

# Titanium-catalysed formation of high molecular weight elastomeric polypropene: evidence for living propene polymerisation

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## Abstract

Catalyst generated from 1:1 mixtures of Cp\*TiMe<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> are highly active for the polymerisation of propene in toluene, light petroleum or liquid propene to give atactic polypropene of unusually high molecular weight (up to  $M_w = 4 \times 10^6$ ) and narrow polydispersity. The polymer is elastomeric. The presence of polymer fractions with  $M_w/M_n = 1.1$ , as revealed by Schulz–Zimm analysis of the GPC data, and the behaviour of the catalyst indicates that a significant proportion of the titanium centres act as living propene polymerisation catalysts. Aluminium trialkyls were found to act as catalyst poisons, reducing polymer yield and molecular weight and substantially broadening the molecular weight distribution. © 1997 Elsevier Science B.V.

## 1. Introduction

Olefin polymerisation catalysts based on Group IV metallocene complexes have attracted considerable attention in recent years [1]. By comparison, half-sandwich complexes of the type CpMX<sub>3</sub> have been less intensely investigated, and their chemistry is less well understood. CpTiCl<sub>3</sub> and Cp\*TiCl<sub>3</sub> activated with a large excess of MAO are well known as catalysts for the polymerisation of conjugated dienes [2] and the syndiospecific polymerisation of styrene [3], as well as for the polymerisation of ethylene and propene [4]. Similarly, Pellecchia et al. [5] found Cp\*TiR<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> mixtures (R = CH<sub>3</sub>, CH<sub>2</sub>Ph) to be highly active MAO-free catalysts for the polymerisation of ethylene, while the system Cp\*Ti(CH<sub>2</sub>Ph)<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlMe<sub>3</sub> polymerised propene to an atactic product. Baird et al. [6] were able to demonstrate the zwitterionic nature of the resting state of this catalyst, Cp\*TiMe<sub>2</sub>(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, which in aromatic solvents is in equilibrium with the arene complexes [Cp\*TiMe<sub>2</sub>(η-arene)]<sup>+</sup> [MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup>. Such systems polymerised ethylene even at very low temperatures (-104°C) but did not

seem to react with propene in toluene solution, while dichloromethane solutions gave polypropene of modest molecular weight ( $M_w \approx 15000$ ) and predominantly syndiotactic structure [7].

As part of our studies concerning the nature of activation and deactivation reactions in MAO-free polymerisation catalysts [8,9], we have reinvestigated the polymerisation of propene with Cp\*TiMe<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in the presence and absence of aromatic solvents. The results are summarised in Tables 1 and 2.

## 2. Results and discussion

In our hands the catalyst was found to be exceedingly active in toluene at temperatures as low as -78°C, giving rise to high molecular weight atactic polypropene (Table 1, entries 1–5). Whereas atactic polypropenes of the type obtained as by-products of the stereospecific propene polymerisation with conventional Ziegler catalysts are typically waxes or oils of comparatively low molecular weight, the material obtained with Cp\*TiMe<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> is a tough, fully amorphous non-sticky elastomer, with  $M_w$  values ranging from  $4 \times 10^5$  to ca.  $4 \times 10^6$  [10]. In toluene solutions the rapid build-up of a reaction exotherm in the initiation phase of the polymerisation is noticeable, while the

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Table 1  
Propene polymerisation with  $\text{Cp}^*\text{TiMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$

Run	Temp. (°C)	Ti ( $\mu\text{mol}$ )	B ( $\mu\text{mol}$ )	Solvent (ml)	Propene	Time (s)	Yield PP (g)	Productivity <sup>a</sup> $\times 10^{-6}$	$M_w \times 10^{-3}$	$M_w/M_n$
1	70	40	40	toluene (20)	1 bar	60	0.134	0.69	32	4.0
2	40	40	40	toluene (20)	1 bar	60	0.09	0.28	43	3.0
3	0	20	20	toluene (60)	1 bar	60	1.366	2.76	518	2.9
4	-20	20	20	toluene (60)	1 bar	45	1.520	2.69	1103	1.4
5	-78	10	10	toluene (20)	10 ml	120	1.068	0.52	1600	1.5
6	0	20	20	petrol (20)	1 bar	180	0.258	<sup>b</sup>	606	1.7
7	20	20	20	petrol (20)	1 bar	180	0.242	<sup>b</sup>	407	1.6

<sup>a</sup> In g PP (mol Ti)<sup>-1</sup> [C<sub>3</sub>H<sub>6</sub>]<sup>-1</sup> h<sup>-1</sup>.

<sup>b</sup> M<sub>w</sub>/M<sub>n</sub> fraction data for [C<sub>3</sub>H<sub>6</sub>] in petrol not available.

reaction in light petroleum is more controlled, with reduced catalyst productivity, giving rise to polymers of very narrow polydispersity. This activity trend evidently reflects the extent of dissociation of the zwitterionic catalyst precursor  $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$  into ionic species, which is high in toluene but not detectable in petroleum. By implication, displacement of toluene in  $[\text{Cp}^*\text{TiMe}_2(\eta\text{-toluene})]^+$  by propene even at pressures as low as 1 bar must be sufficiently fast to allow rapid chain growth.

Particularly high molecular weight products were obtained in liquid propene at the temperature of boiling propene (-45°C) (Table 2). The  $M_w$  values of the aPP obtained under these conditions proved to be roughly proportional to the duration of the experiment and increased from ca.  $1 \times 10^6$  after 1 min to ca.  $4 \times 10^6$  after 4 min. During polymerisations the reaction mixtures became very viscous but remained homogeneous, and in spite of the high molecular weights the polymers remained readily soluble in hydrocarbons, as expected for atactic products.

A comparison of the number of polymer chains produced with this system, as judged from the  $M_n$  values, and the titanium concentration shows that, as an upper limit, no more than 10–20% of metal centres actually participate in chain growth. This is to be anticipated provided the establishment of the dissociation equilibrium discussed above is slow compared with chain propagation. Although the polydispersities indicate that chain transfer does take place to some extent, as one would expect for a Ziegler system, for a signifi-

cant proportion of the chain carrying species this is negligible (cf. Table 1, entries 4 and 5). Such characteristics point towards a living polymerisation system. This was borne out by closer analysis of a typical sample (Table 1, entry 4), obtained in toluene at -20°C. The rather narrow polydispersity of this polymer could be approximated by the superimposition of two Schulz–Zimm distributions [11] of about equal weight (Fig. 1), indicating that 48% of the sample consisted of a fraction with  $M_w/M_n = 1.10$ , as expected for a living polymerisation system. The second fraction shows a rather broader polydispersity of 1.66 and produces most of the lower molecular weight components. The curve fitting parameters are collected in Table 3 and show an acceptable goodness-of-fit. The fit is best on the high molecular weight tail, therefore  $M_w$  and  $M_z$  and the  $M_z/M_w$  ratio correspond well to the measured data. The curve fitting procedure did not include a correction for peak broadening which would further narrow both distributions. The given distribution widths should therefore be considered as upper limits for the real distributions. The results support the notion that, although the catalyst is not entirely uniform, a significant proportion of the titanium centres build only one polymer chain each and remain bound to it during the course of the reaction. Thus in this catalyst most of the active sites exhibit living characteristics during the (relatively short) duration of the reaction.

Generally, in Ziegler catalysts chain termination by  $\beta$ -H elimination is known to be ca. 2–3 orders of magnitude slower than chain growth, and there is no

Table 2  
 $\text{Cp}^*\text{TiMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$  catalysed polymerisation in liquid propene (-45°C)

Ti ( $\mu\text{mol}$ )	B ( $\mu\text{mol}$ )	Propene (ml)	Time (s)	Yield PP (g)	Productivity <sup>a</sup> $\times 10^{-6}$	$M_w \times 10^{-3}$	$M_w/M_n$
20	20	40	40	0.913	4.1	1079	1.7
20	20	100	120	3.47	5.2	2275	2.0
120	120	500	240	42.0	5.25	3966	2.0

<sup>a</sup> In g PP (mol Ti)<sup>-1</sup> h<sup>-1</sup>.

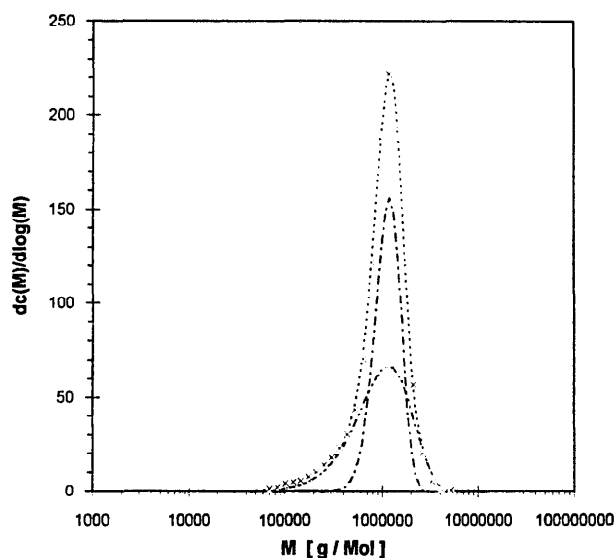


Fig. 1. Curve fitting of the GPC diagram of a sample of aPP (Table 1, entry 4) by the superimposition of two Schulz-Zimm distributions (..... component 1, ..... component 2) of different polydispersities and about equal weight. The resulting fit function (---) closely corresponds to the measured data (×).

reason to entirely discount this pathway in the  $\text{Cp}^* \text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  system. This explains the deviation of the present catalyst from the behaviour of truly living polymerisations with potentially infinite storage lives, for which  $M_w/M_n = 1.0$  can be expected.

A living system would be expected to show a linear increase of molecular weight with time, and of polymer yield with the initiator concentration. This was indeed found. Fig. 2 illustrates the increase of  $M_w$  with time for a  $\text{Cp}^* \text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  catalyst in light petroleum. The deviation from linearity at longer reaction times reflects the increase in viscosity of the solution which reduces stirring rate and monomer take-up. The polymer mass obtained increases linearly with [Ti] (Fig. 3). The fact that the curve does not pass through the origin reflects the 'background level' of impurities in the system, i.e. even under our 'clean' conditions ca. 4–5  $\mu\text{mol}$  titanium complex are irreversibly deactivated before polymerisation can take place. Fig. 4 shows the polymer mass obtained as a function of time; again the increase is linear within experimental error.

The data support the assumption of living propene polymerisation with the  $\text{Cp}^* \text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  catalyst

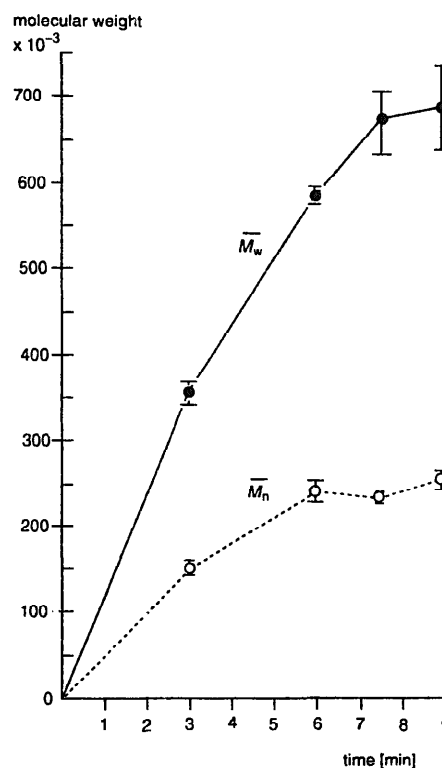


Fig. 2. Dependence of  $M_w$  and  $M_n$  versus reaction time. Conditions: 20  $\mu\text{mol}$   $\text{Cp}^* \text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  in light petroleum, 20°C, 1 bar propene pressure.

system even at comparatively high temperatures. To our knowledge this is the first report of a living Group IV Ziegler polymerisation catalyst. Living propene polymerisation has been found before for vanadium catalysts, such as  $\text{V}(\text{acac})_3/\text{AlEt}_2\text{Cl}$ , at temperatures below  $-65^\circ\text{C}$  [12]. These catalysts have comparatively low activity and give predominantly syndiotactic polymers with polydispersities of 1.1–1.2 and  $M_n$  values below 20000 over a period of several hours. The titanium catalyst described here is about two orders of magnitude more active.

With polymerisation catalysts based on bis(cyclopentadienyl)metal complexes aluminium alkyls are usually added as scavengers, and we have previously shown that isolable binuclear complexes  $[\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+$  are formed which exhibit very high

Table 3

Comparison of the molecular parameters of the fitted functions and the measured GPC data of the polymer

	Component 1	Component 2	Total fit	Sample measurements
$M_n$ ( $\text{g mol}^{-1}$ )	1054000	694000	844000	770000
$k$	9.94	1.51	—	—
Relative amount	0.52	0.48	1	1
$M_w$ ( $\text{g mol}^{-1}$ )	1157000	1153000	1155000	1103000
$M_z$ ( $\text{g mol}^{-1}$ )	—	—	1429500	1363000
$M_z/M_w$	—	—	1.24	1.24
$M_w/M_n$	1.10	1.66	1.37	1.43

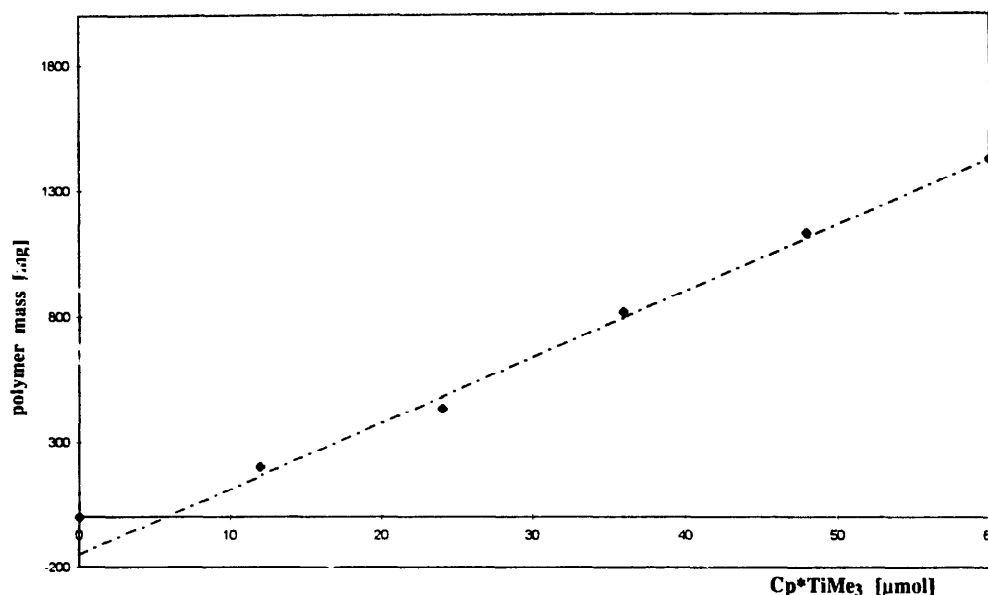


Fig. 3. Dependence of polymer yield on [Ti]. Conditions:  $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  in toluene, 20°C, 1 bar propene pressure.

polymerisation activities [9]. Attempts were therefore made to increase the activity of the  $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  system and its resistance towards impurities by the addition of aluminium trialkyls.

Somewhat surprisingly, trimethyl- and triisobutylaluminium (TIBA) strongly inhibit the catalytic activity of the titanium complexes even at Al:Ti ratios as low as 1:4, i.e. in substoichiometric amounts (Table 4). The polymer yields and the molecular weights are reduced, often to a level where only traces of polymer could be isolated, and the polydispersities are dramatically increased, from values of 2–3 to ca. 10. Gel permeation chromatograms of these polymers (Fig. 5) give a broad

bimodal distribution which contrast sharply with the narrow polydispersities obtained in the aluminium-free system. It has so far not been possible to elucidate the origin of this effect. Although it could reasonably be expected that the 10-electron species  $[\text{Cp}^*\text{TiMe}_2]^+$  would readily form stable adducts with aluminium trialkyls, such as  $[\text{Cp}^*\text{TiMe}(\mu\text{-Me})_2\text{AlMe}_2]^+$  and  $[\text{Cp}^*\text{Ti}\{(\mu\text{-Me})_2\text{AlMe}_2\}_2]^+$ , which might limit the concentration of active species available, variable temperature NMR studies have so far failed to identify such complexes. It is evident that caution must be exercised when extrapolating the chemistry of bis-Cp complexes

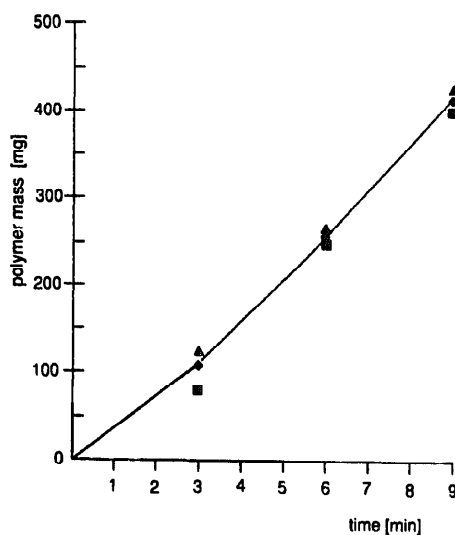


Fig. 4. Polymer yield as a function of reaction time. Conditions: 20  $\mu\text{mol}$   $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  in light petroleum, 20°C, 1 bar propene pressure.

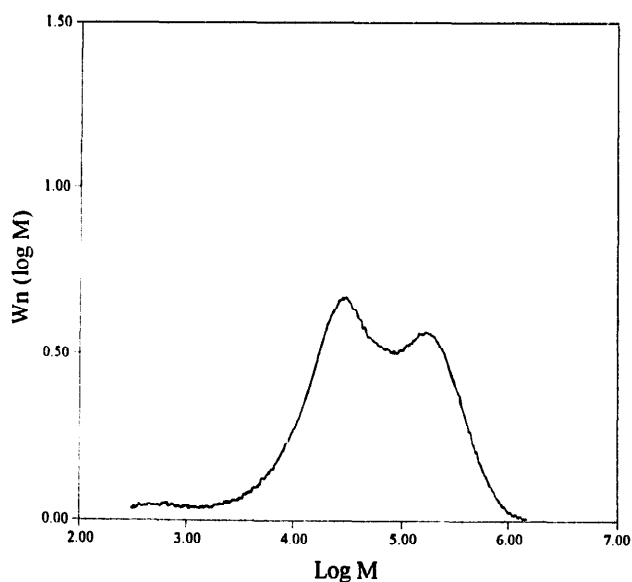


Fig. 5. GPC diagram of a polypropylene sample prepared in the presence of  $\text{AlMe}_3$ . Conditions: 20  $\mu\text{mol}$   $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$ , 10  $\mu\text{mol}$   $\text{AlMe}_3$ , toluene, 20°C, 1 bar propene pressure.

Table 4  
Influence of aluminium alkyls on propene polymerisations with Cp\*TiMe<sub>3</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>

Run	Temp. (°C)	Ti (μmol)	B (μmol)	AlR <sub>3</sub> (μmol)	Toluene (ml)	Time (s)	Yield PP (g)	M <sub>w</sub> × 10 <sup>-3</sup>	M <sub>w</sub> /M <sub>n</sub>
1	0	20	20	0	60	60	1.366	518	2.9
2	0	20	20	AlMe <sub>3</sub> (5)	20	600	trace	118	10.1
3	0	20	20	AlMe <sub>3</sub> (10)	20	120	trace	164	10.2
4	0	10	10	TIBA (10) <sup>a</sup>	20	60	0.509	294	3.3
5	0	20	10	TIBA (10) <sup>b</sup>	20	60	0.322	348	9.9

<sup>a</sup> TIBA injected 30 s after start of reaction.

<sup>b</sup> TIBA injected prior to catalyst addition.

to mono-Cp systems, and there are mechanistic details which are as yet incompletely understood.

### 3. Experimental

#### 3.1. General procedures

All reactions were carried out under inert gas using standard vacuum line techniques. Light petroleum (bp. 40–60°C) was distilled from sodium–potassium alloy, toluene from sodium. Propene was purified by passing through CaCl<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> and stored over Et<sub>2</sub>AlOC<sub>6</sub>H<sub>13</sub>. NMR solvents were stored over 4A molecular sieves under nitrogen or argon and degassed by several freeze–thaw cycles. NMR spectra were recorded on a Bruker DPX300 instrument. <sup>13</sup>C-NMR spectra of polymers were recorded in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120°C. Gel permeation chromatography (GPC) was carried out at 140°C in 1,2-dichlorobenzene using a Waters 150CV instrument fitted with a refractive index detector against polystyrene calibration standards, and in 1,2,4-trichlorobenzene using a Waters 150C chromatograph fitted with an infrared detector Miran 1A CVF (λ = 3.5 μm). With the latter instrument polypropene standards were used which were calibrated by light scattering and end group analysis by <sup>13</sup>C-NMR spectroscopy.

#### 3.2. Propene polymerisations

All polymerisations were conducted in all-glass reactors which had been flame dried in vacuo. Stock solutions (ca. 10<sup>-5</sup> M) of Cp\*TiMe<sub>3</sub> and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in light petroleum were freshly prepared for each series of reactions. Polymerisations in toluene or light petroleum were carried out by equilibrating a given amount of purified and degassed solvent at the stated temperature with 1 bar propene for 30 min. Polymerisation was initiated by injecting an aliquot of Cp\*TiMe<sub>3</sub> followed by an equimolar amount of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and terminated by the injection of 2 ml methanol. Reactions in liquid propene were carried out by condensing the required amount into the reaction vessel at –50°C. On injecting the catalyst the resulting exotherm quickly brought the propene to its boiling point (–45°C). Reactions carried

out in petroleum, toluene or liquid propene become highly viscous during the polymerisation but remain homogeneous. Polymer samples were recovered by precipitation with large amounts of methanol. The rubbery product was collected and dried at 60°C for 24 h. <sup>13</sup>C-NMR analysis of the polymer microstructure at pentad level confirms the atactic nature of the products. Found (calculated) relative pentad intensities were: mmmm 0.07 (0.06), mmmr 0.16 (0.12), rmmr 0.08 (0.06), mmrr 0.11 (0.12), mrrm + rrrr 0.26 (0.25), mrrr 0.15 (0.12), rrrr 0.04 (0.06), rrrm 0.09 (0.12), mrrm 0.04 (0.06) [13].

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