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Authors: Samuel Dagorne

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Bi-functional Squaramides as Organocatalysts for Lactide Polymerization: Catalytic Performance and Comparison with Mono-functional Analogues

David Specklin,[a] Frédéric Hild,[a] Li Chen,[a][b] Lucas Thévenin,[a] Maxime Munch,[a] Françoise Dumas,[b] Franck Le Bideau,*[b] and Samuel Dagorne*[a]

Dedication ((optional))

Abstract: Amino-functionalized squaramides **1** and **2** were prepared and shown to be suitable polymerization organocatalysts for the controlled ROP of *L*-lactide (*L*-LA) in the presence of an alcohol source such as BnOH (acting as initiator) to afford chain-length-controlled and narrowly disperse poly(*L*-lactide) (PLLA) under mild reaction conditions. All ROP experimental and polymer analysis data are consistent with **1** and **2** acting as bifunctional H-bonding catalysts able to activate both the lactide monomer and initiator BnOH thanks to their dual HB acceptor and donor properties. As a comparison, amino-squaramide **3**, a direct analogue of **1** but less HB donor due to the absence of electron-withdrawing NH-substituents, displays little lactide ROP activity, highlighting the key role of monomer activation through HB in the present systems. Unlike amino-squaramides **1** and **2**, related mono-functional squaramides **4** and **5** are inactive in lactide ROP in the presence of BnOH, but the addition of NEt_3, as an external HB acceptor, allows the ROP to proceed with the production of well-defined PLLA. A cooperative dual activation with an activated-monomer/activated chain-end mechanism is most likely operative in the lactide ROP mediated by catalysts **1** and **2** in the presence of BnOH.

Introduction

Poly(lactic acid) (PLA), a biodegradadable polyester composed of lactic acid (*i.e.* a renewable resource) units, is currently attracting attention as a thermoplastic polymer of potential usefulness for a variety of applications ranging from food packaging to electronic devices.[1] Such a material may also constitute a viable alternative to classical petrochemically-based thermoplastics such as polyethylene (PE), polypropylene (PP) and polystyrene (PS). The ring-opening polymerization (ROP) of lactide, a dimer of lactic acid, constitutes the method of choice to access PLA with controllable properties, and may be best performed using either metal-based initiators (organometallic catalysis) and small organic molecules (organocatalysis).[2,3] Industrially, PLA is currently produced *via* the ROP of lactide using a Sn-based catalyst.[4] However, the typical lower toxicity of organic *vs.* metal-based species prompted the development of organocatalyzed ROP of lactide over the past 15 years for the production of metal-free and well-defined PLA material. In this area, non-covalent hydrogen-bonding (HB) ROP of lactide is presently of particular interest as a versatile and mild approach for the efficient production of PLA.[5] An interesting category of HB catalysis lies on the combination of a strong HB donor (for C=O activation of an electrophilic monomer such as lactide) with a Brønsted base acting as a hydrogen-bond acceptor to enhance the nucleophilicity of the initiating moiety (typically an alcohol substrate). Such a dual activation was shown to efficiently promote the ROP of lactide using, most notably, a variety of thiourea-, amidine-, amide-, sulfonamide-based HB donors in association with an amine moiety acting as a HB acceptor for alcohol (initiator) activation.[5,6] These catalytic systems may either be *single-component*, with a discrete bifunctional organo-catalyst containing both HB donor and Brønsted base functions, or, more frequently, *bi-component*, with the involvement of two monofunctional molecular entities (*i.e.* a HB donor and a Brønsted base).[7,8] Ongoing studies in the area also involve the development of new types of HB donor/acceptor catalysts for enhanced HB activation, including acid/base pair binary systems, ionic HB catalysts and bis-/tris-thioureas HB donors.[9,10,11]

Since the first report by Rawal *et al.*[12] and thanks to their specific properties as strong HB donors[13], squaramides with various skeletons have recently being successfully used as bifunctional catalysts for the mediation of various asymmetric organic transformations such as cycloadditions[14], domino/cascade reactions[15], 1,4-conjugate additions and aldol reactions[16]. Therefore, squaramides may stand as a suitable HB ROP catalysts for lactide polymerization and their potential in this area clearly remains unexplored. To date, squaramide-mediated ROP of lactide was reported on one occasion using a squaramide/(–)-sparteine bi-component catalytic mixture.[17a] While the present study was in progress, a Pt-functionalized amino-squaramide was also reported to oligomerize lactide.[Erreur ! Signet non défini.b]

Here we report a complete study on various amine-functionalized squaramides (**1**, **2** and **3**, scheme 1), thus containing a HB donor and a Brønsted base function, able to act as *single-component* organocatalysts for the effective and controlled ROP of lactide in the presence of an alcohol source

[a] Dr. D. Specklin, Dr. F. Hild, Dr. L. Chen, L. Thévenin, M. Munch, Dr. S. Dagorne
Institut de Chimie de Strasbourg
CNRS and Université de Strasbourg
1 rue Blaise Pascal, 67000 Strasbourg, France
E-mail: dagorne@unistra.fr

[b] Dr. F. Dumas, Dr; F. Le Bideau
BioCIS, Univ. Paris-Sud
CNRS and Université Paris-Saclay
92290 Châtenay-Malabry, France

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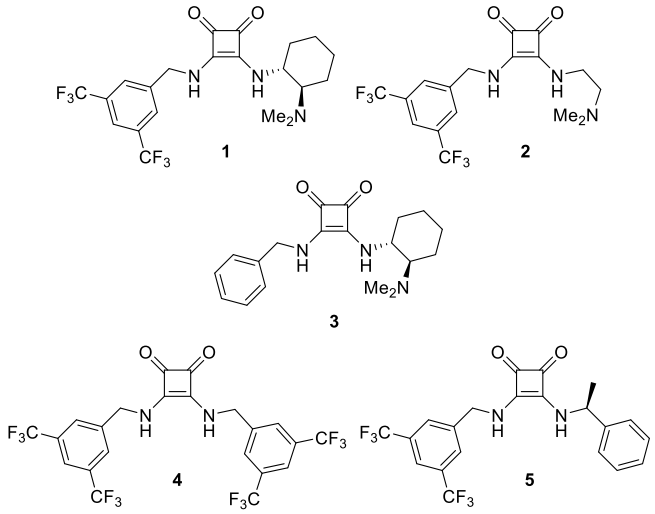
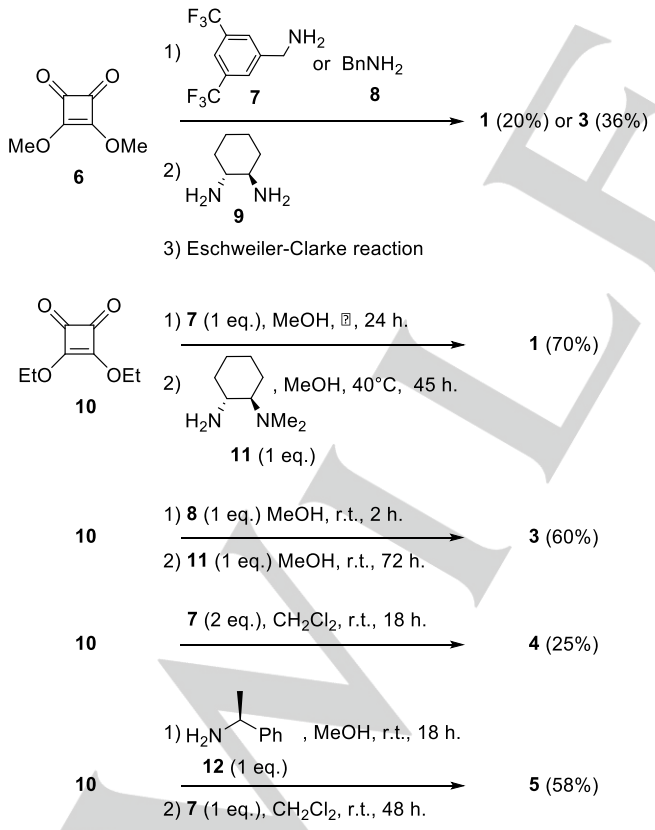
acting as initiator. The catalytic performance of such systems are also compared with that of related *bi-component* squaramide/amine catalysts (using squaramides **4** and **5**, scheme 1).



Scheme 1. Squaramide derivatives used as lactide ROP catalysts in the present study.



Scheme 2. Preparation of the squaramide organocatalysts.

Results and Discussion

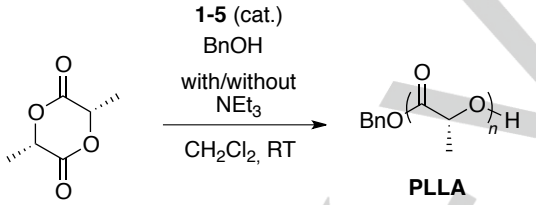
Synthesis of Squaramides 1-5. Catalyst **1** was initially prepared through a three steps protocol starting from dimethylsquarate **6** (Scheme 2) in 20% overall yield following a literature procedure.[18] The rather low yield in **1** is due to the Eschweiler-Clarke reaction (last step, 24% yield) allowing the incorporation of the dimethyl amino group. A low yield one pot synthesis of catalyst **3** (36% yield) was also recently reported. Due to these low yields and the relatively high cost of (*R*,*R*)-diaminocyclohexane **9**, we chose another route to compounds **1** and **3** involving the pre-formation of diamine **11** (obtained in three steps and 69% yield as previously reported[19]). Catalyst **1** (respectively **3**) was thus synthesized *via* a sequential addition of aryl amine **7** (respectively benzylamine **8**) and then compound **11** onto diethylsquarate **10**, in 70% yield (respectively 60% yield) Catalyst **2** was prepared according to a reported procedure.[20] The new squaramide **4** (respectively **5**) was prepared in 25% yield (respectively 58% yield) following a similar procedure with two equivalents of arylamine **7** (respectively sequential addition of 1 equivalent of (*S*)-(–)-methylbenzylamine **12** and arylamine **7**).

Ring-opening polymerization of lactide catalyzed by squaramides 1-5. The amine-functionalized squaramides **1**-**3** and the mono-functional derivatives **4** and **5** were tested as ROP initiators of *L*-lactide under various conditions; *i.e.* in the absence/presence of $PhCH_2OH$ (acting as an initiator) and NEt_3 for initiator activation through HB. The polymerization runs were all performed at room temperature in CH_2Cl_2 and the results are summarized in Table 1. Remarkably, when combined with initiator BnOH (5 equiv *vs.* **1**), the cyclohexylamino-squaramide **1** was found to polymerize 100 equiv *L*-LA at room temperature in a controlled manner in the absence of NEt_3 to afford well-defined and narrow disperse PLLA in high conversion, as deduced from GPC and NMR data (entry 1, Table 1). Increasing the monomer feed from 100 to 600 equiv. (with $[L\text{-LA}]_0/[\text{BnOH}]_0$ = 20) led to the controlled ROP of 450 equiv of *L*-LA within 23 h to afford well-defined PLLA, indicating the effectiveness of catalyst **1** in lactide ROP catalysis (entry 2, Table 1). With $[\text{LA}]_0/[\text{BnOH}]_0$ = 60 and 120 and starting from 600 equiv of *L*-LA (entries 3 and 4, Table 1), the production of narrow disperse PLLA with higher chain length (M_n = 6800 g.mol^{-1}, $Đ$ = 1.13 and M_n = 14600 g.mol^{-1}, $Đ$ = 1.06, respectively) was achieved within 48-72 h at room temperature in CH_2Cl_2. The ROP activity of organocatalyst **1** is thus comparable to that of the thiourea–amine single-component systems developed by Waymouth and Hedrick.[Erreur ! Signet non défini.a] For all runs (entries 1-4, Table 1), the polydispersities ($Đ$) of the produced PLA are below 1.15, with GPC data featuring in all cases monomodal traces (see, for instance, Figures S7 and S7', SI) and the PLA M_n values match reasonably well the expected theoretical values. Besides, kinetic data also support a well-controlled polymerization process including: i) an observed first order reaction rate relative to *L*-LA (Figure 1) and ii) a linear correlation between the M_n of the produced PLA and the monomer-to-polymer conversion (Figure 2; for additional kinetic data, see Figure S6, SI). Regarding the nature of the produced PLA, the NMR along with MALDI-TOF

data agree with the production of linear and OBn-ester-ended PLA. For instance, for the ROP of *L*-LA mediated by catalyst **1** in the presence of 600 equiv of *L*-LA and 10 equiv of BnOH (entry 3, Table 1), the MALDI-TOF mass spectrum only contains equally spaced peaks (by 144 u.a.), thus consistent with the absence of any substantial (and detrimental) transesterification reactions as the ROP proceeds (Figure 3). The mass values also unambiguously agree with the presence of a BnO moiety at the ester end of the formed PLA (Figures S8 and S9, SI).

For further insight on the ROP catalysis mediated by organocatalyst **1** in the presence of BnOH, the dependence of the ROP reaction rate on [**1**] was determined by performing several ROP runs at constant $[L\text{-LA}]_0$ and $[BnOH]_0$ concentrations ($[L\text{-LA}]_0/[BnOH]_0$ = 20) but at different concentrations in **1**, leading to a set of different k_{obs} values. As depicted in figure 4, there is a linear correlation between k_{obs} and [**1**]: this indicates a first order dependence of the reaction rate relative to [**1**], which is in line with compound **1** being the actual catalyst of the ROP process and thus with a dual activation at a single molecular catalyst.[Erreur ! Signet non défini.,Erreur ! Signet non défini.]

Table 1. ROP of *L*-lactide catalyzed by squaramides **1**-**5** in the presence of BnOH [a]



PLLA

Entry	Catalyst	*L*-LA/BnOH/NEt_3	Time (h) [b]	Conv. (%) [c]	$M_{n\ (theo)}$ [d]	$M_{n\ (exp)}$ [e]	$Đ$ [f]
1	**1**	100/5/0	18	95	2750	2300	1.08
2	**1**	600/30/0	23	75	2150	1800	1.16
3	**1**	600/10/0	48	94	8100	6800	1.11
4	**1**	600/5/0	72	90	15600	14600	1.06
5	**2**	100/5/0	18	90	2600	2800	1.13
6	**2**	600/30/0	23	50	1400	1200	1.13
7	**3**	600/30/0	23	10	-	-	-
8	**4**	600/30/1	48	57	1600	1600	1.15
9	**4**	600/30/10	25	93	2700	2600	1.06
10	**4**	600/10/10	32	91	7800	6300	1.10
11	**5**	600/30/1	48	27	800	800	1.02
12	**5**	600/30/10	40	83	2400	2100	1.05
13	**5**	600/10/10	40	48	4150	3700	1.08

[a] $[L\text{-LA}]_0$ = 2 M, CH_2Cl_2, room temperature. [b] Reaction time. [c] Monomer conversion to PLLA as determined by ^1H NMR. [d] Calculated using $M_{n\ (theo)} = [L\text{-LA}]_0/[BnOH]_0 \times M_{L\text{-LA}} \times$ conv. [e] Calculated using $M_{n\ (theo)} = [L\text{-LA}]_0/[BnOH]_0 \times M_{L\text{-LA}} \times$ conv. [e] Measured by GPC in THF (30 °C) using polystyrene standards and corrected by applying the appropriate correcting factor (0.58).[21] [f] Measured by GPC in THF (30 °C).

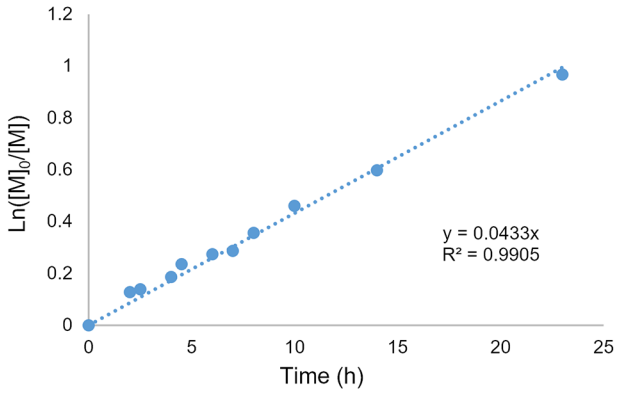


Figure 1. Plot ln([M]$_0$/[M]) (M = monomer = *L*-LA) *versus* time in the ROP of *L*-LA mediated by amino-squaramide **1** in the presence of BnOH. Conditions: *L*-LA/BnOH/**1** = 600/30/1, room temperature, CH_2Cl_2.

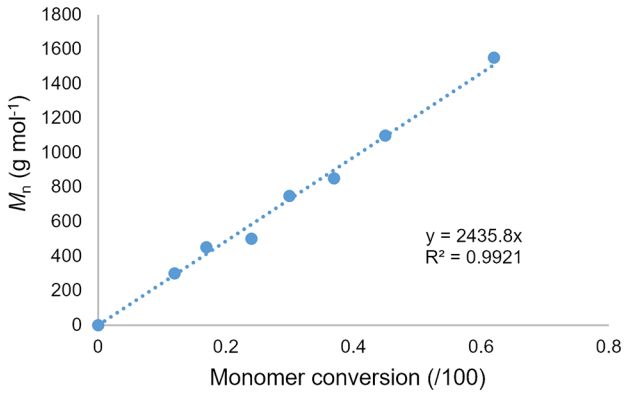


Figure 2. Plot of the M_n (g.mol^{-1}) of the produced PLA *versus* monomer conversion in the ROP of *L*-LA mediated by amino-squaramide **1** in the presence of BnOH. Conditions: *L*-LA/BnOH/**1** = 600/30/1, room temperature, CH_2Cl_2.

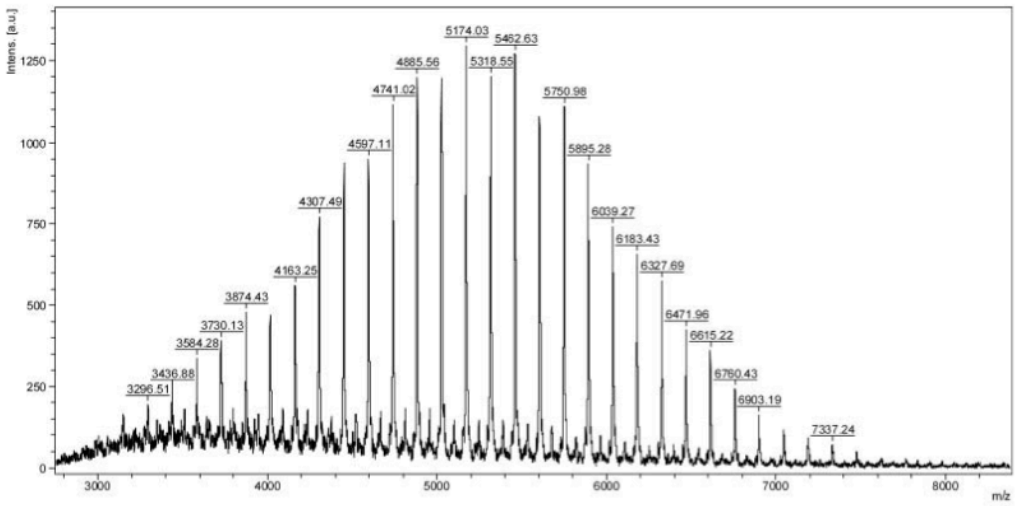


Figure 3. MALDI-TOF analysis of the isolated from the ROP of *L*-LA mediated by amino-squaramide **1** in the presence of BnOH. Conditions: *L*-LA/BnOH/**1** = 600/10/1, room temperature, CH_2Cl_2 (48 h, 94% conv. to PLLA).

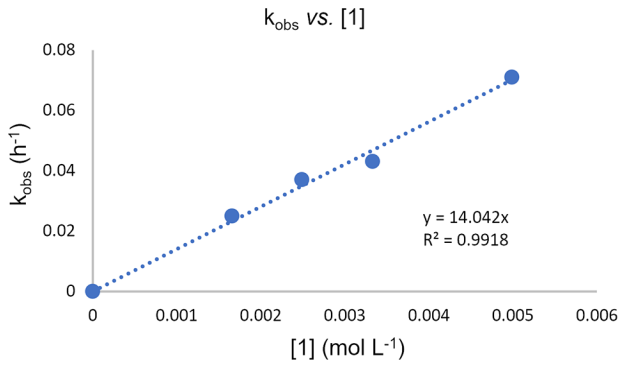


Figure 4. Plot of k_{obs} *versus* [**1**] in the ROP of *L*-LA mediated by amino-squaramide **1** in the presence of BnOH at constant initial concentrations of *L*-LA and BnOH. Conditions: $[L\text{-LA}]_0$ = 2 M, $[L\text{-LA}]_0/[\text{BnOH}]_0$ = 20, room temperature, CH_2Cl_2.

Amino-squaramide **2**, which contains a more flexible CH_2-CH_2-NMe_2 amino side-arm *vs.* that in catalyst **1**, also mediates the ROP of *L*-LA in a controlled manner but is less active than its analogue **1** (entries 5 and 6, Table 1). Thus, in the presence of 600 equiv of *L*-LA and 30 equiv of BnOH, species **2** may polymerize up to 300 equiv of *L*-LA within 23 h (CH_2Cl_2, room temperature) while 450 equiv of monomer are polymerized by catalyst **1** under identical reaction conditions (entry 5 *vs.* 2; Table 1). Kinetic data with catalyst **2** are also consistent with a well-controlled ROP catalysis (Figures S12 and S13, SI) and with catalyst **2** being roughly twice slower than its analogue **1** (Figure S1 *vs.* Figure S12). Polymer analysis data for the ROP

mediated by **2** agree with the formation of BnO-ester-ended PLLA (Figures S11 and S14, SI). When compared to catalyst **2**, the rigidity and the steric bulk of the cyclohexyl backbone in **1** certainly further favors a conformational arrangement in which the NMe_2 moiety lies in the vicinity of the NH amido functions (as depicted in scheme 1 for squaramide **1**), a key feature for an effective bifunctional ROP catalysis (monomer and initiator activation in close proximity). Note that catalysts **1** and **2** also mediate the ROP of *rac*-LA (with a similar reaction rate and polymerization control to that observed with *L*-LA) to afford atactic PLA, while they are both essentially inactive in the ROP of other lactones such as ε-caprolactone.

The nature of the squaramide NH-substituents also appears of importance for an efficient ROP process. Thus, the cyclohexylamino-squaramide **3** (Scheme 1), which bears a $PhCH_2$-NH moiety *vs.* a 3,5-$(CF_3)_2$-$PhCH_2$-NH group in **1**, only displays a moderate ROP activity in the presence of 600 equiv LA, with only a 10% consumption of monomer after 23 h at room temperature (CH_2Cl_2, 30 equiv of BnOH; entry 7, Table 1). The presence of electron withdrawing NH-substituents is thus clearly required to enhance the HB donor character of these bifunctional catalysts and hence ensure an effective monomer activation, as previously observed.[5,7,8]

The bifunctional nature of amino-squaramide catalysts **1** and **2** was further evidenced by comparing their ROP performances with those of their mono-functional counterparts **4** and **5** (Figure 1). Thus, unlike species **1**-**3**, both **4** and **5** are inactive in *L*-LA ROP in the presence of BnOH under various reactions (CH_2Cl_2, room temperature, 100 or 600 equiv of *L*-LA, 10 or 30 equiv of BnOH), highlighting the fact that initiator (*i.e.* BnOH) activation is crucial for the ROP to proceed with the present catalytic systems. Accordingly, the addition of an external Lewis base such as NEt_3 for initiator activation promoted the ROP reaction. Thus, in the presence of 600 equiv of *L*-LA and 30 equiv of BnOH, the 1/1 **4**/NEt_3 catalytic mixture afforded PLA in a controlled manner with a 57% conv. after 48 h at room temperature as deduced from NMR and GPC data (entry 8, Table 1; Figures S15-S17, SI). As a comparison, with an identical monomer/initiator feed, bifunctional catalyst **1** is clearly more effective with a 75% conv. to PLA within 23 h (entry 2 *vs.* entry 8, Table 1), showing that the intramolecular proximity of the HB donor/acceptor sites for monomer and initiator activation is clearly beneficial to ROP catalysis. Comparing the observed ROP rate constant (k_{obs}) of a 1/1 **4**/NEt_3 catalyst *vs.* amino–squaramide **1** (k_{obs} = 0.0173 and 0.0433 h^{-1}, respectively; Figures S15 *vs.* S1), the ROP reaction is 2.5 times faster with the bifunctional catalyst **1** than with the 1/1 **4**/NEt_3 bi-component system. The ROP performance of the **4**/NEt_3 catalytic mixture may be significantly improved upon increasing feed in NEt_3. Thus a 1/10 **4**/NEt_3 catalyst mixture readily polymerizes *L*-LA to afford chain-length controlled PLLA in high conversion in the presence of BnOH as initiator (600 equiv *L*-LA, > 90% conv. to PLLA within 25 or 32 h, 10 or 30 equiv of BnOH; entries 9 and 10, Table 1). All kinetic and polymer characterization data agree with a well-controlled process (Figures S18-S21, SI). The kinetic data for the 1/1 *vs.* 1/10 **4**/NEt_3 catalytic system (k_{obs} = 0.0173 *vs.* 0.111 h^{-1}; Figures S15 and S18, SI) indicate that going from 1 to 10 equiv of NEt_3 increases the ROP reaction rate by a factor of 6.5. To probe this issue further, the ROP reaction rate dependence on [NEt_3] was studied at constant $[L\text{-LA}]_0$, $[BnOH]_0$ and $[\mathbf{4}]_0$ ($[L\text{-LA}]_0/[BnOH]/[\mathbf{4}]_0$ = 600/30/1) but at different NEt_3 concentrations. The observed linear correlation of k_{obs} *vs.* [NEt_3] agree with a first order dependence of the reaction rate on [NEt_3] (Figure 5), thus confirming the beneficial effect (on reaction rate) of an excess of NEt_3. As a comparison and in contrast, Kiesewetter and co-workers showed that cocatalyst binding effects in such bi-component systems, *i.e.* amine/HB donor interactions, may be detrimental to catalytic activity at higher amine/HB donor ratios in the case of DBU/thiourea (DBU = 1,8-dizabicyclo[5.4.0]undec-7-ene) catalytic systems.[Erreur ! Signet non défini.j] In our case, the lower Lewis basicity of NEt_3 (vs. DBU), yet allowing an effective initiator activation, along with the systematic use of an excess initiator (*vs.* squaramide) certainly disfavor substantial NEt_3/**4** HB interactions.

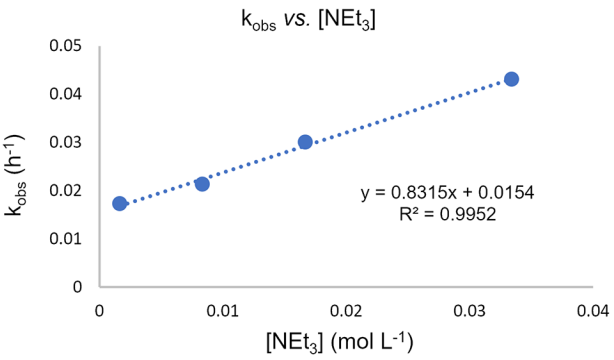
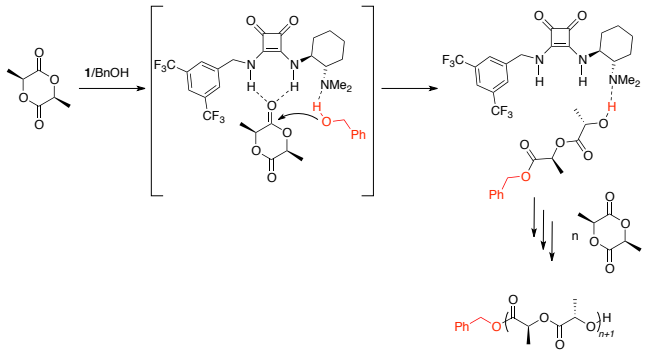


Figure 5. Plot of k_{obs} *versus* [NEt_3] in the ROP of *L*-LA mediated by **4**/NEt_3 at constant initial concentrations of **4**, *L*-LA and BnOH. Conditions: $[L\text{-LA}]_0$ = 1 M, $[L\text{-LA}]_0/[BnOH]_0/\mathbf{4}$ = 600/30/1, room temperature, CH_2Cl_2.

The mono-functional squaramide **5** (Scheme 2), which only bears one electron withdrawing NH-substituent, also mediates the controlled ROP of *L*-LA in the presence of BnOH and NEt_3 (entries 11-13, Table 1; Figures S22-S25, SI) though with a lower activity than analogue **4**, presumably reflecting the lower HB donor ability (for monomer activation) of **5** *vs.* **4**.

Overall, the kinetic and characterization data on *L*-LA ROP catalysis by bifunctional amino-squaramides **1**-**3** (including their comparison with their mono-functional analogues **4** and **5**) clearly hints at a ROP process occurring through a cooperative dual activation of the monomer and initiator/polymer chain-end thanks to the HB donor ability of the squaramide moiety (for lactide activation) and the HB accepting character of the NMe_2 moiety (for initiator/polymer chain-end activation). The proposed bifunctional activation mechanism, *i.e.* activated monomer/activated chain-end mechanism (AM/ACEM)[3h], is depicted in Scheme 3. Such a dual activation at a single molecular catalyst is documented in the literature with other lactide ROP organocatalysts, most notably amino-functionalized thioureas and amidine-type organics.[Erreur ! Signet non défini.]



Scheme 3. Bifunctional activation mechanism for the ROP of *L*-LA catalyzed by amino-squaramides **1** and **2** in the presence of BnOH, taking the example of squaramide **1**.

Conclusions

Amino-functionalized squaramides **1** and **2** are suitable polymerization organocatalysts for the controlled ROP of *L*-LA in the presence of an alcohol source such as BnOH acting as initiator to afford chain-length-controlled and narrowly disperse PLLA. When compared to related mono-functional squaramides **4** and **5** (which require the presence of an external HB acceptor for the ROP to occur), the ROP results with catalysts **1** and **2** agree with a cooperative dual activation ROP mechanism of the type AM/ACEM being operative due to their bifunctional nature (*i.e.* HB donor and acceptor). Given the steric and electronic tunability of squaramide derivatives (through variation of NH substituents) along with their straightforward access *via* well-established synthetic procedures, such HB-based organocatalysts may also be of potential interest for the polymerization of various polar cyclic monomers.

Experimental Section

All experiments were carried out under N_2 using standard Schlenk techniques or in a MBraun Unilab glovebox. Toluene, dichloromethane, and pentane were first dried through a solvent purification system (MBraun SPS) and stored for at least a couple of days over activated molecular sieves (4 Å) in a glovebox prior to use. CD_2Cl_2 was purchased from Eurisotope (CEA, Saclay, France), degassed under a N_2 flow, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. Benzyl alcohol (BnOH) was also dried for 24 h over activated molecular sieves (4 Å) prior to use. All other chemicals were used as received. *L*-lactide was sublimed once prior to use. NMR spectra were recorded on BrukerAC 300 or 400 MHz NMR spectrometers in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Chemical shifts (δ) are given in ppm. Mass spectra were performed at the Mass Spectrometry Department of the University of Strasbourg. Mass spectra were acquired on a time-of-flight mass spectrometer (MALDI-TOF-TOF Autoflex II TOF-TOF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser (λ = 337 nm). An external multi-point calibration was carried out before each measurement with a standard peptide mixture and a standard protein mixture (depending on the mass range analysed). Scan accumulation and data processing were performed with FlexAnalysis 3.4 software. α-cyano-4-hydroxy-cinnamic acid (CHCA), dithranol (DIT) or super-DHB (a 9/1 mixture of dihydroxybenzoid acid/2-hydroxy-5-methoxybenzoic acid) was used as matrix for analysis of the PLA samples. SEC analyses were performed on a SEC system equipped with a Shimadzu RID10A refractometer detector using HPLC-grade THF as an eluent. Molecular weights and dispersities (Đ) were calculated using polystyrene standards. In the case of molecular weight number (M_n), these were corrected with the appropriate correcting factor (0.58) for the M_n values. The synthesis and characterization of squaramides **1**-**5** are described in the Supporting Information.

General procedure for ROP of *L*-lactide mediated by squaramides 1-5 in the presence of BnOH. In a glovebox, the squaramide catalyst **1**-**5** (2 mg, 3.54×10^{-6} mol) was charged in a vial equipped with a TeflonTM-tight screw-cap and dissolved in dichloromethane (0.2 mL). In a separate vial, the appropriate amount of *L*-lactide (from 100 to 600 equiv, 2.12×10^{-3} mol) and of BnOH (from 5 to 30 equiv, 1.06×10^{-4} mol) were dissolved in dichloromethane (0.8 mL) and added all at once to the catalyst solution ($[L\text{-LA}]_0$ = 2 M). In the case of mono-functional squaramides **4** and **5**, NEt_3 (10 equiv, 3.54×10^{-5}, 4.9 µL) was also added to the reaction mixture. The mixture was vigorously stirred at room temperature during the appropriate time and the reaction was monitored by ^{1}H NMR spectroscopy. After the appropriate time, the vial was then removed from the glovebox and the reaction mixture was quenched with an excess of methanol, provoking the precipitation of the polymer which was washed several times with methanol, dried *in vacuo* until constant weight and subsequently subjected to ^{1}H NMR, GPC and MALDI-TOF analysis.

Acknowledgements ((optional))

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Keywords: lactide • polymerization • squaramide • organocatalysis • hydrogen-bonding

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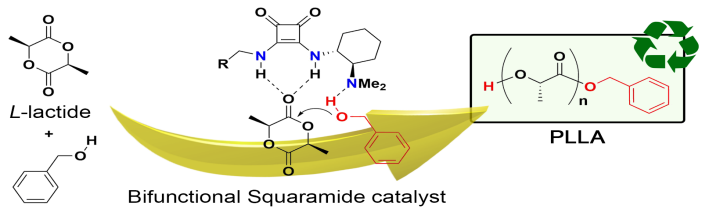

*Author(s), Corresponding Author(s)**

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Title

Single-component amino-squaramides reported herein act as effective bifunctional hydrogen-bonding catalysts for the controlled ROP of lactide under mild conditions in the presence of BnOH. Such organocatalysts perform better in lactide ROP than related squaramide/NEt_3 bi-component catalysts.