

Metal-based catalysts for controlled ring-opening polymerization of macrolactones : high molecular weight and well-defined copolymer architectures

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Metal-Based Catalysts for Controlled Ring-Opening Polymerization of Macrolactones: High Molecular Weight and Well-Defined Copolymer Architectures

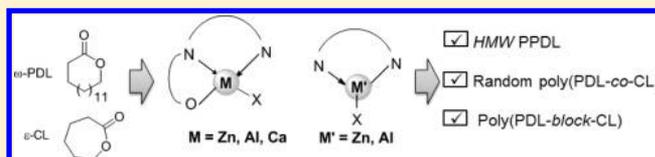
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S Supporting Information

ABSTRACT: This contribution describes our recent results regarding the metal-catalyzed ring-opening polymerization of pentadecalactone and its copolymerization with ϵ -caprolactone involving single-site metal complexes based on aluminum, zinc, and calcium. Under the right conditions (i.e., monomer concentration, catalyst type, catalyst/initiator ratio, reaction time, etc.), high molecular weight polypentadecalactone with M_n up to 130 000 g mol⁻¹ could be obtained. The copolymerization of a mixture of ϵ -caprolactone and pentadecalactone yielded random copolymers. Zinc and calcium-catalyzed copolymerization using a sequential feed of pentadecalactone followed by ϵ -caprolactone afforded perfect block copolymers. The blocky structure was retained even for prolonged times at 100 °C after full conversion of the monomers, indicating that transesterification is negligible. On the other hand, in the presence of the aluminum catalyst, the initially formed block copolymers gradually randomized as a result of intra- and intermolecular transesterification reactions. The formation of homopolymers and copolymers with different architectures has been evidenced by HT-SEC chromatography, NMR, DSC and MALDI-ToF-MS.



INTRODUCTION

The area of aliphatic polyesters derived from renewable feedstock has been dominated for long by polylactide (PLA), a fully bio-based polyester derived from natural L-lactide obtained by fermentation of starch.¹ This polyester was designated to be an alternative for petroleum-based commodity plastics in some high-added value applications. However, due to PLA's intrinsic brittleness and relatively high cost, its range of applications is limited to some specific areas. Polyesters containing long methylene sequences, obtained from readily available fatty acid feedstock, form an interesting alternative class of bio-based polyesters, displaying some interesting properties such as toughness and ductility similar to polyethylene.²

Polyesters containing long methylene sequences can be produced by different methods. Meier's group has extensively studied the use of ADMET to couple olefin-containing monomers.³ Mecking and Gross reported on polycondensation of fatty acid-based diesters + diols or fatty acid-based ω -hydroxy esters.^{2a,4} However, the polycondensation route is an equilibrium process, and the formation of high molecular weight polymers is generally limited. Ring-opening polymerization (ROP) of macrolactones proved to be a very efficient route to high molecular weight polyesters containing long methylene sequences.

So far, most reports on ROP of macrolactones have been based on the use of enzymatic polymerization of macrolactones.^{4a,5} Enzymes can be highly effective in ring-opening of

large-ring lactones affording high molecular weight products, but the enzymatic polymerization also has some limitations such as a poor level of control of the polymer microstructure as a result of transesterification, and they show only a moderate thermal stability. Organic catalysts also promote the polymerization of macrolactones such as polypentadecalactone (PDL) and the copolymerization of PDL and ϵ -caprolactone (CL);⁶ however, they again tend to produce only moderate molecular weight products. Only few examples of metal-catalyzed ROP of macrolactones have been reported, and most reports are generally based on the use of homoleptic tin, zinc, and yttrium complexes, which produced rather low molecular weight polymers.⁷ Thus far, only aluminum salen catalysts have been found to produce high molecular weight polymacrolactones.⁸ All catalyst systems (enzymatic, organic, and metal-based) reported so far undergo competitive intra- and intermolecular transesterification. This obviously prevents the formation of block copolymers of different (macro)lactones and is responsible for the formation of low molecular weight cyclic side products as a result of backbiting.^{6,8}

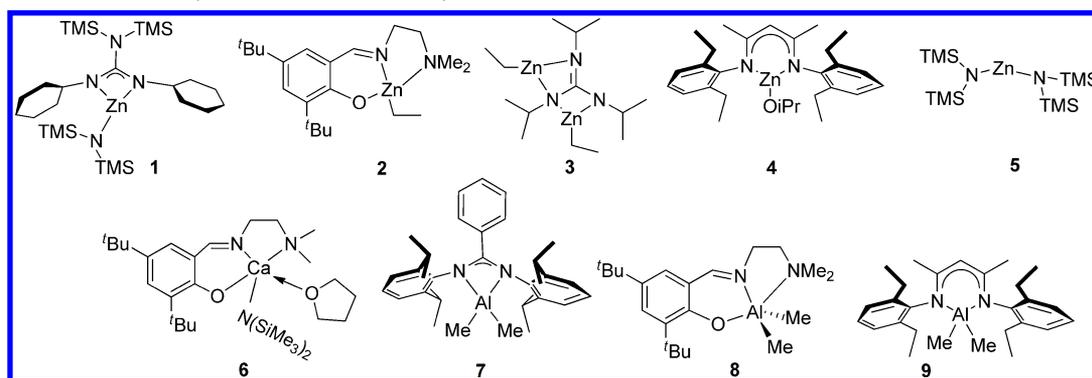
High molecular weight macrolactone-based block copolymers containing a more polar second block could be interesting materials for compatibilization polar–nonpolar polymer blends or for biomedical applications with improved hydrolytic

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Scheme 1. Metal-Based Catalysts Used in This Study

Table 1. Ring-Opening Polymerization of PDL Mediated by Catalysts 1–9^a

entry	cat.	[Mon] ₀ /[M] ₀ /[ROH] ₀ (mole ratio)	time ^b (h)	conv ^c (%)	TOF (h ⁻¹)	<i>M</i> _{n,calc} (kg mol ⁻¹)	<i>M</i> _{n,exp} (kg mol ⁻¹)	PDI
1	1	100/1/1	1.0	70	70	16.8	16.9	1.6
2 ^e	1	100/1/1	1.0	38	38	9.1	15.8	1.5
3 ^f	1	530/1/1	15.0	22	8	9.3	18.8	1.2
4	1	600/1/2	24.0	37	9	26.6	20.4	1.6
5	1	600/1/10	24.0	92	23	13.3	11.2	1.5
6	1	600/1/20	24.0	100	25	7.2	5.2	1.5
7 ^g	1	300/1/1	0.25	99	1200	33.8	9.9	1.7
8	2	240/1/0.5	24.0	53	5	n.d.	38.2	1.7
9	2	100/1/1	1.5	90	60	21.6	17.8	1.6
10	2	100/1/5	1.5	95	63	4.6	6.7	1.4
11 ^e	2	100/1/1	1.5	76	50	18.2	10.3	1.6
12 ^f	2	100/1/1	1.5	65	43	5.2	2.2	1.3
13 ^g	2	100/1/1	0.5	99	198	n.d.	n.d.	n.d.
14	3	100/1/1	1.5	62	41	14.8	2.6	2.5
15	4	100/1/0	1.5	34	22	8.4	9.6	1.8
16	5	100/1/1	2.0	25	13	6.0	14.3	1.7
17	6	100/1/1	0.5	55	110	13.2	28.5	1.7
18	6	200/1/0	1.0	45	90	21.6	35.9	1.6
19 ^g	6	100/1/1	0.5	99	198	n.d.	n.d.	n.d.
20	7	100/1/1	1.5	83	55	19.9	15.2	1.7
21	8	100/1/1	1.5	65	43	15.6	18.6	1.8
22	9	100/1/1	1.5	63	42	15.1	14.1	1.9

^aReactions were conducted in bulk monomer at 100 °C unless noted otherwise using BnOH as initiator. ^bReaction times were not necessarily optimized. ^cConversion of PDL as determined by ¹H NMR from the α -methylene resonances of PDL and PPDL. ^dNumber molecular weight calculated from $[\text{PDL or CL}]_0/[\text{BnOH}]_0 \times \text{conv} \times 240.0$ (or 114 for CL). ^eReaction performed in toluene solution ($[\text{PDL}] = 2.5 \text{ M}$, % weight of monomer (vs weight of toluene) ≈ 0.7). ^fReaction performed using 1,1,1-tris(hydroxymethyl)ethane as initiator. ^gConducted in bulk monomer at 100 °C using CL monomer.

stability compared to the currently used polyesters. To be able to produce block copolymers of different (macro)lactones, the catalyst of choice should show intrinsic living polymerization behavior. At first sight this might seem doable since several living ROP catalyst systems have been reported.⁹ However, the reactivity of the ester functionality in the more or less ring strain-free PDL is likely to be very similar to that of the ester groups in the corresponding polymer. Hence, finding catalysts showing selectivity for ring-opening of macrolactones versus transesterification of the corresponding copolymer might be challenging. Here we report on a study aimed at producing high molecular weight PPDL as well as PDL–CL block copolymers using highly selective metal-based ROP catalysts.

RESULTS AND DISCUSSION

Homopolymerization of ϵ -Caprolactone and Penta-decalactone. Since it is our aim to produce both high

molecular weight aliphatic polyesters and corresponding block copolymers, the ROP catalysts of choice should show intrinsic living polymerization behavior. Preferably, the catalysts should also be stable toward an excess of protic reagents such as alcohols and amines that can be applied as initiator/chain transfer agents affording an immortal catalyst system.^{10,11} Complexes based on Zn, Ca, and Al, previously reported to be active in the controlled (living or immortal) ROP of lactide, lactones, and cyclic carbonates monomers (Scheme 1),^{9–12} were expected to be potential candidates for the production of high molecular weight homopolymers as well as block copolymers of a wide variety of cyclic monomers and have therefore been selected for the PDL homopolymerization and the PDL–CL copolymerization.

In view of the low solubility of PPDL at moderate temperatures, the ROP of PDL is commonly carried out at high temperatures to minimize the constraints related to

monomer diffusion and precipitation of the product. Thus, all metal complexes listed in Scheme 1 have been tested as catalyst for the ROP of PDL at 100 °C, both in toluene solution ($[PDL] = 2.5 \text{ M}$) and in bulk monomer ($[PDL] = 3.8 \text{ M}$).^{9–12} Main group metal alkyls and bulky amides are generally little or not active ROP catalysts, and to effectively initiate the polymerization, addition of a protic substrate, typically an alcohol e.g. benzyl alcohol (BnOH), is crucial.^{10,13} NMR tube experiments have shown that the alcohol reacts instantaneously with the metal alkyl functionality forming the corresponding metal alkoxide, which is the actual active species.^{8b} Catalyst 6 does not require an initiator since in this case the amido substituent also functions as an initiating group, but adding an alcohol does not harm the activity of the catalysts. Representative results are summarized in Table 1 and Figure 1. For 1 and 2, reactions with different amounts of BnOH as

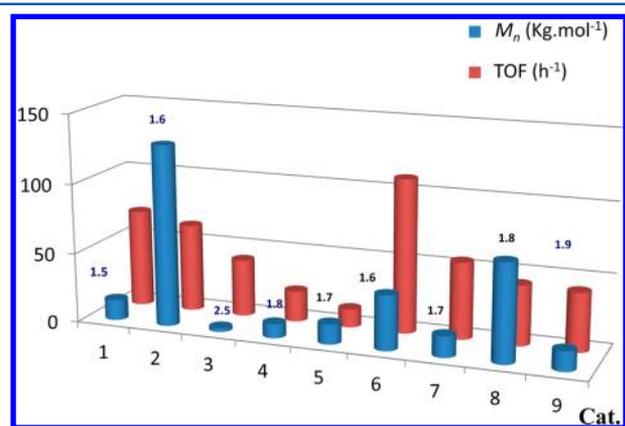


Figure 1. Comparison between M_n , M_w , and PDI of PPDL's prepared using zinc-, calcium-, and aluminum-based catalysts 1–9. Polymerization conditions: bulk monomer, 100 °C, BnOH as initiator (cat.:BnOH = 1:1).

initiator/chain transfer agent have been conducted. The molecular weight of the polymers decreases inversely proportional to the amount of initiator/chain transfer agent added (Table 1, entries 4–6 for 1, entries 8–10 for 2), clearly confirming the immortal character of these catalysts. Increasing the amount of alcohol also appeared to increase the reaction rate, which is most probably due to the reduced viscosity of the

reaction mixture. Replacing the benzyl alcohol by another alcohol did not affect the catalytic performances of the zinc catalysts 1 and 2 for the ROP of PDL. The combination of an equimolar ratio of 1,1,1-tris(hydroxymethyl)ethane and 1 or 2 afforded activities slightly lower than those obtained using BnOH as initiator/chain transfer agent (Table 1, entries 3 and 12). This suggests that by a meticulous choice of the initiator the preparation of PPDL polymers with variable architectures are at reach.^{10,14}

The performances of the catalysts differed significantly, with catalysts 4 and 5 (TOF < 25 h⁻¹) being the least active and catalysts 1 and 6 (TOF > 70 h⁻¹) showing the highest activity. Catalyst 6 was found to be the most active catalyst for pentadecalactone polymerization described so far.^{4–8} Despite the promising results in terms of activities and polymerization control achieved using the guanidinato zinc catalyst 1, all our attempts to obtain high molecular weight polymers using 1 proved futile ($M_n < 20\,000 \text{ g mol}^{-1}$). The zinc catalyst 3 supported by the *i*Pr-guanidinato ligand showed the same trend and invariably produced low molecular weight PPDL's having M_n 's of less than 10 000 g mol⁻¹. By far the most promising catalysts with respect to producing high molecular weight PPDL proved to be the zinc-, calcium-, and aluminum-based catalysts 2, 6, and 8 supported by the tridentate phenoxyimine ligand. These catalysts afforded PPDL's having high molecular weights ($M_n > 35\,000 \text{ g mol}^{-1}$) under the same conditions as used for 1 and 3 (PDL:Zn:BnOH = 240:1:0.5, 100 °C; Table 2, Figure S1). Why 2, 6, and 8 produce high molecular weight products, while 1 and 3 under the same conditions do not, is not well understood. Since the experiments have been carried out in duplicate using the same batches of solvent and PDL for 2, 6, 8, and 1, 3, chain transfer as a result of water initiation for 1 and 3 but not for 2, 6, and 8 can be excluded. Therefore, it is most likely that intramolecular transesterification resulting in low molecular weight cyclic products is somehow favored for 1 and 3.

The effect of various parameters on the molecular weight of the PPDLs obtained using Zn-, Ca-, and Al-based catalysts (2, 6, and 8) was studied further, and results are given in Table 2. For example, high molecular weight PPDL was obtained using a substoichiometric amount of initiator. For example, using 2 in combination with 0.5 equiv of BnOH afforded high molecular weight PPDL with a M_n of 130 000 g mol⁻¹ (Table 2, entries 4,

Table 2. Evolution of PPDL Molecular Weights (M_n) over Time (4, 24 h)

entry	Cat.	$[PDL]_0/[Cat.]_0/[ROH]_0$ (mole ratio)	$[PDL]_0$	4 h		24 h	
				M_n^b (kg mol ⁻¹)	PDI ^b	M_n^b (kg mol ⁻¹)	PDI ^b
1	2	240/1/0.5	3.8	7.6	1.8	38.2	1.7
2	2	240/1/5	3.8	3.7	1.2	6.7	1.4
3 ^c	2	240/1/0.5	1.4	35.0	1.7	69.7	1.9
4	2	530/1/0.5	3.8	n.d.	n.d.	130.0	1.9
5	2	530/1/1	3.8	n.d.	n.d.	45.5	1.8
6	2	530/1/2	3.8	n.d.	n.d.	23.4	1.8
7	6	240/1/0.5	3.8	n.d.	n.d.	60.9	1.9
8	8	240/1/0.5	3.8	53.4	1.9	48.7	2.1
9	8	240/1/2	3.8	21.9	1.8	19.6	1.8
10 ^c	8	240/1/2	1.4	22.4	1.9	25.8	1.7
11	8	530/1/0.5	3.8	n.d.	n.d.	73.0	2.2

^aReactions were conducted in bulk monomer at 100 °C unless noted otherwise using BnOH as initiator. ^bExperimental number-average molecular weight and molecular weight distribution determined by HT-SEC in TCB at 160 °C and referenced to polyethylene standards. ^cReaction performed in toluene solution, % weight of monomer (vs weight of toluene) \approx 0.4.

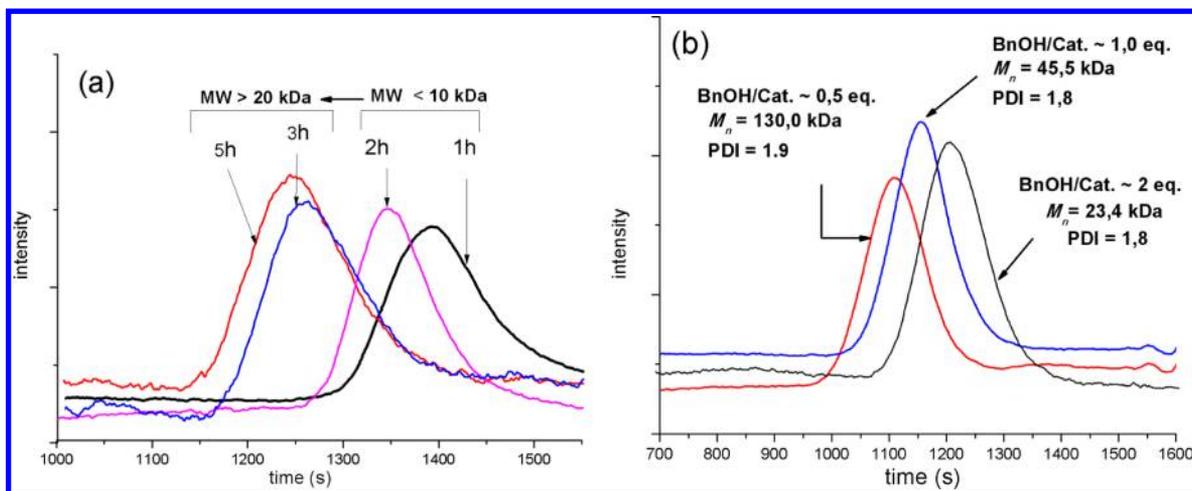


Figure 2. (a) Comparison between SEC traces of the PPDL samples prepared using **2** illustrating the evolution of PPDL molecular weight against reaction time. (b) Comparison of SEC traces of PPDL samples prepared using **2** and varying amounts of BnOH. Polymerization conditions: (a) bulk monomer, 100 °C, molar ratio PDL:Cat. ~ 240:1; (b) bulk monomer, 100 °C, 24 h, molar ratio PDL: Cat. ~ 530:1).

Scheme 2. PDL–CL Copolymerization Using **1**, **2**, **6**, and **8** in the Presence of BnOH as Catalyst Systems

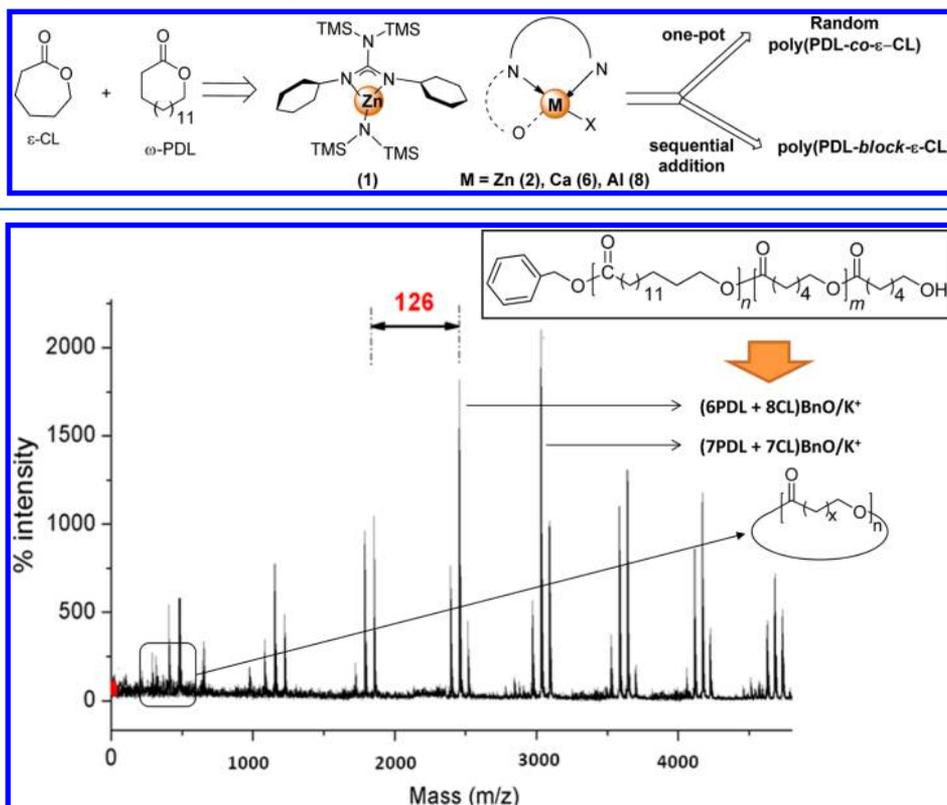


Figure 3. MALDI-ToF-MS of random poly(PDL-co-CL) random copolymer prepared using **2**/BnOH.

and Figure 2b). Under these conditions, the remaining metal alkyl derivatives most probably function as moisture scavengers. The relatively narrow molecular weight distribution ($\text{PDI} \leq 2.0$) reflects some degree of control over the polymerization even for high PDL to catalyst molar ratios (PDL:Zn = 530) and high conversion, which leads to a highly viscous reaction mixture. Under the same conditions, **8** afforded PPDL with a M_n of 73 000 g mol⁻¹, but with a somewhat broader PDI (Table 2, entry 11). Contrarily, the zinc guanidinato catalysts **1** and **3** still afforded relatively low molecular weight products regardless of the lower initiator to catalyst ratio. This is most

probably due to backbiting reactions as it has been observed by MALDI-ToF-MS analysis of PPDL sample prepared using zinc catalyst **3**/BnOH with the presence of two distribution sets corresponding to cyclic and linear oligomers (Figure S2).

The best results with respect to molecular weight were obtained with a combination of prolonged reaction times and substoichiometric amounts of BnOH. The pseudoliving character of these systems is most pronounced for **2**, which showed a significant increase in molecular weight but no increase in PDI for prolonged reaction times (Figure 2a and Table 2). Conversely, for the aluminum analogue **8** increasing

the reaction time did not lead to an increase in the molecular weight (Table 2, entries 8–11). It appeared that **8**, like aluminum salen complexes,⁸ is an effective transesterification catalyst producing significant amounts of low molecular weight cyclic products as a result of intramolecular transesterification.

Pentadecalactone- ϵ -Caprolactone Copolymerization. Most of the catalysts **1**–**9** tested in this study are known to readily ring-open ring-strained cyclic esters and carbonates even under mild conditions.^{10,12,15} To explore the feasibility of preparing well-defined copolymers, we have performed both the bulk and solution copolymerization of PDL and CL using the zinc (**1**, **2**), calcium (**6**), and aluminum (**8**) complexes as catalysts and BnOH as initiator (Scheme 2).

The much higher reaction rate of CL homopolymerization compared to PDL homopolymerization (entries 7, 13, and 19, Table 1) in combination with the similarity of the chain-end structure after insertion of PDL or CL would suggest that tapered or block copolymers would be formed during the copolymerization of a mixture of CL and PDL. However, the copolymerization of a mixture of both lactones led to the formation of pure random poly(PDL-*co*-CL) copolymers. As a result of the cocrystallization over the whole range of comonomer compositions,¹⁶ the obtained poly(PDL-*co*-CL) random copolymers show a gradual decreasing of T_m with increasing CL content (Figures S3 and S4) and remain highly crystalline with melting enthalpies (ΔH_f) ranging from ca. 140 J g⁻¹ (pure PPDL) to ca. 50 J g⁻¹ (pure PCL) as it has been previously observed and reported by Gross et al.^{16c,d} The MALDI-ToF-MS spectra of the poly(PDL-*co*-CL) random copolymers are in agreement with the thermal analysis data; i.e., the individual isotope patterns are separated by 126 g mol⁻¹, which equals the difference in mass between PDL and CL, and the relative content of PDL and CL is in agreement with the initial monomer composition of the feed (Figure 3). Furthermore, there are no signs of PPDL or PCL homopolymers in the MALDI-ToF-MS spectrum, and the end-group analysis showed that in the low molecular weight region only minor a distribution of shorter cyclic chains population is present, while the composition of the higher molecular weight regions exclusively consists of linear chains end-capped by the BnOH initiator.

The sequential addition of PDL followed by CL has successfully been applied for the preparation of poly(PDL-*block*-CL) copolymers as was proven by the combination of SEC, thermal analysis, and MALDI-ToF-MS. The comparison of the SEC chromatograms of the sample removed after the first step (PDL polymerization) and the final product (after copolymerization of subsequently added CL) shows a clear shift from the initial PPDL chromatogram to high molecular weight region of the final produced block copolymers (Figure S5). The DSC curves of the block copolymers prepared using zinc and calcium catalysts **2** or **6** showed two distinct melting temperatures corresponding to the PCL segment with $T_m \sim 55$ °C and the PPDL block with $T_m \sim 90$ °C (Figure S6). The MALDI-ToF-MS spectra of these products were similar to the one in Figure 3, corresponding to PDL-CL copolymers. No signs of homopolymers could be observed in the MALDI-ToF-MS spectra. The fact that even after 18 h at 100 °C the blocky structure of the copolymers has been retained indicates that the zinc and calcium catalysts **2** and **6** do not catalyze intra- or intermolecular transesterification of the formed copolymers. This is rather remarkable knowing that the catalysts readily ring-open PDL, which has little ring-strain, and hence the

reactivity of its ester is expected to be comparable to that of the ester functionalities in the polymer. Clearly, the catalysts show a formidable selectivity for ring-opening of even macrolactones lacking ring strain *without* transesterifying the corresponding (co)polymers.

To further confirm this finding, we have added a 1:1 mixture of the organic catalyst 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and BnOH to a toluene solution of the poly(PDL-*block*-CL) copolymer (TBD/BnOH/copolymer = 1/1/100). The mixture was stirred for 18 h, and samples were taken at defined time intervals (2, 7, and 18 h) and were analyzed by DSC (Figure 4). Under influence of the TBD catalyst, the block

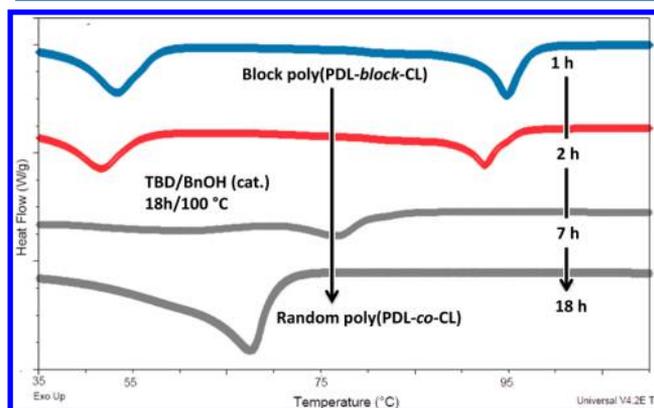


Figure 4. DSC monitoring of the transformation of poly(PDL-*block*-CL) block copolymer prepared using **2**/BnOH (conditions: 100 °C, bulk monomer) into poly(PDL-*co*-CL) random copolymer by transesterification reactions catalyzed by TBD/BnOH (conditions: 100 °C, toluene, 18 h).

copolymer was gradually transformed into a completely random copolymer. The tailing of the melting peak at low temperature is most probably the result of low molecular weight cyclic products formed by intramolecular transesterification.

¹H NMR analyses of the random and block copolymers confirmed the expected structures. The random character of the poly(PDL-*co*-CL) copolymers obtained by one-pot synthesis is evidenced by the presence of only one triplet at δ 4.05 ppm corresponding to the protons of α -methylene groups of both ϵ -CL and PDL units (Figure 5, right expansion). In contrast, the block copolymers obtained by the sequential addition of PDL followed by the addition of CL monomer show two overlapping triplets between δ 4.0 and δ 4.10 ppm (Figure 5, left expansion).

¹³C NMR spectroscopy provides additional information concerning the microstructure of the polymer. The chemical shift of the α -methylene groups CH₂O ($\delta \sim 64$ ppm) as well as of the carbonyl carbons ($\delta \sim 170$ ppm) are highly sensitive and can be used to determine the randomness of the copolymer.^{16d} A schematic representation of copolymer diads of the poly(PDL-*co*-CL) random copolymers and the corresponding linkages between units is shown in Figure 6. The peak at δ 64.37 ppm corresponds to the linkage between two PDL units, whereas the linkage between two CL units is indicated by the signal at δ 64.11 ppm. The linkages between alternate units CL and PDL are shifted at δ 63.99 (CL-PDL) and δ 64.49 ppm (PDL-CL), confirming the random nature of these copolymers.

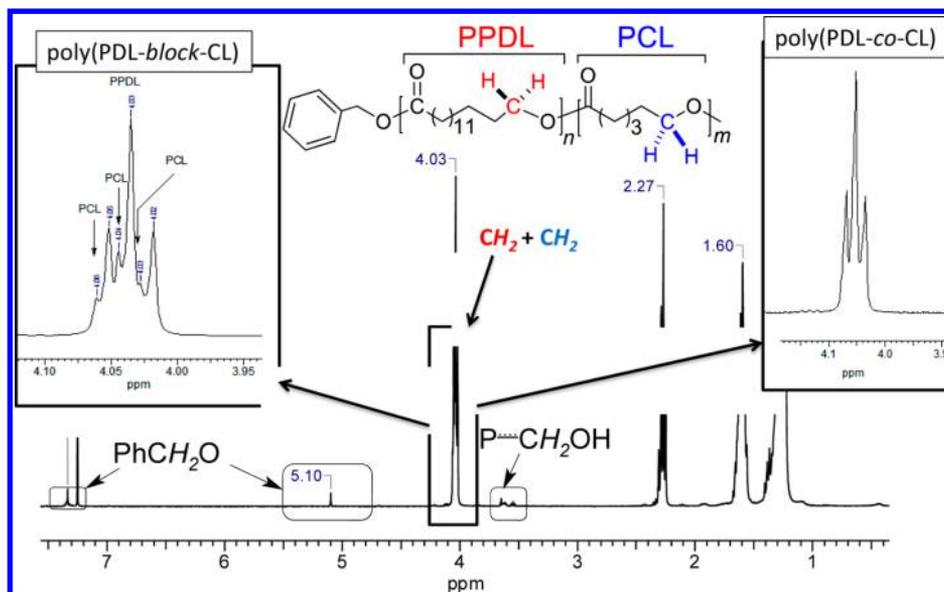


Figure 5. ^1H NMR spectra of poly(PDL-*block*-CL) block copolymer (bottom and top left) illustrating the polymer end groups and the comparison with random poly(PDL-*co*-CL) copolymer (top right).

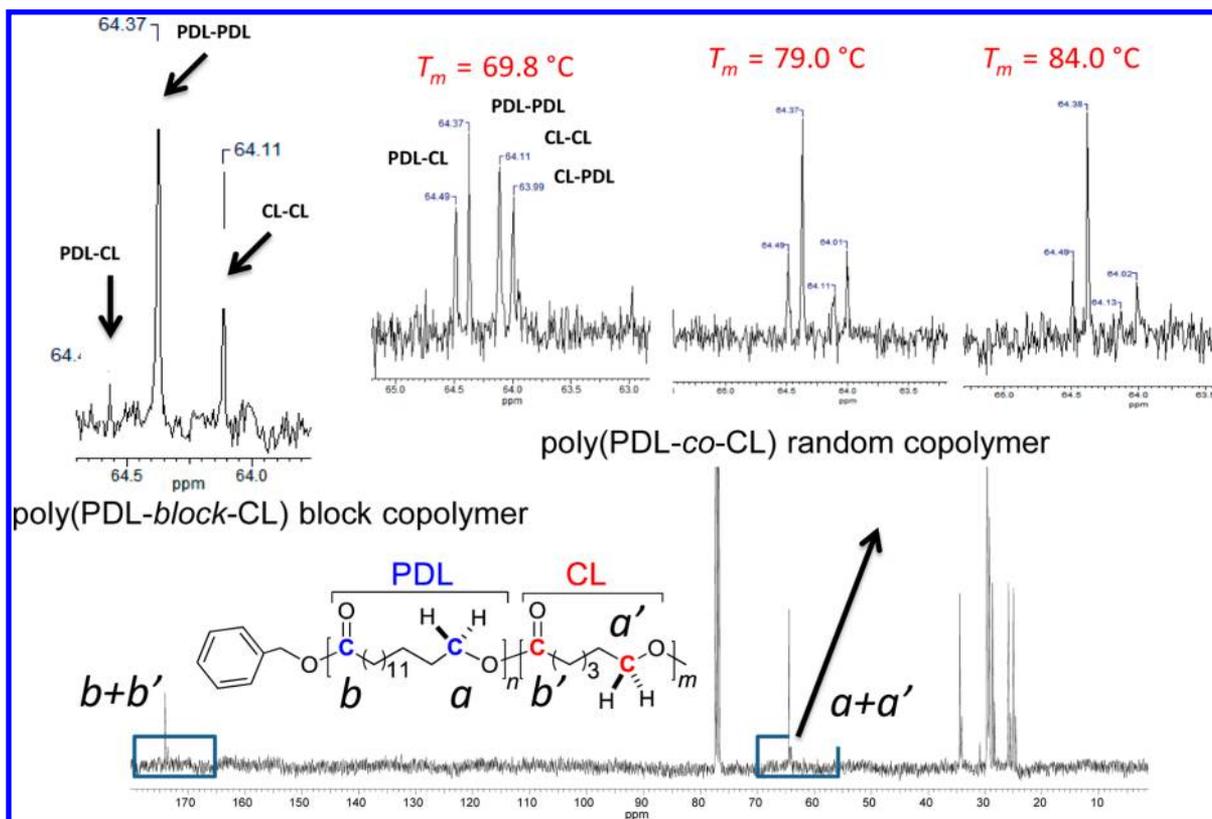


Figure 6. ^{13}C NMR spectra of poly(PDL-*co*-CL) random copolymer (bottom). Expansion of α -methylene group resonance representing the copolymer diads and the corresponding linkages between units for random poly(PDL-*co*-CL) (top right) and block poly(PDL-*block*-CL) (top left).

CONCLUSION

The catalytic behavior of zinc-, calcium-, and aluminum-based complexes, bearing different ancillary ligands (phenoxyimine-amine, guanidinate, amidinate, β -diiminato) in the ROP of (macro)lactones has been studied. From polymerization reactions carried out in bulk and in toluene solution at 100 $^{\circ}\text{C}$, two catalysts (**2**, **6**) have been found as truly efficient in both homopolymerization of PDL to high molecular weight

polypentadecalactone and PDL-CL copolymerization. Furthermore, unlike the aluminum catalysts (**7**–**9**), the zinc (**2**) and calcium (**6**) catalysts were found to show a well-controlled behavior, allowing the formation of both poly(PDL-*co*-CL) random copolymers and poly(PDL-*block*-CL) block copolymers, depending on the polymerization conditions applied. The blocky structure of poly(PDL-*block*-CL) has been randomized by the addition of a catalytic amount of TBD, highlighting the

high degree of polymerization control for the metal catalysts reported in this study. For the random copolymer poly(PDL-co-CL), the linear relationship between the random copolymers melting temperatures (T_m), and comonomer content was revealed by the thermal analysis. Interestingly, high molecular weight polymers could only be obtained using **2** and **6** as catalysts both in PDL polymerization and in PDL-CL copolymerization, while **1** gave only moderate to low molecular weight product as the result of backbiting reactions.

EXPERIMENTAL SECTION

General Considerations. Complexes **1–9** (Scheme 1) were prepared following the experimental procedures described in the literature.^{13,17} Starting materials, such as CaI_2 (anhydrous beads, 99.99%), ZnEt_2 (1.0 M solution in hexanes), and AlMe_3 (1.0 M solution in hexanes), were purchased from Aldrich and used as received. PDL and CL were purchased from Sigma-Aldrich and were freshly distilled from CaH_2 under nitrogen and degassed thoroughly by freeze–thaw–vacuum cycles prior to use. Toluene (Sigma-Aldrich) was passed through purification columns before use. Benzyl alcohol was purchased from Sigma-Aldrich and was distilled from CaH_2 and stored under nitrogen.

Analytical Techniques. ^1H and ^{13}C NMR spectra of PPDL's and PPDL-PCL random and block copolymers were recorded in 5 mm tubes on a Varian Mercury 400 and 200 MHz spectrometers at ambient temperature in CDCl_3 . Chemical shifts are reported in ppm versus tetramethylsilane (SiMe_4) and were determined by reference to the residual solvent. Size exclusion chromatography (SEC) of PPDL's was performed at 160 °C and performed on a Polymer Laboratories PLXT-20 Rapid GPC Polymer Analysis System (refractive index detector and viscosity detector) with 3 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^{-1} . 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. Differential scanning calorimetry (DSC) analyses of PPDLs and PPDL-PCL random and block copolymers were carried out on a DSC Q100 from TA Instruments at a heating rate of 5 °C min^{-1} . First and second runs were recorded after cooling down to ca. –20 °C. The melting temperatures reported correspond to second runs.

MALDI-ToF-MS Analysis. MALDI-ToF-MS analysis was performed on a Voyager DE-STR from Applied Biosystems equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. Mass spectra of 1000 shots were accumulated. The polymer samples were dissolved in CHCl_3 at a concentration of 1 mg mL^{-1} . The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 5 mg mL^{-1} . The matrix used was trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyldiene]-malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL^{-1} . Solutions of matrix, salt, and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflectron mode. All MALDI-ToF-MS spectra were recorded from the crude products.

Typical Procedure for PDL and CL Homopolymerizations. In a glovebox, PDL, metallic catalyst, and an equimolar amount of ROH were placed in a small glass crimp cap vial. Dry toluene was added, and the vial was capped. The reaction mixture was removed from the glovebox and stirred for a given time at 100 °C. For all reactions, an aliquot of crude polymer was withdrawn at the end of the polymerization reaction and dissolved in CDCl_3 in order to determine the conversion by ^1H NMR spectroscopy. The reaction was then stopped by cooling the mixture, removal of toluene under vacuum, and addition of excess methanol (~5 mL) to precipitate the polymer. The produced polymers were isolated and dried in vacuo at RT over 18 h.

Typical Random Copolymerization Reactions. In a glovebox, PDL, CL, catalyst, and initiator were placed simultaneously in a small

glass crimp cap vial. The vial was capped, removed from the glovebox, and heated at 100 °C for a given time (1–18 h). For all reactions, an aliquot of the crude reaction mixture was removed to determine the conversion. The copolymer was then precipitated in THF, dried under vacuum for 18 h, and characterized by size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), and ^1H , ^{13}C NMR spectroscopy.

Typical Copolymerization Reaction for Block Copolymers. PDL monomer and toluene (or bulk PDL) were transferred into a vial under inert nitrogen atmosphere in the glovebox. An equimolar amount of BnOH (to catalyst) was added to the mixture, and the vial was then capped and placed in an oil bath at 100 °C for a predetermined reaction time. At the end of the PDL homopolymerization an aliquot was taken for analysis and CL monomer was added. The resealed vial was then heated at 100 °C for an additional predetermined time. At the end of the polymerization reaction an aliquot of the reaction mixture was taken and dissolved in CDCl_3 for NMR, the mixture was quenched by acidic methanol, and the precipitated copolymer (in THF) was filtered, washed with methanol several times, and dried under vacuum for 24 h before characterization.

ASSOCIATED CONTENT

Supporting Information

Additional SEC chromatograms, DSC spectra, and MALDI-ToF-MS spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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