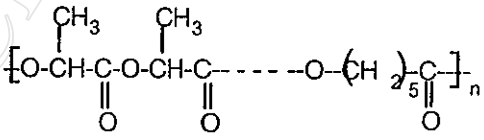
CHAPTER 6

X-RAY DIFFRACTION MEASUREMENTS ON THE P(LC) COPOLYMER FIBRES

A CASE STUDY

This final results chapter of this thesis features a special piece of work which was carried out during a 6 months period of specialist training abroad. The main objective was to expand the scope of the work in some way which could not be done here in Chiang Mai and, at the same time, open up an area for potential research collaboration with the overseas institution.

The area chosen for this case study was X-ray diffraction (XRD), a technique mentioned previously as being of great importance in the study of fibre morphology, particularly crystallinity and crystallite orientation. The work described here was carried out during the 6-month period from July-December 2001 at the Polymer Science Center, University of Reading, UK, under the co-direction of Professor G.R. Mitchell. The material chosen as the subject of this study was the poly(L-lactide-co-ε-caprolactone) 80:20 random copolymer, hereafter referred to simply as the P(LC) copolymer.



$$\left[\text{O-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-O-}\overset{\text{CH}_3}{\overset{|}{\text{CH}}}\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-}\,\text{-}\,\text{-}\,\text{-}\,\text{-O-}(\text{CH}_2)_5\text{-}\underset{\text{O}}{\underset{\|}{\text{C}}}\text{-}\right]_n$$

poly(L-lactide-co-ε-caprolactone) 80:20

P(LL-co-CL) 80:20

Abbreviation used hereafter = P(LC)

6.1 P(LC) Random Copolymer – Fibre Processing

The synthesis and characterization of the P(LC) 80:20 random copolymer was described in Chapter 4. Its actual composition, as determined by ^{1}H-NMR, was L:C = 79:21 (mol%). It was melt-spun into monofilament fibres (at 145-150°C) from pre-formed rods (prepared at 115°C) via a similar procedure to that described for the P(LCG) random terpolymers in Chapter 5. The DSC thermogram of the P(LC) as-spun fibre is shown in Fig. 6.1 and confirms that the as-spun fibre is largely amorphous, as would be expected from the earlier studies of the PL homopolymer.

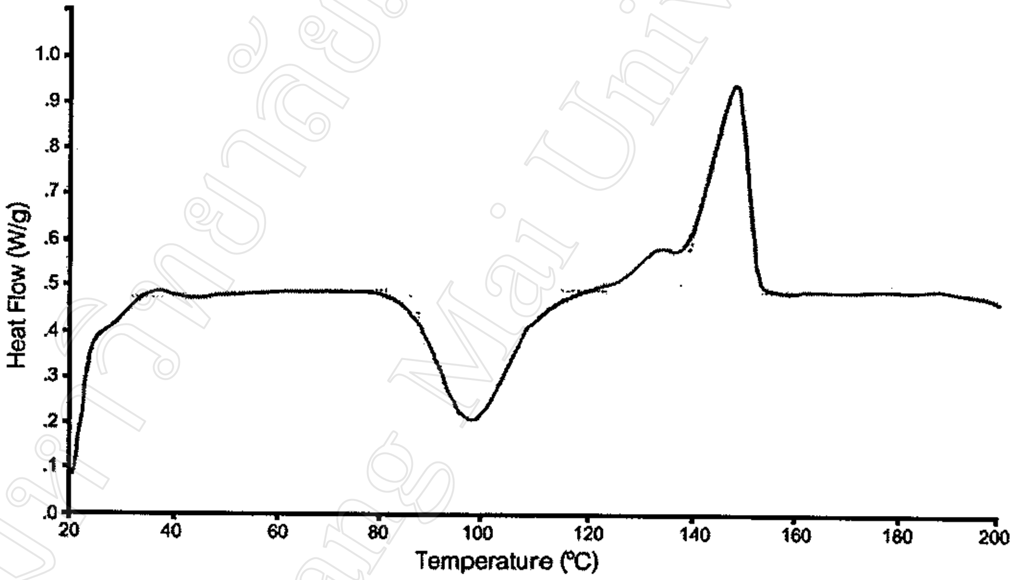


Fig. 6.1 DSC thermogram of the as-spun P(LC) random copolymer fibre.

The as-spun P(LC) fibres were then hot drawn and/or annealed in order to induce an oriented semi-crystalline morphology, thereby improving their tensile properties. Annealing alone at a temperature above T_g was again able to induce crystallisation, as shown in the DSC curves in Fig. 6.2, but because the crystallites were unoriented, the annealed fibres were still weak. In order to produce fibres of reasonable tensile strength, a combination of hot-drawing and annealing was again required. This effect is clearly illustrated in Fig. 6.3 which compares the stress-extension curves for a series of fibres which were first hot-drawn at 65°C to various (off-line) draw ratios (DR) before being annealed at 65°C for 10 hrs. The derived mechanical property values from these stress-extension curves are given in Table 6.1.

Since this series of P(LC) fibres in Fig. 6.3 at various draw ratios exhibited clear and distinct differences in their stress-extension curves, they were considered to be suitable subjects for an X-ray diffraction (XRD) study. The main objective here was to try to correlate the XRD data, relating to fibre morphology, to the corresponding changes in mechanical properties. This XRD work is now described.

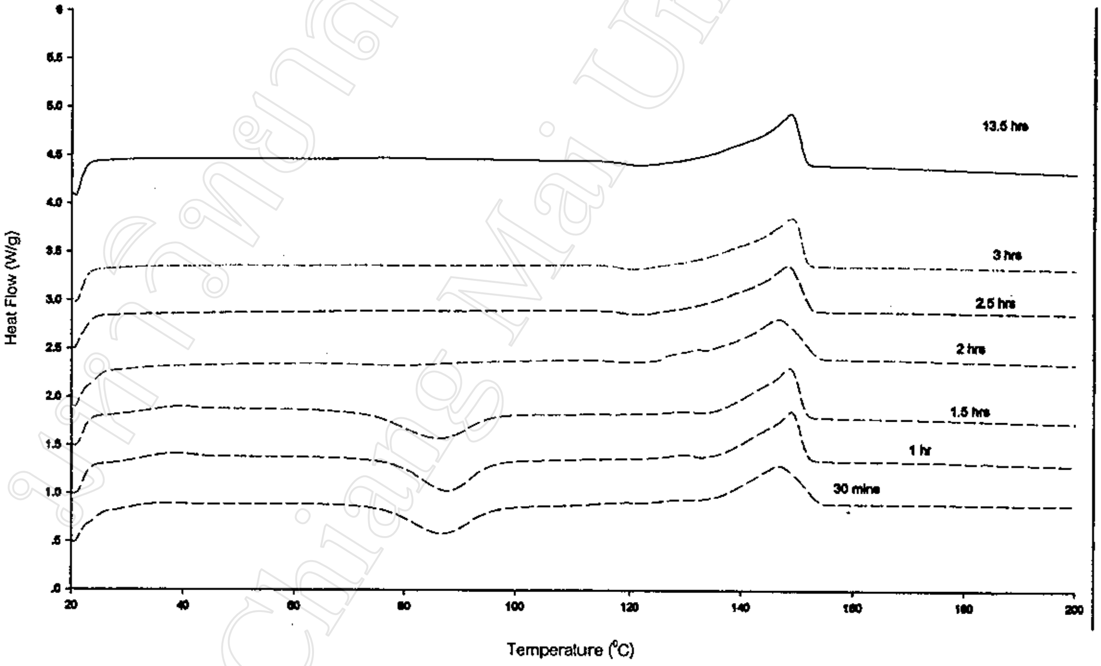


Fig. 6.2 DSC thermograms of the as-spun P(LC) fibres annealed at 60°C for different periods of time.

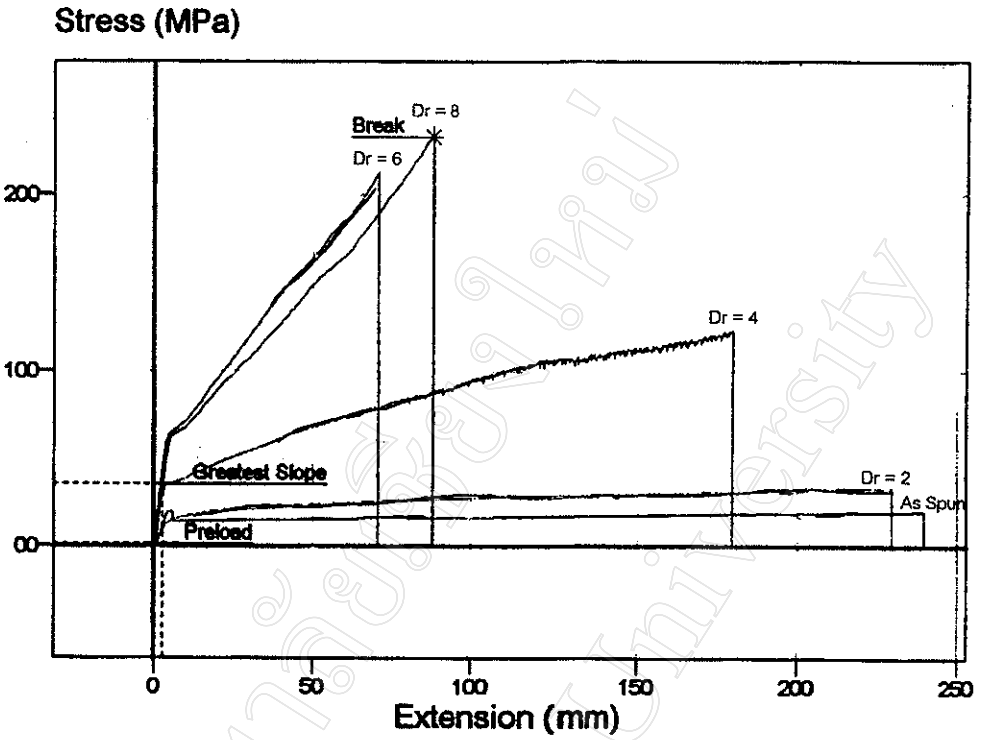


Fig. 6.3 Comparison of examples of the stress-extension curves for a series of P(LC) fibres hot-drawn at 65°C to various draw ratios (DR) before being annealed at 65°C for 10 hours.

Table 6.1 Mechanical property values of the series of P(LC) fibres.

P(LC) Fibre	Young's Modulus (Mpa)	Stress at Break (Mpa)	Strian at Break (%)
As-spun	229.9	20.3	619.3
Draw ratio = 2	192.6	34.4	607.5
Draw ratio = 4	383.3	89.3	504.4
Draw ratio = 6	725.7	220.7	188.4
Draw ratio = 8	599.1	203.5	221.7

Values given are the averages of 5 test results.

6.2 X-Ray Diffraction

6.2.1 Introduction

The extent of sample crystallinity can influence the behaviour of a polymer sample greatly. A particularly effective way of examining partially crystalline polymers is by X-ray diffraction (XRD). When X-rays are focussed on a semi-crystalline polymer sample, two types of scattering occur. One type gives sharp peaks due to scattering from the crystalline regions and is superimposed upon the second type that gives broad diffuse scattering due to the amorphous regions. If the crystallites in the specimen are unoriented, XRD obtained by the Debye-Scherrer technique produces a series of concentric rings from scattering by the crystal planes superimposed on a diffuse background of coherent scattering, as shown in Fig. 6.4 As the degree of crystallinity increases, the rings become more sharply defined and, as the crystallites become oriented (e.g. by drawing), the circles give way to a pattern of arcs and spots more nearly resembling the diffraction patterns of low molecular weight crystalline compounds. 6.5 shows wide-angle X-ray scattering (WAXS) patterns produced on photographic plates for a filament of poly(ethylene terephthalate). These patterns show the changes in morphology at each stage of the fibre's processing.

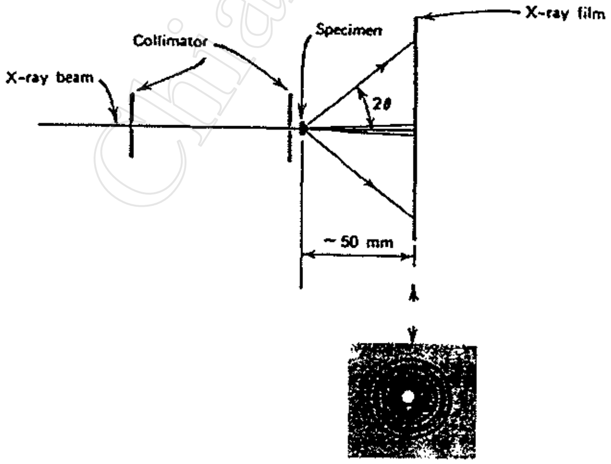
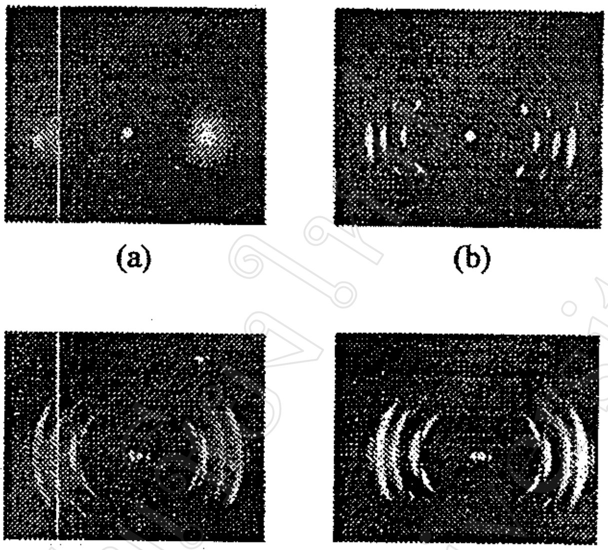


Fig. 6.4 Schematic diagram for X-ray diffraction from a semi-crystalline polymer.



(a) (b)

(c) (d)

Fig. 6.5 Wide angle X-ray scattering (WAXS) patterns of a drawn poly(ethylene terlephthalate) fibre subjected to a series of processing operations [65].

(a) drawn at room temperature to a draw ratio = 5, unannealed

(b) draw ratio = 5, after annealing at 260°C

(c) further drawing at room temperature to a draw ratio = 20, no further annealing

(d) draw ratio = 20, after further annealing at 260°C

The X-ray diffraction photographs in Fig.6.5 show how increasing orientation of the crystallites induced by a mechanical drawing process leads to arcing of the sharp diffraction rings and eventually the establishment of the familiar fibre pattern. This profound change in the pattern provides the basis for accurately quantifying the degree of orientation. However, it is also useful in another respect, in that it is much more straightforward to determine the crystal structure from an oriented fibre pattern than it is from concentric rings characteristic of the unoriented material. Indeed, it is normal practice for crystallographers to orient a crystalline polymer as the first stage in determining its unit cell. So whether the focus of interest is on the structure of the crystallites in the semi-crystalline polymer or on their preferred orientation, which itself can significantly influence mechanical properties, wide angle X-ray diffraction (WAXD) is a broadly applicable technique.

In the field of non-crystalline polymers, however, the situation is markedly different. They are two reasons for this. First, diffraction patterns from non-crystalline substances such as glassy polymers are nothing like as sharply defined as they are from crystalline materials, and the arching which indicates orientation is never as pronounced as in the crystalline case and can be difficult to measure accurately. Secondly, other methods such as birefringence, IR and NMR spectroscopy are relatively more attractive for single-phase polymers where the problems associated with separating the contributions from the two phases of a semi-crystalline material do not arise. In addition, the transparency of many polymer glasses is, of course, an asset in birefringence studies.

X-ray diffraction is also a primary technique for to determining the degree of crystallinity in polymers. The reasons for the lack of structural regularity or crystallinity in synthetic polymers are many. In general, polymers based on atactic chains are 'amorphous', as are materials which have been heavily irradiated with electrons or γ rays. Molten and rapidly quenched polymer systems are also highly disordered. Crystalline polymers often have relatively low degrees of crystallinity and hence contain large proportions of 'non-crystalline' material, as may be seen from their X-ray scattering patterns. Synthetic polymers almost never occur as single crystals. The diffraction pattern from a polymer is almost always either a 'powder' pattern (polycrystalline) or a 'fibre' pattern (oriented polycrystalline).

6.2.2. Description of Orientation [67]

Preferred orientation can occur because, even though a polymeric material may be isotropic in bulk, it will be anisotropic on a sufficiently microscopic or submicroscopic scale. The anisotropy of small orienting units of structure communicates itself to the bulk material as they become mutually aligned. This precept is the basis of the aggregate model discussed by Ward [66]. The first step in describing the development of orientation is to assign unique axes or 'directors' to the orienting units. If the units are crystals, then the directors are appropriately the crystallographic axes, or if the orientation process is being measured by diffraction methods, then normals to the diffracting planes may sometimes be used. With polymers, the direction of the chain axis is of major interest and the orientation distribution for this director with respect to some external axis such as the draw direction is often all the information that is needed. This is very much the case with non-crystalline polymers where, even though each molecule may not have cylindrical symmetry around its axis, there is normally no tendency for mutual alignment on drawing of any directors other than those representing the molecular axes. Hence, in focussing attention on a single director, the assumption of cylindrical symmetry of each orienting unit is implied. This assumption appears to be reasonable for non-crystalline polymers.

Polymers which have been subjected to an external field, whether stress, flow, electric or magnetic, may show a preferred alignment of structural units either about, or normal to, the applied field direction. The quality of alignment achieved is generally not perfect in relation to the field axis. When the probability distribution of unit orientations is symmetrical about any axis, then it can be referred to that axis without the necessity for an external reference frame. Such an axis is known as the director. We shall restrict ourselves initially to situations where this grouping occurs symmetrically about only one axis, in other words a uniaxial system.

It is possible to describe a uniaxial orientation distribution as an angular distribution of the units in polar coordinates (γ, α) where the length γ is proportional to the number of units at angle α. Fig. 6.6 shows such a distribution plot representing the probability of angular distribution $D(\alpha)$. If there were no preferred orientation of the units, the distribution surface would be spherical. The shape of such a distribution surface may be described in a mathematical way. It can be analyzed into spherical harmonics whose functions are of the polar coordinate angles, referred to as the director axis. The first four components, abbreviated as P_0, P_2, P_4, P_6 are defined below and drawn in Fig. 6.7

$$P_0 = 1$$
$$P_2 = (3\cos^2\alpha - 1)/2$$
$$P_4 = (35\cos^4\alpha - 30\cos^2\alpha + 3)/8$$
$$P_6 = (231\cos^6\alpha - 315\cos^4\alpha + 105\cos^2\alpha - 5)/16 \qquad (6.1)$$

The harmonic functions are actually fact the even numbers of a Legendre polynomial series with appropriate amplitudes or coefficients, written as $<P_{2n}(\cos\alpha)>$, which reconstitute the shape of the three-dimensional orientational probability distribution, $D(\alpha)$ where:

$$D(\alpha) \quad = \sum_{n=0}^{\alpha}(4n+1)\left\langle P_{2n}(\cos\alpha)\right\rangle P_{2n}(\cos\alpha) \qquad (6.2)$$

The amplitude of the nth order harmonic is determined as:

$$\left\langle P_{2n}(\cos\alpha)\right\rangle \quad = \int_{0}^{\pi/2} D(\alpha)P_{2n}(\cos\alpha)\sin\alpha\, d\alpha \qquad (6.3)$$

Normally, the amplitudes of the harmonics decrease with increasing order, such that the higher order terms ($n>4$)will be negligible for a lower orientation. As it is the form of the orientation distribution which is of interest rather than the total number of orienting units which make it up, the function $D(\alpha)$ is assumed to integrate to unity over all orientations. If this assumption is not implicit, as in the case of a distribution function such as $I(\alpha)$ which describes the variation of scattered X-ray intensity with orientation at the given scattering angle, then the relation for $<P_{2n}(\cos\alpha)>$ must be calculated, as :

$$\langle P_{2n}(\cos\alpha)\rangle = \frac{\int_{0}^{\frac{\pi}{2}} I(\alpha)P_{2n}(\cos\alpha)\sin\alpha dx}{\int_{0}^{\frac{\pi}{2}} I(\alpha)\sin\alpha dx} \tag{6.4}$$

When the scattering X-ray intensity function, $I(\alpha)$, at a particular scattering angle is collected, it can then be used to determine the spherical harmonics amplitude, $<P_{2n}$ $(\cos\alpha)>$, abbreviated to $<P_{2n}>$, where $<P_{2n}>$ gives the orientation parameters.

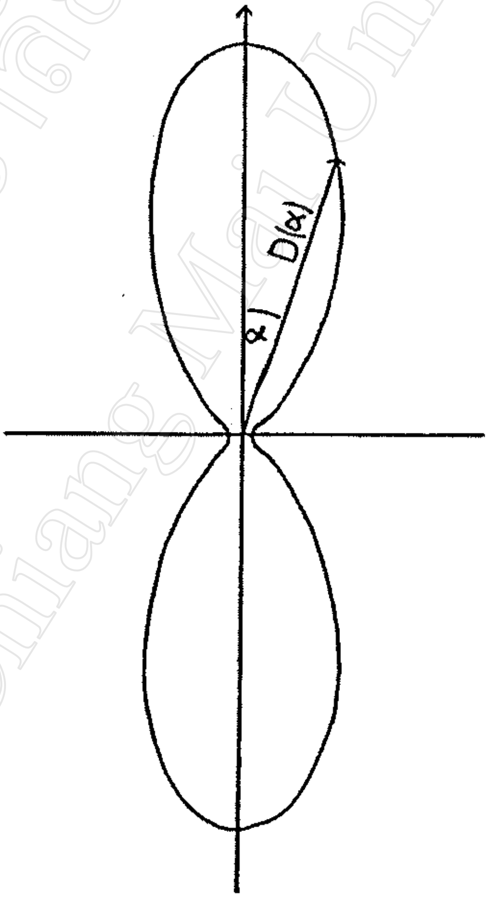


Fig. 6.6 Section through a polar probability plot of a uniaxial orientation distribution [3].

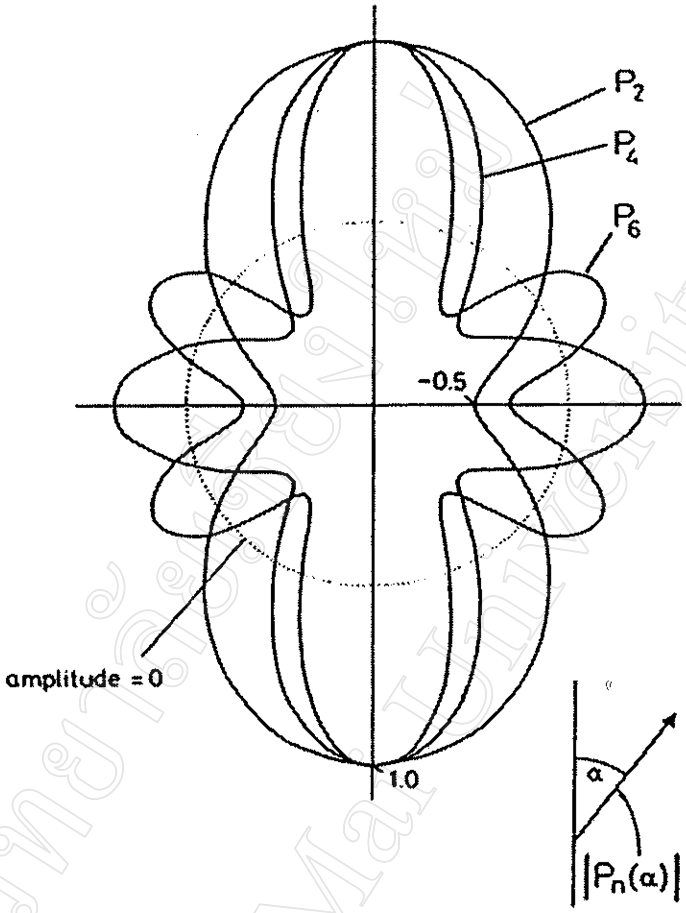


Fig. 6.7 Polar plots of the spherical harmonic functions P_0, P_2, P_4 and P_6 [67].

6.2.3 Experimental Procedure and Diffraction Patterns

In this section, the experimental procedure used to obtain the XRD patterns of the as-spun and processed P(LC) fibres is described. These patterns were then analysed in order to determined each sample's orientation parameters.

Fibre samples were cut into about 2 cm lengths and closely aligned in parallel to cover the 5 mm hole in an aluminum plate, as shown in Fig. 6.8. The plate was then mounted so that the fibers were vertical and perpendicular to the X-ray beam (Cu Kα, 40 kV 40 mA). Using a flat area detector, each sample was exposed to the X-rays for 10 sec. The patterns obtained are shown in Figs. 6.9 (a)(I) - (e)(I). As seen from the patterns, arcing of the broad ring for the as-spun fibre occurs on drawing. More interestingly, at a draw ratio (DR) of higher than 4, the pattern develops into sharp spots which reflects further crystallisation with improved orientation.

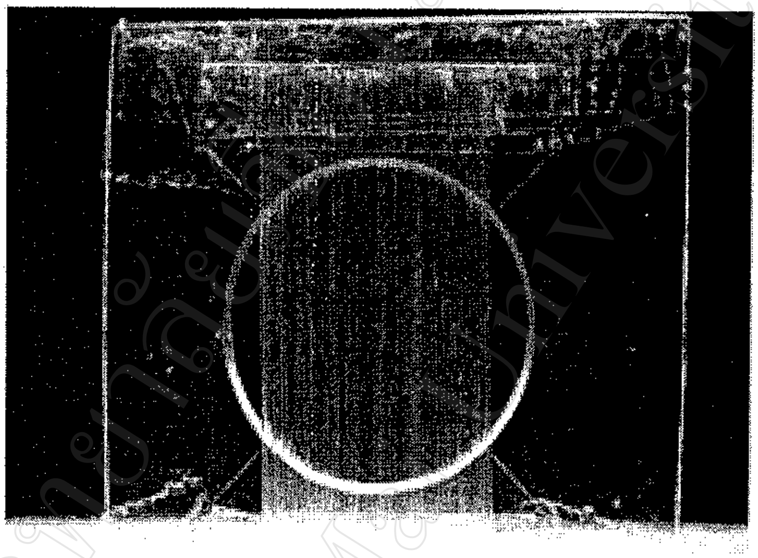


Fig.6.8 P(LC) copolymer fibre sample mounting for X-ray diffraction measurements.

Each of the samples was then tilted towards the X-ray beam by 15° and exposed to the X-rays again for 10 sec. The patterns obtained are shown in Figs. 6.9 (a)(II) -(e)(II). The purpose of doing this was to collect some of the scattering at higher angles along the meridian that was missed previously due to flat-detector technique used. These patterns therefore show other views of the diffraction. As seen in these Figures, there is indeed more scattering in the direction of the meridian although its appears to be quite diffuse along the direction perpendicular to the meridian. This diffuse scattering was eventually shown to be located in between two peaks when the fibre was drawn to higher DR. To obtain orientation information quantitatively, it is necessary to collect a complete set of data in a 2-D section of reciprocal space. To achieve this, data collection was performed using a specially designed piece equipment, a 3-circle X-ray diffractometer, as described in the following section.

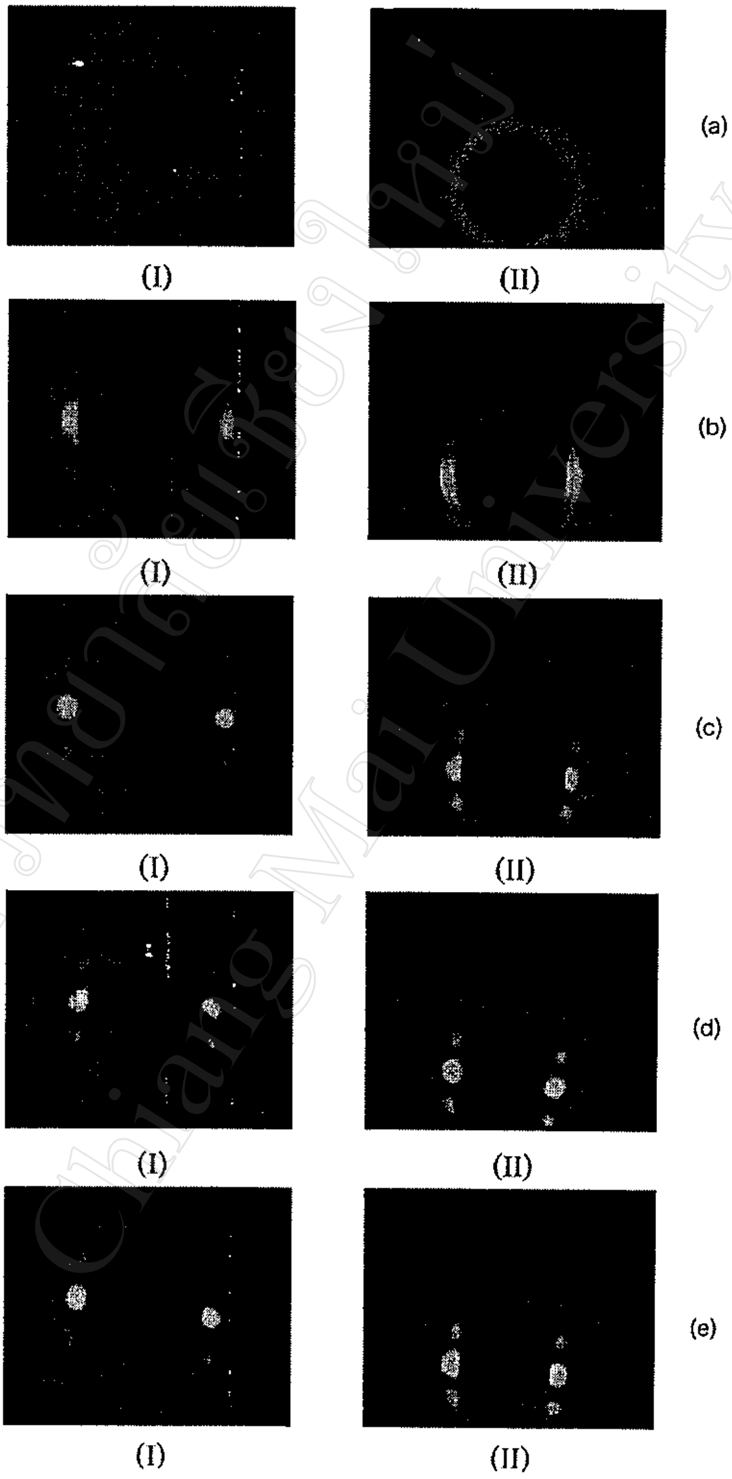


Fig. 6.9 X-ray scattering patterns of the P(LC) copolymer fibres:

(a) as-spun, (b) DR = 2, (c) DR = 4, (d) DR = 6, (e) DR = 8

(I) sample perpendicular to the X-ray beam

(II) sample tilted 15° towards the X-ray beam

6.2.4 Molecular Orientation Parameters

For quantitatively measurements of their molecular orientation parameters, X-ray scattering data for the P(LC) copolymer fibres were collected using a 3-circle X-ray diffractometer developed at Reading University in the UK. The diffractometer is a symmetrical transmission X-ray diffractometer equipped with an incident beam monochromator, pin-hole collimation and step-scanning facilities, as shown in Fig. 6.10 (a). In order to examine samples with a preferred molecular alignment, it is necessary to rotate the sample in its plane, as shown in Fig.6.10 (b). The inclusion of such a rotary stage in a transmission arrangement is relatively straightforward. For these experiments, it was imperative to utilize a symmetrical arrangement (as shown) in order to record an undistorted map of the reciprocal space. The latter restriction precludes the use of film or planar electronic detector-based methods for anything more than a qualitative study of an aligned polymer if the angular range of 2θ exceeds 30°. The instrument operates with a Cu targeted tube with an incident beam graphite monochromator. The collimat or produces a beam at the sample surface of about 1 mm in diameter and with a wavelength of 1.54178 Å. A set of cross-slits is used directly in front of the scintillation detector. A vertical slit of 10 mm is used together with a horizontal slit of 1 mm. The X-ray source uses a Hilton Brooks generator operating at 40 kV and 40 mA with a Hilton Brook shutter control.

Each and sample plate was mounted in the 3-circle X-ray diffractometer and complete 2-D diffraction patterns collected by measuring the scattering X-ray intensity function, $I(Q,\alpha)$, on a grid of $0.2<Q<6.0$ Å^{-1} in 0.02 Å^{-1} steps and $0^{\circ}<\alpha<90^{\circ}$ in 5° steps. Here Q is the scattering vector with $|Q|=4\pi\sin\theta/\lambda$, 2θ is the scattering angle and α is the angle between the scattering vector and the fibre axis. All measurements were made at 25 °C. After background subtraction, each 2-D scattering data set was collected for absorption, polarization and multiple scattering and scaled to electron units. This scaled data was then plotted as a series of contour plots, as shown in Fig. 6.11. These contour plots can be regarded as the corresponding intensity data plots of those in Fig. 6.9 (a)(II) - (e)(II). Besides being more accurate due to having used a scintillation detector, the data plots are also undistorted due to the techniques used. Comparison, of the diffraction patterns in Figs. 6.9 (a)(II) - (e)(II) and the intensity plots in Figs. 6.11(a) - (e) shown them to be essentially equivalent.

To be able to calculate the orientation parameters using the previous equation (6.4), we need to collect the intensity data as a function of α angle ($I(\alpha)$) at a particular Q value. To obtain accurately calculated parameters, the $I(\alpha)$ values used need to be those located at strong peak positions in the 2-D scattering pattern. To locate these peak positions, the scattering intensity data along the equatorial and meridianal axes, I (Q), were collected by a step scanning technique as a function of Q ($Q=4\pi\sin\theta/\lambda$, where 2θ is the angle between the incident and scattered beams, and λ is the wavelength of the X-rays) from 0.2 – 0.6 $\AA^{-1}$ in steps of 0.02 $\AA^{-1}$. The data were obtained at 25°C for all of the fibres. After background subtraction, the I(Q) values were plotted against the corresponding Q values, as shown in Figs. 6.12-6.14 for the P(LC) fibres of draw DR = 8 measured along the equatorial, the meridian and for the as-spun fibre respectively. Consistent with the pattern shown in Fig. 6.9 (e)(II), the scattering from the drawn fibre shows a more intense peak at 1.18 $\AA^{-1}$ along the equator and a less intense peak at 2.26 $\AA^{-1}$ along the meridian. These peaks indicate interchain and intrachain orientation correlations [68]. In contrast, the as-spun fibre shows equivalent broad peaks in both directions which belong to the same broad ring of amorphous scattering (see Fig. 6.9(a)(II) for comparison). These broad peaks, which are equivalent in shape in both directions, indicate that the as-spun fibres were unoriented and amorphous in their morphology.

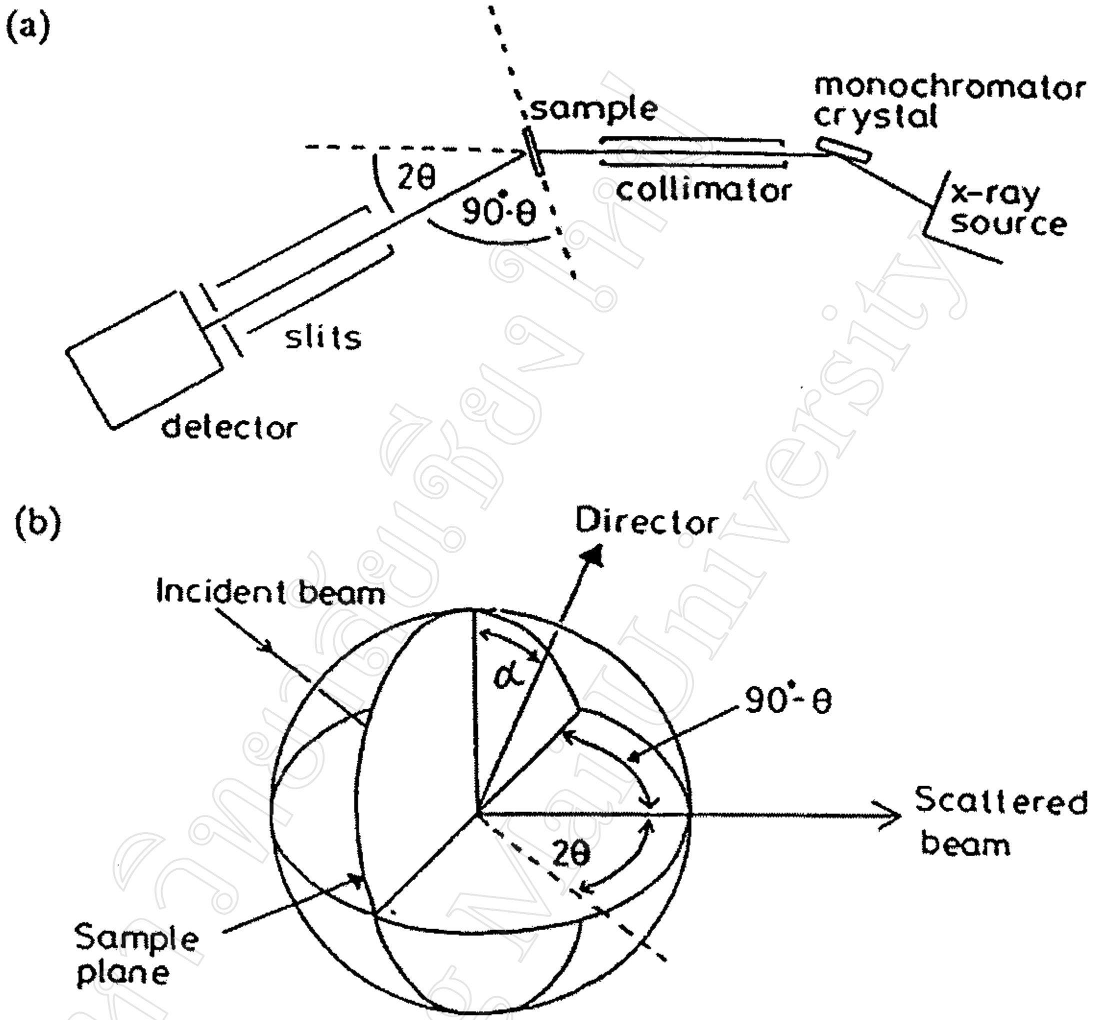


Fig. 6.10 Schematic diagrams of (a) the 3-circle X-ray diffractometer and (b) the scattering geometry, reproduced from Reference [68].

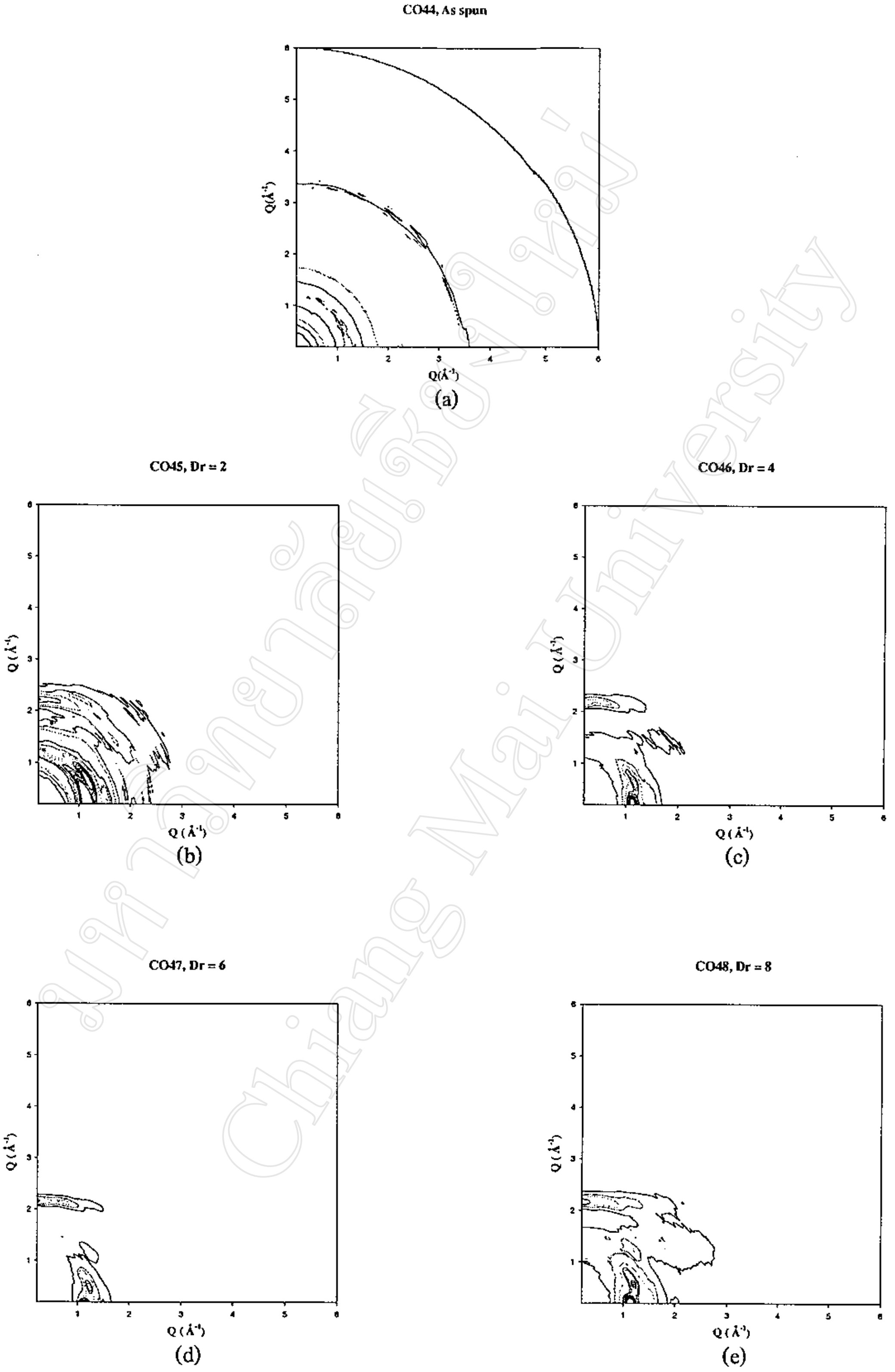


Fig. 6.11 Contour plots of the 2-D diffraction patterns of the P(LC) copolymer fibres: (a) as-spun, (b) DR = Z, (c) DR = 4, (d) DR = 6, (e) DR = 8

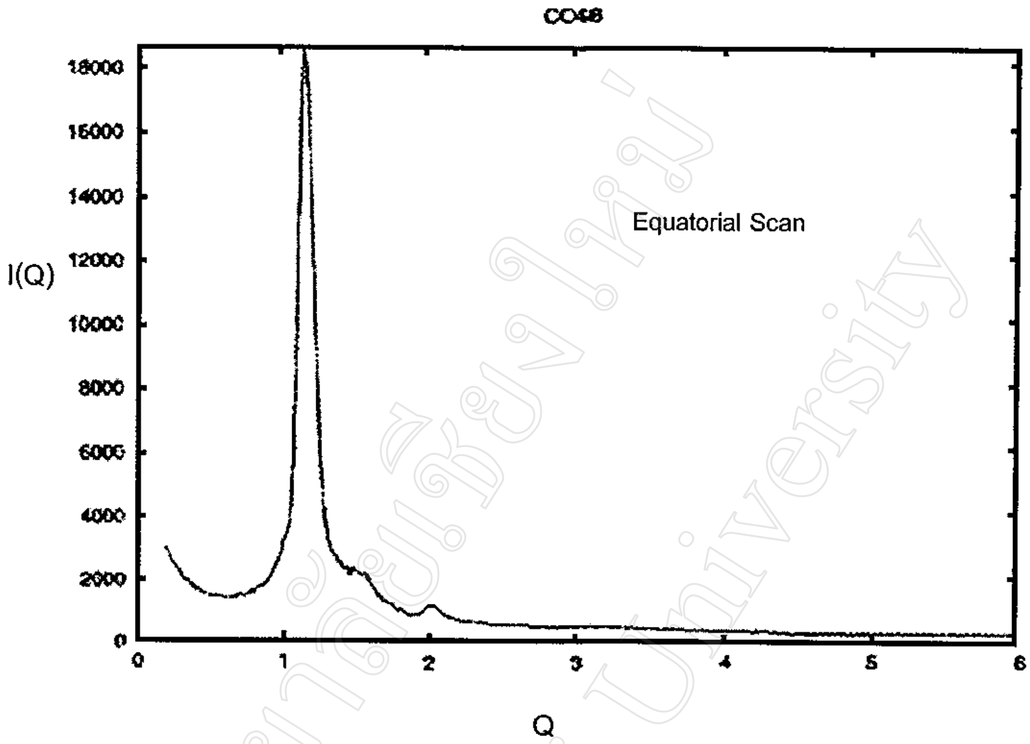


Fig. 6.12 X-ray scattering intensity functions for the P(LC) copolymer fibre of DR=8, as measured along the equatorial.

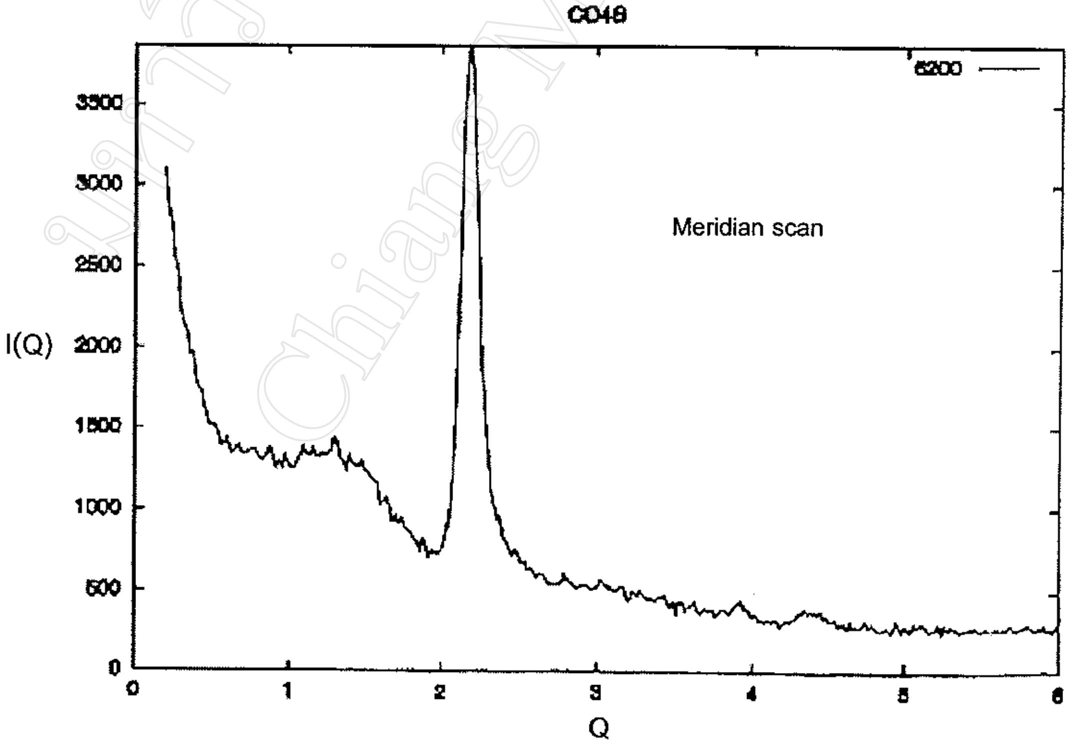


Fig. 6.13 X-ray scattering intensity functions for the P(LC) copolymer fibre of DR=8, as measured along the meridian.

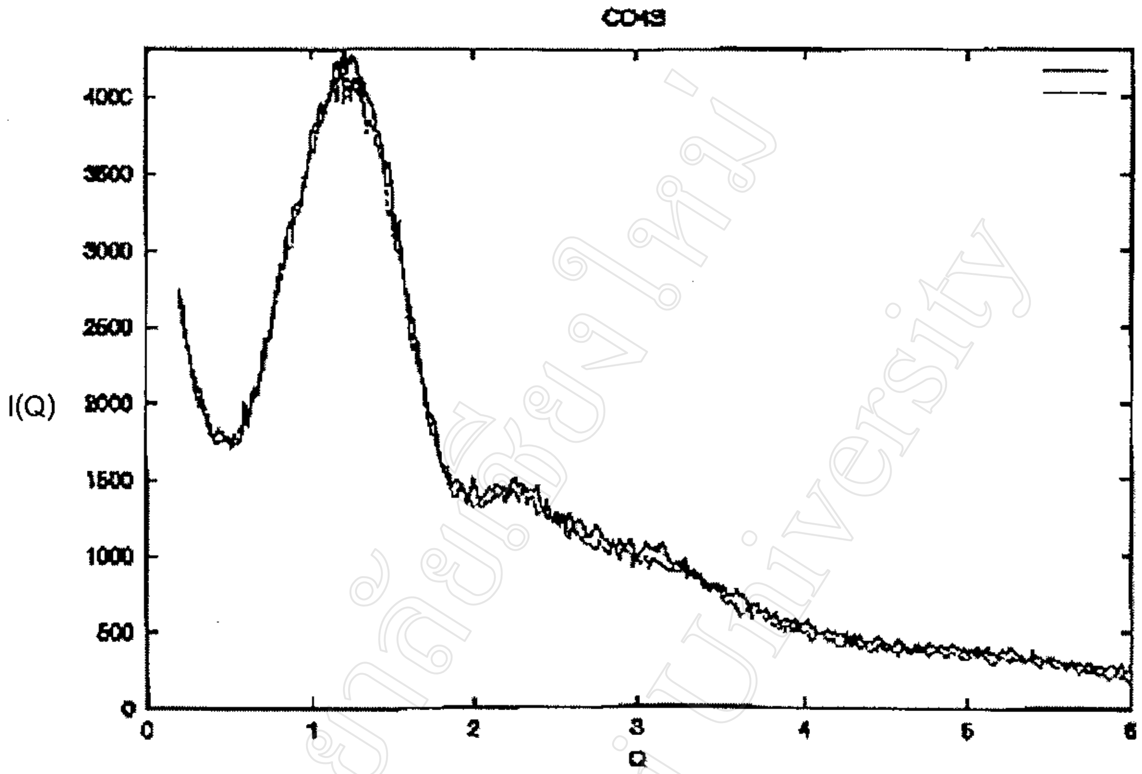


Fig. 6.14 X-ray scattering intensity functions for the as-spun P(LC) copolymer fibre measured along both the equatorial (——)and the meridian (------).

In order to measure the molecular orientation parameters, the scattering intensity function, I(α), at the peak position along the equator at Q = 1.18 Å^{-1} was measured over the whole range of α (0 – 360°). This was done by rotating the sample in steps of 5° and holding the detector at the Q value of 1.18 Å^{-1}. Fig. 6.15 shows a profile of I(α), after being subtracted for the background, for the drawn fibre of DR=8. The scattering data of I(α) were then used to evaluate the spherical harmonic coefficients using equation (6.4). The results of $\langle P_2 \rangle$, $\langle P_4 \rangle$ and $\langle P_6 \rangle$ are shown in Table 6.2. These parameters indicate the overall molecular orientation in the fibres.

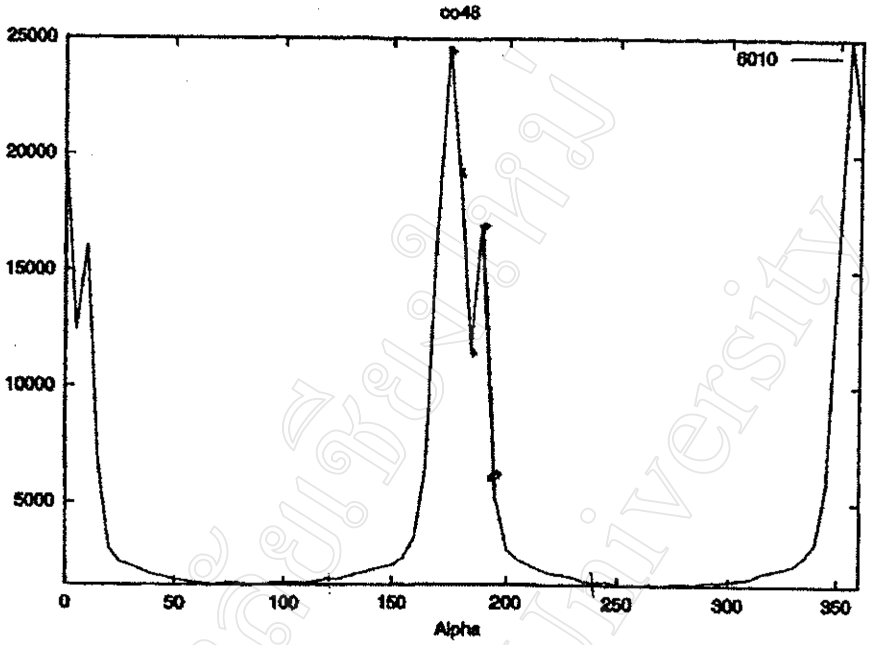


Fig. 6.15 Scattering intensity profile for the P(LC) copolymer fibre of DR=8 at $Q = 1.18$ Å^{-1}.

The $<P_2>$spherical harmonic coefficients in Table 6.2 indicate that the overall molecular orientation increased with draw ratio up to about DR=4. Higher orientation also resulted in higher contributions from the higher order terms $<P_4>$ and $<P_6>$.

These results agree well with previous the tensile testing results in Fig.6.3, i.e. higher orientation resulted in higher strength. However, the drawn fibres of DR=4 showed an average strength in between those for DR=2 of 2 and 6 (Fig. 6.3). It should be mentioned here that mechanical testing was carried out within 1-2 days of processing whereas the X-ray work was not performed at Reading University until after some months has elapsed. It is possible that some additional crystallisation may have occurred during this interim storage period giving rise to the higher orientation parameters from the scattering data analyses. P(LC) random copolymers have been reported [69] to crystallise during storage, especially if they are above their Tg value at room temperature.

Table 6.2 Spherical harmonic coefficients evaluated using I(α) at Q = 1.18 Å^{-1} for the P(LC) copolymer fibres at various draw ratios.

Draw Ratio	Spherical Harmonic Coefficients
(as spun) 1	$<P_2> = 0.298$* $<P_4> = 0.098$* $<P_6> = -0.009$*
2	$<P_2> = 0.806$ $<P_4> = 0.567$ $<P_6> = 0.395$
4	$<P_2> = 0.872$ $<P_4> = 0.700$ $<P_6> = 0.566$
6	$<P_2> = 0.866$ $<P_4> = 0.674$ $<P_6> = 0.493$
8	$<P_2> = 0.886$ $<P_4> = 0.721$ $<P_6> =0.569$

* Values calculated for completion; they are comparatively insignificant from zero.

6.3 Concluding Remarks

This XRD case study has not only expanded the scope of this but also provided a very useful insight into how molecular orientation can be quantitatively determined. The importance of molecular orientation to a fibre's mechanical properties has been emphasized throughout this thesis but mechanical property testing, as such, provides only a qualitative rather than a quantitative measurement. XRD is therefore a powerful analytical tool for understanding at the microscopic level what the molecules of the polymer are doing in response to the various processing operations to which the fibre is subjected.

The X-ray diffraction patterns in this chapter have shown quite clearly how oriented crystallinity can be built into an amorphous fibre matrix though a combination of drawing and annealing steps. Drawing rates and temperatures, draw ratios, and annealing temperatures and times are all influential variables which need to be carefully chosen and precisely controlled. While this work has studied the effects of some of these variables, much more work needs to be done before the optimum conditions for fibre processing can be firmly established.

The X-ray scattering intensity plots and intensity profiles over the complete 0-360° angular range have enabled numerical values to be determined for the spherical harmonic coefficients. When viewed as molecular orientation parameters, these values afford an insight into how molecular orientation, draw ratio and tensile strength can be interrelated. The results obtained here seem to suggest that molecular orientation does not increase continuously with draw ratio but on up to a certain point above which further drawing may have no further advantage as far as the fibre's final properties are concerned. This XRD study has opened up potential avenues of study which are currently being investigated within the Chiang Mai Polymer Research Group.