

Research Article

Ring-Opening Polymerization of Lactones Catalyzed by Silicon-Based Lewis Acid

Yuushou Nakayama , Keiya Katagi, Ryo Tanaka, and Takeshi Shiono

Department of Applied Chemistry, Graduate School of Advanced Science and Technology, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

Correspondence should be addressed to Yuushou Nakayama; yuushou@hiroshima-u.ac.jp

Received 25 November 2022; Revised 25 March 2023; Accepted 24 April 2023; Published 17 May 2023

Academic Editor: Atsushi Sudo

Copyright © 2023 Yuushou Nakayama et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Many catalysts containing various elements at their active sites have been reported for the ring-opening polymerization (ROP) of cyclic esters. However, to our knowledge, silicon-based catalysts for ROP have never been reported. Here we report the ROP of cyclic esters and cyclic carbonates catalyzed by the derivatives of bis(perchlorocatecholato)silane ($\text{Si}(\text{cat}^{\text{Cl}})_2$), which is a neutral silicon-based Lewis acid recently reported by Greb et al. The catalyst systems show high activity for the ROP of seven- and six-membered ring monomers such as ϵ -caprolactone, δ -valerolactone, and trimethylene carbonate to produce the polymers with molecular weights up to 32 kg/mol. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) and nuclear magnetic resonance analysis of the obtained polymers indicates the predominant formation of cyclic polymers.

1. Introduction

Aliphatic polyesters such as poly(ϵ -caprolactone) (PCL) and poly(L-lactide) are mainly synthesized by the ring-opening polymerization (ROP) of the corresponding cyclic ester monomers. One of the most popular catalysts is tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$), which has been widely used in both industrial and academic applications of the ROP of cyclic esters [1–5]. $\text{Sn}(\text{Oct})_2$ is relatively easy to handle because it is bench stable and moderately active. The molecular weights of the resulting polymers can be controlled by using protic compounds such as alcohols as initiators and adjusting the feed ratio of the monomer and the initiator. However, the catalyst residue of $\text{Sn}(\text{Oct})_2$ could potentially be harmful, especially in biomedical applications of biodegradable aliphatic polyesters [6–8]. Therefore, alternative catalysts to $\text{Sn}(\text{Oct})_2$ are required. Various catalyst systems have been developed for the ROP of cyclic esters [9–17]. Several metal-free organocatalysts and enzyme catalysts have also been developed [10, 18, 19]. Among group 14 elements, carbon [10, 18, 19], germanium

[20–23], and lead [24, 25] have also been applied to the active site of the ROP catalysts as well as tin. However, to the best of our knowledge, silicon has never been applied to the reaction site for the catalyst for the ROP of cyclic esters [14]. Silicon is abundant and low in elemental toxicity; therefore, a silicon-based catalyst for the ROP of cyclic esters can be interesting, if it has high catalytic activity.

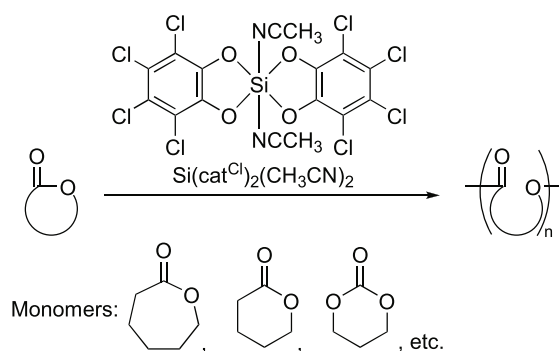
Some Lewis acids have been known to catalyze the ROP of cyclic esters. Methylaluminum bis(phenolate), $\text{MeAl}(\text{OC}_6\text{H}_3\text{Ph}_2-2,6)_2$, promoted the ROP of ϵ -caprolactone (ϵ -CL) to produce PCL with narrow molecular weight distribution [26]. The ROP of ϵ -CL by scandium trifluoromethanesulfonate ($\text{Sc}(\text{OTf})_3$) has been proposed to proceed by a monomer-activation mechanism [27, 28]. A borane Lewis acid, $\text{B}(\text{C}_6\text{F}_5)_3$, promoted the controlled ROP of cyclic esters such as ϵ -CL [29]. We have reported that $\text{Al}(\text{C}_6\text{F}_5)_3(\text{THF})$ can promote the ROP of ϵ -CL, while that of lactide required the combination of $\text{Al}(\text{C}_6\text{F}_5)_3(\text{THF})$ with bulky phosphines [30].

On the other hand, Greb et al. recently reported neutral Si-based Lewis super acids, such as bis(perchlorocatecholato)silane ($\text{Si}(\text{cat}^{\text{Cl}})_2$, **1**), bis(perbromocatecholato)silane ($\text{Si}(\text{cat}^{\text{Br}})_2$, **2**),

and bis(perfluorocatecholato)silane ($\text{Si}(\text{cat}^{\text{F}})_2$, **3**) [31, 32]. Fluoride ion affinity (FIA) is generally used as an indicator of Lewis acidity [33]. The FIA values of **1** (507 kJ/mol), **2** (538 kJ/mol), and **3** (490 kJ/mol) are comparable to those of $\text{Sc}(\text{OTf})_3$ (516 kJ/mol) and higher than that of $\text{B}(\text{C}_6\text{F}_5)_3$ (435 kJ/mol). We expected that the Si-based Lewis acid derivatives could be potential candidates for the Si-based catalysts for the ROP of cyclic esters. Here we report the ROP of cyclic esters and cyclic carbonates by using bis(perhalocatecholato)silane derivatives as Si-based catalysts (Scheme 1).

2. Results and Discussion

2.1. ROP of ϵ -CL. In this work, acetonitrile or diethyl ether adducts of bis(perhalocatecholato)silane derivatives [31, 32] were used as catalysts rather than donor-free ones for the ease of preparation and handling. The results of the ROP of ϵ -CL by $\text{Si}(\text{cat}^{\text{Cl}})_2(\text{MeCN})_2$ (**1a**), $\text{Si}(\text{cat}^{\text{Cl}})_2(\text{Et}_2\text{O})_2$ (**1b**), $\text{Si}(\text{cat}^{\text{Br}})_2(\text{MeCN})_2$ (**2a**), and $\text{Si}(\text{cat}^{\text{F}})_2(\text{MeCN})_2$ (**3a**) are summarized in Table 1. As a result, **1a** was found to catalyze the ROP of ϵ -CL in toluene at 100°C to produce PCL with M_n of 12 kg/mol (run 1). To the best of our knowledge, this is the first example of the ROP of cyclic esters using Si-based catalysts. Because the reported Lewis acid-catalyzed ROPs have often been combined with some alcohols as initiators [26–29], the ROP of ϵ -CL using **1a** was examined in the presence of different amounts of benzyl alcohol (BnOH) (runs 1–3). With increasing feed amount of BnOH, the polymer yields decreased, indicating that BnOH was not necessary for the catalyst system of **1a**, but rather hampered the reaction. This is in sharp contrast to that the polymerization of ϵ -CL catalyzed by $\text{MeAl}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2$ [26], $\text{Sc}(\text{OTf})_3$ [27, 28], and $\text{B}(\text{C}_6\text{F}_5)_3$ [29] can be co-initiated with alcohol. We speculate that the addition of BnOH should cause the decomposition of $\text{Si}(\text{cat}^{\text{Cl}})_2$ by protonolysis. The increased **1a** feed amount enhanced polymer yield and did not affect the molecular weight of the resulting polymer (run 4). The diethyl ether adduct **1b** showed similar activity to that of **1a** to give PCL with lower molecular weight (run 5). The activities of **2a** and **3a** were compared with that of **1a** (runs 6 and 7 vs. run 1). In comparison with **1a**, the polymer yield by **2a** was lower despite the higher Lewis acidity of **2** than that of **1** [31, 32]. We speculate that the lower stability of **2** could result in faster deactivation to cause a lower polymer yield. The gel permeation chromatography (GPC) curve obtained with **2a** showed a peak having a shoulder (Figure S11), while that obtained with **1a** showed a unimodal peak (Figure S10), suggesting a multiplicity of active species in the **2a** system possibly due to the partial decomposition of **2a**. The fluoro-derivative **3a** did not produce PCL under the same conditions. When the ϵ -CL polymerization by **1a** was performed at 60°C (run 8), the polymer yield decreased to 35%, while M_n increased to 17 kg/mol compared with those at 100°C (run 1). The attempted polymerization of ϵ -CL at room temperature (r.t.) did not give PCL (run 9). The increase and decrease of the feed monomer to catalyst ratio (runs 10 and 11 vs. run 1) resulted in lower and higher polymer yield, respectively, and the molecular weight of the resulting



SCHEME 1: Ring-opening polymerization of cyclic esters and cyclic carbonates by $\text{Si}(\text{cat}^{\text{Cl}})_2(\text{CH}_3\text{CN})_2$.

PCL was somewhat decreased in run 11. When the initial monomer concentrations were increased from 0.41 to 3.0 mol/L (runs 12, 1, and 13), quantitative polymer yield was achieved, and the M_n of the resulting PCL increased from 8 kg/mol to 15 kg/mol. Thus, bulk polymerization of ϵ -CL using **1a** was examined (runs 14–17). The bulk ROP of ϵ -CL by **1a** was almost completed within 10 minutes to give PCL with M_n of 29 kg/mol (run 15), which demonstrated high catalytic activity of **1a**. The increased feed monomer to catalyst ratio from 30:1 to 100:1 increased the molecular weight of the resulting polymer (run 15 and 16), while a further increase to 300:1 did not increase the molecular weight (run 17). Perchlorocatechol ($\text{cat}^{\text{Cl}}\text{H}_2$) did not polymerize ϵ -CL under the same conditions, suggesting that the active site in this polymerization catalyst should be the Si-center of **1a**.

The PCL with rather low molecular weight obtained with **1b**-BnOH in run 5 was analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Figure 1). The spectrum of the PCL exhibited a series of repeating peaks separated by the molecular weight of ϵ -CL, which were in good agreement with the formation of cyclic PCLs. This result also suggests that BnOH was not acting as an initiator in this system despite the presence of BnOH in run 5. The MALDI-TOF MS spectrum of the PCL with relatively low molecular weight obtained with **1a** without BnOH (run 12) is shown in Figure S5. The spectrum also exhibited a series of repeating peaks separated by the molecular weight of ϵ -CL. The peaks around $m/z = 1400\text{--}1900$ are in good agreement with cyclic polymers (Figure S5(b)). On the other hand, the peaks of H_2O -terminated species were also observed in the higher m/z region (Figure S5(c)). The MALDI-TOF MS spectrum of the PCL obtained by bulk polymerization with **1a** in run 16 showed the peaks for H_2O -terminated linear PCLs with comparable intensity to those for cyclic PCLs (Figure S6). Thus, the polymerization under lower concentration enhanced the selectivity for cyclic polymers as expected.

The ^1H nuclear magnetic resonance (NMR) spectrum of the PCL (run 1, Figure S1) showed the signals of the methylene protons next to the terminal OH group at 3.65 ppm (*e*) as well as those of the methylene signals in repeating units at 4.0 ppm (*e*). The molecular weights of PCLs determined by GPC (polystyrene standards, THF)

TABLE 1: Polymerization of ϵ -CL by silicon-based Lewis acids.

Run	Cat.	$[M]_0 : [BnOH]_0 : [cat]$	Solvent	$[M]_0$ (mol/L)	Temp. ($^{\circ}C$)	Time (h)	Yield (%)	M_n^a (kg/mol)	\bar{D}^a
1	1a	100:0:1	Toluene	0.82	100	24	59	12	1.5
2	1a	100:1:1	Toluene	0.82	100	24	21	12	1.4
3	1a	100:2:1	Toluene	0.82	100	24	<1	—	—
4	1a	100:1:2	Toluene	0.82	100	24	84	12	1.5
5	1b	100:1:2	Toluene	0.82	100	24	67	6	1.8
6	2a	100:0:1	Toluene	0.82	100	24	46	6	2.0
7	3a	100:0:1	Toluene	0.82	100	24	<1	—	—
8	1a	100:0:1	Toluene	0.82	60	24	35	17	1.5
9	1a	100:0:1	Toluene	0.82	r.t.	24	<1	—	—
10	1a	200:0:1	Toluene	0.82	100	24	19	11	1.6
11	1a	50:0:1	Toluene	0.82	100	24	64	7	1.9
12	1a	100:0:1	Toluene	0.41	100	24	34	8	1.7
13	1a	100:0:1	Toluene	3.0	100	24	>99	15	2.7
14	1a	100:0:1	Bulk	—	100	1	>99	30	1.6
15	1a	100:0:1	Bulk	—	100	1/6	98	29	1.7
16	1a	30:0:1	Bulk	—	100	1/4	97	16	1.6
17	1a	300:0:1	Bulk	—	100	1/6	89	32	1.8
18	cat ^{Cl} H ₂	100:0:1	Bulk	—	100	1	<1	—	—

^aDetermined by GPC analysis calibrated with standard polystyrenes in THF.

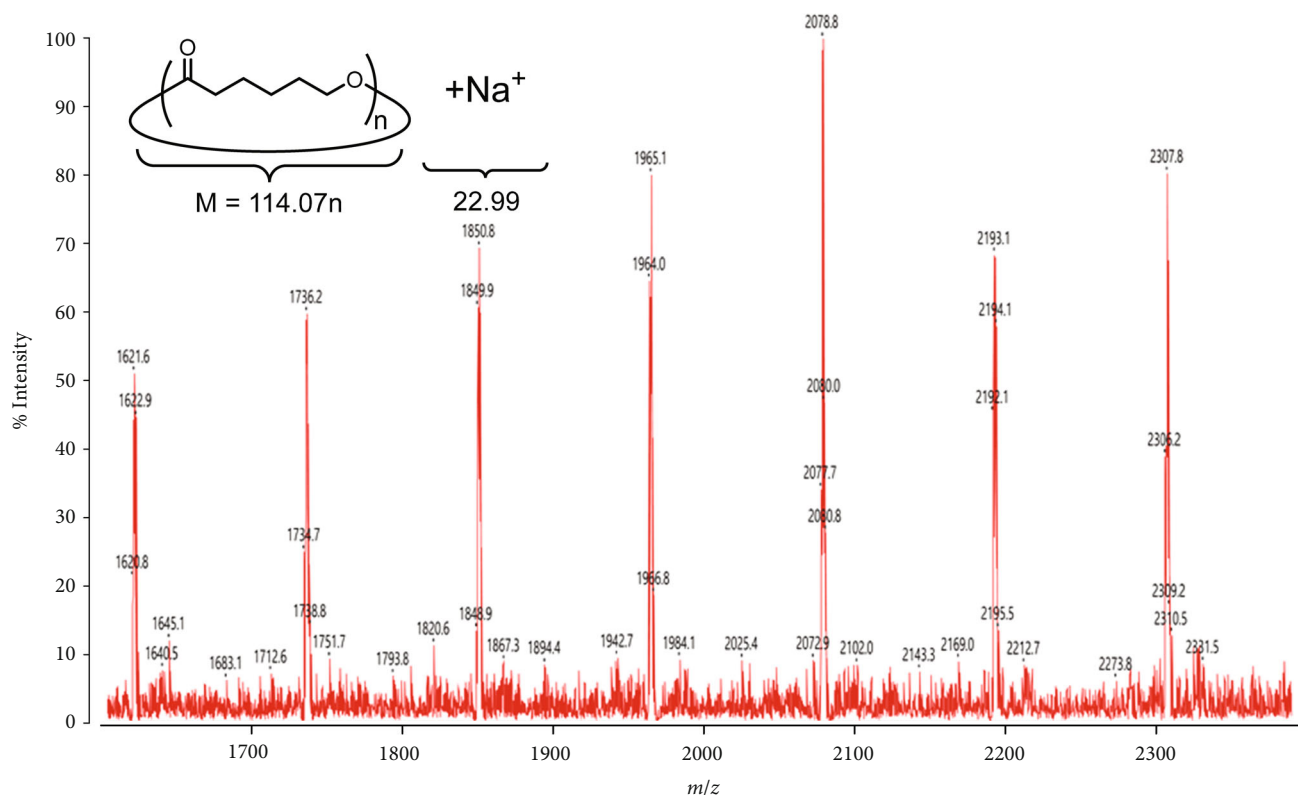


FIGURE 1: MALDI-TOF MS spectrum of the PCL obtained with **1b** (run 5).

TABLE 2: Polymerization of cyclic monomers by **1a**.

Run	Monomer	Time (h)	Yield (%)	M_n^a (kg/mol)	\bar{D}^a
19	δ -VL	1	>99	25	1.4
20		1/6	93	20	1.7
21 ^b		24	12	6	1.4
22 ^c		24	42	12	1.4
23	β -PL	1	24	1.8	1.5
24	β -BL	1	<1	—	—
25	ϵ -DL	1	<1	—	—
26	GL	1	<1	—	—
27	LLA	1	<1	—	—
28	TMC	1/6	99	21	1.6
29 ^d		24	26	7	2.3
30 ^e	DTC	1	22	7	2.0
31 ^f	PO	1	<1	—	—

Conditions: bulk polymerization, $[M]_0 : [\text{cat.}] = 100 : 1$, temp. = 100°C.

^aEstimated by GPC analysis calibrated with standard polystyrenes in THF.

^bSolution polymerization in toluene at $[M]_0 = 0.62$ mol/L.

^cSolution polymerization in toluene at $[M]_0 = 0.82$ mol/L.

^dSolution polymerization in toluene at $[M]_0 = 0.41$ mol/L.

^eTemp. = 120°C.

^fTemp. = 20°C.

were reported to be close to those determined by NMR [34]. From the M_n value in run 1 (12 kg/mol) determined by GPC analysis, the intensity ratio of internal and terminal methylene protons of 105:1 can be expected. However, the observed intensity ratio from the spectrum is approximately 492:1, indicating a much smaller amount of the terminal group than that expected from the molecular weight. This also supports the predominant formation of cyclic polymers. Although the reaction mechanism is not clear yet, the speculated mechanism for the formation of cyclic polymers is shown in Scheme S1.

2.2. ROP of Other Monomers. To elucidate the scope of applicable monomers, **1a** was used for the ROP of various cyclic monomers, δ -valerolactone (δ -VL), β -propiolactone (β -PL), β -butyrolactone (β -BL), ϵ -decalactone (ϵ -DL), glycolide (GL), L-lactide (LLA), trimethylene carbonate (TMC), 2,2-dimethyltrimethylene carbonate (DTC), and propylene oxide (PO) (Table 2). Among these monomers, β -BL (run 24), ϵ -DL (run 25), GL (run 26), LLA (run 27), and PO (run 31) did not give polymers by **1a** under the

TABLE 3: Glass-transition temperatures of the polymers.

Run	Monomer	Catalyst	M_n^a (kg/mol)	\bar{D}^a	T_g^b (°C)
12	ϵ -CL	1a	8	1.7	-46.2
32		Sn(Oct) ₂ ^c	30	1.9	-60.8
21	δ -VL	1a	6	1.4	-34.7
33		Sn(Oct) ₂ ^c	9	1.4	-45.9
23	β -PL	1a	1.8	1.5	-33.9
34		Al(O ^{<i>i</i>} Pr) ₃	4.0	1.3	-20.5
29	TMC	1a	7	2.3	-10.5
35		TBD ^c	17	2.0	-20.4

Conditions: bulk, $[M]_0 : [\text{cat.}] = 100 : 1$, temp. = 100°C.

^aDetermined by GPC analysis calibrated with standard polystyrenes in THF.

^bDetermined by DSC in the second heating scan.

^cInit. = BnOH, $[M]_0 : [\text{Init.}] : [\text{cat.}] = 100 : 1 : 0.25$, $[M]_0 = 2.0$ mol/L.

attempted conditions. Since the silicon center of **1a** is crowded, the substituents on the monomers may hinder their polymerization due to steric hindrance. The small dipole moment of GL could lead to weak interactions with the Lewis acid.

The ROP of δ -VL by **1a** (runs 19–22) proceeded similarly to those of ϵ -CL. Bulk polymerization of δ -VL by **1a** rapidly proceeded to afford poly(δ -VL) with M_n of 20–25 kg/mol, while solution polymerization gave those with lower M_n . The ¹H NMR and MALDI-TOF MS spectra of the resulting poly(δ -VL) (Figures S2 and S7, respectively) indicated their predominant cyclic structure as observed in the case of PCL. The polymerization of β -PL by **1a** gave low molecular weight poly(β -PL) in low yield (run 23). The electrospray ionization mass spectrometry (ESI MS) (Figure S8) and ¹H NMR spectrum (Figure S3) of the obtained poly(β -PL) suggested multiple peaks indicating its complicated chain ends. Bulk polymerization of TMC by **1a** proceeded to produce poly(TMC) with M_n of 21 kg/mol in a quantitative yield within 10 minutes (run 28). The solution polymerization of TMC by **1a** produced poly(TMC) with lower molecular weight (run 29). The bulk polymerization of TMC by **1a** was accompanied by decarboxylation to form some ether linkage (ca. 1.5 mol% in run 28) as indicated by the ¹H NMR and ESI MS analysis of the produced poly(TMC) (Figures S4 and S9, respectively). In comparison with bulk polymerization of TMC, the decarboxylation was hampered in solution polymerization (ca. 0.1 mol% in run 29), although the polymerization rate was much lower. The polymerization of DTC by **1a** (run 30) was slower than that of TMC (run 28) possibly due to steric hindrance and also accompanied by decarboxylation (ether bond content 1.0 mol%).

In general, glass-transition temperatures (T_g s) of linear polymers tend to decrease with decreasing their molecular weights due to the increasing effect of their end groups. In contrast, cyclic polymers generally show little dependence of T_g s on their molecular weights due to their constrained topology and the absence of chain ends, resulting in higher T_g of cyclic polymers than those of linear polymers with relatively low molecular weights [35, 36]. Thus, the T_g values of the polymers synthesized by **1a** were compared with those synthesized by typical catalysts to produce linear polymers

(Table 3). The PCL synthesized by **1a** showed T_g at -46.2°C , which is substantially higher than that of linear PCL (-60.8°C) synthesized by $\text{Sn}(\text{Oct})_2\text{-BnOH}$ [37], supporting its predominant cyclic structure. Similarly, the polymers of δ -VL and TMC produced by **1a** also showed higher T_g than those obtained by $\text{Sn}(\text{Oct})_2\text{-BnOH}$ or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)- BnOH [38, 39]. These results also support the formation of cyclic polymers by **1a**. On the other hand, the poly(β -PL) synthesized by **1a** showed lower T_g than that synthesized with $\text{Al}(\text{O}^i\text{Pr})_3$ [40], suggesting its linear structure.

3. Conclusions

The Si-based Lewis acid, **1a**, was found to exhibit high catalytic activity for the ROP of seven- or six-membered cyclic esters and cyclic carbonates without substituents. **1a** promoted the ROP without an alcoholic initiator and afforded cyclic polymers predominantly. Such Si-based compounds can be promising catalysts for the ROP of cyclic esters and cyclic carbonates due to the high natural abundance and low elemental toxicity of silicon. In comparison with the reported catalyst systems based on other group 14 elements, the present silicon-based catalyst is unique in that cationic polymerization proceeds without proton mediation.

Data Availability

The experimental section and the data used to support the findings of this study are included within the article and the supplementary information file.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This work was supported by the Japan Society for the Promotion of Science KAKENHI (grant no. 21H02002).

Supplementary Materials

Supplementary Materials 1. Experimental section. 2. ^1H NMR spectra of the polymers. Figure S1. ^1H NMR spectrum of poly(ϵ -CL) (run 1). Figure S2. ^1H NMR spectrum of poly(δ -VL) (run 22). Figure S3. ^1H NMR spectrum of poly(β -PL) (run 23). Figure S4. ^1H NMR spectrum of poly(TMC) (run 28). 3. MALDI-TOF MS spectra of the polymers. Figure S5. MALDI-TOF MS spectrum of PCL (run 12). Figure S6. MALDI TOF MS spectrum of PCL (run 16). Figure S7. MALDI-TOF MS spectrum of poly(δ -VL) (run 21). 4. ESI MS spectra of the polymers. Figure S8. ESI MS spectrum of poly(β -PL) (run 23). Figure S9. ESI MS spectrum of poly(TMC) (run 29). 5. GPC curves of the PCL obtained with **1a** (run 12) and **2a** (run 6). Figure S10. GPC curve of the PCL obtained with **1a** (run 12). Figure S11. GPC curve of the PCL obtained with **2a** (run 6). 6. Speculated reaction mechanism. Scheme S1. Speculated reaction mechanism for the polymerization of ϵ -CL catalyzed by $\text{Si}(\text{cat}^{\text{Cl}})_2(\text{CH}_3\text{CN})_2$ (**1a**). 7. References. (*Supplementary Materials*)

References

- [1] S. Penczek, A. Duda, A. Kowalski, J. Libiszowski, K. Majerska, and T. Biela, "On the mechanism of polymerization of cyclic esters induced by tin(II) octoate," *Macromolecular Symposia*, vol. 157, no. 1, pp. 61–70, 2000.
- [2] A. Kowalski, A. Duda, and S. Penczek, "Kinetics and mechanism of cyclic esters polymerization initiated with Tin(II) octoate. 3. Polymerization of L,L-Dilactide," *Macromolecules*, vol. 33, no. 20, pp. 7359–7370, 2000.
- [3] A. Kowalski, J. Libiszowski, T. Biela, M. Cypryk, A. Duda, and S. Penczek, "Kinetics and mechanism of cyclic esters polymerization initiated with tin(II) octoate. Polymerization of ϵ -caprolactone and L,L-lactide co-initiated with primary amines," *Macromolecules*, vol. 38, no. 20, pp. 8170–8176, 2005.
- [4] S. Sosnowski and P. Lewinski, "L-Lactide polymerization catalysed by tin(II) 2-ethyl-hexanoate. A deeper look at chain transfer reactions," *Polymer Chemistry*, vol. 6, no. 35, pp. 6292–6296, 2015.
- [5] H. R. Kricheldorf and S. M. Weidner, "Syntheses of poly lactides by means of tin catalysts," *Polymer Chemistry*, vol. 13, no. 12, pp. 1618–1647, 2022.
- [6] M. C. Tanzi, P. Verderio, M. G. Lampugnani, M. Resnati, E. Dejana, and E. Sturani, "Cytotoxicity of some catalysts commonly used in the synthesis of copolymers for biomedical use," *Journal of Materials Science. Materials in Medicine*, vol. 5, no. 6–7, pp. 393–396, 1994.
- [7] T. Yamada, D.-Y. Jung, R. Sawada, and T. Tsuchiya, "Intracerebral microinjection of stannous 2-ethylhexanoate affects dopamine turnover in cerebral cortex and locomotor activity in rats," *Journal of Biomedical Materials Research Part B Applied Biomaterials*, vol. 87B, no. 2, pp. 381–386, 2008.
- [8] C. S. Hege and S. M. Schiller, "Non-toxic catalysts for ring-opening polymerizations of biodegradable polymers at room temperature for biohybrid materials," *Green Chemistry*, vol. 16, no. 3, pp. 1410–1416, 2014.
- [9] B. J. O'Keefe, M. A. Hillmyer, and W. B. Tolman, "Polymerization of lactide and related cyclic esters by discrete metal complexes," *Journal of the Chemical Society, Dalton Transactions*, no. 15, pp. 2215–2224, 2001.
- [10] N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, and J. L. Hedrick, "Organocatalytic ring-opening polymerization," *Chemical Reviews*, vol. 107, no. 12, pp. 5813–5840, 2007.
- [11] P. Dubois, O. Coulembier, and J.-M. Raquez, *Handbook of Ring-Opening Polymerization*, pp. 227–306, Wiley, Weinheim, 2009.
- [12] A. Arbaouia and C. Redshaw, "Metal catalysts for ϵ -caprolactone polymerisation," *Polymer Chemistry*, vol. 1, no. 6, pp. 801–826, 2010.
- [13] X. Li, C. Chen, and J. Wu, "Lewis pair catalysts in the polymerization of lactide and related cyclic esters," *Molecules*, vol. 23, no. 1, p. 189, 2018.
- [14] D. J. Walsh, M. G. Hyatt, S. A. Miller, and D. Guironnet, "Recent trends in catalytic polymerizations," *ACS Catalysis*, vol. 9, no. 12, pp. 11153–11188, 2019.
- [15] M. L. McGraw and E. Y.-X. Chen, "Lewis pair polymerization: perspective on a ten-year journey," *Macromolecules*, vol. 53, no. 15, pp. 6102–6122, 2020.
- [16] H. Li, R. M. Shakaroun, S. M. Guillaume, and J.-F. Carpentier, "Recent advances in metal-mediated stereoselective ring-opening polymerization of functional cyclic esters towards

- well-defined poly(hydroxy acid)s: from stereoselectivity to sequence-control," *Chemistry – A European Journal*, vol. 26, no. 1, pp. 128–138, 2020.
- [17] X. Dong and J. R. Robinson, "The versatile roles of neutral donor ligands in tuning catalyst performance for the ring-opening polymerization of cyclic esters," *New Journal of Chemistry*, vol. 46, no. 2, pp. 444–453, 2022.
- [18] Y. Liu, L. Song, N. Feng, W. Jiang, Y. Jin, and X. Li, "Recent advances in the synthesis of biodegradable polyesters by sustainable polymerization: lipase-catalyzed polymerization," *RSC Advances*, vol. 10, no. 59, pp. 36230–36240, 2020.
- [19] J. Xu, X. Wang, J. Liu, X. Feng, Y. Gnanou, and N. Hadjichristidis, "Ionic H-bonding organocatalysts for the ring-opening polymerization of cyclic esters and cyclic carbonates," *Progress in Polymer Science*, vol. 125, article 101484, 2022.
- [20] A. Finne, Reema, and A.-C. Albertsson, "Use of germanium initiators in ring-opening polymerization of L-lactide," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 41, no. 19, pp. 3074–3082, 2003.
- [21] A. J. Chmura, C. J. Chuck, M. G. Davidson et al., "A germanium alkoxide supported by a c3-symmetric ligand for the stereoselective synthesis of highly heterotactic polylactide under solvent-free conditions," *Angewandte Chemie, International Edition*, vol. 46, no. 13, pp. 2280–2283, 2007.
- [22] J. Guo, P. Haquette, J. Martin, K. Salim, and D. C. M. Thomas, "Replacing tin in lactide polymerization: design of highly active germanium-based catalysts," *Angewandte Chemie, International Edition*, vol. 52, no. 51, pp. 13584–13587, 2013.
- [23] R. D. Rittinghaus, J. Tremmel, A. Růžička et al., "Undiscovered potential: Ge catalysts for lactide polymerization," *Chemistry – A European Journal*, vol. 26, no. 1, pp. 212–221, 2020.
- [24] L. Wang, S.-C. Roşca, V. Poirier et al., "Stable divalent germanium, tin and lead amino(ether)-phenolate monomeric complexes: structural features, inclusion heterobimetallic complexes, and ROP catalysis," *Dalton Transactions*, vol. 43, no. 11, pp. 4268–4286, 2014.
- [25] L. Wang, S. Fadlallah, C. Bellini et al., "Structurally characterized lead(II) alkoxides as potent ring-opening polymerization catalysts," *Organometallics*, vol. 34, no. 7, pp. 1321–1327, 2015.
- [26] M. Akatsuka, T. Aida, and S. Inoue, "Alcohol/methylaluminum diphenolate systems as novel, versatile initiators for synthesis of narrow molecular weight distribution polyester and polycarbonate," *Macromolecules*, vol. 28, no. 4, pp. 1320–1322, 1995.
- [27] N. Nomura, A. Taira, T. Tomioka, and M. Okada, "A catalytic approach for cationic living polymerization: Sc(OTf)₃-catalyzed ring-opening polymerization of lactones," *Macromolecules*, vol. 33, no. 5, pp. 1497–1499, 2000.
- [28] M. Möller, R. Känge, and J. L. Hedrick, "Sn(OTf)₂ and Sc(OTf)₃: efficient and versatile catalysts for the controlled polymerization of lactones," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 38, no. 11, pp. 2067–2074, 2000.
- [29] J. Xu, J. Song, S. Pispas, and G. Zhang, "Metal-free controlled ring-opening polymerization of ε-caprolactone in bulk using tris(pentafluorophenyl)borane as a catalyst," *Polymer Chemistry*, vol. 5, no. 16, pp. 4726–4733, 2014.
- [30] Y. Nakayama, S. Kosaka, K. Yamaguchi, G. Yamazaki, R. Tanaka, and T. Shiono, "Controlled ring-opening polymerization of L-lactide and ε-caprolactone catalyzed by aluminum-based Lewis pairs or Lewis acid alone," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 55, no. 2, pp. 297–303, 2017.
- [31] R. Maskey, M. Schädler, C. Legler, and L. Greb, "Bis(perchlorocatecholato)silane—a neutral silicon Lewis super acid," *Angewandte Chemie, International Edition*, vol. 57, no. 6, pp. 1717–1720, 2018.
- [32] D. Hartmann, M. Schädler, and L. Greb, "Bis(catecholato)silanes: assessing, rationalizing and increasing silicon's Lewis superacidity," *Chemical Science*, vol. 10, no. 31, pp. 7379–7388, 2019.
- [33] L. O. Müller, D. Himmel, J. Stauffer et al., "Simple access to the non-oxidizing Lewis superacid PhF→Al(ORF)₃ (RF=C(CF₃)₃)," *Angewandte Chemie, International Edition*, vol. 47, no. 40, pp. 7659–7663, 2008.
- [34] Y. Shibasaki, H. Sanada, M. Yokoi, F. Sanda, and T. Endo, "Activated monomer cationic polymerization of lactones and the application to well-defined block copolymer synthesis with seven-membered cyclic carbonate," *Macromolecules*, vol. 33, no. 12, pp. 4316–4320, 2000.
- [35] L. Gao, J. Oh, Y. Tu, T. Chang, and C. Y. Li, "Glass transition temperature of cyclic polystyrene and the linear counterpart contamination effect," *Polymer*, vol. 170, pp. 198–203, 2019.
- [36] J. N. Hoskins and S. M. Grayson, "Cyclic polyesters: synthetic approaches and potential applications," *Polymer Chemistry*, vol. 2, no. 2, pp. 289–299, 2011.
- [37] A. Kowalski, A. Duda, and S. Penczek, "Mechanism of cyclic ester polymerization initiated with tin(II) octoate. 2.† Macromolecules fitted with tin(II) alkoxide species observed directly in MALDI–TOF spectra," *Macromolecules*, vol. 33, no. 3, pp. 689–695, 2000.
- [38] M. Bouyahyi, M. P. F. Pepels, A. Heise, and R. Duchateau, "ω-Pentadecalactone polymerization and ω-pentadecalactone/ε-caprolactone copolymerization reactions using organic catalysts," *Macromolecules*, vol. 45, no. 8, pp. 3356–3366, 2012.
- [39] F. Nederberg, B. G. G. Lohmeijer, F. Leibfarth et al., "Organocatalytic ring opening polymerization of trimethylene carbonate," *Biomacromolecules*, vol. 8, no. 1, pp. 153–160, 2007.
- [40] H. R. Kricheldorf, M. Berl, and N. Scharnagl, "Poly(lactones). 9. Polymerization mechanism of metal alkoxide initiated polymerizations of lactide and various lactones," *Macromolecules*, vol. 21, no. 2, pp. 286–293, 1988.