CHAPTER 3

MONOMER PREPARATION AND INSTRUMENTAL METHODS

3.1 Chemicals, Apparatus and Instruments

3.1.1 Chemicals

The chemicals used in this research project were as shown in Table 3.1 below.

Table 3.1 : Chemicals used in this research project.

Chemical	Usage	Grade	Supplier
Glycolic acid	Monomer precursor	Purum	Fluka AG
δ-Valerolactone	Monomer	Lab. reagent	Fluka AG
Antimony trioxide	Catalyst	Lab. reagent	Fluka AG
Aluminium triethyl	Initiator	Lab. reagent	E. Merck
Stannous oxalate	Initiator	Lab. reagent	E. Merck
Stannous octoate	Initiator	95%	E. Merck
Boron trifluoride etherate	Initiator	Lab. reagent	Aldrich
Ethyl acetate	Solvent	AR Grade	E. Merck
1,4-Dioxane	Solvent	AR Grade	Aldrich
Toluene	Solvent	Extra pure	E. Merck
Ethanol	Solvent	Absolute	E. Merck
n-Hexane	Non-Solvent	AR Grade	E. Merck
Acetone	Solvent	Lab. reagent	E. Merck
Chloroform	Solvent	AR Grade	E. Merck
Benzyl alcohol	Solvent	AR Grade	Fluka AG
Dimethylsulfoxide	Solvent	Lab. reagent	Fluka AG
Sodium di-hydrogen phosphate dihydrate	pH buffer	AR Grade	E. Merck

Table 3.1 : (continued)

Chemical	Usage	Grade	Supplier
Di-sodium hydrogen orthophosphate	pH buffer	AR Grade	BDH Chemicals
Sodium hydroxide	Adjust pH	Lab. reagent	E. Merck
Water	Immersion medium	Deionized	-
Calcium chloride	Drying agent	Lab. reagent	E. Merck
Calcium hydride	Drying agent	Lab. reagent	E. Merck
Molecular sieves Type 4 Å	Drying agent	Lab. reagent	Fluka AG
Benzil	Osmometry calibrant	-	Prolabo

3.1.2 Apparatus and Instruments

The main items of apparatus and instruments used were as given in Table 3.2.

Table 3.2 : Apparatus and instruments used in this research project.

Apparatus and Instruments	Company	Model
Infrared Spectrometer	Jasco	810
Melting Point Determinator	Buchi	SMP-20
FT-IR Spectrometer	Nicolet	510
Differential Scanning Calorimeter	Perkin-Elmer	DSC 7
Thermogravimetric Analyzer	Perkin-Elmer	TGA 7
Vapour Pressure Osmometer	Knauer	-
C-13 Solid-State NMR Spectrometer	Chemagnetics	CMX-200
Elemental Analyzer (CHNS/O)	Perkin-Elmer	PE-2400 Series II
Automatic Viscosity Measuring System	Schott-Gerate	AVS 300
Micro-Ubbelohde Viscometer	Schott-Gerate	537 10
Controlled Atmosphere Glove Box	Labconco	50004
Vacuum Oven	Lab-line Instruments	3620-1
Vacuum Oven	Eyela	VOS-300 SD
Melt Spinning Apparatus	-	-

Table 3.2 : (continued)

Apparatus and Instruments	Company	Model
pH Meter	Radiometer Copenhagen	PHM 61
Incubator	Memmert	-
KBr Press	Jasco	-
Autoclave	Hirayama	HL 42 ADY
Analytical Balance	Sartorious	BA 210S

3.2 Monomer Preparation and Purification

The monomers used in this research project were δ-valerolactone and glycolide. Since glycolide is prohibitively expensive to buy (Polysciences, Inc. : $ US 46.60/10 g), it was synthesized from its much cheaper precursor, glycolic acid. The method of synthesis is described in the following section 3.2.2. δ-Valerolactone is more readily available and was purchased for use in this research project. However, this commercially available monomer may contain a number of impurities or additives that must be carefully removed prior to polymerization.

3.2.1 Purification of δ-Valerolactone by Vacuum Distillation

Commercial δ-valerolactone (Fluka, assay > 98 %) was purified before use by vacuum distillation (see Fig. 3.1), the constant boiling fraction from 82.0-84.0°C/ 2-3 mm Hg pressure being collected (cf. lit. [35] b.pt. = 58.0-60.0°C/ 0.5 mm Hg). Pure δ-valerolactone was obtained as a clear colorless liquid at room temperature and was stored in the refrigerator until required for use in polymerization.

In order to prevent thermal self-polymerization during vacuum distillation, δ-valerolactone should be distilled quickly in small amounts at the lowest temperature and pressure possible.

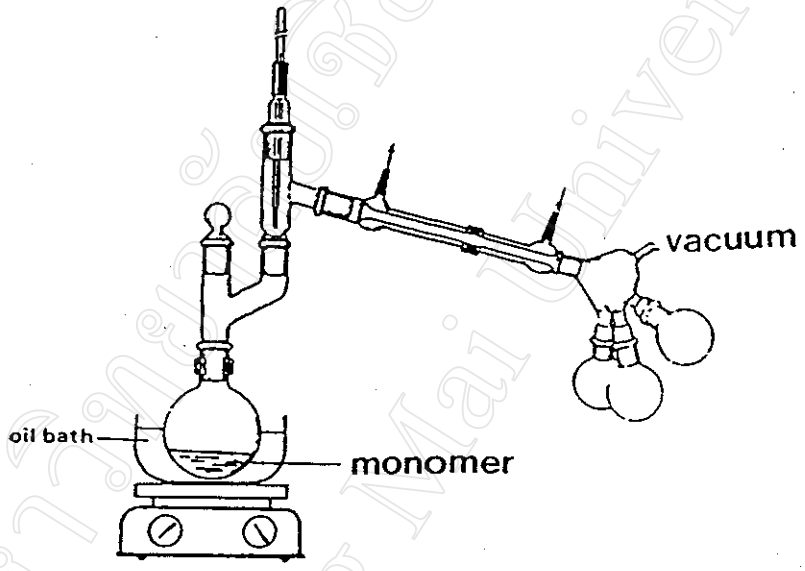


Fig. 3.1 : Vacuum distillation apparatus used for purification of δ-valerolactone.

The IR spectrum of purified δ-valerolactone shown in Fig. 3.2 can be compared with the reference spectrum in Fig. 3.3. The major vibrational peaks are listed in Table 3.3. The spectrum was obtained from a neat sample contained in a NaCl cell.

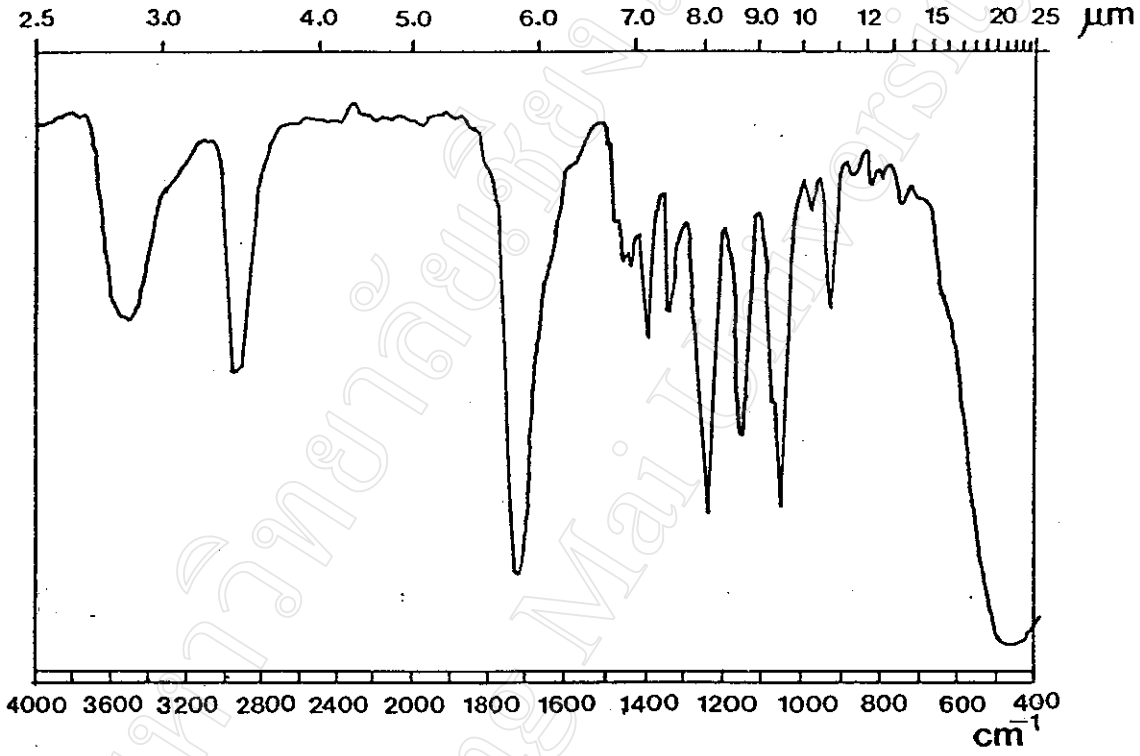


Fig. 3.2 : Infrared spectrum of purified δ-valerolactone.

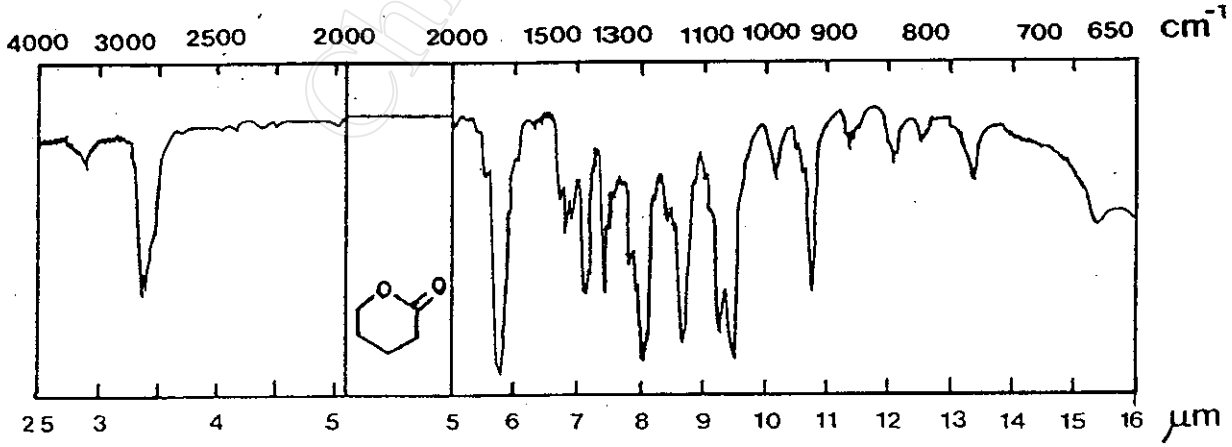


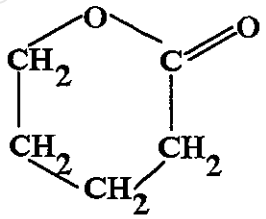
Fig. 3.3 : Reference infrared spectrum of δ-valerolactone [36].

Table 3.3 : Infrared absorption band assignments for purified δ-valerolactone.

Vibrational assignment	Band Intensity *	Wavenumber (cm^{-1})
O-H stretching, in OH	m	3600-3450
C-H stretching, in CH_2	m	2970-2900
C=O stretching	s	1720
C-H bending, in CH_2	m	1440, 1400, 1340
C-O stretching, acyl-oxygen	m	1150
C-O stretching, alkyl-oxygen	m	1050

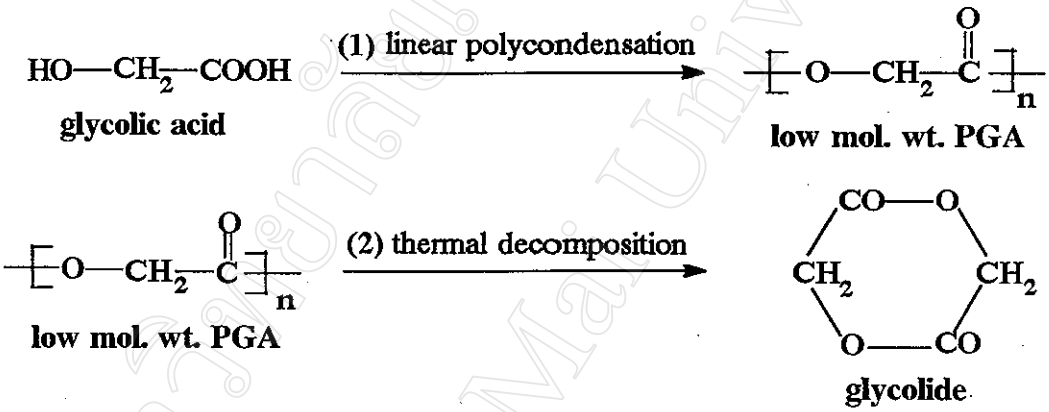
*
m = medium, s = strong

The chemical structure of δ-valerolactone is as shown below :



3.2.2 Synthesis of Glycolide

The synthesis of glycolide dates back to the early 1930s and the pioneering work of Carothers [31]. It is a two-step synthesis involving, firstly, the linear polycondensation of glycolic acid to low molecular weight poly(glycolic acid) followed, secondly, by thermal decomposition of the polymer to yield glycolide as the primary decomposition product, as shown below.



In a typical synthesis reaction in this project, approximately 35 g of glycolic acid together with approximately 0.35 g of antimony trioxide catalyst (1% by weight) were heated at 130°C under a nitrogen atmosphere in a conventional short-path distillation apparatus (see Fig. 3.4 a). Heating was continued for about 3 hours until the water of polycondensation ceased to distill from the flask.

The apparatus was then adapted for vacuum take-off (see Fig. 3.4 b) and heating continued for a further 1 hour at a reduced pressure of 2-3 mm Hg. Over the following 3-4 hours, the heating temperature was increased up to 150°C and then, when the flask contents started to solidify, increased further up to 180°C. The product at this stage was low molecular weight poly(glycolic acid).

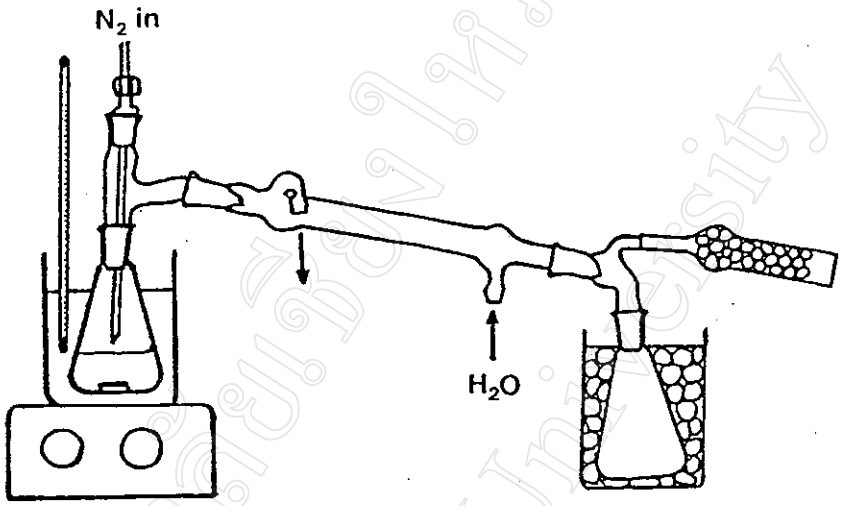
Finally, for an additional period of about 4 hours, the heating temperature was increased up to 300-320 °C in order to thermally degrade the low molecular weight PGA to yield glycolide as the primary product.

Crude glycolide began to distill out of the flask and solidify in the condenser at about 290°C. This crude product was obtained as a pale yellow crystalline solid in approximately 60-70% yield based on the initial glycolic acid. After recrystallization, it had an observed melting range of 80-82°C (cf., lit. [37] m.p. 82-84°C).

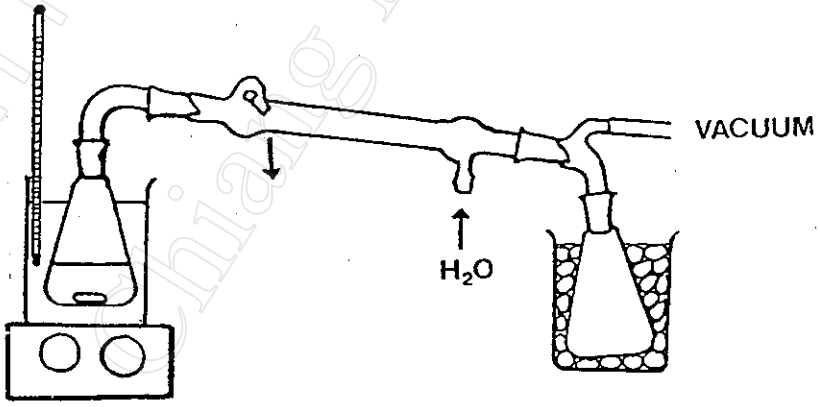
3.2.2.1 Purification and Purity Analysis of Glycolide

The crude glycolide which had collected in the condenser was carefully and quickly removed due to its hygroscopic nature. It was then quickly ground up and purified by recrystallization from distilled ethyl acetate, the purified glycolide being a white, needle-like, crystalline solid. It was dried to constant weight in a vacuum oven at 50°C and stored in a vacuum desiccator. Analysis by differential scanning calorimetry (DSC) showed that purified glycolide had a DSC melting peak from 70 to 88°C with a peak onset of 81.34°C (see Fig. 3.5) and was obtained in approximately 60 % yield.

In order to determine the actual purity of the recrystallized glycolide by the DSC, the instrument's Purity Analysis Software Program was employed [38]. To obtain the best results for purity analysis, a slow scanning rate (2°C per minute or less) and a small sample size in the range of 1-3 mg are recommended [38]. Both the synthesized and commercial (Polysciences, Inc.) glycolide samples were analyzed and their purities compared. From their DSC curves (see Fig. 3.6), purities of 99.65 % (synthesized) and 99.26 % (commercial) were obtained. These results confirm that the glycolide synthesized in this work was of a comparable purity with that of the commercial product and therefore suitable for polymerization.



(a)



(b)

Fig. 3.4 : Apparatus used in the two-stage preparation of glycolide :
(a) glycolic acid polycondensation to low mol. wt. PGA;
(b) thermal decomposition of low mol. wt. PGA to glycolide.

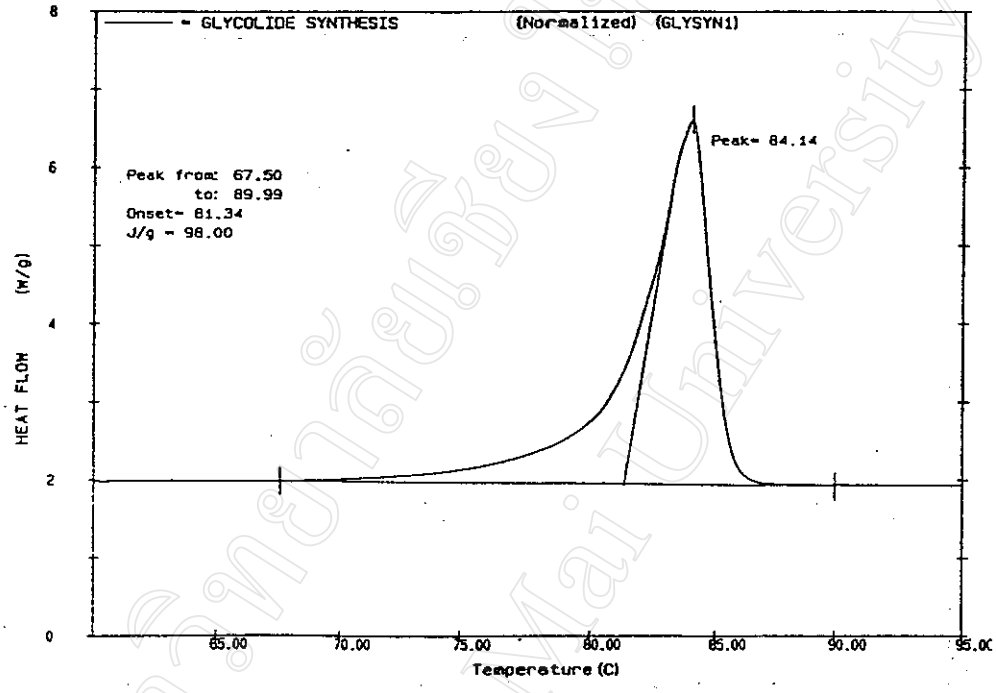
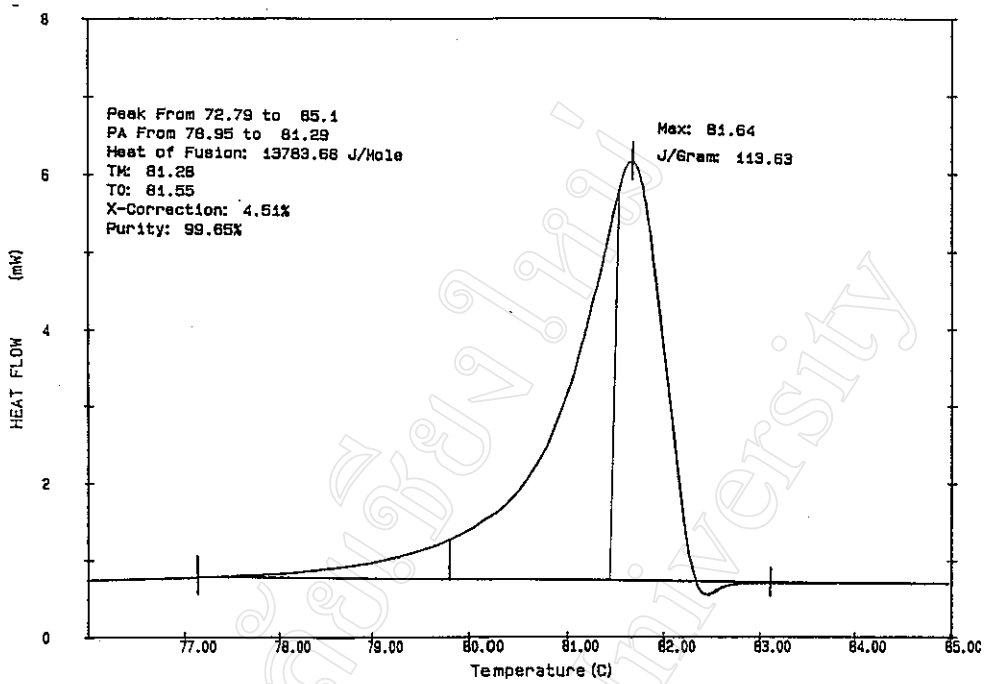
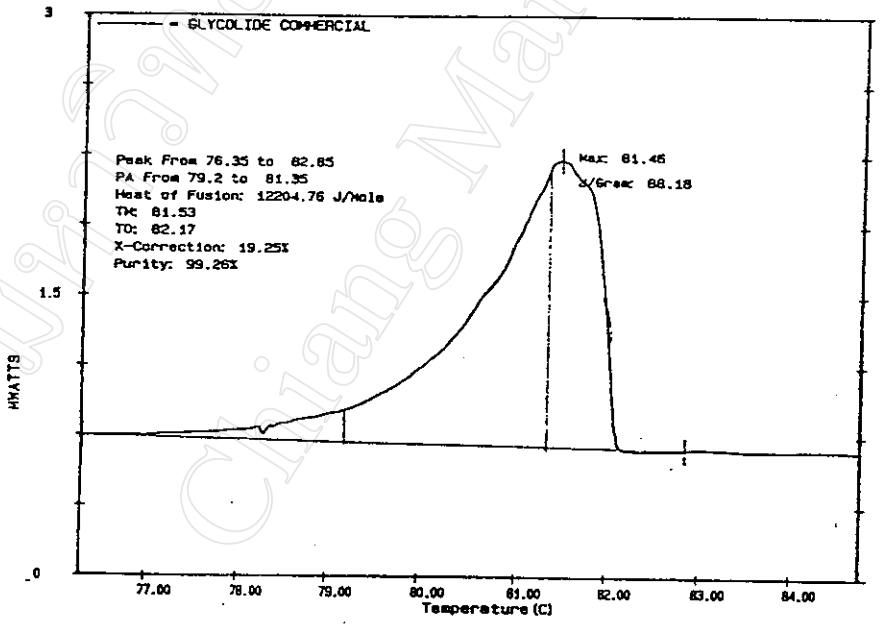


Fig. 3.5 : DSC curve of synthesized glycolide (purified by recrystallization).



(a)



(b)

Fig. 3.6 : DSC curves showing the results of the purity analyses of
(a) purified glycolide (from synthesis)
(b) commercial glycolide (Polysciences, Inc.).

3.2.2.2 Structural Analysis of Glycolide by Infrared Spectroscopy

Fig. 3.7 shows a typical infrared (IR) spectrum of the purified glycolide (from synthesis) compared with commercial glycolide (Polysciences, Inc.). The major vibrational peaks are compared in Table 3.4. Both spectra were obtained with the samples prepared in the form of KBr discs.

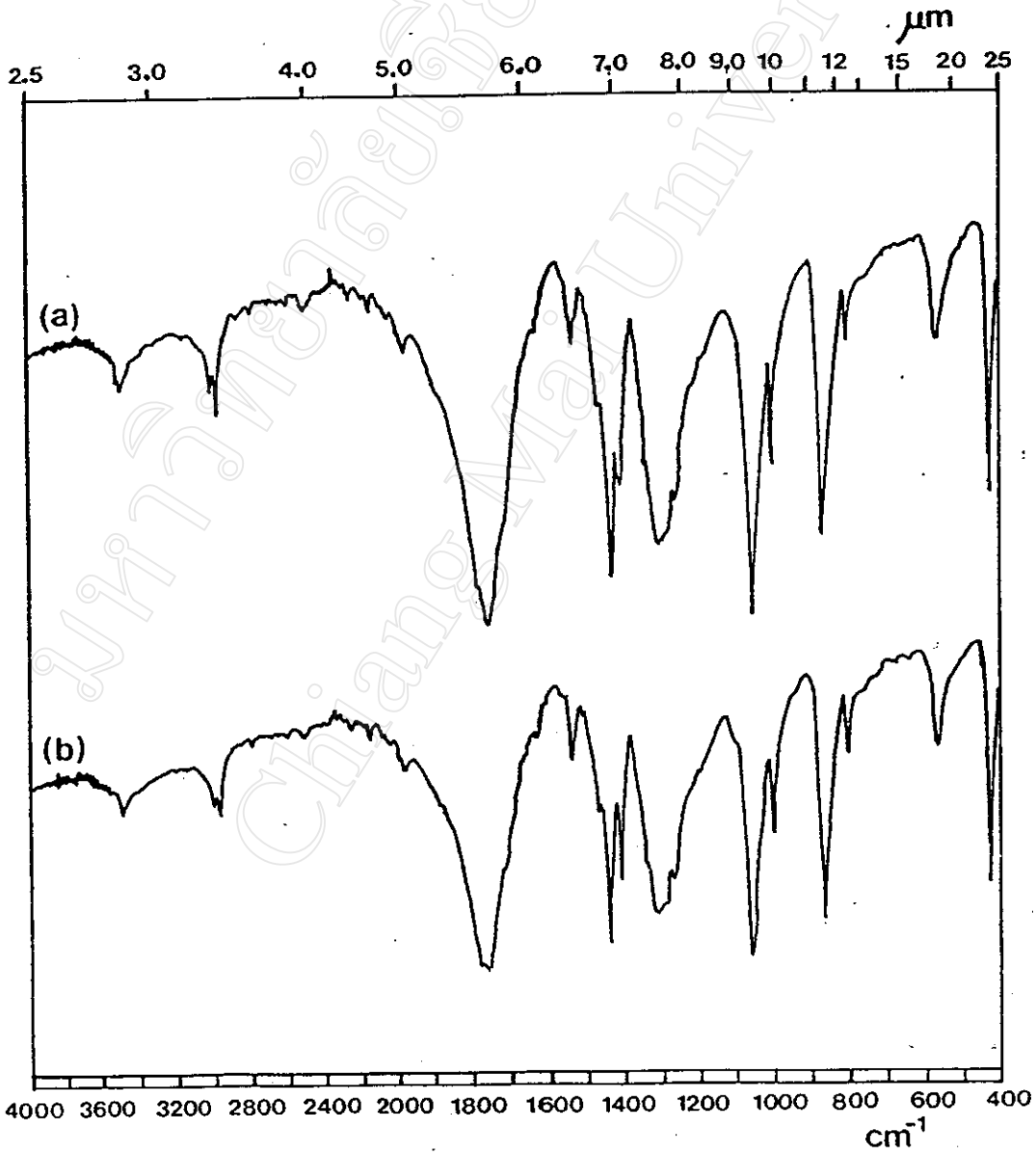
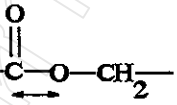
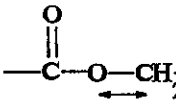


Fig. 3.7 : Infrared spectra of (a) purified glycolide (from synthesis) and (b) commercial glycolide (Polysciences, Inc.).

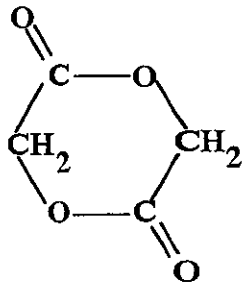
Table 3.4 : Comparison of IR data of purified glycolide (from synthesis) and commercial glycolide (Polysciences, Inc.).

Vibrational Assignment	Band Intensity *	Wavenumber (cm^{-1})	
		Synthesized Glycolide	Commercial Glycolide
C-H stretching, in CH_2	w	3050-2950	3050-2950
C=O stretching	s	1760	1780-1760
C-H bending, in CH_2	m	1440, 1410	1440, 1410
C-O stretching, acyl-oxygen	m	1320-1280 (a)	1320-1280 (a)
C-O stretching, alkyl-oxygen	m	1060 (b)	1060 (b)

* w = weak, m = medium, s = strong

(a) = in  acyl-oxygen, (b) = in  alkyl-oxygen

The chemical structure of glycolide is as shown below:



3.3 Instrumental Methods for Polymer Characterization

In the study of polymers, their characterization is the essential intermediate step between their synthesis and their development as useful materials. In this research project, the polymer products obtained were characterized by the following combination of instrumental methods :

(i) infrared spectroscopy (IR) :
- for structural characterization

(ii) high-resolution nuclear magnetic resonance (NMR) spectrometry (Carbon-13 Solid-State NMR)
- for structural characterization and copolymer composition

(iii) elemental analysis (CHNS/O)
- for copolymer composition

(iv) differential scanning calorimetry (DSC)
- for temperature transitions and crystallinity studies

(v) thermogravimetry (TG)
- for thermal stability studies

(vi) vapour pressure osmometry
- for molecular weight determination

(vii) dilute-solution viscometry
- for intrinsic viscosity determination ($\propto$ molecular weight)

3.3.1 Infrared Spectroscopy [39]

Infrared spectroscopic techniques are widely used in polymer investigations in a variety of applications. In addition to their qualitative analysis for structural characterization, infrared spectra may also be analyzed quantitatively for following microstructural changes (e.g., differences in copolymer composition) by determination of the absorbance ratio of functional groups through their characteristic absorption frequencies.

Fourier transform infrared spectroscopy (FTIR) has proved to be a powerful tool in polymer characterization. However, it has been applied only to the observation of events that are stationary in time, or at least stationary with respect to the measurement time. The multiplex characteristics (the ability to measure all spectral elements) of the interferometer, together with the high energy throughput, provide FTIR with a substantial gain in signal to noise ratio for a given measurement time, as compared to a dispersive instrument. Hence, the use of FTIR to study time-dependent phenomena is feasible, the advantage being that simultaneous measurements of band position, shape and relative intensity are made.

Despite the great improvement in the measurement timescale when FTIR is used, it is impractical, if not impossible, for the interferometer to follow rapidly evolving events with time resolution in the order of milliseconds. The limit is reached when the time period required for one scan of the moving mirror is longer than the time resolution required to describe the physical phenomena. Furthermore, in order to improve the signal to noise ratio, co-adding scan is necessary, a procedure which further degrades the time resolution. Therefore, a number of time-resolved FTIR techniques have been developed to increase the speed of data acquisition to a value suitable for characterizing the dynamics of structural changes in polymers.

In this research project, a Jasco Model IR-810 and a Nicolet FT-IR 510 Infrared Spectrometer, as shown in Figs. 3.8 and 3.9, were used for the recording of infrared spectra.

Fig. 3.8 : The Jasco Model IR-810 Infrared Spectrometer.

Fig. 3.9 : The Nicolet Model FT-IR 510 Infrared Spectrometer.

3.3.2 C-13 Solid-State Nuclear Magnetic Resonance Spectroscopy [39].

Nuclear magnetic resonance (NMR) spectroscopy is a most effective and significant method for observing the structure and dynamics of polymer chains both in solution and in the solid state. In the solid state, where the motions of the chains are relatively slow, the resonances are broad owing to the local dipolar field at each observed nucleus. This phenomenon of dipolar broadening tends to abolish all structural information.

In this research project, carbon-13 solid-state NMR spectra were recorded on a Chemagnetics CMX-200 spectrometer at a frequency of 50.3 MHz under conditions of cross-polarization, high-power proton decoupling and magic-angle spinning (CP/MAS). The relevant operating parameters were as follows:

spectral width	18 kHz
acquisition time	57 msec
contact time	1 msec
recycle delay	20 sec
pulse width	4 μsec

The spectra obtained are the result of 64 scans and are Fourier transformed to 4k data points with a line broadening of 17.6 Hz (= 1/acquisition time).

3.3.3 Elemental (CHNS/O) Analysis [40]

Elemental analysis is particularly useful in copolymer characterization. Since copolymers are usually composed of carbon, hydrogen, and oxygen, the percentages of which can be determined by elemental (CHNS/O) analysis, the corresponding percentages of each monomer in the copolymer can be calculated.

A Perkin-Elmer PE 2400 Series II CHNS/O Analyzer was used in this research project for the rapid determination of the carbon, hydrogen, and oxygen contents in the copolymers. The PE 2400 Series II Analyzer is

capable of operating in multiple analysis modes. These modes include the simultaneous determination of carbon, hydrogen, and nitrogen (option 1, CHN), plus sulphur (option 2, CHNS), and/or the determination of oxygen (option 3, oxygen). Fig. 3.10 shows the PE 2400 Series II CHNS/O Analyzer, Printer, and Perkin-Elmer AD-6 Ultramicrobalance. The specifications for the CHNS/O options used in this project were:

SAMPLE TYPE	:	SOLIDS AND LIQUIDS
TIME	:	8 MINUTES
ACCURACY	:	PLUS/MINUS 0.3 %
SAMPLE SIZE	:	1-2 mg

Fig. 3.10 : The PE 2400 Series II CHNS/O Elemental Analyzer, Data Printer and Perkin-Elmer AD-6 Ultramicrobalance.

In the CHNS operating mode (option 2), the PE 2400 Series II CHNS/O Analyzer employs a combustion method to convert the sample elements to simple gases. The sample is first oxidized in a pure oxygen environment using classical reagents. Products produced in the combustion zone include CO_2, H_2O, N_2, and SO_2. Other elements, such as halogens, are removed in the reduction zone.

In the oxygen operating mode (option 3), the Analyzer performs an oxygen analysis. The sample is pyrolyzed in a helium-hydrogen environment at 1000°C over platinized carbon where the pyrolyzed oxygen products of reaction are converted to carbon monoxide. The carbon monoxide and other gases pass through a scrubber trap where acid gases and water are removed.

The resulting gases are homogenized and controlled to exact conditions of pressure, temperature, and volume. The homogenized gases are allowed to de-pressurize through a column where they are separated in a stepwise steady-state manner and detected as a function of their thermal conductivities. Figs. 3.11 and 3.12 show the separation of gases for the CHNS and oxygen determinations respectively.

3.3.4 Differential Scanning Calorimetry (DSC) [38, 41]

Differential scanning calorimetry is a technique in which the difference in energy input into a substance and a thermally inert reference is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. Some examples of energy changes in polymers which can be determined by DSC are those which are associated with the glass transition temperature (Tg), crystallization temperature (Tc), and melting temperature (Tm). Any transition in the range of -100°C to +600°C which involves the absorption or evolution of heat is amenable to study. Greatest accuracy in temperature measurement is attained by observing the following four considerations :

(1) precise calibration of the instrument
(2) small sample size (< 5 mg)
(3) proper encapsulation of the sample
(4) slow scanning rate (< 10°C/min)

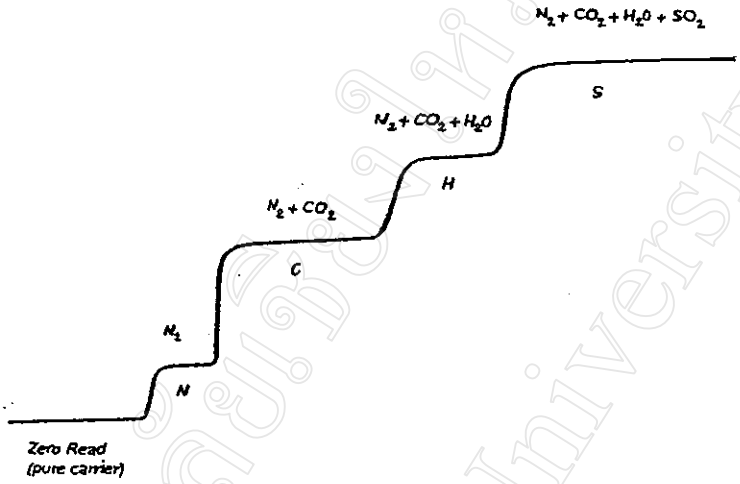


Fig. 3.11 : Separation of gases in elemental analysis for CHNS determinations.

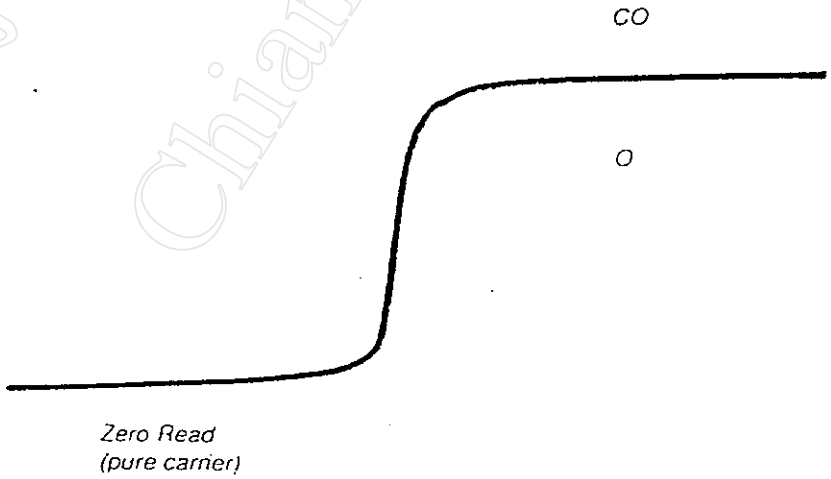


Fig. 3.12 : Separation of gas in elemental analysis for oxygen determinatio

For precise measurements of heats of transition, it is necessary to add two further considerations :

(1) precise weighing (± 0.01 mg)
(2) precise calculation of the peak area lying under the endotherm or exotherm caused by the transition

From the DSC curve, the area under a transition peak is directly proportional to the energy of the change per unit weight.

In this research project, the particular instrument used was a Perkin-Elmer DSC 7 Differential Scanning Calorimeter (see Fig. 3.13). The operating conditions employed for each sample analysis were as shown in Table 3.5. In addition, nitrogen gas (99.9%, dry, oxygen-free grade) was used as the purge gas at a pressure of 20 lbs/in^2 (flow rate ≈ 40.0 ml/min.).

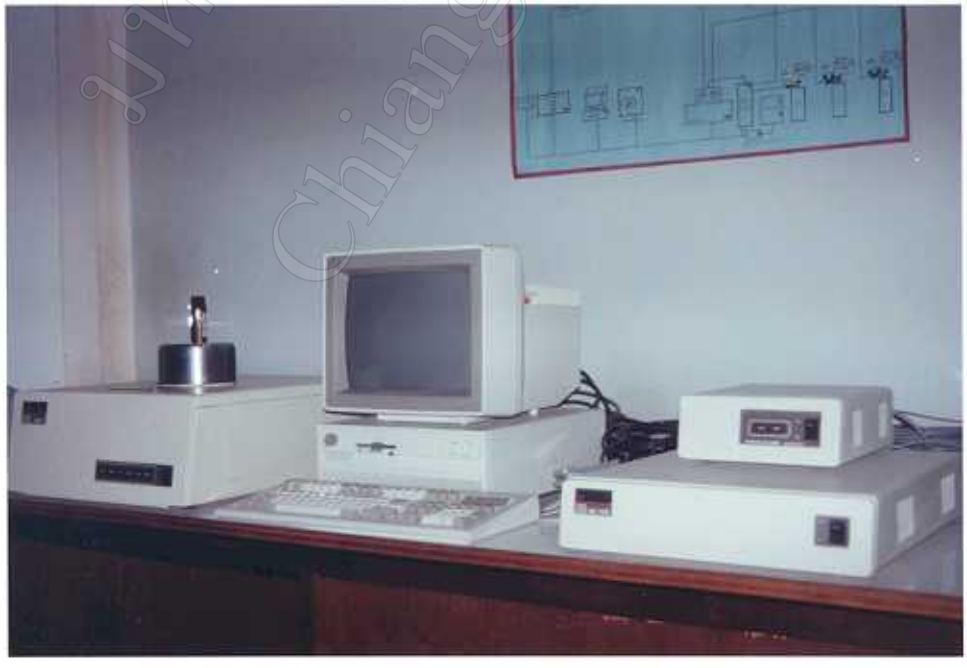


Fig. 3.13 : The Perkin-Elmer DSC 7 Differential Scanning Calorimeter.

Table 3.5 : DSC operating conditions used for polymer analysis.

DSC Method : PVL

Sample Information

Sample ID : PVL/Sn(Octoate)
Operator ID : MONTIRA

Parameters		Conditions	
Final Temp :	230.0 C	End Condition :	Load Temp
Start Temp :	25.0 C	Load Temp :	25.0 C
Scanning Rate :	10.0 C/min.	Go To Temp Rate :	50.0 C/min.
Y Range :	40.0 mW	Event 1 Time :	0.00 min.
*Sample Weight :	4.000 mg.	Event 2 Time :	0.00 min.
		Date Delay :	0.00 min.
		Time at T Start :	0.00 min.
		Time at T Final :	0.00 min.
		Y Initial Value :	10.0 mW

* variable according to sample

3.3.5 Thermogravimetry (TG) [42-44]

Thermogravimetry is a most useful method for the investigation of the thermal decomposition and stability of a polymer. Thermogravimetry is generally defined as a technique in which the weight of a substance is measured as a function of temperature whilst the substance is subjected to a controlled temperature program. Thermogravimetry may be divided into two types :

(1) isothermal thermogravimetry, in which the method is to record the change in weight of the sample as a function of time at a constant temperature, and

(2) non-isothermal (or dynamic) thermogravimetry, in which the change in weight of the sample is recorded as a function of both temperature and time as the temperature is raised at a given heating rate.

Non-isothermal thermogravimetry was used in this research project for the comparison of the thermal stabilities of the various homopolymers and copolymers prepared. A typical non-isothermal TG curve (thermogram) is shown in Fig. 3.14.

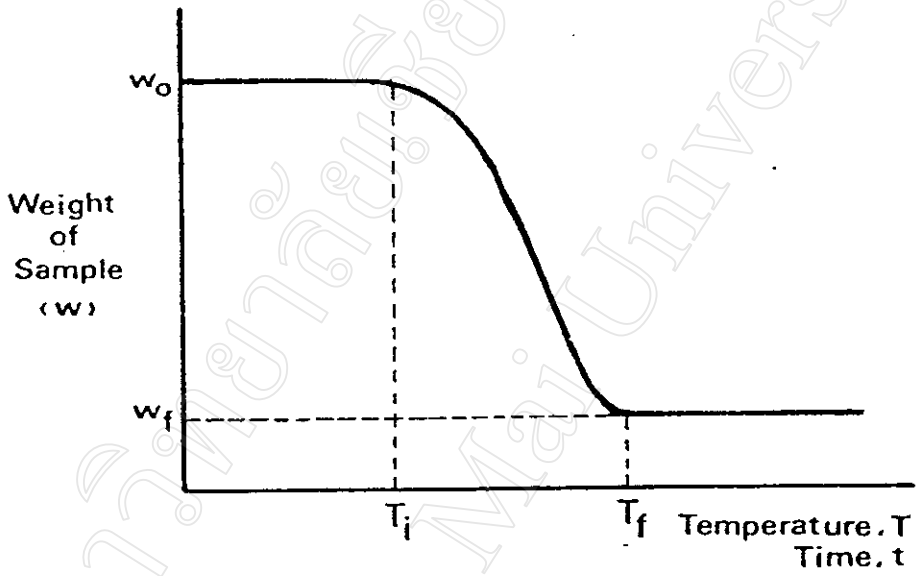


Fig. 3.14 : A typical non-isothermal TG curve for a polymer showing the various reaction parameters derived from the curve.

The various reaction parameters shown in Fig. 3.14 are generally defined as:

w_0	=	initial weight of sample
w_f	=	final weight of sample
w	=	weight of sample remaining at any intermediate time, t, or temp., T
T_i	=	initial decomposition temperature
T_f	=	final decomposition temperature
$T_i \rightarrow T_f$	=	decomposition range

In this research project, the particular instrument used was a Perkin-Elmer TGA 7 Thermogravimetric Analyzer (see Fig. 3.15).

Fig. 3.15 : The Perkin-Elmer TGA 7 Thermogravimetric Analyzer.

The most important variables which need to be controlled in order to obtain meaningful TG data are :

(1) the heating rate (in non-isothermal TG), which must be linear with time and slow enough to separate successive reactions ;
(2) the sample size, which must be kept as small as practicable to minimize mechanical difficulties ;
(3) the atmosphere, which must be either absent (i.e., in vacuo) or inert (usually N_2) to prevent reaction (e.g., oxidation) with the sample.

The non-isothermal TG operating conditions employed for each sample analysis in this project were as shown in Table 3.6. Nitrogen gas

(99.9%, dry, oxygen-free grade) was used as the purge gas at pressures of 30 lbs/in^2 for the sample zone and 50 lbs/in^2 for the balance.

Table 3.6 : Dynamic TG operating conditions used for polymer analysis.

TGA 7 Method : PVL

Sample Information

Sample ID : PVL/Sn(Octoate)
Operator ID : MONTIRA

Parameters		Conditions	
Final Temp :	550.0 C	End Condition :	Load Temp
Start Temp :	50.0 C	Load Temp :	50.0 C
Scanning Rate :	20.0 C/min.	Go To Temp Rate :	200.0 C/min.
Y Range :	100.0 %	Event 1 Time :	0.00 min.
*Sample Weight :	1.526 mg.	Event 2 Time :	0.00 min.
		Delay Time :	0.00 min.

* variable according to sample

3.3.6 Vapour Pressure Osmometry [45]

The relationship between molecular weight and vapour pressure is derived from Raoult's Law

$$\frac{p^\circ - p}{p^\circ} = \frac{x_2}{x_1 + x_2} \qquad (3.1)$$

where **p°** and **p** are the vapour pressures of the solvent and the solute respectively, and $\mathbf{x_1}$ and $\mathbf{x_2}$ are the numbers of mole fractions of each. Since Raoult's Law becomes a reality for real solutions only at infinite dilution where x_2 is very small, it can be re-expressed as

$$\frac{p^\circ - p}{p^\circ} = x_2 \qquad (3.2)$$

Therefore, measurement of the relative lowering of vapour pressure for a dilute, ideal solution of known weight concentration allows the molar mass of the solute to be determined.

The most convenient method in practice for the measurement of vapour pressure lowering is by conversion of the pressure difference into a temperature difference . This approach, the thermoelectric method, forms the basis of most commercial vapour pressure osmometers. The basic principles of the thermoelectric method are as follows. If a drop of solution is exposed to the vapour pressure of pure solvent, then its lower vapour pressure will result in condensation of solvent from the vapour phase; the heat of condensation thus liberated will cause the solution drop to increase its temperature and equilibrium will, theoretically, be obtained when the temperature increase raises the solution vapour pressure to equal that of the pure solvent. The temperature increase is easily measured if the solution drop is placed on a thermistor and a drop of pure solvent is placed on a second (reference) thermistor; both thermistors are mounted in an atmosphere saturated with pure solvent vapour and they are connected as two arms of a Wheatstone bridge circuit. The temperature difference can then be measured as the change in balancing resistance ΔR which occurs when a drop of pure solvent on the measuring thermistor is replaced by a drop of solution. Since the temperature difference to be measured is usually very small, two thermistors are always used and mounted close together; provided that the resistance/temperature characteristics are closely matched, temperature fluctuations in the instrument will affect both thermistors equally and produce no change in the bridge output. The vapour pressure osmometer provides one of the most convenient methods for studying polymers of low molecular weight. Sensitivity limitations place an upper limit of about 25,000 on the number-average molecular weight, $\overline{M}_n$, which can be measured with commercial instruments, whilst the lower limit is set by solute volatility at around 100 g mol^{-1}. Thus, in an ideal vapour pressure osmometer, in which there are no heat losses, the lowering of the vapour pressure produced by the involatile solute will be balanced by an increase in solution temperature to equalize the vapour pressure of solvent and solution. The temperature difference T_2-T_1 (=ΔT) is related to the activity of the solvent through the equation :

$$\Delta T = -K'' \ln a_1 \qquad (3.3)$$

where **K''** is a constant, and **a** is the activity of the solvent in the liquid phase. Furthermore, since the balancing resistance ΔR is proportional to ΔT, the activity of the solvent will be related to ΔR by

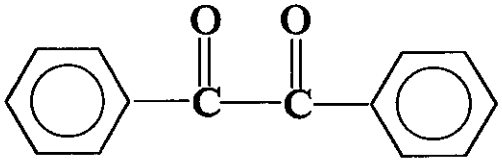
$$\Delta R = -K' \ln a_1 \qquad (3.4)$$

In vapour pressure osmometry, it is conventional to express the solute concentration, **c**, as the weight of solute per unit weight of solution. For most purposes, it is convenient to obtain the polymer molecular weight, $\overline{M}_n$, from the limiting condition :

$$(\Delta R / c)_{c=0} = K / \overline{M}_n \qquad (3.5)$$

where **K** is a calibration constant which is pre-determined from measurements on a calibration standard of known molecular weight. Thus, from the previous equation, a plot of ($\Delta R/c$) against c should be a straight line whose intercept at c=0 enables $\overline{M}_n$ to be calculated, provided that K is already known from a calibration experiment.

In this study, a Knauer Vapour Pressure Osmometer of the type shown in Fig. 3.16 was employed. The calibration standard used was benzil, of the structure and molecular weight shown below.



benzil (mol. wt. = 210.24)

Fig. 3.16 : **Knauer Vapour Pressure Osmometer.**

3.3.7 Dilute-Solution Viscometry [46]

Dilute-solution viscometry is what is known as a secondary method for molecular weight determination, that is to say it is not an absolute method as the primary ones are (e.g., light scattering, ultracentrifugation, osmometry). However, dilute-solution viscometry has the important advantages of being easy to perform and of being a much faster method. Hence, it is still one of the most well-known methods of molecular weight determination used in polymer science.

3.3.7.1 Dilute-Solution Viscosity Measurements

Dilute-solution viscosity measurements are usually carried out in glass capillary viscometers, the most commonly used of which are the Ostwald and Ubbelohde types shown in Fig. 3.17. A Schott-Gerate micro-Ubbelohde viscometer (type No. 537 10, capillary size I) (see Fig. 3.17 b)

was used in this research project in conjunction with a Schott-Gerate AVS 300 Automatic Viscosity Measuring System (Fig. 3.18).

The primary data obtained from these measurements are the so-called "flow-times", t_0 (sec) for the pure solvent and **t** (sec) for each polymer solution of its particular concentration **c** (g/dl). These flow-times then give rise to a range of derived viscosity parameters, as defined in the following section.

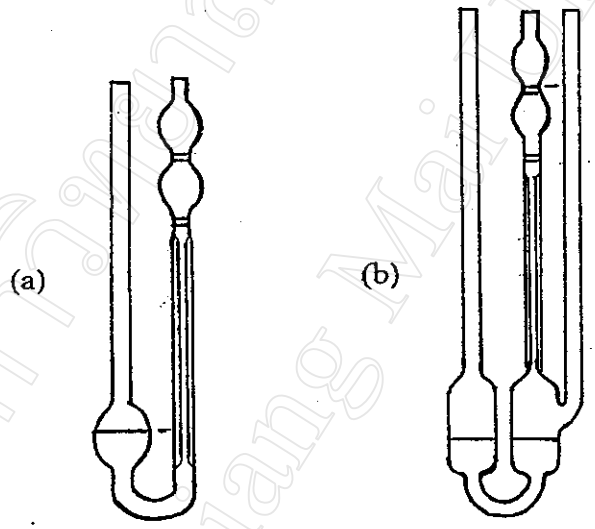


Fig. 3.17 : Viscometers commonly used in polymer chemistry :

(a) Ostwald viscometer

(b) Ubbelohde viscometer

Fig. 3.18 : Schott-Gerate AVS 300 Automatic Viscosity Measuring System.

3.3.7.2 Definitions of Dilute-Solution Viscosity Terms [46,47]

In dilute-solution viscometry, a variety of quantities are to be found in the literature describing the experimental data. There are summarized in Table 3.7.

Table 3.7 : Definitions and nomenclature of dilute-solution viscosity quantities [48].

Common Name	Official Name	Quantity
Viscosity	Viscosity Coefficient	η
Relative viscosity	Viscosity Ratio	$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$
Specific Viscosity		$\eta_{sp} = \eta_r - 1$
Reduced Specific Viscosity	Viscosity Number	$\eta_{red} = \frac{\eta_{sp}}{c}$
Inherent Viscosity	Logarithmic Viscosity Number	$\eta_{inh} = \frac{(\ln \eta_r)}{c}$
Intrinsic Viscosity	Limiting Viscosity Number	$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c}$
Intrinsic Viscosity	Limiting Viscosity Number	$[\eta] = \lim_{c \to 0} \frac{(\ln \eta_r)}{c}$

The relative viscosity, η_r, may be written very simply as a ratio of the viscometer flow-times if the kinetic energy correction is neglected :

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \qquad (3.6)$$

where t and t_0 are the flow-times of the solution and solvent respectively. Obviously, η and η_0 (i.e. t and t_0) must be measured under the same conditions. The relative viscosity is always greater than unity because the presence of the polymeric solute always increases the viscosity. It is appropriate then to define the specific viscosity , η_{sp}, as the fractional increase in viscosity caused by the presence of the dissolved polymer in the solvent, as shown in equation (3.7).

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \qquad (3.7)$$

The specific viscosity and the relative viscosity clearly depend on the concentration of the polymer in solution; they increase in magnitude with increasing concentration. Therefore, η_{sp} can be expressed as a reduced quantity called the reduced viscosity or reduced specific viscosity, η_{red}.

$$\eta_{red} = \frac{\eta_{sp}}{c} \qquad (3.3)$$

A similar relationship exists between the inherent viscosity, η_{inh}, as given by

$$\eta_{inh} = \frac{(\ln \eta_r)}{c} \qquad (3.9)$$

Finally, the intrinsic viscosity, $[\eta]$, is defined as the limits of both the reduced viscosity and the inherent viscosity as the concentration approaches zero, and is therefore given by

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right) \qquad (3.10)$$

$$[\eta] = \lim_{c \to 0} \left(\frac{\ln \eta_r}{c}\right) \qquad (3.11)$$

3.3.7.3 Determination of Intrinsic Viscosity [48].

The intrinsic viscosity term, [η], is the term which is related to the polymer's average molecular weight. Alternative methods of calculating [η] are now described.

(i) Huggins-Kraemer Method

The intrinsic viscosity, [η], is most commonly and conveniently determined via the Huggins Equation [49]

$$\eta_{red} = \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \qquad (3.12)$$

and the Kraemer Equation [50]

$$\eta_{inh} = \frac{(\ln \eta_r)}{c} = [\eta] + k''[\eta]^2 c \qquad (3.13)$$

In these Huggins and Kraemer Equations, **c** is the concentration of the polymer in solution (g/dl), while **k′** and **k″** are constants for a given polymer in a given solvent at a given temperature and are themselves related by the equation :

$$k' - k'' = 0.5 \qquad (3.14)$$

The value of k′ is usually in the range $0.3 < k' < 0.5$ and increases as solvent power decreases.

Thus, the two equations (3.12) and (3.13) should yield linear plots against concentration, c, with their common intercept equal to [η] at c=0, as shown in Fig. 3.19. The double extrapolation facilitates the accurate estimation of [η].

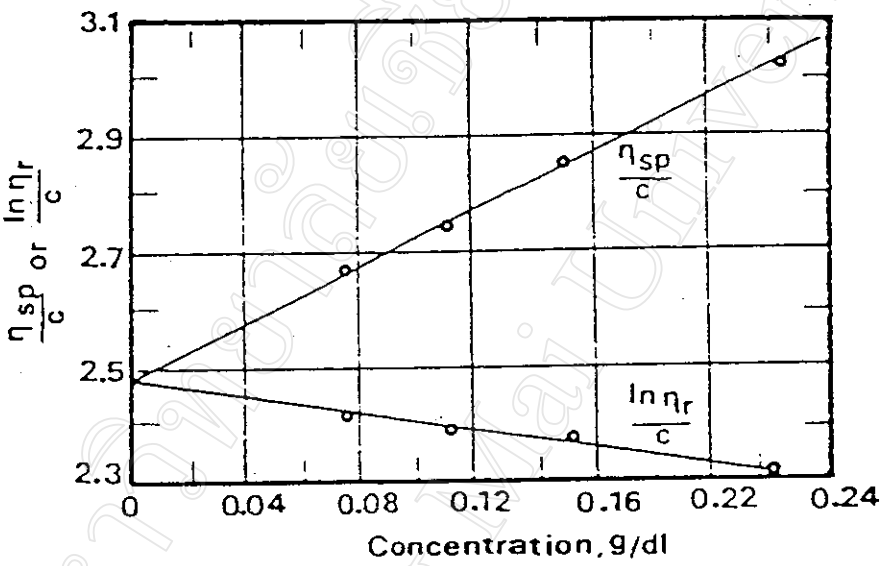


Fig. 3.20 : Reduced and inherent viscosity-concentration plots for a typical polymer sample.

(ii) Solomon-Ciuta One-point Approximation Method [51]

Measurement of the dilute-solution viscosity at only a single solution concentration, c, can enable calculation of the intrinsic viscosity, [η], from the Solomon-Ciuta Equation.

$$[\eta] = \frac{[2(\eta_{sp} - \ln\eta_r)]^{1/2}}{c} \qquad (3.15)$$

This equation is obtained by combination of the previous equations (3.12), (3.13), and (3.14) followed by elimination of k′ and k″. However, this method is accurate only when it is already known that there is a good linear relationship between c and η_{sp}/c and/or $(\ln \eta_r)/c$. This was the method used in this research project for the determination of [η].

3.3.7.4 Intrinsic Viscosity

The intrinsic viscosity, [η], of a polymer in solution is related to its molecular weight by the Mark-Houwink-Sakurada Equation [52]

$$[\eta] = K\overline{M}_V^a \qquad (3.16)$$

where :

K and **a** are constants for the polymer-solvent pair at a given temperature and are usually obtained from the "Polymer Handbook" [37]

$\overline{M}_V$ is the so-called "viscosity-average molecular weight"

Unfortunately, the values of **K** and **a** for the speciality homopolymers and copolymers prepared in this project are not available in the "Polymer Handbook". Consequently, their molecular weights cannot be calculated. from equation 3.16. However, their [η] values still provide useful indications as to the level of their molecular weights. Estimates of the level of molecular weight based on intrinsic viscosity are roughly as follows [32] :

Low $\overline{M}_V$	:	[η] less than 0.2 dl/g
Medium $\overline{M}_V$	:	[η] greater than 0.2 but less than 0.8 dl/g
High $\overline{M}_V$	:	[η] greater than 0.8 dl/g