

‘Link-functionalized’ and triblock polymer architectures through bifunctional organolanthanide initiators: A review

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Received 10 October 1997; accepted 2 March 1998

Abstract

Bimetallic complexes of the type $\text{Cp}_2^*\text{Sm-R-SmCp}_2^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) were used for the living bisinitiated polymerization of methyl methacrylate and ϵ -caprolactone, giving polymers with discrete functionalities at the center of the backbone (‘link-functionalized’). A method was also developed for generating a bifunctional Sm(III) initiator in situ from a (meth)acrylate monomer and a divalent Cp_2^*Sm precursor. Well-defined, syndiotactic ABA triblock copolymers containing both methacrylate and acrylate segments were prepared in 2 monomer addition steps with this methodology. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methacrylate; Lactone; Block copolymerization; Lanthanide; Link-functionalized polymer; Bisinitiation

1. Introduction

Bifunctional polymerization initiators—those which possess 2 covalently linked active sites—offer a number of interesting strategies for the synthesis of polymers with controlled architectures. In addition to possessing an inherent advantage over monoinitiators for the synthesis of ABA triblocks and telechelics, bisinitiators may be used to synthesize polymers with discrete functionalities at the center of their backbone (‘link-functionalized’ polymers or LFPs). Link-functionalized polymers are of interest because chemical alteration of the incorporated groups may provide new routes into biodegradables, functionalized materials, and other special-architecture macromolecules such as star and network polymers.

While bisinitiators have been used extensively in ‘living’ anionic polymerization since 1956 [1–3], systems involving bifunctional coordination–insertion catalysts are quite rare. Metal-mediated poly-

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merizations, in addition to typically possessing a high degree of living character, offer further control of polymer tacticity and microstructure through ligand sphere modification. The combination of these advantages with the synthetic utility of bisinitiated polymerization thus represents a step forward in producing well-defined, architecturally interesting macromolecules.

Organolanthanide complexes of the type Cp_2^*Ln-R ($Cp^* = C_5Me_5$; $Ln =$ lanthanide; $R =$ hydride, alkyl, alkylaluminum) have recently been shown by Yasuda et al. to function as initiators for the living, highly syndiotactic polymerization of methyl methacrylate [4–6]. These lanthanocenes may also be used for the well-controlled polymerization and block copolymerization of ethylene, lactones, and acrylates [6–8]. As part of our general interest in controlling macromolecular architecture through living, bisinitiated transition metal polymerization [9,10] we have developed a new bifunctional initiation system based on the lanthanides, and describe here the use of both preformed bisinitiators and an in situ catalyst generation method to prepare a variety of well-defined polyester and acrylic LFPs and triblock copolymers.

2. Experimental

All manipulations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere using careful Schlenk or drybox techniques. Monomers and solvents were dried before use over sodium benzophenone ketyl or calcium hydride. Polymerizations were carried out in dry THF or toluene for 2–4 h at temperatures ranging from -78 to $0^\circ C$ for (meth)acrylates and $0^\circ C$ to room temperature for ϵ -caprolactone. A typical procedure utilized 3–5 mg catalyst, 0.5–1 ml solvent, and 100–300 μl monomer; an excess of methanol was added to terminate the polymerization. Block copolymerizations were carried out by sequential monomer addition via syringe on a Schlenk line, or preferably by vacuum transfer of monomers onto a solution of initiator through an all-glass apparatus. Specific procedures and instrumentation for polymerizations, characterization of the resultant polymers, selective sidechain deprotection of triblock copolymers, and literature preparation of initiators 1–7 have been previously described in detail [11–13].

3. Results

3.1. 'Link-functionalized' polymers

Link-functionalized polymers have traditionally been prepared by the coupling of 2 end-functionalized polymers [14–17]. This technique is limited by efficiency and fractionation is typically required to remove uncoupled material. When bisinitiation is used, however, it becomes possible to directly incorporate a desired moiety during polymerization.



This is accomplished through modification of the bridging initiating group which links the 2 active centers of the catalyst. Since polymerization occurs simultaneously at both centers, the linking unit

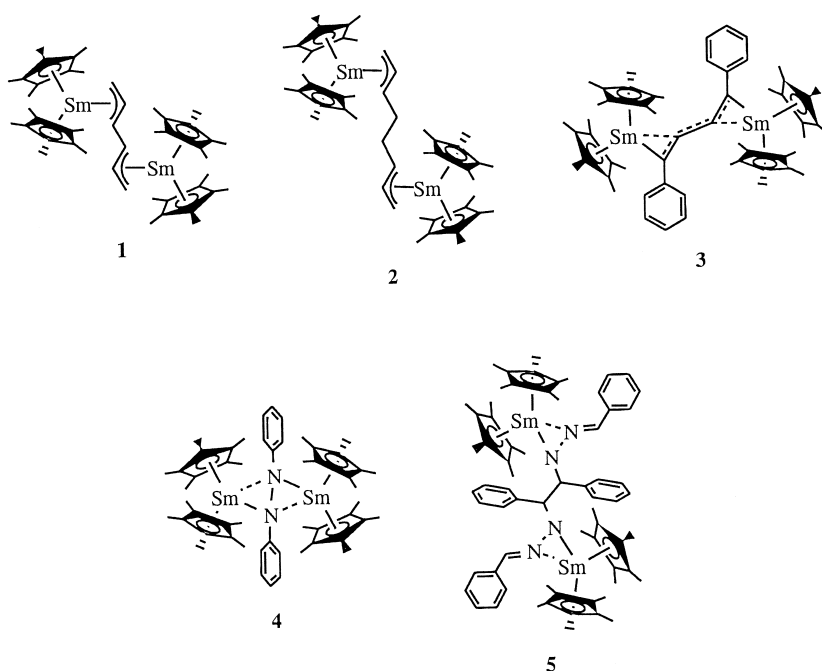


Fig. 1. Bimetallic samarium(III) initiators.

becomes incorporated at the statistical center of the polymer backbone; thus, functionalization of this group in the desired manner produces an LFP. It is important to note that initiation and propagation of polymerization must not be impeded by the linking functionality.

To evaluate the usefulness of lanthanide(III) bisinitiators for LFP synthesis, we selected a representative array of complexes having the structure $Cp_2^*Sm-R-SmCp_2^*$ as initiators for the polymerization of methyl methacrylate (MMA) and ϵ -caprolactone (Fig. 1) [11,18]. For MMA, simple bis-allyl initiators (**1–2**) give high yields of syndiotactic polymethyl methacrylate (PMMA) with low polydispersity (Table 1). Incorporation of the bis-allyl unit into the polymer backbone (most likely as 2 pendant vinyl groups) was confirmed by 1H NMR; the presence of molecular weight control during polymerization was demonstrated by a linear relationship between M_n and monomer to

Table 1
Polymerization of methyl methacrylate with bimetallic samarium(III) initiators

Catalyst	Conditions	Calculated M_n	Observed M_n (GPC)	Observed PDI (GPC)	Yield (%)
1	0°C THF	17180	23 230 ^a	1.15 ^a	100
2	RT toluene	31060	37960 (LS)	1.03 (LS)	95
3	0°C toluene ^d	46570	348060 ^a	1.25 ^a	100
4	0°C toluene	14550	52300 ^b	1.12 ^b	77
5	–78°C toluene	18190	≈ 300000 ^b	≈ 2.0 ^b	100
5	0°C THF	31730	930980 ^c	1.18 ^c	29

^aCHCl₃, vs. PMMA.

^bTHF, vs. polystyrene. M_n is probably somewhat low due to hydrodynamic differences of PMMA and polystyrene in THF.

^cCHCl₃, vs. polystyrene.

^dWith THF as solvent, no polymer was obtained. LS = Light scattering.

Table 2
Polymerization of ϵ -caprolactone with bimetallic samarium(III) initiators

Catalyst	Conditions	Calculated M_n	Observed M_n (GPC)	Observed PDI (GPC)	Yield (%)
1	toluene 0°C	22 140	24 130 ^a (bimodal)	—	100
2	toluene 0°C	48 840	28 230 ^a (bimodal)	—	98
3	toluene 0°C	41 010	29 710 ^a	1.12 ^a	73
5	0°C THF	29 610	≈ 34 080 ^b	1.17 ^a	67

^aTHF, vs. polystyrene. M_n values are corrected as described in Ref. [11].

^bEstimated from GPC (CHCl₃, vs. PS) as described in Ref. [11].

initiator ratio for **1**. Since olefins can be polymerized or easily transformed into other useful groups, these LFPs should be useful precursors for the synthesis of other methacrylate polymer architectures.

In contrast to initiators **1** and **2**, the sterically hindered trienediyl catalyst **3** was found to undergo slow and inefficient initiation of polymerization, producing PMMA with both an inflated and broadened molecular weight distribution (Table 1). The heteroatom initiators **4** and **5** also produced polymers with highly inflated M_n s; this effect was most pronounced for **5** which also contains a highly coordinating imine moiety. Thus, the synthesis of methacrylic LFPs with bimetallic lanthanide(III) initiators seems to involve a number of steric and electronic limitations.

The polymerization of ϵ -caprolactone is much more robust (Table 2); no loss of polymerization control is observed when hindered **3** and electron-rich **5** are used for the synthesis of lactone LFPs containing aryl/trienediyl and amide/imine groups. Similar to its behavior with MMA, complex **3** was found to undergo rather slow initiation as evidenced by NMR kinetics; however, this effect is not large enough to contribute to significant molecular weight inflation or broadening. Backbone incorporation of the trienediyl unit of **3** in a poly(ϵ -caprolactone) (PCL) oligomer was also confirmed by ¹H NMR. Unfortunately, lactone polymerization with allyl complexes **1** and **2** produced PCL having a bimodal molecular weight distribution (a similar effect was seen when the monometallic initiator Cp₂*Sm(η^3 -CH₂CHCH₂) [19] was used). Since related lanthano-cene allyls are capable of Grignard addition to carboxylic substrates [20–23], it is possible that side reactions with lactone monomer occur; catalysts containing less reactive interior allyl groups would perhaps be more satisfactory initiators in this case.

3.2. ABA triblock synthesis: *in situ* bisinitiation

The use of bifunctional initiators allows triblock copolymers to be prepared in 2 monomer addition steps rather than 3, since new polymer is grown from both ends of the existing chain. This produces more symmetric copolymers and minimizes termination from monomer impurities (which leads to contamination by diblocks and homopolymers). While a preformed bisinitiator may be used, the *in situ* formation of a bifunctional catalyst through electron transfer initiation is an improved method: in this instance, an anionic bisinitiator is generated by the addition of a one-electron reducing agent to a vinyl monomer, forming radical anions which couple to give a linked species. Since the actual bisinitiator is not formed until monomer is added, concerns about deactivation of one active center of the catalyst during storage or upon addition of solvent are avoided.

Historically, electron transfer initiation has been limited to anionic polymerization initiated by alkali metals [1–3]. We have extended this methodology to metal-mediated coordination polymeriza-

tion for the first time by taking advantage of the electron-transfer properties of samarium(II) (Fig. 2) [12,18]: When $\text{Cp}_2^* \text{Sm}$ (**6**) or $\text{Cp}_2^* \text{Sm}(\text{THF})_2$ (**7**) is added to an excess of MMA



monomer, one-electron transfer from the samarocene species to monomer occurs, and the resultant radical anions undergo dimerization to form a bimetallic samarium(III) bisenolate which initiates polymerization. Similar electron transfer/dimerization reactions between $\text{Cp}_2^* \text{Sm}$ complexes and other, nonpolymerizable unsaturated substrates are well known [19,24–27].

As predicted by the coupling of the 2 active centers, the molecular weights of PMMA prepared in this manner are near 2 times those calculated from the monomer: initiator ratio. The polymerization is ‘living’ as evidenced by molecular weight control and low polydispersities of the resultant PMMA (≤ 1.15); *n*-hexyl methacrylate, benzyl methacrylate, ethyl acrylate, and *t*-butyl acrylate were also polymerized in this manner (high syndiotacticity was also observed for the higher methacrylates). We were able to exploit the atmospheric sensitivity of samarium complexes to obtain further evidence for

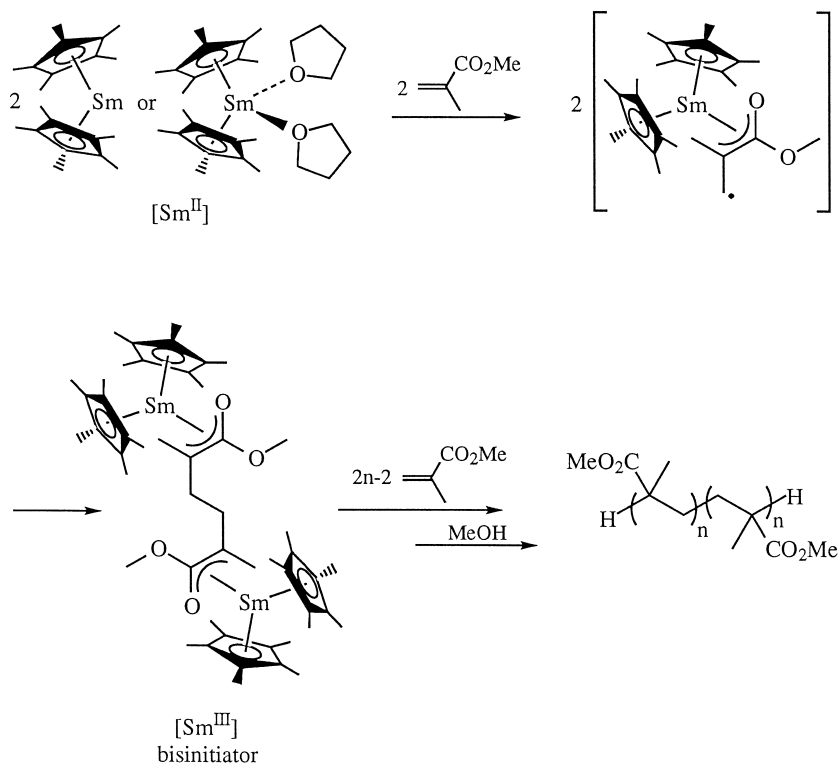


Fig. 2. In situ formation of a bimetallic initiator from $\text{Cp}_2^* \text{Sm}$ and methyl methacrylate.

Table 3

(Meth)acrylic triblock copolymers prepared by in situ bisinitiator formation with **6** and **7**

Block A	Block B	Composition (A:B, wt.%) ^a	Initiator	Yield	M_n (GPC)	PDI (GPC)
Benzyl MA	MMA	50:50	7	100	60860 ^c	1.15 ^{c,d}
MMA	Hexyl MA	53:47	7	83 ^b	31960 ^e	1.16 ^e
MMA	Hexyl MA	77:23	6	84 ^b	70810 ^e	1.12 ^e
Ethyl AC	MMA	49:51	6	88	60540 ^c	1.27 ^c
MMA	<i>t</i> -Butyl AC	54:46	7	72	76490 ^c	1.10 ^{c,d}

^aBy ¹HNMR.^bAfter a second reprecipitation; crude yield was higher.^cTHF, vs. polystyrene.^dGPC/LS PDI = 1.01.^eCHCl₃, vs. PMMA.

a bisinitiated mechanism: the molecular weight distributions of PMMA prepared without rigorous exclusion of air and water exhibit a small second peak at approximately half of the main M_n , consistent with the formation of small amounts of monoinitiator by adventitious termination at 1 active site.

We have used this in situ bisinitiator formation methodology to prepare a variety of well-defined triblock copolymers containing both methacrylic and acrylic segments (Table 3) [12,18]. Controlled monomer crossover from both methacrylate to acrylate and from acrylate to methacrylate was observed, and characterization of the copolymers by ¹HNMR and/or elemental analysis gave composition values near those predicted from feed ratios. The potential for preparing thermoplastic materials can be seen from the successful synthesis of triblocks incorporating poly(*n*-hexyl methacrylate) and poly(ethyl acrylate). It should be noted that previous attempts to synthesize poly(ethyl acrylate-*b*-MMA-*b*-ethyl acrylate) anionically have failed [28].

We have exploited the highly tactic nature of this polymerization system to prepare a methacrylic triblock containing a syndiotactic poly(methacrylic acid) (PMA) segment as well [12]. All-methacrylic block copolymers containing acid or ionomeric segments have been studied as potential thermoplastic elastomers, since these materials tend to undergo phase separation more easily than all-ester blocks [29–31]; syndiotactic PMA should be the most useful as a hard block in this capacity, since it possesses a higher T_g than its *iso*- and atactic analogues and is more resistant to thermolysis than isotactic PMA [32–34]. Selective and quantitative deprotection of the benzyl ester groups in

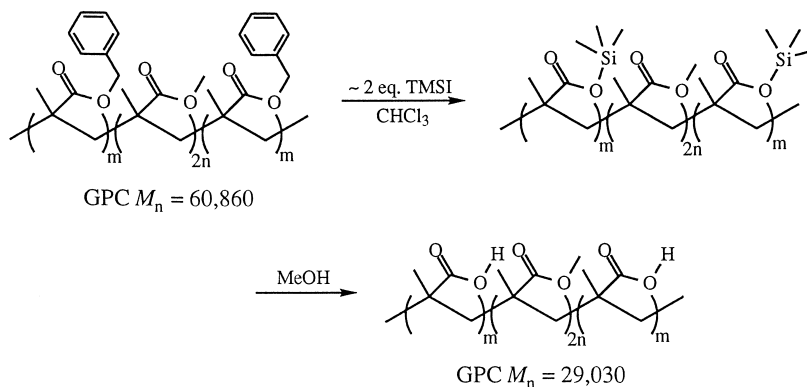


Fig. 3. Deprotection of benzyl ester sidechains with trimethylsilyl iodide/methanol.

poly(benzyl methacrylate-*b*-MMA-*b*-benzyl methacrylate) was carried out with trimethylsilyl iodide (Fig. 3), giving a copolymer with syndiotactic exterior acid segments. A novel triblock containing an inner acid segment was also prepared by selective deprotection of the *t*-butyl groups in poly(MMA-*b*-*t*-butyl acrylate-*b*-MMA) with catalytic *p*-toluenesulfonic acid. Both acid copolymers showed solubility properties characteristic of hydrophilic/hydrophobic materials.

4. Conclusions

A bifunctional initiation system based on bimetallic $\text{Cp}_2^* \text{Sm-R-SmCp}_2^*$ complexes has been developed for the ‘living’ coordination-insertion polymerization of ϵ -caprolactone and (meth)acrylic monomers, allowing for the preparation of useful special-architecture polymers. The synthesis of an unusual structure—‘link-functionalized’ polymers—was accomplished with preformed bimetallic samarium(III) initiators bearing functionalized bisinitiating groups. While PMMA containing internal olefin groups may be prepared in this manner, steric and electronic constraints are apparent for the synthesis of other types of methacrylate LFPs. Analogous preparations of ϵ -caprolactone LFPs, however, are not limited in this manner.

A living Sm(III) polymerization system which generates a bisinitiating catalyst in situ from a divalent samarium precursor and a (meth)acrylate monomer by electron transfer was also developed. This system is analogous to anionic electron-transfer initiation and may be used to prepare monodisperse, highly syndiotactic (meth)acrylic triblock copolymers. When monomers incorporating cleavable sidechains are used, selective deprotection of these groups leads to amphiphilic copolymers containing syndiotactic methacrylic acid segments.

Acknowledgements

The authors acknowledge support for this work from the National Science Foundation, the Materials Research Science and Engineering Center, University of Massachusetts, and the Center for University of Massachusetts-Industry Research on Polymers (CUMIRP). L.S.B. acknowledges the National Science Foundation for a predoctoral fellowship.

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