Synthesis and characterization of bisphenol sodium complexes: An efficient catalyst for the ring-opening polymerization of L-lactide

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ABSTRACT

Two sodium complexes, $[(\mu_3\text{-MDBP})\text{Na}_2(\text{THF})_2]_2[(\mu_3\text{-OCH}_2\text{CH}_2\text{OCH}_3)\text{Na}]_2$ (**1**) and $[(\mu_1\text{-MDBP})\text{Na}(\mu_2\text{-H}_2\text{O})(\text{THF})]_2(\text{THF})_2$ (**2**) have been synthesized and structurally characterized. Experimental results show that complex **1** initiates efficiently the ring opening polymerization of L-lactide in a controlled fashion, yielding polymers with narrow polydispersity indexes in a wide range of monomer-to-initiator ratios.

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Currently, polyesters such as polylactide (PLA) and poly(ϵ -caprolactone) (PCL) are of the most important synthetic biodegradable and biocompatible polymers due to their wide range of biomedical and pharmaceutical applications such as controlled drug delivery, resorbable sutures, medical implants, and scaffolds for tissue engineering [1]. An effective method for the synthesis of PLA and PCL is the ring-opening polymerization (ROP) of related cyclic esters, [2] where metal alkyls, [3] amides, [4] thiolates, [5] aryl oxides, [6] alkoxides [7] and enolates [8] in the presence or absence of alcohol have been used as initiators. Among them, single-site metal alkoxides have the highest activity with a good control over the polymer molecular weight [7].

Metal complexes supported by a variety of ligands such as bisphenol, β -diketiminates, salen, and many others have been developed and used as catalytic/initiating systems for ROP of lactide. And many metal complexes, such as lithium, sodium, magnesium, aluminum, zinc, stannous and trivalent lanthanide derivatives [9] have been reported to be effective initiators of ROP of lactones/lactides giving polymers with both high molecular weights and high yields. However, the cytotoxicity and difficulties in removal of the catalyst from the resulting polymer have limited their utilization when a medical-grade polymer is required. Among these metals, sodium is non-toxic and essential for human life, [10] therefore, sodium complexes are good candidates as catalysts/initiators in the preparation of biomedical grade PLA. However, the reactivity of sodium complexes [11] has barely received

attention. Here, we report synthesis, characterization two novel sodium complexes $[(\mu_3\text{-MDBP})\text{Na}_2(\text{THF})_2]_2[(\mu_3\text{-OCH}_2\text{CH}_2\text{OCH}_3)\text{Na}]_2$ (**1**) and $[(\mu_1\text{-MDBP})\text{Na}(\mu_2\text{-H}_2\text{O})(\text{THF})]_2(\text{THF})_2$ (**2**). And the catalytic activity of complex **1** towards ROP of L-lactide is investigated. As we expected, the complex **1** is a potential initiator for ring-opening polymerization of lactide, which was confirmed by the experiment results.

The unusual sodium aggregate, $[(\mu_3\text{-MDBP})\text{Na}_2(\text{THF})_2]_2[(\mu_3\text{-OCH}_2\text{CH}_2\text{OCH}_3)\text{Na}]_2$ (**1**), was obtained as a white crystalline solid in 73% yield from the reaction of 6,6'-methylenebis(2,4-di-tert-butylphenol) (MDBP-H₂) with 3.5 M equiv of sodium and 1 M equiv of 2-methoxyethanol in toluene, followed by the removal of solvent and crystallization from THF/hexane (10 mL:30 mL) as shown in Scheme 1. The ¹H NMR spectrum (toluene-*d*₈) signals for the corresponding aromatic rings, methylene group, 2-methoxyethanol, as well as the tert-butyl and protons of THF appeared at 7.82, 7.29 (Ar-H), 5.26, 3.44 (Ar-CH₂-), 4.03, 3.26, 2.78 (O-CH₂CH₂OCH₃), 1.51, 1.48 (t-Bu), and 3.20, 1.30 (THF), respectively, supporting the identical chemical environments of these groups and structure of the complex **1**. During preparation of complex **1**, complex **2** shows an interesting structure of $[(\mu_1\text{-MDBP})\text{Na}(\mu_2\text{-H}_2\text{O})(\text{THF})]_2(\text{THF})_2$ which was obtained unexpectedly maybe due to trace water in the reaction solvent. Subsequently, complex **2** was prepared as colorless crystalline solid through two different approaches. The ¹H NMR spectra and microanalyses of complex **2** are consistent with our expectations. Their molecular structures and coordination modes have been further verified by X-ray diffraction studies.

The crystal of complex **1** was obtained from a saturated solution in THF/hexane and only weakly diffracting, which led to a high R factor. Complex **1** is crystallized in orthorhombic space group *Pbca*. The

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Scheme 1. Preparation of complexes 1 and 2.

asymmetric unit is composed of three independent Na centers, one MDBP²⁻ ligand, one 2-methoxyethanolate group, and two coordinated THF molecules in a crystal lattice. As shown in Fig. 1, there are three different Na atoms in the asymmetric unit of **1**. Na1 is coordinated by four oxygen atoms (O1, O2, O3, and O6) from three different ligands with Na1–O bond lengths ranging from 2.241(5) to 2.352(6) Å, and the O–Na1–O bond angles varying from 92.78(15) to 122.08(19)°. Na2 is four-coordinated with distorted tetrahedral environment by two oxygen atoms (O1A and O2) from two different MDBP ligands and two oxygen atoms (O3 and O4) from one 2-methoxyethanolate group. The Na2–O bond lengths extend from 2.264(5) to 2.305(7) Å,

and the O–Na2–O bond angles varying from 76.3(2) to 139.19(19)°, respectively. The Na3 is four-coordinated with distorted tetrahedral coordination geometry by four oxygen atoms (O1A, O2, O3, and O5) from three different ligands with bond lengths Na3–O1 2.355(5), Na3–O2A 2.378(5), Na3–O3 2.253(6) and Na3–O5 2.344(7) Å, respectively. In addition, the asymmetric unit is linked into hexanuclear sodium aggregate by the asymmetric operation of inversion. The hexanuclear structure consists of two six-membered Na₃O₃ rings linked by six Na₂O₂ cores. In these rings, all of the six oxygen atoms (O1, O2, O3, O1A, O2A, and O3A) are triply bridged.

Single crystals of **2** suitable for X-ray structural determination were obtained from a mixture THF and hexane solution at room temperature. Complex **2** crystallizes in monoclinic *P2*(1)/*c* space group. The asymmetric unit is composed of one independent Na center, one MDBP²⁻ ligand, one aqua ligand, one coordinated THF, and one free THF molecule in a crystal lattice. As depicted in Fig. 2, there is one Na atom in the asymmetric unit of **2** with slightly distorted tetrahedral geometry. The Na1 is surrounded by one oxygen (O1) atom from MDBP ligand, one oxygen (O3) atom coordinated THF molecule, and two oxygen atoms (O1W, and O1WA) from two aqua waters. The Na–O bond distances are in the range of 2.356(3)–2.396(3) Å, and the O–Na–O bond angles vary from 86.51(11) to 132.43(13)°. It is interestingly that the binuclear [Na(OH₂)₂]₂ unit with a Na···Na distance of 3.463(4) Å was formed through two μ₂-H₂O molecules to bridging two Na centers. In addition, there exist intramolecular hydrogen bond (O1W–H···O2) and intermolecular hydrogen bond (O1W–H···O4). It is believed that the hydrogen-bonding interactions play an important role in the stabilization of complex **2**.

Although many syntheses of sodium aggregates [11,12] have been reported, mixed-ligand sodium aggregates in ROP of lactide have barely received attention. In this paper, ROP of L-lactide employing **1** (0.02 mmol) as initiator is systematically examined in toluene (40 mL) at 0 °C and 25 °C as shown in Table 1. It was found that complex **1** is an efficient initiator for the ROP of L-lactide. ROP of lactide goes to completion within 0.5 h at room temperature (Table 1, entries 1 and 2), and the reaction rate decreases with decreasing of temperature (Table 1, entries 3–9). Comparing with other hetero-bimetallic bisphenol complexes, complex **1** shows a high activity for the ROP of L-LA under room temperature [6,11,13]. The polymerization time

Fig. 1. Molecular structure of **1** as 30% ellipsoids (carbon atoms of the tert-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Na1–O1 2.330(6), Na1–O2 2.352(6), Na1–O3 2.241(5), Na1–O6 2.290(7), Na2–O2 2.264(5), Na2–O1A 2.279(5), Na2–O3 2.300(6), Na2–O4 2.305(7), Na3–O3 2.253(6), Na3–O5 2.344(7), Na3–O1A 2.355(5), Na3–O2 2.378(5), Na(1)–Na(2) 3.105(3), Na(1)–Na(3) 3.180(3), Na(2)–Na(3) 3.606(4). Symmetry codes: $-x+1$, $-y$, $-z+2$.

Fig. 2. Molecular structure of **2** as 35% ellipsoids (carbon atoms of the tert-butyl groups and all of the hydrogen atoms are omitted for clarity). Selected bond lengths (Å): Na1–O1 2.356(3), Na1–O1W 2.396(3), Na1–O3 2.370(4), Na1–O1WA 2.358(3), Na1–Na1A 3.463(4). Symmetry codes: $-x+1, -y+1, -z$.

required for the hexanuclear aggregate complex **1** is much shorter compared with the other dinuclear or tetranuclear sodium aggregates [11, 12]. This may be attributed to the easily obtained oxygen anion of 2-methoxyethanol when complex **1** is in the toluene, which is an initiator in the anion ROP of L-lactide [14]. However, the polydispersity indexes (PDIs) of poly(L-lactide)s obtained at 0 °C are narrow, ranging from 1.38 to 1.44, and a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) existed (Fig. 3), implying the controlled character of the polymerization process. It is worth noting that the ^1H NMR spectrum (Fig. 4) of PLA-100 shows one 2-methoxyethanolate group and one hydroxyl chain end, suggesting that the initiation occurs through the insertion of the alkoxy group from complex **1** into L-lactide and the backing reactions do not occur in our condition. This is further verified by the following experimental results. First, the homonuclear decoupled ^1H NMR spectrum (Fig. 5) reveals only one resonance at δ 5.16 ppm in the methine region. Second, if cyclization occurs during polymerization, the PDIs of the resulting PLA would be much higher. However, the PDIs of the PLA obtained are in a narrow range. Furthermore, epimerization of the chiral centers in PLA does not occur as

Fig. 3. Polymerization of L-LA catalyzed by **1** in toluene at 0 °C. The relationship between M_n (▲) (PDI (■)) of the polymer and the initial mole ratio $[M]_0/[I]_0$ is shown.

observed by the homonuclear decoupled ^1H NMR studies in the methine region [15]. In addition, the living character of the polymerization has been proved, which was further confirmed by our resumption experiment (Table 1, entry 10) in which another portion of L-LA monomer ($[LA]_0/[I]_0 = 100$) was added after the polymerization of the first addition ($[LA]_0/[I]_0 = 100$) had gone to completion.

In conclusion, there are two novel sodium complexes supported by bisphenol ligand that have been synthesized and fully characterized by spectroscopic methods as well as X-ray diffraction. Experimental results show that complex **1** is an efficient initiator for the ROP of lactide in controlled fashion, yielding polymers with expectative molecular weight and low polydispersity indexes.

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Appendix A. Supplementary material

CCDC 855790 and 860011 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with

Table 1

Ring-opening polymerization of L-lactide initiated by **1**.

Entry	$[M]_0/[I]_0$	Temperature (°C)	Time (h)	M_n (GPC) ^a	M_n (calcd.) ^b	PDI	Conversion (%) ^c
1	250:1	25	0.5	27,300(15,800)	17,700	1.48	98
2	300:1	25	0.5	35,200(20,400)	21,000	1.43	97
3	100:1	0	2	14,600(8500)	7060	1.38	97
4	200:1	0	2	27,300(15,800)	13,900	1.40	96
5	300:1	0	2	41,400(24,000)	21,200	1.39	96
6	400:1	0	3	52,400(30,400)	27,700	1.39	96
7	500:1	0	3	67,400(39,100)	34,600	1.39	96
8	600:1	0	3	77,600(45,000)	41,100	1.40	95
9	700:1	0	3	89,700(52,000)	49,000	1.44	97
10	100(100):1 ^d	0	2(2)	26,400(15,300)	14,100	1.45	98

^a Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58 [16].

^b Calculated from the molecular weight of L-lactide times $[M]_0/2[I]_0$ times conversion yield plus the molecular weight of 2-methoxyethanol.

^c Obtained from ^1H NMR analysis.

^d Prepolymerization of LA with **1** for 2 h, followed by the addition of another portion of L-LA.

Fig. 4. ^1H NMR spectrum of PLA-100 initiated by complex 1.

Fig. 5. Homonuclear decoupled ^1H NMR spectrum reveals only one resonance at δ 5.16 ppm in the methine region in the polymer of PLLA-100.

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