Applications of 3D-NMR In Organosilicon Chemistry

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http://www.chemistry.uakron.edu/magnet/whatsnew.html
Outline

• Introduction/Problems & Practice
  – Why do 3D-NMR
  – Background
  – Experimental Issues
• Heteronuclear $^{1}H/^{13}C/^{29}Si$ Triple Resonance 3D NMR
  – Small Molecules
  – Dendrimers
  – Polymers
• Heteronuclear Double Resonance 3D NMR
  – Applications with unlabeled materials
  – Applications with isotopic labeling
Why Do 3D-NMR?

- Dispersion proportional to $v^3$
  - Resolve resonances
  - Interpretation by simple inspection
- Atomic connectivity information
- Simplification by filtering
  - Selectively examine one part of molecule
- Sensitivity $^1$H-detected
2D-NMR Pulse Sequence

Preparation  Evolution  Mixing  Acquisition

t_1  t_2

Preparation  Evolution  Mixing  Acquisition

t_1  t_2
Array of Spectra Obtained with Different $t_1$ Delays
Resonance Assignments of PIB Using HMQC & HMBC

1D/2D/3D-NMR Sequences

1D
- Preparation
- Evolution
- Mixing
- Acquisition

2D
- Preparation
- Evolution $t_1$
- Mixing
- Acquisition

nD
- Preparation
- Evolution $t_{n-1}$
- Mixing
- Acquisition $t_n$
Sample Considerations in 3D-NMR of Synthetic Polymers

- Occurrence of structural unit
- Abundance of nuclei
- Possibility of labeling
- Molecular weight
- Structural diversity
- Solubility
Relative Signal Strength for $^{1}H-^{13}C-^{29}Si$ Structure Fragments

Log Intensity

NMR Signal Component

- 1H-12C
- 1H-13C
- 1H-13C-29Si
- Minor
- Junction
- Backbone

- Minor
- Junction
- Backbone
HXY 3D-NMR Sequence

Biological 3D-NMR Pulse Sequences

- HNCO
- HCACO
- HCA(CO)N

HNCA

\[ ^{15}\text{N-TOCSY-HMOC} \]

“The devil is in the details.”
Silane Curing Agent

1) HSiCl₃/Catalyst
2) CH₃OH

$^{1}$H/$^{13}$C/$^{29}$Si 1D-NMR of Silane Curing Agent

Relative Signal Strength for Structure Components in $^1$H/$^{13}$C/$^{29}$Si Experiments

$DOD = \log \frac{I_H}{I_{HCSi \text{ fragment}}} = 4-5$

$1J_{CSi} = 140\text{Hz}$
$^{1}H/^{13}C/^{29}Si$ 3D-NMR Pulse Sequence

Projections of $^1$H/$^{13}$C/$^{29}$Si 3D-NMR

$^1J_{CSi} = 140$Hz

$^{1}H/^{13}C/^{29}Si$ 3D-NMR of Silane Curing Agent

$\delta^{29}Si = - 44.97$

$\delta^{29}Si = - 45.57$

$^{1}\text{H}/^{13}\text{C}/^{29}\text{Si}$ 3D-NMR of Silane Curing Agent

$(\text{H}_3\text{CO})_3\text{Si} \quad \delta_{^{29}\text{Si}} = -44.69$

$(\text{H}_3\text{CO})_3\text{Si} \quad \delta_{^{29}\text{Si}} = -45.94$

$^1$H/$^{13}$C/$^{29}$Si 3D-NMR of Silane Curing Agent

$\delta^{29}\text{Si} = -44.65$

$\delta^{29}\text{Si} = -45.00$

Relative Signal Strength for Structure Components in $^{1H}/^{13C}/^{29Si}$ Experiments

$$DOD = \log \left( \frac{I_H}{I_{HCSi\ fragment}} \right) = 4-5$$
$^{1}H/^{29}Si/^{13}C$ 3D-NMR Spectrum With $^{1}J_{csi}$
Generation 2 Dendrimer

$^1$H/$^{29}$Si/$^{13}$C 3D-NMR Spectrum With $^2$J_{csi} Generation 2 Dendrimer

Dimethyl-siloxane Oligomer MD$_3$MH

Chai et al., *Polymer Preprints*, 2001, 42(1), 15.
MD$_3$MH $^1$H/$^{13}$C and $^1$H/$^{29}$Si 2D-NMR

Chai et al., *Polymer Preprints*, **2001**, *42*(1), 15.
Chai et al., *Polymer Preprints*, 2001, 42(1), 15.
Poly(1-phenyl-1-silabutane)

3D-NMR of PPSB

The Power of Conditioning
Relative Signal Strength for Polymer Structure Components in $^1\text{H}/^{13}\text{C}$ & $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ Experiments

$\text{DOD}_{\text{HC}} = \log \left( \frac{I_H}{I_{\text{HC fragment}}} \right) = 4-5$

$\text{DOD}_{\text{HCN}} = \log \left( \frac{I_H}{I_{\text{HCX fragment}}} \right) = 6-7$
DAB-16 1D-NMR Spectra

3D-HMQC-TOCSY Pulse Sequence
3D-HMQC-TOCSY Slices DAB-16

### Possible Triads of Poly(EBC)

Poly(ethylene-co-butylacrylate-co-carbon monoxide)

<table>
<thead>
<tr>
<th>E-centered</th>
<th>B-centered</th>
<th>C-centered</th>
</tr>
</thead>
<tbody>
<tr>
<td>EEE</td>
<td>BBB(3)</td>
<td>CCC</td>
</tr>
<tr>
<td>EEB</td>
<td>EBB(2)</td>
<td>ECC</td>
</tr>
<tr>
<td>BEB(2)</td>
<td>EBE</td>
<td>ECE</td>
</tr>
<tr>
<td>CEE</td>
<td>CBB(2)/BBC(2)</td>
<td>BCC/CCB</td>
</tr>
<tr>
<td>CEC</td>
<td>CBC</td>
<td>BCB(2)</td>
</tr>
<tr>
<td>BEC/CEB</td>
<td>EBC/CBE</td>
<td>ECB/BCE</td>
</tr>
</tbody>
</table>

**E = ethylene  C = carbon monoxide  B = n-butylacrylate**
1D $^{13}$C NMR of Labeled Poly(BCE)
Truncated 3D of Poly(EB*C)

3D Slices HCACO Poly(EB*C)

F3 (ppm)

F1=175.3

F1=174.9

F1=174.7

F1=174.2

ppm

176

175

174

Hardware and Environment Requirements

- Capability of most modern instruments
- Stable magnetic environment
- Stable room temperature
- Vibration-free environment
- Gradient spectroscopy
- Multiple channel instrument
- High sample concentrations
- Computer
## NMR Experiment Sizes & Times

<table>
<thead>
<tr>
<th>Dimensionality</th>
<th>Data Size</th>
<th>File Size (Mbytes)</th>
<th>Experiment Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>64k</td>
<td>0.25</td>
<td>20 sec</td>
</tr>
<tr>
<td>2D</td>
<td>64k x 64k</td>
<td>2,000</td>
<td>300 hours</td>
</tr>
<tr>
<td></td>
<td>4k x 1k</td>
<td>16</td>
<td>4 hours</td>
</tr>
<tr>
<td>3D</td>
<td>4k x 1k x 1k</td>
<td>16,000</td>
<td>80 days</td>
</tr>
<tr>
<td></td>
<td>4k x 32 x 32</td>
<td>16</td>
<td>4 hours</td>
</tr>
</tbody>
</table>
## NMR Experiment Spectral Windows (750 MHz)

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Window</th>
<th>Window (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1D</td>
<td>^1H</td>
<td>Full</td>
</tr>
<tr>
<td></td>
<td>^13C</td>
<td>Full</td>
</tr>
<tr>
<td>2D</td>
<td>^1H</td>
<td>50-80%</td>
</tr>
<tr>
<td></td>
<td>^13C</td>
<td>50%</td>
</tr>
<tr>
<td>3D</td>
<td>^1H</td>
<td>50-80%</td>
</tr>
<tr>
<td></td>
<td>^13C</td>
<td>10-50%</td>
</tr>
<tr>
<td>X</td>
<td>Only few resonance</td>
<td>100-1,000</td>
</tr>
</tbody>
</table>
Data Processing

- Optimal use of folding
- Optimize S:N
- Linear prediction
- Zero filling
- Digital filtering
- Live with poor digital resolution
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