CHAPTER 7

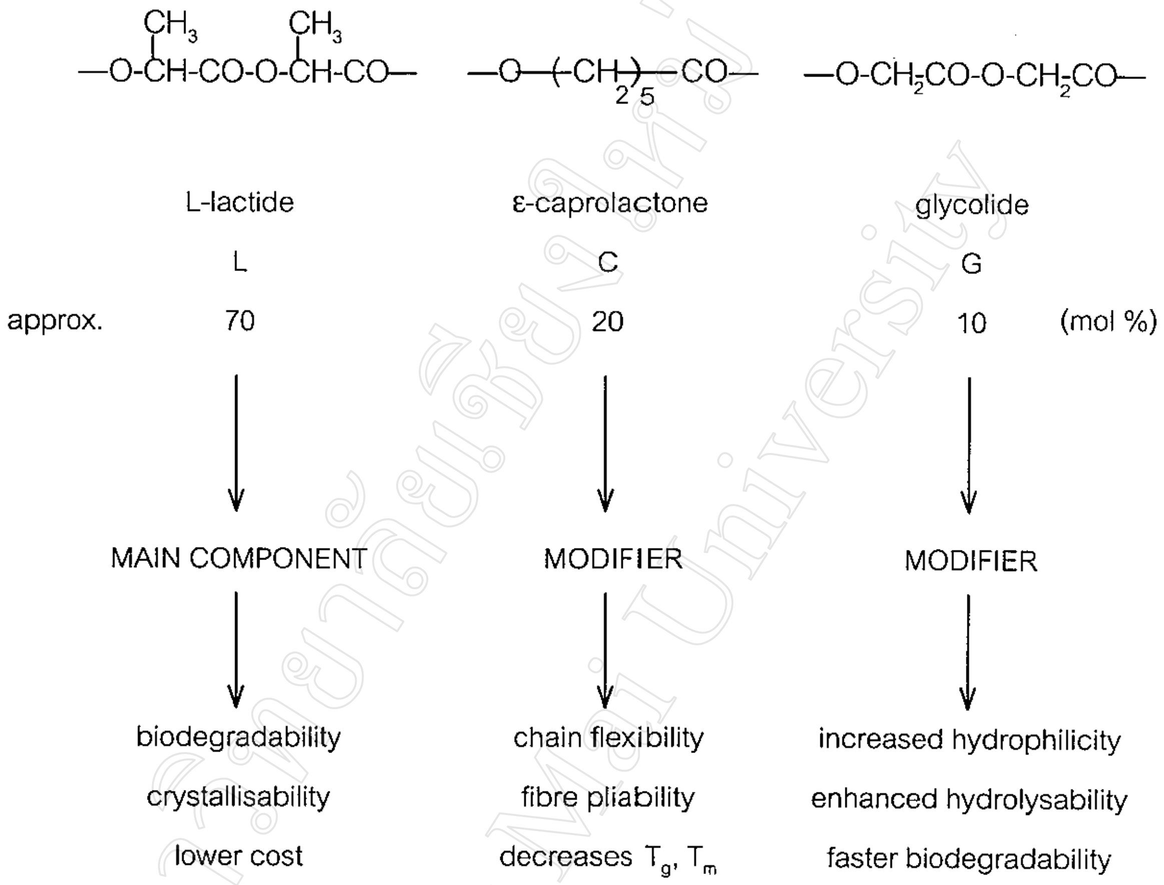
MAIN CONCLUSIONS

Most of the results presented in the preceding Chapters 3-6 have already been discussed along the way. This final chapter of this thesis now aims to bring together the main conclusions and correlate them as far as possible.

7.1 Molecular Design

The first step in the development of speciality polymers, such as those studied in this work, is their molecular design. Generally, the properties required of a speciality polymer are very well defined by the end-use application and the molecular structure of the polymer will be designed to meet these property requirements. In the case of an absorbable surgical suture, a combination of good healing (biodegradability, biocompatibility, minimal tissue reaction) and good handling (pliability, knot security, minimal tissue drag) properties is required.

Although molecular design has not been an integral part of this project as such, the methodology and rationale behind it needs to be understood since it also has an important influence on melt rheology and therefore melt processibility. The P(LCG) terpolymers studied here were composed of the following 3 monomer units :



$-O-CH(CH_3)-CO-O-CH(CH_3)-CO-$ $\quad -O-(CH_2)_5-CO-$ $\quad -O-CH_2CO-O-CH_2CO-$

Thus, each structural unit has its own specific functions which contribute towards meeting the overall property requirements. In addition, the way in which these units are joined together in the terpolymer chain (i.e., the monomer sequencing) is also of vital importance. In this work, both random and segmented triblock chain microstructures have been compared, at the same 70 : 20 : 10 mol % composition, and have been found to have quite different properties, Other microstructural variations such as the monomer sequence distribution, compositional drift and block length, not to mention molecular weight, also affect the properties of the final product.

7.2 Polymer Synthesis

As with the molecular design, the polymer syntheses described in Chapter 4 also drew heavily on previous experience gained within the Chiang Mai Polymer Research Group. The reaction conditions employed here have been shown to give near-quantitative yields with average molecular weights within the so-called "property range" for polyester fibres, The results here confirmed this. The mechanism of the ring-opening polymerisation reaction is believed to be of the "coordination-insertion" type, as shown in the following Scheme 7.1 for the stannous octoate-catalysed, diethylene glycol-initiated polymerisation of L-lactide. Apart from the reaction conditions, the final molecular weight of the polymer is also highly sensitive to monomer purity and the strict exclusion of moisture from the system.

7.3 Polymer Characterisation

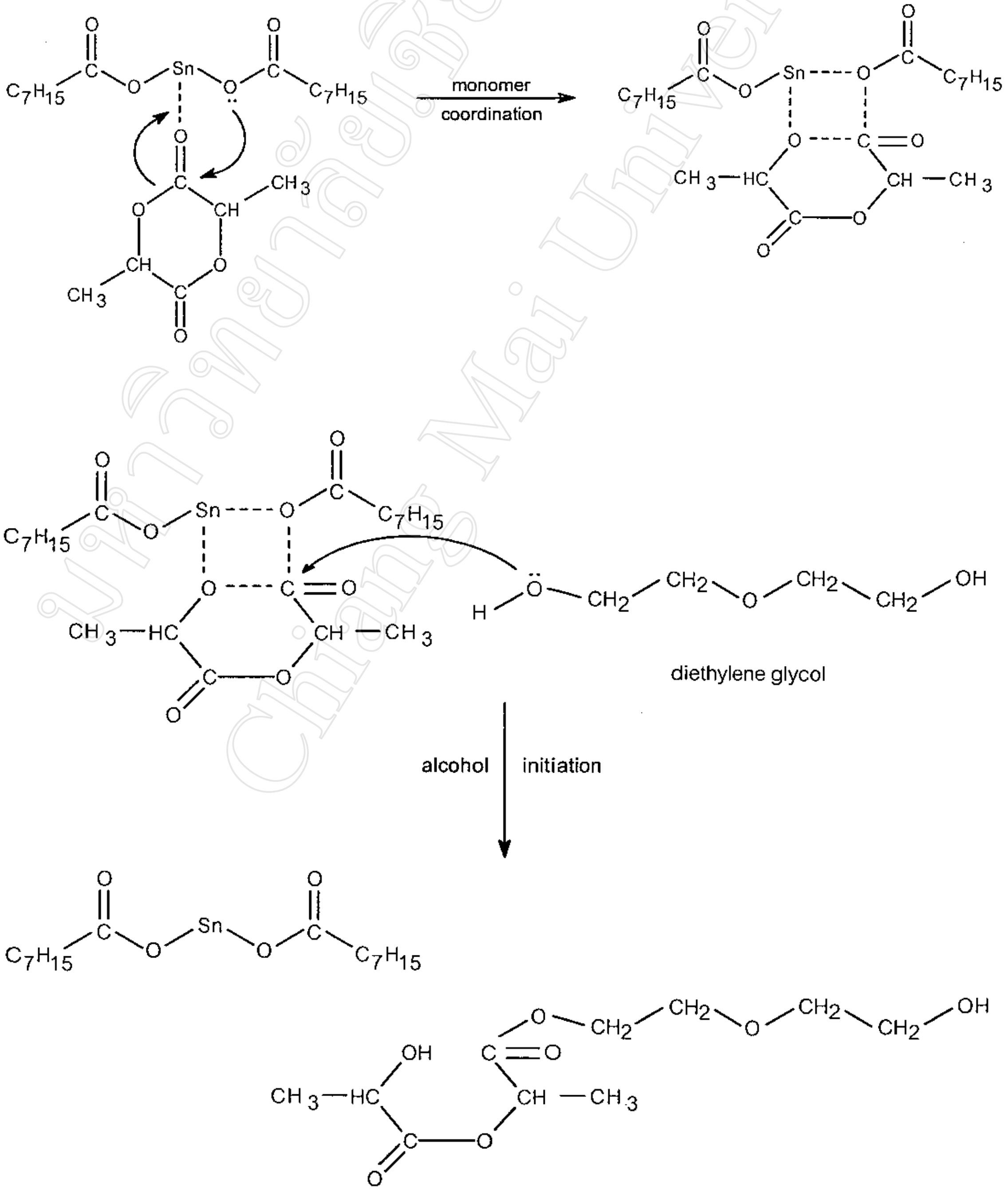
The complete characterisation of a co- or terpolymer in terms of both its chemical and physical microstructure is a challenging task, even allowing for the vast array of modern analytical techniques which are now available. In this work, a combination of techniques were used for the synthesized materials followed by another combination for the as-spun and processed fibres.

For chemical microstructure, ^{1}H-NMR and ^{13}C-NMR formed a powerful combination for co- and terpolymer compositonal analysis and monomer sequencing respectively. The ^{13}C-NMR spectrum, with its much wider ppm range, was able to distinguish between random and blocky structures as a result of the sensitivity of the C=O carbon peak to sequencing effects. Similarly, for physical microstructure, the combination of DSC, XRD and tensile testing was highly effective in monitoring the changes in crystallite formation and orientation brought about during the various stages of fibre processing.

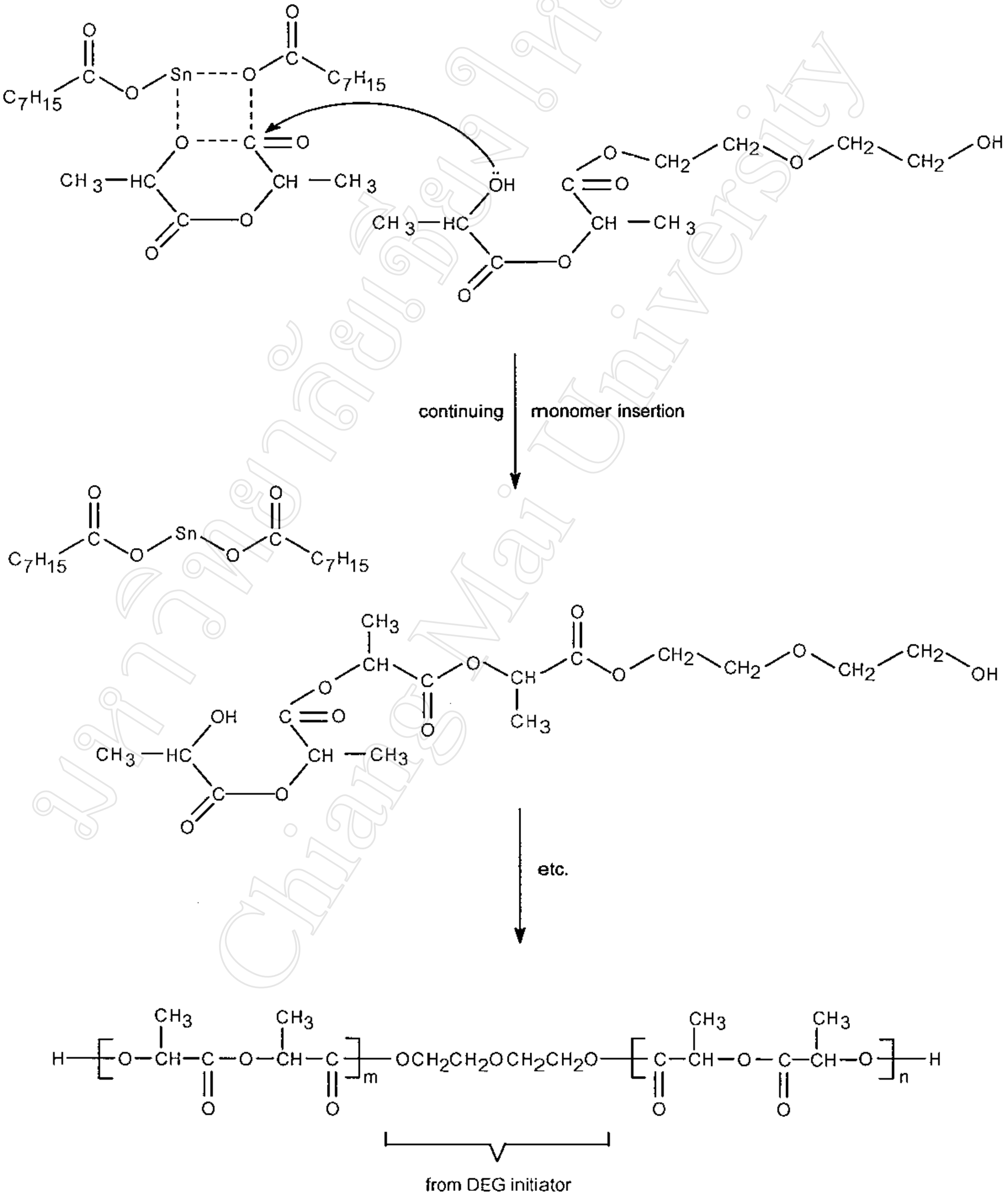
SCHEME 7.1

Coordination-insertion mechanism for the ring-opening polymerization of L-lactide using stannous octoate as catalyst and diethylene glycol as initiator.

INITIATION



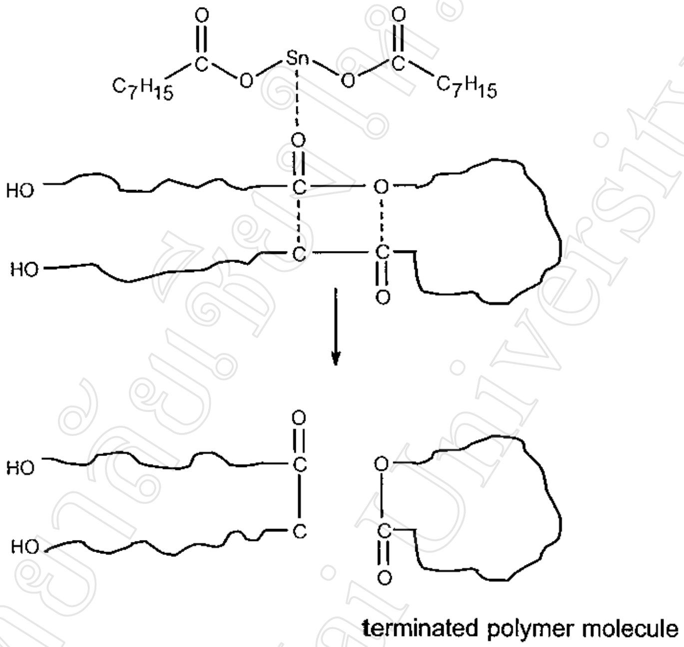
PROPAGATION



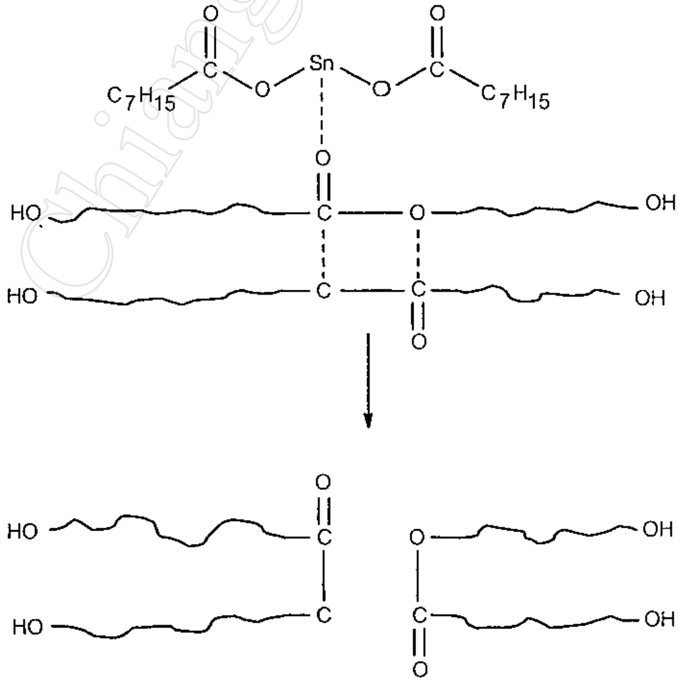
hydroxyl-terminated poly(L-lactide)

TERMINATION

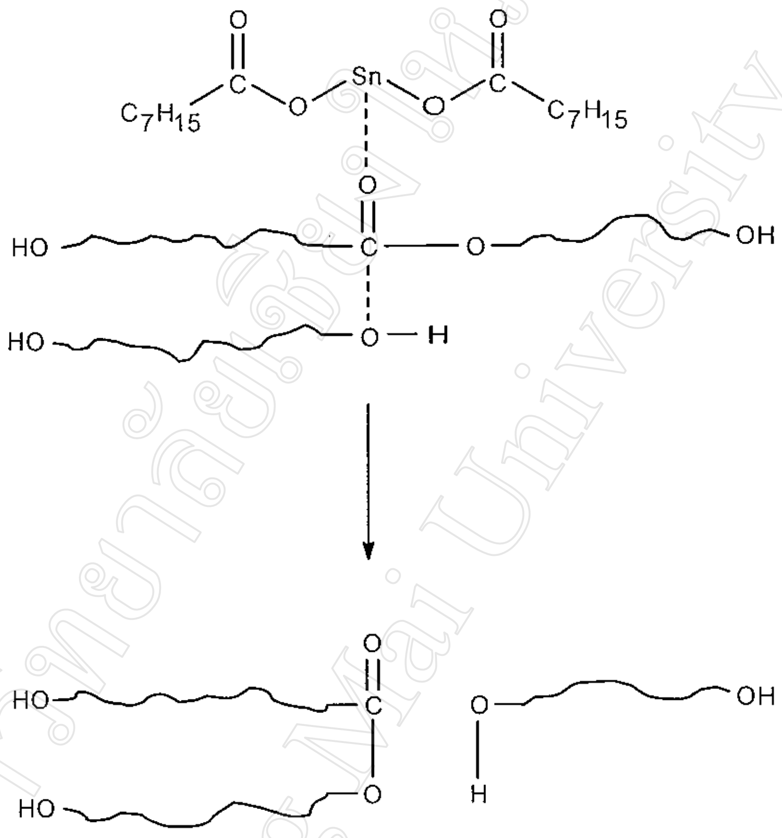
(a) Intramolecular Transesterification



(b) Intermolecular Transesterification

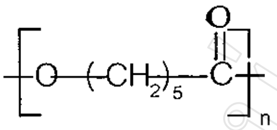


(c) Hydrolysis / Alcoholysis by Moisture / Hydroxy-containing Compounds



7.4 Fibre Processing

Just as polymer synthesis revolves around a myriad of reaction variables, so does fibre spinning around a myriad of processing variables. Fibre spinning is not so much a technology as an art for which there is no substitute for experience. In this project, valuable experience was gained from melt spinning trials on a model commercial polyester, poly(ε-caprolactone) (PCL).



poly(ε-caprolactone), PCL

As described in Chapter 3, melt spinning of PCL demonstrated the importance of balancing the basic processing variables of temperature, extrusion rate and take-up rate in order to obtain a stable filament line of uniform diameter. Melt rheology is clearly of fundamental importance but was not studied in detail apart from the temperature dependence of melt flow index (MFI). In the small-scale melt spinning apparatus used here, the polymer melt was subjected to very little shear action other than being forced through a stainless steel wire mesh before entering the capillary section of the spinnerette. The problem of void formation in the extruded fibre was minimized by spinning from pre-formed rods rather than beads.

Having emerged from the spinnerette, what happened thereafter as the filament cooled and hardened depended mainly on the polymer's physico-chemical characteristics, for example its chemical structure, transition temperatures and crystallisability. In the case of PCL, its rate of crystallisation was so fast that the as-spun fibres were always semi-crystalline. However, because the molecules were still unoriented, the fibres were still very weak and highly extensible. In order to assume recognizable fibre properties, the as-spun fibres needed to be hot-drawn in order to align the crystalline regions along the fibre axis. Thus, the necessity for not just crystallinity but <u>oriented</u> crystallinity was clearly demonstrated. This part of the work has resulted in a paper being accepted for publication in the international journal ***Polymer International*** (see "Supporting Papers" at the end of this thesis).

The knowledge and experience gained from the PCL studies was then applied to the synthesized P(LCG) terpolymers. Even though they were also aliphatic polyesters, their melt spinning characteristics were quite different from PCL and required finer adjustment. Furthermore, the oscillatory instability known as ***draw resonance*** became a problem with the random terpolymers. Due to their structural irregularity and the much slower crystallisability of L-lactide units (the main component), both the random and triblock as-spun fibres were largely if not completely amorphous. This was considered to be advantageous in as much that the required % crystallinity could then be built into the fibres along with orientation through controlled off-line hot-drawing and annealing steps. This was confirmed by DSC, XRD and tensile test measurements.

The key question in all of this seems to be: what are the molecules doing at each stage in the fibre production process? Some of the possible molecular rearrangement processes are visualized in Fig. 7.1 for a typical high-speed commercial production process, e.g. for poly(ethylene terphthalate), PET, fibres. However, for the fibres produced here, very slow speeds were employed so that these changes could be observed more gradually rather than all at once. This was achieved to a certain extent and has allowed an insight to be gained into how fibres with tailored matrix morphologies as well as tailored chemical structures can be obtained.

7.5 Random versus Triblock Terpolymers

Finally, one of the main points of interest in this work has been the comparison between the melt spinning and fibre properties of the random and triblock P(LCG) 70:20:10 terpolymers. From the results in Chapter 5, it can be assumed that, with their compositions and molecular weights being approximately equal, their different chain microstructures must be responsible for their different melt rheologies and fibre properties. Comparing their spinnabilities, the triblock terpolymer seemed to give a smoother filament line with no tendency towards draw resonance. The presence in the melt of discrete blocks of the less mobile L units may have had the effect of increasing the melt's viscous component relative to its elastic component, resulting in a more favourable melt rheology. However, this is just an idea which requires experimental verification. Similarly, these same L blocks enhance the terpolymer's crystallisability on cooling leading to fibres with higher tensile strengths after drawing and annealing. On the face of it, the triblock terpolymer would therefore appear to have the greater potential for further development as an absorbable surgical suture.

Having said this, the random terpolymer, despite its more difficult melt processing, did show great capacity for property improvement off-line. Furthermore, it tended to yield softer, more flexible fibres due to its lower T_g and % crystallinity. However, its tensile strength needs to be increased. The lingering impression gained from this work is that the random terpolymer needs a higher molecular weight. Not only would this increase mechanical strength, it might also have a beneficial effect on its melt rheology. This, of course, means that we would have to return to the synthesis part of the work and consider how the reaction conditions might be improved, a fitting reminder to end this thesis of how synthesis and processing are inextricably linked.

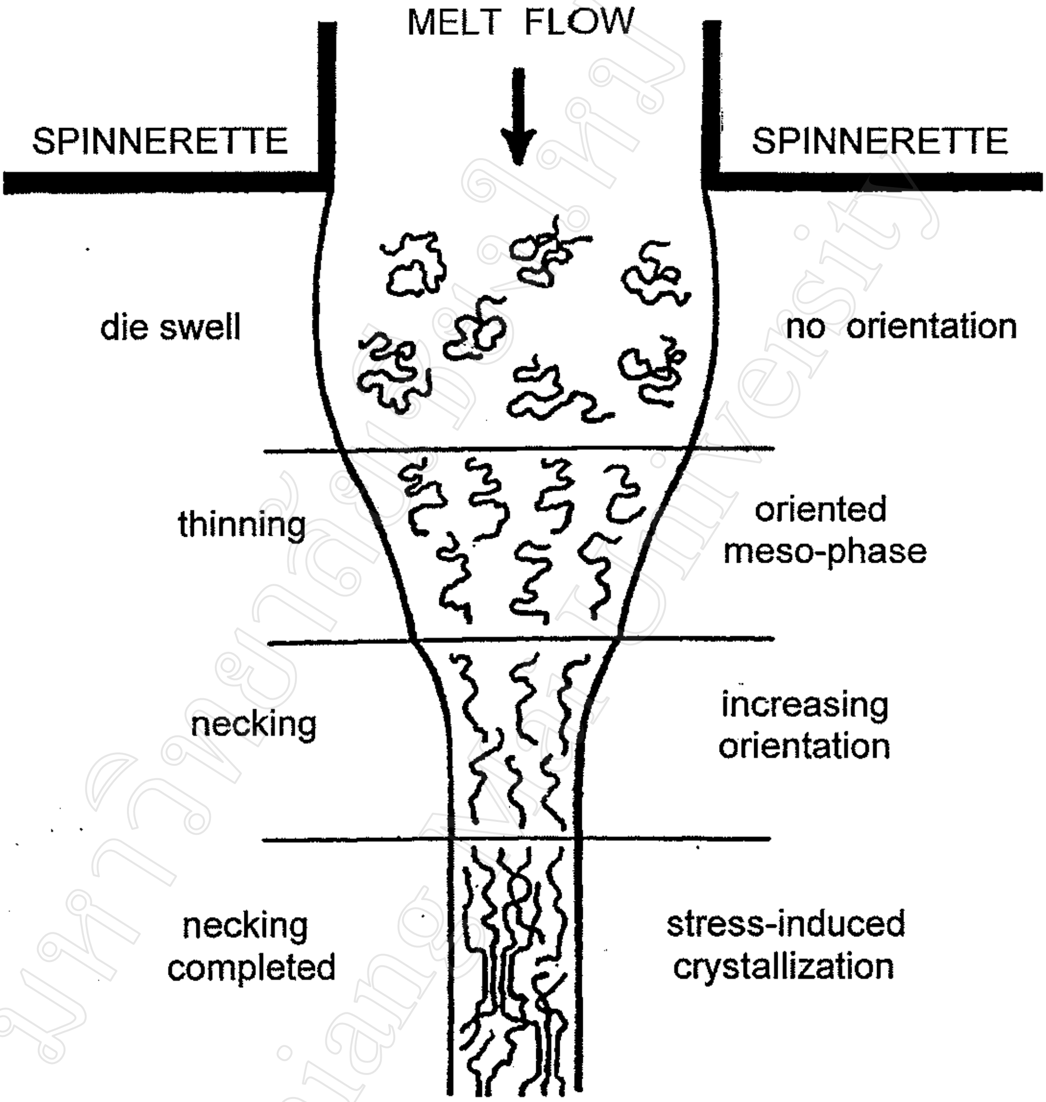


Fig. 7.1 Visualization of the sequence of molecular rearrangement processes which can occur during the melt spinning of a monofilament fibre.

SUGGESTIONS FOR FURTHER WORK

In continuation of the work described in this thesis, the following suggestions for further work are made, some of which have already been mentioned in the preceding text.

(1) Melt Rheology

Melt rheology is obviously central to any melt processing operation. In this work, the melt rheologies of the polymers studied were simply observed qualitatively in terms of the smoothness of extrusion and the stability of the filament line. In order to understand the factors affecting melt rheology more clearly, quantitative measurements should be carried out using techniques such as capillary and/or parallel-plate rheometry.

(2) Polymer Molecular Weight

The polymer molecular weights achieved here have certainly been adequate for fibre spinning and good quality fibres have been obtained. However, if higher molecular weights ($\overline{M}_n > 10^5$) could be obtained, it would be interesting to see what effects this might have on processing and properties.

(3) X-Ray Diffraction

The X-ray diffraction studies carried out at the University of Reading, UK, afforded a unique insight into the way in which an oriented semi-crystalline morphology is gradually developed through drawing and annealing steps. This is a fascinating area of study which is a natural extension of this work. It is also a very challenging area since many of the molecular rearrangement processes involved are both time- and temperature-dependent. The time-temperature superposition principles therefore come into play.

(4) Chemical Microstructure

In this project, a P(LCG) terpolymer composition of L:C:G = 70:20:10 was chosen, based on previous work within the Chiang Mai Polymer Research Group. This composition is constantly being re-appraised and re-adjusted and new materials can be expected to be produced for comparison. In addition to different compositions, different monomer sequence distributions and, in the case of the triblock terpolymer, different block lengths will undoubtedly affect both processing characteristics and fibre properties.

(5) Scale-Up

Finally, scale-up of the synthesis and processing operations is a necessary precursor to potential commercial development. Scale-up can also, in itself, be a processing variable. As the work described here moves towards its logical and, hopefully, successful conclusion, a 10-fold scale-up from the 40-50 g scale to the 400-500 g scale would enable more detailed experiments to be carried out on the same bacth of material, thereby reducing the uncertainty arising from batch-to-batch variations.