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Copolymerization of Ethylene with Norbornene Catalyzed by Cationic Rare-Earth Metal Half-Sandwich Complexes

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ABSTRACT: We report on copolymerizations of ethylene with norbornene with half-sandwich rare-earth metal catalysts generated by activation of dialkyl complexes [Ln(η^5-$C_5Me_4SiMe_2R$)(η^1-CH_2SiMe_3)$_2$(THF)] (Ln = Sc, R = Me (**1**); Ln = Sc, R = C_6F_5 (**2**); Ln = Y, R = C_6F_5 (**3**); Ln = Lu, R = C_6F_5 (**4**)) with [Ph_3C][B(C_6F_5)$_4$]. Complexes **1** and **2** showed excellent activities, whereas complex **3** gave poor activity and **4** was practically inactive. Weak stabilization of metal center by bulkier silyl group of the tetramethylcyclopentadienyl ring in complexes **2** and **3** allows controlled copolymerization (M_w/M_n < 1.3). Mainly atactic alternating P(E-*co*-N) copolymers were obtained with the active catalytic systems. These copolymerizations were well described by first-order Markov statistics.

Introduction

Catalysts based on group 4 metallocenes[1] and, more recently, on postmetallocenes[2,3] led to significant breakthroughs in homogeneous olefin polymerization catalysis, resulting in new types of copolymers. There has been great interest around cyclic olefin copolymers (COCs) in recent years due to their unique properties. Glass-like clarity as well as high moisture barrier and thermal stability make such materials attractive for applications including lenses, vials, monitors, and medical devices and, more recently, for "smart" applications such as the fabrication of microelectronics or microfluidics devices.[4] Among the family of COCs, the copolymers of ethylene (E) with norbornene (N) (P(E-*co*-N)) by addition polymerization represent the most convenient ones for their synthesis in a single-step catalyzed reaction. Unlike those obtained by ring-opening metathesis polymerization (ROMP), these polymers do not require an additional hydrogenation step.[5] Group 4 metallocenes/MAO and group 10 metal catalysts have mainly been used for the synthesis of P(E-*co*-N) copolymers and for elucidating the copolymer structures.[6−8] Recently, the scandium half-sandwich bis(alkyl) complex [Sc(η^5-$C_5Me_4SiMe_3$)(η^1-CH_2SiMe_3)$_2$(THF)] (**1**) has been reported to be converted into the cationic species [Sc(η^5-$C_5Me_4SiMe_3$)(η^1-CH_2SiMe_3)(THF)$_x$]$^+$[B(C_6F_5)$_4$]$^-$ upon treatment with [Ph_3C][B(C_6F_5)$_4$].[9] This system has shown high activity in ethylene/norbornene and dicyclopentadiene copolymerization,[9,10] representing the first example by rare-earth metal catalysts for efficient COC synthesis.[10a]

Cationic organometallic complexes of the rare-earth metals (group 3 metals and the lanthanides) of general formula [$LnR_m(L)_n$]$^{(3-m)+}$ (R = alkyl; m = 1, 2; L = Lewis base) can be easily generated by reacting the neutral complexes [$LnR_3(L)_n$] with Lewis acids such as BR_3 or [Ph_3C][B(C_6F_5)$_4$]. Their enhanced electrophilicity and Lewis acidity make them potentially suitable as homogeneous olefin polymerization catalysts.[11] Thus, cationic rare earth metal (group 3 metal and lanthanide) alkyls are emerging as a new class of catalysts for homo- and copolymerization of various olefins, including copolymerization of styrene with ethylene and hexene.[12] Rare-earth metal half-sandwich complexes analogous to **1** were previously prepared and characterized.[13] Preliminary studies, involving complexes of scandium having a bulky cyclopentadienyl moiety and stabilizing alkyl groups, have shown their potential in copolymerizations of ethylene with norbornene.[14] These systems can yield active polymerization catalysts, both with and without low amounts of aluminum alkyls, which are involved in chain transfer reactions. Thus, the design of such systems could allow for the achievement of living polymerization.[15]

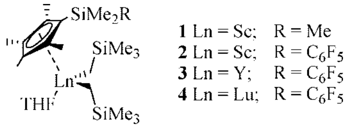

Figure 1. Representative formula of the investigated complexes.

Herein, we report on copolymerizations of ethylene with norbornene by a series of structurally characterized scandium, yttrium, and lutetium compounds of the type [Ln(η^5-$C_5Me_4SiMe_2R$)(CH_2SiMe_3)$_2$(THF)] (Ln = Sc, Y, Lu) with R = Me, C_6F_5 as precatalysts (Figure 1).

Results and Discussion

Copolymers Synthesis and Analysis. Rare-earth metal compounds with various substituents on the silyl group of the cyclopentadienyl ring can allow the evaluation of both steric and electronic effects of the ligand on the polymerization activity. In addition, scandium, yttrium, and lutetium complexes with the same ligands can allow for estimating the influence of metal size and different electronic properties on the catalytic behavior. A series of copolymerization reactions with complexes **2**, **3**, **4**, and **1**, for comparison, were carried out in toluene at atmospheric pressure. Different temperatures (from 0 to 50 °C) and feedstock compositions ([N]/[E] from 2 to 9) were investigated. Active species were generated in situ using [Ph_3C][B(C_6F_5)$_4$] as activator (Scheme 1).

Microstructure and norbornene content in the copolymers were determined by means of ^{13}C NMR spectroscopy. Molecular masses and glass transition temperatures (T_gs) were determined

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Scheme 1. Copolymerization of Ethylene with Norbornene by 1−4/[Ph_3C][$B(C_6F_5)_4$]

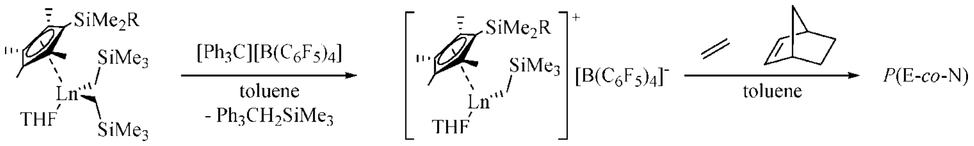


Table 1. Conditions and Results for Ethylene/Norbornene Copolymerization Catalyzed by 1−4/[Ph_3C][$B(C_6F_5)_4$][a]

entry	catalyst	(μmol)	T (°C)	t (min)	activity[b]	N polymer content[c] (mol %)	T_g[d] (°C)	M_n[e] (10^5 Da)	M_w/M_n[e]
1	**1**	10	25	5	1.57	44	117	1.02	1.59
2	**1**	5	25	5	1.12	45	119	1.2	1.48
3	**2**	5	25	5	0.61	39	99	1.19	1.28
4	**2**	5	50	5	0.82	37	92	0.98	1.36
5	**3**	10	25	20	0.04	31	70	0.47	1.18
6	**3**	10	40	20	0.08	34	75	0.41	1.10
7	**4**	10	25	15	inactive				
8	**4**	10	25	30	inactive				

[a] Conditions: $V = 20$ mL of toluene; $p_E = 1.01$ bar; [N]/[E] = 5.6; [Ln]:[Ph_3C][$B(C_6F_5)_4$] = 1:1. [b] Given in 10^6 g of P(E-*co*-N) mol Ln^{-1} h^{-1}. [c] Determined by ^{13}C NMR. [d] Measured by DSC. [e] Determined by SEC in 1,2-dichlorobenzene by using standard polystyrene calibration.

Table 2. Conditions and Results for Ethylene/Norbornene Copolymerization Catalyzed by 2/[Ph_3C][$B(C_6F_5)_4$][a]

entry	T (°C)	[N]/[E] feed	t (min)	activity[b]	N polymer content[c] (mol %)	T_g[d] (°C)	M_n[e] (10^5 Da)	M_w/M_n[e]
9	0	0	5	0.00	0			
10	25	0	5	0.02	0	nd	nd	nd
11	0	5.6	5	0.32	32	82	0.98	1.24
12	25	5.6	5	0.61	39	99	1.19	1.28
13	50	5.6	5	0.34	37	92	0.98	1.36
14	25	2	5	0.91	29	61	1.64	1.27
15	25	9	5	0.54	40	100	1.95	1.31
16	50	9	5	1.22	43	110	1.62	1.49
17	25	9	1	2.50	42	106	1.19	1.22
18	25	9	2	2.14	42	102	1.75	1.31
19	25	9	3	1.88	42	104	2.52	1.35

[a] Conditions: $V = 20$ mL of toluene; **2** = 5 μmol; [**2**]:[B] = 1:1. [b] Given in 10^6 g of P(E-*co*-N) mol Sc^{-1} h^{-1}. [c] Determined by ^{13}C NMR. [d] Measured by DSC. [e] Determined by SEC in 1,2-dichlorobenzene by using standard polystyrene calibration.

by SEC and DSC measurements, respectively. Relevant data for several representative copolymerizations by complexes **1**−**4** are summarized in Table 1. Both scandium complexes were instantaneously activated in contrast to those less electrophilic based on yttrium and lutetium. Excellent yields with both scandium catalysts were obtained. The system **2**/[Ph_3C][$B(C_6F_5)_4$] gave polymerization activities comparable to **1**/[Ph_3C][$B(C_6F_5)_4$], even though slightly lower. Possibly, coordination of the *ortho*-fluorine atom of $-C_6F_5$ to the metal in the active species of **2**/[Ph_3C][$B(C_6F_5)_4$] competes with coordination and insertion of norbornene. Catalyst **3**/[Ph_3C][$B(C_6F_5)_4$] catalyzed copolymerization with low activities, whereas no copolymerization activity was observed with **4**/[Ph_3C][$B(C_6F_5)_4$], at least under these conditions. There is a general decrease in activity by increasing the metal atomic radius, though there is no linear relationship (ionic radii: Sc = 0.745 Å, Y = 0.900 Å, Lu = 0.861 Å; for CN = 6).[16]

Catalyst **1**/[Ph_3C][$B(C_6F_5)_4$] formed copolymers with the highest norbornene content, followed by **2** and **3**, respectively.

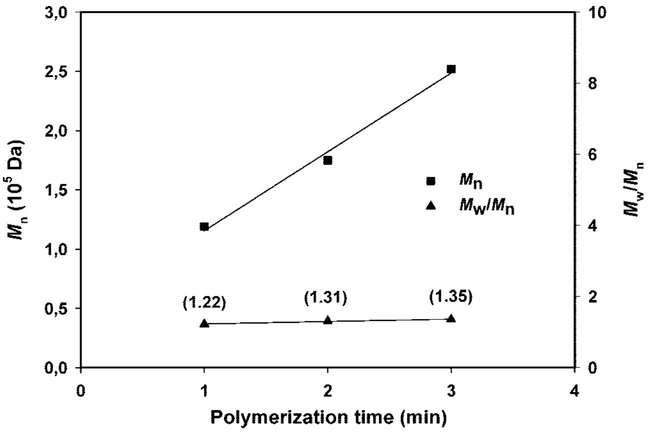
Copolymers with molecular mass as high as 100000 Da were obtained by **2**/[Ph_3C][$B(C_6F_5)_4$] as well as by **1**/[Ph_3C][$B(C_6F_5)_4$] within 5 min, whereas **3**/[Ph_3C][$B(C_6F_5)_4$] gave low molecular mass products. Interestingly, lower M_w/M_n were obtained with complex **3**/[Ph_3C][$B(C_6F_5)_4$].

Catalyst **2**/[Ph_3C][$B(C_6F_5)_4$] was further examined for its high activity as well as high molecular masses and narrow copolymer molar mass distributions. The copolymerization reactions were carried out with **2**/[Ph_3C][$B(C_6F_5)_4$] over the range of temperature from 0 to 50 °C and at feedstock compositions [N]/[E] from 2 to 9. For comparison, catalyst **2**/[Ph_3C][$B(C_6F_5)_4$] was tested in ethylene homopolymerization at 0 and 25 °C. Relevant data are collected in Table 2.

Catalyst **2**/[Ph_3C][$B(C_6F_5)_4$] (entries 10 and 11) was practically inactive in homopolymerization of ethylene at both 0 and 25 °C, whereas catalyst **1** showed activity under similar conditions.[10a] More interestingly, when both ethylene and norbornene were available for the cationic active species, the copolymerization reaction occurred so fast that the solution viscosity increased after a few minutes of reaction. Highest activities and M_n were attained at 25 °C, whereas the copolymerization is best controlled at a low temperature: M_w/M_n slightly increased with temperature due to a common increase of chain transfer side reactions. It should be pointed out that catalyst **2**/[Ph_3C][$B(C_6F_5)_4$] produced copolymers with M_w/M_n constantly lower than **1**/[Ph_3C][$B(C_6F_5)_4$]. The well-controlled nature of copolymerization mediated by **2**/[Ph_3C][$B(C_6F_5)_4$] was confirmed by monitoring M_n and M_w/M_n as a function of reaction time (nos. 17−19). Worth noting is that, as depicted in Chart 1, M_n increased quite linearly within the first 3 min of reaction, keeping quite a narrow M_w/M_n. Subsequently, the controlled nature was lost, probably for the need of more diluted solutions. Moreover, the catalyst was extremely active at the beginning of the reaction so that the linear fit of M_n vs time does not intersect the origin.

A series of experiments were carried out at room temperature, at different feed compositions (entries 12, 14, and 11). While catalyst **2**/[Ph_3C][$B(C_6F_5)_4$] was inactive in E homopolymerization, within the feed ratios considered, the catalytic activities for ethylene/norbornene copolymerization decreased with the [N]/[E] feed ratios as for other catalyst systems (entry 15 < no. 12 < entry 14).[6,17,18] Interestingly, quite narrow molar mass distributions were found at all [N]/[E] feed ratios. Increasing the charged N, the norbornene incorporation in the copolymer raised. Because of the bulkiness or the coordinating effect of

Chart 1. Plots of M_n and M_w/M_n vs Reaction Time with 2/[Ph_3C][$B(C_6F_5)_4$] (Nos. 17−19)



the $-C_6F_5$ substituent on the cyclopentadienyl ligand, **2** required a N/E feed ratio greater than **1** to reach the *plateau* composition (entries 2 and 14).

Figure 2 displays the ^{13}C NMR spectrum of the copolymer formed with complex **2** (M_n 119 000, M_w/M_n 1.22, entry 18 in Table 2). Peak assignments were performed based on a comparison of the observed chemical shifts with our previous data.[18] The spectrum indicated that **2**/[Ph_3C][$B(C_6F_5)_4$] promoted an addition-type copolymerization of N with *exo*−*exo* enchainment. The peak at 45.77 ppm and the peak at 45.17 were assigned to carbons C2 and C3 in the alternating isotactic and alternating syndiotactic units, respectively. The peaks at 39.99 and 39.48 ppm were ascribed to carbons C1 and C4 in the alternating isotactic and syndiotactic units, respectively. The peak at 31 ppm was assigned to C7 in alternating units. The peaks at 28.71 and 27.72 ppm were assigned to the carbons derived from E in the alternating isotactic and syndiotactic NEN units, respectively. Additionally, as illustrated in the dashed inset of Figure 2, the common broad signal assigned to C5 and C6 carbons resulted split into two resolved signals at 28.36 and 28.31 ppm assigned to C6 carbons of isotactic and syndiotactic NENE, respectively.

In summary, the relative peak intensities showed a copolymer containing 42 mol % of N predominantly consisting of alternating NEN sequences; in addition, the copolymer contained some isolated N units present in ENEE sequences and only a small amount of NN diads (see the section below for further details). These results indicate a very high tendency of **2**/[Ph_3C][$B(C_6F_5)_4$] to afford alternating P(E-*co*-N)s. The relative peak intensities also revealed that the copolymer consisted of about 57 syndiotactic and 43 isotactic units, which indicates a random tacticity. Practically, the sterically open nature of an E-last-inserted active species cannot distinguish between coordination of N with a bridging methylene group up or down. The copolymers stemming from **2**/[Ph_3C][$B(C_6F_5)_4$] apparently possess the same microstructure as those obtained by **1**/[Ph_3C][$B(C_6F_5)_4$] under these conditions apart from the N incorporation.

As far as the glass transition temperatures are concerned, in general for random copolymers T_gs increase linearly with norbornene content.[7] The values determined with catalyst **2**/[Ph_3C][$B(C_6F_5)_4$] were correlated with norbornene content and tended to a *plateau* as the N content in the copolymer. Catalyst **1**/[Ph_3C][$B(C_6F_5)_4$] was reported to have unique characteristics, such as unprecedented formation of innovative P(E-*co*-N)-*block*-PE copolymer by complete norbornene conversion during the polymerization reaction so that successive ethylene insertions could occur after all of the norbornene monomer had been consumed. The novel block copolymers, which were the toluene-soluble portion of raw polymers, showed at DSC both the T_gs at 110−114 °C of the amorphous P(E-*co*-N) and the melting point at 126−128 °C of the short crystalline PE fragment.[10] In our experiments DSC analysis did not reveal any melting event for polymers formed neither by **1**/[Ph_3C][$B(C_6F_5)_4$] nor by **2**/[Ph_3C][$B(C_6F_5)_4$] because we never reached extremely high conversions originated by high catalyst concentration and low [N]/[E] feed ratios reported by Hou et al. However, NMR spectra of copolymers obtained by **1**/[Ph_3C][$B(C_6F_5)_4$] revealed the presence of some EEEE tetrads, though ethylene homosequences were not long enough to crystallize.

Polymerization Statistics from Copolymer Microstructure. The analysis of copolymer microstructure at tetrad level allows insight into the copolymerization mechanism. In the past few years, our continuous interest in the investigation of the microstructure of P(E-*co*-N)s by combining the use of NMR techniques with computational methods made it possible to achieve assignments and quantification of isolated, alternating, and blocky norbornene sequences, including differentiation in the tacticities of the sequences. A methodology to completely quantify tetrad and pentad sequence distributions, to determine the copolymerization parameters, and to clarify possible statistical models of copolymerization, discriminating between ultimate and penultimate effects, has been achieved. Here, we used the tetrad description of the microstructure of the alternating copolymers prepared by complexes **1** and **2**, reported in Tables 1 and 2, to understand and visualize differences in copolymerization mechanisms. The main features of the copolymers prepared with the two catalysts are evident in Charts 2 and 3, where the NMR-measured tetrad distributions obtained by our methodology were compared with those calculated according to first- and second-order Markovian models. One representative copolymer sample produced by **1** and one produced by **2** were selected for such a comparison. Entries 1 and 19 contained 44 and 42 mol % of norbornene incorporated, respectively. Entry 1 was produced with catalyst **1** at N/E = 5.6 while entry 19 was produced with catalyst **2** at N/E = 9. The copolymer prepared by **1** is more alternating than the one prepared by **2**: the greatest differences were in NENE and ENEE molar fractions, NENE being 0.67 and 0.59 with **1** and **2**, respectively. In both cases the molar fraction of NENE *racemic* (syndiotactic) sequence was about 1.3 times the one of the *meso* (isotactic) sequence. As expected, the second-order Markov fitting was slightly better, though the first-order Markov statistics seemed to be sufficient to describe these copolymerizations. As to the reactivity ratios, while r_1r_2 were quite similar for the two catalytic systems, the r_1 value was close to 1 for catalyst **1** and about 3 for catalyst **2**, indicating the greater preference of **1** for norbornene. We also note that the greatest error between the molar fractions obtained from NMR and those calculated according to both Markov models occurred for sequence EEEE, where the calculations underestimated the experimental value of the ethylene homosequence. This is an indication that, as observed, catalyst **1** is able to yield P(E-*co*-N)-*block*-*P*E copolymer under norbornene starvation and catalyst excess.

Comparison among Group 3 Metal Catalysts for Ethylene/Norbornene Copolymerization. Activities achieved by **1**−**2**/[Ph_3C][$B(C_6F_5)_4$] were fairly good, though lower than those found by Hou et al. with system **1**, using more diluted reaction solutions.[10a] We too observed a dependence of activity on catalyst concentration, which practically were inversely proportional. Activity strongly depended on the nature of the metal and decreased in the series Sc (**1**−**2**), Y (**3**), and Lu (**4**) with the (η^5-$C_5Me_4SiMe_2C_6F_5$) ligand, in agreement with the literature. With respect to the analogous inactive [Y(η^5-$C_5Me_4SiMe_3$)(η^1-CH_2Si-Me_3)$_2$(THF)],[10b] yttrium complex **3** showed some

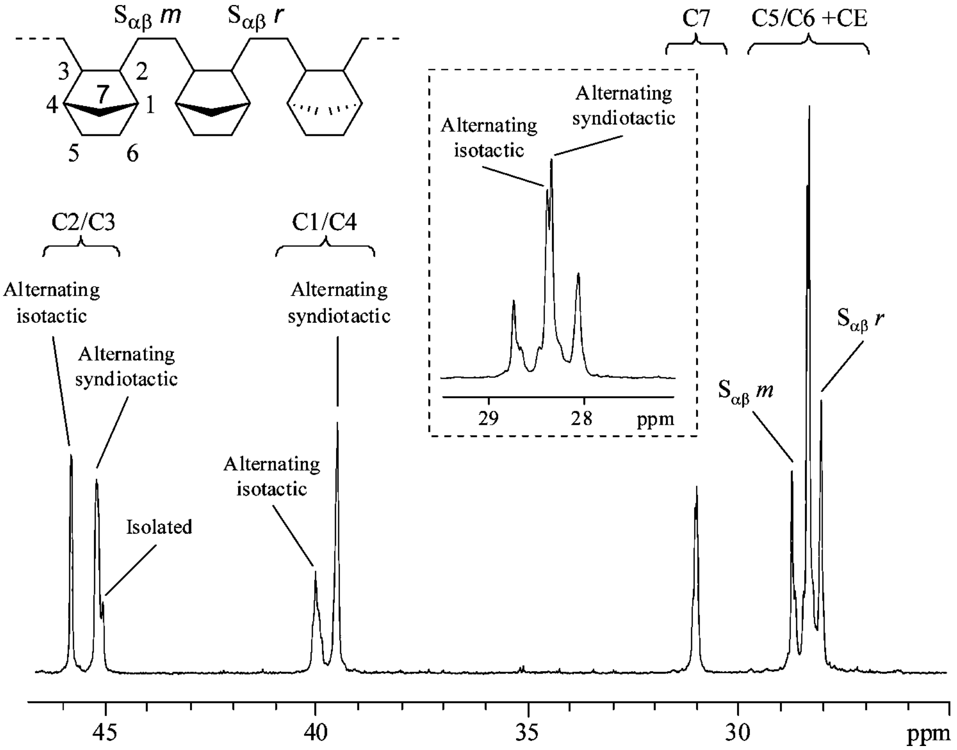
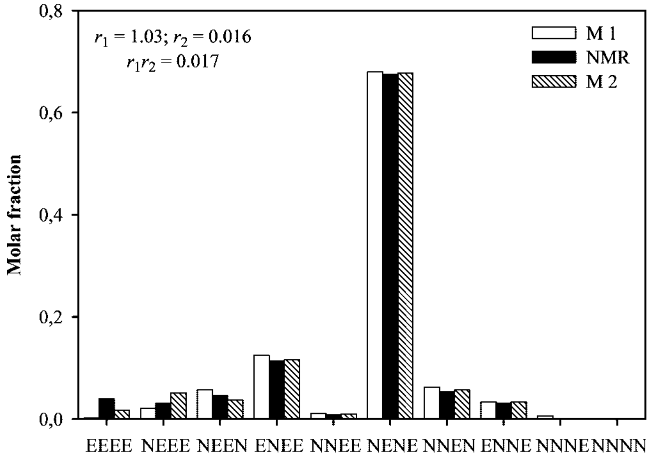


Figure 2. ^{13}C NMR spectrum in $C_2D_2Cl_4$ for the P(E-*co*-N) formed in entry 18.

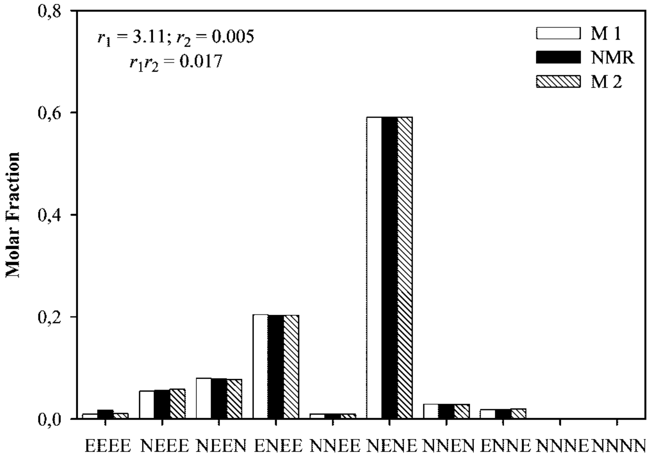
Chart 2. Experimental and Calculated Tetrads Distributions for P(E-*co*-N) Copolymer Sample Prepared with $1/[Ph_3C][B(C_6F_5)_4]$, at Feed Ratio [N]/[E] = 5.6 (Entry 1)[a]



[a] Black: experimental data obtained from NMR; white: according to first-order Markov model; dashed: according to second-order Markov model.

activity and an interesting living character. The molecular masses obtained by **1**−**2**/$[Ph_3C][B(C_6F_5)_4]$ did not depend on the nature of the cyclopentadienyl ligand. By contrast, the cyclopentadienyl ligand influenced both the polydispersity and norbornene incorporation, which follow the order **2** (η^5-$C_5Me_4SiMe_2C_6F_5$) < **1** (η^5-$C_5Me_4SiMe_3$). Finally, Hou et al. reported that catalyst **1**/$[Ph_3C][B(C_6F_5)_4]$ produces a polymer mixture containing P(E-*co*-N)-*block*-*P*E as toluene-soluble fraction. By replacing the (η^5-$C_5Me_4SiMe_3$) ligand with (η^5-$C_5Me_4SiMe_2C_6F_5$), we found that the living character of mono(cyclopentadienyl) rare-earth metal complexes improved when compared with the prototypical system **1**/$[Ph_3C][B(C_6F_5)_4]$.

Chart 3. Experimental and Calculated Tetrads Distributions for P(E-*co*-N) Copolymer Sample Prepared with $2/[Ph_3C][B(C_6F_5)_4]$, at Feed Ratio [N]/[E] = 9 (Entry 19)[a]



[a] Black: experimental data obtained from NMR; white: according to first-order Markov model; dashed: according to second-order Markov model.

Conclusion

In summary, activated half-sandwich complexes of scandium **1** and **2** give mainly atactic, alternating P(E-*co*-N) copolymers in excellent yields. In contrast, yttrium half-sandwich catalyst **3** shows poor activities and lutetium catalyst **4** was practically inactive. Differences in silyl substituents on the cyclopentadienyl ligand have an influence on norbornene incorporation and molar mass distribution. Stabilization of metal by weak coordination of *ortho*-fluorine atom of (η^5-$C_5Me_4SiMe_2C_6F_5$) ligand in complexes **2** and **3** allows controlled copolymerization (M_w/M_n < 1.3), though it slightly affects activity and norbornene incorporation. Atactic alternating P(E-*co*-N) copolymers were obtained with the active catalytic systems. These copolymerizations were well described by first-order Markov statistics.

Experimental Section

Materials. All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk-line techniques or a glovebox. Toluene was fresh-distilled on benzophenone ketyl and stored on molecular sieves and BTS catalysts before each polymerization. The four complexes [Ln(η^5-$C_5Me_4SiMe_2R$)(η^1-CH_2SiMe_3)$_2$(THF)] (Ln = Sc, R = Me (**1**); Ln = Sc, R = C_6F_5 (**2**); Ln = Y, R = C_6F_5 (**3**); Ln = Lu, R = C_6F_5 (**4**)) were prepared following the literature procedure.[13] Trityl tetra(pentafluorophenyl)borate was purchased from Strem Chemicals. Ethylene was purified flowing through BTS catalysts, molecular sieves, and $CaCl_2$. Norbornene, purchased from Aldrich, was distilled on Na/K alloy and used as a stock solution in toluene kept dry by BTS and molecular sieves. $C_2D_2Cl_4$ was purchased from Cambridge Isotope Laboratories, Inc.

Polymerization Procedure. In the glovebox, a Schlenk flask containing a stirring bar was charged with norbornene toluene solution, [Ph_3C][B(C_6F_5)$_4$], and toluene. The reactor was equipped with a dropping funnel containing a toluene solution of catalyst. The reactor was taken off, set in a thermostated water bath, and connected to the Schlenk line. The solution was degassed and then saturated with ethylene for 2 min under vigorous stirring. The catalyst solution was injected through the dropping funnel. The reaction was quenched by addition of methanol (5 mL). Then the polymer was precipitated in methanol (100 mL) and stirred for several hours. The polymer product was collected by filtration, washed with methanol, and then dried in vacuo at 70 °C for several hours.

^{13}C NMR. For ^{13}C NMR analysis about 100 mg of copolymer was dissolved in $C_2D_2Cl_4$ in a 10 mm tube. Hexamethyldisiloxane was used as internal reference. The spectra were recorded on a Bruker NMR Advance 400 spectrometer operating at 100.58 MHz (^{13}C) in the PFT mode working at 103 °C. The applied conditions were the following: 10 mm probe, 90° pulse angle; 64K data points; acquisition time 5.56 s; relaxation delay 20 s; 3−4 K transient. Proton broadband decoupling was achieved with a 1D sequence using bi_waltz_16_32 power-gated decoupling.

Calculation of Tetrad Distribution and Reactivity Ratios. The tetrad level microstructures of the P(E-*co*-N) copolymers presented in this work were analyzed according to the first-order and second-order Markovian statistical models by means of the procedure described elsewhere. The reader is referred to previous work.[18]

DSC. Measurements were performed on a Pyris 1 Perkin-Elmer instrument. The samples (around 8 mg) were heated from 50 to 250 at 20 °C/min, with a nitrogen flow (30 mL/min). A first scan was realized to erase the thermal history of each polymer. T_g was then recorded during a second thermal cycle.

Molecular Mass Measurement. Measurements were performed on about 12 mg of product in *o*-dichlorobenzene at 105 °C by a GPCV2000 high-temperature size exclusion chromatography (SEC) system from Waters (Millford, MA) equipped with two online detectors: a viscometer (DV) and a differential refractometer (DRI). The column set was composed of three mixed Styragel HT columns. The universal calibration was constructed of 18 narrow MMD polystyrene standards, with the molar mass ranging from 162 to 5.48×10^6 Da.

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