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Catalytic Ring-Opening Polymerization of Renewable Macrolactones to High Molecular Weight Polyethylene-like Polymers

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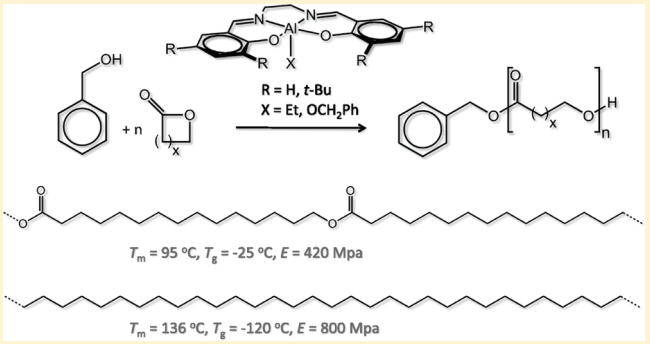
ABSTRACT: The catalytic ring-opening polymerization of macrolactones to polyethylene-like polyesters was investigated using aluminum−salen complexes as the initiators. Contrary to the common understanding that high molecular weights in these reactions can only be achieved by enzymatic ring-opening polymerization due to the absence of ring tension in macrolactones, the aluminum−salen complexes produces poly(pentadecalactone)s with number-average molecular weights (M_n) of over 150 000 g/mol. Moreover, the same catalyst is also active in catalyzing the ROP of small and medium size lactones, which makes these aluminum−salen complexes highly potential catalysts for the cROP of lactones irrespective of ring size. These results show that it is possible to polymerize macrolactones to high molecular weight polyethylene-like polymers using cheap and robust metal-based catalysts. Even the so-called medium-sized lactones (ring size: 9−12) can be polymerized with a reasonably good activity to high molecular weight products, which is truly exceptional. These results complement the common theory of ring-tension-driven cROP.



INTRODUCTION

Polyolefins account for over 65% of the total world demand of plastic materials, a staggering 111 million tons in 2009.[1] The polyolefin industry is heavily reliant on petrochemistry for its raw materials. Moreover, since polyolefins are nondegradable, they cause major environmental problems in places where waste collection is impossible, for example in the marine environment.[2] There are thus strong political, environmental, and economical drivers to develop green, where possible degradable, alternatives for polyolefins. Two approaches can be distinguished for the replacement of polymers from petrochemical resources: (1) Developing an alternative route to the common monomers based on biofeedstock. In the field of polyolefins conversion of biomass (via ethanol) to ethylene has already led to the development of biopolyethylene.[3] (2) Finding an alternative material, which matches the properties and price of existing polymers but is produced from renewable building blocks. The major advantage of this approach is that also other properties can be engineered into the targeted materials. In the case of polyethylene, that could be degradability, which would address one of the long-term key issues as discussed above.

In 2010, Mecking et al. reported an elegant route to the synthesis of polyethylene-like polyesters via methoxy carbonylation of unsaturated fatty acids followed by polycondensation.[4] The difficulty of obtaining high molecular weight products by polycondensation remains, however, a big challenge. Alternatively, ring-opening polymerization (ROP) of large fatty acid-based lactones such as pentadecalactone (PDL) can afford polyethylene-like materials of high molecular weight, crucial for polyethylene-like properties.[5] For example, poly(pentadecalactone) (PPDL), which can be produced via enzymatic ring-opening polymerization (eROP), is a semicrystalline polymer with a T_m around 100 °C similar to that of low-density polyethylene (LDPE) and a T_g well below room temperature (−27 °C). The rapid crystallization from the melt, the high crystallinity (>60%), the crystal structure, and the chemical inertness of PPDL also reveal large similarities with polyethylene.[6]

Metal-catalyzed ROP (cROP) of lactones is a particularly successful method to produce polymers of high molecular weight, low polydispersity, and with controlled microstructure.[7] Seminal work on the cROP of e.g. lactide and ε-caprolactone has given significant mechanistic insight into the chemistry as well as the huge potential of cROP.[8] It is commonly agreed that the driving force behind the cROP of lactones is the release of ring strain in the transition from the cyclic ester to the polyester chain. Consequently, as the ring strain decreases with increasing lactone

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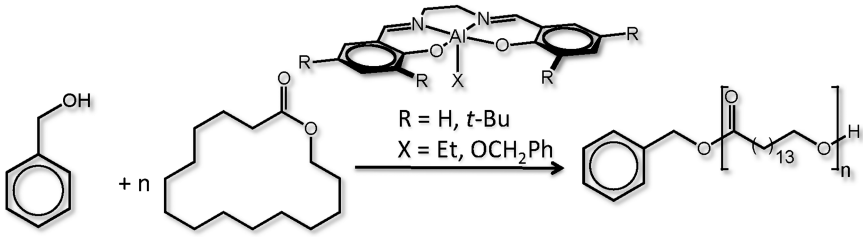
Scheme 1. Aluminum−Salen (R = H, X = Et (1), OCH_2Ph (2); R = *t*-Bu, X = Et (3), OCH_2Ph (4)) Catalyzed Ring-Opening Polymerization of Pentadecalactone (PDL)



size so does the reactivity in cROP.[9] Not surprisingly, only a few examples of cROP of macrolactones have been reported, generally producing only low yields and low molecular weight products.[5,9,10] The situation is inversed for the lipase-catalyzed ROP (eROP).[11] Lipases like *Candida Antarctica* Lipase B (CALB) are highly active in the eROP of lactones,[12] show exceptionally high polymerization rates for macrolactones, and afford high molecular weight products (M_n up to 150 000 g/mol).[13] The drawback of enzymes is that they are expensive, allow little control over the polymerization, and cannot be used at high temperatures (melt polymerization). This severely limits technical developments of the commercial production of theses polyethylene-like materials, and it would therefore be highly desirable to be able to use nonenzymatic catalysts to polymerize these renewable macrolactones to high molecular weight polymers.

Here we report the highly efficient metal-mediated ROP of macrolactones. Moreover, we provide evidence that the catalyst applied is equally efficient in the polymerization of ε-caprolactone and might thus be the first universal catalyst for the polymerization of lactones of various ring sizes.

EXPERIMENTAL SECTION

Materials. Pentadecalactone, caprolactone, and benzyl alcohol were purchased from Aldrich and were distilled before use. Toluene and trichlorobenzene were purchased from Biosolve and dried over an alumina column. The aluminum−salen complexes **1** and **2** were synthesized following a literature procedure.[14] The corresponding benzyloxy complexes **3** and **4** were obtained in quantitative yield by treating **1** and **2** with stoichiometric amounts of benzyl alcohol in toluene at room temperature followed by removal of the solvent.

Methods. ^1H and ^{13}C NMR spectroscopy was performed on a Varian Mercury 400 MHz NMR in $CDCl_3$. Data were acquired using VNMR software. Chemical shifts are reported in ppm relative to tetramethylsilane (^1H NMR). High-temperature size exclusion chromatography (SEC) was performed on a Polymer Laboratories PLXT-20 Rapid GPC Polymer Analysis System (including pump, refractive index detector, and viscosity detector) at 160 °C with three PLgel Olexis (300 × 7.5 mm, Polymer Laboratories) columns in series. 1,2,4-Trichlorobenzene was used as eluent at a flow rate of 1 mL/min. The molecular weights were calculated with respect to polyethylene standards (Polymer Laboratories). A Polymer Laboratories PL XT-220 robotic sample handling system was used as autosampler.

Ring-Opening Polymerization. Catalysts **1** and **2** were applied with an equimolar amount benzyl alcohol, whereas **3** and **4** were used without additional benzyl alcohol. Lactone (4.0 mmol) and the aluminum−salen complex (and benzyl alcohol in the case of **1** and **2**) were added to a vial in a nitrogen-filled MBraum MB-150 GI glovebox. The monomer to initiator ratio was varied from 50 to 500. The vial was then closed and stirred at 100 °C for a set time. For the reactions in solution, toluene (2 mL) was added to the polymerizations prior to heating. After the polymerization the mixture was cooled in an ice bath, and in the case of a solution polymerization, the solvent was evaporated. The products were analyzed without further precipitation.

Table 1. cROP of PDL Catalyzed by 1 in the Presence of an Equimolar Amount of Benzyl Alcohol Using Various Monomer (M) to Initiator (I) ratios ([1] ≈ 15 mM, *T* = 100 °C, *t* = 1 h)

entry	solvent	$[M]_0/[I]_0$	$M_{n,calc}$ [g/mol][a]	$M_{n,GPC}$ [g/mol]	PDI	conversion [%][b]
1		44	11 000	24 000	2.8	>99
2		110	26 000	41 000	2.6	>99
3		212	38 000	99 000	2.1	74
4		424	71 000	118 000	2.5	70
5	toluene	109	22 000	33 000	2.5	>99
6	toluene	213	49 000	100 000	2.4	95
7	toluene	427	58 000	155 000	2.0	57

[a] $[M]_0/[I]_0$ × conversion × *M* (monomer). [b] Determined by ^1H NMR in $CDCl_3$ by comparison of the methylene peak adjacent to the ester group of the monomer (4.14 ppm) and the polymer (4.04 ppm).

Transesterification Experiment. An NMR tube was charged under a nitrogen atmosphere with a [D8]toluene solution (1 mL), ethyl acetate, methyl propionate, and 0.5% of **3** or **1** + benzyl alcohol (1:1). The solution was heated at 100 °C for 1 h, and the ^1H NMR was measured at regular time intervals.

RESULTS AND DISCUSSION

The aluminum−salen complexes have previously been reported in ring-opening polymerizations.[8p−u] The efficiency of **1** (Scheme 1, R = H, X = Et) as catalyst in the cROP of PDL was initially tested in the bulk polymerization of PDL in the presence of benzyl alcohol as an initiator at a 1:1 ratio at 100 °C (just above the melting point of the PDL/PPDL mixture) with increasing monomer to initiator ratios (50−500). A constant reaction time of 4 h was applied after which the reaction was stopped and the polymer analyzed. The high efficiency of the catalyst in these polymerizations was immediately evident from the fast increase in viscosity of the reaction medium and within 20 min agitation stopped completely. Even though a rapid viscosity increase with conversion is known for the eROP of PDL, for a metal catalyst such fast polymerization kinetics for the cROP of macrolactones is remarkable. For the lower monomer to **1** ratios, ^1H NMR spectroscopy showed a near-quantitative monomer conversion within the applied reaction time (Table 1, entries 1 and 2). When the monomer-to-initiator ratio was increased, the monomer conversion leveled off around 74% (Table 1, entries 3 and 4),

possibly due to diffusion limitations caused by the high viscosity of the reaction mixture and concomitant crystallization of the polymer. In order to reach higher conversions, a series of polymerizations were carried out in toluene solution (Table 1, entries 5−7).

The molecular weights of the polymers were analyzed by high-temperature size exclusion chromatography (SEC) in trichlorobenzene as the high crystallinity and (polyethylene-like) hydrophobicity of PPDL dramatically reduced its solubility in common organic solvents. An increasing monomer-to-initiator ratio clearly results in an increase of molecular weight. The number-average molecular weights obtained during bulk polymerizations range from 24 000 g/mol for the monomer-to-initiator ratio of 44 to 118 000 g/mol for the monomer-to-initiator ratio of 424, respectively. Solution polymerizations afford even higher molecular weights compared to the bulk reactions. At a monomer-to-initiator ratio of 427 (entry 7, Table 1) an M_n of 155 000 g/mol was obtained. Noticeable is that the measured molecular weights are higher than the calculated values. Since PPDL and polyethylene, used as calibration standards, are expected to be rather similar, the observed deviation cannot be explained by the difference between PPDL and PE alone, and most probably poor solubility of the catalyst, limiting the number of active sites, plays a role as well. The molecular weights of PPDL obtained with **1** are unprecedented for cROP of macrolactones and match the highest molecular weights reported for similar polyesters obtained by enzymatic polymerization.

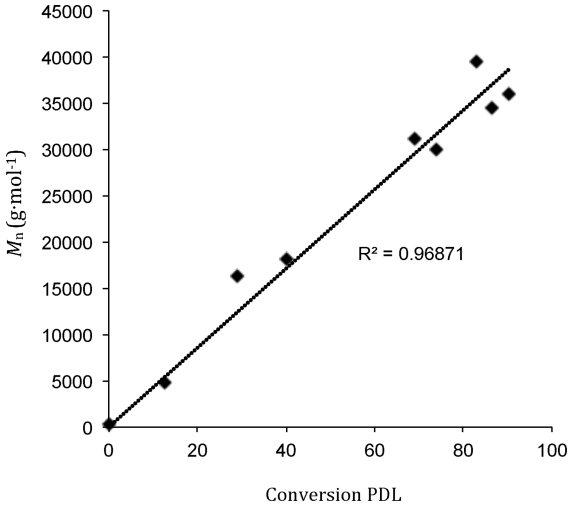


Figure 1. M_n versus conversion plot for PPDL prepared by bulk polymerization using **1** and benzyl alcohol as initiator at a monomer-to-initiator ratio of 100. M_n obtained from HT-SEC in trichlorobenzene.

In order to gain further insight into the polymerization characteristics, samples were withdrawn from a polymerization with a monomer to initiator ration of 100 and analyzed by HT-SEC. Noticeable is that the molecular weight increases linearly with an increasing conversion (Figure 1). This linear correlation between M_n and conversion is characteristic for a living-like catalytic behavior. However, the polydispersity indices (PDI) of the obtained PPDLs are ranging from 2.1 to 2.8 (Table 1), which either suggests slow initiation or concurrent rapid chain transfer via transesterification. The latter is also commonly observed in the otherwise living cROP of lactides and lactones by tin or aluminum catalysts at high conversions.[15] MALDI-ToF-MS measurements on low molecular weight PPDL indeed shows the presence of low molecular weight cyclics as a result of intramolecular transesterification next to the linear $PhCH_2O-[C(=O)(CH_2)_{14}O]-H$ chains (Figure 2). That the salen complexes are efficient transesterification catalysts was further confirmed in a control experiment by mixing equimolar amounts of ethyl acetate and methyl propionate in [D8]-toluene in the presence of a catalytic amount (0.5%) of **3** (or **1** + 1 equiv of benzyl alcohol). Within an hour at 100 °C the equilibrium between methyl acetate, ethyl acetate, methyl propionate, and ethyl propionate was established. Transesterification reactions are thus present under the applied polymerization conditions and most likely responsible for the broad PDI. However, due to the high reaction rate, it is unclear whether transesterification happens during every stage of the polymerization or only at the end of the reaction, i.e., at high monomer conversion when the chain mobility is reduced.

The influence of the ring size of the lactone was also studied using complex **1** with benzyl alcohol as initiator and toluene as solvent (Figure 3 and Table 2). Complex **1** hardly shows any catalytic activity toward β-butyrolactone, and as expected based

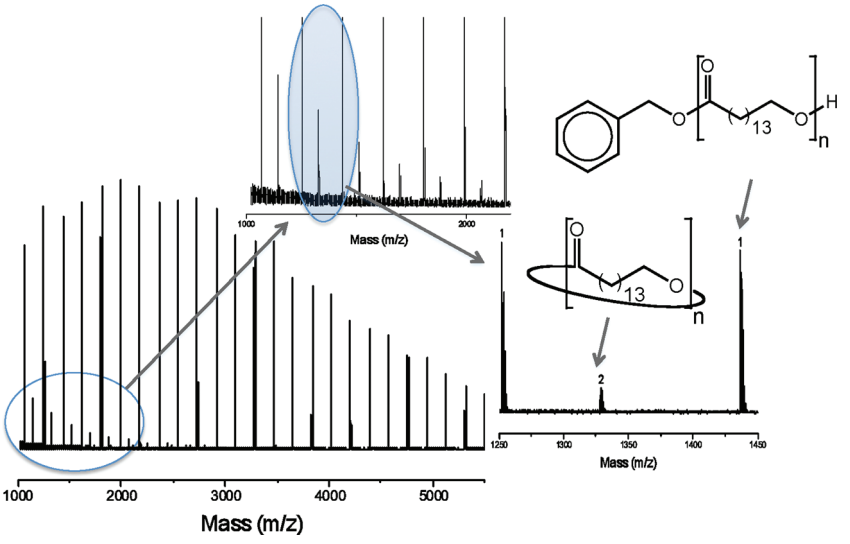


Figure 2. MALDI-ToF-MS spectrum of low molecular weight polypentadecalactone obtained by cROP of **1** and benzyl alcohol (1:1 ratio). See footnote of Table 3 for conditions.

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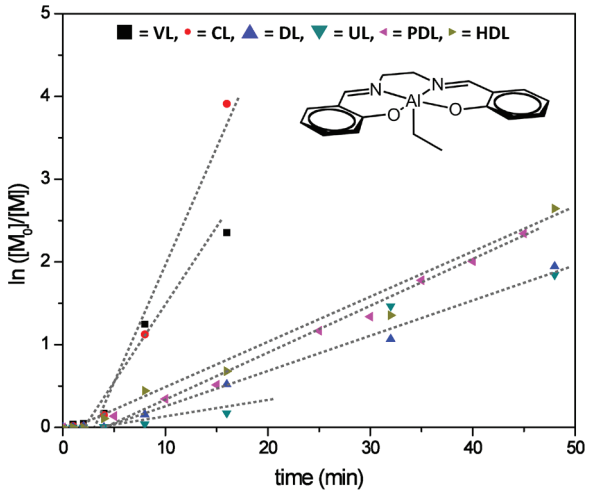

Figure 3. cROP of lactone of different ring-size catalyzed by **1** in the presence of an equimolar amount of benzyl alcohol. VL = δ-valerolactone, CL = ε-caprolactone, DL = decalactone, UL = undecalactone, PDL = pentadecalactone, and HDL = hexadecalactone. See Table 2 for conditions.

Table 2. cROP of Lactone of Different Ring-Size Catalyzed by 1 in the Presence of an Equimolar Amount of Benzyl Alcohol in Toluene[a]

monomer	ring size	k_{app} [min^{-1}]	$M_{n,calc}$ [g/mol][b]	$M_{n,GPC}$ [g/mol]	PDI	conversion [%][c]
β-BL	4		8 600	8 50	2.0	2.5
γ-BL[d]	5		8 600		2.1	
VL	6	0.16 ± 0.01	10 000	10 000	2.3	96
CL	7	0.25 ± 0.03	11 400	13 000	1.7	>99
DL	11	$0.03 \pm 4 \times 10^{-3}$	17 000	24 000	1.6	84
UL	12	$0.01 \pm 2 \times 10^{-3}$	18 400	27 000	1.6	91
PDL	16	$0.03 \pm 2 \times 10^{-3}$	25 600	36 000	1.6	90
HDL	17	$0.04 \pm 5 \times 10^{-3}$		40 000	1.8	98

[a] BL = butyrolactone, VL = δ-valerolactone, CL = ε-caprolactone, DL = decalactone, UL = undecalactone, PDL = pentadecalactone, and HDL = hexadecalactone. [**1**] $\approx$ 15 mM, [lactone]$_0 \approx$ 1.5 M, T = 100 °C, t = 1 h. [b] [Monomer]/[catalyst] × conversion × M (monomer). [c] Determined by ^{1}H NMR in $CDCl_3$. [d] t = 96 h.

on the relative thermodynamic stability of the 5-membered ring,[16] no polymerization of γ-butyrolactone was observed even after 96 h. The small lactones, δ-valerolactone and ε-caprolactone, show higher polymerization rates compared to the larger lactones, which can be explained by either the higher ring strain or by the energetically high cisoid conformation in the 6- and 7-membered lactones. All of these small lactones were consumed within 15 min. Compared to other ROP catalysts for strained ring lactones such as lactide and ε-caprolactone, **1** is only a moderately effective catalysts for these smaller ring-sized lactones.[8,17] Decalactone and undecalactone, the middle-sized lactones, show the lowest polymerization rate of all polymerizable lactones. The trigonal carbonyl group in middle-sized lactones reduces their transannular strain. Consequently, these lactones show a strong resistance to convert the trigonal C═O into a tetragonal C−O, necessary during ring-opening, which increases the activation energy.[18] Nevertheless, the polymerization rate is still

Table 3. Results of the cROP of PDL Using Different Complexes ([Complex] = 0.16 M, [Lactone]$_0$ = 1.5 M, T = 100 °C, t = 4 h)

complex	k_{app} [min^{-1}]	$M_{n,calc}$ [g/mol]	$M_{n,GPC}$ [g/mol]	PDI	conversion [%]
1[d]	$0.2 \pm 2 \times 10^{-2}$	2700	8100	1.7	98
2[d]	$0.01 \pm 2 \times 10^{-3}$	2300	8400	1.5	93
3[e,f]	$0.14 \pm 6 \times 10^{-3}$	2700	17000	1.6	99
4[f]	$0.09 \pm 2 \times 10^{-4}$	2300	10000	1.6	87

[a] [Monomer]/[catalyst] × conversion × M (monomer). [b] Measured in TCB at 160 °C. [c] Determined by ^{1}H NMR in $CDCl_3$ by comparison of the methylene peak adjacent to the ester group of the monomer and the polymer. [d] [BnOH]$_0$ = 0.16 M. [e] Poor solubility of **3**. [f] [BnOH]$_0$ = 0 M.

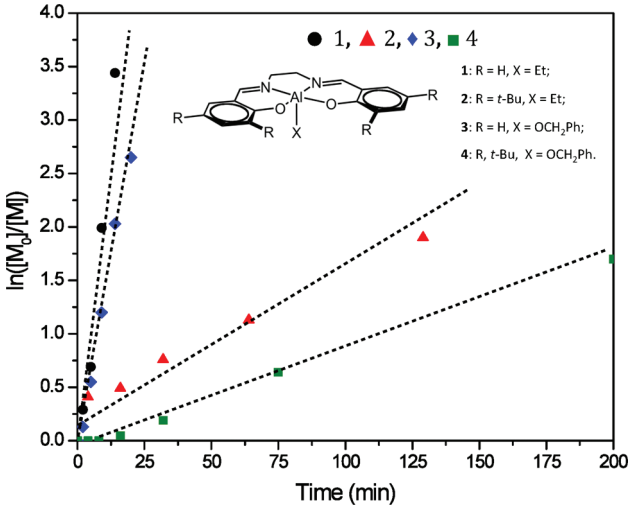

Figure 4. cROP of PDL catalyzed by **1** and **2** in the presence of an equimolar amount of benzyl alcohol or **3** and **4** without benzyl alcohol. See footnote in Table 3 for conditions.

respectable for these middle-sized lactones and considerably higher than for the enzymatic ROP or the rate of alkaline hydrolysis of these monomers.[11,18b] A similar trend was observed in a study by Duda[9a] on the cROP of various size lactones with zinc octoate, but the difference in the relative rates of polymerization are much lower for the aluminum salen complex. For example, HDL polymerizes only six times slower than CL compared to 330 time for the zinc catalyst.

The effect of catalyst structure on the activity of the cROP of PDL was studied by varying the X group at the aluminum and the steric bulk of the ancillary ligand (Table 3 and Figure 4). Whereas the polymerizations using **1** or **3** resulted in full conversion of the PDL within 1 h, for the sterically more hindered complexes **2** and **4**, the highest conversion reached was 93% for **2** and 87% using **4** (Table 2).

The relation between time and the logarithm of the relative concentration is linear for all complexes, implying a constant consumption of monomer and therefore first-order kinetics (Table 3). To investigate the rate of formation of the active species, complexes **1** and **2** were treated with benzyl alcohol to form the corresponding benzyloxy complexes **3** and **4**, respectively, the assumed active species. The difference between using complex **1** plus benzyl alcohol or **3** is negligibly small, indicating

that the active species is formed instantaneously. This excludes the aforementioned possibility that a slow activation process contributes to the broad PDI. It has to be mentioned that for **2** and **4** there is a clear difference in the initial rate. A possible explanation might be that the structure of **4** is actually different, for example, an alkoxide bridged dimer, compared to that of the actual catalytically active species and first has to rearrange.[19]

To exclude any possible artifacts, besides the aluminum salen catalysts **1**−**4**, we also examined the catalytic behavior of previously reported yttrium isopropoxide.[10b] In agreement with the earlier reports, relatively low molecular weight products (<25 000 g/mol) were obtained with this catalyst. Hence, the crucial question is why the salen aluminum system is such a suitable catalyst for the ring-opening polymerization of macrolactones to high molecular weight polymers whereas the common catalysts are not? At this point we can only speculate and more research will be necessary to unravel this issue. Nevertheless, these results show that it is possible to polymerize macrolactones to unprecedentedly high molecular weight (M_n > 150 000 g/mol) polyethylene-like polymers using cheap and robust metal-based catalysts. Even the so-called medium-sized lactones (ring size: 9−12) can be polymerized with a reasonably good activity to high molecular weight products, which is truly exceptional. These results complement the common theory of ring-tension driven cROP. Obviously, these findings offer tremendous opportunities for the development of novel, renewable, polyethylene-like materials with sufficiently high molecular weight to replace polyethylene in selected applications. While ethylene is currently still cheaper than macrolactones, the future economic competitiveness of the material will only be determined by the price of the raw materials and not by the catalyst or production method, as it is the case for the enzymatic route.

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