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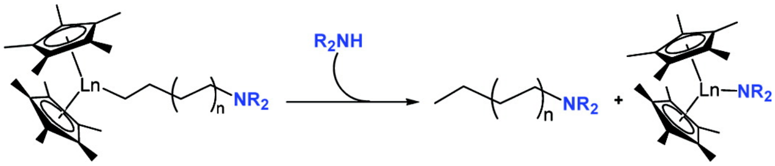

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Organolanthanide-Catalyzed Synthesis of Amine-Capped Polyethylenes

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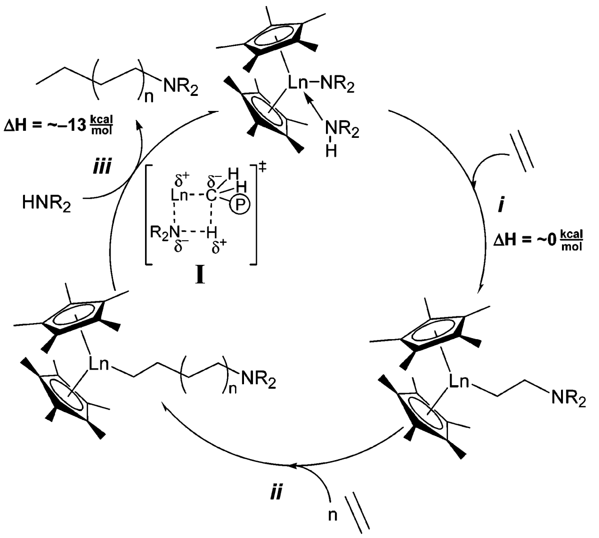
Introduction of reactive functional groups into otherwise chemically inert polyolefins by means of a selective, catalytic pathway represents a significant challenge.[1] Functionalized polyolefins are of considerable interest due to enhanced physical properties such as adhesion, paintability, and compatibility with other more polar materials.[2] One approach to functionalizing polyolefins is the use of chain transfer agents, which can introduce heteroatom functionality at chain ends with concomitant control of molecular weight.[3−8] Previously, electron-deficient/neutral chain transfer agents such as alanes,[3] silanes,[4] and boranes[5] were successfully introduced into catalytic olefin polymerization processes. Regarding functionally analogous processes with electron-rich chain transfer agents, only phosphines have been investigated, and the products are largely of specialized interest.[7] In contrast, amine-terminated polyolefins have broad utility in diverse applications ranging from drug and gene delivery, antibacterial treatments, sensors to adhesives and ion-exchange resins, and are very attractive targets.[9]

Organolanthanide complexes are effective catalysts for both olefin hydroamination[10] and polymerization processes.[11] Thus, lanthanocenes mediate ethylene polymerization with activities as high as 10^6 g polymer/(mol Ln•atm ethylene•h)[12] and efficiently catalyze inter- and intramolecular hydroaminations of diverse C−C unsaturated substrates.[10] These combined characteristics raise the intriguing question of whether the two transformations could be coupled to use amines as chain transfer agents in catalytic olefin polymerization. If viable, this approach would represent a new catalytic synthesis of amine-capped polymers. However, in contrast to electron-deficient chain transfer agents where heteroatom delivery occurs at the end of the polymerization cycle, a cycle for electron-rich chain transfer agents places far greater demands on the sequence of events, requiring sterically-demanding, essentially thermoneutral C-heteroatom bond formation[10] at the initiation of the polymerization cycle (e.g., Scheme 1). Additionally, since Ln−C protonolyses by amines are $\sim 10^4$ times faster than by the corresponding phosphines,[13] careful tuning of the amine chain transfer agent steric and electronic characteristics is essential to achieving efficient chain propagation (Scheme 1, rates *i*, *ii* ≫ rate *iii*). In survey experiments, we find that $HN(SiMe_3)_2$ is too acidic for efficient propagation (Scheme 1, rate *iii* is too large), and only $H(CH_2CH_2)_nN(SiMe_3)_2$ oligomers are formed ($n = 1, 2$), while $HN(^iPr)_2$ is apparently insufficiently encumbered to allow efficient ethylene chain propagation prior to termination, instead forming $H(CH_2CH_2)_nN(^iPr)_2$ oligomers ($n = 10−17$).[14] Furthermore, sterically encumbered and acidic $HN(SiMe_3)(^tBu)$ effects rapid chain termination with slow ethylene propagation, while less bulky, less acidic $HN(^iPr)_2$ and HN(*sec*-Bu)$_2$ effect very rapid chain termination.[14] Nevertheless, as we report here, it is possible to find amines with the correct balance in *i/ii* versus *iii* rates, and lanthanocenes efficiently mediate the aforementioned coupled transformations in the presence of dicyclohexylamine to afford high molecular weight amine-terminated polyethylenes.

Scheme 1. Schematic Catalytic Cycle for Organolanthanide-Mediated Ethylene Polymerization in the Presence of Amine



All polymerizations were carried out at 24 °C with $Cp'_2LnCH(SiMe_3)_2$ or $Cp'_2LnN(C_6H_{11})_2$ precatalysts under rigorously anhydrous/anaerobic conditions using procedures minimizing mass transport effects[14] and with pseudo-zero-order [ethylene] and [dicyclohexylamine]. Polymeric products were characterized by $^1H/^{13}C$ NMR, GPC, and DSC; the data (Table 1) are consistent with linear polyethylenes formed in single-site processes.[14] The proposed catalytic cycle for amine-capped polyethylene synthesis (Scheme 1) is envisioned to proceed via sequences of (i) insertion of C═C unsaturation into the Ln−N bond, (ii) multiple C═C incorporation into the growing polymer chain, and (iii) Ln−polymeryl protonolysis with simultaneous regeneration of the lanthanide amido active species to close the cycle (transition state **I**). ^1H NMR spectra of the product amine-terminated polyethylenes exhibit characteristic amine (δ 2.41), polyethylene backbone (δ 1.2−1.5), and $-CH_3$ chain end (δ 0.98) resonances (Figure 1a), while ^{13}C NMR spectra likewise exhibit characteristic amine (δ 61) and polyethylene backbone (δ 29) resonances. Furthermore, the absence of vinylic resonances in both the ^1H and ^{13}C NMR spectra indicates that chain termination via β-hydride elimination is insignificant, and the ∼1:1 $-CH_2N$ and $-CH_3$ ^1H NMR chain end resonance ratio argues that one amine functional group caps each polyethylene chain.

Polymerization and product characterization data (Table 1) reveal reasonable polymerization activities and surprisingly high product molecular weights. Narrow monomodal polydispersities are also observed in the present polymerization systems, consistent with single-site processes. Assuming for any given reaction, constant [catalyst] and [ethylene], and that rapid reinitiation occurs after chain transfer, where aminolysis is the dominant chain transfer pathway, product polymer M_n should be inversely proportional to [dicyclohexylamine], which is the case (Table 1, entries 5−9; Figure 2),

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Table 1. Organolanthanide-Mediated Ethylene Polymerization in the Presence of Dicyclohexylamine

entry	precatalyst[a]	[precat.] (μM)	[$(C_6H_{11})_2NH$] (mM)	activity[b] ($\times10^4$)	M_n[c] ($\times10^3$)	M_w/M_n[c]	T	T_m[d] (°C)
1	Cp'_2LuR	370	34	<0.01[e]	–	–	24	-
2	Cp'_2YR	330	34	0.01[e]	–	–	24	-
3	Cp'_2SmR	330	34	0.70	260	2.7	24	138
4	Cp'_2LaR	360	34	1.00	200	2.5	24	138
5	Cp'_2LaNCy_2	330	8.4	2.50	1100	2.0	24	139
6	Cp'_2LaNCy_2	290	20	2.03	270	2.1	24	138
7	Cp'_2LaNCy_2	350	42	0.91	130	1.7	25	139
8	Cp'_2LaNCy_2	360	84	0.20	91	1.6	25	137
9	Cp'_2LaNCy_2	360	126	0.10	53	2.1	24	138

[a] $Cp' = Me_5C_5$; polymerization conditions: 30 mL of toluene, 90 min. [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). Cy = cyclohexyl; R= $CH(TMS)_2$ or secondary amine.

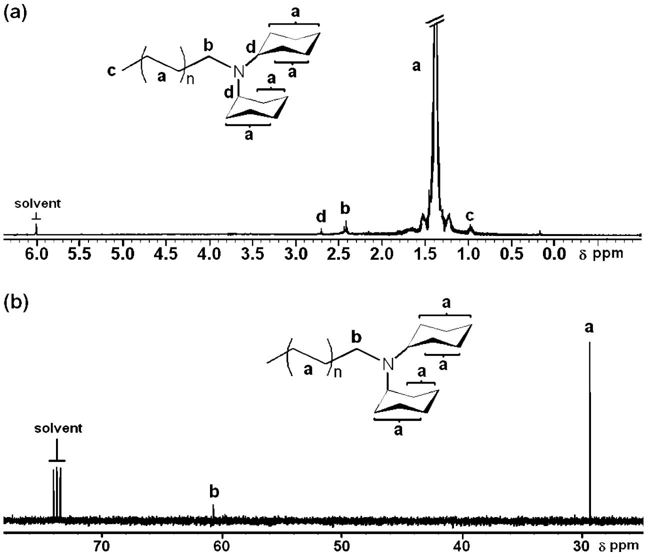

Figure 1. (a) ^1H NMR (400 MHz, $C_2D_2Cl_4$) spectrum and (b) ^{13}C NMR (100 MHz, $C_2D_2Cl_4$) spectrum of a dicyclohexylamine-capped polyethylene (M_n = 131 600) produced by Cp'_2La-mediated polymerization.

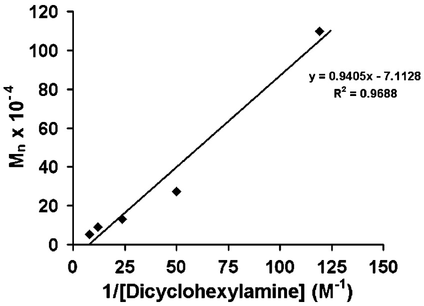

Figure 2. Relationship of polyethylene number-average molecular weight (GPC versus polyethylene) to inverse $(C_6H_{11})_2NH$ concentration at fixed catalyst and ethylene concentrations.

supporting the mechanism in Scheme 1. Similar to the metal ion size trends observed in phosphine-capped polyethylene synthesis,[7] in the present systems, product M_n increases from the larger lanthanum to the smaller samarium ion, doubtlessly reflecting the sensitive steric demands around the electrophilic metal center. Consistent with organolanthanide-catalyzed small molecule hydroamination,[10f] larger lanthanides exhibit the greatest polymerization activity: La > Sm ≫ Y/Lu.[10f] In Cp'_2LnNCy_2 systems, where Ln = Y, Lu, only minor quantities of polymer are produced, likely reflecting the steric constraints around these smaller metal centers which apparently hinder C═C insertion into the Ln−amido active species or render repetitive C═C insertions sluggish.

In conclusion, these results demonstrate that, despite kinetic disadvantages with respect to Ln−C protonolysis by amines, careful amine chain transfer agent selection allows the efficient, catalytic synthesis of dialkylamine-capped polyethylenes. This reaction is a flexible and efficient method for incorporating electron-rich functional groups into polyolefins.

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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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