

## CHAPTER II

### EXPERIMENTAL

#### 2.1 General information

Acryloyl chloride and triethylamine were obtained from Fluka and freshly distilled prior to use.

Pentachlorophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol and 4-chloro-3-methylphenol were obtained from Fluka and used without further purification.

Vinyl acetate was also obtained from Fluka and purified by shaking with 10 percent sodium hydroxide. It was then washed several times with distilled water, dried over anhydrous sodium sulfate and distilled prior to use (28).

Toluene, methanol, n-hexane were commercial grade, but benzene and chloroform were reagent grade and obtained from BDH. All of them were distilled before used.

Melting points were determined by a John-Fisher electrothermal melting point apparatus with cover glass sample holder and are uncorrected.

The following instruments were used to obtain the spectroscopic data and an elemental analysis :

UV-Visible spectrophotometer, Shimadzu, model UV 240 with 10 nm matched quartz cells,

Infrared Spectrophotometer, Perkin-Elmer, model Perkin-Elmer 780, with grating infrared spectrophotometer,

Fourier-transform NMR spectrometer, Jeol, model JNX-FX 90Q,

Mass spectrometer, Jeol, model JMS-DX 300/JMA 2000 , with electron ionization source.

Elemental analyzer, Perkin-Elmer, model Perkin-Elmer 240 CHNO analyzer,

## 2.2 Syntheses of fungicidal acrylate monomers

### 2.2.1 Pentachlorophenyl acrylate (PCPA)

Pentachlorophenyl acrylate was prepared by the reaction of pentachlorophenol and acryloyl chloride in the presence of triethylamine (27, 28, 29). A three-necked round bottom flask (500 ml, equipped with a condenser and nitrogen inlet) was charged with toluene (300 ml), pentachlorophenol (24 g , 0.09 mole) and triethylamine (15.6 ml, 0.11 mole). The solution was then stirred and maintained at 20-25 ° C, while acryloyl chloride (9 ml, 0.11 mole) was slowly added through a dropping funnel . White triethylamine hydrochloride immediately precipitated. The reaction was monitored by thin layer chromatography with silica gel as the adsorbent using chloroform as the eluting solvent. After the reaction was completed (disappearance of starting material as shown by thin layer chromatography), the solution was allowed to warm to room temperature. It was then filtered and washed several times with

distilled water to remove unreacted acryloyl chloride. The toluene layer was dried over anhydrous sodium sulfate and filtered, then removed the toluene by vacuum distillation. The remaining brownish solid was recrystallized from methanol to yield 25 g (87 %) of pentachlorophenyl acrylate as a white solid, m.p. 78-79 °C (58 °C, 75 °C, 82.5 °C).

Spectroscopic data:

IR (KBr)	$\nu$	1760 (s), 1635 (w), 1415 (m), 1385 (s), 1360 (s) 1225 (m), 1140 (s), 1130 (s), 980 (m), 800 (m), 780 (m), 710 (m) $\text{cm}^{-1}$
UV ( $\text{CHCl}_3$ )	$\lambda_{\text{max}}$	240 nm ( $\epsilon$ 5300)
NMR ( $\text{CDCl}_3$ )	$\delta$	6.08-6.89 (m) ppm
MS	m/e	318 ( $\text{M}^+$ )                      % RA 3.00
		320 ( $\text{M}^++2$ )                      % RA 4.68
		322 ( $\text{M}^++4$ )                      % RA 3.00
		324 ( $\text{M}^++6$ )                      % RA 0.97
		55 (base peak)                  % RA 51.95

Elemental analysis

found	:	%C, 33.89 ; %H, 0.87
calcd. for $\text{C}_9\text{H}_3\text{O}_2\text{Cl}_5$	:	%C, 33.70 ; %H, 0.94

2.2.2 2,4,6-Trichlorophenyl acrylate (2,4,6-TCPA)

In the same manner as described in 2.2.1, 2,4,6-trichlorophenol (11.8 g, 0.06 mole) was reacted with acryloyl



chloride (6.1 ml, 0.08 mole) in the presence of triethylamine (10.4 ml, 0.08 mole). When the solvent was removed to give remaining brownish liquid, the residue was purified by column chromatographic method (packed with silica gel) using benzene as an eluent to yield 13.5 g (90 %) of 2,4,6-trichlorophenyl acrylate as colourless liquid. (Decomposition point 120 °C, 10 mmHg)

Spectroscopic data :

IR(neat)	$\nu$	3090 (w), 1760 (s), 1635 (m), 1570 (s), 1450 (s), 1410 (s), 1295 (m), 1225 (s), 1150 (s), 1120 (s), 1015 (s), 980 (s), 895 (s), 855 (s), 820 (s), 770 (s) $\text{cm}^{-1}$
UV ( $\text{CHCl}_3$ )	$\lambda_{\text{max}}$	240 nm ( $\epsilon$ 790 ) $\lambda_{\text{max}}$ 275 nm ( $\epsilon$ 339 ) $\lambda_{\text{max}}$ 285 nm ( $\epsilon$ 307 )
NMR ( $\text{CDCl}_3$ )	$\delta$	6.02-6.82 (m, 3H), 7.36 (s, 2H) ppm
MS	m/e	250 ( $\text{M}^+$ ) % RA 9.68 252 ( $\text{M}^++2$ ) % RA 9.42 254 ( $\text{M}^++4$ ) % RA 3.09 256 ( $\text{M}^++6$ ) % RA 0.36 55 (base peak) % RA 24.27

Elemental Analysis

found	:	%C, 43.22 , %H, 2.15
calcd. for $\text{C}_9\text{H}_5\text{O}_2\text{Cl}_3$	:	%C, 42.94 , %H, 1.99

## 2.2.3 2,4,5-Trichlorophenyl acrylate (2,4,5-TCPA)

In the same manner as described in 2.2.1, 2,4,5-trichlorophenol (23.6 g, 0.12 mole) was reacted with acryloyl chloride (12.2 ml, 0.15 mole) in the presence of triethylamine (20.8 ml, 0.15 mole). When the solvent was removed, the remaining residue was recrystallized from methanol to yield 27.6 g (92%) of 2,4,5-trichlorophenyl acrylate as a white solid, m.p. 63-64 °C.

## Spectroscopic data :

IR (KBr)	$\nu$	3090 (w), 1755 (s), 1630 (m), 1455 (m), 1405 (s), 1350 (m), 1140 (s), 1120 (s), 1080 (s), 990 (m), 895 (m), 795 (m) $\text{cm}^{-1}$
UV ( $\text{CHCl}_3$ )	$\lambda_{\text{max}}$	240 nm ( $\epsilon$ 1800 ) 280 nm ( $\epsilon$ 982 ) 290 nm ( $\epsilon$ 982 )
NMR ( $\text{CDCl}_3$ )	$\delta$	6.00-6.80 (m,3H), 7.34(s,1H), 7.55 (s,1H) ppm
MS	m/e	250 ( $\text{M}^+$ ) % RA 6.06 252 ( $\text{M}^++2$ ) % RA 6.05 254 ( $\text{M}^++4$ ) % RA 1.97 55 (base peak) % RA 50.58

## Elemental analysis

found	:	%C, 42.89 ; %H, 1.92
calcd. for $\text{C}_9\text{H}_5\text{O}_2\text{Cl}_3$	:	%C, 42.94 ; %H, 1.99

## 2.2.4 4-Chloro-3-methylphenyl acrylate (4-Cl-3-MPA)

In the same manner as described in 2.2.1, 4-Chloro-3-methylphenol (10.8 g, 0.08 mole) was reacted with acryloyl chloride (7.7 ml, 0.09 mole) in the presence of triethylamine (13.1 ml, 0.09 mole). When the solvent was removed, the remaining liquid was purified by column chromatographic method (packed with silica gel) using benzene as an eluent to yield 12.75 g (85%) of 4-Chloro-3-methylphenyl acrylate as colourless liquid (decomposition point  $120^{\circ}\text{C}$ , 10 mmHg).

## Spectroscopic data :

IR (neat)	$\nu$	3040 (w), 2920 (w), 1750 (s), 1635 (m), 1610 (m), 1580 (m), 1480 (s), 1405 (s), 1250 (s), 1230 (s), 1160 (s), 900 (m), 800 (m) $\text{cm}^{-1}$
UV ( $\text{CHCl}_3$ )	$\lambda_{\text{max}}$	240 ( $\epsilon$ 2272)
NMR ( $\text{CDCl}_3$ )	$\delta$	2.36 (s, 3H), 5.92-6.53 (m, 3H), 6.69-7.38 (m, 3H) ppm
MS	m/e	196.5 ( $\text{M}^+$ ) Intensity 235.6 198.5 ( $\text{M}^+2$ ) Intensity 71.3 55 (base peak) Intensity 1000.0

## Elemental Analysis

found	: %C, 61.19 ; %H, 4.60
calcd. for $\text{C}_{10}\text{H}_9\text{O}_2\text{Cl}$	: %C, 61.07 ; %H, 4.58

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### 2.3 Preliminary study of copolymerization

#### 2.3.1 Bulk polymerization

A dried test tube (10 ml) was charged with pentachlorophenyl acrylate(PCPA), vinyl acetate(VAc) and benzoyl peroxide( $Bz_2O_2$ ). After the mixture was purged with nitrogen for 10 minutes, the tube was immersed in a constant temperature bath at 60 °C. The observation data are shown in Table 2.1.

Table 2.1 Bulk copolymerization of pentachlorophenyl acrylate with vinyl acetate

PCPA (g)	VAc (g)	$Bz_2O_2$ (g)	time (hr)	observation
0.0172	4.2840	0.0492	5	viscous solution
0.0470	4.2439	0.0488	5	viscous solution
0.0783	4.1861	0.0485	5	viscous solution
0.1088	4.1079	0.0495	5	viscous solution to give rubbery product in hexane
0.1374	4.0640	0.0482	5	opaque solution to give 0.1972 g of white precipitated in hexane
0.1563	4.1950	0.0490	5	opaque viscous solution

After the reaction was worked up, the reaction mixture was diluted with benzene and precipitated in hexane, to give the rubbery material. Attempts to precipitate using other nonsolvent, i.e. ether and light petroleum ether, also gave the same tacky polymer.

Copolymerization between 2,4,5-trichlorophenyl acrylate (2,4,5-TCPA) and vinyl acetate by bulk polymerization technic was also attempted. The similar results were observed (Table 2.2).

Table 2.2 Bulk copolymerization of 2,4,5-trichlorophenyl acrylate with vinyl acetate

2,4,5-TCPA (g)	VAc (g)	Bz <sub>2</sub> O <sub>2</sub> (g)	time (hr)	observation
0.0120	4.2767	0.0485	5	viscous solution
0.0381	4.2686	0.0485	5	viscous solution
0.0614	4.2501	0.0487	5	viscous solution
0.0896	4.2961	0.0493	5	viscous solution to give rubbery product in hexane
0.1291	4.3109	0.0500	2.45	opaque viscous solution to give white precipitate in hexane



### 2.3.2 Solution Polymerization

The polymerization tubes were each charged with  $\alpha,\alpha'$ -azobisisobutyronitrile, benzene (10 ml) and with the quantities of the acrylate monomers and vinyl acetate given in the Table 2.3. Some of the mixtures were purged with nitrogen for 10 minutes in order to scavenge oxygen from the solution before heating. These solutions were then heated at some different temperatures and different length of time. After each of the reactions was quenched, the polymer was precipitated and reprecipitated to obtain white solid. The percent conversion was found to range from 0.45-38.00 %.

The product was dissolved in benzene and then applied on tlc plate. Using methanol as the developing solvent, the chromatogram was obtained. It revealed that no contamination of the starting monomer on the polymer product. Some of these products was also examined by infrared spectroscopy (KBr method). Furthermore, the UV-Visible spectrum (in  $\text{CHCl}_3$ ) of some of these polymers were recorded to determine the incorporation of the fungicidal monomer into the polymer.

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Table 2.3 Solution polymerization

Monomer (M <sub>1</sub> )	weight, W <sub>1</sub> ,g	Vinyl Acetate, W <sub>2</sub> g	Initiator g	time hr	temp °C	Oxygen	Conversion %	F <sub>1</sub> *
PCPA	0.8805	4.0685	0.1072	30	55	absence	38.0	-
PCPA	1.4194	0.0506	0.0080	4	50	presence	0.45	-
PCPA	0.6220	0.6947	0.0160	1	60	presence	11.6	0.5993
2,4,5- TCPA	0.6194	0.2029	0.0160	9	55	absence	23.0	-
2,4,5- TCPA	0.5036	0.6901	0.0160	1	60	presence	8.5	0.5151
2,4,6- TCPA	0.7639	0.6436	0.0160	1	60	absence	7.6	0.573
2,4,6- TCPA	0.4789	0.6990	0.0160	1	60	absence	6.4	0.608
4-C1-3- MPA	0.9792	0.4351	0.0160	1	60	absence	22	0.710
4-C1-3- MPA	1.3064	0.2851	0.0160	1	60	presence	2.89	0.73

\* see section 2.6

F = The mole fraction of the chlorophenyl acrylate in copolymer

## 2.4 Solution copolymerization of fungicidal acrylate monomers with vinyl acetate

### 2.4.1 Pentachlorophenyl acrylate with vinyl acetate

The polymerization was carried out by thoroughly mixing certain amount of vinyl acetate with pentachlorophenyl acrylate in 10 ml of dry benzene in the reaction cell. Eight reaction cells contained different mole fraction of pentachlorophenyl acrylate comonomer in feeding, i.e. 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 and 0.05, respectively (Table 2.4). It was then added 0.0164 g of,  $\alpha, \alpha'$ -azobisisobutyronitrile into each reaction cell. After heating at 60 °C for one hour, the mixture was cooled and dissolved in benzene (about 20 ml). The solution was then added dropwise into 300 ml of hexane with vigorously stirring and the copolymer precipitated as the white powder. The copolymer was filtered, redissolved in benzene, reprecipitated into hexane, and filtered before drying under vacuum to constant weight .

Finally, the dried precipitate was chromatographed on a tlc plate comparing with pentachlorophenyl acrylate and using methanol as the developing solvent. It revealed that neither monomer contaminated with the precipitate. The polymerization for each monomer feeding ratio of pentachlorophenyl acrylate and vinyl acetate was repeated twice. The polymerization data are listed in Table 2.4.

**Table 2.4** Data for copolymerization of pentachlorophenyl acrylate with vinyl acetate in benzene

Poly (PCPA-co-VAc)	PCPA (g)	VAc (g)	copolymer (g)	conversion (%)
first run				
I-1	2.2310	0.2606	0.1669	6.7
II-1	1.9082	0.3490	0.1603	7.1
III-1	1.5699	0.4398	0.1286	6.4
IV-1	1.2918	0.5142	0.1535	8.5
V-1	0.9575	0.6040	0.1500	9.6
VI-1	0.6220	0.6947	0.1527	11.6
VII-1	0.2757	0.7870	0.0202	1.9
VIII-1	0.1496	0.8210	0.0200	2.1
second run				
I-2	2.1714	0.2776	0.219	8.96
II-2	1.8387	0.3670	0.17	7.74
III-2	1.5518	0.444	0.269	13.51
IV-2	1.2108	0.5356	0.266	15.24
V-2	0.9493	0.6059	0.2100	13.45
VI-2	0.4519	0.7395	0.1100	9.21

#### 2.4.2 The novel chlorophenyl acrylate

The same general procedure as that given in 2.4.1 for the copolymerization was used, except the amount of the monomers as shown in Table 2.5, 2.6, and 2.7.

Table 2.5 Data for copolymerization of 2,4,6-trichlorophenyl acrylate with vinyl acetate in benzene

Poly (2,4,6-TCPA-co-VAc)	2,4,6-TCPA (g)	VAc (g)	copolymer (g)	conversion %
first run				
I-1	1.7711	0.2625	0.1973	9.7
II-1	1.5446	0.3450	0.1852	9.8
III-1	1.2708	0.4315	0.1487	8.7
IV-1	1.0186	0.5147	0.1303	8.5
V-1	0.8258	0.5943	0.1250	8.8
VI-1	0.5274	0.6825	0.0980	8.1
VII-1	0.2711	0.7717	0.0079	0.8
VIII-1	0.1221	0.8147	0.0091	1.0
second run				
I-2	1.8034	0.2759	0.2591	12.17
II-2	1.3857	0.3990	0.1409	7.9
III-2	1.2034	0.4625	0.1537	9.8
IV-2	1.1250	0.4870	0.1782	6.18
V-2	0.7639	0.5994	0.1074	7.6
VI-2	0.4789	0.6990	0.0765	6.4
VII-2	0.2372	0.7802	0.02	1.97



Table 2.6 Data for copolymerization of 2,4,5-trichlorophenyl acrylate with vinyl acetate in benzene

Poly (2,4,5-TCPA-co-VAc)	2,4,5-TCPA (g)	VAc (g)	copolymer (g)	conversion %
first run				
I-1	1.7155	0.2739	0.1574	7.9
II-1	1.4495	0.3657	0.1416	7.8
III-1	1.2195	0.4438	0.1763	10.6
IV-1	0.9935	0.5204	0.1269	8.4
V-1	0.7315	0.6116	0.1128	8.4
VI-1	0.5036	0.6901	0.1010	8.5
VII-1	0.2654	0.7702	0.0614	5.9
VIII-1	0.1233	0.8190	0.0113	1.2
second run				
I-2	1.6549	0.2944	0.16	8.2
II-2	1.2826	0.4218	0.16	9.58
III-2	1.1795	0.4571	0.20	12.2
IV-2	0.9305	0.5424	0.113	7.72
V-2	0.6463	0.6396	0.127	9.88
VI-2	0.3848	0.7292	0.113	10.14
VII-2	0.1534	0.8084	0.023	2.45

Table 2.7 Data for copolymerization of 4-chloro-3-methylphenyl acrylate with vinyl acetate

Poly (4-Cl-3-MPA-co-VAc)	4-Cl-3-MPA (g)	VAc (g)	copolymer (g)	conversion %
first run				
I-1	1.5433	0.1942	0.0193	1.11
II-1	1.3064	0.2851	0.0450	2.83
III-1	1.1558	0.3854	0.0190	1.23
IV-1	1.0231	0.4077	0.0228	1.59
V-1	0.7935	0.5207	0.0190	1.45
VI-1	0.5870	0.5969	0.0164	1.39
VII-1	0.4310	0.6946	0.0192	1.71
second run				
I-2	1.2969	0.2927	0.019	1.21
II-2	1.1224	0.3702	0.027	1.81
III-2	0.9268	0.4390	0.017	1.22
IV-2	0.7868	0.5165	0.014	1.06
V-2	0.5502	0.6198	0.014	1.17
VI-2	0.3370	0.6973	0.012	1.11
VII-2	0.167	0.7877	0.013	1.31

## 2.5 Homopolymerization of the chlorophenyl acrylates

By using the procedure described in section 2.4.1, 0.01 mole of each of the chlorophenyl acrylates was homopolymerized in 10 ml of benzene in the presence of  $\alpha, \alpha'$ -azobisisobutyronitrile (0.0164 g) as the initiator. After 2.5 hours of reaction, the corresponding homopolymer was obtained and examined by both thin layer chromatography and infrared spectroscopy. Exceptionally, homopolymerization of pentachlorophenyl acrylate was carried out in toluene instead of benzene. The four homopolymers obtained are listed in Table 2.8.

Table 2.8 Homopolymerization of the chlorophenyl acrylates

monomer	solvent	weight of monomer, (g)	weight of initiator, (g)	weight of product, (g)
PCPA	benzene	3.2028	0.0162	1.6259
PCPA	toluene	3.1977	0.0165	0.9532
2,4,6-TCPA	benzene	2.3654	0.0154	0.7724
2,4,5-TCPA	benzene	2.5192	0.0172	0.7163
4-Cl-3-MPA	benzene	1.9719	0.0174	0.3732



## 2.6 Determination of copolymer composition by UV-Visible spectroscopy

A certain amount of each copolymer and each homopolymer was individually dissolved in chloroform (Table 2.9-2.16). A wavelength was sought at which one homopolymer and its copolymer showed a characteristic peak and the homopolymer of the other constituents did not absorb. It was found that the wavelength at 240 nm is suitable one for all cases. By preparing solutions of various concentrations of one homopolymer, different UV-Visible spectra were recorded. A concentration-absorption profile of the homopolymer was then obtained by plotting the absorbance against the concentration of each homopolymer solutions (Figure 2.1-2.4). The absorbance at wavelength 240 nm of the known concentration of the corresponding copolymeric samples was obtained from their UV-Visible spectra. Thus the concentration of the desired residues in the copolymer was determined from the calibration curve.

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Table 2.9 Relationship between concentration and UV-Visible absorption of poly (PCPA)

concentration (ppm)	absorption peak height* at 240 nm (cm)**
2.150	1.020
5.376	1.880
13.44	4.190
33.60	9.890
84.00	21.16

\* using ASTM part 42 method

\*\* 15 cm equal to 1 Absorbance

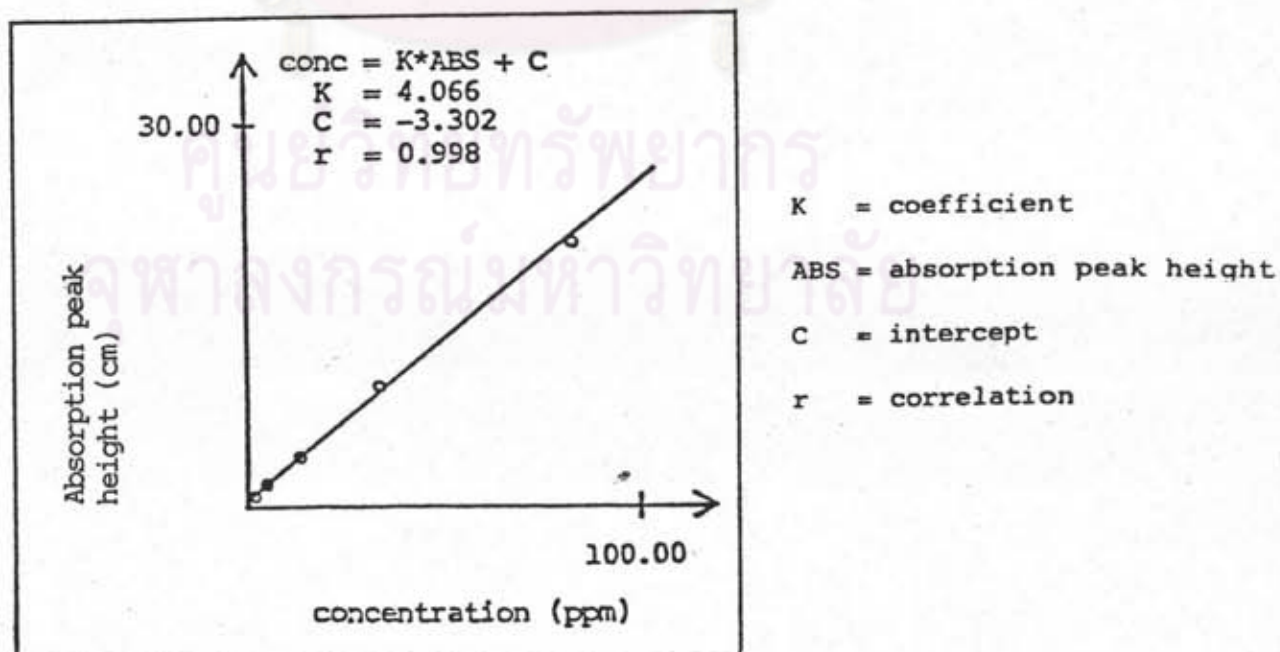


Figure 2.1 The concentration-absorption profile of poly(PCPA)

Table 2.10 Relationship between concentration and UV- Visible absorption of poly(PCPA-co-VAc)

Poly (PCPA-co-VAc)	concentration of copolymer (ppm)	absorption peak height at 240 nm (cm)	concentration of PCPA* (ppm)
first run			
I-1	37.6	9.64	35.89
II-1	54.4	13.38	51.10
III-1	33.6	8.37	30.73
IV-1	47.2	11.25	42.44
V-1	34.4	8.20	30.04
VI-1	28.0	6.65	23.74
VII-1	30.4	6.90	24.75
VIII-1	39.2	8.45	31.06
second run			
I-2	24.0	6.32	22.39
II-2	39.1	9.71	36.18
III-2	32.6	8.20	30.04
IV-2	34.4	8.40	30.85
V-2	28.2	6.93	24.87
VI-2	30.5	7.37	26.66

\* obtained from the concentration-absorption profile in Figure 2.1

Table 2.11 Relationship between concentration and UV - Visible absorption of poly (2,4,6-TCPA)

concentration (ppm)	absorption peak height at 240 nm (cm)
20.68	0.250
51.71	1.050
129.30	3.000
323.20	6.940

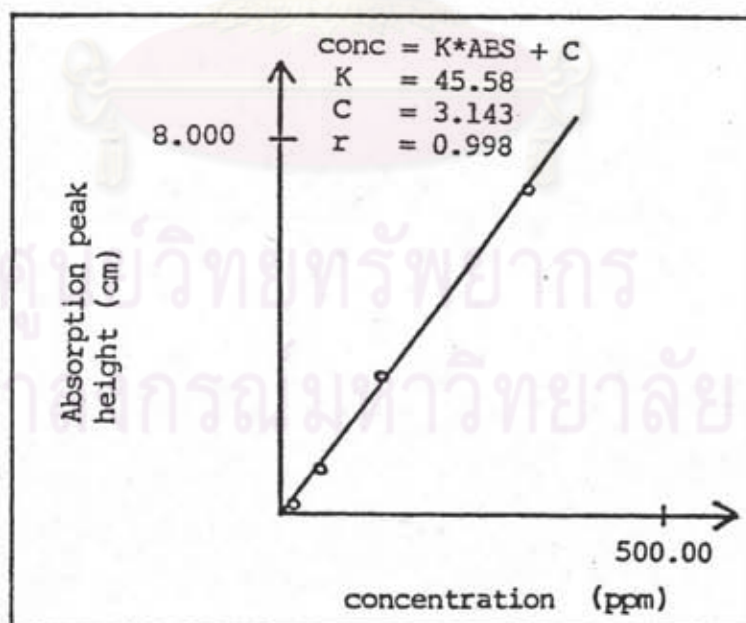


Figure 2.2 The concentration-absorption profile of poly (2,4,6-TCPA)

Table 2.12 Relationship between concentration and UV-Visible absorptiion of poly(2,4,6-TCPA-co-VAc)

Poly (2,4,6-TCPA-co-VAc)	concentration of copolymer (ppm)	absorption peak height at 240 nm (cm)	concentration of 2,4,6-TCPA (ppm)
first run			
I-1	247.2	4.75	219.65
II-1	164.0	3.05	142.16
III-1	181.6	3.30	153.56
IV-1	145.6	2.55	119.37
V-1	156.0	2.65	123.93
VI-1	132.8	2.10	98.86
VII-1	192.0	2.90	135.33
VIII-1	220.0	3.28	152.63
second run			
I-2	177.6	3.4	158.18
II-2	187.2	3.36	156.41
III-2	176.0	3.12	145.32
IV-2	179.2	3.11	144.87
V-2	183.4	3.15	146.65
VI-2	199.6	3.44	159.96
VII-2	171.5	2.58	120.92

\* obtained from the concentration-absorption profile in Figure 2.2

Table 2.13 Relationship between concentration and UV-Visible absorption of poly(2,4,5-TCPA)

concentration (ppm)	absorption peak height at 240 nm (cm)
3.768	0.420
9.421	0.880
23.55	2.750
58.88	6.340

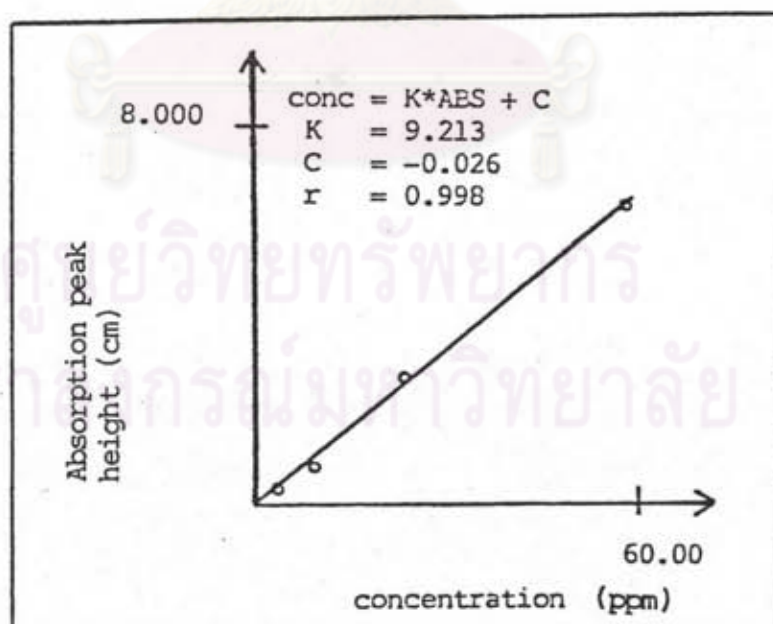


Figure 2.3 The concentration-absorption profile of poly(2,4,5-TCPA)

Table 2.14 Relationship between concentration and UV-Visible absorption of poly(2,4,5-TCPA-co-VAc)

Poly (2,4,5-TCPA-co-VAc)	concentration of copolymer (ppm)	absorption peak height at 240 nm(cm)	concentration of 2,4,5-TCPA (ppm)
first run			
I-1	38.4	3.75	34.52
II-1	49.6	4.70	43.27
III-1	66.4	6.10	56.17
IV-1	74.4	6.60	60.78
V-1	52.8	4.50	41.43
VI-1	50.4	4.14	38.12
VII-1	56.0	4.40	40.51
VIII-1	55.2	4.10	37.75
second run			
I-2	41.6	4.10	37.75
II-2	46.5	4.30	39.59
III-2	41.6	3.8	34.98
IV-2	48.7	4.53	41.71
V-2	64.7	5.39	49.63
VI-2	59.8	5.08	46.78
VII-2	52.9	4.10	37.74

\* obtained from the concentration-absorption profile in Figure 2.3

Table 2.15 Relationship between concentration and UV-Visible absorption of poly(4-Cl-3-MPA)

concentration (ppm)	absorption peak height at 240 nm (cm)
2.294	0.32
5.734	0.55
14.34	1.40
35.84	3.25
89.60	7.25

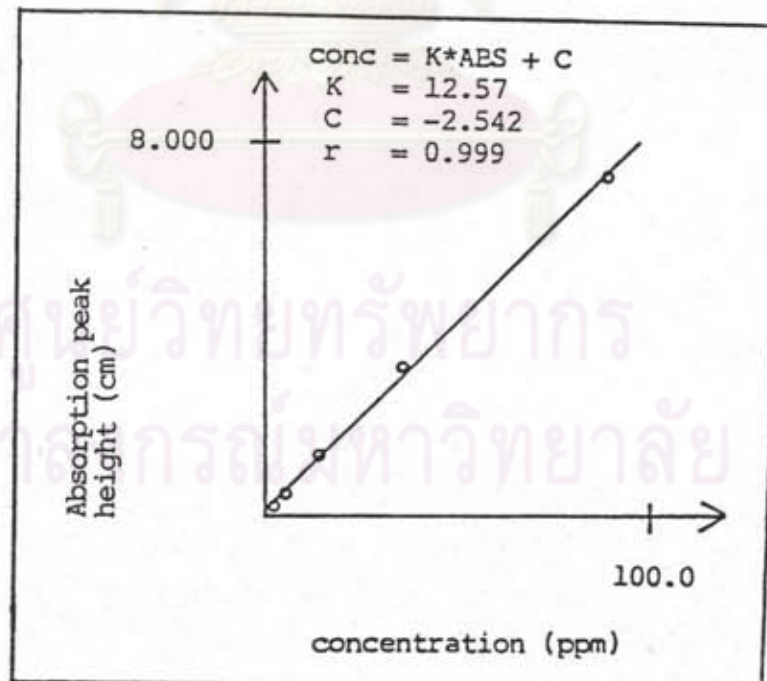


Figure 2.4 The concentration-absorption profile of poly(4-Cl-3-MPA)



Table 2.16 Relationship between concentration and UV-Visible absorption of poly(4-Cl-3-MPA-co-VAc)

Poly (4-Cl-3-MPA-co-VAc)	concentration of copolymer (ppm)	absorption peak height at 240 nm (cm)	concentration of 4-Cl-3-MPA (ppm)
first run			
I-1	60.8	4.51	54.15
II-1	100.8	7.12	86.96
III-1	57.6	4.10	48.99
IV-1	84.8	5.80	70.36
V-1	72.0	4.80	57.79
VI-1	63.2	4.00	47.74
VII-1	69.2	4.20	50.25
second run			
I-2	67.6	4.72	56.84
II-2	77.1	5.09	61.43
III-2	82.3	5.29	63.97
IV-2	49.5	3.12	36.71
V-2	80.8	5.04	60.79
VI-2	54.4	3.45	40.78
VII-2	65.4	3.85	45.88

\* obtained from the concentration-absorption profile in Figure 2.4

## 2.7 Preliminary study of copolymer composition by proton NMR

2,4,5-TPCA (0.1593 g), vinyl acetate (0.1334 g) and poly (methyl methacrylate) (0.0511 g) were mixed with AIBN (0.0070g) in deuterated benzene (2 ml) in the NMR tube (0.5 cm in diameter). After complete dissolution, the tube was inserted in NMR-probe whose temperature was set at 60 °C. The proton NMR spectrum of the mixture was then recorded after a certain length of time during 3 hours of reaction. The condition for proton NMR spectrometer was particular adjusted for this experiment as following.

Observed frequency	89.55	MHz
Obset frequency	54.3	kHz
Spectral width	1000	Hz
Resolution	0.2	Hz
Pulse width	30	s , 60 ° pulse angle
Pulse repetition	30	sec
No. of pulses	6	pulses
Mode of irradiation	Non decoupling	
Sample concentration	1.0	M
Temperature	60	° C

The polymer product remained in the mixture throughout the course of this study.