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APPENDIX I

In the copolymerization of two monomers to high polymer essentially all of the monomer is consumed in the propagation steps involving four different propagation rate constants [k_{11} , k_{22} , k_{12} , k_{21} in Equation (1)-(4)].



Monomer M_1 depleted by reaction (1) and (4), while monomer M_2 depleted by reaction (2) and (3). The rates of depletion of the two monomers which relate with their rates of entry into the copolymer chain are given by

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1] \quad (5)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2] \quad (6)$$

Dividing (5) by (6) yields ratio of rates at which monomer enters copolymer, which is basically the copolymer composition.

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \quad (7)$$

By assuming that the reactivity depends only on the terminal unit and making the steady-state assumption for these free-radical species.

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2] \quad (8)$$

The reactivity ratios are defined as $r_1 = \frac{k_{11}}{k_{12}}$, $r_2 = \frac{k_{22}}{k_{21}}$

equation (7) can be rearranged and combined with equation (8) to yield

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] (r_1[M_1] + [M_2])}{[M_2] ([M_1] + r_2[M_2])} \quad (9)$$

equation (9) is known as the copolymer equation where $\frac{d[M_1]}{d[M_2]}$ is the molar ratio in copolymer and $\frac{[M_1]}{[M_2]}$ is monomer charge ratio.

The copolymer equation [eq.(9)] can be transformed into mole fractions which are frequently more useful, f_1 , f_2 and F_1 , F_2 are mole fractions of monomer M_1 and M_2 in feed and copolymer, respectively.

$$f_1 = 1 - f_2 = \frac{[M_1]}{[M_1] + [M_2]} \quad (10)$$

$$F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad (11)$$

Combining eq.(10) and (11) with eq.(9) yields

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (12)$$

and

$$\frac{F_1}{F_2} = \frac{f_1 (r_1 f_1 + f_2)}{f_2 (r_2 f_2 + f_1)} \quad (13)$$

Equation (12) gives the copolymer composition as the mole fraction of monomer feeding and is often more convenient to use.

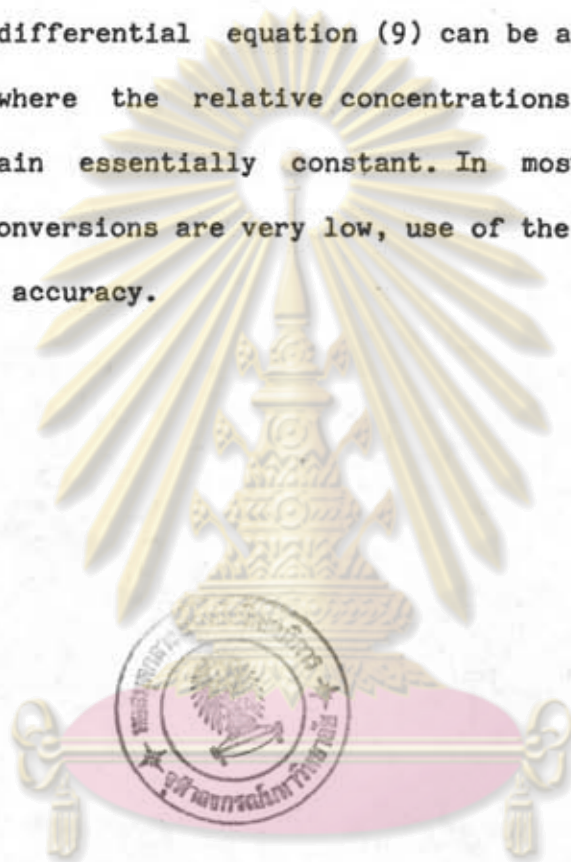
Most procedures for evaluating r_1 and r_2 involve the experimental determination of the copolymer composition for several different comonomer feed compositions. The experimental data can be analysed in several ways. One very useful method involves equation

(13) rearranged in the form

$$\frac{f(F-1)}{F} = r_1 \frac{f^2}{F} - r_2 \quad (14)$$

Equation (14) is known as the Fineman-Ross equation. The left side of this equation is plotted against the coefficient of r_1 to yield a straight line with slope = r_1 and intercept = $-r_2$.

The differential equation (9) can be applied directly in experiments where the relative concentrations of the unreacted monomers remain essentially constant. In most monomer systems, unless the conversions are very low, use of the integrated form is necessary for accuracy.



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APPENDIX II

Equation (9) in Appendix I has been integrated to yield

$$\frac{\log[M_2]}{[M_2]_0} = \frac{r_2}{1-r_2} \frac{\log[M_1][M_2]_0}{[M_2][M_1]_0} - \frac{(1-r_1r_2)}{(1-r_2)(1-r_1)} \frac{\log((r_1-1)([M_1]/[M_2])^{-r_2+1})}{(r_1-1)([M_1]_0/[M_2]_0)^{-r_2+1}} \dots(15)$$

where $[M_1]_0$ and $[M_2]_0$ represent the initial concentrations of monomer M_1 and M_2 , respectively. Direct application of eq.(15) is very difficult, but it has been transformed into

$$r_2 = \frac{\frac{\log[M_2]_0}{[M_2]} - \frac{1}{P} \frac{\log(1-P[M_1]/[M_2])}{(1-P[M_1]_0/[M_2]_0)}}{\frac{\log[M_1]_0}{[M_1]} + \frac{\log(1-P[M_1]/[M_2])}{(1-P[M_1]_0/[M_2]_0)}} \quad (16)$$

where

$$P = \frac{(1-r_1)}{(1-r_2)} \quad (17)$$

Equation (16) is known as the Mayo-Lewis equation for high conversion. The reactivity ratios, r_1 and r_2 , are evaluated graphically as follows. In a single copolymerization, the concentration of monomers at the start of reaction ($[M_1]_0, [M_2]_0$) and at the point where the reaction is stopped ($[M_1], [M_2]$) are determined experimentally and substituted in eq.(16). Since the equation deals only with ratios of concentrations, the concentrations may be expressed in moles per chosen weight or volume. Arbitrary (positive or negative) values of the parameter, P , chosen (at first by trial and error) to give points in a significant

region, are substituted in eq.(16), yielding corresponding values of r_2 ; r_1 is then calculated from equation (17) for each value of P . These values of P are now of no further use. In this study, values of r_1 and r_2 are plotted with r_1 as ordinate and r_2 as abscissa. The plot corresponding to a single experiment is a practically straight line. Other experiment over a wide range of monomer feed compositions is necessary to give an accurate solution for r_1 and r_2 , represented by the center of gravity of the triangular intersection of the three lines.

Sample calculation using equation(16)

For run VIII-80 of the MMA-4-C1-3-MPA system

$$r_2 = \frac{0.3125 - \frac{1}{P} \log(1-0.1236P)}{0.6813 + \frac{\log(1-0.1236P)}{(1-0.2891P)}}$$

For P equal to -0.3, -0.6 and 0.3, respectively, $r_2 = 0.3704, 0.3865$ and 0.3349 . Inserting these respective values of P and r_2 in eq.(17) gives $r_1 = 1.1888, 1.3680$ and 0.8004 . The linear equation of these points (r_1, r_2) is $r_1 = 11.460r_2 - 3.061$ with correlation coefficient = 0.999.

The basic program for determining r_1 and r_2 from equation (16) and(17).

15 REM M₁₀, M₂₀ = INITIAL MONOMER CONC ;M₁, M₂ =
MONOMER CONC AT A GIVEN MOMENT

20 INPUT "M₁₀=";M₁₀

22 INPUT "M₁=";M₁

24 INPUT "M₂₀=";M₂₀

30 INPUT "M₂=";M₂

```

60   INPUT "NO. OF LOOP Z = ";Z
70   FOR I = 1 TO Z
80   INPUT "P=";P
90   A = LOG(M20/M2)
100  B = (1/P)*(LOG((1-(P*X1))/(1-(P*X0))))
110  C = LOG(M10/M1)
120  D = LOG((1-(P*X1))/(1-(P*X0)))
130  PRINT "A=";A, "B=";B, "C=";C, "D=";D
140  R = ((A-B)/(C+D))
150  R2 = R
160  R1 = (1-(P*(1-R2)))
200  PRINT "I=";I, "P=";P, "R2=";R2, "R1=";R1
220  NEXT I
300  END

```

Sample output

I=1 P=0.3 R₂=0.3349604 R₁=0.8004881

P=? -0.3

I=2 P=-0.3 R₂=0.3704037 R₁=1.188879

P=? -1.2

I=3 P=-1.2 R₂=0.4162936 R₁=1.700448

Ok

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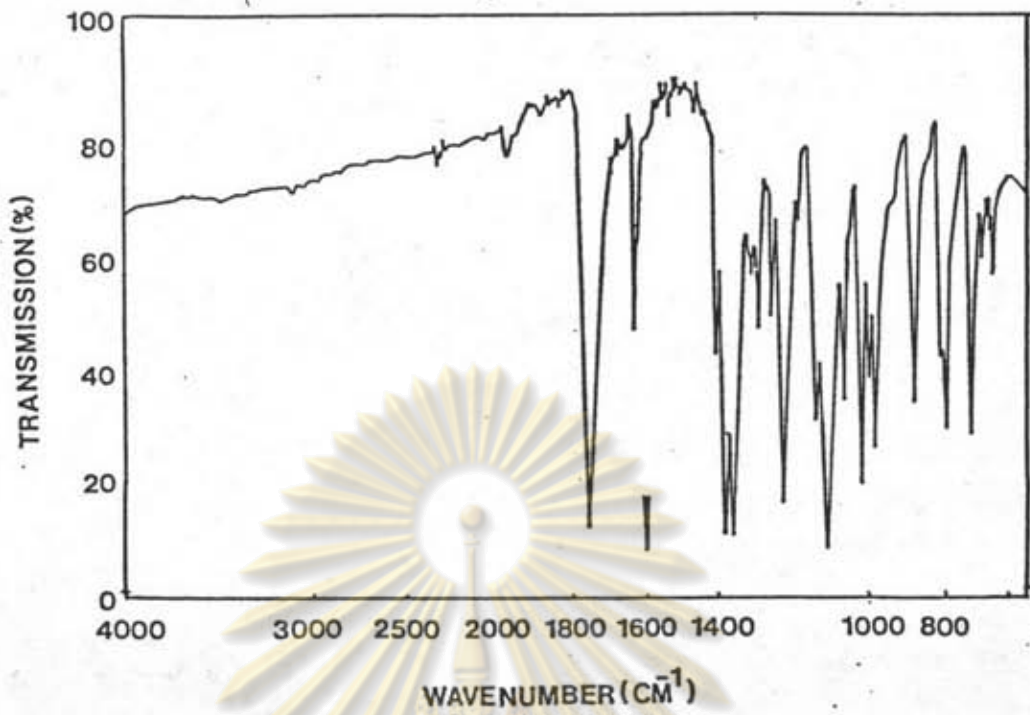


Fig. 1 IR spectrum of PCPA (KBr)

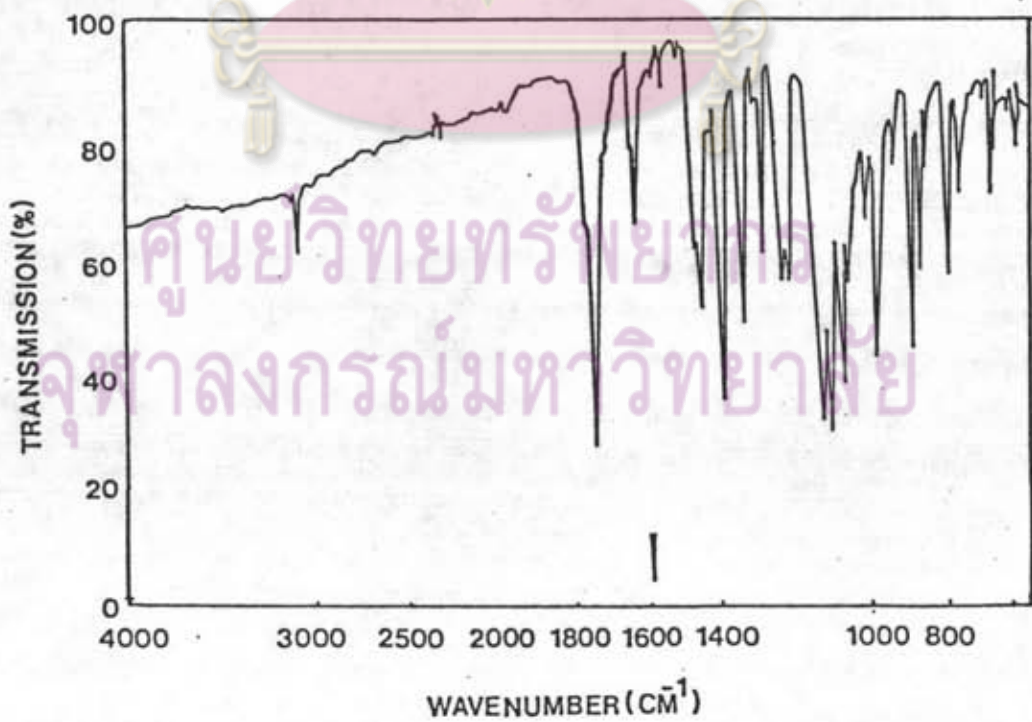


Fig. 2 IR spectrum of 2,4,5-TCPA (KBr)

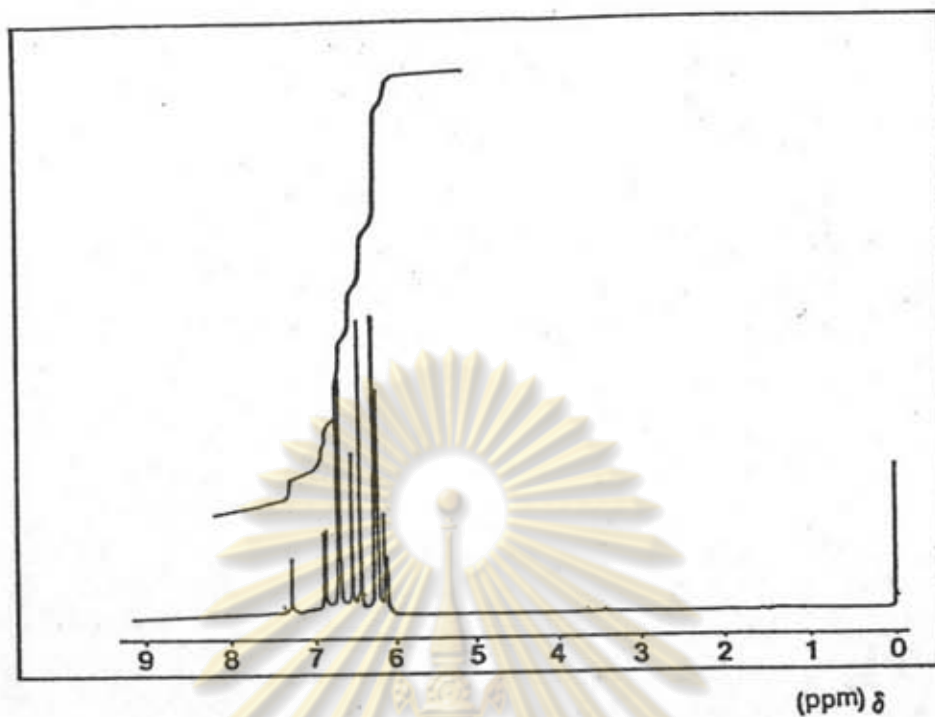


Fig. 5 $^1\text{H-NMR}$ spectrum of PCPA

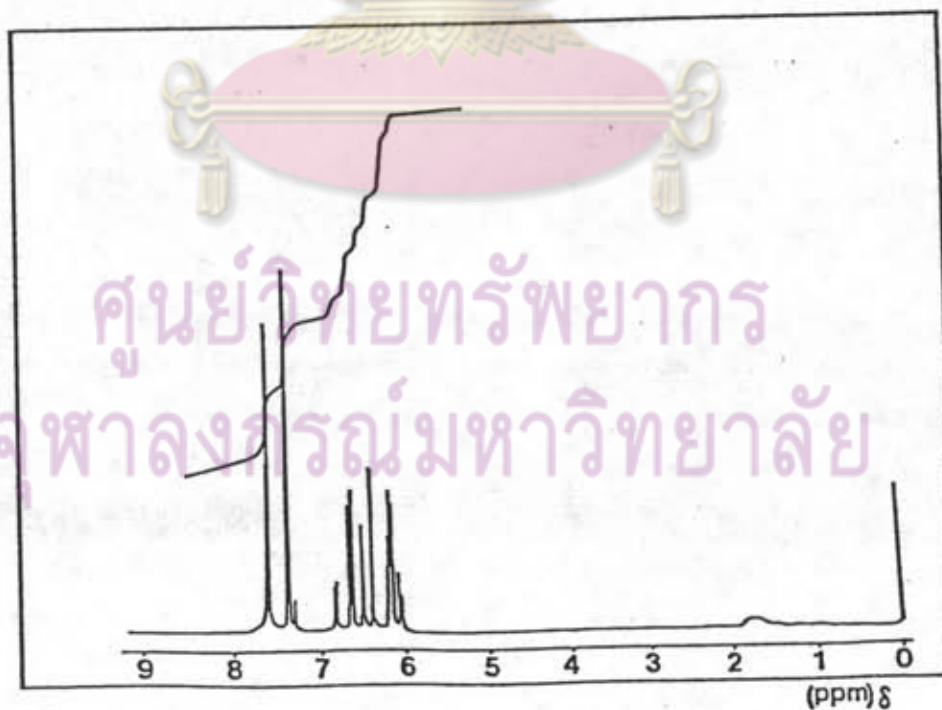


Fig. 6 $^1\text{H-NMR}$ spectrum of 2,4,5-TCPA

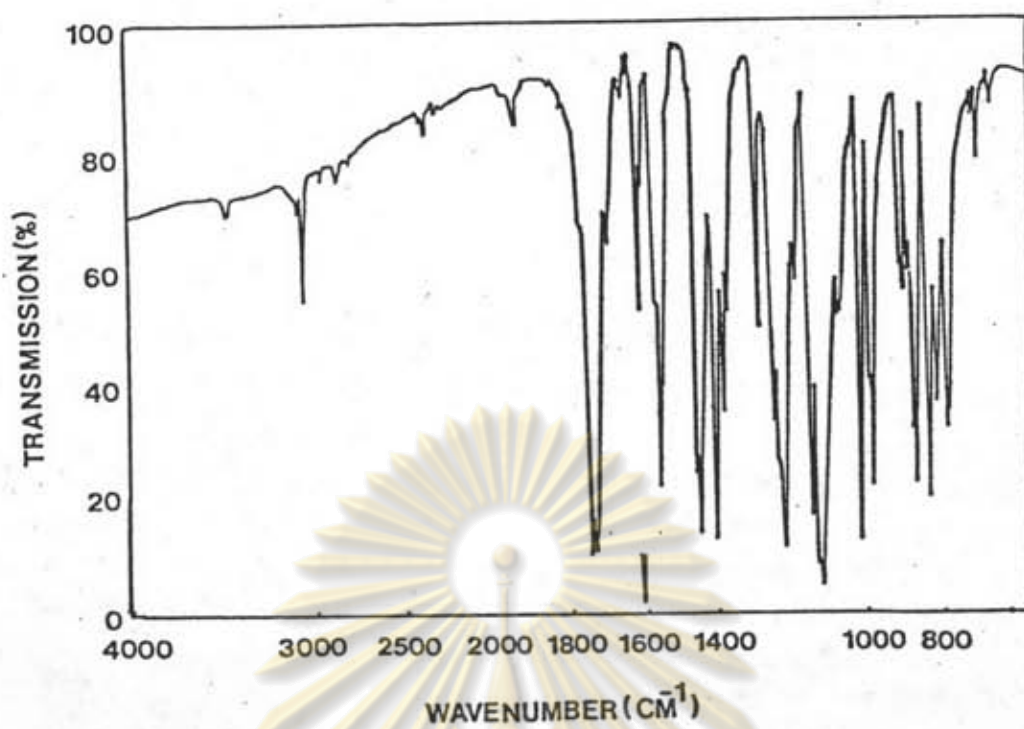


Fig. 3 IR spectrum of 2,4,6-TCPA (NaCl)

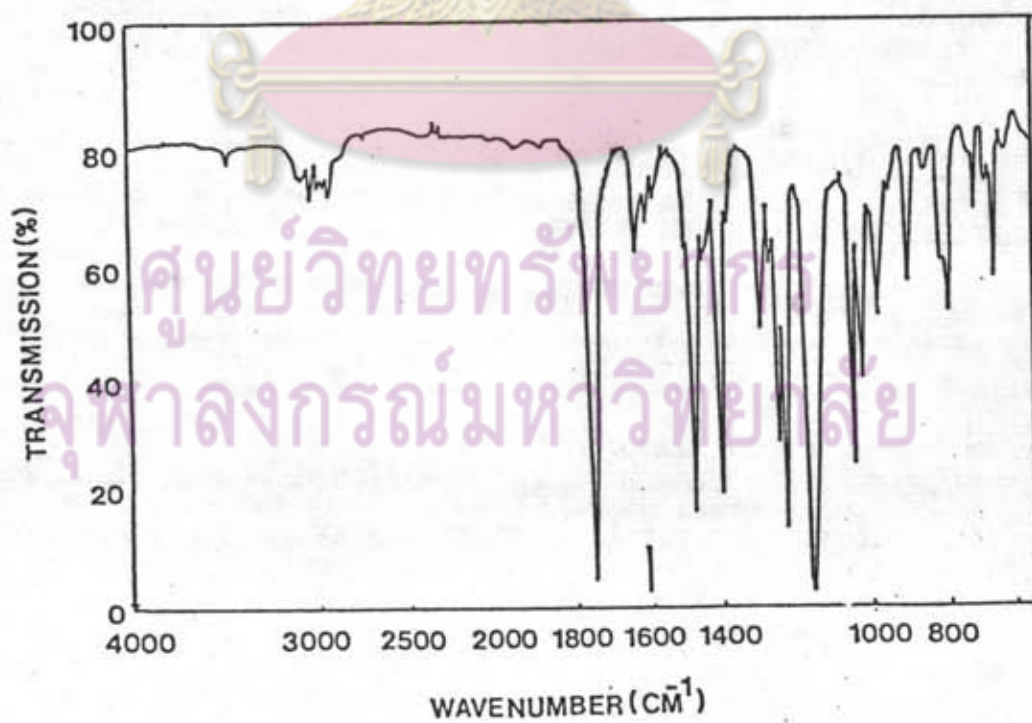


Fig. 4 IR spectrum of 4-Cl-3-MPA (NaCl)

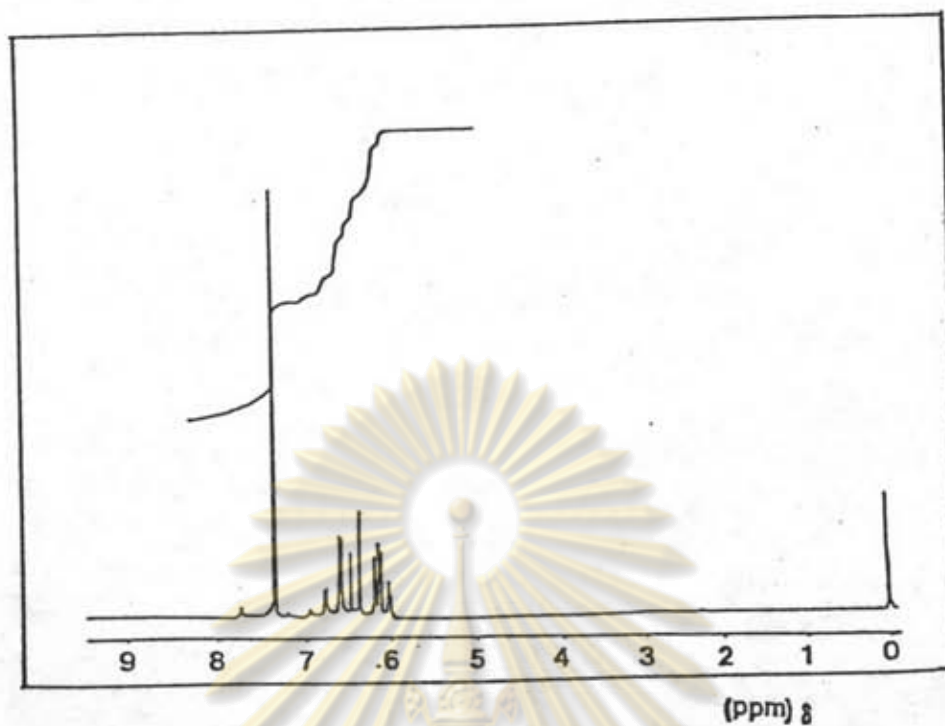


Fig. 7 $^1\text{H-NMR}$ spectrum of 2,4,6-TCPA

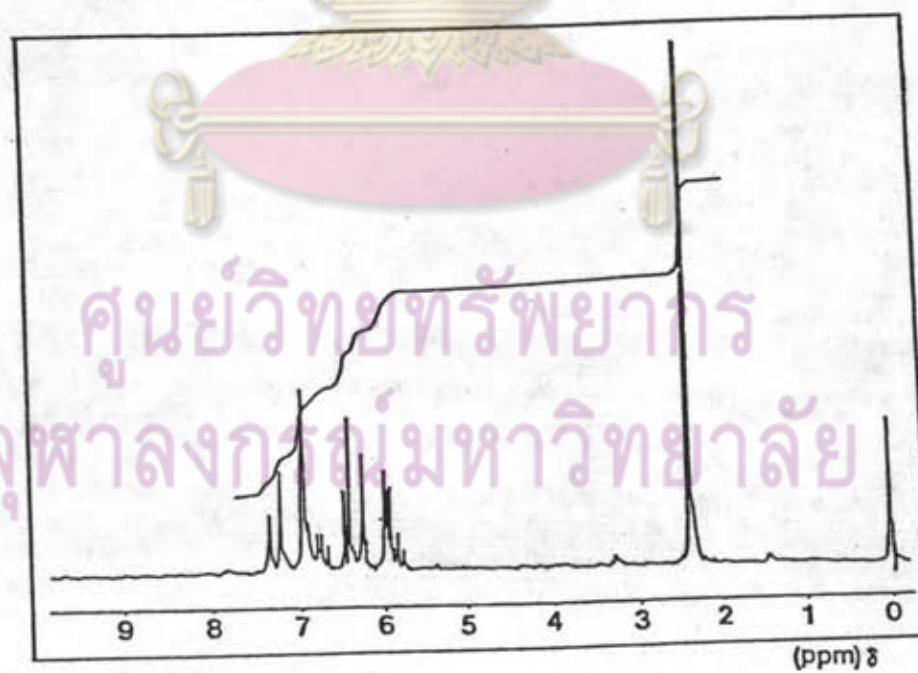


Fig. 8 $^1\text{H-NMR}$ spectrum of 4-Cl-3-MPA

VITA

Miss Penchit Chitnumsub was born on February, 10, 1963 in Samutsakorn. She received her B.Sc. in Chemistry from Faculty of Science, Chulalongkorn University in 1985. Since 1985, she has been a graduate student studying Organic Chemistry in Chulalongkorn University.



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