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Bismuth tris-silylamide: a New Non-Toxic Metal Catalyst for the Ring Opening (Co-)Polymerization of Cyclic Esters under Smooth Conditions

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Abstract.

Ring Opening Polymerization of *rac*-lactide and ϵ -caprolactone as well as their copolymerization was achieved by means of bismuth tris-silylamide in solution and at temperatures below 75 °C. The best performances in terms of control of the polymerisation were obtained in presence of an alcohol as chain transfer agent. A PLA-based copolymer containing up to 23 % ϵ -caprolactone can be prepared. When activated with a borane molecule, bismuth tris-silylamide produces polymers having narrower polymer distributions.

Keywords.

Ring Opening polymerization; bismuth; lactide-lactone copolymer

1. Introduction

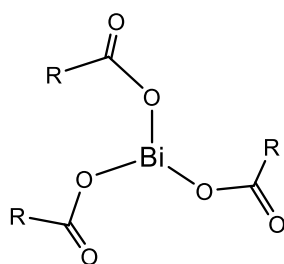
Bismuth compounds have been relatively little used for catalytic purposes by comparison with other elements over the Mendeleiev classification. The bismuth element, which is present in numerous pharmacology formulations, is considered as being of very low toxicity [1]. It is a large size metal having a strong ionic character that offers a Lewis acid

behaviour, therefore standing as effective candidate for the activation of a cyclic ester through Ring Opening Polymerization (ROP) process [2], to afford biodegradable and biocompatible polyesters [3]. This domain of the material science has seen an outstanding expansion because of environmental concerns, relating to both the life cycle of the polymer materials with their impact on ecosystems and the nature of the resources used for their preparation [4]. Polylactide (abbreviated as PLA), derived from lactide (LA), dimer of lactic acid, a renewable resource available from starch, is a major player in this area. It is nowadays industrially prepared by means of stannous octoate-mediated ROP. But tin being considered as toxic, it is of interest to propose other catalytic alternatives based on elements that would fit in a frame of biocompatibility. Bismuth derivatives have been studied quite scarcely in this context. Chart 1 shows the different bismuth compounds used for ROP that were reported in the literature: inorganic derivatives such as BiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) **Ia-c** [5], the homoleptic acetate **IIa** [6], 2-ethylhexanoate **IIb** [7], hexanoate **IIc** [8], triflate **III** [9,10,11] and alkoxides **IVa-c** [12], the heteroleptic subsalicylate **V** [8,13,14], (Salen)bismuth alkoxides **VIa** and **VIb** [15] and the diphenyl bismuth bromide **VII** [16,17]. Among them, a number were also found as efficient catalysts for the copolymerization of lactide with a lactone. Bismuth subsalicylate **V**, which is the main component of Pepto-Bismol®, has shown a particular interest. The recent studies cited above demonstrate its valuable performances toward the ROP of rac-lactide (LA) or ϵ -caprolactone (CL), versus those of tin octoate, in terms of activity or degradation kinetics of the polymer material [18], together with a much lower toxicity [2]. But this compound has a complex polymeric structure and is insoluble in all organic solvents, which may be a limitation to its efficiency [8].

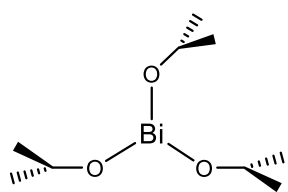
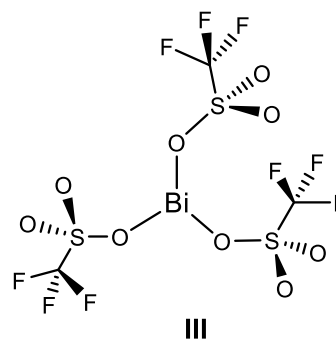
Aiming at assessing an alternate simple and soluble bismuth complex, and considering ROP catalysts based on trisamido derivatives of other metals [19], we turned our attention to $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ (Chart 1, bottom) [20]. This complex is highly soluble in low polar solvents like toluene, which is commonly used for ROP of LA and related cyclic esters. Moreover, we were interested in the possibility to explore the reactivity of this compound in the presence of a borate co-reagent, which is known to easily generate cationic species from a metal-silylamido moiety [21]. The ROP of cyclic esters by cationic catalysts has been the recent subject of a review by Carpentier et al. in which are detailed the potential of such strategy [22].

We present in this contribution our studies devoted to the homo-polymerization of rac-lactide and ϵ -caprolactone with $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ under various experimental conditions, and we also report some results in the statistical co-polymerization of these two monomers.

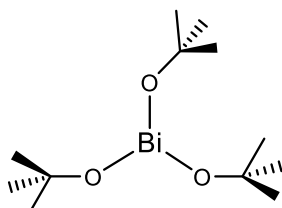
BiX₃
 X = Cl, **Ia**; Br, **Ib**; I, **Ic**



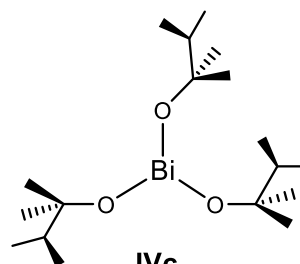
R = Me, **IIa**; n-Pent, **IIb**; Et-2-Pent, **IIc**



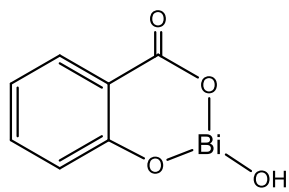
IVa



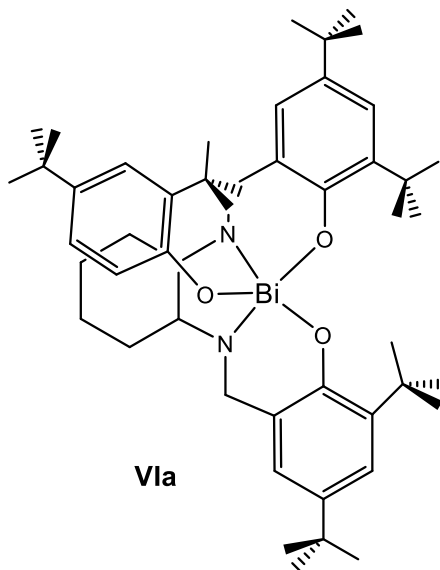
IVb



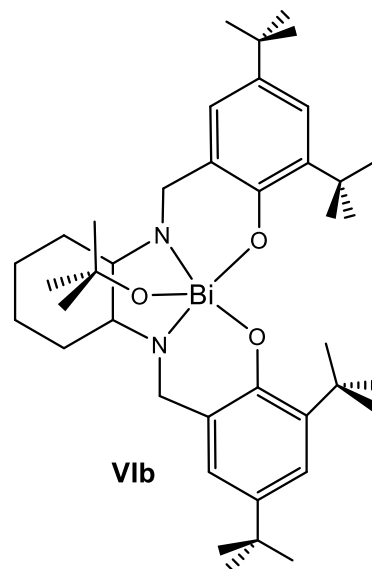
IVc



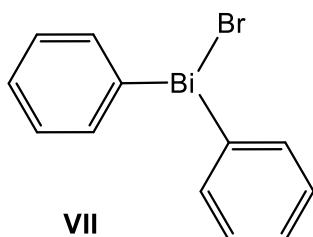
V



VIa



VIb



VII

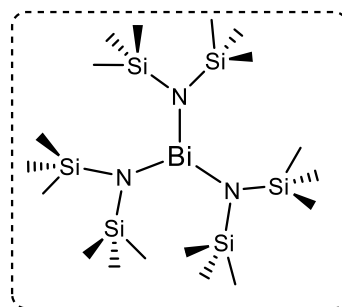


Chart 1. Bismuth complexes used in Ring Opening Polymerization of cyclic polar monomers (bismuth tris(silylamido) used in this work in dot square).

2. Experimental

2.1. Materials and methods

All experiments were done using Schlenk techniques or a glove box (Jacomex). $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ was synthesized as reported [20]. Toluene was purified through alumina column (Mbraun) and stored on molecular sieves in a glove box. E-caprolactone (CL) (Aldrich) was dried over calcium hydride, distilled twice, and stored over molecular sieves in a glove box. *Rac*-lactide (LA) (Aldrich) was purified in two steps by dissolution/evaporation from dry toluene, followed by sublimation of the monomer. NMR (^1H , ^{13}C) spectra were recorded on a Bruker Avance 300 apparatus at room temperature in CDCl_3 . The chemical shifts were calibrated using the residual resonances of the solvent. SEC analyses were performed in THF at 40 °C with a Waters apparatus, calibrated with polystyrene standards, equipped with Waters Styragel columns HR2, HR3, HR5 and HR5E.

2.2. Polymerization procedures and characterization

In a typical polymerization (run 1 taken as an example), a flask was charged in a glove box with the Bi initiator (15 mg, 20 μmol). The solvent (toluene, 1.5 mL), the monomer (for a given monomer to initiator ratio, equal to 100 (0.288 g, 2 mmol) for run 1 and eventually benzyl alcohol (none for run 1), were added in this order. After a given time (2 h) and temperature (75 °C) under stirring, the viscous mixture was treated with a few drops of acidified methanol (methanol containing *ca.* 1% HCl 1M) to quench the reaction, and precipitated in a large excess (200 mL) or methanol. For experiments of LA polymerization or CL/LA co-polymerization carried out in the presence of benzyl alcohol, the reaction mixture was precipitated with a large excess (typically 200 mL) of cold (acetone / liquid nitrogen bath) diethyl ether. The resulting polymeric material was dried under vacuum at room temperature to a constant weight (0.17 g). The yield (59 %) was determined by gravimetry or by conversion by ^1H NMR of a reaction sample withdrawn at a given time. The activity was calculated according to the following formula: $[(\text{monomer conversion}) \times (\text{monomer to catalyst molar ratio}) \times (\text{molar mass of monomer})] / (\text{time of reaction in h})$. The copolymers composition was determined by ^1H NMR by integration of the following signals: δ (ppm) = 3.30 and 4.06 (PCL), 2.64 and 4.23 (CL

monomer), 5.16 (PLA), 5.04 (LA monomer), 2.39 (LA-CL enchainment), 4.13 (CL-LA enchainment) as reported in the literature [23].

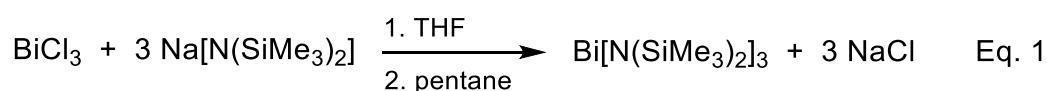
2.3. Polymerization reactions with boron compounds activation of $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$

In some experiments (runs 18-26), a boron compound: $\text{B}(\text{C}_6\text{F}_5)_3$, $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ was added to $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ (10.2, 16.2 and 18.4 mg, respectively, for 1 equiv) before addition of the toluene. Then other reagents were added as described above to proceed to polymerization reactions.

3. Results and discussion

3.1. Homopolymerization of cyclic esters

The bismuth compound $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ used for this study is soluble in non-polar solvents, which fits well with our objective to carry on ROP reactions under smooth experimental conditions. It was synthesized by ionic metathesis according to equation 1 in THF followed by extraction with pentane [20]. LA polymerization experiments were conducted in toluene solution, at 75 °C, so as to achieve a compromise between LA solubility and control of the polymerization, since it was reported that undesired transesterification reactions take place when the ROP is conducted in bulk in neat monomer, which requires high temperatures [24]. These conditions were already utilized in a ROP study of Leskelä et al. with bismuth catalysts, therefore offering a possibility of comparing the results [12].



Selected results are shown in Table 1. First, it can be seen from runs 1 to 5 that $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ displays a good efficiency toward the production of PLA, with an activity of *ca.* 12 kg polymer/mol(Bi)/h (run 5). This result is comparable to other reported bismuth catalysts, under similar solution conditions, and is superior to the activity of $\text{Sn}(\text{oct})_3$ (< 8 kg polymer/mol(Sn)/h) [12]. The experimental molecular weight is higher than the expected theoretical one (calculated for one growing chain per Bi catalyst) in most cases (runs 1-4). This can be related to a rather poor initiation efficiency - the number of polymer chains grown per catalyst - by the Bi-N moiety. With monomer to catalyst ratios higher than 100 (runs 4,5), the initiation efficiency increases up to 1.3, but along with noticeable broadening of the dispersity,

in line with the likelihood of several Bi-N active bonds as already proposed in the case of homoleptic trisamido complexes of other metals [25]. For a given quantity of monomer, the dispersity is also increasing with time, which can be attributed to the likely occurrence of undesired transesterification reactions [26].

Table 1

Solution polymerization of cyclic esters with Bi[N(SiMe₃)₂]₃ as catalyst (runs 1-8, M = LA; runs 9-11, M = CL).

Run ^a	[M]/[Bi]/[BnOH]	t (h)	conv. (%) ^b	M_n (exp) ^c (g/mol)	M_n (th) ^d (g/mol)	N ^e	\bar{D} ^c	ester/amide chain end ^b
1	100/1/0	2	59 ^f	17200	8500	0.5	1.58	
2	100/1/0	4	70 ^f	20000	10000	0.5	1.74	
3	100/1/0	8	93 ^f	26700	13400	0.5	1.85	
4	200/1/0	4	83 ^f	29100	23900	0.8	2.15	
5	400/1/0	4	85 ^f	36200	48800	1.3	2.26	
6	200/1/1	4	98.6	16100	28400	1.8	1.73	5
7	200/1/3	4	98.5	6800	28400	4.2	1.54	13
8	200/1/5	4	98.8	5600	28500	5.1	1.44	18
9	200/1/0	4	36	16500	8200	0.5	2.32	
10 ^g	200/1/0	4	20	36600	4600	0.1	1.85	
11	200/1/3	4	91	9000	20800	2.3	1.28	no amide

^a n(Bi) = 10 μmol, [M]₀ = 0.67 M in toluene, 75 °C.

^b Determined by ¹H NMR of an aliquot of the reaction mixture.

^c Measured by SEC with reference to PS standards and corrected with 0.58 (LA) [27] or 0.56 (CL) [28] factor.

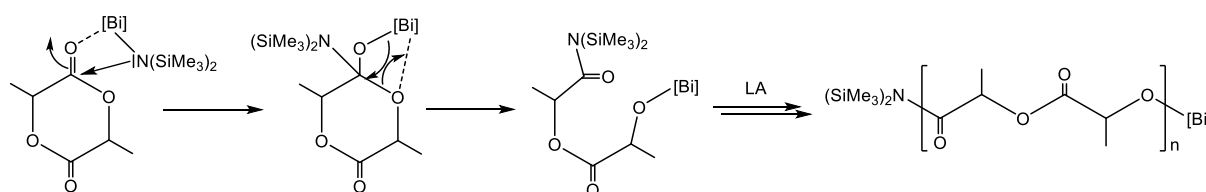
^d M_n (th) = yield x [LA]/[Bi] x 144 or yield x [CL]/[Bi] x 114 (calculated for one polymer chain per Bi).

^e Number of polymer chains per Bi = M_n (th)/ M_n (exp).

^f Determined by gravimetry.

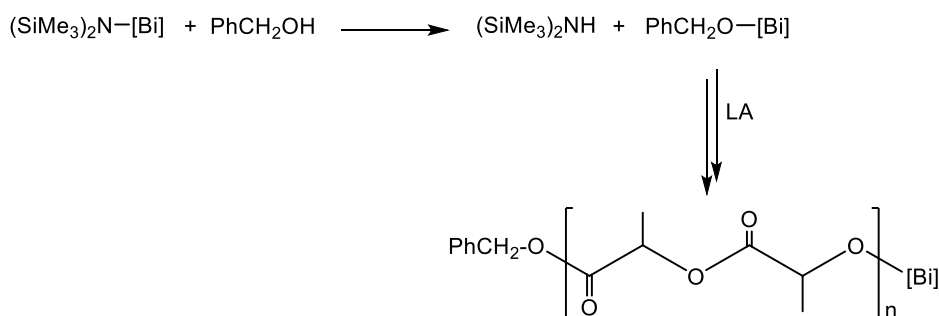
^g T = 25 °C.

With Bi[N(SiMe₃)₂]₃ as catalyst and in absence of alcohol (runs 1-5), the classical coordination-insertion mechanism (Scheme 1) [29] must lead to PLA chains bearing the amide –C(O)–N(SiMe₃)₂. This was actually observed, with the resonance at δ = 0.15 ppm in CDCl₃ (0.035 ppm in C₆D₆) [30], which cannot be confused with the silicone grease residue (δ = 0.07 ppm in CDCl₃ and 0.29 ppm in C₆D₆) [31].



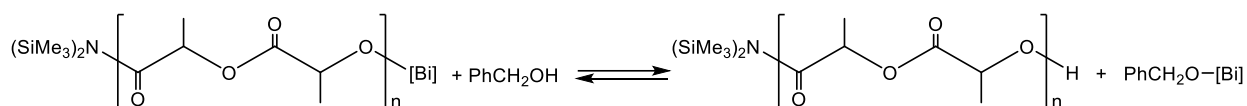
Scheme 1. Coordination-insertion mechanism affording amido-terminated PLA chains.

Reactions were in a second time conducted in the presence of an alcohol source in quantities up to a slight excess, with the aim to better control the polymerization due to anticipated faster initiation of M-O rather than M-N moiety [32] and transfer agent capability of the alcohol [33]. This approach was to our knowledge only reported once in the case of bismuth-mediated ROP [34]. To our delight, the performances were improved, with total conversion within 4 h (1-5 equiv benzyl alcohol, runs 6-8). The projected benzyl end-group of the PLA produced was evidenced by ^1H NMR ($\delta = 7.34$ ppm in CDCl_3 , run 8, Figure 1) [35]. However, the signal at $\delta = 0.15$ ppm was still present, as a minor contribution. From the relative integration of the latter vs that of the signal at $\delta = 7.34$ ppm, for PLA received from run 8, an estimate can be made of 17 out of 18 chains that have an ester chain end, and one chain has an amide chain end. This shows that the benzyl alcohol has a significant effect on the initiation process, and speaks in favor of alcoholysis of a Bi-N bond, prior to the initiation of the polymerization (scheme 2), leading to a $[\text{Bi}]\text{-OCH}_2\text{Ph}$ species that is willing to initiate a PLA chain formation.



Scheme 2. Alcoholysis by BnOH prior to initiation (for one Bi-N bond) affording benzyloxy-terminated PLA chains.

Doing the same analysis for PLAs received from runs 6 and 7 confirmed the presence of both end-groups, in a ratio of 5 and 13 when running the polymerization with 1 and 3 equiv BnOH, respectively. Regarding macromolecular data, a regular decrease of molecular weights along with narrowing of distribution was noticed with the amount of alcohol added, in good agreement with the occurrence of transfer reactions (Scheme 3). In the case of 1 equiv BnOH, the broad distribution can be attributed to several active species working at the same time, as shown by the polymer end-group analysis above. A number of growing chains close to the one expected considering the number of alcohol equiv and one amido group is observed.



Scheme 3. Transfer reaction with benzyl alcohol affording amido-terminated PLA chains

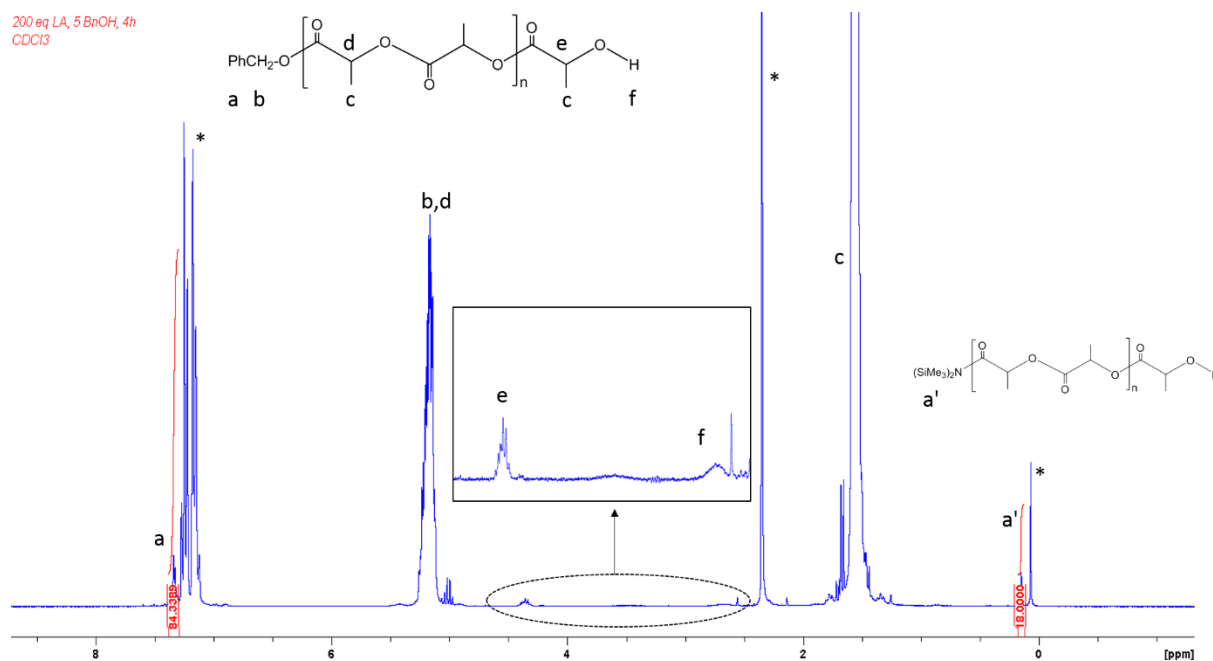


Fig. 1. ¹H NMR spectrum of PLA issued from run 8 for the determination of the chain end (in CDCl₃, * toluene and silicone grease residues).

Under similar conditions as for LA, a low conversion of CL was obtained (run 9, 36%). This result is quite surprising, since CL is known to generally ring open **much** more easily than LA [36] even if some exceptions can be found [37]. At 25°C, the conversion was limited to 20 % within 4 h of reaction. The dispersity is very broad whatever the temperature, which is again an indication of slow initiation *vs.* propagation process. An end-group analysis of low M_n PCL samples performed by ¹H NMR showed the typical resonance of an amido –C(O)-NTMS₂ extremity ($\delta = 0.15$ ppm in CDCl₃, same as in the case of LA), thus establishing the initiation via the [Bi]-NTMS₂ moiety. The polymerization was more controlled in the presence of benzyl alcohol, similarly as observed with LA, with evidence of transfer when looking at the number of polymer chains per bismuth metal (2.3, run 11). The sole end-group was this time a benzyloxy one.

3.2 LA/CL statistical copolymerization:

PLA has some limitations in terms of physico-chemical properties, and these can be upgraded by introducing a co-monomer, a well-known strategy to modulate the properties and improve the potentialities of a polymer material [38]. In general, when LA/CL copolymerizations were attempted under smooth experimental conditions (solution, low temperature) - to avoid undesired transesterification - very few CL was introduced, apart from a very little number of exceptions [23b,39,40]. The polymerization of both monomers introduced together was thus assessed under the same experimental conditions as for homopolymerizations. Selected experiments are gathered in Table 2.

Table 2

Solution statistical co-polymerization of LA/CL with Bi[N(SiMe₃)₂]₃ as catalyst.

Run ^a	[LA]/[CL]/[Bi]/[BnOH]	t (h)	conv. (%) ^b	<i>M_n</i> (_{exp}) ^c (g/mol)	<i>D</i> ^c	CL % ^d	LA-CL/CL-CL% ^d
12	100/100/1/0	4	39	17100	1.81	6	85/15
13	100/100/1/1	4	51	8600	1.92	13	90/10
14	100/100/1/3	4	55	5400	1.60	19	91/9
15	50/150/1/0	16	15	-	-	21	60/40
16	50/150/1/3	4	57	3400	1.52	23	99/1
17	50/150/1/3	22	65	47000	1.68	47	89/11

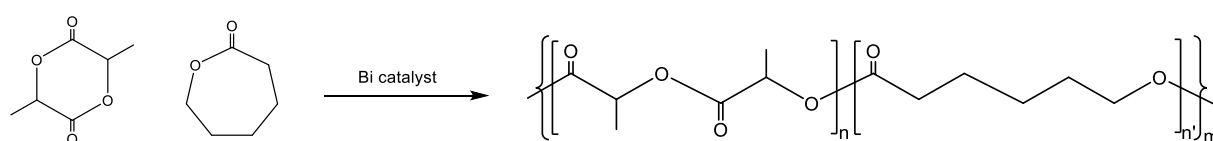
^a n(Bi) = 10 μmol, [LA]₀ = [CL]₀ = 0.67 M in toluene, 75 °C, t = 4h.

^b Total monomer conversion, determined by ¹H NMR of an aliquot of the reaction mixture.

^c Measured by SEC with reference to PS standards and corrected with 0.58 factor.

^d Determined by ¹H NMR.

With equivalent amount of monomers in the feed, some polymer was produced, but the yield was lowered when compared to the polymerization of LA alone (run 12 vs run 4). As shown by the ¹H NMR analysis [40], CL was incorporated at 6 mol% only, which highlights the classical expected preference for LA. A typical copolymer formula is shown in Scheme 4. With a 50/150 feed ratio in favour of CL, the amount of CL in the copolymer increased to 21%, but this was detrimental to the yield (run 15, 15% conversion in 16 h). The probability of CL-CL enchainment (and therefore CL-CL sequences length) was also found higher when feeding the mixture with three times more CL than LA.



Scheme 4. Statistical LA-co-CL copolymer obtained with Bi[N(SiMe₃)₂]₃ catalyst

In the presence of 1 equiv. benzyl alcohol, both the conversion and the CL content were improved (run 13), with twice more CL in the copolymer (13% vs. 6 %, run 13 vs. run 12, respectively). As expected also, the M_n value was significantly reduced (here divided by a factor of two). Increasing the benzyl alcohol amount afforded better conversion and an optimal of CL content of 19% (run 14, Fig. 2), which represents three times the quantity observed in absence of benzyl alcohol (run 12). This result is in line with the recent report from the group of Cui [40], who demonstrated the beneficial role of an alcohol as transfer agent in statistical LA/CL copolymerization, while a similar trend had already been notified in the case of non-polar monomers [41]. Besides, the behavior of the catalytic system resembles to that in homopolymerization: the tightening of dispersities and the gradual decrease of the molar masses decipher effective transfer of polyester alcohols formed, to the catalyst (runs 13, 14). One can note however that with a LA-CL/CL-CL ratio which remains stable at the value of 9 whatever the quantity of benzyl alcohol according to NMR, the possibility to extend the CL sequences is not attained. It seems that the presence of the alcohol will rather impact the CL/LA competition after a LA motive than a CL one. In other terms, the occurrence to insert a CL monomer after a LA is improved, but not the one to insert a second CL monomer subsequently. Running the polymerization with a CL/LA feeding ratio of three and in the presence of 3 equiv. benzyl alcohol afforded after 4 h a polymer with 23 % CL content, together with a good activity (run 16, Fig. 2). It is noteworthy that the CL motive was in this case systematically surrounded by two LA units (LA-CL/CL-CL% = 99/1), while the transesterification was limited to a few % (typical lactyl resonance at $\delta = 171.0$ ppm Figure 3 [42]). When the reaction time was prolonged (run 17, $t = 22$ h), a low M_n polymer material having 47 % CL incorporated with a clear increase of the number of CL-CL junctions was found. This, along with the much higher molecular weight ($M_n = 47000$), speaks in favor of the gradual enrichment of CL sequences in this second stage. The integration signal of the lactyl moiety significantly increased in that case.

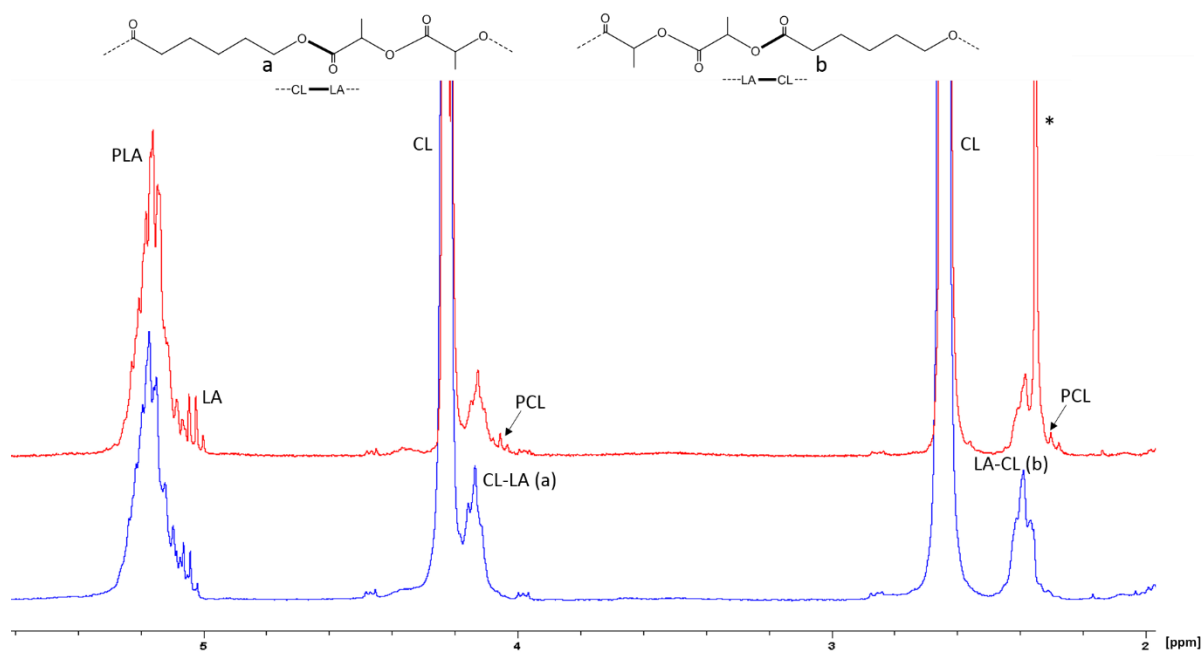


Fig. 2. ^1H NMR spectrum of the reaction mixture issued from run 14 (top, red) and run 16 (down, blue) showing the signals of the junction motives in the copolymer along with those of LA, CL, PLA, PCL (CDCl_3).

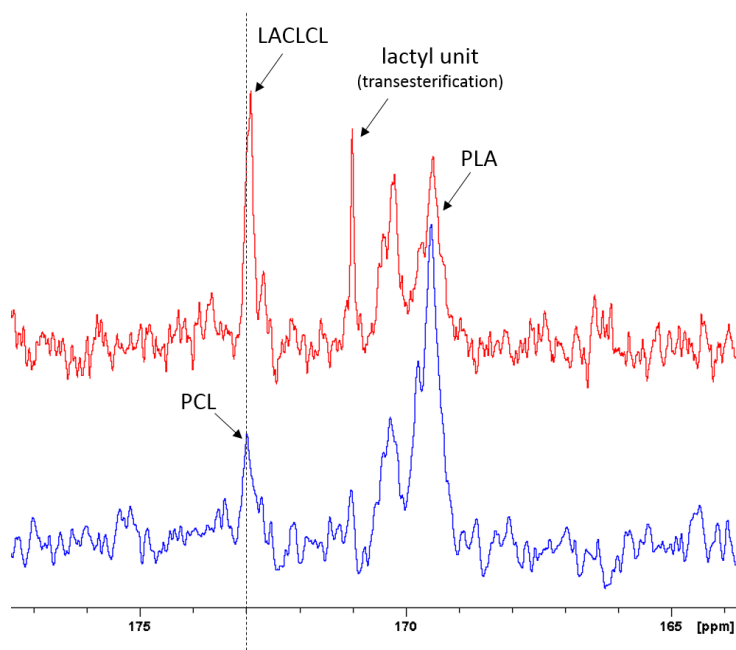


Fig. 3. ^{13}C $\{^1\text{H}\}$ NMR region of copolymers issued from run 16 (bottom, blue) and run 17 (top, red) showing the increase of transesterification (CDCl_3).

3.3. Polymerization reactions in the presence of a boron-based activator

As demonstrated recently by the group of Diaconescu, switching between two redox forms of a metal complex may result in a change in the behavior for each monomer in statistical copolymerization reactions [43]. We thus anticipated that the competition between LA and CL

would possibly be changed by running the polymerization in the presence of a catalyst having higher Lewis acid character. In this frame, the bismuth catalyst $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ was assessed in the presence of a boron reagent, which is known to afford cationic species by the activation of a metal-amide bond [21]. The experimental conditions of polymerization were unchanged vs. previously. Selected experiments are gathered in Table 3.

Table 3

Solution polymerization with $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$ as catalyst activated by a boron compound.

Run ^a	[LA]/[CL]/[Bi]/[BnOH]	Add ^b	conv. (%) ^c	$M_n(\text{exp})^d$	\bar{D}^d	$M_n(\text{th})^e$ (N)	CL % ^f	LA-CL/CL-CL% ^f
18	200/0/1/3	B	86	7000	1.15	24800 (3.5)	-	-
19	200/0/1/5	B	82	4600	1.24	23600 (5.1)	-	-
20	200/0/1/3	2 B	16	2000	1.07	4600 (2.3)	-	-
21	0/200/1/3	B	62	5500	1.36	14100 (2.6)	-	-
22	200/0/1/3	TB	43	1800	1.13	12400	-	-
23	200/0/1/3	HNB	21	67000	1.25	6000	-	-
24	100/100/1/3	B	49	4200	1.16	-	5	93/7
25 ^g	50/150/1/3	B	31	33700	1.24	-	21	84/16
26 ^g	50/150/1/5	B	42	2000	1.24	-	11	98/2

^a $n(\text{Bi}) = 10 \mu\text{mol}$, $[\text{LA}]_0 = [\text{CL}]_0 = 0.67 \text{ M}$ in toluene, $75 \text{ }^\circ\text{C}$, $t = 4 \text{ h}$.

^b Boron additive: B = $\text{B}(\text{C}_6\text{F}_5)_3$, HNB = $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$, TB = $[\text{CPh}_3][(\text{BC}_6\text{F}_5)_4]$.

^c Total monomer conversion, determined by $^1\text{H NMR}$ of an aliquot of the reaction mixture.

^d Measured by SEC with reference to PS standards and corrected with 0.58 or 0.56 factor depending on the monomer (see above).

^e $M_n(\text{th}) = \text{yield} \times [\text{monomer}]/[\text{Bi}] \times 144$ (or 114) (calculated for one polymer chain per Bi).

^f Determined by $^1\text{H NMR}$. ^g $t = 16 \text{ h}$.

Among the three boron reagents assessed, the tri(perfluoro)phenylborane $\text{B}(\text{C}_6\text{F}_5)_3$ gave the most valuable results. The catalytic system was found active, but only in the presence of at least 3 equiv. benzyl alcohol. This can be related to a poor solubility of the compound, presumably cationic, resulting from the activation with the boron derivative, or to a coordination step that wins against the ring opening of the monomer. Notably also, when benzyl alcohol was present in the mixture, the kinetic was not found as rapid as without borane (max 86% conv, run 18 vs. 98%, run 7). An interesting feature however is the narrower distribution (1.07-1.36), which can be related to a better controlled process with faster initiation vs. propagation when the bismuth compound is activated by this procedure. The M_n values are in fair adequation with high level of chain transfer in the course of the polymerization, and match quite well with a number of polymer chains close to the number of BnOH equivalents for both LA (runs 18-20) and CL (run

21) ROP experiments. It must be emphasized that CL was polymerized recently in bulk by a mixture of $B(C_6F_5)_3$ with an alcohol reagent [44]. In our hands, ROP experiments conducted with $Bi[N(SiMe_3)_2]_3/B(C_6F_5)_3$ or $Bi[N(SiMe_3)_2]_3/B(C_6F_5)_3/1$ equiv BnOH failed to afford some polylactide. Regarding the LA/CL copolymerization, one can observe that in absence of boron activator the amount of incorporated CL is limited to 5 % even in the presence of benzyl alcohol (run 24), which marks a true difference with the neutral conditions (run 14, 19 %). A copolymer containing 21 % of CL is obtained by using a 50/150 LA/CL feeding ratio and 3 equiv BnOH (run 25), which appears as an optimum (run 26, 5 equiv BnOH, 11%).

Experiments aiming at a clarification of mechanistic insights with this $Bi[N(SiMe_3)_2]_3/B(C_6F_5)_3/BnOH$ catalytic system are in progress.

4. Conclusion

In this study, Ring Opening Polymerization of *rac*-lactide and ϵ -caprolactone as well as their copolymerization was achieved by means of bismuth tris-silylamide in solution and at temperatures below 75 °C. The performances of this catalyst compare well with other previously studied bismuth derivatives. When the polymerisation is carried out in presence of an alcohol as chain transfer agent, a benefit over the control of the polymerization is noticed, with higher initiation efficiency of the Bi-O vs. the Bi-N moiety. In statistical copolymerisations of these two monomers, the rate of insertion of ϵ -caprolactone into the polylactide backbone is improved of a factor of three in that case. This bismuth catalyst can also be activated by a perfluorotriphenylborane molecule, thus affording much narrower macromolecular distributions. However, the caprolactone content remains limited to ca 20 % in the lactide-caprolactone copolymer.

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Graphical abstract.

