

Supplementary Information for:

**Synthesis and chiral recognition ability of helical polyacetylenes
bearing helicene pendants**

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1. Instruments

The NMR spectra were measured using a Varian AS500 spectrometer (Agilent, Santa Clara, CA) operating at 500 MHz for ^1H using tetramethylsilane (TMS) as the internal standard. The absorption and CD spectra were obtained in a 0.1, 0.5, or 5 cm quartz cell using a JASCO V570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively (JASCO, Tokyo, Japan). The temperature was controlled with a JASCO PTC-423L apparatus. The concentrations of the polymers were calculated based on the monomer units. The size exclusion chromatography (SEC) measurements and fractionations were performed with a JASCO PU-980 liquid chromatograph equipped with a UV-visible detector (300 nm, JASCO UV-1570) and a column oven (JASCO CO-1565). The number-average molecular weight (M_n) and its distribution (M_w/M_n) were determined at 40 °C using a Tosoh TSKgel Multipore H_{XL}-M (0.78 (i.d.) x 30 cm) SEC column (Tosoh, Tokyo, Japan), and tetrahydrofuran (THF) or chloroform (CHCl_3) was used as the eluent at a flow rate of 0.5 or 1.0 mL/min, respectively. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). The chiral HPLC analyses and separations were performed on a JASCO PU-2080 liquid chromatograph equipped with a UV-visible detector (JASCO UV-2075 or MD-2010) and an optical rotation (JASCO OR-2090) or a CD detector (JASCO CD-2095) using Chiracel OD-H, Chiralpak IA and Chiralpak IB columns (0.46 (i.d.) x 25 cm, or 2 (i.d.) x 25 cm, Daicel, Osaka, Japan). The laser Raman spectra were taken on a JASCO RMP-200 spectrophotometer. The matrix-assisted laser desorption/ionisation time-of-flight mass (MALDI-TOF-MS) spectra were taken on a Shimadzu AXIMA-CFR plus spectrometer (Shimadzu, Kyoto, Japan) equipped with a 337 nm N_2 laser.

2. Materials

All starting materials and anhydrous solvents were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), or Tokyo Kasei (TCI, Tokyo, Japan), and were used as received, except for triethylamine (Et_3N) and THF. Et_3N was dried over KOH pellets and distilled onto KOH under nitrogen. THF was dried and deoxygenised by passing through purification columns (Glass Contour Solvent System, Nikko Hansen, Osaka, Japan), distilled onto LiAlH_4 under nitrogen and redistilled under high vacuum just before polymerisation. 2-Ethynyl-carbo[6]helicene (**1-rac**) was synthesised according to the previously reported method.^{S1} The helicene **1-rac** was separated into the enantiomers (**1-P** and **1-M**) using a chiral HPLC column (Chiralpak IB, 2 (i.d.) x 25 cm, *n*-hexane/EtOH = 99:1 (v/v), 11 mL/min),

and the enantiomeric excess (*ee*) values of the **1-P** and **1-M** separated were estimated to be >99% using a chiral HPLC column (Chiralpak IB, 0.46 (i.d.) x 25 cm, *n*-hexane/EtOH = 99:1 (v/v), 1 mL/min) (Fig. S1). (–)-Poly(triphenylmethyl methacrylate) (PTrMA, $[\alpha]_D^{25}$ -336 (*c* 2.0, THF)) was synthesised according to the previously reported method.^{S2} The M_n and M_w/M_n of (–)-PTrMA estimated as its methyl ester (poly(methyl methacrylate)) were 7.0×10^3 and 1.19, respectively, as determined by SEC using poly(styrene) standards in CHCl₃ as the eluent.

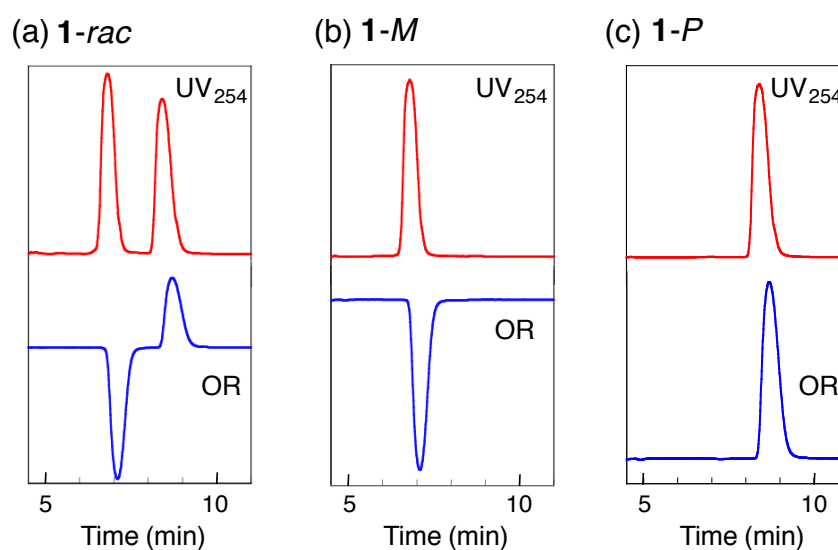


Fig. S1 HPLC traces of **1-rac** (a), **1-M** (b) and **1-P** (c) using a Daicel Chiralpak IB column [*n*-hexane/EtOH = 99:1 (v/v), 1 mL/min].

3. Synthesis of Polymers

Polymerisation. Polymerisations of **1-rac**, **1-P** and **1-M** were carried out according to Scheme 1 in a dry glass ampule under a dry nitrogen atmosphere using [Rh(nbd)Cl]₂ as a catalyst in a similar way as reported previously.^{S3} The polymerisation results are summarised in Table 1. A typical polymerisation procedure is described below.

The monomer **1-M** (50.0 mg, 0.142 mmol) was placed in a dry 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 a mixture of Et₃N (19.8 μ L, 0.142 mmol) and anhydrous THF (0.64 mL) was added with a syringe. To this was added a solution of [Rh(nbd)Cl]₂ (0.06 M) in THF (0.07 mL) at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.2 and 0.006 M, respectively. After 13 h, a

solution of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (0.06 M) in THF (0.07 mL) was added again to complete the polymerisation. After additional 5 h, the resulting polymer (poly-**1-M**) was precipitated into a large amount of Et_2O , washed with Et_2O and collected by centrifugation. The product was purified by reprecipitation from CHCl_3 to Et_2O , and the precipitated poly-**1-M** was washed with Et_2O and dried *in vacuo* at room temperature overnight (23.6 mg, 47% yield) (entry 4 in Table 1). The polymers obtained were soluble in THF under dilute conditions (less than ca. 1 mg/mL). The M_n and M_w/M_n values were 1.8×10^3 and 2.7, respectively, as determined by SEC using polystyrene standards in THF as the eluent. The obtained poly-**1-M** (12 mg) was then subjected to SEC fractionation to obtain four parts with different molecular weights, poly-**1-M_A** (<0.1 mg), poly-**1-M_B** (ca. 4 mg, $M_n = 5.2 \times 10^3$, $M_w/M_n = 1.3$), poly-**1-M_C** (ca. 4 mg, $M_n = 2.1 \times 10^3$, $M_w/M_n = 1.6$) and poly-**1-M_D** (ca. 4 mg, $M_n = 0.79 \times 10^3$, $M_w/M_n = 1.4$). The results of the SEC fractionation are summarised in Table 1.

Spectroscopic data of poly-**1-M** (entry 14 in Table 1): IR (film, cm^{-1}) 3045, 2920, 2850. ^1H NMR (500 MHz, CDCl_3 , 50 °C): δ 8.0 (br, aromatic, C=CH). Anal. Calcd (%) for $(\text{C}_{28}\text{H}_{16})_n$: C, 95.42; H, 4.58. Found: C, 95.61; H, 4.79.

Spectroscopic data of poly-**1-rac** (entry 4 in Table 1): Yield: 46%. IR (film, cm^{-1}) 3045, 2918, 2849. ^1H NMR (500 MHz, CDCl_3 , 50 °C): δ 8.0 (br, aromatic, C=CH). Anal. Calcd (%) for $(\text{C}_{28}\text{H}_{16})_n$: C, 95.42; H, 4.58. Found: C, 95.41; H, 4.70.

Spectroscopic data of poly-**1-P** (entry 9 in Table 1): Yield: 52%. IR (film, cm^{-1}) 3044, 2917, 2849. ^1H NMR (500 MHz, CDCl_3 , 50 °C): δ 8.0 (br, aromatic, C=CH). Anal. Calcd (%) for $(\text{C}_{28}\text{H}_{16})_n$: C, 95.42; H, 4.58. Found: C, 95.32; H, 4.58; N, 0.14.

4. Characterisation of Monomers and Polymers

The ^1H NMR spectra of poly-1s were too broad to determine the stereoregularity. Therefore, their stereoregularities were investigated by laser Raman spectroscopy. Fig. S2 shows the Raman spectra of poly-1-*rac*, poly-1-*P* and poly-1-*M* (Table 1, entries 4, 9 and 14). All the polymers showed intense peaks at 1505, 1311, 873 cm^{-1} (a), 1509, 1310, 882 cm^{-1} (b) and 1508, 1311, 874 cm^{-1} (c), which can be assigned to the C=C, C-C and C-H bond vibrations in the *cis* polyacetylenes, respectively,^{S4} indicating that these polymers possess a highly *cis-transoidal* structure.

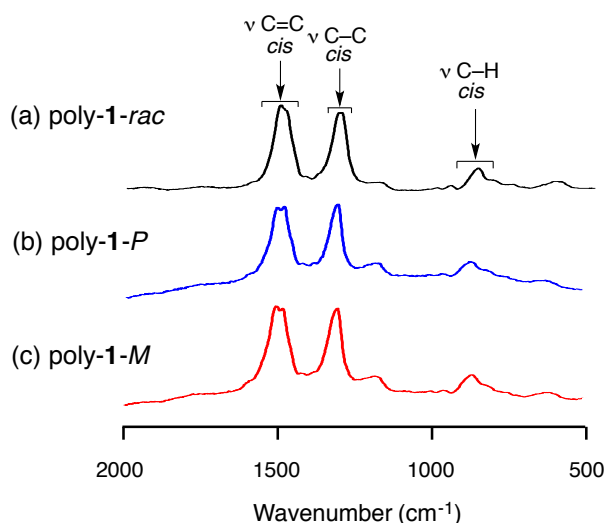


Fig. S2 Raman spectra of poly-1-*rac* (a), poly-1-*P* (b) and poly-1-*M* (c).

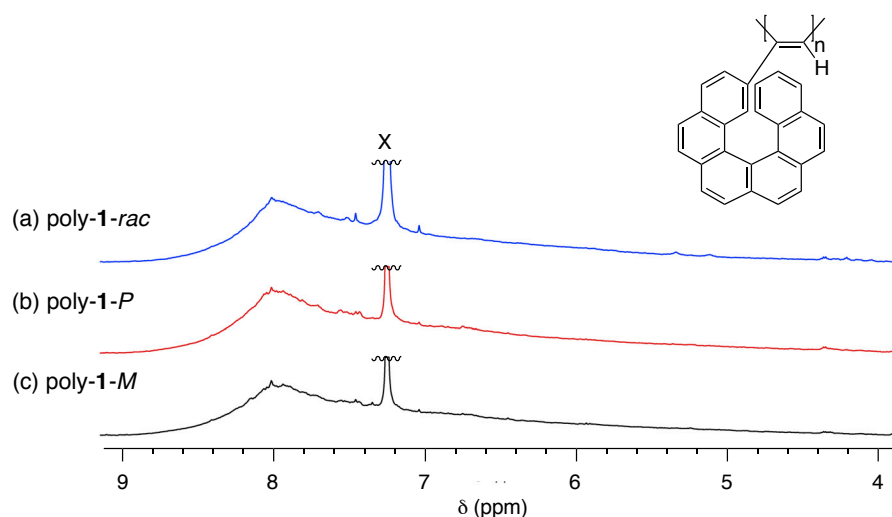


Fig. S3 ^1H NMR spectra of poly-1-*rac* (a), poly-1-*P* (b) and poly-1-*M* (c) in CDCl_3 at 50 $^\circ\text{C}$. X denotes the proton from CHCl_3 .

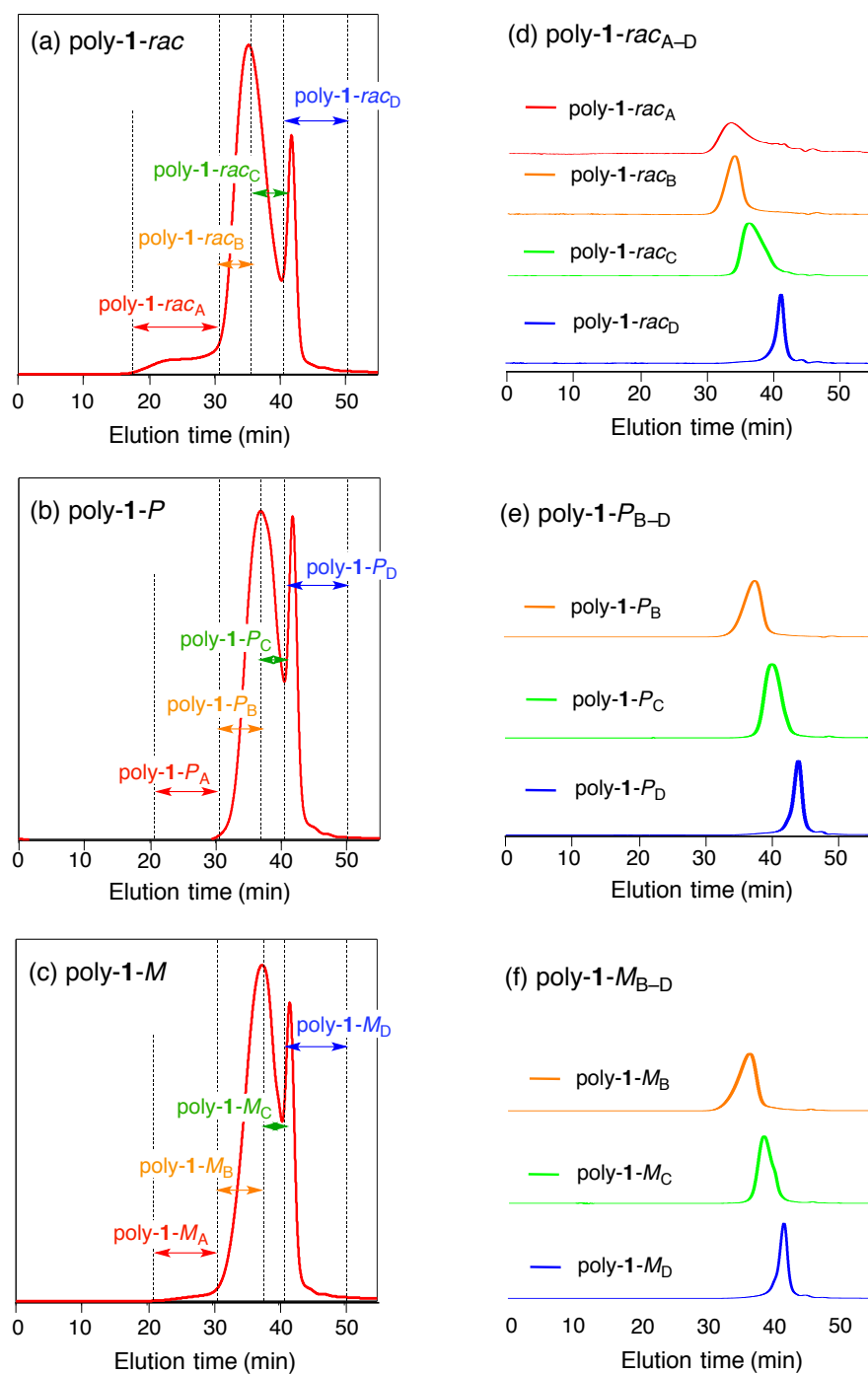


Fig. S4 SEC chromatograms of poly-1-*rac* (a), poly-1-*P* (b), poly-1-*M* (c), poly-1-*rac*_{A-D} (d), poly-1-*P*_{B-D} (e) and poly-1-*M*_{B-D} (f) at 40 °C (column, TSKgel Multipore H_{XL}-M (0.78 (i.d.) x 30 cm; eluent, THF; flow rate, 0.5 mL/min).

Fig. S5 shows the MALDI-TOF MS spectra of poly-**1**- M_B , poly-**1**- M_C and poly-**1**- M_D . The samples were prepared from a THF solution by mixing *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (20 mg/mL) as the matrix, each polymer (10 mg/mL) and AgOCOCF₃ as a cationising agent (2 mg/mL) in a volume ratio of 1:100:1, respectively, according to the reported method.^{S5} As shown in Fig. S5, a series of high molecular weight (MW) peaks up to over 10,000 Da was detected for poly-**1**- M_B and poly-**1**- M_C with an interval of approximately 352 Da corresponding to the *m/z* of a monomer unit, while the degradation of the polyacetylenes took place during the ionisation most likely via intramolecular cyclisation of the main-chain, thus generating the cyclic trimer or its protonated analogue as supported by an intense mass peak of 1062 Da (data not shown). Although it was difficult to determine the number-average MWs of poly-**1**s based on the MALDI-TOF MS spectra because of the degradation of the polymers during the measurements, the MALDI-TOF MS results suggest that the MWs of poly-**1**- M_B , poly-**1**- M_C and poly-**1**- M_D estimated by SEC may be underestimated. Similar tendency was also reported by Kumazawa et al.; the MWs of poly(phenylacetylene)s calculated by MALDI-TOF MS were 1.5 times larger than those estimated by SEC.^{S5}

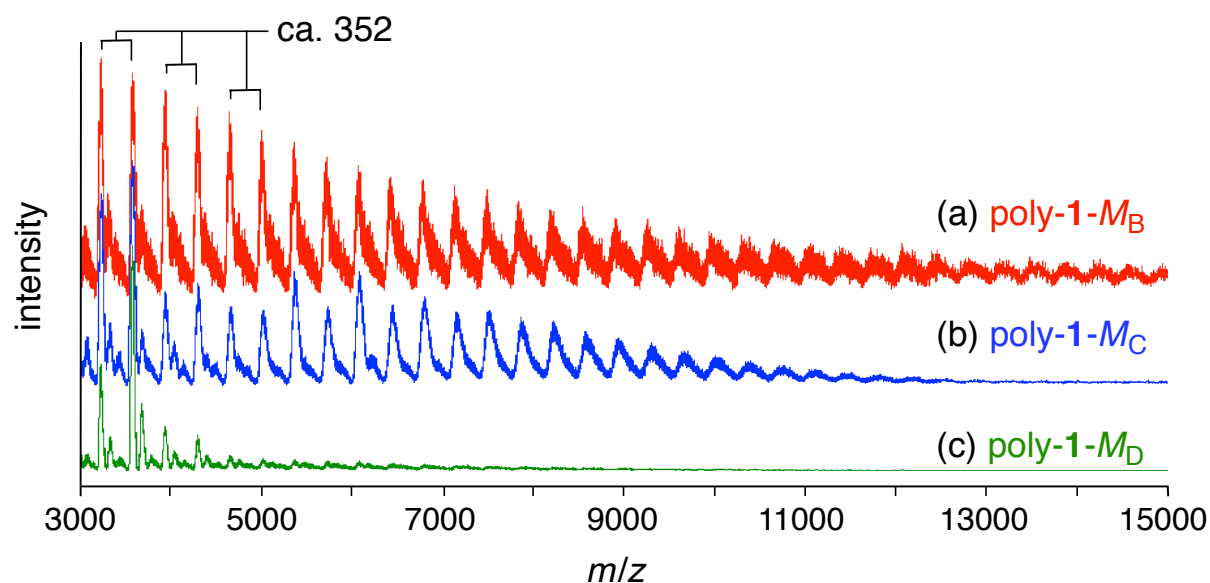


Fig. S5 MALDI-TOF MS spectra of poly-**1**- M_B (a), poly-**1**- M_C (b) and poly-**1**- M_D (c) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile as a matrix and AgOCOCF₃ as a cationising agent.

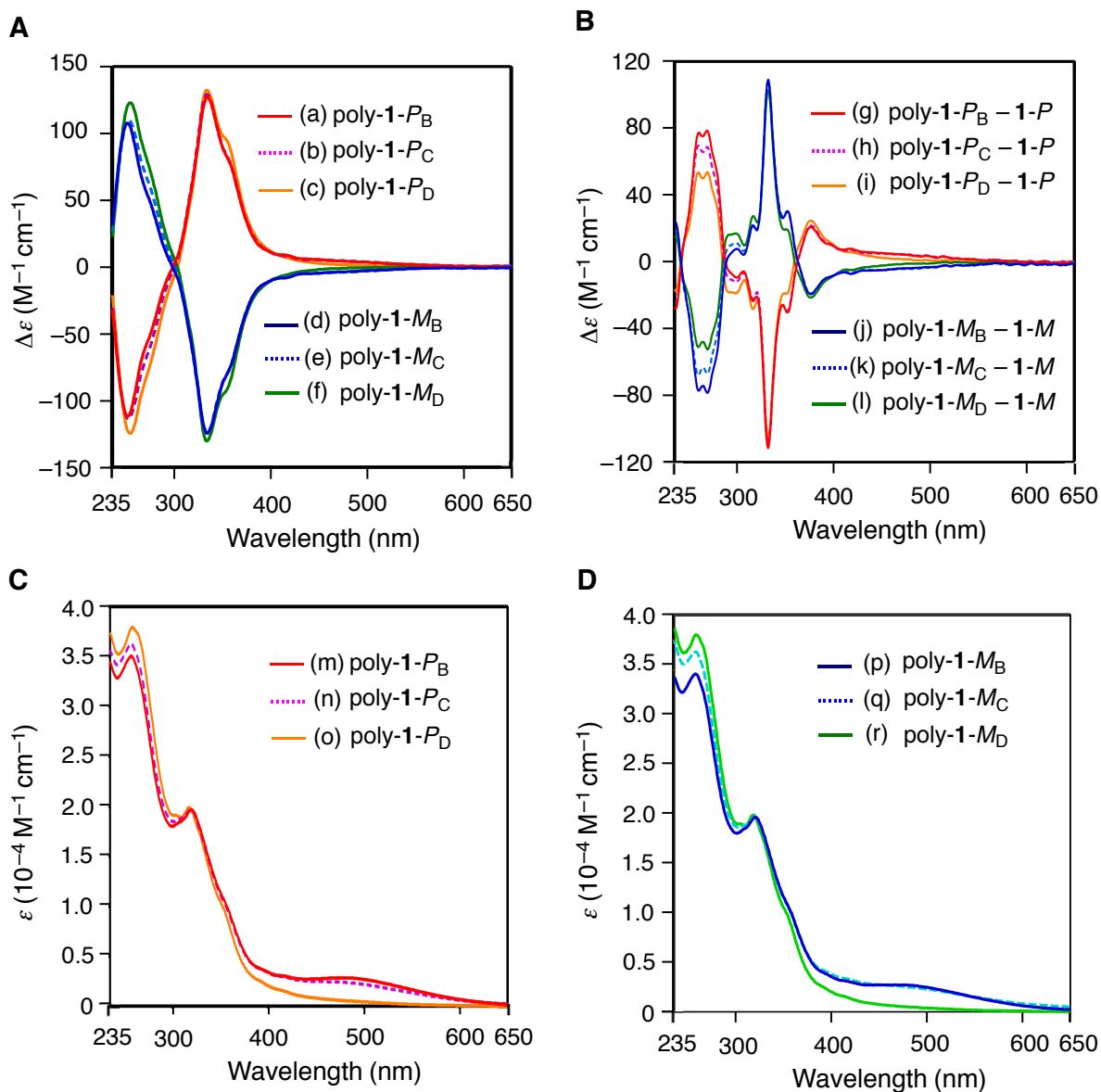


Fig. S6 (A) CD and (C, D) absorption spectra of fractionated poly-**1-P**_{B-D} (a-c, m-o) and poly-**1-M**_{B-D} (d-f, p-r) in THF at 25 °C. (B) Differential CD spectra between fractionated poly-**1-P**_{B-D} and **1-P** and poly-**1-M**_{B-D} and **1-M**, where the CD spectra of **1-P** and **1-M** are subtracted from the observed CD spectra of poly-**1-P**_{B-D} and poly-**1-M**_{B-D}, respectively, without normalisation (see also Fig. 1). The concentrations were 0.02 mg/mL.

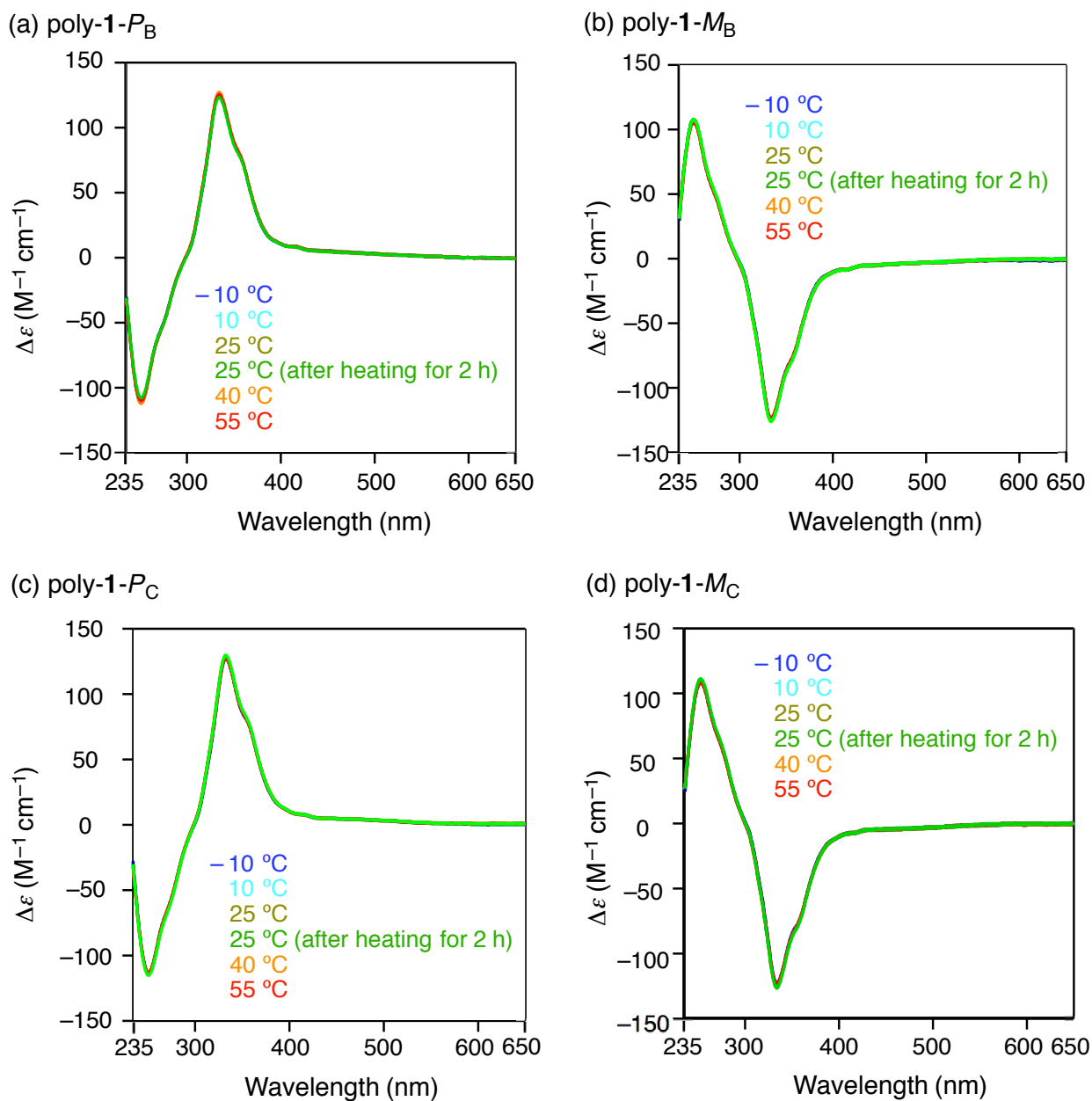


Fig. S7 CD spectra of poly-1- P_B (a), poly-1- M_B (b), poly-1- P_C (c) and poly-1- M_C (d) in THF (0.02 mg/mL) at various temperatures and at 25 °C after heating at 55 °C for 2 h.

5. Molecular Modeling and Calculations

The molecular modeling and molecular mechanics (MM) calculations of poly-**1-M** were conducted with the Compass force field,^{S6} as contained in the MS Modeling software (version 4.4, Accelrys, San Diego, CA) operated using a PC running under Windows XP.

The initial monomer unit structure was constructed using the crystal structure of 2-methyl-carbo[6]helicene.^{S7} The main-chain helix sense of poly-**1-M** in THF where the negative first Cotton effect was observed at the main-chain region (380–600 nm) is assumed to be right-handed on the basis of the CD spectral pattern of the analogous L-alanine-bound helical poly(phenylacetylene) whose helix sense was determined by the direct observation of the helical structure obtained from the high-resolution atomic force microscopy (AFM).^{S8} When the main-chain of poly-**1-M** is right-handed, it possesses an opposite, left-handed helical array of the pendants. The polymer model (40 repeating monomer units) of poly-**1-M** was constructed using the Polymer Builder module in the MS Modeling software. The starting main-chain geometrical parameters such as the bond lengths were defined as a 23 unit/10 turn (23/10) helix on the basis of the helical structure of a cis-transoidal poly(phenylacetylene) bearing *N,N*-diisopropylaminomethyl pendants determined by X-ray analysis.^{S9} The dihedral angle between the main chain and the aromatic residue of the pendant (θ) was varied from 0° to 300° at 60° intervals, and the dihedral angle of the single bond (C=C–C=C) from planarity (ϕ) was set to be 140.3°,^{S9} 150.7°,^{S8b} 160° and 170° (transoid) (Chart S1). The geometrical parameters for the helical poly-**1-M** backbone structure were fixed during the following force field optimisation. The geometry optimisations were performed without any cutoff by the smart algorithm in three steps. First, the starting conformations were subject to the steepest decent optimisation to eliminate the worse steric conflicts. Second, subsequent optimisation until the convergence using a conjugate gradient algorithm was performed. The fully optimised polymer models were obtained by the further energy minimisation using the Newton method with the 0.1 kcal mol⁻¹ Å⁻¹ convergence criterion. The dihedral angles (θ and ϕ) of the optimised helical structure were 310±1° and 160°, respectively. The final right-handed helical poly-**1-M** model as shown in Fig. 2 was reconstructed by adopting the geometry of the central monomer unit of the optimised poly-**1-M** structure to avoid the end-group effect.

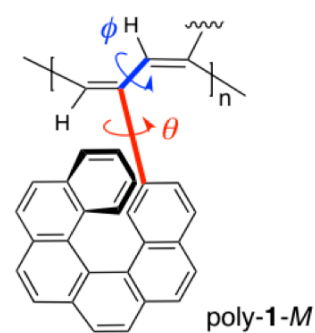


Chart S1

6. Enantioselective Adsorption

Enantioselective Adsorption of Poly-1s by (-)-PTrMA. A typical experimental procedure for the enantioselective adsorption of an equimolar mixture of the enantiomeric poly-1-*P* and poly-1-*M* by (-)-PTrMA is described below. A mixture of (-)-PTrMA (0.4 mg), poly-1-*P* (0.04 mg) and poly-1-*M* (0.04 mg) was dispersed in THF (2 mL) in a screw-capped sample bottle, and to this was added *n*-hexane (8 mL) at ca. 25 °C, affording a white precipitate of (-)-PTrMA on which poly-1 was adsorbed. After centrifugation, the absorption and CD spectra of the supernatant solution were measured to determine the amount and ee of poly-1 (Fig. S8). In the same way, the enantioselective adsorption experiment was performed for poly-1-*rac* and the results are summarised in Table S1.

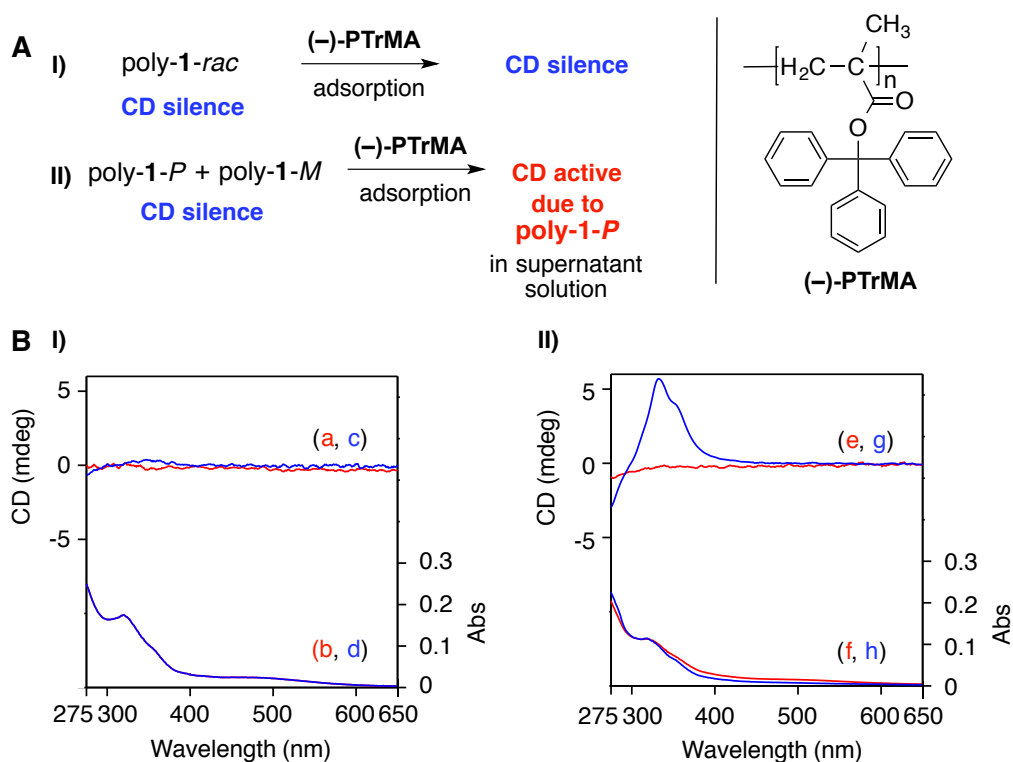


Fig. S8 (A) Experimental procedures for the enantioselective adsorption of (I) poly-1-*rac* and (II) an equimolar mixture of poly-1-*P* and poly-1-*M* by (-)-PTrMA. (B) CD and absorption spectra of poly-1-*rac* (a,b, red lines) and an equimolar mixture of poly-1-*P* and poly-1-*M* (c,d, blue lines) in THF (0.04 mg/mL, 0.1 cm cell) and those of the supernatant solutions after enantioselective adsorption of poly-1-*rac* (e,f, red lines) and the equimolar mixture of poly-1-*P* and poly-1-*M* (g,h, blue lines) by (-)-PTrMA in THF/*n*-hexane (2:8, v/v, 5 cm cell) at 25 °C (see Table S1).

Table S1 Enantioselective adsorption of poly-1s by (-)-PTrMA

Entry	Analyte	Yield of adsorbed analyte (%) ^a	Ee of analyte in supernatant solution (%) ^a
1	poly-1- <i>rac</i>	94.5	<1
2	an equimolar mixture of poly-1- <i>P</i> and poly-1- <i>M</i>	94.3	36.5 (<i>P</i>)

^aDetermined by absorption and CD measurements of the supernatant solution.

Enantioselective Adsorption of 1-*rac* by Poly-1-*P* or Poly-1-*M*. A typical experimental procedure for the enantioselective adsorption of 1-*rac* by poly-1-*M* is described below. A solution of a racemic monomer (1-*rac*) in methanol (0.04 mg/mL, 1 mL) was placed into a screw-capped sample bottle containing poly-1-*M* (2.0 mg, powder), which had been thoroughly washed with a dibutyl ether/THF (80:20, v/v) mixture and then methanol prior to the experiments. After standing at ca. 25 °C for 24 h, the 1-*rac* adsorbed on the poly-1-*M* was recovered by filtration and quickly washed with methanol (1 mL) to remove the racemic solution of 1 attached on the surface of the polymer. The recovered poly-1-*M* was placed into a screw-capped sample bottle containing methanol (5 mL), and the mixture was permitted to stand at ca. 25 °C for 3 h to desorb 1 adsorbed on the poly-1-*M*. This desorption procedure was repeated with methanol (5 mL) and then with a methanol/THF (50:50, v/v) mixture (5 mL), which almost completely desorbed 1 on the poly-1-*M*; the remaining 1 on the poly-1-*M* after the present desorption procedure was found to be negligibly small (< 0.05%) on the basis of SEC fractionation using a Tosoh TSKgel Multipore H_{XL}-M (30 cm) SEC column (THF, 0.5 mL/min) followed by HPLC analysis of 1 adsorbed on the poly-1-*M* after dissolving in THF. The amount and ee of 1 adsorbed on the poly-1-*M* were estimated by chiral HPLC using a Daicel Chiralpak IB column (0.46 (i.d.) x 25 cm, *n*-hexane/EtOH = 99:1 (v/v), 1 mL/min) equipped with UV and CD detectors. The results are summarised in Table 2.

Enantioselective Adsorption of Racemic 2 and 3 by Poly-1-*P* or Poly-1-*M*. A typical experimental procedure for the enantioselective adsorption of racemic 2 is described below. A solution of a racemic 2 in methanol (0.4 mg/mL, 1 mL) was placed into a screw-capped sample bottle containing poly-1-*P* (2.0 mg, powder), which had been thoroughly washed with a dibutyl ether/THF (80:20, v/v) mixture and then methanol prior to the experiments. After standing at ca. 25 °C for 24 h, the analyte adsorbed on the poly-1-*P* was recovered by centrifugation and

quickly washed with methanol (1 mL) to remove the racemic solution of **2** attached on the surface of the polymer. The recovered poly-**1-P** was placed into a screw-capped sample bottle containing methanol (5 mL), and the mixture was permitted to stand at ca. 25 °C for 3 h to desorb **2** adsorbed on the poly-**1-P**. This desorption procedure was repeated with methanol (5 mL) and then with a methanol/THF (50:50, v/v) mixture (5 mL). After evaporation of the solvents, the residue was subjected to SEC fractionation using a Tosoh TSKgel Multipore H_{XL}-M (30 cm) SEC column (THF, 0.5 mL/min) to recover **2**, and the amount and ee of **2** adsorbed on the poly-**1-P** were estimated by chiral HPLC using a Daicel Chiralpak IA column (0.46 (i.d.) x 25 cm, CH₂Cl₂, 0.5 mL/min) equipped with UV and CD detectors. The total amount of the analyte **2** obtained by this procedure was almost coincident with that estimated by the absorption spectral change of the supernatant solution during the enantioselective adsorption experiments. In the same way, the enantioselective adsorption experiment was performed for racemic **3** and the results are summarised in Table 2.

7. Supporting References

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