Polylactic Acid : Synthesis, Properties and Applications

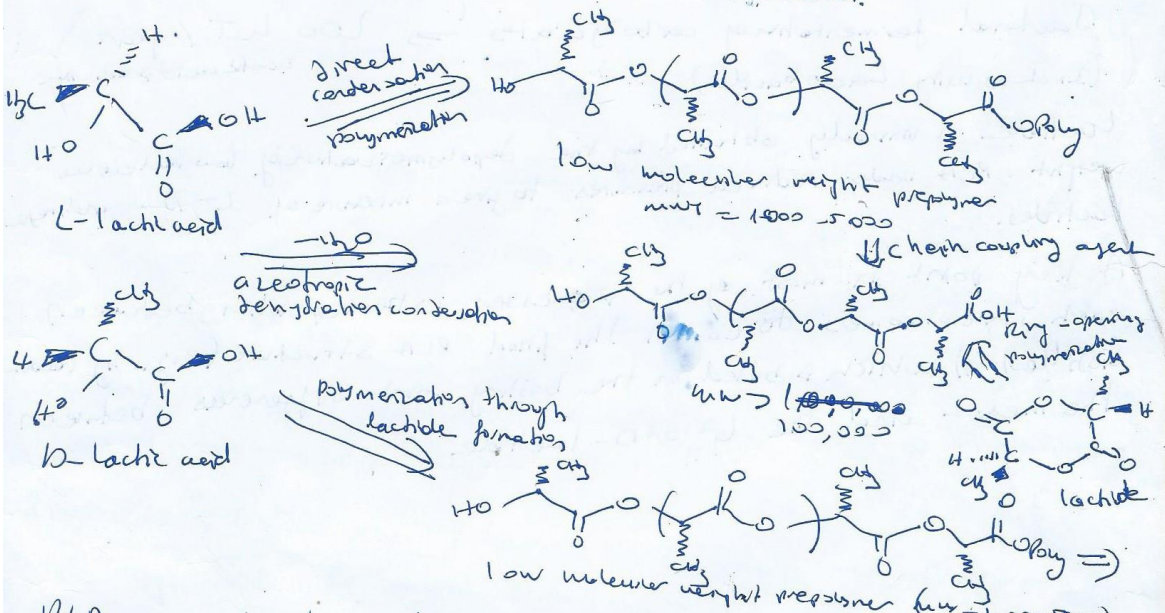
(L. Avérous, Monomers, Polymers and composites from renewable resources, chapter 21)

polylactic acid (PLA) → biodegradable polymers ⇒ large scale production

⇒ application in short-term packaging & biomedical applications (implants, sutures, drug encapsulations...)

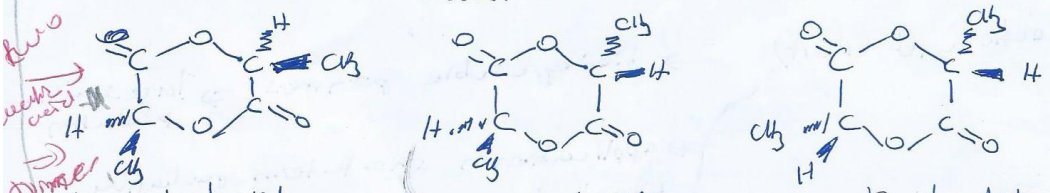
PLA production capacity of Cargill in 2006 → 140 k Ton.
2-5 Euros / kg.

PLA consumption in 2006 was only about 60000 tons/year, at present, only ~30% of lactic acid is used for PLA production.



PLA can be tailored by formulation, mainly adding plasticizers, other biopolymers, fillers, etc.

Lactic acid → mainly used → food industry (as an acidity
19. century started to get industrial scale. cosmetics, pharmaceuticals and animal feed.



L-lactide meso-Lactide D-lactide

Cyclic dimer of lactic acid (combination of two molecule) → boiling point difference

PLA can be obtained either by carbohydrate fermentation or by common chemical synthesis. ↓ operation

bacterial system can produce L and D isomers (Lactic acid)

monomer system only produce L-isomers which is then easily assimilated during metabolism

Bacterial fermentation of carbohydrates (such as using Lactobacilli) ⇒ 200 kT/year. lactic acid production

Lactide is usually obtained by the depolymerization of low molecular weight PLA under reduced pressures to give a mixture of L-, D- and meso lactides.

A key point in most of the processes is the separation between each stereoisomers. to control the final PLA structure (e.g. by vacuum distillation) which is based on the boiling point differences between the meso- and the L- or D- lactide

polymerization

Lactic acid condensation and coupling agent ⟹ least expensive route but low molecular weight

(anhydrides – epoxides – isocyanates) ⇓ use chain extension

very good to obtain telechelic polymer ⟵ (prepolymer end groups should be very controlled (for example HO〰〰C(=O)–OH)

Disadvantage is ⊛ final polymer may contain unreacted chain-extending agents
⊛ oligomers
⊛ residual metallic impurities from the catalyst
⊛ some extending agents could be associated with a lack of biodegradability.

Azeotropic dehydration and condensation ⟹ Mitsui Chemicals (Japan) produced a process

lactic acid ⊕ catalyst —azeotropically dehydrated in a refluxing, high boiling, aprotic solvent under reduced pressures; 30–40 hr at 130°C→ PLA ($M_w \geq 300\,000$)
(diphenyl ether)

⟹ problem is using catalyst ⟹ that can cause degradation & hydrolysis

catalyst toxicity is important in biomedical appl. as well ⟹ It should be removed to some ppm level

Ring Opening Polymerization of Lactide is the only method for producing pure high molecular weight PLA ($M_w \geq 100\,000$).

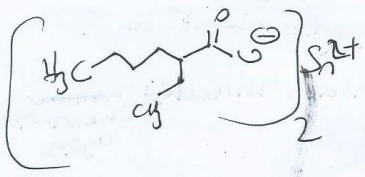
Lactide —trifluoromethane sulphonic acid ($CF_3–SO_2–OH$)→ cationic polymerization.

Controlled anionic polymerization $\xrightarrow{\text{KOMe}}$ well defined polymers with negligible racemization.

Anionic & cationic ROP → should be done in highly purified solvent ⇒ - racemization
- transesterification
- high impurity levels.

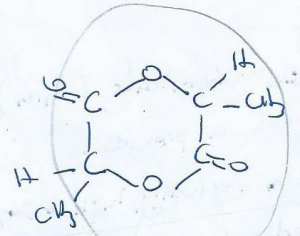
Industrial scale → bulk & melt polymerization ⇒ low levels of non toxic catalyst.

tin, zinc, iron, Aluminum oxides, alkoxides, carboxylates are used.

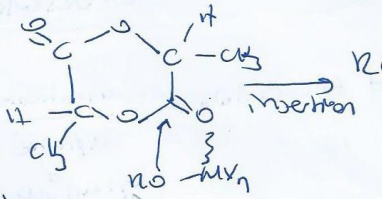


mainly tin(II) bis-2-ethylhexanoic acid (stannous octoate) is used.

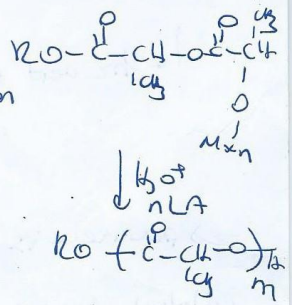
① high catalytic efficiency
② low toxicity
③ food and drug contact approval
④ ability to give high molecular weights with low racemization.



$\xrightarrow[\text{coordination}]{X_nM-OR}$



$\xrightarrow{\text{insertion}}$

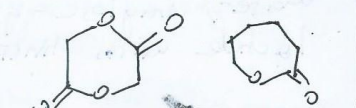


(actively initiated from compounds containing hydroxyl groups such as water and alcohols.)

The interaction between the time and temperature is very significant in terms of limiting the degradation reactions, which affect the molecular weight and the reaction kinetics. It has also been shown that the chain length is directly controlled by the amount of OH-impurities.

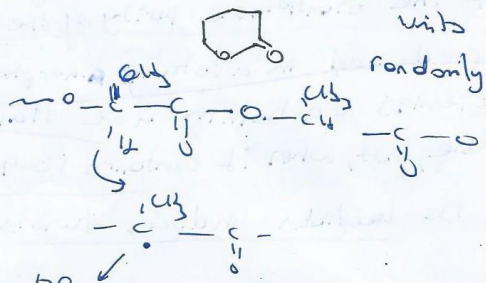
olymers based on lactic acid units

Ring opening copolymerization ; Lactide + glycolide – caprolactone and valerolactone ⇒ the comonomer units can be inserted randomly or in block sequences



grafting / cross-linking

PLA → irradiation or benzoyl peroxide 0,1 – 0,25 wt%



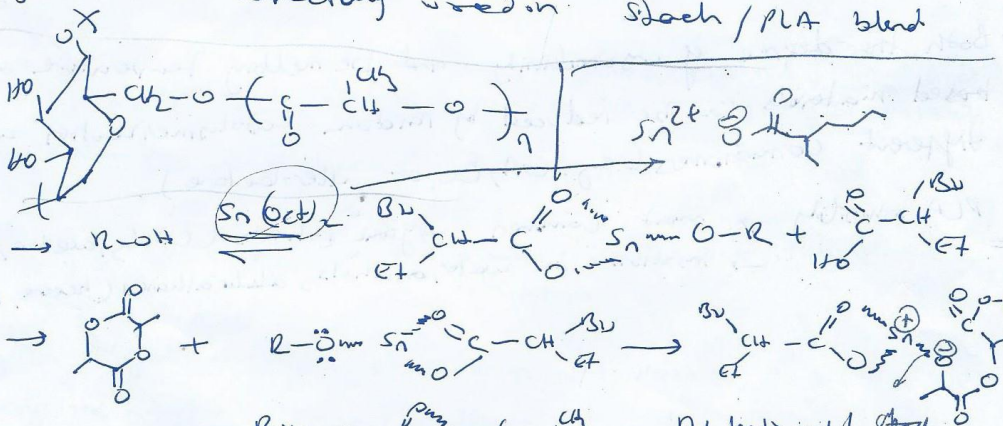
3° radical

Crosslinking occurs.

Irradiation of PLA causes mainly chain-scission or crosslinking reactions, depending on the radiation intensity.

→ grafting (like tarot)

grafting reaction especially used on Starch / PLA blend



After amylose purification to eliminate residual butan
water, amylose-graft-PLA is obtained by the ROP of puri
lactide with tin(II) bis(2-ethylhexanoate) in toluene at 100°C for 20

PLA properties: The physical properties of polylactide are related to the enantiomeric purity of the lactic acid stereopolymers. PLA can be produced in a totally amorphous or with up to 40% crystalline. PLA resins containing more than 98% of L-lactic acid are semicrystalline, but, when it contains 50-93% of it, it is entirely amorphous. Both meso and D-lactides induce twists in the very regular PLLA architecture.

Depending on the preparation conditions, PLA crystallizes in different forms. (α-, β, γ, → space group; helical conformation, chain orientation etc) (Table 21.1 gives PLA crystalline structures)

As PET, PLA can be oriented biaxially by processing and chain orientation increases the mechanical strength of the polymer.

Typical PLA T_g → 50-80°C

T_m → 130-180°C.

Both, the degree of crystallinity and the melting temperature of PLA based materials can be reduced by random copolymerization with different comonomers (e.g. GA, CL or valerolactone)

PLA solubility → most common organic solvents (CHCl$_3$, acetone, THF etc)
→ insoluble in water, alcohols, aliphatic alkanes (hexane, heptane)

permeability packaging

cations in food packaging, its barrier properties (mainly to CO_2, and water vapour) should be investigated

Since diffusion takes place through the amorphous regions of a polymer, an increase in the extent of crystallization will inevitably result in a decrease in permeability.

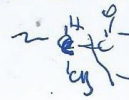
(The CO_2 permeability coefficients for PLA polymers are lower than those reported for crystalline polystyrene at 25°C and 0% relative humidity and higher than those PET.)

Mechanical properties of PLA ⟹ soft – to – elastic materials
stiff – high strength materials
⇓
depends on crystallinity, polymer structure, molecular weight, processing, material formulation

Commercial PLA (such as 92% L-lactide, 8% meso-lactide) → T_g 55°C
addition of plasticizers ⟹ T_g → 10°C.

Degradation : The main abiotic phenomena involve thermal and hydrolysis degradations during the life cycle of the material.

PLA decomposition is between 230°C – 260°C.



T_g → most susceptible bond during thermal hydrolysis.

Hydrolytic degradation is a phenomenon, which can be both desirable (e.g. during the composting stage) or undesirable (e.g. during processing or storage).

water uptake → ester hydrolysis

amorphous region → higher rate of water uptake than crystalline regions

⇒ so undergo hydrolysis before their crystalline regions

⇒ produced low mass degradation products → —COOH ⇒ more water uptake ⇒ autocatalytic effect (more degradation).

The in vivo and in vitro degradations have been evaluated for PLA-based surgical implants. → in vivo studies indicated pH of the ioln plays a key role in the degradation

Enzymes such as proteinase K and pronase have been used to bring about the in vivo PLA hydrolysis. Little enzymatic degradation occurs at the beginning of the process (enzymes are unable to diffuse through the crystalline parts), but pores and fragmentations are produced, widening the accessible area to the different enzymes

...ssary

...major problem in the manufacturing of PLA-based products is the limited thermal stability during the melt processing. To overcome such a drawback or to give PLA new properties, a large number of multiphase materials have been developed, mainly by mixing PLA with others products

PLA → plasticizer is lactide monomer. → but it diffuse very quickly

Oligomeric lactic acid → 20% wt addition
⇒ T_g decreases to 20°C
⇒ modulus decrease 63%.

citrate, maleic anhydride are also used upto 25% wt.

But increasing the plasticizer content can decrease the PLA crystallinity by enhancing chain mobility.

low molecular weight PEG, PPG, fatty acid are also compatible with PLA and can act as plasticizers.

PLA/Starch blend will be discussed in next part. PLA/PEG are miscible with each other when the PLA fraction is below 50%. The PLA/PEG blend consits of two semi-miscible crystalline phases dispersed in an amorphous PLA matrix.