Field Desorption Mass Spectrometry Studies of the Samarium-Catalyzed Polymerization of Ethylene under Hydrogen[1]

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ABSTRACT: The utility of field desorption mass spectrometry (FD-MS) in evaluating organolanthanide-based polymerizations of ethylene is described. The ethylene polymerization reactivity of $(C_5Me_5)_2Sm$, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, $(C_5Me_5)_2Sm(THF)_2$, and related complexes was studied under hydrogen, and oligomers were analyzed which have molecular weights by FD-MS in the 300–1000 Da range. FD-MS was used with this system to study the effects of solvent, temperature, and catalyst precursor on molecular weight, termination steps, and end group identity. The FD-MS data showed that neither β-hydrogen elimination nor solvent metalation was competitive with hydrogenolysis as a termination step under these conditions. Reactions under D_2 led to oligomers which were identified by FD-MS and NMR spectroscopy to cleanly incorporate only two deuterium atoms per polymer chain (i.e., $D-(CH_2CH_2)_n-D$), and reactions conducted with C_2D_4 under hydrogen formed $H-(CD_2CD_2)_n-H$. No deuterium incorporation from the solvent, toluene-d_8, was observed. The similarity of the FD-MS data obtained from different precursors suggests that each of the above organosamarium precursors leads into the same catalytic cycle. Styrene is not polymerized by these samarium compounds, but FD-MS data on styrene and ethylene reactions showed that styrene could be incorporated into the polyethylene.

A variety of organolanthanide compounds have been reported to polymerize ethylene to high molecular weight.[2,3] Since complexes such as the pentamethylcyclopentadienyl lanthanide compounds $(C_5Me_5)_2Sm$,[4] $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[5] and $(C_5Me_5)_2Sm(THF)_2$[2b,6] require no cocatalyst to exhibit high reactivity,[3] they have a potential advantage over the Ziegler–Natta systems which are activated by large excesses of trialkylaluminum compounds or methylaluminoxanes.[7] However, little has been reported about the characteristics of the polyethylene resulting from these organolanthanide polymerizations, since the high molecular weight polymers are relatively difficult to analyze due to limited solubility. As a result, there is a deficiency of information about the basic steps of these ethylene polymerizations and the relationship of the characteristics of the polymers to the specific catalyst precursors and reaction conditions.

We report here the use of field desorption mass spectrometry (FD-MS)[8] as a way to examine olefin polymerization processes with organolanthanide systems. By conducting the lanthanide-based polymerization of ethylene under hydrogen, oligomeric products with molecular weights conveniently analyzed by this technique can be obtained. FD-MS allows solid and liquid samples to be placed directly on the emitter which is subjected to a high field potential (10^7–10^8 V/cm) and resistively heated. Since the resulting valence electron quantum tunneling produces cationic radicals which are not in a highly excited state, little or no fragmentation occurs and molecular ions are observed.[9] Although FD-MS has been demonstrated to produce accurate molecular weight distributions equivalent to those obtained by conventional techniques such as gel permeation chromatography (GPC) only for narrow molecular weight polymeric standards,[10] FD-MS has an advantage over GPC in that polymer chains can be observed as discrete peaks with specific molecular weights rather than as a chromatogram to which approximate molecular weights must be assigned. Analysis of the exact molecular weight of individual polymer chains aids considerably in determining polymer composition and polymer formation processes as demonstrated in this study.

Experimental Section

The lanthanide compounds described below are air- and moisture-sensitive and require handling under argon or nitrogen with the rigorous exclusion of air and water using high-vacuum, Schlenk, and glovebox techniques.

Materials. Toluene, tetrahydrofuran (THF), and hexane were distilled under nitrogen from solutions containing sodium benzophenone ketyl. Toluene-d_8 (Cambridge Isotope Laboratories, 99.6% D) was dried over P_2O_5 and vacuum transferred prior to use. Ethylene (Matheson, research grade, 99.99%), hydrogen (Liquid Air Corp., UHP, 99.999%), and deuterium chloride (Cambridge Isotope Laboratories, 99% D) were used as received. Deuterium (Liquid Carbonic, 99.8% D) and ethylene-d_4 (Cambridge Isotope Laboratories, 98% D) were passed through supported MnO and 4A molecular sieves activated by heating to 200 °C under vacuum before use. $(C_5Me_5)_2Sm$,[4] $(C_5Me_5)_2Sm(THF)_2$,[6] $[(C_5Me_5)_2Sm]_2(PhCHCH_2)$,[11] $[(C_5Me_5)_2Sm]_2(PhCHCHPh)$,[11] $[(C_5Me_5)_2Sm]_2(PhC_2Ph)$,[5] and $[(C_5Me_5)_2Sm]_2(PhC_4Ph)$[12] were prepared as previously described (where Ph = C_6H_5). Eicosane ($C_{20}H_{42}$), triacontane ($C_{30}H_{62}$), and tetratriacontane ($C_{34}H_{70}$) were purchased from Aldrich and used as received. *trans*-Stilbene (Aldrich) was sublimed before use and styrene (Aldrich) was dried over activated 4A molecular sieves and vacuum transferred immediately prior to use.

Physical Measurements. Mass spectra were obtained with a Fisons Autospec mass spectrometer with a high field (4500 Da) magnet. For field desorption, the instrument was operated at 8 kV with an extraction voltage of −4 kV. The mass spectrometer was set at 1500 resolution and scanned at 7 s per decade from *m/z* 4400 to *m/z* 100. The emitter (Linden ChroMasSpec), which is a 10 μm tungsten wire on which carbon microneedles have been grown, is resistively heated while applying the accelerating and extraction voltages. The emitter is loaded by dipping it into a 10 mg/mL solution of the oligomers in hot toluene. The emitter current was programmed from 0 to 50 mA at 1 mA/min after a 1 minute delay. Data were collected in a continuum mode for 50 min and all scans were averaged to obtain the profile of the oligomers produced. No source heater was used. The mass

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Table 1. Reaction Conditions and Results on Polymerizations of Ethylene by Organosamarium Compounds under Hydrogen

expt	catalyst precursor	conc (mM)	C_2H_4 to H_2 ratio	rxn time (h)	special conditions	yield (g)	mol wt[a] (g/mol)	$H(C_2H_4)_nH$[a] n =
1	$(C_5Me_5)_2Sm$	0.9	1:1	17		0.0030	506	17
2	$(C_5Me_5)_2Sm$	1.0	3.9:1	0.9		0.436	563	19
3	$(C_5Me_5)_2Sm$	1.4	8.3:1	2.0		0.742	478	16
4	$(C_5Me_5)_2Sm$	1.2	18:1	0.7		0.978	507	17
5	$(C_5Me_5)_2Sm$	0.8	29:1	1.5		0.441	478	16
6	$(C_5Me_5)_2Sm$	0.9	46:1	0.8		0.462	450	15
7	$(C_5Me_5)_2Sm$	0.7	94:1	2.0		0.512	618	21
8	$(C_5Me_5)_2Sm$	1.0	3.9:1	3.7	D_2, DCl quench[b]	0.102	480	16
9	$(C_5Me_5)_2Sm$	0.7	4.0:1	3.0	ethylene-d_4[b]	0.187	546	17
10	$(C_5Me_5)_2Sm$	0.8	3.8:1	15	93 °C[c]	0.263	478	16
11	$(C_5Me_5)_2Sm$	0.8	3.8:1	3.4	in hexane[d]	0.279	506	17
12	$(C_5Me_5)_2Sm$	0.7	3.8:1	0.6	in toluene-d_8[e]	0.322	478	16
13	$(C_5Me_5)_2Sm(THF)_2$	0.9	3.8:1	1.3		0.327	506	17
14	$(C_5Me_5)_2Sm(THF)_2$	0.9	3.8:1	2.5	4 mL of THF (9%)[f]	0		
15	$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$	0.4	3.8:1	0.8		0.429	478	16
16	$[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$	0.3	3.8:1	1.9	in hexane[d]	0.108	562	19
17	$[(C_5Me_5)_2Sm]_2PhCHCH_2$	0.9	3.8:1	6.3	10 mL of styrene (20%)[f]	0.587	582	17[g]
18	$[(C_5Me_5)_2Sm]_2(PhCH)_2$	0.9	3.8:1	4.2	0.43 g of *trans*-stilbene[f]	0.373	450	15
19	$[(C_5Me_5)_2Sm]_2PhC_2Ph$	1.5	3.8:1	1.7	0.22 g of PhC_2Ph[f]	0.431	506	17
20	$[(C_5Me_5)_2Sm]_2PhC_4Ph$	0.7	3.8:1	2.9		0.340	450	15

[a] The molecular weight and composition cited here are for the largest FD-MS signal. See text regarding molecular weights and supporting information for complete data. [b] In experiment 8, D_2 was substituted for H_2 and in experiment 9, C_2D_4 was substituted for ethylene. [c] The solution was at 65 °C before the gases were introduced. The temperatures was then raised 93 °C. At the end of the reaction, the solution was degassed before it was cooled to prevent polymerization from occurring at temperatures below 65 °C. [d] Hexane was substituted for toluene as the solvent. [e] Instead of toluene, 20 mL of toluene-d_8 was used. The solvent was vacuum transferred to a separate vessel before the solids were isolated. [f] In addition to the standard reaction conditions, these substrates were added. [g] This molecular weight corresponds to a saturated hydrocarbon with one styrene incorporated (i.e., $H-(C_6H_5CHCH_2)(CH_2CH_2)_{17}-H$).

spectrometer was calibrated with cesium iodide using liquid secondary ion mass spectrometry. ^1H NMR spectra were obtained on GE QE 300-MHz or GN 500-MHz NMR spectrometers and chemical shifts were assigned relative to internal solvent resonances ($C_6D_5CD_2H$ at 2.09 ppm). The ^1H NMR spectra of the samples were obtained at 110 °C in toluene-d_8 with a delay time of 15 s.

Synthesis of $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$. $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ can be prepared by hydrogenolysis of a variety of trivalent organosamarium complexes,[3,5,6] but the following synthesis has been shown to be superior in terms of product purity and conversion in our hands. In an ether-free glovebox, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$[3] (52 mg, 0.12 mmol), 10 mL of hexane, and a magnetic stir bar were placed in a 50 mL vessel composed of a 120 mm tube topped with a greaseless high-vacuum stopcock attached to a ground glass joint. The vessel was attached to a high-vacuum line and the solution was degassed by three freeze−pump−thaw cycles. Hydrogen at 1 atm was introduced. The solution slowly turned from red to orange as an orange precipitate formed. After 2 h, the mixture was dried under vacuum to yield $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ as an orange powder (45.8 mg, 97% yield). The compound was identified by ^1H-NMR spectroscopy.[6]

Standard Polymerization Reaction Conditions. In the glovebox, a solution of about 0.04 mmol of the organolanthanide compound in 40 mL of toluene was prepared in a 100 mL round bottom flask which contained a magnetic stir bar and was capped by a high-vacuum stopcock adapter. The vessel was attached to a high vacuum line, the solution was degassed, and magnetic stirring commenced. Ethylene was admitted into the measured volume of the vacuum line (527 mL) to the desired pressure as measured with a mercury manometer. Hydrogen was subsequently added to achieve a total pressure of 1 atm and the desired hydrogen to ethylene ratio. Upon addition of the gas mixture to the reaction vessel, the solution immediately thickened as polyethylene formation occurred. A slow color change to yellow occurred over a period of 30 min as the gas pressure decreased. To maximize the yield of oligomers produced, the reaction was allowed to continue in each case until most of the gas mixture was consumed and no more uptake was observed. The final pressure was typically 40 Torr. The resulting gel was then quenched and the white powder was isolated as described below. Table 1 summarizes the details of the range of experiments which were conducted to examine the effects of ethylene to hydrogen ratio, deuterium labeling, temperature, solvent, and variations in the samarium precursors.

Standard Isolation Procedure. To quench the reaction, the vessel was removed from the vacuum line and opened to air, and water (< 5 mL) was added until the color disappeared. The mixture was poured into 150 mL of methanol to precipitate the oligomer. The slurry was filtered through filter paper on a Buchner funnel and the white powder was air-dried overnight.

Quenching with Deuterium Chloride. In one experiment (Table 1, experiment 8), the gel was evacuated to remove any remaining ethylene or deuterium gas and DCl gas was introduced. The orange gel turned to pink and then colorless in less than a minute, and the colorless gel was isolated as described above.

Results

Mass Spectral Analysis and Calibration. The applicability and accuracy of FD-MS in the analysis of hydrocarbons of the type to be analyzed were assessed using a mixture of three linear hydrocarbons, eicosane ($C_{20}H_{42}$), triacontane ($C_{30}H_{62}$), and tetratriacontane ($C_{34}H_{70}$) in a molar ratio of 0.537:0.276:0.187, respectively. As shown in the top spectrum in Figure 1, each compound gave the molecular ion as the major peak. The bottom spectrum in Figure 1 shows an expanded portion of the spectrum around the molecular ion $[M]^+$ for $C_{30}H_{62}$ at *m/z* 422. The $[M + 1]^+$ and $[M + 2]^+$ ^{13}C isotope peaks for the molecular ion appear at *m/z* 423 and 424 and have the relative intensities (35 and 6%, respectively) expected on the basis of natural abundance. The $[M - 2]^+$ ion at *m/z* 420 could arise from loss of H_2 or the presence of a contaminant in which there is a double bond. It has been suggested previously that $[M - 2]^+$ ions of this type arise due to the presence of olefin impurities,[10] but recent studies show that this ion is a fragment of the alkane and is dependent on the voltages applied.[9] Deuterium labeling experiments described later confirm the latter explanation for this peak. The *m/z* 420 $[M - 2]^+$ ion would be expected to

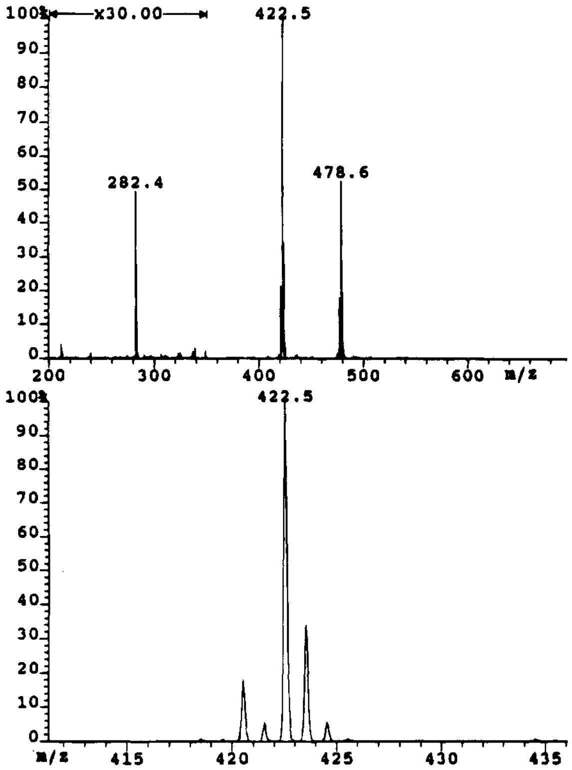


Figure 1. FD-MS data on (top) a mixture of $C_{20}H_{42}$, $C_{30}H_{62}$, and $C_{34}H_{70}$ compounds with the low molecular weight region magnified 30 times and (bottom) an expansion of the molecular ion region for $C_{30}H_{62}$ (mol wt 422).

have a ^{13}C isotope peak at *m/z* 421, $[M - 1]^+$. This is observed with a 22% to 7% relative ratio for the *m/z* 420 and 421 ions, which is consistent with the expected abundance. Interestingly, the relative amount of the $[M - 2]^+$ peak increased as the molecular weight of the $[M]^+$ ion increased in the hydrocarbon samples analyzed (see Figures 2 and 4). This could be due to the higher temperature applied to the emitter to desorb higher molecular weight hydrocarbons.

Although the FD-MS data provide accurate molecular weights on individual chains, this technique does not give a complete picture of a broad molecular weight distribution. In Figure 1, the 168:100 ratio of $C_{30}H_{62}$ peaks to $C_{34}H_{70}$ peaks observed by FD-MS is comparable to the 1.5 molar ratio in the starting material. Hence, in this molecular weight range, intensity is related to abundance. However, even though $C_{20}H_{42}$ comprised over 50% of the mixture, a 30-fold magnification of the $C_{20}H_{42}$ molecular peak at *m/z* 282 was necessary to obtain a signal comparable in intensity to those of the lower volatility components in the mixture. Furthermore, the $C_{20}H_{42}$ molecular ion was observed only in the first few scans taken before the emitter had been appreciably heated (emitter current < 2 mA). This indicates that oligomer chains with molecular weights less than 282 *m/z* are lost under the low-pressure conditions of the instrument and therefore are underrepresented in the spectra generated. Gel permeation chromatography (GPC) and NMR data indicate that high molecular weight polymer chains are also underrepresented due to their lower volatility. Hence, the FD-MS data should not be considered to represent a reliable distribution profile for the polyethylene formed in these reactions. However, the masses of the individual chains are accurate and these data provide insight not available via GPC or NMR.

$(C_5Me_5)_2Sm$ Reactions. $(C_5Me_5)_2Sm$ polymerizes ethylene in the absence of hydrogen to produce polyethylene which is insoluble in refluxing trichlorobenzene and not amenable to analysis by GPC[3] or FD-MS. However, in the presence of hydrogen, $(C_5Me_5)_2Sm$ catalyzes the polymerization of ethylene to form oligomeric products which can be readily analyzed by FD-MS. Reactions were typically performed in 40 mL of toluene with an ethylene to catalyst precursor ratio of greater than 300. Addition of the ethylene and hydrogen gas mixture to the green $(C_5Me_5)_2Sm$ solution immediately leads to thickening of the solution as polymerization of ethylene occurs. There is a slow color change from green to yellow over the course of 30 min as the pressure of gas decreases. This is consistent with the disappearance of the Sm(II) complex and the formation of a Sm(III) species.[13] In order to maximize the yield of product, the reactions were allowed to continue until the gas pressure stopped decreasing, typically at approximately 40 Torr. Depending on the lanthanide complex used and the conditions, this typically occurs in 30 min to 3 h, but in some cases longer reaction times were used. Due to the variable reaction times used and the mass transport problems which decrease the effectiveness of the catalyst as the pressure of the gas mixture decreases, catalyst productivity numbers were not optimized. However, numbers in the range of 11 000 to as high as 34 000 g of polymer/mol of Sm/h were typical for reactions performed less than 1 h (experiments 2, 4, 6, 12, and 15). Details of the reactions are presented in Table 1.

Effect of the Ethylene to Hydrogen Ratio. Experiments numbered 1 to 7 in Table 1 were conducted to determine the effect of varying the ethylene to hydrogen ratio on the oligomers analyzed by FD-MS. As expected, in experiment 1, which has the smallest amount of ethylene, the yield of solid oligomers isolated was the lowest despite the long reaction time. As shown in Figure 2, within the ethylene to hydrogen ratio range of 1:1 to 94:1, there is little effect on the FD-MS data obtained in the 300–1000 Da range. The oligomer envelopes have similar shape and maxima.

The molecular weights obtained by FD-MS correspond to a series of saturated hydrocarbons of formula $H-(CH_2CH_2)_n-H$. For example, in Figure 2, *m/z* 478 corresponds to $C_{34}H_{70}$ ($n = 17$), *m/z* 506 corresponds to $C_{36}H_{74}$ ($n = 18$), and *m/z* 534 corresponds to $C_{38}H_{78}$ ($n = 19$). The 28 mass unit difference between adjacent peaks is as expected for a polymer of ethylene. None of the envelopes observed in these reactions correspond to doubly charged molecular ions. If one envelope was due to molecular ions which were doubly charged, then the spacing between the ions would be 14 rather than the observed 28 and the ^{13}C isotope ions would also occur at half mass values.

Deuterium-Terminated Oligomers. Polymerization of ethylene by $(C_5Me_5)_2Sm$ under deuterium instead of hydrogen followed by quenching with DCl yielded oligomeric products which had molecular weights corresponding to the formula $D-(CH_2CH_2)_n-D$ (Table 1, experiment 8). For example, in the top spectrum of Figure 3, the peak at *m/z* 508 corresponds to $n = 16$. The molecular ions differed by 28 mass units as expected. The data showed that under these conditions two deuterium atoms are cleanly incorporated per chain. The ^1H NMR spectrum of this sample contained a methyl group signal which was broadened and shifted to 0.86 ppm compared to 0.88 ppm for triacontane and

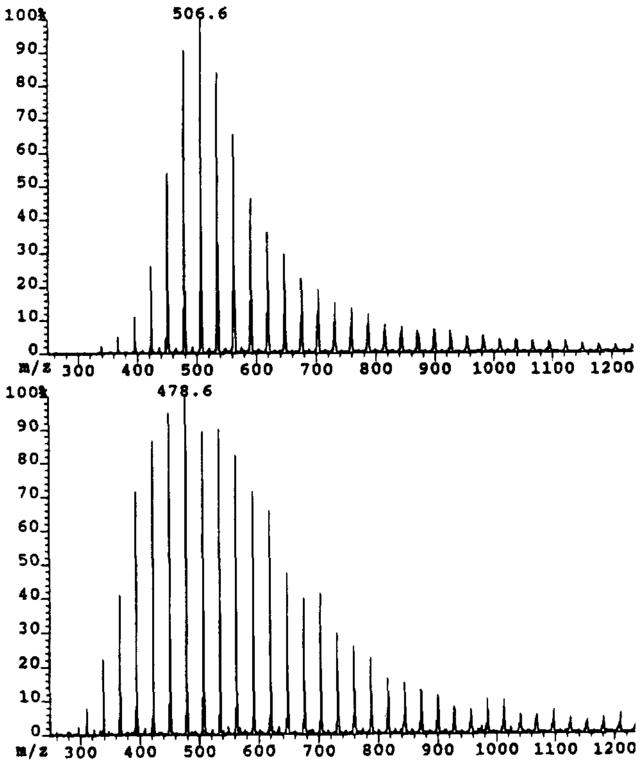


Figure 2. FD-MS data on oligomers produced from $(C_5Me_5)_2$-Sm in toluene using (top) 1:1 and (bottom) 94:1 ethylene to hydrogen gas mixture.

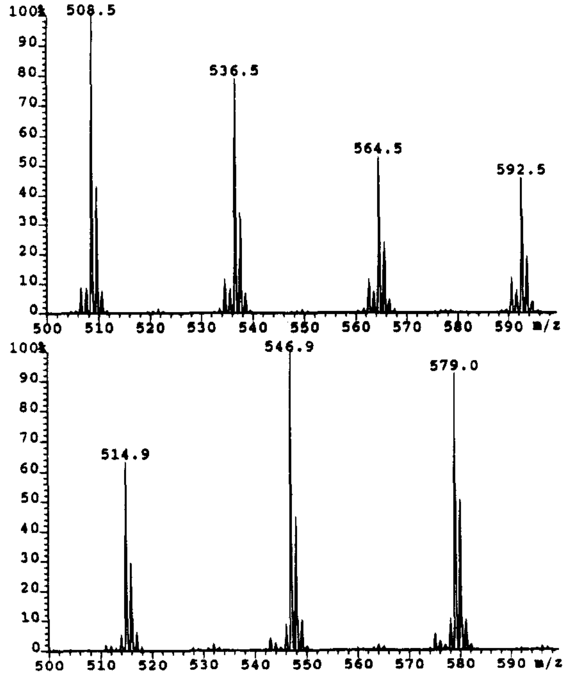


Figure 3. Expanded sections of FD-MS data on oligomers produced using $(C_5Me_5)_2Sm$ in toluene with a 4:1 ratio of (top) ethylene to deuterium and (bottom) ethylene-d_4 to hydrogen.

for the $H-(CH_2CH_2)_n-H$ samples described above. The 0.86 signal is consistent with the presence of CH_2D termini for the oligomer, which is what is expected for a system in which hydrogenolysis with D_2 is the primary chain termination step (see Discussion). The $[M - 1]^+$ ion signals in the top spectrum in Figure 3 are small and can be attributed to residual hydrogen atoms in the deuterium and deuterium chloride gases (99.8% and 99% deuterium labeled, respectively) as well as the ^{13}C isotope for the $[M - 2]^+$ ion.

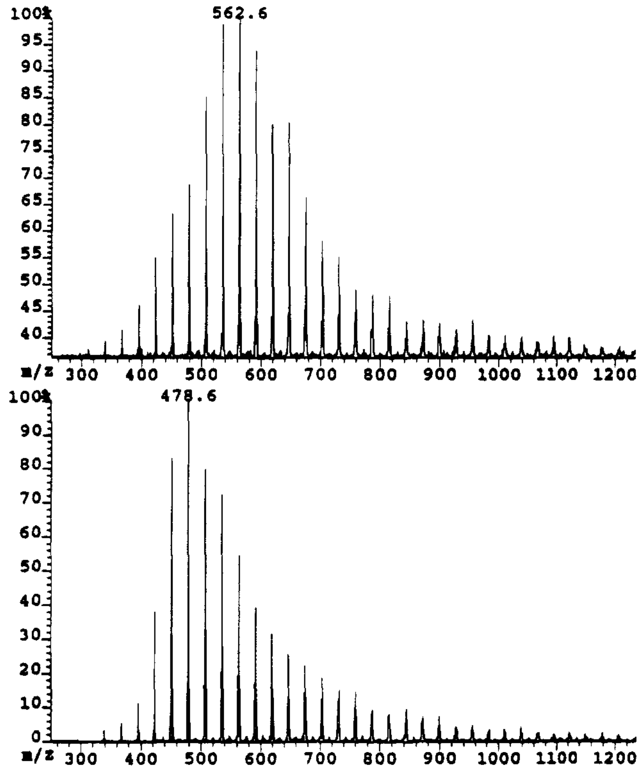


Figure 4. FD-MS data on oligomers produced with an ethylene to hydrogen ratio of 4:1 at (top) 21 °C and (bottom) 93 °C.

Perdeuterioethylene Polymerization. Polymerization of C_2D_4 by $(C_5Me_5)_2Sm$ under hydrogen was also examined (Figure 3, bottom spectrum, experiment 9). The molecular weights of oligomers formed in this reaction correspond to the formula $H-(CD_2CD_2)_n-H$, and the 32 mass unit difference between the molecular ions corresponds to the ethylene-d_4 monomer units. The ^1H NMR spectrum contains very small peaks in the methylene region arising from a small amount of residual hydrogen in the perdeuterioethylene and a large broad methyl signal at 0.82 ppm consistent with CD_2H. Note that in the bottom spectrum in Figure 3, $[M - 4]^+$ signals are observed. These can be assigned to loss of D_2 from $H-(CD_2CD_2)_n-H$ and are analogs of the $[M - 2]^+$ ions found in the spectra of $H-(CH_2CH_2)_n-H$ compounds discussed above. The ion signals at $[M - 3]^+$ and $[M - 2]^+$ are due to the presence of ^{13}C in $[M - 4]^+$ ions. The $[M - 1]^+$ ion is due to residual hydrogen atoms in the perdeuteroethylene (98% deuterium labeled).

Temperature Effects. To examine the possibility that precipitation of the polymer at some molecular weight limit in toluene at room temperature affected the FD-MS data, the polymerization was performed at 93 °C (experiment 10). Since the solubility of the gases in toluene was reduced at this temperature, the yield was diminished. However, polymerization did occur and at the end of the reaction, the mixture of oligomers formed was completely soluble. Subsequent quenching followed by cooling gave a product which had the same FD-MS data as the room temperature product (see experiments 2 and 10 and Figure 4).

Solvent Effects. Changing the solvent from toluene (experiment 2) to hexane (experiment 11) does not influence the FD-MS data on the resulting isolated solid polymer, but it does lower the yield of solid products. This can be attributed to the solubility of the gases. The solubility of both gases is greater in hexane, but the mole fraction of hydrogen increases 110% whereas the mole fraction of ethylene only increases 4%.[14] The increased solubility of hydrogen should favor hydrogenolysis producing lower molecular weight oligomers. Since oligomers of molecular weight < 250 Da are not isolated, the yield of solid oligomers isolated is lowered.

To determine if hydrogen abstraction from toluene occurs during the polymerization,[15] a reaction was performed in toluene-d_8 (experiment 12). The FD-MS spectrum showed no deuterium incorporation into the oligomers obtained. For example, the peak at 478 Da corresponds to the deuterium-free hydrocarbon, $C_{34}H_{70}$. The yield of solids was not significantly altered by using this solvent. The lack of hydrogen abstraction from the toluene is also consistent with the reaction performed in toluene under deuterium (experiment 8) which formed $D-(CH_2CH_2)_n-D$ which was not contaminated by significant amounts of $D-(CH_2CH_2)_n-H$.

Reactions starting with the solvated complex $(C_5Me_5)_2Sm(THF)_2$ were examined (experiment 13) to study the effect of coordinating solvents in the system. The yield and FD-MS data of solids produced from $(C_5Me_5)_2Sm(THF)_2$ were similar to those of products generated from $(C_5Me_5)_2Sm$, although this system requires longer reaction times. Addition of excess THF (9% THF in toluene, 1200 equiv per Sm, experiment 14) to a reaction similar to experiment 13 reduces the reactivity to the point where no uptake of the gas mixture is observed and no solids are isolated.

Trivalent Samarium Precursors. Samarium is often the metal chosen among the lanthanides for a variety of organometallic reactions because it has soluble and reactive divalent complexes like $(C_5Me_5)_2Sm$[4] and $(C_5Me_5)_2Sm(THF)_2$[6] which provide convenient entry into trivalent chemistry.[13,16,17] As part of this study, a variety of Sm(III) organometallic complexes have been examined along with the Sm(II) compounds described above. Since, as discussed below, a trivalent samarium hydride intermediate can be proposed as an active catalytic species in these samarium-based polymerizations, reactions starting with the fully characterized hydride, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[5] were also examined. Reactions starting with this hydride in both toluene (see Figure 5, bottom, experiment 15) and hexane (experiment 16), gave FD-MS data and productivity numbers which were similar to those observed in polymerizations starting with $(C_5Me_5)_2Sm$ (see experiments 2 and 11). Since the compounds $(C_5Me_5)_2Sm$ and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ gave similar results (see Figure 5), $(C_5Me_5)_2Sm$ was chosen for the majority of the other studies because $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is more prone to decomposition.[15]

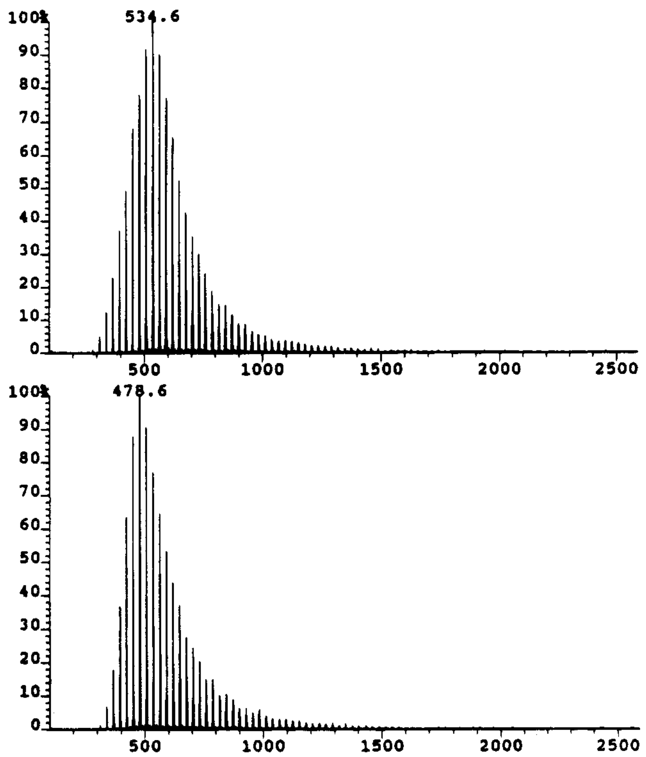


Figure 5. FD-MS data on oligomers produced using (top) $(C_5Me_5)_2Sm$ and (bottom) $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ in toluene with an ethylene to hydrogen ratio of 4:1.

Reactions starting with $[(C_5Me_5)_2Sm]_2(PhCHCH_2)$, $[(C_5Me_5)_2Sm]_2(PhCHCHPh)$, $[(C_5Me_5)_2Sm]_2(PhC_2Ph)$, and $[(C_5Me_5)_2Sm]_2(PhC_4Ph)$ were also examined to determine if they could initiate polymerization and to determine if their styrene-, *trans*-stilbene-, diphenylacetylene-, and 1,4-diphenylbutadiyne-derived components would be incorporated into the oligomers produced. It should be noted that each of these 2:1 metal:substrate complexes is obtained from the reaction of $(C_5Me_5)_2Sm$ with the appropriate unsaturated hydrocarbon, and in no case was $(C_5Me_5)_2Sm$ active in polymerizing that unsaturated hydrocarbon. Each of these complexes was found to function as a precursor for ethylene polymerization (experiments 17–20). For the *trans*-stilbene, diphenylacetylene, and diphenylbutadiyne systems, no evidence for incorporation of the unsaturated hydrocarbon was observed. Even in the presence of excess *trans*-stilbene (experiment 18) and diphenylacetylene (experiment 19), only oligomers of formula $H-(CH_2CH_2)_n-H$ were observed.

However, polymerization of ethylene with hydrogen using the styrene derivative $[(C_5Me_5)_2Sm]_2(PhCHCH_2)$ in toluene with excess styrene present (1100 equiv/Sm) produces an oligomeric sample in which both styrene and ethylene are present. Figure 6 shows the FD-MS data obtained on this product. This differs from all of the reactions in which styrene was absent (experiments 1–16 and 18–20) in that a significant amount of higher molecular weight hydrocarbon chains is present. In addition, there are three distinct envelopes of molecular weights. The molecular weights of the molecular ions present in the largest envelope, as shown in the bottom spectrum in Figure 6, correspond to a copolymer with one styrene incorporated per chain, i.e., a composition of $H-(PhCHCH_2)(CH_2CH_2)_n-H$. The molecular ion at m/z 582 corresponds to $n = 17$. The interval between molecular ions is 28 mass units as expected for oligomers of ethylene. There is no envelope of molecular ions that differ by 104 mass units which would indicate formation of polystyrene. The second envelope contains ions whose molecular weights correspond to homopolymers of ethylene, i.e., $H-(CH_2CH_2)_n-H$. This envelope is very similar to those found in styrene-free reactions (experiments 1–7, 10–16, and 18–20). The molecular ion is at m/z 506 which corresponds to $n = 17$. The third and smallest envelope has molecular ions whose molecular weights correspond to copolymers of ethylene and styrene in which two styrene molecules are incorporated per oligomer chain, i.e., a composition of $H-(PhCHCH_2)_2(CH_2CH_2)_n-H$. Since styrene alone is not polymerized by these samarium systems, the styrene molecules are not likely to be located next to each other. The molecular ion in the third envelope at m/z

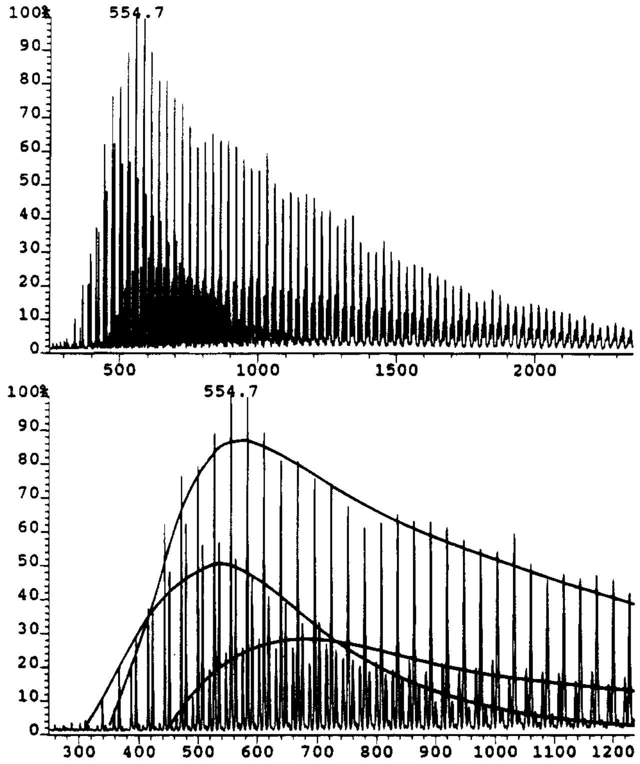
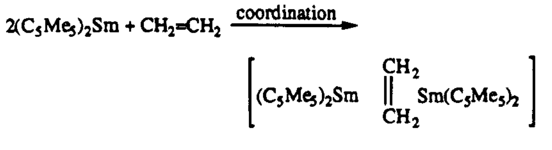


Figure 6. FD-MS data on oligomers produced using $(C_5Me_5)_2Sm$ in toluene with styrene and an ethylene to hydrogen ratio of 4:1: (top) *m/z* 250–2600 and (bottom) *m/z* 300–1170. The largest envelope has incorporation of one styrene unit into the polyethylene chains. The second envelope is polyethylene, and the smallest envelope is a copolymer containing two styrene units in the polyethylene chains.

602 corresponds to an oligomer of 14 ethylene units, 2 styrene units, and the 2 terminal hydrogen atoms.

Discussion

The FD-MS data on organosamarium-based polymerizations of ethylene provide a considerable amount of information on the processes involved in this system. The data are consistent with eqs 1–3 and the set of reactions shown in Scheme 1. Reactions 1–3 show how polymerization can be initiated starting with $(C_5Me_5)_2Sm$, while Scheme 1 demonstrates a catalytic cycle for polymerizations involving a samarium hydride intermediate. Each of these reactions is well precedented in organolanthanide chemistry as described below.



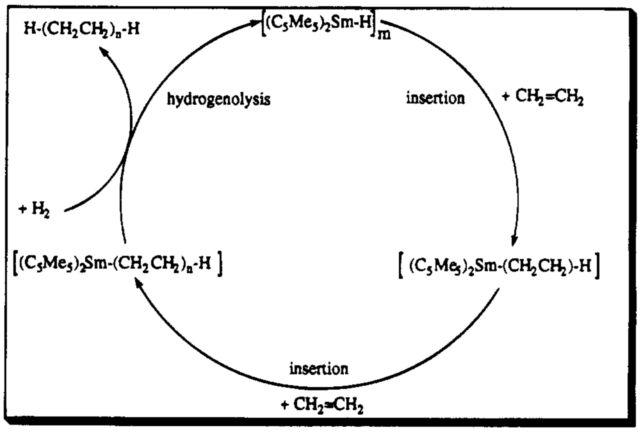
$$2(C_5Me_5)_2Sm + CH_2{=}CH_2 \xrightarrow{\text{coordination}} \left[(C_5Me_5)_2Sm \overset{CH_2}{\underset{CH_2}{\|}} Sm(C_5Me_5)_2\right] \quad (1)$$

$$\left[(C_5Me_5)_2Sm\text{-}CH_2CH_2\text{-}Sm(C_5Me_5)_2\right] + CH_2{=}CH_2 \xrightarrow{\text{insertion}} \left[(C_5Me_5)_2Sm\text{-}(CH_2CH_2)_n\text{-}Sm(C_5Me_5)_2\right] \quad (2)$$

$$\left[(C_5Me_5)_2Sm\text{-}(CH_2CH_2)_n\text{-}Sm(C_5Me_5)_2\right] + H_2 \xrightarrow{\text{hydrogenolysis}} 2\left[(C_5Me_5)_2Sm\text{-}H\right]_m + H\text{-}(CH_2CH_2)_n\text{-}H \quad (3)$$

Equation 1 is based on the precedented tendency of $(C_5Me_5)_2Sm$ to coordinate in a 2:1 manner with unsaturated substrates.[13] Such complexes have been crystallographically confirmed with dinitrogen,[18] azobenzene,[19] styrene,[11] *trans*-stilbene,[11] and diphenylbutadiyne.[12] Reactivity studies with diphenylacetylene[5] and propene[3] are also consistent with the formation of a 2:1 samarium:(unsaturated substrate) complex. In all of these systems, coordination of the unsaturated substrate is accompanied by electron transfer to form a trivalent complex. In the $(C_5Me_5)_2Sm$/ethylene system, this would form a $(C_5Me_5)_2Sm{-}CH_2CH_2{-}Sm(C_5Me_5)_2$ intermediate which has two Sm–C sites for ethylene insertion and polymerization, i.e., it can act as a bisinitiator.[20] The green to yellow color change observed in the $(C_5Me_5)_2Sm$ reactions is consistent with the disappearance of the Sm(II) precursor and formation of trivalent intermediates.[13]

Scheme 1. Proposed Catalytic Cycle for the Organosamarium-Based Polymerization of Ethylene under Hydrogen



Equation 2 involves insertion of an olefin into a lanthanide carbon bond and provides the basis for polymerization. Many examples of the insertion of unsaturated substrates into lanthanide carbon bonds are known.[2,13,15,21–24] The hydrogenolysis shown in eq 3 is also a well-established reaction for lanthanide carbon bonds.[2d,5,22–25] With the dual-site intermediate, termination can occur at one samarium center to form $(C_5Me_5)_2Sm{-}(CH_2CH_2)_n{-}H$, which can continue to polymerize ethylene until a second hydrogenolysis occurs. Once a Sm–H-containing molecule, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_m$ is formed, a catalytic cycle can be written for the polymerization of ethylene in which olefins insert into the lanthanide–hydride bond to form a $Sm{-}(CH_2CH_2){-}H$ unit which can insert ethylene to form $Sm{-}(CH_2CH_2)_n{-}H$ until terminated by hydrogenolysis (Scheme 1). The existence of a dimeric hydride $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ has been crystallographically confirmed[5] and the fact that this hydride can be used to generate an oligomer distribution identical to that obtained from $(C_5Me_5)_2Sm$ is consistent with a hydride intermediate. The degree of aggregation, m, of the hydride intermediate during the polymerizations is not known.[26]

The FD-MS data show that a variety of precursors including $(C_5Me_5)_2Sm$, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$, $[(C_5Me_5)_2Sm]_2(PhCHCHPh)$, $[(C_5Me_5)_2Sm]_2(PhC_2Ph)$, and $[(C_5Me_5)_2Sm]_2(PhC_4Ph)$ give the same FD-MS data. This is consistent with the existence of one common primary catalytic cycle for all of these samarium systems. The fact that the same products can be accessed from Sm(III) precursors as well as highly reducing Sm(II) precursors suggests that trivalent rather than divalent intermediates are involved in the catalytic cycle. Hydrogenolysis of $[(C_5Me_5)_2Sm]_2(PhC_2Ph)$ to form $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$

and PhCHCHPh has previously been reported[5] and would be one way in which this precursor could lead into the catalytic cycle. Scheme 1 is also consistent with the inhibition observed by polar solvents such as THF. Coordination of THF to $(C_5Me_5)_2Sm$ is known to reduce its reactivity[3,13] and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is converted to the catalytically inactive complex $(C_5Me_5)_2Sm(OBu)(THF)$ by a ring-opening reaction on this solvent.[15]

The FD-MS and NMR data on the formation of $D-(CH_2CH_2)_n-D$ from $CH_2{=}CH_2$ under D_2 and $H-(CD_2CD_2)_n-H$ from $CD_2{=}CD_2$ under H_2 are consistent with the termination of the polymerization by hydrogenolysis. The absence of significant amounts of olefinic products suggests that β-hydrogen elimination is not successfully competing with hydrogenolysis as a termination mechanism under these conditions. If termination did occur by β-hydrogen elimination and the resulting olefin was subsequently hydrogenated, the FD-MS data on the $CH_2{=}CH_2/H_2$ reaction would not detect this. However, this should be detectable in the results of the $CH_2{=}CH_2/D_2$ and $CD_2{=}CD_2/H_2$ reactions (experiments 8 and 9, respectively). If β-hydrogen elimination and hydrogenation occurred in experiment 8, the oligomeric products should contain significant amounts of d_1- and d_3-oligomers as well as the d_2- products observed. Likewise, the products of experiment 9 should contain one and three hydrogen atoms rather than the observed two per oligomer chain. The deuterium labeled experiments similarly eliminate the possibility that termination occurs by metalation of solvent, ethylene, or methyl groups on the pentamethylcyclopentadienyl rings. This would be inconsistent with the result of clean formation of $D-(CH_2CH_2)_n-D$ in experiment 8. Hence, the FD-MS data demonstrate that insertion of ethylene and hydrogenolysis are faster processes than metalation under these conditions.

The FD-MS data show no evidence for radical-based polymerization in this system. Hence, there is no deuterium incorporation in reactions performed in toluene-d_8 (experiment 12) and the reaction performed with deuterium (experiment 8) shows no evidence of toluene involvement.

The FD-MS data on the ethylene/styrene reaction (experiment 17) demonstrate the potential of FD-MS to provide information about copolymerization reactivity. The observed incorporation of styrene into the ethylene oligomers was surprising since neither $(C_5Me_5)_2Sm$ nor $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ is a catalyst for styrene polymerization. Styrene could be incorporated into a polymer chain formed according to Scheme 1 by insertion into a Sm–H bond or a $Sm-(CH_2CH_2)_n-H$ bond. Since a normal envelope of $H-(CH_2CH_2)_n-H$ is observed by FD-MS, the intermediates in Scheme 1 are expected to be present in experiment 17. Insertion into Sm–H would be expected to be sterically more favorable. Therefore, the incorporation of one styrene component per oligomer can be rationalized by assuming insertion of styrene into the Sm–H bond of a $(C_5Me_5)_2Sm-H$ intermediate formed during the polymerization. Subsequent ethylene insertion into the $(C_5Me_5)_2Sm-CH_2CHPh-H$ unit would form $(C_5Me_5)_2Sm-(CH_2CH_2)_n-CH_2CHPh-H$. Termination by hydrogenolysis would form the observed $H-(CH_2CH_2)_nCH_2CHPh-H$. The existence of a second set of oligomers whose molecular weights indicated that two styrene molecules were present in some chains suggests that insertion of styrene into Sm–C bonds is also occurring to form the observed composition $(C_5Me_5)_2Sm-CH_2CHPh(CH_2CH_2)_nCH_2CHPh-H$ units. Styrene insertion into lanthanide–carbon bonds has never been previously observed to our knowledge.

Conclusion

Field desorption mass spectrometry has proven to be very valuable in the analysis of the polymerization activity of organolanthanide complexes. By conducting polymerizations of ethylene under hydrogen, oligomers are obtained which can be studied by FD-MS to determine the effects of varying the reaction conditions. Comparisons of several different catalyst precursors can be readily made in this way, both initiation and termination processes can be probed by examining inclusion of end groups and formation of saturated versus unsaturated products, and the effects of using deuterated components and comonomers can be precisely analyzed. FD-MS is particularly valuable compared to GPC or NMR in that it provides exact molecular weight data on individual chains, which gives a more detailed understanding of the polymer composition.

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Supporting Information Available: Additional field desorption mass spectra (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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