

Size does not matter: A highly efficient catalyst for the ring-opening polymerization of macrolactones lacking ring-strain

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SIZE DOES NOT MATTER: A HIGHLY EFFICIENT CATALYST FOR THE RING-OPENING POLYMERIZATION OF MACROLACTONES LACKING RING-STRAIN.

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Introduction

Polyolefins accounts for over 65% of the total volume of world production of plastic materials. The polyolefin industry is heavily reliant on petrochemistry for the raw materials. Nowadays, there are political, environmental and economical reasons to develop green alternatives based on renewable resources. Potential candidates as a polyethylene-like material are polymers obtained from macrolactones of α,ω -hydroxyl fatty acids such as pentadecalactone (PDL), a 15-membered naturally occurring cyclic ester.

Ring-opening polymerization (ROP) of cyclic esters is widely used for the synthesis of aliphatic AB-type polyesters. Particularly successful is metal-mediated ROP as it allows for the control of the polymer molecular weight and end-groups by the use of a nucleophilic initiator.¹ It is commonly agreed that the driving force behind the ROP of lactones is the release of ring-strain in the transition from the cyclic ester to the polyester chain or, in thermodynamic terms, by the negative change of enthalpy. Consequently, as the ring-strain decreases with increasing lactone size so does the reactivity in metal-mediated ROP.² Consequently, only few examples of metal-catalyzed ROP of macrolactones like PDL can be found in literature, which report only low yields and low molecular weights.^{3,4,5}

The situation is inverted for the lipase-catalyzed ROP.^{2,6} Lipases like *Candida Antarctica* Lipase B are highly active in the ROP of lactones and show exceptionally high polymerization rates for macrolactones.^{7,8} The reactivity of lactones in this process is no longer determined by the ring-strain but by the preference of the lipase for hydrophobic (fatty acid-like) substrates. Macrolactones can thus easily be polymerized enzymatically and poly(pentadecalactone)s (PPDL) with molecular weights (M_n) up to 150,000 g/mol have been reported.^{9,10} It is thus commonly accepted (and repeatedly stated) that efficient polymerization of macrolactones is only possible by enzymatic catalysis. Unfortunately, enzymes are expensive, allow little control over the polymerization and cannot be used at high temperatures (melt polymerization). It would therefore be highly desirable to be able to use catalysts to polymerize these renewable macrolactones to high molecular weight polymers with polyethylene-like properties.

In this paper we report for the first time a 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

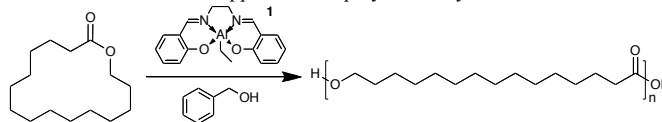
Materials. PDL, ϵ -caprolactone, δ -valerolactone, β -butyrolactone, γ -butyrolactone, benzyl alcohol and toluene were purchased from Aldrich. The aluminum salen complex **1**, decanolactone, undecanolactone and hexadecalactone were synthesized following literature procedures.¹¹

Methods. ¹H and ¹³C NMR spectroscopy was performed on a Varian Mercury 400 MHz NMR in CDCl₃. High temperature Size Exclusion Chromatography 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 3 PLgel Olexis (300 × 7.5 mm, Polymer Laboratories) columns in series. 1,2,4-Trichlorobenzene (Biosolve) was used as eluent at a flow rate of 1 mL/min. The molecular weights were calculated with respect to polystyrene standards (Polymer Laboratories, $M_p = 580$ up to $M_p = 7.1 \times 10^6$ g/mol).

Ring-opening polymerization. Lactone (4 mmol), aluminum salen catalyst and benzylalcohol (co-initiator) were added to a vial under nitrogen atmosphere. The molar ratio of benzyl alcohol to the catalyst was kept constant at 1:1, while the monomer to initiator ratio was varied from 50 to 500. The vial was then closed and stirred at 100 °C for 4 h. For the reactions in solution, toluene (2 mL) was added to the polymerizations prior to heating. After the reaction the mixture was cooled in an ice bath and the solvent was evaporated. The products were analyzed without further precipitation.

Results and Discussion

Poly(pentadecalactone). The aluminum salen complex **1** (Scheme 1) was applied as catalyst in the cROP of PDL. The efficiency of **1** was initially tested in the bulk polymerization of PDL in the presence of benzyl alcohol (BA) as an initiator at a 1:1 ratio at 100 °C with increasing monomer to catalyst ratios (50-500). A constant reaction time of 4 h was applied after which the reaction was stopped and the polymer analyzed.



Scheme 1. Polymerization of pentadecalactone (PDL) using an aluminum salen complex.

The high efficiency of the catalyst in these polymerizations was immediately evident from the fast reaction. The viscosity of the reaction medium increased rapidly within minutes and after about 20 min. agitation stopped. Even though a rapid viscosity increase with conversion is known from enzymatic PPDL synthesis, for a metal catalyst such fast polymerization kinetics are remarkable. For the lower monomer to **1** ratios, ¹H-NMR spectroscopy (Table 1, entry 1 and 2) showed an almost quantitative monomer conversion within the applied reaction time. When the ratio was increased the monomer conversion leveled off between 70 and 74 % (Table 1, entry 4 and 5), most likely due to diffusion limitations caused by the high viscosity of the reaction mixture.

The molecular weight of the polymers was analyzed by Size Exclusion Chromatography (SEC). Due to its high crystallinity and hydrophobicity (polyethylene-like) PPDL has a very low solubility in common SEC solvents. Therefore the polymers were analyzed by high temperature SEC (160 °C) in 1,2,4-trichlorobenzene (PS calibration).¹⁰ A clear shift of the SEC traces to higher molecular weight with an increasing monomer to catalyst ratio can be observed in Figure 1.

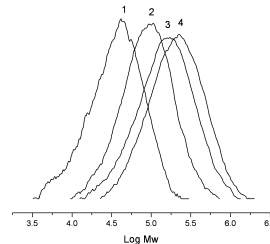


Figure 1. High temperature SEC results of PPDL prepared by bulk polymerization with increasing monomer to catalyst ratio. The numbers refer to entries in Table 1.

The number average molecular weights range from 24,000 g/mol for the monomer to catalyst ratio of 44, to 118,000 g/mol for the monomer to catalyst ratio of 424, respectively. Noticeable is that the molecular weight increases almost linearly with an increasing monomer to initiator ratio. However, without additional insights into the polymerization mechanism, any further discussion as to the control of the polymerization remains speculative. The polydispersity indices (PDI) of the obtained PPDLs are ranging from 2.1 to 2.8, which supports the expectation that the aluminum salen complex is a single-site catalyst. It also suggests either slow initiation or the presence of chain transfer via transesterification. MALDI-ToF-MS indeed shows the presence of a minor contribution of low molecular weight cyclics next to high molecular weight $\text{PhCH}_2\text{O}-[\text{C}(=\text{O})(\text{CH}_2)_{14}\text{O}]-\text{H}$ chains. Due to the high reaction rate, it is unclear at this moment whether these chain transfer reactions happen during the polymerization or at a later stage of the reaction, i.e. at high monomer conversion when the chain mobility is reduced.

In order to circumvent diffusion limitations a series of polymerizations was carried out in solution (toluene). While no complete gelation of the reaction medium was observed in these reactions, the viscosity again increased rapidly. The obtained molecular weights were even higher than for the bulk reactions. At the highest monomer to initiator ratio of 427 (entry 7, Table 1) an M_n of 155,000 g/mol was obtained. The molecular weights of PPDL obtained with **1** are unprecedented for cROP of macrolactones and match the highest molecular weights reported by enzymatic polymerization.

Table 1. cROP of PDL catalyzed by **1** in the presence of an equimolar amount of benzyl alcohol using various monomer to catalyst ratios (M:C).

| Entry | Solvent | M:C | M_n calc. [g/mol] ^a | M_n [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 | 26 000 | 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[monomer]/[catalyst] × conversion × M_n (monomer). ^bDetermined by ¹H-NMR in CDCl₃ by comparison of the methylene peak adjacent to the ester group of the monomer (4.14 ppm) and the polymer (4.04 ppm).

In addition to **1** other aluminum salen complexes were explored (Figure 2). A bulky substituent was placed on the phenyl ring to investigate the influence of steric hindrance at the catalyst on the polymerization rate. Secondly, complexes were pretreated with benzyl alcohol to form the active benzyloxy complex before the polymerization to investigate the rate of formation of the active species. Using aluminum or yttrium isopropoxide or Y[N(SiMe₃)₂]₃, well-known ROP catalysts for ϵ -caprolactone, in the polymerization of PDL invariably resulted in the formation of only low molecular weight products.

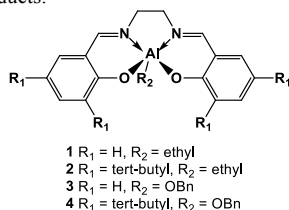


Figure 2. Aluminum salen complexes used in the chemical ring opening polymerization of pentadecalactone.

As can be observed in Figure 3, polymerization using complex **1** or **2** resulted in full conversion. The highest conversion reached using **4** was 87 % and 93 % using **2** (Table 2). Longer reaction times are required to reach higher conversions using **4**. 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 (Figure 3, right). The difference between using complex **1** or **3** (and **2** or **4**) is small, which indicates that the active species is formed instantaneously.

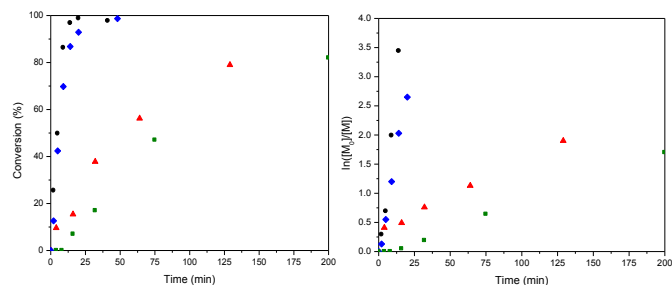


Figure 3. Conversion and the logarithm of the relative concentration vs time plots of the polymerization of pentadecalactone using different salen complexes, ● **1**, ▲ **2**, ◆ **3**, ■ **4**.

To study the influence of the ring size of the lactone polymerized, a kinetic study with various ring sizes was launched (Table 2). All polymerizations were performed under the same conditions (100 °C under inert atmosphere) and the same catalyst: initiator: monomer ratio of 1:1:100 was applied. All polymerizations were carried out using complex **1** with benzyl alcohol as the catalytic system and toluene as solvent. All reactions were run for 1 hour, except the polymerization of γ -butyrolactone, which was followed over 96 h.

Table 2. cROP of lactone of different ring-size catalyzed by **1** in the presence of an equimolar amount of benzyl alcohol.

| Monomer | Ring size | k_{app} [min ⁻¹] | M_n calc. [g/mol] ^a | M_n [g/mol] ^b | PDI | Conversion [%] ^c |
|--------------|-----------|--------------------------------|----------------------------------|----------------------------|-----|-----------------------------|
| β -BL | 4 | - | 8 600 | 850 | 2.0 | 2.5 |
| γ -BL | 5 | - | 8 600 | - | - | - |
| VL | 6 | 0.16 ± 0.01 | 10 000 | 10 000 | 2.1 | 96 |
| CL | 7 | 0.25 ± 0.03 | 11 400 | 13 000 | 2.3 | > 99 |
| DL | 11 | 0.03 ± 4·10 ⁻³ | 17 000 | 24 000 | 1.7 | 84 |
| UL | 12 | 0.01 ± 2·10 ⁻³ | 18 400 | 27 000 | 1.6 | 91 |
| PDL | 16 | 0.03 ± 2·10 ⁻³ | 24 000 | 36 000 | 1.6 | 90 |
| HDL | 17 | 0.04 ± 5·10 ⁻³ | 25 600 | 40 000 | 1.8 | 98 |

[complex] ≈ 15 mM, [lactone]₀ ≈ 1.5 M, T = 100 °C. ^a[monomer]/[catalyst] × conversion × M_n (monomer). ^bMeasured in TCB at 160 °C. ^cDetermined by ¹H-NMR in CDCl₃.

Complex **1** is virtually unreactive towards polymerization of β -butyrolactone. As expected based on the thermodynamic stability of the 5-membered ring, no polymerization of γ -butyrolactone was observed after 96 h.¹² The smaller sized lactones, δ -valerolactone and ϵ -caprolactone, have higher rate constants compared to the larger lactones, which can be explained by either the high ring strain or by the energetically high cisoid conformation in the 6- and 7-membered lactones, however, **1** is clearly not a highly effective catalysts for these smaller ring-sized lactones. Molecular weights obtained are in good agreement with the calculated values. Polydispersities of 2.1 and 2.3, respectively, are quite broad for a living system, which is probably due to transesterification reactions near complete conversion. Decanolactone and undecanolactone, the middle-sized lactones, show the lowest polymerization rate of all polymerizable lactones. Nevertheless, for these unreactive monomers, the polymerization rate is still respectable. It is known that no ring strain and therefore no driving force is present in these larger lactones.¹³ The larger lactones show a somewhat higher polymerization rate than the middle-sized lactones, which can be ascribed to the positive ΔS^\ddagger for polymerization for these macrolactones. Despite the high conversions obtained within an hour (98 % for HDL) the polydispersities are lower than 2, suggesting limited transesterification taking place.

Conclusions

These results show that it is possible to catalytically polymerize macrolactones to high molecular weight ($M_n > 150,000$ g/mol) polymers. Complex **1** even polymerizes the so-called medium-sized lactones (ring size: 9 – 12) with a reasonably good activity to high molecular weight products, which is truly exceptional. These results are unprecedented in the literature and they challenge the common theory of ring-tension driven cROP. Obviously, these findings offer tremendous opportunities for the development of novel, renewable, polyethylene-like materials.

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