Articles

Vinyl Chloride as a Chain Transfer Agent in Olefin Polymerizations: Preparation of Highly Branched and End Functional Polyolefins

Scott G. Gaynor†

The Dow Chemical Co., Polyolefins and Elastomers Research, 2301 N. Brazosport Blvd., Freeport, Texas 77541

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ABSTRACT: Vinyl chloride monomer (VCM) has been employed as a chain transfer agent to yield polyolefins with one vinyl end group per chain; subsequent incorporation of these macromonomers has resulted in the formation of branched polyolefins. The use of VCM as a comonomer in transition-metal-catalyzed olefin polymerizations results in β-chloride elimination, yielding polymers that contain vinyl end groups and a chlorinated catalyst. Through reactivation of the catalyst by advantageous MAO, or other aluminum alkyl, reinitiation of the olefin polymerization can occur; the combination of elimination and reactivation allows for VCM to behave as a chain transfer agent. The use of VCM as a chain transfer agent results in the exclusive formation of vinyl end groups (no vinylidene or internal vinyl end groups) in polyethylenes, both homopolyethylene and copolymers with octene; in propylene polymerizations, vinyl end groups are formed in addition to vinylidene end groups, the result of β-hydride elimination which occurs even in the absence of VCM. The chain transfer constants for VCM in ethylene polymerizations for a variety of single site catalysts were determined and found to be very similar, with $C_s \times 10^4 \sim 30$; for a propylene polymerization using a zirconocene catalyst, $C_s \times 10^4 \sim 700$. It was further observed that the resulting macromonomers formed in the polyethylene polymerizations could be incorporated into the growing polymer chains, resulting in the formation of long chain branches.

Introduction

Currently, the state of the art in new polyolefin materials development relies on the discovery and implementation of new catalysts to control polymer microstructure. Although this is a crucial component to preparing new polymeric materials, it is a lengthy and time-consuming process. Indeed, significant efforts have been undertaken to develop high-throughput techniques to screen catalyst candidates which can lead to the development of new polyolefin materials. Other strategies to prepare new polyolefins have not been as extensively explored, largely due to the lack of ability to control polymer size (M_n), functionality (reactive end groups), and topology (linear vs branched), as compared to the control offered by catalyst modification.

The use of chain transfer agents in olefin insertion polymerization is not widely used, with the exception of hydrogen to control molecular weight. Beyond hydrogen, there are very few examples of reagents providing for clean and controlled end groups in olefin polymerization. For example, various hydrides, such as those based on silane[1−3] or borane,[4−6] have been reported, as has the use of thiophene[7] and, to a limited extent, allylbenzene.[8] However, these reagents are generally exotic and are not readily applicable to use in an industrial process which would require thousands, if not millions, of pounds of highly purified and relatively inexpensive material for use in global scale olefin polymerizations. Although transfer to aluminum alkyls is known, such a reaction produces polymers with aliphatic end groups which cannot undergo further functionalization. Recently, transfer to aluminum alkyls has been used as a route to the generation of low molecular weight polyethylenes with a hydroxyl end group.[9] The use of vinyl chloride monomer as a chain transfer agent can allow for a greater degree of control of the polymer functionality and topology.

Many research groups have been interested in polymerizing vinyl chloride monomer (VCM) with a coordination polymerization catalyst in order to influence the tacticity of the pendant chlorine groups. Similarly, it is desirable to be able to copolymerize VCM with olefins and thus introduce polar functionality to substantially linear polyolefins such as polyethylene, polypropylene, and their copolymers with α-olefins. However, these efforts have been largely unsuccessful due to very fast β-chloride elimination that occurs after 1,2-insertion of the VCM into the metal−polymer bond. Elimination of the β-chlorine appears to be general, as it has been reported previously by Stockland and Jordan with zirconocenes,[10,11] Boone and Mullins with iron-based catalysts,[12] and Strazisar and Wolczanski with tantalum hydrides.[13] Elimination of the halogen (or other β-X group, i.e., ethers, esters, etc.) results in the formation of a vinyl-terminated polymer and a chlorinated catalyst, which is inactive to polymerization until reactivated by metathesis with advantageous aluminum

† Current address: The Dow Chemical Co., Advanced Electronic Materials, 1702 Building, Midland, MI 48674. E-mail: sggaynor@dow.com.

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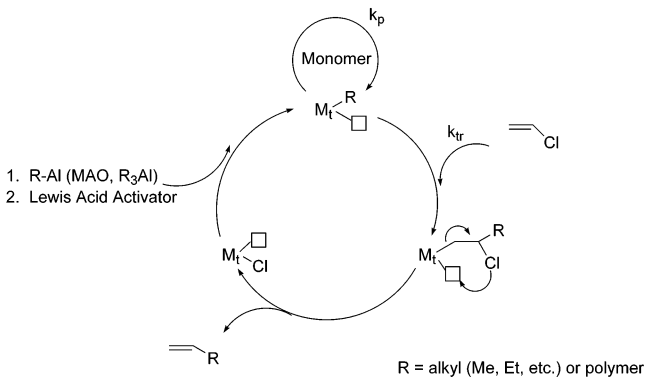
Scheme 1



alkyls, or similar species, and subsequent formation of the cationic species by a Lewis acid (Scheme 1).[10] It is of note that this mechanism has been observed for a variety of catalysts, regardless of the transition metal employed or the catalyst ligand structure.

The behavior of VCM in the polymerization is that of a chain transfer agent. The formation of vinyl-terminated polymer when using VCM as a transfer agent provides the opportunity to develop new polyolefin polymers and materials. For example, branched polymers can be prepared by incorporation of this macromonomer. Since the elimination of the chlorine atom is extremely fast[13] (no chlorine is observed in the final polymer chains[10,12]), the ratio of VCM to olefin monomer can be used to control the molecular weight of the polymer and thereby the concentration of the macromonomer in the reactor. This allows for tuning of the branching distribution and/or number of branches per chain. In multiple reactor configurations, there is the potential to prepare graft copolymers of varying composition, i.e., high-density polyethylene vs low-density polyethylene or low modulus vs high modulus, by synthesizing the macromonomer in the first reactor and introducing it into a second reactor where a polymer backbone of differing composition is formed. Additionally, the vinyl end groups can be readily transformed to other useful functionalities such as epoxides, azides, amines, hydroxyl, and others.

This report focuses on the initial screening of the utility of VCM to act as a chain transfer agent for the polymerization of ethylene (as well as ethylene copolymers with styrene or octene) and propylene using a variety of single site catalysts. The chain transfer constants for ethylene and propylene with VCM were estimated. GPC and rheological analyses have been used to confirm the synthesis of polymers with high levels of long chain branching.

Experimental Section

Vinyl chloride monomer was obtained from Dow Chemical and used without further purification. Ethylene and propylene were passed through an oxygen scrubber prior to introduction to the polymerization reactor. Toluene was purified by passing through molecular sieves and alumina prior to use and stored under nitrogen: catalyst A: ($C_5Me_4SiMe_2N^tBu$)Ti(η^4-1,3-pentadiene); catalyst B: dimethylsilyl(2-methyl-*s*-indacenyl)(*tert*-butylamido)titanium 1,3-pentadiene; catalyst C: *rac*-[dimethylsilylbis(1-(2-methyl-4-phenyl)indenyl)] zirconium 1,4-diphenyl-1,3-butadiene); catalyst D: (1*H*-cyclopenta[1]phenanthrene-2-yl)dimethyl(*tert*-butyl amido)silane titanium dimethyl. All catalysts and methylaluminoxane (MAO) were obtained from The Dow Chemical Co.

Screening Polymerizations. In a drybox, catalyst ($\sim 2 \times 10^{-5}$ mol), methyl di(octadecyl)ammonium tetrakis(pentafluorophenyl)borate (Asahi Glass, 132 μL, 0.1588 M), MAO (390 μL, 6.45 wt %, 25 mg Al) ([M_t]:[B]:[Al] = 1:1.05:46.5), and toluene (5.0 mL) were charged to a 45 mL stainless steel vessel. The vessel was sealed with a pressure transducer and an inlet valve attached to the head. The vessel was connected to a manifold at the inlet valve, and the line was purged of air by three vacuum/nitrogen cycles. After putting the vessel contents under vacuum, the inlet valve was closed and the vessel was weighed. Upon reconnecting the vessel to the manifold (after three vacuum/nitrogen cycles before reopening the inlet valve), VCM was added and the vessel reweighed; the amount of VCM added ($\sim$0.2 g) was determined by the difference. The manifold was pressurized with 150 psi of ethylene, the inlet valve opened, and the pressure allowed to equilibrate. The inlet valve was closed, the vessel disconnected from the manifold, and the vessel placed in a heated (70 °C) shaker. The reaction was run for the desired period of time, and then the reactor was vented. The reaction mixture was washed with 1 M HCl, and the solid polymer was obtained by decanting off the liquid layers. The polymer was washed with 2-propanol and acetone and then dried overnight under vacuum at 80 °C.

Determination of Chain Transfer Constant. The following is a general description of the polymerization procedure using a 300 mL stirred Parr reactor:

A 300 mL Parr reactor was used to conduct polymerizations under better stirring conditions and to provide a slightly larger amount of final product. The Parr reactor consisted of a 300 mL stainless steel vessel with a six-port head and stirrer. The ports were configured as follows: (1) gas inlet/outlet and pressure gauge (0−1000 psi), (2) dip tube into reactor with connection for catalyst/solvent vessels, (3) rupture disk and connection for blow-down tank (1 L), (4) coolant inlet, (5) coolant outlet (the inlet/outlet were connected by SS tubing within the reactor to act as a cooling loop, and (6) a thermocouple. The head was sealed to the vessel body (predried in a 130 °C oven) by two half-moon flanges with three set screws each.

The assembled reactor was connected to the blow-down tank, the catalyst/solvent vessels, recirculating coolant (25 °C), and the manifold line. The reactor was then pressure tested at 150 psi for 5 min to check for leaks. The reactor was then pressurized with nitrogen and vented (3×), placed under vacuum, and heated to 85 °C (using a Glas-coil heating mantle; temperature was measured between the mantle and the reactor body) for 15 min. The catalyst ([cat]$_0 \sim 2.5 \times 10^{-5}$ mol, [M_t]:[B]:[Al] = 1:1.2:4 in the final reaction mixture) and solvent were then charged to the reactor, and the solution was heated to 70 °C (measured using the thermocouple in the reactor). Upon reaching 70 °C, the VCM (added using a HPLC injection loop) and the monomer (ethylene or propylene) were added through the gas inlet valve to the reactor and monomer feed until the reactor pressure was 150 psi. The gas inlet valve was then closed and the reaction allowed to proceed at 70 °C (or higher due to reaction exotherm). When the reaction was completed (or reached the desired pressure drop), the reactor was vented and pressurized with nitrogen three times. The reactor was disassembled and the contents poured into methanol. The product was then isolated and dried under vacuum at 75−90 °C overnight.

Analysis. NMR analyses were performed on a Varian Unity+ 400 MHz spectrometer. Samples were typically prepared as 15% solutions in tetrachloroethane-d_2/1,2-dichlorobenzene (50/50 wt) with 0.025 M chromium acetylacetonate. Instrument parameters were chosen to ensure quantitative collection of the spectrum. Triple detection GPC (3D-GPC) was performed using a Waters 150C chromatograph (with RI detector) in conjunction with a Precision Detectors PDI 2040 light scattering detector and a Viscoteck 150R viscometer. The polymer samples were eluted through Polymer Lab mixed A columns at 1 mL/min at 150 °C in 1,2,4-trichlorotoluene (stabilized with 200 ppm BHT). The number of branches per 1000C was estimated using the method of Zimm and Stockmayer,[14] with $g' = g^{0.5}$.

Table 1. End-Group Analysis of Polymers Obtained in Screening Polymerizations Using VCM with a Variety of Catalysts

catalyst/monomer[a]	mol % vinyl[b]	mol % cis and trans[b]	mol % vinylidene[b]	total mol % unsaturation[b]	M_w (LS)
catalyst A HDPE	not soluble				insoluble
catalyst A HDPE/VCM	0.172	0.0000	0.0000	0.172	36000
catalyst B HDPE	no data	0.0000	0.0000	0.0000	insoluble
catalyst B HDPE/VCM	0.164	0.0000	0.0000	0.164	31000
catalyst C HDPE	no data	0.018	0.0000	0.018	insoluble
catalyst C HDPE/VCM	0.046	0.0000	0.0000	0.046	142000
catalyst C PP	0.0000	0.0000	0.058	0.058	
catalyst C PP/VCM	0.114	0.0000	0.056	0.171	

[a] HDPE = polymerization conducted with ethylene as the monomer; PP = polymerization conducted with propylene as the monomer. [b] Mol % is relative to total $-CH_2CH_2-$ in the polymer.

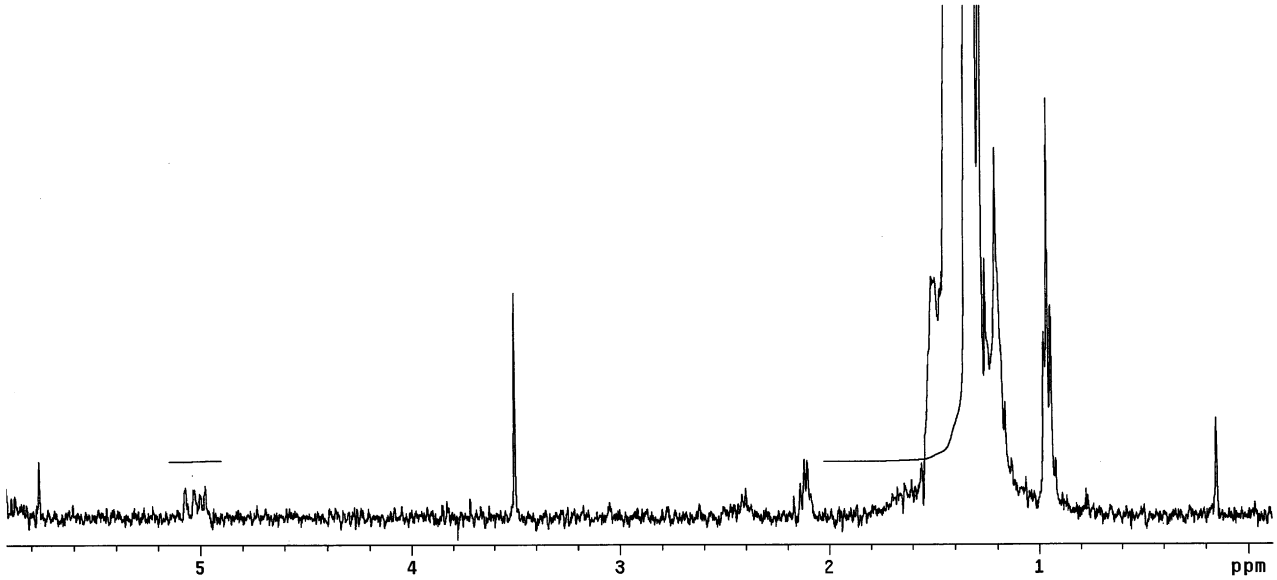


Figure 1. Representative ^{1}H NMR of the polyethylene obtained using catalyst C.

Results and Discussion

Initial Screening Reactions. *Homopolymerizations.* Two titanium-based single site catalysts were selected to evaluate the efficacy of VCM as a chain transfer agent in the polymerization of ethylene. Additionally, a zirconocene catalyst was used both for the polymerization of ethylene and for propylene.

Analysis by ^{1}H NMR (Table 1) showed that the polymerization with VCM produced polymers with vinyl end groups. A representative ^{1}H NMR spectrum of the polyethylene prepared using catalyst C is shown in Figure 1. The only signals resulting from unsaturation in the carbon−carbon chain are those from vinyl end groups (5.0−5.1 ppm); there are no signals observed from vinylidene (4.7−4.8 ppm) or internal olefins (∼5.3 ppm).[15] Also observable is the methyl end groups (0.95 ppm) from MAO (reactivation of the catalyst yields M_t-CH_3 which initiates polymerization of the monomer).

The polymers prepared in the absence of VCM showed very little, if any, vinyl end groups. The vinylidene unsaturation observed for the polypropylene was expected, as β-hydride elimination from the backbone carbon adjacent to the pendent $-CH_3$ group is a common chain termination step in propylene polymerization. Conversely, the polypropylene polymers prepared with VCM showed significant amounts of vinyl end groups. It is notable that, for the ethylene polymers prepared with VCM, the vinyl end groups were the only unsaturations observed. This is in contrast to the use of multiple catalyst systems which employ a catalyst that readily undergoes β-hydride transfer to prepare vinyl macromonomers in the single reactor preparation of branched polyolefins,[15−17] where a significant portion of the unsaturated end groups are vinylidene and internal olefin.

In the propylene polymerization, the mol % of vinylidene end groups remained unchanged upon addition of VCM to the reaction, but the mol % of vinyl end groups increased from 0 to 0.114 mol %, relative to the $-CH_2CH_2-$ units in the polymer. This observation indicates that the presence of the VCM in the reaction mixture did not interfere with the general propagation and termination/transfer mechanisms that are involved in the polymerization of propylene by the catalyst. VCM simply behaved as a chain transfer agent, where VCM insertion/β-Cl elimination was a competing reaction with β-H elimination.

Analysis by GPC showed that the polymers produced with VCM were of significantly lower molecular weight than those prepared in the absence of VCM (the insolubility is due to the high molecular weight of the polymer) (Table 1). The lowered molecular weights were consistent with the hypothesis that the VCM acted as a chain transfer agent.

Copolymerizations. As copolymers of ethylene with various α-olefins are widely used as commercial materials, VCM was evaluated as a chain transfer agent for copolymerizations. Ethylene was copolymerized with styrene or octene in the presence and absence of VCM. The results show (Table 2) that the addition of VCM yielded lower molecular weight polymers with vinyl end groups. Therefore, VCM's utility as a chain transfer

Table 2. Copolymerizations of Ethylene with VCM and Various α-Olefins

		mol % comonomer				
comonomer	catalyst	feed[a]	polymer[b]	mol % VCM[a]	mol % vinyl[b]	$M_{w,LS}$ (M_w/M_n)
octene	catalyst B	20	5	7	0.04	48 300 (6.9)
styrene	catalyst D	55	41	20	0.04	52 800 (8.9)
		55	40	0	nd	67 100 (12.4)
		12	8	38	0.4	92 200 (15.4)
		12	7	0	nd	148 000 (9.2)

[a] Compositions based on estimated 15 mmol of ethylene (40 mL headspace, 150 psi, 70 °C). [b] Compositions determined by ^{1}H NMR. [c] M_w determined by light scattering using triple detection GPC.

agent is independent of the particular olefin being (co)-polymerized.

Determination of Chain Transfer Constants (C_s). To evaluate the ability of VCM to act as a chain transfer agent, the Mayo equation was used to determine the relative rate of reaction of the active center toward monomer (propagation, k_p) vs reaction with the transfer agent (k_{tr}), eq 1.[18] In eq 1, $1/X_n$ is the predicted number-average degree of polymerization, $1/X_{n0}$ is the number-average degree of polymerization in the absence of the transfer agent (under identical conditions), C_s is the chain transfer constant ($C_s = k_{tr}/k_p$), [S] is the concentration of transfer agent (VCM), and [M] is the concentration of monomer.

$$\frac{1}{X_n} = \frac{1}{X_{n0}} + C_s\frac{[S]}{[M]} \qquad (1)$$

Under conditions where the conversion of both monomer and chain transfer agent are kept low, a plot of $1/X_n$ vs [S]/[M] (Mayo plot) yields a straight line where the slope is C_s and the intercept is $1/X_{n0}$. Since C_s is the ratio k_{tr}/k_p, this chain transfer constant can be used to gauge the relative reactivity of the active center toward the chain transfer agent (VCM) with the monomer being polymerized, i.e., ethylene or propylene. For simplicity, the chain transfer constant, C_s, is generally reported as the ratio times 10^4; i.e., for $k_{tr}/k_p = 0.01$, $C_s \times 10^4 = 100$.

To apply the Mayo plot to the current system using VCM, some assumptions were made. The first was that the rate-determining step in the reaction of the catalyst center with VCM was insertion of the VCM double bond into the metal−carbon bond of the propagating polymer chain; elimination of chlorine was presumed to be instantaneous, and no subsequent monomer is polymerized after insertion of VCM into the polymer chain. Such an assumption is likely quite valid, as Jordan[10] and Boone[12] have reported that no polymer containing chlorine has been observed when either homo- or copolymerizing VCM. Wolczanski has determined that the rate of elimination for vinyl halides is at least 100 times faster than propagation for tantalum hydride catalysts.[13] Further, considering that Brookhart has shown that insertion of ethylene into a metal−alkane bond is 6−10 kcal/mol less favorable than for the corresponding hydride[19,20] (translating into a rate ratio difference ($\Delta G = RT\ \ln(k)$) of 10^3−10^6 at 70 °C), β-elimination of the chlorine is likely many orders of magnitude faster than any subsequent propagation.

Another assumption was that VCM did not interfere with propagation of the olefin, other than to act as a chain transfer agent; that is, k_p was constant in either the presence or absence of vinyl chloride. If the reduction in molecular weight was caused by a lowering of k_p, then the chain-breaking process(es) would be the same either with or without added VCM, most notably β-H elimination which would result in the formation of vinyl, vinylidene, and internal (trisubstituted) olefin end groups. As was noted in the above experiments, only vinyl end groups were observed. The observation of only vinyl end groups is consistent with the mechanism for VCM insertion−elimination put forth in the papers by Jordan,[10,11] Boone,[12] and Wolczanski.[13]

Finally, by conducting the reactions for only short times, it was presumed only linear chains would be formed with little incorporation of the vinyl-terminated polymers. If there were significant amounts of branching by incorporation of the formed macromonomers, the number-average molecular weight determined by GPC would be erroneous. As small amounts of branching will more significantly impact M_w and only slightly affect M_n, incorporation of some macromonomer was deemed acceptable for the *estimation* of the chain transfer constants. However, some catalysts were found to incorporate macromonomer more readily than others (vide infra).

As the rate of transfer, k_{tr}, is essentially the rate of reaction of the metal center with VCM, C_s can be used to estimate the reactivity ratio for VCM with the monomer being polymerized. This is possible since the reactivity ratio r_1 is the ratio of the rates of reaction of an active center with attached polymer chain toward monomer vs the rate toward VCM. The rate of reaction with monomer is propagation, k_p, and reaction with VCM is transfer (k_{tr}, again, assuming fast elimination); hence $r_1 = 1/C_s$ (eq 2). The reactivity ratio r_2 is undefined and can be taken as zero since both k_{22} and k_{21} are zero because the active catalyst species M_t−CH_2−CH(Cl)−R does not react with either monomer or VCM but undergoes β-Cl elimination.

$$r_1 = \frac{k_{11}}{k_{12}} = \frac{k_p}{k_{tr}} = \frac{1}{C_s} \qquad (2)$$

The chain transfer constant was expected to be dependent on the catalyst being used to polymerize the olefins, as electronic and steric differences between catalysts may influence the rate of reaction between the catalyst center and VCM, just as is observed with other insertion copolymerizations. To quantify this behavior, ethylene was polymerized with VCM using the following catalysts: catalyst A, catalyst B, and catalyst C; propylene was polymerized with VCM using catalyst C.

Each ethylene polymerization was conducted under identical conditions: 70 °C, 100 mL of toluene in a 300 mL stirred reactor, ~2.5×10^{-5} mol of catalyst, ~3×10^{-5} mol of borate activator, 10^{-4} mol of MAO, and 150 psi of ethylene (reaction stopped after $\Delta = 50$−60 psi, usually less than 2 min). The amount of VCM was varied—500, 100, and 25 μL—and was metered using a HPLC injection loop. Each set of reactions for a given

Table 3. Data Obtained from Triple Detector GPC for Polymerizations of Ethylene or Propylene with VCM Using Various Catalysts

				calculated values from Mayo plots			
catalyst	monomer	VCM (μL)	M_n	$C_s \times 10^4$	$1/X_{n0} \times 10^4$	r_1 ($=1/C_s$)	LCB/1000C[a]
catalyst A	ethylene	500	39 000	52	3.55	192	0.395
		100	58 100				0.282
		25	85 200				0.452
catalyst B	ethylene	500	55 700	36	2.88	279	0.0
		100	85 100				0.206
		25	86 108				0.0
catalyst C	ethylene	500	59 500	25	2.98	402	0.011
		100	77 900				0.006
		25	98 400				0.102
catalyst C	propylene	500	18 900	682	10.7	14.7	nd
		100	30 300				nd
		25	39 300				nd

[a] Determined from triple detection GPC.

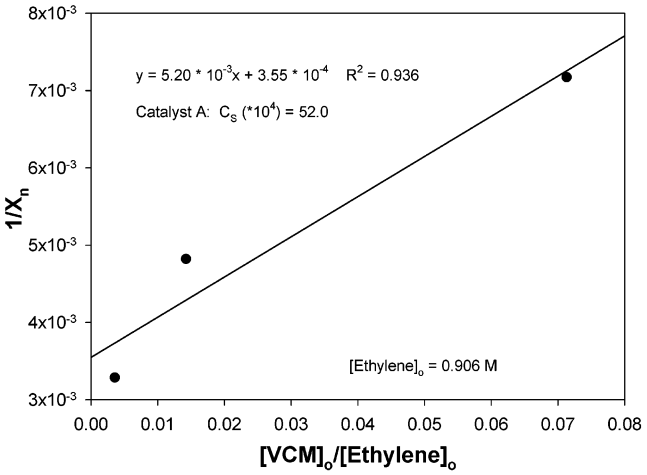


Figure 2. Mayo plot for the polymerization of ethylene in the presence of vinyl chloride using catalyst A.

catalyst was performed on the same day. The concentration of ethylene in the toluene solution was estimated according to Henry's law.[21] Figure 2 is a representative Mayo plot using the results obtained for the ethylene polymerizations with catalyst A. Table 3 is a compilation of the raw data.

The Mayo plots showed reasonably good fits, considering that each reaction required opening and cleaning the reactor after every polymerization and that the catalysts are very sensitive to impurities. The determined $C_s \times 10^4$ values were: catalyst A = 52, catalyst B = 36, and catalyst C = 25. As these values are relatively close to each other, and considering the error in measurement of X_n (due to the presence of long chain branching), $[VCM]_0$, and $[ethylene]_0$, it can be concluded that VCM reacted with these single-site catalysts at nearly the same rates, relative to ethylene, but may exhibit slight differences based on catalyst fine structure. The calculated r_1 values have a much larger spread due to its inverse relationship to C_s. For propylene, the $C_s \times 10^4$ value was calculated to be $C_s \times 10^4 = 682$; $r_1 = 14.7$.

In these reactions, catalyst efficiencies were not measured due to the small scale of the polymerizations and the fact that the reactors were opened to the atmosphere after every reaction to isolate the polymer. Small levels in impurities have significant effects on the catalyst concentration and cause changes in the catalyst efficiencies. Further, the amount of ethylene (or propylene) feed to the reactor could not precisely be repeated; as noted above, the concentrations of monomer in the reactor are estimates. Although the reactor setup was not appropriate to determine catalyst efficiencies, it was sufficient to estimate the relative reactivities of VCM to ethylene (propylene). Additional studies are required in larger batch reactors, or preferably in a continuous polymerization system, to quantify the loss in catalytic activity, if any, due to the formation of the metal chloride catalyst species and its subsequent reactivation by aluminum alkyls.

Branching by Incorporation of Macromonomers. *GPC Analysis.* The mechanism by which VCM acts as a chain transfer agent dictates that the polymers that are formed should have one vinyl end group on each chain. These end groups allow for the polymers to be reincorporated by growing chains, just as any other α-olefin, resulting in a branched polymer where the branch length is dictated by the average length of the macromonomer formed by chain transfer with VCM. Indeed, numerous groups have reported the use of two catalyst systems to prepare branched polyolefins;[17,22−25] one catalyst is used to prepare the vinyl-terminated macromonomer, and the other is used to prepare high polymer which has the macromonomer incorporated as a long chain branch. The reactions that were conducted to construct the Mayo plots were performed for only short reaction times (generally, less than 4 min) so as to minimize the incorporation of such macromonomers.

During the course of the molecular weight determination, it was observed by triple detection GPC (3D-GPC: on-line light scattering, viscometry, and refractive index) that some of the polymers were branched. In particular, those polymers prepared with catalyst A as the catalyst were found to contain significant amounts of long chain branching (Table 3).

Analysis of the GPC chromatograms and the data obtained from the on-line viscometry of those samples prepared using catalyst A was found to detail the amount of branching and its location in the molecular weight distribution. In Figure 3, the distribution of the polymeric species and the viscosities (Mark−Houwink plots) of both the sample and a linear standard are plotted vs molecular weight. Also plotted is the value g' which is the ratio of the viscosity of the sample polymer (η_s) to the linear standard (η_L) at a given molecular weight. This value is used as a sensitive parameter to determine the presence of branching. The maximum value of $g' = 1$ is that of a linear polymer; values below 1 indicate that the polymer at that given molecular weight is branched. The value g' was used to

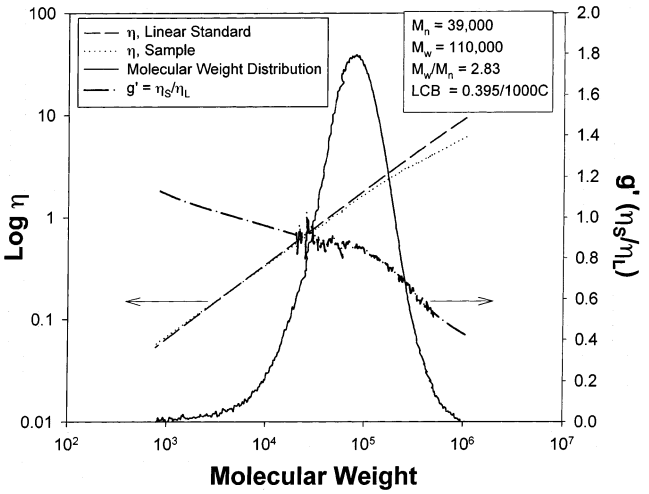


Figure 3. Plot of molecular weight distribution and viscosity data for polymer obtained by polymerization of ethylene with 500 μL of VCM using catalyst A.

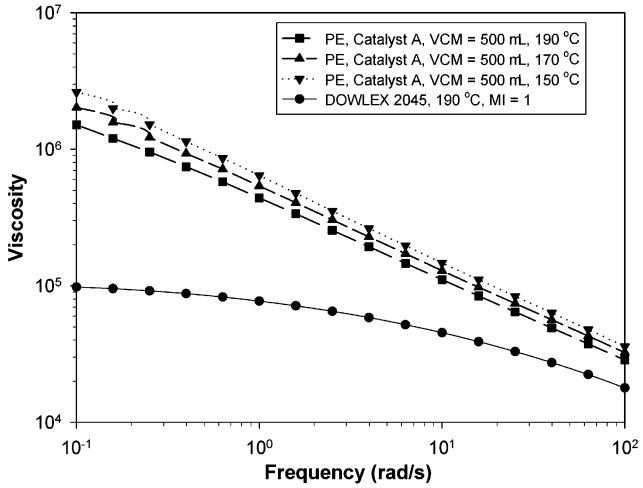


Figure 4. Plot of melt viscosity as a function of frequency for polyethylene prepared using catalyst A and 500 μL of VCM (Figure 1). Unbranched DOWLEX 2045 (MI = 1.0) is shown for comparison. Temperature values indicate temperatures at which melt viscosity was measured.

calculate the number of long chain branches per 1000 C atoms by using the methodology developed by Zimm and Stockmayer.[14]

The Mark−Houwink plot (Figure 3) shows that there is a significant reduction in the viscosity of the higher molecular weight fraction, indicating long chain branching. This is correspondingly reflected in the decrease of g' (an increase in the number of branches per chain) as molecular weight increases. In the middle and lower molecular weight fractions, there is a slight deviation between the viscosity of the sample and the linear standard, but the two are parallel. The g' values and number of branches appear to be at a slight plateau. This could be the result of small inaccuracies in the viscosity measurement or a sign of short chain branching. It is important to remember that this polymer is synthesized from only ethylene; there is no α-olefin comonomer.

It is noted that the amount of long chain branching observed in the polymers varies from catalyst to catalyst and that it does not trend directly with the amount of VCM added to the reaction. The variability of the long chain branching from catalyst to catalyst can be attributed to the ability of the catalyst to incorporate the polyolefin macromonomer—essentially the reactivity ratio of the macromonomer to ethylene. It appears that catalyst A was the most effective at incorporating macromonomer to form long chain branches.

The variability of LCB with $[VCM]_0$ is likely due to continued polymerization of the vinyl-terminated macromolecules at the end of the reaction. The reactions were "stopped" by venting the ethylene, followed by pressuring the reactor with nitrogen and venting (this process was repeated three times). The reactor was then removed from the stirrer and heating assembly and opened. Although the ethylene/VCM was effectively removed from the reaction, there remained active catalyst in the solution which could continue to polymerize the polyolefin macromonomer and increase the level of branching.

Rheology of Branched Polymer Prepared Using VCM as a Branching Agent. The melt viscosity as a function of frequency for the polyethylene sample prepared using catalyst A and 500 μL of VCM, as described in Figure 2, at three different temperatures, is shown in Figure 4, with a similar plot for a commercial linear polyethylene resin, DOWLEX 2045 (melt index (MI) = 1.0) at 190 °C (DOWLEX is a Trademark of The Dow Chemical Co.). The DOWLEX polymer is used as a linear polymer to compare with the results of the branched polyethylene synthesized using VCM. The M_w of the branched polymer was 110 000, which is approximately equal to MI = 1.0 (for linear polymers).

In Figure 4, the viscosities at higher frequencies are slightly offset, implying that the molecular weight of the branched polymer was somewhat higher than the linear analogue (DOWLEX 2045). However, the melt viscosity of the branched polymer prepared with VCM does not plateau (indeed, it does not even begin to plateau) throughout the range of frequencies studied, consistent with the expected behavior of a highly branched polymer.

Conclusion

Vinyl chloride has been shown to be one of the few reagents that act as a good chain transfer agent in olefin polymerization. Others, such as various silanes and borane hydrides, are rather exotic and would be of limited commercial use. However, vinyl chloride is readily available and inexpensive (~$0.20/lb). The only other chain transfer agent similarly available is hydrogen, but its use leaves a saturated chain end, whereas the use of VCM results in the exclusive formation of a vinyl end group which can allow for subsequent functionalization or for branching.

Further work is required to elucidate the effects of the formation of the dormant catalyst after β-Cl elimination. The metal chloride species which was formed cannot add additional monomer until activated, e.g., metathesis with an aluminum alkyl and formation of the active catalyst. Although on the small reactors used for this study there was no noticeable difference in reaction rates with and without the VCM, the effect on catalyst efficiency should be evaluated on larger batch or continuous reactors. Further, the amount and type of added aluminum alkane, either aluminum alkyls (tri-, di-, or mono-) or MAO-type species, should be investigated and optimized.

In this study, it has been shown that the molecular weight of the polymer was inversely proportional to the

concentration of the VCM in the reactor. Mayo plots were used to estimate the chain transfer constant, C_s, for a variety of catalysts polymerizing either ethylene or propylene. Ethylene: catalyst A ($C_s \times 10^4 = 52$), catalyst B ($C_s \times 10^4 = 35$), catalyst C ($C_s \times 10^4 = 27$). Propylene: catalyst C, $C_s \times 10^4 = 682$.

During the process of chain transfer, a polymer with a vinyl end group was formed. Under the appropriate reaction conditions, this newly formed macromonomer could be reincorporated into other growing chains to introduce branches in the polymer chain. By variation of the [VCM]/[monomer], the reaction time, or both, it is possible to design polymers with precise branch lengths and distributions. The ability to control the topology of the polymer in such a manner, coupled with the ability to prepare macromonomers differing in composition from the backbone, i.e., polypropylene or HDPE grafts and LLDPE backbones, allows for the development of novel polyolefinic materials.

To date, the vast majority of work in preparing new olefin polymers has focused on the synthesis of new catalysts to control polymer microstructure and monomer incorporation/reactivity; if a new polymer structure was desired, a new catalyst was prepared. The use of simple chain transfer agents which provide functionality, e.g., vinyl chloride, that can subsequently be used to define the polymer's final mechanical and physical attributes is a new avenue in designing polyolefins. This capability of defining polymer architectures relatively independently of the catalyst structure is a valuable development in polyolefin polymerization and should be explored, and exploited, further.

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Supporting Information Available: Mayo plots for catalysts B and C for ethylene and the Mayo plot for catalyst C with propylene; GPC data (molecular weight distribution and Mark−Houwink plots) for branched and an unbranched polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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