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A Strategy and the Mechanism to Access Hydroxy Functionalized Polypropylene via Coordination Polymerization

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Abstract: Preparation of polyethylene containing hydroxyl groups has been already industrialized through radical copolymerization under harsh conditions followed by alcoholysis. On contrary, the hydroxyl functionalized polypropylene has been a rather challenging project of polymer science. Propylene can't be polymerized via radical mechanism, and its coordination copolymerization with polar monomers is frustrated by the catalyst poison. Herein we report a new strategy to reach this target. The coordination polymerization of allenes by rare-earth metal precursors affords pure 1,2-regulated polyallenes, which are facilely transferred to poly(ally alcohol) analogues followed by hydroboration-oxidation. Strikingly, the copolymerization of allenes and propylene gives the unprecedented hydroxyl functionalized polypropylene after post-polymerization modification. The mechanism elucidated by DFT simulation suggests the kinetically favored rather than thermo dynamical control.

Synthesis of hydroxyl functionalized (co)polymers in particular polyolefins has been the pursuing target of polymer scientists, because hydroxyl group endows the materials with hydrophilicity and excellent surface properties, besides, it is a reactive group to be facilely transferred into other functionality. For instance, polyethylene (PE) is the most famous and widely applied hydrophobic plastics,[1] whilst its hydroxyl functionalized derivatives such as poly(vinyl alcohol) (PVA) and poly(ethylene-vinyl alcohol) (EVOH) possess rather unique properties and apply in different fields.[2] To date the copolymerization of ethylene with a broad scope of functional vinyl monomers has been thoroughly investigated and achieved great successes,[3] except hydroxyl functionalization. Fortunately, radical polymerization of vinyl acetate or copolymerization with ethylene under high temperature and pressure followed by post-polymerization alcoholysis affords PVA and EVOH, which is a rather efficient and industrialized method.[4] On contrary, the synthesis of the corresponding hydroxyl functionalized polypropylene (PP) from the direct polymerization of allylic alcohol (AA) or its copolymerization with propylene encounters serious problems. Although allyl alcohol (AA) is a stable chemical, it is hard to propagate into a high molecular weight PAA via radical polymerization even under the assistance of a Lewis acid;[5] and the anionic and coordination catalysts react with the hydroxyl group prior to the C=C bond. The more efficient manner of getting a linear PAA with high molecular weight (~30 kDa) and a block copolymer with styrene P(AA-St) is reported recently by Hillmyer via the reversible addition-fragmentation chain transfer (RAFT) radical polymerization of the Boc-protected (bis(tert-butyloxy carbonate)) vinyl ester or vinyl amide followed by post-polymerization reduction.[6] The copolymerization of propene with allyl acetate, which is another way to reach PP that includes hydroxyl functionalities after hydrolysis. While the insertion rate of allyl acetate was poor. [7] Therefore, coordination polymerization of the only adopted manner for fabricating PP hasn't been applied to prepare PAA or hydroxy containing PP, since even the Boc-protected polar monomers are poisonous to the employed coordination catalysts.

Allene compounds are widely employed as building blocks in the field of organic synthesis due to the highly active cumulative double bonds.[8] They also attract attention of polymer scientists, since the corresponding polymers possess double bonds that can be transferred into other functionalities via hydrogenation[9], epoxidation[10] and hydrosilylation[11] *etc* post-polymerization modification. However, the high activity of the cumulative double bonds arouses difficulty to control polymer microstructures through either radical or cationic polymerization.[12] The well controlled polymerization of allenes is achieved by using coordination catalysts. Of which the Ti[10] based systems, η^3-allyl NiOCOCF$_3$[13] and the rare-earth metal[14] catalysts display almost pure 2,3-selectivity. Nevertheless, the resultant polymers contain the internal C=C double bonds that are chemically stable and reluctant to be further transferred. In contrast, the 1,2-selective polymerization of allenes gives polymers with the active terminal C=C double bonds, however, which is sterically disfavored.

Herein, we report the highly active and distinguished 1,2-selective coordination polymerization of allene monomers (Chart 1) and its copolymerization with propylene by using the rare-earth metal precursors (Chart 2). The resultant poly(allene)s have high molecular weights, which are facilely transferred into analogous PAAs through hydroboration-oxidation reactions under mild conditions. Strikingly, the copolymerization of propylene and allene monomers is also successul to afford the unprecedented hydroxy functionalized PP after post-polymerization modification. The mechanism for the activity and 1,2-selectivity is elucidated through DFT simulation, indicating a

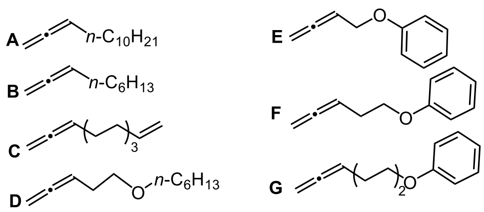

Chart 1. Allene Monomers.

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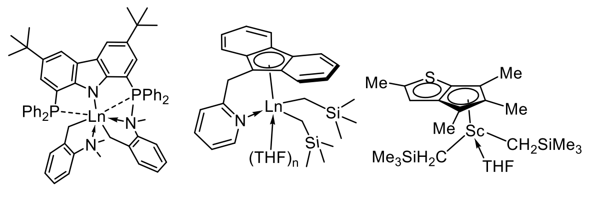


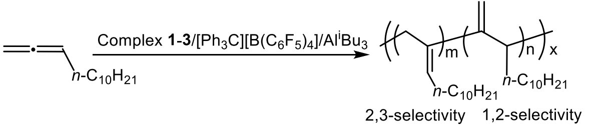
Ln=Sc(**1a**), Y(**1b**)
Ln=Sc (**2a**), n=0
Ln= Y (**2b**), n=1
3

Chart 2. Rare-earth Metal Precursors **1**-**3**.

kinetically favored rather than the thermo dynamical control procedure.

The PNP-carbazolide scandium (**1a**) and yttrium (**1b**) bis(alkyl) complexes, upon activation of $[Ph_3C][B(C_6F_5)_4]$ show distinguished activity and perfect *cis*-1,4-selectivity for the polymerization of conjugated diene monomers.[15] Both were firstly tempted to catalyze *n*-decylallene polymerization (Table 1, entries 1 and 2) but completely inert. Then, the constrained geometry-configuration catalysts (CGC), the methylene pyridine side-armed fluorenyl rare-earth metal bis(alkyl) complexes $(Flu\text{-}CH_2\text{-}Py)Ln(CH_2SiMe_3)_2(THF)_n$ (Ln= Sc, n =0, **2a**; Y, n = 1, **2b**) in combination with $[Ph_3C][B(C_6F_5)_4]$ and Al^iBu_3 were employed. The polymerization of *n*-decylallene with the yttrium precursor **2b** afforded only trace amount of polymer, contrary to its behavior towards phenylallene polymerization reported previously to exhibit high activity and pure 2,3-selectivity.[14] Switching to the more Lewis acidic scandium precursor **2a**, the polymerization was performed efficiently to reach 90% conversion in 24 h. The isolated polymer showed an improved 1,2-regularity (72%) (Table 1, entries 3 and 4). Therefore, we turned to the less bulky half-sandwich thiophene-fused-cyclopentadienyl scandium complex **3** that is highly active for ethylene polymerization.[16] The polymerization went smoothly to reach 92.2% conversion under the same conditions to those using precursors **3** and gave a poly(*n*-decylallene) with a moderate molecular weight (M_n = 1.8×10^4) (Table 1, entry 5). The ^{1}H NMR spectrum of the resultant polymer (Figure 1, top) shows two groups of broad peaks at δ 5.21 and 2.8 assigned to the terminal vinyl protons H_a and methine proton H_b on the 1,2-regulated polymer chains, while the broad resonances within the range of δ 2.0 to 0.5 are attributed to the alkyl $C_{10}H_{21}$ protons. The peak at δ 5.63 assigned to the internal methylene protons H_c is rather weak. The ratio of the integral intensities of $H_a : H_c$ indicates a 94% 1,2-tacticity, higher than those obtained from any other catalysts reported to date. Intrigued by these results, we investigated in details the catalytic performance of complex **3** under various conditions. The representative data were collected in Table 2. Changing the *n*-decylallene-to-Sc ratio from 100:1 to 500:1, the molecular weight of the resultant poly(*n*-decylallene) increased correspondingly from M_n = 1.8×10^4 to 3.6×10^4 while the molecular weight distribution maintained constantly (Table1, entry 5; Table 2, entries 1 and 2). This indicated that the polymerization was controllable and the active species was single-sited, avoiding any side reactions and crosslinking products. Noted that addition of Al^iBu_3 (Al: Sc = 10:1) to the above binary system $[Sc]/[Ph_3C][B(C_6F_5)_4]$ did not show any obvious influence on the catalytic performances (Table 2, entry 3). Lowering the polymerization temperature to 0ºC, a higher molecular weight polymer with a distinguished 1,2-regularity (M_n = 3.7×10^4, 96%) was afforded. Further decreased the temperature to -20ºC and -40ºC, respectively, the polymerization could still perform fluently to achieve an over 85% conversion albeit at a prolonged polymerization time. Meanwhile, the 1,2-selectivity increased strikingly over 99% (Figure 1, middle). In the ^{13}C NMR spectrum the terminal vinyl carbon C_a shows a resonance at δ 109 and the ternary carbon C_b displays a sharp singlet at δ 152, whilst the methine carbon C_c appears at δ 51. There are no resonances from the other regularities, indicating an almost pure 1,2-regularity (Figure 2), which is further confirmed by the HSQC spectrum analysis (Figure S39). Compared to the 2,3-selectivity for allene polymerization the 1,2-selectivity means a spacially disfavored route, therefore, the such recorded high value of 1,2-selectivity, as far as we are aware, is indeed unconventional. The physical property of poly(*n*-decylallene) products is strongly dependent on the microstructure. The polymer having a 94% 1,2-tacticity possesses a T_g value of -27 ºC without melting point (T_m), while that bearing an over 99% 1,2-tacticity gives a melting point T_m= 39 ºC owing to its more regulated microstructure albeit containing long soft alkyl side chains (Figure 3).

Table 1. Polymerization of *n*-decylallene catalyzed by complexes **1**-**3**. [a]



Entry	Cat	Conv.(%)	1,2% [b]	M_n[c]×10^{-4}	PDI[c]	T_g/ T_m[d] (ºC)
1	**1a**	trace	-	-	-	-/-
2	**1b**	0	-	-	-	-/-
3[e]	**2a**	90	72	1.3	1.39	-27/-
4[e]	**2b**	trace	-	-	-	-/-
5[f]	**3**	92.2	94	1.8	1.47	-27/-

[a] Conditions: Cat 10 μmol, Mon/Cat =100, $[Ph_3C][B(C_6F_5)_4]$ 10 μmol, Toluene 0.2mL, T=20 ºC, Time 24h. [b] Measured by ^{1}H NMR in $C_6D_4Cl_2$ at 100 ºC. [c] Determined by GPC in $C_6H_3Cl_3$ at 150 ℃ against polystyrene standard. [d] Determined by DSC. [e] Al^iBu_3 10 μmol. [f] Al^iBu_3 20 μmol.

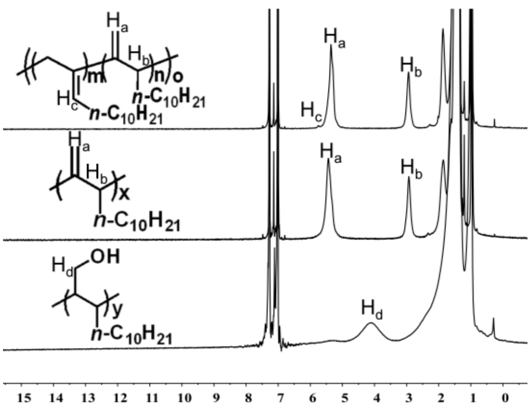


Figure 1. ^{1}H NMR spectrum of poly(*n*-decylallene) obtained at 20 ºC (top, Table 1, entry 5), -40 ºC (middle, Table 2, entry 6) and hydroxylated polymer (bottom) (400MHz, $C_6D_4Cl_2$, 100 ºC).

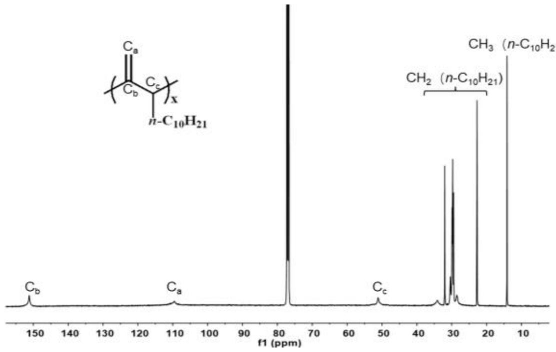


Figure 2. ^{13}C NMR spectrum of poly(*n*-decylallene) obtained at -40 °C (Table 2, entry 6) (125 MHz, $CDCl_3$, 25 °C).

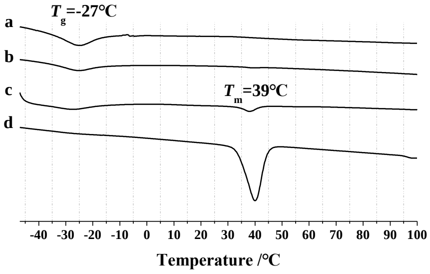


Figure 3. DSC traces of poly(*n*-decylallene)s with different 1,2-tacticities. a: 1,2% = 94% (Table 1, entry 5); b: 1,2% = 96% (Table 2, entry 4); c: 1,2% = 98% (Table 2, entry 5); d: 1,2% > 99% (Table 2, entry 6).

The distinguished performances of complex **3** towards *n*-decylallene drove us to explore the polymerizations of allene derivatives bearing different substituents. Monomer **B** containing *n*-hexyl group was polymerized to give poly(*n*-hexylallene) with the identical 1,2-regularity as poly(n-decylallene), suggesting that the length of the side alkyl chain has no obvious influence on the selectivity (Table 2, entries 8 and 9). The polymerization of monomer **C** possessing a terminal C=C double bond exhibited the regio-selectivity at the allene unit exclusively, indicating the high reactivity of the cumulative double bonds than the discrete double bond (Table 2, entries 10 and 11). To investigate the influence of polar substituents, monomers **D**, **E**, **F** and **G** were synthesized. Monomer **D** has a propyloxo fragment attached to the cumulative double-bonds. During the polymerization the oxygen atom is geometrically available to back-bite the active Sc^{3+} ion together with the cumulative unit, generating a strong chelate to retard the polymerization (Scheme S1). Replacing the *n*-C_6H_{13} species in **D** by a phenyl group is anticipated to avoid oxygen from poisoning the active species, thus, monomer **F** indeed could be polymerized sluggishly to reach 42% conversion in 72h albeit with a rather low 1,2-selectivity (13.0%). This might be attributed to the weak back-biting chelation of the phenoxyl to the active metal center to arouse a crowding and variable coordination-insertion environment. Monomer **E** bearing the methylene unit between the cumulative double bonds and phenoxyl group was completely inert, which coordinates to the active species and then isomerizes to 1-phenoxy-1,3-butadiene through 1,3-hydrogen shift.[17] Strikingly, monomer **G** containing a butyl spacer polymerized rather fluently to generate pure 1,2-tacticity (Table 2, entries 12-16).

Then the mechanism of highly active and chemoselective (1,2 vs. 2,3) performance for the polymerization of allenes **A**, **B**, **C** or **G** was then elucidated at the DFT level (B3PW91) based on catalysts **2a** and **3**. In the following, only insertion of monomer **B** was considered as representative of the allene polymerization. Experimentally, complex **2a** appears to be less 1,2 selective than catalyst **3**. The two first insertions (1,2 and 2,3) were computed for catalyst **2a** (see Figure S64). It is found that there is a clear kinetic competition between the two insertions in line with the moderate selectivity of this complex for the 1,2 insertion. Indeed, the first insertion seems to be 1,2 (barrier of 10.0 vs. 13.6 kcal/mol) whereas the second one might be a 2,3 (11.9 kcal/mol vs. 6.9 kcal/mol). On the other hand, the reactivity of complex **3** seems very different (Scheme 1). Interestingly, the 1,2 insertion appears to be kinetically always more favorable than the 2,3 one (barrier of 7.0 vs. 10.4 kcal/mol for the first insertion and of 0.5 vs. 8.0 kcal/mol for the second one). This is in line with the greater selectivity for the 1,2-insertion observed experimentally. This selectivity appears to be due to the fact that no stable 1,2 adduct can be formed whereas stable 2,3 can. The stability of the later is therefore reducing the 2,3 reactivity. However, it should be noticed that 1,2 selectivity appears to be kinetically driven as the 2,3-insertion product, that appears to be a π-allyl, is thermodynamically favored. Therefore, at high temperature, formation of the thermodynamic product should be observed, reducing the 1,2 selectivity, whereas the 1,2 selectivity should be greater at low temperature (low energy demand for the reaction). This is in perfect agreement with the experimental results (Table 2, entries 8 and 9). Therefore, the reaction sequence is controlled by the kinetically facile 1,2 insertion but not by the coordination of the monomer to the metal center. This finding is quite unusual for classical coordination-insertion mechanisms and is associated to the steric repulsion between the growing polymer chain and the allene, which prevents the formation of a 1,2 adduct.

The hydrolysis of the obtained polymers was performed via hydroboration with BH_3 followed by oxidation with H_2O_2 under mild conditions. In the ^1H NMR spectrum the peak at δ 5.21 assigned to the terminal vinyl protons is almost invisible, while the broad resonance at δ 3.75 is attributed to the methylene CH_2 group adjacent to the hydroxyl group, suggesting the rather high efficiency of this post-polymerization modification (Figure 1, bottom). In the FTIR (cm^{-1}) trace, the characteristic C=C stretching vibration at 1648 arising from 1,2-regulated poly(alkylallene) is nearly absent while a strong and broad resonance at 3300 cm^{-1} is attributed to the stretching vibration of the newly generated O-H bond (Figure S61).

The surface property of the nonpolar poly(alkylallene) is greatly improved after hydrolysis to decyl substituted PAA by giving a smaller static water contact angle (WCA) of 96.2° as compared to 107.7° for poly(alkylallene).[18]

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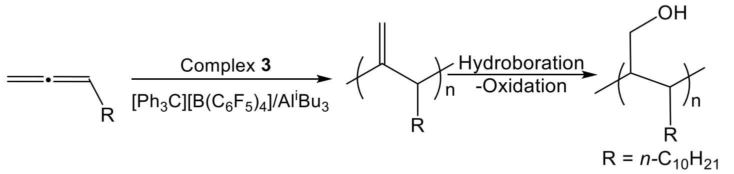
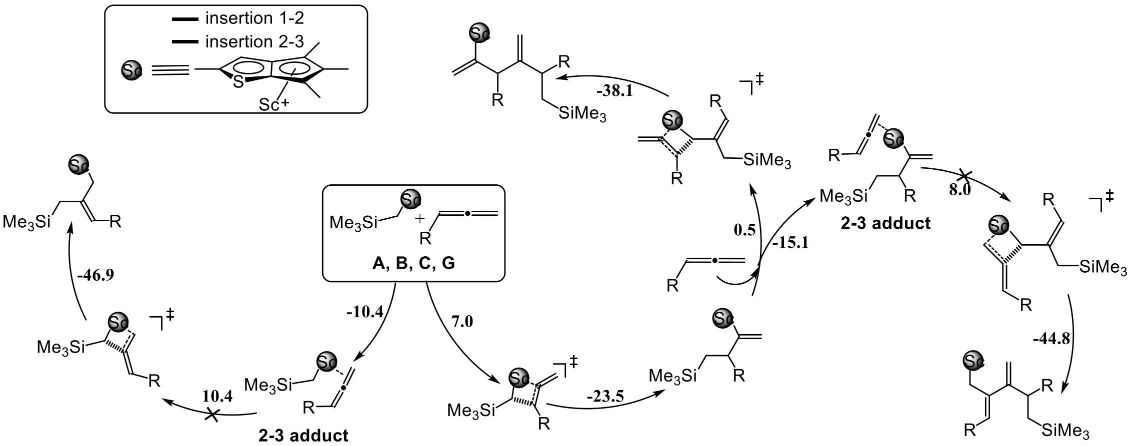
Table 2. Polymerization of allene derivatives catalyzed by the thiophene-fused cyclopentadiene ligated scandium complex **3** and post-functional scheme. [a]



Entry	Mon	Mon/Cat	T/℃	Time/h	Conv. (%)	1,2 %[b]	M_n[c]×10^{-4}	PDI[c]	T_g/ T_m[d] (°C
1	**A**	200	20	24	94.6	94	2.2	1.67	-27/-
2	**A**	500	20	24	82.4	94	3.6	1.67	-27/-
3	**A**[e]	100	20	24	94.8	94	1.9	1.60	-27/-
4	**A**	100	0	24	72.8	96	3.7	1.30	-27/-
5	**A**	100	-20	36	86.6	98	4.6	1.25	-27/39
6	**A**	100	-40	36	85.1	>99	7.6	2.07	-/39
7	**A**	500	-40	96	91.2	>99	25.6	2.62	-/39
8	**B**	100	20	24	83.8	94	1.1	1.71	-10/-
9	**B**	100	-40	36	81.9	>99	5.1	1.56	-/-
10	**C**	100	20	24	89.1	94	1.4	2.19	-32/-
11	**C**	100	-40	36	82.4	>99	5.0	1.82	-/-
12	**D**	100	20	24	0	-	-	-	-/-
13	**E**	100	20	24	0	-	-	-	-/-
14	**F**[f]	50	20	96	41.9	13.0	0.5	1.65	23/-
15	**G**	100	20	36	78.7	84.0	0.8	1.85	-2/-
16	**G**	100	-40	24	65.8	>99	2.8	1.60	-2/-

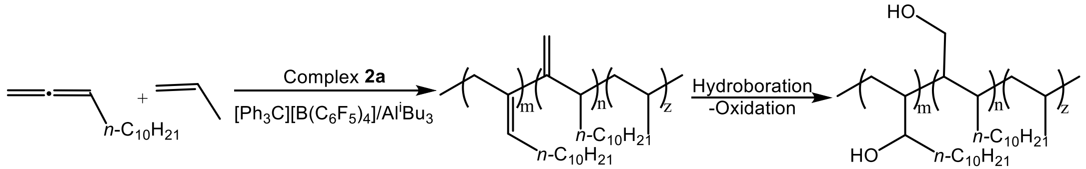
[a] Conditions used for polymerization: [Sc] 10 μmol, $[Ph_3C][B(C_6F_5)_4]$ 10 μmol, Al^iBu_3 20 μmol, Toluene 0.2mL. The data in table are for the polymers before post-functionalization. [b] Measured by ^1H NMR in $C_6D_4Cl_2$ at 100 °C [c] Determined by GPC in $C_6H_3Cl_3$ at 150 °C against polystyrene standard. [d] Determined by DSC. [e] [Sc] 10 μmol, $[Ph_3C][B(C_6F_5)_4]$ 10 μmol, Al^iBu_3 100 μmol. [f] [Sc] 20 μmol.

As compared to the extensive investigations on functionalizing polyethylene via coordination polymerization of ethylene with polar monomers,[3] that for polypropylene is rather rare. For one reason, polypropylene cannot be prepared via radical mechanism, which avoids radical copolymerization with vinyl acetylacetate; another is effcient catalysts for propylene coordination polymerization are very limited as compared to those for ethylene polymerization, thus those can survive in the copolymerization with polar monomers are scarce. The success of highly 1,2-selective polymerization of the nonpolar allene compounds stimulated us to attempt their copolymerization with propylene using the excellent precursor **3**. Unfortunately, trace amount of polymer was obtained, which might be due to the intense competition between the two monomers. Suprisingly to us, complex **2a** upon activation with $[Ph_3C][B(C_6F_5)_4]$ successfully aroused the copolymerization of allene monomer **A** and propylene in a high activity comparable to that of propylene homopolymerization and a rather high 1,2-selectivity (80%). Meanwhile the allene incorporation was sensitive to the propylene fraction in the reaction vessel, which increased with the decreases of propylene pressure and reaction temperature to reach up to 26.5% (Table 3). This meant a polypropylene containing as as high as 26.5% molar fraction of hydroxyl groups has been realized after post-functionalization, for the first time.



Scheme 1. Proposed mechanism for the polymerization of alkylallene monomers **A, B, C** and **G** by catalyst **3** (computed enthalpy of monomer **B** was provided (kcal/mol)).

Table 3. Copolymerization of *n*-decylallene and propylene by complex **2a** and post-functional scheme. [a]



Entry	Propylene (atm)	T/℃	Time/h	Yield/g	Allene %[b]	1,2%[b]	M_n[c] × 10^{-4}	PDI	T_g/T_m [d] (°C)
1	1	20	0.5	0.10	26.5	79	1.0	1.4	-40/-
2	1	20	1	0.26	10.3	79	0.8	1.6	-21/-
3	2	20	1	0.71	7.6	79	0.8	1.5	-17/-
4	4	20	1	1.18	5.1	79	0.9	1.4	-15/-
5	1	0	3	0.36	9.5	84	1.2	1.4	-19/3
6[e]	1	20	1	0.19	0	-	0.8	1.5	-6/-

[a] Conditions used for polymerization: [Sc] 10 μmol, Allene/[Sc]/[Ph$_3$C][B(C$_6$F$_5$)$_4$]=100:1:1 (mol/mol), Toluene, 2mL, Time, 1h, Temperature, r.t. The data in table are for the copolymers before post-functionalization. [b] Measured by ^{1}H NMR in CDCl$_3$ at 25 °C. [c] Determined by GPC in THF at 40 °C against polystyrene standard, [d] Determined by DSC, [e] Homopolymerization of propylene.

In summary, we have demonstrated that the unconventional highly 1,2-selective polymerization of polar and nonpolar alkylallene compounds can be achieved in high activity by using the rare-earth metal based catalytic systems. These alkyl substituted allene monomers are environmentally demanding, thus, from catalytic precursor viewpoint, a more opening coordination sphere is a precondition to show activity for allene polymerization. The half-sandwich thiophene-fused cyclopentadienyl ligated rare-earth metal precursors are sterically less bulky than the pyridinyl methylene fluorenyl and the tridentate PNP ligated rare-earth metal precursors, which exhibit higher activities. From allene monomer viewpoint, the long alkyl chain or a terminal double bond cannot prohibit the polymerization but the polar oxygen atom can terminate the polymerization by chelating steadily to the active metal center. With respect of chemo-selectivity, the 1,2-selective polymerization is kinetically favored rather than the thermo dynamical control. This work paves a new avenue to hydroxyl modification of non polar polymers via copolymerization synthon but to avoid the problem of catalysts being poisoned by the polar groups. Now, the copolymerizations of allenes with styrene and conjugated dienes and other simple olefins, are under investigation.

Acknowledgements

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Keywords: allene • polar monomer • copolymerization • hydroxylated polypropylene • rare-earth metal complex

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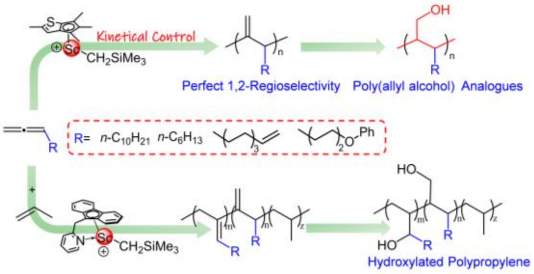
<td>The highly active and excellent 1,2-selective coordination polymerization of allenes has been achieved using rare-earth metal precursors. The resultant polyallens are facilely transferred into the first poly(allyl alcohol) direvatives through hydroboration-oxidation reactions. Strikingly, the copolymerization of propylene and allene monomers are also successul to afford the unprecedented hydroxy functionalized polypropylene after post-polymerization modification. The mechanism elucidated by DFT simulation suggests a kinetically favored rather than thermo dynamical control procedure.</td>
<td>
</td>
<td><i>Yuanhao Zhong,[a,b] Iskander Douair,[c] Tiantian Wang,[a,d] Chunji Wu,*,[a] Laurent Maron*,[c] and Dongmei Cui*,[a]</i>

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A Strategy and the Mechanism to Access Hydroxy Functionalized Polypropylene via Coordination Polymerization</td>
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