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“Link-Functionalized” Polymers: An Unusual Macromolecular Architecture through Bifunctional Initiation

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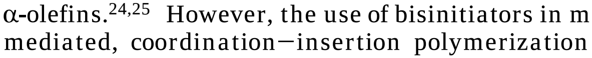
ABSTRACT: Bimetallic complexes of the type $(C_5Me_5)_2Sm{-}R{-}Sm(C_5Me_5)_2$ were used for the living bis-initiated polymerization of methyl methacrylate and ϵ-caprolactone, giving polymers with discrete functionalities at the center of the backbone (“link-functionalized”). Poly(methyl methacrylate) containing olefin units was prepared from $[(C_5Me_5)_2Sm]_2(\mu\text{-}\eta^3\text{-}CH_2CHCH{-})_2$ and related allyl compounds, although slow and/or inefficient initiation of polymerization is observed for complexes in which R is a bulky, heteroatom, or coordinating group. In contrast, the polymerization of ϵ-caprolactone may be carried out with good control in the presence of both sterically hindering and electron-rich moieties. Polylactones incorporating aromatic, cumulene, and amine/imine groups were synthesized through one-step bimetallic initiation in this manner. Differences between lanthanide(III) methacrylate and lactone polymerizations, differences between lanthanide(III) and aluminum(III) lactone polymerizations, and the presence of transesterification in the lactone system are discussed.

Introduction

Polymers with specifically placed functionalities—such as macromonomers, telechelics, and end-functionalized macromolecules—are of great synthetic utility and commercial interest.[1] The reactive sites present in these structures render them useful precursors to triblock copolymers, star and graft polymers, and cross-linked networks. Chain extension, network formation through reaction injection molding, and attachment of a solid support or biologically active molecule may also be carried out at these sites. As part of our work involving the use of living bis-initiated transition metal polymerizations to control polymer architecture,[2−4] we have investigated the synthesis of a more unusual structure: that of polymers containing a discrete, symmetrically located backbone functionality (“link-functionalized” polymers or LFPs).

In contrast to other types of functionalized polymers, LFPs have not been widely prepared. The few reports of these structures which exist, however, clearly demonstrate their potential as useful materials: First, LFPs may serve as building blocks to other architectures. Yagci and co-workers have synthesized polystyrene and polyether LFPs containing a backbone azo functionality which may be cleaved thermally, giving radical-ended polymers which serve as macroinitiators for the subsequent block copolymerization of vinyl monomers.[5−8] Second, LFPs are useful models for the environment experienced by the polymer backbone. The groups of Ediger, Monnerie, and Yamamoto have used macromolecules containing an interior 9,10-anthracene group to study static and dynamic chain stiffness by fluorescence anisotropy decay.[9−13] “Once-broken” worms or rods, helical polymers incorporating a flexible moiety, have also been utilized to gain an understanding of the rigidity of extended-conformation macromolecules such as poly(γ-benzyl α,L-glutamate).[14−17] Third, if an LFP functionality is introduced upon initiation, it may be used to influence the polymerization process itself. This ability was noted by Jérôme, Teyssié, and co-workers for the synthesis of poly(ϵ-caprolactone) with a bifunctional $Et_2Al{-}[S(CH_2)_2S]{-}AlEt_2$ initiator.[18] In this instance, coordinative interactions between sulfur and the aluminum active center resulted in an almost twofold increase in the polymerization rate and the formation of a reversible gel. Finally, a link-functionalized site can be uniquely used to chemically cleave a polymer in half. This feature was demonstrated by Yagci with polyethers and polystyrene[19] and by Steinbrecht and Bandermann with poly(methyl methacrylate).[20] The importance of facile main-chain cleavage may lie in biodegradability for carbon-backbone polymers, which tend to only support good bacterial growth at low molecular weights.[21]

Since it is impossible to place a discrete group along a macromolecular backbone through any polymerization process involving only one active center, the synthesis of LFPs is not trivial. They may be prepared by the coupling of two end-functionalized polymers; however, this method is limited by efficiency, and cumbersome fractionation steps are often required to remove uncoupled material.[9,13,22,23] Additionally, the coupling step itself tends to “use up” any useful functionality which might otherwise be incorporated into the polymer backbone. A more elegant route is through bifunctional initiation (eq 1), a process which employs a catalyst having two active centers which are linked by a bridging initiating group. Polymerization occurs simultaneously at both centers, and the linking unit becomes incorporated at the statistical center of the polymer backbone. Bifunctional initiation has been used extensively in anionic polymerization since Szwarc first utilized styrene dianion for the polymerization of dienes and α-olefins.[24,25] However, the use of bisinitiators in metal-mediated, coordination−insertion polymerization has been quite rare.[2,3,18,26,27]



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Yasuda has shown that organolanthanide complexes of the type $Cp^*{}_2Sm{-}R$ (where $Cp^* = C_5Me_5$ and R = hydride, alkyl, alkylaluminum) function as initiators for the highly syndiotactic, living polymerization of methyl methacrylate (MMA).[28−33] Well-controlled polymeriza-

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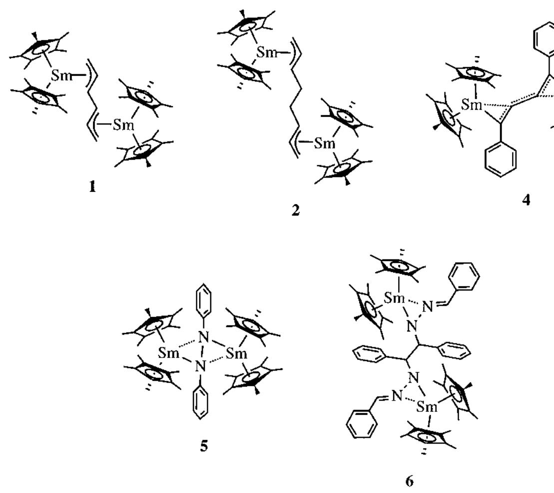
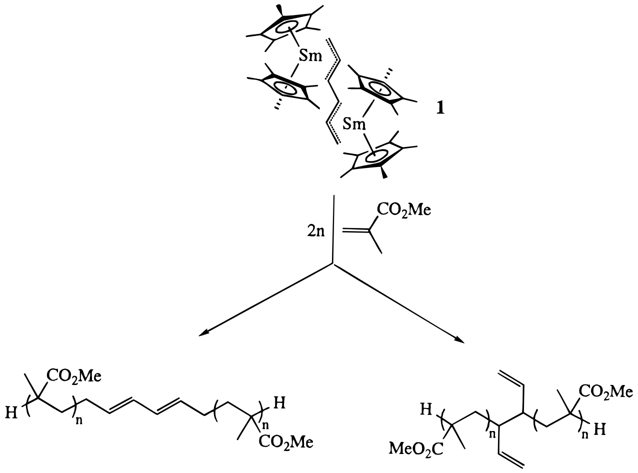


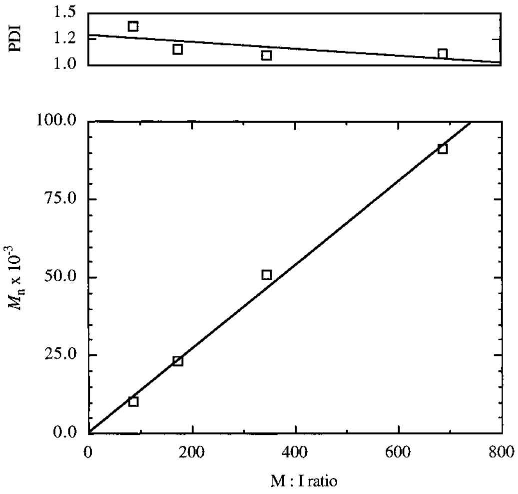
Figure 1. Bimetallic samarium(II) initiators.

Scheme 1. Synthesis of Olefin-Functionalized PMMA with 1



tions and block copolymerizations of acrylates, lactones, and ethylene by these compounds have been reported.[30−37] We have been working to develop new bisinitiating polymerization systems based on the lanthanides and report herein the synthesis of "link-functionalized" poly(methyl methacrylate) (PMMA) and poly(ϵ-caprolactone) (PCL) with bimetallic Cp*$_2$Sm−R−SmCp*$_2$ complexes. An initial report of this work appeared previously in this journal.[38]

The ideal polymerization system for the synthesis of LFPs should possess two distinct characteristics in addition to "living" behavior. First, bisinitiators incorporating a wide range of functionalized bridging initiating groups must be available; secondly, initiation and propagation must be tolerant to these groups. Samarium(III) polymerization is particularly well-suited in regards to the first criterion due to the variety of bimetallic Cp*$_2$Sm^{III} complexes which have been prepared by 2 × 1-electron transfer to organic substrates from decamethylsamarocene.[39−43] We selected a representative array of these complexes to study as initiatiors, choosing those which we felt would both produce interesting LFPs and help us evaluate the generality and usefulness of the system with regards to the second criterion. Additionally, previous lanthanide(III) polymerization studies by Yasuda have involved only hydride and alkyl initiators; we hoped to gain further insight into this polymerization system in general by studying the behavior of other initiating groups.



M : I Ratio	Calculated M_n	Observed M_n[a,b]	Observed PDI[b]	Yield (%)
86	8 590	10 200	1.37	43[c]
172	17 180	23 230	1.15	100
343	34 360	50 870	1.09	100
686	68 720	91 280	1.11	100

[a] THF, 0 °C, 24 h; [1] = 0.00343-0.00458 M; [MMA]$_0$ = 0.377-2.357 M. [b] GPC (CHCl$_3$, vs. PMMA). [c] Low due to partial solubility during precipitation into methanol.

Figure 2. Polydispsersity and molecular weight versus monomer to initiator ratio for the polymerization of MMA with **1**.

Table 1. Polymerization of Methyl Methacrylate with 2 and 3

cat.	calcd M_n	obsd M_n[a,b]	obsd PDI[b]	yield (%)
2	31 060	37 960	1.03	95
3	31 200	55 180	1.01	100

[a] Toluene, room temperature, 16 h. [b] GPC/LS.

Methyl Methacrylate. (A) Allyl Complexes. We began our study of the synthesis of link-functionalized PMMA with the bis-allyl complex [Cp*$_2$Sm(μ-η^3-CH$_2$-CHCH−)]$_2$ (**1**) (Figure 1).[44] Lanthanide(III) allyls are quite reactive, serving as initiators for the polymerization of ethylene[45,46] and precatalysts for the hydroamination of amino olefins.[47,48] Depending on the mode of attack during initiation, the link-functionality resulting from this process should comprise either two pendant vinyl groups or a backbone 1,3-diene unit (Scheme 1). As olefins can be polymerized or easily transformed into other useful groups, these structures would be versatile precursors for the synthesis of other architectures. The diene unit additionally presents a route into main-chain cleavage through ozonolysis.[49] Given that Cp$_2$Sm^{III} allyl complexes (Cp = C$_5$H$_5$) are known to add to ketones through the more substituted carbon,[50,51] the pendant vinyl structure is more likely.

Complex **1** polymerizes MMA in a well-controlled fashion in either toluene or tetrahydrofuran (THF). Temperatures of −78 °C to room temperature may be employed; the use of THF as solvent appears to provide the best control. Quantitative yields of PMMA having low polydispersity (typically ≤1.15) were obtained, and a linear relationship was observed between M_n and the monomer to initiator ratio (Figure 2), demonstrating a lack of chain transfer and good molecular weight control even at high M:I ratios. Polymerization with a second allyl complex, [Cp*$_2$Sm(μ-η^3-CH$_2$CHCHCH$_2$−)]$_2$ (**2**), gave similar results (Table 1). In order to more accurately assess the degree of control present during polymerization, molecular weight analysis of PMMA prepared with **2** was carried out by tandem gel permeation chromatography/light scattering (GPC/LS). The true polydispersity of the resultant polymer was found to be quite narrow (1.03). For comparison, polymerization with a monometallic initiator, $Cp^{*}_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**3**), was also performed (Table 1). Bimetallic initiators **1** and **2** showed the same degree of control as the monometallic initiator, although the GPC/LS PDI of PMMA prepared with **3** was slightly narrower.

The introduction of small amounts of air and water by brief exposure of the polymerization to the atmosphere was also used to obtain evidence of bisinitiation for **1** and **2**. As a general rule, these samarium(III) initiators are highly air and/or moisture sensitive. Although the exact reactions are not fully understood, they rapidly decompose to nonactive complexes. The molecular weight distributions of PMMA synthesized under rigorously air- and water-free conditions with these complexes were monomodal, but those of polymers prepared under less rigorous conditions exhibited lower molecular weight shoulders due to the formation of monoinitiating species by deactivation at one active center. (Any deactivation that might occur at both ends of the initiator would lead to dead molecules that do not contribute to the polymerization behavior.) In contrast, atmospheric contamination during polymerization with monoallyl complex **3** produced PMMA still having a symmetric, although broadened, monomodal molecular weight distribution.

Although all other features of polymerization with **1**, **2**, and **3** are indicative of a "living" process, we did observe that the molecular weights of the PMMA obtained are somewhat higher than calculated values. This effect was most severe for **1** and **3**; however, the exact magnitude of inflation tended to vary depending on the exact conditions and the particular batch of catalyst used. It is likely that catalyst purity plays a large role in this effect, as the complexes are highly soluble and we were not able to obtain reagent quantities of pure material by recrystallization. The synthesis of **1** and **3** is atypical of bimetallic decamethylsamarocene reductions in that reduction of the necessary olefin reagents (1,5-hexadiene and propene, respectively) to allyl moieties necessitates the removal of a hydrogen and results in the formation of byproducts by a mechanism which is not yet fully understood.[45] Extraction is used to remove these species from products **1** and **3**; contamination by undetected noncatalytic impurities may result in an apparent relative inefficiency of this process. (Although inert, any impurities contribute to the "weight of the catalyst" used, and hence, effectively increase the monomer to initiator ratio.) Molecular weight inflation was noticeably less severe with complex **2**, which is prepared by the clean reductive coupling of two 1,3-butadiene units rather than through a mechanism involving hydrogen abstraction. It is possible that side reactions of the allyl species with MMA also contribute to the observed inflation, as $[Ln(\eta^3\text{-}CH_2CHCH_2)_4]^-[Li]^+$ complexes are known to undergo 1,2-addition to nonpolymerizable enones.[52] However, any significant side reaction involving the allyl group would have resulted in an unavoidable bimodal molecular weight distribution for polymerization with bimetallic initiators **1** and **2** due to deactivation of one of the two initiating centers.

To confirm incorporation of the allyl functionality into the polymer, a low molecular weight PMMA oligomer was prepared with **2** and examined by ^1H NMR (Figure 3). The olefin resonances arising from the inserted moiety appear as a multiplet at 5.9−5.8 ppm; unfortunately, resolution is not sufficient to allow distinction between the possible diene and pendant vinyl structures. The spectrum of an end-functionalized oligomer prepared with monoinitiator **3** was also obtained and shows resonances at 6.0−5.9 ppm in a 1:2 ratio representing the internal and inequivalent external protons of the olefin end-functionality (Figure 4). The character and approximate area of the olefin proton peaks remained constant throughout the multiple reprecipitation steps employed for purification.

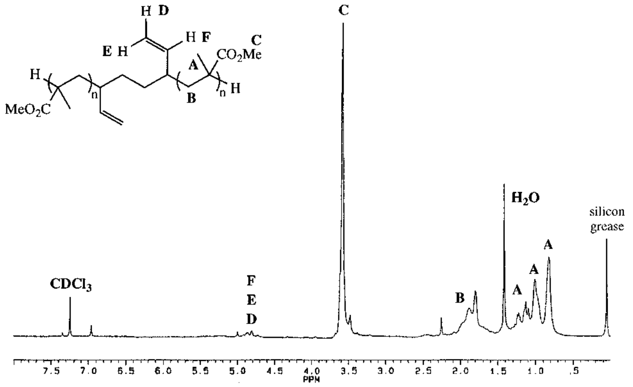
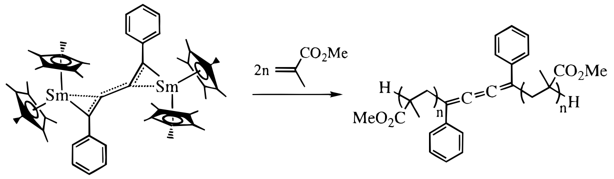


Figure 3. 200 MHz ^1H NMR spectrum of olefin-functionalized PMMA oligomer prepared with **2**.

To further show that these resonances arise from the allyl moiety, the ^1H NMR spectrum of the product of **3** and 2 equiv of MMA in toluene-d_8 was recorded (more than 1 equiv of MMA is necessary to achieve complete insertion due to the dilute conditions and brief time period of the NMR-scale reaction). The resonances arising from the three olefin protons are clearly seen in a 1:2 ratio near 5.4 and 4.8 ppm and are broadened due to interaction with samarium (Figure 5). Due to the presence of multiple insertion products and minor deactivation of the sensitive enolate centers, the region of the spectrum below 3.5 ppm is somewhat complicated. However, the C_5Me_5 protons of the inserted species are easily seen as a broad singlet at 1.14 ppm.

(B) Hindered Carbon Initiators. The controlled synthesis of PMMA with **1** and **2** indicates that bifunctional samarium(III) polymerization is a viable route into methacrylate LFPs. To further assess the types of linking groups which may be used in the system, MMA polymerization with the trienediyl complex $[Cp^{*}_2Sm]_2(\mu\text{-}\eta^2{:}\,\eta^2\text{-}PhC_4Ph)$ (**4**) was investigated (eq 2). This unusual species possesses an electronic structure intermediate between a 1,3-diyne and a butatriene.[53,54] The C_4 moiety is highly sterically protected by four C_5Me_5 rings and two phenyl substituents. Thus, **4** serves as a good model to evaluate the effects of steric hindrance in the synthesis of LFPs, being electronically fairly similar to the unhindered allyl complexes.



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Initiation with **4** would theoretically produce an LFP containing a 1,2,3-butatriene group. Teuben and coworkers have found that the trienediyl units of related cerium and lanthanum complexes are susceptible to rearrangement upon protolysis to form a more thermodynamically stable enyne unit;[55] however, the amount of rearrangement is inversely related to the degree of steric bulk provided by the 1,4-substituents. Given the smaller radius of samarium and the size of the phenyl groups, it seems unlikely that a similar rearrangement

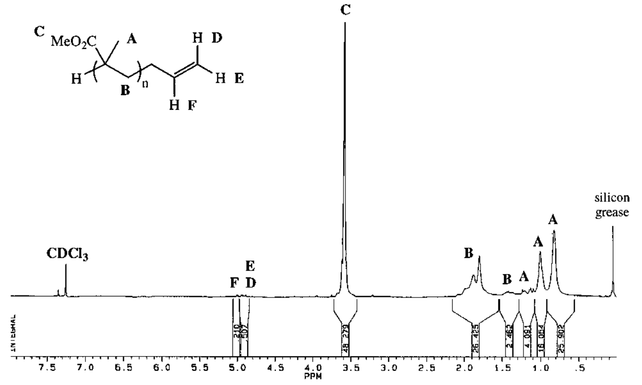


Figure 4. 200 MHz ^{1}H NMR spectrum of olefin end-functionalized PMMA oligomer prepared with **3**.

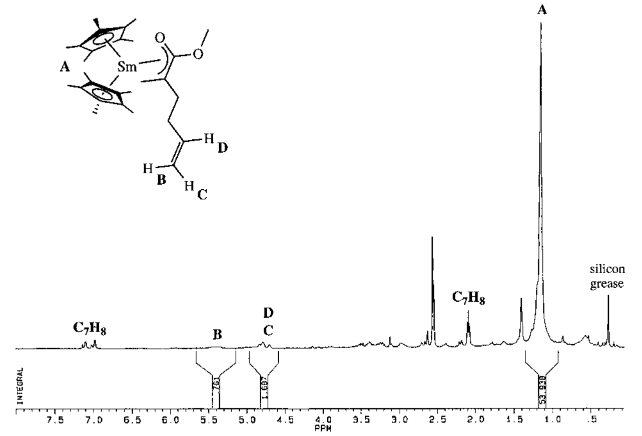


Figure 5. 200 MHz ^{1}H NMR spectrum of the insertion product of **3** with MMA.

would occur during initiation with **4**. If this process was operable, the resultant polymer would possess a 1-(phenylethynyl)-2-phenylethylene link functionality.

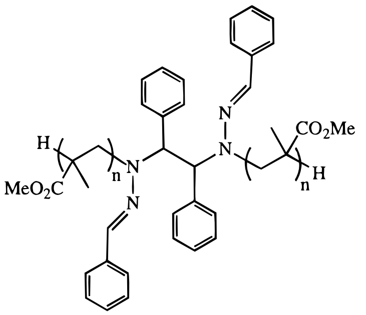
When MMA was added to deep orange **4** in toluene at 0 °C, a slow (10 min) color change to the characteristic enolate yellow was observed. A quantitative yield of PMMA was subsequently isolated, but possessed a GPC molecular weight of over 7 times the calculated value (observed $M_n = 348\ 060$;[56] calculated $M_n = 46\ 570$). The polydispersity of the PMMA was also anomalously high at 1.25.[56] These results indicate that initiation with the trienediyl unit of **4** is slow and quite inefficient. Evidence supporting a steric origin of slow initiation was obtained upon changing the polymerization solvent to THF. With this donor solvent, which competes with monomer for the already limited access to the metal center, no polymer was obtained. It is likely that the inefficiency of the initiation process also reflects steric effects arising from the multihapto nature of the bonding between samarium and the trienediyl.

(C) Heteroatom and Donor Group Initiators. Next, we wished to determine if heteroatom initiators could be used for the synthesis of methacrylate LFPs. Yasuda has noted that lanthanide(III) alkoxides do not catalyze the polymerization of methyl methacrylate, a consequence of the lower basicity of alkoxides as compared to enolates.[30] However, amido compounds are sufficiently basic to act as potential initiators and would produce PMMA containing nitrogen groups which could, for example, be selectively protonated or used as Lewis bases. Precedents for polymerization through lanthanide−nitrogen bonds exist; $Cp^*_2Ln^{III}$ amido complexes are known to insert unsaturated groups such as carbon monoxide and monosubstituted olefins,[57,58] and $Cp^*_2LaNMe_2$ and $Cp^*_2NdNMe_2$ catalyze the polymerization of ethylene.[48,59] Magnesium amides have been used in the same manner as Grignard reagents for the anionic polymerization of MMA.[60]

As no bimetallic $Cp^*_2Sm^{III}$ alkyl or aryl amide compounds are reported in the literature, we chose the azobenzene complex $[Cp^*_2Sm]_2(\mu\text{-}\eta^1\text{:}\ \eta^1\text{-}N_2Ph_2)$ (**5**)[58,61]—which has a relatively simple linker structure—to serve as a representative nitrogen initiator. Polymerization of MMA with **5** in toluene was successful, giving a fairly high yield of monodisperse polymer, but the observed molecular weight of the PMMA was nearly 4 times the expected value (Table 2). However, **5** is not an optimal model to gauge the efficiency of samarium−nitrogen bond initiation. The azobenzene moiety is highly delocalized and weakly bound, and the complex undergoes unusual ligand redistribution or bond cleavage reactions with THF and CO.[58,61]

It is likely that similar reactions play a part in the observed molecular weight inflation. When 1 equiv of azobenzene is added in THF to **5**, which is deep blue, the dimer structure is cleaved to give 2 equiv of a green monomeric complex, $Cp^*_2Sm(\eta^2\text{-}PhN_2Ph)(THF)$.[58] This process involves formal transfer of one electron from the doubly reduced bridging azo moiety to free azobenzene. A similar color change to green, rather than to the usual yellow of the propagating enolate, was seen when MMA was added to **5**. This suggests that formation of the monomeric, singly reduced complex occurred through dimer cleavage and electron transfer to MMA. The second product in this process would be a Cp^*_2Sm-ligated radical enolate anion; coupling of these species to give a bimetallic initiator[38] could then occur (Scheme 2). Since only half of the original samarium centers would be transformed into radical anions and since molecular weight doubling would result from the dimerization of these species, this mechanism is consistent with a 4× inflation of M_n from the calculated value.

We next chose two additional complexes, $[Cp^*_2Sm]_2[\mu\text{-}\eta^2\text{:}\ \eta^2\text{-}(PhHC{=}NNCHPh{-})]_2$ (**6**)[52] and $Cp^*_2Sm(NHPh)(THF)$ (**7**),[63] as improved models. Like **5**, complex **6** possesses a linking group with an N−N bond, but its bridging moiety involves only one metal interaction per unit. Amido complex **7** was selected as a monometallic equivalent for **5.** Both are more stable, undergoing only coordination with THF rather than redistribution.[62,63] PMMA synthesized with **6** would possess a link functionality containing aromatic, amine, and Schiff base-like units (a control reaction of **6** with terminating agents confirmed that the linker structure remains intact upon protolysis):



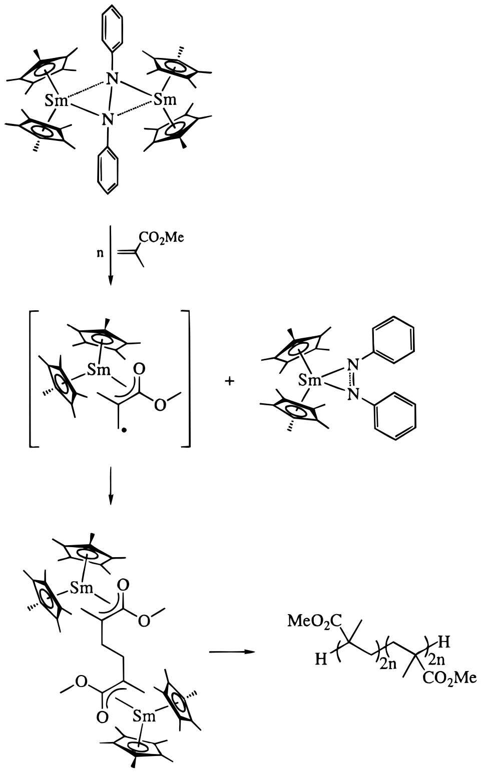
Polymerization of MMA with **6** and **7**, however, also gave inefficient initiation (Table 2). This effect was particularly evident for **6**, which produced polymer having a molecular weight of over 16 times the calculated value when the polymerization was carried out in toluene. In THF, the molecular weight inflation was extremely severe; a polymerization quenched at only

Table 2. Polymerization of Methyl Methacrylate with Samarium(III) Nitrogen Initiators

cat.	conditions	calcd M_n	obsd M_n (GPC)	obsd PDI (GPC)	yield (%)
5	0 °C, 8 h, toluene	14 550	52 300[a,b]	1.12[a]	77
6	-78 °C, 19 h, toluene	18 190	≈300 000[a,b]	≈2.0[a]	100
6	0 °C, 1.5 h, THF	31 730	930 980[c]	1.18[c]	29
7	-78 °C, 3 h, toluene	12 510	88 540[a,b]	1.20[a]	76

[a] THF, vs polystyrene. [b] This value is probably somewhat low due to hydrodynamic differences of PMMA and polystyrene in THF. [c] $CHCl_3$, vs polystyrene.

Scheme 2. Possible Mechanism for Initiation of MMA Polymerization with 5



29% conversion produced PMMA with an M_n approaching one million.

This behavior confirms that initiation of methacrylate polymerization through samarium−nitrogen bonds is not a quantitative process, presumably due to side reactions of the electron-rich nitrogen anion with the highly functionalized monomer. However, the large difference in behavior between **6** and complexes **5** and **7** requires further explanation. It is logical that the imine lone pair present in the bridging moiety of **6** is responsible for this effect, as this highly donating moiety is locked into a favorable position for coordination to a samarium center.[62] Since MMA coordination through the carbonyl oxygen competes unfavorably with binding of the imine, only a small fraction of centers are able to undergo insertion. The further inflation seen in THF supports this conclusion, since this donor solvent would further bias the associative equilibrium against monomer. A preference of lanthanides for unsaturated nitrogen donors over oxygen donors has been recently demonstrated by Evans, who found that *N*-methylimidazole can displace THF from $Cp^*{}_2Sm(THF)_2$ to form $Cp^*{}_2Sm(N\text{-}MeIm)_2$.[64]

To verify that polymerization is impeded by nitrogen donor functionalities, polymerization was attempted with allyl initiator **1** in the presence of 2 equiv of pyridine, which is known to solvate $Cp^*{}_2Ln^{II}$ and $Cp^*{}_2Ln^{III}$ complexes.[65] Only a trace of polymer (<5 mg) was obtained; a second trial gave identical results. Yasuda has observed a similar inhibition of MMA polymerization with $Cp^*{}_2SmMe(THF)$ in pyridine.[29]

Poly(ϵ-caprolactone). Poly(ϵ-caprolactone) is one of the few literature examples of polymers which have been endowed with link-functionality through the use of bisinitiating coordination catalysts.[18,27] To investigate the samarium(III) synthesis of link-functionalized PCL, complexes **1**, **4**, and **6** were chosen. Yasuda has noted that the exact mechanism of initiation for $Cp^*{}_2Ln^{III}$ lactone polymerization differs for alkyl and alkoxide catalysts.[37] In the case of alkoxides a direct ring opening of the first lactone monomer is observed, which is identical to the propagation step of the polymerization. For the alkyl catalysts, addition to the first monomer unit is proposed to occur without ring opening to give a cyclic acetal. Thus, with carbon initiators **1** and **4**, addition to the first lactone molecule without ring opening may be assumed; for **6**, whose nitrogen nucleophile is less electron-rich than an alkoxide, non-ring-opening initiation is likely but not certain.

Treatment of CL with **1**, **4**, and **6** in toluene or THF at 0 °C for 1−3 h, followed by protolysis with 5% aqueous HCl, resulted in the formation of PCL in yields of 67% and higher (Table 3). Subsequent polymerizations with **8** showed that improved yields of polymer can be obtained under more concentrated conditions or after longer reaction times. The PCL prepared with these initiators is telechelic, as α,ω-hydroxy groups are introduced upon termination of the two active centers.

For trienediyl catalyst **4**, incorporation of the bridging PhC_4Ph unit was confirmed by ^1H NMR spectroscopy of a similarly prepared oligomer (Figure 6). The end group CH_2OH protons are also observable in the spectrum of the functionalized oligomer (3.59 ppm, triplet, $J = 6.5$ Hz).[66] Due to the relatively long relaxation times of aromatic centers and the large number of scans (>300) needed to obtain the spectrum of the oligomer, the end groups are more distinctly observed than the linking group.

One feature should be noted regarding molecular weight determinations for PCL, which we carried out by GPC. By comparison with universal calibration values, McLain and Drysdale have determined a correction factor of 0.45 for PCL molecular weights determined in THF versus polystyrene at room temperature.[67,68] The GPC apparatus used in our experiments utilized either THF or chloroform, varyingly, and PCL molecular weights determined in THF were easily corrected to absolute values with this relationship. Unfortunately, a similar factor has not been reported for $CHCl_3$. To determine absolute molecular weights for PCL from chloroform values, available samples were reanalyzed in THF when possible. A conversion factor of 0.20−0.35 from chloroform weights to absolute weights was calculated by this method. However, due to the gradual degradation and hydrolysis of PCL at ambient temperature[69] and random fluctuations of GPC retention times based on thermostating and standardization accuracy, refinement of this range to a specific value was not possible. A factor of 0.3 has been used to convert the M_n values presented here; these figures are marked as approximate (≈).

As determined by these methods, the molecular weights of PCL prepared with **1** and **4** are reasonably near calculated values. Those observed with **6** are inflated to some extent if yield is taken into account. However, it should be noted that uncertainties regarding not only the 0.3 conversion factor but the degree of

Table 3. Polymerization of CL at 0 °C with Bimetallic Samarium(III) Initiators

cat.	solvent	calcd M_n	yield (%)	obsd M_n[a]	PDI[b]	high-MW peak[a]	low-MW peak[a]
4	toluene	41 010	73	29 710	1.12		
6	THF	29 610	67	≈34 080[c]	1.17		
1	toluene	22 140	100	24 130	1.24 (bimodal)		
2	toluene	48 840	98	28 230	1.28 (bimodal)	50 440	22 350
3	toluene	29 000	92	31 220	1.45 (bimodal)	43 660	15 900

[a] From GPC measurements in THF. Reference 67. [b] GPC (THF, vs polystyrene). [c] Estimated from GPC ($CHCl_3$, vs polystyrene) as described.

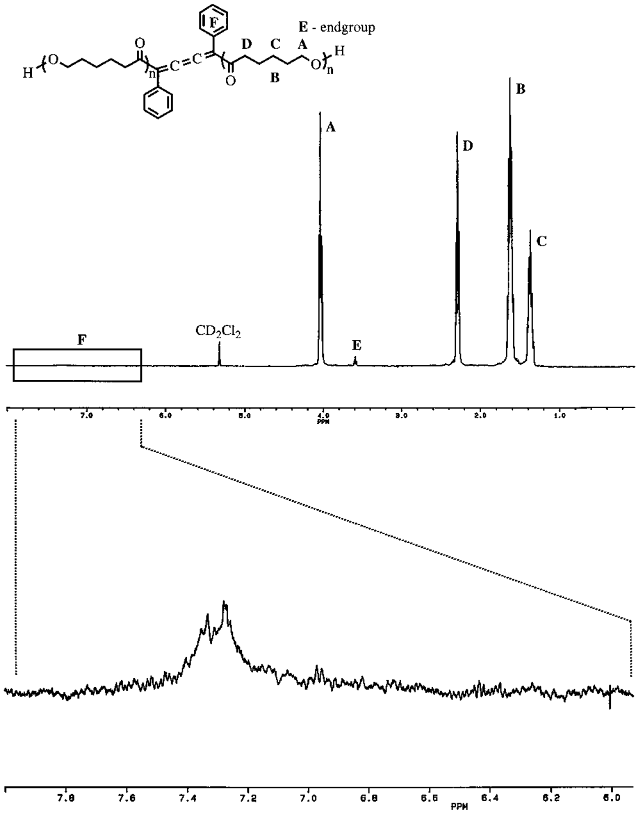


Figure 6. 400 MHz ^{1}H NMR spectrum of PhC_4Ph-functionalized PCL.

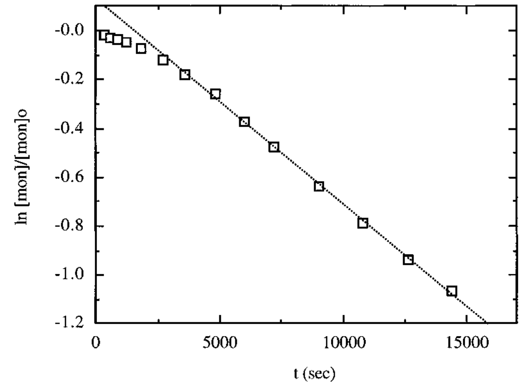


Figure 7. Initial-rate ^{1}H NMR kinetics for CL polymerization with **4**. Toluene-d_8, 0 °C; [**4**] = 0.0182 M; $[CL]_0 = 0.617$ M.

solvation of this catalyst are operative. Complex **6** reportedly crystallizes with 3 THF and $^1/_2$ toluene molecules of solvation per unit, although we did not observe THF species in the ^{1}H NMR spectrum of the "easily desolvated" complex.[62] M_n values were calculated assuming a toluene hemisolvate structure for **6**; the presence of additional weight in the form of undetected THF would act to increase the monomer to initiator ratio. This effect for a full three THF molecules of solvation would cause a 17% inflation from the calculated M_n values.[70]

(A) Allyl Complexes. The molecular weight distributions of link-functionalized PCL prepared with **4** and **6** were monomodal and fairly monodisperse. Surprisingly, with **1** a broad, overlapping, bimodal distribution was seen. We initially attributed this to monoinitiation by some fraction of the **1** molecules and thought that some factor involving the conjugated nature of the two allyl groups might be responsible. However, a similar result was obtained with **2** (Table 3). The GPC molecular weight of the smaller peak was approximately half of the weight of the larger peak, suggesting that the bimodality arose from contamination with a small fraction of monoinitiator. However, the M_n of the larger peak was substantially higher than the calculated value. Additionally, two peaks were seen in the distribution of PCL prepared with monometallic initiator **3**. The molecular weights of the peaks in this case were not related by a factor of 2, although their large degree of overlap may have numerically biased this relationship. The area ratio of the two distributions varied with catalyst; the higher M_n peak was largest for **3** and smallest for **2**. The average molecular weights of the polymers obtained were not inflated as calculated from monomer/initiator ratio, indicating that the majority of the allyl groups are active during initiation.

A possible explanation for this phenomenon, suggested by the inflated molecular weights of the larger polymer species in the distribution, is cross-linking through the incorporated allyl groups to give star polymers, during either polymerization or acid protolysis. A second possibility is disproportionation of the $Cp^*_2Sm(allyl)$ compounds to two active species which catalyze the polymerization at different rates, although C_5Me_5 groups have traditionally been successful at suppressing such reactions in lanthanide chemistry.[71] $Cp_2Sm(allyl)$ complexes are known to add to ketones, aldehydes, and acid chlorides in a manner similar to Grignard reagents;[50,51] however, their behavior toward esters has not been explored.[72] It is possible that catalysts containing less-reactive interior allyl groups would act as more satisfactory initiators.

(B) Hindered Carbon Initiators. Given its behavior with MMA, it is quite interesting that complex **4** carries out lactone polymerization in both toluene and THF with a high degree of control. Although the molecular weights and polydispersity indices of PCL prepared with **4** were no less satisfactory than those obtained with **6** or with monometallic alkyl and alkoxide complexes,[37] we noticed that the behavior of **4** upon monomer addition was slighly different than that of **1**, **2**, **3**, and **6**. When CL was added to an orange solution of **4** in toluene or THF, a transient green color (lasting ≤0.5 s) was often observed before formation of the yellow propagating samarium(III) alkoxide. Initiation thus proceeds through an intermediate which is long-lived enough to be detected visually but still consumed on a time scale equivalent to propagation. Our suspicion of slow initiation was confirmed by studying initial rate kinetics by ^{1}H NMR. As shown in Figure 7, the rate of monomer disappearance is relatively slow at the

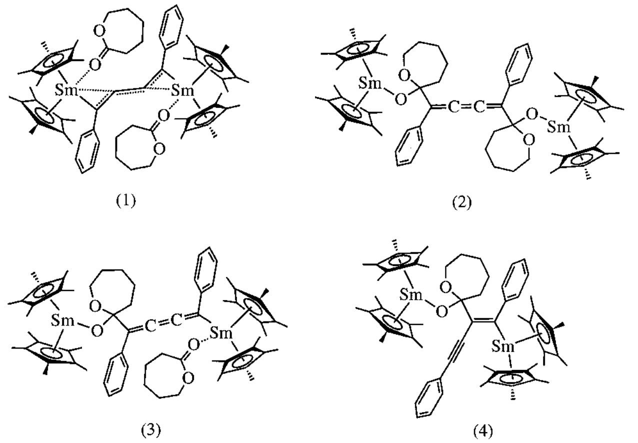


Figure 8. Possible intermediates for CL initiation with **4**.

Table 4. Solvent and Temperature Effects on CL Polymerization with 4

T (°C)	t (h)	solvent	calcd M_n	yield (%)	obsd M_n[c]	PDI[d]
0[a]	2:30	toluene	39 650		≈39 780	1.18
0[a]	2:35	THF	38 520		≈36 040	1.11
0	17	pyridine	70 440	96	≈35 980	1.34
−20[b,e]	11	toluene	31 510	90	≈30 570	1.17
−20[b,f]	17	toluene	33 090	85	≈32 540	1.22

[a] Carried out at $[CL]_0$ = 0.694 M, [**4**] = 0.00201−0.00207 M. [b] Carried out at $[CL]_0$ = 1.621−1.690 M, [**4**] = 0.00586−0.00591 M. [c] Estimated from GPC ($CHCl_3$, vs polystyrene) as described. [d] GPC ($CHCl_3$, vs polystyrene). [e] Initiated at room temperature. [f] Initiated at approximately −25 °C.

beginning of the reaction but reaches a constant value at approximately 1/3 half-life, consistent with a slow initation process in which the number of active centers increases during the early stages of polymerization.[73]

We found that the effects of slow initiation could be observed more readily at lower temperatures. When monomer was added to toluene solutions of **4** at temperatures below −30 °C, a color change from orange to emerald green was observed. The green species persisted until the solution was warmed to approximately −50 to −25 °C,[74] at which the usual color change to yellow was observed along with the production of polymer. This unidentified intermediate is quite stable at low temperature. When 245 equiv of ϵ-caprolactone was added to **4** in toluene at −78 °C and the resultant solution maintained at that temperature for 21 h, no further color change was observed. In contrast, addition of CL to **2** and **6** under identical conditions resulted in an immediate color change to bright yellow, indicating the formation of the alkoxide species.[75]

Barring the possibility that a different mechanism is operative with **4** than with other samarium(III) initiators, a structure for the green species can be proposed. Relatively low energy intermediates are imaginable at three points during the initiation process: (1) after lactone coordination to samarium but prior to insertion; (2) after non-ring-opening insertion of the lactone into the bridging moiety; (3) after insertion at only one samarium center (Figure 8). Since monometallic samarium alkyls add to lactones without ring opening,[37] it is highly probable that structure (2) is present during initiation. However, it is not obvious why such a species would be so electronically dissimilar to the ring-opened propagating alkoxide as to possess a different color. Monoinsertion at one samarium center would produce structure (3), but the loss of the electron density from resonance, the vacation of a coordination site, and the electron-poor nature of the cumulated group would seemingly activate the second samarium center toward initiation, rather than having the opposite effect. If rearrangement of the trienediyl moiety during initiation does occur, enyne structure (4) is also possible. The significant color shift observed could result in part from formation of this highly conjugated unit.

Lactone adduct (1) is the most likely possibility. Complexes of lanthanide(III) chlorides and $(C_5Me_5)_2SmX$ compounds containing coordinated ϵ-caprolactone are well-known,[37,76,77] and insertion is known to be the rate-determining step in aluminum-catalyzed lactone polymerizations.[78] Coordination of two CL groups would increase the electron density at the samarium centers of red **4**, consistent with a deepening of color.[79] The tightness of the tetracyclopentadienyl cavity in **4**[53,54,80] may seem to argue sterically against a low-energy intermediate containing coordinated lactone, especially since this complex is not known to form THF solvates and does not exhibit a similar color change upon dissolution in THF. However, Evans and coworkers have found that ϵ-caprolactone not only is less sterically demanding than THF but is actually preferred as a donor by $LnCl_3$ complexes.[77] Thus, (1) is not necessarily destabilized for steric reasons.[81]

(C) Heteroatom and Donor Initiators. We were especially interested in the controlled behavior of complex **6** toward CL, given the deactivating effect of its samarium−nitrogen bonds and imine groups for MMA polymerization. To confirm the tolerance of lactone polymerization to Lewis basic nitrogenous donors, a polymerization was carried out with **1** in neat pyridine (Table 4). In contrast to the pyridine reaction of **1** with MMA, a 96% yield of PCL was obtained. The more successful competition of CL versus MMA with pyridine for vacant sites around the samarium center is not surprising, since the MMA carbonyl group is comparatively less electron rich due to the double bond. Although we have not studied bis-initiators requiring direct insertion through samarium−oxygen bonds, the ability of Cp^*_2SmOEt(ether) and related complexes to initiate lactone polymerization indicates that polylactones containing oxygenated link functionalities may most likely be prepared as well.[31,32,37]

Moving beyond nitrogenous donors, the effects of Lewis bases were further probed by comparing polymerizations performed in toluene and THF. Under identical conditions of concentration and time, a slower rate of propagation (evidenced by a lower M_n of the resultant PCL) was observed in THF (Table 4). This is consistent with a coordination−insertion mechanism showing increased competition between monomer and donor solvents for active sites and parallels the trend observed for aluminum[82−84] and titanium[85] lactone polymerizations.

Lastly, the differing character of the highly ionic lanthanide initiators and the more covalent "living" aluminum lactone polymerization catalysts of Jérôme and Teyssié is made apparent with initiator **6**. In the latter system Lewis bases present in 1 equiv, including link functionalities, accelerate the rate of lactone polymerization by factors of up to 4 through coordination to aluminum, which increases the nucleophilicity of the propagating center.[18,78,86] In contrast, polymerization with **6** carried out in THF for 190 min produced the same yield of polymer as polymerization carried out with **4** for 170 min under similar conditions.[87]

We hoped that the precedent of successful lactone insertion into a samarium−nitrogen bond indicated that these catalysts would be active toward nitrogen-containing monomers. However, addition of ϵ-caprolactam to **1** in toluene at 0 °C produced no polymer, instead resulting in discoloration of the catalyst. The characteristic yellow color of samarium(III) amide complexes[47] was not seen. In this case, it is possible that reaction of the samarium center with the amide proton of ϵ-caprolactam occurs.[88] Yasuda has attempted the polymerization of acrylonitrile, 4-vinylpyridine, and 2-vinylpyridine with monometallic lanthanide(III) complexes but found the initiators to be inert to these nitrogenous monomers.[32]

Comparison of Methyl Methacrylate and ϵ-Caprolactone. The trends observed for **1**, **4**, **6**, and other catalysts offer some insights to the respective properties of methacrylates and lactones as both polymerization substrates and ligands for lanthanide complexes. Methacrylate initiation is sensitive to both steric and electronic perturbations, while lactone initiation is seemingly influenced by only steric factors. Thus, it appears that the more electron-rich lactones are better ligands for the electrophilic lanthanides, their alkoxide insertion products are favored over enolates, and they occupy a smaller area when acting as carbonyl oxygen donors (this is consistent with the branched carbon α to the MMA carbonyl).

The preference of initiator **6** for CL illustrates an important feature of bimetallic polymerizations. While steric hindrance can obviously act as a deterrent to initiation with monometallic catalysts, the proximity of two pairs of (C_5Me_5) ligands renders bis-initiating samarium(III) complexes uniquely susceptible to steric perturbations. In catalysts such as **6**, the small linking group inside the tetracyclopentadienyl cavity is harder to access, and successful initiation is possible only with relatively small monomers. For free-ion or radical bis-initiators, which contain no spectator ligands, this limitation is not operative. Protection of the initiating groups by a spectator ligand cavity is thus a unique factor for ligated bimetallic coordination–insertion catalysts, and adequate separation of the two initiating centers must be achieved for controlled initiation.

Transesterification in Cp*$_2$Sm^{III} Lactone Polymerization. Anionic and pseudoanionic lactone polymerizations are plagued by transesterification processes.[89–92] These chain transfer reactions occur when the alkoxide propagating species attacks a carbonyl group along the polymer backbone in an intermolecular or intramolecular fashion, causing the ultimate degradation of the PCL to low M_n oligomers. This process has been successfully kinetically controlled through modification of temperature, relative catalyst concentration, polymerization solvent, or the nature of the active end group.[92,93]

In a typical polymerization, the effects of small amounts of chain transfer—slight broadening and lowering of the molecular weight distribution—are not debilitating. For the synthesis of link-functionalized polymers the consequences are more severe. The backbone redistribution which occurs is a random process; thus, a distribution of chains each containing one link-functionality will be transformed into a sample in which some chains have no functionalized groups and others have more than one. Additionally, the linking groups will no longer be at the statistical center of the polymer backbone. For a case where LFP groups activate neighboring monomer carbonyl units to nucleophilic attack, the resultant distribution may contain a disproportionate number of end-functionalized chains.

Because of these considerations, we wished to investigate the nature and magnitude of potential transesterification during the bimetallic Cp*$_2$Sm^{III} CL polymerization. This process is obviously not significant during monometallic Cp*$_2$Sm^{III} CL polymerization, given the “living” behavior and low polydispersities obtained by Yasuda.[37] However, evidence collected by McLain and Drysdale[67] for Ln(OR)$_3$ complexes indicates that lanthanide initiators are susceptible to backbiting *after* the completion of chain growth, and Evans and Katsumata have observed similar degradation for electron-transfer-initiated CL polymerizations with $(C_5Me_5)_2Sm$, especially in the absence of donor solvents.[94] Yasuda has noted that the polydispersity of PCL prepared with $(C_5Me_5)_2SmCH_3(THF)$ at 50 °C is substantially broader than that obtained at 0 °C (1.70 vs 1.08).[37] This does not necessitate the existence of backbiting but is consistent with a system in which it is present but kinetically supressed under typical conditions.

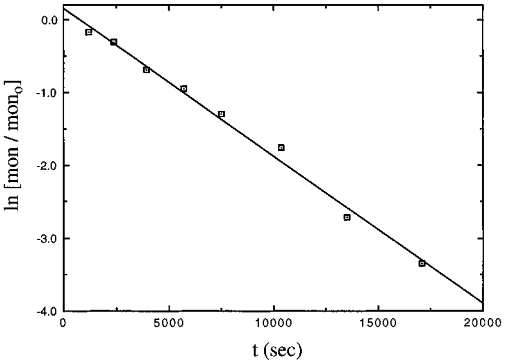


Figure 9. Aliquot kinetics for CL polymerization with **4**. Toluene-d_8, 0 °C; [4] = 0.0187 M]; $[CL]_0$ = 0.617 M.

The low polydispersity indexes (PDIs) obtained with **4** and **6** show that for these initiators, transesterification is not significant when the polymerization is quenched before or near quantitative conversion. To confirm that “living” behavior is maintained for the bis-initiating catalysts, kinetics were carried out with **4**. Aliquot ^{1}H NMR polymerization kinetics showed the first-order monomer dependence expected for a coordination–insertion mechanism; a linear dependence of ln([monomer]/[monomer]$_0$) holds to at least 96% conversion (Figure 9).[95] A rate constant of 2.02×10^{-4} s^{-1} and a half-life of 3 430 s (57 min) were determined for the reaction at $[CL]_0$ = 0.617 M and [**4**] = 0.001 88 M. The linearity of this relationship, indicates the absence of chain termination but does not preclude the presence of chain transfer.[96]

The relationship between molecular weight, polydispersity, and monomer conversion is commonly studied to show a lack of chain transfer.[96] Yasuda has measured PCL molecular weight versus monomer conversion for both alkyl and alkoxide lanthanide(III) catalysts and found a linear relationship in all cases to 90–100%, with polydispersities remaining constant throughout.[37] We observed a similar relationship for **4**, with some experimental complications (Figure 10).[97] Also, the polydispersity of the PCL does not broaden with conversion. Rather, a *decrease* is seen, additional evidence of a slow initiation process being operative for **4**.[98]

To study the effects of backbiting *after* consumption of monomer, four identical polymerizations of CL (0 °C, toluene solvent) with **1** were allowed to proceed to completion. Initiator **1** was chosen because any broadening of molecular weight would be doubly evident for its bimodal distribution of polymer. At completion, one polymerization was quenched and the others were allowed to proceed for additional periods of time. The resultant polymers were weighed for yield and analyzed by GPC (Figure 11); clearly, transesterification does

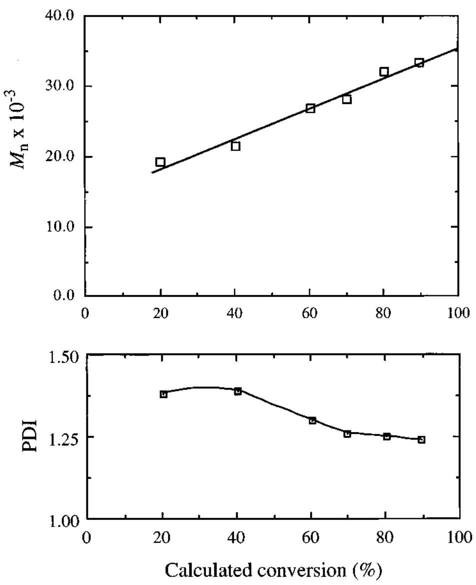
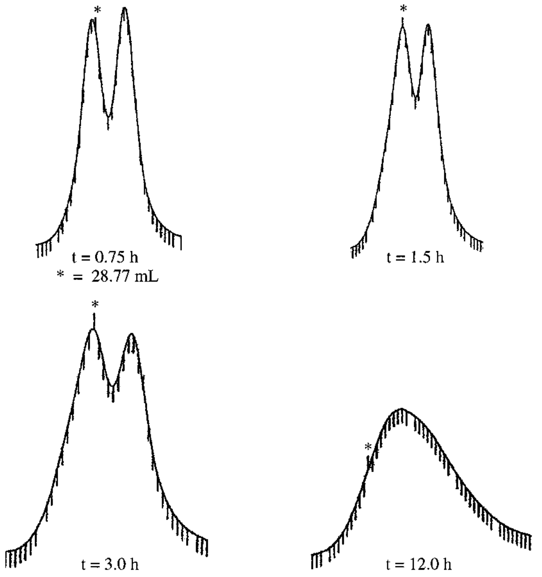


Figure 10. Molecular weight and polydispersity vs conversion for CL polymerization with **4**.



t (h)	Yield (%)	M_n[a]	PDI[b]
0.75	100	24 130	1.24
1.5	100	22 710	1.35
3.0	100	23 470[c]	1.34[c]
12.0	87	8 720	2.03

[a] From GPC measurements in THF. Reference 67. Calculated M_n = 22 140, 0 °C, toluene.

[b] GPC (THF, vs. polystyrene). [c] The limitations of GPC for distinguishing between similar, but broad, distributions are seen here.

Figure 11. Transesterification after complete conversion for CL polymerization with **1**.

occur once monomer is consumed. At 45 min after completion (t = 1.5 h), the PDI of the poly(ϵ-caprolactone) has increased and its molecular weight has decreased slightly. After a total of 16 h the M_n of the high polymer has decreased by two-thirds; at this point the molecular weight distribution is so broad as to appear as a single peak. The yields of polymer obtained by precipitation into hexanes were still quantitative at t = 1.5 and 3 h, but after 12 h only 87% was isolated, with the remaining 13% being converted to hexane-soluble small oligomers.

For confirmation this experiment was repeated with D-lactide, which undergoes transesterification to a much greater extent than CL during polymerization due to its additional carbonyl group.[86,99] A polymerization carried out for 48 h with **1** in toluene at 0 °C (calculated M_n = 30 040) produced only small oligomers (M_n = 1010, PDI = 2.01).[100] As expected, an identical procedure in THF showed a lesser degree of backbiting, but degradation was still severe (M_n = 2510, PDI = 2.22).[100]

We have investigated two strategies for the suppression of transesterification during the final stages of monomer conversion. In contrast to the extreme degradation to oligomeric material seen at 0 °C after 12 h with **1**, a polymerization carried out at −20 °C for 11 h with **4** produced PCL with the expected molecular weight and a PDI of 1.17 (Table 4). A similar polymerization, allowed to proceed for 17 h, showed PDI broadening to only 1.22. Lowering the polymerization temperature even more should further prevent backbiting, until energetic limitations are reached for initiation and propagation (*vide supra*).

A second strategy involves the addition of Lewis bases. Jérôme and Teyssié have found that coordinating additives such as THF and pyridine slow transesterification during aluminum-catalyzed lactone polymerization, in part by competing with the polymer backbone carbonyl groups for metal coordination.[84,86,101] We found the use of strong donors to prevent oligomer formation valid for $Cp^*_2Sm^{III}$ initiators as well. When a CL polymerization was carried out in pyridine for 17 h at 0 °C (Table 4), the resultant polymer had an M_n somewhat lower than the calculated value but a polydispersity of only 1.34, as compared to 2.03 for **1** after 12 h in toluene. Given the tendency of electron donors to slow propagation during other lactone polymerizations when present in excess,[82–85] suppression should be even more effective if only 1 equiv of pyridine is used. In light of this behavior it is again worth noting that the link functionality present in **6** has the ability to bind the active center,[18] which could also have a transesterification-enhancing effect. However, the polydispersity of PCL prepared with **6** was not significantly larger than that seen with **4**.

Conclusions

The synthesis of an unusual macromolecular architecture—"link-functionalized" polymers—was accomplished through the use of preformed bimetallic samarium(III) initiators. PMMA containing interior olefin groups may be prepared in a living manner with bis-allyl complexes such as $[Cp^*_2Sm(\mu\text{-}\eta^3\text{-}CH_2CH\text{-}CH-)]_2$. However, significant constraints are apparent for the synthesis of other types of link-functionalized polymethacrylates. Inefficient initiation is seen with catalysts containing sterically hindered, electron-rich, or coordinating groups; slow initiation is also seen with hindered functionalities. The polymerization of methacrylates is particularly inhibited by strongly donating groups such as imines.

The successful synthesis of link-functionalized polymers containing bulky, electron-rich, and donating groups was carried out with ϵ-caprolactone. In contrast to the electronic and steric interference of initiation seen with MMA, lactone initiation is impeded only sterically and to a much smaller extent. The complex $[Cp^*_2Sm]_2(PhC_4Ph)$ undergoes slow initiation to some degree with both monomers, illustrating the unique susceptibility of bimetallic coordination catalysts to protection of the initiating group in a spectator ligand cavity.

Samarium(III) lactone polymerization is, in general, influenced by the same trends as aluminum alkoxide-based lactone polymerization. This includes susceptibility to transesterification and backbiting at high monomer conversions. These unwanted side reactions are not significant until quantitative conversion is approached and can be suppressed afterward to a large extent by lowering the reaction temperature or adding coordinating groups to the polymerization medium.

Experimental Section

General Procedures and Characterizations. All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of prepurified argon using standard Schlenk techniques. Unless specified otherwise, solvents were removed under Schlenk line vacuum (approximately 0.01 Torr) rather than with a rotary evaporator. Drybox manipulations were performed under argon or nitrogen in a Vacuum Atmospheres HE-432 Dri-Lab equipped with an HE-493 Dri-Train or in a Braun Labmaster 100 drybox equipped with a Labmaster MB130 B-G Inert Gas System, an integrated SPS water-oxygen analyzer, and a −35 °C freezer. ^{1}H NMR spectra were obtained at 200 and 400 MHz with Bruker AM-200 or AM-400 FT NMR spectrometers and are referenced to residual solvent proton peaks. ^{13}C{^{1}H} proton decoupled NMR spectra were measured at 75 MHz on a Bruker MSL-300 spectrometer and are referenced to solvent carbon peaks. Infrared spectra were obtained using a Perkin-Elmer 1600 Series FTIR spectrometer as thin films on NaCl disks and are uncalibrated.

Polymer Characterizations. Gel permeation chromatography (GPC) was performed on a Hewlett-Packard 1050 Series liquid chromatograph pump equipped with an HP Model 1047 refractive index detector and a Hewlett-Packard Model 3396A integrator. Chloroform or THF was used as the mobile phase with a flow rate of 1 mL/min and samples were prepared as 1−2% polymer (w/v) and passed through 0.2 μm filters before injection. Separations were affected by 10^5, 10^4, 10^3, and 500 Å Waters Ultrastyragel or Pacific Column Permagel columns run in series (an additional 10^6 Å column was used in some cases). Molecular weights were calibrated to narrow molecular weight polystyrene standards (M_n = 700−556000) or PMMA standards (M_n = 16200−164700) purchased from Scientific Polymer Products. PCL molecular weights measured in THF were converted to absolute values by applying McLain's correction factor of 0.45.[67] Absolute values for weights measured in $CHCl_3$ were approximated with multiplication by a factor of 0.3. Values for poly(D-lactide) are not corrected. Tandem GPC/light scattering experiments were carried out in THF at 25 °C (flow rate = 1 mL/min) using an HP 1050 Series liquid chromatograph pump equipped with a Wyatt/Optilab Model 903 interferometric refractometer and an 18-angle Wyatt Dawn DSP-F laser photometer operating at 633 nm. GPC/LS data were analyzed using Wyatt ASTRA 1.2 or 1.4 software. Separations were affected and samples were prepared as described above. Molecular weight and polydispersity values were obtained with a literature d*n*/d*c* value of 0.084 for syndiotactic PMMA.[102]

Reagents. Unless indicated, all materials were purchased from commercial suppliers in reagent grade and used without further purification. Tetrahydrofuran (THF), diethyl ether, toluene, mesitylene, hexanes, and toluene-d_8 used for air-sensitive manipulations were vacuum transferred or distilled under nitrogen from purple sodium benzophenone ketyl and stored in Schlenk solvent pots. Alternately, solvents were passed sequentially through columns of activated alumina (LaRoche A-2) and Q-5 supported copper redox catalyst (Engelhard CU-0226S) under a prepurified nitrogen atmosphere.[103] Pyridine was vacuum transferred from CaH_2 after a drying period of 1 week. Methyl methacrylate and ϵ-caprolactone were dried over CaH_2 and vacuum transferred (MMA) or disilled (CL) onto fresh CaH_2 and dried for a second period. MMA was not vacuum transferred for the second time until immediately before use and was protected from heat and incident light during drying and stored below 0 °C in a darkened container. ϵ-Caprolactam was recrystallized from cold toluene and sublimed under dynamic vacuum at 55 °C. D-Lactide, a gift from the DuPont Chemical Co., was sublimed before use.

Samarium initiators were prepared by the methods of Evans et al.: $[Cp^*{}_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{-})]_2$ (**1**), $[Cp^*{}_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$ (**2**), and $Cp^*{}_2Sm(\eta^3\text{-}CH_2CHCH_2)$ (**3**) were prepared from $Cp^*{}_2Sm$[4,104] and 1,5-hexadiene, 1,3-butadiene, and propene, respectively.[45,59] The alkenes used in these syntheses were dried over CaH_2 prior to use; we have also found that the purification/extraction steps of these procedures must be very thorough to obtain catalytic-grade material. $[Cp^*{}_2Sm]_2(\mu\text{-}\eta^2\text{: }\eta^2\text{-}PhC_4Ph)$ (**4**)[58,61] was prepared from $Cp^*{}_2Sm$ and 1,4-diphenylbutadiene (recrystallized from dry hexanes) in a manner similar to that described by Evans from $Cp^*{}_2Sm(THF)_2$[105] and recrystallized from cold toluene as the toluene disolvate.[106,107] $[Cp^*{}_2Sm]_2[\mu\text{-}\eta^2\text{: }\eta^2\text{-}(H_5C_6HC{=}NNCHC_6H_5{-})]_2$ (**6**) was prepared from $Cp^*{}_2Sm(THF)_2$ and benzaldehyde azine (dried over CaH_2 in dry diethyl ether and recrystallized from dry hexanes) and recrystallized from 5:1 toluene/THF.[62] $Cp^*{}_2Sm(NHPh)(THF)$ (**7**) was prepared from 1,4-diphenylhydrazine and $Cp^*{}_2Sm(THF)_2$.[63] The presence of a toluene resonance at 2.10 ppm in the C_6D_6 ^{1}H NMR spectrum of **6**, with crude peak integration corresponding to a stoichiometry of $^1/_2$ toluene molecule per unit, indicated the isolation of the complex as the toluene hemisolvate. The samarium metal used in the synthesis of these compounds was purchased as −40 mesh spheres (Aldrich) and stored under argon.

Experimental Procedures and Characterizations. General Procedure for Polymerization of MMA. Two methods were employed as indicated. Successful polymerizations exhibited an immediate color change from that of the catalyst solution to bright yellow upon addition to monomer, and more concentrated polymerizations (higher than approximately 0.5 M in monomer) became viscous or gelled at high conversion.

Schlenk Procedure (Used with 1, 4, 5, 6, and 7). In the drybox, a 25 or 50 mL Schlenk tube was equipped with a magnetic stirbar. Catalyst (typically 0.002−0.010 mmol, as a solid or aliquot of volumetric solution) was added to the tube, followed by solvent (0.5−2.0 mL). The tube was sealed with a glass stopper and removed to argon on a Schlenk line, where the stopper was replaced with a rubber septum. Alternately, the tube was sealed directly with a degassed rubber septum which was wired tightly to the tube upon removal from the drybox. Monomer (typically 0.9−1.8 mmol) was added to the stirred solution via syringe at 0 or −78 °C. The rubber septum was replaced with a flame-dried glass stopper, and the polymerization was closed from argon and allowed to stir for the appropriate length of time. For monomer to initiator ratio experiments with **1**, multiple polymerizations were initiated simultaneously with aliquots of monomer from a single gas-tight, flame-dried microsyringe which was flushed with several volumes of argon before use.

Drybox Procedure (Used with 2 and 3). In the drybox, the desired amounts of catalyst and solvent were measured directly into a 10 mL round-bottom flask equipped with a stirbar. The flask was sealed with a glass stopper, removed from the drybox, and immediately cooled to the desired temperature.

Polymer Workup. After polymerization was complete, the polymerization vessel was opened to air and an excess of methanol (5−10 times the volume of the polymerization solvent) was added, causing disappearance of the yellow color and precipitation of the PMMA as a white solid. The polymer was isolated by filtration and purified by reprecipitation into methanol from $CHCl_3$, collected on a 0.2 μm filtration apparatus, and rinsed with additional methanol.

Poly(methyl methacrylate). Due to the highly syndiotactic nature of the PMMA, a number of the literature peaks reported for heterotactic PMMA were minor or absent from the ^{13}C{^{1}H} spectrum; minor peaks are noted and major peaks bear carbon assignments. Spectral data are for a sample prepared at −78 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.59 (s, 3 H), 1.87 and 1.80 (both br s, combined 2 H), 1.03 and 0.85 (both br s, combined 3 H). Literature ($CHCl_3$): δ 3.62 (s, C*H*$_3$O−), 1.86 (br, −C*H*$_2$−), 1.07 (br s, heterotactic −C*H*$_3$), 0.93 (br s, syndiotactic −C*H*$_3$).[108] ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz): δ 178.05 (minor peak), 177.76, 176.95 (minor peak), 54.37 (minor peak), 54.12, 51.76, 44.86 (minor peak), 44.56, 18.68 (minor peak), 16.63. Literature ($CDCl_3$): δ 178.0, 177.7, 176.9 ($C{=}O$), 54.4, 53.6, 53.0 ($-CH_2-$), 51.7 ($-OCH_3$), 45.5, 44.9, 44.6 ($-CC{=}O$), 21.1, 18.8, 16.6 ($-CH_3$).[109] IR (thin film from $CHCl_3$): 2995 (m), 2950 (m), 2842 (sh), 1732 (vs), 1636 (sh), 1486 (m), 1448 (m), 1436 (m), 1386 (w), 1273 (m), 1243 (s), 1192 (s), 1150 (s), 1063 (w), 987 (w), 967 (w), 912 (w), 842 (w), 826 (w), 810 (w), 752 (s) cm^{-1}. Literature: 2951, 1730, 1449, 1387, 1240, 1148, 1064, 989, 753 cm^{-1}.[110]

Preparation of Functionalized MMA Oligomers with 2 and 3. Methyl methacrylate (40.0 μL, 37.8 mg, 0.377 mmol) was added to toluene solutions of **3** (8.4 mg, 0.0182 mmol) and **2** (18.4 mg, 0.0194 mmol) using the drybox procedure; polymerization was carried out for 16 h. Upon protolysis solvents were removed *in vacuo* and the white residues extracted with THF and filtered to remove decomposed catalyst species. After removal of the filtrate solvent the oligomers were precipitated from THF into hexanes. The material prepared with **3**, a white powder, was further purified by precipitation from hot methanol into distilled H_2O and lyophilization from benzene. The oligomer prepared from **2**, however, was precipitated as a gummy, yellowish solid. Further purification as described above did not entirely remove the yellow color. GPC/LS analysis of the oligomer was complicated by the presence of nonvolatile decomposed catalyst species. **Mono-oligomer** (prepared with **3**): GPC/LS ($dn/dc = 0.084$): $M_n = 4\,310$; PDI $= 1.27$. GPC (THF, vs polystyrene): $M_n = 2\,810$; PDI $= 1.35$. Calculated $M_n = 2\,120$. **Bis-oligomer** (prepared with **2**): GPC (THF, vs polystyrene): $M_n = 1\,960$; PDI $= 1.20$. Calculated $M_n = 2\,060$.

NMR-Scale Reaction of 3 with MMA. In the drybox, a 0.189 mM stock solution of MMA in toluene-d_8 was prepared in a 1 mL volumetric flask. Separately, a 5 mL round-bottom flask equipped with a stirbar was charged with 3.3 mg (0.0071 mmol) of **5** and ≈0.75 mL of toluene-d_8. While the mixture was stirred, 76 μL of the stock solution (0.014 mmol MMA) was added by syringe. A rapid color change to yellow was observed. The contents of the flask were transferred to a 5 mm NMR tube fitted with an air-free Teflon valve. The tube was sealed, removed from the drybox, and quickly cooled with liquid nitrogen. Following degassing by multiple freeze−pump−thaw cycles (to prevent shattering of the tube upon warming), the tube was again cooled in liquid nitrogen for transport. It was warmed to room temperature immediately prior to recording of the ^{1}H NMR spectrum.

Attempted Polymerization of MMA with 1 in the Presence of Pyridine. In the drybox, a 0.124 M stock solution of dry pyridine in THF was prepared. Separately, **1** (3.2 mg, 0.0035 mmol) was dissolved in 1 mL of THF in a 25 mL Schlenk tube equipped with a magnetic stirbar. A 56 μL (0.0069 mmol) aliquot of the stock solution was added to the tube by syringe. The catalyst solution was then treated with 100 μL of MMA (94.4 mg, 0.943 mmol) at 0 °C (Schlenk procedure). A slow color change to bright yellow was observed, and the reaction was allowed to stir overnight. Protolysis yielded only a trace (<5 mg) of methanol-insoluble material. A second attempt gave identical results.

General Procedure for CL Polymerizations. The drybox and Schlenk methods described for MMA were used. Typically, 2.5−5.0 mmol of catalyst and 1−2 mL of solvent were used. A color change to bright yellow was usually observed upon addition of monomer; an increase in solution viscosity was typically seen by the end of the polymerization period. An excess of 5% aqueous HCl (0.5 mL) was used to quench the polymerization, forming a colorless, biphasic mixture. Hexanes (5−10 mL) were then quickly added to precipitate the white PCL from the organic layer. The polymer was collected by filtration on a 0.2 μm membrane filtration apparatus and purified by reprecipitation from $CHCl_3$ into hexanes. Oligomerization with **4** was carried out similarly at a monomer:initiator ratio of 20:1.

Poly(ϵ-caprolactone): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 4.03 (t, $J = 6.7$ Hz, 2 H), 2.29 (t, $J = 7.5$ Hz, 2 H), 1.62 (br quintet, $J = 7.3$ Hz, 4 H), 1.37 (br m, 2 H). Literature ($CDCl_3$): δ 4.06 (t, OCH_2), 2.31 (t, $-H_2CC{=}O$), 1.65 (m, $OCH_2CH_2CH_2CH_2$-CH_2-), 1.38 (m, $OCH_2CH_2CH_2-$).[27] IR (thin film from $CHCl_3$): 2945 (s), 2898 (sh), 2868 (m), 1729 (vs), 1473 (m), 1463 (sh), 1438 (m), 1401 (m), 1365 (s), 1294 (s), 1239 (s), 1172 (vs), 1108 (m), 1067 (sh), 1047 (s), 961 (m), 935 (sh), 842 (w), 774 (w), 732 (m), 710 (sh), 585 (w) cm^{-1}. Literature (melt): 2945, 1733, 1464, 1363, 1295, 1242, 1165, 1104, 1045 cm^{-1}.[110]

Initial Rate ^{1}H NMR CL Polymerization Kinetics with 4. In the drybox, CL (110 mL, 113 mg, 0.993 mmol) was added to **4** (3.6 mg, 0.0029 mmol) in 1.5 mL toluene-d_8 as described previously. The solution was transferred to a 5 mm NMR tube fitted with an air-free Teflon valve by pipet. The tube was sealed, removed from the drybox, and placed in an ice water bath. One-pulse ^{1}H NMR spectra were immediately recorded on an instrument with a probe precooled to 0 °C. Relative monomer concentration was calculated from the area ratio of the monomer and combined monomer and polymer OCH_2 resonances (3.65 and 3.95 ppm, respectively).

Attempted Polymerization of ϵ-Caprolactam with 1. Using the Schlenk procedure, a solution of ϵ-caprolactam (100 mg, 8.87 mmol) in 2 mL of toluene was added to **1** (3.8 mg, 0.0041 mmol) in 2 mL toluene at 0 °C. The purple catalyst solution, which became less intense and discolored upon addition of monomer, was allowed to stir for 12 h at 0 °C. No solids were isolated upon addition of methanol.

Polymerization of D-Lactide with 1. Using the drybox procedure, a solution of 130 mg (0.902 mmol) of D-lactide in 0.75 mL of THF was added to **1** (4.0 mg, 0.0043 mmol) in 1 mL of THF. The catalyst solution immediately became bright yellow. The polymerization was stoppered and allowed to stir for 48 h at room temperature, after which it had become a gel. Aqueous 5% HCl (10 mL) was added to precipitate a greasy white solid. Solvent was removed *in vacuo* and the polymer purified by reprecipitation from THF into hexanes (72 mg, 56%). Due to autocatalytic hydrolysis during storage,[98] alcoholic end group resonances were observed in the ^{1}H NMR and IR spectra of the polylactide.

Poly(D-lactide): ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.15 (br m, 1 H, OCH), 4.45−4.25 (v br, endgroup CH), 3.72 (br s, endgroup OH), 1.54 (br s, 3 H, CH_3), 1.24 (br s, endgroup CH_3, 0.18 H). Literature ($CDCl_3$): δ 5.1 (br s, CH), 1.3 (br s, CH_3). Alcoholic end group resonances for oligomeric poly(L,L-lactide) ($CDCl_3$): 4.4 (CH), 3.2 (OH), 1.4 (CH_3).[99] IR (thin film from $CHCl_3$): 3503 (w), 2994 (w), 2944 (w), 2886 (sh), 1756 (vs), 1455 (m), 1385 (w), 1383 (w), 1318 (w), 1270 (m), 1187 (s), 1131 (s), 1093 (s), 1051 (m), 956 (w), 867 (w), 756 (w) cm^{-1}. Literature: 3440, 2950−2900, 1750, 1450, 1375, 1275, 1175, 1125, 1090, 1040, 890 cm^{-1}.[99] An identical procedure was utilized with toluene as solvent.

Procedure for CL Polymerization Kinetics with 4. In the drybox, a volumetric solution of **4** (0.00200 M) and mesitylene (0.331 M) in toluene-d_8 was prepared. Measured aliquots of this solution (0.75−1.50 mL) were distributed to 5 mL round-bottom flasks containing stirbars. ϵ-Caprolactone (331 equiv/**4**) was added to each stirred aliquot by syringe at recorded times. To minimize the effect of propagation at room temperature, aliquots designated for longer polymerization times were initiated first. The flasks were sealed with glass stoppers and immediately removed from the drybox to an ice water bath. At appropriate intervals, stirred aliquots were quenched by the addition of 40.0 μL (59.2 mg, 0.519 mmol) trifluoroacetic acid and transferred in entirety to a 5 mm NMR tube. Relative monomer concentration was calculated from the areas of the mesitylene CH and ϵ-caprolactone OCH_2 resonances (6.66 and 3.65 ppm, respectively) in the one-pulse, 400 MHz ^{1}H NMR spectrum. The monomer concentration and time at the first measured point were designated as C_0 and t_0. To ensure that the samarium acetate species formed upon addition of CF_3CO_2H does not function as a catalyst, monomer was added to a quenched aliquot of volumetric solution of **4**. No peaks corresponding to PCL were observed in the ^{1}H NMR spectrum.

Procedure for CL Molecular Weight vs Percent Conversion Experiments with 4. Using the drybox procedure, a CL polymerization with **4** was initiated in toluene in a 25 mL round-bottom flask. The quantities of reagents used were 10.4 mg (0.00847 mmol) of **4**, 4.23 mL of toluene, and 310 μL (319 mg, 2.80 mmol) of ϵ-caprolactone. The polymerization was divided into six equivalent aliquots in 10 mL round-bottom flasks containing stirbars. The flasks were quickly sealed, removed from the drybox, and cooled to 0 °C in an ice water bath. The time which elapsed before thermostating was 397 s. At appropriate intervals, a stirred flask was removed from the bath and quenched with 5% aqueous HCl. The polymer was isolated and purified as described above. Calculated M_n = 37 940.

Low-Temperature Polymerizations of ϵ-Caprolactone with 4. A toluene solution of **4** in a stoppered 10 mL round-bottom flask, prepared in the drybox, was cooled to −35 °C in the drybox freezer. The flask was removed from the freezer and monomer was immediately added to the stirred solution. Monomer was also added to an identically prepared and cooled solution which had been allowed to warm to approximately −20 °C. Both vessels were immediately stoppered, removed from the drybox, and cooled in a liquid nitrogen bath. The flasks were then transferred to a precooled −20 °C circulating glycol/H_2O bath and allowed to stir for the desired length of time.

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(74) The wideness of this range most likely represents concentration effects and/or thermostating inefficiencies.

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(81) We have attempted to characterize the intermediate by stoichiometric reactions of **4** with ϵ-caprolactone. Unfortunately, even at a 1:1 reaction ratio of lactone/**4**, the intermediate was not obtained at ambient temperature. Yasuda has noted that the ϵ-caprolactone adduct of (C$_5$Me$_5$)$_2$YOMe is only stable for 2 h at 0 °C and gradually undergoes ring-opening at room temperature and that for the same reason isolation of the analogous β-propiolactone complex was not possible. We have found **4** to be extremely air-sensitive, to the point that drybox manipulations are preferred over Schlenk techniques for its clean isolation in crystalline form; unfortunately, the conditions of extreme low temperature needed to prepare and study the intermediate were not available with a drybox freezer. See ref 37.

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(87) For **6**: [CL]$_0$ = 1.503 M; [**6**] = 0.00588 M. See Table 3. For **4**: [CL]$_0$ = 1.505 M; [**4**] = 0.00617 M. Calculated M_n = 28 040; observed M_n (GPC, corrected THF vs polystyrene) = 28 430. Both polymerizations gave yields of 67%.

(88) Primary amines are known to protonate samarium allyls. See ref 47.

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