A great deal of my work is just playing with equations and seeing what they give.

Paul Dirac (1902-1984)
Acknowledgements

Mr Keran Chen

Dr Saeid Mehdizabadi
Deconvolution of GPC-IR distributions identifies the minimum number of active sites on Ziegler-Natta catalysts.

This method also estimates the apparent kinetic constants for activation, propagation, deactivation, and comonomer incorporation of each site type.

<table>
<thead>
<tr>
<th>Site</th>
<th>$M_n \times 10^3$</th>
<th>SCB/1000C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>29.6</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>11.3</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>112</td>
<td>4.2</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Ziegler-Natta polyolefins have broad molecular weight and chemical composition distributions.

It should look like this,

but it looks like this,

A reasonable explanation is that there are 2 or more site types, each making polymer with the distribution on the left of the slide.
**Hypothesis:** Different polymer populations are made on each site type
Methodology

Minimize

\[ \sum [(\text{GPC-IR})_{\text{exp}} - (\text{GPC-IR})_{\text{pred}}]^2 \]

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m )</td>
<td>0.0378</td>
<td>0.1800</td>
<td>0.4333</td>
<td>0.2674</td>
<td>0.0815</td>
</tr>
<tr>
<td>( M_n )</td>
<td>7 400</td>
<td>23 900</td>
<td>64 900</td>
<td>164 000</td>
<td>507 000</td>
</tr>
<tr>
<td>SCB/1000C</td>
<td>7.05</td>
<td>1.98</td>
<td>1.10</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>( F_B )</td>
<td>0.0143</td>
<td>0.0040</td>
<td>0.0022</td>
<td>0.0020</td>
<td>0.0020</td>
</tr>
</tbody>
</table>
Polymerization System

- 250 mL SS autoclave reactor
- 90 °C polymerization temperature
- 7 bar ethylene
- 2, 4, or 6 g 1-hexene
- 10, 20, 40, 60 min polymerization time
- $H_2$ used a chain transfer agent
Polymerization Kinetics

2.0 g 1-Hexene

- 10 min
- 20 min
- 40 min
- 60 min

Ethylene Flow Rate (ml/min)

Time (min)

Introduction Method GPC-IR Kinetics Conclusions
Deconvolution Assumptions

- Sites of different types make polymer populations with the same $M_n$ and SCB/1000 C.
- The changes in $M_n$ and SCB/1000C for the whole polymer result from differences in the polymerization kinetics of the distinct site types.
  - Distinct site types have different activation/propagation/deactivation rates that affect the properties of the whole polymer.
GPC-IR Deconvolution

2.0 g 1-Hexene
Deconvolution Results

The fraction of polymer made in high-$M_n$ sites increases.

The fraction of polymer made in low-$M_n$ sites decreases.

<table>
<thead>
<tr>
<th>Site</th>
<th>$M_n (10^3)$</th>
<th>SCB/1000C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>29.6</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>11.3</td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>6.2</td>
</tr>
<tr>
<td>4</td>
<td>112</td>
<td>4.2</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>3.4</td>
</tr>
</tbody>
</table>

2.0 g 1-Hexene
### Results for Other 1-Hexene Concentrations

#### 4.0 g 1-Hexene

<table>
<thead>
<tr>
<th>Site</th>
<th>$M_n (10^3)$</th>
<th>SCB/1000C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>35.1</td>
</tr>
<tr>
<td>2</td>
<td>12.0</td>
<td>13.8</td>
</tr>
<tr>
<td>3</td>
<td>35</td>
<td>9.5</td>
</tr>
<tr>
<td>4</td>
<td>107</td>
<td>7.6</td>
</tr>
<tr>
<td>5</td>
<td>318</td>
<td>6.2</td>
</tr>
</tbody>
</table>

#### 6.0 g 1-Hexene

<table>
<thead>
<tr>
<th>Site</th>
<th>$M_n (10^3)$</th>
<th>SCB/1000C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.5</td>
<td>39.6</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>17.5</td>
</tr>
<tr>
<td>3</td>
<td>36</td>
<td>13.7</td>
</tr>
<tr>
<td>4</td>
<td>101</td>
<td>10.9</td>
</tr>
<tr>
<td>5</td>
<td>290</td>
<td>10.4</td>
</tr>
</tbody>
</table>
1-Hexene Incorporation per Site Type

![Graph showing 1-hexene incorporation per site type. The x-axis represents 1-hexene (g) and the y-axis represents SCB/1000 C. The graph includes data points for Site 1, Site 2, Site 3, Site 4, and Site 5. ]
# Investigating Site Type Kinetics

<table>
<thead>
<tr>
<th>Description</th>
<th>Chemical Equation</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation</td>
<td>( C + Al \rightarrow P_0 )</td>
<td>( k_a )</td>
</tr>
<tr>
<td>Propagation</td>
<td>( P_r + M \rightarrow P_{r+1} )</td>
<td>( k_p )</td>
</tr>
<tr>
<td>1(^{st}) Order Deactivation</td>
<td>( P_r \rightarrow C_d + D_r )</td>
<td>( k_d )</td>
</tr>
</tbody>
</table>

\[
R_p = k_p [M] \frac{\left\{ 1 - \exp\left[ -K_a \left( 1 - \frac{k_d}{K_a} \right) t \right]\right\} \exp(-k_d t)}{1 - \frac{k_d}{K_a}} C_0
\]
Effect of $k_p$
Effect of $k_d$

- Introduction
- Method
- GPC-IR
- Kinetics
- Conclusions
Effect of $K_A$
Polymer Yield in a Semi-Batch Reactor

\[
Y_{\text{whole}} = \sum Y_i
\]

\[
Y = \frac{k_p[M]C_0}{1 - \frac{k_d}{K_a}} \left( \frac{1 - e^{-k_d t}}{k_d} - \frac{1 - e^{-K_d t}}{K_a} \right)
\]

**Introduction**

**Method**

**GPC-IR**

**Kinetics**

**Conclusions**
Partitioning the Polymer Among Active Sites

$t = 20 \text{ min}$

**Whole polymer**

Log MW vs. Log MW distribution.
Ethylene Homopolymerization Site Kinetics

![Graph showing ethylene flow rate over time for different sites and a model comparison.]

- **Introduction**
- **Method**
- **GPC-IR**
- **Kinetics**
- **Conclusions**
Copolymer Yield per Site Type: 2.0 g 1-Hexene
Copolymerization Site Kinetics: 2.0 g 1-Hexene

Graph showing ethylene uptake over time for different sites and the model.
Copolymer Yield per Site Type

4.0 g 1-Hexene

6.0 g 1-Hexene

Introduction Method GPC-IR Kinetics Conclusions
Copolymerization Site Kinetics

4.0 g 1-Hexene

6.0 g 1-Hexene

Introduction
Method
GPC-IR
Kinetics
Conclusions
1-Hexene increases $K_a$

![Graph showing the effect of 1-hexene on $K_a$](image)

- **Ka (min$^{-1}$)**
- **Y-axis**: Ka (min$^{-1}$)
- **X-axis**: 2.0g 1-C6, 4.0g 1-C6, 6.0g 1-C6, Homopolymer
- **Legend**:
  - Site 1
  - Site 2
  - Site 3
  - Site 4
  - Site 5

**Note:**
- Introduction
- Method
- GPC-IR
- Kinetics
- Conclusions
1-Hexene increases $k_p$ of low $M_n$ sites but decreases $k_p$ of high $M_n$ sites
1-Hexene increases $k_d$

![Graph showing the increase in $k_d$ with varying concentrations of 1-hexene and different sites.](image-url)
What is this information good for?
Concluding Remarks

• GPC-IR deconvolution can:
  • Quantify the MWD x SCB/1000 C evolution of polyolefins made with multiple-site catalysts (Ziegler-Natta and Phillips).
  • Assign $M_n$ and SCB for different site types.
  • Estimate apparent $K_a$, $k_p$ and $k_d$ for each site type.

• We must be aware that our conclusions will depend on the hypotheses we made during data analysis.
Questions?