Organolanthanide-Catalyzed Synthesis of Phosphine-Terminated Polyethylenes

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Functionalized polyolefins have highly desirable physical characteristics vs nonfunctionalized polyolefins, such as paintability, adhesion, and compatibility with other materials. However, selective and catalytic incorporation of polar functionalities into such chemically unreactive polymers, produced by highly electrophilic catalysts, remains a significant challenge. One approach to functional polyolefins[1–3] is by employing a chain transfer agent[4–7] to introduce heteroatom groups at chain termini. To date, this transformation has been limited to electron-deficient or electron-neutral reagents, such as boranes,[4] alanes,[5] and silanes,[7] with little success achieved in incorporating potentially important electron-rich species (e.g., groups 15, 16).[6]

Organolanthanide complexes are efficient olefin hydrophosphination[8] and ethylene polymerization catalysts,[9] raising the intriguing question of whether the two transformations can be coupled using electron-rich phosphines as chain transfer agents for single-site olefin polymerization. This would represent a new, efficient way of delivering an electron-rich and chemically versatile fragment to the terminus of a polyolefin chain. With electron-deficient or electron-neutral chain transfer agents, such as boranes[4] and silanes,[7,10] the heteroatom is chain-transferred to the polymer chain at the end of a hydride-based catalytic propagation cycle, with the final C-heteroatom bond-forming step (Scheme 1a, step iii) proposed to occur via four-centered σ-bond metathesis transition state **I**. In contrast, analogy drawn from hydrophosphination[8] and hydroamination[11] mechanistic observations argues that a cycle to incorporate electron-rich fragments would require C-heteroatom bond formation at the initiation of the catalytic cycle (Scheme 1b, step iii), with the Brønsted acidic E−H functionality (E = P, N) effecting protonolytic chain transfer (transition state **II**). We report here the first efficient embodiment of such a process.

The proposed catalytic cycle for lanthanide-mediated synthesis of phosphine-capped polyethylenes (Scheme 1b) involves: (i) insertion of C=C unsaturation into a lanthanide-phosphido bond, (ii) subsequent insertions of ethylene into the resulting Ln−C bond, and (iii) protonolysis of the propagating polyolefin chain by incoming phosphine to close the cycle and regenerate the lanthanide-phosphido species. Polymerizations were carried out at 21°C/1.0 atm ethylene under rigorously anaerobic/anhydrous conditions with $Cp'_2LnCH(SiMe_3)_2$ and $[Cp'_2LnH]_2$ precatalysts ($Cp' = \eta^5\text{-Me}_5C_5$)[12] using procedures minimizing mass transport effects and with [olefin] held constant and [diphenylphosphine] in pseudo-zero-order excess.[13] Since polymers would be produced via ethylene insertion into the Ln−P bond, Cp'_2LnPPh_2 complexes were generated prior to polymerization either in situ or as isolated complexes. For ease of handling, polymer samples were oxidized to the corresponding phosphine oxide-capped derivatives (eq 1) prior to ^{1}H, ^{13}C, and
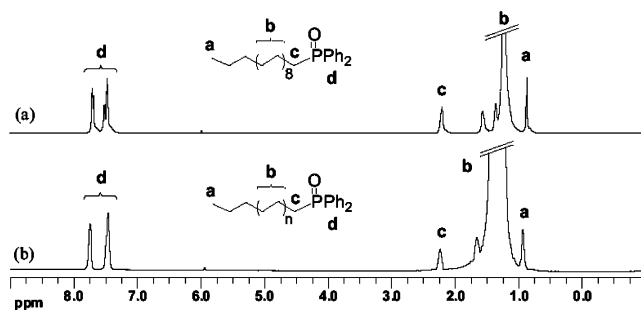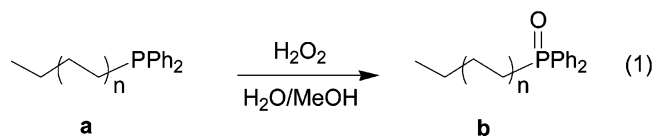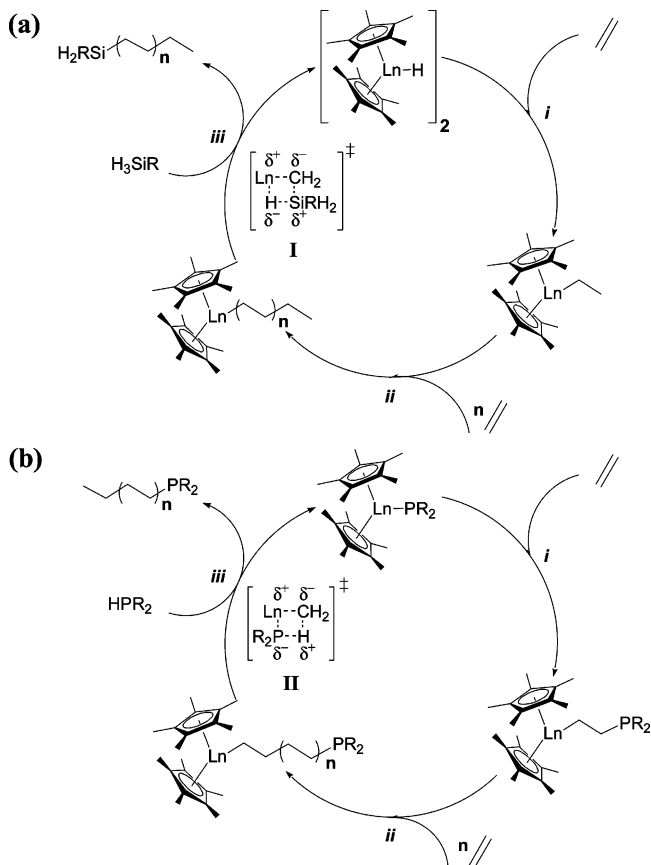
Figure 1. ^{1}H NMR spectra of (a) eicosyldiphenylphosphine oxide and (b) diphenylphosphine oxide-terminated polyethylene synthesized by in situ generated Cp'_2YPPh_2.

Scheme 1. Contrasting Catalytic Cycles for Organolanthanide-Catalyzed Synthesis of (a) Silyl-Terminated and (b) Phosphine-Terminated Polyethylenes.

$$\text{(1)}$$

^{31}P NMR, DSC, and GPC characterization.[13] ^{1}H NMR spectra of the phosphine-terminated polyethylenes produced by in situ generated Cp'_2YPPh_2 (**1**) exhibit characteristic phenyl, polyethylene backbone, and −CH_3 chain end resonances (Figure 1b). Vinylic

Table 1. Organolanthanide-Catalyzed Ethylene Polymerization in the Presence of HPPh₂

entry	precatalyst[a]	[precat.] (μM)	[HPPh₂] (mM)	yield (g)	activity[b] ($\times 10^7$)	M_n[c]	M_w/M_n[c]	T_m[d] (°C)
1	Cp₂′LuR	79	20	0.25	0.73	37500	1.6	137.9
2	Cp′₂YR	78	20	0.70	2.1	25500	1.9	137.6
3	Cp′₂SmR	83	20	0.27	0.76	18900	2.1	137.3
4	Cp′₂LaR	85	20	—[e]	—	—	—	—
5	Cp′₂YPPh₂	36	22	0.48	3.1	29500	1.8	137.6
6	Cp′₂YPPh₂	36	45	0.45	2.9	18800	2.2	137.2
7	Cp′₂YPPh₂	39	67	0.48	2.9	12500	2.3	136.4
8	Cp′₂YPPh₂	35	89	0.41	2.7	11000	2.4	135.3
9	Cp′₂YPPh₂	35	121	0.35	2.3	9400	2.3	134.9
10	Cp′₂YPPh₂	35	154	0.23	1.5	7100	2.3	134.6
11	Cp′₂YPPh₂	33	418	0.070	0.46	3100	2.0	130

[a] Cp′ = η^5-Me₅C₅, R = CH(SiMe₃)₂; polymerization conditions: 50 mL of toluene, average temperature = 21 °C (see Supporting Information for details), 30 s. [b] Units = g/(mol Ln·atm ethylene·h). [c] By GPC in 1,2,4-trichlorobenzene vs polyethylene standards. [d] By DSC. [e] Trace yields of polymer obtained (<10 mg).
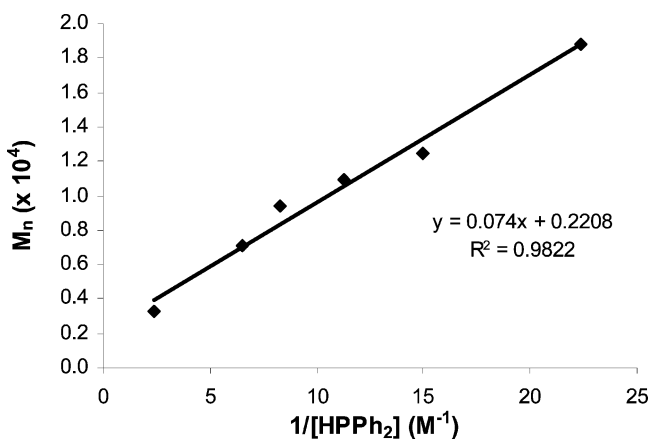
Figure 2. Relationship of polyethylene number average molecular weight (GPC versus polyethylene) to inverse HPPh₂ concentration at fixed catalyst and ethylene concentrations.

chain end resonances are absent in ^{1}H and ^{13}C NMR spectra, suggesting that chain termination via β-H elimination is not significant. Furthermore, the ~1:1 PPh₂ and −CH₃ chain end resonance ratio implies that a phosphine moiety terminates each polymer chain. For comparison, the ^{1}H, ^{13}C, and ^{31}P NMR spectra of the model product 1-eicosyldiphenylphosphine oxide (**2**; Figure 1a)[14] are in good agreement with the polymer spectral assignments.

Polymerization and product characterization data (Table 1) reveal surprisingly high polymerization activities, which are not appreciably depressed over a ~20-fold increase in phosphine concentration. In comparison, the highest activity observed for organolanthanide-mediated ethylene polymerization in the presence of phenylsilane (0.02 M) is 8.97×10^5 g of polymer/(mol Ln·atm ethylene·h).[7] Narrow monomodal polydispersities are also observed in the present case, consistent with a single-site process. At constant [catalyst] and [ethylene], molecular weight is inversely proportional to phosphine concentration (Table 1, entries 6−11; Figure 2), supporting a chain transfer mechanism as in Scheme 1b. With respect to metal ion size effects, it can be seen that product M_n increases with decreasing lanthanide ionic radius, most likely reflecting the steric constraints of the growth-limiting chain transfer process (Scheme 1b, step iii), involving a crowded transition state (**II**). Consistent with these results is the previous observation, for lanthanide-mediated hydrophosphination, that Ln−C protonolysis is more rapid for larger metal radii.[8c] Furthermore the metal ionic radius-activity trend for the present phosphine-capped polyethylene

synthesis is similar to that observed for intramolecular phosphinoalkene hydrophosphination/cyclization:[8c] Y > Sm, Lu > La.[15] In addition, the characteristic orange color of the Y-based polymerization solutions during turnover suggests that the catalyst resting state is a lanthanide-phosphido species (rather than an alkyl).[8,12]

In summary, diphenylphosphine is shown to be an efficient chain transfer agent in organolanthanide-catalyzed ethylene polymerization, yielding phosphine-terminated polyethylenes. This reaction is a versatile, efficient way of incorporating an electron-rich functional group into an otherwise inert polymer. Further investigations of scope and mechanism are currently in progress.

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

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JA045965N