CHAPTER 1

INTRODUCTION

1.1 Biodegradable polymers

Biodegradation refers to degradation induced by the vital activity of an organism, not simply the degradation of a material in a physiological environment. The term biodegradable polymer means a polymer that degrades in the human body [1]. Although this term is preferred, it is often used interchangeably with the terms bioabsorbable and bioresorbable. Bioabsorbability can be defined as the ability of a tissue-compatible material to degrade at some time after implantation into nontoxic products which are eliminated from the body or metabolized therein. Bioabsorbable polymers also are biodegradable but the converse may not be true [2].

Biodegradable polymers are useful for medical applications such as sutures, surgical implants and controlled-release formulations of drugs. Table 1.1 lists some medical applications of biodegradable polymers. Synthetic biodegradable polymers have hydrolytically unstable linkages in the backbone. The most common chemical functional groups with this characteristic are esters, anhydrides, orthoesters, and amides [3].

Biodegradability is achieved by the hydrolysis of the hydrolytically unstable backbone. This take places in two phases. In the first phase, water penetrates the bulk of the device, preferentially attacking the chemical bonds in the amorphous phase and converting long polymer chains into shorter water-soluble fragments. Because this occurs in the amorphous phase initially, there is a reduction in molecular weight without a loss in physical properties, since the device matrix is still held together by thecrystalline regions. In the second phase, enzymatic attack and metabolization of the fragments occur resulting in a rapid loss of polymer mass [3].

Table 1.1 Medical applications for synthetic biodegradable polymers [3].

Application	Trade Name	Composition[a]	Manufacturer
Sutures	Dexon Maxon Vicryl Monocryl PDS Polysorb Biosyn PG suture Sysorb Endofix Arthrex	PG PG-TMC PG-PLL PG-PCL PDO PG-PLL PDO-PG-TMC PG PDLL PG-TMC or PLL PLL	Davis and Geck Davis and Geck Ethicon Ethicon Ethicon U.S. Surgical U.S. Surgical Lukens Synos Acufex Arthrex
Interference screws	Bioscrew Phusiline Biologically Quiet	PLL PLL-PDLL PG-PDLL	Linvatec Phusis Instrument Makar
Suture anchor	Bio-Statak Suretac	PLL PG-TMC	Zimmer Acufex
Anastomosis clip	Lactasorb	PLL	Davis and Geck
Anastomosis ring	Valtrac	PG	Davis and Geck
Dental	Drilac	PDLL	THM Biomedical
Angioplastic plug	Angioseal	PG-DPLL	AHP
Screw	SmartScrew	PLL	Bionx
Pins and rods	Biofix Resor-Pin	PLL or PG PLL-PDLL	Bionx Geistlich
Tack	SmartTack	PLL	Bionx
Plates, mesh, screws	LactoSorb Antrisorb	PG-PLL PDLL	Lorenz Atrix
Guided tissue	Resolut Guidor	PG-DPLL PDLL	W.L. Gore Procordia

[a] Key to material composition :

PLL : Poly(L-lactide)

PDLL : Poly(DL-lactide)

PG : Polyglycolide

PDO : Poly(dioxanone)

PG-TMC : Poly(glycolide-co-trimethylene carbonate)

PG-PLL : Poly(L-lactide-co-glycolide)

PG-PDLL : Poly(DL-lactide-co-glycolide)

PLL-PDLL : Poly(L-lactide-co-DL-lactide)

PDO-PG-TMC : Poly(glycolide-co-trimethylene carbonate-co-dioxanone)

It is their application as suture material which is the focus of this work. Thus, absorbable surgical sutures will now be described in more detail.

1.2 Absorbable surgical sutures

The absorbable surgical suture acts as a temporary scaffold while the process of wound healing is taking place following surgery. The suture is used to hold tissues together until sufficient collagen synthesis has taken place to hold the wound together unassisted [4].

Absorbable sutures can be fabricated as multifilaments or monofilaments that are shown in Fig. 1.1. Whereas multifilament sutures are made up of tiny fibres braided or twisted together, monofilament sutures are single-stranded fibres which have no braiding or twisting. Both have their advantages and disadvantages. Multifilament sutures are soft, flexible and easy to handle, but there are interstices formed by the relatively loose braid of the fibres which permit serum and blood to penetrate the suture and form a perfect refuge for bacteria. Therefore, multifilament sutures should not be used in a wound which is likely to become infected. Moreover, their outer surface is rough which can make it difficult to pull the suture through delicate tissue without tearing the tissue in the process (i.e., causes tissue drag). Monofilament sutures have less affinity for bacteria and a smoother surface which are major advantages in exhibiting less tissue drag. On the other hand, they are quite stiff and difficult to handle and tie, which are disadvantages [5]. On the whole, monofilament sutures are preferable to multifilament ones due to their superior advantages.

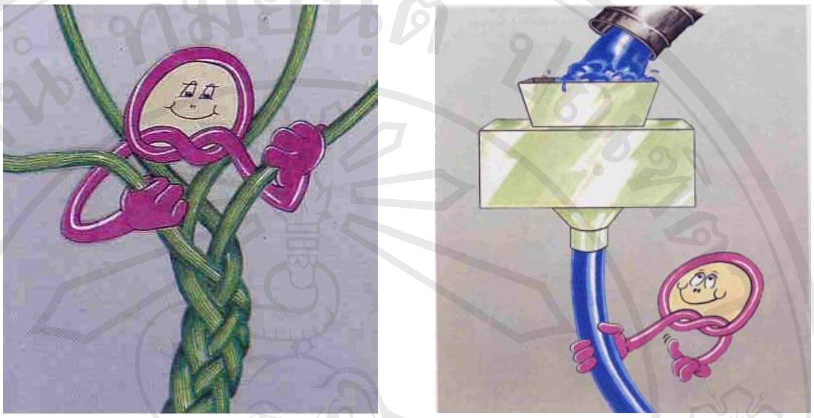


Fig. 1.1 The physical form of a braided multifilament and a monofilament suture [6].

1.3 Property requirements for an ideal absorbable suture

A biodegradable polymer which is to be used in surgical suture must be designed to meet a number of specific property requirements. The polymer needs to be:

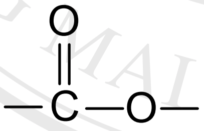
1) non-allergenic
2) resistance to infection
3) minimal tissue reaction
4) superior tensile strength
5) good knot security
6) excellent handling characteristics
7) have predictable absorption throughout the wound-healing process

1.4 Molecular design considerations

Polymer design for use in absorbable surgical suture has to consider the property requirements, as mentioned above. The main structural design consideration is chemical structure and various other microstructural factors also need to be carefully controlled, such as molecular architecture, copolymer composition and monomer sequence distribution, molecular weight and its distribution, and morphology and crystallinity. These factors affect polymeric mechanic properties and each factor is now briefly discussed.

1.4.1 Main chain chemical structure

The chemical structure is the most important single factor in molecular design for making commercial fibre. The chemical structures of the current commercial absorbable surgical sutures are shown in Table 1.3 from which it is possible to gain an insight into the structural considerations which need to taken into account when developing new monofilament absorbable sutures. The polymer structures can be broken down into the following main chain components:



$$-\overset{\displaystyle O}{\overset{\|}{C}}-O-$$

ester group

necessary to confer :

- hydrophilicity
- hydrolysability
- biodegradability
- absorbability
- improved mechanical properties

$-CH_2-$

Methylene link

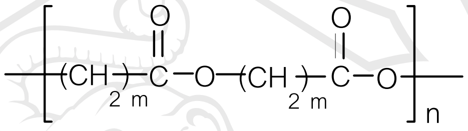
$-O-$

Ether link

necessary to confer :

- main chain flexibility
- fibre flexibility
- improved handling properties as a monofilament suture
- controlled degradation interval

Aliphatic polymer contains ester linkages which is hydrolysable linkages along the main chain are susceptible to biodegradation by microorganisms and enzymatic hydrolysis. In addition, the polarity of ester group, dipole-dipole interaction give rise to the molecular cohesion that polymer molecules be able to pack together closely which resulting mechanical strength. Flexibility is increased when many methylene groups (CH_2) or oxygen atom (-O-) are present between stiffening groups in the chain. Thus, the flexibility of aliphatic polyesters usually increases as **m** is increased [7, 8].



$$-\left[(CH_2)_m-\overset{\overset{O}{\|}}{C}-O-(CH_2)_m-\overset{\overset{O}{\|}}{C}-O\right]_n-$$

Aliphatic polyester

1.4.2 Molecular architecture

Polymer molecules can have different molecular architectures, as represented schematically Fig. 1.2. The particular type of architecture the molecular possess controls the properties of the material. A cross-linked or network polymer is produced that is insoluble and infusible and is therefore called **thermosetting**. Thermoset is heavily cross-linked polymer which is normally rigid and intractable. It can not melt on heating and degrades if the temperature is high enough.

Most linear and branched polymers are **thermoplastic** which is often referred to just as plastics that is, they can be softened or melted by heat and dissolved in appropriate solvents. Thermoplastics can be moulded and remoulded using conventional techniques. Thermoplastics can be sub-divided into those which crystallize on cooling. The ability of the polymers to crystallize depends upon many factors such as the degree of branching and the regularity of the molecules. However, crystalline thermoplastics are invariably only partly (semi-) crystalline and do not crystallize completely when cooled from the melt. In the case of the molecular structure of polymer consists of a lightly cross-linked macromolecular network, they display elastomeric property that is referred to as **rubber**. It is reversibly stretchable to high extensions. The cross-links prevent the molecules from flowing past each other when the material is stretched [9, 10]. However, branching and cross-linking are undesirable for fibre since they disrupt crystalline formation, even though a small amount of cross-linking may increase some physical properties, if effected after the material is drawn and processed.

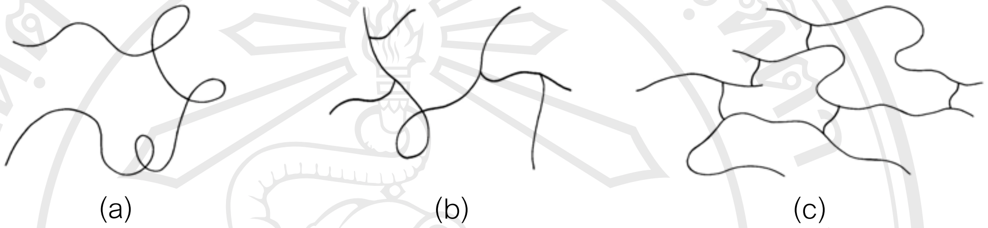


Fig. 1.2 Schematic representation of (a) linear (b) branched and (c) cross-linked or network polymers.

1.4.3 Copolymer composition and monomer sequence distribution

The term polymer is used to mean a particular class of macro-molecules consisting of a set of regularly repeated chemical units of the same type or possibly of a very limited number of different types, joined end to end or sometimes in more complicated ways, to form a chain molecule. If there is only one type of chemical unit the corresponding polymer is a **homopolymer**; if there is more than one type, it is a **copolymer**. Several main types of copolymer are shown in Fig. 1.3.

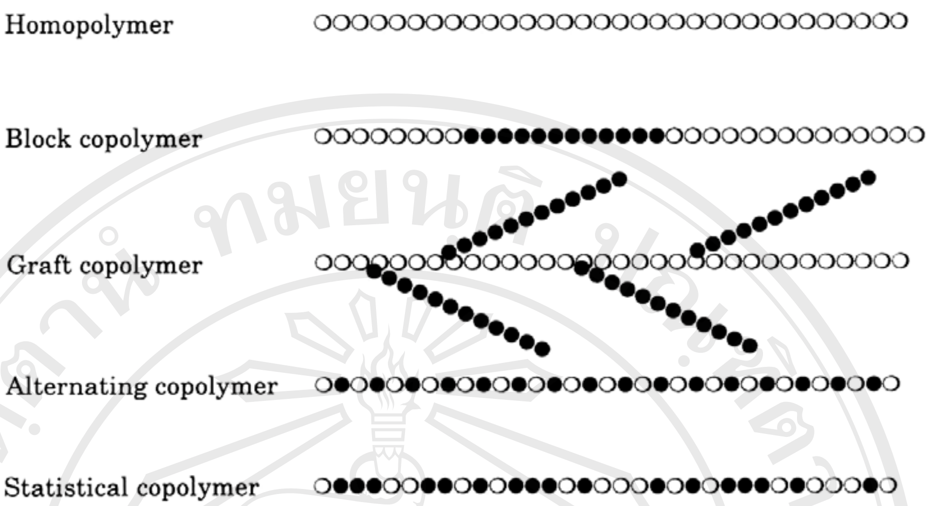


Fig. 1.3 Homopolymer and different types of copolymers. Unit A : o and Unit B : • [11]

Statistical copolymer is copolymer in which the sequential distribution of the repeat unit obeys known statistical laws. **Random copolymer** is a special type of statistical copolymer in which the distribution of repeat units is truly random. The notation for a statistical and random copolymer are poly(A-**stat**-B) and poly(A-**ran**-B) respectively. On the other hand, The nomenclature for unspecified type is referred to as poly(A-**co**-B). When the copolymer is arranged in a regular sequence in the chain, i.e., ABAB the copolymer is called an **alternating copolymer**, poly(A-**alt**-B).

Block copolymer is used to describe copolymer with long sequence or runs of different monomers in the same continuous chain. A molecule of such a block copolymer may consist at the simplest of just two blocks, in an **AB diblock polymer**, or of three blocks, in an **ABA triblock polymer**. **Terpolymer** consists of three different repeating units: A, B and C. The nomenclature for the former is poly(A-**block**-B) or poly(A-**b**-B), the **block or b** inserted to signify the block nature of the product. The term **graft copolymer** is branched polymer in which the branches have different chemical structure to that of the main chain. The nomenclature is designated poly(A-**graft**-B).

In all the above cases the properties of the copolymers are considerably different from those of either of the pure homopolymers. Copolymerization provides a route for making polymers with special, desired property profiles. Regular linear homopolymer are easily crystallized while the tendency of crystallization is reduced in copolymers. Copolymers with random arrangements of repeating units in the polymer chain are generally amorphous. For example, a statistical copolymer consisting of units A and B has in most cases properties in between those of the homopolymers (poly A and poly B). An important deviation from this simple rule arises if either polymer A or polymer B is semi-crystalline. The statistical copolymer is for most compositions fully amorphous. Block and graft copolymers form in most cases a two-phase morphology and the different phases obey properties similar to those of the respective homopolymrs and the properties of block copolymers are also dependent on the length of the sequences of repeating units or domains [11, 12].

1.4.4 Molecular weight and its distribution

Many properties of polymer show a strong dependence upon the size of the polymer chains, therefore it is essential to characterize their dimensions. This is normally done by measuring the **molar mass, M** (g/mol or kg/mol) of polymer. The term **molecular weight** is still often used instead of molar mass by some authors. Fig. 1.4 presents the influence of molar mass on the melting point of polyethylene. Low molar mass substances (oligomers) show a strong increase in melting point with increasing molar mass, whereas a constant melting point is approached in the polymer molar mass range. Other polymers show a similar behaviour. Mechanical properties are also much more dependent on molecular weight over a very broad range, although they too level off at the higher end of the molecular weight spectrum. Where they level off depends on the structure. For polyethylene, where dispersion forces are responsible for mechanical properties, the leveling off occurs at relatively high molecular weight (above 10^5), whereas with very polar polymers such as polyamides, it may occur at a molecular weight as low as about 20,000 to 50,000. Rheological properties such as melt viscosity show a progressive strong increase with increasing molecular weight even at high molecular weight. High molecular weight polymers are difficult to process but they have very good mechanical properties in the final products. This relationship of polymer properties to molecular weight is shown in Fig. 1.5. The working range of commercial polymers shown in the figure is at a molecular weight that gives good mechanical properties at a workable viscosity [11, 13].

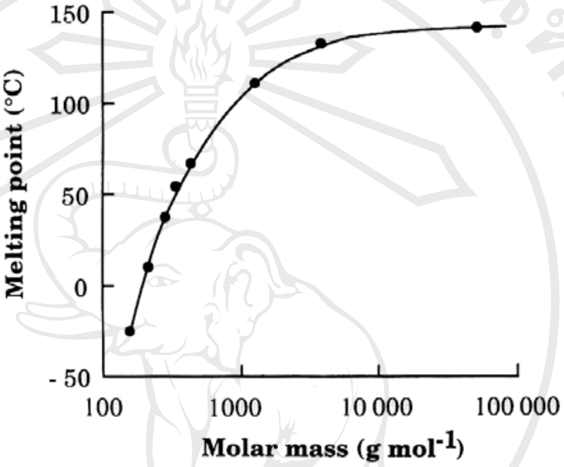


Fig. 1.4 Molar mass dependence of the equilibrium melting point of oligo- and polyethylene [11].

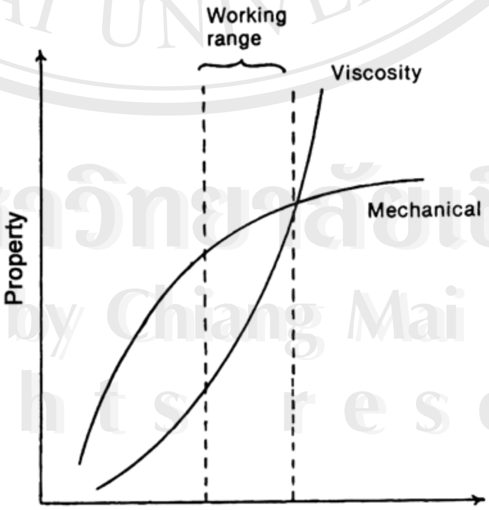


Fig. 1.5 The relationship of polymer properties to molecular weight [14].

1.4.5 Morphology and crystallinity

Polymer morphology is detail of its structure such as molecular arrangement, crystallinity and physical form of polymer molecules. Some polymers have ability to crystallize. The extent to which this occurs varies with the type of polymer and its molecular microstructure. Quite a number of polymers are not able to crystallize due to either its irregularity of molecular chain or some effects that prevents ordering in the structure. Even though, some polymers can crystallize, it is hardly found to be totally single crystals. This is due to the fact that polymers are macromolecules. Especially, in the case of a polymer is crystallized from the melt, imperfect polycrystalline aggregations are formed in association with a substantial amorphous content. This is an effect upon of chain entanglement and the high viscosity of the melt combining to hinder the diffusion of chains into the ordered arrays necessary for crystallite formation. If these restrictions to free movement are reduced, such as in the case of a polymer allowed to crystallize from a dilute solution, it is possible to obtain well-defined single crystals [15]. The solution is necessary to be dilute enough because if it is too concentrated, molecular chains become entangled. When polymer crystallized from a dilute solution, the polymer chains are isolated from each other and free to move and arrange themselves in an ordered crystalline region. Therefore, almost crystallizable polymers found are not single crystals but are in normally semi-crystalline form that contains both crystallinity and amorphous components. Degree of crystallinity, size and arrangement of the crystallites in semi-crystalline polymer have a strong effect upon the mechanical properties of the polymer. In order to explain these properties, it is important to understand the nature of crystalline regions [16].

The first attempts to explain the crystalline structure of a polymer sample produced a model called the fringe-micelle structure (see in Fig. 1.6). The chain was envisaged as meandering throughout the system, entering and leaving several ordered regions along its length [15]. Thus, whole structure was made up of crystallites consisting of pararell polymer chain segments embedded randomly in an amorphous phase. This model has now been almost discarded because this picture can not explain the structure of single polymer crystals which were prepared by several investigators in the 1950s.

Fig. 1.6 Fringed-micelle model of the crystalline - amorphous structure of polymer [17].

Single crystals of polymers are usually grown from dilute solution. Polyethylene is the most widely studied example of polymer single crystals. The single crystals are in the form of thin, flat platelets (lamellae) as shown in Fig. 1.7 [10]. They are too small (~ 10 μm across) to be observed using X-ray techniques and the relative orientation of the polymer molecules within the lamellar crystals can only be determined by electron diffraction. It was found that the molecular chains are perpendicular to the crystal surface. Therefore the feature can only be explained by **chain folding** since as the polymer molecules are about 10^4 Å long and the lamellar thickness is only about 100 Å. Fig. 1.8 shows a schematic picture of flat lamellae of polymer single crystals indicating chain folding. The thickness of the lamellar depends on crystallization temperature and any subsequent annealing treatment. At a given crystallization temperature, the fold length increases with increasing temperature. The fine structure of lamellae and its surface characteristics in semi-crystalline polymers can be described from the models. The models are classified by folding in polymer crystals as illustrated schematically in Fig. 1.9. There are 3 types of adjacent re-entry models i.e. regular folded array with adjacent re-entry of chains, adjacent re-entry with some loose folding and the switchboard model where a molecules leaves and re-enters a crystal randomly [16, 17].

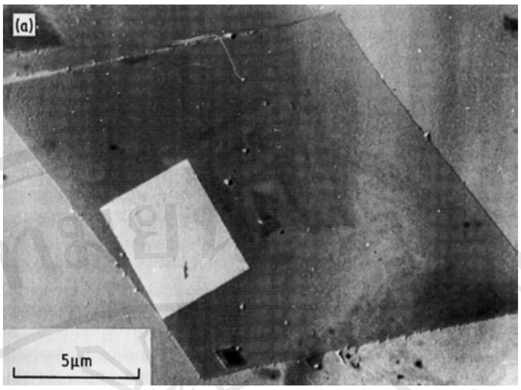


Fig. 1.7 Single crystals of polyethylene [10].

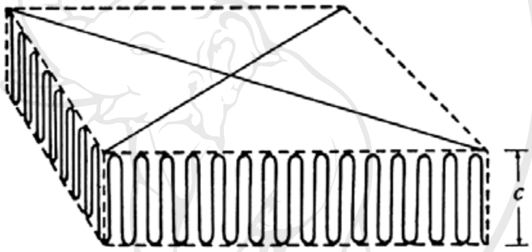


Fig. 1.8 Schematic representation of flat lamellae of polymer single crystals [18]

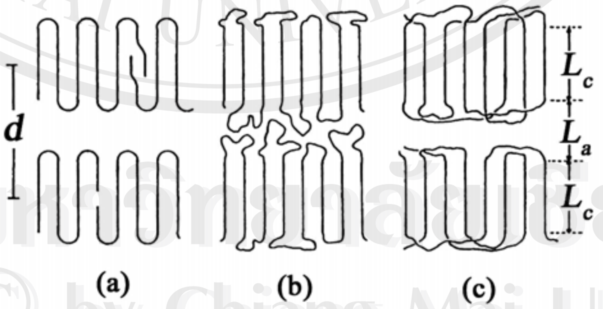


Fig. 1.9 Schematics illustrations of possible chain morphology in a single polymer chain [19]. L_c = Thickness of crystalline lamellae; L_a = Thickness of amorphous cover layers; d = X-ray long periodicity (a) Regular lamellae with sharp folds and crystal defects by chain ends and dislocations (b) Loose fold with adjacent re-entry (c) Switchboard model with random re-entry of chains.

The morphology of the single crystals grown from dilute solutions may be more regular and resemble the first model in Fig. 1.9. However, for melt-crystallized polymers, most of evidence indicates a form of the switchboard model. As in fringed-micelle model, the folded-chain lamellae are embedded in an amorphous phase and they are tied together by interlamellar amorphous chain [20] (see in Fig. 1.10) If is worth to mention that fringed-micelle model is still useful to describe mechanical property development of semi-crystalline polymers.

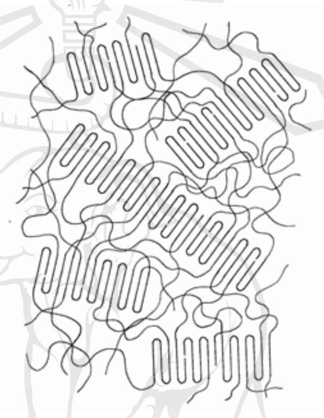


Fig. 1.10 Schematic representation of folded chain lamellae tied together by interlamellar amorphous chains

In addition to the discovery of lamellar structure involving chain folding, it was also found that polymers may crystallize into more complex structures composing of specific arrangements of lamellae such as spherulite structure. When semi-crystalline poymer crystallized from the melt in the form of thin film and viewed in an optical microscope between crossed polaroids, its complex structure can be observed as Maltese cross optical extinction pattern or as ringed structures. Fig. 1.11 is given as an example of Maltese cross pictures of spherulites seen in an optical microscope. Spherulites form by nucleation at different points in the sample and grow as spherical entities. The growth of the spherulites stops when impingement of adjacent spherulites occurs. Therefore, one of the most important parameters to govern the number, size and fine structure of spherulites is the temperature at crystallization of the polymer.

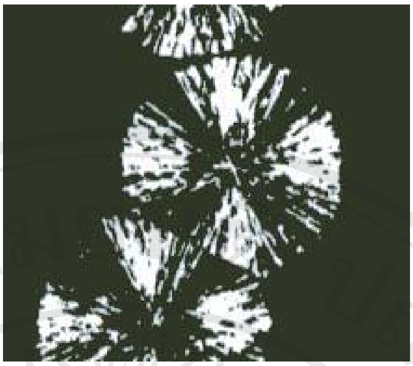


Fig. 1.11 Spherulites growing in poly(ethylene oxide) from the melt [15]

Details of the fine structure of a spherulite can be shown in Fig. 1.12. The spherulite composes of crystals radiating out from a central nucleus. The individual crystals are lamellae. Growth originates from a small crystal nucleus which develops into a fibril. As this fibrillar growth advances, branching takes place. Then branching and twisting produce bundles of diverging and spreading fibrils which eventually fill out into the characteristic spherical structure. In between the branches of the fibrils are amorphous areas and these, along with the amorphous interfacial regions between the lamellae, make up the disordered content of the semi-crystalline polymer [15].

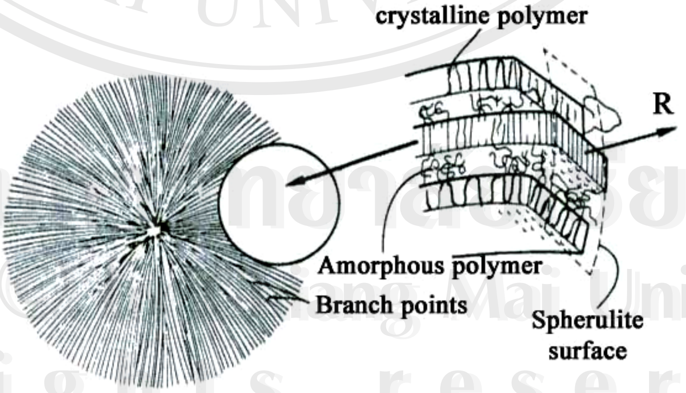


Fig. 1.12 Fully–developed spherulite grown from the melt, comprising chain folded lamellae (magnified section). Most rapid growth occurs in the direction of the spherulite radius R. [15]

The spherulitic morphology occurs commonly when nucleation originates in molten polymer or in concentrated polymer solutions in the absence of external force. If polymer melts or solutions are crystallized under external stress, an entirely different morphology can result such as **Shish-kebab morphology** (see in Fig. 1.13). It takes place during crystallization in the stirred solutions. There are a central block or shish with lamellae overgrowths (Kebabs). Both of them, the polymer molecules are parallel to the shish-kebabs axis [16, 17].

Fig. 1.13 Schematic model of Shish-kebab morphology [17]

When polymer is crystallized in the absence of external force, there is no preferred direction in the specimen. However, if this unoriented crystalline polymer is then applied by external force, it undergoes a rearrangement of the morphology of the semi-crystalline material

The chemical structure determines a given polymer's tendency toward being crystalline or amorphous, or being a mixture of crystalline and amorphous regions in the solid state. In general, crystallinity is favored by symmetrical chain structures that allow close packing of the polymer units to take greater advantage of secondary forces which are distance related. Crystallinity is also favored by high interchain (secondary forces) interactions. For amorphous polymers which are unable to crystallize is commonly their irregular chain structure. Atactic polymers, statistical copolymers and highly branched polymers belong to these amorphous polymers. The differences in crystallinity lead to differences in physical properties of polymers. Table 1.2 shows the relation between the degree of crystallinity and the physical nature. The general lack of difference in physical nature shown by largely crystalline polymers at temperatures below and above the glass transition temperature,T_g is because they lack a significant portion with a T_g. T_g is a characteristic temperature at which glassy amorphous polymers become flexible or rubberlike because of the onset of segmental motion. Moreover, physical factors that increase crystallinity, such as slower cooling and annealing, also tend to increase the stiffness, hardness, and modulus of a polymeric material. Thus, polymers with a least some degree of crystallinity are denser, stiffer and stronger than amorphous polymers. However, the amorphous region contributes to the toughness ad flexibility of polymers [11, 12].

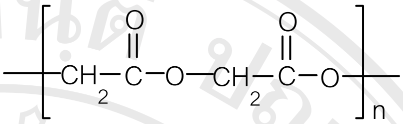
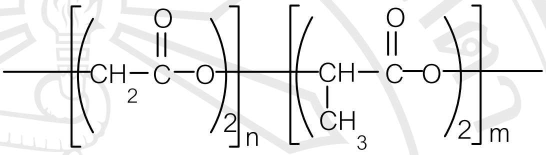
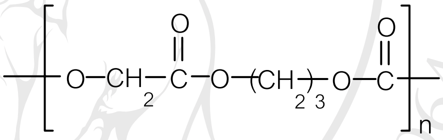
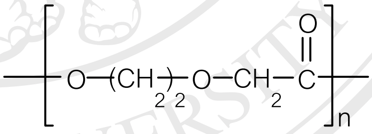
Table 1.2 Effect of crystallinity on physical appearance.

Temperature (°C)	**Degree of crystallinity**		
	Low (< 10%) amorphous	**Intermediate (20 – 70%)**	**High (> 70%) crystalline**
Above T_g	Rubbery	Tough, leathery	Hard, stiff
Below T_g	Brittle, glassy	Tough, horny	Hard, stiff

1.5 Historical development of synthetic absorbable sutures

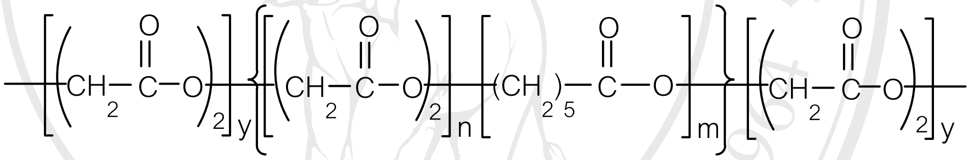
Synthetic biodegradable polyesters have the advantage over natural materials in that they can be tailored to give a wider range of properties. They have been widely used for many biomedical purposes. In this research, attention is focused on absorbable suture applications, the historical development of which is now described in more detail and the chemical structures of some commercial synthetic absorbable suture are listed in Table 1.3

Table 1.3 The chemical structures of some commercial synthetic absorbable sutures.

Trade Name	**CHEMICAL STRUCTURE**
DEXON	 $\left[CH_2-C(=O)-O-CH_2-C(=O)-O \right]_n$ poly(glycolide)
VICRYL	 $\left[\left(CH_2-C(=O)-O \right)_2 \right]_n \left[\left(CH(CH_3)-C(=O)-O \right)_2 \right]_m$ poly(glycolide-co-L-lactide) n : m = 90 : 10 mole %
MAXON	 $\left[O-CH_2-C(=O)-O-(CH_2)_3-O-C(=O) \right]_n$ poly(glycolide-co-trimethylene carbonate)
PDS II	 $\left[O-(CH_2)_2-O-CH_2-C(=O) \right]_n$ poly(p-dioxanone)

The first synthetic absorbable suture was made of polyglycolide by Davis & Geck (USA) and was initially marketed in 1970 under the trade name of DEXON. DEXON is a braided multifilament suture. A similar synthetic absorbable suture to DEXON was developed by Ethicon, Inc. (USA), in 1974 from a 90:10 copolymer of glycolide and L-lactide under the trade name of VICRYL. It was also a braided multifilament suture with properties similar to those of DEXON. However, there are some concerns with braided sutures that relate to tissue drag and the trauma that may cause, as well as the possible potentiation of infection through the interstices of the braid structure.

To eliminate some of the concerns about braided sutures, the absorbable monofilament sutures, PDS II (a homopolymer of p-dioxanone; Ethicon, Inc.) and MAXON (a copolymer of trimethylene carbonate and glycolide; Davis & Geck) were introduced in the 1980s. Subsequently, MONOCRYL appeared on the market as a new, more pliable monofilament. This suture is made from a segmented triblock copolymer of ε-caprolactone (CL) and glycolide (G). The triblocks are comprised of a soft center-block of a random copolymer of P(G -co- CL) with a 55 : 45 mole % composition and two hard end-blocks of polyglycolide to add up to an overall composition of 25 : 75 mole %. The soft center-block provides good handling characteristics while hard end-blocks of polyglycolide provide high strength. The molecular formula of MONOCRYL is shown below [8, 21-22] :



$$-\!\!\left[\left(CH_2-\overset{\overset{\textstyle O}{\|}}{C}-O\right)_2\right]_y\left\{\left[\left(CH_2-\overset{\overset{\textstyle O}{\|}}{C}-O\right)_2\right]_n\left[(CH_2)_5-\overset{\overset{\textstyle O}{\|}}{C}-O\right]_m\right\}\left[\left(CH_2-\overset{\overset{\textstyle O}{\|}}{C}-O\right)_2\right]_y\!\!-$$

poly[glycolide-b-(glycolide-co-ε-caprolactone)-b-glycolide] 'MONOCRYL'

m : n = 45 : 55 mole %

m : n + 2y = 25 : 75 mole %

While MONOCRYL has been shown to have superior handling properties, its breaking strength decreases faster than both PDS II and MAXON [22]. The challenge lies in tailoring the polymer microstructure to give the correct balance of handling and healing characteristics to meet the requirements of the application.

1.6 Mechanism of suture absorption

In general, the various mechanisms of polymer biodegradation can be classified into 4 groups: solubilization, ionization followed by solubilization, enzymatically-catalyzed hydrolysis and simple hydrolysis. The particular mechanism depends on the chemical structure of the polymer and the environment of the reaction. However, the synthetic polyesters which are currently in use as absorbable surgical sutures degrade mainly via simple hydrolysis the ester bonds to yield alcohol and carboxylic acid end-groups.

A simplified view of the various physical, chemical and biological processes which are involved in suture absorption is represented in Fig. 1.14. The first stage in a polymer biodegradation process in which hydrolysis is the dominant mechanism is the adsorption of water and wetting at the polymer surface. The efficiencies and, therefore, the rates of these physical processes depend primarily on the hydrophilicity of the polymer and the amount of surface area available for interaction. During this stage, water diffuses into the bulk interior of the polymer matrix. Ester hydrolysis take places preferentially in the amorphous regions where the chains are loosely packed that in the highly ordered crystalline regions. The second stage, water reacts with the polymer backbone which resulting in cleavage of covalent chemical bonds. The polymer molecular weight and strength decrease until the degradation products are small enough in size to diffuse out of the matrix, resulting in mass loss. Finally, the degradation products are metabolized are excreted through the body's urinary and respiratory systems.

Although Fig. 1.14 represents what is obviously a very simplified picture of suture absorption, it does at least give some idea of the complex of the various physical, chemical and biological processes involved. Since these processes are all interrelated with each other and with all aspects of the sutures's microstructure, even slight variations in polymer characteristics such as molecular weight, % crystallinity, composition and monomer sequence distribution can have quite marked effects on the rate of absorption. This places great demands on the degree of control required in both polymer synthesis and suture processing.

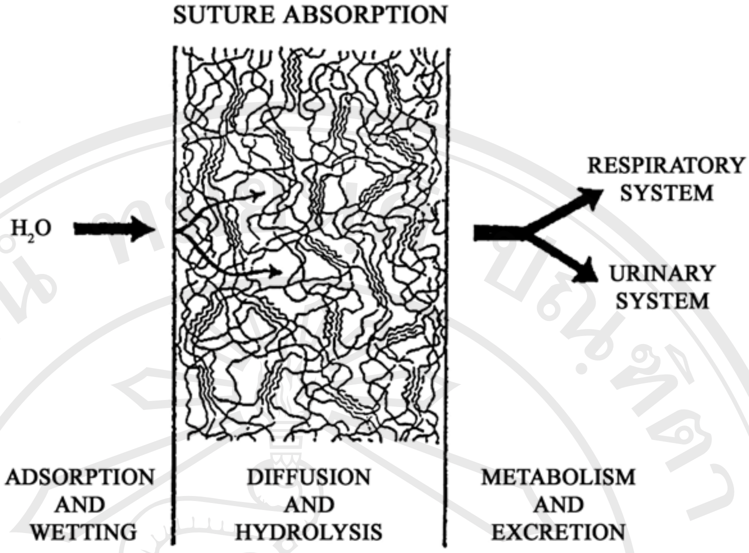
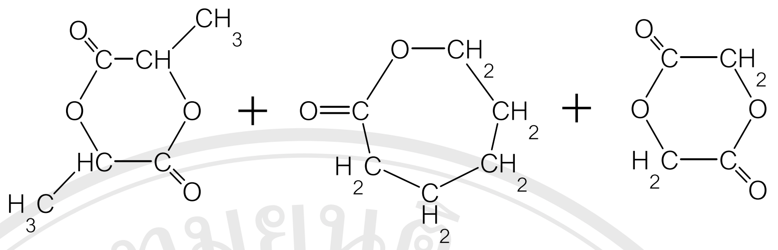


Fig. 1.14 The various physical and chemical processes involved in suture absorption.

1.7 Aims of this study

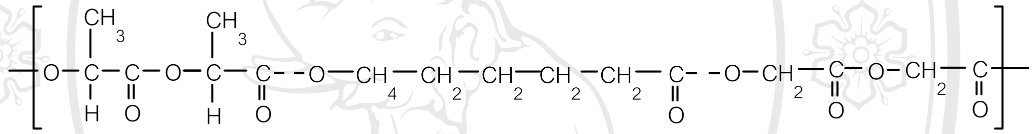
The purpose of this research is to develop a new synthetic monofilament fibre with the appropriate balance of physical and mechanical properties for use as an absorbable surgical suture. The synthetic biodegradable sutures currently in commercial use are polyesters that have the ability to biodegrade by hydrolysis. The products of degradation are non-toxic and can be effectively broken down and excreted via the body's metabolic pathways. The polyesters of particular interest in this research project are terpolymers based on L-lactide (LL), ε-caprolactone (CL) and glycolide (G). L-lactide is the major component due to its low cost while ε-caprolactone and glycolide increase chain flexibility and the degradation rate of the terpolymer respectively. The chemical structures of these 3 monomers are shown below.



L-lactide (LL) + ε-caprolactone (CL) + glycolide (G)

Two types of terpolymer are to be studied, namely:

(1) Random terpolymer of the structure below :



$$\left[-O-CH(CH_3)-C(=O)-O-CH(CH_3)-C(=O)--O-CH_4-CH_2-CH_2-CH_2-CH_2-C(=O)--O-CH_2-C(=O)-O-CH_2-C(=O)-\right]$$

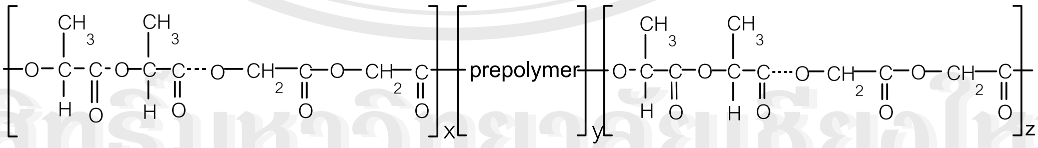
LL : CL : G

70 : 25 : 5 mole %

Poly(L-lactide-co-ε-caprolactone-co-glycolide)

P (LL-co-CL-co-G)

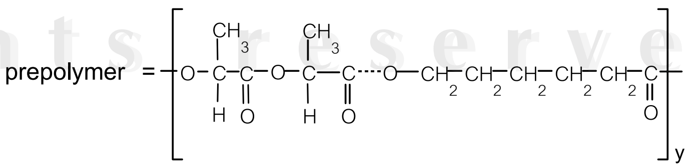
(2) Segmented triblock terpolymer of the structure below :



$$\left[-O-CH(CH_3)-C(=O)-O-CH(CH_3)-C(=O)\cdots O-CH_2-C(=O)-O-CH_2-C(=O)-\right]_x\left[\text{prepolymer}\right]_y\left[-O-CH(CH_3)-C(=O)-O-CH(CH_3)-C(=O)\cdots O-CH_2-C(=O)-O-CH_2-C(=O)-\right]_z$$

(LL-co-G) (LL-co-CL) (LL-co-G)

25 : 2.5 20 : 25 25 : 2.5 mole %



$$\text{prepolymer} = \left[-O-CH(CH_3)-C(=O)-O-CH(CH_3)-C(=O)\cdots O-CH_2-CH_2-CH_2-CH_2-CH_2-C(=O)-\right]_y$$

P(LL-co-CL)

Poly((L-lactide-co-glycolide)-b-(L-lactide-co-ε-caprolactone)-b-(L-lactide-co-glycolide))

P((LL-co-G)-b-(LL-co-CL)-b-(LL-co-G))

Both random and segmented triblock terpolymers of L-lactide, ε-caprolactone and glycolide with the same composition ratio of 70: 25: 5 mole % are to synthesized via controlled ring-opening polymerization reactions. In the case of the random terpolymer, the synthesis reaction is a single-step procedure while for the segmented triblock terpolymer it requires two separate steps with sequential monomer additions. The fabrication process is melt spinning. The crystallinity and molecular orientation of the as-spun fibres will be further developed by annealing and hot-drawing under various conditions to give the required mechanical properties. In this way, this research project aims to study the relationships between microstructure and properties of the monofilament fibres at each stage in its processing.

For simplicity in referring to the segmented triblock terpolymer in the text of this thesis, it will be referred to simply as the block terpolymer from this point onwards.