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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 rubbish 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 polyethylenes. It has been previously found that early transition metal catalysts, such as titanium and zirconium metallocenes, which are excellent catalysts for the polymerization of nonpolar olefins, were easily poisoned by heteroatoms (Fig. 1A). Although some bulky siloxy–containing or aluminum alkoxy–containing α-olefins were reported to copolymerize with ethylene in the presence of group 4 metal catalysts, the polar 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.

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

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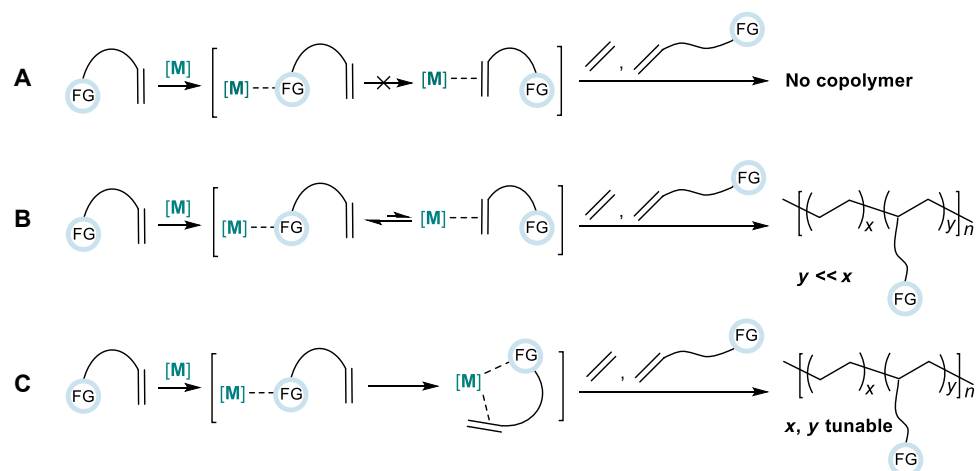
Fig. 1. Possible influences of a heteroatom in the transition metal–catalyzed copolymerization of ethylene with an FG-containing α-olefin. (**A**) A heteroatom (FG) acts as a poison to deactivate the catalyst and hamper the polymerization. [M], transition metal. (**B**) FG acts as a spectator that is 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.
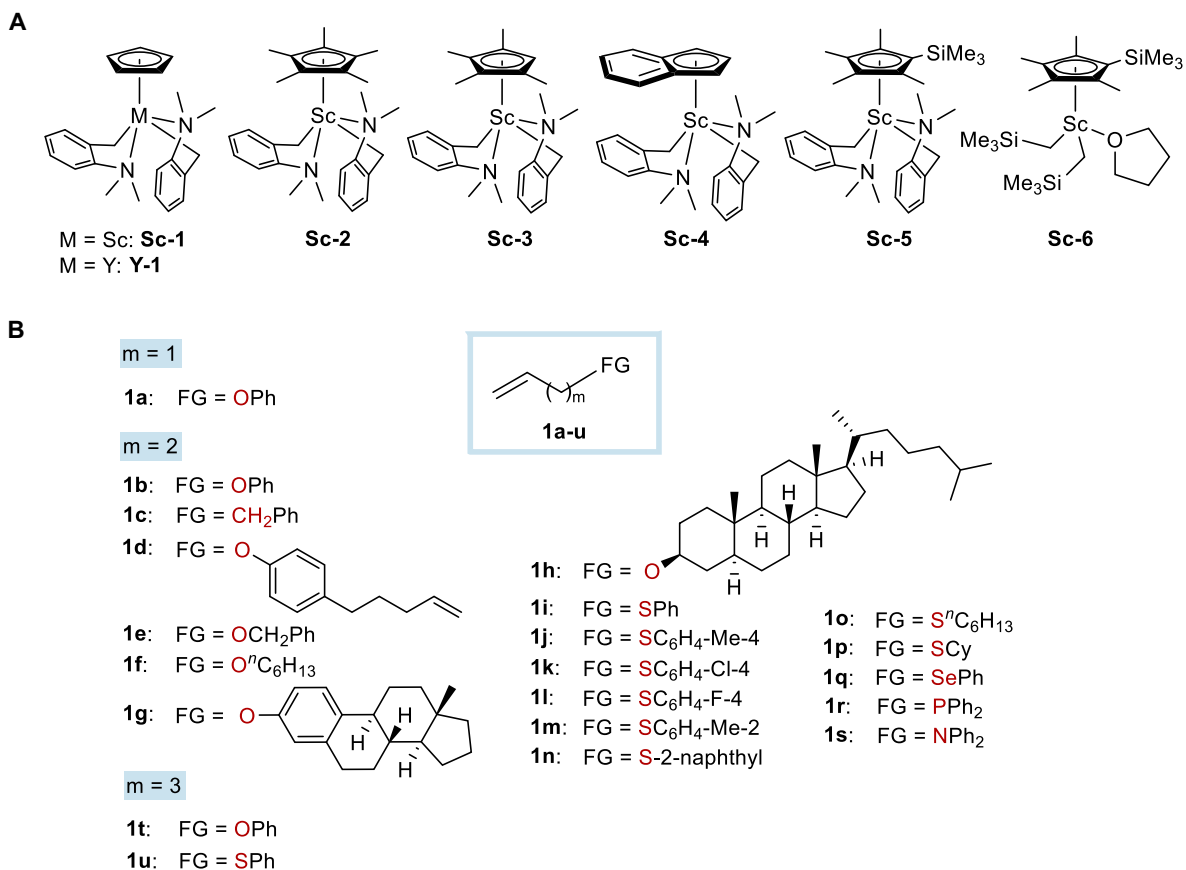
Fig. 2. Catalysts and monomers investigated in this study. (**A**) Rare-earth complexes used as precatalysts in this work. (**B**) Heteroatom-containing α-olefins examined in this work.

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.

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.
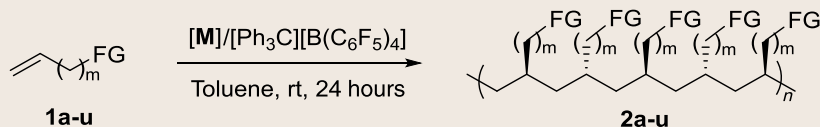
Entry	Monomer 1	[M]	1/[M]	Polymer 2	Yield (%)*	M_n (×10³)†	M_w/M_n†	rrrr (%)‡	T_g (°C)§
1	**1a**	Sc-1	100/1	**2a**	0‖	—	—	—	—
2	**1b**	Sc-1	200/1	**2b**	98	33.6	1.77	>95	9
3	**1b**	Sc-2	200/1	**2b**	0	—	—	—	—
4	**1b**	Sc-3	200/1	**2b**	100	29.8	1.33	>95	5
5	**1b**	Sc-3	500/1	**2b**	78	59.8	1.78	>95	4
6	**1c**	Sc-3	100/1	**2c**	0	—	—	—	—
7	**1d**	Sc-3	500/1	**2d**	93	80.4	2.06	>95	−32
8	**1e**	Sc-3	500/1	**2e**	71	83.6	1.96	>95	−31
9	**1f**	Sc-3	500/1	**2f**	89	74.5	1.76	>95	n.o.
10	**1g**	Sc-3	500/1	**2g**	95	80.4	1.85	>95	98
11	**1h**	Sc-3	100/1	**2h**	Trace	—	—	—	—
12	**1h**	Sc-4	100/1	**2h**	99	30.2¶	1.16¶	>95	n.o.
13	**1i**	Sc-3	200/1	**2i**	100	57.0	2.23	>95	0
14	**1i**	Sc-3	1000/1	**2i**	100	103.2	2.29	>95	0
15	**1i**	Sc-3	2000/1	**2i**	100	133.1	2.20	>95	−1
16	**1i**	Sc-3	5000/1	**2i**	63	189.0	2.03	>95	0
17#	**1i**	Sc-3	200/1	**2i**	100	304.9	1.65	>95	0
18#	**1i**	Sc-3	2000/1	**2i**	93	585.5	1.57	>95	1
19	**1j**	Sc-3	1000/1	**2j**	100	83.4	2.36	>95	−1
20	**1k**	Sc-3	1000/1	**2k**	97	103.5	2.02	>95	12
21	**1l**	Sc-3	1000/1	**2l**	99	132.9	2.52	>95	−5
22	**1m**	Sc-3	1000/1	**2m**	100	118.4	2.87	>95	2
23	**1n**	Sc-3	1000/1	**2n**	99	20.7	2.68	>95	29
24**	**1n**	Sc-3	1000/1	**2n**	99	60.2	2.45	>95	24
25	**1o**	Sc-3	1000/1	**2o**	100	102.0	1.80	>95	n.o.
26	**1p**	Sc-3	1000/1	**2p**	100	123.8	1.84	>95	−8
27	**1q**	Sc-3	500/1	**2q**	100	58.9	2.55	92	−7
28	**1r**	Sc-3	500/1	**2r**	10	4.1	1.56	n.d.	−2
29	**1r**	Sc-1	500/1	**2r**	100	14.6	1.77	n.d.	27
30	**1s**	Sc-3	100/1	**2s**	37	1.5	1.39	n.d.	2
31	**1s**	Sc-1	100/1	**2s**	39	1.2	1.46	n.d.	22
32	**1s**	Sc-4	100/1	**2s**	64	3.1	1.53	n.d.	36
33	**1t**	Sc-1	100/1	**2t**	Trace	—	—	—	—
34	**1t**	Y-1	100/1	**2t**	23	6.8	1.57	88	−5
35	**1u**	Sc-3	200/1	**2u**	40	11.3	1.99	89	−21
36	**1u**	Sc-1	200/1	**2u**	80	8.9	2.16	90	−23
37	**1u**	Sc-4	200/1	**2u**	88	23.5	2.36	>95	−22

*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 ¹³C nuclear magnetic resonance (NMR) analysis.   §Determined by differential scanning calorimetry.   ‖Formation of 1-phenoxy-1-propene (an isomerization product of **1a**) was observed.   ¶Determined by high-temperature GPC in 1,2-dichlorobenzene at 145°C against polystyrene standard.   #−40°C.   **0°C.

RESULTS AND DISCUSSION

Homopolymerization of heteroatom-containing α-olefins

As an initial test of the HOP concept, the polymerization of 3-phenoxy-1-propene (**1a**), which has one methylene (CH$_2$) unit between the C=C double bond and the oxygen atom (Fig. 2B), was first examined by using the C$_5$H$_5$-ligated scandium complex **Sc-1** (Fig. 2A) with [Ph$_3$C][B(C$_6$F$_5$)$_4$] as a cocatalyst. However, no polymer was observed (Table 1, entry 1). It seemed that the isomerization of **1a** to 1-phenoxy-1-propene through 1,3-hydrogen shift took place. We then examined 4-phenoxy-1-butene (**1b**), which has two CH$_2$ 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(phenoxybutene) **2b** in 98% yield in 24 hours (entry 2). In attempts to see the ligand influence, the sterically demanding C$_5$Me$_5$-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 C$_5$Me$_4$H-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% *rrrr*) by stereoregularly orienting 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-butenyloxy)-4-(4-penten-1-yl) benzene (**1d**), which contains both a phenoxybutene unit and an oxygen-free pentene unit in one molecule, the polymerization occurred exclusively at the phenoxybutene 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 benzyloxy (**1e**), hexyloxy (**1f**), and [estra-1,3,5(10)-trien-3-yl]oxy (**1g**) groups also served as efficient promoters for the 1-butene polymerization by **Sc-3**, affording the corresponding functionalized polyolefins **2e** to **2g** in high yields with high molecular weight ($M_n = 7.45 \times 10^4$ to 8.36×10^4), narrow molecular weight distribution ($M_w/M_n = 1.76$ to 1.96), and excellent syndiotacticity (>95% *rrrr*) (entries 8 to 10). In the case of a monomer (**1h**) having the sterically demanding β-cholestanoxy 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 abovementioned 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 1.33×10^5 in 24 hours at room temperature (entries 13 to 15). Further higher molecular weight (M_n of up to 5.86×10^5) was obtained at −40°C, possibly because the β-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 halogen-

ated 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% *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% *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}C NMR analysis.

In the case of 5-phenoxy-1-pentene (**1t**), which has a longer linker (three CH$_2$ 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 (C$_5$H$_5$)Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_2$ (**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 lager 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 [Ph$_3$C][B(C$_6$F$_5$)$_4$] (*31*). It has been revealed that the coordination of the S atom in **1i** to the Sc atom in **Cat** may afford complexes ***si*-C1** and ***re*-C1**, although ***si*-C1** is more favored than ***re*-C1** by 2.2 kcal/mol (Fig. 3). The insertion of the C=C double bond into the Sc–CH$_2$C$_6$H$_4$NMe$_2$-*o* bond in ***si*-C1** or ***re*-C1** 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
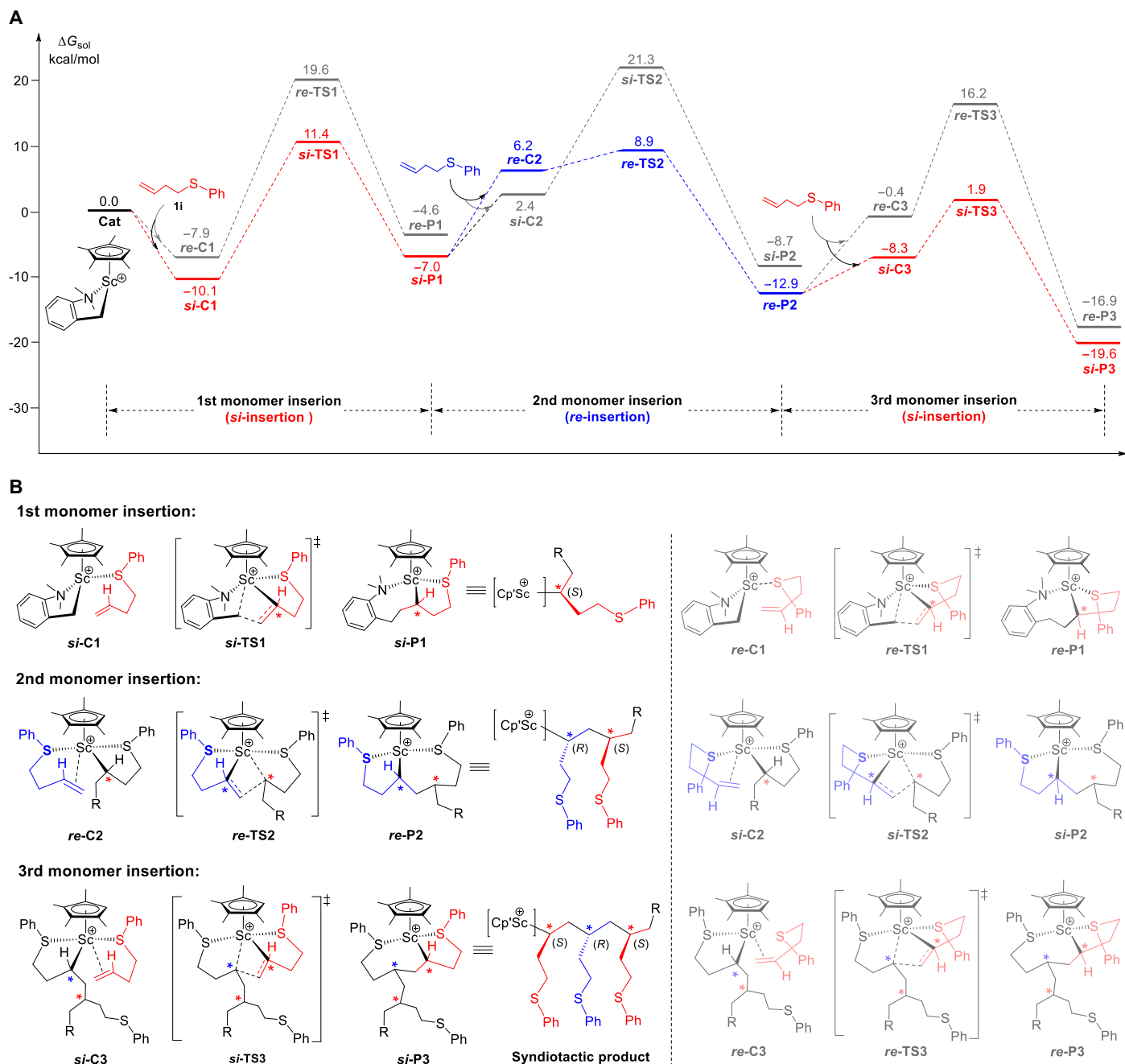
Fig. 3. Computational analysis of the polymerization of 1i by the cationic species Cat generated in the reaction of Sc-3 with [Ph₃C][B(C₆F₅)₄]. (**A**) DFT-calculated energy profile of the polymerization of **1i** by **Cat**. (**B**) Structures of the stationary points shown in the energy profile. The less favored pathway is pale-colored. R = $CH_2C_6H_4NMe_2$-o; **TS**, transition state; ΔG_{sol}, relative Gibbs free energy in solution.

re-P1 (27.5 kcal/mol). The coordination of the second molecule of **1i** to the Sc atom in **si-P1** via both the S atom and the C=C double bond could yield **si-C2** and **re-C2**. Although **re-C2** has a higher energy (6.2 kcal/mol) than **si-C2** (2.4 kcal/mol), the subsequent insertion of the C=C double bond into the Sc–alkyl bond in **re-C2** via **re-TS2** ($\Delta G^{\ddagger}$ = 15.9 kcal/mol) to give **re-P2** (re-insertion; syndiotactic product) is much easier than that in **si-C2** via **si-TS2** ($\Delta G^{\ddagger}$ = 28.3 kcal/mol) to give **si-P2** (si-insertion; isotactic product). Similarly, the insertion of the third **1i** into **re-P2** would take place via **si-C3** and **si-TS3** to give the favorable product

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 α-olefins

After having proved the validity of the HOP concept, we then examined the copolymerization of the heteroatom-containing α-olefins with

Table 2. Copolymerization of heteroatom-containing α-olefins with ethylene. Conditions: [Sc] (0.03 mmol), [Ph₃C][B(C₆F₅)₄] (0.03 mmol), monomer 1, ethylene (1 atm), toluene (50 ml) at 20°C for t hours (unless otherwise stated).
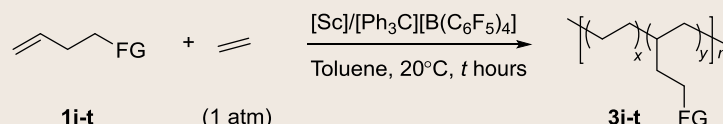
Entry	1	[Sc]	1/[Sc]	t (hour)	3	Yield (g)	Activity*	M_n $(\times10^3)$†	M_w/M_n†	i.r. (%)‡	T_g (°C)§	T_m (°C)§
1	**1i**, FG = SPh	**Sc-3**	100/1	1.5	**3i**	0.12	2.7	14.7	1.76	73.5	−8	n.o.
2	**1i**	**Sc-5**	100/1	2	**3i**	0.64	10.6	20.6	1.39	29.0	−36	125
3	**1i**	**Sc-5**	500/1	20	**3i**	1.95	3.3	57.7	1.92	44.9	−16	128
4	**1i**	**Sc-6**	100/1	5	**3i**	1.11	7.4	82.4	1.69	2.6	−18	124
5	**1i**	**Sc-6**	500/1	20	**3i**	3.48	5.8	31.7	1.96	15.7	−19	119
6	**1i**	**Sc-6**	1000/1	20	**3i**	4.39	7.3	17.0	2.38	38.9	−14	110
7	**1r**, FG = PPh₂	**Sc-5**	100/1	0.33	**3r**	1.03	103.2	54.0	2.20	9.5	2	133
8	**1r**	**Sc-5**	500/1	1.5	**3r**	2.90	64.4	—‖	—‖	32.5	10	124
9	**1b**, FG = OPh	**Sc-5**	100/1	5	**3b**	0	—	—	—	—	—	—
10	**1t**, FG = CH₂OPh	**Sc-5**	100/1	0.5	**3t**	1.36	90.4	124.9	2.29	8.7	-40	127
11	**1t**	**Sc-5**	500/1	5	**3t**	3.07	20.5	89.6	1.95	24.8	−39	114
12	**1t**	**Sc-6**	100/1	5	**3t**	1.78	11.8	154.2	2.71	3.3	−31	124
13	**1t**	**Sc-6**	500/1	20	**3t**	1.22	2.0	83.0	2.23	11.8	−36	119

*10^3 g of copolymer per mole of Sc per hour per standard pressure of ethylene.   †Determined by GPC in 1,2-dichlorobenzene at 145°C against polystyrene standard.   ‡Incorporation ratio of **1**, determined by ¹H NMR analysis.   §Determined by differential scanning calorimetry.   ‖No GPC signal was observed in 1,2-dichlorobenzene at 145°C probably because of oxidation (or other reaction) of the phosphine components at high temperatures inside the GPC columns.

ethylene. Some representative results are summarized in Table 2. When **Sc-3** was used as a catalyst with [**1i**]/[**Sc-3**] = 100/1, the copolymerization of **1i** with ethylene (1 atm) occurred rapidly at room temperature, affording 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 sterically 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 = 2.06×10^4 to 5.77×10^4 and **1i** incorporation = 29.0 to 44.9 mol %, when [**1i**]/[**Sc-5**] was raised from 100/1 to 500/1 (entries 2 and 3). 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 1000/1 (entries 4 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 $r_S = k_{SS}/k_{SE} = 3.02$, where E is ethylene and S is **1i** (32), suggesting that the polymerization of **1i** is faster than that of ethylene. These results are in sharp contrast with the titanium-catalyzed copolymerization of phenyl sulfide–substituted α-olefins with ethylene, in which the incorporation of the sulfur-containing monomer was less than 1 mol % (33).

The copolymerization of the phosphorus-containing monomer **1r** with ethylene was also achieved by using the **Sc-5** catalyst, which afforded the corresponding copolymers (**3r**) with varying phosphorus incorporation ratio (9.5 to 32.5 mol %) as the monomer/catalyst feed was charged with [**1r**]/[**Sc-5**] = 100/1 to 500/1 (entries 7 and 8). As to

oxygen-containing monomers, **1b** did not copolymerize with ethylene (entry 9). In contrast, the copolymerization of **1t** with ethylene by **Sc-5** and **Sc-6** afforded the oxygen-functionalized copolymers (**3t**) in high yields with high molecular weight (M_n = 8.30×10^4 to 1.54×10^5) and controllable **1t** incorporation (3.3 to 24.8 mol %) (entries 10 to 13), although the homopolymerization of **1t** by **Sc-5** or **Sc-6** was very slow. These results suggest that the copolymerization of a functional α-olefin with ethylene can be well performed even if its homopolymerization is not so efficient. This phenomenon has also been observed previously in the scandium-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 polyethylenes prepared by the copolymerization of ethylene with heteroatom-free α-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 polymerization of a series of oxygen-, sulfur-, selenium-, nitrogen-, and phosphorus-containing α-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 α-olefin and the catalyst metal center plays a critically important

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 N_2-filled glove box, a toluene solution (0.5 ml) of $[Ph_3C][B(C_6F_5)_4]$ (28.5 mg, 0.03 mmol) was slowly added to a toluene solution (0.5 ml) of $C_5H_5Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**Sc-1**; 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-1**, respectively.

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

In a N_2-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 system and was saturated in the solution by stirring for 2 min. A toluene solution (2 ml) of $C_5Me_4SiMe_3Sc(CH_2C_6H_4NMe_2\text{-}o)_2$ (**Sc-5**) (15.2 mg, 0.03 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (28.5 mg, 0.03 mmol) was then added through a syringe under vigorous stirring. The polymerization was quenched after 2 hours by adding methanol (200 ml). The polymer product 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 **1i** 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), $C_5Me_4SiMe_3Sc(CH_2SiMe_3)_2$ (THF) (**Sc-6**) was used as a catalyst instead of **Sc-5**. See the Supplementary Materials for detailed experimental conditions, procedures, and spectroscopic analyses.

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