Kinetics and mechanism of methyl acrylate homo- and co-polymerisation catalysed by cyclopentadienyltitanium trichloride–MAO

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Abstract

Methyl acrylate is readily polymerised by the CpTiCl₃–MAO system. A kinetic study shows that the reaction is characterised by a linear dependence of the rate upon methyl acrylate concentration, and by saturation behaviour with respect to both catalyst CpTiCl₃ and co-catalyst MAO. The kinetic behaviour is interpreted in terms of insertion of an O-complexed monomer into a η^3 enolate-Ti growing polymer chain. When a mixed methyl acrylate–styrene monomer system is used, a mechanism resulting in a much slower formation of a random 1:1 co-polymer is proposed.
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1. Introduction

The cyclopentadienyltitanium trichloride–methylaluminoxane (CpTiCl₃–MAO) system effects polymerisation of electron-rich alkenes, such as styrene [1,2], 1-vinylcyclohexene [3], 1,3-butadiene [2] and 4-methylpenta-1,3-diene [2,4] and in some cases, e.g. styrene, this results in a syndiotactic polymer [5]. Generally, the alkenes polymerised or co-polymerised [6] by CpTiCl₃–MAO, metallocene and related homogeneous catalysts have been non-polar electron-rich ones. There have been fewer examples of analogous polymerisation of polar electron-deficient alkenes, although an early patent reported the co-polymerisation of styrene and a variety of acrylates and methacrylates by (Me₅Cp)Ti(OMe)₃–MAO [7].

The mechanism of the syndiotactic styrene polymerisation by CpTiCl₃–MAO and related catalyst systems [8] has been the subject of intense and ongoing study [9], although some aspects still remain unclear. Attention is now turning to polymerisations of polar electron-deficient

alkenes. Of interest here is a recent paper that describes the homo-polymerisation of methyl methacrylate and its co-polymerisation with styrene in the presence of Zn-reduced (Me₅Cp)TiMe₃-Ph₃C⁺B(C₆F₅)₄⁻, and proposes a group transfer protocol-like mechanism for homo-polymerisation, and a sequential conjugate addition mechanism for co-polymerisation [10].

In a recent paper we have reported the efficient polymerisation of methyl acrylate by the CpTiCl₃–MAO system, and also the co-polymerisation of methyl acrylate with styrene and isoprene [11]. Subsequent to this, we have undertaken a research programme to explore the mechanism of these polymerisations, the results of which are presented and discussed here.

2. Experimental

2.1. Materials

Methyl acrylate (Acros, 99% stabilised with 200 ppm monomethyl ether hydroquinone), isoprene (Aldrich, 99%) and cyclopentadienyltitanium trichloride (Aldrich, 97%)

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were used as received. Toluene (BDH) was distilled under N_2 from P_2O_5 (Fisher Scientific) and the fraction at 108 °C collected. Styrene (Aldrich, 99%) was dried by distillation at ca. 30 mm Hg from CaH_2 (Aldrich). The HCl/methanol solution used in the workup was prepared by bubbling HCl gas (generated by dropping hydrochloric acid into concentrated sulphuric acid) into methanol (BDH). The MAO (Aldrich, 10% (w/w) solution in toluene) was used as received, but it did appear to deteriorate with time. Therefore, the MAO solutions were discarded when the methyl acrylate polymerisation rate (see below) dropped significantly below that found using newly purchased solution.

2.2. Polymerisation of methyl acrylate

A three-necked 250 cm³ round-bottomed flask was set-up with a stopper, a septum and a connection to a vacuum pump, manometer and dry N_2 supply. Methyl acrylate (30 cm³, 28.68 g, 333 mmol) and sodium-dried toluene (49 cm³) were placed in the flask along with a stirring bar. The apparatus was thrice evacuated (to ca. 10 mm pressure) and filled with N_2 before a slow flow of N_2 was allowed across the system. Then, 10% MAO/toluene (2.9 cm³, ca. 5 mmol) was added carefully through the septum, with the tip of the needle below the surface of the solvent. The reaction was quickly heated to 50 °C on an oil bath before a solution of cyclopentadienyltitanium trichloride (CpTiCl₃) (0.011 g, 0.053 mmol) in dry toluene (1.0 cm³) was added via a syringe. Samples of approximately 2 cm³ volume were withdrawn via syringe at $t = 0$ and thereafter at 5 min intervals up to 1 h, and the last sample after 4 h. Each aliquot was injected into a pre-weighed sample tube and the exact weight was obtained. The aliquot was then worked up by addition of ca. 2 cm³ of HCl/methanol, allowed to stand for 1 day and the precipitated solid was collected by filtration. The precipitate was washed repeatedly with cold methanol and then dried at room temperature before being weighed.

2.3. Co-polymerisation

The co-polymerisation of methyl acrylate and styrene was carried out similarly, except that methyl acrylate (15 cm³, 14.34 g, 166 mmol) and styrene (15 cm³, 13.635 g,

131 mmol) were used in place of just methyl acrylate. Samples were withdrawn via syringe at $t = 0$ and thereafter at 4 h intervals up to 72 h. Similarly, the co-polymerisation of methyl acrylate and isoprene involved methyl acrylate (15 cm³, 14.34 g, 166 mmol) and isoprene (15 cm³, 10.215 g, 150 mmol).

3. Results and discussion

3.1. Kinetics

It has been shown that heating of methyl acrylate in toluene with CpTiCl₃ and MAO yields poly(methyl acrylate) as a rubbery solid; it showed no evidence of stereoregularity [11]. For kinetic analysis in the current work, polymerisation of methyl acrylate was carried out at 50 °C, under a nitrogen atmosphere, using quantities typified by those in Table 1. The progress of the reaction was monitored by sampling, followed by workup, drying, and weighing of the precipitated polymer.

The results for one particular run are shown in Table 2. The term W_{ppt}/W_{sample} is the weight of the isolated and dried polymer from a given weighed aliquot of reaction solution. The reaction is addition polymerisation, so the term equates to the fraction of the overall reaction weight that has been polymerised. Furthermore, it is related to the molality (moles

Table 2
Yield of polymer versus time[a]

Time (min)	Yield (W_{ppt}/W_{sample})
0	0.011
5	0.02
10	0.02
15	0.031
20	0.031
25	0.041
30	0.047
35	0.042
40	0.05
45	0.065
50	0.061
55	0.07
60	0.067
240	0.225

[a] Reaction conditions: Table 1, $T = 50$ °C.

Table 1
Amounts and calculation of concentration

Compound	RMM	Density	Weight (g)	Volume (cm³)	Amount (mmol)	Concentration (mol dm⁻³)	Concentration (mol kg⁻¹)	Fraction[a]
Methyl acrylate	86	0.956	28.68	30	333	4.02	4.48	0.385
Toluene	92	0.865	43.25	50	470	5.67	6.31	0.581
CpTiCl₃	219.36		0.011		0.050	0.00060	0.00067	0.00015
10 wt.% MAO in toluene	58[b]	0.875	2.5375	2.9	4.38[b]	0.052[b]	0.059[b]	0.034[b]

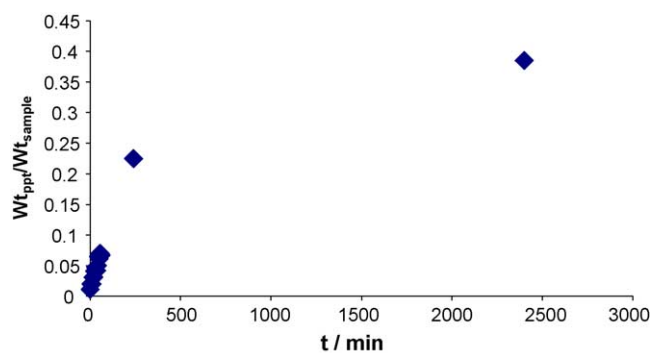[a] Fraction of total weight.

[b] Value relates to MAO rather than its solution in toluene.

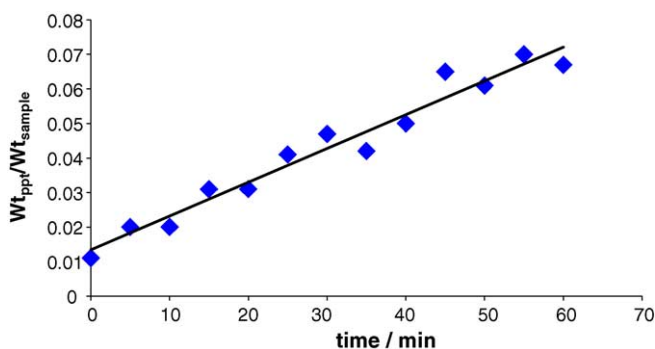Fig. 1. Plot of W_{ppt}/W_{sample} vs. t for the polymerisation of methyl acrylate. Reaction conditions: Table 1, $T = 50\,°C$.

Fig. 2. Plot of W_{ppt}/W_{sample} vs. t for the first 17% of the polymerisation of methyl acrylate. Reaction conditions: Table 1, $T = 50\,°C$.

of methyl acrylate consumed per kg of reaction mixture) of the methyl acrylate consumed.[1]

The W_{ppt}/W_{sample} data over the first 240 min of reaction is plotted against t (min) (Fig. 1). In addition, a reading taken after 240 min is included, as is the theoretical end point of the reaction, $W_{sample(t=\infty)} = 0.385$, calculated by assuming all the monomer (28.68 g), in the total reaction weight (74.48 g) has been polymerised. The 240 min reading corresponds to the half-life of the reaction, so the 'infinity' reading was arbitrarily set as 10×240 min for plotting the figure.

Comparing the $t = 60$ min value (0.067) with the 'infinity' value (0.385), it is clear that the reaction has not progressed beyond the first 17%. Hence, the apparent linearity of the plot when the early data is viewed on an expanded chart as in Fig. 2. From Fig. 2 the slope of the plot (obtained from least squares) gives the initial rate as $V_i = d(W_{ppt}/W_{sample})/dt = 1.63 \times 10^{-5}\,s^{-1}$. This initial rate can be converted to more traditional units and is equivalent to $d[\text{polymer}]/dt = -d[\text{monomer}]/dt = 1.90 \times 10^{-4}\,\text{mol kg}^{-1}\,s^{-1}$. The experiment was repeated three times further, to give an averaged $V_i = d(W_{ppt}/W_{sample})/dt = (1.27 \pm 0.29) \times 10^{-5}\,s^{-1}$, equivalent to $d[\text{polymer}]/dt = -d[\text{monomer}]/dt = (1.48 \pm 0.34) \times 10^{-4}\,\text{mol kg}^{-1}\,s^{-1}$.

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[1] For example, it can be seen from Table 1 that a W_{ppt}/W_{sample} ratio of 0.385 would correspond to $4.48\,\text{mol kg}^{-1}$ of monomer consumed.

Table 3
Variation of rate with [methyl acrylate][a]

[methyl acrylate] (mol kg^{-1})	$d(W_{ppt}/W_{sample})/dt$ ($\times 10^{-5}\,s^{-1}$)	$d[\text{polymer}]/dt$ ($\times 10^{-4}\,\text{mol kg}^{-1}\,s^{-1}$)
0	0	0.00
1.53	0.24	0.28
3.04	1.02	1.19
4.48	1.27	1.48

[a] Reaction conditions: $[\text{CpTiCl}_3] = 0.67\,\text{mmol kg}^{-1}$, $[\text{MAO}] = 0.059\,\text{mol kg}^{-1}$, $T = 50\,°C$.
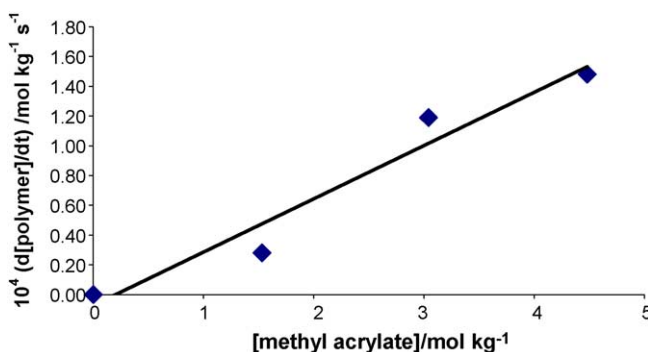

Fig. 3. Variation of rate with [methyl acrylate]. Reaction conditions: $[\text{CpTiCl}_3] = 0.67\,\text{mmol kg}^{-1}$, $[\text{MAO}] = 0.059\,\text{mol kg}^{-1}$, $T = 50\,°C$.

Table 4
Variation of rate with [CpTiCl$_3$][a]

[CpTiCl$_3$] (mmol kg^{-1})	$d(W_{ppt}/W_{sample})/dt$ ($\times 10^{-5}\,s^{-1}$)	$d[\text{polymer}]/dt$ ($\times 10^{-4}\,\text{mol kg}^{-1}\,s^{-1}$)
0.00	0.43	0.50
0.18	0.96	1.12
0.68	1.27	1.48
1.22	1.10	1.28

[a] Reaction conditions: $[\text{methyl acrylate}] = 4.48\,\text{mol kg}^{-1}$, $[\text{MAO}] = 0.059\,\text{mol kg}^{-1}$, $T = 50\,°C$.

The reaction was repeated at two lower levels of methyl acrylate (increasing the solvent toluene accordingly to preserve the overall volume) and the results are summarised in Table 3 and plotted against [methyl acrylate] in Fig. 3 to show linear dependence of rate upon monomer concentration.[2]

An approximate linear relationship is found, implying that $d[\text{polymer}]/dt = -d[\text{monomer}]/dt = k[\text{monomer}]$, where $k = (36 \pm 6) \times 10^{-6}\,s^{-1}$, a first-order rate constant.

Similarly, the variation of rate was determined with $[\text{CpTiCl}_3]$ (Table 4, Fig. 4) and with [MAO] (Table 5, Fig. 5). In both cases, the rate rises as $[\text{CpTiCl}_3]$ or [MAO] increases, only to level off.

Polymerisation of a 50:50 (v/v) methyl acrylate–styrene mixture, under the conditions of Table 1, resulted in much slower reaction than with methyl acrylate alone; similarly for methyl acrylate–isoprene (Fig. 6).

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[2] The reaction was carried out as per Table 1, but with 20 cm^3 of MA and 60 cm^3 of toluene to give $V_i = 1.02 \times 10^{-5}\,s^{-1}$, and with 10 cm^3 of MA and 70 cm^3 of toluene to give $V_i = 0.24 \times 10^{-5}\,s^{-1}$.

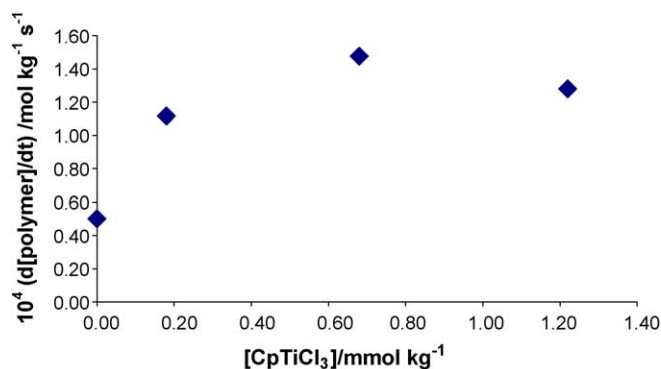Fig. 4. Variation of rate with [CpTiCl$_3$]. Reaction conditions: [methyl acrylate] = 4.48 mol kg^{-1}, [MAO] = 0.059 mol kg^{-1}, T = 50 °C.

Table 5
Variation of rate with [MAO][a]

[MAO] (mol kg^{-1})	d(W_{ppt}/W_{sample})/dt (×10^{-5} s^{-1})	d[polymer]/dt (×10^{-4} mol kg^{-1} s^{-1})
0.000	0	0.00
0.020	0.99	1.15
0.059	1.27	1.48
0.202	1.24	1.44

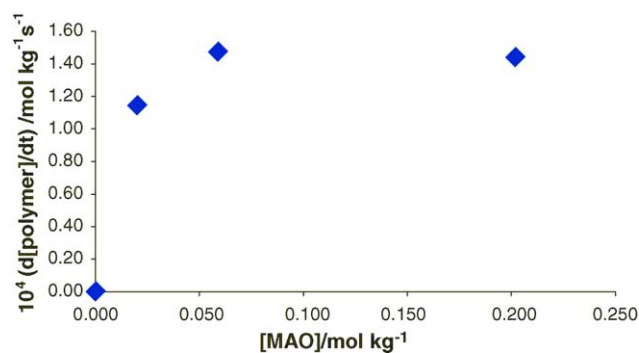[a] Reaction conditions: [methyl acrylate] = 4.48 mol kg^{-1}, [CpTiCl$_3$] = 0.68 mmol kg^{-1}, T = 50 °C.

Fig. 5. Variation of rate with [MAO]. Reaction conditions: [CpTiCl$_3$] = 0.67 mmol kg^{-1}, [methyl acrylate] = 4.48 mol kg^{-1}, T = 50 °C.
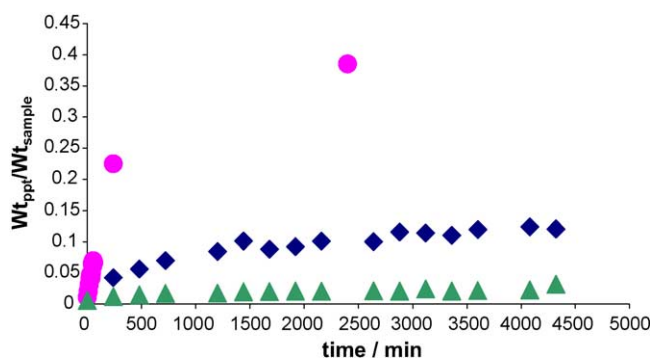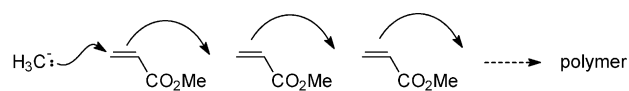

Fig. 6. Plot of W_{ppt}/W_{sample} vs. t for the co-polymerisation of methyl acrylate and styrene (◆), co-polymerisation of methyl acrylate and isoprene (▲) and polymerisation of methyl acrylate alone (●). Reaction conditions: [CpTiCl$_3$] = 0.67 mmol kg^{-1}, [MAO] = 0.059 mol kg^{-1}, T = 50 °C.

Scheme 1. Anionic polymerisation of methyl acrylate.
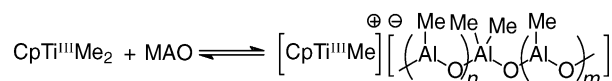
3.2. Mechanism

The interpretation of mechanistic studies on polymerisation of polar alkenes must, as indicated by Boffa and Novak [12], be approached with caution. Traditionally, electron-deficient alkenes were polymerised by anionic initiators such as *tert*-butyllithium/trialkyl aluminium.

The non-zero rate of polymerisation (Table 4 and Fig. 4) with MAO, but no CpTiCl$_3$, might suggest that MAO (a partly hydrolysed trialkyl aluminium derivative) alone is polymerising the methyl acrylate as in Scheme 1. However, the rate of polymerisation increases significantly when CpTiCl$_3$ is added. Therefore, it is clear that a significant fraction of the polymerisation is via a CpTiCl$_3$-catalysed route. Furthermore, it is difficult to see how a simple anionic polymerisation of methyl acrylate could be so greatly inhibited by the presence of styrene co-monomer given the known anionic polymerisation reactivity ratios (acrylate ≫ styrene) [13].

The variation of rate with MAO concentration increases (Fig. 5) up to a concentration of ca. 50 mmol; equivalent to an [MAO]:[CpTiCl$_3$] ratio of ca. 75:1. This optimum ratio of Al/Ti is relatively low compared to other catalysts where, e.g. Al/Zr ratios > 200 are found [14]. The results here, for methyl acrylate polymerisation, are remarkably similar to those found by Newman and co-workers [5], for styrene polymerisation using Cp$_*$Ti(OMe)$_2$ and Cp$_*$Ti(OMe)$_3$ [15]. These catalysts show 'saturation' behaviour at [MAO]:[catalyst] > 100 and saturation kinetic behaviour is common in such systems [9b,16].

The MAO is believed to cause reduction of Ti^{IV} to Ti^{III} [17]. However, ligand exchange equilibria between the Ti catalyst and MAO such as shown in Scheme 2 would account for the saturation kinetics.

The rate of reaction shows an increase with increasing [CpTiCl$_3$] at low levels of catalyst, but appears to fall slightly on further increase. This can be attributed to a reduction in the [MAO]:[CpTiCl$_3$] ratio to well below the optimum 75:1 value. We propose that the 'styrene polymerisation-like' kinetic behaviour with respect to MAO and CpTiCl$_3$ is indicative of the involvement of the same form of the catalyst here. Therefore, we assume, in line with others [9b] that CpTiCl$_3$ initially reacts with MAO to give a partly or fully, methylated derivative, e.g. CpTi(CH$_3$)$_3$, and that dissociation yields an



Scheme 2. Catalyst–MAO equilibrium.
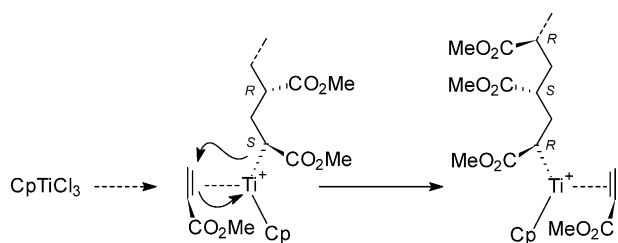
Scheme 3. The Cossee mechanism adapted for methyl acrylate.

active species that is cationic in nature, possibly with Ti reduced from Ti^{IV} to Ti^{III}, e.g. $CpTi(CH_3)^+$ (Scheme 2).

In the light of the above reasoning, it is tempting to argue that the polymerisation of methyl acrylate occurs via the styrene-like Cossee mechanism of Scheme 3 [18] but this is highly unlikely for methyl acrylate polymerisation here. Introduction of an electron-withdrawing group to styrene, e.g. chlorostyrene, is known to greatly reduce the efficiency of polymerisation [5,19] and the electron-withdrawing CO_2Me in place of Ph would reduce, rather than enhance, polymerisation as per Scheme 3.

The second possibility is the 'enolate' mechanism. Zirconium (Zr) and samarium (Sm) catalysts have been found to be effective for polymerisation of methyl methacrylate [20]. An 'enolate' mechanism has been proposed for these polymerisations [12,21] shown adapted from that proposed for Zr-catalysed polymerisation in Scheme 4, and Sm-catalysed polymerisation in Scheme 5.

Marks has argued convincingly for this mechanism in the case of the Zn-reduced $(Me_5Cp)TiMe_3$-$Ph_3C^+B(C_6F_5)_4^-$ system for methyl methacrylate homo-polymerisation [10]. However, this Zr-derived 'enolate' mechanism as shown in Scheme 4 seems unlikely here. It is difficult to envisage the growing Ti-bound polymer attacking a Ti-coordinated monomer intermolecularly, when space is available for monomer coordination to the same Ti-centre, allowing intramolecular reaction. The large polymeric MAO-derived counter-ion, likely to be intimately associated with the active catalyst centre (Scheme 2), would also preclude this bi-
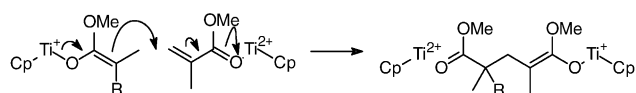
Scheme 4. The Zr-derived enolate mechanism.
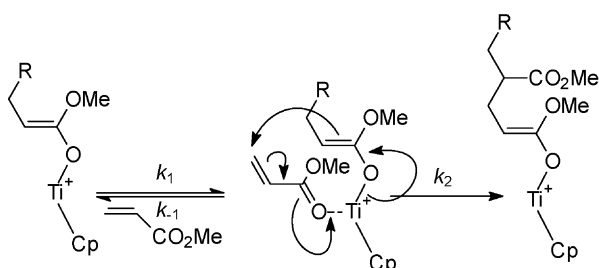
Scheme 5. The Sm-derived enolate mechanism.
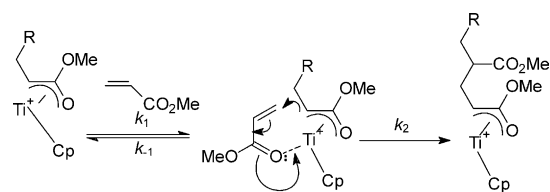
Scheme 6. η^3-mechanism.

molecular mechanism. Finally, it is also difficult to explain why MAO is required in this mechanism; the Ti^{IV} of the $CpTiCl_3$ alone would seem to be a preferable catalyst for this mechanism.

The Sm-based mechanism [20,22], shown in Scheme 5, suffers from the problem that the 'insertion' of the O-coordinated monomer into the attached polymer chain is difficult, since the enolate C is quite distant from the monomer β-C.

This difficulty could be alleviated by either a π-bonded monomer, or some degree of Ti–C bonding in the enolate. The latter seems more likely, especially if a η^3-system is invoked and a mechanism via a η^3-Ti-enolate is proposed in Scheme 6.

Once the polymerisation is established, as in Scheme 6, the key steps are the complexation ($k_1/k_{-1} = K$) of the alkene to the titanium, and the subsequent insertion (k_2) of the complexed alkene into the growing chain. A weak pre-complexation of alkene ($k_1/k_2 = K$) followed by rate-limiting insertion (k_2) is proposed; this would involve a rate equation of the form $V_i = k_2 K[\text{methyl acrylate}]_i[CpTiCl_3]_i$ ($V_i = $ initial rate, $d[\text{polymer}]/dt_{(t=0)}$), i.e. linear in methyl acrylate as observed.

3.3. Co-polymerisation

The methyl acrylate–styrene co-polymerisation product appears to be a random 1:1 co-polymer without stereoregularity. However, the dramatic reduction in rate for co-polymerisation of methyl acrylate–styrene, or for methyl acrylate–isoprene, is intriguing kinetically (Fig. 6).[3] Styrene appears to act as a 'competitive' inhibitor of methyl acrylate polymerisation, presumably by competing efficiently for the active catalyst species. This result is further evidence that the same catalyst active species is involved in polymerisation of styrene and of methyl acrylate. Further, it suggests that complexation of styrene is strong, in contrast to methyl acrylate complexation.

Despite the weaker complexation, methyl acrylate polymerisation is significantly faster overall, so the insertion step for methyl acrylate polymerisation must be very fast compared to the same step for styrene. Since it is difficult to reconcile a Ti-bound enolate or η^3-complex as more nucleophilic than a Ti-bound aryl-stabilised carbanion, this sug-

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[3] Independent studies show that polymerisation of styrene on its own, and isoprene on its own are both much slower that that of methyl acrylate.
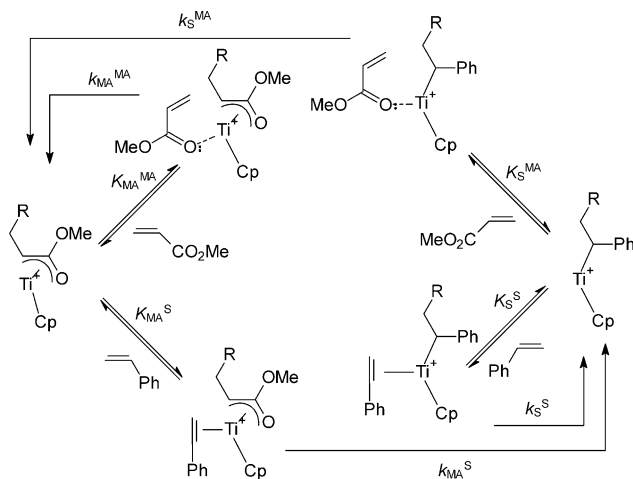
Scheme 7. Competition between methyl acrylate and styrene.

gests that the Ti-bound (via O) methyl acrylate is far more electrophilic than the π-bonded styrene. An idealised co-polymerisation mechanism is shown in Scheme 7 where the 1:1 co-polymerisation can be explained by a balance between predominant co-ordination of the unreactive styrene and the rarer, but more reactive co-ordination of methyl acrylate. While the mechanism proposed here might seem similar to that proposed earlier by Marks for the $(Me_5Cp)TiMe_3$-$Ph_3C^+B(C_6F_5)_4^-$ system, there are two significant differences. In particular, in our system, the catalyst active species favours methyl acrylate over styrene polymerisation, whereas in the latter, styrene polymerisation is favoured.

In conclusion, the mechanism of methyl acrylate polymerisation in the presence of CpTiCl$_3$ and MAO occurs predominantly via the same active catalyst species as proposed for styrene polymerisation, e.g. [Cp–Ti^{III}–R]$^+$. It involves an initial weak association of alkene (via O) with activated catalyst, followed by insertion into the growing polymer chain to give a η^3-complex. The rapidity of the polymerisation is due mainly to the activation of monomer by complexation to the Ti. Co-polymerisation with styrene results in a reduction in the rate due to preferential complexation by less reactive styrene to Ti complex. However, a balance between the complexation ability of styrene and the insertion ability of methyl acrylate results in a 1:1 co-polymer.

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