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Organolanthanide-Mediated Silanolytic Chain Transfer Processes. Scope and Mechanism of Single Reactor Catalytic Routes to Silapolyolefins

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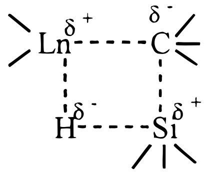
ABSTRACT: This paper reports efficient and selective silanolytic ($PhSiH_3$, *n*-$BuSiH_3$, $C_6H_5CH_2SiH_3$) chain transfer in organolanthanide-catalyzed homogeneous ethylene polymerization and ethylene copolymerization with several α-olefins. The result is a series of silyl-capped polyolefins which have been characterized by $^1H/^{13}C$ NMR and IR spectroscopy as well as by GPC. In $[(Me_5C_5)_2LnH]_2/[Me_2Si(Me_4C_5)_2LnH]_2$-mediated ethylene homopolymerization and ethylene copolymerization, both primary arylsilanes ($PhSiH_3$) and alkylsilanes (*n*-$BuSiH_3$, $C_6H_5CH_2SiH_3$) function as efficient chain-transfer agents. In the case of ethylene polymerization mediated by $[(Me_5C_5)_2SmH]_2$, the mechanism of chain transfer is supported by the observation that M_n of the capped polyethylenes formed at constant [catalyst], [$PhSiH_3$], [ethylene] is inversely proportional to [$PhSiH_3$]. Using silane-activated $Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2$ precatalysts, this chain-transfer process also efficiently produces silyl-endcapped ethylene + 1-hexene copolymers and ethylene + styrene copolymers.

Introduction

The selective and catalytic introduction of functional moieties into the architectures of nonpolar polyolefins via Ziegler−Natta processes[1] currently represents a significant, largely unsolved challenge.[2−5] In the case of olefin hydrosilylation mediated by lanthanocene[6] catalysts,[7] we demonstrated that the mechanism involves rapid, operationally irreversible olefin insertion into the Ln−H bond, followed by turnover-limiting Si−H/Ln−C transposition.[8] One interesting aspect of this reaction pathway is that the organic fragment appended to the metal center is transferred stereospecifically to silicon in the final step, as shown in Scheme 1. With regard to metal−ligand bond enthalpy considerations, the insertion of olefin into a lanthanide hydride bond is estimated to be exothermic,[8,9] while Ln−C/Si−H transpositions are also estimated to be exothermic[8,9] and presumably proceed via four-centered σ bond metathesis transition states (**I**). These observations and the demonstrated competence of such lanthanide complexes for olefin polymerization[10] raise the intriguing question of whether silanes could be used as chain transfer agents in d⁰/f metallocene-catalyzed olefin polymerizations to yield silapolyolefins (Scheme 2). Once formed, the silicon−carbon bond is a versatile precursor for a myriad of polar and nonpolar functional groups.[11] In this paper, we report a full discussion of our studies demonstrating that $PhSiH_3$, *n*-$BuSiH_3$, and $C_6H_5CH_2SiH_3$ are efficient and selective chain-transfer agents in organolanthanide-catalyzed α-olefin polymerizations and copolymerizations, yielding families of new silapolyolefins[12] which have been characterized by $^1H/^{13}C$ NMR and IR spectroscopy as well as by GPC.



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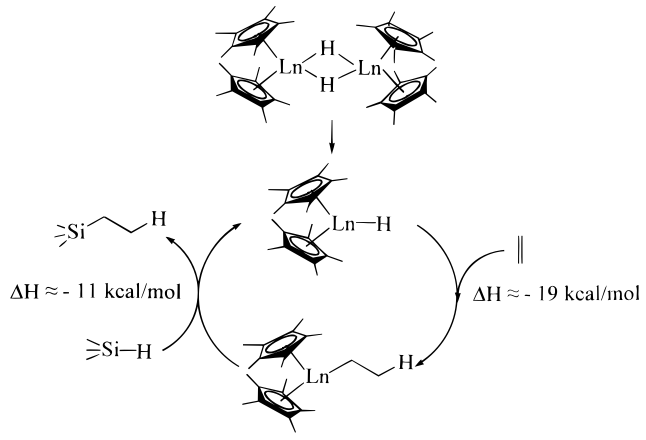
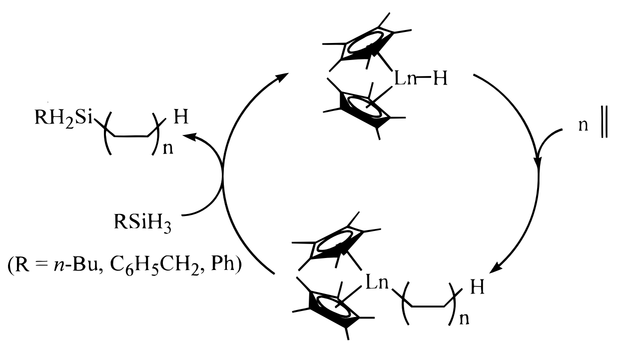
Scheme 1. Demonstrated Mechanistic Scenario for Organolanthanide-Catalyzed Olefin Hydrosilylation



Scheme 2. Proposed Catalytic Cycle for Silyl-Capped Polyolefins Mediated by Organolanthanide Catalysts



Experimental Section

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-

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type glassware on a dual manifold Schlenk line or interfaced to a high-vacuum (10^{-5} Torr) line or in a nitrogen-filled Vacuum Atmospheres glovebox with a high-capacity recirculator (<1 ppm O_2). Argon and ethylene (Matheson, prepurified) were purified by passage through a MnO oxygen-removal column and a Davison 4 A molecular sieve column. Hydrocarbon solvents (toluene, *n*-pentane) were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored in vacuo over Na/K alloy in resealable bulbs. Other olefins (styrene and 1-hexene) for polymerization were obtained from Aldrich, stirred over CaH_2 for 24 h, and vacuum transferred. Phenylsilane was obtained commercially (Aldrich), dried over CaH_2 for 24 h, and distilled prior to use. The reagents $PhCH_2SiH_3$ [13] and *n*-$BuSiH_3$ [14] were prepared according to literature procedures. The organolanthanide catalysts $Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2$ [10c] and $[(Me_5C_5)_2LnH]_2$ [10d] (Ln = Sm, Lu, Y, La) were prepared by published procedures.

Physical and Analytical Measurements. NMR spectra were recorded on either a Varian VXR 300 (FT: 300 MHz, ^1H; 75 MHz, ^{13}C) or a UNITYplus 400 (FT: 400 MHz, ^1H; 100 MHz, ^{13}C) instrument. Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported relative to tetramethylsilane. NMR experiments on air-sensitive samples were conducted in Teflon valve-sealed tubes (J. Young). For ^{13}C NMR analyses of homopolymer microstructures, 40−60 mg polymer samples were dissolved in 0.7 mL of $C_2D_2Cl_4$ with a heat gun in a 5 mm NMR tube, and the samples were immediately transferred to the NMR spectrometer with the probe head preequilibrated at 120 °C. A 45° pulse width and 2.5 s acquisition time were used with a pulse delay of 5 s. For ^{13}C NMR analyses of copolymer microstructures, the samples were prepared by dissolving 50 mg polymer samples in 0.7 mL of $C_2D_2Cl_4$ and spectra were taken at 120 °C with a 10 s pulse delay and a 90° pulse width. GPC analyses of polymer samples were performed at Dow Corning Corp., Midland, MI, relative to polystyrene or polypropylene standards. IR spectra (KBr pellets) were recorded using a Nicolet 520 FT-IR spectrometer with an MCT detector.

PhH_2Si-Capped Polyethylene. Representative Experiment. On the high-vacuum line, toluene (10 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 1.0 mL (8.1 mmol) of $PhSiH_3$ was vacuum transferred into the flask at −78 °C. In the glovebox, a 6 mL sample vial equipped with a septum cap was charged with 12 mg (0.014 mmol) of $[(Me_5C_5)_2SmH]_2$. A measured amount of toluene (1.0 mL) was then syringed into the vial containing the above reagent with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was then quickly syringed under a ethylene counterflow into the rapidly stirred olefin + silane reaction mixture through the septum-sealed reaction flask sidearm at 25 °C. After a measured time interval (2 min), the reaction was quenched by the addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under vacuum; yield, 0.33 g; M_n = 4400, M_w = 18 900 by GPC. ^1H NMR ($C_2D_2Cl_4$, 120 °C, relative intensity): δ 7.50 (Ph, 0.8), 7.20 (Ph, 1.0), 4.33 (SiH_2, 0.7), 1.30 ($-CH_2CH_2-$, 100), 0.92 ($-CH_3$, 1.2), 0.82 ($-CH_2Si$, 0.8). ^{13}C NMR ($C_2D_2Cl_4$, 75.5 MHz, 120 °C): δ 32.5, 31.7, 29.4, 29.3, 29.0, 27.4, 25.4, 25.2, 22.4, 13.8, 13.3, 10.0, 9.1, 8.7.

***n*-BuH_2Si-Capped Polyethylene. Representative Experiment.** On the high-vacuum line, toluene (10 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 0.40 mL (3.0 mmol) of *n*-$BuSiH_3$ was vacuum transferred into the flask at −78 °C. In the glovebox, a 6 mL sample vial equipped with a septum cap was charged with 11 mg (0.013 mmol) of $[(Me_5C_5)SmH]_2$. A measured amount of toluene (2.0 mL) was then syringed into the vial containing the above reagent with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was then quickly syringed under a ethylene counterflow into the rapidly stirred olefin + silane reaction mixture through the septum-sealed reaction flask sidearm at 25 °C. After a measured time interval (2 min), the reaction was quenched by the addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under vacuum; yield, 0.22 g; M_n = 2700, M_w = 5000 by GPC. ^1H NMR ($C_2D_2Cl_4$, 120 °C, relative intensity): δ 3.69 (SiH_2, 1.2), 1.03 ($-CH_2CH_2-$, 100), 0.92 ($-CH_3$, 2.1), 0.71 ($-CH_2Si$, 3.7). ^{13}C NMR ($C_2D_2Cl_4$, 75.5 MHz, 120 °C): δ 32.5, 31.7, 29.4, 29.3, 29.0, 27.4, 25.4, 25.2, 22.4, 13.7, 13.3, 9.1, 8.7.

$C_6H_5CH_2SiH_2$-Capped Polyethylene. Representative Experiment. On the high-vacuum line, toluene (10 mL) was condensed into a flamed, 100 mL reaction flask equipped with a large magnetic stirring bar and a septum-covered sidearm. Next, 0.40 mL (3.0 mmol) of $C_6H_5CH_2SiH_3$ was vacuum transferred into the flask at −78 °C. In the glovebox, a 6 mL sample vial equipped with a septum cap was charged with 20 mg (0.033 mmol) of $Me_2Si(Me_4C_5)_2SmCH(SiMe_3)_2$. A measured amount of toluene (2.0 mL) was then syringed into the vial containing the above reagents with a dry, Ar-purged gastight syringe. The vial was removed from the glovebox immediately prior to the polymerization experiment. The catalyst solution was then quickly syringed under an ethylene counterflow into the rapidly stirred olefin + silane reaction mixture through the septum-sealed reaction flask sidearm at 25 °C. After a measured time interval (90 min), the reaction was quenched by the addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under vacuum; yield, 0.23 g; M_n = 2000, M_w = 4700 by GPC. ^1H NMR ($C_2D_2Cl_4$, 120 °C, relative intensity): δ 7.25 ~7.01 (Ph, 2.9), 3.84 (SiH_2, 0.9), 2.25 ($PhCH_2Si$, 1.0), 1.31 ($-CH_2CH_2-$, 100), 0.92 ($-CH_3$, 1.3), 0.72 ($-CH_2$, 0.9). ^{13}C NMR ($C_2D_2Cl_4$, 75.5 MHz, 120 °C): δ 136.3, 132.4, 128.2, 128.1, 37.9, 35.3, 31.7, 29.4, 29.0, 28.4, 22.4, 13.7, 10.0, 8.5.

$PhSiH_3$ + Ethylene + Styrene Copolymerization. Representative Experiment. In the glovebox, 18 mg (0.031 mmol) of $Me_2Si(Me_4C_5)_2NdCH(SiMe_3)_2$ was loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. After evacuation, 0.2 mL (1.6 mmol) of $PhSiH_3$ and 1.2 mL (10.5 mol) of styrene were vacuum transferred into the flask at −78 °C. The mixture was then warmed to room temperature and exposed to ethylene (1 atm), while being rapidly stirred for 20 h.

Table 1. Organolanthanide-Mediated Ethylene Polymerization in the Presence of $PhSiH_3$

entry	catalyst/precatalyst[a]	$PhSiH_3$ (M)	reacn time (min)	yield (g)	activity (kg of PE/(mol of Ln atm h))	M_n[b] ($\times 10^3$)	M_w/M_n[b]
1	$(Cp'_2SmH)_2$	0.02	3	1.30	897	98.6	1.8
2	$(Cp'_2SmH)_2$	0.03	4	1.55	776	75.1	2.1
3	$(Cp'_2SmH)_2$	0.05	2	0.69	713	57.0	2.1
4	$(Cp'_2SmH)_2$	0.24	2	0.80	827	7.6	4.2
5	$(Cp'_2SmH)_2$	0.74	2	0.33	342	4.4	4.3
6	$(Cp'_2LuH)_2$	0.74	4	0.50[c]	274	2.6[d]	
7	$(Cp'_2YH)_2$	0.74	2	0.35	300	4.9	2.2
8	$(Cp'_2LaH)_2$	0.74	1.5	0.59	828	4.1	3.5
9	$Me_2SiCp''_2SmR$[e]	0.74	25	0.24		2.6	2.9

[a] $Cp' = \eta^5\text{-}Me_5C_5$; $Cp'' = \eta^5\text{-}Me_4C_5$; R = $CHTMS_2$; catalyst concentration range = 1.32−1.45 mM. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards unless otherwise indicated. [c] Contains 33% vinyl-terminated polyethylene. [d] Determined by ^1H NMR. [e] Since the catalytically active hydride is generated in situ, polymerization activities are not strictly comparable.

The reaction was then quenched by the addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under high vacuum; yield, 1.70 g. Polymer composition: 26% styrene incorporation (by ^1H NMR); $M_n = 3300$ by ^1H NMR. ^1H NMR ($C_2D_2Cl_4$, 120 °C, relative intensity): δ 6.95−7.70 (*Ph*, 87), 4.35 (SiH_2, 2.1), 2.30−2.80 ($-CH(Ph)-$, 19), 1.40−1.70 ($-CH_2$-CHPh−, 35), 0.90−1.40 ($-CH_2CH_2-$, 100). ^{13}C NMR ($C_2D_2Cl_4$, 75.5 MHz, 120 °C): δ 146.6, 135.7, 135.6, 135.2, 129.7, 129.6, 129.4, 128.4, 128.2, 128.1, 127.9, 127.2, 127.1, 125.6, 125.0, 46.1, 45.8, 36.8, 36.7, 29.6, 29.4, 27.6, 27.4, 25.4, 22.0, 16.6, 13.8, 10.0.

***n*-BuSiH$_3$ + Ethylene + Styrene Copolymerization. Representative Experiment.** In the glovebox, 23 mg (0.038 mmol) of $Me_2Si(Me_4C_5)_2SmCH(SiMe_3)_2$ was loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. After evacuation, 0.75 mL (5.6 mmol) of *n*-BuSiH$_3$ and 1.2 mL (10.5 mol) of styrene were vacuum transferred into the flask at −78 °C. The mixture was then warmed to room temperature and exposed to ethylene (1 atm), while being rapidly stirred for 20 h. The reaction was then quenched by the addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under high vacuum; yield, 1.40 g. Polymer composition: 7% styrene incorporation (by ^1H NMR); $M_n = 1700$, $M_w = 5000$ by GPC. ^1H NMR ($C_2D_2Cl_4$, 120 °C, relative intensity): δ 7.10−7.35 (*Ph*, 9.6), 3.78 (SiH_2, 0.5), 2.30−2.80 ($-CH(Ph)-$, 0.7), 1.40−1.70 ($-CH_2CHPh-$, 5.6), 1.01−1.40 ($-CH_2CH_2-$, 100), 0.90 ($-CH_2$, 3.9), 0.70 ($-CH_3$, 2.2). ^{13}C NMR ($C_2D_2Cl_4$, 75.5 MHz, 120 °C): δ 146.6, 128.3, 128.2, 128.0, 127.7, 126.9, 125.6, 124.7, 46.0, 38.4, 36.8, 32.7, 29.5, 29.2, 27.5, 22.0, 13.5, 9.2.

***n*-BuSiH$_3$ + Ethylene + 1-Hexene Copolymerization. Representative Experiment.** In the glovebox, 23 mg (0.038 mmol) of $Me_2Si(Me_4C_5)_2SmCH(SiMe_3)_2$ was loaded into a 100 mL round-bottom flask equipped with a large magnetic stirring bar. On the vacuum line, 10 mL of toluene was added to the flask via syringe under an Ar counterflow. After evacuation, 1.0 mL (7.5 mmol) of *n*-BuSiH$_3$ and 5.0 mL (0.040 mol) of 1-hexene were vacuum transferred into the flask at −78 °C. The mixture was then warmed to room temperature and exposed to ethylene (1 atm), while being rapidly stirred for 60 min. The reaction was then quenched by the addition of 2.0 mL of methanol. The polymer was collected by filtration and then washed with methanol and acetone, followed by drying under high vacuum; yield, 0.20 g. Polymer composition: 33% 1-hexene incorporation (by ^1H NMR); $M_n = 1000$, $M_w = 1500$ by GPC. ^1H NMR ($C_2D_2Cl_4$, 120 °C, relative intensity): δ 3.69 (SiH_2, 0.8), 1.40 ($-CH-$, 8.1), 1.30 ($-CH_2CH_2-$, 100), 1.10 ($-CH_3$, 22), 0.90 ($-CH_2$, 2.5), 0.72 ($-CH_3$, 0.9). ^{13}C NMR ($C_2D_2Cl_4$, 75.5 MHz, 120 °C): δ 32.6, 31.8, 29.6, 29.2, 28.5, 27.6, 25.6, 22.5, 13.9, 13.5, 9.2.

Results and Discussion

The goal of this investigation of organolanthanide-mediated silanolytic chain-transfer processes was to examine the scope of silanes viable as chain-transfer agents as well as the scope of applicable olefins and organolanthanides. Relevant to this work were preliminary reports from this laboratory that organolanthanides are efficient olefin hydrosilylation catalysts (Scheme 1).[7] In the present work, we demonstrate that the hydrosilylation and the polymerization processes can be coupled to afford silyl-capped polyolefins (Scheme 2). At relatively high olefin:silane ratios, repeated olefin insertion into Ln−H/C bonds affords lanthanide−polymer chains. Similary to the silanolysis process of the hydrosilylation reactions, Ln−C/Si−H transposition then occurrs and yields silyl-capped polyolefins. It will be seen that silyl functional groups are delivered predominantly if not exclusively to the terminal positions of the polymer chain in the final step of the polymerization reaction.

Silanolytic Chain Transfer with Phenylsilane. Organolanthanide-mediated α-olefin polymerizations and copolymerizations were first studied in the presence of $PhSiH_3$ under rigorously anhydrous/anaerobic high-vacuum-line conditions.[15] The $Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2$ precatalysts require a brief induction period before full catalytic activity is attained. As already shown, the reaction of $Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2$ with $PhSiH_3$ yields the active polymerization/hydrosilylation catalyst $[Me_2Si(Me_4C_5)_2LnH]_2$ and $PhH_2SiCH(SiMe_3)_2$ via Ln−C/Si−H transposition (eq 1).[8] One

$$Me_2Si(Me_4C_5)_2LnCH(SiMe_3)_2 + PhSiH_3 \rightarrow {}^1/_2[Me_2Si(Me_4C_5)_2LnH]_2 + PhH_2SiCH(SiMe_3)_2 \quad (1)$$

complication is the significantly lower solubility of $[Me_2Si(Me_4C_5)_2LnH]_2$ complexes versus the $[(Me_5C_5)_2LnH]_2$ analogues.[10c] Operationally, this requires lower catalyst concentrations, and overall ethylene polymerization yields are correspondingly lower than with the $[(Me_5C_5)_2LnH]_2$ analogues over similar reaction times (Table 1, entries 5−9). In the present study, the concentration of silane was maintained at a pseudo-zero-order level, and

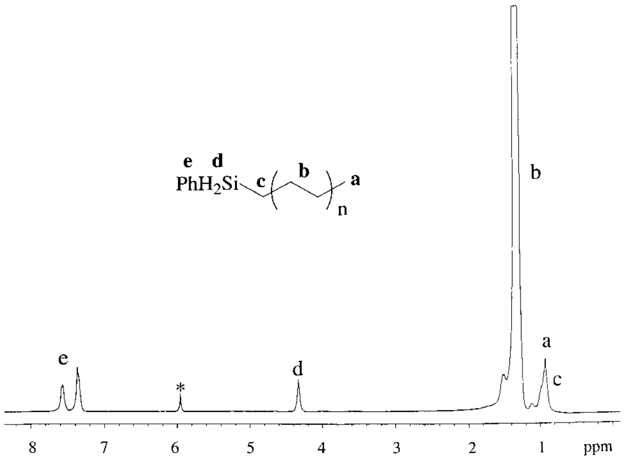


Figure 1. ^1H NMR spectrum (300 MHz) of a $PhSiH_2$-capped polyethylene sample in $C_2D_2Cl_4$ at 120 °C. The asterisk denotes the solvent resonance ($Cl_2HCCDCl_2$).

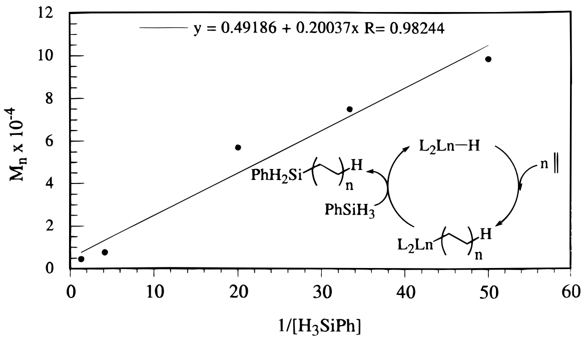
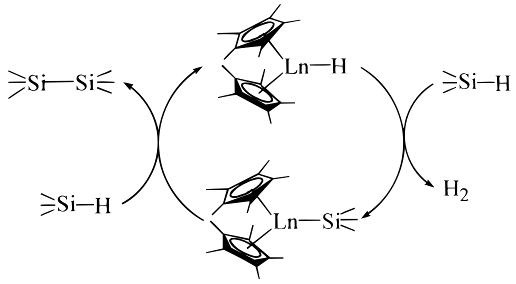
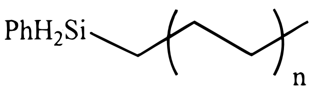


Figure 2. Relationship of polyethylene number average molecular weight (GPC versus polystyrene) to $PhSiH_3$ chain-transfer agent concentration for fixed organolanthanide catalyst $[(Me_5C_5)_2SmH]_2$ and ethylene concentrations. Inset: Proposed catalytic cycle for this process.

Scheme 3. Cycle for Organolanthanide-Catalyzed Dehydrogenative Silane Coupling





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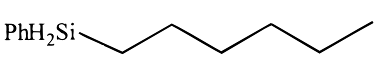
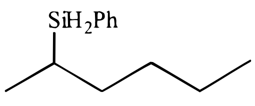


III



IV

the polymerization reactions were halted by quenching with MeOH (see Experimental Section for details). Polymerizations employed rapid stirring and short reaction times to minimize mass-transfer effects.[15] Characterization of the homopolymeric and copolymeric products was carried out by $^1H/^{13}C$ NMR and IR spectroscopies and by GPC versus polystyrene. The microstructures of the PhH_2Si-capped polyethylene (**II**) were characterized by $^1H/^{13}C$ NMR and IR. ^1H NMR (Figure 1) shows a characteristic $PhSiH_2$ resonance[7,8,16] at δ 4.33 coupled to an adjacent CH_2 group (triplet resolvable in low molecular weight samples, $^3J_{H-H} = 3.6$ Hz). The Ph, $SiCH_2$, polyethylene backbone, and chain end CH_3 moieties are assigned by comparison to literature data.[16,17] The SiH_2:$SiCH_2$:CH_3 intensity ratio of 2:2:3 (±8%)[18] argues that silyl-capped polyethylene is the exclusive product of this reaction. Furthermore, end group features associable with conventional[1,10] chain transfer processes (e.g., β-H elimination) are not detectable except in the case of a small Ln^{3+} ion (Table 1, entry 6). Since the same organolanthanide catalysts and $PhSiH_3$ under essentially the same reaction conditions yield mixed 1,2 and 2,1 regiochemistries in α-olefin hydrosilylation (e.g., **III** and **IV** for 1-hexene).[8] The terminus-only regiochemistry of **II** argues that polyolefin functionalization arises from direct chain transfer (Scheme 2) rather than from hydrosilylation of a β-H elimination product. NMR examination of the supernatants after polymer precipitation and washing reveals no evidence of silane coupling products. These observations rule out significant competing chain transfer via H_2[1,10] produced by potentially competing catalytic dehydrogenative silane coupling (Scheme 3).[8,18,19] In the ^{13}C NMR of the capped polyethylenes in $C_2D_2Cl_4$, both the $SiCH_2$ terminus (δ 9.98, $^1J_{C-H} = 118$ Hz, triplet) and the polymer chain end CH_3[17] (δ 13.76, $^1J_{C-H} = 127$ Hz, quartet) groups are readily assigned and are present in essentially equal proportions. The existence of a Si−H functionality is also verified by the observation of strong υ_{Si-H} absorption[20] in the IR at 2109 cm^{-1}. The covalently silyl-capped formulation is also supported by the observation of identical NMR spectra after polymer reprecipitation from hot *o*-dichlorobenzene with MeOH.

Polymerization and characterization data are shown in Table 1. Ethylene polymerization activities are somewhat lower than in conventional homogeneous group 4[1] or lanthanide[10,21] metallocene-catalyzed ethylene homopolymerizations. For the synthesis of silyl-capped polyethylene mediated by $[(Me_5C_5)_2LnH]_2$, the approximate order of reactivity follows decreasing lanthanide ionic radius: La ≫ Sm ≥ Y ≥ Lu, a reactivity trend which was observed for polymerization in the absence of silane.[10d] While silane does not affect the *relative* reactivities of the lanthanide complexes, the absolute polymerization rates of the $[(Me_5C_5)_2LnH]_2$ catalysts are depressed by the presence of silanes as noted above. This may reflect competitive coordination at Lewis acidic lanthanide olefin activation sites by the weakly basic silanes.[8]

The polymer molecular weight data in Table 1 indicate generally narrow polydispersities, consistent with single site processes.[1] Moreover, the number average molecular weight falls as $[PhSiH_3]$ increases (ethylene maintained at 1.0 atm; Table 1 entries 1−5; Figure 2). Assuming constant concentrations of catalyst, olefin, and silane (the latter maintained in pseudo-zero-order concentrations) throughout the polymerization, that rapid reinitiation occurs after chain transfer, and that silanolysis is the dominant chain-transfer mechanism ($k_{Si}[H_3SiR]$ ≫ the rate of other chain-transfer processes),[22] the product number average degree of polym-

Table 2. Organolanthanide-Mediated Ethylene Polymerization in the Presence of n-BuSiH$_3$ or C$_6$H$_5$CH$_2$SiH$_3$

entry	precatalyst[a]	silane	silane (M)	reacn time (min)	yield (g)	M_n[b] ($\times 10^3$)	M_w/M_n[b]
1	Me$_2$SiCp″$_2$SmR	n-BuSiH$_3$	0.85	30	0.15	1.2	1.34
2	Me$_2$SiCp″$_2$SmR	n-BuSiH$_3$	0.23	60	0.21	2.1	2.39
3	Me$_2$SiCp″$_2$SmR	n-BuSiH$_3$	0.080	240	5.04	24.0	1.75
4	Me$_2$SiCp″$_2$SmR	C$_6$H$_5$CH$_2$SiH$_3$	0.27	90	0.23	2.0	2.36
5	Me$_2$SiCp″$_2$SmR	C$_6$H$_5$CH$_2$SiH$_3$	0.54	90	0.79	1.1	2.84

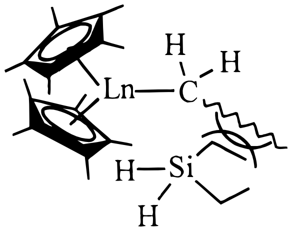
[a] Cp″ = η^5-Me$_4$C$_5$; R = CHTMS$_2$; catalyst concentration range = 2.64–3.28 mM; the catalytically active hydride is generated in situ. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards unless otherwise indicated.

erization, $\bar{P}_n$, at an idealized steady state should obey eq 2, where the first term in the denominator dominates.[23]

$$\bar{P}_n = \frac{k_p[\text{olefin}]}{k_{Si}[H_3SiR] + k_{\text{other chain transfer processes}}[Y]^x} \quad (2)$$

In the synthesis of PhH$_2$Si-capped polyethylene (**II**), the concentrations of olefin and catalyst are held constant and that of PhSiH$_3$ is varied while in pseudo-zero-order excess. Here k_p is the rate constant for propagation, and k_{Si} is the rate constant for silane chain transfer. From Figure 2 it can be seen that Table 1 entries 1–5 obey this relationship with $k_p/k_s \approx 190$.[24] In addition to the control of polymer molecular weight, macromolecule functionalization is simultaneously achieved by silyl group addition to the chain terminus via silanolytic chain transfer.

Silane Generality in Chain Transfer. In complementary work, we focused on exploring the scope of silanes which are effective as chain-transfer agents. In the course of studying chain-transfer agent generality, secondary silanes (PhMeSiH$_2$ and Et$_2$SiH$_2$) were found to be inefficient chain-transfer agents in organolanthanide polymerization systems. In the case of ethylene homopolymerization, uncapped polyethylenes (vinyl-terminated polyethylenes) are produced in the presence of secondary silane derivatives. This result suggests that silane steric encumberance of the chain-transfer agents plays an important role in the chain transfer step. The incoming bulky chain-transfer agents presumably generate unfavorable steric interactions with the metal center in the chain transfer step (**V**), and these interactions would render Sm-polyolefin interception via Si–H/Sm–C transposition inefficient. The heteroatom-containing silane (Me$_3$Si)$_2$NSiH$_3$[25] is found to be a severe poison for these organolanthanide catalysts.



V

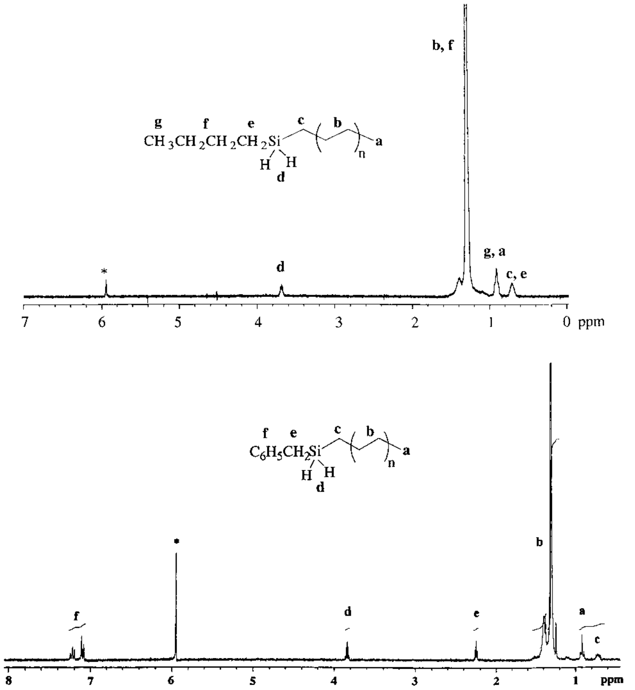
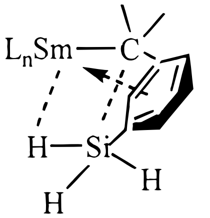
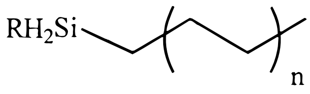


Figure 3. (a) ^{1}H NMR spectrum (300 MHz) of a n-BuH$_2$Si-capped polyethylene sample in C$_2$D$_2$Cl$_4$ at 120 °C. (b) ^{1}H NMR spectrum (300 MHz) of a C$_6$H$_5$CH$_2$SiH$_2$-capped polyethylene sample in C$_2$D$_2$Cl$_4$ at 120 °C. The asterisks denotes the solvent resonance (Cl$_2$HCCDCl$_2$).



VI

On the basis of the efficiency of a primary aryl silane (PhSiH$_3$) as a chain-transfer agent, primary alkyl silanes were also examined as chain-transfer agents in organolanthanide polymerization systems. It is a well-known effect that aromatic substituents can coordinate to electrophilic metal centers and stabilize polyhapto intermediate structures (**VI**).[26] However, this possible aromatic substituent stabilizing effect does not appear to be significant in organolanthanide-mediated chain transfer as judged by the excellent efficiency of primary alkyl silanes as chain-transfer agents. Both n-BuSiH$_3$ and C$_6$H$_5$CH$_2$SiH$_3$ are efficient and selective in organolanthanide-mediated ethylene homopolymerizations, resulting in silyl-capped polyolefins (**VII**). In accord with expectations for n-BuH$_2$Si-capped and C$_6$H$_5$CH$_2$SiH$_2$-capped polyethylenes, the ^{1}H NMR spectra exhibit a characteristic n-BuSiH_2 resonance at δ 3.69 (multiplet, coupled to an adjacent CH$_2$ group), a C$_6$H$_5$CH$_2$SiH_2 resonance at δ 3.84 (quintet, $^3J_{H-H}$ = 3.5 Hz), and a C$_6$H$_5$$CH_2SiH_2$ resonance at δ 2.25 (triplet, $^3J_{H-H}$ = 3.5



R = n-Bu, C$_6$H$_5$CH$_2$

VII

Table 3. Organolanthanide-Mediated Ethylene Polymerization in the Presence of *n*-BuSiH$_3$ or PhSiH$_3$

entry	catalyst[a]	silane	silane (M)	reacn time (min)	yield (g)	activity (kg of PE/(mol of Ln atm h))	M_n[b] ($\times 10^3$)	M_w/M_n[b]
1	$(Cp'_2SmH)_2$	*n*-BuSiH$_3$	0.34	2	0.22	506	2.7	1.87
2	$(Cp'_2SmH)_2$	PhSiH$_3$	0.34	2	0.34	782	3.2	4.54

[a] Cp′ = η^5-Me$_5$C$_5$; catalyst concentration = 2.64mM. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards unless otherwise indicated.

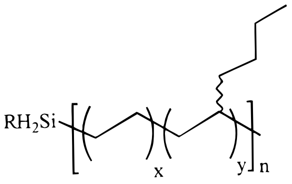
Table 4. Organolanthanide-Mediated Ethylene + 1-Hexene and Ethylene + Styrene Copolymerization in the Presence of Primary Silanes

entry	precatalyst[a]	silane	silane (M)	conomer (M)	reacn time (min)	yield (g)	comonomer incorp (M%)	M_n[b] ($\times 10^3$)	M_w/M_n[b]
1	Me$_2$SiCp″$_2$SmR	PhSiH$_3$	0.41	1.52[c]	180	0.60	12	3.7	2.9
2	Me$_2$SiCp″$_2$SmR	PhSiH$_3$	0.41	2.28[c]	180	0.24	60	0.4	4.9
3	Me$_2$SiCp″$_2$NdR	PhSiH$_3$	0.16	0.98[d]	1200	1.70	26	3.3	
4	Me$_2$SiCp″$_2$SmR	*n*-BuSiH$_3$	0.080	0.32[c]	1200	0.20	0.3	2.5	3.86
5	Me$_2$SiCp″$_2$SmR	*n*-BuSiH$_3$	0.51	1.44[c]	120	1.00	3.0	1.9	2.05
6	Me$_2$SiCp″$_2$SmR	*n*-BuSiH$_3$	2.57	13.3[c]	60	0.20	33	1.0	1.47
7	Me$_2$SiCp″$_2$SmR	*n*-BuSiH$_3$	0.58	1.05[d]	1200	1.40	7.0	1.7	2.95

[a] Cp″ = η^5-Me$_4$C$_5$; R = CHTMS$_2$; catalyst concentration range = 2.64−3.85 mM; the catalytically active hydride is generated in situ. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards unless otherwise indicated. [c] 1-Hexene. [d] Styrene.

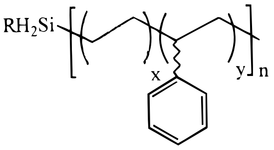
Hz), respectively (Figure 3a,b, respectively). End group analyses by ^{1}H NMR reveal a 2:3 SiH$_2$:CH$_3$ intensity ratio for both C$_6$H$_5$CH$_2$SiH$_3$ + ethylene and *n*-BuSiH$_3$ + ethylene products. These observations suggest that silanolytic chain transfer is the predominant if not exclusive chain termination process, as already observed in the case of PhSiH$_3$ + ethylene. Ethylene polymerization and polymer characterization data are summarized in Table 2. As expected from the aforementioned PhSiH$_3$ + ethylene results, the number average molecular weights of the silyl-capped polyolefins scale approximately inversely with chain-transfer-agent concentration. The highest molecular weight polymers are obtained using the lowest concentration of chain-transfer agent (see Table 2, entry 3). Comparative experiments shown in Table 3 reveal that the yield and molecular weight of *n*-BuH$_2$Si-capped polyethylene is similar to that of PhH$_2$Si-capped polyethylene obtained under identical reaction conditions. This argues that the polymerization activities and chain transfer rates of *n*-BuSiH$_3$ and PhSiH$_3$ are comparable.

Copolymerizations. The present silanolytic chain-transfer process using PhSiH$_3$ and *n*-BuSiH$_3$ is also effective in the formation of silyl-capped ethylene + 1-hexene (**VIII**) and ethylene + styrene (**IX**) copolymers (Table 4). The copolymerizations were carried out with [Me$_2$Si(Me$_4$C$_5$)$_2$LnH]$_2$ complexes, since these catalysts are more active for ethylene + α-olefin copolymerization processes.[10c] ^{13}C and ^{1}H NMR spectroscopy of the ethylene-based copolymers indicates essentially random ethylene + 1-hexene and ethylene + styrene copolymer microstructures.[27] For the *n*-BuH$_2$Si-capped ethylene + 1-hexene copolymer, Si is selectively delivered to the ethylene unit, and the ^{1}H chemical shift of the SiH$_2$ group (δ 3.69) is indistinguishable from that in *n*-BuH$_2$Si-capped polyethylene. Other possible microstructures such as Si delivery to inserted 1-hexene (**X**) are not detected in significant quantities in this system. This selectivity likely reflects similar steric effects observed in earlier studies.[10c] The ethylene + 1-hexene copolymerization reactions carried out under the same reaction conditions in the absence of silanes support this contention, and microstructure unit (**XI**) is the major product.



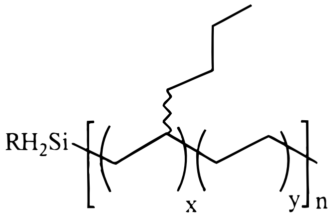
R = *n*-Bu, Ph

VIII



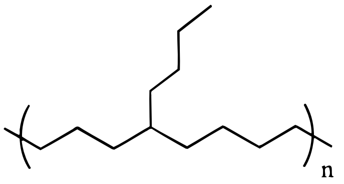
R = *n*-Bu, Ph

IX



R = *n*-Bu, Ph

X

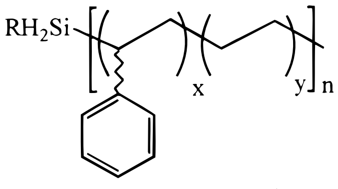


XI

In the case of PhSiH$_3$ + ethylene + styrene copolymerization reactions, silyl substituents are delivered to ethylene units as confirmed by ^{1}H NMR observation of SiH$_2$ as triplets coupled to adjacent CH$_2$ units (δ 4.35, $^3J_{H-H}$ = 3.6 Hz); **IX**; PhH$_2$Si-capped polyethylene = δ 4.33). Silyl substituent attachment to styrenic units (**XII**) instead of ethylene can be ruled out because organolanthanide catalysts effect 2,1 addition to styrenic substituents with complete regiospecificity[8] and because the ^{1}H NMR exhibits no detectable SiH$_2$ resonance coupled to the CH of a styrenic unit (**XII**).

Conclusions

Suitable selection of silane derivatives and α-olefins yields silyl-capped polyolefins via organolanthanide-mediated polymerization/silanolytic chain transfer pro-



R = *n*-Bu, Ph

XII

cesses. The mechanism of this transformation resembles that of the analogous hydrosilylation process, with the formation of Ln−C(polymer chain) bonds, followed by Si−H/Ln−C transposition. Silicon is thereby selectively and catalytically transferred to the terminus of the polymer chain in a final step. These results demonstrate that primary alkyl and primary aryl silanes (*n*-BuSiH$_3$, C$_6$H$_5$CH$_2$SiH$_3$, and PhSiH$_3$) are effective and selective chain-transfer agents yielding silyl-capped ethylene-based polyolefins via chain transfer process in organolanthanide-mediated polymerization systems (Scheme 2). With silanolytic chain-transfer processes, the synthesis of a functionalized polyolefin and the control of the polymer molecular weights are simultaneously achieved. In due course, we will report results with group 4 metals, with other olefins, and with other chain transfer agents.

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