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Silanolytic Chain Transfer in Ziegler−Natta Catalysis. Organotitanium-Mediated Formation of New Silapolyolefins and Polyolefin Architectures

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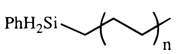
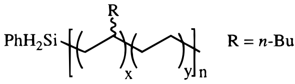
The efficient and selective introduction of polar and/or reactive functional groups into polyolefin chains via homogeneous Ziegler−Natta catalytic processes[1] offers the tantalizing prospect of new polymer properties and architectures.[2−5] We recently reported that organosilanes function as chain transfer agents in lanthanocene-mediated polymerizations to afford silyl-terminated ethylene polymers and copolymers (e.g., **I** and **II**).[6,7] This observation raises intriguing questions of whether such transformations have generality, whether they might be effected by conventional group 4 catalysts (allowing "drop-in" processes), whether the scope can be extended beyond simple ethylene-based polymers, and whether more elaborate macromolecular architectures are accessible. We report here that several classes of organotitanium catalysts are highly and, so far, uniquely competent for producing a variety of new linear, stereoregular, and unusual branched silapolyolefins.

I



II



R = *n*-Bu, Ph

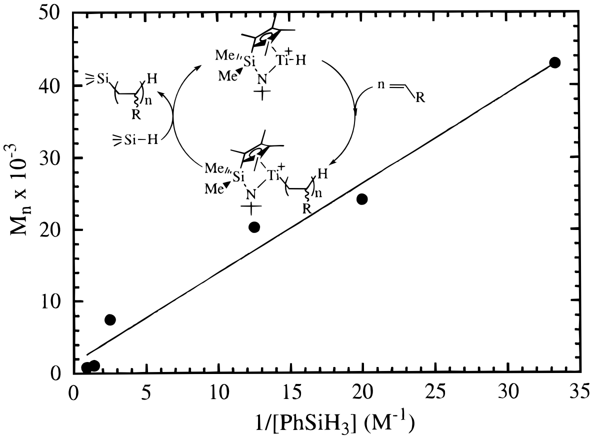
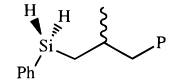
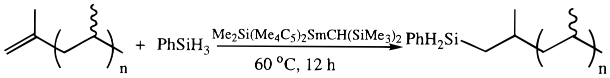


Figure 1. Relationship of polypropylene number average molecular weight (GPC versus polystyrene) to PhSiH$_3$ chain transfer agent concentration for the [Me$_2$Si(Me$_4$C$_5$)^{t}BuN]TiMe$^+$B(C$_6$F$_5$)$_4$$^-$-mediated capping of atactic polypropylene. Catalyst and olefin concentrations are assumed to be constant. Inset: Proposed catalytic cycle for this process.

Polymerization and copolymerizations were carried out in the presence of PhSiH$_3$ under rigorously anhydrous/anaerobic conditions.[4,6] Interestingly, a variety of *zirconium* metallocenes and quasi-metallocenes with a variety of cocatalysts[1,8] produced predominantly or exclusively polyolefins devoid of silyl caps together with dehydrogenative silane coupling[9] products (PhSiH$_2$-SiH$_2$Ph, etc.).[9,10] The behavior of several "cationic" *organotitanium* catalysts is markedly different. Thus, "constrained geometry" catalyst[11] [Me$_2$Si(Me$_4$C$_5$)^{t}BuN]TiMe$^+$B(C$_6$F$_5$)$_4$$^-$ (**1**) mediates the rapid polymerization of propylene with efficient silanolytic chain transfer (Table 1) and no detectable (by ^{1}H, ^{29}Si NMR) silane coupling products. ^{1}H, ^{13}C, and ^{29}Si NMR are in accord with PhSiH$_2$-terminated atactic polypropylene microstructure **III**.[12−14] Further structural proof derives from the synthesis of an authentic sample (with indistinguishable NMR parameters) via organolanthanide-catalyzed hydrosilylation (1,2 regiochemistry expected[10]) of a vinylidene-terminated polypropylene[8a] (eq 1). In regard to mechanism, polymerization coupled with silanolytic chain transfer (Figure 1, inset) having constant catalyst, olefin, and silane concentrations, as well as rapid chain growth after reinitiation, should obey eq 2,[15] where $\bar{P}_n$ is the steady-state number average degree of polymerization, k_p the rate constant for chain propagation, and k_s the rate constant for silanolytic chain

III





(1)

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(12) ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 4.48 (PhSiH_2, t, $^3J = 3.6$ Hz, resolved in lower M_w samples; SiH$_2$ diastereotopism not resolved), 0.75 (SiCH_2, t, $^3J = 3.6$ Hz, resolved in lower M_w samples). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ 1.95 (SiCH$_2$, t, $^1J_{C-H} = 118$ Hz) and 14.53 (−CH$_2$CH$_2$$CH_3$, q, $^1J_{C-H} = 124$ Hz) of approximately equal intensity with NOE suppression.

(13) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982; pp 75−84.

(14) (a) The PhSiH$_2$CH$_2$− spectral parameters[14b] are identical to those obtained in the Me$_2$Si(Me$_4$C$_5$)$_2$Sm-mediated 1,2 hydrosilylation[10,14c] of 2-methyl-1-butene. (b) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1984; pp 512−520. (c) Molander, G. A.; Nicols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416.

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Table 1. Propylene and 1-Hexene Polymerization; Ethylene-1-Hexene and Ethylene-Styrene Copolymerization; Representative Experiments in the Presence of $[Me_2Si(Me_4C_5)(^tBuN)][TiMe^+B(C_6F_5)_4^-]$ [a] and $PhSiH_3$

entry	time (min)/ temp (°C)	monomer (1 atm)	comonomer (M)	$PhSiH_3$ (M)	polymer yield (g)	comonomer incorp (M%)	M_n [b]	M_w/M_n [b]
1	3/25	propylene		0.03	3.0		43 000	3.5
2	3/25	propylene		0.05	2.5		24 200	1.7
3	3/25	propylene		0.08	1.3		20 300	2.0
4	3/25	propylene		0.40	0.4		7 500	2.1
5	3/25	propylene		0.73	3.8		1 100	4.4
6	3/25	propylene		1.13	3.2		890	5.0
7	10/0	propylene		0.020	4.0		67 000	3.1
8	60/25	1-hexene[c]		0.030	3.1		2 500	2.5
9	180/25	ethylene	0.17[d]	0.050	2.8	50	72 000	1.4
10	180/25	ethylene	0.32[e]	0.060	2.6	52	50 000	2.4

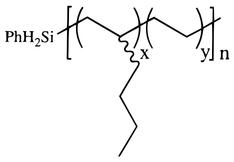
[a] Concentration range of catalyst = 2.64−3.05 mM. [b] By GPC in 1,2,4-trichlorobenzene vs polystyrene standards. [c] Concentration of 1-hexene = 6.00 M. [d] Styrene. [e] 1-Hexene.

transfer. Figure 1 illustrates good adherence to eq 2 (with $k_p/k_s \approx 35$)[16] in a series of experiments in which [**1**] was held constant and [propylene] and [$PhSiH_3$] maintained pseudo-zero-order.

$$\bar{P}_n = \frac{k_p[\text{olefin}]}{k_S[H_3SiR]} \qquad (2)$$

Regarding monomer scope, **1** mediates rapid 1-hexene polymerization to yield atactic, silyl-functionalized poly(1-hexene) (Table 1). Interestingly, **1** fails to effect $PhSiH_3$ chain transfer in ethylene polymerization at 25 °C (uncapped polyethylene is produced instead). That this reflects a subtle interplay of competing kinetic and steric effects is suggested by the following: (1) **1**-mediated chain transfer to polyethylene is effective at −25 °C; (2) **1** mediates efficient 25 °C chain transfer in ethylene + 1-hexene and ethylene + styrene copolymerizations, yielding products with high degrees of comonomer incorporation (Table 1) in which Si is predominantly adjacent to a 1,2-inserted comonomer unit (**IV** and **V**).[17]

IV



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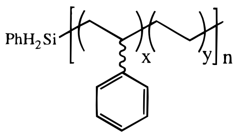
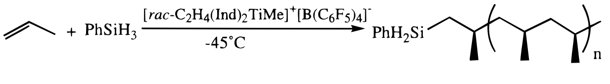


That **1** is not unique in mediating chain transfer and that stereoregular products are accessible is demonstrated by eqs 3 and 4 which yield isotactic silapolypropylene[18] (*mmmm* = 94%) and syndiotactic silapolystyrene (*rrrr* = 98%),[19] respectively.



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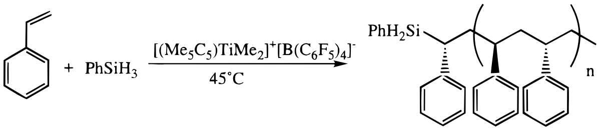
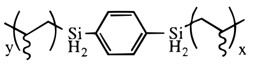


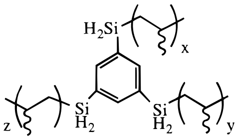
(4)

Finally, **1** + propylene polymerization in the presence of 1,4-disilabenzene[20] and 1,3,5-trisilabenzene[20] reveal that *polyfunctional* chain transfer agents effect assembly of more complex macromolecular architectures (**VI**[21a] and **VII**, [21b] respectively; NMR spectra similar to polymers produced via the corresponding hydrosilylation reactions (cf., eq 1)).

VI



VII



These findings demonstrate that silanolytic chain transfer in olefin polymerizations and copolymerizations can be effected by conventional "cationic" organotitanium catalysts. In addition to endcapping a variety of linear polymers and copolymers, the possibility of catalytically creating unusual, silane-linked multichain polymer connectivities in situ is achieved.

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Supporting Information Available: Details of polymerization procedures and polymer characterization (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(16) For propylene solubility data (toluene), see: Wang, B. P., Ph.D. Dissertation, University of Massachusetts, 1989.

(17) ^{13}C NMR (75 MHz, $C_2D_2Cl_2$): **IV**, δ 14.4 (t, $^1J_{C-H} = 119$ Hz, $PhSiH_2\mathit{C}H_2-$; identical to that in $PhSiH_2$-terminated poly(1-hexene)); **V**, δ 13.5 (t, $^1J_{C-H} = 118$ Hz, $PhSiH_2\mathit{C}H_2CHPh$; identical to that in $PhSiH_2\mathit{C}H_2$-CH_2Ph[10]).

(18) (a) Catalyst: Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015−1018. (b) By NMR: *mmmm* = 94%, $M_n = 8200$; δ $Si\mathit{H}_2 = 4.22$.

(19) (a) Catalyst: Mena, M.; Pellinghelli, M.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118−1119. (b) By NMR (C_6D_6): *rrrr* = 98%, $M_n = 52\,000$, δ $Si\mathit{H}_2 = 4.21$.

(20) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863−6860.

(21) (a) $M_n = 24\,000$ by ^1H NMR (C_6D_6). (b) $M_n = 35\,000$ by ^1H NMR (C_6D_6). See the Supporting Information for further details.