

## Supporting Information

### **Study of the pseudo-polyrotaxane architecture as a route for mild surface functionalization by click-chemistry of poly( $\epsilon$ -caprolactone)-based electrospun fibers**

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## 1. Complementary experimental details

### 1.1. Materials

$\alpha$ -cyclodextrin ( $\alpha$ -CD, Alfa-Aesar) and  $\beta$ -cyclodextrin ( $\beta$ -CD, Sigma-Aldrich) were dried overnight under vacuum at 50°C prior to any chemical reaction.  $\epsilon$ -caprolactone ( $\epsilon$ -CL, Sigma-Aldrich) was dried over calcium hydride and distilled under reduced pressure prior to ring-opening polymerization. Poly(propylene glycol) (PPG, Alfa-Aesar,  $M_w=2000$  g/mol) was dried by azeotropic distillation of moisture with anhydrous toluene. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, Sigma-Aldrich), pentaerythritol (Alfa Aesar), anhydride succinic (Sigma Aldrich), 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMTMM, Sigma Aldrich), triethylamine (TEA, Sigma-Aldrich) and 1-adamantamine (sigma-aldrich) were used as received. 4-(bromomethyl)phenyl isothiocyanate and potassium carbonate ( $K_2CO_3$ ) were purchased from Sigma-Aldrich. N-[(1R,8S,9s)-bicyclo[6.1.0]non-4-yn-9-ylmethoxycarbonyl]-1,8-diamino-3,6-dioxaoctane (amino-BCN, Sigma-Aldrich) was kept in a freezer and used as such. Fluorescein isothiocyanate (FITC) and MegaStokes 673 obtained from Sigma-Aldrich were kept in the dark. A commercially available linear poly( $\epsilon$ -caprolactone) (PCL) with  $M_w \sim 80\,000$  g/mol (CAPA 6806) was supplied by Perstorp and used as received. Dimethylsulfoxide (DMSO), dichloromethane (DCM), toluene and dimethylformamide (DMF) were purchased from Sigma-Aldrich and distilled prior to their use. Acetonitrile (ACN, Sigma-Aldrich) was used without further purification.

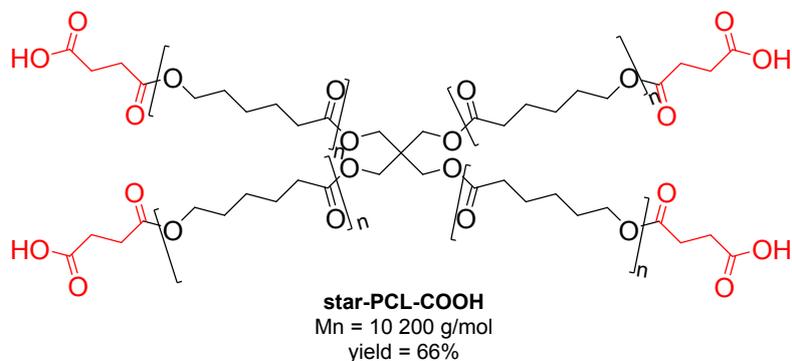
## 1. 2. Syntheses of PCL precursors with different architectures

### *a) Synthesis of the four branched star-PCL by ring opening polymerisation (ROP) of $\epsilon$ -CL*

This reaction was performed in anhydrous conditions in order to avoid any initiation due to water contamination. 0.2 g (1.469 mmol) of pentaerythritol was incorporated into a 100 mL three-neck round flask under an argon atmosphere and stirred at room temperature. Freshly distilled toluene (75 mL) was then added. 0.1022 g (0.734 mmol, 1eq) of TBD is then incorporated to the solution and let to stir until complete dissolution of the catalyst before distilled  $\epsilon$ -CL (16.768 g, 0.147 mol, 200 eq) was incorporated. The temperature was then set to 115°C and the reaction was refluxed for 24 hours before being quenched by adding a few drops of acetic acid. The reaction was let to stir for 30 minutes while cooling down before the solution was concentrated under reduced pressure. 25 mL of tetrahydrofuran (THF) was then used to solubilize the polymer and it was precipitated in 300 mL of cold methanol (MeOH). The obtained polymer was filtered and purified again twice with THF and MeOH. The collected white solid was then vacuum dried overnight at 35°C. A 60%wt yield of star-PCL was achieved. According to SEC analysis, the molecular weight was around  $M_w = 13\ 000$  g/mol with a dispersity of 1.2.  $^1\text{H}$  NMR analysis suggested that  $M_n = 10\ 000$  g/mol and so the degree of polymerization (DP) per branch was 21. The presence of only one singlet at 4.15 ppm as well as the absence of the pentaerythritol peaks corresponding to  $\text{CH}_2\text{-OH}$  and  $\text{CH}_2\text{-OH}$  at 3.77 and 3.55 ppm confirmed that a well-defined four-branched polymer was obtained. Moreover, in  $^{13}\text{C}$  NMR also, only one single peak appeared around 40 ppm.  $^1\text{H}$  NMR (300MHz, T = 296K, acetone- $d_6$  +  $\text{D}_2\text{O}$ , ppm):  $\delta$  4.16 (s, 2H, C- $\text{CH}_2\text{-O}$ - pentaerythritol), 4.04 (t, J = 6.5728 Hz, 2H, - $\text{CH}_2\text{-O}$ - PCL), 3.50 (t, J = 6.44 Hz, 2H, - $\text{CH}_2\text{-OH}$  end chains), 2.29 (m, 2H, O-CO- $\text{CH}_2$ - PCL), 1.56 (m, 4H, - $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-O}$ - PCL), 1.35 (m, 2H, O-CO- $\text{CH}_2\text{-CH}_2$ - PCL).  $^{13}\text{C}$  NMR (300MHz, acetone- $d_6$  +  $\text{D}_2\text{O}$ , ppm):  $\delta$  207.3, 173.78, 64.5, 62.8, 61.9, 42.9, 34.6, 34.4, 34.2, 33.1, 26.1, 25.5, 25.2, 25.1.

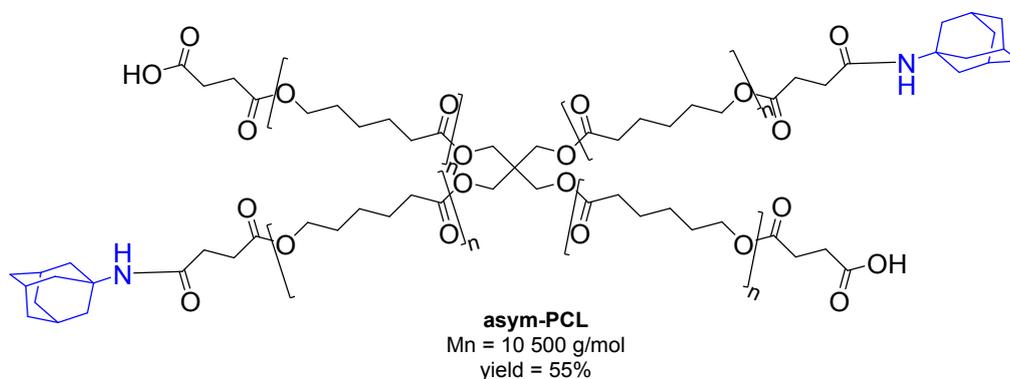
**b) Preparation of the asym-PCL by a two-step modification of the prepared star-PCL**

*Esterification of the end hydroxyl groups of star-PCL with succinic anhydride to obtain Star-PCL-COOH*



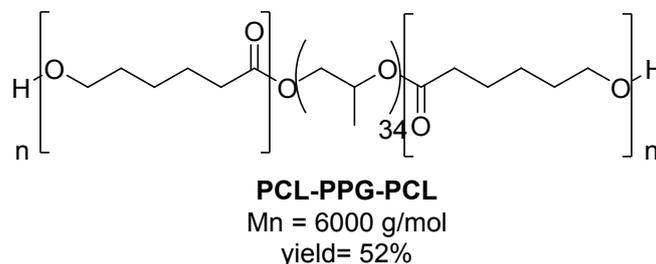
3.0 g of the previously prepared four-branched PCL (0,3 mmol, 1,3 mmol of hydroxyl functions) was dissolved in 25mL of 1,4-dioxane under inert atmosphere. Succinic anhydride (0.2470 g, 2.47 mmol) was then added as well as a few drops of triethylamine (TEA). The reaction was carried out at 70°C for 12 days before being cooled down. The resulting mixture was concentrated under reduced pressure, by evaporation, washed several times with 50 mL of ethyl acetate (EtOAc) and 50 mL of brine, dried over sodium sulphate and filtered. The final product was concentrated with a rotary evaporator. The yellowish product yielded 66%wt.  $^1H$  NMR (300MHz,  $T = 296K$ ,  $CDCl_3$ , ppm):  $\delta$  4.12 (m, 2H), 2.67 (m, 4H), 2.33 (t,  $J = 14,8575$  Hz, 2H), 1.65 (m, 4H), 1.41 (m, 2H).  $^{13}C$  NMR (300MHz,  $T = 296K$ ,  $CDCl_3$ , ppm):  $\delta$  174.34, 174.19, 172.82, 67.74, 65.24, 64.80, 61.04, 34.78, 34.51, 29.01, 28.90, 26.19, 25.23, 25.16, 25.09.

Reaction of the end groups of the star-PCL-COOH with adamantanamine to obtain asym-PCL  
(based on the literature<sup>2</sup>)



1.0 g of star-PCL-COOH (0.096 mmol, 0.385 mmol of COOH functions) was added to 0.029 g 1-adamantanamine (0.192 mmol, 0.5 eq<sub>COOH</sub>). The solids were solubilized under inert atmosphere with 18 mL of freshly distilled dichloromethane. 0.0594 g of 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride hydrate (DMTMM) was then added as well as 2 mL of TEA. The reaction was carried out under stirring for 9 days at 35°C before the solution was concentrated under reduced pressure. The solid was then solubilized in 100 mL of EtOAc and the solution was washed two times with 100 mL of a 1%wt HCl solution, dried over sodium sulphate, filtered and collected before being concentrated at the rotavapor to obtain a white solid (yield = 86%w). <sup>1</sup>H NMR (300MHz, T = 296K, CDCl<sub>3</sub>, ppm): δ 5.34 (s, NH), 4.07 (t, J= 6.68 Hz, 2H PCL), 2.67 (m, 4H succ.), 2.32 (t, J= 7.41 Hz, 2H PCL), 2.07 (m, 3H adamantyl), 2,0 (m, 6H adamantyl), 1.66 (m, 4H PCL + 6H adamantyl), 1.36 (m, 2H PCL). <sup>13</sup>C NMR (300MHz, T = 296K, CDCl<sub>3</sub>, ppm): δ 173.67, 64.29, 41.78, 34.27, 28.51, 25.68, 24.73.

*c) Synthesis of the block PCL-PPG-PCL copolymer by ROP of  $\epsilon$ -CL (inspired by the literature<sup>3</sup>)*



This reaction was performed in anhydrous conditions in order to avoid any initiation due to water contamination. 0.5 g (0.25 mmol) of previously dried poly(propylene glycol) (PPG) was incorporated into a 100 mL three-neck round flask under an argon atmosphere and stirred at room temperature. Freshly distilled toluene (25 mL) was then added. 2.85 g (24.9 mmol, 200 eq) of freshly distilled  $\epsilon$ -CL was then incorporated to the solution and let to stir until an homogenous solution was obtained. The catalyst was then added into the flask (0.0174 g, 0.125 mmol, 1 eq). The reaction was carried out at 25°C for 24 hours before being quenched by adding a few drops of acetic acid. The polymer was then purified by precipitation into 300 mL of cold methanol (MeOH). The obtained solid was filtered out of the solution and purified again twice by solubilisation in THF and precipitation in cold MeOH. The collected white solid was finally vacuum dried overnight at 35°C. A 50%wt yield of PCL-PPG-PCL was achieved. According to SEC analysis, the molecular weight was around Mn = 14 000 g/mol with a dispersity  $\mathcal{D}$  of 1.4. <sup>1</sup>H NMR analysis suggested that Mn = 10 000 g/mol and so the degree of polymerization (DP) per PCL block was 35. <sup>1</sup>H NMR (300MHz, T = 296K, CDCl<sub>3</sub>, ppm):  $\delta$  4.03 (t, J= 6.6779 Hz, 2H of PCL), 3.55 (m, 2H of PPG), 3.38 (m, 1H of PPG), 2.29 (t, J= 14,9465 HZ, 2H of PCL), 1.62 (m, 4H of PCL), 1.34 (m, 2H of PCL), 1.11 (m, 3H of PPG). <sup>13</sup>C NMR (300MHz, T = 296K, CDCl<sub>3</sub>, ppm):  $\delta$  173.51, 75.53, 75.33, 75.12, 73.37, 72.87, 64.13, 34.11, 28.35, 25.53, 17.48, 17.36.

### 1. 3. Preparation of the pPR

#### a) Preparation of star- and mik-pPR.

In a 500 mL three-neck round flask, 100 mL of an aqueous saturated solution of  $\alpha$ -cyclodextrin (150 mg/mL, 15 mmol) was prepared. In another round flask, 2.00g (17.5 mmol  $\epsilon$ -caprolactone monomer unit) of star-PCL or asym-PCL respectively was dissolved in 100 mL of acetone. Once both solid were dissolved in their respective solvent, the polymer solution was added dropwise in the saturated solution of  $\alpha$ -CD. A white precipitate instantly formed. The mixture was then stirred for 48 hours at 70°C before being cooled down to room temperature. The white solid was filtered and washed several times with acetone or distilled water to remove any unreacted asym-PCL or  $\alpha$ -CD, respectively. The so obtained pseudo-polyrotaxanes star-pPR (yield = 35% w) or mik-pPR (yield = 24% w) was then dried in a vacuum oven at 35°C.

*Star-pPR:  $^1\text{H NMR}$  (400 MHz,  $T=353\text{K}$ ,  $\text{DMSO-}d_6$ , ppm):*  $\delta$  5.16 (m, 12H, -O-CH-O- of CD and CH<sub>2</sub>-OH of CD), 4.83 (d,  $J= 3.36$  Hz, 6H, -CH-OH of CD), 4.02 (m, 6H, -CH<sub>2</sub>-O- of PCL), 3.71 (m, 18H, various HO-CH<sub>2</sub>-CH-CO-CH(OH)-CH(OH)- of CD), 3.41 (m, 6H, CHO-CH(OH)-CH(OH)- of CD), 3.33 (m, water and CD), 2.27 (t,  $J= 7.30$  Hz, 2H, O-CO-CH<sub>2</sub>- of PCL), 1.58 (m, 4H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O- of PCL), 1.35 (m, 2H, O-CO-CH<sub>2</sub>-CH<sub>2</sub>- of PCL).  $^{13}\text{C NMR}$  (400 MHz,  $\text{DMSO-}d_6$ , ppm):  $\delta$  171.99, 101.51, 81.79, 72.89, 71.94, 71.87, 62.93, 59.90, 32.98, 27.32, 24.41, 23.54.

*Mik-pPR:  $^1\text{H NMR}$  (300MHz,  $T = 296\text{K}$ ,  $\text{DMSO-}d_6$ , ppm):*  $\delta$  5.52 (d,  $J= 7.02\text{Hz}$ , 6H of CD), 5.44 (s, 6H of CD), 4.80 (s, 6H of CD), 4.47 (m, 6H of CD), 3.98 (m, 2H of PCL), 3.77 (m, 6H of CD), 3.60 (m, 12H of CD), 2.26 (m, 2H of PCL), 1.53 (m, 4H of PCL), 1.26 (m, 2H of PCL).  $^{13}\text{C NMR}$  (300MHz,  $T = 296\text{K}$ ,  $\text{DMSO-}d_6$ , ppm):  $\delta$  172.72, 101.96, 82.07, 73.25, 72.1, 63.47, 59.97, 33.35, 27.79, 24.88, 24.07.

***b) Preparation of  $\beta$ -cyclodextrin copo-pPR (adapted from <sup>5</sup> and <sup>6</sup>).***

In a 500 mL three-neck round flask, 100 mL of an aqueous solution of  $\beta$ -cyclodextrin (3.76 g, 3.3 mmol) was prepared. In another round flask, 2g (6.8 mmol of propylene glycol monomer unit) of PCL-PPG-PCL was dissolved in 100 mL of acetone. Once both solid were dissolved in their respective solvent, the polymer solution was added dropwise in the saturated solution of  $\beta$ -CD. The mixture was then stirred for 24 hours at 70°C under reflux before being cooled down to room temperature. The solution was let to stir for another 24 hours at room temperature. A yellow solid could be seen at the wall of the flask. The solvents were removed by rotary evaporation for several hours to remove the highest amount of DMSO. The so obtained pseudo-polyrotaxane, copo-pPR, (yield = 50% wt) was then dried further dried on a vacuum line.

*<sup>1</sup>H NMR (300MHz, T = 296K, DMSO-d<sub>6</sub>, ppm):  $\delta$  5.75 (3, 14H of CD), 4.88 (s, 7H of CD), 4.03 (m, 2H of PCL), 3.66 (m, 7H of CD), 3.35 (m, 14H of CD), 2.32 (m, 2H of PCL), 1.58 (m, 4H of PCL), 1.34 (m, 2H of PCL), 1.08 (m, 3H of PPG). <sup>13</sup>C NMR (300MHz, T = 296K, DMSO-d<sub>6</sub>, ppm):  $\delta$  121.93, 81.53, 73.03, 72.40, 72.03, 59.9, 24.07.*

## 1.4. Characterization

### *a) NMR Spectroscopy*

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy was performed using a Bruker Advance DRX500 300MHz spectrometer at 296K. Chemical shifts were referenced to the solvent values,  $\delta = 2.50$  ppm in the case of DMSO  $d_6$ ,  $\delta = 7.26$  ppm for  $\text{CDCl}_3$  and  $\delta = 2.04$  ppm for acetone- $d_6$ .

All solutions were prepared several hours prior to the NMR analysis. For the pseudopolyrotaxanes, after the synthesis purifications with water to remove free cyclodextrins and acetone to remove unthreaded PCL, all powders were solubilized at  $50^\circ\text{C}$  in DMSO- $d_6$  for at least several hours to ensure the pPR decomplexation so that all molecules (i.e. CD and PCL) were isolated in the mixture.

### *b) Size Exclusion Chromatography*

Size exclusion chromatography (SEC) measurements were performed in chloroform (HPLC grade) in a Shimadzu liquid chromatograph equipped with a LC-10AD isocratic pump, a DGU-14A degasser, a SIL-10AD automated injector, a CTO-10A thermostated oven with a 5 PLGel Guard column, two PL-gel 5 MIXED-C and a 5  $100 \text{ \AA}$  300mm-columns, and three online detectors : Shimadzu RID-10A refractive index detector, Wyatt Technologies MiniDAWN 3-angle-light scattering detector and Shimadzu SPD-M10A diode array (UV) detector. Samples were dissolved in chloroform (at a concentration 4mg/mL) and filtered through a  $0.2\mu\text{m}$  PTFE membrane. For all analyses the injection volume was  $100\mu\text{L}$ , the flow rate was  $0.8\text{mL}/\text{min}$  and the oven temperature was set at  $25^\circ\text{C}$ . Molar weights and dispersity were calculated from a calibration with polystyrene standard in UV or RI detection.

### *c) FTIR Spectroscopy*

The infrared spectra were obtained by using a Fourier transform infrared spectrometer (FTIR) (Thermo Nicolet 380 FT-IR). The scans (64 scans) were recorded between 4000 and 400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

#### ***d) Thermogravimetric analysis***

Thermogravimetric analyses (TGA) were performed on a TA Instrument Q5000 thermal analysis apparatus. All samples were heated under air up to 650°C at a constant rate of 10°C/min.

#### ***e) Differential Scanning Calorimetry***

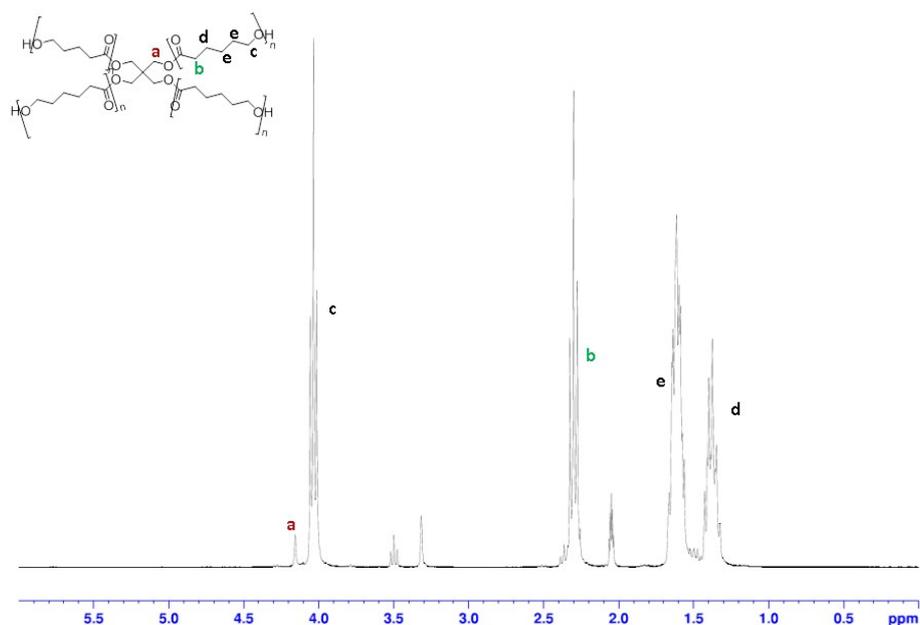
Differential Scanning Calorimetry (DSC) thermograms were obtained using TA Instrument Q200 apparatus. Temperatures were varied from -70°C up to 250°C at a heating rate of 10°C/min. The reported melting point temperatures ( $T_m$ ) were all assessed from the second heating cycle thermogram.

#### ***f) X-ray Diffraction***

Crystalline organization of solids and membranes was determined by X-Ray diffraction (XRD) measurements using a Bruker D8 Advance diffractometer at a scanning rate of 1.6°/min. The detector used for the analyses was a Lynxeye photo diode and the copper source was excited under vacuum.  $2\theta$  angle values were ranging from 5° to 50°.

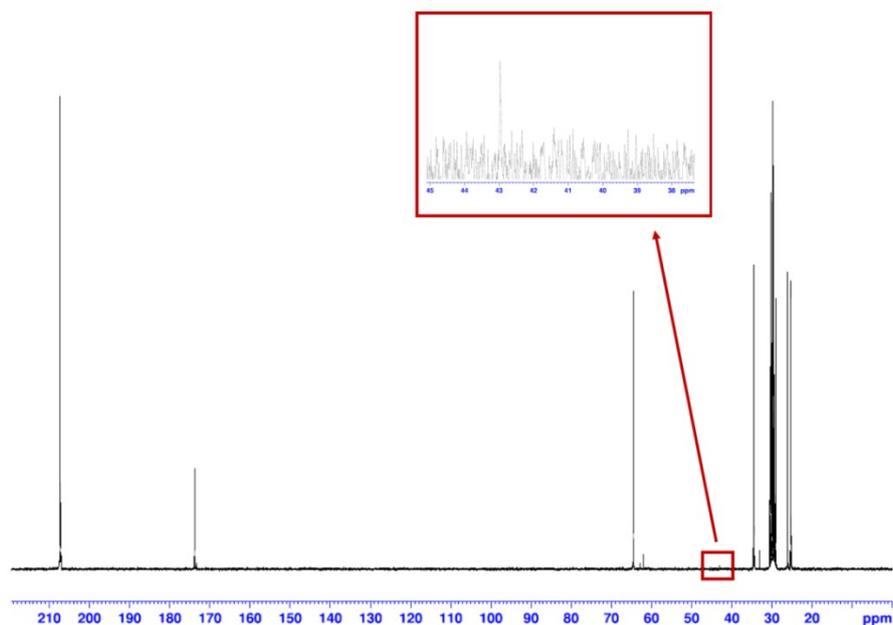
#### ***g) Fluorescent confocal microscopy***

Fluorescent properties of functionalized fibres were assessed by confocal microscopy on a Leica SP5 11 confocal microscope equipped with an oil-immersion objective lens 62x. FITC-labelled fibres were visualized by excitation of the fluorophore at  $\lambda = 488$  nm and at  $\lambda = 561$  nm. Simultaneously, images of the mats under white light were taken. In order to determine that the fluorescent properties were only due to FITC, red and blue images of the mats were also taken to eliminate noises.



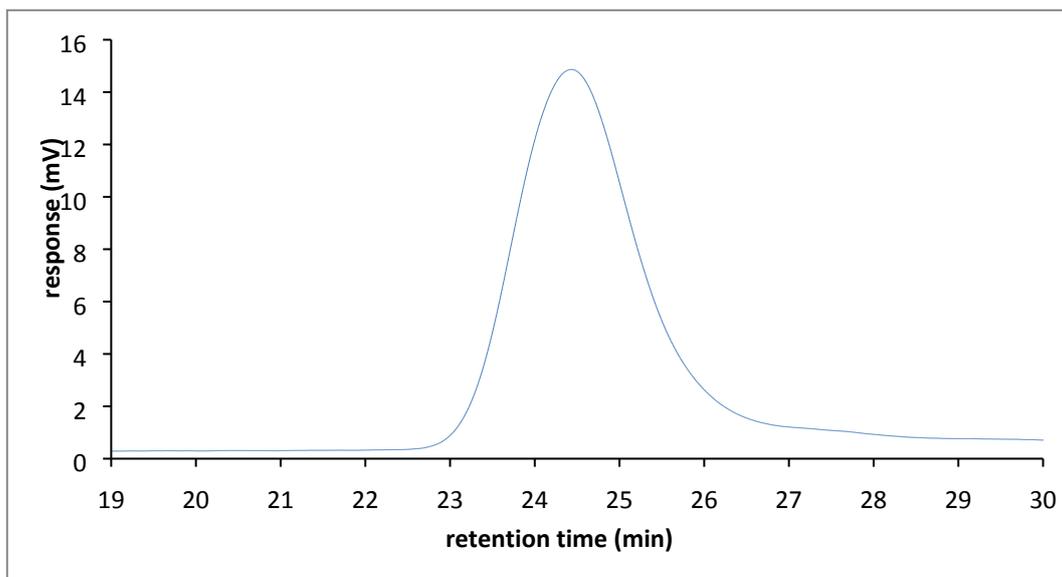
**Figure S1.**  $^1\text{H}$  NMR spectrum of the four-branched PCL (**star-PCL**) in acetone- $\text{d}_6$  with a few drops of  $\text{D}_2\text{O}$ .

The calculated average DP per branch was 21 based on the integral values of peaks a ( $\delta=4.16$ , 2H,  $I=0.093$ ) and b ( $\delta=2.29$ , 2H,  $I=2.00$ ). The DP corresponds to the ratio of  $b/a$ . The presence of one single peak at 4.16 ppm, as well as the absence of remaining peaks from the pentaerythritol at 3.55 and 3.77 ppm confirms the structure of the four-branched PCL.

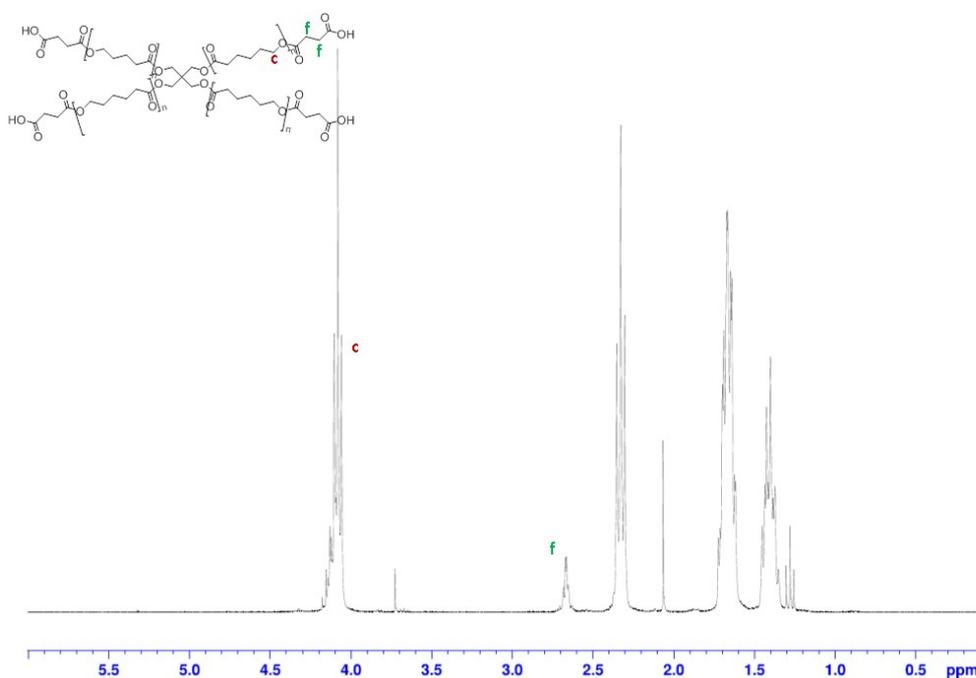


**Figure S2.**  $^{13}\text{C}$  NMR spectrum of the four-branched PCL (**star-PCL**) in acetone- $\text{d}_6$  with a few drops of  $\text{D}_2\text{O}$ .

The presence of a single peak around 40 ppm confirmed the well-defined synthesis of a four-branched PCL.

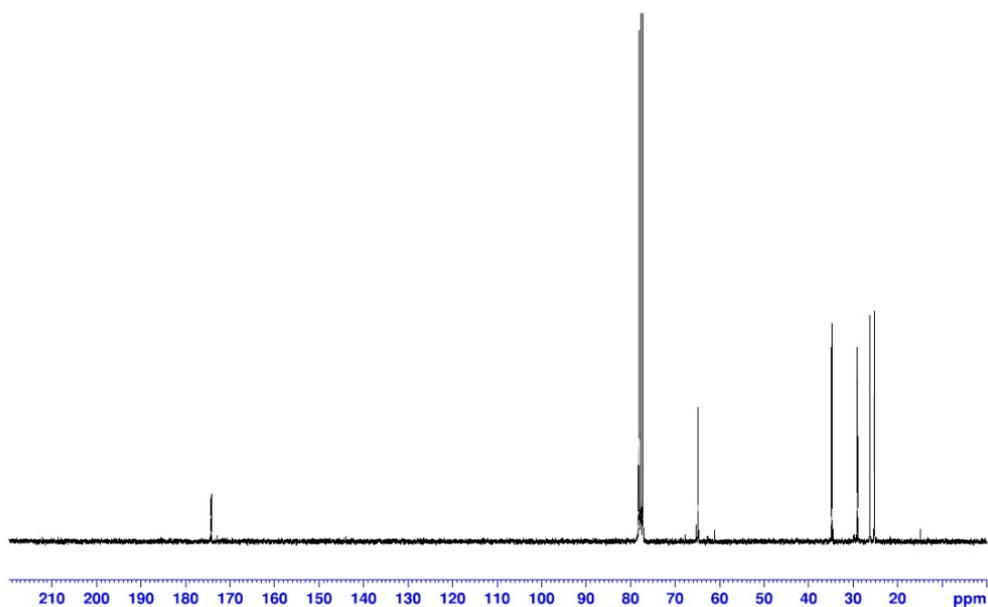


**Figure S3.** Size exclusion chromatograph of the star-PCL in chloroform using the refractive index detector and a polystyrene standard. The SEC analysis indicated a molecular weight of 13 000 g/mol (eq. polystyrene) with a dispersity of 1.2. Based on this molecular weight, the calculated DP of the polymer per branch is 28.

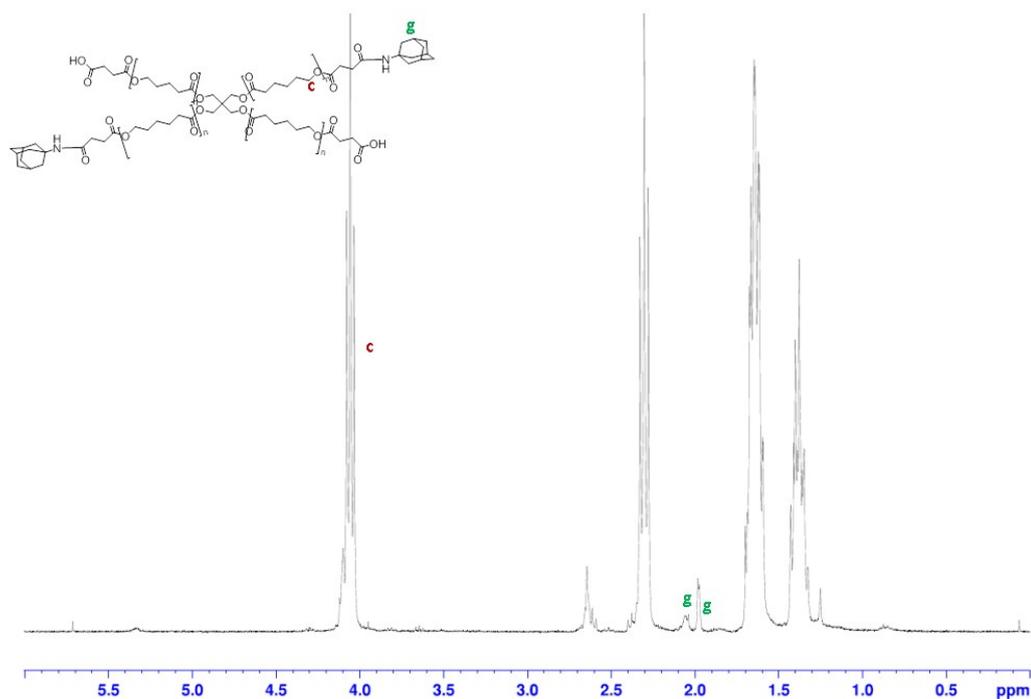


**Figure S4.**  $^1\text{H}$  NMR spectrum of the esterified four-branched PCL (**star-PCL-COOH**) in  $\text{CDCl}_3$ .

To determine the number of esterified branches, the integral value of f ( $\delta=2.67$  ppm, 4H) was fixed at 4.00 and the integral value for c ( $\delta=4.12$  ppm, 2H) was found to be 21 as expected by the DP found previously.

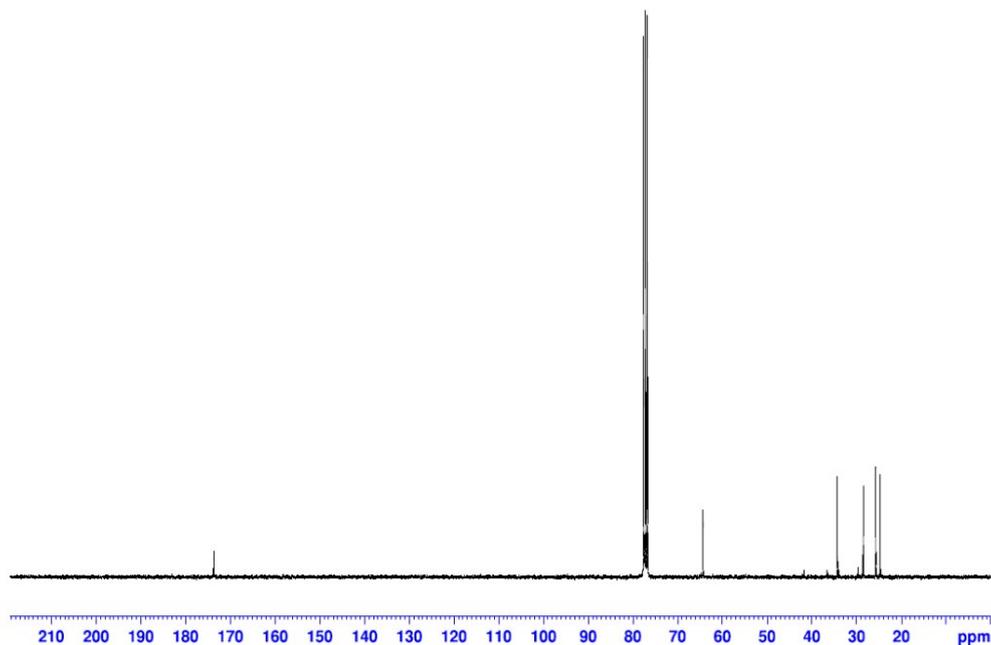


**Figure S5.**  $^{13}\text{C}$  NMR spectrum of the esterified four-branched PCL (**star-PCL-COOH**) in  $\text{CDCl}_3$ .

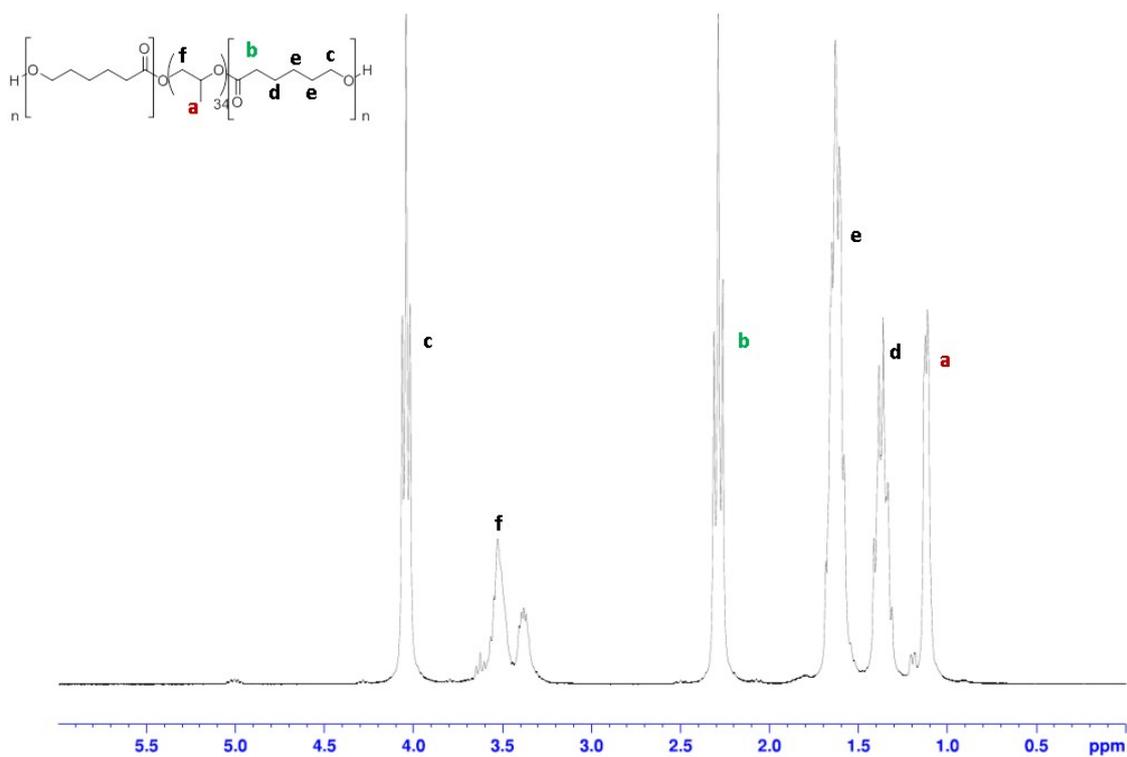


**Figure S6.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of asym-PCL after the adamantane coupling reaction.

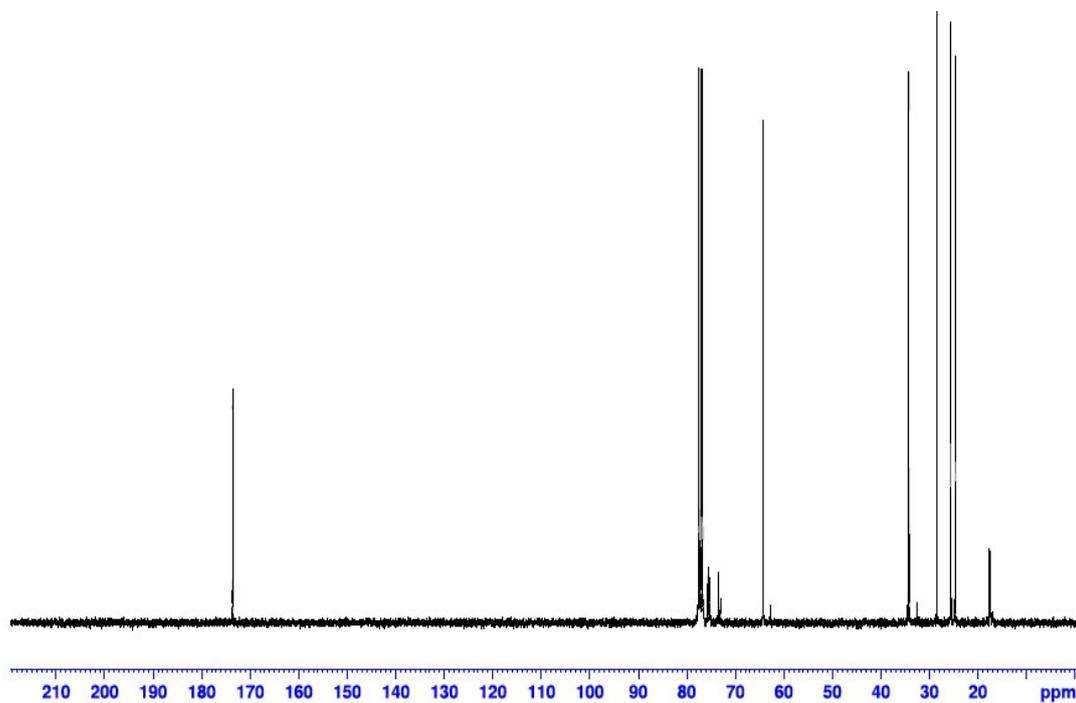
This analysis proved the statistical grafting of two stoppers per star-PCL. Indeed, peak c ( $\delta=4.07$  ppm, 2H PCL) and g ( $\delta=2.0$  ppm, 6H adamantyl group) were used and their integral values were determined (respectively  $I = 2.0$  for the peak at  $\delta=4.12$  ppm and  $I = 0.14$  for the multiplet at  $\delta=2.0$  ppm).



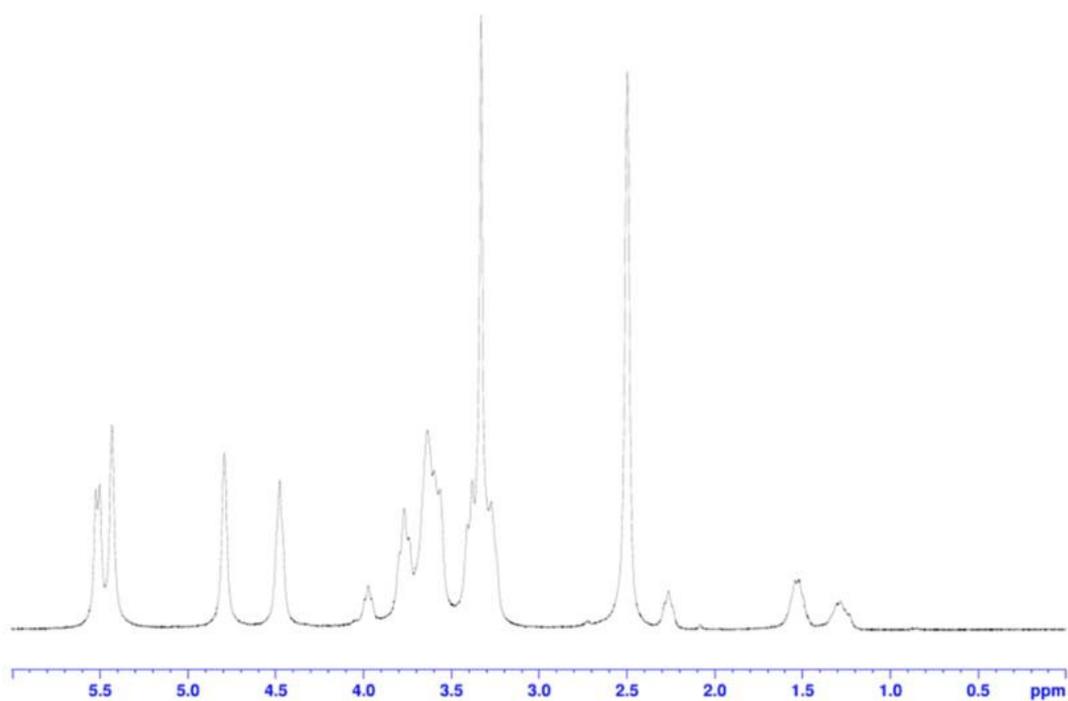
**Figure S7.**  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of asym-PCL after the adamantane coupling reaction.



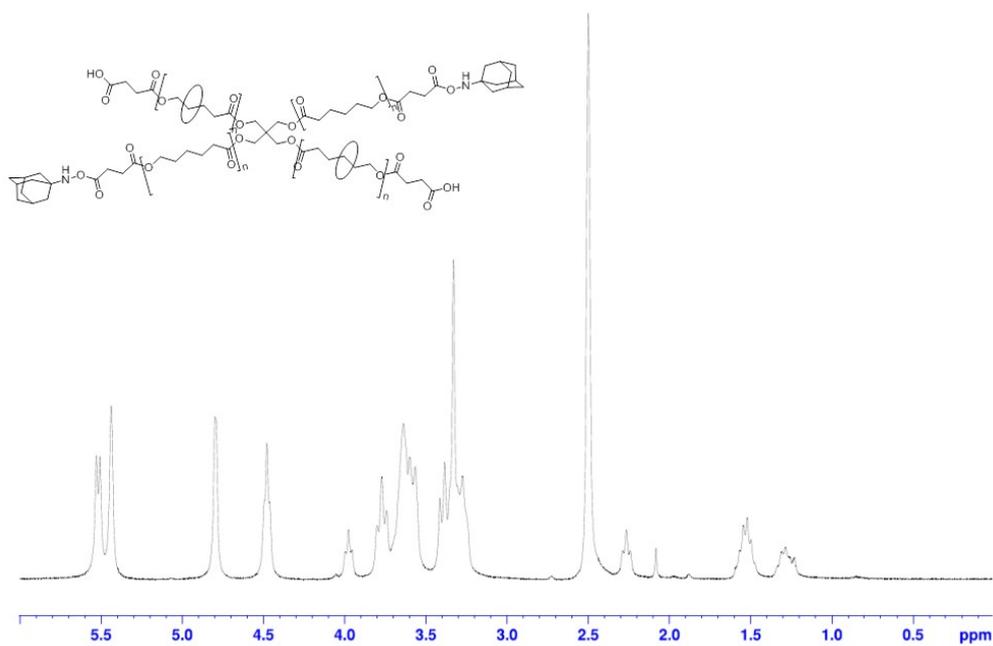
**Figure S8.**  $^1\text{H}$  NMR analysis of PCL-PPG-PCL synthesized by ROP of  $\epsilon$ -caprolactone catalyzed by TBD in toluene. The integral values of a and b were used to determine the DP per branch of the polymer. The DP per branch for each PCL block was determined to be 35.



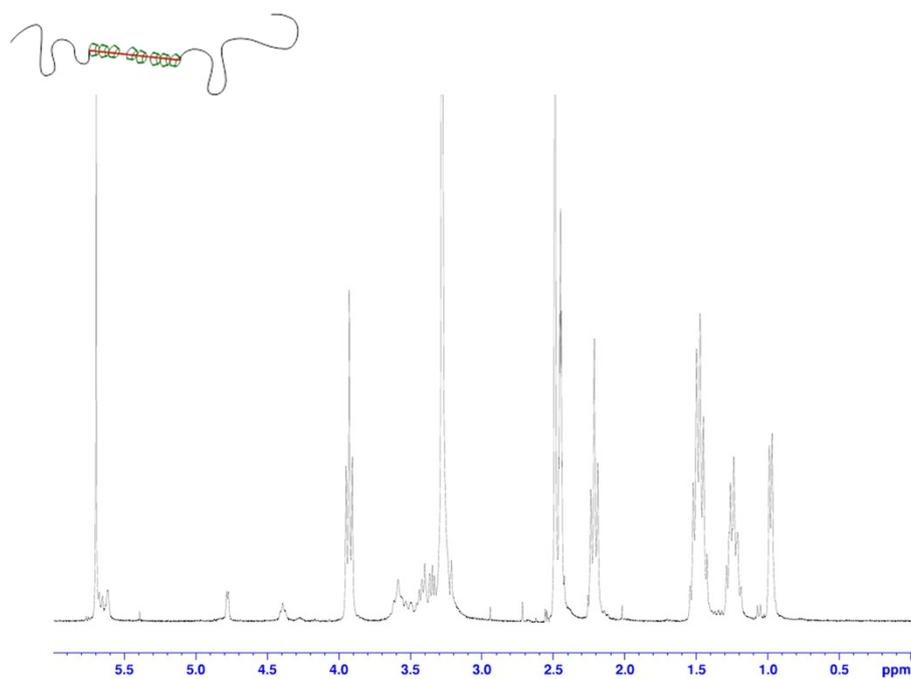
**Figure S9.**  $^{13}\text{C}$  NMR spectrum in  $\text{CDCl}_3$  of the PCL-PPG-PCL block copolymer.



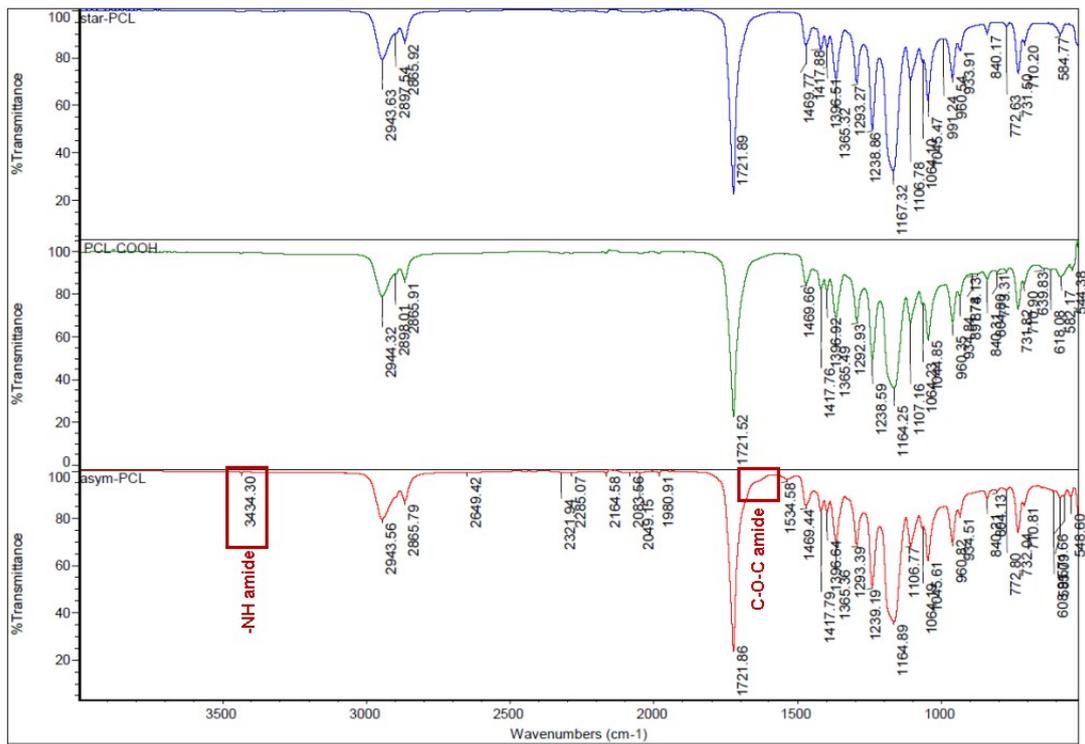
**Figure S10.**  $^1\text{H}$  NMR spectrum of star-pPR in DMSO  $d_6$ . The ratio of  $\alpha$ -CD: $\epsilon$ -CL was determined to be  $\alpha$ -CD: $\epsilon$ -CL = 1 :.



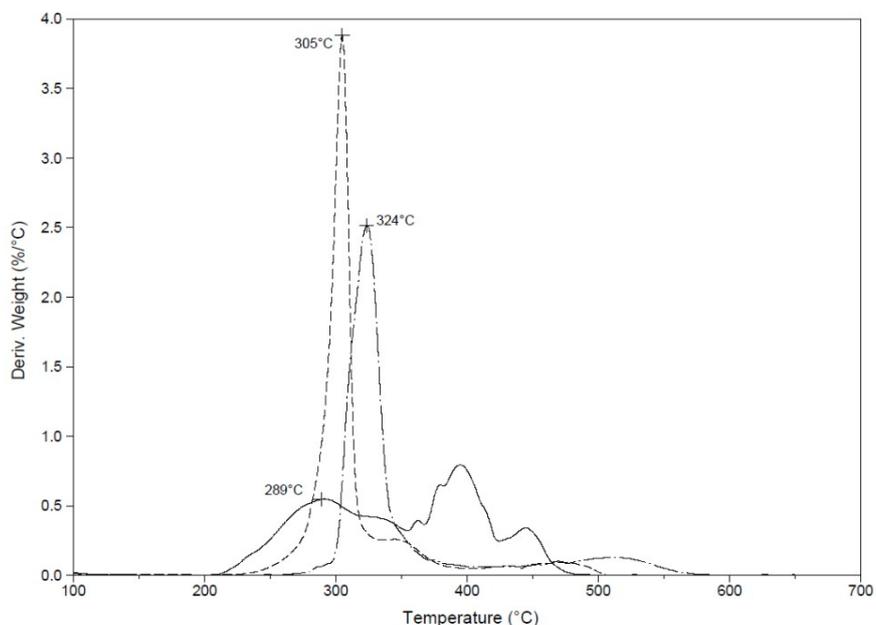
**Figure S11.**  $^1\text{H}$  NMR spectrum of mik-pPR in DMSO- $d_6$ .



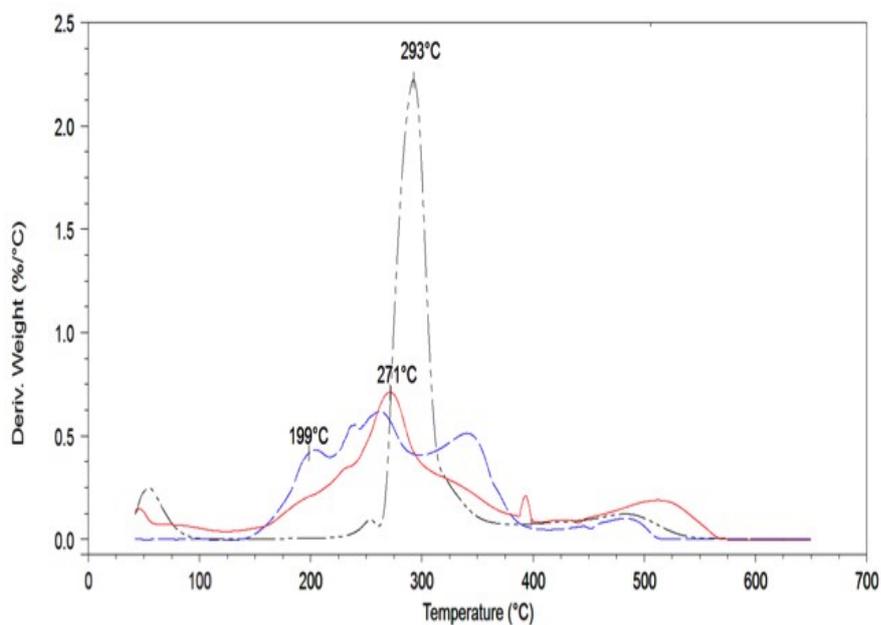
**Figure S12.**  $^1\text{H}$  NMR spectrum of copo-pPR in DMSO- $d_6$ .



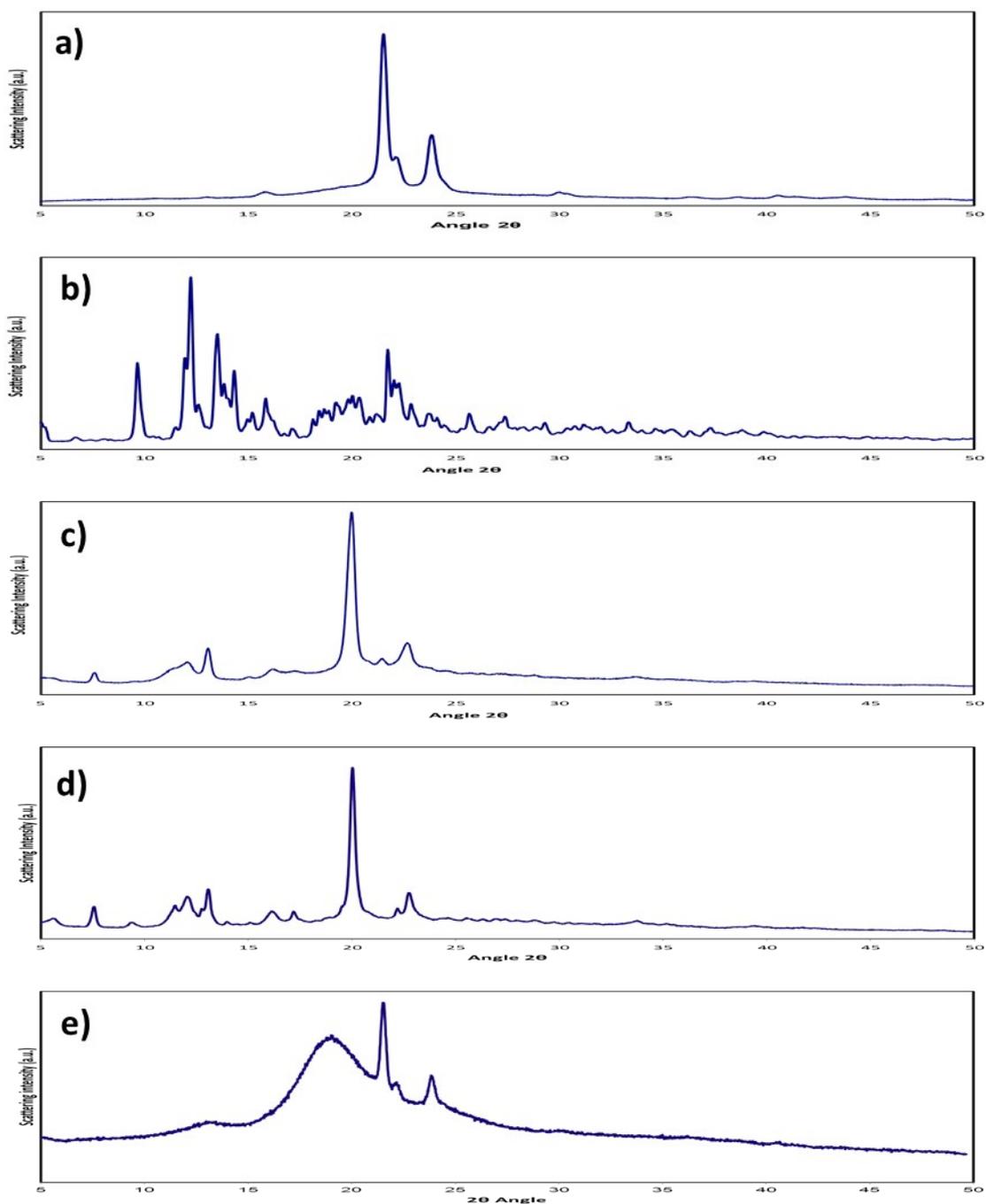
**Figure S13.** FTIR spectra overlay of the star-PCL, the star-PCL-COOH with esterified chain ends and the asym-PCL.



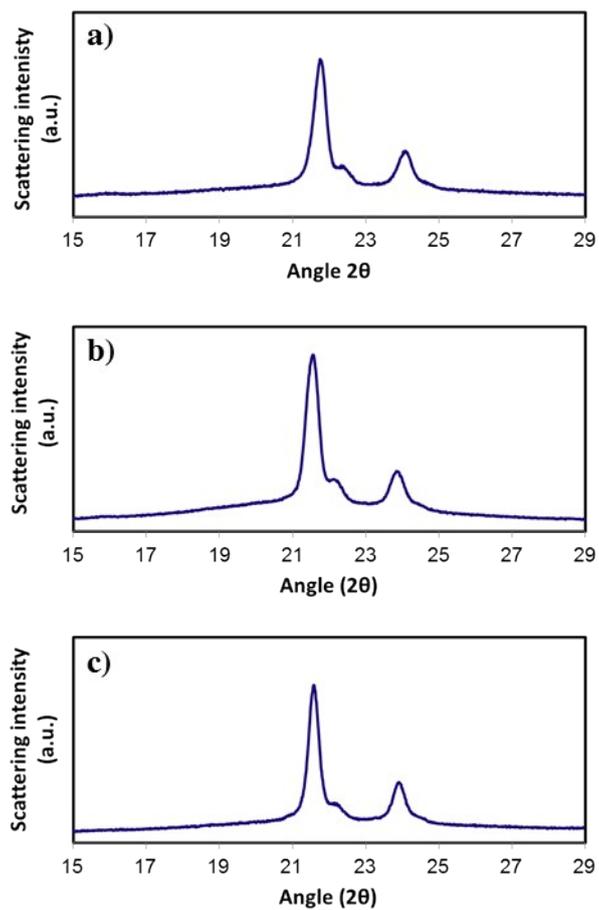
**Figure S14.** Thermal gravimetric evolution of a) asym-PCL (solid line), b) mik-pPR (----), c) alpha-cyclodextrin (-·-·-·-). The difference of degradation temperature is obvious as the derivative curves clearly show the first weight loss of the polymer around 290°C, whereas the mik-pPR first weight loss occurs at 305°C. The pPR thermal properties are thus enhanced.



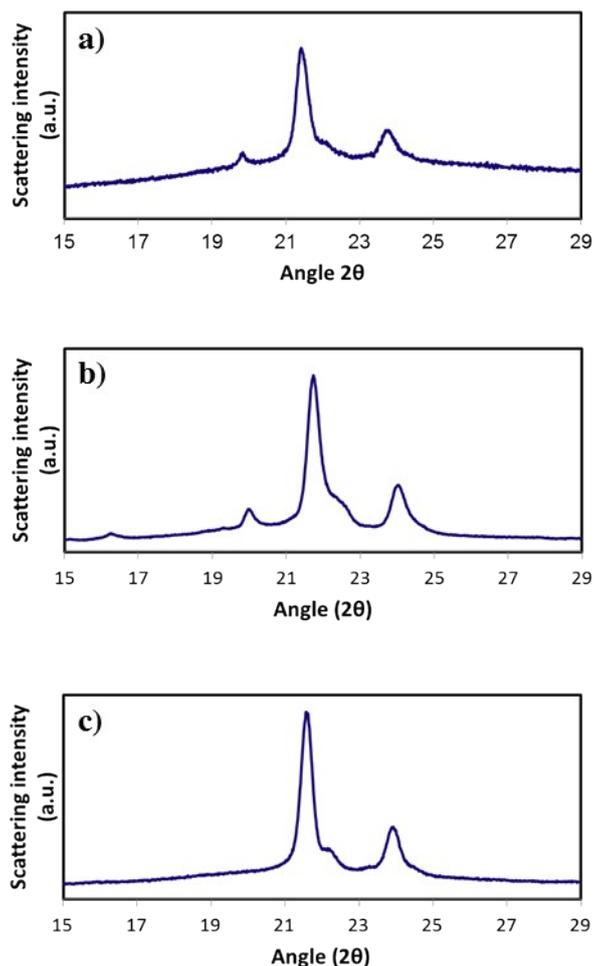
**Figure S15.** Thermal gravimetric evolution of a) copo-pPR (solid line), b) block copolymer (---), c) beta-cyclodextrin (-·-·-·-). The difference of degradation temperature is obvious as the derivative curves clearly show the first weight loss of the polymer around 200°C, whereas the copo-pPR first weight loss occurs at 270°C. The pPR thermal properties are thus enhanced.



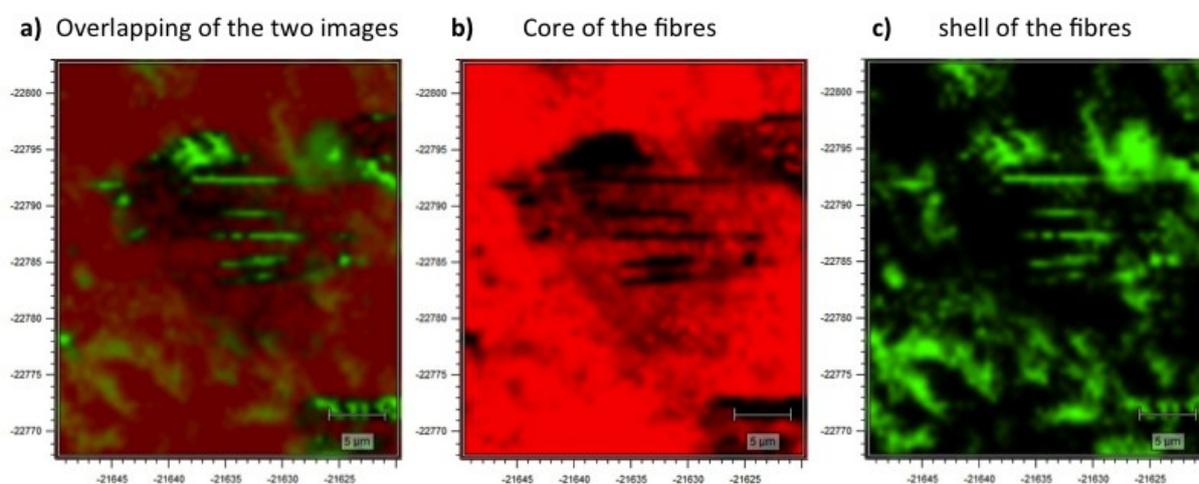
**Figure S16.** XRD diffractograms of a) neat PCL, b) alpha-cyclodextrin, c) star-pPR, d) mik-pPR and e) copo-pPR.



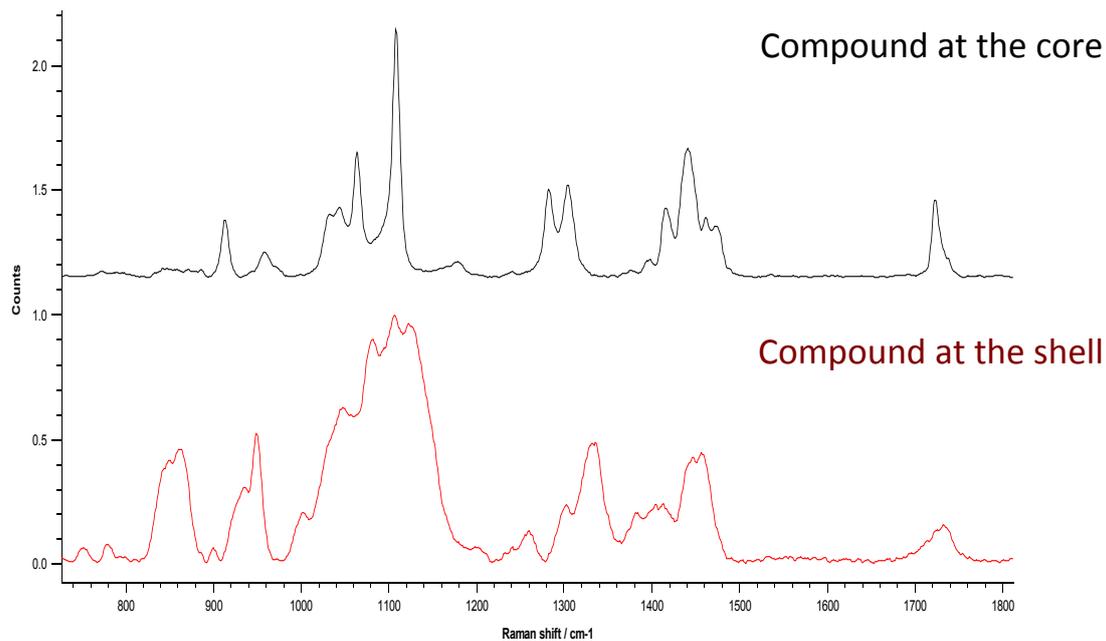
**Figure S17.** XRD spectrograms obtained in the case of the a) 10:1 PCL:star-pPR, b) 10:1 PCL:mik-pPR and c) 10:1 PCL:copo-pPR core:shell electrospun membranes.



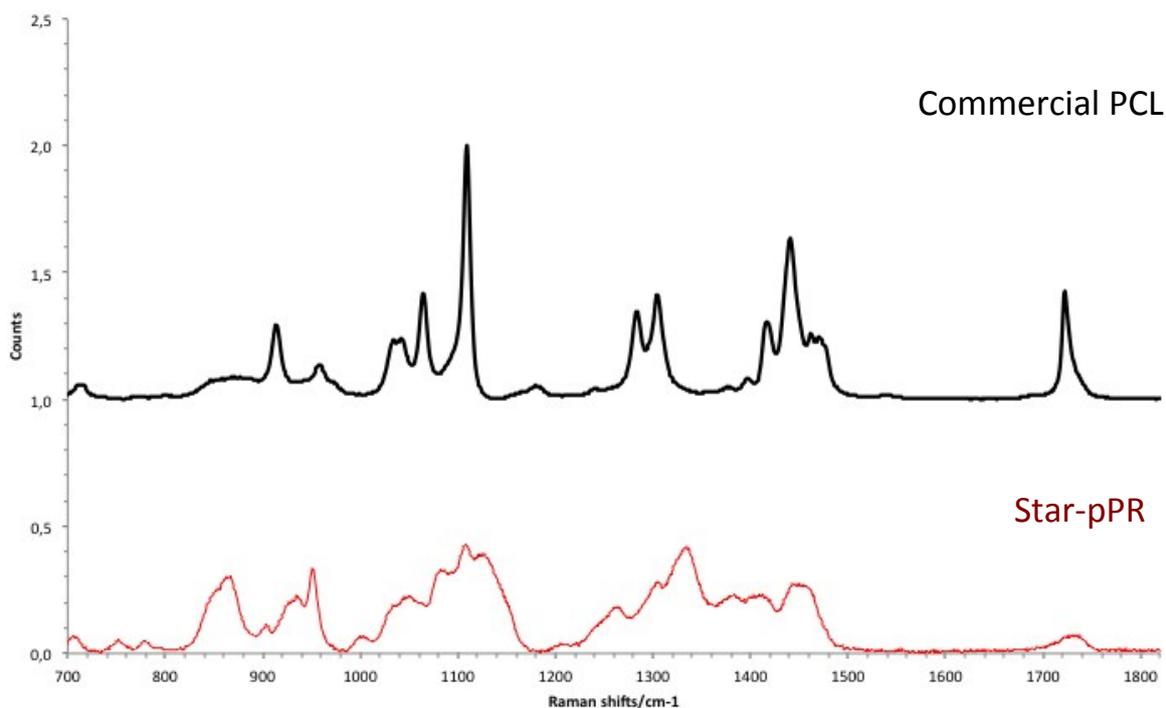
**Figure S18.** XRD spectrograms obtained in the case of the a) 10:3 PCL:star-pPR, b) 10:3 PCL:mik-pPR and c) 10:3 PCL:copo-pPR core:shell electrospun membranes. In the case of 10:3 PCL:star-pPR and 10:3 PCL:mik-pPR fibres, a peak is seen at  $2\theta = 20^\circ$  characteristic of alpha-cyclodextrin channel structure.



**Figure S19.** Raman cartographic images obtained on a) two thick 10:1 PCL:star-pPR fibres. The so-obtained image could be split into two different Raman images where b) the red color was attributed to the component found at the core and c) the green color was attributed to the compound at the shell.

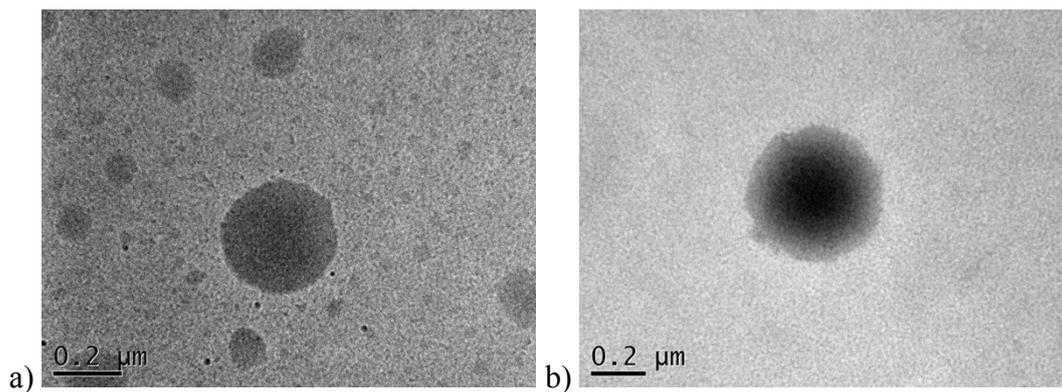


**Figure S20.** Raman spectrograms of the two different compounds that were found and isolated at the core and the shell of the fibers.



**Figure S21.** Raman spectrograms obtained on a) the commercially available PCL and b) the synthesized star-pPR.

From these two spectrograms, we can see that the compound found at the core is indeed the neat PCL and the compound at the shell is star-pPR. This demonstrates that the PCL is located in the core of the fibres and star-pPR is found at the shell of the coaxial electrospun fibres.



**Figure S22.** a) TEM of a cross-section of neat PCL fibers. b) TEM of a cross-section of a single PCL:mik-pPR fibers.

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