Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information for:

Synthesis, Properties, and Crystallization of Alternating Stereo Copolymer Poly(L-lactic acid-*alt*-D-lactic acid) [Syndiotactic Poly(lactic acid)] and its Blend with Isotactic Poly(lactic acid)

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Contents

S1. Synthesis of PLLA (i-PLA)

The synthesis for PLLA was performed corresponding to the same procedure for s-PLA described in the manuscript using the method reported by Stayshich and Meyer.[S1,S2]

S1.1. Methyl (*S*)-2-[(*tert*-butyldiphenylsilyl)oxy]propanoate (1b)

DMAP (0.880 g, 7.20 mmol), Methyl L-(-)-lactate (1.36 mL, 14.4 mmol), TEA (4.03 mL, 28.8 mmol) and *tert*-butylchlorodiphenylsilane (4.10 mL, 16.0 mmol) were used. A colorless liquid (5.18 g, Yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (t, J = 6.8 Hz, 4H), 7.46-7.33 (m, 6H), 4.28 (q, J = 6.9 Hz, 1H), 3.56 (s, 3H), 1.37 (d, J = 6.9 Hz, 3H), 1.09 (s, 9H) ppm.

S1.2. (*S*)-2-[(*tert*-Butyldiphenylsilyl)oxy]propanoic acid (2b)

(*S*)-2-[(*tert*-butyldiphenylsilyl)oxy]propanoate (5.15 g, 15.0 mmol) and $LiOH \cdot H_2O$ (2.52 g, 60.1 mmol) were used. A colorless liquid (3.76 g, Yield: 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.51-7.37 (m, 6H), 4.33 (q, J = 6.8 Hz, 1H), 1.31 (d, J = 6.8 Hz, 3H), 1.18 (s, 9H) ppm.

S1.3. Benzyl (*S*)-2-({(*S*)-2-[(*tert*-butyldiphenylsilyl)oxy]propanoyl}oxy)propanoate (3b)

(*S*)-2-[(*tert*-butyldiphenylsilyl)oxy]propanoic acid (2.60 g, 7.92 mmol), DMAP (0.484 g, 3.96 mmol), Benzyl (S)-(-)-lactate (1.27 mL, 7.92 mmol) were used. A colorless liquid (3.85 g, Yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.63 (m, 4H), 7.45-7.29 (m, 11H), 5.15 (s, 2H), 5.01 (q, J = 6.8 Hz, 1H), 4.38 (q, J = 6.8 Hz, 1H), 1.55 (s, 3H), 1.42 (d, J = 6.8 Hz, 3H), 1.36 (d, J = 6.8 Hz, 3H), 1.09 (s, 9H) ppm.

S1.4. Benzyl (*S*)-2-{[(*S*)-2-hydroxypropanoyl]oxy}propanoate (4b)

(S)-2-({(S)-2-[(tert-butyldiphenylsilyl)oxy]propanoyl)oxy})propanoate (2.14 g, 4.37 mmol), acetic acid (0.375 mL, 6.55 mmol) and TBAF (6.55 mL, 6.55 mmol) were used. A colorless liquid (0.955 g, Yield: 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.31 (m, 5H), 5.27-5.13 (m, 3H), 4.38-4.30 (m, 1H), 2.66 (d,

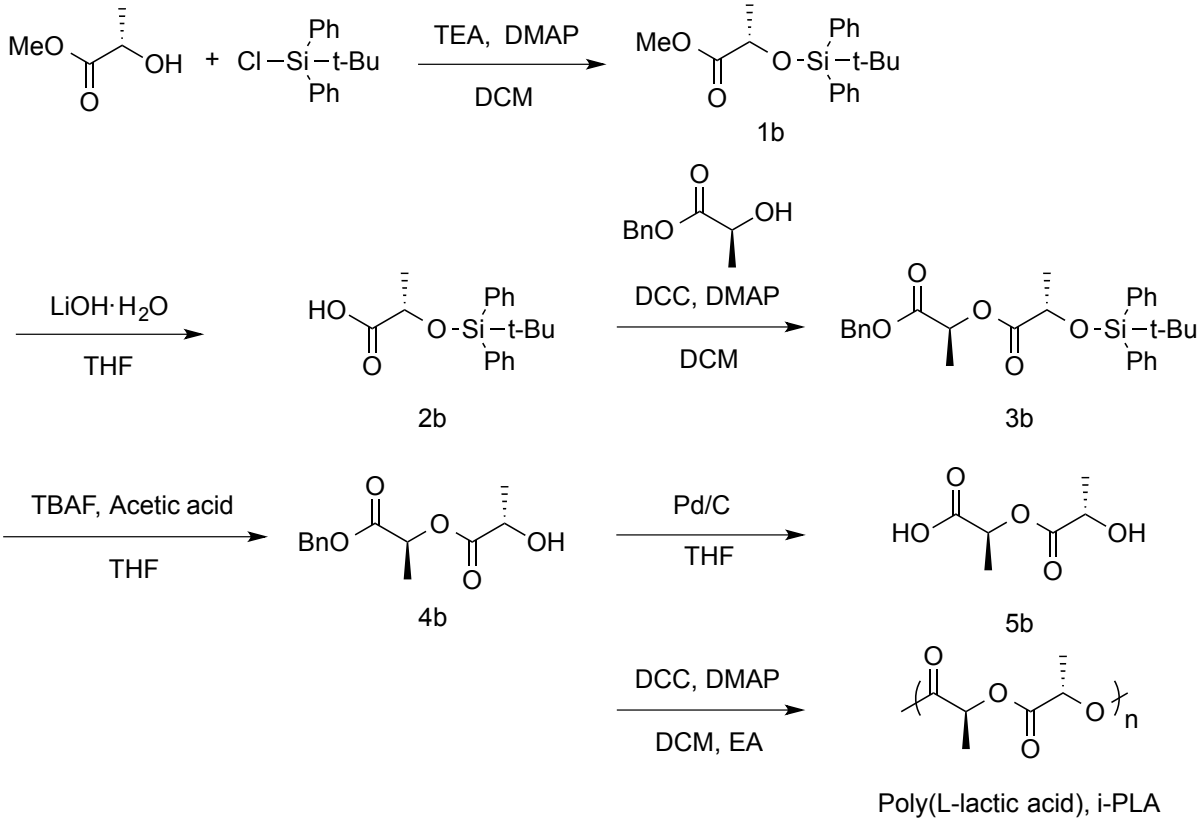
J = 5.6 Hz, 1H), 1.54 (d, *J* = 7.2 Hz, 3H), 1.44 (d, *J* = 6.8 Hz, 3H) ppm.

S1.5. (*S*)-2-{[(*R*)-2-Hydroxypropanoyl]oxy}propanoic acid (5b)

Benzyl (*S*)-2-{[(*R*)-2-hydroxypropanoyl]oxy}propanoate (0.926 g) and Pd/C (0.185 g) were used. A colorless liquid (0.427 g, Yield: 64%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (q, *J* = 7.2 Hz, 1H), 5.0-4.4 (br, 2H), 4.37 (q, *J* = 6.9 Hz, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.49 (d, *J* = 6.9 Hz, 3H) ppm.

S1.6. PLLA (i-PLA)

(*S*)-2-{[(*S*)-2-Hydroxypropanoyl]oxy}propanoic acid (0.310 g, 1.91 mmol), DMAP (18.7 mg, 0.153 mmol) and DCC (0.591 g, 2.87 mmol) were used. A colorless solid (0.142 g, Yield 46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23-5.10 (m, OC*H*CH_3), 4.40-4.31 (m, C*H*CH_3OH), 1.64-1.53 (m, CHC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 69.0, 16.6 ppm.



Scheme S1. Synthetic route for poly(L-lactic acid), i-PLA.

S.2. Schematic representation of the preparation of solvent evaporated i-PLA/s-PLA blend and the procedure of crystallization experiments (Figure S1)

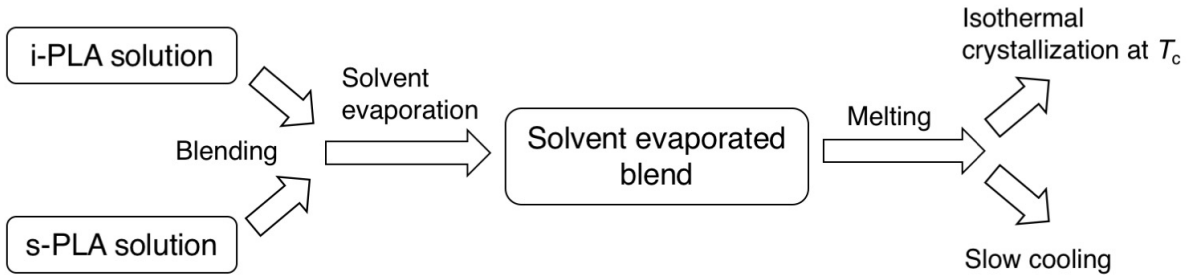


Figure S1. Schematic representation of the preparation of solvent evaporated i-PLA/s-PLA blend and the procedure of crystallization experiments.

References

S1. Stayshich R. M., Meyer T. Y. New Insights into Poly(lactic-*co*-glycolic acid) Microstructure: Using Repeating Sequence Copolymers to Decipher Complex NMR and Thermal Behavior. *J. Am. Chem. Soc.* ***2*****010**, *132*, 10920–10934.

S2. Stayshich R. M., Meyer T. Y. Preparation and Microstructural Analysis of Poly(lactic-*alt*-glycolic acid), *J. Polym. Sci. Part A, Polym. Chem.* 2**008**, *46*, 4704–4711.