



**HAL**  
open science

# Lactide Lactone Chain Shuttling Copolymerization Mediated by an Aminobisphenolate Supported Aluminum Complex and Al(OiPr)<sub>3</sub>: Access to New Polylactide Based Block Copolymers

Julie Meimoun, Choltirosn Sutapin, Gregory Stoclet, Audrey Huret, Pascal Roussel, Marc Bria, Suwabun Chirachanchai, Fanny Bonnet, Philippe Zinck

► **To cite this version:**

Julie Meimoun, Choltirosn Sutapin, Gregory Stoclet, Audrey Huret, Pascal Roussel, et al.. Lactide Lactone Chain Shuttling Copolymerization Mediated by an Aminobisphenolate Supported Aluminum Complex and Al(OiPr)<sub>3</sub>: Access to New Polylactide Based Block Copolymers. Journal of the American Chemical Society, 2021, Journal of the American Chemical Society, 143 (50), pp.21206-21210. 10.1021/jacs.1c09744 . hal-03474097

**HAL Id: hal-03474097**

**<https://hal.univ-lille.fr/hal-03474097>**

Submitted on 13 Nov 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Lactide Lactone Chain Shuttling Copolymerization Mediated by an Aminobisphenolate Supported Aluminum Complex and $\text{Al}(\text{OiPr})_3$ : Access to New Polylactide Based Block Copolymers

Julie Meimoun<sup>†</sup>, Choltirosn Sutapin<sup>‡</sup>, Grégory Stoclet<sup>‡</sup>, Audrey Favrelle<sup>†</sup>, Pascal Roussel<sup>†</sup>, Marc Bria<sup>⊥</sup>, Suwabun Chirachanchai<sup>‡</sup>, Fanny Bonnet<sup>‡\*</sup>, and Philippe Zinck<sup>†\*</sup>

<sup>†</sup> Unité de Catalyse et Chimie du Solide, UMR 8181, Univ. Lille, CNRS, Centrale Lille, Univ. Artois, F-59650, Villeneuve d'Ascq, France

<sup>‡</sup> Bioresources Advanced Materials Research Unit (B2A), The Petroleum and Petrochemical College, Chulalongkorn University Pathumwan, Bangkok, 10330, Thailand

<sup>‡</sup> Unité Matériaux et Transformations (UMET), UMR 8207, Univ. Lille, CNRS, INRAE, Centrale Lille, F-59650, Villeneuve d'Ascq, France

<sup>⊥</sup> Plateforme RMN, Univ. Lille, CNRS, Centrale Lille, Univ. Artois, F-59650, Villeneuve d'Ascq, France

\* Corresponding authors:

E-mail [philippe.zinck@univ-lille.fr](mailto:philippe.zinck@univ-lille.fr), [fanny.bonnet@univ-lille.fr](mailto:fanny.bonnet@univ-lille.fr)

KEYWORDS Chain shuttling copolymerization • Polylactide • Aluminum complex • Block copolymers • Polyesters

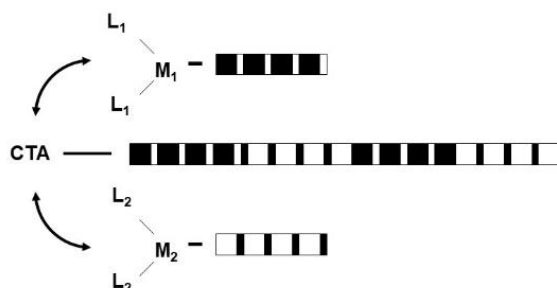
---

**ABSTRACT:** The chain shuttling ring-opening copolymerization of L-lactide with  $\epsilon$ -caprolactone has been achieved using two aluminum catalysts presenting different selectivities and benzyl alcohol as chain transfer agent. A newly synthesized amino-bisphenolate supported aluminum complex affords the synthesis of lactone rich poly(L-lactide-*co*-lactone) statistical copolymeric blocks, while  $\text{Al}(\text{OiPr})_3$  produces semi-crystalline poly(L-lactide) rich blocks. Transalkoxylation is shown to operate efficiently. The crystalline ratio and glass transition temperatures of these new class of polylactide based block copolymers can be tuned by adjusting the catalysts and the comonomers ratio.

---

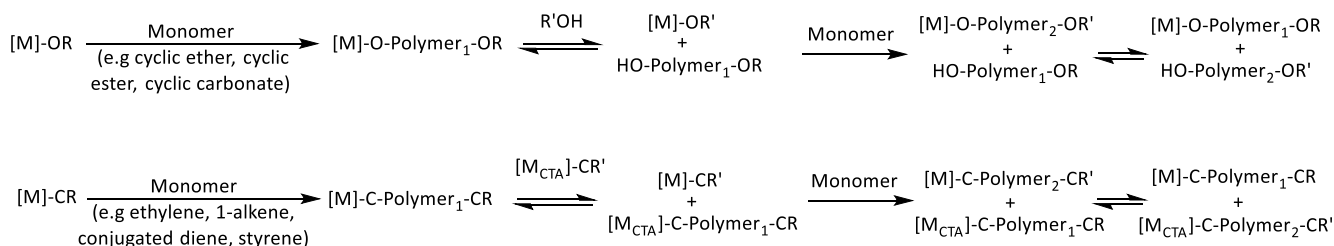
The depletion of petroleum resources and the advent of plastic pollution are growing human concerns. The development of biobased and biodegradable/compostable polymers can help in this regard. Among the different biobased materials available on the market, polylactide is becoming more and more competitive and its production is continuously growing. This compostable, biocompatible and bioresorbable polyester is synthesized by ring-opening polymerization (ROP) of lactide, a cyclic ester obtained from oligomerization-cyclization of lactic acid. L-lactide (Figure 2) is particularly interesting since it leads to a 100 % isotactic poly(L-lactide) or PLLA, a semi-crystalline material which displays mechanical properties close to those of conventional polyethylene terephthalate (PET). The brittleness of PLLA and its low elongation at break (2-6%) hampers however its development for numerous applications.<sup>1</sup> In order to overcome these problems and to allow PLLA to be used for a wider range of applications, it is commonly used in the form of blends with other polymers<sup>1</sup> or in composites.<sup>2</sup> Another strategy consists in copolymerizing L-Lactide with other cyclic esters displaying complementary properties which will enhance the thermomechanical properties of the final material.

A challenge is thus to synthesize advanced high quality polylactide or related structures by dedicated synthesis platforms. In this respect catalytic polymerization is relevant, and more specifically chain shuttling copolymerization (CSP, represented Scheme 1), a powerful tool allowing the access to multiblock / segmented copolymers with original microstructures in a one-pot one-step route.<sup>3</sup>



**Scheme 1.** Chain shuttling copolymerization (CSP). M are metals with their ligands L. CTA is the chain transfer agent.

In this process initially developed for ethylene / 1-alkene systems,<sup>3-6</sup> the growing macromolecular chain is allowed



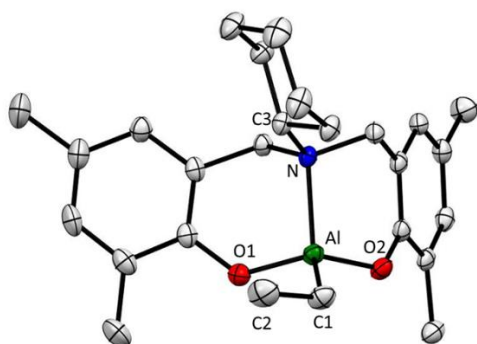
**Scheme 2.** Similarity between Coordinative Chain Transfer Polymerization (bottom) and Immortal Ring-Opening Polymerization (top)

to “shuttle” by transmetalation via an organometallic chain transfer agent (CTA) between two catalysts presenting a difference in comonomers reactivity ratios, and thus leading to statistical copolymeric blocks of different composition (Scheme 1). The block rich in ethylene is semi-crystalline, while the higher amount of 1-alkene hampers the crystallization of the second type of block, giving rise to materials with valuable properties. It is worth mentioning that 1600 polymerizations experiments were realized by high-throughput technology in order to find the adequate catalytic combination based on bis(phenoxyimine) Zr and pyridylamide Hf affording the seminal shuttling.<sup>3</sup>

If chain shuttling homopolymerization systems, where only one monomer is involved, have been well explored,<sup>7-14</sup> it appears that since the seminal work in 2006 on ethylene/1-alkene comonomers,<sup>3</sup> the synthesis of original multiblock microstructures by chain shuttling copolymerization was extended to only one other comonomers combination, *i.e.* styrene / conjugated diene, by rare earth based catalysts.<sup>15-16</sup> This is probably to be ascribed to the complexity of the catalytic system required and the high level of constraints as soon as two different monomers are involved. We present herein the first example of a ring-opening chain shuttling copolymerization of L-lactide with the seven-membered  $\epsilon$ -caprolactone, yield new original PLLA based block copolymers.

Chain shuttling copolymerization is based on Coordinative Chain Transfer Polymerization, or CCTP, a degenerative chain transfer process.<sup>17-18</sup> In CCTP, the growing macromolecular chain transmetalates from the catalyst metal to the metal of the CTA, often a main group metal, via transalkylation, allowing the growth of several chains per catalyst atom (Scheme 2, bottom part). This can be combined with a second catalyst that displaces the growing chain to yield *e.g.* linear  $\alpha$ -olefins.<sup>18</sup> In the present work involving cyclic esters as comonomers, the chemistry is based on the so-called immortal ROP concept introduced by Inoue *et al.* using an aluminium porphyrin/alcohol system and an epoxide as monomer (Scheme 2, top).<sup>20</sup> Immortal ROP presents conceptual similarities with CCTP. The catalyst gives rise to the growth of several polymer chains by reversible transalkoxylation reactions. Immortal ROP was later transposed to cyclic esters,<sup>21</sup> including also other metal complexes (see for example ref.<sup>22</sup>) and their statistical copolymerization.<sup>23</sup>

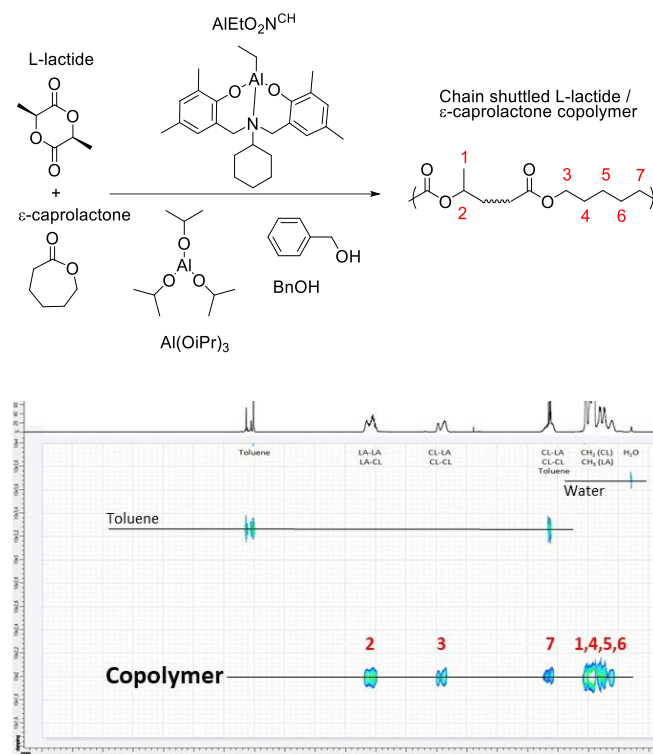
In order to introduce PLLA blocks in the targeted copolymer microstructure, a catalyst displaying a very high selectivity toward lactide has to be introduced in the reactive medium, while the second one will have to statistically copolymerize the two monomers with a substantial incorporation of the lactone. Such different behaviours can be reached by playing on the ligand framework. The metal catalysed statistical copolymerization of lactides with lactones is still quite challenging due to the fact that oxophilic metals involved in this reaction preferentially coordinate the lactide monomer.<sup>24-25</sup> A bulkier ligand is thought to rebalance the reactivity ratios of both comonomers and enables a better incorporation of the typically less reactive lactone.<sup>25</sup> Bulky ligand should thus be considered for a high lactone incorporation, while less hindered catalysts should allow a preferential insertion of the lactide monomer. Both catalysts must also enable reversible transalkoxylation reactions, *i.e.* the immortal-like character



**Figure 1.** Displacement ellipsoid plot of  $\text{AlEtO}_2\text{N}^{\text{CH}}$  (50%). Hydrogen atoms were hidden for clarity. Selected bond lengths (Å) and angles (°): Al-O1 = 1.7510(10); Al-O2 = 1.7408(9); Al-N = 2.0230(10); Al-C1 = 1.9515(13); O1-Al-O2 = 114.74(5); O1-Al-C1 = 110.50(5); O2-Al-C1 = 110.75(5)

We have synthesized a new aminobisphenolate-supported aluminium complex by treatment of *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)cyclohexylamine ( $\text{H}_2\text{O}_2\text{N}^{\text{CH}}$ ) with an equimolar amount of  $\text{AlEt}_3$  in toluene at room temperature. The ORTEP structure is presented in Figure 1, while synthetic and crystallographic details are given in the SI section. This complex, referred to as  $\text{AlEtO}_2\text{N}^{\text{CH}}$  affords, in combination with benzyl alcohol, the statistical copolymerization of L-lactide with  $\epsilon$ -caprolactone with a high lactone insertion, as shown entry 1 in Table 1. Furthermore, in the presence of several equivalents alcohol CTA (entry 2), the good agreement between experimental and calculated number-average molecular weight ( $M_n$ ) highlights an immortal ring-opening statistical copolymerization of L-lactide with  $\epsilon$ -caprolactone. Narrow molecular weight distribution can be noticed in both cases, with a dispersity of 1.11 for entry 2. Regarding the second catalyst required for the chain shuttling copolymerization system,  $\text{Al}(\text{O}i\text{Pr})_3$  has been reported in the literature for its ability to allow immortal-like ROP of both lactide and  $\epsilon$ -caprolactone, together with a very high selectivity for the lactide in the course of statistical copolymerizations.<sup>26</sup> These behaviours are also observed in our experimental conditions, as shown entry 3 in Table 1. Chain shuttling copolymerization experiments performed with the combination of these

two catalysts, represented Figure 2, top part, are reported Table 1, entries 4-7 with increasing quantities of the chain transfer agent. Again, controlled molecular weights can be noticed, with dispersities decreasing down to 1.11 with increasing quantity of CTA, together with a very good agreement between calculated and measured number-average molecular weight. This attests to an efficient transalkoxylation / shuttling reaction occurring during the polymerization.



**Figure 2.** Chain shuttling copolymerization (top) and DOSY analyses of entry 7 (bottom)

A Diffusion Ordered SpectroscopY (DOSY) analysis was performed on a low molecular weight sample (low molecular weight is recommended for DOSY) realized with 9 eq. CTA (entry 7). The measurement of the diffusion coefficient allows to check if lactide and lactone based repeating units are on the same macromolecule or if it is a mixture of PLLA and the statistical copolymer that would have been made separately by the two catalysts. Indeed, in the former case, they will have the same diffusion coefficient, whereas in the latter case, two diffusion coefficients will be detected. The DOSY analysis given in Figure 2 bottom part shows that the lactyl -CH signal, the lactyl -CH<sub>3</sub> and all the caprolactoyl -CH<sub>2</sub> have the same diffusion coefficient, confirming the occurrence of chain shuttling. The splitting of the lactyl -CH signal around 5.1 ppm and that of the caprolactoyl -O-CH<sub>2</sub> signal around 4.1 ppm is attributed to two different enchainments, *i.e.* lactyl / lactyl and lactyl / caprolactoyl for the former, and caprolactoyl / caprolactoyl and caprolactoyl / lactyl for the latter. This can be quantified, and more information about the microstructure is given in the SI section. The thermal analysis of the so formed copolymers shows two glass transition temperatures and one melting temperature. Wide Angle X-ray Scattering (WAXS) analyses given in the

**Table 1. L-Lactide/ $\epsilon$ -caprolactone (LA/CL) statistical and chain shuttling copolymerizations using  $\text{AlEtO}_2\text{N}^{\text{CH}}$  and  $\text{Al}(\text{OiPr})_3$  at 70 °C in toluene, 1 M, 24 h.**

| Entry           | LA/CL/ $\text{AlEtO}_2\text{N}^{\text{CH}}$ /<br>$\text{Al}(\text{OiPr})_3/\text{BnOH}$ | Conv.<br>LA/CL(%) <sup>a</sup> | Yield<br>(%) | $M_{n \text{ calc}}$<br>(g/mol) <sup>b</sup> | $M_{n \text{ exp}}$<br>(g/mol) <sup>c</sup> | $\bar{D}$ <sup>c</sup> | LA/CL<br>(%) <sup>d</sup> | $T_{g1}$<br>(°C) <sup>e</sup> | $T_{g2}$<br>(°C) <sup>e</sup> | $T_m$<br>(°C) <sup>e</sup> | $\Delta H$<br>(J/g) <sup>e</sup> | $\chi_c$<br>(%) <sup>f</sup> |
|-----------------|---|--------------------------------|--------------|--|---|------------------------|---------------------------|-------------------------------|-------------------------------|----------------------------|----------------------------------|------------------------------|
| 1               | 250/250/1/0/1   | 83/61                          | 56           | 47 300                                       | 41 400                                      | 1.22                   | 54/46                     | -6                            | -                             | -                          | -                                | -                            |
| 2               | 250/250/1/0/5   | 79/59                          | 53           | 9 100  | 9 000                                       | 1.11                   | 54/46                     | -5                            | -                             | -                          | -                                | -                            |
| 3               | 250/250/0/1/1   | 86/4                           | 45           | 8 000  | 9 700                                       | 1.19                   | 94/6                      | -                             | 44                            | 144                        | 32                               | 38.5                         |
| 4               | 500/500/1/1/1   | 83/40                          | 58           | 20 600                                       | 20 100                                      | 1.25                   | 68/32                     | 1                             | 48                            | 74/102                     | 2.8                              | 6.2                          |
| 5               | 500/500/1/1/2   | 86/45                          | 65           | 17 500                                       | 16 200                                      | 1.22                   | 67/33                     | 0                             | 47                            | 74/103                     | 1.3                              | 2.9                          |
| 6               | 500/500/1/1/4   | 76/43                          | 57           | 11 300                                       | 11 300                                      | 1.15                   | 66/34                     | 3                             | 48                            | 87                         | 1.6                              | 3.7                          |
| 7               | 500/500/1/1/9   | 79/28                          | 44           | 6 100  | 7 100                                       | 1.11                   | 71/29                     | -1                            | 48                            | 102                        | 2.3                              | 4.5                          |
| 8               | 500/500/1/0.6/1   | 62/29                          | 38           | 21 900                                       | 23 100                                      | 1.16                   | 64/36                     | 7                             | -                             | 110                        | 1.4                              | 3.3                          |
| 9               | 500/500/0.6/1/0.6   | 77/28                          | 46           | 19 900                                       | 21 400                                      | 1.26                   | 78/22                     | 16                            | 47                            | 102                        | 18.1                             | 29.5                         |
| 10              | 700/300/0.6/1/0.6   | 70/20                          | 43           | 21 500                                       | 24 600                                      | 1.27                   | 88/12                     | 6                             | 42                            | 144                        | 30.1                             | 40.7                         |
| 11              | 300/700/0.6/1/0.6   | 77/30                          | 43           | 15 900                                       | 17 300                                      | 1.21                   | 55/45                     | -8                            | 57                            | -                          | -                                | -                            |
| 12 <sup>g</sup> | 1000/1000/0.6/1/0.6   | 77/35                          | 54           | 41 900                                       | 43 300                                      | 1.34                   | 69/31                     | 2                             | 47                            | 99                         | 3.3                              | 6.7                          |
| 13 <sup>g</sup> | 1000/1000/1/1/1   | 77/36                          | 52           | 38 000                                       | 37 900                                      | 1.30                   | 62/38                     | -1                            | 52                            | 111                        | 2.3                              | 6.1                          |
| 14 <sup>g</sup> | 1000/1000/1/1/4   | 78/52                          | 62           | 24 500                                       | 23 300                                      | 1.18                   | 66/34                     | 4                             | 56                            | -                          | -                                | -                            |

<sup>a</sup> Conversion determined by <sup>1</sup>H NMR analysis (see SI). <sup>b</sup>  $M_{n \text{ calc}} = [\text{LA} / (3 \times \text{Al}(\text{OiPr})_3 + \text{BnOH})] \times 144.14 \times \text{conv. LA} + [\text{CL} / (3 \times \text{Al}(\text{OiPr})_3 + \text{BnOH})] \times 114.14 \times \text{conv. CL}$ . <sup>c</sup> Determined by Size Exclusion Chromatography.  $M_n$  corrected by a factor of  $[0.58 \times \text{wt\%LA units} + 0.56 \times \text{wt\%CL unit}]$ . <sup>d</sup> Molar composition of the isolated polymer determined by <sup>1</sup>H NMR (see SI). <sup>e</sup> Determined by Differential Scanning Calorimetry. <sup>f</sup> Estimated PLLA crystalline ratio (see SI). <sup>g</sup> 2M, 48h.

SI have confirmed that the latter corresponds to crystalline PLLA.  $T_{g1}$  is ascribed to the soft poly(L-lactide-co- $\epsilon$  caprolactone) blocks made by the aminobisphenolate complex, while  $T_{g2}$  corresponds to amorphous poly(L-lactide-co- $\epsilon$ -caprolactone) segments rich in lactide produced by  $\text{Al}(\text{OiPr})_3$ .

The thermal properties of the blocks show that the transalkoxylation rate is lower than the insertion rate in these conditions, allowing a multiblock structure with blocks of length sufficient to reach, e.g., the crystallisation of PLLA and the presence of 2 different  $T_g$ . When higher amounts of CTA are introduced, the dispersity goes down, suggesting that, even if lower than the insertion rate, the transfer rate is probably important. From <sup>13</sup>C Nuclear Magnetic Resonance (NMR) analysis we have evidenced that transesterification is not occurring in the course of the polymerization (see SI section for more details).

The ratios of the catalysts and the comonomers were varied in order to assess which extent of microstructure can be reached with this original chain shuttling copolymerization system. An experiment with a lower amount of  $\text{Al}(\text{OiPr})_3$  is reported entry 8. As expected, the lactide conversion is lower, 62% vs. 83% in entry 4. This leads also to a lower conversion of the lactone, probably due to the fact that the concentration of lactide in the reactive medium is higher, and

thus it may be more competitive for the statistical copolymerization on the second catalyst. The  $T_g$  of the soft block increases as a consequence. Decreasing the amount of  $\text{AlEtO}_2\text{N}^{\text{CH}}$  does in turn not affect substantially the amount of lactide in the copolymer, as seen in entry 9, but does decrease the lactone conversion, as expected. As a consequence, the glass transition temperature of the soft block increases by 15 °C. The most important feature of this experiment is the important poly(L-lactide) crystalline ratio reached, with a melting enthalpy of 18.1 J/g, corresponding to a PLLA crystalline ratio close to 30%.  $\chi_c$  can be increased up to 40% by increasing the amount of lactide in the reactive medium, as presented entry 10. The  $T_g$  of the PLLA rich phase decreases down to 42 °C. The high crystalline ratio of the sample leads probably to a lower amount of lactide in the amorphous phase, which may explain the lower  $T_g$ . The increase of the quantity of lactone in the reactive medium leads in turn to the disappearance of the crystalline phase (entry 11), and thus to a fully amorphous block copolymer.

Higher molecular weight can also be reached with this system by increasing the monomer over catalyst ratio, as shown entries 12-13. The immortal-like character of the polymerization is still observed for this ratio, as, in the presence of excess benzyl alcohol, the calculated and theoretical

molecular weights are still in agreement together with a dispersity of 1.18 (entry 14). In this set of experiments, the propagation rate decreases as a consequence of an increased monomer / catalyst ratio, while the transfer rate probably stays constant, which may lead to a decrease of the size of the blocks. In addition, in entry 14 the amount of CTA is increased by a factor 4, which is a second leverage to decrease the size of the blocks, which may explain the disappearance of the crystallinity of the polymer. We thus have a fully amorphous block copolymer with PLA and statistical copolymeric blocks.

The nanostructure of the resulting block copolymers was then assessed via Small Angle X-ray Scattering. The results obtained for entry 6 showed the presence of an organized structure at the nanometer scale (see SI). This nanostructure consists of crystalline PLLA lamellae of thickness around ~5.6nm regularly stacked with a repeating distance of ~23nm as determined from the modeling of the SAXS curves.

**Table 2. Mechanical properties of the copolymers measured by tensile tests**

| Entry | E <sup>a</sup> (MPa) | σ <sub>MAX</sub> <sup>b</sup> (MPa) | ε <sub>B</sub> <sup>c</sup> (%) | Toughness (MJ/m <sup>3</sup> ) |
|-------|----------------------|-------------------------------------|---------------------------------|--------------------------------|
| 9     | 63.2                 | 3.5                                 | 57                              | 1.76                           |
| 10    | 63.6                 | 1.7                                 | 74                              | 1.08                           |
| 12    | 24.6                 | 2.0                                 | 75                              | 1.20                           |
| 14    | 0.8                  | 0.2                                 | 275                             | 0.15                           |

<sup>a</sup> Young modulus. <sup>b</sup> Yield stress. <sup>c</sup> Elongation at break.

We finally assessed the mechanical properties of the new materials. We selected for this purpose samples with the highest crystallinity (entries 9 and 10), a lower crystallinity with a high molecular weight (entry 12) and finally a fully amorphous sample (entry 14). The results are reported in Table 2. All samples revealed a rather high elongation at break, from 50-75% for semi-crystalline samples to ca. 300% for the fully amorphous multiblock. The former exhibited in turn the highest modulus and strain at break, highlighting the key role of crystallinity. Toughness of 1.2-1.76 MJ/m<sup>3</sup> were obtained for semi-crystalline materials. The data also underline the variety of mechanical behavior that can be obtained and the possibility to easily tune them with this new system.

In summary, we report herein for the first time a lactide lactone chain shuttling copolymerization at two different aluminum sites, allowing to access new PLLA based block copolymers, where one of the block consists of a statistical, amorphous copolymer where the T<sub>g</sub> can be varied, while the other block consists of semi-crystalline or amorphous poly(L-lactide) based material. Work is under progress to extend the scope of application of this new synthetic approach, and to characterize thoroughly the structure and properties of the resulting materials.

#### AUTHOR INFORMATION

Corresponding Authors

\* Fanny Bonnet ([fanny.bonnet@univ-lille.fr](mailto:fanny.bonnet@univ-lille.fr)) and Philippe Zinck ([philipe.zinck@univ-lille.fr](mailto:philipe.zinck@univ-lille.fr))

#### Funding Sources

The authors gratefully acknowledge the Agence Nationale de la Recherche (ANR) for partial funding through the PLANAVETTE project (ANR-21-CE06-0024). This work was also partially funded by the FWV ALPO Interreg Grant and the authors thanks the European Regional Development Fund (FEDER) and the University of Lille. Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur de la Recherche et de l'Innovation, Région Hauts de France and CNRS are also acknowledged for supporting and funding partially this work. The French Ministry of Foreign Affairs and the French Embassy in Bangkok is gratefully acknowledged for the French-Thai PHC SIAM project.

#### ACKNOWLEDGMENT

This paper is dedicated to the memory of Prof. André Mortreux, one of the fathers of CCTP, Coordinative Chain Transfer Polymerization, who passed away last year. We also thank Aurélie Malfait and Dr. Jonathan Potier for SEC measurements, Céline Delabre for Elemental Analysis, and Dr. Yohan Champouret and Prof. Marc Visseaux for fruitful discussion on the topic of L-lactide / lactone statistical ring-opening copolymerizations.

#### REFERENCES

- (1) Liu, H.; Zhang, J. Research progress in toughening modification of poly(lactic acid) *J. Pol. Sci. Part B: Polymer Physics* **2011**, *49*, 1051–1083.
- (2) Murariu, M.; Dubois, P. PLA composites: From production to properties. *Adv. Drug. Deliv. Rev.* **2016**, *107*, 17-46.
- (3) Arriola, D.J.; Carnahan, E.M.; Hustad, P.D.; Kuhlman, R.L.; Wenzel, T.T. Catalytic production of olefin block copolymers via chain shuttling polymerization. *Science* **2006**, *312*, 714–719.
- (4) Wei, J.; Zhang, W.; Wickham, R.; Sita, L. R. Programmable Modulation of Co-monomer Relative Reactivities for Living Coordination Polymerization through Reversible Chain Transfer between “Tight” and “Loose” Ion Pairs. *Angew. Chem. Int. Ed.* **2010**, *49*, 9140–9144.
- (5) Descour, C.; Sciarone, T. J. J.; Cavallo, D.; Macko, T.; Kelchtermans, M.; Korobkov, I.; Duchateau, R. Exploration of the effect of 2,6-(*t*-Bu)<sub>2</sub>-4-Me-C<sub>6</sub>H<sub>2</sub>OH (BHT) in chain shuttling polymerization. *Polym. Chem.* **2013**, *4*, 4718-4729.
- (6) Vittoria, A.; Busico, V.; Cannavacciuolo, F. D.; Cipullo, R. Molecular Kinetic Study of “Chain Shuttling” Olefin Copolymerization. *ACS Catal.* **2018**, *8*, 5051–5061.
- (7) Alfano, F.; Boone, H. W.; Busico, V.; Cipullo, R.; Stevens, J. C. Polypropylene “Chain Shuttling” at Enantiomorphous and Enantiopure Catalytic Species: Direct and Quantitative Evidence from Polymer Microstructure. *Macromolecules* **2007**, *40*, 7736–7738.

- (8) Tynys, A.; Eilertsen, J. L.; Seppälä, J. V.; Rytter, E. Stereoblock Polypropylenes Prepared by Efficient Chain Shuttling Polymerization of Propylene with Binary Zirconium Catalysts and *i*Bu<sub>3</sub>Al. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 1364–1376.
- (9) Xiao, A.; Wang, L.; Liu, Q.; Yu, H.; Wang, J.; Huo, J.; Tan, Q.; Ding, J.; Ding, W.; Amin, A. M. A. Novel Linear–Hyperbranched Multiblock Polyethylene Produced from Ethylene Monomer Alone via Chain Walking and Chain Shuttling Polymerization. *Macromolecules* **2009**, *42*, 1834–1837.
- (10) Zhao, W.; Wang, Y.; Liu, X.; Chen, X.; Cui, D.; Chen, E. Y.-X. Protic compound mediated living cross-chain-transfer polymerization of *rac*-lactide: synthesis of isotactic (crystalline)–heterotactic (amorphous) stereomultiblock polylactide. *Chem. Commun.* **2012**, *48*, 6375–6377.
- (11) Liu, B.; Cui, D. Regioselective Chain Shuttling Polymerization of Isoprene: An Approach To Access New Materials from Single Monomer. *Macromolecules* **2016**, *49*, 6226–6231.
- (12) Childers, M. I.; Vitek, A. K.; Morris, L. S.; Widger, P. C. B.; Ahmed, S. M.; Zimmerman, P. M.; Coates, G. W. Iso-specific, Chain Shuttling Polymerization of Propylene Oxide Using a Bimetallic Chromium Catalyst: A New Route to Semicrystalline Polyols. *J. Am. Chem. Soc.* **2017**, *139*, 11048–11054.
- (13) Phuphuak, Y.; Bonnet, F.; Stoclet, G.; Bria, M.; Zinck, P. Isoprene chain shuttling polymerisation between cis and trans regulating catalysts: straightforward access to a new material. *Chem. Commun.* **2017**, *53*, 5330–5333.
- (14) Dai, Q.; Zhang, X.; Hu, Y.; He, J.; Shi, C.; Li, Y.; Bai, C. Regulation of the cis-1,4- and trans-1,4-Polybutadiene Multiblock Copolymers via Chain Shuttling Polymerization Using a Ternary Neodymium Organic Sulfonate Catalyst. *Macromolecules* **2017**, *50*, 7887–7894.
- (15) Pan, L.; Zhang, K.; Nishiura, M.; Hou, Z. Chain-Shuttling Polymerization at Two Different Scandium Sites: Regio- and Stereospecific “One-Pot” Block Copolymerization of Styrene, Isoprene, and Butadiene. *Angew. Chem. Int. Ed.* **2011**, *50*, 12012–12015.
- (16) Valente, A.; Stoclet, G.; Bonnet, F.; Mortreux, A.; Visseaux, M.; Zinck, P. Isoprene–Styrene Chain Shuttling Copolymerization Mediated by a Lanthanide Half-Sandwich Complex and a Lanthanidocene: Straightforward Access to a New Type of Thermoplastic Elastomers. *Angew. Chem. Int. Ed.* **2014**, *53*, 4638–4641.
- (17) Kempe, R. How to Polymerize Ethylene in a Highly Controlled Fashion? *Chem. Eur. J.* **2007**, *13*, 2764–2773.
- (18) Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative Chain Transfer Polymerization. *Chem. Rev.* **2013**, *113*, 3836–3857.
- (19) Gollwitzer, A.; Dietel, T.; Kretschmer, W. P.; Kempe, R. A Broadly Tunable Synthesis of Linear  $\alpha$ -Olefins. *Nature Communications* **2017**, *8*, 1226–1231.
- (20) Asano, S.; Aida, T.; Inoue, S. ‘Immortal’ polymerization. Polymerization of epoxide catalysed by an aluminium porphyrin–alcohol system. *J. Chem. Soc. Chem. Comm.* **1985**, *17*, 1148–1149.
- (21) Endo, M.; Aida, T.; Inoue, S. Immortal polymerization of epsilon-caprolactone initiated by aluminum porphyrin in the presence of alcohol. *Macromolecules* **1987**, *20*, 2982–2988.
- (22) Miola-Delaite, C.; Hamaide, T.; Spitz, R. Anionic coordinated polymerization of  $\epsilon$ -caprolactone with aluminium, zirconium and some rare earths alkoxides as initiators in the presence of alcohols, *Macromol. Chem. Phys.* **1999**, *200*, 1771–1778.
- (23) Li, L.; Liu, B.; Liu, D.; Wu, C.; Li, S.; Liu, B.; Cui, D. Copolymerization of  $\epsilon$ -Caprolactone and l-Lactide Catalyzed by Multinuclear Aluminum Complexes: An Immortal Approach. *Organometallics* **2014**, *33*, 6474–6480.
- (24) Duda, A.; Biela, T.; Libiszowski, J.; Penczek, S.; Meckerreyes, D.; Jérôme, R. Block and random copolymers of  $\epsilon$ -caprolactone. *Polym. Degrad. Stab.* **1998**, *59*, 215–222.
- (25) Stirling, E.; Champouret, Y.; Visseaux, M.; Catalytic metal-based systems for controlled statistical copolymerisation of lactide with a lactone. *Polym. Chem.* **2018**, *9*, 2517–2531.
- (26) Jacobs, C.; Dubois, P.; Jerome, R.; Teyssie, P. Macromolecular Engineering of Polylactones and Polylactides. 5. Synthesis and Characterization of Diblock Copolymers Based on Poly- $\epsilon$ -caprolactone and Poly(L,L or D,L)lactide by Aluminum Alkoxides. *Macromolecules* **1991**, *24*, 3027–3034.

ToC

