CHAPTER 2

Materials and Instrumental Methods

2.1 Chemicals, Apparatus and Instruments

2.1.1 Chemicals

The various chemicals used in this research are as shown in Table 2.1.

Table 2.1 Chemicals used in this research project.

CHEMICAL	USAGE	GRADE	SUPPLIER
ε-Caprolactone	Monomer	99%	Acros
L(-)-Lactide	Monomer	> 99.5%	Polymers Research Unit
Diethylene glycol	Reagent	99%	Merck
Triethylamine	Reagent	99%	Ajax
Tin(II) chloride	Reagent	98%	Acros
Methanol	Solvent	95%	Sigma
Ethyl acetate	Solvent	Commercial	Northern
Acetone	Solvent	Commercial	Northern
Chloroform	Solvent	AR Grade	Northern
Tetrahydrofuran	Solvent	Commercial	ICI
Calcium hydride	Drying Agent	95%	Alfa
Calcium chloride	Drying Agent	Lab Reagent	Aldrich
Molecular sieves Type 4Å	Drying Agent	AR Grade	Merck
Tin(II) Octoate	Initiator	95%	Sigma
Ethylene glycol	Reagent	> 99%	Aldrich
Poly(ethylene glycol 300)	Reagent	Commercial	Fluka
Poly(propylene glycol 400)	Reagent	Commercial	Fluka
Poly(propylene glycol 1200)	Reagent	Commercial	Fluka
Chloroform-d	Solvent	AR Grade	Aldrich
Dimethyl Sulfoxide-d_6	Solvent	AR Grade	CIL
Silicone oil	Heating bath	Commercial	Ajax

2.1.2 Apparatus and Instruments

The main apparatus and instruments used are as listed in Table 2.2.

Table 2.2 Apparatus and instruments used in this research project.

Apparatus and Instruments	Company	Model
Fourier-Transform Infrared Spectrometer (FTIR)	Bruker	TENSOR 27
Nuclear Magnetic Resonance Spectrometer (NMR)	Bruker	DPX 400
Differential Scanning Calorimeter (DSC)	Perkin-Elmer	DSC7
Thermogravimetric Analyzer (TGA)	Perkin-Elmer	TGA7
Gel Permeation Chromatograph (GPC)	Waters	PL-GPC 50 Plus
Ubbelohde Viscometer	Schott-Geräte	532 10
Vacuum Oven	Eyela	VOS-300SD
Controlled Atmosphere Glove Box	Labconco	50801
Rotary Evaporator	Buchi	B-480
Small-scale Melt Spinning Apparatus	Bradford University Research Ltd.	
Universal Mechanical Testing Machine	Lloyds	LRX+

2.2 Monomer Purification

The cyclic ester monomers used in this research are L-lactide and ε-caprolactone which need to be purified prior to the polymerisation. Impurities can act either as initiators or chain terminators during ring-opening polymerisation (ROP) leading to a decrease in the molecular weight of the final product.

2.2.1 Purification and Purity Analysis of L-Lactide

The crude L-lactide was purified at least 3 times by recrystallisation from distilled ethyl acetate. The purified L-lactide was obtained as a white, needle-like, crystalline solid. It was dried in a vacuum oven at 55 ^{o}C before use in polymerisation.

Purity analysis by differential scanning calorimetry (DSC) technique, the instrument’s Purity Analysis Software Program was employed. To obtain the best results from purity analysis, a slow scanning rate of 2 ^{o}C/min and a small sample size in the range of 1-3 mg were used. From its DSC melting peak, purified L-lactide was of a sufficiently high purity (>99.5%) to produce high molecular weight polymer. A DSC thermogram of purified L-lactide showing the melting peak and the Van’t Hoff plot (see Appendix A) from which the % purity was computed are shown in Figures 2.1 and 2.2 respectively.

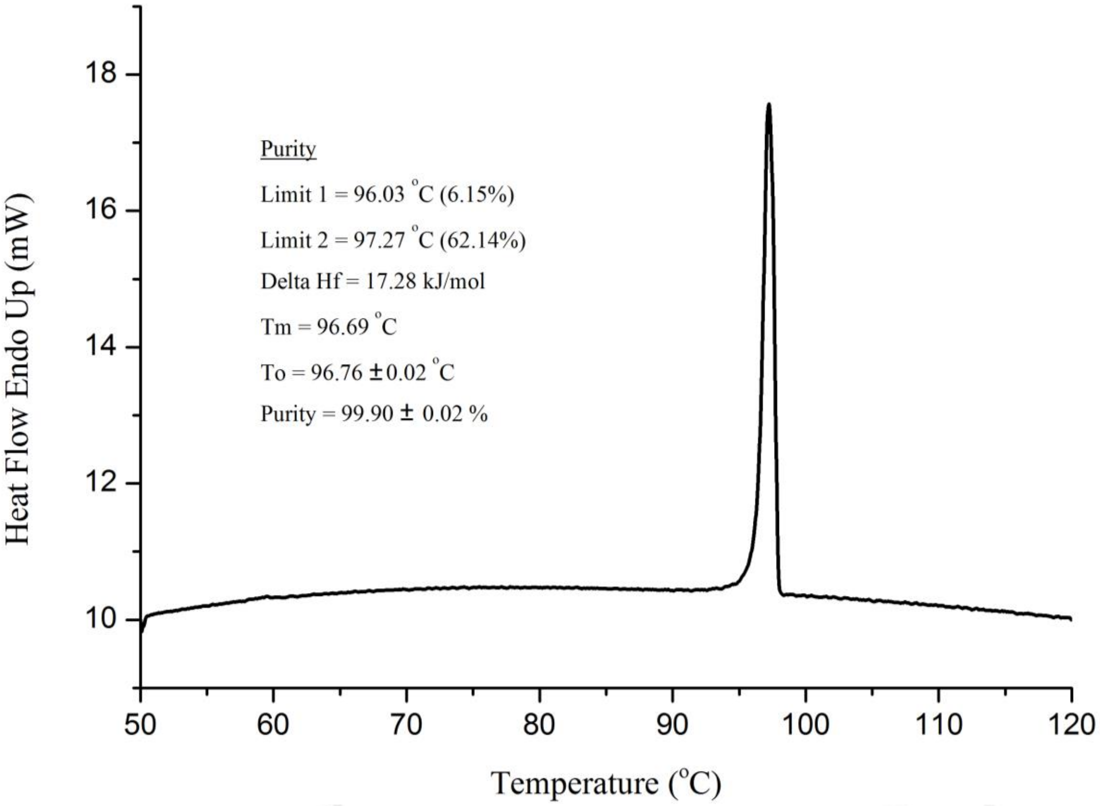


Figure 2.1 DSC thermogram of purified L-lactide showing its melting peak used for purity analysis.

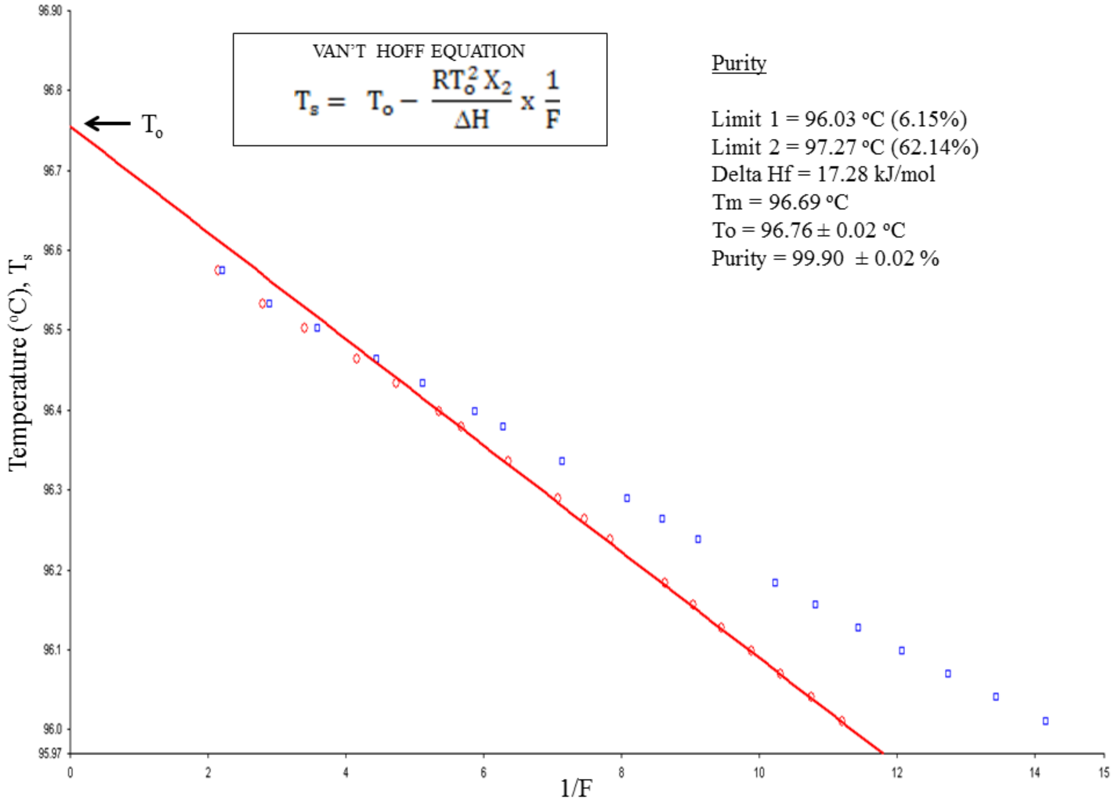


Figure 2.2 Van't Hoff plot derived from the melting peak data in Figure 2.1.

2.2.2 Purification of ε-Caprolactone

Commercial ε-caprolactone (Acros Organics, assay > 99%) was purified by fractional vacuum distillation (Figure 2.3). During its vacuum distillation, the constant boiling fraction at 75 °C / 2 mm Hg (cf., lit. [84] b. pt. = 82 °C / 5.5 mm Hg) was collected. Pure ε-caprolactone was obtained as a clear colourless liquid at room temperature. It was stored over molecular sieves (4 Å) in a refrigerator in a tightly sealed container until required for use in polymerisation.

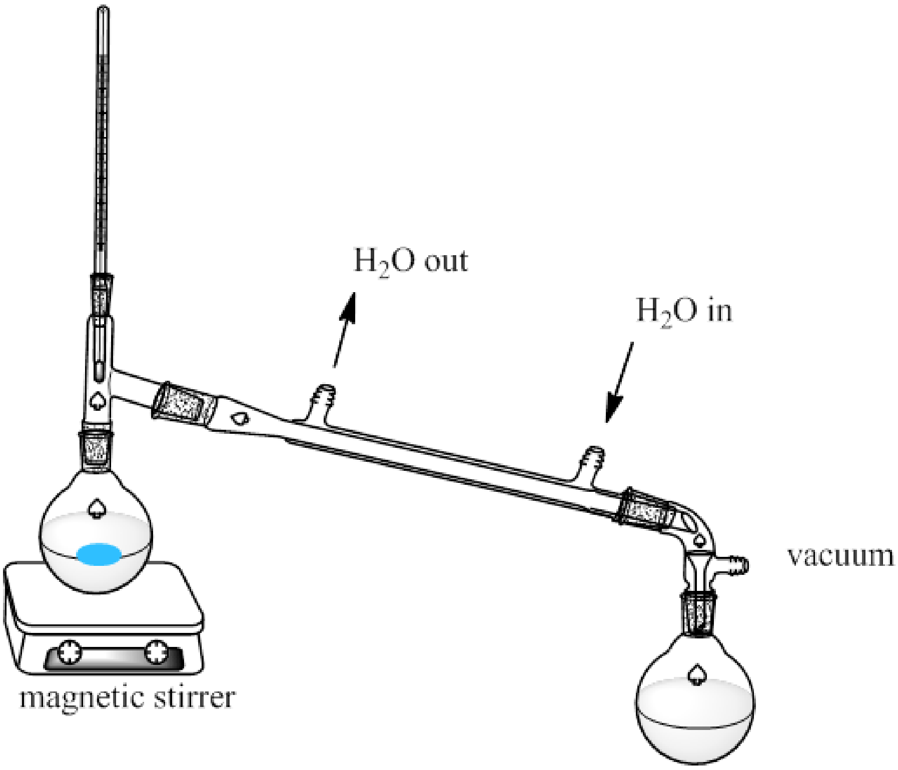


Figure 2.3 Fractional vacuum distillation apparatus used for the purification of ε-caprolactone.

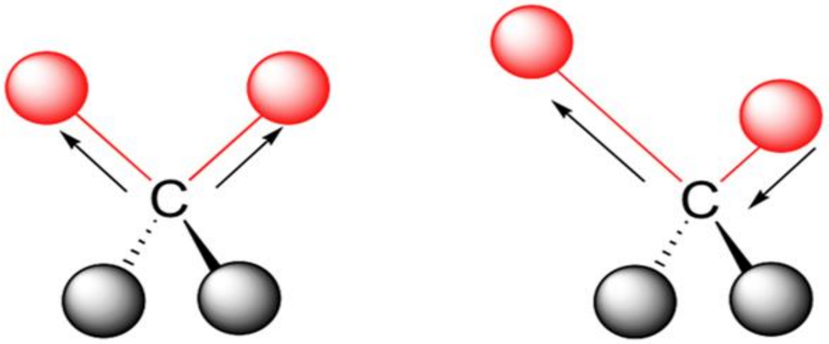
2.3 Instrumental Methods

In this work, the monomers, polymers and the tin(II) alkoxide initiators were characterised by a combination of analytical techniques with respect to their chemical structure by FT-IR, chemical composition by ^{1}H-NMR, chain microstructure by ^{13}C-NMR, temperature transitions by DSC, thermal stability by TGA, and molecular weight by GPC and dilute-solution viscometry. All of these techniques are now described.

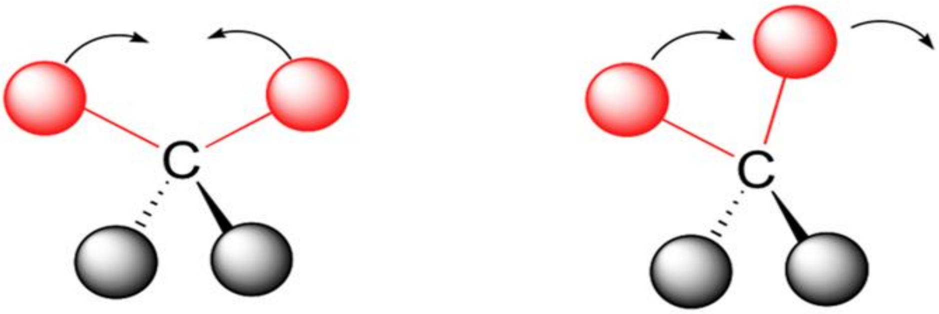
2.3.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy (IR) is probably the most extensively used method for the investigation of chemical structure and the analysis of functional groups. It is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. IR spectrometers can be used to study samples in the gaseous, liquid and solid state, depending on the types of accessories used. Infrared radiation is absorbed when the oscillating dipole moment caused by a molecular vibration interacts with the oscillating electric vector of the infrared beam. A complex molecule has a large number of vibrations of individual bonds or functional groups (localized vibrations) while others may be considered as vibrations of the whole molecule [85].

The major types of molecular vibrations are stretching and bending. Various types of vibrations are illustrated in Figure 2.4. Infrared radiation is absorbed and the associated energy is converted into these type of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions. These combinations lead to the absorption bands, not the discrete lines, commonly observed in the mid IR region [86].



symmetric stretching asymmetric stretching



scissoring (bending) rocking

Figure 2.4 Major vibrational modes for a nonlinear group, CH_2 [87].

Fourier-transform infrared (FT-IR) spectroscopy brings greater versatility to polymer structural studies. This is because spectra can be scanned, recorded and transformed in a matter of seconds. The technique facilitates the study of such polymer reactions as degradation and crosslinking. Moreover, the quality of the spectrum depends on proper care in sample preparation. If the samples are too thick, the spectrum totally absorbs in many frequency regions and much useful information is lost. On the other hand, if the samples are too thin, many of the important features of the spectrum are lost in the background [88].

Identification

There are a number of methods available for examining polymer samples. If the polymer is a thermoplastic, it can be softened by warming and formed in a hydraulic press into a thin film. Alternatively, the polymer may be dissolved in a volatile solvent and the solution allowed to evaporate to give a thin film on an alkali halide plate. Some polymers, such as cross-linked synthetic rubbers, can be microtomed (cut into thin slices with a blade). A solution in a suitable solvent is also a possibility. If the polymer is a surface coating, reflectance techniques may be used. A useful correlation table for polymers is shown in Figure 2.5.

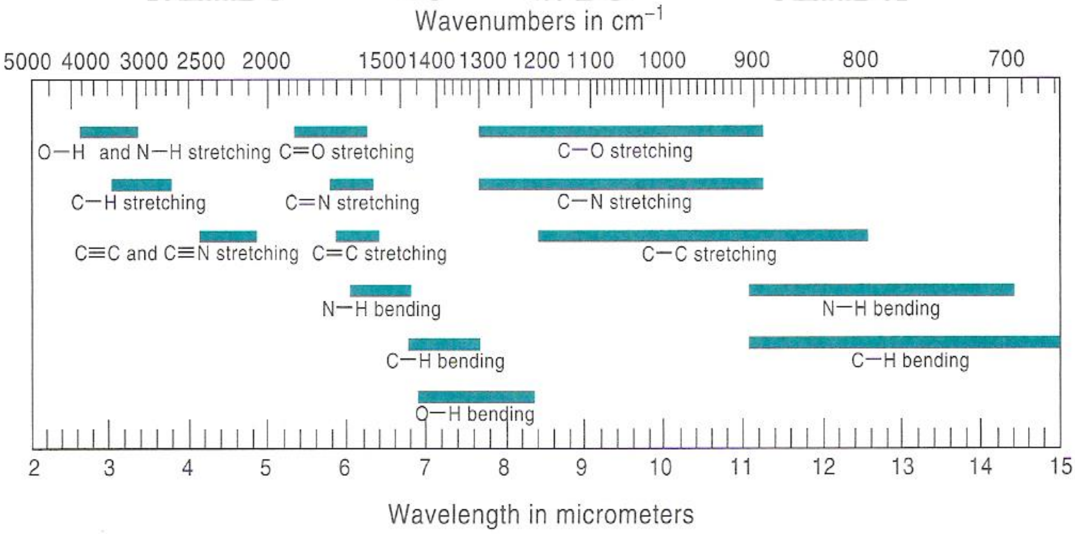


Figure 2.5 Correlation table for the infrared bands [89].

In this thesis, a Bruker Model FT-IR TENSOR 27 Infrared Spectrometer was used for the recording of all infrared spectra. All of the samples were prepared in the form of thin films casting from solution in chloroform onto NaCl discs.

2.3.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Many applications of NMR techniques are similar to those of IR spectroscopy. However, NMR spectroscopy offers much greater scope than IR for elucidating detailed features of molecular microstructure. This is especially true of ^{13}C-NMR spectroscopy which nowadays is by far the most important technique for the microstructural characterisation of polymers [90].

Nuclear magnetic resonance is a physical phenomenon of resonance transition between magnetic energy levels, happening when atomic nuclei are immersed in an external magnetic field and applied an electromagnetic radiation with specific frequency. Nuclei of a particular element that are in different chemical environments within the same molecule generally experience slightly different applied magnetic field strengths due to the shielding and deshielding effects of nearby electrons. As a result, their resonance frequencies differ, and each is defined by a characteristic chemical shift value. The chemical shift is measured in parts per million (ppm) and is designated by the Greek letter delta (δ) [91]. By detecting the absorption signals, one can acquire NMR spectrum. [92].

A general understanding of the trends of chemical shifts is essential for the interpretation of NMR spectra. The chemical shifts of ^{1}H and ^{13}C signals are affected by the proximity of electronegative atoms (O, N, Cl, etc.) in the bonding network and by the proximity to unsaturated groups (C=C, C=O, aromatic) directly through space. Although the range of chemical shifts in parts per million is much larger for ^{13}C than for ^{1}H (0–220 ppm *vs.* 0–13 ppm), there is a rough correlation between the shift of a proton and the shift of the carbon it is attached to (see Figure 2.6) [91].

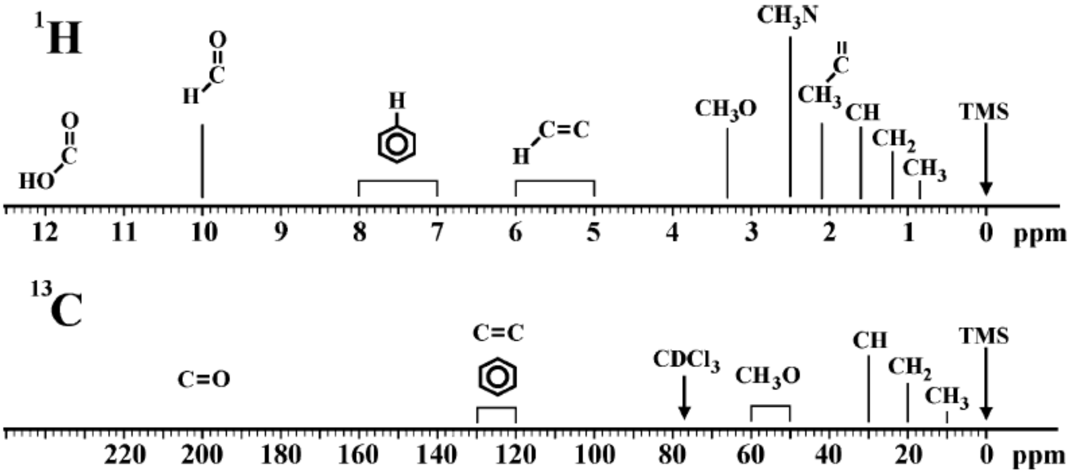


Figure 2.6 Correlation between the shift of a proton and the shift of the carbon.

The goal of nuclear magnetic resonance, NMR, is to study molecular structures, especially in our case it is useful for polymer characterisation, because the signals can be assigned to specific atoms along the polymer's backbone and side chains. In this thesis, the particular instrument used for ^{1}H-NMR analysis was a Bruker Model DRX 400 MHz NMR Spectrometer**.** ^{1}H-NMR analysis of the polymer products in deuterated chloroform ($CDCl_3$) solutions were recorded with tetramethylsilane (TMS) as internal standard at room temperature.

^{13}C-NMR was also used to obtain microstructural information about the copolymers that ^{1}H-NMR was unable to provide. This is made possible by the fact that, in ^{13}C-NMR, the chemical shifts are spread over a wide range of over 200 ppm, as compared with the relatively narrow 10 ppm range in ^{1}H-NMR. Therefore, much smaller differences in chemical environment can be distinguished in ^{13}C-NMR making it a much more powerful technique than ^{1}H-NMR for studying polymer microstructure, in particular monomer sequencing in copolymers. In ^{13}C-NMR polymer spectra, carbonyl (C=O) carbon atoms have been shown to be especially sensitive to sequencing variations, much more so than C-H carbons (methyl, methylene and methine). Therefore, it is the carbonyl region of the spectrum from δ = 165-175 ppm which provides the most information about the copolymer chain microstructures [90].

2.3.3 Thermal Analysis

2.3.3.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) [93] is a thermal analysis technique which measures the amount of energy (heat flow) absorbed or released by a sample as it is heated, cooled or held at a constant (isothermal) temperature. In practice, a polymer sample and an inert reference are heated alongside each other in identical micro furnaces, usually in a nitrogen atmosphere. When an exothermic or endothermic change occurs in the sample, energy is applied or removed to one or both micro furnaces to compensate for the energy change occurring in the sample. The system is thus maintained in a "thermal null" state at all times. The amount of power (energy) required to maintain the system at equilibrium is directly proportional to the energy changes occurring in the sample.

The instrument used for this purpose is called a differential scanning calorimeter, the heart of which is the DSC cell which contains both the sample (S) and the reference (R) material, as shown in Figure 2.7.

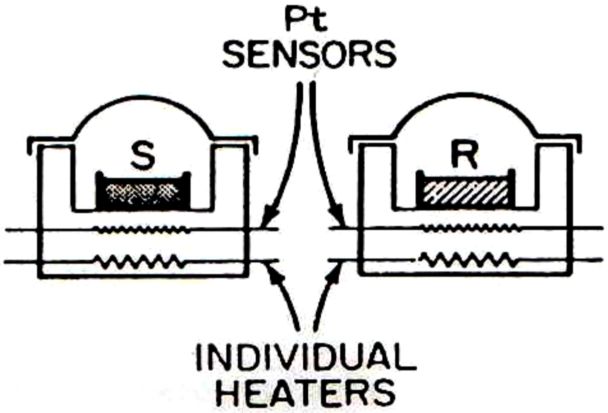


Figure 2.7 Principle components and layout of a power-compensated DSC cell showing the sample (S) and reference (R) micro furnaces.

The principle of operation of a power-compensated DSC is based on keeping the temperature of the sample (T_s) and the reference (T_R) equal throughout the temperature program, i.e.,

$$\Delta T = T_s - T_R = 0$$

Consequently, a DSC curve (more correctly termed a thermogram) is obtained as a plot of heat flow against temperature, as shown in Figure 2.8. The various transitions which occur in the sample appear as deviations from the baseline, either in the upward direction if endothermic or in the downward direction if exothermic.

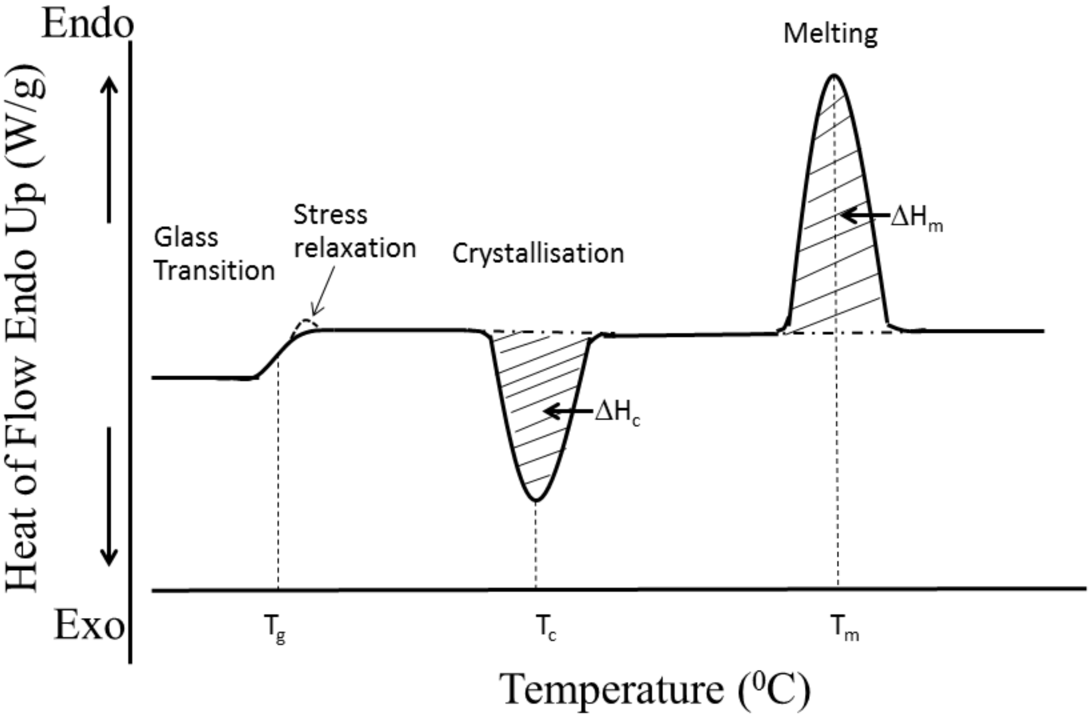


Figure 2.8 DSC thermogram showing the various temperature transitions that can occur in a semi-crystalline polymer.

The DSC technique has many useful applications in polymer science, both qualitative and quantitative, since its thermogram can show thermal properties namely:

- glass transition temperature, T_g
- melting studies, T_m, ΔH_m and % crystallinity ($\propto \Delta H_m$)
- crystallization studies, T_c and ΔH_c
- purity analysis (e.g., monomer purity)

In this project, the particular instrument used was a Perkin-Elmer DSC7 Differential Scanning Calorimeter as shown in Figure 2.9. 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).

Figure 2.9 The Perkin Elmer DSC7 Differential Scanning Calorimeter.

2.3.3.2 Thermogravimetric Analysis (TGA)

Thermogravimetry (TG) is used primarily for determining the thermal stability of polymers. In the analysis, the mass of the sample is recorded continuously while the temperature is (usually) increased at a constant rate (non-isothermal TG). Data is recorded as a thermogram of weight versus temperature. Weight losses occur initially when volatiles absorbed by the polymer are driven off and, at higher temperatures, when degradation of the polymer occurs with the formation of volatile products [94].

The layout of the TG system used is shown schematically in Figure 2.10. The thermobalance can be detected weight changes to 0.1 μg and calibration can be made by using standard masses. Ultra high-purity metals are commonly used for temperature calibration. A typical non-isothermal TG curve (thermogram) is illustrated in Figure 2.11.

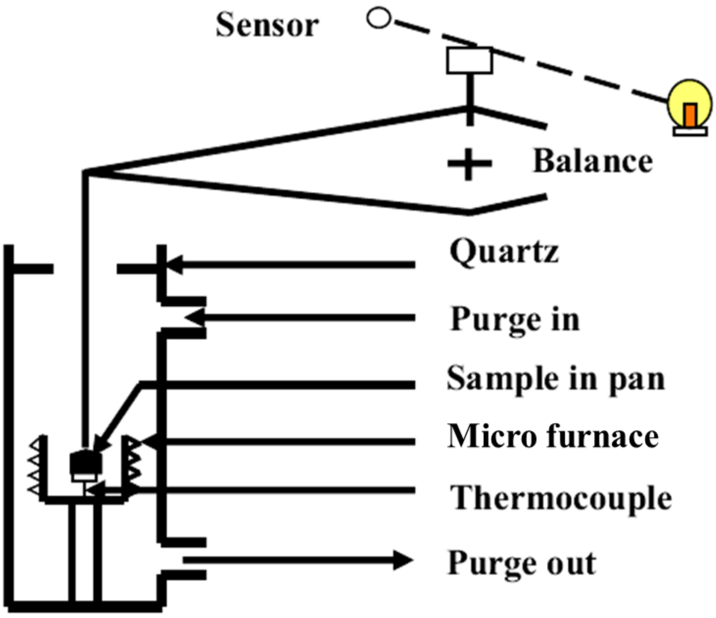


Figure 2.10 Diagram showing the furnace and balance arrangement in the Perkin-Elmer TGA7.

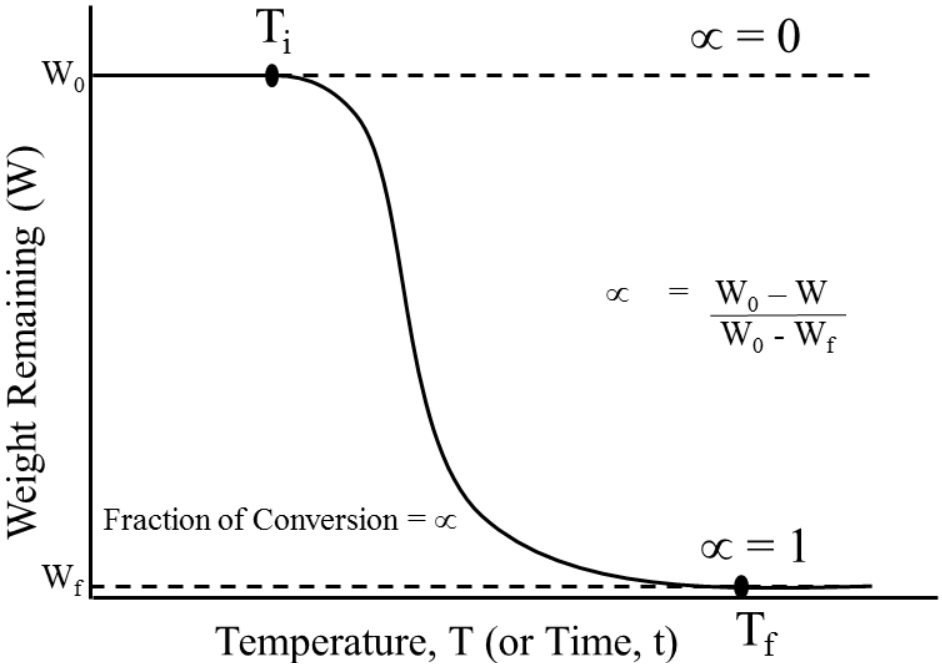


Figure 2.11 A typical non-isothermal TG thermogram for polymer showing the various reaction parameters derived from the curve.

The various parameters illustrated in Figure 2.12 are generally defined as:

W_o = initial weight of sample
W_f = final weight of sample
W = weight of sample remaining at any intermediate time, t ,or
temperature, T
T_i = initial weight loss temperature
T_f = final weight loss temperature
$T_i \rightarrow T_f$ = weight loss temperature (decomposition) range
α = fraction of conversion (or extent of reaction)

In this research, the particular instrument used was a Perkin-Elmer TGA7 Thermogravimetric Analyzer as shown in Figure 2.12. Nitrogen gas (99.99 % purity) 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 zone. The heating rate used was 20°C/min with initial (finely powdered) sample weights in the range of 5-10 mg.

Figure 2.12 The Perkin Elmer TGA7 Thermogravimetric Analyzer.

2.3.4 Molecular Weight Determination

2.3.4.1 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC), also referred to as Size Exclusion Chromatography (SEC), is a mode of liquid chromatography in which the components of a mixture are separated on the basis of size. In GPC-SEC, large molecules elute from the column first, followed by smaller molecules (Figure 2.13). It is an important tool for the analysis of polymers. The essential results are molecular weight data and molecular weight distribution curves which are needed to characterise a polymer with regard to differences in properties [95]. The method of gel permeation chromatography (GPC) depends on the use of mechanically stable, highly crosslinked gels which have a distribution of different pore sizes and can, by means of a sieving action, effect separation of a polymer sample into fractions, as dictated by their molecular volume in solution [96].

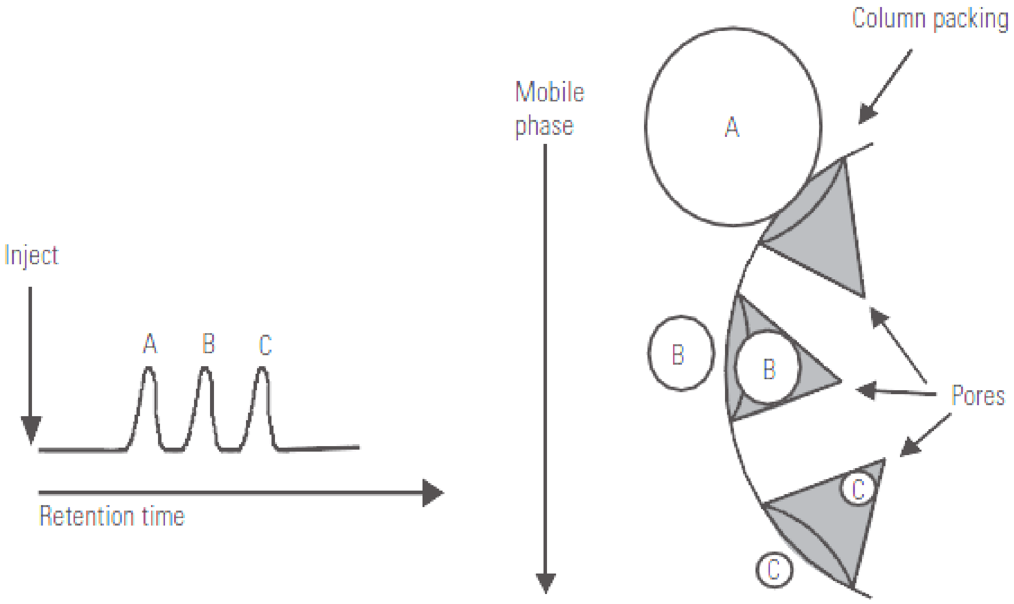


Figure 2.13 GPC-SEC separation mechanism [95].

The technique of gel permeation chromatography (GPC) is an extremely powerful and convenient method for determining the molecular weight distribution and the various molecular weight averages [97]. The molecular weight distribution (MWD) of a polymer sample has a significant influence on its properties and knowledge of the shape of this distribution is fundamental to the complete characterisation of a polymer. In this research project, the GPC instrument used was a PL-GPC 50 Plus Gel Permeation Chromatography (as shown in Figure 2.14) operating under the following conditions:

Polymer solution : 0.1 mg/ml
Solvent : Tetrahydrofuran (THF)
Flow-rate : 1.00 ml/min
Oven Temperature : 40 ^{o}C
Column : PL gel 5 μm mixed-C columns
Detector : Refractive Index (RI) Detector

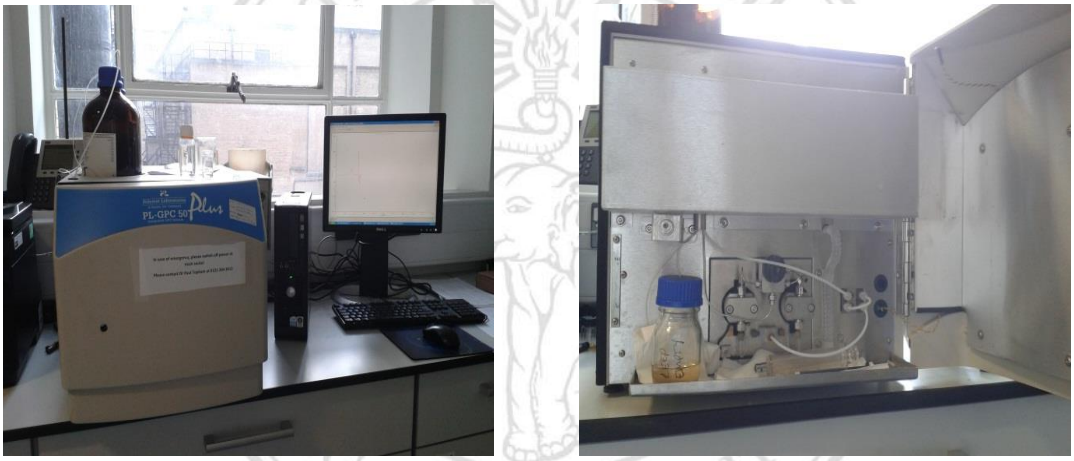


Figure 2.14 PL-GPC 50 Plus Gel Permeation Chromatography.

2.3.4.2 Dilute-Solution Viscometry [90]

Measurements of dilute-solution viscosity provide the simplest and most widely used technique for routinely determining molecular weights. The intrinsic viscosities, $[\eta]$, of the polymer products were measured with a Ubbelohde viscometer in $CHCl_3$ as solvent. The flow-time in seconds is recorded as the time for the meniscus to pass between two designated marks on the viscometer. Viscosities are run at constant temperature at 30.0 ± 0.1°C. Dilute-solution viscosity can be expressed in several ways, as in Table 2.3.

Table 2.3 Dilute-solution viscosity terms currently in use.

Common Name	**IUPAC Name**	**Definition**
Relative viscosity	Viscosity ratio	$\eta_{rel} = \dfrac{\eta}{\eta_0} = \dfrac{t}{t_0}$
Specific viscosity	-	$\eta_{sp} = \dfrac{\eta - \eta_0}{\eta_0} = \dfrac{t - t_0}{t_0} = \eta_{rel} - 1$
Reduced viscosity	Viscosity number	$\eta_{red} = \dfrac{\eta_{sp}}{c} = \dfrac{\eta_{rel} - 1}{c}$
Inherent viscosity	Logarithmic viscosity number	$\eta_{inh} = \dfrac{\ln \eta_{rel}}{c}$
Intrinsic viscosity	Limiting viscosity number	$[\eta] = \left(\dfrac{\eta_{sp}}{c}\right)_{c \to 0} = \left(\dfrac{\ln \eta_{rel}}{c}\right)_{c \to 0}$

The common names are, at the present time, more widely used than the IUPAC-recommended names.

Relative viscosity (η_{rel}) is the ratio of the solution viscosity to the solvent viscosity which is proportional, to a good approximation for dilute solutions, to the ratio of the corresponding flow-times.

Specific viscosity (η_{sp}) is the fractional increase in viscosity due to the polymer alone. Both η_{rel} and η_{sp} are dimensionless quantities. As concentration increases, so does its viscosity. Hence, to eliminate concentration effects, the specific viscosity is divided by concentration and extrapolated to zero concentration to give the intrinsic viscosity $[\eta]$. Not uncommonly, viscosities are determined at a single concentration and the *inherent viscosity* (η_{inh}) is often used as an approximate indication of molecular weight. Inherent viscosity extrapolates to the same $[\eta]$. Concentration, c, in the above expressions is in units of grams per 100 ml of solvent. Thus, the reduced, inherent, and intrinsic viscosities all have units of deciliters per gram. Obviously, the units of concentration must be specified when viscosity data are reported.

The intrinsic viscosity ($[\eta]$) is the most useful of these various viscosity designations because it can be related to molecular weight by the Mark-Houwink Sakurada Equation:

$$[\eta] = K\overline{M}_v^{a}$$

where $\overline{M}_v$ is the viscosity-average molecular weight of the polymer. K and a are viscometric constants.

2.3.5 Kinetic Studies by Dilatometry

For the kinetic investigations of homogeneous polymerisations, a variety of methods and apparatus has been developed, In this work, the considered technique used for kinetic studies of the ROP of ε-caprolactone is dilatometry. The dilatometric method is especially useful on account of its simplicity and general application which provide complementary information about the progress of a polymerisation reaction in term of % conversion and rate of polymerisation.

Dilatometry is the technique most often used to monitor polymerisation reactions and measure the polymerisation rate by exploiting the fact that the density of a polymer is normally greater than that of its corresponding monomer. The sensitivity of the change in volume with conversion can be increased significantly if the shrinkage in volume is observed in a tube of very narrow diameter. Thus, a dilatometer is usually designed with a reservoir to contain a sufficient volume of liquid (to make the total volume change occurring during conversion to be meaningful) and fitted with a capillary tube to make the volume change accompanying the conversion of monomer to polymer readily measurable.

The measurement of the volume change is complicated if there are any gases dissolved in the monomer or polymer which may separate as bubbles at the temperature of polymerisation, or if a gas is generated in the reaction. Dissolved gases should be removed by degassing the monomer and any diluents before polymerisation. Another complication can arise if the polymer is insoluble in the polymerising mixture.

The dilatometer may be constructed in a variety of ways. The principle of operation of a dilatometer may be seen from the apparatus shown in section 4.3.1. The design and construction of these small glass instruments depend on a number of considerations such as the expected volume change and the accuracy with which it must be measured, the rate of polymerisation, the corresponding rate of heat evolution and its effect on temperature uniformity, the viscosity of the polymerising mixture and the need for stirring. The dilatometer is placed in a thermostatically controlled oil bath maintained at the desired reaction temperature. Initially, as the volume of liquid increases by thermal expansion, the liquid will rise up the capillary tube. As soon as the liquid has reached thermal equilibrium, the volume of the liquid will decrease with polymerisation. The change in height of the liquid in the capillary is measured periodically with a cathetometer. The rate of polymerisation can then be determined from the rate of change in the height of the liquid.

For this dilatometry experiment, the polymerisation temperature used was 130 ^{o}C. The various initiators used to study the kinetics of the bulk ring-opening polymerisation (ROP) of ε-CL are as follow:

1) Commercial available Tin(II)Octoate
2) Commercial available Tin(II)Octoate/ROH
3) Synthesised Tin (II)Alkoxides ($[Sn(Oct)]_2DEG$, and $[Sn(Oct)]_2EG$)

2.4 Fabrication of PLC Fibre

2.4.1 Melt Spinning

Copolymer PLC was fabricated into monofilament fibre using melt spinning technique because the purity of the fabricated fibre is crucial for its absorbable surgical suture application. It is also the most economical process but can only be applied to polymer that are sufficiently stable at temperature above their melting point or softening point to be extruded without substantial degradation.

Figure 2.15 shows small-scale melt spinning apparatus used for fibre fabrication. Before fibre fabrication, copolymer material was first converted into a cylindrical rod to avoid problem of air bubble. The cylindrical rod was then put into the extrusion cylinder. By applying pressure to a ram to act as a piston applied to the top of the unmelted polymer rod in the cylindrical well, the rod was then displaced downward through the melting zone. Before reaching the tubular-shaped die, the molten polymer is filtered through metal gauzes in order to remove large particles that might make defect on the wall tubes and provide shearing that can influence rheological behaviour. The extruded tube or fibre of molten polymer is pulled to a cooling zoon where the polymer solidifies to complete the fibre melt spinning process. Figure 2.16 shows a schematic drawing of molecular orientation changes during the fibre formation at the extrusion. The fibre extruded is so-called as-spun fibre which is usually almost completely amorphous and unoriented. Accordingly, its mechanical properties are required to improve further by hot-drawing and annealing under controlled conditions.

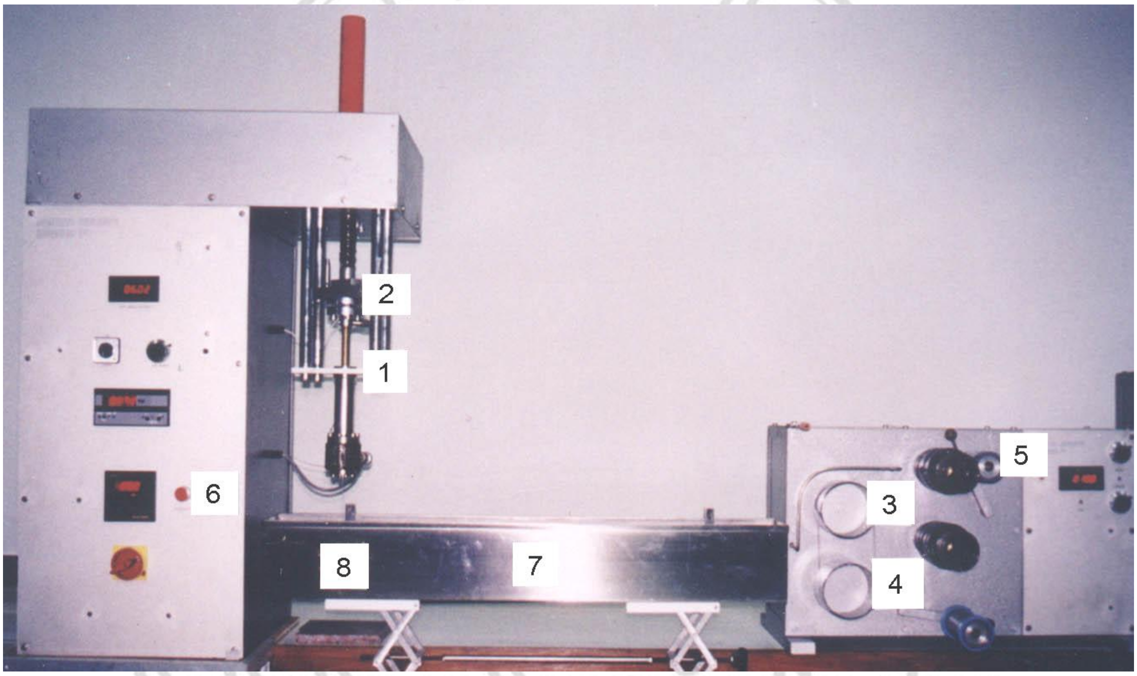


Figure 2.15 Small-scale melt spinning apparatus:

1 = extrusion cylinder and heating block
2 = piston (ram) in raised position
3 = godet
4 = godet

5 = final take-up bobbin
6 = heater control switch
7 = cooling bath (ice-water)
8 = filament guide

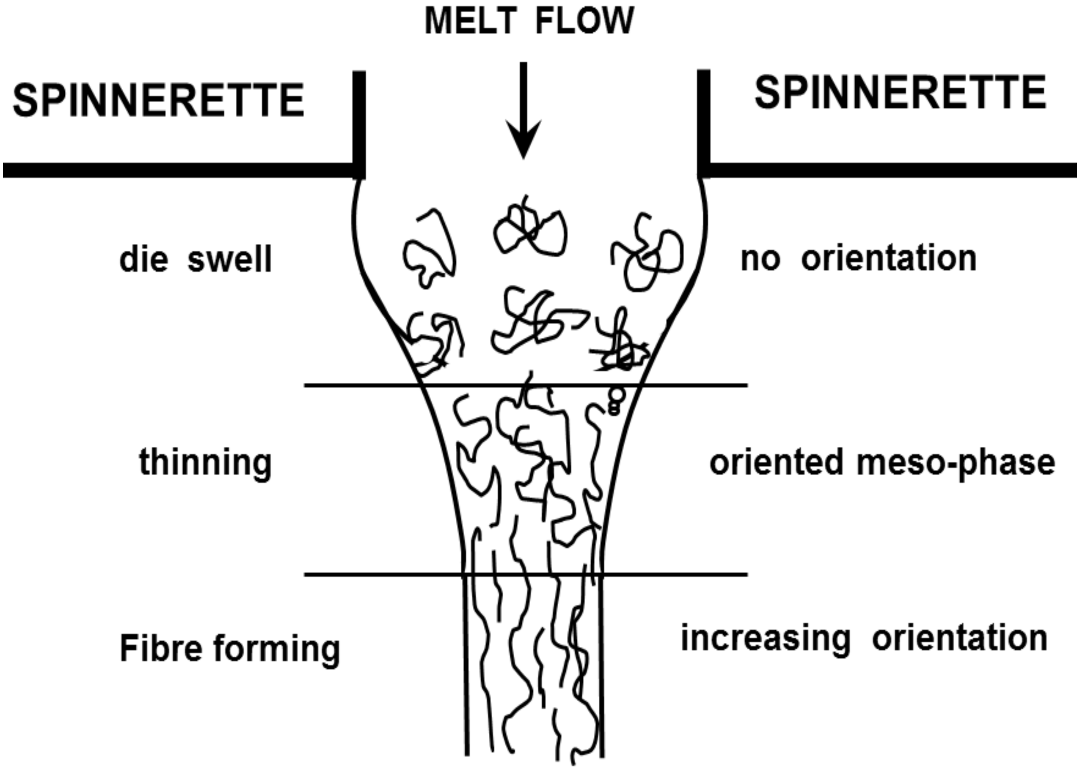


Figure 2.16 A schematic drawing of molecular orientation changes during the fibre formation at the extrusion.

2.4.2 Hot-drawing

Drawing is a common commercial process for improving mechanical properties of fibres. After the polymer has been melt spun, it solidified in an unoriented state or a state of low orientation, so called as-spun fibre. It is weak and high extensible. Subsequent drawing is needed to introduce orientation. Drawing removes the kinks from the polymer chains and extends them along a common axis to promote closer packing at temperature above its glass transition temperature (see Figure 2.17). That is to say that drawing process not only induces orientation of crystallites which has already occurred but also induces orientation in amorphous region immersely and as a result, there appears higher crystallinity [98, 99]. Therefore, mechanical properties of fibre is generally improved by a high degree of crystallinity and by an orientation of both the crystallites and the polymer chain segments in the non-crystalline domains.

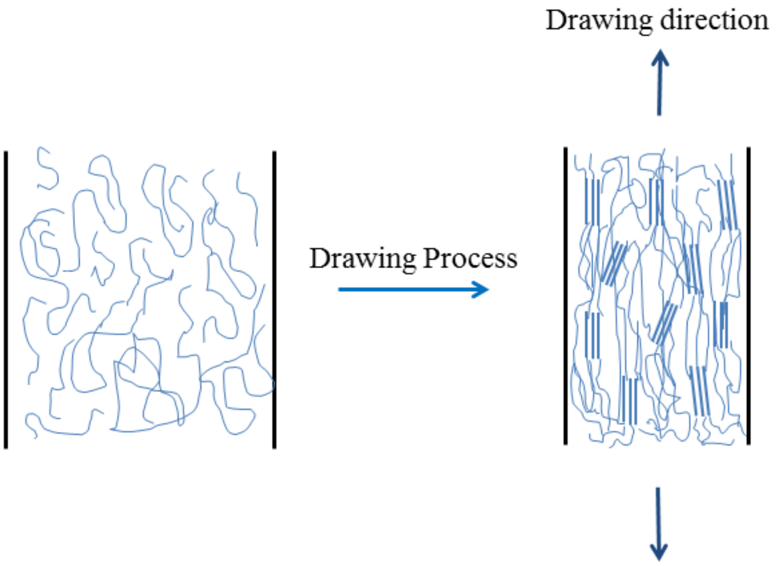


Figure 2.17 Schematic representation of molecular and crystal orientation in polymer fibre developed under drawing process.

Normally, drawing process may be performed either by hand or using instrument at a particular temperature. Drawing at higher than glass transition temperature (T_g) and around crystallisation temperature (T_c) was employed in this project to enable high extensibility and, as a result, high orientation. This drawing at high temperature is well-known as hot-drawing. The extension of the fibre may be represented by a term of draw ratio (λ) evaluated as follows.

$$\lambda = l / l_0$$

where l_0 and l are the initial and final lengths of the drawn fibre.

2.4.3 Annealing

The fine structure and physical properties of synthetic fibres are often further modified by thermo mechanical annealing treatments. Annealing is a process in which a polymer was heated under vacuum or in an inert atmosphere (to prevent oxidation) at a specified temperature to induce crystallization in polymer and molecular relaxation. The temperature for annealing a polymer is usually chosen in between its glass transition temperature (T_g) and melting temperature (T_m).

Annealing fibre may be done in two ways for different particular purposes. One is in which a fibre is annealed under constant tension, so-called free annealing.

The other is annealing a fibre under constant length, so-called fixed annealing. Crystallization of polymer in free annealing process occurs randomly, resulting in brittle and low tensile strength. Figure 2.18 represents a schematic picture for an unoriented amorphous structure in as-spun fibre, then crystallization can occur randomly in solid amorphous fibre through free annealing process. On the other hand, annealing under constant length or fixed annealing induces both crystallization and orientation of crystallites along the fibre axis, as seen in Figure 2.19. This results in higher tensile properties in the fibre direction [98].

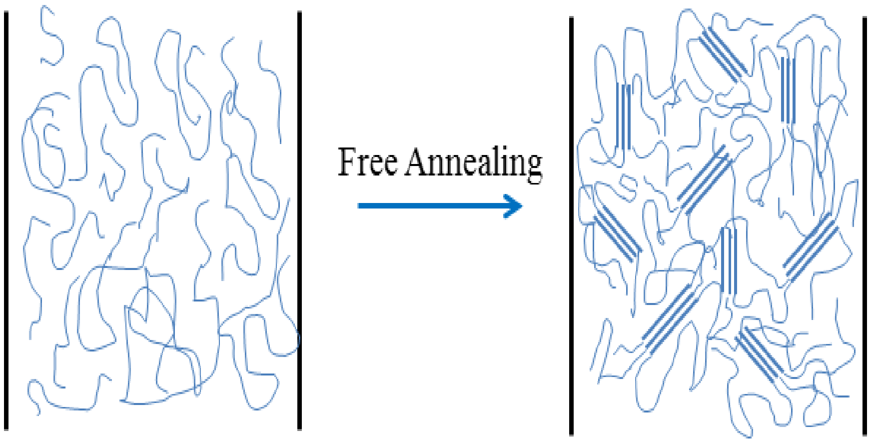


Figure 2.18 Schematic representation of crystallisation in polymer fibre developed under free annealing process.

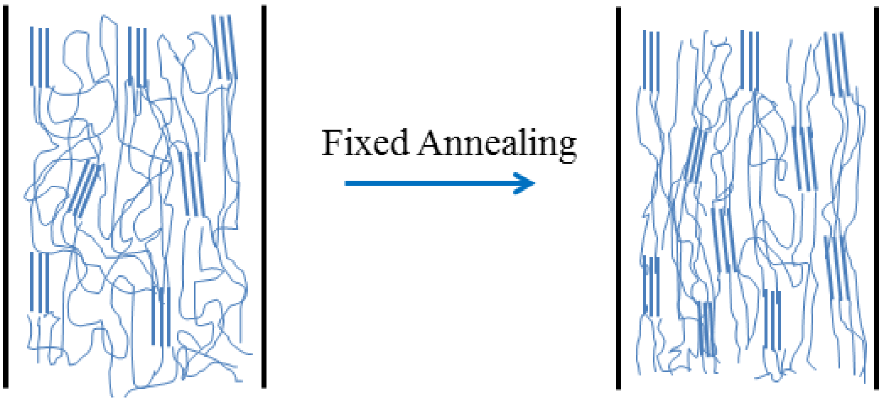


Figure 2.19 Schematic representation of both crystallization and orientation of crystallites along the fibre axis in polymer fibre developed under fixed annealing process.

2.5 Tensile Testing

The mechanical properties of a monofilament fibre are of fundamental interest because they must fall within a specified range for a given application. In this study, mechanical properties such as tensile strength, % elongation at break, and Young's modulus were determined and the results correlated as far as possible with the fibre's chemical microstructure and matrix morphology.

For tensile testing, load is applied to the fibre specimen resulting in the increase in length of the fibre, called as **elongation**. Results of tensile testing are usually illustrated in the form of a stress-strain curve as shown in Figure 2.20. This figure is a typical stress-strain curve that obtained for a number of semi-crystalline polymers. Specific terms such as stress, strain, ultimate strength, yield point, etc., are defined as below.

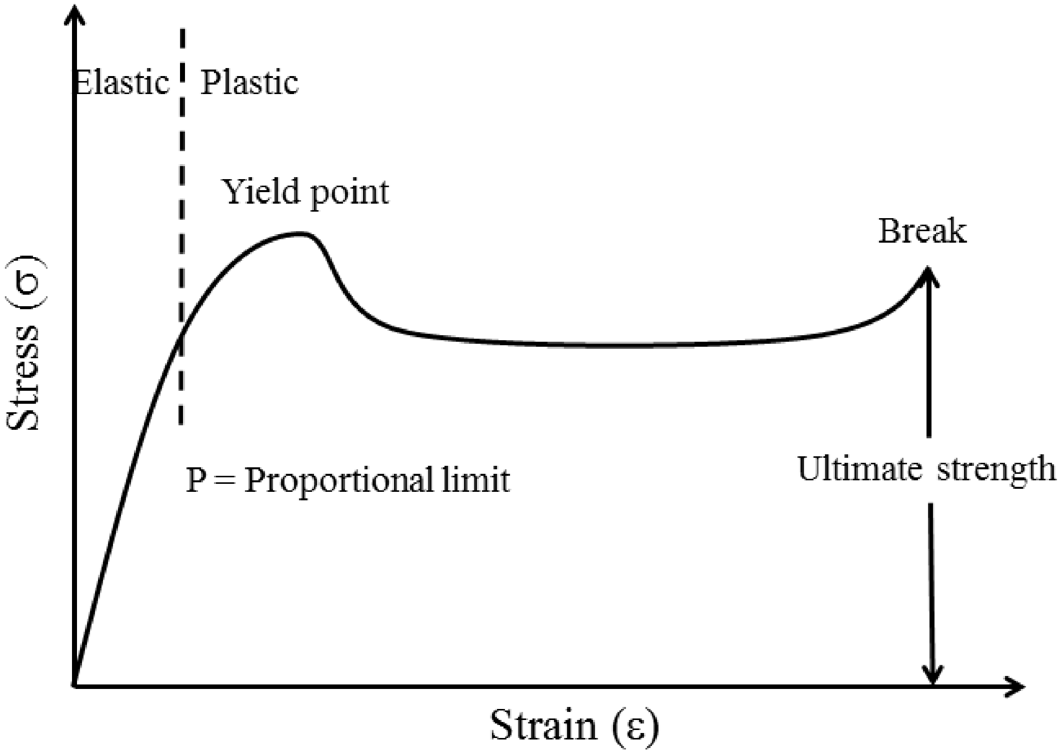


Figure 2.20 A typical stress-strain curve for semi-crystalline polymers.

Stress (σ) is defined as a force applied to produce deformation per unit area of the specimen perpendicular to the direction of force. Stress is therefore a ratio of an applied load to the corresponding perpendicular cross-sectional area. However, for simplicity, the cross-sectional area may be assumed constant, i.e. equivalent to the original cross-section at the beginning of testing. The stress is therefore evaluated as follows.

$$\sigma = F / A_0$$

where F is the instantaneous load applied to the specimen, in units of newtons (N), and A_0 is the original cross-sectional area before any load is applied.

Strain (ε) is defined as a ratio of elongation (Δl) to the gauge length of the specimen, or simply stated as a change in length per unit of the original length, as written below.

$$\varepsilon = \Delta l / l_0$$

where l_0 is the original length before any load is applied, referred to as the gauge length.

Young's modulus (E): In most traditional materials such as metals, their mechanical behavior obeys Hooke's law : stress is proportional to strain.

$$E = \sigma / \varepsilon$$

Proportional limit (P): When the applied load is continuously increased up to a point P, the actual curve starts to deviate from the straight line. Therefore, point P indicates boundary between the elastic and plastic behaviours of the specimen. Point P is so called the proportional limit.

Yield point: The first point on the stress-strain curve at which an increase in strain occurs without the increase in stress. Beyond the yield point, extension occurs by displacement of molecules with respect to one another, intermolecular slippage. The displaced molecules have no tendency to slip back to their original positions. These deformations are permanent and non recoverable and so call plastic deformation.

Yield strength: The stress at the yield point.

Ultimate strength: The maximum stress at which a material will be able to withstand when subjected to an applied load in tension.

Polymers can show various mechanical properties largely depend upon their molecular structures and relative arrangements. A particular polymer can also show all the features of properties such as glassy, brittle, weak or rubbery depending on the conditions of testing, e.g. the rate of application of load, temperature, and time scale of measurement. It is therefore difficult to classify polymers as particular types of materials. However, it is helpful to specify their properties at a particular condition at testing from their stress-strain diagrams as described below. Figure 2.21 illustrates typical stress-strain curves obtained from polymers possessing different properties such as softness, brittleness, hardness and toughness. The area under the stress-strain curve is a measure of toughness of the polymeric material. Definitions of all other terms are as follow[98].

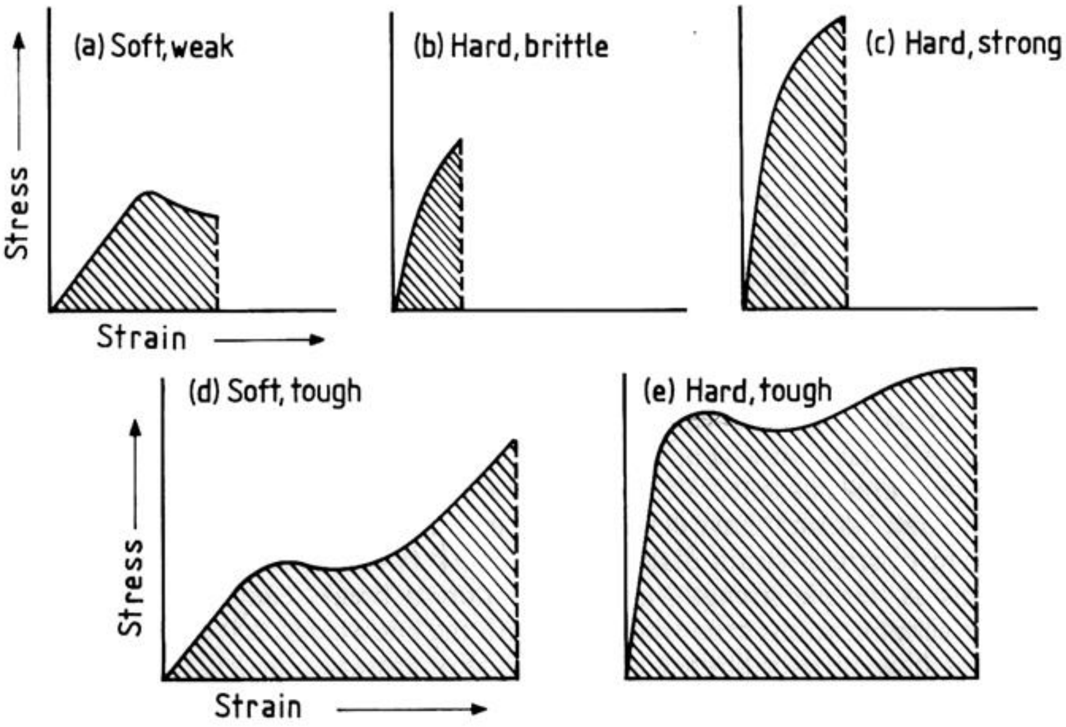


Figure 2.21 Typical stress-strain curves [98].

A soft and weak material is characterised by low modulus, low (or no) yield point and moderate elongation at break.

A hard and brittle material is characterised by high modulus, no yield point and very low elongation at break.

A hard and strong material has high modulus, high yield stress, high ultimate strength and relatively low elongation at break.

A soft but tough material shows low modulus, low yield point but very high elongation and high stress at break.

A hard and tough material is characterised by high modulus, high yield stress relatively high elongation at break and high ultimate strength.

In this research, the mechanical tests were performed on the Universal Mechanical Testing Machine (LLOYD Instrument model LRX), as shown in Figure 2.22. All tests were carried out with the fibre sample wound once around each of two bollard grips at 40 mm gauge length (Figure 2.23).

Figure 2.22 Universal Mechanical Testing Machine used for fibre tensile testings.

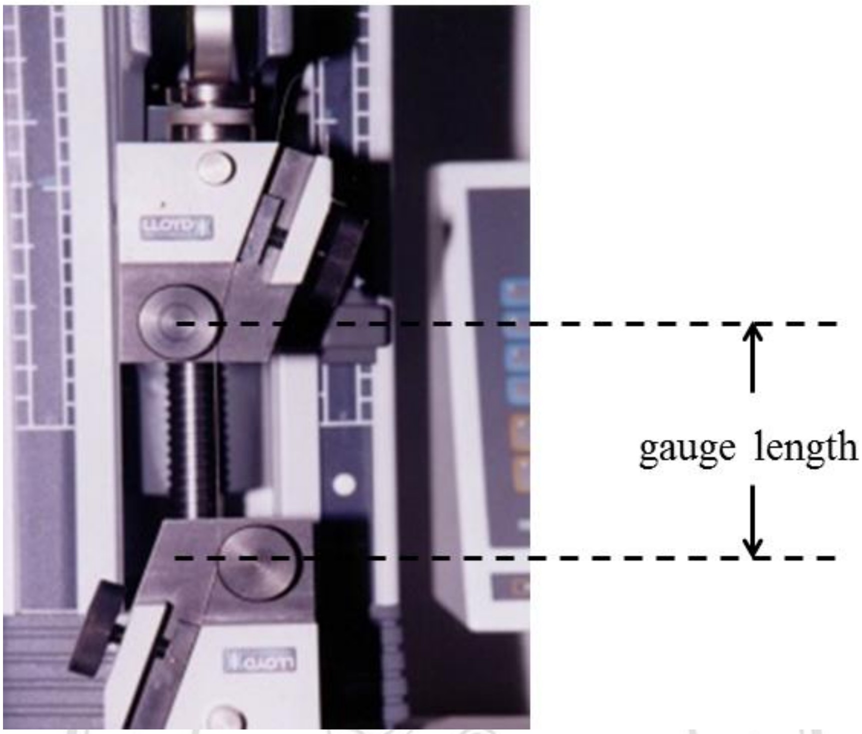


Figure 2.23 Photograph of the bollard grips.

The tensile test conditions used for the monofilament fibre samples were as follows:

Fibre Tensile Test Conditions		
Load cell	:	100 N
Sample grips	:	bollard-type
Initial gauge length	:	40 mm
Crosshead speed	:	80 mm / min
Temperature	:	Ambient (20-25^{o}C)
Humidity	:	50-70 % rh