Supplementary Information:

Crystallization Behavior, Structure, Morphology, and Thermal Properties of Crystalline and Amorphous Stereo Diblock Copolymers, Poly(L-lactide)-*b*-Poly(DL-lactide)

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S1. ^{1}H NMR spectra of synthesized PLLA, PLLA-*b*-PDLLA, and PDLLA polymers (Figure S1)

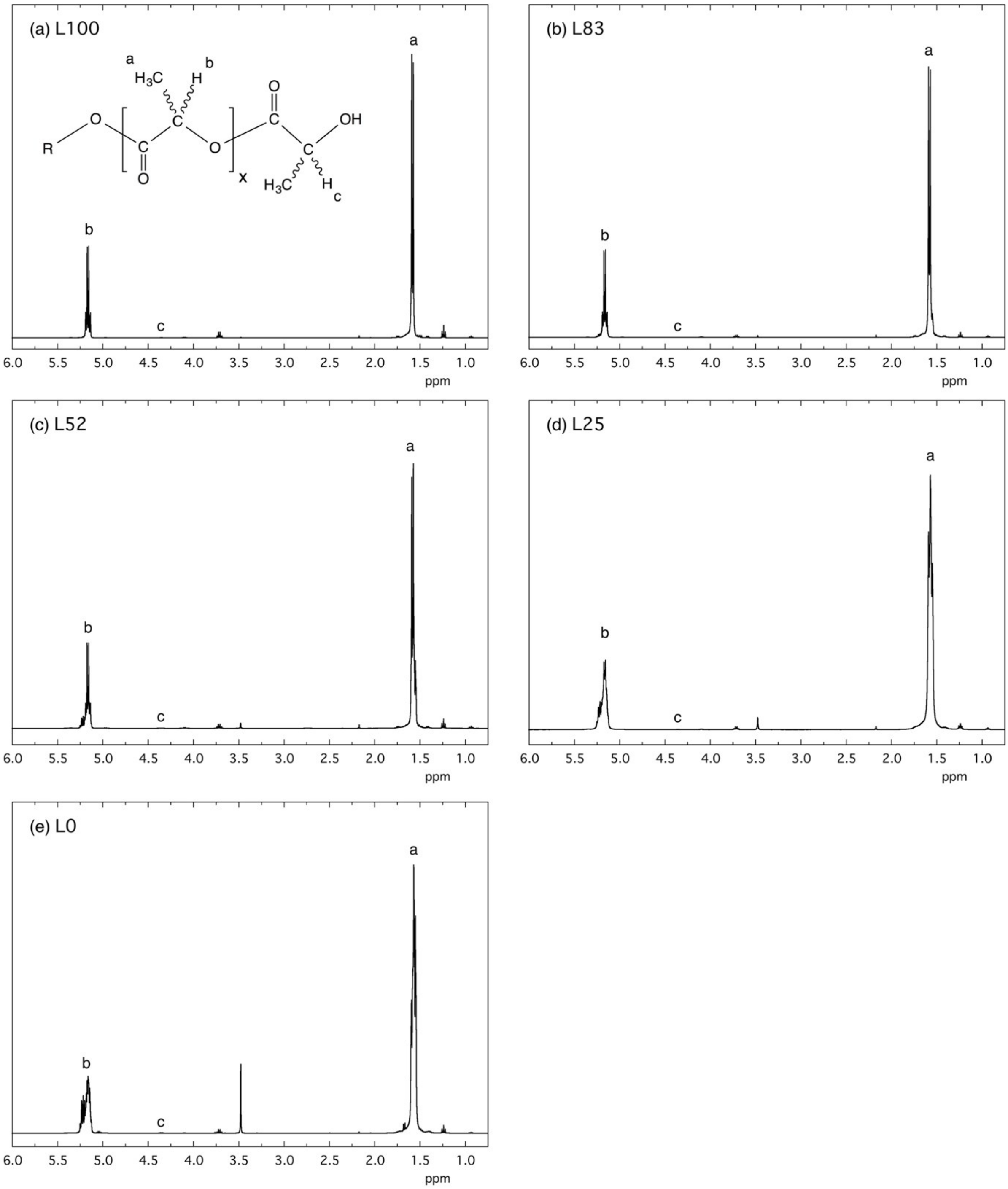

Figure S1. ^{1}H NMR spectra of synthesized L100 (a), L83 (b), L852 (c), L25 (d), and L0 (e) polymers in $CDCl_3$. The peak at 3.5 ppm is ascribed to methyl proton of methanol remaining in polymers.

S2. Thermal properties of PLLA, PLLA-*b*-PDLLA, and PDLLA polymers for heating (Table S1)

Table S1. Thermal properties of PLLA, PLLA-*b*-PDLLA, and PDLLA polymers for heating.

Code	PLLA fraction (%)	Crystallization [a]	T_g [b] (°C)	T_{cc} [b] (°C)	T_m [b] (°C)	ΔH_{cc} [c] (J g^{-1})	ΔH_m [c] (J g^{-1})	ΔH(tot) [d] (J g^{-1})
L100	100	SE	47.5	90.3	173.9	-4.1	68.1	64.0
		Pr	61.2		174.1		62.1	62.1
		MC (160°C)	50.1		182.7[e]		83.3	83.3
		MC (140°C)			163.1, 176.0[e]		79.2	79.2
		MC (120°C)			171.7[e]		68.0	68.0
		MC (110°C)			172.0		68.8	68.8
		MC (100°C)			165.6,[f] 173.7		63.7	63.7
		MC (90°C)			164.0,[f] 173.2		52.9	52.9
		MC (80°C)		135.4	162.7,[f] 172.9	-5.0	56.5	51.5
		MC (0°C) [g]	56.5	98.5	163.5, 173.1	-59.8	59.9	0.1
L83	82.8	SE		132.2	170.0	-3.1	46.5	43.4
		Pr	52.6		158.2, 169.4		38.5	38.5
		MC (160°C)	49.2, 57.5	107.6, 155.1	164.6	-42.1	42.4	0.3
		MC (140°C)	51.1		169.1[e]		51.0	51.0
		MC (120°C)	51.2		163.8,[e] 169.7		52.3	52.3
		MC (110°C)	43.8		155.7,[f] 168.6		48.6	48.6
		MC (100°C)	48.1, 56.3		147.5,[f]168.6		38.8	38.8
		MC (90°C)	55.2	149.7	168.9	-5.3	40.8	35.5
		MC (80°C)	52.0	148.0	169.0	-7.0	44.6	37.6
		MC (0°C) [g]	54.6	107.9, 154.2	168.1	-40.3	41.5	1.2
L52	52.4	SE	43.9	99.2	163.9	-9.7	26.5	16.8
		Pr	50.2		154.8, 164.4		35.5	35.5
		MC (160°C)	48.4, 56.1	125.7	154.5, 163.1	-24.7	25.5	0.8
		MC (140°C)	48.0		162.1[e]		36.1	36.1
		MC (120°C)	50.6		156.9,[e] 163.6		27.6	27.6
		MC (110°C)	47.2		126.0, 154.2,[e] 163.1		29.3	29.3
		MC (100°C)	45.4		119.9, 151.7,[e] 163.3		31.4	31.4
		MC (90°C)	42.1, 54.2	148.0	108.7, 163.4	-2.0	29.1	27.1
		MC (80°C)	51.9	144.5	163.1	-3.9	28.4	24.5
		MC (0°C) [g]	53.6	125.9	154.5, 163.2	-24.8	25.0	0.2
L25	25.4	SE	41.0, 49.1	107.6	147.8	-4.0	4.4	0.4
		Pr	52.8	114.4	144.1, 154.9	-1.0	11.1	10.1
		MC (160°C)	48.1, 54.8					
		MC (140°C)	49.1		152.4		0.7	0.7
		MC (120°C)	48.5		131.5,[e]142.9, 148.6		11.9	11.9
		MC (110°C)	46.6		124.2,[e]138.9, 146.6		13.8	13.8
		MC (100°C)	47.7		116.7,[e] 135.7, 144.5		13.2	13.2
		MC (90°C)	45.3, 53.2		108.2,[e] 131.8, 144.5		11.2	11.2
		MC (80°C)	50.4		146.5		8.2	8.2
		MC (0°C) [g]	50.2					
L0	0	SE	10.1					
		Pr	29.1					
		MC (160°C)	45.9					
		MC (140°C)	52.4					
		MC (120°C)	47.9					
		MC (110°C)	47.8					
		MC (100°C)	48.7					
		MC (90°C)	45.7					
		MC (80°C)	48.4					
		MC (0°C) [g]	48.9					

[a] SE, Pr, and MC indicate that the samples were prepared correspondingly by solvent-evaporation, precipitation, and melt-crystallization at shown T_c.
[b] T_g, T_{cc}, and T_m are glass transition, cold crystallization, and melting temperatures, respectively.
[c] ΔH_{cc} and ΔH_m cold crystallization and melting enthalpies, respectively.
[d] $\Delta H(\text{tot}) = \Delta H_{cc} + \Delta H_m$. [e] T_m values of α-form used to obtain T_m^0 values. [f] T_m values of δ-form used to obtain T_m^0 values.
[g] Melt-quenched samples.

S3. Thermal properties of PLLA, PLLA-*b*-PDLLA, and PDLLA polymers for cooling (Table S2)

Table S2. Thermal properties of PLLA/PDLA, PLLA-*b*-PDLLA blends, and PDLLA for cooling.

Code	PLLA fraction (%)	T_c [a] (°C)	ΔH_c [b] ($J\ g^{-1}$)
L100	100	117.8	-55.6
L83	82.8	105.3	-35.5
L52	52.4		
L25	25.4		
L0	0		

[a] Crystallization temperature.
[b] Crystallization enthalpy.

S4. Magnified WAXD profiles (Cu-Kα) of PLLA and PLLA-*b*-PDLLA polymers (Figure S2)

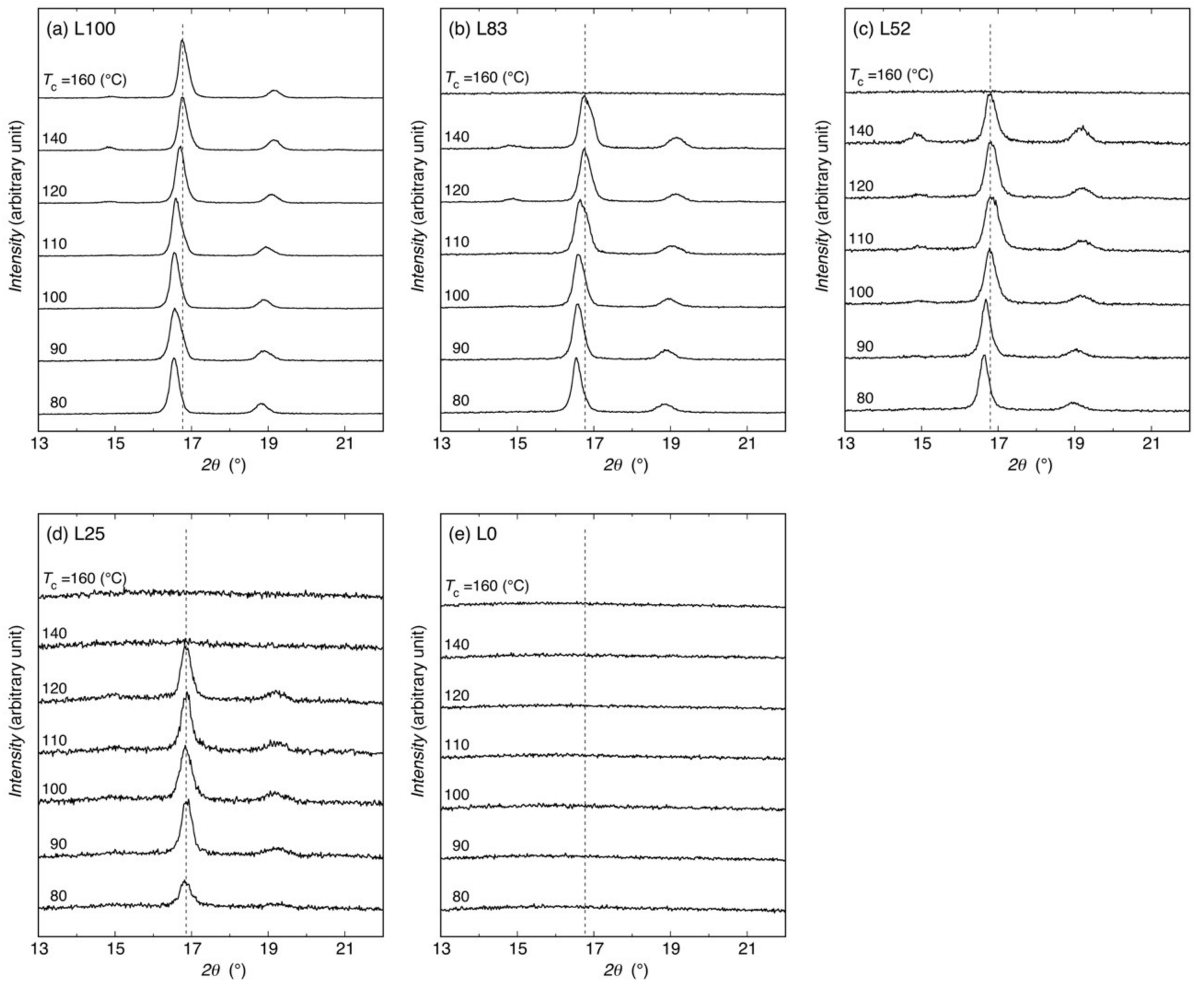

Figure S2. Magnified WAXD profiles (2θ range of 13–22°, Cu-Kα) of PLLA (L100) (a), PLLA-*b*-PDLLA polymers, L83 (b), L52 (c), L25 (d), and PDLLA (L0) (e) crystallized at different crystallization temperature (T_c) values from the melt.

S5. Structural parameters of PLLA and PLLA-*b*-PDLLA polymers (Table S3)

Table S3. Structural parameters of PLLA and PLLA-*b*-PDLLA polymers crystallized at 130ºC for 10h from the melt.

Code	PLLA fraction (%)	L [a] (Å)	d_c [b] (Å)	d_a [c] (Å)	d_{tr} [d] (Å)	X_c (%)
L100	100	168.2	83.5	84.7	32.2	68.1
L83	82.8	182.2	90.4	91.8	34.9	51.9
L52	52.4	231.5	116.4	115.1	44.5	36.3
L25	25.4	270.5	137.3	133.2	51.3	19.6

[a] Long period.
[b] Mean lamellar thickness.
[c] Mean thickness of amorphous layer.
[d] Mean thickness of transition layer between the crystalline and amorphous layers.

S6. Avrami plot of PLLA and PLLA-*b*-PDLLA polymers (Figure S3)

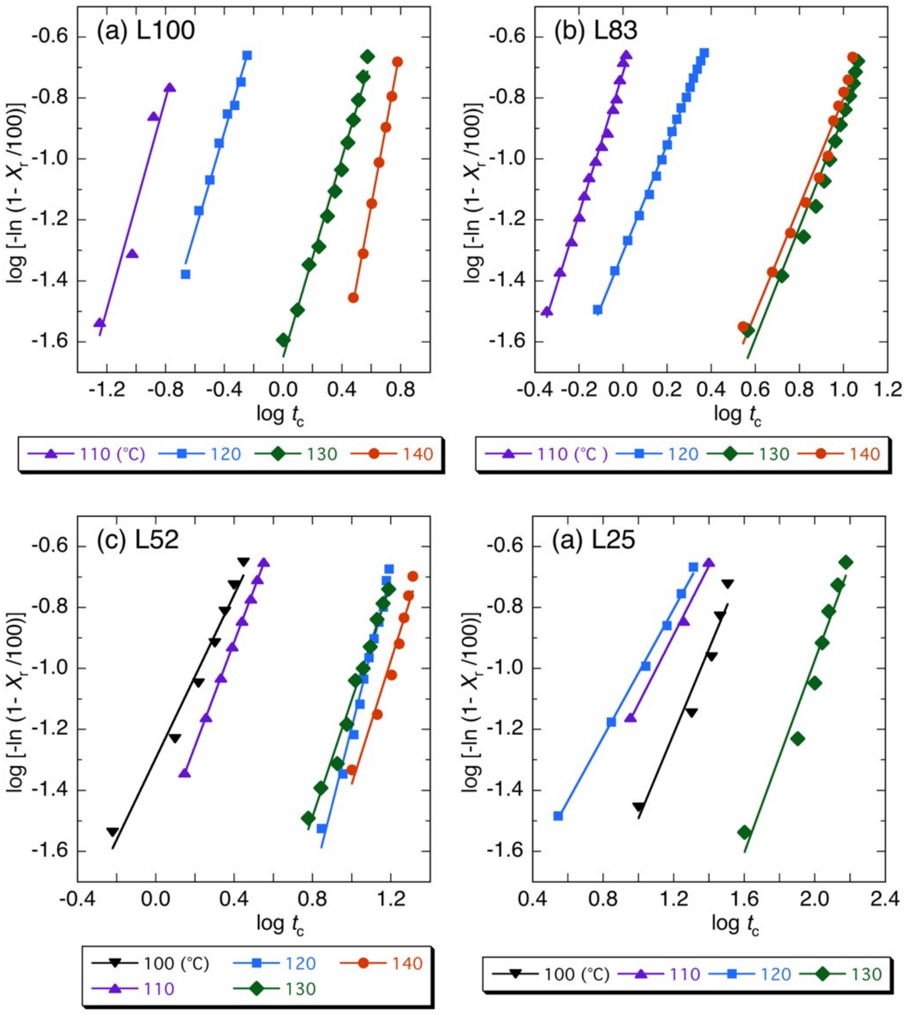

Figure S3. Avrami plot of PLLA (L100) (a), PLLA-*b*-PDLLA polymers, L83 (b), L52 (c), and L25 (d) crystallized at different crystallization temperature (T_c) values from the melt.

S7. WAXD profiles (Mo-Kα) of PLLA and PLLA-*b*-PDLLA polymers (Figure S4)

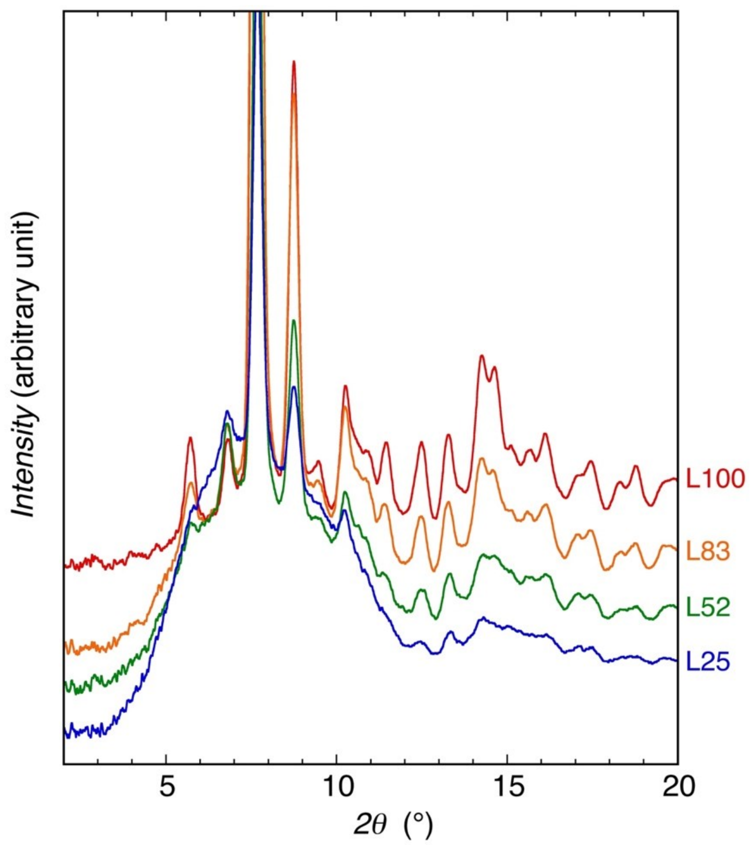

Figure S4. WAXD profiles (Mo-Kα) of PLLA, PLLA-*b*-PDLLA polymers crystallized at 130°C for 10 h from the melt.

S8. WAXD half-width of PLLA and PLLA-*b*-PDLLA polymers (Table S4)

Table S4. WAXD half-width of PLLA and PLLA-*b*-PDLLA polymers (113/203) obtained from Figure S4.

Code	PLLA fraction (%)	Half-width (°)
L100	100	0.299
L83	82.8	0.322
L52	52.4	0.348
L25	25.4	0.355