MODELING OLEFIN POLYMERIZATION USING MONTE CARLO SIMULATION: DETAILED COMONOMER DISTRIBUTION

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Objectives

- To build a Monte Carlo model to describe the polymerization mechanisms of olefin copolymerization using single-site coordination catalyst

- To predict detailed polymer microstructure:
  - The complete chain length distribution;
  - Polydispersity;
  - Average comonomer (B) composition FB;
  - Comonomer composition distribution as function of chain length;
  - Monomer (A) and comonomer (B) segment length distribution as function of chain length;
  - Average triads distribution;
  - Triad distribution as a function of chain length;
Introduction

**Stochastic Modeling & Monte Carlo Simulation**

- Monte Carlo modeling is a convenient method of modeling polymer reaction mechanism and is widely used in polymerization systems (use of probabilities)

- It is useful specially when analytical solutions are not available

**Polyolefins**

- The basic properties of PE (-CH$_2$CH$_2$)$_n$ are determined by the molecular structure

- Depends on degree of crystallinity, degree of polymerization, average molar mass and molar mass distribution
### Catalysts

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>Characteristics</th>
</tr>
</thead>
</table>
| Ziegler Titanium    | - Narrow molecular weight distribution  
                        - Co-catalyst required  
                        - Hydrogen is used for molecular weight control |
| Phillips Chromium   | - Relatively broad molecular weight distribution  
                        - Co-catalyst not required  
                        - Hydrogen is not used for molecular weight control |
| Metallocene Zirconium| - Relatively narrow molecular weight distribution  
                        - Co-catalyst required  
                        - Hydrogen as chain transfer agent |

Catalysts for global PE production (Kashiwa, 2004)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ziegler</td>
<td>26.2 (51%)</td>
</tr>
<tr>
<td>Philips</td>
<td>8.3 (16%)</td>
</tr>
<tr>
<td>Metallocene</td>
<td>0.8 (2%)</td>
</tr>
</tbody>
</table>
Copolymer-Kinetic Equations-Probabilities Calculations

Rate of Propagation:

\[ P_{r=1}^* + n \, M \rightarrow P_{r=1+n}^* \]

\[ R_{pA} = k_{pA} [P_r^*][A] \]
\[ R_{pB} = k_{pB} [P_r^*][B] \]

Rate of Termination:

\[ P_r^* \rightarrow P_H^* + \bar{D}_r \]
\[ R_{tA} = k_{tA} [P_r^*] \]
\[ R_{tB} = k_{tB} [P_r^*] \]

The probability of propagation:

\[ p_p = \frac{(R_{pA} + R_{pB})}{(R_{pA} + R_{pB}) + (R_{tA} + R_{tB})} = \frac{(k_{pA} [P_r^*][A] + k_{pB} [P_r^*][B])}{(k_{pA} [P_r^*][A] + k_{pB} [P_r^*][B]) + (k_{tA} [P_r^*] + k_{tB} [P_r^*])} \]

Knowing that, the number average chain length:

\[ r_n = \frac{R_p}{R_t} = \frac{(R_{pA} + R_{pB})}{(R_{tA} + R_{tB})} \]
Copolymer-Kinetic Equations-Probabilities Calculations

The probability of propagation is related to the number-average chain length:

\[
P_p = \frac{R_p}{R_p + R_t} = \frac{1}{1 + \frac{R_t}{R_p}} = \frac{1}{1 + \frac{1}{r_n}} \approx 1 - \frac{1}{r_n}
\]

And, the probability of chain termination is related to the number-average chain length by:

\[
P_t = \frac{R_t}{R_p + R_t} = \frac{R_p + R_t}{(R_{pa} + R_{pb}) + (R_{ta} + R_{tb})} = \frac{k_{ta} [P_r^*] + k_{tb} [P_r^*]}{(k_{pA} [P_r^*][A] + k_{pB} [P_r^*][B]) + (k_{tA} [P_r^*] + k_{tB} [P_r^*])}
\]

\[
P_t = \frac{R_t}{R_p + R_t} = \frac{1}{R_p + 1} \approx \frac{1}{r_n}
\]
Copolymerization Schematic Flow Chart

Number of chains (1000000)
Number average chain length (3500)
Probability of adding monomer B (0.2)
Random number seed (-1)

AABAA(A)_n B(B)_n

Input

\( P_t \)

\( \text{RAN} \)

\( \text{RAN} < P_t \)

Yes

Store termination Information

Re-calculate \( r, F_B, SLD, \text{Triads} \)

Build another chain?

Yes

End of Program

No

Store propagation Information

\( \text{RAN} \)

\( \text{RAN} > P_B \)

Yes

add A

No

\( \text{add B} \)

Change & Recalculate

Number of chains & Comonomer distribution as a function of chain length
Number of segments (monomer and comonomer) as a function of segment length ..etc
(txt file, open with Excel)
Simulation Model Inputs-Outputs

Model Input:
- Total number of polymer chains
- Number average chain length ($r_n$)
- Average fraction of comonomer ($F_B$)
- Seed to initiate the random number

Model Parameters:
- Probability of termination ($P_t$)
- Probability of adding the comonomer ($P_B$)
- Concentration of monomer [A]
- Concentration of comonomer [B]
- Concentration of the active species, $[P^-]
- Monomer A propagation constant, $k_{pA}$
- Comonomer B propagation constant, $k_{pB}$
- Monomer A termination constant, $k_{tA}$
- Comonomer B termination constant, $k_{tB}$

Model Output:
- Chain length distribution
- Polydispersity
- Average comonomer (B) composition
- Comonomer composition distribution as function of chain length ($r$)
- Monomer and comonomer segment length distribution as function of ($r$)
- Average triads distribution
- Triad distribution as a function of ($r$)

Experimental Measurement:
- Molecular weight
- Degree of polymerization
- Branching
- Crystallinity
  (tensile strength, impact toughness, melting temperature)
Triads Relative Intensities of $^{13}$C-NMR Spectra

Nomenclature and $^{13}$C-NMR Chemical Shift Assignments

Nuclear Magnetic Resonance spectroscopy is a very powerful technique for polymer characterization.

..ABABBBBA...

A = ethylene
B = 1-hexene

LLDPE = Linear Low Density Polyethylene
Tabulated Intensity Equations
Chemical Shifts Assignments

Calculated intensities with respective chemical shift assignments ($r_n = 100.8$ and $F_B = 5\%$)

<table>
<thead>
<tr>
<th>Region</th>
<th>from</th>
<th>to</th>
<th>Contributing Carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>39.5</td>
<td>42</td>
<td>$\alpha$, Methylene</td>
</tr>
<tr>
<td>B</td>
<td>38.1</td>
<td></td>
<td>(Methine)$_{EHE}$</td>
</tr>
<tr>
<td>C</td>
<td>33</td>
<td>36</td>
<td>(Methine)$<em>{EH+HHE}$, (Methine)$</em>{HHH}$, 4B$_4$, $\gamma\gamma$, $\alpha\delta$</td>
</tr>
<tr>
<td>D</td>
<td>28.5</td>
<td>31</td>
<td>$\delta^<em>\delta^</em>$, 3B$_4$, $\gamma\gamma$, $\alpha\delta$</td>
</tr>
<tr>
<td>E</td>
<td>26.5</td>
<td>27.5</td>
<td>$\beta\delta^*$</td>
</tr>
<tr>
<td>F</td>
<td>24</td>
<td>25</td>
<td>$\beta\beta$</td>
</tr>
<tr>
<td>G</td>
<td>23.4</td>
<td></td>
<td>$2B_4$</td>
</tr>
<tr>
<td>H</td>
<td>14.1</td>
<td>1B$_4$</td>
<td>$\gamma\delta^*$, $\alpha\alpha$</td>
</tr>
</tbody>
</table>

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Chain Length & Segment Length Distribution

Case Study

Simulation Results

Triad Distribution

Triads Relative Intensities of $^{13}$C-NMR Spectra
Number Fraction of Chains as a Function of Chain Length and Comonomer Distribution

Four different simulations scenarios

<table>
<thead>
<tr>
<th>$k_{pA}$ (L/mole.s)</th>
<th>$k_{pB}$ (L/mole.s)</th>
<th>$k_{tA}$ (L/mole.s)</th>
<th>$k_{tB}$ (L/mole.s)</th>
<th>$Pp$</th>
<th>$r_n$</th>
<th>$P_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1210</td>
<td>1910</td>
<td>2.70</td>
<td>1.10</td>
<td>0.99901</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2150</td>
<td>3395</td>
<td>1.35</td>
<td>0.91</td>
<td>0.99967</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3220</td>
<td>5080</td>
<td>1.23</td>
<td>0.80</td>
<td>0.99980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3420</td>
<td>5340</td>
<td>0.98</td>
<td>0.56</td>
<td>0.99986</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$[Pr^*]=10 \times 10^{-6}$ (mole/L), $[A]=3$ (mole/L), $[B]=0.1$ (mole/L), $P_B$ = probability of adding comonomer B
Fraction of Monomer Segment Length, $A_n$ ($r_n=5004$, $F_B=3\%$)

Segment < 20 monomer units will not crystallize (Haag et. al., 2003)
Fraction of Comonomer Segment Length $B_n$ ($r_n=5004$, $F_B=3\%$)

$AABBAAABAABBBA$

$\sum_{n} = 20$

Segment $< 20$ monomer units will not crystallize (Haag et. al., 2003)

Monomer B Segment Length = 2

Number Fraction of Segments $B$

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Distribution of Segments $B_{1-6}$, $A_{1-19}$, $A_{>19}$ and total $A_n$ as a Function of Chain Length ($r_n = 5004$, $F_B = 3\%$)

$(A)_n$

Segment < 20 monomer units will not crystallize

$(\text{Haag et. al., 2003})$
Triad Distribution as a Function of Chain Length

\( r_n = 5004, \ F_B = 3\% \)
Case Study

Kinetic parameters used in the case study (representing four different reactor conditions)

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$k_{pA}$ (L/mole.s)</th>
<th>$k_{pB}$ (L/mole.s)</th>
<th>$k_{iA}$ (L/mole.s)</th>
<th>$k_{iB}$ (L/mole.s)</th>
<th>$r_n$</th>
<th>$F_B$</th>
<th>$r_n$</th>
<th>$F_B$</th>
<th>$r_n$</th>
<th>$F_B$</th>
<th>$r_n$</th>
<th>$F_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1210</td>
<td>1910</td>
<td>2.70</td>
<td>1.10</td>
<td>1008</td>
<td>5%</td>
<td>3001</td>
<td>4%</td>
<td>5004</td>
<td>3%</td>
<td>7024</td>
<td>2%</td>
</tr>
<tr>
<td>R2</td>
<td>2160</td>
<td>2700</td>
<td>1.25</td>
<td>1.00</td>
<td>0.00033</td>
<td>0.99967</td>
<td>3001</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>2200</td>
<td>2040</td>
<td>0.79</td>
<td>0.57</td>
<td>0.00020</td>
<td>0.99980</td>
<td>5004</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>3900</td>
<td>2390</td>
<td>0.92</td>
<td>0.78</td>
<td>0.00014</td>
<td>0.99986</td>
<td>7024</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$[Pr^*]=10 \times 10^{-6}$ (mole/L), $[A]=3$ (mole/L), $[B]=0.1$ (mole/L)
Case Study

Effect of product mixing from reactor 1 to reactor 4 on the polymer parameters

<table>
<thead>
<tr>
<th></th>
<th>$r_n$</th>
<th>$r_w$</th>
<th>PDI</th>
<th>$F_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>1008</td>
<td>2001</td>
<td>1.98</td>
<td>5.0%</td>
</tr>
<tr>
<td>$R_1+R_2$</td>
<td>2006</td>
<td>4994</td>
<td>2.49</td>
<td>4.5%</td>
</tr>
<tr>
<td>$R_1+R_2+R_3$</td>
<td>3007</td>
<td>7777</td>
<td>2.59</td>
<td>4.0%</td>
</tr>
<tr>
<td>$R_1+R_2+R_3+R_4$</td>
<td>4009</td>
<td>10513</td>
<td>2.62</td>
<td>3.5%</td>
</tr>
</tbody>
</table>

Kinetic parameters used in the case study after mixing (representing the products with $r_n = 1008$ to 4009 for mixed product from reactor 1 to reactor 4)

<table>
<thead>
<tr>
<th></th>
<th>$k_{pA}$</th>
<th>$k_{pB}$</th>
<th>$k_{tA}$</th>
<th>$k_{tB}$</th>
<th>$P_i$</th>
<th>$P_p$</th>
<th>$r_n$</th>
<th>$P_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>1210</td>
<td>1910</td>
<td>2.70</td>
<td>1.10</td>
<td>0.00099</td>
<td>0.99901</td>
<td>1008</td>
<td>0.05</td>
</tr>
<tr>
<td>$R_1+R_2$</td>
<td>1100</td>
<td>1550</td>
<td>0.92</td>
<td>0.80</td>
<td>0.00050</td>
<td>0.99950</td>
<td>2006</td>
<td>0.045</td>
</tr>
<tr>
<td>$R_1+R_2+R_3$</td>
<td>1308</td>
<td>1650</td>
<td>0.79</td>
<td>0.57</td>
<td>0.00033</td>
<td>0.99967</td>
<td>3007</td>
<td>0.04</td>
</tr>
<tr>
<td>$R_1+R_2+R_3+R_4$</td>
<td>2220</td>
<td>2400</td>
<td>0.94</td>
<td>0.78</td>
<td>0.00025</td>
<td>0.99975</td>
<td>4009</td>
<td>0.035</td>
</tr>
</tbody>
</table>

$[Pr^*]=10^{-6}$ (mole/L), $[A]=3$ (mole/L), $[B]=0.1$ (mole/L)
Case Study
From reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains
Case Study

Number fraction of monomer segments for A₁ to A₁₉ from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length.
ABA triad distribution from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length (varying $r_n$, $F_B$)
Case Study

BBB triad distribution from reactor 1 with 250,000 chains to reactor 4 with 1,000,000 chains as function of chain length (varying $r_n$, $F_B$)
The relative intensities of $^{13}$C-NMR spectra for the branching regions
Fractionated Chain Length Population

- **Low**: $M_n=30,800$ g/mol, $r = 1,100$
- **Medium**: $M_n=282,800$ g/mol, $r = 10,100$
- **High**
**Triads Relative Intensities**

Table-7 Fractionated population classes for the relative intensities with respective regions of reactor 4 after mixing the products from reactor 1 to 4 ($R_1+R_2+ R_3+ R_4$) according to chain length ($r$)

<table>
<thead>
<tr>
<th>Region</th>
<th>Low ($r &lt;1100$)</th>
<th>Medium ($1100 &lt; r &lt;10100$)</th>
<th>High ($r &gt;10100$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.109%</td>
<td>0.080%</td>
<td>0.070%</td>
</tr>
<tr>
<td>A</td>
<td>0.080%</td>
<td>0.059%</td>
<td>0.053%</td>
</tr>
<tr>
<td>B</td>
<td>0.605%</td>
<td>0.446%</td>
<td>0.381%</td>
</tr>
<tr>
<td>C</td>
<td>98.595%</td>
<td>98.964%</td>
<td>99.107%</td>
</tr>
<tr>
<td>D</td>
<td>0.083%</td>
<td>0.061%</td>
<td>0.052%</td>
</tr>
<tr>
<td>E</td>
<td>0.074%</td>
<td>0.054%</td>
<td>0.045%</td>
</tr>
<tr>
<td>F</td>
<td>0.227%</td>
<td>0.167%</td>
<td>0.146%</td>
</tr>
<tr>
<td>G</td>
<td>0.227%</td>
<td>0.167%</td>
<td>0.146%</td>
</tr>
<tr>
<td>H</td>
<td>0.083%</td>
<td>0.061%</td>
<td>0.052%</td>
</tr>
</tbody>
</table>

---

**Graph:***

![Graph showing relative intensities for regions A to H across low, medium, and high chain length categories.](image)
Future Research Work

Model Input:
- Total number of polymer chains
- Number average chain length ($r_n$)
- Average fraction of comonomer ($F_B$)
- Seed to initiate the random number

Model Parameters:
- Probability of termination ($P_t$)
- Probability of adding the comonomer ($P_B$)
- Concentration of monomer [A]
- Concentration of comonomer [B]
- Concentration of the active species, $[P_i^*]$
- Monomer A propagation constant, $k_{pA}$
- Comonomer B propagation constant, $k_{pB}$
- Monomer A termination constant, $k_{tA}$
- Comonomer B termination constant, $k_{tB}$

Experimental Measurement:
- Molecular weight
- Degree of polymerization
- Branching
- Crystallinity (tensile strength, impact toughness, melting temperature)

Model Output:
- Chain length distribution
- Polydispersity
- Average comonomer (B) composition
- Comonomer composition distribution as a function of chain length ($r$)
- Monomer and comonomer segment length distribution as function of ($r$)
- Average triads distribution
- Triad distribution as a function of ($r$)

Parameter Estimation

Future Work
Conclusions

The comprehensive Monte Carlo model which is developed and tested in this research work was able to describe the detailed comonomer distribution in the copolymerization of ethylene-\(\alpha\)-olefins.

For copolymerization, the model was able to predict chain length and comonomer sequence distribution with great detail.

In the case of copolymerization the fraction of monomer B incorporated in the polymer chain was not dependant on the size of the chain, which is in agreement with the polymerization mechanism.

The input information for running the model can be obtained from experimental polymer analysis or through the reaction kinetics.
The input information is used to calculate model probabilities that are then used to determine each event of the polymerization mechanism.

The model demonstrated great ability in predicting the detailed segment length distribution as a function of chain length, as well as the relative intensity for the peaks of the $^{13}$C-NMR.

This is a powerful tool to explore the chemical composition of the polymer in more detail.

Knowing the segment lengths and triads distribution as a function of chain length is an advantage that allows us to study the polymerization mechanism and the properties of the polymer.