Polymerization Catalysts

Alternating Ethylene–Norbornene Copolymerization Catalyzed by Cationic Half-Sandwich Scandium Complexes**

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Cationic alkyl–rare-earth-metal complexes (i.e., Group 3 and the lanthanides) have recently attracted much interest as homogeneous polymerization catalysts.[1–10] A number of cationic alkyl–rare-earth-metal complexes supported by various ancillary ligands such as deprotonated aza crowns,[2] benzamidinates,[3] β-diketiminates,[4] anilido imines,[5] amide-functionalized triazacyclononanes,[6] phosphides,[7] cyclopentadienyls,[8] and crown ethers[9] have been synthesized and their reactivity has been studied. Despite these extensive efforts, however, the olefin-polymerization chemistry of the cationic alkyl–rare-earth-metal complexes is still limited solely to that of ethylene,[2–10] whereas the development of active rare-earth-metal catalysts for the efficient polymerization/copolymerization of higher olefins has remained a challenge.

The copolymer of ethylene with a cyclic olefin such as norbornene (COC) is one of the most important high-performance polymer materials with many desirable properties. Since Kaminsky et al. first described the copolymerization of ethylene (E) with norbornene (NB) by using zirconocene-based catalysts in 1991,[11] extensive studies have been carried out in this area. Most of the catalysts reported so far are complexes based on transition metals such as those of Group 4 and Group 10,[12] whereas no rare-earth-metal complex has been previously used for the copolymerization of ethylene with norbornene.[13]

Herein we report an excellent cationic half-sandwich scandium catalyst for the copolymerization of ethylene with norbornene. This catalyst not only represents the first example of a rare-earth-metal catalyst for ethylene–norbornene copolymerization, but it also shows several unique characteristics, such as extremely high activity for the alternating ethylene–norbornene copolymerization and unprecedented formation of novel poly(ethylene-*alt*-norbornene)-*b*-polyethylene block copolymers.

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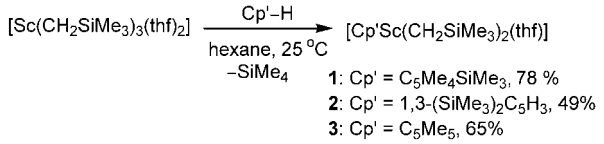
The acid–base reaction between the scandium–tris(alkyl) complex $[Sc(CH_2SiMe_3)_3(thf)_2]$ and the cyclopentadiene ligands Cp′H easily afforded the corresponding mono(cyclopentadienyl)scandium–bis(alkyl) complexes $[Cp'Sc(CH_2SiMe_3)_2(thf)]$ ($Cp' = SiMe_3C_5Me_4$ (**1**); 1,3-$(SiMe_3)_2C_5H_3$ (**2**); C_5Me_5 (**3**); Scheme 1). The X-ray crystal structure of **2** is shown in Figure 1.



Scheme 1. Synthesis of mono(cyclopentadienyl)scandium–bis(alkyl) complexes.

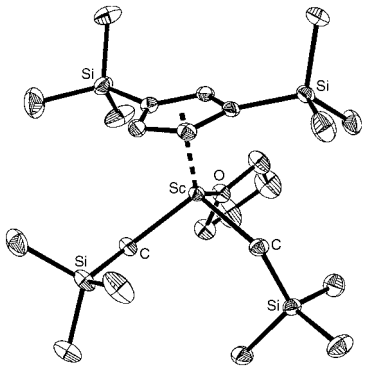


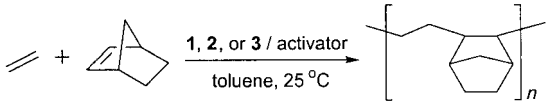
Figure 1. ORTEP drawing of **2** with ellipsoids shown at the 30% level of probability. Hydrogen atoms are omitted for clarity.

Treatment of complexes **1**–**3** with 1 equivalent of $[Ph_3C][B(C_6F_5)_4]$ (**A**) in C_6D_6 at 25 °C led to the immediate formation of $Ph_3CCH_2SiMe_3$ and a cationic scandium alkyl species assignable to $[Cp'Sc(CH_2SiMe_3)(thf)_x][B(C_6F_5)_4]$, as monitored by ^1H NMR spectroscopy. However, attempts to isolate such a cationic Sc species were not successful because of its extremely high reactivity (i.e., instability). Nevertheless, the in situ generated cationic scandium species showed high activity for ethylene polymerization ($\approx 10^5$ g(mol of Sc)$^{-1}$ h^{-1} atm^{-1}; Table 1, entry 1). These species were also active for norbornene polymerization, though the activity was very low ($\approx 10^2$ g(mol of Sc)$^{-1}$ h^{-1} atm^{-1}; Table 1, entry 2). More remarkably, in the presence of both ethylene and norbornene, extremely rapid copolymerization of the two monomers took place ($\approx 10^6$ g(mol of Sc)$^{-1}$ h^{-1} atm^{-1}) to yield the alternating ethylene–norbornene copolymers with a norbornene content of up to around 43 mol% (Table 1, entries 3–5).

Among complexes **1**–**3**, **1** showed the highest activity under the examined conditions. As an activator, $[PhMe_2NH][B(C_6F_5)_4]$ (**B**) was also effective for this copolymerization (Table 1, entry 6), whereas the use of $B(C_6F_5)_3$ (**C**) led to only a trace amount of norbornene incorporation into the polymer product (Table 1, entry 7).[14] In contrast, the neutral bis(alkyl) complexes **1**–**3** alone showed no activity for either norbornene homopolymerization or ethylene–norbornene copolymerization, although they were active for ethylene homopolymerization. None of the boron compounds were active towards ethylene or norbornene. These results clearly indicate that the cationic half-sandwich scandium–alkyl species play a critical role in this ethylene–norbornene copolymerization.

On the basis of the results described above, the **1**/**A** system was chosen to examine the ethylene–norbornene copolymerization under various conditions. The copolymerization can be carried out over a wide range of temperatures (0–70 °C; Table 2, entries 1–4). The activity of the catalyst increased at elevated temperatures, but the molecular weight of the resultant polymer decreased when the polymerization temperature was raised, thus suggesting that chain transfer should occur more rapidly at higher temperatures. Consistent with the above observation that the copolymerization of the two monomers is much faster than the homopolymerization of either monomer, a strong dependence of the activity of the catalyst on the monomer concentration (or the ethylene/norbornene molar ratio in the reaction solution) was observed (Table 2, entries 2, 5–9). Under appropriate conditions (with respect to the ethylene/norbornene molar ratio), the catalytic activity reached as high as 25.2×10^6 g of copolymer (mol of

Table 1: Copolymerization of ethylene with norbornene by half-sandwich scandium catalysts.[a]



Entry	Compound	Activator[b]	$p_{ethylene}$ [atm]	NB [mmol]	Yield [g]	Activity[c]	Product[d]	NB cont.[d] [mol%]	M_n[e] ($\times 10^4$)	PDI[f]	T_g[f] [°C]
1	**1**	**A**	1	0	0.03	0.4	PE		n.d.[g]	n.d.	n.d.
2[h]	**1**	**A**	0	20	0.02	0.0005	P(NB)	100	n.d.	n.d.	n.d.
3	**1**	**A**	1	20	0.67	8.0	P(E-*alt*-NB)	41.2	11.0	1.79	126
4	**2**	**A**	1	20	0.47	5.6	P(E-*alt*-NB)	36.1	4.9	1.89	105
5	**3**	**A**	1	20	0.20	2.4	P(E-*alt*-NB)	42.9	5.8	2.22	101
6	**1**	**B**	1	20	1.18	14.2	P(E-*alt*-NB)	43.6	12.1	2.78	110
7	**1**	**C**	1	20	0.06	0.7	PE		n.d.	n.d.	n.d.

[a] Conditions: Sc (1 μmol), activator (1 μmol), toluene (40 mL), $T = 25$ °C; $t = 5$ min, unless otherwise noted. [b] **A** = $[Ph_3C][B(C_6F_5)_4]$, **B** = $[PhMe_2NH][B(C_6F_5)_4]$, **C** = $B(C_6F_5)_3$. [c] 10^6 g of copolymer (mol of Sc)$^{-1}$ h^{-1} atm^{-1}. [d] NB content determined by ^{13}C NMR spectroscopy. [e] M_n is the number-averaged molecular mass determined by GPC with polystyrene standards. [f] Measured by differential scanning calorimetry (DSC; PDI = polydispersity index). [g] n.d. = not determined. [h] Conditions: Sc (21 μmol), activator (21 μmol), toluene (10 mL), $T = 25$ °C; $t = 2$ h.

Table 2: Alternating copolymerization of ethylene and norbornene by **1**/**A**.[a]

Entry	NB [mmol]	T [°C]	V [mL]	Yield [g]	Activity[b]	NB cont. [mol%][c]	M_n[d] ($\times 10^4$)	PDI[d]	T_g[e] [°C]
1	20	0	40	0.35	4.2	35.7	12.1	1.49	104
2	20	25	40	0.67	8.0	41.2	11.0	1.79	126
3	20	50	40	0.81	9.7	42.5	8.0	1.81	119
4	20	70	40	0.97	11.6	43.2	4.0	2.33	127
5	30	25	40	2.10	25.2	44.2	8.5	2.19	118
6	40	25	40	0.31	3.7	45.5	7.4	1.80	120
7	20	25	60	0.62	7.4	35.8	15.4	1.65	105
8	20	25	20	1.29	15.5	46.4	6.5	1.92	134
9	20	25	10	0.37	4.4	48.1	3.2	2.08	128

[a] Conditions: **1** (1 μmol), **A** (1 μmol), toluene (V mL), $p_{ethylene} = 1$ atm, $t = 5$ min. [b] 10^6 g of copolymer (mol of Sc)$^{-1}$ h^{-1} atm^{-1}. [c] NB content determined by ^{13}C NMR spectroscopy. [d] PDI determined by GPC with polystyrene standards. [e] Measured by DSC.

catalyst)$^{-1}$ h^{-1} atm^{-1} (Table 2, entry 5). To our knowledge, this is the highest activity ever reported for the copolymerization of ethylene and norbornene.[12]

The ^{13}C{^{1}H} NMR spectra of the copolymers show eight singlets at $\delta = 47.99$, 47.37, 42.19, 41.68, 33.14, 30.87, 30.50, and 30.18 ppm, as expected for an alternating ethylene–norbornene copolymer.[12d,e] The copolymers are amorphous and most of them have glass-transition temperature (T_g) values in the range of 118–134 °C. The gel-permeation chromatography (GPC) curves of the copolymers are all unimodal with relatively narrow molecular distributions (1.49–2.78), consistent with the predominance of a single homogeneous catalytic species. Solvent-fractionation experiments reveal negligible quantities of homopolymer impurities.[15]

More remarkably, the alternating ethylene–norbornene copolymerization system presented here could be applied to the preparation of poly(ethylene-*alt*-norbornene)-*b*-polyethylene block copolymers by use of an insufficient amount of norbornene monomer in the copolymerization as successive ethylene insertion can occur after all of the norbornene monomer has been consumed. As shown in Table 3, when the copolymerization reaction of 10 mmol of norbornene with ethylene (1 atm) in the presence of 21 μmol of **1**/**A** was quenched after 0.3 min, pure alternating ethylene–norbornene copolymer with a norbornene content of 45.6 mol% (equivalent to 53.4% conversion of added norbornene) was obtained (Table 3, entry 2). However, when the reaction time was extended to 1.0, 3.5, and 5.0 min under a constant flow of ethylene (1 atm), all of the norbornene was consumed and poly(ethylene-*alt*-norbornene)-*b*-polyethylene block copolymers, which had norbornene contents of 32.1, 25.6, and 19.9 mol% (Table 3, entries 3–5, respectively) were obtained as the major product together with a small amount of homopolyethylene in the case of longer reactions.[16] The new block copolymers showed values for both the glass-transition temperature (110–114 °C) and the melting point (126–128 °C; Table 3, entries 4 and 5) that correspond to the amorphous poly(ethylene-*alt*-norbornene) segment and the crystalline polyethylene segment, respectively.

In summary, the cationic half-sandwich scandium–alkyl species [Cp′Sc(CH_2SiMe_3)(thf)$_x$][B(C_6F_5)$_4$], generated in situ by reaction of **1**, **2**, or **3** with 1 equivalent of an activator such as **A**, act as excellent catalysts for the alternating copolymerization of ethylene and norbornene. Successive norbornene insertion is sluggish in the present catalyst system, possibly due to steric hindrance. However, the insertion of a norbornene monomer into a Sc–CH_2CH_2R 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 a sufficient quantity of norbornene is present. These unique properties lead to rapid and exclusive formation of the alternating ethylene–norbornene copolymer under appropriate ethylene/norbornene molar ratios and also leads to unprecedented formation of poly(ethylene-*alt*-norbornene)-*b*-polyethylene block copolymers when the quantity of the norbornene monomer is low. This work demonstrates, for the first time, that a cationic rare-earth-metal–alkyl species can serve as an excellent catalyst for the copolymerization of ethylene and a cyclic olefin. Further studies on the polymerization/copolymerization of other monomers by this and related rare-earth-metal catalysts are in progress.

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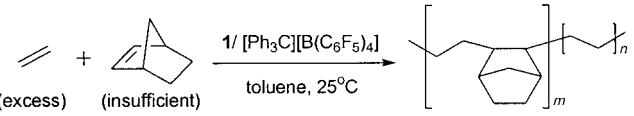
Table 3: Synthesis of poly(ethylene-*alt*-norbornene)-*b*-polyethylene by **1**/**A**.[a]



Entry	NB [mmol]	t [min]	THF-sol[b]	Yield [g] tol-sol[c]	tol-insol[d]	Major product	NB cont. [mol%][e]	M_n[f] ($\times 10^4$)	PDI[f]	T_g[g] [°C]	T_m[g] [°C]
1	0	5.0	0	0	1.57	PE		12.8	3.05		130
2	10	0.3	0.68			P(E-*alt*-NB)	45.6	3.2	1.42	111	n.o.[h]
3	10	1.0	0.12	1.18	trace	P(E-*alt*-NB)-*b*-PE	32.1	6.7	1.29	118	n.o.[h]
4	10	3.5	trace	1.77	0.07	P(E-*alt*-NB)-*b*-PE	25.6	16.6	1.36	114	128
5	10	5.0	trace	2.12	0.22	P(E-*alt*-NB)-*b*-PE	19.9	18.9	1.40	110	126

[a] Conditions: **1** (21 μmol), **A** (21 μmol), $p_{ethylene} = 1$ atm, toluene (40 mL), $T = 25$ °C. [b] THF-soluble portion: P(E-*alt*-NB) without PE block. [c] THF-insoluble, toluene-soluble portion: P(E-*alt*-NB)-*b*-PE. [d] THF-insoluble, toluene-insoluble portion: homo-PE. [e] NB content determined by ^{13}C NMR spectroscopy. [f] Determined by GPC with polystyrene standards. [g] Measured by DSC. [h] n.o. = not observed.

Keywords: alkyl complexes · copolymerization · cyclopentadienyl ligands · scandium

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[14] $B(C_6F_5)_3$ is a weaker activator than $[Ph_3C][B(C_6F_5)_4]$ or $[PhMe_2NH][B(C_6F_5)_4]$ for the generation of a cationic species. The reaction of $[(C_5Me_5)ScMe_2(OPtBu_3)]$ with 1 equivalent of $B(C_6F_5)_3$ in toluene was reported to give a contact ion pair, $[(C_5Me_5)ScMe(OPtBu_3)][MeB(C_6F_5)_3]$, which exhibits a significant $Sc\cdots MeB(C_6F_5)_3$ interaction. See reference [8c].

[15] The alternating ethylene–norbornene copolymers were soluble in toluene, whereas homopolyethylene and homopolynorbornene were insoluble.

[16] The three polymer products P(E-*alt*-NB), P(E-*alt*-NB)-*b*-PE, and PE could be easily separated by solvent fractionation: P(E-*alt*-NB) ($M_n < 4 \times 10^4$) was soluble in THF; P(E-*alt*-NB)-*b*-PE was insoluble in THF but soluble in toluene; PE was insoluble in both THF and toluene.

