J. Am. Chem. Soc. **1995,** *117,* 10747−10748

Silanes as Chain Transfer Agents in Metallocene-Mediated Olefin Polymerization. Facile in Situ Catalytic Synthesis of Silyl-Terminated Polyolefins

Peng-Fei Fu and Tobin J. Marks*

Department of Chemistry, Northwestern University
Evanston, Illinois 60208-3113

Received July 10, 1995

The efficient catalytic introduction of polar and/or reactive backbone or terminal functional groups into polyolefins via Ziegler-Natta processes currently represents a major scientific and technological challenge.[1−4] In a recent mechanistic study[5] of organolanthanide-catalyzed olefin hydrosilylation,[6] we found that the principal reaction channel involves a metal hydride-based cycle in which turnover-limiting Si−H/Ln−C transposition delivers the completed carbon skeletal fragment to silicon (eqs 1−3; L = cyclopentadienyl-type ligation, Ln = lanthanide). We also showed that a succession of Ln-mediated bond-forming steps could be effected within the carbon fragment prior to transposition (eq 2).[5] This raises the intriguing question of

$$\mathrm{L_2LnH} + \text{olefin} \xrightarrow{\text{fast}} \mathrm{L_2LnR} \quad (1)$$

$$(\mathrm{L_2LnR} \xrightarrow{\text{fast}} \mathrm{L_2LnR'}) \quad (2)$$

$$\mathrm{L_2LnR(R')} + \mathrm{HSi{\equiv}} \xrightarrow{\text{turnover-limiting}} \mathrm{L_2LnH} + \mathrm{(R')RSi{\equiv}} \quad (3)$$

whether eq 2 could be a polymerization process and whether silanes could be used as chain transfer agents in d^0/f metallocene-catalyzed olefin polymerizations[7,8] (e.g., Scheme 1). At present, only limited and frequently nonselective in situ chain transfer means are available for such polymerizations (H_2,[7] β-H/alkyl elimination,[7,9] monomer,[8b,10] main group alkyls[7,11]), and we report here that $PhSiH_3$ is an efficient and selective chain transfer agent[12] in lanthanocene-catalyzed α-olefin polymerizations and copolymerizations.

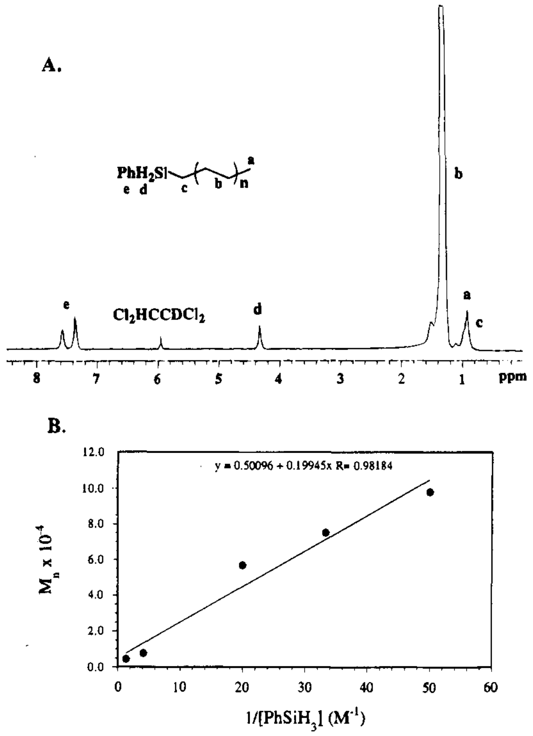
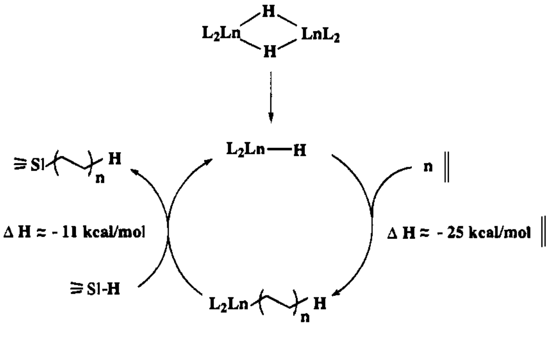


Figure 1. (A) ^1H NMR spectrum (400 MHz) of a $PhSiH_2$-terminated polyethylene sample ($M_n \approx 3000$; catalyst = $(Cp'_2SmH)_2$ in $C_2D_2Cl_4$ at 140 °C). (B) Relationship of polymer number average molecular weight to silane concentration for constant catalyst and olefin concentrations (Table 1, entries 1−5).

Scheme 1



Polymerizations were carried out in toluene under rigorously anhydrous/anaerobic high-vacuum line conditions using procedures described previously.[8b,9a] $(Cp'_2LnH)_2$ ($Cp' = \eta^5\text{-}Me_5C_5$) and $Me_2SiCp''_2LnCHTMS_2$ ($Cp'' = \eta^5\text{-}Me_4C_5$) were prepared as described elsewhere.[8b,c] Polymerization experiments were conducted in a mode designed to minimize mass transport effects (rapid mixing, short reaction times),[8b,9a,13] with olefin and $PhSiH_3$ concentrations maintained at a pseudo-zero-order level.

---

(1) Protected monomer approaches: (a) Stein, K. M.; Kesti, M. R.; Coates, G. W.; Waymouth, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*, 480−481. (b) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679−9680. (c) Datta, S. In *High Value Polymers*; Fawcett, A. H., Ed.; The Royal Society of Chemistry: Cambridge, 1991; pp 37−57.

(2) Borane monomer approaches: (a) Chung, T. C. *CHEMTECH* **1991**, *21*, 496−499. (b) Chung, T. C. *Macromolecules* **1988**, *21*, 865−867.

(3) Ring-opening Ziegler polymerization approaches: (a) Yang, X.; Seyam, A. M.; Fu, P.-F.; Marks, T. J. *Macromolecules* **1994**, *27*, 4625−4626. (b) Yang, X.; Jia, L.; Marks, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 3392−3393.

(4) For non in situ approaches, see: Mülhaupt, R.; Dushek, T.; Rieger, B. *Makromol. Chem., Macromol. Symp.* **1991**, *48−49*, 317−332 and references therein.

(5) Fu, P.-F.; Brard, L.; Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 7157−7168.

(6) (a) Nolan, S. P.; Porchia, M.; Marks, T. J. *Organometallics* **1991**, *10*, 1450−1457. (b) Sakakura, T.; Lautenschlager, H.-J.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1991**, 40−41. (c) Molander, G. A.; Julius, M. *J. Org. Chem.* **1992**, *57*, 6347−6351. (d) Fu, P.-F.; Brard, L.; Marks, T. J. *Abstracts of Papers*, 207th National Meeting of the American Chemistry Society, San Diego, CA, 1994; INOR 40. (e) Molander, G. A.; Nichols, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 4415−4416.

(7) (a) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1−29 and references therein. (b) Kaminsky, W. *Catal. Today* **1994**, *20*, 257−271 and references therein. (c) Marks, T. J. *Acc. Chem. Res.* **1992**, *25*, 57−65 and references therein. (d) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325−387 and references therein.

(8) (a) Watson, P. L.; Herskovitz, T. *ACS Symp. Ser.* **1983**, *212*, 459−479. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091−8103. (c) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103−8110. (d) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51−55. (e) Burger, B. J.; Thompson, M. E.; Cotter, D. W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566−1577.

(9) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015−10031. (b) Resconi, L.; Piemontesi, F.; Franciscono, G.; Abis, L.; Fiorani, T. *J. Am. Chem. Soc.* **1992**, *114*, 1025−1032. (c) Eshuis, J. J.; Tan, Y. Y.; Teuben, J. H.; Renkema, J. *J. Mol. Catal.* **1990**, *62*, 277−287.

(10) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H.-H.; Jüngling, S.; Mülhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964−970.

(11) (a) Kurosawa, H.; Shiono, T.; Soga, K. *Macromol. Chem. Phys.* **1994**, *195*, 3303−3309. (b) Shiono, T.; Kurosawa, H.; Soga, K. *Makromol. Chem.* **1992**, *193*, 2751−2761.

(12) For a mechanistically dissimilar Co-centered approach to similar products, see: Brookhart, M.; De Simone, J. M.; Grant, B. B.; Tanner, M. J. *Macromolecules* **1995**, *28*, 5378−5380.

(13) See supporting information for experimental procedures.

0002-7863/95/1517-10747$09.00/0

Table 1. Ethylene Polymerization and Ethylene−1-Hexene and Ethylene−Styrene Copolymerization in the Presence of $PhSiH_3$

entry	catalyst/ precatalyst[a]	$PhSiH_3$ (M)	comonomer (M)	reactn time (min)	yield (g)	comonomer incorp (M%)	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	$MeSiCp''_2SmR$[e]	0.74		25	0.24			2.6	2.9
10	$MeSiCp''_2SmR$[e]	0.41	1.52[f]	180	0.60	12		3.7	2.9
11	$MeSiCp''_2SmR$[e]	0.41	2.28[f]	180	0.24	60		0.4	4.9
12	$MeSiCp''_2NdR$[e]	0.16	0.98[g]	1200	1.70	26		3.3[d]	

[a] $Cp' = \eta^5\text{-}Me_5C_5$, $Cp'' = \eta^5\text{-}Me_4C_5$, R = $CHTMS_2$; catalyst concentration range = 2.64−2.90 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 active hydride is generated in situ, polymerization activities are not strictly comparable. [f] 1-Hexene. [g] Styrene.

After MeOH quenching, workup, and drying, polymer and copolymer samples were characterized by $^1H/^{13}C$ NMR and GPC. In accord with end-capped $PhSiH_2$−polyethylene microstructures and Scheme 1, the ^1H NMR (Figure 1A) exhibits a characteristic $PhSiH_2$ resonance[5,6,14] at δ 4.33 ($PhSiH_3$ = δ 4.38) coupled to an adjacent CH_2 group (triplet resolvable in low molecular weight samples, $^3J_{^1H\text{-}^1H}$ = 3.6 Hz). Features assignable to the Ph, Si−CH_2, polyethylene backbone,[15] and chain end CH_3[15] moieties are also visible. As expected, the SiH_2:$SiCH_2$:CH_3 intensity ratio is 2:2:3 (±8%).[16] With one exception (Lu, vide infra), end group features associable with conventional (e.g., β-H elimination) chain transfer processes[9,15] are not detectable (Figure 1A). In the ^{13}C NMR in $C_2D_2Cl_4$, both $SiCH_2$ (δ 9.98, $^1J_{^{13}C\text{-}^1H}$ = 118 Hz, triplet)[14] and chain end CH_3 (δ 13.76, $^1J_{^{13}C\text{-}^1H}$ = 127 Hz, quartet)[15] groups are readily assigned and are present in essentially equal proportions. The silyl end group presence is further verified by a strong ν_{Si-H} absorption[17] in the IR at 2109 cm^{-1}. Dissolution of polymer samples in hot *o*-dichlorobenzene followed by MeOH precipitation, washing, and drying yields identical NMR spectra, further supporting the covalently end-capped formulation.

Polymerization and polymer characterization data are set out in Table 1. Polymerization activities are relatively high by metallocene standards,[7,9a] and the rate data parallel Ln^{3+} ion radius−insertion reactivity trends previously established[5,8b,c] in the absence of silanes. Table 1 also indicates that this chain transfer process is applicable to ethylene−1-hexene and ethylene−styrene copolymerizations. Qualitatively, it can be seen that polymer molecular weights fall as [$PhSiH_3$] increases. Assuming constant concentrations of catalyst, olefin, and silane throughout the course of a polymerization experiment, that silanolysis (eq 3) is the dominant chain transfer pathway, and that chain growth reinitiation following chain transfer is rapid, the number average degree of polymerization, $\bar{P}_n$, at steady state should obey eq 4[18] in a series of experiments in which the concentrations of olefin and catalyst are held constant and that of $PhSiH_3$ is varied. Here k_p is the rate constant for chain propagation and k_s is the rate constant for silane chain transfer.

$$\bar{P}_n = \frac{k_p[\text{olefin}]}{k_s[\text{PhSiH}_3]} \tag{4}$$

In accord with Scheme 1, note that Table 1 entries 1−5 obey this relationship (Figure 1B) with $k_p/k_s \approx 190$.[19] As noted above, polymers produced using small Lu^{3+} contain end groups derived from β-H elimination (Table 1, entry 6) as well as the present chain transfer process. In this case, Lu−polyethylene interception via Si−H/Lu−C transposition is apparently sufficiently slow (($Cp'_2LuH)_2$ is a sluggish hydrosilylation[5] and a sluggish polymerization[8b,c] catalyst) that an alternative chain transfer process[8b−d] competes.

These results demonstrate a new "drop-in" chain transfer process for metallocene-catalyzed olefin polymerization and an efficient, selective route to silyl-terminated polyolefins. In due course, we will report results with group 4 metals, other olefins, and other chain transfer agents.

Acknowledgment. We thank the NSF for support under Grant CHE9104112. P. F. thanks Dow Corning for a postdoctoral fellowship. We thank Dr. Gary Burns of Dow Corning for GPC analyses and helpful discussions.

Supporting Information Available: Polymerization procedure (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952252J

---

(14) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1984; pp 512−520.

(15) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic: New York, 1982; pp 78−91.

(16) (a) These ratios rule out significant chain transfer via H_2 produced by competing catalytic dehydrogenative silane coupling.[16b] NMR examination of the supernatants after polymer precipitation and washing reveals no evidence of silane coupling products.[16b] (b) Forsyth, C. M.; Nolan, S. P.; Marks, T. J. *Organometallics* **1991**, *10*, 2543−2545.

(17) Crompton, J. R. In ref 14, pp 416−421.

(18) (a) Tait, P. J. T.; Watkins, N. D. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 4, pp 549−563. (b) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985; Chapter I.

(19) Ethylene solubility data (toluene): Wang, B. P. Ph.D. Dissertation, University of Massachusetts, 1989.