Supporting information

3D Printing via Polymerization-Induced Microphase Separation using Acrylate Macromonomers instead of MacroRAFT Agents

Maxime Michelas [a], Nathaniel Corrigan [a], Cyrille Boyer [a,*]

[a] School of Chemical Engineering, UNSW Sydney, Sydney, New South Wales 2052, Australia; Email: cboyer@unsw.edu.au

I. Materials

Tin(II) 2-ethylhexanoate ($Sn(oct)_2$, 92.5-100.0%, Sigma Aldrich), benzyl alcohol (BnOH, ≥99%, Sigma Aldrich), ethylene glycol (≥99%, Sigma-Aldrich), anhydrous toluene (Tol, 99.8%, Sigma-Aldrich), anhydrous dichloromethane (DCM, 99.8%, Sigma-Aldrich), phenylbis (2,4,6-trimethylbenzoyl)phosphine oxide (TPO, 97%, Sigma-Aldrich), 2-(butylthiocarbonothioylthio) propanoic acid (BTPA, 95%, Boron Molecular), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB, 90%, Boron Molecular), 2-Isocyanatoethyl methacrylate (IEM, 98%, Sigma Aldrich), 2-Isocyanatoethyl acrylate (IEA, 97%, AmBeed), ε-caprolactone (CL, 97%, Sigma Aldrich), acrylic acid (AA, 99%, Sigma Aldrich), *N,N*-dimethylacrylamide (DMA, 99%, Sigma Aldrich), methyl acrylate (MA, 99%, Sigma-Aldrich), isobornyl acrylate (IBoA, technical grade, Sigma-Aldrich) *N*'-(ethylcarbonimidoyl)-*N,N*-dimethylpropane-1,3-diamine hydrochloride (EDC·HCL, ≥99%, AmBeed), 4-dimethylaminopyridine (DMAP, ≥99%, Sigma-Aldrich), sodium chloride (NaCl, ≥99%, Chem-Supply), magnesium sulfate ($MgSO_4$, ≥99%, Chem-Supply), and deuterated chloroform ($CDCl_3$, Cambridge Isotope Laboratories) were used as received. All the solvents were purchased from Chem supply.

II. Methods

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker Avance III 300 or Bruker Avance III 400 with a Prodigy CryoProbe. Signals are reported relative to the residual ^1H NMR signal of CDCl3 (δ = 7.26 ppm).

Size Exclusion Chromatography (SEC) analysis of the molecular weight distributions of the polymers were determined using a Shimadzu modular system composed of an SIL-20A auto-injector, a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm2) followed by three linear PL (Styragel) columns (105, 104 and 103), an RID-10A differential refractive-index (RI) detector, and a UV detector. The eluent was DMAc (containing 0.03% w/v LiBr and 0.05% w/v 2,6-dibutyl-4-methylphenol (BHT)) at 50 °C, run at a flow rate of 1.0 mL/min. The SEC was calibrated using narrow poly(styrene) (PS) standards with molecular weights of 200 – 10^6 g/mol.

Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) spectroscopy was performed to monitor photopolymerization kinetics using a Bruker Alpha FTIR spectrometer equipped with room temperature DTGS detectors. After taking a background reading of the empty plate, 20 μL of polymerization resin was pipetted onto the ATR crystal plate. An absorption spectrum was then obtained by scanning the droplet from 400-4000 cm^{-1}. After an initial reading, the droplet was irradiated with a Thorlabs mounted LED with a collimation adapter (λ_{max} = 405 nm, I_0 = 2.06 mW cm^{-2}) and subsequently the IR absorption spectra

were obtained at various times to determine the integral of the vinylic peak at time tx. Vinyl bond conversions were calculated from the disappearance of the C=C stretching peak at 1630 cm-1 normalized to the C=O stretching peak at 1760 cm^{-1} as an internal standard using Equation S1:

$$Conversion\ (\%) = 100\ \times (1 - \frac{int_x / std_x}{int_0 / std_0}) \quad \text{(S1)}$$

Where int_x is the integral of the 1600-1650 cm^{-1} peak at x min of irradiation, std_x is the integral of the 1670-1800 cm^{-1} peak at x min of irradiation, int0 is the initial integral of the 1600-1650 cm^{-1} peak before irradiation, and std_0 is the initial integral of the 1670-1800 cm^{-1} peak before irradiation. The vinyl bond conversion was monitored using 5 s intervals between 0 to 1 min and 15 s intervals between 1 to 2 min. All FTIR measurements were performed in triplicate.

Small Angle X-ray Scettering (SAXS) experiments were performed on an Anton Paar SAXSPoint 2.0 system with a Cu Kα (λ = 0.154 nm) microfocus X-ray source (50 kV/1 mA) and Dectris Eiger 1M detector. Data was collected at room temperature, under vacuum for 5 min from a sample at a sample-to-detector distance of 0.575 m. Samples were 3D printed at the thickness of 2×100 μm layers. Data was reduced to 1D by radial averaging the 2D detector after converting pixel positions to $q = (4\pi/\lambda)\sin\theta$, where 2θ is the scattering angle). The domain spacing was calculated using Equation S2:

$$d_{SAXS} = \frac{2\pi}{q} \quad \text{(S2)}$$

Scanning Electron Microscopy (SEM). All samples were set on a stub using conductive tape and coated with platinum coating with 15 nm thickness using a Leica ACE600 sputter coater. SEM images were obtained using a field-emission NanoSEM 230 instrument with a 3 kV accelerating voltage and a secondary electron detector.

Dynamic Mechanical Analysis (DMA) was performed using single cantilever testing methodology. The analysis was performed using a TA instruments Q800 dynamic mechanical analyzer. Initially, the 3D printed sample was measured using digital calipers and placed into the single cantilever clamp. The clamp was then tightened. Rectangular prism samples with dimensions of 40 × 8 × 1.5 mm (length × width × thickness) were used for all DMA experiments.

Estimation of the χP(AA-stat-PEGDA)-b-PCL by group molar method

Note 1: χP(AA-*stat*-PEGDA)-*b*-PCL was estimated using Supplementary Equation (S3):

$$\chi_{P(AA-stat-PEGDA)-b-PCL} = (1-x)\chi_{PEGDA-PCL} + x\chi_{PAA-PCL} + x(1-x)\chi_{PAA-PEGDA} \quad \text{(S3)}$$

Where x is the weight fraction of AA in P(AA-stat-PEGDA) block (x = 0.54). $\chi_{1\text{-}2}$ was calculated using Supplementary Equation (S4):

$$\chi_{1-2} = \frac{VN_A}{RT}(\delta_1 - \delta_2)^2 \quad \text{(S4)}$$

Where V is the reference volume (set to 118 Å^3), R is the gas constant (1.987 cal mol^{-1} K^{-1}), T is temperature (set to 298 K), N_A is the Avogadro's number (6.02 × 1023 mol^{-1}), δ ((cal cm^{-3})$^{1/2}$) is solubility parameter estimated using the group molar contribution method proposed by Small[1] using Supplementary Equation (S5):

$$\delta = \frac{d\sum G}{M} \quad \text{(S5)}$$

Where d (g cm^{-3}) is density, M is monomer molecular weight, $\sum G$ is the sum of the molar attraction constants. [1-3] Estimated δ values were as follows: δ_{PCL} = 9.05 cal$^{1/2}$ cm$^{-3/2}$, δ_{PAA} = 9.31 cal$^{1/2}$ cm$^{-3/2}$, δ_{PEGDA} = 5.87 cal$^{1/2}$ cm$^{-3/2}$. Then, χ parameters were calculated using Supplementary Equation (S4): $\chi_{PEGDA\text{-}PCL}$ = 1.211, $\chi_{PAA\text{-}PCL}$ = 0.008, $\chi_{PAA\text{-}PEGDA}$ = 1.42. Subsequently, $\chi_{P(AA\text{-}stat\text{-}PEGDA)\text{-}b\text{-}PCL}$ was calculated using Supplementary Equation (S3): $\chi_{P(AA\text{-}stat\text{-}PEGDA)\text{-}b\text{-}PCL}$ = 0.92.

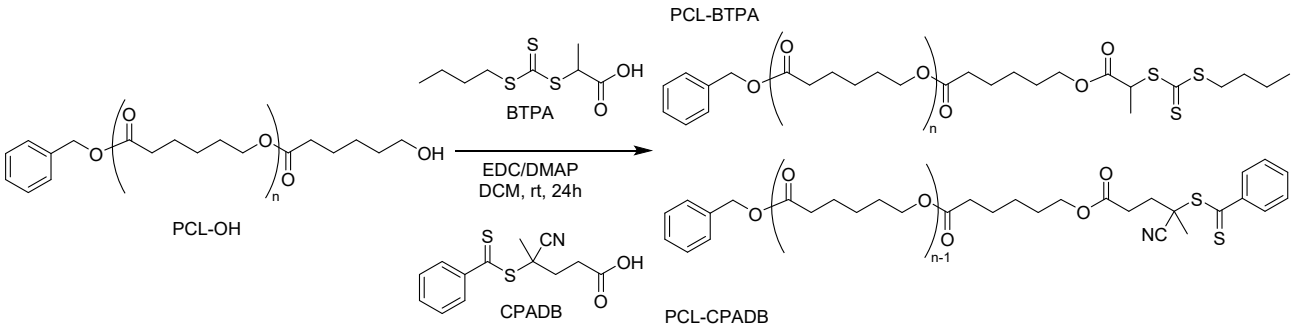
III. Experimental procedures

Poly(ε-caprolactone) synthesis

A Schlenk equipped with magnetic stirrer was flame dried prior to the start of the experiment. ε-caprolactone (15 g, 0.131 mol), $Sn(Oct)_2$ catalyst (0.5 wt% with respect to monomer), BnOH initiator (0.57g, 5.25mmol, 1:25 ratio initiator and monomer) and anhydrous toluene (30 mL, 4.4 mol L^{-1}) were added to the Schlenk while being purged under argon (30 minutes). Then, two freeze-pump cycles were performed by freezing the solution in liquid N_2/Acetone mix. After freezing, the head space was turn under dynamic vacuum for five minutes to ensure a proper inert atmosphere. The reaction performed for 24h at 105 °C. The reaction was monitored by ^{1}H NMR with the shift of the Hε signal from 4.28 ppm to 4.14 ppm until near-complete conversion (see figure **S1**). After completion of the reaction, the solution was concentrated and precipitated in cold diethyl ether, following by drying overnight under vacuum yielding a white powder with final yield of 93%.

End-chain functionalization

RAFT end-chain functionalization

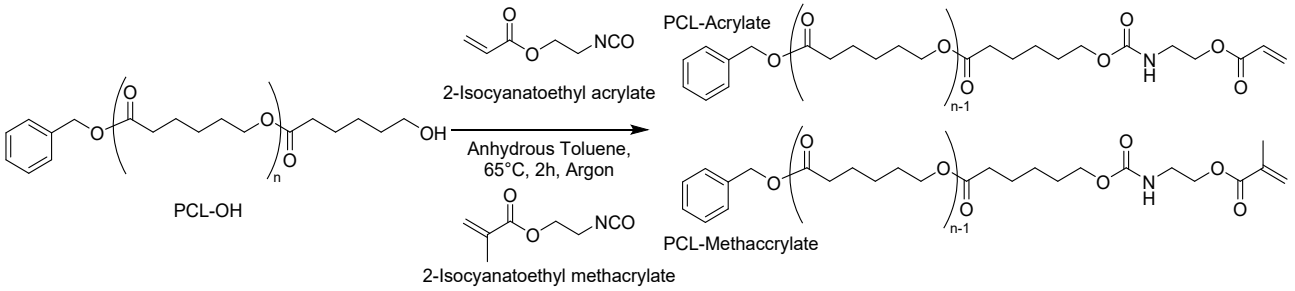


Scheme S 1. Synthesis of RAFT end-chain poly(ε-caprolactone): PCL-BTPA (top) and PCL-CPADB (bottom).

In round bottom flask poly(ε-caprolactone) (PCL-OH) (3 g, 1 mmol, 1eq. M=3000 g mol^{-1}), BTPA (333 mg, 1.4 mmol, 1.4 eq.) or CPADB (391 mg, 1.4 mmol, 1.4eq.), and DMAP (24 mg, 0.2 mmol, 0.2eq.) were added and dissolved in anhydrous DCM (10 mL). The reaction mixture was then cooled to 0 °C using an ice-water bath, and a solution of EDC·HCl (230 mg, 1.2 eq., 1.2 mmol) in DCM (10 mL) was slowly added over 10 min using a syringe. After addition completed, the reaction was stirred for 15 min at 0 °C. Then, the flask was wrapped in aluminium foil and stirred at room temperature (~25 °C) for approximately 24 h. After that, the reaction mixture was successively washed with 1 M HCl (2 × 50 mL), deionized water (2 × 50 mL), and brine (2 × 50 mL), and dried over anhydrous $MgSO_4$. The DCM was removed using a rotary evaporator and dynamic vacuum, followed by solubilization in minimum amount of toluene and precipitation in cold diethyl ether.

Then, dried overnight under vacuum yielding a yellow and pink powders for PCL-BTPA and PCL-CPADB, respectively, with final yield of 53% and 49%. And were characterized by DMAc-SEC and ^{1}H NMR.

Vinyl end-chain functionalization



Scheme S 2. Synthesis of vinyl end-chain poly(ε-caprolactone): PCL-Acrylate (top) and PCL-Methacrylate (bottom).

A Schlenk equipped with magnetic stirrer was flame dried prior to the start of the experiment and poly(ε-caprolactone) (2 g, 0.6 mmol, 1eq.) was added. Then, three cycles vacuum/argon was done before addition of the 2-isocyanatoethyl acrylate (150 mg, 1.06 mmol, 1.6 eq.) or 2-isocyanatoethyl methacrylate (165 mg, 1.06 mmol, 1.6 eq.) solutions. The solution was gently stirred while bubbling argon through the solution for 30 minutes before two freeze pump was performed. The reaction mixtures were stirred at 65 °C for 2 hours. After that, the solutions were concentrated and precipitated in cold diethyl ether following by drying overnight under vacuum yielding a white powder with final yield of 90% and 83% for PCL-acrylate and PCL-methacrylate, respectively. And were characterized by DMAc-SEC and ^{1}H NMR.

Resin formulation for LCD-3D printing

The typical procedure for fabricating 3D printed objects is as follows: A 3D object template was downloaded using Thingiverse platform and the object was exported as an .stl file format. The .stl file was opened using Photon Workshop 64. The Z lift speed and retract speed were both set to 1 mm/s, and the Z lift distance was set to 6 mm. When preparing objects a layer thickness of 50 μm was used. The file was then sliced using Photon Workshop and copied to a flash drive for use with a masked DLP 3D printer (Anycubic Photon S) with a violet (λmax = 405 nm) light LED array (I_0 = 2 mW.cm^{-2}). 20 s/layer cure time was used for PCL-Acrylate and PCL-Methacrylate while 30s/layer cure time was used for PCL-BTPA and control PCL-OH formulation.

Etching of PCL fragment

The printed materials were etched in 5 mL vials. Objects were placed in the vials, followed by the addition of 4 mL of 0.5 M NaOH (aq.) solution. The vials were sealed and gently stirred on an orbital shaker at 60 ℃ for 24 and 48 hours. After etching, the solution was carefully removed by pipette, and 100 μL of water was added to each vial for freeze-drying before preparation for SEM microscopy.

IV. Supplementary data

Poly(ε-caprolactone) characterization

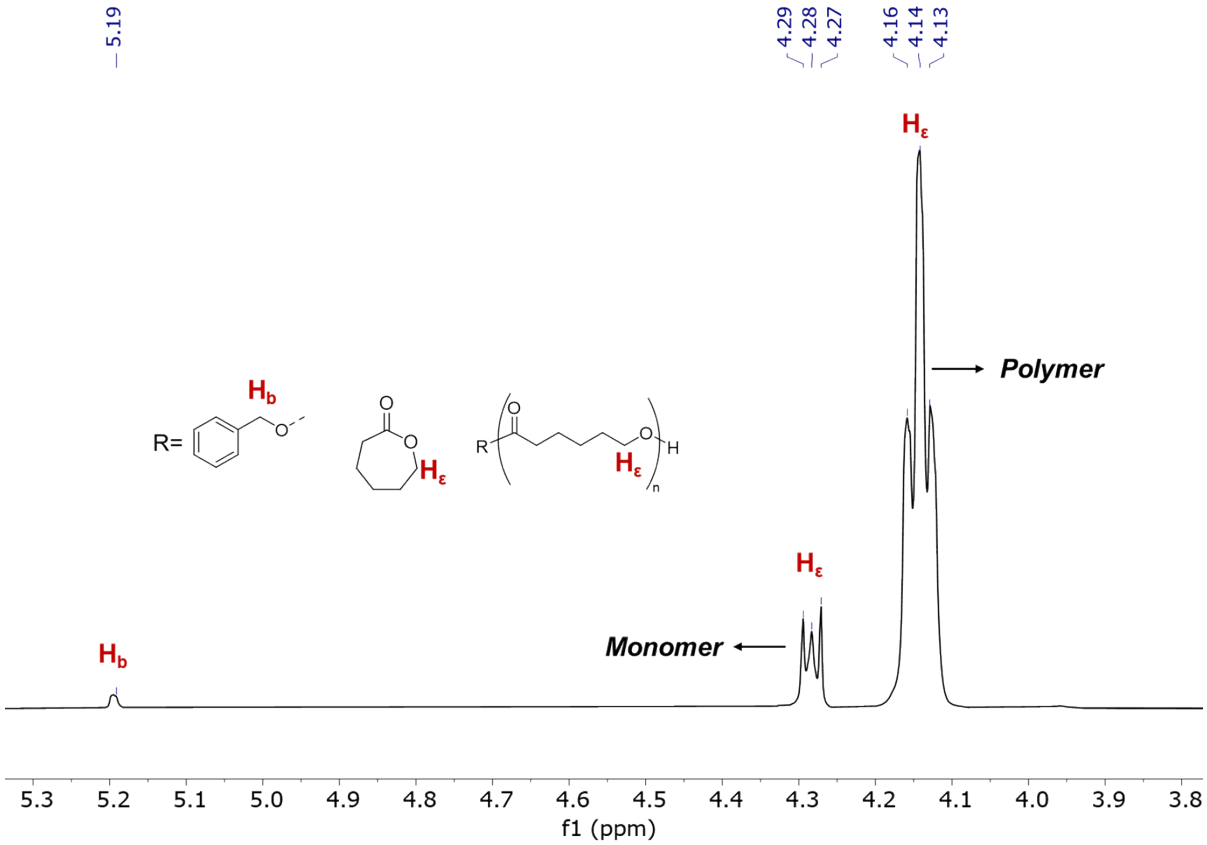


Figure S1. *^{1}H-NMR spectrum displaying the shift/conversion of the Hε protons from ε-caprolactone monomers (4.28 ppm) into those of the synthesized PCL polymer (4.14 ppm), recorded in $CDCl_3$, 400MHz, 298K.*

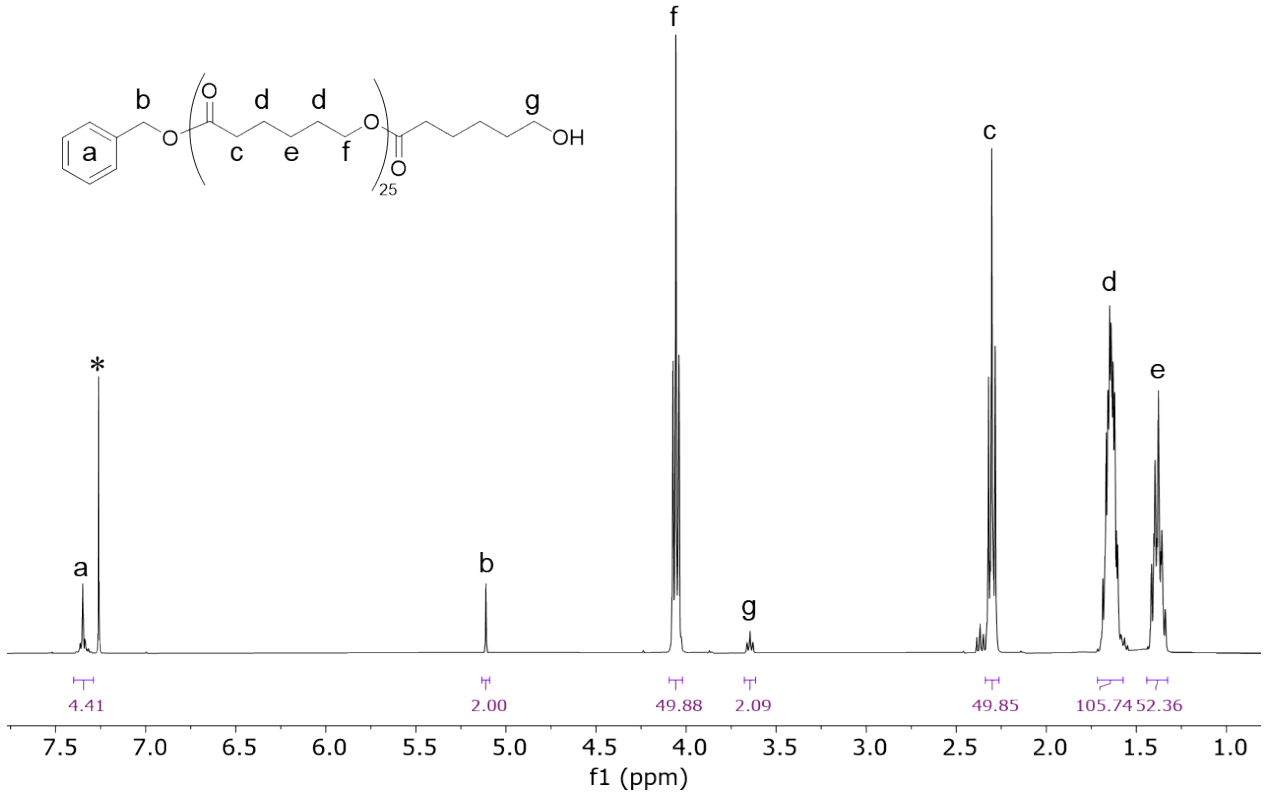


Figure S2. *^{1}H NMR spectrum of purified poly(ε-caprolactone) (PCL_{3k}-OH) recorded in $CDCl_3$ (*), 400MHz, 298K.*

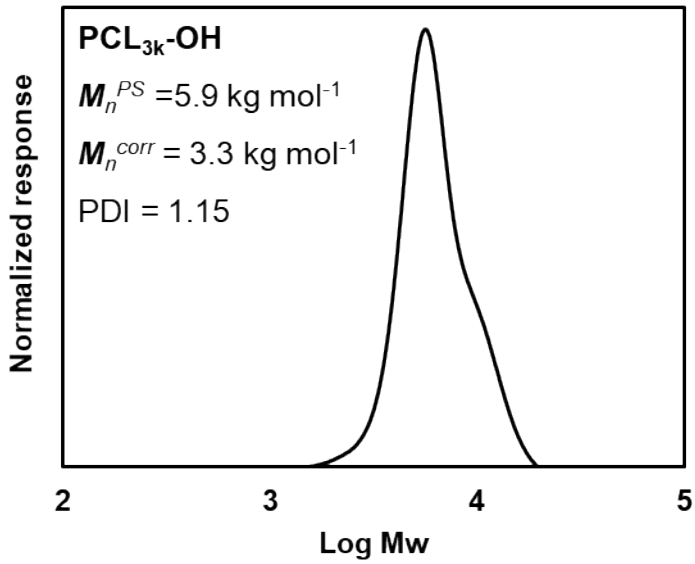


Figure S3. *Molecular weight distribution of poly(ε-caprolactone) (PCL_{3k}-OH) obtained by DMAc-SEC, PS calibration.*

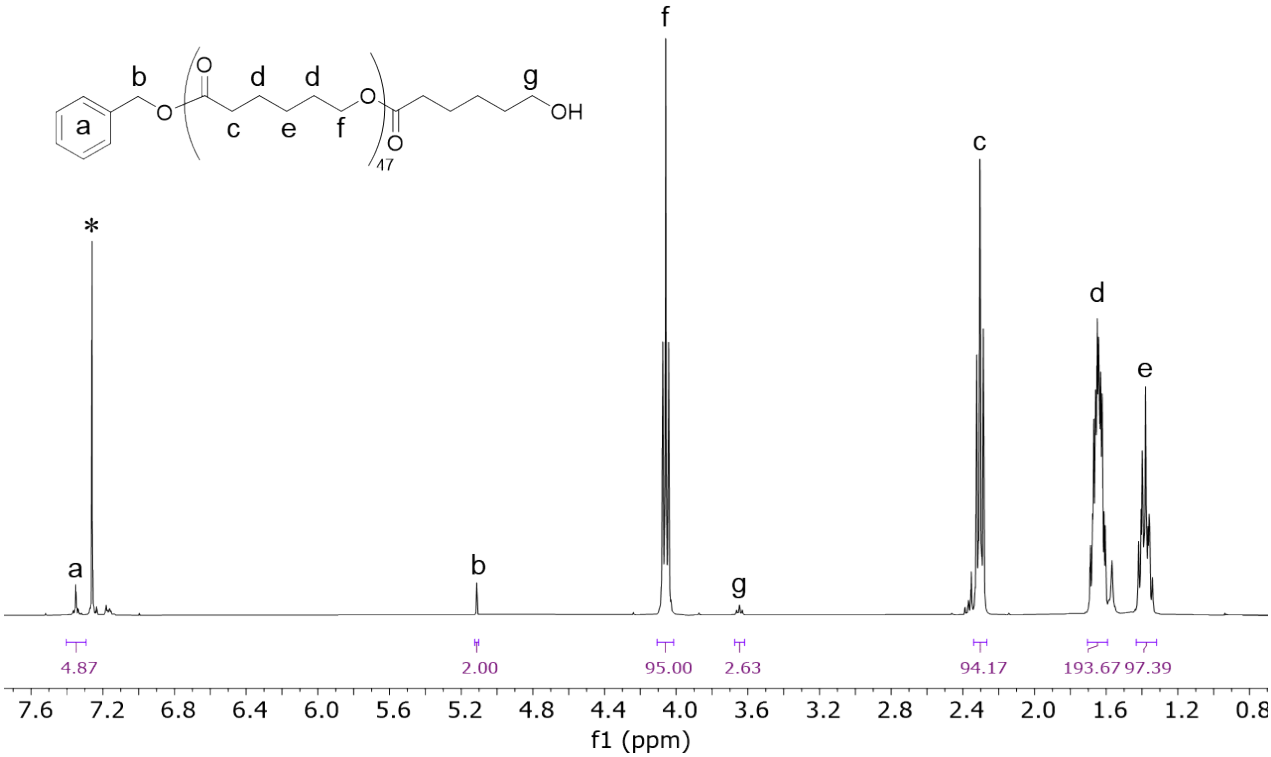


Figure S4. *^{1}H NMR spectrum of purified poly(ε-caprolactone) ($PCL_{5.5k}$-OH) recorded in $CDCl_3$ (*), 400MHz, 298K.*

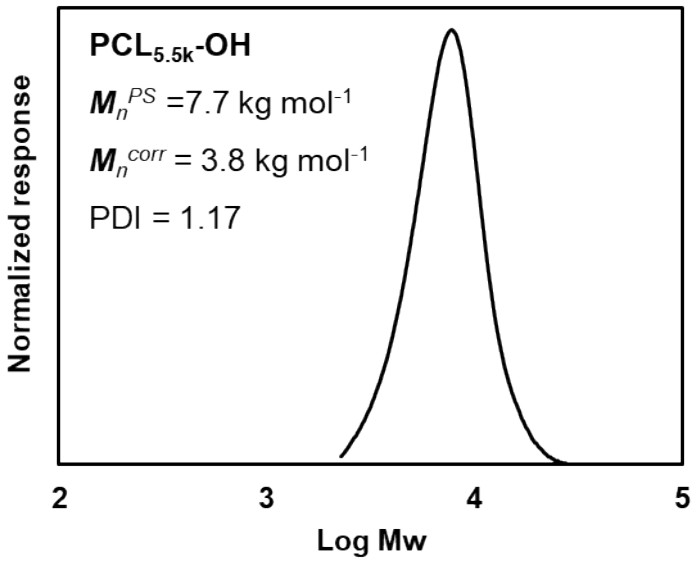


Figure S5. *Molecular weight distribution of poly(ε-caprolactone) ($PCL_{5.5k}$-OH) obtained by DMAc-SEC, PS calibration.*

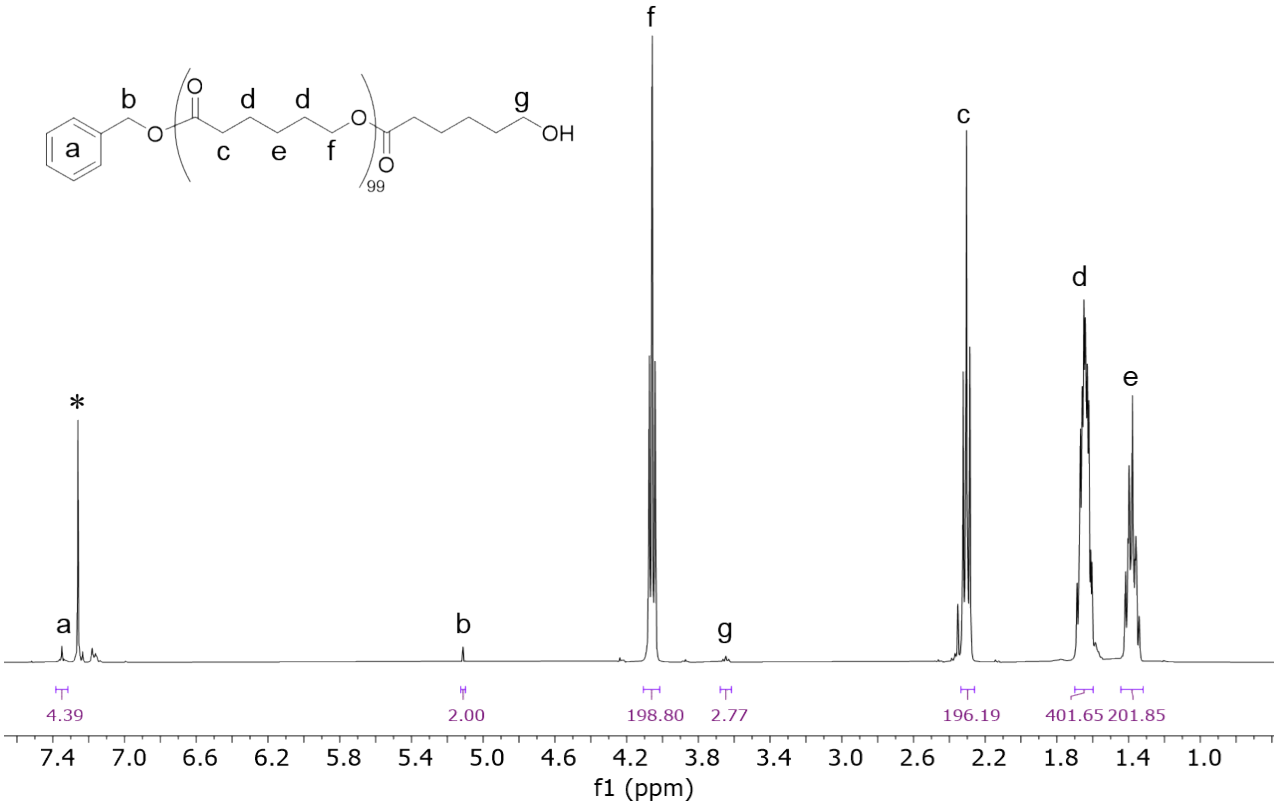


Figure S6. *^{1}H NMR spectrum of purified poly(ε-caprolactone) (PCL_{11k}-OH) in $CDCl_3$ (*), 400MHz, 298K.*

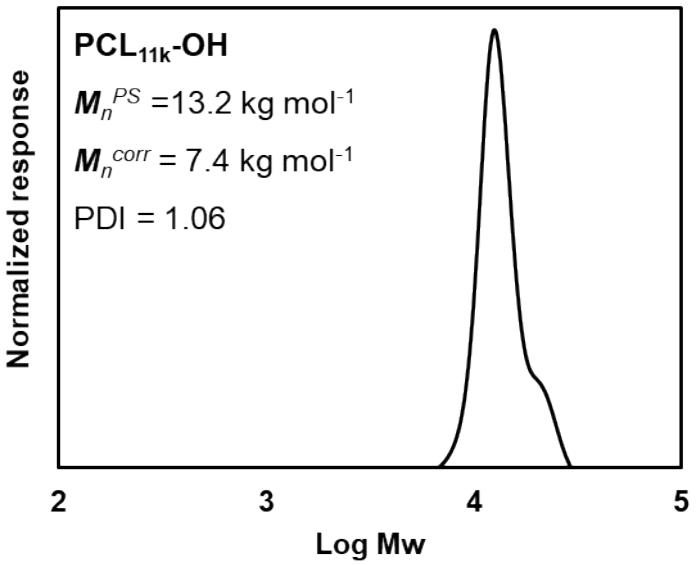


Figure S7. *Molecular weight distribution of poly(ε-caprolactone) (PCL_{11k}-OH) obtained by DMAc-SEC, PS calibration.*

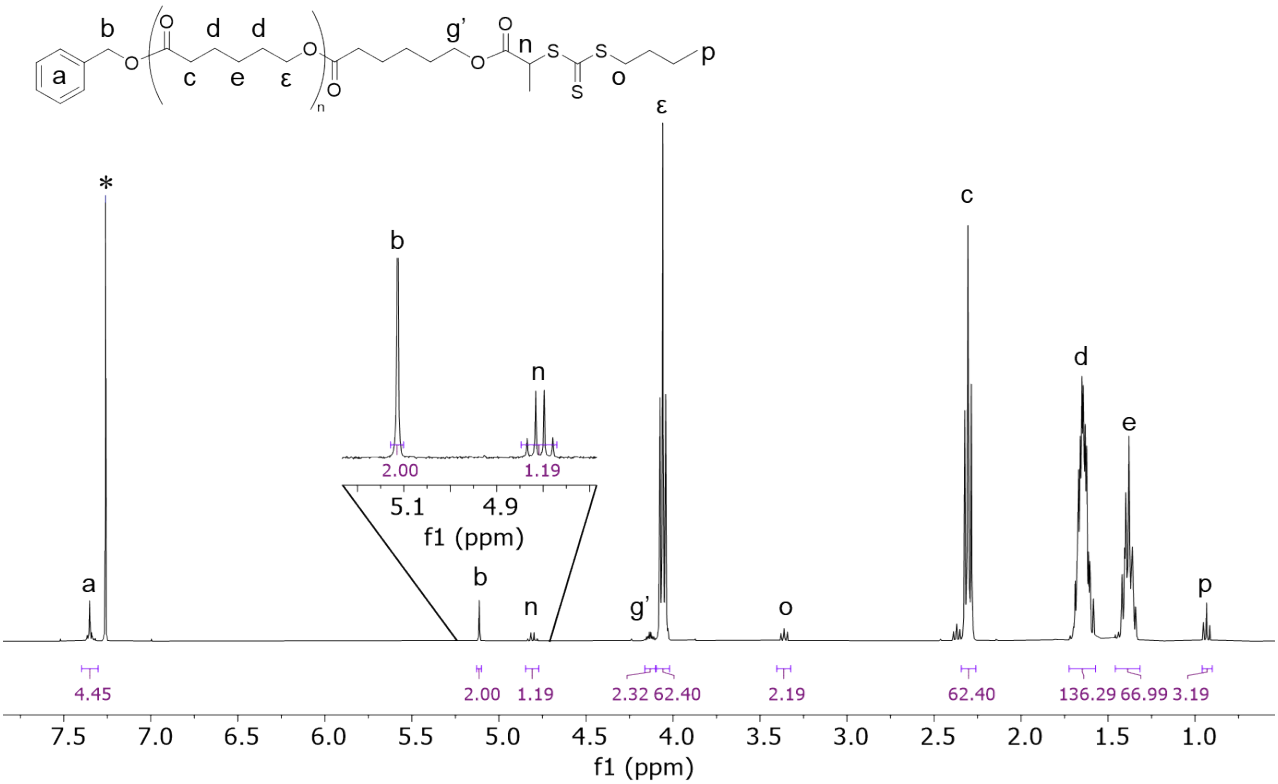


Figure S8. *[1]H NMR spectrum of purified poly(ε-caprolactone)-BTPA (PCL_{3k}-BTPA) recorded in $CDCl_3$ (*), 400MHz, 298K.*

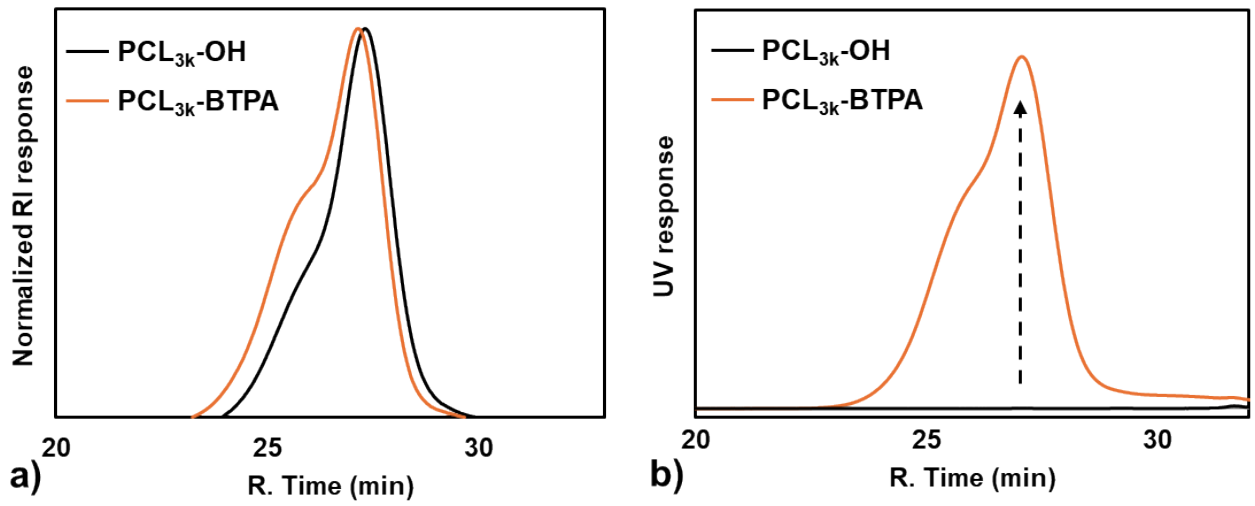


Figure S9. *(**a**) SEC chromatograms of poly(ε-caprolactone)-BTPA (PCL_{3k}-BTPA) obtained by DMAc-SEC, PS calibration, $M_n^{PS\ standard}$ = 7.3 kg mol^{-1}, $M_n^{corr} = M_n^{PS\ standard} x0.56$ = 4.1 kg mol^{-1}, M_w = 8.5 kg mol^{-1}, PDI = 1.17, (**b**) UV response.*

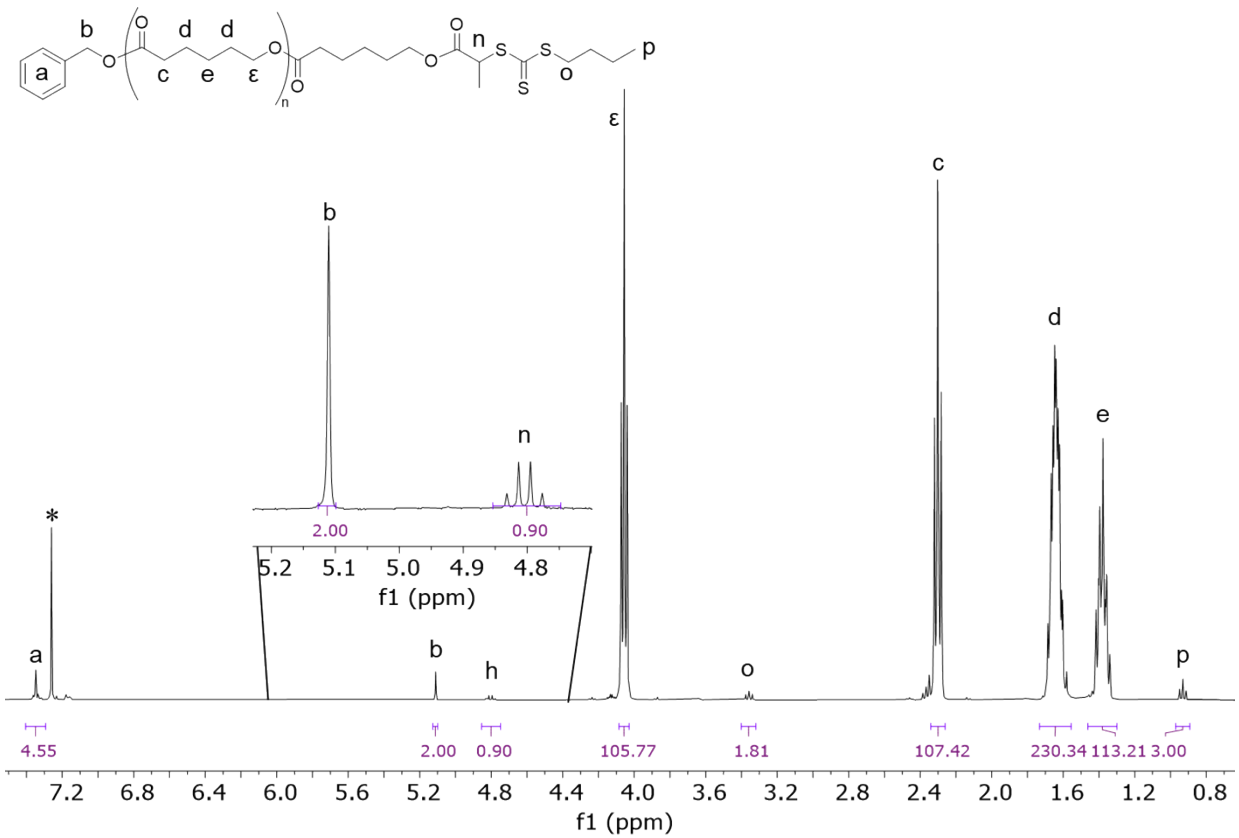


Figure S10. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-BTPA ($PCL_{5.5k}$-BTPA) recorded in $CDCl_3$ (*), 400MHz, 298K.*

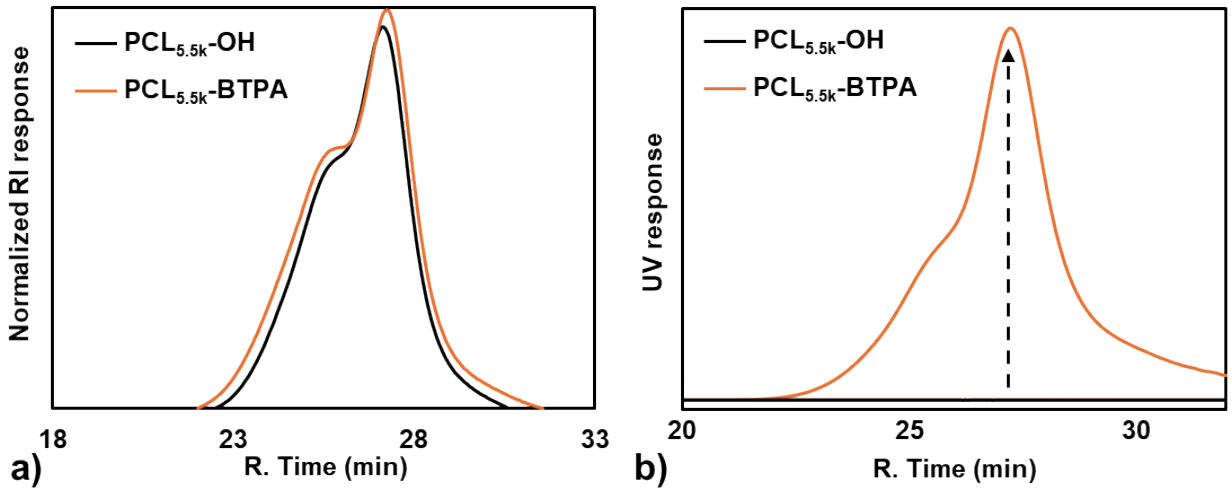


Figure S11. *(**a**) SEC chromatograms of poly(ε-caprolactone)-BTPA ($PCL_{5.5k}$-BTPA) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{PS\ standard} = 7.8\ kg\ mol^{-1}$, $\boldsymbol{M}_n^{corr} = \boldsymbol{M}_n^{PS\ standard} x0.56 = 4.4\ kg\ mol^{-1}$, $\boldsymbol{M}_w = 10.6\ kg\ mol^{-1}$, PDI = 1.17, (**b**) UV response.*

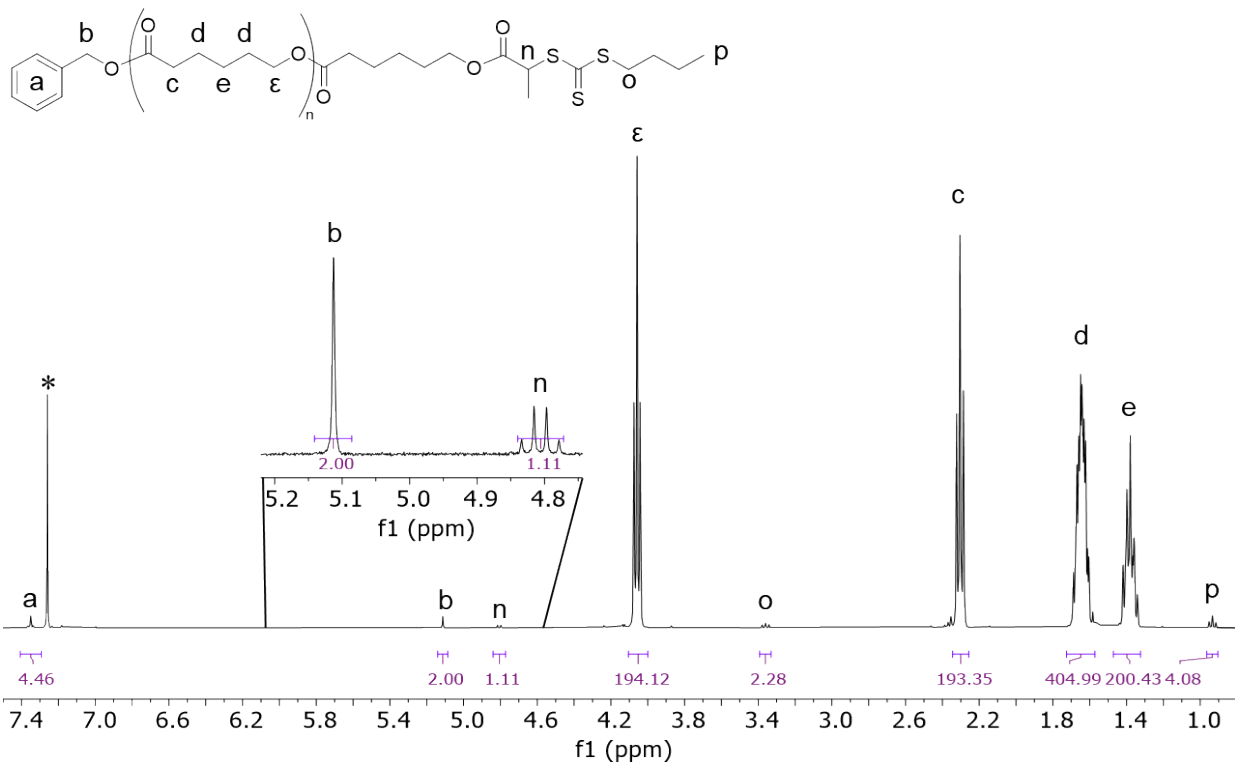


Figure S12. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-BTPA (PCL_{11k}-BTPA) recorded in $CDCl_3$ (*), 400MHz, 298K*

.

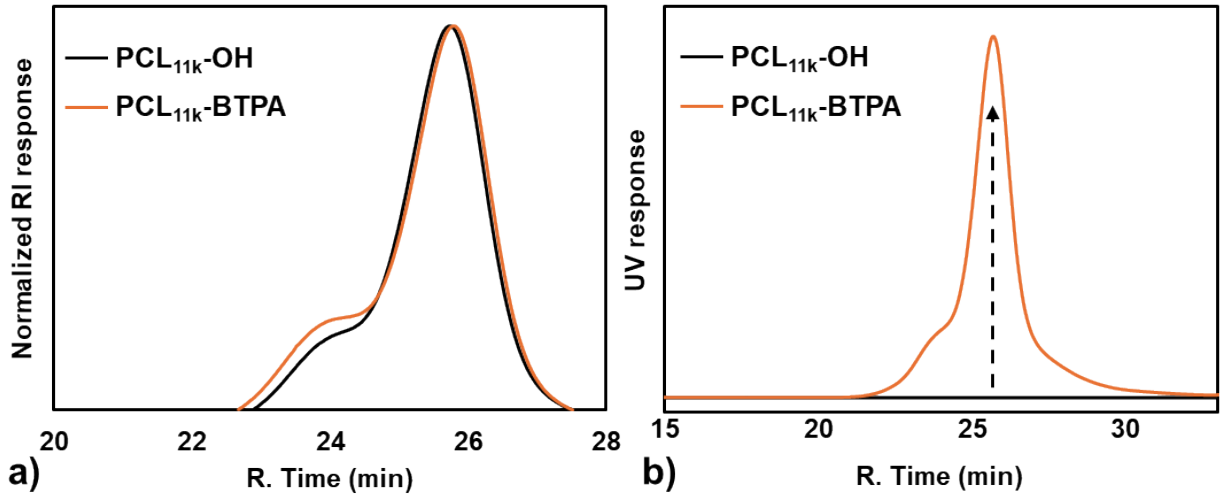


Figure S13. ***(a)*** *SEC chromatograms of poly(ε-caprolactone)-BTPA (PCL_{11k}-BTPA) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{\text{PS standard}} = 13.3$ kg mol^{-1}, $\boldsymbol{M}_n^{corr} = \boldsymbol{M}_n^{\text{PS standard}} \times 0.56 = 7.4$ kg mol^{-1}, $\boldsymbol{M}_w = 14.2$ kg mol^{-1}, PDI = 1.07,* ***(b)*** *UV response.*

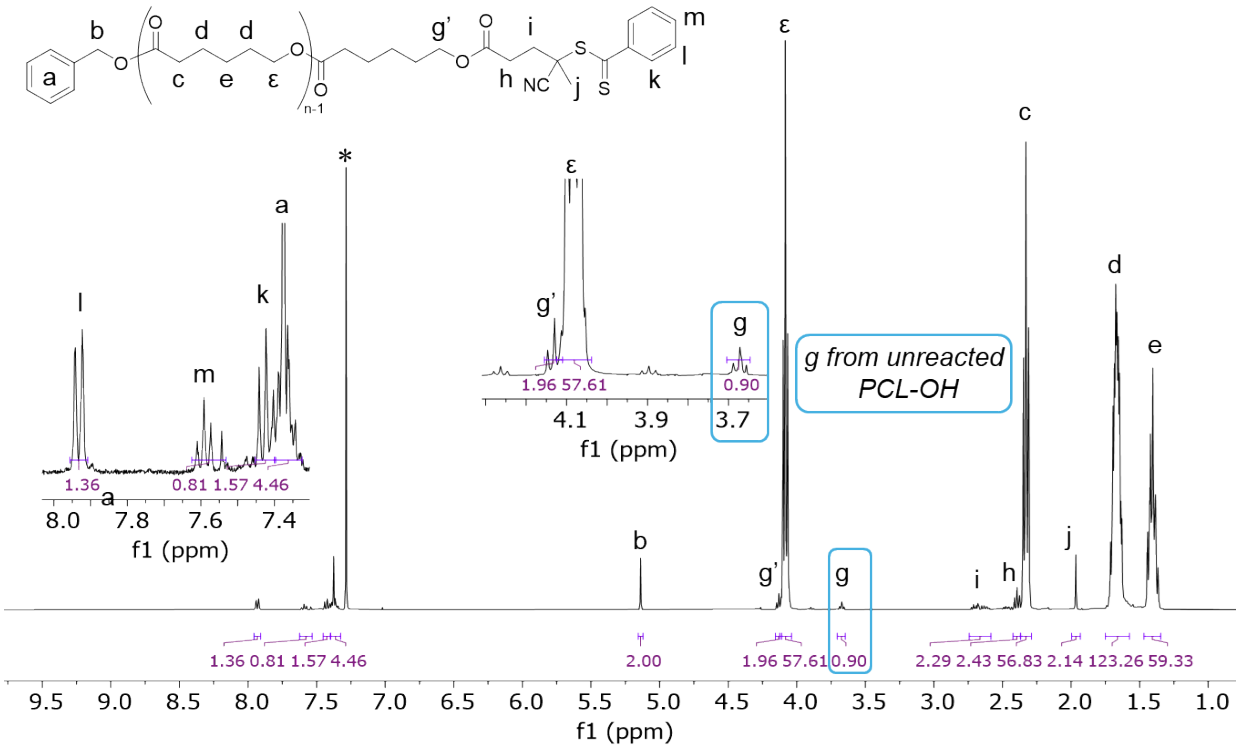


Figure S14. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-CPADB (PCL_{3k}-CPADB) recorded in $CDCl_3$ (*), 400MHz, 298K.*

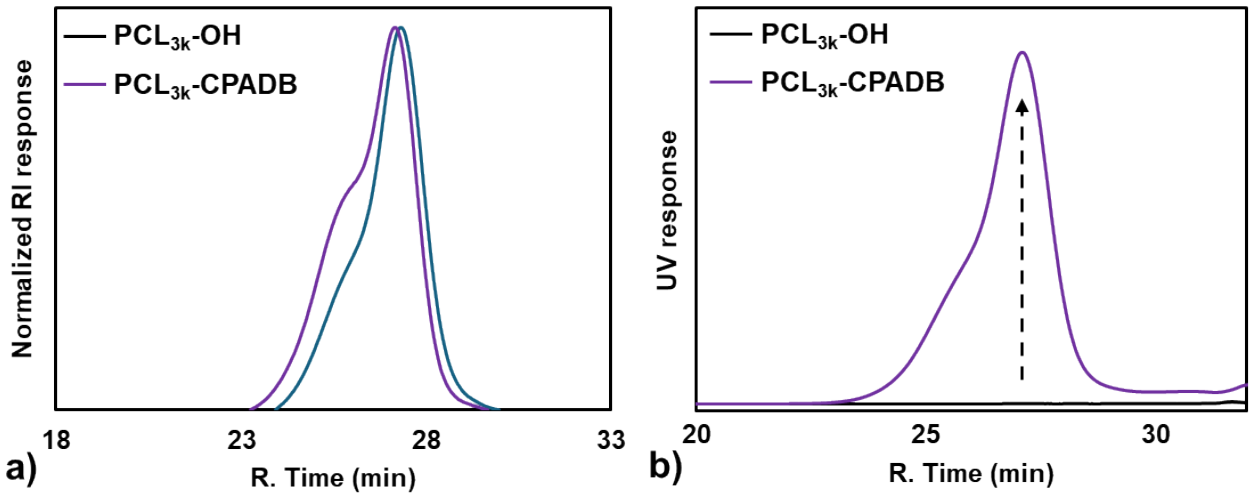


Figure S15. *(**a**) SEC chromatograms of poly(ε-caprolactone)-CPADB (PCL_{3k}-CPADB) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{PS\ standard}$ = 6.9 kg mol^{-1}, $\boldsymbol{M}_n^{corr} = \boldsymbol{M}_n^{PS\ standard}$x0.56 = 3.9 kg mol^{-1}, $\boldsymbol{M}_w$ = 8.5 kg mol^{-1}, PDI = 1.17, (**b**) UV response.*

Poly(ε-caprolactone)-Acrylate/Methacrylate

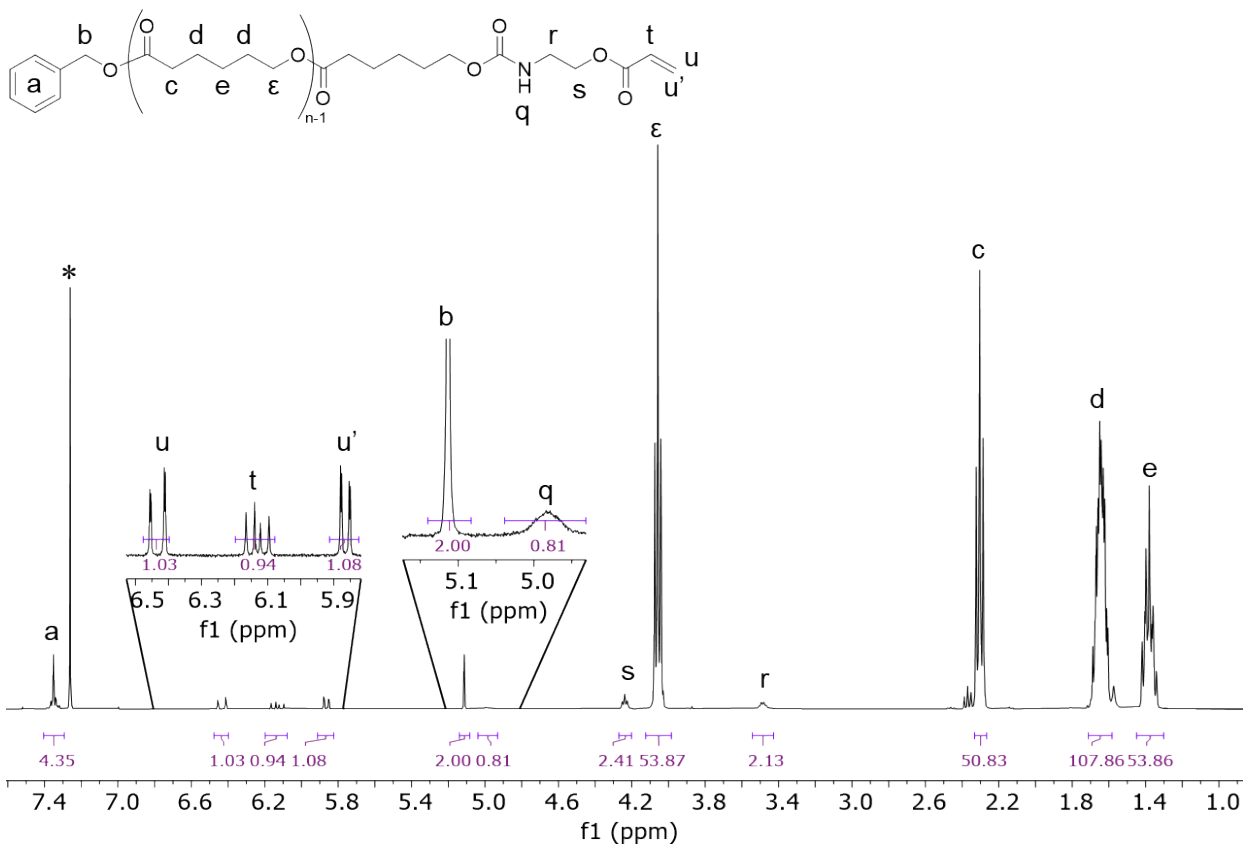


Figure S16. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-Acrylate (PCL_{3k}-Acrylate) recorded in $CDCl_3$ (*), 400MHz, 298K.*

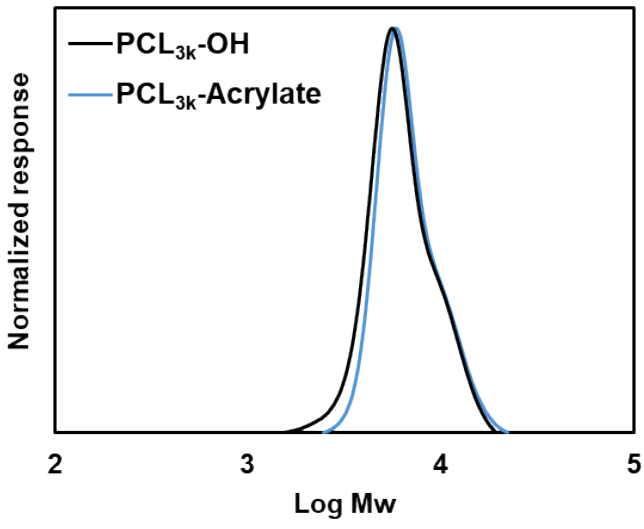


Figure S17. *SEC chromatograms of poly(ε-caprolactone)-Acrylate (PCL_{3k}-Acrylate) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{PS\ standard}$ = 6.5 kg mol^{-1}, $\boldsymbol{M}_n^{corr} = \boldsymbol{M}_n^{PS\ standard}$x0.56 = 3.6 kg mol^{-1}, $\boldsymbol{M}_w$ = 7.4 kg mol^{-1}, PDI = 1.13.*

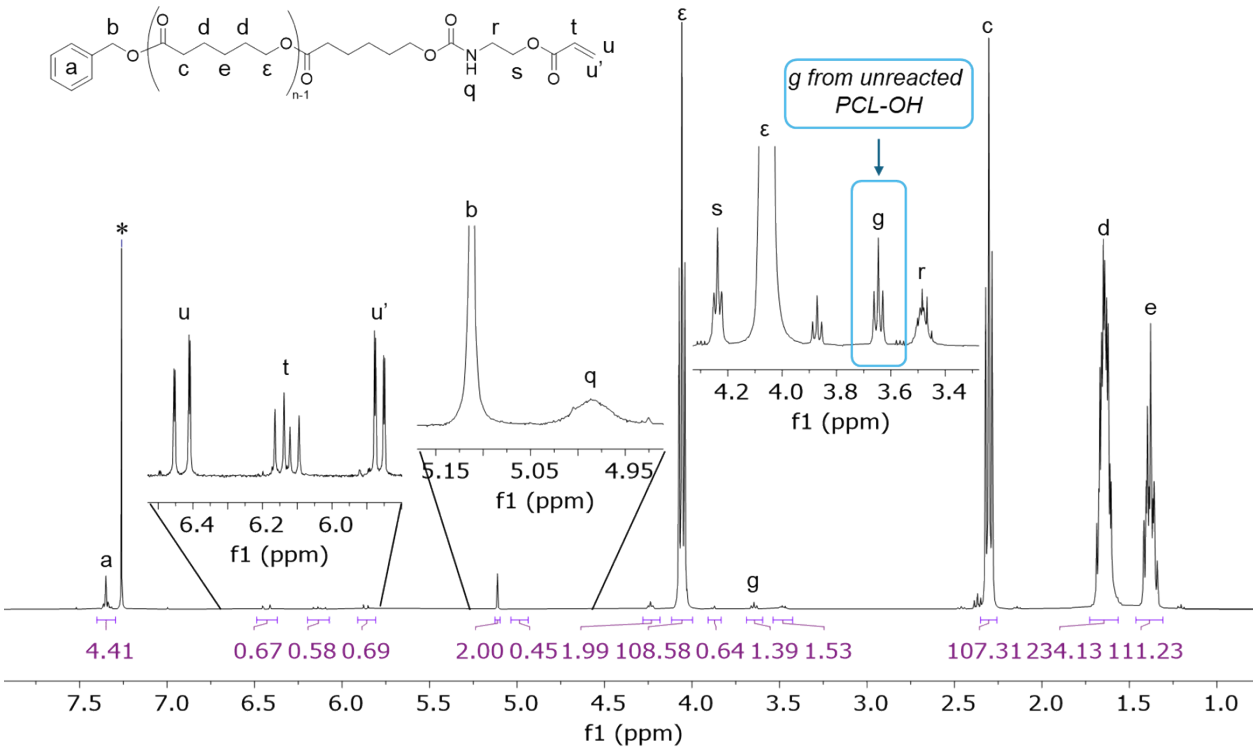


Figure S18. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-Acrylate ($PCL_{5.5k}$-Acrylate) recorded in $CDCl_3$ (*), 400MHz, 298K.*

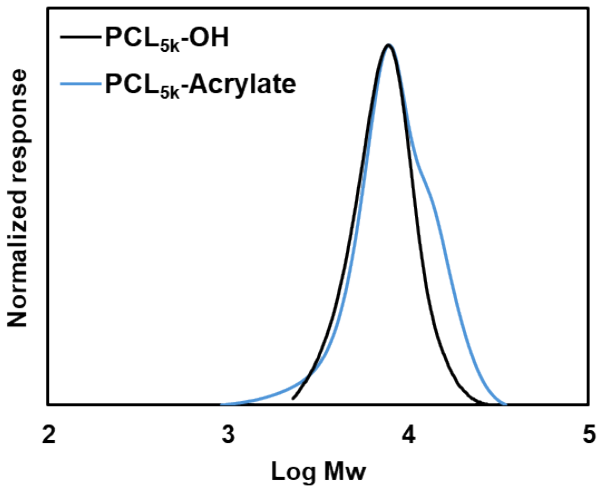


Figure S19. *SEC chromatograms of poly(ε-caprolactone)-acrylate ($PCL_{5.5k}$-acrylate) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{\,PS\ standard} = 7.9$ kg mol^{-1}, $\boldsymbol{M}_n^{\,corr} = \boldsymbol{M}_n^{\,PS\ standard} \times 0.56 = 4.5$ kg mol^{-1}, $\boldsymbol{M}_w = 10.1$ kg mol^{-1}, PDI = 1.27.*

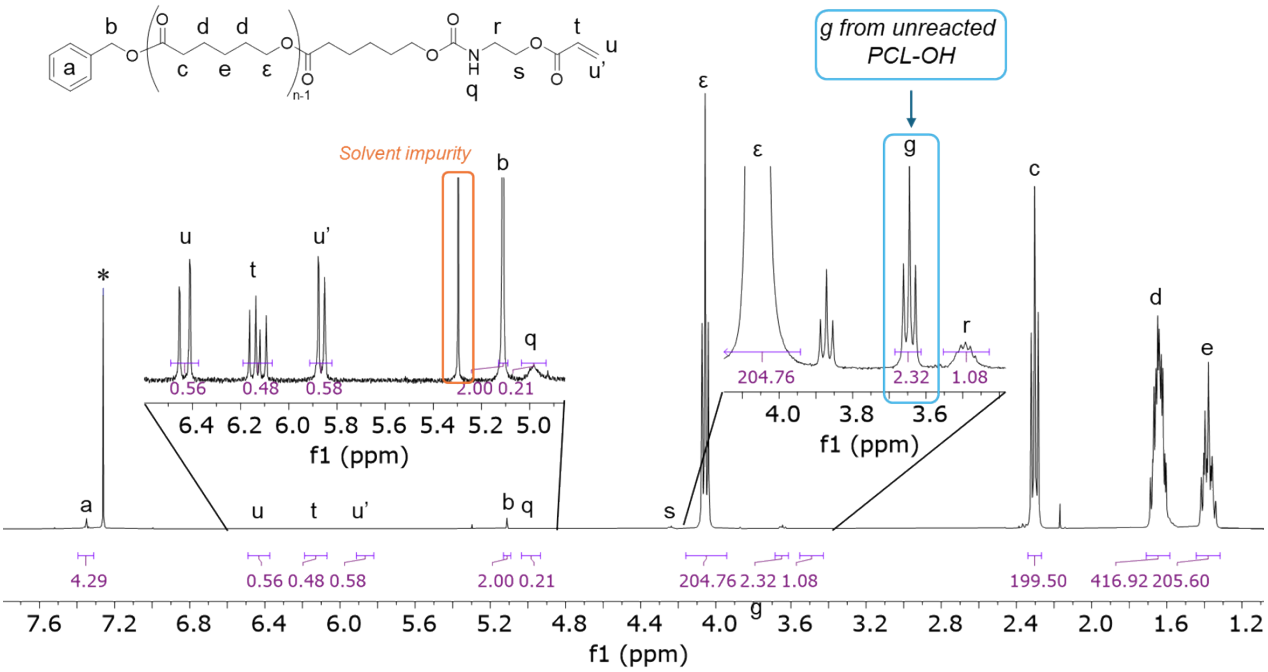


Figure S20. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-Acrylate (PCL_{11k}-Acrylate) recorded in $CDCl_3$ (*), 400MHz, 298K.*

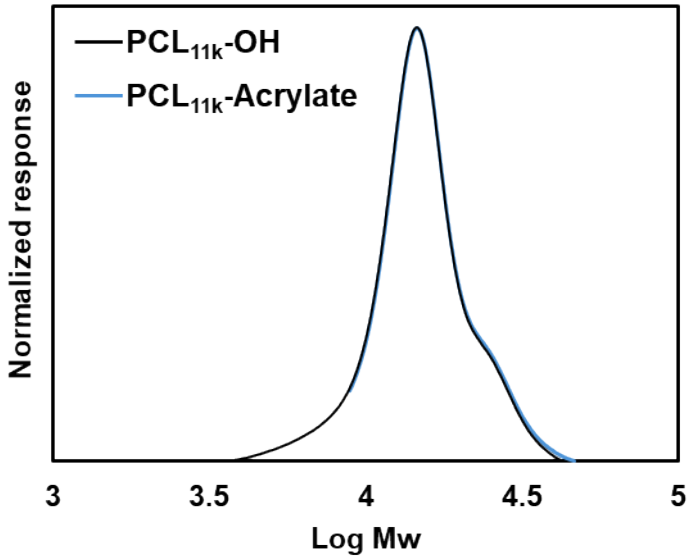


Figure S21. *SEC chromatograms of poly(ε-caprolactone)-acrylate ($PCL_{5.5kk}$-Methacrylate) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{PS\,standard}$ = 14.4 kg mol^{-1}, $\boldsymbol{M}_n^{corr} = \boldsymbol{M}_n^{PS\,standard}$x0.56 = 8.1 kg mol^{-1}, $\boldsymbol{M}_w$ = 16.2 kg mol^{-1}, PDI = 1.13.*

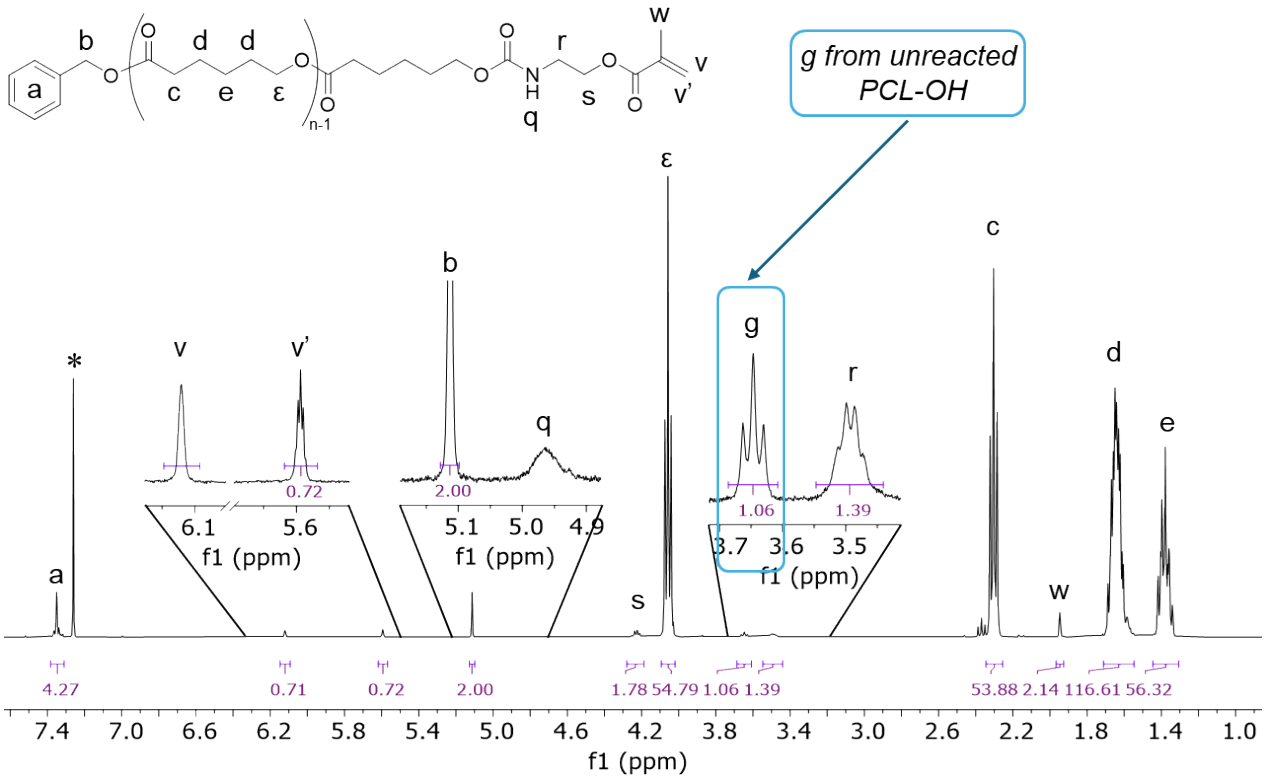


Figure S22. *^{1}H NMR spectrum of purified poly(ε-caprolactone)-Methacrylate (PCL_{3k}-Methacrylate) recorded in $CDCl_3$ (*), 400MHz, 298K.*

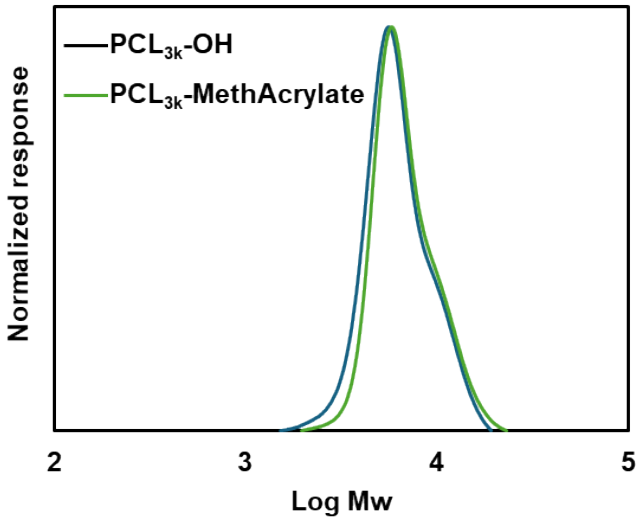


Figure S23. *SEC chromatograms of poly(ε-caprolactone)-Methacrylate (PCL_{3k}-Methacrylate) obtained by DMAc-SEC, PS calibration, $\boldsymbol{M}_n^{PS\ standard}$ = 7.8 kg mol^{-1}, $\boldsymbol{M}_n^{corr} = \boldsymbol{M}_n^{PS\ standard}$x0.56 = 4.4 kg mol^{-1}, $\boldsymbol{M}_w$ = 10.7 kg mol^{-1}, PDI = 1.36.*

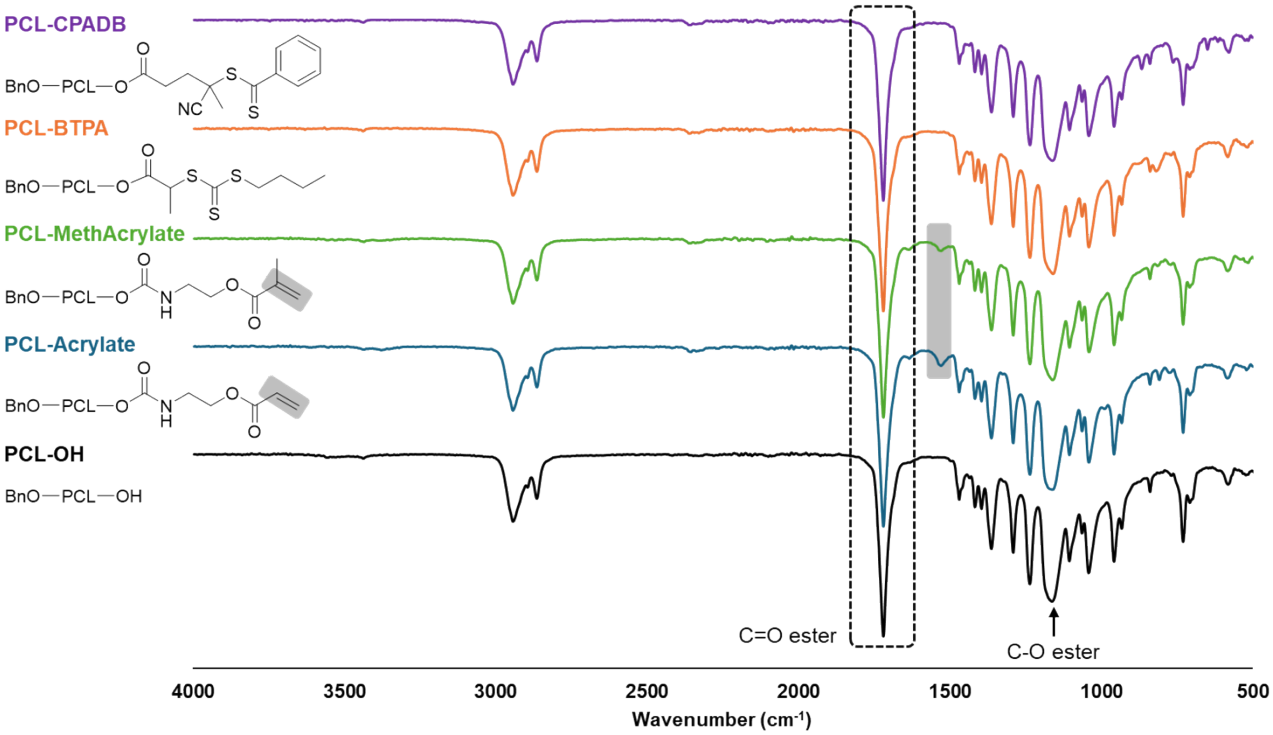
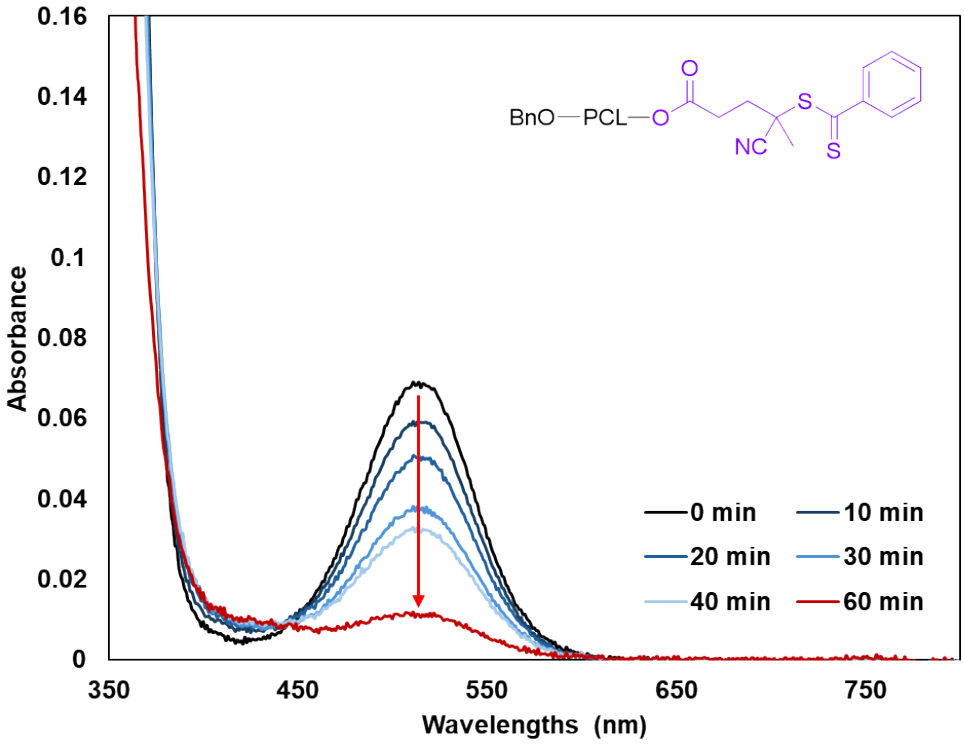


Figure S24. *ATR-FTIR spectra comparison of initial PCL_{3k}-OH (black) and after chain-end modification with Acrylate (blue), Methacrylate (green), BTPA (yellow) and CPADB (orange).*



ff

Figure S 25. *UV-Vis monitoring the PCL_{3k}-CPADB decomposition under 405 nm irradiation. [PCL_{3k}-CPADB] = 1 mmol L^{-1} in dichloromethane, irradiation 20 mW cm^{-2} violet light (λ_{max} = 405 nm).*

LCD-3D printing

Table S1. *Resins molar ratios of [AA]/[PEGDA]/[PCL_{3k}-X] at four loading of PCL_{3k}-X (15, 21, 25 and 35 wt%) and corresponding domain spacing obtained by SAXS. Molar ratio of [AA]/[PEGDA] and TPO was fixed at 9/1 and 1 w%, respectively.*

Chain-End (R)	***Loading of MacroCTA [wt%]***	***Resin composition [wt%]***		***d_{SAXS} (nm)***
		AA	***$PEGDA^{575}$***	
BTPA	15	44	39	15.20
	21	42	36	13.36
	25	40	34	14.13
	35	35	29	13.38
CPADB	21	42	36	No signal
Acrylate	15	44	40	14.54
	21	42	36	14.13
	25	40	34	13.75
	35	35	29	11.28
Methacrylate	15	44	40	No signal
	21	42	36	No signal
	25	40	34	No signal
	35	35	29	No signal

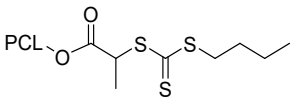
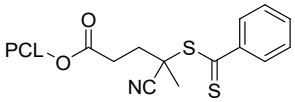
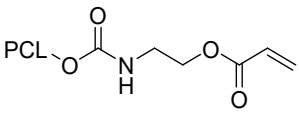
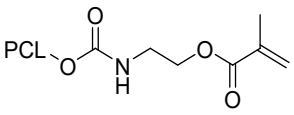
	15 wt%	***21 wt%***	***25 wt%***	***35 wt%***
PCL-BTPA 				
PCL-CPADB 	X		X	X
PCL-Acrylate 				
PCL-Methacrylate 				

Figure S26. *Printed SAXS samples at various loading and different PCL-R.*

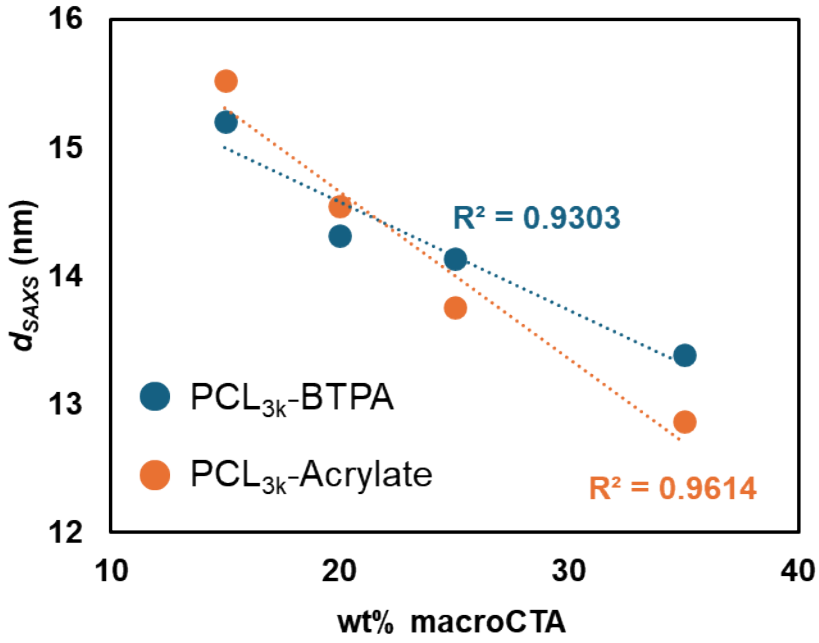


Figure S27. *Plot of the domain spacing (d_{SAXS}) as function of loading for PCL_{3k}-Acrylate (orange) and PCL_{3k}-BTPA (blue).*

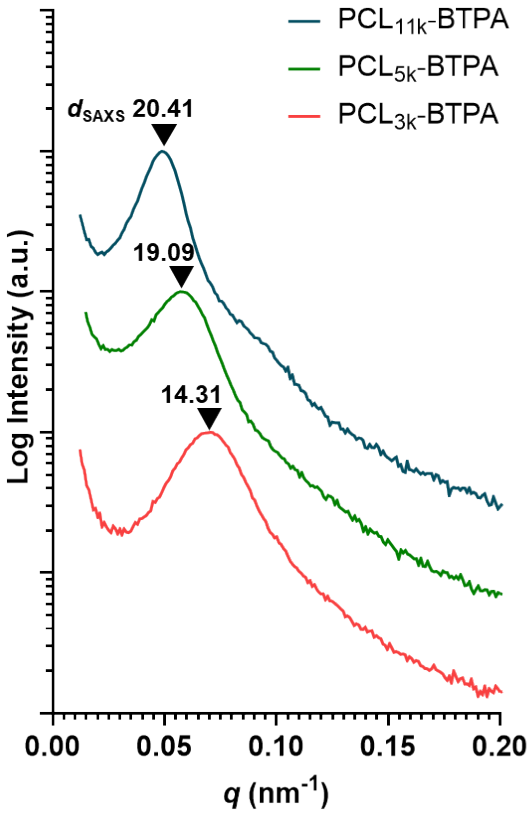


Figure S28. *SAXS profiles and corresponding domain spacing (d_{SAXS}) values of materials 3D printed using varied X_n of PCL-BTPA:3k (red curve, bottom), 5k (green curve, middle), and 11k (blue curve, top).*

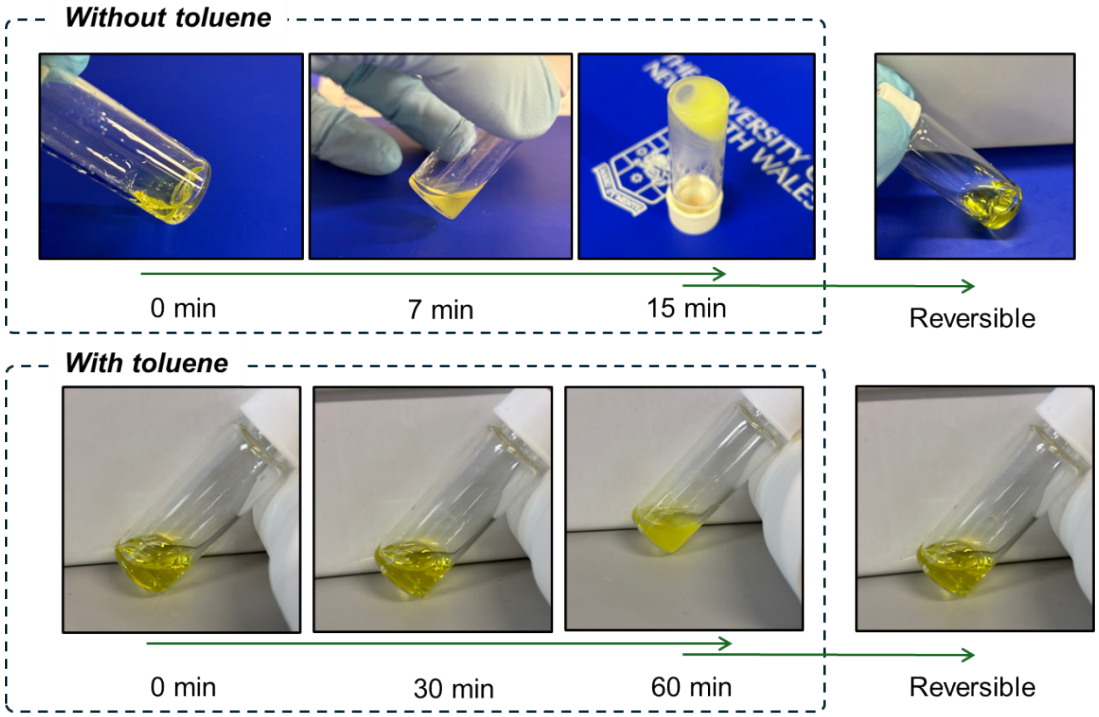


Figure S29. *Gelation effect in formulation PCL_{3k}-BTPA with (bottom) and without (top) 10 wt% toluene. The gel can be reversibly solubilized upon sonication.*

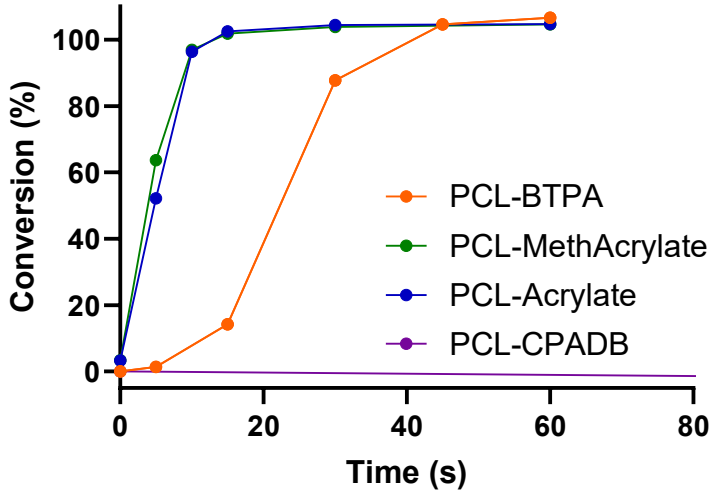


Figure S30. *Photopolymerization kinetics of resin formulated with four different PCL polymers: PCL_{3k}-BTPA (orange), PCL_{3k}-CPADB (purple), PCL_{3k}-Acrylate (blue), PCL_{3k}-Methacrylate (green). The molar ratio of [AA]/[PEGDA], content of PCL-R, toluene, and TPO were fixed at 9/1, 19 wt%, 10 wt% and 1 wt%, respectively. Kinetics experiments were performed in triplicate. Double bond conversion was measured using ATR-FTIR under 2.08 mW cm^{-2} violet light (λ_{max} = 405 nm).*

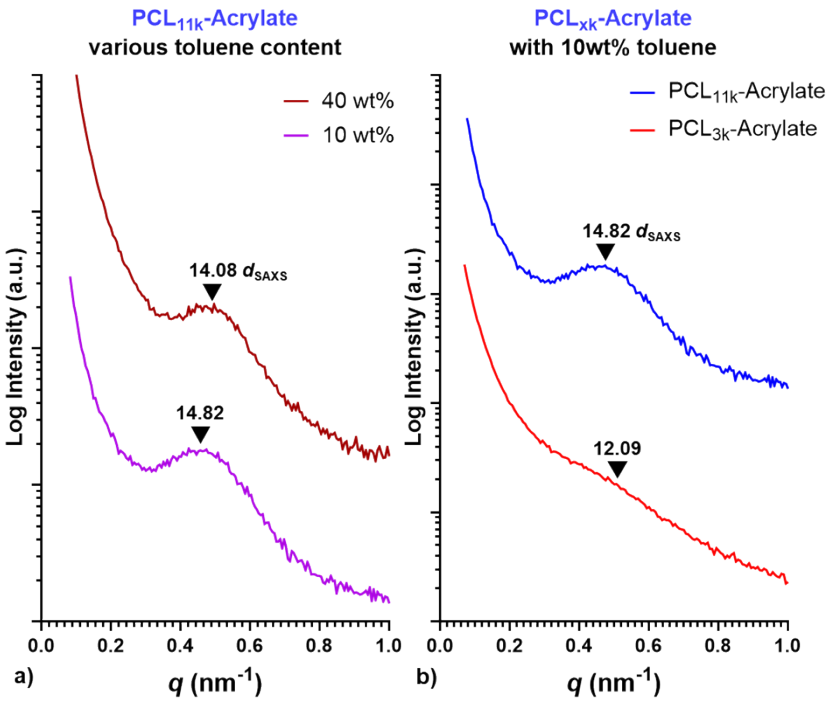


Figure S31. *SAXS profiles and corresponding domain spacing (d_{SAXS}) values of materials 3D printed using a) varied toluene content: 10 wt% (purple curve, bottom) and 40 wt% (red curve, top), b) varied X_n of PCL-Acrylate:3k (red curve, bottom) and 11k (blue curve, top).*

Table S2. *Resin formulations with various monomers, PCL_{3k}-BTPA as macroCTA and corresponding domain spacing obtained by SAXS. Molar ratio of [M]/[PEGDA], macroCTA and TPO was fixed at 9/1, 21 wt% and 1 w%, respectively.*

Monomer	***d_{SAXS} (nm)***
AA	14.31
MA	15.67
DMA	13.86
IBoA	13.38

Table S3. *Resins molar ratios of [AA]/[PEGDA]/[Toluene]/[PCL_{3k}-R] at 10 and 40 wt% of toluene and corresponding domain spacing obtained by SAXS. Molar ratio of [AA]/[PEGDA] and TPO was fixed at 9/1 and 1 w%, respectively.*

Chain-End (R)	***Solvent content [wt%]***	***Resin composition [wt%]***			***d_{SAXS} (nm)***
		MacroCTA	***AA***	***$PEGDA^{575}$***	
BTPA	10	19	37.5	32.5	14.11
	40	12.5	25	21.5	13.36
Acrylate	10	19	37	33	12.09
	40	12.5	25	21.5	13.20
Methacrylate	10	19	37	33	11.67
	40	12.5	25	21.5	11.03

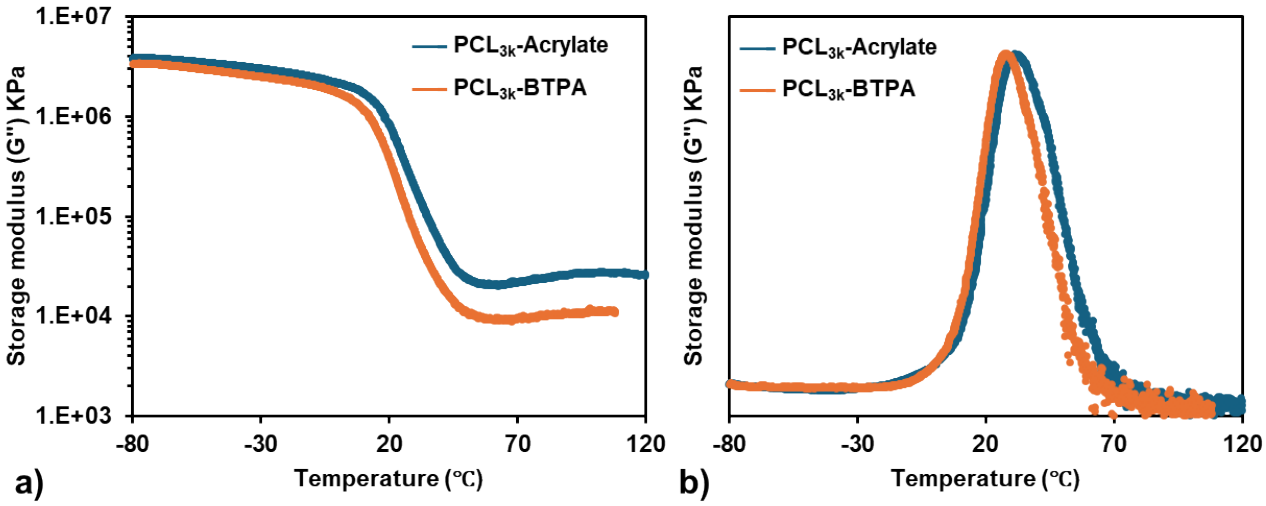


Figure S32. *DMA test results of 3D printed samples with different formulations of a-b) PCL_{3k}-BTPA and PCL_{3k}-Acrylate with AA, PEGDA, toluene a) The storage modulus vs. temperature curve, b) Tan (δ) curves.*

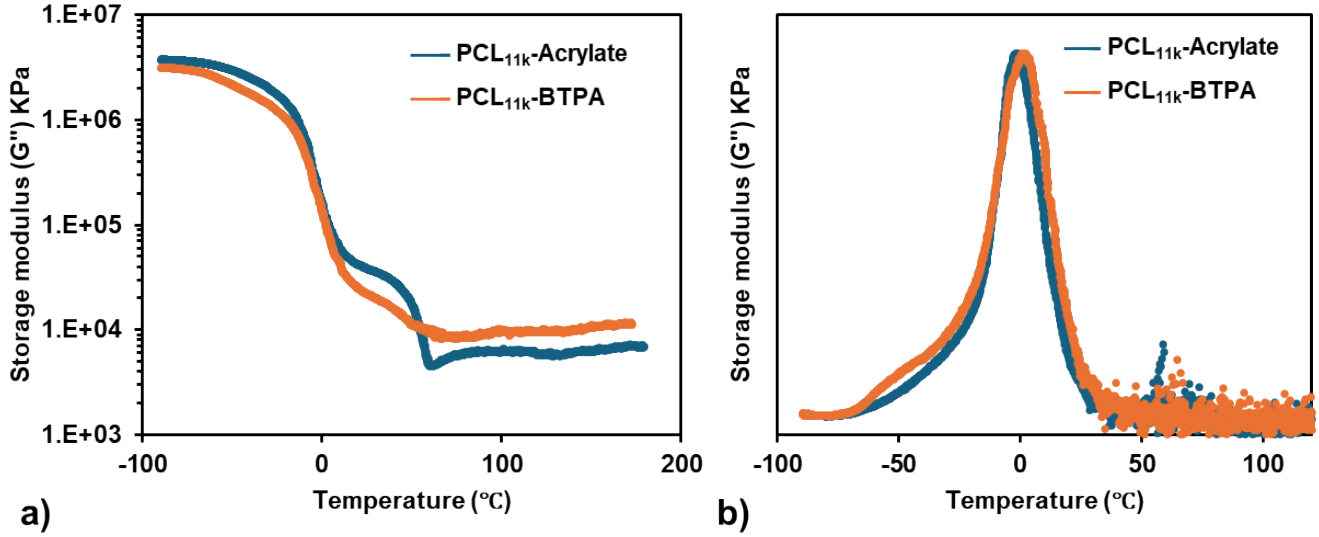


Figure S33. *DMA test results of 3D printed samples with different formulations of PCL_{11k}-BTPA and PCL_{11k}-Acrylate with IBoA, PEGDA, toluene a) The storage modulus vs. temperature curve, b) Tan (δ) curves.*

Etching

Table S 4. *Weight loss after etching in a 0.5 M NaOH aqueous solution at 60 °C of the printed object with PCL_{11k} -BTPA and PCL_{11k} -Acrylate in the presence of IBoA, PEGDA and 10 wt% toluene.*

Time	Experimental % weight loss		Theoretical wt % of PCL +Toluene
	PCL_{11k}-BTPA	PCL_{11k}-Acrylate	
Control	2.1	2.0	29.1
1 day	21.6	7.0	29.1
2 days		25.5	29.1

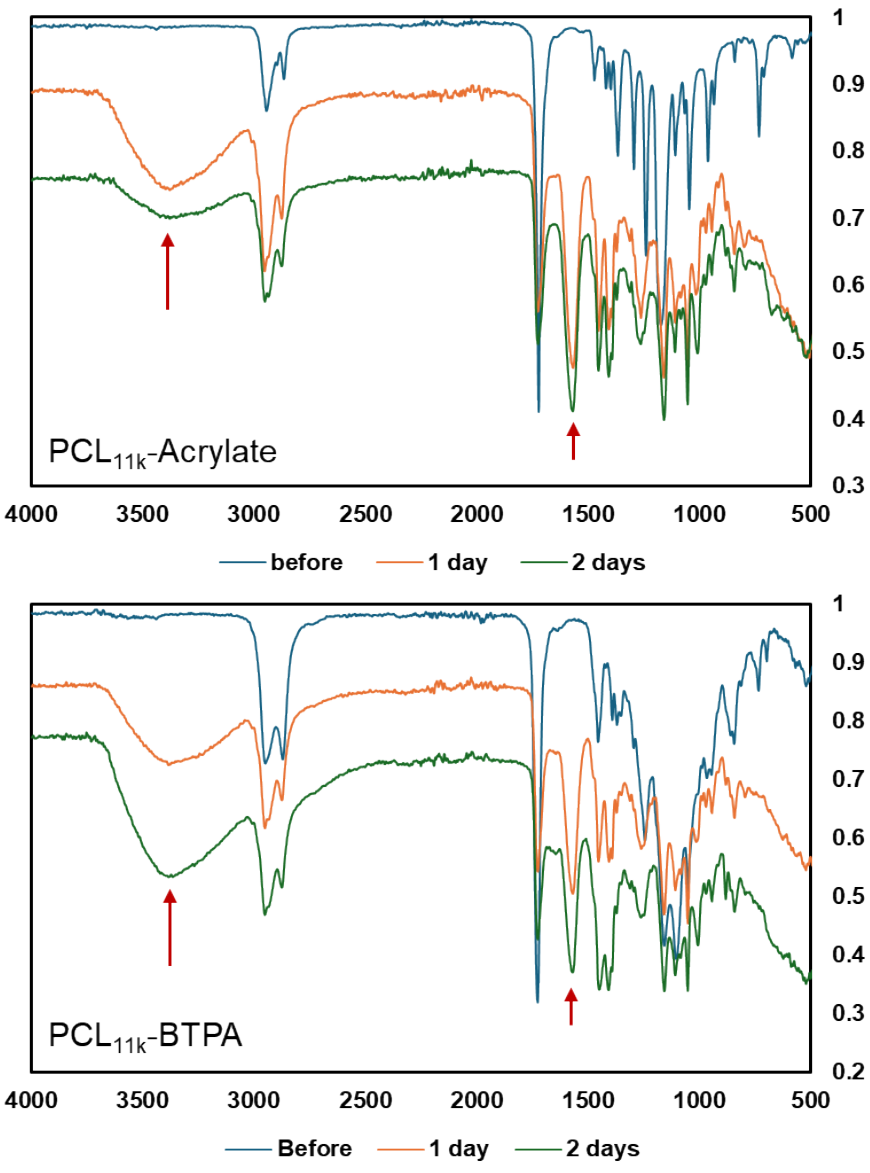


Figure S 34. *ATR-FTIR analyses before and after one and two days of etching for etching in a 0.5 M NaOH aqueous solution at 60 °C of the printed object with PCL11k -BTPA and PCL11k -Acrylate in the presence of IBoA, PEGDA and 10 wt% toluene.*

Supporting Information - References

1. Small, P. A., Some factors affecting the solubility of polymers. *Journal of Applied Chemistry* **2007,** *3* (2), 71-80.
2. Bates, F. S.; Fredrickson, G. H., Block copolymer thermodynamics: theory and experiment. *Annu Rev Phys Chem* **1990,** *41*, 525-57.
3. Mark, J. E., Physical Properties of Polymers Handbook.