CHAPTER 2

KINETICS OF POLYCONDENSATION

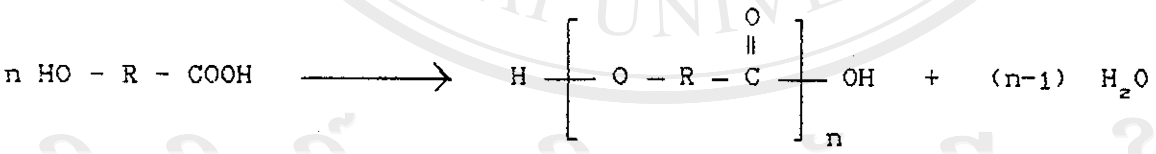
2.1 Introduction

2.1.1 Mechanisms of Polycondensation [2, 3, 18, 20-30]

Polycondensation or step-growth polymerisation proceeds via a step-by-step succession of one or more reactants (monomers) carrying at least two reactive functional groups. Each independent step causes the disappearance of two coreacting centres and creates a new linking unit between a pair of molecules. In this way, large molecules are produced by joining small ones together.

Thus, most of the polycondensation processes which occur via a suitable choice of condensation reactions, such as esterification, follow a step-growth mechanism in which chain growth occurs in a slow, stepwise manner. Initially, the monomer molecules react to form dimers. These dimers can then react with other monomer molecules to form trimers or with other dimers to form tetramers, and so on. This stepwise mechanism causes nearly complete conversion of the original reactants to low molecular weight products early in the reaction. High polymer forms later and more slowly because the concentration of reactive groups decreases as the length of the chains increase. Thus, the average molecular weight and degree of polymerisation of the product increase slowly over a period of time.

An important characteristic of condensation polymerisation is the fact that only linear polymers result from bifunctional reactants. Branched or crosslinked (three-dimensional) structures are formed only via the incorporation of tri- and higher functional reactants. When the monomers have a functionality of two or greater, the adduct formed by the coupling reaction will also have the same functionality and hence coupling reactions can continue to take place indefinitely. In general, bimolecular condensation can potentially lead to either inter- or intracmolecular reactions, the latter leading to ring formation. A good example of a typical condensation polymerisation is the self-condensation of a hydroxy acid which has difunctionality in a single monomer bearing two different functional groups. The product is a polyester.



$$n\ HO - R - COOH \longrightarrow H \left[O - R - \overset{\overset{O}{\|}}{C} \right]_n OH + (n-1)\ H_2O$$

The mechanism of the reaction may be described as follows. Initially, the first step is the disappearance of the monomer by intermolecular esterification to form dimers with elimination of water. As the dimer concentration builds up, trimers are formed in the reaction mixture from the condensation of monomer with dimer. Further reaction in the mixture of monomer, dimer and trimer results in the appearance of tetramer, pentamer and hexamer and, as these species in turn react, the mixture becomes increasingly complex. At any time after the reaction has commenced, the polymerisation can be represented by the series of elementary steps shown below :

$$\begin{array}{c} \text{HORCOOH} \\ \text{(monomer)} \end{array} + \left[\begin{array}{lcl} \text{HORCOOH} & \longrightarrow & \text{H(ORCO)}_2\text{OH} + \text{H}_2\text{O} \\ \text{H(ORCO)}_2\text{OH} & \longrightarrow & \text{H(ORCO)}_3\text{OH} + \text{H}_2\text{O} \\ \vdots & & \\ \text{H(ORCO)}_i\text{OH} & \longrightarrow & \text{H(ORCO)}_{i+1}\text{OH} + \text{H}_2\text{O} \end{array} \right.$$

$$\vdots$$

$$\vdots$$

$$\begin{array}{c} \text{H(ORCO)}_2\text{OH} \\ \text{(dimer)} \end{array} + \left[\begin{array}{lcl} \text{HORCOOH} & \longrightarrow & \text{H(ORCO)}_3\text{OH} + \text{H}_2\text{O} \\ \text{H(ORCO)}_2\text{OH} & \longrightarrow & \text{H(ORCO)}_4\text{OH} + \text{H}_2\text{O} \\ \vdots & & \\ \text{H(ORCO)}_i\text{OH} & \longrightarrow & \text{H(ORCO)}_{i+2}\text{OH} + \text{H}_2\text{O} \end{array} \right.$$

and so on.

Briefly, this set of equations can be summarized as :

$$\text{H(ORCO)}_i\text{OH} + \text{H(ORCO)}_j\text{OH} \longrightarrow \text{H(ORCO)}_{i+j}\text{OH} + \text{H}_2\text{O}$$

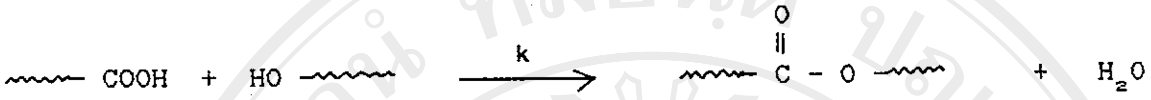
where any value of i can be taken with any value of j [24].

Since most condensation reactions are equilibria, it is obviously essential to provide some method for removal of the water or other by-products if high polymer molecular weights are to be obtained.

2.1.2 **Kinetics of Polycondensation** [2, 3, 18, 20-27]

Kinetic studies of simple esterification reactions show that, as the chain length of the acid component increases in a homogeneous series, the velocity constant for the reaction approaches an asymptotic limit. Results of this type are of fundamental importance to the study of condensation polymerisation since they imply that, for chains of any significant size, the effect of chain length on reactivity is negligible. From the concept of fundamental group reactivity independent of molecular weight or chain length, another fundamental assumption is that the reaction rate is independent of gross factors such as the diffusion rate and the viscosity of the medium. Although the mobility of the entire chain decreases with size, the intrinsic reactivity of the end group does not change. A long chain, then, may be considered simply as a diluent to the reactive end group. What this assumption amounts to kinetically is the proposition that all of the individual steps in a condensation polymerisation have equal rate constants.

Since the rate constant of the condensation polymerisation reaction (or reactivity of two functional groups) is independent of molecular size, it is possible to measure the rate of reaction simply by determining the concentration of functional groups as a function of time. For example, this may be done easily by titration of the unreacted carboxylic acid groups during a polyesterification reaction. Thus, in the polyesterification, the general reaction at any time t is as represented in the equation :



$$\sim\sim\sim\; \mathrm{COOH} + \mathrm{HO} \;\sim\sim\sim \xrightarrow{k} \sim\sim\sim\; \overset{\overset{\displaystyle O}{\|}}{C} - O \;\sim\sim\sim + H_2O$$

and, as the reaction proceeds, the functional groups -COOH and -OH disappear at the same rate. Therefore, samples can be removed from the reaction mixture at various time intervals and the concentration of the remaining carboxylic acid groups can be determined. Hence, the rate of polymerisation, R_p, expressed as the rate of loss of carboxylic acid groups, becomes

$$R_p = -\frac{d[\mathrm{COOH}]}{dt}$$

It is well known in organic chemistry that esterification reactions are catalysed by acids. Polyesterification is no exception. The rate law may then be written as

$$-\frac{d[\mathrm{COOH}]}{dt} = k\,[\mathrm{COOH}]\,[\mathrm{OH}]\,[\mathrm{catalyst}] \qquad (1)$$

The development of kinetic equations for polycondensation reactions depends to a large extent on the nature of the particular reaction being studied. Thus, different kinetic treatments are required for when an external acidic catalyst is or is not added. When a catalyst is added, it is naturally assumed that its concentration remains constant throughout the polymerisation.

2.1.2.1 Case 1 : Self-Catalysed Polyesterification or No External Acidic Catalyst Added

In the absence of an external catalyst, the polymerisation will still take place but a second molecule of the acid in the carboxylic acid groups themselves must function as the acid catalyst and, hence, the concentration of catalyst decreases with conversion. In this case, $[\mathrm{H}^{+}]$ will be proportional to the concentration of acid in the system and the kinetic rate expression becomes

$$-\frac{d[\mathrm{COOH}]}{dt} = k_3 [\mathrm{OH}] [\mathrm{COOH}]^2 \qquad (2)$$

where [COOH] and [OH] represent the total concentrations of carboxyl and hydroxyl groups in the reaction mixture at the particular instant of time and the subscript to k_3 denotes a third-order rate constant.

For an equimolar mixture of carboxyl and hydroxyl groups, as in the case of a single hydroxy carboxylic acid monomer, the COOH and OH groups disappear at the same rate. Therefore, at any time **t**,

$$[OH] = [COOH] = c$$

and the rate equation (2) for the uncatalysed reaction reduces to

$$-\frac{dc}{dt} = k_3 c^3 \qquad (3)$$

This equation can be readily integrated since at $t = 0$, $c = c_o$

$$\int_{c_o}^{c} -\frac{dc}{c^3} = \int_{0}^{t} k_3\, dt \qquad (4)$$

and so

$$\frac{1}{c^2} = \frac{1}{c_o^{\,2}} + 2\,k_3 t \qquad (5)$$

It is convenient to introduce the conversion, or the extent of reaction, **p**, in terms of the fraction of COOH groups (or OH groups) that have reacted at time **t**. Thus, if **p** is the fraction of COOH groups reacted, then

$$p = 1 - \frac{[COOH]}{[COOH]_o} \qquad (6)$$

or

$$p = 1 - \frac{c}{c_o}$$

$$c = c_o (1 - p) \tag{7}$$

Substitution of (7) into (5) gives the result

$$\frac{1}{(1 - p)^2} = 2 c_o^2 k_3 t + 1 \tag{8}$$

When plots are made of experimental values of $1/(1 - p)^2$ versus time t, it is found that (8) is not obeyed from $p = 0$ up to about $p = 0.80$ (i.e., for about the first 80% of the esterification of -COOH and -OH groups). After 80% conversion, the integrated rate expression (8) is obeyed very well. The deviations below 80% conversion are not unique to polyesterifications, however, because they are also observed for the simple esterifications that result when the dicarboxylic acid is replaced by a monocarboxylic acid.

Apparently, the major reason for the nonadherence to (8) below about 80% conversion is that the reaction medium is changing from one of pure reactants initially to one in which the ester product is the solvent. The prevalent (although not universal) view among polymer chemists is that the kinetics of condensation polymerisation have meaning only for the last 20% of the reaction when the reaction medium has become essentially invariant. Hence, the true reaction rate constants are to be obtained from the linear portion of the plot of $1/(1 - p)^2$ versus time [20].

2.1.2.2 Case 2 : Acid-Catalysed Polyesterification

If an acid catalyst is added to the polyesterification system (which contains equal quantities of COOH and OH), under these conditions, the concentration of acid catalyst $[H^+]$ remains constant throughout the polyesterification so that equation (1) becomes :

$$-\frac{d[COOH]}{dt} = [COOH]^2 \left(k_3 [COOH] + k_{cat} [H^+] \right) \qquad (9)$$

where k_3 is the rate constant for the uncatalysed reaction and k_{cat} is the rate constant for the catalysed reaction. From the definition of a catalyst, the $[H^+]$ does not change throughout the course of the reaction and generally $k_{cat} [H^+] >> k_3 [COOH]$. As a result, (9) usually can be approximated by (10), in which the second-order rate constant k_2 is related to k_{cat} by the expression $k_2 = k_{cat} [H^+]$, so that

$$-\frac{d[COOH]}{dt} = k_2 [COOH]^2 \qquad (10)$$

or

$$-\frac{dc}{dt} = k_2 c^2 \qquad (11)$$

where $[COOH] = c$. Integration of (11) leads to

$$\frac{1}{c} = \frac{1}{c_o} + k_2 t \qquad (12)$$

Substitution of (7) then gives

$$\frac{1}{1 - p} = k_2 c_o t + 1 \qquad (13)$$

which is a description of the dependence of the conversion p on reaction time t for a catalysed polyesterification. Thus, $1/(1 - p)$ is linear with time t provided that k_2 does not vary.

2.1.3 Time Dependence of the Average Degree of Polymerisation and the Average Molecular Weight [19, 20, 27]

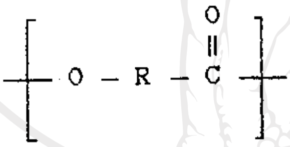
Consider the particular case under investigation in this project of the polyesterification of a bifunctional hydroxy acid monomer containing both functional groups necessary for reaction. Under such conditions, the initial number of COOH groups is equal to the total number of molecules present initially in the system. As a consequence of each esterfication reaction :

$$\text{HO-R-COOH} + \text{HO-R-COOH} \longrightarrow \text{HO-R-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-R-COOH} + H_2O$$

one COOH group disappears, but the total number of molecules present is unchanged. However, if the water formed in the reaction is removed (and this must be done in order to obtain high polymer), then for each COOH group lost, one molecule is removed from the system. Thus, with an efficient removal of water, the number of COOH groups present is equal to the number of molecules present, not only initially, but throughout the reaction. If **N** is the total number of molecules in the system and **V** is the volume, it is possible to write

$$\frac{N}{V} = [COOH] = [COOH]_o\,(1 - p) \qquad (14)$$

The repeating unit of each polyester molecule formed from the monomer HO-R-COOH, namely :



$$\left[-O-R-\overset{\overset{\large O}{\|}}{C}- \right]$$

contains the central structural unit from the hydroxy acid. Structural units are never removed from the system ; therefore, the total number of structural units present at all times is a constant and is equal to the initial number of molecules. Hence, in view of (14), it is also possible to write

$$\frac{N_{\text{structural units}}}{V} = [COOH]_o \qquad (15)$$

The average degree of polymerisation of the system, $\overline{DP}$, is defined as the average number of structural units per molecule or the ratio of the number of starting molecules to the number of product molecules, i.e.

$$\overline{DP} = \frac{\text{number of molecules present initially}}{\text{number of molecules remaining after time } t}$$

$$\overline{DP} = \frac{[COOH]_o}{[COOH]} = \frac{c_o}{c} = \frac{c_o}{c_o\ (1 - p)} = \frac{1}{1 - p} \qquad (16)$$

If M_o is the molecular weight of the structural unit that makes up a repeat unit, then the number-average molecular weight, $\overline{M}_n$, of the polyester is given by

$$\overline{M}_n = \frac{M_o}{1 - p} + 18 \qquad (17)$$

where 18 is added to account for unreacted groups at the end of each polyester chain.

By combining (17) with (8) and (13), the dependence of the polymer molecular weight on reaction time for both the uncatalysed and catalysed polyesterifications respectively is obtained as shown by

Uncatalysed : $\overline{M}_n = M_o (1 + 2 [COOH]_o^2 k_3 t)^{1/2} + 18$ (18)

Catalysed : $\overline{M}_n = M_o (1 + [COOH]_o k_2 t) + 18$ (19)

The kinetic expressions (8) and (13) are obeyed for conversions above about 80%. For conversions of this magnitude, it is generally true that the values of t are sufficiently large that unity in the parentheses of (18) and (19) may be neglected. The approximate equations :

Uncatalysed : $\overline{M}_n \approx M_o [COOH]_o (2k_3)^{1/2} t^{1/2}$ (20)

Catalysed : $\overline{M}_n \approx M_o [COOH]_o k_2 t$ (21)

are then obtained. These equations may be used with the rate constant data to construct curves of number-average molecular weights as a function of time.

2.2 Experimental Aspects [1, 2, 15, 31-35]

2.2.1 Chemicals and Apparatus

(a) Chemicals

Table 2.1 : Chemicals used in the kinetic experiments.

Chemical	Formula	Grade	Supplier
Antimony trioxide	Sb_2O_3	> 98%	Fluka
Benzoic acid	C_6H_5COOH	99.5%	BDH
Benzyl alcohol	$C_6H_5CH_2OH$	> 99.0%	Fluka
Chloroform	$CHCl_3$	Lab	Merck
Ethanol, absolute	C_2H_5OH	99%	Merck
Glycolic acid	$HOOCCH_2OH$	99%	Fluka
Phenol red	–	–	BDH
Sodium hydroxide	NaOH	AR	Merck
p-Toluenesulfonic acid monohydrate	$CH_3C_6H_4SO_3H.H_2O$	99%	Aldrich

(b) Apparatus

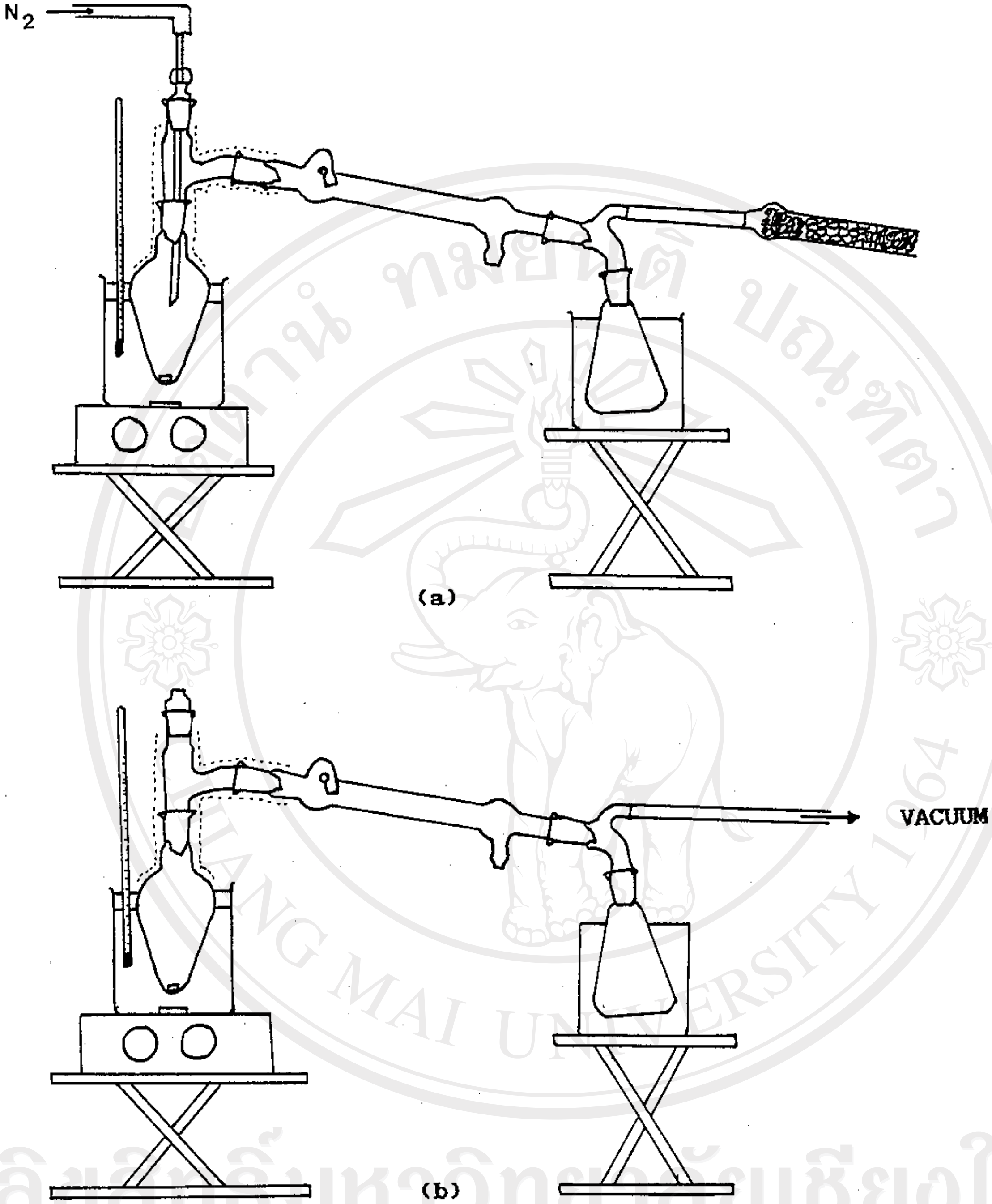


Fig. 2.1 : Apparatus used in the polyesterification of glycolic acid :

(a) polyesterification under an atmospheric pressure of nitrogen gas;

(b) polyesterification under reduced pressure.

2.2.2 Polyesterification Methodology Used in This Work

One method of making a condensation polymer is to heat the monomer above its melting point with a catalyst, if required. By-products are removed from the reaction mixture as they are formed. This method is called "melt or bulk polymerisation" and is usually carried out at high temperature. In addition, the monomer and the polymer must be thermally stable at the reaction temperature, and the polymer must be fusible. Melt polymerisation is usually started at ordinary pressure and then later continued under vacuum to achieve high molecular weights by shifting the reaction equilibrium to the product side. Melt polymerisation is used widely, both commercially and in the research laboratory. This is the method that was used in the polyesterification of glycolic acid studied in this work.

The kinetic course of the reaction can be easily followed by taking samples from the reaction mixture periodically and titrating the unreacted carboxylic acid groups still present. The extent of reaction, p , is then calculated directly from the carboxyl group titre. The most successful procedure for carboxyl end-group titration used in this work was a modification of Pohl's method [34] in which the hot (160-180 °C) polymer solution in benzyl alcohol was poured into chloroform to yield either a cooled (< 50 °C) metastable solution or a fine suspension which could be satisfactorily titrated with alkali in the presence of a suitable indicator [15]. This modified cooled titration procedure is described in detail in the following section 2.2.3.1 : RUN 1.

2.2.3 Uncatalysed Polyesterification of Glycolic Acid

The apparatus used for the uncatalysed polyesterification of glycolic acid to form poly(glycolic acid) was as shown in Fig. 2.1. The water by-product formed on heating was initially removed from the reaction mixture by passing a stream of dry nitrogen gas through the system at atmospheric pressure. A vacuum pump was then connected to the system to reduce the pressure in order to facilitate the further removal of water. According to the kinetic theory of polycondensation previously described, in the absence of added catalyst, the COOH groups of the glycolic acid monomer must themselves act as the acid catalyst. Since the COOH groups are also reactants in the polyesterification, the kinetics of the reaction are therefore third-order in this case. Polymer COOH end-group concentrations were determined by the modified cooled titration method previously mentioned.

2.2.3.1 RUN 1 : At 150 °C under an Atmospheric Pressure of Nitrogen Gas

Approximately 0.5 g of glycolic acid was weighed accurately into a 50 ml pear-shaped flask, connected as shown in Fig. 2.1 (a). The flask and still-head were wrapped with an electric heating tape. The raction flask was immersed in a silicone oil bath at 150 °C ($\pm$ 5 °C) and a slow stream of dry nitrogen gas continuously passed through the system. Heating was continued for varying periods of up to 7 hours, during which time the acid melted and water was evolved. At the end of the reaction period, the flask was removed from the heating bath and allowed to cool to room temperature. The reaction mixture was then rapidly dissolved in about 5-10 ml of benzyl alcohol (more if necessary) at about 160-180 °C. When dissolution was complete, the solution was immediately poured into a 100 ml conical flask containing distilled chloroform in a 1:1 volume/volume ratio at room temperature. The original flask was washed out with a further 5.0 ml of benzyl alcohol which was then transferred to the polymer solution. Five drops of a freshly prepared 0.1% w/v solution of phenol red in absolute ethanol were added as indicator and the mixture stirred. The solution was then titrated with standardized 0.1 M sodium hydroxide in benzyl alcohol until a stable end-point (yellow ⟶ purple) was reached. A blank run on the mixed solvent alone (10.0 ml of benzyl alcohol heated at 160 °C for about 30 minutes before being poured into 10.0 ml of distilled chloroform) gave a background titre which was subtracted from those of the samples solutions.

The results obtained at various time intervals are given in Table 2.2 and analysed in Fig. 2.2 and Fig. 2.3.

Results and Data Analysis

Sample Calculation : Time = 120 mins

weight of glycolic acid = 0.509 g

weight of poly(glycolic acid) sample = 0.385 g

concentration of NaOH solution = 0.0982 M

volume of NaOH used in titration with sample = 7.16 ml

volume of NaOH used in titration with blank = 0.02 ml

corrected volume of NaOH used in titration with sample

= 7.16 - 0.02 ml

= 7.14 ml

moles of NaOH used $= \frac{0.0982 \times 7.14}{1000}$

$= 7.01 \times 10^{-4}$ mole

= g-equilvalents of COOH groups remaining in sample

thus, COOH remaining in 0.385 g of PGA = 7.01×10^{-4} g-equiv.

hence, $[COOH] = \frac{7.01 \times 10^{-4}}{0.385}$ $g.equiv.g^{-1}$

$[COOH] = 1.82 \times 10^{-3}$ $g.equiv.g^{-1}$

Calculation of initial COOH groups in the glycolic acid monomer :

molecular weight of glycolic acid = 76.05

$$\text{moles of glycolic acid used} = \frac{0.509}{76.05}$$

$$= 6.69 \times 10^{-3} \quad \text{moles}$$

Since 1 molecule of glycolic acid contains 1 COOH functional group :

$$\text{initial moles of glycolic acid} = \text{initial g-equiv. of COOH}$$

$$= [\mathrm{COOH}]_o$$

hence,

$$[\mathrm{COOH}]_o = \frac{6.69 \times 10^{-3}}{0.509} \quad \text{g-eqiuv.g}^{-1}$$

$$\mathbf{[COOH]_o = 1.31 \times 10^{-2} \quad g.equiv.g^{-1}}$$

Calculation of fraction of COOH groups reacted, **p :**

$$p = 1 - \frac{[\mathrm{COOH}]}{[\mathrm{COOH}]_o}$$

$$= 1 - \frac{1.82 \times 10^{-3}}{1.31 \times 10^{-2}}$$

$$p = 0.861$$

$$p = \mathbf{86.1\%} \quad \text{conversion}$$

The average degree of polymerisation, $\overline{DP}$, is then given by

$$\overline{DP} = \frac{[COOH]_o}{[COOH]} = \frac{[COOH]_o}{[COOH]_o\ (1-p)} = \frac{1}{1-p}$$

which, for this particular example, gives

$$\overline{DP} = \frac{1}{1 - 0.861}$$

$$\overline{DP} = 7.19$$

It follows from this that the number-average molecular weight of the polymer, $\overline{M}_n$, equals

$$\overline{M}_n = \frac{M_o}{1-p} + 18$$

where M_o is the molecular weight of the structural repeat unit of poly (glycolic acid), $\left[-O-CH_2-CO- \right]_n$, = 58

$$\text{hence,} \quad \overline{M}_n = \left[58 \times \frac{1}{1-p} \right] + 18$$

$$= (58 \times 7.19) + 18$$

$$\overline{M}_n = 435$$

<u>Table 2.2</u> : **Data obtained from RUN 1 : uncatalysed polyesterification of glycolic acid at 150 °C/atm/N_2.**

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)^2}$	$\overline{DP}$	$\overline{M}_n$
30	0.500	0.404	0.0989	14.82	0.05	0.724	13.1	3.63	228
40	0.504	0.426	0.0930	16.64	0.05	0.724	13.1	3.62	228
50	0.500	0.435	0.0930	14.98	0.05	0.757	16.9	4.11	256
60	0.502	0.409	0.0989	11.91	0.05	0.782	21.0	4.58	284
80	0.507	0.381	0.0914	9.04	0.02	0.835	36.7	6.06	370
90	0.502	0.372	0.0932	8.02	0.04	0.847	42.7	6.54	397
100	0.505	0.401	0.0982	7.90	0.02	0.853	46.3	6.80	412
120	0.509	0.385	0.0982	7.16	0.02	0.861	51.8	7.19	435
150	0.505	0.378	0.0982	7.04	0.02	0.861	51.8	7.19	435
180	0.502	0.374	0.0982	6.62	0.02	0.868	57.4	7.58	458
210	0.503	0.360	0.0982	6.09	0.02	0.873	62.0	7.87	474
240	0.553	0.421	0.1090	6.86	0.02	0.865	54.9	7.41	448
270	0.517	0.375	0.1090	5.58	0.02	0.877	66.1	8.13	490
300	0.592	0.490	0.0982	7.80	0.02	0.881	70.6	8.40	505
330	0.576	0.424	0.1090	5.92	0.02	0.884	74.3	8.62	518
360	0.649	0.479	0.0982	8.52	0.02	0.867	56.5	7.52	454
420	0.576	0.435	0.1090	7.61	0.02	0.855	47.6	6.90	418

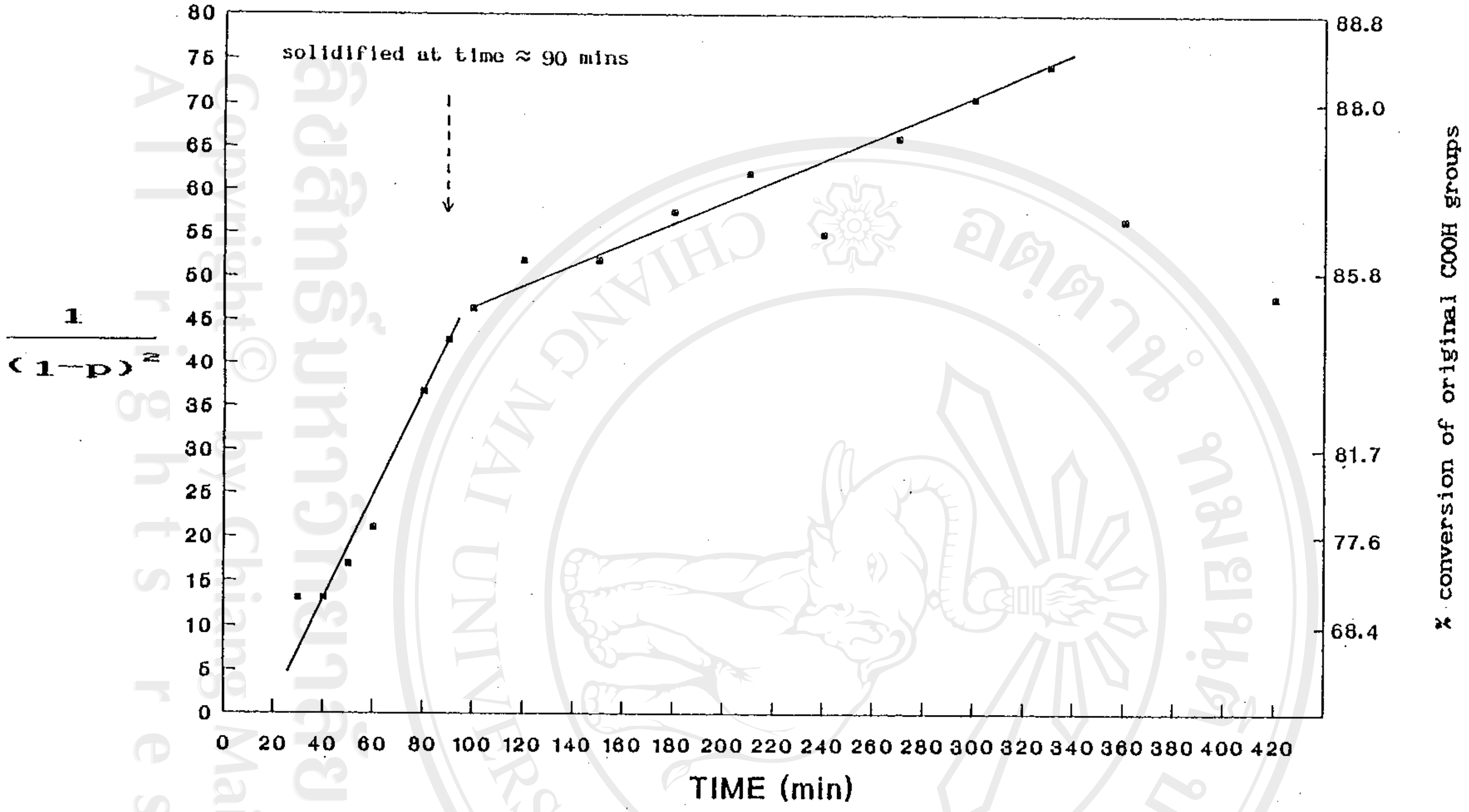
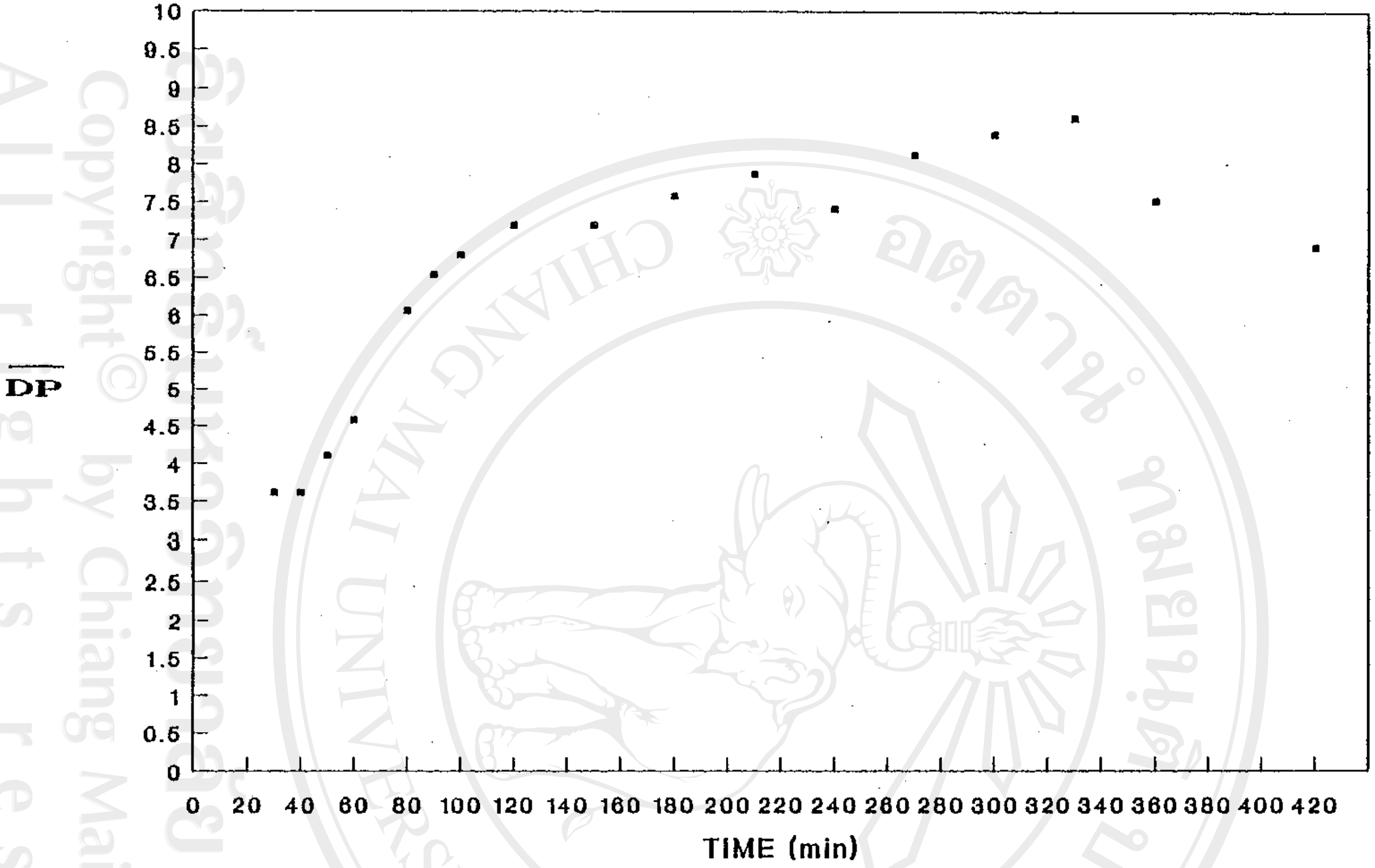


Fig. 2.2 : Third-order rate plot for the uncatalysed polyesterification of glycolic acid at 150 °C/atm/N_2; RUN 1.



<u>Fig. 2.3</u> : Average degree of polymerisation of poly(glycolic acid) as a function of time at 150 °C/atm/N_2 with no catalyst added; RUN 1.

2.2.3.2 RUN 2 : At 150 °C/atm/N_2 followed by at 180 °C/Reduced Pressure

For RUN 2, a modification was made to the conditions used in the previous RUN 1. In this modification, when the reaction flask was heated at 150 °C under an atmospheric pressure of nitrogen gas, the heating was continued only until the reaction mixture solidified. The reaction flask was then quickly transferred to another silicone oil heating bath at 180 °C and the pressure reduced to about 2-4 mbar by connection to a vacuum pump. The remaining experimental procedure was exactly the same as previously described in RUN 1. The conditions for RUN 2 can therefore be summarized as :

STAGE 1		STAGE 2
temperature = 150 °C time = until solidification pressure = atm/N_2 gas	⟶	temperature = 180 °C time = variable pressure = 2-4 mbar

The results obtained and data analysis are presented in Table 2.3, Fig. 2.4 and Fig. 2.5.

Table 2.3 : Data obtained from RUN 2 : Uncatalysed polyesterification of glycolic acid at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2).

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)^2}$	$\overline{DP}$	$\overline{M}_n$
10	0.593	0.444	0.0936	8.78	0.02	0.859	50.3	7.09	429
30	0.522	0.318	0.0936	5.90	0.02	0.868	57.4	7.58	458
60	0.540	0.362	0.0936	5.72	0.02	0.888	79.7	8.93	536
90	0.562	0.231	0.0936	2.14	0.02	0.934	229.6	15.2	900
120	0.585	0.373	0.0936	2.86	0.02	0.946	342.9	18.5	1091
150	0.529	0.345	0.0936	2.70	0.02	0.944	318.9	17.8	1050
210	0.525	0.273	0.1090	2.17	0.02	0.944	318.9	17.8	1050
300	0.539	0.197	0.1090	1.29	0.02	0.954	472.6	21.7	1277
360	0.539	0.290	0.1090	1.82	0.02	0.949	384.5	19.6	1155
420	0.602	0.268	0.0877	2.12	0.03	0.948	369.8	19.2	1132

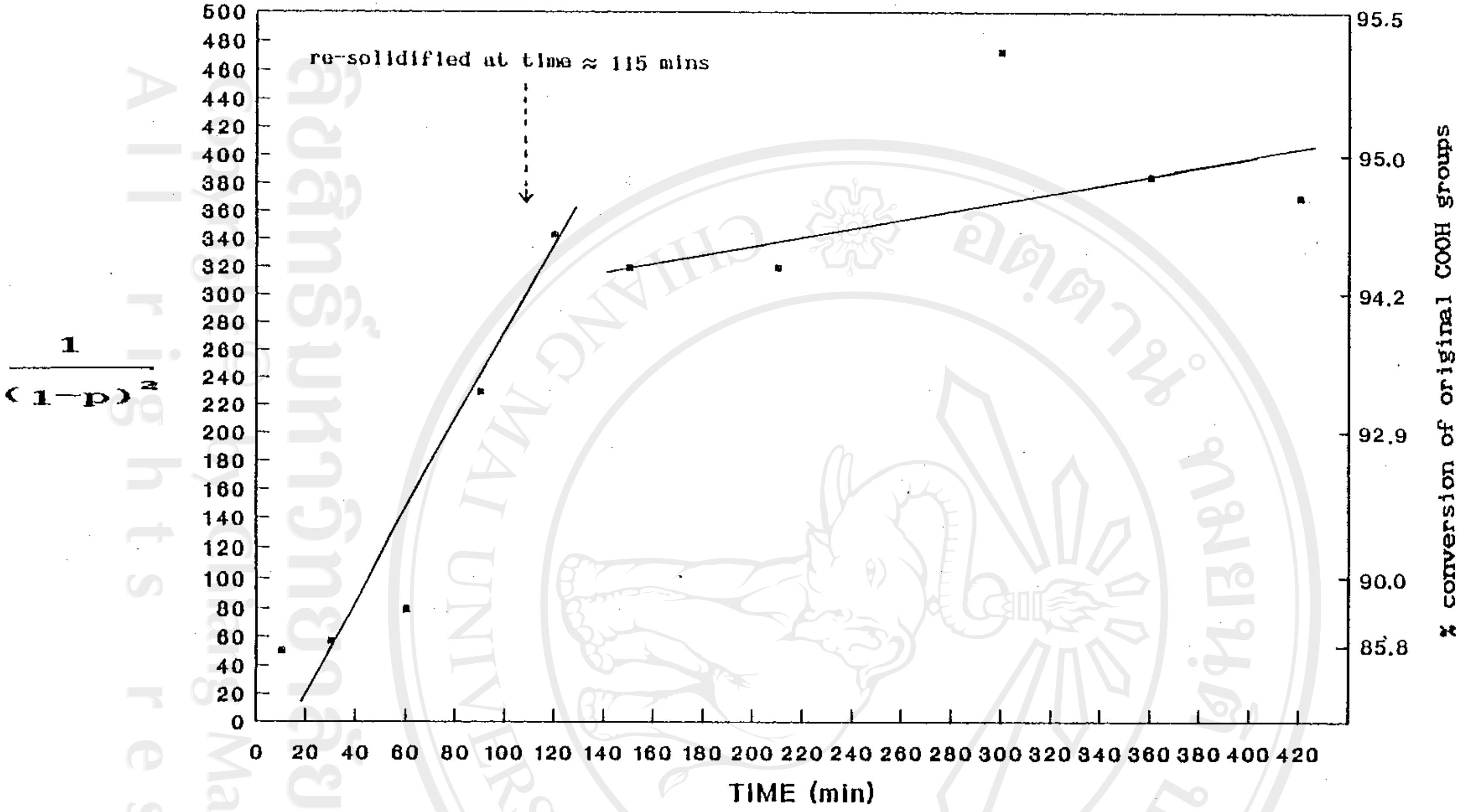
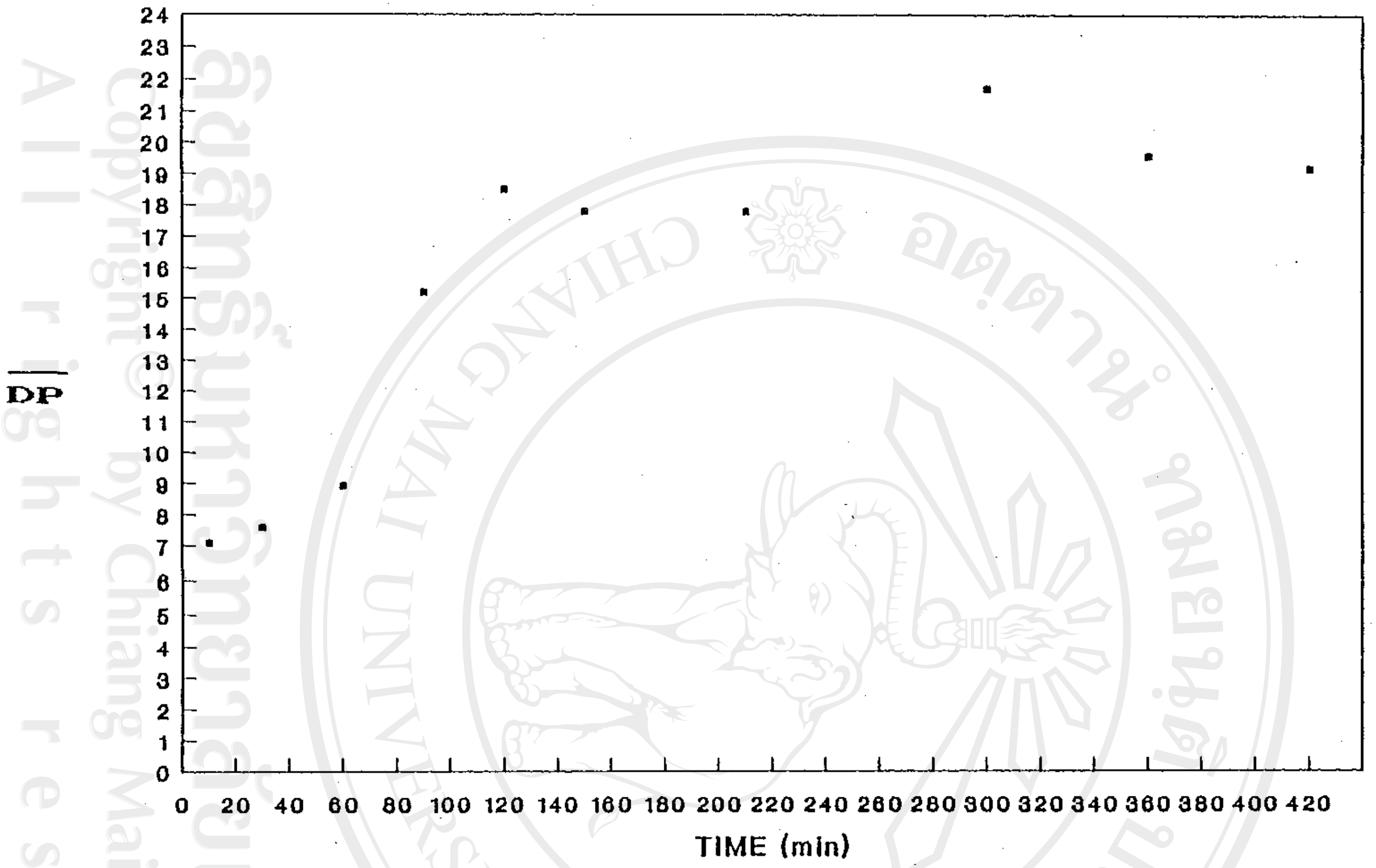


Fig. 2.4 : Third-order rate plot for the uncatalysed polyesterification of glycolic acid at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2); RUN 2.



<u>Fig. 2.5</u> : Average degree of polymerisation of poly(glycolic acid) as a function of time at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2) with no catalyst added; RUN 2.

2.2.3.3 RUN 3 : At 150 °C/atm/N_2 followed by at 200 °C/Reduced Pressure

For RUN 3, the reaction temperature was increased to 200 °C during the second stage of the synthesis which was carried out under reduced pressure. Also, an orthophosphoric acid heating bath was used instead of the silicone oil bath. Apart from this, all other conditions and experimental procedures were the same as previously described in RUN 2. Thus, the conditions for RUN 3 can be summarized as :

STAGE 1		STAGE 2
temperature = 150 °C time = until solidification pressure = atm/N_2 gas	⟶	temperature = 200 °C time = variable pressure = 2-4 mbar

The results obtained and data analysis are presented in Table 2.4, Fig. 2.6 and Fig. 2.7.

Table 2.4 : Data obtained from RUN 3 : uncatalysed polyesterification of glycolic acid at 200 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2).

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)^2}$	$\overline{DP}$	$\overline{M}_n$
10	0.529	0.366	0.0877	7.41	0.03	0.865	54.9	7.41	448
30	0.517	0.233	0.0936	2.73	0.02	0.917	145.2	12.0	714
60	0.588	0.369	0.0877	3.30	0.03	0.941	287.3	16.9	998
90	0.548	0.261	0.0936	2.02	0.02	0.945	330.6	18.2	1074
120	0.528	0.152	0.0936	1.06	0.02	0.951	416.5	20.4	1201
150	0.695	0.438	0.0877	2.98	0.03	0.955	493.8	22.2	1306
180	0.621	0.249	0.0877	1.63	0.03	0.957	540.8	23.2	1364
210	0.536	0.311	0.0936	1.80	0.02	0.959	594.9	24.4	1433
240	0.584	0.364	0.0877	1.90	0.03	0.966	865.0	29.4	1723
300	0.642	0.247	0.0877	1.05	0.03	0.972	1275.5	35.7	2089
360	0.557	0.336	0.0877	1.39	0.03	0.973	1371.7	37.0	2164
420	0.558	0.214	0.0877	0.80	0.03	0.976	1736.1	41.7	2437

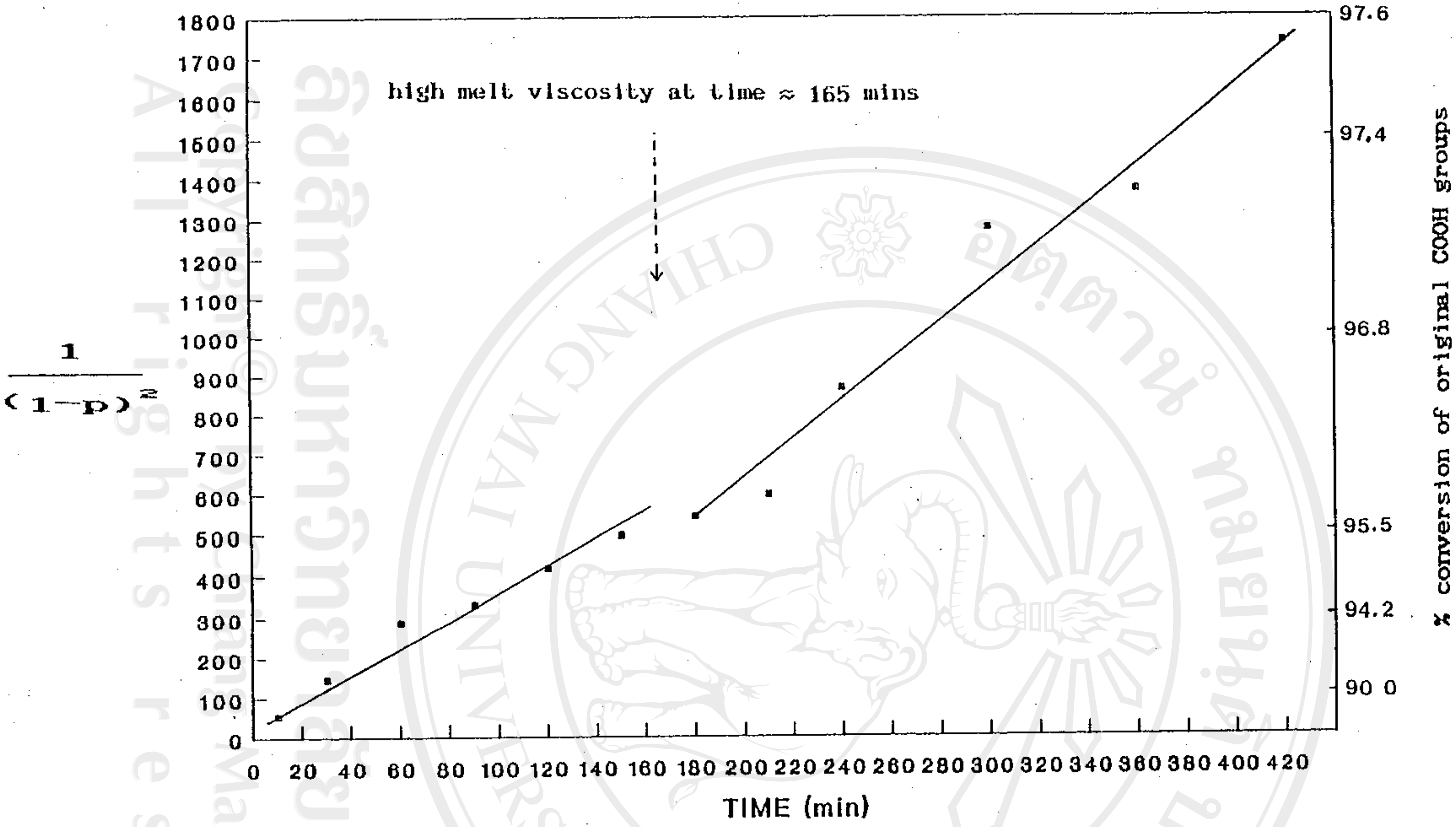


Fig. 2.6 : Third-order rate plot for the uncatalysed polyesterification of glycolic acid at 200°C/reduced pressure (after initial solidification at 150°C/atm/N_2); RUN 3.

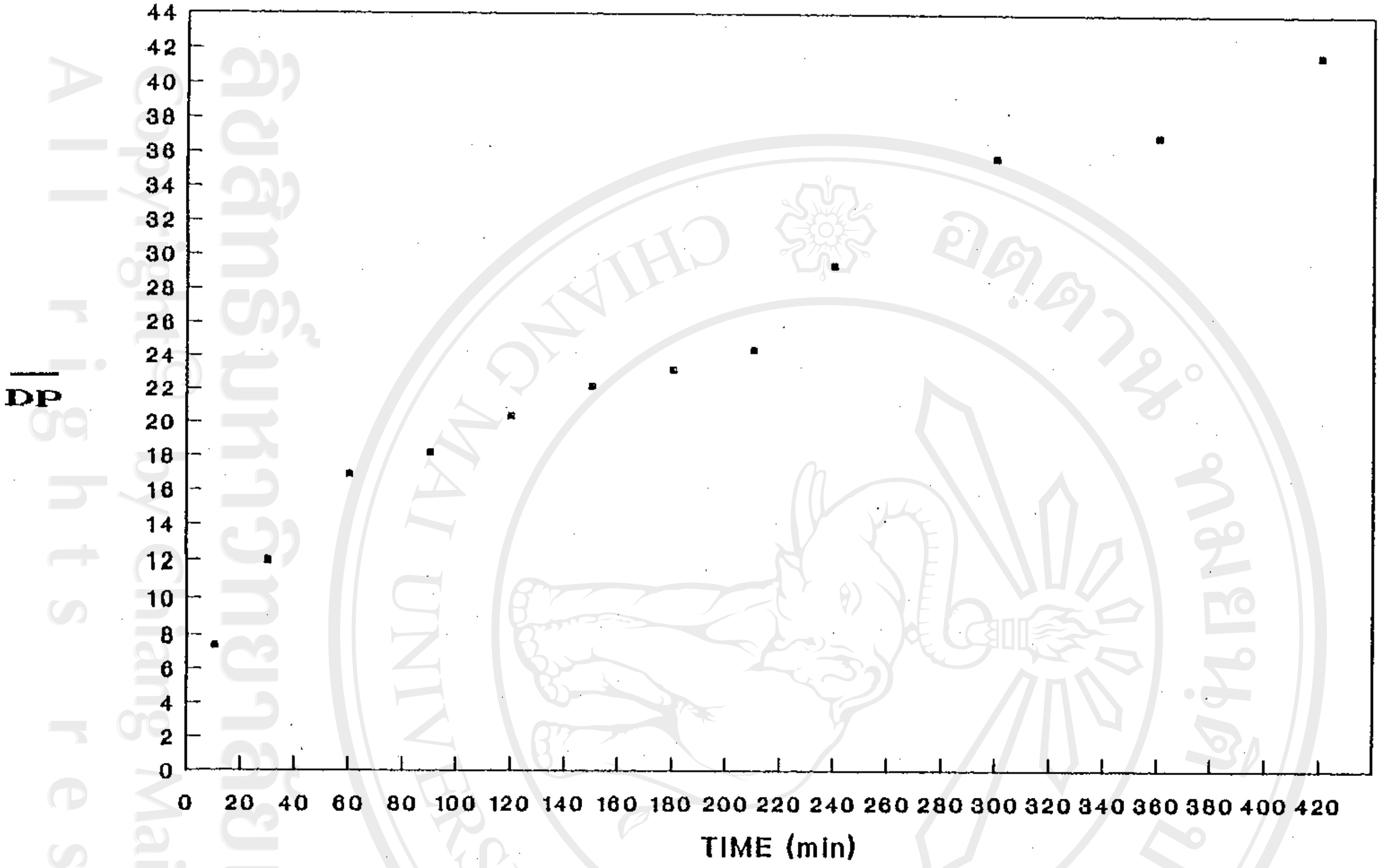


Fig. 2.7 : Average degree of polymerisation of poly(glycolic acid) as a function of time at 200 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2) with no catalyst added; RUN 3.

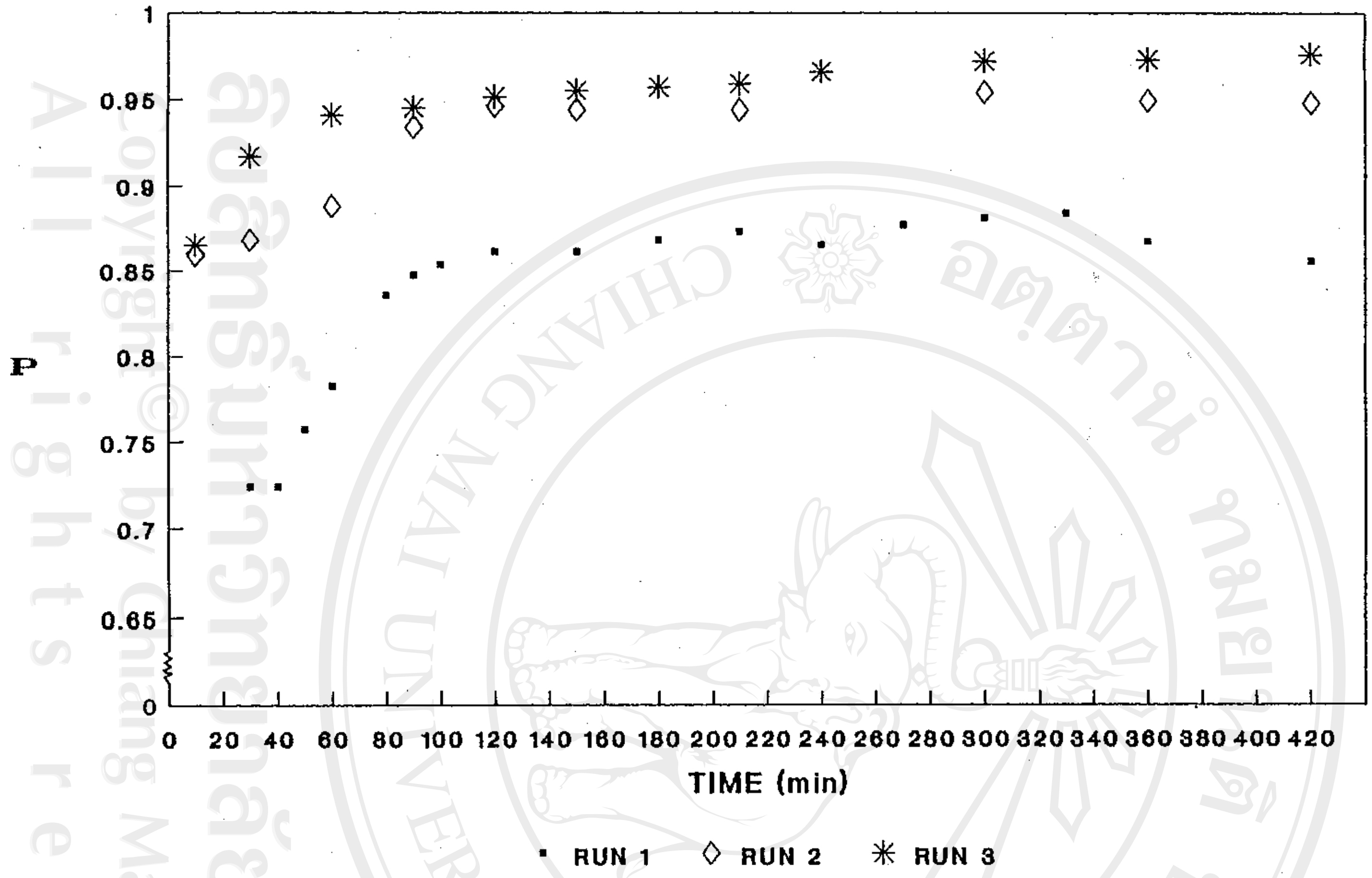


Fig. 2.8 : Extent of reaction of functional groups in the uncatalysed polyesterification of glycolic acid as a function of time : comparison of RUNS 1-3.

RUN 1 : 150 °C/N_2
RUN 2 : 150 °C/N_2 ⟶ 180 °C/N_2
RUN 3 : 150 °C/N_2 ⟶ 200 °C/vac.

2.2.3.4 Discussion of Uncatalysed Polyesterification [2, 3, 18-27]

From the results of the kinetic studies of the uncatalysed polyesterification of glycolic acid in bulk, as shown in Tables 2.2 - 2.4 and Figs. 2.2 - 2.8, the following points for discussion arise. According to the underlying kinetic theory, uncatalysed polyesterification should obey third-order kinetics:

$$\frac{1}{(1-p)^2} = 2c_o^2k_3t + 1 \qquad (8)$$

However, when $1/(1-p)^2$ is plotted against time, t , the adherence to this throry is seen to be rather limited in practice. The relevant plots in Figs. 2.2, 2.4 and 2.6 are approximately linear against time only over limited ranges of conversion.

In RUN 1, Fig. 2.2, it was found that the deviation from linearity was most pronounced in the low conversion region below p = 0.80 (i.e., for the first 80% of the esterification of the COOH and OH groups). The main reason for the nonadherence to equation (8) below about 80% conversion, as previously described, is believed to be mainly due to the reaction medium changing from one of pure reactants initially to one in which the ester product is the solvent. Initially, the glycolic acid medium is an equivalent mixture of alcohol and acid, whereas at complete reaction it is a polyester. Thus, there is a significant change in "solvent" polarity of the reaction medium as the more polar monomer is converted to a less polar polymer. At high conversions, it becomes a dilute solution of carboxyl and hydroxyl groups in a polyester. In addition, because the initial mixture is very concentrated, it is likely to be thermodynamically nonideal. Under these circumstances, the thermodynamic activity may not be proportional to concentration and, consequently, a kinetic analysis based on concentration may be misleading. Thus, the change in the activity coefficients of the end groups with yield could be the cause of this deviation. Therefore, in the low conversion region, a rapid change in polarity of the medium occurs which may cause the reaction mechanism or the value of the kinetic constants to change.

Another important effect which is generally neglected in the kinetic approach is that linked to the volume variations during the course of polyesterification due to the continuous removal of small molecules, such as water in this case. In a recent paper [2], for the case of the irreversible stoichiometric third-order polycondensation of a bifunctional monomer (A-B type), such as glycolic acid, and assuming volume additivity, the derived equations predict nonlinearity in the $1/(1-p)^2$ plot versus time for low extents of reaction, tending towards linearity only at higher conversions. In contrast to the traditional assumptions, the slope of the linear part does not give the true rate constant; the extent of nonlinearity at small conversions and the deviation of the apparent rate constant value from the true one depend on the initial number of A groups and on the density of the leaving molecule. Furthermore, the range of the nonlinear region increases with decreasing rate constant values, for instance, by decreasing the reaction temperature, in agreement with experimental observations. This is supported by comparing the results of this work shown previously in Fig. 2.4 and Fig. 2.6.

Hence, the true reaction rate constants are to be obtained from the linear portions of the plots. This applies to the last stage of the reaction when the concentration of reactive end-groups has been greatly decreased and the dielectric properties of the medium no longer change with conversion. However, deviations in the high-conversion region can also occur which are probably attributable to an increase in the rate of reverse reactions, since polyesterification reactions are reversible. Therefore, in order to drive the reaction to completion, it is necessary to remove totally the water by-product to avoid this deviation.

The rate constants obtained from the slopes and initial concentrations of COOH groups in this study are shown in Table 2.5. The concentration units of the rate constants are in terms of "equivalents per gram"; this is a more convenient measure of concentration than the usual "moles per liter" because the volume of the system decreases significantly with conversion. Calculation of the rate constants is performed as follows:

initial weight of glycolic acid = 0.500 g

molecular weight of glycolic acid = 76.05

moles of glycolic acid used = $\frac{0.500}{76.05}$

= 6.57×10^{-3} moles or equivalents

glycolic acid 0.500 g = 6.57×10^{-3} equivalents of COOH hence, $c_o = [COOH]_o = \dfrac{6.57 \times 10^{-3}}{0.500}$

$= 0.0131$

$c_o = [COOH]_o = 1.31 \times 10^{-2}$ equivalents/g

Table 2.5 : Comparison of kinetic parameters for uncatalysed polyesterification of glycolic acid under different conditions.

RUN	Conditions	p_{max}	P range of slope	Third-order rate constant $k_3 \times 10^{-2}$, $(g/equiv.)^2$ min^{-1}
1	150 °C/atm./N_2	0.884	0.725-0.847	17.5
			0.853-0.884	3.5
2*	180 °C/red.press.	0.954	0.859-0.946	89.7
			0.944-0.948	8.4
3*	200 °C/red.press.	0.976	0.865-0.955	97.0
			0.957-0.976	145.7

* after solidification at 150 °C/atm/N_2

The results from RUN 1 show that long reaction times of about 80 minutes were required before conversions in excess of 80% could be attained. Furthermore, even at much longer reaction times of up to 420 minutes, the conversion was still less than 90%. Consequently, the values of the number-average molecular weight, $\overline{M}_n$, and the average degree of polymerisation, $\overline{DP}$, were still relatively low even at the end of the RUN.

The main reason for these limitations is that, in RUN 1, the reaction was carried out under a flowing atmosphere of nitrogen purge gas at ordinary pressure. Under these conditions, the water by-product is difficult to remove completely and reverse hydrolysis reactions can occur. The increase in the average degree of polymerisation, $\overline{DP}$, with time is shown in Fig. 2.3. According to the theory, by substitution of equation (17) in (18), $\overline{DP}$ is found to be approximately proportional to the square root of time; hence, the rate of increase of molecular weight decreases as the reaction proceeds and the polymer molecules become larger. For this reason, self-catalysed reactions are rarely practical and added catalysts are always preferred.

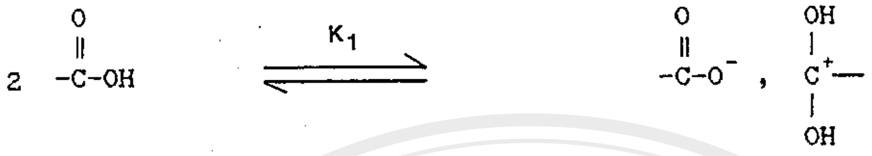
The results from Fig. 2.3 support this view. The $\overline{DP}$ of the polymer increases for about the first 120 minutes, after which it remains fairly constant. This must be due to the limiting conditions of the reaction such as the rapid increase in melt viscosity until the reaction medium solidified at about t = 90 minutes. The resulting decrease in molecular mobility decreases the probability that the remaining functional groups will come close enough to react.

In order to achieve high conversion in polycondensation, one normally has to use high vacuum during the later stages of the reaction, as in RUN 2. As shown in Fig. 2.4, a high conversion was obtained in a very short time; for example, whereas in RUN 1, 86% conversion took about 120 minutes, in RUN 2 this conversion was attained within 10 minutes. Furthermore, in RUN 2, the conversion rose to about 95% within about 3 hours. This was made possible by the remelting of the reaction mixture at the increased temperature of 180 °C together with the more effective removal of water under reduced pressure. Under reduced pressure, the presence of side and reverse reactions is lessened,thus shifting the equilibrium of the reaction towards complete conversion. However, beyond a certain limit, the removal of water is controlled by its diffusion in the reaction mixture; this is particularly true at high molecular weights when the viscosity of the reaction medium is very high. This diffusional rate decreases until, at some limiting value of $\overline{DP}$, the overall reaction becomes diffusion - controlled. Consequently, the maximum molecular weight attainable is strictly correlated to the water content in the system.

Finally, in RUN 3, by increasing the temperature in the reduced pressure stage further to 200 °C, it was found that the % conversion reached 90% within about 30 minutes (see Fig.2.6), compared with about 90 minutes in RUN 2. The higher temperature in RUN 3 meant that the reaction mixture was able to remain molten for a longer time, thus enabling the $\overline{DP}$ to reach a higher level before the polymer's melting point, T_m , exceeded 200 °C and solidification occurred. Continued polymerisation in the solid state is limited by the severe restrictions imposed on molecular motion. Consequently, increasing the reaction temperature provides a means of increasing the ultimate % conversion and, hence, $\overline{DP}$, provided that the temperature is not too high, in which case reverse scission reactions may occur at extended reaction times.

In summary, therefore, the kinetic comparisons in Fig. 2.8 and Table 2.5 show, as expected, that as the reaction temperature increases in the order RUN 1 < RUN 2 < RUN 3, the extent and rate of the reaction increases. However, because of the difficulty in completely removing all of the water formed, together with the possibility of several reactions occurring simultaneously, kinetic studies of this type are often difficult. This probably accounts for the observed deviations of the experimental data from the theoretically predicted third-order kinetics.

Flory, in his pioneering studies [2], found that the uncatalysed irreversible reaction, at least in the latter stages, showed overall third-order kinetics, being second-order in carboxyl and first-order in hydroxyl group concentration. A simplified mechanism consistent with these results is the common Ingold $A_{AC}2$ mechanism. This involves the autoprotolysis of the carboxylic acid with the formation of an ion pair, owing to the low dielectric constant of the medium, equivalent to those found at high conversion during polyesterification, where the presence of free ions can be reasonably excluded.

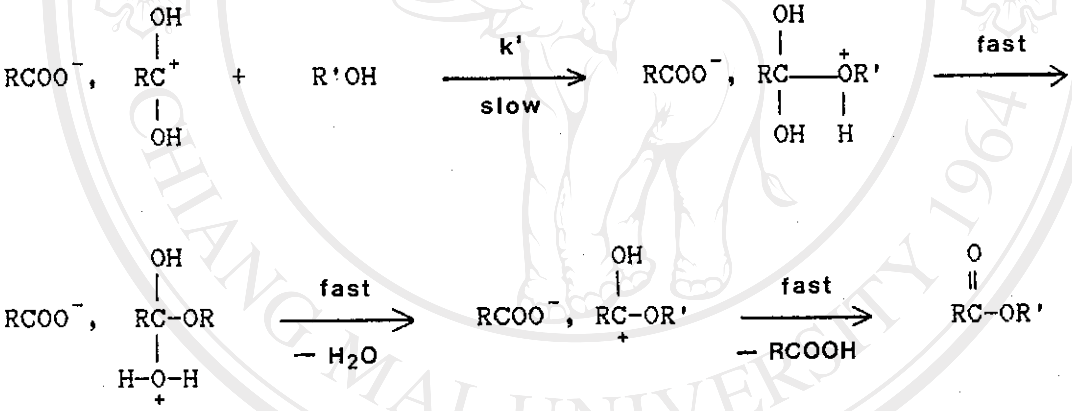


$$2\ \ -\overset{\overset{O}{\|}}{C}-OH \ \xrightleftharpoons{K_1}\ -\overset{\overset{O}{\|}}{C}-O^{-}\ ,\ \ \underset{OH}{\overset{OH}{C^{+}}}-$$

$[\ RCOO^{-}\ ,\ RC(OH)_2^{\ +}\ ]$

ion pair

This is then followed by attack of the alcohol (which represents the rate-determining step) and the elimination of water.



$$RCOO^{-},\ \underset{OH}{\overset{OH}{RC^{+}}}\ +\ R'OH \xrightarrow[\text{slow}]{k'} RCOO^{-},\ \underset{OH}{\overset{OH}{RC}}-\underset{H}{\overset{+}{O}}R' \xrightarrow{\text{fast}}$$

$$RCOO^{-},\ \underset{H-\underset{+}{O}-H}{\overset{OH}{RC}}-OR \xrightarrow[-\ H_2O]{\text{fast}} RCOO^{-},\ \underset{+}{\overset{OH}{RC}}-OR' \xrightarrow[-\ RCOOH]{\text{fast}} \overset{\overset{O}{\|}}{RC}-OR'$$

According to this mechanism, the kinetic rate expression (2) becomes:

$$-\frac{d[COOH]}{dt} \ =\ -\frac{d[OH]}{dt} \ =\ k'\ [OH]\ [RCOO^{-},\ RC(OH)_2^{\ +}]$$

As it is also the case that:

$$K_1 = \frac{[RCOO^-, RC(OH)_2^+]}{[COOH]^2}$$

For this scheme, assuming that the concentration of ion pairs with respect to the overall concentration of COOH and OH is negligible, as would be expected for a medium of such low polarity, the concentration of ion pairs is derived through the equilibrium constant K_1.

$$[RCOO^-, RC(OH)_2^+] = K_1 [COOH]^2$$

When substituted in the above rate expression, the rate equation can alternatively be written as:

$$-\frac{d[COOH]}{dt} = k'K_1 [OH] [COOH]^2$$

hence

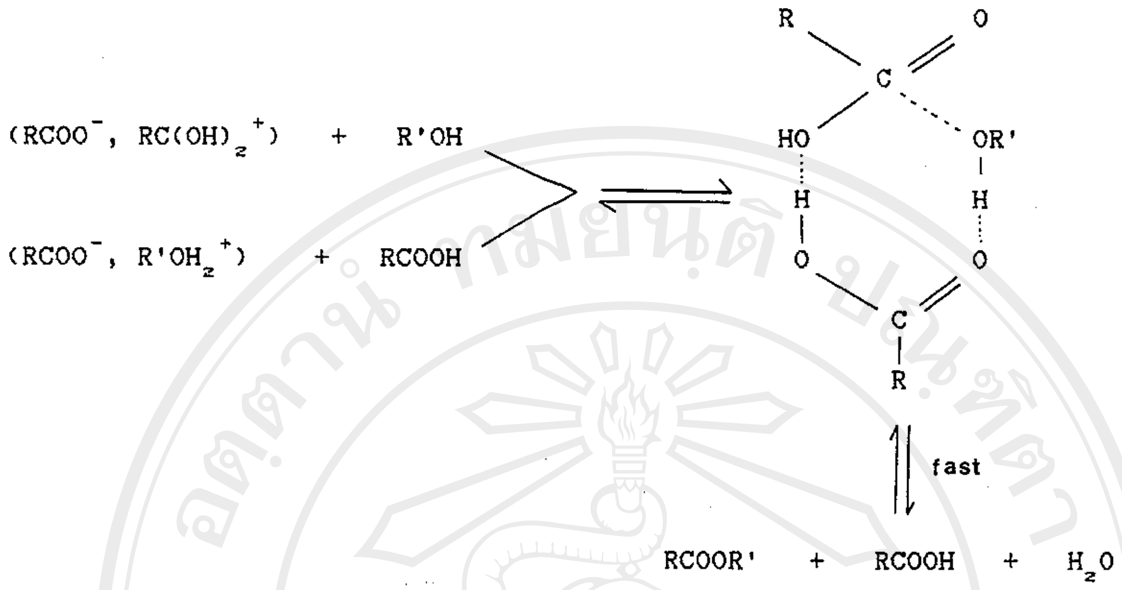
$$-\frac{d[COOH]}{dt} = k_3 [OH] [COOH]^2$$

where $k_3 = k'K_1$

An overall third-order mechanism could also be interpreted by assuming hydrogen-bond adducts according to the equations below:

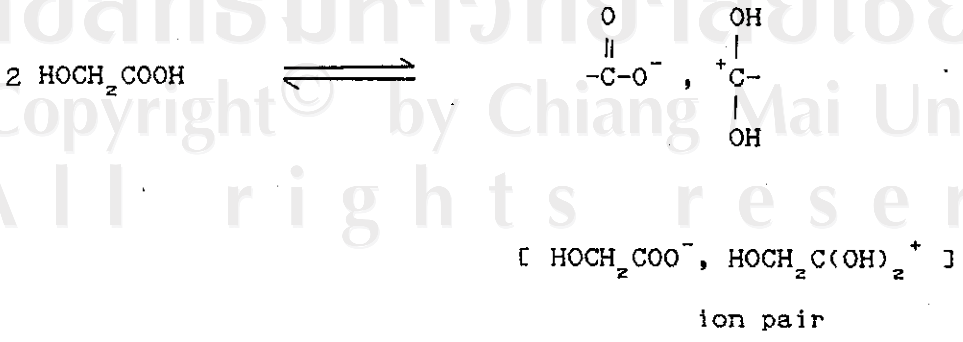
$$2\ RCOOH \rightleftharpoons (RCOO^-, RC(OH)_2^+)$$

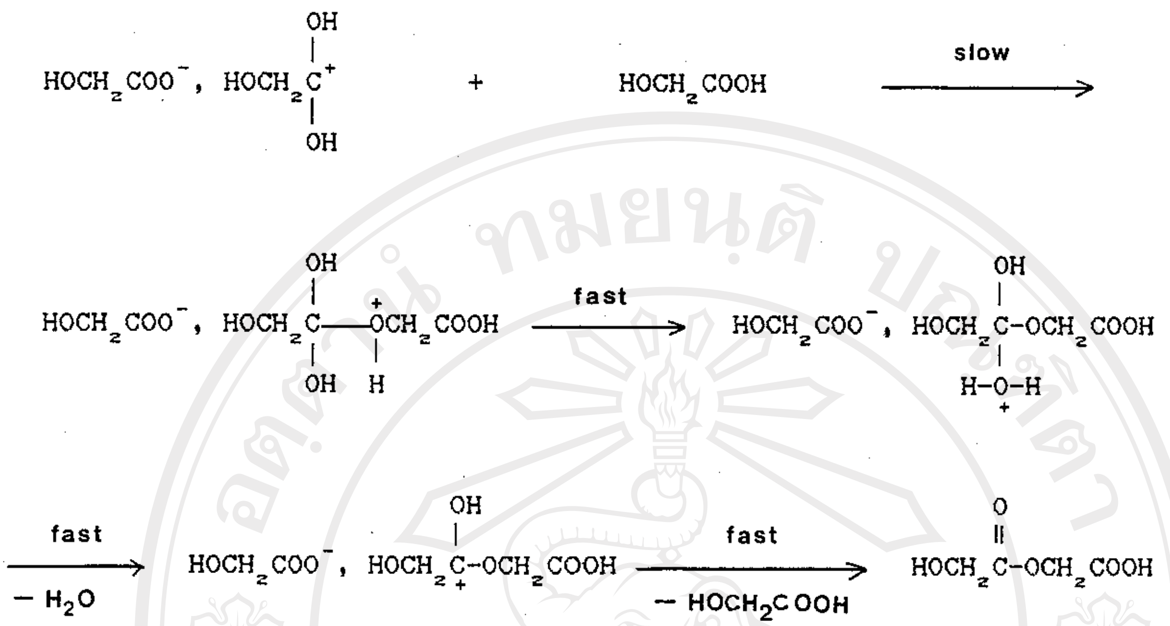
$$RCOOH + R'OH \rightleftharpoons (RCOO^-, R'OH_2^+)$$



Althrough overall third-order is mostly accepted, several studies of uncatalysed polyesterification have been interpreted on the basis of different kinetics: overall second-order, an overall order of 2.5, second followed by third-order in the last stage of the reaction, and even an overall order of six has been reported [2].

On the basis of these proposals, the uncatalysed polyesterification of glycolic acid studied in this work can be expected to proceed along the following mechanistic pathway:





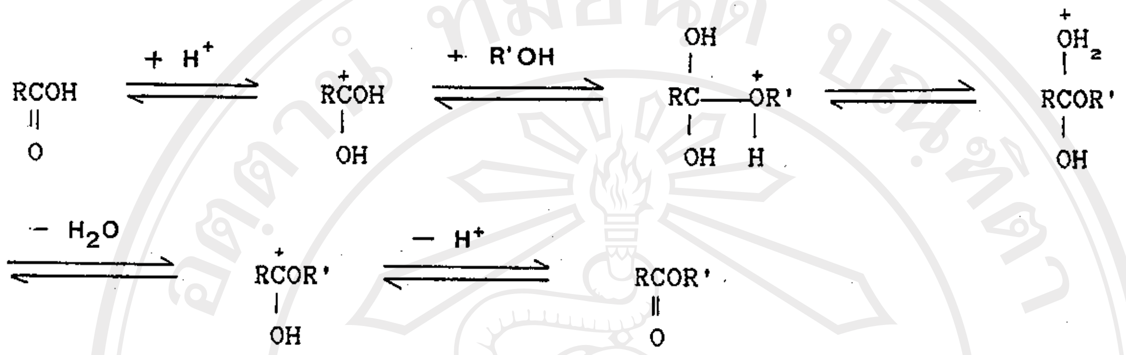
$$\mathrm{HOCH_2COO^-,\ HOCH_2\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C^+}}}\quad + \quad \mathrm{HOCH_2COOH} \xrightarrow{\text{slow}}$$

$$\mathrm{HOCH_2COO^-,\ HOCH_2\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{C}}\!-\!\!-\!\underset{\underset{H}{|}}{\overset{+}{O}}CH_2COOH} \xrightarrow{\text{fast}} \mathrm{HOCH_2COO^-,\ HOCH_2\overset{\overset{OH}{|}}{\underset{\underset{\underset{+}{H-O-H}}{|}}{C}}-OCH_2COOH}$$

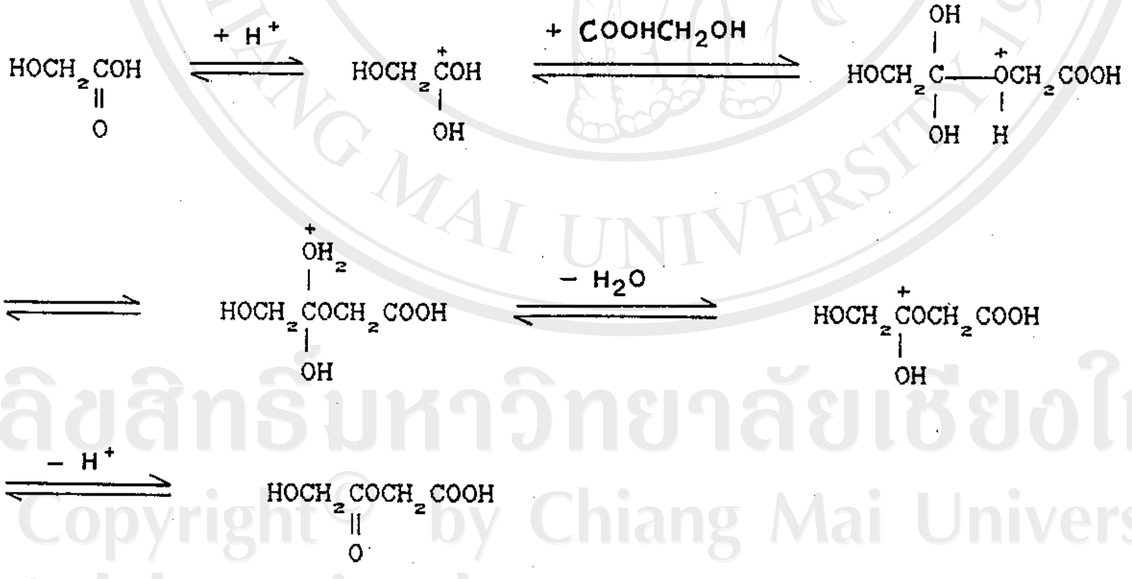
$$\xrightarrow[-\,\mathrm{H_2O}]{\text{fast}} \mathrm{HOCH_2COO^-,\ HOCH_2\overset{\overset{OH}{|}}{\underset{+}{C}}-OCH_2COOH} \xrightarrow[-\,\mathrm{HOCH_2COOH}]{\text{fast}} \mathrm{HOCH_2\overset{\overset{O}{\|}}{C}-OCH_2COOH}$$

As mentioned previously, many other investigations into the kinetics of self-catalysed polyesterifications have been carried out and several different conclusions have been reached regarding the overall reaction order. Even reaction orders which are not constant throughout the course of the reaction have been proposed. Consequently, different reaction mechanisms have been proposed which, for example, take into account the formation of free ions instead of ion pairs. Other proposed mechanisms involve association equilibia between either carboxyl or hydroxyl groups, or the protonation of the alcohol, or the inclusion of a reverse reaction due to the presence of unremoved water. A comprehensive review by Fradet and Marechal is devoted to a careful examination of the literature concerning this subject [2].

If the formation of free ions is considered instead of ion pairs, because of its more general acceptance for proton-catalysed reactions, then the modified mechanism becomes:



In the case of glycolic acid, this free ion mechanism would be represented as:



In conclusion of this section, it would appear from the literature that it is still not clear whether the "ion-pair" or the "free-ion" mechanism is the more correct; indeed, it is possible that the true mechanism may contain features of both. While the results of this work cannot shed any light on this controversy, it is nevertheless relevant to this study that each be considered within the context of this discussion. These mechanisms allow for a better understanding of the factors affecting polyesterification in bulk.

2.2.4 Catalysed Polyesterification of Glycolic Acid [2, 23, 33]

The results from RUNS 1 - 3 showed that uncatalysed polyesterification requires quite long times to reach high degrees of polymerisation and high extents of reaction. Higher rates are achieved by adding to the system a small amount (about 1% w/w) of catalyst whose concentration is constant throughout the reaction process.

In general, for condensation polymerisation, catalysts may be organic or inorganic acids or bases, or different types of metal compounds. Strong protonic acids (mainly sulfuric acid and aromatic sulfonic acids) or carboxylic organic acids are frequently used, as are metal compounds such as alkali metal and alkali earth metal acetates, zinc and manganese acetates, antimony, germanium, lead and tin oxides or organometallic compounds, titanium compounds and others. These catalysts, which in many cases show a very powerful effect, may act as Lewis acids [2, 23]. In this work, p-toluenesulfonic acid and antimony trioxide were used as catalysts and their effects compared.

The reactions were carried out by heating the reactants (monomer and catalyst) together and removing water, usually applying vacuum in the later stages. In this case, the concentration of the catalyst is included in the rate constant term. From the kinetic theory of condensation polymerisation for a catalysed reaction, as previously described, the reaction should follow second-order kinetics.

2.2.4.1 p-Toluenesulfonic Acid-Catalysed Polyesterification

2.2.4.1.1 RUN 4 : At 150 °C under an Atmospheric Pressure of Nitrogen Gas

In RUN 4, the experimental procedure and conditions used were exactly the same as previously described in RUN 1 except that 1% w/w p-toluenesulfonic acid catalyst (4 mmol/mole glycolic acid) was added to the glycolic acid in the reaction flask.

The results obtained and data analysis are presented in Table 2.6 and Fig. 2.9.

Table 2.6 : Data obtained from RUN 4 : p-toluenesulfonic acid-catalysed polyesterification of glycolic acid at 150 °C/atm/N_2.

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)}$	$\overline{M}_n$
10	0.508	0.452	0.1009	4.95	0.06	0.917	12.0	714
30	0.505	0.428	0.1004	3.68	0.05	0.935	15.4	911
40	0.506	0.411	0.0930	3.36	0.05	0.943	17.5	1033
50	0.502	0.410	0.1009	2.54	0.06	0.954	21.7	1277
60	0.503	0.386	0.0989	2.12	0.05	0.960	25.0	1468
80	0.504	0.401	0.0930	2.10	0.05	0.964	27.8	1630
90	0.500	0.368	0.0932	1.58	0.04	0.970	33.3	1949
120	0.505	0.382	0.0932	1.47	0.04	0.973	37.0	2164
150	0.501	0.370	0.0932	1.40	0.04	0.974	38.5	2251
180	0.504	0.377	0.0932	1.57	0.04	0.971	34.5	2019
210	0.503	0.371	0.0932	1.86	0.04	0.965	28.6	1677
240	0.552	0.414	0.0982	2.21	0.02	0.960	25.0	1468
270	0.525	0.411	0.0982	2.01	0.02	0.964	27.8	1630
300	0.533	0.414	0.0982	2.24	0.02	0.960	25.0	1468
330	0.564	0.443	0.0982	2.30	0.02	0.962	26.3	1543
360	0.559	0.420	0.0982	2.53	0.02	0.955	22.2	1306
420	0.543	0.403	0.0982	1.71	0.02	0.969	32.3	1891
480	0.524	0.388	0.0982	1.78	0.02	0.966	29.4	1723
540	0.514	0.391	0.0982	2.27	0.02	0.957	23.3	1369

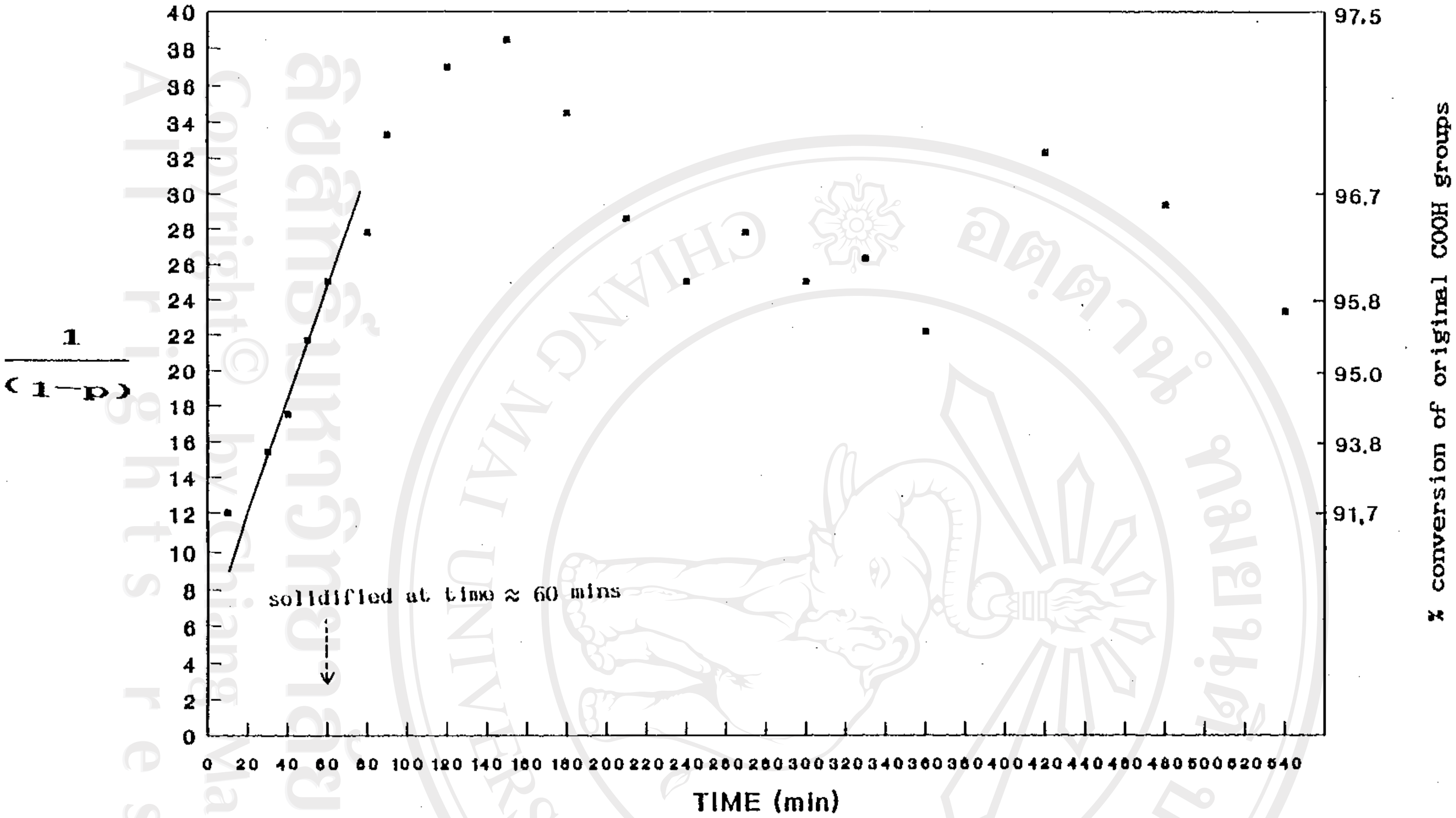


Fig. 2.9 : Second-order rate plot for the p-toluenesulfonic acid-catalysed polyesterification of glycolic acid at 150 °C/atm/N_2; RUN 4.

2.2.4.1.2 RUN 5 : At 150 °C/atm/N_2 followed by at 180 °C/Reduced Pressure

In RUN 5, the experimental procedure and conditions used were identical to those previously employed in RUN 2 except that 1% w/w p-toluenesulfonic acid catalyst (4 mmol/mol) was added to the glycolic acid in the reaction flask.

The results obtained and data analysis are presented in Table 2.7 and Fig. 2.10.

Table 2.7 : Data obtained from RUN 5 : p-toluenesulfonic acid-catalysed polyesterification of glycolic acid at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2).

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)}$	$\overline{M}_n$
10	0.502	0.355	0.1004	3.38	0.05	0.928	13.9	824
20	0.501	0.343	0.0938	3.04	0.05	0.938	16.1	952
30	0.500	0.354	0.1001	2.62	0.06	0.945	18.2	1074
40	0.501	0.338	0.0992	1.94	0.07	0.958	23.8	1398
60	0.504	0.356	0.0992	1.58	0.07	0.968	31.2	1828
80	0.501	0.336	0.0938	1.45	0.05	0.970	33.3	1949
90	0.500	0.338	0.0989	1.36	0.05	0.971	34.5	2019
120	0.501	0.361	0.0992	1.31	0.07	0.974	38.5	2251
150	0.504	0.330	0.0932	1.10	0.04	0.977	43.5	2541
180	0.506	0.347	0.0914	1.40	0.02	0.972	35.7	2089
210	0.507	0.363	0.0914	1.59	0.02	0.968	31.2	1828
240	0.679	0.405	0.1024	1.56	0.04	0.971	34.5	2019
300	0.640	0.418	0.1024	2.05	0.04	0.962	26.3	1543
360	0.600	0.424	0.1024	1.98	0.04	0.964	27.8	1630
420	0.519	0.265	0.1024	1.07	0.04	0.970	33.3	1949

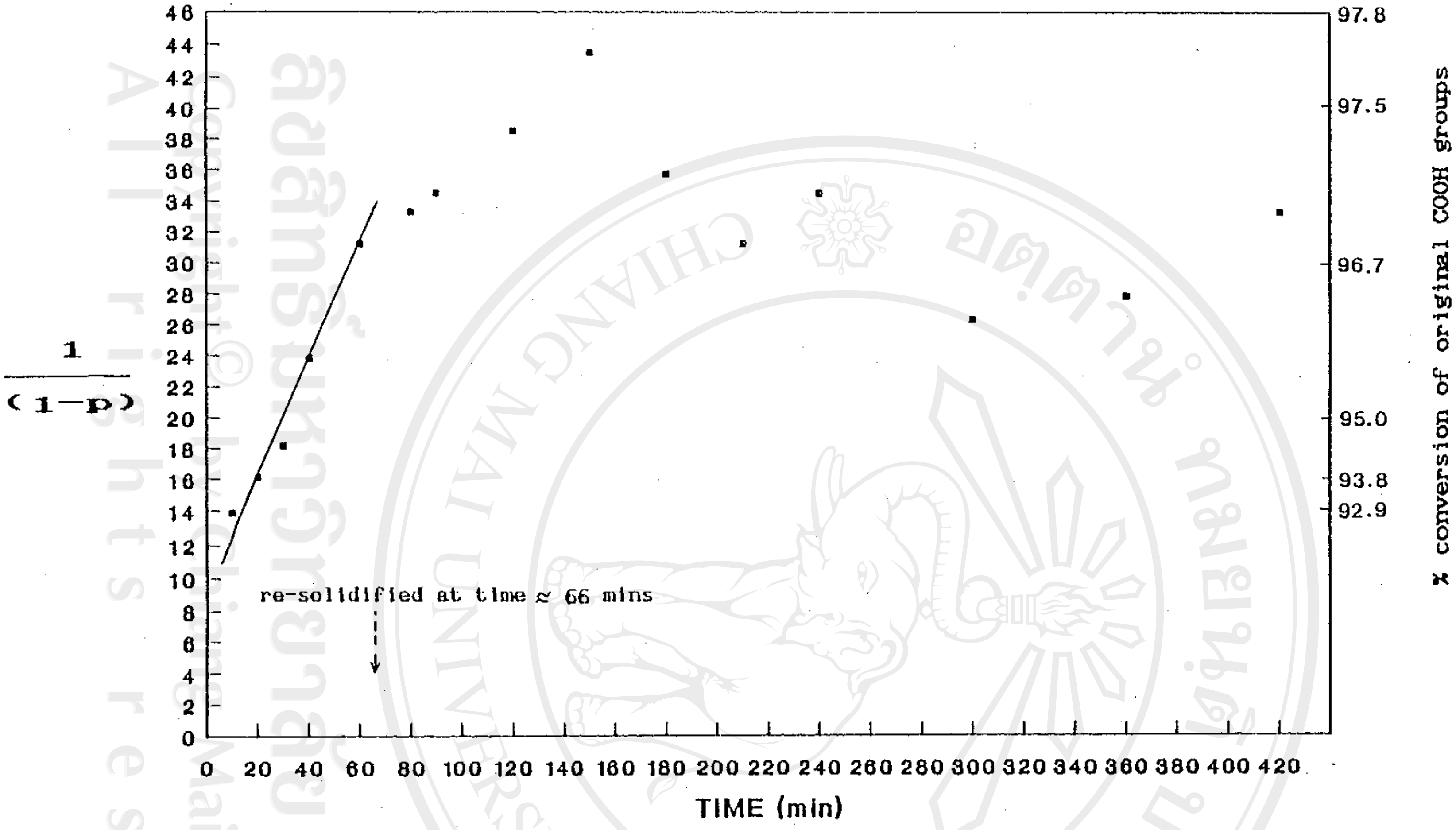


Fig. 2.10 : Second-order rate plot for the p-toluenesulfonic acid-catalysed polyesterification of glycolic acid at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2); RUN 5.

2.2.4.1.3 RUN 6 : At 150 °C/atm/N_2 followed by at 200 °C/Reduced Pressure

In RUN 6, the experimental procedure and conditions corresponded to those previously described in RUN 3 with the addition of 1% w/w p-toluenesulfonic acid catalyst (4mmol/mol) to the glycolic acid in the reaction flask.

The results obtained and data analysis are presented in Table 2.8 and Fig. 2.11.

Table 2.8 : Data obtained from RUN 6 : p-toluenesulfonic acid-catalysed polyesterification of glycolic acid at 200 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2).

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)}$	$\overline{M}_n$
10	0.504	0.313	0.1036	2.12	0.04	0.947	18.9	1114
20	0.504	0.324	0.1036	1.97	0.04	0.953	21.3	1253
30	0.501	0.307	0.1004	1.64	0.05	0.960	25.0	1468
40	0.504	0.317	0.0938	1.46	0.05	0.968	31.2	1827
60	0.500	0.295	0.1036	1.06	0.04	0.973	37.0	2164
70	0.502	0.312	0.0943	1.12	0.02	0.975	40.0	2338
90	0.503	0.347	0.1001	1.13	0.06	0.976	41.7	2437
100	0.500	0.301	0.0938	0.99	0.05	0.978	45.4	2651
120	0.501	0.301	0.0943	0.90	0.02	0.979	47.6	2779
130	0.505	0.310	0.0914	0.96	0.02	0.979	47.6	2779
150	0.502	0.288	0.0933	0.90	0.05	0.979	47.6	2779
180	0.508	0.295	0.0943	0.95	0.02	0.977	43.5	2541
240	0.540	0.297	0.1024	1.04	0.04	0.974	38.5	2251
300	0.698	0.574	0.1024	2.36	0.04	0.968	31.2	1828
360	0.550	0.318	0.1024	1.17	0.04	0.972	35.7	2089
420	0.518	0.260	0.1024	1.18	0.04	0.966	29.4	1723

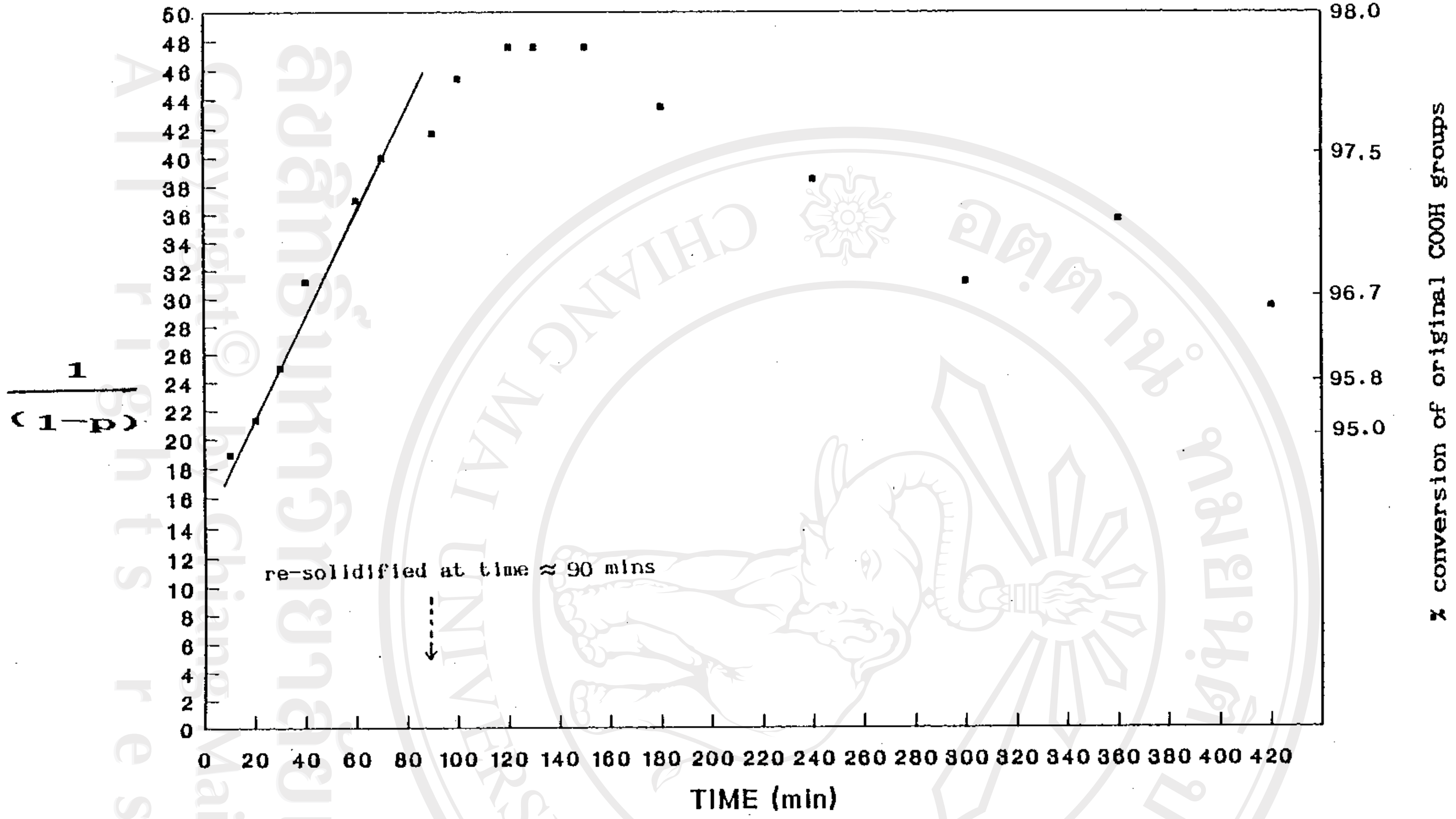


Fig. 2.11 : Second-order rate plot for the p-toluenesulfonic acid-catalysed polyesterification of glycolic acid at 200 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2); RUN 6.

2.2.4.1.4 **Discussion of p-Toluenesulfonic Acid-Catalysed Polyesterification** [2, 3, 18-27, 35]

From the results of the uncatalysed polyesterifications, previously described in RUNS 1-3, long reaction times were required before high extents of reaction could be attained. Various methods are employed to reduce these times, such as adding an external acid catalyst, as employed here in RUNS 4-6. In many cases, it has been found that, at a fixed catalyst concentration, the reaction is first-order in both carboxyl and hydroxyl concentrations, thus giving rise to overall second-order kinetics. However, it should also be pointed out that, strictly speaking, the general form of the rate equation

$$-\frac{d[COOH]}{dt} = k_2 [COOH] [OH]$$

is incomplete, because the uncatalysed reaction, always present, has been neglected. Theoretically, a second term of the type

$$-\frac{d[COOH]}{dt} = k_3 [COOH]^2 [OH]$$

should also be incorporated. However, in practice, the contribution of the uncatalysed term to the overall reaction is considered to be negligible due to the relatively much higher rate constant of the catalysed reaction.

Accordingly, the results here in Fig. 2.9 (RUN 4) show a marked increase in reaction rate resulting from the presence of the p-toluenesulfonic acid catalyst. This can be seen by comparing the respective conversions as a function of time with those of the corresponding uncatalysed RUN 1 in Fig. 2.2. The previous rate equation (13) on page 19 predicts that a plot of $\overline{DP}$ or $1/(1-p)$ versus time should be linear if k_2 is truly constant. It was found in this work that this plot was approximately linear only for the first part, after which $\overline{DP}$ began to decrease slightly. Similar results have been obtained by other workers for simple esterifications and polyesterifications in the presence of strong protonic catalysts. The observed deviations from pseudo-second-order kinetics in the initial region may be attributed, as in the uncatalysed case, mainly to changes in the polarity of the medium and to volume variations during the reaction.

When the temperature was increased and the pressure reduced, as in the second parts of RUNS 5 and 6, the medium was able to re-melt and molecular mobility be restored. The main effect of this was to enable the reaction to continue for a further period in the melt state until the polymer's melting point increased above that of the reaction temperature, whereupon re-solidification occurred. This is reflected in Table 2.9 through the slight increases in the maximum extent of reaction, p_{max}, and the second-order rate constant, k_2. It is also significant to note in Figs. 2.9-2.11 that, under all conditions, the value of p increased slightly even after solidification had occurred. This suggests that a limited amount of additional polycondensation takes place in the solid-state before, at longer times, degradation processes appear to become more important.

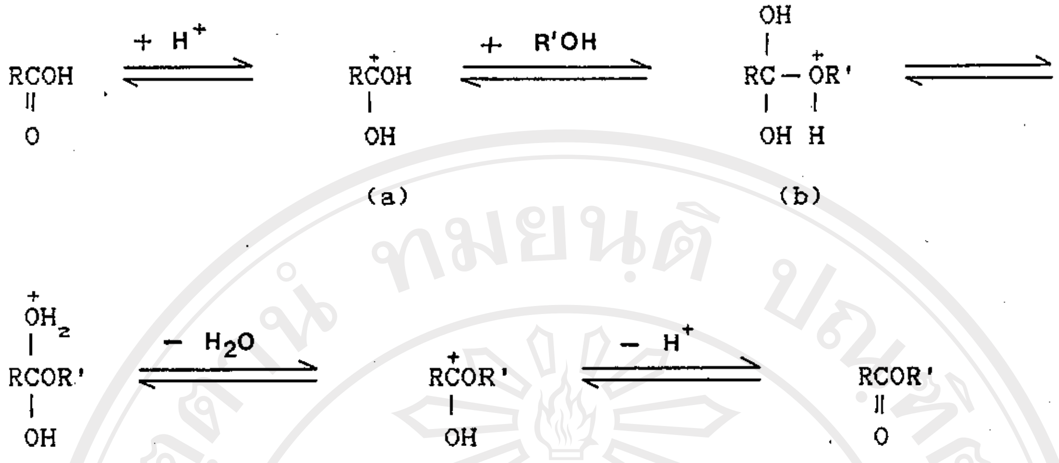
Table 2.9 : Comparison of kinetic parameters for p-toluenesulfonic acid-catalysed polyesterification of glycolic acid under different conditions.

RUN	Conditions	p_{max}	p range of slope	Second-order rate constant k_2 , g/equiv-min
4	150 °C/atm./N_2	0.974	0.917-0.960	26.0
5*	180 °C/red.press.	0.977	0.928-0.968	28.2
6*	200 °C/red.press.	0.979	0.947-0.976	29.0

* after solidification at 150 °C/atm/N_2

When polyesterifications are carried out at high temperatures, many reactions can occur simultaneously, leading to either chain growth or chain scission. The relative rates of these reactions is usually determined by the reaction conditions and by the catalysts employed. This then becomes the most important limiting factor for the molecular weight increase. Kinetic constants of chain growth reactions are generally much higher than those of degradation; however, as conversion approaches unity, the low concentration of terminal groups and the high concentration of ester groups within the chains causes the balance between the overall rates of molecular weight increase and of chain scission to change. This undoubtedly accounts for the slight decreases in molecular weight after the attainment of p_{max} observed in RUNS 4-6.

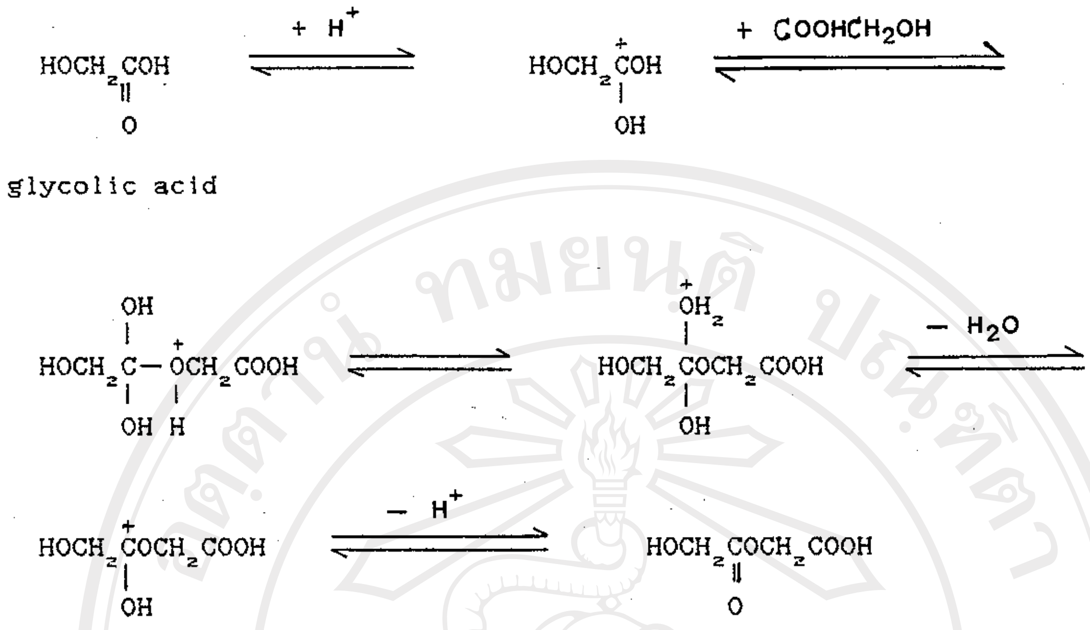
Turning our attention now to the actual mechanism of the reaction, according to classical organic chemistry, direct esterification can be catalysed by either acidic or basic compounds. Ingold [2] has proposed eight different mechanisms, four for acid-catalysed and four for base-catalysed processes. Of these, the acid-catalysed mechanism $A_{AC}2$ is by far the most frequently observed for polyesterification. In the Ingold $A_{AC}2$ mechanism, though the details may vary, it is suggested that acid can promote electron withdrawal from the carbonyl carbon atom through coordination to the oxygen atom. The use of an acidic catalyst, either in the form of a protonic or a Lewis acid, adds an additional equilibrium reaction to the overall mechanism resulting from coordination of the catalyst to the carbonyl oxygen atom. It can be assumed that the role of the catalyst is to increase the positive charge on the carbonyl carbon atom.



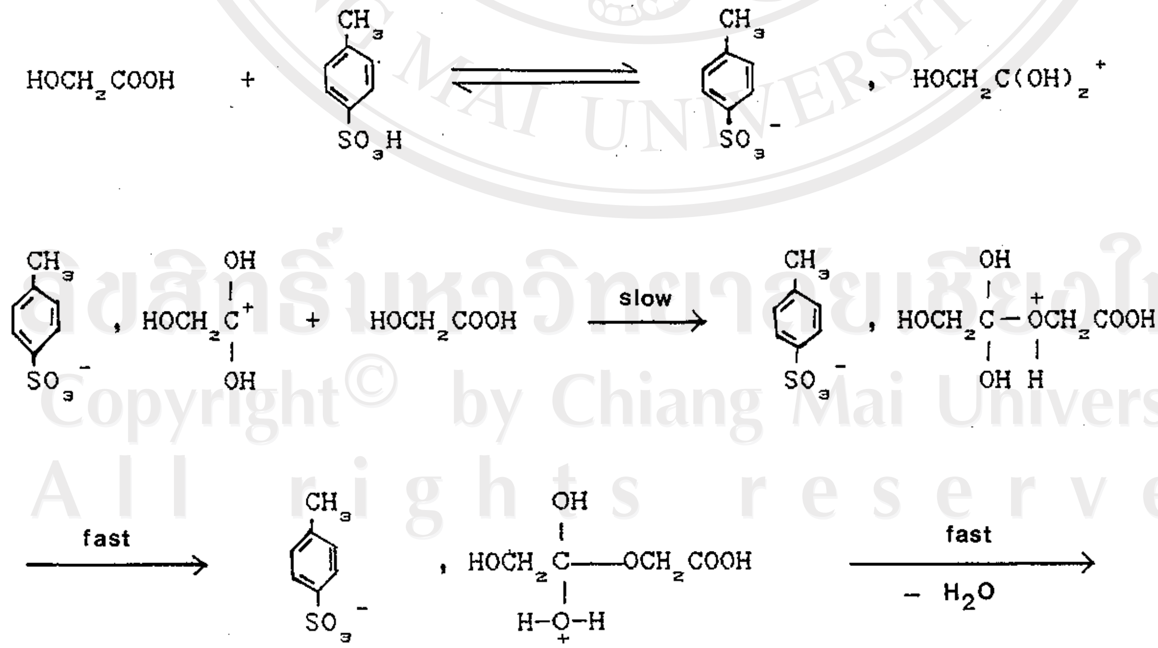
In this "free ion" scheme, the reaction of the protonated form (a) of the carboxylic acid with the hydroxy compound to give the addition intermediate (b) is usually the rate-controlling step. This mechanism is usually extrapolated to proton-catalysed direct polyesterification.

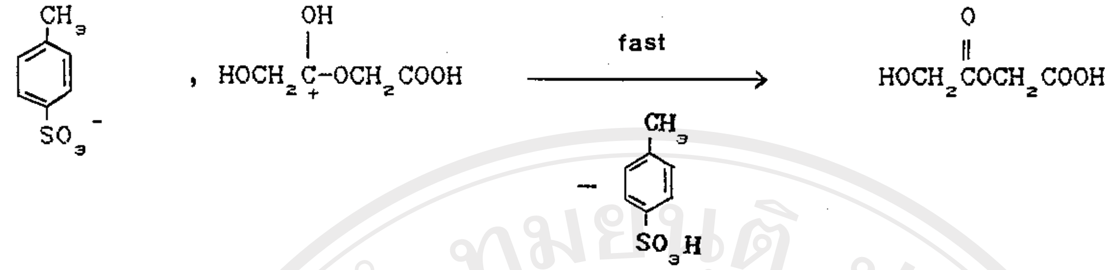
In the case of the p-toluenesulfonic acid (PTSA) catalysed polyesterification of glycolic acid studied here, the above "free ion" mechanism can be written as :

PTSA



However, since at high conversion, the contribution of the accompanying uncatalysed reaction usually becomes negligible, the mechanism may tend towards proton transfer from the catalyst with the formation of an "ion pair" (rather than free ions):





Whilst an exact solution to this "free ion versus ion pair" controversy is beyond the scope of this project, it is interesting to compare and contrast the different mechanisms within the context of this work.

2.2.4.2 Antimony Trioxide-Catalysed Polyesterification

2.2.4.2.1 RUN 7 : At 150 °C under an Atmospheric Pressure of Nitrogen Gas

For RUN 7, the experimental procedure and conditions of synthesis were the same as used in RUN 1 except that 1% w/w antimony trioxide catalyst was added to the glycolic acid.

The results obtained and data analysis are presented in Table 2.10 and Fig. 2.12.

Table 2.10 : Data obtained from RUN 7 : antimony trioxide-catalysed polyesterification of glycolic acid at 150 °C/atm/N_2.

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)}$	$\overline{M}_n$
10	0.501	0.452	0.1035	5.68	0.02	0.901	10.1	603
20	0.502	0.401	0.0919	6.86	0.02	0.880	8.33	501
30	0.500	0.402	0.0919	6.73	0.02	0.883	8.55	514
40	0.504	0.408	0.0919	6.36	0.02	0.891	9.17	550
60	0.505	0.386	0.1024	4.86	0.04	0.903	10.3	615
90	0.554	0.441	0.0919	5.73	0.02	0.909	11.0	656
120	0.506	0.382	0.0982	5.42	0.02	0.894	9.43	565
150	0.500	0.405	0.0919	6.32	0.02	0.891	9.17	550
180	0.501	0.377	0.0919	5.44	0.02	0.899	9.90	592
210	0.502	0.381	0.0919	5.09	0.02	0.907	10.8	644
240	0.529	0.381	0.0936	5.75	0.02	0.892	9.26	555
270	0.525	0.389	0.1090	5.73	0.02	0.878	8.20	494
300	0.593	0.444	0.1090	6.19	0.02	0.885	8.70	523
330	0.537	0.410	0.1090	6.88	0.02	0.861	7.19	435
360	0.522	0.379	0.1090	5.82	0.02	0.873	7.87	474
420	0.531	0.391	0.1090	5.92	0.02	0.875	8.00	482

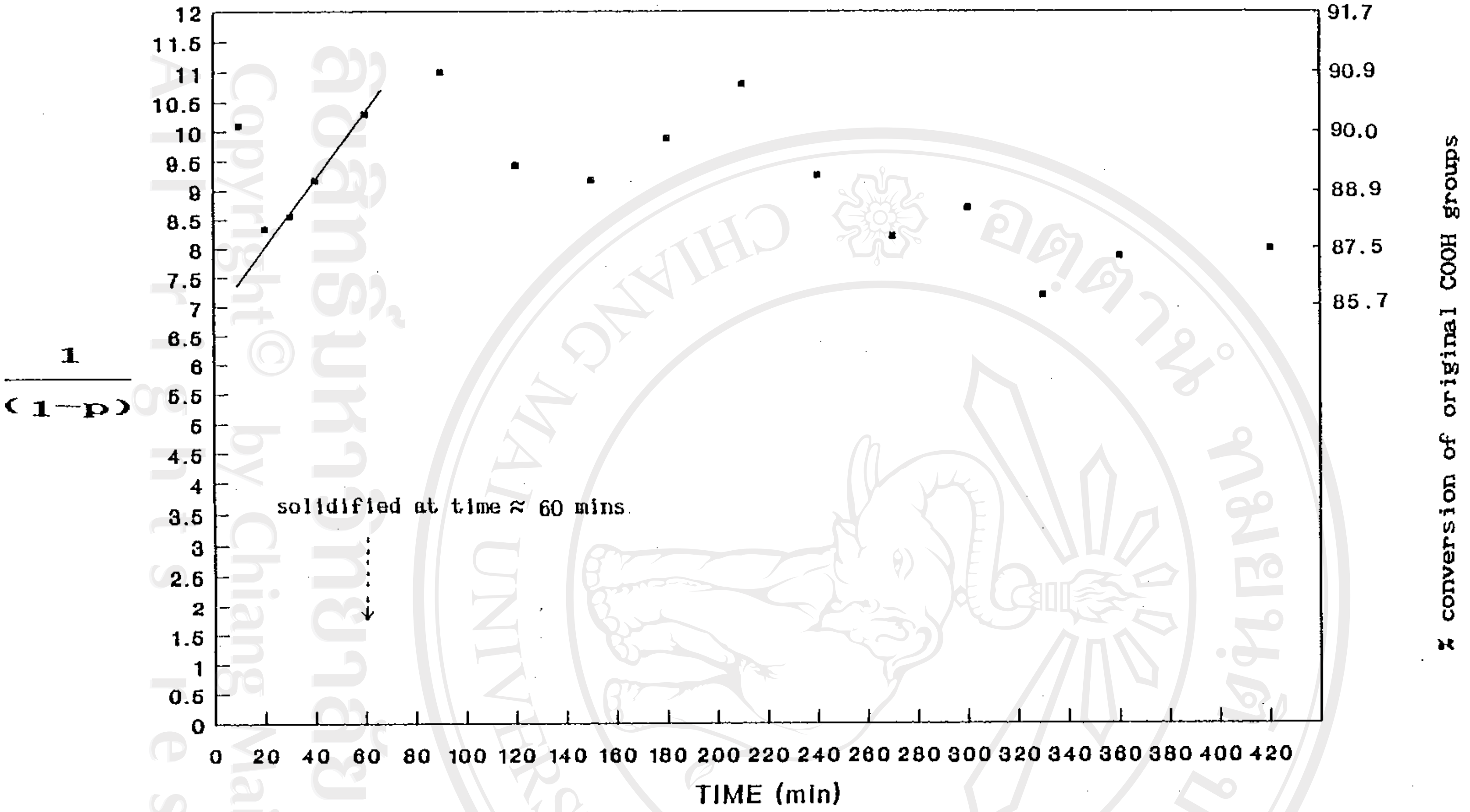


Fig. 2.12 : Second-order rate plot for the antimony trioxide-catalysed polyesterification of glycolic acid at 150 °C/atm/N_2 ; RUN 7.

2.2.4.2.2 **RUN 8 : At 150 °C/atm/N_2 followed by at 180 °C/Reduced Pressure**

In RUN 8, the experimental procedure and conditions of synthesis corresponded to those previously used in RUN 2 except that 1% w/w antimony trioxide catalyst was added to the glycolic acid.

The results obtained and data analysis are presented in Table 2.11 and Fig. 2.13.

Table 2.11 : Data obtained from RUN 8 : antimony trioxide-catalysed polyesterification of glycolic acid at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2).

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)}$	$\overline{M}_n$
10	0.571	0.337	0.0976	6.20	0.02	0.863	7.30	441
20	0.567	0.386	0.0976	5.71	0.02	0.891	9.17	550
30	0.538	0.345	0.0976	4.37	0.02	0.906	10.6	633
40	0.503	0.306	0.0976	3.62	0.02	0.912	11.4	679
60	0.521	0.352	0.0976	3.52	0.02	0.926	13.5	801
90	0.502	0.343	0.0976	4.62	0.02	0.900	10.0	598
150	0.502	0.333	0.0976	4.76	0.02	0.894	9.43	565
210	0.535	0.353	0.0976	4.60	0.02	0.904	10.4	621
300	0.587	0.335	0.0936	3.99	0.02	0.915	11.8	702
420	0.532	0.310	0.1090	3.11	0.02	0.917	12.0	714

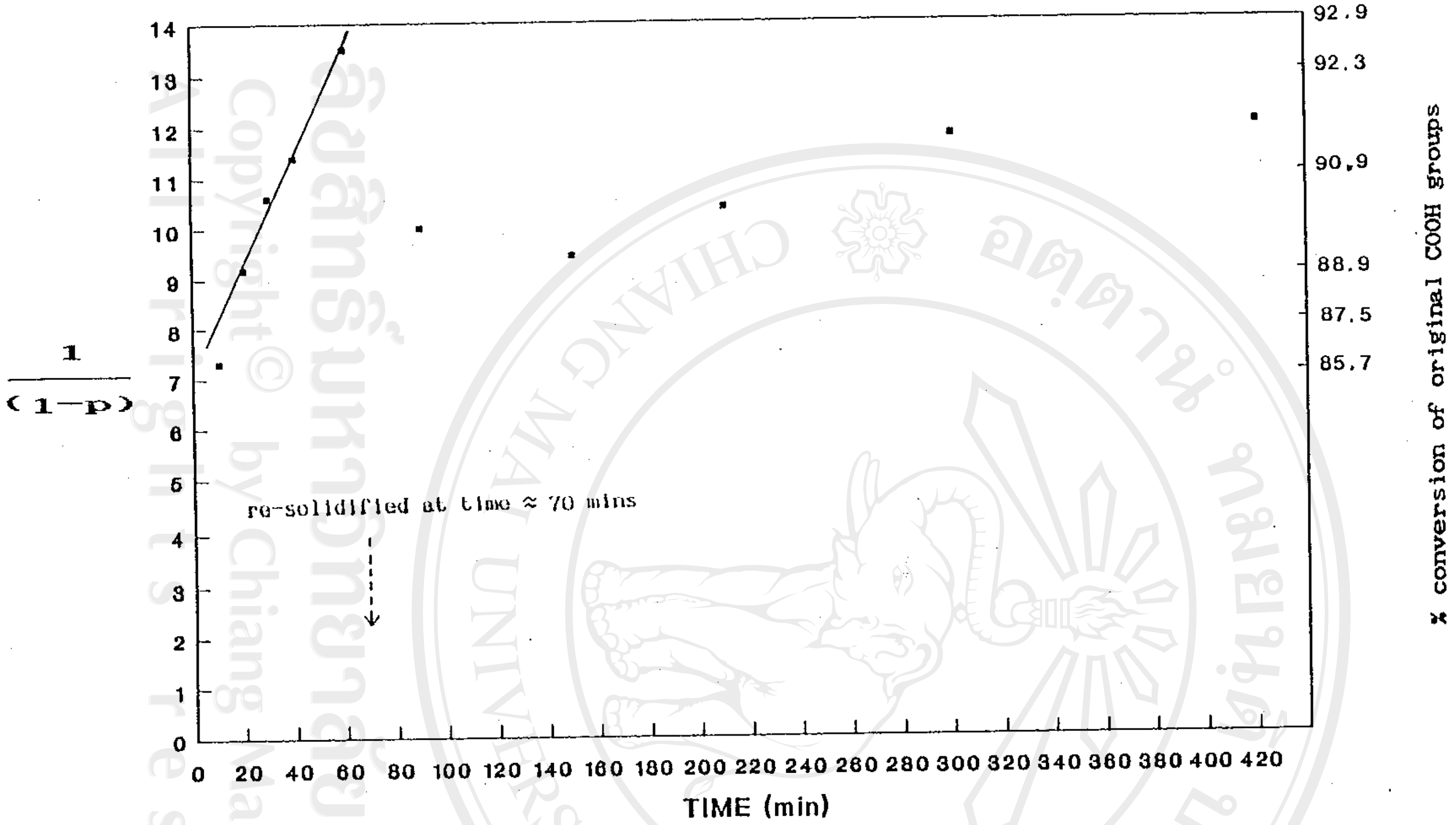


Fig. 2.13 : Second-order rate plot for the antimony trioxide-catalysed polyesterification of glycolic acid at 180 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2); RUN 8.

2.2.4.2.3 **RUN 9 : At 150 °C/atm/N_2 followed by at 200 °C/Reduced Pressure**

In RUN 9, the experimental procedure and conditions used were identical to those previously employed in RUN 3 except that 1% w/w antimony trioxide catalyst was added to the glycolic acid.

The results obtained and data analysis are presented in Table 2.12 and Fig. 2.14.

<u>Table 2.12</u> **:** **Data obtained from RUN 9 : antimony trioxide-catalysed polyesterification of glycolic acid at 200 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2).**

Time (min)	Weight of GA (g)	Weight of PGA (g)	[NaOH] (M)	NaOH used for PGA (ml)	NaOH used for blank (ml)	p	$\frac{1}{(1-p)}$	$\overline{M}_n$
10	0.570	0.445	0.1024	5.00	0.04	0.913	11.5	685
20	0.505	0.272	0.1098	3.85	0.03	0.883	8.55	514
30	0.583	0.398	0.0877	6.14	0.03	0.897	9.71	581
60	0.568	0.387	0.0976	3.90	0.02	0.926	13.5	801
90	0.592	0.343	0.0877	4.16	0.03	0.919	12.3	731
120	0.560	0.242	0.0976	2.58	0.02	0.921	12.7	755
150	0.536	0.180	0.0877	1.78	0.03	0.935	15.4	911
180	0.544	0.266	0.1090	2.24	0.02	0.931	14.5	859
210	0.589	0.296	0.0877	2.52	0.03	0.944	17.9	1056
300	0.608	0.089	0.0877	0.58	0.03	0.959	24.4	1433
360	0.601	0.159	0.0877	0.94	0.03	0.962	26.3	1543
420	0.581	0.066	0.0877	0.50	0.03	0.952	20.8	1224

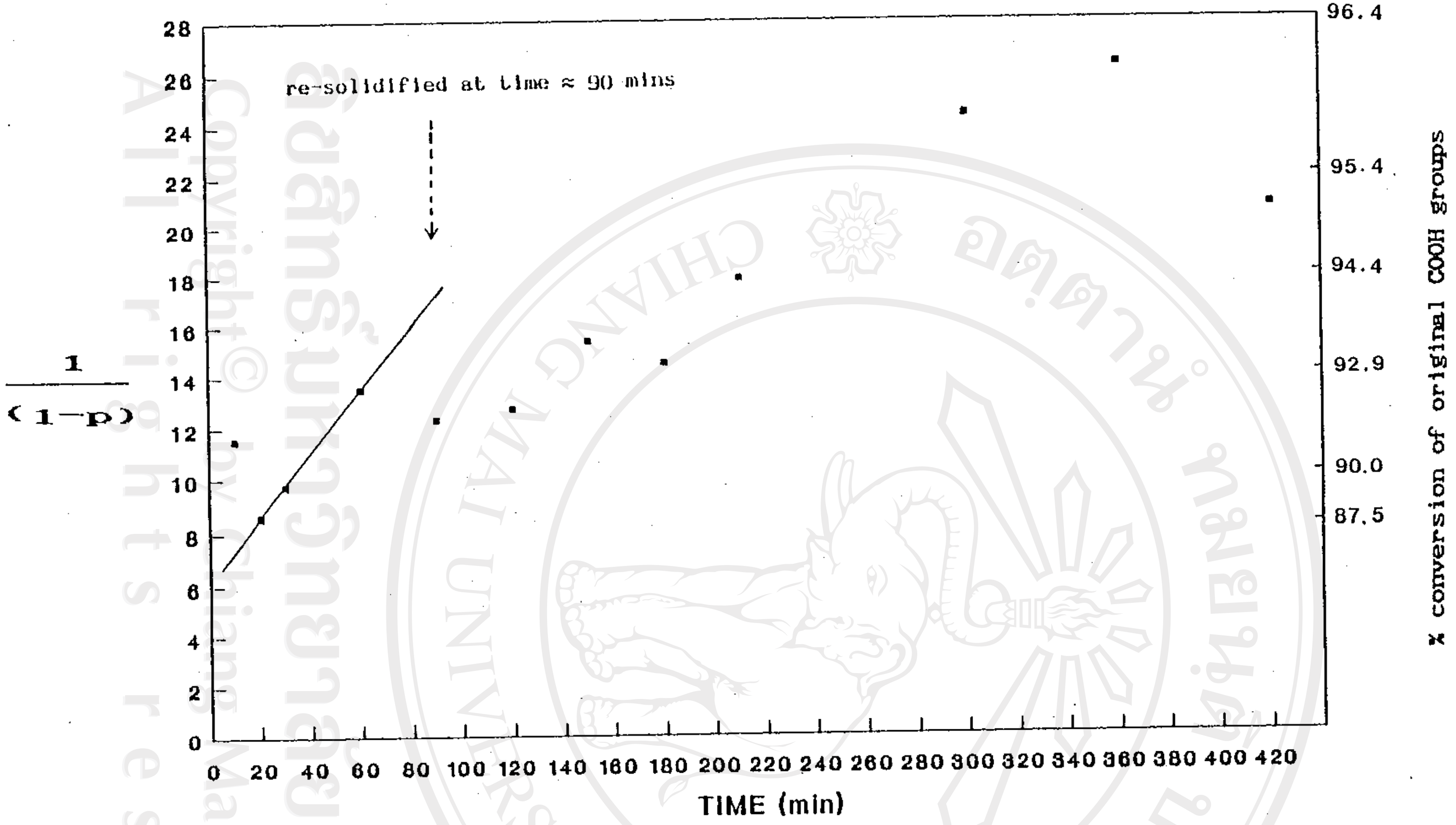


Fig. 2.14 : Second-order rate plot for the antimony trioxide-catalysed polyesterification of glycolic acid at 200 °C/reduced pressure (after initial solidification at 150 °C/atm/N_2); RUN 9.

2.2.4.2.4 Discussion of Antimony Trioxide-Catalysed Polyesterification [2, 36-38]

From the results in Tables 2.10-2.12 and Figs. 2.12-2.14, the antimony trioxide (Sb_2O_3) catalysed polyesterification of glycolic acid is seen to be less amenable to kinetic analysis than the previous uncatalysed and PTSA-catalysed systems. For example, there appears to be considerably more scatter in the data points in the second-order rate plots. However, from the initial steps of the plots, before solidification occurred, it is still possible to estimate the second-order rate constants even though there is a degree of uncertainty involved. The results for RUNS 7-9 are compared in Table 2.13.

Table 2.13 : **Comparison of kinetic parameters for antimony trioxide-catalysed polyesterification of glycolic acid under different conditions.**

RUN	Conditions	p_{max}	p range of slope	Second-order rate constant k_2 , g/equiv-min
7	150 °C/atm./N_2	0.909	0.901-0.903	4.3
8*	180 °C/red.press.	0.926	0.863-0.926	8.4
9*	200 °C/red.press.	0.962	0.913-0.919	9.2

* after solidification at 150 °C/atm/N_2

The kinetic parameters in Table 2.13 show, as expected, that as the final reaction temperature increases in the order RUN 7 < RUN 8 < RUN 9, the extent and rate of reaction increases.

The catalytic activity of Sb_2O_3 is confirmed by the fact that the initial increase in p is much faster than in the uncatalysed case. However, it is interesting to note that the maximum value of p attainable is less. This is probably due to some reverse reaction (depolymerisation) by chain scission at longer reaction times since Sb_2O_3 is known to be a catalyst for this reaction too, a fact used to advantage later on in this work.

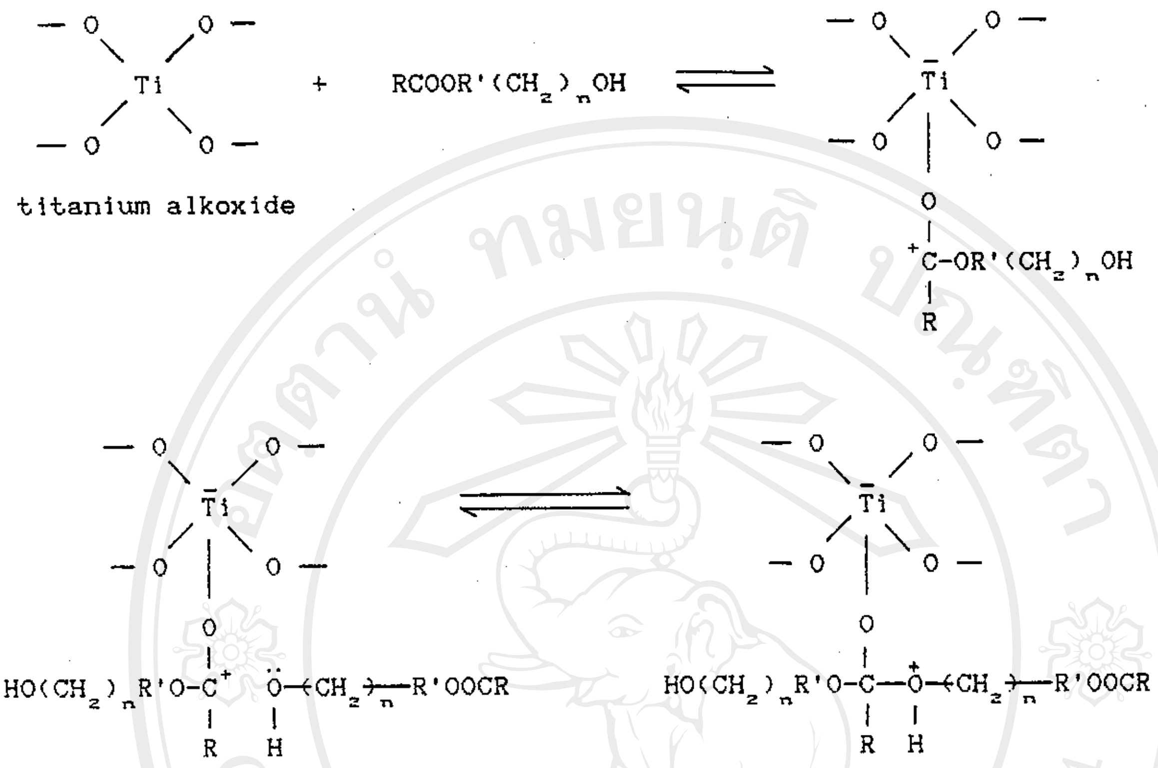
On the other hand, when compared to the PTSA-catalysed initial rates (see Table 2.9), the Sb_2O_3-catalysed rates under the same conditions (see Table 2.13) are slower by about a factor of 3. A possible explanation for this may lie in the fact that Sb_2O_3, as an ionically - bonded inorganic compound, is insoluble in the organic reaction medium. Thus, its catalytic role is heterogeneous in nature. In contrast, PTSA is a covalently-bonded organic compound which is soluble in the medium and therefore homogeneous in nature. This may explain not only why Sb_2O_3 is a less efficient catalyst but also why the kinetic data from the Sb_2O_3-catalysed RUNS 7-9 is less reliable.

Despite these potential drawbacks, many metal derivatives have been found to be effective catalysts for direct esterification at high temperature. Yet our knowledge of their mechanisms and kinetics is far from being definitive. Due to the economic relevance of alcoholysis, a large number of compounds of almost all the elements have been tested as catalysts and an enormous number of patents have been published. Comparison of the catalytic activity of various metal catalysts has been reported [2], among these, acetates of lead (II), lead (IV), zinc, manganese, calcium, cobalt and cadmium; oxides such as antimony trioxide and germanium dioxide; and titanium alkoxides. Their overall catalytic activity is probably the result of many different factors : extent of solubility in the reaction medium, exchange-reaction capability of the original ligands with reactants, and effects on concomitant reactions are probably the most relevant. Furthermore, each of these factors can obviously be affected by reaction conditions such as type and concentration of functional groups and reaction temperature.

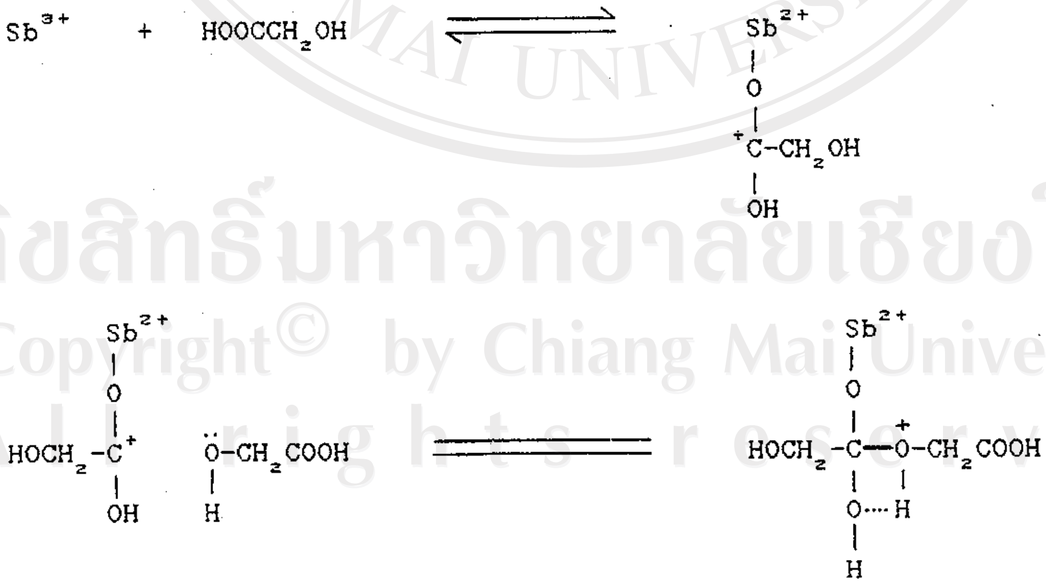
Analogously to proton catalysis, which introduces a positive charge into a substrate, distorting the electronic distribution in the molecule and thus making reactions feasible, metal compounds, when they can form a complex with a substrate, may also introduce a positive charge into a molecule. However, many experimental results suggest that the behavior of these catalysts in the reacting system is rather more complex. Examples of exchange reactions between the metal ligands with compounds bearing OH or COOH groups are well known in the literature; additional evidence is the absence of catalytic activity for metal derivatives which cannot undergo exchange reactions with the substrate, implying that exchange of ligands is a prerequisite to catalytic activity.

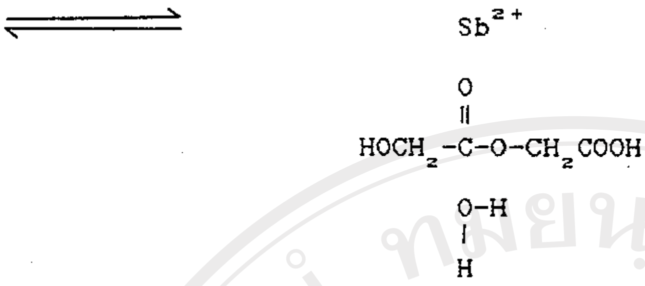
On the other hand, when exchange is possible the catalytic effect does not depend on the nature of the ligands unless the ligands resulting from the exchange are too bulky; in this latter case, they can hinder coordination with the metal resulting in a decrease of catalytic effectiveness. Association or condensate forms of the catalyst can be either already present in the initial catalyst or can be formed during the reaction and are probably in equilibrium with the species bearing OH and COOH groups and with water. Accordingly, the catalyst can be present in various forms which may change with the composition of the reaction system and therefore with conversion; the effective number of catalytic sites and the catalytic activity of the various forms are generally unknown and can differ from that corresponding to the amount of catalyst introduced. As a result, it is often no longer possible to speak of kinetic orders owing to the complexity of the kinetic equations; however, under particular conditions, the kinetic equations can reduce to simpler forms.

Many questions are still unanswered about the true catalytic mechanism of most metal catalysts. On reason is that the original catalyst often undergoes exchange reactions with reactants leading to products of unknown concentration and catalytic activity; the overall catalytic activity is therefore the result of a complex set of reaction and coordination equilibria involving catalyst and functional groups. In addition to their effect on growing reeactions, metal catalysts may also affect side reactions, and compounds with good catalytic activity towards growing reactions can be unsuitable owing to their effect on side reactions. This is the case for titanium alkoxides, for example, which have been found to be the most efficient and are frequently used to prepare polyesters by the process of direct esterification or ester interchange. In this case, the catalytic mechanism may involve the initial formation of an adduct between a carbonyl group and the titanium atom. The consequent decrease in the electron density at the carbonyl carbon atom should facilitate its subsequent electrophilic attack on the hydroxyl oxygen of a second molecule. The proposed mechanism is shown in the following scheme for a model compound study [2].



By analogy with this mechanism, the Sb_2O_3-catalysed polyesterification of glycolic acid may therefore be envisaged as :





$$\rightleftharpoons \qquad \begin{array}{c} Sb^{2+} \\ O \\ \| \\ HOCH_2\text{-}C\text{-}O\text{-}CH_2COOH \\ O\text{-}H \\ | \\ H \end{array}$$

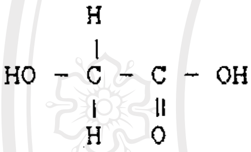
In this mechanism, the Sb^{3+} ion is clearly acting as a Lewis acid. Also, considering the insolubility of Sb_2O_3 in the reaction medium, the reaction must presumably occur at the Sb_2O_3 crystal surface. Due to its limited surface area, this may help to explain its somewhat different kinetics from those of the PTSA-catalysed reaction.

2.2.5 **Structural Analysis of Low Molecular Weight Poly(glycolic acid) by Infrared Spectrometry** [39-42]

The polyesterification of glycolic acid to form poly(glycolic acid) can be confirmed by structural analysis using infrared spectrometry.

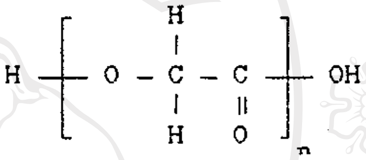
In Fig. 2.15, the infrared (IR) spectra of the glycolic acid monomer and the poly(glycolic acid) product obtained from RUN 3 (uncatalysed polyesterification at 150 °C/atm/N_2 followed by at 200 °C/ reduced pressure for 150 minutes) are compared; their interpretations are detailed in Table 2.14. The spectra were obtained with the samples in the form of KBr discs. The corresponding reference spectra are shown in Fig. 2.16, as obtained from the literature [41] for glycolic acid and from a commercial sample (Polysciences, Inc., USA) for poly(glycolic acid).

Comparison of Structures :



$HO-CH_2-C(=O)-OH$

glycolic acid



$H-[O-CH_2-C(=O)]_n-OH$

poly(glycolic acid)

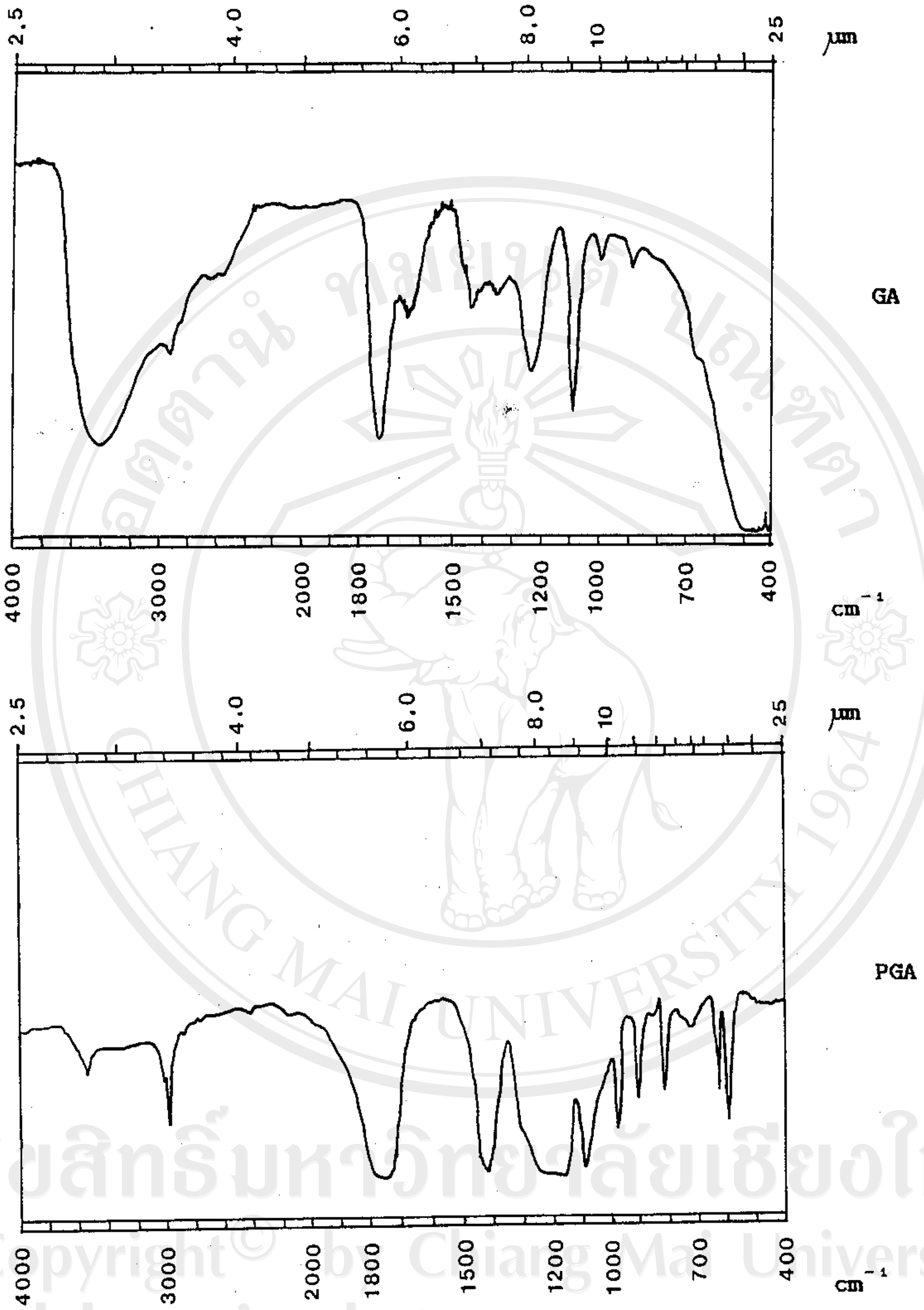
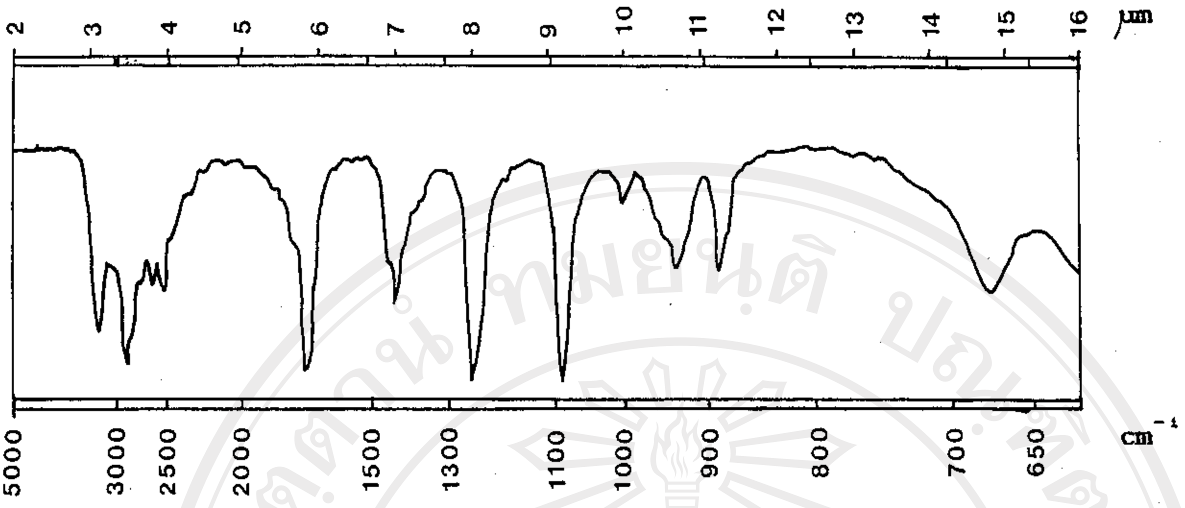
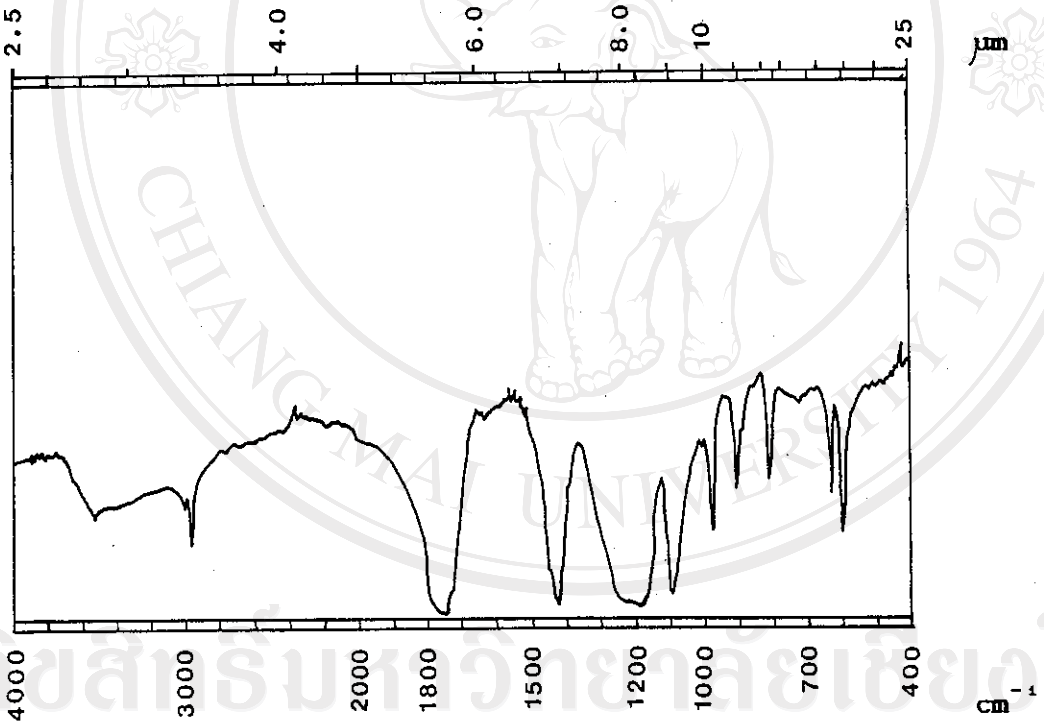


Fig. 2.15 : Comparison of the infrared spectra of the glycolic acid starting material and the poly(glycolic acid) product (from RUN 3).



(a)



(b)

Fig. 2.16 : Reference infrared spectra of :

(a) glycolic acid [41];

(b) commercial poly(glycolic acid) sample (Polysciences, Inc.).

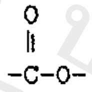
Table 2.14 : **Infrared spectra interpretation for glycolic acid and poly(glycolic acid).**

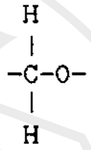
Vibrational Assignments	Wavenumber (cm^{-1})	
	GLYCOLIC ACID	POLY(GLYCOLIC ACID)
O-H str. in OH and COOH, overlapping	3700 - 2400	3700 - 3450
C-H str. in CH_2	2930 (superimposed upon the broad O-H stretching band)	2980
C=O str.	1740 - 1720	1800 - 1720
C-H out-of plane bend.	1440 , 1350	1450 - 1400
O-H in-plane bend.	1440 , 1350 (coupled with C-H out-of-plane bend)	1450 - 1400
C-O str.	1260 - 1200 (a) 1100 - 1080 (b)	1260 - 1150 (c) 1100 - 1080 (d)
O-H out-of-plane bend.	1000 - 880	980 - 820

NOTES :

a = in COOH

b = in OH

c = in acyl-oxygen bonds (i.e.,  $-\overset{\overset{\displaystyle O}{\|}}{C}-O-$)

d = in alkyl-oxygen bonds (i.e.,  $-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-$)

str. = stretching

bend. = bending

From the IR spectra in Fig. 2.15 and the peak assignments in Table 2.14, the most obvious differences which confirm that glycolic acid polyesterification did, in fact, occur are:

(1) the prominent O-H stretching peaks in glycolic acid, appearing at 3700 - 2400 cm^{-1} (in -OH and -COOH, overlapping), are greatly reduced in the polymer due to the relatively low concentration of remaining -OH and -COOH chain-ends;

(2) the slight shift in the carbonyl C=O stretching peak from 1740 - 1720 cm^{-1} in glycolic acid to 1800 - 1720 cm^{-1} in the polymer is due to the change in chemical environment from C=O in acid (-COOH) to C=O in ester (-COO-).