CHAPTER 4

EXPERIMENTAL ASPECT

4.1 Chemicals, Apparatus and Instruments

4.1.1 Chemicals

The chemicals used in this research project were as shown in Table 4.1 below.

Table 4.1 Chemicals used in this research project

Chemicals	Usage	Grade	Supplier
Disodium hydrogen phosphate	Immersion Medium	AR Grade	Carlo Erba
Potassium dihydrogen phosphate	Immersion Medium	AR Grade	E. Merck
Sodium chloride	Immersion Medium	Lab Reagent	E. Merck
Sodium hydroxide	Adjust pH	AR Grade	Akzo Noble
MONOCRYL suture	Commercial Suture		Ethicon
MAXON suture	Commercial Suture		Davis&Geck
PDS II suture	Commercial Suture		Ethicon
Poly(L-lactide-*ran*-ε-caprolactone-*ran*-glycolide)	Studied Material		
Water	Immersion Medium	Deionized	
Chloroform	Solvent	Commercial Grade	E. Merck

4.1.2 Apparatus and Instrument

The main items of apparatus and instruments used were as given in Table 4.2

Table 4.2 Apparatus and instruments.

Apparatus and Instruments	Company	Model
Incubator	Memmert	
pH Meter	Radiometer Copenhagen	PHM 61
Vacuum Oven	Lab-line Instruments	3620-1
Automatic Viscosity Measuring System	Schott-Gerate	AVS 300
Micro-Ubbelohde Viscometer	Schott-Gerate	537 10
Universal Tensile Testing Machine	LLOYD Instrument	LRX
60 MHz ^{1}H-NMR Spectrometer	Bruker	R-1500
Differential Scanning Calorimeter	Perkin-Elmer	DSC7
Scanning Electron Microscopy	JEOL	JSM-840A

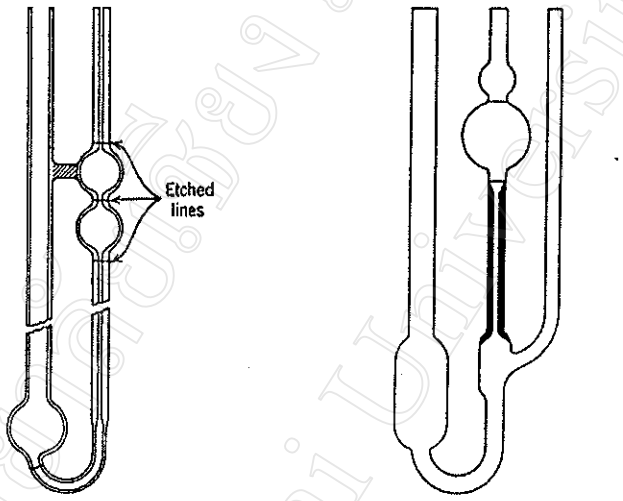
4.2 Instrumental Methods

4.2.1 Dilute-Solution Viscometry [3]

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.

4.2.1.1 Dilute-Solution Viscosity Measurements

Dilute-solution viscosity measurements are usually carried out in glass capillary viscometers, the most commonly used of which are the Oswald and Ubbelohde types shown in Fig. 4.1. A Schott-Gerate micro-Ubbelohde viscometer (type No. 537 10, capillary size I) (See Fig. 4.1b) was used in this research project in conjunction with a Schott-Gerate AVS300 Automatic Viscosity Measuring System (Fig. 4.2).



(a) (b)

Fig. 4.1 Viscometer commonly used in polymer chemistry:

(a) Ostwald viscometer

(b) Ubbelohde viscometer

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). This flow-times then give rise to a range of derived viscosity parameter, as defined in the following section.

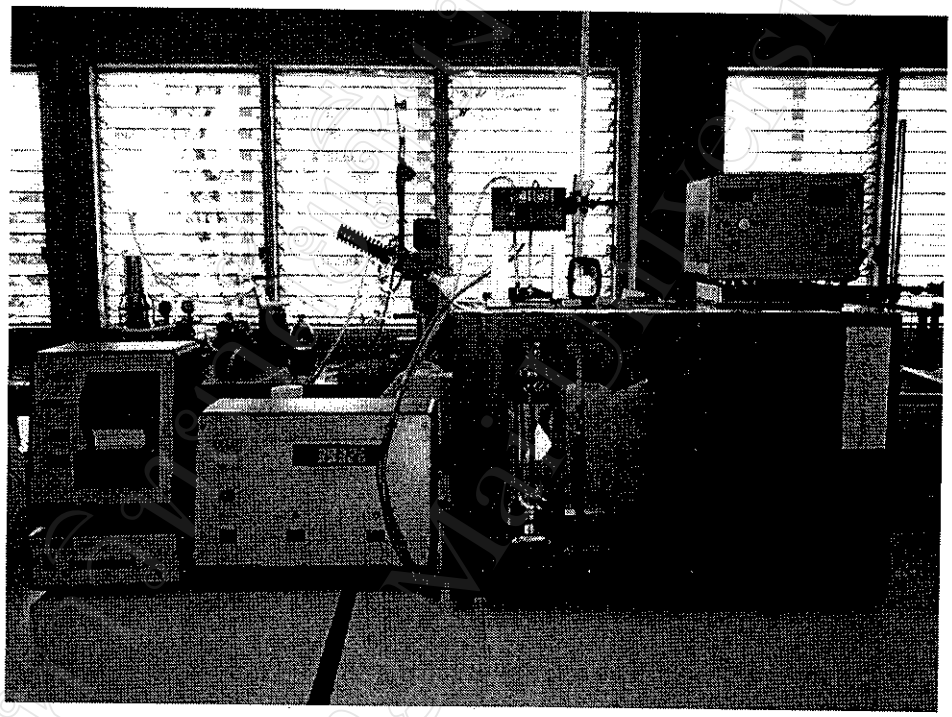


Fig. 4.2 Schott-Gerate AVS300 Automatic Viscosity Measuring System.

4.2.1.2 Definitions of Dilute-Solution Viscosity Terms

In dilute-solution viscometry, a variety of quantities are to be found in the literature describing the experimental data. There are summarized in Table 4.3

Table 4.3 Definitions and nomenclature of dilute-solution viscosity quantities.

Common Name	Official Name	Quantity
Viscosity	Viscosity Coefficient	η
Relative Viscosity	Viscosity Ratio	$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$
Specific Viscosity		$\eta_{sp} = \eta_r - 1$
Reduce 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 simple as a ratio of the viscometer flow-times if the kinetic energy correction is negleted:

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \qquad (4.1)$$

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 (4.2)

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \qquad (4.2)$$

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 **reduce_viscosity** or **reduced specific viscosity**, η_{red}

$$\eta_{red} = \frac{\eta_{sp}}{C} \qquad (4.3)$$

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

$$\eta_{inh} = \frac{(\ln \eta_r)}{C} \qquad (4.4)$$

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

$$[\eta] = \lim_{C \to o} \frac{\eta_{sp}}{C} \qquad (4.5)$$

$$[\eta] = \lim_{C \to o} \frac{\ln \eta_r}{C} \qquad (4.6)$$

4.2.1.3 Determination of Intrinsic Viscosity

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

(i) Huggins-Kraemer Method

The intrinsic viscosity, $[\eta]$, is most commonly and conveniently determined via the Huggins Equation

$$\eta_{red} = \frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \qquad (4.7)$$

and the Kraemer Equation

$$\eta_{inh} = \frac{(\ln \eta_r)}{C} = [\eta] + k'' [\eta]^2 C \qquad (4.8)$$

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:

$$k' - k'' = 0.5 \qquad (4.9)$$

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

Thus, the two equation (4.7) and (4.8) should yield linear plots against concentration, c, with their common intercept equal to $[\eta]$ at C=0, as shown in Fig. 4.3. The double extrapolation facilitates the accurate estimation of $[\eta]$.

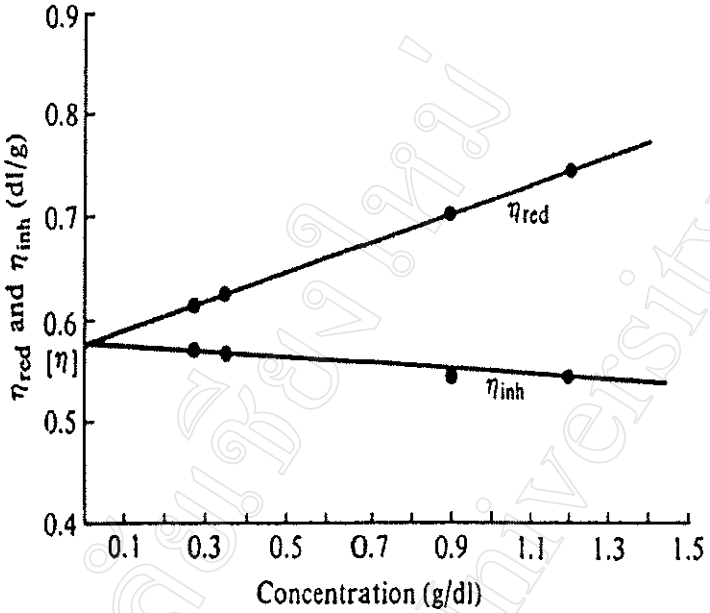


Fig. 4.3 Reduced and inherent viscosity-concentration plots for a typical polymer sample

(ii) Solomon-Ciuta One-point Approximation Method

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

$$[\eta] = \frac{[2(\eta_{sp} - \ln\eta_r)]^{1/2}}{C} \qquad (4.10)$$

This equation is obtained by combination of the previous equations (4.7), (4.8) and (4.9) 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 (ln η_r)/C. This was the method used in this research project for determination of $[\eta]$.

4.2.1.4 Intrinsic Viscosity

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

$$[\eta] = K \overline{M}_v^a \qquad (4.11)$$

Where:

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

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

Unfortunately, the value of K and a or the speciality copolymers prepared in this project are not available in the "Polymer Handbook". Consequently, their molecular weights can not be calculated from equation (4.11). However, their $[\eta]$ 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 follow:

Low $\overline{M}_v$: $[\eta]$ less than 0.2 dl/g

Medium $\overline{M}_v$: $[\eta]$ greater than 0.2 but less than 0.8 dl/g

High $\overline{M}_v$: $[\eta]$ greater than 0.8 dl/g

4.2.2 Differential Scanning Calorimetry [3,5]

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat absorbed by a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. DSC techniques are commonly used to measure the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) of polymers. DSC methods can also be applied to the direct measurement of the energy absorbed or evolved in studies of heats of fusion, heat of reaction (including polymerization, oxidation and combustion), and specific heats. Greatest accuracy in temperature measurement is attained by observing the following four considerations:

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

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

(1) precise weighing ($\pm$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.

Polymeric materials, however, inherently melt over a temperature range rather than at a single temperature. This broad melting behavior is related to crystalline size or imperfections throughout the polymer and is not necessarily evidence of impurity.

In this research project, the particular instrument used was a Perkin-Elmer DSC7 Differential Scanning Calorimeter (Fig.4.4). Nitrogen gas (99.99% purity) was used as the purge gas at a pressure of 20 lbs/in^2 (flow rate ≈40.0 ml/min).

Fig. 4.4 The Perkin-Elmer DSC7 Differential Scanning Calorimeter.

4.2.3 SCANNING ELECTRON MICROSCOPY [18]

Scanning electron microscopy (SEM) is an electron optical imaging technique that yields both topographic images and elemental information when used in conjunction with energh-dispersive X-ray analysis (EDX) or wavelength-dispersive X-ray spectrometry (WDS). SEM is useful for characterizing the size and morphology of microscopic specimens. Together, image and X-ray analyses are important for the identification of small particles. Elemental analyses using SEM/EDX or SEM/WDS are useful for qualitative and semiquantitative determination of elemental content. Accurate quantitation is possible only for bulk samples with smooth surfaces and thus is not practical for particle specimens.

Typically, SEM analysis requires a small amount, $\approx 10^{-10}$ to 10^{-12}g, of a solid specimen that is coated with a conductive substance to inhibit sample charging. The sample is placed in an evacuated chamber and scanned in a controlled rate pattern by an electron beam. Interaction of the electron beam with the specimen produces a variety of physical phenomena that, when detected, are used to form images and provide elemental information about the specimen. Secondary electrons and reflection of back-scattered electrons are the most important phenomena for constructing SEM images. Secondary electrons are emitted from a specimen surface as the result of inelastic collisions between incident electrons and electrons within a specimen. Back-scattered electrons are incident electrons that have been reflected from the sample.

Primarily, the SEM is an instrument for the examination of surfaces (crystallographic information may be obtained from macroscopic crystals, in the form of electron channeling patterns) and, as such, appropriate samples may be examined directly with little or no prior preparation. However, polymer do present some specific problems. Firstly, most polymers are poor conductors of electricity and, as a result, charge rapidly builds up on the surface of the sample as the electron beam is scanned across it. The resulting field then interacts with the incident electron beam, resulting in image distortion. The second problem concerns the molecular changes that are induced in the sample by the impinging electrons. Such effects serve to restrict the operating conditions under which particularly sensitive specimens may be examined.

For stable images to be formed it is essential that the charge deposited on the sample surface by the electron beam is able to leak away to earth. Thus, for polymer, it is usually desirable to coat the specimen with a conducting film prior to examination. In many circumstances the coating material chosen is gold, a film of which is applied either by evaporation or, more conveniently, by sputtering. Such a film provides many advantages: it is easy to apply, give a good leakage path to earth, and gives a high secondary electron yield. However, gold is not ideal in all respects, and for particular problems other materials may be preferable (e.g., gold-palladium alloy or carbon).

4.2.4 Universal Mechanical Testing Machine [19]

The mechanical tests were performed on a Lloyds LRX+ Universal Mechanical Testing Machine, illustrated in Fig. 4.7. Fiber samples were cut into 32 cm lengths and their diameters measured accurately ($\pm$0.001 mm) with a digital micrometer. All tests were carried out with the fiber sample wound once around two bollard grips, as illustrated in Fig. 4.7.

Fig. 4.5 Photograph of the Lloyds LRX+ Universal Testing Machine used for fiber mechanical testing.

Fig. 4.6 Photograph of the bollard grips.

Tensile Test Conditions

In mechanical testing, the choice of an appropriate set of testing conditions and standard procedure is the essential first step in obtaining accurate and meaningful results. In this study, the tensile test conditions used for the monofilament fiber samples were as follows:

Load cell	=	100 N
Sample grips	=	Bollard-type
Initial guage length	=	40 mm
Crosshead speed	=	20 mm/min
Temperature	=	Ambient (20-25^{o}C)
Humidity	=	Ambient (50-70% rh)

The main advantage of bollard-type grip is that the tensile stress is distributed more uniformly around the bollards rather than concentrated at the points of contact. Consequently, the fiber samples failed within the gauge length. This was considered to be a mode of failure more representative of the fiber's true properties and was the main criterion used in choosing bollard type.

However, bollard grips also have their disadvantages, the main one being the uncertainty in the "true" gauge length. This arises from the fact that the fiber can stretch to a certain extent around the bollard's circumference. Consequently, since the gauge length is taken as the distance between the 2 mid-points of the bollards, i.e. the 2 initial points of contact, the measured gauge length (in this work, 40 mm) will be somewhat less than the "true" gauge length. This will inevitably introduce an element of error into the absolute mechanical property values obtained but comparisons between different samples under the same test conditions will be valid.