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Highly Isospecific Polymerization of Methyl Methacrylate with a Bis(pyrrolylaldiminato)samarium Hydrocarbyl Complex

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*Summary: New types of samarium alkyl complexes, $L_2SmMe(THF)$ (**2**) and $L_2SmCH_2SiMe_3(THF)$ (**3**), supported by the pyrrolylaldiminato ligand L (L = $[2\text{-}(2,6\text{-}iPr_2C_6H_3N{=}CH)\text{-}5\text{-}tBuC_4H_2N]^-$), were prepared from the corresponding chloride $L_2SmCl(THF)$ (**1**) with the appropriate alkyllithium reagents; the corresponding yttrium alkyl $L_2YCH_2SiMe_3$ (**4**) was prepared similarly. The molecular structures of **1** and **3** were determined by X-ray single-crystal analyses. Compound **3** initializes the stereospecific polymerization of MMA to yield highly isotactic PMMA (mm triad 94.8%) with high molecular weight and narrow molecular distribution at room temperature while **2** is inactive. The possible initial step of the polymerization reaction was proposed.*

A substantial amount of work has been devoted to the development of well-defined single-component catalytic systems for polymerization of polar functional monomers in a controlled fashion.[1] Pioneering work by Yasuda and Collins has shown that lanthanocenes[2] and cationic zirconocenes[3] are excellent precursors for the controlled polymerization of methyl methacrylate (MMA). Recent studies have shown that *ansa*-metallocenes of cationic group 4 enolates and multiple-component catalytic systems can polymerize MMA stereospecifically under certain conditions.[3−5] In addition, a number of lanthanocenes have been reported to generate syndiorich poly(methyl methacrylates) (PMMAs) under mild conditions;[6−15] while C_1-symmetric ansa-bridged lanthanocenes were reported to induce isospecific polymerization of MMA at low temperature.[8] However, none of the known lanthanide systems show high stereoregularity (*mm* or *rr* triad >90%) for MMA polymerization at room temperature, which is a current strategic objective.

We communicate herein that a non-metallocene, one-component lanthanide system initializes polymerization of MMA to generate highly isotactic PMMA with high molecular weight even at elevated temperature. The system is based on a bulky pyrroylaldiminato ligand[16] and does not contain any chiral groups.

The samarium chloride $L_2SmCl(THF)$ (**1**) was obtained by the reaction of KL (L = $[2\text{-}(CH{=}NC_6H_3\text{-}2,6\text{-}i Pr_2)\text{-}5\text{-}t BuC_4N]^-$) with $SmCl_3$ in THF. The corresponding hydrocarbyls $L_2SmR(THF)$ (R = Me (**2**), CH_2SiMe_3 (**3**)) were prepared in high yield by the reaction of **1** with the appropriate alkyllithium in toluene (Scheme 1). The ^{1}H NMR spectra of the paramagnetic **2** and **3** include the broad resonances of one coordinated THF molecule and the α-protons for the alkyl moieties. The yttrium compound $L_2YCH_2SiMe_3$ (**4**) was prepared similarly. Compound **4** is THF free, is monomeric (doublet of CH_2SiMe_3, δ 44.61, 44.17; $^1J_{Y,C} = 44.2$ Hz), and is produced as one diastereomer, as indicated by its ^{1}H and ^{13}C NMR spectra. Attempts to prepare the methyl derivative in this case have, thus far, been unsuccessful. The NMR spectrum of compound **4** is unperturbed by addition of several equivalents of THF in C_6D_6, and the solid compound shows no evidence of coordinated solvent when isolated in the presence of THF.

The molecular structures of **1** and **3**, as determined by single-crystal X-ray analyses,[17] are shown in Figure 1, along with selected bond distances and angles. Both **1** and **3** adopt a distorted-octahedral geometry with the THF oxygen located trans to one pyrrole nitrogen (O−Sm−N angle 160.4(2)° in **1** and 160.37(9)° in **3**). The most striking features are the acute N−Sm−N angles (average 70.3° in **1** and 69.12° in **3**) of the chelating ligand. Importantly, both compounds display molecular C_1 symmetry while the two pyrrolyaldiminato ligands adopt an approximate C_2 arrangement. The Sm−C bond length in **3** is comparable to those found in a handful of samarium alkyls characterized by X-ray diffraction analysis, $(C_5Me_5)_2SmR(THF)$ (R = Me, 2.484(14) Å; R = benzyl, 2.498(5) Å; R = Ph, 2.511(5) Å),[18−20] and

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(17) See the Supporting Information for X-ray crystal data for complexes **1** and **2**.

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Scheme 1

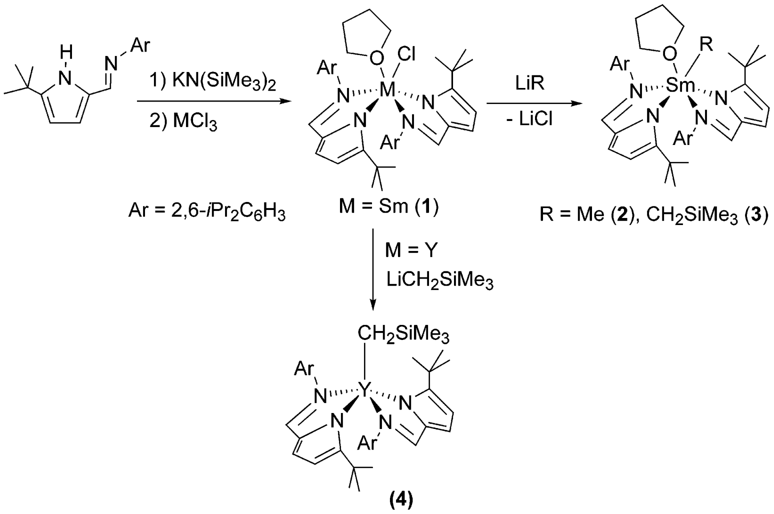

Table 1. Summary of Polymerization Results and Polymer Properties with Complexes 3 and 4

initiator	entry	MMA/**3** (mol/mol)	time (h)	T (°C)	yield (%)	$10^{-4}M_n$[c]	M_w/M_n[c]	T_g[e] (°C)	[mm][d] (%)	[mr] (%)	[rr] (%)	2[rr]/[mr]
3	1[a]	500	1	40	100	3.27	1.48		93.8	5.2	1.0	0.38
3	2[a]	500	2	0	100	5.92	1.24	56.4	97.3	2.1	0.6	0.57
3	3[a]	1000	1	23	65	0.75	1.65		94.5	4.7	0.8	0.33
3	4[a]	2000	1	23	60	1.35	1.86		94.7	4.3	1.0	0.47
3	5[a]	3000	2	23	60	15.8	1.98	59.6	94.8	4.1	1.1	0.54
3	6[a]	1000	2	65	30	4.47	1.47	47.2	91.3	6.7	2.0	0.60
3	7[a]	1000	3	23	75	10.6	1.63	55.4	94.9	3.9	1.2	0.62
3	8[a]	1000	10	23	80	20.2	1.57	57.5	94.9	4.3	0.8	0.37
3	9[a]	1000	4	0	100	16	1.40		97.8	1.7	0.5	0.58
3	10[b]	1000	0.5	23	80	141	1.31		91.8	6.1	2.1	0.69
4	11	1000	2	23	100	1.49	1.72		81.9	12.3	5.8	0.94
4	12	1000	2	0	100	0.92	1.46		84.9	10.2	4.8	0.94
4	13	1000	8	−30	60	6.23	1.48		87.2	8.7	4.1	0.94

[a] Polymerization in toluene solution. [b] Bulk polymerization. [c] From GPC relative to polystyrene standards. [d] From ^{1}H NMR in $CDCl_3$. [e] From DSC.

the ate complex $Li(THF)_2[Sm(OAr)_3(CH_2SiMe_3)_2]$ (2.451(10) Å, Ar = 2,6-$i$$Pr_2C_6H_3$).[21] The ^{1}H NMR spectrum of the paramagnetic **3** in toluene-d_8 shows two broad singlets (δ 10.9, 12.4 ppm) for the diastereotopic protons of the methylene group in CH_2SiMe_3, consistent with the solid-state C_1-symmetric structure.

The alkyl compounds **2**−**4** have been investigated as initiators for the polymerization of methyl methacrylate (MMA). Compounds **3** and **4** were found to be highly active and isospecific for the MMA polymerization in toluene (Table 1, entries 1−9) and in bulk MMA (entry 10), as shown by the triad contents obtained from the ^{1}H NMR spectra[22,23] (Table 1). The samarium species **3** showed excellent stereoregularity in a wide range of temperatures (−40 to +65 °C, *mm* triad content ranging from 91.3 to 97.8%). This feature sets compound **3** apart from known lanthanocenes, which generated syndio-rich or atactic PMMA at normal temperature. The isotacticity of the PMMA samples obtained declined slightly with increasing reaction temperature. At 65 °C, the PMMA yield is relatively low, presumably due to thermally induced chain termination steps. The high isotacticity is observed even in the bulk polymerization process, although the *mm* triad content (91.8%) is slightly low due to high exothermicity of the polymerization reaction.

Remarkably, the bulk polymerization with **3** generates very high molecular weight isotactic PMMA (M_n = 1.41 × 10^6, PDI = 1.31), which, to the best of our knowledge, has not been obtained with known catalytic systems. As can be seen in Table 1, the yttrium complex **4** shows relatively low selectivity. The polydispersity of the PMMA is relatively narrow (1.24−1.98), indicating a single-site catalytic system. (For comparison, chiral lanthanocene systems that yield isotactic PMMA show PDIs in the range 1.8−7.9.[8]) The PDI is slightly higher with an increase in the MMA/**3** ratio and reaction temperature. The T_g values are consistent with the reported values for isotactic PMMA.[4] The ^{1}H NMR spectra of the PMMA samples showed characteristic traces of the $SiMe_3$ group (δ 0.04 ppm), suggesting that the initial step of polymerization proceeds by a coordination insertion mechanism (Scheme 2). Furthermore, MS analysis of a hydrolyzed sample of the reaction mixture from **3** and MMA (1:5 molar ratio) exhibited ions of the formula $HC(Me)(CO_2Me)CH_2[C(Me)(CO_2Me)$-

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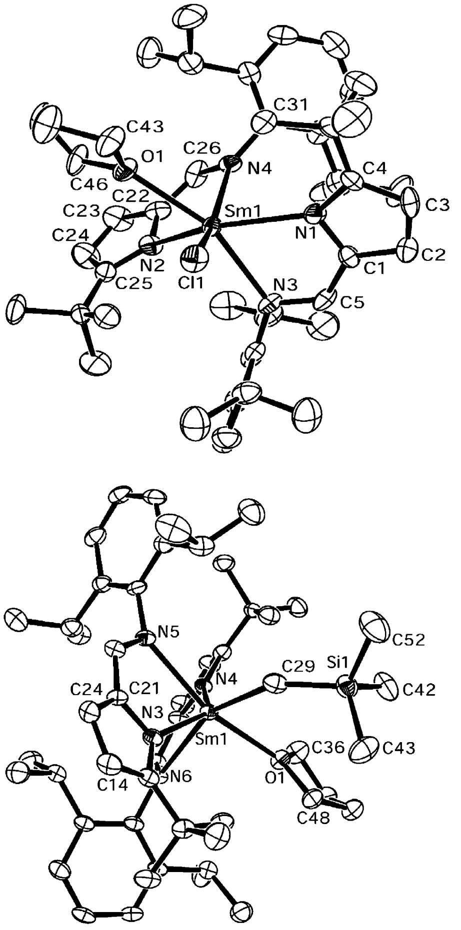


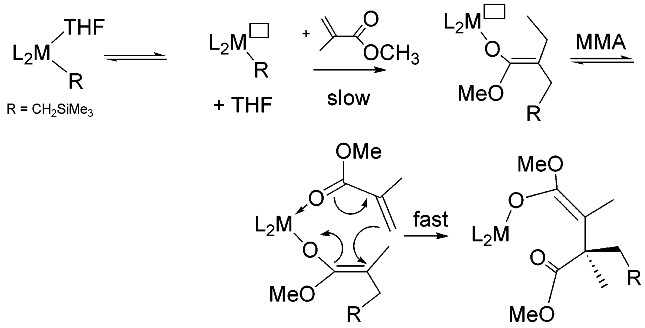
Figure 1. ORTEP drawings of **1** (top) and **3** (bottom) with thermal ellipsoids at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1**: Sm1−Cl1 = 2.625(2), Sm1−O1 = 2.497(6), Sm1−N1 = 2.426(7), Sm1−N2 = 2.429(1), Sm1−N3 = 2.537(7), Sm1−N4 2.570(7); = N1−Sm1−N3 = 69.9(3), N2−Sm−N4 = 70.7(3), O1−Sm1−N3 = 160.4(2), Cl1−Sm1−N4 = 156.0(2), N1−Sm1−N2 = 141.6. Selected bond lengths (Å) and angles (deg) for **3**: Sm1−C29 = 2.455(4), Sm1−O1 = 2.578(3), Sm1−N3 = 2.464(3), Sm1−N4 = 2.467(3), Sm1−N5 = 2.588(3), Sm1−N6 = 2.626(3); N3−Sm1−N5 = 69.13(10), N4−Sm1−N6 = 69.11(9), O1−Sm1−N5 = 160.37(9), N3−Sm1−N4 = 141.70(10), N6−Sm1−C29 = 155.6(1).

$CH_2]_nCH_2SiMe_3$ ($n = 0-6$), corresponding to the oligomers resulting from the initial insertion of the CH_2SiMe_3 group into the MMA molecules.

The reaction of **3** and **4** with 1 equiv of MMA in C_6D_6 only led to the consumption of ca. 20% of **3** and **4**, respectively. ^1H NMR spectra revealed that even when a large excess (40 equiv) of MMA was employed, a trace of the initiator was always observed, indicating that the first step of the reaction (MMA insertion into the M−C bond to form lanthanide enolate[2]) is much slower than chain propagation.

In contrast, compound **2** is inactive for MMA polymerization. Instead, it reacts completely with 1 equiv of MMA immediately in C_6D_6. The ^1H NMR spectrum indicates the presence of multiple compounds that have eluded characterization to date. One possible explanation is that **2** does not form an active enolate species with MMA, due to a slower rate of dissociation of the coordinated THF. Instead, the methyl group may directly attack the MMA carbonyl to deactivate the initiator. Consistent with this notion, we saw no evidence for polymerization when the same procedures were conducted in THF or in toluene/THF (15:1 v:v) solutions of **3** and **4**. Further experiments to probe the mechanism are in progress.

Scheme 2



The triad and pendant content tests of the PMMA samples obtained from initiator **3** indicate that the stereocontrol mechanism conforms to neither enantiomorphic site control nor chain end control, while those from **4** are produced by an enantiomorphic site control mechanism (2[*rr*]/[*mr*] close to 1).[24] Although the detailed stereocontrol mechanism is not available at this stage, it is assumed that the steric environment around the metal center may hinder isomerization of lanthanide enolate species and thus MMA coordination always takes place at a fixed site (Scheme 2). This mechanism has been proposed previously for a chiral lanthanocene catalytic system.[8]

In summary, we have developed a new type of lanthanide system incorporating a bulky pyrroylaldiminato ligand, which exhibits unprecedented stereoregularity for the polymerization of MMA at ambient temperatures. The polymerization proceeds initially by a coordination insertion mechanism. Further studies on kinetics and mechanistic details of the polymerization as well as on other applications of these type of complexes are in progress.

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Supporting Information Available: Text and tables giving crystallographic data for complexes **1** and **3**, experimental details for the synthesis and characterization of **1**−**4**, and details of the polymerization process. This material is available free of charge via the Internet at http://pubs.acs.org.

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