

Single-site metal alkoxide catalysts for ring-opening polymerizations.

Poly(dilactide) synthesis employing $\{\text{HB}(3\text{-Bu}^t\text{pz})_3\}\text{Mg}(\text{OEt})$

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$\{\text{HB}(\text{Bu}^t\text{pz})_3\}\text{Mg}(\text{OEt})$ in CH_2Cl_2 at 22°C acts as a catalyst precursor for the fast, stereoselective, ring-opening polymerization of *L,L*-dilactide by the acyl cleavage mechanism yielding isotactic poly(*L,L*-dilactide) with PDI ≈ 1.2 .

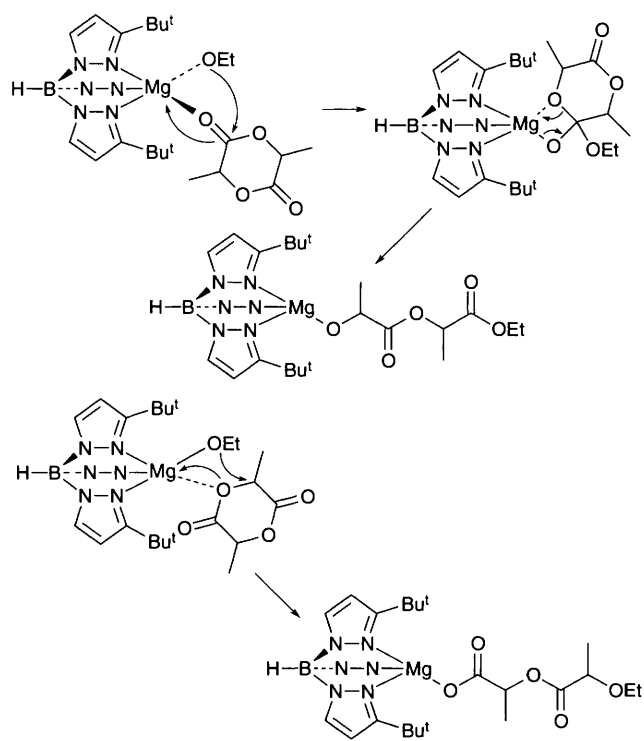
Ring-opening polymerizations of strained cyclic ethers and esters are typically carried out by so-called 'coordinate catalysts' which are ill-defined when it comes to a knowledge of intimate mechanism and structure. For example, the Union Carbide calcium amide/alkoxide process for the polymerization of ethylene oxide or propylene oxide involves a heterogeneous reaction mixture and the stereochemistry of the ring opening is not known.¹ Similarly, in the polymerization of dilactide, **I**, to give polydilactide, which finds numerous applications as a biodegradable² and biocompatible polymer,³ the most common catalysts are tin or zinc octanoates, $\text{M}(\text{O}_2\text{CR})_2$, whose structures and detailed modes of reaction are unknown. Indeed, evidence has been presented that in polymerization of dilactides involving the tin and zinc octanoates, it is a hydrolysis product, present as a minor component, that is the active catalyst.⁴ There is therefore a target of opportunity for coordination chemists to design discrete complexes of the form $\text{L}_n\text{M}(\text{OR})$ that may act as catalyst precursors for ring-opening polymerization in an analogous manner to the recent development of ROMP catalysts precursors such as $[\{\text{Me}_2(\text{CF}_3)\text{CO}\}_2(\text{Ar}'\text{N})\text{Mo}=\text{CHBu}^t]$.⁵ We describe here our initial investigations of the reactivity of $\{\text{HB}(3\text{-Bu}^t\text{pz})_3\}\text{Mg}(\text{OEt})$, **II**, as a catalyst precursor. This compound, originally prepared by Parkin and Han,⁶ has several attractive features. The elements Mg and B are biologically benign. The $\{\text{HB}(3\text{-Bu}^t\text{pz})_3\}\text{Mg}$ fragment is kinetically inert with respect to the Schlenk equilibrium and the Mg^{2+} ion is not prone to redox reactions or β -hydrogen atom abstraction from alkoxide ligands. The reaction between the substrate and growing polymer should occur in a *cis*-migratory insertion manner due to steric requirements of the tripodal $\eta^3\text{-}\{\text{HB}(3\text{-Bu}^t\text{pz})_3\}$ ligand in **II**.

Compound **II** was found to be monomeric in benzene by the Signer method and is assumed to be monomeric in the more polar solvent dichloromethane which was used for studies of the polymerization of **I** at room temperature. Typical polymerizations were carried out employing 10^{-2} mol dm^{-3} solutions of **II** and 1.1 mol dm^{-3} solutions of dilactide **I**. Aliquots of the solutions were removed with time and the polymerization reaction was quenched by the addition of methanol yielding a precipitate of poly(dilactide). The solvent

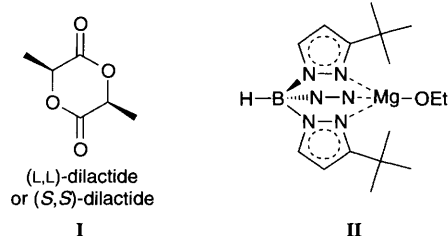
was removed under a dynamic vacuum from these aliquots and the residue was examined by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. In $[\text{D}_6]\text{benzene}$ poly(dilactide) is soluble up to $M_w \approx 15\,000$ and monomer and polymer are distinguishable by their methine resonances: δ 3.74 for *L,L*-dilactide vs. δ 5.02 for poly(dilactide). From the integrations of the methine signals for the monomer and polymer we determined the kinetics of the reaction to be first-order in *L,L*-dilactide and, from changing the concentrations of **II**, the polymerization was also shown to be first-order in catalyst precursor. These studies also revealed a small induction period before the onset of linear kinetics and this period was smaller with higher concentrations of **II**. We propose the most likely explanation for the induction period is that the appearance of the methine signal at δ 5.02 requires several ring-opening events.

At various times during the polymerization the M_w of the polymer was examined by GPC using thf as an eluent, which has commonly been used, with polystyrene as a calibrant for poly(dilactide). These studies revealed a linear relationship between the observed M_w and that predicted by a single polymer chain per Mg centre at a given percentage conversion. The PDI remained constant at *ca.* 1.2 up to polymerization of 1000 equiv. of **I**.

Ring opening of dilactide can occur by either acyl cleavage or alkyl cleavage as shown in Scheme 1. The acyl cleavage leads to an ester end group bearing the alkoxide ligand of **II** whereas the alkyl cleavage generates an ether end group. To distinguish

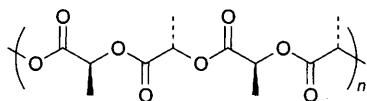


Scheme 1



between these modes of reaction we used ^1H NMR spectroscopy in CDCl_3 . In this solvent the methine resonances of both **I** and poly(dilactide) occur at δ 5.03. The sequential addition of three equivalents of L,L-dilactide to **II** resulted in the disappearance of the $\text{MgOCH}_2\text{CH}_3$ quartet at δ 4.16 and the appearance of the methylene end group in the oligomer at δ 4.18. The chemical shift of the latter is consistent with an ester end group and not an ether end group $\text{MeCHCOCH}_2\text{CH}_3$ for which $\delta \approx 3.4$ would be expected.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the poly(dilactide) shows just one sharp resonance for each of the ketonic, methyl and methine carbons indicative of the formation of the isotactic polymer poly(L,L-dilactide) **III**.⁸



isotactic poly(L,L)-dilactide

III

Formation of the isotactic polymer is consistent with the acyl cleavage mechanism for polymer growth and our inability to detect any syndiotactic linkages shows that base-promoted epimerization of the cyclic dilactide or the polymer chain is insignificant.

In conclusion, we have shown that $\{\text{HB}(3\text{-Butpz})_3\}\text{Mg}(\text{OEt})$ acts as an efficient catalyst precursor for the ring-opening polymerization of L,L-dilactide in CH_2Cl_2 at room temperature. The rate of polymerization compares favourably with all other catalyst systems and is notably better than the Sn and Zn catalyst systems noted earlier which require heating to 110–120 °C (often melt polymerizations). The use of a discrete

coordination catalyst precursor with a single active site MOP, where P = growing polymer, allows control of the polymerization reaction and eliminates unwanted side-reactions such as epimerizations and transesterification reactions. The virtues of an $L_n\text{M}(\text{OR})$ single-site catalyst precursor are many and clearly warrant further study. When the $L_n\text{M}$ template and substrate are both chiral the potential for block copolymers derived from polymerization of the racemic mixture of the monomer exists.

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