Electronic Supplementary Information for:

Helical polymer brushes with a preferred-handed helix-sense triggered by a terminal optically active group in the pendant

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1. Instruments

NMR spectra were recorded on JEOL ECA500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) or LA400 (400 MHz for ^{1}H) spectrometers (Tokyo, Japan) in $CDCl_3$ using TMS as an internal standard. Number- (M_n) and weight-average (M_w) molecular weights of polymers were determined by size-exclusion chromatography (SEC) on a Tosoh TSKgel MultiporeH$_{XL}$-M column (Tokyo, Japan) using $CHCl_3$ as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained using polystyrene standards (Tosoh). IR spectra were recorded with a JASCO Fourier Transform IR-460 spectrophotometer (Hachioji, Japan). Absorption and circular dichroism (CD) spectra were measured in a quartz cell with a path length of 0.1 or 0.5 cm on a JASCO V-570 spectrophotometer and a JASCO J-725 spectropolarimeter, respectively. The temperature (-10–40 °C) was controlled with a JASCO ETC 505T (for absorption spectral measurements) and a JASCO 348WI apparatus (for CD spectral measurements). VCD spectra were measured in a 0.15-mm BaF_2 cell with a Jasco JV-2001YS spectrometer equipped with a temperature controller (EYELA NCB-1200). Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

2. Materials

Pyridine (Aldrich), pyrrolidine (Wako), and (*S*)-2-(methoxymethyl)pyrrolidine ((*S*)-MMP) (TCI) were dried over calcium hydride and distilled under high vacuum. TEA (Kanto Kagaku) was dried over KOH pellets under nitrogen and distilled onto 4 Å molecular sieves. These amines were stored under nitrogen. Anhydrous THF, DMSO, and CH_2Cl_2 were purchased from Kanto Kagaku. As the polymerization solvent, the as-purchased anhydrous THF was further dried over $LiAlH_4$ under nitrogen and vacuum-transferred to a dry glass ampoule just before polymerization. 3-Methoxyphenyl isocyanate (3MeOPI) (TCI) was dried over calcium hydride and distilled under high vacuum just before polymerization. Oxalyl chloride, *tert*-butyllithium (1.7 M in pentane), and anhydrous $CHCl_3$ were purchased from Aldrich. 4-Ethynylbenzoic acid[1] and $Rh^{+}(nbd)[(\eta^{6}\text{-}C_6H_5)B^{-}(C_6H_5)_3]$[2] were synthesized according to previously reported methods.

3. Synthetic Procedures

4-Ethynylbenzoyl chloride.[3] To a solution of 4-ethynylbenzoic acid (7.42 g, 49.7 mmol) in CH_2Cl_2 (150 mL) were added oxalyl chloride (8.4 mL, 100 mmol) and a catalytic amount of DMF. The reaction mixture was then stirred under nitrogen at room temperature overnight. After removal of the solvent, the residue was purified by distillation under reduced pressure to give 3.20 g of 4-ethynylbenzoyl chloride in 39% yield (bp 97 °C/10 mmHg).

Synthesis of macromonomers. Macromonomers macro-$\mathbf{1}_m$ (m represents the degree of polymerization (DP)) were synthesized by the polymerization of 3MeOPI with the lithium amide of (*S*)-MMP as an initiator (Scheme 1) in a similar manner to that reported previously.[4] Polymerization was carried out in a dry glass ampule under a dry nitrogen atmosphere in THF at -98 °C. A typical polymerization procedure is described below.

3MeOPI (0.92 mL, 7.2 mmol) and THF (8.4 mL) were placed in a glass ampoule with a three-way stopcock using a syringe and then the solution was cooled to -98 °C. Polymerization was initiated by adding the lithium amide of (*S*)-MMP (Li-(*S*)-MMP) in THF (0.55 M), which was prepared by adding an equimolar amount of *tert*-butyllithium in pentane to a solution of (*S*)-MMP in THF at 0 °C, with a syringe. The reaction mixture was rapidly stirred for 50 min at -98 °C, and then polymerization was terminated by adding an excess amount of 4-ethynylbenzoyl chloride (4.2 mmol) in THF and pyridine (3.0 mmol). The reaction mixture was held at -98 °C for 15 min and then at -78 °C for 1 h to ensure complete termination. The mixture was poured into a large amount of MeOH, and then the precipitated polymeric product was collected by centrifugation and dried *in vacuo* at room temperature. The obtained product was dissolved in DMF and stirred for 24 h at 40 °C to remove any -NH terminated polymers that had not been capped with a 4-ethynylbenzoyl group. The solution was poured into a large amount of hexane-ethanol (3/1, v/v) to remove depolymerization products. The precipitated macromonomer (macro-$\mathbf{1}_{m}$) was collected by centrifugation and dried *in vacuo* at room temperature overnight (0.46 g, 43% yield). The complete removal of -NH terminated products was confirmed by the disappearance of the signal from the -NH group (at ca. 10.5 ppm) in the ^{1}H NMR spectrum of the macromonomer (Fig. S1).[4] The DP of the obtained macromonomer was calculated to be 29 by ^{1}H NMR analysis using the peak intensity of the pendant phenyl proton resonances (4H, o + p + q + r, 5.6–7.2 ppm) relative to that of the aromatic proton resonances of the terminal phenylacetylene residue (4H, b + c, 7.7 and 7.4 ppm) (Fig. S1).

Spectroscopic data of macro-$\mathbf{1}_{29}$: IR (KBr): ν 1721 (C=O of polyisocyanate) cm^{-1}. Anal. Calcd for $C_6H_{12}NO(C_8H_7NO_2)_{29}C_9H_5O\cdot 2H_2O$: C, 64.43; H, 4.90; N, 9.13. Found: C, 64.46; H, 4.97; N, 8.89. For ^{1}H NMR, see Fig. S1(A).

Other macromonomers with different DPs (macro-$\mathbf{1}_{48}$ and macro-$\mathbf{1}_{70}$) were synthesized in the same manner as macro-$\mathbf{1}_{29}$; the results of polymerization are summarized in Table 1. ^{1}H NMR spectra of macro-$\mathbf{1}_{48}$ and macro-$\mathbf{1}_{70}$ are shown in Fig. S1(B) and Fig. S1(C), respectively.

Synthesis of polymer brushes. Polymer brushes (poly-$\mathbf{1}_{m}$) were synthesized by polymerization of the corresponding macromonomers macro-$\mathbf{1}_{m}$ using $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ as a catalyst (Scheme 1). A typical experimental procedure is described below.

Macro-$\mathbf{1}_{29}$ (63 mg, 0.014 mmol) was placed in a dry ampoule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated three times, anhydrous THF (0.08 mL) was added to the ampoule with a syringe to dissolve macro-**1**$_{29}$. A solution of $Rh^+(nbd)[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (3.95 mM) in THF at 30 °C was added, giving a concentration of macro-**1**$_{29}$ and rhodium catalyst of 0.105 and 0.0015 M, respectively. After 5 h at 30 °C, the resulting polymer brush was precipitated by addition of a large amount of MeOH, collected by centrifugation, and dried *in vacuo* at room temperature overnight (59 mg, 93% yield). Poly-**1**$_{29}$ was soluble in DMSO, THF, and $CHCl_3$. The molecular weight (M_n) and distribution (M_w/M_n) of the poly-**1**$_{29}$ were estimated to be 5.9×10^5 and 2.02, respectively, as determined by SEC using a polystyrene standard and $CHCl_3$ as the eluent. The stereoregularity of poly-**1**$_{29}$ was investigated by NMR and Raman spectroscopies. However, it was difficult to evaluate the stereoregularity of poly-**1**$_{29}$ from its ^{1}H NMR spectrum (Fig. S2) because the signals from the main chain protons, which are highly useful for assigning the conformation and configuration of the polyacetylene backbone,[5] could hardly be observed because of their very weak intensities relative to those of the protons of the pendant polyisocyanates. The Raman spectrum of poly-**1**$_{29}$ gave useful information and exhibited intense peaks at 1576, 1338, and 972 cm^{-1}, which are characteristic of *cis* polyacetylenes and can be assigned to the C=C, C-C and C-H bond vibrations, respectively, while those consistent with *trans* polyacetylenes were not observed (Fig. S3).[6] This indicates that the obtained poly-**1**$_{29}$ possesses a highly *cis-transoidal* structure.

Spectroscopic data of poly-**1**$_{29}$: IR (KBr): ν 1726 (C=O of polyisocyanate) cm^{-1}. Anal. Calcd for $C_6H_{12}NO(C_8H_7NO_2)_{29}C_9H_5O\cdot4H_2O$: C, 63.93; H, 4.95; N, 9.05. Found: C, 64.00; H, 4.86; N, 8.75. For ^{1}H NMR, see Fig. S2(A).

Poly-**1**$_{48}$ and poly-**1**$_{70}$ were synthesized by the polymerization of macro-**1**$_{48}$ and macro-**1**$_{70}$, respectively, using the same procedure described for poly-**1**$_{29}$; polymerization results are summarized in Table 2. In the case of polymerization of macro-**1**$_{48}$ and macro-**1**$_{70}$, SEC measurements of the components that were insoluble in MeOH showed a bimodal SEC trace, suggesting that these polymers contain the unreacted macromonomers. To remove these unreacted macromonomers, this component was dissolved in THF and then the solution was poured into a large amount of MeOH-THF (3:2 (v/v) for poly-$\mathbf{1}_{48}$ or 1:1 (v/v) for poly-$\mathbf{1}_{70}$). The resulting precipitate was collected by centrifugation and dried *in vacuo* at room temperature overnight to give poly-$\mathbf{1}_{48}$ and poly-$\mathbf{1}_{70}$ with unimodal SEC traces. ^{1}H NMR spectra of poly-$\mathbf{1}_{48}$ and poly-$\mathbf{1}_{70}$ are shown in Fig. S2(B) and Fig. S2(C), respectively.

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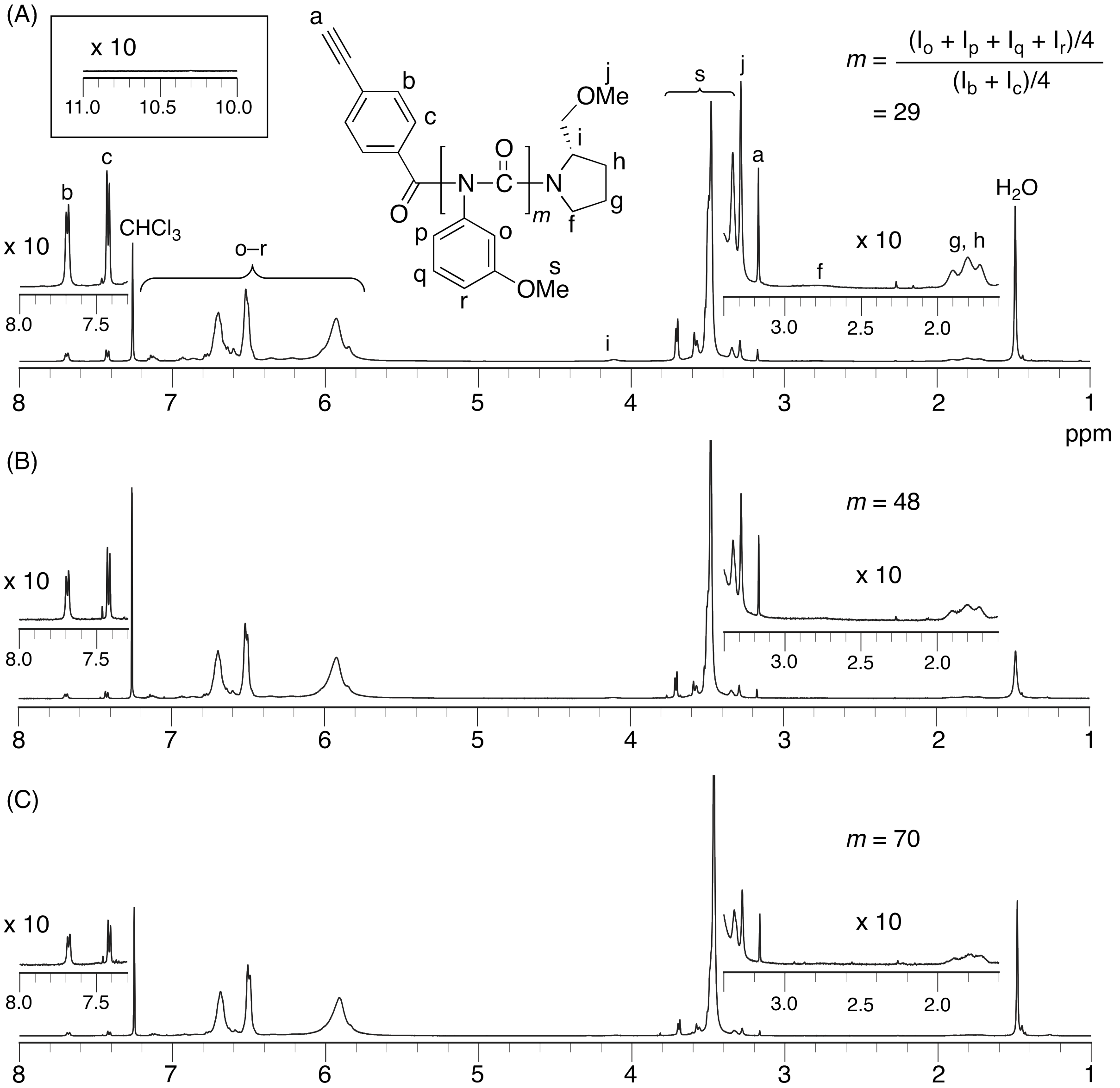

Fig. S1 ^{1}H NMR (500 MHz) spectra of macro-**1**$_{29}$ (A), macro-**1**$_{48}$ (B), and macro-**1**$_{70}$ (C) in CDCl$_3$ at 50 °C.

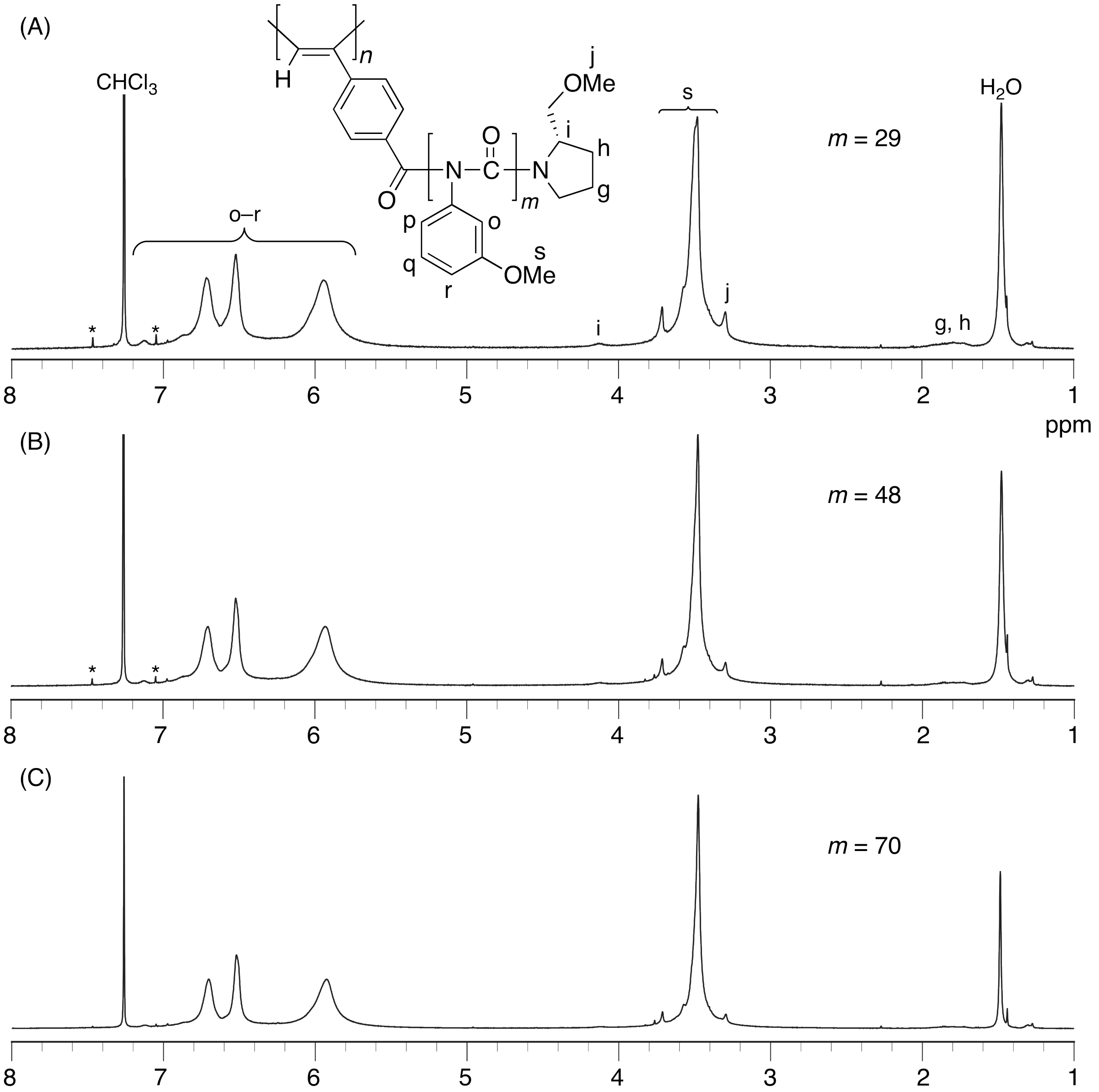

Fig. S2 ^{1}H NMR (500 MHz) spectra of poly-**1**$_{29}$ (A), poly-**1**$_{48}$ (B), and poly-**1**$_{70}$ (C) in $CDCl_3$ at 50 °C. "*" denotes the spinning side band.

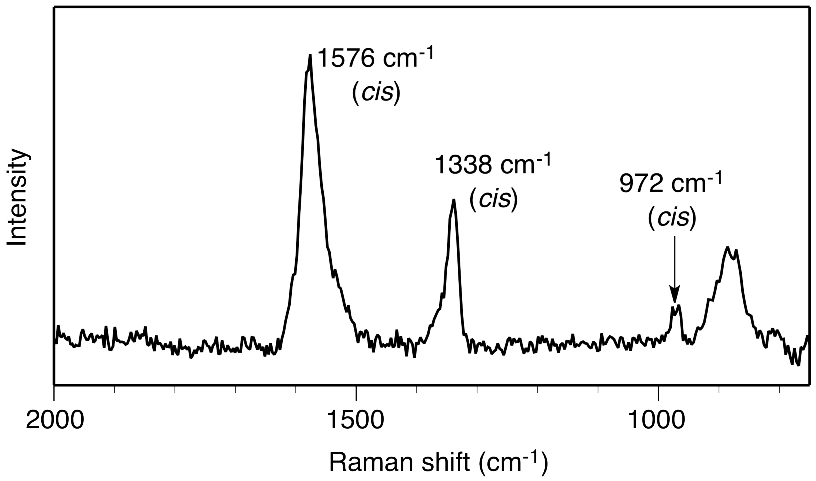

Fig. S3 Raman spectrum of poly-$\mathbf{1}_{29}$ in the film state.

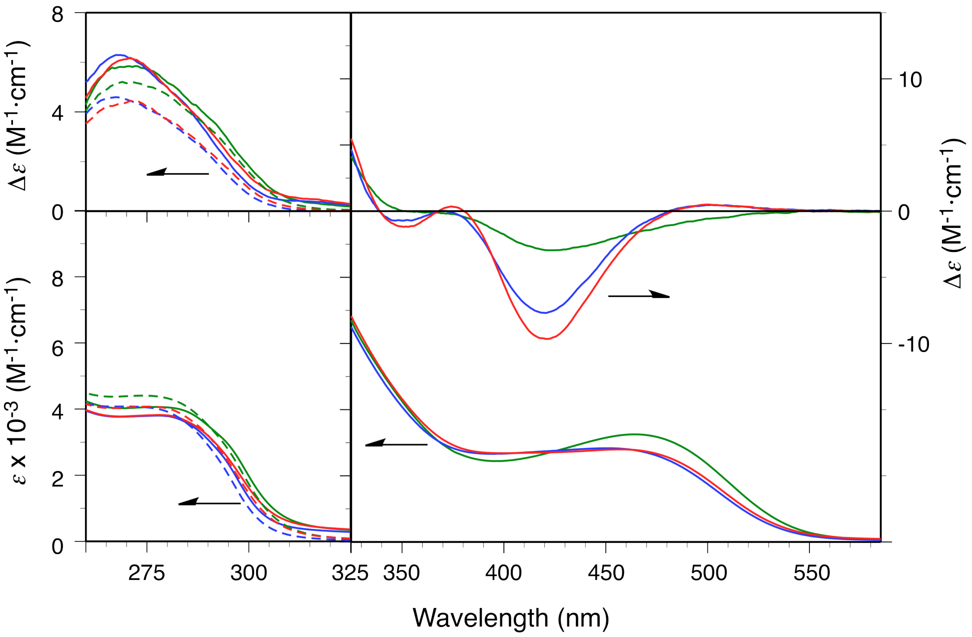

Fig. S4 CD and absorption spectra of macro-$\mathbf{1}_{29}$ (dotted line) and poly-$\mathbf{1}_{29}$ (solid line) in DMSO (red), THF (blue), and $CHCl_3$ (green) at 25 °C. The molar ellipticity ($\Delta\varepsilon$) and molar absorption coefficient (ε) were calculated using the molar concentration of 3MeOPI (260–325 nm) and macro-$\mathbf{1}_{29}$ (> 325 nm).

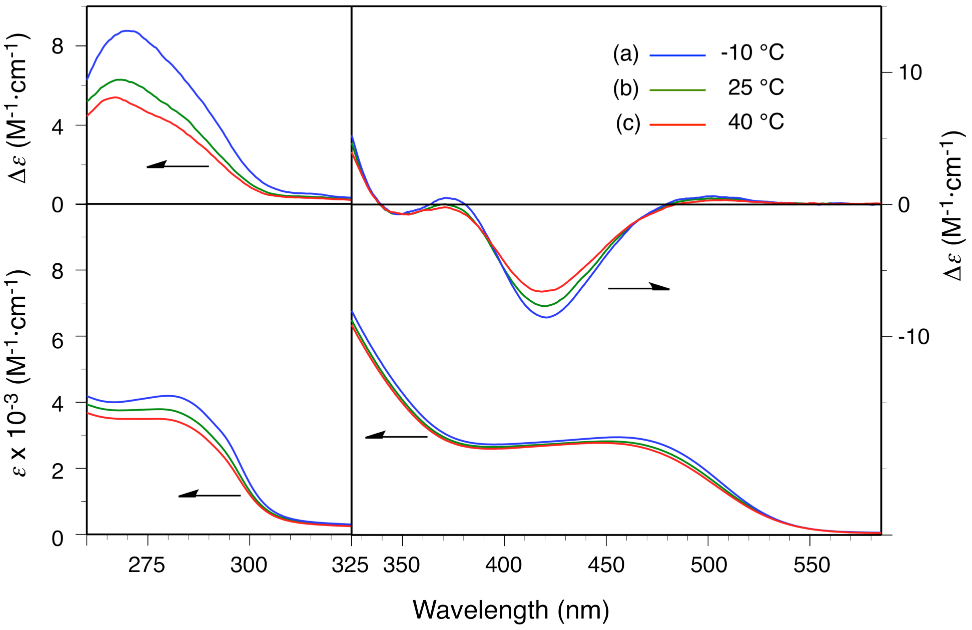

Fig. S5 CD and absorption spectra of poly-$\mathbf{1}_{29}$ in THF at -10 (a, blue), 25 (b, green), and 40 °C (c, red). The molar ellipticity (Δ*ε*) and molar absorption coefficient (*ε*) were calculated using the molar concentration of 3MeOPI (260–325 nm) and macro-$\mathbf{1}_{29}$ (> 325 nm).

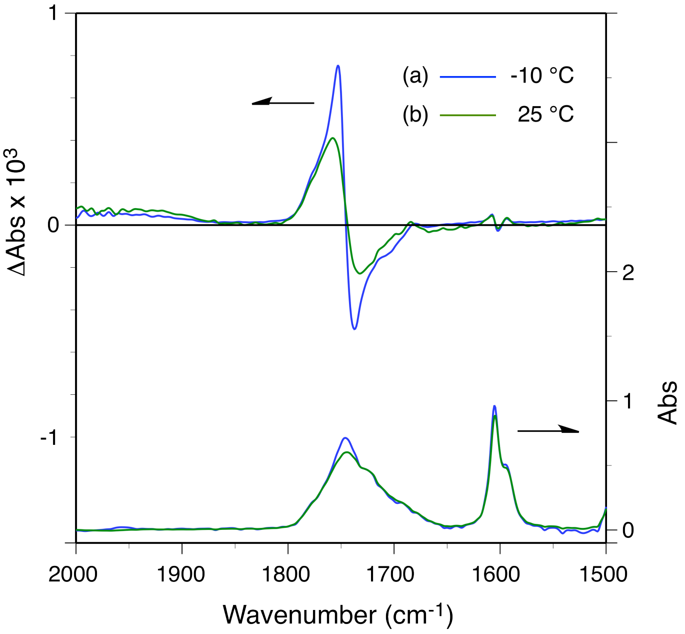

Fig. S6 VCD and IR spectra of poly-$\mathbf{1}_{29}$ in THF at -10 (a, blue) and 25 °C (b, green). The concentration of poly-$\mathbf{1}_{29}$ was 25 mg/mL in THF. All spectra were collected for ca. 3 h at a resolution of 4 cm^{-1}.