

Rare-Earth Half-Sandwich Dialkyl and Homoleptic Trialkyl Complexes for Rapid and Stereoselective Polymerization of a Conjugated Polar Olefin

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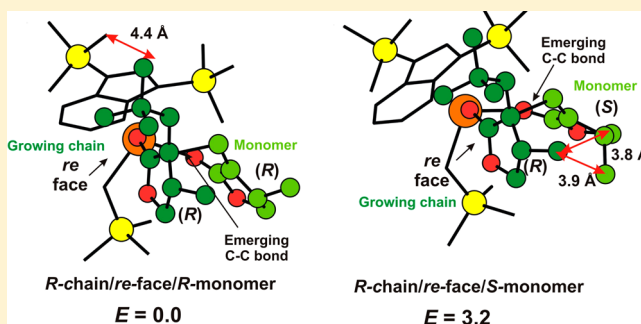
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Supporting Information

ABSTRACT: Under ambient conditions, discrete half-sandwich rare-earth (RE) dialkyls, $[\eta^5\text{-(1,3-(SiMe}_3)_2\text{C}_9\text{H}_5)]\text{RE-(CH}_2\text{SiMe}_3)_2\text{(THF)}$ (RE = Sc, Y, Dy, Lu), catalyze rapid and stereoselective coordination polymerization of β -methyl- α -methylene- γ -butyrolactone (β MMBL), a conjugated polar olefin and a member of the naturally occurring or biomass-derived methylene butyrolactone family. Within the present RE series, the complex of the largest ion (Dy^{3+}) exhibits the highest activity, achieving a high turnover frequency of 390 min^{-1} , and also produces the highly isotactic polymer $\text{P}_{\beta}\text{MMBL}$ ($mm = 91.0\%$). This stereoregular polymer is thermally robust, with a high glass-transition temperature of 280°C , and is resistant to all common organic solvents. Other half-sandwich RE catalysts of the series are also highly active and produce polymers with a similarly high isotacticity. Intriguingly, even simple homoleptic hydrocarbyl RE complexes, $\text{RE(CH}_2\text{SiMe}_3)_3\text{(THF)}_2$ (RE = Sc, Y, Dy, Lu), also afford highly isotactic polymer $\text{P}_{\beta}\text{MMBL}$, despite their much lower polymerization activity, except for the Lu complex, which maintains its high activity for both types of complexes. Computational studies of both half-sandwich and simple hydrocarbyl yttrium complexes have revealed a stereocontrol mechanism that well explains the observed high stereoselectivity of β MMBL polymerization by both types of catalysts. Specifically, the experimental stereoselectivity can be well rationalized with a monometallic propagation mechanism through predominantly chain-end stereocontrol in the coordination–addition polymerization. In this mechanism, formation of an isotactic polymer chiefly originates from interactions between the methyl groups on the chiral β -C atom of the five-membered ring of both the coordinated monomer and the last inserted β MMBL unit of the chain, and the auxiliary ligand on the metal makes a negligible contribution to the stereocontrol of the polymerization.



INTRODUCTION

Coordination–addition polymerization of conjugated polar olefins, or acrylics, by discrete, single-site metal catalysts has attracted growing interest due to its precision in the catalyst-site-regulated stereochemical and architectural control as well as its ability to produce new classes of polymeric materials unattainable by other means of polymerization.¹ In this type of polymerization catalysis, cationic group IV metal complexes and their isoelectronic, neutral rare-earth (RE) complexes are the two best-known classes of highly active, efficient, and controlled catalysts for the coordination–addition polymerization of acrylics such as methyl methacrylate (MMA), acrylates, acrylonitrile, and acrylamides.^{1,2} On comparison of these two

classes of bis(η^5 -cyclopentadienyl) and related sandwich metallocene catalysts, cationic group IV metallocenium catalysts have the advantage of achieving high activity and precise control over stereochemistry of polymerization, often at ambient temperature, while neutral RE metallocene catalysts typically require no cocatalysts and are more effective for acrylate polymerization and are more tolerant toward polar donor media.^{1,2} Such important features of RE catalysts render them especially effective in polymerizing biomass-derived,

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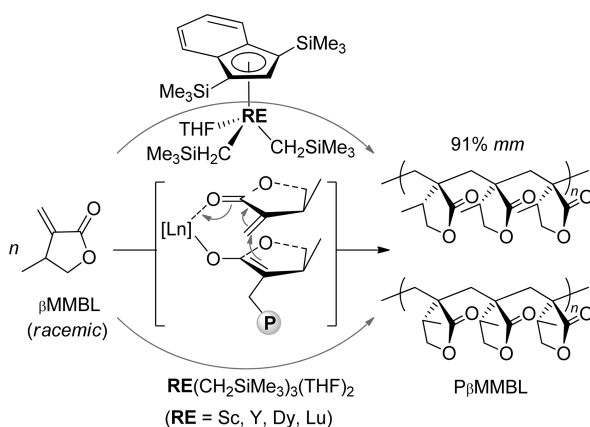
oxygenated polar feedstocks,^{3–5} such as α -methylene- γ -butyrolactone (MBL)⁶ and γ -methyl- α -methylene- γ -butyrolactone (β MMBL),⁷ because such renewable monomers resemble more acrylates than methacrylates in reactivity and polar donor solvents, such as *N,N*-dimethylformamide (DMF), are needed for the polymerization due to solubility constraints of the resulting polymers. Such sustainable polymers offer not only an alternative to petroleum-based acrylic polymers such as PMMA⁸ but also superior materials properties.^{3–5}

Of many types of RE catalysts that have been developed for molecular catalysis⁹ and for polymerization catalysis of acrylics,¹⁰ bis(η^5 -pentamethylcyclopentadienyl) (Cp^*) and related sandwich lanthanocenes, such as $[\text{Cp}^*_2\text{SmH}]_2$ and $\text{Cp}^*_2\text{LnMe}(\text{THF})$, typically exhibit the highest polymerization activity and control.¹⁰ In comparison, single- Cp -type, half-sandwich RE catalysts,¹¹ despite their remarkable versatility demonstrated in the polymerization and copolymerization of olefins, especially styrene and isoprene, leading to a series of new polymeric materials,¹² have been shown to be much less active and effective than the prototype sandwich lanthanocene catalysts for polymerization of acrylics.¹ Likewise, several different types of *ansa*-RE metallocenes are also considerably less active and effective than the unbridged RE metallocene system.¹ However, for the biomass-derived monomers MBL and β MMBL, which can be considered as cyclic analogues of MMA, we found that RE half-metallocenes⁴ and *ansa*-half-metallocenes⁵ can promote extremely rapid polymerization of such cyclic acrylics without lactone ring-opening side reactions, with a high turnover frequency (TOF) up to 500 min^{-1} .

Polymers derived from free-radical polymerization of the β -methyl derivative of methylene butyrolactones, β -methyl- α -methylene- γ -butyrolactone (β MMBL), have been shown to exhibit superior materials properties as plastic optical fibers in comparison to other acrylic polymers.¹³ Radical polymerization of β MMBL initiated by 2,2-azobis(isobutyronitrile) (AIBN) yields an atactic polymer, which is soluble in common organic solvents such as DMF and DMSO.¹⁴ We reported recently that coordination polymerization of β MMBL by chiral C_2 -ligated zirconocenium ester enolate catalysts afford highly isotactic (95% *mm*) $\text{P}\beta\text{MMBL}$ to stereoperfect (>99% *mm*) $\text{P}\beta\text{MMBL}$.¹⁵ The highly isotactic polymer is thermally robust, with a high glass-transition temperature (T_g) up to 290 $^\circ\text{C}$, and resistant to all common organic solvents at room temperature or refluxing conditions. However, such chiral zirconocenium catalysts exhibit only modest activity, with $\text{TOF} = 4 \text{ min}^{-1}$.¹⁵ On the other hand, we found that *ansa*-half-sandwich RE dialkyl complexes supported by an ethylene-bridged fluorenyl-*N*-heterocyclic carbene (NHC) ligand, $\text{C}_2\text{H}_4(\eta^5\text{-Flu-}\kappa^1\text{-NHC})\text{RE}(\text{CH}_2\text{SiMe}_3)_2$ ($\text{RE} = \text{Y, Lu}$), also promote stereoselective polymerization of β MMBL to produce the isotactic polymer $\text{P}\beta\text{MMBL}$, with an isotacticity of 91% *mm*.⁵ Although the isotacticity of the polymer is lower than that by the chiral zirconocenium catalysts, the *ansa*-half-sandwich RE catalyst exhibits much higher activity, with a high TOF of 75 min^{-1} .⁵

These earlier interesting observations prompted us to investigate the characteristics of β MMBL polymerization by unbridged half-sandwich RE dialkyl complexes incorporating a disilylated indenyl ligand: $[\text{Ind}]\text{RE}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$, $[\text{Ind}] = \eta^5\text{-}(1,3\text{-(SiMe}_3)_2\text{C}_9\text{H}_5)$, $\text{RE} = \text{Sc},^{16} \text{Y},^{17} \text{Dy},^{17} \text{Lu}^{17}$ (Scheme 1). As controls and comparative examples, we also examined simple homoleptic hydrocarbyl RE complexes, $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ($\text{RE} = \text{Sc, Y, Dy, Lu}$). Most significantly, our combined experimental and theoretical study described in

Scheme 1. Stereoselective Polymerization of β MMBL by Half-Sandwich RE Dialkyls and Simple RE Hydrocarbyl Complexes



the current report has revealed that (a) half-sandwich RE catalysts promote rapid *and* stereoselective coordination polymerization of β MMBL at ambient temperature, (b) simple hydrocarbyl RE complexes also produce the highly isotactic polymer $\text{P}\beta\text{MMBL}$, and (c) the stereoselectivity of this monometallic coordination polymerization originates chiefly from interactions between the methyl groups on the chiral β -C atom of the five-membered ring of both the coordinated monomer and the last inserted β MMBL unit of the chain.

EXPERIMENTAL SECTION

Materials and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon or nitrogen-filled glovebox. HPLC-grade organic solvents were sparged extensively with nitrogen during filling of the solvent reservoir and then dried by passage through activated alumina (for Et_2O , THF, and CH_2Cl_2) followed by passage through Q-5-supported copper catalyst (for toluene and hexanes) stainless steel columns. HPLC-grade *N,N*-dimethylformamide (DMF) was degassed and dried over CaH_2 overnight, followed by vacuum transfer (no distillation). The NMR solvents CDCl_3 and $\text{DMSO}-d_6$ were dried over activated Davison 4 Å molecular sieves, and NMR spectra were recorded on a Varian Inova 300 (FT 300 MHz, ^1H ; 75 MHz, ^{13}C), a Varian Inova 400 MHz, or an Inova 500 MHz spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane.

Acetaldehyde (freshly distilled), methyl acrylate, *N*-bromosuccinimide, dimethyl sulfide, 1,4-diazabicyclo[2.2.2]octane (DABCO), formaldehyde (37 wt % in water), tin powder, and *p*-toluenesulfonic acid were purchased from Sigma-Aldrich and used as received. AIBN (2,2-azobis(isobutyronitrile)) was purchased from Alfa Aesar. Literature procedures were employed to prepare the following compounds: $[\eta^5\text{-(1,3-(SiMe}_3)_2\text{C}_9\text{H}_5)]\text{RE}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ ($\text{RE} = \text{Sc},^{16} \text{Y},^{17} \text{Dy},^{17} \text{Lu}^{17}$) and $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ($\text{RE} = \text{Sc, Y, Dy, Lu}$).¹⁸

Preparation of β MMBL. Literature procedures^{5,14} were modified to prepare β -methyl- α -methylene- γ -butyrolactone (β MMBL) as detailed below. The purified monomer was stored in brown bottles inside a glovebox freezer at $-30 \text{ }^\circ\text{C}$.

Step 1: Methyl 2-Methylidene-3-hydroxybutanoate. Freshly distilled acetaldehyde (44.1 g, 1.00 mol), methyl acrylate (95.5 g, 1.11 mol), and DABCO (12.3 g, 0.110 mol) were stirred at room temperature for 10 days. The solution was diluted with diethyl ether (200 mL), washed with water ($2 \times 100 \text{ mL}$) and 10% aqueous hydrochloric acid (50 mL), and then rinsed with water ($2 \times 50 \text{ mL}$).

Table 1. Selected Results of β MMBL Polymerization by RE (Sc, Y, Dy, Lu) Catalysts^a

run no.	RE cat.	gelation time (min)	reaction time (min)	isolated yield (%)	TOF (min ⁻¹)	T _g (°C)
1	[Ind]Sc(CH ₂ SiMe ₃) ₂ (THF)	<1	2	93	190	299
2	[Ind]Y(CH ₂ SiMe ₃) ₂ (THF)	<1	2	88	180	295
3	[Ind]Dy(CH ₂ SiMe ₃) ₂ (THF)	<1	1	97	390	280
4	[Ind]Lu(CH ₂ SiMe ₃) ₂ (THF)	<1	2	93	190	304
5	Sc(CH ₂ SiMe ₃) ₃ (THF) ₂	N.A.	30	28	3.7	N.D.
6	Y(CH ₂ SiMe ₃) ₃ (THF) ₂	N.A.	30	35	4.7	N.D.
7	Dy(CH ₂ SiMe ₃) ₃ (THF) ₂	N.A.	30	9	1.2	N.D.
8	Lu(CH ₂ SiMe ₃) ₃ (THF) ₂	<1	2	88	180	300

^aAll runs were carried out in 4.0 mL of CH₂Cl₂ at room temperature (~25 °C) with a catalyst loading of 0.25 mol % and $[\beta\text{MMBL}]/[\text{RE}] = 400/1$. N.A. = not applicable. N.D. = not determined.

The organic phase was dried over magnesium sulfate. The remaining methyl acrylate and diethyl ether were removed in vacuo. Fractional distillation of the residue afforded 91.0 g (0.70 mol, 59% yield) of methyl 2-methylidene-3-hydroxybutanoate as a clear liquid at 66–68 °C/1.0 mmHg. ¹H NMR (300 MHz, CDCl₃): 6.18 (s, 1H), 5.76 (s, 1H), 4.54 (q, 1H), 3.70 (s, 1H), 3.15 (s, 3H), 1.25 (d, 3H).

Step 2: Methyl (Z)-2-Bromomethyl-2-butenolate. N-Bromosuccinimide (97.9 g, 0.550 mol) in dry dichloromethane (600 mL) was chilled to 0 °C, and dimethyl sulfide (44.0 mL, 0.599 mol) in dry dichloromethane (100 mL) was added dropwise under nitrogen while the solution was kept below 5 °C, after which the solution was cooled to –20 °C, and methyl 2-methylidene-3-hydroxybutanoate (65.0g, 0.50 mol) in dichloromethane (100 mL) was added dropwise over 1 h. Then this mixture was stirred for 48 h at room temperature to give a clear, pale yellow solution. The solution was diluted with hexanes (600 mL) and poured into an ice/water/NaCl mixture (800 mL total, 200 g of ice, and 100 g of NaCl). The organic phase was separated and washed with saturated aqueous KCl (2 × 150 mL). The two aqueous portions were combined and extracted with diethyl ether (2 × 150 mL), and the separated ether phase was dried over MgSO₄. All organic phases were combined, and the solvent was removed on a rotary evaporator to give 100 g of the crude product as a clear, yellow liquid. ¹H NMR (300 MHz, CDCl₃): 7.14 (q, 1H), 4.20 (s, 2H), 3.72 (s, 3H), 1.84 (d, 3H). This crude product was used directly in the next step.

Step 3: β MMBL. The above crude ester product (23.80 g, ~90% purity, 21.4 g, 0.111 mol of the ester), formaldehyde (37 wt % in water, 12 mL, 0.161 mol), and tin powder (14.6 g, 0.123 mol) were added to a mixture of THF (100 mL) and saturated aqueous ammonium chloride (40 mL). The mixture was stirred and gently refluxed at 75 °C for 28 h. After the mixture was cooled to room temperature, it was extracted with a 5/4 (v/v) mixture of diethyl ether and hexanes (3 × 300 mL), and the combined organic phase was washed with water (4 × 100 mL) and dried over MgSO₄ with added hydroquinone (0.05 g, 0.454 mmol). After removal of the solvents, *p*-toluenesulfonic acid (0.25 g, 1.3 mmol) and dry toluene (50 mL) were added to the residue. The mixture was stirred at room temperature for 5 h, diluted with diethyl ether (50 mL), washed with water (3 × 10 mL), and dried over MgSO₄. After toluene was removed by rotary evaporation, successive fractional distillations (at 40–50 °C/0.5–1 mmHg) of the crude product gave the crude MMBL (about 5 mL). Then the crude product was purified on a silica column (the eluent was an 8.5/1.5 mixture of hexanes and ethyl acetate). The product from the column was dried over CaH₂ (a little amount of hydroquinone was added) overnight and distilled under reduced pressure (~40 °C/0.5 mmHg), giving about 4 mL of the pure product. ¹H NMR (300 MHz, CDCl₃): 6.14 (d, 1H), 5.52 (d, 1H), 4.42 (t, 1H), 3.66 (dd, 1H), 3.10 (m, 1H), 1.28 (d, 3H).

General Polymerization Procedures. Polymerizations were performed in 30 mL glass reactors inside the glovebox at ambient temperature (ca. 25 °C). In a typical polymerization procedure, a predetermined amount of RE metal catalyst (0.0103 mmol for runs with a $[\beta\text{MMBL}]/[\text{RE}]$ ratio of 400) was dissolved in a solvent (4.0 mL of CH₂Cl₂). With vigorous stirring, monomer (β MMBL, 4.11 mmol) was quickly added to the above catalyst solution via syringe to

start the polymerization. After the measured time interval, the polymerization was immediately quenched by addition of 5 mL of 5% HCl-acidified methanol. The quenched mixture was precipitated into 100 mL of methanol, stirred for 1 h, and filtered, and the product was washed with methanol and dried in a vacuum oven at 50 °C overnight to a constant weight.

Polymer Characterizations. Glass-transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) on a DSC 2920 TA Instrument. Polymer samples were first heated to 250 °C at 20 °C/min, equilibrated at this temperature for 4 min, and reheated to 320 °C at 10 °C/min. All T_g values were obtained from the second scan after the thermal history was removed from the first scan.

The tacticity of the atactic P β MMBL produced by the radical polymerization was measured by ¹³C NMR either in DMSO-*d*₆ at 100 °C or in trifluoroacetic acid (TFA)-*d* at 70 °C, while the tacticity of the isotactic P β MMBL produced by the coordination polymerization with the RE catalysts was measured in TFA-*d* at 70 °C. (Note that the isotactic P β MMBL is insoluble in DMSO-*d*₆ but soluble in TFA at 70 °C, and there was no evidence for ring opening of the butyrolactone ring or polymer hydrolysis under the NMR conditions.) The assignments of the triads were based on the backbone quaternary carbon resonances, following the literature.^{5,15}

¹³C NMR (TFA-*d*, 125 MHz, 70 °C) for P β MMBL (by AIBN): δ 184 (m, C=O), 73.9 (OCH₂), 50.4, 50.0, 49.2 (m, quaternary carbon, *rr*, *mr*, *mm*), 39.5 (m, main-chain CH₂), 35.8 (CH), 8.90 (CH₃). ¹³C NMR (TFA-*d*, 125 MHz, 70 °C) for P β MMBL (by the Dy catalyst): δ 185 (C=O), 74.1 (OCH₂), 50.6, 50.2, 49.5 (quaternary carbon, *rr*, *mr*, *mm*), 40.2 (main-chain CH₂), 35.6 (CH), 9.52 (CH₃).

Computational Details. Calculations followed the procedures described in our prior publications.^{15,19} All the density functional theory (DFT) calculations were performed using the Gaussian09 package.²⁰ The BP86 GGA functional of Becke and Perdew was used.^{21,22} Geometry optimizations were performed with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, C, Si, and O atoms (SVP keyword in Gaussian),²³ while the quasi-relativistic small-core Stuttgart ECP with the associated triple- ζ valence basis set was used for yttrium (SDD keyword in Gaussian09). The reported energies have been obtained via single-point energy calculations with the M06 functional and the triple- ζ basis set of Ahlrichs (TZVP keyword in Gaussian09). Solvent effects, CH₂Cl₂ and DMF, were included with the default Gaussian PCM implementation.²⁴ The transition states were confirmed by analytical frequency calculations.

RESULTS AND DISCUSSION

Results of β MMBL Polymerization. With a low catalyst loading of 0.25 mol % ($[\beta\text{MMBL}]/[\text{RE}] = 400/1$) in CH₂Cl₂ at ambient temperature (~25 °C), all polymerizations by the four [Ind]RE(CH₂SiMe₃)₂(THF) complexes proceeded rapidly, leading to gelation (due to polymer precipitation) within 1 min of reaction. The isolated polymer yields by Sc (2 min), Y (2 min), Dy (1 min), and Lu (2 min) complexes were 93%,

88%, 97%, and 93%, respectively (runs 1–4, Table 1). The complex of the largest ion of this series (Dy^{3+}) gave the highest activity, with a high turnover frequency of $\text{TOF} = 390 \text{ min}^{-1}$ (run 3); however, there was no particular activity trend as a function of ionic radii of the RE metals (Table 1). The resulting polymer, $\text{P}_{\beta}\text{MMBL}$, is insoluble in CH_2Cl_2 or other common organic solvents tested, including DMF, DMSO, acetonitrile, and dichlorobenzene, at room temperature or refluxing temperatures. The insolubility of the $\text{P}_{\beta}\text{MMBL}$ produced herein limited our ability to characterize the polymers by gel-permeation chromatography (GPC), but our previous work on the GPC characterization of βMMBL -containing soluble copolymers produced by *ansa*-RE catalysts showed that the RE catalysts afford polymers with a typical polydispersity index (PDI) of ~ 2 ,⁵ characteristic of single-site catalysis.

The observed excellent solvent resistance of the $\text{P}_{\beta}\text{MMBL}$ produced by coordination polymerization with the current RE catalysts points to the formation of stereoregular polymers.^{5,15} Such polymers are in sharp contrast to the amorphous, atactic $\text{P}_{\beta}\text{MMBL}$ prepared by free-radical polymerization initiated by AIBN, which is readily soluble in common organic solvents including DMF, DMSO, or acetonitrile, even at ambient temperature.¹⁴ The extremely high T_g value of 280°C (Table 1 and Figure S4 (Supporting Information)) for the $\text{P}_{\beta}\text{MMBL}$ produced by $[\text{Ind}]\text{Dy}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ is consistent with the value observed for the highly isotactic $\text{P}_{\beta}\text{MMBL}$.^{5,15} The T_g 's of βMMBL polymers produced by Sc, Y, and Lu catalysts are even higher (Table 1). Further characterization of this stereoregular polymer by 500 MHz NMR in trifluoroacetic acid ($\text{TFA}-d$) at 70°C confirmed it being indeed a highly isotactic polymer. Figure 1 depicts an overlay of ^{13}C NMR spectra (125

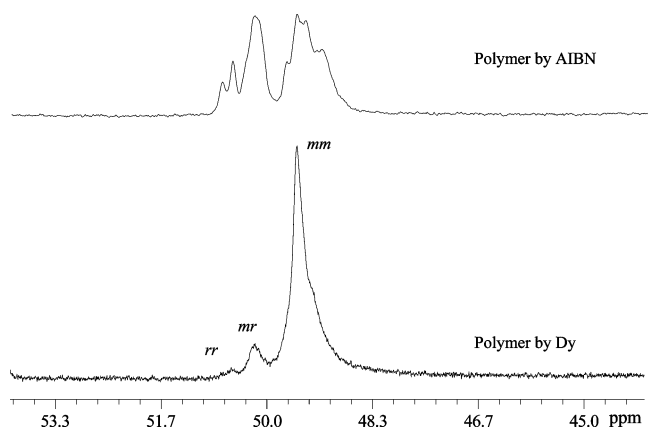


Figure 1. Overlay of ^{13}C NMR ($\text{TFA}-d$, 125 MHz, 70°C) spectra of the atactic $\text{P}_{\beta}\text{MMBL}$ (top) produced radically by AIBN and the highly isotactic $\text{P}_{\beta}\text{MMBL}$ (bottom) produced by coordination polymerization using the RE catalyst $[\text{Ind}]\text{Dy}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$, in the backbone quaternary carbon (*rr*, *mr*, *mm*) region.

MHz) of the $\text{P}_{\beta}\text{MMBL}$ samples produced by AIBN and $[\text{Ind}]\text{Dy}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ in the main-chain backbone quaternary carbon triad region. Analysis of ^{13}C NMR spectra (Figure 1) of the polymers clearly shows that the polymer produced by free-radical polymerization is an iso-rich atactic polymer with 56.5% *mm*, 35.5% *mr*, and 8.0% *rr*, whereas the polymer by $[\text{Ind}]\text{Dy}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ is a highly stereoregular, isotactic polymer, with 91.0% *mm*, 7.9% *mr*, 1.1% *rr*. Likewise, the other three RE catalysts of this series produced

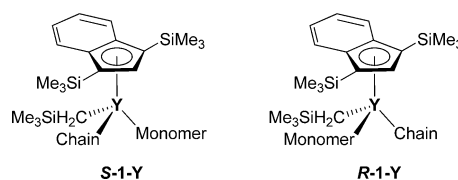
the polymers with a similar isotacticity, despite their variations in polymerization activity.

The formation of the highly stereoregular polymer by the *achiral* half-sandwich RE precatalysts $[\text{Ind}]\text{RE}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ led to a hypothesis that this stereoselective polymerization is largely chain-end controlled. To provide further evidence to support this hypothesis, we also investigated the polymerization characteristics of simple homoleptic hydrocarbyl RE complexes, $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ ($\text{RE} = \text{Sc}, \text{Y}, \text{Dy}, \text{Lu}$). The polymerization results (runs 5–8, Table 1) showed that Sc, Y, and Dy complexes experienced a substantial activity drop on going from the substituted indenyl-ligated half-sandwich complexes to the simple hydrocarbyl complexes, with the Dy complex incurring the largest activity drop from a high TOF of 390 min^{-1} for the half-sandwich complex (run 3) to a low TOF of only 1.2 min^{-1} for the hydrocarbyl complex (run 7). This drastic activity reduction is due to rapid catalyst deactivation shown by the simple hydrocarbyl complexes of Sc, Y, and Dy, as evidenced by the similar polymer yields achieved for the polymerization (by Sc, for example) between 3 min (24%) and 30 min (28%) of reaction. On the other hand, the Lu complex nearly maintained its activity on going from the half-sandwich type to the simple hydrocarbyl type: $\text{TOF} = 180 \text{ min}^{-1}$ (run 8) vs $\text{TOF} = 190 \text{ min}^{-1}$ (run 4). Most significantly, the simple Lu hydrocarbyl complex also produced highly isotactic $\text{P}_{\beta}\text{MMBL}$, with isotacticity similar to that afforded by the half-sandwich complex.

Stereocontrol Mechanism in βMMBL Polymerization.

To understand the stereocontrol mechanism governing these polymerization reactions, we performed computational studies of βMMBL polymerization catalyzed by $[\text{Ind}]\text{Y}(\text{CH}_2\text{SiMe}_3)_2$. We assumed the monometallic propagation mechanism established previously⁵ and considered the general model, depicted in Scheme 2, as *S*-1-Y and *R*-1-Y, in that the metal

Scheme 2. General Model for the Monometallic Propagation Mechanism for the Polymerization of βMMBL by Half-Sandwich RE Dialkyl Complexes



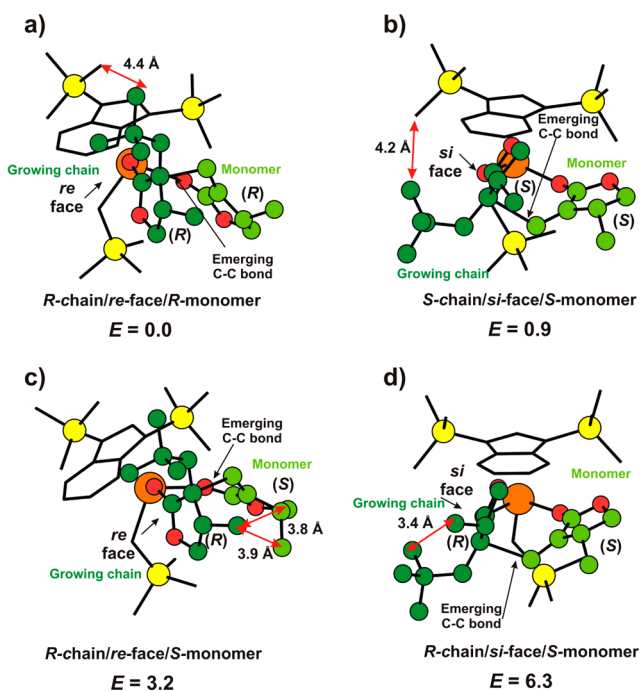
center is tetracoordinated with the indenyl ligand and the $-\text{CH}_2\text{SiMe}_3$ ligand from the starting complex, as well as a new growing enolate βMMBL polymer chain and a coordinated βMMBL monomer. We focused on the transition state (TS) for monomer addition with an *S* configuration at the chiral metal of the catalyst (*S*-1-Y).²⁵ For the *S*-1-Y system we considered addition of both *R* and *S* βMMBL monomers at both *re* and *si* prochiral faces of the growing chain with both *R* and *S* configuration of the chiral $\beta\text{-C}$ atom of the five-membered ring of the last inserted βMMBL unit (*R* or *S* chain) and both *trans* and *cis* geometries, which indicates the relative orientation of the O atoms of the five-membered rings of the monomer and of the chain.^{15,19} The energies of the competitive transition states calculated for *S*-1-Y are reported in Table 2, and the reported energies included effects of the solvents CH_2Cl_2 and DMF.

Table 2. Energy (kcal/mol) of the Possible Transition States for β MMBL Addition on S-1-Y

entry	R chain			ΔE	
	chain face	β MMBL	chain/ β MMBL	CH ₂ Cl ₂	DMF
1	<i>re</i>	R	<i>cis</i>	0.0	0.0
2	<i>re</i>	S	<i>cis</i>	3.2	3.2
3	<i>si</i>	R	<i>cis</i>	6.3	6.4
4	<i>si</i>	S	<i>cis</i>	7.4	7.5
entry	S chain			ΔE	
	chain face	β MMBL	chain/ β MMBL	CH ₂ Cl ₂	DMF
5	<i>re</i>	R	<i>cis</i>	4.8	4.9
6	<i>re</i>	S	<i>cis</i>	6.7	6.8
7	<i>si</i>	R	<i>trans</i>	3.3	3.4
8	<i>si</i>	S	<i>cis</i>	0.9	0.9

The energy differences reported in Table 2 indicate that, for an S metal, system S-1-Y, an R chain favors addition of another R β MMBL molecule on the *re* face of the growing chain (entry 1 vs entries 2–4), while an S chain favors addition of another S β MMBL molecule on the *si* face of the growing chain (entry 8 vs entries 5–7). In short, consecutive addition of β MMBL molecules with the same configuration (R or S) at the same chain enantioface (*re* or *si*) is strongly favored, which indicates that stereoselectivity is determined by the configuration of the last inserted monomer. This finding rationalizes the formation of the isotactic P β MMBL observed experimentally with the half-sandwich RE catalysts. For monomer additions to the growing enolates of both R and S chains, the two competitive TSs, namely addition of S β MMBL on the *re* face of the R growing chain (entry 2) and addition of R β MMBL on the *si* face of the S growing chain (entry 7), which lead to consecutive addition of β MMBL molecules with opposite configuration, are roughly 3 kcal/mol higher in energy than the TSs for the correct additions, namely the R-chain/*re*-face/R-monomer (entry 1) and S-chain/*si*-face/S-monomer additions (entry 8), entry 2 vs 1 and entry 7 vs 8. Finally, the relative energies in CH₂Cl₂ and in DMF are quite close, indicating that the polarity of the solvent has a minor impact on the relative energy of the various TSs.

The two largely favored R-chain/*re*-face/R-monomer and S-chain/*si*-face/S-monomer TS geometries in presence of an S metal are compared in Figure 2. These TS geometries differ in the orientation of the growing chain: in the S-chain/*si*-face/S-monomer TS it is oriented toward the bulky –SiMe₃ group of the indenyl ligand, whereas in the R-chain/*re*-face/R-monomer TS it is oriented toward the sterically less demanding –CH₂SiMe₃ groups bound to the metal. Calculations also indicate that in the case of an S metal the R-chain/*re*-face/R-monomer TS is slightly preferred over the S-chain/*si*-face/S-monomer TS in both solvents by 0.9 kcal/mol (entry 1 vs 8). The two TSs leading to consecutive addition of β MMBL molecules with the same configuration are of higher stability because the emerging C–C bond and its substituents are oriented away from the metal and from the ligand, as shown by the large distances between the reacting atoms and the metal ligands in Figure 2a,b, as well as in Figure S1a,b (Supporting Information).²⁰ These results indicate that the stereoselectivity should involve only interactions between the monomer and the chain. Indeed, steric interactions involving the β -methyl groups of the monomer and the chain favor addition of the R monomer over the S monomer on the *re* face of the R chain

**Figure 2.** Transition state geometries for the competitive β MMBL addition on S-1-Y. Energies (kcal/mol) refer to the values in CH₂Cl₂ (Table 1). The ^tBu group was used to model the remainder of the growing chain.

and of the S monomer over the R monomer on the *si* face of the S chain (Figure 2a vs Figure 2c and Figure S2 (Supporting Information)). Moreover, as previously reported for β MMBL polymerization catalyzed by the C₂-symmetric cationic metallocene systems,¹⁵ the combinations R-chain/*si*-face and S-chain/*re*-face are disfavored because of steric interaction within the growing chain. These interactions involve the methyl group on the last inserted monomer unit and the growing chain, which pushes the corresponding TSs at 6.3 and 3.9 kcal/mol over the favored R-chain/*re*-face/R-monomer and S-chain/*si*-face/S-monomer TSs (Figure 2a vs Figure 2d).

In short, calculations indicate that the origin of stereoselectivity can be ascribed to the configuration of the chiral β -C atom of the five-membered ring of the last added monomer, which dictates the selection between the two chain faces (*re* or *si*) and between the two monomer configurations (R and S) in the addition steps. Specifically, the last added R β MMBL molecule on the *re* chain favors addition of another R β MMBL molecule on the *re* chain, independent of the metal configuration. The end result is that the formed P β MMBL should display regularity in the sequence of the configurations of the chiral β -C atom of the five-membered ring and should be isotactic. Further, since the configuration of the metal seems to play a minor role, i.e. the R-chain/*re*-face/R-monomer and the S-chain/*si*-face/S-monomer TSs are favored on either metal configuration, our results suggest that no strict requirement for regular chain migratory or regular back-skip of the growing chain at each insertion step is needed. This result, together with the calculated ΔE_{stereo} value of about 3 kcal/mol (Table 2), is in agreement with the experimentally observed isotactic P β MMBL with 91% of *mm* triads. Finally, a mistake in the selectivity of the monomer configuration or of the chain face at the addition step should switch between R and S chains and thus between R and S selectivity of monomer addition. This consideration

indicates that the formed P_{β} MMBL should present a microstructure consistent with a chain-end stereocontrol.

Next, we considered a scenario where the chain initiation involves both $-\text{CH}_2\text{SiMe}_3$ groups in the $[\text{Ind}]\text{Y}(\text{CH}_2\text{SiMe}_3)_2$ complex so that two growing chains could propagate on one metal center (1-Y). The addition reactions of R_{β} MMBL monomer on the system with two chains, one R chain and one S chain, is sketched in Scheme 3. The competitive TS

Scheme 3. General Model for Considering Two Growing Chains Propagating on One Metal Center

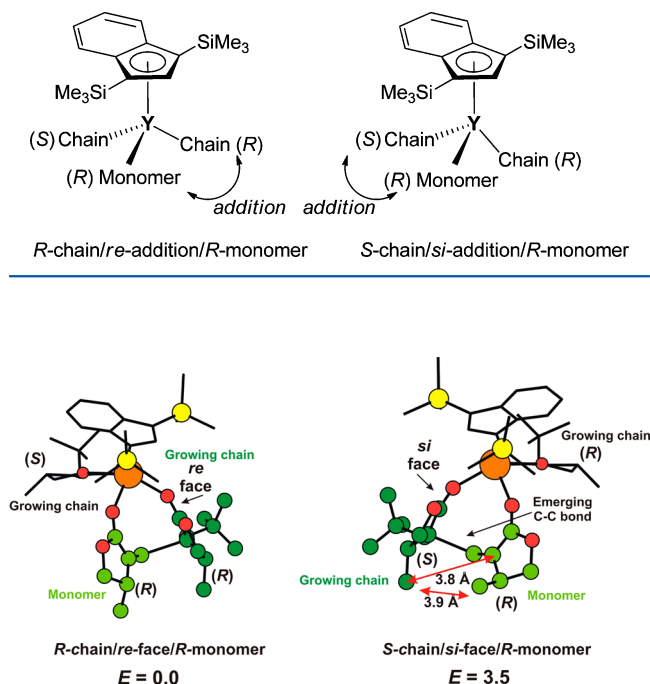


Figure 3. Transition state geometries for the competitive β MMBL addition on 1-Y with one R chain and one S chain on the same metal center. Energies (kcal/mol) refer to the values in CH_2Cl_2 . The $t\text{Bu}$ group was used to model the remainder of the growing chain.

geometries are compared in Figure 3. By replacing the $-\text{CH}_2\text{SiMe}_3$ group on R -1-Y with a more bulky growing chain (R or S) (Scheme 2 vs 3), the metal ligands are still away from the reacting atoms (see Figure S3 (Supporting Information)) so that there is no meaningful difference in the competitive TS additions, and the resulting ΔE_{stereo} value remains approximately 3 kcal/mol (3.5 kcal/mol in both solvents) (Figure 3). Hence, the presence of two growing chains on the 1-Y system should not change the proposed mechanism of stereocontrol, since the monomer prevailing reacts with the chain having the same configuration of the β -C atom of the five-membered ring, and the combinations of R -chain/ re -face/ R -monomer and S -chain/ si -face/ S -monomer are still largely favored, thus still yielding isotactic P_{β} MMBL.

As further evidence of the negligible contribution of the metal ligands in the stereocontrol mechanism operating in the current half-sandwich RE complexes, we obtained essentially the same results with the simple hydrocarbyl complexes $\text{Y}(\text{CH}_2\text{SiMe}_3)_3$ (2-Y, Scheme 4). As shown in Figure 4, where the competitive TS geometries are compared, the calculated ΔE_{stereo} is again close to 3 kcal/mol (3.5 kcal/mol in CH_2Cl_2 , 3.3 kcal/mol in DMF), suggesting that a similarly high

Scheme 4. General Model for the Monometallic Propagation Mechanism for the Polymerization of β MMBL by Simple Hydrocarbyl RE Complexes

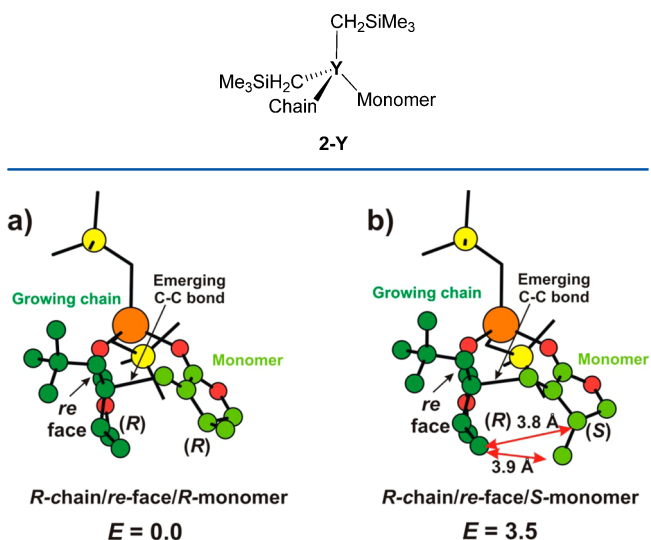


Figure 4. Transition state geometries for the competitive β MMBL addition on 2-Y. Energies (kcal/mol) refer to the values in CH_2Cl_2 . The $t\text{Bu}$ group was used to model the remainder of the growing chain.

isotactic P_{β} MMBL should result, which is in excellent agreement with the experiment.

CONCLUSIONS

Half-sandwich RE dialkyl complexes, $[\eta^5-(1,3-(\text{SiMe}_3)_2\text{C}_9\text{H}_5)]\text{-RE}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (RE = Sc, Y, Dy, Lu), promote rapid polymerization of β MMBL at ambient temperature. The complex of Dy, the largest ion of this Ln series, exhibits the highest activity, thus achieving nearly quantitative polymer yield (97%) within 1 min of reaction that employs a low loading of catalyst (0.25 mol %), corresponding to a high TOF of 390 min^{-1} . More significantly, this highly active coordination polymerization system also affords the highly stereoregular polymer β MMBL having an isotacticity of 91.0% mm , in contrast to the atactic polymer produced by radical polymerization initiated by AIBN. Other half-sandwich RE catalysts of the current series are also highly active and produce polymers with a similarly high isotacticity. The resulting isotactic P_{β} MMBL is thermally robust, with a high T_g of 280 $^{\circ}\text{C}$, and resistant to all common organic solvents at ambient or elevated temperature.

Intriguingly, simple homoleptic hydrocarbyl RE complexes, $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (RE = Sc, Y, Dy, Lu), also produce highly isotactic polymer P_{β} MMBL. Their polymerization activity is, however, much lower than that of the corresponding half-sandwich dialkyl complexes, with the exception of the Lu complex, which maintains its high activity for both types of complexes.

Computational studies of both half-sandwich and simple hydrocarbyl yttrium complexes have led to a stereocontrol mechanism that well explains the observed high stereoselectivity of β MMBL polymerization by the current catalysts. Concisely, in the proposed monometallic propagation mechanism, formation of an isotactic polymer originates chiefly from interactions between the methyl groups on the chiral β -C atom of the five-membered ring of both the monomer and the last inserted β MMBL unit of the chain, and the auxiliary ligand on

metal exerts negligible contribution to the stereocontrol exhibited by the current half-sandwich RE complexes. This mechanism is in good agreement with the current experimental results and is further supported by the prior results that the coordination polymerization of methylene butyrolactones without the β -Me substituent, including MBL and γ MMBL, catalyzed by the same half-sandwich RE dialkyl complexes under the same reaction conditions, yields essentially atactic polymers.⁴

■ ASSOCIATED CONTENT

■ Supporting Information

Additional figures and computational details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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