CHAPTER 2

EXPERIMENTAL METHODS

2.1 Small-Scale Fibre Melt Spinning

In any fibre-forming process, the morphology and molecular orientation within the fibre at the microscopic level can be controlled by the processing method and conditions used. This, in turn, controls the fibre properties at the macroscopic level. In this study, melt spinning, off-line hot-drawing and annealing were used in the production of monofilament fibres.

Polymer samples were melt-spun using a modular-design, small-scale melt spinning apparatus manufactured by Ventures & Consultancy Bradford Ltd. (formerly Bradford University Research Ltd.), Bradford, UK. It could handle batch sizes of as small as 5 – 20 g depending on the size of the cylinder that was used. A schematic diagram and photograph of the apparatus are shown in Figs. 2.1 and 2.2 respectively.

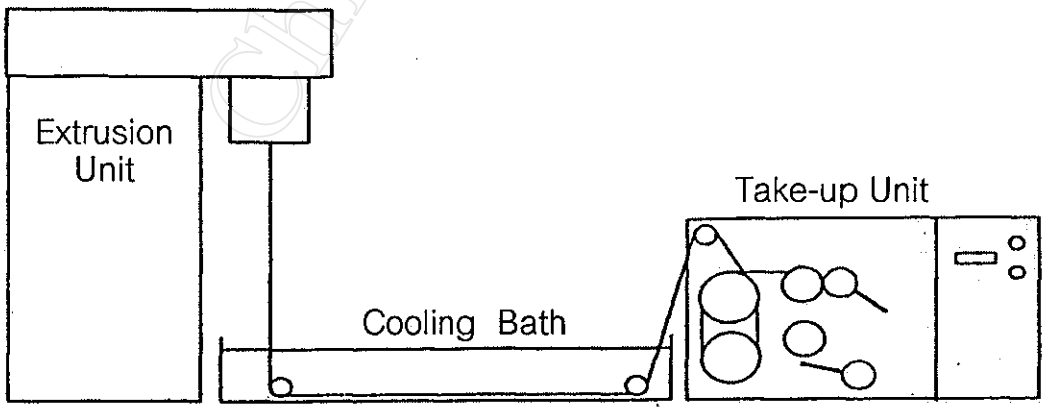

Fig. 2.1 Schematic diagram of the small-scale melt spinning apparatus.

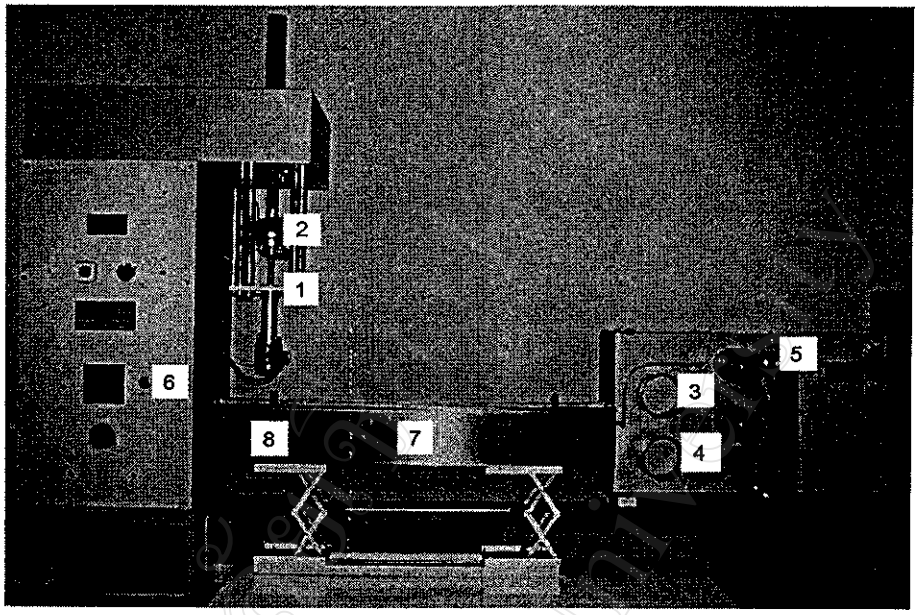

Fig. 2.2 Photograph of the small-scale melt spinning apparatus

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

A closer view of the various accessories used is shown in the photograph in Fig. 2.3, while Fig. 2.4 shows a more detailed diagram of the compression, melting and metering zones.

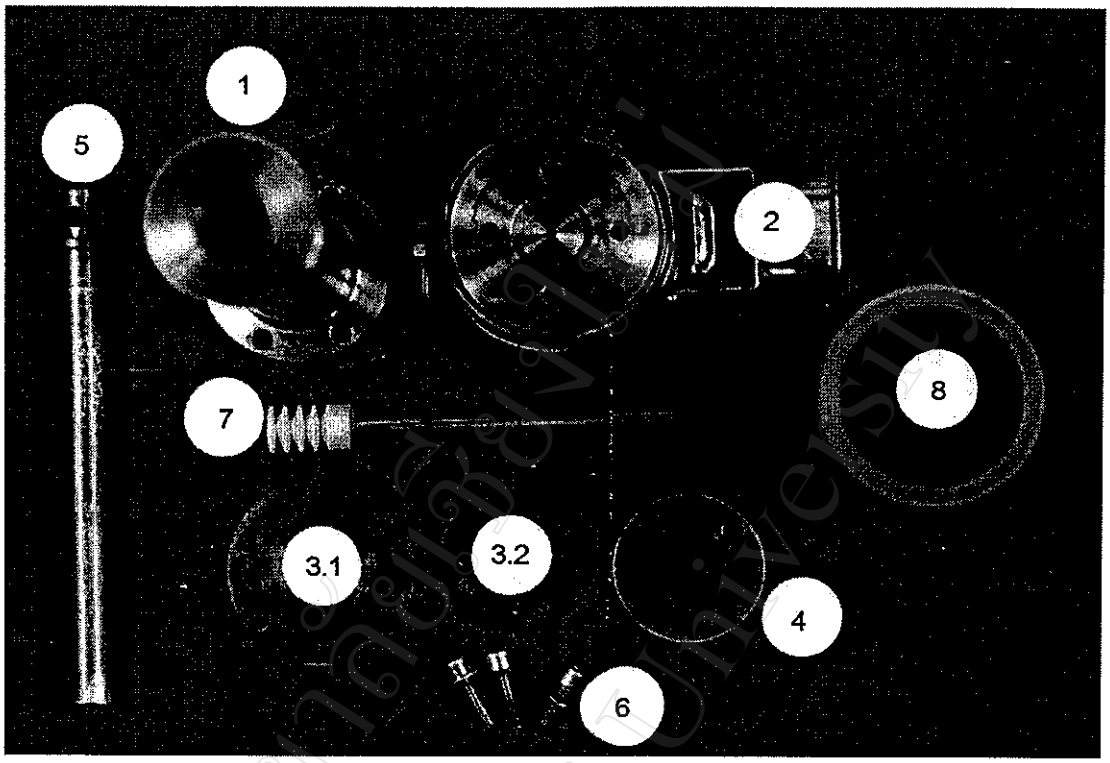

Fig. 2.3 Photograph showing some of the various accessories used in the small-scale melt spinning apparatus.

Key to figure :

1 = 15 ml extrusion cylinder

2 = heating block fitted with band heater

3 = copper gaskets

3.1 = gasket used between the extrusion cylinder and the heating block

3.2 = gasket used between the heating block and the spinnerette

4 = spinnerette (single hole; 1, 1.5, 2 or 2.5 mm diameter)

5 = piston (ram)

6 = cap screws

7 = filament guide

8 = final take-up bobbin (spool)

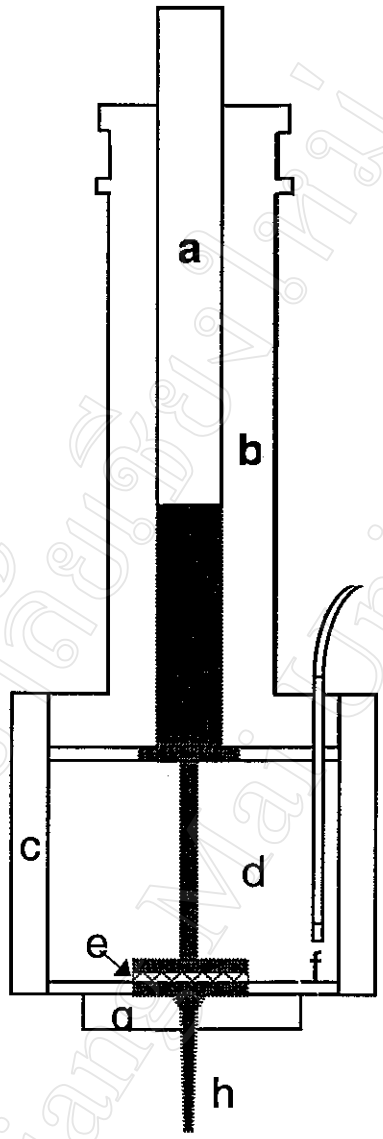

Fig. 2.4 Schematic diagram of the compression, melting and metering zones showing the (a) ram, (b) cylinder, (c) band heater, (d) heating block, (e) stainless steel filter mesh, (f) thermocouple, (g) spinnerette, and (h) extruded monofilament fibre.

With reference to Figs. 2.1-2.4, the melt spinning procedure employed in this work can be summarized as follows. The extrusion cylinder was attached to the heating block by means of 6 × 10 mm cap screws that were lubricated with anti-seizure compound. The spinnerette then was bolted to the lower face of the heating block.

A circular disk of fine stainless steel gauze (~ 300 mesh) was inserted in the centre of the heating block as a means of shearing the polymer melt, thereby assisting the molten polymer to flow more smoothly through the spinnerette. In this way, the stainless steel gauze served a similar purpose to a screen pack in a conventional extruder.

The extrusion cylinder was placed in the extrusion unit with the thermocouple and band heater in place. After switching on the heater and setting the temperature controller to a few degrees below the nominal melting point of the polymer, some loose granules of the polymer were placed in the cylinder, the ram placed in its raised position and then brought down so as compress the polymer. As the temperature approached the set value, the polymer started to melt, followed soon after by extrusion from the spinnerette. Initially, the temperature was cautiously adjusted in steps of 1-2°C until an appropriate melt viscosity was obtained which gave a stable filament line and smooth extrusion.

As the molten polymer emerged from the spinnerette, the monofilament was first cooled by contact with the room air before being passed through an ice-water quenching bath (10-15°C). The vertical distance from the spinnerette to the water bath was 4 cm. Finally, the monofilament was wound 4 to 5 times in a clockwise direction around the two godets and then led on to the final take-up bobbin via a traversing roller, as illustrated in Figs. 2.1 and 2.2.

2.2 Polymer Characterisation and Fibre Testing

2.2.1 Instruments Used

The main items of equipment used in this project were as listed in Table 2.1.

Table 2.1 Instruments used in this research project.

INSTRUMENT	COMPANY	MODEL
FT-IR Spectrometer	Nicolet	510
^{1}H-NMR Spectrometer	Bruker	DPX 300
^{13}C-NMR Spectrometer (75 MHz)	Bruker	DPX 300
Differential Scanning Calorimeter	Perkin-Elmer	DSC7
Thermogravimetric Analyzer	Perkin-Elmer	TGA7
Gel Permeation Chromatograph	Waters	150-CV
Automatic Viscosity Measuring System	Schott-Gerate	AVS 300
Universal Testing Machine	Lloyds	LRX+

2.2.2 Instrumental Methods

In this research project, the random and block terpolymer products obtained were characterised by the following combination of instrumental methods:

(i) infrared spectroscopy (IR)

- for qualitative structural characterisation

(ii) nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR)

- for quantitative compositional and microstructural characterisation

(iii) differential scanning calorimetry (DSC)

- for temperature transitions and crystallisability studies

(iv) thermogravimetry (TG)

- for thermal stability

(v) gel permeation chromatography (GPC)

- for molecular weight determination (averages and distribution)

(vi) dilute-solution viscometry

- for molecular weight determination (intrinsic viscosity)

(vii) mechanical testing

- for determining the tensile properties of the fibres obtained

2.2.1.1 Infrared Spectroscopy (IR) [31,32]

Vibrational spectroscopy, particularly infrared (IR) spectroscopy, is one of the most important methods for the identification and characterisation of polymeric materials. It has been widely used to identify polymers, to quantitatively analyze their chemical composition, and to specify steric and geometric isomerism, configuration, branching, end-groups, and crystallinity. In addition, the identification and analysis of additives, residual monomers, fillers and plasticizers can been accomplished, while chemical reactions such as polymerisation, vulcanization, degradation and weathering have also been studied.

Fourier-transform infrared (FT-IR) spectroscopy brings greater versatility to polymer structural studies. 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. The very small sample-size requirement facilitates coupling of the FT-IR instrument with a microscope for analysis of highly localized sections of a polymer sample. In addition, the capability for digital subtraction allows one to generate otherwise "hidden" spectra. An example of spectral subtraction is shown in Fig. 2.5 for isotactic polystyrene. Spectrum A is that of the semicrystalline polymer obtained by annealing; B is that of the same polymer heated above the T_m and quenched in the amorphous state. Spectrum C, obtained by subtraction of B from A, reveals more well-defined absorbances characteristic of the crystalline regions where the benzene rings are "frozen" into relatively specific conformations.

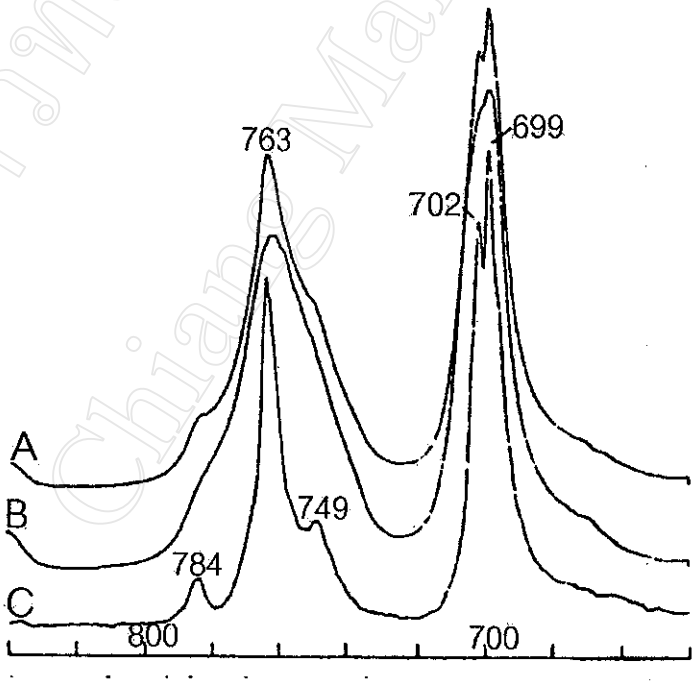

Fig. 2.5 FT-IR spectra of isotactic polystyrene in the 640 to 840 cm^{-1} region: (A) semicrystalline; (B) amorphous; and (C) the difference spectrum obtained by subtracting B from A.

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. With the development of FT-IR, sampling requirements are less restrictive due to the high energy throughput of the instrument; for example, suitable spectra can be obtained with only 1% transmission through the sample. Additionally, very thin samples can be examined due to the high signal-to-noise ratio available and ordinate scale expansion capabilities. However, the benefits of FT-IR can only be achieved with proper sample preparation.

In this research project, FT-IR was used mainly for the structural characterisation of the random and block terpolyesters. A Nicolet FT-IR 510 Fourier-transform Infrared Spectrometer was used for the recording of all FT-IR spectra. Wherever possible, the samples were prepared as thin films cast from solution in chloroform. These thin films generally gave better quality spectra than, for example, compressed discs of the polymer in admixture with potassium bromide (KBr).

2.2.2.2 Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR and ^{13}C-NMR) [32]

Nuclear magnetic resonance (NMR) spectroscopy is perhaps the most powerful technique available for studying the environment of individual atoms within a polymer chain. Many of the applications of this technique are the same as those of IR spectroscopy. Thus, both ^{1}H and ^{13}C-NMR are widely used for routine purposes such as polymer identification, confirmation of molecular structure and evaluation of average copolymer composition. NMR spectroscopy, however, offers much greater scope than IR spectroscopy 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.

The NMR spectra of linear polymers of low molecular weight often show unique absorptions due to the end-groups. By referencing these absorptions to those of the nuclei in the repeat units, it is possible to obtain the ratio of the number of end-groups to the number of repeat units and thereby to evaluate the number-average molecular weight ($\overline{M}_n$) of such polymers.

However, the power of NMR spectroscopy (especially ^{13}C-NMR) is most clearly demonstrated by its ability to yield quantitative information on features of molecular microstructure not accessible by other techniques. These features include: (i) head-to-tail and head-to-head repeat unit linkages, (ii) different types of isomerism, (iii) isotactic and syndiotactic sequences, (iv) chain branching and (v) in copolymers, the sequence distribution of the different repeat units present along the copolymer chains.

In this research project, NMR spectroscopy was used for terpolymer compositional analysis by ^{1}H-NMR and microstructural analysis by ^{13}C-NMR. The ^{1}H and ^{13}C-NMR spectra were recorded in $CDCl_3$ as solvent using a Bruker Advance FT-NMR DPX 300 MHz Nuclear Magnetic Resonance Spectrometer which could be adapted for both ^{1}H-NMR and ^{13}C-NMR analyses.

2.2.2.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) 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 microfurnaces, usually in a nitrogen atmosphere. When an exothermic or endothermic change occurs in the sample, energy is applied or removed to one or both microfurnaces 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 sample container most commonly used is a very small aluminium pan (gold or graphite is used for analyses above 500°C) and the reference is either an empty pan or a pan containing an inert material in the temperature range of interest, such as anhydrous alumina. The sample size usually varies from about 0.5 to 5 mg.

DSC is generally used to measure the glass transition temperature (T_g), crystallisation temperature (T_c), and melting temperature (T_m) of polymers. The major advantage of DSC is that peak areas are directly related to the corresponding enthalpy changes in the sample. Therefore, it can also be applied to measurements of heat capacities, heats of melting, enthalpies of reactions (including polymerisation, oxidation and combustion), purities of monomers, % crystallinity, and rates of reaction.

Precise temperature measurement is obviously essential in DSC and attained by observing the following:

(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 accurate 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

In this research project, the particular instrument used was a Perkin-Elmer DSC 7 Differential Scanning Calorimeter. Nitrogen gas (99.99% purity) was used as the purge gas at a pressure of 20 lbs/in^2 (flow rate $\approx$ 40 ml/min). The heating rate used was 10°C/min with a sample size typically in the range of 3-5 mg.

2.2.2.4 Thermogravimetry (TG)

Thermogravimetry (TG) is used primarily for determining the thermal stability of polymers. The most widely used TG method is based on the continuous measurement of weight on a sensitive balance (called a thermobalance) as sample temperature is increased in air or in an inert atmosphere (nitrogen gas) at a constant heating rate. This method is referred to as *non-isothermal TG*. Data is recorded as a thermogram of weight versus temperature. Weight loss may arise initially from evaporation of residual moisture or solvent, then at higher temperatures from polymer decomposition. Besides providing information on thermal stability, TG may also be used to characterise polymers through loss of a known entity, such hydrogen chloride (HCL) HCl from poly(vinyl chloride). Thus, weight loss can be correlated with the % vinyl chloride content in a copolymer.

A variation of the non-isothermal method is to record weight loss with time at a constant temperature. Referred to as *isothermal TG*, this is less commonly used than non-isothermal TG. A typical non-isothermal TG curve (thermogram) is illustrated in Fig. 2.6.

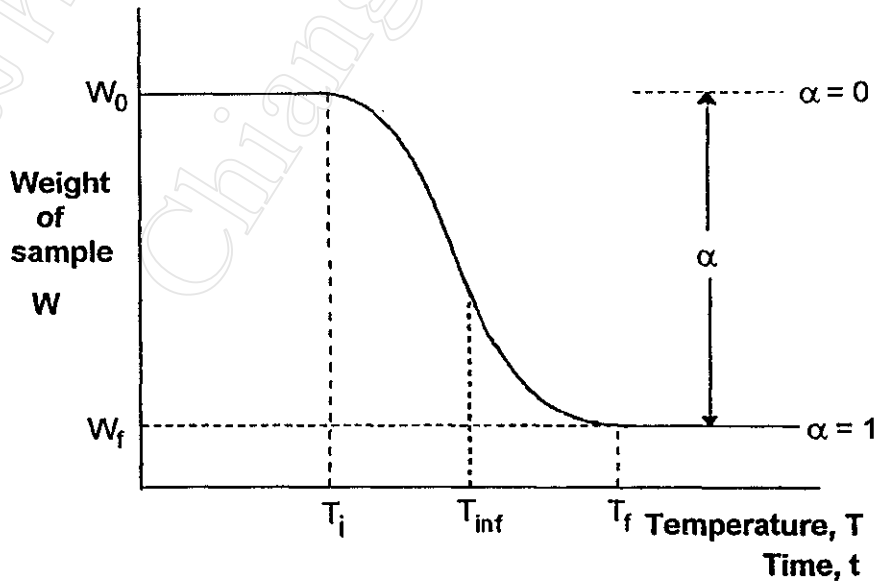

Fig. 2.6 A typical non-isothermal TG thermogram for a polymer showing the various reaction parameters derived from the curve.

The various reaction parameters illustrated in Fig. 2.6 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 temperature, T

T_i = initial weight loss temperature

T_f = final weight loss temperature

$T_i - T_f$ = weight loss temperature range

T_{inf} = inflection point temperature, i.e. the temperature at which the maximum rate of weight loss, $(dW/dt)_{max}$, occurs

α = fraction of conversion (or extent of reaction)

$$\alpha = \frac{W_0 - W}{W_0 - W_f}$$

In this work, the non-isothermal TG thermograms of the terpolyesters were obtained using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. The most important variables which must be controlled in order to obtain meaningful TG data are:

(1) the heating rate (in non-isothermal TG), which must be linear with time (i.e., dT/dt = constant) and slow enough to separate successive reactions

(2) the initial sample size, which must be kept as small as practicable to minimize mechanical and heat transfer difficulties

(3) the sample particle size, which should also be as small as possible to increase surface area and thereby minimize diffusion-controlled processes

(4) the atmosphere, which must be either absent (i.e., *in vacuo*) or inert (usually N_2) to prevent reactions (e.g., oxidation) with the sample

In this project, 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.

2.2.2.5 Gel Permeation Chromatography (GPC) [33]

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. 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. In GPC, a dilute polymer solution is injected into a solvent stream which then flows through a column packed with beads of a porous gel. The porosity of the gel is of critical importance and typically is in the range 50-10^6 Å. The small solvent molecules pass both through and around the beads, carrying the polymer molecules with them where possible. The smallest polymer molecules are able to pass through most of the pores in the beads and so have a relatively long flow-path through the column. However, the largest polymer molecules are excluded from all but the largest of the pores because of their greater molecular size and consequently have a much shorter flow-path. Thus, GPC is a form of size-exclusion chromatography in which the polymer molecules elute from the column in order of decreasing molecular size in solution. The concentration of polymer in the elute is monitored continuously and the chromatogram obtained is a plot of concentration against elution volume, which provides a qualitative indication of the molecular weight distribution.

The volume of solvent contained in a GPC system from the point of solution injection, through the column to the point of concentration detection can be considered as the sum of a void volume V_0 (i.e. the volume of solvent in the system outside the porous beads) and an internal volume V_i (i.e. the volume of solvent inside the beads).

The volume of solvent required to elute a particular polymer species from the point of injection to the detector is known as its retention (elution) volume V_R and on the basis of separation by size-exclusion is given by the equation

$$V_R = V_0 + K_{se}V_I \qquad (2.1)$$

where K_{se} is the fraction of the internal pore volume penetrated by those particular polymer molecules. Thus, $K_{se} = 0$ for very large molecules of ($V_R = V_0$) and rapid elution takes place, whereas $K = 1$ for very small molecules which can penetrate all the available pore volume. This is shown schematically in Fig. 2.7 and clearly the technique cannot discriminate among the molecular sizes with $V_R \leq V_0$ or $V_R \geq V_0 + V_I$. For samples which fall within the appropriate range, it has been suggested that a universal calibration curve can be constructed to relate V_R and molecular weight M by assuming that the hydrodynamic volume of a polymermolecule is related to the product $[\eta]$ M, where $[\eta]$ is the intrinsic viscosity of the polymer in the carrier solvent used at the temperature of measurement.

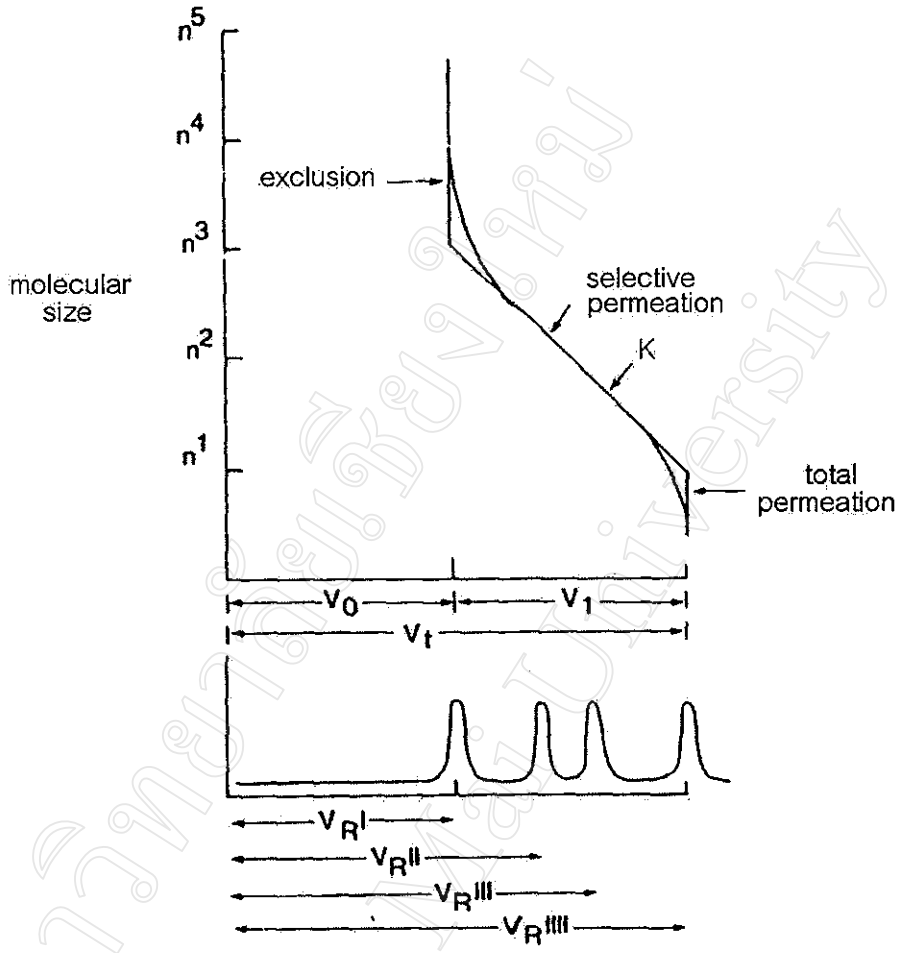

Fig. 2.7 GPC elution curve showing schematically the range of elution volumes which are valid for a particular column. (In this case, molecules with a molecular size > n^3 are totally excluded and eluted without discrimination, while those < n^1 tend to become absorbed or are partitioned if a mixed solvent is used.) [33]

A universal calibration curve is then obtained by plotting log [η] M against V_R for a given carrier solvent at a fixed temperature. Experimental verification of this is shown in Fig. 2.8 for a variety of different polymers and can be utilized in the following way.

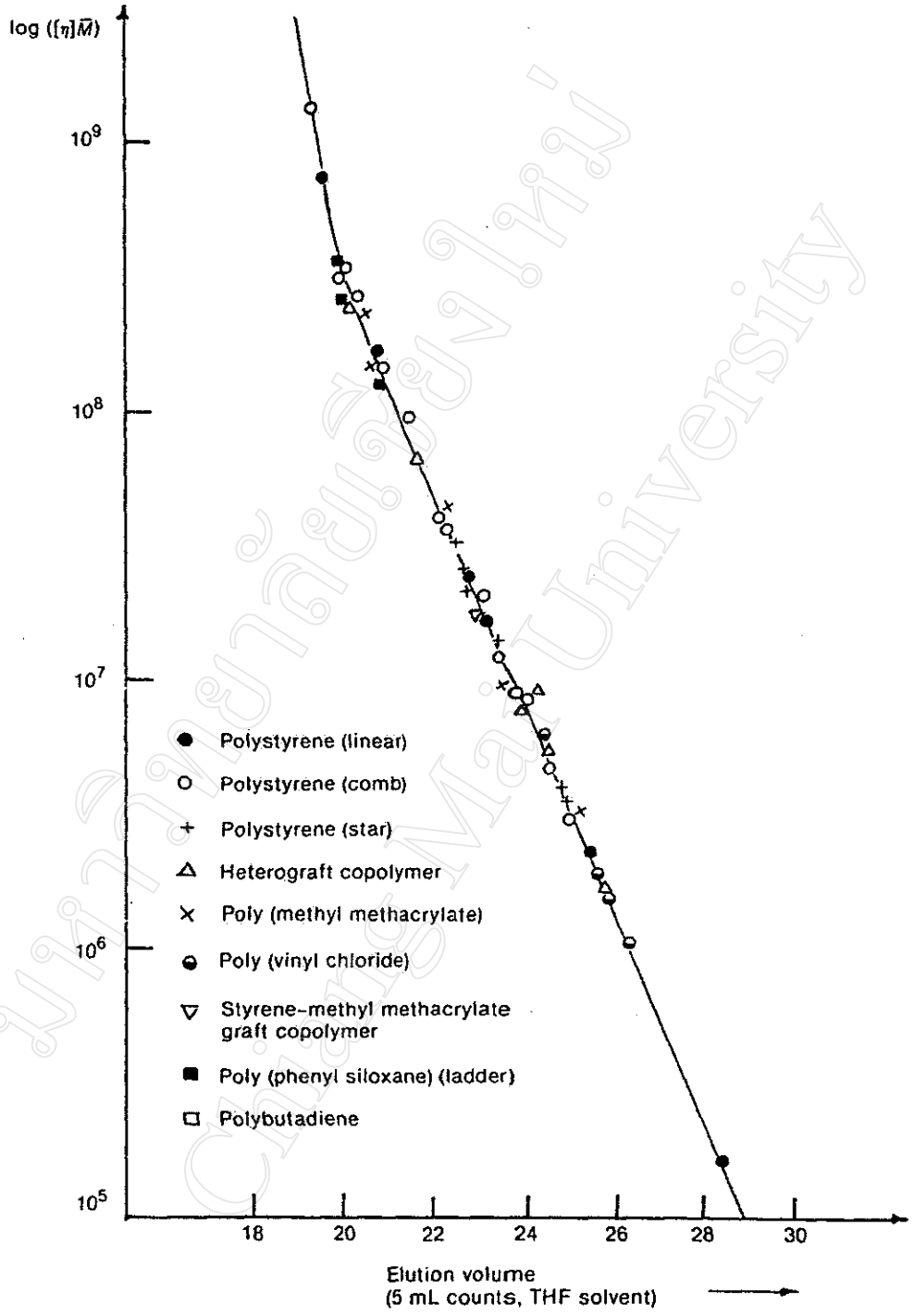

Fig. 2.8 Universal GPC calibration curve for several polymers in tetrahydrofuran as solvent at 30°C [33].

To obtain the MWD, the weight of the polymer being eluted must be measured. This can be achieved continuously using refractive index, UV or IR detectors which will give a weight distribution as a function of V_R. It is still necessary to estimate the molecular weight of each fraction before the MWD curve can be constructed. If the universal calibration curve is valid for the system, then

$$[\eta]_s M_s = [\eta]_u M_u \qquad (2.2)$$

where the subscripts s and u denote the standard calibration and the polymer under study respectively.

From the Mark-Houwink-Sakurada Equation

$$[\eta]_s = K_s M_s^{a_s} \qquad (2.3)$$

$$[\eta]_u = K_u M_u^{a_u} \qquad (2.4)$$

Combining these equations and solving for log M_u gives

$$\log M_u = \left(\frac{1}{a_u + 1}\right) \log\left(\frac{K_s}{K_u}\right) + \left(\frac{a_s + 1}{a_u + 1}\right) \log M_s \qquad (2.5)$$

To determine the molecular weight (M_u) at a given retention volume, the column must first be calibrated with standard polystyrene fractions (same solvent, same temperature). The constants K and a are normally obtainable from the "Polymer Handbook". By substituting the value of M_s for a particular retention volume from the calibration plot and the values of K and a in the above equation, M_u can be readily calculated.

When using GPC, care must be taken not to overload the columns with too large a polymer sample as this results in a non-linear response, characterised by losses in resolution and column efficiency.

In this research project, the GPC instrument used was a Waters Model 510 Gel Permeation Chromatograph operating under the following conditions:

type of column	:	Ultrastyragel®
solvent	:	chloroform
eluent flow-rate	:	1.0 ml/min
temperature	:	30°C
calibration	:	universal (narrow MWD polystyrene standards)

2.2.2.6 Dilute-Solution Viscometry [34]

Measurements of dilute-solution viscosity provide the simplest and most widely used technique for routinely determining molecular weights. However, dilute-solution viscometry is not an absolute method; each polymer system must first be calibrated with absolute molecular weight determinations (usually by light scattering) run on fractionated polymer samples. Viscosities are usually measured at concentrations of up to 1 g/100 ml of solvent by determining the flow-time of a certain volume of solution through a capillary of fixed length. 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, for example at 30.0 ± 0.1°C.

Three typical viscometers are shown in Fig. 2.9. Of the three, the Ubbelohde-type is more convenient to use in that it is not necessary to have exact volumes of solution to obtain reproducible results. Furthermore, additional solvent can be added (assuming that the reservoir is large enough); thus, the solution concentration can be reduced without having to empty and refill the viscometer.

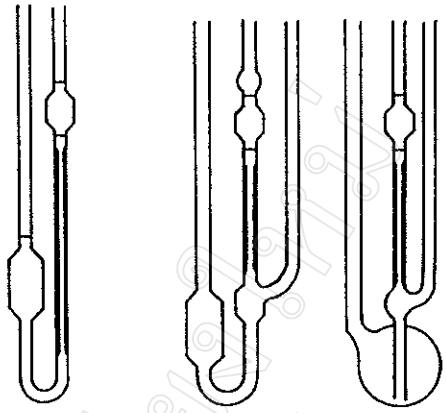

Fig. 2.9 Diagrams of (a) an Ostwald U-tube viscometer, (b) a Ubbelohde suspended-level viscometer, and (c) a modified Ubbelohde viscometer with a larger reservoir bulb for dilutions.

Dilute-solution viscosity can be expressed in several ways, as in Table 2.2 :

Table 2.2 Dilute-solution viscosity terms currently in use.

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

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 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:

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

where $\bar{M}_v$ is the viscosity-average molecular weight of the polymer and is defined as:

$$\bar{M}_v = \left(\frac{\sum_{i=1}^{\infty} N_i M_i^{1+a}}{\sum_{i=1}^{\infty} N_i M_i} \right)^{\frac{1}{a}}$$

The constants K and a are the intercept and slope, respectively, of a plot of log $[\eta]$ versus log $\bar{M}_v$ (or log $\bar{M}_n$ of a series of fractionated polymer samples). Such plots are linear (except at low molecular weights) for linear polymers, thus:

$$\log [\eta] = \log K + a \log \bar{M}_v$$

In addition, K and a are constants for a given polymer-solvent pair at a given temperature and are usually obtained from the "Polymer Handbook". Unfortunately, K and a for the specialty terpolymers prepared in this project are not available in the "Polymer Handbook". Consequently, their molecular weights cannot be calculated. However, their $[\eta]$ values still provide useful indications as to the level of their molecular weight.

In this research project, intrinsic viscosities were measured in chloroform as solvent at 30°C with a Schott-Gerate Ubbelohde-type viscometer (type No. 532 00, capillary No. 0) in conjunction with the Schott-Gerate AVS 300 Automatic Viscosity Measuring System.

2.2.2.7 Mechanical (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 (tensile) modulus were determined and the results correlated as far as possible with the fibre's chemical microstructure and matrix morphology.

In this research, the mechanical (tensile) tests were performed on a Lloyds LRX+ Universal Testing Machine, as illustrated in Fig 2.10 Fibre samples were cut into 35 cm lengths and their diameters measured accurately (± 0.001 mm) with a digital micrometer. All tests were carried out with the fibre sample wound once around each of two bollard grips, as shown in Fig. 2.11.

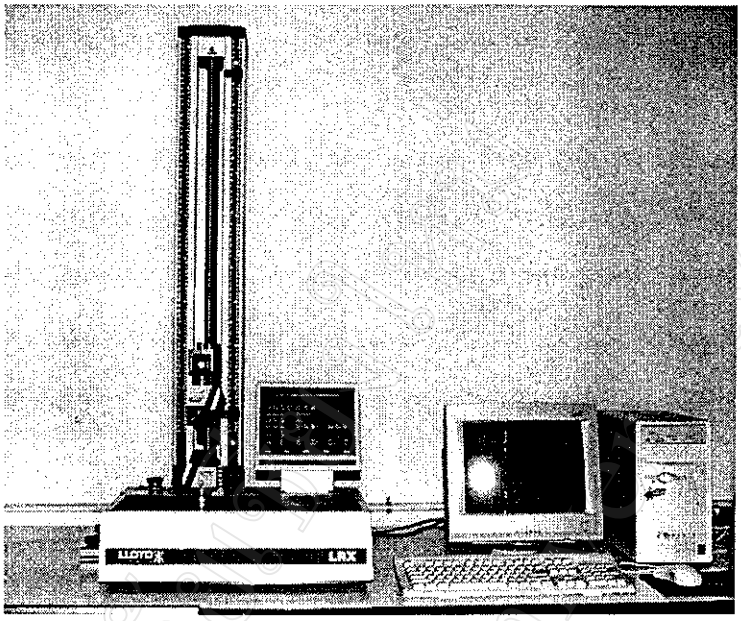

Fig. 2.10 Photograph of the Lloyds LRX+ Universal Testing Machine used for fibre tensile testing.

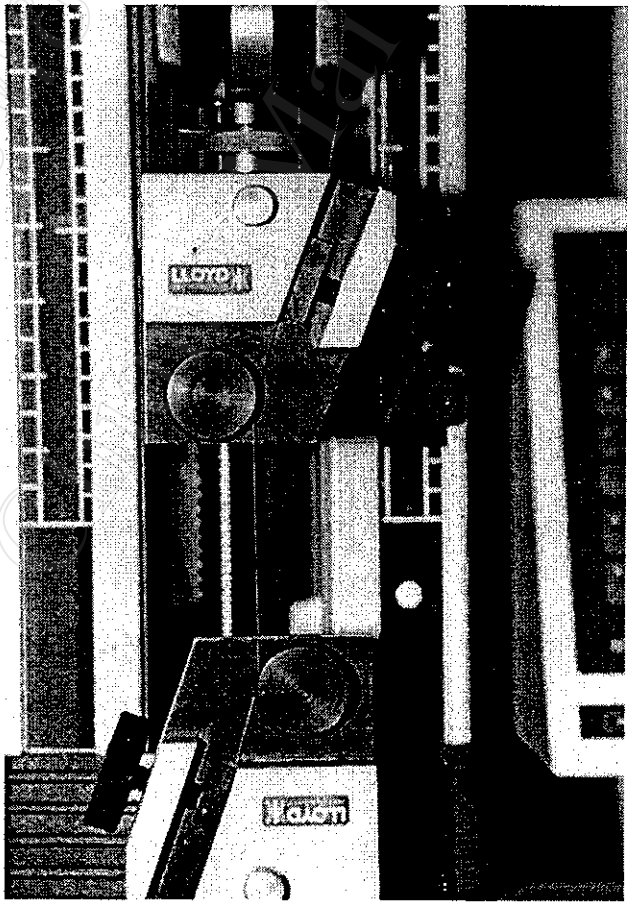

Fig. 2.11 Close-up photograph of the bollard grips showing the fibre sample mounted in position at the start of a test.

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 fibre samples were as follows:

FIBRE TENSILE TEST CONDITIONS		
load cell	=	100 N
sample grips	=	bollard-type
initial gauge length	=	40 mm
crosshead speed	=	20 mm/min
temperature	=	ambient (20-25°C)
humidity	=	ambient (50-70% rh)

Bollard-type grips, as shown in Fig. 2.11, were preferred to vice-action grips (manual tightening) because the latter tended to pinch the samples, especially the softer as-spun fibres, causing the applied stress to be concentrated at the grips. Hence, a fibre sample tested using vice-action grips would fail consistently at one of the two grips. Since the sample's cross-sectional area was distorted by lateral compression in each grip, the results were widely variable and unreliable. In contrast, the main advantage of bollard-type grips is that the tensile stress is distributed more uniformly around the bollards rather than concentrated at the points of contact. Consequently, the fibre samples failed within the gauge length. This was considered to be a mode of failure more representative of the fibre's true properties and was the main criterion used in choosing bollard-type rather than vice-action grips.

However, bollard grips too have their disadvantages, the main one being the uncertainty in the "true" gauge length. This arises from the fact that the fibre can stretch to a certain extent around the bollard's circumference. Consequently, since the gauge length is nominally 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.