

Supporting information

Block Copolymers of Macro/Small Lactones by a “Catalyst-Switch” Organocatalytic Strategy. Thermal Properties and Phase Behaviour

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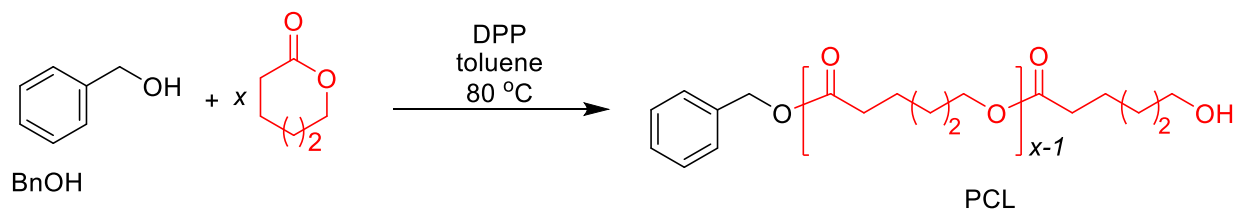
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Scheme S1. ROP of CL catalyzed by DPP ($[\text{CL}]_0 = 1 \text{ M}$, $[\text{OH}]_0:[\text{DPP}]_0 = 1:2$, $80 \text{ } ^\circ\text{C}$).

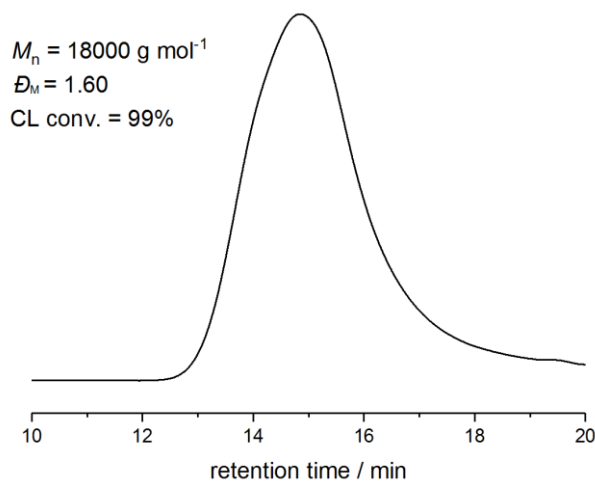


Figure S1. GPC trace of PCL prepared by ROP with DPP as catalyst (THF, $35 \text{ } ^\circ\text{C}$, PS standards).

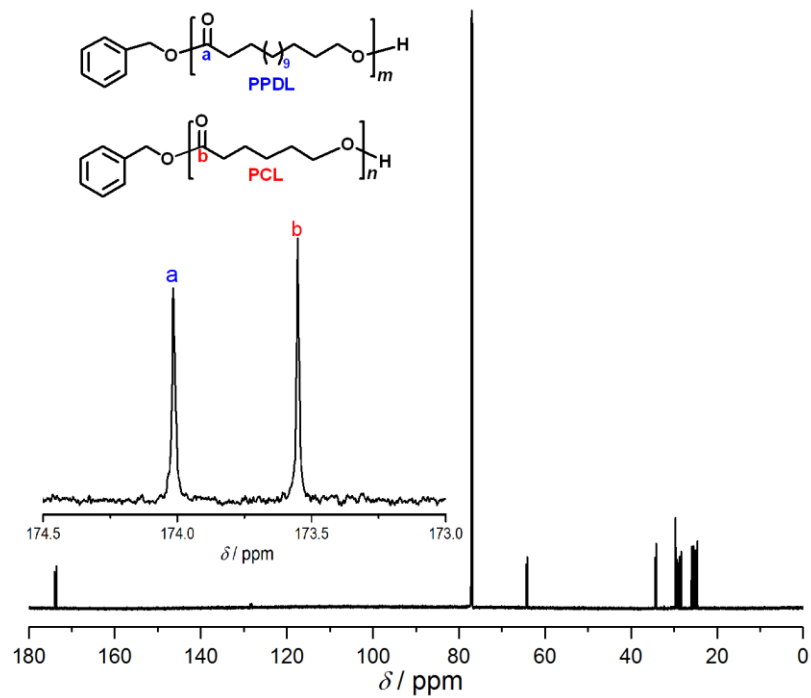


Figure S2. 239 MHz ^{13}C NMR spectrum of PPDL:PCL mixture in CDCl_3 at room temperature (rt).

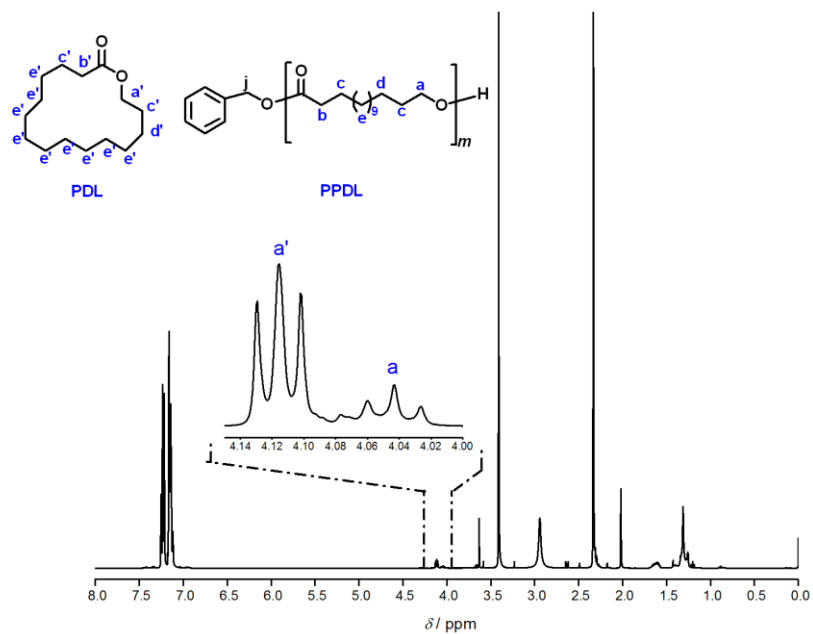


Figure S3. Determination of PDL conversion to PPDL from ^1H NMR spectrum of reaction mixture after 10 min by 500 MHz spectrometer (CDCl_3 , rt).

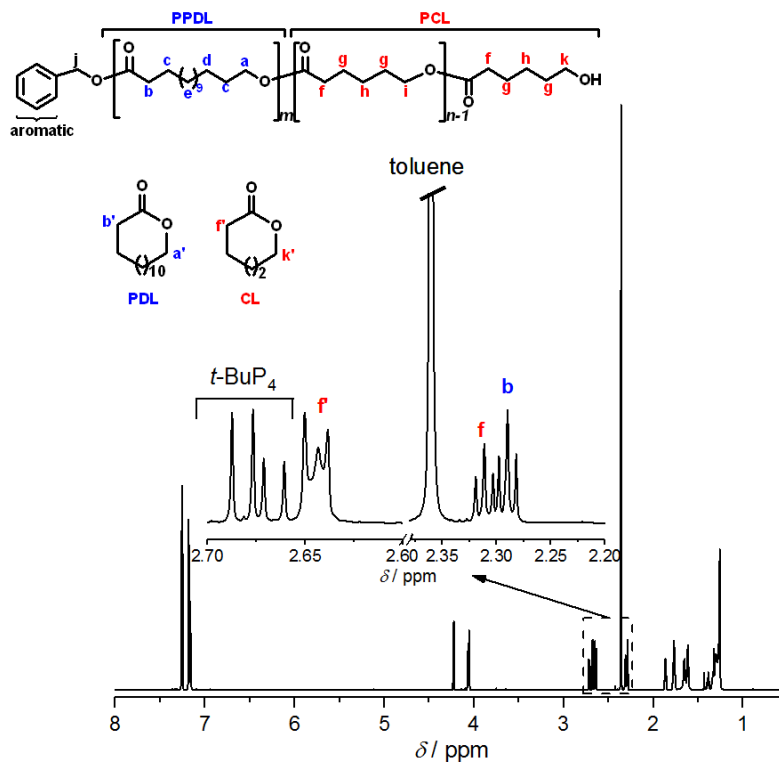


Figure S4. Determination of PCL conversion during the catalyst-switch synthesis of PPDL-*b*-PCL from ^1H NMR spectrum of reaction mixture after 6 h by 950 MHz (CDCl_3 , rt).

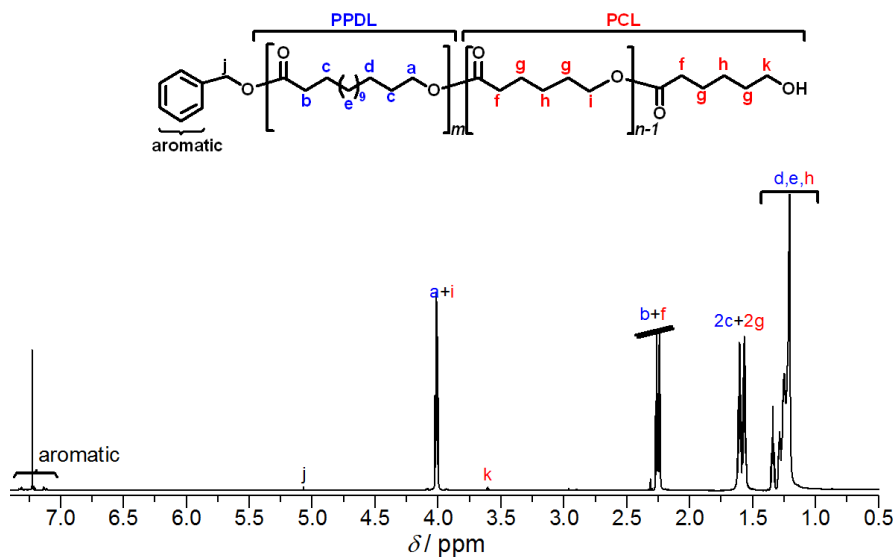


Figure S5. 950 MHz ^1H NMR spectrum of PPDL-*b*-PCL (entry 1, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt).

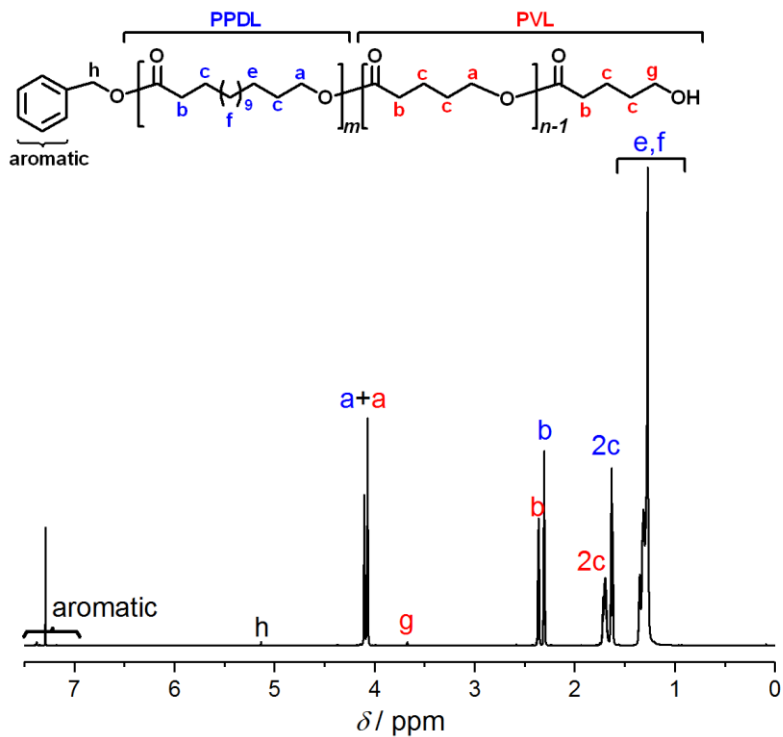


Figure S6. 950 MHz ^1H NMR spectrum of PPDL-*b*-PVL (entry 2, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt).

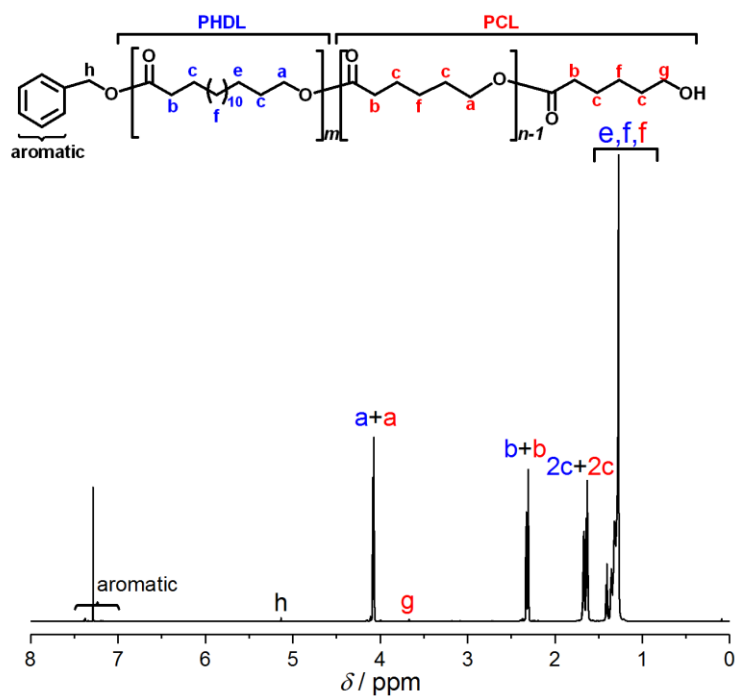


Figure S7. 950 MHz ^1H NMR spectrum of PHDL-*b*-PCL (entry 3, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt).

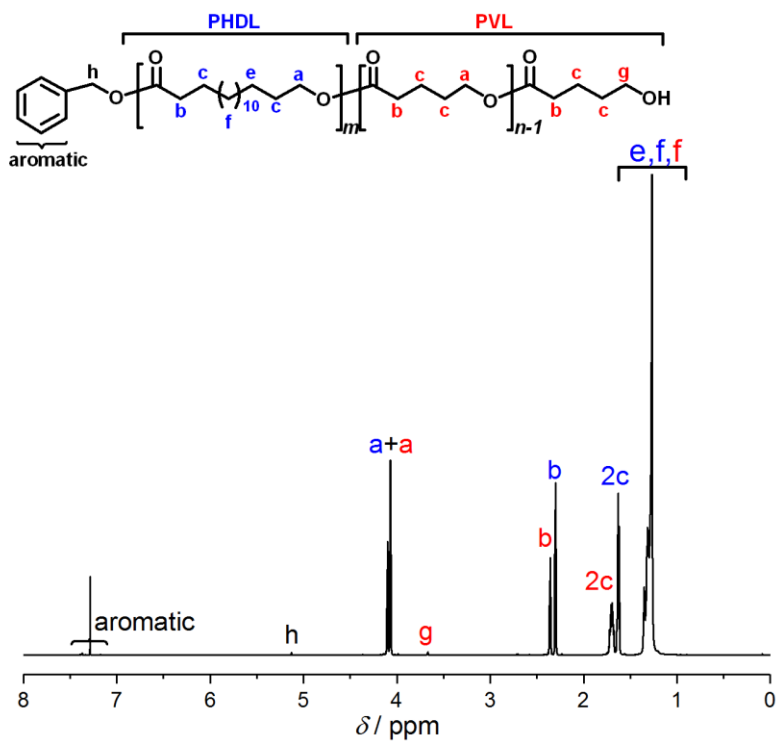


Figure S8. 950 MHz ^1H NMR spectrum of PHDL-*b*-PVL (entry 4, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt).

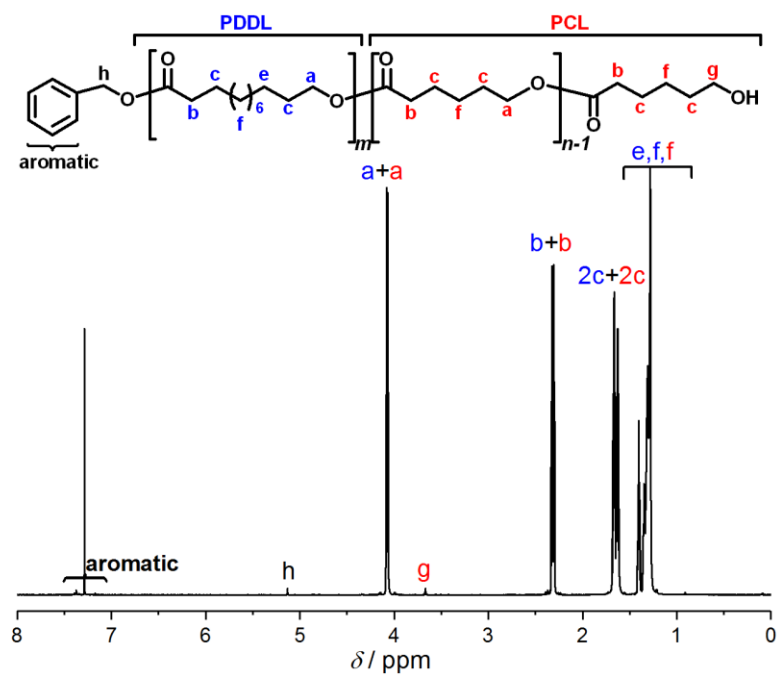


Figure S9. 950 MHz ^1H NMR spectrum of PDDL-*b*-PCL (entry 5, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt).

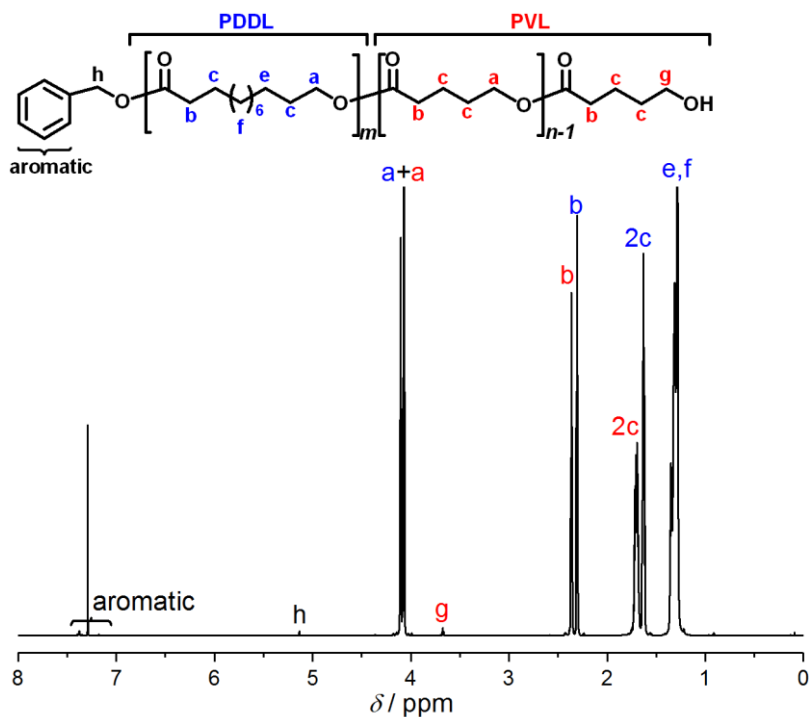


Figure S10 950 MHz ¹H NMR spectrum of PDDL-*b*-PVL (entry 6, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt).

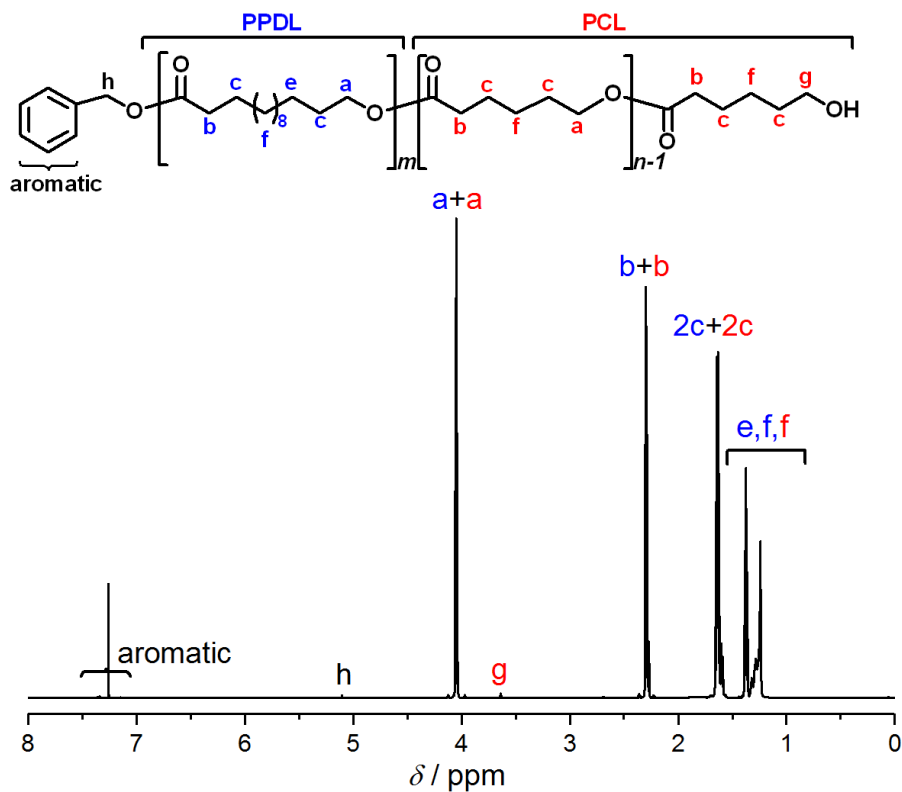


Figure S11. 950 MHz ¹H NMR spectrum of PPDL₅₀-*b*-PCL₄₀₀ (entry 7, Tale 2) prepared by catalyst-switch strategy (CDCl₃, rt)

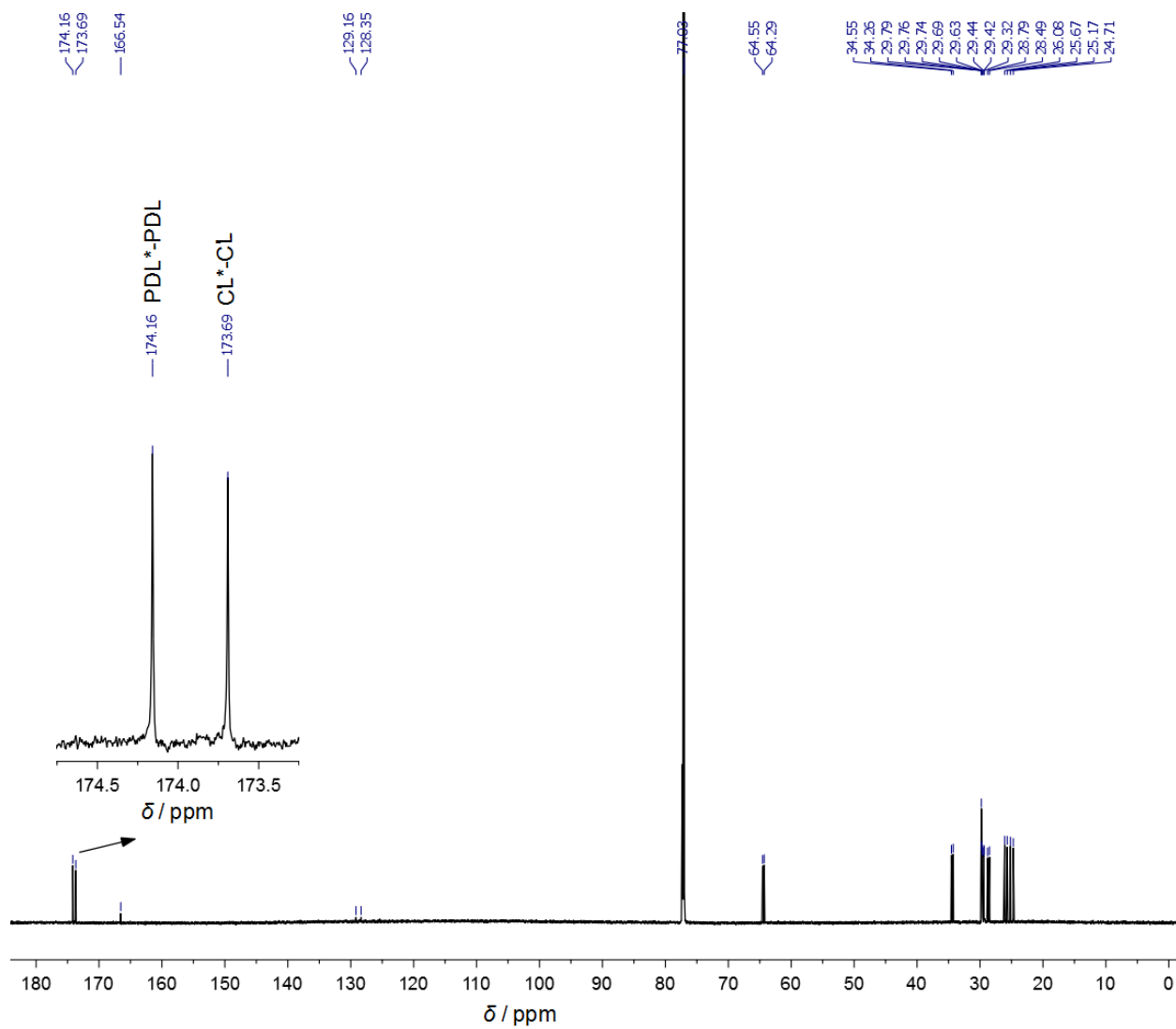


Figure S12. 239 MHz ^{13}C NMR spectrum of PPDL-*b*-PCL (entry 1, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt).

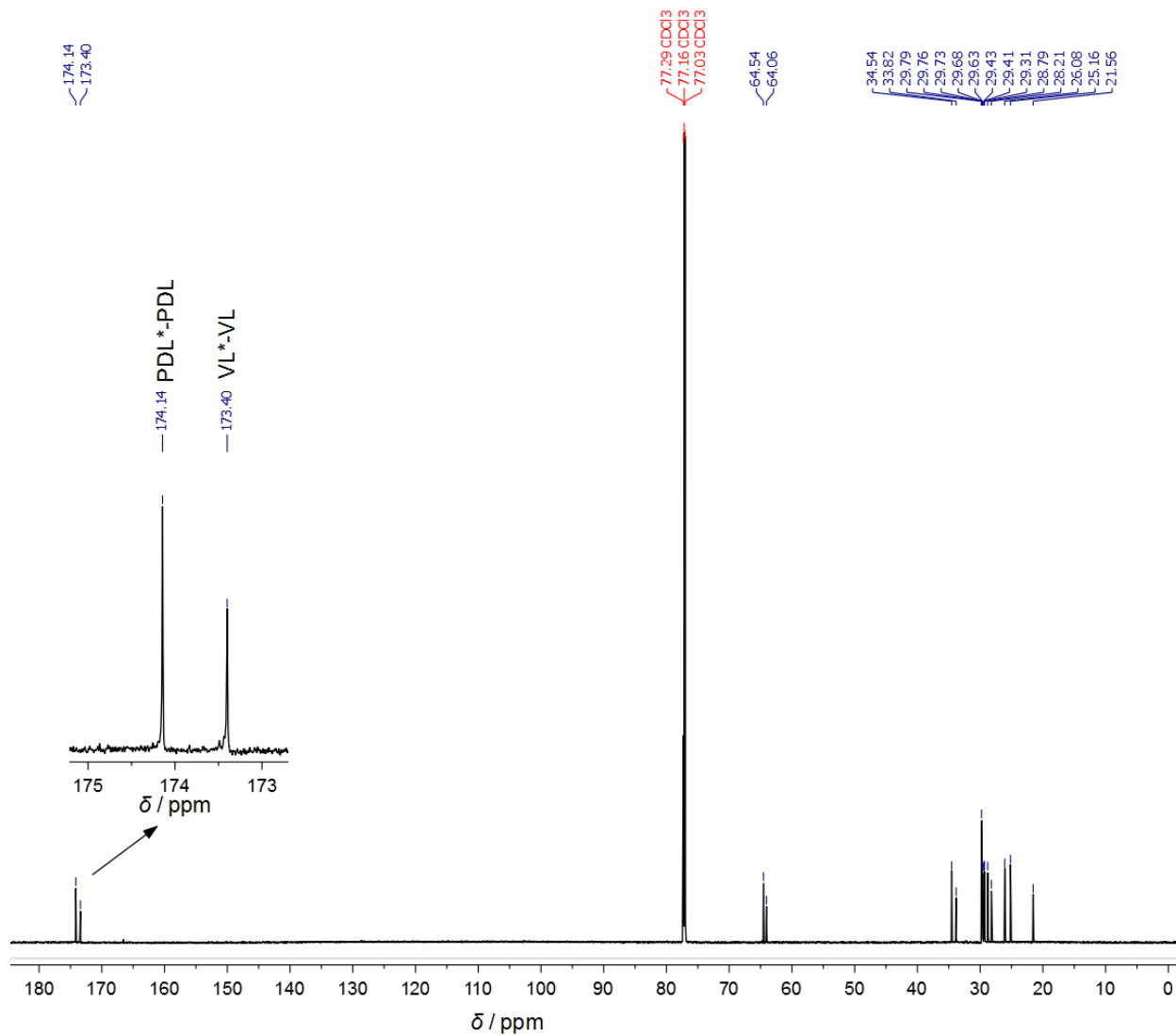


Figure S13. 239 MHz ¹³C NMR spectrum of PPDL-*b*-PVL (entry 2, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt).

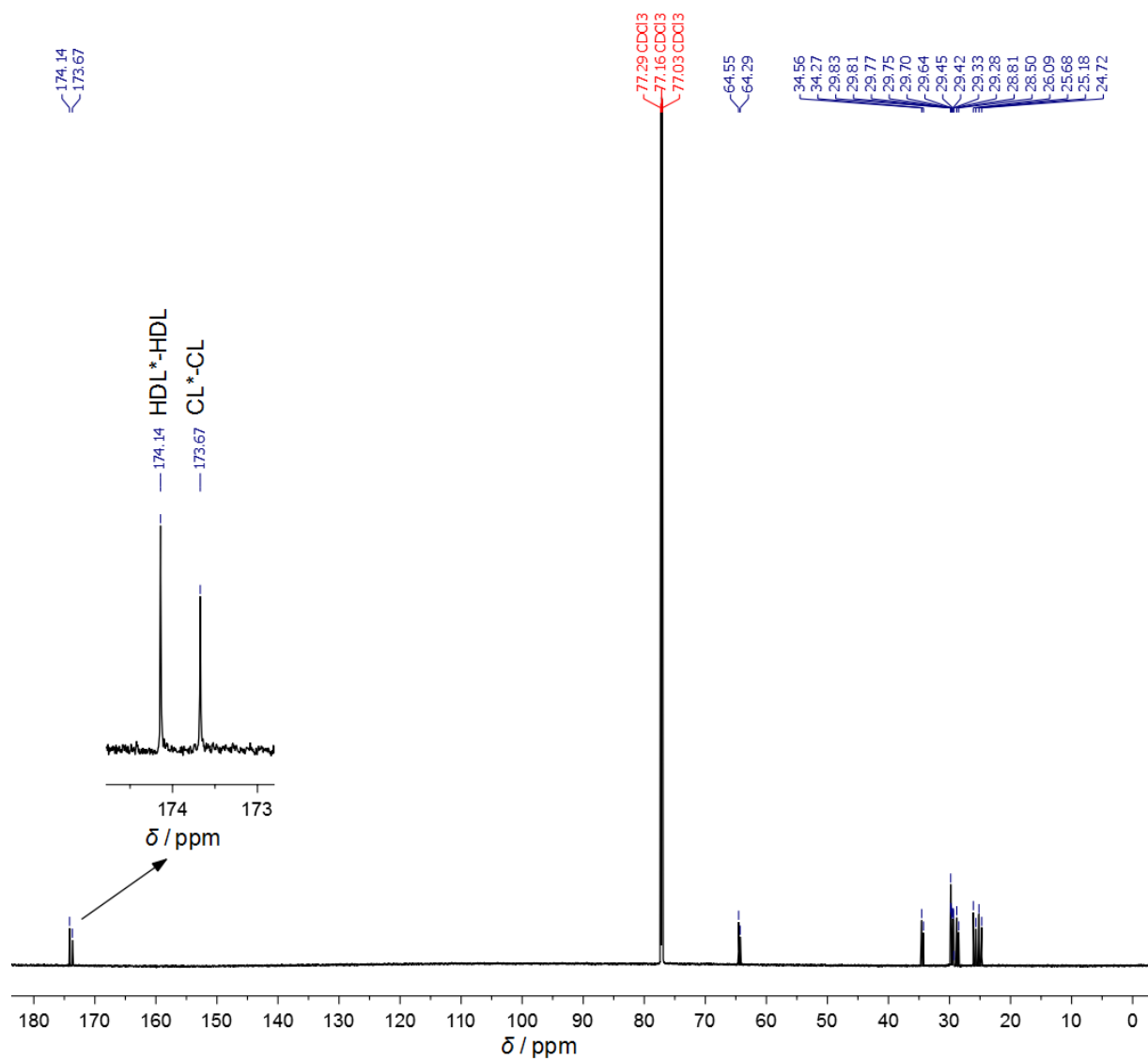


Figure S14. 239 MHz ¹³C NMR spectrum of PHDL-*b*-PCL (entry 3, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt)

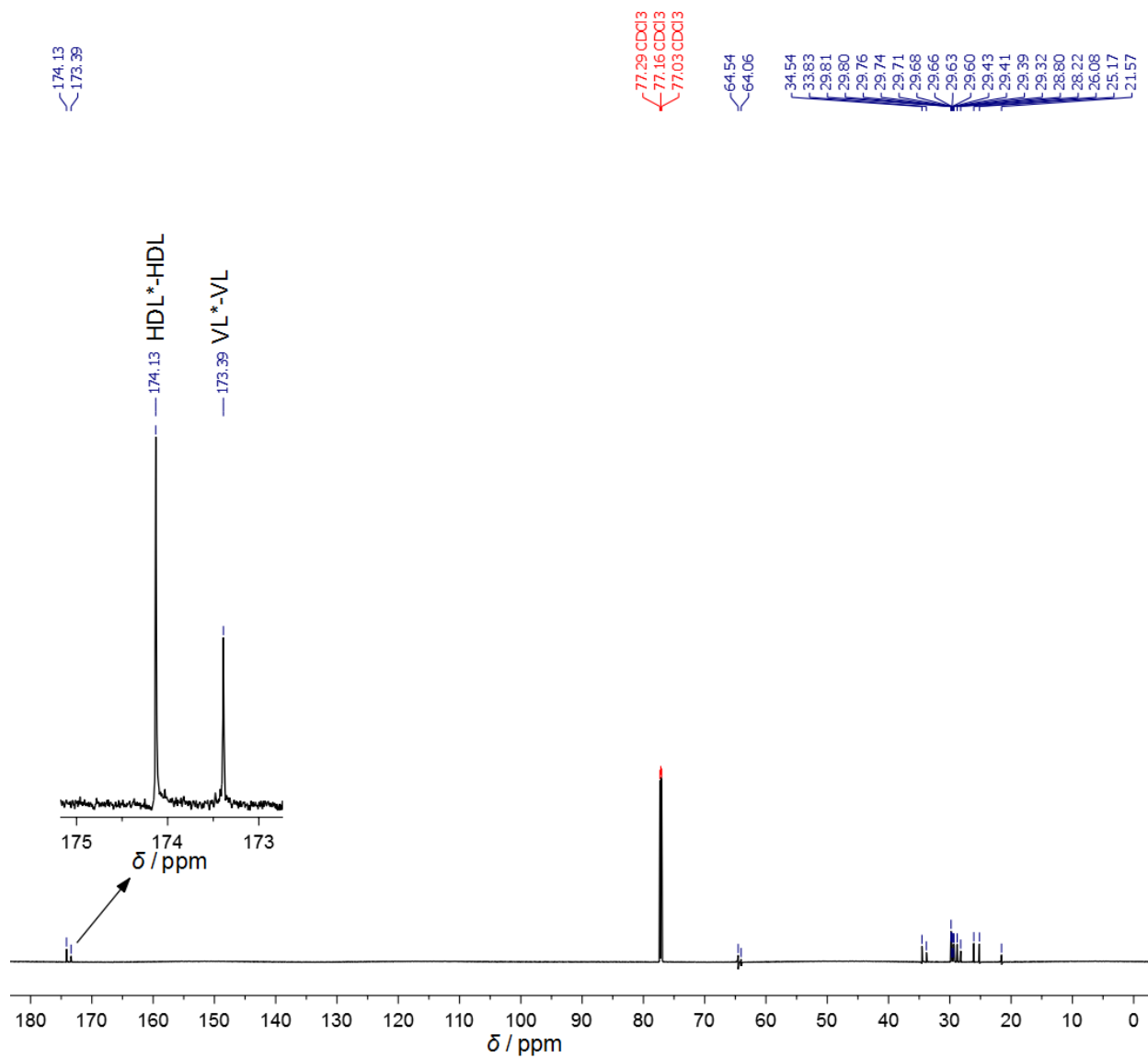


Figure S15. 239 MHz ¹³C NMR spectrum of PHDL-*b*-PVL (entry 4, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt)

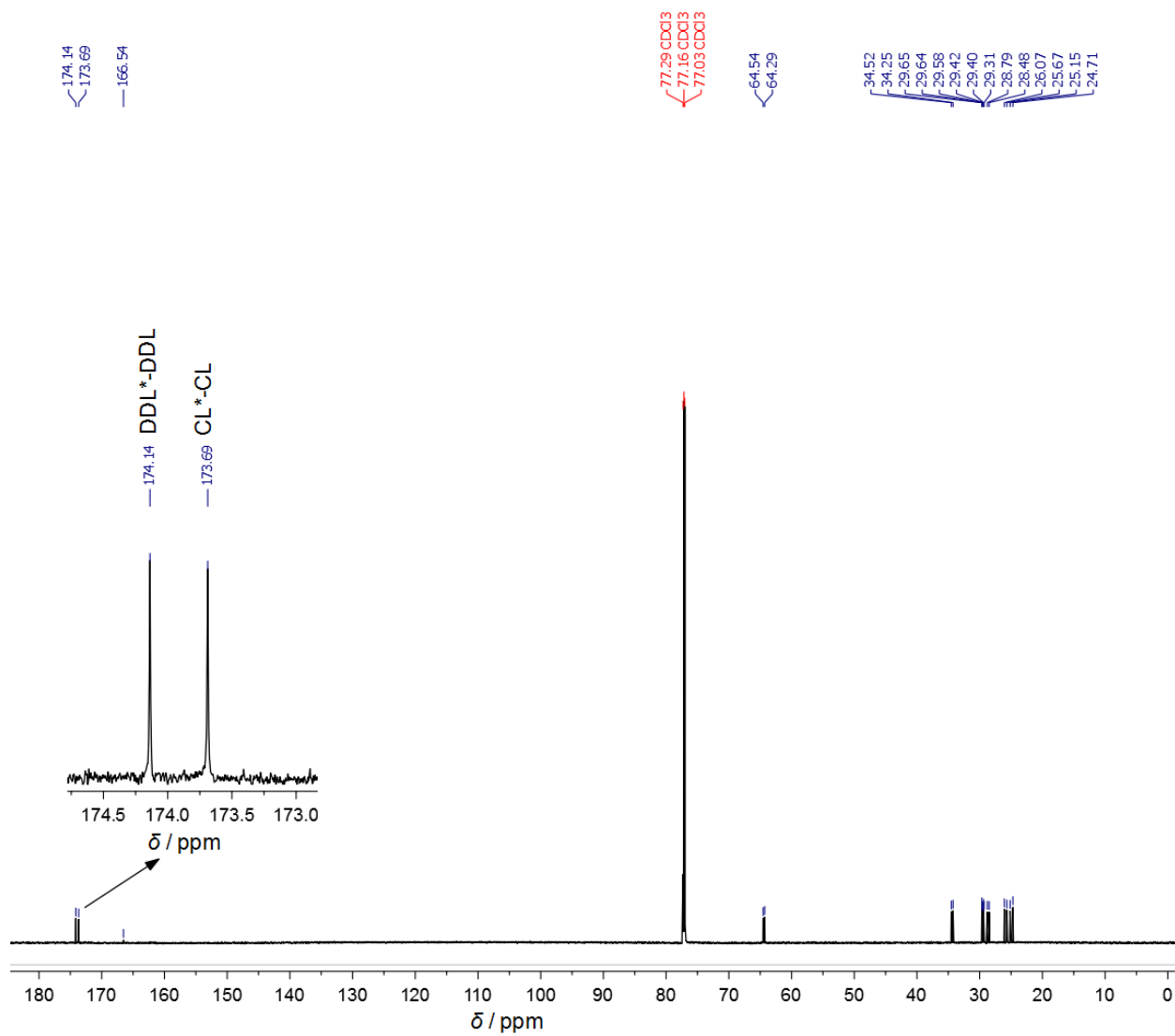


Figure S16. 239 MHz ^{13}C NMR spectrum of PDDL-*b*-PCL (entry 5, Table 2) prepared by catalyst-switch strategy (CDCl_3 , rt)

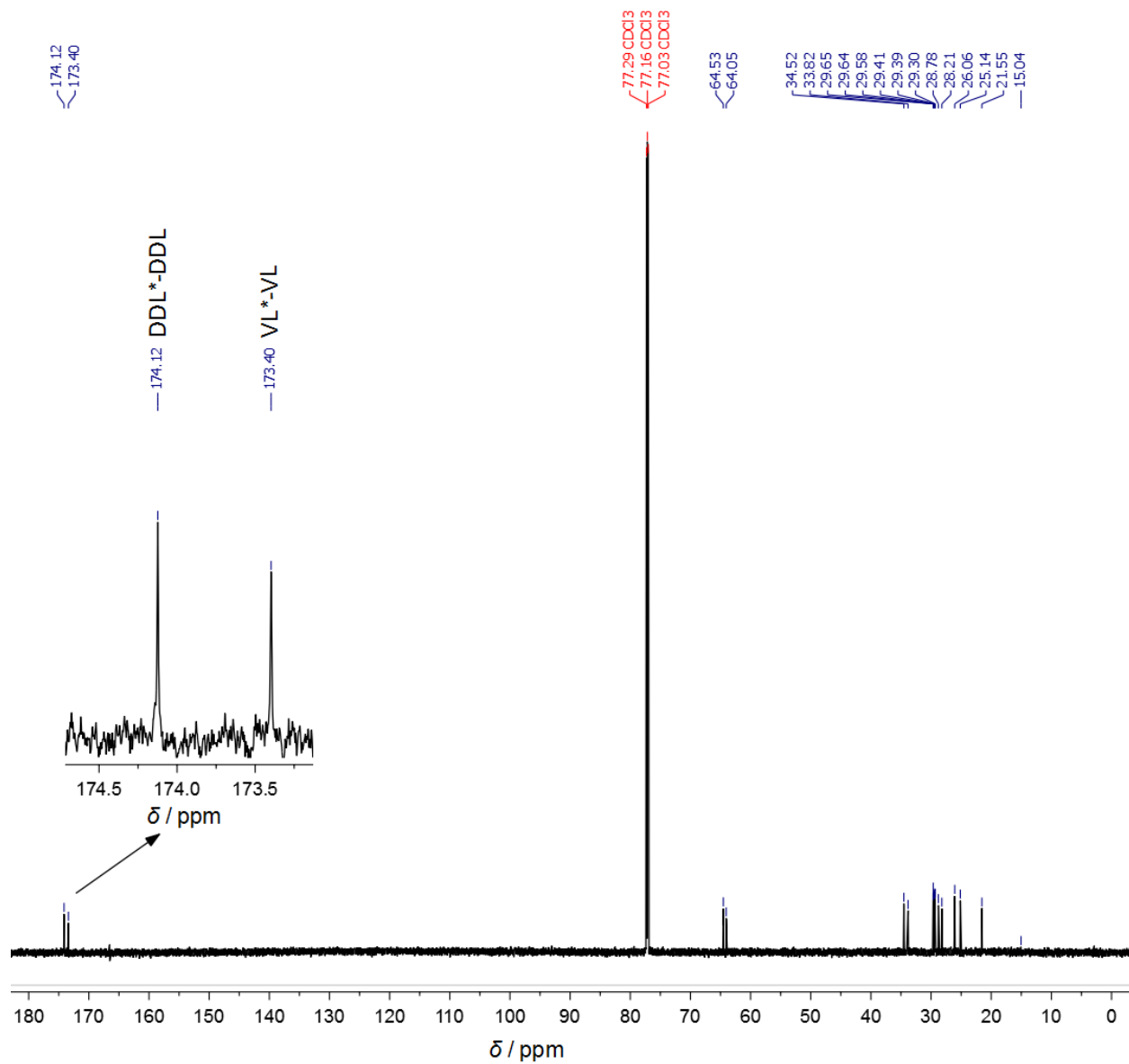


Figure S17. 239 MHz ¹³C NMR spectrum of PDDL-*b*-PVL (entry 6, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt)

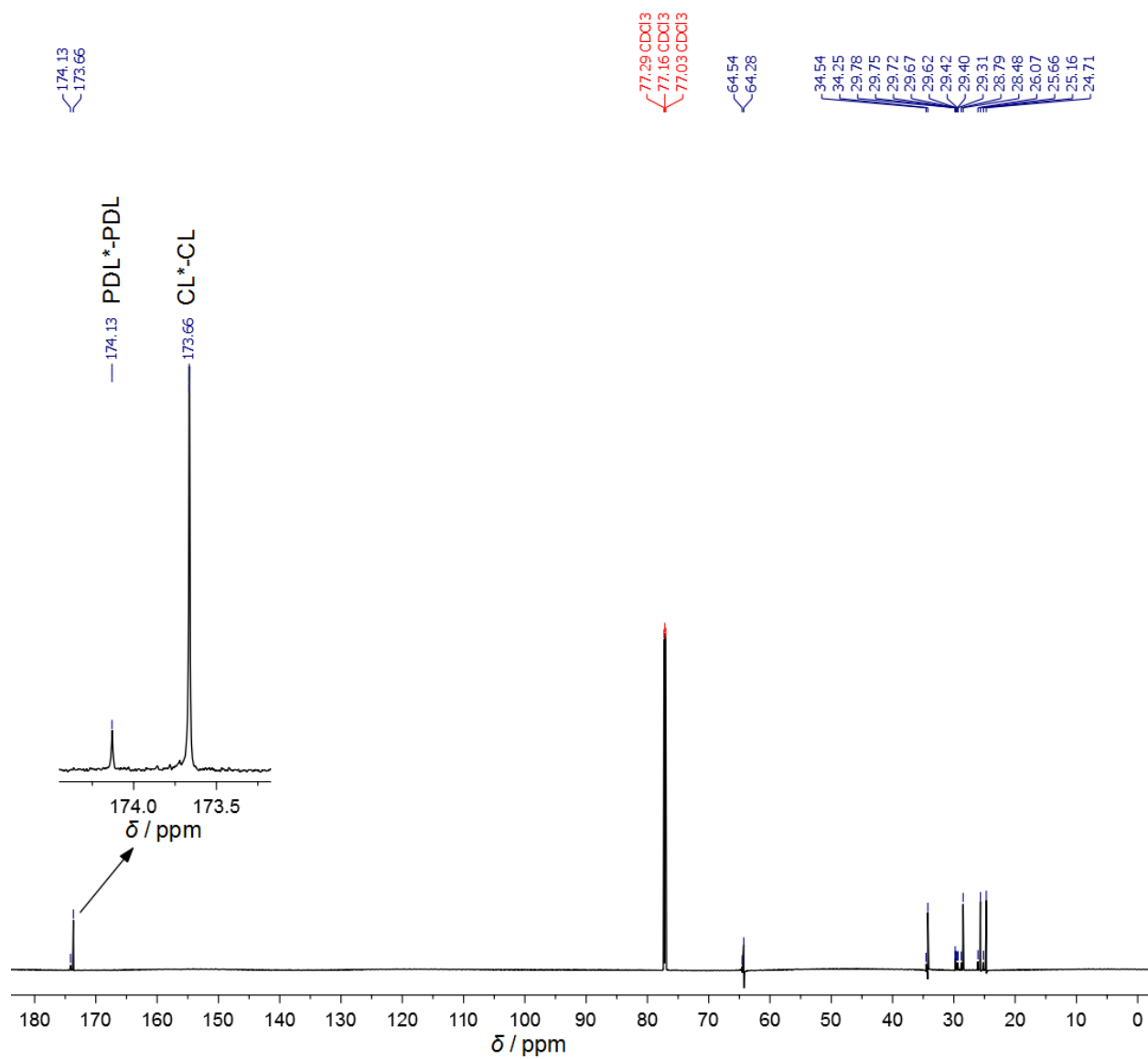


Figure S18. 239 MHz ¹³C NMR spectrum of PPDL₅₀-*b*-PCL₄₀₀ (entry 7, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt)

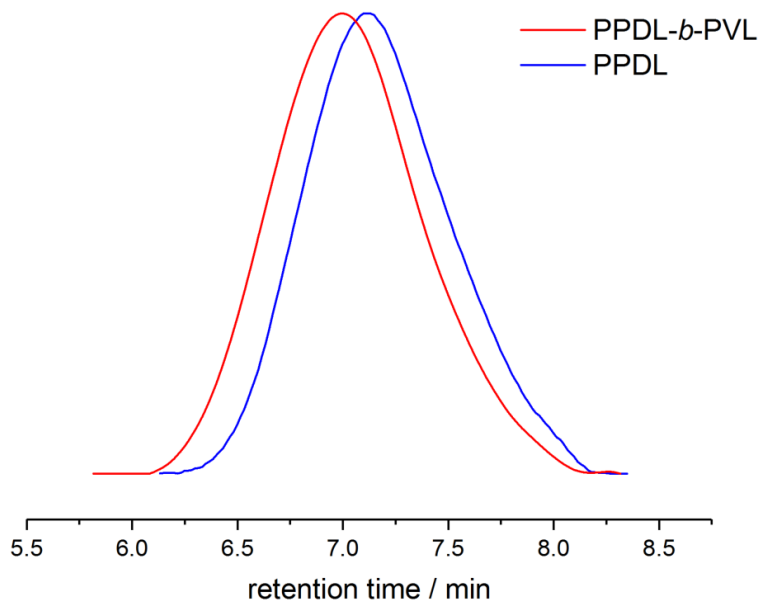


Figure S19. HT-GPC traces of PPDL (blue) macroinitiator and PPDL-*b*-PVL (red, entry 2, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

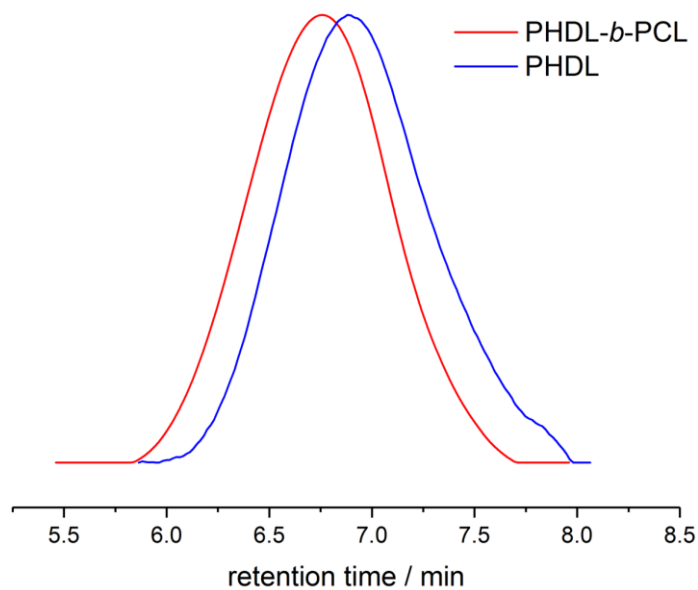


Figure S20. HT-GPC traces of PHDL (blue) macroinitiator and PHDL-*b*-PCL (red, entry 3, Table 2) prepared by catalyst switch-strategy (TCB, 150 °C, PS standards).

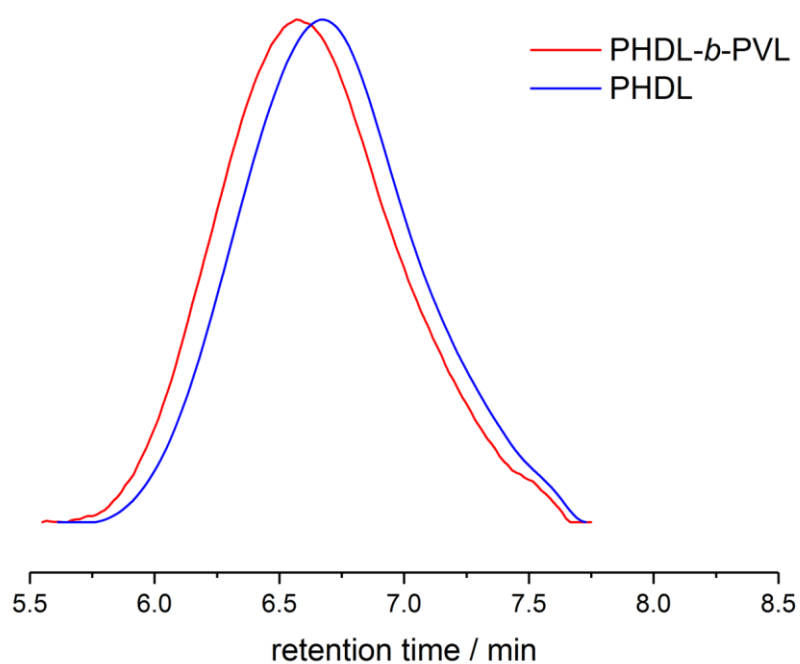


Figure S21. HT-GPC traces of PHDL (blue) macroinitiator and PHDL-*b*-PVL (red, entry 4, Table 2) prepared by catalyst switch-strategy (TCB, 150 °C, PS standards).

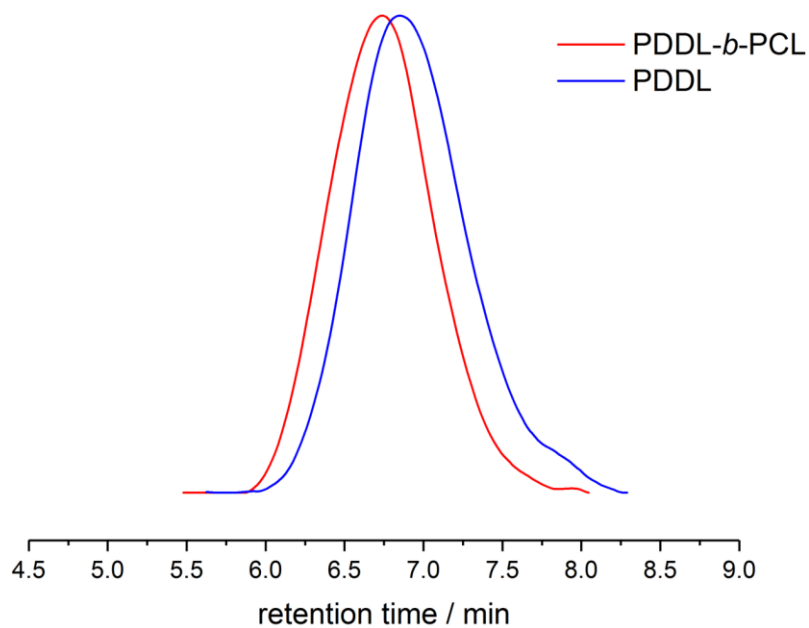


Figure S22. HT-GPC traces of PDDL (blue) macroinitiator and PDDL-*b*-PCL (red, entry 5, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

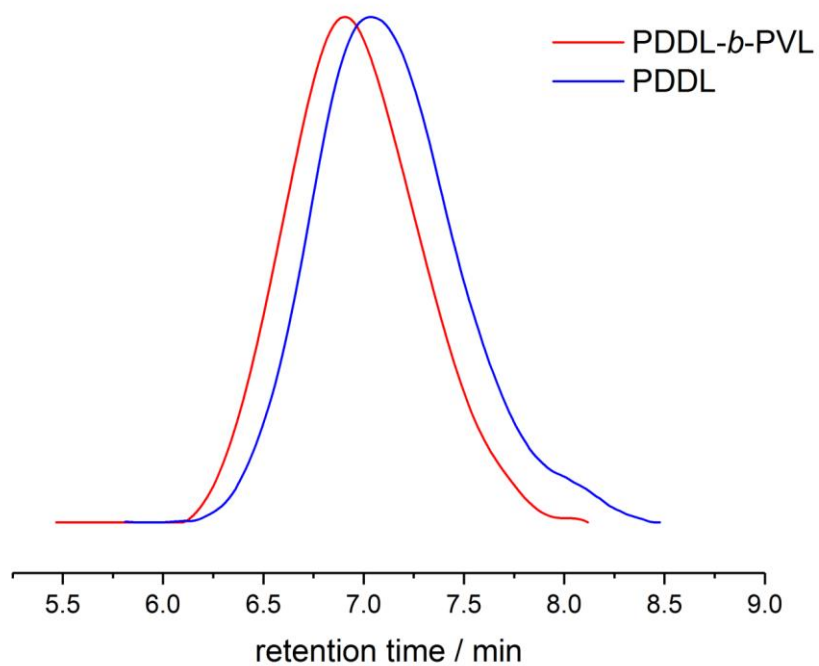


Figure S23. HT-GPC traces of PDDL (blue) macroinitiator and PDDL-*b*-PVL (red, entry 6, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

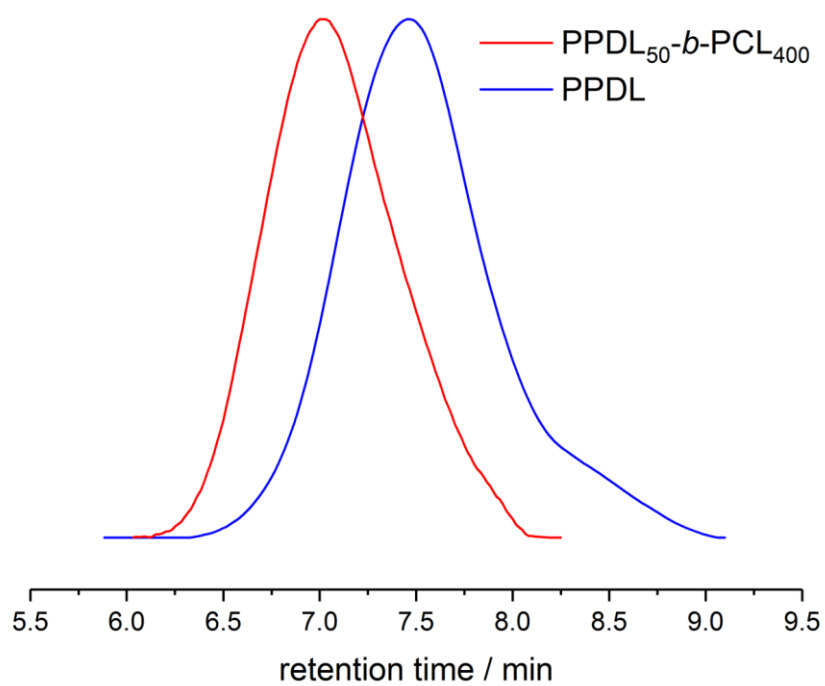


Figure S24. HT-GPC traces of PPDL (blue) macroinitiator and PPDL₅₀-*b*-PCL₄₀₀ (red, entry 7, Table 2) prepared by catalyst-switch strategy (TCB, 150 °C, PS standards).

Table S1. Properties of PMLs:PSLs blends

entry	sample	mass (mg)		PSL (°C)		PML (°C)		ΔH_m^a (J g ⁻¹)	
		PSL	PML	T_c^a	T_m^a	T_c^a	T_m^a	PSL	PML
1	PPDL:PCL	1.2	2.8	38.5	53.7	79.6	92.6	-23.8	-78.6
2	PPDL:PVL	1.0	3.0	39.5	57.2	78.9	92.7	-20.3	-80.4
3	PHDL:PCL	1.0	3.0	43.9	55.7	76.2	91.6	-16.8	-86.2
4	PHDL:PVL	0.8	3.2	44.7	58.0	76.3	90.8	-12.9	-89.6
5	PDDL:PCL	1.4	2.6	36.5	53.6	67.7	83.4	-28.8	-65.9
6	PDDL:PVL	0.8	3.2	38.3	55.6	67.0	83.3	-16.5	-79.8
7	PPDL ₅₀ :PCL ₄₀₀	3.2	0.8	37.2	53.8	80.5	93.0	-68.4	-17.3

^aMeasured by DSC under air with heating rate 10 °C min⁻¹.

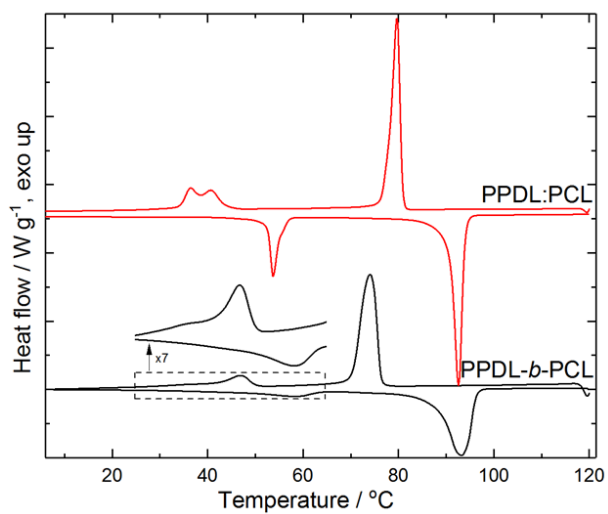


Figure S25. DSC traces of PPDL-*b*-PCL (black, entry 1, Table 2) prepared by catalyst-switch strategy and PPDL: PCL blend (red) (under air, 10 °C min⁻¹).

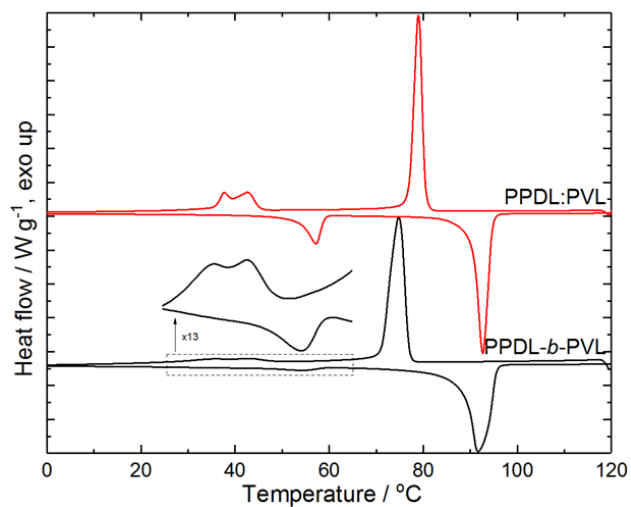


Figure S26. DSC traces of PPDL-*b*-PVL (black, entry 2, Table 2) prepared by catalyst-switch strategy and PPDL: PVL blend (red) (under air, 10 °C min⁻¹).

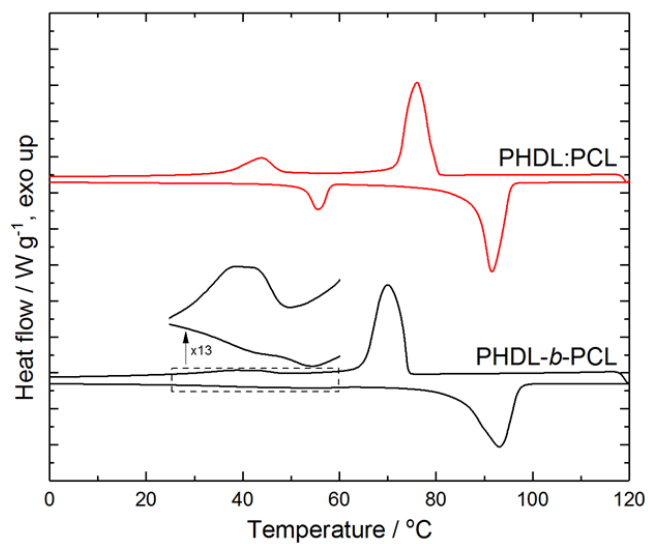


Figure S27. DSC traces of PHDL-*b*-PCL (black, entry 3, Table 2) prepared by catalyst-switch strategy and PHDL: PCL blend (red) (under air, 10 °C min⁻¹).

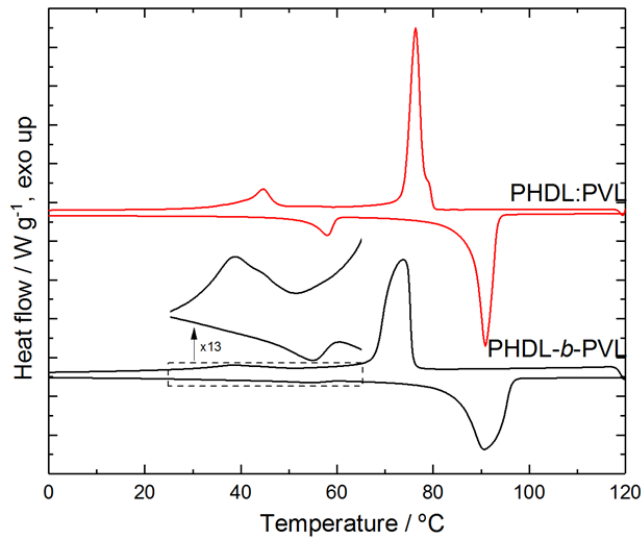


Figure S28. DSC traces of PHDL-*b*-PVL (black, entry 4, Table 2) prepared by catalyst-switch strategy and PHDL: PVL blend (red) (under air, 10 °C min⁻¹).

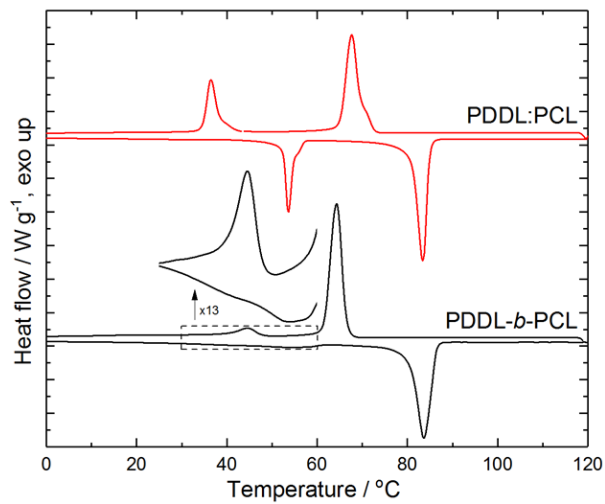


Figure S29. DSC traces of PDDL-*b*-PCL (black, entry 5, Table 2) prepared by catalyst-switch strategy and PDDL: PCL blend (red) (under air, 10 °C min⁻¹).

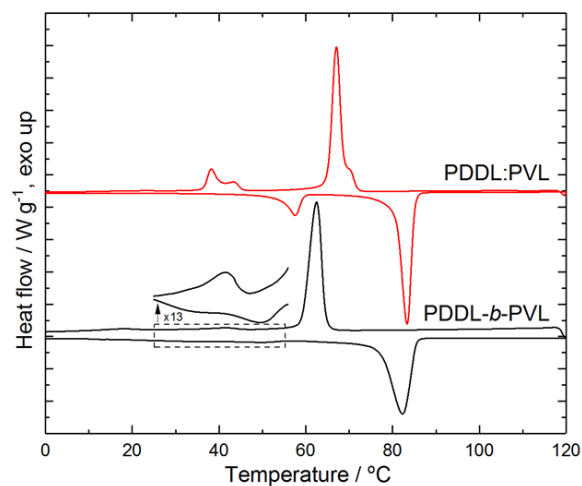


Figure S30. DSC traces of PDDL-*b*-PVL (black, entry 6, Table 2) prepared by catalyst-switch strategy and PDDL: PVL blend (red) (under air, $10\text{ }^{\circ}\text{C min}^{-1}$).

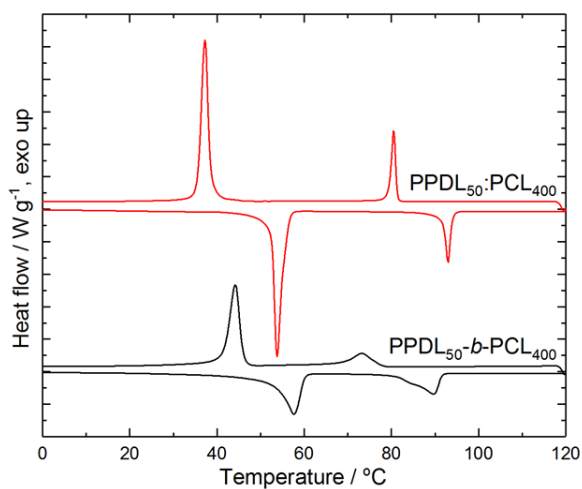


Figure S31. DSC traces of PPDL₅₀-*b*-PCL₄₀₀ (black, entry 7, Table 2) prepared by catalyst-switch strategy and PPDL₅₀:PCL₄₀₀ blend (red) (under air, $10\text{ }^{\circ}\text{C min}^{-1}$).

Table S2. Peaks position of PMLs and PSLs in XRD spectra

run	sample	Peak 1 ^a (2θ)	Peak 2 ^a (2θ)
1	PPDL- <i>b</i> -PCL	21.6	24.0
2	PPDL- <i>b</i> -PVL	21.6	24.0
3	PHDL- <i>b</i> -PCL	21.5	23.9
4	PHDL- <i>b</i> -PVL	21.6	24.0
5	PDDL- <i>b</i> -PCL	21.5	24.0
6	PDDL- <i>b</i> -PVL	21.6	24.0
7	PPDL ₃₀ - <i>b</i> -PCL ₂₀₀	21.5	23.8
8	PCL	21.5	23.7
		22.1	
9	PVL	21.7	24.4
10	PPDL	21.6	24.0
11	PHDL	21.5	23.9
12	PDDL	21.5	23.9

^aDetermined by XRD under ambient condition.