Telechelic Polyethylene

DOI: 10.1002/anie.201208756

Telechelic Polyethylene from Catalyzed Chain-Growth Polymerization**

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Since the discovery of the Ziegler–Natta catalyst[1,2] for the coordinative polymerization of ethylene, continual chemical and process optimizations have led to a broad range of commodity polyolefins with enhanced properties.[3–5] Despite these extensive efforts and numerous breakthroughs, telechelic polyethylenes (PEs), in which both chain ends feature the same functional group (X-PE-X) or chemically distinct groups (X-PE-Z), are yet to be accessed using catalytic ethylene polymerization. Telechelic polymers have important commercial applications as cross-linkers, chain linkers, or building blocks,[6] highlighting the opportunities reliant on the development of telechelic PE production. In this context, catalytic polymerization of ethylene, producing many PE chains per transition-metal center, is the best route to overcome the cost limitation[7] presented by other strategies, while reliably attaining the crystalline, insoluble, thermoplastic properties of high density PE.

Previous methods to produce telechelic PE have involved polymerization of butadiene followed by functionalization and hydrogenation,[8] partial hydrogenation of polybutadiene followed by metathesis degradation of the interior olefin groups,[9] ring-opening metathesis polymerization of a cyclic olefin followed by functionalization and hydrogenation,[10,11] and the living coordinative polymerization of olefins.[12,13] These techniques have produced valuable materials for the fundamental understanding of structure–property relationships. They are, however, either multistep processes, noncatalytic (using stoichiometric quantities of high-cost initiators), or employ monomers, such as butadiene or cyclic olefins, that are expensive compared to ethylene and consequently incompatible with the prerequisites of industrial production.

In the field of catalytic ethylene polymerization, the scope of end-functional PE production using high-volume methods is limited by both the range of efficient, quantitative, and selective transformations of transition-metal-bound polymer chain ends and by competition from chain-transfer reactions, in particular β-hydrogen transfer, that deactivate the chain end. Approaches to overcoming these limitations have emphasized the exploitation of the reactivity of the polymer–metal bond present in living systems,[14,15] in which chain transfer reactions are absent. The development of complexes that mediate catalyzed chain growth (CCG)[16] of PE chains on a main-group metal has facilitated the introduction of PE end functions under catalytic conditions. In CCG polymerization, reversible PE chain transfer, which is rapid in comparison to propagation, occurs between a catalytic amount of a transition metal (on which the chains propagate) and a main-group metal used as the chain-transfer agent (CTA).[17–19] A PE-Mg-PE intermediate can be produced by CCG on magnesium using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ in combination with a dialkyl magnesium as CTA.[20,21] The nucleophilic Mg−C bonds of PE-Mg-PE can then be exploited to install functional polymer chain ends.[22] Using this strategy, continuing investigations have revealed the potential of end-functional, linear PE blocks (PE-Z) to form part of more complex architectures.[23–25] Alternatively, end-group transformations with small-molecule reagents have been demonstrated,[26–32] through which the reactivity, secondary structure, or surface properties of PE can be modified.

The production of telechelic PE presents the additional challenge of introducing potential reactivity at both ends of the polymer chain, prior to or during polymerization. The established reactivity of PE-Mg-PE towards electrophiles and the behavior of dialkyl magnesium cocatalysts (MgR_2) as CTAs in coordinative ethylene polymerization, offer a synthetic pathway to 1,ω-difunctional PE, provided that R features a functional group that remains a spectator during ethylene polymerization. Bis(pentamethylcyclopentadienyl)-neodymium catalysts have shown no propensity to incorporate α-olefins into predominantly PE chains,[33] which raised the possibility of employing *exo*-alkenyl magnesium CTAs. We describe herein the use of a bis(*exo*-alkenyl) magnesium CTA in controlled CCG polymerization of ethylene, thereby installing a vinyl functionality prior to the polymerization. We then demonstrate the synthesis of 1,ω-heterodifunctional, linear PE (X-PE-Z) by CCG polymerization of ethylene followed by single-step, in situ functionalization.

Bis(3-butenyl)magnesium (B-3-BM) was produced by adaptation of a precedent Grignard disproportionation procedure.[34] Reaction of a THF solution of 3-butenylmagnesium bromide with 1,4-dioxane caused the rapid precipitation of $\{MgBr_2(O_2C_4H_8)_2\}_n$, leaving a THF solution of B-3-BM upon filtration. To preclude a suppressive effect of THF, both on the polymerization activity of the Nd-based catalyst and on the level of functionality attainable upon post-polymerization functionalization, the THF solvent was removed and replaced

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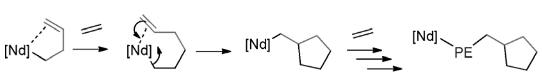
[**] The financial support from the University Claude Bernard Lyon 1 is acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201208756.

with di-*n*-butyl ether. Polymerization of ethylene at 3 bar pressure using a combination of $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ and B-3-BM (Mg/Nd = 150) in toluene with 2.5 % di-*n*-butyl ether proceeded rapidly with an activity of $2.7\times 10^5\,g\,mol^{-1}\,h^{-1}\,bar^{-1}$.

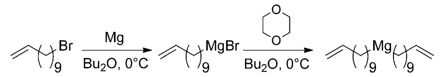
The PE produced during the polymerization was found to have $M_n = 1450\,g\,mol^{-1}$ and a low $Đ$ (1.12). The ^1H NMR spectrum was observed to contain no resonances corresponding to vinyl end groups, which was attributed to the intramolecular insertion of vinyl chain ends into the neodymium–carbon bonds, forming organometallic species that retained the capacity to insert ethylene. Related alkylneodymium species have been shown to insert vinyl units across the Nd−C bond during ethylene–butadiene copolymerization, leading to the formation of cyclohexyl moieties, after which propagation continued.[35,36]

The ^{13}C NMR spectra indicated the selective cyclization and formation of cylcopentane rings at the chain end (Supporting Information, Figure S1). The formation of cyclopentyl groups occurs after the first ethylene insertion by the mechanism shown in Scheme 1, which is consistent with behavior reported for the related alkyl neodymium species during ethylene–butadiene copolymerization.



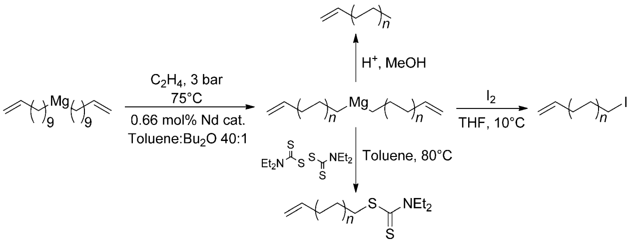
Scheme 1. Formation of cyclopentyl end groups after ethylene insertion.

The use of longer terminal alkenyl chains in the CTA was proposed to limit the potential for insertion of the vinyl chain ends by precluding the formation of thermodynamically favored 5 or 6-membered rings. 11-bromo-1-undecene was treated with a magnesium suspension in di-*n*-butyl ether to form a solution of 10-undecenylmagnesium bromide (UMB), which was converted into a bis(10-undecenyl)magnesium (BUM) solution by addition of dioxane to trigger $MgBr_2$ precipitation (Scheme 2). The ^1H NMR spectrum showed that the carbon–magnesium bond was Mg-alkyl, and no rearrangement to an Mg-alkenyl species had occurred. The concentration of magnesium-bound chains capable of chain transfer was estimated by titration with pyrene-1-acetic acid.



Scheme 2. Synthesis of bis(10-undecenyl)magnesium.

Polymerization of ethylene using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ and BUM (Mg/Nd = 150) in toluene with 2.5 % di-*n*-butyl ether, commencing at 75 °C, proceeded rapidly to produce bis(vinylpolyethylenyl)magnesium (Vin-PE)$_2$Mg. The (Vin-PE)$_2$Mg intermediate was then subjected to one of three in situ treatments (Scheme 3): 1) cooling to ambient temperature, followed by quenching with methanol (No. 1, Table 1); 2) cooling to 10 °C, followed by stirring with an iodine solution in THF for 1 h (No. 2, Table 1); or 3) addition of a solution of *N,N,N′,N′*-tetraethylthiuram disulfide (disulfuram) in toluene, followed by stirring at 80 °C for 2 h (No. 3, Table 1).



Scheme 3. Synthesis of $CH_2{=}CH{-}(CH_2)_9{-}PE{-}Z$, where Z = H, I, or $SC(S)N(Et_2)_2$.

The polymer produced by quenching the intermediate (Vin-PE)$_2$Mg with methanol was analyzed by HT-SEC and ^1H and ^{13}C NMR spectroscopy in 2:1 TCE/C_6D_6 at 90 °C (TCE = tetrachloroethylene). The narrow molecular-weight distribution observed ($Đ = 1.13$) and molecular weight close to that targeted ($M_n = 1150\,g\,mol^{-1}$, $M_{n,target} = 1000\,g\,mol^{-1}$) indicate a well-controlled polymerization with efficient initiation and chain transfer to Mg and a low rate of termination, consistent with the CCG mechanism. The ^1H NMR spectrum featured multiplet resonances at 4.88 ppm and 5.69 ppm of intensity consistent with quantitative retention of the terminal olefin moiety throughout polymerization, which led to the structural assignment of the expected PE product $CH_2{=}CH{-}(CH_2)_9{-}(CH_2CH_2)_n{-}H$, that was confirmed by ^{13}C NMR analysis (Supporting Information, Figure S2).

The heterogeneous reaction between excess solution-phase iodine and precipitated (Vin-PE)$_2$Mg, as previously established for monofunctional PE-I synthesis,[27] produced $CH_2{=}CH{-}(CH_2)_9{-}PE{-}I$ as a pale brown powder. The ^1H NMR spectra of the polymers produced contained multiplet resonances at 4.88 ppm and 5.69 ppm of intensities consistent with quantitative retention of the vinyl end group through polymerization and post-polymerization iodination (Figure 1; Supporting Information, Figure S3). It was found to be necessary to limit the temperature (10 °C) and reaction

Table 1: Polymerizations performed at 75 °C using the precatalyst $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ with bis(10-undecenyl)magnesium as cocatalyst, and subsequent in situ functionalization to give polymers of the form vinyl-PE-Z.[a]

No.	Quenching agent	Z	Quenching time [h/°C]	M_n ($Đ$)[b] [g mol^{-1}]	Vinyl[c]	Z[c]	Me[c]
1	MeOH	H	0.5/20	1150 (1.13)	1	1	–
2	I_2 (THF)	I	1/10	1500 (1.14)	1	0.96	0.04
3	$[Et_2NC(S)S]_2$	SC(S)NEt$_2$	3/80	1550 (1.15)	1	0.87	0.13

[a] Polymerization conditions: $P = 3$ bar, [Nd] = 42 μmol L^{-1}, Mg/Nd = 150, toluene/*n*Bu$_2$O 40:1.
[b] Determined by HT-SEC in 1,2,4-trichlorobenzene at 150 °C, with reference to PE standards.
[c] Determined by ^1H NMR at 90 °C (TCE/C_6D_6 2:1).

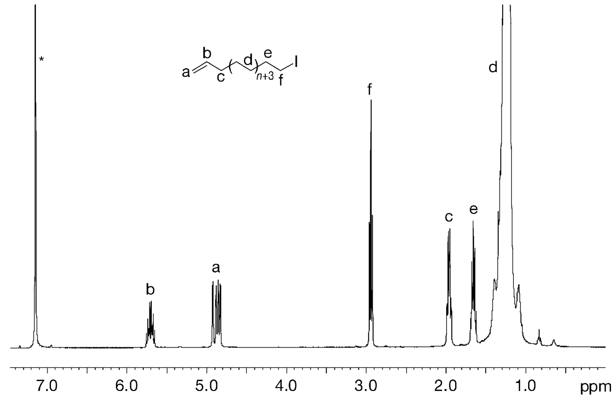


Figure 1. ^{1}H NMR spectrum of $CH_2{=}CH{-}(CH_2)_9{-}PE{-}I$. ⋆ = residual proton signal of C_6D_5H.

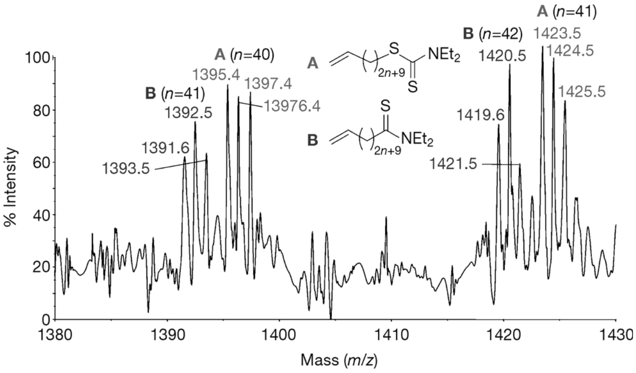


Figure 3. Expansion of the MALDI-TOF mass spectrum of $CH_2{=}CH{-}(CH_2)_9{-}PE{-}SC(S)NEt_2$ showing $n = 40$ and $n = 41$ peak envelopes.

time (1 hour) of the iodination to prevent a small proportion of chains from undergoing iodine addition to the olefinic double bond.

Attachment of a dithiocarbamate end group to a PE chain presents the most high-yielding route (by a quantitative reduction) to thiol-terminated PE, which may be further transformed to access a large number of potential structures using thiol–ene chemistry.[32] The solution-phase reaction between $(Vin\text{-}PE)_2Mg$ and disulfuram at 80 °C was used to produce $CH_2{=}CH{-}(CH_2)_9{-}PE{-}SC(S)NEt_2$ in a method similar to that used to prepare monofunctional PE$-$SC(S)NEt$_2$.[26]

The polymer produced (molecular weight $M_n = 1550\ g\,mol^{-1}$) had a molecular weight distribution $Đ = 1.15$, which is characteristic of a well-controlled polymerization. The ^{1}H NMR spectrum features signals corresponding to terminal vinyl proton resonances, along with those assigned to CH_2S, NCH_2CH_3, and NCH_2CH_3 protons (Figure 2). The integral ratios of these resonances were used to estimate chain-end functionalities, which indicated the formation of 87 % of $CH_2{=}CH{-}(CH_2)_9{-}PE{-}SC(S)NEt_2$. The presence of the dithiocarbamate terminus was corroborated by ^{13}C NMR and FTIR spectroscopy (Supporting Information, Figures S4, S5). The FTIR spectrum of $CH_2{=}CH{-}(CH_2)_9{-}PE{-}SC(S)NEt_2$ revealed absorbance at $\nu = 1414\ cm^{-1}$, which is characteristic of the dithiocarbamate C=S stretching mode. The Lewis basic sulfur and nitrogen sites located on the dithiocarbamate terminus allowed the analysis of polymer composition by MALDI-TOF mass spectrometry. The mass spectrum (Figure 3) featured a distribution of peaks **A** with m/z ratios corresponding to the structure $[CH_2{=}CH_2\text{-}(CH_2)_{2n+9}SC(S)NEt_2 + H]^+$ ($[MH]^+$), where n is the number of ethylene units enchained during the polymerization step. An additional distribution of peaks **B** was observed, of generally slightly lesser intensity, which appears to shadow the higher intensity peak series at m/z ratios of $\mathbf{B} = \mathbf{A} - 32$. These signals are suspected to arise from the loss of a sulfur atom by fragmentation and recombination reactions to give ions of structure $[CH_2{=}CH_2(CH_2)_{2n+9}C(S)NEt_2 + H]^+$, occurring during the MALDI process prior to polymer protonation, as previously reported for dithiocarbamate-terminated PE.[26]

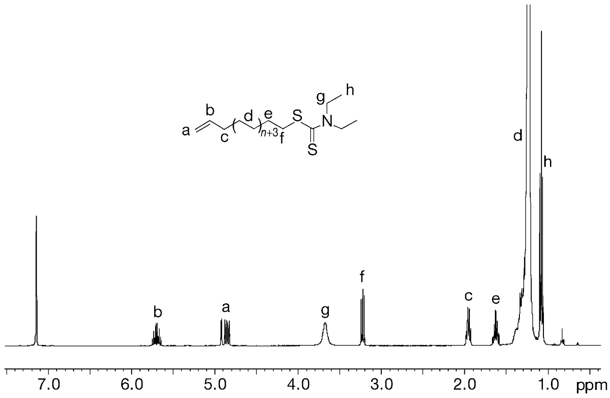


Figure 2. ^{1}H NMR spectrum of $CH_2{=}CH{-}(CH_2)_9{-}PE{-}SC(S)N(Et_2)_2$. ⋆ = residual proton signal of C_6D_5H.

Following strategies employed in our laboratories,[27] $CH_2{=}CH{-}(CH_2)_9{-}PE{-}I$ was further quantitatively transformed into $CH_2{=}CH{-}(CH_2)_9{-}PE{-}N_3$, which can be further reduced in $CH_2{=}CH{-}(CH_2)_9{-}PE{-}NH_2$ (see the Supporting Information, Figures S6–S9 and the general polymerization procedure).

In summary, a route to linear, well-defined telechelic PEs by CCG polymerization has been established. A bis(*exo*-alkenyl)magnesium chain-transfer agent, featuring vinyl functionality, has been developed to quantitatively produce vinyl functionalized PE, free from cyclized byproducts, after simple deactivation of the resultant $(Vin\text{-}PE)_2Mg$ intermediate with methanol. Efficient, single-step functionalization reactions between the $(Vin\text{-}PE)_2Mg$ intermediate and electrophiles of the form Z_2 allowed access to 1,ω-heterodifunctional PE, Vin-PE-Z. Telechelic PEs $CH_2{=}CH{-}(CH_2)_9{-}PE{-}I$ and $CH_2{=}CH{-}(CH_2)_9{-}PE{-}SC(S)NEt_2$ were produced with quantitative retention of the chain-end vinyl function and Z functionality of 96 % and 87 %, respectively. After one simple and quantitative chemical transformation, azide and amine can further be introduced. The catalytic nature of the polymerization and use of ethylene as the monomer enhance the economic viability of this route to low-molecular-weight telechelic PEs. Access to telechelic PEs in a cost-effective process can potentially boost the development of existing applications of functional waxes, such as imaging, inks, coatings, personal-care products, and oil and plastics additives,[37] and provide new "crystalline" building blocks to be incorporated in greater structures.

Received: October 31, 2012

Keywords: chain growth · homogeneous catalysis · polyethylene · polymers · telechelic polymers

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