Supplementary Information:

Synthesis and Stereocomplex Formation of Enantiomeric Alternating Copolymers with Two Types of Chiral Centers, Poly(lactic acid-*alt*-2-hydroxybutanoic acid)s

Hideto Tsuji^{*}, Kazuya Nakayama, and Yuki Arakawa

Department of Applied Chemistry and Life Science, Graduate School of Engineering, Toyohashi University of Technology, Tempaku-cho, Toyohashi, Aichi 441-8580, Japan E-mail: ht003@edu.tut.ac.jp

Contents

- S1. Experimental Section
- S1.1. Materials and synthesis
- S1.2. Sample preparation
- S1.3. Physical measurements and observation
- S2. ¹H NMR spectra of P(LLA-*alt*-L-2HB), P(DLA-*alt*-D-2HB), P(L-2HB), P(LLA-*co*-L-2HB), and PLLA (Figure S1)
- S3. ¹³C NMR spectra of P(LLA-alt-L-2HB) and P(DLA-alt-D-2HB) (Figure S2)
- S4. ¹³C NMR spectra of P(L-2HB), P(LLA-*co*-L-2HB), and PLLA (Figure S3)
- S5. WAXD profile of *N*,*N*-diisopropylurea (DIU) (Figure S4)
- S6. Interplanar distance and crystalline diffraction angle values of samples (Table S1)
- S7. Crystallinity and thermal properties of samples (Table S2)
- S8. FTIR spectroscopy (Figure S5 and Table S3)

S1. Experimental Section

S1.1. Materials and synthesis

Unless otherwise stated, commercially available chemicals were used without further purification. 4-(Dimethylamino)-pyridinium-*p*-toluene sulfonate (DPTS) was synthesized referring to Ref. S1. All the synthesized molecules (intermediates, monomers, and polymers) were synthesized according to Scheme 1 and referring to Refs. S1-S4. The synthetic procedures for L-configured isomers are representatively described as below. The D-configured isomers were basically prepared by the same procedures.

L-2HB

L-2-Aminobutyric acid (2.00 g, 19.4 mmol) and 0.5 M H₂SO₄ aqueous solution (80 mL) were put in a round flask, and the mixture was cooled to 0 °C in an ice bath. NaNO₂ (8.03 g, 116.4 mmol) dissolved in distilled water (27 mL) was added to the flask at 0 °C. The mixture was stirred at 0 °C for 3 hours, and subsequently was stirred at ambient temperature for 3 days. The reaction mixture was diluted with ethyl acetate (EA), washed with water and brine. The organic phase was dried over MgSO₄, and the volatiles were removed *in vacuo*, to yield L-2HB without further purification. Yield: 85%. ¹H NMR (400 MHz, CDCl₃) δ 4.27 (q, 1H), 2.02-1.69 (m, 2H), 1.03 (q, 3H) ppm.

D-2HB

Yield: 98%. ¹H NMR (400 MHz, CDCl₃) δ 4.26 (q, 1H), 2.02-1.66 (m, 2H), 1.02 (q, 3H) ppm.

Bn-L-2HB

In a two-necked flask, L-2HB (1.60 g, 15.4 mmol), KOH (0.99 g, 17.7 mmol), and dehydrated *N*,*N*-dimethylformamide (DMF) (40 mL) were stirred at 100 °C under argon atmosphere. After 1 hour, benzyl bromide (2.21 mL, 18.5 mmol) was added to the flask, and the mixture was stirred at 100 °C for 24 hours. The reaction mixture was diluted with dichloromethane (DCM), and washed with water and brine. The organic phase was dried over MgSO₄, and the volatiles were evaporated *in vacuo*. The residue was

purified by column chromatography on silica gel with a mixed solvent [DCM/hexane = 4:1(v/v)] as an eluent, to yield Bn-L-2HB. Yield: 66%. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.33 (m, 5H), 5.22 (q, 2H), 4.20 (q, 1H), 1.91-1.66 (m, 2H), 0.94 (t, 3H) ppm.

Bn-D-2HB

Yield: 63%. ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.32 (m, 5H), 5.22 (q, 2H), 4.20 (q, 1H), 1.91-1.65 (m, 2H), 0.94 (t, 3H) ppm.

TBDPS-LLA-Me

Methyl L-(-)-lactate (1.10 mL, 11.6 mmol), 4-dimethylaminopyridine (DMAP) (0.880 g, 7.20 mmol), dehydrated DCM (40 mL), and triethylamine (TEA) (4.03 mL, 28.8 mmol) were added to a two-necked flask purged with argon gas and the mixture was cooled to 0 °C in an ice bath. *tert*-Butyldiphenylchlorosilane (TBDPSCl) (3.29 mL, 12.8 mmol) was added dropwise to the flask at 0 °C. The mixture was stirred at ambient temperature for 12 hours under argon atmosphere. The reaction mixture was diluted with DCM, and the organic phase was washed with water and brine, and dried over MgSO₄. The volatiles were removed *in vacuo*, and the residue was purified by column chromatography on silica gel with a mixed solvent [DCM/hexane = 1:1 (v/v)] as an eluent, to yield TBDPS-LLA-Me. Yield: 97%. ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.66 (m, 4H), 7.44-7.35 (m, 6H), 4.29 (q, 1H), 3.56 (s, 3H), 1.37 (d, 3H), 1.10 (s, 9H) ppm.

TBDPS-DLA-Me

Yield: 98%. ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.65 (m, Ar-*H*, 4H), 7.44-7.35 (m, Ar-*H*, 6H), 4.29 (q, *J*=6.8 Hz, C-*H*, 1H), 3.56 (s, O-C*H*₃, 3H), 1.37 (d, *J*=6.8 Hz, C-C*H*₃, 3H), 1.10 (s, C-(C*H*₃)₃, 9H) ppm.

TBDPS-LLA

TBDPS-LLA-Me (4.92 g, 14.4 mmol) and tetrahydrofuran (THF) (80 mL) were added to a round flask, and the mixture was cooled to 0 °C in an ice bath. Then, LiOH•H₂O (2.42 g, 57.6 mmol) dissolved in distilled water (50 mL) was added to the flask at 0 °C, and the mixture was stirred at ambient temperature for 5 hours. The reaction mixture was diluted with distilled water and neutralized with 1M hydrochloric acid. The resulting organic phase was diluted with diethyl ether, washed with water and brine, and dried over MgSO₄. The volatiles were removed *in vacuo*, to yield TBDPS-LLA without further purification. Yield: 75%. ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.63 (m, 4H), 7.48-7.37 (m, 6H), 4.32 (q, 1H), 1.32 (d, 3H), 1.11 (s, 9H) ppm.

TBDPS-DLA

Yield: 82%. ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.61 (m, 4H), 7.49-7.38 (m, 6H), 4.33 (q, 1H), 1.30 (d, 3H), 1.11 (s, 9H) ppm.

TBDPS-LLA-L-2HB-Bn

TBDPS-LLA (4.28 g, 13.0 mmol), Bn-L-2HB (2.52 g, 13.0 mmol), DPTS (0.76 g, 2.6 mmol), and dehydrated DCM (40 mL) were added to a two necked flask, and the mixture was cooled to 0°C in an ice bath. Then, *N*,*N*'-diisopropylcarbodiimide (DIC) (3.06 mL, 19.5 mmol) was added to the flask at 0°C, and the mixture was stirred at ambient temperature for 24 hours. The reaction mixture was filtrated to remove the precipitated urethane, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with a mixed solvent [DCM/hexane = 1:1(v/v), which was gradually changed to 2/3]] as an eluent, to yield TBDPS-LLA-L-2HB-Bn. Yield: 56%. ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (m, 4H), 7.45-7.29 (m, 11H), 5.13 (q, 2H), 4.87 (t, 1H), 4.34 (q, 1H), 1.74 (m, 2H), 1.37 (d, 3H), 1.09 (s, 9H), 0.80 (t, 3H) ppm.

TBDPS-DLA-D-2HB-Bn

Yield: 60%. ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.65 (m, 4H), 7.45-7.29 (m, 11H), 5.13 (q, 2H), 4.87 (t, 1H), 4.34 (q, 1H), 1.74 (m, 2H), 1.37 (d, 3H), 1.09 (s, 9H), 0.81 (t, 3H) ppm.

LLA-L-2HB-Bn

TBDPS-LLA-L-2HB-Bn (3.40 g, 6.74 mmol), dehydrated THF (50 mL) and acetic acid (0.69 mL, 12.1 mmol) was added to a two-necked flask that was purged with an argon gas, and cooled to 0° C in an ice bath. Tetrabutylammonium fluoride (1 M in THF) (TBAF) (10.1 mL, 10.1 mmol) was added dropwise to the flask, and the mixture was stirred at ambient temperature for 6 hours. The reaction mixture was diluted with diethyl ether, washed with water and brine, and dried over MgSO₄. After the volatiles were removed in vacuo, the residue was purified by column chromatography on silica gel with a mixed solvent [EA/hexane = 1/6 (v/v), which was gradually changed to 1/1] as an eluent, to yield LLA-L-2HB-Bn. Yield: 87%. ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.32 (m, 5H), 5.17 (q, 2H), 5.09 (t, 1H), 4.36 (q, 1H), 1.92 (m, 2H), 1.44 (d, 3H), 0.97 (t, 3H) ppm.

DLA-D-2HB-Bn

Yield: 73%. ¹H NMR (400 MHz, CDCl₃) δ 7.40-7.31 (m, 5H), 5.18 (q, 2H), 5.09 (t, 1H), 4.36 (q, 1H), 1.92 (m, 2H), 1.44 (d, 3H), 0.97 (t, 3H) ppm.

LLA-L-2HB

LLA-L-2HB-Bn (1.59 g, 5.97 mmol) and Pd/C (79.5 mg, 5wt%) were put in a two-necked flask, which was purged with hydrogen gas. Dried EA (30 mL) was added to the flask, and the mixture was stirred at room temperature for 24 hours under hydrogen atmosphere. The reaction mixture was filtered with Celite[®], and the solvent was removed *in vacuo*, to yield LLA-L-2HB. Yield: 94%. ¹H NMR (400 MHz, CDCl₃) δ 5.09 (q, 1H), 4.39 (q, 1H), 2.01-1.90 (m, 2H), 1.50 (d, 3H), 1.04 (t, 3H) ppm.

DLA-D-2HB

Yield: 97%. ¹H NMR (400 MHz, CDCl₃) δ 5.09 (q, 1H), 4.39 (q, 1H), 2.01-1.91 (m, 2H), 1.50 (d, 2H), 1.04 (t, 3H) ppm.

Poly(LLA-alt-L-2HB)

LLA-L-2HB (400 mg, 2.27 mmol), DPTS (131.6 mg, 0.45 mmol), and dehydrated DCM were put in a two-necked flask, which was purged with argon gas, and the mixture was cooled to 0 °C in an ice bath. Then, DIC (0.51 mL, 3.41 mmol) was added dropwise into the mixture at 0 °C and the mixture was stirred at ambient temperature for 24 hours. The reaction mixture was filtrated to insoluble urethane, and the volatiles were remove *in vacuo*. The residue was purified by extraction with methanol, to yield Poly(LLA-*alt*-L-2HB). Yield: 34%. ¹H NMR (400 MHz, CDCl₃) δ 5.21 (q, 1H), 5.07 (q, 1H), 2.03-1.92 (m, 2H), 1.58 (d, 3H), 1.03 (t, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 168.9, 73.6, 68.2, 24.3, 16.7, 9.2 ppm.

Poly(DLA-alt-D-2HB)

Yield: 20%. ¹H NMR (400 MHz, CDCl₃) δ 5.21 (q, 1H), 5.04 (q, 1H), 2.04-1.92 (m, 2H), 1.58 (d, 3H), 1.03 (t, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 168.9, 73.6, 68.9, 24.3, 16.7, 9.2 ppm. 3, 16.7, 9.2 ppm.

S1.2. Sample preparation

The purified polymers were dried under reduced pressure for at least six days before sample preparation. The crystallization of neat (unblended) and blended polymers was carried out by the following two methods: solvent evaporation (casting) and precipitation. Equimolar binary polymer blend was prepared by the procedure stated in the previous papers.^{S5–S7} Briefly, each solution of the two enantiomeric polymers was prepared separately to have a polymer concentration of 1 g dL⁻¹ and then admixed at 1:1 (w:w) ratio under vigorous stirring for preparation of blend samples. Dichloromethane (guaranteed grade, Nacalai Tesque Inc.) was used as the solvent. The mixed solution was cast onto a petri-dish,

followed by solvent evaporation at 25°C for approximately one day. The obtained polymer blend was further dried under reduced pressure for at least six days. The precipitated samples were prepared by dissolving solvent-evaporated samples at a concentration of 2 g dL⁻¹ (10 mg/0.5 mL) in dichloromethane and reprecipitation with stirred methanol (5 mL) as the nonsolvent.^{58,59}

S1.3. Physical measurements and observation

The weight- and number-average molecular weights (M_w and M_n , respectively) of the polymers were evaluated in chloroform at 40°C using a Tosoh (Tokyo, Japan) gel permeation chromatography (GPC) system with two TSK gel columns (GMH_{XL}) and polystyrene standards. Therefore, the M_w and M_n values are given relative to polystyrene.^{S6} The ¹H and ¹³C NMR spectra were measured in deuterated chloroform (50 mg mL⁻¹) by a Bruker BioSpin (Kanagawa, Japan) AVANCE III 400 using tetramethylsilane as the internal standard.^{S10,S11} The specific optical rotation ([a]²⁵₅₈₉) of the polymers was 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.^{S6}

The glass transition, cold crystallization, and melting temperatures (T_g , T_{cc} , and T_m , respectively) and the enthalpies of cold crystallization and melting (ΔH_{cc} and ΔH_m , respectively) were determined with a Shimadzu (Kyoto, Japan) DSC-60 differential scanning calorimeter under a nitrogen gas flow at a rate of 50 mL min⁻¹.^{S6} The samples (ca. 3 mg) were heated from 0 to 250°C at a rate of 10°C min⁻¹). ^{S6} Wide angle X-ray diffraction (WAXD) measurements were carried out at 25°C using a RINT-2500 (Rigaku Co., Tokyo, Japan) equipped with a Cu-K_a source [wave length (λ) = 1.5418 Å].^{S6} In a 2 θ range of 5–30°, the crystalline diffraction peak areas of respective crystalline species relative to the total area between a diffraction profile and a baseline were used to estimate the X_c values.^{S6} Fourier transform infrared (FTIR) spectra were obtained using a JASCO (Tokyo, Japan) FT/IR-4200 by the KBr (For Infrared Spectrophotometry, Wako Pure Chemical Industries, Ltd., Osaka, Japan) method.^{S7}

S2. ¹H NMR spectra of P(LLA-alt-L-2HB), P(DLA-alt-D-2HB), P(L-2HB), P(LLA-co-L-2HB),



and PLLA (Figure S1)

Figure S1. ¹H NMR spectra of (a) P(LLA-*alt*-L-2HB), P(DLA-*alt*-D-2HB), (b) P(L-2HB), P(LLA*co*-L-2HB) (56/44) random copolymer, and PLLA in CDCl₃. The spectra in Figure S2(b) were reproduced from ref. S9 with permission from Elsevier.



S3. ¹³C NMR spectra of P(LLA-alt-L-2HB) and P(DLA-alt-D-2HB) (Figure S2)

Figure S2. ¹³C NMR spectra of (a) carbonyl, (b) methine, (c) methylene, (d) methyl carbons of P(LLA-*alt*-L-2HB) and P(DLA-*alt*-D-2HB) in CDCl₃.



S4. ¹³C NMR spectra of P(L-2HB), P(LLA-*co*-L-2HB), and PLLA (Figure S3)

Figure S3. ¹³C NMR spectra of (a) carbonyl, (b) methine, (c) methylene, (d) methyl carbons of P(L-2HB), P(LLA-*co*-L-2HB) (56/44) random copolymer, and PLLA in CDCl₃. The spectra in Figure S4(a) were reproduced from ref. S9 with permission from Elsevier.

S5. WAXD profile of *N*,*N*'-diisopropylurea (DIU) (Figure S4)



Figure S4. WAXD profile of *N*,*N*-diisopropylurea (DIU).

S6. Interplanar distance and crystalline diffraction angle values of samples (Table S1)

Crystallization ^{a)}) $d(\text{\AA})[2\theta(^{\circ})]$			Refs.
	$9^{\circ} \leq 2\theta \leq 12^{\circ}$	$16^{\circ} \leq 2\theta \leq 21^{\circ}$	$19^{\circ} \leq 2\theta \leq 24^{\circ}$	
SE	7.72 [11.46]	4.47 [19.88]	3.90 [22.83]	Present
Pr	7.89 [11.21]	4.54 [19.57]	3.93 [22.63]	study
MC ($T_{\rm c} = 160^{\circ}$ C)	7.85 [11.28]	4.52 [19.63] 4.42 [20.10]	3.92 [22.71]	S12
SE	7.69 [11.51]	4.45 [19.95]	3.88 [22.95]	
MC ($T_{\rm c} = 70^{\circ}{\rm C}$)	8.35 [10.59]	4.81 [18.45] 4.64 [19.12]	4.17 [21.32]	S6
SE	8.25 [10.72]	4.71 [18.83]	4.14 [21.46]	
Pr	8.31 [10.65]	4.77 [18.61]	4.14 [21.46]	
MC ($T_{c} = 120^{\circ}C$)	8.43 [10.50]	4.86 [18.25] 4.68 [18.95]	4.21 [21.11]	S13
MC $(T_{\rm c} = 80^{\circ}{\rm C})$	8.39 [10.55]	4.86 [18.27] 4.66 [19.06]	4.21 [21.10]	
SE	8.27 [10.70]	4.79 [18.51] 4.64 [19.11]	4.17 [21.31]	
MC ($T_c = 130^{\circ}C$)	7.42 [11.93]	4.29 [20.72]	3.71 [23.99]	S14
MC ($T_c = 130^{\circ}C$)	8.28 [10.68]	4.78 [18.56] 4.60 [19.29]	4.14 [21.46]	S15
$MC(T_c = 130^{\circ}C)$	9.16 [9.66]	5.28 [16.79] 5.01 [17.72]	4.57 [19.44]	S16
	Crystallization ^{a)} SE Pr MC ($T_c = 160^{\circ}C$) SE MC ($T_c = 70^{\circ}C$) SE Pr MC ($T_c = 120^{\circ}C$) MC ($T_c = 80^{\circ}C$) SE MC ($T_c = 130^{\circ}C$) MC ($T_c = 130^{\circ}C$) MC ($T_c = 130^{\circ}C$)	Crystallization a) $9^{\circ} \leq 2\theta \leq 12^{\circ}$ SE7.72 [11.46]Pr7.89 [11.21]MC ($T_c = 160^{\circ}$ C)7.85 [11.28]SE7.69 [11.51]MC ($T_c = 70^{\circ}$ C)8.35 [10.59]SE8.25 [10.72]Pr8.31 [10.65]MC ($T_c = 120^{\circ}$ C)8.43 [10.50]MC ($T_c = 80^{\circ}$ C)8.39 [10.55]SE8.27 [10.70]MC ($T_c = 130^{\circ}$ C)7.42 [11.93]MC ($T_c = 130^{\circ}$ C)8.28 [10.68]MC ($T_c = 130^{\circ}$ C)9.16 [9.66]	$\begin{array}{c c} \mbox{Crystallization}^{a)} & d(\mbox{Å}) [2\theta(\mbox{°})] \\ \hline g^{\circ} \leqq 2\theta \leqq 12^{\circ} & 16^{\circ} \leqq 2\theta \leqq 21^{\circ} \\ \hline g^{\circ} \leqq 2\theta \lessgtr 12^{\circ} & 16^{\circ} \leqq 2\theta \leqq 21^{\circ} \\ \hline g^{\circ} \oiint 2\theta \And 12^{\circ} & 16^{\circ} \And 2\theta \And 21^{\circ} \\ \hline g^{\circ} \And 2\theta \And 12^{\circ} & 16^{\circ} \end{Bmatrix} 2\theta \leqq 21^{\circ} \\ \hline g^{\circ} \And 2\theta \And 12^{\circ} & 16^{\circ} \end{Bmatrix} 2\theta \And 21^{\circ} \\ \hline g^{\circ} \And 2\theta \And 12^{\circ} & 16^{\circ} \end{Bmatrix} 2\theta \And 2\theta \And 21^{\circ} \\ \hline g^{\circ} \end{Bmatrix} 2\theta \And 12^{\circ} & 16^{\circ} \end{Bmatrix} 2\theta \And 2\theta \And 21^{\circ} \\ \hline g^{\circ} \end{Bmatrix} 2\theta \end{Bmatrix} 12^{\circ} & 16^{\circ} \end{Bmatrix} 2\theta \And 2\theta \end{Bmatrix} 2\theta \end{Bmatrix} 12^{\circ} & 16^{\circ} \end{Bmatrix} 112^{\circ} & 4.47 [19.88] \\ \hline MC(T_{c} = 160^{\circ}C) & 7.85 [11.28] & 4.52 [19.63] & 4.42 [20.10] \\ g^{\circ} \And 8.25 [10.72] & 4.51 [18.45] & 4.64 [19.12] \\ g^{\circ} \end{Bmatrix} 8.25 [10.72] & 4.71 [18.83] \\ Pr & 8.31 [10.65] & 4.77 [18.61] \\ MC(T_{c} = 120^{\circ}C) & 8.43 [10.50] & 4.86 [18.25] & 4.68 [18.95] \\ MC(T_{c} = 80^{\circ}C) & 8.39 [10.55] & 4.86 [18.27] & 4.66 [19.06] \\ g^{\circ} \end{Bmatrix} 8.27 [10.70] & 4.79 [18.51] & 4.64 [19.11] \\ MC(T_{c} = 130^{\circ}C) & 7.42 [11.93] & 4.29 [20.72] \\ MC(T_{c} = 130^{\circ}C) & 9.16 [9.66] & 5.28 [16.79] & 5.01 [17.72] \\ \end{array}$	$\begin{array}{c c} Crystallization^{a} & d(Å) [2\theta(°)] \\ \hline g \circ \leqq 2\theta \leqq 12^{\circ} & 16^{\circ} \leqq 2\theta \leqq 21^{\circ} & 19^{\circ} \leqq 2\theta \leqq 24^{\circ} \\ \hline SE & 7.72 [11.46] & 4.47 [19.88] & 3.90 [22.83] \\ Pr & 7.89 [11.21] & 4.54 [19.57] & 3.93 [22.63] \\ MC (T_c = 160^{\circ}C) & 7.85 [11.28] & 4.52 [19.63] & 4.42 [20.10] & 3.92 [22.71] \\ SE & 7.69 [11.51] & 4.45 [19.95] & 3.88 [22.95] \\ MC (T_c = 70^{\circ}C) & 8.35 [10.59] & 4.81 [18.45] & 4.64 [19.12] & 4.17 [21.32] \\ SE & 8.25 [10.72] & 4.71 [18.83] & 4.14 [21.46] \\ Pr & 8.31 [10.65] & 4.77 [18.61] & 4.14 [21.46] \\ MC (T_c = 120^{\circ}C) & 8.43 [10.50] & 4.86 [18.25] & 4.68 [18.95] & 4.21 [21.11] \\ MC (T_c = 80^{\circ}C) & 8.39 [10.55] & 4.86 [18.27] & 4.66 [19.06] & 4.21 [21.10] \\ SE & 8.27 [10.70] & 4.79 [18.51] & 4.64 [19.11] & 4.17 [21.31] \\ MC (T_c = 130^{\circ}C) & 7.42 [11.93] & 4.29 [20.72] & 3.71 [23.99] \\ MC (T_c = 130^{\circ}C) & 9.16 [9.66] & 5.28 [16.79] & 5.01 [17.72] & 4.57 [19.44] \\ \end{array}$

Table S1. Interplanar	distance (d) and crystalli	ne diffraction angle (2θ)	values of samples.
-----------------------	----------------------------	----------------------------------	--------------------

^{a)} MC, SE, and Pr indicate that the samples were prepared by melt-crystallization at shown T_c, solvent-evaporation, and precipitation, respectively. ^{b)} The 2θ values as peak-top angles were estimated using the intersection of two contacting lines of higher and lower angle

sides for each peak.

S7. Crystallinity and thermal properties of samples (Table S2)

Table S2.	Crystallinity	and thermal	properties of	samples.
	2 2		1 1	1

Sample	Preparation	Xc ^{a)} (%)	Tg ^{b)} (°C)	<i>T</i> _m ^{b)} (°C)	$ \frac{\Delta H_{\rm m}^{\rm c)}}{({\rm J~g}^{-1})} $
P(LLA-alt-L-2HB)	Purification	0	21.6		
	Solvent-evaporation	0	17.6		
	Precipitation	0	40.4		
P(DA-alt-D-2HB)	Purification	0	20.9		
. ,	Solvent-evaporation	0	19.7		
	Precipitation	0	15.5, 29.4		
P(LLA-alt-L-2HB)/P(DLA-alt-D-2HB) blend	Solvent-evaporation	66.7	36.3	187.9	65.4
	Precipitation	60.8	33.7	187.5	55.8

^{a)} Crystallinity estimated by WAXD. ^{b)} $T_{\rm g}$, $T_{\rm m}$, and $\Delta H_{\rm m}$ are glass transition and melting temperatures and melting enthalpy, respectively.

S8. FTIR spectroscopy (Figure S5 and Table S3)

The FTIR spectra of solvent-evaporated neat P(LLA-*alt*-L-2HB), P(DLA-*alt*-D-2HB), and P(LLA-*alt*-L-2HB)/P(DLA-*alt*-D-2HB) blend are shown in Figure S5, along with assignments of LA and 2HB units reported in the literatures for PLLA^{S17-S20} and a book chapter for FTIR (δ CH₂).^{S21} The assignments were for both LA and 2HB units, except for δ CH₂ for 2HB units. The solvent evaporated samples were chosen for the measurements because the solvent-evaporated P(LLA-*alt*-L-2HB)/P(DLA-*alt*-D-2HB) blend had higher *X*_c value than that of precipitated one. The peak frequencies of the FTIR spectra are tabulated in Table S3. As seen in Table S3, all peak frequencies of P(LLA-*alt*-L-2HB)/P(DLA-*alt*-D-2HB) blend were different from those of neat P(LLA-*alt*-L-2HB) and P(DLA-*alt*-D-2HB). Since the P(LLA-*alt*-L-2HB)/P(DLA-*alt*-D-2HB) blends can form SC crystalline phase but the neat P(LLA-*alt*-L-2HB) and P(DLA-*alt*-D-2HB) were amorphous, such large frequency changes of FTIR spectra can be ascribed to the stronger interaction between P(LLA-*alt*-L-2HB) and P(DLA-*alt*-D-2HB) than that between P(LLA-*alt*-L-2HB) or P(DLA-*alt*-D-2HB) chains, resulting in SC formation.



Figure S5. FTIR spectra of solvent-evaporated unblended P(LLA-*alt*-L-2HB), P(DLA-*alt*-D-2HB), and P(LLA-*alt*-L-2HB)/P(DLA-*alt*-D-2HB) blend and peak assignments.

The frequency change of vC=O peak is frequently utilized to monitor SC crystallization. The frequency change of vC=O peak of P(LLA-*alt*-L-2HB)/P(DLA-*alt*-D-2HB) blend (1761 to 1759 cm⁻¹) by SC crystallization was smaller than those of PLLA/PDLA blends (1754 to 1749 cm⁻¹ or 1756 to 1751 cm⁻¹)^{S19,S20} but larger than that of P(LLA-*alt*-GA)/P(DLA-*alt*-GA) blend (1760 to 1760 cm⁻¹, no change).^{S7} These frequency changes cannot be simply compared, since in the case of P(LLA-*alt*-L-2HB) and P(DLA-*alt*-D-2HB), frequency changes were those between stereocomplexed blends and amorphous L- or D-configured neat polymers, whereas in the cases of PLLA and PDLA and of P(LLA-*alt*-GA) and P(DLA-*alt*-GA), L- or D-configured, frequency changes were those between stereocomplexed blends and homo-crystallized L- or D-configured neat polymers.

Table S3. The	peak frequ	uencies of	FTIR s	pectra of sam	ples.
---------------	------------	------------	--------	---------------	-------

Assignments	FTIR Frequencies (cm ⁻¹)				
	P(LLA-alt-L-2HB)	P(DLA-alt-D-2HB)	Average ^{a)}	Blend	
vC=0	1761	1760	1761	1759	
$\delta CH + \nu COC$	1262	1261	1262	1263	
VasCOC	1211	1209	1210	1215	
VasCOC	1184	1183	1184	1181	
$ ho_{ m as} m CH_3$	1126	1126	1126	1131	
<i>v</i> _s COC	1091	1092	1192	1089	
vC-CH ₃	1044	1044	1044	1040	

^{a)} The averages of the peak frequencies of P(LLA-alt-L-2HB) and P(DLA-alt-D-2HB).

References

- S1. J. S. Moore and S. I. Stupp, *Macromolecules*, 1990, 23, 65-70.
- S2. R. M. Stayshich and T. Y. Meyer, J. Polym. Sci. A, 2008, 46, 4704–4711.
- S3. R. M. Stayshich and T. Y. Meyer, J. Am. Chem. Soc., 2010, 132, 10920-10934.
- S4. H. Tsuji and Y. Arakawa Polym. Chem., 2018, 9, 2446-2457.
- S5. H. Tsuji, N. Masaki, Y. Arakawa, K. Iguchi and T. Sobue, *Cryst. Growth Des.*, 2018, 18, 521– 530.
- S6. H. Tsuji, K. Osanai and Y. Arakawa, Cryst. Growth. Des., 2018, 18, 6009-6019.
- S7. H. Tsuji, M. Yamasaki and Y. Arakawa, ACS Appl. Polym. Mater., 2019, 1, 1476–1484.
- S8. H. Tsuji, S. Noda, T. Kimura, T. Sobue and Y. Arakawa, Sci. Rep., 2017, 7, Article number: 45170.
- S9. H. Tsuji and T. Sobue, Polymer, 2015, 72, 202–211.
- S10. Y. Sakamoto and H. Tsuji, Polymer, 2013, 54, 2422-2434.
- S11.H. Tsuji, Y. Arakawa and N. Matsumura, Polym. Bull., 2019, 76, 1199-1216.
- S12. H. Tsuji and T. Sobue, RSC Adv., 2015, 5, 83331–83342.
- S13.H. Tsuji, K. Osanai and Y. Arakawa, Cryst. Growth. Des., 2020, 20, 1047–1057.
- S14. L. Bouapao and H. Tsuji, Macromol. Chem. Phys., 2009, 210, 993-1003.
- S15.H. Tsuji and A. Okumura, *Macromolecules*, 2009, 42, 7263–7266.
- S16. H. Tsuji and T. Sobue. Polymer, 2015, 69, 186-192.
- S17.G. Kister, G. Cassanas and M. Vert, Polymer, 1998, 39, 267-273.
- S18.C. M. B. Gonçalves, J. A. P. Coutinho and I. M. Marrucho, in *Poly(lactic acid): Synthesis, structures, properties, processing, and applications (Wiley Series on Polymer Engineering and Technology)*, ed. R. Auras, L. -T. Lim, S. E. M. Selke and H. Tsuji, John Wiley & Sons, Inc., NJ, 2010, Chapter 8. pp. 97–112.
- S19. J. Zhang, H. Sato, H. Tsuji, I. Noda and Y. Ozaki, *Macromolecules*, 2005, 38, 1822–1828.
- S20. J. Zhang, H. Sato, H. Tsuji, I. Noda and Y. Ozaki, J. Mol. Struct., 2005, 735-736, 249-257.
- S21.R. M. Silverstein, F. X. Webster, D. J. Kiemle and D. L. Bryce, Spectrometric Identification of Organic Compounds, 8th Edition, John Wiley & Sons, Inc., NJ, 2014, Chapter 2, Infrared Spectroscopy, pp. 71–125.