Cyclic and Spirocyclic Polyacetal Ethers from Lignin-Based Aromatics
Alexander G. Pemba, Mayra Rostagno, Tanner A. Lee and Stephen A. Miller*

The George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida
Gainesville, Florida 32611-7200, USA

Electronic Supplementary Information (ESI)

Supplementary Information Available: Complete polymer characterization data.

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Summary of Polymerization Data

Table S1. Thermal and molecular weight data for spirocyclic (1–4) and cyclic (5–8) polyacetal ethers.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer</th>
<th>Yield (%)</th>
<th>$M_w$ (Da)</th>
<th>$M_n$ (Da)</th>
<th>PDI</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_{95}$ (°C)</th>
<th>Residue (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>P-BB</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>n.o.</td>
<td>n.o.</td>
<td>328</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>P-VV</td>
<td>90</td>
<td>23,700</td>
<td>10,600</td>
<td>2.2</td>
<td>129</td>
<td>n.o.</td>
<td>308</td>
<td>19</td>
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<tr>
<td>3</td>
<td>P-SS</td>
<td>90</td>
<td>36,000</td>
<td>18,600</td>
<td>1.9</td>
<td>152</td>
<td>n.o.</td>
<td>307</td>
<td>17</td>
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<tr>
<td>4</td>
<td>P-EE</td>
<td>83</td>
<td>47,800</td>
<td>18,500</td>
<td>2.6</td>
<td>108</td>
<td>n.o.</td>
<td>326</td>
<td>23</td>
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<tr>
<td>5</td>
<td>D-BB</td>
<td>81</td>
<td>3,500</td>
<td>2,600c</td>
<td>1.4</td>
<td>n.o.</td>
<td>259</td>
<td>349</td>
<td>8.3</td>
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<td>6</td>
<td>D-VV</td>
<td>90</td>
<td>44,200</td>
<td>22,200</td>
<td>2.0</td>
<td>80</td>
<td>n.o.</td>
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<td>8.2</td>
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<td>7</td>
<td>D-SS</td>
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<td>34,600</td>
<td>21,600</td>
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<td>n.o.</td>
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<td>8</td>
<td>D-EE</td>
<td>83</td>
<td>42,100</td>
<td>19,300</td>
<td>2.2</td>
<td>68</td>
<td>n.o.</td>
<td>333</td>
<td>10</td>
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*Polymerization conducted in refluxing methylene chloride at 40 °C, except as noted. Molecular weight data obtained by GPC in hexafluoroisopropanol (HFIP) solvent. For DSC data, n.o. indicates a thermal transition not observed. *Polymerization conducted in refluxing 1,1,2,2-tetrachloroethane at 146 °C. Although insolubility prevented GPC analysis for P-BB, $^1$H NMR spectroscopy confirmed the absence of aldehydic hydrogens characteristic of the monomer. *Thermogravimetric analysis conducted under nitrogen; temperature reported upon 5% mass loss; residue (%) reported at end of TGA experiment. *Acidity of HFIP degraded the sample before GPC analysis of D-BB. Nonetheless, $^1$H NMR spectroscopy confirmed the absence of aldehydic hydrogens characteristic of the monomer.
Gel Permeation Chromatography (GPC) Analysis (in hexafluoroisopropanol, HFIP)

<table>
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<tr>
<th>Peak</th>
<th>Mp</th>
<th>Mn</th>
<th>Mw</th>
<th>Mz</th>
<th>Mz+1</th>
<th>Mv</th>
<th>PD</th>
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<tbody>
<tr>
<td>Peak 1</td>
<td>22636</td>
<td>10601</td>
<td>23713</td>
<td>35882</td>
<td>49249</td>
<td>34180</td>
<td>2.237</td>
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Peak information

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<th>Start (mins)</th>
<th>End (mins)</th>
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<tr>
<td>Baseline region 1</td>
<td>21.79</td>
<td>24.79</td>
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<tr>
<td>Baseline region 2</td>
<td>52.23</td>
<td>55.23</td>
</tr>
<tr>
<td>Peak 1</td>
<td>30.00</td>
<td>39.47</td>
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<table>
<thead>
<tr>
<th>Peak</th>
<th>Trace</th>
<th>Peak Max RT (mins)</th>
<th>Peak Area (mV s)</th>
<th>Peak Height (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak 1</td>
<td>RI</td>
<td>33.96</td>
<td>8261878.103</td>
<td>35693.014</td>
</tr>
</tbody>
</table>

Chromatogram

Figure S1. GPC Chromatogram of P-VV (Table S1, entry 2).
Figure S2. GPC Chromatogram of P-SS (Table S1, entry 3).
Figure S3. GPC Chromatogram of P-EE (Table S1, entry 4).
Figure S4. GPC Chromatogram of D-BB (Table S1, entry 5).
Figure S5. GPC Chromatogram of D-VV (Table S1, entry 6).
Figure S6. GPC Chromatogram of D-SS (Table S1, entry 7).
Figure S7. GPC Chromatogram of D-EE (Table S1, entry 8).
Differential Scanning Calorimetry (DSC) Thermograms

Figure S8. DSC Thermogram of P-BB (Table S1, entry 1).

Figure S9. DSC Thermogram of P-VV (Table S1, entry 2).
Figure S10. DSC Thermogram of P-SS (Table S1, entry 3).

Figure S11. DSC Thermogram of P-EE (Table S1, entry 4).
Figure S12. DSC Thermogram of D-BB (Table S1, entry 5).

Figure S13. DSC Thermogram of D-VV (Table S1, entry 6).
Figure S14. DSC Thermogram of D-SS (Table S1, entry 7).

Figure S15. DSC Thermogram of D-EE (Table S1, entry 8).
Thermogravimetric Analysis (TGA) Thermograms

Figure S16. TGA Thermogram of P-BB (Table S1, entry 1).

Figure S17. TGA Thermogram of P-VV (Table S1, entry 2).
Figure S18. TGA Thermogram of P-SS (Table S1, entry 3).

Figure S19. TGA Thermogram of P-EE (Table S1, entry 4).
Figure S20. TGA Thermogram of D-BB (Table S1, entry 5).

Figure S21. TGA Thermogram of D-VV (Table S1, entry 6).
Figure S22. TGA Thermogram of D-SS (Table S1, entry 7).

Figure S23. TGA Thermogram of D-EE (Table S1, entry 8).
**1H NMR Spectra**

Figure S24. 1H NMR spectra of **BB** (top, red trace) and **D-BB** (black, bottom trace) in TCE-\(d_2\). Absence of the aldehydic proton (ca. 10 ppm) in the **D-BB** trace suggests that the monomer (**BB**) has been completely consumed and has been converted to high molecular weight polymer.

Figure S25. 1H NMR spectrum of **P-VV** in DMSO-\(d_6\) (Table S1, entry 2).
Figure S26. $^1$H NMR spectrum of P-SS in DMSO-d$_6$ (Table S1, entry 3).

Figure S27. $^1$H NMR spectrum of P-EE in DMSO-d$_6$ (Table S1, entry 4).

Figure S28. $^1$H NMR spectrum of D-BB in TCE-d$_2$ (Table S1, entry 5).
Figure S29. $^1$H NMR spectrum of D-VV in TCE-$d_2$ (Table S1, entry 6).

Figure S30. $^1$H NMR spectrum of D-SS in TCE-$d_2$ (Table S1, entry 7).
Figure S31. $^1$H NMR spectrum of D-EE in TCE-$d_2$ (Table S1, entry 8).
$^{13}$C NMR Spectra

Figure S32. $^{13}$C NMR spectrum of P-VV in DMSO-$d_6$ (Table S1, entry 2).

Figure S33. $^{13}$C NMR spectrum of P-SS in DMSO-$d_6$ (Table S1, entry 3).
Figure S34. $^{13}$C NMR spectrum of P-EE in DMSO-$d_6$ (Table S1, entry 4).

Figure S35. $^{13}$C NMR spectrum of D-BB in TCE-$d_2$ (Table S1, entry 5).
Figure S36. $^{13}$C NMR spectrum of D-VV in TCE-$d_2$ (Table S1, entry 6).

Figure S37. $^{13}$C NMR spectrum of D-SS in TCE-$d_2$ (Table S1, entry 7).
Figure S38. $^{13}$C NMR spectrum of D-EE in TCE-$d_2$ (Table S1, entry 8).
Fourier Transform Infrared Spectroscopy (FTIR) Spectra

Figure S39. Comparative FTIR spectra for **BB** (monomer), **P-BB**, and **D-BB**.

Figure S40. Comparative FTIR spectra for **BB** (monomer), **P-BB**, and **D-BB** for carbonyl area (magnified), showing no carbonyl peak in either polymer.
Figure S41. Comparative FTIR spectra for VV (monomer), P-VV, and D-VV.

Figure S42. Comparative FTIR spectra for SS (monomer), P-SS, and D-SS.

Figure S43. Comparative FTIR spectra for EE (monomer), P-EE, and D-EE.
Degradation Studies via Dynamic Light Scattering (DLS)

**Figure S44.** Degradation studies of P-VV / DMSO solution with 0.5% aqueous concentrated HCl.

**Figure S45.** Degradation studies of P-VV / DMSO solution with 0.5% 2M aqueous HCl.

**Figure S46.** Degradation studies of D-VV / DMSO solution with 0.5% aqueous concentrated HCl.
Figure S47. Degradation studies of D-VV / DMSO solution with 0.5% 2M aqueous HCl.