

Highly Branched Poly(α -Methylene- γ -Butyrolactone) from Ring-Opening Homopolymerization

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Abstract

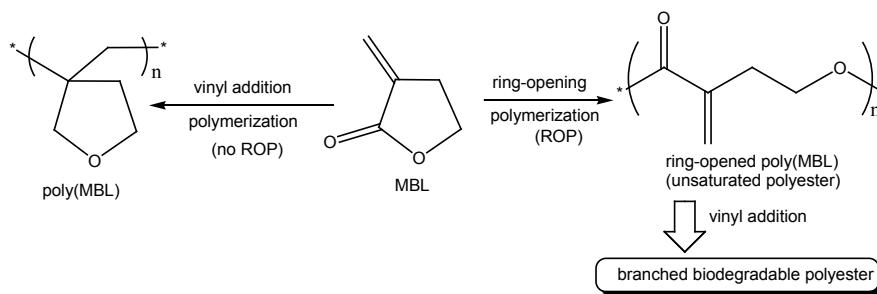
New heteroleptic lanthanide complex $[L^{III}LaN\{Si(CH_3)_2\}]$ (**1**) containing tridentate [ONO] ancillary ligand was synthesized from an acid-base ligand exchange reaction with ligands H_2L^I and corresponding homoleptic lanthanide compound $La[N\{Si(CH_3)_2\}_3]$. Meanwhile, dimeric complexes $[L^I LaCl]$ (**2**) and $[L^{III} LaCl]$ (**3**) were prepared from salt metathesis reaction between one equivalent of ligands H_2L^{III} , three equivalent of $NaN\{Si(CH_3)_2\}_3$ and one equivalent of $LaCl_3$. These compounds were characterized by nuclear magnetic resonance (300 MHz) and elemental analysis. These complexes were used as catalysts in the ring-opening homopolymerization of α -methylene- γ -butyrolactone. While compound **1** did not show any significant reactivity, compounds **2** and **3** gave significant amount of highly branched poly(α -methylene- γ -butyrolactone) as confirmed by 1H NMR spectroscopy and Malvern's triple detector GPCMax analysis in DMSO with molecular weights of over 500,000 Dalton. The glass-transition temperatures of the branched polymer samples were determined using a Dynamic Mechanical Analyzer, DMA Q800.

Keywords

Lanthanide, α -Methylene- γ -Butyrolactone, Polyesters, Ring-Opening Polymerization

1. Introduction

Due to their good mechanical properties, hydrolyzability and biocompatibility, aliphatic saturated polyesters have been extensively investigated with great applications in packaging, drug delivery and medical implantation devices [1]-[10].



The best and most reliable method of synthesizing high molecular weight polyesters is via ring-opening polymerization (ROP) of lactones with a relatively high strain energy using metal initiators for chain-growth polymerization [11]-[35].

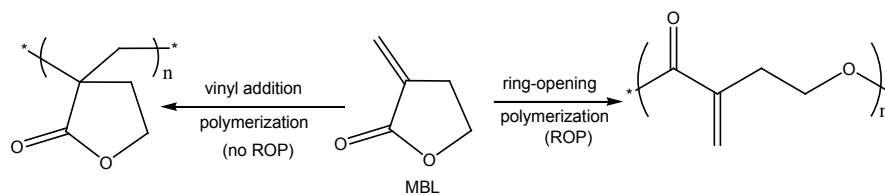
Unsaturated polyesters are of high scientific and technological interest for producing tailor-made functionalized biodegradable materials of commercial importance [36] [37] [38]. Preferably, they are easily synthesized via ring-opening polymerization (ROP) of unsaturated lactones [38]. α -Methylene- γ -butyrolactone (α -MBL), also known as Tulipaline A, has received much interest in the synthesis of sustainable unsaturated polyesters since it is the simplest member of a class of naturally occurring sesquiterpene lactones found in tulips [37]-[46]. α -MBL can also be produced chemically from biomass feed stocks making it naturally renewable [47]. When polymerized, α -MBL can either undergo vinyl addition polymerization at the highly reactive exocyclic double bond or ROP of the γ -butyrolactone (γ -BL) five-membered ring (Scheme 1). γ -BL is non-polymerizable due to its low strain energy [48] [49] [50] [51].

Because vinyl-addition is favored over ring-opening at room temperature due to the stability of five membered rings, special conditions and reagents must be used to favor the ring-opening polymerization. In fact, ring-opening copolymerization of α -MBL and other highly strained lactones to obtain unsaturated polyesters have been reported [39] [42] [46]. However, the ring-opening homopolymerization of α -MBL has not been reported in the literature. Herein, we report the ring-opening homopolymerization of α -methylene- γ -butyrolactone into highly branched polyester using heteroleptic lanthanide initiators at 0°C.

2. Experimental Procedure

2.1. Materials and Measurements

All air- or moisture-sensitive reactions were carried out under a dry nitrogen atmosphere, employing standard Schlenk line and glovebox techniques. Anhydrous solvents were purchased and used as received under nitrogen. α -MBL was purchased from Acros, stored under an inert atmosphere, and used as received. Deuterated solvents were purchased from Alfa Aesar and used as received. 3,5-di-tert-butyl-2-hydroxybenzaldehyde was purchased from Alfa Aesar while (*R*)-2-phenylglycinol was purchased from Acros Organic and used as



Scheme 1. Vinyl addition polymerization versus ROP of MBL.

received. (*L*)-Valinol[(*S*)-(+)-2-Amino-3-methyl-1-butanol] was purchased from TCI and used as received. All ^1H and ^{13}C NMR spectra were recorded on a JEOL-300 NMR spectrometer and referenced to CDCl_3 , C_6D_6 or $\text{C}_4\text{D}_8\text{O}$. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Optical rotations were recorded on a Rudolph Autopol III polarimeter with sodium D-line (589 nm) at room temperature. GC-MS analyses were performed on Bruker Scion 436-GC systems at 50°C with electron impact ionization (70 eV). Gel permeation chromatography (GPC) analyses were performed using Malvern Malvern Viscotek GPCMax TDA 305 triple detection system (refractive index, right angle light scattering, and viscometer). Thermal analysis was done using TA Walters DMA Q800.

2.2. Synthesis of Ligands

2.2.1. (*R*)-(+)-2-Phenyl-2-Imino-1-Ethanol-2,4-Di-Tert-Butyl-Phenol (H_2L^1)

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (4.00 g, 0.017 mol), and (*R*)-(+)-2-phenylglycinol (2.33 g, 0.017 mol) were dissolved in methanol (50 mL). The resulting solution was heated at reflux for 18 h and then cooled to room temperature. Solvent and water were removed using high vacuum Schlenk line to obtain yellow oil. The ligand was purified by column chromatography using hexane-ethyl acetate mixture (9:1) (5.56 g, 92.5 %). $[\alpha]_{\text{D}} + 0.332$ ($c = 0.005$, toluene). Elemental analysis: (Found: C 76.80, H 9.12, N 3.16. $\text{C}_{23}\text{H}_{31}\text{NO}_2$ requires C 78.15, H 8.84, N 3.96%). ^1H NMR (300 MHz; CDCl_3 ; 298 K) 1.36 (s, 9H, Ar^tBu), 1.49 (s, 9H, Ar^tBu), 3.96 (br, 2H, $\text{ArCH}=\text{NCH}(\text{Ph})\text{OH}$), 4.50 (br, 1H, $\text{ArCH}=\text{NCH}(\text{Ph})\text{CH}_2\text{OH}$), 7.18 (s, 1H, ArH), 7.36 (s, 1H, ArH), 7.40 - 7.48 (br, 5H, ArH), 8.56 (s, 1H, $\text{ArCH}=\text{N}$), 9.81 (s, 1H, ROH), 11.62 (s, 1H, ArOH). GC-MS m/z calcd for $\text{C}_{23}\text{H}_{31}\text{NO}_2$: 353.51; found 353.5.

2.2.2. (*S*)-(+)-3-Methyl-2-Imino-1-Butanol-2,4-Di-Tert-Butyl-Phenol (H_2L^{11})

3,5-Di-tert-butyl-2-hydroxybenzaldehyde (3.00 g, 0.013 mol), and *L*-valinol [(*S*)-(+)-2-Amino-3-methyl-1-butanol] (1.32 g, 0.013 mol) were dissolved in methanol (50 mL). The resulting solution was heated at reflux for 18 h and then cooled to room temperature. Solvent and water were removed using high vacuum Schlenk line to obtain yellow oil. Recrystallization from methanol at -10°C (freezer) yielded yellow solid (4.025 g, 98.4%). Mp: $103.9^\circ\text{C} - 104.0^\circ\text{C}$; $[\alpha]_{\text{D}} + 0.006$ ($c = 0.005$, toluene). Elemental analysis: (Found: C 75.32, H 10.16,

N 4.58. $C_{20}H_{33}NO_2$ requires C 75.19, H 10.41, N 4.38 %). 1H NMR (300 MHz; $CDCl_3$; 298 K) 0.95 (dd, 6H, $J = 6.51$ Hz, $MeCHMe$) 1.32 (s, 9H, Ar^tBu), 1.44 (s, 9H, Ar^tBu), 1.93 (m, 1H, $J = 6.51$ Hz, $MeCHMe$), 3.03 (br, 2H, $ArCH=NCH(^iPr)CH_2OH$), 3.80 (br, 1H, $ArCH=NCH(^iPr)CH_2OH$), 7.14 (s, 1H, ArH), 7.42 (s, 1H, ArH), 8.38 (s, 1H, $ArCH=N$), 9.87 (s, 1H, ROH), 11.65 (s, 1H, $ArOH$). $^{13}C\{H\}$ NMR (75 MHz; $CDCl_3$; 298 K) 18.9 ($ArCMe_3$), 19.9 ($ArCMe_3$), 29.5 ($ArCMe_3$), 30.2 ($MeCHMe$), 31.6 ($ArCMe_3$), 34.3 ($MeCHMe$), 35.1 ($ArCH=NCH(^iPr)CH_2OH$), 64.8 ($ArC=NCH(^iPr)CH_2OH$), 117.8, 126.3, 127.3, 136.8, 140.3, 158.2 (all ArC), 167.2 ($ArCH=N NCH(^iPr)CH_2OH$). GC-MS m/z calcd for $C_{20}H_{33}NO_2$: 319.49; found 319.4.

2.3. Synthesis of Lanthanide Complexes

2.3.1. $[L^{II}LaN\{Si(CH_3)_3\}_2]THF(1)$

A 50 mL Schlenk flask was obtained and dried in the oven. To a colorless THF solution (20 mL) of $La[N(SiMe_3)_2]_3$ (0.25 g, 0.40 mmol) at $-50^\circ C$ (acetone/dry ice mixture), a clear yellow toluene solution (10 mL) of ligand H_2L^{II} (0.128 g, 0.40 mmol) was added drop-wise under nitrogen using a Schlenkline. The resulting orange solution was stirred gently for 4 hours. Volatiles were removed *in vacuo* without heating to afford an orange-yellow solid that was dried under high vacuum to afford compound **1** (0.109 g, 44.80%); Mp: $184^\circ C$; $[\alpha]_D -0.026$ ($c = 0.01$, toluene). Elemental analysis: (Found: C 52.00, H 7.39, N 3.74. $C_{30}H_{57}N_2O_3Si_2La$ (**1**) requires C 52.31, H 8.34, N 4.07 %). 1H NMR (300 MHz; C_4D_8O ; 298 K) 0.2 ppm (br, 18H, $-N[Si(CH_3)_3]_2$), 0.9 ppm (d, 6H, $-CH(CH_3)_2$), 1.5 ppm (s, 9H, $-(CH_3)_3$), 1.7 ppm (s, 9H, $-(CH_3)_3$), 2.0 ppm (m, 1H, $NCH(^iPr)CH_2O$), 3.2 ppm (m, 1H, $NCH(^iPr)CH_2O$), 3.7 ppm (m, 2H, $NCH(^iPr)CH_2O$), 7.3 ppm (s, 1H, ArH), 7.5 ppm (s, 1H, ArH), and 8.2 ppm (s, 1H, $Ar-CH=N$).

2.3.2. $[L^I LaCl](2)$

A 100 mL Schlenk flask was obtained and dried in the oven. To a colorless THF solution (20 mL) of $NaN(SiMe_3)_2$ (0.77 g, 4.20 mmol) at room temperature, a clear yellow toluene solution (10 mL) of ligand H_2L^I (0.50 g, 1.40 mmol) was added drop-wise under nitrogen using a Schlenkline. The resulting orange-yellow solution was stirred gently for 4 hours. $LaCl_3$ (0.34 g, 1.40 mmol) was added and the solution was refluxed overnight at $78^\circ C$. White precipitate of $NaCl$ was visible at bottom of flask. The supernatant clear greenish-yellow solution was decanted into another Schlenk flask. Volatiles were removed *in vacuo* to afford a greenish-yellow solid, which was further extracted with hexanes and dried under high vacuum to afford compound **2** (0.332 g, 42.86%); Mp: $170^\circ C$; $[\alpha]_D + 0.008$ ($c = 0.01$, toluene). Elemental analysis: (Found: C 51.79, H 6.01, N 2.21. $C_{23}H_{29}NO_2LaCl$ (**2**) requires C 52.53, H 5.56, N 2.66 %). 1H NMR (300 MHz; C_4D_8O ; 298 K) 1.16 (br, 9H, Ar^tBu), 1.35 (br, 9H, Ar^tBu), 2.95 (br, 2H, $ArCH=NCH(Ph)CH_2O$), 4.37 (br, 1H, $ArCH=NCH(Ph)$), 6.85 (s, 1H, ArH), 7.32 - 7.38 (br, 5H, ArH), 7.84 (br, 1H, ArH), 8.58 (s, 1H, $ArCH=N$).

2.3.3. [L^{II}LaCl] (**3**)

A 100 mL Schlenk flask was obtained and dried in the oven. To a colorless THF solution (20 mL) of NaN(SiMe₃)₂ (0.88 g, 4.80 mmol) at room temperature, a clear yellow toluene solution (10 mL) of ligand H₂L^{II} (0.5 g, 1.6 mmol) was added drop-wise under nitrogen using a Schlenk line. The resulting orange-yellow solution was stirred gently for 4 hours. LaCl₃ (0.39 g, 1.6 mmol) was added and the solution was refluxed overnight at 78 °C. White precipitate of NaCl was visible at bottom of flask. The supernatant clear greenish-yellow solution was decanted into another Schlenk flask. Volatiles were removed *in vacuo* to afford a greenish-yellow solid, which was further extracted with hexanes and dried under high vacuum to afford compound **3** (0.324 g, 41.25%); Mp: 180 °C; [α]_D + 0.003 (c = 0.01, toluene). Elemental analysis: (Found: C 49.39, H 7.06, N 2.81. C₂₀H₃₁NO₂LaCl (**3**) requires C 48.84, H 6.35, N 2.85 %). ¹H NMR (300 MHz; C₄D₈O; 298 K) 1.0 ppm (br, 6H, -CH(CH₃)₂), 1.2 ppm (s, 9H, -(CH₃)₃), 1.4 ppm (s, 9H, -(CH₃)₃), 2.3 ppm (br, 1H, NCH(ⁱPr)CH₂O), 2.9 ppm (br, 1H, NCH(ⁱPr)CH₂O), 3.4 ppm (m, 2H, NCH(ⁱPr)CH₂O), 7.2 ppm (s, 1H, ArH), 7.3 ppm (s, 1H, ArH), and 8.4 ppm (s, 1H, Ar-CH=N).

1) General polymerization procedure

All materials were prepared in a glovebox and all reactions (air- and moisture-sensitive) were carried out in flamed Schlenk-type glassware on a Schlenk line. The monomer/initiator ratio employed was 500:1. In a 25 ml flame dried Schlenk flasks, 1.0 g of the monomer (α -methylene- γ -butyrolactone) was added to the calculated ratio of the catalyst along with 8.0 ml of DMSO. The polymerization reaction was maintained at 0 °C using acetone and ice. After the desired reaction time, the reaction was quenched with 2.0 ml of 5% acidified methanol (HCl/MeOH) and the solid was allowed to precipitate in the freezer (-15 °C) overnight. The white polymer product was filtered, dried and characterized by ¹H NMR spectroscopy (d₆-DMSO), Gel Permeation Chromatography (DMSO) to obtain polymer microstructure, and molecular weights (M_n and M_w), respectively. Thermal analyses of polymer were done using DMA Q800 to obtain Tg.

2) Gel Permeation Chromatography (GPC) data procedure

GPC analyses were performed on a Malvern Viscotek GPCMax TDA 305 triple detection system (RI, RALS, and viscometer) using a two mixed bed D6000M columns. Dimethyl Sulfoxide (DMSO) was used as the dissolution solvent and mobile phase at a flow rate of 0.75 mL·min⁻¹. The temperature of the detectors and columns were set at 50 °C. The calibration method used was triple detection. Samples were dissolved at concentration between 1 - 5 mg/mL and dissolved overnight. Allowing for dissolution overnight, the samples were not fully in solution, so heat at 50 °C for 1 hour was applied and the samples were allowed to cool. Samples were filtered through a 0.2 μ m Nylon syringe filter prior to analysis.

3) Dynamic Mechanical Analyzer (DMA) data procedure

Melting temperature, T_m, of polymer samples was done using melting point apparatus while glass transition temperature was obtained using TA Walters

Dynamic Mechanical Analyzer, DMA Q800. Tg was obtained as Tan Delta value from DMA Q800 Multi-Frequency-Strain Mode using a powder clamp Temperature Ramp method mounted onto a dual cantilever at 3.00°C /min from 25°C to 150°C and 20.00 µm Amplitude.

3. Results and Discussion

3.1. Synthesis of Ancillary Ligands

This project discusses the synthesis of cross-linked biodegradable polyesters using new heteroleptic lanthanide catalytic system with three main components LLaX: where L is a chiral dianionic multidentate ancillary ligand, H_2L^I and H_2L^{II} (see **Figure 1**), La is a highly electropositive trivalent lanthanum metal and X is an initiator (trimethylsilylamide, chloride) that initiates ring-opening of cyclic ester monomer. In order to initiate ROP, the initiating group, X, must be a good nucleophile and monodentate with labile coordination to lanthanide. The ancillary ligand, L, is to stabilize the metal catalyst during ROP as it remains bound to the lanthanide metal during coordination–insertion mechanism for ROP of lactones.

Newly synthesized ligands H_2L^I and H_2L^{II} (**Figure 1**) will be employed as L component in the catalytic system LLaX [41] [49] [50] [51] [52] [53]. Deprotonation of phenolic hydrogens in H_2L^I and H_2L^{II} will afford dianionic multidentate ancillary ligands with different steric and electronic demands. The ligands were synthesized *via* Mannich condensation reactions using 3,5-Di-tert-butyl-2-hydroxybenzaldehyde and chiral auxiliary, (*R*)-(+)-2-phenylglycinol (H_2L^I) and [(*S*)-(+)-2-Amino-3-methyl-1-butanol (H_2L^{II})] (**Scheme 2**). The synthesized ligands were characterized by NMR, and elemental analysis.

3.2. Synthesis of Lanthanide Complexes

Attachment of ligands H_2L^I and H_2L^{II} to homoleptic lanthanum amide offers new heteroleptic metal complexes for metal catalyzed ring-opening polymerization of MBL. A diverse array of synthetic strategies for the different catalyst precursors is proposed from ligand exchange reactions (see **Scheme 3**) to salt elimination metathesis (see **Scheme 4**). The synthesis of catalysts *via* acid–base ligand exchange reaction (**Scheme 3**) offers a superior, cleaner approach over

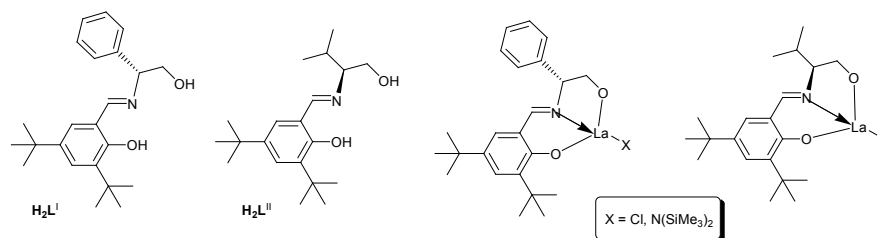
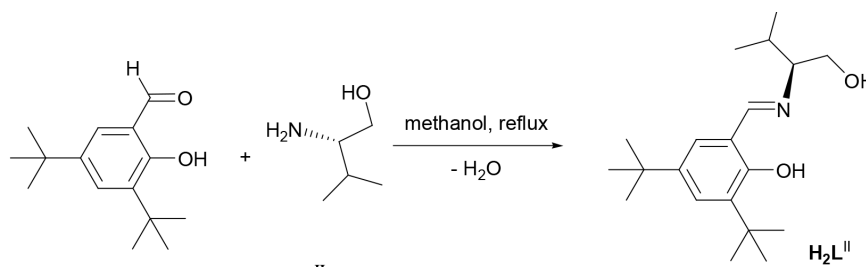
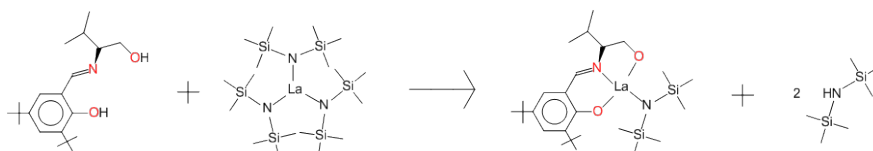


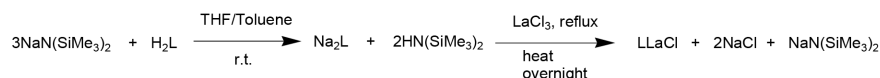
Figure 1. New [ONO] ancillary phenolate ligands and intended heteroleptic Lanthanide Catalyst System showing catalytic pocket around metal coordination site.



Scheme 2. Synthesis of ligand H_2L^{II} via condensation reaction.



Scheme 3. Synthesis of compound **1** via ligand exchange reactions.



Scheme 4. Synthesis of $LLaCl$ catalyst via salt metathesis reactions.

salt metathesis reactions (**Scheme 4**) since the by-products from acid-base reactions can be readily removed, making it easier to obtain analytically pure compounds.

New lanthanum compound **1** was synthesized using homoleptic $La\{N(SiMe_3)_2\}_3$ and ligand H_2L^{II} in toluene and THF to afford $[L^{II}LaN\{Si(CH_3)_3\}_2] THF$ **1** (**Scheme 3**). The synthesized heteroleptic lanthanum compound was fully characterized by NMR spectroscopy, elemental analysis and melting point (see experimental). Meanwhile, compounds **2** and **3** were isolated via salt metathesis reaction using one equivalent of ligands H_2L^{II} , three equivalent of $NaN\{Si(CH_3)_3\}_2$, and one equivalent of $LaCl_3$ in refluxing THF for 18 h (**Scheme 4**). The goal was to synthesize the amido compounds but heterolepticlanthanide chloride was isolated presumably as slight amount of water from the 99% dry THF solvent must have reacted with some of the sodium amide. 1H NMR spectroscopy of compound **1** in d_8 -THF(C_4D_8O) revealed one L^{II} molecule and asilylamide ligand (**Figure 2**) while NMR spectroscopy of **2** and **3** in d_8 -THF(C_4D_8O) also confirmed their formulation. This was supported by elemental analysis results and chloride test. Compound **1** gave a negative chloride test while **2** and **3** gave white precipitate with $AgNO_3$ indicative of the presence of chloride. It was very difficult to isolate good single crystals for X-ray determination.

3.3. Ring-Opening Homopolymerization of MBL Using New Lanthanide Complexes

Unsaturated aliphatic polyesters, which can be synthesized from ROP of naturally available α -methylene- γ -butyrolactone (MBL), are of scientific and

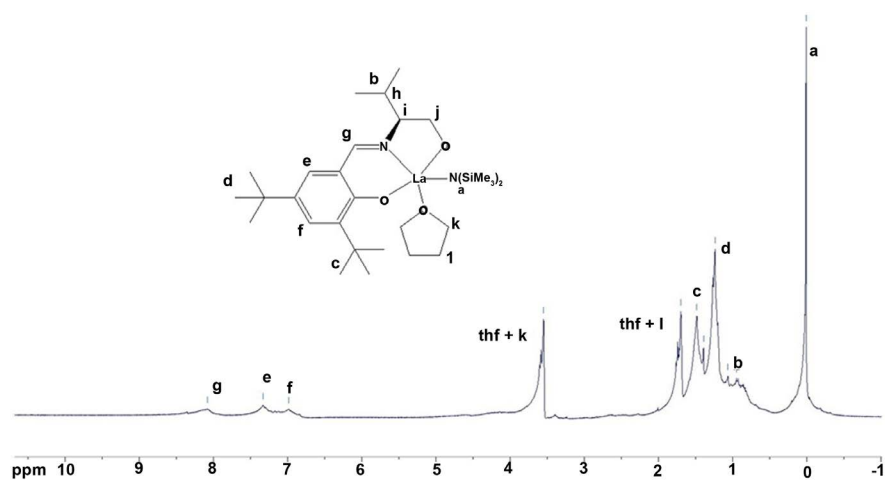
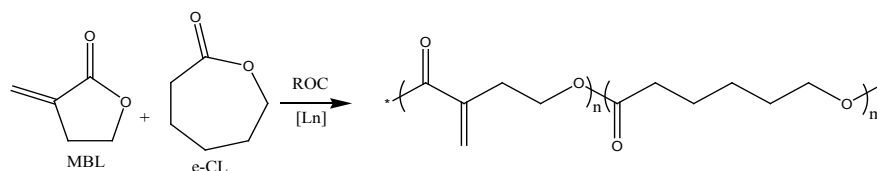


Figure 2. ^1H NMR of $\text{L}^{\text{II}} \text{La}(\text{NSiMe}_3)_2 \text{THF}$ (**1**) in $\text{d}_8\text{-THF}$.

technological interest for producing tailor-made functionalized biodegradable shape memory materials. The unfavorable thermodynamics involved in the ROP of MBL results in too small negative change of enthalpy (ΔH) to offset a large negative entropy change (ΔS). As a result, MBL prefers vinyl addition polymerization to ROP.

Hong and Chen recently reported the first Ring-Opening Copolymerization (R $^\circ$ C) of MBL with ϵ -caprolactone (ϵ -CL) catalyzed by homoleptic lanthanide tris(bistrimethylsilyl)amide $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$, that produced exclusively an unsaturated copolyester PMBL-co-PCL (**Scheme 5**) [42]. Despite the non-homopolymerizability of unsaturated gamma lactones toward ring-opening polymerization due to the relative low ring-strain energy (high thermodynamic stability) of its five-membered ring, copolymerization with ϵ -CL using lanthanide coordination catalytic system, coupled with appropriate reaction conditions (relatively nonpolar solvent and low temperature at 0°C to -20°C) was an effective way of shutting down the vinyl-addition pathway *via* conjugate addition across the ex Cyclic C=C double bond (ring retention). After carrying out extensive investigations, Hong and Chen also reported that non polar solvents such as toluene was able to suppress the competing vinyl-addition polymerization while copolymerization with a high strain lactone and low reaction temperature favored ROP of the five-membered unsaturated lactones [42]. Using similar reaction conditions with newheteroleptic lanthanide complexes LLaX using the ligands $\text{H}_2\text{L}^{\text{I}}$ and $\text{H}_2\text{L}^{\text{II}}$, ring-opening polymerization of MBL was achieved. Homoleptic LnX_3 such as $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ has shown to catalyze ROP very rapidly without any polymerization control due to lack of a stabilizing ancillary ligand such as $\text{H}_2\text{L}^{\text{I}}$ and $\text{H}_2\text{L}^{\text{II}}$, and as a result form competing vinyl-addition polymerization and ROP (**Scheme 1**) where copolyester PMBL-co-PCL recorded high molecular weight distribution with polydispersity up to 2.77 [42]. The high Lewis acidity and coordination number of the lanthanides (desirable for monomer coordination and activation) and the high nucleophilicity of amides and alkoxides (desirable

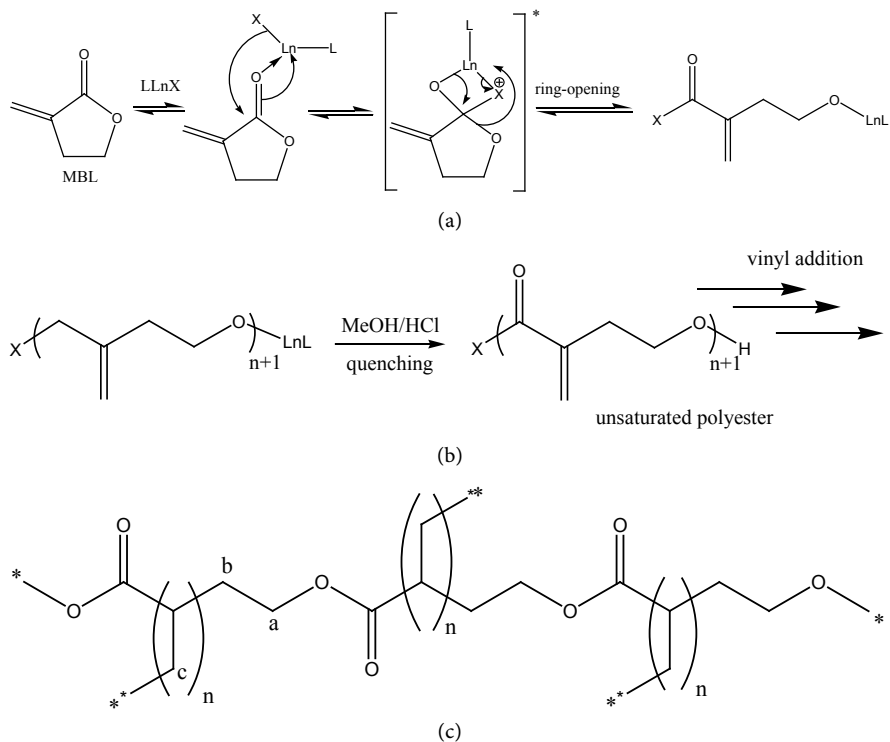


Scheme 5. Ring Opening Copolymerization (ROC) of MBL and ϵ -CL to form PMBL-co-PCL.

for chain initiation) is illustrated in the mechanism presented in **Scheme 6**.

Compounds **1**, **2**, and **3** were treated with MBL and the results are summarised in Table 1 below. All polymerization reactions were performed in DMSO at 0°C. Entry 1 is the control reaction which shows no polymerization, even after 24 h. Furthermore, there was no polymer formation with compound **1** after 1 hour which is probably due to slow initiation process as a result of bulky amide-group and non-polymerizability of MBL (**Table 1**, entry 2). However, compound **2** and **3** gave significant polymer formation after 1 hour (**Table 1**, entries 3 - 4). All polymerization reactions were quenched with acidified methanol. Due to high solubility of this polymer in DMSO, the reaction flask was kept in freezer overnight to allow precipitation of the white PMBL product. This reactivity suggests that the chloride is better at initiating ROP of MBL than the bulky amide. ¹H NMR analysis of the polymer obtained showed that the methylene protons of exocyclic C=C bond at 5.7 ppm and 6.0 ppm were significantly absent indicative of vinyl addition reactions to form branched polymer (see **Figure 3**).

GPC analysis of the polymer obtained supports highly branched polyester with a very high molecular weight, about 25 times larger compared to the expected linear unsaturated polyester. The hydrodynamic volume was also very large. Because these compounds were so large compared to expected linear polymers and to ensure reproducibility in analysis since these polymers are novel, a comparison of the samples was repeated with a 73 kDa Dextran polymer standard at different concentrations and the following chromatograms were obtained showing similar molecular weight as previously analyzed (see **Figure 4**). All these samples displayed a much larger hydrodynamic size than the 73 kDa Dextran standard. Sample #2 (**Table 1**, entry 4) showed higher molecular weight of 754 kDa while sample #1 gave 577 kDa (**Table 1**, entry 3). Both polymeric samples gave a narrow polydispersity of 1.3. The GPC was analyzed using Malvern Viscotek GPCMax triple detector system (refractive index, light scattering and viscometer) which has been proven to successfully determine the absolute molecular weight of polymeric materials. The only explanation to the large molecular weight is the production of highly branched polymer through vinyl addition of the C=C double bonds bringing many linear PMBL polymers into one unit. This is supported by ¹HNMR spectra of the polymers, which showed a significant reduction and in some cases disappearance of the exocyclic CH=CH double bond proton signals. This also explains the difficulty in solubility of these branched polymers. Due to its higher molecular weight, sample #2 gave higher



Scheme 6. Proposed Mechanism for ROP of MBL.

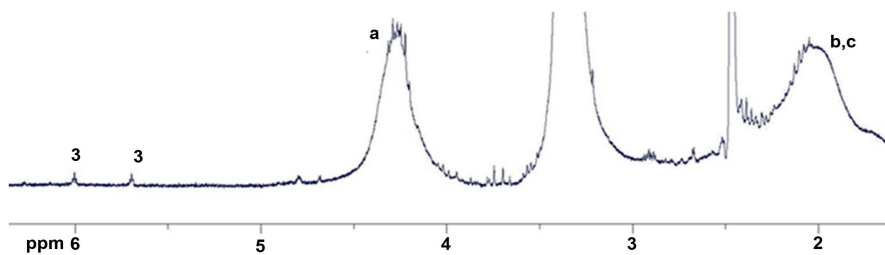


Figure 3. ^1H NMR of PMBL (Table 1, entry 3) in d_6 -DMSO.

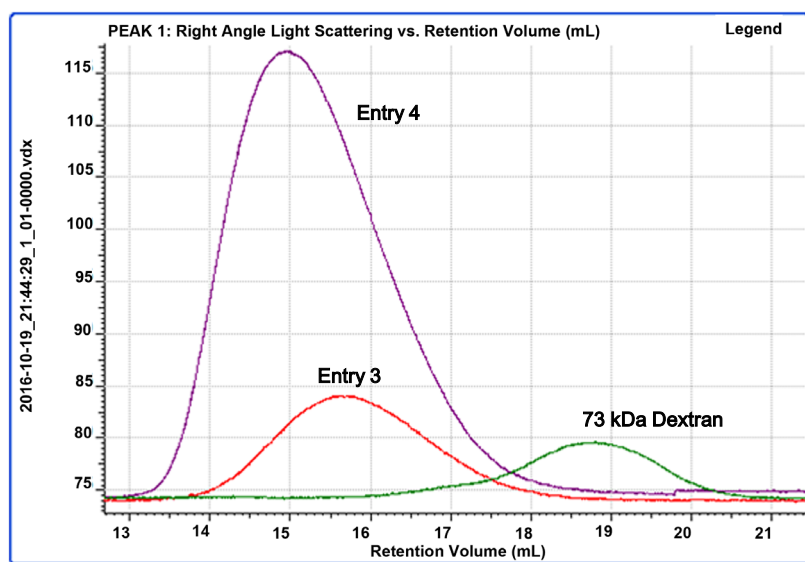


Figure 4. GPC Data of newly synthesized branched PMBL.

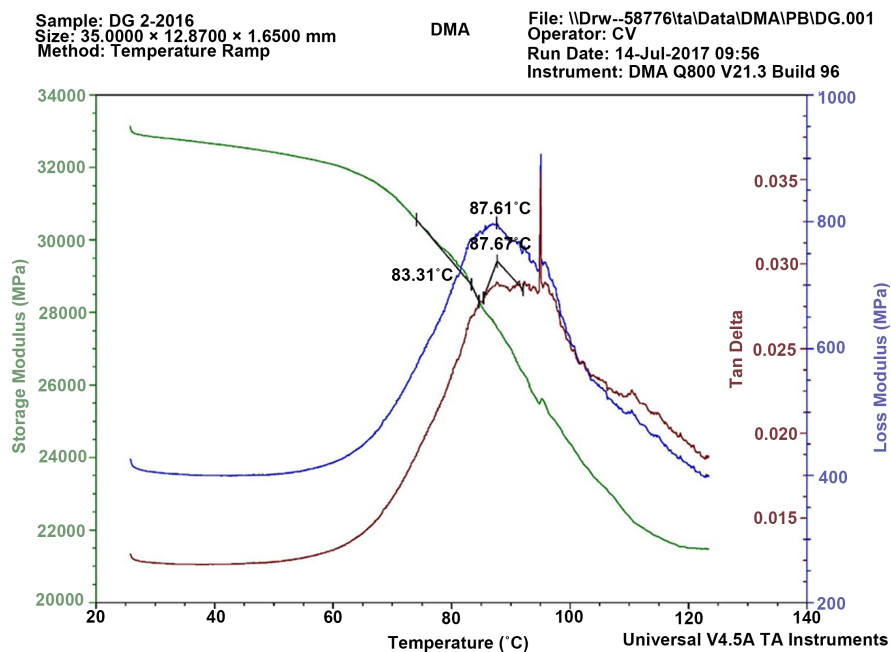


Figure 5. DMA Data of newly synthesized branched PMBL showing T_g values for entries 3.

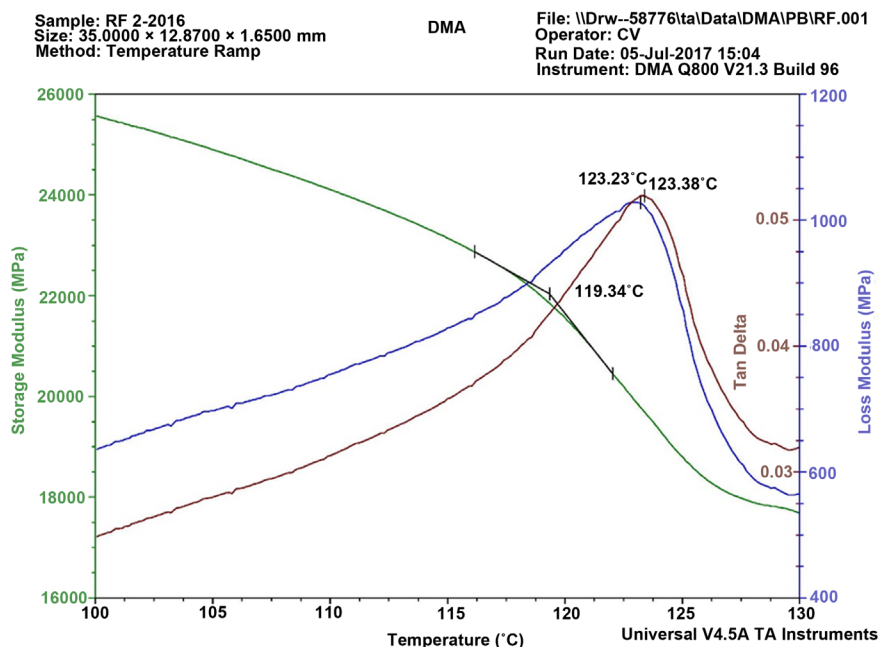


Figure 6. DMA Data of newly synthesized branched PMBL showing T_g values for entries 4.

melting and glass transition temperatures than sample #1 (**Figure 5** and **Figure 6**). The T_g for sample #1 was 87.61 °C while that for sample #2 was 123.38 °C.

4. Conclusion

New heteroleptic lanthanide complexes supported by newly synthesized tridentate dianionic [ONO] aminophenolate ligands were characterized by NMR and

Table 1. Polymerization of MBL using La complexes at 0 °C.

Entry	Initiator	[MBL]/[I] ^a	Solvent	Time (min)	Yield (g)	M _w (kDa) ^b	M _n (kDa) ^b	PDI ^b	T _m (°C)	T _g (°C)
1	None	-	DMSO	120	0	-	-	-	-	-
2	[L ^{II} LaN{Si(CH ₃) ₃ } ₂]/THF (1)	500	DMSO	120	0	-	-	-	-	-
3	[L ^I LaCl] (2)	500	DMSO	120	0.185	577	430	1.34	110	87.61
4	[L ^{II} LaCl] (3)	500	DMSO	120	0.100	754	570	1.32	199	123.38

^a: Monomer to initiator ratio. ^b: M_w and M_w/M_n (PDI) of polymer determined by GPC; PDI = polydispersity index.

elemental analysis. We also report for the first time, the ring-opening homopolymerization of α -methylene- γ -butyrolactone into highly branched polyester using lanthanide initiators at 0 °C. GPC analysis of the newly synthesized branched polymer gave large molecular weight above 500,000 g/mol and a narrow polydispersity of 1.3. The glass-transition temperatures of the polymer samples were recorded at 87.61 °C and 123.38 °C using a Dynamic Mechanical Analyzer, DMA Q800. The newly synthesized polyester is suitable candidates for medical implantation devices and shape memory materials.

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