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The kinetics of propene and hexene polymerisation with $[(SBI)ZrR]^+X^-$: evidence for monomer-dependent early or late transition states†

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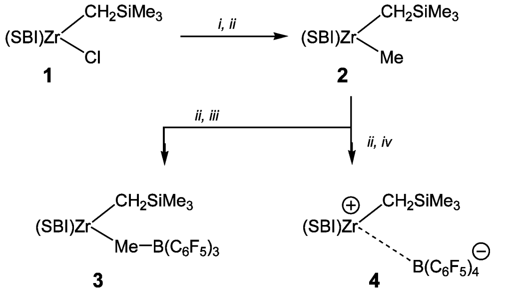
Whereas the rates of propene polymerisation catalysed by zirconocene ion pairs are strongly anion-dependent, hexene polymerisations are not; the findings demonstrate the existence of very different kinetic regimes for two closely related reactions.

Various kinetic techniques have recently furnished unprecedented insight into the mechanistic details of the polymerisation of 1-alkenes catalyzed by metallocenes.[1–3] In particular, the importance of the "non-coordinating" counteranion X in $[L_2ZrR^+\cdots X^-]$ ion pair catalysts has been emphasised.[4–9] Some of these systems are among the most active propene polymerisation catalysts known; *e.g.* $(SBI)ZrMe_2/CPh_3[B(C_6F_5)_4]$ in the presence of TIBA affords propagation rates $k_p^{obs} \approx 10^3$–10^4 s^{-1} (SBI = *rac*-$Me_2Si(1\text{-Ind})_2$, TIBA = Al^iBu_3) under very mild conditions (25 °C, 1 bar).[9a] On the other hand, elegant work by Landis using the $(EBI)ZrMe_2/B(C_6F_5)_3$ catalyst suggested that the polymerisations of 1-hexene and propene proceed with very similar rates, with propene, as the less hindered monomer, reacting only about three times faster than 1-hexene (EBI = *rac*-$C_2H_4(1\text{-Ind})_2$).[10,11] These results prompted us to re-examine our propene polymerisation data in comparison with those for hexene.

Previous kinetic experiments had been conducted using the system $(SBI)ZrMe_2/TIBA/CPh_3[CN\{B(C_6F_5)_3\}_2]$ (1:100:1).[2] Although this system is extremely active with excellent reproducibility, it is complicated by the nature of the reaction products between the zirconocene alkyl and TIBA and the uncertain structure of the *in-situ* generated catalyst. We therefore wished to develop a system that allowed us to study polymerisation kinetics in the absence of TIBA, under well-controlled conditions.

The complexes $(SBI)Zr(CH_2SiMe_3)X$ provide such a system [X = $MeB(C_6F_5)_3$, $B(C_6F_5)_4$].‡ They are readily accessible from the mixed alkyl compound **2** which reacts with $B(C_6F_5)_3$ or $CPh_3[B(C_6F_5)_4]$ to give **3** and **4**, respectively (Scheme 1). The only by-product observed was a trace of $SiMe_4$ in the case of **4**. Both compounds are stable at room temperature; toluene solutions of **4** containing 10 vol% 1,2-difluorobenzene showed no change or deterioration over a period of days. Propene polymerisations with catalyst **3** were conducted in toluene at 20 °C under 1 bar propene ($[C_3H_6]$ = 0.71 mol L^{-1}) and follow the established rate law.[1,2] Since this system does not contain a scavenger, partial catalyst deactivation by background impurities must be taken into account. A plot of polymer mass as a function of [Zr] is linear but does not pass through the origin; the intercept indicates that of the 10 μmol **3** added initially, 6.6 μmol have been deactivated. This difference has been taken into account in calculating the propagation rate constant, k_p(**3**-P) = 20 L mol^{-1} s^{-1}.[12] Kinetic data are summarised in Table 1.

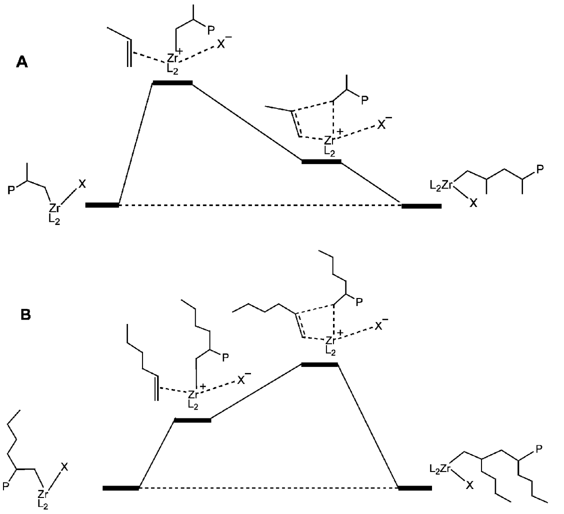


Scheme 1 *Reagents and conditions*: (i) MeMgCl, toluene–THF; (ii) room temperature; (iii) 1 equiv. $B(C_6F_5)_3$, toluene-d_8; (iv) $[CPh_3][B(C_6F_5)_4]$, toluene-d_8–1,2-$C_6H_4F_2$ (9:1).

Hexene polymerisations with **3** show slightly less catalyst deactivation, 3.4 μmol. The data give a rate constant of k_p(**3**-H) = 4.8 L mol^{-1} s^{-1} which confirms that for the zwitterionic catalyst **3** the rate of polymerisation shows little dependence on the bulkiness of the monomer, with propene polymerisation proceeding *ca.* four times faster than hexene, in agreement with the results of Sillars and Landis.[10]

A rather different situation is, however, found for the ion pair **4**. Under scavenger-free conditions propene polymerisations with this system proceed 60–70 times faster than with **3**. By contrast, **4** polymerises hexene at about the same rate as catalyst **3**, k_p(**4**-H) = 15 L mol^{-1} s^{-1}.

There are therefore two distinct kinetic scenarios: *hexene* polymerisation, at least with the pair of catalysts under investigation here, is *not* significantly influenced by the nature of the anion



Scheme 2 Qualitative reaction pathways for the insertion of propene (A) and 1-hexene (B) into $[(SBI)ZrR^+\cdots B(C_6F_5)_4^-]$ ion pairs.

Table 1 Kinetic parameters of propene and hexene polymerisations with $(SBI)Zr(CH_2SiMe_3)X$[a]

X	Monomer	k_p/L mol^{-1} s^{-1}
$[MeB(C_6F_5)_3]^-$	Propene	20 ± 1
$[B(C_6F_5)_4]^-$	Propene	1360 ± 12
$[MeB(C_6F_5)_3]^-$	1-Hexene	4.8 ± 0.1
$[B(C_6F_5)_4]^-$	1-Hexene	15 ± 1

[a] [Zr] = [B] = 1 × 10^{-4} mol L^{-1}, 100 mL toluene, 20 °C, $[C_3H_6]_0$ = 0.71 mol L^{-1}; $[C_6H_{12}]_0$ = 0.8 mol L^{-1}.

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† Electronic supplementary information (ESI) available: Experimental results and rate calculations. See http://www.rsc.org/suppdata/cc/b3/b314845a/

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and proceeds with about equal rates whether the anion is more strongly coordinating, as in the case of $MeB(C_6F_5)_3^-$, or not. The rate of *propene* polymerisation, on the other hand, is highly sensitive to anion structure and greatly accelerated by reducing anion nucleophilicity. We believe these findings point to differences in the transition states. For propene, transfer of the polymeryl chain to the monomer is fast since both these ligands are sterically comparatively undemanding, and, for $MeB(C_6F_5)_3^-$ at least, anion displacement is therefore likely to be the rate limiting step (Scheme 2(A)). This is slow for X = $MeB(C_6F_5)_3^-$ but much accelerated for $B(C_6F_5)_4^-$.[13] For the more bulky 1-hexene, on the other hand, chain transfer is a slower process which benefits little from faster anion displacement (Scheme 2(B)).

Therefore, while catalysts for small monomers such as ethene and propene are enhanced by anion engineering, hexene polymerisation catalysts may be primarily improved by modifying the ligand structure. It remains to be seen if these conclusions also hold in the case of more open half-sandwich catalysts.

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Notes and references

‡ **1**: To a suspension of (SBI)$ZrCl_2$ (1.1 g, 2.5 mmol) in 50 mL of toluene at 0 °C was added $ClMgCH_2SiMe_3$ (1.63 mL, 1.5 M in diethyl ether). After stirring for 10 h at room temperature and filtration, **1** was isolated as orange crystals. ^1H NMR (300 MHz, 25 °C, $CDCl_3$): δ 6.6–7.5 (10 H, Ind-C_6), 6.05 (d, 1H, *J* 3.3 Hz, Ind), 5.72 (d, 1H, *J* 3.1 Hz, Cp H), 0.94 (s, 3H, $SiMe_2$), 0.84 (s, 3H, $SiMe_2$), 0.15 (d, 1H, *J* 11.6 Hz, $ZrCH_2$), −0.30 (s, 9H, $SiMe_3$), −2.07 (d, 1H, *J* 11.6 Hz, $ZrCH_2$). ^{13}C NMR ($DCCl_3$): δ 133–86 (Ind), 58.2 ($ZrCH_2$), 2.4 ($SiMe_3$), −0.72 ($SiMe_2$), −1.77 ($SiMe_2$).

2: *Method 1*: To a solution of (SBI)Zr(Cl)CH_2SiMe_3 from the above reaction in 50 mL of toluene was added MeMgCl (3.0 mmol, 1 mL, 3 M in THF) at room temperature. After 1 h, **2** was isolated from the filtrate as an orange solid which was recrystallised in light petroleum (bp 40–60 °C). *Method 2*: To an orange suspension of (SBI)$ZrCl_2$ (5.2 g, 11.6 mmol) in 150 mL of toluene at −20 °C was added $ClMgCH_2SiMe_3$ in diethyl ether (11.7 mmol, 7.8 mL, 1.5 mol L^{-1}). The reaction mixture was stirred for 1 h at −20 °C and for 16 h at room temperature. After filtration, MeMgCl in THF (12.0 mol, 4.0 mL, 3 mol L^{-1}) was added, the mixture was stirred for 10 h, filtered and concentrated to give crystalline **2** (4.1 g, 8.6 mmol, 74.1%). ^1H NMR (300 MHz, 25 °C, toluene-d_8): δ 7.2–6.6 (10 H, Ind), 5.65 (d, 1H, *J* 3.3 Hz, Ind-C_5), 5.57 (d, 1H, *J* 3.3 Hz, Ind-C_5), 0.60 (s, 3H, $SiMe_2$), 0.57 (s, 3H, $SiMe_2$), 0.05 (s, 9H, $SiMe_3$), −0.22 (d, 1H, *J* 11.4 Hz, $ZrCH_2$), −1.09 (s, 3H, ZrMe), −2.15 (d, 1H, *J* 11.4 Hz, $ZrCH_2$).

3: (SBI)Zr(Me)CH_2SiMe_3 (5.0 mg, 10.0 µmol) and $B(C_6F_5)_3$ (5.2 mg, 10.0 µmol) were loaded into a 5 mm NMR tube and dissolved in 0.6 mL of toluene-d_8. ^1H NMR (300 MHz, 20 °C, toluene-d_8): δ 7.5–5.6 (Ind), 0.59 (br, 3H, $SiMe_2$), 0.47 (br, 3H, $SiMe_2$), −0.09 (s, $SiMe_3$) −0.17 (d, 1H, *J* 10.2 Hz, $ZrCH_2$), −0.20 (br, 3H, µ-Me), −0.72 (d, 1H, *J* 10.2 Hz, $ZrCH_2$).

4: Deuterated toluene was dried by stirring over Na/K alloy followed by trap-to-trap distillation. 1,2-$F_2C_6H_4$ was dried over 4Å molecular sieve. (SBI)Zr(Me)CH_2SiMe_3 (5 mg, 10 µmol) and $[Ph_3C][B(C_6F_5)_4]$ (9.3 mg, 10 µmol) were loaded into a 5 mm NMR tube and dissolved in 0.6 mL of C_7D_8 containing 10 vol% of 1,2-$F_2C_6H_4$. ^1H NMR (300 MHz, 20 °C, toluene-d_8–$F_2C_6H_4$): δ 7.5–5.0 (Ind), 2.59 (d, 1H, *J* 12.3 Hz, $ZrCH_2$), 1.98 (s, 3H, Ph_3C*Me*), 0.72 (s, 6H, $SiMe_2$), −0.22 (d, 1H, *J* 12.3 Hz, $ZrCH_2$), −0.61 (s, 9H, $SiMe_3$). A trace of $SiMe_4$ was also observed.

1 (*a*) Z. Liu, E. Somsook and C. R. Landis, *J. Am. Chem. Soc.*, 2001, **123**, 2915; (*b*) Z. Liu, E. Somsook, C. B. White, K. A. Rosaaen and C. R. Landis, *J. Am. Chem. Soc.*, 2001, **123**, 11193; (*c*) C. R. Landis, K. A. Rosaaen and J. Uddin, *J. Am. Chem. Soc.*, 2002, **124**, 12062; (*d*) C. R. Landis, K. A. Rosaaen and D. R. Sillars, *J. Am. Chem. Soc.*, 2003, **125**, 1710.

2 F. Song, R. D. Cannon and M. Bochmann, *J. Am. Chem. Soc.*, 2003, **125**, 7641.

3 For earlier kinetic studies of metallocene catalyzed alkene polymerisations, see: (*a*) D. Schnell and G. Fink, *Angew. Makromol. Chem.*, 1974, **39**, 131; (*b*) G. Fink and W. Zoller, *Makromol. Chem.*, 1981, **182**, 3265; (*c*) G. Fink and D. Schnell, *Angew. Makromol. Chem.*, 1982, **105**, 31; (*d*) R. Mynott, G. Fink and W. Fenzl, *Angew. Makromol. Chem.*, 1987, **154**, 1; (*e*) G. Fink, W. Fenzl and R. Mynott, *Z. Naturforsch., Teil. B*, 1985, **40**, 158.

4 (*a*) E. Y. X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391; (*b*) M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255; (*c*) M. Bochmann, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1181.

5 (*a*) S. Beck, A. Geyer and H. H. Brintzinger, *Chem. Commun.*, 1999, 2477; (*b*) S. Beck, S. Lieber, F. Schaper, A. Geyer and H. H. Brintzinger, *J. Am. Chem. Soc.*, 2001, **123**, 1483.

6 N. Herfert and G. Fink, *Makromol. Chem.*, 1992, **193**, 773.

7 (*a*) V. Busico, R. Cipullo, F. Cutillo, M. Vacatello and V. Van Axel-Castelli, *Macromolecules*, 2003, **36**, 4258; (*b*) V. Busico, V. van Axel-Castelli, P. Aprea, R. Cipullo, A. Segre, G. Talarico and M. Vacatello, *J. Am. Chem. Soc.*, 2003, **125**, 5451.

8 M. Mohammed, M. Nele, A. Al-Humydi, S. Xin, R. Stapleton and S. Collins, *J. Am. Chem. Soc.*, 2003, **125**, 7930.

9 (*a*) J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thornton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223; (*b*) S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. L. Hughes and M. Bochmann, *Organometallics*, 2002, **21**, 451–453.

10 D. R. Sillars and C. R. Landis, *J. Am. Chem. Soc.*, 2003, **125**, 9894.

11 k_p(hexene, 20 °C) ≈ 6.3 ± 0.3 L mol^{-1} s^{-1} (ref. 1*b*).

12 This value is in excellent agreement with the k_p value of 10 L mol^{-1} s^{-1} obtained by Sillars and Landis by extrapolation to 20 °C (ref. 10).

13 Although, strictly speaking, for the $B(C_6F_5)_4^-$ anion our data here do not allow us to distinguish whether anion displacement or alkyl chain migration is rate-limiting, the observation of strong anion effects on rates in propene polymerisations (ref. 9*a*) supports the assumption of an early transition state in our view.