

During the reaction, the disappearance of the reactant and the formation of the product were monitored by thin layer chromatography in comparison with each chlorophenol. By this method, four chlorophenyl acrylates were obtained with high yield as shown in Table 3.1.

Table 3.1 The chlorophenyl acrylates

$\begin{array}{c} \text{CH}_2 = \text{CH} \\ \\ \text{C} \\ // \quad \backslash \\ \text{O} \quad \text{O-Ar} \end{array}$	Yield (%)	m.p./b.p. (°C)
$\text{Ar} = \begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{C}_6\text{H}_2 \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}, \text{PCPA}$	83	75-76(s)
$\text{Ar} = \begin{array}{c} \text{Cl} \\ \\ \text{C}_6\text{H}_3 \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array}, \text{2,4,5-TCPA}$	86	63-64(s)
$\text{Ar} = \begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{C}_6\text{H}_3 \\ \\ \text{Cl} \end{array}, \text{2,4,6-TCPA}$	91	120(dec. at 10 mmHg)
$\text{Ar} = \begin{array}{c} \text{C}_6\text{H}_4 \\ \\ \text{Cl} \end{array} \text{CH}_3, \text{4-Cl-3-MPA}$	87	120(dec. at 10 mmHg)

Pentachlorophenyl acrylate and 2,4,5-trichlorophenyl acrylate were white solid with melting points 75-76° and 63-64° C, respectively, while 2,4,6-trichlorophenyl acrylate and 4-chloro-3-methylphenyl acrylate were colour liquid with the same decomposition point at 120° C (10 mmHg). The formation of these acrylates was clearly indicated by the IR and ¹H-NMR spectra (see Appendix III) (38). It should be mentioned here that pentachlorophenyl acrylate

has been synthesized by the other research groups, different melting points, 58°C (21), 75°C (20), 78°C (38) and 82.5°C (39) were however reported.

3.2 Structural Identification of the Synthesized Chlorophenyl

Acrylates

All four chlorophenyl acrylates exhibited the similar IR absorption at ν_{\max} (cm^{-1}) : 1760-1750 (s, $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$) and 1640-1635 (m, C=C) (see Appendix III). Normally, the latter band is a characteristic peak of vinyl monomer in chain polymerization and disappears when a polymer is formed.

The $^1\text{H-NMR}$ spectra of the chlorophenyl acrylates (see Appendix III) in deuteriochloroform all showed the absorption peaks in the range at δ 6-7 (m, 3H) ppm which due to the vinylic protons. While the $^1\text{H-NMR}$ spectrum of pentachlorophenyl acrylate showed only a multiplet (δ 6.08-6.86 ppm), the $^1\text{H-NMR}$ spectra of the other chlorophenyl acrylates displayed the additional signals in the aromatic region; i.e., δ 7.34(s, 1H) and 7.55(s, 1H) for 2,4,5-trichlorophenyl acrylate, δ 7.38 (s, 2H) for 2,4,6-trichlorophenyl acrylate and δ 6.82-7.36 (m, 3H) for 4-chloro-3-methylphenyl acrylate. Moreover, the $^1\text{H-NMR}$ of 4-chloro-3-methylphenyl acrylate exhibited a singlet at δ 2.34 ppm which was assigned to the methyl protons.

These spectroscopic data are consistent with the ones reported by Miss Tongjaroensirikul (38). Accordingly, the structures of four chlorophenyl acrylates are individually confirmed.

3.3 Homopolymerization of the Chlorophenyl Acrylate Monomers

The homopolymer of each chlorophenyl acrylate monomer was prepared by solution polymerization technic. The reaction was carried out in benzene at 50°C, and benzoyl peroxide of 0.5 mole percent of the total monomer content used for polymerization of PCPA while α, α' -azobisisobutyronitrile of 0.5, 0.6 and 1.0 mole percent used for polymerization of 2,4,5-TCPA, 4-Cl-3-MPA and 2,4,6-TCPA, respectively. It was found that these conditions were good for 47-71% conversion. The product was then precipitated from benzene into hexane several times until no corresponding monomer contaminated in the homopolymer as mentioned by thin layer chromatography. Since the synthesized homopolymers will be used only as the standards for the determination of the copolymer composition, no attempt had been made on low conversion homopolymers.

The disappearance of monomer or appearance of polymer could also be followed by spectroscopic means, infrared and ultraviolet absorption spectroscopy. Therefore, after the homopolymer was dried under vacuum, the infrared spectrum of each homopolymer was recorded. Figure 3.1 to 3.4 showed the infrared spectra of the homopolymers of pentachlorophenyl acrylate, of 2,4,5-trichlorophenyl acrylate, of 2,4,6-trichlorophenyl acrylate, and of 4-chloro-3-methylphenyl acrylate, respectively. Each spectrum also confirmed that no contamination of the acrylate monomer was found in each purified homopolymer. The examination was performed by monitoring the absence of the absorption bands near 1640, 1350 and 900 cm^{-1} which corresponding to C=C stretching, CH_2 vibration and C-H stretching of the olefinic end group, respectively. Simultaneously, the vibration of the CH_2 group

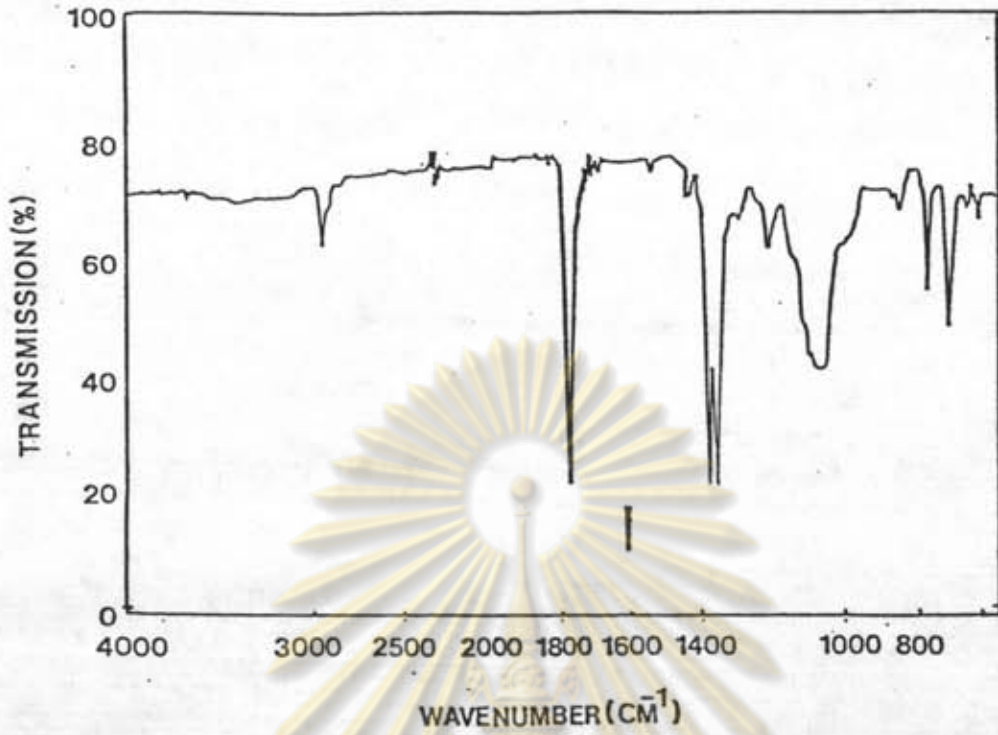


Fig. 3.1 IR spectrum of poly (PCPA)

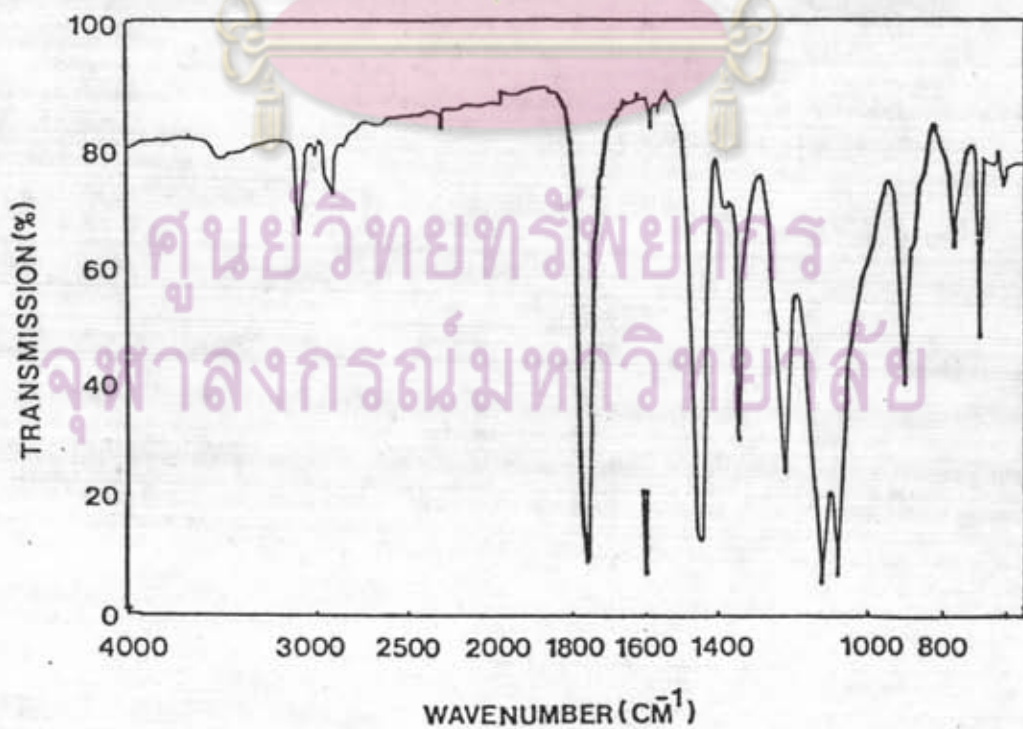


Fig. 3.2 IR spectrum of poly (2,4,5-TCPA)

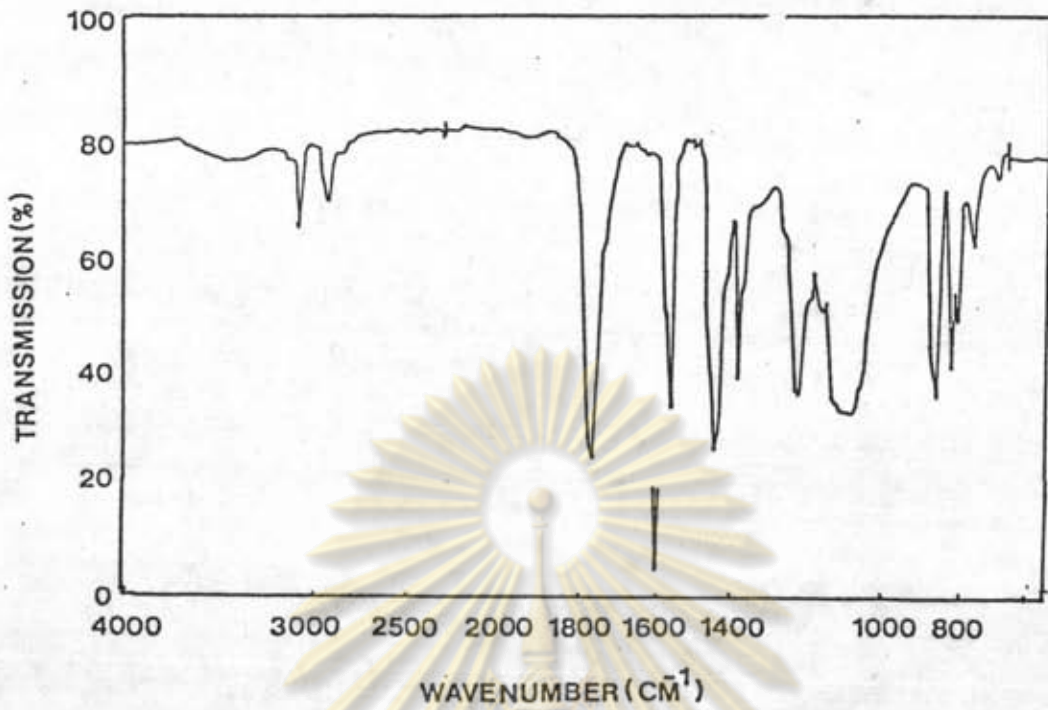


Fig. 3.3 IR spectrum of poly (2,4,5-TCPA)

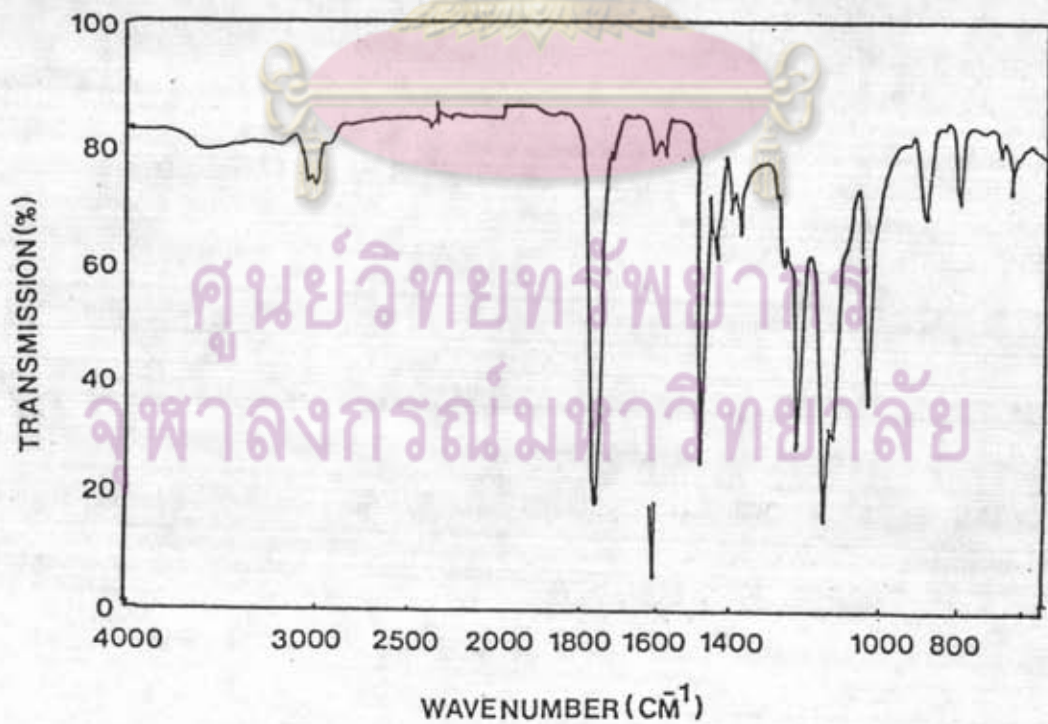


Fig. 3.4 IR spectrum of poly (4-Cl-3-MPA)

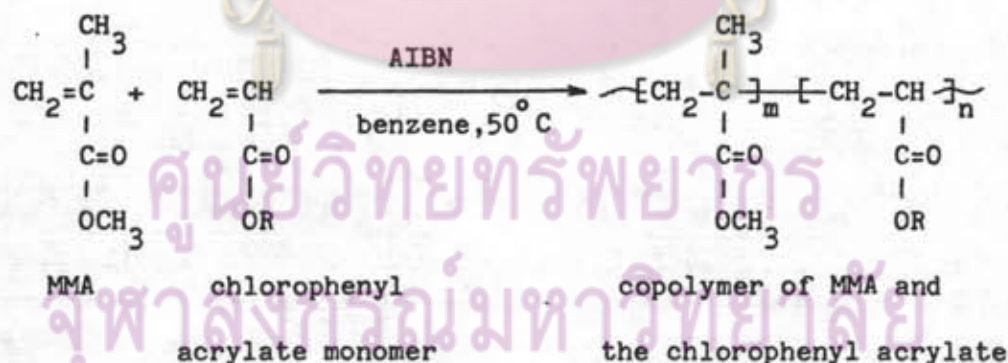
in the polymer chain appeared at 750 cm^{-1} . Such feature was a characteristic of the formation of a polymer. Consequently, the infrared spectra suggest that homopolymers of pentachlorophenyl acrylate, of 2,4,5-trichlorophenyl acrylate, of 2,4,6-trichlorophenyl acrylate and of 4-chloro-3-methylphenyl acrylate were obtained.

3.4 Copolymerization of the Chlorophenyl Acrylate and Methyl Methacrylate

3.4.1 Low-Conversion Copolymerization

The chlorophenyl acrylate was copolymerized with methyl methacrylate (MMA) at various monomer-feed compositions. Attempts to prepare the copolymer by bulk polymerization technique gave unsatisfactory results. However, by solution polymerization in benzene using α, α' -azobisisobutyronitrile (AIBN) as the initiator, each of the synthesized chlorophenyl acrylates was successfully copolymerized with methyl methacrylate (scheme 3.2).

scheme 3.2



The reaction was carried out in the same manner as for homopolymerization (50°C , AIBN 0.5 mole%). A series of each copolymer was prepared under such condition. It should be pointed out that the low degrees of conversion (less than 15 wt%) of the comonomers to the copolymer has been made to minimize errors in the use of the

differential copolymer equation. The examination of the purity and the identification of all copolymers have been performed. Figure 3.5 to 3.12 showed the infrared spectra of each copolymer. Each spectrum also confirms that no contamination of the chlorophenyl acrylate monomer was found in each purified copolymer. No absorption bands near 1640 , 1350 and 900 cm^{-1} were observed in all spectra. This, clearly, indicated the absence of the olefinic end group. Concomitantly, the band near 750 cm^{-1} is undoubtedly observed in all spectra.

Since both monomers are ester compounds, the infrared spectrum of each copolymer showed the absorption bands in the same region as that of the chlorophenyl acrylate monomer. Nevertheless, the spectrum resembles that of polymethyl methacrylate (Figure 3.13) rather than the corresponding chlorophenyl acrylate monomer.

It should be pointed out that two absorption bands appeared in the carbonyl region in the infrared spectrum of PCPA-MMA copolymer (Figure 3.5,3.6). The band at 1780 cm^{-1} was presumably due to the carbonyl stretching of PCPA unit while the band at 1730 cm^{-1} is assigned to that of MMA unit. Similarly, the infrared spectra of 2,4,5-TCPA-MMA copolymer (Figure 3.7,3.8) and 2,4,6-TCPA-MMA copolymer (Figure 3.9,3.10) showed the absorption bands at 1770 cm^{-1} and 1730 cm^{-1} which due to carbonyl stretching of 2,4,5-TCPA or 2,4,6-TCPA and MMA, respectively. For 4-Cl-3-MPA-MMA copolymer (Figure 3.11,3.12), the absorption bands in the carbonyl region were very close up. However, it could be pointed out that the band at 1740 cm^{-1} was due to carbonyl stretching of 4-Cl-3-MPA unit while at 1730 cm^{-1} was assigned to that of MMA unit.

Furthermore, it should be noticed that the peak heights at the carbonyl region of all copolymers proportionally varied with the mole fraction of the monomer feeding. For instance, Figure 3.5 revealed that poly (PCPA-co-MMA), PC-III, containing PCPA moiety was less than MMA while the peak height of each carbonyl in poly (PCPA-co-MMA), PC-V, was rather equal as seen in Figure 3.6. Indeed, the mole fractions of PCPA in the feeding were 0.3, 0.5, respectively.

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



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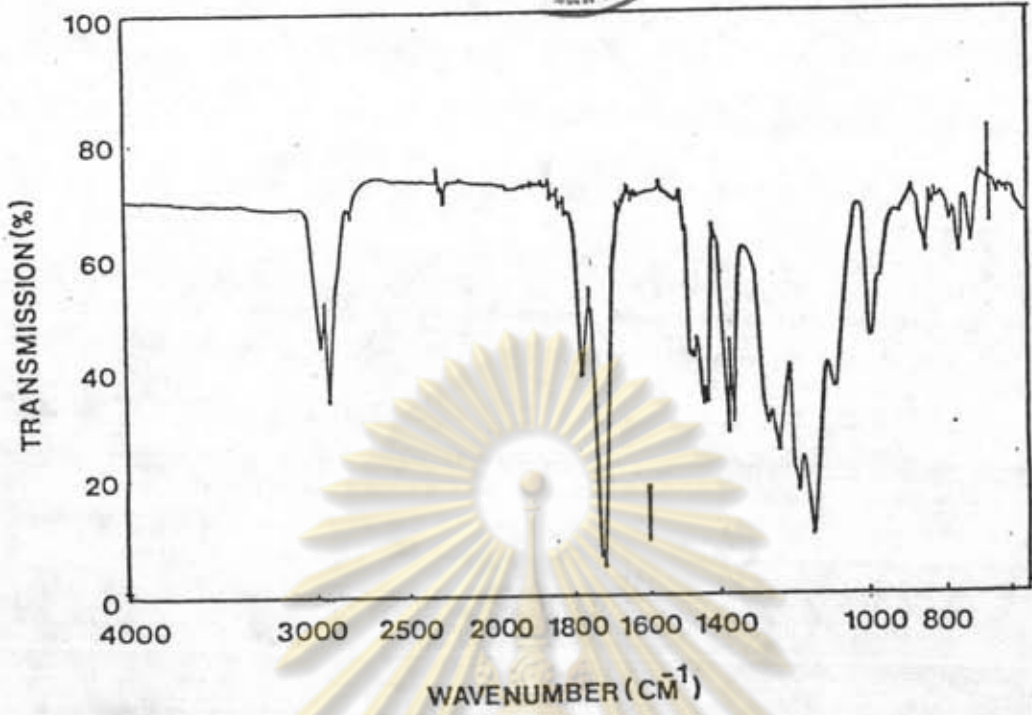


Fig. 3.5 IR spectrum of poly (PCPA-co-MMA), PC-1-I

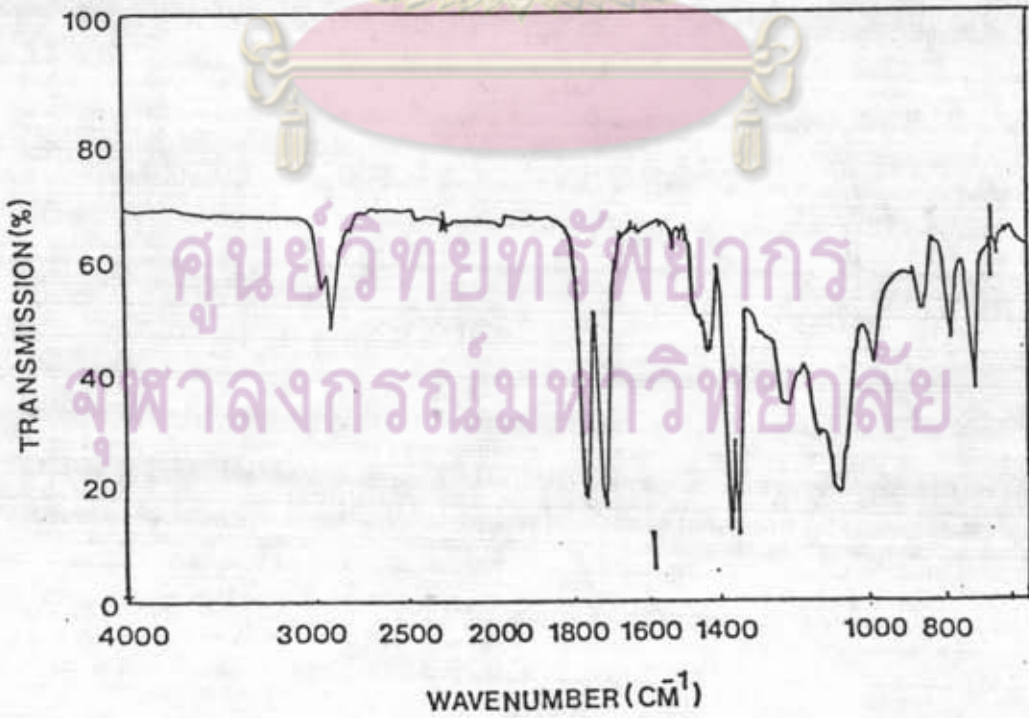


Fig. 3.6 IR spectrum of poly (PCPA-co-MMA), PC-1-V

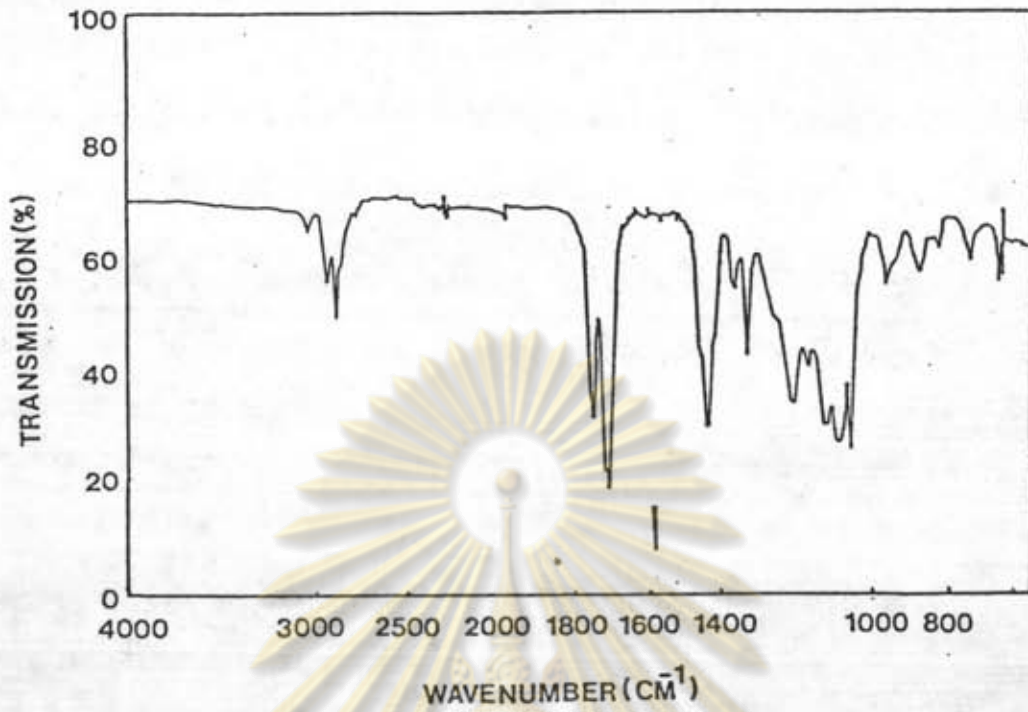


Fig. 3.7 IR spectrum of poly(2,4,5-TCPA-co-MMA), TC-1-IV

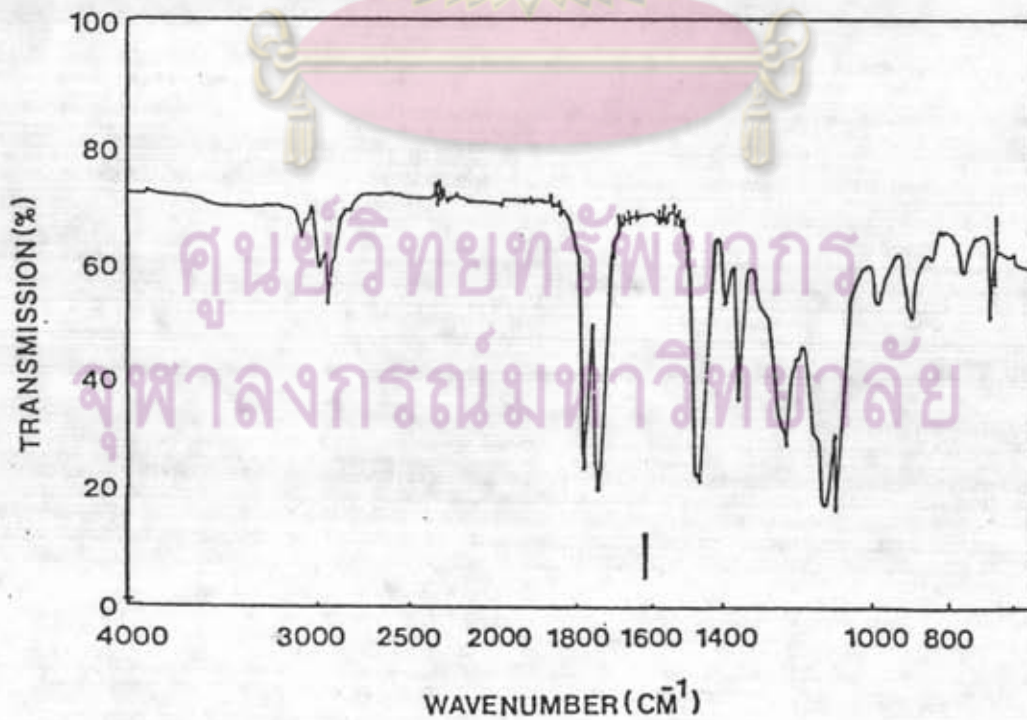


Fig. 3.8 IR spectrum of poly(2,4,5-TCPA-co-MMA), TC-1-VI .

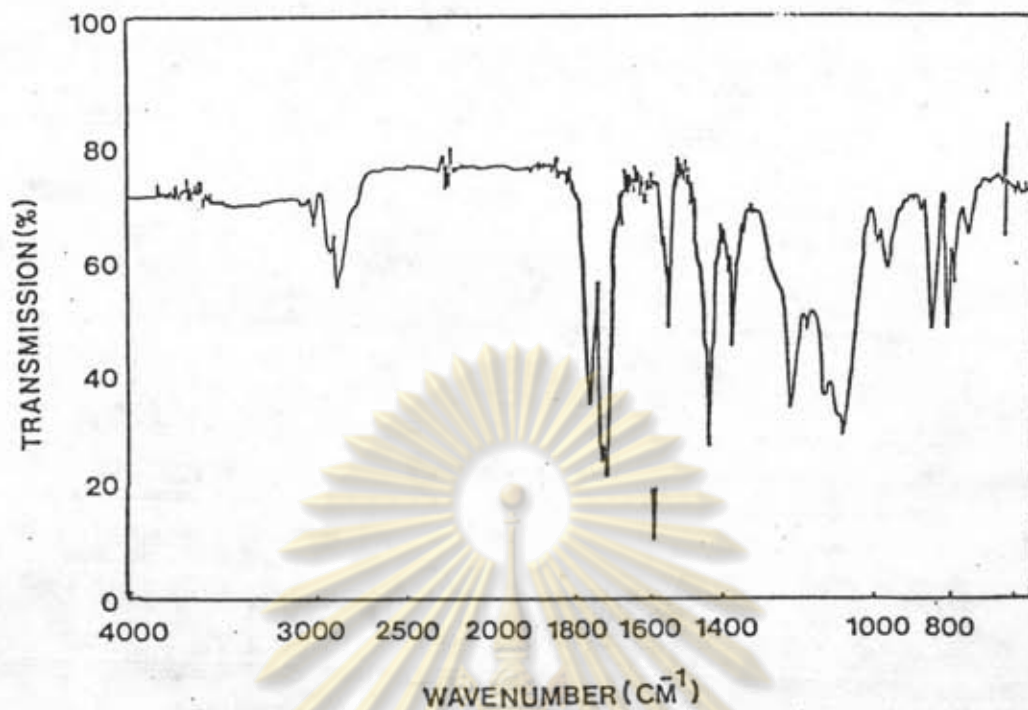


Fig. 3.9 IR spectrum of poly (2,4,6-TCPA-co-MMA) TP-1-V

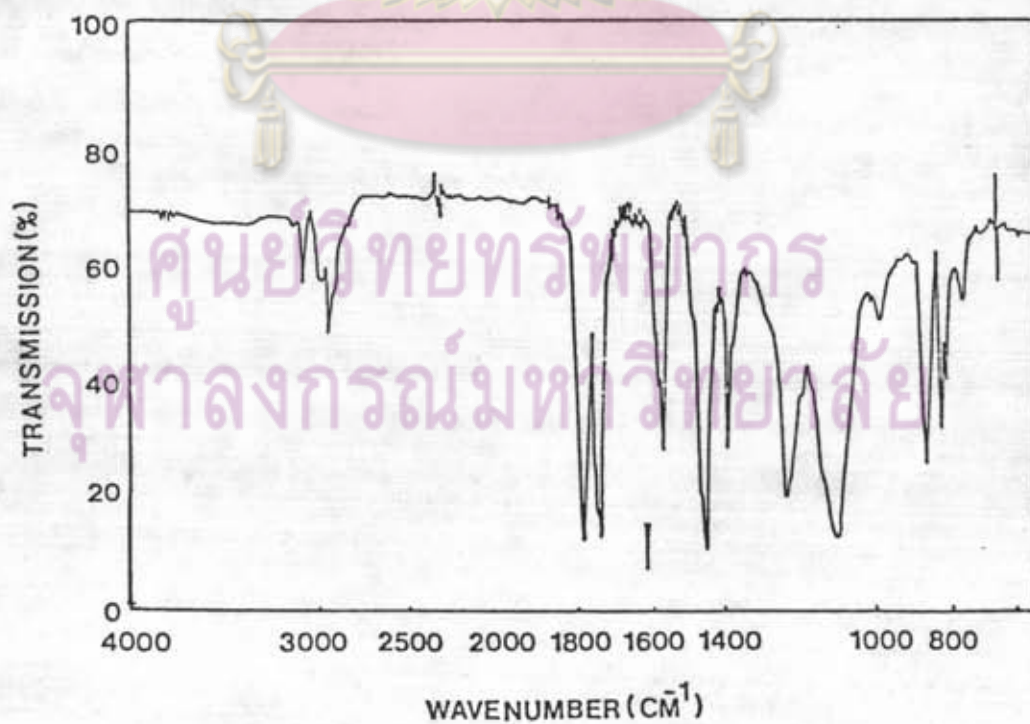


Fig. 3.10 IR spectrum of poly (2,4,6-TCPA-co-MMA) TP-1-VII

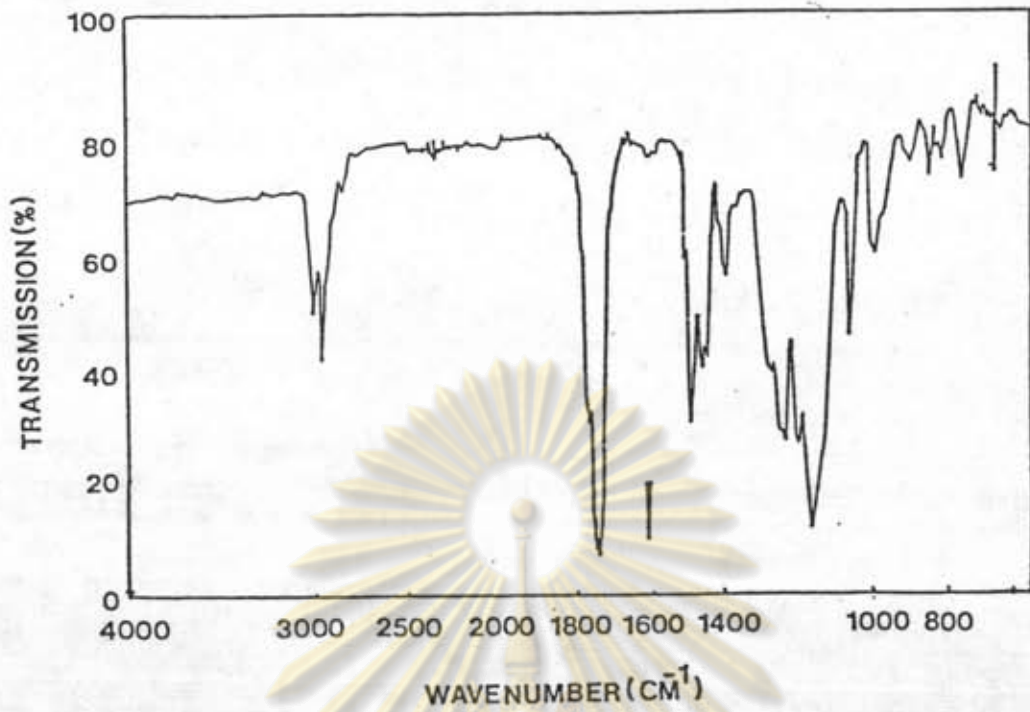


Fig. 3.11 IR spectrum of poly(4-Cl-3-MPA-co-MMA) CM-1-II

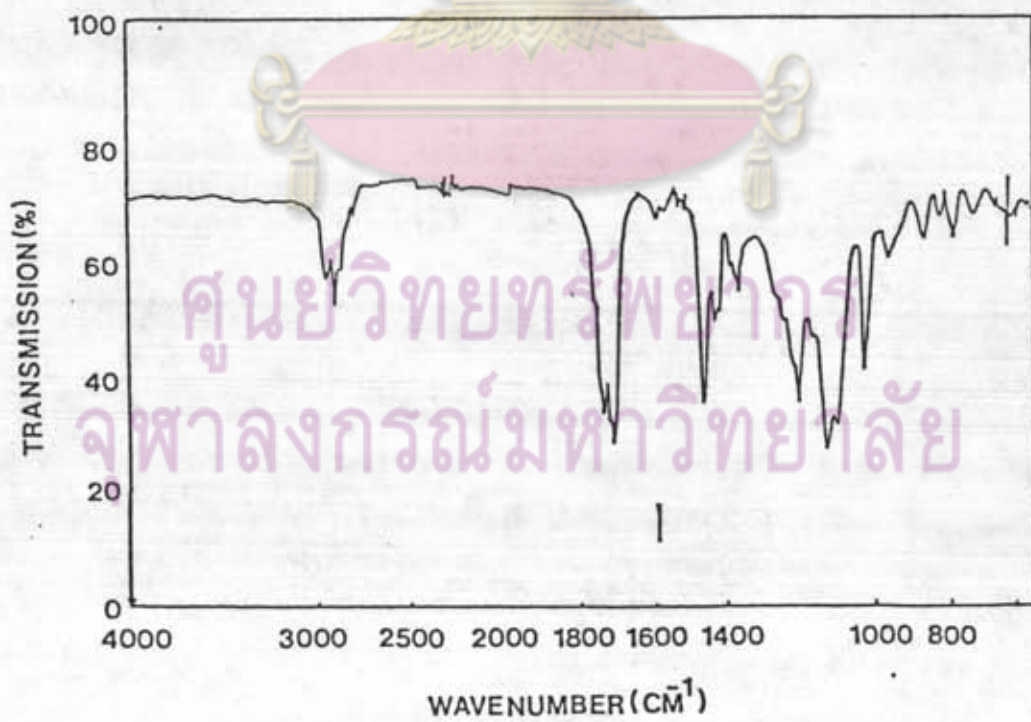
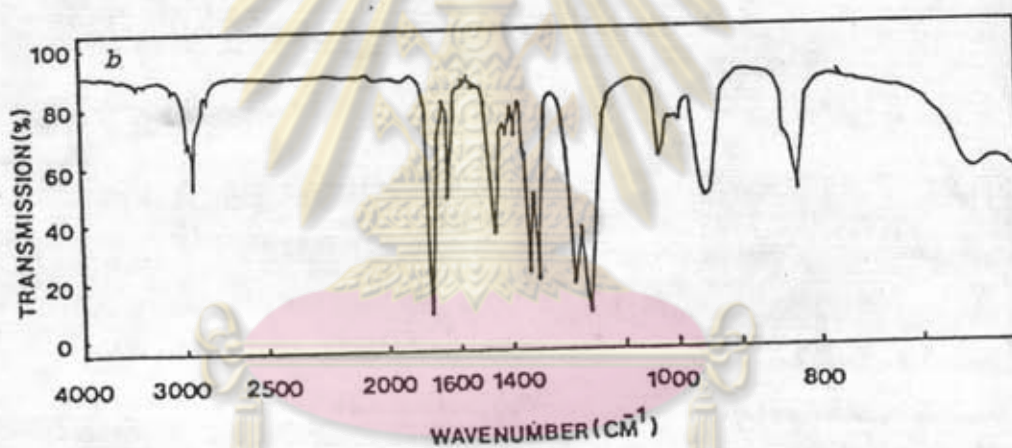
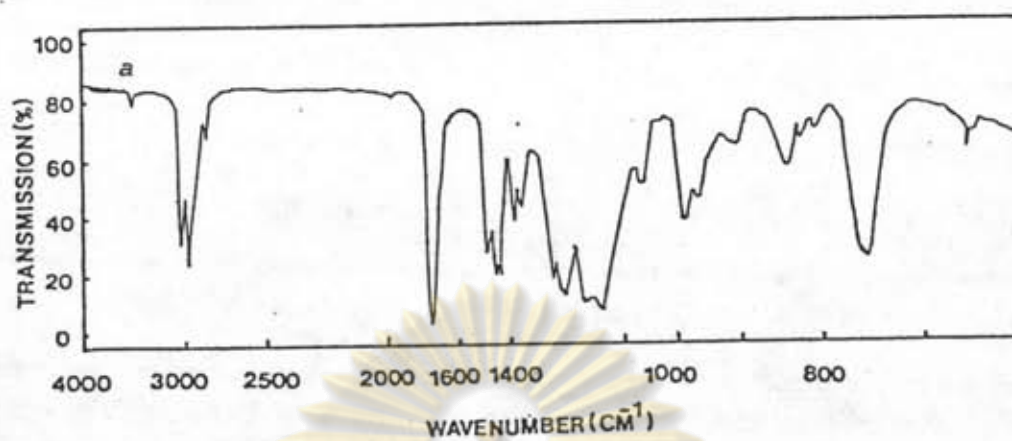


Fig. 3.12 IR spectrum of poly(4-Cl-3-MPA-co-MMA) CM-1-V



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Fig. 3.13 IR spectra of

- a) Poly (MMA)
- b) MMA

3.4.2 High-Conversion Copolymerization

The high-conversion copolymers of all four chlorophenyl acrylate monomers with methyl methacrylate were prepared in the same manner as for the low-conversion copolymerization, except much more AIBN was needed to reduce the reaction time. After the reaction was quenched, the monomer left in the solution will be determined by using quantitative gas liquid chromatographic technic. In this case, n-dodecane was used as the internal standard because its retention time is considerably different from that of all monomers which want to analyze and it does not interfere the copolymerization. After the concentration of each residual monomer was monitored, some copolymers were precipitated and their IR spectra were recorded. Indeed, the two carbonyl absorption bands and no trace of the carbon-carbon double bond stretching band were observed in either case. Accordingly, the IR spectrum of each high-conversion copolymer was considerably similar to that of the corresponding low-conversion copolymer.

3.5 Determination of Copolymer Composition

It has been known that different monomers have different tendencies to undergo copolymerization. Therefore, the composition of a copolymer in most instances is found to be different than that of the comonomer feed from which it is produces. And the copolymer composition can not be determined from a knowledge of the homopolymerization rates of the two monomers. Although there are a number of methods for analysis of copolymers, including infrared spectroscopy, elemental analysis, NMR and UV - Visible spectroscopy, all methods except UV - Visible spectroscopy are troublesome.

Attempts to analyze copolymers by using 90 MHz $^1\text{H-NMR}$ spectroscopic technic was unsuccessful. In this research work, incorporation of the fungicidal chlorophenyl acrylate monomer into the copolymer is thus investigated by using UV-Visible spectroscopic technic. However, UV-Visible spectroscopy is an attractive choice 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.

All four fungicidal chlorophenyl acrylate compounds give UV-Visible absorption bands in the range of 200-320 nm, but not methyl methacrylate. Preliminary investigations reveal that both copolymers and homopolymers show the same UV-Visible absorption pattern as the corresponding chlorophenyl acrylate monomers. The fraction of the chlorophenyl acrylate monomer in the copolymer could thus be obtained by comparison of the absorbance, at certain wavelength, of the copolymer with that of the corresponding fungicidal monomer, and even better, its homopolymer.

Since only the fungicidal chlorophenyl acrylate monomer unit absorbs the light at 241-243 nm, the absorption at the wavelength by the copolymer correlates directly with the numbers of the fungicidal monomer units in the copolymer. Therefore, the number of the fungicidal monomers incorporated into the copolymer can be obtained by comparison of the UV-Visible absorption of the copolymer with the homopolymer of the corresponding fungicidal monomers. Certainly, the concentration-absorption profiles of each homopolymer have to be

constructed.

When the absorption of a certain concentration solution of each copolymer was measured, concentration of the fungicidal monomer could be obtained from the corresponding concentration-absorption profile and subsequent calculation. Finally, mole fraction of the fungicidal monomer in the copolymer can be established.

3.5.1 Pentachlorophenyl Acrylate Unit in Methyl Methacrylate and Pentachlorophenyl Acrylate Copolymer

Polypentachlorophenyl acrylate, prepared as mentioned in section 2.3, was not dissolved in any solvent, though it was attempted to increase its solubility by raising the temperature. Pentachlorophenyl acrylate is thus chosen as a reference instead of polypentachlorophenyl acrylate because it shows the same absorption pattern of maximum absorption at 243 nm in chloroform as MMA-PCPA copolymer, Polymethyl methacrylate and methyl methacrylate, of course, do not show any absorption region above wavelength 200 nm.

As mentioned above, the number of the pentachlorophenyl acrylate monomers incorporated into the copolymer were obtained by comparison of the absorption at 243 nm of the copolymer with pentachlorophenyl acrylate monomer. The concentration-absorption profile of pentachlorophenyl acrylate standard monomer has been shown in Figure 2.1. The ultraviolet cutoff wavelength of chloroform is at 245 nm near the characteristic peak of the chlorophenyl acrylate unit. Therefore, the absorption was detected by the double beam UV-Visible spectrometer. The UV-Visible spectra of PCPA and MMA-PCPA

copolymer in chloroform were measured in the range of 200-350 nm (Figure 3.14). The concentration of the pentachlorophenyl acrylate monomer in the copolymer solution was obtained from the concentration-absorption profile of PCPA. The mole fraction of PCPA unit in copolymer was established (Table 3.2).

3.5.2 The Other Chlorophenyl Acrylate Unit in the Corresponding Copolymer

Similarly, The concentration of three chlorophenyl acrylate monomers in the corresponding copolymers was obtained from the concentration-absorption profile of their relevant homopolymer. Both 2,4,5-trichlorophenyl acrylate and 2,4,6-trichlorophenyl acrylate monomer unit show the same absorption at 241 nm, while 4-chloro-3-methylphenyl acrylate monomer unit show the absorption at 242 nm. Fortunately, the copolymers and their corresponding homopolymers show similar absorption pattern. Figure 3.15, 3.16 and 3.17 show the UV-Visible spectra of MMA - 2,4,5-TCPA copolymer, MMA - 2,4,6-TCPA copolymer and MMA - 4-Cl-3-MPA copolymer, respectively and the corresponding homopolymer as a part in the Figure. The mole fraction (F_2) of 2,4,5-TCPA, 2,4,6-TCPA and 4-Cl-3-MPA unit in the copolymers was listed in Table 3.3, 3.4 and 3.5, respectively.

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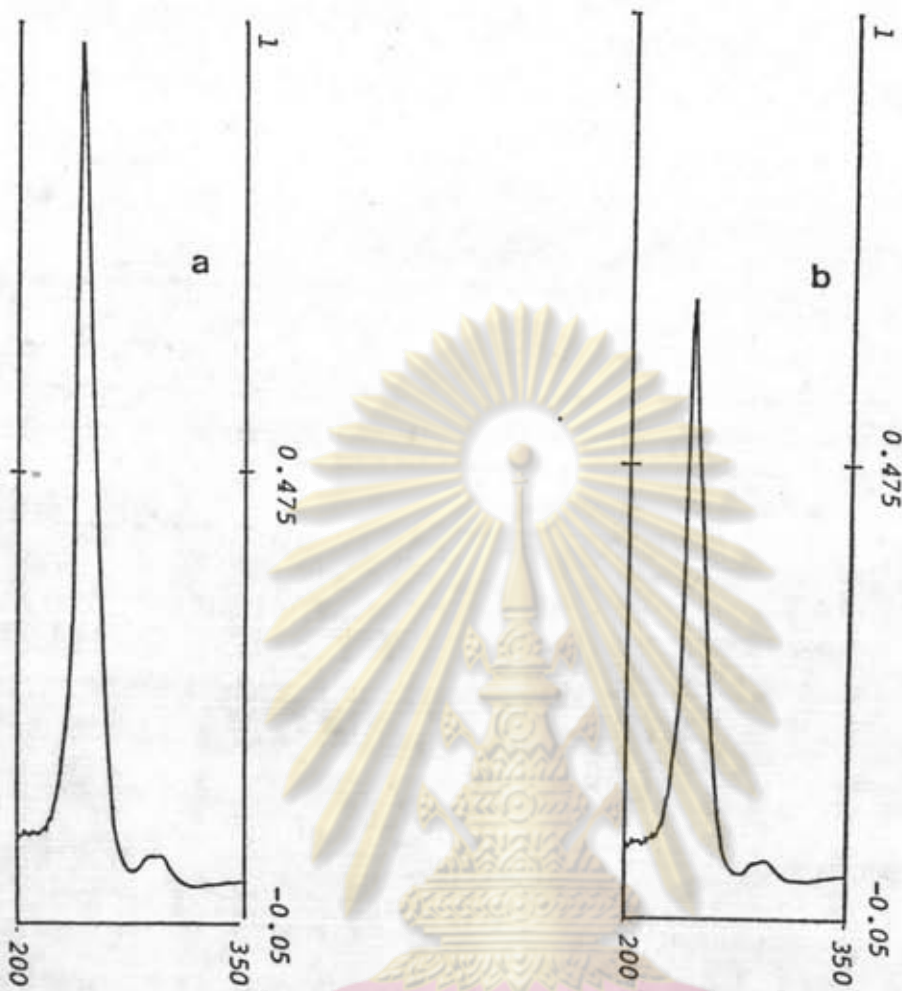
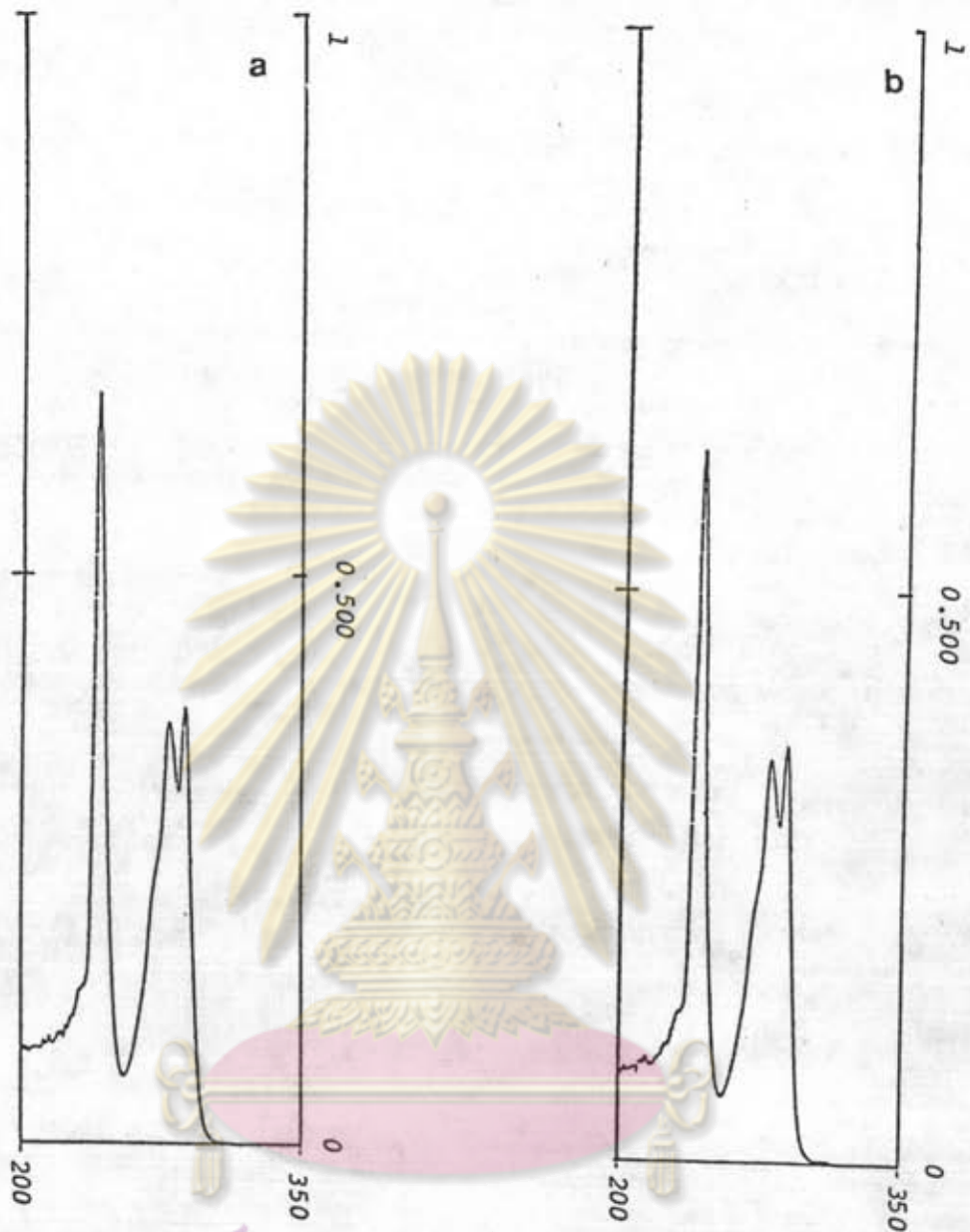


Fig. 3.14 UV-Visible spectra in chloroform of

a) PCPA

b) poly (PCPA-co-MMA)

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Fig. 3.15 UV-Visible spectra in chloroform of

a) poly (2,4,5-TCPA)

b) poly (2,4,5-TCPA-co-MMA)

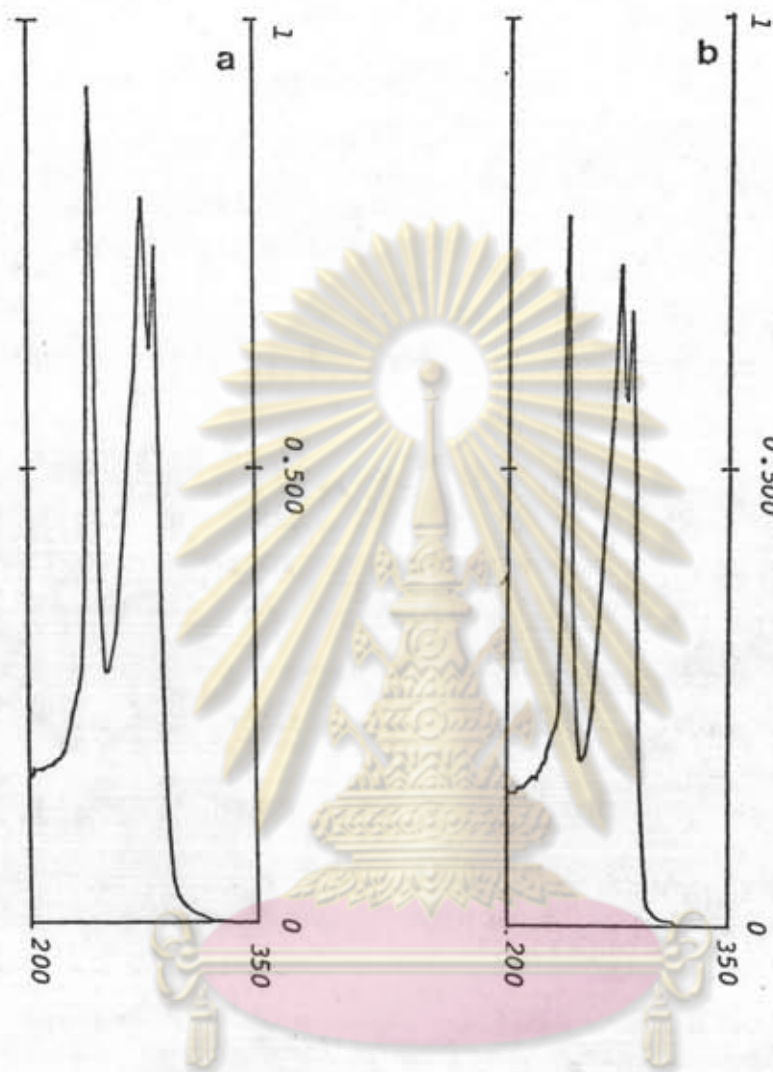
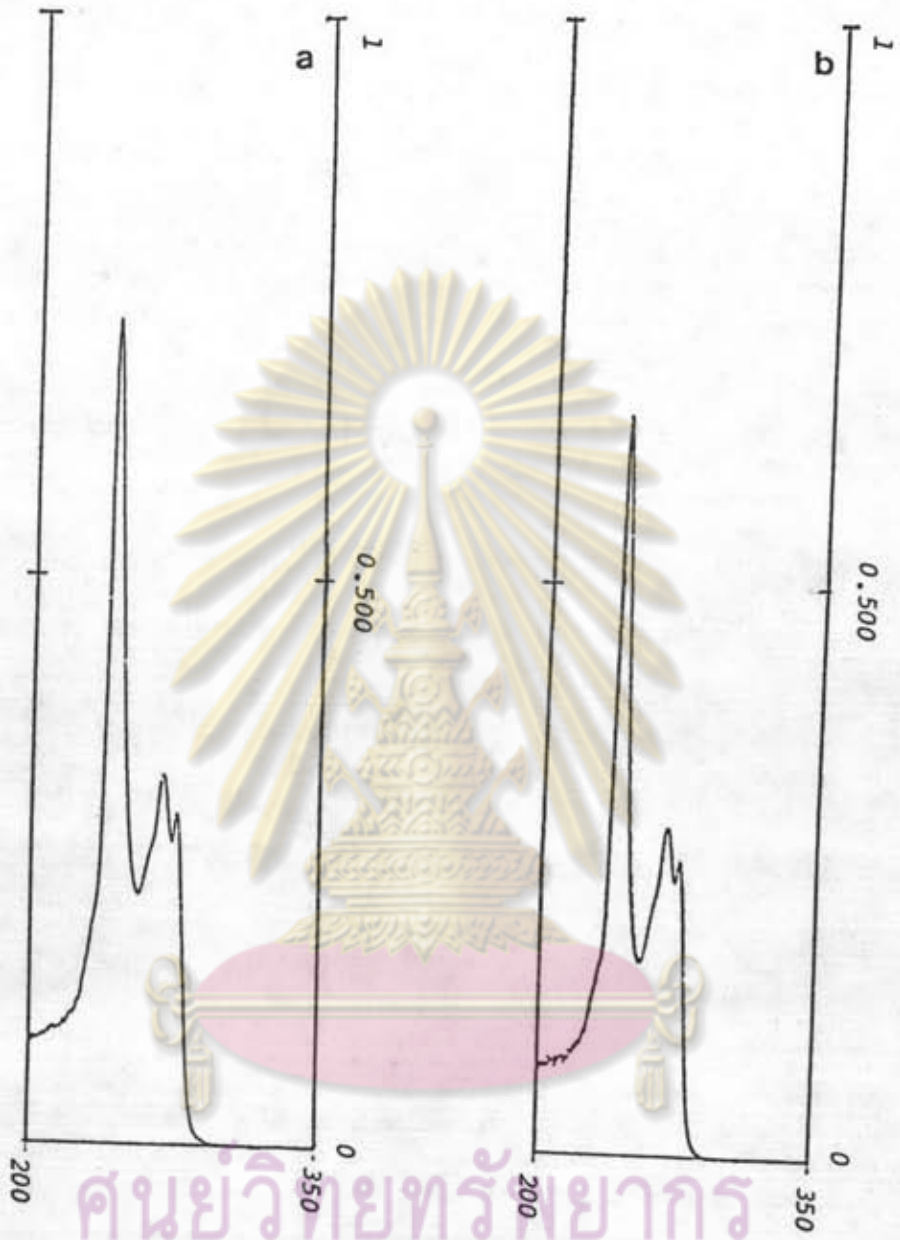


Fig. 3.16 UV-Visible spectra in chloroform of

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

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

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Fig. 3.17 UV-Visible spectra in chloroform of

a) poly (4-Cl-3-MPA)

b) poly (4-Cl-3-MPA-co-MMA)

Table 3.2 The incorporation of the PCPA monomer into the MMA-PCPA copolymer

Poly (MMA-co-PCPA)	PCPA monomer unit	
	in solution ($\times 10^{-5}$ mole/l)	in copolymer (mole%)
PC-1-I	9.9926	8.79
PC-1-II	11.7895	15.96
PC-1-III	9.2056	21.10
PC-1-IV	11.7152	27.84
PC-1-V	8.4334	27.25
PC-1-VI	9.0274	56.25
PC-1-VII	12.0568	41.09
PC-2-I	9.7402	8.67
PC-2-II	11.7152	15.82
PC-2-III	11.2549	22.03
PC-2-IV	10.3787	26.86
PC-2-V	8.3146	28.08
PC-2-VI	12.9775	55.65
PC-2-VII	13.7645	35.88

Table 3.3 The incorporation of the 2,4,5 -TCPA monomer into the MMA - 2,4,5-TCPA copolymer

Poly (MMA-co-2,4,5-TCPA)	2,4,5 -TCPA monomer unit	
	in solution ($\times 10^{-4}$ mole/l)	in copolymer (mole%)
TC-1-I	3.6444	10.92
TC-1-II	4.6574	19.30
TC-1-III	5.3140	28.18
TC-1-IV	4.8111	33.64
TC-1-V	5.0905	40.84
TC-1-VI	4.6224	51.40
TC-1-VII	5.6564	55.31
TC-2-I	4.3798	10.88
TC-2-II	3.4907	19.25
TC-2-III	4.0216	27.74
TC-2-IV	5.3210	33.41
TC-2-V	5.5935	34.28
TC-2-VI	4.3919	43.33
TC-2-VII	4.7412	53.80

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Table 3.4 The incorporation of the 2,4,6-TCPA monomer into the
MMA - 2,4,6-TCPA copolymer

Poly (MMA-co-2,4,6-TCPA)	2,4,6 -TCPA monomer unit	
	in solution ($\times 10^{-3}$ mole/l)	in copolymer (mole%)
TP-1-I	2.3886	14.14
TP-1-II	2.1584	29.67
TP-1-III	2.3945	35.91
TP-1-IV	1.6802	44.78
TP-1-V	2.2630	52.40
TP-1-VI	2.2092	55.20
TP-2-I	2.3165	14.08
TP-2-II	2.2750	29.24
TP-2-III	2.4214	35.82
TP-2-IV	2.2720	45.67
TP-2-V	2.7413	52.74
TP-2-VI	2.5679	55.89

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Table 3.5 The incorporation of the 4-Cl-3-MPA monomer into the MMA - 4-Cl-3-MPA copolymer

Poly (MMA-co-4-Cl-3-MPA)	4-Cl-3-MPA monomer unit	
	in solution ($\times 10^{-4}$ mole/l)	in copolymer (mole%)
CM-1-I	3.4124	22.72
CM-1-II	6.1768	30.28
CM-1-III	6.9391	35.98
CM-1-IV	6.3054	46.70
CM-1-V	6.6544	45.07
CM-1-VI	6.5625	49.51
CM-2-I	4.8846 ^a	22.97
CM-2-II	5.6426 ^a	30.44
CM-2-III	5.9478 ^a	36.62
CM-2-IV	6.0856 ^a	47.12
CM-2-V	7.6279	47.02
CM-2-VI	5.8592	46.01

a) calculated from equation: $\text{conc} = (9.8440\text{OABS} - 1.0710) \times 10^{-4}$ mole/l



3.6 Determination of Monomer Feed Composition

When the formation of copolymer occurred, monomers were considerably differently consumed. Consequently, the monomer feed compositions at different time are usually not the same except for the case that the degrees of conversion to copolymer are low. Several instrumentation methods, for examples, gas-liquid chromatography and $^1\text{H-NMR}$ spectroscopy, can be applied to investigate the monomer feed composition. However, preliminary $^1\text{H-NMR}$ investigation of the mixture solution of methyl methacrylate and the chlorophenyl acrylates in benzene revealed that no signals of each monomer clearly separated without interference to each other. For this reason, $^1\text{H-NMR}$ spectroscopy is not suitable to this work. Thus gas-liquid chromatography is preferred to $^1\text{H-NMR}$ spectroscopy and applied to this research.

Preliminary quantitative GLC investigation of the copolymerization solution has been attempted at various conditions, i.e., temperature, time and carrier gas flow rate to achieve the optimum condition to use in this work. A good resolution of each peak was found from the following condition: column, 10%SE-30; carrier gas, nitrogen; flow rate, 30ml/min; column temperature, 40°C (4 min) to 230°C in 16 min; detector mode, FID, 230°C ; injection mode, 1 μl 230°C . The analytical system was calibrated by reference samples of the pure monomers, i.e., methyl methacrylate and the corresponding fungicidal chlorophenyl acrylate, and the internal standard compound, n-dodecane. Each mixture solution is composed of benzene, MMA, n-dodecane and the chlorophenyl acrylate. A series of each monomer solution was investigated under such condition.

Table 3.6 shows the retention time of each compound. It has been known that the retention time of each compound depended on its boiling point and polarity. In fact, it was found that the more molecular weight of compounds give the more retention time. The chromatogram of each monomer solution showed the same pattern. The number of methyl methacrylate and the chlorophenyl acrylate monomer residues can be obtained by comparison of the peak area of the certain monomer with that of the relevant standard monomer. Certainly, the concentration-peak area profile of each standard monomer have to be constructed. By using the internal standard method, therefore the peak area was referred to the ratio of peak area of each monomer and n-dodecane.

Table 3.6 Retention time

Compound	retention time (min)
Benzene	2.95
MMA	4.42
PCPA	17.52
2,4,5,-TCPA	15.03
2,4,6,-TCPA	14.60
4-Cl-3-MPA	13.76
n-dodecane	11.75

When the peak area of each monomer solution was monitored, concentration of MMA and the chlorophenyl acrylate monomer could be

attained from the corresponding concentration-peak area profile. Finally, the degree of total conversion of monomers to copolymers could be established from the following equation:

$$\% \text{conversion} = \frac{[M_1]_0 - [M_1] + [M_2]_0 - [M_2]}{[M_1]_0 + [M_2]_0}$$

3.6.1 The Chlorophenyl Acrylate and Methyl Methacrylate

Figure 3.18-3.21 showed analysis of monomer feed composition in the following system, i.e., MMA-PCPA, MMA-2,4,5-TCPA, MMA-2,4,6-TCPA and MMA-4-Cl-3-MPA, respectively. Subsequently, the concentration of each monomer was summarized in Table 3.7-3.10 in the same order where $[M_1]_0, [M_2]_0$ and $[M_1], [M_2]$ are the molar concentration of methyl methacrylate (M_1) and the chlorophenyl acrylate (M_2) at before and after copolymerization, respectively.

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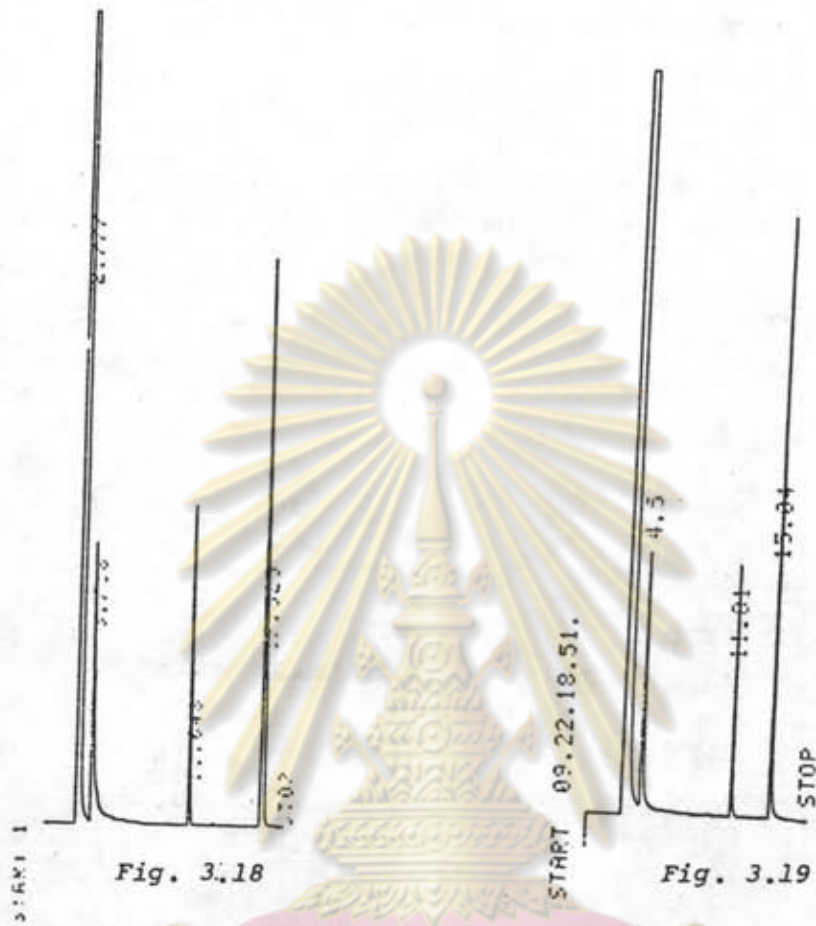


Fig. 3.18 Chromatogram of analysis of the PCPA-MMA

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copolymerization in benzene

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Fig. 3.19 Chromatogram of analysis of the 2,4,5-TCPA-MMA

copolymerization in benzene

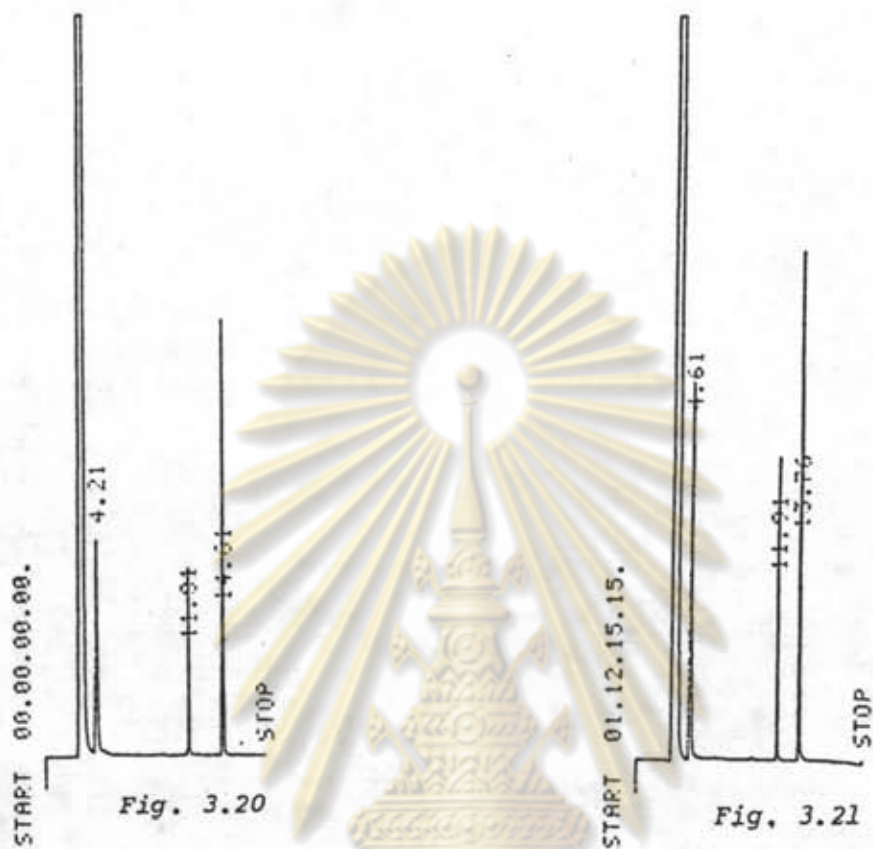


Fig. 3.20 Chromatogram of analysis of the 2,4,6-TCPA-MMA copolymerization in benzene

Fig. 3.21 Chromatogram of analysis of the 4-Cl-3-MPA-MMA copolymerization in benzene

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Table 3.7 Monomer feed compositions of the copolymerization^a of methyl methacrylate (M_1) and pentachlorophenyl acrylate (M_2)

	$[M_1]_0$	$[M_2]_0$	TIME(hr)	$[M_1]$	$[M_2]$	CONV (%)
I-5	1.0352	0.0622	12.00	0.7648	0.0461	26.11
II-5	1.0352	0.0622	13.30	0.5849	0.0377	43.27
III-15	0.8449	0.1101	11.00	0.5763	0.0758	31.60
IV-18	0.6745	0.1518	9.05	0.3876	0.0954	40.28
V-50	0.4218	0.4700	10.00	0.2298	0.3535	34.59
VI-50	0.4218	0.4700	11.00	0.2091	0.3447	37.90

a) each run was initiated with 1 mole% AIBN

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Table 3.8 Monomer feed compositions of the copolymerization^a of methyl methacrylate (M_1) and 2,4,5-trichlorophenyl acrylate (M_2)

	$[M_1]_0$	$[M_2]_0$	TIME(hr)	$[M_1]$	$[M_2]$	CONV(%)
I-6	0.8118	0.0534	8.00	0.5417	0.0339	33.73
II-9	1.0437	0.1033	8.00	0.6717	0.0645	35.82
III-40	0.5738	0.4032	6.00	0.3077	0.2313	27.21
IV-60	0.4370	0.5856	6.00	0.1931	0.3270	49.14
V-65	0.2999	0.5811	6.00	0.1486	0.3727	40.83

a) each run was initiated with 1 mole% AIBN

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Table 3.9 Monomer feed compositions of the copolymerization^a of methyl methacrylate (M_1) and 2,4,6-trichlorophenyl acrylate (M_2)

	$[M_1]_0$	$[M_2]_0$	TIME(hr)	$[M_1]$	$[M_2]$	CONV(%)
I-10	1.1385	0.1127	13.00	1.0356	0.0993	9.29
II-10	1.1385	0.1127	14.00	0.9664	0.0913	15.46
III-50	0.2887	0.3297	10.00	0.1026	0.2052	50.25
IV-50	0.2887	0.3297	11.00	0.0803	0.1551	61.93
V-80	0.1253	0.4335	9.00	0.0649	0.3265	29.95

a) each run was initiated with 0.7 mole% AIBN

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Table 3.10 Monomer feed compositions of the copolymerization^a of methyl methacrylate (M_1) and 4-chloro-3-methyl-phenyl acrylate (M_2)

	$[M_1]_0$	$[M_2]_0$	TIME(hr)	$[M_1]$	$[M_2]$	CONV(%)
I-10	0.9488	0.0939	10.00	0.5830	0.0493	35.82
II-10	0.8682	0.0995	7.30	0.7013	0.0778	19.69
III-30	0.6745	0.2800	7.30	0.5005	0.2082	25.73
IV-40	0.4803	0.3884	9.30	0.2789	0.2331	40.73
V-80	0.2242	0.7756	9.30	0.0467	0.3777	57.53

a) each run was initiated with 0.7 mole% AIBN

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3.7 Evaluation of Monomer Reactivity Ratio of the Chlorophenyl Acrylate and Methyl Methacrylate

3.7.1 The Fineman - Ross Method

When the copolymer composition has been known, the monomer reactivity ratios can then be evaluated. Among several methods (1,4,40), the linearization method developed by Fineman and Ross is the most common one for low conversion copolymerization (see Appendix I), which was chosen to be applied to this work as well. In the Fineman and Ross method, the reactivity ratios r_1 and r_2 for the monomer pair M_1 and M_2 can be determined by using the following equation:

$$f(F-1)/F = r_1(f^2/F) - r_2$$

where f and F are the ratios of the mole fractions of monomer M_1 and M_2 in feeding and copolymer, respectively. Consequently, if one plots $f(F-1)/F$ and f^2/F , the straight line will be obtained with the slope of r_1 and the intercept of $-r_2$. The errors involved in the reactivity ratio values were derived from the standard deviations in the slope and intercept of the straight line.

3.7.1.1 Pentachlorophenyl Acrylate and Methyl

Methacrylate

As mentioned in section 2.5 and 3.5, the mole fraction of PCPA unit in each of eight copolymers was determined by ultraviolet-visible spectroscopy. Thus the terms of $f(F-1)/F$ and f^2/F were attained (Table 3.11). Then the plot of $f(F-1)/F$ and f^2/F led to the straight line (Figure 3.22). From the slope and the intercept of this straight line, monomer reactivity

ratios of the MMA(M_1)-PCPA(M_2) copolymer were obtained, i.e., $r_1 = 1.07 \pm 0.03$ and $r_2 = 0.08 \pm 0.11$.

It has been known that the reactivity of a monomer toward a radical depends on the reactivities of both the monomer and the radical. The MMA reactivity ratio (r_1) revealed that the value of the rate constant k_{11} closed up to k_{12} . So, the MMA radical had a similar reactivity tendency toward its own and the other monomer (PCPA). This could be concluded that methyl methacrylate monomer can form both homopolymer and copolymer in the same rate. However, in the copolymerization, the reactivity of the monomer pair (PCPA; r_2) is essential to be considered as mentioned above. The value of PCPA reactivity (r_2) indicated that the rate constant k_{22} is much less than k_{21} . A decrease in PCPA radical reactivity toward its own monomer is probably due to the steric hindrance of the chlorophenyl pendant group between it and its radical to which it is adding. Thus the PCPA propagating species preferentially added the other monomer, MMA. Although methyl methacrylate and pentachlorophenyl acrylate radical chain ends appear to have tendency toward alternation which was supported by the $r_1 r_2$ product, 0.08, methyl methacrylate monomer is preferentially incorporated into propagating copolymer chain. Therefore, the copolymer will contain a larger proportion of MMA monomer.

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 the copolymer equation.

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)$$

The calculated F_1 values of each copolymer were listed in Table 3.12. Figure 3.23 showed the copolymer composition as a function of methyl methacrylate in the feeding based on the experimentally determined reactivity ratios in the copolymerization of methyl methacrylate and pentachlorophenyl acrylate. The curve illustrates an interesting characteristic of copolymerization with a tendency toward alternation. Most experimental values (F_1 obsd) fit well to the theoretical curve (F_1 calcd) with $r_1 = 1.07$ and $r_2 = 0.08$, while some observed F_1 values (*) show a drift from the calculated. This observation may be due to a shift in the monomer feed ratio as the degrees of conversion to copolymer increase but the Fineman and Ross equation requires a constant composition of the relevant monomer feed.

Roman et al. (41) reported the reactivity ratios of 2-chlorophenyl acrylate-methyl methacrylate copolymer and that of 4-chlorophenyl acrylate-methyl methacrylate copolymer, i.e., $r_{2-Cl-PA} = 0.42 \pm 0.02$, $r_{MMA} = 1.30 \pm 0.05$, and $r_{4-Cl-PA} = 0.30 \pm 0.04$, $r_{MMA} = 1.08 \pm 0.05$, respectively. The reactivity ratios of ethyl acrylate (M_1) and PCPA copolymer were $r_1 = 0.88 \pm 0.19$ and $r_2 = 0.21 \pm 0.06$ reported by Pittman et al. (20). In three cases, the reactivity ratios show that both methyl methacrylate and ethyl acrylate have same tendency to continue the chain more easily than the chlorophenyl acrylate which corresponded with the reactivity ratios of MMA-PCPA copolymer in this study.

3.7.1.2 2,4,5-Trichlorophenyl Acrylate and Methyl Methacrylate

As mentioned in section 2.5 and 3.5, the

incorporation of the chlorophenyl acrylate monomer into the polymer of each of MMA-2,4,5-TCPA copolymer was determined by using UV-Visible spectroscopic technic. Therefore, the terms of $f(F-1)/F$ and f^2/F were attained (Table 3.13). The Fineman-Ross plot between $f(F-1)/F$ and f^2/F (Figure 3.24) gave $r_1 = 0.84 \pm 0.11$ and $r_2 = 0.36 \pm 0.05$. The reactivity ratios showed that each monomer preferred to cross-propagate, thus the copolymer would exhibit a tendency to alternate as well as that of MMA-PCPA copolymer. But $r_1 r_2 (0.27)$ of MMA-2,4,5-TCPA copolymer greater than that of MMA-PCPA copolymer, thus the alternation tendency in MMA-2,4,5-TCPA copolymer is smaller than that in MMA-PCPA copolymer. In this sense, the copolymerization will be intermediate between alternating and random. Comparison of the experimentally observed and the calculated F_1 value (Table 3.14) was done to verify the obtained values of r_1 and r_2 . For this case, the values of r_1 and r_2 are less than unity the F_1 versus f_1 curve (Figure 3.25) crosses the line representing $F_1 = f_1$ (the diagonal line). At this intersection or crossover point the copolymer and feed composition are the same and copolymerization occurs without a change in the feed composition.

3.7.1.3 2,4,6-Trichlorophenyl Acrylate and Methyl Methacrylate

Similarly, the reactivity ratios of this system were calculated (Table 3.15 and Figure 3.26). The reactivity ratios of MMA(M_1)-2,4,6-TCPA copolymer, r_1 is 0.58 ± 0.01 and r_2 is 0.20 ± 0.05 . Certainly, the calculated F_1 values were determined, then compared with the observed F_1 values to verify the value of r_1 and r_2 (Table 3.16). Moreover, the copolymer composition curve (Figure 3.27) showed the same characteristic as that of MMA-2,4,5-

TCPA copolymer.

3.7.1.4 4-Chloro-3-Methylphenyl Acrylate and Methyl Methacrylate

The reactivity ratios of MMA(M_1)-4-Cl-3-MPA copolymer were calculated in the same manner as shown in Table 3.17 and Figure 3.28. It was found that $r_1 = 0.67 \pm 0.02$ and $r_2 = 0.33 \pm 0.02$. Similarly, the F_1 values were calculated by using the obtained r_1 and r_2 and listed in Table 3.18. Figure 3.29 showed the plot of F_1 versus f_1 .

The reactivity ratios of all four copolymer systems lead to deduction that all four copolymer systems shows the small tendency towards alternation of monomeric units and methyl methacrylate trends to continue the chain more easily than chlorophenyl acrylate.



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Table 3.11 Variables for the evaluation of the reactivity ratios of the MMA-PCPA copolymer by the Fineman-Ross method

mole ratio		f^2/F	$f(F-1)/F$
in feed, f	in copolymer, F		
8.9273	10.3885	7.6717	8.0679
4.0079	5.2668	3.0499	3.2469
2.3515	3.7388	1.4790	1.7226
1.5007	2.5923	0.8688	0.9218
1.0078	2.6692	0.3805	0.6302
0.6719	0.7779	0.5803	-0.1918
0.4356	1.4339	0.1323	0.1318
9.0229	10.5358	7.7271	8.1665
4.0087	5.3205	3.0203	3.2552
2.3165	3.5393	1.5161	1.6619
1.5045	2.7229	0.8313	0.9519
1.0104	2.5609	0.3986	0.6158
0.6719	0.7969	0.5664	-0.1711
0.4352	1.7872	0.1059	0.1917

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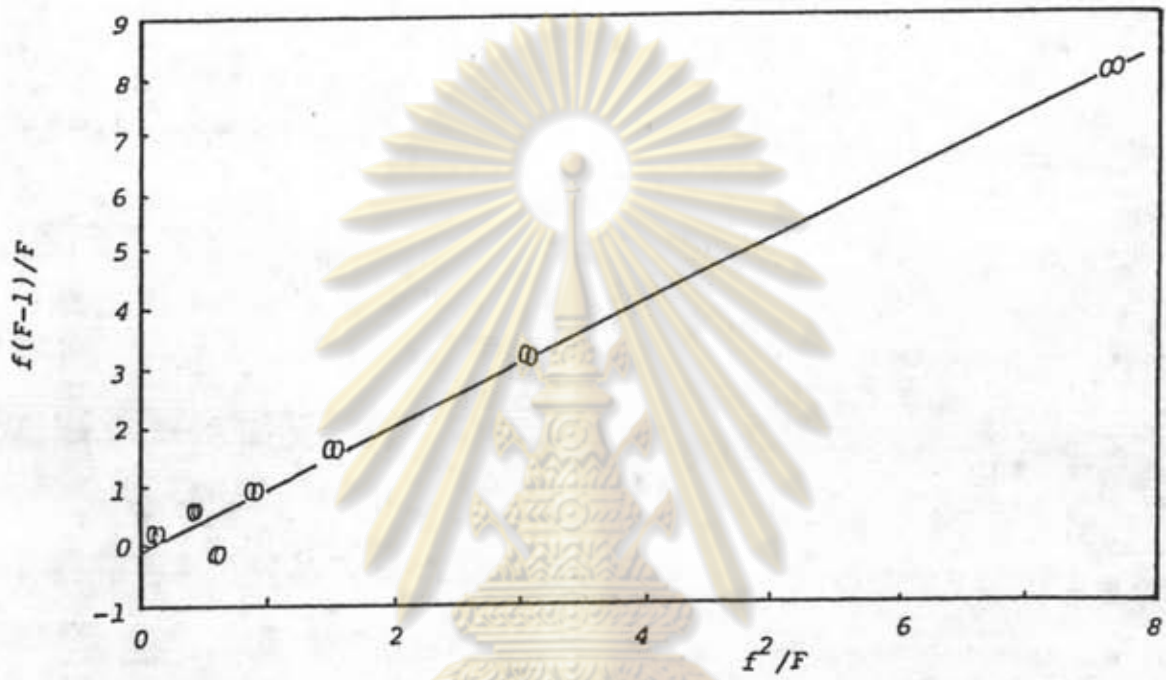


Fig.3.22 Fineman-Ross plot for the determination of reactivity

ratios for the copolymerization of MMA with PCPA

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Table 3.12 Low-conversion copolymerization of pentachlorophenyl acrylate (M_2) and methyl methacrylate (M_1)

f_{MMA} (feed)	conversion (%)	F_{MMA} (copolymer)	
		obsd	calcd
0.8993	8.54	0.9121	0.9128
0.8003	10.71	0.8404	0.8386
0.7016	14.90	0.7890	0.7736
0.6001	14.49	0.7216	0.7121
0.5019	15.00	0.7275	0.6602*
0.4018	10.75	0.4375	0.6088*
0.3034	2.68	0.5891	0.5581
0.9002	14.80	0.9133	0.9135
0.8004	1.40	0.8418	0.8384
0.6985	4.00	0.7797	0.7708
0.6008	7.85	0.7314	0.7138
0.5026	14.35	0.7192	0.6585*
0.4019	11.16	0.4435	0.6057*
0.3032	15.00	0.6412	0.5532*

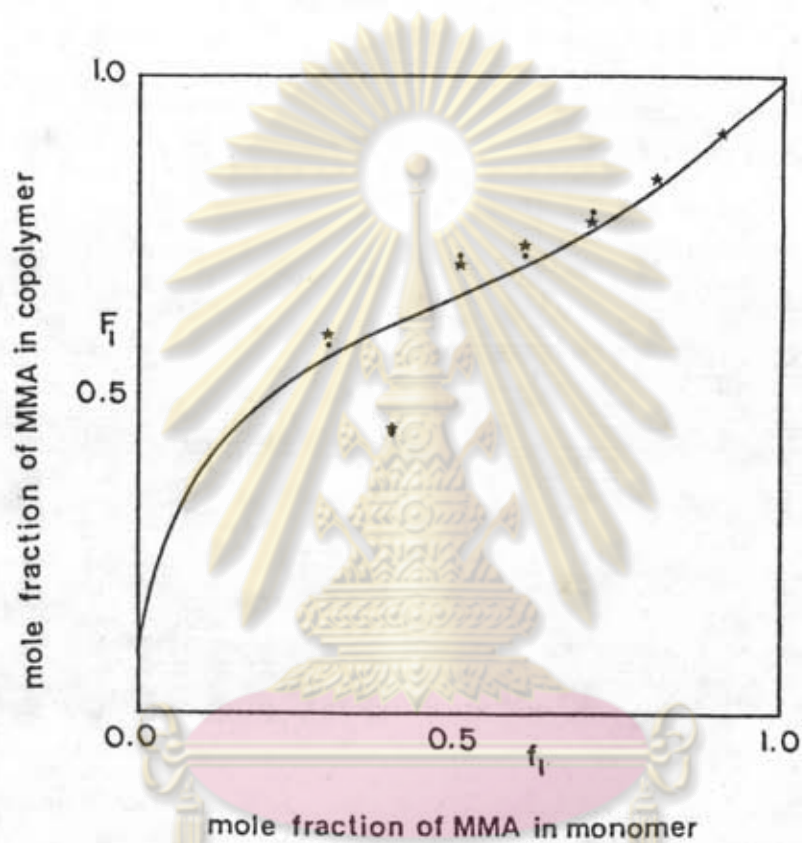


Fig. 3.23 copolymer composition curve for the copolymerization

of MMA (M_1) and PCPA (M_2) in benzene at 50°C

(•) first run, (*) second run, (-) theoretical

Table 3.13 Variables for the evaluation of the reactivity ratios of the MMA-2,4,5-TCPA copolymer by the Fineman-Ross method

mole ratio		f^2/F	$f(F-1)/F$
in feed, f	in copolymer, F		
8.9179	8.1853	9.7095	7.8257
4.0365	4.1790	3.8989	3.0706
2.3395	2.5483	2.1478	1.4214
1.5049	1.9723	1.1483	0.7419
0.9951	1.1767	0.8414	0.1494
0.6720	0.9452	0.4778	-0.0389
0.4292	0.8077	0.2281	-0.1022
8.9874	8.1605	9.8991	7.8861
3.9668	4.1941	3.7516	3.0209
2.3267	2.6048	2.0784	1.4335
1.5196	1.9930	1.1586	0.7571
1.5127	1.9164	1.1940	0.7233
1.0041	1.3086	0.7703	0.2368
0.6819	0.8586	0.5416	-0.1123

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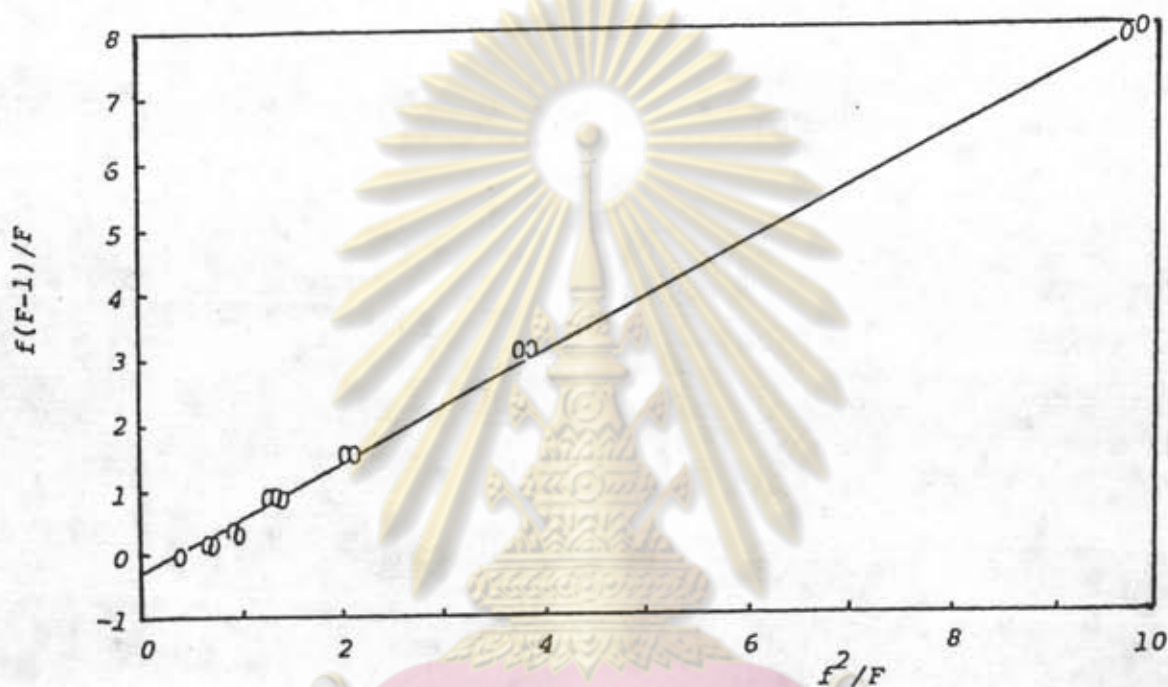


Fig. 3.24 Fineman-Ross plot for the determination of reactivity ratios for the copolymerization of MMA with 2,4,5-TCPA

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Table 3.14 Low-conversion copolymerization of 2,4,5-trichlorophenyl acrylate (M_2) and methyl methacrylate (M_1)

f_{MMA} (feed)	CONVERSION (%)	F_{MMA} (copolymer)	
		obsd	calcd
0.8999	15.00	0.8908	0.8916
0.8014	10.22	0.8070	0.8012
0.7005	7.67	0.7182	0.7198
0.6008	3.50	0.6636	0.6463
0.4988	4.90	0.5916	0.5742
0.4019	4.30	0.4860	0.5046
0.3003	10.64	0.4469	0.4253
0.8992	11.72	0.8912	0.8920
0.7986	10.32	0.8075	0.8006
0.6994	8.22	0.7226	0.7213
0.6031	3.21	0.6659	0.6507
0.6020	14.00	0.6572	0.6499
0.5010	6.87	0.5667	0.5788
0.4055	14.10	0.4620	0.5108

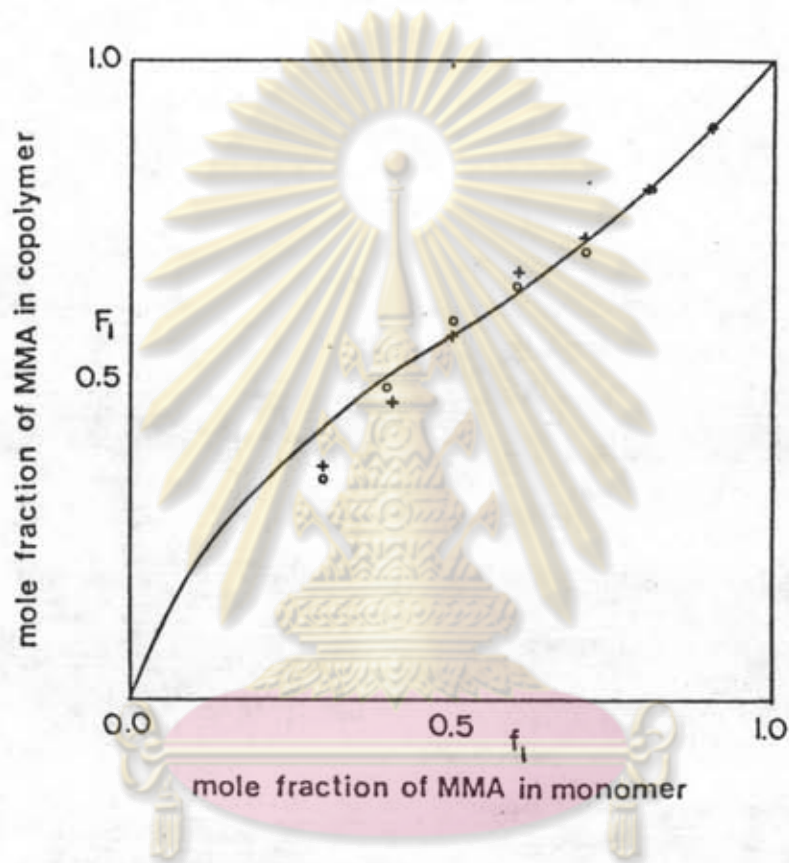


Fig. 3.25 copolymer composition curve for the copolymerization

of MMA(M_1) and 2,4,5-TCPA(M_2) in benzene at 50°C

(o) first run, (+) second run, (-) theoretical

Table 3.15 Variables for the evaluation of the reactivity ratios of the MMA-2,4,6-TCPA copolymer by the Fineman-Ross method

mole ratio		f^2/F	$f(F-1)/F$
in feed, f	in copolymer, F		
8.9550	6.0579	13.2376	7.4767
2.2907	2.3699	2.2141	1.3241
1.4920	1.7843	1.2476	0.6558
1.0140	1.2331	0.8338	0.1917
0.6658	0.9084	0.4880	-0.0671
0.4392	0.8109	0.2378	-0.1024
9.0207	6.1016	13.3363	7.5423
2.3356	2.4193	2.2548	1.3702
1.5536	1.7911	1.3476	0.6862
1.0445	1.1895	0.9172	0.1664
0.6618	0.8959	0.4889	-0.0769
0.4294	0.7891	0.2336	-0.1147

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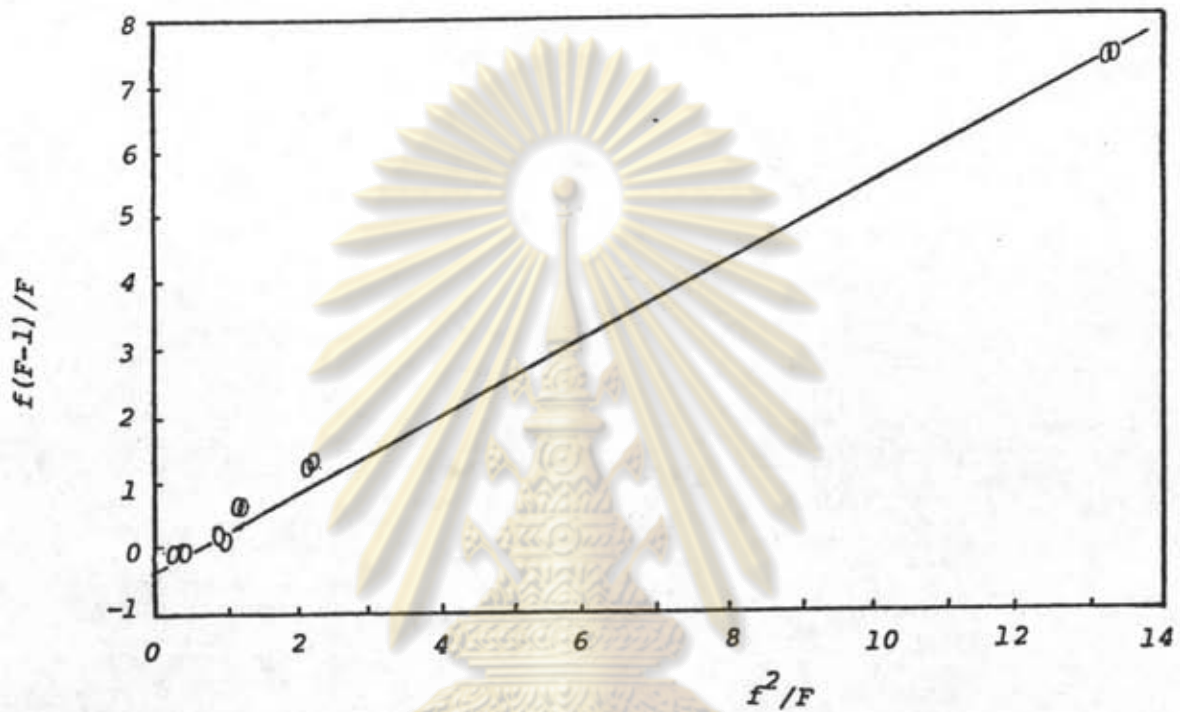


Fig. 3. 26 Fineman-Ross plot for the determination of reactivity ratios for the copolymerization of MMA with 2,4,6-TCPA

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Table 3.16 Low-conversion copolymerization of 2,4,6-trichlorophenyl acrylate (M_2) and methyl methacrylate (M_1)

f_{MMA} (feed)	CONVERSION (%)	F_{MMA} (copolymer)	
		obsd	calcd
0.8995	10.14	0.8586	0.8629
0.6961	10.28	0.7033	0.6807
0.5987	10.45	0.6409	0.6219
0.5035	7.92	0.5522	0.5702
0.3997	7.25	0.4760	0.5159
0.3052	6.67	0.4480	0.4630
0.9002	9.48	0.8592	0.8590
0.7002	12.97	0.7076	0.6844
0.6084	3.52	0.6418	0.6275
0.5109	8.83	0.5433	0.5740
0.3982	7.73	0.4726	0.5152
0.3004	7.76	0.4411	0.4601

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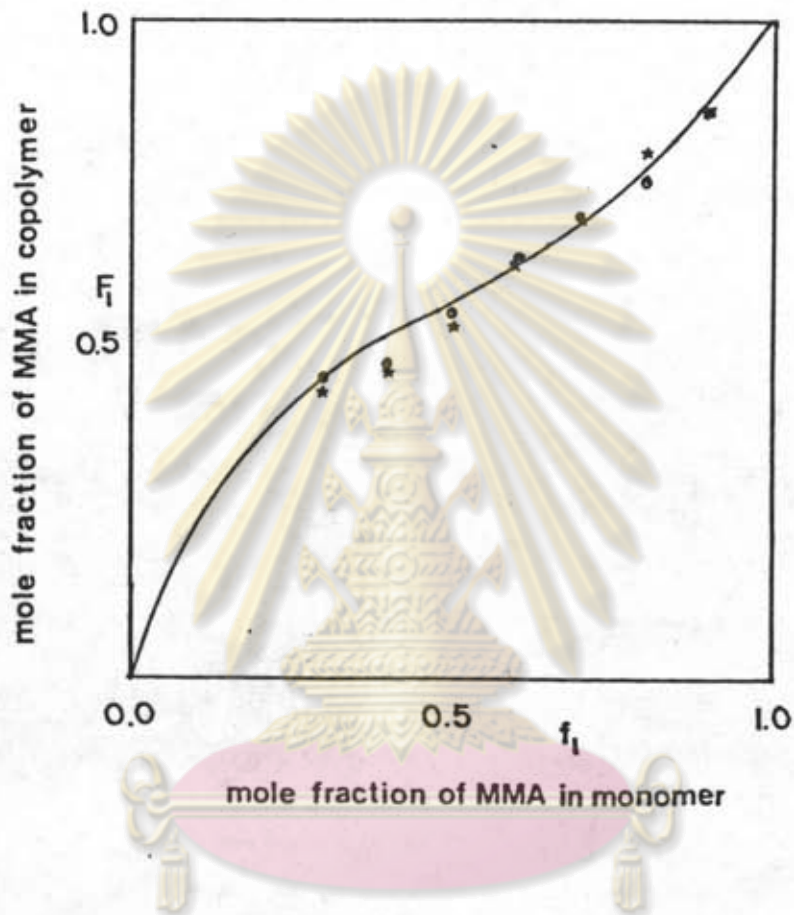


Fig. 3.27 copolymer composition curve for the copolymerization of MMA (M_1) and 2,4,6-TCPA (M_2) in benzene at 50°C
(o) first run, (*) second run, (-) theoretical

Table 3.17 Variables for the evaluation of the reactivity ratios of the MMA-4-Cl-3-MPA copolymer by the Fineman-Ross method

mole ratio		f^2/F	$f(F-1)/F$
in feed, f	in copolymer, F		
3.9754	3.4018	4.6450	2.8067
2.3245	2.3015	2.3477	1.3145
1.5012	1.7788	1.2669	0.6573
1.0064	1.1411	0.8875	0.1245
0.9986	1.2185	0.8184	0.1791
0.6490	1.0195	0.4131	0.0124
3.9514	3.3529	4.6566	2.7728
2.3187	2.2847	2.3532	1.3038
1.4992	1.7308	1.2984	0.6330
1.0060	1.1220	0.9020	0.1094
1.0028	1.1266	0.8925	0.1127
0.6673	1.1730	0.3796	0.0984

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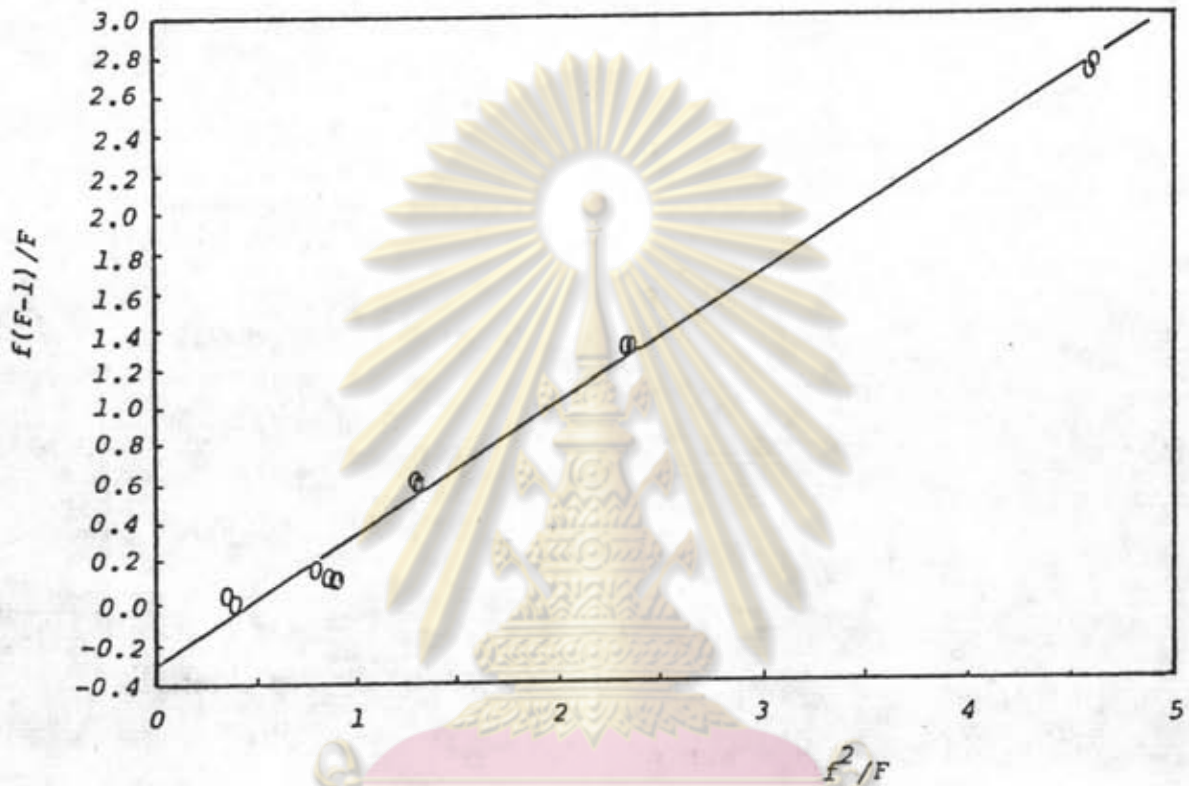


Fig. 3.28 Fineman-Ross plot for the determination of reactivity ratios for the copolymerization of MMA with 4-Cl-3-MPA

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Table 3.18 Low-conversion copolymerization of 4-chloro-3-methyl-phenyl acrylate (M_2) and methyl methacrylate (M_1)

f_{MMA} (feed)	CONVERSION (%)	F_{MMA} (copolymer)	
		obsd	calcd
0.7990	12.79	0.7728	0.7737
0.6992	8.63	0.6972	0.6932
0.6000	12.38	0.6402	0.6235
0.5015	10.76	0.5330	0.5591
0.4997	14.82	0.5493	0.5579
0.3936	8.68	0.5049	0.4886
0.7980	14.95	0.7703	0.7709
0.6987	5.10	0.6956	0.6909
0.5999	13.11	0.6338	0.6216
0.5015	11.46	0.5288	0.5576
0.5007	9.73	0.5298	0.5571
0.4003	6.63	0.5399	0.4920

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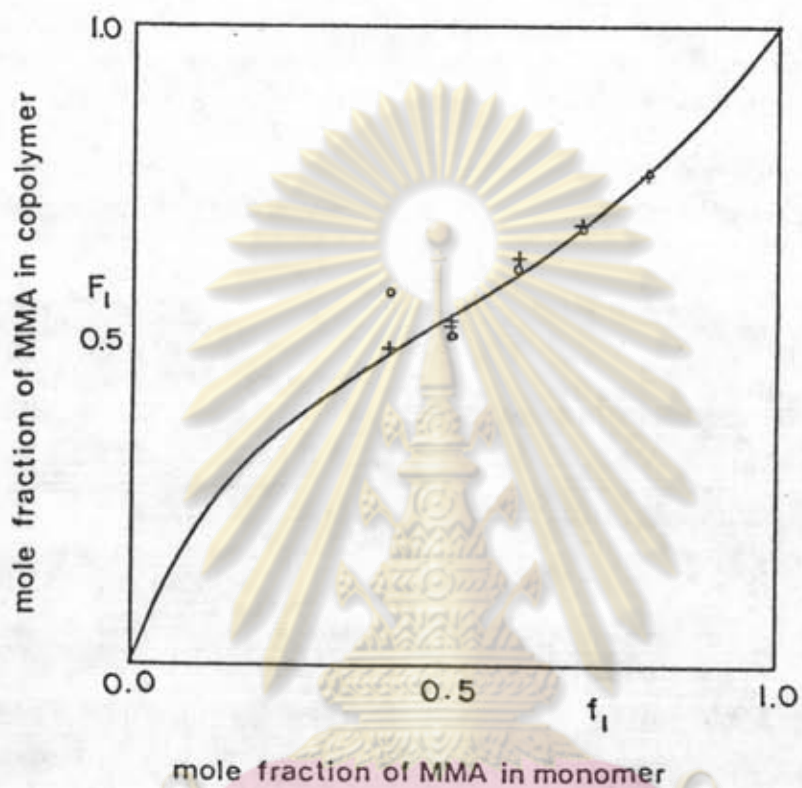


Fig. 3.29

copolymer composition curve for the copolymerization
of MMA (M_1) and 4-Cl-3-MPA (M_2) in benzene at 50°C

(+) first run, (o) second run, (-) theoretical

3.7.2 The Mayo-Lewis Method

3.7.2.1 Pentachlorophenyl Acrylate and Methyl Methacrylate

In evaluation of the monomer reactivity ratios from monomer concentrations at the start and end of copolymerization experiments, an integrated form, eqs. (16) and (17) in Appendix II, of the copolymer equation is used. In the Mayo and Lewis method (11) appropriate values of P are inserted into eqs. (16) and (17) to give a series of r_1 and r_2 values for each copolymerization experiment. Plots of r_1 versus r_2 are then constructed for values calculated from the results of each experiment. The center of gravity of the triangular intersection then defines the reactivity ratios for the system. This is illustrated in Figure 3.30 for data obtained in MMA-PCPA copolymerization studies (Table 3.7). It can be seen that the plots of r_1 versus r_2 are straight line.

The hand calculation of r_1 and r_2 coordinates from eqs. (16) and (17) is tedious. Many points must be calculated, and considerable experimenting is required before appropriate P values are selected. Therefore, the computer program has been written to simplify the calculation involved in such studies (see Appendix II). The input values of P were varied and a large number of r_1 and r_2 coordinates, given the concentration of the initial and final monomer mixture, were then calculated. Values of r_1 and r_2 coordinates suitable for manual plotting could then be selected from the output. The equations for the straight lines passing through the calculated r_1 and r_2 coordinates were determined by a linear

least-squares technic (Table 3.19). The three lines with different proportions of monomer and given the smallest size of area bounded by these lines were then chosen. The monomer reactivity ratios were then determined from the center of gravity of the triangular intersection of these three lines.

It was noticed that the slopes of these lines are positive and increase as $[MMA]/[PCPA]$ increase. The lines with least and greatest slope correspond, respectively, to experiments which initially contained 50 and 95 mole % of MMA. The monomer reactivity ratios of this system are $r_1 = 1.00$ and $r_2 = 0.08$. Although these values (i.e., r_1 and r_2) as determined by the Fineman-Ross and Mayo-Lewis method are not equal, they at least exhibit a similar tendency toward alternation.

3.7.2.2 2,4,5-Trichlorophenyl Acrylate and Methyl Methacrylate

By analogy with the MMA-PCPA system, the monomer reactivity ratios of the MMA-2,4,5-TCPA system were determined. Table 3.20 summarized linear equation from Mayo-Lewis plot. Figure 3.31 exhibits the straight line obtained by using Mayo and Lewis method. The slopes of these lines are positive and increase as $[MMA]/[2,4,5-TCPA]$ increase as well. In this system $r_1 = 0.92$ and $r_2 = 0.42$, in accord with the values determined by Fineman and Ross method. The values of r_1 and r_2 of both methods are of the same order as those of similar copolymer systems that contain acrylate and MMA as described in section 3.7.1.1.

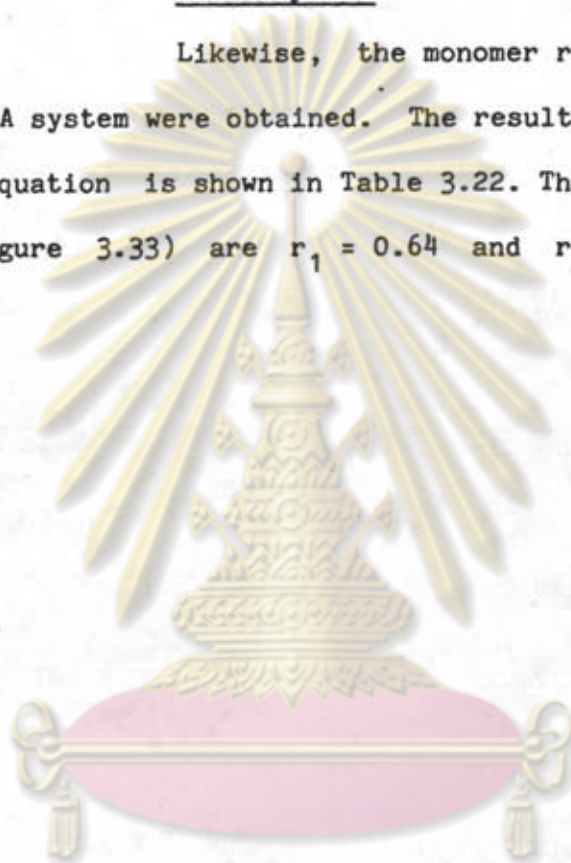
3.7.2.3 2,4,6-Trichlorophenyl Acrylate and Methyl Methacrylate

The monomer reactivity ratios of MMA-2,4,6-

TCPA system were similarly determined. Linear equation of a series of r_1 and r_2 coordinates is list in Table 3.21. The r_1 and r_2 values obtained (Figure 3.32) are $r_1 = 0.63$ and $r_2 = 0.12$.

3.7.2.4 4-Chloro-3-Methylphenyl Acrylate and Methyl Methacrylate

Likewise, the monomer reactivity ratios of MMA-4-Cl-3-MPA system were obtained. The results calculated by the Mayo-Lewis equation is shown in Table 3.22. The r_1 and r_2 values obtained (Figure 3.33) are $r_1 = 0.64$ and $r_2 = 0.37$.



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Table 3.19 Linear equation of Mayo-Lewis plot from the copolymerization of MMA (M_1) and PCPA (M_2)

	equation
I	$r_1 = 0.137 r_2 + 0.873$
II	$r_1 = 0.072 r_2 + 1.076$
III	$r_1 = 0.138 r_2 + 0.891$
IV	$r_1 = 0.281 r_2 + 0.958$
V	$r_1 = 2.811 r_2 + 0.816$
VI	$r_1 = 3.048 r_2 + 0.914$



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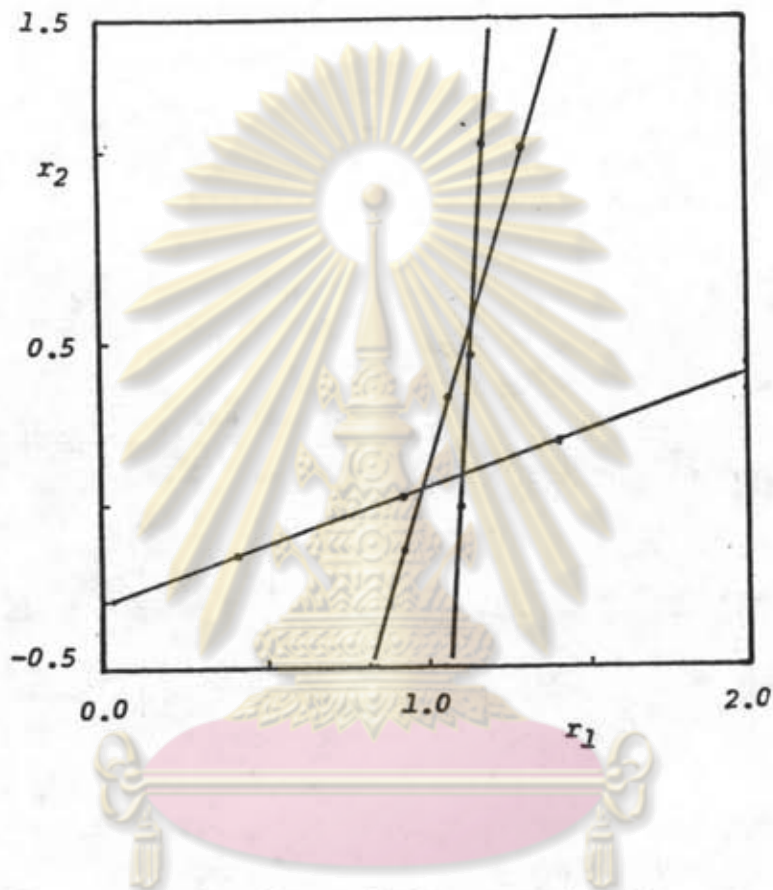


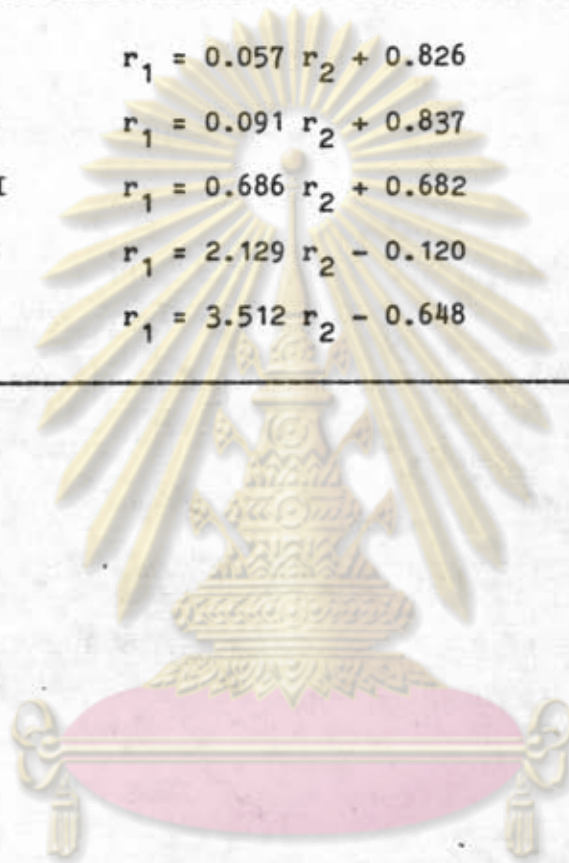
Fig. 3.30 Mayo-Lewis plot ; high-conversion data for

คunyvitayathayakr
methyl methacrylate-pentachlorophenyl acrylate copolymer

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Table 3.20 Linear equation of Mayo-Lewis plot from the copolymerization of MMA (M_1) and 2,4,5-TCPA (M_2)

	equation
I	$r_1 = 0.057 r_2 + 0.826$
II	$r_1 = 0.091 r_2 + 0.837$
III	$r_1 = 0.686 r_2 + 0.682$
IV	$r_1 = 2.129 r_2 - 0.120$
V	$r_1 = 3.512 r_2 - 0.648$



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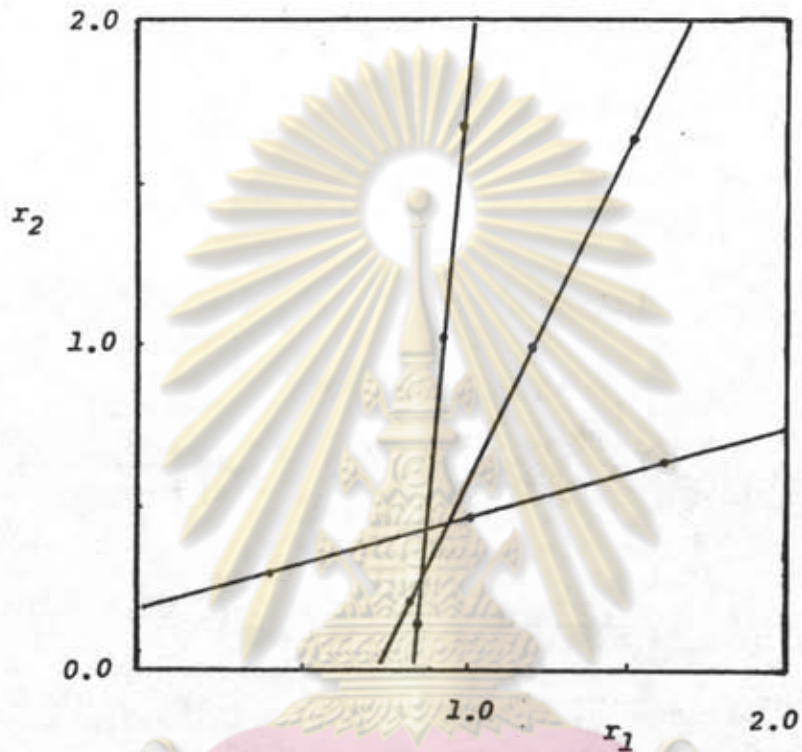


Fig. 3.31 Mayo-Lewis plot ; high-conversion data for

methyl methacrylate-2,4,5-trichlorophenyl acrylate copolymer

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Table 3.21 Linear equation of Mayo-Lewis plot from the copolymerization of MMA(M_1) and 2,4,6-TCPA (M_2)

	equation
I	$r_1 = 0.074 r_2 + 0.655$
II	$r_1 = 0.076 r_2 + 0.683$
III	$r_1 = 4.967 r_2 + 0.519$
IV	$r_1 = 2.424 r_2 + 0.254$
V	$r_1 = -4.890 r_2 + 1.053$

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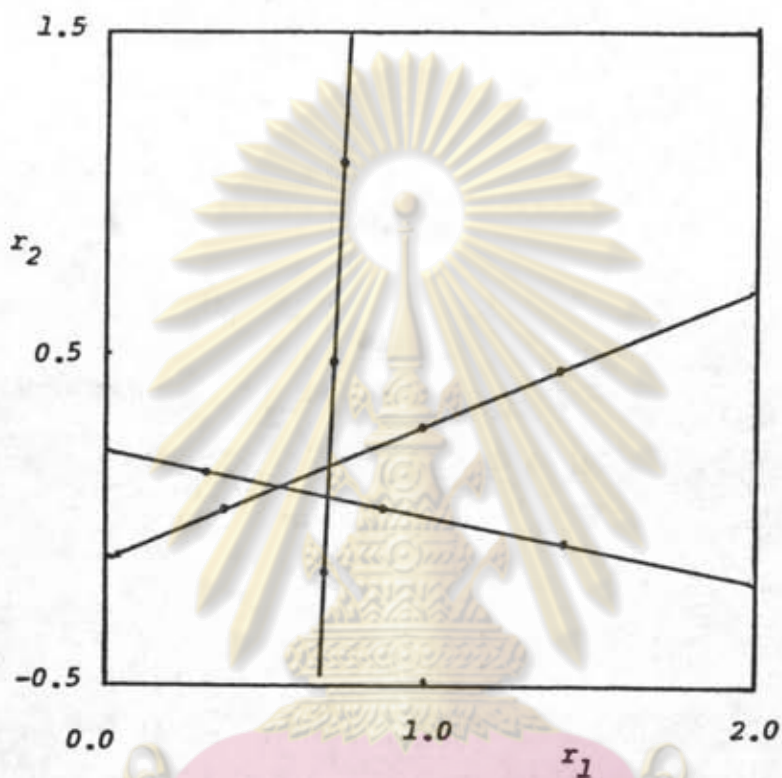


Fig. 3.32 Mayo-Lewis plot ; high-conversion data for methyl methacrylate-2,4,6-trichlorophenyl acrylate copolymer

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Table 3.22 Linear equation of Mayo-Lewis plot from the copolymerization of MMA(M_1) and 4-Cl-3-MPA (M_2)

	equation
I	$r_1 = 0.069 r_2 + 0.664$
II	$r_1 = 0.099 r_2 + 0.753$
III	$r_1 = 0.418 r_2 + 0.592$
IV	$r_1 = 0.872 r_2 + 0.246$
V	$r_1 = 11.46 r_2 - 3.061$

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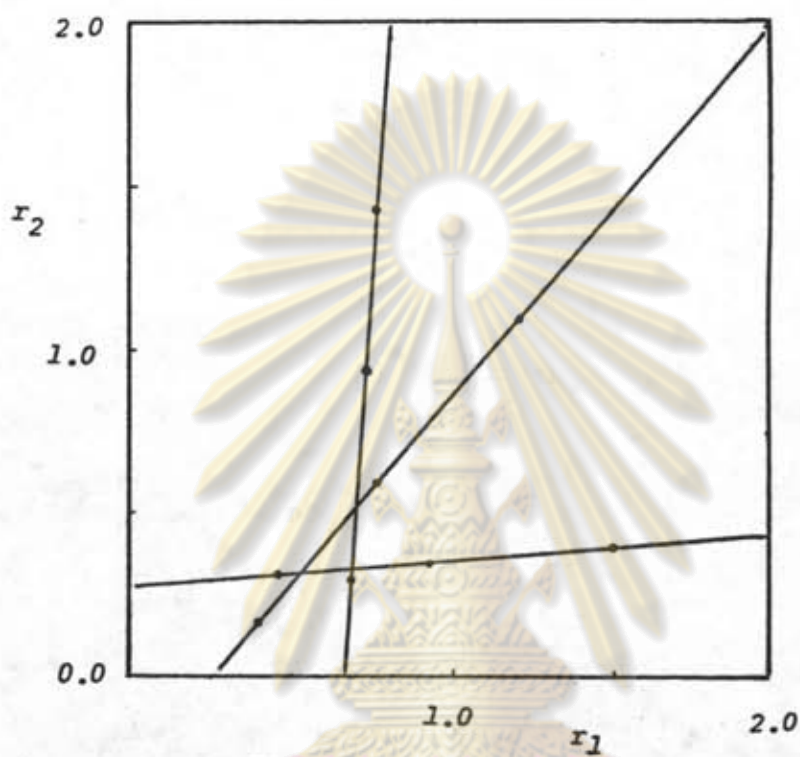


Fig. 3.33 Mayo-Lewis plot ; high-conversion data for

methyl methacrylate-4-chloro-3-methylphenyl acrylate copolymer

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