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Living and immortal polymerization of seven and six membered lactones to high molecular weights with aluminum salen and salan catalysts

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ABSTRACT

The ring-opening polymerization (ROP) of seven membered aliphatic cyclic esters with aluminum salen (MeAl[salen]) and salan (MeAl[salan]) catalyst is reported. While the controlled polymerization of lactide and β-butyrolactone is known for these systems, the living polymerization of ε-caprolactone (ε-CL) was poorly controlled. We now report excellent levels of control upon optimization of reaction concentration, time and temperature. High molecular weight polycaprolactone (PCL), up to 175 kDa, was also prepared with exceptional dispersity control. Immortal polymerization was also studied, with up to 100 equivalents of chain transfer alcohol and 10,000 monomer equivalents tolerated without any sacrifice to polymer control. 6-Methyl-ε-caprolactone (6-Me-ε-CL) and 2,6-dimethyl-ε-caprolactone (2,6-Me-ε-CL) were subjected to ROP conditions and low rates of polymerization were observed. Polymerization of 4-(4-benzyloxybutyl)-ε-caprolactone (4-BOB-ε-CL) was achieved with excellent control over dispersity and molecular weight, allowing introduction of functional groups into the polymer backbone. A block copolymer with 4-BOB-ε-CL and ε-CL was also prepared to produce a family of polymers with predictable composition.

1. Introduction

Fuelled by both their industrial importance and a fundamental interest in their chemistry and properties, significant advances in biodegradable polymers have been made in recent years [1]. In particular, catalyst development has been especially popular and powerful, with Lewis acidic catalysts reported for many metal centers [2]. Despite the ever-increasing number of catalysts, very few have shown to be effective for a wide range of monomers; often a system will have been screened for only one or two monomers. It is concomitantly more difficult to take a complex from the literature and quickly generate the desired complex macromolecule, limiting the impact of designer catalysts.

The aluminum salen and salan systems are certainly versatile [3]: aluminum salen complexes were first reported in ROP to produce poly(3-hydroxybutyrate) (P3HB) from β-butyrolactone (β-BL) using a catalyst based on the simplest salen ligand (N,N′-bis(salicylidene)-1,2-ethanediimine) [4]. Polymerization of β-BL produced only oligomeric P3HB, consistent with low monomer conversion. Extending this system to *rac*-lactide gave high conversions and produced isotactic enriched poly(lactic

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acid) (PLA) [5]. Modification of the salen ligand by Gibson has allowed for tunability of rates, dispersity (Đ) and isoselectivity (P_m) in ROP of *rac*-lactide, with *tert*-butyl phenoxy substitution offering the highest P_m (0.88) [6]. Our group demonstrated that modifying the ligand to incorporate even bulkier *ortho*-adamantyl groups could yield even higher isoselectivities (P_m = 0.94) [7]. Furthermore, using MeAl[salen] and MeAl[salan] (Fig. 1) for β-BL polymerization could give high conversion and low dispersities under optimized reaction conditions. Building from this work, the polymerization of β-lactones with much longer alkyl-substituents (Et, β-VL; ^{n}Bu, β-HL; $C_{10}H_{21}$, β-TDL) was possible using the same MeAl[salen] and MeAl[salan] catalysts [8].

Surprisingly, ε-caprolactone (ε-CL) has received little attention in ROP with aluminum salen and aluminum salan complexes. Cao and coworkers were of the first to polymerize ε-CL with an aluminum salen complex, as well as its dimer [9]. While these catalysts did facilitate the polymerization at 100 °C with high conversion, dispersities were relatively broad (Đ = 1.21–1.65). Yingming and coworkers reported two piperazine-bridged aluminum salan complexes for ε-CL [10]. Polymerizations showed a slight improvement in control (Đ = 1.17–1.89), although lower dispersities corresponded to very low conversions. Jones and coworkers have also studied aluminum salan complexes for ε-CL ROP [11]. Five homopiperazine-bridged aluminum salan complexes were tested with broad molecular weight distributions seen in most cases. Low dispersity was obtained for one catalyst, though only low conversion was achieved. Feijen has studied the polymerization of ε-CL as well as two methyl-substituted derivatives (Fig. 2, 4-methyl-ε-caprolactone, 4-Me-ε-CL and 6-methyl-ε-caprolactone, 6-Me-ε-CL) using a chiral aluminum complex based on Jacobsen's ligand [12]. Polymerization of ε-CL was found to have moderate dispersity control (1.21) with molecular weight nearly double the theoretical value. This report suggested a surprisingly rapid polymerization, reaching 96% conversion after just 2.5 h at 90 °C. Switching the monomer to 4-Me-ε-CL resulted in an increased reaction time and less control. When the methyl group is closer to the active site of ring-opening in 6-Me-ε-CL, reaction times are increased even longer: well-controlled polymerization of 6-Me-ε-CL required 336 h to reach high conversion (96%).

With this in mind, we herein investigate MeAl[salen] and MeAl[salan] in the ROP of a range of aliphatic polyesters and show that, under optimized reaction conditions, they are exceptional catalysts for the ROP of a variety of ε-CLs and δ-VL to produce well-controlled polymers.

2. Experimental procedures

Representative living polymerization: In a glovebox, ε-CL (234 mg, 2.04 mmol), MeAl[salen] (11.2 mg, 0.02 mmol) and BnOH (2.1 μL, 0.02 mmol) were added to an ampoule in 1.5 mL toluene. The ampoule was sealed, and placed in a preheated oil bath at 70 °C for six hours. After six hours, 0.5 mL of a 10% MeOH in CH_2Cl_2 solution was added to the ampoule and the solution was allowed to stir and cool to room temperature. A crude sample was removed and concentrated for ^{1}H NMR spectroscopic analysis. The remaining solution was added dropwise to stirring cold MeOH. The precipitate was collected by filtration and dried under reduced pressure to constant weight. ^{1}H NMR analysis indicated >98% conversion and GPC analysis indicated M_n = 8990 ($M_{n,th}$ = 11,520) and Đ = 1.39. Polymerizations of substituted caprolactones were set up similarly with appropriate temperatures, concentrations and reaction times.

NMR data for the known polymer products matched previous literature reports [12,13].

Poly(4-(4-benzyloxybutyl)caprolactone): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (m, 4H, *o*-,*m*-Ar*H*), 7.26 (m, 1H, *p*-Ar*H*), 4.48 (s, 2H, OCH_2Ph), 4.02 (m, 2H, $CH_2CH_2CH_2O$), 3.44 (bt, 2H, $CH_2CH_2CH_2O$), 2.22 (bd, 2H, C(O)CH_2CH), 1.87 (m, 1H, C(O)CH_2C*H*), 1.59 (m, 4H), 1.33 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.27, 138.81, 128.50, 127.50, 127.64, 73.04, 70.39, 64.62, 39.04, 34.79, 33.70, 30.22, 30.11, 25.98, 23.33.

Representative immortal polymerization: In a nitrogen filled glovebox, ε-CL (114 mg, 1.0 mmol), MeAl[salen] (0.2 mg, 4×10^{-4} mmol) and BnOH (1.0 μL, 1.0 mmol) were added to toluene (600 mg). The solution was added to an ampoule and removed from the glovebox. ^{1}H NMR spectroscopy of crude aliquots was used to monitor the reaction. Once the polymerization had reached 95% monomer conversion, 0.5 mL of a 10% MeOH in CH_2Cl_2 was added to quench polymerization. The solution was then added dropwise to cold methanol and the precipitate was filtered and dried until constant weight.

NMR scale polymerization for reaction kinetics: In a glovebox, ε-CL (109 mg, 0.94 mmol), MeAl[salen] (5.4 mg, 0.01 mmol) and BnOH (1.0 μL, 0.01 mmol) were dissolved in 0.6 mL C_6D_6 and added to a Young's tap NMR tube and sealed and placed in a preheated oil bath (at desired temperature, if desired). The NMR tube was then analyzed at various time points to determine conversion. Once the reaction was complete, the solution was added to stirring cold MeOH and the precipitate was removed by filtration and dried under reduced pressure to constant weight. GPC analysis was then performed on the purified polymer.

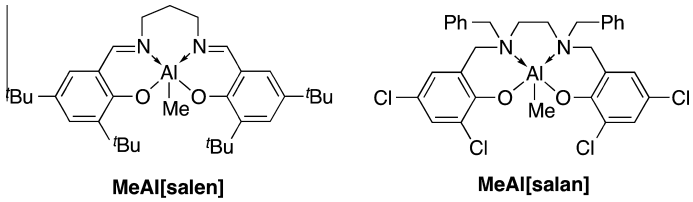

Fig. 1. Structure of MeAl[salen] and MeAl[salan] precatalysts.