Heteroatom-assisted olefin polymerization by rare-earth metal catalysts

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Heteroatom-functionalized polyolefins are of fundamental interest and practical importance. This has spurred investigations of the copolymerization of polar and nonpolar olefins. We report the first syndiospecific polymerization of a series of heteroatom-containing α-olefins and their copolymerization with ethylene catalyzed by half-sandwich rare-earth complexes. We have found that the interaction between a heteroatom in a functional α-olefin monomer and a rare-earth metal catalyst can significantly raise the olefin polymerization activity and thereby promote its copolymerization with ethylene. By using this heteroatom-assisted olefin polymerization (HOP) strategy, we have successfully synthesized a series of heteroatom (O, S, Se, N, and P)-functionalized polyolefins with high molecular weights and controllable functional monomer contents. The mechanistic aspect of the HOP process has been elucidated by computational studies. We expect that our findings will guide the design of new catalyst systems for the synthesis of various desired functional polyolefins.

INTRODUCTION
Polyolefins, such as polyethylene, are ubiquitous in modern society, ranging from food packing to rubber disposal bags, toys, power cables, and agricultural films (1–3). Nevertheless, the application scope of polyolefins is still limited compared to their potential because of the lack of functional polar groups that can make them compatible with other types of materials, such as oxygen- and nitrogen-containing polymers, polar pigments, glass fibers, clays, and metals. Therefore, the incorporation of chemical functionality or polar groups into polyolefins to improve their performance and properties has been the target of extensive studies in both academia and industry over the past decades (4–9). In this context, the copolymerization of ethylene with heteroatom-containing functional α-olefins has been examined by using various transition metal catalysts because this approach is, in principle, the most straightforward and atom-efficient route for the synthesis of functionalized polyolefins. It has been previously found that early transition metal catalysts, such as titanium and zirconium metallocenes, are excellent catalysts for the polymerization of nonpolar olefins, were easily poisoned by heteroatoms (Fig. 1A). Although some bulky siloxy-containing or aluminum alkoxo-containing α-olefins were reported to copolymerize with ethylene in the presence of group 4 metal catalysts, the polymer monomer incorporation ratio or the copolymer molecular weight was low (10–15). Late transition metal catalysts, such as nickel and palladium complexes, could show relatively higher tolerability toward polar functional groups (Fig. 1B) (16–23), but the polar monomer incorporation ratio or the copolymer molecular weight was still low and far from desired because the polymerization activity of a polar α-olefin is usually much lower than that of ethylene. The synthesis of functionalized polyolefins having both high molecular weight and high functional monomer content in a controllable fashion has remained a challenge to date.

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Increasing polymerization activity of a functional α-olefin is obviously of critical importance to achieve high functional monomer incorporation and high copolymer molecular weight in the copolymerization with ethylene. In principle, if the interaction between the heteroatom in a functional α-olefin and the catalyst metal center could facilitate the catalyst-olefin interaction through an intramolecular chelation, the polymerization activity of the functional α-olefin may be enhanced, which would thereby promote the incorporation of the functional α-olefin into polyethylene in the copolymerization reaction (Fig. 1C). However, in contrast to extensive studies on the tolerability or survivability of the catalysts toward heteroatoms in the copolymerization of polar and nonpolar olefins (10–23), the potential of heteroatoms as promoters to enhance the polymerization activity of a functional α-olefin has remained unexplored to date. Obviously, to make the heteroatom-assisted olefin polymerization (HOP) mechanism operative, it is highly important to search for new catalysts that can show not only appropriate interactions with the heteroatom/olefin units but also high activity for olefin insertion (polymerization).

We have previously shown that organo–rare-earth (group 3 and lanthanide) metal complexes, such as half-sandwich scandium alkyls bearing monocyclopentadienyl ligands, serve as efficient catalysts for the polymerization and carbometalation of a wide range of olefins as well as for the C–H addition of heteroatom-containing aromatic compounds (such as anisoles, pyridines, and N,N-dimethylanilines) to olefins (24–29). In many of these transformations, the coordination of a heteroatom (such as O and N) as well as an olefin C=C double bond to the rare-earth metal ion was essential to achieve reactivity and selectivity. These results encouraged us to examine whether the unique heteroatom affinity and olefin affinity of the rare-earth metal ions together with the high olefin insertion activity of the rare-earth metal alkyls could promote the polymerization of heteroatom-containing α-olefins. Here, we report our studies on the heteroatom-assisted polymerization of a series of oxygen-, sulfur-, selenium-, nitrogen-, and phosphorus-containing α-olefins catalyzed by the half-sandwich rare-earth catalysts (Fig. 2, A and B). We have found that the interaction between the heteroatom in an α-olefin and the rare-earth metal atom in a catalyst not only can significantly raise the...
olefin polymerization activity but also can enable the efficient co-polymerization of the heteroatom-containing α-olefins with ethylene. Moreover, the intramolecular interaction (chelation) of both the heteroatom and the olefin unit with the catalyst metal center can induce unique stereoselectivity (syndiotacticity) in the polymerization process. By using this HOP strategy, we have synthesized a new family of heteroatom-functionalized polyolefins having both high molecular weights and a broad range of functional monomer contents. The mechanistic aspect of the HOP process has been elucidated by density functional theory (DFT) studies.

Fig. 1. Possible influences of a heteroatom in the transition metal–catalyzed copolymerization of ethylene with an FG-containing α-olefin. (A) A heteroatom (FG) acts as a poison to deactivate the catalyst and hamper the polymerization. [M], transition metal. (B) FG acts as a spectator that is compatible with the catalyst. (C) FG acts as a promoter to enhance the polymerization activity of the α-olefin monomer and facilitate its incorporation into polyethylene through the heteroatom-assisted catalyst-olefin interaction. This HOP could serve as a useful strategy for polar-nonpolar olefin copolymerization, as demonstrated in this work.

Fig. 2. Catalysts and monomers investigated in this study. (A) Rare-earth complexes used as precatalysts in this work. (B) Heteroatom-containing α-olefins examined in this work.
Table 1. Polymerization of heteroatom-containing α-olefins. Conditions: [M] (0.03 mmol), [Ph3C][B(C6F5)4] (0.03 mmol), 1 (1.5 M), toluene, room temperature (rt), 24 hours (unless otherwise noted). n.o., not observed; n.d., not determined.

| Entry | Monomer 1 | [M] | 1/[M] | Polymer 2 | Yield (%)* | $M_n$ ($\times 10^3$)† | $M_w/M_n$† | $\%rrrr$‡ | $T_g$ (°C)§ |
|-------|-----------|-----|-------|----------|------------|---------------------|------------|-----------|-------------|
| 1     | 1a        | Sc-1| 100/1 | 2a       | 0‡         | —                   | —          | —         | —           |
| 2     | 1b        | Sc-2| 200/1 | 2b       | 100        | 29.8               | 1.33       | >95       | 5           |
| 3     | 1c        | Sc-3| 500/1 | 2c       | 71         | 83.6               | 1.96       | >95       | 31          |
| 4     | 1d        | Sc-3| 500/1 | 2d       | 78         | 165.0              | >95        | 98        | —           |
| 5     | 1e        | Sc-3| 100/1 | 2e       | 95         | 80.4               | 1.63       | >95       | 10          |
| 6     | 1f        | Sc-3| 500/1 | 2f       | 89         | 71.8               | 1.76       | >95       | 98          |
| 7     | 1g        | Sc-3| 100/1 | 2g       | 95         | 80.4               | 1.63       | >95       | 10          |
| 8     | 1h        | Sc-4| 100/1 | 2h       | Trace      | —                   | —          | —         | —           |
| 9     | 1i        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 10    | 1j        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 11    | 1k        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 12    | 1l        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 13    | 1m        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 14    | 1n        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 15    | 1o        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 16    | 1p        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 17    | 1q        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 18    | 1r        | Sc-3| 200/1 | 2i       | 100        | 30.2               | 1.16       | >95       | 98          |
| 19    | 1s        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 20    | 1t        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 21    | 1u        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 22    | 1v        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 23    | 1w        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 24    | 1x        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 25    | 1y        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 26    | 1z        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 27    | 1a        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 28    | 1b        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 29    | 1c        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 30    | 1d        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 31    | 1e        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 32    | 1f        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 33    | 1g        | Sc-3| 1000/1| 2i       | 93         | 189.0              | >95        | 98        | —           |
| 34    | 1h        | Y-1 | 100/1 | 2t       | 23         | 6.8                | 1.57       | 88        | −5          |
| 35    | 1i        | Y-1 | 100/1 | 2t       | 23         | 6.8                | 1.57       | 88        | −5          |
| 36    | 1j        | Y-1 | 100/1 | 2t       | 23         | 6.8                | 1.57       | 88        | −5          |
| 37    | 1k        | Y-1 | 100/1 | 2t       | 23         | 6.8                | 1.57       | 88        | −5          |

*Weight of polymer obtained/weight of monomer used. †Determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at room temperature against polystyrene standard. ‡Determined by $^1$H nuclear magnetic resonance (NMR) analysis. §Determined by differential scanning calorimetry. ¶Formation of 1-phenyloxy-1-propene (an isomerization product of 1a) was observed. #$^0$C. **0°C.
RESULTS AND DISCUSSION
Homopolymerization of heteroatom-containing α-olefins

As an initial test of the HOP concept, the polymerization of 3-phenoxymethylene-1-propene (1a), which has one methylene (CH₂) unit between the C-C double bond and the oxygen atom (Fig. 2B), was first examined by using the C₅H₅-C₂H₅-ligated scandium complex Sc-1 (Fig. 2A) with [Ph₃C][B(C₆F₅)₄] as a cocatalyst. However, no polymer was observed (Table 1, entry 1). It seemed that the isomerization of 1a to 1-phenoxymethylene-1-propene through 1,3-hydrogen shift took place. We then examined 4-phenoxymethylene-1-butene (1b), which has two CH₂ units as a spacer between the C-C double bond and the oxygen atom. With the monomer/catalyst feed ratio [1b]/[Sc-1] = 200/1, the polymerization occurred smoothly at room temperature, affording poly(phenoxymethylene) 2b in 98% yield in 24 hours (entry 2). In attempts to see the ligand influence, the sterically demanding C₅Me₅-ligated scandium complex Sc-2 was used in place of Sc-1, but no polymer product was formed under the same conditions (entry 3). When the slightly smaller C₅Me₅H₂-ligated scandium complex Sc-3 was used, the polymer product 2b with number-average molecular weight \( M_n = 2.98 \times 10^4 \) and molecular weight distribution \( M_w/M_n = 1.33 \) was quantitatively obtained under the same conditions (entry 4). These results suggest that the polymerization activity of a heteroatom-containing α-olefin is significantly influenced not only by the spacer length between the olefin unit and the heteroatom but also by the steric hindrance of the catalyst ligand. Remarkably, the polymer produced by either Sc-1 or Sc-3 showed high syndiotacticity (>95% \( \text{rrrr} \)) by stereoregularly orientating the heteroatom-containing side chains opposite each other along the polymer main chain. In contrast, the oxygen-free analog 5-phenyl-1-pentene (1c) showed no polymerization activity with either Sc-1 or Sc-3 under the same conditions (entry 6), suggesting that the oxygen atom in 1b played a critically important role in the present polymerization. In the case of 1-(3-butenyloxyl)-4-(4-penten-1-yl)benzene (1d), which contains both a phenoxymethylene unit and an oxygen-free pentene unit in one molecule, the polymerization occurred exclusively at the phenoxymethylene unit, whereas the oxygen-free pentene moiety remained intact (entry 7), again demonstrating the importance of an oxygen atom in the present polymerization. Similar to a phenoxy unit (1b or 1d), the benzoxoyl (1e), hexyloxy (1f), and [estra-1,3,5(10)-trien-3-y]oxy (1g) groups also served as efficient promoters for the 1-butenyl polymerization by Sc-3, affording the corresponding functionalized polyolefins to 2g in high yields with high molecular weight \( M_n = 7.45 \times 10^4 \) to 8.36 \times 10^4), narrow molecular weight distribution \( M_w/M_n = 1.76 \) to 1.96), and excellent syndiotacticity (>95% \( \text{rrrr} \)) (entries 8 to 10). In the case of a monomer (1h) having the sterically demanding \( \beta \)-cholestanoyl substituent, Sc-3 showed almost no activity (entry 11), whereas the indenyl-ligated analog Sc-4 quantitatively produced the corresponding syndiotactic polymer in 2 hours under the same conditions (entry 12), again suggesting that the polymerization activity may be tuned by changing the catalyst ligand.

On the basis of the above-mentioned observations, we then examined sulfur-containing α-olefins and found that sulfur is even more efficient than oxygen as a promoter for the olefin polymerization. With Sc-3 as a catalyst, up to 2000 equivalents of 4-phenylthio-1-butene (1i) were quantitatively converted to the corresponding polymer 2i with an \( M_n \) of up to \( 1.33 \times 10^5 \) in 24 hours at room temperature (entries 13 to 15). Further higher molecular weight \( M_w \) of up to \( 5.86 \times 10^5 \) was obtained at \(-40^\circ \text{C} \), possibly because the \( \beta \)-hydride elimination (a possible chain termination process) was suppressed at a lower temperature (entries 17 and 18) (30). 4-Arylthio-1-butenes bearing halogen substituents at the phenyl ring (1k and 1l) were also selectively converted to the corresponding halogenated sulfur-containing polymers, thus providing new opportunities for further functionalization of the polymer products (entries 20 and 21). The sterically demanding 2-methylphenyl (1m) or 2-naphthyl (1n) substituent at the sulfur atom did not hamper the polymerization (entries 22 to 24). Aliphatic (either linear 1o or cyclic 1p) sulfide-substituted 1-butenes were also applicable (entries 25 and 26). In all cases, excellent syndiotacticity (>95% \( \text{rrrr} \)) was observed, similar to the oxygen-containing analogs described above. Remarkably, selenium also served as a promoter for the olefin polymerization because 4-phenylselenyl-1-butene (1q; 500 equivalents) was quantitatively converted to the corresponding polymer 2q in a syndiotactic fashion (92% \( \text{rrrr} \)) by Sc-3 (entry 27).

Compared to the oxygen-, sulfur-, and selenium-containing 1-butenes, the phosphorus-substituted analog 1r showed relatively lower activity, giving the polymer product 2r in only 10% yield when Sc-3 was used as a catalyst with [1r]/[Sc-3] = 500/1 in 24 hours (entry 28). The lower polymerization activity of 1r was possibly due to the steric hindrance of the two phenyl substituents at the phosphorus atom. When the smaller Sc-1 was used in place of Sc-3, the phosphorus-containing polymer 2r was obtained quantitatively under the same conditions (entry 29). The nitrogen-containing olefin 1s was less active than its phosphorus analog 1r. Less than 40% of 1s was converted to the corresponding polymer 2s when Sc-1 or Sc-3 was used as a catalyst with a monomer/catalyst feed ratio of 100/1 (entries 30 and 31). The indenyl-ligated Sc-4 showed somewhat better performance for the polymerization of 1s, which afforded the polymer 2s in 64% yield under the same conditions (entry 32). The syndiotacticity of the phosphorus- and nitrogen-containing polymers 2r and 2s was relatively low and difficult to determine by the \(^{13}\text{C} \) NMR analysis.

In the case of 5-phenoxymethylene-1-pentene (1t), which has a longer linker (three CH₂ units) between the oxygen atom and the olefin unit than 1b, only a trace amount of the polymer product 2t was observed with either Sc-1 or Sc-3 as a catalyst (entry 33). The use of \( \left(\text{C}_2\text{H}_5\right)\text{Y}\left(\text{CH}_2\text{C}_6\text{H}_4\text{NM}_{2}\text{-o}\right)_2 \) (Y-1) as a catalyst in place of Sc-1 afforded the polymer product 2t in 23% yield (entry 34). The higher activity of Y-1 is probably due to the larger yttrium atom (than scandium), which could lead to an easier interaction with the oxygen atom as well as the C-C double bond in 1t. In contrast, 5-phenylthio-1-pentene (1u), a sulfur analog of 1t, was converted to the corresponding polymer product 2u under similar conditions (entries 35 to 37), probably because of the larger radius of the sulfur atom, which could bring about sufficient interactions with the scandium atom even with a longer linker.

The present heteroatom-promoted polymerization of α-olefins catalyzed by the rare-earth catalysts stands in sharp contrast with the group 4 metal–catalyzed polymerization of ether-containing α-olefins reported previously, in which no promotion effect of a heteroatom was observed (10–12, 14, 15). To have a better understanding of the mechanistic aspect of the present HOP reaction, we performed the DFT calculations of the polymerization of 1i catalyzed by the cationic species (Cat) generated by the reaction of Sc-3 with 1 equivalent of [Ph₃C][B(C₆F₅)₄] (31). It has been revealed that the coordination of the S atom in 1i to the Sc atom in Cat may afford complexes si-1 and re-1, although si-1 is more favored than re-1 by 2.2 kcal/mol (Fig. 3). The insertion of the C–C double bond into the Sc–CH₂C₆H₄NM₂-o bond in si-1 or re-1 via the transition state si-TS1 (si-insertion) or re-TS1 (re-insertion) could yield si-P1 or re-P1, respectively. Obviously, the formation of si-P1 is more favored both thermodynamically and kinetically than that of re-P1 because si-P1 is more stable than re-P1 by 2.4 kcal/mol and the energy barrier for the formation of si-P1 (21.5 kcal/mol) is 6.0 kcal/mol lower than that for the formation of...
The coordination of the second molecule of 1i to the Sc atom in \textit{si}-P1 via both the S atom and the C=C double bond could yield \textit{re}-C2 and \textit{si}-C2. Although \textit{re}-C2 has a higher energy (6.2 kcal/mol) than \textit{si}-C2 (2.4 kcal/mol), the subsequent insertion of the C=C double bond into the Sc–alkyl bond in \textit{re}-C2 via \textit{re}-TS2 (\(\Delta G^\ddagger = 15.9\) kcal/mol) to give \textit{re}-P2 (re-insertion; syndiotactic product) is much easier than that in \textit{si}-C2 via \textit{si}-TS2 (\(\Delta G^\ddagger = 28.3\) kcal/mol) to give \textit{si}-P2 (si-insertion; isotactic product). Similarly, the insertion of the third 1i into \textit{re}-P2 would take place via \textit{si}-C3 and \textit{si}-TS3 to give the favorable product \textit{si}-P3 (si-insertion; syndiotactic product). Repetition of these alternating re- and si-insertion modes would therefore afford the syndiotactic polymer product (see the Supplementary Materials), in agreement with the experimental observations.

**Copolymerization of ethylene with heteroatom-containing \(\alpha\)-olefins**

After having proved the validity of the HOP concept, we then examined the copolymerization of the heteroatom-containing \(\alpha\)-olefins with...
ethylene. Some representative results are summarized in Table 2. When Sc-3 was used as a catalyst with [III]/[Sc-3] = 100/1, the copolymerization of 1i with ethylene (1 atm) occurred rapidly at room temperature, afforded the corresponding sulfur-functionalized copolymer 3i with the sulfur monomer content as high as 73.5 mole percent (mol %) (Table 2, entry 1). To lower and better control the incorporation of 1i, we then used the more stericly demanding Sc-5 in place of Sc-3. Remarkably, Sc-5 showed high activity and good tunability for the copolymerization of 1i with ethylene, yielding the sulfur-functionalized copolymers with \( M_n = 2.06 \times 10^4 \) to \( 5.77 \times 10^4 \) and \( \text{incorporation} = 29.0 \) to 44.9 mol %, when [1i]/[Sc-5] = 100/1. The THF-containing analog Sc-6 also showed good activity and tunability for the copolymerization of 1i with ethylene, affording the copolymers with 1i incorporation = 2.6 to 38.9 mol % at [1i]/[Sc-6] = 100/1 to 500/1 (entries 1 to 6). The Fineman-Ross plot of the copolymerization of 1i with ethylene by Sc-5 established the reactivity ratios of \( r_E = k_{EE}/k_{ES} = 0.94 \) and \( r_S = k_{ES}/k_{SE} = 3.02 \), where \( E \) is ethylene and \( S \) is 1i (32), suggesting that the copolymerization of 1i is faster than that of ethylene.

These results are in sharp contrast with the titanium-catalyzed copolymerization of norbornene with ethylene (34). Most of the heteroatom-functionalized copolymers obtained above showed a melting point of 110 to 128°C, which is comparable with those of the typical linear low-density polyethylene prepared by the copolymerization of ethylene with heteroatom-free \( \alpha \)-olefins, such as 1-butene, 1-hexene, and 1-octene (3).

**CONCLUSION**

By using half-sandwich rare-earth metal catalysts, such as Sc-3 and Sc-5, we have achieved for the first time the syndiospecific copolymerization of a series of oxygen-, sulfur-, selenium-, nitrogen-, and phosphorus-containing \( \alpha \)-olefins as well as their copolymerization with ethylene. This protocol has efficiently afforded a new family of heteroatom-functionalized polyolefins, which were difficult to prepare previously. Experimental and computational studies have revealed that an appropriate interaction between the heteroatom in an \( \alpha \)-olefin and the catalyst metal center plays a critically important role in these catalytic systems.
role in achieving the olefin polymerization activity and stereoselectivity. Obviously, the success of the present HOP and copolymerization highly relies on the unique heteroatom affinity and olefin affinity of the rare-earth metal ions as well as the high activity of the rare-earth alkyl species toward an olefin unit. This reaction mechanism may also work for other catalysts and functional olefins, if appropriate interactions between the catalyst and the heteroatom/C=C units in an olefin are achievable. We expect that our findings in the present HOP will guide design of new catalysts and functional monomers for synthesis of various desired functional polyolefins. Studies along this direction are currently in progress.

MATERIALS AND METHODS

General procedure for homopolymerization of functionalized α-olefins

In a N₂-filled glove box, a toluene solution (0.5 ml) of [Ph₃C][B(C₆F₅)₄] (28.5 mg, 0.03 mmol) was slowly added to a toluene solution (0.5 ml) of C₆H₅Sc(CH₂C₆H₄NMe₂-2)₂ (Sc-i; 11.4 mg, 0.03 mmol) under magnetic stirring in a 20-ml Schlenk tube. After stirring the mixture for 5 min, α-olefin 1b (889.2 mg, 6.0 mmol, 1.5 M in toluene) was added into the reaction solution. The Schlenk tube was sealed and kept stirred in the glove box for 24 hours at room temperature. The Schlenk tube was taken outside, and the polymerization was quenched by addition of methanol (10 ml). Then, the mixture was poured into methanol (200 ml) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60°C to a constant weight (871.4 mg, 98% yield; Table 1, entry 2). The homopolymerization of other functionalized α-olefins follows the same procedure, only except that the monomers and the reaction time are different. In the cases of monomers 1h, 1r, 1s, 1t, and 1u, Sc-2, Sc-3, Sc-4 or Y-1 was used as a catalyst instead of Sc-i, respectively.

General procedure for the copolymerization of functionalized α-olefins with ethylene

In a N₂-filled glove box, a toluene solution (50 ml) of 1i (492.8 mg, 3 mmol) was charged into a three-necked flask with a magnetic stir bar. The flask was taken outside, set in a water bath (20°C), and connected to a well-purged Schlenk ethylene line and a mercury-sealed stopper by using a three-way cock. Ethylene (1 atm) was introduced into the reaction solution. The Schlenk tube was sealed and kept stirred in the glove box for 24 hours at room temperature. The Schlenk tube was taken outside, and the polymerization was quenched by addition of methanol (10 ml). Then, the mixture was poured into methanol (200 ml) to precipitate the polymer product. The precipitated polymer was collected by filtration, washed with methanol, and then dried under vacuum at 60°C to a constant weight (0.64 g; Table 2, entry 1). The resulting polymer was soluble in hot toluene, dichlorobenzene, and 1,1,2,2-tetrachloroethane. Solvent fractionation experiments suggest that the formation of homopolymers (2i or polyethylene) was almost negligible (<2%). The 1H content in the copolymer was calculated from the 1H NMR analysis. The copolymerization of other functionalized α-olefins (1r and 1t) with ethylene follows the same procedure of 1i, only except that the monomers and the reaction time are different. In the case of entries 4 to 6, 12, and 13 (Table 2), C₆Me₅SiMe₂Sc(CH₂SiMe₃)₂ (THF) (Sc-6) was used as a catalyst instead of Sc-5. See the Supplementary Materials for detailed experimental conditions, procedures, and spectroscopic analyses.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/7/e1701011/DC1

Supplementary Materials and Methods

fig. S1. Fineman-Ross plot for the copolymerization of ethylene and monomer 1i with Sc-5/[Ph₃C][B(C₆F₅)₄] at 20°C.
fig. S2. Sulfor and vinyl coordination complexes and their relative free energies (in kilocalories per mole).
fig. S3. Chain initiation and chain propagation processes of the polymerization of 1i with relative free energies (in kilocalories per mole) shown under the structures.
fig. S4. Coordination site analysis for the incoming monomer.
fig. S5. Schematic representations of the transition states showing steric hindrance influences.
table S1. Homopolymerization of oxygen-containing α-olefin 1b by different rare-earth catalysts.
table S2. Homopolymerization of sulfur-containing α-olefin 1i by different rare-earth catalysts.
table S3. Data for Fineman-Ross plot.
table S4. Energy decomposition analyses of transition states (energy in kilocalories per mole).

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