Cationic Organomagnesium Complexes as Highly Active Initiators for the Ring-Opening Polymerization of ε-Caprolactone

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Species of the form [LH]+[Br₄]− (R = pentafluorophenyl, phenyl, 1) were synthesized by reaction of Brønsted acids with a novel bis-phosphinimine ligand ([L = 4,6-(MesN=PPh₂)₂dibenzo[3]furan]). Corresponding cationic complexes [LMgBu]⁺[Br₄]− (2) were produced by reaction of [MgBrBu]− with [LH]⁺[Br₄]−. Organomagnesium species 2a and 2b exhibit extremely high activity as initiators for the polymerization of ε-caprolactone, yielding near-quantitative conversion of monomer to high molecular weight (> 2.0 × 10⁵ g/mol) polymer in 4 min at ambient temperature.

Introduction

Poly lactones are an important class of biodegradable materials that hold the potential to reduce waste associated with the disposal of conventional plastics. ¹ The advancement of polylactone technology, including the development of new homogeneous catalysts for lactone polymerization, is thus an important goal for many researchers, and many excellent reviews are available. ² Of the commercially viable polylactones (poly(ε-caprolactone), polylactide, and polyglycolide), poly(ε-caprolactone) is particularly attractive, as it is produced from an inexpensive precursor, may be processed under mild conditions (mp ∼ 60 °C), and is readily degraded by naturally occurring microorganisms. ³

Magnetism- and zinc-based homogeneous catalyst systems are particularly attractive for lactone polymerization because of their low toxicity and cost paired with high activity. Magnesium catalysts, however, generally exhibit higher activity than more electron-rich zinc analogues. ²a Therefore, development of sterically and electronically unsaturated magnesium complexes presents an opportunity to achieve even higher levels of polymerization catalytic activity. Catalyst activation by alkide abstraction from organometallic species (which results in a sterically and electronically unsaturated metal center) is well established for olefin polymerization. ⁵ Only preliminary efforts have been reported for extending similar strategies to lactones. ⁶

Herein we describe the synthesis and characterization of a family of cationic organomagnesium complexes that are extremely active initiators for ε-caprolactone polymerization. While some well-characterized examples of formally cationic magnesium complexes have been reported, ⁷ and a variety of neutral organomagnesium species have been applied to lactone polymerization, ⁸ to the best of our knowledge the results described herein constitute the first successful use of a cationic organomagnesium species in ε-caprolactone polymerization.

The polymerization of ε-caprolactone using a cationic organomagnesium initiator may conceptually follow either of two mechanisms: coordination–insertion or activated chain-end (Scheme 1). ⁸b–g ⁹ Typical organomagnesium catalysts have been shown to polymerize lactones via the former


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**Scheme 1.** Possible Mechanisms for the Polymerization of ε-Caprolactone via a Cationic Organomagnesium Initiator: Coordination–Insertion (above) or Activated Chain-End (below)

![Scheme 1](image)


In an effort to utilize this methodology for the preparation of analogous organomagnesium cations, isolable salts of L, [[(L)H][BR$_4$]]$^-$ ([R = C$_6$F$_5$ (1a), Ph (1b)], were generated in high yield (1a: 80.1%, 1b: 86.3%) by reaction of L with an appropriate Brønsted acid (Scheme 2). The doubly protonated species 1c was prepared in a parallel fashion in 91.2% yield. Though 1a and 1b were not sufficiently crystalline in our hands for single-crystal X-ray diffraction, crystals of 1c were isolated and the molecular structure was determined (Figure 2). By comparison to the structure of L (P–N = 1.549(1) Å), the P–N bonds of 1c (P–N = 1.639(2) Å) are elongated as a result of protonation of the phosphinimine nitrogen atoms.

**Figure 1.** Molecular structure of L (50% probability ellipsoids, H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): P(1)–N(1) 1.549(1), P(2)–N(2) 1.565(1); P(1)–N(1)–C(25) 129.5(1), P(2)–N(2)–C(46) 122.9(1).

**Scheme 2.** Synthesis of 1a, 1b, and 1c by Protonation of L Using (i) [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$], (ii) Na[BPh$_4$] and H$_2$O, and (iii) 2 Na[BPh$_4$] and 2 HCl, and Synthesis of Complexes 2a and 2b by Addition of (iv) [Mg(Bu$_2$)$_4$].

$^a$ R = anionic functionality, L = neutral ancillary.
The species L, 1a, 1b, and 1c all display C$_2$ symmetry in solution, as indicated by a single $^{31}$P NMR resonance at δ = 15.0 ppm. The broad resonance reflects a slow exchange process between two species, prepared by the exchange of di-n-butylmagnesium with 1 equiv of diphenylphosphino dibenzofuran. The structure of 1c (50% probability ellipsoids; Figure 2). In each case, $C_{symmetry}$ was preserved, and a large downfield shift in the $^{31}$P NMR resonance (δ = 1.32 (CH2CH2), 0.99 (CH3), and −0.13 (MgCH3) ppm, respectively) is observed. The molecular symmetry established spectroscopically suggests that the N–H protons of 1a and 1b are rapidly exchanging between the two nitrogen atoms on the NMR time scale. The X-ray diffraction study (Figure 3). The ligand is well resolved by $^{1}H$ NMR spectroscopy, giving rise to diagnostic resonances at δ ≈ 1.3, 1.8, and 2.5 ppm. The δ = 0.96 ppm resonance arises from the C₂ symmetry was maintained, and an apparent broadening was observed. Complexes 2a and 2b were isolated in $^{19}$F NMR spectroscopy as extremely weakly interacting ion pairs, and although anions can have a significant effect on polymerization,17 that does not appear to be the case here.

Polymerization of ε-Caprolactone. Preliminary examination of 2a and 2b in the ring-opening polymerization of ε-caprolactone revealed remarkably high activity. Investigations were conducted at initiator concentrations of 0.4 mM (0.77 mol % relative to the lactone monomer) in benzene-δ$_{6}$. In both cases, $^1H$ NMR spectroscopy indicated >90% conversion of ε-caprolactone to poly-(ε-caprolactone) in 4 min at ambient temperature (Table 1). As the BR$_4^-$ anions were established to be extremely weakly coordinating, they were not expected to substantially influence the polymerization process. Indeed, similar activity was observed for 2a and 2b at 23 °C (Table 1). Hence, subsequent reactions focused on the less expensive initiator 2b. Notably, 2b maintains impressive activity at reduced concentrations (0.37 mM and loading (0.19%). Likewise, high activity and a linear relationship between ln[monomer] and time (pseudo-first-order kinetics) were observed at 0 °C. In fact, 2b was active at temperatures as low as −40 °C; however, at temperatures less than 0 °C the exceedingly high viscosity of the reaction mixture rendered it difficult to achieve complete conversion.

The polymerization of ε-caprolactone by 2a and 2b was studied by NMR spectroscopy in an attempt to elucidate the operative polymerization mechanism (Scheme 1). In situ examination of the polymerization process indicated cleavage of the Mg−C bond in both cases (evidenced by...
disappearance of a characteristic Mg–CH2 resonance at \( \delta = 0.13 \) in the \(^1H\) NMR spectrum, and while the methylene resonances could not be detected due to overlapping polymer signals, the \( n \)-butyl–CH2 resonance is clearly visible at \( \delta 0.86 \) in the \(^1H\) NMR spectrum. However, this same \( n \)-butyl resonance could not be detected in the spectra of isolated oligomer samples (generated using 10 mol % 2b), clearly demonstrating that the polymer does not bear an \( n \)-butyl end group. Corroboration of these results via MALDI-ToF mass spectrometry was not successful despite an exhaustive examination of a variety of polymer samples.\(^{2b,18}\) Thus, while the ultimate fate of the initiator is unknown, the absence of an \( n \)-butyl end group on isolated oligo(\( \varepsilon \)-caprolactone) samples suggests that lactone polymerization occurs via an activated chain-end process (Scheme 1).

Poly(\( \varepsilon \)-caprolactone) samples produced using 2b (0.24\%\%, 23 \(^\circ\)C) possessed average molecular weights (\( M_n \)) as high as 2 \( \times 10^5 \) g/mol and PDI 1.6 or less, as determined by GPC analysis (Table 2).\(^{2a}\) The average molecular weights of the polymers were higher than expected (i.e., a controlled polymerization utilizing 0.24 mol \% initiator would be expected to afford polymer with a molecular weight of 4.8 \( \times 10^3 \) g/mol), which may be attributed to slow initiation relative to propagation in the polymerization process, and therefore only moderate initiator efficiency. A relatively slow initiation step is also consistent with the observed polydispersity values. This could occur in the context of an activated chain-end mechanism, whereby the cationic chain end may be less stable and more reactive than the initiating cationic magnesium species.

### Conclusion

Cationic organomagnesium species (2a and 2b), prepared by treating \( \text{di-}n \)-butylmagnesium with novel species 1a and 1b, respectively, have demonstrated exceptionally high activity for the polymerization of \( \varepsilon \)-caprolactone. The observed results are extremely promising, and future generations of this initiator will be designed in hopes of maintaining high activity while giving enhanced molecular weight control.

### Experimental Section

#### General Procedures.

All manipulations of air-sensitive materials and reagents were conducted using high-vacuum techniques\(^{19}\) under a purified argon atmosphere or in a glovebox (MBraun Labmaster 130). Proteo solvents were purified using an MBraun solvent purification system (MB-SPS), stored in Teflon-sealed glass vessels over appropriate drying agents, and vacuum transferred directly to reaction vessels. Deuterated solvents (Cambridge Isotopes) were dried with appropriate drying agents, vacuum transferred, and stored under an inert atmosphere prior to use. \( \varepsilon \)-Caprolactone was dried over CaH2, distilled, and stored under an inert atmosphere prior to use. All other materials were obtained in high purity (Sigma-Aldrich) and used without additional purification. NMR spectra \( (^1H, 300.13 \mathrm{MHz}, ^{13}C[^1H], 75.47 \mathrm{MHz}, ^{31}P[^1H], 121.48 \mathrm{MHz}, ^{19}F(282.42 \mathrm{MHz}), ^{11}B(96.29 \mathrm{MHz}) \) were collected using a Bruker Avance II NMR spectrometer equipped with a variable-temperature unit. Spectra were collected at ambient temperature unless otherwise noted and referenced to residual proto solvent resonances \( (^1H, \text{solvent} ^{13}C[^1H]) \), or an external standard (triphenylphosphine \( ^{31}P[^1H] \)), trifluorotoluene \( ^{19}F \), or boron trifluoride diethyl etherate \( ^{19}F \)) depending on the nucleus of interest. \(^1H\) and \(^{13}C\) NMR peak assignments were facilitated by DEPT-45, DEPT-90, DEPT-135, COSY, and HSQC experiments. X-ray crystal structures were collected using a Bruker AXS SMART APEX II single-crystal X-ray diffractometer (Mo Ka \( (\lambda = 0.71073 \AA) \)). Elemental analyses were performed using an Elementar Vario Microcube.

#### Synthesis of 4,6-(PPh\(_2\)_2)dibenzofuran.

The ligand precursor 4,6-(PPh\(_2\)_2)dibenzofuran was prepared as described by Kraneburg et al.\(^{20}\) with several modifications. A 250 mL round-bottom flask was charged with 2.6869 g (15.974 mmol) of dibenzofuran, to which 100 mL of diethyl ether was added by vacuum transfer at \(-78 \, ^\circ\mathrm{C}\). Tetramethylethylenediamine (TMEDA) was injected slowly (7.2 mL, 5.6 g, 48 mmol), and the suspension was allowed to warm to ambient temperature over approximately 20 min. The dibenzofuran fully dissolved to afford a light yellow solution. This solution was cooled back to \(-78 \, ^\circ\mathrm{C}\), and a solution of sec-butyllithium (35 mL at 1.4 mol/L in heptane, 49 mmol) was added dropwise. The reaction mixture was stirred for 2 h, producing a light green suspension, which became dark green upon slow warming to ambient temperature. The reaction mixture was stirred for an additional 6 h and then cooled to \(-78 \, ^\circ\mathrm{C}\). Beginning 9 h after the initial injection of sec-butyllithium, 9.0 mL (11 g, 50 mmol) of neat chlorodiphenylphosphate was injected rapidly. An immediate color change from green to white was noted. The reaction mixture was gradually warmed back to ambient temperature and stirred for an additional 14 h, during which a light brown suspension formed. The solvent was removed in vacuo. All subsequent manipulations were performed under aerobic conditions. The resulting light brown oil was dissolved in 80 mL of dichloromethane and quenched with 50 mL of distilled water. The aqueous phase was removed, and the organic phase was washed with three subsequent 50 mL fractions of distilled water. The organic phase was dried thoroughly in vacuo, affording 6.06 g (11.3 mmol, 70.9\%) of the desired product. \(^1H\) and \(^{31}P[^1H]\) NMR spectra matched published results.\(^{19,20}\) \(^1H\) NMR (chloroform-d\(_6\), dq 16.8 (s), \(^1H\) NMR (chloroform-d\(_6\)): \( \delta 7.95 \) (d, \( \delta 1H = 7.5 \, ^\circ\mathrm{Hz}\), 2H, dbf-C\(_{176}\)), \( 7.35 \) to \( 7.20 \) (ov m, 22H, dbf-C\(_{176}\)).

#### Synthesis of 4,6-(MesN=P=PPh\(_2\))dibenzofuran (L).

A 500 mL Teflon-sealed glass reaction vessel was charged with 5.7732 g (10.760 mmol) of 4,6-(PPh\(_2\)_2)dibenzofuran. The precursor dissolved fully in 110 mL of toluene, and then excess neat 2,4,6-trimethylphenylazide (mesityl azide, MesN\(_3\)) (4.255 g, 26.39 mmol) was added. Evolution of a colorless gas was noted within

| Table 2. GPC Results for Poly(\( \varepsilon \)-caprolactone) Produced Using Initiator 2b: Weight Average (\( M_w \)) Number Average (\( M_n \)) and Corresponding PDI (\( M_w / M_n \)) Values |
| --- | --- | --- |
| batch | \( M_w \) | \( M_n \) | PDI (\( M_w / M_n \)) |
| 1 | \( 1.9 \times 10^5 \) | \( 1.2 \times 10^5 \) | 1.6 |
| 2 | \( 2.1 \times 10^5 \) | \( 1.3 \times 10^5 \) | 1.5 |

\(^{18}\) Fontaine, F.-G. Personal communication. High molecular weight poly(\( \varepsilon \)-caprolactone) has proven impossible for the Fontaine group to observe by MALDI-ToF mass spectrometry.


Under aerobic conditions, two solutions of \( \text{dbf-C}_1/9 \) (chloroform-\( m \)mol) of \([\text{H}-4,6-(\text{MesN}) \_\text{acac}] \) were added, and the reaction mixture was allowed to stir at 65 °C until the \( ^{31} \text{P} \) NMR spectrum of crude reaction mixture aliquots indicated that the reaction had reached completion (approximately 2 additional h). The solution was cooled to ambient temperature and transferred to a 100 mL round-bottom flask in two fractions of approximately 60 mL each. The solvent was removed in vacuo between fractions and after the full volume had been transferred, yielding an oily yellow solid. All subsequent manipulations were conducted under aerobic conditions. The product was washed five times with 50 mL fractions of hexane. During each washing procedure, the mixture was sonicated and vigorously stirred for approximately 5 min prior to filtration. The product was collected as a white powder and dried in vacuo. Total yield was 93.9% (8.10 g, 10.1 mmol). \(^{31} \text{P} \) NMR (benzene-\( d_6 \)) and the reaction mixture was allowed to stir at 65 °C for 60 min. The temperature was then gradually raised to 65 °C with occasional venting, for 60 min. The temperature was then roughly dried in vacuo for 14 h, yielding the desired product as an amorphous yellow solid in 86.26% yield (7.1136 mmol, 11.1336 mmol). \(^{31} \text{P} \) NMR (benzene-\( d_6 \)) of the organic layer was then thoroughly washed, resulting in "in vacuo" for 14 h, yielding the desired product as an amorphous yellow solid in 86.26% yield (7.1136 mmol, 11.1336 mmol). \(^{31} \text{P} \) NMR (benzene-\( d_6 \)) of the organic layer was then thoroughly washed, resulting in "in vacuo" for 14 h, yielding the desired product as an amorphous yellow solid in 86.26% yield (7.1136 mmol, 11.1336 mmol). \(^{31} \text{P} \) NMR (benzene-\( d_6 \)) of the organic layer was then thoroughly washed, resulting in "in vacuo" for 14 h, yielding the desired product as an amorphous yellow solid in 86.26% yield (7.1136 mmol, 11.1336 mmol). \(^{31} \text{P} \) NMR (benzene-\( d_6 \)) of the organic layer was then thoroughly washed, resulting in "in vacuo" for 14 h, yielding the desired product as an amorphous yellow solid in 86.26% yield (7.1136 mmol, 11.1336 mmol). \(^{31} \text{P} \) NMR (benzene-\( d_6 \)) of the organic layer was then thoroughly washed, resulting in "in vacuo" for 14 h, yielding the desired product as an amorphous yellow solid in 86.26% yield (7.1136 mmol, 11.1336 mmol).
MgCH₂CH₂CH₂CH₃), 12.0 (s, Mg(CH₂CH₂CH₂CH₃). B-(C₆F₅)₃, resonances not reported. ³¹P{¹H} NMR (benzene-d₆): δ = 130.7 (d, ³²JHP = 11 Hz, 8F, o-C₆F₅), -161.7 (t, ³³JHP = 22 Hz, 4F, p-C₆F₅), -165.5 (m, 8F, m-C₆F₅). ¹¹B NMR (benzene-d₆): δ = -15.8 (br s). Anal. Calcd [%] for C₈₃H₇₁BF₂₃O₂Mg₂N₂OP₂: C, 62.99; H, 3.68; N, 1.79. Found: C, 62.17; H, 3.86; N, 1.84.

Synthesis of [4,6-(Mes=ΨPPh₂)-dibenzo furylamgMgBu][BPh₄] (2b). Under argon, a 100 mL round-bottom flask was charged with 0.7422 g (0.6608 mmol) of 1b to which 40 mL of benzene was added. A solution of Di(n-butyl)magnesium (0.67 mmol of 1.0 M solution in heptane, 0.67 mmol) in 4 mL of benzene was added. The solution was stirred for 30 min at ambient temperature. The solvent was removed in vacuo, yielding the desired material as a white solid (0.7242 g, 0.6017 mmol, 91.07%). ³¹P{¹H} NMR (benzene-d₆): δ = 23.2 (s). ¹¹H NMR (benzene-d₆): δ = 8.09–8.01 (br m, 8H, o-Ph₂), 7.64 (d, ³²JHH = 6.0 Hz, 2H, dbf-C₁αH), 7.26 (dd, ³²JHH = 12 Hz, ³³JHH = 9.1 Hz, 8H, o-Ph₂), 7.19 (m, 3.1H₄), 7.09–6.97 (br m, 14H, o-Ph₂), 6.97–6.84 (br m, 10H, o-Ph₂), 6.35 (s, 4H, m-Mes), 2.03 (s, 6H, p-Mes), 1.52 (s, 12H, p-Mes), 1.38–1.32 (m, 4H, MgCH₂CH₂CH₂CH₄), 0.99 (t, ³²JHH = 7.3 Hz, 3H, MgCH₂CH₂CH₂CH₄), 0.13 (t, ³²JHH = 9.2 Hz, 2H, MgCH₂CH₄CH₂CH₃), 1.17 (¹³C{¹H} NMR (benzene-d₆): δ = 165.4 (1:1:1:1 q), 165.4 (1:1:1:1 q). ¹⁵N{¹H} NMR (benzene-d₆): δ = 68.8 (s, dbf-quaternary), 140.2 (s, m-Ph₂), 137.5 (s, m-Ph₂), 135.7 (t, ³²JCP = 6.8 Hz, dbf-quaternary), 133.9 (m, o-Ph₂), 133.8 (s, 133.1 (d, ³²JCP = 9.1 Hz, dbf-C₁α), 129.9 (s, m-Mes), 129.7 (s), 129.5 (s), 128.1 (s), 126.5 (s), 126.2 (s, o-Ph₂), 125.4 (d, ³²JCP = 8.3 Hz), 122.2 (s, p-Ph₂), 112.2 (d, ³²JCP = 107 Hz, ipso-Ph), 12.0, 30.2 (s, MgCH₂CH₂CH₂CH₃), 20.6 (s, p-Mes (CH₃)), 20.3 (s, o-Mes (CH₂)), 14.0 (s, MgCH₂CH₂CH₂CH₃), 11.9 (s, MgCH₂CH₂CH₂CH₃). Dibf-C₁α not observed. ¹¹B NMR (benzene-d₆): δ = 5.6 (br s). Anal. Calcd [%] for C₈₃H₇₁BF₂₃O₂Mg₂N₂OP₂: C, 81.81; H, 6.46; N, 2.33. Found: C, 80.85; H, 6.33; N, 2.72.

General Procedures for the Polymerization of ε-Caprolactone. Both 2a and 2b were found to be active in the polymerization of ε-caprolactone. Representative procedures for examination of polymerization activity by NMR spectroscopy and preparation of polymer samples for GPC analysis are described herein. GPC analyses were performed using a Viscotek Triple Detector GPC system outfitted with a model 270 Dual Detector Platform (four-capillary viscometer and light-scattering detector). Polymer samples were run in THF at a concentration of 1 mg/mL.

In Situ NMR Analysis of ε-Caprolactone Polymerization. A representative procedure for the polymerization of ε-caprolactone by 2b is described herein. All NMR-scale polymerization procedures using 2a and 2b made use of similar methods. Polymerization reactions at low temperature (~40 to 0 °C) were performed by allowing the solution containing initiator to equilibrate within the precooled instrument for 20 min prior to monomer injection. Low-temperature reactions were run in toluene-d₈ rather than benzene-d₆.

An NMR tube was charged with 0.0010 g (0.00083 mmol) of 2b to which 2.2 mL of benzene-d₈ was added. The tube was capped with a rubber NMR tube septum, which was then wrapped in parafilm and shaken vigorously. Dry, distilled ε-caprolactone (48 μL, 0.43 mmol, 5.2 × 10² equiv) was measured under an inert atmosphere into a 100.0 μL gastight micro-syringe, which was sealed by inserting the needle into a rubber septum until immediately before addition to the reaction mixture. Prior to monomer injection, all appropriate instrumental parameters were set and NMR spectra of the initiator were collected. The sample was then removed from the instrument, injected with the monomer, shaken, and reinserted into the NMR spectrometer. Collection of NMR data began within 60 s of injection of the monomer. Conversion percentages were determined by integration of the most downfield methylene resonance (ε-COCH₂–) of the polymer (¹³C{¹H} NMR (benzene-d₆): δ = 3.98 (t, ³²JHH = 6.1 Hz, 2H)) relative to those of the residual monomer (¹¹H NMR (benzene-d₆): δ = 3.59 (t, ³²JHH = 6.1 Hz, 2H)), as these resonances were most clearly resolved from all other monomer, polymer, initiator, and residual solvent resonances.

Preparation of Isolated Poly(ε-caprolactone) Samples. A representative procedure for the polymerization of ε-caprolactone by 2b is described herein. All preparations of polymer and oligomer samples for GPC, NMR, or MALDI-ToF analysis used a similar methodology.

Under an inert atmosphere, a 50 mL round-bottom flask was charged with 0.0310 g (0.0258 mmol) of 2b, to which 10 mL of benzene was added. The solution was stirred rapidly, and 1.20 mL (1.24 g, 10.8 mmol, 418 equiv) of ε-caprolactone was injected, resulting in the immediate formation of a thick gel. After 30 min, the reaction mixture was transferred to a 60 mL syringe and added to 100 mL of rapidly stirring methanol under aerobic conditions. This resulted in the immediate precipitation of polymer, which formed a single solid mass that could easily be mechanically separated. The polymer was dried in vacuo, yielding 0.700 g of material (~57%).

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Supporting Information Available: Supporting experimental and X-ray crystallographic data in PDF format and CIF files are available free of charge via the Internet at http://pubs.acs.org.