Supplementary Information for:

Impact of a minority enantiomer on the polymerization of alanine-based isocyanides with an oligothiophene pendant

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1. Materials

Anhydrous solvents (dichloromethane, chloroform, dimethyl sulfoxide (DMSO), ethanol and tetrahydrofuran (THF)), the common organic solvents and 1-hydroxybenzotriazole (HOBt) were purchased from Kanto Kagaku (Tokyo, Japan). Nickel(II) perchlorate hexahydrate ($Ni(ClO_4)_2 \cdot 6H_2O$) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) were purchased from Wako Pure Chemical Industries (Osaka, Japan). L-*N*-Formylalanine and *N*-methylmorpholine were purchased from Nacalai (Kyoto, Japan). D-*N*-Formylalanine was from Watanabe Chemical Industries (Hiroshima, Japan). Diphosgene and tetrabutylammonium bromide were from Sigma-Aldrich (St. Louis, MO, USA). DL-*N*-Formylalanine was from Tokyo Kasei Kogyo (TCI) (Tokyo, Japan). A ethylamine compound with an oligothiophene unit ($R\text{-}NH_2$ in Scheme S1) was prepared according to the procedure in the literature.[1] Chiralpak IA (25 cm × 2.0 cm (i.d.)) and Chiralpak IE (25 cm × 0.46 cm (i.d.)) were purchased from Daicel (Tokyo, Japan). The enantiomeric excess (ee) of the optically active **1L** and **1D** was confirmed to be >99.8% and 99.4%, respectively, by chiral high-performance liquid chromatography (HPLC).

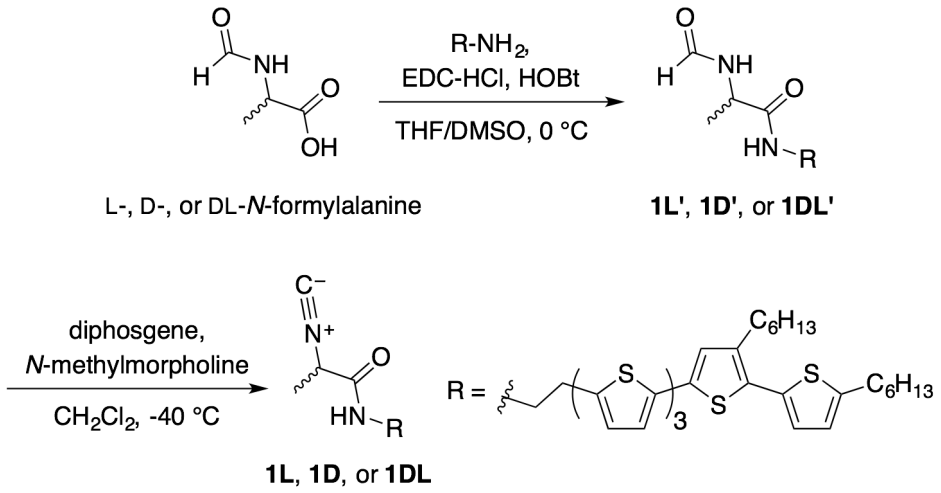
2. Instruments

NMR spectra were taken on a JNM-ECA 500 (JEOL, Tokyo, Japan) (500 MHz for ^1H, 125 MHz for ^{13}C) or a JNM-ECA 600 (JEOL) (600 MHz for ^1H) spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Melting points were measured on a Yanako melting point apparatus and were uncorrected. IR spectra were obtained using a JASCO (Hachioji, Japan) Fourier Transform IR-460 spectrophotometer with a KBr pellet. The molecular weights and distributions of the polymers were estimated using size-exclusion chromatography (SEC) equipped with TSKgel α-M column and TSKgel GMH_{HR}-H(20) (Tosoh, Tokyo, Japan), a JASCO PU-2080 Plus HPLC pump, a JASCO UV-970 UV/VIS detector at 300 or 400 nm and a JASCO CD-2095 CD detector at 300 nm, where THF containing 0.25 wt % tetrabutylammonium bromide was used as the eluent. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). The optical

rotation was measured at 25 °C with a JASCO P-1030 polarimeter. Absorption and circular dichroism (CD) spectra were measured in chloroform at 25 °C with a 1.0 mm quartz cell using a JASCO V-570 and a JASCO J-725 spectrometers, respectively. The temperature was controlled using a JASCO ETC-505T (absorption spectroscopy) and a JASCO PTC-348WI apparatus (CD spectroscopy). Chromatographic separations of the enantiomeric monomers (**1L** and **1D**) were performed using a JASCO PU-2080 Intelligent HPLC pump equipped with a JASCO MD-2018 and a polarimetric detector (JASCO OR-990, Hg-Xe without filter) at *ca.* 20 °C. A solution of a chiral compound was injected into the chromatographic system by a Rheodyne Model 7125 injector (Rheodyne, Rohnert Park, CA, USA). The % ee values of the isolated **1L** and **1D** were determined by HPLC analysis on Chiralpak IE (eluent, hexane/ethyl acetate (70/30, v/v); flow rate, 0.5 mL min^{-1}; temperature, *ca.* 20 °C; $t_{\mathbf{1L}}$, 23.0 min, $t_{\mathbf{1D}}$, 32.2 min). Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan. A probe-scan-type atomic force microscope (AFM) (5500 AFM, Keysight Technologies, CA, USA) was used for molecular imaging in the dynamic (tapping) mode with a cantilever (OMCL-AC240TS, Olympus Corp., Tokyo, Japan) having a spring constant of 1.7 N m^{-1} and resonance frequency of 70 kHz (typical values).[2–5] The set point was optimized for the gentle-touch imaging. A specimen for AFM imaging was prepared by a spin-cast method (*ca.* 1500 rpm), and mica was used as a substrate. A dilute polymer solution of chloroform (*ca.* 10^{-6} M, 50 μL) was used. AFM imaging was carried out at 25 ± 1 ºC in air.

3. Synthesis of monomers

Alanine-based optically active isocyanide monomers bearing a quinquethiophene unit (**1L** and **1D**) and the corresponding racemic monomer (**1DL**) were prepared according to Scheme S1.



Scheme S1 Synthesis of alanine-based isocyanide monomers bearing a quinquethiophene unit (**1**).

1L'. L-*N*-Formylalanine (218 mg, 1.86 mmol) was added to a solution of R-NH_2 (1.16 g, 1.86 mmol) and HOBt (277 mg, 2.05 mmol) in THF/DMSO (2/1, v/v) (27 mL) and the mixture was cooled to 0 °C under a nitrogen atmosphere. To this mixture was added EDC-HCl (393 mg, 2.08 mmol). After stirring at 0 °C for 5 h, the reaction system was diluted with dichloromethane and the solution was washed with saturated $NaHCO_3$ aqueous solution and brine and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using ethyl acetate as the eluent to give **1L'** as an orange solid (1.23 g, 92% yield). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.17 (s, 1H, CHO), 7.07-6.97 (m, 6H, ArH), 6.93 (d, J = 3.4 Hz, 1H, ArH), 6.75 (d, J = 3.4 Hz, 1H, ArH), 6.73 (d, J = 3.4 Hz, 1H, ArH), 6.22 (d, J = 7.5 Hz, 1H, NH), 6.12 (t, J = 6.0 Hz, 1H, NH), 4.51 (quint, J = 7.1 Hz, 1H, CH), 3.63-3.49 (m, 2H, NHCH_2), 3.02 (t, J = 6.6 Hz, 2H, $NHCH_2CH_2$), 2.81 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.72 (t, J = 7.7 Hz, 2H, $ArCH_2$), 1.74-1.61 (m, 4H, CH_2), 1.45-1.28 (m, 15H, $CHCH_3$, CH_2), 0.94-0.85 (m, 6H, CH_3).

1D'. The title compound **1D'** was prepared from D-*N*-formylalanine in the same way for **1L'** and obtained in 87% yield as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.17 (s, 1H, CHO), 7.08-6.98 (m, 6H, ArH), 6.93 (d, J = 3.4 Hz, 1H, ArH), 6.75 (d, J = 3.4

Hz, 1H, ArH), 6.73 (d, J = 3.4 Hz, 1H, ArH), 6.19 (d, J = 6.5 Hz, 1H, NH), 6.07 (t, J = 5.5 Hz, 1H, NH), 4.51 (quint, J = 7.1 Hz, 1H, CH), 3.63-3.49 (m, 2H, NHCH_2), 3.02 (t, J = 6.6 Hz, 2H, $NHCH_2CH_2$), 2.82 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.72 (t, J = 7.7 Hz, 2H, $ArCH_2$), 1.75-1.61 (m, 4H, CH_2), 1.45-1.28 (m, 15H, $CHCH_3$, CH_2), 0.94-0.86 (m, 6H, CH_3).

1DL'. The title compound **1DL'** was prepared from DL-*N*-formylalanine in the same way for **1L'** and obtained in 88% yield as an orange solid. ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 8.17 (s, 1H, CHO), 7.08-6.98 (m, 6H, ArH), 6.93 (d, J = 3.4 Hz, 1H, ArH), 6.77-6.71 (m, 2H, ArH), 6.18 (d, J = 5.5 Hz, 1H, NH), 6.05 (t, J = 5.5 Hz, 1H, NH), 4.51 (quint, J = 7.3 Hz, 1H, CH), 3.62-3.50 (m, 2H, NHCH_2), 3.02 (t, J = 6.6 Hz, 2H, $NHCH_2CH_2$), 2.81 (t, J = 7.4 Hz, 2H, $ArCH_2$), 2.72 (t, J = 7.7 Hz, 2H, $ArCH_2$), 1.74-1.60 (m, 4H, CH_2), 1.44-1.27 (m, 15H, $CHCH_3$, CH_2), 0.95-0.85 (m, 6H, CH_3).

1L. To a solution of **1L'** (628 mg, 0.87 mmol) in dichloromethane (174 mL) was added *N*-methylmorpholine (0.38 mL, 3.5 mmol) and the mixture was cooled to –40 °C under a nitrogen atmosphere. To this mixture was added a solution of diphosgene (58 μL, 0.48 mmol) in dichloromethane (5.7 mL) over a period of 1 h and the reaction was quenched by adding an aqueous saturated $NaHCO_3$ solution (5 mL). After vigorous stirring for 5 min, the resulting mixture was diluted with dichloromethane and washed with saturated $NaHCO_3$ aqueous solution and brine and then dried over Na_2SO_4. After filtration, the solvent was removed by evaporation and the crude product was purified by silica gel chromatography using dichloromethane as the eluent to give **1L** as an orange solid (500 mg, 82% yield). **1L** was further purified by chiral HPLC on Chiralpak IA (eluent, hexane/dichloromethane (55/45, v/v); flow rate, 10 mL min^{-1}; temperature, *ca.* 20 °C) to enhance its enantiopurity up to >99.8% ee. Mp: 140.5–140.8 °C. $[\alpha]^{25}_D$ +10.3 (*c* 1.0, chloroform). IR (KBr, cm^{-1}): 2140 (N≡C), 1667 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.08-7.01 (m, 5H, ArH), 6.99 (s, 1H, ArH), 6.93 (d, J = 4.0 Hz, 1H, ArH), 6.78 (d, J = 4.0 Hz, 1H, ArH), 6.73 (d, J = 3.4 Hz, 1H, ArH), 6.64-6.51 (br, 1H, NH), 4.25 (q, J = 7.3 Hz, 1H, CH), 3.60 (q, J = 6.3 Hz, 2H, NHCH_2), 3.07 (t, J = 6.6 Hz, 2H, $NHCH_2CH_2$), 2.81 (t, J = 7.7 Hz, 2H, $ArCH_2$), 2.72 (t, J = 8.0 Hz, 2H, $ArCH_2$), 1.74-1.61 (m, 7H, $CHCH_3$, CH_2), 1.43-1.28 (m, 12H, CH_2), 0.94-0.85 (m, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt):

δ 166.25, 161.45, 146.53, 139.88, 139.85, 136.47, 136.24, 136.20, 136.02, 135.68, 134.18, 133.29, 130.69, 126.75, 126.69, 125.70, 124.57, 124.46, 124.37, 124.30, 124.16, 123.85, 53.68, 41.21, 31.82, 31.72, 30.67, 30.30, 29.99, 29.49, 29.38, 28.96, 22.77, 22.73, 19.92, 14.26. Calcd for $C_{38}H_{44}N_2OS_5$: C, 64.73; H, 6.29; N, 3.97. Found: C, 64.75; H, 6.16; N, 3.97.

1D. The title compound **1D** (99.4% ee) was prepared from **1D'** in the same way for **1L** and obtained in 85% yield as an orange solid (500 mg, 85% yield). Mp: 140.2–140.6 °C. $[\alpha]^{25}_{D}$ –10.1 (*c* 1.0, chloroform). IR (KBr, cm^{-1}): 2142 (N≡C), 1663 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.07-7.00 (m, 5H, ArH), 6.99 (s, 1H, ArH), 6.93 (d, *J* = 3.4 Hz, 1H, ArH), 6.78 (d, *J* = 3.4 Hz, 1H, ArH), 6.73 (d, *J* = 3.4 Hz, 1H, ArH), 6.65-6.54 (br, 1H, NH), 4.25 (q, *J* = 7.1 Hz, 1H, CH), 3.59 (q, *J* = 6.5 Hz, 2H, NHC*H*$_2$), 3.06 (t, *J* = 6.9 Hz, 2H, $NHCH_2CH_2$), 2.81 (t, *J* = 7.7 Hz, 2H, $ArCH_2$), 2.71 (t, *J* = 7.7 Hz, 2H, $ArCH_2$), 1.74-1.60 (m, 7H, CH*CH*$_3$, CH_2), 1.44-1.28 (m, 12H, CH_2), 0.96-0.84 (m, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 166.24, 161.37, 146.51, 139.86, 139.83, 136.44, 136.21, 136.18, 135.99, 135.65, 134.16, 133.27, 130.67, 126.71, 126.64, 125.71, 124.56, 124.49, 124.38, 124.29, 124.14, 123.86, 53.68, 41.19, 31.80, 31.71, 30.66, 30.28, 29.97, 29.48, 29.37, 28.95, 22.76, 22.73, 19.93, 14.26. Calcd for $C_{38}H_{44}N_2OS_5$: C, 64.73; H, 6.29; N, 3.97. Found: C, 64.43; H, 6.12; N, 3.95.

1DL. The title compound **1DL** was prepared from **1DL'** in the same way for **1L** and obtained in 91% yield as an orange solid. Mp: 132.4–132.7 °C. IR (KBr, cm^{-1}): 2140 (N≡C), 1661 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.08-7.00 (m, 5H, ArH), 6.98 (s, 1H, ArH), 6.93 (d, *J* = 3.4 Hz, 1H, ArH), 6.77 (d, *J* = 3.4 Hz, 1H, ArH), 6.72 (d, *J* = 3.4 Hz, 1H, ArH), 6.66-6.53 (br, 1H, NH), 4.25 (q, *J* = 7.3 Hz, 1H, CH), 3.59 (q, *J* = 6.5 Hz, 2H, NHC*H*$_2$), 3.06 (t, *J* = 6.6 Hz, 2H, $NHCH_2CH_2$), 2.81 (t, *J* = 7.7 Hz, 2H, $ArCH_2$), 2.71 (t, *J* = 7.7 Hz, 2H, $ArCH_2$), 1.75-1.60 (m, 7H, CH*CH*$_3$, CH_2), 1.47-1.27 (m, 12H, CH_2), 0.96-0.83 (m, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, rt): δ 166.23, 161.36, 146.49, 139.83 (2C), 136.43, 136.19, 136.17, 135.98, 135.64, 134.15, 133.27, 130.66, 126.70, 126.63, 125.70, 124.55, 124.48, 124.37, 124.32, 124.13, 123.84, 53.62, 41.18, 31.80, 31.70, 30.65, 30.28, 29.96, 29.47, 29.37, 28.94, 22.75, 22.73, 19.92, 14.25. Calcd for $C_{38}H_{44}N_2OS_5 \cdot 0.1H_2O$: C,

64.57; H, 6.30; N, 3.96. Found: C, 64.33; H, 6.13; N, 4.01.

4. Synthesis of poly(1L$_r$-*co*-1D$_{1-r}$)

Poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$), poly(**1L**$_{0.003}$-*co*-**1D**$_{0.997}$) and poly(**1L**$_{0.50}$-*co*-**1D**$_{0.50}$) were synthesized by the polymerization of **1L**, **1D** and **1DL**, respectively, using $Ni(ClO_4)_2 \cdot 6H_2O$ as a catalyst according to our previous procedure.[1] The optically active copolymers, poly(**1L**$_r$-*co*-**1D**$_{1-r}$) containing nonracemic chiral repeating units, were synthesized by the copolymerization of **1L** and **1D** at various feed ratios (Scheme 1). The synthetic procedure of poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$) is described below as a typical example.

To a solution of **1L** (15.0 mg, 21.3 μmol) and **1D** (1.5 mg, 2.1 μmol) in chloroform (665 μL) was added a chloroform/ethanol (50/1, v/v) mixed solution (93 μl) containing $Ni(ClO_4)_2 \cdot 6H_2O$ (0.09 mg, 0.26 μmol) and the mixture was stirred at 20 °C under a nitrogen atmosphere. In predetermined intervals, a portion of the reaction mixture was withdrawn from the vessel and diluted with THF or chloroform (2.0 mL) to terminate the polymerization.[6] The monomer conversion was determined from the concentration of a residual monomer measured by SEC equipped with TSKgel G1000H$_{HR}$ (Tosoh) using a chloroform as the internal standard, where THF containing 0.25 wt % tetrabutylammonium bromide was used as the eluent and the chromatograms were recorded with UV detection at 254 nm (e.g., for 380 min, 36% conversion). The % ee of residual monomer was determined by chiral HPLC equipped with a Chiralpak IE column (e.g., for 380 min, 91% ee). After almost complete consumption of the monomer, the reaction mixture was poured into a large amount of ethanol and the resulting precipitate was collected by centrifugation to give the target polymer poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$) as a red solid (M_n = 1.3 × 10^5, M_w/M_n = 2.4). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.11-5.63 (br, 9H, ArH), 4.21-2.09 (br, 9H, CH, CH_2), 2.01-0.57 (br, 25H, CH_2, CH_3). Anal. Calcd for $(C_{38}H_{44}N_2OS_5 \cdot 0.2H_2O)_n$: C, 64.40; H, 6.32; N, 3.95. Found: C, 64.15; H, 6.21; N, 3.95.

Other isocyanide-based copolymers with different compositions were synthesized using the same procedure. As for poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$), poly(**1L**$_{0.995}$-*co*-**1D**$_{0.005}$),

poly(**1L**$_{0.98}$-*co*-**1D**$_{0.02}$) and poly(**1L**$_{0.003}$-*co*-**1D**$_{0.997}$), the spectroscopic data could not be obtained due to their insolubility after isolation.

Spectroscopic data of poly(**1L**$_{0.70}$-*co*-**1D**$_{0.30}$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.12-5.45 (br, 9H, ArH), 3.70-2.08 (br, 9H, CH, CH_2), 1.83-0.40 (br, 25H, CH_2, CH_3). Anal. Calcd for $(C_{38}H_{44}N_2OS_5 \cdot 0.2H_2O)_n$: C, 64.40; H, 6.32; N, 3.95. Found: C, 64.20; H, 6.15; N, 3.94.

Spectroscopic data of poly(**1L**$_{0.50}$-*co*-**1D**$_{0.50}$). ^{1}H NMR (500 MHz, $CDCl_3$, rt): δ 7.10-5.72 (br, 9H, ArH), 3.91-2.10 (br, 9H, CH, CH_2), 1.88-0.56 (br, 25H, CH_2, CH_3). Anal. Calcd for $(C_{38}H_{44}N_2OS_5 \cdot 0.1H_2O)_n$: C, 64.57; H, 6.30; N, 3.96. Found: C, 64.31; H, 6.19; N, 3.98.

Spectroscopic data of poly(**1L**$_{0.09}$-*co*-**1D**$_{0.91}$). ^{1}H NMR (600 MHz, $CDCl_3$, rt): δ 7.02-5.70 (br, 9H, ArH), 4.32-2.03 (br, 9H, CH, CH_2), 1.84-0.67 (br, 25H, CH_2, CH_3). Anal. Calcd for $(C_{38}H_{44}N_2OS_5 \cdot 0.3H_2O)_n$: C, 64.24; H, 6.33; N, 3.94. Found: C, 64.00; H, 6.17; N, 3.95.

5. Monomer-addition experiment

To examine whether or not the random conformation in a polymer chain can be changed into the helical one during polymerization, a fresh feed of **1L** (100 mol % against the total monomer concentration in the first-step reaction) dissolved in chloroform was added to the polymerization solution when the polymerization ([**1L**]$_0$/[**1D**]$_0$ = 93/7) was almost completely finished (conversion >99%). **1L** poured into the reaction system was almost completely consumed in the additional 30 min. The SEC curve of the polymer shifted to higher molecular weight almost keeping the distributions (M_w/M_n: from 2.1 to 2.3).

6. Molecular modeling

All-atom molecular dynamics (MD) simulations were carried out using the Forcite module of the BIOVIA Materials Studio 8.0 (Dassault Systèmes BIOVIA, San Diego, CA, USA) on the supercomputer system (PRIMERGY CX250, Fujitsu, Tokyo, Japan). Before MD simulation, the initial structure of a polymer chain model was generated at torsion angle of +70 degree, orientation of head-to-tail, degree of polymerization of 50 using the repeating unit. The MD cell was built by means of usual procedure of the Amorphous Cell module. Here, single-polymer-chain was put in the center of the cell, and the solvent molecules of chloroform were packed in the cell at density of 1.492 g cm^{-3}. Sequentially, the geometry of the MD cell was optimized. Simulation in the NPT ensemble (constant number of atoms, pressure and temperature in the cell) was conducted at 298 K for 200 ps (time step of 0.2-fs, 1,000,000 steps) to equilibrate the MD cell at fixed pressure of 1.0×10^{-4} GPa. The Nose thermostat was used to control the temperature. After the equilibration, simulation in the NVT ensemble (constant number of atoms, volume and temperature) was conducted at 800 K for 2050 ps (time step of 1.0-fs, 2,050,000 steps) as the sampling. The COMPASS II (ver. 1.2) forcefield was used, and the charges were assigned by the forcefield.

7. Supporting data

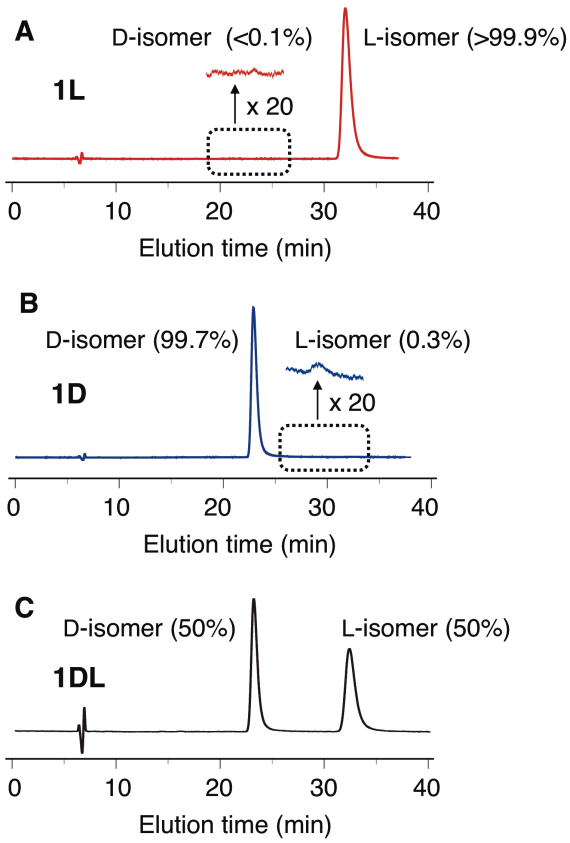


Fig. S1 Resolution results of **1L** (A), **1D** (B) and **1DL** (C) on Chiralpak IE. The chromatograms depict UV traces recorded at 415 nm (column, 25 cm × 0.46 cm (i.d.); eluent, hexane/ethyl acetate (70/30, v/v); flow rate, 0.5 mL min^{-1}; temperature, 20 °C).

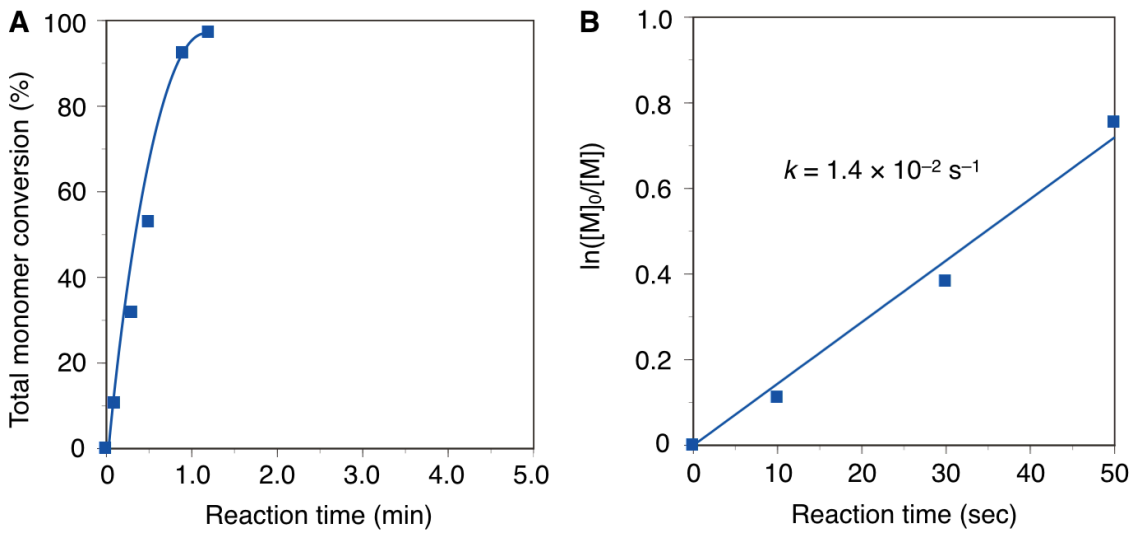


Fig. S2 Time-conversion curve (A) and first-order kinetic plot (B) for the polymerization of **1D** (99.4% ee) with a nickel(II) complex in a chloroform/ethanol mixture at 20 °C.

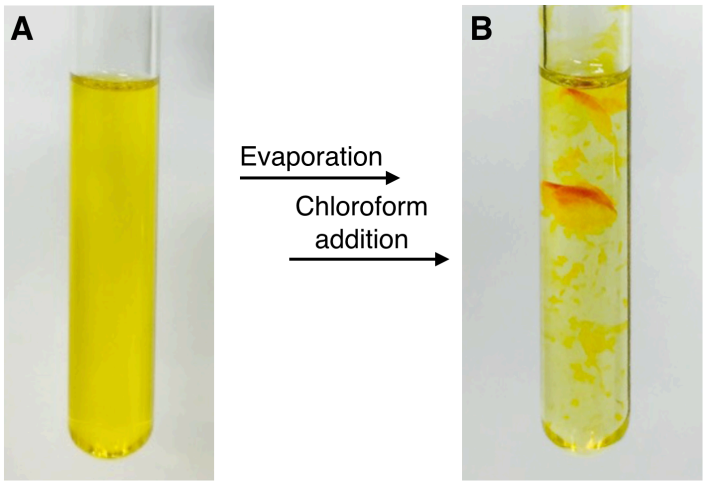


Fig. S3 Photographs of the poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$) solution prepared by dilution of the completed polymerization system with chloroform ([poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$)] = *ca.* 10^{-5} M) (A) and the poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$) dispersed solution prepared by evaporation of the solvent in (A) and then adding chloroform (B).

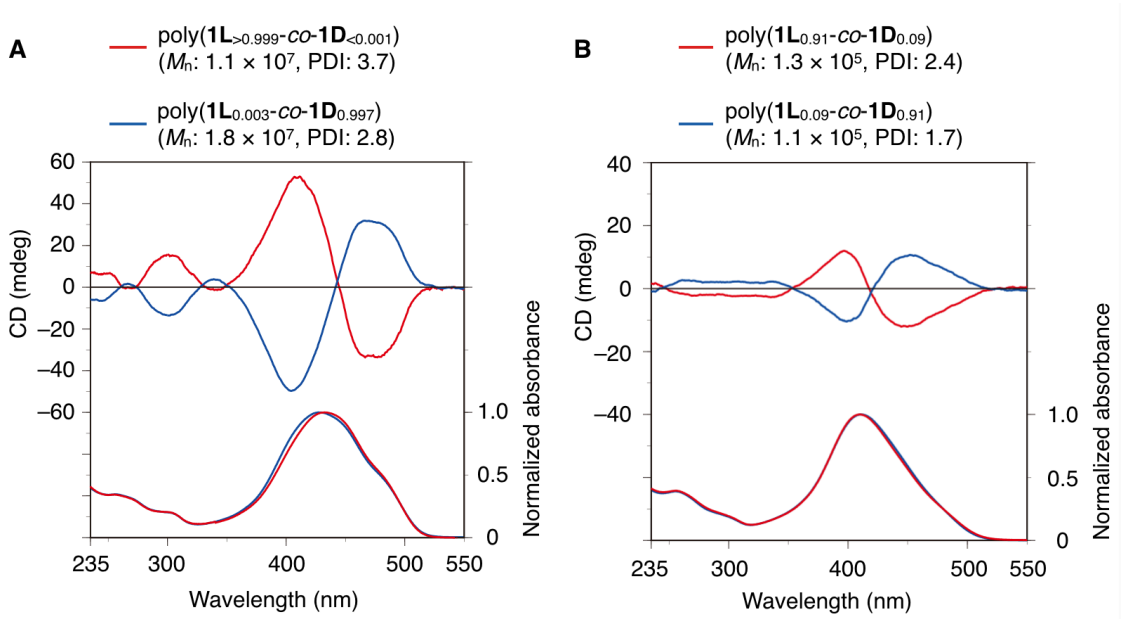


Fig. S4 CD (upper) and absorption (lower) spectra of poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$) (A, red), poly(**1L**$_{0.003}$-*co*-**1D**$_{0.997}$) (A, blue), poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$) (B, red) and poly(**1L**$_{0.09}$-*co*-**1D**$_{0.91}$) (B, blue) in chloroform at 25 °C.

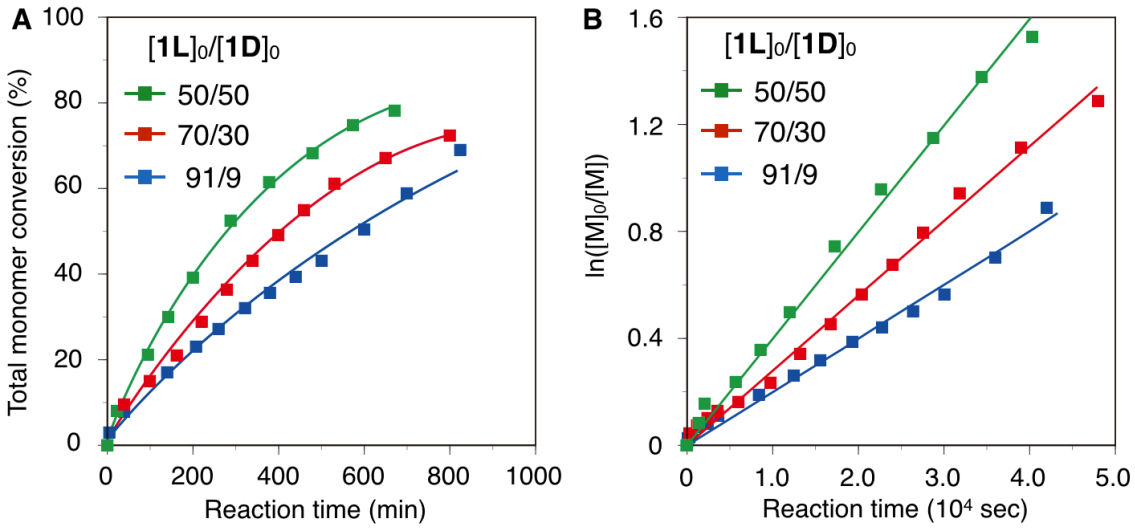


Fig. S5 Time-conversion curves (A) and first-order kinetic plots (B) for the copolymerizations of **1L** and **1D** with a nickel(II) complex in a chloroform/ethanol mixture at 20 °C. [**1L**]$_0$/[**1D**]$_0$ = 91/9 (blue, $k = 2.0 \times 10^{-5}$ s^{-1}), 70/30 (red, $k = 2.8 \times 10^{-5}$ s^{-1}) and 50/50 (green, $k = 4.0 \times 10^{-5}$ s^{-1}).

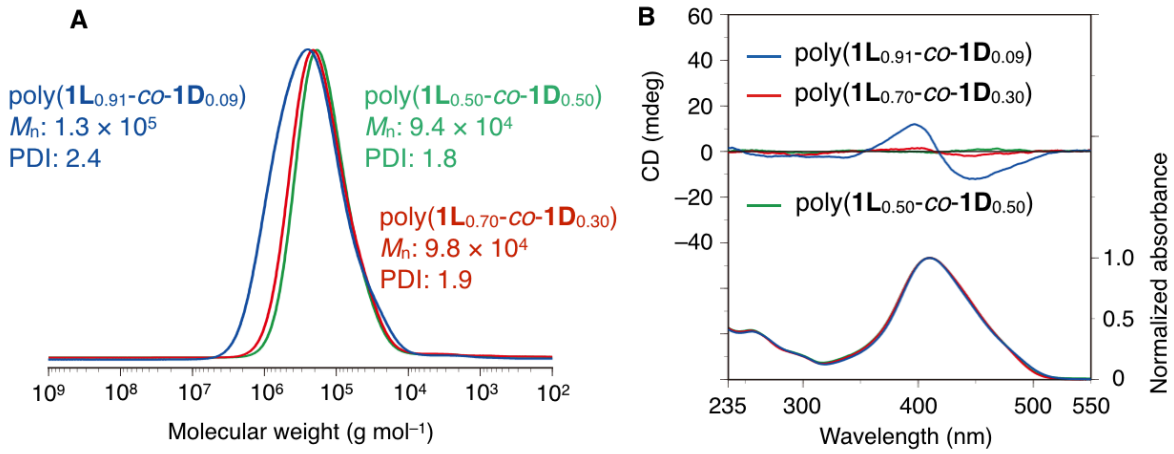


Fig. S6 (A) SEC traces of poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$) (blue), poly(**1L**$_{0.70}$-*co*-**1D**$_{0.30}$) (red) and poly(**1L**$_{0.50}$-*co*-**1D**$_{0.50}$) (green) (eluent, THF containing 0.25 wt % tetrabutylammonium bromide; polystyrene standards). (B) CD (upper) and absorption (lower) spectra of poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$) (blue), poly(**1L**$_{0.70}$-*co*-**1D**$_{0.30}$) (red) and poly(**1L**$_{0.50}$-*co*-**1D**$_{0.50}$) (green) in chloroform at 25 °C.

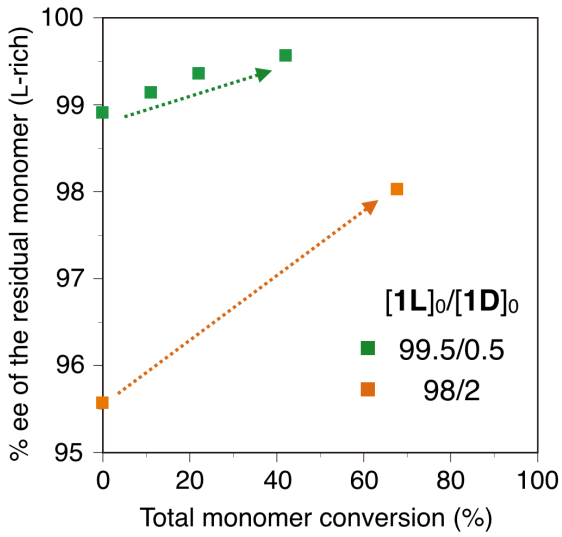


Fig. S7 Changes in the % ee of the residual monomer during the copolymerizations of **1L** and **1D**. [**1L**]$_0$/[**1D**]$_0$ = 95.5/0.5 (green) and 98/2 (orange).

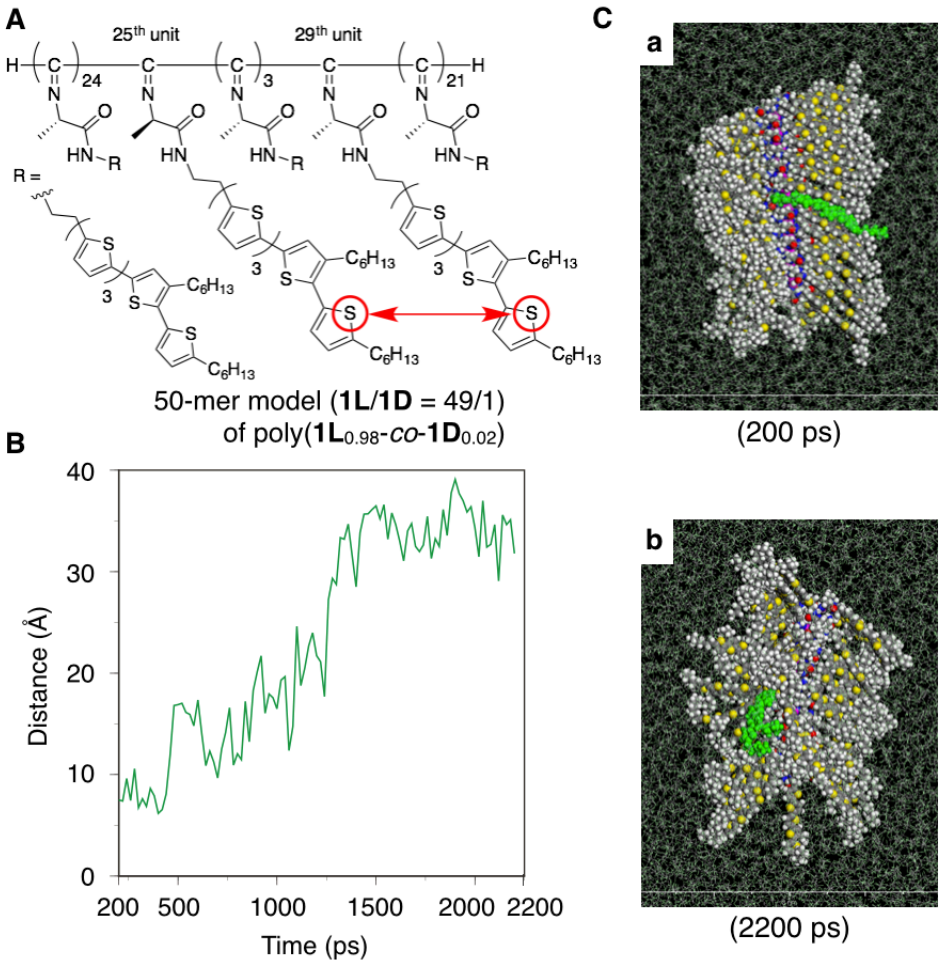


Fig. S8 (A) Structure of the 50-mer model of poly(**1L**$_{0.98}$-*co*-**1D**$_{0.02}$) containing the **1D** component at the 25th unit. (B) Plots of the interatomic distance between sulfur atoms indicated by the arrow in (A), as a function of the calculation time. (C) Molecular models of poly(**1L**$_{0.98}$-*co*-**1D**$_{0.02}$) at 200 ps (a) and 2200 ps (b) in MD simulations represented by space-filling models. The **1D** component in the poly(**1L**$_{0.98}$-*co*-**1D**$_{0.02}$) model is highlighted in green. Countless chloroform solvent molecules are represented by stick models.

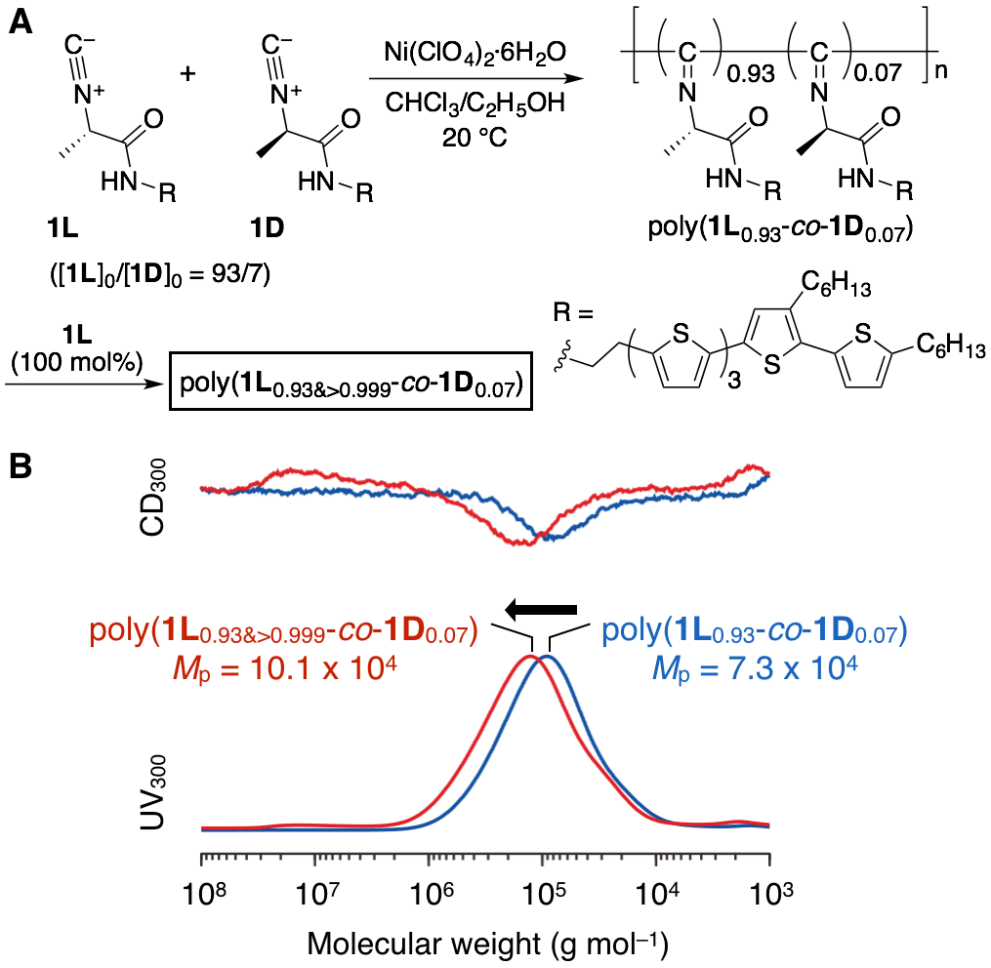


Fig. S9 (A) Synthesis of poly(**1L**$_{0.93\&>0.999}$-*co*-**1D**$_{0.07}$) through the addition of the enantiopure **1L** after completion of the copolymerization of **1L** and **1D** ([**1L**]$_0$/[**1D**]$_0$ = 93/7). (B) SEC traces of poly(**1L**$_{0.93}$-*co*-**1D**$_{0.07}$) (blue) and poly(**1L**$_{0.93\&>0.999}$-*co*-**1D**$_{0.07}$) (red). The upper and lower chromatograms depict UV and CD traces recorded at 300 nm, respectively (eluent, THF containing 0.25 wt % tetrabutylammonium bromide; polystyrene standards).

8. NMR spectral data

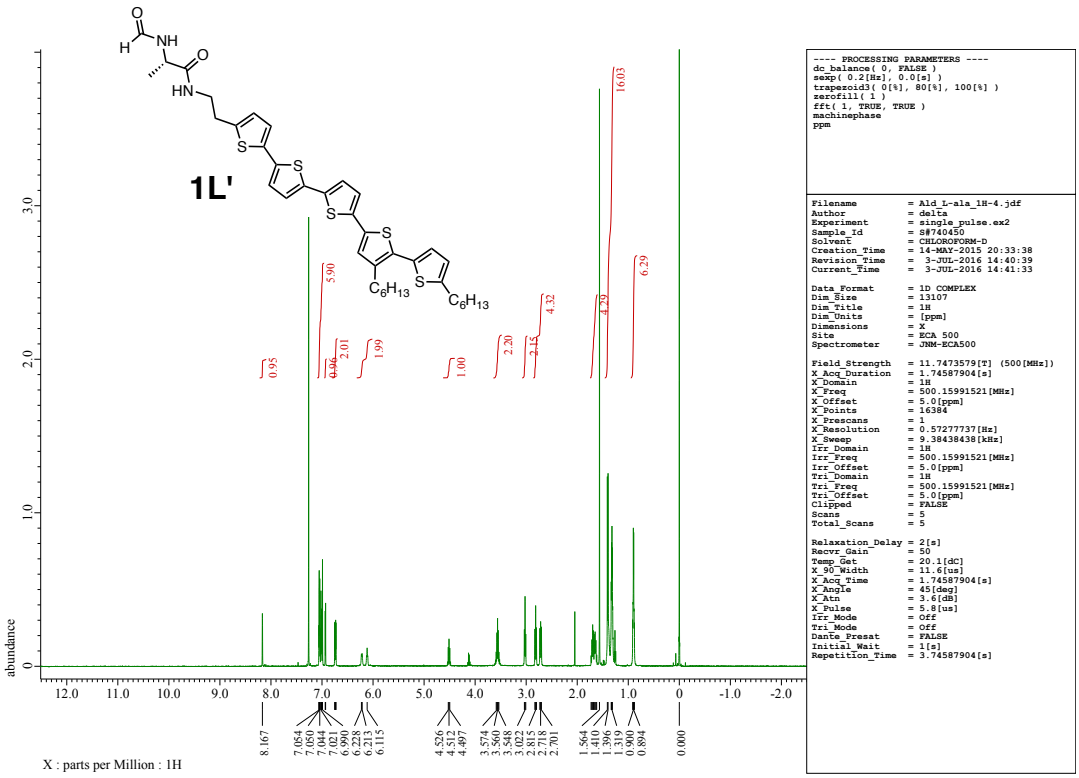


Fig. S10 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **1L'**.

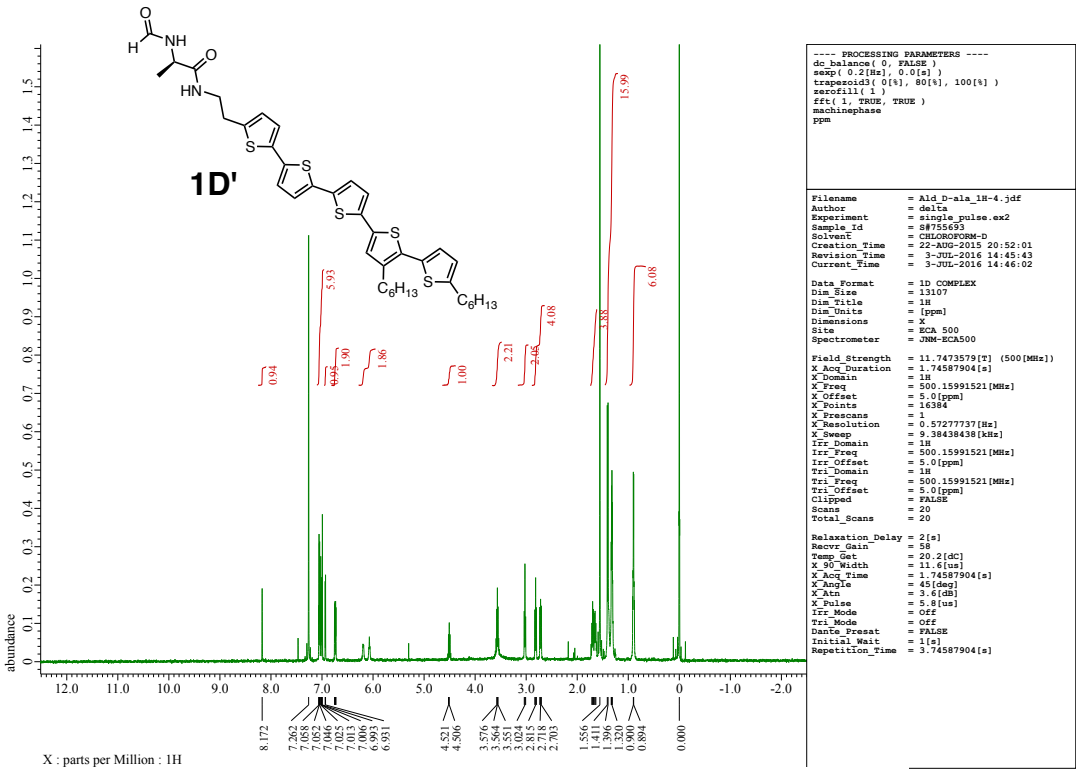


Fig. S11 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **1D'**.

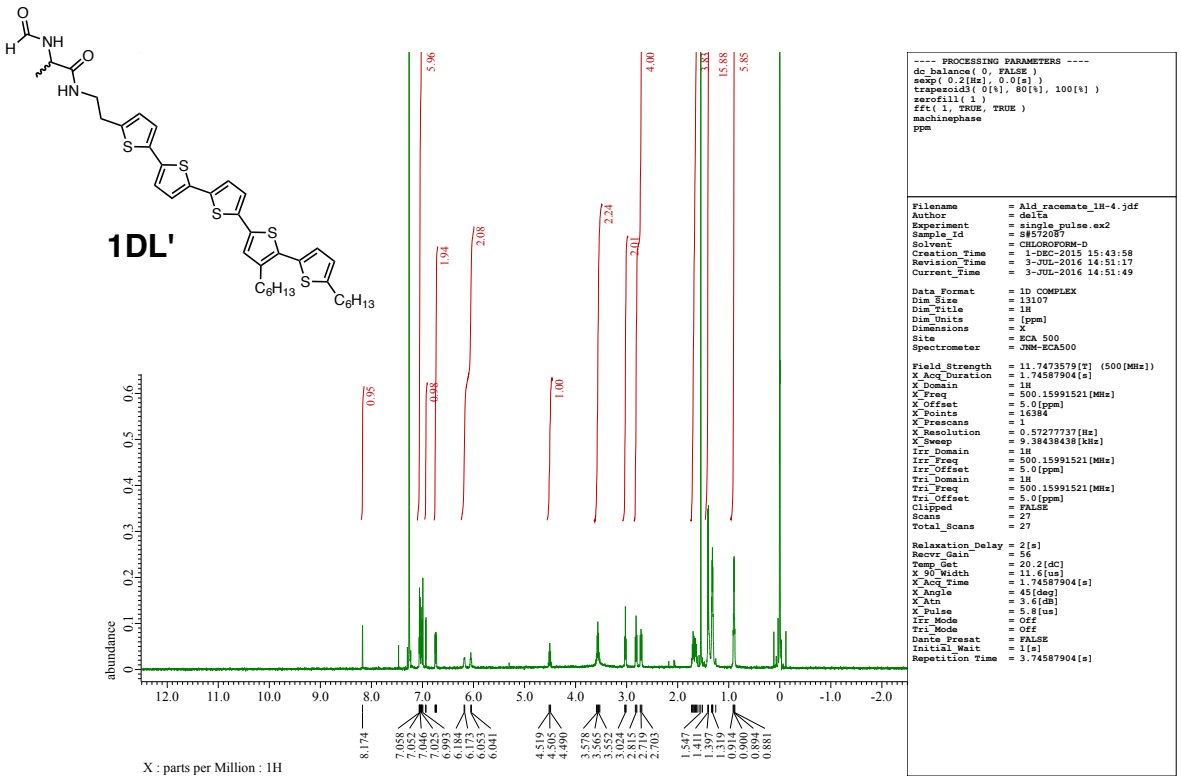


Fig. S12 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **1DL'**.

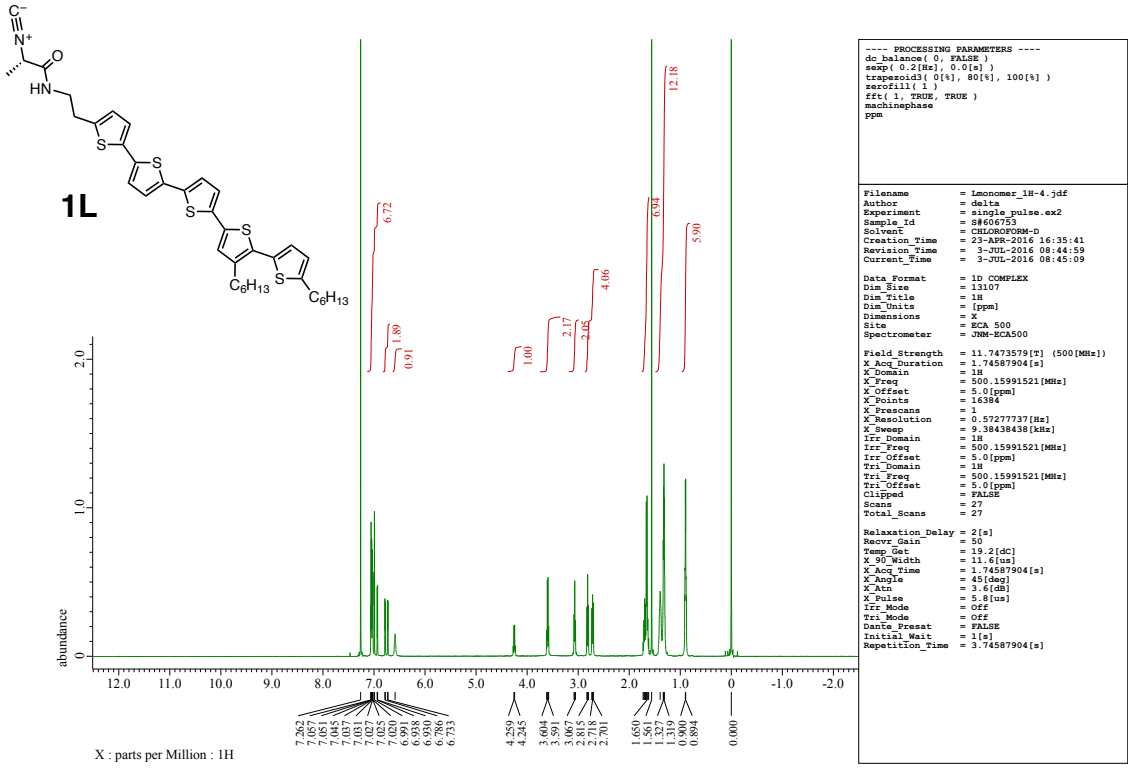


Fig. S13 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **1L**.

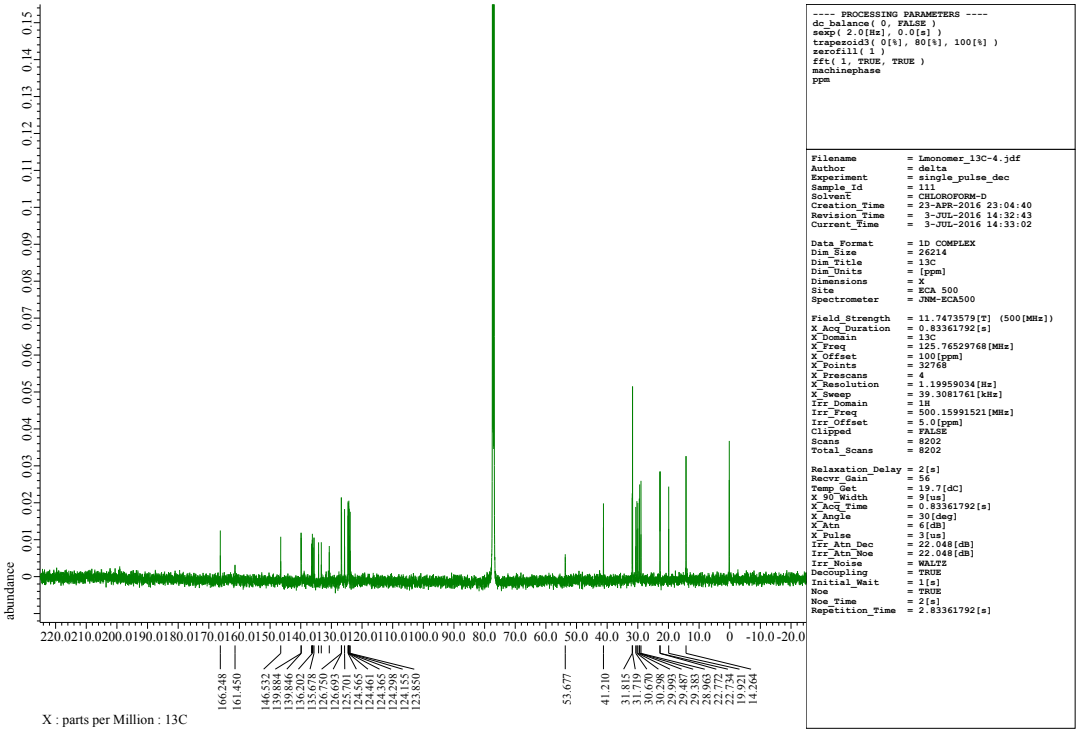


Fig. S14 ^{13}C NMR ($CDCl_3$, 125 MHz, rt) spectrum of **1L**.

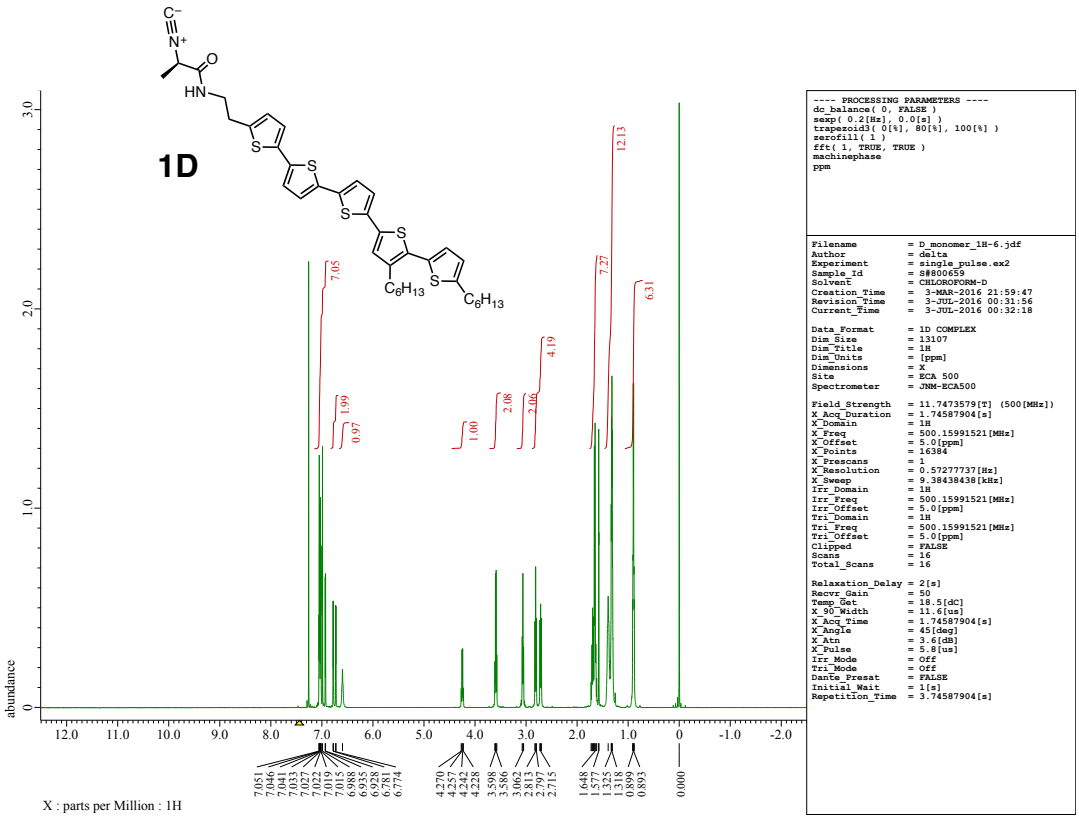


Fig. S15 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **1D**.

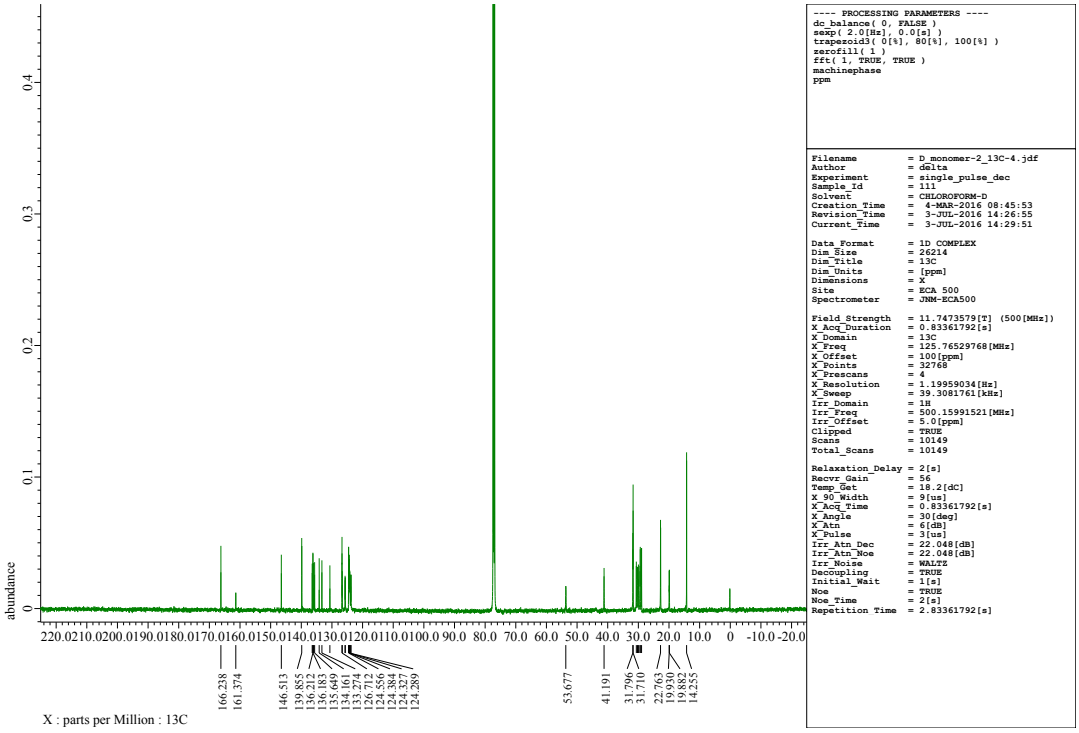


Fig. S16 ^{13}C NMR ($CDCl_3$, 125 MHz, rt) spectrum of **1D**.

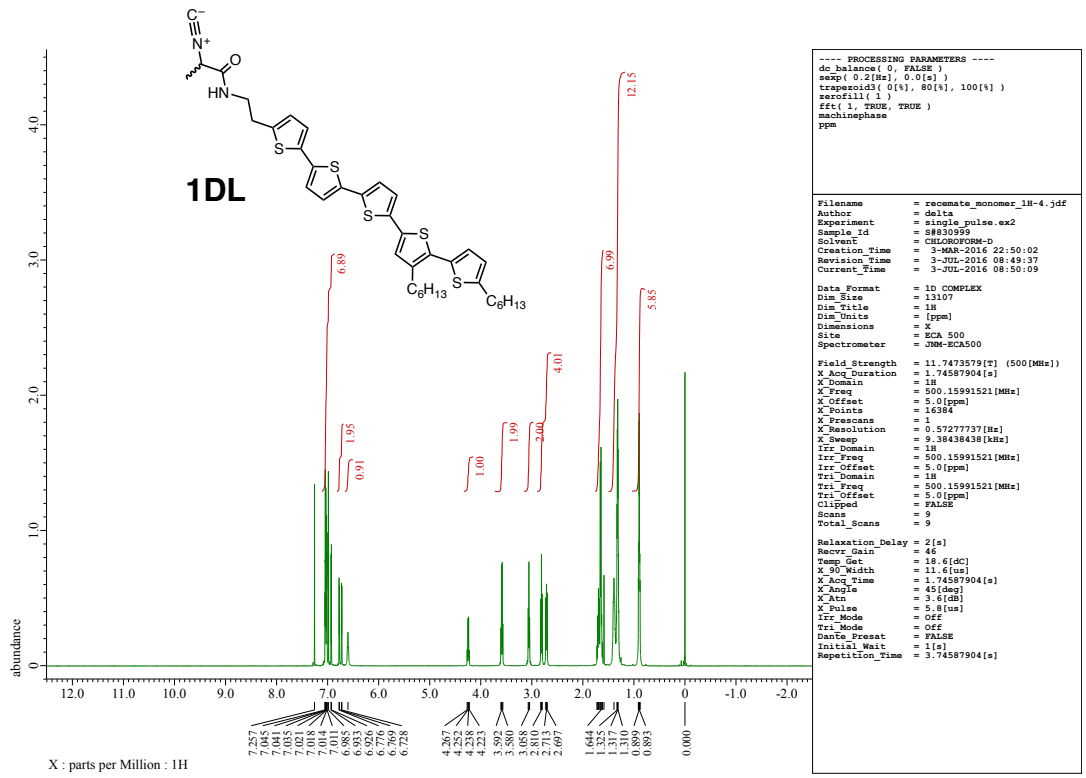


Fig. S17 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of **1DL**.

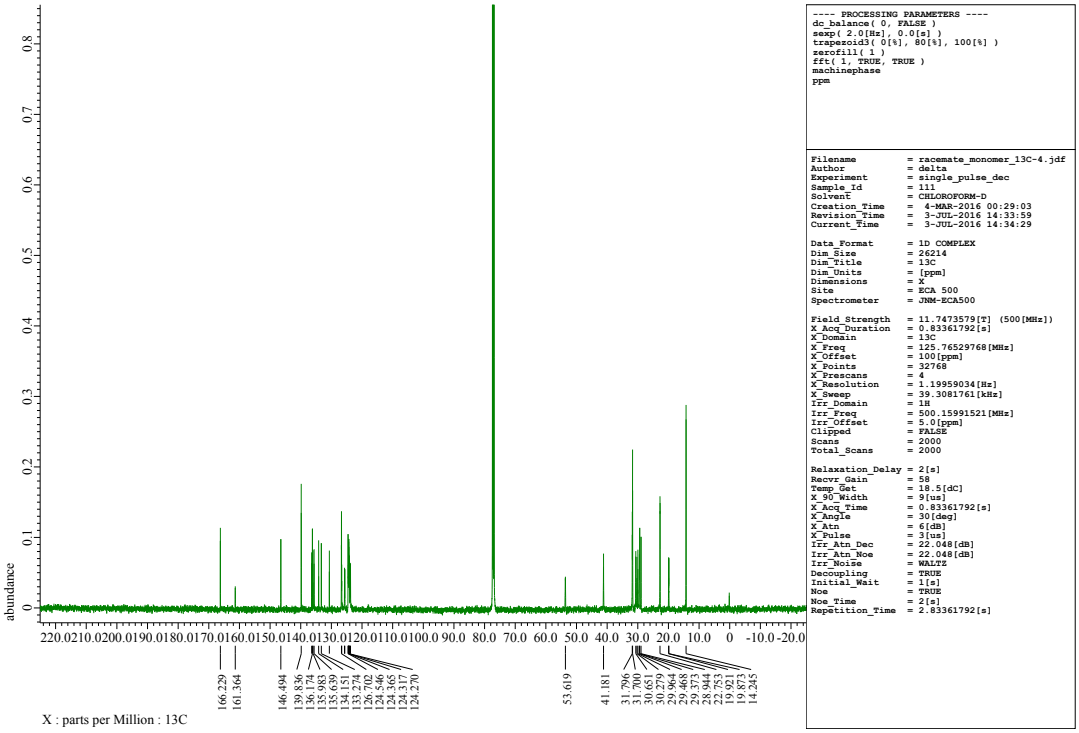


Fig. S18 ^{13}C NMR ($CDCl_3$, 125 MHz, rt) spectrum of **1DL**.

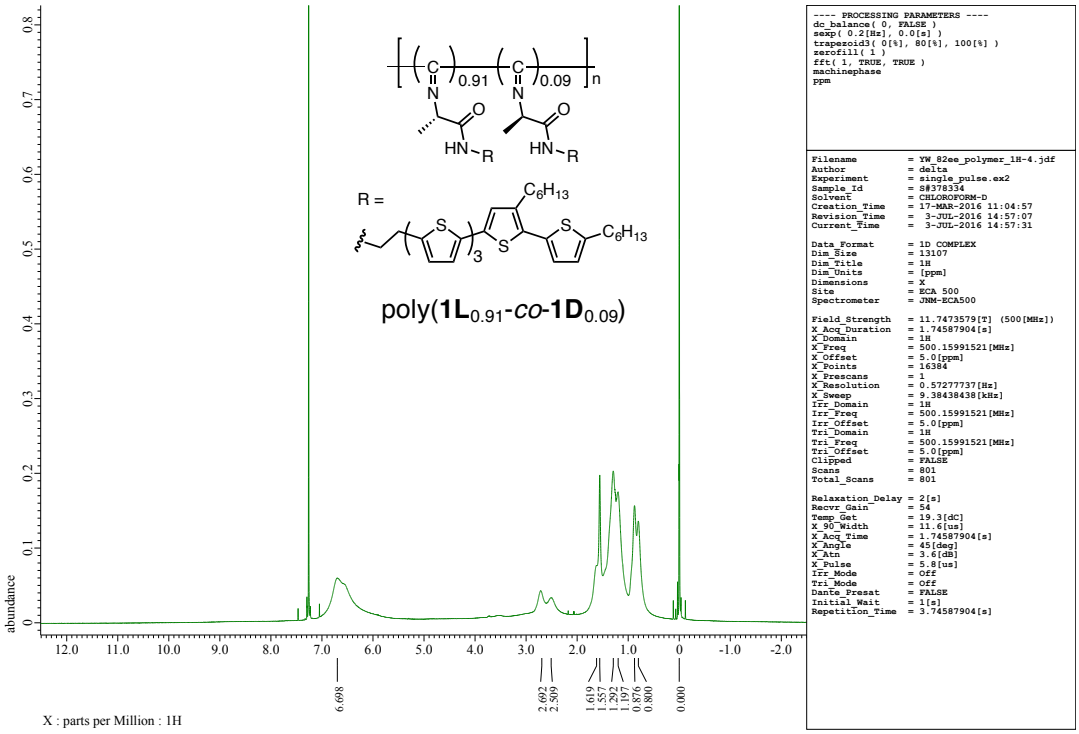


Fig. S19 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$).

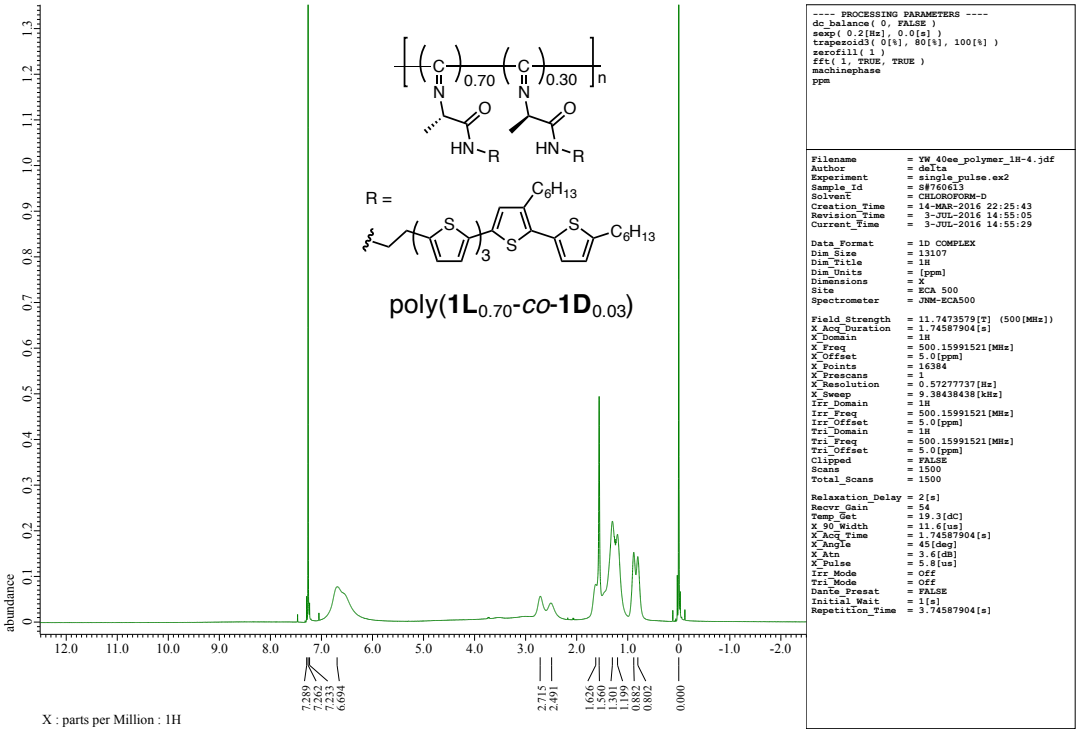


Fig. S20 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of poly(**1L**$_{0.70}$-*co*-**1D**$_{0.30}$).

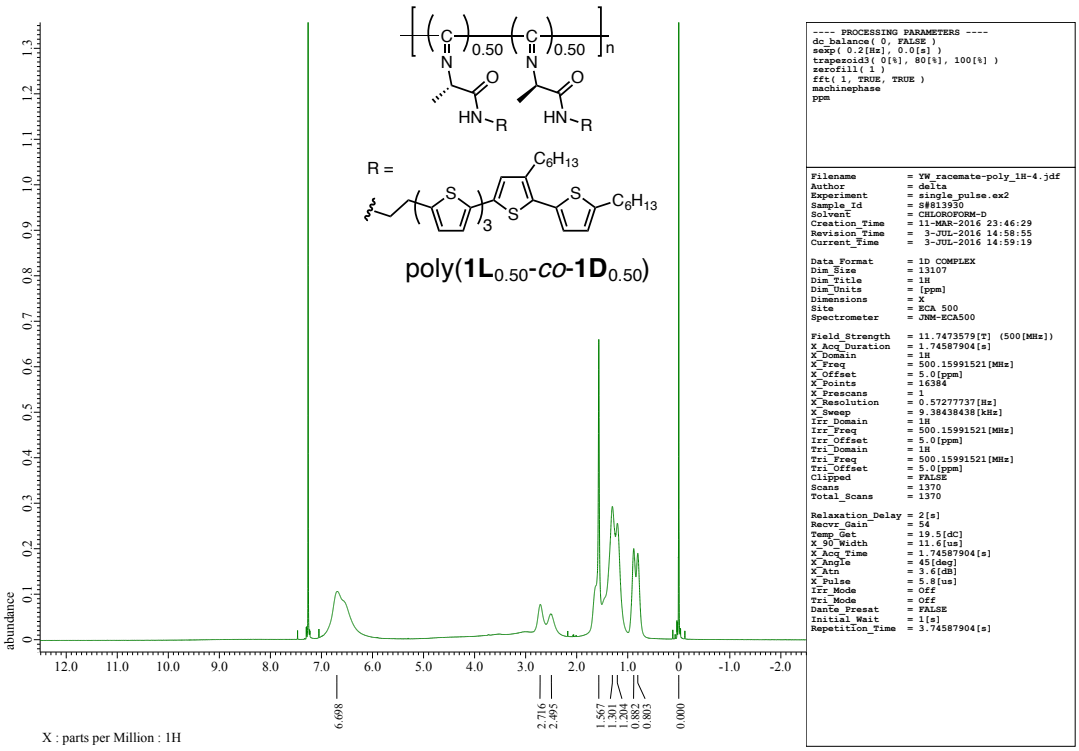


Fig. S21 ^{1}H NMR ($CDCl_3$, 500 MHz, rt) spectrum of poly(**1L**$_{0.50}$-*co*-**1D**$_{0.50}$).

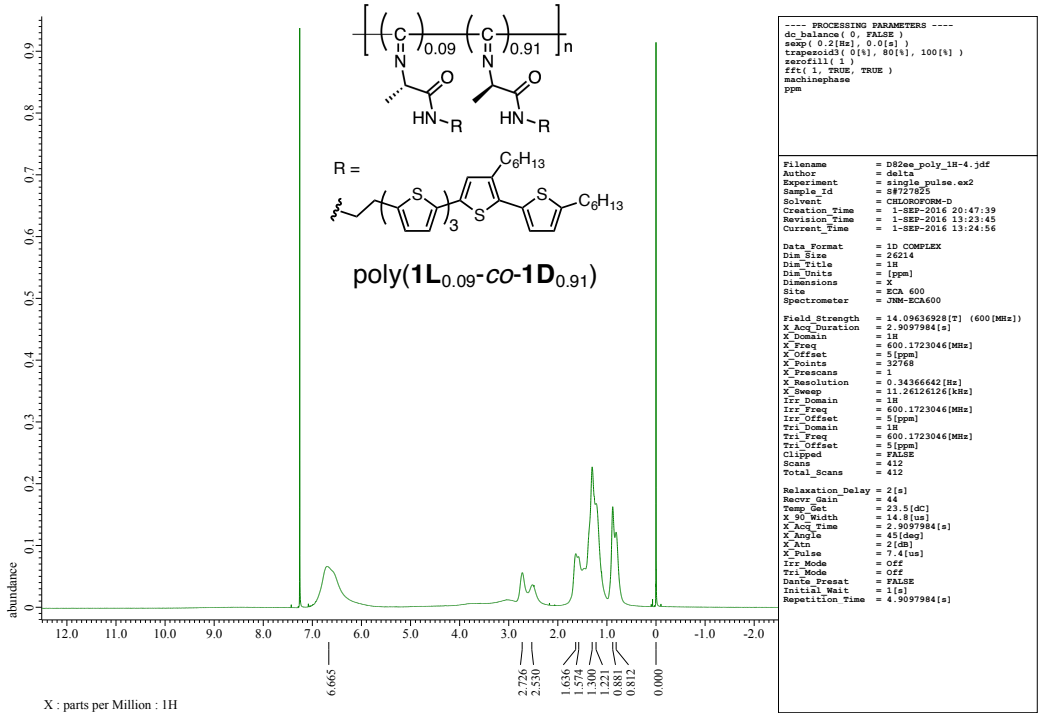


Fig. S22 ^{1}H NMR ($CDCl_3$, 600 MHz, rt) spectrum of poly(**1L**$_{0.09}$-*co*-**1D**$_{0.91}$).

9. Captions for supporting movies

Movie S1 An animation of all-tom MD simulation in the NVT ensemble at 800 K of the 50-mer model of poly(**1L**$_{>0.999}$-*co*-**1D**$_{<0.001}$) (CPK model) in chloroform (stick model) at 200–2250 ps as the sampling. The cell density and pressure were 1.318 g cm^{-3} and 0.264 GPa. See the supporting information for detail.

Movie S2 An animation of all-atom MD simulation in the NVT ensemble at 800 K of the 50-mer model of poly(**1L**$_{0.91}$-*co*-**1D**$_{0.09}$) (CPK model) in chloroform (stick model) at 200–2250 ps. The cell density and pressure were 1.341 g cm^{-3} and 0.289 GPa. The **1D** components in the model were highlighted in green. See the supporting information for detail.

Movie S3 An animation of all-atom MD simulation in the NVT ensemble at 800 K of the 50-mer model of poly(**1L**$_{0.98}$-*co*-**1D**$_{0.02}$) (CPK model) in chloroform (stick model) at 200–2200 ps. The cell density and pressure were 1.333 g cm^{-3} and 0.282 GPa. The **1D** components in the model were highlighted in green. See the supporting information for detail.

10. References

1 T. Ikai, Y. Takagi, K. Shinohara, K. Maeda and S. Kanoh, *Polym. J.*, 2015, **47**, 625–630.

2 K. Shinohara, S. Yamaguchi and T. Wazawa, *Polymer*, 2001, **42**, 7915–7918.

3 K. Shinohara, S. Yasuda, G. Kato, M. Fujita, and H. Shigekawa, *J. Am. Chem. Soc.* 2001, **123**, 3619–3620, Editors' Choice, *Science* 2001, **292**, 15.

4 K. Shinohara, N. Kodera and T. Oohashi, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 4103–4107.

5 K. Shinohara. Patent WO 2014/104172 A8, July 3, 2014.

6 We confirmed that the monomer consumption did not proceed at all even in 3 days after a 100-fold dilution of the polymerization system with chloroform.