Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Selective *O*-acyl Ring-Opening of β-Butyrolactone Catalyzed by Trifluoromethane Sulfonic Acid: Application to the Preparation of Well-defined Block Copolymers

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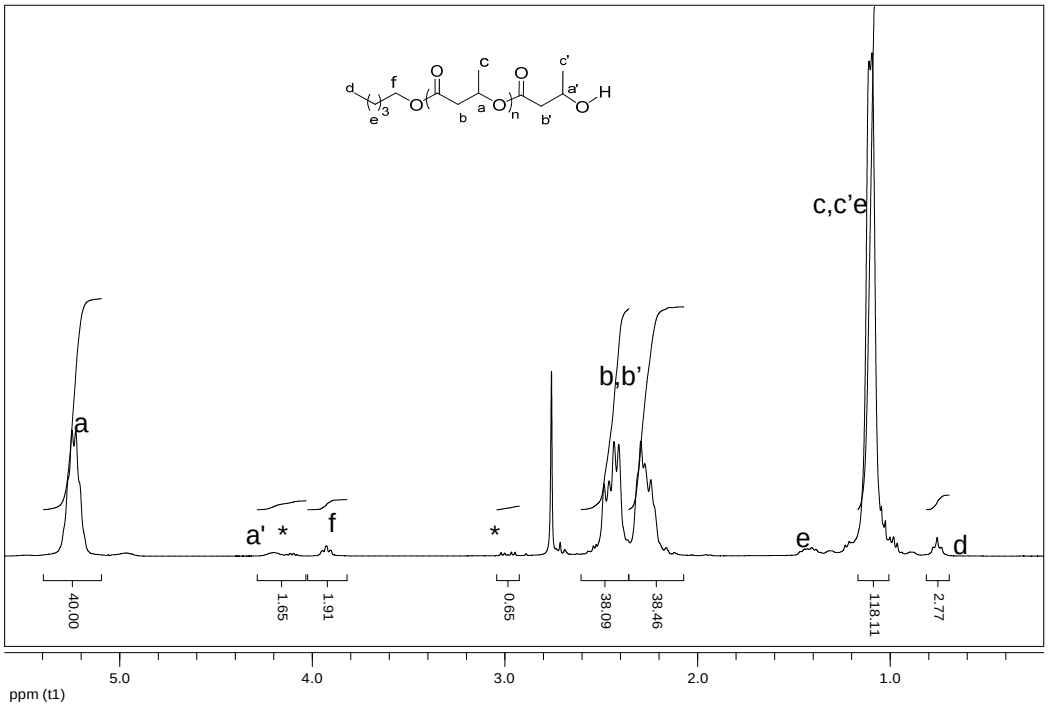


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of a PBL prepared with MSA as catalyst. Polymerization conditions: Run 2 in Table 1. * Residual monomer.

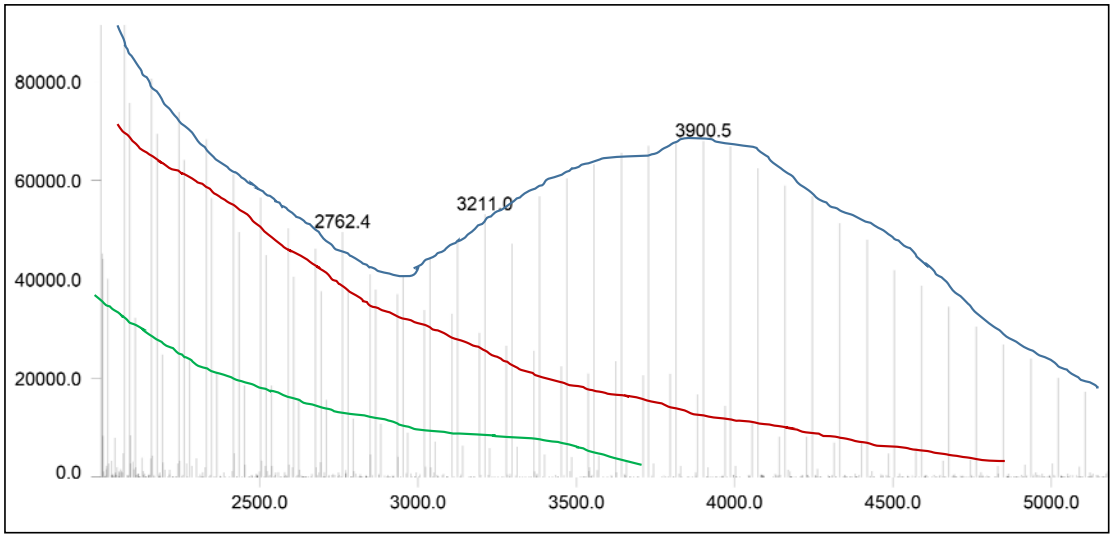


Figure S2. MALDI–TOF mass spectrum (Region m/z 2 000 to 5 000) of a PBL_{40} polymer. (Polymerization conditions: Run 2 Table 1). Blue: population of polymer chains initiated by *n*-pentanol M = 88($M_{n–pentOH}$) + n × 86.09($M_{β\text{-}BL}$) + 23(Na+). Red: population of cyclic polymer chains; Green: population of polymer chains initiated by *n*-pentanol and resulting from crotonisation reaction M = 88($M_{n–pentOH}$) + n × 86.09($M_{β\text{-}BL}$) + 23(Na+) + 69 (M_{C4H5O}).

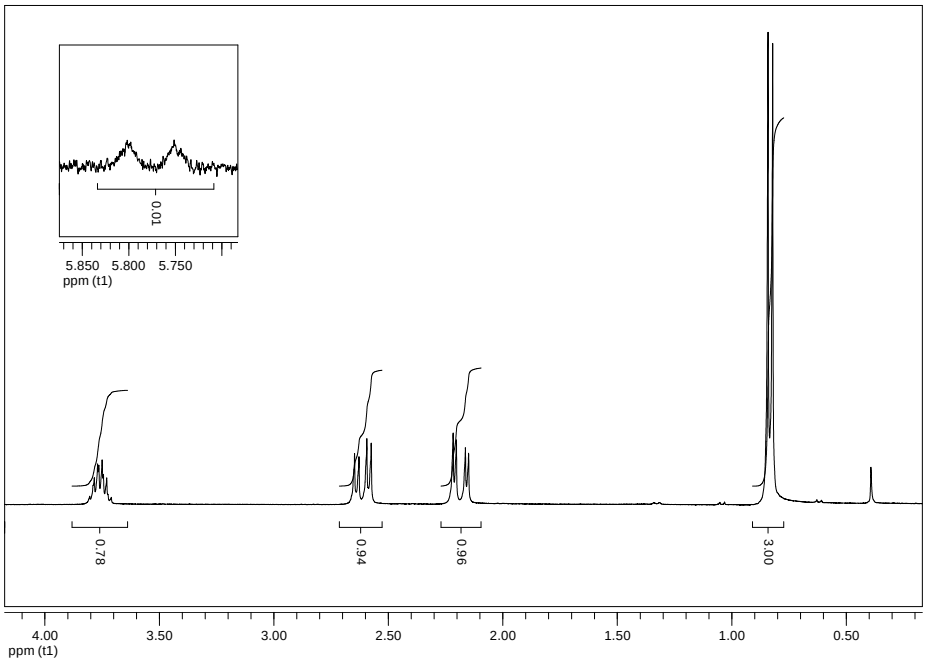


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 300MHz) of distilled β-BL. Signal at δ 5.77 ppm corresponds to olefinic H atoms resulting from crotonisation reactions.

Table S1. β-BL/ε-CL copolymerization reactions catalysed by HOTf[a]

run	Init.	[BL]/[CL]	% β-BL[b]	M_n[c] (g/mol)	$Đ$[c]
1	$C_5H_{11}OH$	20/20[d]	47	5 160	1.16
2	$C_5H_{11}OH$	20/20	46	6 670	1.21
3	$C_5H_{11}OH$	60/60	48	14 690	1.30
4	$C_4H_8(OH)_2$	120/0	100	10 730	1.18
		120/160	42	28 700	1.33
5	$PEG_{10000}(OH)_2$	60/0	100	16 730	1.23
6	$PEG_{1500}(OH)_2$	60/0	100	5 600	1.26
		60/60	51	9 900	1.46
7	Krazol LBH-P	60/0	100	9 870	1.21
		60/60	49	16 790	1.40

[a]Polymerization of of β-butyrolactone carried out at 30 °C in C_6D_6 solution.

[b]Determined by ^{1}H NMR spectroscopy.

[c]Obtained from size exclusion chromatography analysis in tetrahydrofuran using polystyrene standards.

[d]PCL-*b*-PBL prepared by ROP of ε-CL first.

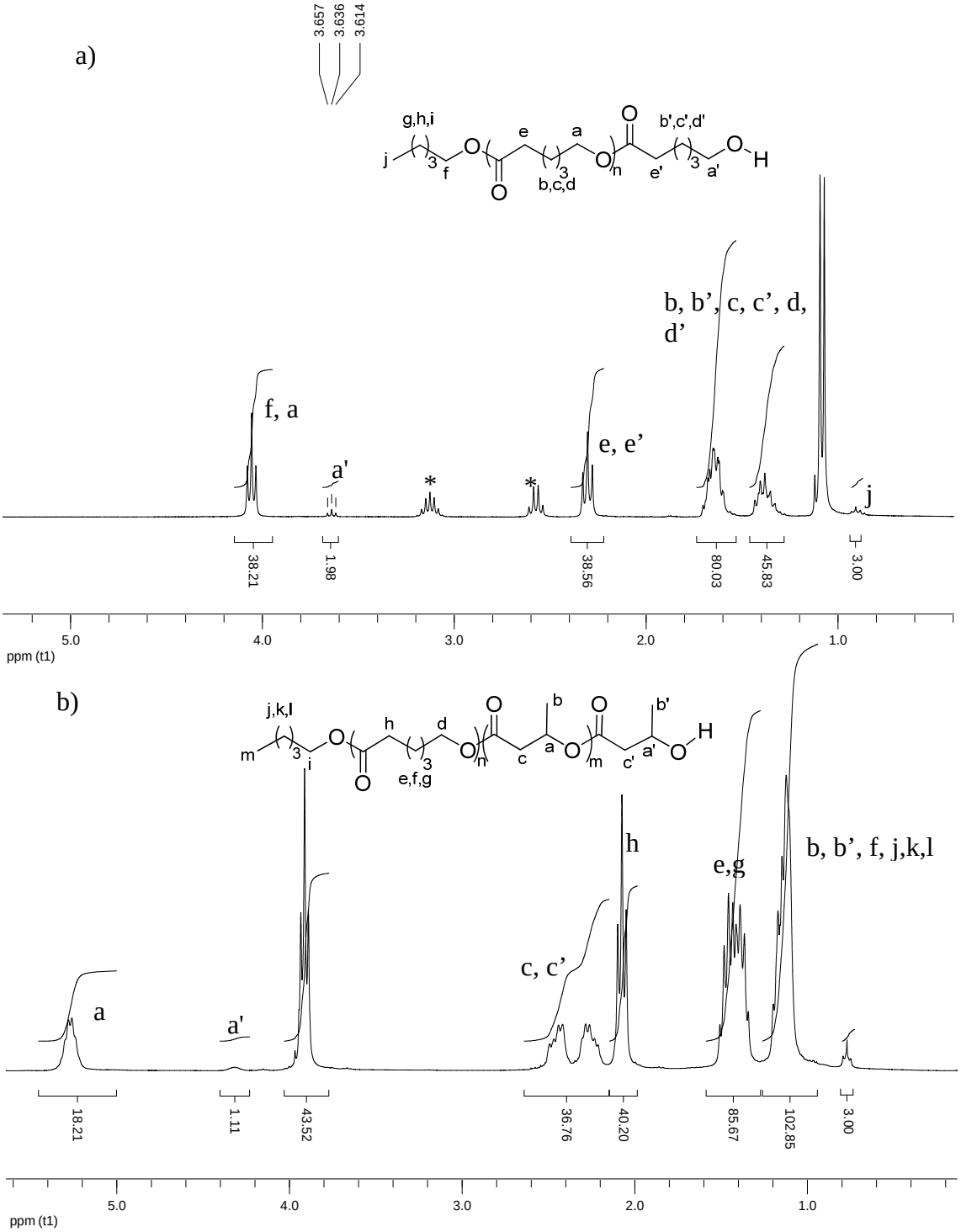


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of the block copolymer PCL_{20}–*b*–PBL_{20} (M_n = 5 160 g/mol): a) After polymerization of the ε-CL initially feed. b) ^{1}H NMR spectrum of the final PCL_{20}–*b*–PBL_{20} copolymer. Polymerization conditions: Run 1 in Table S1. * refers to the DIEA.HOTf salt.

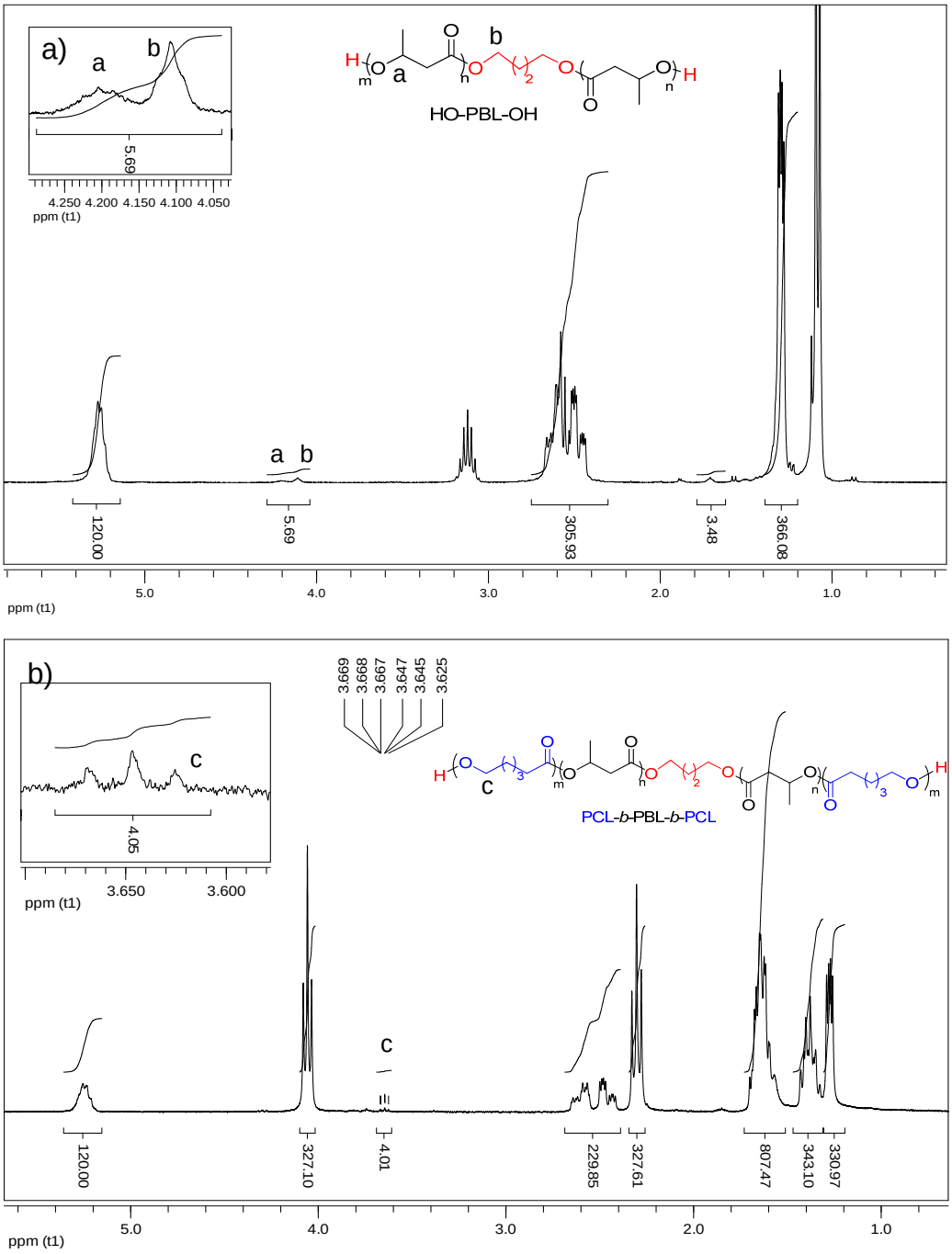


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of the telechelic HO-PBL-OH (a) and of the triblock copolymer PCL–*b*–PBL–*b*–PCL (b) (M_n = 28 700 g/mol): Polymerization conditions: Run 4 in Table S1.

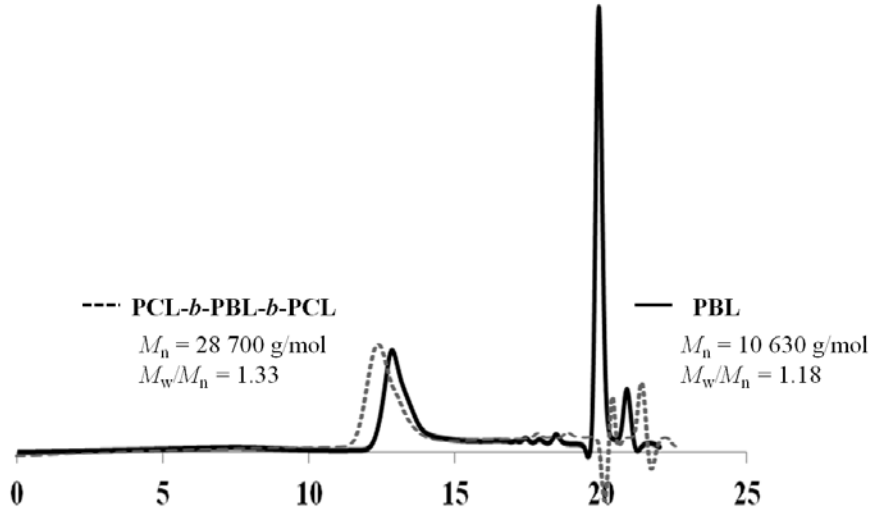


Figure S6. SEC traces of the telechelic HO-PBL-OH block and final PCL–*b*–PBL–*b*–PCL copolymer

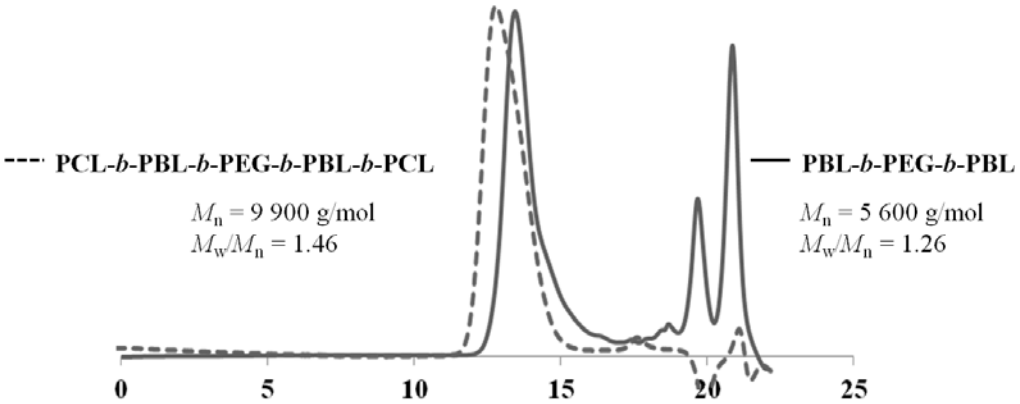


Figure S7. SEC traces of the telechelic HO-PBL-*b*-PEG-*b*-PBL-OH block and final PCL–*b*–PBL–*b*–PEG–*b*–PBL–*b*–PCL copolymer

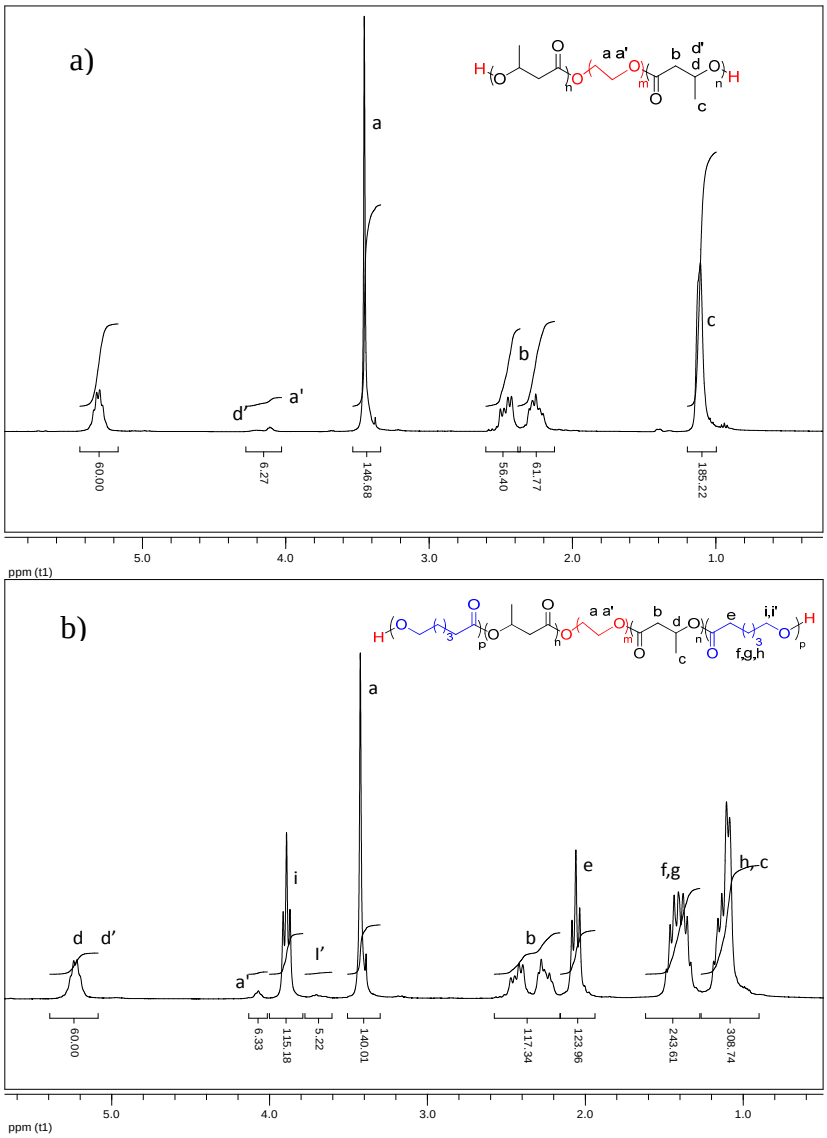


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of the block copolymer PCL–*b*–PBL–*b*–PEG–*b* –PBL–*b*–PCL: Polymerization conditions: Run 6 in Table S1. a) PBL–*b*–PEG–*b* –PBL; b) PCL–*b*–PBL–*b*–PEG–*b* –PBL–*b*–PCL

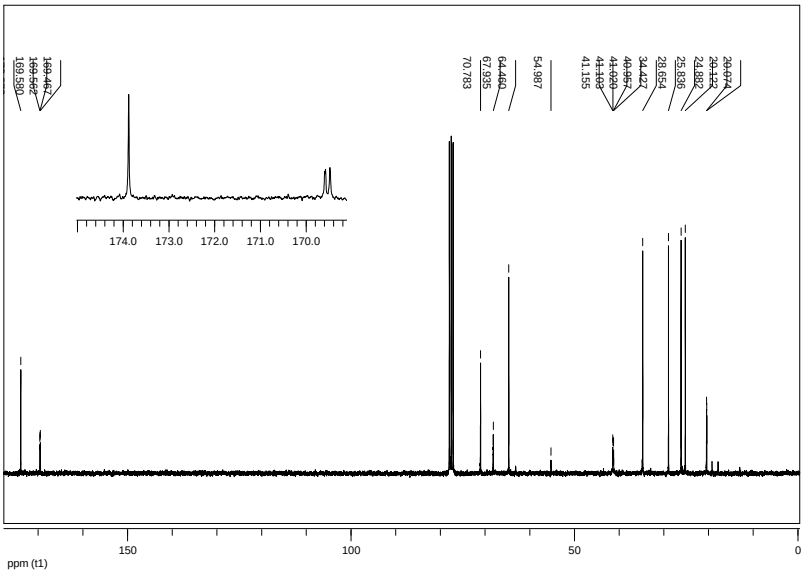
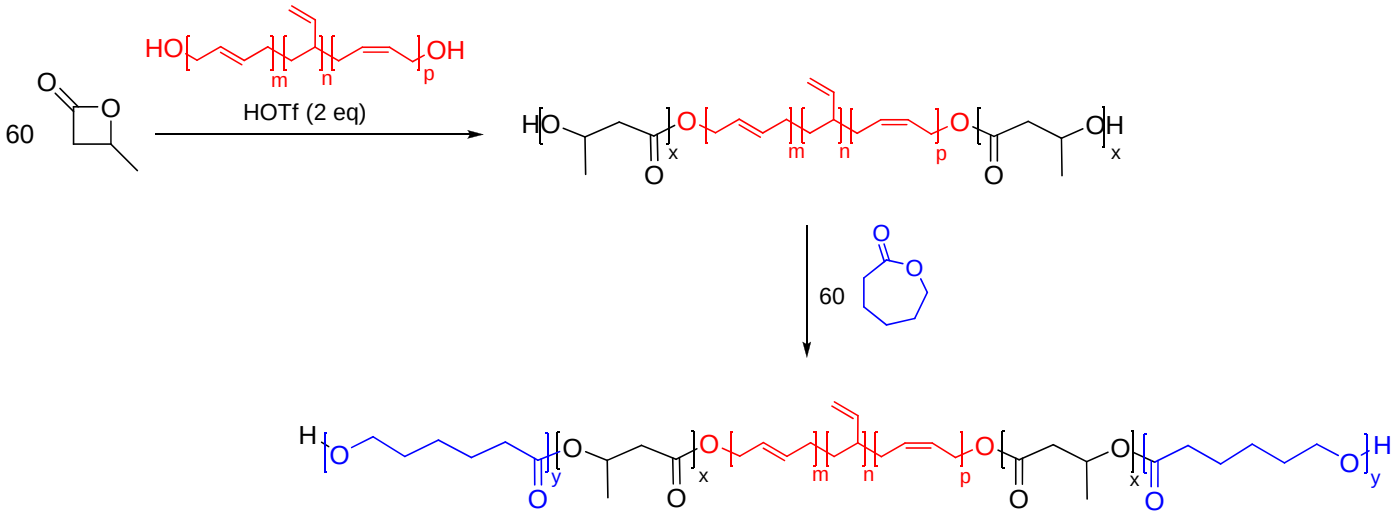


Figure S9. ^{13}C NMR spectrum ($CDCl_3$, 75 MHz) of the block copolymer PCL–*b*–PBL–*b*–PEG–*b*–PBL–*b*–PCL: Polymerization conditions: Run 6 in Table S1.



Scheme S1. Preparation of the block copolymer PCL–*b*–PBL–*b*–PBD–*b*–PBL–*b*–PCL: Polymerization conditions: Run 7 in Table S1.

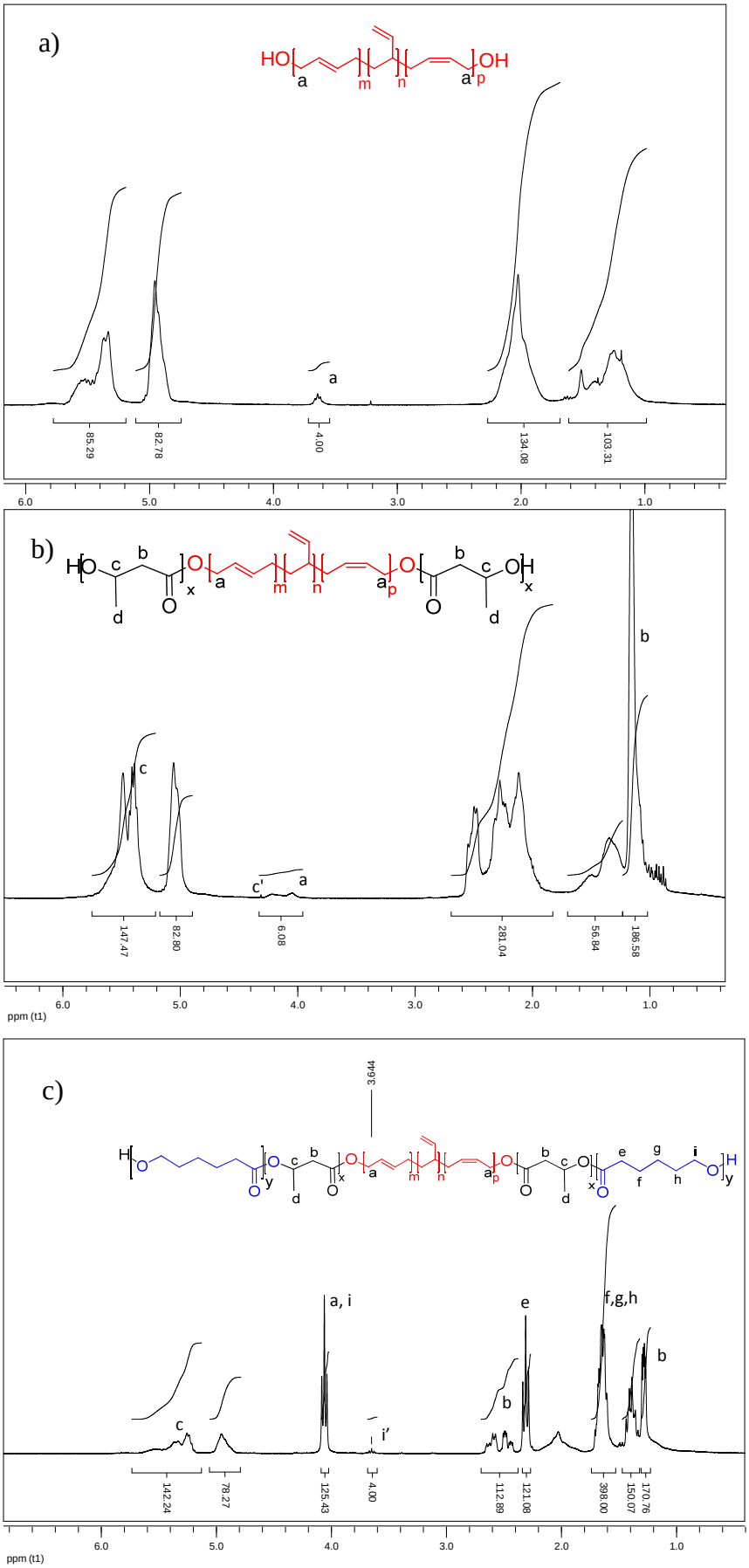


Figure S10. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of the block copolymer PCL–*b*–PBL–*b*–PBD–*b*–PBL–*b*–PCL: Polymerization conditions: Run 7 in Table S1. a) PBD; b) PBL–*b*–PBD–*b*–PBL; c) PCL–*b*–PBL–*b*–PBD–*b*–PBL–*b*–PCL.

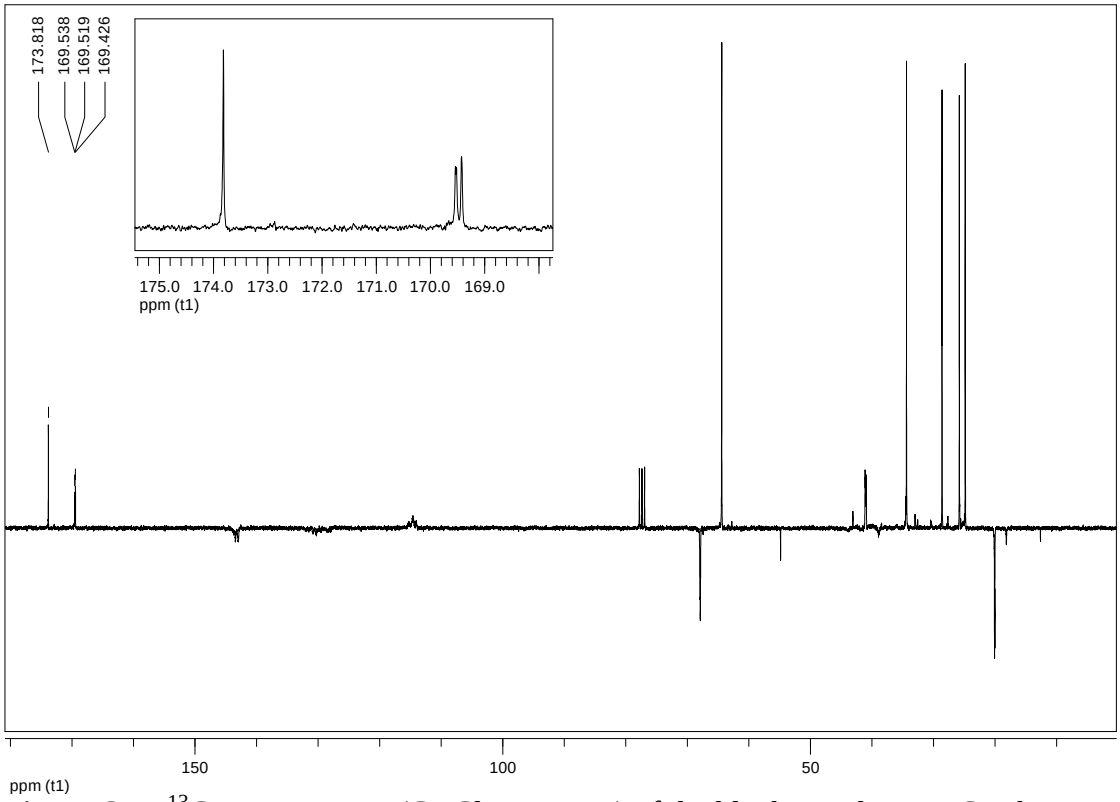


Figure S11. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of the block copolymer PCL–*b*–PBL–*b*–PBD–*b*–PBL–*b*–PCL: Polymerization conditions: Run 7 in Table S1.

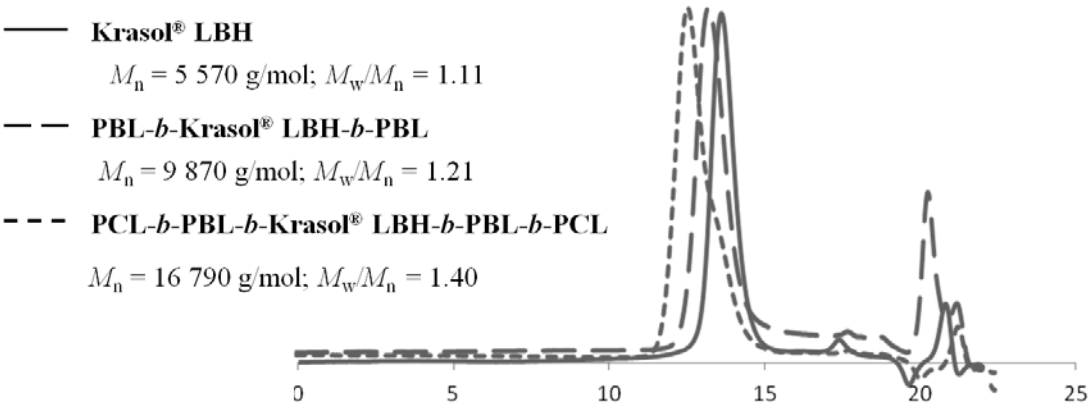


Figure S12. SEC traces of the telechelic HO-PBL-*b*-PBD-*b*-PBL-OH block and final PCL–*b*–PBL–*b*–PBD–*b*–PBL–*b*–PCL copolymer.