

Highly Iseoselective Coordination Polymerization of *ortho*-Methoxystyrene with β -Diketiminato Rare-Earth-Metal Precursors**

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Abstract: Stereoselective coordination/insertion polymerization of the polar *ortho*-methoxystyrene has been achieved for the first time by using the cationic β -diketiminato rare-earth-metal species. High activity and excellent isoselectivity (*mmmm* > 99 %) were achieved. The unmasked Lewis-basic methoxy group does not poison the Lewis-acidic metal center, but instead activates the polymerization through σ - π chelation to the active species together with the vinyl group, thus lower the coordination and activation energies as compared with those of styrene derivatives lacking the methoxy group.

Homo- or co-polymerization of polar vinyl monomers is driven by the future technology needs of the chemical industry. Polymers bearing polar functionalities are highly desired materials for completely new areas of applications as compared with their nonfunctionalized analogues because of the unique range of surface properties.^[1] However, it has been a challenging and long-standing project in academia because the Lewis-basic polar groups usually poison the Lewis-acidic metal centers of the catalysts as a result of coordination of the functional group of the penultimate repeat unit which is incorporated from the polar monomer. Therefore, to protect the active species by introducing bulky substituents to mask the functional groups,^[2] or pre-complexion of the functional groups with Lewis acids such as alkylaluminum^[3] and MAO^[4] is a prerequisite. Separating the functional groups from the olefinic locus of the insertion by a long spacer unit is another adopted practice.^[3–5] An alternative strategy is the manipulation of the less oxophilic late-transition-metal catalysts

bearing anionic ancillary ligands for the direct copolymerization of ethylene and the functional monomers with or without protection.^[6] Despite these achievements, synthesis of high-molecular-weight copolymers with tunable incorporation of the functional groups, preferably with consecutive insertions of polar vinyl monomers occurring in a stereoselective way, is still an open research area, and the specific selective homopolymerization of polar vinyl monomers, despite some excellent pioneering work,^[2a,b,5b,d,7] has been far from successful.

Herein we report the unprecedented coordination polymerization of *ortho*-methoxystyrene (*o*MOS) with high activity by using the cationic β -diketiminato yttrium and lutetium systems. The strong Lewis-basic polar methoxy group, which is a typical poison to the transition-metal-based catalysts, behaves as an activator to the hard Lewis-acidic rare-earth metal catalyst since it remains to coordinate to Y³⁺ throughout the procedure. This coordination was determined based on DFT simulations, and is in striking contrast to the above mentioned strategies. More remarkably, the resultant P(*o*MOS) has a high molecular weight with excellent isotacticity (*mmmm* > 99 %), and thus provides a new approach to optically active helical materials^[8] and polystyrene-based functional materials. Note that, *o*MOS can be polymerized by cationic (e.g. AlCl₃/Et or Et₂O·BF₃) and radical catalysts (e.g. BPO) without selectivity^[9] or anionic catalysts (e.g. *n*BuLi), thus giving enriched isotacticity at very low temperature.^[10] To date, only one heterogeneous Ziegler–Natta catalyst and two homogenous catalyst systems (the cationic OSSO-tetradentate titanium complex and the neutral lanthanidocenes [(IndCMe₂Ind)Ln-(allyl)(THF)]) have been reported to provide isoselectivity for styrene polymerization,^[11] although syndiospecific polymerization of styrene has proven successful with the invention of various homogeneous catalysts derived from Group 3 and 4 metals.^[12]

Treatment of rare-earth-metal tris(alkyl)s with bis(2,6-dimethyl anilido)ketimine (BDI) in *n*-hexane afforded the corresponding bis(alkyl) complexes solvated by one THF molecule [(BDI)Ln(CH₂SiMe₃)₂(THF)] [Ln = Y (**1**),^[13] Lu(**2**)] and the non-solvated scandium complex **3**, [(BDI)Sc(CH₂SiMe₃)₂] (for ¹H and ¹³C NMR spectra of **2** and **3** see Figures S1–S4 in the Supporting Information). The structure of the lutetium complex **2** was defined by X-ray diffraction analysis and adopts a distorted trigonal-bipyramido geometry (see Figure S6 in the Supporting Information). Treatment of **1–3** with the organoborate [Ph₃C][B(C₆F₅)₄] in toluene results in abstraction of one alkyl moiety to generate, in situ, the cationic complexes [(BDI)Ln(CH₂SiMe₃)(THF)_{*n*}][B(C₆F₅)₄] [*n* = 1, Ln = Y (**4**), Lu (**5**); *n* = 0, Ln = Sc (**6**)]. These metal

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alkyl species give resonances around $\delta = -0.24$ ppm for Y-CH₂, $\delta = -0.53$ ppm for Lu-CH₂, and $\delta = 0.45$ ppm for Sc-CH₂, thus indicating a downfield shift of resonances compared to those of their precursors. The reaction between **1–3** and [Et₃NH][BPh₄] in THF afforded the more stable cationic complexes [(BDI)Ln(CH₂SiMe₃)(THF)_n][BPh₄] [*n* = 2, Ln = Y (**7**), Lu (**8**); *n* = 1, Sc (**9**)], thus allowing successful isolation of the complex **8**, [(BDI)Lu(CH₂SiMe₃)(THF)₂][BPh₄], which might mimic the structure of the true active species **4** and **5** (Scheme 1). An X-ray diffraction study established **8** as a monoalkyl ion pair where the ligand in combination with the alkyl moiety and the solvated THF molecules form the distorted trigonal-bipyramido geometry around Lu³⁺ (Figure 1). The above characterization suggested the formation of the cationic complexes **4–9** by abstraction of the alkyl moiety and not the BDI ligand.

The cationic complexes **4–6** were unfortunately inert to styrene polymerization, even with the assistance of excess amounts of the alkylaluminum, and despite our earlier reports on the cationic yttrium based system catalyzing the highly *cis*-1,4 selective polymerization of isoprene.^[13] To our surprise, both the cationic yttrium and lutetium complexes **4** and **5**, respectively, showed moderate to high activity for the polymerization of polar *o*MOS (0.19×10^5 g mol⁻¹ h⁻¹ versus 1.08×10^5 g mol⁻¹ h⁻¹; entries 2 and 3 in Table 1), although the cationic scandium complex **6** still remained inactive owing to the sterically bulky environment around the small Sc³⁺ ion. We were delighted that addition of alkyl aluminum to **4** tripled the activity (3.1×10^5 g mol⁻¹ h⁻¹).

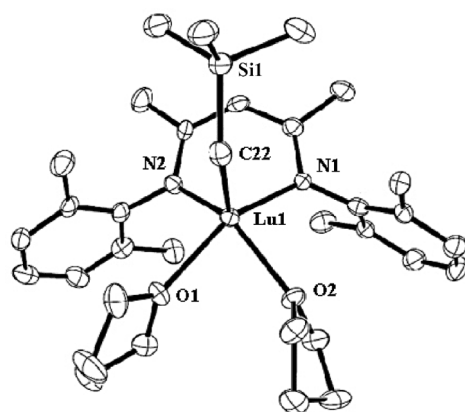
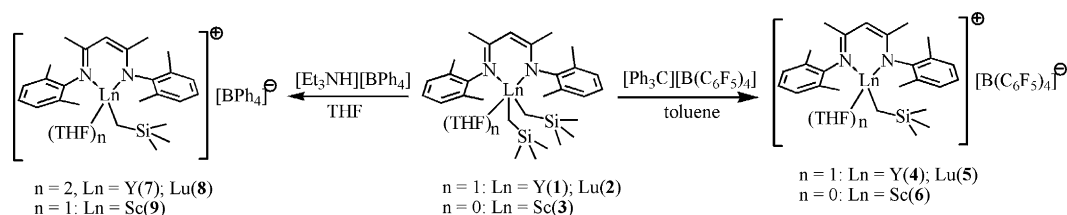


Figure 1. ORTEP drawing of the cationic part of the complex **8**. Thermal ellipsoids shown at 35% probability.

Meanwhile, the molecular weight of the resultant P(*o*MOS) increased correspondingly with the monomer-to-Y ratio thus going as high as $M_n = 123\,000$. The molecular-weight distribution (see Figures S24–26 in the Supporting Information) was narrow, thus suggesting a controllable polymerization mode and the single-sited nature of the active species.

Remarkably, this polymerization provided specific selectivity and gave P(*o*MOS) with excellent isotacticity as determined by the quintet centered at $\delta = 2.56$ ppm and multiplet centered at $\delta = 1.38$ ppm, which are assignable to



Scheme 1. Synthesis of neutral and cationic rare-earth metal complexes **1–9**.

Table 1: Isotactic polymerization of *ortho*-methoxystyrene with the cationic rare-earth metal precursors **4–6**

Entry	Cat.	Monomer	[M]/[Y]	Conv. [%]	Activity ^[b]	TON ^[c]	$M_n^{[d]}$ [$\times 10^{-4}$]	$M_w/M_n^{[d]}$	<i>mmmm</i> ^[e] [%]	$T_g/T_m^{[f]}$ [°C]
1	4–6	St	600	–	–	–	–	–	–	–
2 ^[g]	4	<i>o</i> MOS	600	34	1.08	204	10.4	1.33	> 99	87/299
3 ^[h]	5	<i>o</i> MOS	600	24	0.19	144	5.82	1.17	> 99	86/301
4 ^[h]	6	<i>o</i> MOS	600	–	–	–	–	–	–	–
5	4	<i>o</i> MOS	150	100	0.80	150	2.88	1.51	> 99	88/293,302 ^[i]
6	4	<i>o</i> MOS	300	93	1.48	279	5.10	1.60	> 99	88/295,299,303 ^[i]
7	4	<i>o</i> MOS	600	73	2.32	438	8.07	1.91	> 99	86/299
8	4	<i>o</i> MOS	1200	48	3.10	576	12.3	2.07	> 99	86/299
9	4	<i>m</i> MOS/ <i>p</i> MOS	600	–	–	–	–	–	–	–

[a] General reaction conditions: 10^{-3} mol of a Ln complex; [Al]/[Ln] = 10; [Ph₃C][B(C₆F₅)₄]/[Ln] = 1 ([Al] = AlⁱBu₃), in 1 mL toluene, for 15 min.

[b] Given in 10^5 g polymer mol⁻¹ h⁻¹. [c] Turnover number (TON): mol of *o*MOS consumed by per mol of catalyst. [d] Determined by GPC in THF at 40 °C against a polystyrene standard. [e] Determined by ¹³C NMR spectroscopy. [f] Determined by DSC. [g] No AlⁱBu₃. [h] No AlⁱBu₃; time (60 min).

[i] Multiple *T_m* values.

the methine proton and the asymmetric methylene protons, respectively (Figure 2A). It also correlates with the sharp singlet for the *ipso*-carbon peak at $\delta = 136.0$ ppm in the ^{13}C NMR spectrum, thus indicating an isotacticity of $mmmm > 99\%$ (Figure 2B).^[14] The highly isotactic P(*o*MOS) is an excellent precursor for the synthesis of the optically active helical products if induced by a chiral compound.^[8] Notably, *o*MOS could only be polymerized through cationic and radical mechanisms to give the atactic polymer,^[9] and an isotactic-enriched product was obtained by anionic polymerization at very low temperature (-78°C).^[10] P(*o*MOS) is also an excellent building block for constructing topological and functional macromolecules. For instance, when treated with boron tribromide at -20°C , P(*o*MOS) was swiftly transformed into the isotactic poly(*o*-hydroxystyrene) [P(*o*HOS)].^[15] The signal associated with the methoxy groups of P(*o*MOS) at $\delta = 3.47$ ppm is no longer present in the ^1H NMR spectrum of P(*o*HOS) (see Figure S11 A and B in the Supporting Information), and the resonance around $\delta = 4.60$ ppm is assigned to the hydroxy group, thus indicating the complete transformation from P(*o*MOS) into P(*o*HOS).

To investigate the mechanism for this novel polymerization, DFT calculations were employed. The energy profiles for the different stages of polymerization are shown in Figure 3 and in Figures S27 and S28 (see the Supporting Information). Firstly, one *o*MOS monomer coordinates to the active metal center Y^{3+} through its oxygen atom and C=C bond in a σ - π mode. 2,1-Insertion of *o*MOS via the transition-state **TS1M** is preferred to 1,2-insertion, which is lower by $10.6\text{ kcal mol}^{-1}$, to afford the intermediate **3M_{THF}** where the methoxy oxygen atom remains in contact with Y^{3+} (Figure S27). In these steps, the coordination of THF to the metal center is reversible, and might explain why the THF-solvated cationic lutetium and yttrium systems displayed a moderate to high activity in the absence of the aluminum coactivator.

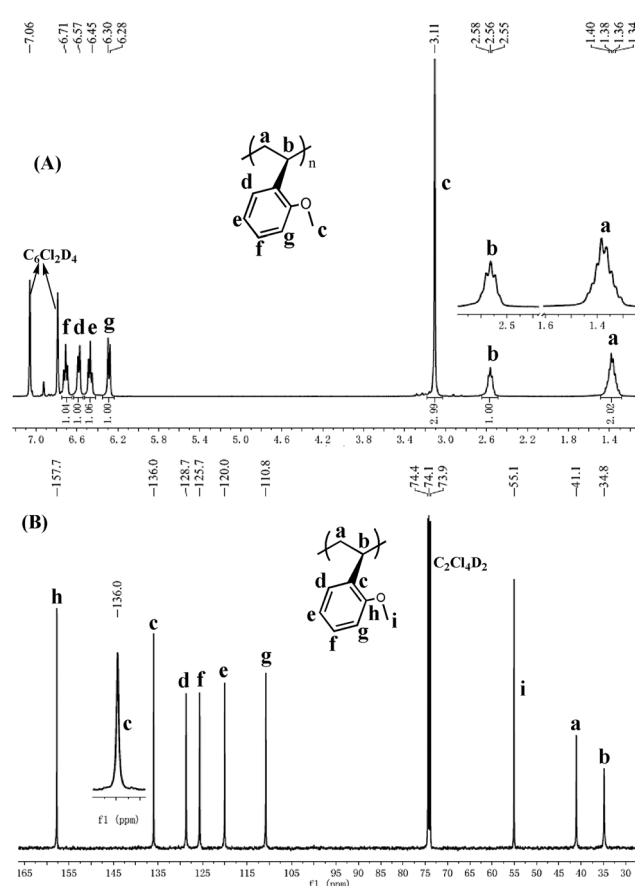


Figure 2. A) ^1H NMR spectrum ($\text{C}_6\text{Cl}_2\text{D}_4$, 120°C) and B) ^{13}C NMR spectrum of isotactic poly(*o*MOS) ($\text{C}_2\text{Cl}_4\text{D}_2$, 120°C). See entry 2 of Table 1.

3M_{THF} adopts a second molecule of *o*MOS on either the *re*-face or *si*-face through bonding of Y^{3+} with the oxygen atom

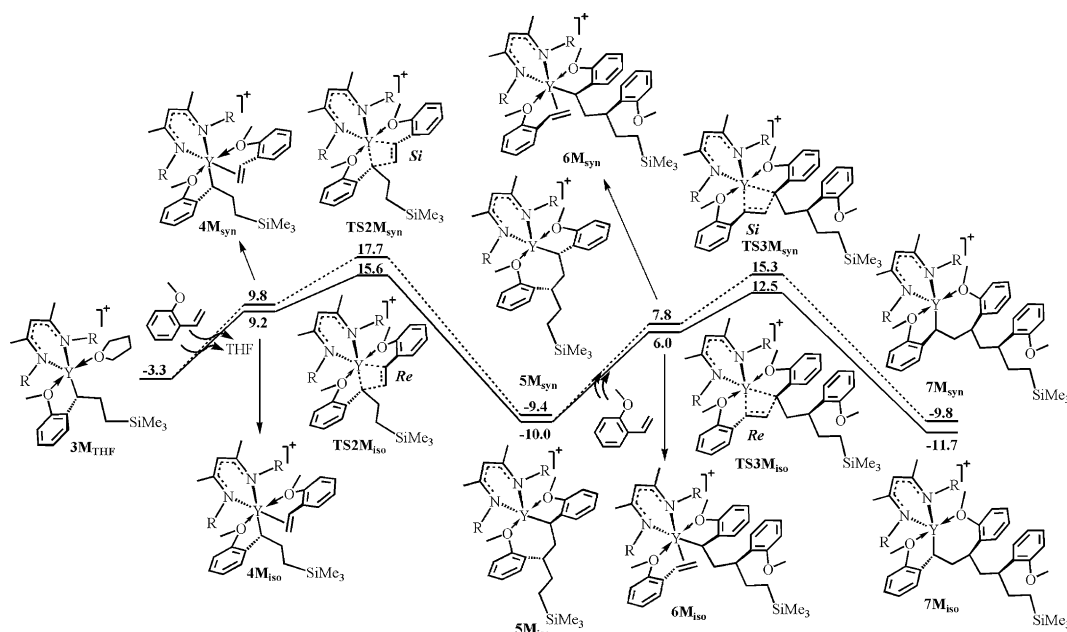


Figure 3. Energy profiles for 2,1-insertion of *o*MOS and generation of stereoregularity. R = 2,6-dimethylphenyl.

and vinyl group to afford either the intermediate $5M_{iso}$ or $5M_{syn}$, respectively. Since the transition-state $TS2M_{iso}$ (for $5M_{iso}$) is 2.1 kcal mol⁻¹ lower in energy than the transition-state $TS2M_{syn}$ (for $5M_{syn}$), the isoselective route is favored (Figure 3), and parallels the influence of the C₂-symmetric BDI ligand on the selectivity of its attached metal center.^[16] This pathway is confirmed further by the energy profiles for coordination (*re*-face) of a third *o*MOS molecule to $5M_{iso}$, thus generating an isotactic unit which needs to overcome 22.5 kcal mol⁻¹ of energy ($TS3M_{iso}$) as compared with 25.3 kcal mol⁻¹ ($TS3M_{syn}$) for the *si*-face coordination to $5M_{iso}$ to form the syndiotactic unit (Figure 3). It is noteworthy that in the process the methoxy groups of the last and the penultimate units continuously coordinate to the Y³⁺ by forming five/five metalocycles in the transition states and the five/seven metalocycles in the intermediates. This arrangement could explain why 2,1-insertion of *o*MOS is more favored than 1,2-insertion, as the former is geometrically convenient for forming a stable five-membered metalocycle while the latter gives an encumbered six-metalocycle.

In contrast, styrene coordinates to the active metal center Y³⁺ without a polar group chelation and result in an energy which is 6.2 kcal mol⁻¹ higher than that of *o*MOS. To complete the first insertion an activation energy of 32.1 kcal mol⁻¹ needs to be overcome, and it is much higher than the 24.8 kcal mol⁻¹ for *o*MOS (see Figure S28 in the Supporting Information). This data agrees well with the experimental result that both **4** and **5** were inactive towards styrene polymerization. When extending the monomers to the *meta*-methoxy-substituted styrene (*m*MOS) and *para*-methoxy-substituted styrene (*p*MOS), surprisingly, the polymerization did not take place at all. This result is contrary to all previous reports that the closer the polar group to the active metal center is, the lower the possibility is for polymerization.^[5b,c] For instance, the polymerization of polar vinyl olefins bearing ether or halogen polar groups, having σ -bonds to the active metal center, leads to β -elimination (elegantly proved by the isolation of the intermediate)^[7b] to provide the multiple-insertion or oligomerization product. The efficient and controllable polymerization of the naked *o*MOS suggests that the σ -coordination of the polar group to the active metal center does not always poison, but may activate the polymerization if it does not inhibit the vinyl group from π -bonding to the active species.

In summary, we have demonstrated the unprecedented coordination/insertion polymerization of the polar aromatic olefin, *ortho*-methoxystyrene (*o*MOS), by using the cationic β -diketiminate yttrium and lutetium systems. The cationic systems demonstrate high activity and give a high-molecular-weight product with excellent isotacticity. The DFT calculations suggest that the strong Lewis-basic polar methoxy group activates the hard Lewis-acidic rare-earth-metal active species by σ - π bonding to the active center Y³⁺ together with the vinyl group. The acid–base interaction lowers both the coordination and the activation energy as compared with those polar and nonpolar styrene derivatives lacking such interactions. This coordination may also lead to the stereoisotacticity of the resultant polymer in addition to the influence of the C₂-symmetric geometry of the BDI ligand.

This work is in striking contrast to the previous strategies for achieving (co)polymerization of polar monomers, strategies which avoiding contact between the polar group and the active centers. Thus, the chemistry reported herein provides a new route for the synthesis of homo- and co-polymers bearing polar groups through the combination of properly chosen catalysts and polar monomers. The (co)polymerization of other polar vinyl monomers is under investigation.

Keywords: β -diketiminate ligand · density functional calculations · isoselective polymerization · *ortho*-methoxystyrene · rare-earth metal complex

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- [14] Assigning the isotacticity of P(oMOS) was done according to the reference: V. Busico, R. Cipullo, *Prog. Polym. Sci.* **2001**, *26*, 443. For isotactic polymers, the two protons of the methylene group are magnetically unequivalent, thus the methylene resonance is usually split in two multiplets (e.g. isotactic polypropylene) or one multiplet (e.g. isotactic polystyrene, see Ref. [11b] and [12a]) in the ^1H NMR spectrum. Meanwhile, for syndiotactic polymers, the two protons of the methylene group are magnetically equivalent, and they give rise to one triplet in the ^1H NMR spectrum. The NMR spectrum of P(oMOS) is also typical. For the isotactic P(oMOS), the multiplet resonance for the methylene CH_2 appears at $\delta = 1.38$ ppm as compared with the syndiotactic P(oMOS), prepared by other catalyst system, which has a triplet at $\delta = 1.52$ ppm (see Figure S8 in the Supporting Information).
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