Electronic Supporting Information (ESI)

Fully bio-derived CO₂ polymers for non-isocyanate based polyurethane synthesis

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1. Characterization of PBDs

1.1 Summarized properties of PBD1 - PBD4

Table S1. Detailed properties of PBD1 - PBD4.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_n$ [kg/mol]$^a$</th>
<th>$D^b$</th>
<th>double bond units [%]$^c$</th>
<th>double bond units [%]$^d$</th>
<th>double bonds [mmol/g]$^e$</th>
<th>$T_g$ (°C)$^f$</th>
<th>$T_d$ (°C)$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1,4- cis</td>
<td>1,4- trans</td>
<td>1,2- cyclic</td>
<td>1,2- cis-trans</td>
<td>1,2- cyclic/vinyl</td>
</tr>
<tr>
<td>PBD1</td>
<td>1.14</td>
<td>2.3</td>
<td>40.8</td>
<td>30.1</td>
<td>29.1</td>
<td>40.7</td>
<td>59.3</td>
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<tr>
<td>PBD2</td>
<td>2.63</td>
<td>2.5</td>
<td>44.4</td>
<td>36.6</td>
<td>1.1</td>
<td>18.9</td>
<td>81.4</td>
</tr>
<tr>
<td>PBD3</td>
<td>11.0</td>
<td>1.1</td>
<td>42.1</td>
<td>44.0</td>
<td>0.4</td>
<td>13.5</td>
<td>88.1</td>
</tr>
<tr>
<td>PBD4</td>
<td>39.4</td>
<td>1.1</td>
<td>45.8</td>
<td>43.9</td>
<td>0.2</td>
<td>10.2</td>
<td>91.6</td>
</tr>
</tbody>
</table>

$^a$Measured by GPC (THF, RT) using polystyrene standards. $^b$Determined by $^1$H NMR analysis using normalized proton areas (A): $X_{\text{double bond type}}(\%) = \frac{A_{\text{double bond type}}}{A_{\text{total}}} \cdot 100$. $^c$Determined by $^{13}$C gated NMR analysis using normalized carbon areas (A): $X_{1,4- \text{ cis} / \text{ trans}}(\%) = \frac{A_{1,4- \text{ cis} / \text{ trans}} - A_{\text{styrene}}}{A_{\text{total}} - A_{\text{styrene}}} \cdot 100$. $^d$Measured by epoxide titration (see Supporting Information Section 3). $^e$Determined by DSC; data are taken from the second heating. $^f$Decomposition temperature ($T_d$) determined by TGA at 1% weight loss.
1.2 Spectroscopic analysis

1.2.1 PBD1

Figure S1. $^1$H NMR spectrum of PBD1 in CDCl$_3$ (Table S1).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) = 7.50-6.85 (m, 5H, 1-CH), 6.1-5.69 (m, 1H, 17-CH), 5.69-5.49 (m, 1H, 9-CH), 5.49-5.23 (m, 2H, 4-CH, 5-CH), 5.23-4.50 (m, 2H, 10-CH$_2$, 18-CH$_2$), 3.00-2.57 (m, 2H, 2x2-CH), 2.57-0.48 (m, 16H, 2x3-CH, 2x6-CH, 2x7-CH, 8-CH, 2x11-CH, 12-CH, 13-CH, 2x14-CH, 15-CH, 2x16-CH).
Figure S2. $^{13}$C NMR spectrum of PBD1 in CDCl$_3$ (Table S1).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm) = 145.0-141.8 (1x1-C (styrene end group), 9-C, 17-C), 132.5-123.2 (5x1-C (styrene end group), 4-C, 5-C), 115.7-111.5 (10-C, 18-C), 46.7-6.05 (2-C, 3-C, 6-C, 7-C, 8-C, 11-C, 12-C, 13-C, 14-C, 15-C, 16-C).
**Figure S3.** IR spectrum of PBD1 (Table S1).
1.2.2 PBD2

Please note the peak assignments in Figure S1 and S2. The signal for 1, 4-cis and 1,4-trans double bonds splits into the signals at $\delta$ (ppm) = 5.42 (m, 2H (trans)) and 5.38 (m, 2H, (cis)).

Figure S4. $^1$H NMR spectrum of PBD2 in CDCl$_3$ (Table S1).

Figure S5. $^{13}$C NMR spectrum of PBD2 in CDCl$_3$ (Table S1).
Figure S6. IR spectrum of PBD2 (Table S1).
Please note the peak assignments in Figure S1 and S2. The signal for 1,4-cis and 1,4-trans double bonds splits into the signals at $\delta$ (ppm) = 5.46 (m, 2H (trans)) and 5.41 (m, 2H, (cis)).

**Figure S7.** $^1$H NMR spectrum of PBD3 in CDCl$_3$ (Table S1).

**Figure S8.** $^{13}$C NMR spectrum of PBD3 in CDCl$_3$ (Table S1).
Figure S9. IR spectrum of PBD3 (Table S1).
1.2.4 PBD4

Please note the peak assignments in Figure S1 and S2. The signal for 1, 4-cis and 1, 4-trans double bonds splits into the signals at δ (ppm) = 5.45 (m, 2H (trans)) and 5.40 (m, 2H, (cis)).

Figure S10. $^1$H NMR spectrum of PBD4 in CDCl$_3$ (Table S1).

Figure S11. $^{13}$C NMR spectrum of PBD4 in CDCl$_3$ (Table S1).
1.3 Thermal analysis

1.3.1 PBD1

Figure S12. IR spectrum of PBD4 (Table S1).

Figure S13. Thermogravimetric analysis of PBD1 (Table S1).
Figure S14. Differential Scanning Calorimetry trace of PBD1 (Table S1).

1.3.2 PBD2

Figure S15. Thermogravimetric analysis of PBD2 (Table S1).
Figure S16. Differential Scanning Calorimetry trace of PBD2 (Table S1).

1.3.3 PBD3

Figure S17. Thermogravimetric analysis of PBD3 (Table S1).
Figure S18. Differential Scanning Calorimetry trace of PBD3 (Table S1).

1.3.4 PBD4

Figure S19. Thermogravimetric analysis of PBD4 (Table S1).
2. Characterization of PE-PBDs

2.1 Summarized properties of PE-PBD1 - PE-PBD4

Table S2. Detailed properties of PE-PBD1 - PE-PBD4.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ [kg/mol]</th>
<th>D*</th>
<th>Epoxide units [%]</th>
<th>EP-number [mmol/g]</th>
<th>$T_g$ (°C)*</th>
<th>$T_d$ (°C)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>total</td>
<td>1,4- cis epoxide</td>
<td>1,2- cis epoxide</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>trans cyclic/vinyl</td>
<td>(%)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>PE-PBD1</td>
<td>1.10</td>
<td>2.43</td>
<td>13.9</td>
<td>6.50</td>
<td>1.47</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>10.9</td>
<td></td>
<td>7.20</td>
<td>3.85</td>
<td>0.39</td>
<td>1.33</td>
</tr>
<tr>
<td>PE-PBD2</td>
<td>2.64</td>
<td>2.56</td>
<td>8.26</td>
<td>7.20</td>
<td>0.39</td>
<td>1.33</td>
</tr>
<tr>
<td>PE-PBD3</td>
<td>11.5</td>
<td>1.16</td>
<td>11.8</td>
<td>11.2</td>
<td>0.07</td>
<td>1.96</td>
</tr>
<tr>
<td>PE-PBD4</td>
<td>39.7</td>
<td>1.13</td>
<td>10.7</td>
<td>9.70</td>
<td>0.20</td>
<td>1.51</td>
</tr>
</tbody>
</table>

*Measured by GPC (THF, RT) using polystyrene standards. Determined by $^1$H NMR analysis using normalized proton areas for epoxy unit analysis:

$$X_{1,2 \text{- cyclic/vinyl epoxide}} \text{ or } X_{1,4 \text{- cis epoxide}}(\%) = \frac{A_{\text{epoxide type}}}{A_{\text{total}} - A_{\text{methylene group, styrene}}} \times 100$$

$$X_{1,4 \text{- trans epoxide}}(\%) = \frac{A_{\text{epoxide type}} - A_{\text{methylene group, styrene}}}{A_{\text{total}} - A_{\text{methylene group, styrene}}} \times 100$$

**Determined by $^{13}$C gated NMR analysis using normalized carbon areas of epoxides and double bonds:**

$$X_{\text{epoxide}}(\%) = \frac{A_{\text{epoxide}}}{A_{\text{total}} - A_{\text{styrene}}} \times 100$$

*Measured by epoxide titration (see Supporting Information Section 3). Determined by DSC; data are taken from the second heating. Decomposition temperature ($T_d$) determined by TGA at 1% weight loss.
2.2 Spectroscopic analysis

2.2.1 PE-PBD1

Figure S21. $^1$H NMR spectrum of PE-PBD1 in CDCl$_3$ (Table S2).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) = 7.50-6.85 (m, 5H, 1-CH), 6.0-5.69 (m, 1H, 17-CH), 5.69-5.49 (m, 1H, 9-CH), 5.49-5.22 (m, 2H, 4-CH, 5-CH), 5.23-4.50 (m, 2H, 10-CH$_2$, 18-CH$_2$), 3.25-3.00 (m, 2H, 9'-CH, 17'-CH), 3.00-2.80 (m, cis epoxide, 2H, 4'-CH, 5'-CH), 2.80-2.57 (m, trans epoxide, 4H, 2x2-CH, 4'-CH, 5'-CH), 2.57-0.48 (m, 36H, 2x3-CH, 2x3'-CH, 2x6-CH, 2x6'-CH, 2x7-CH, 2x7'-CH, 8-CH, 8'-CH, 2x10'-CH, 2x11-CH, 2x11'-CH, 12-CH, 12'-CH, 13-CH, 13'-CH, 2x14-CH, 2x14'-CH, 15-CH, 15'-CH, 2x16-CH, 2x16'-CH, 2x18'-CH).

Signals from side reactions e. g. epoxide ring opening (-OH formation) and cross-linking (C-O-C formation) typically between $\delta$ (ppm) = 3 - 6 ppm were not observed for all samples.
Figure S22. $^{13}$C NMR spectrum of PE-PBD1 in CDCl$_3$ (Table S2).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm) = 145.0-141.8 (6x1-C (styrene), 9-C, 17-C), 132.5-123.2 (4-H, 5-C), 115.7-111.5 (10-C, 18-C), 66.0-63.5 (9'-C, 17'-C), 59.5-51.0 (4'-C, 5'-C), 46.7-6.05 (10'-C, 18'-C, 2-C, 3-C, 3'-C, 6-C, 6'-C, 7-C, 7'-C, 8-C, 8'-C, 10-C, 11'-C, 12-C, 12'-C, 13-C, 13'-C, 14-C, 14'-C, 15-C, 15'-C, 16-C, 16'-C).
Signals from side reactions e. g. epoxide ring opening (-OH formation) and cross-linking (C-O-C formation) typically between 3600 - 3200 cm$^{-1}$ and 1300 - 1000 cm$^{-1}$ were not observed for all samples.

**Figure S23.** IR spectrum of PE-PBD1 (Table S2).
2.2.2 PE-PBD2

Please note the peak assignments in Figure S21 and S22. The signal for 1, 4-cis and 1, 4-trans double bonds splits into the signals at $\delta$ (ppm) = 5.45 (m, 2H (trans)) and 5.42 (m, 2H, (cis)).

Figure S24. $^1$H NMR spectrum of PE-PBD2 in CDCl$_3$ (Table S2).

Figure S25. $^{13}$C NMR spectrum of PE-PBD2 in CDCl$_3$ (Table S2).
Figure S26. IR spectrum of PE-PBD2 (Table S2).
2.2.3 PE-PBD3

Please note the peak assignments in Figure S21 and S22. The signal for 1, 4-cis and 1, 4-trans double bonds splits into the signals at \( \delta \) (ppm) = 5.36 (m, 2H (trans)) and 5.32 (m, 2H, (cis)).

Figure S27. \(^1\)H NMR spectrum of PE-PBD3 in CDCl\(_3\) (Table S2).

Figure S28. \(^{13}\)C NMR spectrum of PE-PBD3 in CDCl\(_3\) (Table S2).
Figure S29. IR spectrum of PE-PBD3 (Table S2).
2.2.4 PE-PBD4

Please note the peak assignments in Figure S21 and S22. The signal for 1, 4-cis and 1, 4-trans double bonds splits into the signals at $\delta$ (ppm) = 5.40 (m, 2H (trans)) and 5.36 (m, 2H, (cis)).

Figure S30. $^1$H NMR spectrum of PE-PBD4 in CDCl$_3$ (Table S2).

Figure S31. $^{13}$C NMR spectrum of PE-PBD4 in CDCl$_3$ (Table S2).
Figure S32. IR spectrum of PE-PBD4 (Table S2).
2.3 Thermal analysis

2.3.1 PE-PBD1

Figure S33. Thermogravimetric analysis of PE-PBD1 (Table S2).

Figure S34. Differential Scanning Calorimetry trace of PE-PBD1 (Table S2).
2.3.2 PE-PBD2

Figure S35. Thermogravimetric analysis of PE-PBD2 (Table S2).

Figure S36. Differential Scanning Calorimetry trace of PE-PBD2 (Table S2).

S27
2.3.3 PE-PBD3

Figure S37. Thermogravimetric analysis of PE-PBD3 (Table S2).

Figure S38. Differential Scanning Calorimetry trace of PE-PBD3 (Table S2).
2.3.4 PE-PBD4

Figure S39. Thermogravimetric analysis of PE-PBD4 (Table S2).

Figure S40. Differential Scanning Calorimetry trace of PE-PBD4 (Table S2).
3. Determination of PBDs double bond contents

EP-numbers of several partly epoxidized PBDs were determined by the titration technique described in the Experimental Section. The relative amounts of converted double bonds were calculated by $^1$H NMR analysis. Both results were applied to the graph shown in figure S41.

![Figure S41. EP-numbers of partly epoxidized PBDs and relative amount of epoxidized double bonds applied to a graph and linearly fitted.](image)

Linear fitting and extrapolation leads to the EP-values expectable at 100 % epoxide conversion. This is equated with the total amount of double bonds in the polymers, respectively. The results are summarized in table S3. All samples differ from the theoretical value of 18.5 mmol/g.

**Table S3.** Summary of data derived by linear fit and extrapolation.

<table>
<thead>
<tr>
<th>PBD</th>
<th>slope, $a$ [mol/100g/100g]</th>
<th>coefficient of determination, $R^2$</th>
<th>EP-value at 100% epoxide conversion [mol/100g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD1</td>
<td>0.0117</td>
<td>0.9990</td>
<td>1.17</td>
</tr>
<tr>
<td>PBD2</td>
<td>0.0160</td>
<td>0.9998</td>
<td>1.60</td>
</tr>
<tr>
<td>PBD3</td>
<td>0.0167</td>
<td>0.9967</td>
<td>1.67</td>
</tr>
<tr>
<td>PBD4</td>
<td>0.0142</td>
<td>0.9962</td>
<td>1.42</td>
</tr>
</tbody>
</table>
4. Characterization of PC-PBDs

4.1 Spectroscopic analysis

4.1.1 PC-PBD1

Figure S42. $^1$H NMR spectrum of PC-PBD1 in CDCl$_3$ (Table 2).

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) = 7.39-6.85 (m, 5H, 1-CH), 6.25-5.68 (m, 1H, 17-CH), 5.68-5.49 (m, 1H, 9-CH), 5.49-5.23 (m, 2H, 4-CH, 5-CH), 5.23-4.73 (m, 2H, 10-CH$_2$, 18-CH$_2$), 4.73-3.85 (m, 8H, 4''-H, 5''-H, 9''-H, 10''-H, 17''-H, 18''-H), 3.25-3.00 (m, 2H, 9'-CH, 17'-CH), 3.00-2.80 (m, cis-epoxide, 2H, 4'-CH, 5'-CH), 2.80-2.57 (m, trans-epoxide, 4H, 2x2-CH, 4'-CH, 5'-CH), 2.57-0.48 (m, 52H, 2x3-CH, 2x3'-CH, 2x3''-CH, 2x6-CH, 2x6'-CH, 2x6''-CH, 2x7-CH, 2x7'-CH, 2x7''-CH, 8-CH, 8'-CH, 8''-CH, 2x10'-CH, 2x11-CH, 2x11'-CH, 2x11''-CH, 12-CH, 12'-CH, 12''-CH, 13-CH, 13'-CH, 13''-CH, 2x14-CH, 2x14'-CH, 2x14''-CH, 15-CH, 15'-CH, 15''-CH, 2x16-CH, 2x16'-CH, 2x16''-CH).
Figure S43. $^{13}$C NMR spectrum of PC-PBD1 in CDCl$_3$ (Table 2).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ (ppm) = 145.0-141.8 (6x1-C (styrene), 9-C, 17-C), 132.5-123.2 (4-H, 5-C), 115.7-111.5 (10-C, 18-C), 83.0-77.7 (4''-C, 5''-C, 9''-C, 10''-C, 17''-C, 18''-C), 66.0-63.5 (9'-C, 17'-C), 59.5-51.0 (4'-C, 5'-C), 46.7-6.05 (2-C, 3-C, 3'-C, 3''-C, 6-C, 6'-C, 6''-C, 7-C, 7'-C, 7''-C, 8-C, 8'-C, 8''-C, 11-C, 11'-C, 11''-C, 12-C, 12'-C, 12''-C, 13-C, 13'-C, 13''-C, 14-C, 14'-C, 14''-C, 15-C, 15'-C, 15''-C, 16-C, 16'-C, 16''-C).
Figure S44. IR spectrum of PC-PBD1 (Table 2).
4.1.2 PC-PBD2

Please note the peak assignments in Figure S42 and S43.

Figure S45. $^1$H NMR spectrum of PC-PBD2 in CDCl$_3$ (Table 2).

Figure S46. $^{13}$C NMR spectrum of PC-PBD2 in CDCl$_3$ (Table 2).
Figure S47. IR spectrum of PC-PBD2 (Table 2).
4.1.3 PC-PBD3

Please note the peak assignments in Figure S42 and S43.

Figure S48. $^1$H NMR spectrum of PC-PBD3 in CDCl$_3$ (Table 2).

Figure S49. $^{13}$C NMR spectrum of PC-PBD3 in CDCl$_3$ (Table 2).
Figure S50. IR spectrum of PC-PBD3 (Table 2).
4.1.4 PC-PBD4

Please note the peak assignments in Figure S42 and S43.

Figure S51. $^1$H NMR spectrum of PC-PBD4 in CDCl$_3$ (Table 2).

Figure S52. $^{13}$C NMR spectrum of PC-PBD4 in CDCl$_3$ (Table 2).
Figure S53. IR spectrum of PC-PBD4 (Table 2).
4.2 Thermal analysis

4.2.1 PC-PBD1

Figure S54. Thermogravimetric analysis of PC-PBD1 (Table 2).

Figure S55. Differential Scanning Calorimetry trace of PC-PBD1 (Table 2).
4.2.2 PC-PBD2

Figure S56. Thermogravimetric analysis of PC-PBD2 (Table 2).

Figure S57. Differential Scanning Calorimetry trace of PC-PBD2 (Table 2).
4.2.3 PC-PBD3

Figure S58. Thermogravimetric analysis of PC-PBD3 (Table 2).

Figure S59. Differential Scanning Calorimetry trace of PC-PBD3 (Table 2).
4.2.4 PC-PBD4

Figure S60. Thermogravimetric analysis of PC-PBD4 (Table 2).

Figure S61. Differential Scanning Calorimetry trace of PC-PBD4 (Table 2).
5. Selectivities towards the conversion of 1,2-cyclic/vinyl, 1,4-cis and 1,4-trans epoxides depending on reaction conditions demonstrated by epoxide residues in the partyl carboxylated PE-PBDs

![Figure S62](image_url)

**Figure S62.** Epoxide ratios in partly carboxylated PE-PBD1 after the application of different reaction conditions, solvents and reaction times.
Figure S63. Epoxide ratios in partly carboxylated PE-PBD2 after the application of different reaction conditions, solvents and reaction times.

Figure S64. Epoxide ratios in partly carboxylated PE-PBD3 after the application of different reaction conditions, solvents and reaction times.
Figure S65. Epoxide ratios in partly carboxylated PE-PBD4 after the application of different reaction conditions, solvents and reaction times.
6. GPC analysis

Figure S66. GPC analysis of the sequential transformation a) from PBD1 to PC-PBD1, b) PBD2 to PC-PBD2, c) PBD3 to PC-PBD3 and d) PBD4 to PC-PBD4.
7. IR Characterization NIPU reactions

Figure S67. IR-spectra of PC-PBD1 cured with PDA (1/1) at 70 °C and 130°C for 16h.

Figure S68. IR-spectra of PC-PBD1 cured with ODA (1/1) at 70 °C and 130°C for 16h.
**Figure S69.** IR-spectra of PC-PBD2 cured with PDA (1/1) at 70 °C and 130 °C for 16h.

**Figure S70.** IR-spectra of PC-PBD2 cured with ODA (1/1) at 70 °C and 130 °C for 16h.