Terminal Functionalization of Polypropylene by Radical-Mediated Thiol−Ene Addition

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ABSTRACT: The radical-mediated addition of alkanethiols to the terminal unsaturation of polypropylene (PP) is used to prepare functional polyolefin derivatives without altering the molecular weight of the parent material. The sulfide product of thiol−ene addition, as well as the internal olefin resulting from a remarkable thiyl radical-mediated olefin migration, is characterized using a model hydrocarbon, 2,4-dimethylhept-1-ene. The yield of 3-mercaptopropyltrimethoxysilane (MPTMS) addition to atactic-PP is examined in detail, and the functionalization of high molecular weight isotactic-PP is used to produce moisture-curing resins that bind to siliceous fillers. The limited unsaturation content of PP, along with the high temperatures needed to modify the resin in its melt state, is shown to impact negatively on the reaction conversion due to the reversibility of thiyl radical attack on olefin.

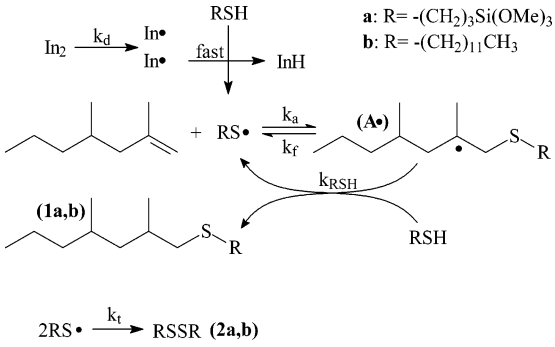
Introduction

Radical-mediated polymer modifications are robust and inexpensive methods for preparing functionalized commodity materials of added value.[1] A leading example is the grafting of vinyltrialkoxysilanes to polyethylene to create moisture-curing resins that adhere covalently to siliceous fillers.[2] Unfortunately, the selectivity of this process is inadequate for polypropylene (PP) modifications. Because of the propensity of tertiary macroradicals to undergo β-scission,[3] a high degree of PP degradation is typically incurred to attain a significant amount of monomer incorporation.[4,5] The products have very low melt strength, and they cannot be moisture-cured to the point of large-scale gel formation.[6]

We have explored a synthetic approach that has the potential to be free of such limitations, which involves the radical-mediated addition of functional thiols to the terminal unsaturation of the polymer.[7,8] This process exploits the well-established principles of thiol addition to olefins (Scheme 1),[9] wherein rapid hydrogen atom donation by RSH is exploited in combination with favorable thiyl radical (RS•) addition kinetics to generate a closed reaction sequence.[10,11] Because the chain-carrying species is a thiyl radical as opposed to the polymeric alkyl radical species that support conventional vinylsilane grafting processes, the functionalization of PP by a thiol−ene process is not expected to suffer from polymer fragmentation.[12]

In this report we describe the addition of alkyl mercaptans to polypropylene homopolymers and compare this modification strategy to conventional monomer grafting processes. Unambiguous characterization of polymer reaction products is provided by analyses of the products derived from 2,4-dimethyl-1-heptene (DMH), which serves as a model for the terminal unsaturation of PP. These structural investigations are extended to studies of low molecular weight atactic-PP modifications in which issues related to kinetic chain length and polymer fragmentation are addressed. The functionalization of high molecular weight isotactic-PP is demonstrated by silica-binding and moisture-curing experiments.

Scheme 1. Radical-Mediated Thiol−Ene Addition to DMH



Experimental Section

Materials. Dicumyl peroxide (DCP, 98%), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%), 1-dodecanethiol (98%), (3-mercaptopropyl)trimethoxysilane (MPTMS, 95%), mercaptosuccinic acid (MSA, 97%), 11-mercaptoundecanoic acid (MUA, 95%), and vinyltrimethoxysilane (VTMS, 98%) were used as received from Sigma-Aldrich. Dibutyltin dilaurate (94%, Alfa Aesar), 2,4-dimethylhept-1-ene (DMH, 99%, ChemSampCo), 2,4-dimethylheptan-2-ol (**5**, 98%, ChemSampCo), and Hi-Sil 233 (PPG) were used without purification. 2,2′-Azobis(isobutyronitrile) (AIBN), 2,5-dimethyl-2,5-di(*tert*-butylperoxyl)hexane (L-101, Elf Atochem), and 3,3,5-trimethyl-1,1-bis(*tert*-butylperoxy)cyclohexane (L-231, Elf Atochem) were stored under refrigeration. Isotactic polypropylene (*i*-PP, $M_n = 50\,000$, polydispersity = 3.8, Sigma-Aldrich) was used as received for thiol addition experiments but purified by dissolving in hot xylenes and precipitating from solution by the addition of acetone for conventional vinylsilane grafting work. Atactic polypropylene (*a*-PP, $M_n = 3300$, polydispersity = 3.0, [$R_2C{=}CH_2$] = 0.29 mmol/g, Scientific Polymers Products) was purified by dissolution−precipitation (toluene−acetone) prior to use.

[3-(2,4-Dimethylheptylthio)propyl]trimethoxysilane (1a). DMH (1 g, 7.9 mmol), MPTMS (1.56 g, 7.9 mmol), and L-231 (0.001 g, 3.3 μmol) were degassed by three freeze−pump−thaw cycles and heated to 125 °C for 60 min under a nitrogen atmosphere. Unconsumed reagents were removed by Kugelrohr distillation (0.03 mmHg, 70 °C) to yield a pale

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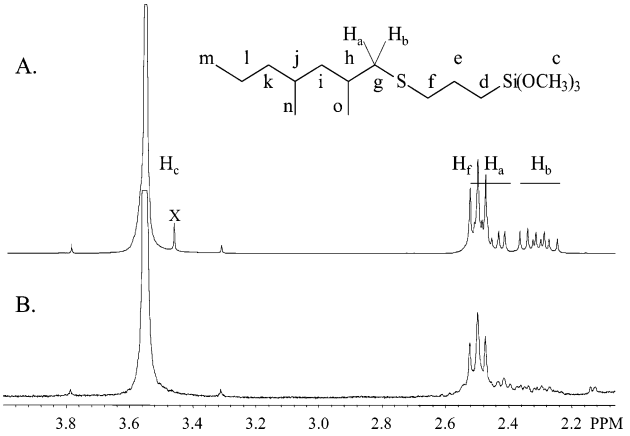


Figure 1. Downfield ^{1}H NMR spectra ($CDCl_3$): (A) **1a**; (B) *a*-PP-*g*-MPTMS (X = MeOH).

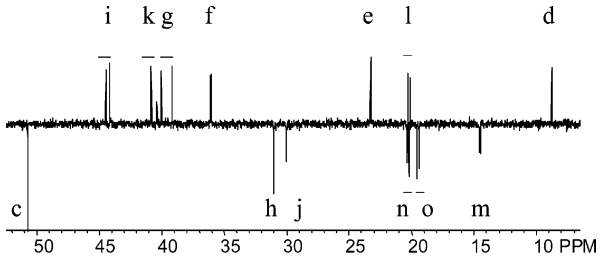


Figure 2. JMOD ^{13}C NMR spectrum of **1a**; assignments as shown in Figure 1.

yellow liquid, **1a**. MS analysis: required for $C_{15}H_{34}SSiO_3H^+$ *m/e* 322.199; found *m/e* 322.192. ^{1}H NMR ($CDCl_3$, Figure 1): δ 3.55 (s, 9H, $-OCH_3$), δ 2.52−2.44 (t, 2 H, $-CH_2-S-$), δ 2.50−2.38 (m, 1H$_a$, $-CH_aH_b-S-$), δ 2.35−2.22 (m, 1H$_b$, $-CH_aH_b-S-$), δ 1.8−1.6 (m, 3H, $-CH-$, $-CH_2$), δ 1.5−1.0 (m, 7H, $-CH_2-$, $-CH_2-$, $-CH_3$), δ 1.0−0.5 (m, 11H, $-CH_3$, $-CH_3$, $-CH_3$, $-CH_2-$). ^{13}C NMR ($CDCl_3$, Figure 2): δ 8.8 (CH_2), δ 14.4(CH_3), δ 19.4 (CH_3), δ 20.1 (CH_2), δ 20.2 (CH_3), δ 23.2 (CH_2), δ 30.0 (CH), δ 31.0 (CH), δ 36.0 (CH_2), δ 39.6 (CH_2), δ 40.5 (CH_2), δ 44.3 (CH_2), δ 50.7 (OCH_3).

Reaction yield studies were conducted as described above, using thiol and initiator concentrations listed in Table 1. Normalized integration of ^{1}H NMR spectra provided the relative concentration of residual DMH (δ 4.55−4.75, 2H, $=CH_2$), the sulfide **1** (δ 2.5−2.2, 4H, $-S-CH_2-$), and the disulfide **2** (δ 2.6, 4H, $-S_2-CH_2-$) to within ±5%.

Disulfide (2a). MPTMS (1 g, 5.09 mmol) was heated with AIBN (0.83 g, 5.09 mmol) to 90 °C for 60 min. Unconsumed reagents were removed by Kugelrohr distillation (0.03 mmHg, 60 °C). ^{1}H NMR ($CDCl_3$): δ 3.55 (s, 18H, $-OCH_3$), δ 2.59−2.63 (t, 4H, $-CH_2-S-$), δ 1.64−1.69 (m, 4H, $-CH_2-$), δ 0.54−0.66 (t, 4H, $-CH_2-Si-$).

2,4-Dimethylhept-2-ene (3). A solution containing a 2:1 ratio of dodecanethiol (0.64 g, 3 mmol) and 1,1-di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane (L-231, 0.48 g, 1.5 mmol) was added dropwise via a syringe pump to DMH (1 g, 7.9 mmol) at 140 °C over 8 h. An olefin mixture containing DMH (89%) and 2,4-dimethylhept-2-ene (11%) was recovered from the distillate of a Kugelrohr distillation (0.03 mmHg, 40 °C).

Selective Olefin Hydration.[13] The desired olefin (DMH, or DMH + **3** mixtures, 0.075 g, 0.6 mmol) was mixed a 1 M solution of borane in tetrahydrofuran (1 mL) under nitrogen for 30 min at 25 °C before quenching with water (1 mL). The resulting organoborane was oxidized by addition of 1 mL of 3 N sodium hydroxide and 1 mL of 30% aqueous hydrogen peroxide. The solution was stirred for 30 min at 25 °C prior to the addition of CH_2Cl_2 (20 mL). The organic layer was washed with saturated NaCl solution (3 × 20 mL), and the aqueous phase was extracted with CH_2Cl_2 (20 mL). The organic extracts were combined and dried over $MgSO_4$, and the resulting alcohols were isolated by rotary evaporation.

GC analysis employed a Supelco SPB-1 microbore column, with injector and detector temperatures of 225 and 300 °C, respectively. The oven temperature profile involved 40 °C for 6 min, ramp to 150 °C at 1 °C/min, ramp to 280 °C at 12 °C/min, and hold for 5 min. Helium carrier gas was used at 2 mL/min. Retention times for the diastereomers of a 2,4-dimethyl-1-heptanol (**4**) standard were 22.492 and 23.003 min, while those of a 2,4-dimethyl-3-heptanol (**5**) standard were 14.083 and 14.803 min. Retention times observed for the hydrated mixture of DMH + **3** were 13.819, 14.730 as well as 22.443, 22.950 min.

Sulfide Stability. DMH-S-dodecane (**1b**) (1.61 g, 5 mmol) was heated with dodecanethiol (1.01 g, 5 mmol) at 150 °C for 1 h with DCP (2.093 mg, 7.74 μmol or 6.27 mg, 0.002 mmol). ^{1}H NMR revealed the unreacted sulfide and dodecyl disulfide as the principal reaction products.

***a*-PP-*g*-MPTMS.** *a*-PP (1 g), MPTMS (0.094 g, 0.48 mmol), and AIBN (0.004 g, 30.4 μmol) were heated under a nitrogen atmosphere to 90 °C for 60 min. Residual thiol was removed by Kugelrohr distillation (0.03 mmHg, 100 °C) to yield a sticky, pale yellow product. ^{1}H NMR ($CDCl_3$, Figure 1): δ 3.5 (s, 9H, $-OCH_3$), δ 2.55−2.45 (m, 2H, $-CH_2-S-$), δ 2.50−2.38 (m, 1H$_a$, $-CH_aH_b-S-$), δ 2.35−2.20 (m, 1H$_b$, $-CH_aH_b-S-$), δ 1.7−1.5 (m, 3H, $-CH-$, $-CH_2$), δ 1.5−0.5 (m, $-CH-$, $-CH_2-$, $-CH_3$). Studies of *a*-PP conversion to sulfide were conducted as described above, using the reaction conditions listed in Table 1 and in Figure 3. Normalized integration of ^{1}H NMR spectra provided the relative concentration of residual olefin (δ 4.6−4.8, 2H, $=CH_2$) and the sulfide analogous to **1a** (δ 2.45−2.55, 4H, $-CH_2-S-CH_2-$) to within ±5%.

Poisoning of Thiol−Ene Additions. The model compound formulations listed in Table 2 were degassed by three freeze−pump−thaw cycles and heated to 125 °C for 60 min under nitrogen. Analogous polymer formulations were similarly treated at 150 °C for 60 min.

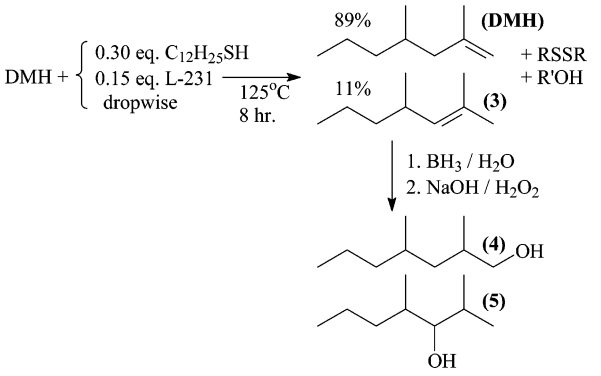
***i*-PP-*g*-MPTMS.** Ground *i*-PP (0.75 g) was tumble-mixed with L-101 (0.001 g, 3.4 μmol) and the required amount of MPTMS. Reactions were conducted in the cavity of an Atlas Laboratory mixing molder at 180 °C for 15 min, yielding *i*-PP-*g*-MPTMS. Radical-mediated *i*-PP degradations were conducted by mixing *i*-PP (45 g) and the desired amount of DCP at 180 °C within a Haake Polylab R600 internal batch mixer for 15 min at 60 rpm.

Moisture Curing of *i*-PP-*g*-MPTMS. Polymer (1.0 g) and xylenes (20 mL) were heated to reflux prior to the addition dibutyltin dilaurate (10 μL, 20.2 μmol) and water (0.5 mL). The mixture was maintained at a reflux condition for 20 min, after which the polymer was recovered from solution by precipitation with acetone (150 mL) and dried in vacuo. Gel content was determined by extracting cured products with refluxing xylenes from 120 mesh sieve cloth. Extraction solutions were stabilized with 100 ppm of 2,6-di-*tert*-butyl-4-methylphenol (BHT), and the procedure was conducted for a minimum of 2 h, with longer times having no effect on the results. Unextracted material was dried under vacuum to constant weight, and gel content was calculated as the weight percent of insoluble polymer.

Silica Immobilization of *i*-PP-*g*-MPTMS. Polymer (1.0 g), xylenes (20 mL), and precipitated silica (0.4 g) were heated to reflux for 30 min, after which the polymer and silica were recovered from solution by precipitation with acetone (150 mL) and dried in vacuo. Gel content was determined as described above, with the data presented as weight percent of insoluble polymer after correcting for the silica content of the sample.

Analysis. NMR spectra were recorded with a Bruker AM-400 spectrometer (400.13 MHz ^{1}H, 100.62 MHz ^{13}C) in $CDCl_3$ with chemical shifts referenced to tetramethylsilane. Mass spectra were recorded with a Fisons VG Quattro triple-quadrupole instrument with chemical ionization (*i*-C_4H_{10}). Melt flow rate (MFR) values are reported as grams of resin extruded in 10 min, as determined using a Tinius Olsen apparatus at 230 °C with a 2.16 kg load, unless otherwise noted. The relative viscosity of toluene solutions containing 5 g/100 mL of polymer was determined at 25 °C using an Eubelohde

Scheme 2



capillary viscometer. Since elution times exceeded 200 s for all solutions, kinetic energy corrections were not required.

Results

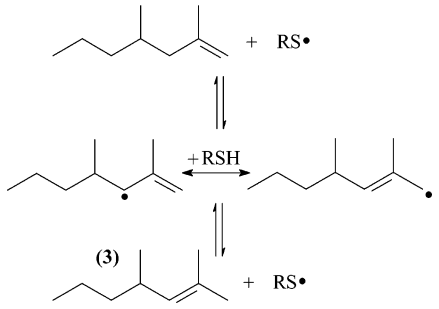
Model Thiol−Ene Additions. The products resulting from thiol addition to PP have been characterized by comparisons to a model compound, 2,4-dimethyl-1-heptene (DMH), whose structure is consistent with the terminal unsaturation of the polymer (Scheme 1). Two principal reaction products were isolated from the modification process: the desired sulfide (**1**) and a disulfide resulting from thiol oxidation (**2**).

The sulfide generated by reaction of DMH and 3-mercaptopropyltrimethoxysilane (MPTMS) is the expected anti-Markovnikov addition product (**1a**) whose ^{1}H and ^{13}C NMR spectra are illustrated in Figures 1a and 2, respectively. Of particular analytical value is the downfield ^{1}H NMR resonances derived from residual terminal unsaturation and from methylene groups adjacent to sulfur ($-CH_2-S-CH_2-$). However, the two asymmetric centers within **1a** complicate the multiplicity of the sulfide ^{1}H NMR resonances for H_a and H_b (Figure 1). Given that the protons of this methylene group are diastereotopic, they exhibit geminal coupling. Additionally, the four stereoisomers of compound **1a** constitute two pairs of diastereomers, with each pair being represented in an NMR spectrum. As a result, two sets of resonances for each methylene proton are observed by ^{1}H NMR, and two sets of signals are recorded for each carbon in the ^{13}C NMR spectrum that is proximal to an asymmetric center. Peak assignments were confirmed by 2-dimensional COSY ^{1}H NMR and HSQC ^{1}H−^{13}C NMR analysis.

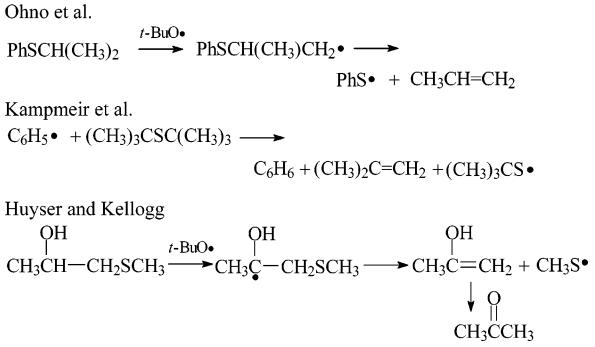
In addition to the desired sulfide, we were surprised to discover small quantities of 2,4-dimethyl-2-heptene (**3**) in the products of model reactions that employed low thiol concentrations. Much higher yields of this isomerization product were achieved by introducing thiyl radicals to DMH in the absence of significant amounts of free thiol (Scheme 2). These conditions generated dodecyl disulfide (**2b**) as the principal sulfur-containing product and resulted in an 11% conversion of DMH to **3**. Unambiguous characterization of **3** required a selective hydration of the olefin mixture,[13] followed by gas chromatography analysis of the resulting secondary and primary alcohols.

While the extent olefin migration may not be substantial under standard thiol−ene addition conditions, its occurrence is of considerable fundamental importance, since it involves hydrogen atom transfer between thiyl and allylic species (Scheme 3). Although thiols are widely recognized as efficient hydrogen donors, abstraction by alkyl thiyl radicals has been documented for thermodynamically favorable benzylic[14,15] and allylic systems[16] as well as for other C−H activated compounds.[17] The present case involves a similarly favorable allylic hydrogen abstraction, which is followed by trapping of the intermediate allyl radical by thiol to generate the observed internal olefin.

Scheme 3. Thiyl Radical-Mediated Olefin Migration



Scheme 4



In contrast to conventional grafting reactions that accommodate relatively insoluble reagents such as maleic anhydride, thiol additions are highly sensitive to modifier solubility.[8] Soluble thiols such as MPTMS could be added to DMH with conversions exceeding 90%. On the other hand, poorly soluble reagents such as mercaptoundecanoic acid (MUA) and mercaptosuccinic acid (MSA) were completely inactive in the absence of a cosolvent. Only when DMH and MUA were rendered miscible by dissolving both reagents in chlorobenzene was a modest olefin conversion achieved. Therefore, the scope of solvent-free additions of thiols to polyolefins may be considerably less than anticipated, given the apparent incompatibility of thiol−ene reactions involving nonpolar hydrocarbons and polar modifiers.

Stability of Sulfide Addition Products. The temperatures required to chemically modify and process isotactic polypropylene are well in excess of those commonly used for thiol−ene additions, which may raise concerns regarding sulfide stability. In fact, there are many reports of sulfide decomposition, three of which are illustrated in Scheme 4. The studies of Ohno et al.[18] and Kampmeir et al.[19] initiated fragmentation by abstracting β-hydrogen from the sulfide, leading to a rapid elimination of a thiyl radical. These decompositions possessed no chain character, presumably due to the inability of the eliminated thiyl radical to abstract hydrogen in the manner of *tert*-butoxyl and phenyl radicals. However, Huyser and Kellogg[20] succeeded in producing a chain sulfide decomposition by exploiting the C−H bond activation brought on by an α-hydroxyl group. Quantitative decomposition of their hydroxy thioether was achieved due to the tautomerization of

Table 1. Silane Modification of *a*-PP

modifier	initiator loading (μmol/g)	modifier loading (mmol/g)[a]	silane graft content (mmol/g)	olefin conversion (%)	relative viscosity[b]
MPTMS	30.4	0.48	0.16	57	1.74
MPTMS	30.4	0.96	0.23	82	1.78
MPTMS	16.5	0.48	0.12	43	1.75
MPTMS	16.5	0.96	0.19	66	1.76
MPTMS	18.5	0.48	0.08	34	1.86
MPTMS	18.5	0.96	0.17	58	1.75
VTMS	18.0	0.48	0.34		1.04

[a] 0.48 and 0.96 mmol/g represent 2.0 and 4.0 thiol equivalents, respectively. [b] Toluene; 5 g of polymer/100 mL; 25 °C; unmodified *a*-PP relative viscosity = 1.75.

the enol product, which prevented the readdition of eliminated thiyl radicals.

The stability of the sulfides of interest under the reaction conditions used in this work was confirmed by exposing the compounds to a variety of treatments, none of which led to the regeneration of DMH. As an illustrative example, sulfide **1b** was maintained at 125 °C for 8 h while a solution containing 0.25 equiv of dodecanethiol and 0.12 equiv of L-231 was added with a syringe pump at a uniform rate. This treatment exposed **1b** to a steady concentration of thiyl radicals under thiol-starved reaction conditions, thereby favoring sulfide decomposition. Nevertheless, dodecyl disulfide was the only significant reaction product. The sulfide **1b** was recovered in very high yield, and only trace amounts of olefins that did not include DMH were detected by ^{1}H NMR analysis.

Further evidence of stability was provided by the observed inactivity of **1** with respect to sulfide exchange. Heating **1a** with 1 equiv of dodecanethiol and L-231 to 125 °C had no effect. The only significant product of this treatment was dodecyl disulfide, which was accompanied by trace amounts of unisolable olefinic byproducts. Similar behavior was observed at 150 °C using DCP as initiator.

We attribute the high-temperature stability of compound **1** its polymer analogues to the inefficiency of the β-hydrogen abstraction that facilitates sulfide cleavage. Given that this hydrogen transfer involves an alkyl mercaptan (RS−H bond dissociation energy ≈86 kcal/mol) and a tertiary alkyl hydrocarbon (R_3C−H ≈91 kcal/mol), the process energetically unfavorable. Indeed, Walling and Rabinowitz have reported limited yields for *n*-butyl thiyl radical abstraction from isooctane,[14] and one would, therefore, expect the decomposition of sulfides such as **1a** to demonstrate a limited kinetic chain length, as reported for similarly unactivated systems.[18,19]

Atactic-PP Modifications. Toward the synthesis of silane-modified, isotactic materials of industrial interest, we extended our model compound investigations to an atactic polypropylene material (*a*-PP) having a M_n of approximately 3300 g/mol. This polymer was amorphous, and its substantial terminal olefin content (0.29 mmol/g) allowed the extent of olefin conversion to sulfide to be monitored by solution ^{1}H NMR. Moreover, any polymer degradation that accompanied the modification process could be detected by dilute solution viscosity.

^{1}H NMR analysis of *a*-PP-*g*-MPTMS (Figure 1b) confirmed that the structure of its functional moiety is consistent with that of the model sulfide (**1a**). The yields of the desired product were acceptable given the low olefin concentrations imposed by the polymeric substrate (Table 1), and the concentration of olefin migration products was negligible under the conditions used to produce the derivative. Furthermore, the silane-modified polymer was generated without altering its relative viscosity, meaning that no gross changes to molecular weight were inflicted by the process. In contrast, the conventional radical-mediated addition of vinyltrimethoxysilane (VTMS) to *a*-PP resulted in severe viscosity losses due to macroradical fragmentation (Table 1).

Figure 3 illustrates the influence of thiol loading, temperature, and initiator concentration on sulfide yields. As expected, increased thiol concentrations improved olefin conversions under all the conditions investigated. However, this sensitivity to thiol concentration precluded the use of poorly soluble mercaptans such as MUA and MSA. Just as they were ineffective in the model compound system, these modifiers were completely inactive for *a*-PP functionalization under solvent-free conditions.

The effect of reaction temperature is of particular interest since isotactic polypropylene modifications must operate above the 160 °C melting point of the material. The data plotted in Figure 3 show a sharp decline in olefin conversion on moving from 90 to 125 °C and further to 150 °C. We note that the half-lives of AIBN, L-231, and DCP are nearly equivalent at the temperatures employed ($t_{1/2}$ = 14.6, 18.6, and 15.0 min, respectively) and that initiation efficiencies should be exceptionally high given the hydrogen-donating properties of thiols. Therefore, pseudo-steady-state radical concentrations are not expected to vary considerably between the three series of experiments. Since the decline in yield with temperature cannot be attributed to radical concentration effects on kinetic chain length, this effect likely stems from the reversibility of thiyl radical attack on olefins, as argued in the Discussion section.

Although the initiation of thiol−ene addition reactions is commonly written as shown in Scheme 1, knowledge of the details of the initiation process is lacking. This may be due, in part, to the particular sensitivity of thiol additions to low-yielding radical generation reactions, given their exceptional kinetic chain lengths. In fact, we observed substantial MPTMS addition to *a*-PP in the absence of initiator (Figure 3), which is not seen for conventional vinylsilane and maleic anhydride additions to polyethylene.[21] Since the sulfide adduct is an anti-Markovnikov addition product of a radical-mediated reaction, this baseline radical activity could be attributed to trace amounts of peroxide/hydroperoxide within *a*-PP, as others have proposed for the addition of thiols to unpurified olefins.[22] It should be noted, however, that spontaneous radical formation has been reported for thiol−ene mixtures held in the absence of daylight and oxygen,[23] possibly due to a molecule-assisted homolysis mechanism, as proposed by Pryor and co-workers.[24]

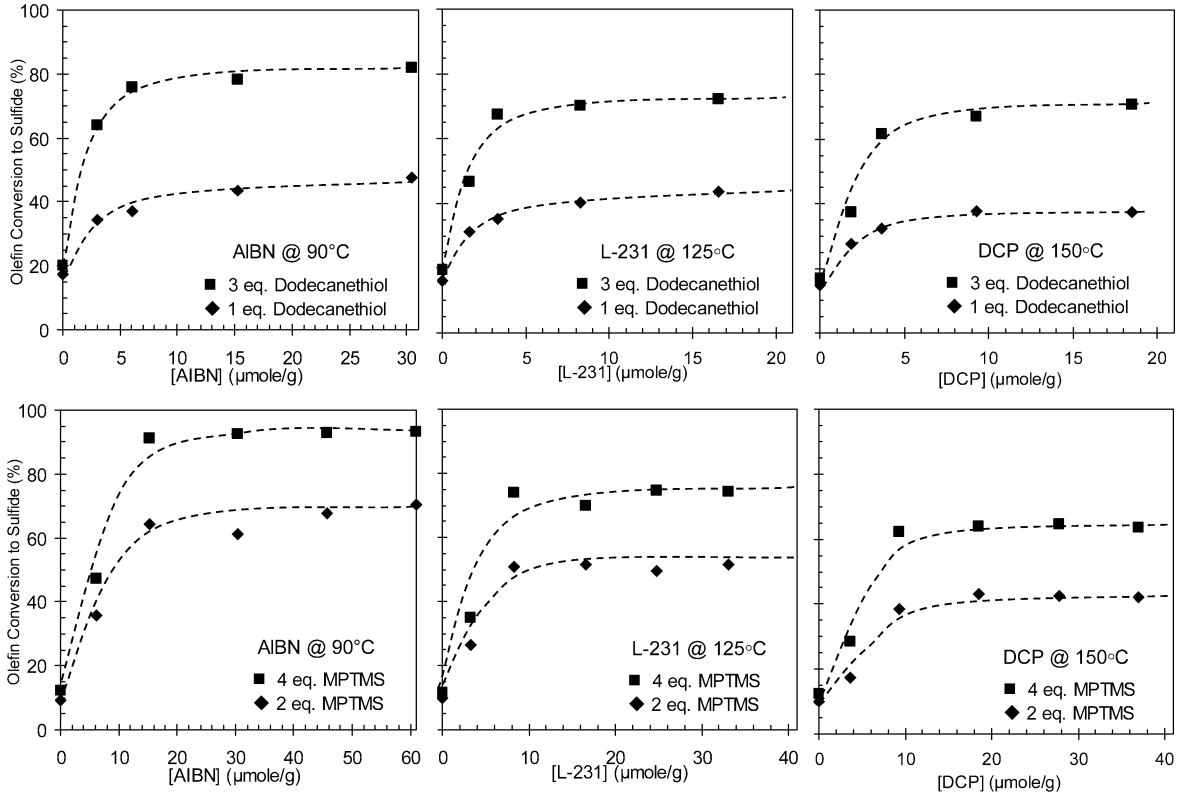


Figure 3. *a*-PP conversion of terminal vinylidene to sulfide as a function of initiator and thiol loadings.

Table 2. Thiol−Ene Poisoning Trials

thiol modifier	[thiol] (equiv)[a]	potential poison	[poison] (equiv)[a]	conv (%)
DMH; [L-231] = 0.1 wt %; T = 125 °C; 60 min				
MPTMS	1.0	none		71
MPTMS	1.0	sulfide **1a**	0.19	73
MPTMS	1.0	sulfide **1a**	0.46	70
MPTMS	1.0	disulfide **2a**	0.15	73
a-PP; [DCP] = 0.24 wt %; T = 150 °C; 60 min				
n-$C_{12}H_{25}SH$	3.0	none		67
n-$C_{12}H_{25}SH$	3.0	*a*-PP-*g*-$C_{12}H_{25}SH$	0.44	65
n-$C_{12}H_{25}SH$	3.0	disulfide **2b**	0.42	68

[a] Molar equivalents relative to olefin.

Table 3. Silane Modification of *i*-PP[a]

modifier	modifier loading (mmol/g)	product MFR[b] (g/10 min)	cured gel content (wt %)	bound polymer (wt %)
	0.00	>700	0	0
MPTMS	0.10	38	0	5
MPTMS	0.20	37	10	8
MPTMS	0.20	37	12	14
MPTMS	1.00	40	32	35
VTMS	0.20	>700	0	38
VTMS	0.33	>700	0	45

[a] [L-101] = 3.4 μmol/g; T = 170 °C; 15 min. [b] MFR measured at 230 °C using a 2.16 kg load. MFR of unmodified *i*-PP = 35 g/10 min.

Further anomalies are observed at high initiator loadings, as the incremental response of sulfide yield to additional initiator decreased dramatically beyond a relatively low threshold concentration. This observation is consistent with data reported by Ciardelli et al. for AIBN-initiated additions of functional thiols to diene-based elastomers.[12] On the basis of the simple mechanism presented in Scheme 1, one would expect to observe a half-order dependence of the sulfide formation rate on the concentration of initiator.[25] As a result, the sulfide yield should continue to increase with increasing initiator loading as long as both olefin and thiol are available. In an effort to define this initiator issue in greater detail, we have considered potential complications derived from the interaction of major reaction products with the initiator or propagating radical intermediates. Table 2 lists the olefin conversions recorded for a series of model compound and *a*-PP experiments wherein different amounts of sulfide or disulfide were included in the reaction mixture. Neither reaction product influenced sulfide yields, meaning that further work is required to characterize the yield plateau behavior illustrated in Figure 3.

Isotactic-PP Modifications. The principles demonstrated with the model compound and *a*-PP can be applied to commercial grades of high-molecular-weight isotactic polypropylene (*i*-PP). For this substrate, the extent of MPTMS functionalization was determined by coupling the modified polymer to precipitated silica and by moisture-curing the modified resin. Given that only silane-functionalized chains participate in these reactions, these assays fractionate the polymer into its grafted and unmodified components and provide an accurate and meaningful measure of the extent of PP modification.

The data presented in Table 3 confirm that radical chemistry can be used to functionalize *i*-PP while retaining the melt viscosity of the parent resin. The MPTMS addition products reacted extensively with precipitated silica, providing bound polymer contents of up to 35 wt %. However, the MPTMS loadings required to produce this degree of polymer functionalization were high when compared to a conventional VTMS grafting process, which provided relatively high bound polymer contents at low modifier loadings. The key difference between the two modification approaches is revealed by

Table 4. MPTMS Addition to Degraded *i*-PP[a]

[DCP] for degradation (μmol/g)[b]	degraded *i*-PP MFR[c] (g/10 min)	sulfide MFR[c] (g/10 min)	cured gel content (wt %)	bound polymer (wt %)
d	9	11	32	35
0.0	57	59	53	48
1.8	170	170	72	75
3.7	420	430	86	83

[a] [MPTMS] = 1.0 mmol/g; [L-101] = 3.4 μmol/g; T = 170 °C; 15 min. [b] Controlled *i*-PP degradation prior to MPTMS modifications; T = 180 °C; 15 min. [c] MFR measured at 190 °C using 2.16 kg load. [d] No degradation.

melt flow rate (MFR) and gel content analyses. Samples of *i*-PP-*g*-VTMS demonstrated grossly reduced melt viscosities and an inability to moisture-cure to the gel point, while the MPTMS-grafted products retained the MFR of the parent resin and could be cured to a significant extent.

It is obvious that the transformation of *i*-PP into a moisture-curable polymer by thiol−ene addition is affected by the vinylidene content of the resin. The catalyst technology used to prepare the polymer dictates the end-group functionality, thereby establishing an upper limit on the sulfide concentration that one can achieve through a thiol−ene addition approach.[7] In a final series of experiments, the radical-mediated degradation of *i*-PP prior to MPTMS addition was explored as a means of increasing the olefin content of the resin[26] and, by extension, the amount of thiol addition to the polymer. Heating *i*-PP with various amounts of DCP in the absence of thiol resulted in a substantial degree of polymer fragmentation, as revealed by increases in MFR (Table 4). Despite reducing the molecular weight of the resin, degradation increased the olefin content of the polymer substantially, thereby leading to a higher bound polymer contents in silica-coupling reactions and to a more extensive siloxane network in a moisture-curing process.

Discussion

The functionalization of PP with MPTMS would be a straightforward application of the thiol−ene addition reaction if not for the extraordinary conditions that are imposed by the substrate. For example, a commercial grade of *i*-PP with a M_n of 50 000 may contain a terminal unsaturation content of 20 μmol/g, which is far less than the concentrations employed for standard sulfide preparations. The high melting temperature of *i*-PP also imposes stress on the process since the reaction must be carried out in the melt state. Aside from unresolved issues regarding initiation, the mechanism illustrated in Scheme 1 adequately accounts for the consequences of these imposed conditions on a thiol−ene derivatization. Thermodynamic and kinetic analyses must, however, be limited to qualitative arguments, given a lack of thermochemical data and rate constants for the compounds and temperatures that are relevant to PP functionalization.

What distinguishes the thiol−ene approach from conventional monomer grafting methods is the reversibility of thiyl radical addition to olefin. This reversibility underlies well-established methods for the *E*,*Z*-rearrangement of internal olefins, wherein catalytic amounts of thiol are activated by standard radical initiators to isomerize large quantities of olefin at the expense of trace amounts of sulfide addition product.[27] The extent to which reversibility influences the dynamics of MPTMS additions to PP depends on the ratio k_f/k_{RSH}[RSH], which reflects the rate of thiyl radical elimination from the carbon-centered radical adduct (A•) relative to the rate at which thiol traps this adduct (Scheme 1). The small amount of quantitative data on this subject has been discussed by Chatgilialoglu et al. in the course of studying ambient temperature reactions of monounsaturated fatty acid esters.[28] A ratio of k_f/k_{RSH} = 15.0 M^{-1} was reported for thiyl radical elimination to *E*-isomers of this system, and a value of 2.2 M^{-1} was assigned to fragmentations leading to the corresponding *Z*-isomers. Walling and Helmreich have recorded values of k_f/k_{RSH} = 84.9 and 19.8 M^{-1} at 60 °C for the elimination of $CH_3S^•$ to generate the *E*- and *Z*-isomers of 2-butene, respectively.[29]

Both studies confirm that the rate of adduct radical fragmentation greatly exceeds that of hydrogen transfer when low thiol concentrations are employed. However, these values reflect the reactivity of adducts carrying β-substituents, which is not the case in the present system. McPhee et al. derived a very crude estimate of k_f/k_{RSH} = 0.034 M^{-1} for reactions of 1-octene and *tert*-butyl thiyl radicals at 25 °C.[30] This value suggests that fragmentation may have a minor effect on the addition of thiols to unsubstituted terminal olefins. However, given the expected differences between the activation energies for thiyl radical elimination vs that of hydrogen transfer, we propose that fragmentation is much more favorable at the high temperatures employed for PP modifications.

If this premise is valid, then the addition and elimination of thiyl radicals should maintain a pseudo-equilibrium condition throughout the grafting process. The position of this equilibrium is dictated by $K_1 = k_a/k_f$, whose dependence on temperature is defined by a negative enthalpy of reaction (Scheme 1).[30] Consequently, K_1 declines as the reaction temperature is increased, and the equilibrium is displaced away from the desired adduct toward thiyl radical + olefin. The net result of this displacement is a decline in sulfide production with temperature, as observed throughout our studies of the *a*-PP-*g*-MPTMS system.

The reversibility of thiyl radical addition to the unsaturation within PP also creates a pronounced sensitivity to thiol concentration. Mercaptans of low solubility in PP (such as MUA and MSA) have a limited potential to trap carbon-centered adduct radicals. Without efficient hydrogen donation, the rate of sulfide formation declines to such an extent that disulfide becomes the predominant reaction product. Conventional graft additions of maleic anhydride proceed quite well despite limited modifier solubility because alkyl radical attack on the monomer is irreversible, and the hydrogen donor in these systems is not the poorly soluble modifier, but the polymeric substrate.

It is interesting to contemplate a further potential consequence of the reversibility of thiyl radical attack on carbon−carbon double bonds. We note that the overall thiol−ene addition process could be reversible if the hydrogen atom transfer component of the propagation cycle shown in Scheme 1 is also reversible. This possibility has been alluded to by Walling, who depicted thiol addition in this manner without exploring the potential consequences of reversible hydrogen transfer reactions on the overall dynamics of the process.[31] Since thiol−ene additions to PP are high-temperature, exothermic processes conducted under dilute conditions,

these reactions are reasonable candidates for an equilibrium limitation. However, our studies have shown the sulfide addition product is stable with respect to radical-mediated fragmentation. Since the kinetics of sulfide cleavage are not competitive with those of sulfide formation, a mechanism wherein sulfide formation and fragmentation constitute a dynamic equilibrium is inapplicable to this process.

Conclusions

The addition of alkanethiols to the terminal unsaturation of polypropylene yields functional derivatives without affecting molecular weight. However, the reversibility of thiyl radical attack on olefin results in an inverse relationship between temperature and reaction yield and restricts the scope of this chemistry to soluble modifiers that trap intermediate adduct radicals efficiently. MPTMS is particularly well-suited to this process and yields moisture-curing products that bind to siliceous fillers.

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References and Notes

(1) Russell, K. E. *Prog. Polym. Sci.* **2002**, *27*, 1007−1038.
(2) Munteanu, D. In *Reactive Modifiers for Polymers*; Al-Malaika, S., Ed.; Blackie Academic and Professional: London, 1997; pp 196−265.
(3) Moad, G. *Prog. Polym. Sci.* **1999**, *24*, 81−142.
(4) Hu, G. H.; Flat, J. J.; Lambla, M. In *Reactive Modifiers for Polymers*; Al-Malaika, S., Ed.; Blackie Academic and Professional: London, 1997; pp 196−265.
(5) Nachtigall, S. M. B.; Stedile, F. C.; Felix, A. H. O.; Mauler, R. S. *J. Appl. Polym. Sci.* **1999**, *72*, 1313−1319.
(6) Huang, H.; Lu, H. H.; Liu, N. C. *J. Appl. Polym. Sci.* **2000**, *78*, 1233−1238.
(7) Mulhaupt, R.; Duschek, T.; Rieger, B. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 317−332.
(8) Boileau, S.; Mazeaud-Henri, B.; Blackborow, R. *Eur. Polym. J.* **2003**, *39*, 1395−1404. (b) Gorski, U.; Maenz, K.; Stadermann, D. *Angew. Makromol. Chem.* **1997**, *253*, 51−64.
(9) Kharasch, M. S.; Read, A. T.; Mayo, F. R. *Chem. Ind.* **1938**, 752. (b) Sivertz, C.; Andrews, W.; Elsdon, W.; Graham, K. *J. Polym. Sci.* **1956**, *19*, 587−588.
(10) Griesbaum, K. *Angew. Chem., Int. Ed.* **1970**, *9*, 273−287. (b) Walling, C. In *Free Radicals in Solution*; Wiley: New York, 1957. (c) Stacey, F. W.; Harris, J. F. *Org. React.* **1963**, *13*, 150−376. (d) Sosnovsky, G. In *Free Radical Reactions in Preparative Organic Chemistry*; MacMillan: New York, 1964; pp 62−119.
(11) Back, R.; Trick, G.; McDonald, C.; Sivertz, C. *Can. J. Chem.* **1954**, *32*, 1078−1091.
(12) Ciardelli, F.; Aglietto, M.; Passaglia, E.; Picchioni, F. *Polym. Adv. Technol.* **2000**, *11*, 371−376.
(13) Zweifel, G.; Brown, H. C. *Org. React.* **1963**, *13*, 33.
(14) Walling, C.; Rabinowitz, R. *J. Am. Chem. Soc.* **1959**, *81*, 1137−1143.
(15) Bickel, A. F.; Kooijman, E. C. *Nature (London)* **1952**, *170*, 211−212. (b) Wang, C. H.; Cohen, S. G. *J. Am. Chem. Soc.* **1957**, *79*, 1924−1929. (c) van Zwet, H.; Kooyman, E. C. *Recl. Trav. Chim.* **1968**, *87*, 45−48. (d) Pryor, W. A.; Gojon, G.; Stanley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 945−946. (e) Pryor, W. A.; Gojon, G.; Church, D. F. *J. Org. Chem.* **1978**, *43*, 793−800.
(16) Lunazzi, L.; Placucci, G.; Grossi, L. *J. Chem. Soc., Chem. Commun.* **1979**, *12*, 533−534. (b) Schoeneich, C.; Asmus, K.-D.; Dillinger, U.; Bruchhausen, F. *Biochem. Biophys. Res. Commun.* **1989**, *161*, 113−120.
(17) Zhao, R.; Lind, J.; Merenyi, G.; Eriksen, T. E. *J. Am. Chem. Soc.* **1994**, *116*, 12010−12015. (b) Robins, M. J.; Ewing, G. J. *J. Am. Chem. Soc.* **1999**, *121*, 5823−5824. (c) Nauser, T.; Schoneich, C. *J. Am. Chem. Soc.* **2003**, *125*, 2042−2043.
(18) Ohno, A.; Kito, N.; Ohnishi, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 463−467.
(19) Kampmeier, J. A.; Geer, R. P.; Meskin, A. J.; D'Silva, R. M. *J. Am. Chem. Soc.* **1966**, *88*, 1257−1265.
(20) Huyser, E. S.; Kellogg, R. M. *J. Org. Chem.* **1966**, *31*, 3366−3369.
(21) Parent, J. S.; Tripp, M.; Dupont, J. *Polym. Eng. Sci.* **2003**, *43*, 234−242.
(22) Jones, S. O.; Reid, E. E. *J. Am. Chem. Soc.* **1938**, *60*, 2452−2455. (b) Overberger, C. G.; Mulvaney, J. E.; Marshall, B. *J. Org. Chem.* **1956**, *21*, 1311−1312.
(23) Sensfuss, S.; Friedrich, M.; Klemm, E. *Makromol. Chem.* **1991**, *192*, 2895−2900.
(24) Pryor, W. A.; Coco, J. H.; Daly, W. H.; Houk, K. N. *J. Am. Chem. Soc.* **1974**, *96*, 5591−5593. (b) Pryor, W. A.; Lasswell, L. D. In *Advances in Free-Radical Chemistry*; Williams, G. H., Ed.; Academic Press: New York, Vol. 5, pp 27−99.
(25) This assumes a steady-state concentration of thiyl radicals and an equilibrium distribution between thiyl- and carbon-centered adduct radical species.
(26) Thompson, M. R.; Tzoganakis, C.; Rempel, G. L. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 3083−3086.
(27) Golub, M. A. *J. Polym. Sci.* **1957**, *25*, 373−377. (b) Huyser, E. S.; Kellogg, R. M. *J. Org. Chem.* **1965**, *30*, 2867−2868.
(28) Chatgilialoglu, C.; Altieri, A.; Fischer, H. *J. Am. Chem. Soc.* **2002**, *124*, 12816−12823.
(29) Walling, C.; Helmreich, W. *J. Am. Chem. Soc.* **1959**, *81*, 1144−1148.
(30) McPhee, D. J.; Campredon, M.; Lesage, M.; Griller, D. *J. Am. Chem. Soc.* **1989**, *111*, 7563−7567.
(31) Walling, C. In *Fifty Years of Free Radicals/Cheves Walling*; American Chemical Society: Washington, DC, 1995; p 57.

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