Supporting Information for

Enhanced stereocomplex formation of enantiomeric polylactides grafted on a polyrotaxane platform

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Experimental

Materials. L-Lactide and D-lactide were purchased from PURAC Biochem BV (Gorinchem, The Netherlands) and used without further treatment. Poly(ethylene glycol) bis-amine (NH_2-PEG-NH_2, M_n: 35 kDa) was purchased from Aldrich. α-cyclodextrin (α-CD), anhydrous ethanol, naphthalene, anhydrous tetrahydrofuran (THF), anhydrous dimethyl sulfoxide (DMSO), *N*,*N*'-carbonyldiimidazole (CDI), 4-(*N*,*N*-dimethylamino)-pyridine (DMAP) purchased from Wako Pure Chemical Co. were used as received. The other synthetic reagents were used as received without further purification.

Synthesis of PRX. The polyrotaxane of PEG was prepared by mixing α-CD (12.0 g, 12.3 mmol) and NH_2-PEG-NH_2 (1.1 g, 31 μmol) in DMF, followed by capping with 10 eq of Z-Tyr (0.28 g, 620 μmol) at room temperature in the presence of 1.2 eq of benzotriazol-1-yloxytris(dimethylamino)phosphomium hexafluorophosphate (BOP, 0.032 g, 74 μmol), 1-hydroxybenzotriazole (HOBt, 0.01 g, 74 μmol), and *N*,*N*'-diisopropylethylamine (DIEA, 0.01 g, 74 μmol) in 70 mL of DMF. After stirring at room temperature over 12 h, the mixture was poured into excess methanol, filtered, and washed with acetone two times to remove BOP, HOBt, DIEA, and unreacted NH_2-PEG-NH_2. The resulting precipitate was dried *in vacuo* at 60 ºC to obtain a polyrotaxane (PRX, yield 60%). Number averaged threading α-CDs in a PEG was estimated to be 148 by ^{1}H-NMR spectroscopy (DMSO-d_6, JEOL GSX-400, internal reference:

TMS). M_n was estimated by following equation; M_n = MW (972) of α-CD × 148 + 35 kDa + MW of Z-Tyr (315) = 180 kDa. Molecular weight distribution (M_w/M_n) of the PRX was estimated to be 1.6 by gel permeation chromatography [GPC; Tosoh GPC-8020 series system (column: TSK-GEL ALPHA-5000 × 2, eluent: DMSO, detector: refractive index, standard: pullulan)]. ^{1}H-NMR (DMSO-d_6): 7.45–6.45 (m, aromatics of Z-Tyr), 4.87 (s, C(1)H of α-CD), 3.84–3.36 (m, C(3), C(6), C(5), C(2), and C(4)H of α-CD), 3.54 (s,-OCH_2CH_2- of PEG).

Synthesis of PLA-CI. Mono-hydroxy terminated PLLA and PDLA were synthesized by ring-opening polymerization of L-lactide or D-lactide using ethanol as an initiator, as shown in Scheme S1. The following anionic polymerization was carried out in a glove box purged with dry argon. A hydroxyl end group of ethanol was transformed to the potassium alkoxide end group with potassium (K)/naphthalene in dry THF. Naphthalene (1.96 g, 15.3 mmol) and small amount potassium were added to dry THF (7.7 mL, 95 mmol) and then stirred to obtain a THF solution of K/naphthalene (deep green). 7.7 mL of K/naphthalene THF solution added to a THF solution (5.0 mL, 61.7 mmol) of ethanol (180 μL, 5.1 mmol) and stirred for 60 min to prepare potassium ethoxide. 30.6 mL of L-lactide or D-lactide (14.69 g, 102 mmol) of THF solution was added to the resulting potassium ethoxide solution. After 15 min, the polymerization of L-lactide or D-lactide was terminated by addition of 517 μL (10.2 mmol) of acetic acid to the reaction mixture. The product was precipitated in diethyl ether and dried under vacuum overnight to yield the white solid of mono-hydroxyl terminated PLLA or PDLA with DP 19 ± 2. M_n and M_w/M_n of the PLAs was estimated by GPC (eluent: DMF, standard: PS)]. Degree of polymerization was estimated by ^{1}H-NMR spectroscopy ($CDCl_3$).

To couple the PLA to PRX, the hydroxyl group of the PLA was activated using CDI. In brief, CDI (1.07 g, 6.2 mmol) was dissolved in dry chloroform (5 mL) in a nitrogen atmosphere. PLLA-OH or PDLA-OH (6.84 g, 2.5 mmol) was dissolved in chloroform (7 mL) and added to the CDI solution. The reaction mixture was stirred for 6 h at room temperature in a nitrogen atmosphere. Then, the reaction mixture was washed with a large amount of ethanol to remove the excess CDI and imidazole. The precipitate was collected by centrifugation and dried under vacuum overnight to yield the white solid of PLLA-CI or PDLA-CI with DP 19 ± 2.

Synthesis of PLLA- or PDLA-Grafted PRX. PLLA- or PDLA-grafted PRX (PRX-*g*-PLLA or PRX-*g*-PDLA) was synthesized through a coupling reaction between PRX and PLA-CI. In brief, PRX (117 mg, 4.9 μmol) and DMAP (5.7 mg, 5.5 μmol) were dissolved in dry DMSO (5 mL, 70.4 mmol) containing 5% LiCl. PLLA-CI or PDLA-CI (DP 19, 100 mg, 370 μmol) dissolved in dry DMSO (5 mL, 70.4 mmol) was added. The solution was stirred at room temperature for 4 days in a nitrogen atmosphere, after which the reaction was stopped by addition of concentrated HCl (150 μL, 4.9 mmol) to neutralize DMAP and imidazole. The reaction mixture was washed with large amount of acetone to remove traces of uncoupled PLAs. The precipitate was collected by centrifugation and dried under vacuum overnight to yield the yellow solid of PRX-*g*-PLLA or PRX-*g*-PDLA graft copolymers. The coupling reactions were confirmed by GPC (standards: pullulan, eluent: DMSO). Number averaged PLLA or PDLA chains grafted on a PRX were calculated using ^{1}H-NMR spectroscopy (DMSO-d_6). M_n of PRX-*g*-PLLA or PRX-*g*-PDLA was estimated following equation; M_n of PRX + M_n of PLA × number averaged PLA grafts.

Preparation of Cast Films of PRX-*g*-PLA. Films of PRX-*g*-PLLA or PRX-*g*-PDLA were prepared by the usual casting method. 50 mg of PRX-*g*-PLLA or PRX-*g*-PDLA were dissolved in DMSO and the solutions were cast on a Teflon dish to 30 mm in diameter, and then dried at 60 ºC for 24 hours, followed by thorough drying for 6 days *in vacuo*. Blend films of PRX-*g*-PLLA and PRX-*g*-PDLA with similar molecular compositions were also prepared by a casting method. A solution of PRX-*g*-PLLA (4 wt%) in DMSO was mixed with PRX-*g*-PDLA solution in DMSO (4 wt%). The mixed solution was stirred at 55 ºC for 12 h. The resulting solution was poured into a large amount of cooled methanol, and the resulting precipitate was dried under vacuum overnight to give a white solid. The solid was dissolved in DMSO (4 wt%), cast on a Teflon dish to 30 mm in diameter, and then dried at 60 ºC for 24 hours, followed by thoroughly drying for 6 days *in vacuo*. The thicknesses of the PRX-*g*-PLA films and the blend films were in the range of 80–100 μm.

Measurements of PRX-*g*-PLA Films. Thermal properties of PRX-*g*-PLA films and blend films were measured by a differential scanning calorimeter (DSC; Shimadzu DSC-60, TA-60WS). After the film was quenched with liquid nitrogen, two consecutive heating runs were conducted from 0 ºC to 220 ºC at a rate of 10 ºC/min. The crystallinity assigned to the PEG crystals ($X_{c,PEG}$) in the films was calculated with the aid of the enthalpy of fusion for perfectly crystalline PEG ($\Delta H_{100\%,PEG}$: -202.4 J/g) according to the equation: X_c (%) = $(\Delta H_{sample}/\Delta H_{100\%,PEG}) \times 100$. The crystallinity assigned to homo-PLLA or -PDLA crystals ($X_{c,PLA}$) in the films was calculated with the aid of the enthalpy of fusion for perfectly crystalline homo-PLLA or -PDLA ($\Delta H_{100\%,PLA}$: -93.7 J/g) according to the equation: X_c (%) = $(\Delta H_{sample}/\Delta H_{100\%,PLA}) \times 100$. The crystallinity assigned to the SC crystals ($X_{c,SC}$) in the films was calculated with the aid of the enthalpy of fusion for perfectly crystalline SC ($\Delta H_{100\%,SC}$: -142.5 J/g) according to the equation: X_c (%) = $(\Delta H_{sample}/\Delta H_{100\%,SC}) \times 100$. The surfaces of the films were observed by SEM (JEOL JSM-35). The optical properties of the polymer films were measured with an optical microscope (Olympus BHS-751P) under cross-polarized conditions at 25 ºC. Wide angle X-ray diffraction analysis of the polymer films was performed using M18XHF22-SRA (MAC Science Co.) with CuK_α source ($\lambda = 1.54$ Å) at 25 ºC.

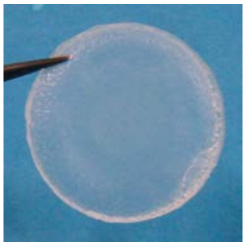

Figure S1. Photographs of a PRX film at 25 ºC.

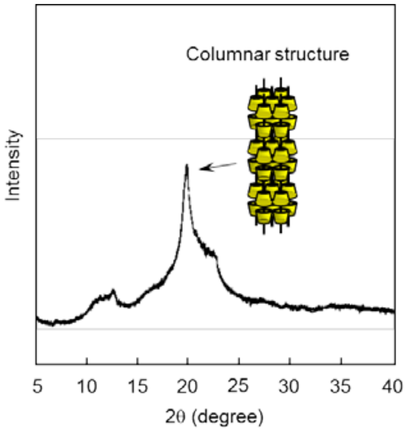

Figure S2. WAXD spectra of a PRX film at 25 ºC.

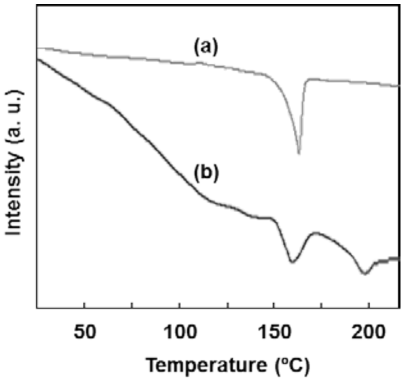

Figure S3. DSC curves of (a) $PLLA_{19}$ and (b) a blend film of $PLLA_{19}$ and $PDLA_{20}$.