Performance and Bioinspired Elastomers

Biomass-based Plastics and Chemically Recyclable Materials

Advanced Precision Architectures and Assemblies for Energy Storage

FSU REU Photochemistry Café
July 7, 2023
“As petroleum came to the relief of the whale,” so “has celluloid given the elephant, the tortoise, and the coral insect a respite in their native haunts; and it will no longer be necessary to ransack the earth in pursuit of substances which are constantly growing scarcer.” ~J. W. Hyatt

3,500 elephants in 3 years  
~ New York Times (1867)
Humans have found utility in polymers since the beginning.

**Cellulose** – the most abundant organic polymer in cotton (90%) and wood (~45 ± 5%).
- Repeat unit is D-glucose
- \( n = 7,000 – 15,000 \)
- Semi-crystalline and strong
- Linear polymer

**Lignin**
- In hardwood (~28 ± 3%)
- In softwood (~20 ± 4%)
- \( “n” = \text{infinity} \) (network)
- Extremely strong
- Crosslinked
- Hydrophobic

**Hemicellulose** – many isomers (one example)
- In wood (~28 ± 3%)
- \( n = 500 – 3000 \)
- Amorphous and weak
- Branched
The first “man-made” polymers were modifications to natural polymers

Natural Rubber (NR)

Vulcanized NR (sulfur treated) ~1839

Utilizing the chemistry of olefins, Charles Goodyear treated NR with sulfur and temperature/pressure, creating a network polymer therefore stronger than NR.

Note* - 100% cis conformation
The nitration of cellulose

[Cellulose structure]

Nitric Acid → cellulose trinitrate (gun cotton)

KNO₃, H₂SO₄ → cellulose mononitrate (celluloid) more stable
- industrial use (movie films, pool balls)

ignition → CO₂, CO, N₂, H₂O
all gases!!

“smokeless” gun powder

nitrate film (early movies)
The first synthetic polymer - Bakelite

Leo Baekeland - 1910’s (only a century ago)

“Bakelite” – Phenolic Resins

\[
\text{phenol} + \text{formaldehyde} \xrightarrow{\text{lots of heat / pressure}} \text{Bakelite}
\]

\[
\text{OH} \quad + \quad \overset{\text{O}}{\text{C}} \quad \overset{\text{H}}{\text{H}}
\]

remind you of anything you just saw?

Bakelite

Lignin!
Hermann Staudinger

Born: 23 March 1881 (Worms, Germany)
Died: 8 September 1965

1920: First predicted that polymers (rubber, cellulose, starch) were long chains of covalently bonded repeating units

"macromolecules"

WATER
mol. mass = 18
boils at 100 °C
(212 °F)

METHANE
mol. mass = 16
boils at -162 °C
(-258 °F)

Nobel Prize Chemistry 1953
World War II & the Birth of the Polymer Enterprise

Synthetic Rubbers
Polyesters
Polystyrene
Nylons
Vinyl
Acrylics
Saran
POLYETHYLENES
Post-war Era – Rebranding of Plastics
The World of Polyethylenes

ethylene + catalyst + pressure → polyethylene

The exact same chemistry, the only difference is molecular architecture leading to a wide range of properties from one type of chemical.
Polyethylene Terephthalate (PET or PETE)
2013 NAFTA* PRODUCTION OF MAJOR COMMODITY POLYMERS – 74.3 BILLION POUNDS

Doesn’t include PETE, which comprises most of your beverage bottles.

*North American Free Trade Agreement (includes Mexico, US, and Canada)
The growing realization that polymers are a bit TOO popular...

Laborer rests at a recycling plant in Jiaxing, China

A Graphical Perspective by Type of Plastic


400 Mtn = 882 BILLION POUNDS
A Graphical Perspective of Waste by Application


330 BILLION POUNDS of plastic packaging waste
Equivalent to 10,000 adult blue whales
PETE, HDPE, LDPE, PVC, PP, PS

A Positive Trend: Recycling

Our Increasing Dependence on Fossil Fuels

Global Petroleum Reliance (~125 million barrels in 2018)

harder to get locations...

limited geographic availability...

World

Much of Global Oil Production Comes from the Middle East
Oil production as a % of world total as of 2009

Source: BP (Statistical Review of World Energy, 2010), Barclays Capital
...and...of course, this!
OK, LET'S TAKE A DEEP BREATH...
..where would we be today without polymers...
..we are polymers...
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The Challenges of ROMP on Low Strain Rings

\[ \Delta G_{pol} = \Delta H_{pol} - T \Delta S_{pol} \]

- \( \Delta H = 31 \text{ kJ mol}^{-1} \)
- \( \Delta S = 9 \text{ J mol}^{-1} \text{ K}^{-1} \)

- \( \Delta H = 28 \text{ kJ mol}^{-1} \)
- \( \Delta S = 70 \text{ J mol}^{-1} \text{ K}^{-1} \)

Neary, W. J. & JGK. ACS Macro Lett. 2019, 8, 46
**Cyclopentene ROMP**

**A need for:**

- Better control - (dispersity, targeted molar mass, high conversion)

- Monomer development - More derivatives that undergo ROMP

- Material Properties - Especially on functionalized derivatives

- Advanced architectures - with control = block, gradient, or grafted polymers

Reviewed in: Neary, W. J. & JGK ACS Macro Lett. 2019, 8, 46
Why Go Through All the Trouble?

- Even numbered ring
- Regioregularity required unless symmetric disubst.
- semi-crystalline
- Cyclopentane-tethered backbone
- Enhanced rigidity ($T_g = 40 \, ^\circ\text{C}$)

- Odd numbered ring
- Flexible backbone ($T_g = -44 \, ^\circ\text{C}$)
Divergent Possibilities from Cheap Starting Materials

- Odd numbered ring
- Flexible backbone ($T_g = -44 \, ^\circ\text{C}$)

**Line 1:**

- **homoallylic (achiral)**
- **allylic (chiral)**

**Line 2:**

- *precision polyolefins*
- *precision elastomers*
- *precision and isotactic polyolefins*
Polypentenamers are **Chemically Recyclable**

Monomer favored at high temp
- diluted

Polymer favored at low temp, concentrated

Due to the low ceiling temperature ($T_c$), depolymerization is possible under reverse conditions.

Where to Begin?: 4-Phenylcyclopentene (4PCP)

\[
\text{O} + \text{CH}_2=\text{SiMe}_3 \xrightarrow{\text{TiCl}_4, \text{MeNO}_2, \text{DCM}} \xrightarrow{-90 \text{ to } 60 \text{ °C}} \xrightarrow{\text{DCM dil., } 23 \text{ °C}} \xrightarrow{\text{HG2, tol., } \Delta T} \xrightarrow{?}
\]

\[
\begin{align*}
\Delta H_p &= -21.3 \text{ kJ mol}^{-1} \\
\Delta S_p &= -79.5 \text{ J mol}^{-1} \text{ K}^{-1}
\end{align*}
\]

ring strain slightly less than CP

\[
\begin{align*}
\Delta H_p &= -23.4 \text{ kJ mol}^{-1} \\
\Delta H_p &= -25.9 \text{ kJ mol}^{-1}
\end{align*}
\]


**monitoring [M]_{eq} at varying T by \textsuperscript{1}H NMR**

\[
\ln[M]_e = \frac{\Delta H_p}{RT} - \frac{\Delta S^\circ}{R}
\]

\[
y = -2.569x + 9.592 \\
R^2 = 0.9992
\]

in toluene-\textit{d}_8; [M]_0=2.50 M; 0.23 mol\% HG2

(VT-\textsuperscript{1}H NMR; 5, 7.5, 10, 12.5, 15 °C)

Neary, W. J. & JGK Macromol. Rapid Commun. 2016, 37, 975

Effect of Temperature on Ru-based ROMP

- colder temperature = higher conversion but loss of control
- standard deviation values represent duplicate trials (repeatable!)
- each material had 85 ± 3% trans olefins
- dispersities are consistent with previous Ru-ROMP reports

**Table:**

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Conv. (%)$^a$</th>
<th>$M_{n,\text{theo}}$ (kg mol$^{-1}$)$^b$</th>
<th>$M_{n,\text{SEC}}$ (kg mol$^{-1}$)$^c$</th>
<th>$D^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>62.3 ± 0.3</td>
<td>39.1</td>
<td>47.9 ± 2.7</td>
<td>1.51 ± 0.02</td>
</tr>
<tr>
<td>5</td>
<td>67.2 ± 0.3</td>
<td>42.1</td>
<td>47.6 ± 0.5</td>
<td>1.65 ± 0.03</td>
</tr>
<tr>
<td>0</td>
<td>72.2 ± 0.4</td>
<td>45.3</td>
<td>50.9 ± 0.6</td>
<td>1.63 ± 0.01</td>
</tr>
<tr>
<td>-5</td>
<td>75.0 ± 0.1</td>
<td>47.1</td>
<td>67.4 ± 1.4</td>
<td>1.60 ± 0.01</td>
</tr>
<tr>
<td>-10</td>
<td>78.9 ± 1.2</td>
<td>49.5</td>
<td>72.1 ± 0.5</td>
<td>1.60 ± 0.15</td>
</tr>
<tr>
<td>-15</td>
<td>84.6 ± 0.4</td>
<td>53.1</td>
<td>92.3 ± 3.3</td>
<td>1.63 ± 0.03</td>
</tr>
</tbody>
</table>

$^a$ determined by $^1$H-NMR analysis (CDCl$_3$) following termination with ethyl vinyl ether.

$^b$ based on [M]$_0$/[cat]$_0$ adjusted for % conversion.

$^c$ determined by SEC analysis in THF.

[4PCP]$_0$ = 4.5 M
[cat] = 0.23 mol %
rxn time = 12 h

Neary, W. J. & JGK Macromol. Rapid Commun. 2016, 37, 975
A Precision Styrenic-Rubber \( \rightarrow \) Precision ES Copolymer

access to ES Interpolymers with varying %S (w/w)

**Pros:**
- large scope of material properties
- variety of applications: compatibilizers, packaging, foams, bitumen modifiers

**Cons:**
- homopolymer formation
- aggressive reaction conditions
- batch repeatability

*cons increase when higher S content targeted*

Elucidating Precision Material Properties

\[ M_n = 44 \text{ kg/mol} \]
\[ D = 1.80 \]
\[ \rho_{90^\circ C} = 0.999 \text{ g/cm}^3 \]

\[ M_n = 51 \text{ kg/mol} \]
\[ D = 1.68 \]
\[ \rho_{90^\circ C} = 0.980 \text{ g/cm}^3 \]

\[ M_e = 10 \text{ kg/mol} \]
\[ G_N^o = G' \text{ at min tan } \delta \]

\[ M_e = 3.6 \text{ kg/mol} \]

Elastic at Low Strain Rate
Polystyrene Sulfonate (PSS)

Where might more flexible versions of PS be useful?


Asrar, J. Macromolecules 1992, 25, 5150-5156

T_g ≈ 105 °C

T_g > 200 °C

T_g = 17 ± 2 °C

T_g > T_d

A Precise and More Flexible PSS Analog?

\[
\text{Product Formation} \
\text{90 °C, ~48 hrs}
\]

Aaron Kendrick

Thermal Properties

- Increasing thermal stability with size of counter-cation
- Two-step loss of acid form suspected to be desulfonation

**DSC ANALYSIS**

3rd heating at 30°C min⁻¹

- $T_g = 268 ^\circ C$
- $T_g = 17 ^\circ C$
- $T_g = 109 ^\circ C$


Collaboration: Percolated Ion Networks

Karen Winey  Amalie Frischknecht

Collaboration: Fluorine-free PEMs