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Solid state polymerization of poly(lactic acid): Some fundamental parameters

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ABSTRACT

Poly(lactic acid) (PLA) was submitted to solid state polymerization (SSP) in a fixed bed reactor under nitrogen flow, so as to examine technique efficiency for increasing the molecular weight and hence permitting the reduction of the melt polymerization residence times. In order to use a suitable starting material, SSP prepolymers of low and medium molecular weight were first prepared through solid state hydrolysis of commercial PLA grade under acidic and alkaline conditions. During these degradation runs, hydrolysis involved the random scission of ester groups in the polymer backbone, while the relevant kinetics and the resulting thermal properties were also examined. In a subsequent step, the prepolymers obtained were subjected to SSP at three temperatures, approximately 2.5–25.0 °C below their melting point. The process achieved an increase of up to 1.7 times the initial molecular weight, however, with different trends depending on the prepolymer characteristics, reaction temperature and time, as well as the pH of the hydrolysis medium. In addition to molecular weight build up, the effect of the SSP process on end product thermal properties was also investigated.

1. Introduction

Poly(lactic acid) (PLA) comprises one of the most promising materials from renewable resources, serving as an alternative for fossil-based polymers. Regarding thermal properties, the enantiomerically pure PLA is a semicrystalline thermoplastic with glass transition temperature (T_g) in the range of 50–80 °C and melting point (T_m) at 130–175 °C, the latter being lower than that of polystyrene and PET rendering PLA processing much easier. Regarding mechanical properties, they can vary to a large extent, ranging from soft and elastic PLA plastics to stiff and high strength materials. PLA may have numerous applications in packaging, consumer goods, fibers and biomedicine because of its transparency, biosafety, as well as adjustable hydrolyzability [1–5].

There are two established routes for the synthesis of PLA, according to Fig.1: ring opening (ROP) of the lactide and direct polycondensation (DPC) of the lactic acid. ROP can be through cationic, anionic, coordination or free radical polymerization, while DPC usually comprises two stages: first an oligomer is prepared through esterification and then polycondensation follows in the presence of a catalyst at lower pressure and higher temperature. Tin and titanium based catalysts, e.g. tin (II) chloride dihydrate and titanium tetrabutoxide ($Ti(BuO)_4$), are typically used in both routes; tin compounds are also combined with proton acids (binary systems), such as *p*-toluenesulfonic acid (TSA) [1,3,5,6]. A pertinent mechanism on Sn-TSA catalysis has been assumed by Moon et al. [7]. Ring opening is commercially applied but involves usually high costs due to the complicated purification process of the lactide, the traces of which may deteriorate PLA mechanical properties, cause corrosion of the processing machines and increase polymer degradation rate [8]. On the other hand, polycondensation of lactic acid presents significant drawbacks to allow its wide commercialization: competitive reaction of lactide formation, degradation reactions due to high temperatures, increase of melt viscosity, heat and mass transfer limitations, all leading to inability of formation of PLA with sufficiently high molecular weight [3,5,9].

Some of these drawbacks are overcome with a combination of melt polycondensation and solid state polymerization (SSP), i.e. the melt polycondensation is interrupted and the molecular weight (MW) is further increased by heating the solid polymer under inert atmosphere at temperatures lower than T_m but higher than T_g. In particular, SSP involves polycondensation reactions in the amorphous regions of the semicrystalline prepolymer, where the chain mobility is high enough; any formed condensate is excluded in the

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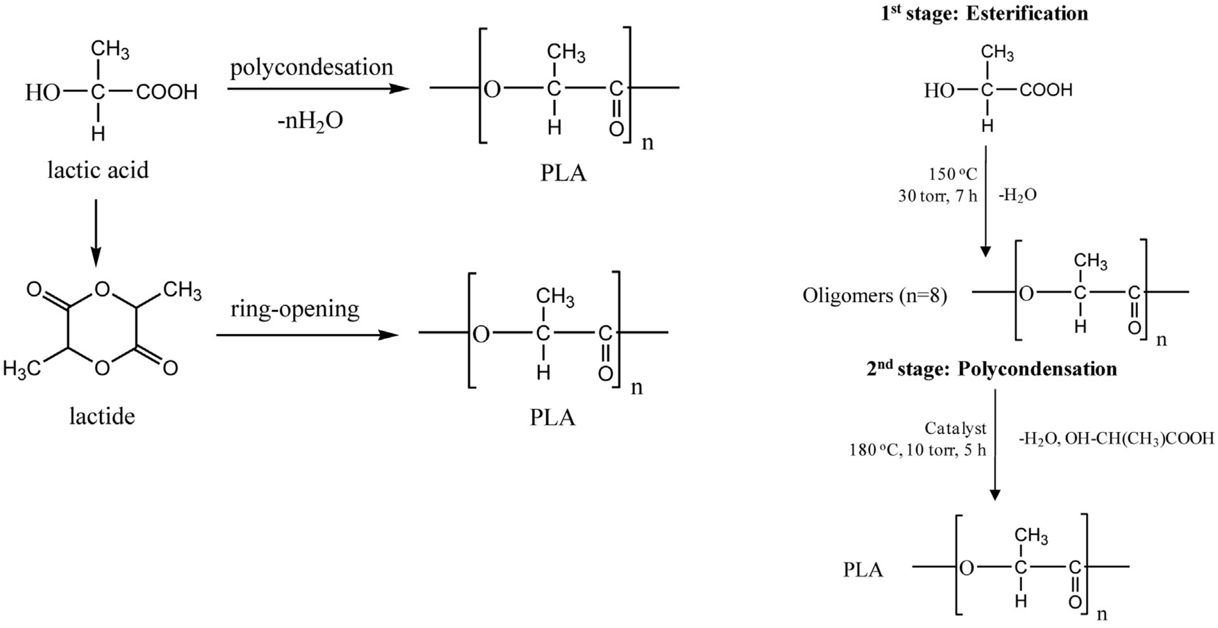

Fig. 1. PLA production through direct polycondensation (DPC) and ring opening (ROP). Indicative DPC conditions used by Moon et al. [6].

amorphous phase along with end groups, oligomers and preferably catalysts, and is removed through convection caused by passing inert gas or by maintaining reduced pressure. SSP can be considered as a Green Polymerization Technology, since energy consumption is low due to the reduced reaction temperatures, no solvent is used, it requires simple equipment and can be a continuous operation [10–13].

Especially for the case of PLA, indicative works on SSP are presented in Table 1, referring to vacuum processes and synthesized PLA grades, while in some works SSP served also as a method for monomer removal from ROP-derived PLA. In other words, crystallization occurring simultaneously with SSP may result in excluding reactive ends and monomer in the amorphous regions and reaching thus polymerization conversion of 100% [8]. In Table 1, input is also given on prepolymer pretreatment. More specifically, precrystallization is usually applied prior to PLA SSP, so as to increase prepolymer melting point and to avoid sintering phenomena, as well as to exclude monomer and catalyst in the amorphous regions of the polymer in order to accelerate SSP reactions [3,6,15]. This pretreatment is already widely applied during PET SSP for the same reasons [10].

In the current paper, PLA SSP process at different reaction conditions was studied under nitrogen flow in a new SSP batch assembly; pertinent systems are suitable for continuous operations and already industrially applied for other commercial polycondensation polymers, such as polyamides and PET. Furthermore, prepolymers were produced through solid state hydrolysis of high-molecular-weight commercial PLA, potentially all-hydroxyl- or all-carboxyl-terminated grade [1], so as to provide starting materials of appropriately reactive carboxyl and hydroxyl end groups. This approach can be also considered as a model to assess SSP efficiency as a PLA recycling technique, i.e. to examine if SSP can serve as a molecular weight build-up process for used/hydrolyzed PLA grades. This is the case in industrially applied processes for PET bottle-to-

Table 1
Indicative literature conditions for melt synthesized PLA solid state polymerization.

Ref.	Prepolymer	Precrystallization	SSP conditions	Vacuum/ flowing N_2	Range of molecular weight		PDI[a]
					Initial	Final[a]	
[8]	PLLA		$T = 100–140$ °C, $t = 9$ h, catalyst: stannous 2-ethyl hexanoate	n.a./n	$\overline{M_n} = 40{,}000–10{,}000$	52,000–74,000	2.2
[6]	PLLA	1–2 h, 105 °C, 0.5 torr	$T = 130–155$ °C, $t = 10–55$ h, catalyst: $SnCl_2 \cdot 2H_2O$/TSA	0.5 torr/n	$\overline{M_n} = 13{,}000$	670,000	2.8
[14]	PLLA	1 h, 105 °C, 0.5 torr	$T = 150$ °C, $t = 10$ h, catalyst: $SnCl_2 \cdot 2H_2O$/TSA	0.5 torr/n	$\overline{M_n} = 13{,}000$	320,000	
[15]	PLLA	15–90 min, 105 °C	$T = 135$ °C, $t = 15–50$ h, catalyst: $SnCl_2 \cdot 2H_2O$/TSA	n.a./n	$\overline{M_n} = 18{,}000$	80,000	
[16]	PLA		$T = 98–150$ °C, $t = 5–12$ h, catalyst: tin octanoate	n.a./n	$\overline{M_n} = 26{,}000$	228,000	
[17]	PLA nanocomposites (clay)		$T = 150–160$ °C, $t = 5–10$ h, catalyst: tin octanoate clay: cloisite 20 A	n.a./n	$\overline{M_n} = 21{,}000$	138,000	1.46
[18]	PLLA/PDLA		$T = 140–160$ °C, $t = 30$ h, catalyst: $SnCl_2 \cdot 2H_2O$/TSA	0.5 torr/n	$\overline{M_n} = 22{,}000$	141,000	5.6
[19]	PLLA/PDLA (1:1 wt)		$T = 140–160$ °C, $t = 30$ h, catalyst: $SnCl_2 \cdot 2H_2O$/TSA	0.5 torr/n	$\overline{M_n} = 31{,}000$	202,000	

PLLA: poly(L-lactic acid).
PDLA: poly(D-lactic acid).
n.a. non available.
[a] Maximum value.

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