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Characterizing and Tailoring Polymers using Nuclear Magnetic Resonance

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TARA MEYER, PhD
Professor, Chemistry Department and the McGowan Center for Regenerative Medicine, University of Pittsburgh

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Characterizing and Tailoring Polymers using Nuclear Magnetic Resonance

ACS PMSE Webinar
Thursday, April 6, 2023

Spider Silk: Sequence Yields Desirable Materials Properties

Spider Silk: Sequence Yields Desirable Materials Properties

Vollrath, Polymer, 2009, 50, 5623

Random PLGAs

poly(lactic-co-glycolic acid)

Biodegradable – Biocompatible – FDA Approved

Random copolymer
Sequence Classes

**Structural Sequence**

- Homopolymer
- Alternating
- Periodic sequence
- Block copolymer
- Random

**Stereosequence**

- Isotactic
- Syndiotactic
- Periodic sequence + stereoblock
- Periodic sequence + syndiotactic

**Structural Sequence + Stereosequence**

- *For polymers whose symmetry does not allow the assignment of absolute chirality, tacticity refers to the relationship of the pseudochiral substituents on adjacent monomers*

---

Synthesis of Polymers: Segmer Assembly

**Trimeric Segmer**

\[
\text{HO} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{R} \quad \text{O} \\
\text{R} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{OH}
\]

R: H or CH₃

1.5 eq DIC
0.2 eq DPTS
3.0 M, CH₂Cl₂
3 h

**RSC Polymer**

\[
\text{R} \quad \text{O} \quad \text{O} \quad \text{R} \\
\text{O} \quad \text{R} \quad \text{O} \\
\text{R}
\]

R: H or CH₃

---

Using NMR to Characterize Microstructure in PP

Polypropylene

\[ m = \text{meso} \rightarrow \text{isotactic} \]
\[ r = \text{racemo} \rightarrow \text{syndiotactic} \]

\(^1\text{H} \text{ NMR} \]

syndiotactic

isotactic

\[^{13}\text{C} \text{ NMR} \]

methylene

atactic

methyl


Using NMR to Characterize Microstructure in PLA


Using NMR to Characterize Microstructure in PLGA

Assigning structures past the dyad level is challenging even when stereosequence is not a variable

$^{13}$C NMR (Isotactic)

$^1$H NMR (Isotactic)


Poly LG: Sequenced Copolymer

 poly(L-lactic acid) (L) poly(R-lactic acid) (L ) Glycolic acid (G) t = isotactic s = syndiotactic

<table>
<thead>
<tr>
<th>Tetrads</th>
<th>i i i</th>
<th>i s</th>
<th>s s</th>
<th>i s</th>
<th>s i</th>
<th>i i</th>
</tr>
</thead>
<tbody>
<tr>
<td>LG</td>
<td>i i i</td>
<td>i i i</td>
<td>s s s</td>
<td>i i i</td>
<td>i i i</td>
<td>i i i</td>
</tr>
<tr>
<td>L_{iso}G</td>
<td>i i i</td>
<td>i s</td>
<td>s s</td>
<td>i s</td>
<td>s i</td>
<td>i i</td>
</tr>
<tr>
<td>GLGL_R</td>
<td>i i i</td>
<td>i i i</td>
<td>s s s</td>
<td>i i i</td>
<td>i i i</td>
<td>i i i</td>
</tr>
</tbody>
</table>

60% LG + 40% L_{iso}G


^1H NMR Spectra of Poly LGs

S-lactic acid (L) R-lactic acid (L ) Glycolic acid (G)
Nearly Tetrad Level Resolution

<table>
<thead>
<tr>
<th>Tetrad</th>
<th>Shift</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>4.857</td>
<td>(1,2)</td>
</tr>
<tr>
<td>III</td>
<td>4.857</td>
<td>(1,2) or (3,4)</td>
</tr>
<tr>
<td>III</td>
<td>4.855</td>
<td>(1,2) or (3,4)</td>
</tr>
<tr>
<td>III</td>
<td>4.855</td>
<td>(1,2) or (3,4)</td>
</tr>
<tr>
<td>III</td>
<td>4.813</td>
<td>6 or 7</td>
</tr>
<tr>
<td>III</td>
<td>4.809</td>
<td>6 or 7</td>
</tr>
<tr>
<td>III</td>
<td>4.808</td>
<td>5 or 8</td>
</tr>
<tr>
<td>III</td>
<td>4.804</td>
<td>5 or 8</td>
</tr>
</tbody>
</table>

*CDCl₃ at 600 MHz.

Diasterotopic protons

Tetrad level resolution = 8 combinations

Poly LLG Stereoisomers

\[ \text{L}_{2}\text{L}_{2}\text{G} \quad \text{2x Stereopure S-lactic} + \text{G} \]
\[ \text{L}_{n}\text{L}_{n}\text{G} \quad \text{2x Stereopure R-lactic} + \text{G} \]
\[ \text{L}_{2}\text{L}_{2}\text{G} \quad \text{Stereopure S-lactic} + \text{R-lactic} + \text{G} \]
\[ \text{L}_{n}\text{L}_{2}\text{G} \quad \text{Stereopure R-lactic} + \text{S-lactic} + \text{G} \]
\[ \text{L}_{\text{rac}}\text{L}_{4}\text{G} \quad \text{rac-lactic} + \text{stereopure R-lactic} + \text{G} \]
\[ \text{L}_{2}\text{L}_{\text{rac}}\text{G} \quad \text{Stereopure R-lactic} + \text{rac-lactic} + \text{G} \]
\[ \text{L}_{\text{rac}}\text{L}_{\text{rac}}\text{G} \quad \text{2x rac-lactic} + \text{G} \]

Tacticity in Poly LLG

\[ \text{Poly LLG} \]

Adj. Dist.

- **G-centered octad**
  - \[ i \quad S \quad S \quad i \quad i \quad S \quad S \]

- **L^C-centered octad**
  - \[ i \quad S \quad S \quad i \quad i \quad S \quad S \]

- **L^0-centered octad**
  - \[ i \quad S \quad S \quad i \quad i \quad S \quad S \]

- **Central tetrad**

- **S-lactic acid (L)**
- **R-lactic acid (L^R)**
- **Glycolic acid (G)**

- \[ i \] = isotactic
- \[ s \] = syndiotactic

- **L^C** Lactic unit on C-side of Glycolic unit
- **L^0** Lactic unit on O-side of Glycolic unit

- Adj. Adjacent relationship
- Dist. Distant relationship

- Center of the polyad
### Possible Tacticity in Poly LLGs

<table>
<thead>
<tr>
<th>Tetrads</th>
<th>Poly LLG</th>
<th>Poly LaLG</th>
<th>Poly L(RGLLG</th>
<th>Poly LaLG (LGLLG</th>
<th>Poly L(LGLLG</th>
<th>Poly L(RG)LG</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>iiii</td>
<td>sssss</td>
<td>sssss</td>
<td>iiii i</td>
<td>iiii i</td>
<td>iiii i</td>
</tr>
<tr>
<td>Hexads</td>
<td>iiii i</td>
<td>sssss</td>
<td>sssss</td>
<td>iiii i</td>
<td>iiii i</td>
<td>iiii i</td>
</tr>
<tr>
<td>Octads</td>
<td>iiii i</td>
<td>sssss</td>
<td>sssss</td>
<td>iiii i</td>
<td>iiii i</td>
<td>iiii i</td>
</tr>
</tbody>
</table>

### 1H NMR for a Selection of LLG Polymers

- Poly LLG
- Poly LaLG
- Poly L(RGLLG
- Poly L(LGLLG
- Poly L(RG)LG

![NMR Spectra](image-url)
Resolution Depends on Sequence

Octad Level Resolution in Poly LLG

30 backbone atoms
Assigning L units in Poly $L_x$LGs

2D HMBC NMR Spectra

$^1$H-$^{13}$C correlation (3 bonds)
A – Poly LLG
B – Poly $L_p$LLLG
C – Poly $L_p$LG

$^{13}$C Spectra of LLGs
Mixtures of Structural Sequences

- Stereochemistry controlled
- Structural sequence mixed

Glycolic methylene region of a mixed $^1$H NMR spectrum for mixed sample (1:1:1) of poly LG, GLG and LLG at 600 MHz in CDCl$_3$.

Mixtures of Stereosequences

- Stereochemistry mixed
- Structural sequence controlled

Glycolic methylene region of poly L$_{rac}$L$_{rac}$G at 700 MHz in CDCl$_3$. 
**1H NMR Sensitivity to Conformation**

Diastereotopic glycolic acid protons exhibit significant shift differences in the ring-closed and ring-opened version.

**Sensitivity: Structural vs. Stereo**

Hexad
- iisi
- LLGLL

Octad
- siiiss
- GLLGLGG

Hexad
- iisi
- LLGLL

Octad
- iiiiiii
- GLLGLGG

Hexad
- iiiiiii
- LLGLL

Octad
- iiiiiiiii
- LLLGLLL
Sensitivity: Structural vs. Stereo

Structural ≠ Stereo =

Hexad

Octad

LLLGLLL

LLLGLLL

GLLGGG

GLLGGG

LLLGLLL

LLLGLLL

Structural ≠ Stereo =
Sensitivity: Structural vs. Stereo

Structural  =
Stereo    ≠

Hexad

iiisii
LLGLL

L_R L_R G L_S L_S G

Octad

siisiis
GLGGLLL

iiisii
LLGGL

L_R L_R L_R G L_S L_S G

iii
LLGL

iiisi
LLGLG

L_R L_R G R L_R L_R G

iiiii
LLGGL

iiiiii
LLGLL

L_R L_R L_R G L_R L_R G

ppm

4.85
4.80
4.75
4.70
4.65
4.60
Conclusions: Distinctive Fingerprints

Poly $L_{\text{rac}}LG$

Poly $LL_{\text{rac}}G$

Conclusions: Conformational Control

- Each sequence exhibits different conformational preferences in CDCl$_3$
- Spectra exhibit unusually good resolution for polymeric chains
- Conformation is affected more by stereosequence than structural sequence
Conclusions: Assignment Challenges

Chemical shifts assignments made from complex mixtures do not perfectly correlate with those made based on isolated sequences.

Conclusions: Goldilocks System

- Monomer backbone is short (3 atoms)
- Sufficient # of protons to encode information but not so many that information is lost due to overlap
- Strong conformational preferences
- Stereoactive monomers
- Diastereotopic protons whose shift responds to conformational changes
Current Students
Megan Clark
Anneliese Schmidt
Jordan Fitch
Sarah Craig
Emily Barker
Charis White
Michael Cole

Former students involved in this project
Dr. Ryan M. Stayshich
Dr. Ryan Weiss
Dr. Michael Washington
Dr. Jamie Nowalk
Dr. Jordan Swisher

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