Supplementary Information

Nucleobase-Monofunctionalized Supramolecular Poly(L-lactide): Controlled Synthesis, Competitive Crystallization, and Structural Organization

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Experimental

Synthesis of nonfunctionalized PLLA. A typical synthetic procedure of nonfunctionalized PLLA with a designed M_n of 2.0 kDa is shown as follows. Benzyl alcohol (0.54 g, 0.005 mol) and L-lactide (9.44 g, 0.066 mol) were added into a flask and further dried under reduced pressure at 60 °C for 1 h, followed by the addition of $Sn(Oct)_2$ (0.04 g, 0.10 mmol). Polymerization was allowed to proceed at 120 °C for 12 h under an argon atmosphere. After reaction, the reaction mixture was precipitated into excess of cold ether (250 mL); the precipitate was dried at 50 °C *in vacuo* for 24 h to attain the benzyl-terminated PLLA, denoted as the nonfunctionalized PLLA. Nonfunctionalized PLLA was coded as $PLLA_{xk}$, with *x* representing the $M_{n,PLLA}$ (in kDa) of PLLA block measured by ^1H NMR. ^1H NMR of $PLLA_{1.9k}$ ($CDCl_3$): δ = 7.34 (t, 5H, $-C_6H_5$), 5.18 (t, 28H, $-CH(CH_3)-O-$), 4.37 (t, 1H, $-CH(CH_3)-OH$), 1.75–1.25 (m, 87H, $-CH-CH_3-$).

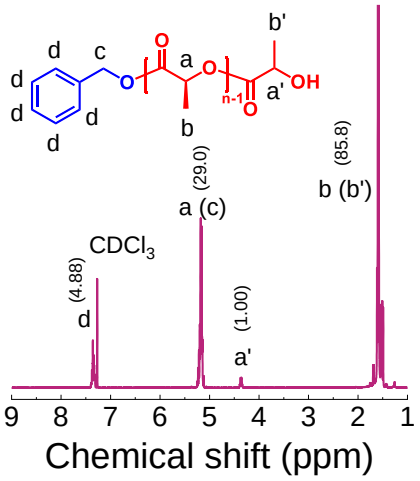

Fig. S1 ^1H NMR spectra of nonfunctionalized $PLLA_{1.9k}$. The numerals in brackets denote the integrated area of each peak.

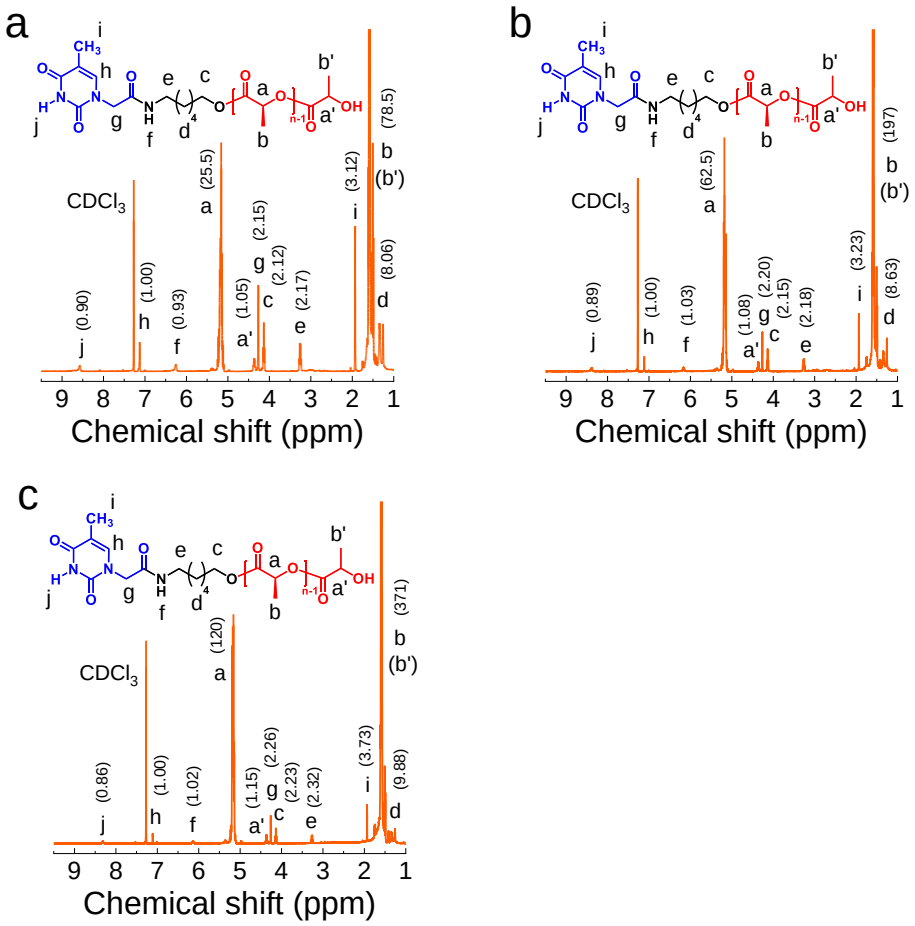

Fig. S2 ^{1}H NMR spectra of (a) PLLA $_{1.7k}$-Thy; (b) PLLA $_{4.1k}$-Thy; (c) PLLA $_{7.4k}$-Thy. The numerals in brackets denote the integrated area of each peak.

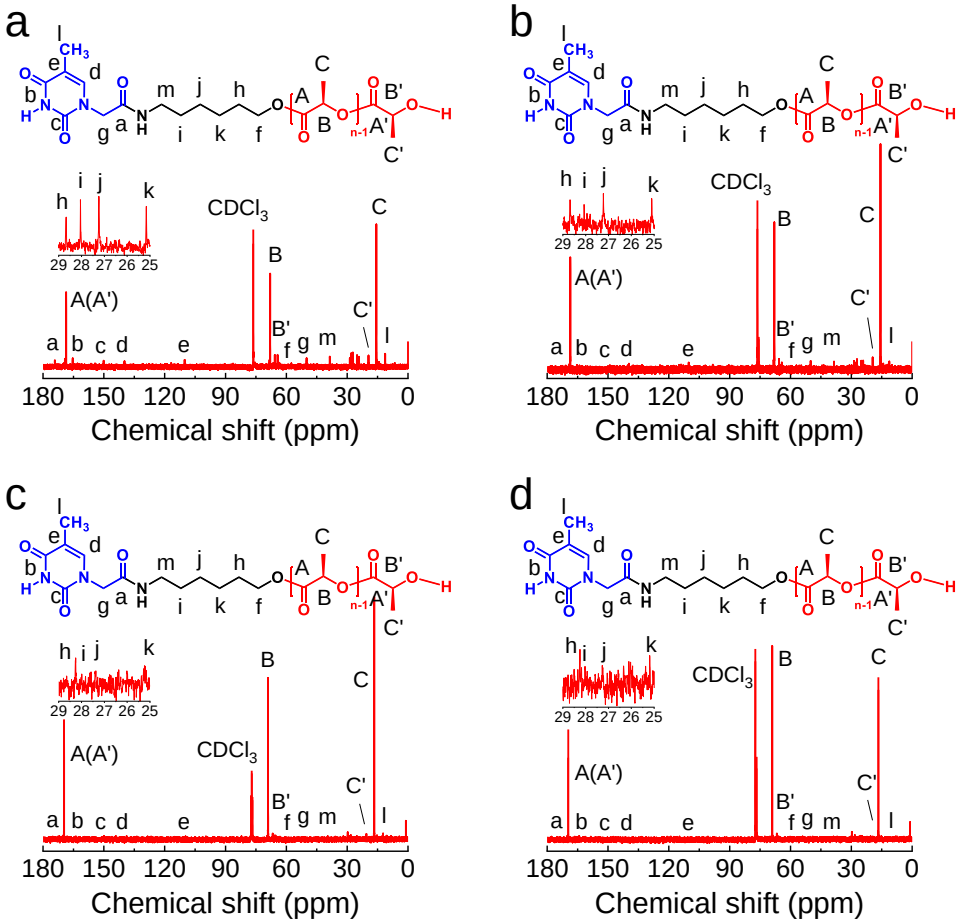

Fig. S3 ^{13}C NMR spectra of (a) PLLA$_{0.8k}$-Thy; (b) PLLA $_{1.7k}$-Thy; (c) PLLA $_{4.1k}$-Thy; (d) PLLA $_{7.4k}$-Thy.

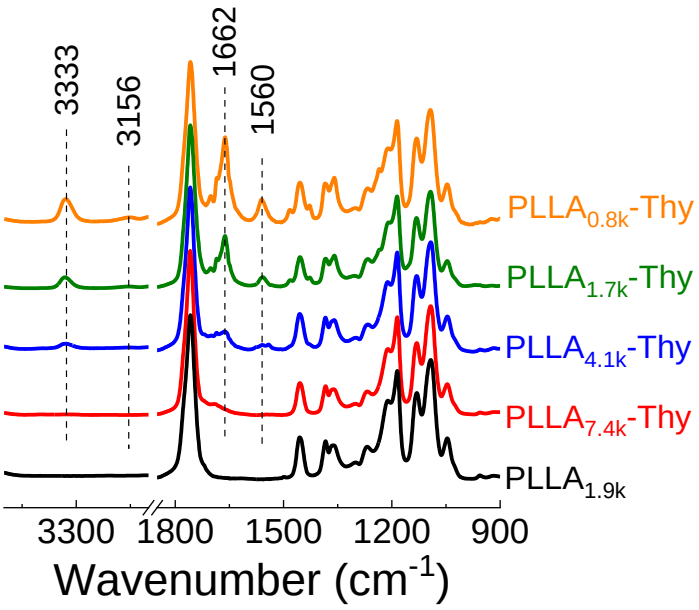

Fig. S4 FTIR spectra of PLLA-Thy and nonfunctionalized PLLA.

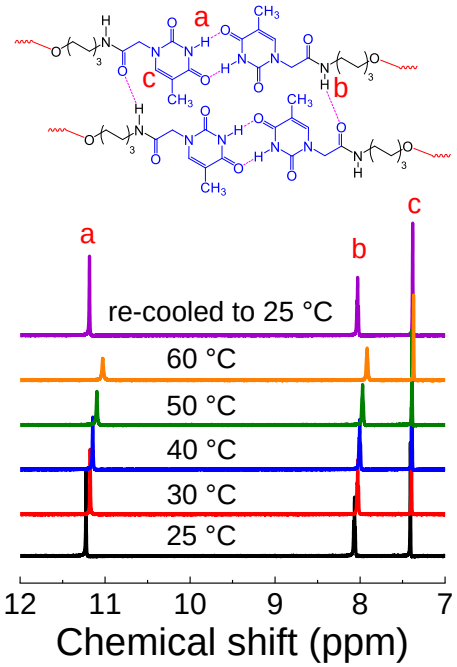

Fig. S5 Temperature-dependent ^{1}H NMR spectra of PLLA$_{1.7k}$-Thy in DMSO-d_6. Sample was equilibrated for 10 min at each temperature before measurement.

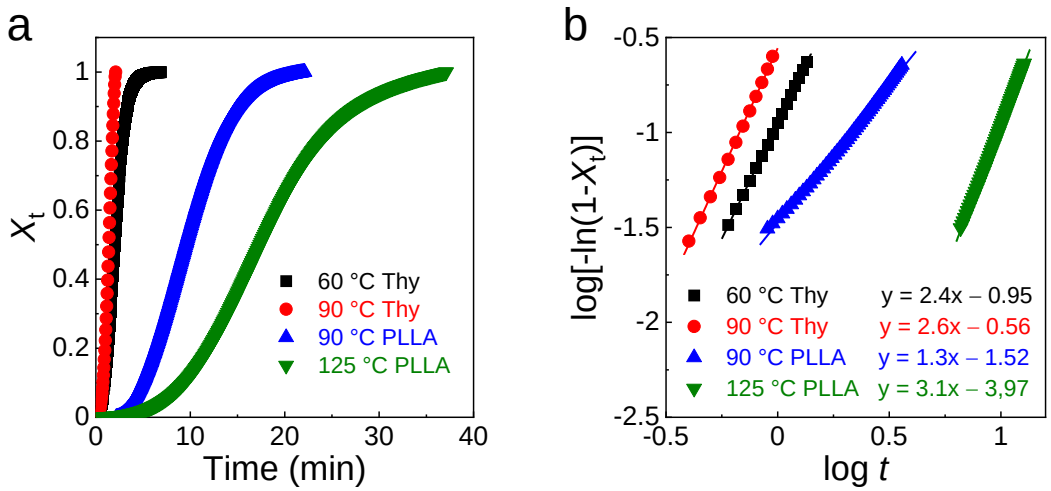

Fig. S6 Analysis of isothermal crystallization kinetics of PLLA$_{1.7k}$-Thy at different T_c's. (a) Changes of relative crystallinity (X_t) of thymine unit and PLLA block; (b) Plot of lg[−ln(1−X_t)] against lg$t$.

Table S1. Scattering data of $PLLA_{0.8k}$-Thy after isothermal melt crystallization at different T_c's.

T_c (°C)	Characteristic reflection	q (nm^{-1})	d[a] (nm)
60	Thy	13.3	0.47
		16.7	0.38
70	Thy	13.3	0.47
		16.7	0.38
80	Thy	13.3	0.47
		16.7	0.38
90	Thy	13.3	0.47
		16.7	0.38
100	Thy	13.3	0.47
		16.7	0.38
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
110	Thy	13.3	0.47
		16.7	0.38
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
120	Thy	13.3	0.47
		16.7	0.38
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41

[a]d was evaluated from the q value of characteristic reflection by Bragg equation ($d = 2\pi/q$).

Table S2. Scattering data of $PLLA_{1.7k}$-Thy after isothermal melt crystallization at different T_c's.

T_c (°C)	Characteristic reflection	q (nm^{-1})	d[a] (nm)
60	Thy	13.3	0.47
		16.7	0.38
70	Thy	masked	
	PLLA $\alpha'_{110/200}$	13.3	0.47
	PLLA α'_{203}	15.2	0.41
80	Thy	masked	
	PLLA $\alpha'_{110/200}$	13.3	0.47
	PLLA α'_{203}	15.2	0.41
90	Thy	masked	
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
100	Thy	masked	
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
110	Thy	masked	
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
120	Thy	masked	
	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41

[a] d was evaluated from the q value of characteristic reflection by Bragg equation ($d = 2\pi/q$).

Table S3. Scattering data of $PLLA_{4.1k}$-Thy after isothermal melt crystallization at different T_c's.

T_c (°C)	Characteristic reflection	q (nm^{-1})	d[a] (nm)
60	PLLA $\alpha'_{110/200}$	13.3	0.47
	PLLA α'_{203}	15.2	0.41
70	PLLA $\alpha'_{110/200}$	13.3	0.47
	PLLA α'_{203}	15.2	0.41
80	PLLA $\alpha'_{110/200}$	13.3	0.47
	PLLA α'_{203}	15.2	0.41
90	PLLA $\alpha'_{110/200}$	13.3	0.47
	PLLA α'_{203}	15.2	0.41
100	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
110	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41
120	PLLA $\alpha_{110/200}$	13.5	0.47
	PLLA α_{203}	15.3	0.41

[a]d was evaluated from the q value of characteristic reflection by Bragg equation ($d = 2\pi/q$).