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Alkenylsilane Effects on Organotitanium-Catalyzed Ethylene Polymerization. Toward Simultaneous Polyolefin Branch and Functional Group Introduction

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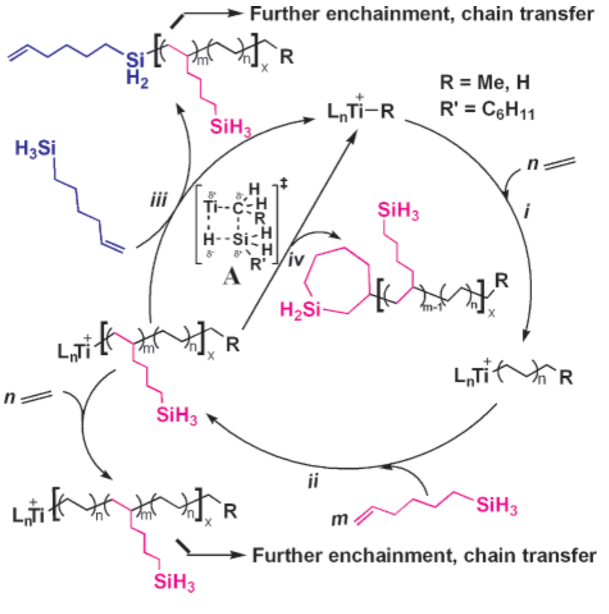
Polyolefins containing longer-chain branches or reactive functionality have a myriad of desirable properties, such as increased melt-fracture resistance, adhesion, elasticity, and compatibility with other materials.[1] Despite recent advances in homogeneous olefin polymerization, precise tailoring of such polymer microstructures remains largely unrealized.[2] A potential approach to simultaneously control branching and reactive functionality would be by manipulating specific polymerization chain transfer pathways.[3−7] However, to date, introduction of a comonomer having the ability both to undergo rapid insertion (propagation) as well as to effect chain transfer to introduce reactive functionality has not to our knowledge been explored.

Organotitanium complexes, such as "constrained geometry catalysts", are efficient α-olefin polymerization agents.[8] They also effect silanolytic chain transfer,[4] raising the intriguing question of whether the two transformations could be coupled, using alkenylsilanes as comonomers (i.e., Scheme 1). This would provide a means of simultaneously introducing branching and versatile reactive functionality[9] into polyolefins. For electron-deficient chain transfer agents, such as silanes and boranes,[4,5] the heteroatom is delivered to the polymer chain terminus at the end of each polymerization cycle, with the final C-heteroatom bond-forming step (Scheme 1, steps iii and iv) proposed to occur via a four-centered σ-bond metathesis transition state (**A**). Although organotitanium catalysts effectively mediate silanolytic chain transfer for many polymerization processes, they are conspicuously inefficient in ethylene polymerization, for reasons not entirely understood.[4a] Thus, silanes containing α-olefinic functionality offer the intriguing potential of holding reactive groups in closer proximity to the Ti−C bond to afford silane-capped, branched polyolefins, all using a single reagent/comonomer. We report here that organotitanium-mediated ethylene polymerization in the presence of 5-hexenylsilane efficiently effects the aforementioned coupled transformations to produce new polymer microstructures.

Scheme 1. Proposed Catalytic Cycle for Organotitanium-Mediated 5-Hexenylsilane/Ethylene Copolymerization



All polymerizations were carried out under rigorously anhydrous/anaerobic conditions using procedures minimizing mass transport effects,[10] with pseudo-zero-order [ethylene] and [5-hexenylsilane]. Polymeric products were characterized by ^{1}H/^{13}C NMR, GPC, and DSC; data are compiled in Table S1 and are consistent with single-site processes.[10] The proposed catalytic cycle for silane-capped ethylene/5-hexenylsilane copolymer synthesis (Scheme 1) is envisioned to proceed via sequences of (i) multiple insertions of C═C unsaturation into Ti−alkyl bonds, (ii) insertion of 5-hexenylsilane into the growing polymer chain, and/or (iii) *inter*molecular silanolytic chain transfer of the copolymer chain, and/or (iv) *intra*molecular silanolytic chain transfer of the copolymer chain, to close the cycle. ^{13}C NMR spectra of the silane-terminated ethylene + 5-hexenylsilane copolymers produced by $CGCTiMe_2/Ph_3C^+B(C_6F_5)_4^-$ exhibit characteristic *n*-butylsilane and polyethylene backbone resonances (Figure 1a). Terminal vinylic chain resonances are below the detection limits (Figure 1), indicating that chain termination via β-hydride elimination is negligible.[4a,7a] Furthermore, the ~3:1 $-CH_2SiH_3$:$-CH_2SiH_2$ ^{13}C NMR intensity ratio suggests

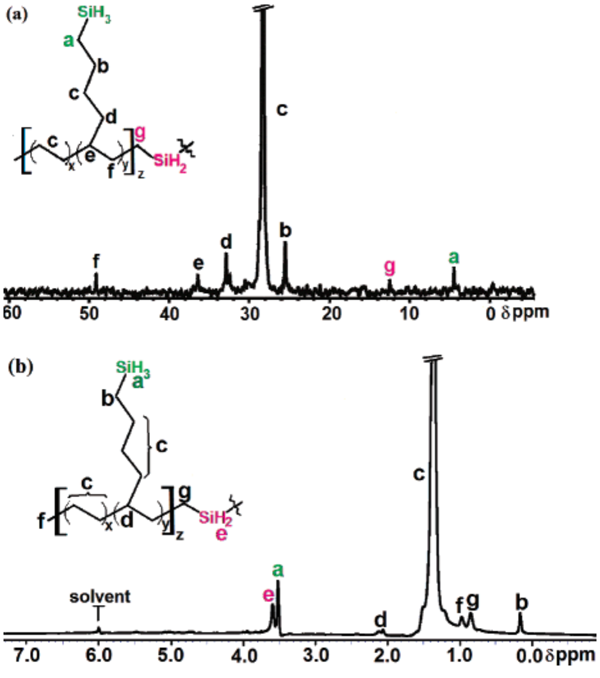


Figure 1. (a) ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) spectrum[13] and (b) ^{1}H NMR (400 MHz, $C_2D_2Cl_4$) spectrum[4a] of the ethylene/5-hexenylsilane copolymer produced by $CGCTiMe_2/Ph_3C^+B(C_6F_5)_4^-$.

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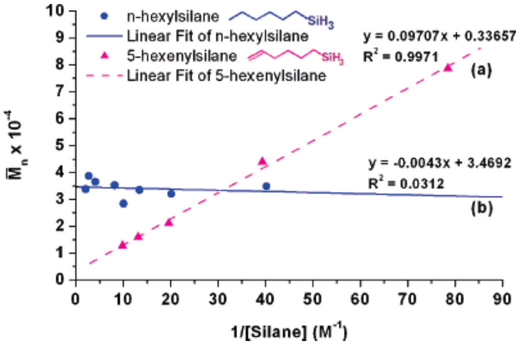

Figure 2. Relationship of polyethylene number average molecular weight (GPC versus polyethylene) to (a) inverse $C_6H_{11}SiH_3$ concentration at fixed catalyst and ethylene concentrations, and (b) inverse $C_6H_{13}SiH_3$ concentration at fixed catalyst and ethylene concentrations.

that 5-hexenylsilane readily undergoes insertion into the polymer chain as well as effects intramolecular chain termination.

Previously, it was found that organotitanium-mediated ethylene polymerization in the presence of alkyl- or arylsilanes fails to produce silyl-capped polyethylenes, and that instead, vinyl-terminated polyethylenes are produced, implicating β-hydride elimination as the dominant chain transfer mechanism.[4a] Assuming for any given reaction, constant [silane], [ethylene], and [catalyst] and that rapid reinitiation occurs after chain transfer, where silanolysis is the dominant chain transfer pathway, the number average degree of polymerization P_n at ideal steady-state in [II] should obey eq 1.[10-12] Here k_p and k_{Si} are the rate constants for chain propagation and (inter/intramolecular) silanolytic chain transfer, respectively. Note from Figure 1 that 5-hexenylsilane is an efficient chain transfer agent for organotitanium-mediated ethylene polymerizations at 25 °C. With the polymerizations carried out at constant catalyst and monomer concentration and a pseudo-zero-order excess of 5-hexenylsilane, Figure 2a shows that eq 1 is obeyed.[11,12] Using this result and the data in Figure 1a yields $k_p^{5-\text{hexenylsilane}}/k_{Si}^{\text{total}} \approx 5$ and $k_p^{\text{ethylene}}/k_{Si}^{\text{total}} \approx 180$, arguing that chain transfer predominantly occurs after 5-hexenylsilane enchainment.[13]

$$P_n = \frac{\sum k_p^{\text{total}}\,[\text{olefin}]}{k_{Si}^{\text{inter}}[\text{5-hexenylsilane}] + k_p^{5-\text{hexenylsilane}}[\text{5-hexenylsilane}]} \qquad (1)$$

To assess any role for the silane C═C functionality in chain transfer, control polymerizations were next carried out using *n*-hexylsilane as chain transfer agent. ^{1}H NMR integration of SiH_2 versus vinyl resonances indicates predominantly vinyl-terminated polyethylenes (Table S2), consistent with literature precedent.[4a] Furthermore, the plot of M_n versus 1/[*n*-hexylsilane] evidences nonideal chain transfer (Figure 2b) with the near-zero slope, indicating that $k_{Si}/k_p \approx 0$ (Figure 2b), and that silanolytic chain transfer is no longer the dominant termination pathway. Silanolytic chain transfer is then most likely competitive with β-hydride elimination. That 5-hexenylsilane is a more efficient chain transfer agent than *n*-hexylsilane ($k_p/k_{Si}^{\text{total}}$ for *n*-hexylsilane is 150-fold that of 5-hexenylsilane) indicates that the olefinic moiety is essential in 5-hexenylsilane chain transfer. An attractive explanation is that the chain transfer rates are enhanced by high local silane concentrations in proximity to the electrophilic Ti center. Using eq 1 and the data in Figure 2 yields $k_{Si}^{5-\text{hexenylsilane}}/k_{Si}^{n-\text{hexylsilane}} \geq 150$, indicating that efficient silanolysis is both inter- and intramolecular when the silyl group is held proximate to the Ti center either by insertion into the growing polymer chain or by interaction of the weakly basic silyl group to the Ti center (presumably via Scheme 1, steps iii and iv).

These results show 5-hexenylsilane to be a versatile comonomer with the ability to both incorporate into a growing polyolefin chain as well as to terminate growing polymer chains, thereby producing branched, silyl-capped polyethylenes. This comonomer allows coupled olefin enchainment and silanolytic chain transfer, thus increasing the probability of branch formation.

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Supporting Information Available: Detailed experimental procedures, kinetic analysis, and polymer characterization data (Tables S1, S2) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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