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Tantalum- and Titanium-Based Catalytic Systems for the Synthesis of Hyperbranched Polyethene

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Abstract: Hyperbranched polyethene was synthesized using a novel $TaCl_5$/alkylaluminum halide catalyst system. The polymers were viscous oils with a ratio of methyl hydrogens/total alkyl hydrogens of 0.25−0.40 and weight-average molecular weights of 600−4000 daltons. Both branching and molecular weight can be varied by changing reaction conditions and catalyst composition. The system can also be modified to synthesize 1-alkenes (principally, 1-hexene). A second system, involving $TiCl_4$/alkylaluminum halide, also gave hyperbranched polyethene, with a ratio of methyl hydrogens/total alkyl hydrogens of 0.10−0.25. Weight-average molecular weights varied from 900 to 1800 daltons. Higher selectivity to liquid product was achieved through the addition of dihydrogen. The mechanism of the formation of branched polyethene appears to involve, for the most part, oligomerization of ethene to 1-alkenes (principally 1-hexene) by a transition metal alkyl species followed by cationic oligomerization of the 1-alkenes by Lewis acidic species. The addition of tetraalkylammonium chloride to the $TaCl_5/Et_3Al$ system resulted in a change in product selectivity from all polyethene to >65% 1-hexene. The highly selective trimerization of ethene by the tantalum system is unusual.

An important goal in the polymerization of alkenes is the synthesis of low molecular weight (ca. 500−5000 daltons) hyperbranched polymers from inexpensive monomers such as ethene and propene. Such polymers are useful in the lubricant industry as base stocks and precursors to lubricant additives. Indeed, the demand for synthetic lubricant materials is rising.[1] Almost half of all synthetic lubricant base stocks are polymers of higher 1-alkenes, usually 1-decene. Despite the increasing demand for synthetic lubricants, 1-alkene capacity has not increased significantly. The advent of a lubricant material synthesized directly from a plentiful and less expensive monomer such as ethene is, therefore, of great current interest.

We have recently reported the synthesis of hyperbranched polymers from ethene using nickel and palladium catalysts.[2] The polymers synthesized had weight-average molecular weights (relative to polystyrene standards) ranging from 400 to 1100 daltons and ratios of methyl hydrogens to total aliphatic hydrogens (H_{Me}/H_{tot}, obtained from integration of ^{1}H NMR spectra) from 0.4 to 0.65 ($H_{Me}/H_{tot} = 0$ for totally linear polyethene). However, the reactions catalyzed by nickel compounds were highly exothermic, and both the nickel and palladium catalysts produced a significant amount of butenes that essentially represented wasted monomer. Because of the higher tendency of late transition metal alkyls to undergo β-hydrogen abstraction, we examined early transition metal compounds as possible catalysts for the synthesis of hyperbranched polyethene. The titanium-based synthesis of branched polymers from ethene has been reported previously; however, the detailed structures of the polymers and the reaction mechanism were not investigated.[3,4]

Our catalytic systems involve two components: an early transition metal halide and an alkylaluminum halide. Unlike trialkylaluminum, alkylaluminum halides are fairly strong Lewis acids, a property that appears to be essential for the formation of hyperbranched polyethene.

Experimental Section

Materials. C.P. or higher grade chemicals were used as received unless otherwise noted. Ethylaluminum dichloride (1 M solution in hexanes), diethylaluminum chloride (1 M solution in hexanes), and ethylaluminum sesquichloride, $TiCl_4$, and $TaCl_5$ (each 99.999% pure) were purchased from Aldrich. Aluminum trichloride was purchased from Strem or Aldrich. 2,6-Di-*tert*-butylpyridine was purchased from Aldrich and was dried over molecular sieves and freeze−thaw degassed before use. Hex-1-ene, obtained from Chevron, was distilled from CaH_2 and freeze−thaw degassed before use. Distearyldimethylammonium chloride was purchased from TCI. Dihydrogen was purchased from MG Industries. Ethene was purchased from MG Industries or Air Products. Chlorobenzene and hexanes used for polymerizations were dried over calcium hydride, distilled under vacuum or nitrogen, and freeze−thaw degassed.

General Methods. All catalyst manipulations and polymerization setups were performed in a nitrogen-filled glovebox. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker WP-200 or a AM-300 (later upgraded to DPX-300) FT-NMR spectrometer. DEPT 135 spectra were obtained on a Bruker AMX-500 FT-NMR spectrometer. Liquids were analyzed in $CDCl_3$ solution at ambient temperature; solids were analyzed in 1,2-dichlorobenzene (a DMSO-d_6 capillary was used for obtaining a lock) at 120 °C. Chemical shifts were referenced to hexamethyldisiloxane or to the residual protic chloroform resonance at 7.27 ppm. Molecular weights of polymers were measured in $CHCl_3$ on a Waters Associates liquid/gel permeation chromatograph equipped with Styragel columns and a differential refractometer detector. Polystyrene standards were used for calibration. GC analyses of reactions involving 2,6-di-*tert*-

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Table 1. Ethene Polymerization Results via $TaCl_5/EtAlCl_2$ Catalysis[f]

entry	equiv of $EtAlCl_2$[a]	solvent	pressure (psi)	temp (°C)	liquid yield (g)[b]	M_n[c]	M_w[c]	M_w/M_n[c]	H_{Me}/H_{tot}
1	1	C_6H_5Cl	700	45	4.2	1310	2070	1.6	0.30
2	10	C_6H_5Cl	700	45	2.5	1240	1590	1.3	0.32
3	0.1	C_6H_5Cl	700	45	0.2	570	660	1.2	0.34
4	1	C_6H_5Cl	150	45	2.0	1540	2020	1.3	0.32
5	1	C_6H_5Cl	700	25	2.7	2040	3870	1.9	0.33
6	1	C_6H_5Cl	700	75	5.6	890	1310	1.5	0.27
7[d]	1	hexanes	700	45	1.4	970	1300	1.3	0.40
8[d]	1	C_6H_5Cl	700	45	4.1	1060	1590	1.5	0.40
9[e]	1	C_6H_5Cl	700	45	4.4	1010	1440	1.4	0.31

[a] 1 M solution in hexanes. [b] After evaporation at 0.1 Torr, 25 °C. [c] Determined by GPC in $CHCl_3$ solvent, relative to polystyrene standards. [d] 2.00 mmol of $AlCl_3$ added. [e] 10 psi single hydrogen charge added before monomer. [f] Conditions: 0.20 mmol of $TaCl_5$; 10 mL of solvent; 16 h; 125 mL stainless steel autoclave.

Table 2. Effect of Changing Cocatalyst in Ta-Based Catalytic Ethene Polymerization[d]

entry	cocatalyst	liquid yield (g)[a]	M_n[b]	M_w[b]	M_w/M_n[b]	H_{Me}/H_{tot}
1	$EtAlCl_2$[c]	4.2	1310	2070	1.6	0.30
2	$Et_3Al_2Cl_3$	2.4	1780	3080	1.7	0.32
3	Et_2AlCl[c]	2.5	920	1410	1.5	0.32

[a] After evaporation at 0.1 Torr, 25 °C. [b] Determined by GPC in $CHCl_3$ solvent, relative to polystyrene standards. [c] 1 M solution in hexanes. [d] Conditions: 0.20 mmol of $TaCl_5$; 1 equiv of Al; 16 h; 10 mL of C_6H_5Cl solvent; 700 psi constant feed of ethene; 45 °C; 125 mL stainless steel autoclave.

Table 3. 1-Hexene Polymerization Results via $TaCl_5/EtAlCl_2$ Catalysis[a]

entry	$TaCl_5$ (mmol)	$EtAlCl_2$ (mmol)	yield (g)	H_{Me}/H_{tot}
1	0.20	0.20	1.95	0.29
2	0.20		0.53	0.35
3		0.20	0.25	0.27

[a] Conditions: 2.0 g of 1-hexene; 10 mL of C_6H_5Cl; 700 psi of N_2; 45 °C; 16 h; 125 mL stainless steel autoclave.

butylpyridine were performed on a Hewlett-Packard HP5980 Series II gas chromatograph coupled to a Hewlett-Packard HP 5972 Series mass selective detector. The GC was equipped with a flame ionization detector and a J & W Scientific DB-5 MS fused silica capillary column (30 m × 0.25 mm). The temperature was ramped as follows: initial temperature of 35 °C for 4 min, ramp at 6 deg C/min to 310 °C, followed by holding at 310 °C for 20 min. GC analyses for reactions involving distearyldimethylammonium chloride were performed on a Varian Model 3700 gas chromatograph equipped with a flame ionization detector and a Supelco 10% SP-2100 on 100/120 Supelcoport packed column. The temperature was ramped as follows: initial temperature of 30 °C for 5 min, ramp at 2 deg C/min to 250 °C, followed by holding at 250 °C until all volatiles had eluted. Thermal analyses were performed under an argon purge on a Perkin-Elmer DSC7 differential scanning calorimeter; a heating rate of 20 deg C/min was used.

General Procedure for the Tantalum-Catalyzed Polymerization of Ethene (See Tables 1 and 2 for Specific Details). $TaCl_5$ (72 mg, 0.20 mmol) and the appropriate amount of alkyl aluminum cocatalyst were combined in 10 mL of solvent in a glass autoclave liner equipped with a Teflon-coated stir bar to give a brown mixture. The 125 mL stainless steel autoclave was assembled then heated to the specified temperature. A constant feed of ethene was introduced, and the mixture was stirred for 16 h. The autoclave was then vented of excess ethene, and a small amount of methanol was added to quench the reaction. The product mixture was taken into approximately 40 mL of chloroform and filtered (usually, less than 5% of the total product was insoluble waxy solid). The filtrate was passed through neutral alumina or silica and dried under vacuum to yield the liquid product as a colorless to yellow oil. ^1H NMR ($CDCl_3$) (ppm): 1.3 (br), 0.8 (br).

Tantalum-Catalyzed Polymerization of Ethene: Catalyst Lifetime Study. $TaCl_5$ (72 mg, 0.20 mmol) and $EtAlCl_2$ solution (0.20 mL of a 1 M solution in hexanes, 0.20 mmol) were combined in 10 mL of chlorobenzene in a glass autoclave liner equipped with a Teflon-coated stir bar to give a brown mixture. The 125 mL stainless steel autoclave was then assembled and heated to 45 °C. The autoclave was charged to 700 psi with ethene, and the reaction mixture was stirred at 45 °C. Ethene was recharged at 16, 40, and 62 h. Pressure drops were noted before each recharge and at the end of the reaction (86 h). At the end of the reaction, the autoclave was vented of excess ethene, and a small amount of methanol was added to quench the reaction. The product mixture was taken into approximately 40 mL of chloroform and filtered. The filtrate was passed through neutral alumina and dried under vacuum to give 6.7 g of soft, highly viscous, cloudy white material. ^1H NMR ($CDCl_3$) (ppm): 5.8 (m), 4.9 (m), 1.9 (br), 1.3 (br), 0.8 (br).

General Procedure for the Tantalum-Catalyzed Polymerization of 1-Hexene in Chlorobenzene (See Table 3 for Specific Details). $TaCl_5$ (72 mg, 0.20 mmol) was dissolved in 10 mL of chlorobenzene in a glass autoclave liner equipped with a Teflon-coated stir bar to give a pale yellow solution. Ethylaluminum dichloride (150 mg, 0.20 mmol) was added and turned the solution to dark brown. A portion of 1-hexene (2.0 g, 24 mmol) was then added to the solution, with no visible signs of change. The 125 mL stainless steel autoclave was charged with 700 psi of dinitrogen, and the mixture was stirred at 45 °C for 16 h. The autoclave was then chilled in ice for 30 min and vented of dinitrogen, and a small amount of methanol was added to quench the reaction (the product mixture turned from brown to colorless). The product mixture was taken into 20 mL of chloroform and filtered. The filtrate was passed through neutral alumina and dried under vacuum to yield the liquid product as a cloudy, colorless oil. ^1H NMR ($CDCl_3$) (ppm): 2.0 (br), 1.2 (br), 0.8 (br).

General Procedure for the Titanium-Catalyzed Polymerization of Ethene in Chlorobenzene (See Tables 4 and 5 for Specific Details). $TiCl_4$ (38 mg, 0.20 mmol) was dissolved in 10 mL of chlorobenzene in a glass autoclave liner equipped with a Teflon-coated stir bar to give a yellow solution. Ethylaluminum dichloride (0.20 mL of a 1 M solution in hexanes, 0.20 mmol) was added and turned the solution to darker yellow. The 125 mL stainless steel autoclave was assembled and stirred at room temperature for 12 h under a constant 50 psi feed of ethene. The autoclave was then vented of excess ethene, and a small amount of methanol was added to quench the reaction (the product mixture turned from red-brown to colorless). The product mixture was taken into approximately 40 mL of chloroform and filtered. The filtrate was passed through neutral alumina or silica and dried under vacuum to yield the liquid product as a colorless to yellow oil. ^1H NMR ($CDCl_3$) (ppm): 5.4 (br), 5.0 (br), 1.3 (br), 0.9 (br).

Addition of Tetraalkylammonium Chloride to the $TaCl_5/AlEt_3$ Catalyst System. $TaCl_5$ (72 mg, 0.20 mmol) was partially dissolved in 10 mL of chlorobenzene in a glass autoclave liner equipped with a magnetic stir bar to give a pale yellow mixture. Triethylaluminum (23 mg, 0.20 mmol) was added, turning the mixture deep brown. Distearyldimethylammonium chloride (122 mg, 0.21 mmol) was also added. The autoclave was assembled and heated to 45 °C, and a constant 700 psi feed of ethene was introduced for 16 h. The autoclave was then chilled in ice for 30 min and vented of excess ethene, and a small amount of methanol was added to quench the reaction (the product mixture turned from brown to colorless). The liquid portion was analyzed by GC and was found to contain approximately 1.35 g of

Table 4. Ethene Polymerization Results via $TiCl_4/EtAlCl_2$ Catalysis: Liquid Fractions[h]

entry	equiv of $EtAlCl_2$[a]	addnl. cocatalys	solvent	liquid yield (g)[b]	M_n[c]	M_w[c]	M_w/M_n[c]	H_{Me}/H_{tot}
1	5		C_6H_5Cl	3.0	920	1420	1.5	0.23
2	5		hexanes	nil				
3	5	10 $AlCl_3$	C_6H_5Cl	4.1	1220	1800	1.5	0.23
4	5	5 dtbp[d]	C_6H_5Cl	1.3	820, 140[e]	980, 150[e]	1.2, 1.1[e]	0.13
5[f]	1	20 $AlCl_3$	hexanes	3.7	1140	1560	1.4	0.23
6[f]	5	H_2[g]	C_6H_5Cl	4.5	850	1300	1.5	0.23

[a] 1 M solution in hexanes. [b] After evaporation at 0.1 Torr, 25 °C. [c] Determined by GPC in $CHCl_3$ solvent, relative to polystyrene standards. [d] dtbp = 2,6-di-*tert*-butylpyridine. [e] Bimodal distribution: data are for each peak. [f] 17 h reaction. [g] 10 psi single charge. [h] Conditions: 0.20 mmol of $TiCl_4$; 10 mL of solvent; 50 psi constant feed of ethene; room temperature; 12 h; 125 mL stainless steel autoclave.

Table 5. Ethene Polymerization Results via $TiCl_4/EtAlCl_2$ Catalysis: Solid Fractions[c]

entry	equiv of $EtAlCl_2$[a]	addnl. cocatalyst	solvent	solid yield (g)	T_m (°C)	H_{Me}/H_{tot}
1	5		C_6H_5Cl	1.3	87, 119	0.16
2	5		hexanes	4.6	127	0.07
3	5	10 $AlCl_3$	C_6H_5Cl	1.5	86, 121	0.19
4	5	5 dtbp[b]	C_6H_5Cl	4.5	125	0.02

[a] 1 M solution in hexanes. [b] dtbp = 2,6-di-*tert*-butylpyridine. [c] Conditions: 0.20 mmol of $TiCl_4$; 10 mL of solvent; 50 psi constant feed of ethene; room temperature; 12 h; 125 mL stainless steel autoclave.

1-hexene, which comprised approximately 87% of the volatile liquid product. The remaining product solution was filtered, and the filtrate was dried under vacuum to yield 0.2 g of viscous oil ($H_{Me}/H_{tot} = 0.11$). The solid portion of the product was washed with 1.5 M methanolicHCl, followed by methanol, then dried under vacuum to yield 0.2 g of white solid.

Addition of Tetraalkylammonium Chloride to the $TiCl_4/AlEt_3$ Catalyst System. Triethylaluminum (31 mg, 0.27 mmol) and distearyldimethylammonium chloride (156 mg, 0.27 mmol) were dissolved in 10 mL of chlorobenzene in a glass autoclave liner equipped with a magnetic stir bar to give a colorless solution. $TiCl_4$ (5.5 μL, 0.05 mmol) was added, turning the solution orange. The autoclave was assembled and a constant 50 psi feed of ethene was introduced. The reaction was allowed to proceed for 12 h at room temperature, after which the autoclave was vented to reveal a brown solution. An aliquot of the liquid portion was analyzed by ^1H NMR and showed no new products. The volatiles were evaporated to yield only catalyst residue.

Results and Discussion

A. Tantalum-Based Catalyst System. 1. Hyperbranched Polyethene Synthesis Catalyzed by $TaCl_5$/Alkylaluminum Halide.

The results are shown in Table 1. $TaCl_5$ is partially soluble (giving a pale yellow solution) in chlorobenzene and insoluble in hexanes. However, when $EtAlCl_2$ was added, the catalyst mixture turned brown in chlorobenzene and green-brown (slurry) in hexanes. We hypothesize that alkylation of tantalum, in addition to coordination and/or insertion of ethene, allows the catalyst to dissolve and react with appreciable activity.

For the reaction at 75 °C (Table 1, entry 6), 5.6 g of branched liquid was obtained from a catalyst loading of 0.20 mmol of tantalum, translating to an activity of 1.8 kg of polyethene/mol of Ta per h, or about 60 turnovers/h.

Ethylaluminum dichloride is indeed essential for polymer synthesis to proceed. One to five equivalents per tantalum appears to be optimal. The use of 0.1 equiv of $EtAlCl_2$ gave less polymer, and the polymer molecular weight was drastically reduced (Table 1, entry 3). On the other hand, raising the concentration of $EtAlCl_2$ from 1 to 10 equiv resulted in reduced yield with approximately the same molecular weight (Table 1, entry 2).

Changing the aluminum cocatalyst from $EtAlCl_2$ to other alkylaluminum halides (Table 2) reduced yields somewhat, but branching was unaffected. Halide content (and therefore, Lewis acidity) in the cocatalyst was essential for liquid production, as the use of $AlEt_3$ as a cocatalyst resulted in almost completely solid product (however, see the section on chloride effect).

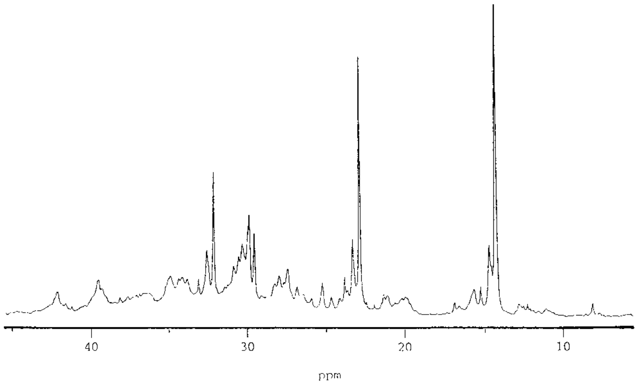

Figure 1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum of hyperbranched polymer synthesized via $TaCl_5/EtAlCl_2$ catalysis.

When a small amount of dihydrogen was added to the catalyst mixture, the molecular weight decreased slightly (Table 1, entry 9). In an effort to vary polymer branching, $AlCl_3$ was added as a third catalyst component (Table 1, entry 8). The increased Lewis acidity of the system did indeed result in an increase in branching to $H_{Me}/H_{tot} = 0.40$, compared to 0.30 when no $AlCl_3$ was used.

An increase in reaction temperature resulted in higher yields and lower molecular weights (Table 1, entries 1, 5, and 6). The ability to vary molecular weight would be advantageous when a change in product viscosity is desired. A decrease in pressure (and therefore, monomer concentration) resulted in a decreased yield, as expected (Table 1, entry 4 vs 1).

When the polymerization reaction was run in hexanes without a third cocatalyst, no product was formed. When the reaction was run in hexanes (Table 1, entry 7) with 10 equiv of $AlCl_3$ added, the yield was still low, as was expected due to the low solubility of $TaCl_5$ and $AlCl_3$ in nonpolar solvents.

The ^{13}C NMR spectrum ($CDCl_3$ solvent, Figure 1) of the polymer synthesized in chlorobenzene is fairly complex, but some comments can be made based on previous reports.[5] The following resonances (ppm) can be attributed to long ($\geq C_5$) branches: 32.4 [$(CH_2)_n\mathbf{CH_2}CH_3CH_3$], 30.2 and 29.9 ($CH_2$ groups near the middle of long branches), 23.2 [$(CH_2)_nCH_2\mathbf{CH_2}CH_3$], and 14.6 [$(CH_2)_nCH_2CH_2\mathbf{CH_3}$], where $n \geq 2$.

The CH_2 resonance at 30.2 ppm can be ascribed to both CH_2 groups in long branches, as well as in the main chain. There are many smaller peaks in the spectrum that could correspond to shorter branches, but they are not sufficiently resolved. The

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[5] Nelson, L. T. J.; McCord, E. F.; Johnson, L. K.; McLain, S. J.; Ittle, S. D.; Killian, C. M.; Brookhart, M. Presented at the 213th National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, 1997; POLY.

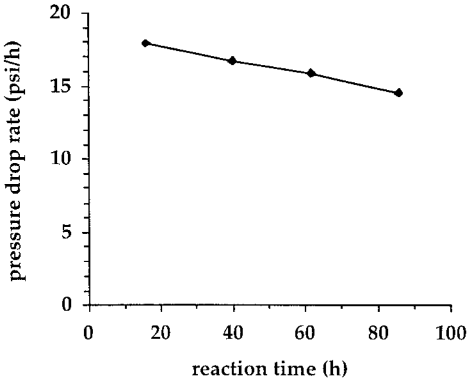

Figure 2. Tantalum catalyst lifetime: ethene pressure drops versus time.

lack of a visible baseline throughout the aliphatic region of the ^{13}C NMR spectrum suggests that cationic rearrangements and/or oligomerization may be involved in the polymerization mechanism (vide infra).

To examine the robustness of the catalyst, a catalyst lifetime experiment was conducted, in which ethene was charged into an autoclave containing $TaCl_5$ and $EtAlCl_2$. Approximately every 20 h, the autoclave was repressurized. Ethene was charged a total of four times. The rate of pressure drop versus time is plotted in Figure 2. The graph shows that ethene consumption decreases slightly with time, which would indicate decreasing catalyst activity. However, the situation is complicated by issues such as dynamic solvent polarity (solvent becomes less polar as product is synthesized) and mass transfer. Additionally, the product obtained after multiple ethene charges contained a significant amount of 1-alkenes (vide infra), as evidenced by ^1H and ^{13}C NMR spectroscopy. Indeed, the product was less branched ($H_{Me}/H_{tot} = 0.25$) than the product typically obtained after reactions of shorter duration. Lower branching is to be expected if there is a significant amount of 1-alkenes present in addition to the hyperbranched polymer. Thus, while the tantalum catalyst may be very robust, it is the subsequent cationic polymerization (vide infra) that is shorter-lived, resulting in large amounts of unconverted 1-alkenes.

2. Mechanistic Considerations. There are two possible mechanistic scenarios for the formation of a branched polymer from ethene. The first involves β-hydrogen abstraction from a growing polymer chain, followed by readdition of the resultant coordinated vinyl-ended polymer to the metal hydride, a process that competes with polymer chain growth.[6] The second mechanism involves ethene oligomerization to 1-alkenes followed by their cationic rearrangement and/or oligomerization (eq 1).

$$CH_2{=}CH_2 \xrightarrow{TaCl_5/R_xAlCl_{3-x}} \text{1-alkenes} \xrightarrow{TaCl_5/R_xAlCl_{3-x}} \text{hyperbranched polyethene} \qquad (1)$$

The compound 2,6-di-*tert*-butylpyridine is known to inhibit cationic rearrangements and oligomerizations by acting as a proton sponge.[7] Accordingly, to test the validity of the mechanism shown in eq 1, 2,6-di-*tert*-butylpyridine was added (1 equiv per Al) to a 1:1 mixture of $TaCl_5$ and $EtAlCl_2$ in chlorobenzene. After 16 h of stirring at 45 °C under a constant 700 psi feed of ethene, 1-hexene (45%) along with a Schulz-Flory distribution[8] of 1-alkenes (55%) having $\alpha = 0.73$ was obtained (see Figure 3 for a gas chromatogram of the higher boiling fraction). In the gas chromatogram, minor peaks corresponding to other products were also present. The peaks between the major (linear 1-alkenes) peaks correspond to branched 1-alkenes, while the other extraneous peaks correspond to products formed by alkylation of chlorobenzene (solvent). *The high selectivity for 1-hexene is particularly intriguing.* To our knowledge, apart from a few chromium-based systems,[9] the selective trimerization of ethene has not been observed with other transition metal catalysts.

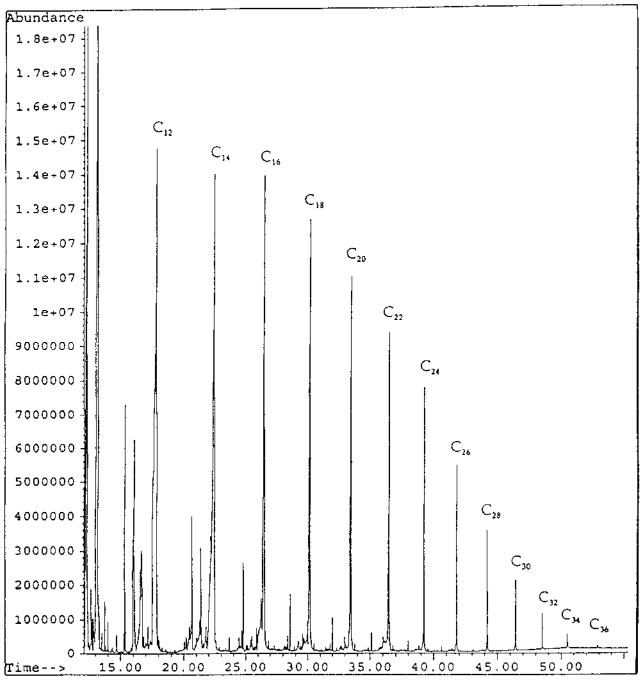

Figure 3. Gas chromatogram for the higher boiling fraction of the 1-alkene product obtained from tantalum-catalyzed ethene oligomerization in the presence of 2,6-di-*tert*-butylpyridine.

The formation of 1-alkenes (principally 1-hexene), rather than branched polymer, upon the addition of 2,6-di-*tert*-butylpyridine suggests that hyperbranched polyethene synthesis catalyzed by $TaCl_5$/alkylaluminum halide proceeds by the two-step mechanism shown in eq 1. To confirm this possibility, the polymerization of 1-hexene was attempted under similar conditions. As detailed in Table 3, viscous liquids with branching and NMR spectra similar to those derived from ethene were obtained.

B. Titanium-Based Catalyst System. 1. Hyperbranched Polyethene Synthesis Catalyzed by $TiCl_4$/Alkylaluminum Halide. The results are shown in Tables 4, 5, and 6. Under the conditions employed by us, the use of $TiCl_4$ and $EtAlCl_2$ gave a hyperbranched ($H_{Me}/H_{tot} = 0.23$) liquid polymer (1.3 kg of liquid polyethene/mol of Ti per h). However, 30% of the product was a waxy solid. Therefore, we explored the use of a third catalyst component in an effort to effect higher selectivity to liquid product and, perhaps, tailor branching.

The use of dihydrogen, a common chain transfer agent in the coordination polymerization of alkenes,[10] resulted in 50%

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Table 6. Ethene Polymerization via $TiCl_4/EtAlCl_2$ Catalysis: Concentration Effects[e]

entry	solvent vol (mL)	liquid yield (g)[a]	M_n[b]	M_w[b]	M_n/M_w[b]	H_{Me}/H_{tot}
1[c]	10	4.5	850	1670	1.5	0.23
2[d]	40	18.9	910	1300	1.4	0.23

[a] After evaporation at 0.1 Torr, 25 °C. [b] Determined by GPC in $CHCl_3$ solvent, relative to polystyrene standards. [c] Peformed in a 125 mL autoclave. [d] Performed in a 300 mL autoclave. [e] Conditions: 0.20 mmol of $TiCl_4$; 1.00 mmol of $EtAlCl_2$ (1 M in hexanes); 10 psi feed of single hydrogen charge; 50 psi constant feed of ethene; C_6H_5Cl solvent; room temperature; 16 h.

more liquid product and only a small amount of solid (Table 4, entry 6).

Lowering the catalyst concentration resulted in higher activity, as shown in Table 6. Using the $TiCl_4/EtAlCl_2/H_2$ system, an increase in solvent from 10 mL to 40 mL (in a larger, mechanically stirred reactor with all other conditions being the same) yielded quadruple the amount of branched liquid (molecular weights and branching of the products were nearly equal). The activity for the reaction in 10 mL of chlorobenzene was 1.4 kg of polyethene/mol of Ti per h (Table 6, entry 1), whereas the activity in 40 mL of solvent was 5.9 kg of polyethene/mol of Ti per h (Table 6, entry 2).

As with the tantalum-based system, the use of the less Lewis acidic $AlEt_3$ resulted in a typical Ziegler system with linear polyethene as the sole product. On the other hand, the addition of 10 equiv of $AlCl_3$ to the $TiCl_4/EtAlCl_2$ mixture resulted in an increase in the amount of liquid product but not in the amount of solid polyethene (Table 4, entry 3; Table 5, entry 3). Interestingly, the degree of branching of the liquid was unchanged while the molecular weight was significantly higher.

The choice of solvent appears to have a profound influence on the course of the polymerization. Under the conditions employed by us, the substitution of hexanes for chlorobenzene resulted in essentially total selectivity to solid product (Table 4, entry 2; Table 5, entry 2). Additionally, the degree of branching in the solid product was lower. However, when a large excess of the Lewis acid $AlCl_3$ was added to the reaction mixture in hexanes, the product branching increased and the molecular weight decreased, giving near total selectivity to a viscous liquid product (Table 4, entry 5).

The reactions in Table 5 all gave significant amounts of solid product (insoluble in $CHCl_3$). The reaction in entry 2, performed in hexanes, gave a nongreasy, fluffy solid with a single T_m at 127 °C and a 99 J/g heat of melting, indicating that the polymer was lightly branched. This conclusion was confirmed by NMR analysis which yielded $H_{Me}/H_{tot} = 0.07$.

The solids from entries 1 and 3, however, were fairly greasy and each showed two melt transitions. Not surprisingly, the solid from entry 3, in which $AlCl_3$ was added to the catalyst mixture, had lower enthalpies of melting as a result of lower crystallinity due to higher branching.

The solid from entry 4, which was formed using a catalyst mixture that contained 2,6-di-*tert*-butylpyridine, a proton scavenger, was moderately crystalline with $T_m = 125$ °C and a very low branching ($H_{Me}/H_{tot} = 0.02$). The linearity of this polymer has mechanistic implications (vide infra).

The liquid polymer obtained using the titanium-based system was highly branched with a variety of branches. However, ^{13}C (Figure 4) and DEPT ^{13}C (Figure 5) NMR spectra (in $CDCl_3$), when compared to previously reported spectra for branched hydrocarbon polymers,[5] provide us with a fairly clear picture of the polymer microstructure.

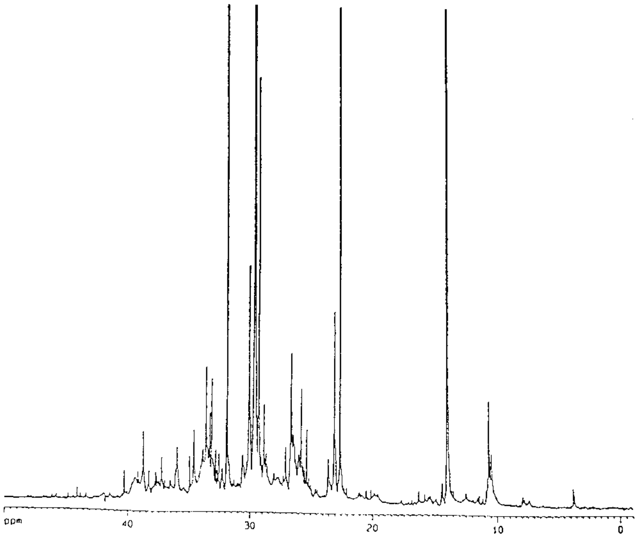

Figure 4. $^{13}C\{^1H\}$ NMR ($CDCl_3$) spectrum of hyperbranched polymer synthesized via $TiCl_4/EtAlCl_2$ catalysis.

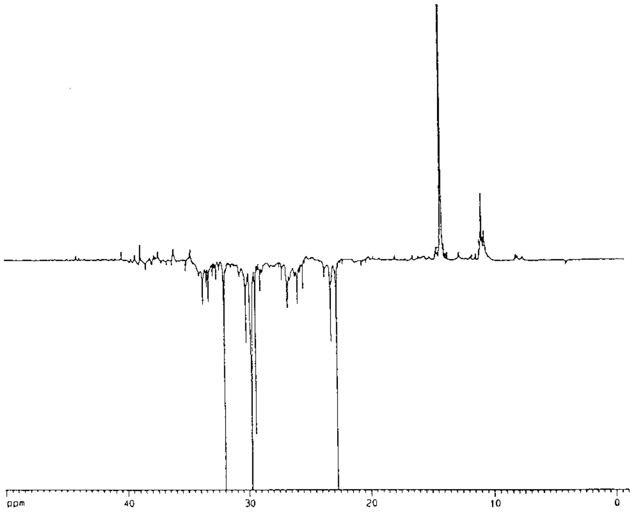

Figure 5. DEPT-135 ^{13}C NMR spectrum of hyperbranched polymer synthesized via $TiCl_4/EtAlCl_2$ catalysis.

The polymer contains ethyl branches as evidenced by resonances at 10.6 ($CH_2\mathbf{CH_3}$) and 26.4 ppm ($\mathbf{CH_2}CH_3$). Propyl branches may be present in low amounts: peaks at 14.4 ($CH_2CH_2\mathbf{CH_3}$), 21.0 ($CH_2\mathbf{CH_2}CH_3$), and 36.0 ($\mathbf{CH_2}CH_2CH_3$) appear in fairly low intensity. Butyl branches are apparent from the peaks at 14.1 ($CH_2CH_2CH_2\mathbf{CH_3}$), 23.1 ($CH_2CH_2\mathbf{CH_2}CH_3$), 30.1 ($CH_2\mathbf{CH_2}CH_2CH_3$), and one of the resonances between 32 and 34 ppm ($\mathbf{CH_2}CH_2CH_2CH_3$). It should be noted that the methyl resonance at 14.0 ppm is quite intense, and we ascribe this peak to the terminal methyls of linear branches that are C_4 and higher.

As the branch length increases, the methylene units in the middle of the branch tend to have the same chemical shift as that of linear polyethene (29.6 ppm). For branches longer than C_4, we ascribe the following resonances (ppm): 14.0 [$CH_2CH_2(CH_2)_nCH_2CH_2\mathbf{CH_3}$], 22.6 [$CH_2CH_2(CH_2)_nCH_2\mathbf{CH_2}CH_3$], 31.9 [$CH_2CH_2(CH_2)_n\mathbf{CH_2}CH_2CH_3$], 26.6 [$CH_2\mathbf{CH_2}(CH_2)_nCH_2CH_2CH_3$], and 32−34 [$\mathbf{CH_2}CH_2(CH_2)_nCH_2CH_2CH_3$].

There also remains the question of the polymer backbone. To the unbranched portions of the backbone can be assigned the methylene resonance at 29.6 ppm. We assign the methine signal at 40.4 ppm to ethyl branch points on the main chain, while the methine resonance at 37.1 ppm may be ascribed to branch points for longer branches. The methylene peaks at 35.0 and 36.0 ppm may be due to the carbons α to a branch.

2. Mechanistic Considerations. As with the tantalum-based system, an experiment was conducted in which the proton scavenger, 2,6-di-*tert*-butylpyridine, was added to confirm or deny the possibility of cationic rearrangements and/or oligomerization as the source of branching. The resultant product had both liquid and solid components, as in the absence of added 2,6-di-*tert*-butylpyridine (Table 4, entry 4; Table 5, entry 4). However, the branching was much lower than in the case of the reaction with no scavenger (0.13 versus 0.23 for the liquid and 0.02 versus 0.16 for the solid).

As can be seen from the branching data, the solid produced by the scavenged system is essentially linear polyethene. In addition, the oil produced from the scavenged system contains distinctly 1-alkene end groups. The gel permeation chromatogram for the oil shows two peaks, the lower molecular weight component[11] presumably being the 1-alkene. Additionally, it is likely that the lightly branched polyethene results from a predominantly insertion mechanism. Thus, unlike the tantalum-based system, both insertion and cationic mechanisms operate. The solid polyethene is formed predominantly via an insertion mechanism, whereas the liquid product is a result of ethene oligomerization followed by cationic rearrangements and/or oligomerization.

C. The Chloride Effect. As discussed above, replacing triethylaluminum with an alkylaluminum halide as the cocatalyst in our systems results in a dramatic change in product selectivity. Instead of polyethene, lower molecular weight 1-alkenes are formed (which subsequently undergo cationic oligomerization). The effect is more clear-cut in the tantalum-based system. This observation raises the interesting question of what causes the lowering of the molecular weight of the primary product (i.e., increases the rate of β-hydrogen abstraction relative to propagation). Since the only real difference between a "traditional" Ziegler system and ours is the presence of alkylaluminum halide cocatalyst in the latter, we hypothesized that the presence of chloride ions may, in part, be responsible for the effect.[12] Accordingly, we have examined the effect of added chloride ions on the $TaCl_5/Et_3Al$ and $TiCl_4/Et_3Al$ systems.

The addition of 1 equiv of distearyldimethylammonium chloride to a 1:1 mixture of $TaCl_5$ and Et_3Al in chlorobenzene resulted in the formation of >90% liquid product. *The observation that >75% of the liquid was 1-hexene and not a typical Schulz−Flory distribution of 1-alkenes was again intriguing.* While further studies are clearly in order, it is obvious that chloride ions have an interesting and significant effect on the system that includes a considerable lowering of the molecular weight of the primary product.

The effect of adding distearyldimethylammonium chloride to a mixture of $TiCl_4$ and Et_3Al in chlorobenzene was also briefly examined. In this case, the result was an essentially complete cessation of catalytic activity.

Conclusions

Polymeric oils of varying molecular weights and branching have been synthesized from ethene using $TaCl_5$/alkylaluminum halide and $TiCl_4$/alkylaluminum halide catalyst systems. Molecular weight and branching can be tuned by varying reaction conditions and the composition of the catalyst mixture. The mechanism of the formation of branched polyethene appears to involve, for the most part, oligomerization of ethene to 1-alkenes (principally 1-hexene) by a transition metal alkyl species followed by cationic oligomerization of the 1-alkenes by Lewis acidic species. The addition of chloride ions to the $TaCl_5/Et_3Al$ system results in a change in product selectivity from all polyethene to >65% 1-hexene. The highly selective trimerization of ethene by the tantalum system is unusual and clearly merits further study.

The hyperbranched polymers from both systems have great potential as lubricant components because of the systems' variability and use of the inexpensive ethene monomer.

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[11] Because the lowest calibration standard used was $M_n = 208$, this data point is outside the calibration range and should be treated as an approximate number.

[12] A similar effect has been reported for a metallocene-based 1-alkene oligomerization system: Christoffers, J.; Bergman, R. G. *Inorg. Chim. Acta* **1998**, *270*, 20.