## **Supplementary Information**

## Photoinduced Topological Transformation of Cyclized Polylactides for Switching the Properties of Homocrystals and Stereocomplexes

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**Figure S1.** <sup>1</sup>H NMR spectra of **3L**, **3D**, **4L**, **4D**, **5L**, and **5D**.



Figure S2. SEC traces of 3L, 3D, 4L, 4D, 5L, and 5D. Broken and solid lines in 5L and 5D show the products obtained before and after SEC fractionation, respectively.



Figure S3. MALDI–TOF mass spectra of 3L, 3D, 4L, 4D, 5L, and 5D.  $DP_n$  denotes the number of a half of lactide units.



**Figure S4.** SEC traces of (a) **3L** (before photoirradiation) and **7L** (after photoirradiation for 30 min in the respective solvents at a concentration of 0.5 mg/mL) and (b) **3D** (before photoirradiation) and **7D** (after photoirradiation for 30 min in the respective solvents at a concentration of 0.5 mg/mL). At the bottom of (b), a THF solution of **3D** was irradiated in the presence of butylated hydroxy toluene (BHT, 0.05% solution).



**Figure S5.** SEC traces of cyclic **5L** and **5D** (before photoirradiation), and linear **6L** and **6D** (after photoirradiation for 2 h). BHT (0.05% solution) was used as a radical scavenger.



**Figure S6.** Photoisomerization of an *ortho*-nitrobenzyl (NB) group into an *ortho*-nitrosobenzaldehyde group and the subsequent dimerization



**Figure S7.** <sup>1</sup>H NMR spectra of **3D** (before photoirradiation), **5L** (before photoirradiation), **6L** (after photoirradiation on **5L**), and **7D** (after photoirradiation on **3D**). Asterisk indicates residual protons in deuterated chloroform.



Figure S8. WAXD profiles of 1L, 1D, 2L, 2D, 1L/1D, 1L/2D, and 2L/2D.



Figure S9. SAXS profiles of 1L, 1D, 2L, 2D, 1L/1D, 1L/2D, and 2L/2D.

Table S1. Properties of non-photocleavable linear and cyclic polylactides determinedby SAXS and WAXD

	description	L (nm)	l <sub>c</sub> (nm)	$M_{\rm n}$ for $l_{\rm c}$ (kDa)	l <sub>a</sub> (nm)	Xc
1L	non-photocleavable linear PLLA ( $M_n \sim 3 \text{ kDa}$ )	12	8.2	2.0	2.1	63%
1D	non-photocleavable linear PDLA ( $M_n \sim 3 \text{ kDa}$ )	12	9.4	2.3	2.5	58%
<b>2</b> L	non-photocleavable cyclic PLLA ( $M_n \sim 3 \text{ kDa}$ )	6.3	3.9	1.0	2.4	64%
2D	non-photocleavable cyclic PDLA ( $M_n \sim 3 \text{ kDa}$ )	6.1	3.6	0.9	2.5	50%
1L/1D	blend of 1L and 1D	12	10	2.5	2.1	79%
1L/2D	blend of 1L and 2D	8.8	7.2	1.8	1.6	62%
2L/2D	blend of <b>2L</b> and <b>2D</b>	7.0	5.4	1.3	1.6	69%