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Alkali Metal Complexes for the Controlled Synthesis of Bioplastics: Tuning the Metal Environment and the Reaction Conditions

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Abstract: Polylactide (PLA) is one of the most prominent bioplastics, derived from renewable feedstocks and noted for its biocompatibility. Yet, the full potential of PLA has not been fulfilled due to limitations in its production processes, especially the dependence on traditional toxic catalysts such as tin(II) octanoate. Recent studies have highlighted the advantages of alkali metal complexes as efficient, non-toxic, and versatile catalysts for the ring-opening polymerization (ROP) of lactide. Historically, alkali metals were considered too reactive or poorly controlled to be effective in ROP catalysis. However, recently it has been demonstrated that this limitation can be overcome through judicious ligand design and reaction engineering, transforming alkali metals into powerful tools for sustainable polymer chemistry. As such, the use of bulky ligands can tune the metal environment and assert a better control over the polymerization. As well, depending on the presence or not of the co-initiator, the polymerization mechanism varies significantly which influences the control of the stereoregularity of the polymers obtained, and poly-*L*-lactide (PLLA) with different *D*-lactide units can be obtained. This stereoregularity determines the thermal and mechanical properties and hence the applications of the PLLA. Furthermore, using chiral alkali compounds and controlling the aggregation, isoselective *rac*-lactide polymerization can be achieved. Hence, catalyst design and reaction conditions can be combined to tune polymer microstructure, molecular weight, and tacticity, advancing PLA toward a sustainable and circular material future. Furthermore, the alkali metal compounds described herein not only enable rapid lactide polymerization, but also promote PLA depolymerization under mild conditions, thereby connecting synthesis with chemical recycling.

Keywords: Alkali metals · Biobased polymers · Catalysis · PLA

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1. Bio-Based Polymers

Since the early 20th century, conventional polymers derived from fossil fuels have revolutionized our modern life due to their durability, versatility, and cost-effectiveness. Unfortunately, these very properties have also led to a staggering accumulation of persistent plastic waste in ecosystems worldwide. Microplastic pollution, greenhouse gas emissions from production, and the finite nature of fossil feedstocks, all underline the need for developing more sustainable alternatives.[1]

In this context, bioplastics arise as a more environmentally friendly alternative. They can be derived from renewable feedstocks and can also be biodegradable.[2,3] However, these materials come with some drawbacks, such as generally higher manufacturing costs compared to traditional plastics.[4] Hence, the development of a more efficient synthesis remains an open challenge. In this context, catalysis enables a very effective pathway to enhance the production efficiency.[5]

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Among bioplastics, polylactic acid or polylactide (PLA) occupies an outstanding position. Derived from lactic acid, itself produced *via* fermentation of renewable resources such as corn or sugarcane, PLA combines biodegradability with biocompatibility. It has already found commercial applications in packaging, single-use items, and biomedical devices.[6,7] However, several challenges hinder its broader applications. PLA often displays lower thermal resistance and brittleness compared to petroleum-based plastics, and its end-of-life management is far from straightforward. Although theoretically biodegradable, industrial composting conditions are typically required, while degradation in natural environments is slow and incomplete.[8]

PLA is commonly produced through the catalytic Ring-Opening Polymerization (ROP) of lactide, a cyclic dimer of lactic acid, as displayed in Fig. 1.[9] The performance and structure of the resulting polymer — its molecular weight, dispersity, tacticity, and crystallinity — depend heavily on the catalyst used.[10] Currently, the industrial catalyst of reference is tin(II) octanoate ($Sn(Oct)_2$). While effective, this compound raises concerns regarding toxicity and environmental impact, particularly for biomedical applications where catalyst residues may come in contact with living systems.[11]

Hence, the development of sustainable, non-toxic, and highly controllable catalytic systems is of great interest. Among the promising candidates are alkali metal compounds based on sodium and potassium. These elements are earth-abundant, inexpensive, and biocompatible. Furthermore, recent studies have demonstrated that their catalytic potential, once overlooked in favour of heavier metals, can be harnessed by careful ligand design and reaction condition optimization.

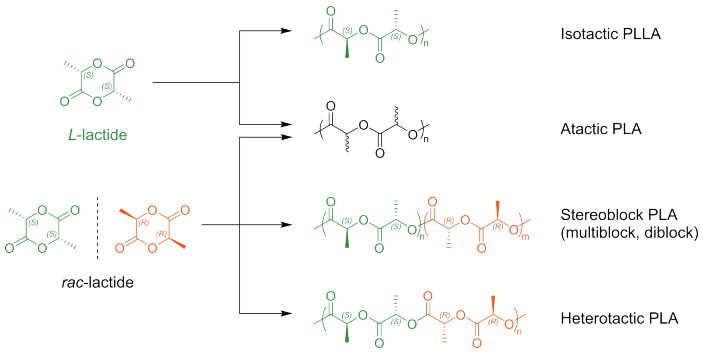


Fig. 1. Ring-opening polymerization of *L*-lactide (analogous for *D*-lactide) and *rac*-lactide.

2. Alkali Metal Complexes for Sustainable PLA Production *via* ROP

The use of sodium and potassium in catalysis benefits from several intrinsic properties. Both metals are abundant and inexpensive, ensuring economic viability. They are also non-toxic and biocompatible, qualities that are particularly valuable for polymers intended for medical or food-contact applications. In contrast to many transition metal catalysts, which may leave behind hazardous residues, alkali metals present minimal risk.

In most reported cases of alkali metal complexes as ROP catalysts, the ligands are aryloxides,[12–21] and less frequently O- and/or N- donor species such as amino-phenolates,[22–25] amidinates,[26,27] and quinolinolates.[28] Other neutral donor ligands such as sulfonamides[29] or calixarenes[30] have also been explored. Interestingly, only a few examples with chiral ligands have been described.

In our group, we have focused on O- and O-/N- donor ligands. In particular, we have prepared a family of sodium and potassium aryloxide complexes stabilized by bulky diphenylmethyl-substituted ligands. The bulky ligand provides steric protection around the metal centre, influencing both activity and selectivity.[31] Among the N- and O- donor ligands, we have explored oximates, a class of ligands that has previously been overlooked. Oximates are characterized by the presence of two adjacent donor atoms, which can show different coordination modes as well as an interesting reactivity due to cooperative effects.[32,33] We have investigated both the non-toxic commercial acetophenone oximate[34] and an oximate ligand derived from limonene to introduce chirality (Fig. 2).[35]

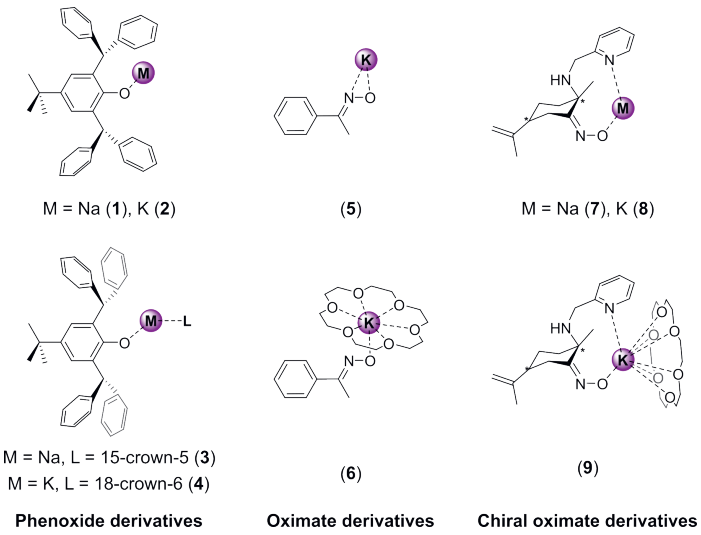


Fig. 2. Structures of alkali metal-based catalysts developed in our group.

These alkali metal derivatives have proven to be extremely active catalysts for the ROP of lactide. In particular, the aryloxide compounds, **1** and **2**, can achieve full conversion of *L*-lactide within minutes under ambient conditions (Table 1). Sodium complexes were generally more active than their potassium counterparts. However, the control over the polymerization it is not high and polymers with molecular weights significantly higher that the theoretical ones and dispersity values (Đ) over 1.5 are obtained. This behaviour could agree with a catalyst aggregation in solution, which would lead to less active centres available, reducing the polymer chains that are initiated which eventually leads to polymers with higher molecular mass.

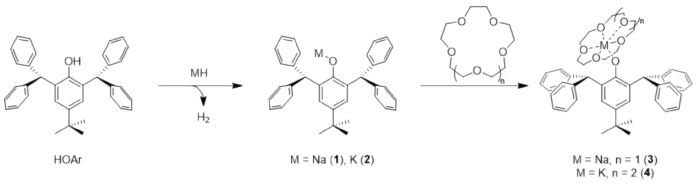
Table 1. ROP of LLA using alkali metal derivatives as catalysts.[a]

Ent.	Cat.	[LLA]: [Cat]	t (min)	conv.[b] (%)	$M_{n,theo.}$ [c](kDa)	$M_{n,exp.}$ [d] (kDa)	Đ [d]
1	**1**	100:1	0.5	>99	14.4	70.5	1.9
2	**1**	200:1	1	>99	28.8	99.0	1.8
3	**1**	400:1	2	>99	57.6	165.4	1.7
4	**1**	800:1	8	76	87.6	86.8	1.7
5	**2**	100:1	1.5	>99	14.4	57.5	2.0
6	**2**	200:1	2	>99	28.8	63.9	1.9
7	**2**	400:1	4	88	50.5	81.5	1.7

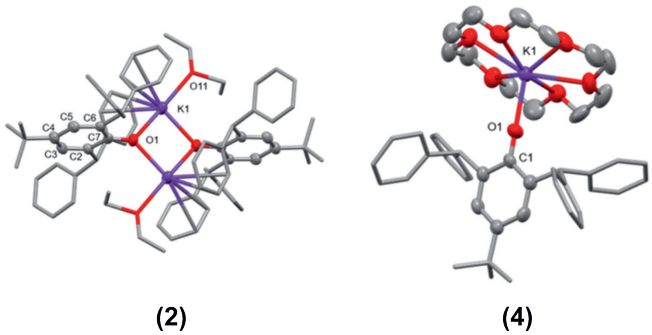
[a]All polymerizations were performed in CH_2Cl_2 at room temperature, [LLA] = 2 M. [b]Determined by ^1H NMR spectroscopy in $CDCl_3$. [c]$M_{n,theo} = ([LLA]_0/[Cat]_0) \cdot MW_{LLA} \cdot \%Conv.$ [d]Determined by GPC in THF, using polystyrene standards (Đ = Mw/Mn).

3. Polymerization Studies: Control Through the Use of Crown Ethers and Co-Initiators

The influence of the crown ether in potassium compounds used for lactide ROP has been described by Sipos and Zsuga, who observed that the presence of this cyclic unit significantly reduced the polydispersity of the polymers obtained.[36] The incorporation of crown ethers significantly alters the catalyst nuclearity and the aggregation. As shown in Scheme 1, compounds [NaOAr(15-crown-5)] (**4**) and [KOAr(18-crown-6)] (**5**) can be prepared *via* reaction with the appropriate crown ether, and while compound **2** is dinuclear, the crown ether coordination leads to mononuclear species, as evidenced by the structure determination using single crystal X-ray diffraction (Fig. 3).



Scheme 1. Synthesis of the alkali metal-based compounds with aryloxide ligands.



(2) (4)

Fig. 3. ORTEP plot of (**2**) and (**4**) showing thermal ellipsoid plots (30% probability). For clarity hydrogen atoms have been omitted, the phenoxide ligand substituents and the coordinated ether molecule are depicted as sticks.

This structural change has direct consequences for polymerization control: the crown ether–stabilized complexes exhibit lower activity but afford polymers with narrower Đ and M_n values, closer to the theoretical values (Table 2).

Another approach to enhance the control over the polymerization is the use of a co-initiator such as the benzyl alcohol, BnOH, widely used in ROP processes. Although the polymerizations conducted in the presence of BnOH showed similar conversions and reaction times compared to the results without co-initiator (Table 1), the molecular weights and dispersity values indicated a more controlled process. This effect was particularly evident in the full conversion reactions, where the M_n values were closer to the theoretical ones (Table 3).

Table 2. LLA polymerization employing crown ether derivatives.[a]

Ent.	Cat.	[LLA]: [Cat]	t (min)	conv.[b] (%)	$M_{n,theo}$[c] (kDa)	$M_{n,exp}$[d] (kDa)	Đ[d]
1	**3**	100:1	4	>99	14.4	17.2	1.6
2	**3**	200:1	6	95	28.8	22.8	1.5
3	**4**	100:1	8	83	12.0	12.0	1.5
4	**4**	200:1	16	70	20.1	13.7	1.5

[a]All polymerizations were performed in CH_2Cl_2 at room temperature, [LLA] = 2 M. [b]Determined by ^{1}H NMR spectroscopy in $CDCl_3$. [c]$M_{n,theo}$ = ([LLA]$_0$/[Cat]$_0$) · MW_{LLA} · %Conv. [d]Determined by GPC in THF, using polystyrene standards (Đ = Mw/Mn).

Table 3. LLA polymerization in the presence of BnOH.[a]

E	Cat.	[LLA]: [Cat]: [BnOH]	t (min)	conv.[b] (%)	$M_{n,theo}$[c] (kDa)	$M_{n,exp}$[d] (kDa)	Đ[d]
1	**1**	200:1:2	1	>99	14.5	11.8	1.4
2	**1**	400:1:2	2	>99	28.9	22.9	1.4
3	**1**	800:1:2	4	99	57.8	41.7	1.6
4	**2**	200:1:2	1	>99	14.5	19.4	1.5
5	**2**	400:1:2	2	>99	28.9	31.3	1.6
6	**2**	800:1:2	6	65	37.5	31.4	1.7

[a]All polymerizations were performed in CH_2Cl_2 at room temperature, [LLA] = 2 M. [b]Determined by ^{1}H NMR spectroscopy in $CDCl_3$. [c]$M_{n,theo}$ = ([LLA]$_0$/[Cat]$_0$) · MW_{LLA} · %Conv. [d]Determined by GPC in THF, using polystyrene standards (Đ = Mw/Mn).

4. Polymerization Mechanism

The polymerization pathway varies significantly depending on the presence or not of the co-initiator. To gain further insight into the mechanisms, end-groups analysis using MALDI-TOF experiments can provide key information. In our case, for the polymerizations using BnOH as co-initiator, the presence of benzyloxide as an end-chain group was evident in the mass spectrum (Fig. 4, top). It was also detected in the ^{1}H NMR spectrum (Fig. 5a). In an experiment performed with a LLA:Cat:BnOH ratio of 1:1:2 it was possible to detect benzyl lactate in the ^{1}H NMR spectrum, confirming that the polymerization goes *via* an activated monomer mechanism, (Scheme 2).[31]

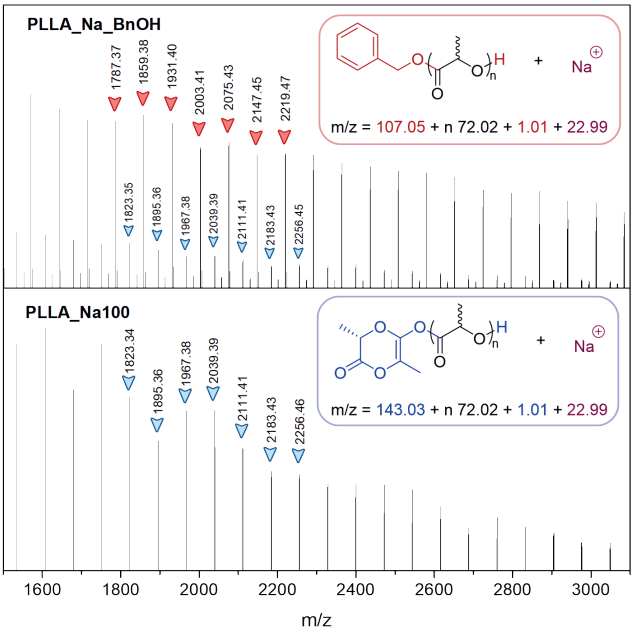
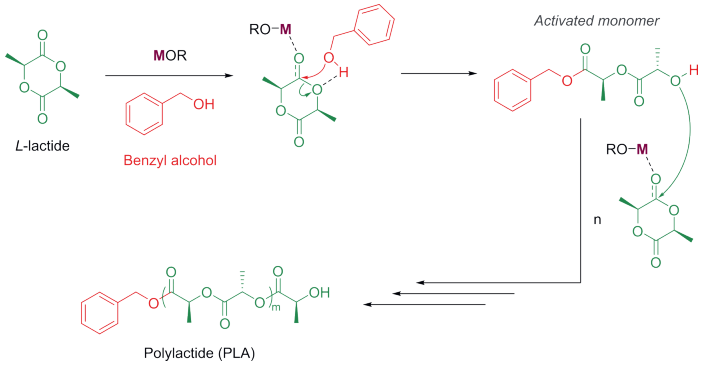


Fig. 4. MALDI-TOF spectra for PLLA obtained (top) with co-initiator (Entry **1**, Table 3) and (bottom) without (Entry **2**, Table 1).



Scheme 2. Activated monomer mechanism in the presence of the co-initiator.

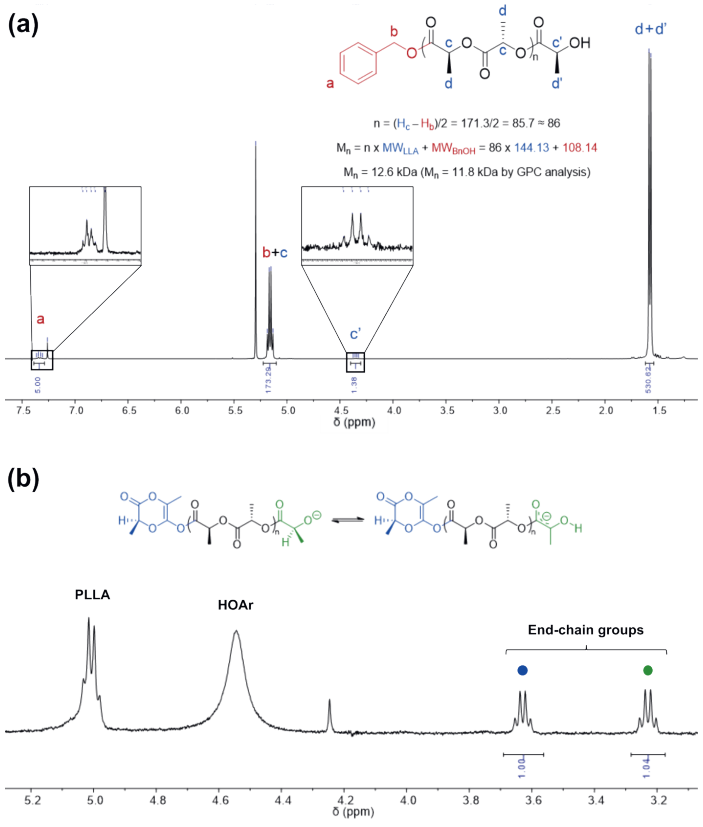
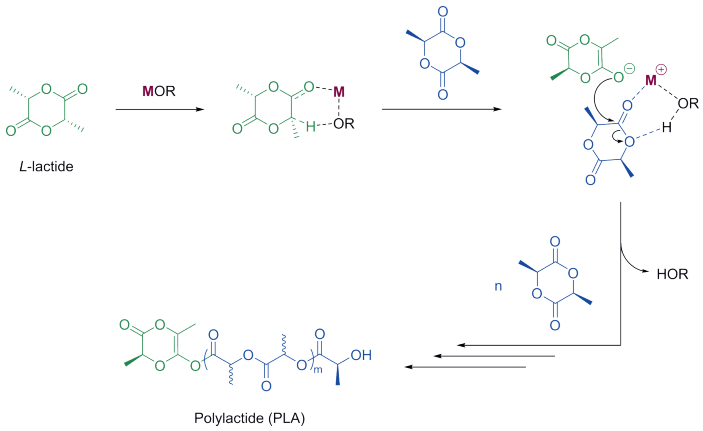


Fig. 5. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of (a) isolated PLLA obtained in the presence of BnOH ([LLA]:[**3**]:[BnOH] = 200:1:2) and (b) from the reaction between LLA and **1** using a ratio of 1:1 at –70 °C.

In the absence of the co-initiator, the mechanism may proceed *via* an anionic pathway, as it is often observed for alkali metal complexes.[37] In such case, the deprotonation of the lactide may generate an anionic fragment that would be responsible for the chain propagation. Again, NMR can give light on the pathway taking place, as such, a ^{1}H NMR experiment without BnOH allowed the detection of the protonated ligand, HOAr (see Fig. 5b). This indicates that the lactide was deprotonated by the ligand, leading to the formation of a lactide enolate. The formation of such species was further confirmed by a ^{13}C NMR spectrum, where a signal at 57.6 ppm was observed, corresponding to the methyl group of one of the resonant forms of the lactide enolate.[31,38,39] Besides, in the ^{1}H NMR spectrum of the polymer obtained with the LLA:catalyst ratio of 1:1, the CH proton of the chain end-group -CH(CH_3)OH could be identified (see Fig. 5b). Hence, the polymer obtained has a linear structure with enolate and -OH end-groups in agreement with the mechanism proposed in Scheme 3.



Scheme 3. Anionic mechanism in the presence of alkali-based catalysts without co-initiator.

A similar result was obtained both for the oximate and the aryloxide derivatives. These findings agree with an anionic ROP *via* monomer deprotonation, then the resonant form of the enolate initiates the polymerization propagation step (Scheme 3). This result shows that the basic character of the oximate or the aryloxide group is prevalent to the nucleophilic one, favouring the deprotonation instead of the nucleophilic attack to the carbonyl group of the lactide. Since the same behaviour has been observed across different ligands, it may be ascribed to the highly basic character of the ligands, motivated by a strong ionic component of their bond to the alkali metal.

Interestingly, for these systems, the addition of just one equivalent of BnOH results in the coexistence of two competing mechanisms, the anionic and the activated-monomer pathways. As such, in the ^{13}C NMR spectrum of the reaction with a LLA:Cat:BnOH 1:1:1 ratio, signals corresponding to both the benzyloxide and the enolate groups were observed, consistent with distinct end-groups of different polymer chains. To ensure that the polymerization proceeds only *via* an activated-monomer mechanism, at least two equivalents of BnOH per catalyst equivalent are required.[31,34]

5. PLLAs Characterization

The mechanism has a strong influence on the microstructure of the polymer formed. As mentioned above, in the absence of BnOH, the polymerization follows an anionic pathway, often leading to side reactions such as epimerization of the lactide units. In contrast, in the presence of BnOH, the mechanism shifts towards an activated monomer pathway, reducing epimerization and yielding polymers with higher isotacticity ($P_m \approx 1$). Hence this catalytic system gives the opportunity of modulating the polymer microstructure and, consequently, the material properties. As such, varying the reaction conditions (temperature, ratio or presence of co-initiator), allows control of the degree of epimerization and thus the incorporation of *D*-lactide units within predominantly *L*-lactide polymers. This directly affects the crystallinity, thermal behaviour, and mechanical properties of the PLA produced. Indeed, increased *D*-content lowers crystallinity and enhances flexibility, which is potentially useful for specific applications where brittleness is undesirable.

To evaluate the influence of molecular weight, end-chain groups and microstructure, thermal and mechanical characterization were performed on polymers produced using **1** and **2** without BnOH at different monomer-to-catalyst ratios (1:100 and 1:200), as well as the most comparable polymers, in terms of weight average molecular weight (M_w), obtained in presence of BnOH as co-initiator. Since epimerization was detected in several samples, their specific optical rotation was measured to determine the *D*-isomer percentage present in the polymeric chains. In accord-

ance with the NMR spectra, the polymers produced using BnOH as co-initiator maintain stereoregularity along the polymer chain, and the resulting PLLAs are highly isotactic with low *D*-content (< 2%, P_m > 0.97). However, for the polymerizations without the co-initiator epimerization took place, being more favoured as the temperature was increased. Comparing the activity of both catalysts, **2** induced more epimerization than **1**, resulting in values of *D*-content around 12%, confirming the trend observed by homodecoupled ^{1}H NMR spectra.[31,35]

In Table 4, the selected polymers are shown with their M_w, *D*-contents and thermal properties. The evaluation of their thermal transitions by Differential Scanning Calorimetry (DSC) corroborated clear differences between those with the benzyloxide end-chain group and those synthesized *via* an anionic mechanism. As shown in Fig. 6, the samples obtained in the presence of BnOH displayed higher melting temperatures (T_m) and crystallinity degrees (χ_c) compared to the other polymers.

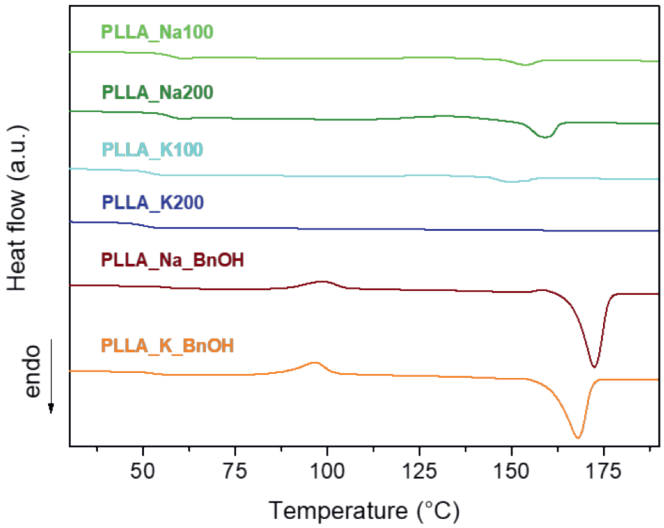


Fig. 6. DSC 2nd heating scans of the selected PLLAs produced by aryloxide derivatives.

These observations are attributed to the formation of bigger crystals with a more defined morphology, which would agree with the isotactic microstructure, as previously observed by homodecoupled ^{1}H NMR. As shown in Table 4, the presence of the *D*-isomer clearly disrupts the crystallinity of the polymer and induces a decrease in the T_g, T_m and χ_c values up to the point of hindering the PLLA crystallization, giving completely amorphous polymers for *D*-contents higher than 10%, as previously reported.[40–42]

6. Polymerization Studies: Control Using a Chiral Oximate Ligand

Another powerful strategy to control the microstructure of the final polymer is the use of chiral catalysts that exert higher constrains on the metal environment. In our group we have prepared oximate derivatives using terpene derived preligands, (complexes **7** and **8**, Fig. 2).[35] The ligand chosen has a pyridine group as a substituent on the nitrogen, which provides an additional coordination point to the metal and affects the nuclearity of the compounds in solution, as evidenced by DOSY 2D NMR studies.[35] Besides, the aggregation can be further limited by the addition of a crown ether ligand, which leads to the formation of the monometallic derivative **9** (see Fig. 2).

In this case we explored the activity of these chiral compounds towards *rac*-lactide ROP to check if there was a preferential activity towards one of the lactide isomers. These derivatives were also shown to be highly active, achieving high conversions within minutes, although full conversions were not reached under any conditions (Table 5) which could imply a preference for just one lactide isomer. As observed before, in the absence of co-initiator, higher molecular weights than the theoretical ones were attained. In fact, using a 1:200 catalyst-to-monomer ratio, the polymers obtained reached molecular weights over 100 kDa within a few minutes. This behaviour, similar to that observed for the aryloxide compounds **1** and **2**, can also be attributed to aggregation processes in solution.

Table 4. Intrinsic thermal properties of the selected PLLAs produced by aryloxide derivatives.[a]

PLLA sample	M_w[a] (kDa)	P_m[b]	T_g[c] (ºC)	T_{cc}[c] (ºC)	T_m[c] (ºC)	X_c[c] (%)
Na100	97.0	0.96	56	131	154	0.6
Na200	217.1	0.97	56	133	159	1.6
K100	93.8	0.88	52	129	150	0.8
K200	108.8	0.79	49	-	144	0.4
Na_ BnOH	65.1	0.98	57	99	172	46.0
K_ BnOH	53.4	0.97	53	97	168	38.9

[a]Determined by GPC in THF, using polystyrene standards. [b]Determined by homonuclear decoupled ^{1}H {^{1}H }NMR spectroscopy, as previously reported.[31,43] [c]Determined by DSC (2nd heating scans).[31,44]

Table 5. ROP of rac-lactide in the presence of limonene-based oximate derivatives.[a]

Ent.	Cat.	[*rac*-LA]: [Cat]: [BnOH]	t (min)	conv.[b] (%)	$M_{n,theo}$[c] (kDa)	$M_{w,exp}$[d] (kDa)	Đ[d]
1	**7**	100:1:0	2	70	10.1	27.4	1.6
2	**7**	200:1:0	25	65	18.7	101.9	1.4
3	**7**	300:1:0	5	62	26.8	90.7	1.2
4	**7**	300:1:1	2	59	25.5	48.5	1.6
5	**8**	100:1:0	2	58	8.4	16.1	1.5
6	**8**	200:1:0	3	60	17.3	106.8	1.7
7	**8**	300:1:0	5	62	26.8	26.4	1.7
8*	**8**	300:1:0	6	59	25.5	73.8	1.4
9	**8**	300:1:1	2	59	25.6	31.7	1.5

[a]All polymerizations were performed in toluene at room temperature, [Cat] = 0.01 M. *Entry 8 performed at 0 ºC [b]Determined by ^{1}H NMR spectroscopy. [c]$M^{n,theo}$ = $([LLA]_0/[Cat]_0) \cdot MW_{LLA} \cdot$ %Conv. or $M_{n,theo}$ = $([LLA]_0/[BnOH]_0) \cdot MW_{LLA} \cdot$ %Conv. + M_w(BnOH). [d]Determined by GPC-MALS in THF (Đ = M_w/M_n).

The potassium compound **8** shows some tendency to give isotactic polymers with P_m values around 0.6. To achieve a higher control of the stereoselectivity, we performed the polymerization at low temperatures (T = 0 ºC). As the temperature decreased, the molecular weight of the polymer increased as an indication that fewer active centres are available due to aggregation (26.4 *vs*

73.8 kDa). This effect takes place as the temperature decreases until –70 °C, when the catalyst is inactive and no conversion is observed, suggesting that the aggregation also occurs for **8**. To address this problem, we studied the polymerization activity of its crown ether derivative (**9**), in which the potassium atom is saturated by a 18-crown-6 ether.

Compound **9** is an active catalyst in toluene, even at –70 °C, giving nearly complete conversions (see Table 6). Furthermore, this catalyst exhibits a high stereocontrol on the process and produces highly isotactic PLA with remarkable P_m values in the 0.85–0.93 range. These values match the highest ones reported for PLA generated from *rac*-lactide with potassium compounds and **9** achieves these results remarkably quickly.[12–14,22,26]

Table 6. ROP of *rac*-lactide using **9** as catalyst.[a]

Ent.	[*rac*-LA]: [Cat]: [BnOH]	t (min)	Conv.[b] (%)	$M_{n,theo}$[c] (kDa)	$M_{w,exp}$[d] (kDa)	Đ[d]	P_m[e]
1	100:1:0	180	>99	14.4	61.1	1.1	0.85
2	100:1:1	100	>99	14.5	18.0	1.1	0.89
3	100:1:5	30	>99	3.0	8.9	1.1	0.86
4	100:1:10	10	>99	1.6	3.6	1.1	0.93

[a]All polymerizations were performed in toluene at - 70 °C, [Cat] = 0.01 M. [b]Determined by ^{1}H NMR spectroscopy. [c]$M_{n,the}o$ = ([LLA]0/[Cat]0) · MW_{LLA} · %Conv. or $M_{n,theo}$ = ($[LLA]_0/[BnOH]_0$) · MWLLA · %Conv. + Mw(BnOH). [d]Determined by GPC in THF calibrated versus polystyrene standards using a correction factor of 0.58 (Đ = M_w/M_n). [e]Determined by homonuclear decoupled ^{1}H{^{1}H} NMR spectroscopy, as previously reported.[31,43]

The formation of isotactic polylactide from *rac*-lactide is a consequence of the enantiomeric behaviour of the catalyst or initiator. To explore this behaviour for **9**, different experiments with both enantiomers, (1*S*,4*R*)-**9** and (1*R*,4*S*)-**9**, toward *L*-lactide and *rac*-lactide were carried out. The results displayed in Table 7 evidence that (1*S*,4*R*)-**9** exhibits a preference for *L*-lactide, as such, the polymerization takes place in 5 minutes. However, 180 minutes are needed to achieve the same conversion for *rac*-lactide. Hence, for (1*S*,4*R*)-**9** the polymerization of the *levo* monomer is kinetically favoured. For its part, the enantiomer (1*R*,4*S*)-**9** polymerized *L*-lactide more slowly, reaching only 63% after 120 minutes, which is an indication of a higher tendency to polymerize *D*-lactide.

Table 7. Enantiomeric experiments with both isomers of **9**.[a]

Ent.	Catalyst	Monomer (LA)	t (min)	conv.[b] (%)
1	(1*S*,4*R*)-**9**	*rac*-lactide	180	>99
2	(1*S*,4*R*)-**9**	*L*-lactide	5	>99
3	(1*R*,4*S*)-**9**	*L*-lactide	120	63

[a]All polymerizations were performed in toluene at –70 °C. [b]Determined by ^{1}H NMR spectroscopy.

Hence when the polymerization is performed with (1*S*,4*R*)-**9** the polymerization of both lactide isomers *L* and *D* would take place sequentially, first the *L* isomer, which is more favoured, and then the *D* isomer. The resulting polymer could be considered a block copolymer PLLA-PDLA. This type of isotactic polylactide may form stereo-complexes due to the strong interactions between both blocks. These structures exhibit higher thermal resistance and melting points than the other PLA microstructures. Considering the P_m values obtained when using **9** as catalysts, DSC studies were carried out to analyse the possible formation of stereo-complexes. As shown in Table 8 (entry 1), very high melting points are observed for the polymer with the highest P_m value, indicating the tendency to form stereo-complexes.

Table 8. Thermal properties of the PLLAs produced with the enantiomers (1*S*,4*R*)-**9** and (1*R*,4*S*)-**9**.[a]

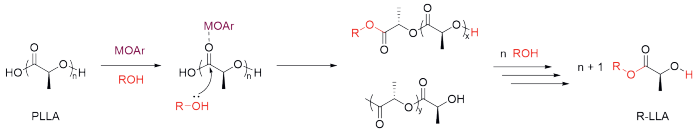
Ent.	Reaction conditions	conv.[b] (%)	T_m[c] (ºC)
1	*rac*-LA: (1*S*,4*R*)-**9**:BnOH (100:1:5), –70 ºC	>99	184
2	*rac*-LA: (1*S*,4*R*)-**9**:BnOH (100:1:0), –70 ºC	>99	178
3	*rac*-LA: (1*S*,4*R*)-**9**:BnOH (100:1:0), 25 ºC	>99	167
4	*L*-LA: (1*S*,4*R*)-**9**:BnOH (100:1:0), –70 ºC	>99	109
5	*L*-LA: (1*R*,4*S*)-**9**:BnOH (100:1:0), –70 ºC	63	92

[a]All polymerizations were performed in toluene, [Cat] = 0.01 M. [b]Determined by ^{1}H NMR spectroscopy. [c]Obtained by DSC 2nd heating.

Hence, our potassium derivative, (1*S*,4*R*)-**9**, bearing 18-crown-6 as an auxiliary ligand, is able to generate isotactic polylactide from *rac*-lactide with excellent conversions in short reaction times. The striking difference to compound **7**, that does not have a crown ether, provides evidence of the crucial role of this ligand. The nature of the terpenoid ligand used is also key in the process, and for **9**, the improvement of the process control and the stereoregularity of the polymers is also related to the coordination of the pyridine group to the metal.

7. Chemical Upcycling *via* Alcoholysis

Beyond polymerization, these alkali metal aryloxides and oximates also catalysed the alcoholysis of PLA, enabling its chemical upcycling into alkyl lactates such as methyl or ethyl lactate (Scheme 4).



Scheme 4. Proposed mechanism for alcoholysis of PLLA in the presence of alkali-based complexes (R = Me, Et or Bn).

These products are valuable as solvents, flavouring agents, or chemical intermediates.[46] In particular, for the aryloxide derivatives, strikingly, depolymerization occurred within 15 minutes at room temperature, far outperforming many previously reported systems where higher temperatures, longer reaction times, and excess reagents are required.

8. Conclusions

This article highlights some key advances in this emerging area. Although alkali metals have been considered less active than transition metals, our bulky aryloxide alkali metal complexes are capable of promoting a very fast polymerization of *L*-lactide to give high-molecular-weight poly-*L*-lactic acid (PLLA). By manipulating the aggregation of the catalyst using crown ethers and employing co-initiators like BnOH, it is possible to control the polymerization mechanism and to influence the stereoregularity of the resulting PLLA. This control affects the thermal and mechanical properties of the polymer and hence its applications. Additionally, using chiral alkali metal compounds permits isoselective polymerization of *rac*-lactide, yielding isotactic PLA. Together, these studies illustrate how ligand architecture and reaction conditions can be tuned to achieve high levels of control of lactide polymerization promoted by alkali metal compounds.

Furthermore, the dual capability — efficient polymerization and facile depolymerization — illustrates the potential of alkali metal compounds to support closed-loop PLA lifecycles, aligning production with sustainability goals.

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