlorophenyl acrylate

The infrared spectrum and the assignment of 2,4,6-trichlorophenyl acrylate are shown in Figure 3.6 and Table 3.4, respectively. Similarly, it should be pointed out here that the absorption band at 1635 cm^{-1} , which is due to C=C stretching, will disappear if a polymer is formed.

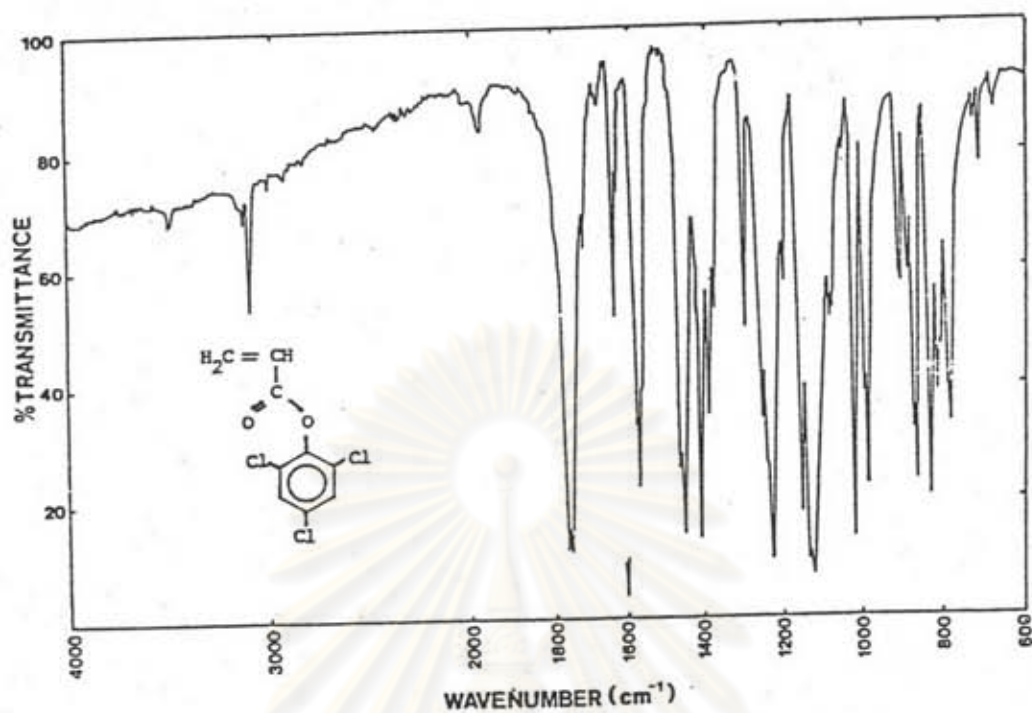


Figure 3.6 Infrared spectrum of 2,4,6-trichlorophenyl acrylate (neat)

Table 3.4 Assignment of the various important bands in the infrared spectrum of 2,4,6-trichlorophenyl acrylate

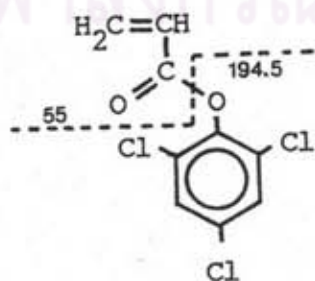
Absorption bands (cm^{-1})	assignments
3090 (w)	aromatic C-H stretching vibration
1760 (s)	C=O stretching vibration
1635 (m)	C=C stretching vibration, vinyl terminal
1450 (s), 1390 (s), 1410 (s)	C-H stretching vibration
1225 (s), 1120 (s)	C-O-C stretching vibration
970 (w)	=C-H bending vibration
855 (s), 820 (s)	C-Cl stretching vibration

2,4,6-trichlorophenyl acrylate also exhibits ultraviolet absorption maximum at λ_{\max} 240 nm (ϵ 790 $\text{mole}^{-1}.\text{cm}^{-1}$), with additional absorption at λ_{\max} 285 nm (ϵ 307 $\text{mole}^{-1}.\text{cm}^{-1}$) and λ_{\max} 275 nm (ϵ 339 $\text{mole}^{-1}.\text{cm}^{-1}$) (Figure 3.7). This is consistent with the presence of a benzene ring in the molecule.

The NMR spectrum of 2,4,6-trichlorophenyl acrylate in deuteriochloroform is similar to that of pentachlorophenyl acrylate with the addition of one singlet at δ 7.36 ppm (2H). This is assigned to the phenylic protons meta to the oxygen atom in benzene ring which are both equivalent (Figure 3.8).

The remaining signals in the spectrum, δ 6.02-6.82 ppm, with an integration for total three protons are due to the vinylic protons. Within the multiplets in this region, two pairs of doublets are clearly observed. This pattern is thus indicative of the vinylic geminal protons.

The mass spectrum of this compound also exhibits (Figure 3.9). The molecular ion at m/e 250 shows characteristic of 3 chlorine atoms ($M^+ : M+2 : M+4 = 100.0 : 97.8 : 31.9$). The base peak at m/e 55 due to the vinyl acylium ion which is formed by the cleavage of the C-O bond, the same as in the case of pentachlorophenyl acrylate. It also shows the other fragment ion, 2,4,6-trichlorophenolicium ion at m/e 194.



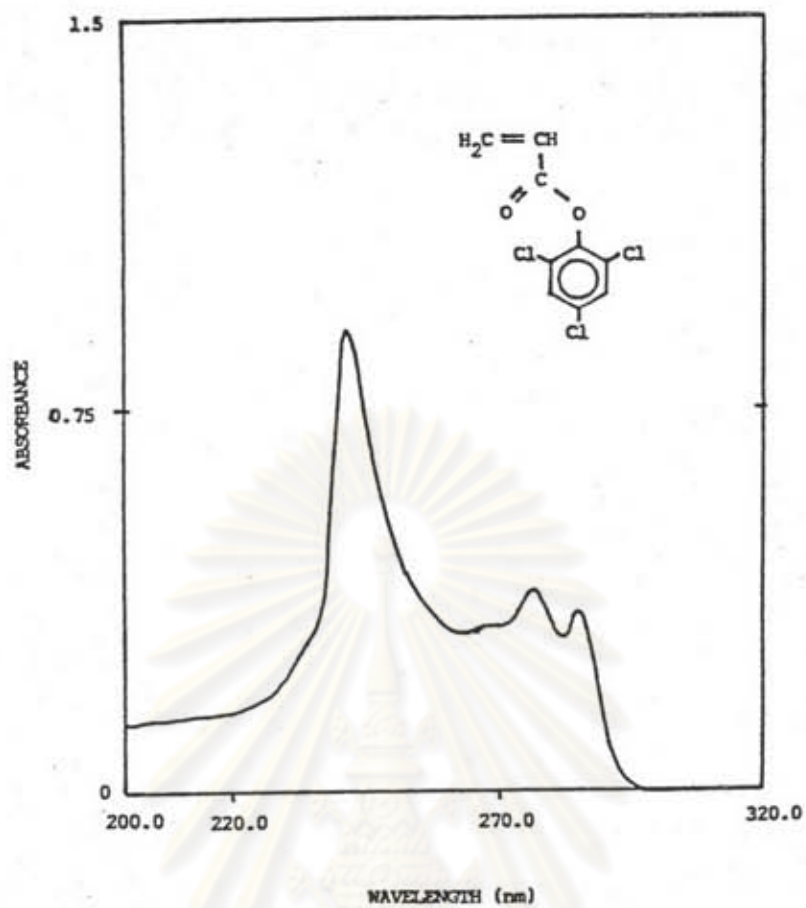


Figure 3.7 UV-Visible spectrum of 2,4,6-trichlorophenyl acrylate (CHCl_3)

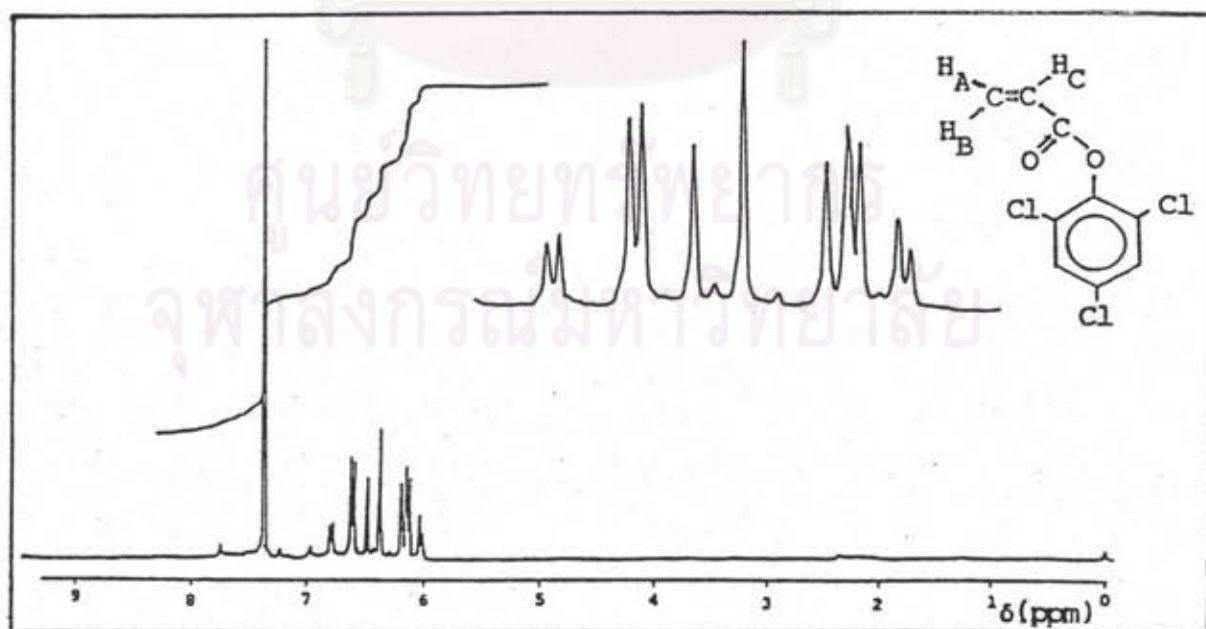
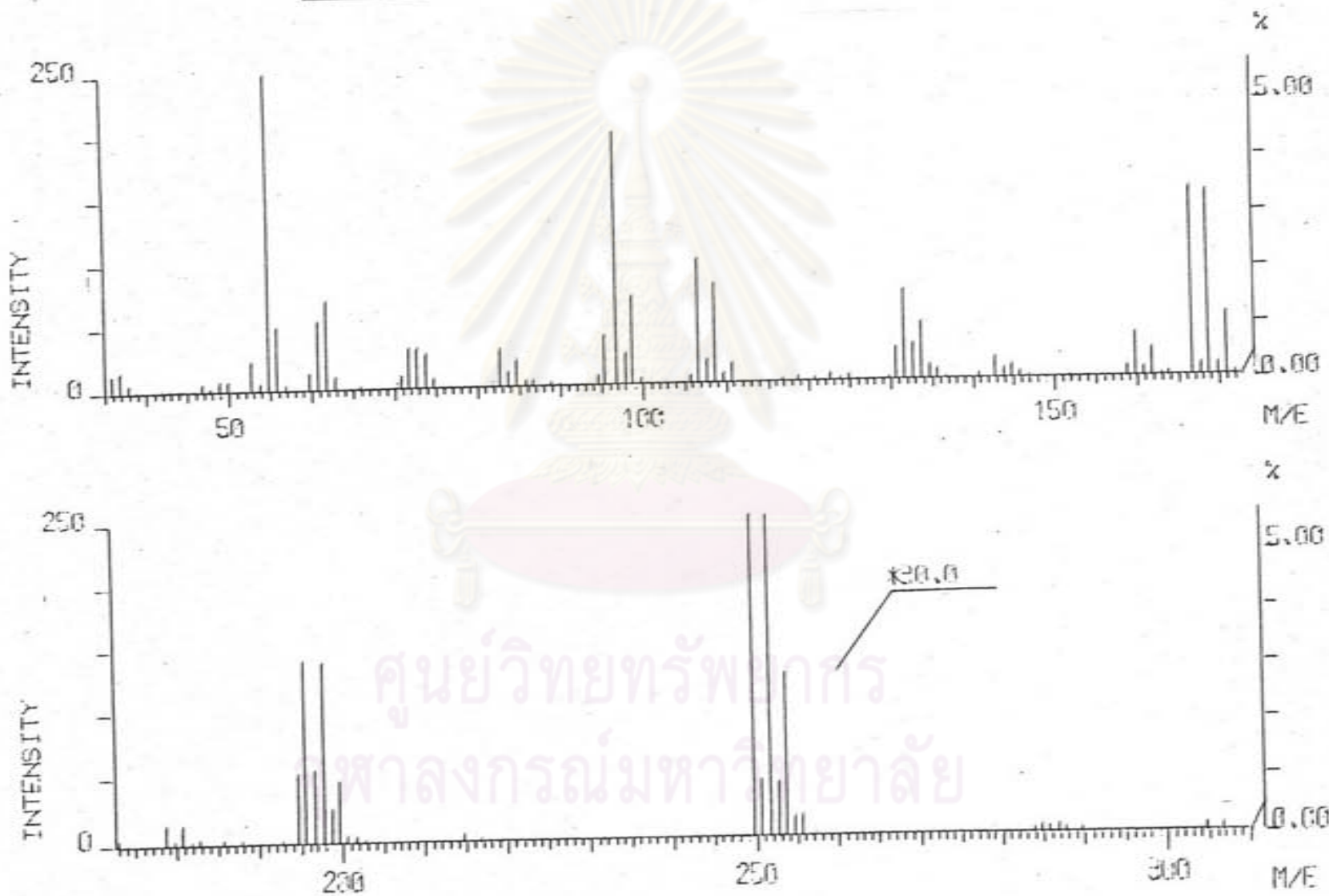


Figure 3.8 $^1\text{H-NMR}$ spectrum of 2,4,6-trichlorophenyl acrylate (CDCl_3)

Figure 3.9 Mass spectrum of 2,4,6-trichlorophenyl acrylate



3.1.2.3 2,4,5-Trichlorophenyl acrylate

Figure 3.10 and Table 3.5 are the infrared spectrum of 2,4,5-trichlorophenyl acrylate and its assignments, respectively. The C=C stretching also appears clearly at wavelength 1630 cm^{-1} in the spectrum.

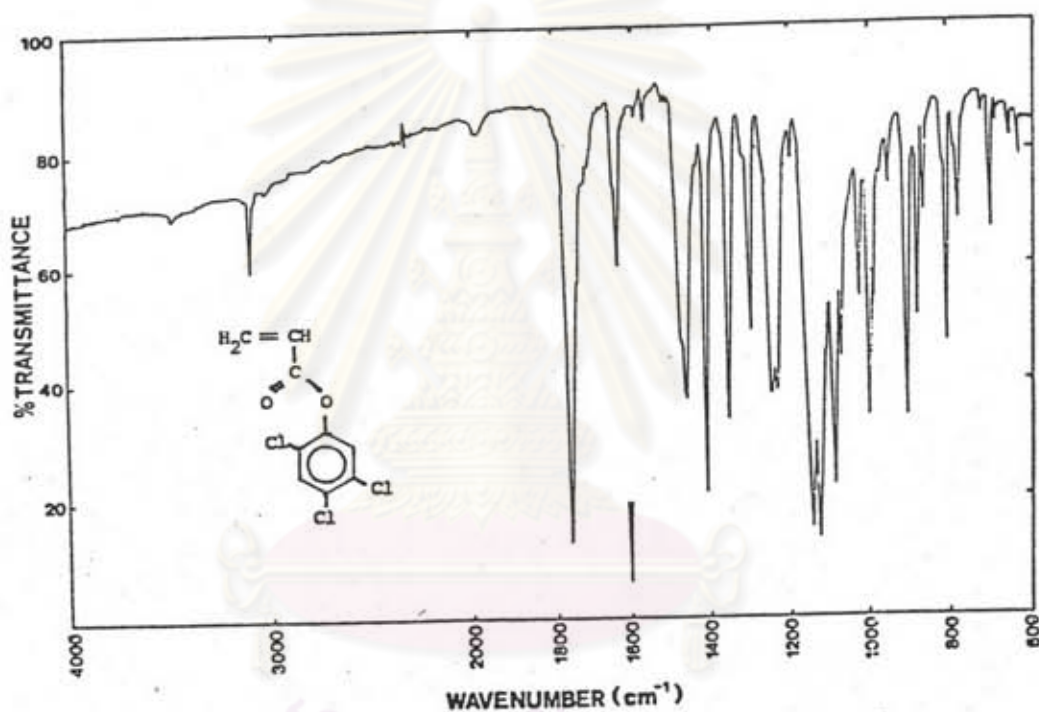


Figure 3.10 Infrared spectrum of 2,4,5-trichlorophenyl acrylate (KBr)

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Table 3.5 Assignment of the various important bands in the IR spectrum of 2,4,5-trichlorophenyl acrylate (value in cm^{-1})

Absorption bands (cm^{-1})	assignments
3045 (w)	aromatic C-H stretching vibration
1755 (s)	C=O stretching vibration
1630 (m)	C=C stretching vibration, vinyl terminal
1405 (m), 1350 (m), 1300 (m)	C-H bending vibration
1240 (m), 1220 (m), 1140 (s), 1120 (s)	C-O-C stretching vibration
990 (m)	=C-H bending vibration
890 (m), 800 (m), 760 (m), 680 (m)	C-Cl stretching vibration

2,4,5-trichlorophenyl acrylate exhibits the ultraviolet absorption band at λ_{max} 240 nm (ϵ 1800 $\text{mole}^{-1} \cdot \text{cm}^{-1}$), λ_{max} 280 nm (ϵ 392 $\text{mole}^{-1} \cdot \text{cm}^{-1}$) and λ_{max} 290 nm (ϵ 982 $\text{mol}^{-1} \cdot \text{cm}^{-1}$) (Figure 3.11) which is similar to both mentioned compounds.

In the NMR spectrum of 2,4,5-trichlorophenyl acrylate (Figure 3.12), the pattern of the vinylic geminal protons which is two pairs of doublets can again be identified easily. The two singlets at δ 7.34 (1H) and 7.55 (1H) ppm are assigned to the phenylic protons ortho- and meta- to the oxygen atom. Therefore the

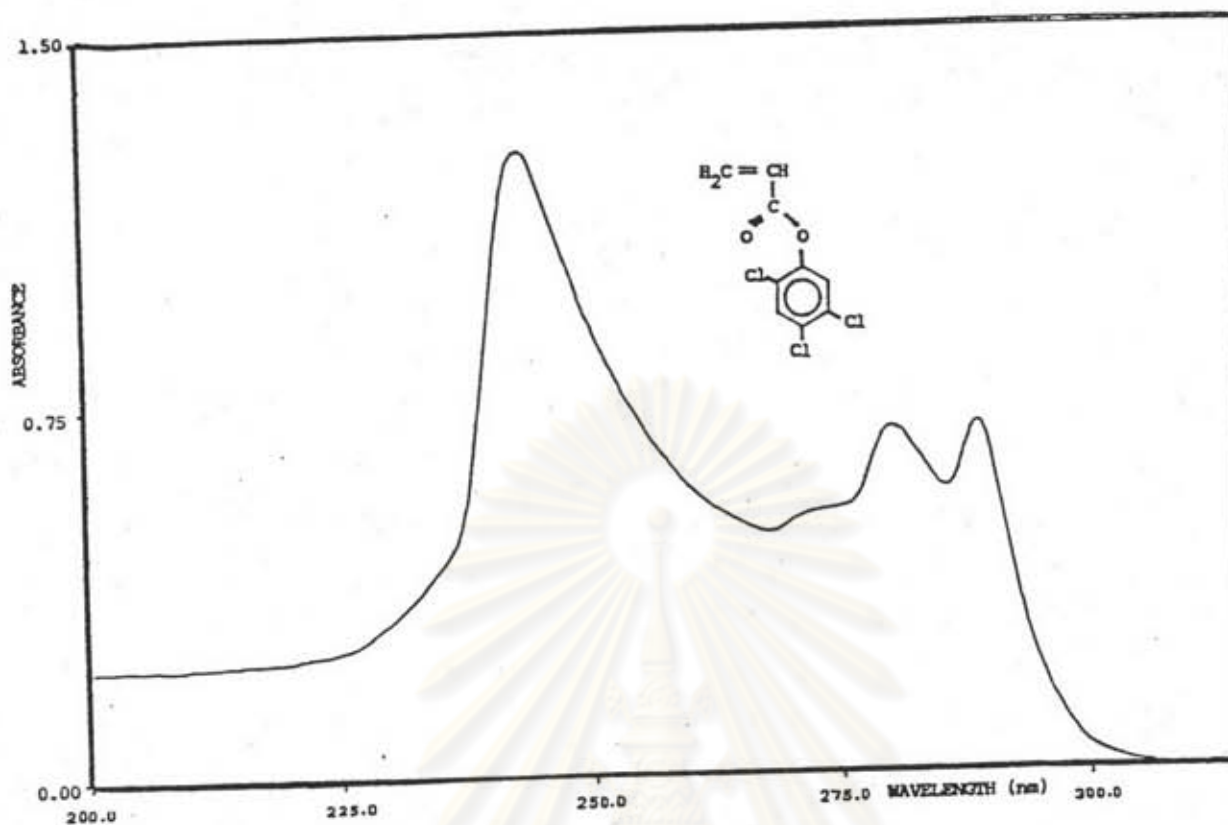


Figure 3.11 UV-Visible spectrum of 2,4,5-trichlorophenyl acrylate (CHCl_3)

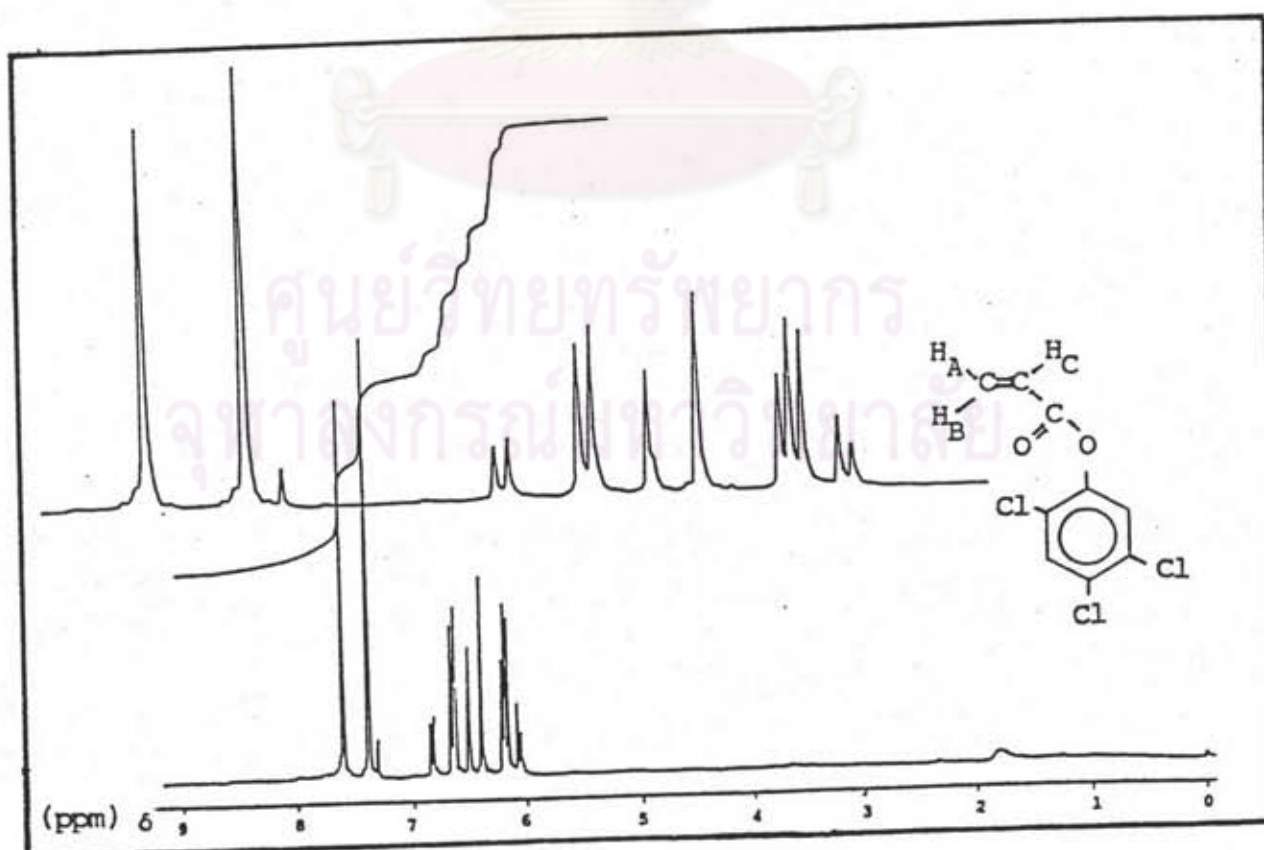
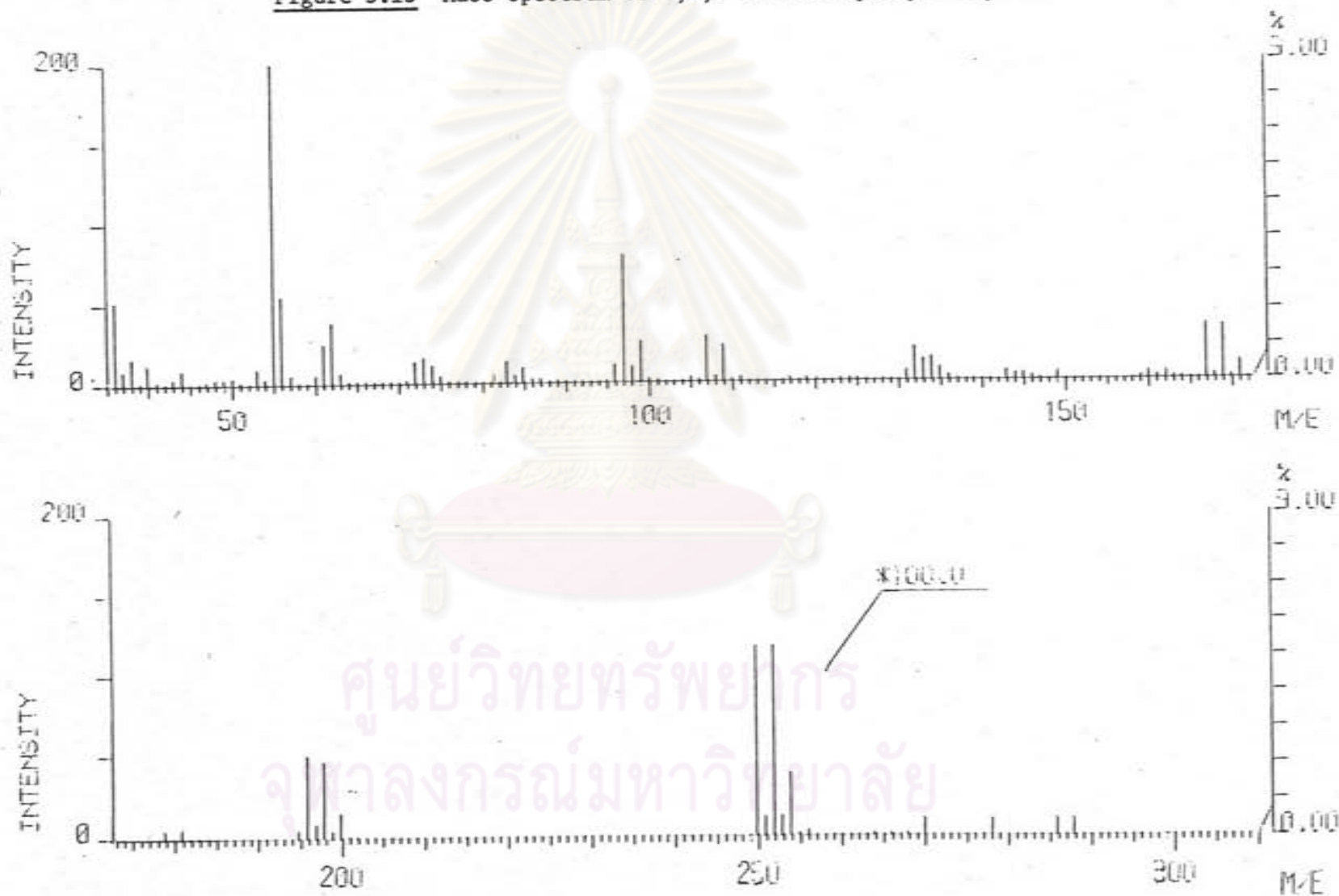


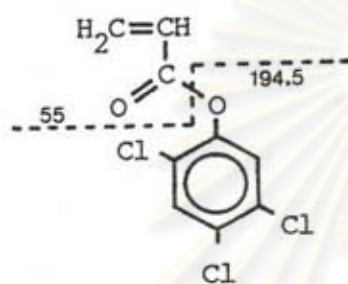
Figure 3.12 $^1\text{H-NMR}$ spectrum of 2,4,5-trichlorophenyl acrylate (CDCl_3)

Figure 3.13 Mass spectrum of 2,4,5-trichlorophenyl acrylate



NMR spectrum seems to support the structure of 2,4,5-trichlorophenyl

The mass spectrum of 2,4,5-trichlorophenyl acrylate (Figure 3.13) exhibits the molecular ion peak at m/e 250. The ratio of $M^+ : M+2 : M+4$ is 100 : 97.8 : 31.9 which show the characteristic of the molecule contains 3 chlorine atoms. The base peak at m/e 55



accounts for the formation of the vinyl acylium ion. It also shows the peak of 2,4,5-trichloropheno-licium ion at m/e 195 which confirms the presence of 3 chlorine atoms.

The above spectral information of this compound thus leads to the deduction that it is 2,4,5-trichlorophenyl acrylate.

3.1.2.4 4-Chloro-3-methylphenyl acrylate (4-Cl-3-MPA)

Figure 3.14 and Table 3.6 are the infrared spectrum of 4-chloro-3-methylphenyl acrylate (4-Cl-3-MPA) and its assignments, respectively. A sharp absorption band at 1635 cm^{-1} is obviously identified. This is due to C=C stretching vibration. In addition, two absorption bands at 1610 and 1580 cm^{-1} are also observed. These bands are belong to the aromatic C=C stretching.

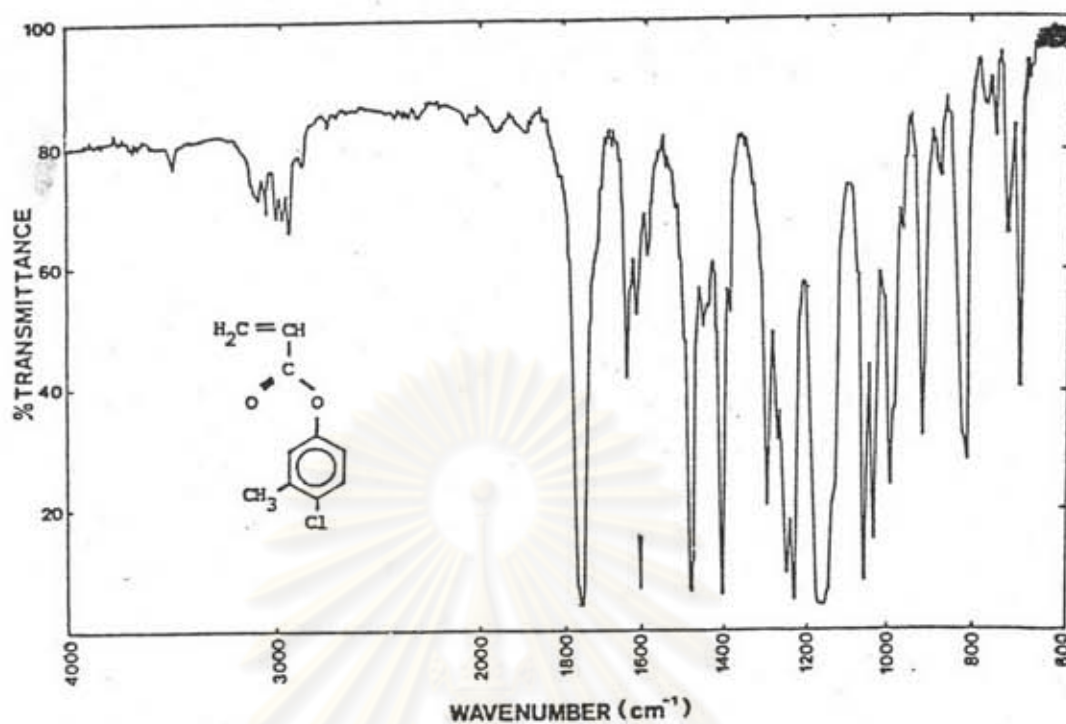


Figure 3.14 Infrared spectrum of 4-chloro-3-methylphenyl acrylate (neat)

Table 3.6 Assignment of the various important bands in the infrared spectrum of 4-chloro-3-methylphenyl acrylate

Absorption Bands (cm ⁻¹)	assignments
3050 (w), 2950 (w)	C-H stretching of CH ₃ , aromatic C-H stretching
1750 (s)	C=O stretching vibration
1635 (m)	C=C stretching vibration, vinyl terminal
1480 (s)	C-H bending vibration, CH ₃ , aromatic
1409 (s), 1300 (m)	C-H bending vibration, vinyl terminal
1250 (s), 1230 (s), 1150 (s)	C-O-C stretching vibration
985 (m), 900 (m)	=C-H bending vibration
800 (m), 680 (m)	C-Cl stretching vibration

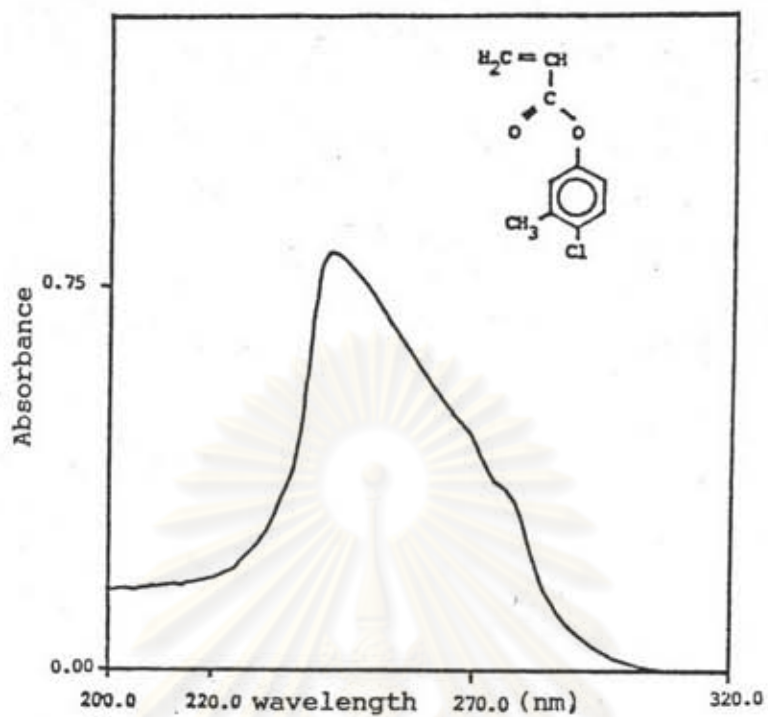


Figure 3.15 UV-Visible spectrum of 4-chloro-3-methylphenyl acrylate (CHCl_3)

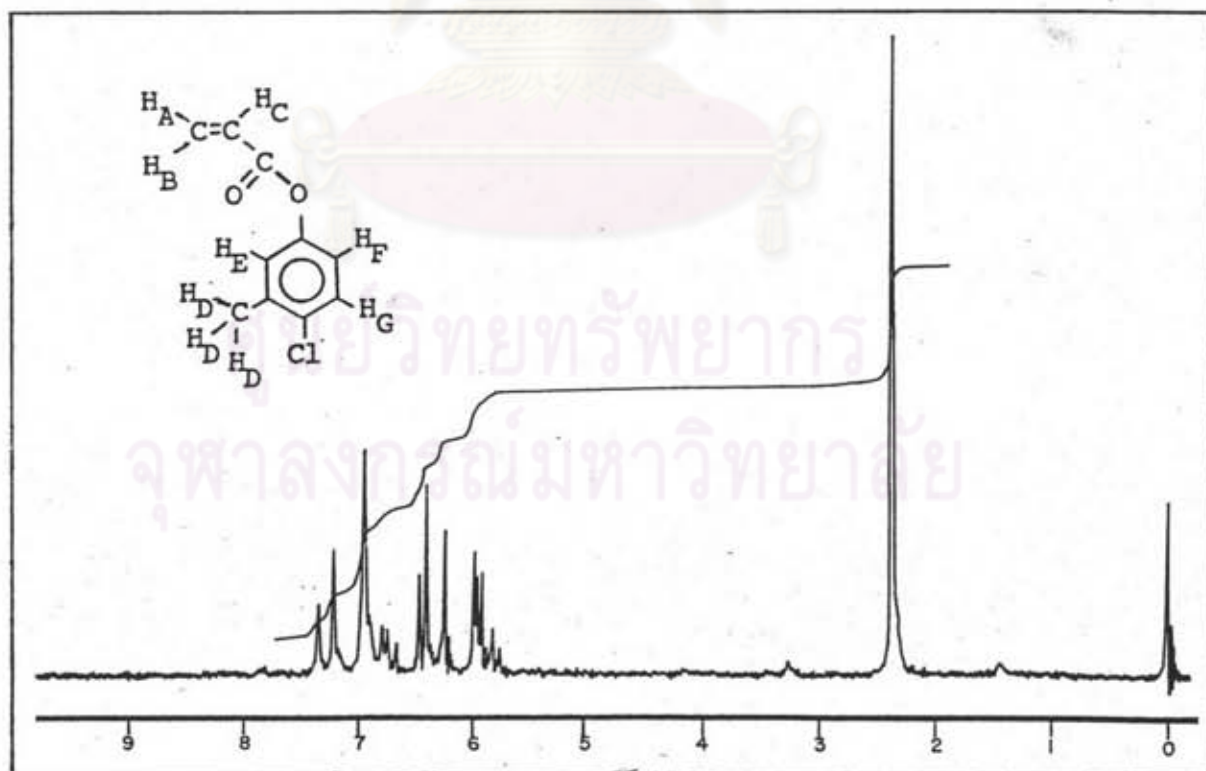


Figure 3.16 $^1\text{H-NMR}$ spectrum of 4-chloro-3-methylphenyl acrylate (CDCl_3)

4-Chloro-3-methylphenyl acrylate also exhibits the ultraviolet absorption band at λ_{max} 240 nm (ϵ 2272 mole⁻¹.cm⁻¹). (Figure 3.15) Thus a benzene ring is confirmed to be in the molecule

The proton NMR spectrum of 4-chloro-3-methylphenyl acrylate in deuteriochloroform (Figure 3.16) shows two pairs of doublets at δ 5.94, 6.04 ppm and δ 6.52, 6.71 ppm. This pattern is characteristic peak of geminal vinylic protons. The multiplets at δ 6.84–7.38 ppm with the integration of total 3 protons are due to the aromatic protons. The remaining signal at δ 2.36 ppm for total 3 protons are assigned to the methyl groups.

The mass spectrum of 4-chloro-3-methylphenyl acrylate (Figure 3.17) shows the molecular ion at m/e 196.5 ($M^+ : M+2 = 100 : 32.6$). The base peak at m/e at 55 which is due to the vinyl acylium

ion. The 4-chloro-3-methylphenyl cation ion is observed at m/e 141.5 which confirms the presence of 1 chlorine atom. It also shows the high intensity peak at m/e 195.5 which corresponds to the fragmentation of 4-chloro-3-methylacrylatium ion by losing the hydrogen atom, as following

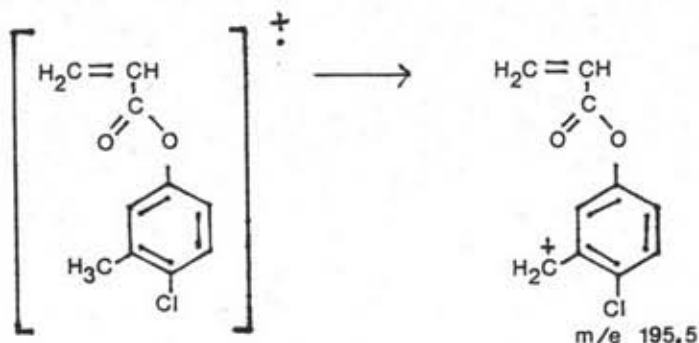
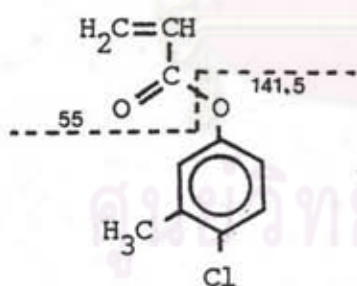
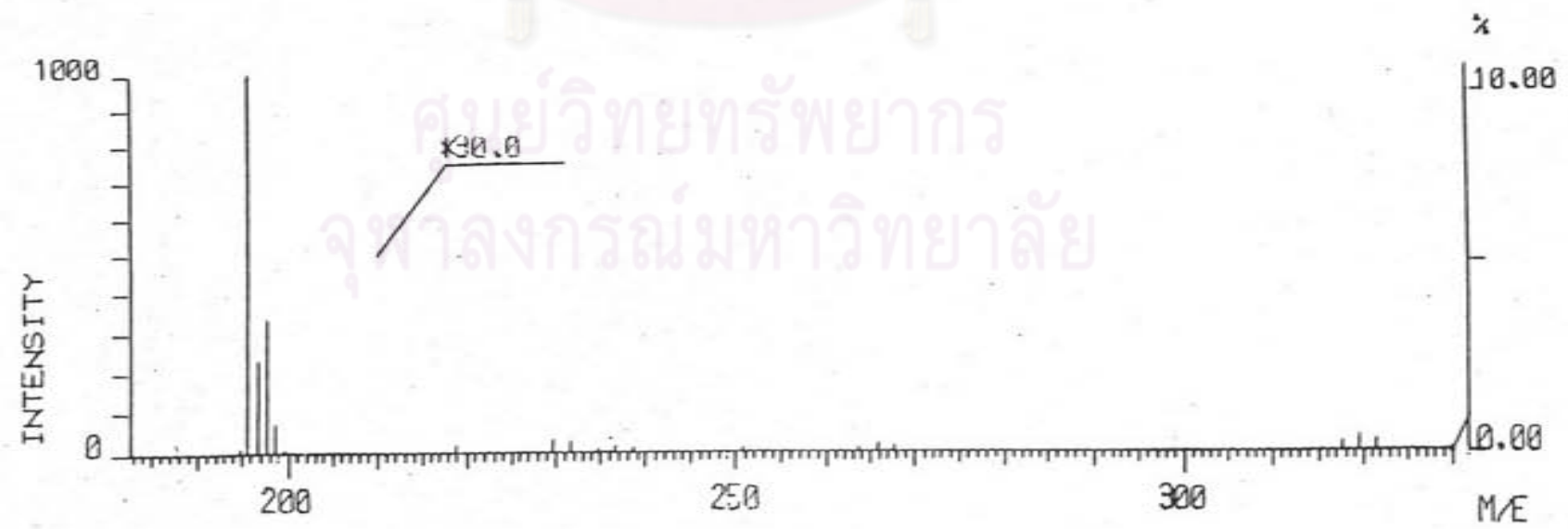
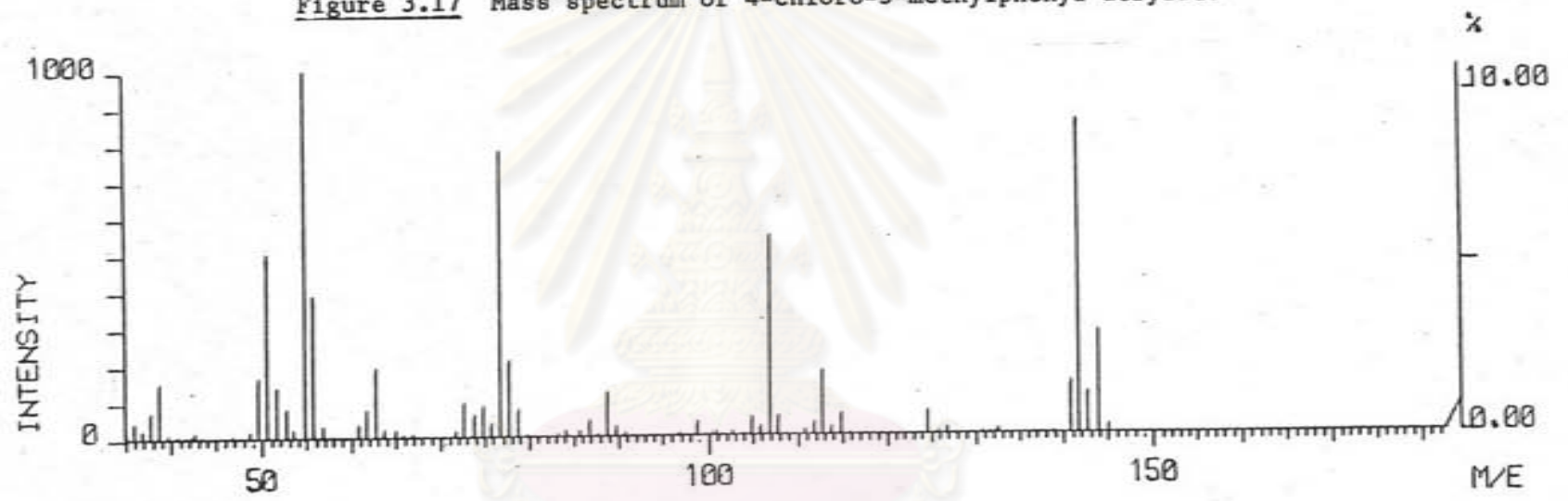


Figure 3.17 Mass spectrum of 4-chloro-3-methylphenyl acrylate

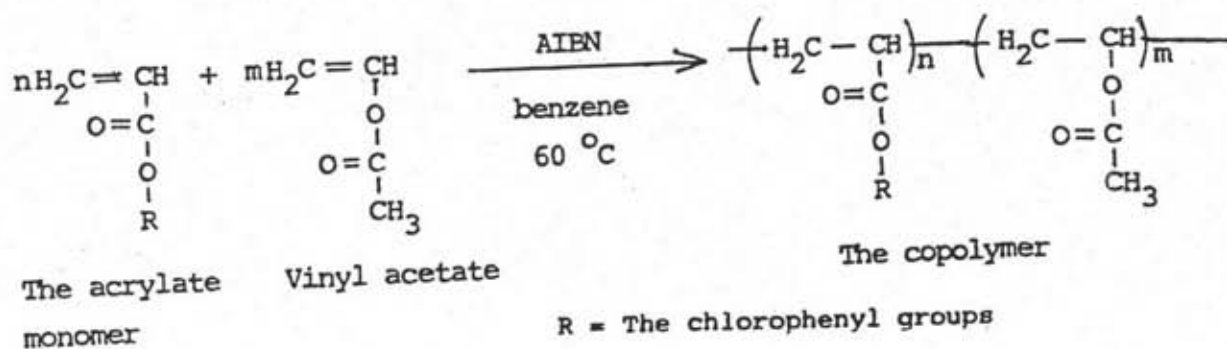


ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

3.2 Preliminary study of copolymerization

Firstly, pentachlorophenyl acrylate (PCPA) was copolymerized with vinyl acetate by bulk polymerization technic . It was found that solubility of pentachlorophenyl acrylate in vinyl acetate could not be more than one percent mole at 60 °C. Attempts to prepare poly(PCPA-co-VAc) with various percent mole higher than one percent mole by bulk polymerization technic were thus unsuccessful. The same problem was also observed for the preparation of poly(2,4,5-TCPA-co-VAc). Because of the solubility limit of the acrylates in vinyl acetate, polymerization was therefore attempted in benzene.

AIBN is known to be a good initiator for polymerization of vinyl monomer (1). This is due to its reactive radical. It also shows essentially not enter into the transfer reactions. It decomposes at almost the same rate in benzene and essentially is unaffected by inhibitor in such solvents. Therefore AIBN was chosen to be the initiator for copolymerization between the fungicidal acrylate monomers and vinyl acetate . The following equation represents such reaction.



Several different conditions for copolymerization between the acrylate and vinyl acetate in benzene were tried out. The temperature, the reaction time and the amount of AIBN were varied. The condition leading to low conversion (less than 15 %) is desired which is necessary for the determination of the monomer reactivity ratios defined by Fineman and Ross (3). It was finally found that at 60 °C, one hour of reaction time and AIBN at one percent mole of the total monomer content is the suitable condition for this study.

Since oxygen has been known to scavenge the radicals, the copolymerizations were carried out both in the presence and in the absence of oxygen by purging the solution mixture with N₂ gas for 10 minutes before heating the reaction. Both cases showed that the acrylate monomer could enter into the copolymer much more than vinyl acetate (Table 2.3). The results of the series of the reactions in the presence of oxygen, however, were inconsistency. This was presumably due to the loss of vinyl acetate during the removal oxygen. The loss of vinyl acetate from each mixture unequally, of course altered the sequence of the monomer ratios in the feed which subsequently affected to the incorporation of the monomer into the polymer. Since oxygen causes only the low conversion of the polymer and its effect on the monomer incorporation into the polymer was never been reported, it is therefore not necessary to eliminated oxygen from the solutions before polymerizations.

3.3 Copolymerization of the fungicidal acrylate monomers with vinyl acetate

3.3.1 Pentachlorophenyl acrylate with vinyl acetate

The copolymerization between pentachlorophenyl acrylate and vinyl acetate had been carried out with various monomer feeding ratios at 60 °C for one hour. The purity of each copolymer was indicated by both thin layer chromatography and its infrared spectrum (Figure 3.18 and 3.19). For quick monitoring by thin layer chromatography, methanol was used as the developing solvent. Usually, the acrylate monomer appears near the solvent front, while copolymer, which does not dissolve in methanol, stays at the starting line. No contamination of a monomer on a copolymer was found in every cases. This was further confirmed by the infrared spectra with the absence of the absorption bands near 1635 and 980 cm^{-1} which correspond to the olefinic moiety. It is of interest to observe two carbonyl absorption bands at 1740 and 1780 cm^{-1} in the spectrum. These bands are assigned to the C=O stretching of the carbonyl group in vinyl acetate and pentachlorophenyl acrylate moieties, respectively. These assignments are verified by spectra of poly(vinyl acetate) (Figure 3.16) and poly(pentachlorophenyl acrylate) (Figure 3.20)

Furthermore, it should be noticed that the peak heights at wave number 1740 and 1780 cm^{-1} proportionally vary with the mole fraction of the monomer feeding. For instance, Figure 3.18 shows that poly(PCPA-co-VAc)I-1 contains PCPA moiety much more than

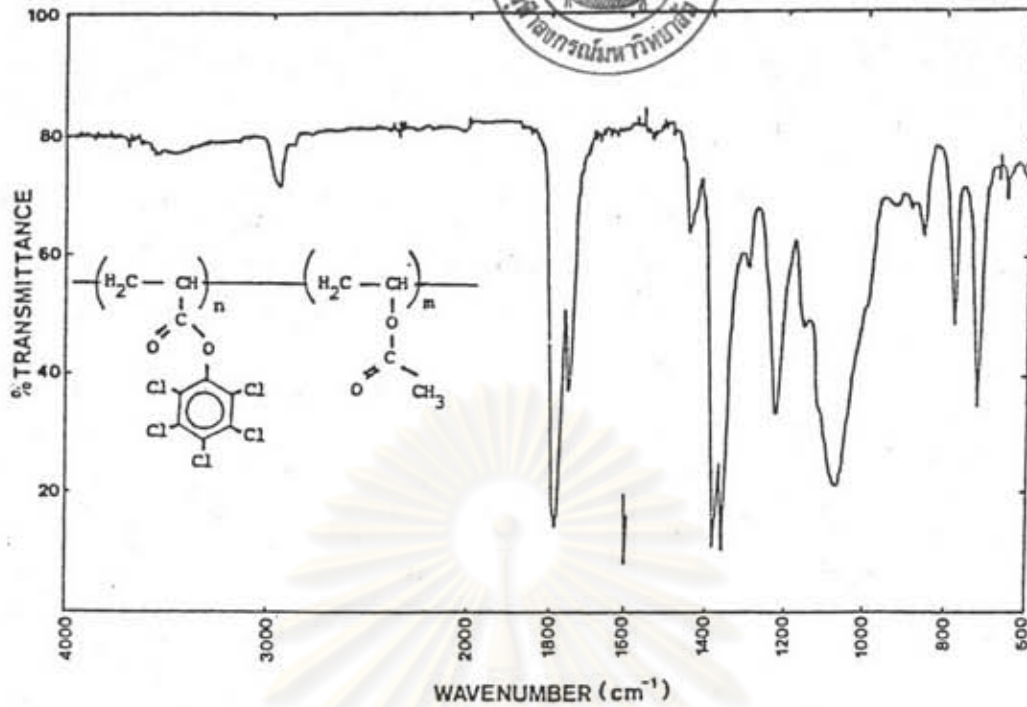


Figure 3.18 Infrared spectrum of poly(PCPA-co-VAc) I-1 (KBr)

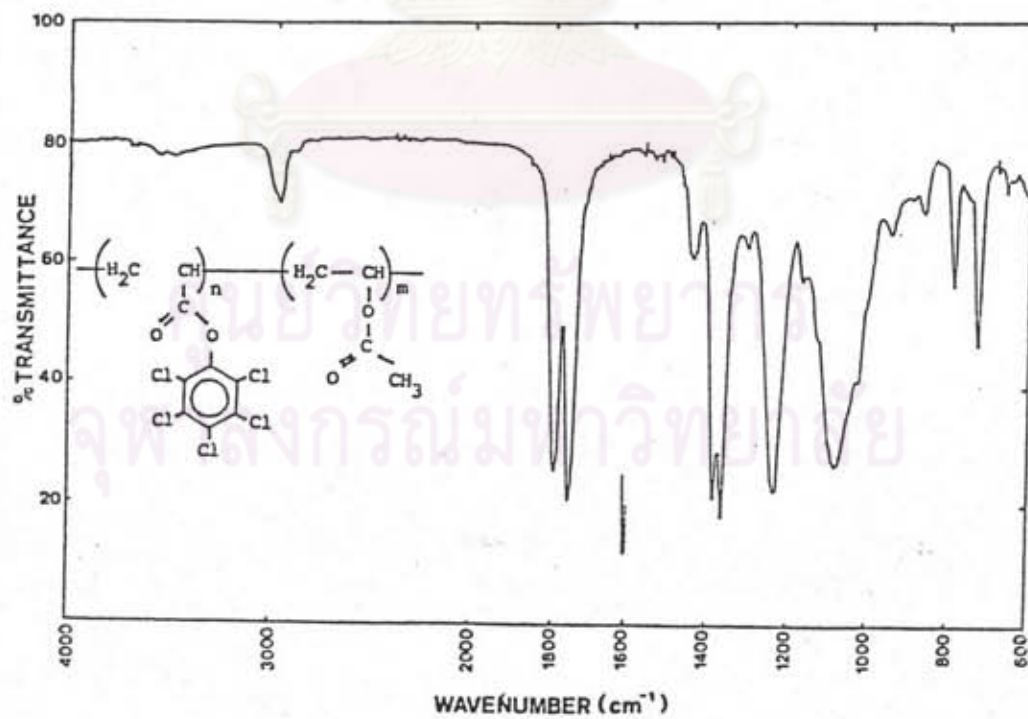


Figure 3.19 Infrared spectrum of poly(PCPA-co-VAc) VIII-1 (KBr)

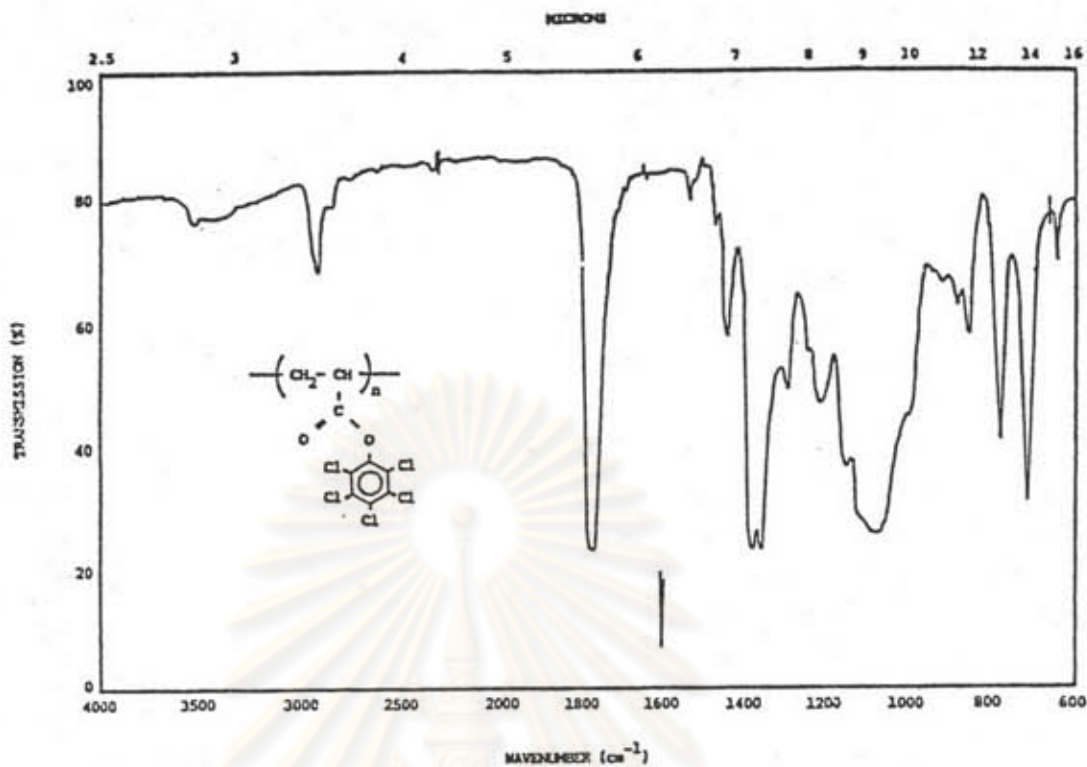


Figure 3.20 Infrared spectrum of poly(PCPA) (KBr)

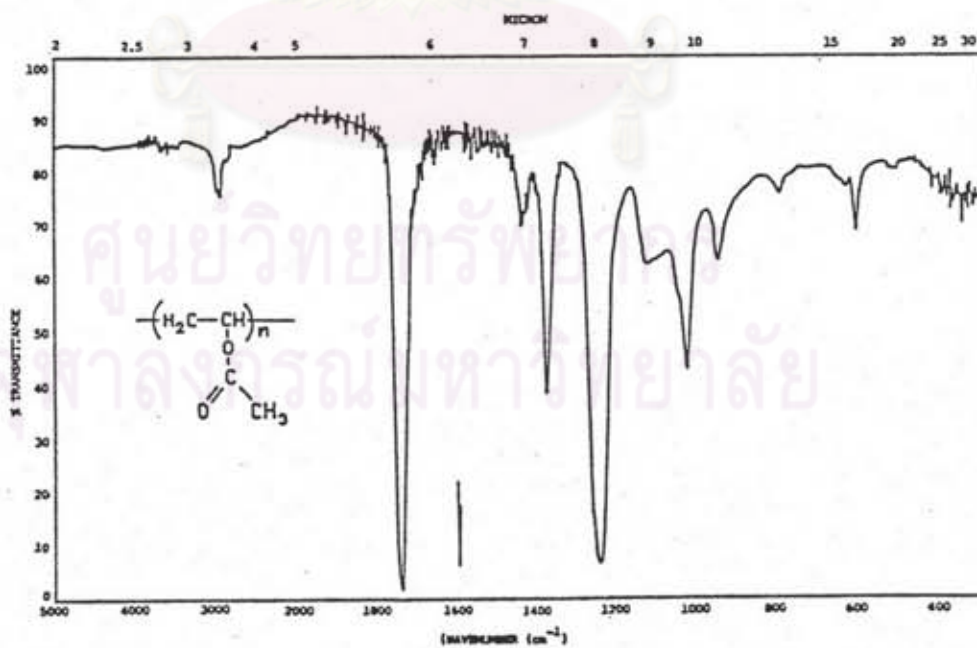


Figure 3.21 Infrared spectrum of poly(VAc) (film)

VAc, while approximately the equal amount of each monomer in poly(PCPA-co-VAc)VIII-1 is shown in Figure 3.19. Indeed, the mole fractions of PCPA in the feeding are 0.7 and 0.05, respectively.

However, the infrared spectroscopy technic is not applicable for determination of the copolymer composition in this study. This is because those two absorption peaks seem to overlap to some extent for each copolymer. Thus it is difficult to clarify each portion which is necessary for further calculation.

3.3.2 2,4,6-Trichlorophenyl acrylate with vinyl acetate

Similarly, poly(2,4,6-TCPA-co-VAc) I-VIII were obtained. Figure 3.22 and 3.23 are the infrared spectra of poly(2,4,6-TCPA-co-VAc) I-1 and VIII-1, respectively.

Besides the absence of the absorption bands near 1635, 1300 and 1015 cm^{-1} which corresponding to olefinic moiety, the presence of two carbonyl absorption bands at 1770 and 1740 cm^{-1} appear in each spectrum as well. These are attributed to C-O stretching vibration of carbonyl group in 2,4,6-TCPA and VAc moieties, respectively. Again, the variation of the peak height in the carbonyl region is observed which depends on the mole fraction of the feeding.

3.3.3 2,4,5-Trichlorophenyl acrylate with vinyl acetate

In the same manner, poly(2,4,5-TCPA-co-VAc) I-VIII were prepared. The absence of the absorption bands near 1630, 1405, 1300 and 990 cm^{-1} (Figure 3.24 and Figure 3.25) obviously indicates the generation of a polymer and no contamination of a monomer. Two absorption bands at 1770 and 1740 cm^{-1} are indicative of the C=O stretching vibrations of two carbonyl groups in the copolymers. These are due to the 2,4,5-TCPA and VAc portions, respectively.

3.3.4 4-Chloro-3-Methylphenyl acrylate with vinyl acetate

Poly(4-Cl-3-MPA-co-VAc) I-VIII were similarly prepared. All their infrared spectra show the absence of the absorption bands near 1635, 1405, 1300 and 985 cm^{-1} . However, only one strong absorption band at wavenumber 1750 cm^{-1} is observed (Figure 3.26 and Figure 3.27). The reason is that the carbonyl absorption of a poly(4-Cl-3-MPA) is at wave number 1750 cm^{-1} which is very close to the one of poly(VAc), i.e. 1740 cm^{-1} .

It should be pointed out here that the copolymerization between 4-chloro-3-methylphenyl acrylate and vinyl acetate gave very low conversion comparing to the other three polymerizations mentioned above. This is probably due to chain transfer reaction which will be discussed in more detail in section 3.4.

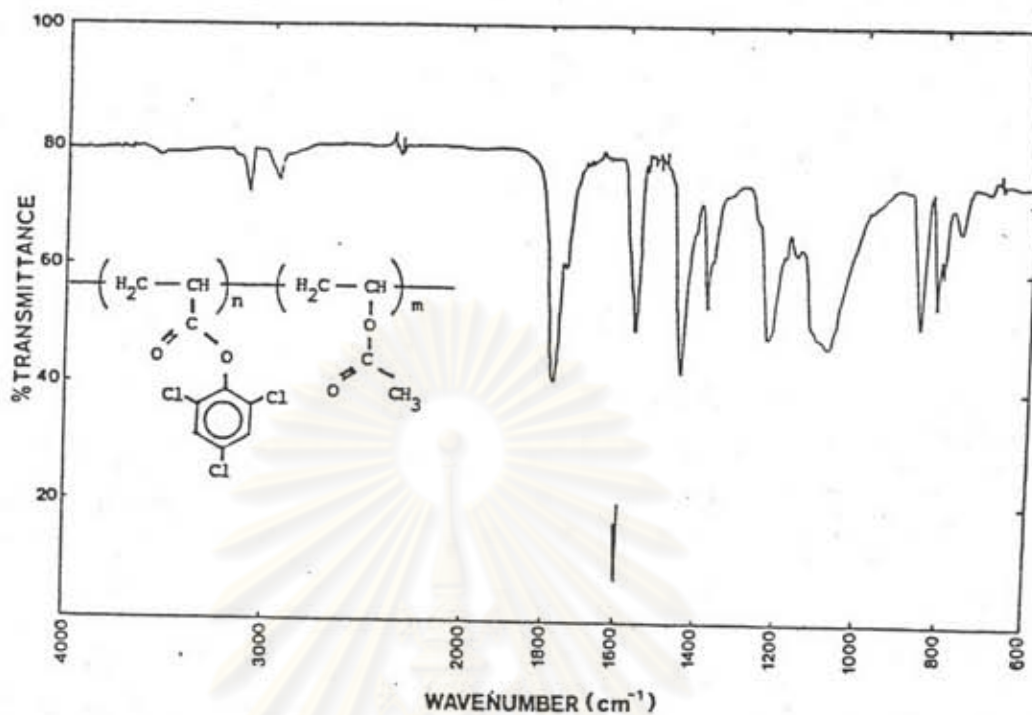


Figure 3.22 Infrared spectrum of poly(2,4,6-TCPA-co-VAc) I-1 (KBr)

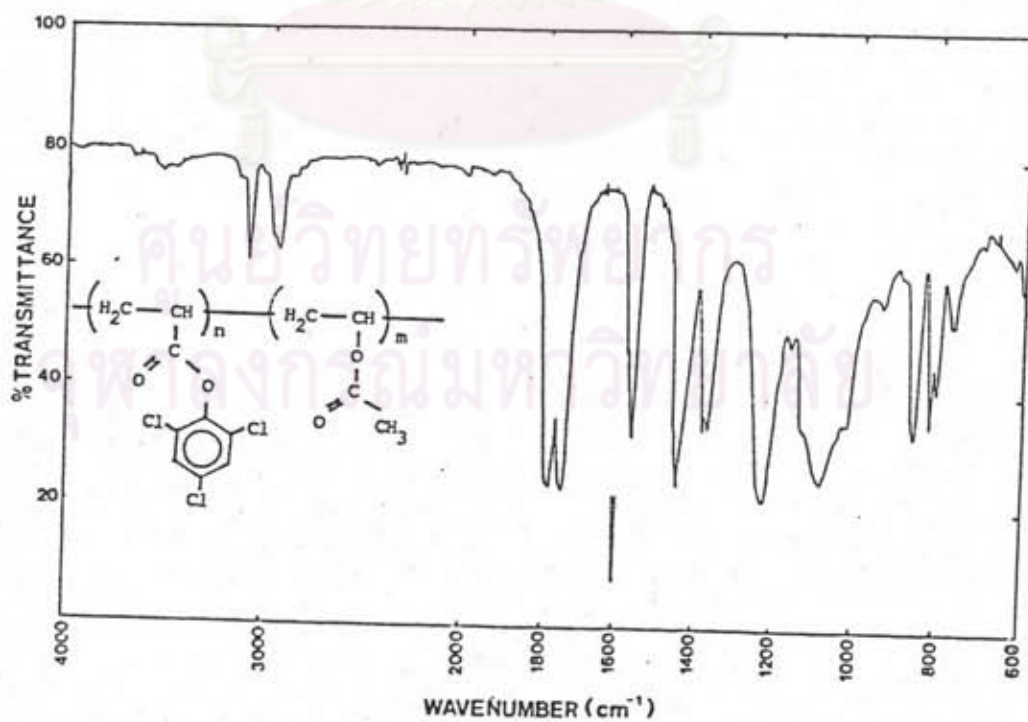


Figure 3.23 Infrared spectrum of poly(2,4,6-TCPA-co-VAc) VIII-1 (KBr)

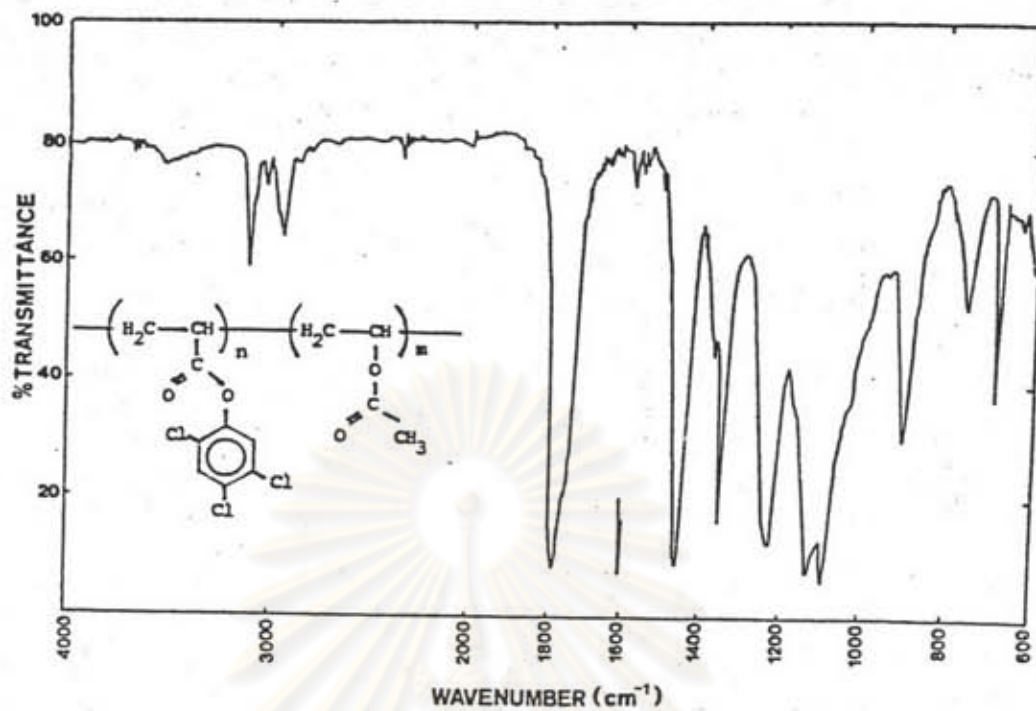


Figure 3.24 Infrared spectrum of poly(2,4,5-TCPA-co-VAc) I-1 (KBr)

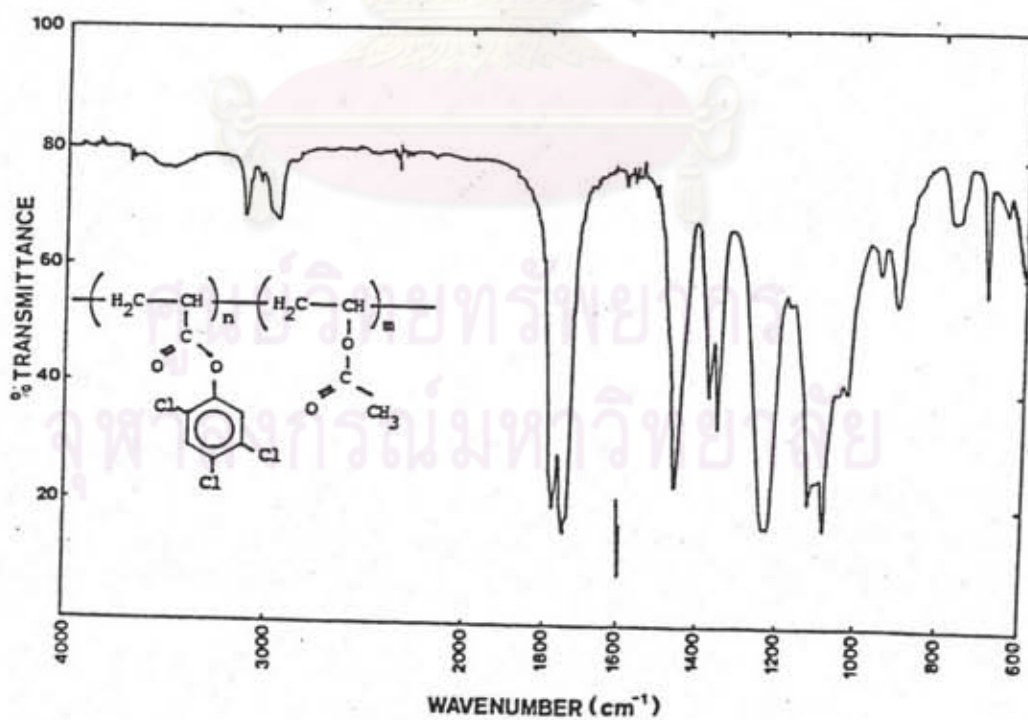


Figure 3.25 Infrared spectrum of poly(2,4,5-TCPA-co-VAc) VIII-1 (KBr)

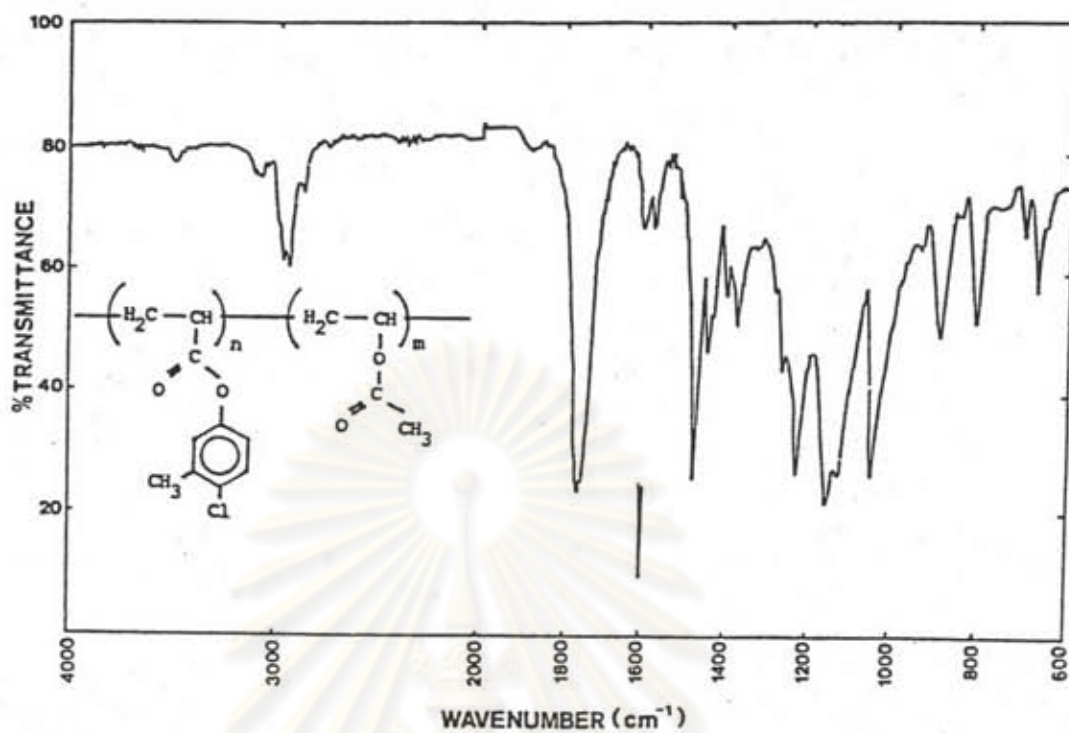


Figure 3.26 Infrared spectrum of poly(4-Cl-3-MPA-co-VAc) I-1 (KBr)

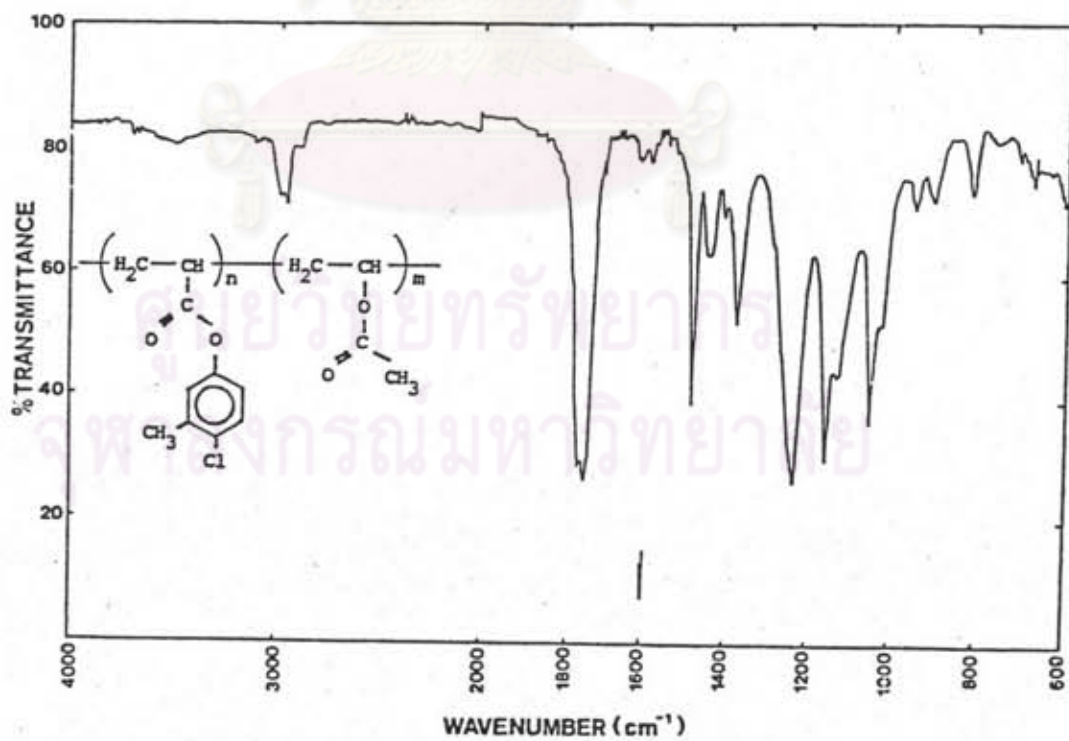


Figure 3.27 Infrared spectrum of poly(4-Cl-3-MPA-co-VAc) VII-1 (KBr)

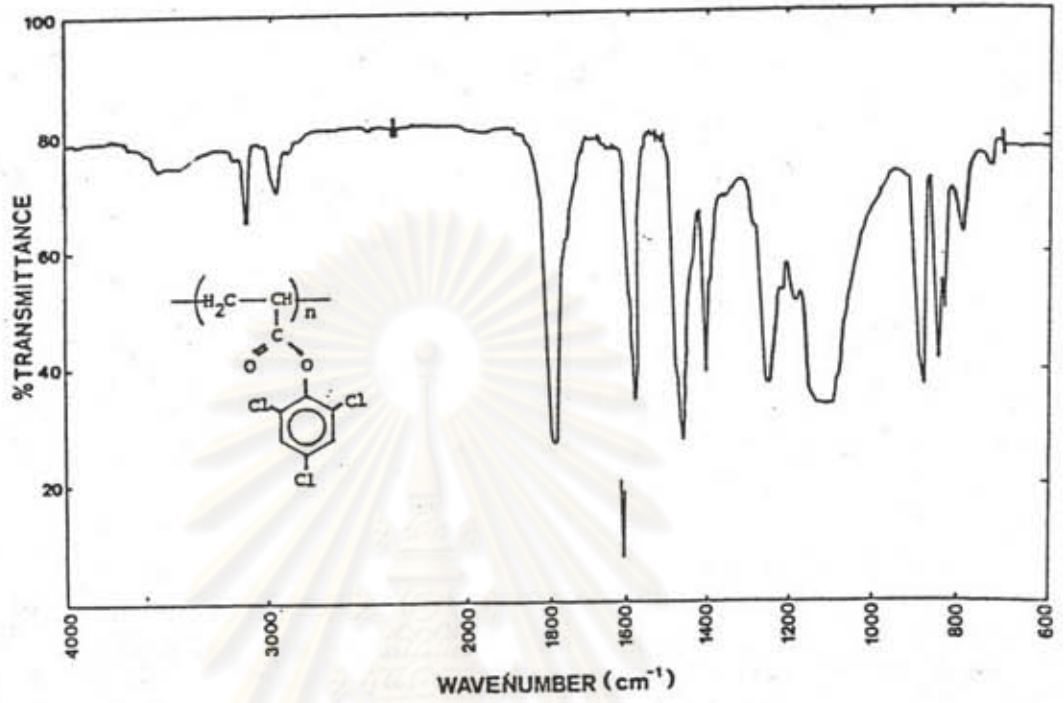


Figure 3.28 Infrared spectrum of poly(2,4,6-TCPA) (KBr)

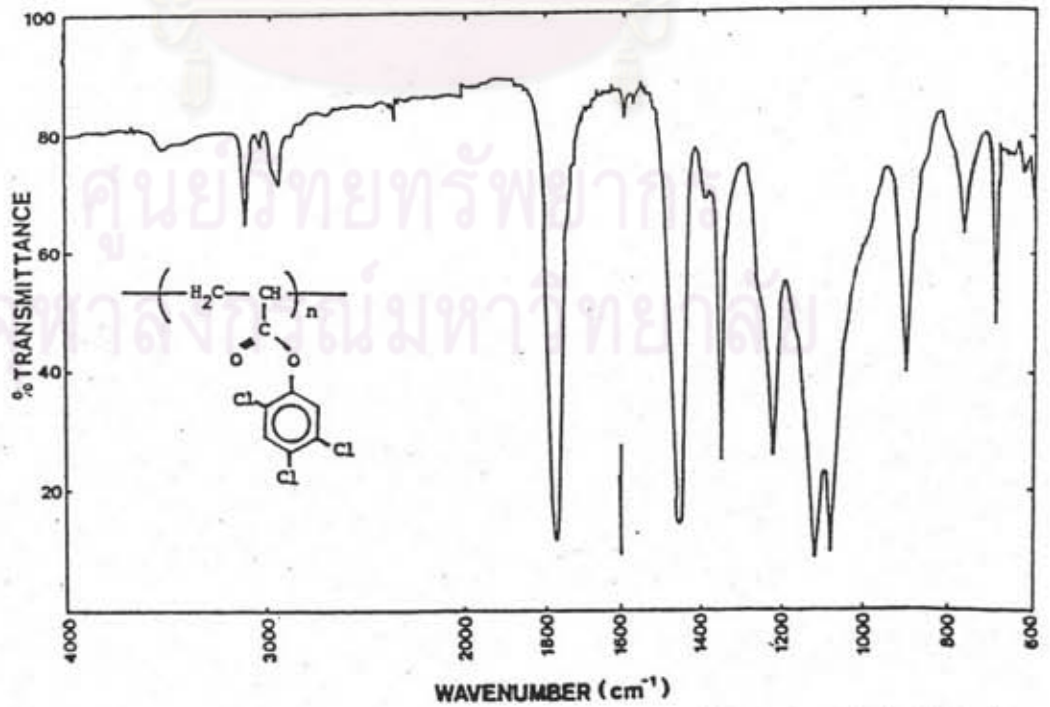


Figure 3.29 Infrared spectrum of poly(2,4,5-TCPA) (KBr)

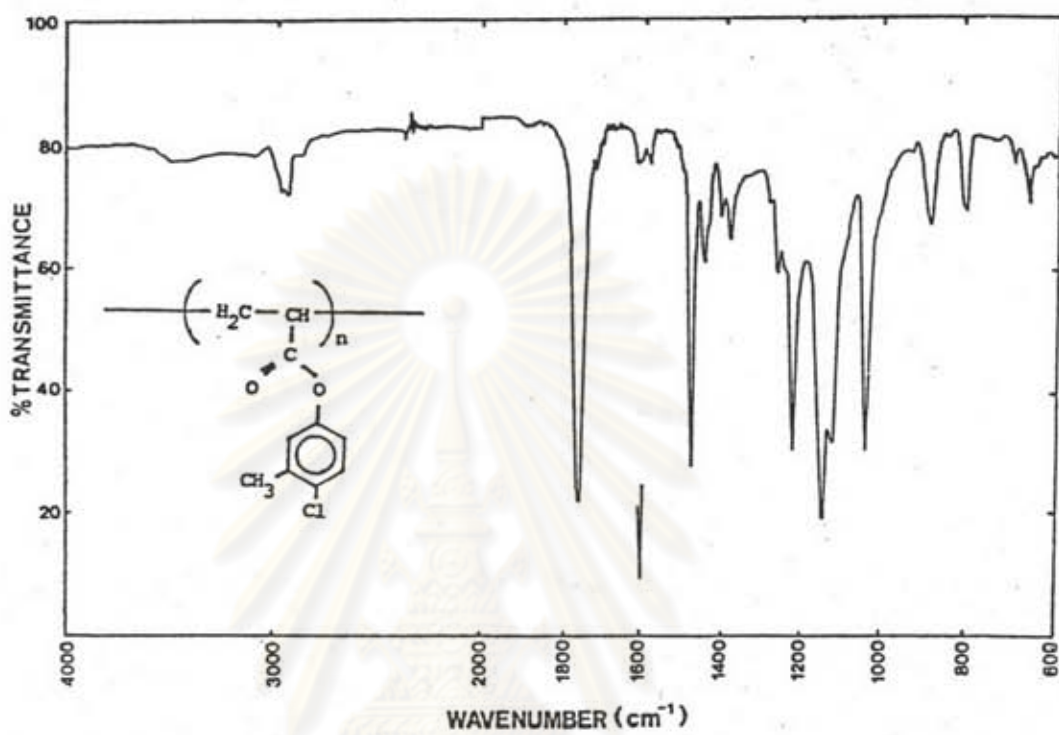


Figure 3.30 Infrared spectrum of poly(4-Cl-3-NPA) (KBr)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

3.4 Homopolymerization of the fungicidal acrylate monomer

All homopolymerization was carried out in benzene in the presence of equal amount of initiator, 0.0164 g of AIBN. Since the purpose of this preparation is for being a standard for the determination of copolymer composition, no attempt to control the degree of conversion was made. The mixture was heated at 60 °C for 2.5 hours. All the polymers remained in the solution during the reaction, except for poly(PCPA) which precipitated after 10 minutes of the reaction. After the precipitation, the polymers were obtained (Table 3.7)

TABLE 3.7 The chlorophenyl acrylate homopolymers

Polymer	conversion (%)
Poly(PCPA)	50.76
Poly(2,4,6-TCPA)	32.65
Poly(2,4,5-TCPA)	28.43
Poly(4-Cl-3-MPA)	18.93

The infrared spectra of all these homopolymers (Figure 3-20 , 3.28, 3.29, 3.30) are similar to their corresponding monomers (Figure 3.1, 3.6, 3.10, 3.14) except the disappearance of the absorption bands near 1630 and 980 cm^{-1} , which are due to the olefinic part. By thin layer chromatographic technic , the purity of each homopolymer was confirmed.

3.5 Determination of the copolymer composition

3.5.1 Pentachlorophenyl acrylate composition in copolymer

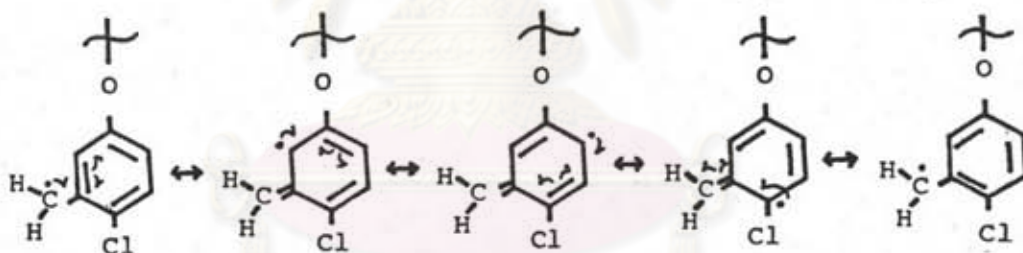
It has been known that two monomers differ markedly in their tendencies to enter into copolymers. Therefore the fractions of both monomers in the copolymer are usually not the same as in the monomer feed. There are several methods to investigate the polymer formation. In this research work, the incorporation of the fungicidal monomer into the copolymer is thus determined by using UV-Visible spectroscopic techniques.

However, UV-Visible spectroscopy is an attractive choice only when the following conditions can be met : (1) the backbone units must not have overlapping absorbance maxima; (2) solutions can be prepared in nonopaque solvents, (3) there are not major shifts in spectral intensity or position of one backbone unit due to the presence of the other .(32)

Unfortunately, poly(PCPA), prepared as described in Section 3.4, did not dissolve in any solvent. Attempts to increase its solubility by raising the temperature gave the unsatisfactory result. This is probably due to its high molecular weight . Therefore, poly(PCPA) of lower molecular weight was prepared. The reaction was performed in methanol which is the non-solvent. Poly(PCPA) was precipitated during the polymerization course. The polymer of low molecular weight was thus obtained. These products were able to dissolve in chloroform.

It is of interest to notice that poly(4-Cl-3-MPA) has the lowest percent of conversion. The resemble result was observed before (see Section 3.3.4). The copolymerization of 4-Cl-3-MPA with vinyl acetate gave significantly lower percent of conversion comparing to the ones of the other three chlorophenyl acrylate monomers with vinyl acetate.

The rationalization for the above observation is that the growing chain radical was transferred to another species in the reaction. Since 4-Cl-3-MPA has the benzylic protons, it can therefore act as a chain transfer agent. This benzylic radical is more stable than the other aliphatic radical due to its resonance stabilization by benzene.



Since toluene also has a benzylic proton, it can be a chain transfer agent. Therefore if homopolymerization of pentachlorophenyl acrylate is carried out in toluene, low conversion of the polymer product should be observed. Indeed, 29.81 percent of conversion was obtained when PCPA was polymerized in toluene. Consequently, this result confirms the observation of the lower percentage conversion of 4-Cl-3-MPA.

Preliminary investigation reveals that with poly(PCPA) and poly(PCPA-co-VAc) have the same absorption pattern of maximum absorbance at 240 nm in chloroform (Figure 3.31 a, b). Vinyl acetate or poly(VAc), of course, does not have any absorption above 200 nm. Consequently, only the PCPA units in poly(PCPA-co-VAc) absorbs the light. Subsequently, the number of PCPA units in poly(PCPA-co-VAc) can be obtained directly from the absorbance of poly(PCPA-co-VAc) solution of known concentration by comparing to poly(PCPA) which contains only the PCPA units in the chain.

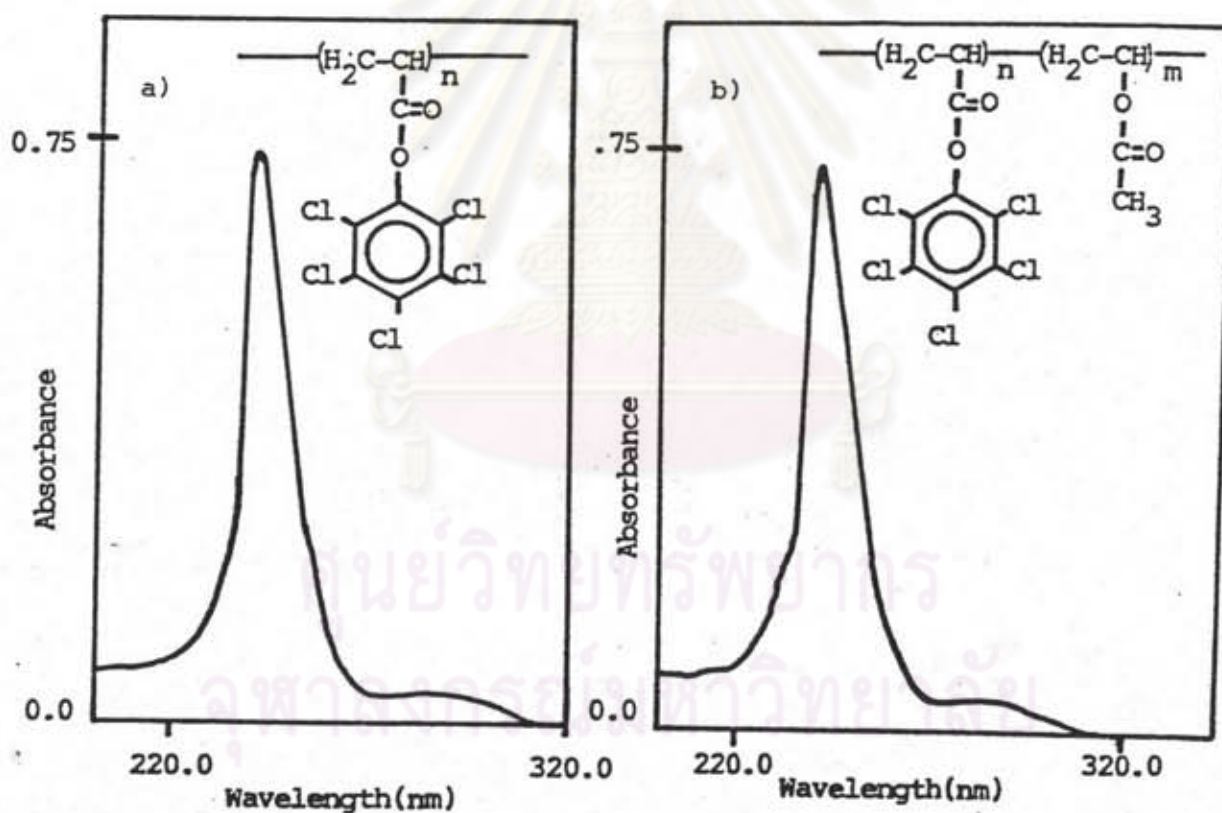


Figure 3.31 UV-Visible spectra in CHCl_3 of

a) poly(PCPA)

b) poly(PCPA-co-VAc)



3.5.2 The novel chlorophenyl acrylate in the copolymers

The determination of the other three chlorophenyl acrylates in copolymers was performed in the same manner as mentioned before. Fortunately, the copolymers and its corresponding homopolymers have the same absorption patterns with maximum absorption at 240 nm. as shown in Figure 3.32 to Figure 1.34. Therefore, all the measurements were made at 240 nm.

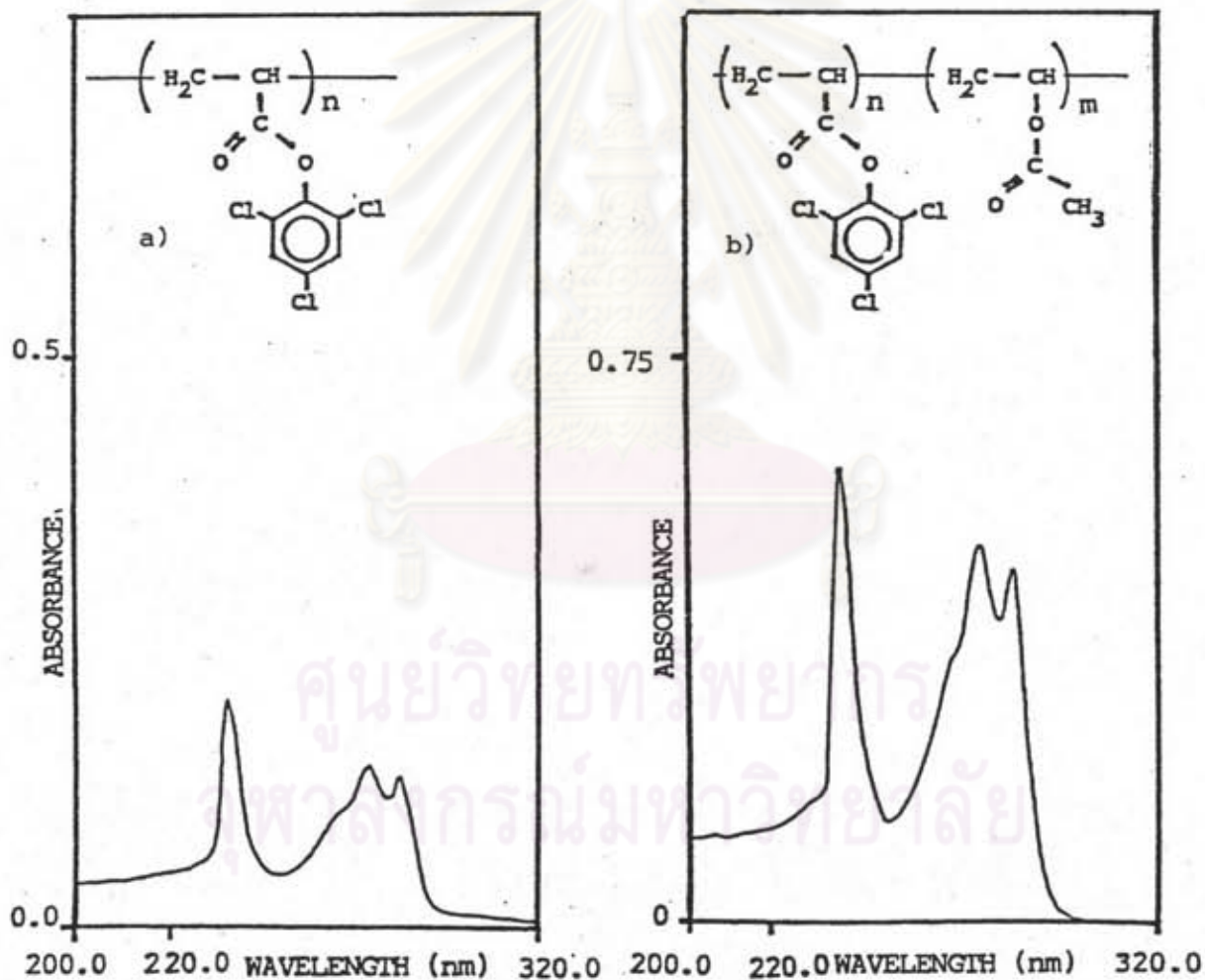


Figure 3.32 UV-Visible spectra in CHCl_3 of

a) poly(2,4,6-TCPA)

b) poly(2,4,6-TCPA-co-VAc)

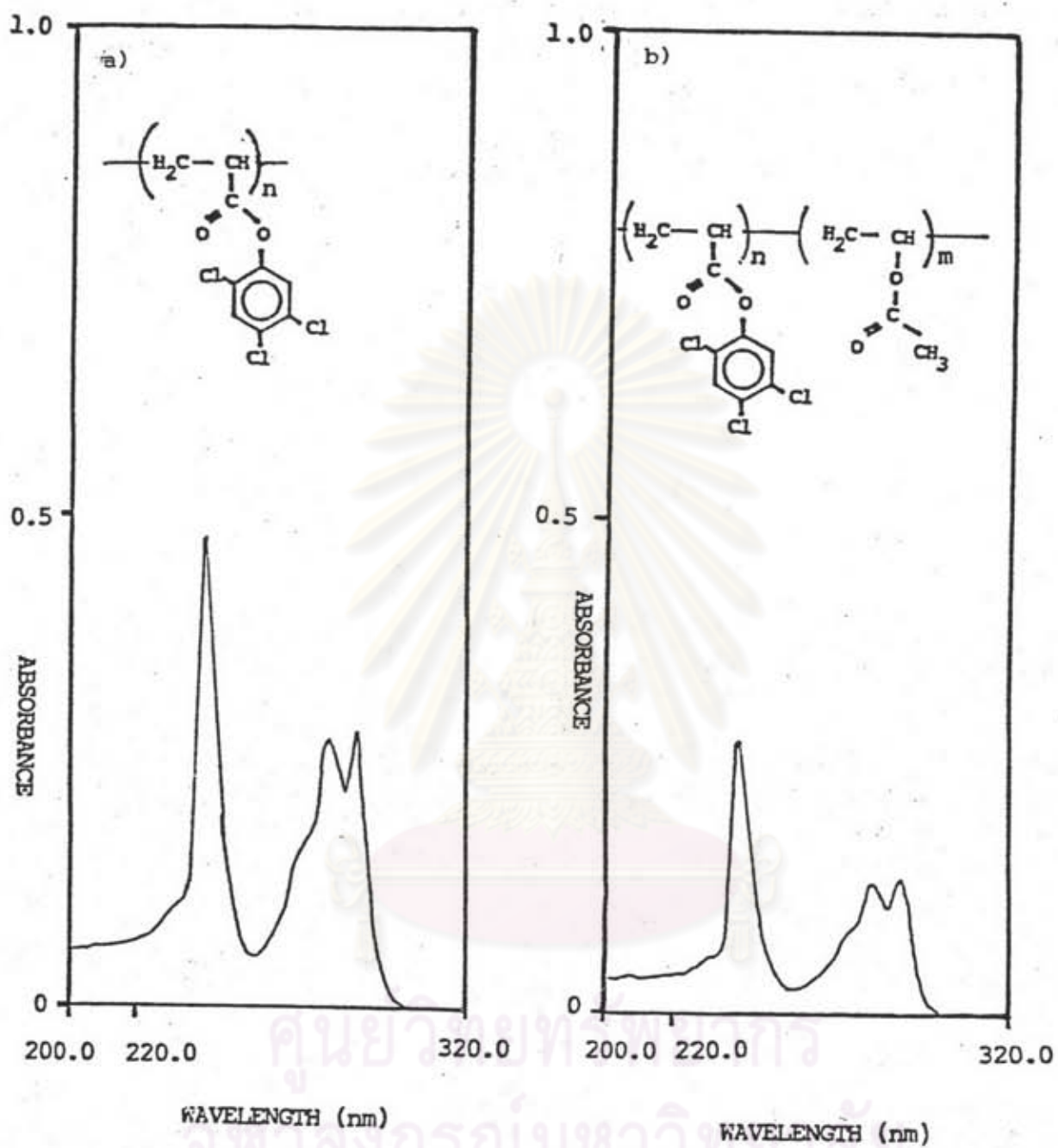


Figure 3.33 UV-Visible spectra in CHCl_3 of
 a) poly(2,4,5-TCPA)
 b) poly(2,4,5-TCPA-co-VAc)

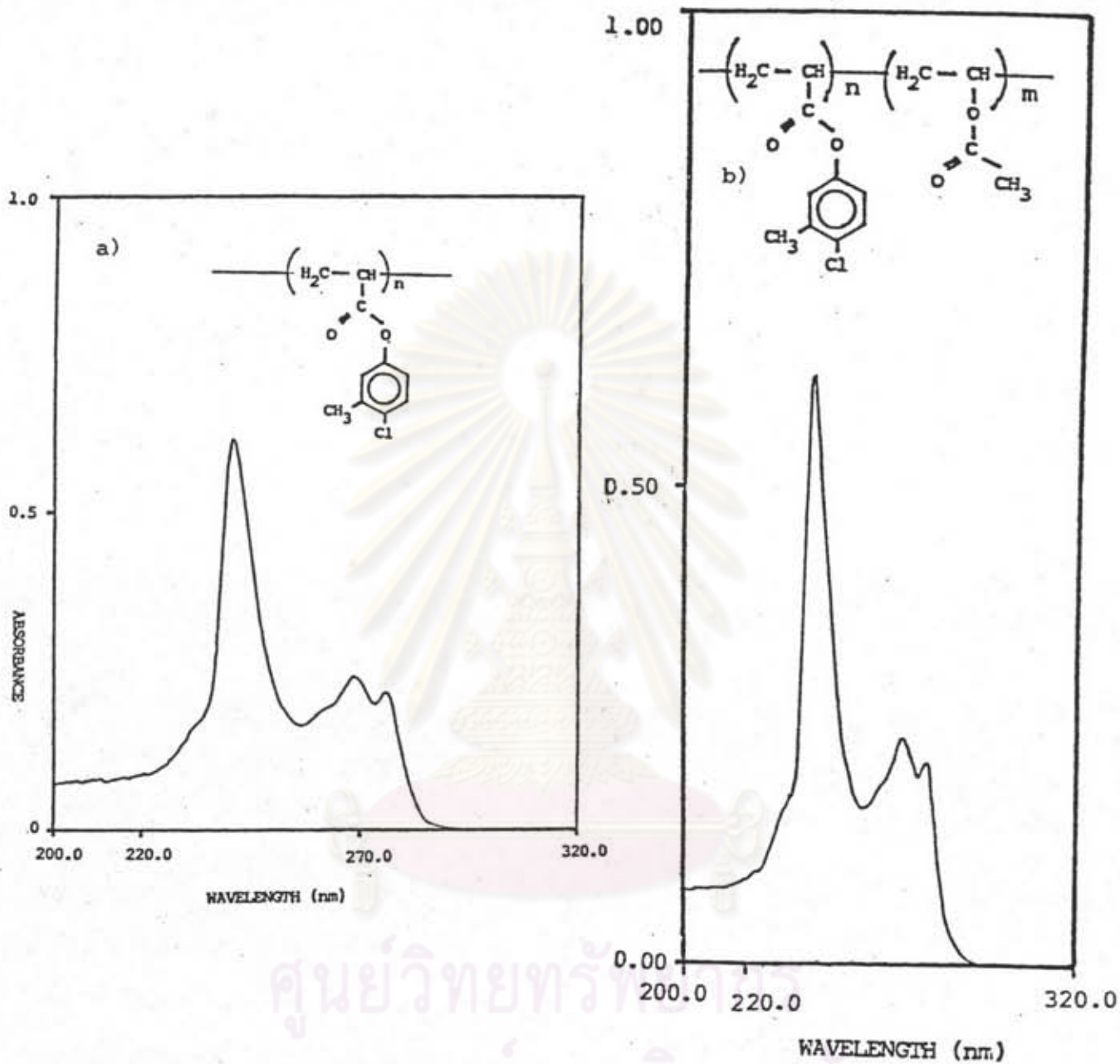


Figure 3.34 UV-Visible spectra in CHCl_3 of
 a) poly(4-Cl-3-MPA)
 b) poly(4-Cl-3-MPA-co-VAc)

3.6 Preliminary study of copolymer composition by ¹H-NMR

The progress of polymerization can be followed by ¹H-NMR spectroscopy. The amount of each monomer left in the solution which, in turn, leads to the one incorporated, into the polymer chain can also be obtained at any interval of the reaction. This is, however, successful only when the monitoring proton, which is olefinic, of each monomer appears at different chemical shift and not interfere with other protons.

Figure 3.3 a illustrates the 90-MHz proton NMR spectrum of 2,4,5-TCPA-VAc (30 percent mole of 2,4,5-TCPA in the feed) in deuteriated benzene solution. This spectrum was recorded after 30 minutes of the reactions at 60°C. The olefinic protons of 2,4,5-TCPA (δ 5.51-6.63 ppm) clearly appear at different chemical shifts from the geminal methylene protons of vinyl acetate (δ 4.35-4.9 ppm). Two signals at δ 3.54 and 3.63 ppm are due to the methoxy protons of two conformers of poly (methyl methacrylate) which was added to the mixture as a reference to calibrate the signal.

Figure 3.3 b and Figure 3.3 c exhibit the similar spectra with the exception of the changing relative intensities of the signals. These alterations are due to the polymerization of 2,4,5-TCPA and vinyl acetate. The signals responsible for the olefinic protons of both compounds decreases with reaction time.

This is concomitant with the rising signals of the aliphatic methylene protons of the polymer product. Accordingly, the ratio of

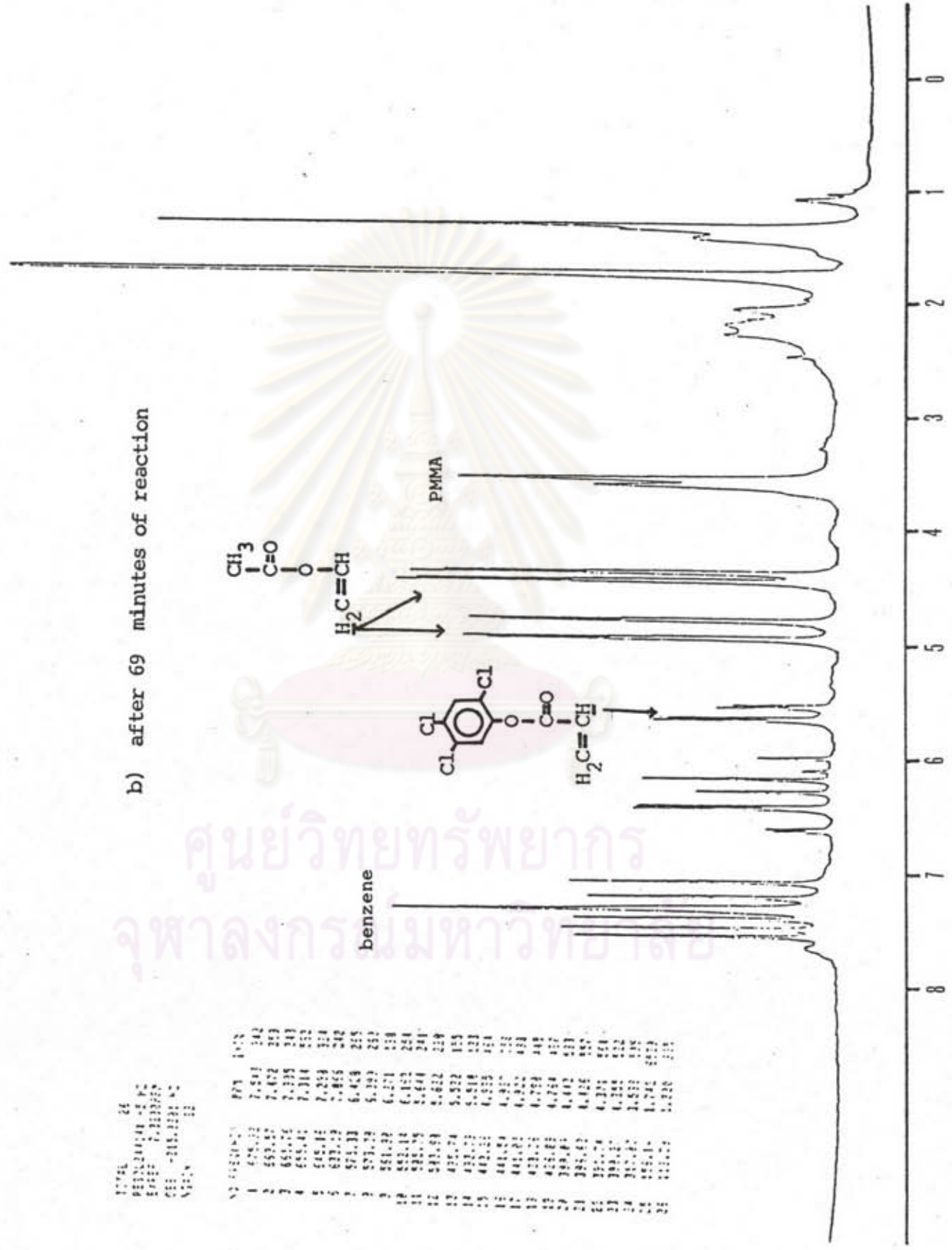
Figure 3.35 The NMR spectrum of the mixture of 2,4,5-TCPA and vinyl acetate in benzene- d_6 and in the presence of PMMA at 60°C

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

174L
 00000000-00
 0000 000000
 CH - 015.0000
 0000

b) after 69 minutes of reaction

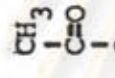
NO	PPM	INTEG
1	7.581	1.02
2	7.472	1.03
3	7.335	1.03
4	7.314	1.02
5	7.254	1.04
6	7.055	1.02
7	6.459	1.05
8	5.193	1.01
9	5.179	1.01
10	5.170	1.01
11	5.159	1.01
12	5.148	1.01
13	5.137	1.01
14	5.126	1.01
15	5.115	1.01
16	5.104	1.01
17	5.093	1.01
18	5.082	1.01
19	5.071	1.01
20	5.060	1.01
21	5.049	1.01
22	5.038	1.01
23	5.027	1.01
24	5.016	1.01
25	5.005	1.01
26	4.994	1.01
27	4.983	1.01
28	4.972	1.01
29	4.961	1.01
30	4.950	1.01
31	4.939	1.01
32	4.928	1.01
33	4.917	1.01
34	4.906	1.01
35	4.895	1.01
36	4.884	1.01
37	4.873	1.01
38	4.862	1.01
39	4.851	1.01
40	4.840	1.01
41	4.829	1.01
42	4.818	1.01
43	4.807	1.01
44	4.796	1.01
45	4.785	1.01
46	4.774	1.01
47	4.763	1.01
48	4.752	1.01
49	4.741	1.01
50	4.730	1.01
51	4.719	1.01
52	4.708	1.01
53	4.697	1.01
54	4.686	1.01
55	4.675	1.01
56	4.664	1.01
57	4.653	1.01
58	4.642	1.01
59	4.631	1.01
60	4.620	1.01



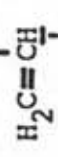
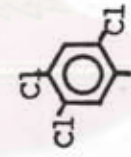
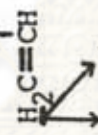
ศูนย์วิทยทรัพยากร
 จุฬาลงกรณ์มหาวิทยาลัย

c) after 165 minutes of reaction

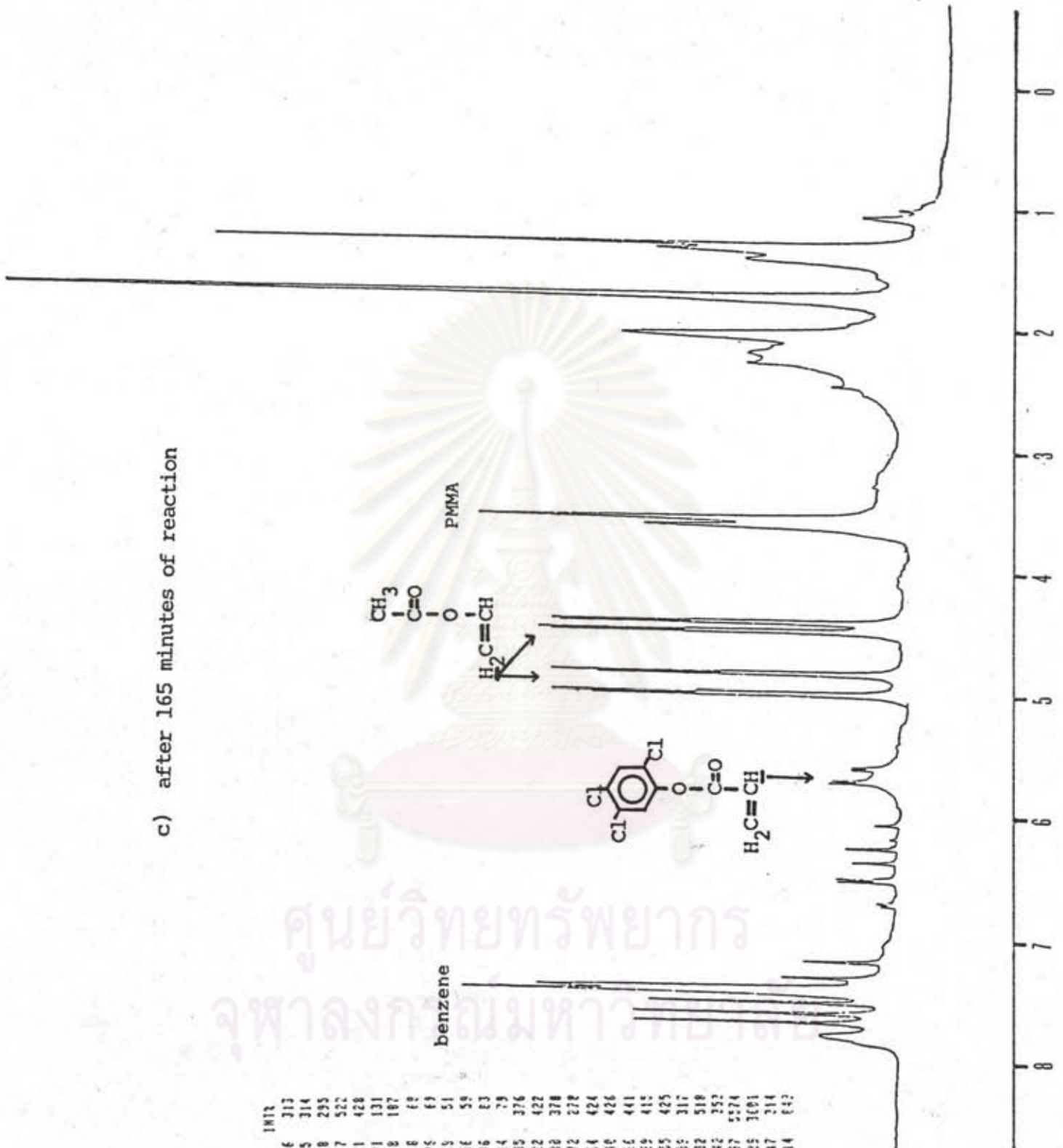
NO	FREQ(CY)	PPM	INTG
1	676.16	7.546	313
2	669.81	7.475	314
3	662.20	7.398	295
4	655.65	7.317	522
5	652.48	7.281	428
6	644.42	7.191	131
7	632.46	7.058	187
8	625.65	6.918	62
9	617.12	6.798	69
10	611.61	6.709	51
11	605.65	6.558	58
12	598.62	6.436	83
13	593.67	6.314	79
14	482.59	4.935	376
15	481.95	4.922	422
16	455.35	4.780	378
17	432.63	4.772	278
18	426.83	4.764	424
19	397.84	4.848	426
20	354.62	6.426	441
21	351.85	4.369	415
22	348.71	4.355	425
23	321.67	3.866	317
24	316.59	2.932	519
25	182.20	2.842	352
26	161.65	1.737	574
27	144.82	1.725	3081
28	130.74	1.347	314
29	11.11	1.214	643



PMMA



benzene



ศูนย์วิทยุทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

both compounds at any time of the reaction can be figured out directly from the NMR spectrum.

In this case, a pair of doublets of one proton centered at δ 5.581 ppm and two pairs of doublets centered at δ 4.85 and δ 4.398 ppm were taken for the measurement of each compound. These signals are accountable for one mole of 2,4,5-TCPA and one mole of vinyl acetate, respectively. Consequently, the mole fractions of both 2,4,5-TCPA and vinyl acetate at several interval of reaction time were calculated as exhibited in Table 3.8.

Table 3.8 Mole fractions of 2,4,5-trichlorophenyl acrylate and vinyl acetate at time t

time (min)	$F_{2,4,5\text{-TCPA}}$	F_{VAc}	$F_{2,4,5\text{-TCPA}}/F_{\text{VAc}}$
3	0.2394	0.7606	0.3147
30	0.2909	0.7091	0.4102
69	0.2504	0.7496	0.3340
105	0.2000	0.8000	0.2500
135	0.1588	0.8412	0.1888
165	0.1205	0.8795	0.1370

Figure 3.36 shows the plot of $F_{2,4,5\text{-TCPA}}/F_{\text{VAc}}$ against time. it can be observed that during the induction period (36 minutes) the line shows positive slope and after this time the slope changes

to be negative.

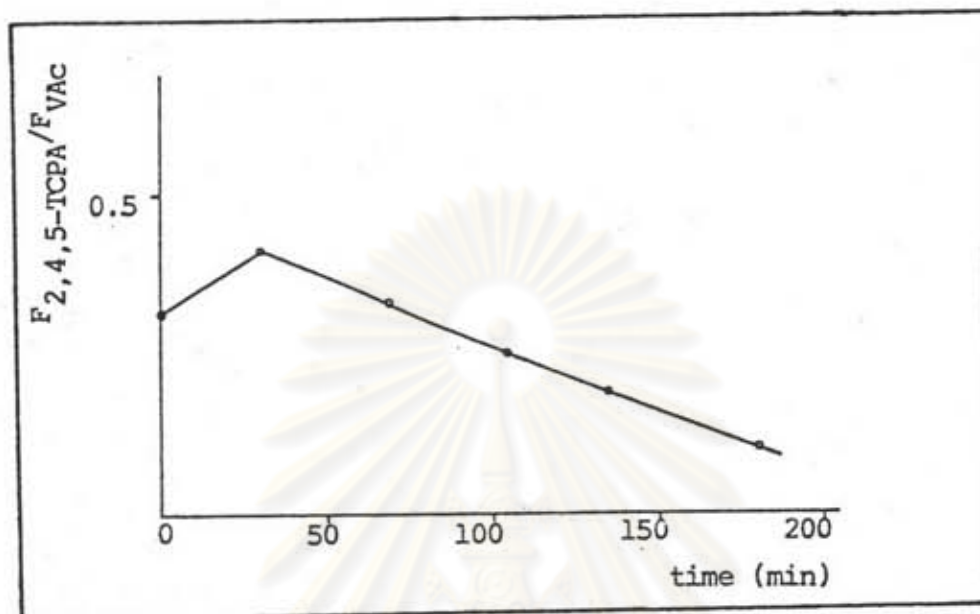


Figure 3.36 The mole ratio of 2,4,5-TCPA and VAc at time t

It can be rationalized that the first period is the retardation time. In this period oxygen, as impurity in the reaction scavenges the radical initiator. Furthermore, it is due to the equilibration of the decomposition of initiator. In this period the polymerization hardly occurs. Additionally, the amount of $F_{2,4,5-TCPA}/F_{VAc}$ increases with time. This is due to the mole fraction of vinyl acetate decreasing against time. The decreasing of vinyl acetate bases on the evaporation of low boiling point vinyl acetate (71-73 °C). After 36 minutes, the slope changes to be negative which implies that 2,4,5-TCPA decreased quicker than vinyl acetate. This is because of the higher reactivity of the acrylate.

The calculation of the copolymer composition has been tried. The mole fraction of 2,4,5-TCPA at 30 minute is 0.2909 which is

used to be the feeding mole fraction. This is due to the polymerization reaction occurred in equilibrium condition after the retardation time (36 minutes). The polymer compositions at time 69 minutes are calculated. The difference between the peak area of the 2,4,5-trichlorophenyl acrylate at time 30 minutes and 69 minutes leads to the one incorporated into the polymer chain. While the difference between the peak area of the vinyl acetate at that time leads to the one incorporated into the polymer chain and the one that is lost by evaporation. The correction of evaporation is made by compared with the difference between the peak area of vinyl acetate during the retardation time. It is, therefore, the copolymer contains 0.49 mole fraction of the 2,4,5-trichlorophenyl acrylate at 69 minutes. This value is consistent with the calculation from UV-Visible spectroscopic technic.

However, the proton NMR study of copolymerization is very interesting. By the limitation of time the investigation was preliminarily studied. To obtain the reliable results, the following idea must be obtained: 1) the relaxation time of the monomers must be considered 2) the chosen internal standard should be hexamethylene disiloxane which give the signal of proton NMR spectrum at δ 0.5 ppm which does not interfere other signals of the monomers 3) the proton NMR tube must be sealed to get rid of evaporation of vinyl acetate 4) the equilibrium between gas phase and liquid phase of vinyl acetate in the seal tube should be studied.

3.7 Monomer reactivity ratios of the chlorophenyl acrylate and vinyl acetate

3.7.1 Pentachlorophenyl acrylate and vinyl acetate

When the copolymer composition has been known, the monomer reactivity ratios can, however, be considered by several methods. (1-5) One of the common methods is the linearization method developed by Fineman and Ross (see APPENDIX). In the Fineman and Ross equation f_1 and f_2 are the mole fractions of the monomer feeding,

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}r_1 \quad \text{-----(eq.1)}$$

while F_1 and F_2 are the mole fractions of the corresponding comonomer in the copolymer. Consequently, if one plots $f_1(1-2F_1)/(1-f_1)F_1$ and $f_1^2(F_1-1)/(1-f_1)^2F_1$, the straight line will be obtained with a slope of r_1 and an intercept r_2 .

As mentioned in section 2.6,3.5, the mole fraction (F_1) of PCPA in each copolymer was determined by UV-Visible spectroscopy. Thus the terms of $f_1(1-2F_1)/(1-f_1)F_1$ and $f_1^2(F_1-1)/(1-f_1)^2F_1$ were attained. In order to acquire the reliable values of the monomer reactivity ratio, the data from all the sets of experiments were obtained. The straight line was indeed obtained from the plot of $f_1(1-2F_1)/(1-f_1)F_1$ and $f_1^2(F_1-1)/(1-f_1)^2F_1$ (Figure 3.31). Its slope and intercept are 2.18 and 0.02 which are the monomer reactivity ratio of PCPA and VAc, respectively.

In order to verify the values of r_1 and r_2 , F_1 was calculated by using the following equation which was rearranged from copolymer equation. The calculated F_1 values of each copolymer were

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \text{-----(eq.2)}$$

shown in Table 3.9 . By comparison with the observed F_1 , on agreement is indeed obtained between two sets of values. This is obviously seen from the plots of both F_1 observed and F_1 calculated against f_1 as shown in Figure . As mentioned in section 2.2 , copolymerization of pentachlorophenyl acrylate with vinyl acetate has been studied by Pittman and coworkers(29). They reported that r_1 and r_2 for comonomers were 1.44 and 0.039 .These values were known , obtained using non-linear least square method developed by Tidwell and Mortimer, which was different from this work. Nevertheless, it is not usually that the monomer reactivity ratio of the same comonomer system are reported not identical, when different methods of data treatment have been used.

The data from this research could match with the literature, but r_1 and r_2 were different. It probably due to different data treatment process. The method of non linear least square is based on the variation of parameter in the equation that can fit with the observed values. It is different from the linearization method which based on simple copolymerization kinetics.

Table 3.9 Copolymerization of pentachlorophenyl acrylate (F_1) and vinyl acetate (F_2)

f_1	f_2	(conv. %)	F_{1obsd}	F_{1calcd}
first run				
0.6969	0.3031	6.7	0.8497	0.8563
0.5949	0.4051	7.1	0.8062	0.8056
0.4895	0.5105	6.4	0.7420	0.7517
0.4029	0.5971	8.5	0.7055	0.7059
0.2986	0.7014	9.6	0.6492	0.6481
0.1939	0.8061	11.6	0.5993	0.5846
0.0860	0.9140	1.9	0.5408	0.4985
0.0467	0.9533	2.0	0.5060	0.4401
second run				
0.6775	0.3225	9.0	0.7888	0.8468
0.5737	0.4263	7.7	0.7689	0.7949
0.4842	0.5158	13.5	0.7591	0.7489
0.3778	0.6222	15.2	0.7000	0.6923
0.2962	0.7038	13.5	0.6673	0.6467
0.1410	0.8590	9.2	0.6509	0.5476

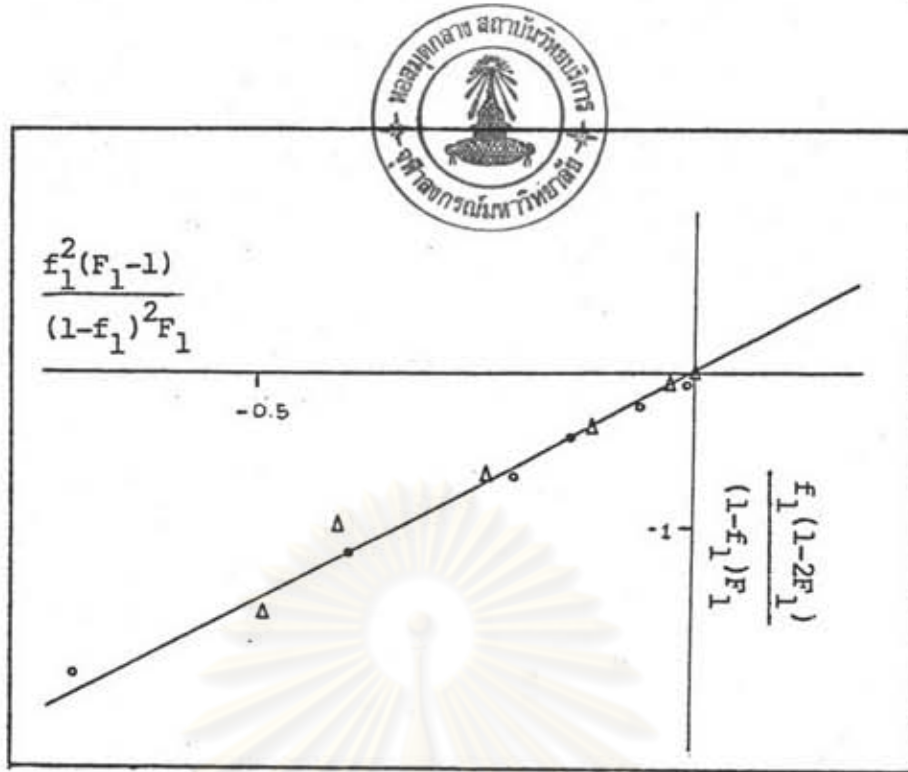


Figure 3.37 Plot of $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$ vs $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ according to equation (1), the data of PCPA-VAc

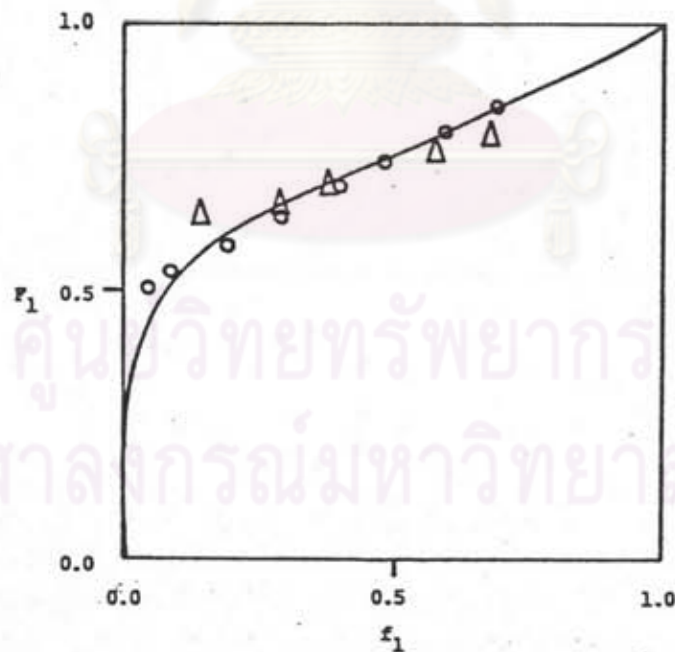


Figure 3.38 Dependence of copolymer composition F_1 on the comonomer composition f_1 : (o) observed value from the first run (Δ) observed value from the second run (-) predicted from equation (2) using $r_1 = 2.18$ and $r_2 = 0.02$ as the parameter values.

It investigates the two parameter from the average value. It was revealed from literature that r_1 and r_2 which calculate from the different method gave the different value. Cywar and coworker worked on the styrene-acrylonitrile system, they reported that the monomer reactivity ratio were 0.09 and 0.63, respectively, as determined by penultimate model. (33) Doak and coworker suggest for the same system that they were 0.40 and 0.04 with the simple copolymerization method (5).

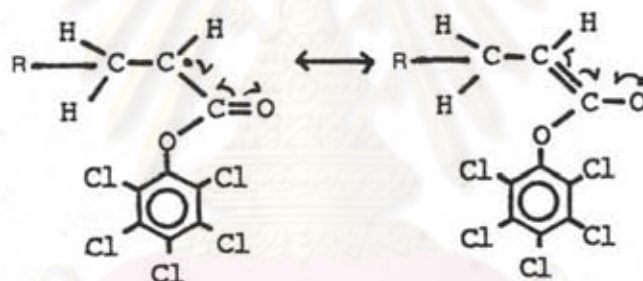
Gruber and Elias analysed several identical samples of styrene-methyl methacrylate copolymer by five different analytical methods. (Table 3.10) These results clearly show that bias in analytical procedures does exist and that it has a powerful influence on the r_1 and r_2 values. (32)

Principal causes for the inconsistencies evident in the literature on reactivity ratios are the used of either bias polymer assay procedures or a model which fail to described the copolymerization system used to create the polymer.

Table 3.10 Copolymerization reactivity ratios calculated from the data of Gruber and Elias

Assay method	r_1	r_2
C,H,O	0.52	0.46
Infrared	0.60	0.45
Ultraviolet	0.23	0.48
NMR	0.49	0.26
dn/dc	0.56	0.40

However, the evaluation of r_1 and r_2 for the PCPA-VAc system by both two methods are at least in the same trend. That is r_1 is much greater than r_2 . This implies that PCPA is more reactive than VAc toward propagating free radical species. The plausible explanation is that the free radicals of the PCPA can be stabilized by its conjugating structure. Therefore, pentachlorophenylacrylate monomer was reactive to free radical initiator.



In the case of vinyl acetate, its radical has low resonance stabilization. It is due to steric inhibition of resonance with the carbon-carbon double bond which actually occurs in vinyl acetate monomer was unreactive to free radical initiator but the free radical adduct of low resonance stabilization has high reactivity with materials that can trap free radical such as oxygen.

3.7.2. 2,4,6-Trichlorophenylacrylate and vinyl acetate

By analogy with the PCPA-VAc system, the monomer reactivity ratios of the 2,4,6-TCPA-VAc system were determined (Table 3.11). Figure 3.39 exhibits the straight line obtained by using Fineman and Ross method. It should be pointed out here that the data from two sets of experiments were used in order to attain the reliable results.

Therefore the slope and the intercept of the straight line was measured which were equal to r_1 and r_2 . Accordingly, r_1 is 0.80 and r_2 is 0.03. Figure 3.40 is the fitting between the calculated values and the observed one.

3.7.3 2,4,5-Trichlorophenylacrylate and vinyl acetate

Likewise, the monomer reactivity ratios of the 2,4,5-TCPA-VAc system were obtained as shown in Table 3.12 and Figure 3.41. In this system r_1 is 0.981 and r_2 is 0.035.

3.7.4 4-Chloro-3-methylphenyl acrylate and vinyl acetate

The monomer reactivity ratios of 4-Cl-3-MPA - VAc system were similarly obtained (Table 3.13 and Figure 3.43). In this system r_1 is 0.808 and r_2 0.01.

Table 3.11 Copolymerization of 2,4,6-trichlorophenyl acrylate (F_1) and vinyl acetate (F_2)

f_1	f_2	(conv. %)	F_{1obsd}	F_{1calcd}
first run				
0.6978	0.3022	9.7	0.7318	0.7376
0.60510	0.3949	9.8	0.6902	0.6858
0.5020	0.4980	8.7	0.6521	0.6369
0.4038	0.5962	8.5	0.6091	0.5962
0.3223	0.6777	8.8	0.5695	0.5649
0.2092	0.7908	8.1	0.4993	0.5211
0.1073	0.8927	0.8	0.4497	0.4673
0.0488	0.9512	1.0	0.4369	0.3965
second run				
0.7231	0.2769	12.5	0.7360	0.7533
0.5431	0.4569	7.9	0.6349	0.6555
0.4711	0.5289	9.2	0.6185	0.6236
0.4415	0.5585	11.0	0.5909	0.6113
0.3037	0.6963	7.9	0.5773	0.5579
0.1900	0.8100	6.5	0.5801	0.5129
0.0943	0.9057	2.0	0.4500	0.4568

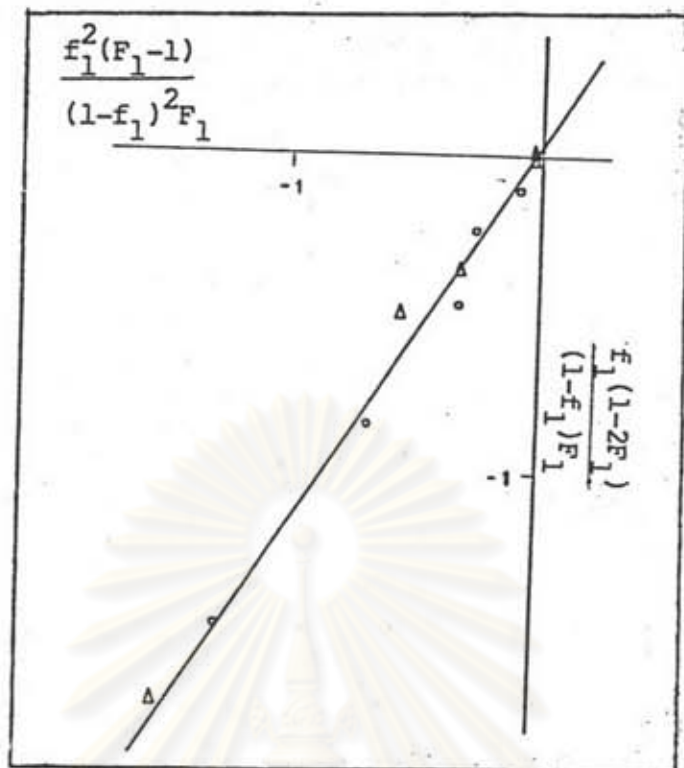


Figure 3.39 Plot of $f_1(1-2F_1) / (1-f_1)F_1$ vs $f_1^2(F_1-1)/(1-f_1)^2 F_1$ according to equation (1), the data of 2,4,6-TCPA-co-VAc

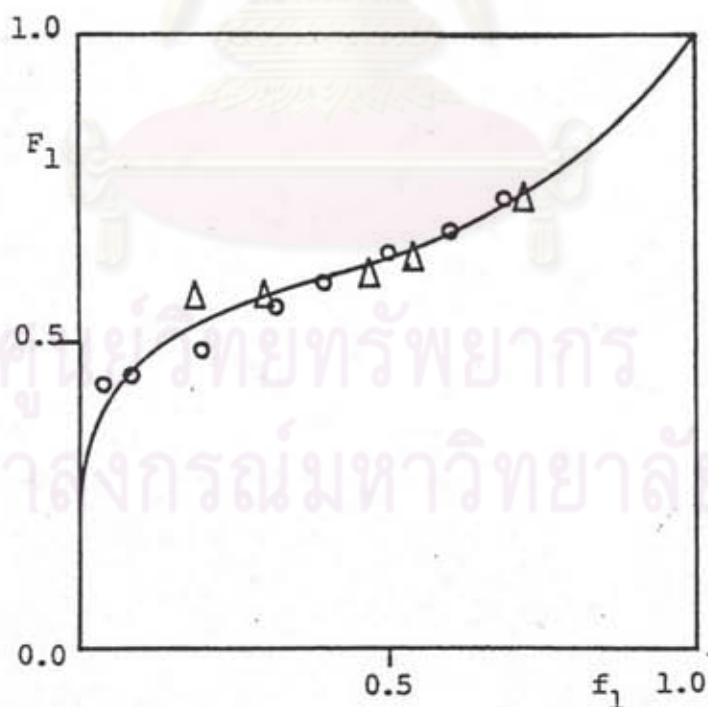


Figure 3.40 Dependence of copolymer composition (F_1) on the comonomer composition (f_1): (°) observed from the first run (Δ) observed from the second run (-) predicted from equation (2) using $r_1 = 0.80$ and $r_2 = 0.03$ as the parameter values

Table 3.12 Copolymerization of 2,4,5-trichlorophenyl acrylate (F_1) and vinyl acetate (F_2)

f_1	f_2	(conv. %)	$F_{1\text{obsd}}$	$F_{1\text{calcd}}$
first run				
0.6819	0.3181	7.9	0.7530	0.7530
0.5757	0.4243	7.8	0.7008	0.6944
0.4847	0.5153	10.6	0.6528	0.6495
0.3952	0.6048	8.4	0.6044	0.6090
0.2905	0.7095	8.4	0.5551	0.5635
0.1999	0.8001	8.5	0.5151	0.5220
0.1055	0.8945	5.9	0.4724	0.4625
0.0490	0.9510	1.2	0.4254	0.3852
second run				
0.6580	0.3420	8.2	0.7705	0.7393
0.5100	0.4900	9.4	0.6623	0.6616
0.4690	0.5310	12.2	0.6440	0.6423
0.3700	0.6300	7.67	0.6713	0.5980
0.2570	0.7430	9.87	0.5299	0.5488
0.1530	0.8470	10.1	0.5515	0.4695
0.0610	0.9390	2.4	0.4600	0.4087

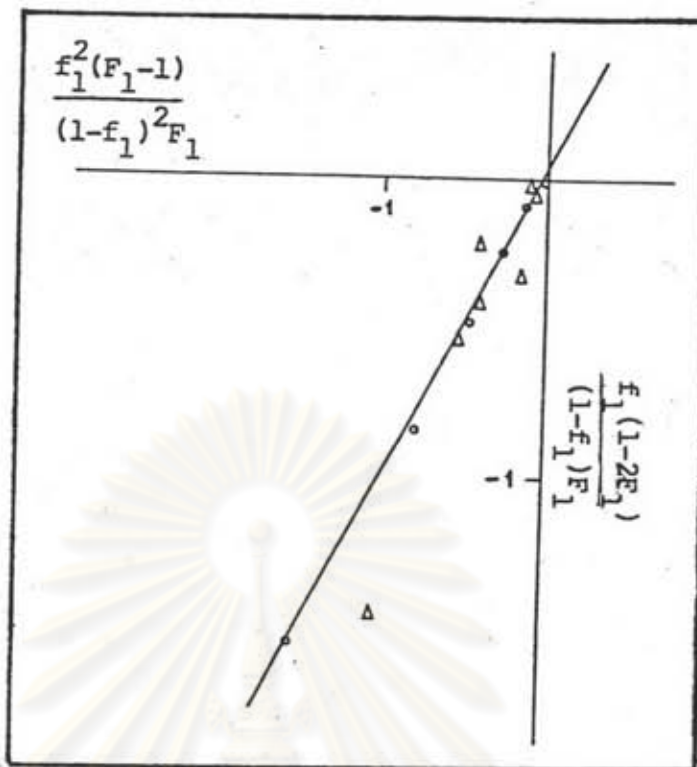


Figure 3.41 Plot of $f_1(1-2F_1) / (1-f_1)F_1$ vs $f_1^2(F_1-1)/(1-f_1)^2F_1$ according to equation (1), the data of 2,4,5-TCPA-co-VAc

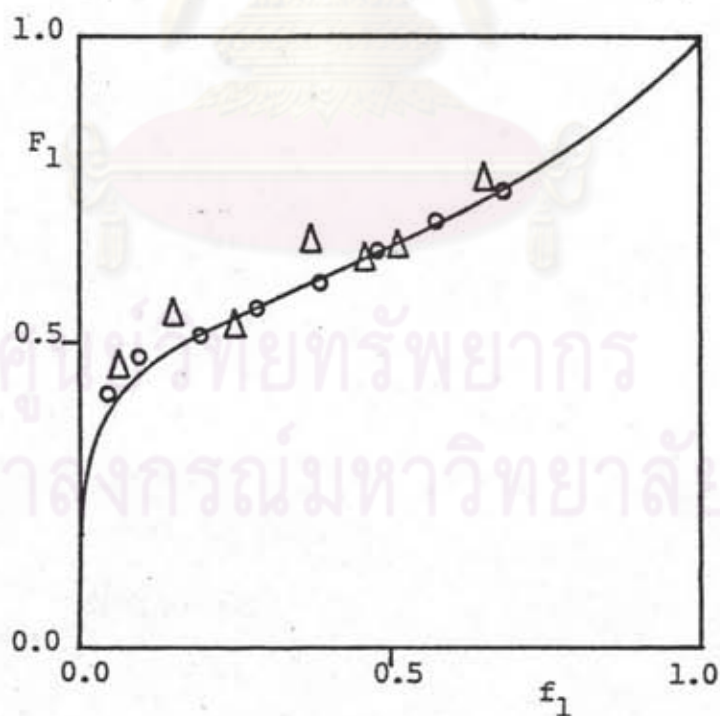


Figure 3.42 Dependence of copolymer composition (F_1) on the comonomer composition (f_1): (•) observed from the first run (▲) observed from the second run (-) predicted from equation (2) using $r_1 = 0.981$ and $r_2 = 0.035$ as the parameter values

Table 3.13 Copolymerization of 4-chloro-3-methylphenyl acrylate (F_1) and vinyl acetate (F_2)

f_1	f_2	(conv. %)	F_{1obsd}	F_{1calcd}
first run				
0.7769	0.2231	1.11	0.7810	0.7918
0.6675	0.3325	2.89	0.7335	0.7230
0.5678	0.4322	1.23	0.7138	0.6717
0.5237	0.4763	1.59	0.6811	0.6517
0.4004	0.5996	1.45	0.6406	0.6026
0.3011	0.6989	1.39	0.5749	0.5685
0.2137	0.7863	1.71	0.5375	0.5404
second run				
0.6606	0.3400	1.19	0.6983	0.7187
0.5705	0.4295	1.81	0.6230	0.6727
0.4900	0.5100	1.21	0.6046	0.6374
0.4003	0.5997	1.07	0.5570	0.6026
0.2800	0.7200	1.17	0.5710	0.5710
0.1915	0.8085	1.12	0.5674	0.5337
0.0850	0.9150	1.36	0.5073	0.4925
—				

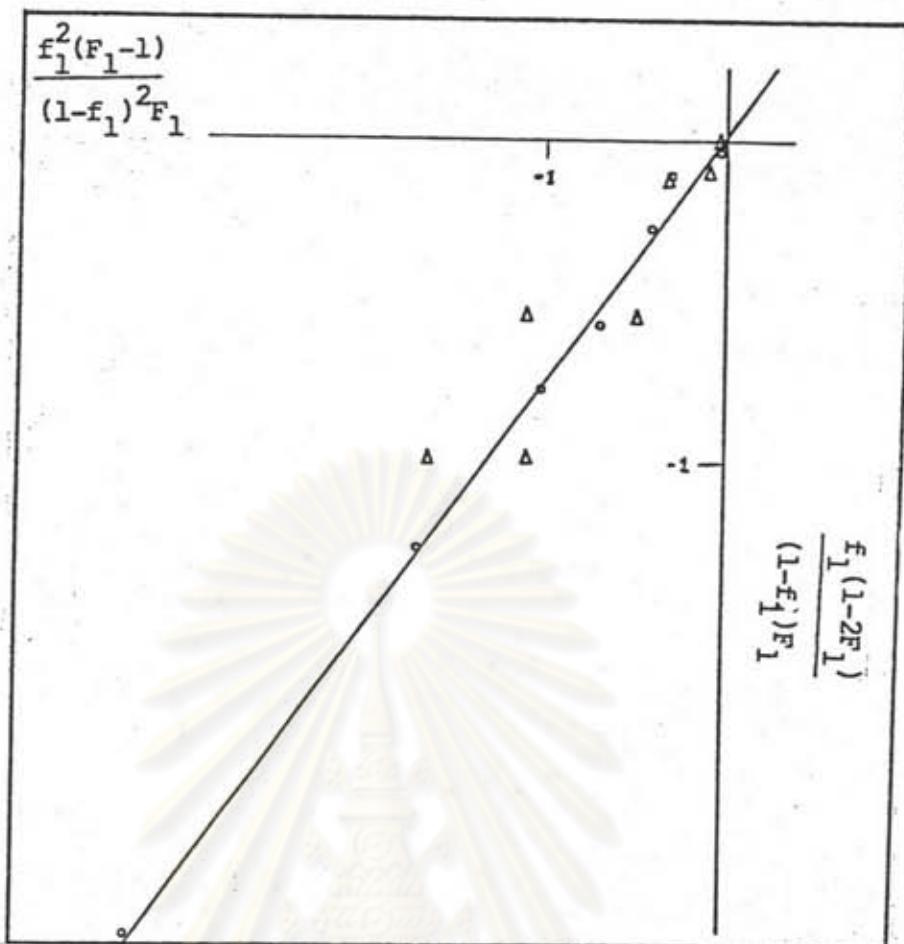


Figure 3.43 Plot of $f_1(1-2F_1) / (1-f_1)F_1$ vs $f_1^2(F_1-1)/(1-f_1)^2 F_1$ according to equation (1), the data of 4-Cl-3-MPA-co-VAc

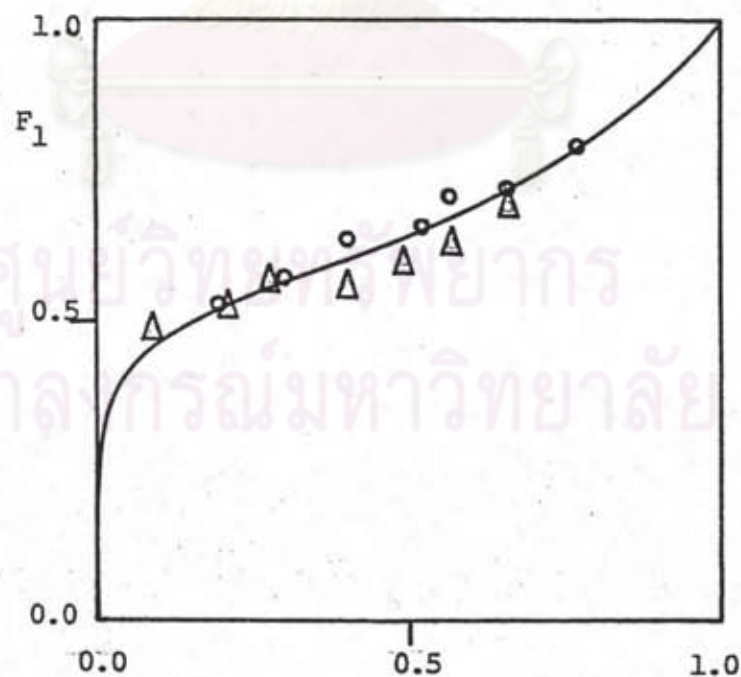


Figure 3.44 Dependence of copolymer composition (F_1) on the comonomer composition (f_1): (°) observed from the first run (Δ) observed from the second run (-) predicted from equation (2) using $r_1 = 0.808$ and $r_2 = 0.01$ as the parameter values