

**$\alpha,\omega$ -Di(glycerol carbonate) Telechelic Polyesters and Polyolefins  
as Precursors to PolyHydroxyUrethanes: an Isocyanate-free approach**

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## Electronic Supplementary Information

### $\alpha,\omega$ -Di(glycerol carbonate) Telechelic Polyesters and Polyolefins

#### as Precursors to PolyHydroxyUrethanes: an Isocyanate-free approach

**Figure S1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (\* stands for residual solvent resonances)

**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (\* stands for residual solvent resonances)

**Figure S3.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectra of  $\text{PPG}_{400,1600,2800}\text{-GC}_2$  prepared from the reaction of the corresponding  $\text{PPG}_{400,1600,2800}\text{-OH}_2$  with GC-OTS.

**Figure S4.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of  $\text{PPG}_{400}\text{-OH}_2$  (\* stands for residual solvent resonances, and x stands for an unidentified impurity).

**Figure S5.**  $^1\text{H}\text{-}^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of  $\text{PPG}_{400}\text{-GC}_2$ .

**Figure S6.**  $^1\text{H}\text{-}^{13}\text{C}$  (DEPT) HMQC NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25 °C) of  $\text{PPG}_{400}\text{-GC}_2$ .

**Figure S7.** (a)  $^1\text{H}$  (500 MHz,  $\text{CDCl}_3$ , 25 °C) and (b)  $^{13}\text{C}\{^1\text{H}\}$  (125 MHz,  $\text{CDCl}_3$ , 25 °C) NMR spectra of  $\text{PEG}_{400}\text{-OH}_2$ .

**Figure S8.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of the  $\text{PEG}_{400}\text{-GC}_2$ .

**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of the  $\text{PEG}_{400}\text{-GC}_2$ .

**Figure S10.**  $^1\text{H}\text{-}^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of the  $\text{PEG}_{400}\text{-GC}_2$ .

**Figure S11.** FTIR spectra of  $\text{PEG}_{400}\text{-OH}_2$  (black trace) and the resulting  $\text{PEG}_{400}\text{-GC}_2$  (red trace).

**Figure S12.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of the  $\text{PEE}\text{-OH}_2$ .

**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of the  $\text{PEE}\text{-OH}_2$ .

**Figure S14.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PEE-GC<sub>2</sub> (\* marker stands for residual toluene and \*\* for the starting reagent).

**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PEE-GC<sub>2</sub> (\* marker stands for residual toluene).

**Figure S16.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25 °C) of PEE-GC<sub>2</sub>.

**Figure S17.**  $^1\text{H}$ - $^{13}\text{C}$  (DEPT) HMQC NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25 °C) of PEE-GC<sub>2</sub>.

**Figure S18.** FTIR spectra of PEE-OH<sub>2</sub> (black trace) and the resulting PEE-GC<sub>2</sub> (red trace).

**Figure S19.** MALDI-ToF MS spectrum of PEE-GC<sub>2</sub>.

**Figure S20.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PBD-OH<sub>2</sub>.

**Figure S21.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PBD-GC<sub>2</sub> (\* marker stands for residual toluene).

**Figure S22.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PBD-GC<sub>2</sub>.

**Figure S23.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PBD-GC<sub>2</sub>.

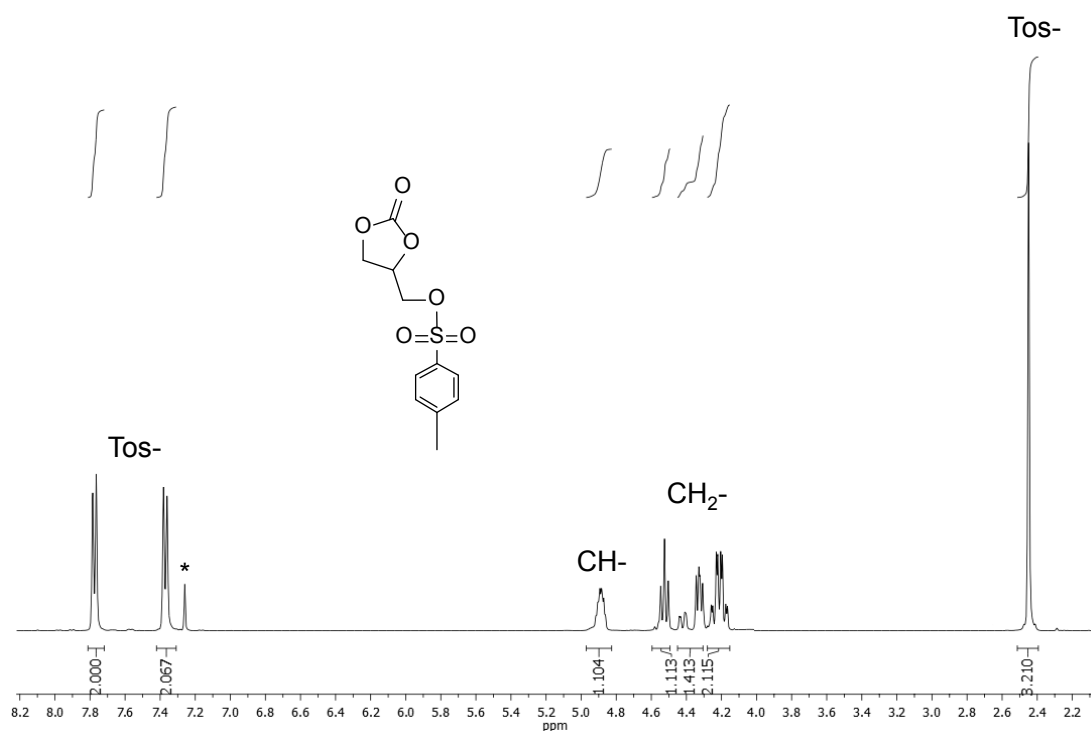
**Figure S24.** FTIR spectra of PBD-OH<sub>2</sub> (black trace) and the resulting PBD-GC<sub>2</sub> (red trace).

**Scheme S1.** Synthesis of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs).

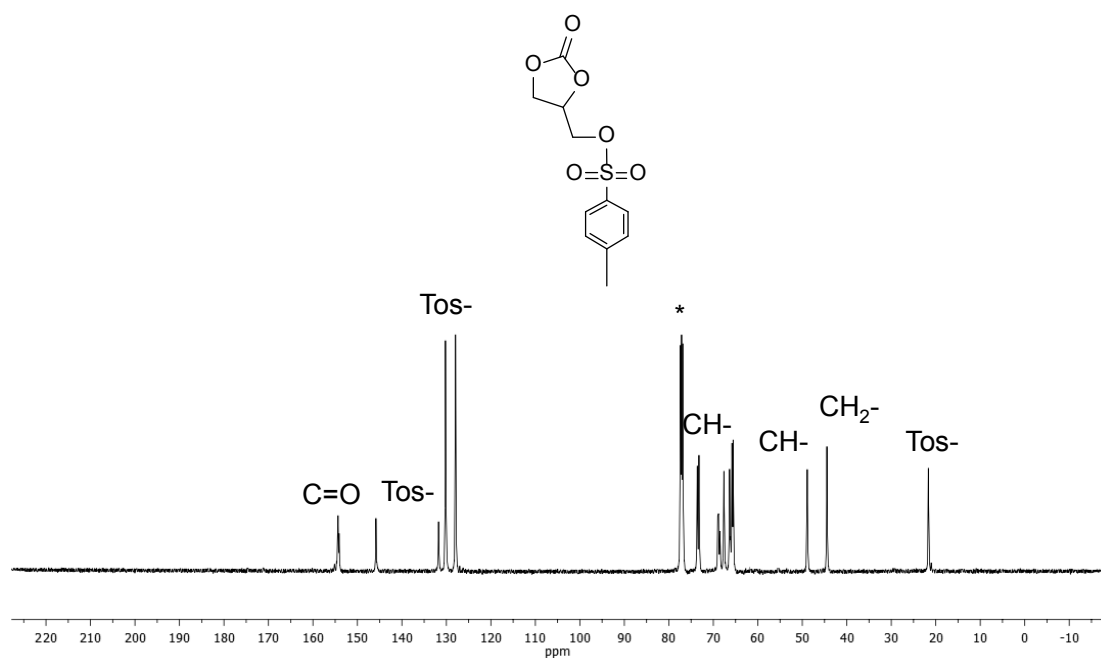
**Table S1.**  $\alpha,\omega$ -Dihydroxy and dicyclocarbonate telechelic PEGs characteristics.

**Table S2.**  $\alpha,\omega$ -Dihydroxy and dicyclocarbonate telechelic PEE characteristics.

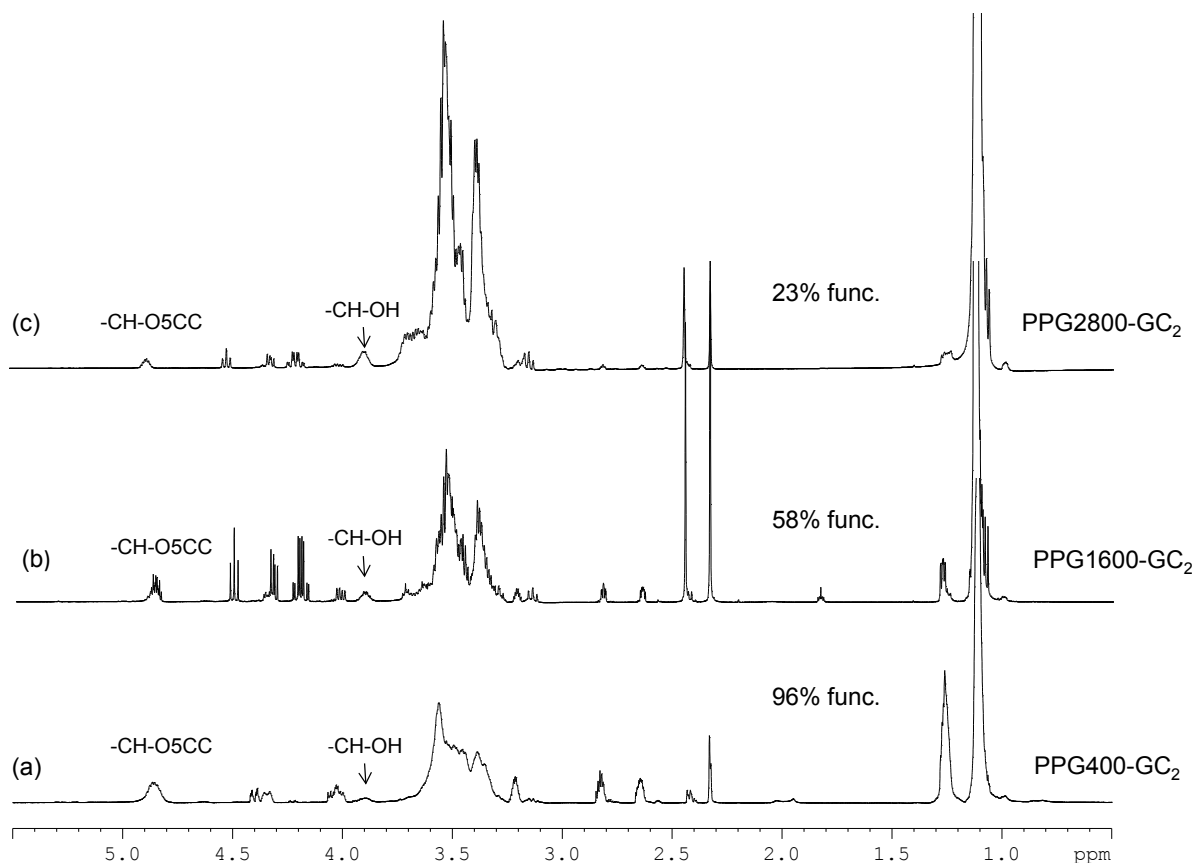
**Table S3.**  $\alpha,\omega$ -Dihydroxy and dicyclocarbonate telechelic PBD characteristics.



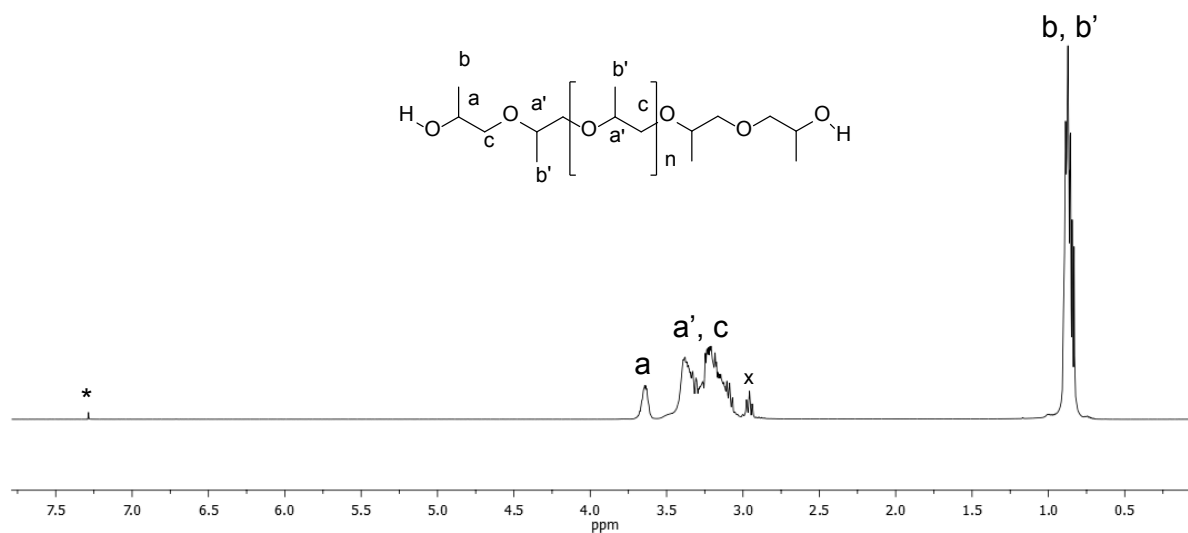
**Figure S1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (\* stands for residual solvent resonances).



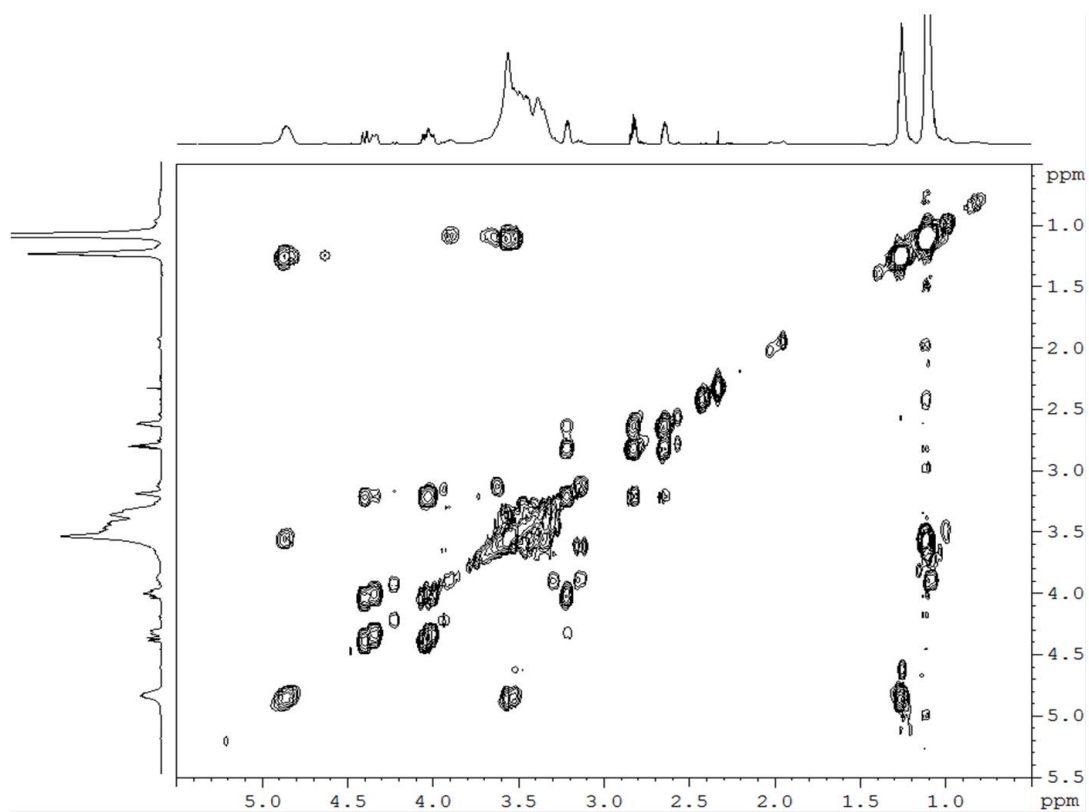
**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (\* stands for residual solvent resonances).



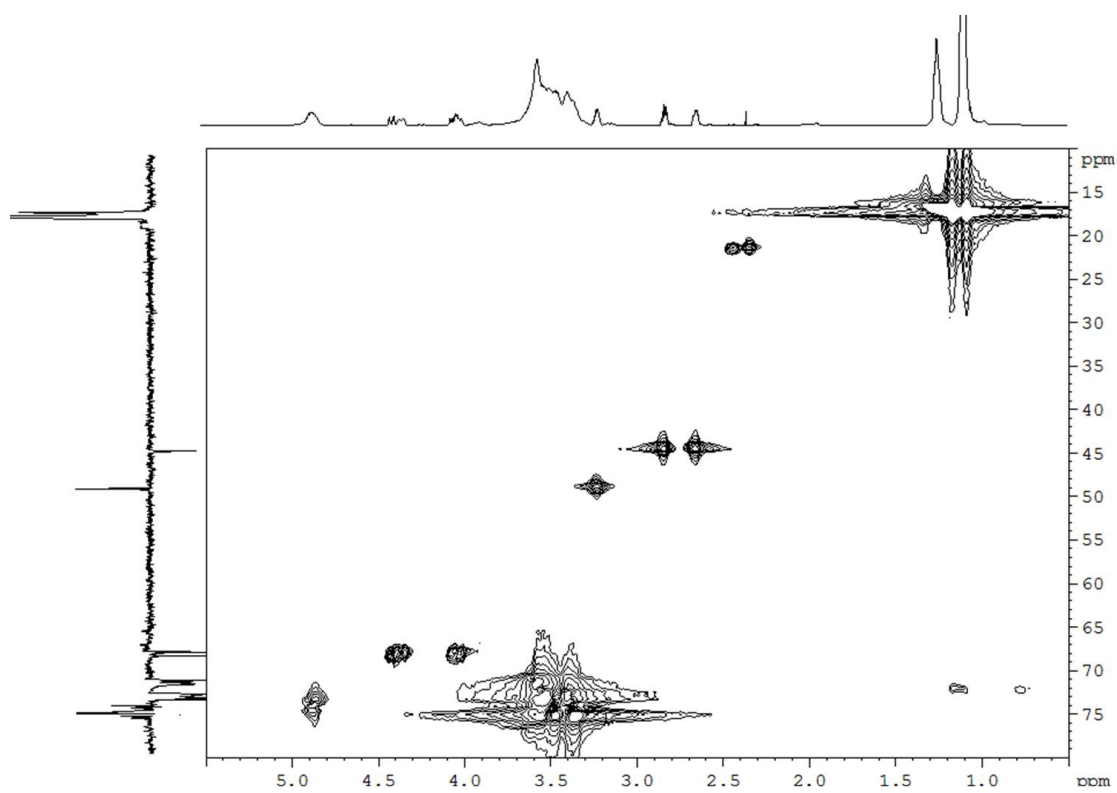
**Figure S3.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectra of  $\text{PPG}_{400,1600,2800}\text{-GC}_2$  prepared from the reaction of the corresponding  $\text{PPG}_{400,1600,2800}\text{-OH}_2$  with GC-OTS.



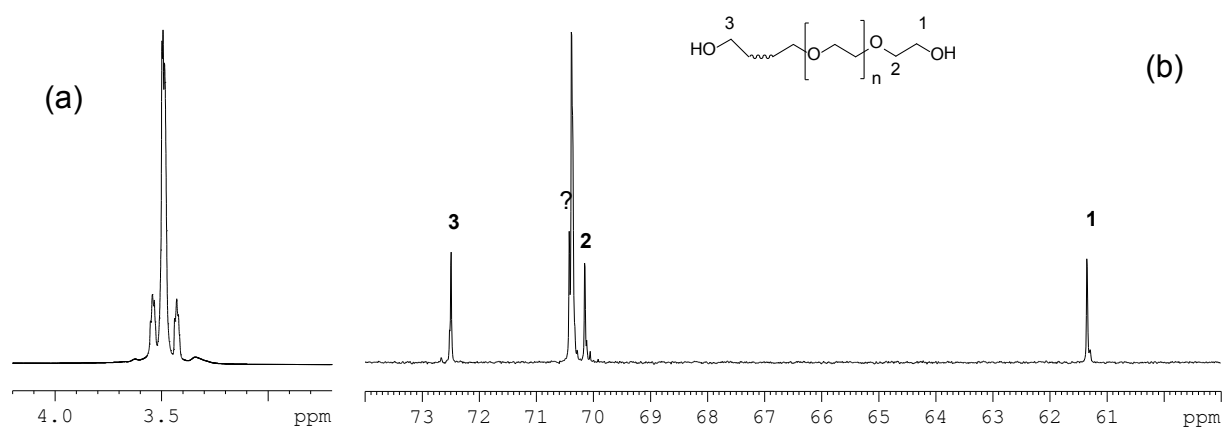
**Figure S4.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of  $\text{PPG}_{400}\text{-OH}_2$  (\* stands for residual solvent resonances, and x stands for an unidentified impurity).



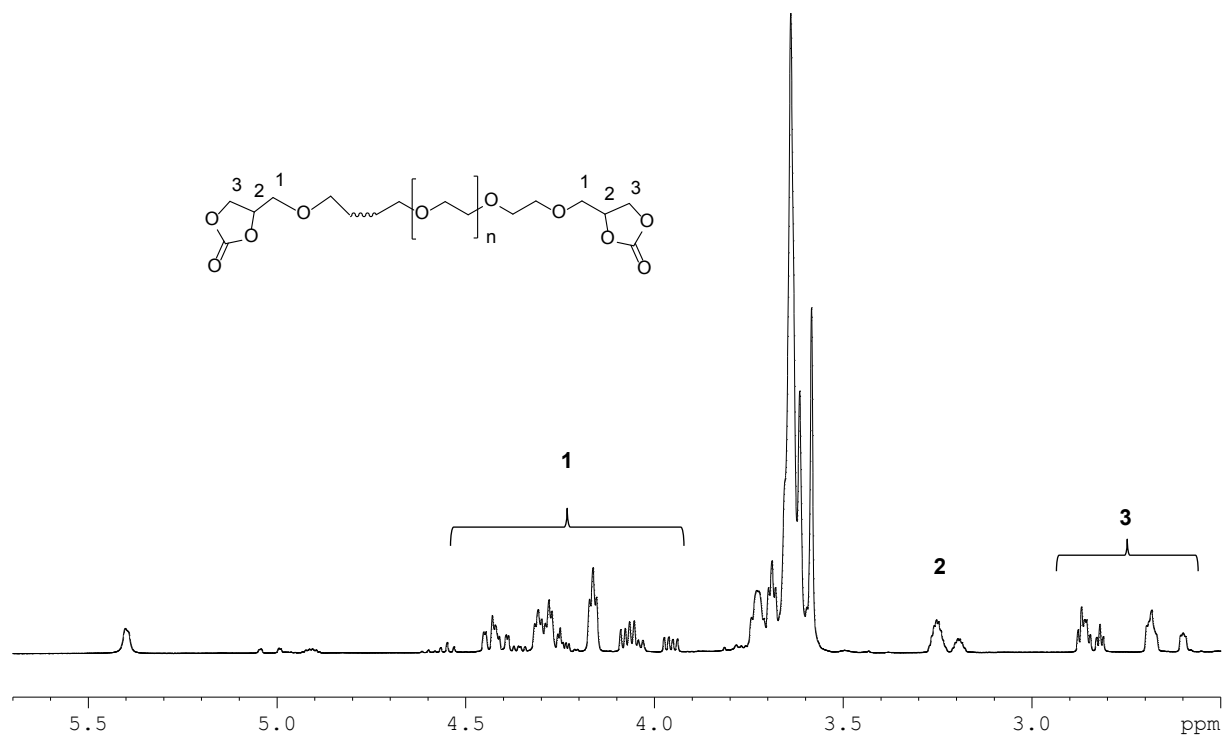
**Figure S5.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PPG<sub>400</sub>-GC<sub>2</sub>.



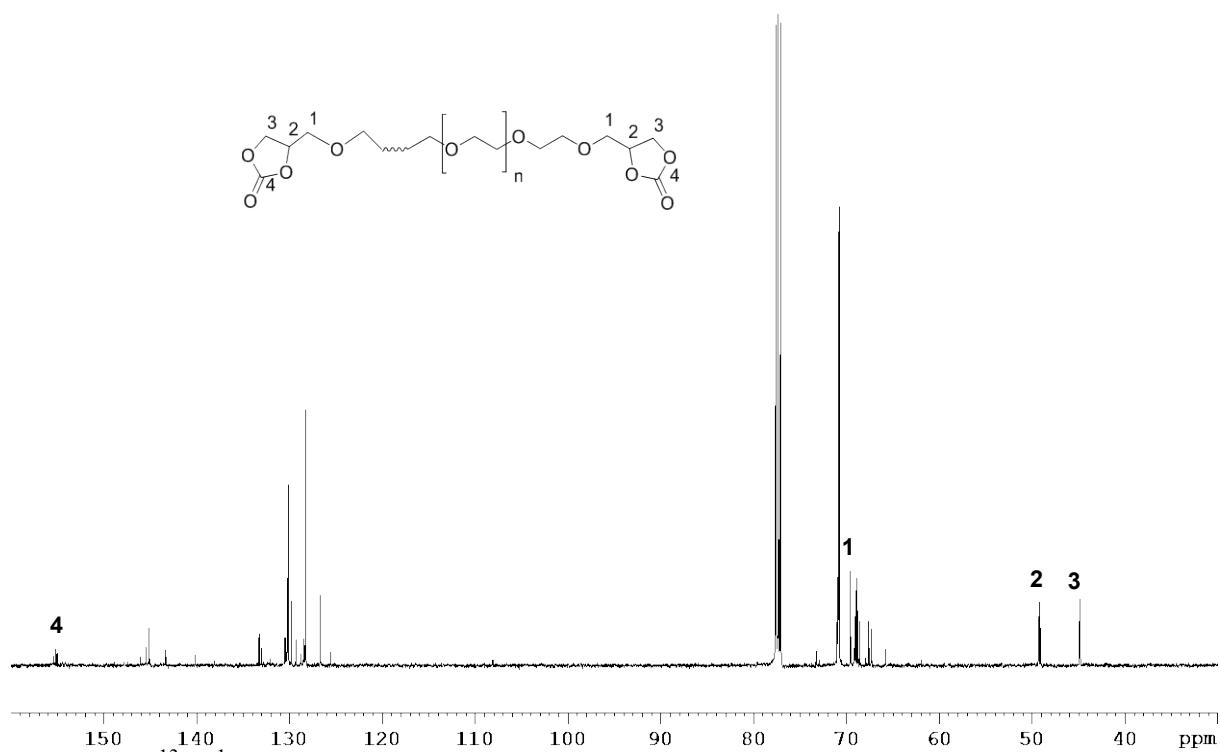
**Figure S6.**  $^1\text{H}$ - $^{13}\text{C}$  (DEPT) HMQC NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25 °C) of PPG<sub>400</sub>-GC<sub>2</sub>.



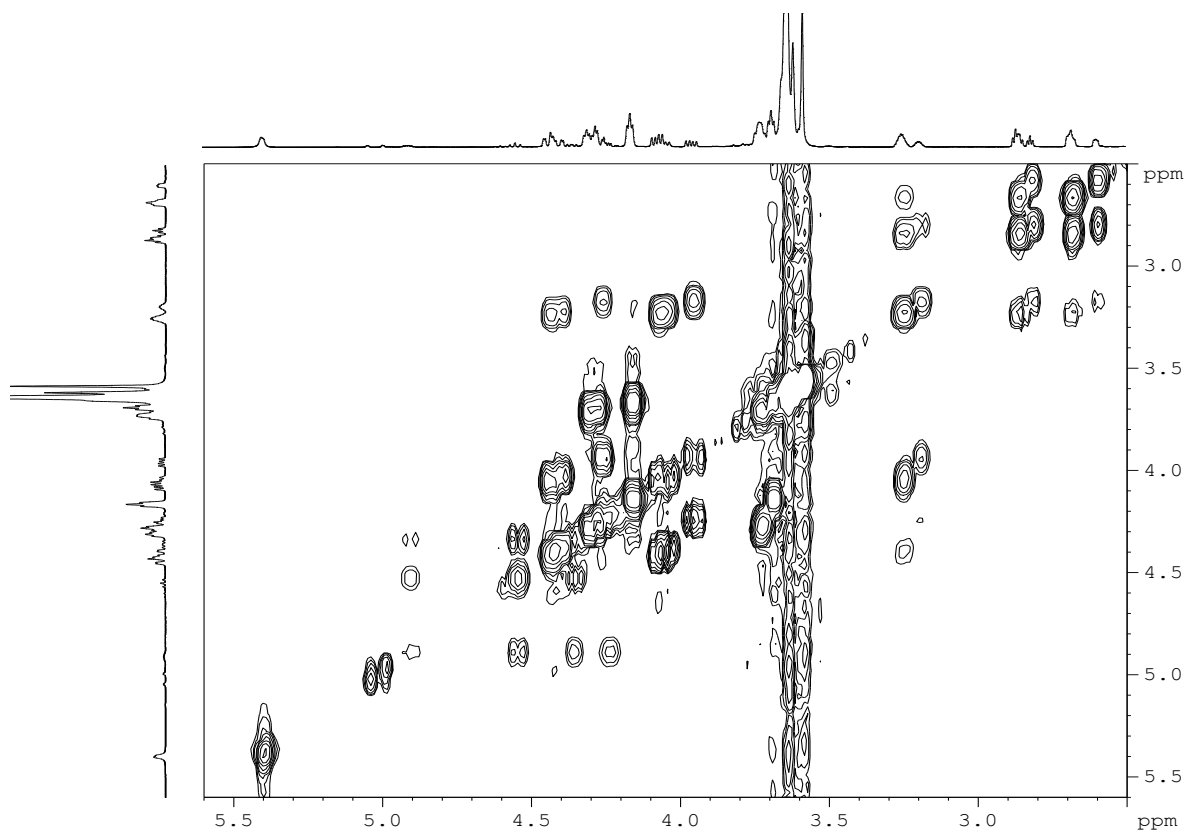
**Figure S7.** (a) <sup>1</sup>H (500 MHz, CDCl<sub>3</sub>, 25 °C) and (b) <sup>13</sup>C {<sup>1</sup>H} (125 MHz, CDCl<sub>3</sub>, 25 °C) NMR spectra of PEG<sub>400</sub>-OH<sub>2</sub>.



**Figure S8.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of the PEG<sub>400</sub>-GC<sub>2</sub>.

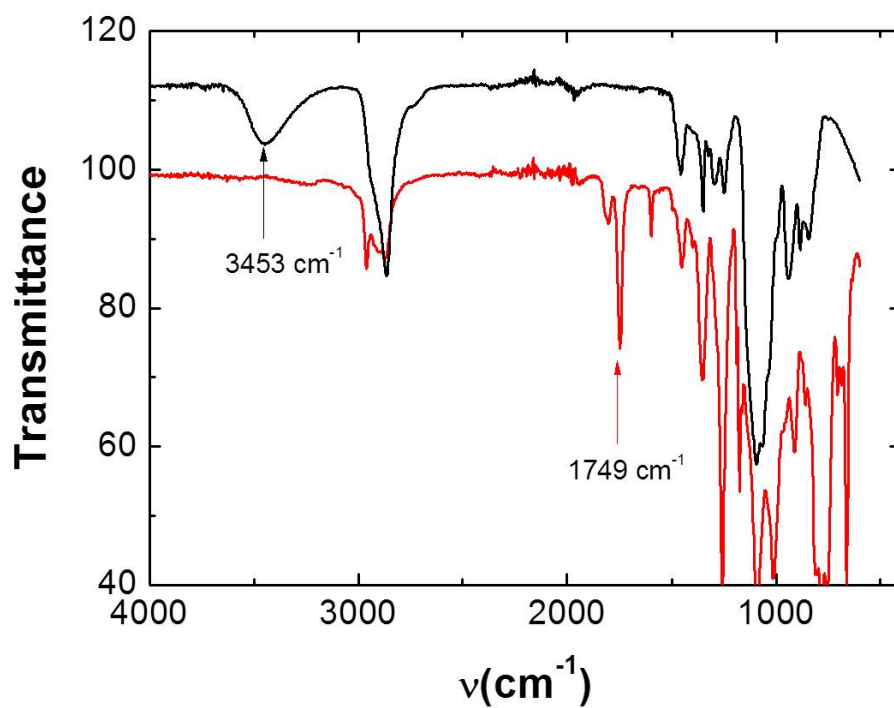


**Figure S9.** <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of the PEG<sub>400</sub>-GC<sub>2</sub>.

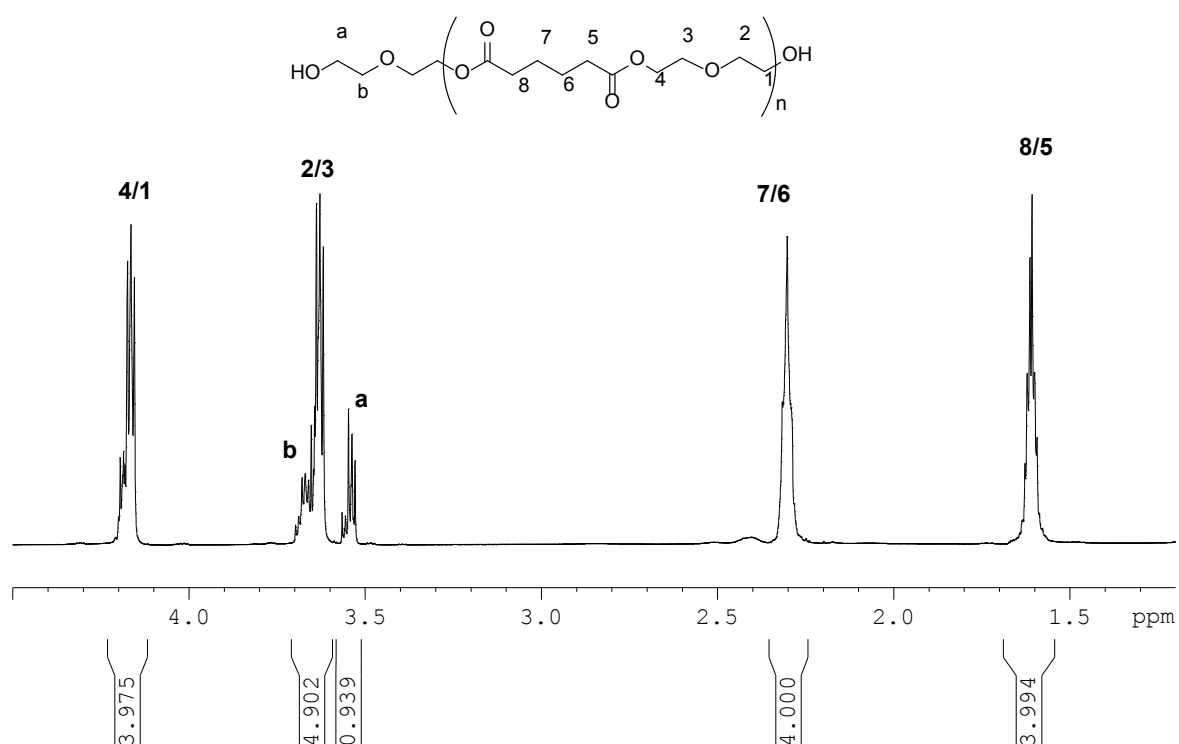


**Figure S10.** <sup>1</sup>H-<sup>1</sup>H COSY NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of the PEG<sub>400</sub>-GC<sub>2</sub>.

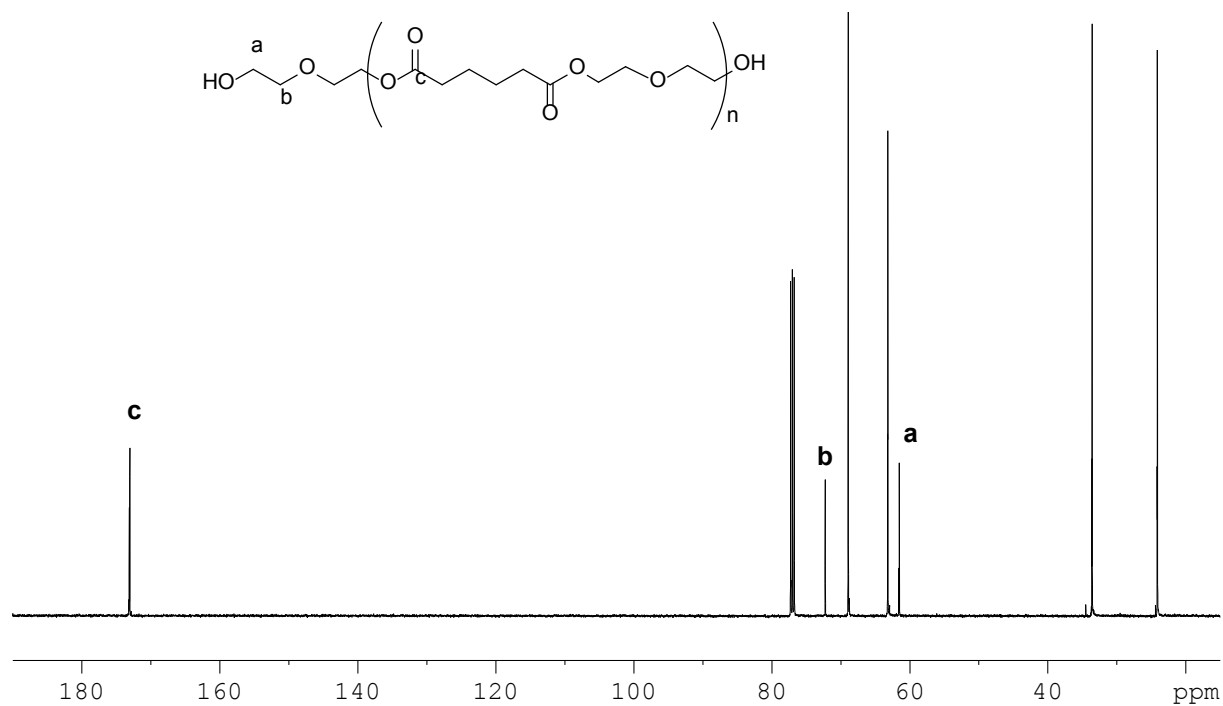




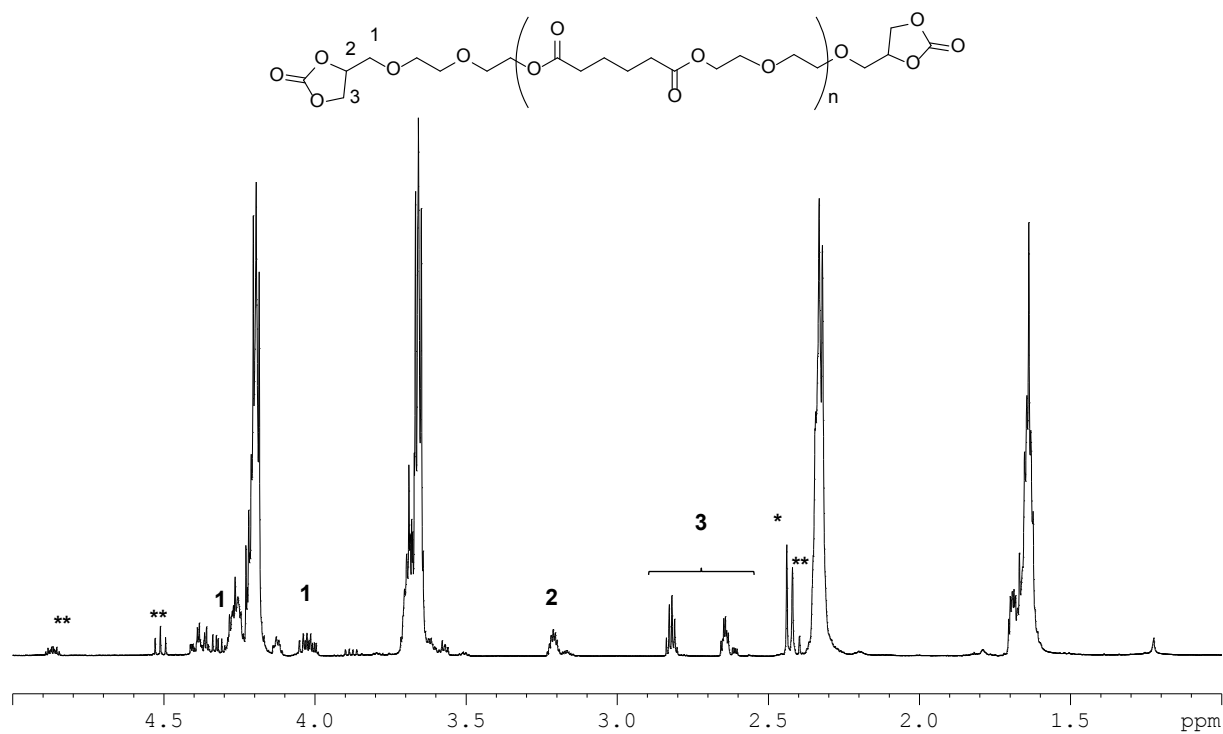
**Figure S11.** FTIR spectra of PEG<sub>400</sub>-OH<sub>2</sub> (black trace) and the resulting PEG<sub>400</sub>-GC<sub>2</sub> (red trace).



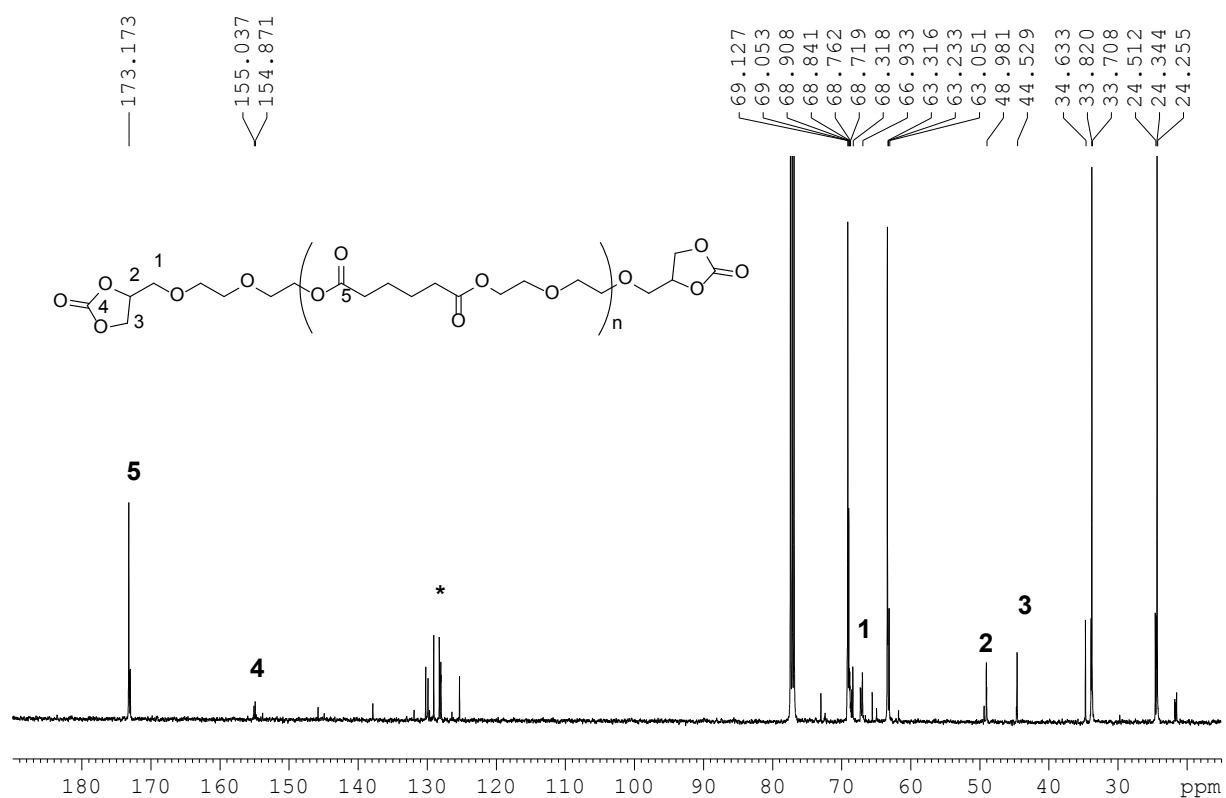
**Figure S12.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of the PEE-OH<sub>2</sub>.



**Figure S13.** <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of the PEE-OH<sub>2</sub>.



**Figure S14.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of PEE-GC<sub>2</sub> (\* marker stands for residual toluene and \*\* for the starting reagent).



**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , 25 °C) spectrum of PEE-GC<sub>2</sub> (\* marker stands for residual toluene).

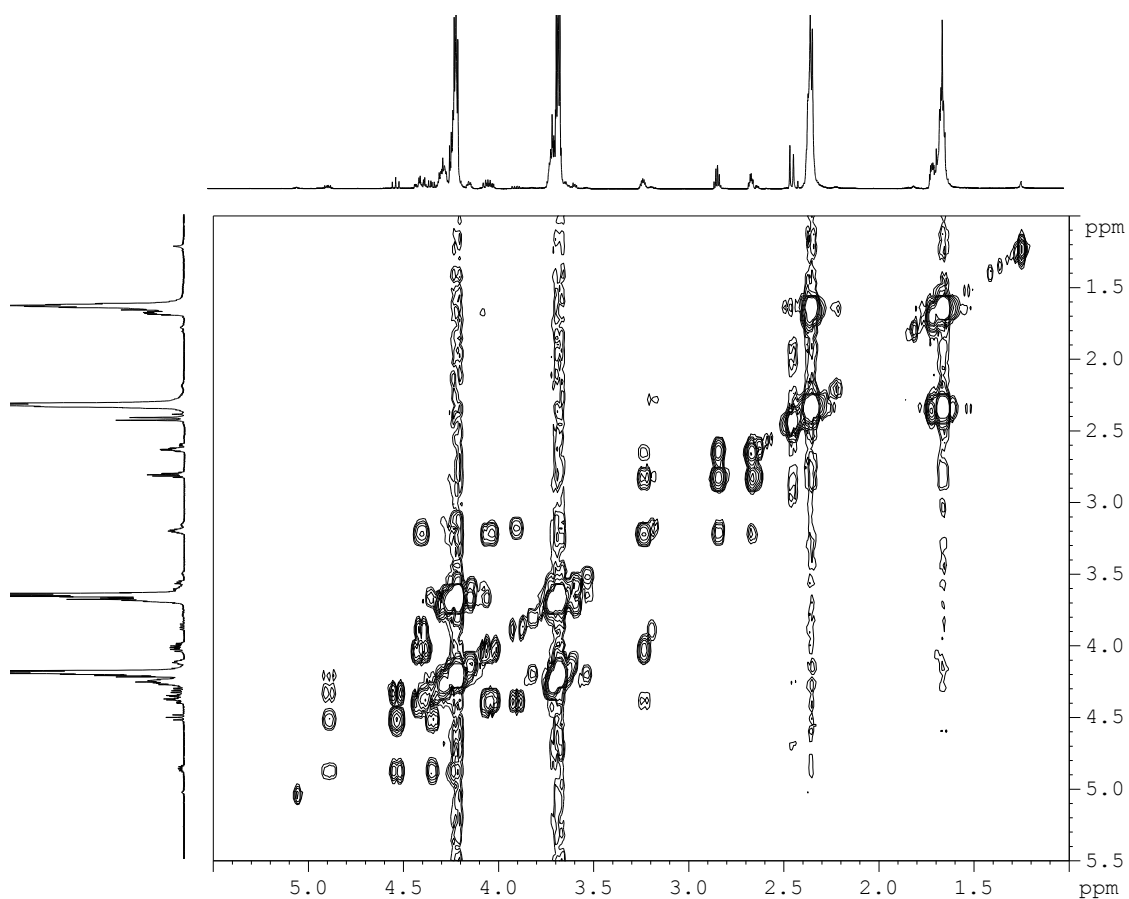


Figure S16.  $^1\text{H}$ - $^1\text{H}$  COSY NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25 °C) of PEE- $\text{GC}_2$ .

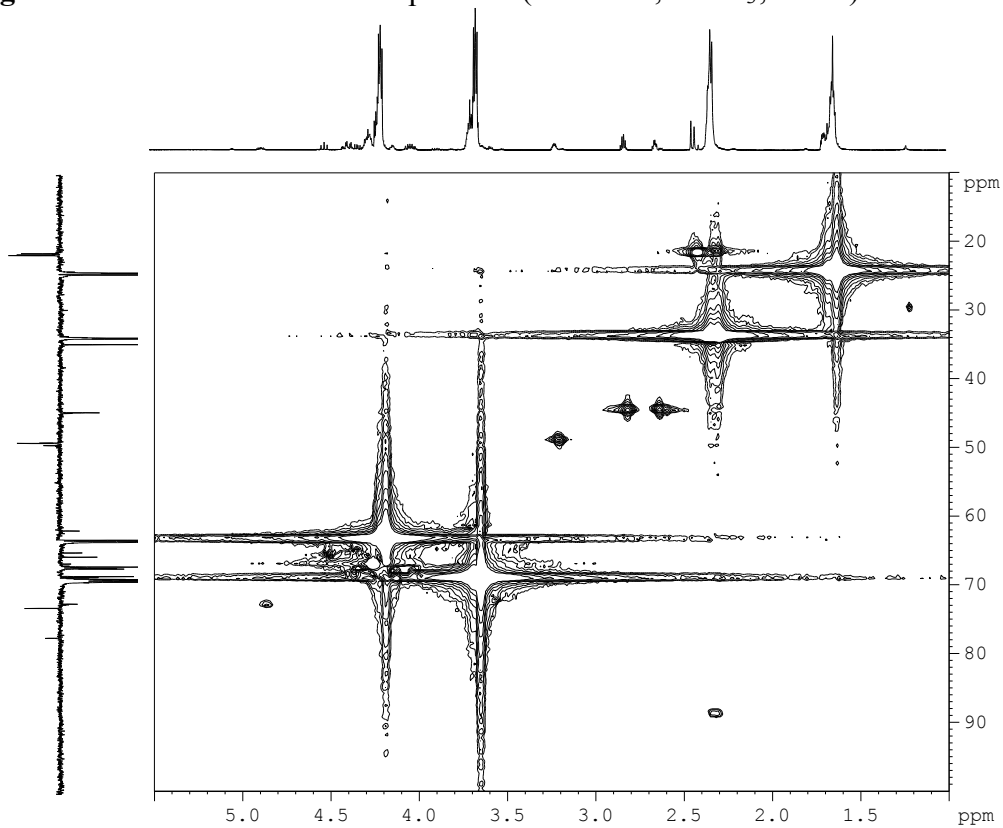


Figure S17.  $^1\text{H}$ - $^{13}\text{C}$  (DEPT) HMQC NMR spectrum (500 MHz,  $\text{CDCl}_3$ , 25 °C) of PEE- $\text{GC}_2$ .

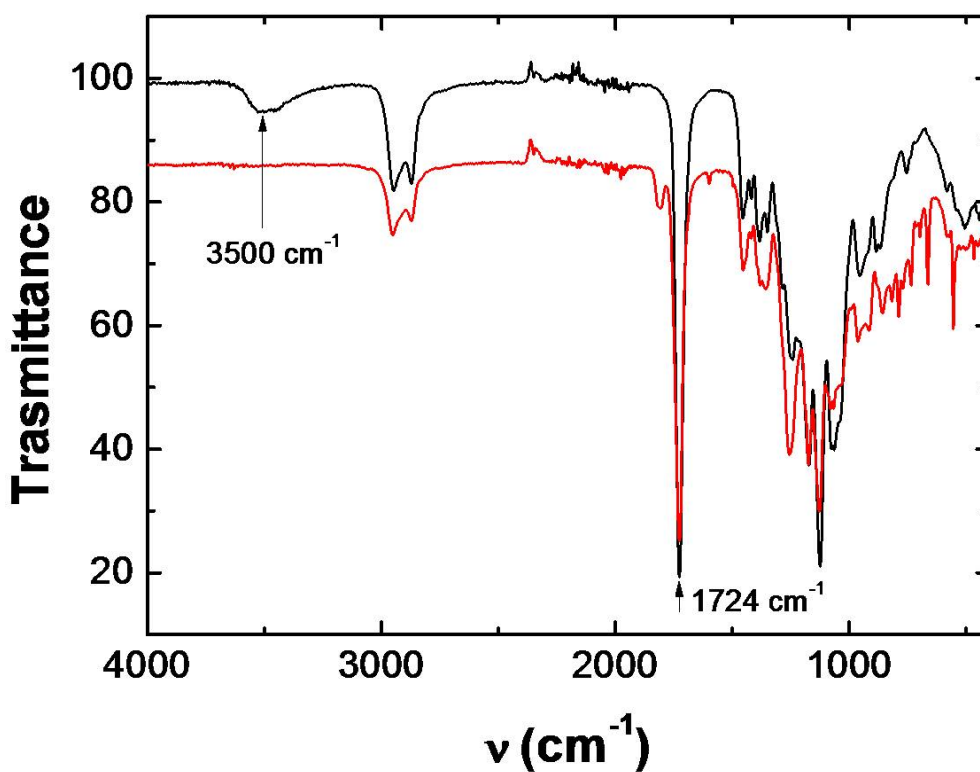


Figure S18. FTIR spectra of PEE-OH<sub>2</sub> (black trace) and the resulting PEE-GC<sub>2</sub> (red trace).

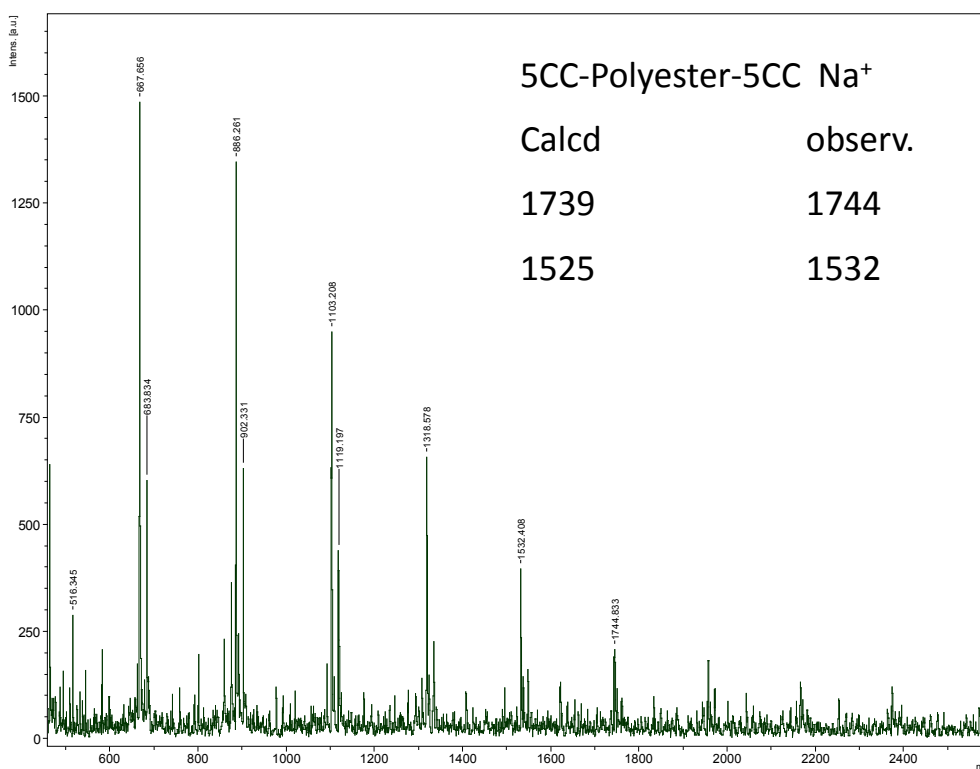
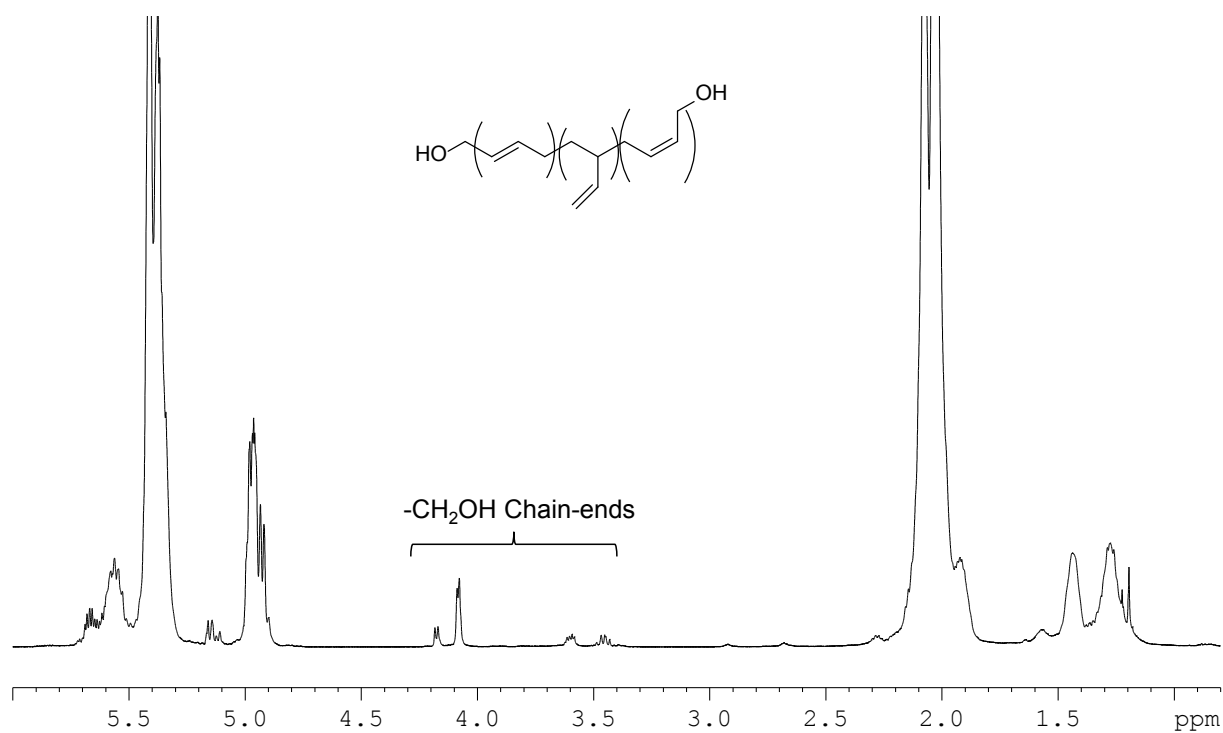
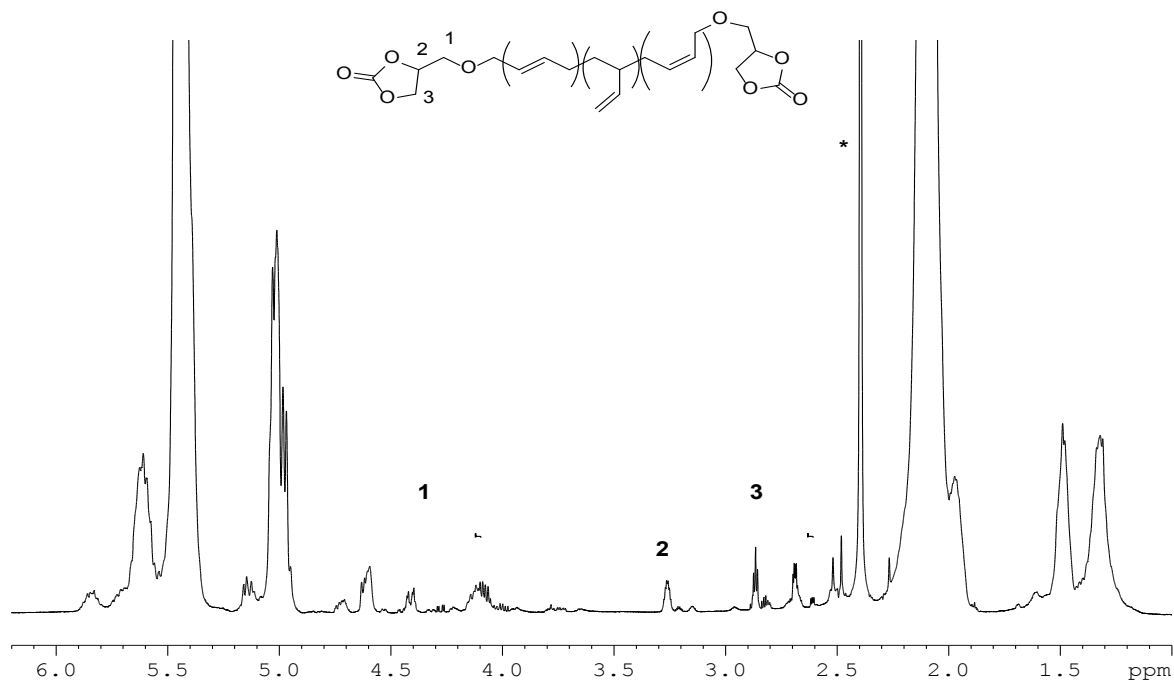


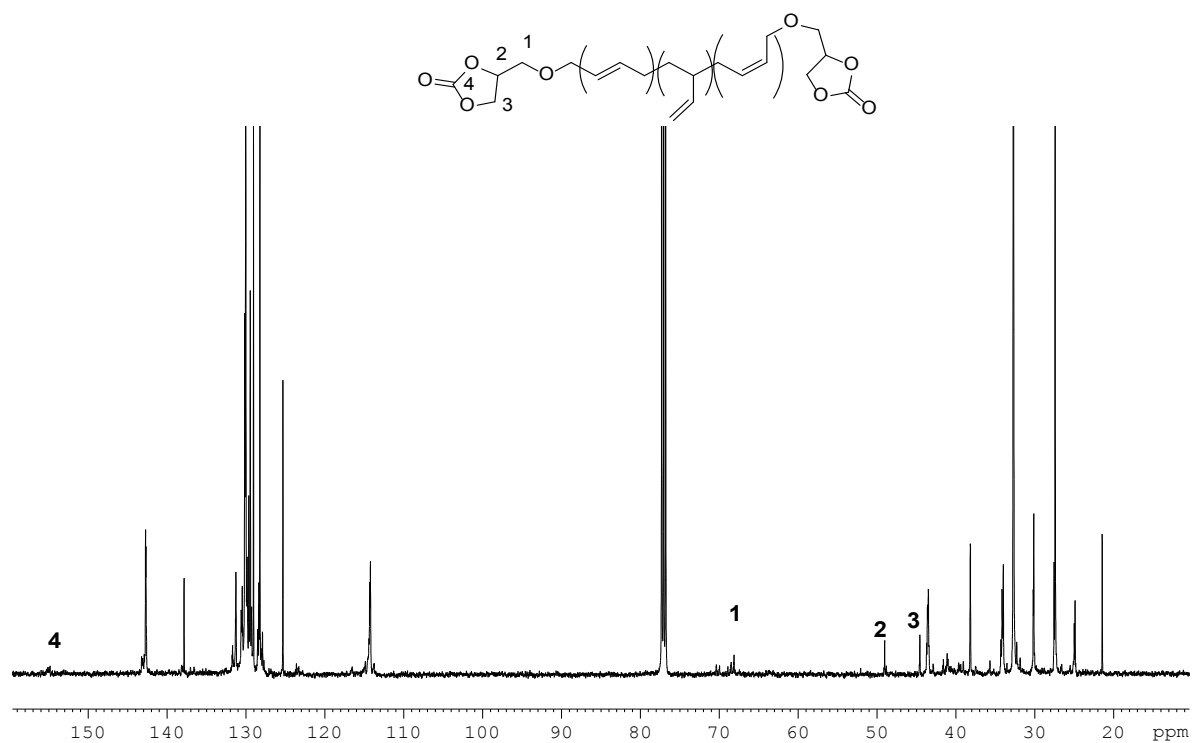
Figure S19. MALDI-ToF MS spectrum of PEE-GC<sub>2</sub>.



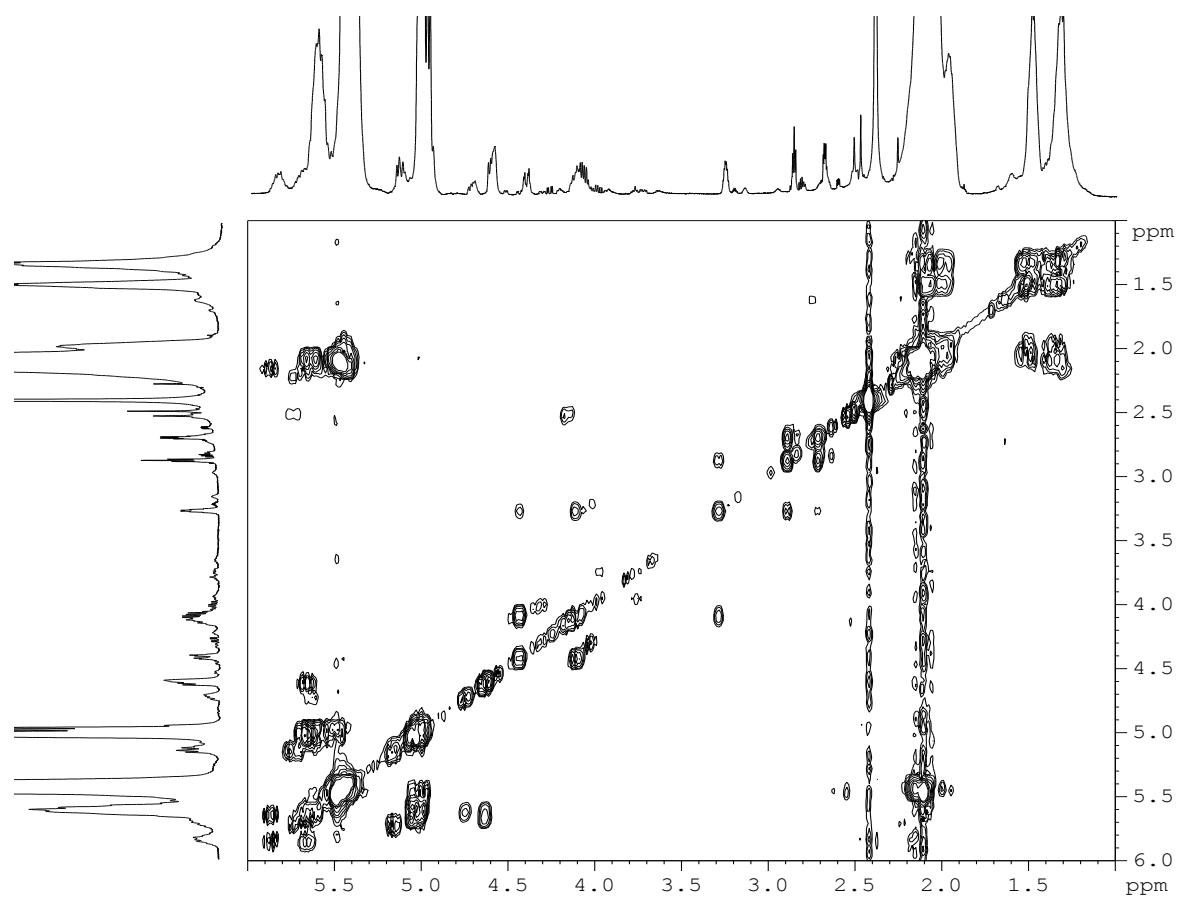
**Figure S20.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of PBD-OH<sub>2</sub>.



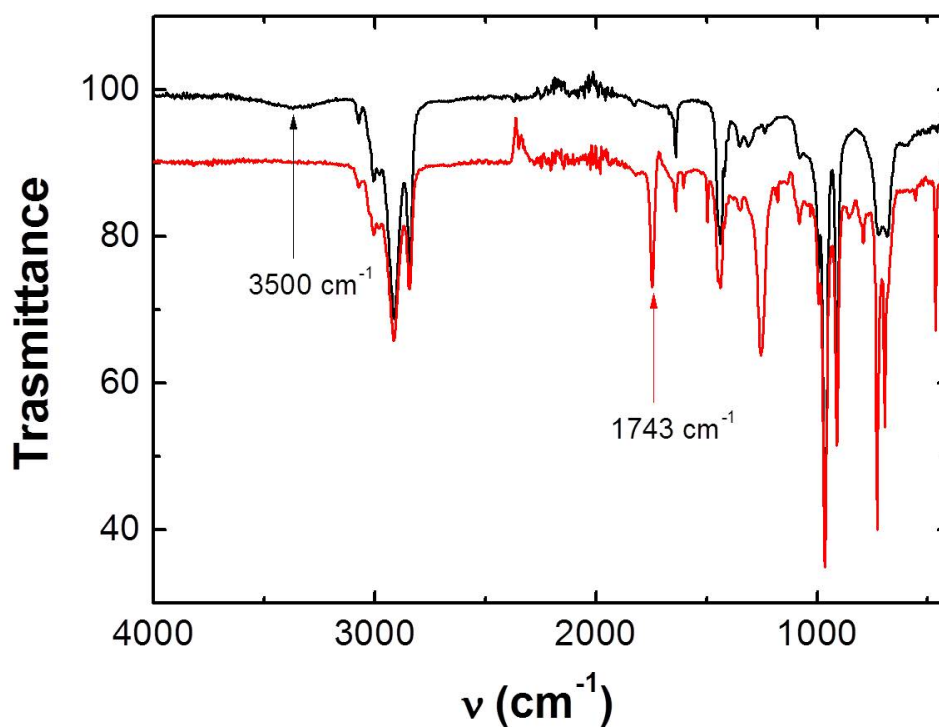
**Figure S21.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of PBD-GC<sub>2</sub> (\* marker stands for residual toluene).



**Figure S22.** <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of PBD-GC<sub>2</sub>.

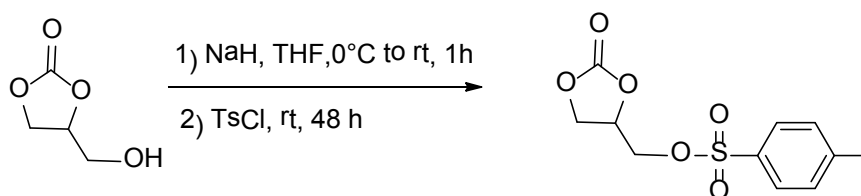


**Figure S23.** <sup>1</sup>H-<sup>1</sup>H COSY NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) spectrum of PBD-GC<sub>2</sub>.



**Figure S24.** FTIR spectra of PBD-OH<sub>2</sub> (black trace) and the resulting PBD-GC<sub>2</sub> (red trace).

**Scheme S1.** Synthesis of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs).



**Table S1.**  $\alpha,\omega$ -Dihydroxy and dicyclocarbonate telechelic PEGs characteristics.

	$M_{n,SEC}^b$	$D_M^b$
PEG <sub>400</sub> -OH <sub>2</sub>	-	-
PEG <sub>400</sub> -GC <sub>2</sub>	-	-
PEG <sub>4000</sub> -OH <sub>2</sub>	3950	1.10
PEG <sub>4000</sub> -GC <sub>2</sub>	4400	1.18

<sup>a</sup> Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected  $M_n$  values).



**Table S2.**  $\alpha,\omega$ -Dihydroxy and dicyclocarbonate telechelic PEE characteristics.

	$M_{n,NMR}^a$	$M_{n,SEC}^b$	$D_M^b$
PEE-OH <sub>2</sub>	1000	1040	2.24
PEE-GC <sub>2</sub>	1200	1090	2.14

<sup>a</sup> Determined by NMR analysis of the isolated polymer, from <sup>1</sup>H resonances of both terminal groups <sup>b</sup> Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected  $M_n$  values).

**Table S3.**  $\alpha,\omega$ -Dihydroxy and dicyclocarbonate telechelic PBD characteristics.

	$M_{n,SEC}^a$	$D_M^a$	% 1,4-cis units	% 1,4-trans units	% 1,2 units
PBD-OH <sub>2</sub>	3450	2.4	20.0	60.0	20.0
PBD-GC <sub>2</sub>	3800	2.29	20.0	60.0	20.0

<sup>a</sup> Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected  $M_n$  values).