

Accelerated Polymerization of Lactide Driven by a DBU-based Salt and a 15-Crown-5 Ether Sacrificial Kinetic Booster

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The recent advances in polymerization of lactide (LA) from organic salts enriched the toolbox to prepare well-defined materials. Herein we report the use of crown ether (CE) as an additive to polymerize the L-LA when initiated by 12-hydroxydodecanoic acid (HDA) activated by one equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). While both size and

structure of the ether additive play an important role on the overall rate of reaction, the CE decomplexation is crucial to outpace transfer reactions and also permit the process to be moderately conducted under air atmosphere by an efficient water trapping process.

Introduction

Since the beginning of the year 2000, the field of polymer chemistry has been fueled by the use of organic catalysts.^[1] This side of catalysis has evolved to the point that organic molecules now supplant metal- and enzyme-based catalytic routes.^[2] Especially for ring-opening polymerization (ROP) processes, the field of organic catalysis has expanded rapidly, and a wide range of choices for which to choose an appropriate catalyst now exist.^[3] Organic catalysts are simple, commercially available molecules that are typically easily purified and well suited to a range of reaction conditions as a consequence of their acidic or basic nature. Over the years, it soon became apparent that those acid and base components were complementary in terms of control, activity and types of monomers that could be polymerized.^[4] Consequently, and certainly inspired by Nature, compounds composed of mixtures of organic acids and bases have started to be studied. Such a facile approach provides a wide range of possibilities, since both stoichiometric and non-stoichiometric acid-base mixtures can be prepared giving protic ionic mixtures or Non-Eutectic Mixture Organocatalysts (NEMOs).^[5] These cooperative and synergistic components combinations are very versatile and have the dual functionality that may show a stronger acidic or basic nature, depending on the stoichiometry and the chemical nature of the compounds.


On account of its high activity, low cost, non-toxicity and excellent control over various polymerization processes, the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is rapidly becoming the workhorse of the organic base catalyst in ROP processes.^[3,6]

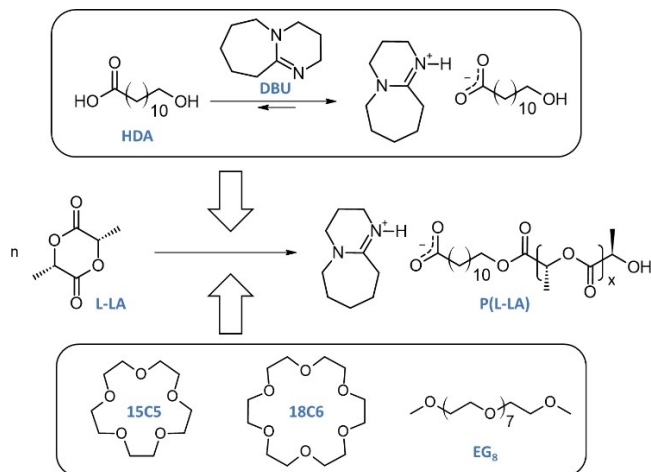
Especially for lactides (LA) ROP, the very high polymerization activity of DBU, even under mild experimental conditions, leads to an extremely rapid monomer polymerization sometimes unable to provide a narrow molar mass distribution. In 2011, Hedrick demonstrated that the addition of one equivalent of benzoic acid (BA) results on the formation of a stable DBU/BA organic salt involving a bifunctional catalytic mechanism between LA and an exogenous initiating alcohol where both the monomer carbonyl and nucleophilic hydroxyl group are activated via hydrogen bonding.^[7] No experimentally discernible transesterification could be observed allowing for narrow dispersity values and targeted poly(lactide) (PLA) molecular weights to be produced.

Recently, the development of such organic salts offered great opportunities to not only simplify the preparation of polyesters in high temperature industrial conditions,^[5] but also access polymer materials that were difficult to prepare using conventional methods. The ability of a RCOO^- , DBU.H^+ salt to act as catalyst by activating hydroxyl functions during a 6-membered lactone ROP is indeed complemented by its ability to efficiently initiate 4-membered lactone anionic processes.^[8,9] Well-defined copolyesters with complex structures were therefore synthesized in a one-pot efficient manner, which is difficult by conventional methods.^[9,10] Nevertheless, as (the only) drawback, the linear polymerization of LA from an exogenous alcohol is still relatively slow, necessitating hours of reaction to get a polymerization degree (DP) of 100. Since the basicity of the DBU-based salt carboxylate ion is crucial to activate the hydroxyl propagating group and based on our recent works,^[11] we reasoned that a catalyst promoting the DBU.H^+ cation and the RCOO^- carboxylate anion separation would further accelerate the polymerization.

Herein we report the accelerated and partially air-tolerant polymerization of L-lactide (L-LA) from 12-hydroxydodecanoic acid (HDA) activated by one equivalent of DBU and complexed by crown ethers (CE) and a linear analog (Scheme 1). While both size and structure of the ether play an important role on the overall rate of reaction, the kinetics of CE decomplexation is

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 Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.202300666>



Scheme 1. General polymerization scheme of L-LA in presence of a DBU/HDA initiator and ether catalysts.

crucial to outpace transfer reactions and also permit the process to be moderately conducted under air atmosphere.

Results and Discussion

To demonstrate the effect of CE, we arbitrarily decided to begin our studies with the 18-crown-6 ether (18 C6) complexing agent. To help on the complexation, the 18 C6 was priorly mixed with a DBU/HDA equimolar mixture in DCM in a 1:1 molar ratio at a relatively high concentration ($[18\text{ C6}]_0 \sim 0.23\text{ M}$). Since complexation rates for the interaction of CE could be slow, the tripartite mixture was kept under agitation for 10 minutes before adding it to a L-LA solution in DCM, targeting a DP ($[L\text{-LA}]_0/[HDA]_0$) of 40 ($[L\text{-LA}]_0 = 1.63\text{ M}$; $[HDA]_0 = [DBU]_0 = [18\text{ C6}]_0 = 0.041\text{ M}$). In sharp contrast to the polymerization performed in absence of 18 C6 under identical conditions, the reaction surprisingly appeared much slower, with only 39% conversion after 15 minutes (Figure 1, Table S1 in Supporting Information, SI).

Hydrogen bonding and dipolar interaction can contribute to the stabilization of CE with neutral molecules. In 1992, Stoddart already reported the complexation of alcohols by a monoprotonated azaCE hosting agent, concluding that in presence of methanol, the as-obtained complex is 40 times more stable than with the non-protonated CE.^[12] In the present case, we hypothesized that the 18-membered ring has the correct number of heteroatoms for a complementary arrangement of donor and acceptor atoms for hydrogen bonding with the hydroxyl group of the initiating/propagating alcohol specially in presence of the trapped amidinium proton (Scheme 2). Diminishing the propension of the propagating alcohol to be openly activated by the carboxylate group ("open" complex) and sequestering the propagating site in a bulky environment ("close" complex), such interaction should lower the overall kinetics of polymerization.

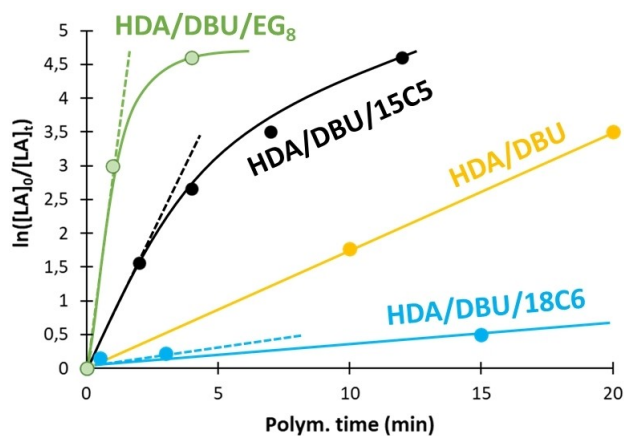
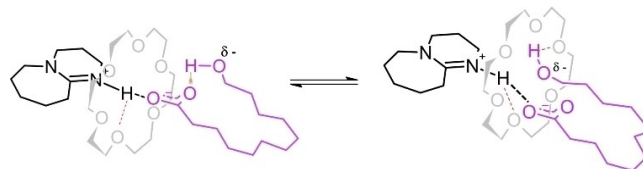


Figure 1. Semilogarithmic plots of L-LA polymerizations initiated with HDA activated by DBU (●) and complexed with 18 C6 (●), 15 C5 (●) and EG₈ (●). Conditions of polymerizations: $[L\text{-LA}]_0/[HDA/DBU]_0/[additive]_0 = 40/1/1$, $[L\text{-LA}]_0 = 1.63\text{ M}$, DCM solvent, 21 °C.



Scheme 2. Equilibrium between an "open" (left) and "close" (right) DBU/HDA/18 C6 mixture complex possibly involved during L-LA ROP in DCM. Note that both inter- and intramolecular complexation could occur. The intramolecular complex has been drawn for schematic simplicity.

To get more insight into such hydroxyl complexation, the DBU/HDA/18 C6 tripartite complex was tentatively studied by ¹H NMR spectroscopy in CDCl₃. Because CDCl₃ could compete with the guest for the CE host cavity binding site,^[13] ¹H NMR analysis was quickly performed after solubilization of a preformed complex at relatively high concentration ($[HDA]_0 = [DBU]_0 = [18\text{ C6}]_0 \sim 0.16\text{ M}$) also mimicking the polymerization procedure. As envisaged, the recorded ¹H NMR spectrum appears complex with a split methylene hydroxyl signal and a high degree of CE dissymmetry supporting the hypothesis that a DBU/HDA/18C6 "open" complex is in equilibrium with its "close" form, limiting then informative interpretation (Figure S1 in SI).

Reasoning that during the course of the polymerization the propensity of the alcohol end-group to be trapped by the CE is mainly dependent on its ring-size, the effect of a smaller 15-crown-5 ether (15 C5) on the DBU/HDA initiating system has then been evaluated. For sake of comparison, ¹H NMR analyses were also recorded in CDCl₃ for an initial concentration of 0.16 M (Figure 2). In presence of pristine DBU, the HDA methylene carboxy protons were most affected, as indicated by a change in chemical shift of the $-\text{CH}_2\text{CO}_2\text{H}$ resonance (H_a , $\Delta\delta = 0.13\text{ ppm}$, Figure 2b), confirming that the formation of the HDA/DBU salt takes place. The presence of the DBU.H⁺-based carboxylate end-group causes a downfield shift of the meth-

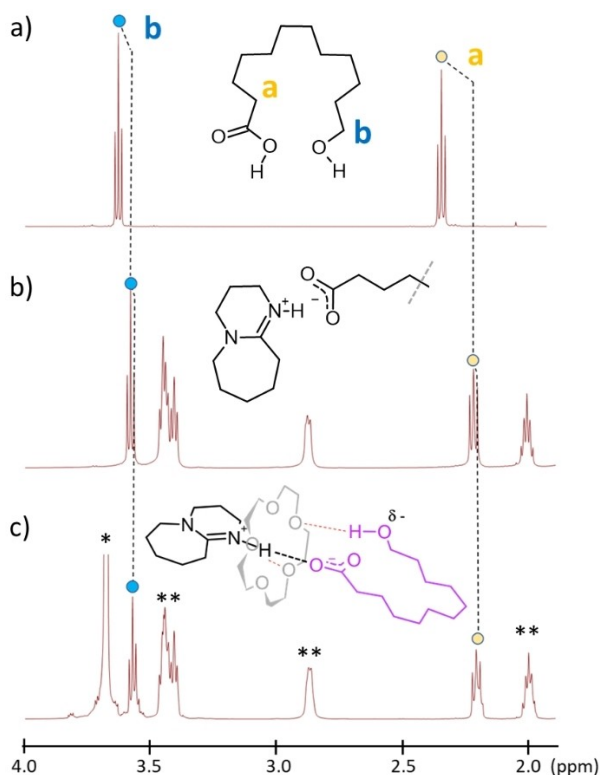


Figure 2. ¹H NMR spectra (zoomed between δ = 2 ppm and δ = 4 ppm) of pristine HDA (a), DBU/HDA salt (b) and DBU/HDA/15 C5 complex (c), recorded in CDCl₃ at 21 °C for an initial concentration of 0.16 M (Note that both inter- and intramolecular complexation could occur. The intramolecular complex has been drawn for schematic simplicity). * refers to the 15 C5 methylene protons and ** refers to the DBU methylene protons.

ylene hydroxy protons (H_b, Δδ = 0.05 ppm) confirming that the carboxylate efficiently activates the hydroxyl group of the HDA.^[9] As expected, the activation appears slightly more pronounced in presence of the 15 C5 since upon addition of 1 molar equivalent of CE, both H_a and H_b signals still move substantially by 0.01 ppm (Figure 2c). Finally, as compared to the use of the 18 C6, the ¹H NMR spectrum appears much simpler, reinforcing the hypothesis of complex structuring when using a larger CE.

With this complex in hands, we reiterated the L-LA ROP in the same experimental conditions than formerly used (Figure 1, Table S1 in SI). As compared to a polymerization proceeding without CE or in presence of 18 C6, the reaction appears faster, reaching a monomer conversion of ~80% within 2 minutes, generating a well-defined P(L-LA) with predictable molecular mass ($M_n, SEC = 8100$ g/mol) and narrow dispersity index ($D_M = M_w/M_n = 1.13$). Pushing the reaction to higher conversions results in a kinetic plot in semilogarithmic coordinates exhibiting a continuous deviation from the straight line. Although such a behavior is typical of transfer and/or termination reactions competing with the chain growth, the obtained M_n however increases linearly suggesting the maintained end-group fidelity throughout the polymerization process (Figure S2 in SI). Because such a slowing down effect could not be

explained by an adventitious loss of control, at least for conversions lower than 95%, we hypothesized that the kinetic stability of the DBU/HDA/15 C5 catalytic complex during the course of the polymerization could cause reactional kinetic turbulences.

Most of the applications of CE are based on their ability to form stable complexes with neutral or charged species and their selectivity towards them. From both a practical and mechanistic point of view, the dynamic characteristics of the process of complexation and decomplexation are important and strongly influence the system.^[14] Since performing the L-LA ROP in absence of CE conducts to a linear semi-log kinetic plot (Figure 1), possible intrinsic electrostatic modification of the RCOO⁻, DBU.H⁺ ion pair, *i.e.* an equilibrium displacement between ion pairs and free ions, during the polymerization course is excluded. This thus suggests that the slowing down effect observed with the DBU/HDA/15 C5 complex is mainly attributed to a modification of the 15 C5 complexation-decomplexation equilibrium with the DBU/HDA salt. Dynamics of coordination of R₃NH⁺ species in crown ether cavities reveal that ammonium undergoes facile rotation in the three dimensional space, leading to frequent changes in the NH bonds involved in the overall coordination.^[15] The reduced host-guest symmetry matching of the 15 C5 enhances the reorientation dynamics making easier the CE decomplexation and more especially here for an amidinium cation already in strong interaction with its carboxylate counter-anion. The appearance of P(L-LA) from the lactone monomer could also have a strong impact in the weak functional group interactions especially if the 15 C5 mobility is influenced by the polymer. Mimicking the polymerization medium in terms of lactidyl units concentration, *i.e.* for a [L-LA]₀ = [P(L-LA)]₀ of 1.6 M, we briefly evaluated the mobility of the CE in presence of both monomer and polymer by comparing the Δv_{1/2} associated to the methyleneoxy CE protons signal (Figure S3 in SI). As compared to its mobility when interacting with the DBU/HDA salt only, the 15 C5 motion is diminished by a factor of ~3.7 when interacting with L-LA and ~5.4 in presence of P(L-LA). This thus suggests that when the DBU/HDA/15 C5 initiator complex is injected into the L-LA solution, the monomer initially keeps safe the complexation of the DBU/HDA salt by limiting the 15 C5 motion. As a consequence, the initiation of the polymerization is really fast improving the overall control of the process, explaining then the samples narrow dispersities. With time, however, due to the weak interactions of the tripartite complex, the inescapable decomplexation of the 15 C5 is more and more pronounced keeping the CE free into the polymer solution since it strongly limits the CE mobility and, as a consequence, the 15 C5 ability to reactivate the DBU/HDA salt.

Many of the dilute solution properties and the bulk material properties of cyclic molecules are significantly different than their linear analogues.^[16] Reasoning that the cyclic rigidity of the 15 C5 is one of the factors influencing its mobility into the polymerization medium, attempts to reduce the kinetic deceleration factor were envisaged by using a more flexible linear oligomeric analog, *i.e.* the octaethylene glycol dimethyl ether, EG₈. Slightly longer but more flexible than CEs, the EG₈ was

mixed with a DBU/HDA equimolar mixture in DCM in a 1:1 molar ratio for a $[EG_8]_0$ of 0.23 M. As for the other polymerizations, after 10 minutes of agitation, the complex was added to a L-LA solution in DCM, targeting a theoretical DP of 40 ($[L-LA]_0 = 1.63$ M; $[HDA]_0 = [DBU]_0 = [EG_8]_0 = 0.041$ M, Table S1 in SI). As highlighted by the Figure 1, the structure of the ethyleneoxy catalyst appears crucial for a fast and expected less decelerated polymerization kinetics, as the EG_8 catalyst allows for a conversion of 95% to be obtained in 1 minute ($M_n, SEC = 8900$ g/mol, $D_M = 1.1$). Rather than very interesting to get low mass P(L-LA)s (DP < 40), trials to reduce the deceleration effect for higher DP values (DP of 100) failed when using an equimolar tripartite complex and an excess of EG_8 ($[EG_8]_0/[DBU]_0 = 5$) was necessary to maintain a fast polymerization kinetics (Figure S4 and Table S1 in SI).

The ability of a CE to interact with molecules of proton-donor solvents in complexing reaction has an appreciable effect on the thermodynamic parameters of these reactions.^[13] In 1985, Golovkova and coll. already measured the ability of various CEs to coordinate with water in chloroform.^[17] They demonstrated that, although less efficient than 18 C6, 15 C5 presents an appreciable capacity to trap free water in solution with an association constant (K) of ~ 5 dm³·mol⁻¹. During our investigation, the ability of the 15 C5 to efficiently trap water was serendipitously highlighted after analyzing its ¹H NMR spectrum when solubilized in undried CDCl₃. Very interestingly, we observed that the proton signal of water shifted from $\delta = 1.56$ ppm to $\delta = 2.77$ ppm demonstrating the ability of 15 C5 to form a stable complex with H₂O (Figure S5 in SI).^[17] Taking advantage of the situation, we reasoned that a DBU/HDA/15C5 tripartite complex could be potentially efficient to get rid of adventitious termination when the polymerization medium is exposed to air (and then traces of poisoning protic adjuvants such as water). After having played its role as a kinetic booster, when the polymerization medium atmosphere is switched from nitrogen to air, the free 15C5 could indeed act as a water trap, preventing then premature terminations and/or transfer reactions induced by water. To verify such hypothesis, the adopted strategy was then to initiate a L-LA ROP under nitrogen, following both kinetics and M_n evolution in that conditions, before switching N₂ by an air atmosphere. To demonstrate the expected effect of the 15 C5, another polymerization free of CE was also performed under the same experimental conditions. Polymerizations were targeting a DP of 200 ($[L-LA]_0/[HDA]_0 = 200$) for an initial $[DBU]_0/[HDA]_0/[15 C5]_0$ ratio of 1 (Table S1 in SI). To get rid of fast initial decomplexation of the CE, the 15 C5 was priorly mixed with a DBU/HDA equimolar mixture in DCM for a concentration of ~ 0.34 M. After 10 minutes, the complex was quickly added under N₂ to a L-LA solution in DCM ($[L-LA]_0 = 1.63$ M) to initiate the polymerization process. As expected, under nitrogen, the reaction performed in presence of 15 C5 is substantially faster (~ 11 times) than the one without CE (Figure 3a). When both polymerization media reached a conv. of 50–60%, solutions were then exposed to an air atmosphere (volume of air ~ 5 to 6 cm³) and corresponding kinetics were recorded. As compared to the fast deceleration observed in absence of CE (Figure 3a), the presence of the

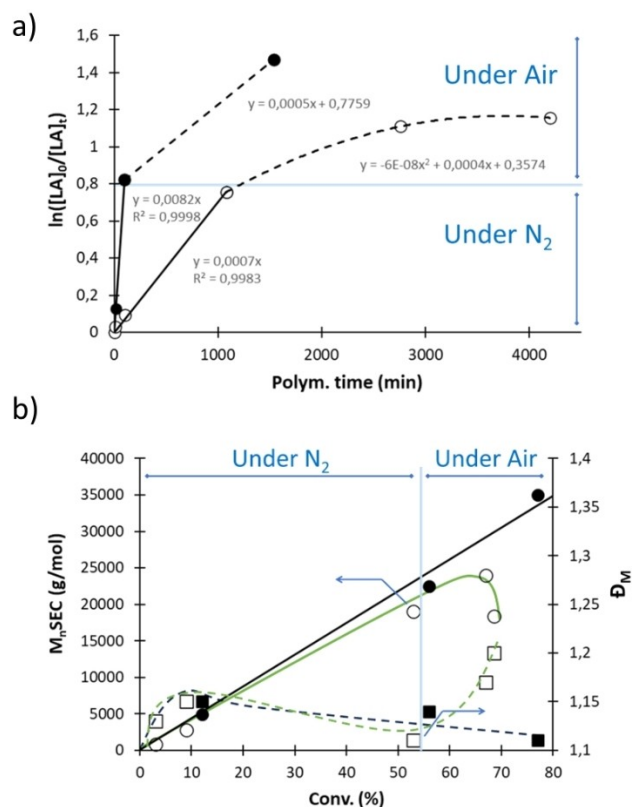


Figure 3. a) Semilogarithmic plots of L-LA polymerizations initiated with DBU/HDA/15C5 (●) and DBU/HDA (○) under N₂ (full line) and air (dash line). Conditions of polymerizations: $[L-LA]_0/[HDA]_0 = 200$, $[L-LA]_0 = 1.6$ M, DCM solvent, 21 °C; b) SEC experimental molar mass (M_n , circles) and dispersity (D_M , squares) in function of the conversions recorded during the DBU/HDA/15C5 (●, ■) and DBU/HDA (○, □) under N₂ and air DBU/HDA/15C5 complex-catalysed ROP of L-LA in DCM at 21 °C under N₂ and air. Conditions: $[L-LA]_0/[DBU]_0/[HDA]_0/[15C5]_0 = 200/1/1/1$; $[L-LA]_0 = 1.6$ M.

sacrificial 15 C5 kinetic booster plays its role allowing a final P(L-LA) sample to be obtained with a molar mass in perfect adequation to the recorded conversion (Figure 3b). Importantly, in absence of 15C5, adventitious water molecules probably act as transesterification agents diminishing the P(L-LA) molar mass while increasing the dispersity values (Figure 3b).

Finally, the ability of the 15C5 to react with water molecules has also been indirectly highlighted by comparing the semi-logarithmic plots recorded from a “nitrogen-to-air” system to the one obtained from a comparative reaction performed under nitrogen only (Figure S6). Under nitrogen, the kinetic plot in semi-logarithmic coordinates exhibits, as already observed in Figure 1, a characteristic and gentle deviation from the straight line. Comparatively, when the atmosphere of the system is switched from nitrogen to air, the 15C5 decomplexes easily by reaction with exogenous water molecules diminishing then the overall kinetics.

Conclusions

In summary, we reported the CE-activated polymerization of L-LA when initiated from a HDA/DBU complex. While the cyclic structure of the CE plays a crucial role in the catalysis, with the 15C5 enabling the fastest polymerization, the kinetics of CE decomplexation has been demonstrated crucial to outpace transfer reactions and also permit the process to be moderately conducted under air atmosphere.

Experimental Section

Materials. L-Lactide (L-LA) (Corbionpurac) was recrystallized three times from toluene and dried under vacuum. 12-Hydroxydodecanoic acid (HDA, Aldrich, 97%) and octaethylene glycol dimethyl ether (EG₈) were dried by three successive azeotropic distillations by addition of toluene. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich, 98%) was pre-dried over BaO and distilled before a successive drying process over CaH₂ and a final distillation under vacuum. 15-Crown ether-5 (15 C5, 98%, Acros) was dried by heating at 80 °C under vacuum for 24 hours. 18-Crown ether-6 (18 C6, 99%, Acros) was first pre-dried by heating at 80 °C under vacuum for 24 hours, then dried by three azeotropic distillations of tetrahydrofuran (THF). Compounds were all stored in a glove box (O₂ ≤ 6 ppm, H₂O ≤ 1 ppm). DCM, toluene and THF solvents were dried using a MBraun Solvent Purification System (model MB-SPS 800) equipped with alumina drying columns.

General Polymerization Procedure. In a glove box, a dried vial equipped by a stirrer is charged with HDA (15 mg, 6.9 × 10⁻⁵ mol), DBU (10.6 mL, 6.9 × 10⁻⁵ mol) and 15 C5 (15.3 mg, 6.9 × 10⁻⁵ mol) in 0.3 g of dry DCM ([DBU]₀ = [HDA]₀ = [15 C5]₀ = 0.3 M). After 10 min, the solution was quickly added to another solution of L-lactide in DCM (0.4 g of LA, 2.8 × 10⁻³ mol and 1 g of dry DCM) to get a polymerization degree of 40. The sealed vial is then maintained under agitation and several withdrawals are performed to follow the kinetics by SEC.

Characterizations. ¹H NMR-spectra were recorded using a Bruker AVANCEII 500 apparatus at r.t. in CDCl₃ (10 mg/0.6 mL). Size exclusion chromatography (SEC) was performed in THF at 35 °C using a Triple Detection Polymer Laboratories liquid chromatograph equipped with a refractive index (ERMA 7517), a UV detector (254 nm), a capillary viscometry, a light scattering RALS (Viscotek T-60) (Polymer Laboratories GPC-RI/CV/RALS) and an automatic injector (Polymer Laboratories GPC-RI/UV) and four columns : a PL gel 10 μm guard column and three PL gel Mixed-B 10 μm columns (linear columns for separation of MwPS ranging from 500 to 10⁶ Daltons).

Acknowledgements

This work was support by the AXA Research Funds. O.C. is Senior Research Associate for the F.R.S.-FNRS and AXA Professor in Chemistry.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: L-LA · ROP · DBU · crown ether

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Manuscript received: May 22, 2023

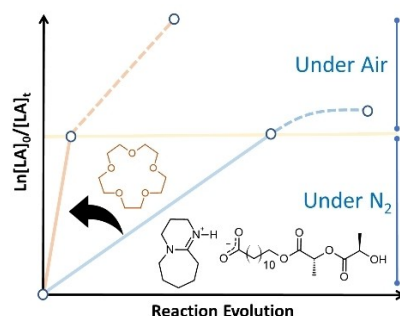
Revised manuscript received: June 22, 2023

Accepted manuscript online: June 23, 2023

Version of record online: ■■■■■

RESEARCH ARTICLE

Crown ether benefits: The 15 C5 has been demonstrated excellent catalyst for the L-LA ROP in presence of alcohol and a DBU ion pair salt. Its decomplexation is vital to prevent transfer reactions, enabling air-friendly process with water trapping effect.



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