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Synthesis and chiroptical properties of helical polystyrenes stabilized by intramolecular hydrogen bonding

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Measurements

The ¹H and ¹³C NMR spectra were recorded using a Bruker 600 MHz or 400 MHz spectrometer {H}. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of two linear TSK gel GMH_{HR}-H columns. Molecular weight (M_n) and its polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. Circular dichroism (CD) spectra were obtained in a 1.0 cm or 1.0 mm quartz cell using a JASCO J1500 spectropolarimeter. The polymer concentration was calculated on the basis of the monomer units and was 0.2 mg/mL. The UV-vis absorption spectra were recorded on a UNIC 4802 UV/vis double beam spectrophotometer. The optical rotations were measured in CHCl₃ at room temperature using a 10.0 cm quartz cell on a WZZ-2B polarimeter. Transmission electron microscopy (TEM) was performed on a JEM-2100F operating at 200 kV accelerating voltage. Scanning electron microscopy (SEM) was performed on a SU8020 operating at 5.0 kV accelerating voltage. Dynamic light scattering (DLS) was recorded using a Nano-ZS 90 Zetasizer of Malvern (UK) instrument. X-ray differaction (XRD) was performed on D/max2500 VB2+/PC Xray diffractometer (Rigaku) using Cu Ka radiation. An E600POL polarizing optical microscope (Nikon, Tokyo, Japan) equipped with a DS-5 M CCD camera (Nikon) connected to a DS-L1 control unit (Nikon) was used to perform the POM observations.

Materials

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals were purchased from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The materials L-2, D-2, and A-2 were prepared according to the reported literatures and the structures were confirmed by ¹H NMR.¹⁻⁴

Synthesis of L-1: Under dry nitrogen atmosphere, L-2 (1.55 g, 6.76 mmol) and 4ethenyl-benzoic acid (1.10 g, 7.44 mmol) were dissolved in CH₂Cl₂ (60 mL). To this solution, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 1.25 g, 6.54 mmol) and 4-dimethylaminopyridine (DMAP, 2.78 g, 8.93 mmol) were added. After the resulting mixture was stirred at room temperature for 2 h, the reaction solution was diluted with CH₂Cl₂, washed with water and brine. The combined organic layer was dried over Na₂SO₄ and evaporated to dryness. The residue was purified by column chromatography using petroleum ether and EtOAc as eluent (v/v = 6/1) to give L-1 as a white solid (1.94 g, 80% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.77 (d, J = 6.0 Hz, 2H, ArH), 7.46 (d, J = 6.0 Hz, 2H, ArH), 6.74 (m, 2H, CHCH₂ and NH), 5.83 (d, 1H, J = 18.0 Hz, CH₂), 5.35 (d, 1H, J = 6.0 Hz, CH₂), 4.78 (m, 1H, CHCH₃), 4.17 $(m, 2H, CO_2CH_2), 1.66 (m, 2H, CH_2), 1.53 (d, 3H, J = 6.0 Hz, CH_2CH_3), 1.26 (m, 14H, 12H, 12H) = 0.0 Hz, CH_2CH_3), 1.26 (m, 14H), 1.26$ CH₂), 0.88 (t, 3H, J = 6.0 Hz, CH₃).¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 173.48, 166.47, 140.97, 133.19, 127.48, 126.43, 116.11, 65.92, 48.72, 32.01, 29.83, 29.63, 29.62, 29.42, 29.32, 28.68, 25.95, 22.80, 18.91, 14.22. $[\alpha]^{25}_{D} = +4.1$ (*c* = 0.2, CHCl₃). FT-IR (KBr, 25 °C): 3283, 2929, 2855, 1743, 1649, 1544, 1463, 1344, 1282, 1214, 1121

cm⁻¹. MS m/z calcd for C₂₂H₃₄NO₃ [M + H]⁺: 360.2460; Found: 360.2537. Anal. Calcd
(%) for C₂₂H₃₃NO₃: C, 73.50; H, 9.25; N, 3.90. Found (%): C, 73.55; H, 9.14; N, 4.17. Monomer D-1 and A-1 were prepared followed the same procedure by using D-2 and A-2 as the starting materials, respectively. The characterization data for D-1 and A-1 are showed bellowed.

D-1: 80% yield. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.77 (d, *J* = 6.0 Hz, 2H, ArH), 7.47 (d, *J* = 6.0 Hz, 2H, ArH), 6.75 (m, 2H, C<u>H</u>CH₂ and NH), 5.83 (d, 1H, *J* = 18.0 Hz, CH₂), 5.36 (d, 1H, *J* = 12.0 Hz, CH₂), 4.78 (m, 1H, C<u>H</u>CH₃), 4.18 (m, 2H, CO₂CH₂), 1.66 (m, 2H, CH₂), 1.53 (d, 3H, *J* = 6.0 Hz, CHC<u>H₃</u>), 1.26 (m, 14H, CH₂), 0.88 (t, 3H, *J* = 6.0 Hz, CH₂C<u>H₃</u>). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 173.51, 166.48, 140.99, 136.07, 133.09, 127.48, 126.46, 116.16, 65.96, 48.73, 32.02, 29.84, 29.65, 29.64, 29.44, 29.34, 28.68, 22.82, 18.97, 14.25. [α]²⁵_D = -4.1 (*c* = 0.2, CHCl₃). FT-IR (KBr, 25 °C): 3315, 2911, 2852, 1746, 1613, 1507, 1447, 1361, 1275, 1216, 1169 cm⁻¹. MS m/z calcd for C₂₂H₃₄NO₃ [M + H]⁺: 360.2460; Found: 360.2594. Anal. Calcd (%) for C₂₂H₃₃NO₃: C, 73.50; H, 9.25; N, 3.90. Found (%): C, 73.80; H, 9.55; N, 4.18.

A-1: 80% yield. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.74 (d, *J* = 6.0 Hz, 2H, ArH), 7.46 (d, *J* = 6.0 Hz, 2H, ArH), 6.86 (s, 1H, NH), 6.74 (m, 1H, C<u>H</u>CH₂), 5.83 (d, *J* = 12.0 Hz, 1H, CH₂), 5.35 (d, *J* = 12.0 Hz, 1H, CH₂), 4.18 (t, *J* = 6.0 Hz, 2H, CO₂CH₂), 1.70 (s, 6H, C(CH₃)₂), 1.65 (m, 2H, CO₂CH₂C<u>H₂</u>), 1.25 (m, 14H, CH₂), 0.88 (t, *J* = 6.0 Hz, 3H, CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 175.34, 166.44, 140.95, 136.28, 134.05, 127.56, 126.58, 116.21, 66.20, 57.36, 32.21, 30.03, 29.84, 29.64, 29.54, 28.85, 26.19, 24.95, 23.02, 14.45. FT-IR (KBr, 25 °C): 3258, 2923, 2855, 1736, 1625, 1531, 1506, 1463, 1332, 1270, 1146 cm⁻¹. MS m/z calcd for C₂₃H₃₆NO₃ [M + H]⁺: 374.2617; Found: 374.2650. Anal. Calcd (%) for C₂₃H₃₅NO₃: C, 73.96; H, 9.44; N, 3.75. Found (%): C, 73.75; H, 9.46; N, 3.75.

Synthesis of L-H: Palladium on activated carbon (10%, 0.38 g) was added to the solution of L-1 (1.00 g, 2.78 mmol) in methanol at room temperature. The reaction mixture was then stirred under an atmosphere of hydrogen for 4 h. The reaction solution was then filtered through celite and the filtrate was evaporated to dryness under reduced pressure, afforded L-H as a white solid (0.95 g, 95% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.73 (d, *J* = 6.0 Hz, 2H, ArH), 7.27 (d, *J* = 6.0 Hz, 2H, ArH), 4.78 (m, 1H, C<u>H</u>CH₃), 4.17 (m, 2H, CO₂CH₂), 2.69 (m, 2H, ArCH₂), 1.66 (m, 2H, CH₂), 1.52 (d, *J* = 6.0 Hz, 3H, CHC<u>H₃</u>), 1.25 (m, 17H, CH₂ and ArCH₂C<u>H₃</u>), 0.88 (t, *J* = 6.0 Hz, 3H, CH₃). ¹³C NMR (150 MHz, CDCl₃, 25 °C): δ 173.73, 167.06, 148.65, 131.67, 128.33, 127.44, 66.05, 43.83, 32.18, 29.80, 29.60, 29.50, 29.09, 28.84, 26.12, 22.98, 19.09, 15.62, 14.42. [α]²⁵_D = +3.7 (*c* = 0.2, CHCl₃). FT-IR (KBr, 25 °C): 3289, 2929, 2849, 1743, 1631, 1531, 1460, 1338, 1280, 1214, 1102 cm⁻¹. MS m/z calcd for C₂₂H₃₆NO₃ [M + H]⁺: 362.2617; Found: 362.2635. Anal. Calcd (%) for C₂₂H₃₅NO₃: C, 73.09; H, 9.76; N, 3.87. Found (%): C, 73.35; H, 9.67; N, 3.89.

Synthesis of D-H: This compound was prepared under the same synthetic procedure of L-H in 95% yield. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 7.73 (d, *J* = 12.0 Hz, 2H, ArH), 7.27 (d, *J* = 12.0 Hz, 2H, ArH), 4.79 (m, 1H, CHCH₃), 4.17 (m, 2H, CO₂CH₂), 2.70 (m, 2H, ArCH₂), 1.66 (m, 2H, CH₂), 1.52 (d, *J* = 12.0 Hz, 3H, CHCH₃), 1.25 (m, 17H, CH₂ and ArCH₂CH₃), 0.88 (t, *J* = 6.0 Hz, 3H, CH₃). ¹³C NMR (150 MHz, CDCl₃,

25 °C): δ 176.07, 169.39, 151.00, 134.01, 130.67, 129.77, 68.39, 51.17, 34.52, 32.13, 31.93, 31.84, 31.43, 31.17, 28.45, 25.32, 21.43, 17.96, 16.75. [α]²⁵_D = -3.7 (*c* = 0.2, CHCl₃). FT-IR (KBr, 25 °C): 3296, 2923, 2855, 1743, 1637, 1544, 1450, 1338, 1288, 1208, 1121 cm⁻¹. MS m/z calcd for C₂₂H₃₆NO₃ [M + H]⁺, 362.2617; Found: 362.2530. Anal. Calcd (%) for C₂₂H₃₅NO₃: C, 73.09; H, 9.76; N, 3.87. Found (%): C, 73.25; H, 9.84; N, 3.89.

Synthesis of poly-L-1₈₀: A 10 mL oven dried and nitrogen-filled flask was charged with monomer L-1 (0.050 g, 0.14 mmol), azodiisobutyronitrile (AIBN, 0.28 mg, 0.0017 mmol), 3-(benzylthiocarbonothioylthio)propanoic acid (0.47 mg, 0.0017 mmol) and toluene (1.4 mL). After the resulting mixture was stirring at 90 °C for 3 h, it was poured into a large amount of methanol, which caused a white solid to precipitate. The solid was then isolated via filtration, washed with methanol and dried under vacuum at room temperature to afford poly-L-1₈₀ (30 mg, 60% yield). ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.27–7.77 (br, 1H, NH), 7.76–7.26 (br , 2H, ArH), 6.69–6.23 (br, 2H, ArH), 4.82–4.57 (br, 1H, CHCH₃), 4.25–4.10 (m, 2H, CO₂CH₂), 2.18–1.86 (br, 1H, CH), 1.76–1.46 (m, 5H, CH₂ and CH₃), 1.44–1.08 (br, 16H, CH₂), 0.93–0.76 (br, 3H, CH₃). [α]²⁵_D = +69.33 (*c* = 0.2, CHCl₃). FT-IR (KBr, 25 °C): 3302, 2923, 2855, 1743, 1637, 1531, 1456, 1338, 1164 cm⁻¹.

Followed the similar procedure, poly-D- $\mathbf{1}_m$ was prepared. The characterization data were showed below.

Poly-D-1_m: 63% yields. ¹H NMR (600 MHz,CDCl₃, 25 °C): δ 8.25–7.74 (br, 1H, NH), 7.72–7.20 (br, 2H, ArH), 6.70–6.04 (br, 2H, ArH), 4.90–4.55 (br, 1H, C<u>H</u>CH₃), 4.26– 4.10 (m, 2H, CO₂CH₂), 2.22–1.86 (br, 1H, CH), 1.70–1.42 (m, 5H, CH₂ and CH₃), 1.42– 1.10 (br, 16H, CH₂), 0.98–0.72 (br, 3H, CH₃). [α]²⁵_D = -69.33 (*c* = 0.2, CHCl₃). FT-IR (KBr, 25 °C): 3305, 2926, 2849, 1751, 1635, 1545, 1455, 1346, 1160 cm⁻¹.

Synthesis of poly(*L*-1₈₀-*co*-3₁₀): A solution of cross-linker ethane-1,2-diyl bis(2methylacrylate (3.37 mg, 0.017 mmol) in toluene and AIBN (0.28 mg, 0.0017 mmol) was added to a solution of poly-L-1₈₀ (50 mg) in toluene. After the resulting mixture was stirring at 90 °C for 2 h, it was poured into a large amount of methanol, which caused a white solid to precipitate. The solid was then isolated via filtration, washed with methanol and dried under vacuum at room temperature to afford poly(L-1₈₀-*co*-**3**₁₀). SEC: M_n = 38.6 kDa, M_w/M_n = 1.32. ¹H NMR (600 MHz, CDCl₃, 25 °C): δ 8.18– 7.64 (br, 1H, NH), 7.62–7.01 (br, 2H, ArH), 6.62–6.01 (br, 2H, ArH), 4.84–4.54 (br, 1H, C<u>H</u>CH₃), 4.24–4.04 (m, 2H, CO₂CH₂), 2.18–1.74 (br, 1H, CH), 1.75–1.42 (m, 5H, CH₂ and CH₃), 1.41–1.08 (br, 16H, CH₂), 0.97–0.73 (br, 3H, CH₃). FT-IR (KBr, 25 °C): 3301, 2924, 2852, 1746, 1646, 1540, 1500, 1460, 1354, 1269, 1163 cm⁻¹.

Typical procedure for enantioselective crystallization: The racemic D/Lthreonine (800 mg) was first dissolved in deionized water (4 mL) to get a supersaturated solution, and the solution was heated to 35 °C under stirring for complete dissolution. Approximately 5 mg of poly(L-1₈₀-*co*-3₁₀) was placed into the supersaturated solution and stirred/sonicated for about 30 min, then the dispersion was left for ambient cooling till to room temperature (approximately 25 °C). For several hours, needle crystals were gradually formed from the solution standing in an open vial at room temperature. The crystal was collected via filtration, washed with cold deionized water, and then dried under vacuum at room temperature to afford L-threonine (175 mg, 22% yield). The *ee* value was determined to be 95% via the comparison of the molar CD intensity at 210 nm of the induced crystal with the commercial available enantiopure L-threonine, which was also confirmed by the value of optical rotation $[\alpha]^{25}_{D} = -26.5$ (*c* = 6 mol/L, water, 25 °C).

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Fig. S1 ¹³C NMR (150 MHz) spectrum of L-1 measured in CDCl₃ at 25 °C.



Fig. S2 FT-IR spectrum of L-1 measured at 25 °C using KBr.



Fig. S3 ¹H NMR (600 MHz) spectrum of D-1 measured in CDCl₃ at 25 °C.



Fig. S4 ¹³C NMR (150 MHz) spectrum of D-1 measured in CDCl₃ at 25 °C.



Fig. S5 FT-IR spectrum of D-1 measured at 25 °C using KBr.



Fig. S6 ¹H NMR (600 MHz) spectrum of A-1 measured in CDCl₃ at 25 °C.



Fig. S7 ¹³C NMR (150 MHz) spectrum of A-1 measured in CDCl₃ at 25 °C.



Fig. S8 FT-IR spectrum of A-1 measured at 25 °C using KBr.



Fig. S9 ¹H NMR (600 MHz) spectrum of L-H measured in CDCl₃ at 25 °C.



Fig. S10 ¹³C NMR (150 MHz) spectrum of L-H measured in CDCl₃ at 25 °C.



Fig. S11 FT-IR spectrum of L-H measured at 25 °C using KBr.



Fig. 12 ¹H NMR (600 MHz) spectrum of D-H measured in CDCl₃ at 25 °C.



Fig. S13 ¹³C NMR (150 MHz) spectrum of D-H measured in CDCl₃ at 25 °C.



Fig. S14 FT-IR spectrum of D-H measured at 25 °C using KBr.



Fig. S15 (a) SEC chromatograms of poly-L-1_{ms} prepared from L-1 with different initial feed ratio of monomer to CAT. (b) Plots of M_n and M_w/M_n values of isolated poly-L-1_{ms} as a function of the initial feed ratio of L-1 to CAT. M_n and M_w/M_n were determined by SEC with polystyrene standard (SEC conditions: eluent = THF, temperature = 40 °C).



Fig. S16 FT-IR spectrum of poly-L-180 measured at 25 °C using KBr.



Fig. S17 CD spectra of poly-L-1₈₀ recorded in CHCl₃ at 25 °C at different concentrations.



Fig. S18 ¹H NMR (600 MHz) spectrum of poly-D-1₈₀ measured in CDCl₃ at 25 °C.



Fig. S19 FT-IR spectrum of poly-D-180 measured at 25 °C using KBr.



Fig. S20 (a) XRD pattern of poly-L- $\mathbf{1}_{80}$ (b) Polarized optical micrograph of poly-L- $\mathbf{1}_{80}$ in CHCl₃ solution taken at room temperature.



Fig. S21 CD and UV-vis spectra of poly-L-1₈₀ measured in CHCl₃ from 60 °C to 0 °C (c = 0.2 mg/mL).



Fig. S22 CD and UV-vis spectra of poly-L-1₈₀ in CHCl₃ and EtOH, and the recovered sampled from EtOH re-dissolved in CHCl₃ at 25 °C (c = 0.2 mg/mL).



Fig. S23 DLS curves of poly-L-1₈₀ measured in different solvents at 25 °C (c = 0.2 mg/mL).



Fig. S24 (a) CD and UV-vis spectra of poly(L-1_n-*co*-A-1_{100-n}) in different monomer compositions measured in CHCl₃ at 25 °C. (b) Plot of $\Delta \varepsilon_{248}$ values of poly(L-1_n-*co*-A-1_{100-n})s as a function of the composition of chiral units (c = 0.2 mg/ mL).



Fig. S25 ¹H NMR (600 MHz) spectrum of poly(L- 1_{80} -co- 3_{10}) measured in CDCl₃ at 25 °C.



Fig. S26 FT-IR spectrum of poly(L-1₈₀-*co*-3₁₀) measured at 25 °C using KBr.



Fig. S27 Time-dependent CD spectra of the solution of enantioselective crystallization of racemic threonine in deionized water induced by chiral poly(L-1₈₀-*co*-3₁₀) at room temperature.