

Review

Poly(lactic acid) (PLA): Research, development and industrialization

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Poly(lactide) (PLA) is a biodegradable, aliphatic polyester derived from lactic acid. It has similar mechanical properties to polyethylene terephthalate, but has a significantly lower maximum continuous use temperature. PLA products can be recycled after use either by remelting and processing the material a second time or by hydrolyzing to lactic acid, the basic chemical. In this review, the technologies for polymerization of the lactic acid and the comparison of physical, thermal and mechanical properties, biodegradability, and biocompatibility of the PLA and copolymers with other similar polymers are described.

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1 Introduction

Poly(lactide) (PLA) is a biodegradable, aliphatic polyester derived from lactic acid made from renewable resources, such as corn starch or sugarcane [1, 2]. Lactide is the cyclic dimer of lactic acid, and is produced by a combined process of oligomerization and cyclization [3]. PLA has similar mechanical properties to polyethylene terephthalate (PET), but has a significantly lower maximum continuous use temperature. Poly(L-lactide) (PLLA) is the most important PLA. It is a semicrystalline polymer and has a crystallinity ~37%, a glass transition temperature (T_g) of ~67°C and a melting

temperature (T_m) of ~180°C [4]. PLA can be processed like all other thermoplastic polymers using extrusion, injection molding, blow molding, or fiber spinning into various products [5, 6]. The products can be recycled after use either by remelting and processing the material a second time, or by hydrolysis to lactic acid, the basic chemical. Another possibility is to compost the PLA to introduce it into the natural life cycle of all biomass, where it degrades into CO₂ and water. PLA can therefore be recycled in traditional ways, composted like all other organic matter, burnt in an incineration plant (a process that is not harmful to the environment) or introduced into a classical waste management system [7, 8].

PLA can be prepared by direct polycondensation of lactic acid [6]. However, it is usually difficult to obtain high molecular weight polymer by polycondensation [9]. Because each step of polymerization generates one molecule of water, the presence of water degrades the forming polymer chain and results in the generation of low molecular weight PLA. Therefore, water has to be removed during the polycondensation to generate PLA of high molecular weight. Yamaguchi *et al.* [10] have reported the synthesis of high molecular weight PLA using a molecular sieve to remove water during direct polycondensation. However, long reaction times

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Abbreviations: P3HB, poly(3-hydroxybutyrate); PCL, poly(ϵ -caprolactone); PCLA, poly(L-lactic acid-co- ϵ -caprolactone); PDLA, poly(D-lactide); PET, polyethylene terephthalate; PGA, poly(glycolide); PLGA, poly(glycolic acid-co-lactic acid); PLLA, poly(L-lactide); P_m , probability of meso linkages; P_r , probability of racemic linkages; PTMC, poly(trimethylene carbonate); rac-LA, 1:1 mixture of L-LA and D-LA; ROP, ring-opening polymerization; T_g , glass transition temperature; T_m , melting temperature

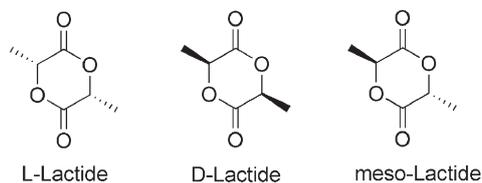


Figure 1. Stereoisomers of lactide.

and high temperatures are required in lactic acid polycondensation [11].

Ring-opening polymerization (ROP) of lactide is a preferred route to prepare PLA because of the higher controllability of the polymerization [12]. Indeed, high molecular weight PLA can be obtained by ROP of lactide [13]. Because one lactide molecule has the two chiral carbon atoms, three stereoisomers of lactide can be generated (L, D, and meso-lactide) (Fig. 1). The 1:1 mixture of L and D-lactide is racemic-lactide (rac-LA).

Since lactide monomer is chiral, the control of PLA stereochemistry is easily achieved by the polymerization of L, D and meso-lactide stereochemical forms. Modulation of the polymer stereochemistry leads to PLA with dramatically different properties. For example, PLLA is a semicrystalline polymer (T_g at 67°C, melting transition at 180°C), while poly(rac-lactide) is an amorphous material (T_g at 58°C). The degree of crystallinity of PLA decreases dramatically as the L content decreases over a narrow compositional range from 100% to 92%. The degree of crystallinity of PLA with 85% L content was amorphous [14].

2 Technologies for polymerization of the lactic acid

Figure 2 depicts the known routes of lactic acid production, oligomer formation, ROP, synthesis of high

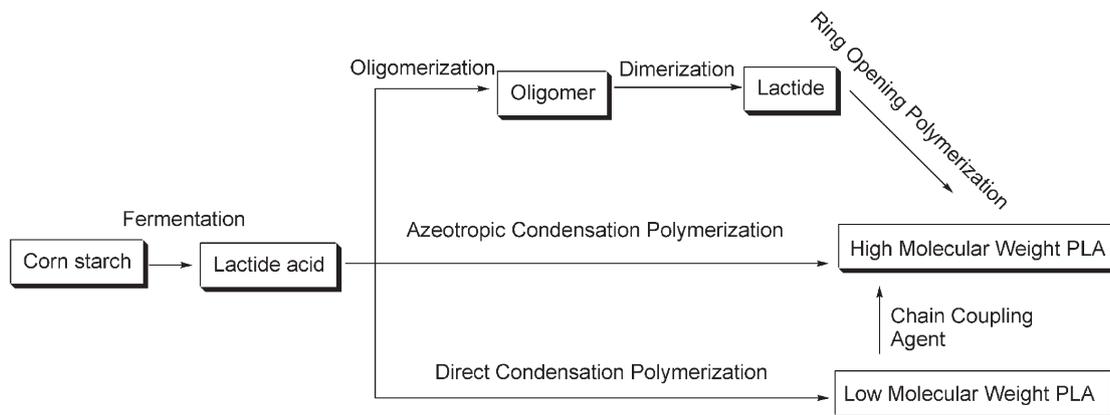


Figure 2. Synthesis methods for PLA.

molecular weight PLA from low molecular weight PLA.

2.1 Condensation polymerization of lactic acid

Condensation polymerization of lactic acid usually yields low molecular weight, brittle, glassy PLA, which is unusable for applications as it is. External coupling agents, such as esterification-promoting adjuvants and chain-extending agents, are used to obtain higher molecular weight PLAs [15].

Dicyclohexylcarbodiimide (DCC), carbonyl diimidazole and bis(trichloromethyl) carbonate have been used as esterification-promoting adjuvants. The disadvantages of these adjuvants are the necessity for dangerous solvents, the inability to form copolymers with different functional groups, and higher costs due to the increase number of reaction and separation steps. The use of chain-extending agents can help to overcome many of these disadvantages. However, polymers also contain unreacted chain-extending agents or residual metal, and the extending agents are not biodegradable or bioabsorbable.

A one-step azeotropic condensation polymerization of lactic acid can yield high molecular weight polymer without the use of additional chain extenders or adjuvants. After removing the solvent, high molecular weight PLAs can be isolated for use as is or for further purification [16–18].

2.2 ROP of lactide

The ROP of lactide was first demonstrated by Carothers in 1932 [19], but high molecular weights were not obtained until in 1954, when the purification techniques of lactide were developed by Dupont [20].

Classified by reaction mechanism, cationic, anionic and coordination-insertion ROP were defined

[5, 21, 22]. It is very difficult to obtain high molecular weight PLA by cationic ROP of lactide. Moreover, anionic mechanism ROP of lactide usually leads to problems in controlling the molecular weight and molecular weight distribution of the PLA, which is mainly caused by side reactions and inter-/intra-molecular transesterification reactions [23]. Therefore, the study of metal complexes that catalyze lactide polymerization via a coordination-insertion mechanism has become an important topic [22].

Metal alkoxide-catalyzed coordination-insertion mechanism involves four steps, as depicted in Fig. 3. The most widely used catalyst for the industrial production of PLA is tin(II) bis(2-ethylhexanoate), usually referred to as tin(II)octanoate or $\text{Sn}(\text{Oct})_2$ [24–26]. Aluminum alkoxides have also been proven to be efficient initiator/catalysts for the ROP of lactide [27–29]. Although these metal alkoxides are efficient catalyst/initiators for the ROP of lactide, there is no preference for one of the three different stereoisomers of lactide, so the polymers obtained by these catalysts have a random placements of lactide monomers. Stereoregular polymers can be obtained only by using enantiopure L-lactic acid or D-lactic acid monomer.

Since stereocomplex polymers formed by an equal mixture of PLLA and poly(D-lactide) (PDLA) have many advantages, such as higher T_m (230°C) [7], many efforts have been made to obtain crystalline PLA via direct ROP of racemic lactide using stereoselective catalysts [5, 30–38]. Stereoregular PLA can be prepared from rac- or meso-LA using a variety of single-site metal complexes, which function via two different mechanisms (i) a chain-end-control mechanism, with which isotactic PLA is obtained from rac-LA and heterotactic PLA by using meso-LA, or heterotactic PLA is obtained from rac-LA and syndiotactic PLA from meso-LA [33]; or (ii) an enantiomeric site-control mechanism, in which only isotactic or syndiotactic PLA can be obtained from rac- or meso-LA, respectively [35, 36].

Several types of stereoselective catalysts that catalyze the polymerization of rac-LA to form isotactic/stereoblock PLAs have been investigated. The most important breakthrough in the field of stereoselective polymerization of lactide was made by Spassky *et al.* [39]. They discovered that in an enantiomerically pure Schiff base aluminum methoxide (R,R)-1-initiated rac-LA polymerization, the polymerization rate of (R,R)-LA was 19 times higher than that of (S,S)-LA. The resulting PLA had a tapered stereoblock microstructure, in which the stereoblock distribution changed from all (R,R) units to all (S,S) units over the polymer

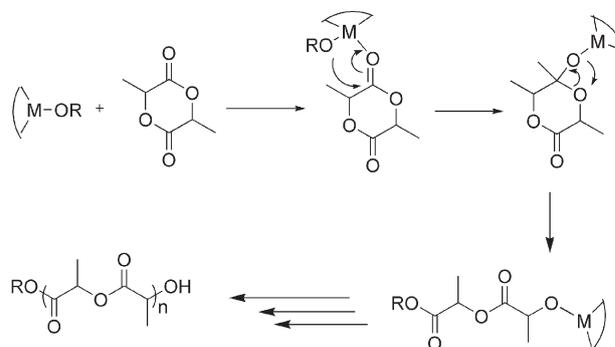


Figure 3. Mechanism of a coordination-insertion mechanism in the ROP of lactide.

chain. Since then, it has been demonstrated that single-site metal alkoxides supported by various kinds of auxiliary ligand frameworks have unique advantages in carrying out well-controlled, and in certain cases stereoselective, polymerization of lactides. Coates and Ovitt [31, 34] prepared compound 1 and 2. They reported that the polymerization of rac-LA using rac-2 at 70°C gave a stereoblock PLA material (Fig. 4). Schiff base aluminum isopropoxides (R,R)-3 and rac-3 were reported by Feijen and colleagues [35, 36] (Fig. 4). (R,R)-3 showed a strong preference for the polymerization of (S,S)-LA ($k_{SS}/k_{RR} = 14$), and rac-3 initiated and catalyzed the polymerization of rac-LA to form a stereoblock PLA with a probability of meso linkages (P_m) value of 0.93 at 85% conversion of rac-LA. This excellent stereocontrol was still maintained even in a bulk polymerization (130°C, $P_m = 0.88$). This was the first time that a highly isotactic PLA was obtained under bulk polymerization conditions from rac-LA. Nomura *et al.* [33] reported on the stereoselective polymerization of rac-LA using *in situ*-formed aluminum alkoxides from the achiral Schiff base aluminum ethyls 4 and 5 with bulky tert-butyl groups at the ortho and para positions of the phenol group. Using benzyl alcohol as an initiator, complexes 4 and 5 catalyzed rac-LA polymerization via a chain-end-control mechanism. Complex 5 furnished PLA with an isotacticity ($P_m = 0.91$) higher than that of PLA obtained with complex 4. Chen and colleagues [37] reported that complex 6 has a high isoselectivity in the polymerization of rac-LA, generating a stereoblock PLA with a P_m value of 0.90. They also synthesized complex 7 [37], which gave the same isoselectivity and polymerization rate constant as that of 6/2-propanol. Further polymerizations carried out by Nomura and coworkers [40] showed that compound 7 maintained a high isoselectivity in bulk polymerization of rac-LA. Nomura *et al.* [41] have reported a Schiff base aluminum complex 8

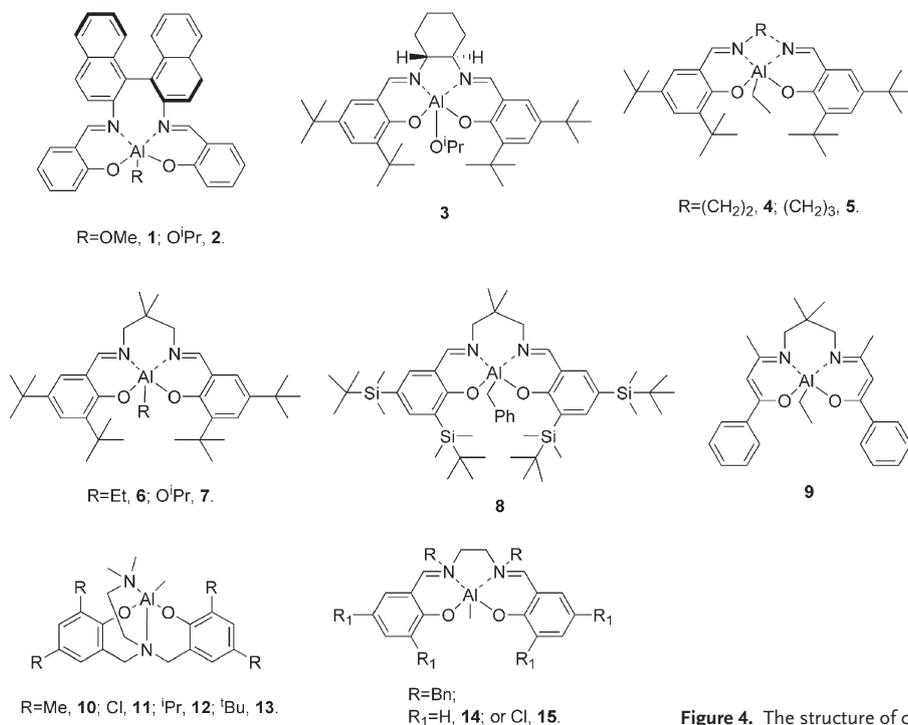


Figure 4. The structure of catalysts 1–15.

with flexible, but bulky, ^tBuMe₂Si substituents at the ortho and para positions of the phenol groups. This catalyst induced stereoblock PLA formation from rac-LA with a P_m value of 0.98. Up to now, this is the highest isotactic stereoblock PLA that has been prepared using an achiral catalyst/initiator system in rac-LA polymerization. Chen and colleagues [38, 42] also reported a series of tetradentate enolic Schiff base aluminum ethyl complexes, and found that lengthening the ethylene diimine bridge to a propylene diimine bridge and the presence of electron-withdrawing substituents at the 5-position in the diketone skeleton resulted in a remarkable enhancement of both stereoselectivity and polymerization rate. Using 2-propanol as an initiator, complex **9** polymerized rac-LA to form isotactic enriched PLA with a P_m of 0.78. A family of aluminum methyl complexes supported by tetradentate aminophenoxide ligands has been prepared by Gibson (Fig. 4) [43]. Complexes **10** and **12** furnished isotactic-biased PLA with P_m values of 0.73 and 0.65, respectively. However, complex **13** led to a slight heterotactic polymerization of rac-LA, affording PLA with a probability of racemic linkages (P_r) value of 0.57. Complex **11** only gave an atactic material from rac-LA. Heterotactic PLA can be produced by stereoselective catalysis of rac-LA polymerization. Gibson and coworkers [44] have found a remarkable stereocontrol of achiral aminophenoxide aluminum methyl complexes in the

ROP of rac-LA. Using benzyl alcohol as an initiator, these complexes catalyzed rac-LA polymerizations and afforded highly isotactic PLA with a P_m value of 0.88 using complex **14**, and highly heterotactic PLAs with a P_r value of 0.96 using complex **15**. This was the first time that aluminum complexes were found to furnish a highly heterotactic PLA, and the first time that a dramatic switch in tacticity of the resulting PLA was observed upon changing the substituent pattern at the ortho and para positions of the phenol group in the complexes.

Coates and coworkers [31, 45] reported zinc isopropoxide (compound **16**) and zinc methyl lactate (compound **17**) (Fig. 5). They were both efficient initiators for lactide polymerization, producing PLAs with predictable molecular weights and narrow molecular weight distributions. Notably, complex **16** initiated the stereoselective ROP of rac-LA via a chain-end-control mechanism, yielding highly heterotactic microstructures with a P_r value up to 0.90 at room temperature and 0.94 at 0°C. The monomeric zinc triphenylsilanoxide (complex **18**) supported by a β -diketiminato ligand [46] with a tetrahydrofuran (THF) molecule coordinated to the central zinc atom was shown to have the same heteroselectivity toward rac-LA in THF as that of the dinuclear zinc complex **16** in CH₂Cl₂. Although the magnesium complexes **19** and **20** as reported by Chisholm *et al.* [47, 48] do not show stereoselectivity toward rac-LA either in CH₂Cl₂ or ben-

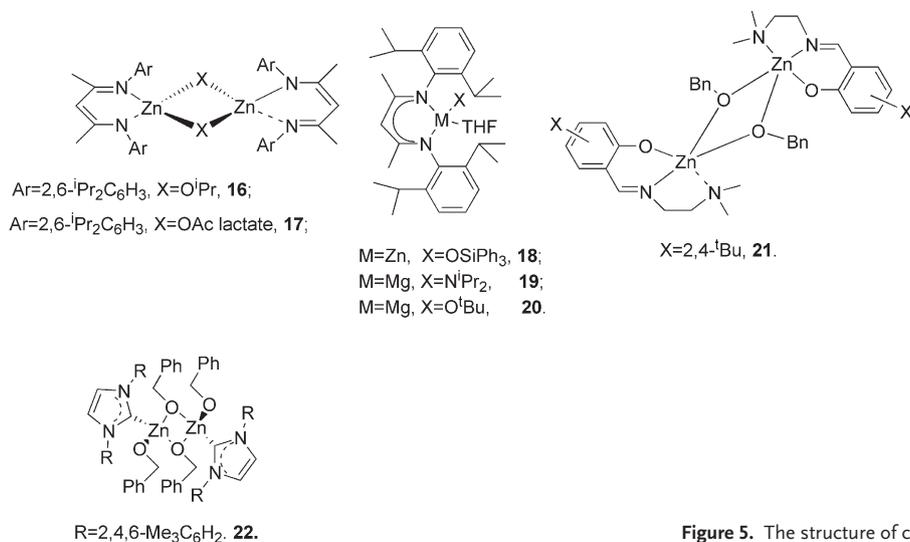


Figure 5. The structure of catalysts 16–22.

zene, they have a similar heteroselectivity to that with complex 16 in THF. It seems that the THF molecule coordinated to the central metal atom plays an important role in enhancing the heteroselectivity of the β -diketiminato zinc or magnesium complexes. Lin and coworkers [49] synthesized dinuclear zinc complexes supported by a *N,N,O*-tridentate Schiff base ligand framework. The reactivities of these complexes were dramatically affected by both the electronic and steric properties of the substituents at the ortho and para positions. All these complexes furnished heterotactic PLA from rac-LA. Notably, a heterotactic PLA with a high P_r value up to 0.91 can be obtained at -55°C using complex 21. Tolman, Hedrick and colleagues [50–52] discovered that the dinuclear zinc complex 22 furnished heterotactic-biased PLA with a P_r value of 0.60 at room temperature in rac-LA polymerization.

Chisholm *et al.* [53] used trispindazolyl(Tp)-hydroborate ligands to coordinate calcium to form efficient initiators for lactide polymerization, as shown in Fig. 6. Complex 23 revealed rapid polymerizations of rac-LA, achieving 90% conversion within 5 min. Complex 24 produced an extremely rapid rac-LA polymerization, achieving 90% conversion in less than 1 min. Moreover, complex 25 furnished a heterotactic PLA material from rac-LA with a P_r value of 0.90. A germanium alkoxide, complex 26, supported by a C_3 -symmetric amine-(trisphenolate) ligand was recently reported by Davidson and colleagues [54]. This compound has been applied in the bulk polymerization of rac-LA at 130°C and the polymers produced revealed a strong heterotactic bias ($P_r = 0.78$ – 0.82). This was

the first example of a highly heteroselective polymerization of rac-LA under solvent-free conditions at a relatively high temperature. Okuda [55, 56] synthesized a series of scandium complexes supported by 1, ω -dithiaalkanediy bridged bis(phenolate) ligands. It was found that both using THF as solvent and bulky substituents at the ortho position of the phenol group largely improved the heterotacticity of the isolated PLAs. Moreover, the complex with a propylene dithialkane bridge improved the heteroselectivity. At 25°C in THF, complex 27 furnished heterotactic PLA from rac-LA with a P_r up to 0.96. Carpentier and coworkers [56–58] introduced bulky substituents at the ortho and para positions of the phenol group and changed the donor group on the pendent chain from methoxy ether to a dimethyl substituted amine group. Complex 28 produced substantially heterotactic PLAs with a P_r of up to 0.90 at 20°C . Cui and colleagues [59] also reported a series of THF-solvated lanthanide (mono)alkyl complexes supported by *O,N,N,O*-tetradentate diamine bis(phenolate) ligands. Complexes 29 and 30 displayed modest activity but high stereoselectivity in the polymerization of rac-LA to give highly heterotactic PLA with P_r values ranging from 0.95 to 0.99. Free carbene complex 31-catalyzed polymerization produced isotactic enriched PLA with a P_m value of 0.75 from rac-LA in CH_2Cl_2 at -20°C . Most notably, achiral carbene complex 32 produced highly isotactic PLA with a P_m value up to 0.90 from rac-LA at -70°C , and heterotactic-biased material with a P_r value of 0.83 from meso-LA at -40°C . Both enantiomerically pure and racemic carbene complex 33 furnished highly isotactic poly(rac-LA) at -70°C with a P_m value of 0.88.

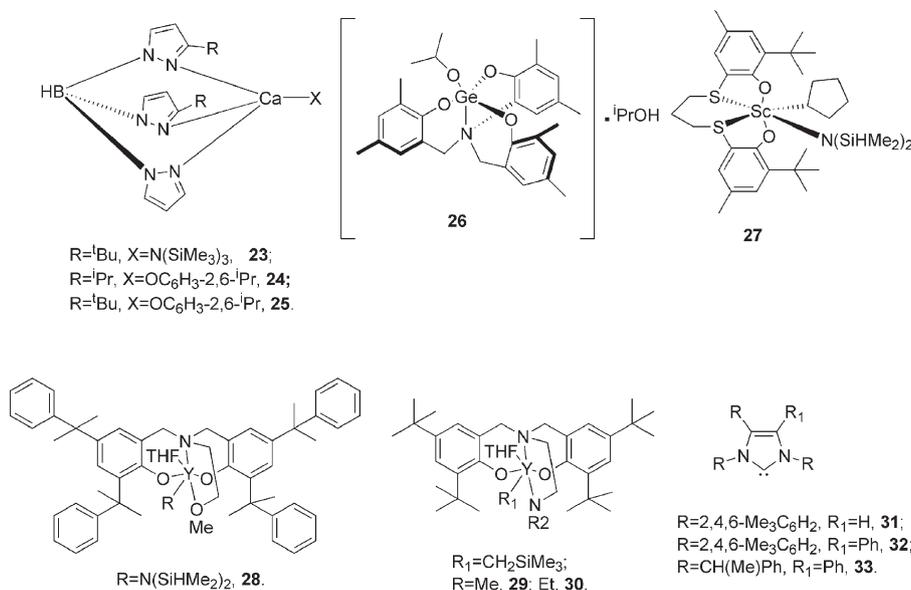


Figure 6. The structure of catalysts 23–33.

3 Comparison of properties of PLA and copolymers with other similar polymers

3.1 Physical, thermal and mechanical properties

The physical, thermal and mechanical properties of PLA and its copolymers are very dependent on the molecular weight, molecular weight distribution, and composition. In the solid state, the PLA can be either amorphous or semicrystalline depending on the stereochemical composition and thermal history. Thus, a variety of PLA with different physical properties can be easily achieved by controlling polymerization of different optical monomers to form different stereochemical make-ups. The most common polymers are the homopolymer PLLA and its enantiomer PDLA, which can be synthesized by direct ROP of the corresponding L-lactide and D-lactide monomers. Crystalline PLLA and PDLA show a typical T_g at about 58°C and a T_m in the 170–180°C range (Table 1 summarizes the properties of PLA and some other polyesters). The wide T_m range is due to the small and imperfect crystallites, slight racemization and some impurities in the polymer [60]. As shown in Table 1, PLA, poly(glycolide) (PGA), and aromatic polycarbonates have a T_g above the room temperature, rendering them hard and brittle, whereas poly(ϵ -caprolactone) (PCL), poly(3-hydroxybutyrate) (P3HB) and poly(trimethylene carbonate) (PTMC) have a lower T_g and show tougher properties. The mechanical properties of PLA exhibit tensile strength and modulus higher than other polyesters.

However, the toughness is poor with less than 10% elongation at break, which limits the applications of PLA [61]. To address this issue and increase the range of applications of the PLA materials, numerous efforts have been made to modify PLA, including stereocomplexes of PLLA/PDLA, copolymerization and blending. The correlation of the properties with the polymer composition are discussed briefly below.

Stereocomplex formation between PLLA and PDLA enhanced the mechanical properties, the thermal resistance, and the resistance to hydrolysis of the PLA-based materials due to the strong interaction between L-lactyl unit sequences and D-lactyl unit sequence [62]. Tsuji *et al.* [63] demonstrated the formation of a favorable stereocomplex by equimolar mixing of PLLA and PDLA. The T_m of the stereocomplex increased to around 230°C (Table 1), which is 40–50°C higher than that of PLLA, showing its potential for high-performance applications. It has been reported that the tensile properties (including tensile strength, Young's modulus and elongation at break) could be improved by stereocomplexation of enantiomeric PLAs of either low or high molecular weight [64]. The thermal stability could also be improved by the stereocomplexation revealed by T_g measurements. The ΔE_{td} (the activation energy for thermal degradation) of stereocomplexes were reported to be 82–110 kJ/mol more than the average ΔE_{td} values of nonblended PLLA and PDLA [65].

Copolymerization is the most direct and effective route towards PLA-based materials with a wide range of properties. Some common polyesters

Table 1. Physical properties of PLA and some polyesters^{a)}.

Properties	Stereocomplexed PLA	PLLA or PDLA	PGA	PCL	P3HB	PC
T_g (°C)	65–72	58	40	–60	5	140–155 ^{b)} –15––26 ^{c)}
T_m (°C)	220–230	170–190	225–230	60	180	–
ΔH_m (J/g)	142, 146	40–50, 93	180–207	142	146	–
$T_{decomposition}$ (°C)	–	310	360	350, 402	–	–
Density (g/cm ³)	–	1.25–1.29	1.50–1.69	1.07–1.20	1.17–1.26	1.20
Tensile strength (GPa)	0.88 ^{d)}	0.12–2.3 ^{d)}	0.08–1 ^{d)}	0.004–0.78	0.18–0.20 ^{d)}	0.06
Young's modulus (GPa)	8.6 ^{d)}	7–10 ^{d)}	4–14	0.21–0.44	5–6	0.118
Elongation at break (%)	30 ^{d)}	4–7	30–40	20–1000	50–70	110

a) Modified from [55, 62, 70, 87, 88]. ΔH_m , Enthalpy of melting of crystal having infinite size, $T_{decomposition}$, decomposition temperature; PC, polycarbonate.

b) Aromatic PC

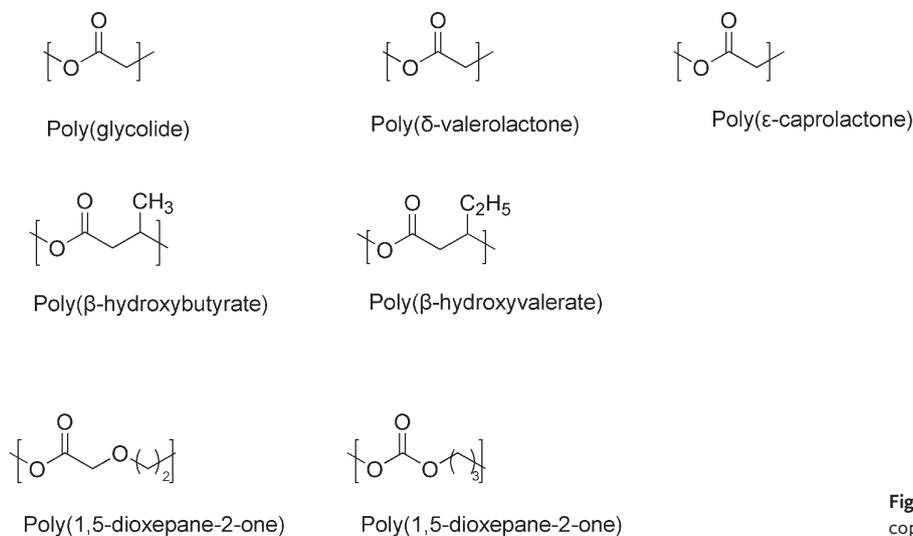
c) PTMC

d) Oriented fiber

used for copolymerization with PLA are illustrated in Fig. 7. The incorporation of a polyester backbone with PLA leads to a decrease of the crystallinity and melting point, while the mechanical properties of the copolymers can be varied to a large extent ranging from soft and elastic plastics to stiff and high strength materials [66]. For example, copolymerization of ϵ -caprolactone with lactide leads to poly(ϵ -caprolactone-co-lactide) (PCLA). The crystallinity decreases quickly from 73% (PCL) to 31% (PCLA containing 20 wt % LA units) and does not occur if the LA content is higher than 30 wt% [67]. The T_g of PCLA also shows a LA content-dependent feature, increasing with the increase LA unit content and fitting well with the Fox equation [67, 68]. The mechanical properties of PCLA differ, widely depending on the compositions [68]. The tensile strength and modulus of the copolymers is lower than PLLA homopolymer, whereas nearly all

copolymers possess a higher maximum strain (>100%). The elongation at break of the PCLA copolymers is in the range 0.1–10, which is lower than PCL but comparable to PLLA.

Polymer blending is another method extensively used to modify PLA-based materials to obtain the desired properties. A variety of materials such as plasticizers, olefin polymers/fiber, inorganic materials, natural polymers, and biodegradable polyesters have been used to blend with PLA [61]. The properties of the PLA blends are highly dependent on nature of the components as well as the composition. Taking PLA blended with PCL as an example, the mechanical properties can be tuned through the variation of blend compositions. The modulus and ultimate tensile strength increase almost linearly as a function of PLA composition when the PLA mass fraction is above 0.4. The strain-at-failure decreases with increasing PLA

**Figure 7.** Common repeating units of PLA-based copolymers.

content, becoming flat above PLA mass fraction reaches 0.6 [69].

3.2 Biodegradability and biocompatibility

Biodegradability of the polyester plays a prominent role in biomedical applications as well as eco-materials. The biodegradation of the PLA and its copolymers has been shown to be dependent, among others, on the chemical structure of the backbone and end group, molecular weight and its distribution, and the condition under which the biodegradation is conducted [67, 70, 71]. Table 2 summarizes the degradation rate of PLA and some other synthetic polyesters, revealing that the degradation rate of PLA is lower than that of PGA as well as poly(glycolic acid-co-lactic acid) (PLGA) and PCLA copolymers. The relatively slow degradation rate is due to the poor water permeability of the semicrystallinity PLA. The hydrolytic degradation of PLA initially occurs in the amorphous parts because of their higher rate of water take-up than in the crystalline regions [66]. The degradation can be autocatalytic due to the production of carboxylic end groups that catalyze further hydrolysis [70]. The faster degradation rate of PLA of low molecular weight or containing oligomers and lactide can be ascribed to autocatalysis. The degradation rate of PLA also increases on heating since the polymer chains become more flexible at elevated temperatures [66]. Tsuji *et al.* [72] tested the degradation of PLLA in different media at pH 2.0, 7.4 and 12, and showed that the degradation rate in alkaline media is faster than that in acid and neutral media. The degradation rate was also shown to be accelerated in the presence of microorganisms and enzymes [71, 73]. However, the PLLA/PDLA stereocomplex has been reported to have a higher hydrolysis resistance than that of PLLA and PDLA alone [64].

PLA is the most extensively studied and used biocompatible polymer since it exerts no toxic or carcinogenic effects in local tissues [61]. Moreover, the ultimate degradation product of PLA is lactic acid, which is then incorporated into tricarboxylic acid cycle and excreted, showing non-toxicity [74]. Other aliphatic polyesters and their copolymers, including PGA and PLGA, PCL and PCLA, PTMC and poly(trimethylene carbonate-co-D,L-lactide), have also been assessed and shown to be non-toxic and tissue compatible [75–77]. Although PLA and its copolymers are sufficiently biocompatible for a wide range of biomedical applications, their hydrophobicity and lack of functional groups are still limitations for certain applications of PLA-based materials. Surface modification of PLA is a direct

Table 2. Biodegradation rate of some polyesters^{a)}

Polymers	Mol. mass/kDa	Degradation rate
PLLA	100–300	(SC) 50% in 1–2 years
PGA	–	(C) 100% in 2–3 months
PLGA	40–100	(A) 100% in 50–100 days
PCL	40–80	(SC) 50% in 4 years
PCLA	100–500	(A) 100% in 3–12 months
PTMC	14	(SC) 9% 30 weeks

a) Modified from [73, 88]; C, crystalline; SC, semicrystalline; A, amorphous.

route to obtain PLA-based materials with improved biocompatibility. A variety of materials including biomimetic apatite, extracellular proteins like fibronectin, collagen, vitronectin, and entacin, and RGD peptides have been attached onto the surface of PLA through either non-covalent or covalent attachment to control the interaction between PLA materials and cells [61].

4 PLA has lower carbon footprint than petroleum-based plastics

The vast majority of existing polymer materials are based on non-renewable petrochemical resources, *e.g.*, PET, polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyamide (PA). These sources will eventually be exhausted. Manufacturing synthetic polymers and disposal by incineration produces CO₂, and emission of CO₂ is considered a potential threat in the form of global warming. For all industrial processes, the energy input required normally results in the production of CO₂. While not unique to the plastics industry, if the threat of global warming is to be taken seriously, steps must be taken to reduce CO₂ emissions. Today, public concerns about the environment, climate change and limited fossil fuel resources have become more important drivers. For these reasons, PLAs are of increasing commercial interest because they are derived from corn-based starch, sequester significant quantities of CO₂ relative to petrochemical-based materials, conserve energy, and easily degrade. Scientists have demonstrated that PLA shows lower fossil resource consumption, and global warming and summer smog values.

PLA presents numerous advantages, including (a) its preparation from a lactide monomer that can be obtained from a renewable agricultural source [78, 79]; (b) its consumption of quantities of CO₂, the leading greenhouse gas [80]; (c) its help in reducing landfill volumes and improvement of farm

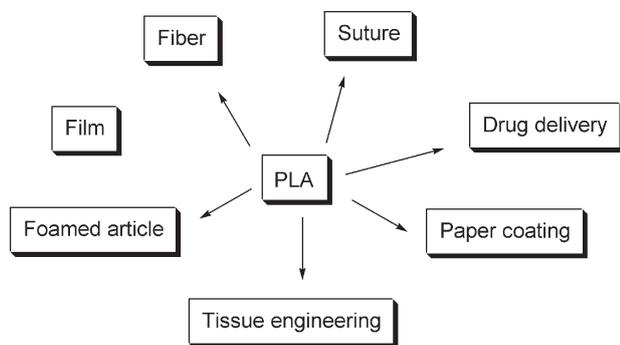


Figure 8. Applications of PLA.

economies as it is bio-based, and (d) its comparable mechanical and physical properties to those of PET and PS [81, 82].

5 Applications for PLA and its copolymers

PLA is a highly versatile environmentally friendly polymer. Due to its renewability, biodegradability, transparency, processability, and mechanical properties, it is finding increasing applications in situations where recycling, reuse and recovery of products are not feasible [83]. Since the production costs for PLA manufacturing processes are decreasing, PLA may find use in different applications for a broad array of products (Fig. 8).

Fiber is one of the largest potential application areas for PLA. PLA is readily melt spinnable, stress crystallizes upon drawing, and can be designed for many fiber applications. Its first commercial success as a fiber material was its use as resorbable sutures. PLA has subsequently been widely studied for use in other medical applications because of its bioresorbability and biocompatible properties in the human body. In addition, PLA fibers have now been developed for use as, for example, filament yarns, and spun yarns for apparel.

Use as a film is the second largest application field for PLA. The crystallization kinetics and physical properties for a broad range of applications can be modified by D, L or meso-co-monomer incorporation, branching, and molecular weight change, which make PLA extremely versatile.

PLA films can be prepared by the blown double bubble technology or, preferably, cast-tentering. Cast-tentered films have very low haze, excellent gloss, and gas (O₂, CO₂, and H₂O) transmission rates desirable for consumer packaging materials. For example, Dannon and McDonald's (Germany) pioneered the use of PLA as a packaging material in

yogurt cups and cutlery. Nature works LLC polymers have been used for a range of packaging applications such as high-value films, rigid thermoformed containers, and coated papers [84].

Currently, new applications such as foamed articles and paper coatings [85] are being pursued. Since the raw materials for PLA are based on agricultural feedstock, the increased demand for PLA resins will create a positive impact on the global agricultural economy.

Nevertheless, a number of areas still need to be improved, especially use as a substitution for existing thermoplastics [86]. For instance, the brittleness and biodegradability may result in unpredictable performance in some applications under conditions of uncontrollable abusive temperature and humidity.

Some of these challenges may be overcome through coating with high barrier materials, blending PLA, copolymers and impact-modified products, and polymer modification. Development in these fields may further expand the applications as high-performance biodegradable materials. With the increasing petroleum prices, the implementation of environmental policies, and the development of raw material sources, such as biomass and other low-value byproduct waste, the use of PLA will be driven forward.

6 Conclusions

Because PLA is biocompatible and bioresorbable, it can be used in a number of biomedical applications, such as sutures, implants, fracture fixation, drug delivery, and tissue engineering. Because PLA is biodegradable, it can also be employed in the preparation of bioplastics, useful for producing loose-fill packaging, compost bags, food packaging, disposable tableware, upholstery, disposable garments, awnings, feminine hygiene products, and nappies. As the depletion of petrochemical feedstocks draws near, PLA is becoming an environmentally sustainable alternative to petrochemical-derived products because of its biodegradable characteristics and the renewable nature of its feedstock.

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