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**α,ω -Di(glycerol carbonate) Telechelic Polyesters and Polyolefins
as Precursors to PolyHydroxyUrethanes: an Isocyanate-free approach**

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Abstract

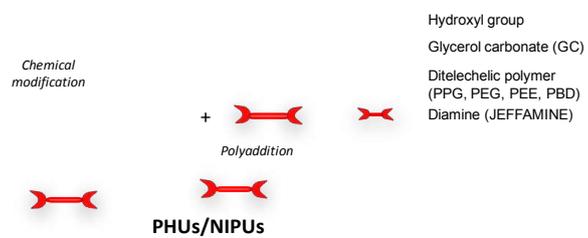
α,ω -Di(glycerol carbonate) telechelic poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG), poly(ester ether) (PEE), and poly(butadiene) (PBD) have been synthesized upon chemical modification of the corresponding α,ω -dihydroxy telechelic polymers (PPG-OH₂, PEG-OH₂, PEE-OH₂ and PBD-OH₂, respectively). Tosylation of the polymer diols with 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) afforded, in high yields, the desired PPG, PEG, PEE and PBD end-capped at both termini with five-membered ring cyclic glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, GC). The GC-functionalization of the polymers at both chain-ends has been confirmed by NMR (¹H, ¹³C, 1D and 2D) and FTIR spectroscopies. Using PPG-GC₂ to demonstrate the concept, the corresponding polyhydroxyurethanes (PHUs/non-isocyanate polyurethanes (NIPUs)) have been subsequently prepared following a non-isocyanate method, upon ring-opening catalyst-free polyaddition of the PPG-GC₂ with JEFFAMINEs ($M_n = 230$ -2000 g.mol⁻¹). The effect of various additives introduced during the polyaddition reaction has been studied at different temperatures. In particular, addition of LiBr (5 mol%) to the reaction medium was found to slightly promote the cyclocarbonate/amine reaction. The polymerization process was supported by FTIR and by SEC analyses.

Keywords

Diol, Glycerol carbonate, telechelic polymers, hydroxy telechelic polymers, non-isocyanate polyurethane (NIPU), poly(hydroxy urethane) (PHU), poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), poly(butadiene) (PBD), polyester

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Synthesis of α,ω -di(glycerol carbonate) telechelic polyesters, polyethers and polydienes as precursors to polyhydroxyurethanes in a catalyst-free, isocyanate-free procedure.



Introduction

With a global market reaching 14 million tons in 2011, polyurethanes (PUs) are attracting much attention both in industry and in academia. Indeed PUs are used in a wide range of applications as commodity or specialty polymer materials, including adhesives, coatings, sealants, foams, thermoplastics, thermorigid, elastomers, or implantable biomedical devices.¹ PUs featuring pendant functional and reactive hydroxy groups, namely polyhydroxyurethanes (PHUs), have also become increasingly investigated for their appealing mechanical and degradation properties.² PHUs exhibit, in comparison to PUs, greater thermal stability (degradation temperature of a urethane unit *ca.* 230 °C) as the result of the absence of biuret (degradation temperature *ca.* 150 °C) or allophanate (degradation temperature *ca.* 120 °C) groups. Also, the intermolecular and intramolecular hydrogen bondings between the hydroxyl groups and the β -carbonyl oxygens within urethane repeating units render PHUs more resistant to organic solvents. In addition, the hydroxyl groups provide greater hydrophilicity and decreased crystallinity, thus making the polymer less vulnerable to environmental degradation. Besides, in regard of general “green considerations”, such PHUs are harmless in terms of toxicity. Finally, chemical modification of the pendant OH groups further provides several opportunities.^{1,2}

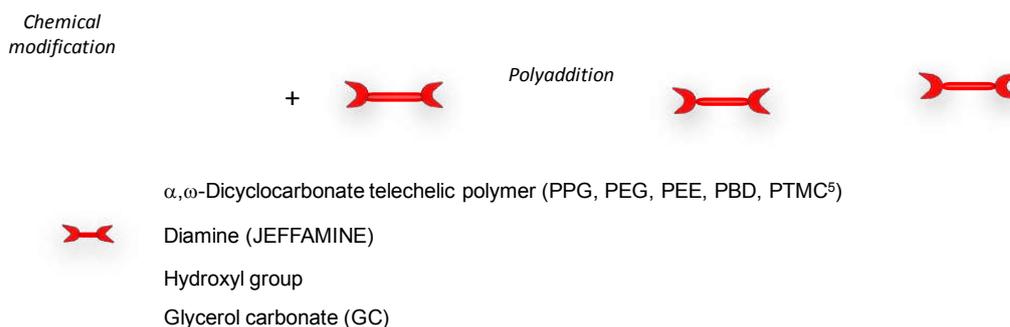
The common method for the production of PUs involves the reaction of isocyanates with diols/polyols catalyzed by a tin compound (most commonly, dibutyl tin laurate (DBTL)). In this process, the use of hazardous isocyanates and phosgene has raised severe toxicity and environmental issues.¹ However, within the recent scientific eagerness towards biofriendly PUs, current attention is being focused on the development of non-isocyanate polyurethanes (NIPUs).^{2,3} Sustainable routes to NIPUs essentially revolve around the valorization of various renewable natural oil polyols (referred to as NOPs) derived from plants. Extensive work aims at chemically modifying vegetable oils (triglycerides, i.e. soybean, sunflower, palm, linseed

oils...) so as to establish a chemical platform as non-petrochemical feedstock for the synthesis of NIPUs.⁴ This approach certainly presents numerous advantages among which the major one is the accessibility to renewable triglycerides which remain the cheapest and most abundant biological sources available. However, the one significant limitation of these NIPU precursors remains their molar mass which cannot be fine-tuned – as it is essentially dictated by the natural oil itself – which restrains their range of properties and therefore of applications.

Within our ongoing studies on NIPUs derived from synthetic polymers, we are developing such polymer materials with a tunable/controlled soft segment molar mass.^{5,6} Our general strategy involves the synthesis of α,ω -dicyclocarbonate end-functionalized pre-polymers which are subsequently reacted with a diamine in a polyaddition reaction to provide PHUs in an isocyanate-free process (Scheme 1). Following the pioneering studies of, in particular Endo, on the ring-opening of five-, six- or seven-membered ring cyclic carbonates by amines affording PHUs/NIPUs of molar mass in the range of $M_n = 20,000\text{--}30,000 \text{ g.mol}^{-1}$,^{7,8} there is currently a reemergence of this “cyclic carbonate/amine” route. One of our approaches consists in the direct synthesis of five-membered ring cyclic glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, GC) end-capped polyolefins, from the ring-opening metathesis polymerization (ROMP) using GC derivatives as chain transfer agents.⁶ In particular, acryloyl-GC smoothly enabled the preparation of well-defined α,ω -di(glycerol carbonate) telechelic poly(cyclooctene) with $M_{n,\text{NMR}}$ up to 49,200 g.mol^{-1} and $D_M = 1.54$. Besides this direct route, our earlier achievement enabled the synthesis of poly(trimethylene carbonate) (PTMC) end-capped at both termini by GC (PTMC-GC₂), obtained upon chemical modification of the analogous α,ω -dihydroxy telechelic PTMC (PTMC-OH₂) – itself prepared by ring-opening polymerization of the corresponding trimethylene carbonate monomer derived from glycerol.^{5,9,10} The corresponding high molar mass ($M_{n,\text{SEC}} = 68,100 \text{ g.mol}^{-1}$; D_M

= 1.20) poly(TMC hydroxyurethane) was next prepared upon ring-opening polyaddition with 1,6-hexanediamine. We currently aim at extending this latter original route to NIPUs, using other dihydroxy- and subsequently dicyclocarbonate-telechelic pre-polymers, as well as other diamines such as the Jeffamines, ultimately offering NIPUs/PHUs featuring various properties. (Scheme 1). To our knowledge, besides these two examples,^{5,6} dicyclocarbonate telechelic polymers remain rare. Another objective of our work is to valorize GC a cheap bio-resourced alcohol obtained from glycerol, a side-product formed during the production of biodiesel and available in large quantities, as well as to promote a “greener” route. Indeed, GC is a versatile building block, nowadays driving many investigations aimed at its valorization, including in the polymer field.¹¹ Note that NIPUs have otherwise been prepared from a biscarbonate urethane featuring a glycerol carbonate moiety at each extremity and a diamine.¹²

Also, one major flaw of the glycerol carbonate/amine reaction that prevents large-scale industrial production is the high stability of the five-membered ring which considerably slows down the polymerization. Catalysts or additives are thus highly desirable to accelerate this polyaddition, although their exact operating mode remains unclear. Besides tin-based compounds (such as dibutyltinlaurate, DBTL), the use of salts that may enhance the nucleophilic addition to oxacyclic compounds or of simple bases have been reported. Also, weak yet oxophilic Lewis acids are expected to coordinate the carbonyl group of GC, possibly weakening/activating it by increasing its electrophilicity.^{7c,g,i,l,8} In particular, LiBr, and to a lesser extent KO^tBu or TBD have been shown as the most potent additives. Finally, the other main challenge to overcome for the carbonate/amine route to be competitive with the traditional isocyanate-based preparation of PUs, is to access high molar mass polymers.



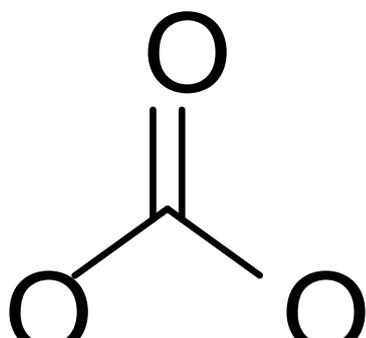
Scheme 1. Concept for the preparation of NIPUs/PHUs from the carbonate/amine reaction.

In the present contribution, we report the synthesis of α,ω -di(glycerol carbonate) telechelic poly(propylene glycol) (PPG-GC₂), poly(ethylene glycol) (PEG-GC₂), poly(ester ether) (PEE-GC₂), and poly(butadiene) (PBD-GC₂), upon reaction of the corresponding α,ω -dihydroxy telechelic polymers (PPG-OH₂, PEG-OH₂, PEE-OH₂ and PBD-OH₂, respectively; Scheme 2) with glycerol carbonate tosylate (GC-OTs). As a conceptual demonstration, the PPG thus end-capped at both termini with GC were subsequently reacted with JEFFAMINEs as diamines of different molar mass, at different temperatures and over different reaction times, thereby affording upon ring-opening polyaddition, the desired PHUs/NIPUs (Scheme 3). Our present investigations also address the efficiency of several additives to promote the carbonate/amine reaction.



Scheme 2. α,ω -Dihydroxy- and α,ω -di(glycerol carbonate) telechelic pre-polymers used towards the synthesis of PHUs/NIPUs.

Step 1: Synthesis of the GC



Scheme 3. Synthesis of PPGHU prepared from PPG-OH₂ via PPG-GC₂ (for the sake of clarity, all possible regioisomers of PPGHU obtained upon ring-opening of the cyclocarbonate ring are not represented).

Experimental section

Methods and Materials

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, GC) was purchased from ABCR chemicals and used as received. 4-Chloromethyl-1,3-dioxolan-2-one was synthesized according to the reported literature procedure.¹³ Glycerol carbonate tosylate (GC-OTs) was synthesized in 65% yield from GC through deprotonation with NaH and subsequent tosylation with TsCl (Scheme S1).¹⁴ NMR spectra are in agreement with reported data (Figures S1 and S2 for ¹H and ¹³C NMR spectra, respectively).¹⁵ α,ω -Dihydroxy telechelic poly(propyleneglycol) (VORANOL Polyol, Bostik, PPG-OH₂), poly(ethyleneglycol) (Bostik, PEG-OH₂), poly(ester ether) (REALKYD XTR 10410, Cray Valley, PEE-OH₂; a polymer produced from the polycondensation of adipic acid and diethyleneglycol), and poly(butadiene) (POLYBD R45 HTLO, Cray Valley, PBD-OH₂) featuring various molar mass values (Tables 1, S1–S3) were used as received. JEFFAMINEs (EDR 176, Huntsman; JA₂₃₀, JA₄₀₀, JA₂₀₀₀; $M_n = 230, 400, \text{ and } 2000 \text{ g}\cdot\text{mol}^{-1}$, respectively) were used as received.

Instrumentation and measurements

¹H (500 MHz) and ¹³C{¹H} (125 MHz) NMR spectra were recorded on a Bruker Avance AM 500 spectrometer at 25 °C in CDCl₃ using a relaxation delay of 3 s to enable quantitative analysis. ¹H and ¹³C NMR spectra were referenced internally relative to SiMe₄ (δ 0 ppm) using the residual solvent resonances.

Average molar mass ($M_{n,SEC}$) and dispersity ($D_M = M_w / M_n$) values of the polymers were determined by size-exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL·min⁻¹) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μ m MIXED-C 300 \times 7.5 mm columns. The polymer samples were dissolved in THF (2 mg·mL⁻¹). Average molar mass and dispersity values of high molar mass PHUs were determined by SEC in DMF with LiBr (1 g·L⁻¹) at

60 °C (flow rate = 0.8 mL.min⁻¹) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore PLgel 3 μm MIXED-D 300 × 7.5 mm columns. The polymer samples were dissolved in DMF (2 mg.mL⁻¹). All elution curves were calibrated with eleven monodisperse polystyrene standards (range of 300 to 380,000 g.mol⁻¹), and $M_{n,SEC}$ values of the polymers were uncorrected for the potential difference in hydrodynamic radius vs. polystyrene.

The molar mass of short-chain PPG samples was determined by ¹H NMR analysis in CDCl₃ from the relative intensities of the signals of the PPG main-chain methyl hydrogens (CH₃CH, δ 1.11 ppm) and those of the chain-end methylene hydrogens of GC (–CHOC(O)OCH₂–, δ 2.82, 2.64 ppm) signals.

Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF) mass spectra were recorded on an AutoFlex LT high-resolution spectrometer (Bruker) equipped with a pulsed N₂ laser source (337 nm, 4 ns pulse width) and time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron mode and an accelerating voltage of 20 kV. The polymer sample was dissolved in THF (HPLC grade, 10 mg.mL⁻¹). A saturated solution of α-cyano-4-hydroxycinnamic acid (Aldrich, 99%; 10 mg.mL⁻¹) in acetonitrile (HPLC grade) was prepared. This latter solution was then mixed in a 3:2 volume ratio with a 0.1% trifluoroacetic acid (TFA) solution in water. Both solutions were deposited sequentially on the sample target and then air-dried. Bruker Care Peptide Calibration and Protein Calibration 1 Standards were used for external calibration.

FTIR spectra of the polymers were acquired (32 scans) with a resolution of 4 cm⁻¹ on a Shimadzu IRAffinity-1 equipped with an ATR.

Synthesis of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs). NaH (1.5 g, 65 mmol) was slowly added to a solution of glycerol carbonate (7.0 g, 59 mmol) in THF (80 mL) at 0 °C. The resulting suspension was stirred at 0 °C for 20 min, then warmed to room temperature

and next stirred over 40 min. A solution of tosyl chloride (11.3 g, 59 mmol) in THF (50 mL) was then added, and the resulting white suspension was stirred at room temperature over 48 h. Then, a few drops of a saturated aqueous solution of NH_4Cl were added at 0 °C. The product was next extracted with toluene (3×50 mL); the organic fraction was dried over Na_2SO_4 and the solvent distilled off by rotary evaporation. The recovered material was purified by silica gel chromatography (pentane:ethyl acetate, 1:4 as eluent) to afford 4-tosylmethyl-1,3-dioxolan-2-one as a white powder (10.5 g, 65%). ^1H NMR (CDCl_3 , 25 °C): δ 2.45 (3H, s, Ph-CH_3), 4.20-4.55 (4H, m, $\text{CH}_2\text{-CH-}$ and CH_2OSO_2), 4.86 (1H, m, $\text{CH}_2\text{-CH-OCOO}$), 7.48 (2H, d, $o\text{-C}_6\text{H}_5$), 7.78 (2H, d, $J = 9$ Hz, $m\text{-C}_6\text{H}_5$) (Figures S1). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 25 °C): δ 21.7 (CH_3), 65.8, 68.9, 44.5 ($\text{CH}_2\text{-GC}$), 73.2, 48.9 (CH-GC), 127.9, 130.2, 131.8, 145.8 (Ar-C), 154.3 (O=COO) (Figure S2).

Functionalization of PPG-OH₂ with GC-OTs. NaH (0.150 g, 6.5 mmol) was slowly added to a solution of PPG-OH₂ (Figure S4 and Table 1; 1.00 g, 2.5 mmol) in THF (100 mL) at 0 °C. The resulting suspension was stirred at 0 °C over 20 min, then warmed to room temperature and next stirred over 60 min. GC-OTs (1.40 g, 5.1 mmol) was then added and the resulting white suspension was stirred at room temperature for 48 h. A few drops of a saturated aqueous solution of NH_4Cl were then added at 0 °C. The product was extracted with toluene (3×50 mL), the organic fraction was dried over Na_2SO_4 and the solvent distilled off. The recovered material was next dissolved in ether (50 mL) and the precipitate was removed by filtration. The filtrate was dried under vacuum to remove the solvent. A clear light-yellow oil was thus recovered (0.90 g, 90%). The final polymer was characterized by 1D and 2D NMR and FTIR, evidencing the almost quantitative functionalization (96%) of PPG-OH₂, and by SEC analysis (Table 1 and Figures 1, 2, 3 and Figures S5,S6).

Functionalization of PEG-OH₂ with GC-OTs. NaH (0.240 g, 10.0 mmol) was slowly added to a solution of PEG-OH₂ (Figure S7; 2.00 g, 5.0 mmol) in THF (30 mL) at 0 °C. The

resulting suspension was stirred at 0 °C over 20 min, then slowly warmed at room temperature and next stirred over 90 min in order to ensure complete deprotonation. GC-OTs (2.85 g, 10.5 mmol) was next added and the resulting white suspension was stirred at room temperature for 48 h. The desired product was recovered following the same procedure as described above for the isolation of PPG-GC₂. A colorless oil was thus recovered (1.62 g, 81%). The final polymer was characterized by 1D and 2D NMR, and FTIR analyses, evidencing the almost quantitative functionalization (99 %) of PEG-OH₂, and by SEC analysis (Figures S8, S9, S10, S11).

Functionalization of PEE-OH₂ with GC-OTs. NaH (0.120 g, 5.1 mmol) was added to a solution of α,ω -dihydroxy telechelic poly(ester ether) (PEE-OH₂, $M_n = 1,000 \text{ g}\cdot\text{mol}^{-1}$; Figures S12, S13 and Table S2; 2.30 g, 2.3 mmol) in THF (30 mL) at 0 °C. The resulting suspension was stirred at room temperature over 2 h. GC-OTs (1.27 g, 4.65 mmol) was then added and the resulting white suspension was stirred at room temperature for 48 h. The desired product was recovered following the same procedure as described above for the isolation of PPG-GC₂. A clear light oil was thus recovered (2.07 g, 90%). The final polymer was characterized by 1D and 2D NMR, FTIR and MALDI-ToF MS evidencing the almost quantitative functionalization (98%) of the PEE-OH₂, and by SEC analysis (Table S2 and Figures S14, S15, S16, S17, S18,S19).

Functionalization of PBD-OH₂ with GC-OTs. NaH (0.080 g, 3.3 mmol) was slowly added to a solution of PBD-OH₂ (2.90 g, 0.85 mmol; Figure S20) in THF (40 mL) at 0 °C. The resulting suspension was stirred at room temperature 3 h in order to ensure complete deprotonation. GC-OTs (0.50 g, 1.8 mmol) was next added and the resulting white suspension was stirred at room temperature over 6 days. The desired product was recovered following the same procedure as described above for the isolation of PPG-GC₂. A very viscous light-yellow oil was recovered (2.17 g, 75%). The final polymer was fully characterized by 1D and 2D

NMR spectroscopy, showing almost quantitative functionalization (98%) of PBD-OH₂, and by SEC analysis (Figures S21, S22, S23, S24).

All the polymer-GC₂ samples were recovered as colorless to light yellow oils.

Poly(hydroxyurethane)s synthesis. In a typical polymerization, PPG-GC₂ (0.150 g, 0.224 mmol) and JEFFAMINE ($M_n = 230 \text{ g}\cdot\text{mol}^{-1}$, 0.051 g, 0.224 mmol; 1.0 equiv.) were mixed together as neat reagents (*i.e.*, bulk reaction) at 80 °C over 16 h (Table 2, entry 9). Various additives and molar mass of JEFFAMINE have been instigated. Monitoring of the reaction by FTIR then showed the complete disappearance of the 1,3-dioxolan-2-one (GC) band concomitant with the appearance of the urethane band at $\nu 1740 \text{ cm}^{-1}$. The PHUs/NIPUs were then characterized by SEC either in THF at 35 °C (low molar mass PHUs) or in DMF at 80 °C (high molar mass PHUs).

Results and Discussion

The poly(hydroxyurethane)s (PHUs) were prepared following a two-step strategy involving: 1) the chemical modification of preformed α,ω -dihydroxy telechelic polymers into the corresponding α,ω -di(glycerol carbonate) telechelic pre-polymers, and 2) their subsequent reaction with JEFFAMINEs (Schemes 1-3).

In the first step, the aliphatic α,ω -diols pre-polymers, namely PPG-OH₂, PEG-OH₂, PEE-OH₂, and PBD-OH₂, were each reacted with GC-OTs (Schemes 2,3). The terminal hydroxyl groups were first deprotonated upon reaction with sodium hydride in THF at 23 °C and next coupled with GC-OTS resulting in the formation of the polymers-GC₂ upon elimination of sodium tosylate (Scheme 2). The latter reagent is known to provide convenient linking with alcohols, thiols, amines and other nucleophiles.¹³⁻¹⁵ In fact, almost quantitative conversion (96-99 % yields) of both hydroxyl chain-end groups was achieved with each of the polymer diols.

Using PPG-OH₂ pre-polymers of different molar mass (Table 1) as models, we observed, unsurprisingly, that the higher the molar mass of the PPG-OH₂, the less accessible the terminal hydroxyl groups for tosylation, and thus the lower their reactivity (Figure S3). The GC-OTs functionalization procedure did not affect the polymers integrity as evidenced by unchanged molar mass values in SEC (Table 1, and Table S1, S2, S3).

Formation of the various GC-functionalized polymers was then demonstrated from NMR (¹H, ¹³C, COSY, DEPT) and FTIR spectroscopic and MALDI-ToF mass spectrometric analyses. As illustrated Figure 1 in the case of PPG₄₀₀-OH₂ (Table 1), the characteristic ¹H NMR signal of the methylene hydrogens (δ 3.65 ppm; Figure S4) adjacent to the terminal hydroxyl group completely disappeared, concomitantly to the appearance of the new signals diagnostic of the methylene (δ 2.64, 2.82 and 4.27, 4.07 ppm) and methine (δ 3.22 ppm) hydrogens of the GC end-moieties. Correspondingly, the ¹³C{¹H} NMR spectrum of PPG₄₀₀-GC₂ similarly displayed the characteristic carbonyl peak of GC (δ 154.3. ppm), along with the awaited –CH and (δ 68.3 ppm) and –CH₂ (δ 48.0, 44.2 ppm) signals (Figure 2). Both the ¹H-¹H COSY and ¹H-¹³C (DEPT) ¹H-¹³C HMQC NMR spectra of α,ω-dicyclocarbonate end-functionalized PPGs corroborated the chemical structure of the polymers and of their termini (Figures S5-S6). The disappearance of the terminal hydroxyl group of PPG₄₀₀-OH₂ precursor (ν_{OH} 3500 cm⁻¹) was clearly evidenced by FTIR which also further confirmed the presence of the GC end-carbonyl group with its typical strong ν_{C=O} observed at 1724 cm⁻¹ (Figure 3).

Table 1. α,ω-Dihydroxy (PPG-OH₂) and di(glycerol carbonate) (PPG-GC₂) telechelic PPGs characteristics.

	$M_{n,NMR}^a$ (g.mol ⁻¹)	$M_{n,SEC}^b$ (g.mol ⁻¹)	D_M^b
PPG ₄₀₀ -OH ₂	430	450	1.13
PPG ₄₀₀ -GC ₂	670	500	1.26
PPG ₁₆₀₀ -OH ₂	1600	1450	1.10

PPG ₁₆₀₀ -GC ₂	1850	1800	1.21
PPG ₂₈₀₀ -OH ₂	2800	3200	1.04
PPG ₂₈₀₀ -GC ₂	3100	3550	1.19

^a Determined by NMR analysis of the isolated polymer, from ¹H resonances of both terminal groups (refer to the Experimental Section). ^b Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).

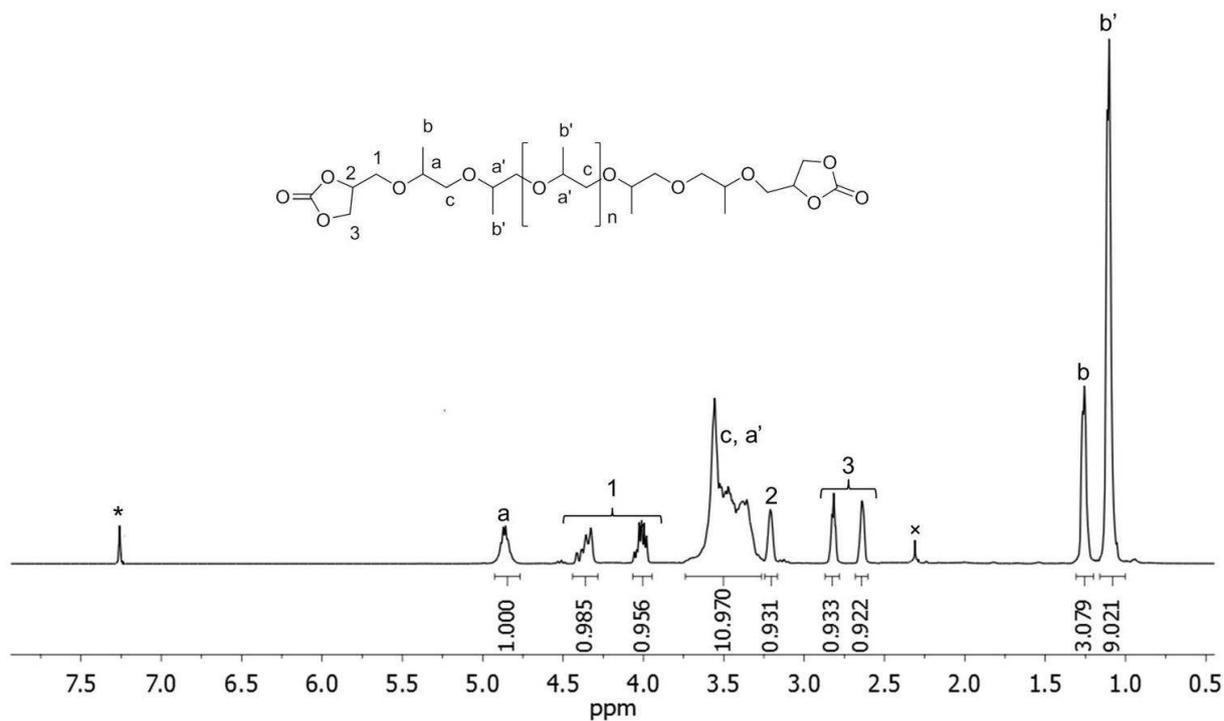


Figure 1. ¹H NMR (500 MHz, CDCl₃, 25 °C) spectrum of PPG₄₀₀-GC₂ (* stands for residual solvent resonances, ^x stands for some unidentified impurity).

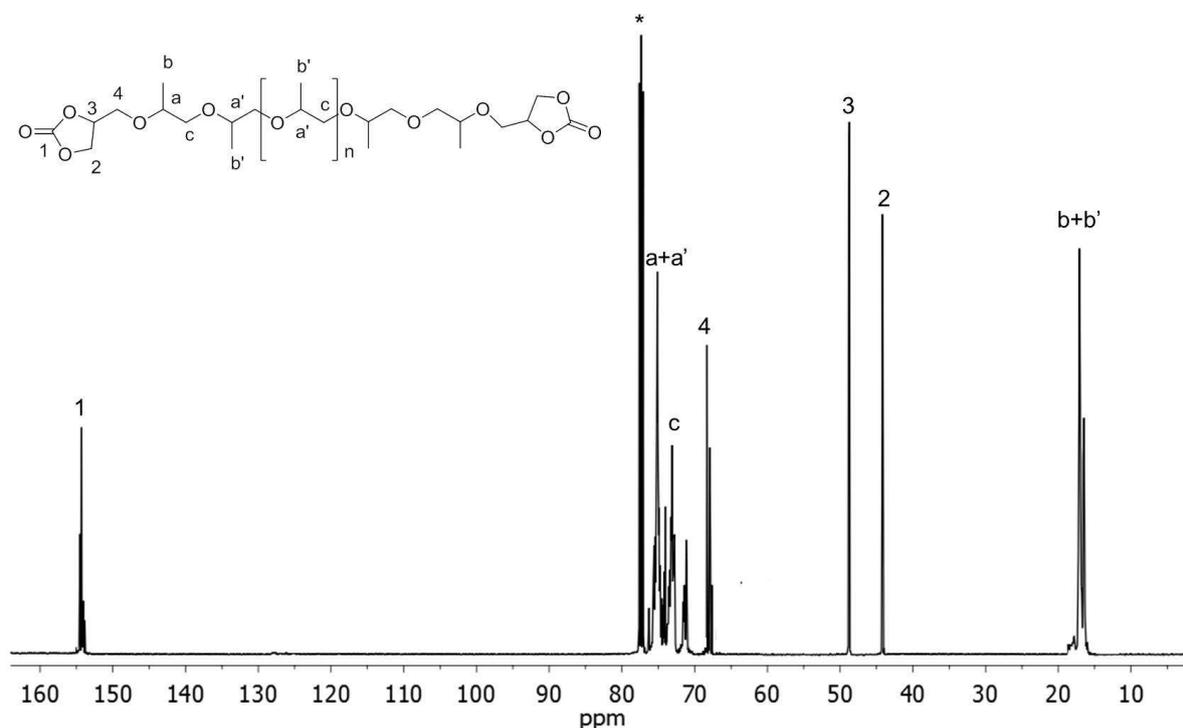


Figure 2. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of PPG₄₀₀-GC₂ (* stands for residual solvent resonances).

In a same approach, α,ω -dihydroxy telechelic PEGs with different molar mass (PEG₄₀₀, PEG₄₀₀₀) were chemically modified (*ca.* 80% yield) at both hydroxyl termini into the corresponding PEG-GC₂, without alteration of the polyester backbone (Scheme 2; Table S1). Characterizations of the PEG-GC₂ samples by NMR (¹H, ¹³C, ¹H-¹H COSY) and FTIR, in comparison to the corresponding PEG-OH₂ analyses (PEG₄₀₀-OH₂; Figure S7), clearly showed the selective functionalization of the hydroxyl chain-end groups by the desired GC moiety (Figures S8, S9, S10, S11). Also, α,ω -dihydroxy telechelic poly(ester ether), PEE-OH₂ ($M_n = 1000 \text{ g}\cdot\text{mol}^{-1}$; Figures S12, S13) was used in a same procedure to prepare the corresponding α,ω -di(glycerol carbonate) telechelic poly(ester ether), PEE-GC₂ ($M_n = 1200 \text{ g}\cdot\text{mol}^{-1}$; Table S2). Spectroscopic analyses of this PEE-GC₂ by NMR (Figures S14, S15, S16, S17), FTIR (Figure S18) and MALDI-ToF MS (Figure S19) similarly supported the quantitative functionalization (>98% yield) of the diol precursor into the expected PEE-GC₂.

Motivated by the generalization of the procedure to other non-polyester type polymers and by the possibility to access materials with reactive internal C=C bonds, the approach was next extended to a polydiene. Modification of an α,ω -dihydroxy telechelic poly(butadiene), PBD-OH₂ (Figure S20), into the corresponding GC-end capped polymer, PBD-GC₂, using the GC-Ts route, revealed also efficient). The polymer backbone remained unaffected by the reaction, and the successful functionalization by GC (98% yield) was attested by NMR (¹H, ¹³C, COSY) and FTIR analyses (Figures S21, S22, S23, and S24 and Table S3, respectively).

In a second step, the primary polyether-diamines differing in molar mass, JEFFAMINEs (JA), were reacted with the α,ω -di(glycerol carbonate) PPG₄₀₀ pre-polymer, using a constant equimolar polymer/amine ratio, thereby affording the corresponding PHUs/NIPUs, PPG₄₀₀HU. Several PHUs were thus prepared from PPG₄₀₀-GC₂ ($M_{n,NMR} = 670$ g.mol⁻¹; Table 1) used as model, while varying the molar mass of the amine (JA₂₃₀, JA₄₀₀, JA₂₀₀₀ with $M_n = 230, 400, \text{ and } 2000$ g.mol⁻¹, respectively), the nature of the additive (LiBr, ZnCl₂, ^tBuOK, LiOTf, Sc(OTf)₃, Al(OTf)₃, In(OTf)₃, dibutyl tin laurate (DBTL) with OTf = CF₃SO₃), the reaction time (16 h or 48 h), or the reaction temperature (25, 50 or 80 °C) (Scheme 3).

In the absence of any additive, the reaction temperature demonstrated a more significant impact on the efficiency of the polyaddition of PPG₄₀₀-GC₂ with JA₂₃₀, than a prolonged reaction time. Indeed, the conversion of PPG₄₀₀-GC₂ monitored over 16 h progressively increased from 25 to 67% upon going from 25 to 80 °C, respectively (Table 2, entries 1-3), whereas for a given reaction temperature (25, 50 or 80 °C), the conversion of the PPG₄₀₀-GC₂ into the corresponding PPG₄₀₀HU was hardly improved with a longer reaction time period (16 to 48 h; Table 2 entries 2 vs 4 and 3 vs 5). With JA₂₃₀, under these experimental conditions, the PPG₄₀₀HU molar mass did not exceed $M_{n,SEC} = 20,000$ g.mol⁻¹. FTIR monitoring of the polymerization from PPG₄₀₀-OH₂ via PPG₄₀₀-GC₂ (*vide supra*) to

PPGHU₄₀₀ ultimately showed, the broadening of this C=O stretch absorption to also encompass a urethane-amide I band $\nu_{\text{C=O}}$ at 1740–1720 cm^{-1} , while the corresponding amide II band was observed at $\nu_{\text{C-N}}$ 1550 cm^{-1} , along with the increase of the ν_{NH} band at 3330 cm^{-1} somewhat overlapping with the ν_{OH} at 3500 cm^{-1} , as hinted by the spectrum of the PPG₄₀₀-OH₂ precursor (possibly suggesting the occurrence of hydrogen bonding in the PHU samples) (Figure 3). Use of higher molar mass JEFFAMINEs (JA₄₀₀ and JA₂₀₀₀; $M_n = 400$ and 2000 $\text{g}\cdot\text{mol}^{-1}$, respectively), still in absence of any added additive, at 50/80 °C and over 48 h, enabled the formation of PHUs of significantly higher molar mass ($M_{n,\text{SEC}}$ up to 68,000 $\text{g}\cdot\text{mol}^{-1}$) as determined by SEC in DMF (Table 2, entries 6-9). The dispersity of all the PPG₄₀₀HUs prepared remained below $D_M = 2.6$ (Table 2).

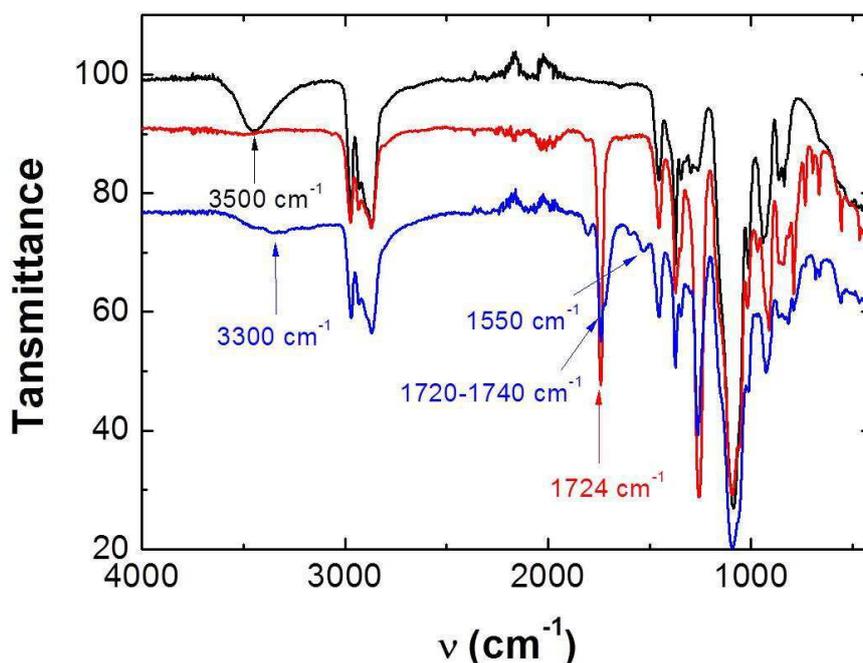


Figure 3. FTIR spectra of PPG₄₀₀-OH₂ (top black trace) and of the resulting PPG₄₀₀-GC₂ (middle red trace) and PPG₄₀₀HU after reaction with JA₂₃₀ (bottom blue trace) (Table 2, entry 5).

Table 2. Reaction of PPG₄₀₀-GC₂ with JEFFAMINEs at different reaction temperatures without an additive.^a

Entry	Temp. (°C)	Reaction time (h)	JEFFAMINE	Conv. ^b (%)	$M_{n,SEC}$ ^c (g.mol ⁻¹)	D_M ^c
1	25	16	JA ₂₃₀	25	1100	1.8
2	50	16	JA ₂₃₀	50	1900	2.3
3	80	16	JA ₂₃₀	67	6050	2.3
4	25	48	JA ₂₃₀	31	5900	2.0
5	50	48	JA ₂₃₀	59	10,700	2.4
6	80	48	JA ₂₃₀	78	20,000	2.2
7	50	48	JA ₄₀₀	89	25,000	2.5
8	80	48	JA ₄₀₀	- ^d	49,000	2.4
9	50	48	JA ₂₀₀₀	- ^d	45,000	2.6
10	80	48	JA ₂₀₀₀	- ^d	68,000	2.3

^a Polymerization conditions: PPG₄₀₀-GC₂ = 0.150 g; [PPG₄₀₀-GC₂]/[JA] = 1.0. ^b Determined by NMR analysis of the isolated polymer. ^c Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected M_n values). ^d The low intensity of the chain-end signals precluded accurate determination of the conversion.

In order to promote the cyclocarbonate/amine reaction, different additives were evaluated in the present study, namely LiBr, ZnCl₂, ^tBuOK, LiOTf, M(OTf)₃ (M = Sc, Al, In), or DBTL, to assess their influence on the PPG-GC₂/diamine reaction. The role of these additives in promoting the formation of PHU/NIPU from PPG₄₀₀-GC₂ has been evaluated by performing three sets of experiments at different temperatures: 25 °C, 50 °C and 80 °C (Tables 3, 4, 5, respectively). No matter the reaction temperature, LiBr revealed the most efficient (yet still modestly) additive, affording the highest PPG₄₀₀-GC₂ conversion, as evaluated by NMR monitoring of the signals of the GC chain-end groups. Using 5 mol% of LiBr, the conversion was slightly improved to 45–80% as compared to the LiBr-free (25–67%) PPG₄₀₀-GC₂/JA₂₃₀ polyaddition (Tables 3–5, entries 1 vs. 2). Along with such an enhanced reactivity, the procedure ran at 80 °C afforded a higher molar mass PHU/NIPU (M_n = 15,700 g.mol⁻¹, Table 5, entry 2) as compared to the oligomers formed without LiBr at 20 °C (M_n = 1100 g.mol⁻¹; Table 3, entry 1). At the opposite, In(OTf)₃ seemed ineffective, affording a conversion varying from 22 to 65% upon raising the temperature from 25 to 80 °C

(Tables 3–5, entry 8), similar to that obtained in absence of an additive (Tables 3–5, entry 1). All other additives evaluated all ranked in between these two extremes, with LiOTf, DBTL and ^tBuOK standing higher than the other metal triflates (M = Sc, Al, In) or ZnCl₂. The tentative rationalization of such an order of reactivity among these additives is that LiBr supposedly provides (to some extent, *vide infra*) better fluidity to the reaction medium than the others, upon cleaving more effectively the hydrogen bonds formed concomitantly to the synthesis of the PHUs/NIPUs. Finally, the synthesis of PPGHUs from PPG₄₀₀-GC₂ was carried out in presence of a few of these additives (5 mol%), at 80 °C in presence of the various JEFFAMINEs over 16h (Table 6). The experiments were preferentially run over a shorter reaction time (16h vs. 48h) so as to avoid the increase in viscosity of the reaction medium. Indeed, longer reaction times would most likely afford higher molar mass PHUs as observed in Table 2, but the objective of the present work was rather to demonstrate the feasibility of the approach rather than focusing on longer PHUs. Increasing the molar mass of the diamine resulted in a significant increase of the viscosity of the reaction medium and in higher molar mass PHUs. As a consequence, the low intensity of the chain-end signals in the NMR spectra precluded accurate determination of the conversion. The molar mass of the JEFFAMINE did not affect significantly the molar mass and the dispersity values of the PHUs recovered remained within the same range, regardless of the additive used. Under such operating conditions, high molar mass PPGHUs ($M_{n,SEC} \leq 52,300 \text{ g}\cdot\text{mol}^{-1}$) were prepared with $D_M \leq 2.6$.

Table 3. Reactions of PPG₄₀₀-GC₂ with JEFFAMINE JA₂₃₀ at 25 °C over 16 h, in presence of various additives.

Entry	Additive ^a (5 mol%)	Conv. ^b (%)	$M_{n,SEC}$ ^c (g·mol ⁻¹)	D_M ^c
1	-	25	1100	1.8
2	LiBr	45	4300	2.3

3	ZnCl ₂	30	2800	2.3
4	^t BuOK	40	3200	2.4
5	LiOTf,	35	2800	2.2
6	Sc(OTf) ₃	30	3500	2.5
7	Al(OTf) ₃	28	2900	2.4
8	In(OTf) ₃	22	1200	2.6
9	DBTL	38	3800	2.3

^a Polymerization conditions: PPG₄₀₀-GC₂ = 0.150 g; PPG₄₀₀-GC₂ : JA = 1. ^b Determined by NMR analysis. ^c Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected M_n values).

Table 4. Reaction of PPG₄₀₀-GC₂ with JEFFAMINE JA₂₃₀ at 50 °C over 16 h, in presence of various additives.

Entry	Additive ^a (5 mol%)	Conv. ^b (%)	$M_{n,SEC}$ ^c (g.mol ⁻¹)	\mathcal{D}_M ^c
1	-	50	1900	2.3
2	LiBr	66	6300	2.2
3	ZnCl ₂	53	4800	2.3
4	tBuOK	57	5200	2.3
5	LiOTf,	60	5600	2.2
6	Sc(OTf) ₃	52	2900	2.6
7	Al(OTf) ₃	55	3700	2.2
8	In(OTf) ₃	52	2900	2.5
9	DBTL	60	5800	2.4

^a Polymerization conditions: PPG₄₀₀-GC₂ = 0.150 g; PPG₄₀₀-GC₂ : JA = 1. ^b Determined by NMR analysis of the isolated polymer. ^c Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected M_n values).

Table 5. Reaction of PPG₄₀₀-GC₂ with JEFFAMINE JA₂₃₀ at 80 °C over 16 h, in presence of various additives.

Entry	Additive ^a (5 mol%)	Conv. ^b (%)	$M_{n,SEC}$ ^c (g.mol ⁻¹)	\mathcal{D}_M ^c
1	-	67	6030	2.3
2	LiBr	80	15,700	2.2
3	ZnCl ₂	69	12,300	2.3
4	tBuOK	71	13,100	2.3
5	LiOTf,	73	15,300	2.2
6	Sc(OTf) ₃	70	13,200	2.6
7	Al(OTf) ₃	75	12,800	2.2

8	In(OTf) ₃	65	5600	2.5
9	DBTL	73	14,600	2.4

^a Polymerization conditions: PPG₄₀₀-GC₂ = 0.150 g; PPG₄₀₀-GC₂ : JA = 1. ^b Determined by NMR. ^c Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected *M_n* values).

Table 6. Reactions of PPG₄₀₀-GC₂ with various JEFFAMINE JA₄₀₀ and JA₂₀₀₀ at 80 °C over 16 h, in the presence of various additives.

Entry	JEFFAMINE	Additive ^a (5 mol%)	Conv. ^b (%)	<i>M_{n,SEC}</i> ^c (g.mol ⁻¹)	<i>D_M</i> ^c
1	JA ₄₀₀	-	57	15,000	2.2
2	JA ₄₀₀	LiBr	- ^d	35,700	2.5
3	JA ₄₀₀	ZnCl ₂	- ^d	30,300	2.3
4	JA ₄₀₀	LiOTf,	- ^d	37,800	2.2
5	JA ₄₀₀	Sc(OTf) ₃	- ^d	30,400	2.4
6	JA ₄₀₀	Al(OTf) ₃	- ^d	28,800	2.3
7	JA ₂₀₀₀	-	- ^d	22,200	1.9
8	JA ₂₀₀₀	LiBr	- ^d	45,100	2.3
9	JA ₂₀₀₀	ZnCl ₂	- ^d	32,400	2.5
10	JA ₂₀₀₀	LiOTf,	- ^d	40,800	2.6
11	JA ₂₀₀₀	Sc(OTf) ₃	- ^d	28,700	2.5
12	JA ₂₀₀₀	Al(OTf) ₃	- ^d	52,300	2.4

^a Polymerization conditions: PPG₄₀₀-GC₂ = 0.150 g; PPG₄₀₀-GC₂ : JA = 1. ^b Determined by NMR analysis. ^c Determined by SEC in THF at 30 °C or DMF at 60 °C vs. polystyrene standards (uncorrected *M_n* values). ^d The low intensity of the chain-end signals in the NMR spectra precluded accurate determination of the conversion.

Conclusion

The chemical modification of various polymer-diols, PPG-, PEG-, PEE-, or PBD-OH₂, into the corresponding polymers α,ω -end functionalized by glycerol carbonate, through reaction with GC-OTs, provides a convenient and effective direct procedure, which can be applied to different families of polymers, namely polyethers, polyesters and polydienes. This original simple strategy towards polymers-GC₂ is a more straightforward pathway than the previously established two-step approach involving the successive modification of the

hydroxyl termini into carboxylic groups subsequently coupled to glycerol carbonate.⁵ Also, it offers a valuable complementary pathway toward the preparation of similarly GC-telechelic polydienes, which can be obtained by ruthenium-catalyzed ROMP of cycloolefins in the presence of a glycerol carbonate derivative as chain transfer agent.⁶

Polyhydroxyurethanes were next synthesized in a catalyst-free and isocyanate-free single step, through the neat (*i.e.* solvent-free) carbonate/amine polyaddition of the α,ω -dicyclocarbonate telechelic PPGs (selected for a conceptual demonstration) and JEFFAMINEs ($M_n = 230\text{-}2000 \text{ g}\cdot\text{mol}^{-1}$). A higher reaction temperature or a higher molar mass diamine enabled to prepare higher molar mass PHUs/NIPUs. When the polymerization was carried out in the presence of LiBr introduced as an additive, a slight improvement of the conversion was observed. Well-defined high molar mass PHUs/NIPUs with M_n up to 68,000 $\text{g}\cdot\text{mol}^{-1}$ were thus smoothly and easily prepared. The selectivity of the polymerization process was confirmed by NMR, FTIR and SEC analyses.

Although the main objective was not to target high molar mass values, the PHUs/NIPUs prepared from polymers-GC₂ pre-polymers rather easily provided, following this one-step carbonate/amine catalyst-free strategy, a large range of molar masses varying from $10,000 < M_{n,\text{SEC}} < 68,000 \text{ g}\cdot\text{mol}^{-1}$. These molar mass values are, to our knowledge, significantly higher than those reached for PHUs/NIPUs derived from natural vegetable oils through a same five-membered ring cyclic carbonate/diamine isocyanate-free procedure (typically $< 20,000 \text{ g}\cdot\text{mol}^{-1}$)^{1,2} and, along with the prior examples reported by Keul,^{3b} among the highest ones obtained for PHUs/NIPUs prepared from the amine/carbonate concept (Scheme 1).¹⁶

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Electronic Supplementary Information (ESI) available: Complementing ^1H , ^{13}C , COSY DEPT NMR spectra of GC-OTs, PPG₄₀₀-OH₂, PEG₄₀₀-OH₂, PEG₄₀₀-GC₂, PEE-OH₂, PEE-GC₂, PBD-OH₂, PBD-GC₂, FTIR spectra of PEG₄₀₀-OH₂, PEG₄₀₀-GC₂, PEE₄₀₀-OH₂, PEE₄₀₀-GC₂, PBD-OH₂, PBD-GC₂, and MALDI-ToF MS of PEE-GC₂ and SEC data for the PEG, PEE, PBD-OH₂ and -GC₂ polymers.

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Electronic Supplementary Information

α,ω -Di(glycerol carbonate) Telechelic Polyesters and Polyolefins

as Precursors to PolyHydroxyUrethanes: an Isocyanate-free approach

Figure S1. ^1H NMR (500 MHz, 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, CDCl_3 , 25 °C) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances)

Figure S3. ^1H NMR (500 MHz, 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. ^1H NMR (500 MHz, 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, 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, CDCl_3 , 25 °C) of $\text{PPG}_{400}\text{-GC}_2$.

Figure S7. (a) ^1H (500 MHz, CDCl_3 , 25 °C) and (b) $^{13}\text{C}\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 °C) NMR spectra of $\text{PEG}_{400}\text{-OH}_2$.

Figure S8. ^1H NMR (500 MHz, CDCl_3 , 25 °C) spectrum of the $\text{PEG}_{400}\text{-GC}_2$.

Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 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, 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. ^1H NMR (500 MHz, CDCl_3 , 25 °C) spectrum of the $\text{PEE}\text{-OH}_2$.

Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of the $\text{PEE}\text{-OH}_2$.

Figure S14. ^1H NMR (500 MHz, CDCl_3 , 25 °C) spectrum of PEE-GC₂ (* marker stands for residual toluene and ** for the starting reagent).

Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of PEE-GC₂ (* marker stands for residual toluene).

Figure S16. ^1H - ^1H COSY NMR spectrum (500 MHz, CDCl_3 , 25 °C) of PEE-GC₂.

Figure S17. ^1H - ^{13}C (DEPT) HMQC NMR spectrum (500 MHz, CDCl_3 , 25 °C) of PEE-GC₂.

Figure S18. FTIR spectra of PEE-OH₂ (black trace) and the resulting PEE-GC₂ (red trace).

Figure S19. MALDI-ToF MS spectrum of PEE-GC₂.

Figure S20. ^1H NMR (500 MHz, CDCl_3 , 25 °C) spectrum of PBD-OH₂.

Figure S21. ^1H NMR (500 MHz, CDCl_3 , 25 °C) spectrum of PBD-GC₂ (* marker stands for residual toluene).

Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of PBD-GC₂.

Figure S23. ^1H - ^1H COSY NMR (500 MHz, CDCl_3 , 25 °C) spectrum of PBD-GC₂.

Figure S24. FTIR spectra of PBD-OH₂ (black trace) and the resulting PBD-GC₂ (red trace).

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

Table S1. α,ω -Dihydroxy and dicyclocarbonate telechelic PEGs characteristics.

Table S2. α,ω -Dihydroxy and dicyclocarbonate telechelic PEE characteristics.

Table S3. α,ω -Dihydroxy and dicyclocarbonate telechelic PBD characteristics.

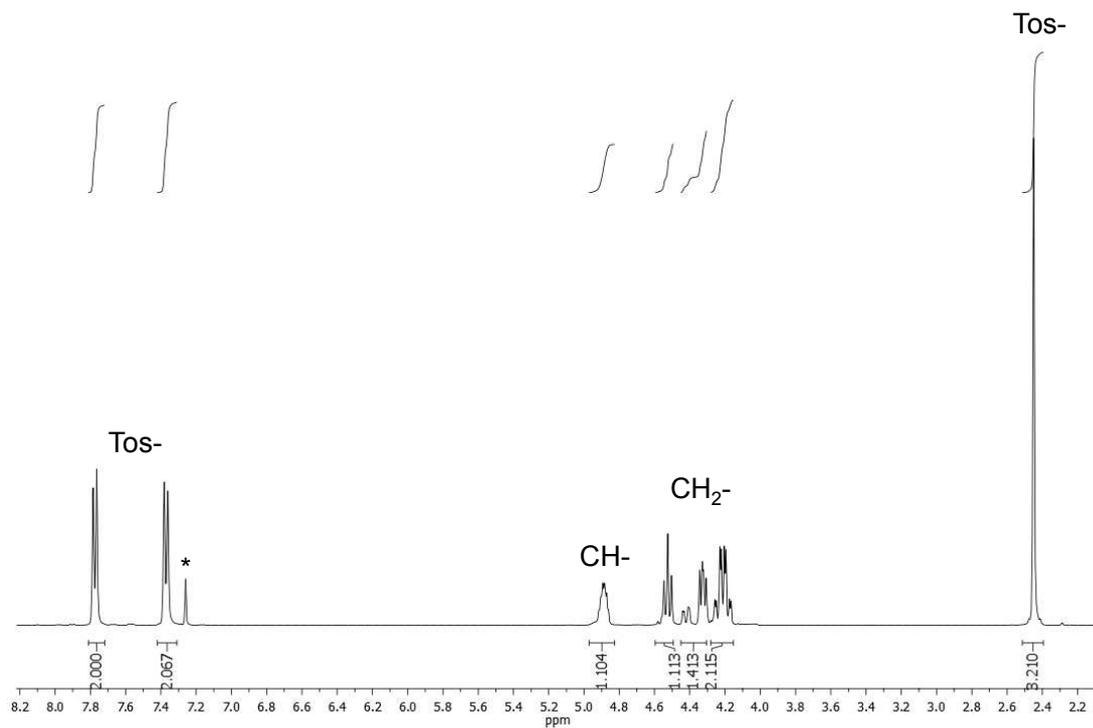


Figure S1. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances).

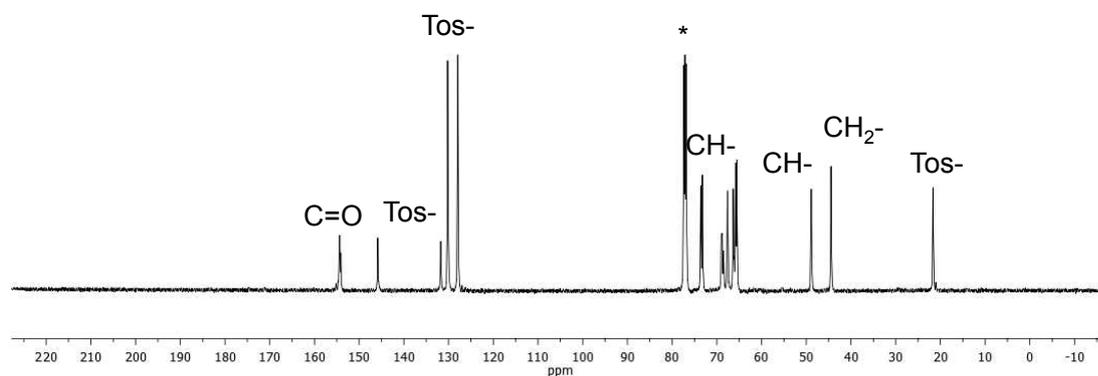


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of 4-tosylmethyl-1,3-dioxolan-2-one (GC-OTs) (* stands for residual solvent resonances).

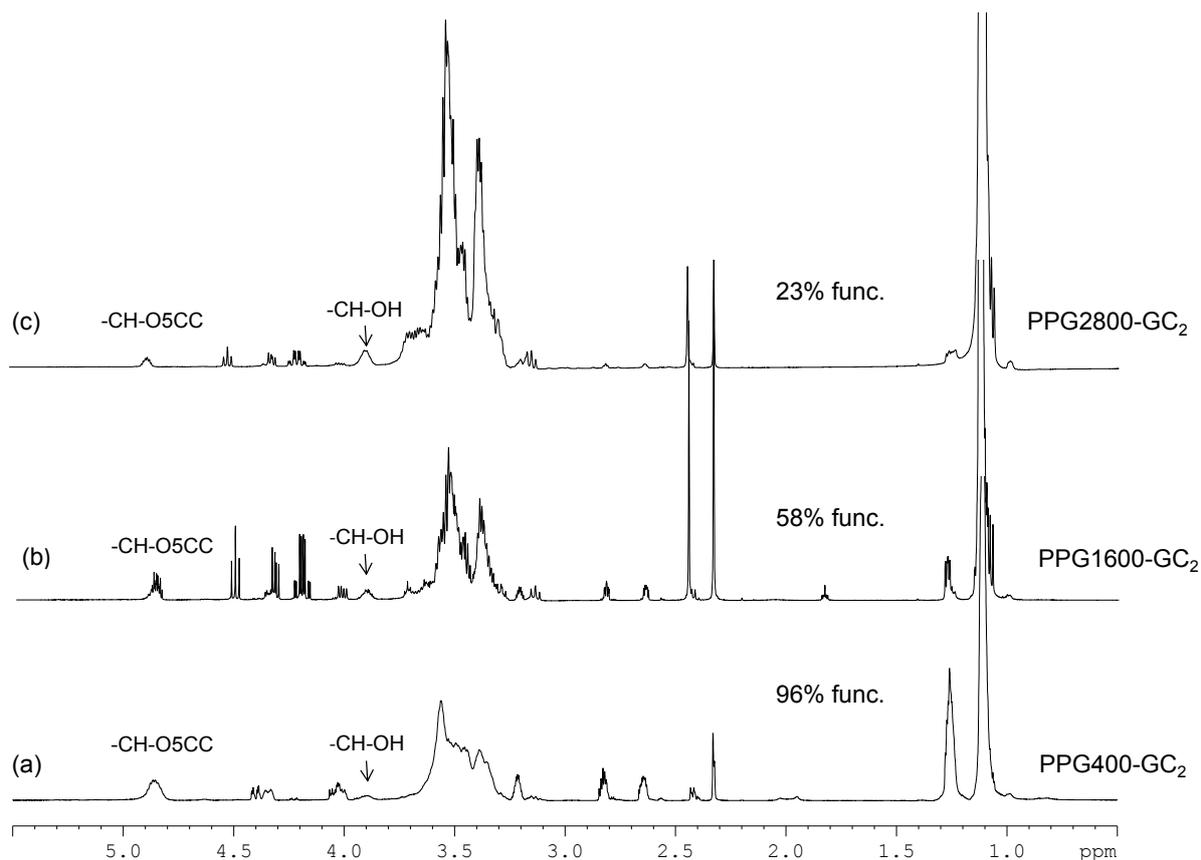


Figure S3. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectra of $\text{PPG}_{400,1600,2800}\text{-GC}_2$ prepared from the reaction of the corresponding $\text{PPG}_{400,1600,2800}\text{-OH}_2$ with GC-OTS.

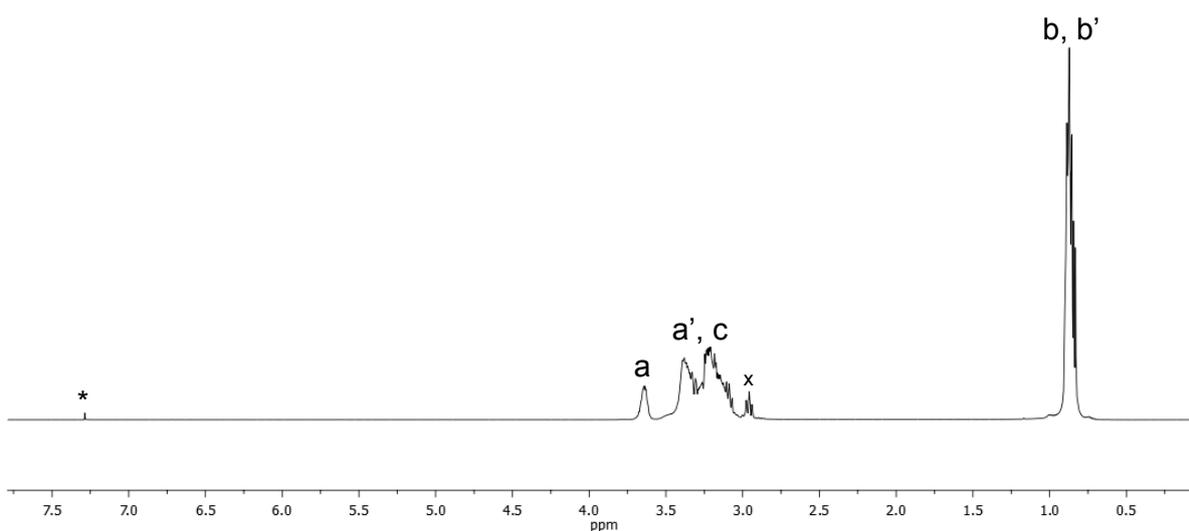


Figure S4. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of $\text{PPG}_{400}\text{-OH}_2$ (* stands for residual solvent resonances, and x stands for an unidentified impurity).

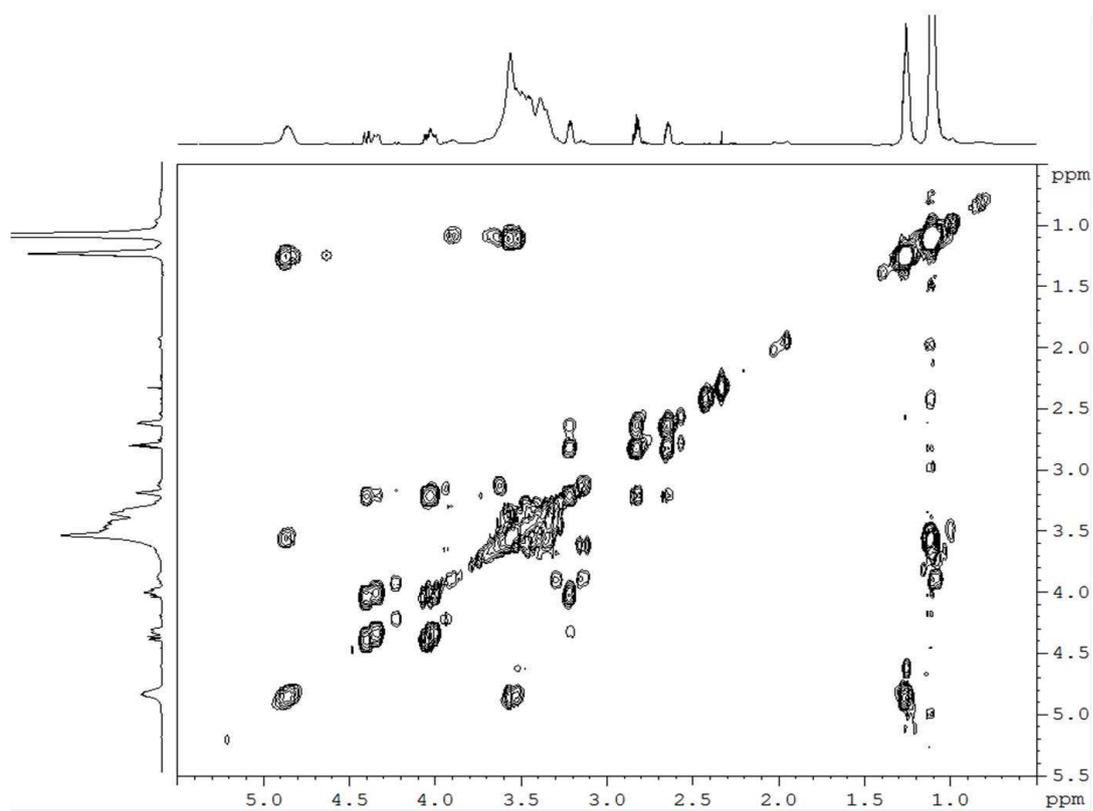


Figure S5. ^1H - ^1H COSY NMR (500 MHz, CDCl_3 , 25 °C) spectrum of $\text{PPG}_{400}\text{-GC}_2$.

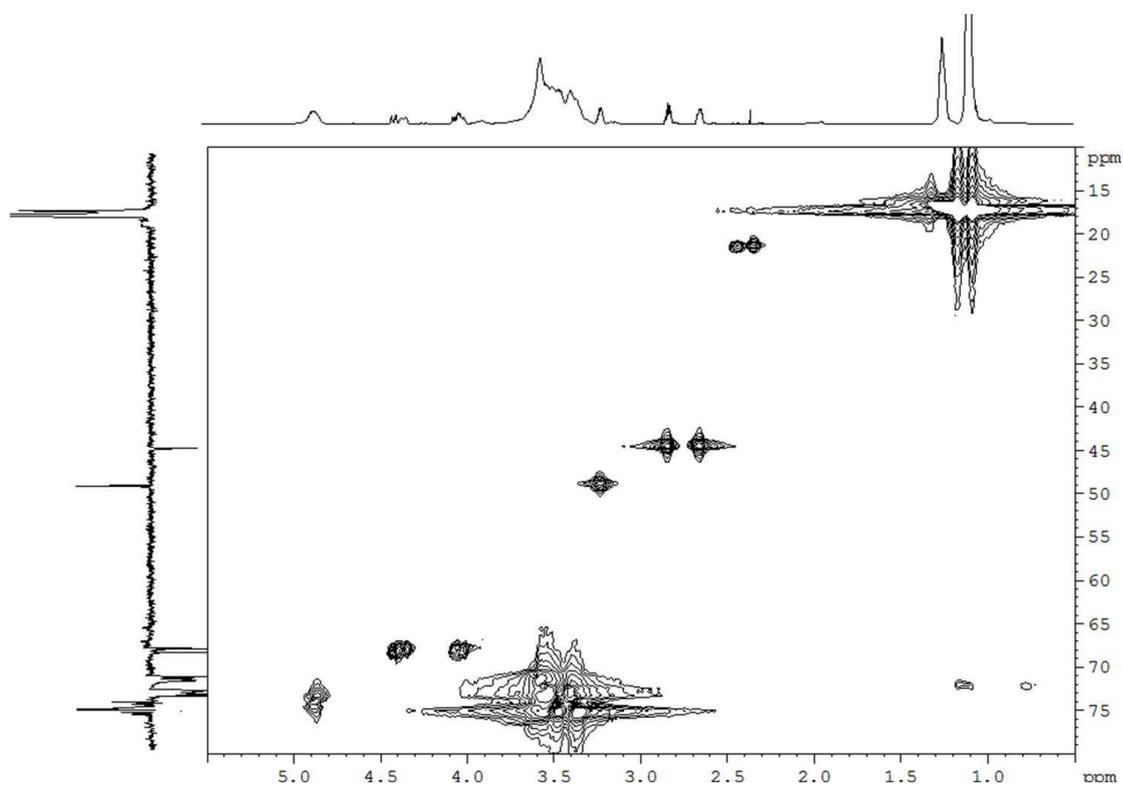


Figure S6. ^1H - ^{13}C (DEPT) HMQC NMR spectrum (500 MHz, CDCl_3 , 25 °C) of $\text{PPG}_{400}\text{-GC}_2$.

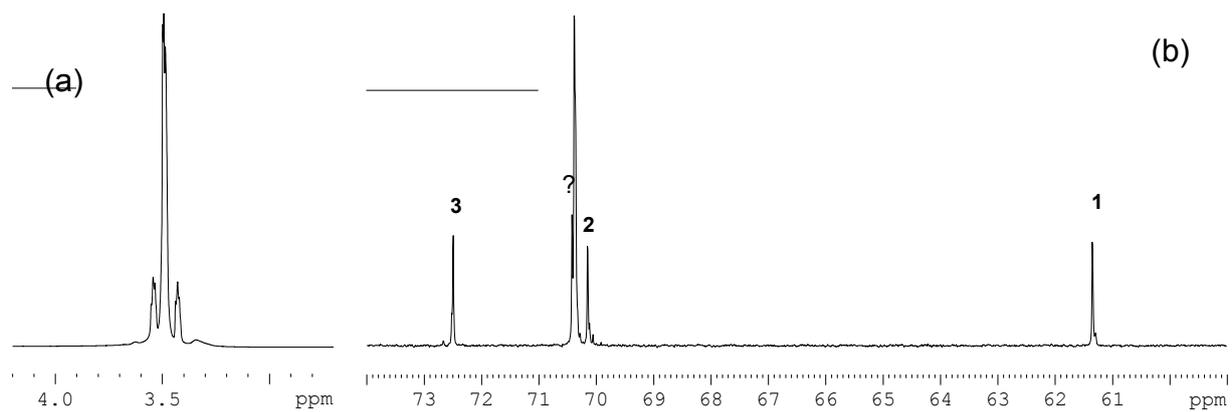


Figure S7. (a) ^1H (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) and (b) ^{13}C $\{^1\text{H}\}$ (125 MHz, CDCl_3 , 25 $^\circ\text{C}$) NMR spectra of $\text{PEG}_{400}\text{-OH}_2$.

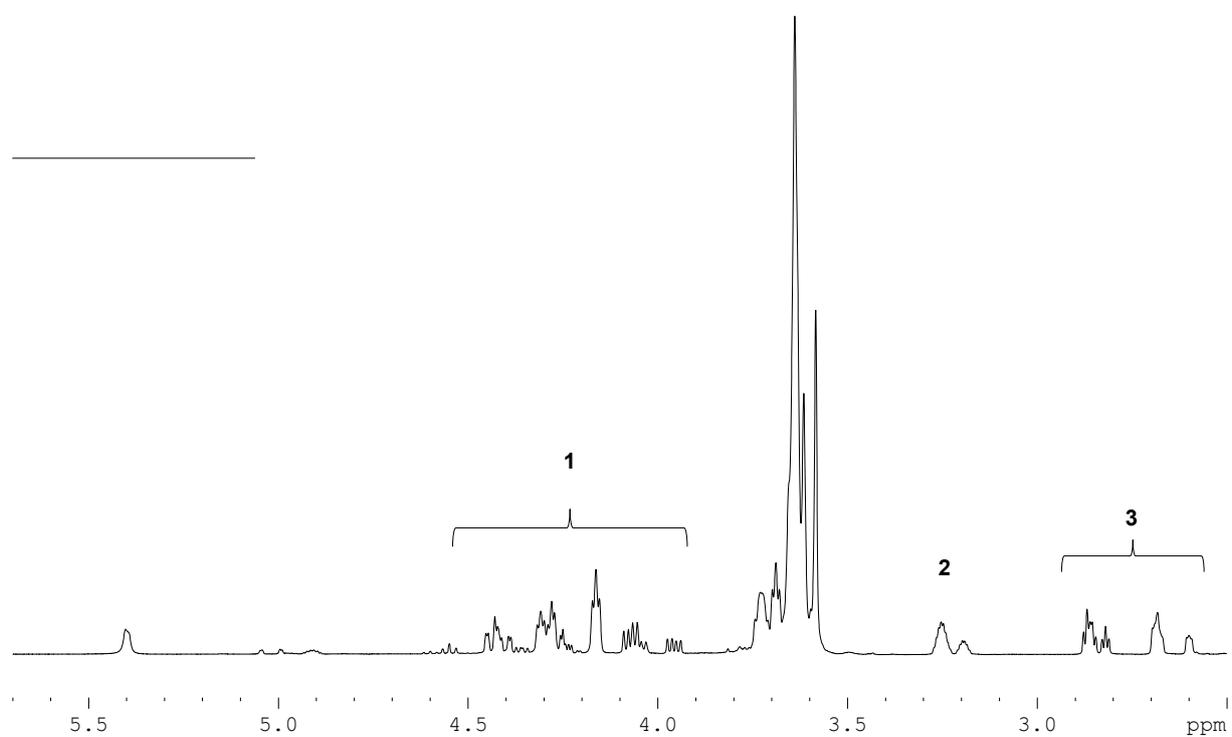


Figure S8. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$) spectrum of the $\text{PEG}_{400}\text{-GC}_2$.

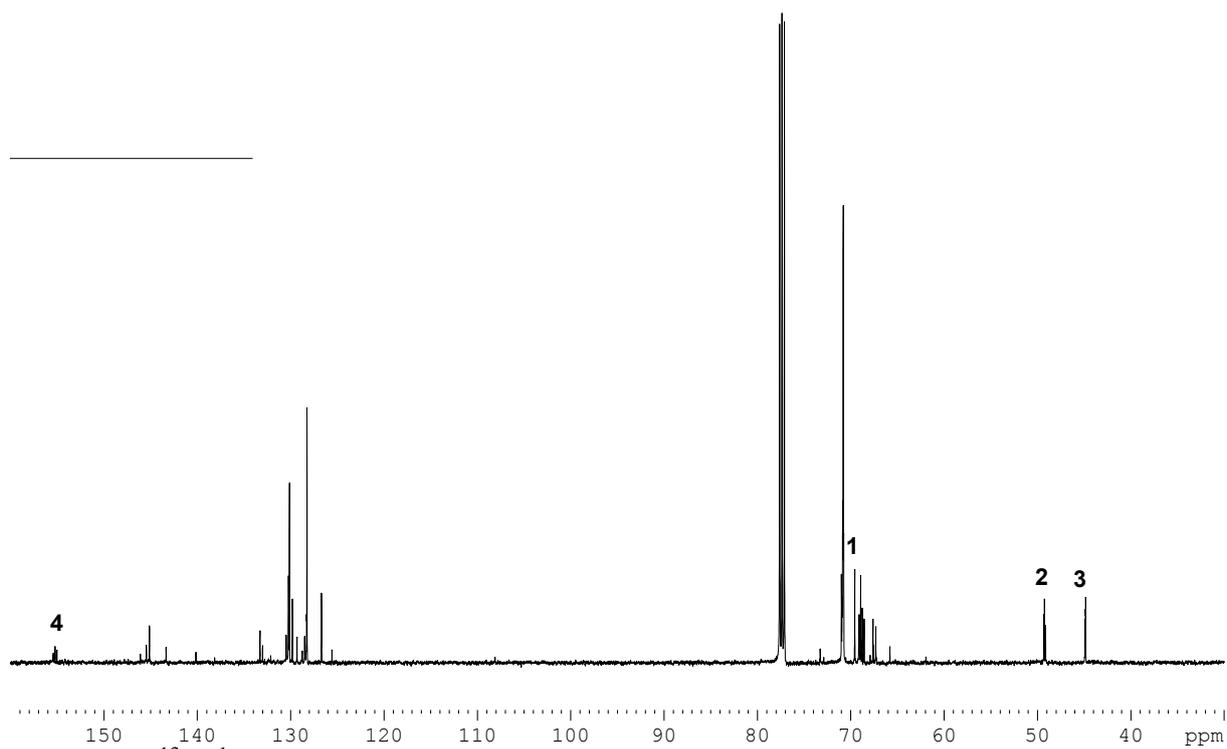


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of the PEG₄₀₀-GC₂.

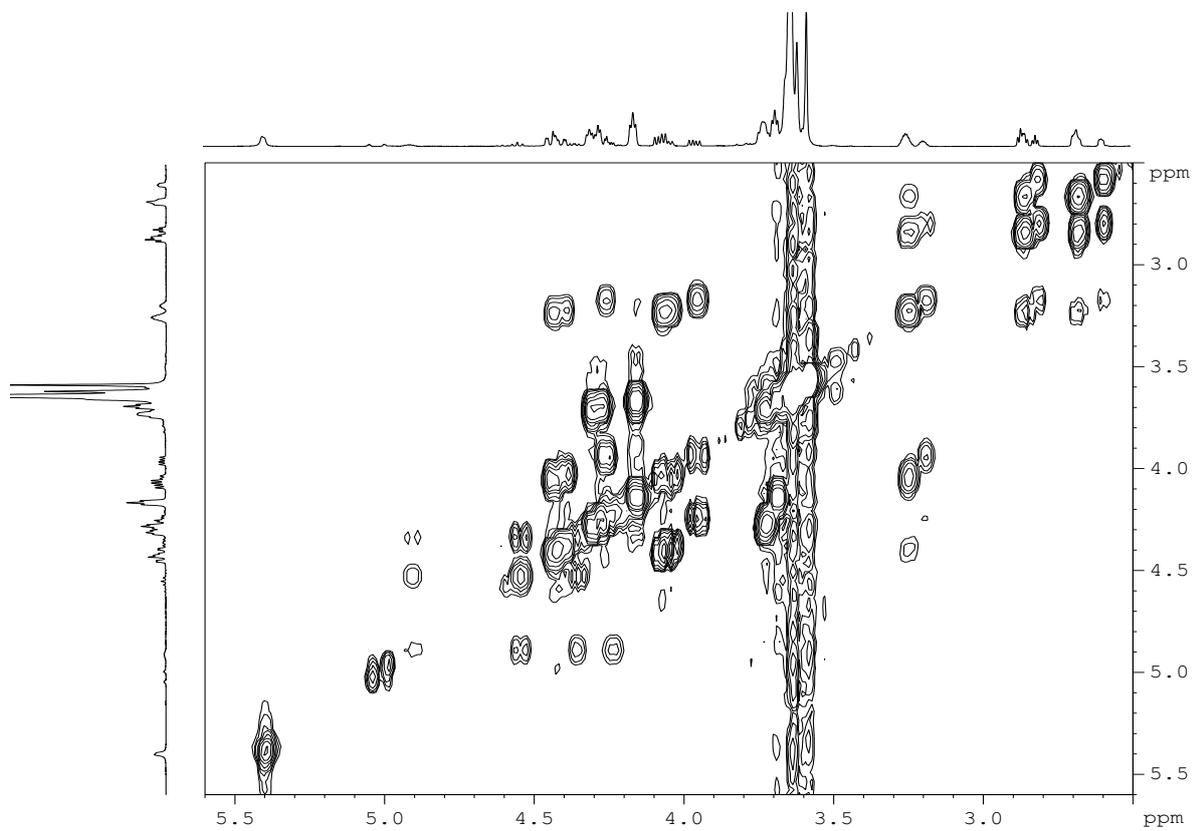


Figure S10. ^1H - ^1H COSY NMR (500 MHz, CDCl_3 , 25 °C) spectrum of the PEG₄₀₀-GC₂.

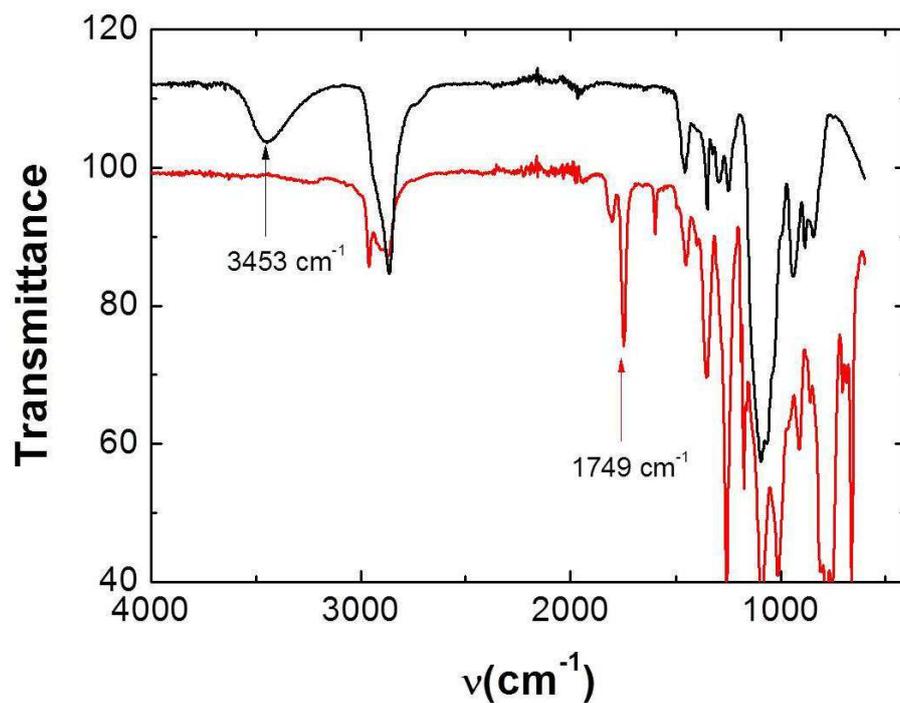


Figure S11. FTIR spectra of PEG₄₀₀-OH₂ (black trace) and the resulting PEG₄₀₀-GC₂ (red trace).

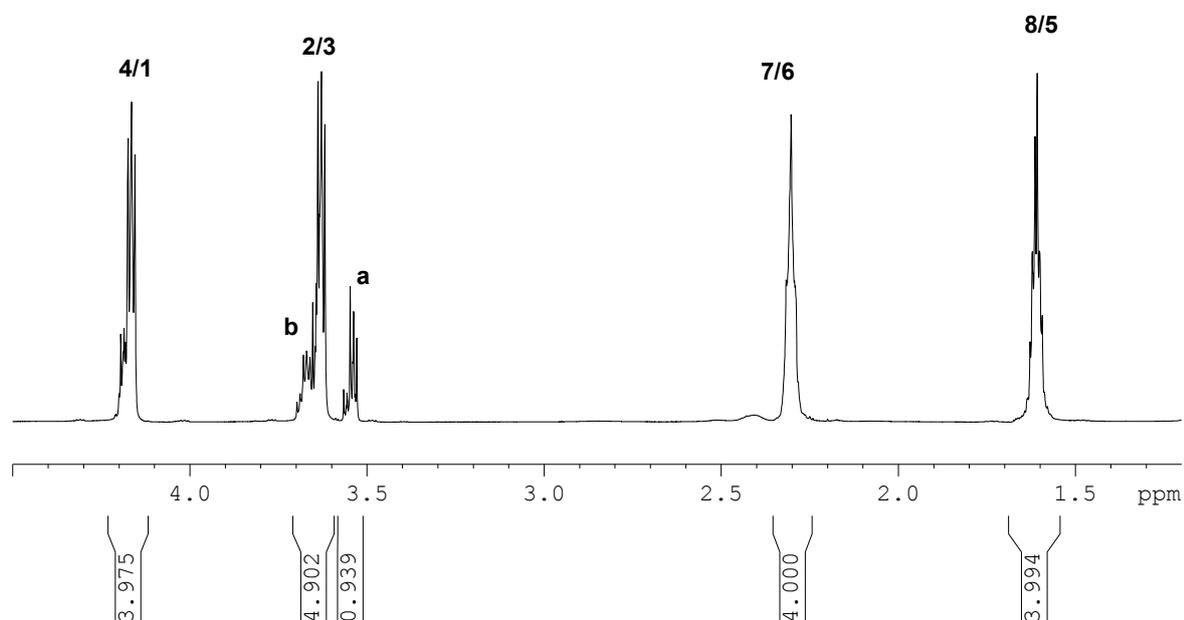


Figure S12. ¹H NMR (500 MHz, CDCl₃, 25 °C) spectrum of the PEE-OH₂.

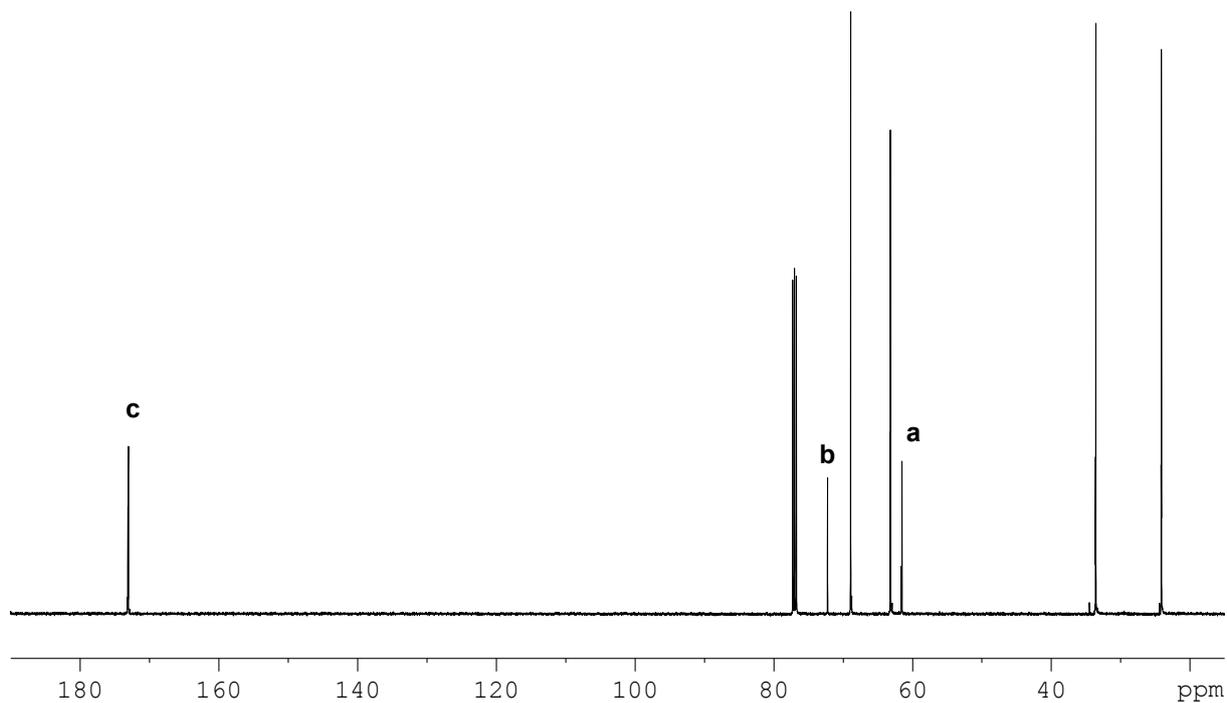


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of the PEE- OH_2 .

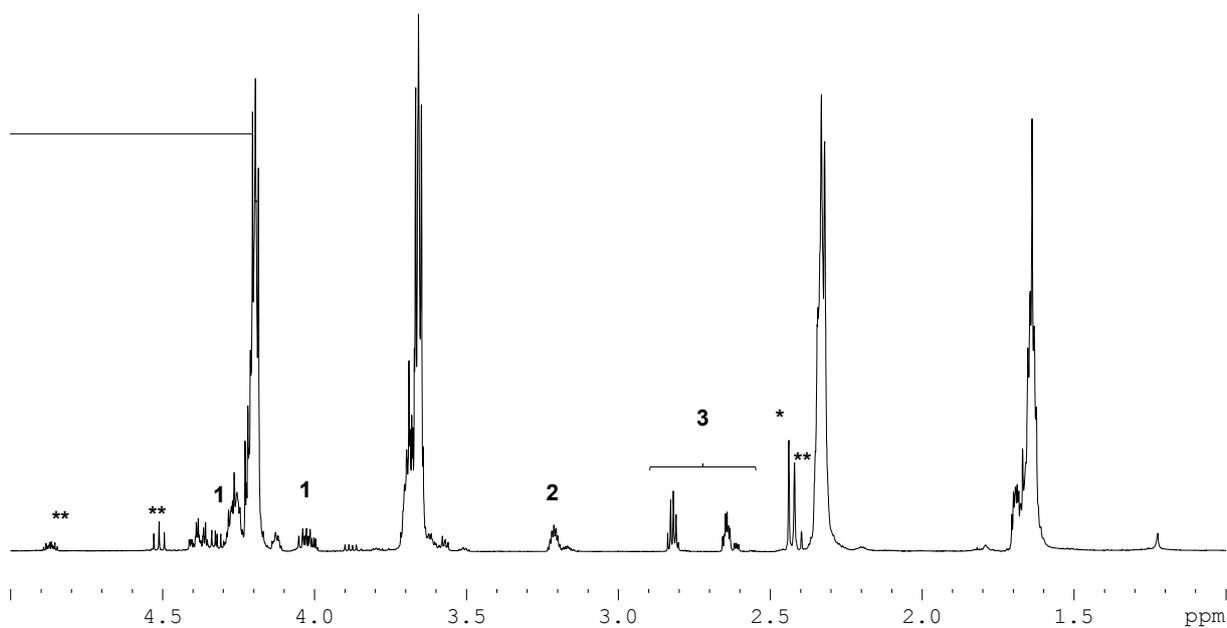


Figure S14. ^1H NMR (500 MHz, CDCl_3 , 25 °C) spectrum of PEE- GC_2 (* marker stands for residual toluene and ** for the starting reagent).

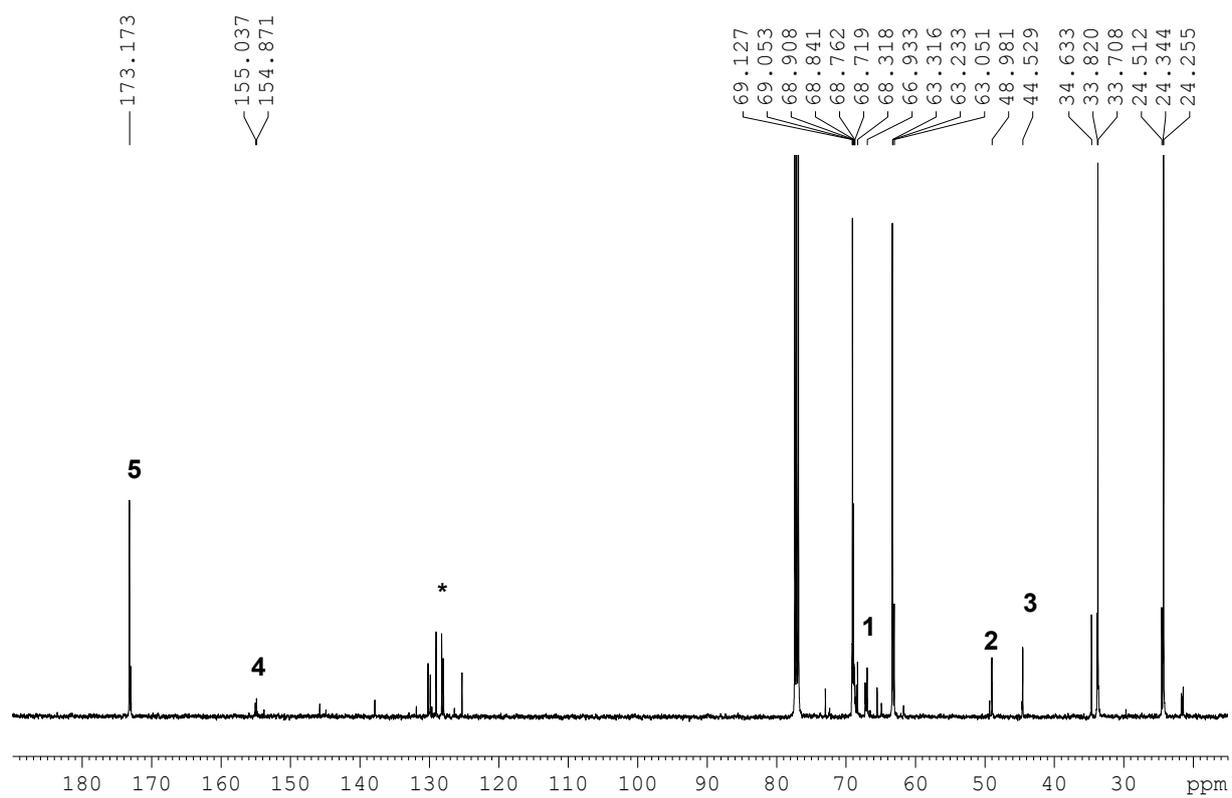


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of PEE- GC_2 (* marker stands for residual toluene).

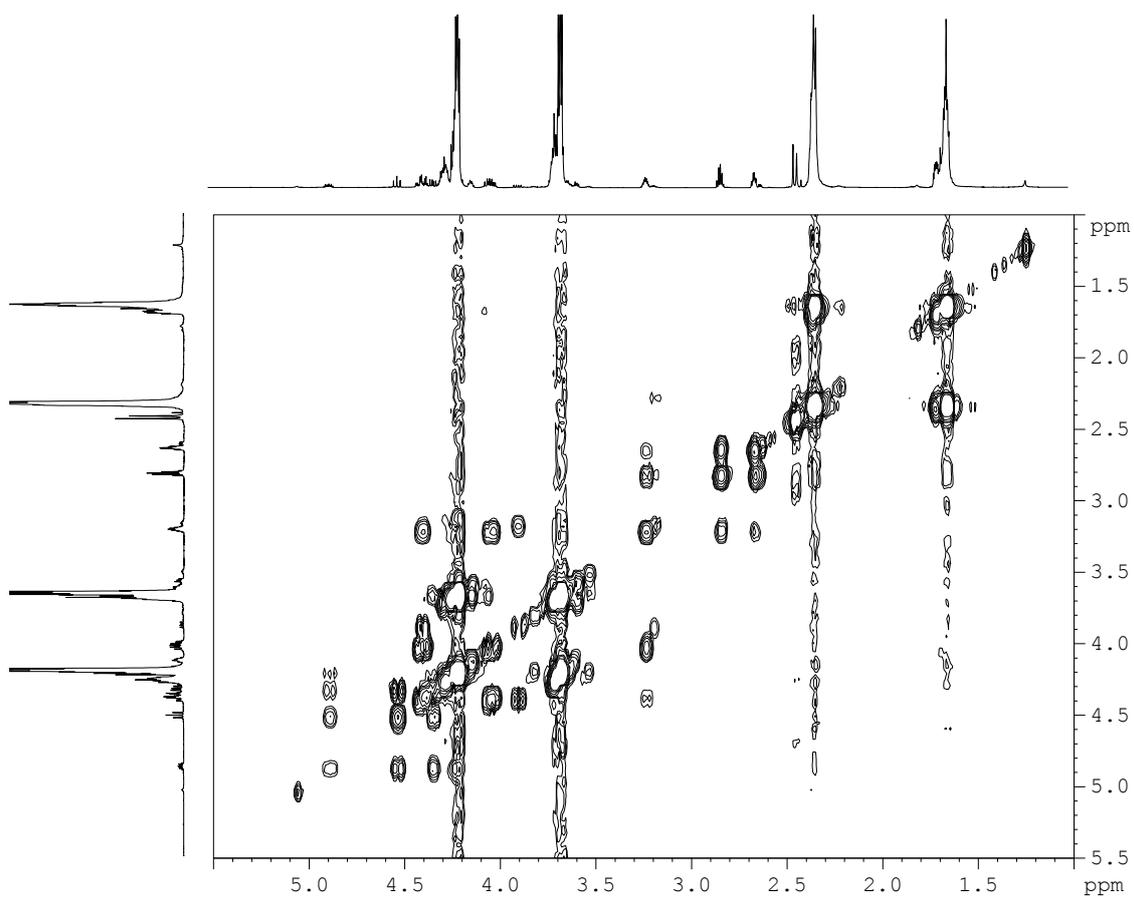


Figure S16. ^1H - ^1H COSY NMR spectrum (500 MHz, CDCl_3 , 25 °C) of PEE-GC₂.

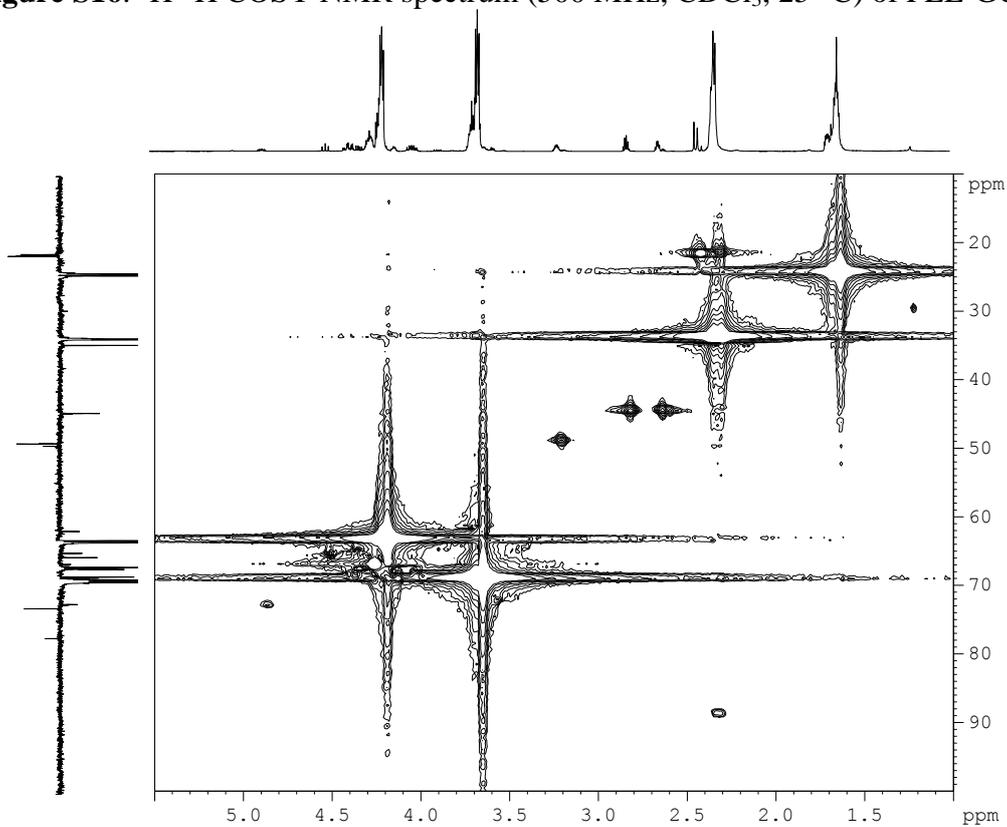


Figure S17. ^1H - ^{13}C (DEPT) HMQC NMR spectrum (500 MHz, CDCl_3 , 25 °C) of PEE-GC₂.

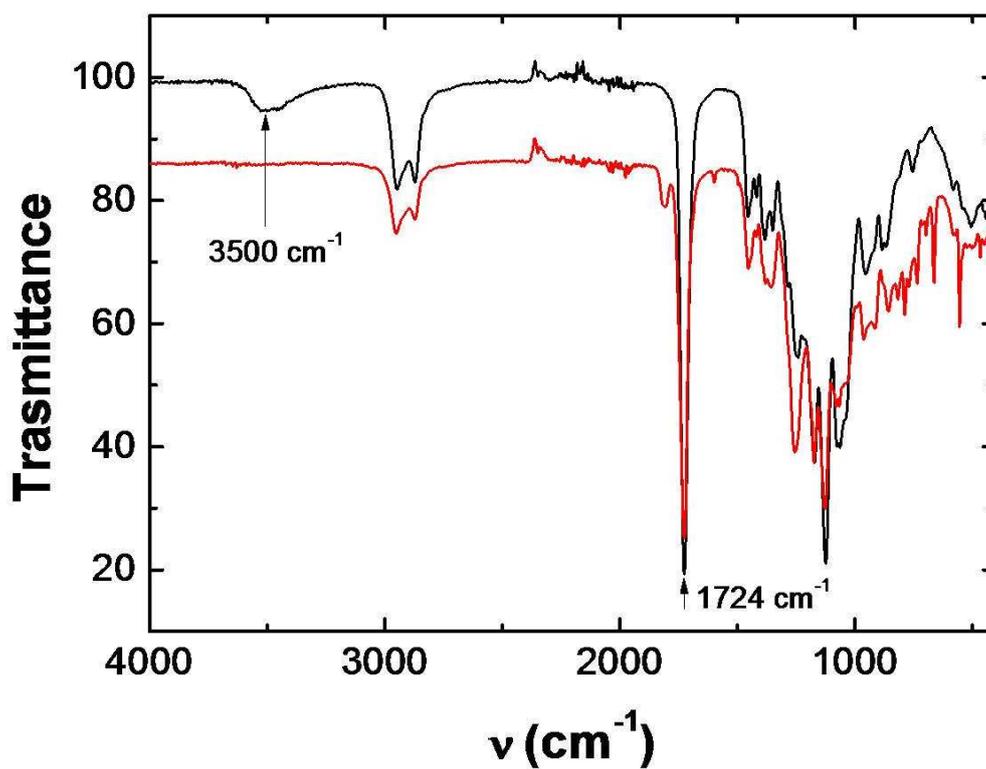


Figure S18. FTIR spectra of PEE-OH₂ (black trace) and the resulting PEE-GC₂ (red trace).

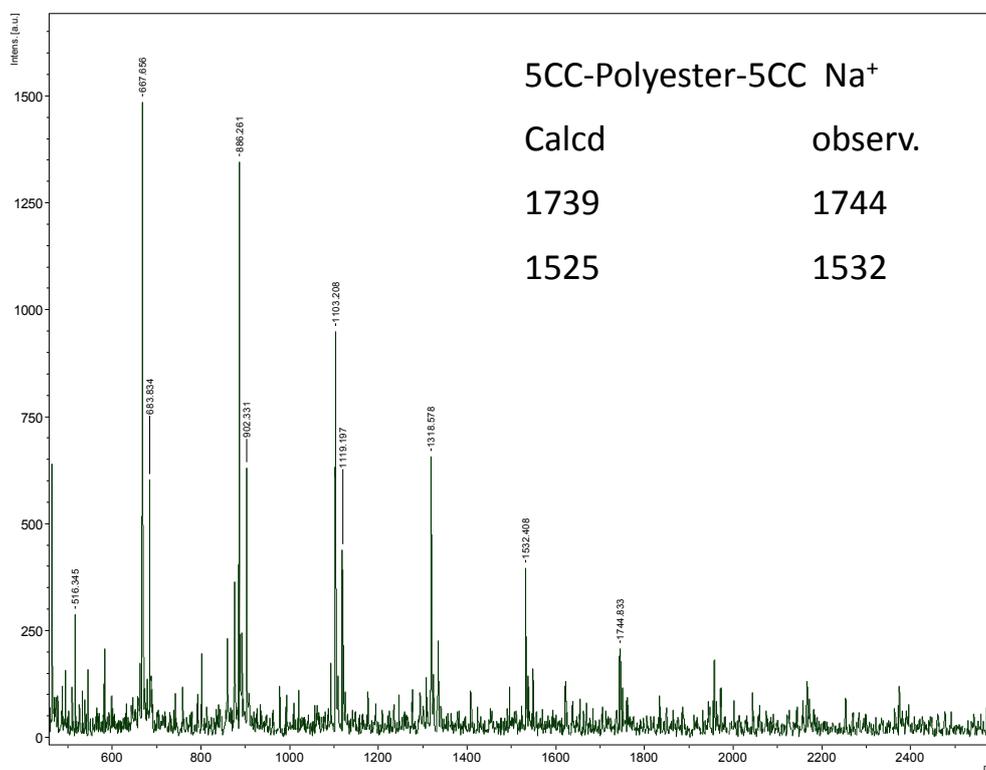


Figure S19. MALDI-ToF MS spectrum of PEE-GC₂.

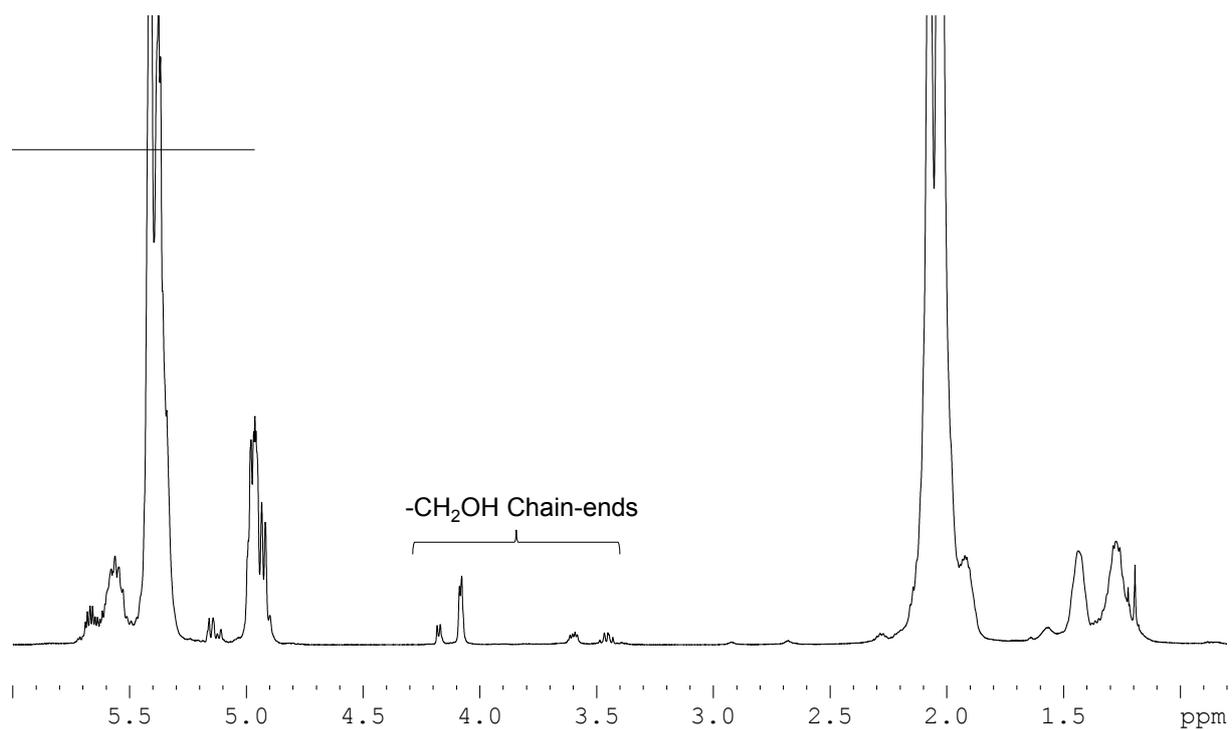


Figure S20. ¹H NMR (500 MHz, CDCl₃, 25 °C) spectrum of PBD-OH₂.

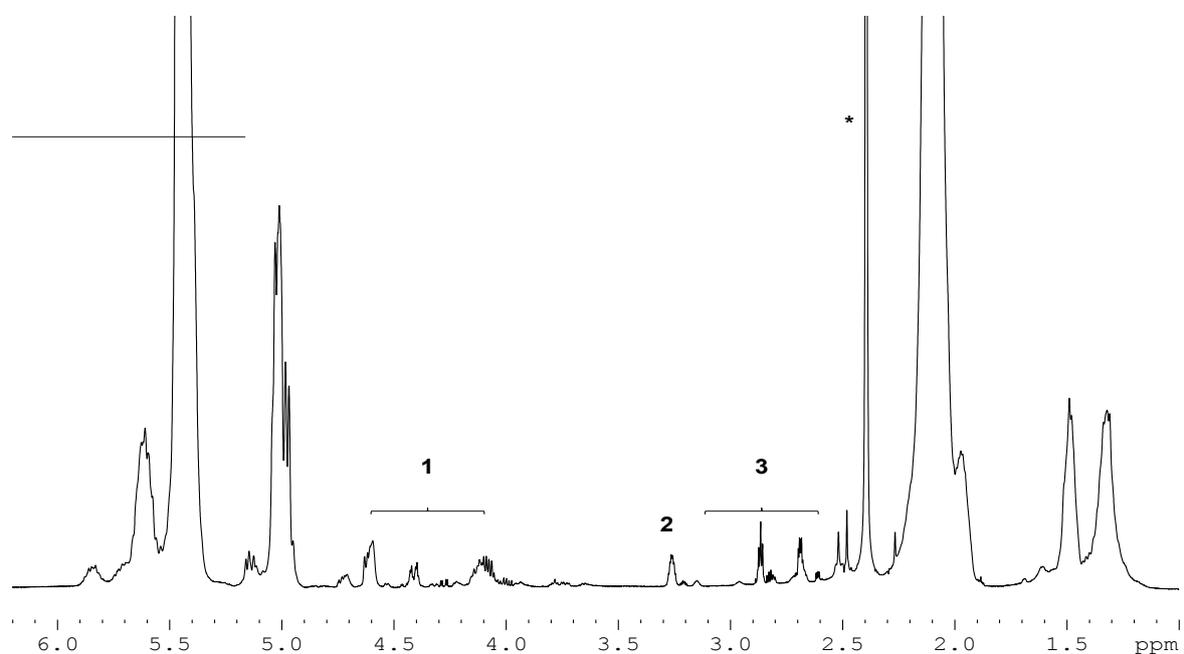


Figure S21. ¹H NMR (500 MHz, CDCl₃, 25 °C) spectrum of PBD-GC₂ (* marker stands for residual toluene).

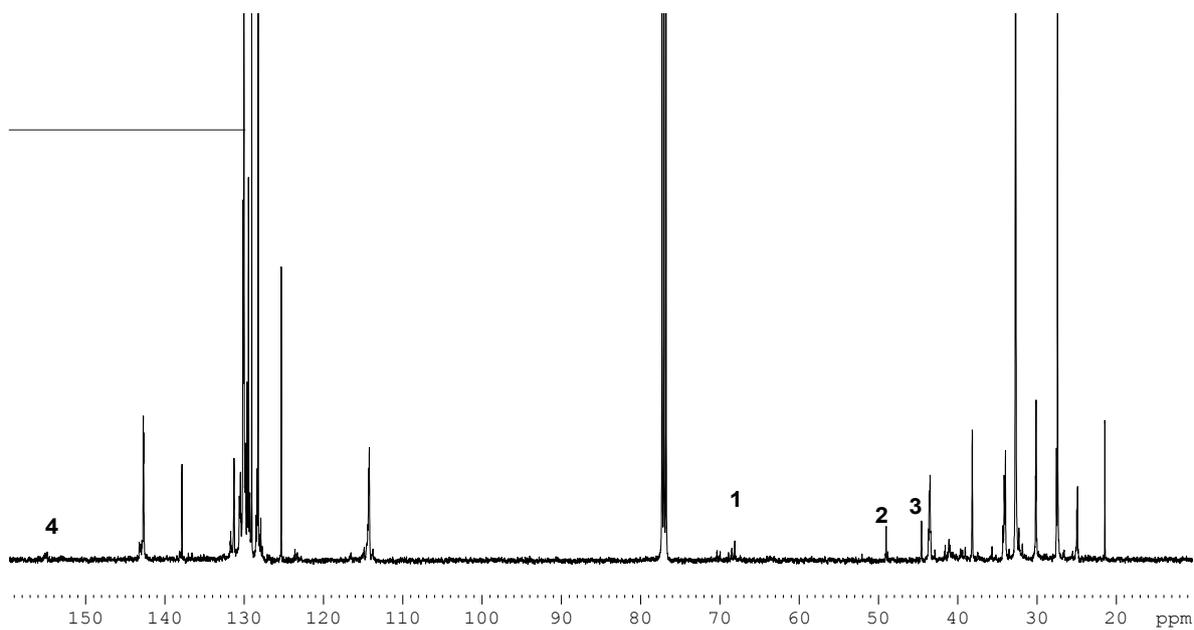


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3 , 25 °C) spectrum of PBD- GC_2 .

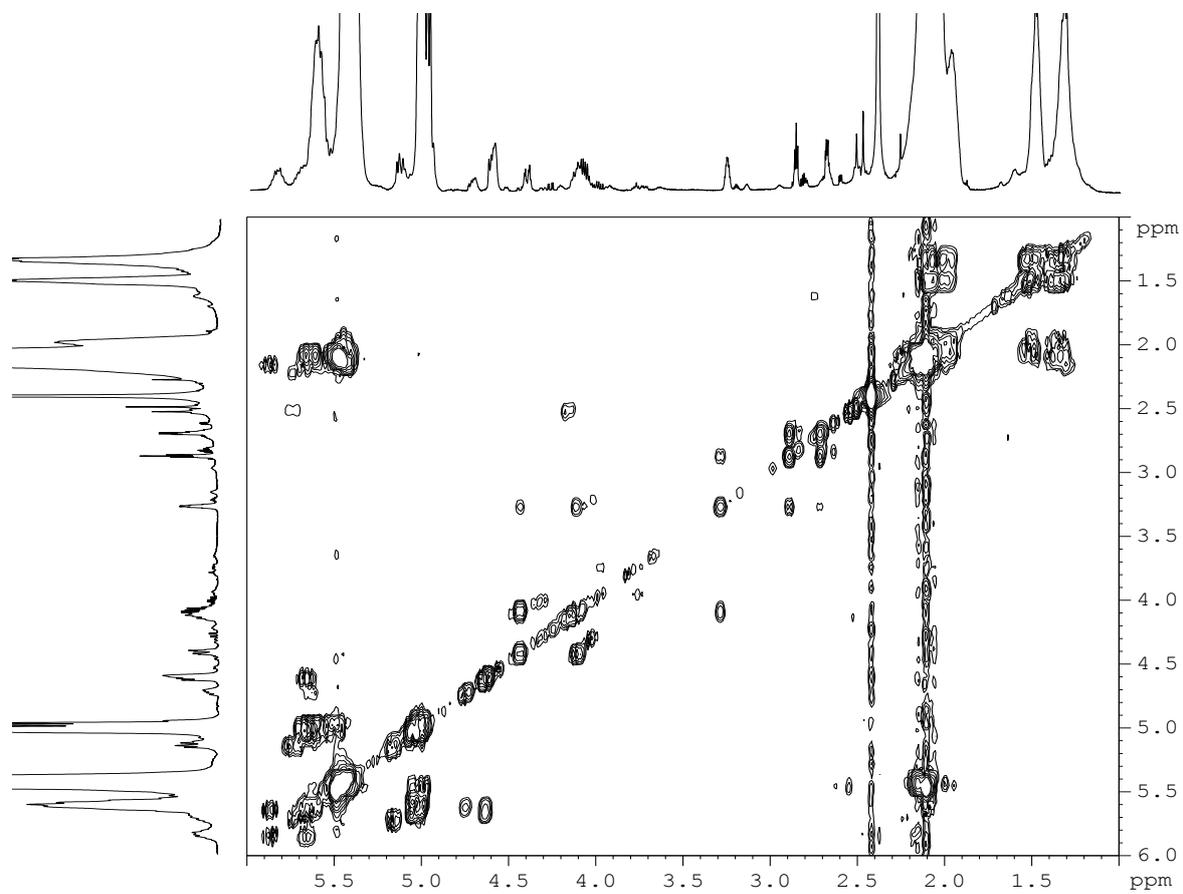


Figure S23. ^1H - ^1H COSY NMR (500 MHz, CDCl_3 , 25 °C) spectrum of PBD- GC_2 .

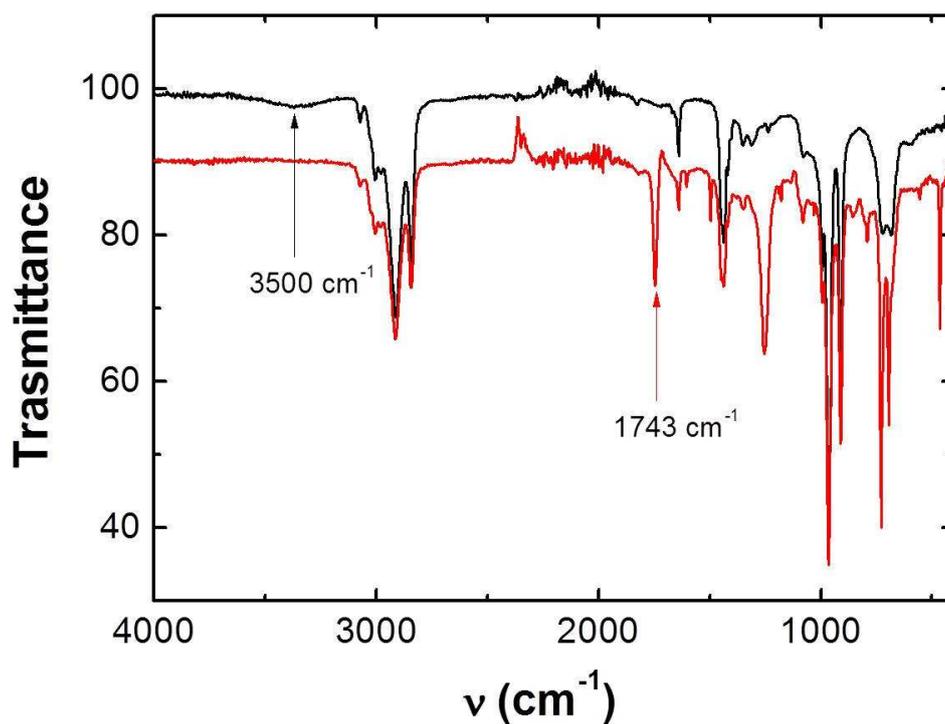


Figure S24. FTIR spectra of PBD-OH₂ (black trace) and the resulting PBD-GC₂ (red trace).

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

Table S1. α,ω -Dihydroxy and dicyclocarbonate telechelic PEGs characteristics.

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

^a Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).

Table S2. α,ω -Dihydroxy and dicyclocarbonate telechelic PEE characteristics.

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

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

Table S3. α,ω -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 ₂	3450	2.4	20.0	60.0	20.0
PBD-GC ₂	3800	2.29	20.0	60.0	20.0

^a Determined by SEC in THF at 30 °C vs. polystyrene standards (uncorrected M_n values).