Supporting Information

Helix Formation of Poly(phenylacetylene)s Bearing Azide Groups through Click Polymer Reaction with Optically Active Acetylenes

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Experimental Section

Materials

Triethyl amine (Et_3N) was dried over KOH pellets and distilled onto KOH under nitrogen. Chloroform ($CHCl_3$) was dried over calcium hydride, distilled, and stored under nitrogen. Et_3N and $CHCl_3$ were redistilled from KOH and calcium hydride under high vacuum just before polymerization, respectively. Anhydrous tetrahydrofuran (THF) and methanol (MeOH) (water content < 0.005%), 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), and (*S*)-(+)-mandelic acid ((*S*)-**5**) were purchased from Wako (Osaka, Japan). Anhydrous dimethyl sulfoxide (DMSO) (water content < 0.005%), (*R*)- and (*S*)-1-phenyl-2-propyn-1-ol, and bis[(norbornadiene)rhodium(I) chloride] ([Rh(nbd)Cl_2]) were obtained from Aldrich (Milwaukee, WI). Sodium azide (NaN_3), copper(I) iodide (CuI), and (*R*)-(–)-mandelic acid ((*R*)-**5**) were obtained from Kishida (Osaka, Japan). (Trimethylsilyl)acetylene was kindly supplied from Shinetsu Chemical (Tokyo, Japan). 1-Bromomethyl-4-(trimethylsilylethynyl)benzene was synthesized according to the previously reported method (78% yield).[1]

Measurements

IR spectra were recorded using a JASCO Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). 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 and 125 MHz for ^{13}C) spectrometer with a solvent residual peak or tetramethylsilane (TMS) as the internal standard. The absorption and CD spectra were measured in a 0.1-cm quartz cell using a JASCO V-560 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The concentrations of the polymers were calculated based on the monomer units. Size exclusion chromatography (SEC) measurements were performed with a JASCO PU-2080 liquid chromatograph equipped with a UV-visible (254 nm, JASCO UV-2075) detector and a column oven (JASCO CO-2060). A Tosoh TSKgel MultiporeH_{XL}-M GPC column (30 cm) was connected and $CHCl_3$ was used as the eluent at a flow rate of 0.5 mL/min. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh).

Momomer Synthesis

Preparation of 1. Compound **1** was synthesized according to the reported method (46 % yield).[2] IR (neat, cm^{-1}): 2101 ($\nu_{N=N=N}$). ^1H NMR (300 MHz, $CDCl_3$, rt): δ 3.08 (s, 1H, ≡CH), 6.98 (d, J = 8.7 Hz, 2H, aromatic), 7.48 (d, J = 8.7 Hz, 2H, aromatic). Anal. Calcd for $C_8H_5N_3$: C, 67.12; H, 3.52; N, 29.35. Found: C, 66.85; H, 3.33; N, 29.56.

Preparation of 1-azidomethyl-4-(trimethylsilylethynyl)benzene. 1-Bromomethyl-4-(trimethylsilylethynyl)benzene (4.00 g, 15.0 mmol) was added to a solution of NaN_3 (1.02 g, 15.7 mmol) in DMSO (31.4 mL), and the reaction mixture was stirred at ambient temperature for 11 h. Water and diethyl ether were added to the reaction mixture and the ether layer was washed with water and then dried over $MgSO_4$. After filtration, the solvent was removed by evaporation. The crude product was purified by silica gel chromatography with hexane to give 1-azidomethyl-4-(trimethylsilylethynyl)benzene as a yellow liquid (2.74 g, 80% yield). IR (neat, cm^{-1}): 2100 ($\nu_{N=N=N}$). ^1H NMR (500 MHz, $CDCl_3$, rt): δ 0.25 (s, 9H, CH_3), 4.34 (s, 2H, CH_2), 7.25 (d, J = 8.2 Hz, 2H, aromatic), 7.48 (d, J = 8.3 Hz, 2H, aromatic).

Preparation of 2. To a solution of 1-azidomethyl-4-(trimethylsilylethynyl)benzene (2.5 g, 11 mmol) in MeOH (168 mL) was added 1 M aqueous NaOH solution (56 mL), and the mixture was stirred at ambient temperature for 3 h. After evaporating the solvent, the crude product was diluted with diethyl ether, and the solution was washed with water and dried over $MgSO_4$. After filtration and evaporation of the solvent, the residue was distilled under reduced pressure (bp: 36-38 °C/0.05 mmHg) to give **2** as a colorless liquid (1.18 g, 69% yield). IR (neat, cm^{-1}): 2100 ($\nu_{N=N=N}$). ^1H NMR (500 MHz, $CDCl_3$, rt): δ 3.10 (s, 1H, ≡CH), 4.35 (s, 2H, CH_2), 7.28 (d, J =10.0 Hz, 2H, aromatic), 7.51 (d, J = 10.0 Hz, 2H, aromatic). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 54.4, 77.8, 83.1, 122.2, 128.1, 132.6, 136.1. Anal. Calcd for $C_9H_7N_3$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.63; H, 4.38; N, 26.85.

Polymerization

Polymerization was carried out according to Scheme 1 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.

A solution of **1** in $CHCl_3$ (0.67 M, 0.63 mL) was placed in a dry glass ampule equipped with a three-way stopcock under dry nitrogen. To this was added a solution of $[Rh(nbd)Cl]_2$ (0.0050 M) containing Et_3N ($[Et_3N]/[Rh] = 200$) in $CHCl_3$ at 30 ˚C. The concentrations of the monomer and the rhodium complex were 0.5 and 0.0025 M, respectively. After 30 min, the resulting polymer was precipitated into a large amount of MeOH and collected by centrifugation. The obtained polymer was dissolved in a small amount of $CHCl_3$, and the solution was re-precipitated into hexane. The precipitated polymer was collected by centrifugation and dried in vacuo at room temperature overnight to give poly-**1** in 68% yield. The stereoregularity of the obtained polymer was confirmed to be a highly *cis-transoidal* by ^{1}H NMR spectroscopy[3-8] The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the obtained polymer were 7.40×10^3 and 3.27, respectively, as determined by SEC using polystyrene standards in $CHCl_3$ as the eluent. In the same way, poly-**2** was prepared in 78% yield and its M_n and M_w/M_n values were 2.33×10^5 and 3.37, respectively.

Poly-**1**: IR (KBr, cm^{-1}): 2097 ($\nu_{N=N=N}$). ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): δ 5.75 (s, 1H, =CH), 6.62–6.69 (m, 4H, aromatic). Anal. Calcd for $(C_8H_5N_3)_n$: C, 67.12; H, 3.52; N, 29.35. Found: C, 66.83; H, 3.50; N, 29.13.

Poly-**2**: IR (KBr, cm^{-1}): 2098 ($\nu_{N=N=N}$). ^{1}H NMR (500 MHz, $CDCl_3$, 60 °C): δ 4.10 (s, 2H, $-CH_2$), 5.81 (s, 1H, =CH), 6.65 (d, 2H, aromatic), 6.89 (d, 2H, aromatic). Anal. Calcd for $(C_9H_7N_3)_n$: C, 68.78; H, 4.49; N, 26.74. Found: C, 68.61; H, 4.46; N, 26.85.

Click Polymer Reaction of Poly-1 and Poly-2

A typical experimental procedure is described below.

Synthesis of poly-(*S*)-3. To a solution of poly-**1** (10.4 mg, 0.0727 mmol) in THF (730 μL) were added (*R*)-1-phenyl-2-propyn-1-ol (13.6 μL, 0.110 mmol), CuI (4.2 mg, 0.022 mmol), and DBU (5.4 μL, 0.036 mmol) and the reaction mixture was stirred at ambient temperature for 1.5 h. The resulting polymer was precipitated into a large amount of MeOH, collected by centrifugation, and dried in vacuo at room temperature overnight. The polymer was then washed with MeOH and hexane, collected by centrifugation, and dried in vacuo at room temperature overnight (16.9 mg, 85% yield).

Poly-(*S*)-**3** (85% yield): ^{1}H NMR (500 MHz, DMSO-d_6 / TFA-*d* (99/1, v/v), 60 °C): δ 5.83 (s, 2H, CH, =CH), 6.40-7.80 (br, 9H, aromatic), 8.23 (s, 1H, =CH). Anal. Calcd for $(C_{17}H_{13}N_3O)_n$: C, 74.17; H, 4.76; N, 15.26. Found: C, 73.99; H, 4.60; N, 15.11.

Poly-(*R*)-**3** (81% yield): ^{1}H NMR (500 MHz, DMSO-d_6 / TFA-*d* (99/1, v/v), 60 °C): δ 5.83 (s, 2H, CH, =CH), 6.40-7.80 (br, 9H, aromatic), 8.23 (s, 1H, =CH). Anal. Calcd for $(C_{17}H_{13}N_3O)_n$: C, 74.17; H, 4.76; N, 15.26. Found: C, 73.89; H, 4.54; N, 15.01.

Poly-(*S*)-**4** (>99% yield): ^{1}H NMR (500 MHz, DMSO-d_6 / TFA-*d* (99/1, v/v), 60 °C): δ 5.15 (s, 2H, CH_2), 5.58 (s, 1H, CH), 5.78 (s, 1H, =CH), 6.47 (s, 2H, aromatic), 6.74 (s, 2H, aromatic), 7.08-7.30 (m, 5H, aromatic), 7.73 (s, 1H, =CH). Anal. Calcd for $(C_{18}H_{15}N_3O)_n$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.55; H, 5.04; N, 14.41.

Poly-(*R*)-**4** (95% yield): ^{1}H NMR (500 MHz, DMSO-d_6 / TFA-*d* (99/1, v/v), 60 °C): δ 5.15 (s, 2H, CH_2), 5.58 (s, 1H, CH), 5.78 (s, 1H, =CH), 6.47 (s, 2H, aromatic), 6.74 (s, 2H, aromatic), 7.08-7.30 (m, 5H, aromatic), 7.73 (s, 1H, =CH). Anal. Calcd for $(C_{18}H_{15}N_3O)_n$: C, 74.72; H, 5.23; N, 14.52. Found: C, 74.51; H, 5.03; N, 14.37.

Almost complete conversions of poly-**1** and poly-**2** to poly-**3** and poly-**4**, respectively, were confirmed by their IR spectra that showed almost the disappearance of the azide signals of poly-**1** and poly-**2** (Figures S4 and S5). The elemental analyses of the polymers agreed satisfactorily with the calculated values. The stereoregularities of poly-**3** and poly-**4** were confirmed to be *cis-transoidal* by ^{1}H NMR spectroscopy (Figure S1).[3-8]

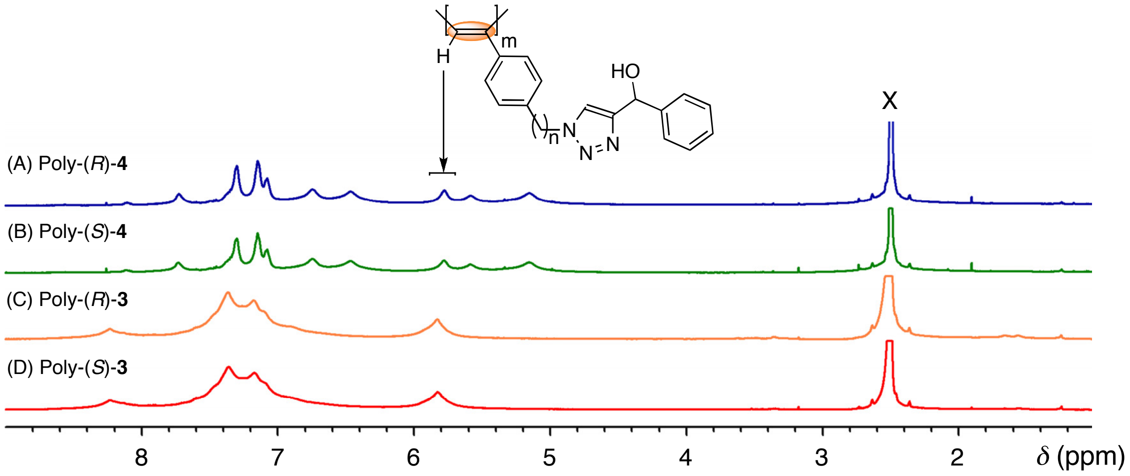

Figure S1. ^{1}H NMR spectra of poly-(*R*)-**4** (A), poly-(*S*)-**4** (B), poly-(*R*)-**3** (C), and poly-(*S*)-**3** (D) in DMSO-d_6 / TFA-*d* (99/1, v/v) at 60 °C. X denotes protons from solvent.

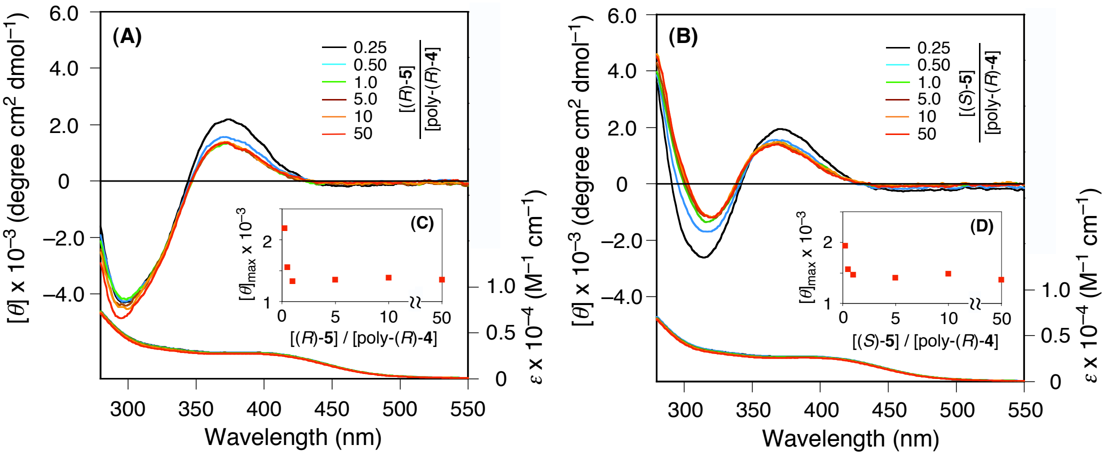

Figure S2. CD and absorption spectral changes of poly-(*R*)-**4** with (*R*)- (A) and (*S*)-**5** (B) in DMSO in a 0.1-cm quartz cell at 25 °C; the molar ratio of **5** to monomer units of poly-(*R*)-**4** is 0.25, 0.50, 1.0, 5.0, 10, and 50. Polymer concentration is 0.5 mg/mL. Insets show the titration plots of $[\theta]_{\max}$ (1st Cotton effect) in the complexation of poly-(*R*)-**4** with (*R*)- (C) and (*S*)-**5** (D).

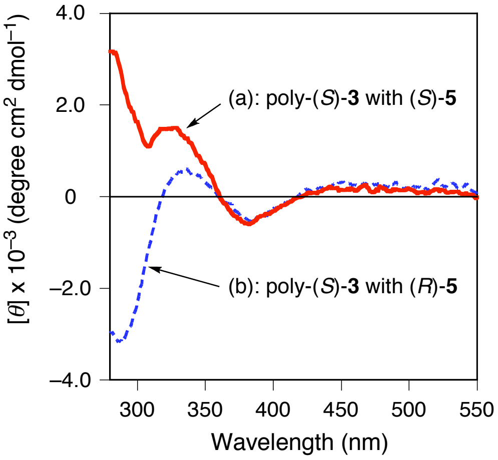

Figure S3. CD spectra of poly-(*S*)-**3** with (*S*)- (a) and (*R*)-**5** (b) (50 equiv) in DMSO in a 0.1-cm quartz cell at 25 °C. Polymer concentration is 0.2 mg/mL.

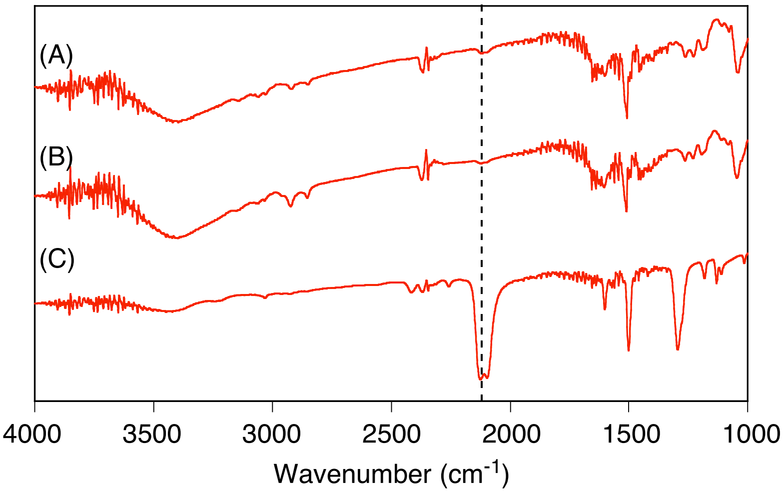

Figure S4. IR spectra of poly-(*R*)-**3** (A), poly-(*S*)-**3** (B), and poly-**1** (C) (KBr).

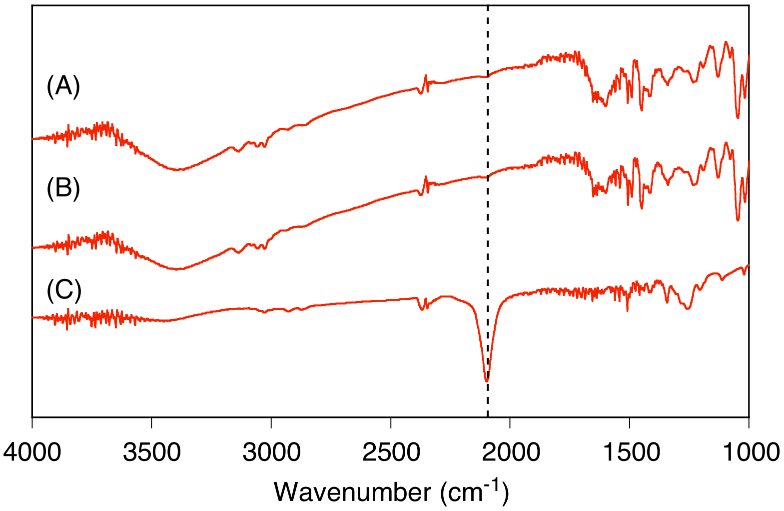

Figure S5. IR spectra of poly-(*R*)-**4** (A), poly-(*S*)-**4** (B), and poly-**2** (C) (KBr).

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