

Composition distribution in poly(ethylene-*graft*-vinyltrimethoxysilane)

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Abstract

Insight into the composition distribution created by free-radical mediated addition of vinyltrimethoxysilane (VTMS) to high-density polyethylene (HDPE) has been gained using physical methods of polymer characterization as well as detailed structural studies of a model hydrocarbon system. Analysis of poly(ethylene-*graft*-vinyltrimethoxysilane), or HDPE-*g*-VTMS, by moisture curing and by differential scanning calorimetry–successive self-nucleation and annealing (DSC–SSA) indicated that the distribution of pendant alkoxy silane grafts amongst polymer chains was non-uniform. Fractionation and characterization of a graft-modified model compound, tetradecane-*g*-VTMS, showed that composition distributions were influenced strongly by intramolecular hydrogen atom abstraction, yielding multiple grafts per chain in the form of single pendant units as opposed to oligomeric grafts. Chain transfer to the methoxy substituent of bound VTMS was found to contribute significantly to the product distribution.

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Keywords: Polymer synthesis; Vinylsilane; Melt grafting

1. Introduction

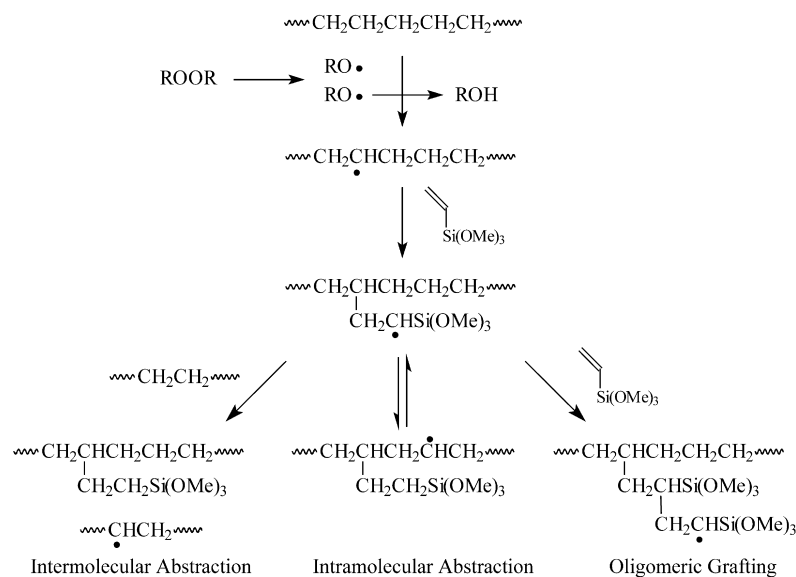
The free-radical mediated addition of functional monomers to polyolefins is a widely practiced method of generating value-added polymers [1]. A leading commercial example is the graft modification of high-density polyethylene (HDPE) with vinyltrimethoxysilane (VTMS) to yield moisture-curable resins that bond to siliceous fillers [2]. Although the distribution of silane grafts amongst polymer chains is expected to affect the physical and chemical properties of a modified polymer, little is known about the structure of HDPE-*g*-VTMS resins. Given the close relationship between the mechanism of VTMS addition and the placement of silane grafts, knowledge of HDPE-*g*-VTMS composition distribution may improve our understanding of melt grafting chemistry as well as the technological properties of graft-modified polymers.

The challenges associated with the analysis of polymers containing a low concentration of functional groups have led researchers to focus on model compound systems as a means of studying grafting chemistry [1]. Of particular interest is the work of Forsyth et al., in which the radical-

mediated addition of VTMS to dodecane has been examined as a model for HDPE modification [3]. Graft-modified dodecane was found to contain an average of 2.4 silane grafts per molecule, and as many as five grafts per molecule were detected by mass spectrometry (MS). Their data were consistent with a graft propagation cycle controlled by extensive intramolecular hydrogen atom abstraction, as opposed to intermolecular abstraction or oligomeric grafting (Scheme 1).

Radical-mediated grafting operates through a chain reaction sequence that produces multiple silane grafts from a single initiation event. Therefore, although hydrogen abstraction by oxygen-centered radicals initiates the grafting process, it does not exert the greatest influence on the composition distribution of the product. Rather, it is the hydrogen atom abstraction tendencies of the vinylsilane-derived radicals that are expected to control the structure of graft-modified polymers (Scheme 1). Intramolecular hydrogen atom abstraction leads to repeated functionalization of a single chain, while intermolecular abstraction serves to modify multiple chains. Hydrogen atom abstraction from the methoxy groups of bound VTMS (referred to as degradative chain transfer) may also contribute to the structure of silane-modified resins (Scheme 2) by adding further vinylsilane groups to a functionalized chain [4].

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Scheme 1.

At the present time there exists no single technique to define the composition distribution of graft-modified polymers. The aim of this work was to gain insight into the structure of HDPE-*g*-VTMS by integrating physical methods of polymer characterization with structural analyses of a model compound system. Measurements of the yield of HDPE-*g*-VTMS moisture cures have been interpreted along with differential scanning calorimetry–successive self-nucleation and annealing (DSC–SSA) data to probe the distribution of silane grafts between, and within, polymer chains. Conclusions drawn from a physical analysis of the polymeric system have been reinforced by structural analysis of tetradecane-*g*-VTMS. Fractionation of tetradecane-*g*-VTMS according to silane graft content has allowed the number distribution of grafts amongst model hydrocarbon chains to be measured directly.

2. Experimental section

2.1. Materials

High-density polyethylene (HDPE, Sclair 2907, MFI = 14.5 g/10 min at 190 °C, 5 kg load) was used as supplied. Phenyllithium (1.8 M in 70:30 cyclohexane:ether) and dicumyl peroxide (DCP, 98%) were used as received from Sigma-Aldrich and stored under refrigeration. Tetradecane (99%+) and vinyltrimethoxysilane (97%), and octyltrimethoxysilane (96%) were used as received from Sigma-Aldrich.

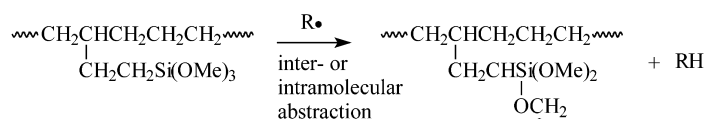
2.2. Preparation of HDPE-*g*-VTMS

Dicumyl peroxide (DCP, 0.1 g, 0.37 mmol) was dissolved in the desired quantity of VTMS and added to HDPE (200 g) prior to tumble-mixing for 30 min. Grafting was conducted in a Haake Rheomix single screw extruder (heating zone set points of 150, 180 and 180 °C, 10 min residence time) equipped with a strand die. The extrudate was cooled with an air stream and stored within a desiccator. Soxhlet extraction of select samples with xylene ensured that no gel formation was incurred during the graft modification.

HDPE-*g*-VTMS samples (5 g) for graft-content analysis were purified by dissolution in hot xylene (120 ml) and precipitating with acetone (400 ml). The isolated polymer was dried in vacuo (80 °C, 0.04 bar), the graft content of thin films was determined by an infrared spectroscopy method [5] based on the 750–850 cm^{−1} absorbance of the silane relative to the 1988–2098 cm^{−1} internal standard region originating from polyethylene [6]. Instrument calibrations were developed using prepared mixtures of HDPE and octyltrimethoxysilane. Graft content data are reported as weight percent of VTMS in the modified resin, and represent an average of three independent measurements on each sample.

2.3. Stabilization of HDPE-*g*-VTMS

The conversion of trimethoxysilane groups to triphenylsilane moieties was done to prevent moisture-induced



Scheme 2.

curing of graft-modified resins during thermal analysis. HDPE-g-VTMS (2 g) was added to dry xylene (100 ml) and the mixture was heated to reflux under nitrogen. Upon complete dissolution of the polymer, an excess of PhLi (7.2 mmol in 70:30 cyclohexane:ether) was added drop-wise and the solution was refluxed for 24 h. The mixture was cooled and excess phenyllithium was quenched with a saturated aqueous solution of NH_4Cl . The polymer was recovered by precipitation in methanol (300 ml), rinsed with acetone, vacuum filtered, and dried in vacuo (80 °C, 0.04 bar). Soxhlet extraction of select product samples with xylene verified that no crosslinking resulted from the arylation process.

2.4. Preparation of tetradecane-g-VTMS

Tetradecane (35 ml, 135 mmol), the desired quantity of VTMS (1.8, 5.4 or 9.1 mmol) and dicumyl peroxide (0.045 g, 0.17 mmol) were sealed in a glass reaction tube and agitated within an air bath for 45 min at 170 °C. Volatile components were removed by Kugelrohr distillation (100 °C, 0.3 mbar) to yield clear yellow oil. The overall silane graft content of the isolated tetradecane-g-VTMS was determined from ^1H NMR spectra by integrating the methoxy resonance (3.57 ppm) relative to the aliphatic region (0.40–1.50 ppm) [3].

2.5. Stabilization and fractionation of tetradecane-g-VTMS

Tetradecane-g-VTMS (0.3 g) was mixed with a 70:30 mixture of cyclohexane-ether (10 ml) prior to establishing a nitrogen atmosphere. Excess PhLi (4 equivalents relative to silane grafts; in 70:30 cyclohexane:ether) was added to the solution and the mixture was stirred at room temperature for 24 h prior to the addition of a saturated aqueous solution of NH_4Cl (5 ml). Hexanes were added to the mixture before isolating the organic phase, which was subsequently dried with Na_2SO_4 and concentrated in vacuo to yield clear yellow oil, tetradecane-g-vinyltriphenylsilane (tetradecane-g-VTPS).

Tetradecane-g-VTPS was fractionated on the basis of silane graft content by semi-preparative, normal-phase HPLC using a Waters Model 400 instrument equipped with UV–Vis and refractive index detectors (10% ethyl acetate, 90% hexanes eluent, Supelcosil PLC-Si column). The fractionation was insensitive to structural isomers, allowing materials of a given graft content to be isolated. The amount of each product collected from repeated 200 μl injections of tetradecane-g-VTPS was determined gravimetrically. Graft content was measured by integration of the aromatic region (7.0–7.8 ppm) relative to the aliphatic region (0.4–1.8 ppm) of ^1H NMR spectra acquired in acetone- d_6 .

2.6. Moisture-curing of HDPE-g-VTMS

HDPE-g-VTMS (2 g) was dissolved in water-saturated xylene (100 ml) within a mechanically stirred flask. Dibutyltin dilaurate (12 μl , 0.02 mmol) was added and the mixture was refluxed for 4 h. The polymer was precipitated from solution with acetone (300 ml) and dried in vacuo (80 °C, 0.04 bar). Gel content was determined by weighing dry polymer (2 g) into a Soxhlet thimble (Whatman, single thickness cellulose) and placing the assembly in a standard Soxhlet extraction apparatus. Xylene (75 ml) was charged to the round bottom, and the system heated to reflux for 18 h. The thimble was then dried under vacuum to a constant weight, and the results reported as weight percent of insoluble polymer. Note that prolonged extraction produced no change in the gel content measurements for select samples, and HDPE-g-VTMS samples that had not been moisture-cured contained no gel.

2.7. Differential scanning calorimetry

DSC analysis was conducted under a dry nitrogen atmosphere using heating/cooling rates of 5 °C/min. To erase any thermal history, samples were held at 170 °C for 5 min and cooled to 30 °C. A subsequent reheating of the sample to 170 °C was recorded for standard DSC characterizations. The successive self-nucleation and annealing (DSC–SSA) protocol is illustrated in Fig. 1. The reported data are the result of heating the annealed samples to 170 °C at 5 °C/min.

2.8. Instrumentation

DSC analysis was conducted with a Seiko DSC 220u instrument. FT-IR spectra were acquired using a Nicolet Avatar 360 FTIR ESP, while NMR spectra were recorded with a Bruker AM-400 spectrometer in CDCl_3 or acetone- d_6 , with chemical shifts referenced to tetramethylsilane. Low-resolution mass spectra were recorded with a Fisons VG Quattro triple-quadrupole instrument with chemical ionization (NH_3).

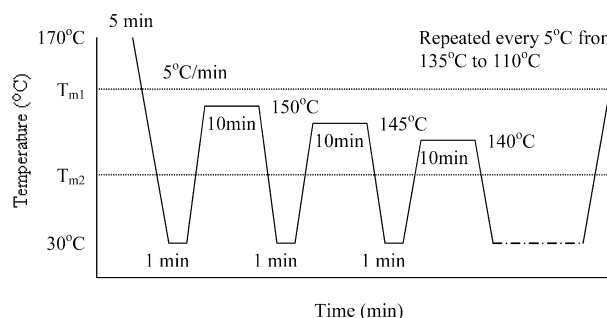


Fig. 1. SSA protocol for DSC analysis.

3. Results and discussion

3.1. HDPE-g-VTMS composition distribution

Single-screw extrusion of HDPE/VTMS/DCP masterbatches containing different silane loadings was used to prepare five HDPE-g-VTMS samples with graft contents ranging from 0.6 to 1.9 wt%. At the fixed dicumyl peroxide concentration of 0.05 wt%, the graft yield increased linearly with the amount of VTMS in the masterbatch (Fig. 2). The peroxide graft yield (defined in this work as the number of silane grafts per cumyloxy radical generated by DCP homolysis) increased from a low of 16.4 in the 1.0 wt% VTMS experiment to a high of 49.2 for the 5.0 wt% VTMS trial. These are conservative estimates, given the frequency of cumyloxy radical fragmentation through β -scission to generate methyl radicals of relatively poor initiation efficiency [7]. While the aforementioned peroxide graft yields are likely to be much higher than the reported values, they show that each initiation event yielded multiple silane grafts. As a result, the hydrogen atom abstraction reactions of silane-derived radical intermediates (Scheme 1) are expected to exert considerable influence on the composition distribution of HDPE-g-VTMS.

As a first step towards characterizing this distribution, the HDPE-g-VTMS samples were moisture-cured and subjected to gel content analysis (Fig. 3). Of particular interest is the asymptotic approach of gel content towards a maximum of 80 wt%. This result indicates that neither hydrogen atom abstraction by cumyloxy radical initiation, nor intermolecular chain transfer by alkyl macroradicals, was capable of generating grafting activity in 20 wt% of the polymer. Furthermore, graft contents beyond the 1.0 wt% level had little influence on the mass of functionalized chains. It is reasonable to conclude that if intermolecular hydrogen abstraction was a significant reaction pathway, the gel content would approach the 100 wt% level. That the gel content approached a plateau of 80% therefore indicates that the intermolecular pathway was not controlling. Rather,

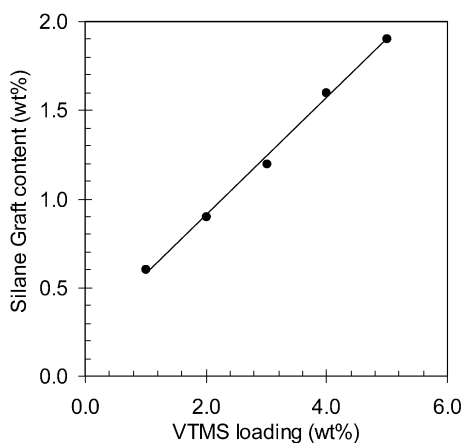


Fig. 2. Effect of vinylsilane loading on HDPE-g-VTMS graft content (0.05 wt% DCP, 180 °C).

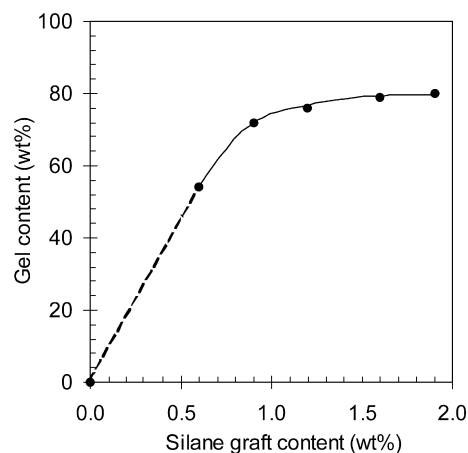


Fig. 3. Gel content as a function of HDPE-g-VTMS graft content.

graft modification must propagate predominantly through intramolecular hydrogen-atom abstraction, oligomeric graft formation and/or degradative chain transfer (Schemes 1 and 2), leading to a non-uniform composition distribution.

3.2. DSC analysis of HDPE-g-VTMS

The relationship between silane graft content and attainable HDPE-g-VTMS gel content reflects, in a qualitative manner, the intermolecular distribution of grafts amongst complete polymer chains. That is, the experiment fractionates the resin crudely into its grafted and unmodified components. Of equal interest is the relationship between silane graft content and short chain branching (SCB) distribution. While it is clear that the introduction of pendant silane groups generates a SCB distribution within HDPE-g-VTMS, the nature of this distribution is unknown. Whether grafts are oligomeric, located in close proximity, or distributed uniformly within a polymer chain relates to the intramolecular composition distribution of HDPE-g-VTMS. Given the reported utility of DSC methods for characterizing SCB in linear low-density polyethylene (LLDPE), we have adopted these techniques for the analysis of HDPE-g-VTMS.

Successive self-nucleation and annealing (SSA) is designed to fractionate semi-crystalline polymers according to lamellar thicknesses of polymer crystals and/or by methylene sequence length [8,9]. By minimizing the extent of cocrystallization between dissimilar chain segments, the SSA process enhances the sensitivity of differential scanning calorimetry (DSC) to the effects of polymer microstructure. This benefit has been exploited for the study of short-chain branching distributions in LLDPE [8], the nature of diethyl succinate groups within graft-modified LLDPE [10], and the placement of succinic anhydride grafts in functionalized polyethylene [9]. While DSC–SSA has little effect on the melting behaviour of HDPE [11], this analysis has provided some knowledge of relationship

between graft content and the SCB distribution within HDPE-*g*-VTMS.

Three samples of HDPE-*g*-VTMS were prepared by reactive extrusion, analyzed for silane graft content, and stabilized by reaction with phenyllithium. Note that comparative DSC tests between HDPE-*g*-VTMS and its stabilized derivative revealed no significant differences. The data listed in Table 1 show that the degree of crystallinity declined with increasing silane content up to the 1.8 wt% level, beyond which no measurable effect was observed. As expected, DSC–SSA produced higher degrees of crystallinity than observed by standard DSC analysis due to the reduction of cocrystallization effects [12].

Evidence of the enhanced resolution provided by SSA is provided in Fig. 4 for sample PE-0.9G. Whereas standard DSC analysis yielded a broad melting peak with a maximum at 134 °C, DSC–SSA resolved the endotherm into a series of sharper melting peaks. After SSA treatment, the majority of the polymer melted at a temperature 2 °C greater than the maximum recorded under standard analysis, while significant low-temperature peaks were observed at the annealing points (115, 120, 125 °C; Fig. 1). Based upon similar conclusions derived from SCB analyses of linear and grafted ethylene copolymers [8–10], we suggest that the methylene sequences that melted at high temperature were relatively long, and were largely unaffected by the presence of proximal grafts. Those chain segments melting at the low annealing temperatures were influenced by the chain defects introduced by pendant silane grafts, which served to reduce the methylene sequence length/lamellar thickness.

Comparisons between unmodified HDPE and HDPE-*g*-VTMS must be made with caution, given that peroxide mediated processes can introduce changes to polyethylene structure through radical combination [13]. However, the peroxide graft yields recorded for the modification process ranged from 16.4 to 49.2 silane grafts per cumyloxy radical. This implies that structural changes imposed by graft modification greatly outnumbered those derived from macroradical termination reactions. Variations amongst DSC–SSA profiles originated mainly from silane addition. These changes are illustrated in Fig. 5, which demonstrates the influence of graft content on DSC–SSA melting endotherms.

Due to the low SCB content of HDPE, little segregation

Table 1
DSC analysis of HDPE-*g*-VTMS

Sample code	Graft content (wt %)	Crystallinity (%)	Crystallinity SSA (%)
HDPE	0.0	56	62
PE-0.9G	0.9	54	59
PE-1.8G	1.8	46	50
PE-2.7G	2.7	47	51

0.05 wt% DCP initiator, $T_1 = 150$ °C, $T_2 = T_3 = 180$ °C; stabilized with PhLi.

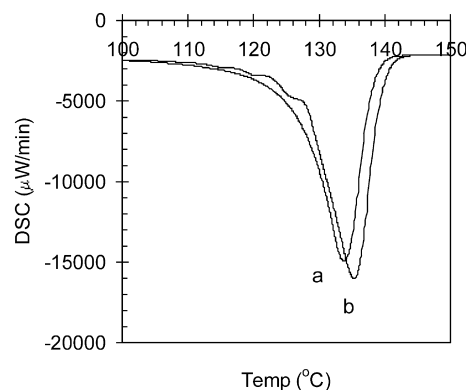


Fig. 4. Sample PE-0.9 (a) DSC and (b) DSC–SSA endotherms following PhLi stabilization.

was achieved in the DSC–SSA analysis of the unmodified polymer. Significant differences between grafted and unmodified resins were observed but, more importantly, the incremental effect of additional grafts declined continuously. We noted that an increase of graft content from 1.8 to 2.7 wt% had little effect on the DSC–SSA endotherm, and the relative area of the low-temperature peaks did not rise appreciably with the degree of polymer functionalization. This result suggests that additional grafts were located in close proximity and, therefore, had a marginal impact on methylene sequence lengths. While this DSC–SSA analysis is not conclusive proof of the tendency of graft modifications to proceed through extensive intramolecular abstraction or oligomerization, the results are consistent with the conclusions drawn from the gel content experiments. More direct information regarding the graft propagation sequence is accessible from model hydrocarbon studies, as detailed below.

3.3. Nature of tetradecane-*g*-VTMS grafts

The structure of silane grafts and their distribution amongst chains was studied using a model compound for which the isolation and characterization of reaction products was technically feasible. Model compounds are used widely to assist with the characterization of graft-modified

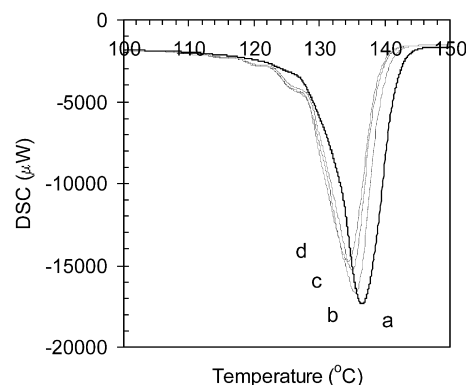


Fig. 5. DSC–SSA endotherms for (a) HDPE; (b) PE-0.9G; (c) PE-1.8G; and (d) PE-2.7G following PhLi stabilization.

polymers [14] and the study of radical grafting dynamics [15–17]. In the present case, the graft modification of tetradecane was intended to provide insight into two key features of HDPE modification. In the first place, structural characterization tetradecane-*g*-VTMS provided knowledge of how intramolecular hydrogen abstraction and oligomerization may generate multiple silane additions to a single molecule. Secondly, the relative rates of intramolecular and intermolecular abstraction by a silane-derived radical could be more easily assessed, given that the probability of repeated intermolecular hydrogen abstraction from tetradecane is much lower than that encountered in a macromolecule.

As was done for the HDPE system, tetradecane-*g*-VTMS samples of different silane content were prepared to investigate the relationship between graft content and composition distribution. Although direct, quantitative comparisons between polymer and model grafting yields are not the objective of this study, model compound experiments were conducted using conditions that are relevant to HDPE grafting operations. For example, a temperature of 170 °C was used to approximate the temperature profile used in the HDPE extrusion work ($T_1 = 150$ °C, $T_2 = T_3 = 180$ °C), and similar reagent concentrations were used in both studies.

Aside from evidence of degradative chain transfer (discussed later), the structural elements of isolated tetradecane-*g*-VTMS were consistent with those reported by Forsyth et al. [3]. ^1H NMR spectrum integration of the methoxy proton resonance (3.57 δ) relative to the remaining hydrocarbon protons (0.40–1.50 δ) was used to estimate the average silane graft content of graft-modified material. For tetradecane-*g*-VTMS sample MC-4.2G, this analysis revealed an average of 4.2 silane grafts per molecule (Fig. 6). Mass spectral data for this material (not shown) revealed tetradecane-*g*-VTMS compounds containing up to five grafts per chain. Fragmentation of higher molecular weight materials during MS analysis precluded the characterization of more extensively grafted products.

The data within Table 2 summarize the key features of the tetradecane-*g*-VTMS samples prepared in this study. Graft content estimates derived from ^1H NMR analysis provide the average molecular weights needed to convert the mass of grafted products into moles of tetradecane-*g*-VTMS. It is interesting to note the similarities between the model and polymer systems. Just as higher silane graft

contents failed to increase the mass of functionalized polyethylene (Fig. 3), increased extents of tetradecane modification resulted in a marginal increase in the yield of modified chains. An important difference between the model and polymeric systems lies in the probability of multiple grafting by intermolecular abstraction. There is little doubt that multiple grafts to tetradecane did not originate from repeated intermolecular hydrogen abstractions, because the tetradecane-*g*-VTMS concentration was insignificant relative to that of unmodified hydrocarbon.

It is also unlikely that multiple monomer additions to tetradecane resulted from oligomeric graft formation, given the low yields and degrees of polymerization reported for several vinylsilane homopolymerizations [18,19]. Of particular interest is the observation of Seyferth et al., that only VTMS oligomers ($M_n = 607$ g/mol) could be generated using a solvent-free, γ -radiation initiated process [4]. Our efforts to polymerize a 5 wt% solution of VTMS in trichlorobenzene (170 °C, 0.1 wt% DCP initiator) produced similar results. A low-molecular weight product was generated in 7% yield, which when compared to the 55% conversion recorded in the preparation of MC-4.2G (Table 1), confirms the limited potential for VTMS oligomerization.

Forsyth et al., drew the same conclusion from a ^1H NMR study of dodecane-*g*-VTMS [3]. Their reasoning was based on integrations of the 0.40–0.65 δ region ($-\text{CH}_2-\text{Si}$) relative to the resonance at 3.57 δ (CH_3-O). Single grafts [$-\text{CH}_2\text{Si}(\text{OCH}_3)_3$] are expected to yield a 2:9 ratio of these regions. ^1H NMR analysis of samples MC-1.5G, MC-2.6G and MC-4.2G revealed ratios of 2:9.7, 2:9.9 and 2:10, respectively, thereby supporting the original finding that most VTMS grafts existed as single units as opposed to the oligomeric grafts illustrated in Scheme 1.

Further insight into the nature of VTMS grafts has been gained by ^{13}C NMR analysis of samples MC-1.5G and MC-4.2 G (Fig. 7). Given that chemical shift assignments have already been developed for dodecane-*g*-VTMS [3], only the loss of methylene and methine resonances (14.0–41.0 δ) with increasing graft content is of present interest. Repeated VTMS additions to propagating oligomeric grafts should have little effect on the aliphatic region of the spectrum. Therefore, the simplified spectrum recorded for sample MC-4.2G is inconsistent with an oligomerization pathway. However, this is the expected result for the repeated addition of single grafts to tetradecane. This mechanism of VTMS incorporation would generate a very large number of structural isomers and stereoisomers whose detection by ^{13}C NMR would be made difficult by the low concentration of each product within a tetradecane-*g*-VTMS sample.

Although little VTMS was grafted through a standard oligomerization mechanism, degradative chain transfer (Scheme 2) contributed significantly to the composition distribution of tetradecane-*g*-VTMS. The multiplet at 3.72 δ in the ^1H NMR spectrum (Fig. 6) was found in a two-dimensional $^1\text{H}-^{13}\text{C}$ chemical shift correlation spectrum

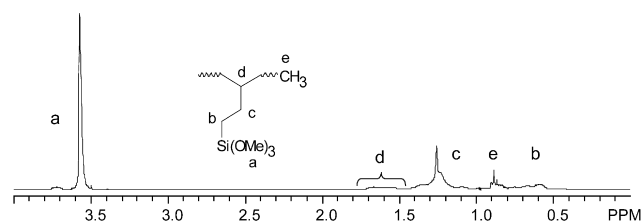


Fig. 6. ^1H NMR spectrum (CDCl_3) of tetradecane-*g*-VTMS sample MC-4.2G.

Table 2
Tetradecane-*g*-VTMS data

Sample code	VTMS loading (wt %)	Tetradecane- <i>g</i> -VTMS Yield (g)	Average grafts/chain	Tetradecane- <i>g</i> -VTMS Yield (mmoles)	VTMS conversion (%)
MC-1.5G	1.0	0.33	1.5	0.77	65
MC-2.6G	3.0	0.65	2.6	1.10	53
MC-4.2G	5.0	0.93	4.2	1.13	53

0.1 wt% DCP initiator, 170 °C.

(not shown) to correlate with the ^{13}C NMR resonance at 65.6 δ (Fig. 7). This is consistent with the $-\text{O}-\text{CH}_2-\text{R}$ group noted by Seyferth et al. [4]. Integration of the $-\text{CH}_2\text{O}-$ multiplet (3.72 δ) within the ^1H NMR spectrum relative to the $\text{CH}_3\text{O}-$ resonance (3.57 δ) yielded a ratio of 0.37:3 for sample MC-4.2G. This indicates that approximately 1 in every 5 VTMS additions were made to the radicals formed through degradative chain transfer. Similarly, 1 in every 8 additions in sample MC-1.5G occurred through this mechanism, and one in every seven silane grafts within sample MC-2.6G were produced by this means.

Physical analyses of HDPE-*g*-VTMS and structural characterizations of the model system have provided compelling evidence of the controlling influence of intramolecular hydrogen atom abstraction on composition distribution. However, the significance of the 1,5-intramolecular abstraction illustrated in Scheme 1 is difficult to establish due to the structural complexity of tetradecane-*g*-VTMS [20,21]. The favorability of the 1,5-intramolecular hydrogen atom abstraction over its intermolecular counterpart is well established for auto-oxidations of branched hydrocarbons [22,23]. In cases where different groups are accessible by 1,5-abstraction, tertiary sites have been shown to be favoured over secondary and primary [24]. This suggests that VTMS modifications may engage in ‘back-

biting’ to the tertiary sites established in a previous graft addition sequence.

3.4. Tetradecane-*g*-VTMS composition distribution

Given that tetradecane-*g*-VTMS is amenable to chromatographic separation according to graft content, the composition distribution of the model system is accessible. It was therefore characterized in order to further our understanding of the hydrogen atom abstraction tendencies of VTMS-derived radicals (Schemes 1 and 2). Prior to fractionation, the tetradecane-*g*-VTMS samples MC-1.5G, MC-2.6G and MC-4.2G were modified with phenyllithium to prevent moisture-induced coupling and potential reactions with the high-pressure liquid chromatography (HPLC) column packing. A significant consequence of this reaction is the cleavage of those grafts formed through degradative chain transfer. That is, VTMS incorporated by addition to the $-\text{OCH}_2$ radicals formed by degradative chain transfer is inevitably cleaved from the tetradecane backbone by the arylation reaction. Although it would be desirable to study the contributions of degradative chain transfer in the model system, the need to stabilize tetradecane-*g*-VTMS before fractionation precluded this possibility.

Normal-phase HPLC was used to fractionate stabilized tetradecane-*g*-VTMS samples according to triphenylethyl-

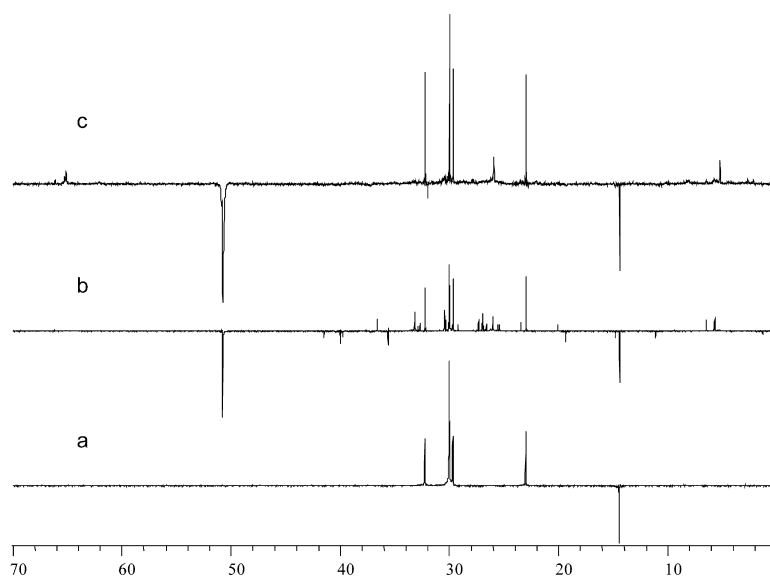


Fig. 7. J-MOD ^{13}C NMR spectra (CDCl_3) of (a) tetradecane; (b) MC-1.5G and (c) MC-4.2G.

silane graft content. Presented in Fig. 8 is the differential refractive index (DRI) instrument response for the separation of sample MC-2.6G. Note that a DRI instrument responds to analyte mass as opposed to its molar concentration [25]. That each fraction consisted of tetradecane-*g*-VTMS of a single graft content was confirmed by MS analysis (Fig. 8) and integrations of ^1H NMR spectra (not shown).

Knowledge of the mass of each fraction and its molecular weight was used to calculate the number distribution of grafts amongst tetradecane chains (Fig. 9). Unfortunately, compounds containing greater than six grafts per chain could not be resolved by HPLC, nor could they be characterized by MS. For sample MC-4.2G, the cleavage of grafts originating from degradative chain transfer, coupled with our inability to quantify compounds of very high graft content, resulted in approximately half of the material being unrepresented. In spite of these limitations, the data present a clear picture of the low-graft content range of the composition distribution that is relevant to commercial HDPE-*g*-VTMS materials.

A histogram such as that recorded for sample MC-1.5G can be generated by a chain sequence in which the probability of VTMS addition to a propagating alkyl radical

is nearly independent of graft content. According to this model, the probability of converting a mono-graft material to di-graft would be equivalent to that of converting di-graft to tri-graft, and so on. This probability is expected to depend upon the rate of VTMS addition to an alkyl macroradical relative to the rates of radical termination and intermolecular chain transfer. These reactions rates are, in turn, dependent upon the instantaneous radical and monomer concentrations in a manner that is presently not understood.

The effect of increasing VTMS concentrations on the graft-modification process is reflected in the composition distributions of samples MC-2.6G and MC-4.2G. Considering that higher VTMS loadings did not increase the molar yield of tetradecane-*g*-VTMS, the observed shift of the composition distribution towards higher graft content is to be expected. A less obvious feature of the recorded distributions is the evidence of different silane addition rates between unmodified tetradecane and tetradecane-*g*-VTMS. Mono-grafted material is generated through a bimolecular initiation event, while successive monomer additions are supported by a supposedly more rapid intramolecular abstraction process. The rate of tetradecane initiation is, therefore, likely to be less than the rate of continued monomer additions. This is reflected in samples

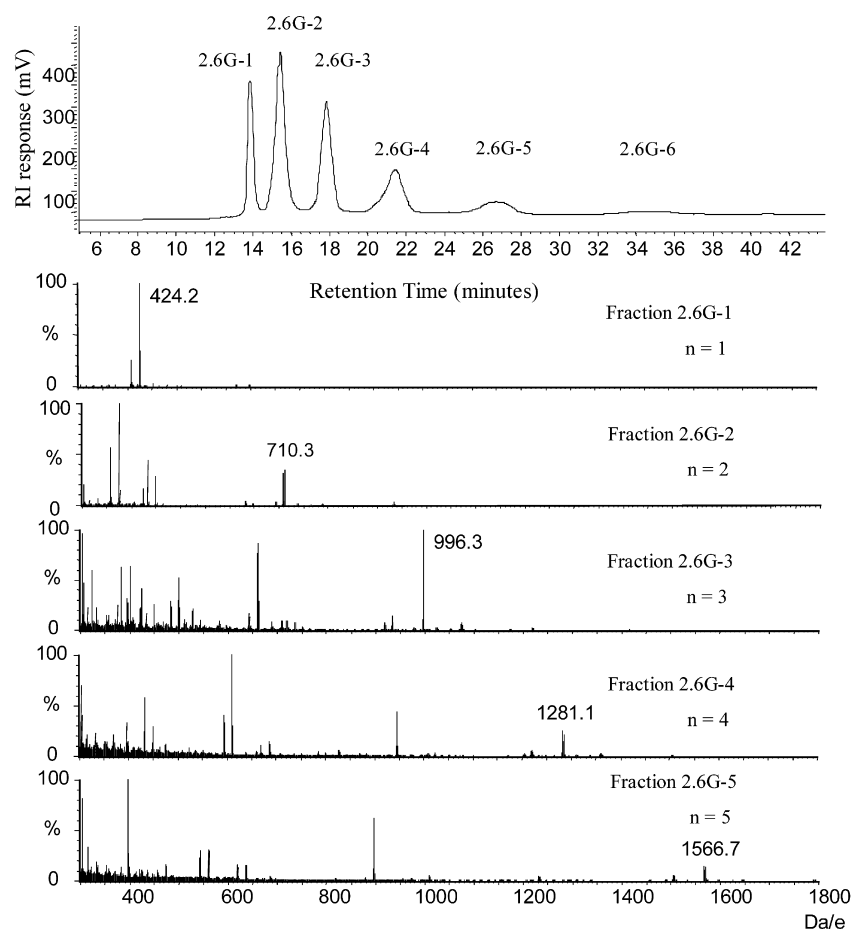


Fig. 8. DRI response for the HPLC fractionation of PhLi-stabilized sample MC-2.6G, and MS spectra for isolated fractions (n = number of silane grafts; Da/e values represent $n = 1-5$ less C_6H_5 , plus ammonia).

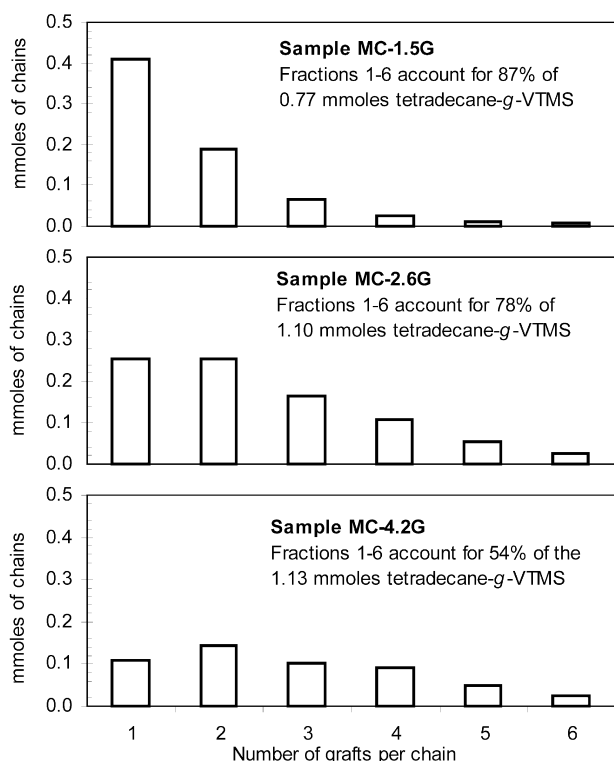


Fig. 9. Composition distribution of grafts for samples MC-1.5G, MC-2.6G and MC-4.2G following PhLi stabilization.

MC-2.6G and MC-4.2G, in which the proportion of di-graft material was greater than that of mono-graft material.

4. Conclusions

Physical characterizations of modified polyethylene and structural analyses of an appropriate model compound indicate that the radical-mediated addition of VTMS to HDPE yields multiple grafts per chain in the form of single, pendant units as well as units derived from degradative chain transfer. The use of elevated VTMS concentrations in the grafting process increases the extent of polymer functionalization without affecting the number of modified chains, due to the predominance of intramolecular chain transfer in the graft propagation mechanism.

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