Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 7495–7503 **7495**
DOI: 10.1021/ma101265t

Thiol-End-Functionalized Polyethylenes

Jérôme Mazzolini,[†] Ilham Mokthari,[†] Rémi Briquel,[†] Olivier Boyron,[†] Frédéric Delolme,[‡] Vincent Monteil,[†] Denis Bertin,[§] Didier Gigmes,[§] Franck D'Agosto,*[,†] and Christophe Boisson*[,†]

[†]*Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Equipe LCPP Bat 308F, 43 Bd du 11 Novembre 1918, F-69616 Villeurbanne, France,* [‡]*Institut de Biologie et de Chimie des Protéines, CNRS UMR 5086 Université Lyon 7, Passage du Vercors, 69367 Lyon Cedex 7, France, and* [§]*Laboratoire Chimie Provence, UMR 6264, Universités d'Aix-Marseille I, II et III-CNRS, Equipe Chimie Radicalaire Organique et Polymères de Spécialité, Case 542, Av. Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France*

Received June 7, 2010; Revised Manuscript Received August 12, 2010

ABSTRACT: Synthesis of well-defined and highly thiol-end-functionalized polyethylene (PE-SH) was performed using olefin polymerization by coordination chemistry and robust functionalization chemistries. Using a Nd-based catalyst in combination with *n*-butyloctylmagnesium (BOMg), dipolyethylenylmagnesium compounds (PE-Mg-PE) were first prepared by catalyzed polyethylene chain growth on magnesium. Taking advantage of the reactivity of the carbon−magnesium bonds so formed, several functionalization strategies were assessed with the main aim of producing the targeted PE-SH in the simplest and most efficient way. In particular, polysulfurs and thiothiocarbonylated-end-functionalized polyethylenes were successfully obtained and reduced by lithium aluminum hydride ($LiAlH_4$) to give the desired PE with up to 90% thiol chain end functionality.

Introduction

The importance of polyolefins (principally polyethylenes (high density (PEHD) and linear low density (LLDPE)) and isotactic polypropylene (*i*-PP)) in the world of polymer thermoplastics cannot be underestimated. Many of the properties associated with this class of polymers cannot be achieved by other polymers at a reasonable cost. Polyolefins exhibit such unique mechanical properties that they remain unavoidable for many applications. In addition to the favorable mechanical properties, the very high productivity related to the catalytic feature of the polymerization systems that produce polyolefins are attractive to industry. There are however areas for which more expensive polymers or cost-effective post-treatments of polyolefins are required to balance their lack of polarity, adhesion, or compatibility with other materials. The possibility of tuning polyolefin properties to a wider range of applications partially relies on the discovery of new macromolecular architectures incorporating polyolefin segments. Polyolefin building blocks in which functionalities have been easily and efficiently introduced and that can further readily react with other materials are in this context very promising macromolecules.

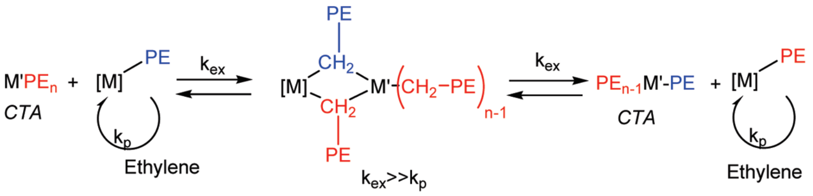
Descriptions of the use of thiols in chemical reactions extend well over 100 years, encompassing a number of fields ranging from biochemistry to polymer science. As an example, thiol can advantageously be involved in reactions toward alkene functionality through a free radical process. This chemistry, better known as thiol−ene free radical chemistry, dates from the late 1930s to the early 1950s.[1] In the polymer field, thiol−ene chemistry is mainly known for the production of networks through thiol−ene step growth polymerizations involving a reaction between multifunctional thiol and ene (vinyl) monomers.[2] The most salient feature of thiol−ene chemistry is that almost any type of ene can participate. Thiol propionate, thiol glycolate, and alkyl thiols have been reported for this chemistry. The marked and reported insensitivity of this chemistry to oxygen contamination together with the versatility of free radical processes and their tolerance to a large variety of functionalities makes this method an efficient way to produce films and thermoset plastics industrially with unprecedented physical and mechanical properties. Because of these unique features, an extension of this chemistry has been proposed in the particular field of polymer functionalization and consists of a one-step modification of polymer precursors bearing a vinyl group (ene) by free radical addition of ω-functional mercaptans (thiols).[3] This cheap and very robust strategy allows for preparing functionalized commodity materials of added value. Finally, thiol−ene chemistry is witnessing a renewal of interest particularly in polymer science in the recent literature where its power is discussed[4] and advantageously used for polymer conjugations and macromolecular architecture design.[5]

The simplicity and the efficacy of this chemistry are two key advantages when trying to functionalize polyolefin-based materials. As a result, appropriately functionalized polyolefins could be perfect candidates as starting materials in the aforementioned thiol−ene chemistry. As far as we know, only two recent papers on the functionalization by a thiol containing silane of commercial PP or PE carrying low loadings of ene end functionality have been reported.[6] Considering that the main-chain stopping event occurring in an olefin polymerization by coordination chemistry produces end unsaturation, polyolefins with high content of ene functionalities could be synthesized and efficiently functionalized using thiol-containing molecules of interest. This strategy is being researched in our laboratories. In the same vein, the introduction of a thiol end group on a polyolefin is also an appealing technique. This, however, requires identification of a catalytic olefin polymerization system that would allow high thiol functionalization rates utilizing simple chemistry.

---

*Corresponding authors. E-mail: dagosto@lcpp.cpe.fr (F.D.); boisson@lcpp.cpe.fr (C.B.).

Scheme 1. Catalyzed Chain Growth (CCG) Concept in Catalytic Ethylene Polymerization by Coordination Chemistry Using a Main Group (M′) Organometallic Species as Reversible Chain Transfer Agent (CTA) and a Transition Metal (M) Catalyst



The catalyzed polyolefin chain growth (CCG) on main group metal is indeed a very powerful tool to end functionalize polyolefins. This polymerization system is depicted in Scheme 1 in the case of ethylene and relies on the use of a catalyst based on a transition metal (M) in conjunction with an efficient chain transfer agent based on a main group metal (M′). A rapid and reversible chain transfer is operating between these two metal centers. In the absence of any irreversible chain stopping events, the system is turned into a pseudoliving polymerization of ethylene.[7] This is indeed the only way to control the polymerization of ethylene under true catalytic conditions and is conceptually similar to reversible addition−fragmentation chain transfer (RAFT) in the controlled radical polymerization area.[8] The reactivity of polyolefins formed via CCG is useful since all the chains are linked to a metal. One can thus take advantage of the reactivity of the end metal−carbon bond to introduce a variety of functional or reactive end groups. We recently showed that catalyzed polyethylene chain growth on magnesium can be used to very efficiently and easily introduce end functional groups in polyethylene chains[9] such as iodine, azide, amines, (meth)acrylate, alkoxyamines, and thiocarbonylthio groups.[10]

We report here on our investigations to introduce thiol end groups on polyethylene chains using CCG.

Experimental Section

Materials. Toluene (Acros Organics, 99%) was dried over activated 3 Å molecular sieve (SDS) under argon bubbling. Tetrahydrofuran (THF, Fisher) was distilled over sodium/benzophenone. Elemental sulfur (S_8, Aldrich), *n*-butyloctylmagnesium 20 wt % solution in *n*-heptane (BOMg, Crompton), iodine (I_2, 99.5%, Aldrich), *N,N*- dimethylformamide (DMF, Fisher Scientific, 99,9%), diethyl ether (Aldrich), potassium xanthic acid salt (KSC(=S)OEt, 97%, ACROS), tetraethylthiuram disulfide (97%, Aldrich), sodium hydrogenosulfide (NaSH, Aldrich), lithium aluminum hydride ($LiAlH_4$, 95%, Aldrich), and magnesium sulfate ($MgSO_4$, 99.5%, Aldrich) were purchased and used as received.

Analytical Techniques. High-resolution liquid ^1H and ^{13}C NMR analyses were performed on a Bruker DRX 400 spectrometer. Spectra were obtained with a 5 mm QNP probe at 363 K. A mixture of tetrachloroethylene (TCE) and perdeuteriobenzene (C_6D_6) (2/1 v/v) was used as solvent. Chemical shift values (δ) are given in ppm in reference to the solvent residual peak (C_6H_6, 7.16 ppm).

High-temperature SEC analyses were performed using a Waters Alliance GPCV 2000 chromatograph equipped with three columns (two Styragel HT6E and one Styragel HT2). Samples (1 mg mL^{-1}) were eluted with trichlorobenzene with a flow rate of 1 mL min^{-1} at 150 °C. Online detection was performed by refractometric and viscosimetric measurements using Waters equipments with polyethylene standards (395, 750, 1110, and 2155 g mol^{-1}).

MALDI-TOF mass spectrometry analyses were recorded in the linear and the reflectron mode using an Applied Biosystems Voyager DE-STR equipment using a nitrogen laser (wavelength 337 nm) and an accelerating voltage of 20 kV. The positive ions were detected in all cases. The spectra were the sum of 200 shots, and an external mass calibration was used (mixture of peptides standards, Sequazyme kit). The samples were deposited on a stainless steel target and dried. Samples were prepared by dissolving the polymer in freshly distilled tetrahydrofuran (THF) at a concentration of 10 g L^{-1}. The matrix was used without further purification and dissolved in distilled THF (10 g L^{-1}). The samples were prepared by mixing a solution of polymer in THF (10 mg mL^{-1}) and a solution of matrix in THF (20 mg mL^{-1}), with a volumetric ratio in the ratio 1/10 (Vsample/Vmatrix). 1 mL of the resulting mixture was placed onto the sample plate, and the solvent was evaporated at room temperature.

Synthesis of $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$. The neodymocene-complex was synthesized as described in the literature.[11]

Polymerization Procedure: Synthesis of PE-Mg-PE. Ethylene polymerization was carried out in toluene in a 500 mL reactor connected to an ethylene reservoir equipped with a pressure sensor. The reactor was charged with a mixture of the chloroneodymocene complex $(C_5Me_5)_2NdCl_2Li(OEt_2)_2$ (8.3×10^{-5} mol L^{-1}) and butyloctylmagnesium (BOMg) in a 400 mL toluene solution. The molar ratio Mg/Nd was adjusted with respect to the targeted molar mass and the concentration of the polymer in the reactor (M_n = 1000 g mol^{-1}, Mg/Nd = 265; M_n = 2000 g mol^{-1}, Mg/Nd = 200). The solution was rapidly set to the polymerization temperature (80 °C) and then to an ethylene pressure of 3 bar. The consumption rate of ethylene was measured from the observed drop of pressure in the reservoir. The reaction was assumed to reach completion when the amount of ethylene consumed corresponds to the expected amount of polymer according to the targeted polymerization degree (DP_n). The latter is calculated using the equation $DP_n = N_{ethylene}/(2N_{CTA})$, where $N_{ethylene}$ is the number of moles of ethylene consumed and N_{CTA} is the number of moles of chain transfer agent (CTA) used, i.e., BOMg.

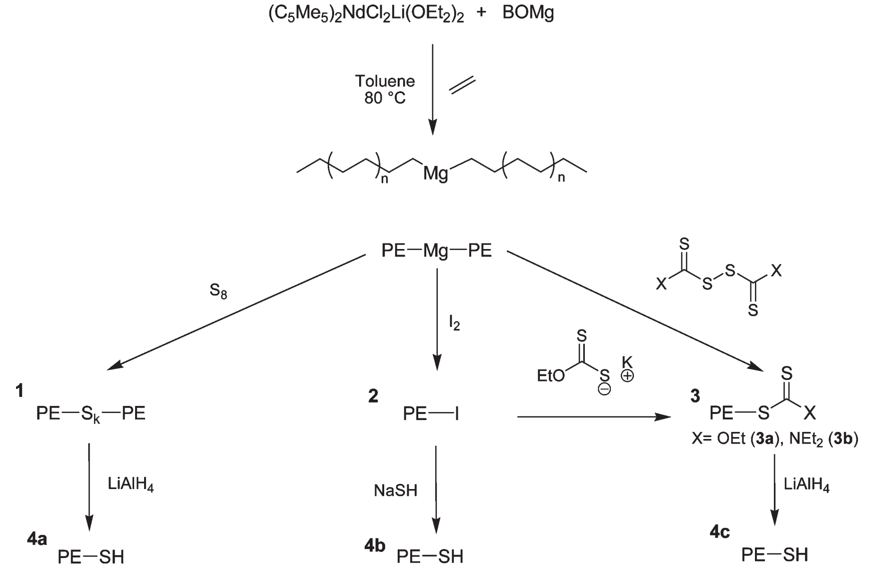
Synthesis of Polysulfur ($PE\text{-}S_k\text{-}PE$) (1). Once ethylene polymerization was assumed to have reached completion, the reactor was degassed with argon. A solution containing elemental sulfur (4−8 mol equiv of S compared to PE-Mg-PE, in 50 mL of THF) was added, and the resulting mixture was stirred under argon at 80 °C for 1 h. Then, the reactor was cooled to room temperature, the mixture was poured into a large amount of methanol, and the polymer was collected by filtration. After washing three times with 200 mL of methanol, the precipitate was dried under reduced pressure. A polysulfur $PE\text{-}S_k\text{-}PE$ was recovered as a fine light yellow powder. ^1H NMR 400 MHz (TCE/C_6D_6, 363 K), δ: 0.85 (t, $CH_3{-}CH_{2n}$), 1.30 (br, $(-CH_2{-}CH_2)_n-$), 1.45 (quint, $CH_2{-}CH_2{-}S$), 1.65 (quint, $CH_2{-}CH_2{-}S_{k>1}$), 2.40 (t, $CH_2{-}S$), 2.60 (t, $CH_2{-}S{-}S$), 2.78 (t, $CH_2{-}S_3$), 2.85 (m, $CH_2{-}S_{k>3}$).

Synthesis of Bis-*O*-ethyl Xanthate. An aqueous iodine solution (18.72 mL, 18.72 mmol) was added dropwise to potassium xanthic acid salt (5.0 g, 31.2 mmol) dissolved in water (50 mL) with the immediate formation of a bright yellow precipitate. The mixture was extracted with diethyl ether (3 × 100 mL). The organic extracts were dried with $MgSO_4$, filtered, and concentrated to afford 2.83 g (75%) of a light yellow oil.

^1H NMR ($CDCl_3$, 298 K), δ: 1.45 (6H, t, $CH_3{-}CH_2$); 4.69 (4H, q, $CH_2{-}O$).

Synthesis of Iodine-End-Functionalized Polyethylene (PE-I) (2). Once ethylene polymerization was assumed to have reached completion, the reactor was degassed with argon. After cooling to room temperature, an iodine solution (4 mol equiv of I_2

Scheme 2. Various Strategies Employed To Synthesize PE-SH Using Catalyzed Polyethylene Chain Growth on Magnesium



compared to PE-Mg-PE, in 50 mL of THF) was added, and the resulting mixture was stirred under argon at 20 °C for 2 h. The mixture was then poured into a large amount of methanol, and the polymer was collected by filtration. After washing three times with 200 mL of methanol, the precipitate was dried under reduced pressure for 10 h. A fine white powder was then recovered. ^{1}H NMR 400 MHz (TCE/C$_6$D$_6$, 363 K), δ: 0.85 (t, CH_3−CH$_2$−); 1.30 (br, CH_2−CH_2)$_n$−); 1.66 (m, CH_2−CH$_2$−I); 2.95 (t, CH_2−I).

Synthesis of Thiothiocarbonylated End-Functionalized Polyethylene (PE−SC(=S)−X) (3a, 3b). Once ethylene polymerization was assumed to have reached completion, the reactor was degassed with argon. Then, a solution of XC(S)S−S(S)CX disulfide (molar ratio XC(S)S−S(S)CX/PE-Mg-PE = 2:1) in toluene was added, and the resulting mixture was stirred at 80 °C for 2 h. The final polymer was collected by precipitation into methanol, washed with methanol, and dried under vacuum at room temperature for 10 h.

3a: PE−SC(=S)−OEt: ^{1}H NMR 400 MHz (TCE/C$_6$D$_6$, 363 K), δ: 0.85 (t, CH_3−CH$_2$−); 1.30 (br, CH_2−CH_2)$_n$−); 1.57 (m, CH_2−CH$_2$−S); 3.05 (t, CH_2−S); 4.51 (q, CH_2−O).

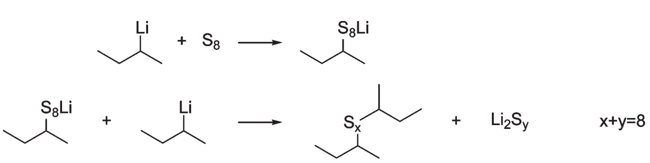
3b: PE−SC(=S)−N(Et)$_2$: ^{1}H NMR 400 MHz (TCE/C$_6$D$_6$, 363 K), δ: 0.85 (t, CH_3−CH$_2$−); 1.08 (t, CH_3−CH$_2$−N); 1.30 (br, CH_2−CH_2)$_n$−); 1.66 (m, CH_2−CH$_2$−S); 3.28 (t, CH_2−S); 3.69 (q, CH_2−N).

PE−SC(=S)−OEt (**3a**) was also obtained by an alternative strategy. A solution of PE-I in toluene was heated up to 90 °C. Solution of potassium xanthic salt (2 equiv) in DMF was added to the previous solution. After 2 h of reaction at 90 °C, the resulting mixture was slowly cooled down to room temperature and filtered, and the product was washed with methanol and dried under vacuum. A fine white powder was then recovered.

Synthesis of Thiol-End-Functionalized Polyethylenes (PE-SH) 4a and 4c. A solution of PE-S$_k$-PE or PE−SC(=S)−X in toluene (200 mL) was heated up to 90 °C. A solution of LiAlH$_4$ (10 equiv) in THF (100 mL) was added to the previous solution. After 4 h of reaction at 90 °C, the resulting mixture was filtrated at 90 °C in order to remove the excess of LiAlH$_4$ and aluminum salts formed during the reaction. 300 mL of methanol was then added to the filtrate in order to precipitate polyethylene. After filtration and washing twice with methanol, the product was dried under vacuum. A fine white powder was recovered.

The following analyses are given for PE-SH obtained in experiment 11, Table 4: ^{1}H NMR 400 MHz (TCE/C$_6$D$_6$, 363 K), δ: 0.85 (3H, t, CH_3−CH$_{2n}$), 1.03 (1H, t, −SH), 1.30 (2nH, br, CH_{2n}), 1.45 (4H, quint, CH_2−CH$_2$−SH), 2.33 (4H, t, CH_2−SH). ^{13}C NMR 100.58 MHz (TCE/C$_6$D$_6$, 363 K), δ: 14.1 (CH$_3$−CH$_2$), 22.9 (CH$_3$−CH$_2$), 24.6 (CH$_2$−SH), 28.7 (CH$_2$−CH$_2$−CH$_2$−SH), 29.4 (CH$_3$−CH$_2$−CH$_2$−CH$_2$), 29.7 (CH$_2$−CH$_2$−CH$_2$−CH$_2$−SH), 30.0 ((CH$_2$)$_n$), 32.3 (CH$_3$−CH$_2$−CH$_2$), 34.4 (CH$_2$−CH$_2$−SH). MALDI-ToF MS: m/z (C$_{78}$H$_{158}$S, M = 1128 g mol^{-1}); [MH]$^+$ = 1128.0.

Scheme 3



Synthesis of Thiol-End-Functionalized Polyethylene (PE-SH) 4b. A solution of PE-I in toluene was heated up to 100 °C, and a solution of NaSH (10 equiv) in DMF (1 mL) was added. After 90 min of reaction at 100 °C, the resulting mixture was cooled down slowly to room temperature and filtered, and the product washed with methanol and dried under vacuum.

Results and Discussion

The introduction of a thiol end group onto polyethylene is an interesting end functionalization since it has not been reported as far as we know for polyethylene. In addition, the attractiveness of the resulting material relies on the reactivity of the introduced end group that could further be used in various fields.

The routes that have been investigated for that purpose are summarized in Scheme 2.

They are all based on a first step that consists in Nd-catalyzed polyethylene chain growth on magnesium. The resulting dipolyethylenyl magnesium compounds (PE-Mg-PE) are then employed in various synthetic pathways as depicted below.

As mentioned in the Introduction, the chemical strategies dealing with the functionalization of polyethylenes need to be not only simple and efficient but also as cheap as possible. An old industrial process of functionalization of ethylene oligomers is the Alfol synthesis which provides fatty primary alcohols.[12] In this process, ethylene is oligomerized using trialkylaluminium under harsh conditions (120 °C, 120−140 bar). An oxidative work-up of the Al−C bonds followed by hydrolysis provides the corresponding alcohols. Other reported examples of oxidative work up of the metal−C bonds that are produced during ethylene polymerization allowed the synthesis of hydroxyl-end-functionalized PE.[13,14]

Table 1. Molar Mass Characteristics of Polyethylenes (1) Obtained after Addition of Elemental Sulfur on PE-Mg-PE and Corresponding Functionalities

expt no.	S/Mg	$M_n{}^a$ (g mol^{-1})	$M_n{}^b$ (g mol^{-1})	PDI^b	PE-Sat (%)^c	PE-Vt (%)^c	PE-S-PE (%)^c	PE-S-S-PE (%)^c	PE-S$_{k>2}$-PE (%)^c
1	4	1000	2280	1.3	6.8	2.1	16.3	28.7	46.1
2	8	1000	2070	1.3	2.2	1.8	20.0	18.9	57.1
3	4	2000	4420	1.3	8.7	6.2	19.8	25.9	39.4
4	8	2000	3950	1.3	7.6	6.1	16.4	20.5	49.4

[a] Theoretical M_n of polyethylene chains. [b] Determined by high-temperature (150 °C) SEC with trichlorobenzene as eluent (1 mL min^{-1}) with a calibration with PE standards. [c] In mol % determined by ^{1}H NMR analyses.

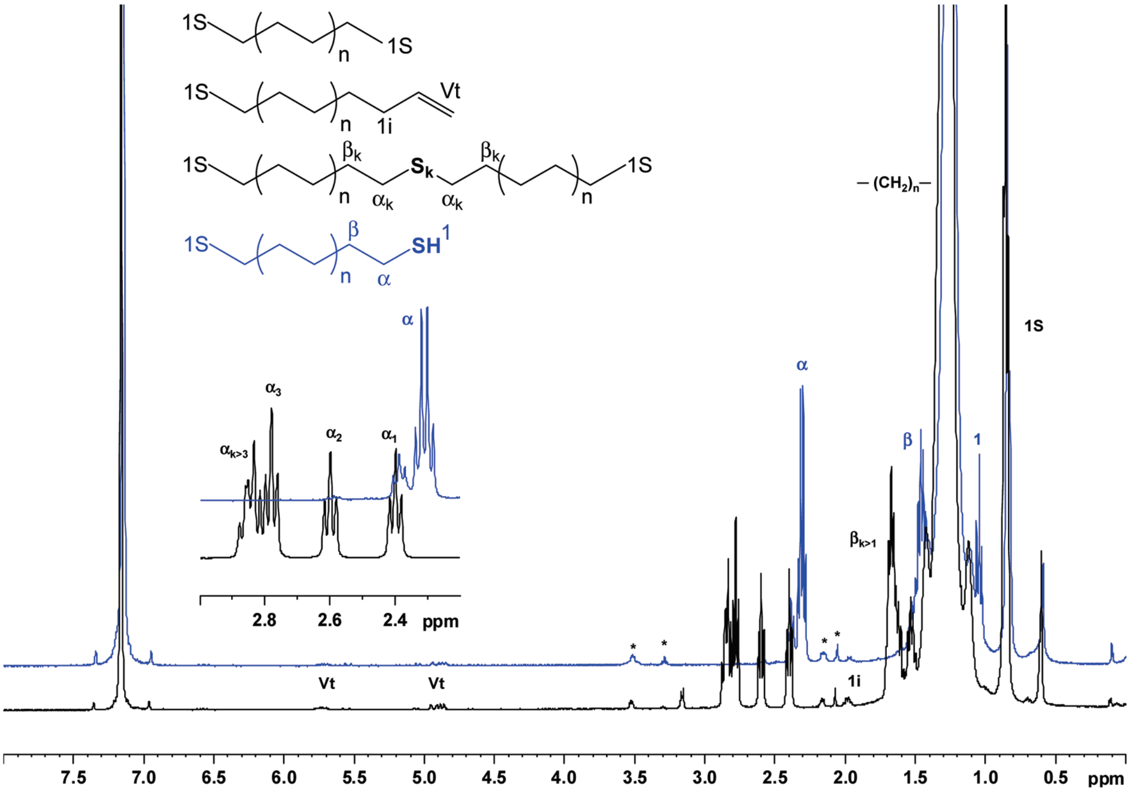
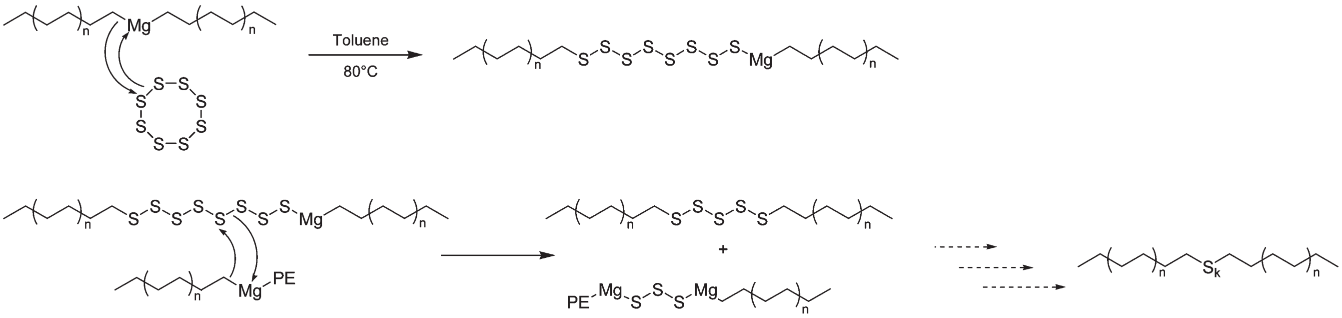


Figure 1. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of a polyethylene obtained by addition of elemental sulfur before (black) (**1**) and after reduction (blue) by $LiAlH_4$ (**4a**). Starred peaks are solvent impurities.

Scheme 4



On the basis of this reaction concept, we envisioned the use of elemental sulfur (S_8) after the catalyzed polyethylene chain growth on magnesium. Boscato et al.[15] reported that the reaction of a benzene solution of S_8 onto carbanions such as *sec*-butyllithium[16] was very fast and led to the precipitation of lithium polysulfides formed by a mechanism shown in Scheme 3 . The characterizations of the resulting organic products showed structures corresponding to *sec*-butyl-S$_x$-*sec*-butyl with $1 < x < 5$ when the stoichiometry of S_8 to the C−Li bonds was less than 1.

Experiments were then carried out (Table 1) in which S_8 was added when the polymerization of ethylene was complete. PE chains with molar masses around 1000 g mol^{-1} (entries 1 and 2) and 2000 g mol^{-1} (entries 3 and 4) were targeted. In each case two stoichiometries of S to PE-Mg-PE (4 and 8) were employed. In all cases, SEC analyses performed on the precipitated polymers were consistent with the mechanism proposed in Scheme 4 since the addition of elemental sulfur to PE-Mg-PE clearly leads to PE chains that exhibit molar masses twice that for a single PE chain (see Table 1).

^{1}H NMR analyses confirmed the SEC measurements (Figure 1). The spectrum corresponding to the polysulfur products revealed the presence of the expected signals corresponding to PE such as the methyl 1S at 0.85 ppm and the methylenes of the repetitive

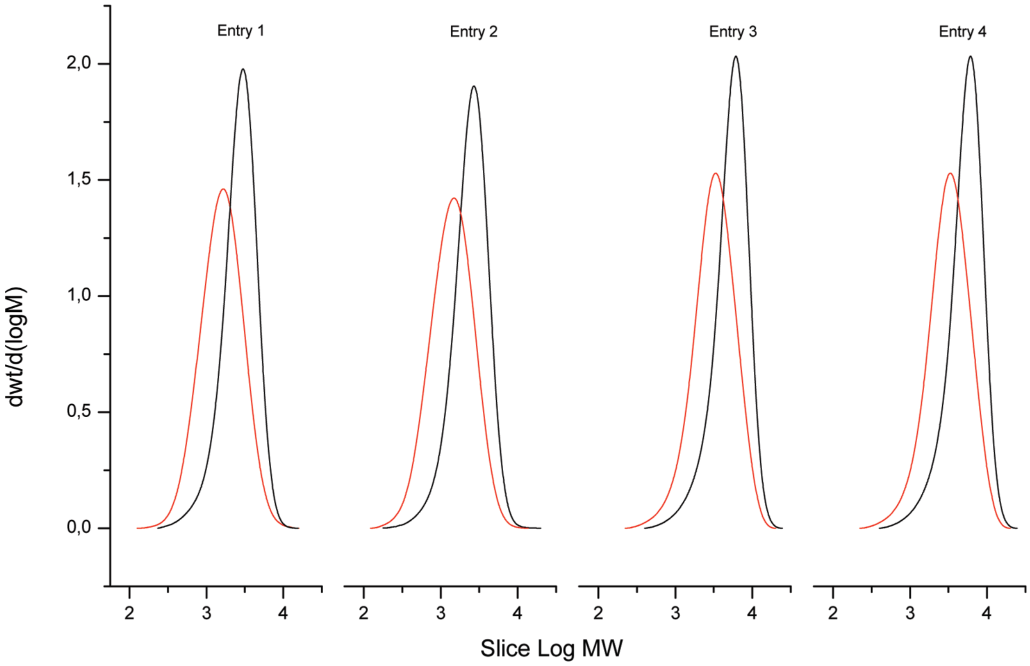


Figure 2. High-temperature SEC (PE standards) chromatograms of polyethylenes obtained by addition of elemental sulfur before (black) (**1**) and after reduction (red) by $LiAlH_4$ (**4a**).

Table 2. Molar Mass Characteristics of End-Functionalized Polyethylene and Thiol-End-Functionalization of Polyethylenes (4a) Obtained after Reduction of Polysulfurs (1)

expt no.[a]	M_n[b] (g mol^{-1})	PDI[b]	PE-Sat (%)[c]	PE-Vt (%)[c]	PE-SH (%)[c]	PE-S-PE (%)[c]	PE-S-S-PE (%)[c]
5 (1)	1300	1.5	6.9	1.4	70.6	18.0	3.1
6 (2)	1130	1.5	5.1	2.2	72.7	18.7	1.3
7 (3)	2570	1.5	12.0	5.2	56.9	19.5	6.4
8 (4)	2270	1.4	15.9	4.2	63.4	13.9	2.6

[a] Experiment number corresponding to the reduction step of the experiment in parentheses (see Table 1). [b] Determined by high-temperature (150 °C) SEC with trichlorobenzene as eluent (1 mL min^{-1}) with a calibration with PE standards. [c] In mol % determined by ^{1}H NMR analyses.

Table 3. Molar Mass Characteristics of End-Functionalized Polyethylene (4b) Obtained after Reaction of NaSH with PE-I

expt no.	M_n[a] (g mol^{-1})	PDI[a]	PE-Vt (%)[b]	PE-SH (%)[b]	PE-S-PE (%)[b]	PE-S-S-PE (%)[b]
9 (air)	1710	1.2	1.6	11.0	2.1	68.5
10 (argon)	1360	1.4	1.7	48.7	26.4	15.7

[a] Determined by high-temperature (150 °C) SEC with trichlorobenzene as eluent (1 mL min^{-1}) and calibration with PE standards. [b] Determined by of ^{1}H NMR analyses. The remaining chains are saturated PE.

Table 4. Molar Mass Characteristics and End-Functionalization Rates of Starting PE-I (2) or PE-SC(═S)-X (3) and Resulting PE-SH (4c)

expt no.	M_n[a] (g mol^{-1})	PDI[a]	PE-I (**2**) (%)[b]	PE-SC(═S)-OEt (**3a**) (%)[b]	PE-SC(═S)-NEt$_2$ (**3b**) (%)[b]	PE-SH (**4c**) (%)[b]	reduction yield (%)[b]
11	1240	1.3	95.0	91.8		88.4	96.2
12	1940	1.2	88.0	88.6		69.3	78.2
13	1270	1.5		81.8		82.7	100
14	2410	1.3		71.8		71.4	99.6
15	1270	1.3			95.5	88.0	92.1
16	1860	1.2			91.1	82.7	90.8

[a] Determined by high-temperature (150 °C) SEC with trichlorobenzene as eluent (1 mL min^{-1}) and a calibration with PE standards. [b] Determined by ^{1}H NMR analyses. The remaining chains are saturated and unsaturated PE.

unit between 1.05 and 1.45 ppm. Additional signals were showing up between 2.4 and 3.0 ppm that were all corresponding to the methylenes adjacent to one sulfur atom in the different polysulfurs formed. The very small fractions (around 6%) of vinyl chain ends formed by β-H elimination during the catalyzed polyethylene chain growth process[9] were characterized by the presence of resonances of vinyl protons at 4.90 and 5.70 ppm and of the adjacent methylene protons at 1.95 ppm.

A proposed mechanism for the formation of polysulfurs PE-S_k-PE ($k < 8$) by addition of S_8 onto PE-Mg-PE and based on the previous works of Boscato[15] is shown in Scheme 4.

In order to obtain the targeted thiol end groups, a reduction of these polysulfurs with $LiAlH_4$ was performed.

The resulting products were again analyzed by SEC (Figure 2) and ^{1}H NMR (Figure 1), and the corresponding data were compared to the starting polysulfurs. The reduction step seemed

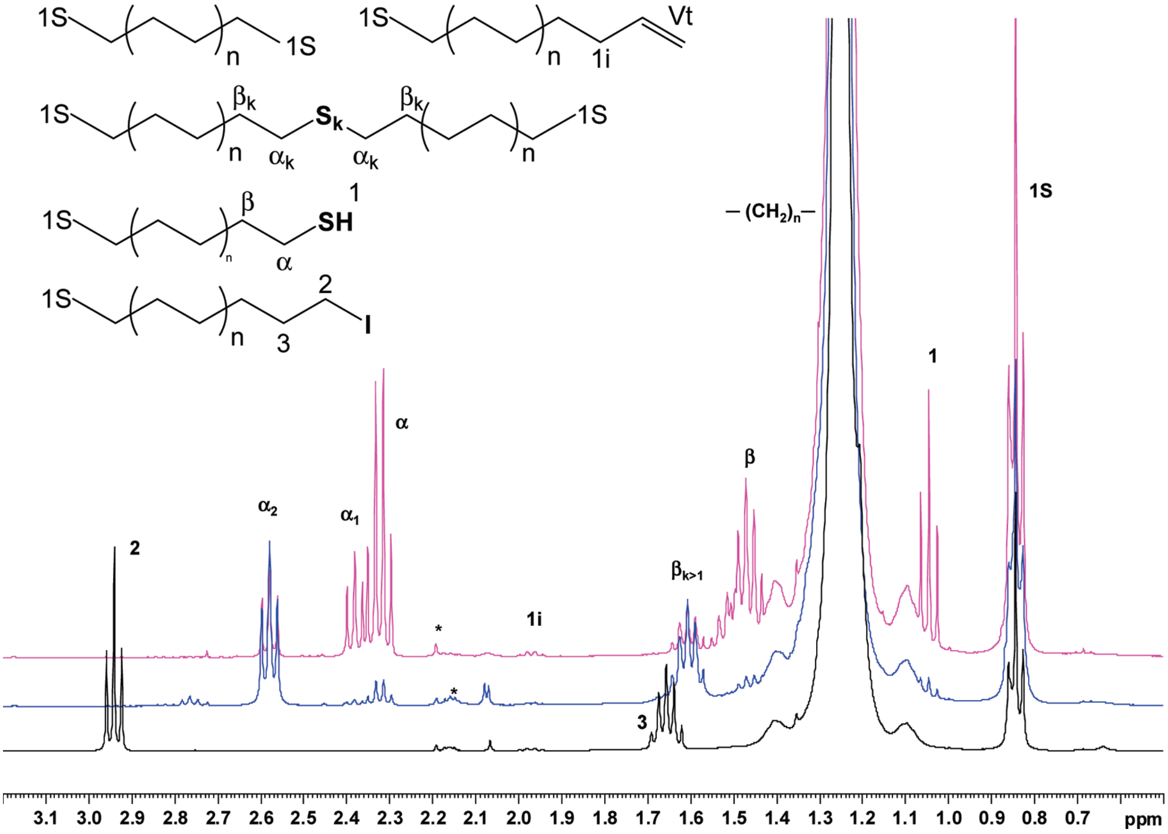


Figure 3. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE-I (black) and thiol-end-functionalized polyethylenes (**4b**) obtained by addition of sodium hydrogenosulfide on PE-I (**2**) under air (blue) and argon (pink). Starred peaks are solvent impurities.

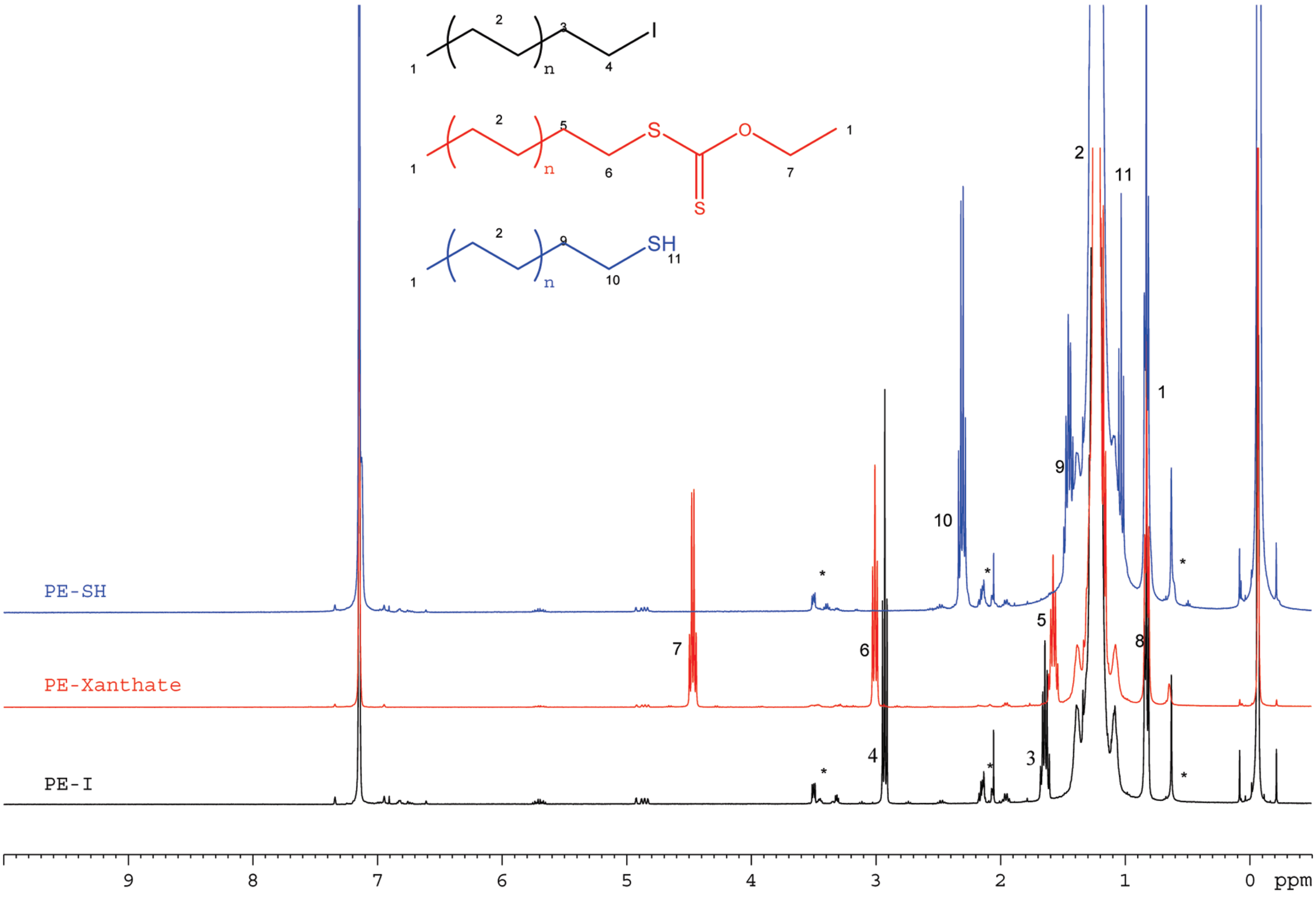


Figure 4. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE-I (**2**) (black), PE-SC(=S)-OEt (**3a**) (red) and PE-SH (**4c**) (blue).

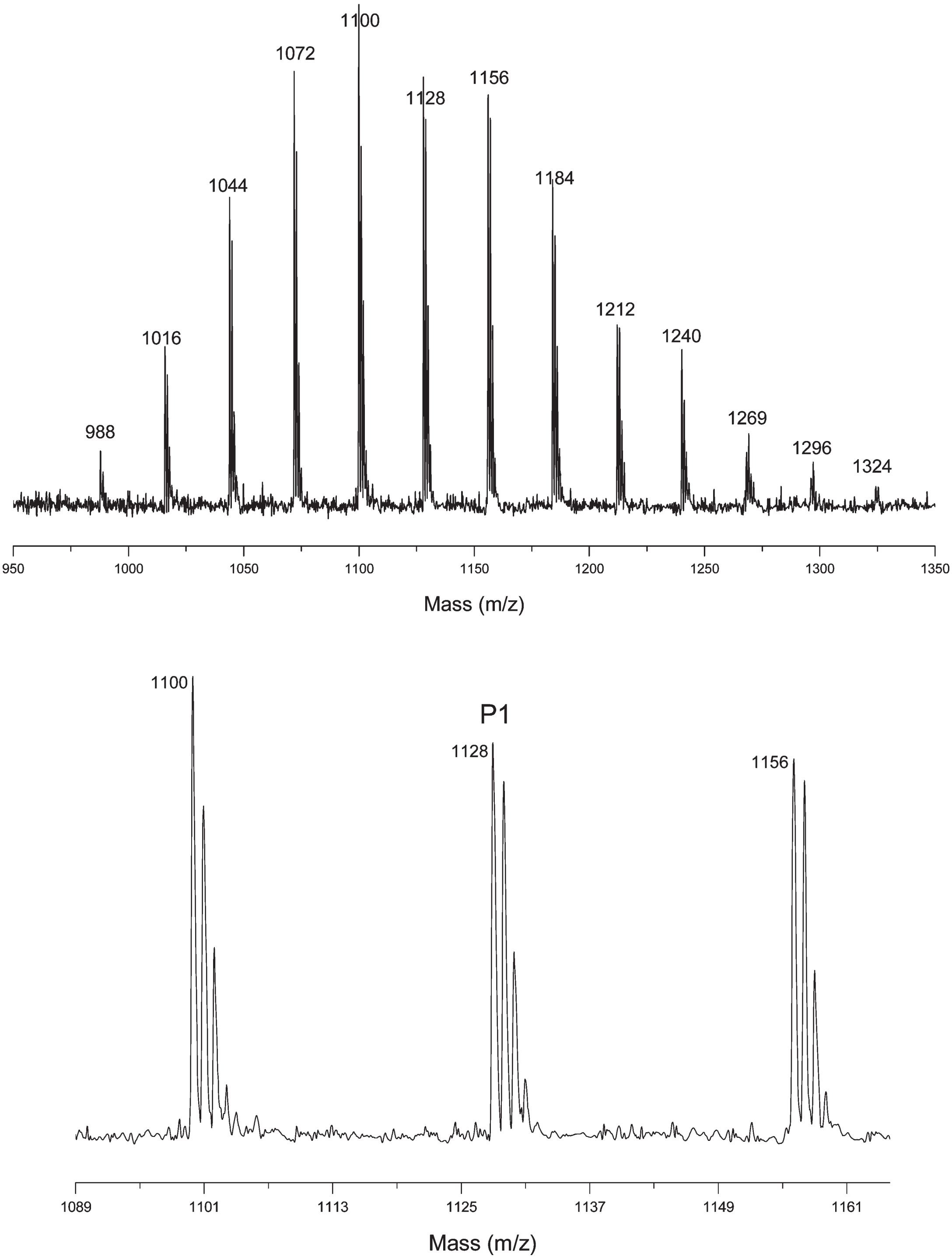


Figure 5. MALDI-TOF mass spectrometry spectrum of PE-SH (**4c**) (entry 11 in Table 4) in reflectron mode and corresponding enlargement between 1089 and 1165 Da. P1 = expected population.

to occur as the SEC analyses of the corresponding polymers systematically exhibited molar masses half that of the starting product (Figure 2).

^{1}H NMR analyses showed the complete disappearance of the signals corresponding to polysulfurs ($k > 2$). The presence of a quadruplet at 2.33 ppm and a triplet at 1.03 corresponding to a methylene adjacent to a thiol group and the proton of the thiol function at 1.03 ppm confirmed the success of the reduction. The remaining triplet at 2.40 ppm corresponds to thioether compounds PE-S-PE that were not reduced by $LiAlH_4$. The determinations of the integrals of the different signals allowed to quantify the polysulfur and thiol end group contents before and after the reduction step, respectively. The corresponding values are compiled in Tables 1 and 2.

A slightly higher thiol-end-functionalization rate was obtained for PE of low molar masses (entries 5 and 6 around 70%) compared to PE of higher molar masses (entry 7 and 8 around 60%). The formed polysulfur compounds were however always efficiently reduced into thiol-end-functionalized PE. However, these functionalization rates were minimized by the systematic and unavoidable formation of thioether compounds that do not undergo reduction. An attempt to increase the stoichiometry of S_8 did not decrease the thioethers content (entries 6 and 8). Thus, although this strategy is a useful, simple, and cheap way to synthesize PE-SH, it suffers from the unavoidable formation of thioethers which limits thiol-end-functionalization rates.

Alternatives were then envisioned, and the reactivity of iodo-end-functionalized polyethylene (PE-I, **2**) was considered. The preparation of PE-I was previously reported by our group.[10a] High functionalities (up to 97% depending on PE molar masses) were obtained by a simple addition of I_2 on PE-Mg-PE right after the ethylene polymerization step. For example, the reactivity of PE-I was used to introduce, almost quantitatively, an azide group at the chain end of polyethylene via reaction with NaN_3. Using a similar procedure, PE-I (95%) was reacted with NaSH in a toluene/DMF mixture at 100 °C. The resulting products (**4b**) were analyzed by ^{1}H NMR (Figure 3), and the proportion of the different products formed was assessed (Table 3). Disulfide PE chains were formed together with the expected PE-SH. However, the yield was poor (11%) when the reaction was performed under air (entry 9, Table 3). A very small fraction of thioether (2.1%) was also observed and may correspond to the reaction of the formed PE-SNa with PE-I. The high proportion of disulfides observed is directly linked to the well-known oxidation coupling reaction of thiol compounds particularly favored under air.[17] This first experiment indeed showed that almost 80% of PE-SH is potentially formed by addition of NaSH onto PE-I. Consequently, an additional experiment was carried out under inert atmosphere (entry 10, Table 3). A higher selectivity toward the formation of the expected thiol-end-functional polyethylenes (PE-SH) was observed (48.7%). However, the proportion of thioethers was higher (26.4%). Indeed, under air, PE-SH was rapidly transformed into PE-S-S-PE which prevented the formation of PE-SNa and its further reaction with PE-I to give PE-S-PE. The reaction between PE-SNa and PE-I is probably more favored under argon. This results in a higher thioether content in the final polymer mixture.

A third strategy to efficiently and easily introduce thiol end functions on PE was investigated. It relies on our previous results based on the synthesis of thiothiocarbonylated PE.

In the field of controlled radical polymerization, the introduction of functionalities at polymer chain ends quantitatively and selectively is of particular interest. In the case of the RAFT process, polymers bearing thiothiocarbonylated end groups (dithioesters, dithiocarbamates, dithiocarbonates, and trithiocarbonates) are obtained and readily reduced to thiols.[18] The reduction with a source of hydride has been depicted as a valuable strategy. With regard to the double objective of preparing macro-RAFT agents based on polyethylene[10e] and precursors of PE-SH, the reaction of PE-I with the potassium salt of xanthic acid KSC(=S)-OEt was investigated. Polyethylenes bearing a dithiocarbonate end group (**3a**) were obtained in quasi-quantitative yields as shown in entries 11 and 12 in Table 4. After a reduction step with $LiAlH_4$, clean PE-SH were obtained as attested by ^{1}H NMR analyses (Figure 4) and MALDI-TOF mass spectrometry (Figure 5) in which only the expected PE-SH population was observed making this strategy a really powerful method for PE-thiol-functionalization.

However, it required three chemical steps (see Scheme 2, PE-I (**2**), PE-SC(=S)-OEt (**3a**) and reduction into PE-SH (**4c**)). We already reported the synthesis of thiothiocarbonylated polyethylenes by an alternative route using a direct functionalization of $MgPE_2$. Similarly, the reactivity of Grignard reagent toward nitroxyl radical was used for the preparation of macroalkoxyamine,[10d] and the reaction of $MgPE_2$ with thiocarbonylthio disulfide provided a range of end-thiothiocarbonylated PE (dithioesters, dithiocarbamates, dithiocarbonates, and trithiocarbonates).[10e] The best rates of functionalization were obtained when dithiocarbonate (PE-SC(=S)-OEt) and dithiocarbamate (PE-SC(=S)-NEt_2) were targeted. These polymers were synthesized here using this strategy. PE-dithiocarbamate appeared to be the best candidate to be reduced to thiol since it is obtained in a one-step reaction using a commercial disulfide (difulfiram) and in high yields (entries 15 and 16, Table 4). The same reduction procedure was then applied with $LiAlH_4$ and successfully led to highly thiol-functionalized polyethylenes (reduction step yields >90%) in a minimum of chemistry steps, making this last route the most valuable of the tested ones.

Conclusion

Several strategies for the preparation of thiol-end-functionalized polyethylenes were assessed. They all rely on the use of catalyzed polyethylene chain growth on magnesium that gives rise to PE-Mg-PE compounds. The reactivity of these compounds is utilized in the direct addition of sulfur at the end of the polymerization process. PE-SH can be obtained in moderate yields (70%) after an additional reduction step of the formed polysulfurs. Alternatively, PE-Mg-PE can be used to synthesize PE-I. The use of this highly functionalized intermediate in substitution reactions with NaSH was evaluated. However, a dipolyethylenyl disulfide and a dipolyethylenyl thioether were obtained in high yields under air and argon, respectively, due to side reactions. The synthesis of polyethylenes bearing a dithiocarbonate end group via reaction of PE-I with the potassium xanthic acid salt is appealing as reduction of the product provided PE-SH in high yields. Taking advantage of this last result, the direct synthesis of end-thiothiocarbonylated (dithiocarbamate and dithiocarbonate) polyethylenes was re-examined by adding the corresponding disulfides directly onto PE-Mg-PE. The reduction of these functional PEs led, almost quantitatively, to PE-SH. The best route seems to be the direct preparation of PE-dithiocarbamate which is obtained in high yield (>90%) using commercial difulfiram and can efficiently be reduced into PE-SH with $LiAlH_4$ (reduction yields >90%). The reactivity of those synthesized PE-SH toward ene-containing compounds is currently being investigated in our group.

Acknowledgment. The authors thank Dr. Fernande Boisson (Service de RMN du Réseaux des Polyméristes Lyonnais, CNRS UMR 5223) and Dr. Hank Debruyn (The University of Sydney) for fruitful discussions. The financial support from the French National Agency for Research (ANR 08-JCJC-Tricky-0115-01) and competitiveness clusters Plastipolis and Axelera is acknowledged.

References and Notes

(1) (a) Kharasch, M. S.; Mayo, F. R. *Chem. Ind.* **1938**, *57*, 752. (b) Marvel, C. S.; Chambers, R. R. *J. Am. Chem. Soc.* **1948**, *70*, 993–998. (c) Marvel, C. S.; Caesar, P. D. *J. Am. Chem. Soc.* **1951**, *73*, 1097–1099. (d) *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974. (e) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology III*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier: London, 1993; Chapter 7, pp 219–268.

(2) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301–5338.

(3) (a) Serniuk, G. E.; Banes, F. W.; Swaney, M. W. *J. Am. Chem. Soc.* **1948**, *70*, 1804–1808. (b) Cunneen, J. I.; Shipley, F. W. *J. Polym. Sci.* **1959**, *36*, 77–90. (c) Ceausescu, E.; Bittman, S.; Fieroiu, V.; Badea, E. G.; Gruber, E.; Ciupitoiu, A. *J. Macromol. Sci., Chem.* **1985**, *22*, 525–539. (d) Boutevin, B.; Hervaud, Y.; Mouledous, G. *Polym. Bull.* **1998**, *41*, 145–151. (e) Boutevin, G.; Ameduri, B.; Boutevin, B.; Joubert, J. P. *J. Appl. Polym. Sci.* **2000**, *75*, 1655–1666. (f) Boileau, S.; Mazeaud-Henri, B.; Blackborow, R. *Eur. Polym. J.* **2003**, *39*, 1395–1404.

(4) Koo, S. P. S.; Stamenovic, M. M.; Prasath, R. A.; Inglis, A. J.; Prez, F. E. D.; Barner-Kowollik, C.; Camp, W. V.; Junkers, T. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 1699–1713.

(5) (a) Lutz, J.-F.; Schlaad, H. *Polymer* **2008**, *49*, 817–824. (b) Lowe, A. B. *Polym. Chem.* **2010**, *1*, 17–36. (c) Dondoni, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 2–5.

(6) (a) Sengupta, S. S.; Parent, S. *J. Polym. Eng. Sci.* **2006**, *46*, 480–485. (b) Parent, S. J.; Sengupta, S. S. *Macromolecules* **2005**, *38*, 5538–5544.

(7) (a) Kempe, R. *Chem.—Eur. J.* **2007**, *13*, 2764–2773. (b) Sita, L. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2464–2472.

(8) D'Agosto, F.; Boisson, C. *Aust. J. Chem.* **2010**, *63*, 1155–1158.

(9) Mazzolini, J.; Espinosa, E.; D'Agosto, F.; Boisson, C. *Polym. Chem.* **2010**, *1*, 793−800.

(10) (a) Briquel, R.; Mazzolini, J.; Bris, T. L.; Boyron, O.; Boisson, F.; Delolme, F.; D'Agosto, F.; Boisson, C.; Spitz, R. *Angew. Chem., Int. Ed.* **2008**, *47*, 9311–9313. (b) Godoy Lopez, R.; Boisson, C.; D'Agosto, F.; Spitz, R.; Boisson, F.; Gigmes, D.; Bertin, D. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2705–2718. (c) Godoy Lopez, R.; D'Agosto, F.; Boisson, C. *Prog. Polym. Sci.* **2007**, *32*, 419–454. (d) Godoy Lopez, R.; Boisson, C.; D'Agosto, F.; Spitz, R.; Boisson, F.; Bertin, D.; Tordo, P. *Macromolecules* **2004**, *37*, 6540–6542. (e) Godoy Lopez, R.; Boisson, C.; D'Agosto, F.; Spitz, R.; Boisson, F.; Gigmes, D.; Bertin, D. *Macromol. Rapid Commun.* **2006**, *27*, 173–181.

(11) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267–3270.

(12) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, 4th completely revised version; Wiley VCH Verlag GmbH & Co. KGaA: Weinheim, 2003.

(13) Byun, D.-J.; Kim, S. Y. *Macromolecules* **2002**, *35*, 8923–8925.

(14) Kaneyoshi, H.; Inoue, Y.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 5425–5435.

(15) Boscato, J. F.; Catala, J. M.; Franta, E.; Brossas, J. *Tetrahedron Lett.* **1980**, *21*, 1519–1520.

(16) Hallensleben, M. *Makromol. Chem.* **1974**, *175*, 3315–3317.

(17) Moad, G.; Chong, Y. K.; Postma, A.; Rizzardo, E.; Thang, S. H. *Polymer* **2005**, *46*, 8458–8468.

(18) Chong, Y. K.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2007**, *40*, 4446–4455.