Supporting Information

Ring-Opening Polymerization of ω-6-Hexadecenlactone by Salicylaldiminato Aluminum Complex: a Route to Semicrystalline and Functional Poly(ester)s

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Figure S25. X-ray diffraction pattern of: (a) poly(6-ω-hexadecenlactone); (b) poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone).

Figure S26. GPC chromatogram of poly(6-ω-hexadecenlactone).

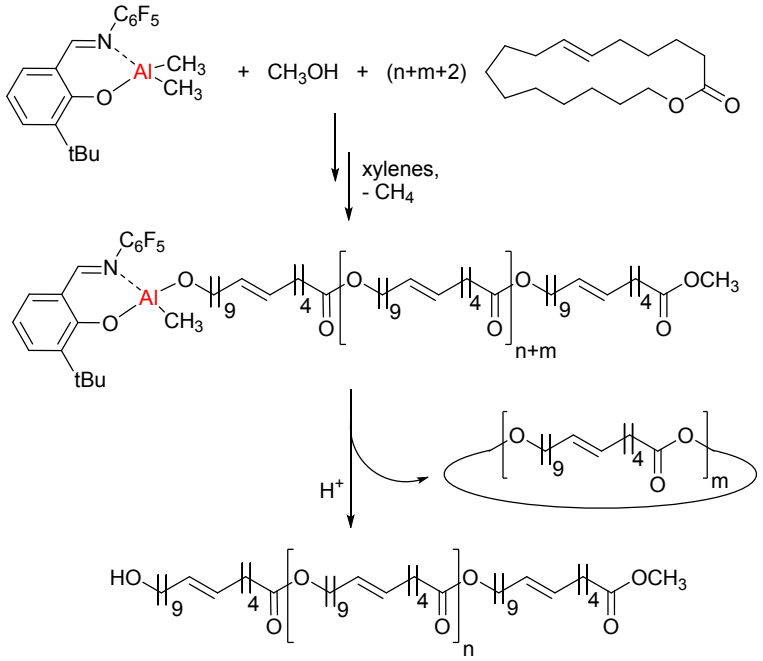
Figure S27. GPC chromatogram of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)].

Figure S28. GPC chromatogram of poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone).

Figure S29. GPC chromatogram of poly(6-ω-hexadecenlactone)-*block*-(*rac*-lactide).

Figure S30. GPC chromatogram of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide).

Figure S31. MALDI-ToF-MS of poly(6-ω-hexadecenlactone).



Scheme S1. Polymerization of 6-ω-hexadecenlactone by compound **1**.

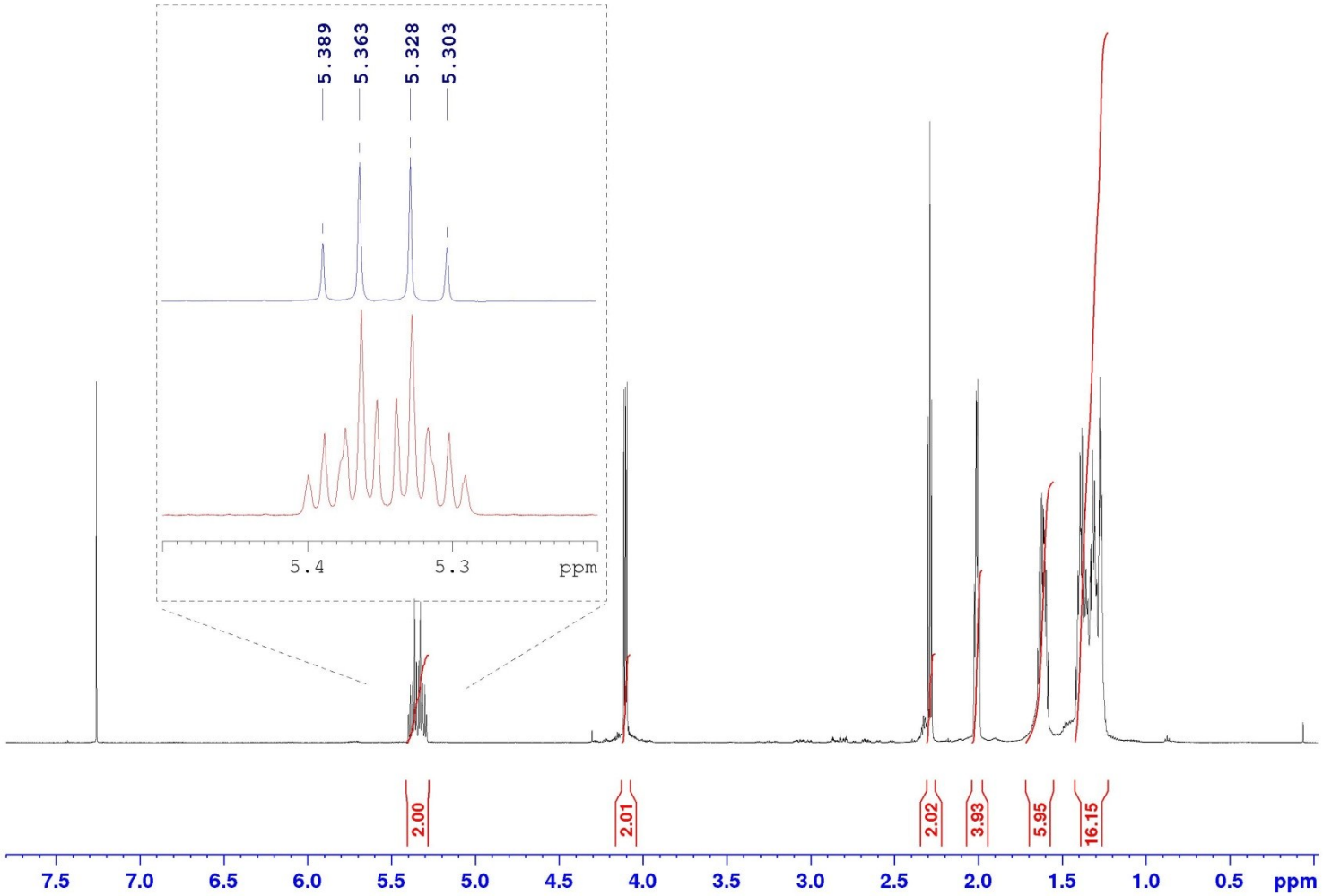


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$, RT) of 6-ω-hexadecenlactone. In the enlargement: comparison between ^{1}H NMR (red) and homonuclear-decoupled ^{1}H NMR (blue) of olefinic region irradiating allylic protons (2.0 ppm).

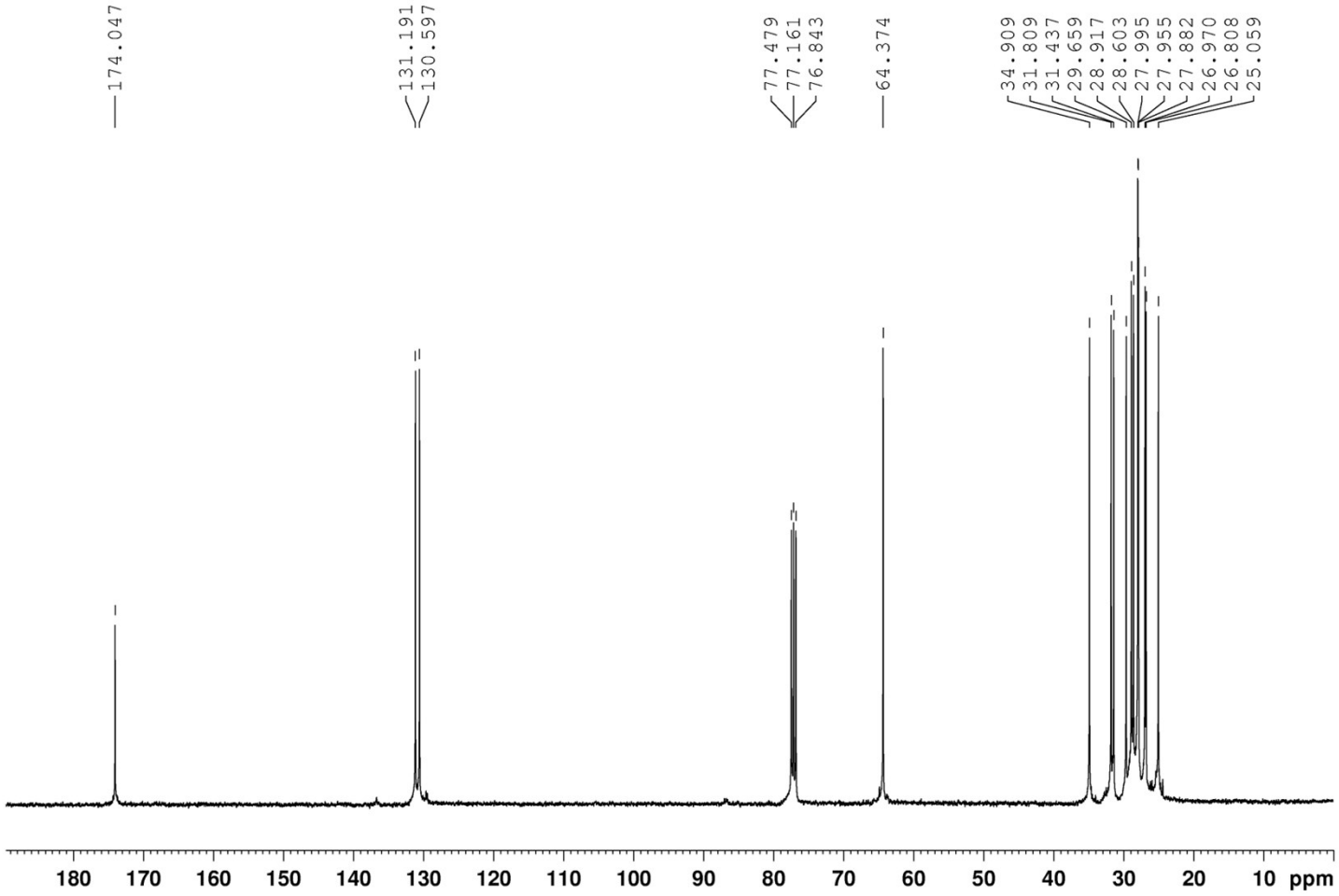


Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, RT) of: 6-ω-hexadecenlactone.

Table S1. Polymerization of ω-6-hexadecenlactone. [a]

Run	$[6HDL]_0/[Cat]/[MeOH]$[b]	T (°C)	t (h)	Conv (%)[c]	Yield (%)	$M_{n,th}$[d] (kDa)	$M_{n,NMR}$ (kDa)
9	100/1/0.5	100	27	33	31	16.7	24.3
10	100/1/2	100	27	41	36	5.2	7.5
11	100/1/4	100	27	36	39	2.3	4.3
12	10/1/1	100	18	87	nd	2.2	2.7

Polymerization conditions: [a]Xylenes = 0.8 mL; precatalyst = 12 μmol. [b]Mol ratio of monomer to precatalyst to MeOH in the feed. [c]Determined by ^{1}H NMR from the ω-methylene resonances of monomer and obtained polymer. [d]Calculated from $([6HDL]_0/[MeOH]_0)$ x conv x 252.4.

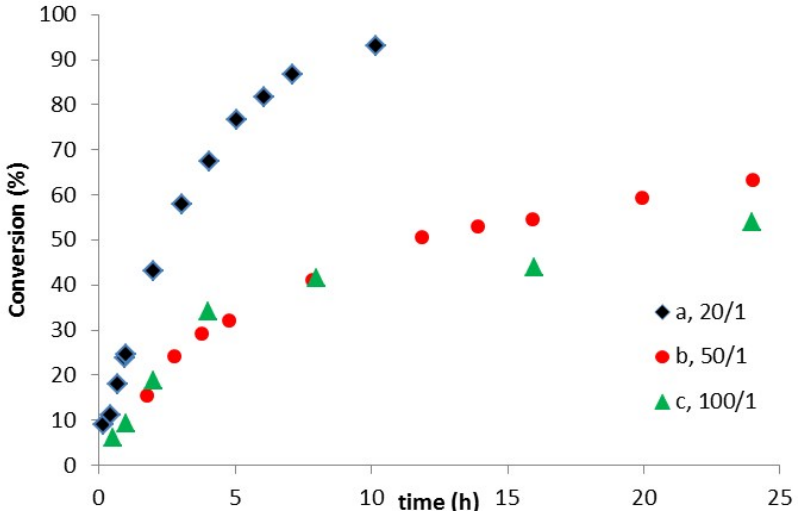


Figure S3. Conversion (%) versus time (h) plot of ROP of ω-6-hexadecnlactone determined by ^{1}H NMR spectra varying mol ratio of monomer to precatalyst in the feed. (a) [Cat] = 5 x 10^{-2} M; [6HDL] = 1.0 M; [MeOH] = 2 x 10^{-2} M; T = 80 °C; toluene-d_8 as solvent. (b) [Cat] = 2 x 10^{-2} M; [6HDL] = 1.0 M; [MeOH] = 2 x 10^{-2} M; T = 80 °C; toluene-d_8 as solvent. (c) [Cat] = 1.5 x 10^{-2} M; [6HDL] = 1.5 M; [MeOH] = 1.5 x 10^{-2} M; T = 100 °C; xylenes as solvent.

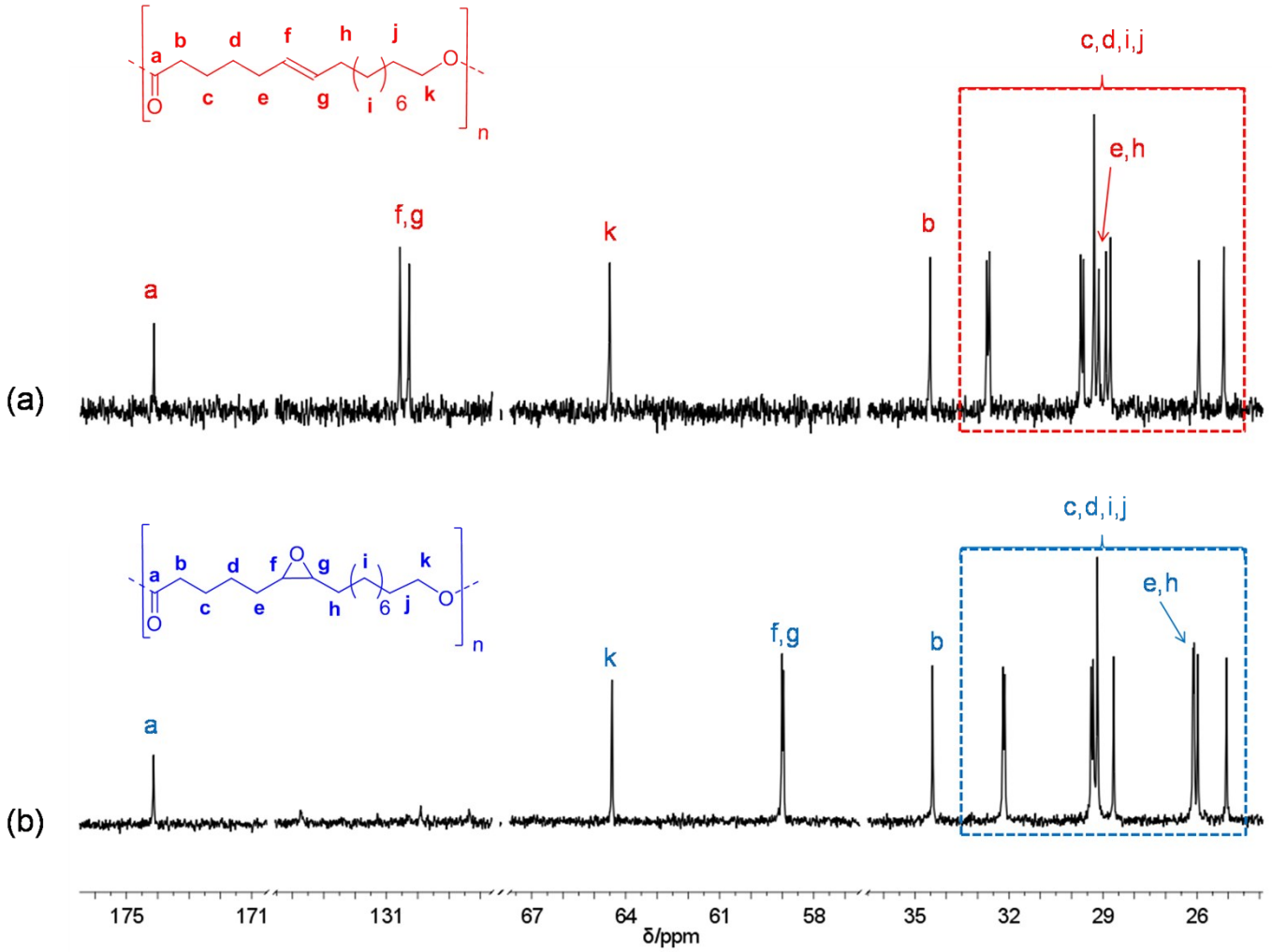


Figure S4. ^{13}C NMR (75 MHz, $CDCl_3$, RT) of: poly(6-ω-hexadecenlactone) and poly(6,7-epoxy-ω-hexadecalactone) (***b***).

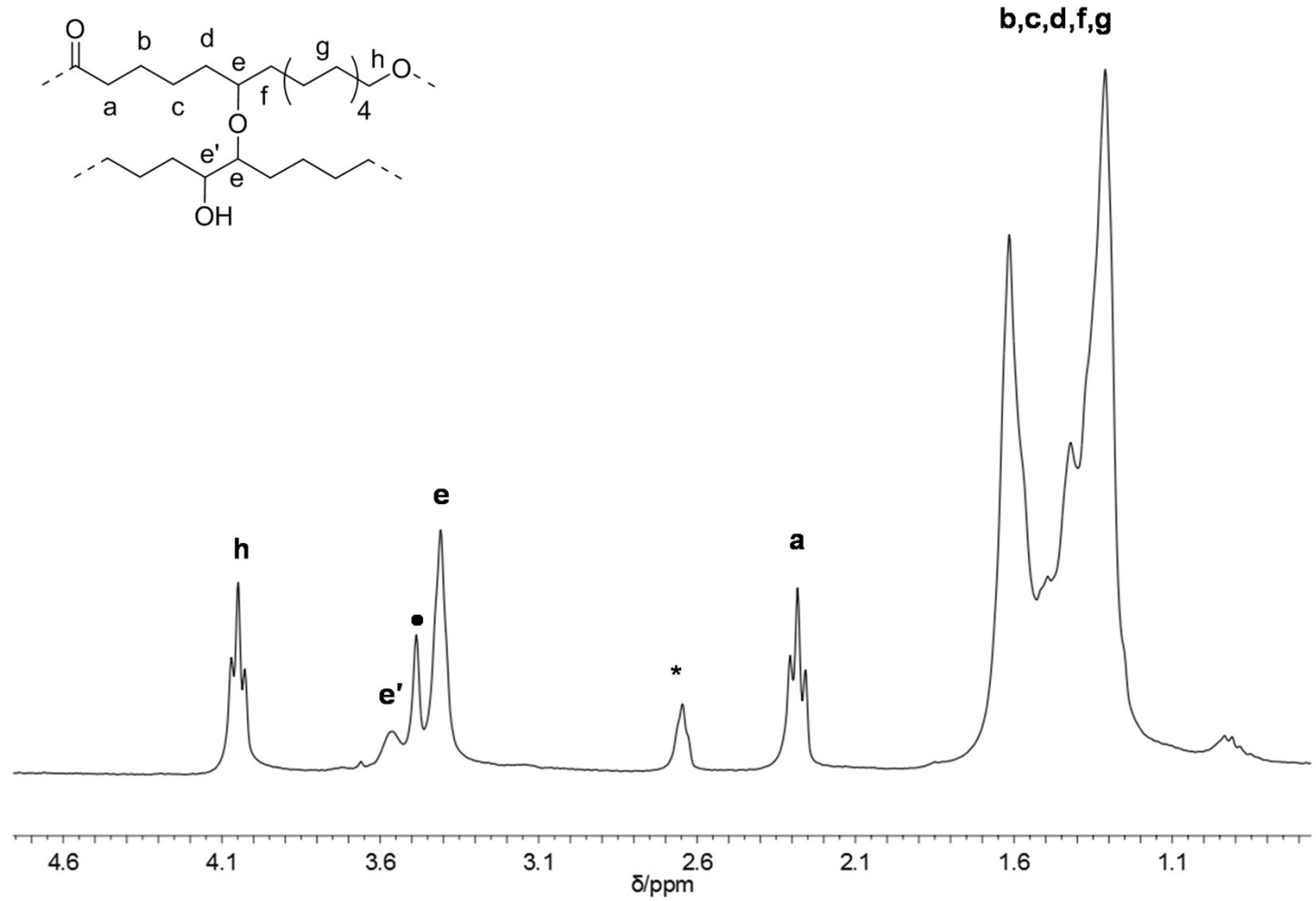


Figure S5. ^{1}H NMR (300 MHz, $CDCl_3$, RT) spectrum of poly(hydroxy-ω-hexadecalactone) (***c***). *: traces of starting poly(6,7-epoxy-ω-hexadecalactone). •: methanol.

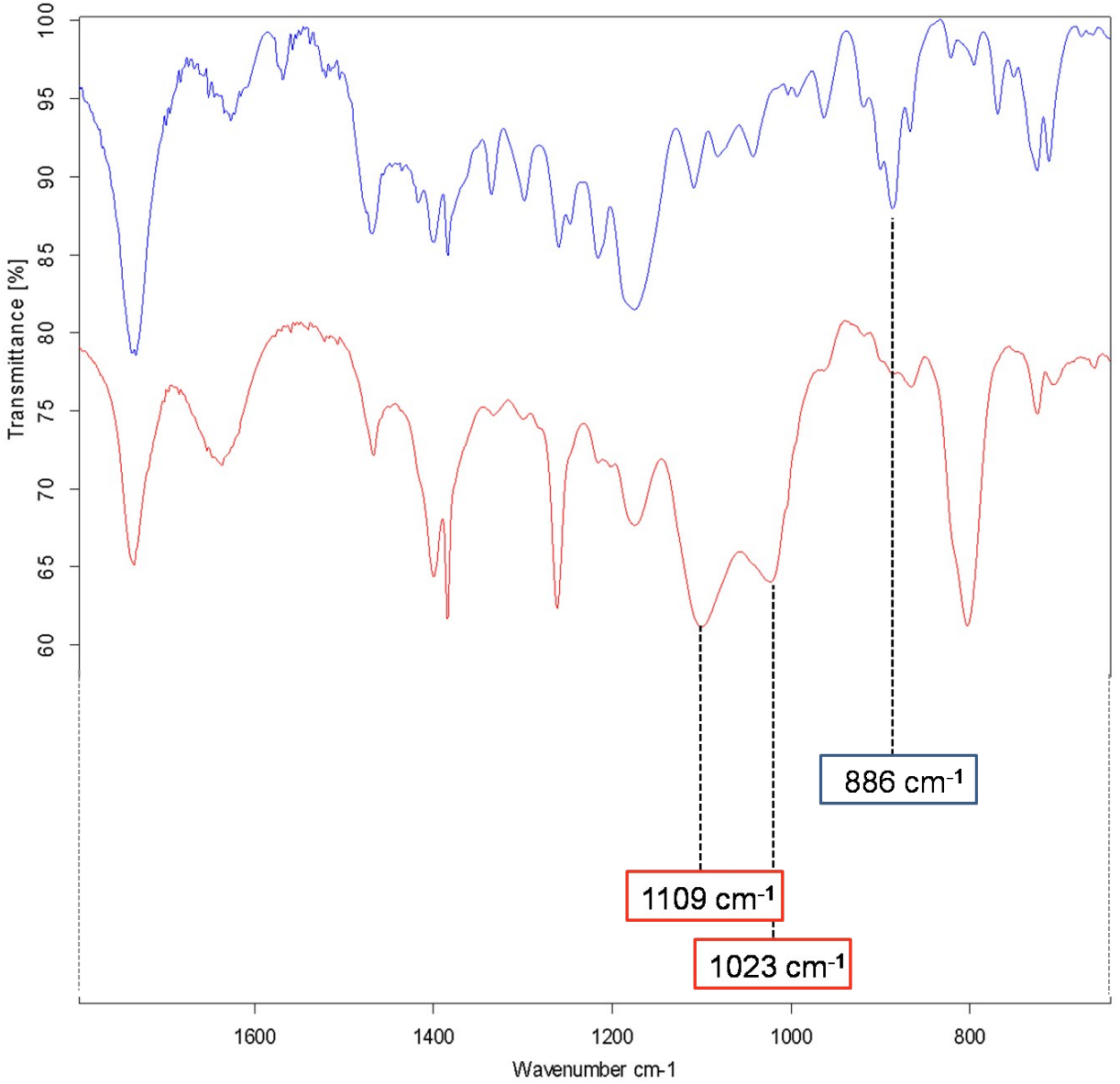


Figure S6. FT-IR spectrum of: (top, blue) poly(6,7-epoxy-ω-hexadecalactone) (***b***) and (bottom, red) poly(hydroxy-ω-hexadecalactone) (***c***).

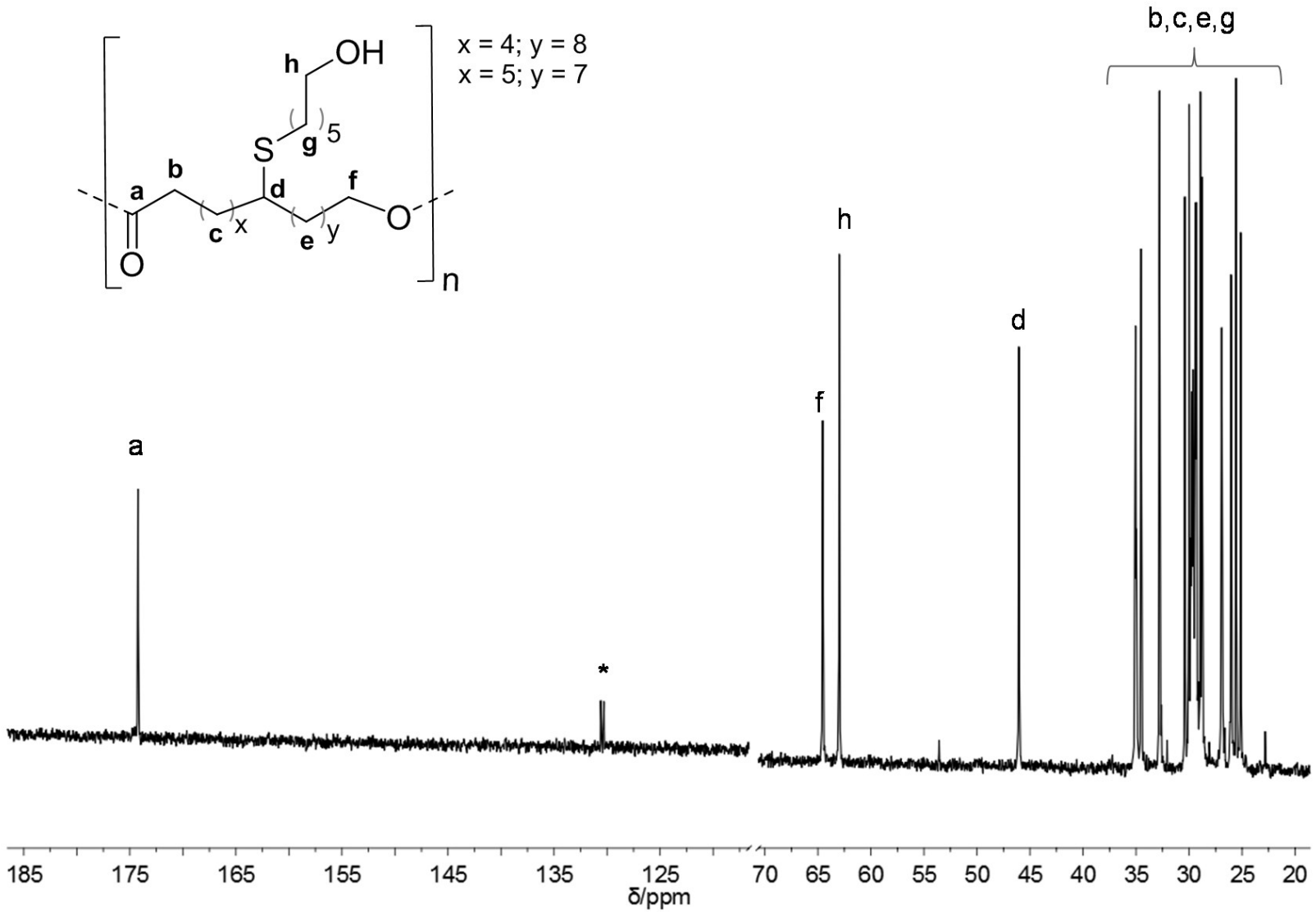


Figure S7. ^{13}C NMR (75 MHz, $CDCl_3$, RT) spectrum of poly(ω-hexadecalactone) with 6-mercapto-1-hexanol groups (***d***). *****: double bond carbons of starting poly(6-ω-hexadecenlactone).

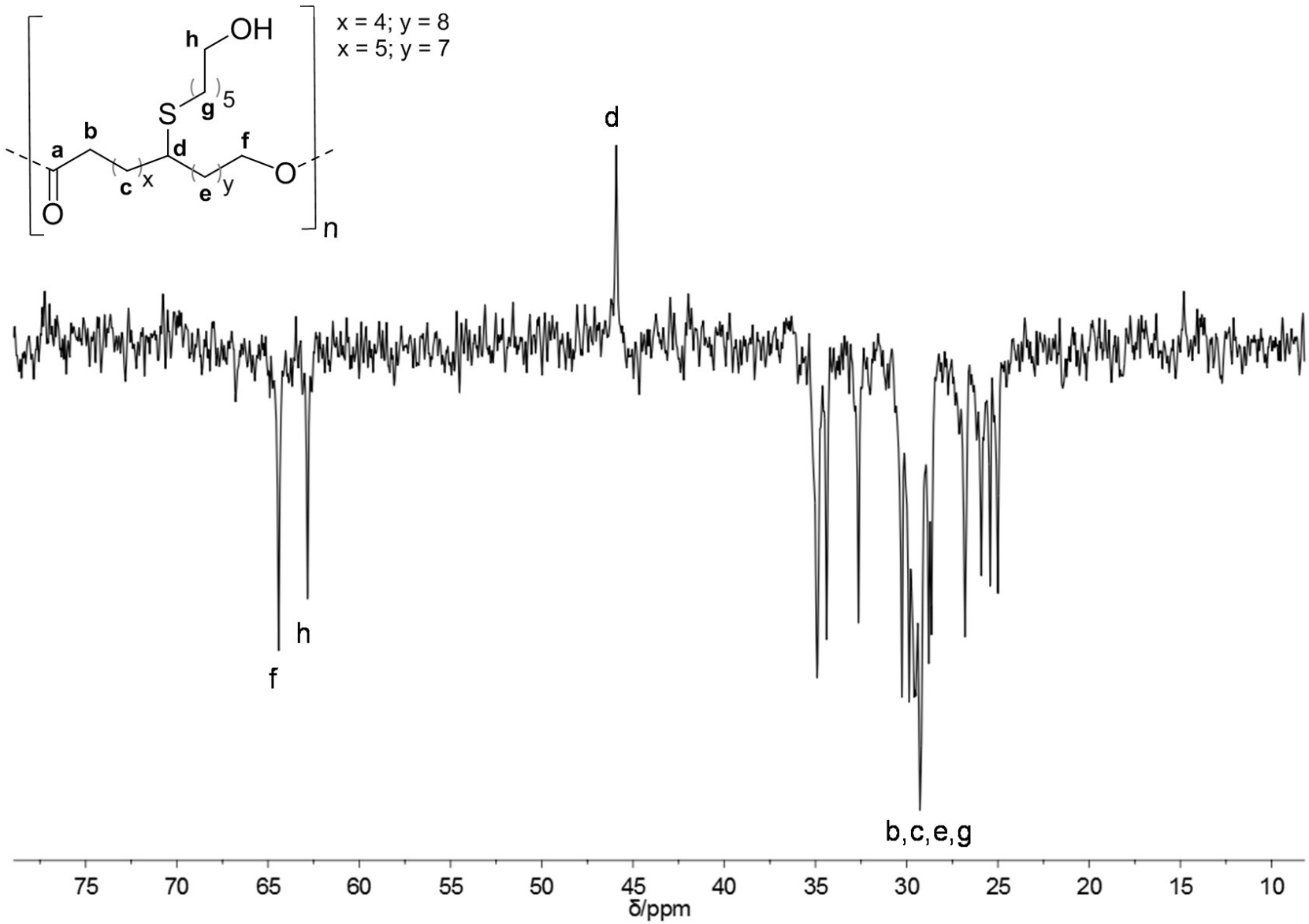


Figure S8. DEPT-135 NMR (75 MHz, $CDCl_3$, RT) spectrum of poly(ω-hexadecalactone) with 6-mercapto-1-hexanol groups (***d***).

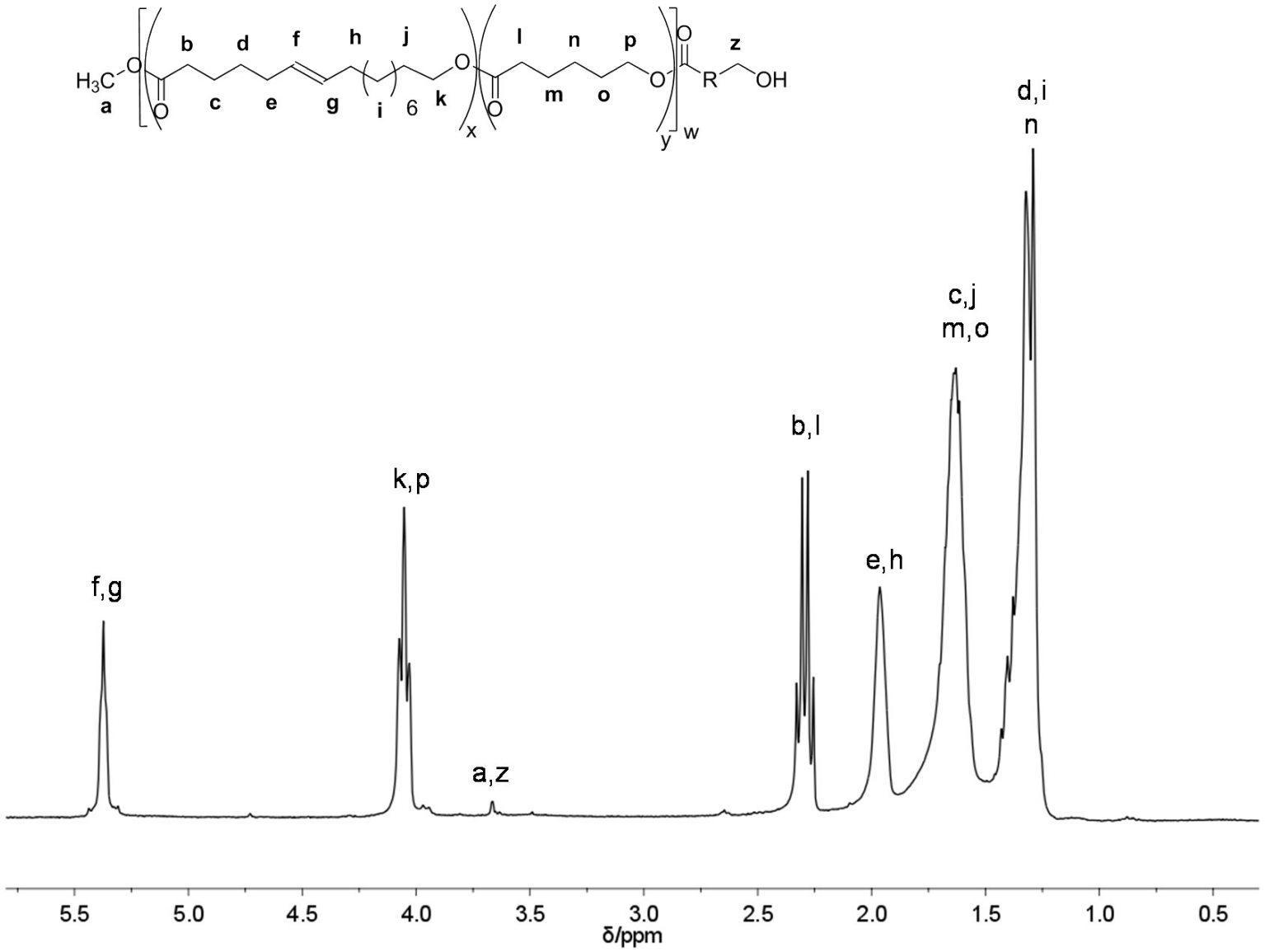


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$, RT) of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)].

Table S2. Di-block copolymerization experiments.

Polymer sample	F_{HDL}[a]	F_{CL}[a]	F_{LA}[a]	L_{HDL}[a]	L_{LA}[a]	L_{CL}[a]	$M_{n,NMR}$ (kDa)[a]	$M_{n,GPC}$ (kDa)[b]	M_w/M_n[b]	T_m (°C)[c]	ΔH_m (Jg-1)[c]
PCL	-	100	-	-	-	-	8.5	23.4	1.5	56.1	76.6
PHDL-*block*-PCL	19	81	-	34	-	120	22.3	37.5	1.9	55.6	78.4
PHDL-*block*-PCL'	62.5	37.5	-	33	-	20	10.6	19.1	2.4	54.1	93.4
PHDL-*block*-PLA	35	-	65	66	125	-	28.4	24.3	1.5	49.3	37.2
P(HDL-*ran*-CL)-*block*-PLA	22	43	35	1.7	58	2.9	26.5	29.1	2.0	38.8	46.9

[a]Determined by 1H NMR spectra. [b]Determined by GPC in THF vs polystyrene standards. [c]Value reported for the second heating cycle.

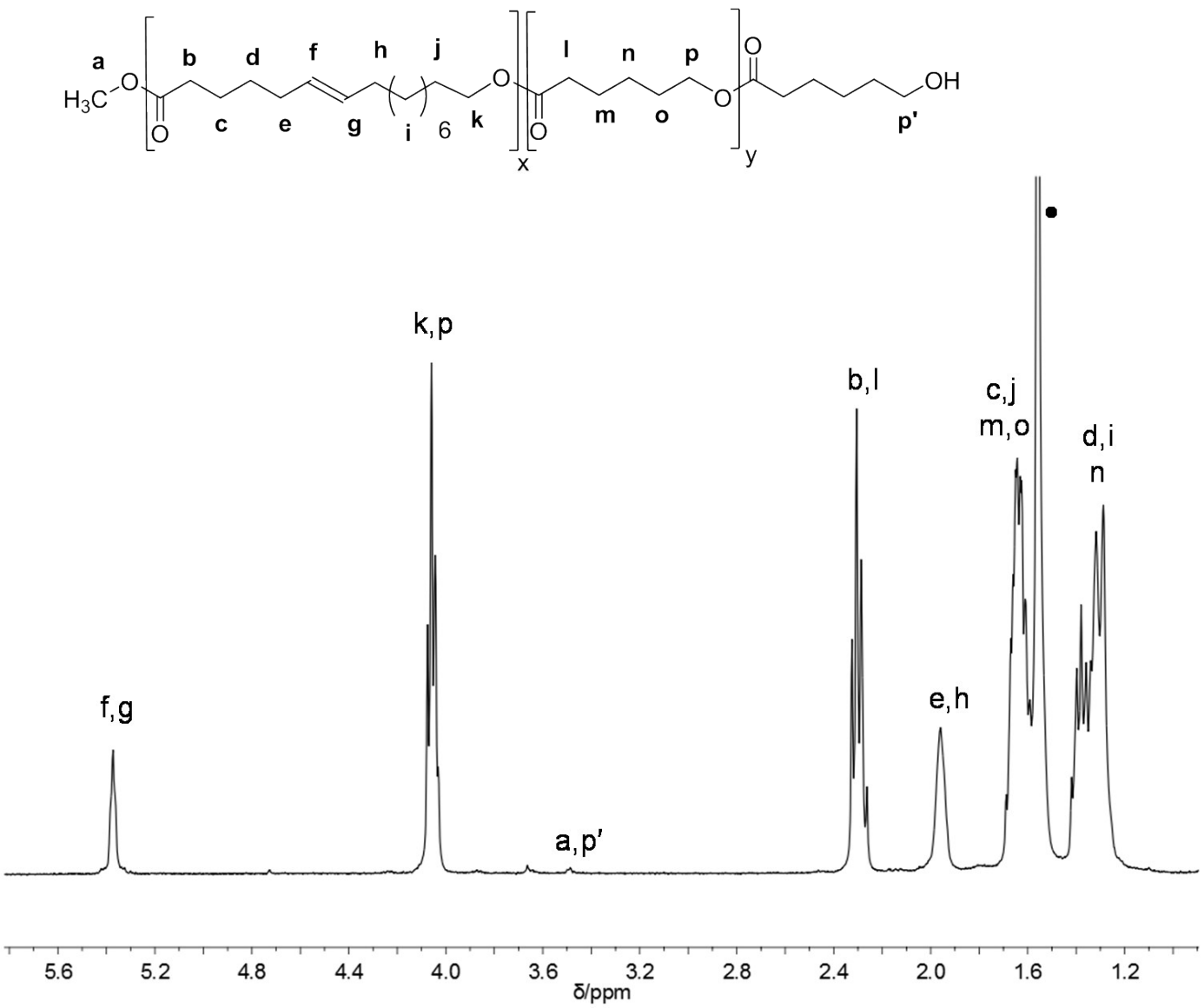


Figure S10. [1] H NMR (300 MHz, $CDCl_3$, RT) of poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone). •: adventitious water.

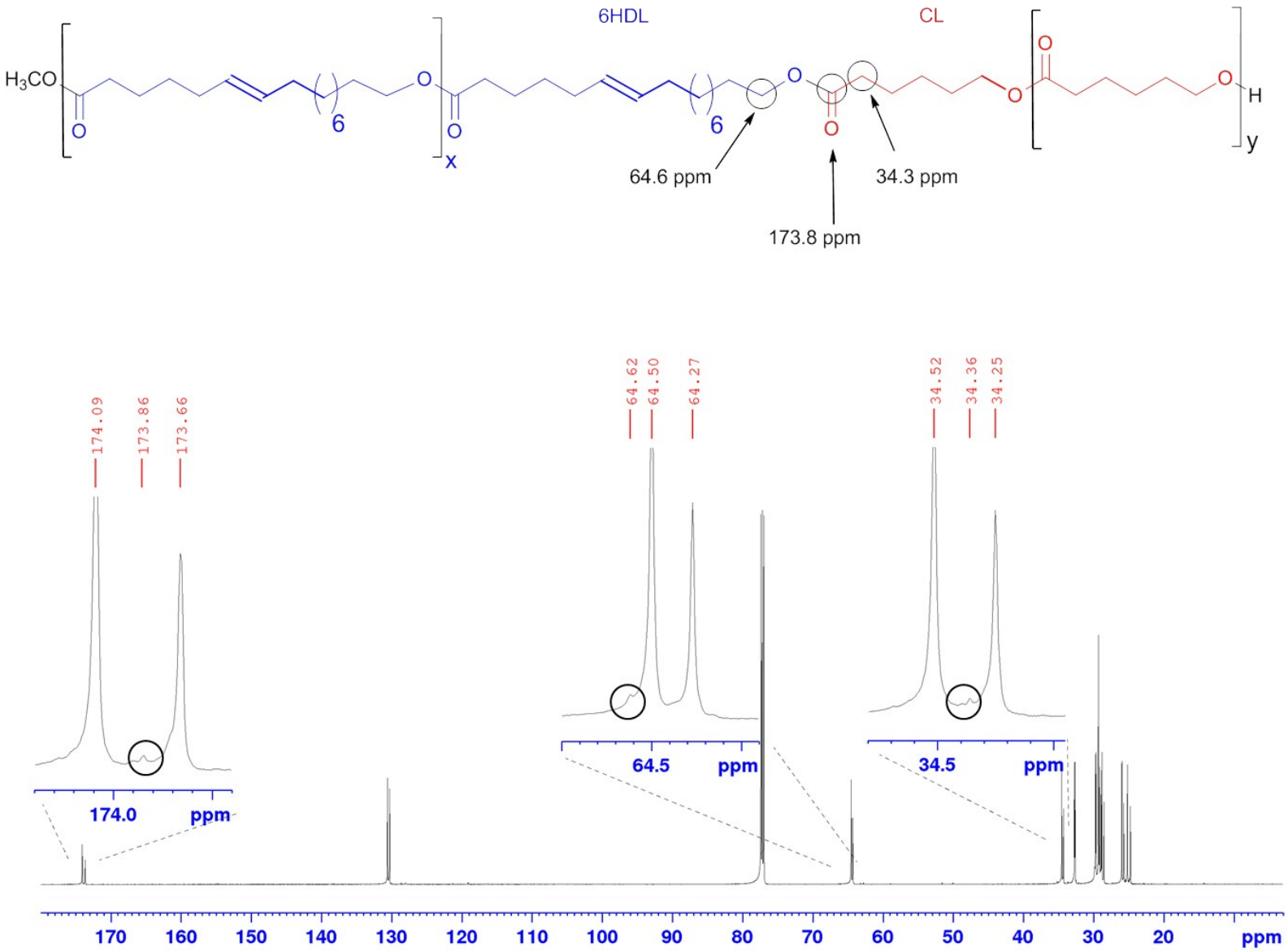


Figure S11. ^{13}C NMR (600 MHz, $CDCl_3$, RT) of poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone) (sample PHDL-*block*-PCL', Table S2).

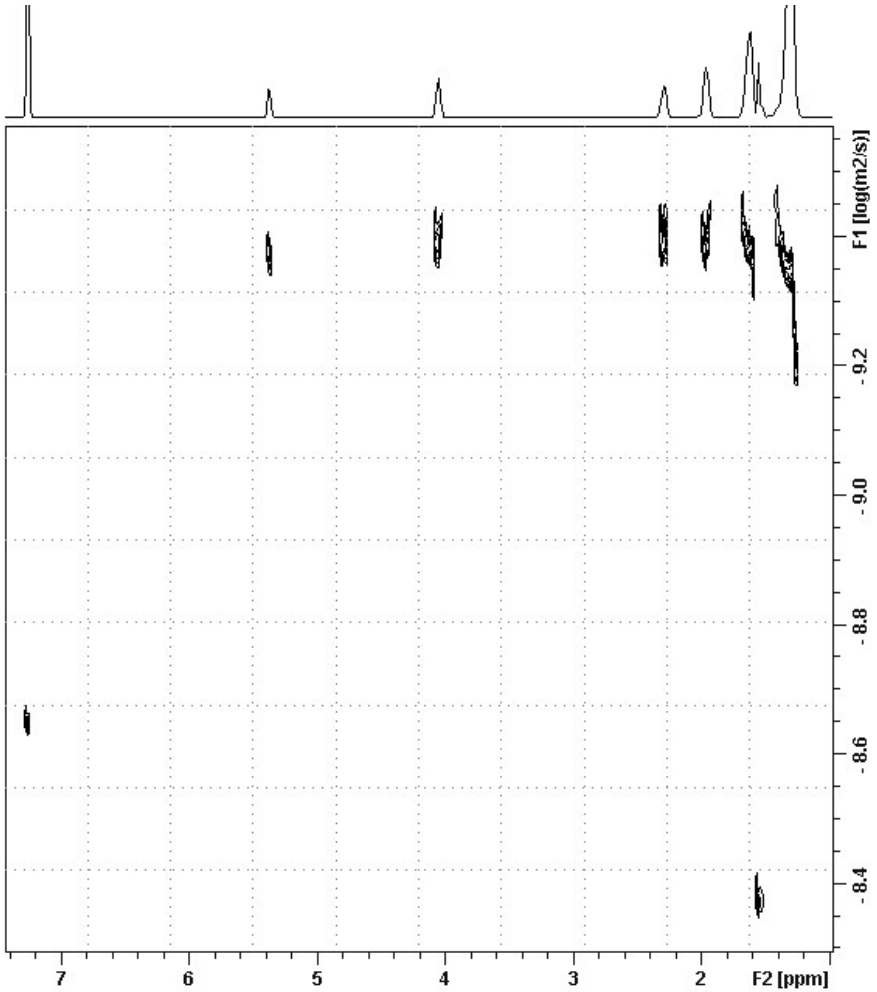


Figure S12. 2D DOSY NMR (400 MHz, $CDCl_3$, RT) of poly(6-ω-hexadecenlactone)-*block*-(ε-caprolactone), recorded employing δ = 1700 μs and Δ = 0.1 s. Signals at 7.26, 1.56 and 1.26 ppm are relative to deuterated solvent residual protic signal ($CHCl_3$), adventitious water and *n*-heptane, respectively.

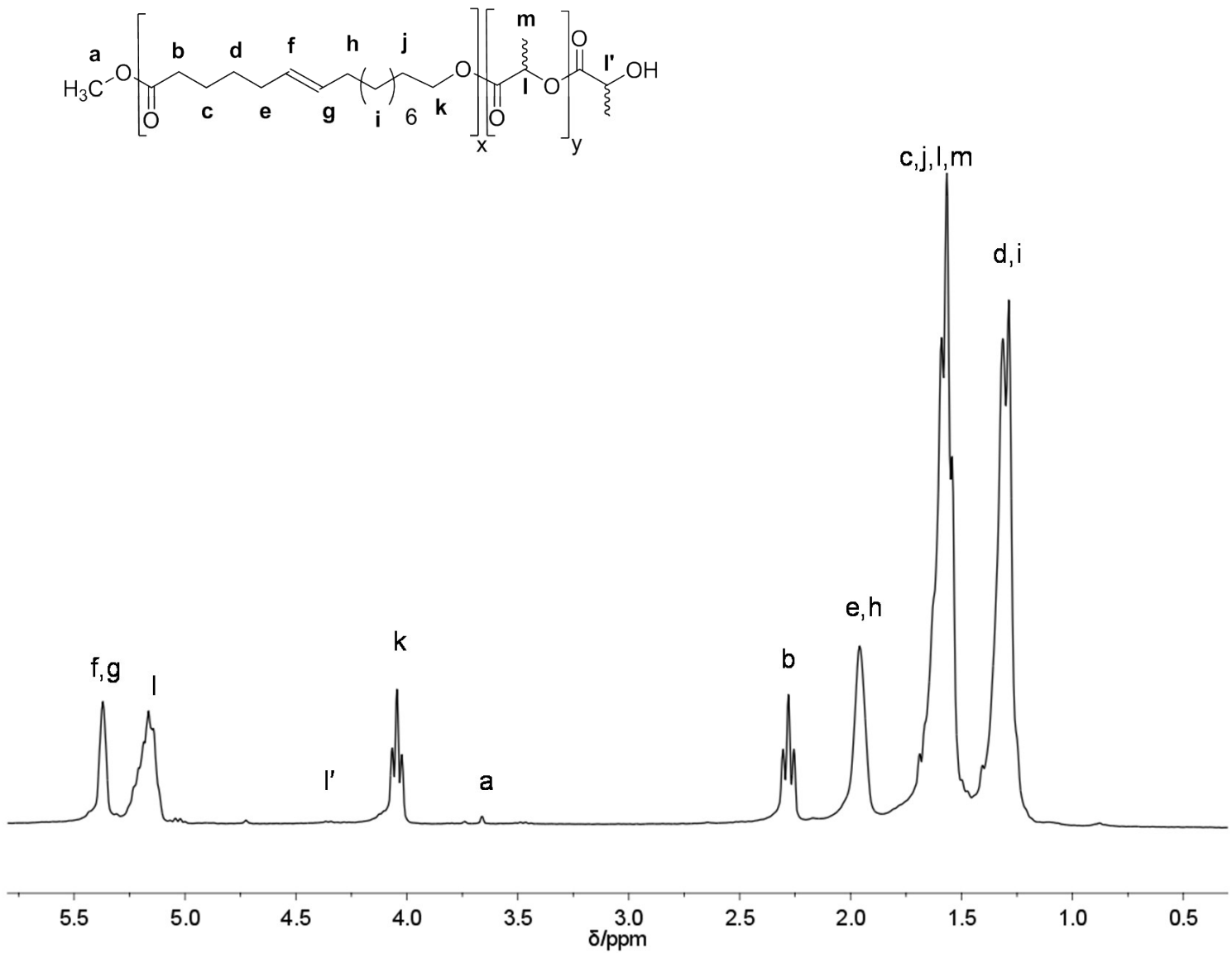


Figure S13. ^{1}H NMR (300 MHz, $CDCl_3$, RT) of poly(6-ω-hexadecenlactone)-*block*-poly(*rac*-lactide).

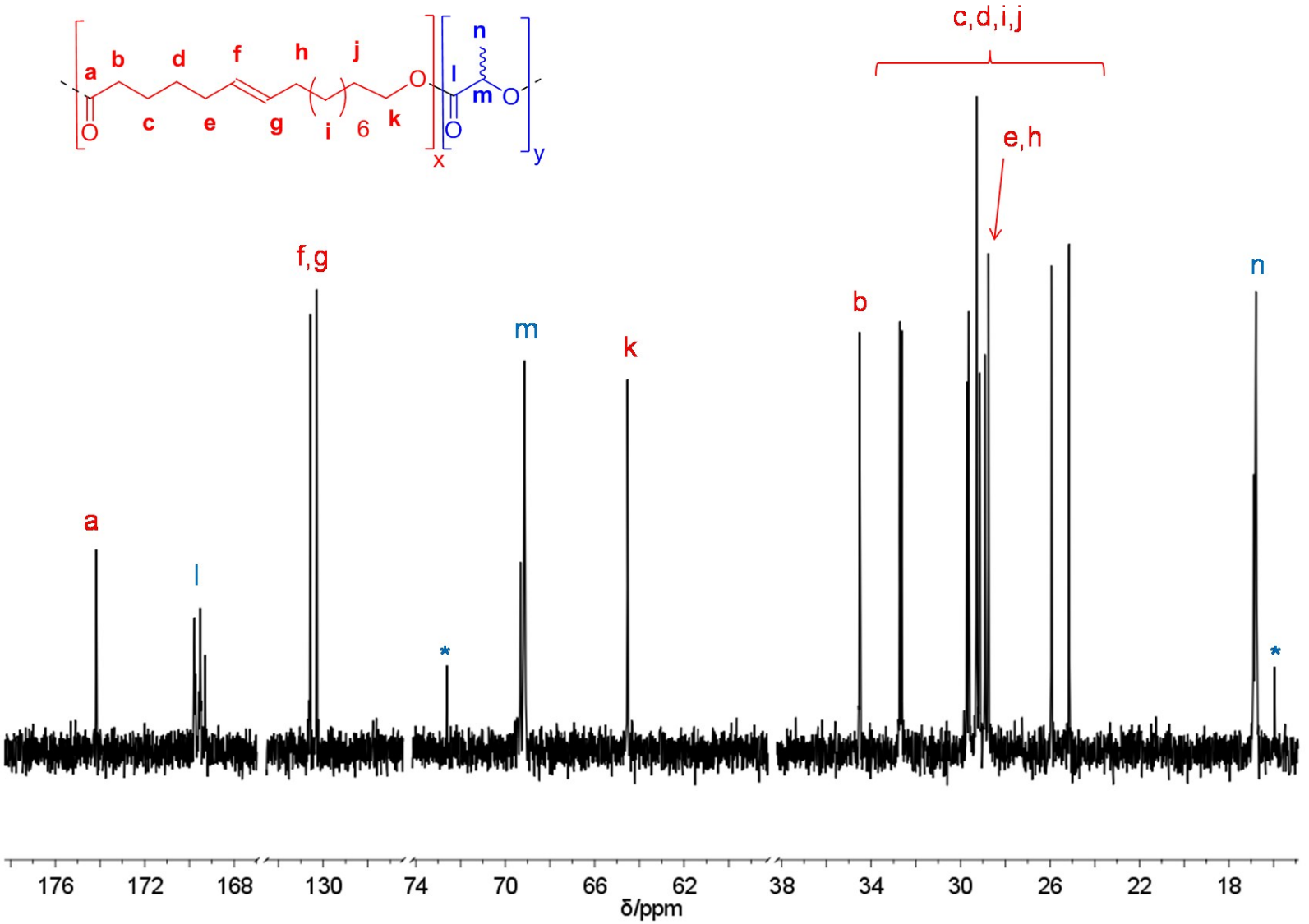


Figure S14. ^{13}C NMR (75 MHz, $CDCl_3$, RT) of poly(6-ω-hexadecenlactone)-*block*-poly(*rac*-lactide). *: *rac*-lactide monomer.

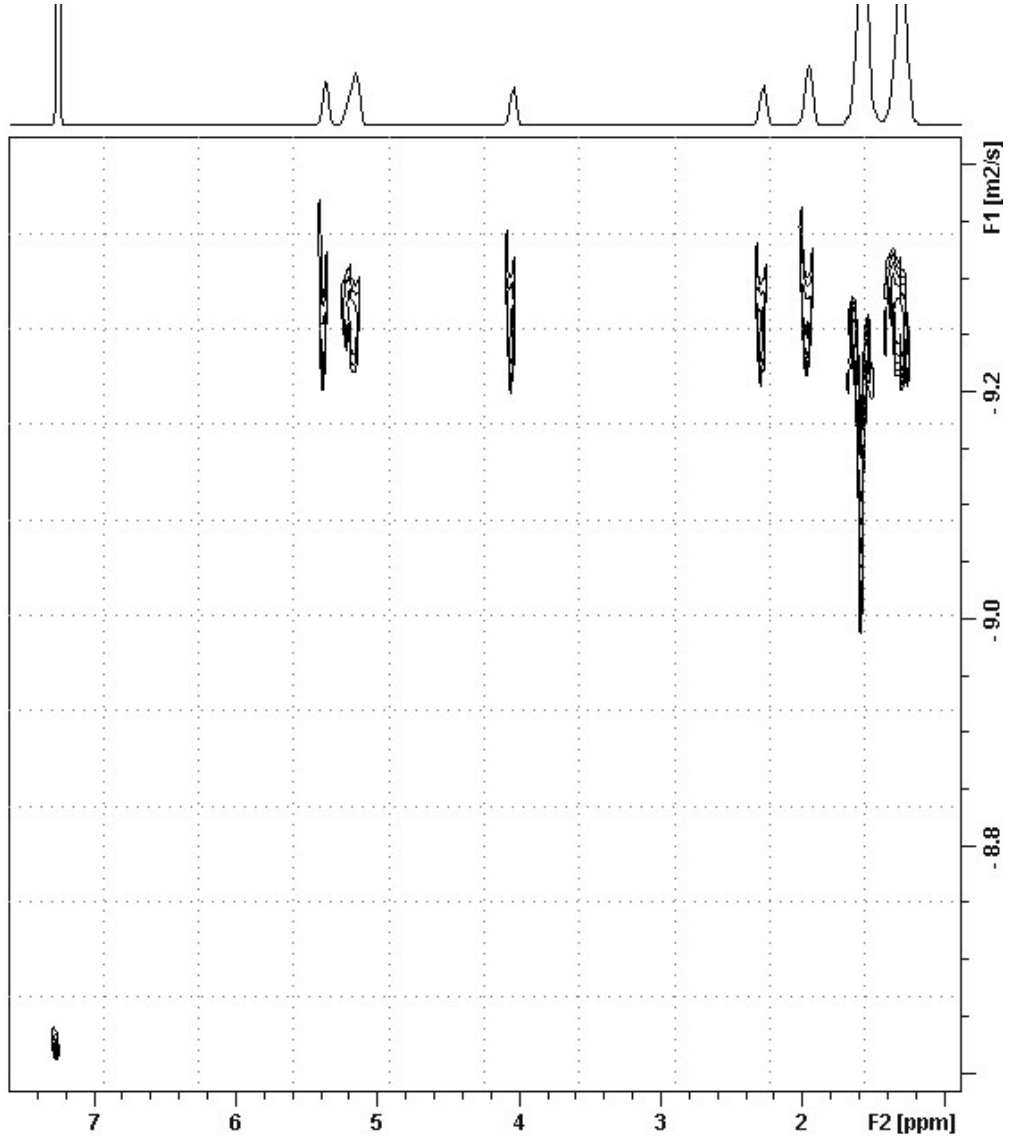


Figure S15. 2D DOSY NMR (400 MHz, $CDCl_3$, RT) of poly(6-ω-hexadecenlactone)-*block*-poly(*rac*-lactide), recorded employing δ = 1000 μs and Δ = 0.5 s. Signals at 7.26 and 1.56 ppm are relative to deuterated solvent residual protic signal ($CHCl_3$) and to adventitious water, respectively.

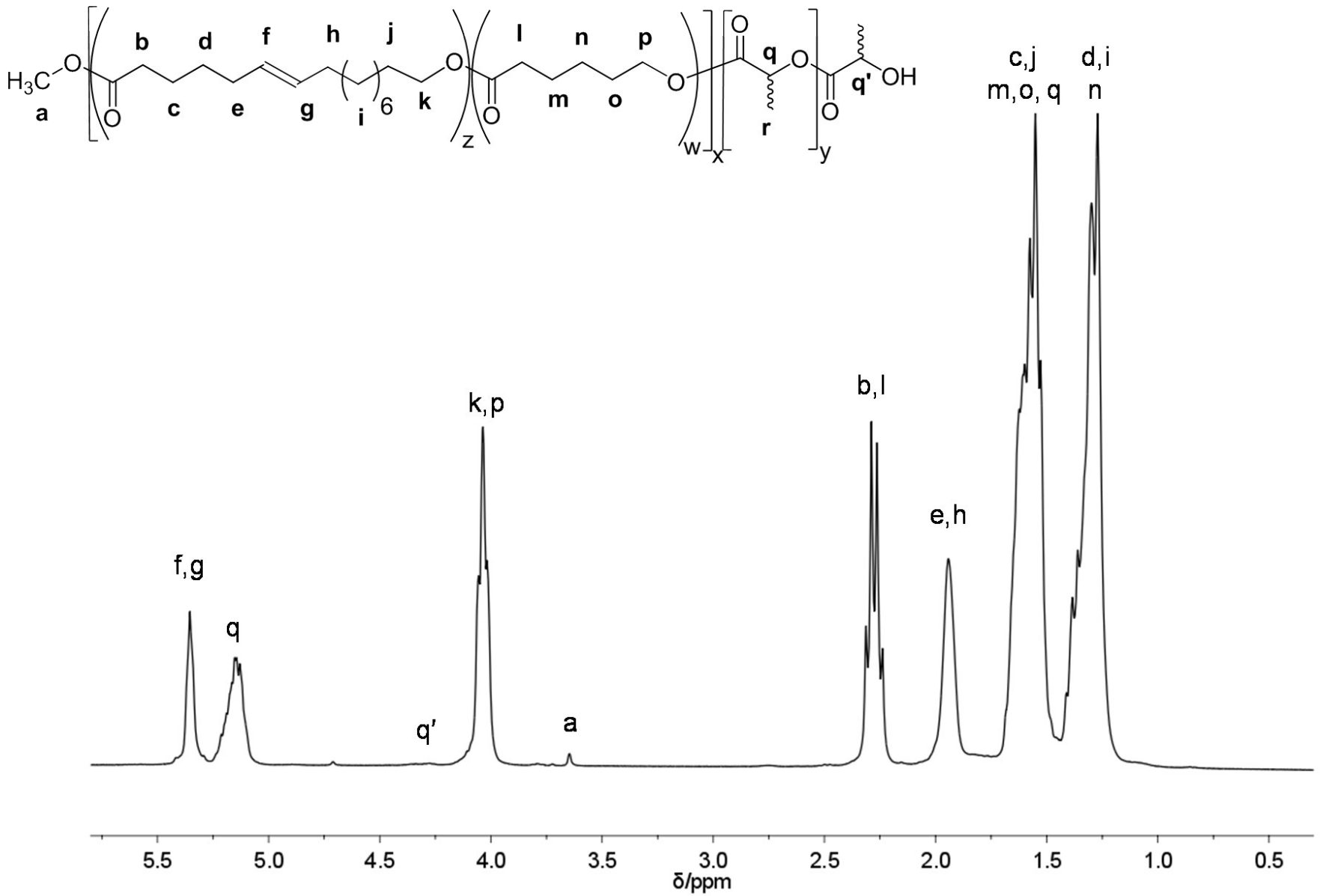


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$, RT) of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide).

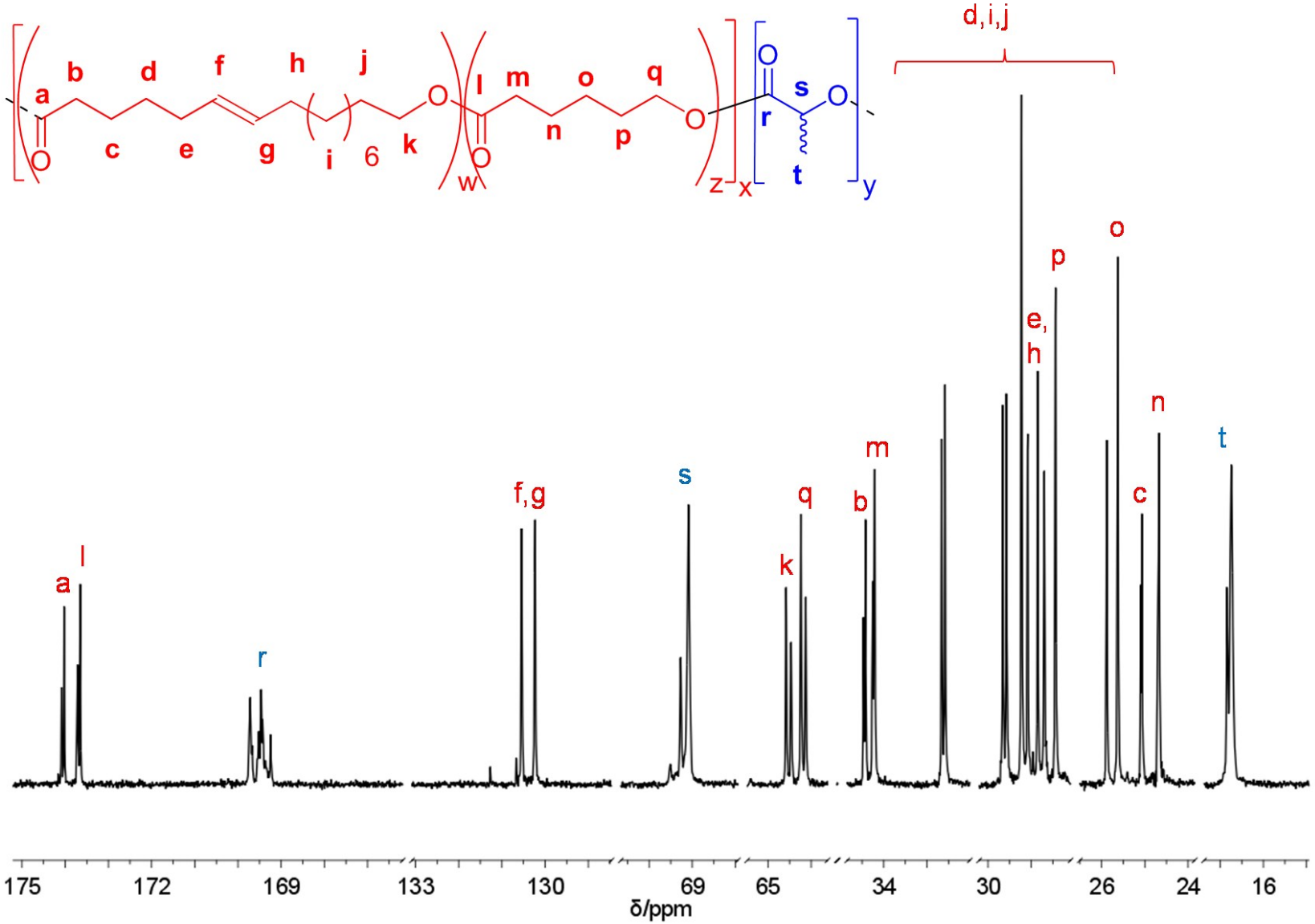


Figure S17. ^{13}C NMR (75 MHz, $CDCl_3$, RT) of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide).

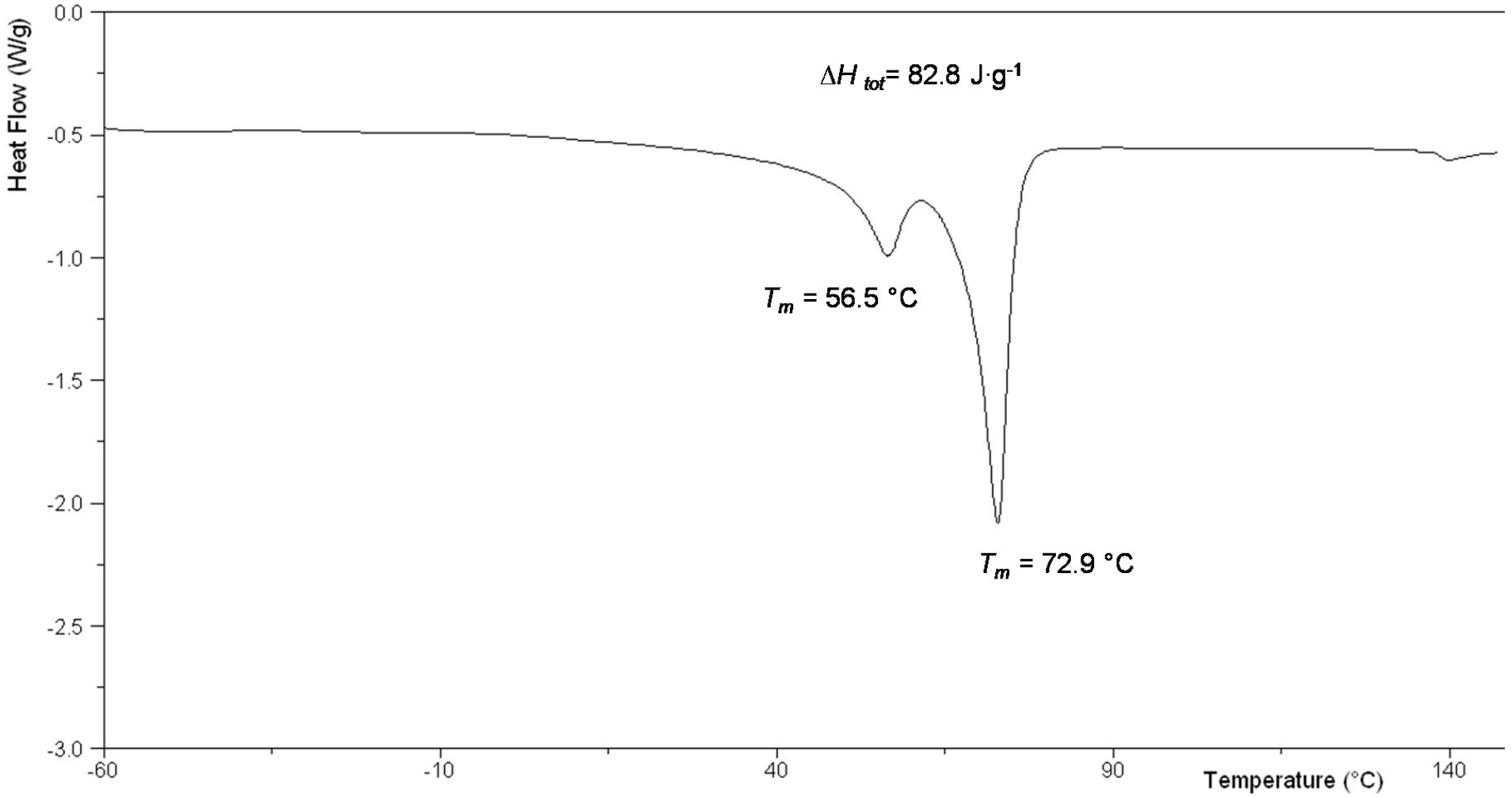


Figure S18. DSC thermogram (II run) of poly(6,7-epoxy-ω-hexadecalactone) (***b***).

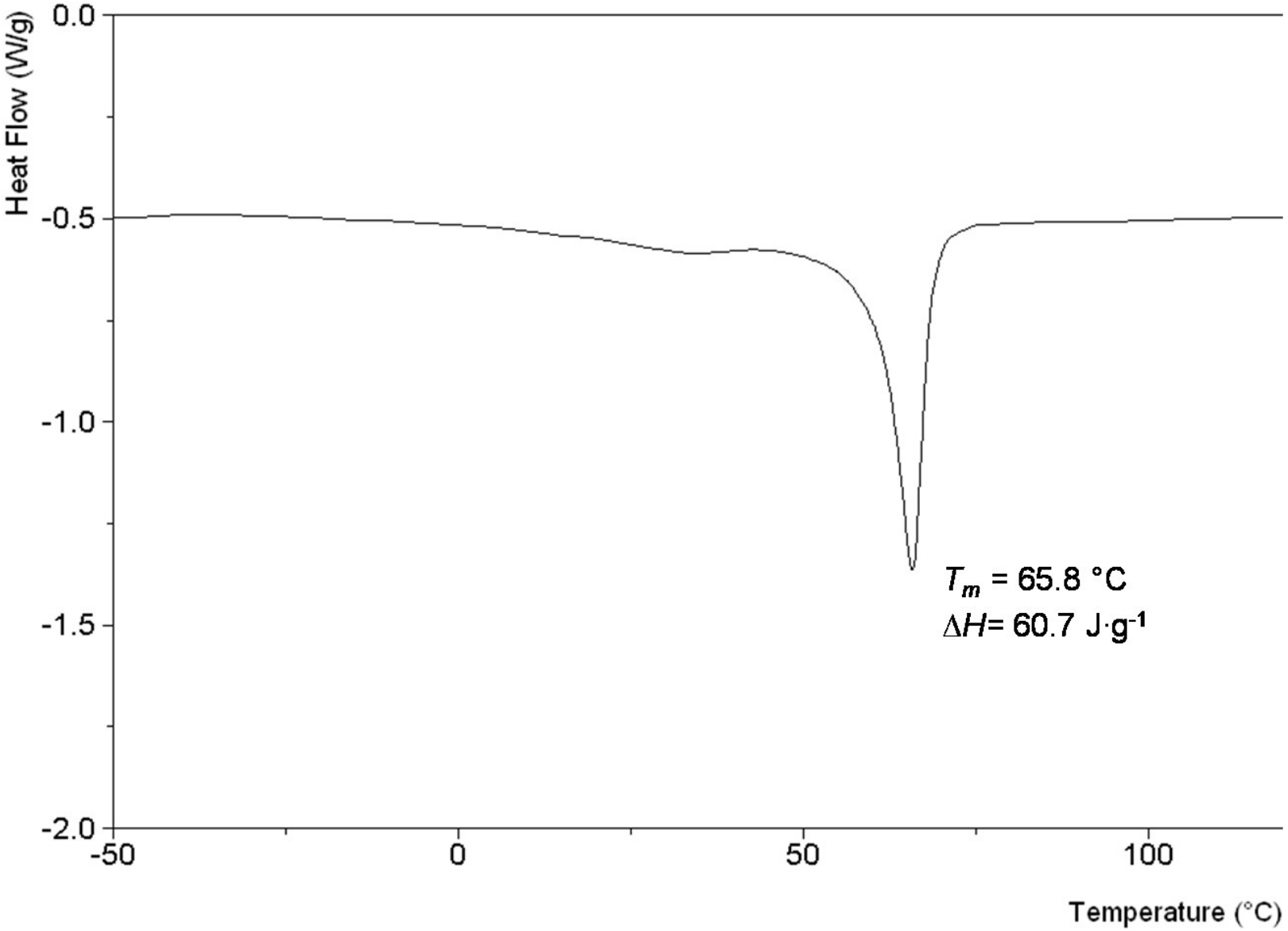


Figure S19. DSC thermogram (II run) of poly(hydroxy-ω-hexadecanlactone) (***c***).

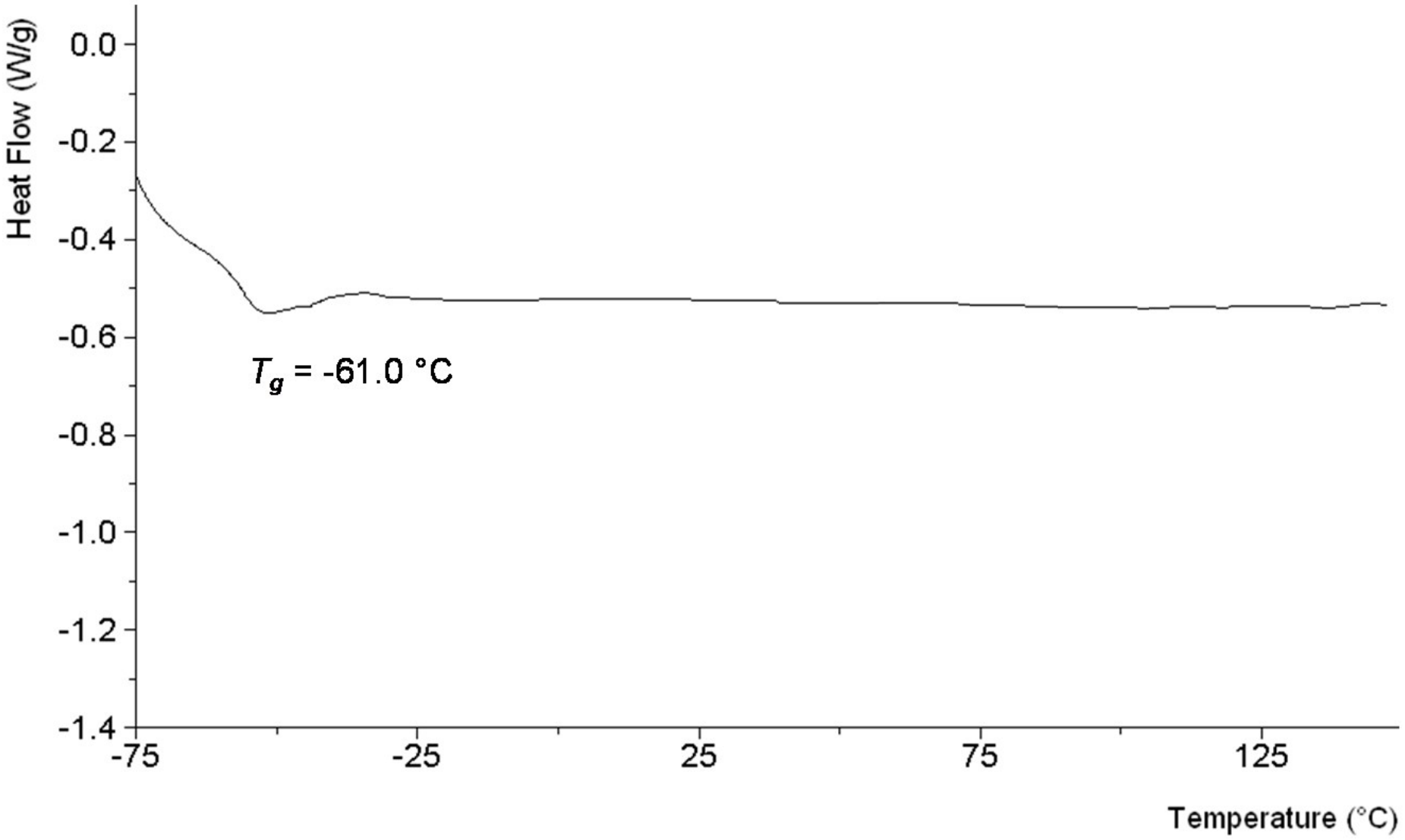


Figure S20. DSC thermogram (II run) of poly(ω-hexadecalactone) with with 6-mercapto-1-hexanol groups groups (***d***).

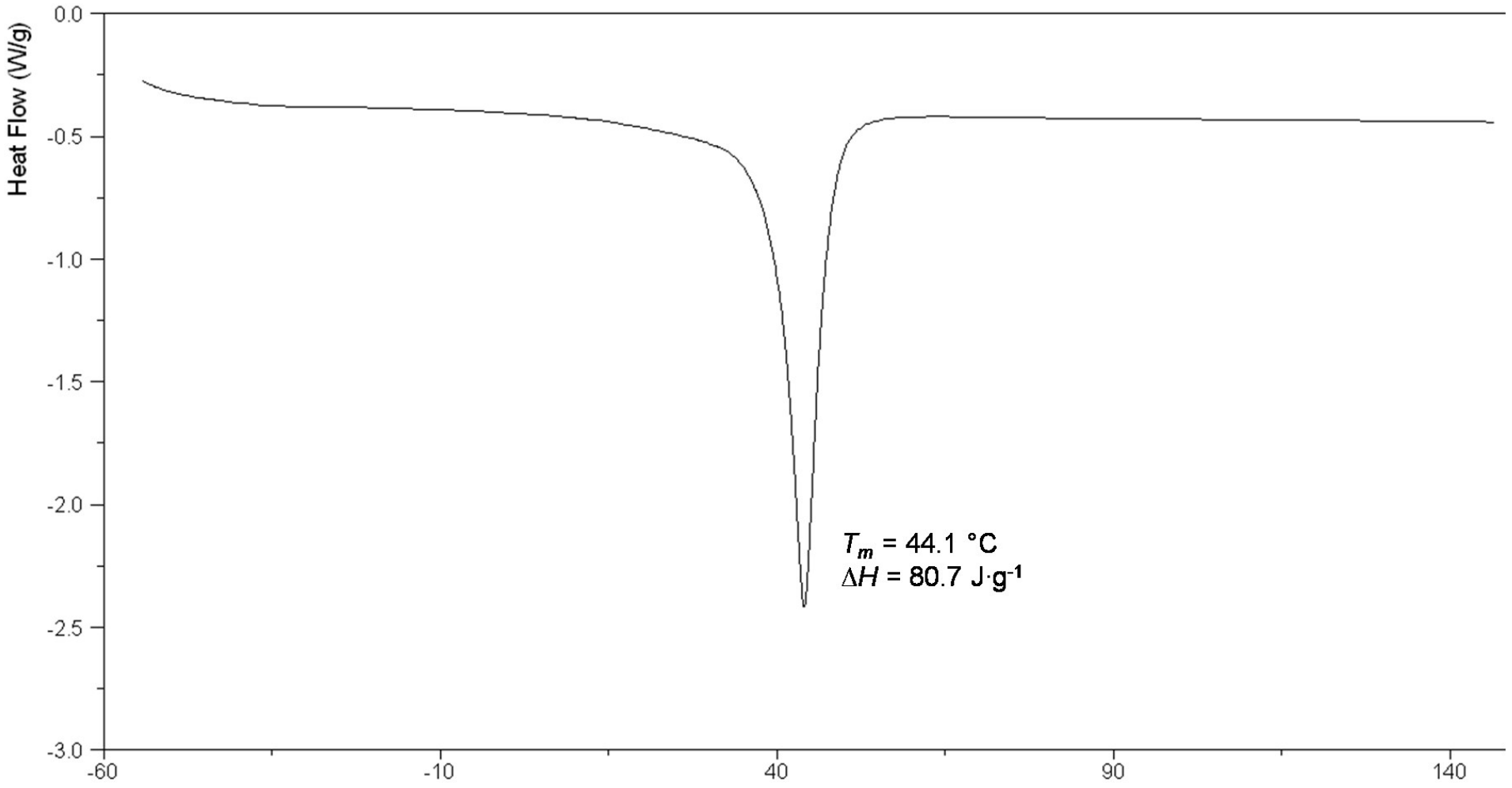


Figure S21. DSC thermogram (II run) of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)].

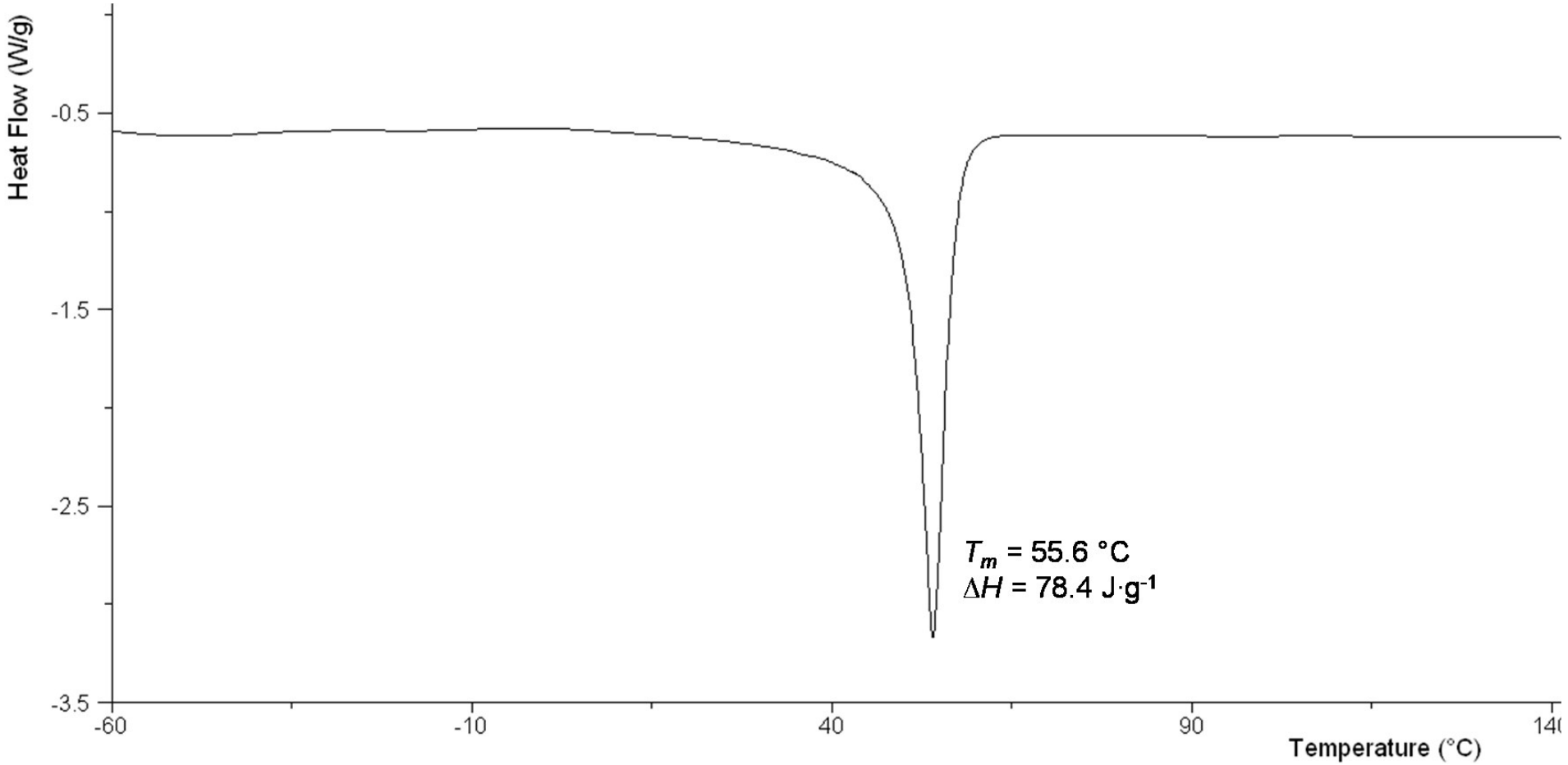


Figure S22. DSC thermogram (II run) of poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone).

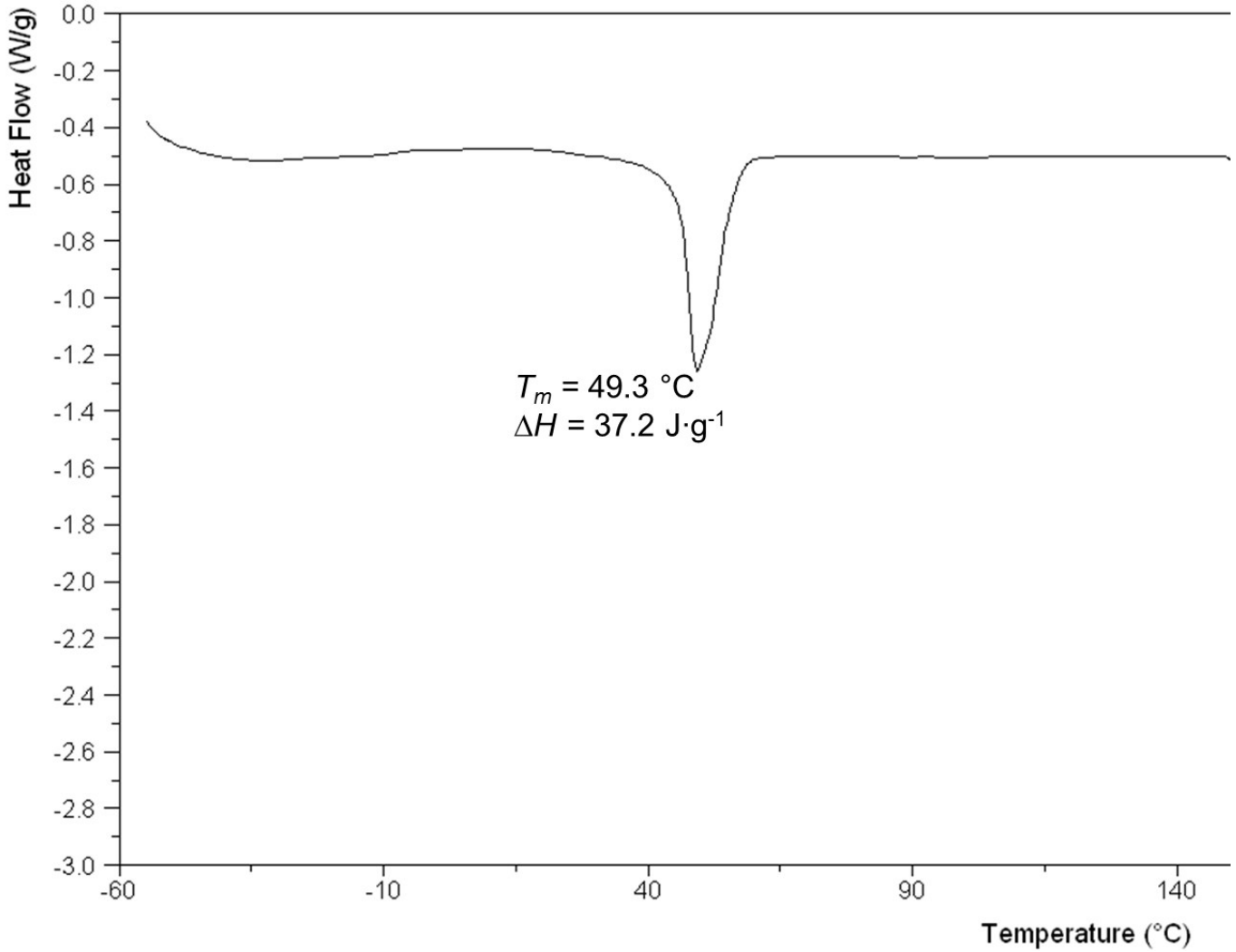


Figure S23. DSC thermogram (II run) of poly(6-ω-hexadecenlactone)-*block*-poly(*rac*-lactide).

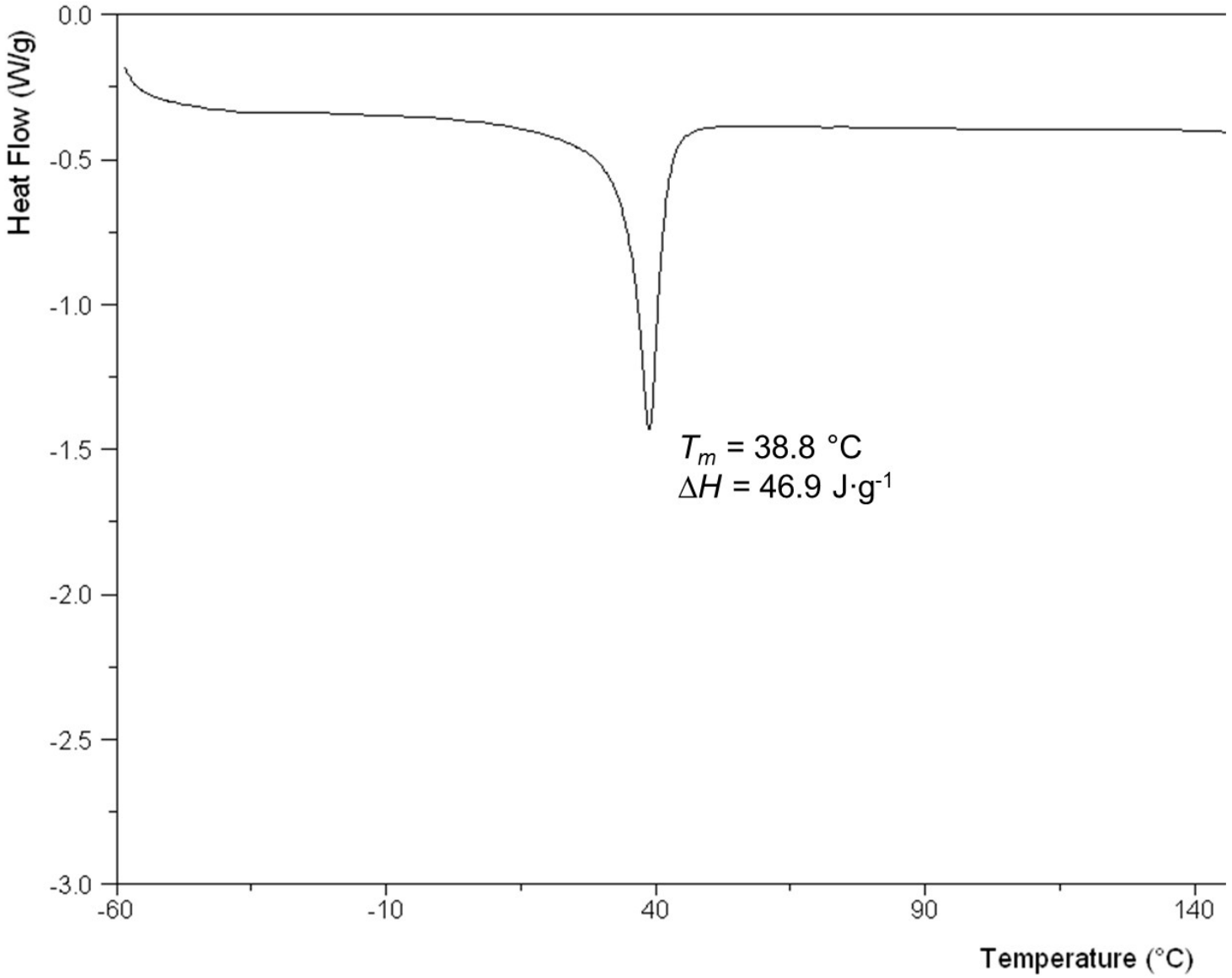


Figure S24. DSC thermogram (II run) of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide).

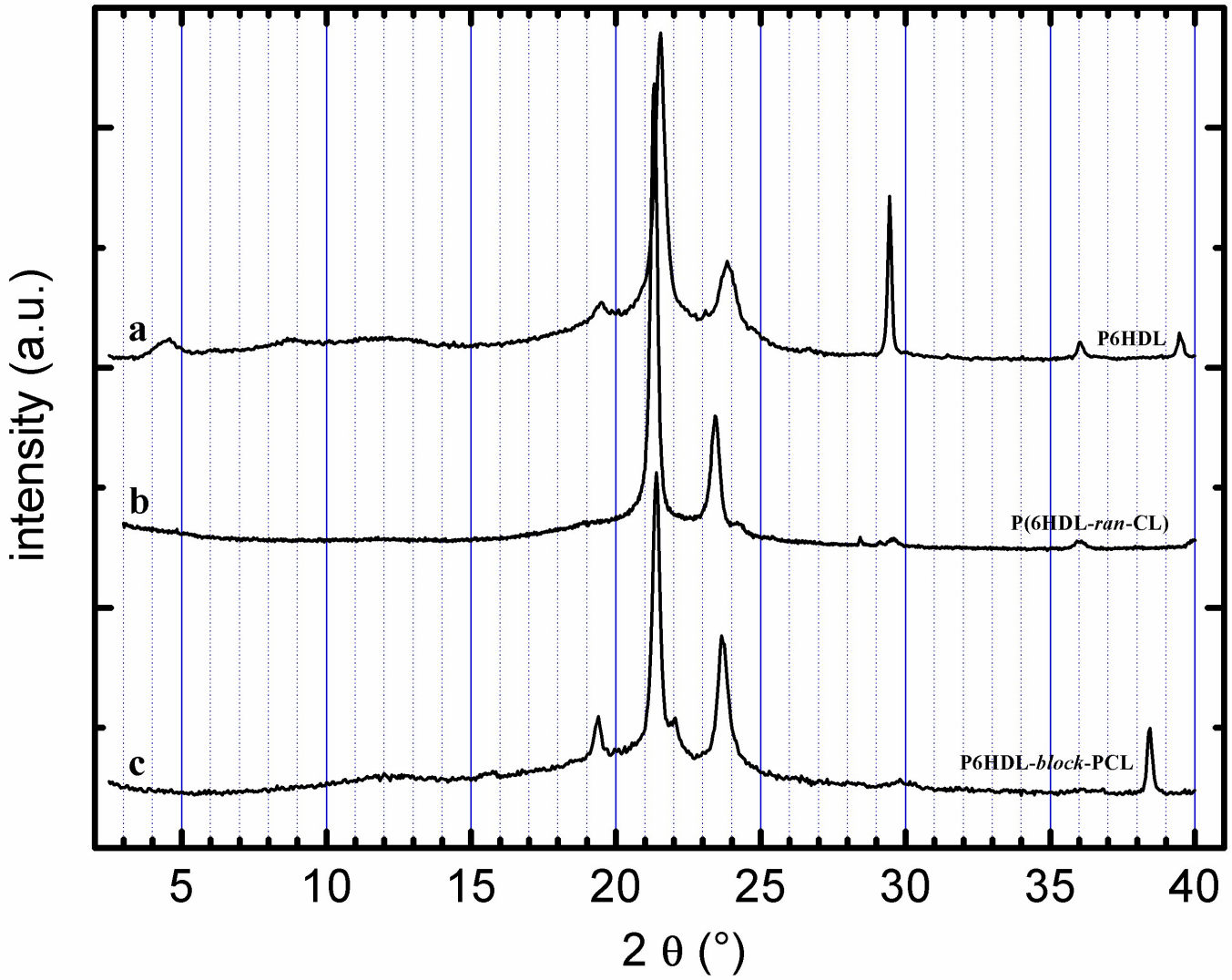
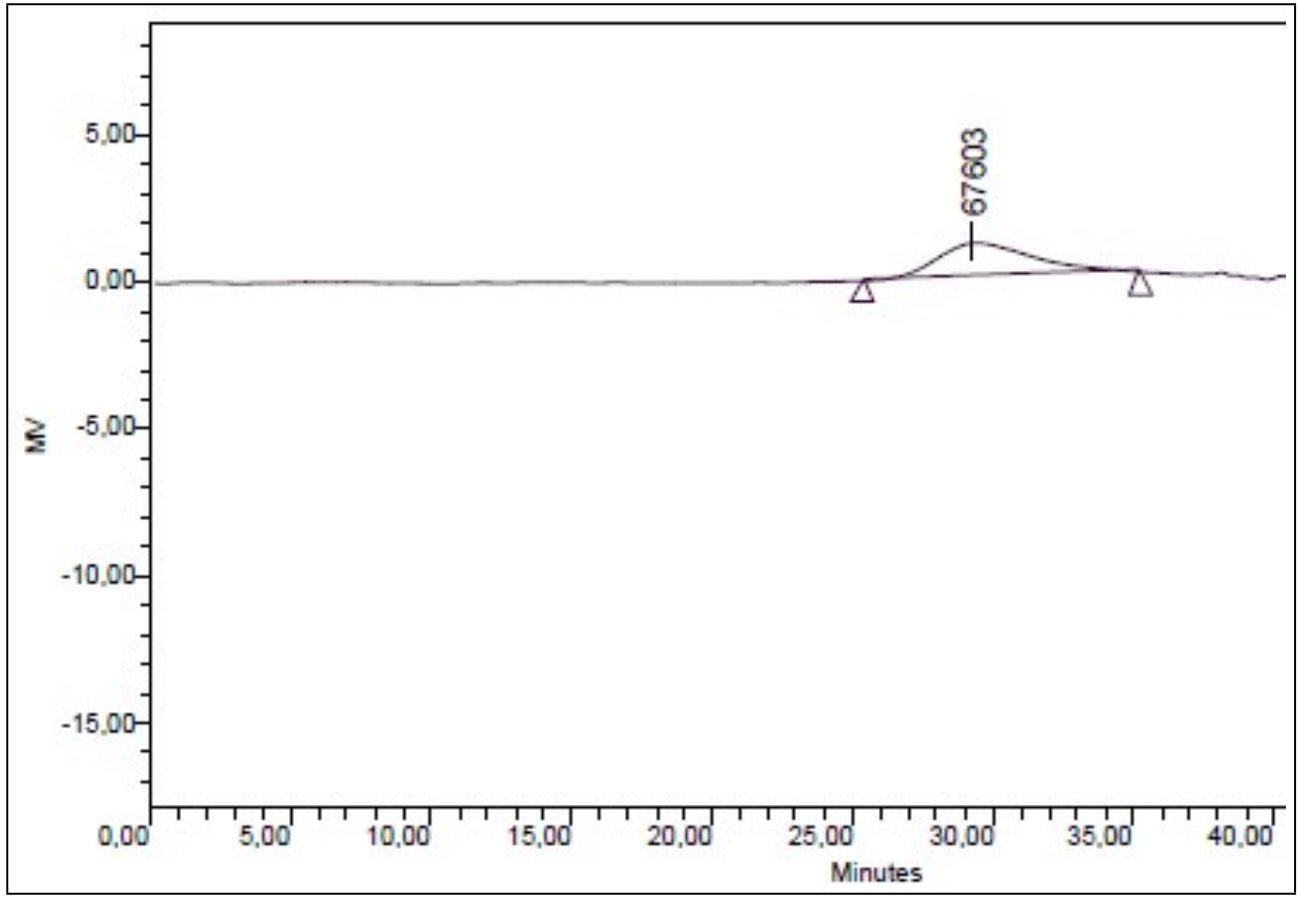
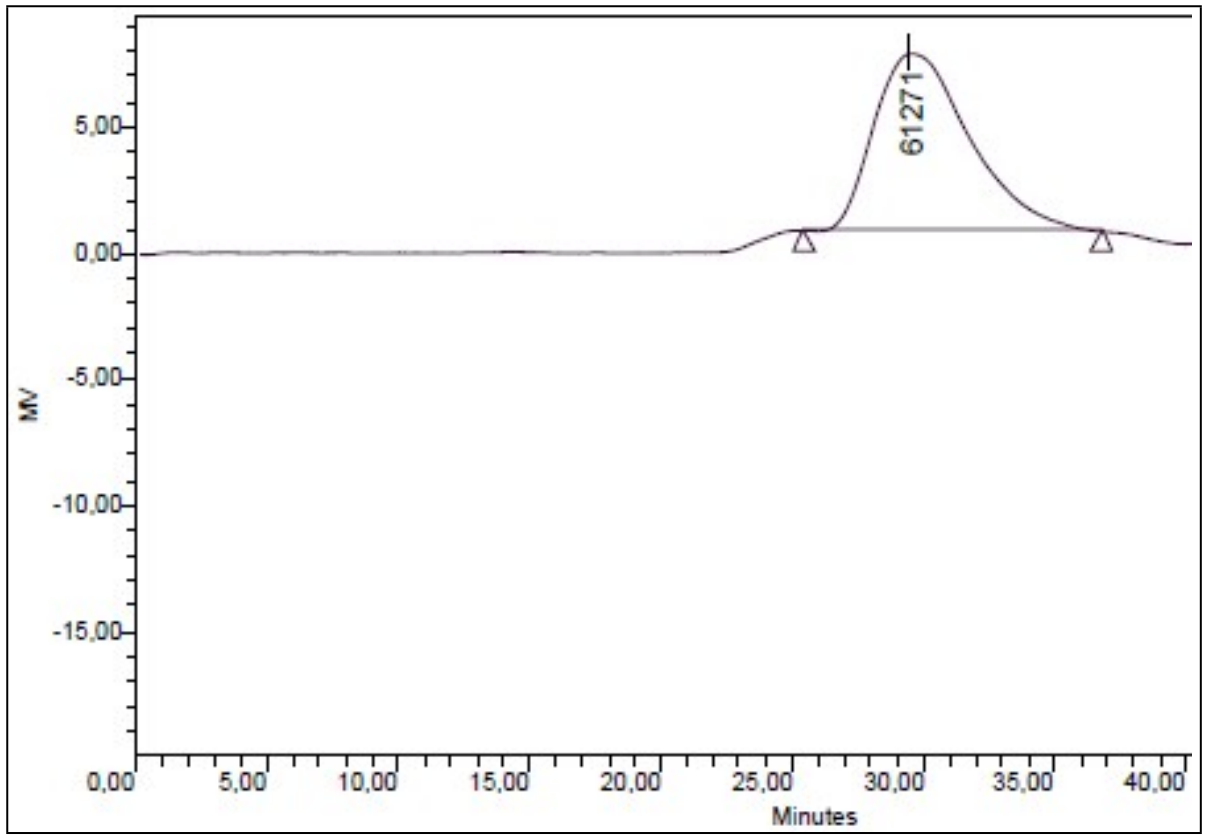


Figure S25. X-ray diffraction pattern of: (a) poly(6-ω-hexadecenlactone); (b) poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]; (c) poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone).



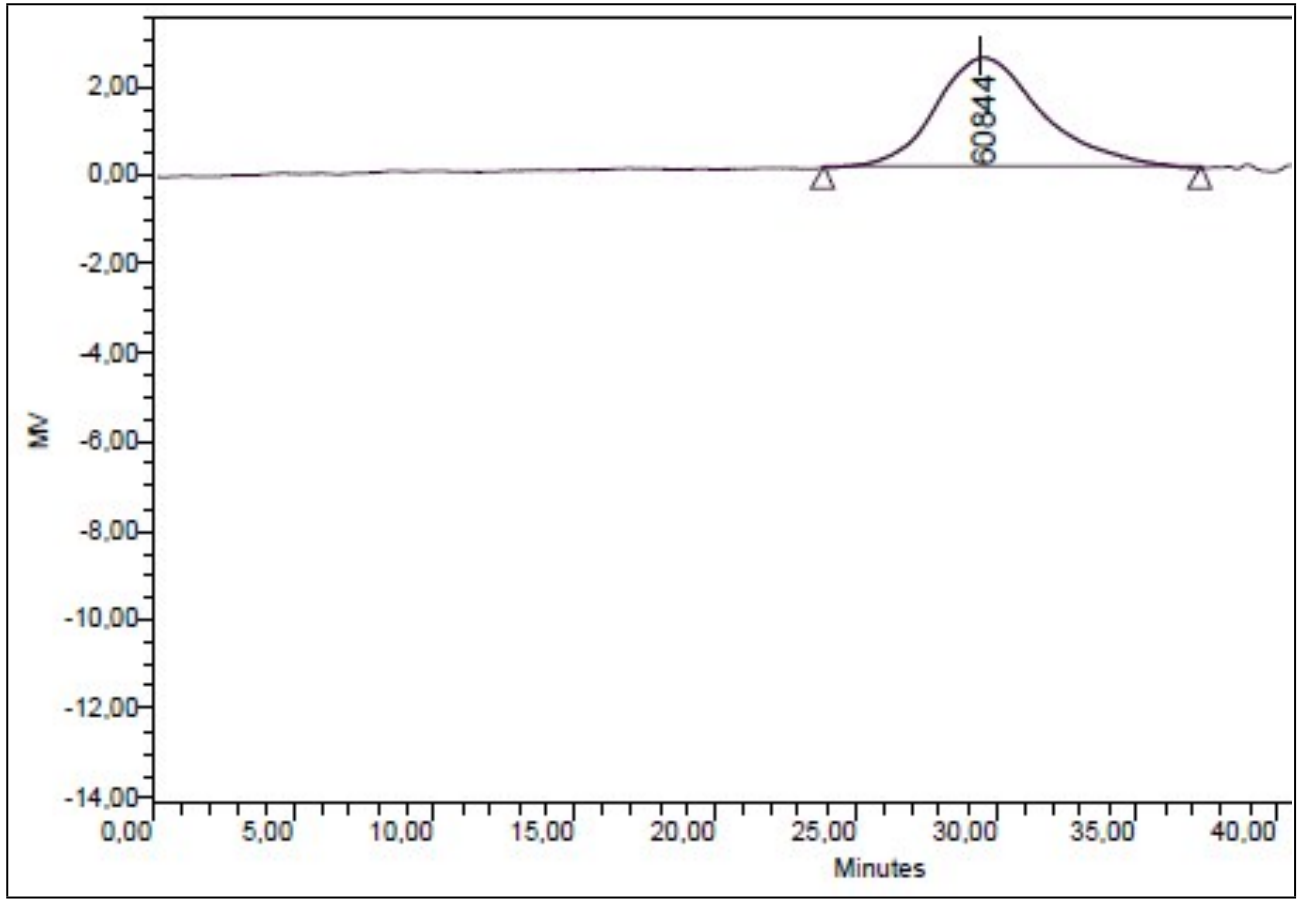
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		40045	64834	67603	94570	125843	1,619029	1,458645	1,941001

Figure S26. GPC chromatogram of poly(6-ω-hexadecenlactone).



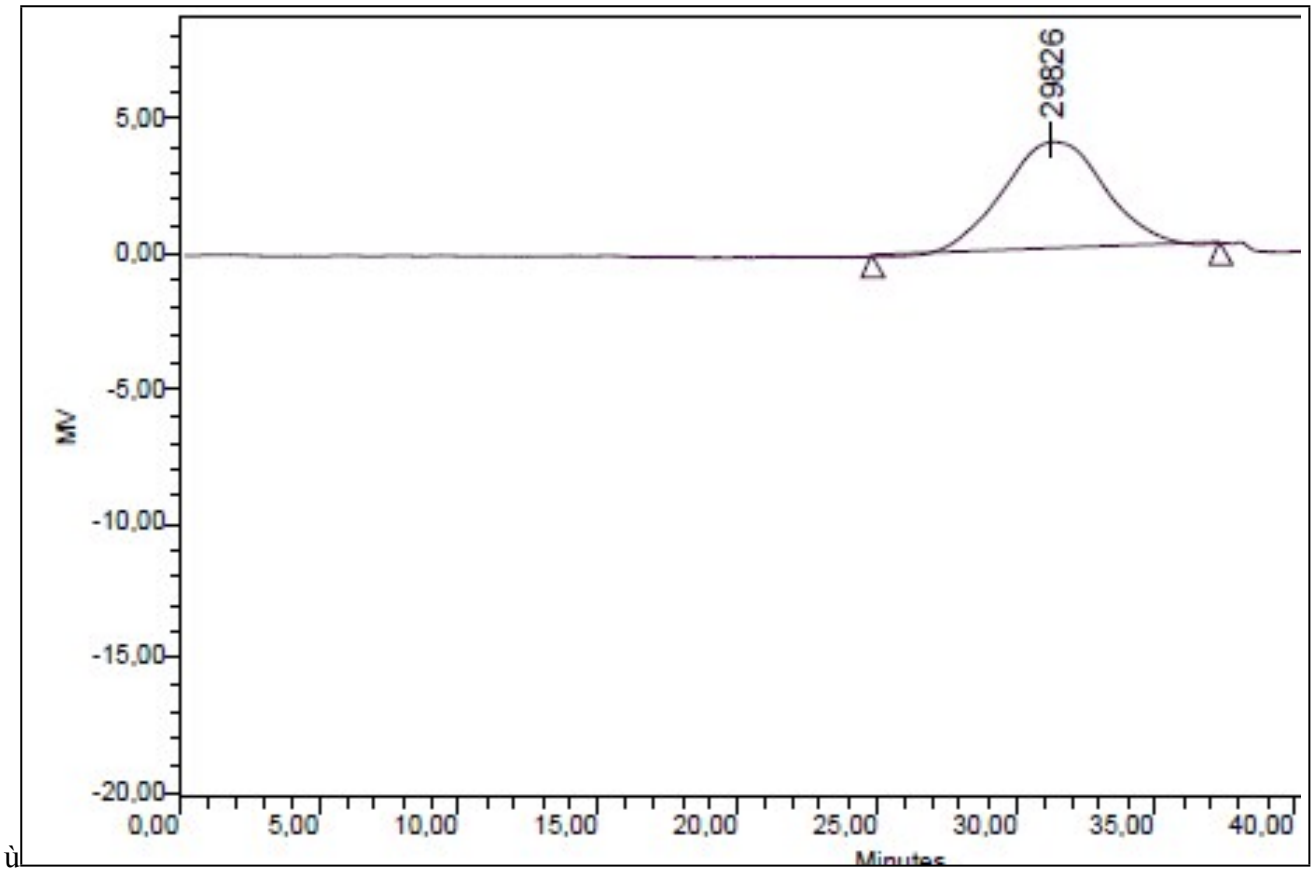
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		36009	58765	61271	83498	106812	1,631946	1,420883	1,817619

Figure S27. GPC chromatogram of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)].



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		37521	72252	60844	132028	234102	1,925649	1,827312	3,240052

Figure S28. GPC chromatogram of poly(6-ω-hexadecenlactone)-*block*-poly(ε-caprolactone).



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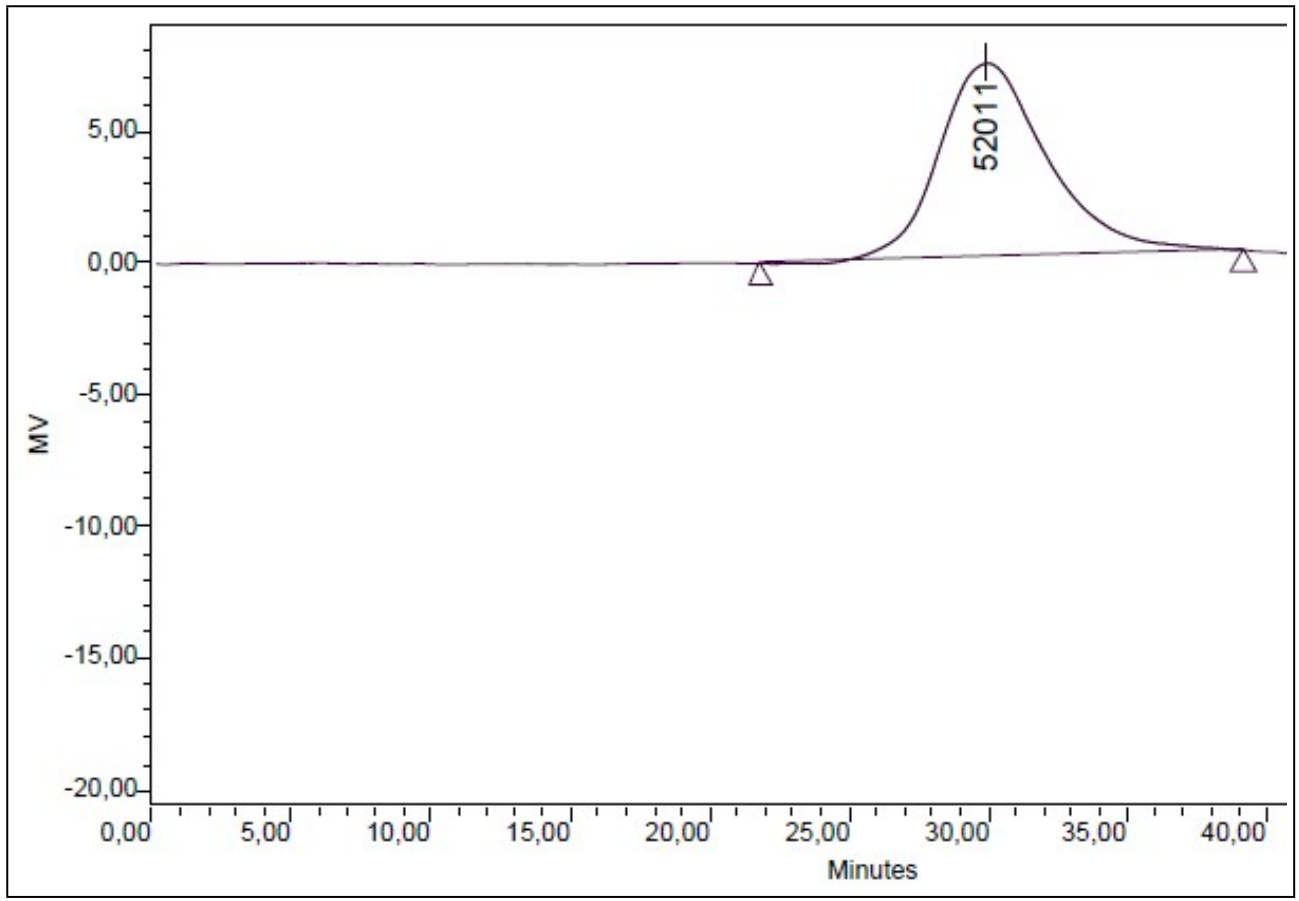
	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		24288	36916	29826	55859	79566	1,519940	1,513131	2,155316

Figure S29. GPC chromatogram of poly(6-ω-hexadecenlactone)-*block*-(*rac*-lactide).



	Distribution Name	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity	Mz/Mw	Mz+1/Mw
1		29113	58949	52011	103505	171264	2,024844	1,755853	2,905298

Figure S30. GPC chromatogram of poly[(6-ω-hexadecenlactone)-*ran*-(ε-caprolactone)]-*block*-poly(*rac*-lactide).

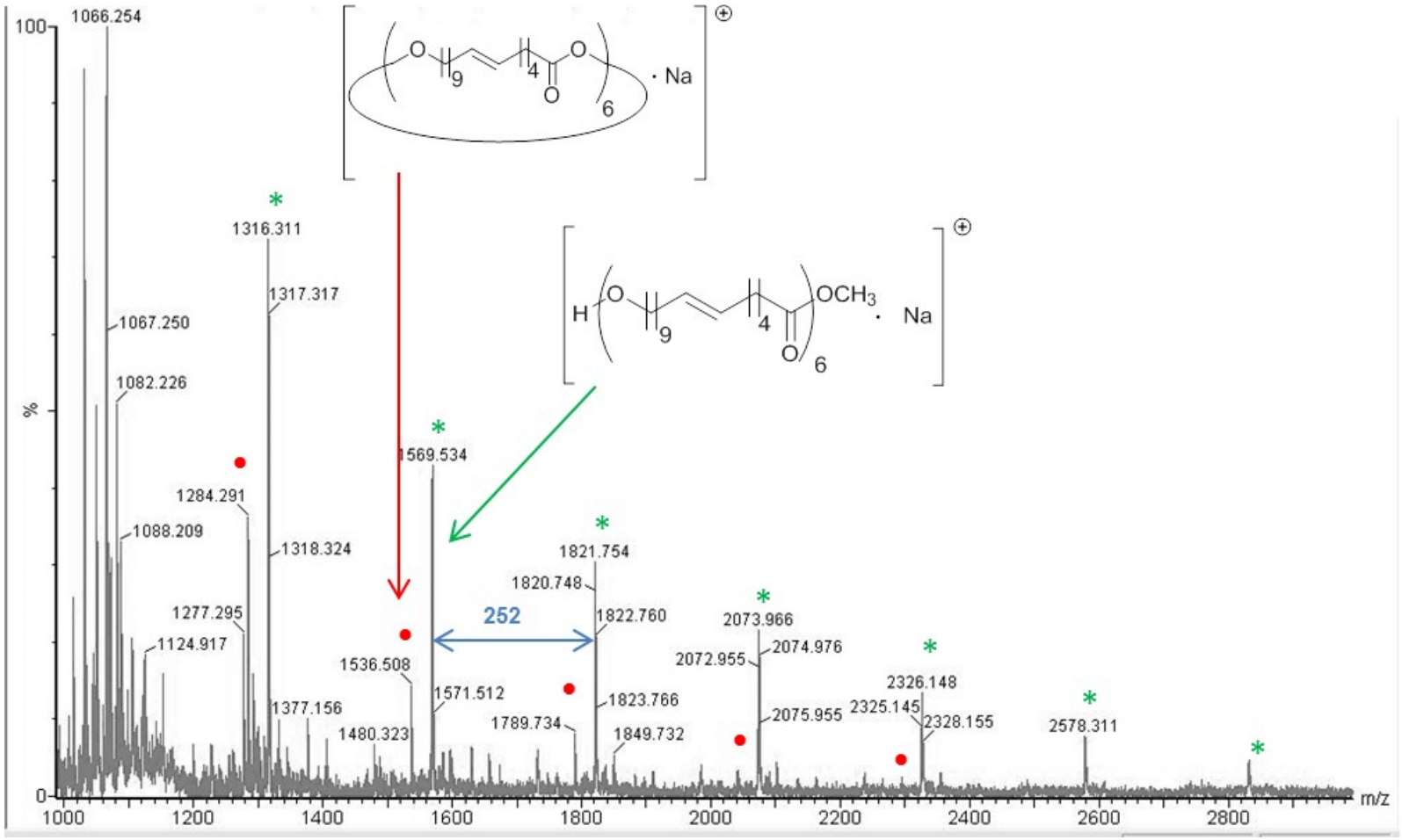


Figure S31. MALDI-ToF-MS of crude poly(6-ω-hexadecenlactone) (run 12, Table S1). Two sets of peaks corresponding to the linear and cyclic polymer species (doped with Na^+) are marked with asterisk (*) and dagger (•) symbols, respectively.