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An Investigation into the Identities and the Relative Concentrations of the Zr−Polymeryl Species Present during Ethylene and Propylene Polymerizations by Zirconocene-Based Ziegler Catalysts

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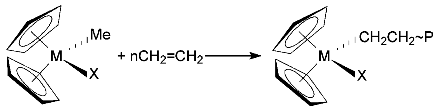
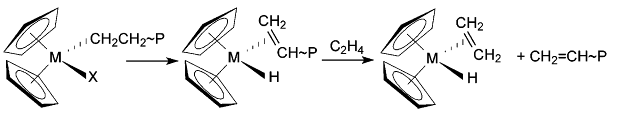
ABSTRACT: A protocol is described in which zirconocene-catalyzed alkene polymerization reactions are terminated by bromine to give polymers containing brominated end groups, Br−polymeryl. Using NMR spectroscopy, the Br−polymeryl groups can be identified as primary or secondary, thus providing information concerning the nature of the Zr−polymeryl linkage(s), and (via integrations) quantified, thus giving information about the relative concentration(s) of the Zr−polymeryl linkage(s). The procedure can in principle give very useful information concerning the nature and concentrations of Zr−polymeryl groups in existence during polymerization processes and is tested through ethylene polymerization by the $Cp_2ZrMe_2/B(C_6F_5)_3$ catalyst system and propylene polymerization by the $Cp_2ZrMe_2/B(C_6F_5)_3$, $(indenyl)_2ZrMe_2/B(C_6F_5)_3$, and *rac*-$\{C_2H_4(1\text{-indenyl})_2\}ZrMe_2/B(C_6F_5)_3$ catalyst systems. To this point the resulting data concerning Zr−polymeryl concentrations are generally consistent with data in the literature but are rather more easily obtained.

There has in recent years been considerable research into the utilization of metallocene complexes of the type $[Cp'_2MR]^+X^-$ (M = Ti, Zr, Hf; Cp′ = substituted η^5-cyclopentadienyl group; R = alkyl group; X^- = weakly coordinating anion) as homogeneous catalysts for coordination (Ziegler−Natta) polymerization of olefins.[1] There is widespread consensus with respect to mechanisms of the general processes involved in the initiation, propagation, chain transfer, and termination steps, and it is believed that these catalysts function as in eq 1 (∼P = long chain alkyl or polymeryl group), the methyl group being converted to a long chain, primary polymeryl group via repeated ethylene insertion steps.[1] Chain transfer then may involve β-hydrogen migration to release a polymer with a terminal olefinic end group (eq 2), although the reversible reinsertion−deinsertion of eq 3 can result in both secondary polymeryl groups and internal olefins.[1]



(1)



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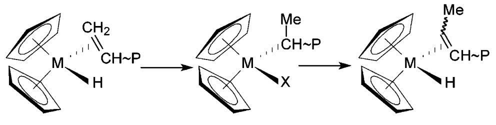
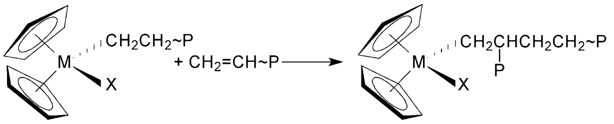


(3)

Alternatively, reinsertion of the terminal olefinic products $CH_2{=}CH{\sim}P$ into a propagating polymer chain can result in long chain branching, as in eq 4.



(4)

In fact, however, there is actually very little direct experimental information available concerning these and other possible species, and there remains much to be learned about intimate details of the polymerization process, as for example, the nature of active species and the concentration of the catalyst actively involved in polymer chain growth at any one time.

Experimentation designed to gain such information has taken several approaches, and it has recently been shown that it is possible to observe some such species directly.[2] Thus, by use of in situ ^1H and ^{13}C NMR spectroscopic studies, the latter involving ^{13}C-enriched catalyst and/or monomer, the presence of the primary $Zr{-}CH_2CH(R){-}$polymeryl species during the polymerization reaction (R = H, CH_3, C_4H_9, C_7H_{15}, C_8H_{17}) has been demonstrated.[2] A second approach for the acquisition of information concerning the intermediates present during the polymerization process involves kinetics studies.[3] Although the complexities of many catalyst processes can make it very difficult to obtain well-defined overall rate laws,[3c] quenched flow kinetics studies have been used recently to deduce the nature and number of active sites in the initial stage of some polymerization processes.[3c,e]

A complementary general approach has involved the use of quenching agents containing radioactive labels such as CH_3O^3H and ^{14}CO.[4,5] The former is believed to cleanly and efficiently replace the metal of a $[Cp'_2MCH_2{\sim}P]^+$ moiety with a single tritium label to give $CH_2{}^3H{\sim}P$, which can be quantified and related to the sum of the concentrations of all species present which contain metal−carbon σ bonds.[4] Carbonylation reactions, on the other hand, were expected to result in coordination of ^{14}CO to the vacant site of the metal in

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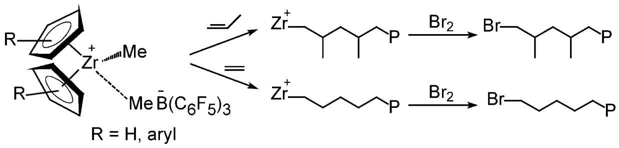
Scheme 1



the $[Cp'_2MCH_2{\sim}P]^+$ moiety followed by a migratory insertion to give an acyl species of the type $[Cp'_2M^{14}\text{-}COCH_2{\sim}P]^+$.[5a] It was anticipated that protic cleavage of the resulting acyl species would result in the formation of labeled aldehyde, whence again the sum of the concentrations of the $[Cp'_2MCH_2{\sim}P]^+$ propagating species could be determined.[5] Although these methods have been generally accepted and used for quantification of metal−polymeryl groups, they do have the limitation that they do not yield information concerning the nature of the end groups bearing the radioactive labels. Moreover, it has been demonstrated[6] that CO does not necessarily terminate polymerization but that it can participate in alkene−CO copolymerization such that more than one CO molecule is absorbed per metallocene unit.[5b,6] If this were the situation generally, then estimates of numbers of active sites obtained using ^{14}CO would be higher than those obtained using CH_3O^3H. However, in some cases the reverse is true,[4a] and thus the general applicability of this method remains suspect.

Recently, to complement a kinetics study,[3a,7] CH_3O^2H has been utilized as a quenching agent to determine the nature and relative concentrations of intermediates present during catalysis at the time of quench by using ^2H NMR techniques. In one particular case, involving 1-hexene polymerization using *rac*-$\{C_2H_4(1\text{-indenyl})_2\}Zr(Me)(\mu\text{-}Me)B(C_6F_5)_3$, the $-CH_2{}^2H$ end group resulting from termination following a 1,2-insertion was the only end group detected. In addition, estimations of its concentration made it possible to show that the number of active sites was approximately equal to the catalyst concentration for the system under study. However, this method suffers from poor sensitivity of ^2H NMR techniques, and taking into account all the above observations, clearly a general and efficient method for determination of the relative concentrations and nature of the propagating polymeryl species is still needed.

With a view to developing a simple, rapid method for the detection and the identification of metal−polymeryl groups present during a polymerization reaction, we have been exploring the use of bromine to label in a useful manner polymer chain ends. Bromine has long been known to rapidly cleave metal−carbon σ bonds,[8a] the products being organic bromides and the corresponding metal bromides as in eq 5 (M = metal; R = alkyl group; L = ligands).

$$L_nM{-}R + Br_2 \rightarrow L_nM{-}Br + RBr \qquad (5)$$

Zirconocene compounds of the type Cp_2ZrRCl have been shown to be cleaved similarly via an S_E2 process,[8b,c] and thus bromine would be expected to react with polymerization reaction mixtures containing Cp_2Zr^{IV}−polymeryl linkages, as in Scheme 1, to form Br−polymeryl end groups which may be identified as primary or secondary alkyl bromides on the basis of chemical shifts.[9]

Furthermore, if indeed it can be shown that Cp_2Zr^{IV}−polymeryl species are converted quantitatively to Cp_2ZrBr_2,[10] then integration of a ^1H NMR spectrum of a reaction mixture would result in an estimate of the amounts of all Br−polymeryl groups in solution and hence in quantitative estimates of all Cp_2Zr^{IV}−polymeryl species in solution at the time of quenching. Thus, in principle, the method should make it possible to identify and quantify every type of Zr−C σ-bonded moiety in solution at the time of termination. The methodology seems rather more appealing than e.g. termination reactions which replace the metal with ^2H or ^3H as the protocol utilizes ^1H NMR spectroscopy rather than the inherently less sensitive ^2H NMR spectroscopy, and of course, it does not require the use of radioactive materials. Also, losses to evaporation of alkyl bromide oligomers are less critical than would possibly be the case with the hydrocarbon analogues obtained via polymeryl labeling with ^2H or ^3H; thus, the quantification of polymeryl species would be more reliable.

We now describe the results of an investigation into the nature and relative concentrations of the Cp_2Zr^{IV}−polymeryl species present in solution during olefin polymerizations by Cp_2ZrMe_2[11a,b] (ethylene and propylene), $(indenyl)_2ZrMe_2$[11a,c] (propylene), and *rac*-$\{C_2H_4(1\text{-indenyl})_2\}ZrMe_2$[11d,e] (propylene) activated with $B(C_6F_5)_3$.[11f]

Experimental Section

Syntheses were carried out under purified argon using standard Schlenk line and glovebox techniques. ^1H and $^{13}C\{^1H\}$ NMR spectra were run on Bruker AV300, -400, or -600 spectrometers, chemical shifts being referenced using the residual proton signals of the deuterated solvents. Differential scanning calorimetry analyses were conducted on a Perkin-Elmer DSC-7 instrument at a heating rate of 5 °C/min. Samples were heated to 160 °C and cooled to 30 °C, and then a second scan was recorded. Toluene was dried by refluxing over sodium/benzophenone and distillation under argon. Chlorobenzene was dried by distillation under argon from calcium hydride prior to use. Deuterated solvents were obtained from Cambridge Isotope Laboratories (>99% atom % D). All NMR solvents were dried over CaH_2 or activated alumina, stored over molecular sieves, and handled in a glovebox. The compounds $B(C_6F_5)_3$,[11f] Cp_2ZrMe_2,[11a,b] $(indenyl)_2ZrMe_2$,[11a,c] *rac*-$\{C_2H_4(1\text{-indenyl})_2\}ZrMe_2$,[11d,e] and $BrCH_2CH(Me)CH_2CH(Me)(n\text{-}Pr)$[9b] were prepared via published procedures. Polymerization grade ethylene (99+% purity, Air Products) and propylene (99.5 wt % purity, liquid phase, Praxair) were dried by passage through a column of activated 4 Å molecular sieves prior use.

Polymerization Procedures. In a typical ethylene polymerization, a solution of 10 mg (0.04 mmol) of Cp_2ZrMe_2 in 1 mL of toluene or chlorobenzene was saturated with ethylene (1 atm, 21 °C) and then treated with a solution of 20 mg (0.04 mmol) of $B(C_6F_5)_3$. The reaction mixture became yellow and then cloudy as the polyethylene began to precipitate. The reactions were run for 10−60 s, and then the ethylene flow was stopped and the polymerization was quenched with a solution (0.4 M) of bromine in CH_2Cl_2 or chlorobenzene. All volatiles were removed under reduced pressure, and the resulting white polymer was dried. In some cases, the polyethylene was purified by dissolution in hot chlorobenzene followed by precipitation with methanol, filtration, and drying as above. ^1H NMR spectra were run at 100 °C in 1,1,2,2-$C_2D_2Cl_4$ or at 120 °C in chlorobenzene-d_5.

In a typical propylene polymerization, a solution of 0.11 g of $B(C_6F_5)_3$ (0.22 mmol) in 2 mL of chlorobenzene was injected into a polymerization flask containing a solution of 0.07 g of $(indenyl)_2ZrMe_2$ (0.2 mmol) in 8 mL of chlorobenzene saturated with propylene (1 atm). On the addition of the $B(C_6F_5)_3$, there was an immediate change in color (from yellow to dark red), and after a measured reaction time, the polymerization reaction was quenched by addition of a solution of Br_2 in chlorobenzene. The polymerization mixture was stirred for 10 more min, and the solvent was removed in vacuo. The

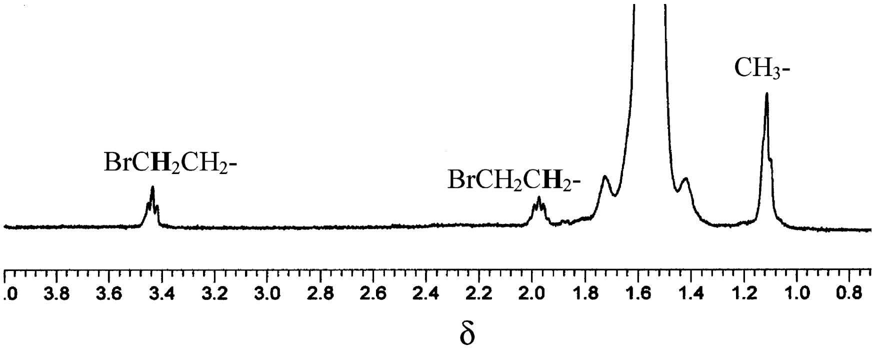


Figure 1. ^{1}H NMR spectrum of brominated polyethylene in C_6D_5Cl (400 MHz, 120 °C).

polymerization product was dissolved in hexane and purified by passage through a short silica column to give a light yellow atactic polypropylene.

Results and Discussion

Model Studies. As a test of the procedure, we initially investigated the bromination of Cp_2ZrMe_2 in $CDCl_3$, CD_2Cl_2, C_6D_6, and toluene-d_7. As anticipated, the reaction of 2 equiv of bromine per Cp_2ZrMe_2 proceeded rapidly and quantitatively as in eq 6.

$$Cp_2ZrMe_2 + 2Br_2 \rightarrow Cp_2ZrBr_2 + 2MeBr \quad (6)$$

Unfortunately, addition of excess bromine to solutions of Cp_2ZrMe_2 in $CDCl_3$, CD_2Cl_2, and C_6D_6 resulted in the apparent slow cleavage of the cyclopentadienyl rings, as indicated by the appearance of weak multiplets in the region δ 4.5–4.8. This problem did not arise in toluene-d_7 and could be avoided in the other solvents by slowly adding the bromine to a solution of Cp_2ZrMe_2 just to the point where its intense brown-red color did not fade.

As a proxy for a polymerization catalyst involving Cp_2ZrMe_2, we reacted this compound in CD_2Cl_2 with $B(C_6F_5)_3$ to form $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$,[12] which we then brominated as above. As hoped, the reaction proceeded rapidly and quantitatively as in eq 7.

$$Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3 + 2Br_2 \rightarrow Cp_2ZrBr_2 + 2MeBr + B(C_6F_5)_3 \quad (7)$$

The results defined by eqs 6 and 7 are important because they imply that species of the types $Cp_2Zr(polymeryl)(\mu\text{-}Me)B(C_6F_5)_3$ will be cleaved rapidly and quantitatively by bromine to give Cp_2ZrBr_2 and Br–polymeryl, confirming the validity of this method.

Ethylene Polymerizations. We began our study with experiments involving ethylene polymerization at room temperature, 1 atm, using the $Cp_2ZrMe_2/B(C_6F_5)_3$ polymerization system[2a,12] in two different solvents, toluene (ϵ 2.38)[13] and chlorobenzene (ϵ 5.68).[13] Polymerizations were typically carried out for 10–60 s in order to obtain data for the early stages of the process, and the polyethylene which was obtained was characterized as the crude or purified by standard precipitation methods. ^{1}H NMR spectra of the resulting polyethylene were run at 100 °C in 1,1,2,2-tetrachloroethane-d_2 or at 120 °C in chlorobenzene-d_5, and a typical ^{1}H NMR spectrum of a brominated polyethylene obtained after 10 s polymerization time in chlorobenzene-d_5 is presented in Figure 1.

In addition to the methylene polymer backbone resonance at δ 1.57 and terminal methyl resonance at δ 1.11 (br t), there are a weak triplet at δ 3.44 and multiplet at 1.97, attributed respectively to the anticipated $Br(\mathbf{CH_2}CH_2){\sim}P$ and $Br(CH_2\mathbf{CH_2}){\sim}P$ end-group hydrogens.

Two procedures were carried out in order to gain estimates of the concentrations of Cp_2Zr–CH_2polymeryl groups during these polymerization reactions. In one approach, utilized for the reactions carried out in toluene, all volatiles were removed from the reaction mixtures and ^{1}H NMR spectra of unpurified samples of polymers which retained the Cp_2ZrBr_2 product were run in 1,1,2,2-$C_2D_2Cl_4$ at 100 °C. Integrations of the resonance at δ 3.41 of several such polymeric products and comparison of their intensities with that of the Cp resonance of the Cp_2ZrBr_2 (δ 6.55) showed that the Zr–polymeryl concentration varied between 0.5% and 5% of the total catalyst present. There appeared to be no correlation of Zr–polymeryl concentration with time, but it seemed quite likely that entrapment of zirconium-containing compounds in the precipitating polyethylene may have resulted in reduced concentrations of Zr–polymeryl groups.

In the second approach, utilized subsequently for the reactions carried out in chlorobenzene, the polymers were purified by reprecipitation from hot chlorobenzene, and the concentration of the $BrCH_2{\sim}P$ groups relative to the amount of catalyst used was obtained from the ^{1}H NMR spectrum (120 °C, C_6D_5Cl) using 1,1,2,2-tetrachloroethane (δ 5.80) as an internal standard. Again, the Zr–polymeryl concentrations were low, in the range 4–10%, although higher than in toluene.

These results seem reasonably consistent with those of Tritto et al.,[2a] who observed what appeared to be the Zr–$^{13}CH_2$polymeryl resonance on treating the $Cp_2Zr(^{13}CH_3)_2/B(C_6F_5)_3$ catalyst system with highly enriched $^{13}C_2H_4$. The ^{13}C resonances of the natural abundance Cp and the enriched Zr–$^{13}CH_2$ groups appear to be comparable in intensity in the NMR spectra shown, consistent with the Zr–$^{13}CH_2$polymeryl groups being present in very low concentrations. We also note that Busico et al.,[3c] in a kinetics study of ethylene polymerization using the C_2-symmetric catalyst system *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}indenyl)_2ZrCl_2$/MAO, deduced Zr–polymeryl relative concentrations of 5–25%.

For all polymer samples obtained in toluene, the ratio of the intensity of the methyl resonance to that of the $BrCH_2$– group was always ≫3:2, varying from ~10:1 at 10 s to ~40:1 at 60 s. Similarly, for samples obtained in chlorobenzene, the ratio of the intensity of the methyl resonance to that of the $BrCH_2$– group varied from 2:1 at 10 s to 32:1 at 60 s. These observations, coupled with observations that the NMR spectra of the brominated polymers exhibited weak or no ^{1}H NMR resonances of

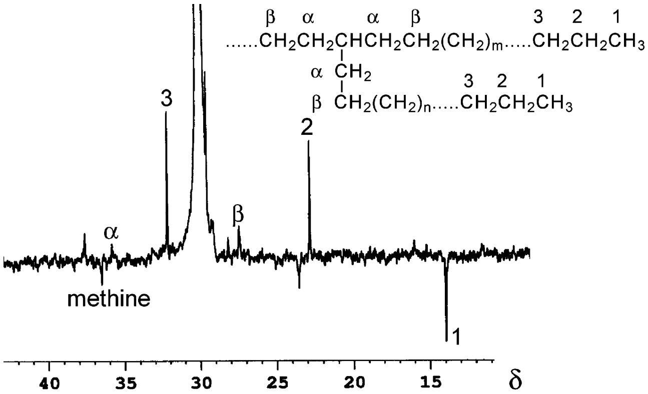


Figure 2. APT-^{13}C NMR spectrum of a sample of brominated polyethylene obtained after a 50 s polymerization time.

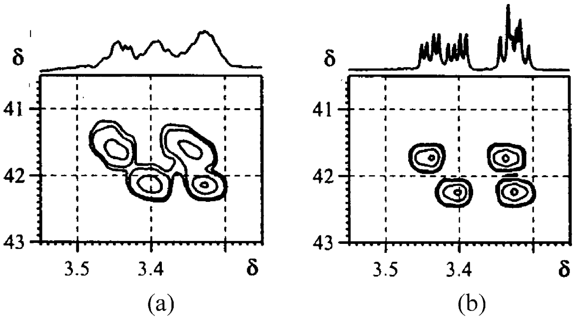
vicinal dibromides[9a,c] and that polyethylene obtained via conventional methanol quenching contained no or very weak olefinic end groups, imply that while a significant degree of chain transfer via β-hydrogen elimination to form α-olefins does occur, the thus formed α-olefins must be efficiently incorporated into the growing polymer chains as long chain branches (eq 4).

To investigate this possibility, ^{13}C{^{1}H} NMR spectra of representative samples were obtained, and a typical APT-^{13}C NMR spectrum of a sample of brominated polyethylene, obtained after 50 s polymerization time in chlorobenzene-d_5, is shown in Figure 2, with assignments.

As can be seen, the spectrum exhibits a weak resonance at δ 36.47, which indicates the presence of a methine resonance; in conjunction with the α and β methylene resonances at δ 35.80 and 27.44, respectively, there is firm evidence for long chain branching.[14a−d] Interestingly, resonances of short chain methyl, ethyl, propyl, and butyl chain branches[14] were not observed in this spectrum, although there is an as yet unassigned methyl resonance at δ 23.52.[14e] The presence of branches in the polyethylene can also be confirmed from DSC analysis as it is known that branches affect the crystalline structure, and as a result the melting temperature and crystallinity are reduced.[15a] Thus, T_m measurements showed that the polyethylene samples prepared in chlorobenzene all melted at 128.6 ±1.3 °C, values indicative of HDPE containing small amounts of long chain branches.[15b]

These results are in themselves interesting as it is generally believed that polymers containing olefinic end groups should be major species in this type of polymerization reaction[1] *unless* the polymerizations involve alkylaluminum cocatalysts such as MAO. In this case polymeryl transfer to aluminum followed by hydrolysis can result in saturated polymers,[16a−c] and observation of the latter tends to be taken as evidence for processes involving chain transfer to aluminum.[3c,14a] In fact, our observations suggest that this interpretation may not always be correct; saturated polymers can be obtained in the absence of alkylaluminum compounds, and the presence of saturated polymers need not necessarily require chain transfer to aluminum.

Propylene Polymerizations. We next turned our attention to propylene polymerization by the $Cp_2ZrMe_2/B(C_6F_5)_3$[12a,b] and $(indenyl)_2ZrMe_2/B(C_6F_5)_3$[11a,c] catalyst systems which are known to give atactic polypropylene;[12a,b,17,18] the latter is quite soluble and therefore easier to investigate than polyethylene. In these experiments the anticipated brominated end groups would be $BrCH_2CH(Me)CH_2CH(Me){\sim}P$ (δ ~3.4),[9b] following a 1,2-insertion, although the presence of $BrCH(Me)CH_2CH_2CH(Me){\sim}P$ (δ ~4.2) end groups,[9a] resulting from an ultimate 2,1-insertion would also be possible. Furthermore, given that chain transfer following a 1,2-insertion yields predominantly vinylidene end groups ($CH_2{=}CMe{\sim}P$),[18] the presence of dibromo species $CH_2BrCBrMe{\sim}P$ (δ ~3.9) was also anticipated.



(a) (b)

Figure 3. HSQC spectra of (a) the brominated end-group region of polypropylene and (b) 1-Br-2,4-dimethylheptane (model compound).

Polymerizations were generally begun at room temperature and terminated with excess bromine after reaction times varying from 10 s to 4 min. After termination, the volatiles were removed under reduced pressure, and the residues were extracted with hexanes and passed through a short silica column to remove catalyst. The solvent was then removed to give oily, atactic materials which were characterized, on the basis of comparison with model compounds,[9] by ^{1}H NMR (600 MHz) and correlation spectroscopy.

In all of ^{1}H NMR spectra of the brominated polymeric products, the Br−(**CH$_2$**CHMe)polymeryl group resonance was observed as expected in the region δ 3.3−3.5, but as three broad, unresolved multiplets with an approximately 1:1:2 ratio of intensities (Figure 3a).

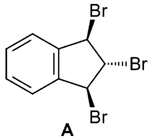
This pattern arises from the overlapping of two pairs of multiplets, as shown by an HSQC experiment (Figure 3a) in which one pair of protons at δ 3.34 and 3.44 was found to correlate with a carbon resonance at δ 41.7 and the other pair of protons at δ 3.32 and 3.40 with a carbon resonance at δ 42.2. The presence of the primary alkyl bromide group was also confirmed on the basis of comparison with the spectrum of the model compound $Br(CH_2CHMe)_2(CH_2)_2Me$,[9b] for which two overlapping pairs of doublets of doublets attributable to the diastereotopic hydrogen atoms are also observed at δ 3.3−3.45 (Figure 3b; note the similarity in ^{13}C chemical shifts between parts a and b of Figure 3). The greater complexity in the case of the spectrum of the polymeric sample reasonably results from the presence of various pentads terminated by *r* and *m* diads, a stereochemical feature which is not present in the model compound which contains only two chiral centers.

The primary alkyl bromide group results from the cleavage of a Zr−C bond after a primary (1,2) insertion and two overlapping pairs of multiplets (*m* and *r* terminal diads) of approximate 1:1 ratio for this group in the brominated polypropylene are consistent with an atactic polymer. To assign the two terminal diads as *m* or *r*, a propylene polymerization in the presence of *rac*-$\{C_2H_4(1\text{-indenyl})_2\}ZrMe_2/B(C_6F_5)_3$[2b,c,4e] was carried out. This system was chosen as it gives isotactic polypropylene,[4e,19] and therefore, by quenching the propylene polymerization with bromine, we expected a change in the relative intensities of the above-mentioned pairs of resonances. On the basis of relative intensities in the ^{1}H NMR and HSQC spectra of the resulting polymer, the pairs of peaks at δ 3.32 and 3.40, δ 3.34 and 3.44, were assigned as *r* and *m* terminal diads, respectively.

While the two achiral catalysts studied have generally been found to be highly regiospecific in favor of primary (1,2) insertion,[17a,20] occasional secondary (2,1) insertions[21] are also possible and would result in secondary Zr−polymeryl linkages. Although the latter have long been considered to represent likely dormant species because of the probability of steric hindrance to further propylene coordination,[22] there is in fact no direct evidence of their presence in polymerization mixtures, and their existence has only been implied from analyses of polymer microstructures[23] and end groups.[3e,18,24] Interestingly, however, a recent study by Landis et al.[2d] showed that a Zr−*sec*-butyl compound was not particularly inert to insertion of propylene, and thus the dormancy of secondary Zr−polymeryl species is currently under debate.

On addition of bromine to our propylene polymerization mixtures, any secondary Zr−polymeryl species present would cleave to give secondary alkyl bromide end groups; these are expected to give resonance at about δ 4.2 on the basis of the ^{1}H NMR spectrum of 2-bromodecane as a model compound.[9a] Unfortunately, the polymers formed contained vinylidene end groups which do not brominate cleanly to give the above-mentioned vicinal dibromo products. The anticipated dibromo produts are unstable under the reaction conditions and are known to produce a mixture of products.[25] Hence, all of our ^{1}H NMR spectra exhibited a plethora of relatively intense resonances in the region δ 3.8−4.6, completely obscuring the δ 4.2 region. However, while an HSQC experiment with 2-bromodecane showed that the CH resonance at δ 4.16 couples with the C-2 resonance at δ 52, similar experiments on several of the polymers obtained using $Cp_2ZrMe_2/B(C_6F_5)_3$ and $(indenyl)_2ZrMe_2/B(C_6F_5)_3$ revealed no coupling of any proton resonances in the region δ 3.8−4.5 with carbon resonances in the region δ 46−55. Furthermore, no 2-butenyl end groups, the products anticipated from β-H elimination after a secondary insertion,[18] were detected in the olefinic region of polymers when propylene polymerization was quenched with methanol. Thus, for $Cp_2ZrMe_2/B(C_6F_5)_3$ and $(indenyl)_2ZrMe_2/B(C_6F_5)_3$, at least, we find no evidence for Zr−polymeryl products of secondary 2,1-insertion. These results are consistent with in situ $^1H\{^{13}C\}$ NMR experiments[2] in which the presence of only primary Zr−polymeryl species have been detected.

In contrast to the situation with ethylene polymerization, where very little olefinic products were present in solution and only slight excesses of bromine were required to quench polymerizations, large excesses of bromine were required in the case of propylene polymerizations because of the presence of the vinylidene end groups arising from chain transfer. However, control experiments involving $(indenyl)_2ZrMe_2/B(C_6F_5)_3$ and $(indenyl)_2ZrBr_2$ showed that the indenyl groups of these compounds are very readily cleaved by excess bromine to form the tribromo species **A**, identified crystallographically and by NMR spectroscopy.[26] For this reason we could not use the resonances of $(indenyl)_2ZrBr_2$ as an internal standard for integrations.


A

To estimate the relative concentrations of the Zr−CH$_2$CHMe∼P groups present during propylene polymerization, the multiplet at δ 3.3−3.5 was therefore integrated relative to the peak of an added internal standard, 1,1,2,2-tetrachloroethane (δ 5.91). Accordingly, with Cp_2ZrMe_2 as catalyst, the relative concentration of the Zr−polymeryl groups was found to be low, ∼10%, and almost constant for polymerization times from 20 to 60 s. With $(indenyl)_2ZrMe_2$, on the other hand, a relatively high value of 84% was reached within 20 s, after which it decreased to much lower values for longer polymerization times (32% after 4 min, see Figure 4).

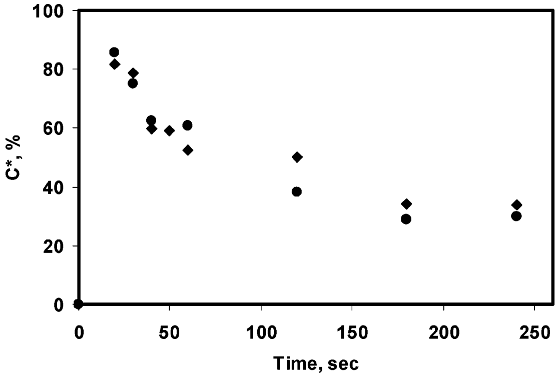


Figure 4. Variation of the relative concentrations of Zr−polymeryl groups with polymerization time (two runs).

The higher values with the $(indenyl)_2ZrMe_2/B(C_6F_5)_3$ than with the $Cp_2ZrMe_2/B(C_6F_5)_3$ catalyst system may be related to the higher polymerization activity of the former, which generally gave polymer yields several times greater than did the latter. Similar results have been reported elsewhere.[1a,27] Although propylene polymerization with the $Cp_2ZrMe_2/B(C_6F_5)_3$ and $(indenyl)_2ZrMe_2/B(C_6F_5)_3$ catalyst systems have been well investigated with respect to the polymerization mechanism, kinetics, end-group analyses, and catalyst activities,[1a,d,j,2a,12b,27,28] to our knowledge there are no reports on the concentration of active species during propylene polymerization with these particular systems, and thus a direct comparison of our results is not possible. However, our results are quite reproducible and are therefore reliable.

Somewhat similar values have, however, been reported for propylene polymerization by stereoselective catalysts. Thus, Landis et al. used a quench methodology to obtain a value of 25% for propylene polymerization by *rac*-$\{C_2H_4(indenyl)_2\}ZrMe_2/B(C_6F_5)_3$ at 20 °C,[3a] although much lower values were obtained by Chien et al. using *rac*-$\{C_2H_4(indenyl)_2\}ZrMe_2$ activated with $Ph_3C[B(C_6F_5)_4]$ at 0 °C.[4e] We were, in fact, unable to detect any BrCH$_2$CHMe∼P end groups at all in reactions carried out at 0 °C and lower, consistent with previous reports that Zr−polymeryl concentrations increase with increasing temperature.[4a,5b]

Summary

Termination by bromine of ethylene and propylene polymerization reactions involving the $Cp_2ZrMe_2/B(C_6F_5)_3$

and (indenyl)$_2$ZrMe$_2$/B(C$_6$F$_5$)$_3$ catalyst systems results in polymers with primary brominated end groups which can be readily identified and quantified using ^{1}H NMR spectroscopy. The procedure gives very useful information concerning the nature and concentrations of zirconium−polymeryl groups in existence during the polymerization process, and to this point the resulting data concerning Zr−polymeryl concentrations are generally consistent with data in the literature.

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