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Metal-catalysed Polymerisation

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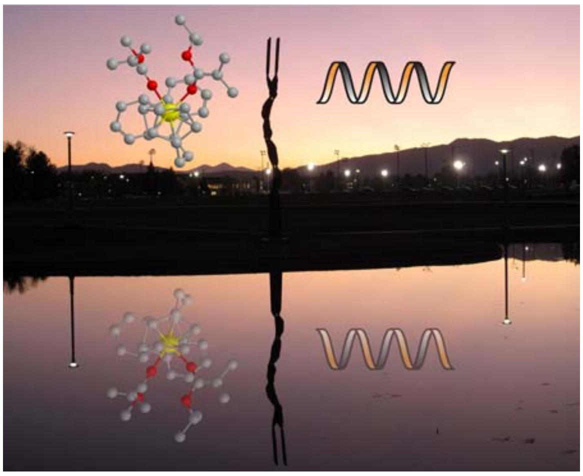

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An investigation of the influence of R on the abilities of the polar monomers $CH_2{=}CH(CH_2)_8OR$ (R = Me, $PhCH_2$, Ph_3C, Me_3Si, Ph_3Si) to participate in O- rather than η^2-coordination to metallocene alkene polymerization catalysts; an unanticipated role for ether oxygen coordination in *promoting* polymerization

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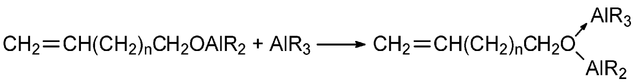
Copolymerization of ethylene and propylene with polar monomers of the types $CH_2{=}CH(CH_2)_nOH$ (n = 1–12) in order to introduce polar functionality into the resulting polymers is possible in principle if the hydroxyl groups of the polar monomers are masked such that they cannot coordinate to Lewis acidic catalyst sites and prevent η^2-alkene coordination. Although the use of hydrolysable ethers of the types $CH_2{=}CH(CH_2)_nOR$ (R = alkyl, silyl; n = 1–12) is a protecting group strategy, which has been investigated *somewhat*, in fact this approach has not been investigated systematically and little is known of the effectiveness of various R groups in hindering oxygen coordination to *e.g.* metallocene polymerization catalyst systems. We report here the results (a) of an NMR study of reactions of an archetypal metallocene polymerization catalyst, $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, with the polar monomers $CH_2{=}CH(CH_2)_8OR$ (R = Me, $PhCH_2$, Ph_3C, Me_3Si, Ph_3Si), all protected versions of the readily available, long chain polar monomer 9-decen-1-ol, and (b) of an investigation of the copolymerization reactions of these same polar monomers with ethylene and propylene catalyzed by the well known *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO catalyst system. While increasing the steric requirements of the groups R does decrease the apparent abilities of the ethers to displace $[BMe(C_6F_5)_3]^-$ from the $[Cp_2ZrMe]^+$ cation, there is no correlation of size of R with the degrees of incorporation of the polar monomers into copolymers of ethylene and propylene. Instead, a heretofore unsuspected role for catalyst *activation* by the ether linkage is suggested.

Introduction

The incorporation of monomers containing polar functionality into polyolefins is currently of great interest and importance, both industrially and academically, since random incorporation of polar groups such as ester, halo, cyano, hydroxyl, *etc.*, into *e.g.* polyethylene and polypropylene is expected to result in significant enhancement of properties such as oil resistance, adhesion, paintability and miscibility with polar polymers such as polyesters and polyamides.[1] Unfortunately the types of Ziegler catalysts, which are most effective for the homopolymerization of ethylene and propylene do not perform well in the presence of monomers containing the above-mentioned polar groups because most such catalysts are strong Lewis acids, which are extremely susceptible to coordination of a polar functional group to a vacant site on the metal. Thus, the "wrong" end of the polar monomer coordinates preferentially and polymerization is prevented.[1] Therefore new methodologies for the synthesis of random copolymers containing polar and non-polar segments are desirable.

Catalytic systems based on cationic metallocene complexes of the type $[Cp'_2M(Me)]^+$ (Cp′ = substituted cyclopentadienyl; Me = CH_3; M = Ti, Zr, Hf)[2] are obvious choices for copolymerization studies involving ethylene as they readily copolymerize ethylene with 1-alkenes to form various types of linear low density polyethylene.[3a–d] By proper tailoring of the ligands, they also offer high degrees of stereochemical control during propylene polymerization to *i*-PP in addition to forming copolymers of propylene with 1-alkenes.[3e–h] In principle, therefore, appropriate masking of the polar functionality of a polar 1-alkene monomer prior to copolymerization should provide a route to interesting new materials, and this approach has been investigated with a number of hydroxyl terminated 1-alkenes of the type $CH_2{=}CH(CH_2)_nCH_2OH$ (n = 0–12). One approach to masking has involved the use of aluminum alkyl compounds, which can both convert the hydroxyl group to an alkoxy group (eqn (1)) and coordinate to the oxygen as in eqn (2).[4,5]

$$CH_2{=}CH(CH_2)_nCH_2OH + AlR_3 \longrightarrow CH_2{=}CH(CH_2)_nCH_2OAlR_2 + RH \tag{1}$$



$$CH_2{=}CH(CH_2)_nCH_2OAlR_2 + AlR_3 \longrightarrow CH_2{=}CH(CH_2)_nCH_2O\begin{matrix}\nearrow AlR_3\\ \searrow AlR_2\end{matrix} \tag{2}$$

A combination of these two processes results in significantly increased steric encumbrance around the oxygen atom, thus inhibiting its coordination to the active site of the catalyst and

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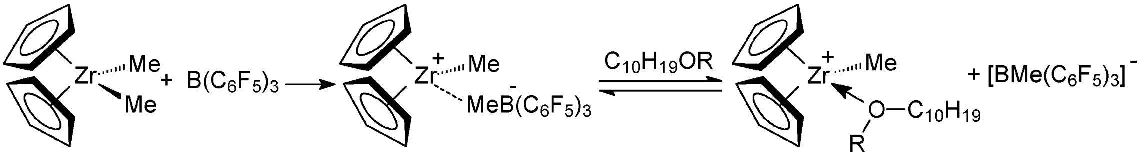


(3)

decreasing the extent of deactivation of the catalyst. Ultimately the hydroxyl end groups may be restored *via* hydrolysis.

To date, many attempts at utilizing this approach to produce random copolymers of ethylene and propylene with monomers containing hydroxyl end groups have been reported. For instance, in a series of studies Löfgren, Seppälä *et al* have made copolymers of ethylene and propylene with a number of short and long chain hydroxyl functionalized alkenes using a variety of dichlorozirconocenes activated with methylaluminoxane (MAO).[4a–i] Reported polar monomer incorporations have been, however, invariably rather low, from 1 wt% to 3.6 mol% with incorporation being highest for the longer chain polar monomers. It was also found that addition of increasing amounts of polar monomer generally resulted in catalyst deactivation, manifested by reduction of both yields and molecular weights, and that the ratios of MAO to both zirconium and polar monomer as well as pretreatment of the latter with MAO had some effect on activities while addition of triisobutylaluminum to MAO-activated systems was in some cases found to be beneficial. Interestingly, in one study, the surface of a material which contained a small proportion of hydroxyl groups was shown to exhibit improved adhesive properties.[4h]

Similar results have been reported by other groups using a variety of aluminum alkyls and zirconocene-based catalysts,[5] although findings vary concerning the usefulness of trimethylaluminum (TMA) as an additive;[5e–g,k] whether or not the addition of TMA is beneficial seems to depend on the metallocene used. Some very high incorporations of longer chain protected polar monomers have been reported in some cases (*e.g.* 10,[5e] 37,[5g,51] 50,[5f,k] mol%), with interesting properties attributable to comonomer incorporation. In one case, for instance, the surface of the copolymer was found to be hydrophilic.[5k]

A complementary approach to the masking of hydroxyl end groups involves the utilization of hydrolysable ethers, a tactic first used many years ago with $TiCl_3$-based catalysts[6a,b] and more recently extended to metallocene-based catalytic systems.[4g,5s,t,6c–g] Although significant improvements in degrees of incorporation, conversions and molecular weights have not to this point been observed, the approach would appear to have merit because of decreased need for alkylaluminum protecting groups. We have therefore embarked on an investigation into the utilization of a series of alkyl and silyl ethers of the types $CH_2{=}CH(CH_2)_nOR$ (n = 2–10; R = alkyl, silyl), anticipating that enhanced steric requirements of the groups bonded to the ether oxygen atoms would result in inhibition of ether coordination and hence in increased incorporation of the polar monomer. In addition, the ability of silicon to efficiently delocalize the π electrons on oxygen through π-bonding renders the oxygen atoms of the two silyl ethers less basic than might be anticipated on the basis of simple electronegativity considerations.[6h,i]

We now describe a ^1H NMR spectroscopic assessment of the effects of varying the steric requirements of the ether substituents on the abilities of the 1-alkene monomers $CH_2{=}CH(CH_2)_8OMe$ (**A**), $CH_2{=}CH(CH_2)_8OCH_2Ph$ (**B**), $CH_2{=}CH(CH_2)_8OCPh_3$ (**C**) $CH_2{=}CH(CH_2)_8OSiPh_3$ (**D**) and $CH_2{=}CH(CH_2)_8OSiMe_3$ (**E**) to coordinate *via* the oxygen atoms to an archetypal catalyst, the $[Cp_2ZrMe]^+$ cation, generated in situ *via* $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (eqn (3)).[2l,7a,b]

We also describe a series of copolymerization experiments of the monomers with ethylene and propylene using the *rac*-$C_2H_4(Ind)_2ZrCl_2$[8a–c] catalyst system.

Experimental

Catalyst manipulations were carried out in an Mbraun glove box filled with purified nitrogen, while all reactions were carried out under purified argon using standard Schlenk line techniques. Deoxygenated toluene, hexanes, CH_2Cl_2 and THF (all Aldrich) were dried by passage through dried alumina columns, and THF and CH_2Cl_2 were further dried by storage over activated 4 Å molecular sieves. $CDCl_3$, CD_2Cl_2 and chlorobenzene-d_6 were dried over activated 4 Å molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were run on Bruker AV300, 400 or 500 spectrometers, chemical shifts being referenced to the residual proton signals of the deuterated solvents. Electrospray mass spectrometry experiments were run in positive ion modes on a Quattro VG with nitrogen as the nebulizing gas and CH_2Cl_2 as the carrier solvent. Differential scanning calorimetry (DSC) was run on a Perkin Elmer DSC 7 (TAC 7/DX), ramping at a rate of 5.00 °C min^{-1} or 10.00 °C min^{-1}, starting at a temperature range of 25 and going up to 250 °C. Elemental analyses were carried out by Canadian Microanalytical Services of Delta, British Columbia. The compounds *rac*-$C_2H_4(Ind)_2ZrCl_2$,[8a–c] NaH, CH_3I, $CHPh_2Br$, Ph_3CCl and $LiClO_4$ (all Aldrich) were used as received and 9-decen-1-ol (98% Alfa Aesar), $SiHPh_3$, $NH(Me_3Si)_2$ and benzyl chloride (all Aldrich) were degassed and dried over activated 4 Å molecular sieves prior to use, while Cp_2ZrMe_2[8d] and $B(C_6F_5)_3$[8f] were prepared as in the literature. Basic alumina (150 mesh, 58 Å, Aldrich) was dried under vacuum overnight and stored in the glove box. MAO was obtained from Aldrich (10 wt%) and Akzo Nobel (6.9 wt%); solutions from the two sources were used interchangeably for ethylene polymerizations.

Synthesis of 10-methoxy-dec-1-ene (A)

This monomer was synthesized as in the literature,[9a] but with modifications. To a slurry of 3.38 g NaH (0.14 mol, 1.1 equiv.) in 250 mL dry THF was added 20.0 g 9-decen-1-ol (0.128 mol, 1.0 equiv.) dropwise at 0 °C. After stirring for 2 h at room temperature, 18.2 g methyl iodide (0.13 mol, 1.0 equiv.) was added at 0 °C. The solution was stirred overnight, the volatiles were removed under reduced pressure, and 100 mL dry hexanes were added. The resulting mixture was filtered to remove NaI, and the filtrate was then eluted through a 6 cm column of activated alumina. The solvent was then removed under reduced pressure to give colourless, liquid product (13.7 g, 63% yield). ^{1}H NMR ($CDCl_3$) δ/ppm: 5.82 (m, 1 H), 4.95 (m, 2 H), 3.37 (m, 2 H), 3.34 (s, 3 H), 2.04 (m, 2 H), 1.56 (m, 2 H), 1.3–1.4 (m, 10 H). As a test for the presence of residual hydroxyl-containing impurities such as water or unreacted 9-decen-1-ol, a solution of **A** in C_6D_6 was treated with 0.2 molar equiv. of the OH-sensitive Cp_2ZrMe_2. In addition to the resonances of 9-decen-1-ol, the resulting NMR spectrum exhibited only the resonances of Cp_2ZrMe_2 (δ 5.73, –0.14). Not observed was the Cp resonance of $(Cp_2ZrMe)_2O$ at δ 5.74 or the resonance of methane at δ 0.24, and thus no cleavage of the Zr-Me bonds in Cp_2ZrMe_2 had occurred.

Synthesis of 10-benzyloxy-dec-1-ene (B)[9b]

This monomer was synthesized essentially as above using 0.77 g NaH (0.032 mol, 1.0 equiv.) in 150 mL dry THF, 5.00 g 9-decen-1-ol (0.032 mol, 1.0 equiv.) and 4.05 g benzyl chloride (0.032 mol, 1.0 equiv.). Yield 1.5 g (20%). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.39–7.26 (m, 5 H), 5.83 (m, 1 H), 4.96 (m, 2 H), 4.52 (s, 2 H), 3.48 (t, *J* 7 Hz, 2 H), 2.05 (m, 2 H), 1.61 (m, 2 H), 1.34 (m, 10 H). The purified product was tested as above for hydroxylic impurities.

Synthesis of 10-trityloxy-dec-1-ene (C)

This was obtained as a colourless oil as above using 5.58 g Ph_3CCl. Yield 3.19 g (40%). ^{1}H NMR ($CDCl_3$) δ/ppm: 7.2–7.6 (m, 5 H), 5.84 (m, 1 H), 4.99 (m, 2 H), 3.08 (t, *J* 7 Hz, 2 H), 2.06 (m, 2 H), 1.65 (m, 2 H), 1.3–1.4 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ/ppm: 145.0, 139.6, 129.1, 128.2, 127.2, 114.5, 86.7, 64.1, 34.2, 30.4, 29.9, 29.8, 29.5, 29.3, 26.7. The purified product was tested as above for hydroxylic impurities. Anal. calcd for $C_{29}H_{34}O$: C 87.39, H 8.60. Found: C 87.18, 8.65.

Synthesis of 10-triphenylsiloxy-dec-1-ene (D)

This was synthesized as in the literature.[9c] To a mixture of 6.00 g 9-decen-1-ol (0.038 mol, 1 equiv.) and 10.00 g $HSiPh_3$ (0.038 mol, 1 equiv.) in 150 mL of dry toluene was added drop wise a solution of 0.786 g $B(C_6F_5)_3$ (1.5 mmol, 0.04 equiv.) in 10 mL toluene. Aliquots of the reaction were periodically analyzed by ^{1}H NMR spectroscopy, and it was determined that the reaction was complete after stirring for 68 h at room temperature. The reaction mixture was filtered, the solvent was removed under reduced pressure and the resulting solid was dissolved in 50 mL hexanes. The solution was eluted through a 6 cm of activated alumina and the solvent was removed under reduced pressure to yield the product as a viscous, colourless oil (12.6 g, 80%). The purified product was tested as above for hydroxylic impurities. ^{1}H NMR ($CDCl_3$) δ/ppm: 7.4–7.8 (m, 15 H), 5.92 (m, 1 H), 5.7 (d, 2 H), 3.91 (t, *J* 7 Hz, 2 H), 2.14 (m, 2 H), 1.70 (m, 2 H), 1.40 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ/ppm: 139.6, 135.8, 134.9, 130.3, 128.2, 114.6, 64.4, 34.2, 32.9, 29.8, 29.7, 29.5, 29.3, 26.2. TOF-EI-MS ($[M + H]^+$, calcd 415.2444, found 415.2457) Anal. calcd for $C_{28}H_{34}OSi$: C 81.10, H 8.27. Found: C 80.98, 7.93.

Synthesis of 10-trimethylsiloxy-dec-1-ene (E)

This monomer was synthesized as in the literature.[9d] To a mixture of 7.22 g $(Me_3Si)_2NH$ (0.044 mol, 0.7 equiv.) and 3.4 g $LiClO_4$ (0.032 mol, 0.5 equiv.) was added 10.00 g 9-decen-1-ol (0.064 mol, 1 equiv.). The mixture was stirred at room temperature overnight, following which 50 mL CH_2Cl_2 was added and the reaction mixture was filtered. The resulting solution was eluted through a 6 cm column of activated alumina and the solvent was then removed under reduced pressure to yield the colourless liquid product (13 g, 89%). The purified product was tested as above for hydroxylic impurities. ^{1}H NMR ($CDCl_3$) δ/ppm: 5.78 (m, 1 H), 4.93 (m, 2 H), 3.55 (t, *J* 7 Hz, 2 H), 2.02 (m, 2 H), 1.50 (m, 2 H), 1.3–1.4 (m, 10 H), 0.9 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ/ppm: 139.3, 114.4, 62.9, 34.1, 33.0, 29.8, 29.7, 29.4, 29.2, 26.1. TOF-EI-MS (M^+, calcd 228.1909, found 228.1904).

Procedure for NMR monitoring of reactions of the compounds $CH_2{=}CH(CH_2)_7CH_2OR$ (R = Me, $PhCH_2$, Ph_3C, Me_3Si, Ph_3Si) with $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$

To a nitrogen filled 5 mm NMR tube was added first a solution of 14 mg $B(C_6F_5)_3$ (27.8 µmol) in 0.50 mL of C_6D_5Cl or CD_2Cl_2 and then a solution of 7 mg Cp_2ZrMe_2 (27.8 µmol) in 0.25 mL of the same solvent. A ^{1}H NMR of this solution was taken, and then 5–10 molar equiv. of a polar monomer was added. The sample was shaken and placed quickly in the probe of an NMR spectrometer, and the NMR spectrum of the solution was obtained.

General procedure for copolymerizations

In a typical experiment (method A), ethylene or propylene was bubbled for 2 min into a solution containing 5 mg of *rac*-$C_2H_4(Ind)_2ZrCl_2$[8a–c] in 15 mL of dry toluene in a flame-dried, 50 mL Schlenk tube; 1000 equiv of MAO were then added and the solution was stirred for a further 5 min. The comonomer was then added drop wise over one min, and the reaction mixture was stirred for 30 min while bubbling of ethylene or propylene was continued. The copolymerizations were quenched with 70 mL of a HCl–ethanol (5% HCl in ethanol) mixture, the resulting mixtures were stirred overnight, and the precipitated copolymers were filtered, washed with ethanol, dried under vacuum at 60 °C for 12–15 h and analyzed by ^{1}H and ^{13}C NMR spectroscopy and IR spectroscopy and by differential scanning calorimetry. Alternatively, (method B), an ethylene- or propylene-saturated toluene solution of *rac*-$C_2H_4(Ind)_2ZrCl_2$ and the polar comonomer was stirred for 5 min and then 1000 equiv. of MAO were added. The subsequent procedure was as above.

Results and discussion

In order to develop methodologies for the incorporation of polar monomers into polyolefins, we chose to work initially with ethers of 9-decen-1-ol, $CH_2{=}CH(CH_2)_7CH_2OR$ (R = Me, $PhCH_2$, Ph_3C, Me_3Si, Ph_3Si). Previous researchers have found that higher incorporations of polar monomers are generally achieved with longer chain monomers,[1b,4c–e,6b] possibly because of the greater separation of the polar functionality from the C=C bond, but to date there has been little research into the effects of varying the nature of the ethers as masking agents for the hydroxyl group. We have chosen to work with the methyl, benzyl, trityl, trimethylsilyl and triphenylsilyl ethers of 9-decen-1-ol, encompassing a range of alkoxy and siloxy group steric requirements, as we wished to test an hypothesis that bulkier substituents would hinder ether oxygen coordination and would thereby inhibit (co)polymerization the least. Also, as noted above, the two silyl ethers are expected to exhibit lowered basicity for purely electronic reasons having to do with π-bonding between the silicon and oxygen atoms.[6h,i] Of the ethers utilized, $CH_2{=}CH(CH_2)_8OMe$ (**A**),[9a] $CH_2{=}CH(CH_2)_8OCH_2Ph$ (**B**),[9b] $CH_2{=}CH(CH_2)_8OSiPh_3$ (**D**)[9c] and $CH_2{=}CH(CH_2)_8OSiMe_3$ (**E**)[9d] and are known compounds while $CH_2{=}CH(CH_2)_8OCPh_3$ (**C**) has not been prepared previously. All were characterized spectroscopically, **D** and **E** by elemental analyses also.

In addition, as a guarantee of the thoroughness of the purification procedures, all of the ethers were tested to ensure that they were free of trace hydroxylic impurities (water, unreacted alcohol) which would coordinate preferentially to $[Cp_2ZrMe]^+$ and thus interfere with the chemistry to be studied. To this end, a deficiency of the OH-sensitive compound Cp_2ZrMe_2 was added to a benzene-d_6 solution of each and the resulting solutions were monitored by ^1H NMR spectroscopy. In no case was cleavage of the Zr–Me bonds of the Cp_2ZrMe_2 indicated by the appearance of new resonances in the Cp or methyl regions of the spectra, or by the appearance of the resonance of methane at δ 0.24.

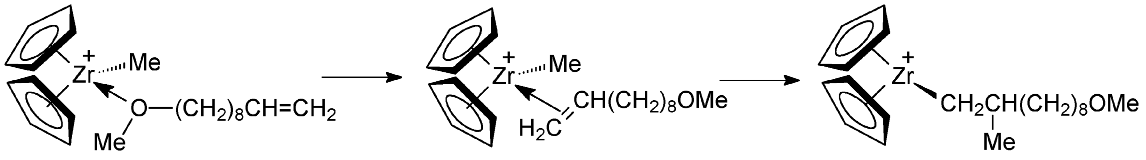
Coordinating abilities of polar monomers A–E

In an attempt to assess the relative coordinating abilities of the protected polar 1-alkene monomers **A–E** with a representative early metal metallocene catalyst system, an NMR study was undertaken of reactions of the monomers with the zwitterionic compound $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$. The latter is formed *via* methyl carbanion abstraction from Cp_2ZrMe_2 by $B(C_6F_5)_3$, and is a precursor of the Lewis acidic polymerization catalyst $[Cp_2ZrMe]^+$, which is expected to coordinate to poorly protected ether oxygen atoms (eqn (3)).[2l,7a,b] The NMR studies involved addition of 5 equiv. of each of the polar monomers **A–E** to solutions of the zwitterionic $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ in C_5D_5Cl or CD_2Cl_2 at room temperature. Similar behaviours were observed in both solvents but precipitation of the zwitterionic intermediate occurred in toluene-d_8 and thus this solvent could not be used.

The results of a typical experiment are shown in Fig. 1 which shows (a) the ^1H NMR spectrum of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, (b) the ^1H NMR spectrum of 1-methoxy-9-decene (**A**), and (c) the ^1H NMR spectrum of a reaction mixture containing one equiv. of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ and 5 molar equiv. of **A** immediately after mixing. As can be seen, the three resonances of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ at δ 5.91 (Cp), 0.46 (Zr–*Me*) and 0.32 (B–*Me*) disappeared on the addition of **A** and were replaced by a new Cp resonance at δ 5.95, a new Zr–*Me* resonance at δ 0.58 and a new B–*Me* resonance of the free $[BMe(C_6F_5)_3]^-$ anion at δ 1.1, identified by the apparent quadrupolar broadening. Equally important, the CH_2CH_2-O-CH_3 triplet, the CH_2-O-CH_3 singlet and the CH_2CH_2O multiplet of **A** at δ 3.25, 3.16 and 1.55, respectively, all broadened significantly, suggesting at least partial substitution of the borate anion from the inner coordination sphere of the zirconium by the ether oxygen of **A** *and* rapid exchange between free and O-coordinated **A** as in eqn (3) (R = Me). Thus, the observed resonances are weighted averages of the chemical shifts of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, of **A** and of the ether complex of **A**. We also note that the CH_2CH_2-O-CH_3, CH_2-O-CH_3 and CH_2CH_2O resonances at δ 3.25, 3.16 and 1.55 all shifted slightly upfield rather than downfield as might be expected on coordination to a strongly Lewis acidic metal ion. This result is presumably a result of ring current effects from the aromatic Cp ligands,[7b,c] and provides further evidence for O-coordination.

Interestingly, and highly important, the olefinic multiplet resonances of **A** at δ ~4.9 and ~5.8 did *not* shift or broaden in the presence of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ (Fig. 1c), and thus coordination of the olefinic group to the metal does not occur significantly under these conditions. With longer reaction times (over 24 h, not shown), these olefinic resonances did weaken and eventually disappeared as new, broad resonances appeared in the aliphatic region (δ 1–2.2). These spectral changes are consistent with slow reorganization of the O-bonded ether complex to the η^2-alkene isomer and migratory insertion, as in eqn (4), followed by oligomerization of **A** as in eqn (5).

A relatively strong, sharp singlet also appeared slowly at δ 4.80. The chemical shift and singlet nature of this resonance are characteristic of vinylidene compounds of the type $H_2C{=}CRR'$ (R and R′ = long chain alkyl groups),[10] and the presence of this type of alkene product is consistent with formation *via* a β-elimination reaction of the unsaturated oligomer shown as a product in eqn (6).



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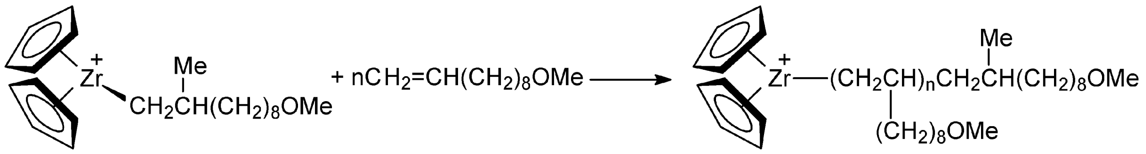

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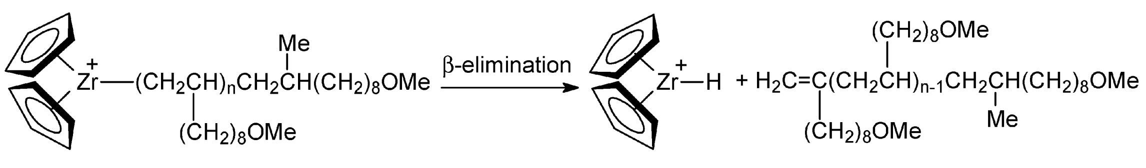

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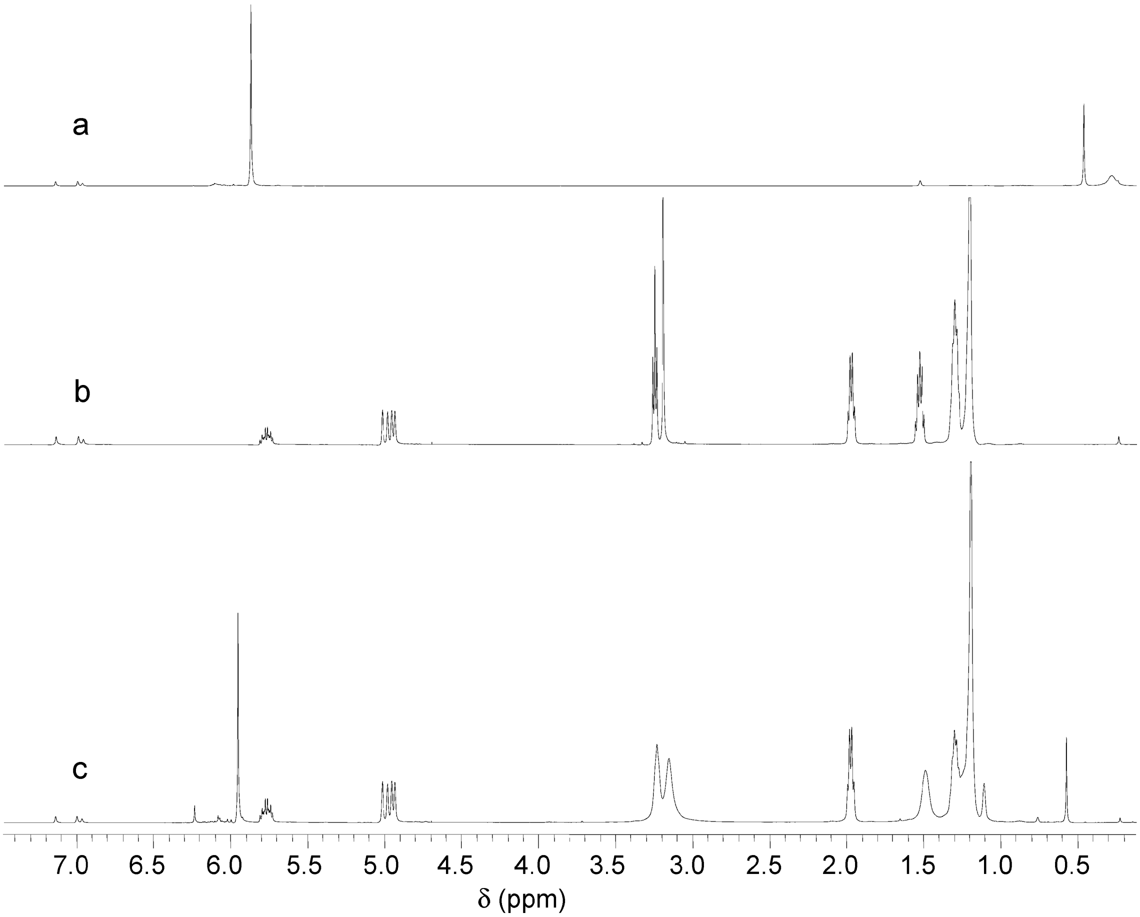

Fig. 1 ^{1}H NMR spectra (500 MHz, C_6D_5Cl) (a) of 1-methoxy-9-decene, (b) of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, and (c) of a solution containing one equivalent of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ with 5 equiv. of 10-methoxy-1-decene immediately after mixing.

The resulting cationic zirconocene hydride is expected to exhibit a Zr–*H* singlet resonance in the region δ 6–8,[11] but several weak resonances are observed in this region and the hydride resonance could not be identified. However, the cationic hydride shown would certainly behave as an oligomerization catalyst and may have been present in very low concentrations. Small amounts of oily materials could be isolated from NMR reactions on removal of the solvent, but these were not investigated because our interest was in comparing the clearly poor protecting ability of the methyl group to those of the bulkier groups.

Similar experiments, involving the addition of a 5-fold molar excess of monomer **B**, with a somewhat larger benzyl protecting group, to solutions of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ showed again that the resonances of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ disappeared, indicating at least a degree of displacement of the $[BMe(C_6F_5)_3]^-$ anion by the ether group. In this case the O–CH_2CH$_2$ triplet and O-CH_2Ph singlet were not broadened or shifted noticeably, suggesting that the benzyl ether does not coordinate to the same extent as does the methyl ether, but the olefinic resonances of **B** did slowly weaken as broad resonances appeared in the aliphatic region of the spectrum. Thus slow oligomerization did appear to take place over 24 h although a possible vinylidene peak at δ ~4.7 did not gain significant intensity. This system was not studied further, but the results do imply that the benzyl group is also not a very good protecting group.

Rather different results were obtained with 1-trityloxy-9-decene (**C**), 10-triphenylsilyloxy-1-decene (**D**) and 10-trimethylsilyloxy-1-decene (**E**, Fig. 2), which contain much larger ether protecting groups and which were therefore expected to exhibit much greater steric protection to the ether oxygen atoms than is the case for **A** or **B**. A typical NMR spectrum, for **E**, is shown in Fig. 2 where it is clear that the ^{1}H resonances of **E** are not affected by the presence of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$. In particular the O–$CH_2$ resonance did not broaden or shift significantly. Furthermore, unlike the situations with **A** and **B**, there was very little or no weakening of the olefinic resonances of **C**, **D** and **E** over 24 h. Thus, relatively little oligomerization occurs with these monomers.

In summary, the above NMR experiments involving monomers **A–E** suggest major differences in the abilities and the extents to which the various groups inhibit displacement of the $[BMe(C_6F_5)_3]^-$ anion and hence allow coordination of the ether oxygen atoms to the $[(\eta^5\text{-}C_5H_5)_2ZrMe]^+$ cation. The differences correlate significantly with the steric requirement of the various groups, and, in the section below, we assess the abilities of these same protecting groups to inhibit polar monomer incorporation

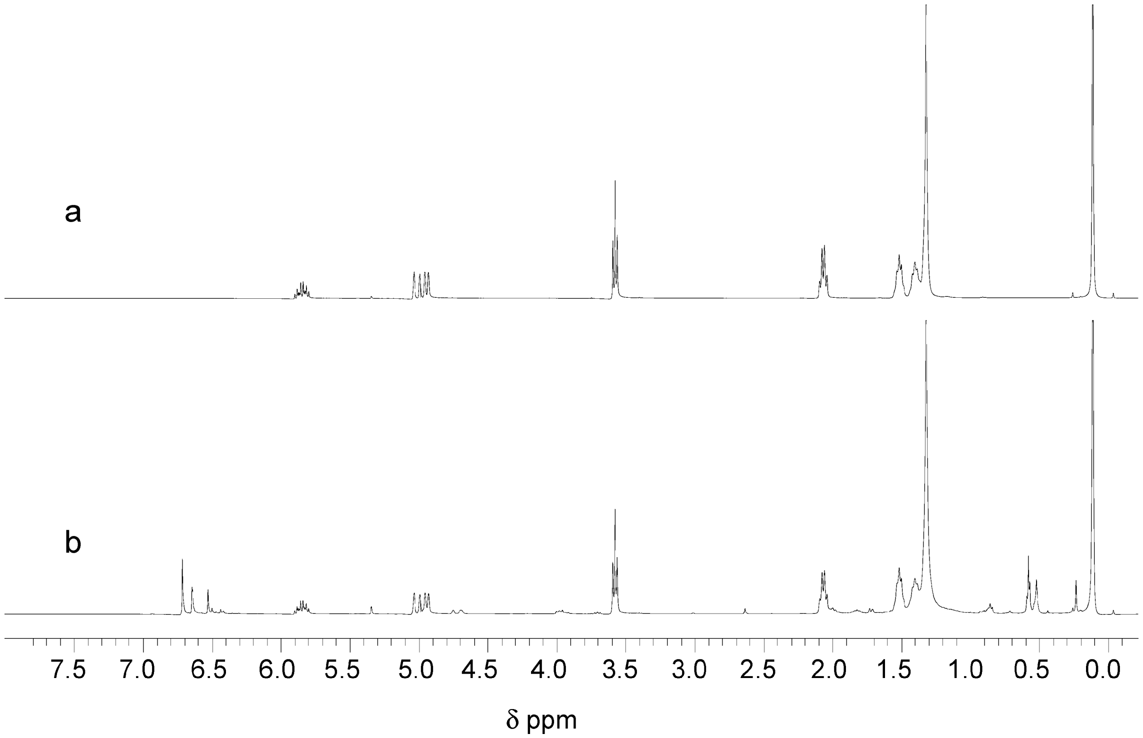

Fig. 2 ^{1}H NMR spectra (400 MHz, CD_2Cl_2) (a) of 1-trimethylsilyloxy-9-decene, (b) of a solution containing one equivalent of $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ with 5 equiv. of 1-trimethylsilyloxy-9-decene immediately after mixing.

during attempted copolymerization reactions of the five polar monomers with ethylene and propylene.

Copolymerization studies of polar monomers A–E

After examining the nature and extent of the interactions of monomers **A–E** with a simple early metal catalyst system, the $[(\eta^5\text{-}C_5H_5)_2ZrMe]^+$ cation, our focus shifted to an investigation of the abilities of the various ether functional groups to influence the incorporation of polar monomers into polyolefins, in particular polyethylene and polypropylene. We wished to test an hypothesis that the bulkier substituents which hinder ether oxygen coordination the most would likewise inhibit copolymerization the least. We chose to work initially with ethers of 9-decen-1-ol as this monomer is less inexpensive than many shorter chain analogues and also because previous researchers have found that higher incorporations of polar monomers are generally better achieved with monomers containing long chains, possibly because of the greater separation of the polar functionality from the C=C bond.[1b,4c–e,6b]

Our initial study involved copolymerizations with ethylene and propylene using *rac*-$C_2H_4(Ind)_2ZrCl_2$. When activated with MAO, this is an excellent catalyst for the homopolymerization of ethylene and the isospecific polymerization of propylene to isotactic polypropylene (*i*-PP),[8a–c] and it also exhibits better activities for alkene polymerization than does the $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ system. We utilized two copolymerization procedures, method A involving treatment of an ethylene- or propylene-saturated toluene solution of *rac*-$C_2H_4(Ind)_2ZrCl_2$ and MAO with polar monomer 5 min after addition of MAO. Initiation of homopolymerization processes is often slower than propagation[12] and we thought it possibly desirable to induce polymerization prior to addition of polar monomer. Although this procedure resulted in some polyethylene or isotactic polypropylene forming in the reaction mixtures, the new copolymers were found to be sufficiently soluble that they could be readily separated from the relatively insoluble polyethylene or isotactic polypropylene. An alternative procedure (method B) involved addition of MAO to an ethylene- or propylene-saturated solution containing *rac*-$C_2H_4(Ind)_2ZrCl_2$ and polar monomer.

In each copolymerization experiment, ethylene or propylene was continuously fed into the reaction mixture until termination of the reaction, which was accomplished after 30 min by quenching with acidified ethanol to destroy the active catalyst and residual MAO. The resulting mixture was then stirred overnight to ensure complete MAO quenching and precipitation of the polymeric products and, following filtration, the solid products were dried in a vacuum oven overnight at 60 °C. The copolymers were characterized by ^{1}H and, in some cases, ^{13}C NMR spectroscopy in tetrachloroethane-d_2 (TCE-d_2) or *o*-dichlorobenzene–C_6D_6, either at room or at high temperatures depending on solubilities. The ^{1}H NMR spectra were used to determine the mole percent incorporations of the polar monomers as outlined below.

Copolymerization studies with ethylene

Copolymerization reactions with ethylene were attempted with all five polar comonomers, and generally proceeded rapidly to give white materials which were purified of aluminum byproducts, collected by filtration and dried. Fig. 3 shows a representative ^{1}H NMR spectrum of the materials obtained utilizing comonomer **A**. As can be seen, the spectrum exhibits somewhat broadened yet

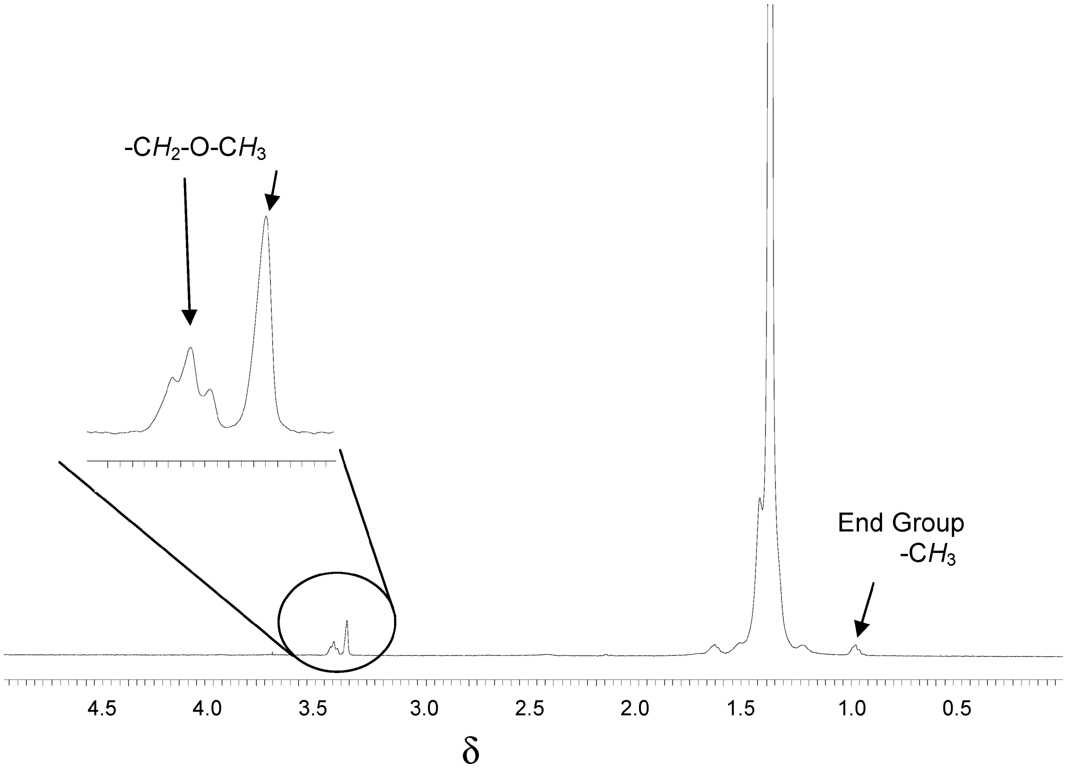

Fig. 3 Representative ^{1}H NMR spectrum (400 MHz, TCE-d_2, 120 °C) of the isolated copolymer of experiment 1.

prominent OCH_2CH_2 and OCH_3 resonances at δ 3.43 and 3.37, respectively, in accord with literature values of δ 3.33 and 3.27[4g] and clear evidence for incorporation of **A** and, by integration, making possible determination of the degree of incorporation Also observed are the main chain polyethylene $(-CH_2-)_n$ resonance at δ 1.38 and the polymer methyl end group at δ 0.98, which was used for the calculation of number average molecular weight, M_n.

Fig. 4 shows a representative ^{1}H NMR spectrum of the copolymers obtained utilizing comonomer **E**; in this case the protecting group is hydrolyzed to a hydroxyl group during the work up procedures. In Fig. 4, the OCH_2CH_2 resonance is observed at δ 3.69, consistent with literature data (δ 3.58[4g]) for similar copolymers of ethylene and 10-undecen-1-o1, but all the remaining resonances due to the polymer main chain and polymer end groups are similar to those in Fig. 3. Again integration of the OCH_2CH_2 resonance made possible determination of the degree of incorporation.

Table 1 summarizes the data obtained for the copolymerization reactions involving ethylene. As can be seen, very low degrees of incorporation (0.004–1.2%) of the polar comonomers were achieved whether the catalyst was activated in the presence of comonomer or prior to comonomer addition. Note that monomer **B** is not included in Table 1 because *no* incorporations were observed in several attempts. For reasons not clear, the degrees of incorporation found here are somewhat lower than those reported elsewhere (0.7–3.6%) for this catalyst with 10-undecen-1-ol protected by MAO from a different source.[4g] However, under the conditions utilized here, it seems that none of the polar comonomers can compete effectively with the relatively small ethylene molecule and, as a result, the resulting low degrees of branching are reflected in values of T_m, which are all very similar to that of high density polyethylene (120–130 °C).[13] The M_n values of the copolymers in Table 1 seemingly varied from 2170 to 51 000 and were consistently high with the trityl protecting group monomer **C** although the observation of two T_m values suggests that bimodal distributions of homopolymers were obtained. However, determination of M_n involved comparing integrations of resonances of very different intensities and the errors involved are unknown. In any case, since the low degrees of incorporation of polar monomers generally rendered comparisons of the data in Table 1 to be of little value, we continued with propylene copolymers.

Table 1 Copolymerizations of ethylene with polar monomers $CH_2{=}CH(CH_2)_7CH_2OR$, where R = Me (**A**), Ph_3C (**C**), Ph_3Si (**D**) Me_3Si (**E**), using the catalyst *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO

Experiment #[a]	Comonomer	Yield/g	Incorp. (mol%)	T_m/°C[b]	M_n
1*	**A**	2.0	0.12	128	2170
2**	**A**	1.7	0.93	123	4520
3*	**C**	2.5	0.004	128	2870
4**	**C**	1.6	1.1	112, 126	11 500
5*	**C**	1.6	0.1	106, 130	25 410
6*	**E**	2.8	0.4	129	51 000
7**	**E**	1.3	1.2	121	8660
8*	**D**	3.0	0.2	127	6820
9**	**D**	4.1	0.1	126	5360

[a] * = Method A, ** = method B. [b] 5.00 °C min^{-1} ramping.

Copolymerization studies with propylene

In contrast to the above results with ethylene, it was hoped that the use of the somewhat bulkier propylene would permit

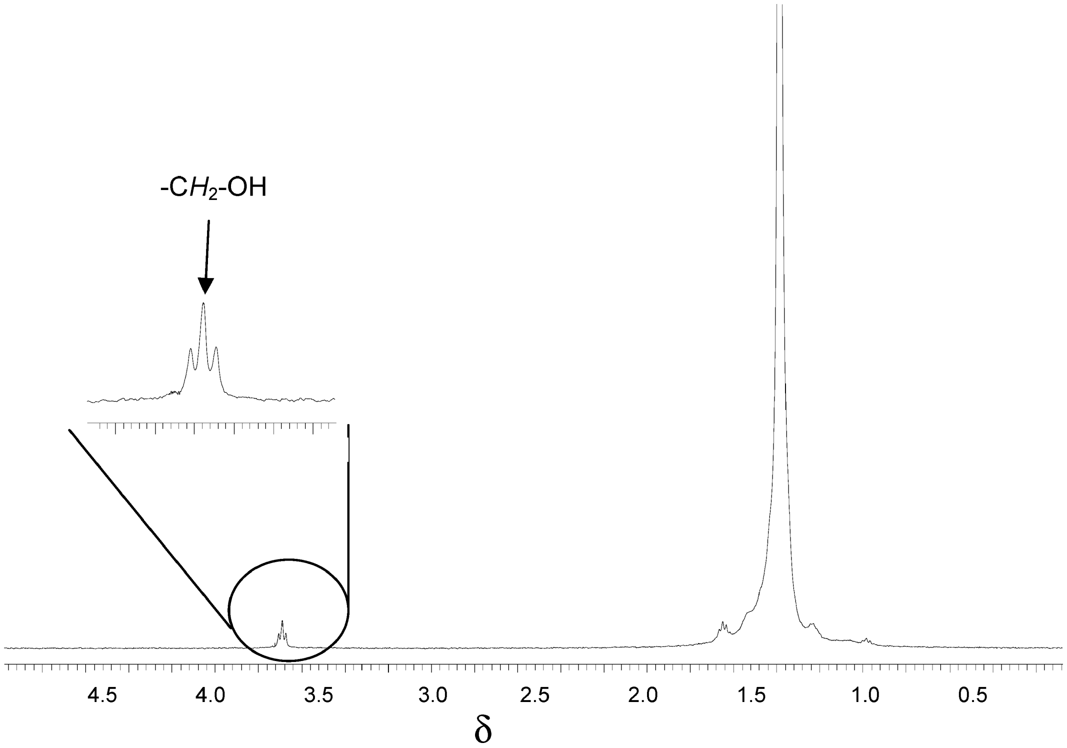

Fig. 4 Representative ^{1}H NMR spectrum (400 MHz, TCE-d$_2$, 120 °C) of the isolated copolymer of experiment 7.

greater incorporation of the polar monomers and hence better discrimination between them. Propylene is also of interest with *rac*-$C_2H_4(Ind)_2ZrCl_2$ as a catalyst, of course, because of the possibility of synthesizing isotactic copolymers[8a–c] which would be interesting and potentially useful materials. The copolymerization reactions involving propylene were carried out using method B, described above, and yielded solid white materials. All polymerization experiments were repeated at least twice and all products were, where possible, characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy and differential scanning calorimetry (DSC). The MAO used for these experiments was from Aldrich (10 wt% in toluene).

The ^{1}H NMR spectrum of the copolymer obtained using comonomer **A**, shown in Fig. 5, exhibits the expected OCH_2CH_2 and OCH_3 resonances at δ 3.37 and 3.34, respectively, in addition to the resonances characteristic of isotactic polypropylene at δ 1.72, 1.40 and 0.87.[14] The resonances of the long chain of the polar monomer are obscured by the much stronger resonances of the polypropylene chains. The ^{1}H NMR spectra of the products obtained using copolymers **B–E** were very similar to that shown in Fig. 5 but, as expected given the nature of the work up procedures, exhibited only a triplet attributable to the OCH_2CH_2 group (δ 3.52–3.61) in addition to the strong resonance of the polypropylene backbone. Polymer spectra generally also exhibited two vinylidene end group resonances at δ ~4.7, barely visible in Fig. 5, which were used for the calculation of number average molecular weights, M_n. As with the ethylene copolymers, the integrated intensities of the OCH_2CH_2 groups were used to determine the degrees of incorporation.

Table 2 lists the results of copolymerization experiments involving propylene, including control runs in which no comonomer was added (experiment 10, 11). The odd numbered experiments are all repeats of the preceding even numbered experiments and, as can be seen, reproducibility was generally very good. Interestingly, addition of the comonomers to propylene polymerization reaction mixtures did not result in either decreased polymer product yields or decreased values of M_n, as has been reported elsewhere for similar experiments.[4] In addition, to our surprise, the greatest degree of incorporation was observed with methoxy monomer **A**, containing the smallest protecting group. Materials obtained with comonomer **B** (benzyl protecting group) exhibited incorporations

Table 2 Copolymerizations of propylene with polar monomers $CH_2{=}CH(CH_2)_7CH_2OR$, where R = Me (**A**), $PhCH_2$ (**B**), Ph_3C (**C**), Ph_3Si (**D**) Me_3Si (**E**), using the catalyst *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO

Experiment #[a]	Comonomer (100 equiv.)	Time/ min	Yield/g	Incorp. (mol%)	T_m/°C	M_n
10	None	30	3.9	—	120	900
11	None	30	3.7	—	118	1200
12	**A**	30	2.6	2.0	127	6300
13	**A**	30	3.0	1.7	126	4700
14	**B**	30	4.6	0.5	128	3100
15	**B**	30	5.2	0.2	124	2500
16	**C**	30	4.2	0.4	121	1000
17	**C**	30	4.1	0.5	123	950
18	**E**	30	2.7	0.9	128	5800
19	**E**	30	2.8	0.7	128	7100
20	**D**	30	4.9	—	121	1340
21	**D**	30	4.9	—	118	1600
22[a]	**E**	30	1.9	0.4	96	1960
23[a]	**E**	30	2.0	0.3	102	2160
24[a]	**D**	30	3.0	—	n.t.	1500
25[a]	**D**	30	3.0	—	n.t.	1460

[a] Copolymerization performed at 60 °C; n.t. = no transition (*i.e.* amorphous).

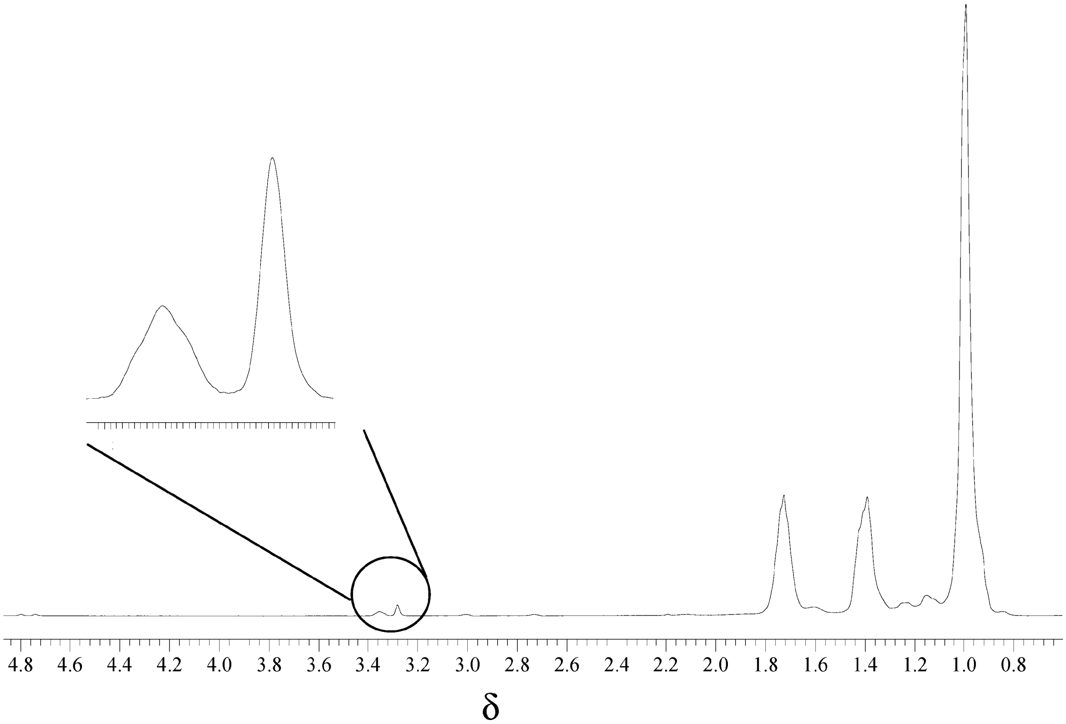

Fig. 5 ^{1}H NMR spectrum (400 MHz, ODCB–C_6D_6, 80 °C) of copolymer from experiment 12.

of polar monomer that were low (up to 0.5 mol%), and similar incorporations were obtained materials containing comonomer **C** (trityl protecting group). These results suggest that bulkier protecting groups do not promote more incorporation of polar monomer within the polypropylene. The degrees of incorporation for copolymers containing comonomer **E** (trimethylsilyl protecting group) were slightly higher (up to 0.9 mol%), but no incorporation was observed for comonomer **D** (triphenylsilyl protecting group) as essentially homopolymer was isolated.

In an effort to determine if greater polar monomer incorporation could be achieved, experiments 22–25 were carried out at a higher starting temperature (60 °C). The products obtained in experiment 22 and 23 were copolymers (up to 0.4 mol% incorporation), but the incorporations were actually lower than those done at 21 °C and increasing the temperature for this particular system clearly did not increase the polar monomer content. This phenomenon was further evident in the products of experiments 24 and 25, where only homopolymer was isolated. In addition, increasing the amount of added polar monomer to 500 equiv. resulted in *no* incorporation of polar monomer; only homopolymer was formed.

The ^{13}C NMR spectra of the copolymers exhibit resonances with chemical shifts consistent with their being copolymers. For example, for the product of experiment 19, there are three major resonances of the isotactic propylene backbone at δ 47.1, 29.5 and 23.3 and for the polar monomer at δ 44.5, 34.6, 31.9, 31.5, 31.2, 27.6, 27.0 and 26.0. These peak assignments are based on literature assignments of similar copolymers[4b] and on comparisons with the ^{13}C NMR spectra of the polar monomers and of polypropylene itself. The resonance at δ 64.8 is diagnostic of the $CH_2\mathit{CH}_2OH$ group of the polar monomer, signifying incorporation and effective protecting group hydrolysis. For the product of experiment 12, containing polar monomer **A** (methoxy group), resonances are observed at δ 58.6 and 73.2, corresponding to the $CH_2\mathit{CH}_2O$ and $O\mathit{CH}_3$ groups, respectively.

Infrared spectra of the copolymers were prepared by placing a few drops of a chloroform solution of each copolymer on a KBr disk and allowing the solvent to evaporate to form thin films. The IR spectra of polypropylene (Fig. 6a) and of the copolymers obtained in experiments 12 and 13 (with methoxy groups) exhibited the characteristic C-H stretching modes of the polypropylene backbone at 2950–2840 cm^{-1}, in addition to C–H bending modes at 1457 and 1376 cm^{-1}. In addition to these peaks, bands at 1120–1017 cm^{-1} (C–O stretch) are observed in the IR spectrum of the two copolymers. For copolymers of polar monomers **B–D**, containing hydroxyl groups, a distinct broad peak at ~3400 cm^{-1} is indicative of hydrogen bonding within the copolymer (Fig. 6b).

The melting temperatures (T_m) of the various materials listed in Table 2 were determined by DSC measurements. The isotactic polypropylene samples synthesized in the control experiments of this study (experiments 10, 11), as well as in two of the copolymerization attempts which yielded only homopolymer (experiments 20, 21), exhibited T_m values (118–121 °C) which are comparable with the range of T_m values reported elsewhere with this catalyst under varying conditions.[15] Perhaps surprisingly, many of the copolymers obtained exhibited slightly higher T_m values although decreases would be expected in polypropylene containing long branches because of loss of crystallinity. Materials formed at higher temperatures (experiments 22–25) exhibited lower values of T_m, as has been noted elsewhere,[15c] and that formed in the presence of **D** exhibited no melting transition at all. There is no obvious trend in the molecular weights M_n, and the values obtained are generally comparable or slightly lower than reported

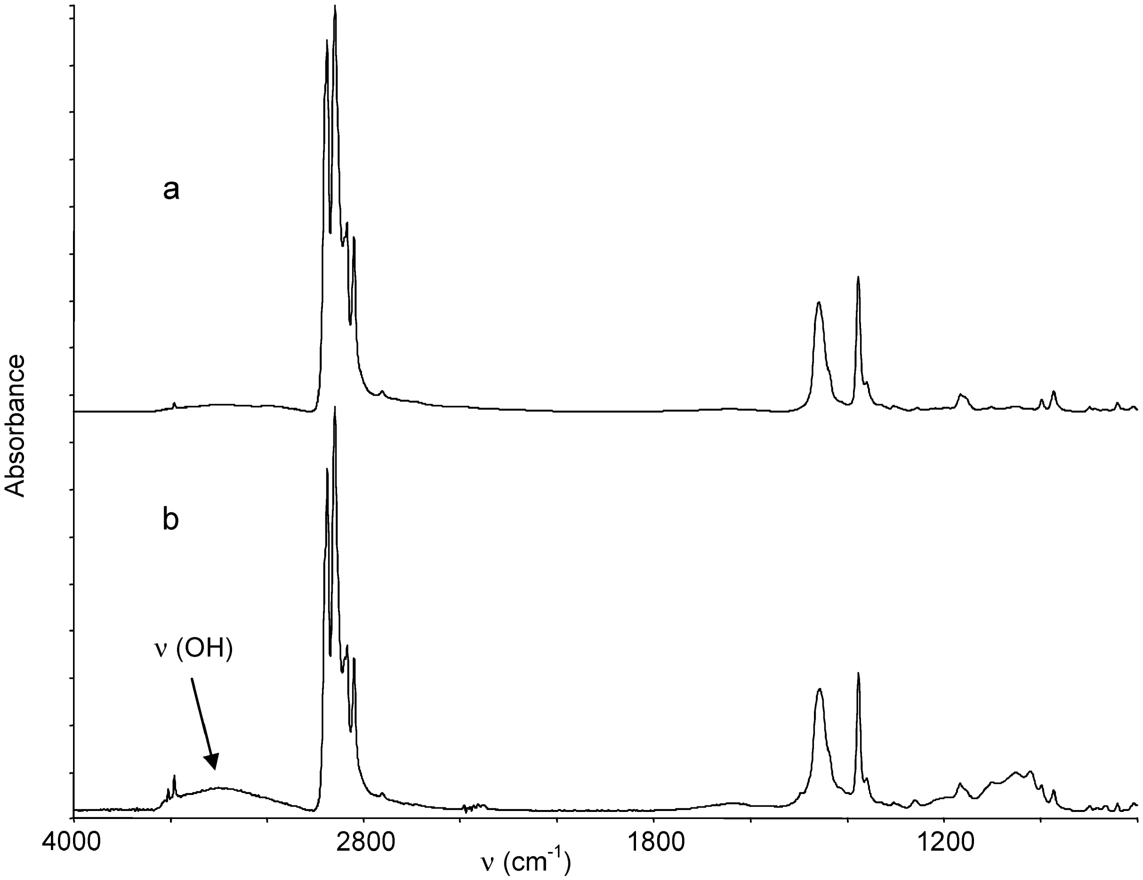

Fig. 6 Absorbance infrared spectra (films) of (a) pure polypropylene and (b) copolymer from experiment 18.

elsewhere from polymerizations carried out at higher pressures of propylene.[15b–15d]

As noted above, the highest degrees of polar monomer incorporation were achieved with the methoxy comonomer **A** (1.7, 2.0 mol%), and the next closest was the trimethylsilyl comonomer **E** (up to 0.9 mol% in experiment 18), while the trityl (experiments 16, 17) and triphenylsilyl (experiments 20, 21) comonomers, containing much greater steric hindrance near the ether oxygen, actually resulted in lower degrees of incorporation or none at all. These findings are unexpected as one would anticipate, as we have hypothesized above, that the presence of sterically more demanding protecting groups would result in higher degrees of incorporation of polar comonomers. We wondered, therefore, if the presence of ether linkages might play an unexpectedly positive role during the polymerization of 1-alkenes by the *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO catalyst system under the conditions utilized here, and we therefore carried out a series of similar copolymer experiments of propylene with 1-hexene in the absence and the presence of the *saturated* methoxy ether, *n*-decyl methyl ether.

Copolymerization reactions of 1-hexene with propylene, with and without added *n*-decyl methyl ether

A series of copolymerization experiments was carried out as above but utilizing 1-hexene rather than polar monomers. The products were all white solids, and typical ^{1}H and ^{13}C NMR spectra are shown in Fig. 7 and 8, respectively. The ^{1}H NMR spectrum is not very informative because of the overlapping of resonances, but propylene (P) resonances at δ 1.72, 1.40 and 0.87 are obvious and some 1-hexene (H) resonances are observed at δ 1.1 and 1.2. Also apparent are two vinylidene end group resonances at δ ~4.8, which were used for the calculation of number average molecular weights, M_n. The ^{13}C NMR spectrum also exhibits resonances attributable to propylene and 1-hexene units,[16] and the relative intensities of these were utilized to calculate the degrees of incorporation of 1-hexene into the polypropylene copolymers.[16]

Table 3 Propylene copolymerizations with 1-hexene using *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO in toluene

Experiment #	Equiv. of 1-hexene added	Yield/g	Incorp. (mol.%)	T_m/°C	M_n
34	—	2.53	—	120	2780
35[a]	100	4.38	2.9	106	2366
36[b]	100	4.03	1.7	127	1089
37[a]	500	4.00	9.1	n.t	2184
38[b]	500	4.67	13.0	n.t	1592

[a] Precatalyst and hexene combined prior to addition of MAO. [b] 1-Hexene added 5 min after MAO addition. n.t–no transition.

Table 3 presents data for representative copolymer samples and, as is seen, the yields, % incorporation (2.9, 1.7% in experiments 35 and 36, respectively) and T_m values are all comparable with those in Table 2. Thus polar monomer incorporations into polypropylene actually rival the degree of incorporation of the

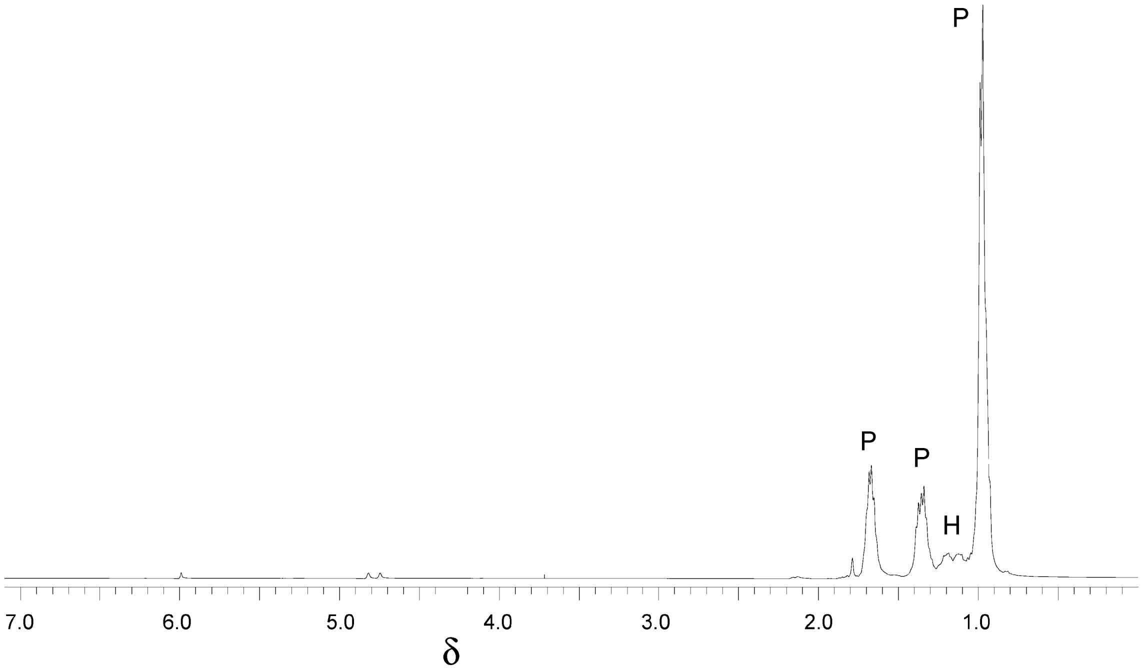

Fig. 7 High temperature ^{1}H NMR spectrum (400 MHz, TCE-d$_2$, 120 °C) of a copolymer of polypropylene with 2.9% of 1-hexene (experiment 35).

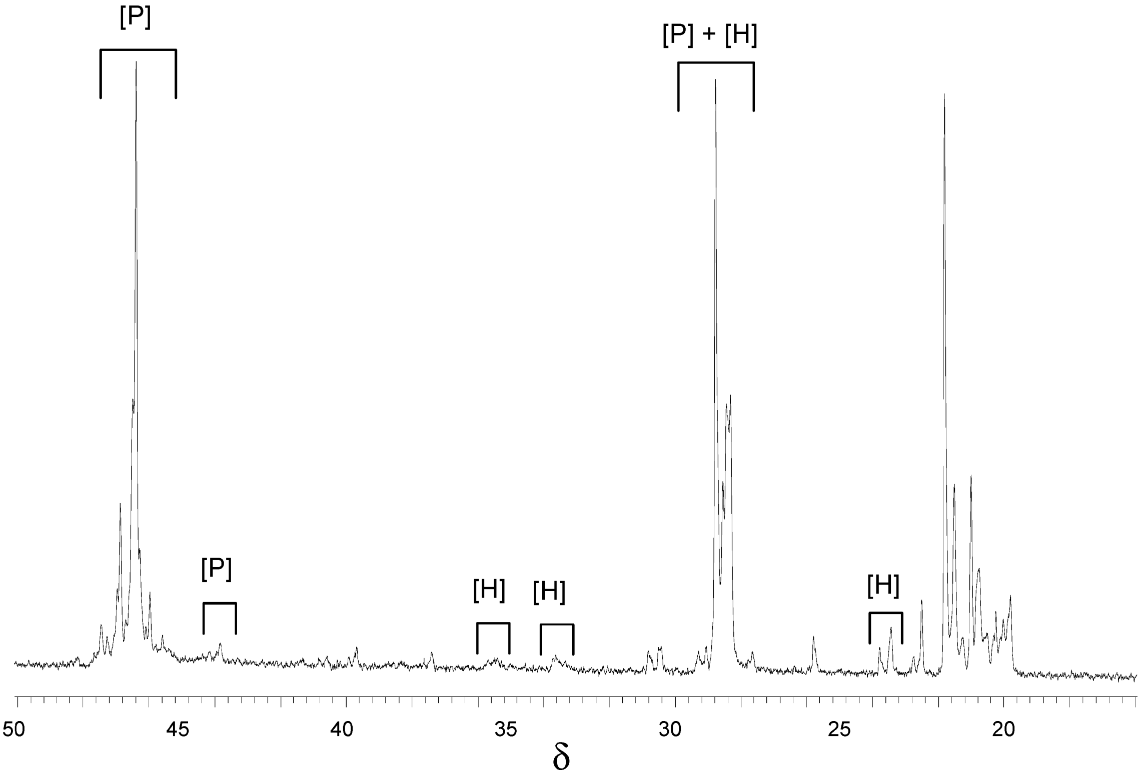

Fig. 8 High temperature ^{13}C NMR spectrum (125 MHz, ODCB–C$_6$D$_6$, 80 °C) of a copolymer of polypropylene with 13.0% of 1-hexene (experiment 38).

non-polar 1-hexene and it would seem that ether functionalities in the former do not hinder polar monomer incorporation, at least not in a straightforward manner. The 1-hexene copolymerizations did differ somewhat in that addition of 500 equiv. of 1-hexene resulted not in catalyst degradation, as with the polar monomers, but in higher degrees of incorporation to give non-crystalline polymers.

Given the apparent lack of correlation of degrees of incorporation of the decenyl ethers with the steric requirements of the series of R groups or with even the presence of an ether group, we

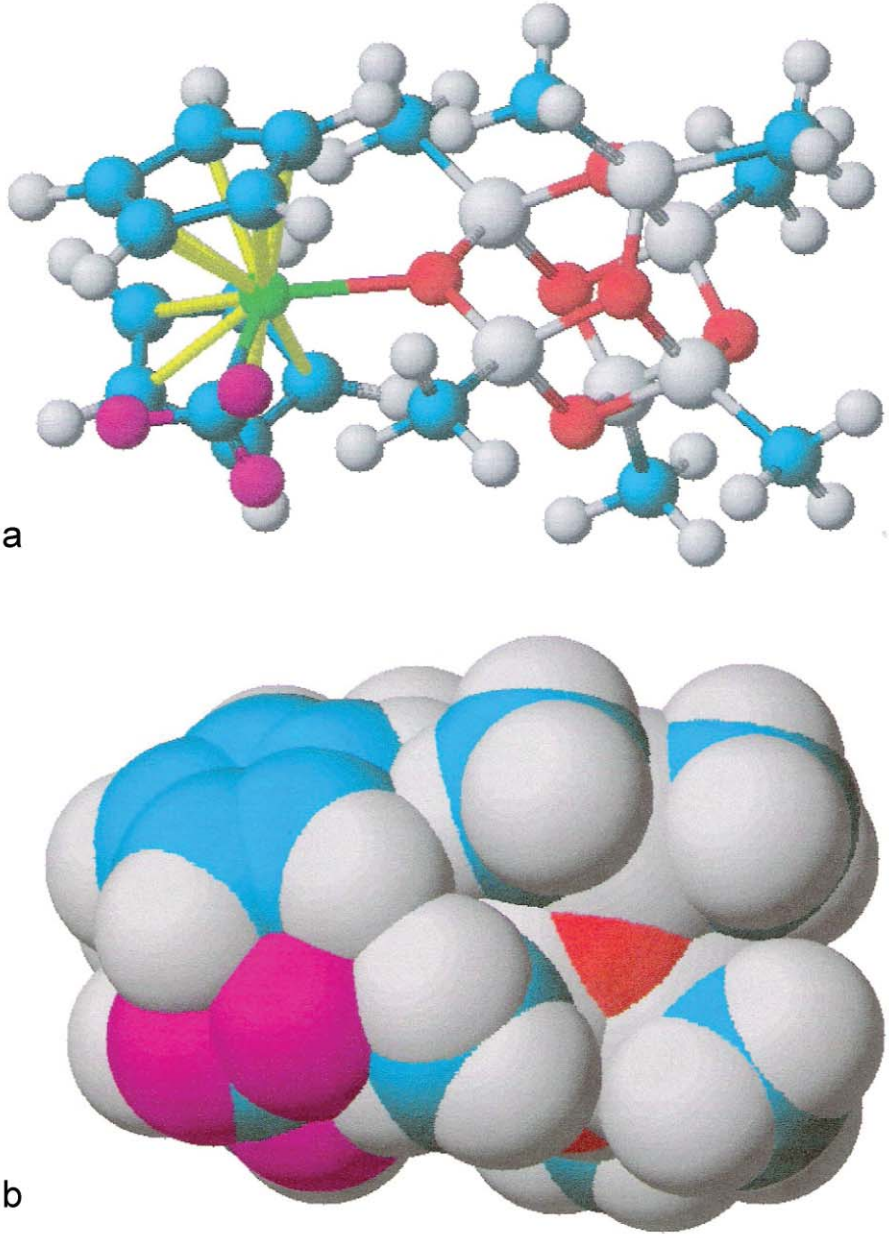

Fig. 9 Molecular models showing the tight ion pair formed when a MAO anion with a typical cage structure[17] coordinates to $[Cp_2ZrMe]^+$: (a) ball and stick model with green = Zr, cyan = C, small grey = H, magenta = Zr–Me, large grey = Al, red = O; and (b) space filling model. The perspective chosen is that of a reasonable trajectory for an attacking alkene.

wondered if the presence of an ether group is actually as deleterious as has long been suspected. We therefore carried out a series of propylene-1-hexene copolymerization reactions, as above but in the presence of *n*-decyl methyl ether, a *saturated* ether, which would have an ether-donor property essentially identical to that of comonomer **A**, which incorporates to the greatest extent.

Shown in Table 4 are the results of four such experiments. The ^1H and ^{13}C NMR spectra of the materials obtained were assigned as above and the percent incorporations of 1-hexene were determined as before. As can be seen, while the yields of copolymers were uniformly lower, the degrees of incorporation of 1-hexene and the

Table 4 Propylene copolymerizations with 1-hexene in the presence of 100 equiv. of *n*-decyl methyl ether

Experiment #	1-Hexene equiv.	Yield/g	Incorp. (mol%)	T_m/°C	M_n
39[a]	100	1.11	5.1	118	1.4×10^4
40[b]	100	1.29	6.5	122	1.5×10^4
41[a]	500	1.03	20	n.d.	6426
42[b]	500	1.32	18	n.d.	2449

[a] Pre-catalyst and hexene combined prior to addition of MAO. [b] 1-Hexene added 5 min after MAO addition; n.t = no transition.

values of M_n of the copolymers are all significantly higher. Perhaps somewhat surprising given the greater number of branches in the copolymers obtained, the values of T_m for experiments 39 and 40 are also somewhat higher than those observed for the products of experiments 35 and 36, although the expected lack of crystallinity is observed for experiments 41 and 42, with incorporations of 20 and 18%, respectively.

Thus addition of *n*-decyl methyl ether to the copolymerization reactions does not result in decreases in either molecular weights or degrees of incorporation, as conventional wisdom would presume, but rather in the formation of copolymers of higher molecular weights and containing greater incorporations of 1-hexene. As a possible rationale of this behaviour, we note that while details of the structure(s) of MAO are not known, it is generally believed to exist in solution as an equilibrium mixture of very bulky anions.[12b] Thus formation of a contact ion pair between a metallocenium cation and a MAO anion, as in Fig. 9, will almost certainly result in considerable steric hindrance to the approach of an alkene to the active site on the metal. To illustrate this point, Fig. 9a shows, from the perspective of an alkene approaching the position *cis* to the Zr–Me group, the optimized (molecular mechanics) ball and stick structure of the contact ion pair between the $[Cp_2ZrMe]^+$ cation and the hexamethyl equivalent of the cage structure determined experimentally for the $[Al_6O_6(Bu^t)_6Me]^-$ anion.[17] Fig. 9b shows the analogous space filling structure with conventional van der Waals radii for all atoms and, as is clear from the latter, even though this particular MAO anion is one of the smaller known,[12b] the metal ion is completely blocked from view and apparently not very accessible to an alkene.

Given that ether oxygen atoms probably have higher affinity for hard zirconocene cations than do alkene π electron pairs, we tentatively hypothesize that a sterically rather unencumbered methoxy group may be able to manoeuvre itself into the space between a bulky MAO-based counter anion and the cationic catalytic site on zirconium, eventually displacing the MAO anion and binding to the metal. Once anion-cation separation has been achieved, the olefinic ether can perhaps exchange ends (as in eqn (4)) such that the C=C bond coordinates and migratory insertion can ensue. Such a process would not be possible with the non-polar 1-hexene and would probably also be more difficult with the much bulkier phenyl-containing ethers. Once polymerization has begun, of course, the steric requirements of the growing chain can presumably keep the MAO anion at a distance.

Summary

Reported here are the results (a) of an NMR study of reactions of the archetypal metallocene polymerization catalyst, $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$, with the polar monomers $CH_2{=}CH(CH_2)_8OR$ (R = Me, $PhCH_2$, Ph_3C, Me_3Si, Ph_3Si), protected versions of the readily available, long chain polar monomer 9-decen-1-ol, and (b) of an investigation of the copolymerization reactions of these same polar monomers with ethylene and propylene catalyzed by the *rac*-$C_2H_4(Ind)_2ZrCl_2$/MAO catalyst system. While increasing the steric requirements of the groups R does decrease the apparent abilities of the ethers to displace $[BMe(C_6F_5)_3]^-$ from the $[Cp_2ZrMe]^+$ cation, there is no correlation of size of R on the degrees of incorporation of the polar monomers into copolymers of ethylene and propylene. Instead, a heretofore unsuspected role for catalyst *activation* by the ether linkage is suggested.

Acknowledgements

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