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# Polylactides
# "NatureWorks™ PLA"

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|---|---|
| AATCC | American Association of Textile Chemists and Colorists |
| BON | biaxially oriented Nylon |
| CD | cross-direction |
| COF | coefficient of friction |
| Den | denier |
| EVA | ethylene vinyl acetate |
| GPPS | general-purpose polystyrene |
| GRAS | generally recommended as safe |
| HDPE | high-density polyethylene |
| HIPS | high-impact polystyrene |
| LDPE | low-density polyethylene |
| MD | machine direction |
| Mn | number average molecular weight |
| OPET | oriented polyethylene terephthalate |
| OPLA | oriented polylactic acid |
| OPP | oriented polypropylene |
| PET | polyethylene terephthalate |
| PLA | polylactic acid (or polylactide) |
| PP | polypropylene |
| PS | polystyrene |
| ROP | ring-opening polymerization |
| $T_g$ | glass transition temperature |
| VA EVA | vinyl acetate/ethylene vinyl acetate copolymer |
| WVTR | water vapor transmission rate |

## 1
## Introduction

Polylactic acid (PLA) is a highly versatile aliphatic, compostable polymer derived from 100% annually renewable resources. Because such resources replace oil as the feedstock, PLA requires 20–50% less fossil resources than comparable petroleum-based plastics. With PLA, $CO_2$ is removed from the atmosphere when growing the feedstock crop, and returned to the Earth when PLA is degraded. Since the process recycles the Earth's carbon, PLA has the potential to reduce atmospheric $CO_2$ levels. Disposal of PLA fits with existing systems, including the additional option of composting. Long term, with the correct infrastructure, PLA products could be recycled back to a monomer and into polymers.

The land mass necessary for feedstock production is minimal. Producing 500,000 tonnes of PLA requires less than 0.5% of the annual US corn crop. Since corn is a cheap

dextrose source, the current feedstock supply is more than adequate to meet foreseeable demand.

In spite of PLA's excellent balance of properties and environmental benefits, its commercial viability has been limited traditionally by high production costs (more than $4 per kg). Until recently, PLA has enjoyed little success in replacing petroleum-based plastics outside of biomedical applications such as sutures (Lipinsky and Sinclair, 1986). The recent formation of Cargill Dow LLC in 1997 has brought focus to the development and production of Nature-Works™ PLA. Although the development of PLA is clearly in its early stages compared with conventional plastic, this new company is significantly reducing production costs while expanding the use of PLA beyond biomedical applications.

## 2
## Historical Outline

Somewhat surprisingly, PLA has been the subject of many investigations for over a century. In 1845, Pelouze condensed lactic acid by distillation of water to form low molecular-weight PLA and the cyclic dimer of lactic acid, lactide (Pelouze, 1845). About 50 years later, an attempt was made to prepare PLA from lactide, but without success (Bischoff and Walden, 1894). In 1932, although another group was able to polymerize lactide to PLA, the method was unsuitable for practical use (Carothers et al., 1932). Later, Watson published a review on the possible uses of PLA for coatings and as a constituent in resins (Watson, 1948). Even though PLA has been known for over 100 years, its commercial viability or usefulness had not been practical. In 1986, PLA was described as having potential as a commodity plastic (Lipinsky and Sinclair, 1986).

In 1988, Cargill Incorporated began an investigation into lactic acid, lactide, and PLA and concluded that although PLA was an interesting material, it was not practical with the then-known technology. Consequently, Cargill began to address the manufacturing, melt processing and cost issues, and in 1994 commenced operation of a semi-works with 4000 tonnes annual capacity, together with large-scale trials on conventional polymer processing equipment. In 1997, Cargill and The Dow Chemical Company formed Cargill Dow LLC in order to develop and bring to full commercialization the PLA technology and products. It is planned that Cargill Dow will commence full commercial manufacture of PLA in November 2001.

## 3
## Production of PLA

PLA can be prepared by both direct condensation of lactic acid and by the ring-opening polymerization (ROP) of the cyclic lactide dimer (Figure 1). Because the direct condensation route is an equilibrium reaction, difficulties in removing trace amounts of water during the late stages of polymerization generally limit the ultimate molecular weight achievable by this approach. Most work has focused on the ROP, although Mitsui Toatsu Chemicals has patented an azeotropic distillation process using a high-boiling solvent to drive the removal of water in the direct esterification process to obtain high molecular-weight PLA (Enomoto et al., 1995; Ichikawa et al., 1995; Kashima et al., 1995; Ohta et al., 1995).

Cargill Dow LLC has developed a patented, low-cost continuous process for the production of lactic acid-based polymers (Gruber et al., 1992a,b, 1993a,b,c, 1994, 1996). The process combines the substantial environ-
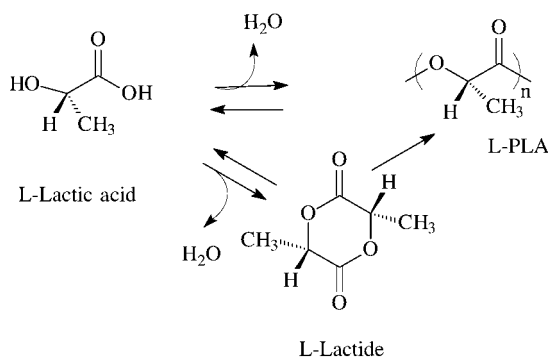
**Fig. 1** Polymerization routes to polylactic acid.

mental and economic benefits of synthesizing both lactide and PLA in the melt rather than in solution and, for the first time, provides a commercially viable compostable commodity polymer made from annually renewable resources. The process starts with a continuous condensation reaction of aqueous lactic acid to produce low molecular-weight PLA prepolymer (Figure 2). Next, the prepolymer is converted into a mixture of lactide stereoisomers using tin catalysis to enhance the rate and selectivity of the intramolecular cyclization reaction. The molten lactide mixture is then purified by vacuum distillation. Finally, PLA high polymer is produced using a tin-catalyzed, ring-opening lactide polymerization in the melt, completely eliminating the use of costly and environmentally unfriendly solvents. After the polymerization is complete, any remaining monomer is removed under vacuum and recycled to the beginning of the process (Figure 3). This process is currently in operation at a 6000 tonnes per year market development facility in Minnesota. The construction of a 140,000 tonnes per year commercial-scale PLA plant in North America was recently announced by Cargill Dow
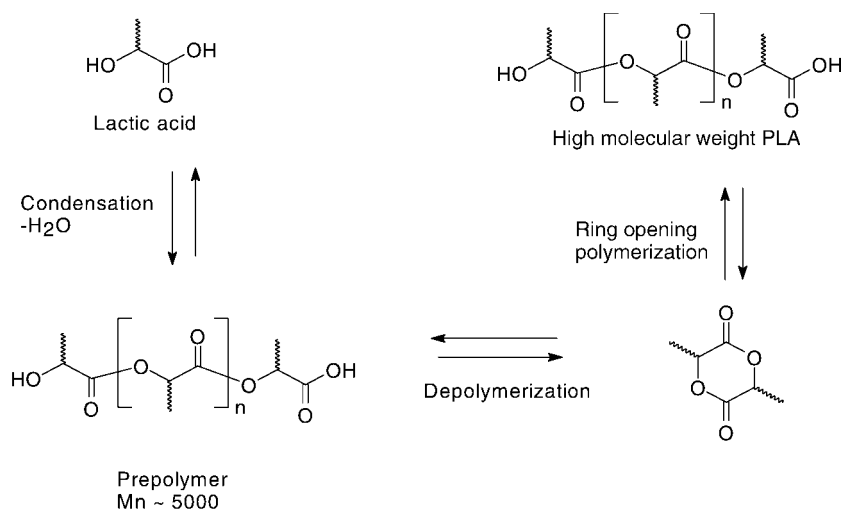


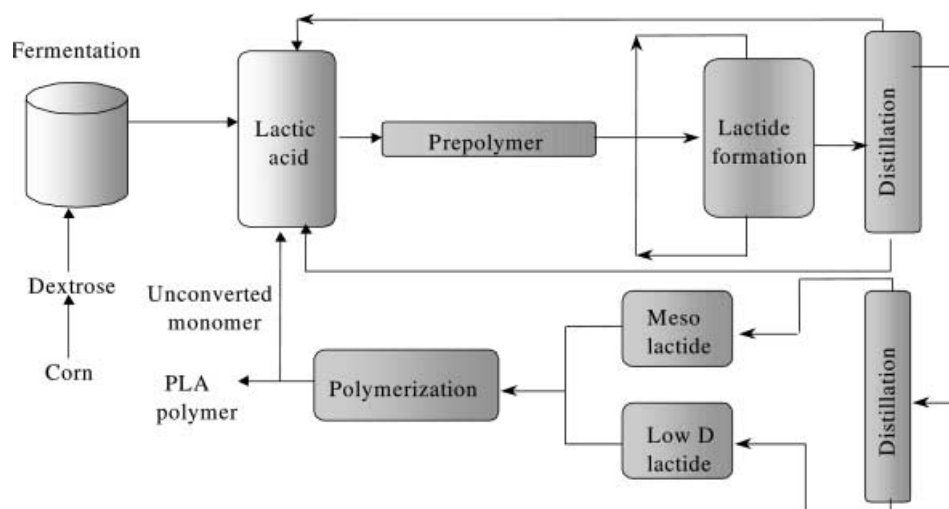**Fig. 2** Schematic of PLA production via prepolymer and lactide.

**Fig. 3** Non-solvent process to prepare polylactic acid.

LLC for start-up in the fourth quarter of 2001, with plans to construct an addition plant in Europe in the near future.

## 3.1
## Polymerization of Lactide

Many catalyst systems have been evaluated for the polymerization of lactide, including complexes of aluminum, zinc, tin, and lanthanides. Even strong bases such as metal alkoxides have been used with some success. Depending on the catalyst system and reaction conditions, almost all conceivable mechanisms [cationic (Kricheldorf and Krieser, 1986), anionic (Kurcok et al., 1992), coordination (Kricheldorf et al., 1995; Nijenhuis et al., 1995), etc.] have been proposed to explain the kinetics, side reactions, and nature of the end groups observed in lactide polymerization. Tin compounds, especially tin(II) bis-2-ethylhexanoic acid (tin octoate), are preferred for the bulk polymerization of lactide due to their solubility in molten lactide, high catalytic activity, and low rate of racemization of the polymer. Conversions of > 90% and less than 1% racemization can be obtained while providing polymer of high molecular weight.

The polymerization of lactide using tin octoate is generally thought to occur via a coordination–insertion mechanism (Kricheldorf et al., 1995; Nijenhuis et al., 1995), with ring opening of the lactide to add two lactic acid molecules to the growing end of the polymer chain (Figure 4).
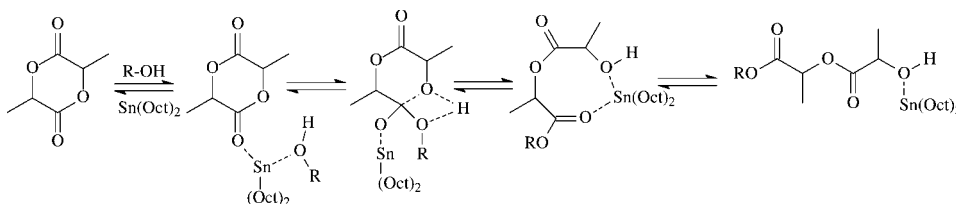


**Fig. 4** Copolymerization of lactide and caprolactone.