Review

Cationic rare earth metal alkyls as novel catalysts for olefin polymerization and copolymerization

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Abstract

Cationic rare earth metal alkyl species, generated by the treatment of mono(cyclopentadienyl) bis(alkyl) rare earth metal complexes with 1 equiv. of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$, act as an excellent catalyst for the polymerization and copolymerization of various olefins such as ethylene, 1-hexene, styrene, norbornene, dicyclopentadiene, and isoprene. These catalysts show unprecedented activity and regio- and stereo-selectivity and afford a series of new polymers which are difficult to be prepared previously.
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Keywords: Cationic rare earth metal alkyls; Olefin polymerization; Metallocene catalysis; Cyclic olefins; Styrene; Isoprene

## Contents

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1. Introduction

Cationic alkyl complexes of group 4 and late transition metals have been the subject of intensive investigations over the past two decades, because of their crucial importance in catalytic olefin polymerization [1]. In contrast, cationic alkyl species of rare earth (group 3 and lanthanide) metals are much less developed [2,3]. Compared to most transition metals which can show variable (different) oxidation states, rare earth metals usually adopt the 3+ oxidation state as the most stable oxidation state, which is not easily changed to other oxidation states under normal conditions. This nature could make rare earth metals unique candidates for formation of true "single-site" polymerization catalysts. This paper summarizes our recent studies on the olefin polymerization chemistry of cationic half-sandwich rare earth metal alkyl catalysts, with emphasis being placed on the unique features of rare earth metal catalysts [4–6].

## 2. Synthesis of half-sandwich rare earth metal bis(alkyl) complexes

The isolation of a half-sandwich rare earth metal bis(alkyl) complex bearing one cyclopentadienyl ligand is generally much more difficult than that of a mono(alkyl) complex with two cyclopentadienyl ligands, because of ligand redistribution problems [2,7]. An appropriate metal/ligand combination is rather critical. In the case of scandium, which is the smallest one in ion size in the rare earth series, the bis(trimethylsilymethyl) complexes bearing different cyclopentadienyl ligands, such as $[Cp'Sc(CH_2SiMe_3)_2(thf)]$ ($Cp' = C_5Me_4SiMe_3$ (**1**), $C_5H_3(SiMe_3)_2$-1,3 (**2**), C_5Me_5 (**3**)), have been prepared by the acid–base reaction between the scandium tris(alkyl) complex $[Sc(CH_2SiMe_3)_3(thf)_2]$ and one equiv. of the cyclopentadiene ligands $Cp'H$ (Scheme 1) [4]. For larger rare earth metal ions, the corresponding bis(alkyl) complexes bearing the $[C_5Me_4SiMe_3]^-$ ligand, $[(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(thf)]$ (Ln = Y (**4**), Gd (**5**), Dy (**6**), Ho (**7**), Er (**8**), Tm (**9**), Lu (**10**)), can be obtained in an analogous way (Scheme 2) [4,8]. However, when less sterically demanding ligands such as $C_5H_3(SiMe_3)_2$-1,3, C_5Me_5, or C_5H_5 are used for these metals, a mixture of mono(cyclopentadienyl)-coordinated and bis(cyclopentadienyl)-coordinated complexes is usually formed. The reaction of the silylene-linked cyclopendienyl-phosphine $Me_2Si(C_5Me_4H)PH(Cy)$ (Cy = cyclohexyl) with an equimolar amount of $Ln(CH_2SiMe_3)_3(THF)_2$
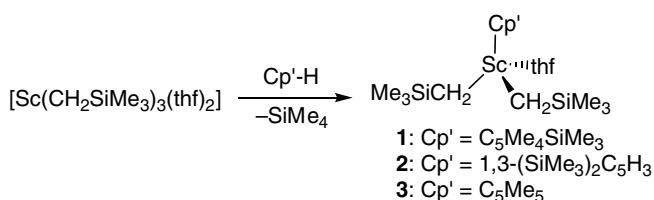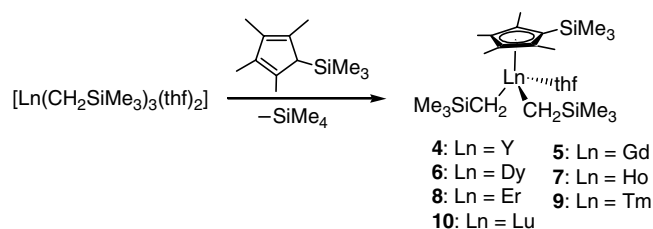
Scheme 2.
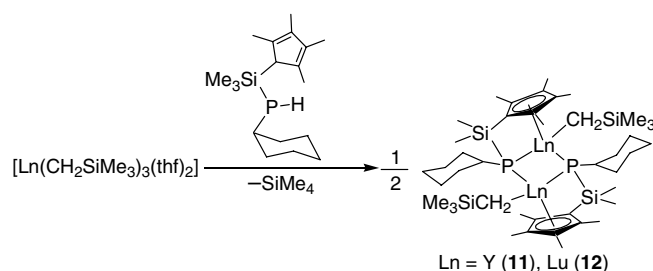
Scheme 3.

afforded the binuclear dialkyl complexes $[Me_2Si(C_5Me_4)\text{-}P(Cy)Ln(CH_2SiMe_3)]_2$ (Ln = Y (**11**), Lu (**12**)) (Scheme 3) [5]. Complexes **1**–**12** have all been structurally characterized by X-ray crystallographic studies.

3. Syndiospecific polymerization and copolymerization of styrene with ethylene

3.1. Syndiospecific, living polymerization of styrene

The neutral half-sandwich rare earth metal bis(alkyl) complexes $(C_5Me_4SiMe_3)Ln(CH_2SiMe_3)_2(thf)$ alone did not show activity for styrene polymerization at room temperature in toluene. When treated with 1 equiv. of $[Ph_3C]$-$[B(C_6F_5)_4]$, however, all of these complexes became active for the syndiospecific polymerization of styrene, with the activity being dependent on both the ion size of the central metals and the ancillary ligands (see Scheme 4) [4b]. Among the scandium complexes **1**–**3**, complex **1** showed the highest activity (up to 1.36×10^4 kg/(mol-Sc h)), which can be compared with the most active catalysts ever reported for syndiospecific styrene polymerization [9–12]. The true active species in the present catalyst systems is believed to be a cationic half-sandwich metal alkyl species, such as $[(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)][B(C_6F_5)_4]$. Compared to scandium complexes, other rare earth metal complexes such as **4**, **5**, and **10** showed much lower activity.

In the present polymerization, neither atactic nor isotactic polystyrene was observed, and therefore, solvent
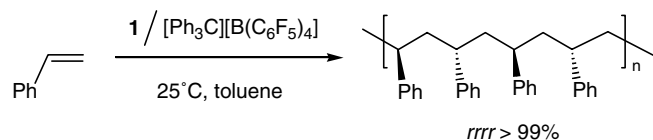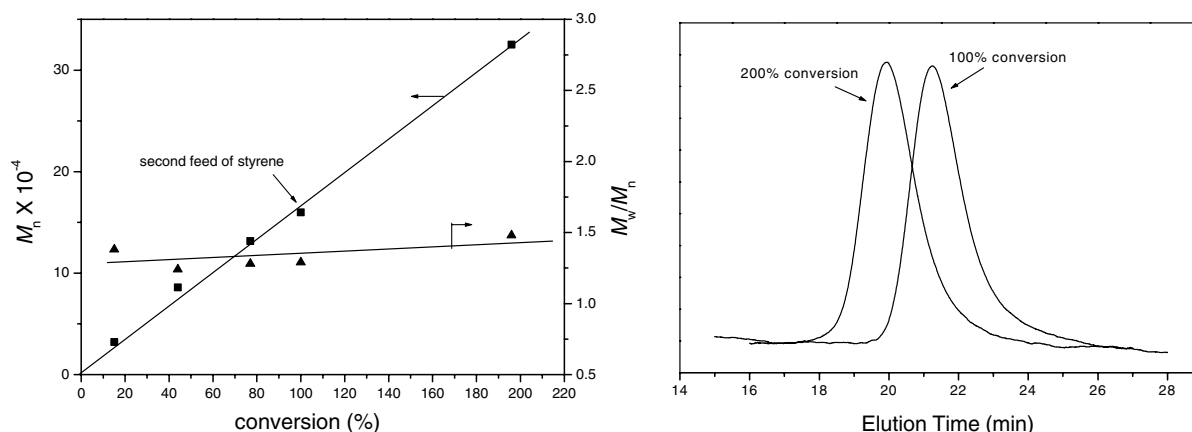

Scheme 1.

Scheme 4.

Fig. 1. Plots of M_n and M_w/M_n versus styrene conversion with 1/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (left) and GPC profiles before and after the second feed of styrene (right) ([St]/[Sc] = 1000; 1, 25 μmol; toluene, 50 mL; 25 °C).

fractionation was not required to obtain pure sPS (*rrrr* > 99% for all polymers obtained). When 1/[Ph$_3$C][B(C$_6$F$_5$)$_4$] was used as a catalyst, the molecular weight of the resulting polymers increased almost linearly as the monomer-to-catalyst ratio was increased, while the molecular weight distribution remained narrow, suggesting that this catalyst system has a "living" character. This "living" character became clearer, when the polymerization was carried out at a lower catalyst concentration, as shown in Fig. 1. The "livingness" of the present syndiospecific styrene polymerization catalyst system has been successfully used for the preparation of styrene–ethylene copolymers having syndiotactic styrene–styrene sequences, as described below.

3.2. Syndiospecific copolymerization of styrene with ethylene

Syndiotactic polystyrene (sPS) is a very promising polymer material for a large number of applications in industry, because of its high melting point (ca. 270 °C), high crystallinity, high modulus of elasticity, low dielectric constant, and excellent resistance to heat and chemicals [9,10]. A drawback that limits the application scope of sPS, however, is its brittleness. Since the discovery of syndiotactic polystyrene by use of homogeneous titanium catalysts in 1986 by Ishihara et al. [9], extensive studies on the copolymerization of styrene with ethylene have been carried out to improve the toughness of this new polymer [10,12–14]. However, attempts to obtain a styrene–ethylene copolymer having syndiotactic styrene–styrene sequences by use of titanium-based catalyst systems were not successful,

because the titanium catalysts usually contained a mixture of different active species, in which the species to produce sPS (probably a Ti(III) species) and that to produce polyethylene (probably a Ti(IV) species) were different from that to yield styrene–ethylene copolymers (unknown species) [13]. In many cases, mixtures of homopolyethylene, homopolystyrene, and varying amounts of styrene–ethylene copolymers with no regio- or stereo-regular styrene-styrene sequences were obtained.

In striking contrast, the scandium-based catalyst system such as 1/[Ph$_3$C][B(C$_6$F$_5$)$_4$] showed excellent activity and selectivity for the syndiospecific copolymerization of styrene with ethylene, as a result of true "single-site" catalysis by a Sc(III) species. As shown in Scheme 5, a sequential polymerization of styrene and ethylene by 1/[Ph$_3$C]-[B(C$_6$F$_5$)$_4$] afforded straightforwardly the corresponding A-B diblock styrene–ethylene copolymers with a syndiotactic polystyrene block [15]. The polystyrene content (or the length of the polystyrene block) in the copolymers could be easily controlled by changing the styrene feed.

When the copolymerization reactions were carried out in the presence of both ethylene and styrene, multi-block styrene–ethylene copolymers which consist of syndiotactic styrene–styrene sequences (blocks) connected by repeated ethylene units were obtained (Scheme 6) [4b]. The styrene

Scheme 5.

Coplymer selectivity: 100%
sPS content: 13–87 mol%
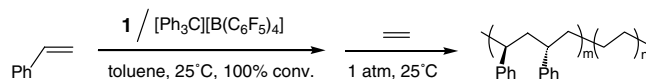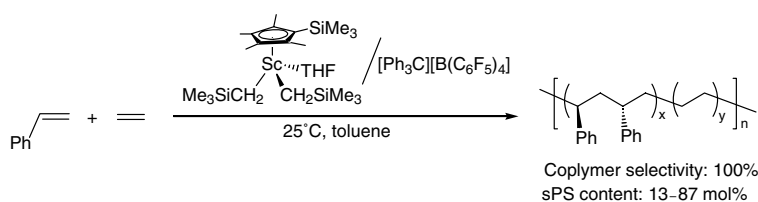
Scheme 6.

content in the copolymers could be controlled simply by changing the initial styrene feed under 1 atm of ethylene. Solvent fractionation experiments confirmed that the copolymer products did not contain homopolymers. ^{13}C NMR analyses did not show any tail-to-tail or head-to-head styrene sequences in the copolymers. The GPC curves of the copolymers were all unimodal with very narrow molecular weight distributions ($M_w/M_n = 1.14–1.26$), indicative of single homogeneous catalyst behavior. This is the first example of syndiospecific copolymerization of styrene with ethylene.

4. Polymerization of 1-hexene and copolymerization of 1-hexene with ethylene

The combination of the half-sandwich scandium bis(alkyl) complexes **1–3** with 1 equiv. of [Ph$_3$C][B(C$_6$F$_5$)$_4$] also showed high activity for the polymerization of 1-hexene, with an activity order of **1 > 3 > 2** [16]. The average number molecular weight (M_n) of the polymers obtained at room temperature was rather low ($M_n = 4800–5800$), and was independent of the amount of monomer consumed. However, when the polymerization was carried out at low temperatures, the molecular weight of the resulting polymers increased dramatically, and reached as high as 332.5×10^3 at $-40\ ^\circ$C. These results suggest that a chain transfer reaction must occur rapidly at room temperature but could be suppressed efficiently at lower temperatures. The ^{1}H NMR analysis of the polymer product (oligomer) obtained at room temperature revealed that the present polymerization reactions proceeded in both 1,2- and 2,1-insertion fashions, with β-hydrogen elimination as a chain termination reaction. Under the same conditions, complexes **4–10** did not show activity for 1-hexene polymerization, demonstrating again the metal dependence of the catalyst activity.

Very recently, dicationic scandium alkyl complexes bearing non-Cp ligands were also reported to show high activity for 1-hexene polymerization [3b,3c]. However, neu-
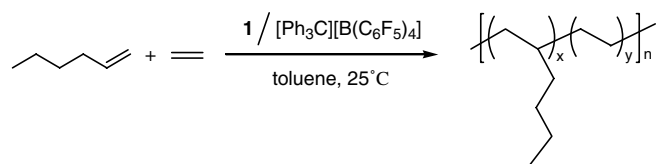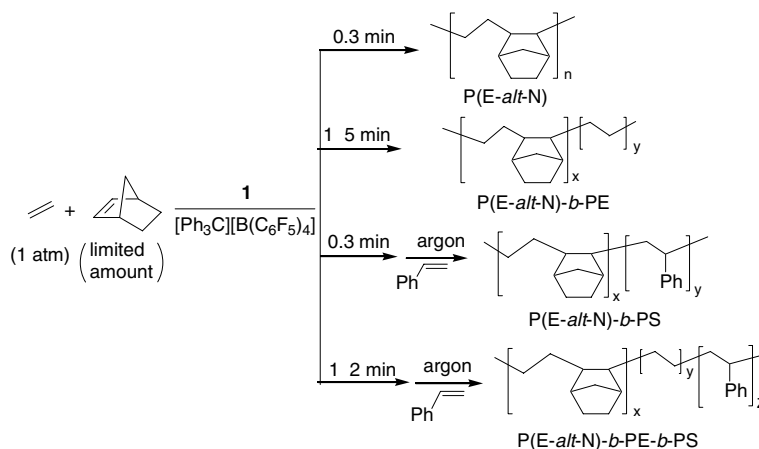

Scheme 7.

tral rare earth metal complexes usually show no or very low activity for the polymerization of α-olefins [14b,17].

The **1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] catalyst system also showed high activity for the copolymerization of 1-hexene with ethylene to produce ethylene/1-hexene copolymers containing isolated butyl branches in the chain backbone (Scheme 7) [16]. When 1-hexene feed was raised under 1 atm of ethylene, the incorporation of 1-hexene increased significantly. It is also noteworthy that the polymerization activity of the present catalyst was also increased significantly with the increase of 1-hexene feed, which thus constitutes a rare example of a homogeneous polymerization catalyst that shows significant positive "comonomer effect" in the copolymerization of ethylene with an α-olefin [18]. The activity of the present catalyst system for the copolymerization of 1-hexene with ethylene could reach as high as ca. 2.3×10^3 kg/(mol-Sc atm h) at room temperature, which ranks the highest ever reported for a rare earth metal catalyst for ethylene–1-hexene copolymerization [17], and could be compared with those reported for the most active group 4 metal catalysts [18].

In the case of **3**, the incorporation of 1-hexene was much lower (2 mol%) under the same conditions, while in the case of **2**, no incorporation of 1-hexene was observed. These results are consistent with the activity of these catalysts for 1-hexene homopolymerization.

5. Alternating copolymerization of norbornene with ethylene

On treatment with 1 equiv. of [Ph$_3$C][B(C$_6$F$_5$)$_4$], complexes **1–3** all showed very high activity for the alternating copolymerization of norbornene with ethylene, with an

Scheme 8.

activity order of **1** > **2** > **3** [4c]. A strong dependence of the copolymerization activity on the monomer concentration (or the ethylene/norbornene molar ratio in the reaction solution) was observed. Under appropriate (ethylene/norbornene molar ratio) conditions, the catalytic activity could reach as high as 25.2×10^3 kg/(mol-Sc h atm), which as far as we are aware, is the highest ever reported for the copolymerization of ethylene and norbornene.

Possibly due to steric hindrance, successive norbornene insertion or homopolymerization of norbornene is sluggish in the present catalyst system. However, the insertion of a norbornene monomer into a Sc–CH$_2$CH$_2$R bond and that of an ethylene monomer into a Sc–norbornyl bond could be very fast, and the former could be even more preferred to successive ethylene insertion when an adequate amount of norbornene is present. This unique nature led to rapid and exclusive formation of the alternating ethylene–norbornene copolymer under appropriate ethylene/norbornene molar ratios. When a relatively small amount of norbornene was used under 1 atm of ethylene, poly(ethylene-*alt*-norbornene)-*b*-polyethylene block copolymers could be obtained (Scheme 8). Analogously, poly(ethylene-*alt*-norbornene)-*b*-polystyrene block copolymers and poly(ethylene-*alt*-norbornene)-*b*-polyethylene-*b*-polystyrene triblock copolymers could also be obtained by use of the procedures shown in Scheme 8.

6. Random terpolymerization of norbornene, ethylene, and styrene

Although the incorporation of an aromatic monomer such as styrene into COCs is of much interest, random terpolymerization of ethylene, styrene, and a cyclic olefin was hardly explored [19] Since the cationic half-sandwich scandium catalysts showed unique activity for both the copolymerization of ethylene with styrene and the copolymerization of ethylene with norbornene, the activity of this new catalyst system for the terpolymerization of ethylene, norbornene, and styrene was further examined [4d,20].

The **1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] combination did not copolymerize styrene and norbornene, which yielded only homopolystyrene in the presence of both monomers. In contrast, the random terpolymerization of ethylene, styrene, and norbornene took place rapidly under the coexistence of the three monomers (Scheme 9). By changing the norbornene/styrene feed ratios under 1 atm of ethylene, the corresponding terpolymers with styrene contents of 7–53 mol% and norbornene contents of 7–27 mol% could be easily prepared. Complexes **2** and **3** were also active for this terpolymerization reaction, although their activity and incor-
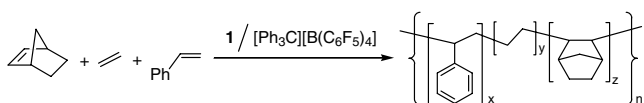
poration of styrene or norbornene were lower than those of **1** under the same conditions.

^{13}C NMR analyses showed the terpolymer products are random terpolymers containing isolated or alternating NB units, isolated styrene units and syndiotactic styrene–styrene sequences. No styrene–NB sequences were found in the terpolymer backbone. These results are consistent with what was observed for the two-component copolymerization reactions. The high and controllable incorporation of styrene in the present terpolymerizations is particularly noteworthy, and is in striking contrast with what was observed for the only previously reported titanium catalyst for the terpolymerization of ethylene, styrene, and norbornene, in which the maximum incorporation of styrene was less than 3 mol% [19].
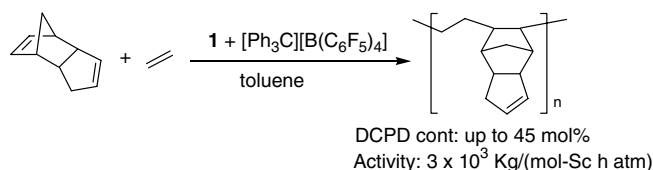
7. Alternating copolymerization of dicyclopentadiene (DCPD) with ethylene

Cyclic olefin copolymers (COCs) have so far been dominated by those of strained cyclic olefins such as norbornene and cyclopentene [21,22]. In comparison with norbornene and cyclopentene, dicyclopentadiene (DCPD) is a very promising and attractive cyclic olefin monomer, because it contains both a norbornene unit and a cyclopentene unit, and is industrially available at a much lower price. Moreover, if only one of the two C–C double bonds in DCPD selectively participates in the copolymerization with another monomer such as ethylene, further functionalization of the remaining C–C double bonds in the resulting copolymers is possible to introduce polar groups into the polymer backbone, giving a broad range of new functionalized polymers with improved properties. Nevertheless, the copolymerization of ethylene with DCPD has been far less extensively studied, and the alternating copolymerization of ethylene with DCPD has not been reported previously in the literature [23]. Cross-linking appeared to be a major problem often encountered in DCPD copolymerization [23c] and, therefore, the search for a catalyst system that is not only sufficiently active but can also distinguish a norbornene unit from a cyclopentene unit is critically important to achieve ethylene–DCPD copolymerization in a controlled fashion. A cationic half-sandwich scandium alkyl system, such as **1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$], proved to be such an excellent catalyst for the copolymerization of DCPD with ethylene (Scheme 10) [4d].

In the presence of **1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] in toluene, the copolymerization of DCPD with ethylene took place very

Scheme 9.

DCPD cont: up to 45 mol%
Activity: 3×10^3 Kg/(mol-Sc h atm)

Scheme 10.

$M_n = 20.4 \times 10^4$, $M_w/M_n = 2.25$ $M_n = 22.4 \times 10^4$, $M_w/M_n = 2.27$
$T_g = 125°C$ $T_g = 193°C$
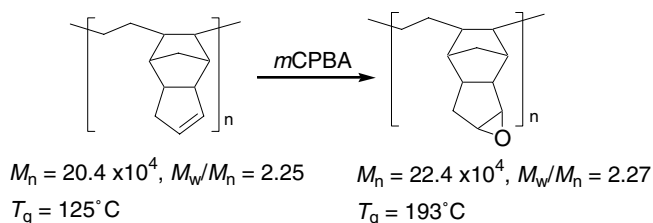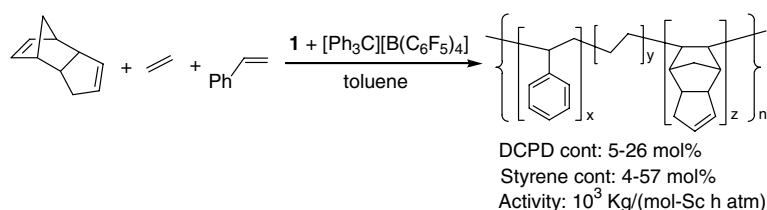
Scheme 11.

rapidly at a wide range of temperatures (0–70 °C) to yield the corresponding alternating copolymers, although DCPD homopolymerization was very slow under similar conditions [4d]. The DCPD content of the resulting copolymers increased as the DCPD monomer feed was raised under 1 atm of ethylene, and reached as high as 45 mol% when 50 mmol of DCPD was used. The catalytic activity also increased as the DCPD monomer feed was increased in the range of 20–40 mmol, while the use of more DCPD (50 mmol) led to decrease in activity. These results suggest that the ethylene–DCPD alternating copolymerization is more preferred than the homopolymerization of either monomer, similar to what was observed in the scandium-catalyzed ethylene–norbornene copolymerization [4c].

^{1}H and ^{13}C NMR analyses revealed that the resulting ethylene–DCPD copolymers contained cyclopetene units, suggesting that the copolymerization proceeded through enchainment of the norbornene ring. Their GPC curves are all unimodal with relatively narrow molecular weight distributions (1.73–2.69), consistent with the predominance of a single homogeneous catalytic species and the good selectivity in the copolymerization.

Epoxidation of an ethylene–DCPD alternating copolymer could be easily achieved by use of m-chloroperbenzoic acid (mCPBA) as an oxidant, which quantitatively converted the olefinic groups into epoxy groups (Scheme 11).

8. Terpolymerization of dicyclopentadiene, ethylene, and styrene

Similar to that of norbornene, ethylene, and styrene, the terpolymerization of DCPD, ethylene, and styrene could also be achieved by use of 1/[Ph₃C][B(C₆F₅)₄] as a catalyst (Scheme 12) [4d]. The terpolymers with styrene contents of 4–57 mol% and DCPD contents of 5–26 mol% could be easily prepared by changing the DCPD/styrene feed ratio under 1 atm of ethylene, ^{13}C NMR analyses revealed that
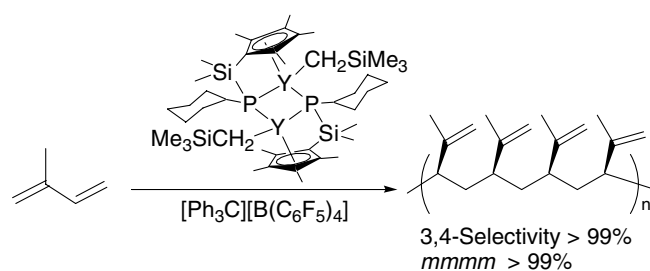
the terpolymers are random copolymers that contain isolated or alternating DCPD units, isolated styrene units, and syndiotactic styrene–styrene sequences, while no styrene–DCPD sequences were observed. These results are in agreement with those observed for the ethylene–DCPD [4c], styrene–DCPD, and ethylene–styrene [4b] two-component copolymerizations, and are similar to those of the terpolymerization of norbornene, ethylene, and styrene.

9. Isospecific 3,4-polymerization of isoprene

The isospecific 3,4-polymerization of isoprene has been achieved for the first time by use of a combination of a binuclear rare earth metal dialkyl complex such as $[Me_2Si(C_5Me_4)(\mu\text{-PCy})YCH_2SiMe_3]_2$ (Cy = cyclohexyl) (11) and an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ as a catalyst system (Scheme 13) [5a]. When the polymerization was carried out at −20 °C by addition of $[Ph_3C][B(C_6F_5)_4]$ to a mixture of 11 (one molar equiv.) and isoprene (600 equiv.) in C_6H_5Cl, a polyisoprene polymer with almost perfect isotactic 3,4-microstructure (3,4-selectivity 100%, mmmm > 99%), high molecular weight ($M_n = 5 \times 10^5$), and unimodal narrow molecular weight distribution ($M_w/M_n = 1.6$) was obtained. No evidence for other structures was observed in ^{1}H and ^{13}C NMR. The isotactic 3,4-polyisoprene obtained is a new polymer, which is crystalline as shown by XRD, and has a melting point at 162 °C. A DFT calculation suggested that a binuclear monocationic monoalkyl species, such as $[Me_2Si(C_5Me_4)(\mu\text{-PCy})Y(\mu\text{-CH}_2Si\text{-}Me_3)Y(\mu\text{-PCy})(C_5Me_4)SiMe_2]^+$, in which the alkyl group bridges the two metal centers, could be a true catalyst species [5a].

Previously, various metal catalysts or initiators have been reported for the polymerization of isoprene, but most of them yielded predominantly 1,4-polyisoprene and none were reported to show isospecific 3,4-selectivity [24,25].

3,4-Selectivity > 99%
mmmm > 99%

Scheme 13.

DCPD cont: 5–26 mol%
Styrene cont: 4–57 mol%
Activity: 10³ Kg/(mol-Sc h atm)

Scheme 12.

10. Conclusion

The cationic rare earth metal alkyl species, generated by reaction of a half-sandwich rare earth metal bis(alkyl) complex such as $Cp'Ln(CH_2SiMe_3)_2(thf)$ or $[Me_2Si(C_5Me_4)(\mu\text{-}PCy)YCH_2SiMe_3]_2$ with 1 equiv. of a borate compound such as $[Ph_3C][B(C_6F_5)_4]$, acts as an excellent catalyst system for the regio- and stereospecific polymerization and copolymerization of various olefins, such as syndiospecific living polymerization of styrene, syndiospecific copolymerization of styrene with ethylene, alternating copolymerization of ethylene with norbornene (or dicyclopentadiene), random and block terpolymerization of ethylene, norbornene (or dicyclopentadiene), and styrene, isospecific 3,4-polymerization of isoprene, etc. Most of these polymerization reactions are unique to the rare earth catalysts, and are difficult to be achieved by previously known catalyst systems. These results demonstrate well the high potential of organo rare earth metal complexes in polymerization catalysis.

Acknowledgement

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