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# Scandium-Catalyzed Regio- and Stereoselective Cyclopolymerization of Functionalized $\alpha,\omega$ -Dienes and Copolymerization with Ethylene

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Supporting Information Placeholder

**ABSTRACT:** The precise control of regio- and stereochemistry in the cyclopolymerization of heteroatom-functionalized  $\alpha,\omega$ -dienes is of much interest and importance, but has remained a challenge to date. We report herein the regio-, diastereoselective and stereoregular cyclopolymerization of ether- and thioether-functionalized 1,6-heptadienes by a half-sandwich scandium catalyst. The polymerization of 4-benzyloxy-1,6-heptadiene selectively afforded the corresponding benzyloxy-functionalized cyclic polymer composed of 1,2,4-*cis*-substituted-ethylenecyclopentane (ECP) microstructures in an isospecific fashion (95% *mmm*). In contrast, the polymerization of 4-phenylthio-1,6-heptadiene exclusively yielded 1,2-*trans*-1,4-*cis*-ECP units with high isotacticity (95% *rrr*). The DFT calculations revealed that an interaction between the scandium atom in the catalyst and the heteroatom in a diene monomer played an important role in controlling the regio- and stereochemistry of the diene cyclopolymerization. The copolymerization of functionalized 1,6-heptadienes with ethylene has also been achieved in a controlled fashion.

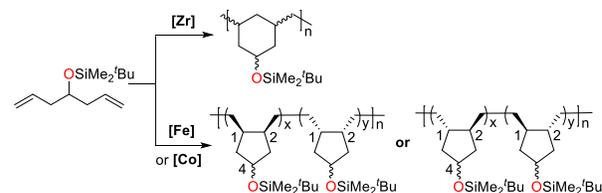
## INTRODUCTION

Organic polymers with cyclic repeating units in the polymer backbone are of much interest and importance in both academic research and industrial applications.<sup>1</sup> Cyclic polyolefins bearing heteroatom functional groups are of special interest, as they may show improved beneficial properties compared to the heteroatom-free polymers. The cyclopolymerization of  $\alpha,\omega$ -dienes such as 1,5-hexadiene and 1,6-heptadiene by transition metal catalysts has demonstrated particular utility for the preparation of cyclopolyolefins.<sup>2-5</sup> In this transformation, the precise control of the regio- and stereochemistry is highly important to obtain high-performance polymers. However, compared to the polymerization of unsubstituted  $\alpha,\omega$ -dienes, it is usually difficult to control the regio- and stereoselectivity of the cyclopolymerization of heteroatom-functionalized  $\alpha,\omega$ -dienes, because of the lack of suitable catalysts that can not only show good compatibility with the heteroatom functional group but can also govern the stereochemistry of the heteroatom-substituent in addition to the regio- and stereoselectivity control of the common cyclization process. It has been previously reported that zirconocene catalysts could show compatibility with some sterically demanding siloxy-substituted  $\alpha,\omega$ -dienes, such as 4-*tert*-butyldimethylsiloxy-1,6-heptadiene. However, the resulting siloxy-functionalized polymer products consisted of a mixture of *trans*- and *cis*-fused 1,3-methylenecyclohexane (MCH) units without showing stere-

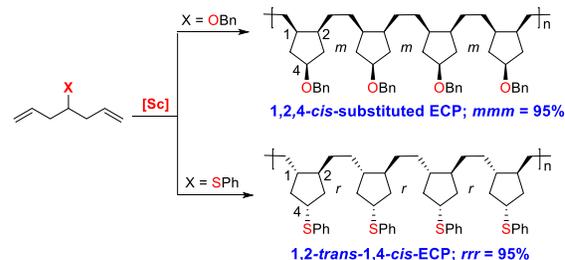
oselectivity at either the 1,3-dimethylene skeleton or the 5-siloxy substituent (Scheme 1a, top).<sup>4</sup> The cyclopolymerization of 4-*tert*-butyldimethylsiloxy-1,6-heptadiene by Fe and Co catalysts has been reported to yield polymers containing the five-membered ring 1,2-ethylene-4-siloxycyclopentane (ECP)

## Scheme 1. Transition-Metal-Catalyzed Cyclopolymerization of Heteroatom-Functionalized 1,6-Heptadienes

a) Previous studies: Cyclopolymerization of siloxy-substituted 1,6-heptadiene by Zr,<sup>4</sup> Fe,<sup>5b</sup> and Co<sup>5b</sup> catalysts



b) This work: Regio-, diastereoselective and stereoregular cyclopolymerization of ether- and thioether-substituted 1,6-heptadienes by a Sc catalyst



units (Scheme 1a, bottom).<sup>5b</sup> Although 1,2-*cis*- or 1,2-*trans* diastereoselectivity could be achieved by choosing a Fe or Co catalyst, respectively, a control of the stereoselectivity on the 4-siloxy substituent was not achieved and no stereoregular (tacticity) of the repeating ECP units was observed. Despite continued interest and recent advances in this area, the precise control of the regio- and stereochemistry in the cyclopolymerization of heteroatom-functionalized  $\alpha,\omega$ -dienes has remained a challenge to date.<sup>6</sup>

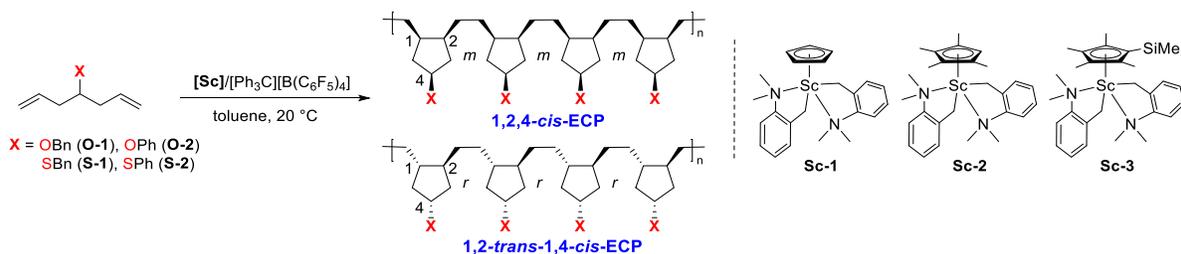
We have recently found that organo rare-earth metal catalysts can show unique activity and selectivity in various transformations of heteroatom-containing organic substrates,<sup>7,8</sup> including the regio-, stereospecific polymerization of heteroatom-functionalized  $\alpha$ -olefins,<sup>8a-f</sup> because of the unique heteroatom-affinity of the rare-earth metal ions. These findings have promoted us to examine the cyclopolymerization of heteroatom-functionalized  $\alpha,\omega$ -dienes by rare-earth metal catalysts. We report herein the regio-, diastereoselective and stereoregular cyclopolymerization of heteroatom-functionalized 1,6-heptadienes by a half-sandwich scandium catalyst, in which the regio- and stereoselectivity is uniquely controlled through the interaction between the catalyst metal center and the heteroatom. This protocol has efficiently afforded a new family of functionalized cyclic polyolefins with unprecedentedly high regio- and diastereoselectivity at all of the three chiral carbon centers together with highly stereoregular orientation of the cyclic ECP units (Scheme 1b). The cyclopolymerization of the heteroatom-functionalized 1,6-heptadienes with ethylene is also described.

## RESULTS AND DISCUSSION

### Homopolymerization of Heteroatom-Functionalized 1,6-Heptadienes by Half-Sandwich Scandium Catalysts.

At first, we examined the polymerization of 4-benzyloxy-1,6-heptadiene (**O-1**) by using a combination of the C<sub>5</sub>H<sub>5</sub>-ligated scandium complex **Sc-1** and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] as a catalyst.<sup>9</sup> With the monomer to catalyst feed ratio [O-1]/[Sc-1] = 100/1, the polymerization slowly took place at room temperature, reaching 35% conversion in 24 h (Table 1, run 1). The resulting polymer contained a mixture of cyclized and uncyclized units, as shown by the NMR analyses. When the larger C<sub>5</sub>Me<sub>4</sub>H-ligated scandium complex **Sc-2** was employed, rapid polymerization was observed under the same conditions, selectively affording the cyclic polymer product with  $M_n = 28.8 \times 10^3$  g mol<sup>-1</sup> and  $M_w/M_n = 2.50$  (Table 1, run 2). When the [O-1]/[Sc-2] feed ratio was raised to 500/1, the monomer was quantitatively converted within 3 h, but an insoluble polymer product (1,2-dichlorobenzene at 145 °C) was yielded probably due to cross-linking (Table 1, run 3). The use of a further sterically demanding C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>-ligated scandium complex **Sc-3** with [O-1]/[Sc-1] = 100/1 yielded the cyclic polymer product with a narrower molecular distribution ( $M_n = 18.7$  kg/mol and  $M_w/M_n = 1.50$ ) (Table 1, run 4). As the [O-1]/[Sc-3] feed ratio was raised to 500/1, the number average molecular weight ( $M_n$ ) of the resulting polymer showed a pronounced increase to  $86.5 \times 10^3$  g mol<sup>-1</sup>, and no cross-linked insoluble product was observed (Table 1, run 5). The polymerization of **O-1** by **Sc-3** proceeded even at -20 °C, affording the cyclic polymer product with higher stereoselectivity (Table 1, run 6). At 50 °C, the polymerization took place more rapidly but with slightly lower stereoselectivity (Table 1, run 7).

**Table 1.** Sc-Catalyzed Cyclopolymerization of Heteroatom-Functionalized 1,6-Heptadienes<sup>a</sup>



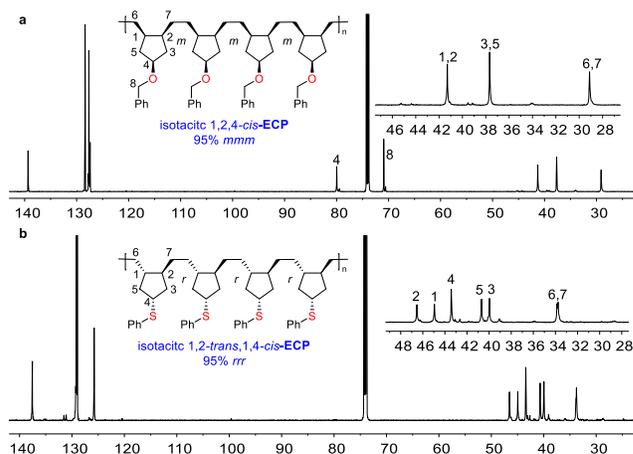
run	diene (D)	[Sc]	D/[Sc]	temp.	time (h)	conv. (%) <sup>b</sup>	$M_n^c$ ( $\times 10^3$ g mol <sup>-1</sup> )	$M_w/M_n^c$	1,2- <i>trans</i> -1,4- <i>cis</i> / 1,2,4- <i>cis</i> <sup>d</sup>	tacticity <sup>d</sup>	$T_g^e$ (°C)	$T_m^e$ (°C)
1	O-1	Sc-1	100/1	20	24	35	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>
2	O-1	Sc-2	100/1	20	0.5	100	28.8	2.50	6/94	95% <i>mmm</i>	10	122
3	O-1	Sc-2	500/1 <sup>g</sup>	20	3	100	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>	n.d. <sup>f</sup>
4	O-1	Sc-3	100/1	20	1	100	18.7	1.50	6/94	95% <i>mmm</i>	11	122
5	O-1	Sc-3	500/1 <sup>g</sup>	20	48	70	86.5	2.20	6/94	95% <i>mmm</i>	11	125
6	O-1	Sc-3	100/1	-20	12	84	17.1	2.89	2/98	98% <i>mmm</i>	11	124
7	O-1	Sc-3	100/1	50	0.5	99	19.8	1.90	12/88	90% <i>mmm</i>	13	116
8	O-2	Sc-3	100/1	20	24	64	12.8	1.86	9/91	atactic	50	n.o. <sup>h</sup>
9	O-2	Sc-2	100/1	20	96	30	6.7	1.98	11/89	80% <i>mmm</i>	47	122
10	S-1	Sc-3	100/1	20	48	57	17.9	2.05	75/25	n.d. <sup>f</sup>	13	n.o. <sup>h</sup>
11	S-2	Sc-3	100/1	20	3	100	7.1	2.13	94/6	95% <i>rrr</i>	28	160
12	S-2	Sc-3	500/1 <sup>g</sup>	20	3	98	10.1	2.73	94/6	95% <i>rrr</i>	31	162

<sup>a</sup> Conditions: [Sc] (0.02 mmol), [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.02 mmol), diene (0.5 M), 20 °C. <sup>b</sup> Weight of polymer obtained/weight of monomer used. <sup>c</sup> Determined by gel permeation chromatography (GPC) in tetrahydrofuran at room temperature against polystyrene standard. <sup>d</sup> Determined by <sup>13</sup>C NMR analysis. <sup>e</sup> Determined by differential scanning calorimetry (DSC). <sup>f</sup> n.d. = not determined. <sup>g</sup> diene (1.0 M). <sup>h</sup> n.o. = not observed.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses revealed that the cyclopolymer products (poly(O-1)) were exclusively composed of 1,2,4-*cis*-substituted ECP units (94%) (Figure 1a; see also Figures S9-S16). In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, the signal of the C1 atom in the ECP ring was identical to that of the C2 atom ( $\delta$  41.2), and the C3 signal was identical to that of the C5 atom ( $\delta$  37.5), suggesting that the C6 and C7 methylene substituents on the C1 and C2 atoms in the ECP ring should be *cis* to each other (Figure 1a). The benzyloxy-substituted carbon atom C4 showed a sharp signal at  $\delta$  80.0, indicating that the configuration of the benzyloxy substituent was also well fixed. A well-expanded NOESY spectrum showed distinct correlation between the C4H proton (3.98 ppm) and the C1H as well as C2H proton (1.78 ppm) (Figure S16), suggesting that the benzyloxy group on C4 should be stereoselectively oriented *cis* to the  $\text{CH}_2$  substituents on the C1 and C2 atoms in the ECP ring. These results are indicative of a highly regulated 1,2,4-*cis* diastereoselective ECP configuration. More remarkably, the  $^{13}\text{C}\{^1\text{H}\}$  NMR signals of all the carbon atoms in the ECP units appeared as well-resolved singlets, suggesting that the ECP units were oriented with high stereoregularity (*mmm* = 95%, isotactic).<sup>10</sup> The DSC analysis of the polymer products revealed melting temperatures ( $T_m$ ) at 122–125 °C (Table 1, runs 2–7; Figures S18, S20, S22), in agreement with the high stereoregularity of the ECP units.

The cyclopolymerization of 4-phenoxy-1,6-heptadiene (O-2) by Sc-3 also took place in a regio- and diastereoselective fashion, selectively affording the corresponding phenoxy-substituted poly(ECP) in a 1,2,4-*cis* fashion (91%), but the reaction was much slower than that of the benzyloxy analog O-1 under the same conditions (Table 1, run 8). In contrast with the high tacticity of poly(O-1), poly(O-2) synthesized by Sc-3 showed poor stereoregularity (atactic) (Figure S32). These results suggest that the substituent on the oxygen atom in an ether-substituted 1,6-heptadiene could show significant influences on the activity and stereoregularity of the cyclopolymerization of the diene unit.<sup>8q</sup> The use of the smaller  $\text{C}_5\text{Me}_4\text{H}$ -ligated Sc-2 catalyst improved the tacticity (80% *mmm*), but the reaction remained sluggish (30% conversion in 96 h) (Table 1, run 9, Figure S38). It is also worth noting that the cyclopolymerization of the oxygen-free 1,6-heptadiene by Sc-3 yielded the six-membered ring MCH units (91%) with no stereoselectivity,<sup>3f</sup> standing in sharp contrast with the exclusive formation of the five-membered ring ECP units in the polymerization of the ether-functionalized 1,6-heptadienes O-1 and O-2. These results suggest that the ether group may show critical influences not only on the stereoselectivity but also on the regioselectivity of the diene cyclopolymerization.

To further probe the heteroatom effects, we then examined sulfur-functionalized 1,6-heptadienes by using catalyst Sc-3. Compared to O-1, the sulfur analog 4-benzylthio-1,6-heptadiene S-1 was much less active and less selective under the same conditions, which afforded ploy(S-1) composed of a 75:25 mixture of the 1,2-*trans*- and 1,2-*cis*-ECP units with 57% conversion in 48 h (Table 1, run 10; Figures S45-S46). By contrast, 4-phenylthio-1,6-heptadiene (S-2) showed much higher activity and higher stereoselectivity than S-1, selectively yielding the thioether-functionalized cyclic polymer consisting of isotactic 1,2-*trans*-, 1,4-*cis*-ECP units with *rrr* = 95% (Table 1, runs 11 and 12; Figure 1b).<sup>10,11</sup> In the  $^{13}\text{C}\{^1\text{H}\}$  NMR



**Figure 1.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (125 MHz,  $1,1,1,2\text{-C}_2\text{D}_2\text{Cl}_4$ , 26.8 °C). (a) Poly(O-1) (Table 1, run 4), (b) Poly(S-2) (Table 1, run 11).

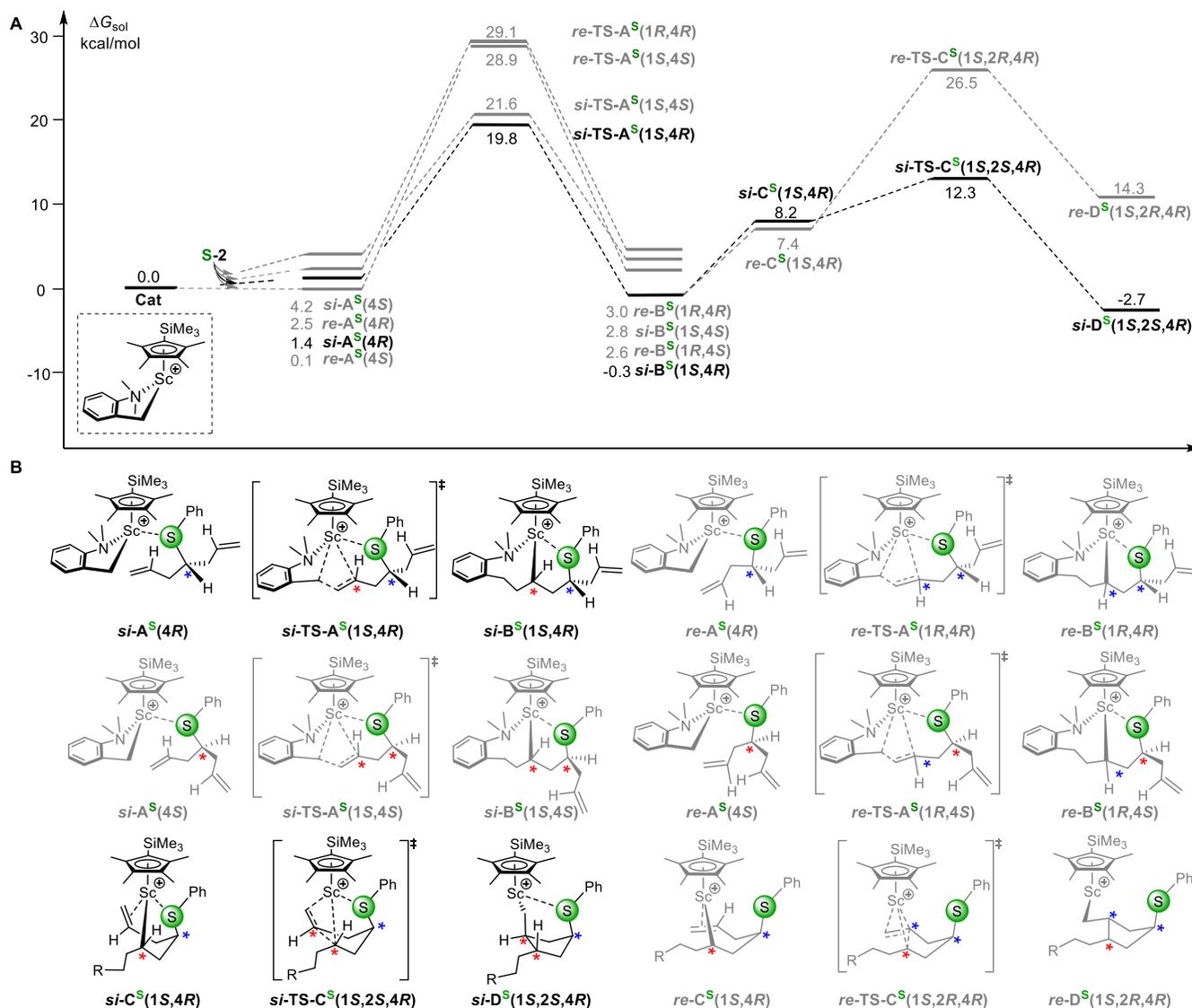
spectrum of poly(S-2), the chemical shifts of the C1 ( $\delta$  44.9) and C2 ( $\delta$  46.5) carbon atoms in the ECP ring were significantly different, and so were those of the C3 ( $\delta$  39.9) and C5 ( $\delta$  40.7) atoms, suggesting that the C6 and C7 methylene substituents on the C1 and C2 atoms should be *trans* to each other (Figure 1b). In the HETCOR spectrum, the difference in chemical shift between the two protons on the C5 atom ( $\delta$  40.7, 1.2 and  $\delta$  40.7, 2.4) was much bigger than on the C3 atom ( $\delta$  39.9, 1.7 and  $\delta$  39.9, 1.9) (Figure S53), probably because of the influence of the PhS substituent on the C4 atom. This suggests that the PhS substituent on the C4 should be diastereoselectively oriented *cis* to the C1 and *trans* to the C2 substituents on the ECP ring (*i.e.*, 1,2-*trans*, 1,4-*cis* configuration). The  $^{13}\text{C}\{^1\text{H}\}$  NMR signals of all the carbon atoms in the ECP units appeared as well-resolved singlets, suggesting that the ECP units should be oriented in a highly stereospecific fashion (*rrr* = 95%, isotactic). In agreement with the high stereoregularity, ploy(S-2) showed high melting temperatures ( $T_m$ ) at 160–162 °C and apparent crystallization temperature at 83–86 °C (Table 1, runs 11 and 12; Figures S59, S61). The selective formation of the 1,2-*trans*, 1,4-*cis*-ECP units in the polymerization of S-2 stands in sharp contrast with the exclusive formation of the 1,2,4-*cis* ECP configurations in the case of O-1 and O-2, again demonstrating the significant influence of the heteroatom in the present polymerization.

#### DFT Calculations of the Cyclopolymerization of S-2 and O-1.

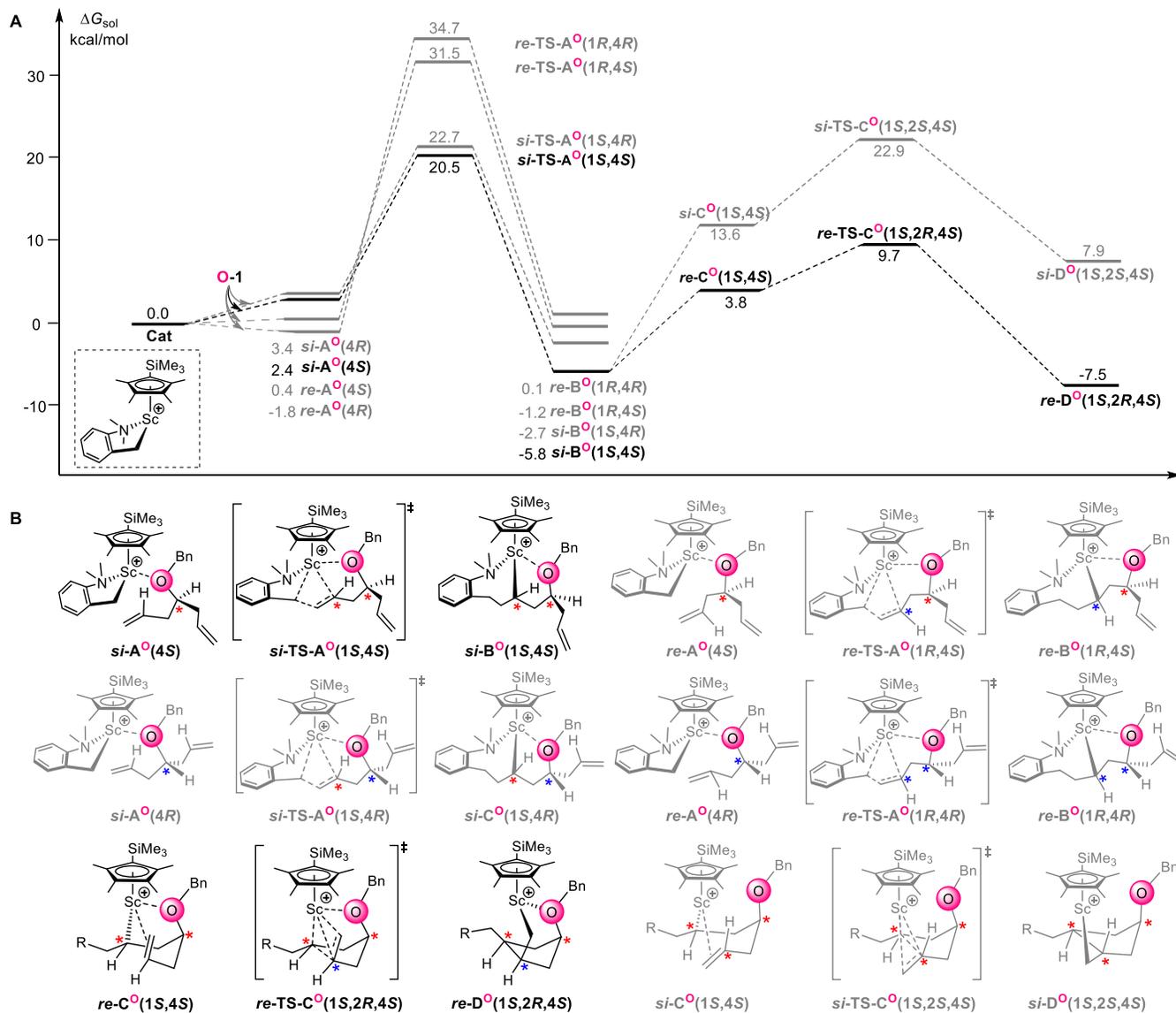
To acquire insights into the high regio- and stereoselectivity observed above, we performed the DFT calculations of the cyclopolymerization of S-2 and O-1 catalyzed by the cationic species (Cat) generated by the reaction of Sc-3 with 1 equivalent of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . In the case of S-2, once the sulfur atom and a vinyl group in the diene are coordinated to the Sc center, the S-bonded prochiral C4 atom in S-2 becomes chiral because of desymmetrization. Two coordination configurations (*i.e.*,  $\text{A}^{\text{S}}(\mathbf{4R})$  and  $\text{A}^{\text{S}}(\mathbf{4S})$ ) of C4 were therefore considered for the insertion/cyclization reactions, respectively (Figure 2). In both pathways, the *si*-coordination insertion mode was calculated to be more kinetically favorable than the *re*-fashion (19.8 and 21.6 vs 29.1 and 28.9 kcal/mol, Figure 2), which is consistent with the previous DFT analyses of the Sc-catalyzed polymerization of 4-phenylthio-1-butene.<sup>8q</sup> It has also been found that *si*- $\text{A}^{\text{S}}(\mathbf{4R})$  is more stable than *si*- $\text{A}^{\text{S}}(\mathbf{4S})$  by 2.8

kcal/mol and the formation of *si-B*<sup>S</sup>(1*S*,4*R*) is more favored both kinetically and thermodynamically in comparison with *si-B*<sup>S</sup>(1*S*,4*S*) (barriers of 19.8 vs 21.6 kcal/mol and reaction energies of -0.3 vs 2.8 kcal/mol, Figure 2). Once the more stable *si-B*<sup>S</sup>(1*S*,4*R*) was generated, different coordination/insertion fashions (*re*- or *si*-) of the remaining C=C bond could yield two diastereo-cyclic products with different configurations. The intramolecular coordination of the remaining C=C bond to the Sc atom in *si-B*<sup>S</sup>(1*S*,4*R*) could yield *si-C*<sup>S</sup>(1*S*,4*R*) or *re-C*<sup>S</sup>(1*S*,4*R*). Although *si-C*<sup>S</sup>(1*S*,4*R*) is 0.8 kcal/mol higher in energy than *re-C*<sup>S</sup>(1*S*,4*R*), the subsequent insertion of the C=C double into the Sc-alkyl bond in *si-C*<sup>S</sup>(1*S*,4*R*) via *si-TS*-

*C*<sup>S</sup>(1*S*,2*S*,4*R*) ( $\Delta G^\ddagger = 12.6$  kcal/mol) to give *si-D*<sup>S</sup>(1*S*,2*S*,4*R*) (*si*-insertion, 1,2-*trans*-1,4-*cis* product) is more favorable than the pathway of *re-C*<sup>S</sup>(1*S*, 4*R*)  $\rightarrow$  *re-TS-C*<sup>S</sup>(1*S*,2*R*,4*R*)  $\rightarrow$  *re-D*<sup>S</sup>(1*S*,2*R*,4*R*) (*re*-insertion, energy barrier of 26.8 kcal/mol, 1,2-*cis*-1,4-*trans* product). A further calculation of the reaction of the second S-2 monomer with *si-D*<sup>S</sup>(1*S*,2*S*,4*R*) also indicated more favorable *si*-insertion and subsequent *si*-cyclization process to give a second 1,2-*trans*-1,4-*cis* ECP unit (Figure S118). Repetition of these *si*-insertion and *si*-cyclization modes would therefore afford the isotactic polymer product, being in agreement with the experimental observation.



**Figure 2.** Computational analysis of the insertion/cyclization of first molecule of S-2 by the cationic species (Cat) generated by the reaction of Sc-3 with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . (A) DFT-calculated energy profile. (B) Structures of the stationary points shown in the energy profile. The less favored pathway is pale-colored. R =  $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o}$ , TS: transition state,  $\Delta G_{\text{sol}}$ : Relative Gibbs free energy in solution.



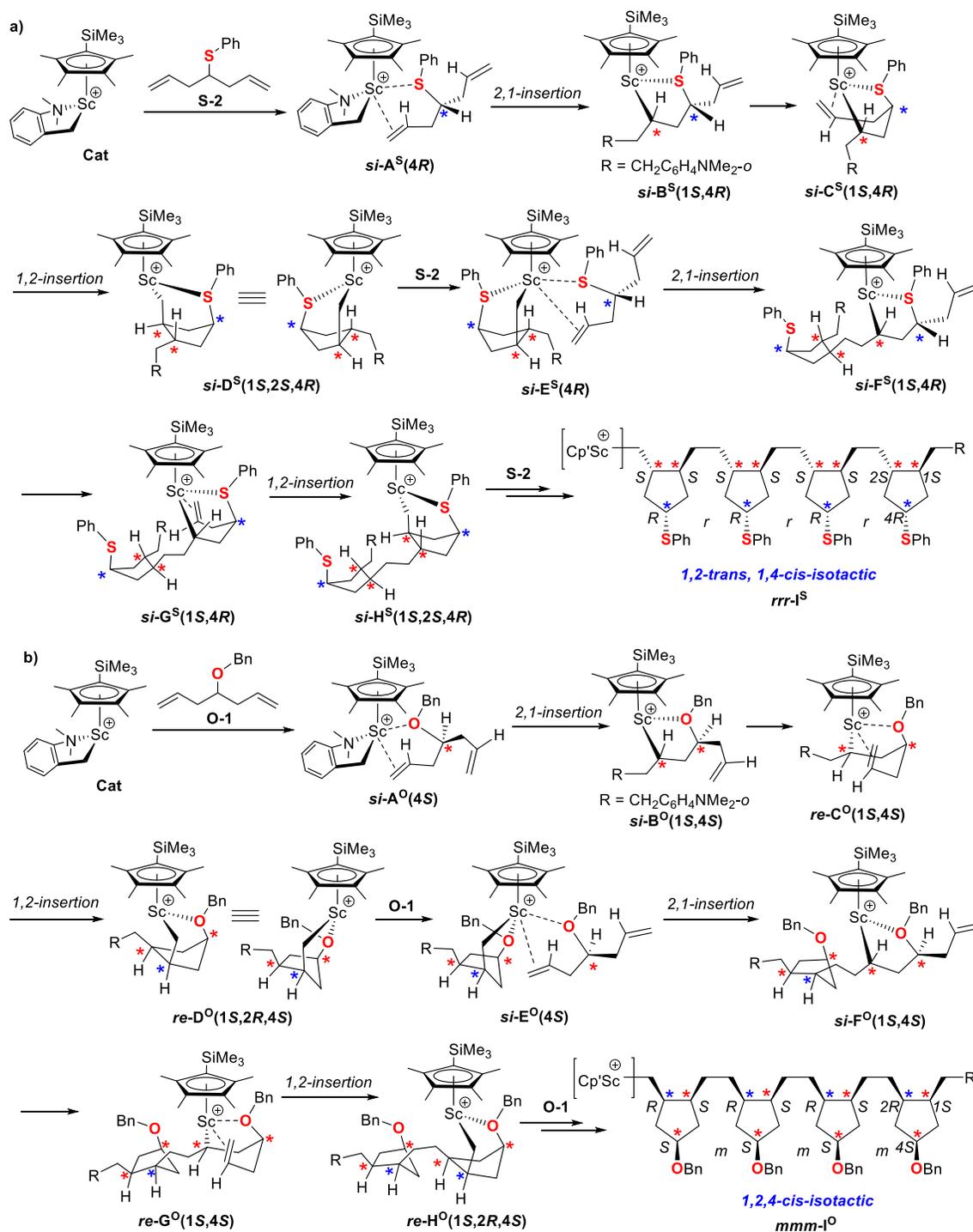
**Figure 3.** Computational analysis of the insertion/cyclization of first molecule of O-1 by the cationic species (Cat) generated by the reaction of Sc-3 with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . (A) DFT calculated energy profile. (B) Structures of the stationary points shown in the energy profile. The less favored pathway is pale-colored. R =  $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_{2-o}$ , TS: transition state,  $\Delta G_{\text{sol}}$ : Relative Gibbs free energy in solution.

In the case of O-1 (Figure 3), the *si*-coordination insertion mode of the first C=C bond is also more kinetically favorable than the *re*-fashion. In contrast to S-2, however, in the two *si*-coordination insertion modes, the pathway of  $si\text{-A}^0(4S) \rightarrow si\text{-TS-A}^0(1S,4S) \rightarrow si\text{-B}^0(1S,4S)$  is more energetically favored than that of  $si\text{-A}^0(4R) \rightarrow si\text{-TS-A}^0(1S,4R) \rightarrow si\text{-B}^0(1S,4R)$  (Figure 3). This indicates that the *S* configuration on the C4 atom of O-1 becomes more favorable during the *si*-coordination insertion of the first C=C bond. In the cyclization step, the  $re\text{-C}^0(1S,4S)$ -involved intramolecular insertion of the remaining C=C bond into the Sc-alkyl bond is significantly more favorable than that of  $si\text{-C}^0(1S,4S)$  (barriers of  $9.7 + 5.8 = 15.5$  vs  $22.9 + 5.8 = 28.7$  kcal/mol, Figure 3). The incorporation of the second O-1 monomer was also calculated to favor the similar way as the first monomer adopted (Figure S119). Repetition of these *si*-insertion and *re*-cyclization modes could therefore afford the isotactic polymer product, being in line with the experimentally observed selectivity.

#### Mechanism of the Sc-Catalyzed Cyclopolymerization of S-2 and O-1.

On the basis of the DFT calculations described above, the possible scenarios of the regio- and stereospecific cyclopolymerization of S-2 and O-1 by Sc-3 are shown in Schemes 2a and 2b, respectively. The chelation of the Sc atom by S-2 with the S atom and a C=C bond occurs in a *si*-coordination fashion to give the most favorable  $si\text{-A}^s(4R)$  configuration (Scheme 2a). The subsequent 2,1-insertion of the Sc-coordinated C=C bond into the Sc- $\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_{2-o}$  bond would generate the  $si\text{-B}^s(1S,4R)$  intermediate. The intramolecular *si*-coordination of the remaining C=C bond to the Sc atom followed by 1,2-sinsertion into the Sc-C  $\sigma$  bond via  $si\text{-C}^s(1S,4R)$  may then take place to give the thermodynamically and kinetically favored 1,2-*trans* cyclopentane species  $si\text{-D}^s(1S,2S,4R)$ . Similarly, the *si*-coordination of the second monomer S-2 to the Sc atom (to give  $si\text{-E}^s(4R)$ ) and the subsequent *si*-2,1-insertion would yield  $si\text{-F}^s(1S,4R)$ . The intramolecular *si*-1,2-insertion (cyclization) of the remaining C=C bond via  $si\text{-G}^s(1S,4R)$  should generate another ECP unit (see  $si\text{-H}^s(1S,2S,4R)$ ) with a configuration

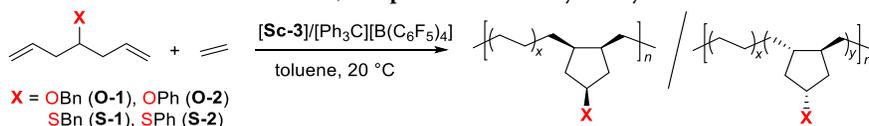
## Scheme 2. Possible Mechanisms of Regio- and Stereoselective Cyclopolymerization of S-2 (a) and O-1 (b) by Sc-3



identical to that in **si-D<sup>S</sup>(1S,2S,4R)**. The incorporation of the third S-2 monomer into **si-H<sup>S</sup>(1S,2S,4R)** in the same manner should then afford the 1,2-*trans*, 1,4-*cis*-fused ECP microstructures with isotactic stereoregularity (**rrr-I<sup>S</sup>**).

In the case of monomer O-1 (Scheme 2b), the chelation of the Sc atom with the O atom and a C=C bond would preferably give the **si-A<sup>O</sup>(4S)** configuration, as shown by the DFT analysis. The subsequent 2,1-insertion of the Sc-coordinated C=C bond into the Sc-CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2-o</sub> bond should yield

the **si-B<sup>O</sup>(1S,4S)** intermediate. The intramolecular *re*-recoordination of the remaining C=C bond to the Sc atom followed by 1,2-insertion into the Sc-C σ bond via **re-C<sup>O</sup>(1S,4S)** could give the thermodynamically and kinetically favored 1,2,4-*cis*-substituted ECP species **re-D<sup>O</sup>(1S,2R,4S)**. Similarly, the successive incorporation of the second and third O-1 monomers in a *si*-2,1-/*re*-1,2-insertion/cyclization manner would afford the isospecific 1,2,4-*cis*-fused ECP units **mmm-I<sup>O</sup>**.

Table 2. Copolymerization of Heteroatom-Functionalized 1,6-Heptadienes with Ethylene by Sc-3<sup>a</sup>

run	diene (D)	D/[Sc-3]	time (min)	yield (g)	diene conv. (%)	activity (g mol <sup>-1</sup> Sc <sup>-1</sup> h <sup>-1</sup> atm <sup>-1</sup> )	$M_n^b$ ( $\times 10^3$ g mol <sup>-1</sup> )	$M_w/M_n^b$	i.r. <sup>c</sup> (%)	1,2- <i>trans</i> -1,4- <i>cis</i> / 1,2,4- <i>cis</i> <sup>d</sup>	$T_g^e$ (°C)	$T_m^e$ (°C)
1	O-1	100/1	10	0.30	74	-	14.1	1.53	100	6/94	10	116
2	O-2	100/1	5	0.47	50	282	55.9	2.05	9	7/93	-19	126
3	O-2	500/1	30	2.16	62	216	100.8	2.20	15	7/93	-17	127
4	O-2	1000/1	45	3.56	65	153	147.9	1.74	25	7/93	-9	n.o. <sup>f</sup>
5	S-1	100/1	90	0.40	88	13.3	24.4	1.88	74	75/25	8	n.o. <sup>f</sup>
6	S-2	100/1	0.5	0.40	62	2400	29.6	1.45	19	94/6	14	120
7	S-2	200/1	1.5	0.79	77	1580	18.5	2.35	35	94/6	21	113/139
8	S-2	500/1	3	2.00	94	2000	14.7	3.89	77	94/6	29	n.o. <sup>f</sup>

<sup>a</sup> Conditions: [Sc-3] (0.02 mmol), [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.02 mmol), ethylene (1 atm), toluene (50 mL) at 20 °C. <sup>b</sup> Determined by GPC in 1,2-dichlorobenzene at 145 °C against polystyrene standard. <sup>c</sup> Incorporation ratio of D, determined by <sup>1</sup>H NMR analysis. <sup>d</sup> Determined by <sup>13</sup>C NMR analysis. <sup>e</sup> Determined by DSC. <sup>f</sup> n.o. = not observed.

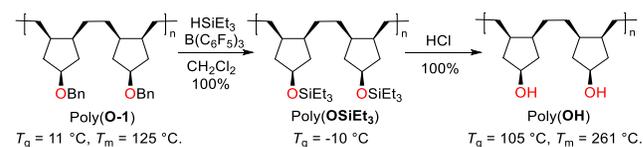
**Copolymerization of Heteroatom-Functionalized 1,6-Heptadienes with Ethylene.** With the establishment of the regio- and stereoselective cyclopolymerization of the heteroatom-functionalized 1,6-heptadienes, their copolymerization with ethylene was also examined (Table 2). Under the coexistence of O-1 and ethylene (1 atm) with [O-1]/[Sc-3] = 100/1, only the homopolymer of O-1 was formed (Table 2, run 1). This is probably due to the strongly coordinating ability of the benzyloxy group in O-1, which may hamper the coordination/insertion of ethylene at the catalyst metal center. By contrast, the copolymerization of the phenoxy-substituted monomer O-2 with ethylene occurred rapidly under the same conditions, although the homopolymerization of O-2 was less efficient. With [O-2]/[Sc-3] = 100/1 under 1 atm of ethylene at room temperature, a copolymer product with  $M_n = 55.9 \times 10^3$  g mol<sup>-1</sup> and O-2 incorporation of 9 mol% was obtained in 5 min (Table 2, run 2). As the [O-2]/[Sc-3] ratio was raised to 500/1 and 1000/1, the molecular weight ( $M_n$ ) of the resulting copolymers significantly increased to  $100.8 \times 10^3$  g mol<sup>-1</sup> and  $147.9 \times 10^3$  g mol<sup>-1</sup>, and the O-2 incorporation ratio increased to 15 mol% and 25 mol%, respectively (Table 2, runs 3 and 4). The <sup>13</sup>C{<sup>1</sup>H} NMR analyses revealed that the copolymers contained predominantly isolated 1,2,4-*cis* ECP units (Figures S74-S81). Uncyclized pendency vinyl group was not observed, suggesting that the cyclization step competed well against ethylene insertion in the present copolymerization.

The copolymerization of S-1 and ethylene (1 atm) with [S-1]/[Sc-3] = 100/1 afforded the corresponding sulfur-functionalized copolymer with 74 mol% incorporation of the S-1 monomer and a 75/25 mixture of the 1,2-*trans*-1,4-*cis*- and 1,2,4-*cis*-ECP units (Table 2, run 5). The copolymerization of S-2 and ethylene with [S-2]/[Sc-3] = 100/1, 200/1, and 500/1 gave the copolymers with the S-2 incorporation ratio = 19, 35, and 77 mol%, respectively (Table 2, runs 6-8). The copolymers possessed predominantly the 1,2-*trans*, 1,4-*cis*-ECP units, similar to the homopolymerization of S-2.

**Transformations of a Cyclic Polymer.** Replacement of the benzyl groups in poly(O-1) ( $M_n = 86.5 \times 10^3$  g mol<sup>-1</sup>, Table 1, run 4) with the triethylsilyl group could be achieved by reaction with Et<sub>3</sub>SiH in the presence of a catalytic amount of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, quantitatively affording the Et<sub>3</sub>SiO-substituted

poly(OSiEt<sub>3</sub>) (Scheme 3). Poly(OSiEt<sub>3</sub>) exhibited a much lower  $T_g$  (-10 °C) than that of poly(O-1) ( $T_g = 11$  °C) without showing a  $T_m$  or  $T_c$  in the DSC profile (Figure S111). The protonolysis of poly(OSiEt<sub>3</sub>) by aqueous HCl in THF gave the corresponding HO-functionalized polymer poly(OH). Poly(OH) demonstrated excellent thermal stability ( $T_g = 105$  °C,  $T_m = 261$  °C,  $T_d$  (decomposition temperature) = 400 °C; Figures S114 and S115) and excellent solvent resistance (insoluble in dichlorobenzene at 145 °C).

### Scheme 3. Transformations of Poly(O-1)



## CONCLUSION

In summary, we have achieved for the first time the regio-, diastereoselective and highly stereoregular cyclopolymerization of ether- and thioether-functionalized 1,6-heptadienes and their copolymerization with ethylene by using a half-sandwich scandium catalyst such as Sc-3. The unprecedented diastereoselectivity and stereoregularity could be ascribed to the unique interaction between the catalyst metal center and the heteroatom in a diene monomer, as shown by DFT calculations. This protocol has afforded a new family of heteroatom-functionalized cyclic polyolefins which were difficult to prepare previously. Our findings may also help design and synthesize new catalysts for efficient and regio-, stereoselective cyclopolymerization and related transformations of various functional dienes.

## EXPERIMENTAL SECTION

**Materials and methods.** All manipulations of air and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen-filled Mbraun glovebox. Nitrogen was purified by being passed through a Dryclean column DC-A4 (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (97%) was purchased from Strem Chemical Corporation and used without purification. Rare-earth catalysts Cp\*Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-

o)<sub>2</sub> (Sc-1: Cp' = C<sub>5</sub>H<sub>5</sub>, Sc-2: Cp' = C<sub>5</sub>Me<sub>4</sub>H, and Sc-3: C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>), were synthesized according to the literatures.<sup>9,12</sup> 4-Functionalized-1,6-heptadienes (O-1, O-2, S-1 and S-2) were synthesized from 4-hydroxy-1,6-heptadien (purchased from Aldrich) according to the literatures.<sup>8a,13</sup> 4-Functionalized-1,6-heptadienes (O-1, O-2, S-1, and S-2) were purified by distillation from Al(octyl)<sub>3</sub> (25 wt.% in hexanes) before use.

The deuterated solvents benzene-d<sub>6</sub> (99.6 atom % D), CDCl<sub>3</sub> (99.8 atom % D), and 1,1,2,2-tetrachloroethane-d<sub>2</sub> (99.6 atom % D) were obtained from Kanto Chemical Co. Inc. and Cambridge Isotope. The NMR data of the polymers were obtained on a Bruker AVANCE III HD 500 NMR (FT, 500 MHz for <sup>1</sup>H; 125 MHz for <sup>13</sup>C) spectrometer with CDCl<sub>3</sub> (at 26.8 °C) or 1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (at 120 °C) as a solvent. The chemical shifts for <sup>1</sup>H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.16 ppm for C<sub>6</sub>D<sub>6</sub>, 7.26 ppm for CDCl<sub>3</sub>, 6.0 ppm for 1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>). The chemical shifts for <sup>13</sup>C{<sup>1</sup>H} NMR were recorded in ppm downfield using the central peak of C<sub>6</sub>D<sub>6</sub> (128.06 ppm), CDCl<sub>3</sub> (77.16 ppm), 1,1,2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> (73.78 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. The abbreviations *s*, *d*, *t*, *q* and *m* stand for singlet, doublet, triplet, quartet and multiplet in that order.

The molecular weights and the molecular weight distributions of homopolymers were determined at 40 °C by gel permeation chromatography (GPC) on a HLC-8320 GPC apparatus (Tosoh Corporation). THF was employed as an eluent at a flow rate of 0.35 mL/min. The molecular weights and the molecular weight distributions of all the copolymers were determined at 145 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8321GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene (DCB) was employed as an eluent at a flow rate of 1.0 mL/min. The calibration was made by use of polystyrene standard (Tosoh Corporation). The DSC measurements were performed on a DSC 7000X (HITACHI) at a rate of 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 180 °C (or 300 °C), cooling at 10 °C/min to -100 °C (or -30 °C) and then recording the second DSC scan. TGA was recorded on TGA-50 thermogravimetric analyzer (Shimadzu). The temperature range is 30 to 500 °C at the heating rate of 10 °C min<sup>-1</sup>.

**General procedure for the homopolymerization of functionalized dienes.** Polymerization of O-1 (Table 1, run 3): In a THF-free glovebox, a toluene solution (2 mL) of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (18.4 mg, 0.02 mmol) was slowly added to a toluene solution (2 mL) of (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> (Sc-3, 10.1 mg, 0.02 mmol) under magnetic stirring in a 10 mL glass tube with cap. After the mixture was stirred for 5 min, O-1 (404.0 mg, 2.0 mmol) was added into the reaction solution. The tube was sealed and kept stirring in the glovebox at room temperature for 1 hour. The polymerization was quenched by addition of methanol (10 mL). Then the mixture was poured into methanol (50 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60 °C to a constant weight (404 mg, 100% yield).

**General procedure for the copolymerization of functionalized dienes with ethylene (Table 2, run 2).** In a THF-free glovebox, a toluene solution (45 mL) of O-2 (376 mg, 2 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 paraffin oil-sealed stopper by use of 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 (5 mL) of (C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-o)<sub>2</sub> (Sc-3) (10.1 mg, 0.02 mmol) and [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (18.4 mg,

0.02 mmol) was then added through a syringe under vigorous stirring. The polymerization was quenched after 5 minutes by adding methanol (50 mL). The polymer product was collected by filtration, washed with methanol, and then dried in vacuum at 100 °C to a constant weight (0.47 g). The resulting polymer was soluble in toluene, dichlorobenzene and 1,1,2,2-tetrachloroethane. Solvent fractionation experiments suggest that no homopolyethylene was formed. The phenoxy substituted cyclic unit content in the copolymer was calculated from the <sup>1</sup>H NMR analysis.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.xxxxxx.

Experimental and computational details, NMR spectra and other characterization data, including Figures S1-S119 (PDF).

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### Notes

The authors declare no competing financial interests.

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## TOC graphic

