Metalation as a Termination Step in Polymerization Reactions Involving α-Olefins and Ethylene As Detected by Field Desorption Mass Spectrometry[1]

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Field desorption mass spectroscopy (FD-MS) in conjunction with NMR spectroscopy has been used to study how olefins larger than ethylene are incorporated into polyethylene using $(C_5Me_5)_2Sm$-based catalysts under hydrogen. Polymerization reactions of propene, 1-pentene, *cis*- and *trans*-2-pentene, 1-heptene, *trans*-2-heptene, *trans*-3-heptene, 1-octene, and 1-nonadecene with ethylene under H_2 and with $CD_2{=}CD_2$ under D_2 were studied as well as reactions of ethylene with propene-d_6 and 3,3,3-propene-d_3 using $(C_5Me_5)_2Sm$ and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ precursors where R = H, Et, and Bu. For the olefins listed above, the combined analytical techniques with the appropriate deuterium labeling indicate that one olefin is selectively incorporated per polyethylene chain and that incorporation occurs by insertion into a Sm−H bond in the system rather than via an allyl group. Metalation of the olefin by growing polymer chains was found to be competitive with hydrogenolysis as a termination step and can be used to control molecular weight. 2-Pentene and 2-heptene do not incorporate as readily as their α-olefin analogs and 3-heptene incorporation was not detectable, but these internal olefins are effective termination agents via metalation.

Introduction

The incorporation of α-olefins into polyethylene is an important method for modifying the properties of this polymer.[2] Optimization of such designer copolymers depends upon developing the capability to selectively incorporate olefins in a controlled fashion. Although organolanthanide complexes have been shown to polymerize ethylene,[3−22] to model Ziegler−Natta polymerization systems,[23] and to effect polymerization without the addition of cocatalysts as in Ziegler−Natta and Kaminsky systems,[2,24,25] organolanthanides have not been extensively explored as copolymerization catalysts for ethylene and α-olefins. This is due, in part, to the inadequacy of lanthanide compounds in polymerizing α-olefins and, in part, to the difficulty in obtaining mechanistic information on these system in order to improve them. Characterization of high molecular weight polyethylene in which relatively small amounts of α-olefin have been incorporated is generally done by analyzing bulk properties, and this information gives little insight into the reaction mechanisms which are occurring.

Recently, field desorption mass spectrometry (FD-MS) has been used to analyze ethylene polymerization initiated by $(C_5Me_5)_2Sm$-based systems.[20] It appeared that this technique could be very useful in studying

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Table 1. Conditions and Results for Reactions of Ethylene and Propene with $(C_5Me_5)_2Sm$ under Hydrogen inToluene

expt no.	amt of Sm (μmol)	C_2H_4 to C_3H_6 to H_2 ratio	rxn time (h)	other conditions	yield oligomer (g)	% odd C chains
1	44	12:1:2	1.7		0.539	20
2	25	9:1:1.5	2.7		0.469	60
3	22	6:1:1	3.5		0.434	75
4	39	6:1:1	0.9	propene-d_6[a]	0.506	45
5	33	11:1:2	0.8	3,3,3-propene-d_3[a]	0.437	60

[a] Deuterium-labeled propene was substituted for propene.

copolymerization reactions as well. To test the utility of FD-MS in analyzing mixed olefin polymerization systems and to develop a better understanding of olefin incorporation into polyethylene in general, organosamarium-initiated polymerization reactions of ethylene with various alkenes were investigated.

On the basis of prior knowledge of the reactivity of $(C_5Me_5)_2Sm$-containing systems, incorporation of olefins larger than ethylene into polyethylene was not expected to be very favorable. Both the divalent initiator, $(C_5Me_5)_2Sm$,[26] and the hydride, $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$,[27,28] which is central to the catalytic cycle (vide infra),[20] had been found to react with a variety of olefins including propene, 2-butene, allylbenzene, 1,3-butadiene, and 1,5-hexadiene to form allyl complexes $[(C_5Me_5)_2Sm(CH_2CHCHR)]_n$,[13] and they do not polymerize these α-olefins at atmospheric pressure. The isolated and crystallographically characterized allyl compounds derived from propene and butadiene, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ and $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{—})]_2$, were shown to polymerize ethylene, but no information on incorporation of the allyl units into the polyethylene was available.[13] Copolymerization reactions involving ethylene and 1-hexene initiated by $[(C_5Me_5)_2Ln(\mu\text{-}H)]_2$ complexes of other lanthanide metals, namely lanthanum, neodymium, and lutetium, were reported over 10 years ago, but the molecular weight distribution, extent of incorporation of 1-hexene, and reaction mechanisms were not analyzed in this complicated system.[6] Recently, ring-opening polymerization has been combined with ethylene polymerization to generate copolymers of ethylene with significantly different types of monomers.[18,21,29]

We report here the utility of FD-MS in analyzing a mixed olefin polymerization system and the reactivity of a variety of olefins on the polymerization of ethylene initiated by $(C_5Me_5)_2Sm$. This compound was used as an initiator, since it is highly soluble, it can be prepared in high purity, and it is more stable than other equivalent precursors such as the hydride $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$.[27,28] All reactions were run under hydrogen (or deuterium) to limit the molecular weight of the product which aids in the analysis by FD-MS,[20] NMR spectroscopy, and gel permeation chromatography (GPC).

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. $(C_5Me_5)_2Sm$[26] must be handled in an environment free of ethers and other coordinating solvents.

Materials. Toluene and hexanes were distilled under nitrogen from solutions containing sodium benzophenone ketyl. Benzene-d_6 and toluene-d_8 (both from Cambridge Isotope Laboratories, 99.6%), ethylene (Matheson, research grade, 99.99%), hydrogen (Liquid Air, UHP, 99.999%), and deuterium chloride (Cambridge Isotope Laboratories, 99%) were used as received. Deuterium (Liquid Carbonic, 99.8%), ethylene-d_4, propene-d_6, 3,3,3-propene-d_3 (all from Cambridge Isotope Laboratories, 98%), and propene (Matheson, research grade, 99.995%) were passed through supported MnO[30] and activated 4A molecular sieves before use. $(C_5Me_5)_2Sm$[26] and $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$[13] were prepared as previously described. All liquid alkenes were purchased from Aldrich, dried with sodium, degassed on a high-vacuum line with three freeze−pump−thaw cycles, and vacuum transferred prior to use. 1-Nonadecene was dried under vacuum before use.

Physical Measurements. Mass spectra were obtained with a Fisons Autospec mass spectrometer having a high field (4500 Da) magnet as previously described.[20] ^1H NMR spectra were obtained on GE QE 300-MHz and GN 500-MHz NMR spectrometers. The ^1H NMR spectra of the polymer samples were obtained at 110 °C in toluene-d_8 with a delay time of 15 s. Elemental analyses were obtained from Analytische Laboratorien, Gummersbach, Germany.

Procedure for Reactions of $(C_5Me_5)_2Sm$ with Ethylene and Propene under Hydrogen. In an ether-free glovebox, a solution of $(C_5Me_5)_2Sm$ 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, stirring was started, and the green solution was degassed. Ethylene was admitted into a measured volume of the vacuum line (527 mL) to the desired pressure as determined with a mercury manometer. The appropriate amount of propene was subsequently added followed by addition of hydrogen to achieve a total pressure of 1 atm and the desired hydrogen to propene to ethylene ratio. Upon addition of the gas mixture to the reaction vessel, the solution immediately thickened as polymer formation occurred. A color change to orange-yellow occurred over a period of 10 min as the gas pressure decreased. To maximize the yield of oligomers produced, the reactions were allowed to continue until most of the gas mixture had been consumed and no more uptake was observed. The final pressure was typically 40 Torr. The resulting orange-yellow gel was then quenched by opening the reaction vessel to air and adding water (<5 mL) 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. Table 1 summarizes the details of the experiments involving propene. For all of the tables, the percentage of odd carbon oligomer chains was calculated by dividing a summation of the FD-MS relative intensities (in percent) of the odd chains by a summation of the FD-MS relative intensities of

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Table 2. Conditions and Results for Reactions of Olefins with Ethylene and Hydrogen (4:1) Using $(C_5Me_5)_2Sm$ in Toluene

expt no.	amt of Sm (μmol)	olefin added	olefin amt (mmol)	rxn time (h)	yield oligomer (g)	% odd C chains
1	42	1-pentene	0.38	0.6	0.412	15
2	44	1-pentene	0.78	0.5	0.418	55
3	44	1-pentene	1.6	1.0	0.431	55
4	43	1-pentene	2.3	0.8	0.499	55
5	44	1-pentene	3.1	1.8	0.458	60
6	43	1-pentene	9.1	0.5	0.319	85
7	44	*c,t*-2-pentenes	0.39	1.1	0.348	5
8	42	*c,t*-2-pentenes	0.79	0.8	0.323	5
9	37	*c,t*-2-pentenes	1.6	0.9	0.374	10
10	42	*c,t*-2-pentenes	2.4	0.9	0.375	10
11	30	*c,t*-2-pentenes	3.2	0.5	0.406	10
12	46	1-heptene	0.3	0.5	0.471	15
13	42	1-heptene	0.55	0.8	0.364	25
14	44	1-heptene	1.3	1.7	0.462	60
15	44	1-heptene	2.2	0.8	0.469	65
16	42	1-heptene	3.3	1.1	0.452	60
17	42	*t*-2-heptene	0.56	0.9	0.386	5
18	42	*t*-2-heptene	1.1	0.9	0.342	10
19	42	*t*-2-heptene	2.2	0.9	0.352	5
20	44	*t*-2-heptene	3.4	0.8	0.360	10
21	41	*t*-3-heptene	0.55	0.9	0.340	3
22	41	*t*-3-heptene	1.1	0.8	0.347	3
23	43	*t*-3-heptene	2.1	1.0	0.332	3
24	39	*t*-3-heptene	3.3	0.9	0.322	3
25	29	1-octene	250[a]	0.6	0.547	15[b]
26	44	1-nonadecene	29	1.6	0.424	15

[a] 1-Octene was substituted for toluene as the solvent. [b] 1-Octene will not produce an odd carbon envelope, but this polymer sample did contain poly(octene) in the given percentage.

the even and odd chains, multiplying by 100, and rounding to the nearest 5%.

Procedure for Reactions of $(C_5Me_5)_2Sm$ with Ethylene and Alkenes Other Than Propene under Hydrogen. In an ether-free glovebox, $(C_5Me_5)_2Sm$ and the alkene were combined in 40 mL of toluene. The red solution was placed in the reaction vessel, and a mixture of ethylene and hydrogen (4:1 ratio) was added to the degassed solution as described above. The reactions typically began with 390 equiv of ethylene per Sm, and uptake of the gas mixture was completed in less than 1 h. The resulting orange gel was quenched, and the white powder was isolated as described earlier. Table 2 summarizes the details of the reactions involving olefins other than propene.

Synthesis of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ Complexes. In an ether-free glovebox, solid $(C_5Me_5)_2Sm$ (0.1−0.2 mmol) was weighed and an excess (7−40 mmol) of the appropriate cooled (−40 °C) liquid alkene (1-pentene, *cis*- and *trans*-2-pentene, 1-heptene, *trans*-2-heptene, and *trans*-3-heptene) was added. The mixture immediately turned dark red and was allowed to stir and warm to room temperature over the course of 1 h before the volatile compounds were removed under vacuum. The dark red oily solid was extracted with a minimal amount of hexanes (<5 mL), and trace amounts of insoluble yellow samarium oxide, $[(C_5Me_5)_2Sm]_2(\mu\text{-}O)$,[31] were discarded. The red hexanes extract was dried under vacuum to isolate the oily red allyl product (0.06−0.1 g).

$(C_5Me_5)_2Sm(CH_2CHCHEt)$ from $(C_5Me_5)_2Sm$ and 1-Pentene or *cis*- and *trans*-2-Pentene. ^1H NMR (C_6D_6): δ 14.91 (br s, 1H, $CH_2C\mathit{H}CHEt$), 10.85 (br s, 1H, $C\mathit{H_2}CHCHEt$), 7.20 (br s, 1H, $C\mathit{H_2}CHCHEt$), 5.84 (br s, 1H, $CH_2CHC\mathit{H}Et$), 1.24 (br s, 15 H, $C_5\mathit{Me}_5$), 1.06 (br s, 15 H, $C_5\mathit{Me}_5$), −1.89 (br s, 1H, $CH_2CHCHC\mathit{H_2}Me$), −3.25 (br s, 3H, $CH_2CHCHCH_2\mathit{Me}$), −4.62 (br s, 1H, $CH_2CHCHC\mathit{H_2}Me$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 173.2 ($CH_2\mathit{C}HCHEt$), 115.6 (C_5Me_5), 52.0 ($CH_2CH\mathit{C}HEt$), 34.9 ($CH_2CHCH\mathit{C}H_2Me$), 25.6 ($\mathit{C}H_2CHCHEt$), 16.0 ($C_5\mathit{Me}_5$), 12.8 ($CH_2CHCHCH_2\mathit{Me}$). IR (neat): 2910 s, 2860 s, 1560 m, 1440 m, 1380 m, 1260 w, 1150 w, 1090 m, 1020 m, 800 m cm^{-1}. Anal. Calcd for $SmC_{25}H_{39}$: Sm, 30.69; C, 61.29; H, 8.02. Found: Sm, 30.85; C, 61.06; H, 7.90.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHBu)$ from $(C_5Me_5)_2Sm$ and 1-Heptene or *trans*-2-Heptene. ^1H NMR (C_6D_6): δ 14.84 (br s, 1H, $CH_2C\mathit{H}CHBu$), 10.83 (br s, 1H, $C\mathit{H_2}CHCHBu$), 7.25 (br s, 1H, $C\mathit{H_2}CHCHBu$), 6.13 (br s, 1H, $CH_2CHC\mathit{H}Bu$), 1.24 (br s, 15 H, $C_5\mathit{Me}_5$), 1.07 (br s, 15 H, $C_5\mathit{Me}_5$), −0.34 (br s, 3H, $CH_2CHCH(CH_2)_3\mathit{Me}$), −0.95 (br s, 1H), −1.74 (br s, 1H), −1.76 (br s, 1H), −2.84 (br s, 1H), −4.05 (br s, 1H), −4.96 (br s, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 173.3 ($CH_2\mathit{C}HCHBu$), 115.7 (C_5Me_5), 114.4 (C_5Me_5), 52.0 ($CH_2CH\mathit{C}HBu$), 35.0 ($CH_2CHCH(\mathit{C}H_2)_3Me$), 34.6 ($CH_2CHCH(\mathit{C}H_2)_3Me$), 25.7 ($\mathit{C}H_2CHCHBu$), 24.4 ($CH_2CHCH(\mathit{C}H_2)_3Me$), 16.1 ($C_5\mathit{Me}_5$), 12.8 ($CH_2CHCH(CH_2)_3\mathit{Me}$). IR (neat): 2920 s, 2850 s, 1550 w, 1430 m, 1375 m, 1250 w, 1150 w, 1100 m, 1015 w, 950 w, 800 w cm^{-1}. Anal. Calcd for $SmC_{27}H_{43}$: Sm, 29.03; C, 62.60; H 8.37. Found: Sm, 29.30; C, 62.27; H 8.27.

$(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHBu)$ and $(C_5Me_5)_2Sm(\eta^3\text{-}MeCHCHCHPr)$ from $(C_5Me_5)_2Sm$ and *trans*-3-Heptene. ^1H NMR (C_6D_6) resonances were as for $(C_5Me_5)_2Sm(CH_2CHCHBu)$ plus δ 15.17 (br s, 1H, $MeCHC\mathit{H}CHPr$), 9.50 (br s, 1H, $MeC\mathit{H}CHCHPr$), 8.90 (br s, 1H, $MeCHCHC\mathit{H}Pr$), 1.15 (br s, 15 H, $C_5\mathit{Me}_5$), 1.10 (br s, 15 H, $C_5\mathit{Me}_5$), 0.40 (br s, 1H), −0.07 (br s, 1H), −1.42 (br s, 3H, *Me*), −3.17 (br s, 3H, *Me*), −3.80 (br s, 1H), and −4.00 (br s, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 173.3 ($\mathit{C}H$), 115.6 (C_5Me_5), 114.5 (C_5Me_5), 50.0 ($\mathit{C}H$), 41.3 ($\mathit{C}H$), 34.9 ($\mathit{C}H_2$), 34.6 ($\mathit{C}H_2$), 31.6 ($\mathit{C}H_2$), 25.6 ($\mathit{C}H_2$), 24.4 ($\mathit{C}H_2$), 20.9 ($\mathit{C}H_2$), 16.1 ($C_5\mathit{Me}_5$), 14.3 (*Me*), 12.8 (*Me*). IR (neat): 2950 s, 2860 s, 1440 m, 1370 m, 1250 w, 1150 m, 1090 m, 1010 w, 950 w, 800 w cm^{-1}.

Procedure for Polymerization of Ethylene under Hydrogen Using Samarium Allyl Compounds as Initiators. In an ether-free glovebox, the organosamarium allyl compound, $(C_5Me_5)_2Sm(CH_2CHCHR)$ (R = H, Et, or Bu), was dissolved in 40 mL of toluene. The reddish-orange solution was placed in the reaction vessel, and a mixture of ethylene and hydrogen (4:1 ratio) was added to the degassed solution as described earlier. The resulting yellow gel was quenched, and the white powder was isolated as described above. Table 3 summarizes the details of these reactions.

Procedure for Reactions of $(C_5Me_5)_2Sm$ with Ethylene-*d*$_4$ and Olefins under Deuterium. The reactions were prepared as described above except deuterium and ethylene-*d*$_4$ were substituted for hydrogen and ethylene, respectively, and a 240 mL gas mixture volume was used. These reactions were quenched by evacuating the vessel containing the polymer gel and adding gaseous DCl. The orange gels turned pink and then colorless in less than 1 min, and the colorless gels were isolated as described above. Table 4 summarizes the details of these experiments.

Results

Both $(C_5Me_5)_2Sm$ and $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ have previously been shown by FD-MS to generate catalytic systems which polymerize ethylene under hydrogen to give saturated oligomers of formula $H(CH_2CH_2)_nH$ with an even number of carbon atoms.[20] These $(C_5Me_5)_2Sm$-based ethylene polymerizations under hydrogen can be understood on the basis of a single scheme involving a samarium hydride intermediate as shown in Scheme 1. Copolymerization studies were performed primarily with olefins containing an odd number of carbon atoms since incorporation of any odd number of these olefins can be immediately detected by FD-MS by the presence of oligomer chains containing an odd number of carbon atoms, i.e. $CH_3(CH_2CH_2)_nH$.

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Table 3. Reaction Conditions and Results for Polymerization of Ethylene under Hydrogen (4:1) with Samarium Allyl Complexes Toluene

expt no.	$(C_5Me_5)_2Sm(\eta^3\text{-allyl})$ precursor allyl	amt of Sm (μmol)	rxn time (h)	yield of poly (g)	NMR M_n	max possible % odd chains[a]	actual % odd chains
1	CH_2CHCH_2	118	0.4	0.547	5400	100	5
2	CD_2CDCD_2	44	0.9	0.388	1300	15	<1
3	$CH_2(CH)_2CH_2CH_3$[b]	94	1.5	0.288	3400	100	3
4	$CH_2(CH)_2(CH_2)_3Me$[c]	184	2.1	0.446	2200	91	2[d]
5	$CH_2(CH)_2(CH_2)_3Me$[e]	96	1.2	0.324	1900	56	2
6	C_7H_{13}[f]	64	1.0	0.253	1000	25	2

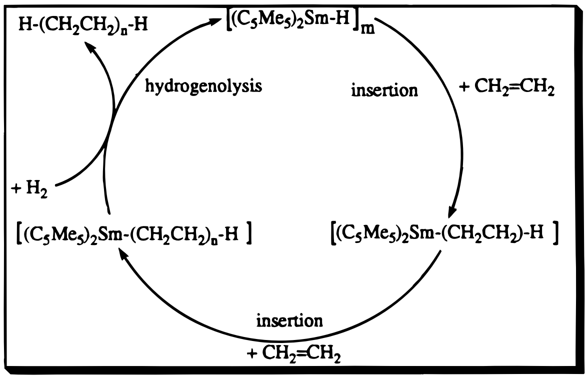
[a] Maximum possible percentage of odd carbon chains calculated from (mmol allyl complex)/(mmol polymer) × 100% using M_n determined by NMR spectroscopy. [b] Formed from $(C_5Me_5)_2Sm$ and *cis*- and *trans*-2-pentene. [c] Formed from $(C_5Me_5)_2Sm$ and 1-heptene. [d] Signals are observed for poly(heptene) which was formed during the synthesis of the starting allyl complex from $(C_5Me_5)_2Sm$ and 1-heptene. [e] Formed from $(C_5Me_5)_2Sm$ and *trans*-2-heptene. [f] A mixture of allyl complexes from $(C_5Me_5)_2Sm$ and *trans*-3-heptene.

Table 4. Conditions and Results for DCl-Quenched Reaction of Olefins with Ethylene-d_4 under Deuterium (4:1) by $(C_5Me_5)_2Sm$

expt no.	amt of Sm (μmol)	olefin added	olefin amt (mmol)	rxn time (h)	yield of oligomer (g)	% odd C chains
1	45	none	0.0	2.7	0.203	0
2	48	1-pentene	3.6	8.9	0.126	75
3	39	1-pentene	4.6	7.6	0.162	95
4	45	*c*,*t*-2-pentenes	4.6	8.0	0.203	30
5	43	1-heptene	3.6	3.3	0.149	60
6	47	*t*-2-heptene	3.6	5.6	0.151	10
7	53	*t*-3-heptene	3.6	3.7	0.228	<10
8	52	1-octene	3.2	2.0	0.291	75[a]

[a] 1-Octene will not produce an odd carbon envelope.

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



Polymerization of Ethylene with Propene. As shown by the FD-MS data in Figure 1, the polymerization of ethylene with propene initiated by $(C_5Me_5)_2Sm$ yields two different types of oligomer chains as indicated by the two different sets of signals. The molecular weights in the largest set of signals, the "primary envelope", in Figure 1 (top spectrum) correspond to a series of saturated hydrocarbons of formula $H(CH_2CH_2)_nH$ (i.e. $C_{32}H_{66}$ at m/z 450, $C_{34}H_{70}$ at m/z 478, and $C_{36}H_{74}$ at m/z 506). The 28 mass unit difference between adjacent peaks corresponds to the molecular weight of ethylene as expected. The secondary envelope of molecular weights also has a 28 mass unit difference between adjacent peaks, but the molecular weight of this series corresponds to saturated hydrocarbons with at least one molecule of propene incorporated per chain, $H(CH_2CHCH_3)_m(CH_2CH_2)_nH$, where m is an odd number (i.e. $C_{33}H_{68}$ at m/z 464, $C_{35}H_{72}$ at m/z 492, and $C_{37}H_{76}$ at m/z 520). Although, as discussed previously, FD-MS cannot provide complete molecular weight distribution data for polyethylene,[20,32] it does provide compositional information not available from the usual methods of polymer molecular weight characterization. For example, GPC would be unable to detect underlying envelopes of polymer chains with odd versus even numbers of carbon atoms.

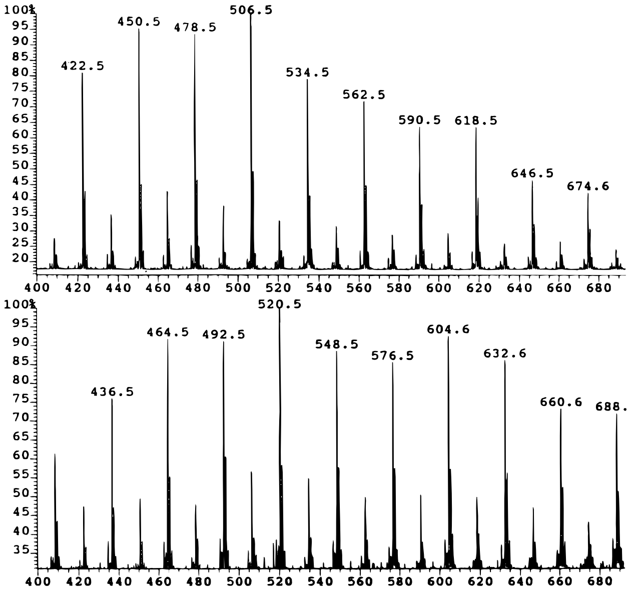


Figure 1. FD-MS data on the reaction of $(C_5Me_5)_2Sm$ with ethylene and propene under hydrogen in a 12:1:2 (top) and 6:1:1 (bottom) ratio.

The productivity numbers for the catalytic species in this system are in the 10 000−20 000 g polymer/mol Sm/h range and are low estimates since mass transport problems decrease the effectiveness of the catalyst as the pressure of the gas mixture decreases and the solution becomes more viscous. Two major signals are observed in the ^1H NMR spectrum of the isolated polymer product: a large resonance at 1.33 ppm due to the methylene groups and a triplet in the methyl region at 0.88 ppm. Comparison of the areas of the methylene and methyl peaks gives a number average molecular weight (M_n) for the oligomers shown in Figure 1 (top spectrum) of 3600 g/mol.

As the relative amount of propene is increased from an ethylene to propene ratio of 12:1 to 9:1 to 6:1 (Figure 1), the amount of oligomer chains with an odd carbon number increases from 20 to 60 to 75% (Table 1, expt 1−3). The FD-MS technique is very useful in determining this trend, which is as expected. However, the data do not reveal how much propene is incorporated per

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(32) Evans, W. J.; DeCoster, D. M.; Greaves, J. Submitted for publication in *J. Am. Soc. Mass Spectrom.*

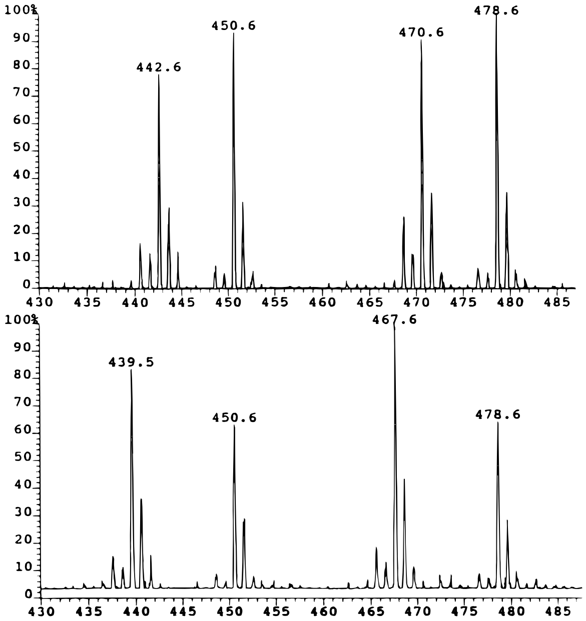

Figure 2. Expansion of the FD-MS data for reaction of $(C_5Me_5)_2Sm$ with ethylene, propene, and hydrogen in the ratios shown: (Top) propene-d_6 (6:1:1); (bottom) 3,3,3-propene-d_3 (11:1:2).

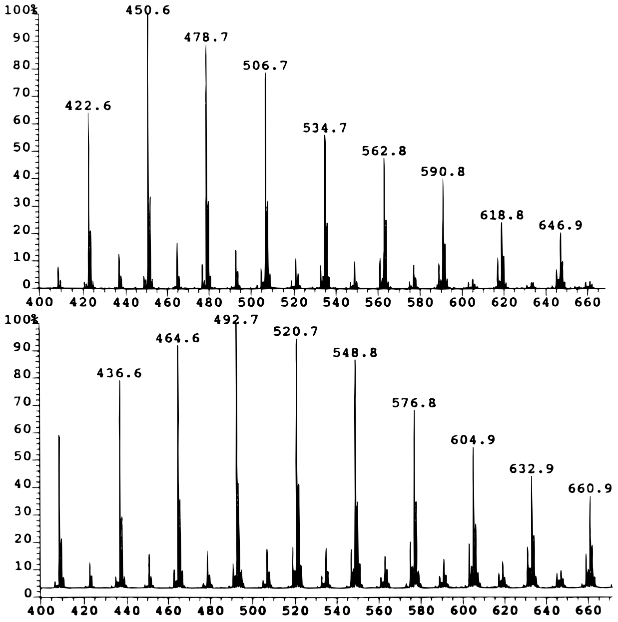

Figure 3. FD-MS data on the reaction of $(C_5Me_5)_2Sm$ and 9 (top) and 210 (bottom) equiv of 1-pentene/Sm with ethylene and hydrogen (4:1).

polymer chain, since the molecular weight of a chain containing an even number of propene units matches that of an even carbon chain containing no propene. Similarly, incorporation of any odd number of propene units is indistinguishable from incorporation of only one.

To determine how many propene units were being incorporated, studies with deuterium-labeled propene were performed. When a 6:1 ratio of ethylene to propene-d_6 was used, the molecular weights of the secondary envelope of odd carbon oligomer peaks in the FD-MS data (Figure 2, top spectrum) corresponded to the incorporation of one propene unit per chain. For example, the signal at *m*/*z* 470.6 corresponds to $C_{33}H_{62}D_6$. At the detection limit, no evidence was found for a third envelope arising from the incorporation of two propene units per chain. Double incorporation would generate signals at, for example, *m*/*z* 462.6 for $C_{32}H_{54}D_{12}$. The signal intensities for peaks of this type were <1% in this sample, which had 45% of the chains incorporating one propene unit.

It is important to note that the FD-MS data show the incorporation of the entire C_3D_6 unit without loss or replacement of any deuterium atoms or addition of any hydrogen. If the deuterated propene reacted to form an allyl complex of formula $(C_5Me_5)_2Sm(\eta^3\text{-}CD_2CDCD_2)$ and this allyl unit were incorporated into the polyethylene, then signals corresponding to the formula $H(CH_2CH_2)_n(CD_2CDHCD_2)H$ would be expected. This is not observed. For example, close examination of the peaks around the $[M]^+$ molecular ion signal at *m*/*z* 470.6 for $H(CH_2CH_2)_{15}(CD_2CDCD_3)H$, reveals no significant peak at *m*/*z* 469.6 corresponding to $H(CH_2CH_2)_{15}(CD_2CDHCD_2)H$. The signals at *m*/*z* 471.6 and 472.6 have 34% and 6% intensities, respectively, which are consistent with the natural abundance of ^{13}C. The ion at *m*/*z* 468.6, $[M - 2]^+$, occurs due to loss of H_2, a fragmentation pattern previously found in FD-MS data on hydrocarbons.[20,33] This $[M - 2]^+$ ion would be expected to have a ^{13}C isotope peak at *m*/*z* 469.6, and there should also be a small contribution to the *m*/*z* 469.6 peak due to residual protons in the propene-d_6 (98%). The ratio of intensities of the 25% *m*/*z* 468.6 peak and the 13% *m*/*z* 469.6 peak (1.9:1 ratio) is consistent with the expected abundance of these isotopically-substituted species.

Polymerization of ethylene with 3,3,3-propene-d_3 in a 11:1 ratio gives results similar to those obtained with propene-d_6. As shown in Figure 2 (bottom spectrum), the molecular weight of the major envelope corresponds to incorporation of one propene-d_3 per chain. For example, the signal at *m*/*z* 467.6 corresponds to $C_{33}H_{65}D_3$ and there is no significant intensity at *m*/*z* 456.6 which would correspond to $C_{32}H_{60}D_6$.

Polymerization of Ethylene with Larger Alkenes. $(C_5Me_5)_2Sm$-initiated polymerizations of ethylene under hydrogen in the presence of olefins larger than propene were examined to see if the results for propene were general and to evaluate the differences between terminal and internal olefins. The results are presented in Table 2.

α-Olefins. The reactions involving 1-pentene (Table 2, expt 1−6) and 1-heptene (expt 12−16) gave similar results. In each case the products were saturated hydrocarbons and the size of the odd carbon envelope increased with increasing α-olefin concentration. As shown in Figure 3, as the amount of 1-pentene increased from 9 to 210 equiv/Sm, the odd carbon envelope changed from being the secondary to the primary envelope. For 1-heptene reactions, molecular weights were obtained by GPC and showed that M_n decreased from 3300 to 1300 to 750 g/mol as the amount of 1-heptene was increased from 0 to 5 to 250 equiv/Sm.

A significantly longer odd carbon alkyl chain α-olefin, 1-nonadecene, $C_{19}H_{38}$, was also examined to determine if the length of the alkyl group had any effect on the extent of incorporation. In a reaction (Table 2, expt 26) using 7 equiv of 1-nonadecene per Sm, odd carbon chains accounted for 15% of the sample, which is

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(33) Heine, C. E.; Geddes, M. M. *Organic Mass Spectrom.* **1994**, *29*, 277−282.

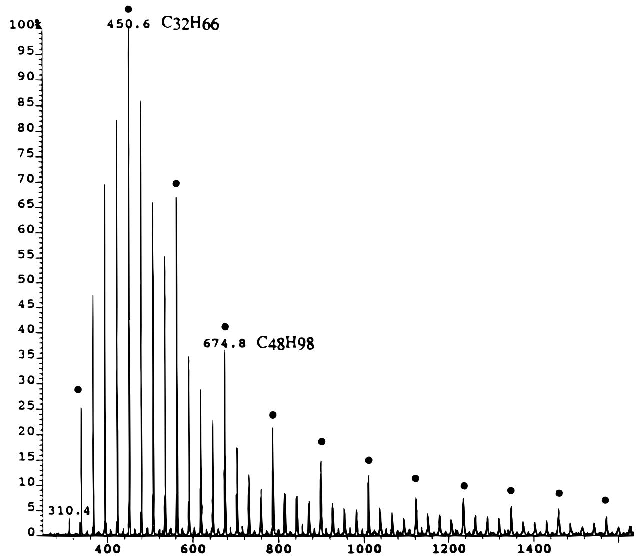


Figure 4. FD-MS data on the reaction of $(C_5Me_5)_2Sm$ with ethylene under hydrogen (4:1) in neat 1-octene.

comparable to the results with 9 equiv of 1-pentene/Sm and 6 equiv of 1-heptene/Sm.

Although incorporation of even carbon olefins cannot be determined by FD-MS without deuterium labeling, some even carbon systems were examined for completeness and to confirm the expectation that only even carbon chains would be formed. This was observed, but FD-MS provided additional information on this system, which, in contrast to the reactions described above, used the olefin as the solvent. The product of this 1-octene reaction (expt 25) differed from the polymers produced in the other reactions in that it was stickier and waxier. The FD-MS data, Figure 4, contained the expected signals of only even carbon saturated hydrocarbon chains, but the intensities of several of these peaks (marked by dots in Figure 4) were unusually high. The signals with excess intensity were separated by 112.1 mass units, which is the molecular weight of 1-octene. These signals, which are substantially larger than the other signals in the spectrum, have molecular weights corresponding to a homopolymer of octene. For example, the signal at *m/z* 786.9 corresponds to $H(CH_2CH_2)_{28}H$ and $H(C_8H_{16})_7H$. This was the first indication that homopolymerization of α-olefins could be achieved in this system. Since the 1-octene and $(C_5Me_5)_2Sm$ were in contact for 20 min before the ethylene and hydrogen gas mixture were added, the homopolymerization could have occurred during that time.

Internal Olefins. Reactions involving *cis*- and *trans*-2-pentene (Table 2, expt 7−11) and *trans*-2-heptene (expt 17−20) also showed formation of two envelopes of saturated hydrocarbons, but the percentages of odd carbon chains were significantly smaller than those observed for α-olefins. As the amount of 2-pentenes was increased from 9 to 110 equiv/Sm, the percentage of odd carbon envelope increased only slightly from 5 to 10% (Figure 5). A similar increase was observed with *trans*-2-heptene. GPC analysis on the isolated product of the reaction with 13 equiv of *trans*-2-heptene/Sm (expt 17) indicated a M_w of 4700, a M_n of 2600 g/mol, and a narrow polydispersity of $M_w/M_n = 1.8$.

3-Heptene. No significant incorporation of *trans*-3-heptene into the polyethylene was observed (expt 21−24). As the amount of *trans*-3-heptene was increased from 13 to 85 equiv/Sm, the odd carbon envelope remained at the same low level of about 3%.

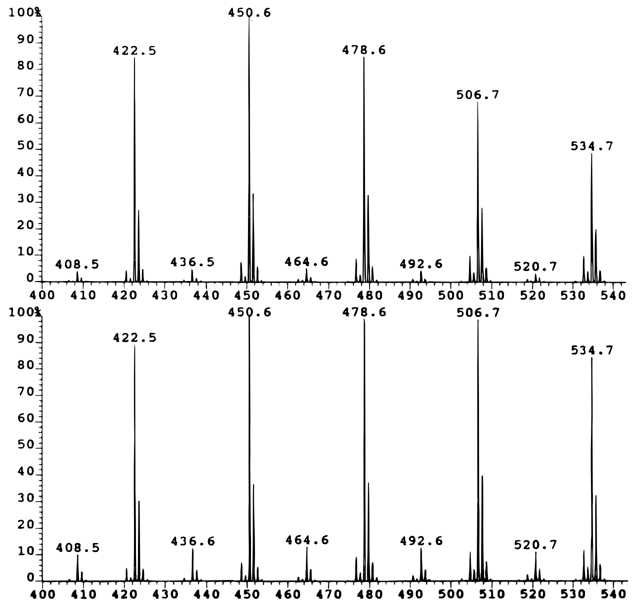


Figure 5. FD-MS data on the reaction of $(C_5Me_5)_2Sm$ with ethylene under hydrogen (4:1) and 9 (top) and 110 (bottom) equiv of *cis*- and *trans*-2-pentene/Sm.

Reactions Involving Samarium Allyl Compounds. Since allyl complexes are likely to form during the olefin/ethylene polymerizations, it was desirable to examine reactions starting with isolated allyl compounds under the same conditions as the reactions initiated with $(C_5Me_5)_2Sm$. This required synthesis of some new allyl complexes.

Synthesis. Pentenes and heptenes react with $(C_5Me_5)_2Sm$ to form allyl complexes as has previously been shown to occur for propene, butene, and allylbenzene.[13] The reaction for forming these allyl compounds is illustrated for propene in eq 1. When $(C_5Me_5)_2Sm$ is

$$2(C_5Me_5)_2Sm + 3CH_2{=}CHCH_3 \rightarrow 2(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2) + CH_3CH_2CH_3 \quad (1)$$

reacted in a sealed tube with a mixture of *cis*-2-pentene and *trans*-2-pentene, pentane and a samarium allyl complex are formed. The allyl complex formed from this 2-pentene mixture is identical by NMR spectroscopy to that obtained from $(C_5Me_5)_2Sm$ and 1-pentene. The number and integration of resonances corresponds to the unsymmetrical complex $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHEt)$ rather than the symmetrical $(C_5Me_5)_2Sm(\eta^3\text{-}MeCHCHCHMe)$. The reactions of $(C_5Me_5)_2Sm$ with 1-heptene and 2-heptene are similar in that only one product is formed and the number of resonances by NMR spectroscopy suggests the formation of $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHBu)$ rather than $(C_5Me_5)_2Sm(\eta^3\text{-}MeCHCHCHPr)$ or $(C_5Me_5)_2Sm(\eta^3\text{-}EtCHCHCHEt)$. The formation of a single isomer in each case from these 1- and 2-alkene reactions is consistent with preferential loss of a hydrogen of a methyl rather than a methylene group in the 2-alkene reactions which leads to the same allyl complex obtained from the 1-alkenes.

Since the formation of an allyl complex from 3-heptene cannot occur by loss of hydrogen from a methyl group, products such as $(C_5Me_5)_2Sm(\eta^3\text{-}EtCHCHCHEt)$ and $(C_5Me_5)_2Sm(\eta^3\text{-}MeCHCHCHPr)$ were likely. A

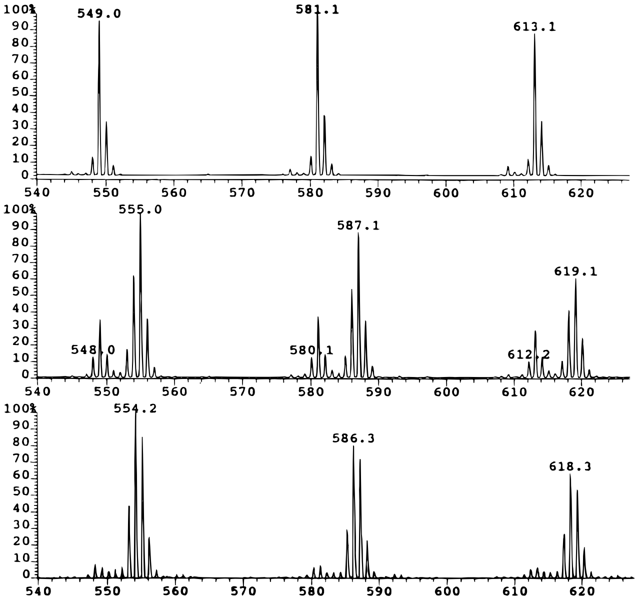


Figure 6. Expansion of the FD-MS data of the DCl-quenched reactions of $(C_5Me_5)_2Sm$ with ethylene-d_4 and deuterium (4:1 ratio) and 0 (top), 75 (middle), and 120 (bottom) equiv of 1-pentene/Sm.

mixture of products was observed by NMR spectroscopy, but surprisingly, one set of resonances matches the signals obtained for $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHBu)$ formed by reaction of $(C_5Me_5)_2Sm$ with 1-heptene or 2-heptene. Hence, isomerization must be occurring during the reaction.

Reactivity. The data on reactions initiated by allyl complexes are summarized in Table 3. For an ethylene polymerization initiated by $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$, very little incorporation of the C_3 unit as measured by the amount of odd carbon chains (5%) was found compared to what could have occurred (100%) based on the amount of starting $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCH_2)$ and the amount of isolated polymer. The amount of odd carbon chain formation observed for the other substituted allyl derivatives tested, namely, $(C_5Me_5)_2Sm(\eta^3\text{-}CD_2CDCD_2)$, $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHCH_2CH_3)$, and $(C_5Me_5)_2Sm(\eta^3\text{-}C_7H_{13})$, was even lower. These allyl compounds showed no significant amount of odd carbon products (<3%). These results suggested that under the conditions of the mixed olefin reactions, the allyl groups produced from the olefins are not incorporated in significant amounts into polyethylene.

Reactions with Ethylene-*d*$_4$ and Deuterium. Additional information on the extent of incorporation of olefins larger than propene into polyethylene could be obtained by using deuterated versions of the larger olefins. However, deuterated analogs of C_3D_6 and $C_3D_3H_3$ are not readily available for larger olefins. To obtain equivalent information, polymerization of ethylene-d_4 under deuterium in the presence of protioolefins was examined with quenching by DCl. With this combination of protio and deuterio species, the ^{1}H NMR spectra of these products were more informative since the only signals present had to arise from the protioolefin. Data on the ethylene-d_4 systems are summarized in Table 4.

Initially, a control reaction involving $(C_5Me_5)_2Sm$ with an ethylene-d_4 to deuterium ratio of 4:1 and no added olefin was examined (Figure 6, top spectrum). The data are as expected for perdeuteriopolyethylene. The molecular weights of the carbon chains correspond to a series of saturated hydrocarbons of formula $D(CD_2CD_2)_nD$ (i.e. $C_{34}D_{70}$ at *m*/*z* 549.0, $C_{36}D_{74}$ at *m*/*z* 581.1, etc.), and the 32 mass unit difference between adjacent peaks corresponds to the molecular weight of CD_2CD_2. The molecular ion, $[M]^+$, of the largest signal in the spectrum appears at 581.1 mass units. The signals at *m*/*z* 582.1 and 583.1 are due to the natural abundance of ^{13}C isotopes and have the expected relative intensities of 40 and 10%, respectively. The ion at *m*/*z* 577.1, $[M - 4]^+$ occurs due to loss of D_2 as a fragment. The $[M - 4]^+$ ion has ^{13}C isotope peaks at *m*/*z* 578.1 and 579.1. The 14% signal at *m*/*z* 580.1 can be attributed to the residual protons in the deuterio-labeled gases ethylene-d_4 (2%), deuterium (0.2%), and hydrogen chloride-d_1 (1%). The ^{1}H NMR spectrum of this product shows no notable resonances other than the solvent peaks.

Table 5. Percentages of Odd Carbon Chains and Chains with Deuterium Replaced by Hydrogen in Products of Reactions with 75 and 120 equiv 1-Pentene/Sm

	odd C chains	chains with one H in place of D
75 equiv of 1-pentene/Sm	45% $C_nD_{2n+2}C_5H_{10}$ 30% $C_nD_{2n+1}C_5H_{11}$	5% $C_nD_{2n+1}H$ 30% $C_nD_{2n+1}C_5H_{11}$
tot.	75%	35%
120 equiv of 1-pentene/Sm	35% $C_nD_{2n+2}C_5H_{10}$ 60% $C_nD_{2n+1}C_5H_{11}$	5% $C_nD_{2n+1}H$ 60% $C_nD_{2n+1}C_5H_{11}$
tot.	95%	65%

α-Olefins. 1-Pentene. When 1-pentene (75 equiv/Sm) is reacted with a mixture of ethylene-d_4 and deuterium (4:1 ratio) using $(C_5Me_5)_2Sm$ and the reaction is quenched with DCl, two envelopes of signals are observed (Figure 6, middle spectrum) as in the analogous protio reaction. The even carbon set of peaks corresponds to perdeuteriopolyethylene with no 1-pentene incorporation, and the odd carbon set of peaks corresponds to incorporation of 1 equiv of 1-pentene into each perdeuteriopolyethylene chain. Within each envelope the peaks differ by 32 mass units as expected.

Although the envelope pattern is similar in this deuterium-labeled experiment, the isotope pattern of the molecular ions in both odd carbon and even carbon envelopes is dramatically different from the control reaction. For example, the signal at *m*/*z* 587.1, $[M]^+$, corresponds to the incorporation of 1 equiv of 1-pentene into perdeuteriopolyethylene and conforms to the formula $C_{37}D_{66}H_{10}$. The signal at *m*/*z* 588.1 is as expected based on the natural abundance of ^{13}C. However, the signal at $[M - 1]^+$, which corresponds to $C_{37}D_{65}H_{11}$ and is expected to be around 14% due to the residual hydrogen in the starting deuterio-labeled gases, is 61% of the molecular ion! Similarly, the $[M]^+$ signal at *m*/*z* 581.1 for $C_{36}D_{74}$, an even carbon perdeuterated polyethylene chain, has an associated *m*/*z* 582.1 signal of the appropriate intensity for ^{13}C natural abundance, but the signal at *m*/*z* 580.1 corresponding to $C_{36}D_{73}H$ is much larger than expected. The percentage of carbon chains, both odd and even, with an extra hydrogen in place of deuterium is 35%, whereas 75% of the chains incorporated 1-pentene (see Table 5).

The ^{1}H NMR spectrum of this product contains two resonances in the methylene region, a shoulder at 1.28 and a peak at 1.27 ppm, and two resonances in the methyl region, a triplet at 0.88 and a small unresolved multiplet at 0.82 ppm. Previous studies of the reaction of $(C_5Me_5)_2Sm$ with ethylene-d_4 and H_2 (4:1 ratio) have shown that the 0.82 ppm signal arises from CD_2H methyl groups as in $H(CD_2CD_2)_nH$.[20]

When the amount of 1-pentene is increased to 120 equiv/Sm and the copolymerization is repeated under the same conditions, the amount of oligomers with one proton in place of a deuterium is increased to the extent that these species are now the largest peaks in the spectrum (Figure 6, bottom spectrum). For example, the signal at *m*/*z* 587.1 for perdeuteriopolyethylene containing one 1-pentene unit, $C_{37}D_{66}H_{10}$, is smaller than the signal at *m*/*z* 586.1, which corresponds to $C_{37}D_{65}H_{11}$. This indicates that significant amounts of saturated oligomer chains have incorporated one hydrogen in place of one deuterium. The same is true for the *m*/*z* 581.1 $C_{36}D_{74}$ and *m*/*z* 580.1 $C_{36}D_{73}H$ signals.

As expected with the larger amount of 1-pentene, the percentage of oligomer chains which have molecular weights which correspond to the incorporation of one 1-pentene unit also increases. The percentage of odd carbon chains in this reaction is 95%, and the amount of carbon chains with an extra hydrogen is 65%. The ^1H NMR spectrum is the same as that of the 75 equiv reaction.

Other α-Olefins. As in the protio systems, reactions with 1-heptene paralleled those with 1-pentene. Hence, a reaction with 83 equiv of 1-heptene /Sm with $CD_2{=}CD_2$ under D_2 produced a product with 60% of the chains incorporating one 1-heptene unit and 45% of the chains with an extra hydrogen in place of a deuterium.

Using the $CD_2{=}CD_2/D_2$ system with 1-octene allowed the amount of incorporation of this even hydrocarbon to be determined. Using 62 equiv of 1-octene/Sm (Table 4, expt 8), 75% of the polymer incorporated one 1-octene per oligomer chain. Hence, this even carbon olefin gives results analogous to the odd carbon analogs. In this sample, 45% of the oligomer chains had hydrogen substituted for deuterium.

Internal Olefins. Reactions of the $CD_2{=}CD_2/D_2$ system with 2-pentenes, 2-heptene, and 3-heptene gave results similar to the protio reactions described above in that the amount of odd carbon chains was less than with α-olefins (Figure 7). In each case, the primary envelope in the deuterated system has no internal olefin incorporation and arises from perdeuteriopolyethylene. Both the primary even carbon and secondary odd carbon envelopes have peak patterns which show the substitution of one hydrogen for one deuterium in many of the chains. Hence, with 100 equiv of 2-pentene/Sm, 30% of the oligomer chains have incorporated one 2-pentene unit and 65% have a hydrogen substituted for deuterium. With 77 equiv of 2-heptene/Sm 10% of the oligomer chains have incorporated one 2-heptene unit and 35% of the chains have an extra hydrogen. With 68 equiv of *trans*-3-heptene/Sm, less than 10% of the oligomer chains have odd numbers of carbon atoms and 50% of oligomer chains have one hydrogen substituted for deuterium. Consistent with this result, the ^1H NMR spectrum contains no methylene resonances but it does contain the 0.82 ppm signal associated with CD_2H groups.

Discussion

The FD-MS data on $(C_5Me_5)_2Sm$-based reactions of ethylene with deuterated propene under hydrogen and the reactions of protioolefins larger than ethylene with $CD_2{=}CD_2$ and D_2 show that the main reaction which occurs when an olefin larger than ethylene is added to these systems is selective incorporation of one olefin into the polyethylene chains. A second general result which is observed is that many of the chains also have one hydrogen in place of a deuterium. Since the amounts of olefin incorporation and hydrogen replacement by deuterium are not correlated, these processes appear to be independent. As described in the following paragraphs, there are several pathways by which one and only one olefin could be incorporated into a polyethylene chain. Evaluation of these routes by FD-MS and NMR reveals the reaction pathways traversed in this system and the power of the FD-MS technique to probe complicated systems. The data also show how the hydrogen replacement can occur, a process which has implications for α-olefin/ethylene copolymerization reactions in general. In the following discussion, the general term olefin will refer to olefins larger than ethylene.

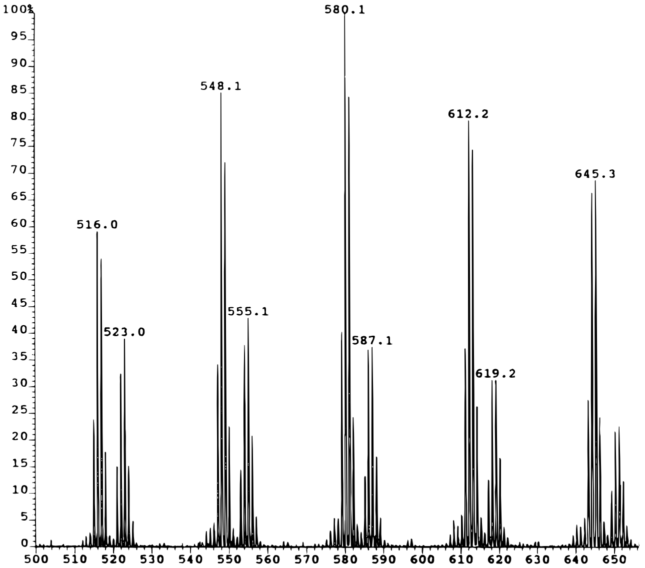
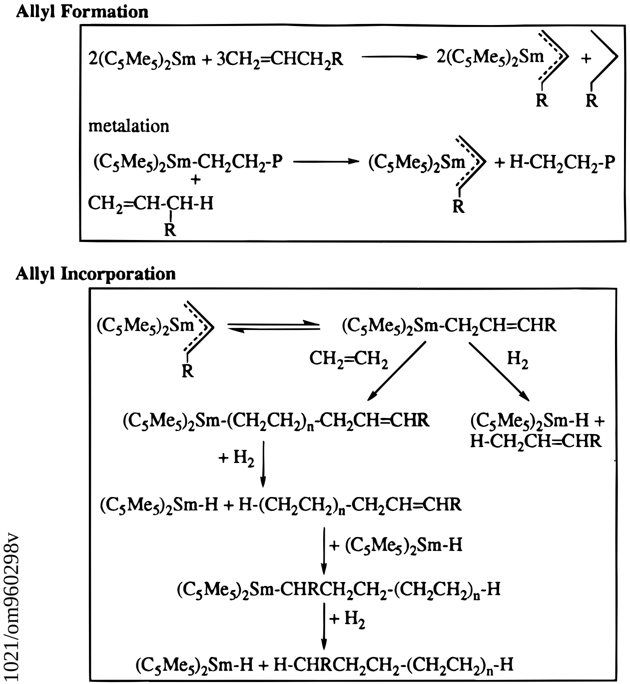


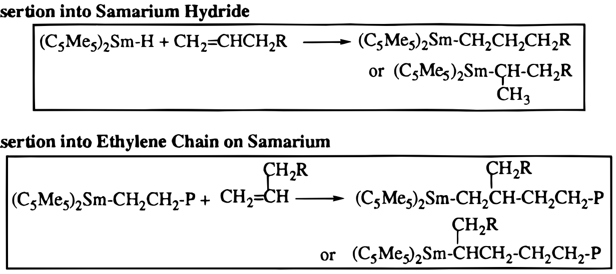
Figure 7. Expansion of the FD-MS data of the DCl-quenched reactions of $(C_5Me_5)_2Sm$ with ethylene-d_4 and deuterium (4:1 ratio) with 100 equiv of *cis*- and *trans*-2-pentene per Sm.

Routes for Olefin Incorporation. One route of olefin incorporation involves the intermediacy of samarium allyl compounds, $(C_5Me_5)_2Sm(RCHCHCHR')$, as illustrated in Scheme 2. The allyl complex can be formed by reaction of the olefin with the $(C_5Me_5)_2Sm$ starting material, as has been demonstrated here and elsewhere,[13] or by metalation of the olefin by a growing polymer chain, a process which terminates the polymer. Isomerization of the allyl group from an η^3- to η^1-bonding mode would form a samarium carbon single bond into which ethylene could insert. Further insertion of ethylene would form the polyethylene chain which would grow until it is terminated by hydrogenolysis or metalation of an olefin. No evidence for β-hydride elimination was observed in these reactions. Incorporation of a single olefin via this allyl route would yield oligomer chains which have an unsaturated group at the beginning of the chain. However, since the molecular weights of the isolated oligomer chains correspond to saturated hydrocarbons, subsequent hydrogenation of the unsaturated oligomer chains as shown in Scheme 2 is required for this route of olefin incorpo-

Scheme 2. Possible Pathway of Incorporation of α-Olefins into Polyethylene via Allyl Complex Formation and Subsequent Insertion of Ethylene (R = H, Propene; R = Et, Pentene; R = Bu, Heptene)



Scheme 3. Possible Pathways of Incorporation of α-Olefins into Polyethylene by Insertion into a Samarium−Hydride Bond or a Samarium−Carbon Bond (P = Polymer Chain; R = H, Propene; R = Et, Pentene; R = Bu, Heptene)



ration to match the data. Incorporation of the olefin by this allyl route seems less likely because polymerization reactions initiated with the samarium allyl complexes, $(C_5Me_5)_2Sm(\eta^3\text{-RCHCHCHR}')$, do not form significant amounts of odd carbon polymer chains as shown in Table 3. However, this pathway must be considered since it does provide a route for incorporation of only one olefin per oligomer chain and allyl complexes are likely to be present during the reaction.

Two other routes for olefin incorporation involve insertion of the olefin into either a samarium hydride bond or a samarium carbon bond as illustrated in Scheme 3. Insertion could either occur in 1,2-fashion to form a linear alkyl product or in the sterically more hindered 2,1-fashion. If insertion into a Sm−H bond occurs, this would put the olefin at the beginning of the chain. Insertion of ethylene into the resulting samarium alkyl moiety would propagate the chain which could subsequently be terminated by hydrogenolysis or metalation to form the observed product. Since only one Sm−H is involved per chain, this would explain why only one olefin is incorporated. To explain why only one olefin is incorporated if insertion into a Sm−C bond occurred, it must be argued that the olefin is at the end of the chain. If insertion of the α-olefin forms an alkyl complex so sterically crowded that further ethylene or α-olefin insertion does not occur, then the only reaction possible is termination by hydrogenolysis or metalation.

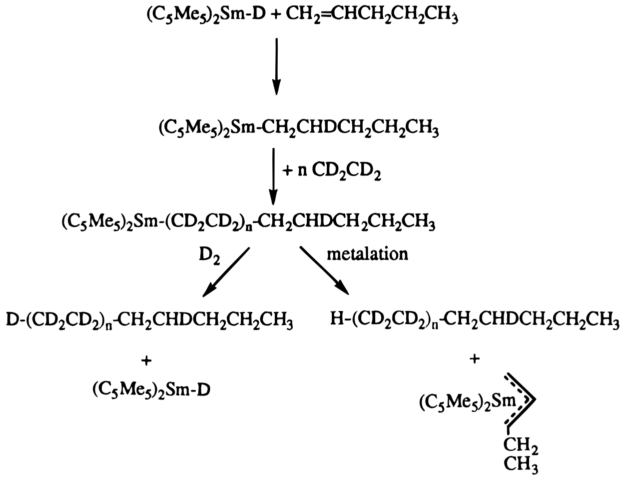
Table 6. Molecular Weights of Possible C_{36} and C_{37} Oligomer Chains Formed from the Reaction of Ethylene-d_4 with 1-Pentene under Deuterium

	n	M_w
No Incorporation		
(1) $D(CD_2CD_2)_nD$	18	581.1
Incorporation as Allyl		
(2) $D(CD_2CD_2)_nCH_2CH{=}CHCH_2CH_3$	16	584.1
(3) $D(CD_2CD_2)_nCH_2CHDCHDCH_2CH_3$	16	588.1
Insertion into Sm−D		
(4) $D(CD_2CD_2)_nCH_2CHDCH_2CH_2CH_3$	16	587.1
Insertion into $Sm(CD_2CD_2)_nD$		
(5) $DCH_2CH(CH_2CH_2CH_3)(CD_2CD_2)_nD$	16	587.1
(6) $D(CD_2CD_2)_mCH_2CH\text{-}(CH_2CH_2CH)_3(CD_2CD_2)_{n-m}D$	16	587.1

Evaluation Using 1-Pentene. These three pathways can be differentiated by a combination of FD-MS and NMR analysis of reactions of the protioolefins with ethylene-d_4 and deuterium. The argument presented here will use the 1-pentene reaction as an example and will focus on the mass range for C_{36} and C_{37} products. Data for the other olefins and for other mass ranges give the same result. Table 6 lists the various possibilities for products of the 1-pentene/$CD_2{=}CD_2/D_2$ reaction in this mass range. (1) If there is no incorporation of olefin, then a signal at m/z 581.1 for perdeuteriopolyethylene should be observed by FD-MS and the product should show no ^1H NMR resonances. (2) If 1-pentene is incorporated as an allyl group, a m/z signal at 584.1 should be observed. (3) If this unsaturated polymer is hydrogenated under the conditions of the reaction, then an FD-MS signal at m/z 588.1 should be observed since the hydrogenation will be done with D_2. (4) If 1-pentene is inserted into a samarium deuteride bond, a signal at m/z 587.1 should be observed and the oligomer should show two types of methylene groups, CH_2 and CHD, by ^1H NMR spectroscopy. (5,6) If 1-pentene is inserted into the Sm−C bond of a growing polymer chain, a signal at m/z 587.1 should again be observed as in case 4. However, these cases can be differentiated by NMR spectroscopy. (5) If 1-pentene insertion into a Sm−C bond is followed by hydrogenolysis with D_2, the NMR spectrum would contain a methine group and a CH_2D methyl group which resonates at 0.86 ppm. (6) If insertion into the Sm−C bond is followed by insertion of ethylene-d_4, then observation of a methine group in the ^1H NMR spectrum is expected. The identity of the 0.86 ppm shift was independently determined by a separate reaction of $(C_5Me_5)_2Sm$ with ethylene under deuterium with a DCl quench which cleanly yields oligomer chains terminated by deuterium, $D(CH_2CH_2)_nD$.[20] The 0.86 ppm shift of the methyl groups in this product can be compared with the 0.88 ppm resonance observed for CH_3 groups in protiopolyethylene and the 0.82 ppm shift for CD_2H groups of $H(CD_2CD_2)_nH$ prepared from $CD_2{=}CD_2$ under hydrogen.[20]

The major peak in the FD-MS spectrum of the $(C_5Me_5)_2Sm$ reaction of 120 equiv of 1-pentene/Sm with $CD_2{=}CD_2$ under D_2 followed by a DCl quench was

Scheme 4. Reaction Pathways Which Conform to the Observed Results of Reactions of 1-Pentene with Ethylene-d_4 under Deuterium



observed at *m*/*z* 586.1 (Figure 6, bottom spectrum), which is none of the possibilities in Table 6! However, there is a signal at *m*/*z* 587.1 which is consistent with incorporation of 1 equiv of 1-pentene into the perdeuteriopolyethylene to form $C_{32}D_{66}(C_5H_{10})$ by insertion into a Sm−D (case 4) or Sm−C bond (cases 5 or 6). Since the signal at *m*/*z* 588.1 has intensity appropriate only for ^{13}C derivatives of the molecular ions at *m*/*z* 586.1 and 587.1, the incorporation of the 1-pentene as an allyl group which gets hydrogenated (case 3) can be excluded. Since no unsaturated products are observed, incorporation of the olefin as an allyl group which is not hydrogenated (case 2) is also eliminated.

^{1}H NMR spectroscopy indicates that the insertion occurs into a Sm−D bond instead of into a Sm−C bond since no methine signals are observed and two signals are observed in the methylene region at 1.28 and 1.27 ppm consistent with the presence of CH_2 and CHD. The absence of a methine resonance also indicates that the insertion into the Sm−D bond occurs in the sterically less hindered 1,2-fashion.

Although these data indicate that insertion into the Sm−D bond proceeds as outlined in the top and left-hand side of Scheme 4, another process must be occurring which gives the *m*/*z* 586.1 signal which corresponds to $C_{32}D_{65}H(C_5H_{10})$. The ^{1}H NMR spectrum is also consistent with the existence of another process, since it contains two types of methyl peaks: the 0.88 resonance expected for a CH_3 group of the incorporated 1-pentene and a resonance at 0.82 ppm which corresponds to a CD_2H group.

The FD-MS spectra of the 1-pentene, $CD_2{=}CD_2$, and D_2 reaction products also contain, in the secondary envelope of even carbon peaks, a peak at *m*/*z* 581.1 which corresponds to a $C_{36}D_{74}$ chain into which no 1-pentene has incorporated. This peak, like the *m*/*z* 587.1 peak described above, also has associated with it a peak one mass unit lower which has significant intensity. This peak, at *m*/*z* 580.1, corresponds to $C_{36}D_{73}H$, i.e. a product with hydrogen substituted for deuterium. Hence, the FD-MS data show that both types of polymers in the sample, i.e. in both polyethylene and polyethylene containing 1-pentene, have chains with masses consistent with the presence of an extra hydrogen in place of deuterium.

Table 7. Summary of Number Average Molecular Weight with Varying Ethylene to Hydrogen Ratio and Addition of 1-Heptene

ethylene to hydrogen	1-heptene equiv/Sm	M_n by GPC (g/mol)
100:0		18 000
94:1		7 500
4:1		3 300
4:1	6	1 300
4:1	250	750

Metalation as a Termination Step. A process which is independent of the olefin incorporation mechanism and which explains the presence of an extra hydrogen in place of deuterium is termination of the oligomer chains by metalation of 1-pentene. Metalation of the protio-1-pentene would form an allyl complex and a polymer with one less deuterium and one more hydrogen as shown in the right-hand side of Scheme 4. All of the data obtained on the copolymerization systems support this mechanism. The control reaction of $CD_2{=}CD_2$ with $(C_5Me_5)_2Sm$ under D_2 with a DCl quench established that, in the absence of 1-pentene, no CD_2H products are observed by either FD-MS or NMR. Hence, the extra hydrogen in the $C_nD_{2n+1}H$ chains must come from the 1-pentene, the only new source of hydrogen. Decreasing the amount of 1-pentene should decrease not only the amount of insertion but also the amount of metalation. This is observed. As the 1-pentene is decreased from 120 to 75 equiv/Sm, the amount of odd carbon chains decreased from 95 to 75% and the amount of chains which have one hydrogen in place of deuterium increased from 65 to 35% (Table 5). The fact that the decrease in odd carbon chains differs from the decrease in chains with H in place of D is consistent with the proposal that these reactions are separate processes. The separate nature of these processes is also supported by the fact that the polyethylene which contains no incorporated α-olefin also has hydrogen in place of deuterium.

Since metalation is a termination step as shown in Scheme 4, increasing the amount of olefin should decrease the molecular weight of the product. This is also observed as summarized in Table 7. Reaction of $(C_5Me_5)_2Sm$ with ethylene in the absence of hydrogen with quenching after 5 min produces a polymer with a M_n of 18 000. Addition of hydrogen (94:1 ethylene to hydrogen) reduces M_n to 7 500. Increasing the amount of hydrogen (4:1 ethylene to hydrogen) produced a polymer with a M_n of 3 300. Addition of 6.5 equiv of 1-heptene per Sm to a reaction of ethylene and hydrogen (4:1) reduces M_n to 1300, and 250 equiv of 1-heptene per Sm reduces M_n further to 750 g/mol. These data show that metalation is competitive with hydrogenolysis as a termination step.

Although metalation has been mentioned in the literature in the past as one of several possible termination steps,[34] this is the first definitive evidence for this process occurring during a reaction forming solid polymers. This result is consistent with the observation in other lanthanide-based polymerization studies that, as the concentration of olefin is increased in copolymerization reactions, the average molecular weight of the polymer decreases.[18,21]

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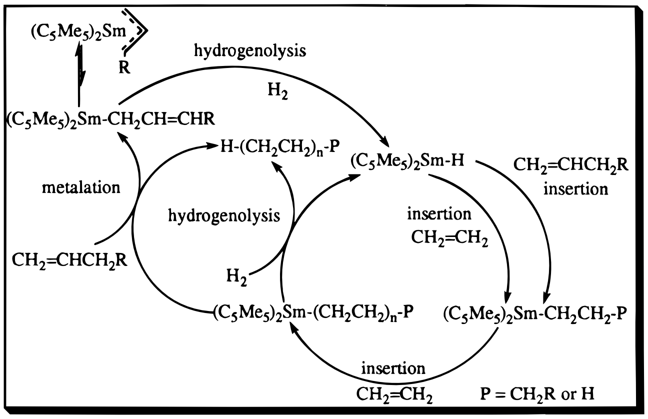
(34) For example see ref 7, p 8110.

Scheme 5. Proposed Catalytic Cycle for Reactions of Olefins with Ethylene under Hydrogen Using Samarium (R = H, Propene; R = Et, Pentene; R = Bu, Heptene)



Internal Alkene Reactions. The validity of Scheme 4 can be examined using the data on internal alkenes. Internal alkenes should also undergo metalation, but smaller amounts of incorporation should occur. This is observed for all of the internal olefins examined. For example, reactions with *cis*- and *trans*-2-pentene yielded FD-MS data and ^1H NMR signals similar to those obtained with 1-pentene, i.e. signals with one hydrogen in place of deuterium were significant, except that less incorporation of olefin was observed. Since insertion of 2-pentene into a Sm−D bond should generate a methine resonance in the ^1H NMR spectrum and this is not observed, it is likely that 2-pentene is isomerized to 1-pentene before incorporation occurs.

Summary. All of this information can be condensed into a single catalytic scheme as shown in Scheme 5. Overall, olefin incorporation occurs by insertion of the olefin into a Sm−H bond. This is the most sterically accessible insertion. In addition, this is consistent with the slow homopolymerization of α-olefins by $(C_5Me_5)_2Sm$, which indicates that insertion of substituted olefins into Sm−C bonds is not facile in this system.

The catalytic cycle can be entered by generation of a samarium hydride,[20] which can occur by hydrogenolysis of either a samarium allyl unit or a samarium carbon bond of a growing chain. Insertion of either ethylene or $CH_2{=}CHCH_2R$ into the samarium hydride bond leads to a saturated alkyl group at the beginning of the polymer. Insertion of ethylene grows the polymer chain and insertion of $CH_2{=}CHCH_2R$ is not competitive with ethylene insertion. Termination by hydrogenolysis forms a saturated hydrocarbon oligomer chain and regenerates the starting samarium hydride. Termination by metalation of an olefin also forms a saturated hydrocarbon and generates a samarium allyl complex. The $(C_5Me_5)_2Sm$ units in the allyl complexes can get back into the catalytic cycle by hydrogenolysis of the allyl group to form a samarium hydride bond.

As a consequence of this overall mechanism, the olefins are incorporated into the polyethylene as chain extensions and not branches. Therefore, olefins could be used as alternatives to hydrogen for controlling molecular weight without affecting any of the properties of the polymer.

On the basis of these results, some information about relative rates can be deduced for this $(C_5Me_5)_2Sm$-based system. First, several statements about insertion rates can be made. The rate of insertion of $CH_2{=}CHCH_2R$ olefins into samarium alkyl bonds is slower than the rate of insertion of ethylene. This is indicated by the fact that the oligomerization of α-olefins occurs slowly over a period of days, whereas ethylene polymerization occurs in less than 1 h. This is consistent with steric expectations and the results in many other systems.[2] The importance of steric factors on the insertion process is consistent with the fact that insertion into a Sm−H bond is preferred over insertion into a Sm−C bond. Since the rate of insertion of olefins into a Sm−H bond should be less sensitive to steric factors, insertion of both olefins and ethylene appears to occur readily. The relative observed rates will depend on the concentration of olefin and ethylene present. Since the concentration of liquid olefins can be higher at the catalytic center than that of ethylene, olefin insertion can occur in the presence of the more favored ethylene insertion. This is consistent with the fact that amount of odd chain hydrocarbons can be controlled by varying the concentration of olefin.

Second, some statements about the chemistry of the allyl compounds in this system can be made. If the isomerization of the samarium allyl from η^3 to η^1 is the rate-determining step for initiation, then the resting state of the catalytic cycle would be in the red $(C_5Me_5)_2Sm(\eta^3\text{-}CH_2CHCHR)$ form. This is consistent with the orange color observed during the copolymerization reactions in this study in comparison to the yellow color found for polymerization reactions without olefin.[20] The products observed in this system indicate that the rate of hydrogenolysis of an η^1-allyl unit is faster than insertion of ethylene, which is much faster than insertion of olefin. This is why incorporation of the allyl group is not observed during the copolymerization reactions under hydrogen even though allyl groups are being generated by the termination reaction.

Third, some comments about termination can be made. The observed rates of termination by hydrogenolysis and metalation of the olefin must be competitive at the concentrations used during these copolymerization reactions since the FD-MS signals due to chains terminated by metalation can be larger or smaller than the signals due chains terminated by hydrogenolysis depending on the olefin concentration. Although the rate constant of hydrogenolysis may be much larger than that of metalation, the observed rate will depend on the limited solubility of hydrogen in toluene.[35] β-Hydrogen elimination is not competitive under the conditions of these reactions as discussed previously.[20]

Conclusion

Using a combination of FD-MS and NMR spectroscopy, it has been shown that $(C_5Me_5)_2Sm$-based reactions of ethylene with propenes, pentenes, heptenes, octene, and nonadecene primarily lead to polymers in which only one olefin per chain is selectively incorporated. α-Olefins were found to incorporate more readily with ethylene than internal olefins in the expected order

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(35) The mole fraction solubility of ethylene is 0.0153 and the mole fraction solubility of hydrogen is 0.000 317 in toluene at 298.2 K and 1.013 bar: Fogg, P. G. T.; Gerrand, W. In *Solubility of Gases in Liquids*; John Wiley and Sons: New York, 1991; pp 133−138, 300−312.

1-alkene ≫ 2-alkene > 3-alkene. The incorporation of olefins was found to occur by insertion into a samarium−hydride bond to form a saturated polymer rather than from an allyl group. Allyl complex formation does occur in this system by metalation of the olefin by samarium alkyl moieties in a chain termination step.

This study demonstrates that metalation of olefins can be an important termination process in ethylene/olefin copolymerization reactions. Metalation is competitive with hydrogenolysis as a termination process, and the amount of olefin present can control the molecular weight. Since the results show that metalation can be as effective as hydrogenolysis as a termination process and since hydrogenolysis is much faster than β-hydrogen elimination, this means that metalation can be used to control the molecular weight in polyethylene systems without the use of hydrogen. Since the results show that the olefin is incorporated as a chain extension of polyethylene, using the olefin as a termination agent should not affect the properties of polyethylene other than the molecular weight distribution.

Finally, this study also shows how much information can be gained by field desorption mass spectrometry on reaction mechanisms leading to solid products in a complicated polymerization system. It seems that FD-MS has considerable potential for application to other complex reactions which form solids.

Acknowledgment. We thank the National Science Foundation for support of this research and Professor Kenneth J. Shea for helpful discussions.

Supporting Information Available: Additional field desorption mass spectra (28 pages). Ordering information is given on any current masthead page.

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