Selectivity of metallocene catalyzed olefin polymerization: a combined experimental and quantum mechanical study, 1. Non-chiral bis(cyclopentadienyl) systems

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Supporting Information

1. Derivation of eq. (2) in the text

Scheme SS1 shows all possible chain propagation steps in a propene/ethene copolymerization, under the plausible assumptions that:

i) the copolymerization statistics is first order Markovian;

ii) chain stereochemistry (when the last inserted unit is a propene one) does not affect the insertion rates;

iii) chain transfer and termination processes can be neglected.
Let us define now:

$C_{n,p}^*$ = concentration of growing chains with degree of polymerization n, in which the last inserted monomeric unit is a 1,2 propene one;

$C_{n,s}^*$ = concentration of growing chains with degree of polymerization n, in which the last inserted monomeric unit is a 2,1 propene one;

$C_{n,E}^*$ = concentration of growing chains with degree of polymerization n, in which the last inserted monomeric unit is an ethene one.

In the hypothesis of stationary state, and that the reaction order with respect to all monomers (1,2 propene, 2,1 propene and ethene) is 1, one can immediately derive the equations below:
\[
\begin{align*}
\frac{dC_{n,p}^*}{dt} &= 0 = \\
&\quad k_{pp}C_{(n-1),p}^*[P] + k_{sp}C_{(n-1),s}^*[P] + k_{ep}C_{(n-1),e}^*[P] \\
&\quad - k_{pp}C_{n,p}^*[P] - k_{sp}C_{n,p}^*[P] - k_{pe}C_{n,p}^*[E] \\
&\quad (S1) \\
\frac{dC_{n,s}^*}{dt} &= 0 = \\
&\quad k_{ps}C_{(n-1),s}^*[P] + k_{ss}C_{(n-1),s}^*[P] + k_{es}C_{(n-1),e}^*[P] \\
&\quad - k_{sp}C_{n,s}^*[P] - k_{ss}C_{n,s}^*[P] - k_{se}C_{n,s}^*[E] \\
&\quad (S2)
\end{align*}
\]

where \([P] ([E]) = \) concentration of propene (ethene) in the reaction phase.

For all catalysts considered here, propene insertion is predominantly 1,2, and occasional 2,1 misinsertions tend to remain isolated. This means that \(k_{pp} \gg k_{ps} \gg k_{es}\). Moreover, in our reaction conditions, due to the very low \([E]/[P]\) mole ratio in the feed (see Table 2 and Fig. 2), it is also true that \(k_{pe}[E] \ll k_{ep}[P]\). Therefore, Eqs. S1 and S2 can be approximated as follows:

\[
\begin{align*}
\frac{dC_{n,p}^*}{dt} &= 0 = k_{pp}C_{(n-1),p}^*[P] + k_{ep}C_{(n-1),e}^*[P] - k_{pp}C_{n,p}^*[P] \\
&\quad (S3) \\
\frac{dC_{n,s}^*}{dt} &= 0 = k_{ps}C_{(n-1),s}^*[P] + k_{es}C_{(n-1),e}^*[P] - k_{sp}C_{n,s}^*[P] - k_{se}C_{n,s}^*[E] \\
&\quad (S4)
\end{align*}
\]

Solving them for \(C_{n,p}^*\) and \(C_{n,s}^*\) gives:

\[
\begin{align*}
C_{n,p}^* &= (k_{pp}C_{(n-1),p}^*[P] + k_{ep}C_{(n-1),e}^*[P])/k_{pp}[P] \\
&\quad (S5) \\
C_{n,s}^* &= (k_{ps}C_{(n-1),s}^*[P] + k_{es}C_{(n-1),e}^*[P])/(k_{sp}[P] + k_{se}[E]) \\
&\quad (S6)
\end{align*}
\]

If one assumes that \(k_{ep} = k_{pp}\) and \(k_{es} = k_{ps}\), dividing Eq. S5 by Eq. S6 leads to:

\[
C_{n,p}^*/C_{n,s}^* = (k_{sp}[P] + k_{se}[E])/k_{ps}[P] \\
&\quad (S7)
\]

Finally, considering that the ratio \(Q_{pe}/Q_{se}\) between the amounts of ethene units inserted after a 1,2 or a 2,1 propene unit, respectively, is given by:

\[
Q_{pe}/Q_{se} = (k_{pe}C_{n,p}^* + k_{es}[E])/k_{ps}[P] \\
&\quad (S8)
\]

combination of Eqs. S7 and S8 yields Eq. S9 below (Eq. 2 in the text):

\[
Q_{pe}/Q_{se} = (k_{pe}/k_{se})(k_{sp}/k_{ps}) + (k_{pe}/k_{ps})[E]/[P] \\
&\quad (S9)
\]
2. Total energies

Table S1. Total energies for metallocene alkyls, olefin complexes and transition states.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Mode</th>
<th>( \text{Cp}_2\text{Ti} )</th>
<th>( \text{Cp}_2\text{Zr} )</th>
<th>( \text{H}_2\text{SiCp}_2\text{Zr} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethene</td>
<td></td>
<td>-78.16105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>propene</td>
<td></td>
<td>-117.26726</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{Cp}_2\text{M}\text{Et}^+)</td>
<td></td>
<td>-519.14969</td>
<td>-793.86429</td>
<td>-793.86429</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{M}\text{Pr}^+)</td>
<td></td>
<td>-558.24697</td>
<td>-832.96379</td>
<td>-832.96379</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{M}(\text{Et})(\text{ethene})^+)</td>
<td></td>
<td>-597.31664(^a)</td>
<td>-872.05113(^a)</td>
<td>-872.05113(^a)</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{M}(\text{Et})(\text{propene})^+)</td>
<td></td>
<td>-636.42593(^b)</td>
<td>-911.15580(^d)</td>
<td>-911.15580(^d)</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{M}(\text{iPr})(\text{ethene})^+)</td>
<td></td>
<td>-636.41031(^a)</td>
<td>-911.14569(^e)</td>
<td>-911.14569(^e)</td>
</tr>
<tr>
<td>(\text{Cp}_2\text{M}(\text{iPr})(\text{propene})^+)</td>
<td></td>
<td>-675.51961(^c)</td>
<td>-950.25360(^f)</td>
<td>-950.25360(^f)</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{Et}...\text{ethene})^+)</td>
<td></td>
<td>-597.31283</td>
<td>-585.85646</td>
<td>-872.04275</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{Et}...\text{propene})^+)</td>
<td>2,1 \text{syn}</td>
<td>-636.40871</td>
<td>-624.95251</td>
<td>-911.13885</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{Et}...\text{propene})^+)</td>
<td>2,1 \text{anti}</td>
<td>-636.40946</td>
<td>-624.95530</td>
<td>-911.14028</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{Et}...\text{propene})^+)</td>
<td>1,2 \text{syn}</td>
<td>-636.41115</td>
<td>-624.95343</td>
<td>-911.14002</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{Et}...\text{propene})^+)</td>
<td>1,2 \text{anti}</td>
<td>-636.41714</td>
<td>-624.96048</td>
<td>-911.14696</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{iPr}...\text{ethene})^+)</td>
<td></td>
<td>(no barrier)</td>
<td>-624.95447</td>
<td>-911.14224</td>
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<tr>
<td>TS (\text{Cp}_2\text{M}(\text{iPr}...\text{propene})^+)</td>
<td>2,1</td>
<td>-675.50472</td>
<td>-664.05145</td>
<td>-950.23971</td>
</tr>
<tr>
<td>TS (\text{Cp}_2\text{M}(\text{iPr}...\text{propene})^+)</td>
<td>1,2</td>
<td>-675.50693</td>
<td>-664.05345</td>
<td>-950.24088</td>
</tr>
</tbody>
</table>

\(^{a}\text{bs} \), \(^{b}\text{bs}, 1,2 \), \(^{c}\text{bs}, 2,1 \), \(^{d}\text{fs}, 1,2 \), \(^{e}\text{syn} \), \(^{f}\text{fs} \), \(^{g}\text{fs}, 2,1 \) GAMESS-UK development version 6.2.1, 1999. Results calculated with earlier or later versions may differ slightly because of changes in the numerical integration schemes used in the DFT module.