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Silanolytic Chain Transfer in Olefin Polymerization with Supported Single-Site Ziegler−Natta Catalysts

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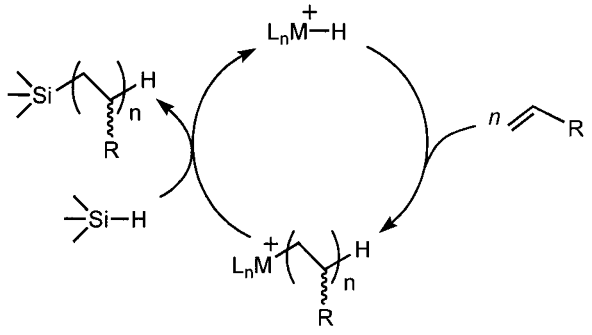
The in-situ introduction of versatile functional groups into nonpolar polyolefin macromolecules offers an attractive approach[1] for modifying interfacial properties via surface segregation of the polar functional groups. In addition to surface-modifying characteristics, robust, linking functional groups, especially at chain ends, offer a means to construct a variety of polymer architectures such as block and graft copolymers. Chain transfer processes to organometalloids[2−4] offer an excellent means to achieve this end because they introduce organometalloid functionality at chain termini via an in-situ catalytic cycle that simultaneously achieves molecular weight control. Silanes are promising candidates for organometalloid chain transfer processes because of their efficiency as chain transfer agents, structural diversity and tunability, environmental stability as building block linkers, and versatility in subsequent functional group transformations.[2] We recently demonstrated efficient “drop-in” silanolytic chain transfer processes for α-olefin polymerization using single-site homogeneous organotitanium and organolanthanide catalysts (Scheme 1).[2] These results raise intriguing questions about catalyst and monomer generality, especially in regard to catalysts suitable for slurry and gas-phase polymerization processes, and chain transfer to ethylene homopolymers, which is not efficient for homogeneous group 4 systems.[2a,c] In this communication, we report initial observations extending the scope of silanolytic chain transfer processes to *heterogeneous* single-site Ziegler−Natta catalysts, which are currently of considerable scientific and technological interest.[5]

Supported catalysts were prepared with rigorous exclusion of air and moisture via the following procedure.[5] (1) Preparation of SiO_2/MAO: Calcined silica (Davison Grade 62, specific surface area, ~250 m^2/g, dried at 320−380 °C for 14 h under high vacuum) was stirred with an MAO solution (Aldrich, 10 wt % in toluene) at 90 °C for 4 h. The solid was then collected by filtration under inert atmosphere and washed thoroughly with toluene. The anchored MAO coverage on the silica was ~3 mmol Al/g solid. (2) Metallocene or quasi-metallocene chemisorption: Solutions of the single-site catalyst precursors, Cp_2ZrCl_2 (**1**), *rac*-$[CH_2CH_2(\text{indenyl})_2]ZrCl_2$ (**2**), $[Me_2Si(Me_4C_5)(^t\text{BuN})]TiMe_2$ (**3**), and $(Me_5C_5)TiMe_3$ (**4**), were stirred with SiO_2/MAO slurries (Al/Zr, Al/Ti ≈ 90−130) in toluene at 80 °C for 2 h (**1**, **2**) and at 45 °C for 1 h for (**3**, **4**) to yield yellow to dark-red fine powders. Nonchemisorbed catalyst components in the supernatants were removed by filtration and several washings with hot toluene. The supported catalysts were then dried under high vacuum.

Scheme 1. Proposed Catalytic Cycle for Silanolytic Chain Transfer Coupled to Single-Site Olefin Polymerization



Polymerizations were carried out in toluene slurries under rigorously anhydrous/anaerobic high-vacuum line conditions.[2c] A weighed portion of a completely dried solid catalyst was charged into a 100 mL flame-dried flask equipped with a large stirring bar in a nitrogen-filled Vacuum Atmospheres glovebox (<1 ppm of O_2). Measured quantities of toluene and silane (in pseudo-zero-order stoichiometric excess) were then vacuum-transferred into the flask on a high-vacuum (10^{-5} Torr) line, and monomer gas was introduced at 25 °C with rapid stirring. After a measured time interval, polymerizations were terminated by injecting 2 mL of methanol, and the reaction mixtures were then poured into a large quantity of methanol. The products were collected by filtration, washed with methanol and acetone, and dried on a high-vacuum line. To completely remove the catalyst residue,[6] the white solid products were slurried in *o*-xylene at 120−140 °C with silica gel and slowly cooled to ambient temperature, which caused the dissolved polymers to deposit on the silica gel in the form of thin layers. The slurries were next packed into a column, and the deposited polymers were eluted with *o*-xylene, which was slowly increased in temperature to 100−140 °C. The eluted polymers were then reprecipitated with methanol. The precipitated polymers were collected by filtration, washed with methanol and acetone, and dried under high vacuum at room temperature. The recovery of product polymers averaged ~74% (~85% excluding entries 6, 12, and 15 in Table 1, which appear to have very high molecular weights) by this method, whereas negligible quantities could be extracted from the catalyst residues by conventional Soxhlet techniques. Control NMR-scale experiments indicate negligible reaction between Et_2SiH_2 and SiO_2 over 5 h at 140 °C, arguing that reaction of the polymer silane end groups with the SiO_2 of the column is negligible.

Polymerization data are summarized in Table 1. Catalyst SiO_2/MAO/**1** exhibits reasonable activity in the absence of silane, 3.44 g of polyethylene/(g of catalyst·atm·h), which is comparable to literature results without additional alkylaluminum as the cocatalyst.[5] The molecular weight of the product is significantly higher than that produced by comparable homogeneous systems,[5] and the PDI is slightly larger than 2.0; both are common observations in supported organometallic olefin polymerization systems.[5] Polymerization activity was decreased to <0.3x, and the product molecular weights were also depressed as the *n*-hexyl-SiH_3 concentration was increased (entries 1−5; run to approximately

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Table 1. Ethylene and Propylene Polymerization with Heterogeneous Ziegler−Natta Catalysts in the Presence of Various Silanes

entry	catalyst precursor[a]	catalyst (mg)	monomer	silane	toluene (mL)	silane (M)	rxn time (min)	polymer yield (mg)	activity[b]	M_w[c] × 10^{-3}	M_w/M_n[c]	MeOH soluble fraction (mg)
1	Cp_2ZrCl_2, **1**	401	ethylene		30	0	10	230	3.44	374	3.99	n.d.
2	Cp_2ZrCl_2, **1**	405	ethylene	*n*-hexyl-SiH_3	30	0.093	45	230	0.74	26	2.95	0
3	Cp_2ZrCl_2, **1**	400	ethylene	*n*-hexyl-SiH_3	30	0.200	45	280	0.93	39	3.98	130
4	Cp_2ZrCl_2, **1**	401	ethylene	*n*-hexyl-SiH_3	30	0.682	60	370	0.92	7	1.57	180
5	Cp_2ZrCl_2, **1**	510	ethylene	*n*-hexyl-SiH_3	30	1.436	90	550	0.72	6	1.44	460
6	Cp_2ZrCl_2, **1**	388	ethylene	$PhSiH_3$	22	0.111	390	180	0.07	n.d.	n.d.	100
7	Cp_2ZrCl_2, **1**	400	ethylene	Et_2SiH_2	22	0.168	15	220	2.20	57	3.61	n.d.
8	Cp_2ZrCl_2, **1**	260	ethylene	Et_2SiH_2	30	1.074	60	260	1.00	30	3.20	40
9	Cp_2ZrCl_2, **1**	404	ethylene	Et_2SiH_2	30	2.410	120	440	0.54	18	2.74	50
10	Cp_2ZrCl_2, **1**[d]	8.7	ethylene	*n*-hexyl-SiH_3	30	0.413	60	850	28.56[e]	10	1.80	40
11	*r*-Et(ind)$_2$ZrCl$_2$, **2**	418	ethylene	*n*-hexyl-SiH_3	30	0.337	20	390	2.81	n.d.	n.d.	360
12	*r*-Et(ind)$_2$ZrCl$_2$, **2**	404	propylene	*n*-hexyl-SiH_3	30	0.511	1320	820	0.09	14	1.95	760
13	$CGCTiMe_2$, **3**	252	ethylene	-	15	0	15	250	3.97	n.d.	n.d.	n.d.
14	$CGCTiMe_2$, **3**	308	ethylene	$PhSiH_3$	15	0.081	150	400	0.52	216	5.10	100
15	Cp*$TiMe_2$, **4**	474	ethylene	*n*-hexyl-SiH_3	30	0.748	60	130	0.27	n.d.	n.d.	140

[a] Supported on SiO_2/MAO, *r*-Et(ind)$_2$ = *rac*-CH_2CH_2(indenyl)$_2$, CGC = $Me_2Si(Me_4C_5)(N^tBu)$, Cp* = Me_5C_5. [b] In g of polymer/(g of catalyst·atm·h). [c] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards unless otherwise indicated. [d] Homogeneous reaction as a control. Al/Zr = 150. [e] In g of polymer/(mmol of Zr·atm·h).

constant conversion). A small portion of polymer exhibits GPC elution characteristics indistinguishable from those of the polymer produced without *n*-hexylsilane (entries 2 and 3). This nonuniformity of reaction products likely reflects variations in active site structures and *n*-hexyl-SiH_3 local concentrations within the solid catalyst. Such effects have ample precedent.[5] The depressed activity as silane concentration is increased is reasonably ascribed to the Lewis basicity of this reagent.[2,8b] Microstructural analysis of the polymeric product reveals *n*-hexyl-SiH_2-capped polyethylene [^1H NMR in $C_2D_2Cl_4$, at 120 °C: δ 3.72 (SiH_2); ^{13}C NMR in $C_2D_2Cl_4$, at 120 °C: δ 9.09 (CH_2SiH_2); ^{29}Si NMR in $C_2D_2Cl_4$, at 120 °C: δ −29.8 (SiH_2); IR in a KBr pellet: 2020 cm^{-1} (ν_{Si-H})), which compares favorably with an authentic capped polyethylene sample produced using *n*-hexyl-SiH_3 and an effective homogeneous polymerization/chain transfer catalyst, $[Me_2Si(Me_4C_5)_2]SmCH(SiMe_3)_2$.[2b] It can be seen from the ^1H NMR spectrum of the polyethylene produced from SiO_2/MAO/**1** in the presence of *n*-hexyl-SiH_3 (Figure 1) that the combined intensity of the CH_3 groups (d + h) at the saturated chain end, overlapping with the *n*-hexylsilyl CH_3 signal, is larger than the CH_3:CH_2Si:SiH_2 intensity ratio of 6.0: 4.0:2.0 expected from Scheme 1. These observations indicate that this polymer sample is a mixture of *n*-hexyl-SiH_2-capped polyethylene (~53%) and uncapped polyethylene with saturated end groups (~47%).[7] Because of overlap between the CH_3 and polyethylene backbone resonances, we estimate uncertainties in this assay of ±5% and ±10% for high and low silane concentrations, respectively.

NMR and GC/MS analyses of the methanol-soluble polymerization reaction byproducts isolated from workup reveal linear and cyclic silane coupling products[8] and *n*-alkanes having exclusively even carbon numbers between 14 and 26. It is well-known that cationic organo-group 4 complexes catalyze dehydrogenative silane coupling to produce polysilane oligomers (Scheme 2, cycle B).[8] It is reasonable that the H_2 byproduct of this reaction functions as a chain transfer agent, resulting in saturated polyethylene chain ends (Scheme 2, cycle A). Various conceivable mechanistic scenarios for this coupling reaction give rates of H_2 production which scale to either first-order[8] or second-order in silane concentration, while the rate of chain transfer should scale linearly with [silane].[2] In the present study, it is found that increasing [*n*-hexyl-SiH_3] does not result in higher silyl group incorporation levels, and the relative ^1H NMR CH_2SiH_2 group:CH_3 group intensity ratio decreases with increasing *n*-hexyl-SiH_3 concentration,[7] while M_w generally declines (Table 1). The absence of detectable unsaturated polyethylene chain ends and the presence of even carbon number *n*-alkanes in the methanol-soluble products argue that any other chain transfer pathways such as β-H elimination or Zr−CH_2CH_2(polymer)/Me−Al(MAO) transposition (eq 1)

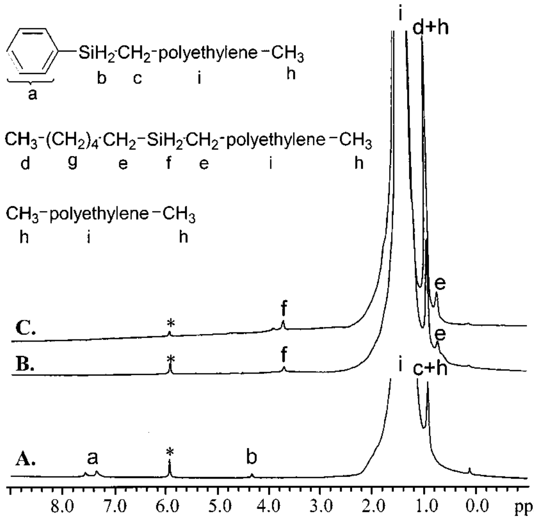
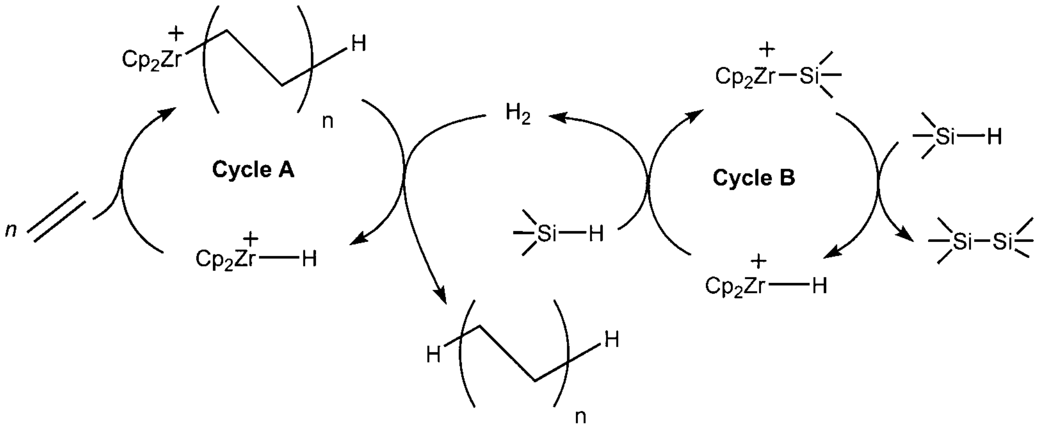


Figure 1. (A) ^1H NMR spectrum (400 MHz) of a $PhSiH_2$-capped polyethylene sample in $C_2D_2Cl_4$ at 120 °C. (B) ^1H NMR spectrum (400 MHz) of an *n*-hexyl-SiH_2-capped polyethylene sample in $C_2D_2Cl_4$ at 120 °C. Synthesized with [*n*-hexyl-SiH_3] = 0.09 M. (C) ^1H NMR spectrum (400 MHz) of an *n*-hexyl-SiH_2-capped polyethylene sample in $C_2D_2Cl_4$ at 120 °C. Synthesized with [*n*-hexyl-SiH_3] = 0.68 M. Asterisk denotes the solvent resonance ($Cl_2HCCDCl_2$).

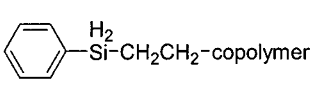
$$Cp_2Zr^+{-}CH_2CH_2{-}polymer + MAO{-}CH_3 \rightarrow Cp_2Zr^+{-}CH_3 + MAO{-}CH_2CH_2{-}polymer \quad (1)$$

are not the dominant chain termination steps in this

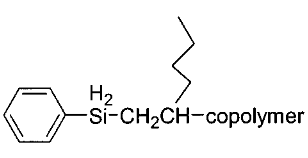
Scheme 2. Proposed Cycle for Catalytic Olefin Polymerization (Cycle A), Dehydrogenative Silane Coupling (Cycle B), and Formation of Saturated Chain-End Polymeric Products



system. In the case of $PhSiH_3$, which is an effective chain transfer agent in homogeneous organolanthanide[2a,b,e]- and organotitanium[2a,c,d]-catalyzed olefin polymerizations, the present product polymers are a mixture of silyl-capped and uncapped saturated polyethylenes (Figure 1). Copolymerization of ethylene and 1-hexene with the supported catalyst system forms partially silyl-capped copolymers, in which the phenylsilyl group is incorporated adjacent to an ethylene subunit (**I**) and *not adjacent* to a 1-hexene subunit (**II**)[9] as in the case of the homogeneous organolanthanide chain transfer systems.[2b,e]



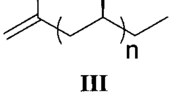
I



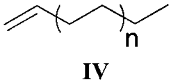
II

Sterically more hindered secondary silanes generally exhibit lower reactivity in the present silanolytic chain transfer reactions.[2] For the supported $SiO_2/MAO/\mathbf{1}$ catalyst, Et_2SiH_2 decreases the product molecular weight, although there are no spectroscopically observable (IR, ^1H, ^{13}C, ^{29}Si NMR) silyl end groups. The even-numbered *n*-alkanes detected in the methanol-soluble fractions suggest that the secondary silane also produces H_2 through dehydrogenative silane coupling. Interestingly, the homogeneous counterpart of this catalyst, $MAO/\mathbf{1}$, with *n*-hexyl-SiH_3 yields exclusively noncapped polyethylene with saturated chain ends (Table 1, entry 10).[10]

Polyethylene and isotactic polypropylene formation mediated by $SiO_2/MAO/\mathbf{2}$ in the presence of *n*-hexyl-SiH_3 does not yield silyl-capped polymers. Vinylidene chain ends (**III**) instead of silyl groups are observed in the case of polypropylene and vinyl chain ends (**IV**) in the case of polyethylene. We additionally observe CH_3 chain ends in higher quantities than unsaturated chain end groups, although the methanol-soluble products in these polymerizations do not include *n*-alkanes. Interestingly and in sharp contrast to the homogeneous chain transfer systems, the supported single-site organotitanium catalysts $SiO_2/MAO/\mathbf{3}$ and $SiO_2/MAO/\mathbf{4}$ do not afford silyl-capped polyethylenes. The polyethylene from $SiO_2/MAO/\mathbf{4}$ contains vinyl chain ends (**IV**) and negligible *n*-alkanes in the methanol-soluble part. In these organotitanium systems, all product polymers have relatively high molecular weights, and chain transfer with H_2 is clearly not extensive, even though small quantities of oligosilane coupling products are detected by GC/MS. The classical heterogeneous Ziegler−Natta catalysts, $TiCl_3 \cdot {}^1/_3AlCl_3-Et_2AlCl$ and $MgCl_2/TiCl_4/(ID)-Et_3Al-(ED)$[11] (ID = diisobutyl phthalate as an internal donor; ED = diphenyldimethoxysilane [$Ph_2Si(OMe)_2$] as an external donor), were also examined with added $PhSiH_3$ in ethylene and propylene polymerization experiments. Negligible yields of silyl-capped polyolefins are obtained from these catalyst systems.



III



IV

These results show that the scope of silanolytic chain transfer can be extended to heterogeneous Zr olefin polymerization catalysts. While the breadth of applicability appears to be somewhat narrower than the case of homogeneous single-site catalysts,[2] the first group 4 systems capable of functioning in the slurry mode and of producing functionalized ethylene homopolymers have been developed. Moreover, there are clearly distinct and large differences in mechanism and regiocontrol between the homogeneous and silica-supported heterogeneous systems.

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Supporting Information Available: Detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) CH_3:CH_2Si integral ratios in the ^1H NMR spectra indicate that ~53% of the polymer chains have *n*-hexylsilyl groups at the chain ends in the polymerization with [*n*-hexyl-SiH_3] = 0.09 M, ~62% at 0.20 M, ~26% at 0.68 M, and ~9% at 1.43 M silane. These values may include appreciable uncertainties because of significant overlap with a ^1H polyethylene main chain signal.

(8) There are two proposed mechanisms for group 4 cationic metallocene-mediated dehydrogenative silane coupling. Metal−hydride and metal−silyl species are involved in both mechanisms, and the only difference is the elementary step in which silanes are coupled. For a photochemical redox mechanism, see: (a) Dioumaev, V. K.; Harrod, J. F. *Organometallics* **2000**, *19*, 583−589. (b) Gauvin, F.; Harrod, J. F.; Woo, H. G. *Adv. Organomet. Chem.* **1998**, *42*, 363−405. For a σ-bond metathesis mechanism, see: (c) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168. (d) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543−2545. (e) Watson, P. L.; Tebbe, F. N. U.S. Patent 4,965,386, 1990. (f) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22−29 and references therein. (g) Corey, J. Y.; Huhmann, J. L.; Zhu, X.-H. *Organometallics* **1993**, *12*, 1121−1130 and references therein. (h) Woo, H. G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047−7055. (i) Harrod, J. F. In *Inorganic and Organometallic Polymers with Special Properties*; Laine, R. M., Ed.; Kluwer Academic Publishers: Amsterdam, 1991; Chapter 14, and references therein. (j) Kobayashi, T.; Sakakura, T.; Hayashi, T.; Yumura, M.; Tanaka, M. *Chem. Lett.* **1992**, 1157−1160.

(9) $PhSiH_2-CH_2CH_2-$ chain ends were confirmed by ^{13}C NMR; no $PhSiH_2-CH_2CH(n\text{-butyl})-$ chain ends were detected.

(10) That minor peaks from *n*-alkanes having odd carbon numbers in the GC/MS are observed implies MAO also functions as a chain transfer agent in this system.

(11) $MgCl_2$-supported catalysts were provided by Mitsui Chemicals, Inc.

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