Polymerization of 1-hexene by $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$

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Abstract

Polymerization of 1-hexene by $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ results in the formation of low yields of high molecular weight polymer at $-78°C$ but higher yields of lower molecular weight material at $0°C$ and $22°C$. ^1H and $^{13}C\{^1H\}$ NMR spectra of the atactic polymers formed at $-78°C$ are consistent with chain initiation via a 1,2-insertion but predominant chain termination via β-hydrogen elimination largely after a 2,1-misinsertion. In contrast, β-hydrogen elimination following 1,2-insertion becomes increasingly important at higher temperatures. © 1998 Elsevier Science B.V.

The utilization of metallocenes as homogeneous olefin polymerization catalysts has received considerable attention in recent years, in large part because of the high degrees of stereoregularity and narrow molecular weight distributions which are possible [1–5]. Of relevance here is the utilization of metallocenes to prepare homo- and copolymers of 1-hexene [6–14], of interest both from the perspective of understanding mechanisms of α-olefin polymerization and because of a high degree of commercial interest in e.g. materials such as ethylene-*co*-1-hexene polymers as linear low-density polyethylene.

Recently, we have reported the utilization of a monocyclopentadienyl olefin polymerization system based on activation of Cp^*TiMe_3 by the highly electrophilic borane $B(C_6F_5)_3$. The active species, $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ (I), behaves as a source of the cationic complex $[Cp^*TiMe_2]^+$, which is an extremely active

initiator for both Ziegler–Natta and carbocationic polymerization reactions [15–22]. Although surprisingly little attention has been previously devoted to polymerization of long chain α-olefins such as 1-hexene by monocyclopentadienyl metal compounds [23,24], we find that **I** is an extremely active initiator for the polymerization of 1-hexene. We describe in this communication the activity of **I** for 1-hexene polymerization, and provide insight into the mechanism with which this process occurs.

Polymerizations were typically carried out by dissolving 14 mg of Cp^*TiMe_3 (0.06 mmol) in 2–5 ml of 1-hexene. If the polymerization was done in neat 1-hexene, this solution was added directly to 31 mg (0.06 mmol) of $B(C_6F_5)_3$. Alternatively, 31 mg of $B(C_6F_5)_3$ dissolved in 2–5 ml of toluene were added to the aforementioned solution of Cp^*TiMe_3. The reactions were normally stirred for 20–30 min at $-78°C$, $0°C$ or $22°C$, and then terminated by the addition of methanol. The room temperature reactions are very rapid and, if not controlled, be-

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come quite hot. The precipitated products were redissolved in toluene and reprecipitated with methanol, and then dried overnight at 60°C, weighed and characterized by GPC measurements and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

The poly(1-hexene) materials obtained were all sticky liquids which were determined to be purely atactic by NMR spectroscopy (see below). In general, it was found that the polymer formed at −78°C was obtained in low yields (≤ ∼ 5%; < 1 g polymer/mmol catalyst/h), although higher yields could be obtained with longer reaction times. The purified low temperature polymer exhibited relatively high molecular weights and narrow molecular weight distributions ($M_w \sim 3 \times 10^4$, $M_w/M_n \sim 2.1$). At 0°C and 22°C, much higher yields of crude material (∼ 50%; ∼ 50 g polymer/mmol catalyst/h) were obtained; the crude materials were multimodal, for reasons not yet clear, but purified materials contained major fractions exhibiting reasonably high molecular weights and narrow molecular weight distributions ($M_w \sim 1 \times 10^4$, $M_w/M_n \sim 2.4$). These results are generally comparable with results reported for metallocene catalysts systems [6–14]; no polymer

was formed when monomer solutions were treated only with B(C$_6$F$_5$)$_3$.

The tacticities of the polymers formed, crude and purified, were assessed by ^{13}C NMR and ^{1}H NMR spectroscopy utilizing procedures described previously [11,25–27]. The ^{13}C{^{1}H} NMR spectrum of the poly(1-hexene) formed at −78°C is illustrated in Fig. 1; as can be seen, the spectrum is dominated by six multiplet resonances centered at ∼ δ 40.5 (C$_1$), 32.2 (C$_2$), 34 (C$_3$), 28.5 (C$_4$), 23.3 (C$_5$) and 14.3 (C$_6$) (A). The breadth of the resonances of C$_1$–C$_4$ indicates the presence of comparable amounts of all possible pentads [25] and identifies the material as

$$—(C_1—C_2)_n—$$
$$\underset{\displaystyle C_3—C_4—C_5—C_6}{|}$$

A
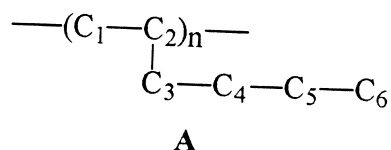
atactic polymer. In contrast, the ^{13}C{^{1}H} NMR spectrum of the polymer formed at 22°C (Fig. 1) is much more complicated. Although much broadened resonances attributable to C$_1$–C$_6$ are

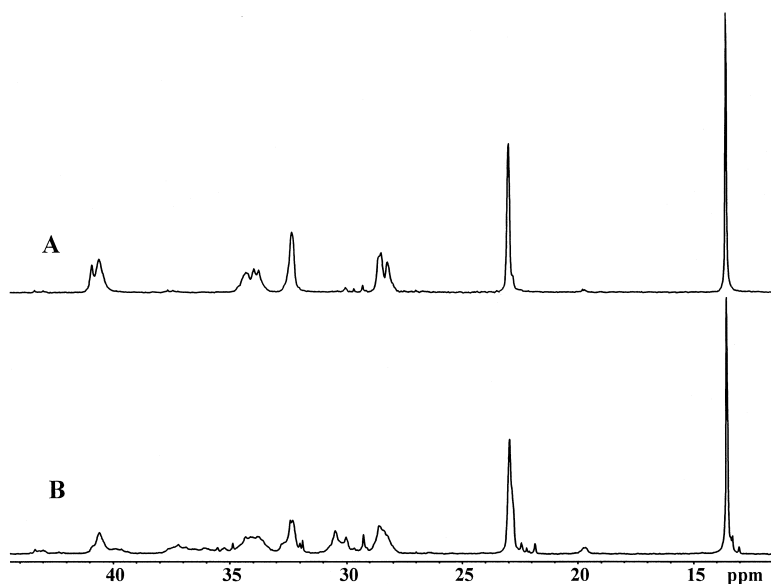Fig. 1. ^{13}C{^{1}H} NMR spectra of poly(1-hexene) prepared at: (A) −78°C, and (B) 22°C.

clearly present at chemical shifts similar (but not identical) to those discussed above, strong, very broad resonances also appear in the regions δ 30–31 and 35–38, as well as weaker resonances elsewhere. Clearly the polymerization process at higher temperatures is much more complicated than that at $-78°C$, but speculation seems pointless until the resonances can be assigned via further NMR experiments to either main chain anomaly or end group resonances.

As is the case generally for polymers of α-olefins [1], the preferred mode of chain propagation seems to involve 1,2-insertions. Evidence that initiation involves 1,2-migratory insertions of 1-hexene into a titanium–methyl bond of **I** is found in the $^{13}C\{^{1}H\}$ NMR spectra of crude samples still containing low molecular weight products. The spectra exhibit weak resonances attributable to C_1 (δ 42.8), C_2 (δ 30.1), C_3 (δ 37.4), C_4 (δ 29.6) and C_7 (δ 20.2), aliphatic end groups resulting from the expected initial 1,2-insertion of 1-hexene into a Ti–Me bond (**B**). Although tentative, these assignments were buttressed by chemical shift calculations [28].

$$Cp^*MeTi^{+}\!\!-\!C_1\!-\!C_2\!-\!C_7$$
$$\qquad\qquad\quad |$$
$$\qquad\qquad\quad C_3\!-\!C_4\!-\!C_5\!-\!C_6$$

B
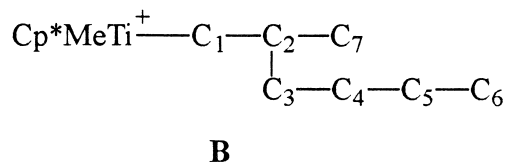
The resonances of C_5 and C_6, calculated to be at δ 23.4 and 14.0, respectively, would be obscured by the resonances of C_5 and C_6 of the side chains of poly(1-hexene). The methyl resonance expected for the ethyl side chain which would result from an initial 2,1-insertion process should be observable ($\delta \sim 11$–12 [11,28]) but was absent.

Assuming chain termination/-transfer proceeds via β-hydrogen elimination processes (see below), chain propagation would involve 1,2- and/or 2,1-insertion into the resulting Ti–H

bonds. While the resonances of the 1-hexyl end group anticipated if the former occurs would be obscured by the main resonances of the polymer, the resonance of the methyl branch of the 2-hexyl group anticipated from 2,1-insertions should occur at $\delta \sim 18$ [28] and is not observed.

The inverse dependence of temperature on M_w of the polymer produced suggests that chain termination becomes more facile relative to chain propagation at elevated temperatures, as has been noted elsewhere with metallocene systems [6–14]. It is also clear from the results that the activity of the catalyst varies little in the range 0–22°C but is greatly reduced at $-78°C$.

End group analyses by ^{1}H NMR spectroscopy in the olefinic regions reveal much about the mechanisms of chain termination. Multiplet resonances of comparable intensities in the ^{1}H NMR spectrum at $\delta \sim 5.3$ and ~ 4.7 in the spectra of polymers formed at 0°C may be attributed to internal olefinic and vinylidene groups, respectively, assignments which are also consistent with the $^{13}C\{^{1}H\}$ NMR spectra. The internal olefinic products result in large part from 2,1-misinsertions followed by β-hydrogen elimination, while the vinylidene end group is a consequence of β-hydrogen elimination following a normal 1,2-insertion of 1-hexene monomer. Interestingly, in the spectrum of the polymer formed at $-78°C$, the multiplet attributable to internal olefins ($\delta \sim 5.4$) is significantly more intense than the vinylidene multiplet ($\delta \sim 4.7$). Thus the proportion of vinylidene end groups increases with increasing temperature, as reported elsewhere for other catalysts [11,23]. This result suggests that chain termination/transfer processes involving 2,1-misinsertions followed by β-hydrogen elimination are rather more important than are 1,2-insertions followed by β-hydrogen elimination. The catalyst site could well be deactivated for steric reasons after a 2,1-misinsertion, resulting in an increased rate of chain transfer relative to chain propagation. The ^{1}H NMR spectrum also indicates an increased production of different kinds of trisubstituted olefins ($\delta \sim 5.1$) for those polymeriza-

tions initiated at 0°C and above, suggesting various isomerization processes at this temperature and consistent with the $^{13}C\{^1H\}$ NMR results.

Acknowledgements

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