CHAPTER II
LITERATURE REVIEW

2.1 General Information of Poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) is in the family of aliphatic polyesters commonly made from Lactic acid or 2-hydroxypropinoic acid which is obtained from the fermentation of engineered microbes of the *genus Lactobacillus*. These microorganisms are highly efficient sources of lactic acid. Lactic acid is the simplest hydroxy acid with an asymmetric carbon atom and exists in two optically active configuration. The optically active lactic acid are "*D*" and "*L*" stereoisomers (figure 2.1). Synthesized PLA from chemical synthesis of lactic acid results in the *racemic*- mixture (50% *D* and 50% *L*). Native PLA typically consists of 99.5% of the *L*-isomer and 0.5% of the *D*-isomer (Vert *et al.*, 1995; Vink *et al.*, 2003).

L-Lactic acid *D*-Lactic acid

Figure 2.1 Stereoisomers of lactic acids.

PLA is a thermoplastic with high strength and high modulus that can be made from renewable resources for use in many applications such as industrial packaging, biomedical items, agricultural field , and textiles. It is easily processed on standard plastic equipment to yield molded parts, films, or fibers (Hartmann, 1998).

Poly(lactic acid) has glass-transition and melt temperature of about 55°C and 175°C, respectively. They require processing temperatures in excess of 185-190°C (Spinu *et al.*, 1996). At these temperatures, unzipping and chain scission reactions leading to loss of molecular weight, as well as thermal degradations, are known to occur. The most widely used method for improving PLA processability is

based on melting point depression by the random incorporation of small amounts of lactide enantiomer with opposite configuration into the polymer (i.e., adding a small amount of *D*-lactide to the *L*-lactide to obtain PDLLA). Unfortunately, the melting point depression is accompanied by a significant decrease in crystallinity and crystallization rates (Garlotta, 2001).

2.2 Synthesis of PLA

The synthesis of lactic acid into high-molecular weight PLA can follow two different routes of polymerization (Figure 2.2).

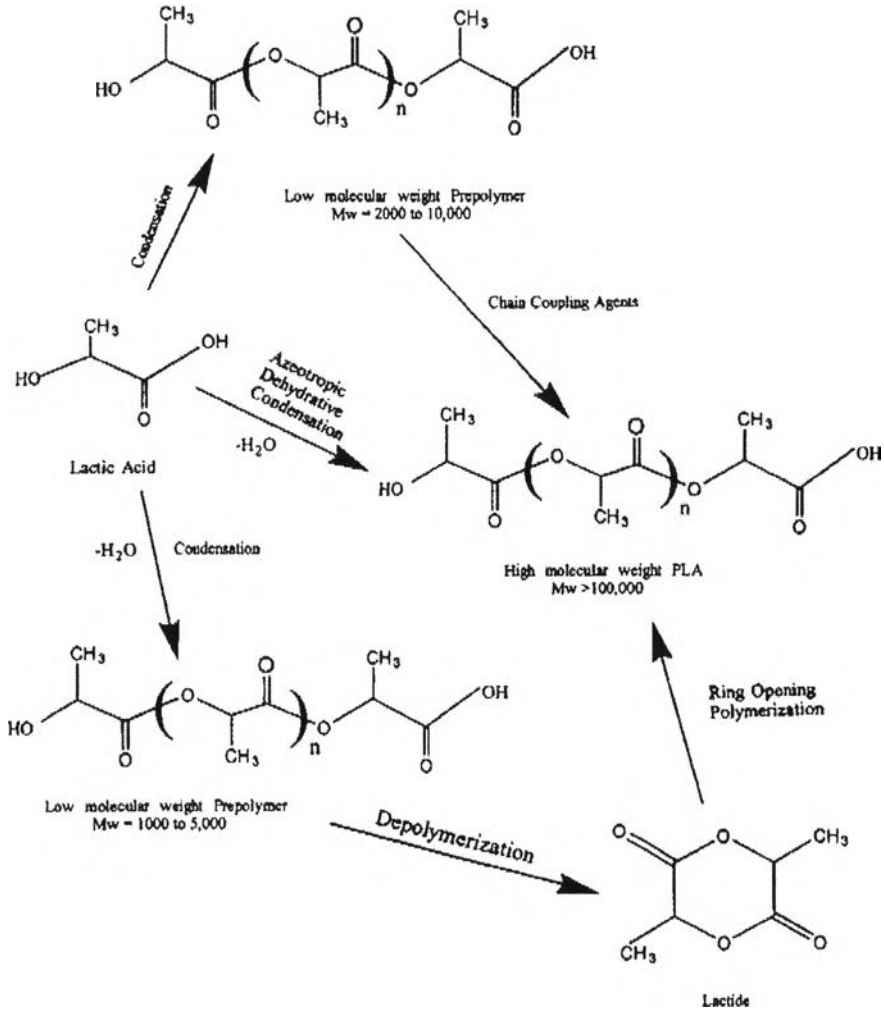

Figure 2.2 Synthesis methods for high-molecular weight PLA.

2.2.1 Direct Melt Polycondensation of Lactic Acid

Direct melt polycondensation is conventionally to produce aliphatic polyesters such as PET. The method is currently also utilized in the production of biodegradable polymers.

Lactic acid is condensation polymerized to yield a low molecular weight with low mechanical properties which, for the most part, is unusable for any applications unless external coupling agents are used to increase the molecular weight of the polymer. The molecular weight of this condensation polymer is low due to viscous polymer melt, presence of water impurities, statistical absence (low concentration) of reactive end-groups, and "back-biting" equilibrium that forms the six-member lactide ring.

The main benefit of direct melt polycondensation of lactic acid is the simplicity of the process due to the decreased steps of reaction, as compared to the Ring-opening polymerization (ROP) route (Moon *et al.*, 2000; Gao *et al.*, 2002).

The disadvantages of bulk polymerization of lactic acid in the melt phase include long reaction times, low reaction yields (typically < 80%), side reactions resulting in coloured bodies, and the low molar masses typically obtained (Hummel, 1982). The main reasons for the low molar masses are the high viscosity of the polymer melt and the presence of water and impurities in the reaction mixture (Kricheldorf *et al.*, 1996). The statistically decreasing probability of the chain ends to react as the polymerization proceeds and the ring-chain equilibrium leading to the formation of lactide and other oligomers have also negatively affects to achieve high molar mass. In direct polymerization reactions M_w/M_n typically approaches 2 at high conversion (Kricheldorf *et al.*, 2005).

2.2.2 Ring-opening Polymerization (ROP) of Lactide

The second route of producing PLA is to ring-open polymerize (ROP) lactide to yield high-weight (Mw>100,000) PLA collect and purify. The lactide method was the only method of producing pure and high-molecular-weight PLA until Mitsui Toatsu Chemicals recently commercialized a process wherein lactic acid and catalyst are azeotropically dehydrated in a refluxing (high-boiling and aprotic

solvent) under reduced pressures to obtain PLA with weight-average molecular weights greater than 300,000 (Garlotta, 2001).

The ROP process involves four main steps: (1) production of a low molar mass oligomer by direct melt polymerization (2) depolymerization of lactic acid oligomer into lactide by the back-biting mechanism, (3) purification of lactide, and (4) polymerization of lactide into high molar mass PLA (M_w> 100,000 g mol^{-1}) by the ROP mechanism (Broderick *et al.*, 2011). Bulk and melt ROP reactions are conducted below and above the melting point of PLA (typically 16 °C), respectively. (Kricheldorf and Serra, 1985) screened 24 different oxides, carbonates, and carboxylates in the bulk polymerization of lactide at 120, 150, and 180 °C. It was found that the most effective catalyst with respect to yield, molecular weight, and racemization were tin(II) oxide or octoate, lead(II) oxide, antimony octoate, and bismuth octoate. The best results were obtained from tin oxide and octoate at 120-150 °C with conversions up to 90%.

In solution polymerization, the reaction is conducted in an organic solvent. The large number of production steps of the ROP route is generally considered as drawback in comparison to the direct melt polymerization of lactic acid. The properties of the formed polymer are strongly dependent on the optical purity of the lactide used. Lactide is a ring-formed dimer that can exist in three different forms, L,L-, D,D-, and D,L-lactide. A 50:50 mixture of D,D and L,L-lactide is called *racemic (rac)*-lactide (Gregson *et al.*, 2006) as depicted in Figure 2.1. Lactide is manufactured by depolymerisation of poly(lactic acid), which is produced by direct melt polymerization and has a molecular weight in the range of 400–2500 g mol^{-1}. The depolymerization reaction is typically conducted at 130–230 °C at reduced pressure in the presence of 0.05–1.0 wt% tin dust in a continuous process.

2.3 Advantages and Limitations of PLA

2.3.1 PLA Advantages

2.3.1.1 Eco-friendly Polymer

PLA is biodegradable, recyclable, and compostable (Drumright *et al.*, 2000). Its production also consumes carbon dioxide (Dorgan *et al.*,

2001). These sustainability and eco-friendly characteristics make PLA an attractive biopolymer.

2.3.1.2 Biocompatibility

The most attractive aspect of PLA, especially with respect to biomedical applications, is its biocompatibility. A biocompatible material should not produce toxic or carcinogenic effects in local tissues. Also, the degradation products should not interfere with tissue healing. Moreover, PLA degradation products are non-toxic (at a lower composition) that is why it a natural choice for biomedical applications (Athanasiou *et al.*, 1996).

2.3.1.3 Processibility

PLA has better thermal processibility compared to other biopolymers such as poly(hydroxyl alkanoates) (PHAs), poly(ethyele glycol) (PEG), poly(ε-caprolactone) (PCL), etc. PLA can be processed by injection molding, film extrusion, blow molding, thermoforming, fiber spinning, and film forming (Auras *et al.*, 2004).

2.3.1.4 Energy Savings

PLA requires 25–55% less energy to produce than petroleum based polymers and some estimations show that this can be further reduced to less than 10% in the future (Vink *et al.*, 2003). Lower energy use makes PLA production potentially advantageous with respect to cost as well.

Although PLA is an eco-friendly bioplastic with excellent biocompatibility, processibility, and less energy dependence, it has drawbacks as well, which limit its use in certain applications.

2.3.2 PLA Limitations

2.3.2.1 Poor Toughness

PLA is a very brittle material with less than 10% elongation at break (Rasal and Hirt, 2008). Although its tensile strength and elastic modulus are comparable to poly(ethylene terephthalate) (PET), the poor toughness limits its use in the applications which need plastic deformation at higher stress levels.

2.3.2.2 Slow Degradation Rate

PLA degrades through the hydrolysis of backbone ester groups and the degradation rate depends on the PLA crystallinity, molecular weight, molecular weight distribution, morphology, water diffusion rate into the polymer, and the stereoisomeric content (Janorkar *et al.*, 2004). The degradation rate is often considered to be an important selection criterion for biomedical applications(Tokiwa and Calabia, 2006). The slow degradation rate leads to a long in vivo life time, which could be up to years in some cases (Bergsma *et al.*, 1995). There have been reports of a second surgery almost 3 years after implantation to remove a PLA-based implant (Incardona *et al.*, 1996). The slow degradation rate is a serious problem with respect to disposal of consumer commodities as well.

2.3.2.3 Hydrophobicity

PLA is relatively hydrophobic, with a static water contact angle of approximately 80 degree. This results in low cell affinity, and can elicit an inflammatory response from the living host upon direct contact with biological fluids (Burg *et al.*, 1999).

2.3.2.4 Lack of Reactive Side-chain Groups-PLA

PLA is chemically inert with no reactive side-chain groups making its surface and bulk modifications a challenging task.

2.4 Nucleating Agents for PLA

The good method for increasing the PLA crystallization rate is blending PLLA with nucleating agent. There were many reports showing potential nucleating agents. The nucleating agent can be classified into five types, i.e., inorganic, organic, stereocomplex of PLLA and PDLA, polymers, and supramolecular polymers.

2.4.1 Inorganic Compounds

Inorganic compounds, such as talc, calcium carbonate ($CaCO_3$) and clay, have been used as nucleating agents. Li *et al.* (2007) studied effect of nucleating agent by adding talc, sodium stearate and calcium lactate in PLLA. The isothermal data showed that talc was highly effective to nucleate PLLA at range 80-120 ^{o}C. Suksut *et al.* (2011) studied the effect of $CaCO_3$ and talc as nucleating agents

in PLLA to improve mechanical properties of PLLA. Both nucleating agents increased the degree of crystallinity of PLLA but decreased spherulite size. The optical micrographs are shown in Figure 2.3.

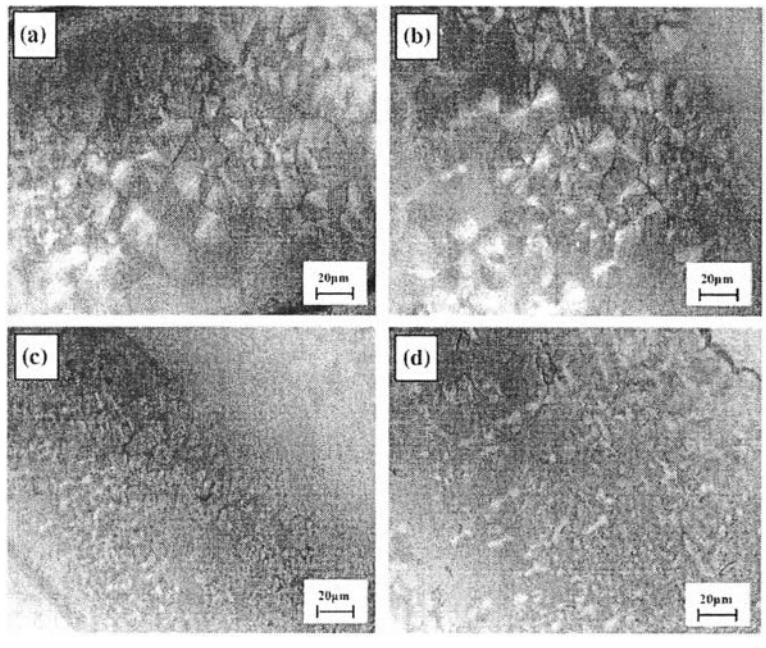

Figure 2.3 Optical micrographs of (a) neat PLLA, and PLLA with nucleating agents of (b) $CaCO_3$, (c) talc, and (d) α-CD at the isothermal crystallization temperature of 127 °C.

2.4.2 Organic Compounds

Organic compounds such as starch, cellulose, and N-aminophthalimide were reported as nucleating agents. Cai *et al.*(2011) studied the effect of thermoplastic starch (TPS) as nucleating agent for TPS/PLLA composites by isothermal crystallization kinetics. The TPS was found to improve the crystallinity of PLLA in composites. Kang *et al.* (2008) studied the effect of chemically modified thermoplastic starch (CMPS) based on the thermal properties of PLLA. The crystallinity and crystallization rate of PLLA were found to increase although the effect of CMPS as a nucleating agent was less than that of talc. Sobkowicz *et al.* (2008) studied the cellulose derived carbon nanospheres (CNS) as nucleating agents. The CNS increased nucleation and crystallization rate of PLLA. The crystallization of PLLA was increased up to 40% leading an increase of impact

resistance. Pei *et al.* (2010) studied how cellulose nanocrystals (CNC) and silylated cellulose nanocrystals (SCNC) could be nucleating agents for PLLA. It was found that modulus and tensile strength of the PLLA/SCNC nanocomposite films were higher than those of PLLA for 20% with only 1 wt.% well-dispersed SCNC. Kim *et al.* (2010) studied the effect of multi-walled carbon nanotube (MWCNT) by melt blending with MWCNT to find that the crystallization was occurred rapidly.

It should be noted that the inorganic and organic nucleating agents may induce phase separation in PLLA matrix.

2.4.3 Stereocomplexation of PLLA and PDLA

As poly(lactic acid) has a chiral center, the molecule can be L and D forms (Figure 2.4).

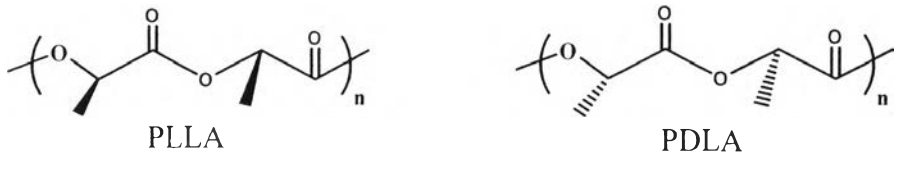

Figure 2.4 Structures of poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA).

In general, the fermentation of starch brings L-lactic acid. In some specific condition D-lactic can produced such as the use of L. delbrueckii, L. jensenii, and L. salivarius (Garlotta, 2001). Stereocomplex PLLA-PDLA can be prepared by simply mixing PLLA with PDLA. Polymer complex between two isomers is a good alternative to increase crystallization rate. A number of studies showed improvements of crystallization rate of PLLA under stereocomplex structure. Tsuji *et al.* (2006) found that an overall crystallization rate of PLLA stereocomplex is much higher than that of pure PLLA or PDLA. Brochu *et al.* (1995) found that PLLA showed the melting temperature (T_m) at 170-180 °C but the stereocomplex PLLA-PDLA showed T_m at 220-230 °C when the content of PDLA was only 10 wt%. Schmidt *et al.* (2001) and Yamane *et al.* (2003) confirmed that the stereocomplex PLLA-PDLA increased the number of PLLA spherulites and the

crystallization rate.

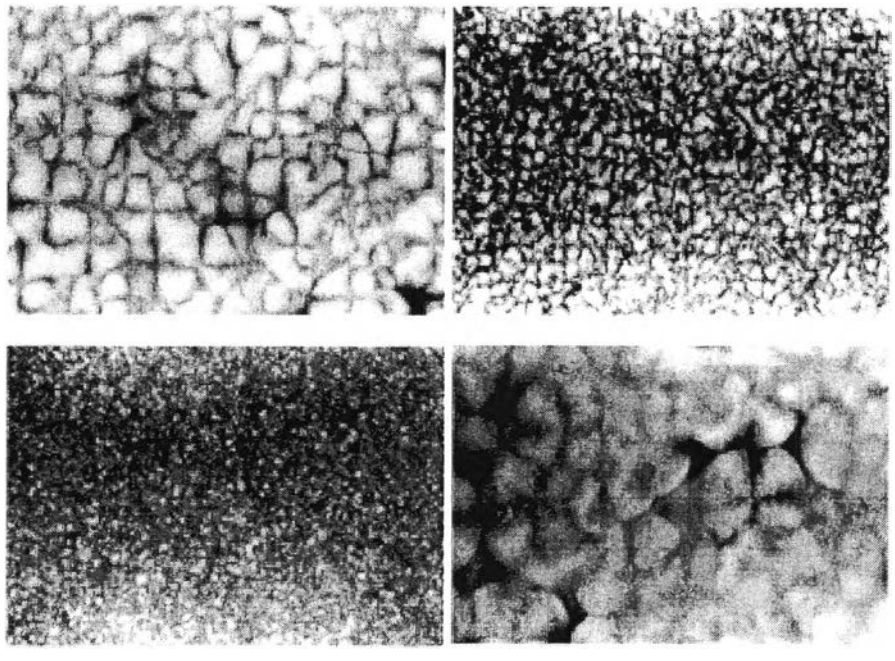

Figure 2.5 Optical micrographs of PLLA-PDLA blends grown isothermally at 120 °C after cooling from 200 °C.

Anderson *et al.* (2006) studied melt preparation and nucleation efficiency of stereocomplex PLLA-PDLA. In addition, Chen, *et al.* (2011) reported that the stereocomplex PLLA-PDLA prepared by melt mixing of PLLA and PDLA enhanced the melting point and spherulite growth rate as compared to PLLA and PDLA. The only problem is the high cost of PDLA.

2.4.4 Polymers

Sarazin *et al.* (2008) studied the blends of PLLA, polycaprolactone(PCL) and thermoplastic starch to improve their mechanical properties. It was found that ternary blend increased impact and elongation at break as compared to the pure PLLA. At the same time, Yokohara *et al.* (2008) studied binary blends of PLLA and poly(butylenes succinate) (PBS) to find that although PLLA and PBS were immiscible, PBS accelerated the crystallization of PLLA and at that time the molten PBS droplets acted as crystallization nuclei for PLLA.

2.4.5 Supramolecular PLLA

Supramolecular polymers including dendritic polymer, hyperbranched polymer and multi-arm star polymers are expected as an effective nucleating agent because of their multi-functional groups.

Wen *et al.* (2010) studied the effect of p-tert-butylcalix[8]arene (TBC8-eb) as a novel active nucleating agent on the isothermal crystallization of poly(lactic acid) (PLLA). The chemical structure is presented in Figure 2.6.

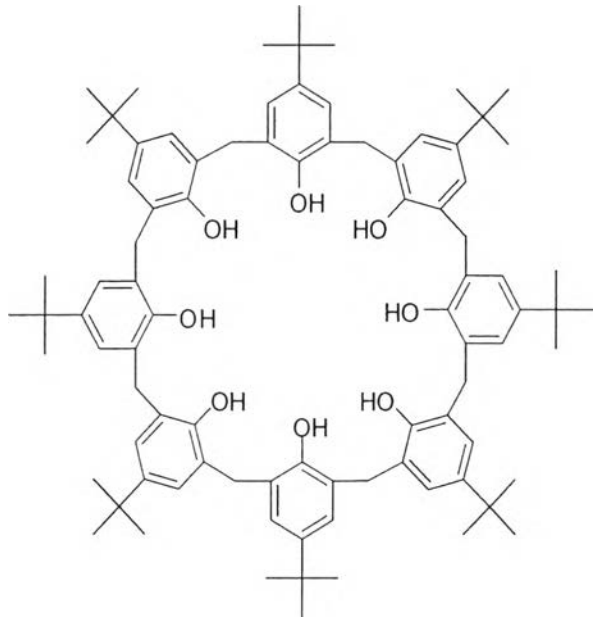

Figure 2.6 Structure of p-tert-butylcalix[8]arene (TBC8-eb).

It was explained that TBC8-eb initiated the conformational order of PLLA in the isothermal crystallization based on the interaction between methyl group and PLLA chains. A couple of methyl groups which formed a short helical structure improved PLLA crystallization rate. Zhang, *et al.* (2004) studied the effect of dendritic hyperbranched polymer (DHP) for using as a nucleating agents. The chemical structure is presented in Figure 2.7.

DHP can improve tensile strength and elongation at break of PLLA. In addition, DHP acted as nucleation agents and significantly increased crystallization rate and crystallinity of PLLA.

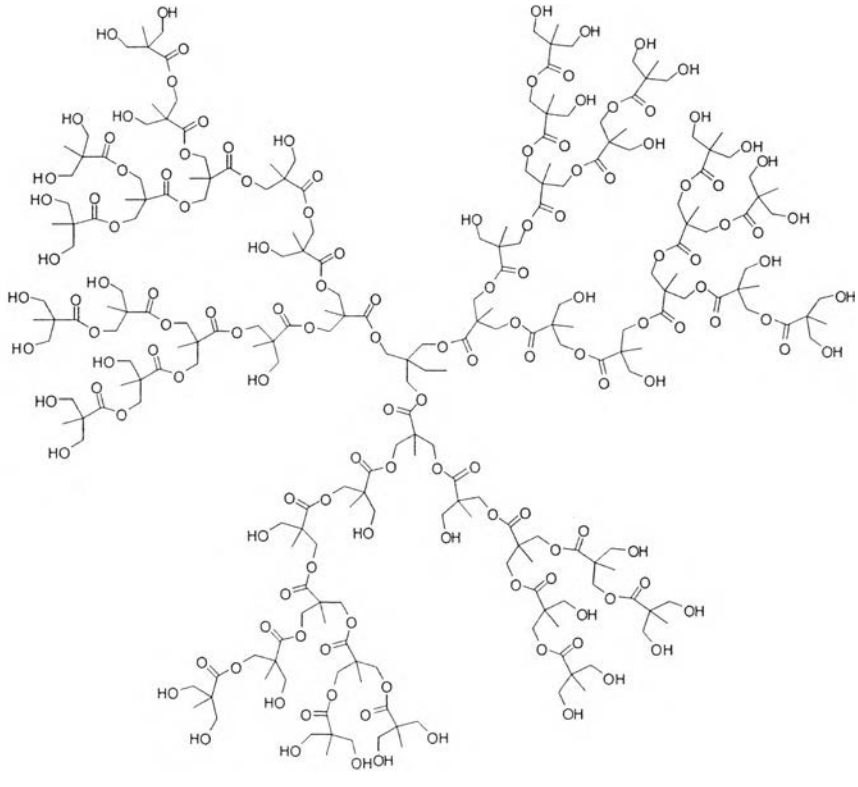

Figure 2.7 Structure of dendritic hyperbranched polymer (DHP).

The preparation of hyper-branched polymers could be accomplished generally in two important synthetic methods; there are the "arm-first" and "core-first" approach. Hao *et al.* (2005) studied synthesis of star-shaped PLLA by "core-first" approach. The 3- to 6-armed star-shaped PLLAs were synthesized through ring-opening polymerization of L-lactide with natural sugar alcohols of glycerol, erythritol, xylitol, and sorbitol as initiators (Figure 2.8). In addition, they studied crystallization kinetic of star-shaped PLLAs, the results showed that the more arms of a star-shaped polymer had lower spherulite growth rate.

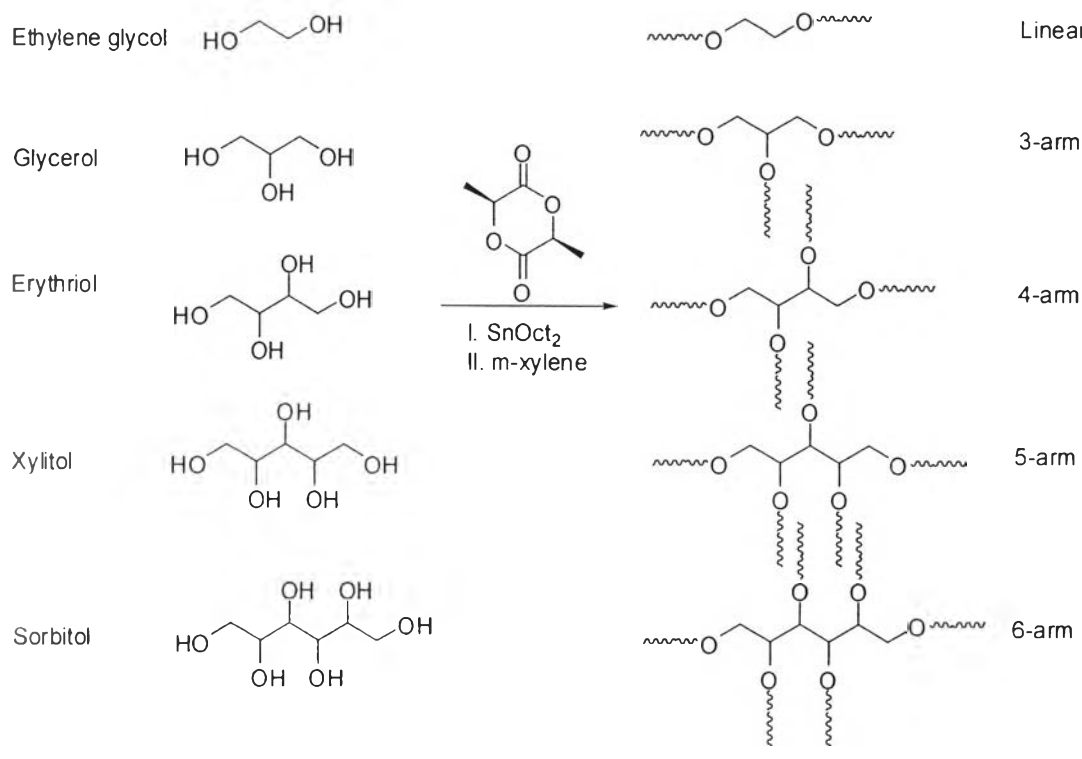

Figure 2.8 Chemical preparation of star-shaped PLLAs initiated with diverse reduced sugar alcohols.

2.5 Plasticization of PLA

Amorphous PLA exhibits the glass transition temperature (T_g) in the range of 50–60 °C. Below that temperature PLA is rigid and brittle having the elastic modulus about 3 GPa and low ability to plastic deformation.The brittleness and stiffness of PLA are major drawbacks for some application. Any factor influencing PLA crystallinity, such as isomer ratio, could disturb the distribution and compatibility of plasticizers with PLA which leads to low efficiency and phase separation (Labrecque *et al.*, 1997; Ljungberg and Wesslén, 2003). Crystallinity, if developed, increases slightly the modulus of elasticity and further decreases the drawability (Perego *et al.*, 1996). To modify the properties, PLA has been blended with other polymers including poly(3-methyl-1,4-dioxan-2-one)(Bechtold *et al.*, 2001), starch (Martin and Avérous, 2001), poly-3-caprolactone (Tsuji *et al.*, 2009), poly(vinyl acetate) (Gajria *et al.*, 1996), poly(methyl methacrylate) (Eguiburu *et al.*,

1998), poly(hydroxy butyrate) (Focarete *et al.*, 1998) and poly(ethylene oxide) (Nijenhuis *et al.*, 1996). Citrate esters (Labrecque *et al.*, 1997; Ljungberg and Wesslén, 2003), and poly(ethylene glycol) (PEG) (Jacobsen and Fritz, 1999; Hassouna *et al.*, 2011) were found to be efficient plasticizers for PLA. Recent studies of PLA plasticized with PEG have demonstrated the increase in efficiency of plasticization with a decrease of PEG molecular weight; low molecular weight plasticizer enables increased miscibility with PLA and more efficient reduction of T_g. The transition from brittle to ductile behavior of plasticized PLA occurred when T_g was shifted to 35 °C. The cold-crystallization temperature of PLA decreased in parallel with the shift in T_g (Baiardo *et al.*, 2003). These effects are enhanced not only by the lower molecular weight of PEG but also by its higher content. However, at certain PEG content, dependent on its molecular weight, blends of PLA with PEG undergo phase segregation. As it has been reported recently (Hu *et al.*, 2003), blends of PLA with low stereo-regularity at 30 wt% of PEG having molecular weight of 8000 g mol^{-1} were unstable. This relates to the slow crystallization of PEG that depletes the amorphous phase of the plasticizer. Blends of PLA with a high stereo-regularity of 30 wt% of the same plasticizer undergo the phase separation with little or no crystallization (Hu *et al.*, 2003).

Lactide monomer an effective plasticizer for PLA, but lead to high migration due to their small molecularsize. Oligomeric lactic acid (OLA) seems to be a better answer, since it shows low migration and high efficiency(Martin and Avérous, 2001). For instance, adding 20 wt% of OLA to poly(92%L-lactide, 8% *meso*-lactide) induced low T_g and modulus decreases of 20°C and 63%, respectively. A significant improvement of PLA flexibility was accomplished by the incorporation of different types of citrates (Labrecque *et al.*, 1997; Ljungberg and Wesslén, 2003; Ljungberg and Wesslén, 2005) or maleates (Zhang and Sun, 2004) whose efficiency was evaluated in terms of T_g shift and mechanical properties improvement. These plasticizers were miscible with PLA up to 25 wt%, but increasing the plasticizer content can rise the PLA crystallinity by enhancing chain mobility (Martin and Avérous, 2001). Polypropylene glycol (PPG) (Piorkowska *et al.*, 2006) and fatty acid are also compatible with PLA and can act as plasticizers. In the case of plasticized PLA with PPG, it was found that the PPG enhanced the spherulite growth rate

(Kulinski and Piorkowska, 2005). In contrast, the lower M_w plasticizer enables increased miscibility with more effective reduction of Tg of PLA. The Tg value was decreased with increasing of PEG content. The cold crystallization peak (T_c) were narrowed and shifted to lower temperature. T_c values depended on the plasticizer content but were independent to the molecular weight. T_c values of PLA were decreased when the PEG content increased (Kulinski and Piorkowska, 2005; Piorkowska *et al.*, 2006).(Sobkowicz *et al.*, 2008)