

Synthesis and Structure of a Molecular Barium Aminebis(phenolate) and Its Application as an Initiator for Ring-Opening Polymerization of Cyclic Esters

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The synthesis and structural characterization of an unusual trinuclear barium aminebis(phenolate) complex are reported along with its application as an initiator for the ring-opening polymerization of ϵ -caprolactone and L-lactide.

The ring-opening polymerization (ROP) of cyclic esters, such as ϵ -caprolactone (ϵ -CL) and lactide (LA), has recently attracted a great deal of attention.¹ This is mainly because the resultant aliphatic polyesters are easily degradable and biocompatible and have potential as environmentally friendly alternatives to current commodity polymers. Polycaprolactone and polylactide are presently used as biocompatible materials (sutures, stents, and controlled drug-delivery systems)² and as packaging materials.^{1c} To initiate the polymerization, an assortment of molecular metal complexes has recently been exploited.³ Among the most active and controlled initiators reported to date are complexes of magnesium⁴ and calcium.⁵ Strontium initiators have also been reported recently,⁶ but to our knowledge, no well-defined barium complexes have thus far been examined as initiators for the ROP of cyclic esters. This is perhaps due to the high ionicity and large size of barium, which favors the formation of insoluble, polymeric materials, increases the propensity for its compounds to cleave ethereal solvents,⁷ and leads to unplanned association of metal centers via oxo bridges.⁸ These features, which make the isolation and utilization of well-defined molecular complexes challenging, are reflected

in the paucity of simple molecular barium species available.⁹ Recent notable exceptions include the isolation of a barium heteroleptic pentafluorophenyltriazenide complex,¹⁰ the synthesis and characterization of barium diphenylmethanide,¹¹ and the synthesis and utility of dibenzyl barium.¹² More pertinent to our work are recent developments in barium phenolate chemistry: Sobota et al. have recently prepared a homoleptic barium benzofuranolate,¹³ and in 2000, Deacon et al. reported the structure of a barium homoleptic 2,6-diphenylphenolate complex.¹⁴ Here we report the utilization

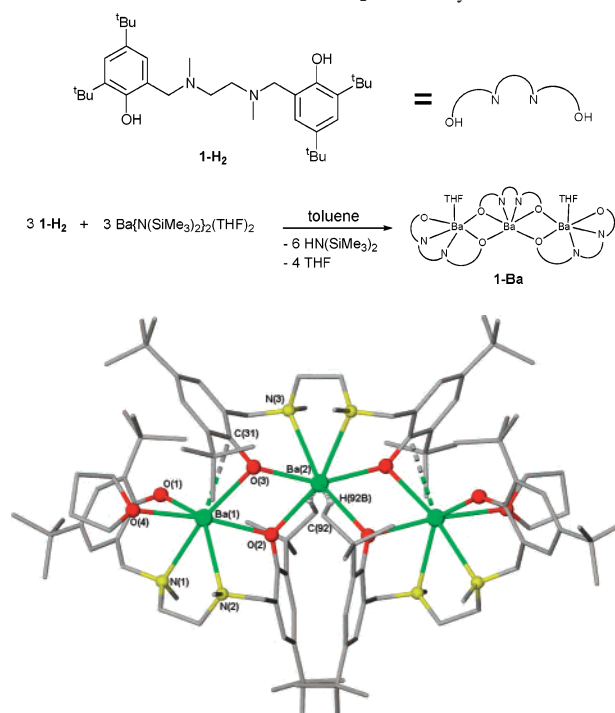
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Scheme 1. Molecular Formula of **1-H₂** and the Synthesis of **1-Ba****Figure 1.** Molecular structure of **1-Ba**. For clarity, all H atoms (except H92B), solvent of crystallization, and THF disorder have been deleted. Key bond lengths and angles are provided in the Supporting Information.

of a bulky aminebis(phenolate) ligand in the isolation and structural characterization of a well-defined, molecular, trinuclear barium complex and the subsequent use of this complex as an initiator for ROP of ϵ -CL and L-LA.

The bis(phenol) ligand used in this study (**1-H₂**) was prepared as described previously (Scheme 1).¹⁵ Complex **1-Ba** was prepared by treating **1-H₂** with freshly prepared $\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$ (THF = tetrahydrofuran)¹⁶ in toluene at ambient temperature and leaving the product to crystallize for 24 h. Complex **1-Ba** crystallizes as a bis(THF)-solvated trinuclear species in the monoclinic space group $C2/c$ (Figure 1).¹⁷ A mirror plane dissects Ba(2); hence, the two outer Ba atoms [Ba(1)] are crystallographically equivalent. The Ba(1) atoms are formally seven-coordinate and bind to one THF molecule, one μ_1 -O, two μ_2 -O, two N moieties, and the C_{ipso} atom (π interaction) of a bridging phenoxide group. Interestingly, the bridging phenoxide ligands bind to Ba(1) asymmetrically; only one of them binds to the metal via an additional π -Ba interaction. The effect that this interaction has on the structure can be gauged in two ways. First, the Ba(1)- μ_2 -O bonds are significantly different [Ba(1)-O(1) and Ba(1)-O(2) are 2.629(2) and 2.753(2) Å, respectively]. The shortest of these interactions is for the phenoxide ligand, which does not appear to provide π donation to the metal

center. Second, the C_{ipso}-O-M angle can be compared to emphasize the tendency of one phenolate group to tilt toward Ba(1) [C(31)-O(3)-Ba(1) and C(31)-O(3)-Ba(2) angles are 98.4(2)° and 140.6(2)°, respectively], while the other bridging ligand, although not perfectly perpendicular to the Ba(1)···Ba(2) axis tilts much less toward Ba(1) [C(21)-O(2)-Ba(1) and C(21)-O(2)-Ba(2) angles are 119.7(2)° and 131.3(2)°, respectively]. The Ba(1)-C(31) π bond [3.228(3) Å] is comparable in length to those in the aforementioned triazene complex [$\text{Ba}(\text{C}_6\text{F}_5)\{\text{N}_3(2,6\text{-Mes}_2\text{-C}_6\text{H}_3)(2\text{-Mes-C}_6\text{H}_4)\}$] (3.286–3.430 Å)¹⁰ and the phenolate complex [$\text{Ba}_2(\text{O-2,6-Ph}_2\text{C}_6\text{H}_3)_4$] [3.075(3)–3.449(4) Å],¹⁸ although in these complexes, the barium metal enjoys a full complement of η^6 -arene interactions. The central metal atom, Ba(2), is formally eight-coordinate. Its coordination sphere contains four μ_2 -O and two N atoms and is completed by incorporating two agostic Ba···H(CH₂) [Ba(2)-H(92) is 2.854 Å] interactions (Figure S10 in the Supporting Information). These are intermediate in length when compared with those found in a series of five barium silylamides (range 2.32–3.23 Å).¹⁹ In contrast to Ba(1), the Ba(2)-O bond distances are more uniform and the Ba(2)-N bond distances are, within experimental error, identical with the Ba(1)-N distances. Upon examination of the metal-heteroatom connectivity of **1-Ba**, the molecular framework may be viewed as a fusion of 13 different four-, five-, and six-membered homo- or heteroatomic rings (Figure S10 in the Supporting Information). Complex **1-Ba** is a rare example of a distinct trinuclear barium species. To the best of our knowledge, only three other examples are known, all of which are barium siloxide complexes.²⁰

In an effort to determine the solution structure of **1-Ba**, ¹H and ¹³C{¹H} NMR spectra of the complex were obtained (in benzene-*d*₆, toluene-*d*₈, and THF-*d*₈ solutions). Previously, we have shown that the ¹H and ¹³C{¹H} NMR spectra for the related **1-Mg**²¹ are complicated, both by the retention of an oligomeric structure in solution and by the presence of diastereotopic H atoms. With respect to **1-Ba**, it is logical to assume that the ¹H NMR spectrum in an arene solvent would have an even greater number of resonances because there are now three crystallographically unique phenolate groups (as opposed to two in **1-Mg**). This was indeed found to be the case. A variable-temperature ¹H NMR spectroscopic study was conducted in an effort to reveal whether the complex retained its solid-state structure in solution. However, in toluene-*d*₈, the complexity of the spectrum at 300 K hindered a complete structural resolution. The additional complexity presumably arises as a result of intramolecular

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dynamic processes and/or the existence of an equilibrium between two or more different oligomers, both of which are commonly observed for molecular alkaline-earth metal species. For example, Izod and co-workers²² have shown that a series of alkaline-earth metal phosphanides are subject to monomer–dimer equilibria in an arene solution. Also, Westerhausen et al.²³ revealed that, because of broad and overlapping signals, ¹H and ¹³C NMR spectroscopy could not be used to elucidate the solution structure of the trimeric magnesium phosphenide, Mg₃{P(SiMe₃)₂}₆; however, a dimer–trimer equilibrium was observed by means of a ³¹P-¹H NMR experiment. When **1-Ba** was dissolved in THF-*d*₈, considerably simplified ¹H, ¹³C, and COSY NMR spectra were obtained: these data suggest deaggregation of the higher oligomer(s) to a THF-stabilized monomer or to a dimeric species containing rapidly exchanging terminal and bridging aryloxide groups (Figures S1–S3 in the Supporting Information).

Complex **1-Ba** was tested as an initiator for ROP of both L-LA and ϵ -CL. Polymerizations using the former were conducted in the neat monomer at 130 °C, with a 900:1 ratio of lactide to initiator, while those involving the latter were performed in a toluene solution at ambient temperature, utilizing a 300:1 ratio of monomer to initiator. Polymerization of LA produced PLA in moderate yield (60% after 3.5 h) with a reasonable degree of control ($M_n = 25\,500$; PDI = 1.57). However, higher levels of conversion were inhibited under these conditions by the increased viscosity of the melt. For ϵ -CL, a number of experiments were performed to assess the degree of control over polymerization and the nature of the initiating species. The linear evolution of the polymer molecular weight with time and the low variation of the molecular weight distribution (Graph S1 and Table S1 in the Supporting Information) suggest that the ROP of ϵ -CL is well-controlled. However, these experiments produced a polymer with a bimodal molecular weight distribution, possibly suggesting the availability of more than one active site, giving rise to more than one rate of initiation and/or propagation of ROP.²⁴ While it is unlikely that the solid-state structure remains intact in solution in the presence of Lewis basic ϵ -CL, this observation is consistent with the NMR data obtained for **1-Ba** in THF, which suggest that both terminal and bridging aryloxides may still be present in coordinating solvents. Prolonged reaction times resulted in a unimodal but broad molecular weight distribution, presumably because of significant transesterification occurring subsequent to consumption of the monomer. An in situ NMR study was also undertaken (Figure 2 and Table S2 in the Supporting Information), which indicates that the polymerization proceeds with first-order kinetics and with little or no induction period.

The use of benzyl alcohol (BnOH) as a coinitiator was assessed (Table S1 in the Supporting Information). Again,

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 (24) Another potential cause of bimodality is transesterification. See: (a) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Rapid Commun.* **1997**, *18*, 325–333. (b) Penczek, S.; Duda, A.; Szymanski, R. *Macromol. Symp.* **1998**, *132*, 441–449. (c) Baran, J.; Duda, A.; Kowalski, A.; Szymanski, R.; Penczek, S. *Macromol. Symp.* **1997**, *123*, 93–101. This possibility, which relies on the bimolecular chain transfer being slower than the rate of propagation, cannot be unequivocally discounted.

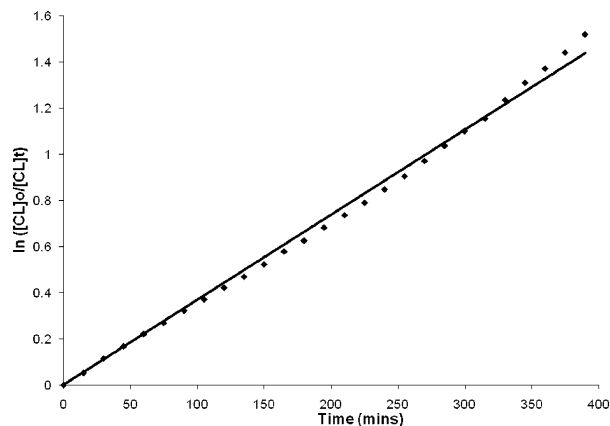


Figure 2. First-order rate plot (by ¹H NMR spectroscopy at 298 K) for the polymerization of ϵ -CL using **1-Ba** in C₆D₆. $r^2 = 0.995$.

the PLA produced showed a bimodal molecular weight distribution. Characterization of this polymer by MALDI-TOF mass spectrometry and NMR end-group analysis revealed two series of polymers: one of higher molecular weight initiated by insertion into a Ba–O(L) aryloxide bond and one of lower molecular weight initiated via insertion into a Ba–OCH₂Ph bond (Figures S17–S19 in the Supporting Information). Observation of the latter benzyl ester terminated polymer suggests that initiation can be preceded by proton transfer (or at least strong intramolecular hydrogen bonding) from barium-coordinated PhCH₂OH to the aminebis(phenolate) ligand (a related process has recently been proposed for the titanium-catalyzed ROP of ϵ -CL).²⁵ Because this process is not exclusively observed, it is implied that active Ba–O(L) sites remain in the presence of a coinitiator. This is consistent with the presence of at least two “active site” environments being available within an oligomeric initiating species and is supported by NMR spectra of **1-Ba** in the presence of excess BnOH (Figure S22 in the Supporting Information), which show that, upon the addition of BnOH to a hydrocarbon solution of **1-Ba**, new barium aminebis(phenolate) species are formed. Finally, we observed that polymerization of ϵ -CL does not occur in neat THF after 90 min, suggesting that coordination of ϵ -CL is inhibited by the presence of excess donor solvent, which is able to competitively bind to the otherwise active metal centers.

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Supporting Information Available: Details of general experimental procedures, synthesis and characterization of **1-H₂**, **1-Ba**, and polymers, structural parameters, ORTEP figures, additional key NMR spectra, gel permeation chromatography and MALDI-TOF data, and a file of X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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