New catalysis for fast bulk ring-opening polymerization of lactide monomers

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SUMMARY : The ring-opening polymerization of lactides has been studied in bulk using either 2-ethylhexanoic acid tin(II) salt, $Sn(Oct)_2$, or aluminum triisopropoxide, $Al(OiPr)_3$, as the initiator over a wide range of temperature and monomer-to-initiator molar ratio. A high increase in the bulk polymerization rate has been observed when the initiator was added with an equimolar amount of a Lewis base, such as triphenylphosphine ($P(\phi)_3$) and 4-picoline (C_6H_7N) added to $Sn(Oct)_2$ and $Al(OiPr)_3$, respectively. Melt stable polylactides of high molecular weight and reasonably narrow molecular weight distribution have been accordingly prepared. The use of the $Sn(Oct)_2.P(\phi)_3$ equimolar combination has allowed for reaching an acceptable balance between propagation and depolymerization rates, so that the polymerization is fast enough to be performed through a continuous single-stage process in a twin-screw extruder. A global activation mechanism is proposed and discussed by comparison with both investigated initiation systems.

Introduction

Polylactides (PLA) constitute a very important representative of aliphatic polyesters. Based on lactic acid building blocks they have been first designed to serve as resorbable biomaterials in surgery (sutures, implants) and chemotherapy (drug delivery systems).[1-4)] Actually, for those biomedical applications, there was no specific requirement for reducing the cost of the marketed products. It is worth recalling the price for one kg of crude PLA, i.e., pellets of the so called biomedical grade PLA, which easily exceeds 1,000 US$. The need for biodegradable materials for environment opens up new markets of opportunities for PLA polymers.[5,6)] This potential market as life respecting materials implies large production

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volumes and therefore requires an economically viable manufacturing process. A continuous one-stage polymerization appears to be essential to the large scale commercial production of polylactides.

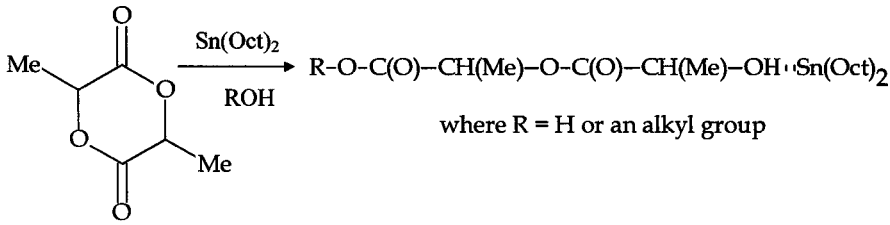
Aliphatic polyesters in general, and polylactides in particular, can be synthesized by two different pathways : either the step-polycondensation of, e.g., ω-hydroxyacids, or the ring-opening polymerization (ROP) of cyclic esters, lactones or dilactones (lactides for instance). In contrast to the more traditional polycondensation, that usually requires long reaction times, high temperature, and continuous removal of by-products such as water, to finally recover quite low molecular weight polyesters with ultimately poor mechanical properties, (di)lactones ROP provides a direct and easy access to the corresponding high molecular weight polyesters.[7] Compared to the polymerization of most unsaturated and cyclic monomers, the lactides (LA) ROP enthalpy is low : $|\Delta H| = 29$ kJ/mol against 70-90 kJ/mol, which allows the controlled implementation of their bulk polymerization.[8-10] The ring-opening polyaddition of lactides is known to be promoted by various inorganic and organic compounds that have been classified in two categories depending on their apparent activation mechanism. In combination with protic compounds, Lewis acid type catalysts such as metals, metal halogenides, oxides, aryls, and carboxylates, activate the lactide ROP. These metal derivatives, with tin(II) bis(2-ethylhexanoate) ($Sn(Oct)_2$) as the main representative, do not initiate the ROP, since it has been reported that the true initiators are protic compounds such as water, alcohols, thiols, and amines (Scheme 1a).[11,12]

However, alkoxides of metals containing free p, d and f orbitals of a favorable energy, e.g., Sn, Ti, Zn, Zr, Y, Nd, Sm, and Al, have been considered as initiators for the ROP of lactides.[7,13] Initiation proceeds through the cleavage of one acyl-oxygen bond of LA in such a way that the opened monomer molecule is attached to the metal through an alkoxide linkage, whereas the other extremity is capped by an ester carrying the alkoxide group of the initiator, $M(OR')X_n$ as shown in Scheme 1b. However, the course of polymerization is perturbed by side intra- and intermolecular transesterification reactions, the extent of which strongly depends on the metal and the acidity of the organometallic compound. Owing to their moderate reactivity, aluminum alkoxides, as simple as the commercially available Al isopropoxide ($Al(OiPr)_3$), have proved to be highly efficient in promoting the "living" ROP of lactides in solution[14] and in bulk.[15]

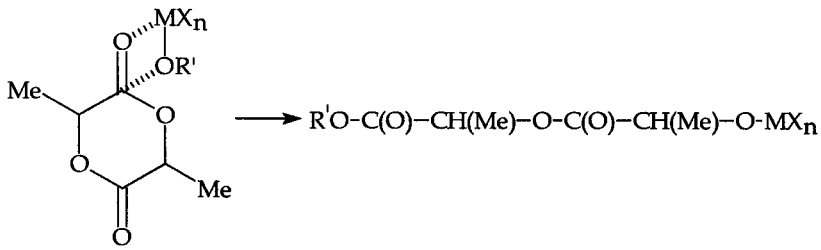
As aforementioned, the current objectives are to make the manufacturing of PLA economically viable. In this respect, the development of a continuous one-stage process is highly desirable, and reactive extrusion could be a very attractive approach. However, this

technique requires that the bulk polymerization is close to completeness within a very short residence time (5 to 7 minutes) and that the PLA stability is high enough at the processing temperature. Even though $Sn(Oct)_2$ can promote quite fast LA polymerization , it is also known to have adverse effects on the PLA molecular weight and properties, as a result of back-biting and intermolecular transesterification reactions, not only during the LA polymerization but also on the occasion of any further melt processing.[16,17] On the other hand, although the moderate reactivity of $Al(OiPr)_3$ has a beneficial effect on the polymerization control, it is responsible for a relatively low polymerization rate.[15]

a) Lewis Acid Catalysts : $Sn(Oct)_2$



b) Metal (with free p-, d- or f- orbitals) alkoxides : $R'O\text{-}MX_n$



Scheme 1

The present paper aims at reporting on the favorable effect of some Lewis bases (LB) on the kinetics of lactide bulk polymerization promoted by $Sn(Oct)_2$ or $Al(OiPr)_3$, without adversely enhancing transesterification/depolymerization reactions. The thermal stability of the so-obtained PLA has also been investigated by thermogravimetric analysis. Comparison of the effect of the studied additives tends to show that both metal derivatives, i.e., Sn dicarboxylate and Al trialkoxide, would activate the lactides ROP by a very similar "coordination-insertion"

mechanism, meaning that polymerization promoted by $Sn(Oct)_2$ would proceed on a tin(II)-alkoxide bond. This tin(II) alkoxide, $(RO)_nSn(Oct)_{2-n}$, would be *in situ* generated by reaction of an alcohol, ROH, and $Sn(Oct)_2$.

Experimental part

Materials. (L,L)-lactide (L-LA) was purchased from Biochem C.C.A. and recrystallized twice from 40 w/v % solution in dried toluene. Monomer was dried for 24h at room temperature under reduced pressure (10^{-2} mmHg) before use. $Sn(Oct)_2$ (from Th. Goldschmidt) was used without further purification and diluted in dry toluene. $Al(OiPr)_3$ from Fluka was purified by distillation and then dissolved in dry toluene. The solution was titrated as previously described.[15] Equimolar solutions of $Al(OiPr)_3$ with 4-picoline (C_6H_7N from Aldrich) and $Sn(Oct)_2$ with C_6H_7N or triphenylphosphine ($P(\phi)_3$ from Aldrich) were prepared by adding the requested volume of the catalyst solution to a well-known amount of dry C_6H_7N and $P(\phi)_3$. C_6H_7N was dried over BaO for 48h and distilled under reduced pressure just before use. $P(\phi)_3$ was dried by three azeotropic distillations of dry toluene. Ultranox 626 was kindly provided by GE Specialty Chem. and used without further purification.

Polymerization procedure. Bulk polymerization of L-LA performed in 20 ml sealed glass ampoules under magnetic stirring has been described elsewhere.[15]

Measurements. Lactide conversion was estimated by FTIR, ^{1}H-NMR and SEC.[15] PLA molecular weight and molecular weight distribution were measured by SEC in THF or $CHCl_3$ at 35°C, in reference to a universal calibration by using polystyrene standards and the related Mark-Houwing parameters.[15,18] Thermogravimetric measurements were carried out under an air flow with a TGA 51 analyzer from T.A. Instruments (heating rate = 10°C/min and isotherm at 210°C).

Results and discussion

Polymerization of L-LA initiated by $Al(OiPr)_3.C_6H_7N$ complex

An equimolar combination of $Al(OiPr)_3$ with 4-picoline as a Lewis base, i.e., $Al(OiPr)_3.C_6H_7N$, has been used to initiate the bulk polymerization of L-LA.[19] The lactide ROP has been investigated for initial monomer-to-initiator molar ratio ranging from 520 to 2,085 at 125°C (Table 1). As expected, the polymerization rate increases with the initiator concentration. In reference to the "livingness" of the lactide bulk polymerization initiated by

$Al(OiPr)_3$,[15] M_n increases proportionally with the $[L\text{-}LA]_o/[Al]$ ratio and the molecular weight distribution is kept rather narrow, at least until the polymerization is complete. No cyclic oligomer, i.e., back-biting reaction, could be detected. Compared to L-LA bulk polymerization initiated by neat $Al(OiPr)_3$, initiation and propagation are substantially activated by C_6H_7N in the whole range of initial monomer-to-Al ratios investigated, while maintaining the control of the polymerization.

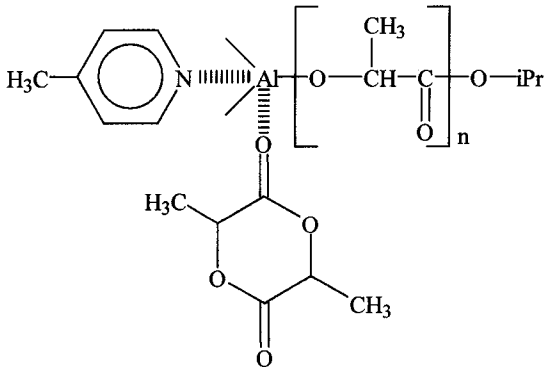
When the polymerization temperature is increased to 180°C, M_n first increases, passes through a maximum at a monomer conversion close to 100%, and then it decreases for longer reaction times. In parallel, the molecular weight distribution broadens indicating that intermolecular transesterifications occur but no back-biting reaction.[19] This general behavior is comparable to that one observed when neat $Al(OiPr)_3$ is the initiator,[15] except for the time required to reach complete monomer conversion: 1h compared to 17h in the absence of C_6H_7N (entry 5 in Table 1).

Tab. 1. Effect of the initiator on the time required for complete L-LA polymerization (t_{100}) and PLA molecular parameters for various initial monomer-to-initiator molar ratios at 125°C.

$[LA]_o/[Al]$	$Al(OiPr)_3$			$Al(OiPr)_3.C_6H_7N$		
	t_{100} (h)	M_n	M_w/M_n	t_{100} (h)	M_n	M_w/M_n
520	40	35,000	1.5	1	34,000	1.4
835	50	58,000	1.5	2	54,000	1.3
1560	83	69,000	1.5	6	77,000	1.4
2085	112 [a]	94,000	1.3	8	99,000	1.4
2085 [b]	17	83,000	1.7	1	95,000	1.8

[a] Polymerization time for 95% monomer conversion.
[b] Polymerization carried out at 180°C.

Accordingly, the equimolar addition of an electron-donating compound such as 4-picoline, onto $Al(OiPr)_3$ allows for activating the Al-OiPr bond toward the monomer insertion and for promoting a substantial enhancement of the L-LA polymerization rate. This kinetic effect has been accounted for by coordination of this Lewis base onto the Al atom, polarizing the metal alkoxide bond and making easier the monomer insertion (Scheme 2). It is also worth noting that, although the reactivity of the active sites is increased by C_6H_7N, the extent of the transesterification reactions is decreased, possibly for steric considerations.[19-21]



Scheme 2

Thermal stability has been investigated for the as-polymerized PLA samples, i.e., without previous purification by extraction of the metal residues and precipitation in cold methanol. The temperature dependence of the weight loss of PL-LA recovered after complete monomer conversion agrees with a sigmoidal single stage process.[22] For sake of comparison, the main degradation characteristics of PL-LA samples synthesized with the same monomer-to-initiator molar ratio (2,085) are listed in Table 2.

Tab. 2 Thermal stability of as-polymerized PL-LA (monomer-to-initiator molar ratio = 2,085) as determined by thermogravimetric analysis under air flow.

initiator	MDT/°C [a]	T_{95}/°C [b]	Degradation rate [c] in 10^{-3}%.min^{-1}
$Al(OiPr)_3$	369	326	10
$Al(OiPr)_3.C_6H_7N$	362	312	10
$Al(OiPr)_3$ [d]	365	308	25
$Sn(Oct)_2$	297	264	260

a) Maximum decomposition temperature defined as the temperature at the inflection point of the temperature dependence of the weight loss.

b) Temperature at which a weight loss of 5% is observed (beyond the volatilization of the residual monomer, in case of $Sn(Oct)_2$).

c) Slope of the time dependence of weight loss (linear portion) under isothermal conditions at 210°C.

d) After purification by solvent extraction of the metal residues and precipitation in cold methanol.

In addition to the maximum decomposition temperature (MDT) and the temperature at which a weight loss of 5% (T_{95}) is observed, the degradation rate expressed in 10^{-3}%.min^{-1} has been calculated from the slope of the time dependence of the weight loss under isothermal conditions at 210°C. Clearly, the addition of 4-picoline to $Al(OiPr)_3$ has no detrimental effect on the polymer thermal stability, which is remarkably higher compared to PL-LA chains promoted by $Sn(Oct)_2$ (compare entries 1,2 and 4 in Table 2). It is worth pointing out that the thermal stability of PL-LA prepared with $Al(OiPr)_3$ as initiator is not enhanced by purification of the as-polymerized material, which rather shows some more ability to degrade (entry 3 in Table 2), in agreement with previously published data.[23,24)]

Polymerization of L-LA catalyzed by $Sn(Oct)_2$.LB equimolar combination

Although $Sn(Oct)_2$ catalyzes a quite fast L-LA polymerization in bulk and at high temperature, e.g., 180°C, it is also known to adversely promote transesterification/degradation side reactions, not only during the lactide polymerization but also during any further melt processing.[16,17,23,24)] In order to optimize the balance between propagation and competing side reactions, two Lewis bases, i.e., 4-picoline and triphenylphosphine, have been added in an equimolar amount to $Sn(Oct)_2$ for promoting the L-LA polymerization at 180°C (Table 3).

Tab. 3 Effect of C_6H_7N and $P(\phi)_3$ on the L-LA bulk polymerization catalyzed by $Sn(Oct)_2$ at 180°C.

$[L\text{-}LA]_o$/ $[Sn(Oct)_2.LB]$	Co-catalyst (LB)	t_{90} [a)] (min.)	t_{100} [a)] (min.)	M_{n100} [b)]	M_w/M_n
5,000	None	27	60	102,000	2.0
	C_6H_7N	42	70	105,000	2.1
	$P(\phi)_3$	20	45	153,000	1.6
1,000	None	15	35	87,000	2.1
	$P(\phi)_3$	10	18	131,000	1.6
10,000	None	48	150	128,000	1.8
	$P(\phi)_3$	36	120	259,000	1.5

a) Polymerization time required to reach 90% conversion (t_{90}) and the maximum monomer conversion (t_{100}), respectively.

b) M_n of PL-LA when the monomer conversion is maximum.

With an initial monomer-to-$Sn(Oct)_2$.LB molar ratio of 5,000, the addition of C_6H_7N surprisingly decreases the polymerization rate compared to neat $Sn(Oct)_2$, whereas $P(\phi)_3$ acts as an accelerator. Indeed, the time required to reach 90% monomer conversion (t_{90}) is decreased from 27 to 20 min. when $Sn(Oct)_2.P(\phi)_3$ is substituted for $Sn(Oct)_2$. In parallel, the time required to reach the highest monomer conversion (t_{100}) drops from 60 down to 45 min. Furthermore the molecular weight observed when the monomer conversion levels off is substantially increased in the presence of $P(\phi)_3$, i.e., 102,000 up to 153,000. This beneficial effect of $P(\phi)_3$ has been confirmed at various monomer-to-$Sn(Oct)_2.P(\phi)_3$ molar ratios (entries 4,5 and 6,7 in Table 3).

Therefore, the overall effect of $P(\phi)_3$ used as a co-catalyst is a faster and a better controlled polymerization, i.e., leading to PL-LA of higher molecular weight and narrower molecular weight distribution, at least within the time required for reaching maximum monomer conversion. The key question to be addressed now is to check the effect of this co-catalyst on the thermal stability of the as polymerized PL-LA, i.e., polylactides contaminated by the residual tin-based catalytic complex (Table4).

Tab. 4 Effect of $P(\phi)_3$ on the thermal stability of as-polymerized PL-LA (monomer-to-$Sn(Oct)_2$ molar ratio = 5,000, at 180°C) as determined by thermogravimetric analysis under air flow.

initiator	MDT/°C [a]	T_{95}/°C [b]	Degradation rate [c] in 10^{-3}%.min^{-1}
$Sn(Oct)_2$	314	260	160
$Sn(Oct)_2.P(\phi)_3$	317	264	200
$Sn(Oct)_2.P(\phi)_3$ [d]	377	280	25

a) Maximum decomposition temperature defined as the temperature at the inflection point of the temperature dependence of the weight loss.

b) Temperature at which a weight loss of 5% is observed (beyond the volatilization of the residual monomer, in case of $Sn(Oct)_2$).

c) Slope of the time dependence of weight loss (linear portion) under isothermal conditions at 210°C.

d) L-LA bulk polymerization carried out by reactive extrusion, in the presence of 0.5 wt % Ultranox 626 (see text).

At a monomer-to-catalyst molar ratio of 5,000, the thermal stability is not much influenced by the co-catalyst $P(\phi)_3$ since both the maximum decomposition temperature (MDT) and the temperature at which the weight loss is 5% (T_{95}) remain unchanged (entries 1 and 2, Table 4). Only the degradation rate calculated from the time dependence of the weight loss at 210°C, increases from 160 up to 200 10^{-3}%.min^{-1} when $P(\phi)_3$ is added to $Sn(Oct)_2$. Thus, at this ratio of 5,000, the equimolar combination of $Sn(Oct)_2$ and $P(\phi)_3$ allows to meet both kinetic and thermal stability requirements. Practically, it opens the way to the ROP of lactides in an extruder through a continuous single-stage process, as it will be reported in a forthcoming paper.[25)]

Indeed, it is worth mentioning the up-scaling of the L-LA bulk polymerization in a typical low capacity closely intermeshed co-rotating twin-screw extruder. The investigated twin-screw extruder was a Berstorff ZE 25 with a screw diameter of 25 mm and a L/D ratio of 48, equipped with a Sulzer static mixer at the end of the screws, in order to homogenize the materials. In addition to the screw configuration, several parameters have been varied to optimize the polymerization process, such as the screw rotation speed (RS) from 50 to 200 rpm, the throughput rate (TR) from 0.75 to 1.25 kg/h, and the extruder head pressure (HP) from ca. 30 to 85 bars.[25)] As a typical example, the L-LA polymerization was catalyzed by $Sn(Oct)_2.P(\phi)_3$ at 180°C with an initial monomer-to-tin(II) molar ratio of 5,000 and in the presence of 0.5 wt % bis(2,4-di-*t*-butylphenyl) penthaerythritol diphosphite (Ultranox 626) used as an antioxidant. The extruder parameters were set up as follows : RS = 100 rpm, TR = 1.00 kg/h, and HP ~ 85 bars. Under these experimental conditions, a PL-LA with a M_n of 86,000 and a M_w/M_n of 1.8 was continuously produced within an average residence time of ca. 7 min. Of important interest is the thermal stability of the as-polymerized PL-LA, which is characterized by a MDT and T_{95} value of 377°C and 280°C, respectively (entry 3 in Table 4). Remarkably, the degradation rate at 210°C is as low as 25 10^{-3}%.min^{-1} allowing for any further thermal processing without undergoing drastic polylactide degradation. Mechanical properties of the resulting polylactides will be extensively reported in a near future.[25)]

Polymerization mechanism for the lactide ROP promoted by $Sn(Oct)_2.P(\phi)_3$

Kinetic experiments have thus pointed out the favorable effect of the addition of one equivalent of $P(\phi)_3$ to $Sn(Oct)_2$ on the L-LA polymerization kinetics and the control of the polylactide molecular parameters. Interestingly enough, the effect of the addition of an alcohol or a carboxylic acid on the course of the L-LA bulk polymerization has been studied

as well. Increasing amounts of either 2-ethylhexanol or hexanoic acid have been added to $Sn(Oct)_2.P(\phi)_3$ at 180°C, while keeping constant the monomer-to-catalyst molar ratio at 5,000 (Table 5). An increase of the alcohol concentration does not affect the monomer conversion that remains close to completion after a 105 min. reaction time, but substantially decreases the number average molecular weight available However, hexanoic acid reduces the rate of L-LA bulk polymerization without significantly modifying the PLA molecular weight, which is kept around 90,000. These observations attest for the decelerator effect of carboxylic acids on the course of L-LA ROP, and for the participation of the alcohol molecules to the initiation step or at least as transfer agent.

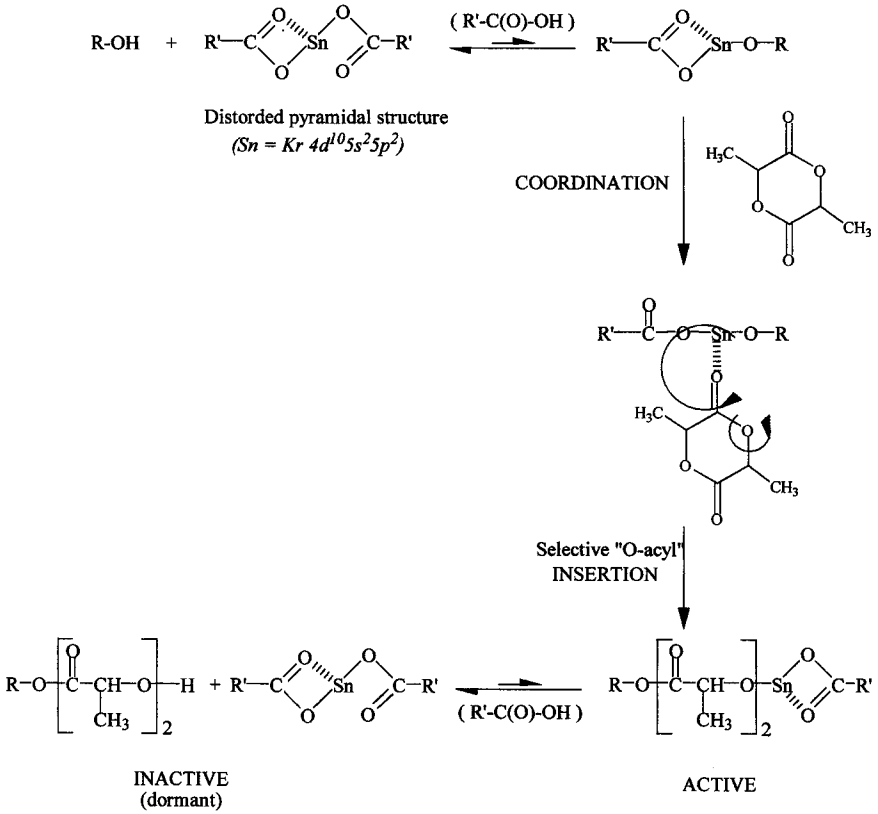
Tab. 5 Effect of 2-ethylhexanol and hexanoic acid on the course of L-LA bulk polymerization promoted by $Sn(Oct)_2.P(\phi)_3$ at 180°C. $[L\text{-}LA]_o/[Sn(Oct)_2.P(\phi)_3]$ = 5,000; polymerization time = 105 min.

Additive	$[Add.]_o/[Sn]$	Conversion (%)[a)]	M_n	M_w/M_n
Alcohol	1	99	174,000	1.5
	2	98	162,000	1.5
	5	98	123,000	1.6
	10	98	103,000	1.6
Acid	1	99	99,000	1.8
	2	97	95,000	1.8
	5	88	84,000	1.9
	10	74	90,000	1.7

[a)] As determined by polymer precipitation from cold methanol

Actually, very recent works by some of us,[26)] and by Duda and Penczek[27)] tend to show that $Sn(Oct)_2$ would react by a reversible way with hydroxyl compounds present in the reaction medium, e.g., residual lactic acid or its opened dimer, so as tin alkoxides such as $(RO)_nSn(Oct)_{2-n}$ (with n = 1 or 2) would be made available even at a very low steady state concentration (Scheme 3). It is worth pointing out that a very similar reaction has been recently reported between dibutyltin(IV) di(2-ethyl hexanoate) and alcohols in the frame of urethane synthesis.[28)] Indeed, the active species in the tin(IV)-catalyzed reaction of isocyanates with alcohols are more likely the *in situ* generated tin(IV) (mono)alkoxides.

By analogy to the (di)lactone ring opening polymerization promoted by aluminum alkoxides (see Scheme 1b), the *in situ* formed tin(II) alkoxides could initiate the polymerization of lactides through a very similar "coordination-insertion" mechanism involving the selective rupture of the oxygen-acyl bond of the monomer. Accordingly, an increase of the alcohol concentration is expected to shift the equilibrium between the alcohol (or dormant ω-hydroxyl PL-LA chains) and the active tin(II)alkoxide towards the right hand side (Scheme 3). It results a reduction of the polylactide molecular weight, as the number of initiation sites is increased. On the contrary, addition of carboxylic acids, e.g. hexanoic acid, will reduce the steady state concentration of tin(II)alkoxides (equilibrium still more shifted to the left hand side), which in turn decreases the global polymerization rate.



Scheme 3

Consequently, the beneficial kinetic effect of $P(\phi)_3$, when added in stoichiometric amount to $Sn(Oct)_2$, might be compared to the rate increase observed in the (di)lactone polymerization as initiated by aluminum tri- or monoalkoxides added with one equivalent of pyridine (or its derivatives) (Scheme 2).[19-21,29] The coordination of a nucleophile such as $P(\phi)_3$ onto the metal atom could polarize the *in situ* generated metal alkoxide in such a way that the insertion of the growing chain alkoxide end group into the oxygen-acyl bond of the cyclic ester monomer is made easier and faster. Such a mechanism would justify that the main kinetic effect is observed only for a $Sn(Oct)_2.P(\phi)_3$ equimolar combination. An excess of nucleophile would compete with lactide monomer for coordinating the metal atom and thus reduce down the overall polymerization rate, in perfect agreement with the experimental observations[18]. However, one can also propose that $P(\phi)_3$ behaves as a Lewis base that could trap carboxylic acid functions, either initially present in the reaction medium (e.g., lactic acid) or 2-ethylhexanoic acid *in situ* formed by reaction of hydroxyl compounds and $Sn(Oct)_2$. Even though the "$Sn(Oct)_2$ - $(RO)_nSn(Oct)_{2-n}$" equilibrium is largely shifted towards the tin(II) dicarboxylate side, the reaction of carboxylic acids and $P(\phi)_3$ should be favorable to the formation of the tin(II) alkoxide species, enhancing their steady state concentration and therefore the overall polymerization rate. However, while an increase of the $P(\phi)_3$-to-$Sn(Oct)_2$ molar ratio should accordingly enhance the polymerization kinetics, a phosphine excess has proved to decrease the rate of the L-LA bulk polymerization.[18] In order to shed more light on the actual polymerization mechanism, a multinuclear NMR study of the $Sn(Oct)_2$-catalyzed ring-opening polymerization of L-LA and the dynamic behavior of the $Sn(Oct)_2.P(\phi)_3$ complex is under current investigation.[26]

In conclusion, this study has shown that the addition of an equimolar amount of a Lewis base, particularly 4-picoline and triphenylphosphine onto aluminum triisopropoxide($Al(OiPr)_3$) and 2-ethylhexanoic acid tin(II) salt ($Sn(Oct)_2$), respectively, significantly enhances the lactide polymerization rate in bulk. This kinetic effect has been accounted for by coordination of the Lewis base onto the metal atom of the initiator, making easier the insertion of the monomer into the metal alkoxide bond of the initiator. As far as $Sn(Oct)_2$ is concerned, the Sn-OR bond would be *in situ* formed by reaction of the alcohol (ROH) and the tin(II) dicarboxylate. It comes out from the above results, that whatever the metal derivatives used to promote the L-LA polymerization, i.e., Al alkoxides or Sn carboxylates, the ROP would proceed via the same "coordination-insertion" mechanism involving the selective oxygen-acyl cleavage of the cyclic ester monomer. The addition of one equivalent of triphenylphosphine onto $Sn(Oct)_2$

allows for reaching an acceptable balance between propagation and depolymerization rates, so that the polymerization is fast enough to be performed through a continuous single-stage process in an extruder. Melt stable PL-LA has been continuously produced, the molecular weight of which being tunable by the addition of alcohol.

Acknowledgments

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