

Chapter 1

Introduction

1.1 Introduction

In the past decades, commercial polymers were mainly non-degradable, which required an excessive process to recycle. Recently, one group of polymers, degradable polymers, is renovating the roles of commonly known polymers. Among these Polylactide (PLA) has led to the introduction of possible ways to create plastics that are more environmental friendly. These polymers are no longer an extreme threat to the atmosphere, which is something very crucial for the future of healthy planet environment. However, the disadvantage of polylactide is that it is more expensive than conventional polymers and is commonly used in the biomedical field. In recent years, polylactide has received vast attention commercially and has been found in items that consist of plastic substances such as packaging materials and has emerged in other consumer products.

Figure 1.1 illustrates life cycle of PLA. Its monomer, lactic acid ($\text{CH}_3\text{C}_2\text{H}_2\text{O}(\text{OH})_2$), can be obtained from renewable starch-containing resources, such as, corn, wheat, or sugar cane, by fermentation and chemical synthesis. With the monomers being composed of these rich natural resources, it is thus a valuable polymer that benefits both the environment and the people. After the completion of the process of bacterial fermentation, lactic acid is produced. Lactic acid is then dehydrated to form lactide. The dehydration process of polylactide consists of chemically oligomerized process and catalytically dimerized process, in which now there are two identical net portions of the newly produced ring, which enables it to be ready for the ring-open polymerization process.

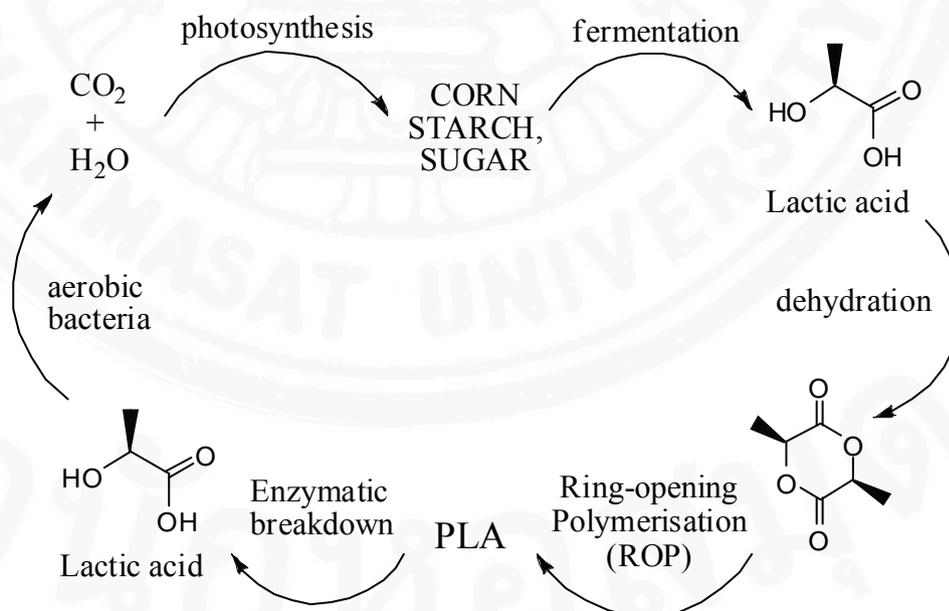


Figure 1.1 Life cycle of degradable PLA

Organo-metallic compounds are used in order to catalyze the ring-open polymerization of polylactide as shown in figure 1.2. At first these initiators were thought to involve in anionic or cationic polymerization, however, with time and improvement of scientific knowledge, it has been classified that most metals trigger the chain reaction through one of the intermolecular forces, covalent bonding. Of these metals, there exists two types of groups that affect the ring-open polymerization of polylactide; Lewis-acid catalysts and metal alkoxides.

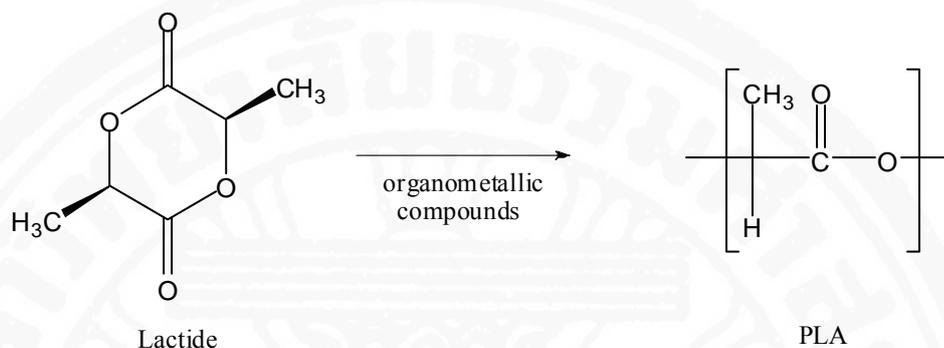


Figure 1.2 Ring-opening polymerization of lactide.

In the group of Lewis-acid, Tin(II)octoate or Sn(II) di(ethyl-2-hexanoate) is conventionally utilized as a catalyst in synthesis of polylactide. Other initiators involved in the same group include metal-halides, carboxylates, and oxides. Hydroxyl groups, such as water and alcohols, are also thought to be possible initiators for the ring-open polymerization for polylactide. Compounds containing these possible initiators can be found in lactide feed or can be exerted into the catalyst itself for the initiation of the process. One advantage that the Lewis-acid-catalysts have is that they are able to trigger more than one chain, without chemically bonding with the expanding chain.

Poly(lactic acid) (PLA) is a rigid thermoplastic polymer that can be semicrystalline or totally amorphous, depending on the stereopurity of the polymer backbone. L(-)-lactic acid is the natural and most common form of the acid, but D(-)-lactic acid can also be produced by microorganisms or through. Ultimately PLA may be the polymer with the broadest range of applications because of its ability to be stress crystallized, thermally crystallized, impact modified, filled, copolymerized, and processed in most polymer processing equipment. It can be formed into transparent films, fibers, or injection molded into blowmoldable preforms for bottles, like PET. PLA also has excellent organoleptic characteristics and is excellent for food contact and related packaging applications.

Poly(ethylene terephthalate), PET, is aromatic polyester that is widely used in many applications, e.g. textile and packaging. PET production process involves two different starting reactions. As summarized in figure 1.3, the first starting reaction is an esterification reaction where terephthalic acid (TPA) reacts with ethylene glycol (EG) at a temperature of between 240 °C and 260 °C and a pressure between 300 and 500 kPa (Fig.1.3a). The second reaction is trans-esterification reaction where dimethyl terephthalate (DMT) is reacted with EG at 150 °C, 180 °C –210 °C, 140–220 °C and 100 kPa. (Firas Awaja, 2005) Trans-esterification is the much preferred process due to easier purification (Fig.1.3b). The output of these processes is bis(hydroxyethyl) terephthalate (BHET) prepolymer. The pre-polymerisation step follows, in which BHET is polymerised to a degree of polymerization (DP) of up to 30. Pre-polymerisation reactions conditions are 250–280 °C and 2–3 kPa. The third stage is the polycondensation process

where the DP is further increased to 100 (Fig.1.3d). The polycondensation process conditions are 280–290 °C, 270–285 °C and 50–100 Pa. Up to this stage, PET is suitable for applications that do not require high molecular weight (MW) or intrinsic viscosity $[\eta]$ such as fibres and sheets. (Firas Awaja, 2005)

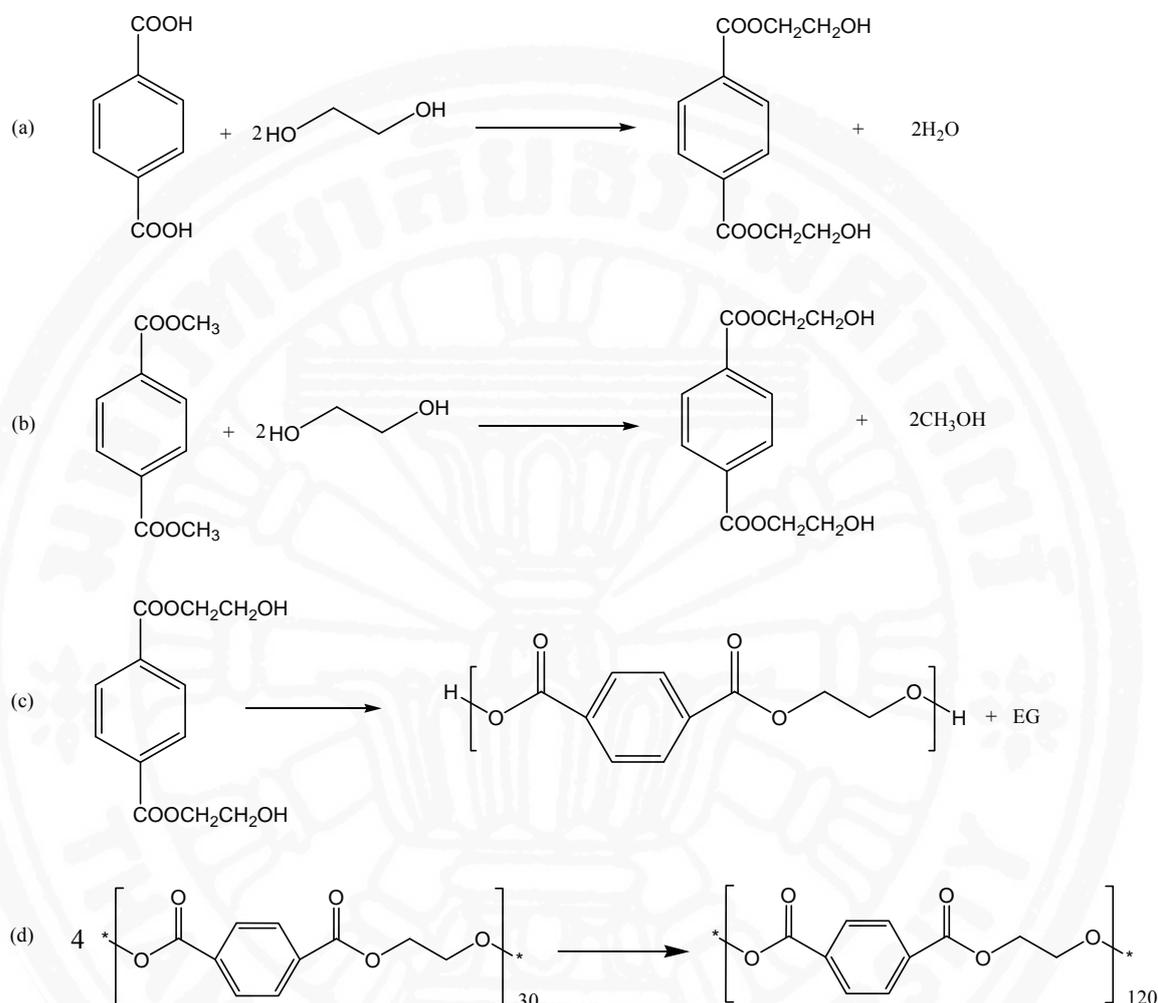


Figure 1.3 Synthesis reactions of PET: (a) esterification reaction of terephthalic acid (b) trans-esterification reaction of dimethyl terephthalate (c) condensation reaction to be oligomer and (d) condensation to be polymer.

1.2 Concepts and significances

Poly(lactic acid) is a biodegradable, thermoplastic, aliphatic polyester derived from renewable resources. PLA can be easily produced in a high molecular weight form through ring-opening polymerization using most commonly a stannous octoate catalyst. In order to improve the mechanical properties of PLA and retain its advantages of degradability and high availability of monomer resources, copolymerization of lactic acid and dimethyl terephthalate.

Aliphatic/aromatic copolyesters have been recognized as a valuable concept in modifying the properties of homopolyester. Especially, the degradable aliphatic

poly(lactic acid) (PLA). Despite its versatility, the properties of PLA can only be slightly modified by varying the molecular weight or crystallinity. The incorporation of other groups e.g. aromatic ester, are therefore required to provide the materials with wider range of properties. Dimethyl terephthalate (DMT) have been shown to increase the glass transition temperature (T_g) of PLA, a result from the incorporation of its stiffness of repeat structure to flexible PLA chain. (Mecerreyes, 1999)

In this study, PLA-based aliphatic/aromatic copolyesters are prepared and their properties are characterized. The synthesis of these copolymers require 3 components; LA, DMT, and diols. Effects of diols and comonomer ratios on the polycondensation were investigated. The incorporation of degradable aliphatic can produce degradable materials with good mechanical properties. Depending on comonomer ratios and chain microstructure, the resulting materials are suitable for wide range of applications. Ratios of L-lactic acid (LLA) dimethyl terephthalate (DMT) and diol of 1/1/2, 1/2/4, and 2/1/2 were employed, respectively.

1.3 Objective of the study

The main objective of this study is to synthesize degradable lactic acid-based copolyesters from lactic acid, diols (ethylene glycol, propylene glycol, 1,3-propanediol and 1,4-butanediol) and dimethyl terephthalate. Chemical structure, physical properties and degradability of the copolymers are then characterized. The resulting high molecular weight PLA-based aliphatic-aromatic copolyesters can be used in many applications taking advantages of the improved physical properties.

1.4 Scope of the study

The scope of this study includes the synthesis and characterizations of PLA-based aliphatic/aromatic copolyesters to incorporate the degradability of PLA and good mechanical properties of aromatic species. The synthesis procedure is summarized in figure 1.4, where polycondensation of lactic acid, dimethyl terephthalate (DMT), and various diols is employed using stannous(II)octoate as a catalyst. Four types of diols with different methylene lengths are used, i.e., ethylene glycol (EG), propylene glycol (PG), 1, 3-propanediol (PD) and 1, 4-butanediol (BD). Effects of diols and comonomer molar ratios on the polycondensation and the molecular weight of resulting copolymers are investigated. Diacids /diol ratios of L-lactic acid (LLA), dimethyl terephthalate (DMT) and diol of 1/1/2, 1/2/4, and 2/1/2 are employed, respectively. Characterizations on chemical structure, molecular weight, thermal properties and degradability of the resulting copolymers are conducted by FTIR, NMR, TGA and DSC experiments.

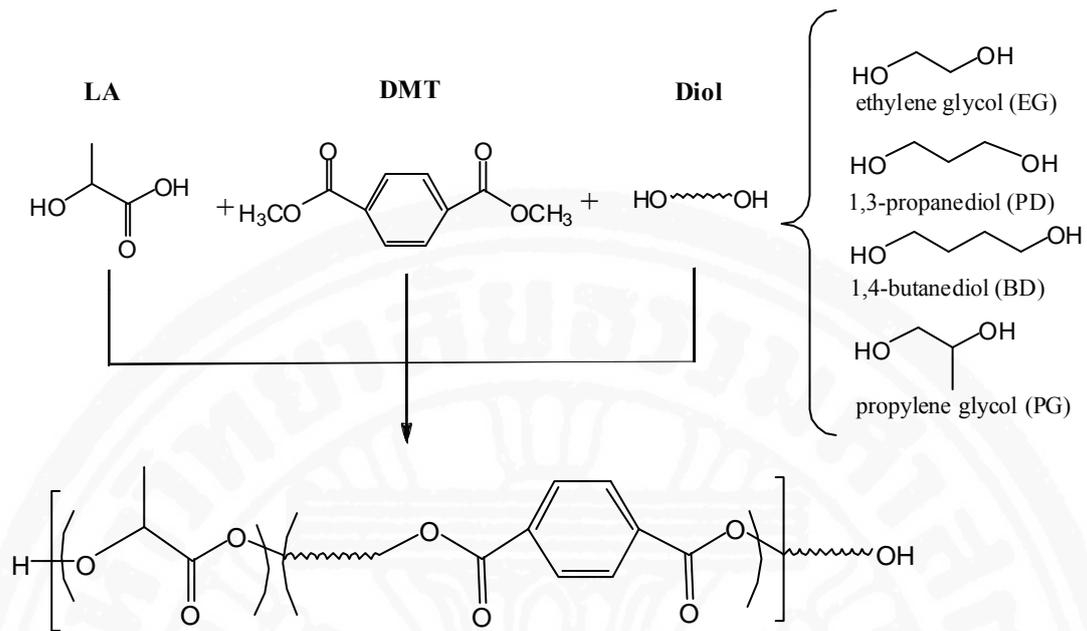


Figure 1.4 Summary of the synthesis reaction of aliphatic-aromatic copolyesters.