

Supporting Information

**Tunable intramolecular H-bonding promotes benzoic acid
active in polymerizations: inspiration from nature**

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I. Preparation of catalyst

General method

^1H NMR spectra were recorded on a Bruker-AV-400 (400 MHz) at ambient temperature, using the chemical shift of a residual protic solvent (CHCl_3 at 7.26 ppm or DMSO at 2.50 ppm) as an internal reference. All shifts are quoted in parts per million (ppm) relative to CHCl_3 or DMSO. The multiplicity of the signal is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), quint. (quintet), sext. (sextet), sept. (septet) and br (broad). ^{13}C NMR spectra were recorded on a Bruker AV-400 (100 MHz) using the central resonance of the triplet of DMSO_3 at δ 29.52 ppm as an internal reference.

All solvents were purified by distillation and A, F and G was synthesized by a method described in previous report.^{1, 2}

o,o'-bis(pivalamido)toluene

To a THF solution (10 mL) of o,o'-diaminotoluene (0.252 g, 2.06 mmol, 1 eq) and triethylamine (1.2 mL, 8.24 mmol, 4 eq) was added pivaloyl chloride (0.99 mL, 8.24 mmol 4 eq) at 0 °C. After 30 min, volatile materials were removed under reduced pressure. Water was added and white precipitates obtained were collected by filtration. The precipitates were recrystallized by hot methanol. Yield 0.48 g (80%). ^1H NMR (400 MHz, DMSO-d_6) δ 8.98 (s, 2H, NH), 7.12 (t, 1H, ArH), 7.02 (d, 2H, ArH), 1.94 (s, 3H, Me), 1.23 (s, 18H, *t*-Bu). ^{13}C NMR (400 MHz, DMSO-d_6) δ 176.4, 137.2, 131.1, 124.9, 27.4, 12.7.

o,o'-bis(pivalamido)benzoic acid (A)

Potassium permanganate (0.52 g, 3.3 mmol, 2 eq) and o,o'-bis(pivalamido)toluene (0.48 g, 1.64 mmol, 1 eq) in pyridine/water (1:1, 40 mL) was heated at reflux with constant stirring for 4 h, or until the purple colour of the permanganate had disappeared. The reaction mixture was allowed to cool to room temperature, water (100 mL) added, then the solution filtered to remove the dark brown precipitate of hydrated manganese dioxide. The pale yellow

filtrate was concentrated to near dryness under reduced pressure and water (150 mL) added. The insoluble residue of unchanged *o,o'*-bis(pivalamido)toluene was filtered off, concentrated hydrochloric acid (4 mL) added to the filtrate and the precipitate of *o,o'*-bis(pivalamido)benzoic acid as white solid. Yield: 0.50 g (40%). Melting point = 186.6-187.0 °C; ¹HNMR (400 MHz, CDCl₃) δ 10.42 (s, 2H, NH), 8.26 (d, ³J=8.4 Hz, 2H, ArH), 7.49 (t, ³J=8.4 Hz, 1H, ArH), 1.32 (s, 18H, CH₃). ¹³CNMR (400 MHz, CDCl₃) δ 178.0, 169.8, 140.8, 134.5, 117.6, 107.1, 40.5, 27.6. MS (ESI) calcd for C₁₇H₂₄N₂O₄ [M+Na]⁺ 343.1628, found 343.1646

***o,o'*-bis(benzamido)toluene**

To a THF solution (80 mL) of *o,o'*-diaminotoluene (1.26 g, 10.3 mmol, 1 eq) and triethylamine (6 mL, 41.2 mmol, 4 eq) was added benzoyl chloride (4.8 mL, 41.2 mmol 4 eq) at 0 °C. After 30 min, volatile materials were removed under reduced pressure. Water was added and white precipitates obtained were collected by filtration. The precipitates were recrystallized by hot methanol. Yield 2.45 g (72 %). ¹HNMR (400 MHz, DMSO-d₆) δ 10.03 (s, 2H, NH), 8.00-8.03 (t, 4H, ArH), 7.51-7.62(t, 6H, ArH), 7.26-7.30(t, 3H, ArH), 2.14 (s, 3H, CH₃). ¹³CNMR (400 MHz, DMSO-d₆) δ 165.4, 137.1, 134.5, 131.5, 131.0, 128.4, 127.6, 125.3, 125.0, 13.2.

***o,o'*-bis(benzamido)benzoic acid (F)**

Potassium permanganate (2.0 g, 12.6 mmol, 2 eq) and *o,o'*-bis(benzamido)toluene (2.08 g, 6.3 mmol, 1 eq) in pyridine/water (1:1, 100 mL) was heated at reflux with constant stirring for 4 h, or until the purple colour of the permanganate had disappeared. The reaction mixture was allowed to cool to room temperature, water (200 mL) added, then the solution filtered to remove the dark brown precipitate of hydrated manganese dioxide. The pale yellow filtrate was concentrated to near dryness under reduced pressure and water (150 mL) added. The insoluble residue of unchanged *o,o'*-bis(benzamido)toluene was filtered off, concentrated hydrochloric acid (8 mL) added to the filtrate and the precipitate of *o,o'*-bis(benzamido)benzoic acid as

white solid. Yield: 1.04 g (46%). Melting point = 206.3-206.4 °C; ¹HNMR (400 MHz, DMSO-d₆) δ 11.17 (s, 2H, NH), 7.95-7.97 (m, 6H, ArH), 7.55-7.63 (m, 7H, ArH). ¹³CNMR (400 MHz, DMSO-d₆) δ 169.1, 164.9, 138.8, 134.6, 132.0, 131.9, 128.7, 127.3, 118.7, 114.9. MS (ESI) calcd for C₂₁H₁₆N₂O₄ [M-H]⁻ 359.1037, found 359.1105

o,o'-bis(4-fluorobenzamido)toluene

To a THF solution (80 mL) of o,o'-diaminotoluene (1.26 g, 10.3 mmol, 1 eq) and triethylamine (6 mL, 41.2 mmol, 4 eq) was added 4-fluorobenzoyl chloride (4.9 mL, 41.2 mmol 4 eq) at 0 °C. After 30 min, volatile materials were removed under reduced pressure. Water was added and white precipitates obtained were collected by filtration. The precipitates were recrystallized by hot methanol. Yield 2.87 g (76 %). ¹HNMR (400 MHz, DMSO-d₆) δ 10.03 (s, 2H, NH), 8.09-8.12 (m, 4H, ArH), 7.24-7.37 (m, 7H, ArH), 2.16 (s, 3H, CH₃). ¹³CNMR (400 MHz, DMSO-d₆) δ 165.2, 164.5, 163.2, 137.1, 131.1, 131.0, 130.4, 125.4, 125.1, 115.4, 115.2, 48.6, 13.3.

o,o'-bis(4-fluorobenzamido)benzoic acid (G)

Potassium permanganate (2.7 g, 14.3 mmol, 2 eq) and o,o'-bis(4-fluorobenzamido)toluene (2.62 g, 7.1 mmol, 1 eq) in pyridine/water (1:1, 100 mL) was heated at reflux with constant stirring for 4 h, or until the purple colour of the permanganate had disappeared. The reaction mixture was allowed to cool to room temperature, water (200 mL) added, then the solution filtered to remove the dark brown precipitate of hydrated manganese dioxide. The pale yellow filtrate was concentrated to near dryness under reduced pressure and water (150 mL) added. The insoluble residue of unchanged o,o'-bis(4-fluorobenzamido)toluene was filtered off, concentrated hydrochloric acid (8 mL) added to the filtrate and the precipitate of o,o'-bis(4-fluorobenzamido)benzoic acid as white solid. Yield: 1.50 g (53 %). Melting point = 248.7-248.9 °C; ¹HNMR (400 MHz, DMSO-d₆) δ 11.17 (s, 2H, NH), 8.01-8.05 (m, 4H, ArH), 7.90-7.92 (m, 2H, ArH), 7.57 (t, J=8.2 Hz, 1H, ArH), 7.40 (t, J=8.8 Hz, 4H, ArH). ¹³CNMR (400 MHz, DMSO-d₆) δ 168.9, 165.2, 163.9, 163.2, 138.6, 131.7, 131.1, 130.0,

129.9, 119.1, 115.7, 115.5. MS (ESI) calcd for $C_{21}H_{14}N_2O_4F_2$ [M-H]⁻ 395.0849, found 395.0915.

II. Ring opening polymerization of δ -valerolactone catalyzed by *o,o'*-bis(pivalamido)benzoic acid

materials

δ -Valerolactone (VL; 99 %) and ϵ -caprolactone (CL; 99 %) were distilled over CaH_2 under reduced pressure in an inert environment. Trimethylene carbonate (TMC; 98 %) was recrystallized from benzene–*n*-hexane at least three times to afford white crystals. Toluene (> 99 %; water content, < 0.001 %) was purified by refluxing on sodium under an argon atmosphere, and further dried over 3 Å molecular sieve pellets for 48 h before use. Benzyl alcohol (BnOH; Acros, 99 %) was refluxed over CaH_2 prior to distillation. All reagents and chemicals, except for the ones specified, were purchased from Sinopharm Chemical Reagent Co.

characterizations

¹H NMR spectra were recorded on a Bruker-AV-400 spectrometer at 400 MHz in $CDCl_3$ to determine the monomer conversion and the number-average molecular weight ($M_{n,NMR}$). ¹³C NMR spectra were measured at 100 MHz in DMSO to investigate the mechanism of the polymerizations.

Size exclusion chromatography (SEC) was performed at room temperature in tetrahydrofuran (THF) at a flow rate of 0.70 mL min⁻¹, using a SSI 1500 pump equipped with a Waters Styragel HR 2.5 μ m, 300 mm \times 7.8 mm column, Wyatt Optilab rEX differential refractive index (DRI) detector with a 658 nm light source. The number-average molecular weight (M_n) and dispersities (M_w/M_n) were obtained using a calibration with standard polystyrene samples.

Matrix assisted laser desorption/ionization time-of-flight mass spectra (MALDI-

ToF-MS) were obtained using a mass spectrometer (Ultraflextreme; Bruker Co.) with a Smartbeam/ Smartbeam II modified Nd:YGA laser. Mass spectra of five hundred shots were accumulated for the spectra at a 25 kV acceleration voltage. The polymer sample was dissolved in CHCl_3 at a concentration of 5 mg mL^{-1} , while the matrix 2,5-DHBA (2,5-dihydroxybenzoic acid) was dissolved in a solution of trifluoroacetic acid and acetonitrile with a volume ratio of 70 : 30 in $10 \text{ }\mu\text{L}$ of water (1 %). Samples for the MALDI-ToF-MS were prepared by mixing the matrix and polymer solutions with a volume ratio of 1 : 1. The MALDI target was spotted with $1.0 \text{ }\mu\text{L}$ of solution and allowed to air-dry.

General procedure for polymerizations

All reactions were conducted under a dry nitrogen stream at room temperature. At first, VL (0.27 mL , 3.0 mmol , 30 equiv.) was dissolved in toluene ($[\text{VL}]_0 = 3.0 \text{ mol L}^{-1}$). Then, accurately weighed *o,o'*-bis(pivalamido)benzoic acid (**A**) (0.0320 g , 0.1 mmol , 1.0 equiv.) was added as a catalyst. Third, the benzyl alcohol ($10.3 \text{ }\mu\text{L}$, 0.10 mmol , 1.0 equiv.) was added as an initiator. Finally, the mixture was stirred at room temperature under an argon atmosphere. The reaction mixture was evaporated under reduced pressure. The obtained polymer was dissolved in a minimum amount of dichloromethane and separated out from cold methanol.

III. Diblock copolymerization of δ -Valerolactone (VL) and trimethylene carbonate (TMC)

At first, VL (0.27 mL , 3.0 mmol , 30 equiv.) was dissolved in dichloromethane ($[\text{VL}]_0 = 3.0 \text{ mol L}^{-1}$). Then, accurate weighed *o,o'*-bis(pivalamido)benzoic acid (**A**) (0.0320 g , 0.10 mmol , 1.0 equiv.) was added as a catalyst and dissolved completely. Third, the benzyl alcohol ($10.3 \text{ }\mu\text{L}$, 0.10 mmol , 1.0 equiv.) was added as an initiator. The mixture was stirred at room temperature under an argon atmosphere. After 12 h, the TMC (0.306 g , 3.0 mmol , 30 equiv.) was

added to start the block copolymerization to obtain poly(δ -valerolactone)-block-poly(trimethylene carbonate) under the same conditions. At the end of the polymerization, an excess of triethylamine was added to terminate the reaction. Polymers were obtained by removing the solvents under vacuum evaporation. The raw polymer was dissolved in a minimum amount of dichloromethane and separated out from cold methanol.

Table S1. ROP of δ -valerolactone (VL) with benzyl alcohol (BnOH) as the initiator in different solvents.^a

entry	Cat.	solvent	Time / h	Conv. ^b (%)	M_n , calcd ^c (kg mol ⁻¹)	M_n , NMR ^b (kg mol ⁻¹)	M_w/M_n ^d
1	A	Toluene	10	95	2.96	3.05	1.05
2	A	Dichloromethane	20	94	2.93	3.20	1.06
3	A	Tetrahydrofuran	45	91	2.84	3.12	1.05
4	A	Acetonitrile	100	92	2.87	3.51	1.12
5	F	Toluene	24	-	-	-	-
6	F	Dichloromethane	24	-	-	-	-
7	F	Tetrahydrofuran	24	-	-	-	-
8	F	Acetonitrile	24	-	-	-	-
9	G	Toluene	24	-	-	-	-
10	G	Dichloromethane	24	-	-	-	-
11	G	Tetrahydrofuran	24	-	-	-	-
12	G	Acetonitrile	24	-	-	-	-

^a $[M]_0 = 3.0 \text{ mol L}^{-1}$; room temperature. ^b Determined by ^1H NMR in CDCl_3 . ^c Calculated from $([M]_0/[BnOH]_0) \times \text{conv.} \times (M_w \text{ of VL}) + (M_w \text{ of BnOH})$. ^d Determined by SEC in THF using polystyrene standards.

Figure S1. Effect of functional groups on the increase of Brønsted acidity of the catalyst.

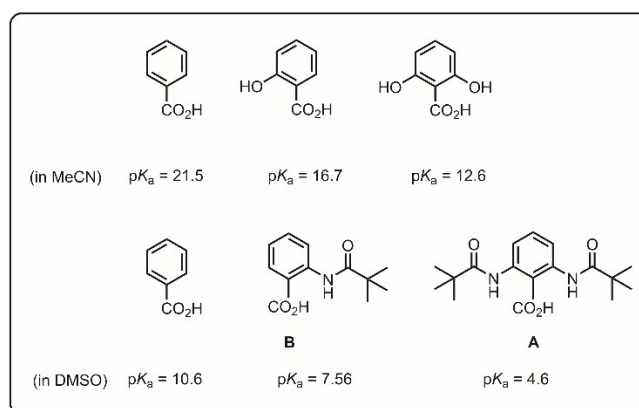


Figure S2. ^1H NMR spectrum of *o,o'*-bis(pivalamido)benzoic acid (**A**).

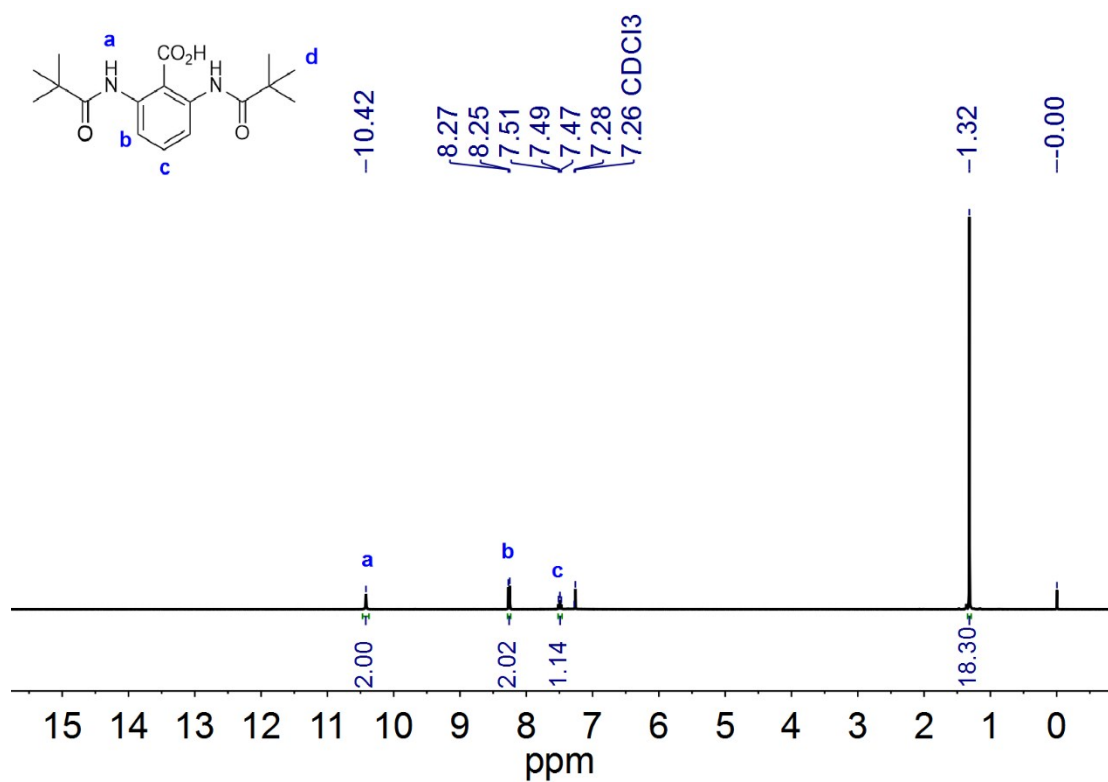


Figure S3. ^{13}C NMR spectrum of *o,o'*-bis(pivalamido)benzoic acid (**A**).

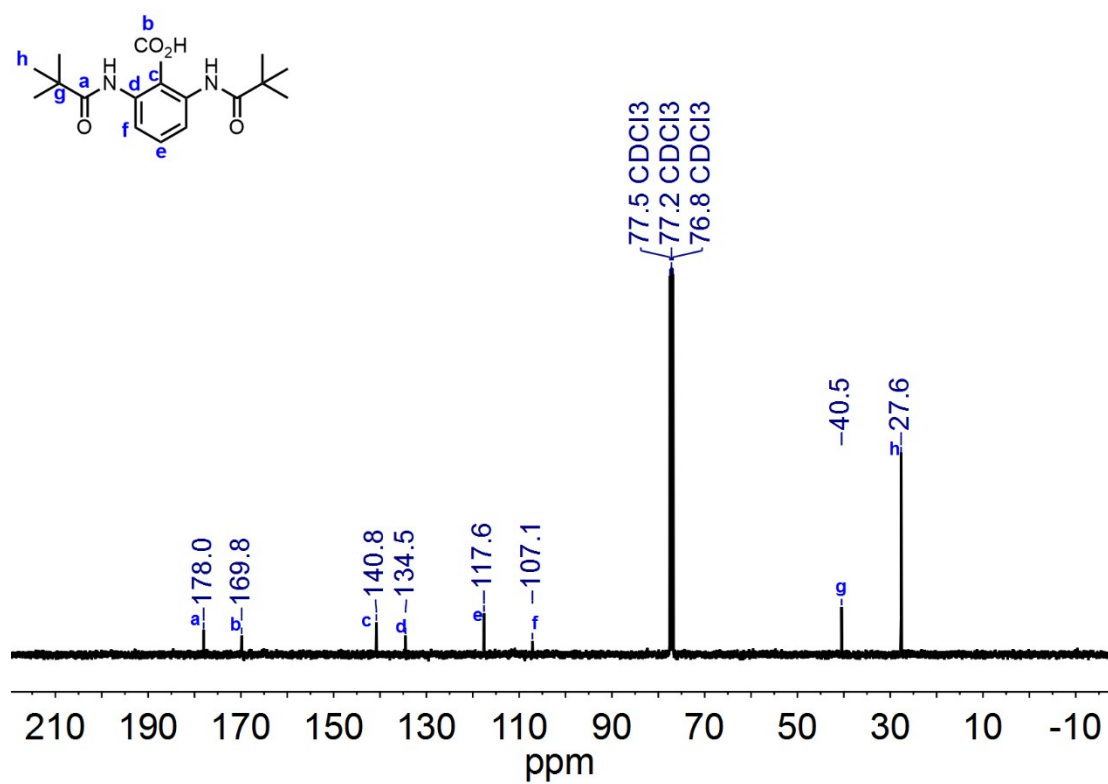


Figure S4. Electrospray ionization-time of flight (ESI-TOF) of *o,o'*-bis(pivalamido)benzoic acid (A).

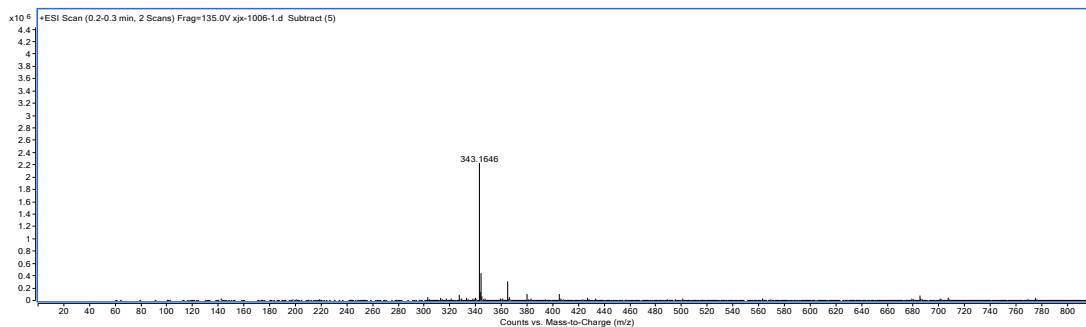


Figure S5. ¹H NMR spectrum of *o,o'*-bis(benzamido)benzoic acid (F).

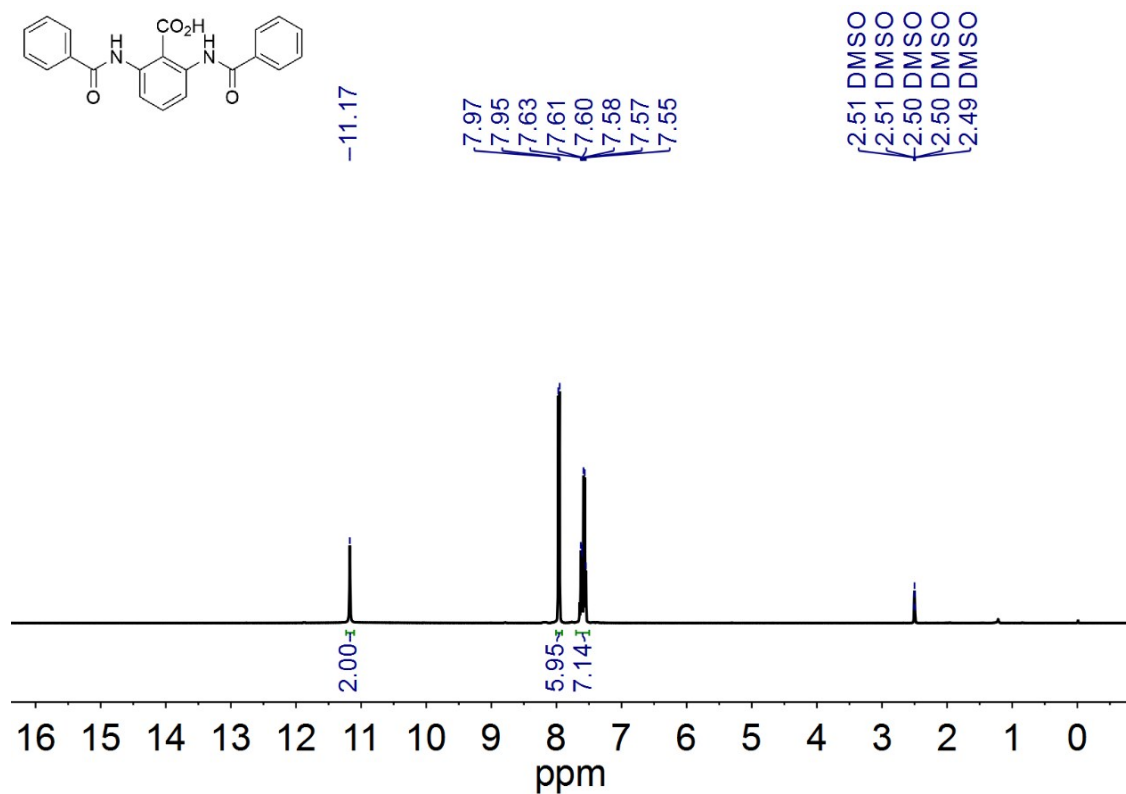


Figure S6. ^{13}C NMR spectrum of *o,o'*-bis(benzamido)benzoic acid (**F**).

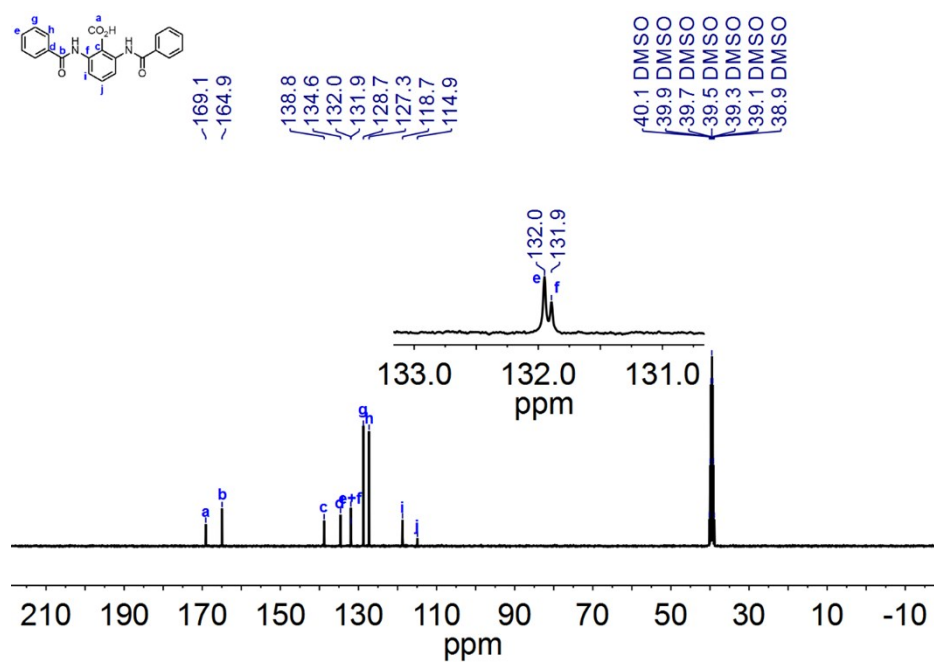


Figure S7. Electrospray ionization-time of flight (ESI-TOF) of *o,o'*-bis(benzamido)benzoic acid (**F**).

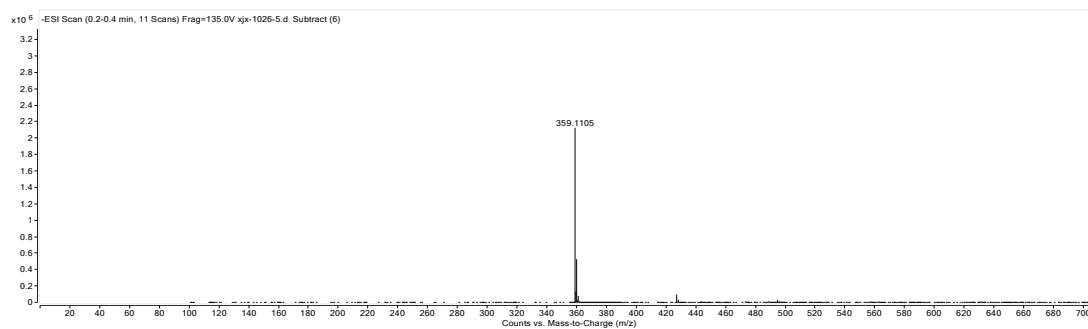


Figure S8. ¹H NMR spectrum of *o,o'*-bis(4-fluorobenzamido)benzoic acid (**G**).

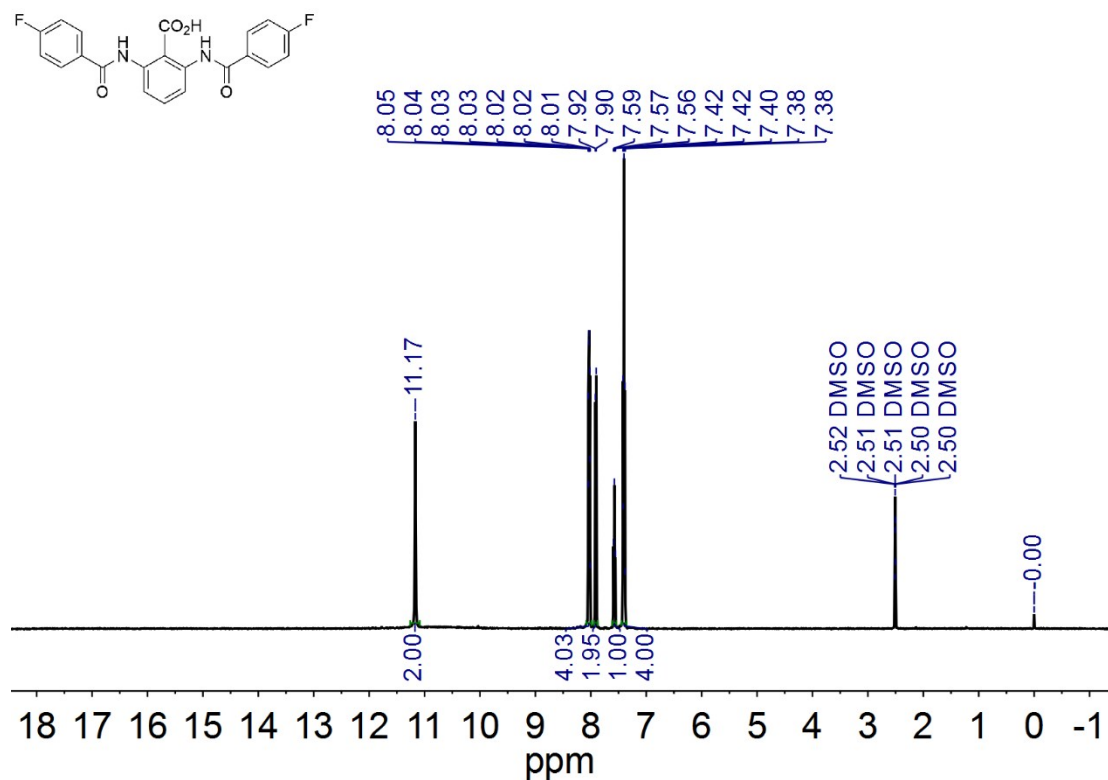


Figure S9. ¹³C NMR spectrum of *o,o'*-bis(4-fluorobenzamido)benzoic acid (**D**).

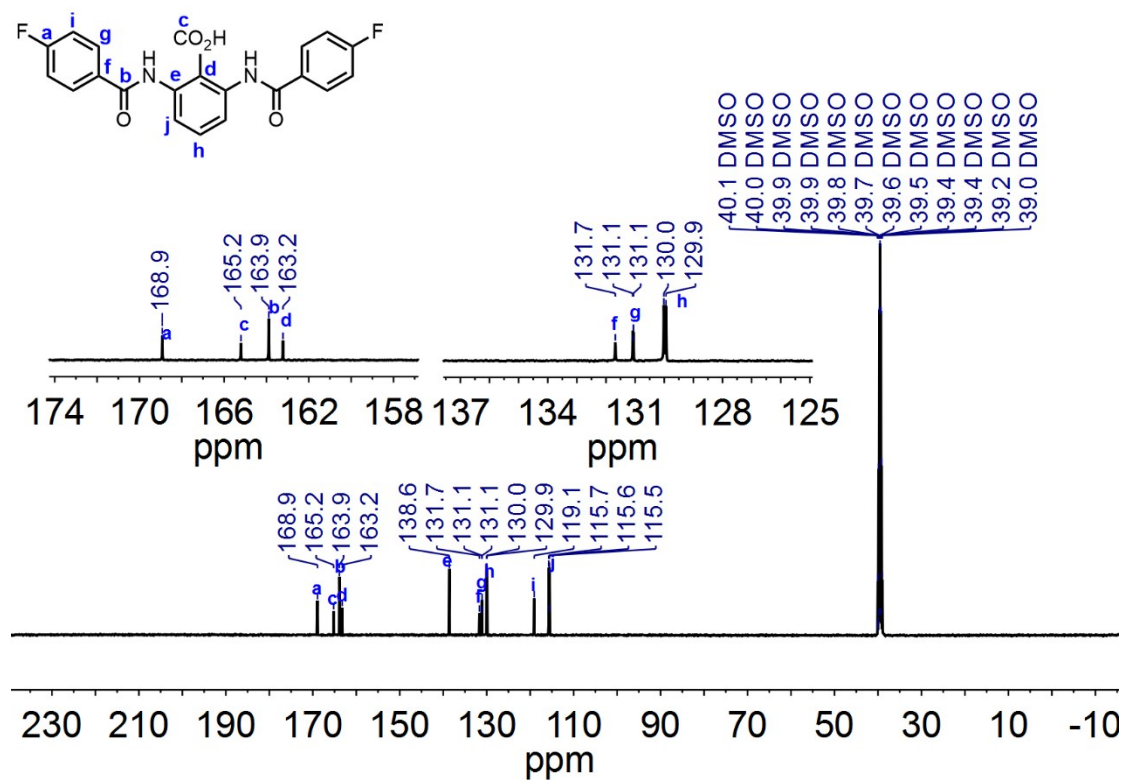


Figure S10. Electrospray ionization-time of flight (ESI-TOF) of *o,o'*-bis(4-fluorobenzamido)benzoic acid (**G**).

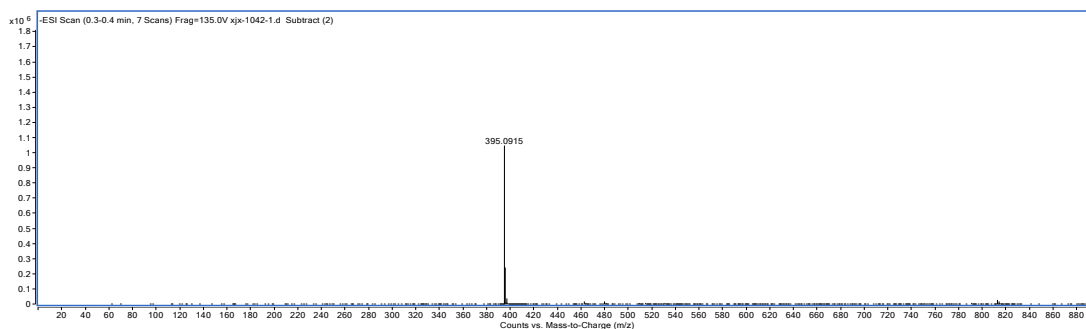


Figure S11. ¹H NMR spectrum of the poly(δ -valerolactone) (PVL)-block-poly(ϵ -caprolactone) (PCL).

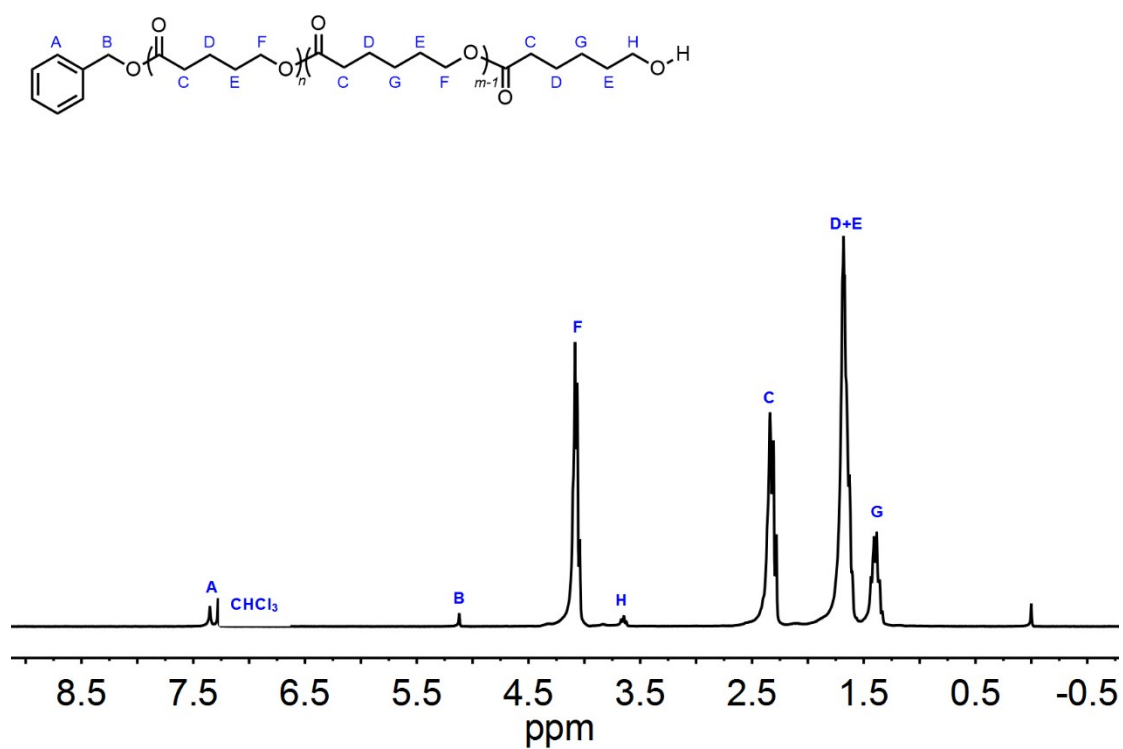


Figure S12. ^{13}C NMR spectrum of the poly(δ -valerolactone) (PVL)-block-poly(ϵ -caprolactone) (PCL).

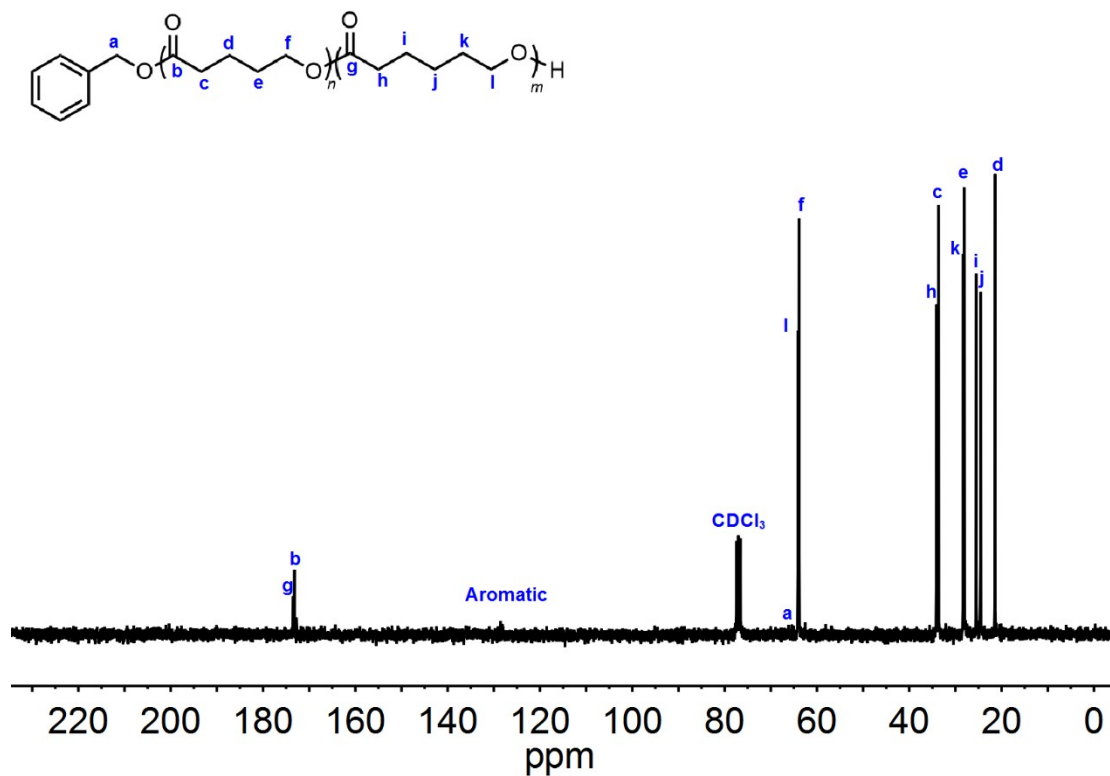


Figure S13. ^1H NMR spectrum of the poly(δ -valerolactone) (PVL)-block-poly(trimethylene carbonate) (PTMC).

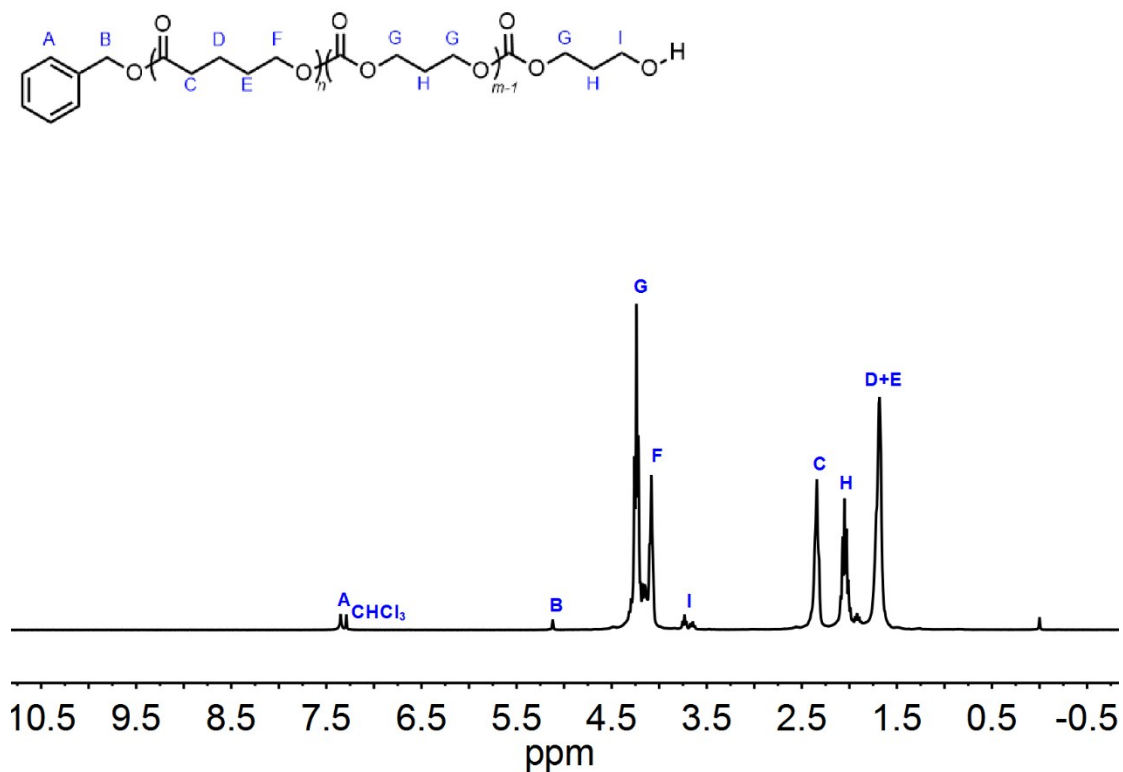


Figure S14. ^{13}C NMR spectrum of the poly(δ -valerolactone) (PVL)-block-poly(trimethylene carbonate) (PTMC).

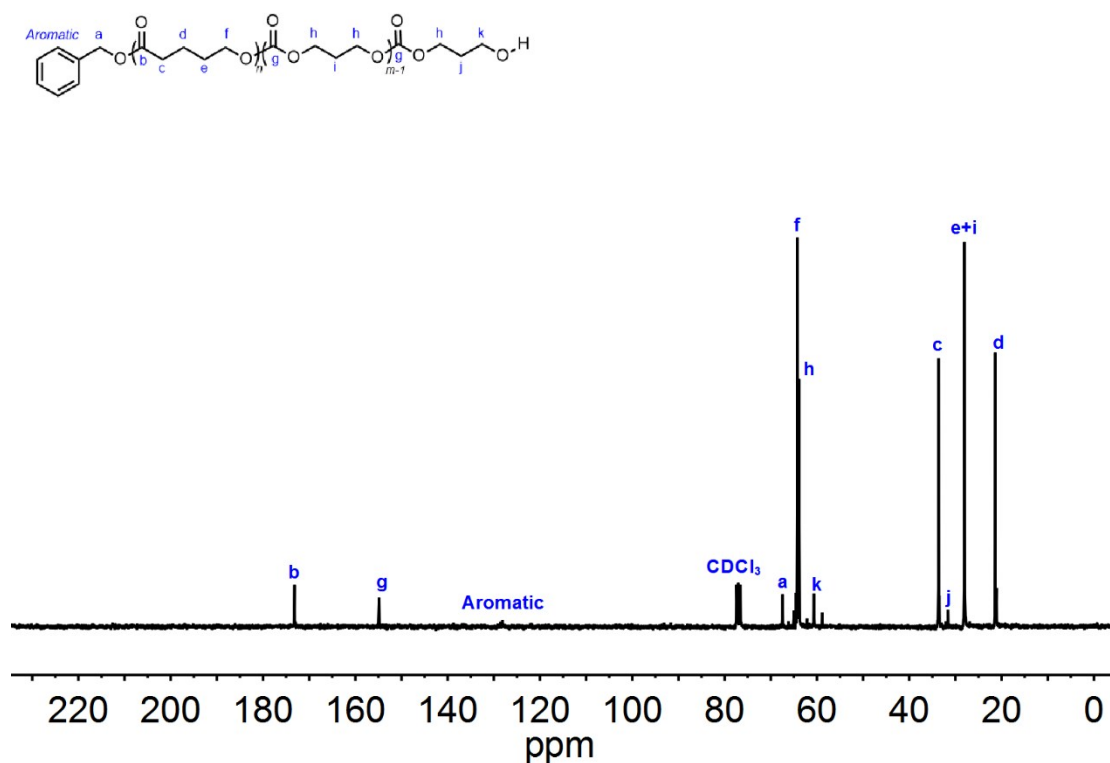


Figure S15. ^1H NMR spectrum of the poly(ϵ -caprolactone) (PCL)-block-poly(δ -valerolactone) (PVL).

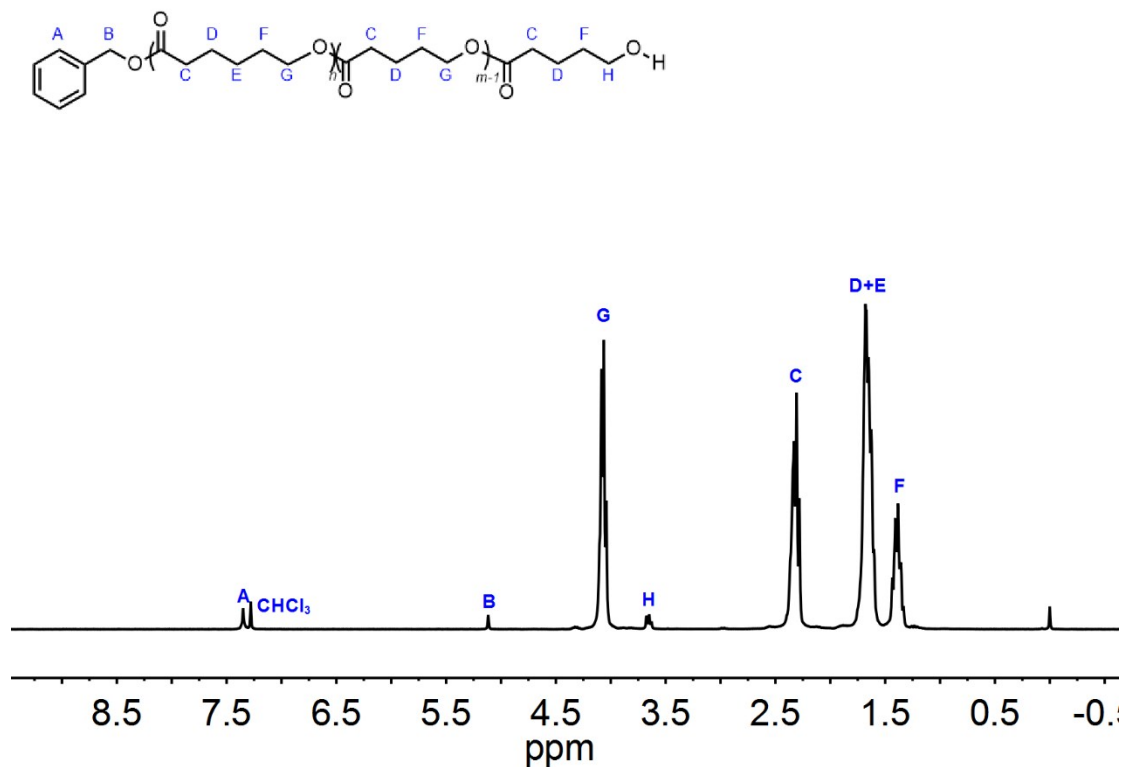


Figure S16. ^{13}C NMR spectrum of the poly(ϵ -caprolactone) (PCL)-block-poly(δ -valerolactone) (PVL).

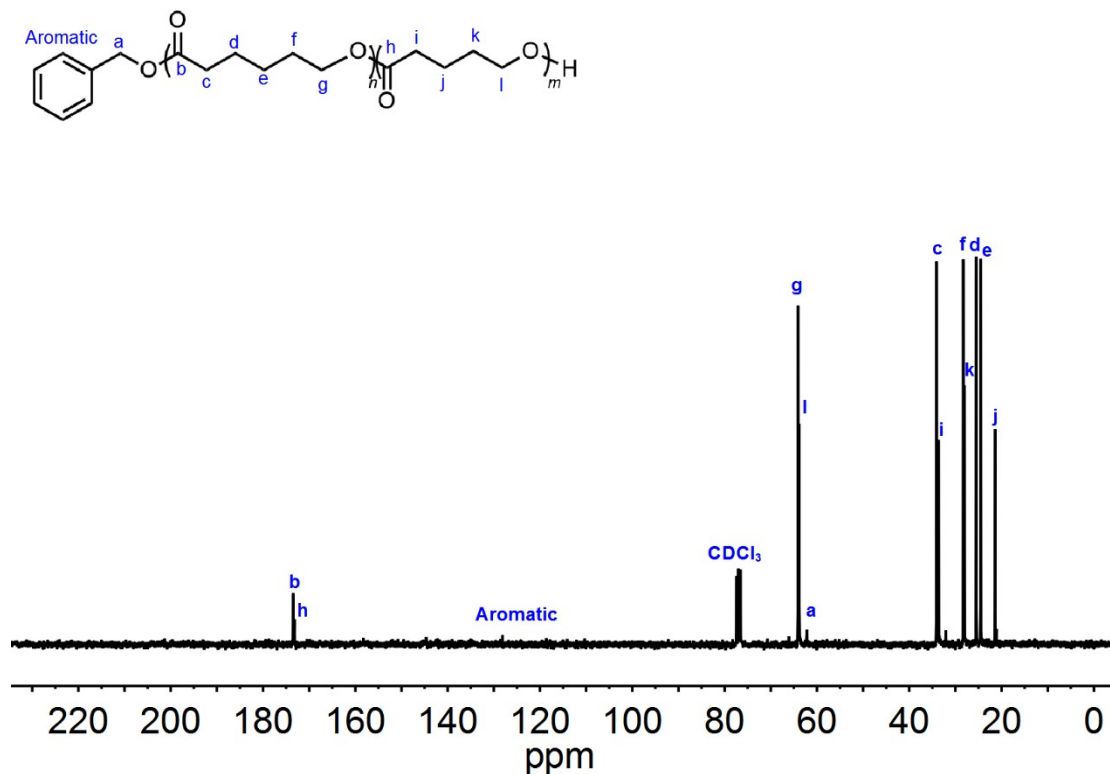


Figure S17. ^1H NMR spectrum of the poly(ϵ -caprolactone) (PCL)-block-poly(trimethylene carbonate) (PTMC).

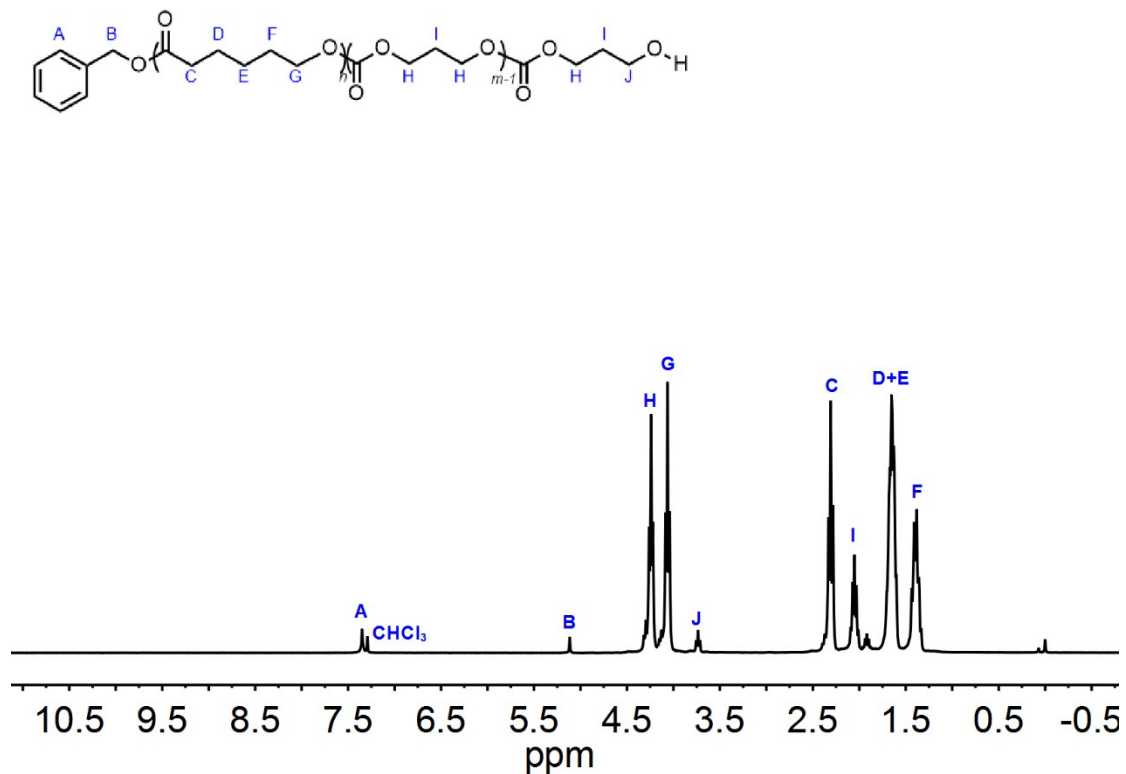


Figure S18. ^{13}C NMR spectrum of the poly(ϵ -caprolactone) (PCL)-block-poly(trimethylene carbonate) (PTMC).

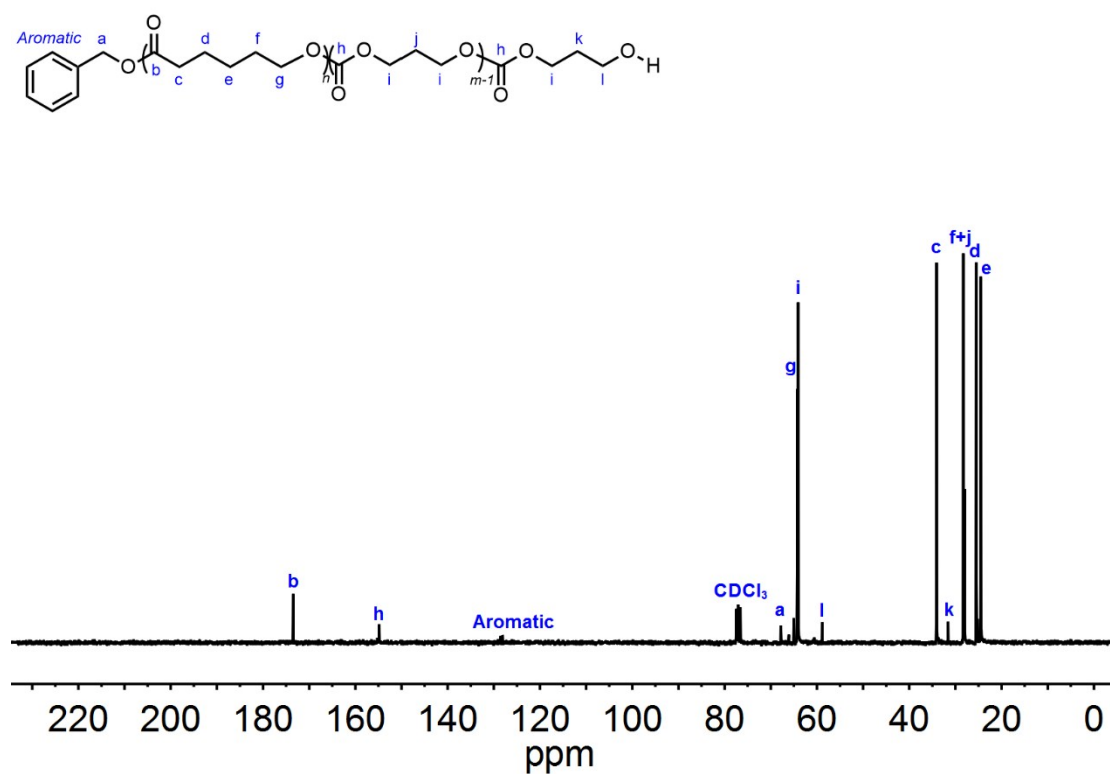


Figure S19. ^1H NMR spectrum of the poly(trimethylene carbonate) (PTMC)-block-poly(δ -valerolactone) (PVL).

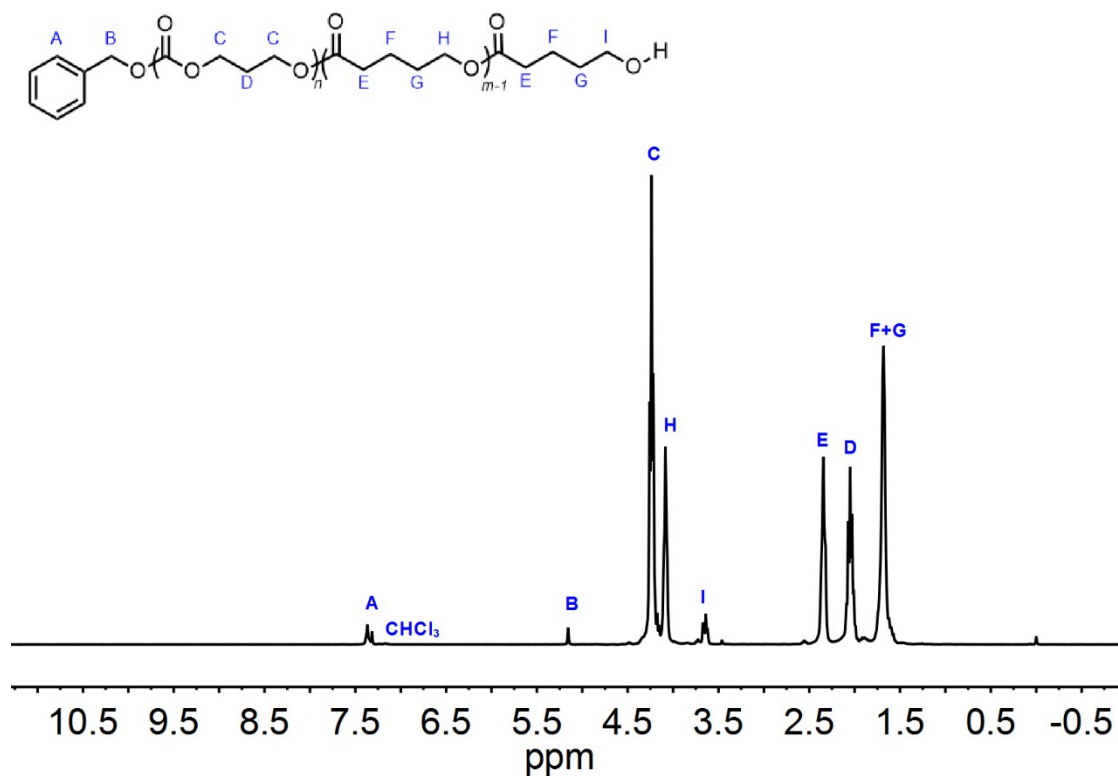


Figure S20. ^{13}C NMR spectrum of the poly(trimethylene carbonate) (PTMC)-block-poly(δ -valerolactone) (PVL).

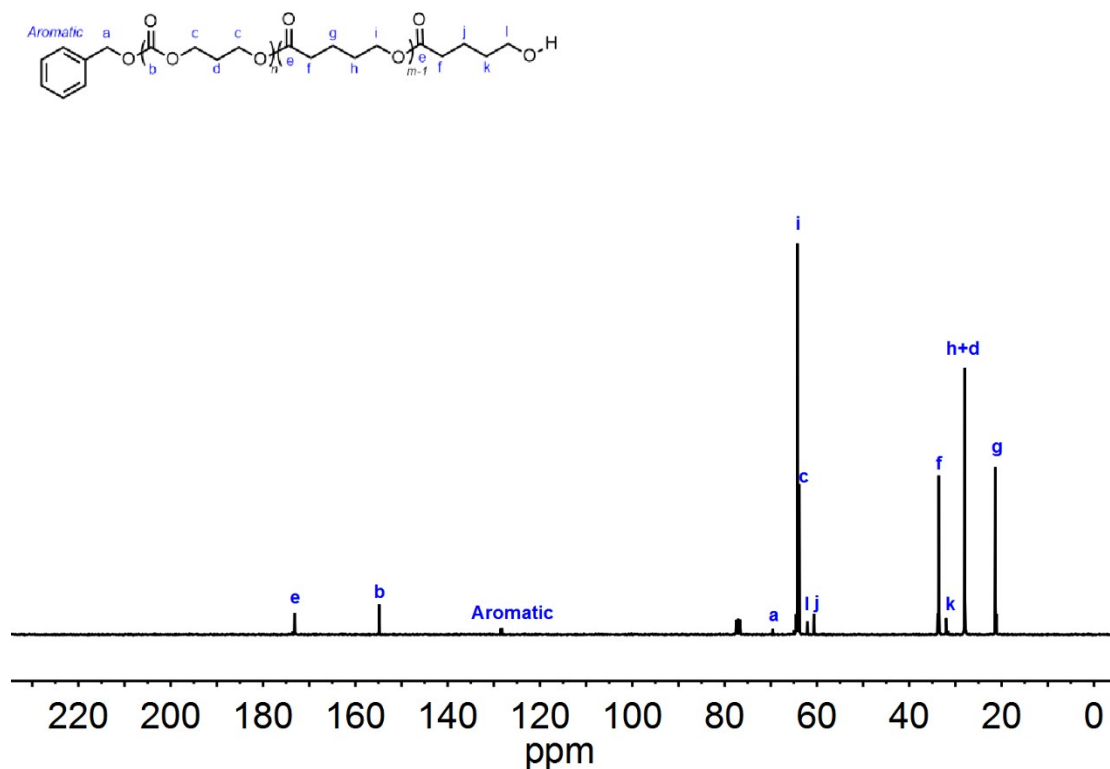


Figure S21. ^1H NMR spectrum of the poly(trimethylene carbonate) (PTMC)-block-poly(ϵ -caprolactone) (PCL).

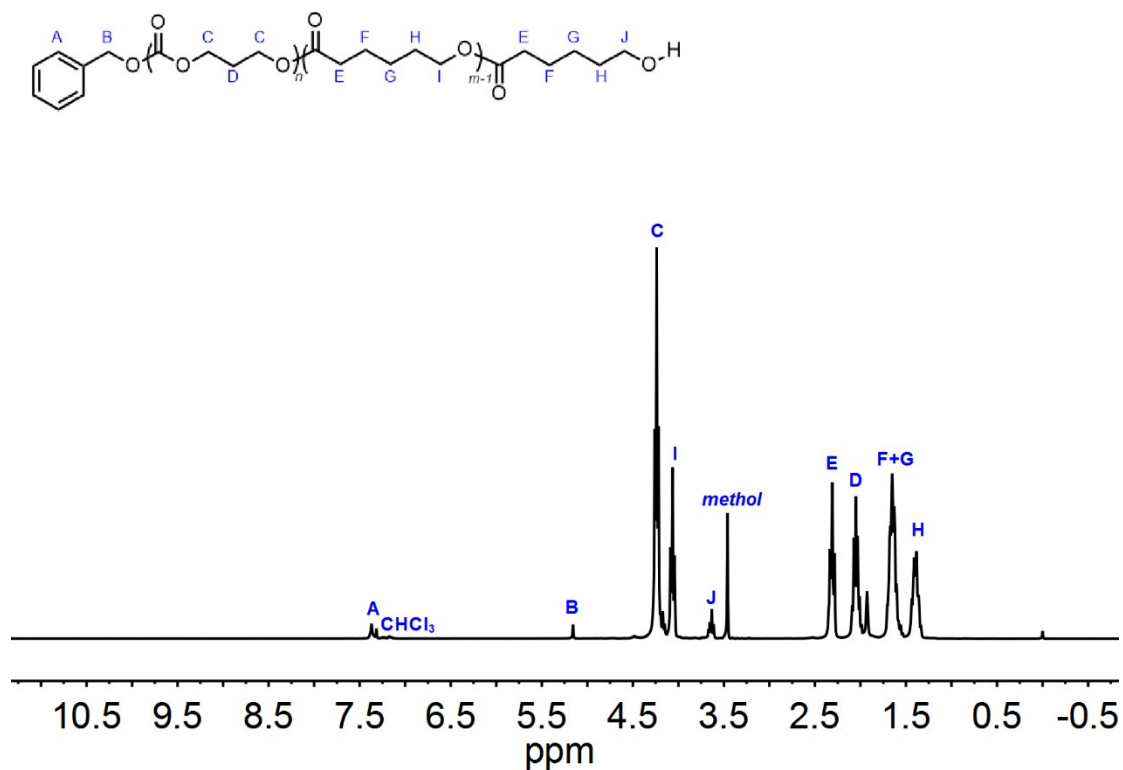


Figure S22. ^{13}C NMR spectrum of the poly(trimethylene carbonate) (PTMC)-block-poly(ϵ -caprolactone) (PCL).

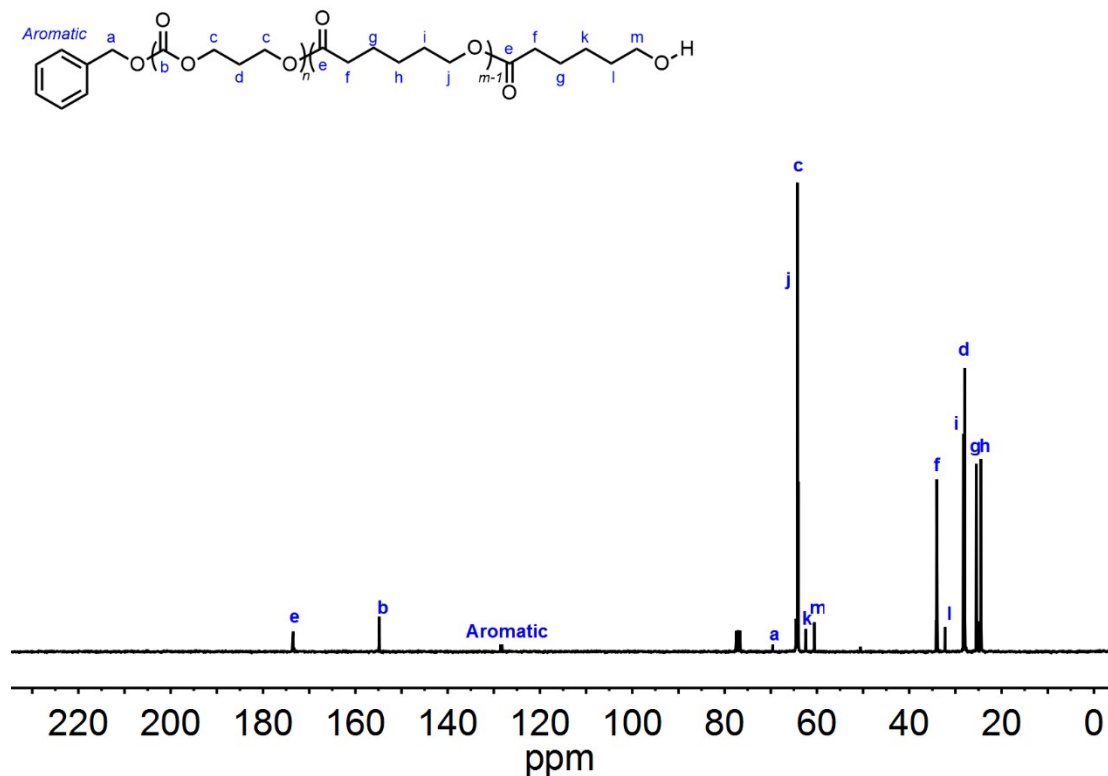


Figure S23. Size exclusion chromatography (SEC) traces for the polymerizations: SEC traces of poly(δ -valerolactone) (PVL; black line) and poly(δ -valerolactone)-block-poly(ϵ -caprolactone) (PVL-*b*-PCL; red line)

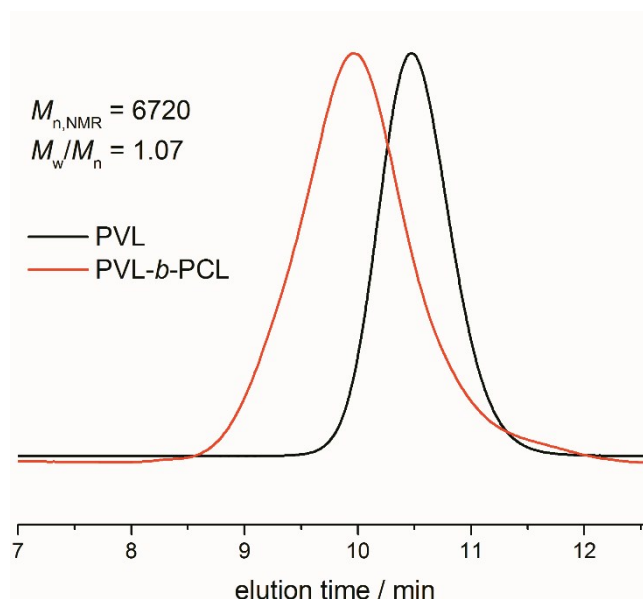


Figure S24. Size exclusion chromatography (SEC) traces for the polymerizations: SEC traces of poly(δ -valerolactone) (PVL; black line) and poly(δ -valerolactone)-block-poly(trimethylene carbonate) (PVL-*b*-PTMC; red line)

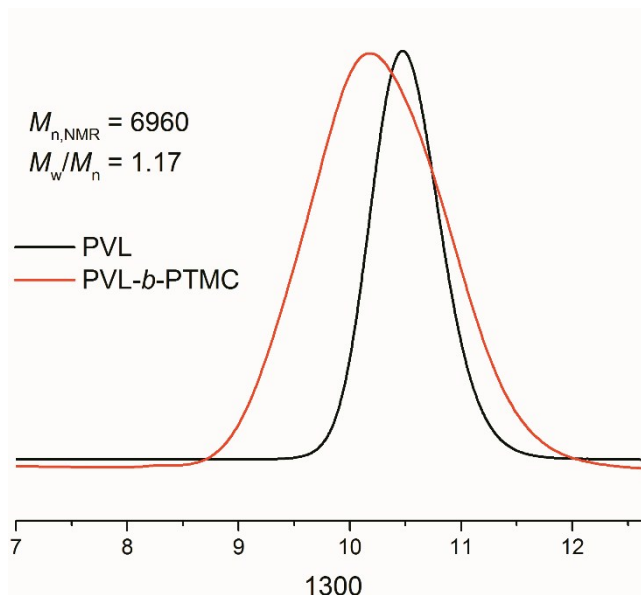


Figure S25. Size exclusion chromatography (SEC) traces for the polymerizations: SEC traces of poly(ϵ -caprolactone) (PCL; black line) and poly(ϵ -caprolactone)-block-poly(δ -valerolactone) (PCL-*b*-PVL; red line)

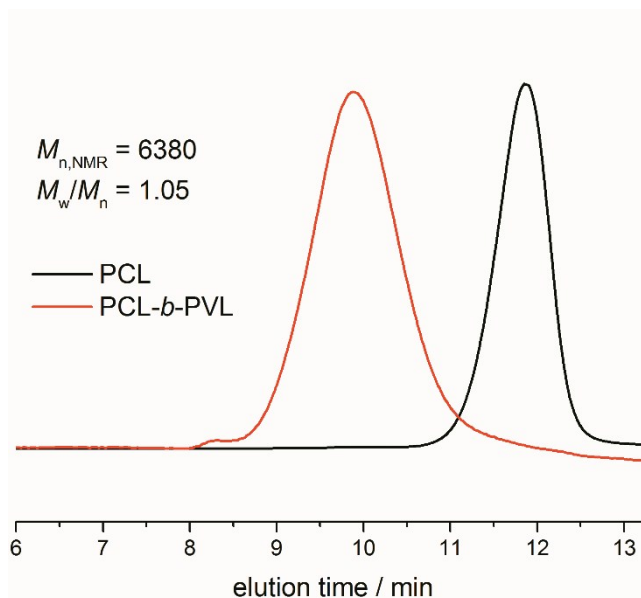


Figure S26. Size exclusion chromatography (SEC) traces for the polymerizations: SEC traces of poly(ϵ -caprolactone) (PCL; black line) and poly(ϵ -caprolactone)-block-poly(trimethylene carbonate) (PCL-*b*-PTMC; red line)

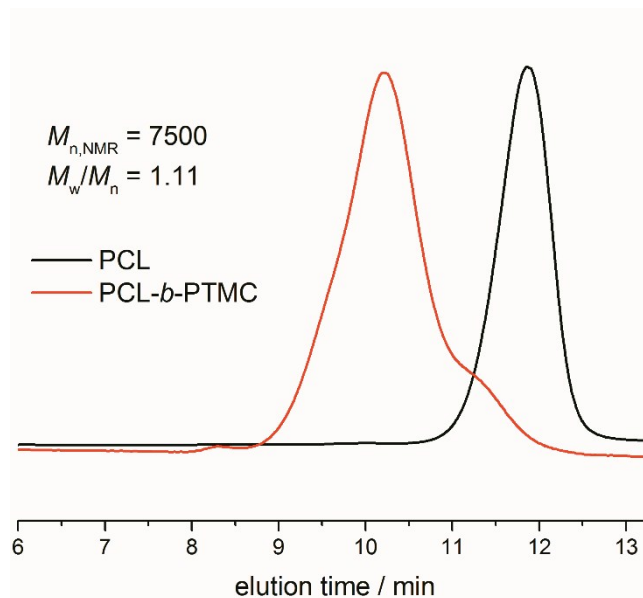


Figure S27. Size exclusion chromatography (SEC) traces for the polymerizations: SEC traces of poly(trimethylene carbonate) (PTMC; black line) and poly(trimethylene carbonate)-block-poly(δ -valerolactone) (PTMC-*b*-PVL; red line)

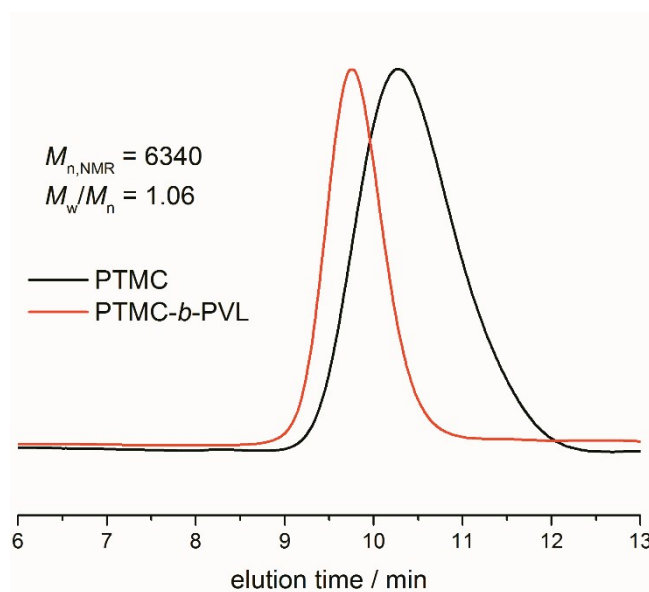
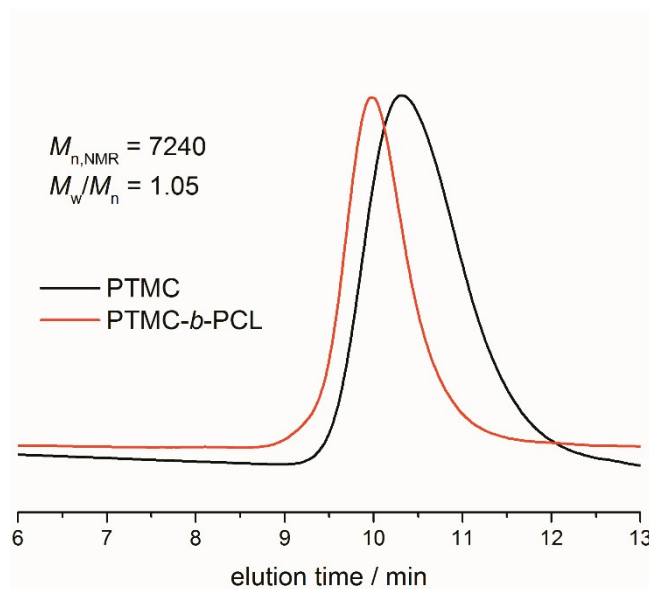


Figure S28. Size exclusion chromatography (SEC) traces for the polymerizations: SEC traces of poly(trimethylene carbonate) (PTMC; black line) and poly(trimethylene carbonate)-block- poly(ϵ -caprolactone) (PTMC-*b*-PCL; red line)



1. J. D. Crane, D. J. Moreton and E. Rogerson, *Eur. J. Inorg. Chem.*, 2004, DOI: 10.1002/ejic.200400441, 4237-4241.
2. A. Onoda, Y. Yamada, J. Takeda, Y. Nakayama, T. Okamura, M. Doi, H. Yamamoto and N. Ueyama, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 321-329.