Supporting information

Block Copolymers of Macro/Small Lactones by a "Catalyst-Switch" Organocatalytic

Strategy. Thermal Properties and Phase Behaviour

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



Figure S1. GPC trace of PCL prepared by ROP with DPP as catalyst (THF, 35 °C, PS standards).



Figure S2. 239 MHz¹³C NMR spectrum of PPDL:PCL mixture in CDCl₃ 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 (CDCl₃, 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 (CDCl₃, rt).



Figure S5. 950 MHz ¹H NMR spectrum of PPDL-*b*-PCL (entry 1, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt).



Figure S6. 950 MHz ¹H NMR spectrum of PPDL-*b*-PVL (entry 2, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt).



Figure S7. 950 MHz ¹H NMR spectrum of PHDL-*b*-PCL (entry 3, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt).



Figure S8. 950 MHz ¹H NMR spectrum of PHDL-*b*-PVL (entry 4, Table 2) prepared by catalyst-switch strategy (CDCl₃, rt).



Figure S9. 950 MHz ¹H NMR spectrum of PDDL-*b*-PCL (entry 5, Table 2) prepared by catalyst-switch strategy (CDCl₃, 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 catalystswitch strategy (CDCl₃, rt)



Figure S12. 239 MHz ¹³C NMR spectrum of PPDL-*b*-PCL (entry 1, Table 2) prepared by catalyst-switch strategy (CDCl₃, 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 ¹³C NMR spectrum of PDDL-*b*-PCL (entry 5, Table 2) prepared by catalyst-switch strategy (CDCl₃, 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).

entry	sample -	mass (mg)		PSL (°C)		PML (°C)		$\Delta H_{\rm m}{}^{\rm a}({\rm J}{\rm g}^{-1})$	
		PSL	PML	$T_{\rm c}{}^{\rm a}$	$T_{\rm m}{}^{\rm a}$	$T_{\rm c}{}^{\rm a}$	$T_{\rm m}{}^{\rm a}$	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

 Table S1.
 Properties of PMLs:PSLs blends

^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, $10 \degree C \min^{-1}$).



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, $10 \degree C \min^{-1}$).



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, $10 \degree C \min^{-1}$).



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, $10 \degree C \min^{-1}$).



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, $10 \degree C \min^{-1}$).



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, $10 \degree C \min^{-1}$).



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, $10 \degree C \min^{-1}$).

run	sample	Peak $1^{a} (2\theta)$	Peak $2^{a} (2 \theta)$	
1	PPDL-b-PCL	21.6	24.0	
2	PPDL-b-PVL	21.6	24.0	
3	PHDL-b-PCL	21.5	23.9	
4	PHDL-b-PVL	21.6	24.0	
5	PDDL-b-PCL	21.5	24.0	
6	PDDL-b-PVL	21.6	24.0	
7	PPDL ₃₀ -b-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	

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

^aDetermined by XRD under ambient condition.