Supporting Information

for

Stereocomplex Formation between Enantiomeric Substituted Poly(lactide)s: Blends of Poly[(S)-2-hydroxybutyrate] and Poly[(R)-2-hydroxybutyrate]

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Appendices for Synthetic Procedure and Characterization of P(S-2HB) and P(R-2HB)

Synthetic Procedure. The polycondensation of (S)- or (R)-2-hydroxybutanoic acid was carried out with 2.5 wt% of p-toluenesulfonic acid under a constant nitrogen gas flow and atmospheric pressure for 5 hours, and then at a reduced pressure of 2.2 kPa (17 mmHg) for 24 hours. The polycondensation reaction was carried out in the molten state of (S)- or (R)-2-hydroxybutanoic at 130˚C, which is above the melting temperature (T_m) of (S)- or (R)-2-hydroxybutanoic (45-50˚C).

Polarimetry. The specific optical rotation ($[\alpha]^{25}_{589}$ per unit mass or per unit mol) values of synthesized P(S-2HB) and P(R-2HB) were measured in chloroform at a concentration of 1 g dL^{-1} and 25°C using a JASCO P-2100 polarimeter at a wave length of 589 nm. The $[\alpha]^{25}_{589}$ values per unit mass of P(S-2HB) and P(R-2HB) were -117 and 114 deg dm^{-1} g^{-1} cm^3, respectively, confirming optical activity of the synthesized polymers. These values were slightly lower than 130 and -121 deg dm^{-1} g^{-1} cm^3 of PLLA and PDLA having similar M_n values of 2.7 and $3.0x10^3$ g mol^{-1}, respectively. The $[\alpha]^{25}_{589}$ values of PLLA and PDLA with M_n exceeding 10^5 g mol^{-1} were reported to be -156 and 156 deg dm^{-1} g^{-1} cm^3, respectively, whose absolute values are respectively 26 and 35 deg dm^{-1} g^{-1} cm^3 higher than those with having lower M_n values of 2.7 and $3.0x10^3$ g mol^{-1}. That is, the higher number of end groups of low-molecular-weight PLLA and PDLA per unit mass is suggested to reduce the absolute $[\alpha]^{25}_{589}$ values.[21] Considering this effect of overall molecular weight, the absolute $[\alpha]^{25}_{589}$ values of P(S-2HB) and P(R-2HB) with M_n exceeding 10^5 g mol^{-1} may be several tens of deg dm^{-1} g^{-1} cm^3 higher than those in the present study. However, the lower absolute $[\alpha]^{25}_{589}$ values per unit mass of P(S-2HB) and P(R-2HB) compared to those of PLLA and PDLA are mainly

due to the relatively higher molecular weight of the monomer unit (86.1 g mol^{-1}) of P(2HB) compared to that of PLA (72.1 g mol^{-1}). The $[\alpha]^{25}_{589}$ values per unit mass of P(S-2HB) and P(R-2HB) can be converted to those per unit mol (-1.0x10^4 and 9.8x10^3 dm^{-1} mol^{-1} cm^3, respectively). These values are very similar to the $[\alpha]^{25}_{589}$ values per unit mol of PLLA and PDLA (-9.4x10^3 and 8.7x10^3 dm^{-1} mol^{-1} cm^3, respectively) and in agreement with the $[\alpha]^{25}_{589}$ values per unit mol of PLLA and PDLA (-1.0x10^4 and 9.3x10^3 dm^{-1} mol^{-1} cm^3), which values are corrected to remove the effect of the incorporated coinitiator (dodecanol) unit. This finding suggests that the helical nature of P(S-2HB) and P(R-2HB) in solution is very similar to that of PLLA and PDLA and the very high optical purities of P(S-2HB) and P(R-2HB), comparable to those of PLLA and PDLA (ca.95% or higher).

^{1}H NMR Spectroscopy. The 400 MHz ^{1}H NMR spectra of synthesized P(S-2HB) and P(R-2HB) were obtained in deuterated chloroform (50 mg mL^{-1}) by a Varian UNITY-400P Spectrometer using tetramethylsilane as the internal standard. The methine triplet, methylene multiplet, and methyl triplet peaks were observed at around 5.1, 2.0, and 1.0 ppm, respectively.

Table S1. Thermal properties of P(S-2HB), P(R-2HB), P(S-2HB)/P(R-2HB) stereocomplexes, PLLA, PDLA, and PLLA/PDLA stereocomplex during heating from 0°C

Specimen	Crystallization conditions		T_g [b]	T_{cc} [b]	T_m [b]	ΔH_{cc} [c]	ΔH_m [c]	$\Delta H_{cc}+\Delta H_m$ [c]
	Method [a]	Temp. (°C)	(°C)	(°C)	(°C)	(J g^{-1})	(J g^{-1})	(J g^{-1})
P(S-2HB)	S	25	26.7	70.1	102.5, 116.6	-6.3	34.7	28.4
P(R-2HB)			26.9	79.5	101.0, 115.3	-6.1	36.0	29.9
P(S-2HB)/P(R-2HB) SC [d]			40.9	-	211.7	0	63.9	63.9
P(S-2HB)	M	70	- [e]	-	103.2	0	36.6	36.6
P(R-2HB)		70	- [e]	-	101.6	0	35.1	35.1
P(S-2HB)/P(R-2HB) SC [d]		130	38.8	-	198.2	0	64.0	64.0
PLLA [f]	M	120	- [e]	- [e]	111.1, 131.9	-2.8	48.2	45.4
PDLA [f]			- [e]	60.5	107.1, 138.2	-5.7	35.8	30.1
PLLA/PDLA SC [d,f]			43.2	-	194.8	0	91.0	91.0

[a] S and M represent solution- and melt-crystallization, respectively.

[b] T_g, T_{cc}, and T_m are glass transition, cold crystallization, and melting temperatures, respectively.

[c] ΔH_{cc} and ΔH_{cc} are enthalpies of cold crystallization and melting, respectively.

[d] Stereocomplex.

[e] Too diffuse to be evaluated.

[f] Unpublished data for PLLA (M_n=2.7x10^3 g mol^{-1}, M_w/M_n=1.5) and PDLA (M_n=3.0x10^3 g mol^{-1}, M_w/M_n=1.9) crystallized at T_c of 120°C from the melt (pure PLLA, PDLA, PLLA/PDLA blend specimens and the procedures for obtaining WAXS and DSC data are the same as those reported in *Macromol. Chem. Phys.,* **2009**, *210*, 993-1002).

Table S2. The interplane distance (*d*) values of P(S-2HB), P(R-2HB), P(S-2HB)/P(R-2HB) stereocomplex crystals, assuming that the P(2HB) specimens have the same crystalline lattice types as those of the PLA specimens, together with those of the PLA specimens

Specimen	Crystallization conditions		*d* (nm) [2θ (degrees)]				
	Method [a]	Temp. (°C)	(100)	(110)/(200)	(203)	(110)	(210)
P(S-2HB)	S	25		0.599 [14.8]	0.513 [17.3]		
P(R-2HB)				0.603 [14.7]	0.516 [17.2]		
P(S-2HB)/P(R-2HB) SC [b]			0.827 [10.7]			0.480 [18.5], 0.460 [19.3]	0.415 [21.4]
P(S-2HB)	M	70		0.603 [14.7]	0.516 [17.2]		
P(R-2HB)		70		0.603 [14.7]	0.516 [17.2]		
P(S-2HB)/P(R-2HB) SC [b]		130	0.827 [10.7]			0.480 [18.5], 0.460 [19.3]	0.413 [21.5]
PLLA [c]	M	120		0.531 [16.7]	0.467 [19.0]		
PDLA [c]				0.531 [16.7]	0.465 [19.1]		
PLLA/PDLA SC [b,c]			0.744 [11.9]			0.429 [20.7]	0.372 [23.9]

[a] S and M represent solution- and melt-crystallization, respectively.

[b] Stereocomplex

[c] Unpublished data for PLLA (M_n=2.7x10^3 g mol^{-1}, M_w/M_n=1.5) and PDLA (M_n=3.0x10^3 g mol^{-1}, M_w/M_n=1.9) crystallized at T_c of 120°C from the melt (pure PLLA, PDLA, PLLA/PDLA blend specimens and the procedures for obtaining WAXS and DSC data are the same as those reported in *Macromol. Chem. Phys.,* **2009**, *210*, 993-1002).