Supplementary Information

Macromolecular helicity inversion of an optically active helical poly(phenylacetylene) by chemical modification of the side groups

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Experimental Section

Materials. Anhydrous tetrahydrofuran (THF), methanol (MeOH), dimethylformamide (DMF), and pyridine (water content < 0.005%) and sodium borohydride (NaBH₄) were purchased from Wako (Osaka, Japan). Triethylamine (Et₃N) and diethylamine (Et₂NH) were dried over KOH pellets and distilled onto KOH under nitrogen. THF and the amines were redistilled from LiAlH₄ and KOH, respectively, under high vacuum just before polymerization. Isopropenyl acetate, phenyl isocyanate, and [(norbornadiene)rhodium(I) chloride]₂ ([Rh(nbd)Cl]₂) were obtained from Aldrich (Milwaukee, WI). Isopropenyl acetate was dried over K₂CO₃, distilled onto molecular sieves 4Å (MS 4A) under nitrogen, and redistilled under high vacuum just before use. Novozyme 435 was purchased from Sigma. Triphenylphosphine (PPh₃) and copper(I) iodide (CuI) were obtained from Kishida (Osaka, Japan). Naphthyl isocyanate, benzoyl chloride, 4-iodoacetophenone, bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh₃)₂Cl₂), and tetrabutylammonium fluoride (TBAF, 1 M in THF) were purchased from Tokyo Kasei (Tokyo). (Trimethylsilyl)acetylene was kindly supplied from Shinetsu Chemical (Tokyo, Japan). Bis(cyclooctadiene)rhodium(I) tetrafluoroborate (Rh(cod)₂BF₄) were prepared from [Rh(cod)Cl]₂ according to the reported method.¹
1-(4-Iodophenyl)ethanol. To a suspension of 4-iodoacetophenone (20.3 g, 82.6 mmol) in MeOH (29 ml) was slowly added NaBH₄ (1.56 mg, 40 mmol). The reaction mixture was stirred at ambient temperature for 2 h before evaporating the solvent. After water was added, the crude product was extracted with ether. The ethereal layer was then washed with aqueous NaCl and water, and dried over Na₂SO₄. After the solvent was evaporated under the reduced pressure, the obtained crude product was purified by recrystallization from hexane-ethyl acetate (20/1, v/v) to yield 10.9 g of 1-(4-iodophenyl)ethanol as a white solid in 53% yield. ¹H NMR (300 MHz, CDCl₃): δ 1.47 (d, J = 6.6 Hz, 3H, CH₃), 1.80 (d, J = 3.6 Hz, 1H, OH), 4.86 (m, 1H, CH), 7.10-7.16 (m, 2H, aromatic protons), 7.64-7.72 (m, 2H, aromatic protons).

1-(4-((Trimethylsilyl)ethynyl)phenyl)ethanol. To a solution of 1-(4-iodophenyl)ethanol (10.8 g, 43.5 mmol), Pd(PPh₃)₂Cl₂ (0.125 g, 0.178 mmol), PPh₃ (0.183 g, 0.698 mmol), and CuI (0.199 g, 1.04 mmol) in Et₃N (145 ml) was added (trimethylsilyl)aceylene (7.4 ml, 53 mmol). The reaction mixture was stirred at ambient temperature for 4 h. After filtration, the solvent was evaporated under the reduced pressure. The crude product was then purified by silica gel chromatography with hexane-ethyl acetate (7/1, v/v) as the eluent to give 10.0 g of 1-(4-((trimethylsilyl)ethynyl)phenyl)ethanol as orange oil in 100% yield. This product was used for the next reaction without further purification. ¹H NMR (300 MHz, CDCl₃): δ 0.25 (s, 9H, Si(CH₃)₃), 1.47 (d, J = 6.3 Hz, 3H, CH₃), 1.82 (d, J = 3.6 Hz, 1H, OH), 4.89 (m, 1H, CH), 7.27-7.33 (m, 2H, aromatic protons), 7.42-7.47 (m, 2H, aromatic protons).

1-(4-Ethynylphenyl)ethanol (rac-1). To a solution of 1-(4-((trimethylsilyl)ethynyl)phenyl)ethanol (9.74 g, 44.6 mmol) in THF (45 ml) was added a THF solution of TBAF (1 M) (4.1 ml). The solution was stirred at ambient temperature for 30 min before evaporating the solvent. The crude product was diluted with ether, and the ethereal solution was washed with 1% aqueous HCl and water, and dried over MgSO₄. After filtration, the solvent was removed by evaporation. The residue was purified by silica gel chromatography with hexane-ethyl acetate (7/1, v/v) as the eluent and further distilled under the reduced pressure to give 4.4 g of rac-1 in 68% yield (bp 62-70 °C, 0.1-0.12 mmHg). IR (neat, cm⁻¹): 3291 (≡C-H), 2107 (C≡C). ¹H NMR (300 MHz, CDCl₃): δ 1.48 (d, J = 6.6 Hz, 3H, CH₃), 1.90 (d, J = 3.7 Hz, 1H, OH), 3.07 (s, 1H, ≡CH), 4.90 (m, 1H, CH), 7.31-7.36 (m, 2H, aromatic protons), 7.46-7.50 (m, 2H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃): δ 25.32, 70.19, 77.21, 83.63, 121.26, 125.49, 132.43, 146.67. HRMS (EI) calcd for C₁₀H₁₀O

**Kinetic Resolution of rac-1 and Polymerization.** The kinetic resolution of rac-1 and succedent polymerization were carried out under a nitrogen atmosphere. A typical procedure is described below.

Novozyme 435 (258 mg), MS 4A (277 mg), and rac-1 (187 mg, 1.28 mmol) were placed in a dry two-necked flask and dry THF (7.7 mL) was added with a syringe. To this was added isopropenyl acetate (0.28 mL, 2.54 mmol) and the reaction mixture was stirred at 40 °C. After 5 h, a small portion of the mixture was withdrawn to determine the conversion of rac-1 and enantiomeric excess (ee) of (S)-1 and (R)-2 using ¹H NMR and chiral HPLC. After an almost 50% of rac-1 was converted to (R)-2, the reaction mixture was filtrated and the solvent was then removed by evaporation to yield the mixture of (S)-1 and (R)-2. The obtained (S)-1 and (R)-2 were dispersed in a mixture of MeOH (0.1 mL) and water (1.6 mL), and Et₃NH (0.38 mL, 3.7 mmol) was added with a syringe. To this was added a solution of Rh(cod)₂BF₄ (0.025 M) in water at 30 °C. The concentrations of the monomers and the rhodium complex were 0.5 and 0.0025 M, respectively. The polymerization heterogeneously proceeded. After 26 h, the solvent was removed by lyophilization. The obtained polymer was then dissolved in a small amount of THF and the THF solution was poured into a large amount of diethyl ether. The precipitated yellow polymer (poly((S)-1-co-(R)-2)) was collected by centrifugation and dried *in vacuo* at ambient temperature overnight (181 mg, 85% yield).

The stereoregularity of poly((S)-1-co-(R)-2) was confirmed to be a highly cis-transoidal by ¹H NMR spectroscopy (Fig. S3). The composition of (S)-1 and (R)-2 units in poly((S)-1-co-(R)-2) was estimated to be 53:47 on the basis of its ¹H NMR spectrum and elemental analysis. The molecular weight (Mₙ) and its distribution (Mₘ/Mₙ) were 8.9 x 10⁴ and 2.0, respectively, as determined by size exclusion chromatography (SEC) using poly(ethylene oxide) and poly(ethylene glycol) standards in DMF containing 10 mM LiCl as the eluent.

Spectroscopic data of poly((S)-1-co-(R)-2). IR (KBr, cm⁻¹): 1735 (C=O). ¹H NMR (500 MHz, DMSO-<d₆>, 30 °C): δ 1.15 (s, CH₃, 1.59H), 1.24 (s, CH₃, 1.41H), 1.89 (s, COCH₃, 1.41H), 4.51 (s, CH, 0.53H), 4.90 (s, OH, 0.53H), 5.60 (s, CH, 0.47H), 5.72 (s, =CH, 1H), 6.49 (s, aromatic protons, 2H), 6.93 (s, aromatic protons, 2H). Anal. Calcd for (C₁₀₉₄H₁₀₉₄O₁₄.₄•7/20H₂O)n: C, 76.28; H, 6.81. Found: C, 76.11; H, 6.43.

Poly((S)-1-co-(R)-2) (20.0 mg, 0.12 mmol) was dissolved in dry pyridine (2.0 mL) and to this was added naphthyl isocyanate (0.05 mL, 0.35 mmol, [naphthyl isocyanate]/[(S)-1 in poly((S)-1-co-(R)-2)] = 5.5) at ambient temperature. After 20 h, the solvent was removed by evaporation. The residue was washed with MeOH and then dissolved in a small amount of DMSO. The DMSO solution was then poured into a large amount of methanol, and the resulting yellow polymer (poly((S)-3-co-(R)-2)) was collected by centrifugation and dried \textit{in vacuo} at ambient temperature overnight (20 mg, 64\% yield).

Spectroscopic data of poly((S)-3-co-(R)-2). IR (film, cm\(^{-1}\)): 1714 (C=O), 1539 (amide II). 1H NMR (500 MHz, DMSO-\(d_6\), 30 \(^\circ\)C): \(\delta\) 1.18 (br, CH\(_3\), 3H), 1.78 (s, COCH\(_3\), 1.41H), 5.64 (br, CH and =CH, 2H), 6.50–7.40 (m, aromatic protons, 7.7H), 9.52 (s, NH, 0.53H). Anal. Calcd for (C\(_{16.77}\)H\(_{14.65}\)N\(_{0.53}\)O\(_2\)\(\cdot\)13/14H\(_2\)O)\(\_n\): C, 73.24; H, 6.16; N, 2.70. Found: C, 73.04; H, 5.45; N, 2.62.


Poly((S)-4-co-(R)-2) was prepared from poly((S)-1-co-(R)-2) (20.0 mg, 0.12 mmol) with phenyl isocyanate (0.05 mL, 0.35 mmol, [phenyl isocyanate]/[(S)-1 in poly((S)-1-co-(R)-2)] = 6) in the same way for the synthesis of poly((S)-3-co-(R)-2) in 72\% yield (20 mg).

Spectroscopic data of poly((S)-4-co-(R)-2). IR (film, cm\(^{-1}\)): 1714 (C=O), 1540 (amide II). 1H NMR (500 MHz, DMSO-\(d_6\), 30 \(^\circ\)C): \(\delta\) 1.18 (br, CH\(_3\), 3H), 1.78 (s, COCH\(_3\), 1.41H), 5.64 (br, CH and =CH, 2H), 6.50–7.40 (m, aromatic protons, 7.7H), 9.52 (s, NH, 0.53H). Anal. Calcd for (C\(_{14.65}\)H\(_{13.59}\)N\(_{0.53}\)O\(_2\)\(\cdot\)3/10H\(_2\)O)\(\_n\): C, 75.04; H, 6.10; N, 3.17. Found: C, 74.87; H, 5.85; N, 3.31.


Poly((S)-5-co-(R)-2) (20.0 mg, 0.12 mmol) was dissolved in dry pyridine (2.0 mL) and to this was added benzoyl chloride (0.04 mL, 0.34 mmol, [benzoyl chloride]/[(S)-1 in poly((S)-1-co-(R)-2)] = 5) at ambient temperature. After 20 h, the solvent was removed by evaporation. The residue was then dissolved in a small amount of DMF, and the DMF solution was poured into a large amount of methanol. The resulting yellow polymer (poly((S)-5-co-(R)-2)) was collected by centrifugation and dried \textit{in vacuo} at ambient temperature overnight (22 mg, 82\% yield).

Spectroscopic data of poly((S)-5-co-(R)-2). IR (film, cm\(^{-1}\)): 1717 (C=O). 1H NMR (500 MHz, CDCl\(_3\), 30 \(^\circ\)C): \(\delta\) 1.27 (br, CH\(_3\), 3H), 1.87 (s, COCH\(_3\), 1.41H), 5.59–5.92 (m, CH and =CH, 2H),
6.55–7.92 (m, aromatic protons, 7.7H). Anal. Calcd for (C_{14.65}H_{13.06}O_{2}•3/10H_{2}O)n: C, 77.68; H, 6.08. Found: C, 77.97; H, 5.80.

**Isolation of (S)-1 and (R)-2.** The mixture of (S)-1 and (R)-2 obtained by the kinetic resolution of rac-1 (1.0 g, 6.8 mmol) (see above) was separated into crude (S)-1 (480 mg) and (R)-2 (650 mg) as a colorless oil by silica gel chromatography with hexane-ethyl acetate (10/1, v/v), followed by ethyl acetate as the eluents. Crude (S)-1 was further purified by distillation to give 430 mg of pure (S)-1. The ee values of (S)-1 and (R)-2 were >99 and 91%, respectively.

Spectroscopic data of (S)-1. IR (neat, cm⁻¹): 3294 (≡C-H), 2108 (C≡C). ¹H NMR (300 MHz, DMSO-­d₆): δ 1.30 (d, J = 6.3 Hz, 3H, CH₃), 4.10 (s, 1H, ≡CH), 4.72 (m, 1H, CH), 5.22 (d, J = 4.2 Hz, 1H, OH), 7.33-7.43 (m, 4H, aromatic protons). ¹³C NMR (DMSO-d₆, 75 MHz): δ 25.57, 67.60, 79.88, 83.53, 119.71, 125.47, 131.31, 148.26. HRMS (EI) calcd for C_{10}H_{10}O [M⁺] 146.0732, found 146.0742. Anal. Calcd for C₁₀H₁₀O: C, 82.16; H, 6.89. Found: C, 81.96; H, 6.94. [α]₀^D −49° (c 0.5, CHCl₃).

Spectroscopic data of (R)-2. IR (neat, cm⁻¹): 3290 (≡C-H), 2108 (C≡C), 1739 (C=O). ¹H NMR (300 MHz, CDCl₃): δ 1.52 (d, J = 3.9 Hz, 3H, CH₃), 2.08 (s, 3H, COCH₃), 3.07 (s, 1H, ≡CH), 5.86 (m, 1H, CH), 7.30-7.48 (m, 4H, aromatic protons). ¹³C NMR (75 MHz, CDCl₃): δ 21.38, 22.21, 71.99, 77.44, 83.50, 121.85, 126.17, 132.45, 142.61, 170.29. HRMS (EI) calcd for C_{10}H_{10}O [M⁺] 188.0837, found 188.0829. Anal. Calcd for C_{12}H_{12}O₂ · 1/5H₂O: C, 75.14; H, 6.52. Found: C, 75.06; H, 6.41. [α]₀^D +127° (c 0.5, CHCl₃).

**Synthesis of Poly((S)-1), Poly((R)-2), and Poly((S)-3).** The polymerization of the isolated (S)-1 and (R)-2 was carried out in a dry glass ampule under a dry nitrogen atmosphere using [Rh(nbd)Cl]₂ as a catalyst. A typical polymerization procedure is described below.

Monomer (S)-1 (30 mg, 0.21 mmol) was placed in a dry glass ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, a three-way stopcock was attached to the ampule and dry THF (0.33 mL) was added with a syringe. To this was added a solution of [Rh(nbd)Cl]₂ (0.005 M) containing Et₃N ([Et₃N]/[Rh] = 200) in THF at 30 °C. The concentrations of the monomer and the rhodium complex were 0.5 and 0.00125 M, respectively. The polymerization rapidly proceeded and an orange polymer was precipitated within a few seconds. After 12 h, the solvent was removed by evaporation. The residue was dissolved in a
small amount of methanol, and the solution was poured into a large amount of diethyl ether. The resulting yellow polymer (poly((S)-1)) was collected by filtration and dried in vacuo at ambient temperature overnight (31 mg, 100% yield). The polymerization of (R)-2 was performed in the same way to yield poly((R)-2) quantitatively.

Spectroscopic data of poly((S)-1). $^1$H NMR (500 MHz, DMSO-$d_6$, 30 °C): $\delta$ 1.14 (s, CH$_3$, 3H), 4.51 (s, CH, 1H), 4.90 (s, OH, 1H), 5.72 (s, =CH, 1H), 6.49 (s, aromatic protons, 2H), 6.89 (s, aromatic protons, 2H). Anal. Calcd for (C$_{10}$H$_{10}$O•3/10H$_2$O)$_n$: C, 79.23; H, 7.05. Found: C, 78.99; H, 6.82.

Spectroscopic data of poly((R)-2). IR (KBr, cm$^{-1}$): 1735 (C=O). $^1$H NMR (500 MHz, CDCl$_3$, 30 °C): $\delta$ 1.31 (d, CH$_3$, 3H), 1.94 (s, COCH$_3$, 1.41H), 5.71 (d, CH, 1H), 5.76 (s, =CH, 1H), 6.56 (s, aromatic protons, 2H), 6.96 (s, aromatic protons, 2H). Anal. Calcd for (C$_{12}$H$_{12}$O$_2$•1/20H$_2$O)$_n$: C, 76.21; H, 6.45. Found: C, 76.29; H, 6.44.

Poly((S)-3) was prepared from poly((S)-1) in the same way for the synthesis of poly((S)-3-co-(R)-2).

Spectroscopic data of poly((S)-3). IR (film, cm$^{-1}$): 1704 (C=O), 1538 (amide II). $^1$H NMR (500 MHz, CDCl$_3$, 30 °C): $\delta$ 1.20 (br, CH$_3$, 3H), 5.61 (br, CH and =CH, 2H), 6.53–7.87 (m, aromatic protons, 11H), 9.29 (s, NH, 1H). Anal. Calcd for (C$_{21}$H$_{17}$NO$_2$)$_n$: C, 79.98; H, 5.43; N, 4.44. Found: C, 79.82; H, 5.31; N, 4.31.

**Instruments.** IR spectra were recorded using a Jasco Fourier Transform IR-620 spectrophotometer (Hachioji, Japan). Optical rotation was measured in a 5-cm quartz cell on a Jasco P-1030 polarimeter. NMR spectra were taken on a Varian Mercury 300 operating at 300 MHz for $^1$H or a Varian VXR-500 (500 MHz for $^1$H) spectrometer with TMS (for CDCl$_3$) or a solvent residual peak (for DMSO-$d_6$) as the internal standard. The absorption and CD spectra were measured in a 0.5-cm quartz cell unless otherwise noted using a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter, respectively. The temperature was controlled with a liquid nitrogen-controlled quartz cell (0.5 cm) in a cryostat. The concentrations of the polymers were calculated based on the monomer units and 0.1 mg/mL unless otherwise stated. The polymer concentrations at low temperatures in THF were corrected by using the density of THF at the given temperature. Chiral HPLC analyses were performed with a Jasco PU-1580 liquid chromatograph equipped with a UV-visible detector (254 nm,
Jasco UV-1570) using Chiralpak AD-H and Chiralcel OD-H columns (25 x 0.46 (i.d.) cm) connected in series at room temperature. Hexane–2-propanol mixture (98/2, v/v) was used as the eluent at a flow rate of 0.8 mL/min. SEC measurements were performed with a Jasco PU-980 liquid chromatograph equipped with UV-visible (300 nm, Jasco UV-970) and RI (Jasco RI-930) detectors and a column oven (Jasco CO-965). The $M_n$ and its $M_w/M_n$ values were determined at 40 °C using Tosoh TSK-GEL α-3000 (30 cm) and α-5000 (30 cm) SEC columns connected in series, and DMF containing 10 mM LiCl was used as the eluent at a flow rate of 0.5 mL/min. The molecular weight calibration curve was obtained with poly(ethylene oxide) and poly(ethylene glycol) standards (Tosoh).

References


Fig. S1 $^1$H NMR spectra of rac-1 (A) and the mixture of (S)-1 and (R)-2 obtained by lipase-catalyzed kinetic resolution of rac-1 (B) in CDCl$_3$. 
**Fig. S2** HPLC chromatograms for the enantioseparation of rac-1 and rac-2 (A) and (S)-1 and (R)-2 obtained by lipase-catalyzed kinetic resolution of rac-1 (B) using chiral columns (Chiralpak AD-H and Chiralcel OD-H) with hexane/2-propanol (98/2, v/v) as the eluent.
**Fig. S3** $^1$H NMR spectrum of poly((S)-1-co-(R)-2) in DMSO-$d_6$ at 30 °C. X denotes protons from solvent.
Fig. S4 (A) CD spectra of poly((S)-1) in THF/DMF (9/1, v/v), and poly((R)-2) and poly((S)-1-co-(R)-2) ([1]/[2] = 53/47) in THF measured at –10 °C, and the sum of the CD spectra of the homopolymers (poly((S)-1) + poly((R)-2)) ([1]/[2] = 53/47). (B) CD spectra of poly((S)-3) and poly((R)-2), poly((S)-3-co-(R)-2) ([3]/[2] = 53/47) measured in THF at –10 °C, and the sum of the CD spectra of the homopolymers (poly((S)-3) + poly((R)-2)) ([3]/[2] = 53/47).