# CHAPTER 6

# MAIN CONCLUSIONS

The objective of this proposed research project has been to develop a new synthetic monofilament fibre with the appropriate balance of physical and mechanical properties for use as an absorbable surgical suture. Since the fibre's mechanical properties such as tensile strength, modulus, elongation at break, etc., are heavily dependent upon its morphology, it is logical to try to control the morphology as far as possible. The morphology of any linear polymer is governed initially by its microstructure, both chemical and physical. Structural composition, tacticity, monomer sequence distribution, and molecular weight and its distribution all have important influences on other internal structural characteristics such as crystallinity, multiphases and molecular orientation. All of these characteristics enable us to visualize the fibre's morphology. Hence, to control the morphology, it is essential to be able to control all of these characteristics. Therefore, to be able to produce a monofilament fibre suitable for this special end-use, its structural characteristics need to be controlled at each of the various stages of its production, such as molecular design, polymerization conditions, fibre fabrication and further morphology modification.

The results obtained by characterization at each stage of the production have already been discussed in detail. This final chapter brings them all together for clarity and summarizes how optimizing the processing conditions for the final products to be used as absorbable surgical sutures can be achieved.

## 6.1 Molecular design and polymer products

The chemical structure of molecular chain was initially designed to achieve required properties of biodegradability suitable for wound healing. L-lactide (LL), ε-caprolactone (CL) and glycolide (G) were chosen as the monomers to synthesize terpolymers with the composition ratio of 70:25:5 mol %. These monomers have the ability to biodegrade by hydrolysis but with different rates [3]. L-lactide was the major component due to its low cost and crystallizability at higher composition (≥ 70 mol %) [80]. The roles of ε-caprolactone and glycolide were to enhance fibre's flexibility and degradation rate respectively, as mentioned in section 1.7.

Two different molecular architectures, namely a random arrangement of the three monomers and a segmented triblock arrangement along the molecular chain were designed to investigate their microstructure-property relationships. These different microstructures were controlled during synthesis as described in section 2.4. Molecular characterization by IR, $^1$H and $^{13}$C-NMR found that the monomer compositions were LL:CL:G = 76:19:5 mol % for the random and 71:25:4 mol % for the block terpolymer respectively. L-lactide was present more than in the initial monomer feed ratio due to its relatively higher reactivity [24, 41-42].

The monomer sequence lengths were analyzed by $^1$H and $^{13}$C-NMR as shown in Table 2.10. It was found that the block showed a much higher proportion of the CCC triad than that observed for the random, with 60% for the block and 37% for the random. The difference was based on the method used to synthesize the materials. The caprolactone in the block was also restricted to one middle block while it was spread over the entire chain in the random. There also appeared to be a lower average lactidyl sequence length for the block polymer. We attributed this result to transesterification affecting on the lactidyl units. More effect of transesterification was found for the glycidyl units. Even though the sequence length of LL ($l_{LL}$) was lower than expected in the block terpolymer and even lower than that in the random, (see Table 2.10) this estimated value was of the average sequence length involving an average over the whole three blocks. Thermal analysis results obtained by DSC confirmed that the two terpolymers synthesized were of different microstructures (see Table 2.11). The block terpolymer showed higher $T_g$ and $T_m$ with much higher energy of melting. From the results, it was clear that the block terpolymer was much more crystalline. From their different characteristics, fibres made from these two terpolymers would be expected to have different morphologies and, as a result, different mechanical properties.

## 6.2 Fibre characterization

As-spun fibres of the terpolymers obtained by melt-spinning were of different diameters : 0.630-0.770 mm for the random and 0.330-0.370 mm for the block. This is a consequence of the differences in the melt-spinning conditions (see Table 3.1) adjusted to obtain monofilaments with smooth surfaces and constant dimensions. As-spun fibres were largely amorphous with low crystallinity and orientation. However, from the DSC analyses, the as-spun block terpolymer fibre had a much higher level of crystallinity (see section 5.2 and Tables 5.1-5.2). Higher crystallinity occurred originally in the as-spun fibre before the DSC heating treatment and also higher crystallinity found in the material of the block after synthesis (see Table 2.11) indicated that the block terpolymer was more readily crystallize with a higher rate of crystallization (see section 4.3.2 and 4.4). However, crystallinity could be induced by drawing to reach a maximum of about the same level for both terpolymers, as seen in Table 5.8. This is an interesting result. Furthermore, it has been proved that they both crystallized in the same crystal form ($\alpha$-phase) of poly(L-lactide) but with different crystallization rates due to their different chemical microstructures compared to the homopolymer poly(L-lactide) with the random terpolymer being the most affected (see sections 4.3 and 4.4). The block terpolymer crystallized more rapidly than the random, presumably due to the greater regularity of the end blocks. In addition, the SAXS pattern of the as-spun fibre of the block terpolymer indicated no microphase segregation in the melt which might affect the rate of crystallization. Moreover, the random terpolymer displayed more highly developed and better defined crystals, as seen from the SAXS patterns in Fig. 4.29, while the two-phase crystalline/non-crystalline structure was rather ill-defined in the block case. This could be attributed to the range of block lengths present in the polymer chains and the rather disrupting effect of the highly disordered central block containing very short sequences of both lactide and caprolactone. In contrast, the random terpolymer exhibited a rather well-defined two-phase structure which was attributed to the greater extent that non-lactide units could be incorporated into the interfaces of lamellar crystals to provide a smoother crystal face.

## 6.3 Morphology development

The morphology of a polymer fibre is easily modified by drawing and annealing. In this work, a novel approach to WAXD patterns of the terpolymer fibres was employed and was able to confirm that drawing did not induce any changes to the crystal structure other than the level of preferred orientation and degree of crystallinity (see section 5.3). Annealing also induced crystallinity and the crystal size depended upon the annealing temperature. Even though these two techniques were normally used for further modification of the polymer morphology, only drawing was employed to improve the fibre's mechanical properties (see Table 3.2). Annealing induced high crystallinity resulting in brittleness which is undesirable for suture applications.

As-spun fibres of both terpolymers were very weak and showed large extension before break due to their low crystallinity and orientation. After hot-drawing to a high draw ratio, dramatic changes in molecular orientation occurred and also crystallization was induced at different rates depending upon the chain microstructure. As a result, the hot-drawn fibres obtained were much stronger with less extension and higher stiffness. The higher the draw ratio, the stronger the fibre. However, the various drawing parameters were interrelated. For example, the draw rate needed to be high enough to overcome molecular motion due to their thermal energy at high draw temperature. In other words, the draw rate must be high enough to induce high orientation in both the amorphous and crystalline phases. However, too high a draw rate could cause defect creation. These parameters at drawing, such as draw rate, draw temperature and draw ratio needed to be optimized. Moreover, the average molecular weight of the polymer was also an important factor. The higher the molecular weight, the easier it was to draw to a higher draw ratio without tearing.

The strongest fibre was obtained by drawing at 50°C with draw rate of 2150 %/min to a draw ratio of 5.6 for random and drawing at 70°C with draw rate of 5280%/min to a draw ratio of 7.5 for block. As seen in Fig. 5.21, the block terpolymer fibre showed a higher potential for reaching the desired strength. In addition, on the whole tensile properties for the block case were found to be better (see Table 5.8). Its morphology was much different from that of the random due to their different molecular architectures. This was easily seen from the SEM micrographs. From characterization, the strongest fibre of the block terpolymer had larger and thicker crystal lamellae and a higher level of crystallinity than the random. From the SAXS patterns, there appeared to be a lamellar stack arrangement in the block.

By comparison of the structural characteristics of the random and block terpolymer fibres, useful information could be obtained. Important factors necessary for the fibre's strength are crystallinity, crystal size, lamellar stack structure and orientation in both crystalline and amorphous. For a particular chemical structure of a polymer with high enough molecular weight, crystallinity and crystal size can be increased by annealing. In the case of the random, its strength may be increased by fixed-annealing at a suitable temperature. In the case of the block, as mentioned above, higher molecular weight terpolymer needed to facilitate hot-drawing at higher temperature to a higher draw ratio which would result in higher strength of the fibre obtained.

In conclusion, there are many important factors influencing the physical and mechanical properties of the final product. They have to be controlled at various stages of production. Before the production, molecular design needed to control biodegradability by choosing monomers with the appropriate composition and sequencing. The synthesis step is crucial in controlling the polymer product. Important factors are the method of addition of each monomer, the initiator used, and the time and temperature of polymerization. These factors control the yield, monomer composition and sequencing obtained, as well as the molecular weight and its distribution. In melt spinning, the spinnerette diameter, spinning temperature, on-line draw ratio and cooling bath temperature are controlled to obtain an almost amorphous as-spun fibre with a smooth surface and constant dimensions. Controlled development of morphology in the fibre can be achieved by off-line drawing and/or annealing processes. Different properties can be obtained at this final stage. Mechanical properties depend upon various characteristics as mentioned above. Important factors in drawing which need to be carefully controlled are the draw rate, draw temperature and draw ratio. For annealing, temperature and the length of time are important. These factors affect crystallinity, crystal size and orientation in both the crystalline and amorphous regions. More importantly, they are interrelated and therefore need to be optimized for each type of polymer to obtain fibres with properties tailored to meet the requirements of the intended application.

# SUGGESTIONS FOR FURTHER WORK

In continuation of the work described in this thesis, the following suggestions for further work are made as follows.

(1) In the case of the block terpolymer, higher molecular weight is necessary. High molecular weight provides higher possibility to draw to a higher draw ratio without tearing due to their higher chain entanglement.

(2) For the random terpolymer, increased crystallinity and crystal size by fixed-annealing after hot-drawing could improve mechanical strength. However, temperature and the period of time at annealing need to be examined.

(3) It will be very useful if *in situ* experiments can be employed during drawing and/or annealing. All the characteristics of the hot-drawn fibres in this thesis work were obtained after the drawing process. *In situ* study of structural changes during continuous hot-drawing and/or annealing processes is useful for better understanding of crystallization behavior and molecular orientation development during the processes. The information and understanding obtained will enable us to better control processing conditions to reach the optimum for the best quality of fibre.

(4) Finally, it is necessary to investigate the fibre's biodegradability by *in vitro* hydrolysability testing of both terpolymers. Results of testing provide a time scale of fibre's strength which is an important indicator for its application as a suture for a particular part of the body.