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Polyethylene End Functionalization Using Radical-Mediated Thiol–Ene Chemistry: Use of Polyethylenes Containing Alkene End Functionality

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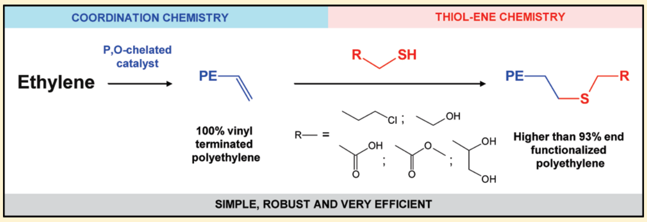
Supporting Information

ABSTRACT: Synthesis of highly end-functionalized polyethylene chains was accomplished using both coordination chemistry and radical mediated thiol–ene chemistry. A vinyl end-terminated polyethylene (M_n =1440 g·mol^{-1}, PDI = 1.8) with a functionalization rate of 100% was synthesized using a P,O-chelated catalyst [Ni{$Ph_2PC(COOEt)$=$C(C_6H_5)O$}$Ph(PPh_3)$]. Thiol–ene reactions were subsequently undertaken between vinyl-terminated polyethylene and the thiol-containing molecules thioglycolic acid, 2-mercaptoethanol, 1-thioglycerol, chloropropanethiol, and methyl thioglycolate. A range of end-functionalized polyethylenes was thus prepared using simple reaction conditions and exhibiting degrees of functionalization higher than 93%.



INTRODUCTION

The use of thiols in chemical reactions is a well-established concept that has been applied to a number of fields ranging from biochemistry to polymer science. In an example, thiols react with an alkene functionality through a free radical process. This chemistry, better known as thiol–ene free radical chemistry, dates from the late 1930s with significant investigation occurring by 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] This chemistry is relatively insensitive to oxygen contamination and tolerant to large variety of functionalities. Because of these features, an extension of this chemistry has been proposed in the 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]

The simplicity and the efficacy of this chemistry are key advantages when trying to functionalize nonreactive polyolefin based materials. As an example, when polyisobutylenes carrying vinylidene end groups became synthetically available, their functionalization with thiols was shown to be selective.[4] The formation of a stable thioether link between the polymer and the introduced functionality is of particular interest in the case of polymers such as polyolefins that need to be processed at high temperature. In addition, the use of chemistry to introduce efficiently functional groups to polyolefins is an ongoing challenge.

With this in mind, ene- or thiol-terminated polyolefins could be perfect candidates as starting materials for the aforementioned thiol–ene chemistry. We recently reported the successful introduction of a thiol end group on polyethylene[5] (PE) by taking advantage of the catalyzed polyethylene chain growth process.[6] Considering that the β-H elimination chain transfer reaction that occurs in an olefin polymerization by coordination catalysis produces an unsaturated chain-end, polyolefins chains with a high proportion of ene end functionalities can also be easily envisioned. As far as we know, the only example of thiol–ene chemistry performed on PE was reported by Parent et al.,[7] who used commercial LDPE in conjunction with 3-mercaptopropyl-trimethoxysilane at 150 °C in the molten phase. In the field of ethylene polymerization via coordination chemistry, Fujita et al. managed to synthesize highly vinyl functionalized PE chains.[8] This was achieved by the fine-tuning of the polymerization conditions and the type of catalysts used (FI catalysts). A monocomponent catalyst system for ethylene polymerization is particularly appealing because in the absence of potential chain transfer agents, β-H elimination is the only process competing with polymerization. This should lead to PE chains exclusively exhibiting vinyl chain ends. An example of such a system is the P,O-chelated nickel catalyst [Ni{$Ph_2PC(COOEt)$=$C(C_6H_5)O$}-$Ph(PPh_3)$].[9] It was found to produce vinyl-terminated PE which

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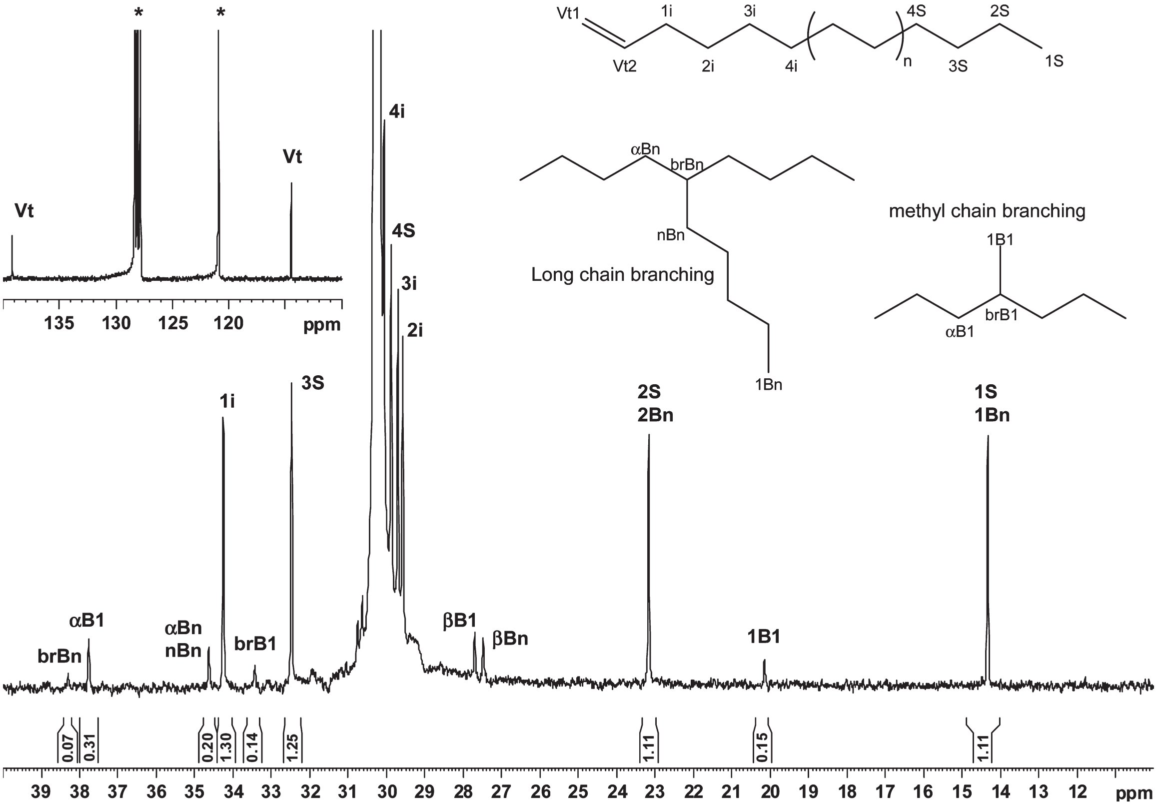


Figure 1. ^{13}C NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 4000 scans, 363 K) of PE−ene.

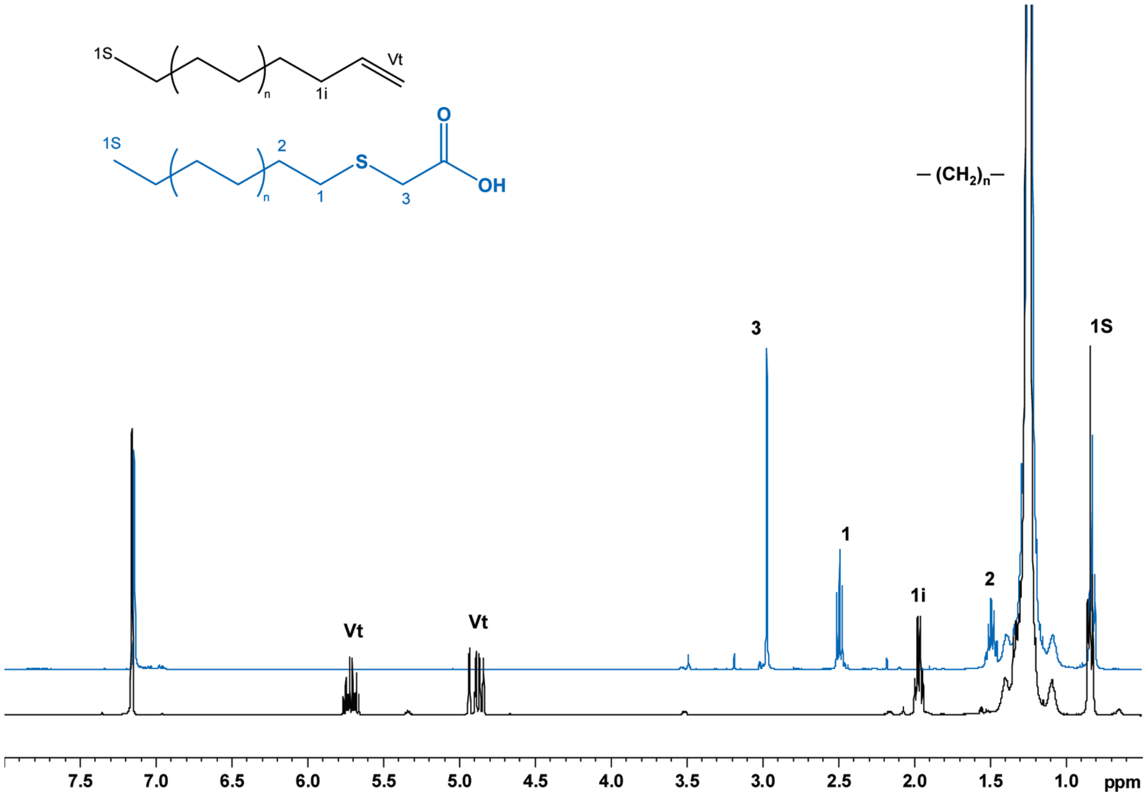


Figure 2. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE−ene (bottom) and PE-COOH (top) corresponding to entry 9 in Table 1.

could be used as starting material for further functionalization using thiol containing molecules.

In the present Article, the synthesis of quantitatively vinyl end-functionalized PE chains using P,O-chelated catalyst $[\mathrm{Ni}\{\mathrm{Ph_2PC(COOEt){=}C(C_6H_5)O}\}\mathrm{Ph(PPh_3)}]$ was performed, and the resulting polymers were functionalized with a range of thiol-containing molecules.

EXPERIMENTAL SECTION

Materials. Toluene (Acros Organics, 99%) was dried over activated 3 Å molecular sieve (SDS) and degassed by argon bubbling. Thioglycolic acid (Sigma, 98%), 2-mercaptoethanol (Sigma, 99%), 1-thioglycerol (Sigma, 97%), chloropropanethiol (Sigma, 98%), and methyl thioglycolate (Sigma, 95%) were purchased and used as received. 2,2′-Azobis-(isobutyronitrile) (AIBN, Fluka, 98%) was purified by recrystallization from ethanol at 40 °C.

Table 1. Influence of the Quantity of Thioglycolic Acid on the Thiol−Ene Reaction between PE−Ene and Thioglycolic Acid

entry	Eq−SH[a]	M_n (g·mol^{-1}) (PDI)[b]	% PE−ene[c]	% PE-COOH[c]
1		1440 (*1.8*)	98.8	
2	1	1600 (*1.7*)	68.9	21.8
3	1.25	1570 (*1.7*)	50.9	38.5
4	1.5	1480 (*1.7*)	29.0	58.7
5	2	1480 (1.7)	13.2	73.2
6	3	1440 (*1.7*)	1.3	86.7
7	4	1380 (*1.8*)	1.1	90.2
8	5	1350 (*1.8*)	1.1	92.7
9	10	1350 (*1.8*)	1.5	95.1

[a] Molar ratio thioglycolic acid/PE−ene. [b] M_n (PDI) value of functionalized PE determined by high-temperature (150 °C) SEC with trichlorobenzene as eluent (1 mL·min^{-1}). [c] Molar percentages of vinyl (PE−ene) and carboxylic acid (PE-COOH)-terminated chains in the product mixture were determined by ^{1}H NMR spectroscopy.

Analytical Techniques. High-resolution liquid NMR spectroscopy was carried out with a Bruker DRX 400 spectrometer operating at 400 MHz for ^{1}H and 100.6 MHz for ^{13}C. Spectra were obtained with a 5 mm QNP probe at 363 K. Polymer samples were examined as 10−15% (w/w) solutions. A mixture of tetrachloroethylene (TCE) and perdeuterobenzene (C_6D_6) (2/1 v/v) was used as solvent. Chemical shift values (δ) are given with respect to the internal reference, tetramethylsilane (TMS).

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 equipment and using polyethylene standards for calibration.

Synthesis of $[\mathrm{Ni}\{\mathrm{Ph_2PC(COOEt){=}C(C_6H_5)O}\}\mathrm{Ph(PPh_3)}]$. The catalyst was synthesized as described in the literature.[9f]

Polymerization Procedure − Synthesis of PE−Ene. 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 solution of $[\mathrm{PhNi(Ph_2PC(C_6H_5){=}C(COOEt)O}]$ (5 μmol) in toluene (250 mL). The solution was heated to the polymerization temperature (70 °C), and ethylene was introduced at a pressure of 10 bar. The pressure drop in the reservoir was recorded to assess activity and productivity data. At the end of the polymerization, the contents of the reactor was added to methanol (600 mL), and the polymer was collected by filtration.

General procedure for Thiol−Ene Reactions. A solution of PE−ene (1 equiv), −SH (10 equiv), and AIBN (0.5eq) in 8 mL of toluene was first degassed with argon for 15 min and then heated to 85 °C. After 4 h, the reaction mixture was slowly cooled to room temperature, precipitated in methanol, and filtered, and the product was washed with methanol and dried under vacuum.

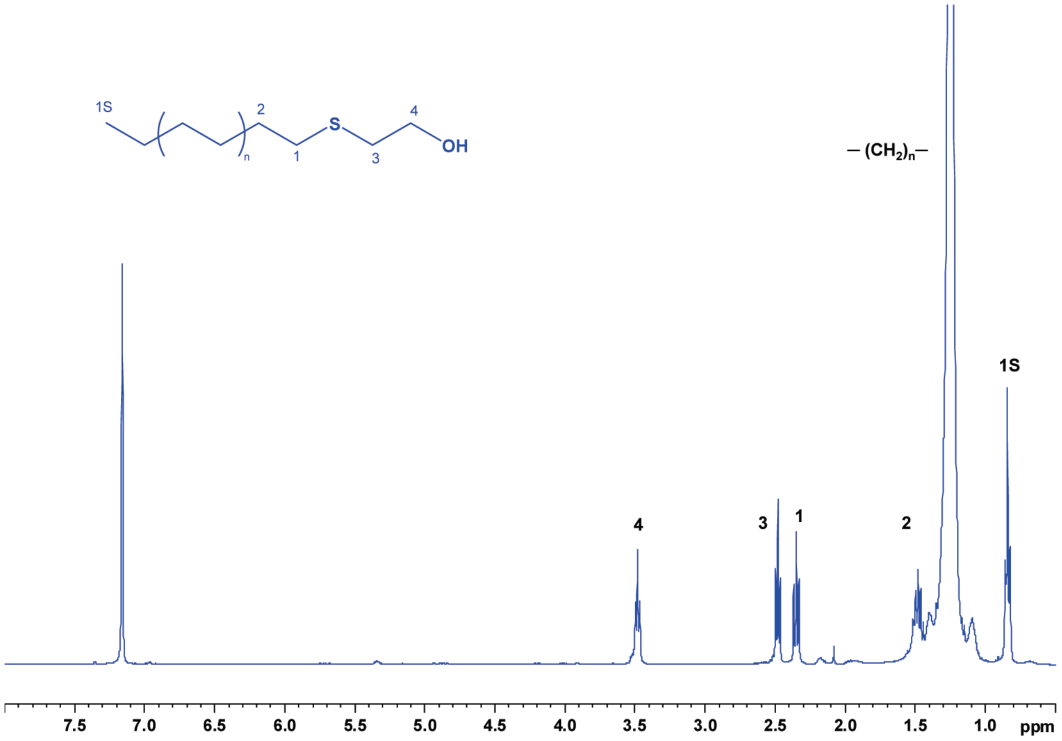


Figure 3. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE−OH.

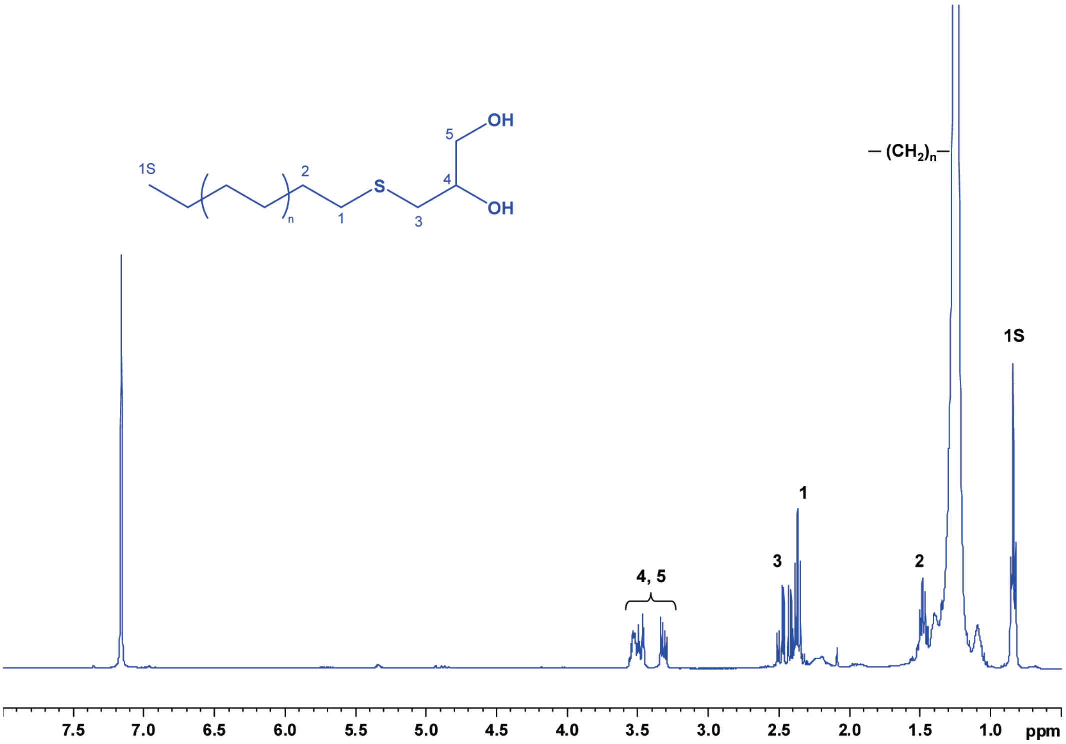


Figure 4. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE-(OH)$_2$.

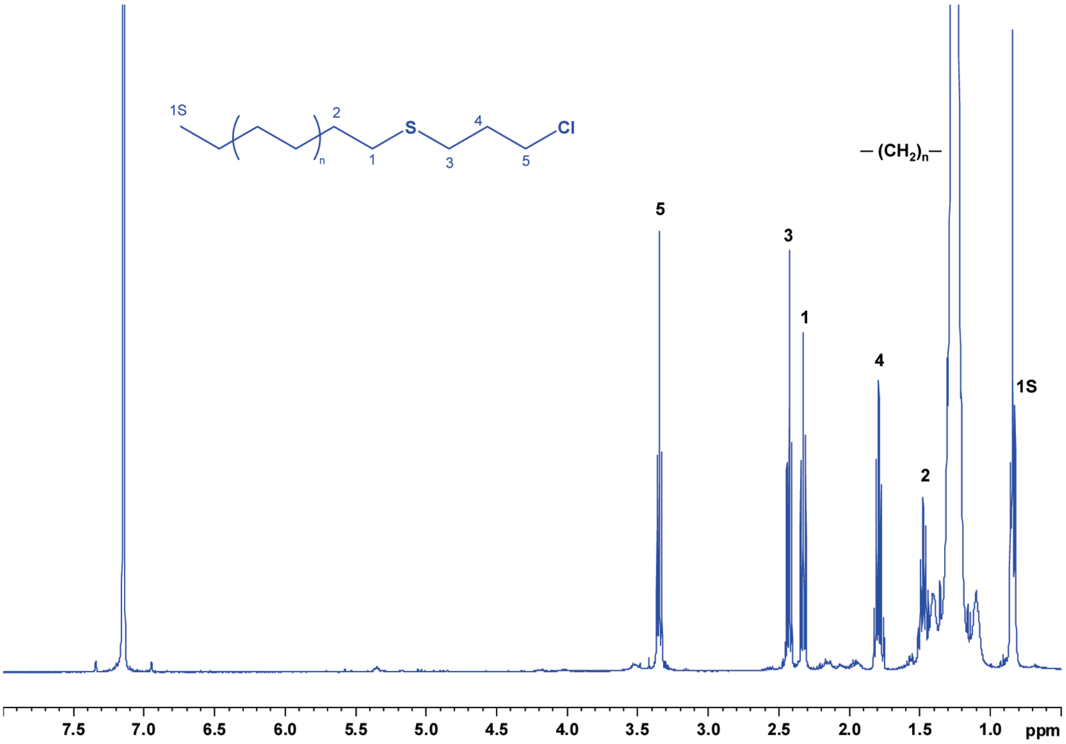


Figure 5. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE-Cl.

■ RESULTS AND DISCUSSION

Synthesis of PE–Ene. The monocomponent catalyst [Ni{$Ph_2PC(COOEt){=}C(C_6H_5)O$}Ph($PPh_3$)] was used for the production of vinyl-terminated PE. The ^{13}C NMR spectrum (Figure 1) of the obtained PE shows the resonances of the vinyl chain ends, as expected, but also reveals the presence of branching (mainly methyl branching). The assignments and notations of chain branching carbons and chain ends carbons are

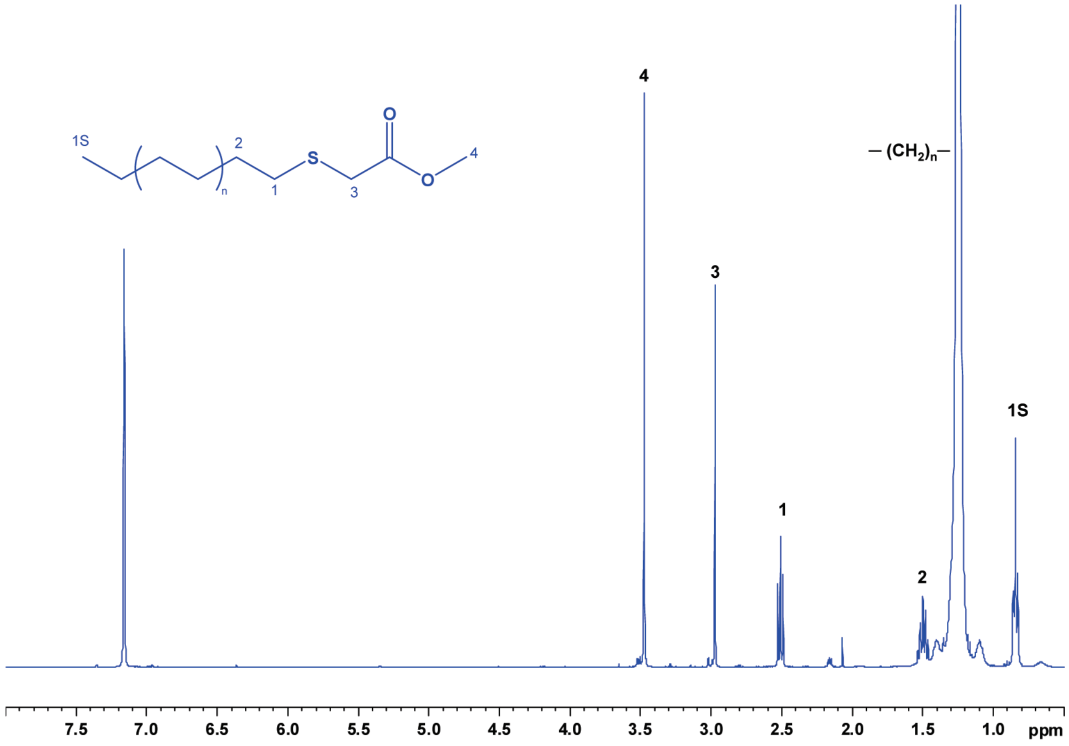
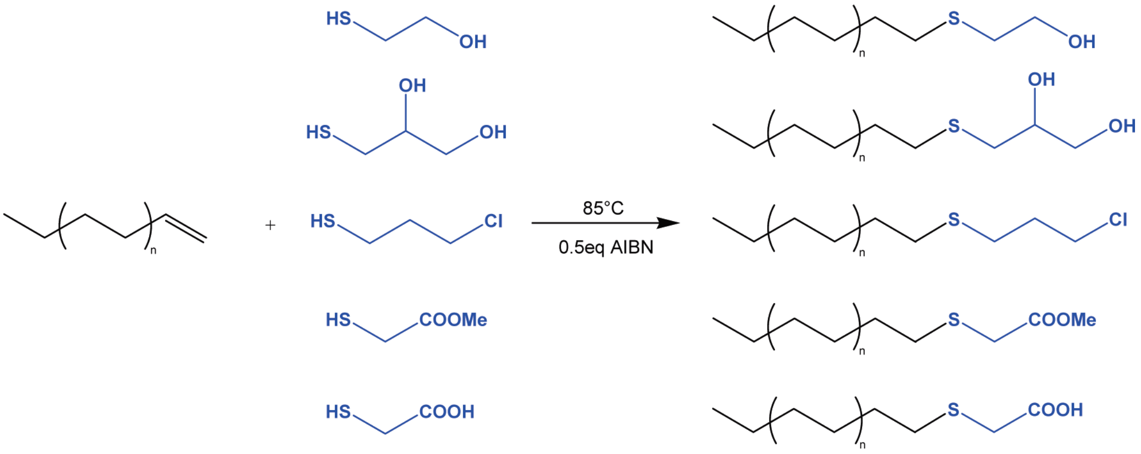


Figure 6. ^{1}H NMR (C_6D_6/TCE 1/2 v/v, 400 MHz, 512 scans, 363 K) of PE-COOMe.

Scheme 1. Thiol—Ene Reactions between PE—Ene and Thiols Containing Functional Groups



based on previous investigations by Galland et al.[10] and Llauro et al.,[11] respectively. The total number of methyl groups per chain was assessed by measuring the peak integrals of carbons of the same type (αB1, αBn+nBn, and 2S+2Bn) and assuming that those carbons exhibit similar relaxation times. An average of 1.21 methyl groups per chain was determined. The percentage of PE chains end-capped by a vinyl unit was then determined by ^{1}H NMR using the resonances of vinyl and methyl groups (Figure 2) and found to be close to 100%. Using ^{1}H NMR analysis, a molar mass value has also been determined (1420 g·mol^{-1}) that is in good agreement with the molar mass determined by HT SEC analysis (1440 g·mol^{-1}, PDI = 1.8).

The resulting vinyl-terminated polyethylene was then used as a reactant in radical-initiated thiol—ene reactions.

Thiol—Ene Reactions Using PE—Ene. In an initial experiment of investigated thiol—PE—ene reactions, vinyl-terminated polyethylene was treated with thioglycolic acid in toluene at 85 °C, in the presence of 0.5 equiv AIBN. The degree of functionalization was calculated using ^{1}H NMR data recorded on the polymer (PE-COOH) recovered by precipitation after cooling the reactor to room temperature and addition of methanol. The success of the reaction was illustrated by the ^{1}H NMR spectrum of the recovered polymer (Figure 2). Resonances corresponding to the vinyl chain-end protons, originally between 4.7 and 6.0 ppm in PE—ene (Vt in Figure 2), were absent

Table 2. Polymer Characteristics of PE-SX Produced from PE−Ene and Various Thiols

entry	thiol	M_n ($g \cdot mol^{-1}$) (PDI)[a]	% PE−SX[b]
1	$HS(CH_2)_2OH$	1680 (*1.7*)	95.5
2	$HSCH_2CH(OH)CH_2OH$	1580 (*1.7*)	95.6
3	$HS(CH_2)_3Cl$	1550 (*1.8*)	93.0
4	$HSCH_2COOCH_3$	1580 (*1.7*)	94.1

[a] M_n (PDI) determined by high-temperature (150 °C) SEC with trichlorobenzene as eluent (1 $mL \cdot min^{-1}$) calibrated using polyethylene standards. [b] Molar percentage of thioether-functionalized PE determined by ^1H NMR spectroscopy.

in the product spectrum. The presence of a triplet (1 in Figure 2) at 2.5 ppm and a singlet at 2.9 ppm corresponding to methylene protons adjacent to the formed thioether link were characteristic of the expected reaction. The resonance corresponding to the methylene protons in a β position to the formed thioether link is observed at 1.5 ppm (2 in Figure 2).

A complete assignment by ^{13}C NMR was also performed. (See the Supporting Information.)

When only 1 equiv of thioglycolic acid was used, the degree of thioether functionalization achieved was only 21.8% (Entry 2, Table 1). A systematic study was then undertaken to optimize the degree of thioether formation by varying reaction stoichiometry. An increased conversion to PE-COOH was observed when an excess of thioglycolic acid was used, with a maximum functionality of 95.1% attained with 10 equiv. Degrees of functionalization were calculated using the integrations of the resonances corresponding to the vinyl protons, the methylene α to the end groups, and the terminal and branch methyls (see above, 1.21 methyl per chain, and the corresponding assignments in Figures 2−6). The majority of PE chains were found to be functionalized with vinyl or $-S-CH_2-COOH$ end groups (Table 1). The remainder were assumed to be the products of unidentified side reactions. When performing postpolymerization modification reactions, it is desirable to minimize side reactions that could lead to a broadening of the molecular weight distribution or result in less-well-defined structures than that of the polymer starting material. The M_n of the starting PE−ene as measured by high-temperature SEC was 1440 $g \cdot mol^{-1}$ (PDI = 1.8, entry 1, Table 1), whereas that for the PE-COOH (entries 2 to 9) was always in the same range with symmetric, unimodal chromatograms (not shown) and similar PDI as the starting PE−ene.

In light of the high conversion attained in the reaction between PE−ene and thioglycolic acid, a series of reactions were carried out between PE−ene and various thiols (Scheme 1).

The resulting polymers were isolated and characterized by ^1H NMR (Figures 3−6) and ^{13}C NMR spectroscopy. (See the Supporting Information.) In all cases, the resonances corresponding to vinyl chain-end protons completely disappeared and the degrees of thioether functionalization calculated were >93% in each product (Table 2). The fact that these thiol−ene couplings did not significantly affect the molar mass of the resulting polymers further demonstrates the low occurrence of side reactions during such end-group modification.

CONCLUSIONS

The aim of this Article was to demonstrate that for the first time the robust and well-documented thiol−ene chemistry could be extended in scope to include vinyl-terminated PE as a reactant while using simple conditions. This required the synthesis of well-defined vinyl end-functionalized polyethylene chains, achieved using a monocomponent P,O-chelated nickel catalyst. Although not really exploited to this end, the resulting ethylene polymerization system was reported in the literature to undergo only β-H elimination in the absence of any other chain transfer reactions. We took advantage of this feature to produce vinyl-terminated polyethylene models exhibiting quantitative end-functionalization. The resulting chains were used in radical mediated thiol−ene reactions with functional thiols. Polyethylenes bearing different end groups such as −COOH, −OH, $-(OH)_2$, −Cl, and COOMe were readily recovered exhibiting degrees of functionalization greater than 93%. These functional polymers can serve as building blocks in macromolecular design as well as in material science.

This study is not limitative, and the use of a catalyst that would provide much higher molecular weight products via the same transfer reaction can be envisaged for various applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information. ^{13}C NMR analyses of PE-COOH, PE-OH, PE-$(OH)_2$, PE-Cl and PE-COOMe. This material is available free of charge via the Internet at http://pubs.acs.org.

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