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Communications to the Editor

Bimetallic Samarium(III) Initiators for the Living Polymerization of Methacrylates and Lactones. A New Route into Telechelic, Triblock, and "Link-Functionalized" Polymers[1]

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Bifunctional polymerization initiators—those with two covalently linked active sites—provide a number of unique strategies in polymer synthesis. The use of bisinitiators dates back to Szwarc, who first demonstrated the utility of the styrene dianion in "living" diene and α-olefin polymerizations.[2] Metal-based bisinitiators are less common; however, systems based on titanium,[3] nickel,[4] and aluminum[5] have been used to prepare a number of unusual polymers.

In addition to possessing an inherent advantage over monometallic species in the preparation of triblocks and telechelics, bisinitiators offer the possibility of synthesizing macromolecules with special functionality in the center of their backbone ("link-functionalized" polymers). We are interested in these polymers because chemical alteration of the incorporated groups, such as cross-linking or cleavage, may present new synthetic routes for the production of star polymers, networks, biodegradables, and functionalized materials.

In an elegant study, Yasuda has shown that organosamarium(III) compounds of the type $Cp^*_2Sm{-}R$ (where $Cp^* = C_5Me_5$ and R = hydride, alkyl, alkylaluminum) function as initiators for the living polymerization of methyl methacrylate (MMA).[6] Well-controlled polymerizations and block copolymerizations of acrylates, lactones, and ethylene by these compounds have also been reported.[7] We are currently working to develop new bisinitiating polymerization systems based on the lanthanides and report in this Communication that the compounds $Cp^*_2Sm(C_4Ph_2)SmCp^*_2$[8] (I) and $[Cp^*_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCH\text{-})]_2$[9] (II) polymerize ϵ-caprolactone and methacrylates, respectively, from both chain ends, in a well-controlled, living fashion. We also discuss generation of a bimetallic bisenolate samarium initiator *in situ* and report the synthesis of triblock copolymers prepared in this manner.

The polymerization of methyl methacrylate by $Cp^*_2Sm\cdot THF_2$[10] **(III)** and other lanthanide(II) complexes has been noted by Yasuda.[6a,b] Although the degree of control of these catalysts is about the same as with trivalent complexes, very low initiator efficiencies (<40%) and greatly inflated molecular weights are observed. The proposed polymerization mechanism involves *in situ* formation of a lanthanide(III) hydride initiator. After reexamining this system, we propose that the actual mechanism of the polymerization proceeds via the formation of a *bisinitiator.* According to our mechanism, the samarocene catalyst undergoes one-electron transfer to a molecule of MMA forming a radical anion. Subsequent dimerization of these radical anions gives a bimetallic bisenolate, which then acts to initiate the polymerization (Scheme 1). Since the two metal centers are now linked, the resultant polymer has a molecular weight twice that predicted for monometallic polymerization, and the initiator appears to be $\leq 50\%$ efficient. Reductive dimerizations of unsaturated compounds by Cp^*_2Sm and its THF solvates are well known,[11] and their ability to initiate polymerization of ϵ-caprolactone by electron transfer has been recently reported.[12]

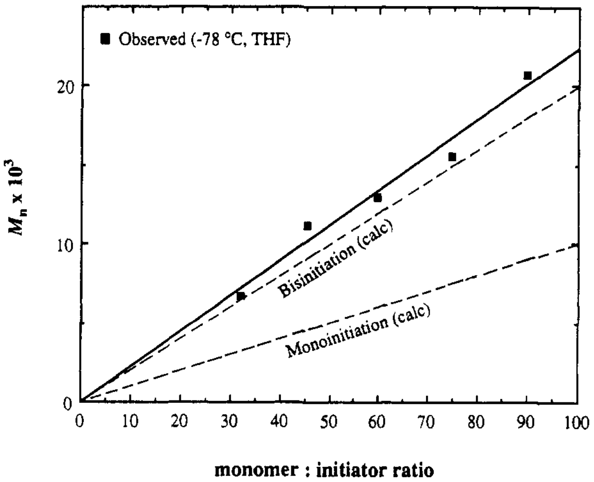

Figure 1. Molecular weight as a function of the monomer: initiator ratio for the polymerization of methyl methacrylate initiated using **III**. Polymerizations were run in THF at −78 °C. Catalyst concentrations ranged from 1.75×10^{-2} to 2.0×10^{-2} M.

Evidence in support of this mechanism for MMA polymerizations was obtained by monitoring the molecular weight of poly(methyl methacrylate) (PMMA) produced with **III** versus the monomer to initiator ratio (Figure 1). As expected M_n(obs)[13] was near that predicted for a linked, bisinitiated polymerization. Bimetallic catalyst efficiencies as high as 96% are seen with the rigorous exclusion of air and water. Living polymerizations at monomer to initiator (M:I) ratios higher than 90:1 can also be achieved; however, the extremely sensitive nature of the organosamarium species results in an increasing degree of molecular weight inflation from calculated values. The polydispersities of the PMMA produced are near 1.1 and are not dependent on the monomer to initiator ratio.

To improve initiator efficiencies and to expand the utility of these lanthanide complexes, we have prepared and isolated preformed bissamarium complexes and examined their polymerization characteristics. To this end, the diyne complex $Cp^*_2Sm(PhC_4Ph)SmCp^*_2$ **(I)** was screened as a methacrylate polymerization initiator. Unfortunately, this complex undergoes slow and/or inefficient initiation, as evidenced by a gradual (10 min) change from the deep orange color of **I** to the bright yellow of the enolates species present as the propagating species in methacrylate polymerizations. A test polymerization in

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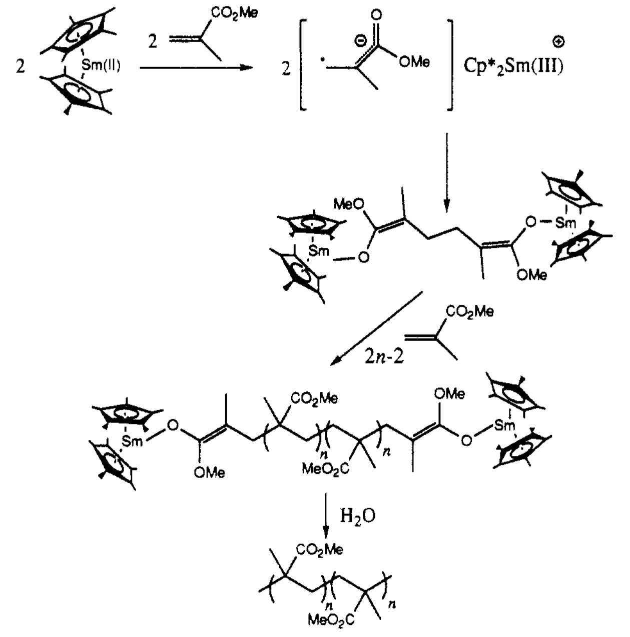
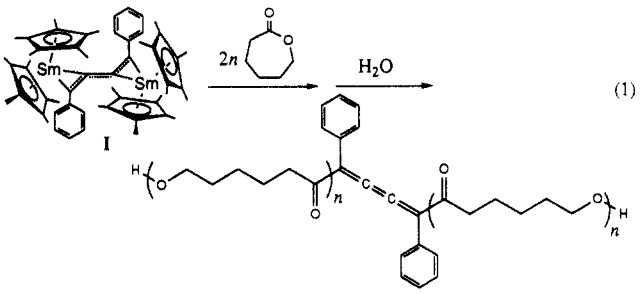
Scheme 1



toluene at 0 °C with M_n(calc) = 46 400 yielded PMMA with a molecular weight of 348 000 and a PDI of 1.25. With THF as the solvent, no polymerization occurred.

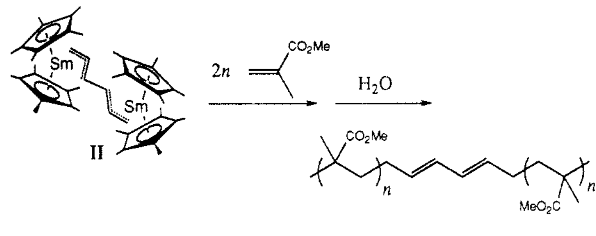
We did find, however, that **I** mediates the polymerization of ε-caprolactone in a well-controlled fashion (eq 1).



(1)

Quantitative yields of poly(ε-caprolactone) (PεCL) are obtained in THF and toluene at 0 °C, with molecular weights[14] near those calculated for bisinitiation and polydispersities of 1.3 or less. NMR aliquot kinetics of the polymerization show the expected first-order dependence on monomer (toluene, 0 °C, [Sm^{III}] = 3.76 × 10^{-3} M: k_{obs} = 2.0 × 10^{-4} s^{-1}; $t_{1/2}$ = 57 min).[15] The activity of this catalyst at low temperatures allows for the suppression of unwanted side reactions. For example, our studies of the polymerization at conversions of up to 95% show no significant degradation of the polymer by transesterification. The PεCL formed with **I** retains the diyne bridge as a cumulated 1,4-diphenyl-1,2,3-butatriene moiety in the center of the polymer backbone. The presence of this linker in a highly-purified representative oligomer was confirmed using NMR spectroscopy.[16] In this case, the bisinitiator approach allows for the direct formation of telechelic diol polymers.

Returning to the methacrylate problem, we found that the preformed bisallyl initiator [Cp*$_2$Sm(μ-η^3-CH$_2$CHCH)]$_2$ (**II**), with its reduced sterics, polymerizes MMA in a living fashion (eq 2).[17] In this case the resultant polymer is "link-functionalized" with a 1,3-butadiene group in its center as a result of the catalyst's bisallyl initiating bridge. Quantitative yields of PMMA with polydispersities of approximately 1.1 are obtained in both THF and toluene after 2 h at 0 °C or 8 h at −78 °C.



(2)

Complex **II** exhibits molecular weight control as well: a plot of observed M_n versus monomer to initiator ratio shows the linearity expected for a polymerization propagating in the absence of chain transfer. Complex **II** can be difficult to purify, however, which sometimes results in the formation of polymers with molecular weights higher than those calculated from the M:I ratio assuming pure bisinitiator.

We have also prepared ABA triblock copolymers with this bimetallic process. Because of the great interest in thermoplastic elastomers, we chose A and B monomers with dissimilar glass transition temperatures (T_gs).[18] Poly(ethyl acrylate-*b*-methyl methacrylate-*b*-ethyl acrylate) synthesized with the samarocene (bisenolate) initiator possessed a molecular weight roughly additive to those of representative homopolymers made with the same catalyst,[19] and quantitative incorporation of both monomers into the polymer backbone was confirmed by NMR spectroscopy. The solubility properties of the triblock were intermediate between those of the homopolymers.[20] Previous attempts to make poly(ethyl acrylate-*b*-methyl methacrylate-*b*-ethyl acrylate) anionically have failed.[21]

We incorporated the crystalline methyl methacrylate segment at the center of the triblock mentioned above, despite the more useful architecture of the "reverse" copolymer, because methacrylate polymerizations are generally more well-controlled than acrylate polymerizations. However, the use of low-T_g poly(alkyl methacrylate) segments[21,22] circumvents this problem entirely, and we have synthesized poly(methyl methacrylate-*b*-hexyl methacrylate-*b*-methyl methacrylate) triblocks in this way as well. An approximately 1:1 by weight copolymer (M_n(obs) = 31 960; PDI = 1.16) exhibited the expected ratio of incorporated monomers and solubility properties.[23] No formation of poly(hexyl methacrylate) (PHMA) homopolymer was observed.[24] The molecular weight of the triblock, however, was somewhat higher than the expected value. It is not clear whether this is due to inadequate exclusion of air during the polymerization (a small amount of diblock copolymer was detected by GPC) or a difference in hydrodynamic radii between the triblock and the PMMA standards used to determine molecular weight.

In conclusion, we have demonstrated the well-controlled polymerization of methyl methacrylate with a preformed bimetallic samarium (III) catalyst and a bisinitiator generated *in situ* from Cp*$_2$Sm·THF$_2$. A third bimetallic complex polymerizes ε-caprolactone. This system incorporates both the high activity and versatility of lanthanide catalysts and the unique advantages of bisinitiating polymerization systems and can be used to produce triblock and "link-functionalized" polymers.

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(13) All molecular weights were determined by gel permeation chromatography (GPC) and are relative to PMMA standards unless otherwise indicated.

(14) Corrected, vs polystyrene: McLain, S. J.; Drysdale, N. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 174.

(15) Monomer loss as a function of time was monitored by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

(16) Oligomerization was run at M:I = 20:1, and the product was purified to a colorless material through reprecipitation. Polycaprolactone oligomer: ^{1}H NMR (CD_2Cl_2) δ 4.03 (t, 2H), 2.28 (t, 2H), 1.62 (m, 4H), 1.36 (m, 2H). The ten phenyl protons of the bridge appear as a broad multiplet, δ 7.3.

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(18) Glass transition temperatures: poly(methyl methacrylate), 105 °C; poly(ethyl acrylate), −24 °C; poly(hexyl methacrylate), −5 °C. *Polymer Handbook*, 3rd ed.; Brandrup J., Immergut, E. H., Eds.; Wiley: New York, 1989.

(19) PEA_{100}–$PMMA_{200}$–PEA_{100}: M_n = 60540; PDI = 1.27. PMMA (M:I = 100): M_n = 24570; PDI = 1.10. PEA (M:I = 100): M_n = 42300; PDI = 1.12. Molecular weights are relative to polystyrene. PEA:PMMA(calc) for triblock = 1.00:1; PEA:PMMA(obs) = 1.03:1 by ^{1}H NMR.

(20) Poly(methyl methacrylate) is insoluble or only slightly soluble in hot methanol, while poly(ethyl acrylate) is soluble in the cold solvent. The triblock copolymer was moderately soluble in methanol at room temperature and dissolved completely upon heating.

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(23) $PMMA_{53}$–$PHMA_{62}$–$PMMA_{53}$: PMMA:PHMA(calc) = 1.71:1; PMMA:PHMA(obs) = 1.94:1 by ^{1}H NMR. M_n(calc) = 21 000; M_n(expected from the sum of representative homopolymers relative to PMMA standards) = 23 960. The triblock dissolves in hot 2-propanol but not in hexanes; PHMA is soluble in both cases while PMMA is not.

(24) The absence of PHMA was determined by comparison of the GPC traces of the unpurified triblock and a sample of PHMA homopolymer prepared using the same monomer in initiator ratio used in the triblock (M:I = 30; M_n(vs PMMA) = 13 370). No evidence of polymer corresponding to the molecular weight or elution time of the PHMA sample was found in the GPC trace of the triblock.