**Supplementary Information**

# Polymerization of an Optically Active Phenylacetylene Derivative Bearing an Azide Residue by Click Reaction and with a Rhodium Catalyst

Shinzo Kobayashi, Ken Itomi, Kazuhide Morino, Hiroki Iida and Eiji Yashima*

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan.

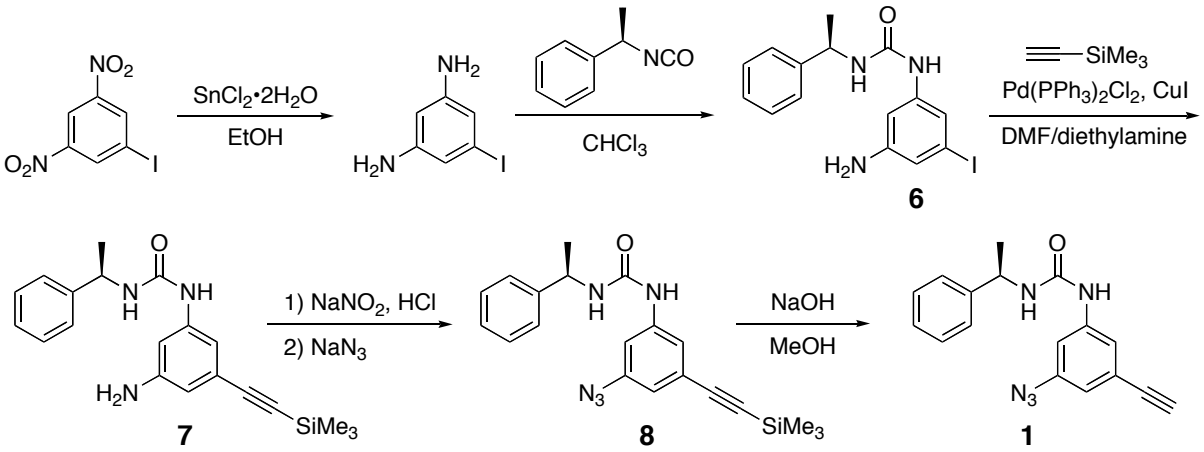
E-mail: yashima@apchem.nagoya-u.ac.jp

Fax: +81-52-789-3185; Tel: +81-52-789-4495

## Experimental Section

**Materials.** Triethylamine ($Et_3N$) and diethylamine ($Et_2NH$) were 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), methanol, dimethylformamide (DMF), sodium L-ascorbate, and L-ascorbic acid were purchased from Wako (Osaka, Japan). (*R*)-$\alpha$-Methylbenzyl isocyanate, (*R*)- and (*S*)-1-phenyl-2-propyn-1-ol ((*R*)- and (*S*)-**2**), (*R*)-1-octyn-3-ol ((*R*)-**3**), 1-iodo-3,5-dinitrobenzene, and bis[(norbornadiene)rhodium(I) chloride] ($[Rh(nbd)Cl]_2$) were obtained from Aldrich (Milwaukee, WI). Tin(II) chloride dihydrate ($SnCl_2•2H_2O$), sodium nitrite ($NaNO_2$), sodium azide ($NaN_3$), copper(II) sulfate pentahydrate ($CuSO_4•5H_2O$), copper(I) iodide (CuI), and lithium chloride anhydrous (LiCl) were obtained from Kishida (Osaka, Japan). Bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) and (*S*)-1-octyn-3-ol ((*S*)-**3**) were purchased from Tokyo Kasei (TCI, Tokyo, Japan). (Trimethylsilyl)acetylene was kindly supplied from Shinetsu Chemical (Tokyo, Japan). 5-Iodo-*m*-phenylenediamine was synthesized by the reduction of 1-iodo-3,5-dinitrobenzene with $SnCl_2•2H_2O$.[1] Model **1** was prepared by addition reaction of aniline with (*R*)-$\alpha$-methylbenzyl isocyanate.

Monomer **1** was prepared according to Scheme S1.




**Scheme S1**

**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 a solvent residual peak or tetramethylsilane (TMS) as the internal standard. The absorption and CD spectra were measured in a 0.2- or 0.5-cm quartz cell using a JASCO V-560 or V-570 spectrophotometer and a JASCO J-725 or J-820 spectropolarimeter, respectively. The temperature was controlled with a JASCO PTC-348WI apparatus or a liquid nitrogen-controlled quartz cell (0.5 cm) in a cryostat. The concentrations of the polymers were calculated based on the monomer units. Fluorescence spectra were measured in a 10-mm quartz cell on a JASCO FP 6500 spectrofluorometer. Size exclusion chromatography (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 number-average molecular weight ($M_n$) and its distribution ($M_w/M_n$) 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). Laser Raman spectra were measured on a JASCO RMP-200 spectrophotometer. Dynamic light scattering (DLS) measurements were performed on a DLS-7000HK (Otsuka Electronics Co. Ltd., Japan) equipped with a 10 mW He-Ne Laser (632.8 nm) at 25 ˚C. Microwave reactions were performed in a Milestone MicroSYNTH Labstation multimodal microwave reactor

equipped with a continuous power source (1000 W max) and a fiber-optic temperature sensor that allowed direct monitoring of the internal temperature of a reaction vessel.

**Synthesis of 6.** To a solution of 5-iodo-*m*-phenylenediamine (2.9 g, 12 mmol) in $CHCl_3$ (195 mL) was added (*R*)-$\alpha$-methylbenzyl isocyanate (2.3 mL, 16 mmol), and the reaction mixture was stirred at ambient temperature for 48 h. After the solvent was evaporated under the reduced pressure, the crude product was washed with $CHCl_3$ and then purified by recrystallization from ethanol to give 1.6 g of **6** as a white solid in 34% yield. Mp 204.8–205.6 °C. IR (KBr, $cm^{-1}$): 1631 (amide I), 1560 (amide II). $^1H$ NMR (300 MHz, DMSO-$d_6$, rt): $\delta$ 1.36 (d, $J$ = 7.2 Hz, $CH_3$, 3H), 4.76 (m, CH, 1H), 5.20 (s, $NH_2$, 2H), 6.48 (m, aromatic, 2H), 6.58 (d, $J$ = 7.2 Hz, NH, 1H), 7.01 (t, $J$ = 1.5 Hz, aromatic, 1H), 7.21–7.36 (m, aromatic, 6H), 8.23 (s, NH, 1H).

**Synthesis of 7.** Compound **7** was prepared in a similar way as previously reported.[2] To a solution of **6** (1.5 g, 3.9 mmol), $Pd(PPh_3)_2Cl_2$ (61 mg, 0.087 mmol), and CuI (33 mg, 0.18 mmol) in DMF (15 mL) were added $Et_2NH$ (6.2 mL, 60 mmol) and (trimethylsilyl)acetylene (0.62 mL, 4.4 mmol), and the reaction mixture was stirred at ambient temperature. After 9 h, the solvent was evaporated under the reduced pressure. The crude product was diluted with $CHCl_3$, and the solution was washed with water, and then dried over $Na_2SO_4$. After filtration, the solvent was removed by evaporation. The crude product was purified by silica gel chromatography with hexane–ethyl acetate (1/1, v/v) as the eluent to give 1.2 g of **7** as a brown solid in 87% yield. Mp 82.8–83.9 °C. IR (KBr, $cm^{-1}$): 2155 ($\nu_{C\equiv C}$), 1648 (amide I), 1559 (amide II). $^1H$ NMR (300 MHz, DMSO-$d_6$, rt): $\delta$ 0.19 (s, $Si(CH_3)_3$, 9H), 1.37 (d, $J$ = 6.9 Hz, $CH_3$, 3H), 4.76 (m, CH, 1H), 5.13 (s, $NH_2$, 2H), 6.20 (t, $J$ = 1.8 Hz, aromatic, 1H), 6.51–6.55 (m, aromatic and NH, 2H), 6.75 (t, $J$ = 1.8 Hz, aromatic, 1H), 7.20–7.37 (m, aromatic, 5H), 8.17 (s, NH, 1H).

**Synthesis of 8.** Compound **8** was prepared in a similar method as previously reported.[3] To a suspension solution of **7** (1.1 g, 3.1 mmol) in conc. HCl (5.5 mL) and water (5.5 mL) was added 4.8% aqueous $NaNO_2$ (5 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and 11% aqueous $NaN_3$ (3.5 mL) was then added to the reaction mixture. After stirring at 0 °C for 1 h, the precipitate was collected by filtration and then purified by silica gel chromatography with $CHCl_3$-ethyl acetate (1/10, v/v) as the eluent to give 526 mg of **8** as a brown solid in 45% yield. Mp 154.2–155.3 °C. IR (KBr, $cm^{-1}$): 2162 ($\nu_{C\equiv C}$), 2110 ($\nu_{N=N=N}$), 1648 (amide I), 1559 (amide II). $^1H$ NMR (300 MHz, DMSO-$d_6$, rt): $\delta$ 0.22 (s,

$Si(CH_3)_3$, 9H), 1.39 (d, $J$ = 6.6 Hz, $CH_3$, 3H), 4.79 (m, CH, 1H), 6.67 (m, aromatic, 1H), 6.78 (d, $J$ = 7.8, NH, 1H), 7.18–7.34 (m, aromatic, 7H), 8.66 (s, NH, 1H).

**Synthesis of 1.** To a solution of **8** (397 mg, 1.13 mmol) in methanol (40 mL) was added 1 M aqueous NaOH (5.5 mL), and the solution was stirred at ambient temperature for 2 h before evaporating the solvent. The crude product was diluted with ethyl acetate, and the solution was washed with water, and dried over $Na_2SO_4$. After filtration, the solvent was removed by evaporation to give 317 mg of **1** as a brown solid in 99% yield. Mp 101.6–102.2 °C. IR (KBr, $cm^{-1}$): 2188 ($\nu_{C\equiv C}$), 2107 ($\nu_{N=N=N}$), 1638 (amide I), 1560 (amide II). $^1$H NMR (300 MHz, DMSO-$d_6$, rt): $\delta$ 1.38 (d, $J$ = 6.9 Hz, $CH_3$, 3H), 4.24 (s, ≡CH, 1H), 4.80 (m, CH, 1H), 6.69 (m, aromatic, 1H), 6.77 (d, $J$ = 8.1 Hz, NH, 1H), 7.22–7.34 (m, aromatic, 7H), 8.68 (s, NH, 1H). $^{13}$C NMR (75 MHz, DMSO-$d_6$, rt): $\delta$ 22.9, 48.7, 81.2, 82.7, 108.3, 114.5, 117.1, 123.3, 125.8, 126.7, 128.4, 140.3, 142.1, 144.9, 154.1. Anal. Calcd for $C_{17}H_{15}N_5O$: C, 66.87; H, 4.95; N, 22.94. Found: C, 66.87; H, 4.79; N, 23.24. $[\alpha]_D^{25}$ +67° ($c$ 0.5, $CHCl_3$).

**Polymerization: Synthesis of Poly-1T.** Poly-**1T** was prepared according to Scheme 1.[4] A typical polymerization procedure is described below (see Scheme 1).

Monomer **1** (97.4 mg, 0.319 mmol) was placed in a glass 12-mL microwave reaction vessel and dry DMF (2 mL) and water (2 mL) were added with a syringe. To this were added sodium L-ascorbate (32.4 mg, 0.164 mmol) and $CuSO_4$•$5H_2O$ (4.1 mg, 0.016 mmol), and the vessel was placed in the microwave reactor and irradiated (1000 W maximum power) at 130 °C for 0.5 h. After cooling, the resulting polymer was precipitated into a large amount of methanol, collected by filtration, and dried in vacuo. The obtained polymer was dissolved in a small amount of DMSO and the DMSO-insoluble part was separated by filtration. The DMSO-soluble part was then poured into a large amount of toluene, and the precipitated polymer was collected by centrifugation, and dried in vacuo at room temperature overnight (24 mg, 25% yield). The $M_n$ and $M_w/M_n$ values were 4.3 x $10^4$ and 3.8, respectively, as determined by SEC using poly(ethylene oxide) and poly(ethylene glycol) standards in DMF containing 10 mM LiCl as the eluent.

Spectroscopic data of poly-**1T**. IR (KBr, $cm^{-1}$): 1656 (amide I), 1543 (amide II). $^1$H NMR (300 MHz, DMSO-$d_6$, 60 °C): $\delta$ 1.42 (d, $J$ = 6.0 Hz, $CH_3$, 3H), 4.88 (m, CH, 1H), 6.71 (d, $J$ = 5.5 Hz, NH, 1H), 7.13–7.41 (m, aromatic, 5H), 8.07 (s, aromatic, 1H), 8.11 (s, aromatic,

1H), 8.19 (s, aromatic, 1H), 8.87 (s, NH, 1H), 9.33 (s, =CH, 1H). Anal. Calcd for $(C_{17}H_{15}N_5O)_n$: C, 66.87; H, 4.95; N, 22.94. Found: C, 66.89; H, 5.15; N, 22.74.

**Polymerization: Synthesis of Poly-1A.** Polymerization 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 (see Scheme 1).

Monomer **1** (169 mg, 0.553 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 $CHCl_3$ (0.72 mL) was added with a syringe. To this was added a solution of $[Rh(nbd)Cl]_2$ (0.0065 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 0.00125 M, respectively. After 12 h, the resulting polymer was precipitated into a large amount of methanol, washed with hexane, collected by centrifugation, and dried in vacuo at room temperature overnight (146 mg, 87% yield).

The stereoregularity of poly-**1A** was confirmed to be a highly *cis-transoidal* by $^1$H NMR and Raman spectroscopies (Fig. S7 and S9A, respectively).[5] The $M_n$ and $M_w/M_n$ values were 1.6 x $10^5$ and 3.9, respectively, as determined by SEC using poly(ethylene oxide) and poly(ethylene glycol) standards in DMF containing 10 mM LiCl as the eluent.

Spectroscopic data of poly-**1A**. IR (KBr, $cm^{-1}$): 2109 ($\nu_{N=N=N}$), 1655 (amide I), 1544 (amide II). $^1$H NMR (500 MHz, DMSO-$d_6$, 60 °C): $\delta$ 1.26 (s, $CH_3$, 3H), 4.75 (s, CH, 1H), 5.71 (s, =CH, 1H), 5.89 (s, aromatic, 1H), 6.45 (s, NH and aromatic, 2H), 7.14 (s, aromatic, 1H), 7.21 (s, aromatic, 5H), 8.25 (s, NH, 1H). Anal. Calcd for $(C_{17}H_{15}N_5O)_n$: C, 66.87; H, 4.95; N, 22.94. Found: C, 66.69; H, 4.95; N, 22.84.

**Chemical Modification of Poly-1A.** A typical experimental procedure is described below (see Scheme 1).

**Synthesis of Poly((*S*,*R*)-4).** Poly-**1A** (20.0 mg, 0.0655 mmol) and (*R*)-**2** (173 mg, 1.31 mmol) were dissolved in dry DMF (0.3 mL) and to this were added L-ascorbic acid (23.1 mg, 0.131 mmol) in DMF (0.131 mL) and $CuSO_4$•$5H_2O$ (16.4 mg, 0.0655 mmol) in DMF (0.262 mL), and the reaction mixture was stirred at ambient temperature. After 12 h, L-ascorbic acid (23.1 mg, 0.131 mmol) in DMF (0.131 mL) and $CuSO_4$•$5H_2O$ (16.4 mg, 0.0655 mmol) in DMF (0.262 mL) were added again to the reaction mixture, and the reaction mixture was further stirred at ambient temperature for 9 h. The resulting polymer

was then precipitated into a large amount of methanol and collected by centrifugation. The obtained polymer was dissolved in a small amount of DMF containing LiCl and the solution was poured into a large amount of methanol. The polymer was collected by centrifugation and dried in vacuo at room temperature overnight (26.8 mg, 93% yield). Complete conversion of poly-**1A** to poly((*S*,*R*)-**4**) was confirmed by the IR spectrum which showed the disappearance of the azide signal of poly-**1A** (Fig. S8). The elemental analysis of the polymer agreed satisfactorily with the calculated values. The stereoregularity of the poly((*S*,*R*)-**4**) was investigated by NMR and Raman spectroscopies. However, we could not estimate the stereoregularity of the poly((*S*,*R*)-**4**) by its $^1$H NMR spectrum because of the broadening of the main chain protons (Fig. S10A). The Raman spectrum of poly((*S*,*R*)-**4**) gave useful information and showed intense peaks, which can be assigned to the C=C, C–C, and C–H bond vibrations in the *cis*-polyacetylenes, indicating that poly((*S*,*R*)-**4**) possesses a highly *cis-transoidal* structure (Fig. S9B).

Spectroscopic data of poly((*S*,*R*)-**4**). IR (KBr, cm$^{-1}$): 1656 (amide I), 1544 (amide II). $^1$H NMR (Fig. S10A). Anal. Calcd for $(C_{26}H_{23}N_5O_2)_n$: C, 71.38; H, 5.30; N, 16.01. Found: C, 71.38; H, 5.21; N, 16.03.

Poly((*R*,*R*)-**4**), poly((*R*,*R*)-**5**), and poly((*S*,*R*)-**5**) were prepared from poly-**1A** in the same way for the synthesis of poly((*S*,*R*)-**4**).

Spectroscopic data of poly((*R*,*R*)-**4**). IR (KBr, cm$^{-1}$): 1656 (amide I), 1551 (amide II). $^1$H NMR (Fig. S10B). Anal. Calcd for $(C_{26}H_{23}N_5O_2)_n$: C, 71.38; H, 5.30; N, 16.01. Found: C, 71.38; H, 5.22; N, 15.88.

Spectroscopic data of poly((*R*,*R*)-**5**). IR (KBr, cm$^{-1}$): 1685 (amide I), 1544 (amide II). $^1$H NMR (Fig. S10C). Anal. Calcd for $(C_{25}H_{29}N_5O_2)_n$: C, 69.58; H, 6.77; N, 16.23. Found: C, 69.42; H, 6.51; N, 16.04.

Spectroscopic data of poly((*S*,*R*)-**5**). IR (KBr, cm$^{-1}$): 1677 (amide I), 1550 (amide II). $^1$H NMR (Fig. S10D). Anal. Calcd for $(C_{25}H_{29}N_5O_2)_n$: C, 69.58; H, 6.77; N, 16.23. Found: C, 69.45; H, 6.60; N, 16.06.

**CD Measurements: Effect of Solvent on ICD of Poly-1T.** A typical experimental procedure is described below. A stock solution of poly-**1T** (4 mg/2 mL) in DMF was prepared in a 2-mL flask equipped with a stopcock. A 200 μL aliquot of the poly-**1T** solution was transferred to the 2-mL flasks equipped with stopcocks. To each flask was added appropriate amounts of DMF using a Hamilton microsyringe, respectively, and the

solutions were diluted with $CHCl_3$ so as to keep the poly-**1T** concentration at 0.2 mg/mL. The absorption and CD spectra were taken for each flask. In the same way, effect of methanol and DMSO–$CHCl_3$ on ICD of poly-**1T** was investigated.

**CD Measurements: Effect of LiCl Concentration on ICD of Poly(phenylacetylene) Derivatives.** A typical experimental procedure is described below. A stock solution of poly-**1A** (1 mg/mL) in DMF was prepared in a 2-mL flask equipped with a stopcock. A 100 μL aliquot of the poly-**1A** solution was transferred to several 1-mL flasks equipped with stopcocks. To each flask was added appropriate amounts of DMF containing LiCl using a Hamilton microsyringe, and the solutions were diluted with DMF so as to keep the LiCl concentration arbitrary and the poly-**1A** concentration at 0.1 mg/mL. The absorption and CD spectra were taken for each flask. In the cases of poly((*S,R*)-**4**), poly((*R,R*)-**4**), poly((*R,R*)-**5**), and poly((*S,R*)-**5**), stock solutions of the polymers (1 mg/mL) in DMF containing 1 mM LiCl were used, and the effect of LiCl concentration on their ICDs of the polymers was investigated in the same way.

**Dynamic Light Scattering Measurements.** A stock solution of poly-**1T** (2 mg/mL) in DMSO was prepared in a 2-mL flask equipped with a stopcock. The 600 μL aliquots of the stock solution were transferred to 6-mL flasks equipped with a stopcock using a Hamilton microsyringe. To the flasks were added DMSO (5.4 mL) or DMSO (1.2 mL) and $CHCl_3$ (4.2 mL), respectively, so as to keep the total volume (6 mL) and the poly-**1T** concentration at 0.2 mg/mL. After 48 h, the solutions were filtered through a 3 μm syringe filter (Toyo Roshi, Japan) prior to use, and then the DLS measurements of the samples were performed at a fixed scattering angle of 90° at ambient temperature. The corresponding hydrodynamic diameter ($d_H$) was calculated using the Stokes-Einstein equation: $d_H = k_B T/(3\pi\eta D)$, where $k_B$, $\eta$, and $T$ are the Boltzmann constant, the solvent viscosity, and the absolute temperature, respectively. The $\eta$ value for DMSO-$CHCl_3$ (3/7, v/v) at 25 °C was separately determined to be 1.07 mPa•s. The weight and number average hydrodynamic diameters ($d_H$) of the aggregates of poly-**1T** were estimated to be 11.6 ± 9.4 and 8.5± 1.8 nm in DMSO and 95.6 ± 34.6 and 75.6 ± 18.9 nm in DMSO–$CHCl_3$ (3/7, v/v), respectively, indicating the formation of supramolecular aggregates upon the addition of $CHCl_3$. The number average histograms are shown in Fig. S5.

**IR Measurements.** IR spectra of poly-**1T** and its model compound (model **1**) were measured at ambient temperature (26–28 °C) in DMSO–$CHCl_3$ (1/1, v/v) with a

concentration of 2 mg/mL or in DMSO with a concentration of 4 mg/mL in a 0.15-mm $BaF_2$ cell or in the solid state, and that of model **1** was also measured in $CHCl_3$ with a concentration of 4 mg/mL in a 0.15-mm $BaF_2$ cell. All spectra were collected at a resolution of 4 $cm^{-1}$.

**References**

1 M. Kakimoto, M. Yoneyama and Y. Imai, *J. Polym. Sci., Part A: Polym. Chem.*, 2000, **38**, 3911.

2 M. Erdélyi and A. Gogoll, *J. Org. Chem.*, 2001, **66**, 4165.

3 H. Tomioka and S. Sawai, *Org. Biomol. Chem.*, 2003, **1**, 4441.

4 A. D. Moorhouse, A. M. Santos, M. Gunaratnam, M. Moore, S. Neidle and J. E. Moses, *J. Am. Chem. Soc.*, 2006, **128**, 15972.

5 (*a*) C. I. Simionescu, V. Percec and S. Dumitrescu, *J. Polym. Sci: Polym. Chem. Ed.*, 1977, **15**, 2497; (*b*) C. I. Simionescu and V. Percec, *Prog. Polym. Sci.*, 1982, **8**, 133; (*c*) A. Furlani, C. Napoletano, M. V. Russo and W. J. Feast, *Polym. Bull.*, 1986, **16**, 311; (*d*) S. Matsunami, T. Kakuchi and F. Ishii, *Macromolecules*, 1997, **30**, 1074; (*e*) T. Kishimoto, P. Eckerle, T. Miyatake, M. Kainosho, A. Ono, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1999, **121**, 12035; (*f*) V. Percec and J. G. Rudick, *Macromolecules*, 2005, **38**, 7241.

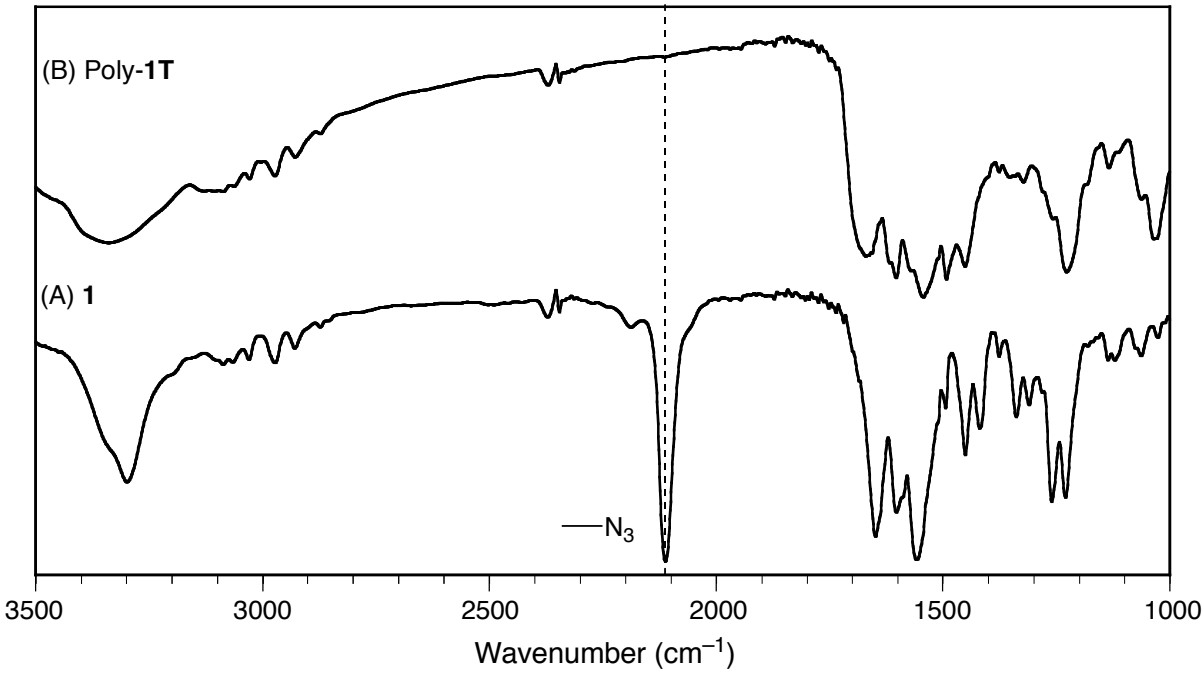



**Fig. S1** IR spectra of **1** (A) and poly-**1T** (B) (KBr).

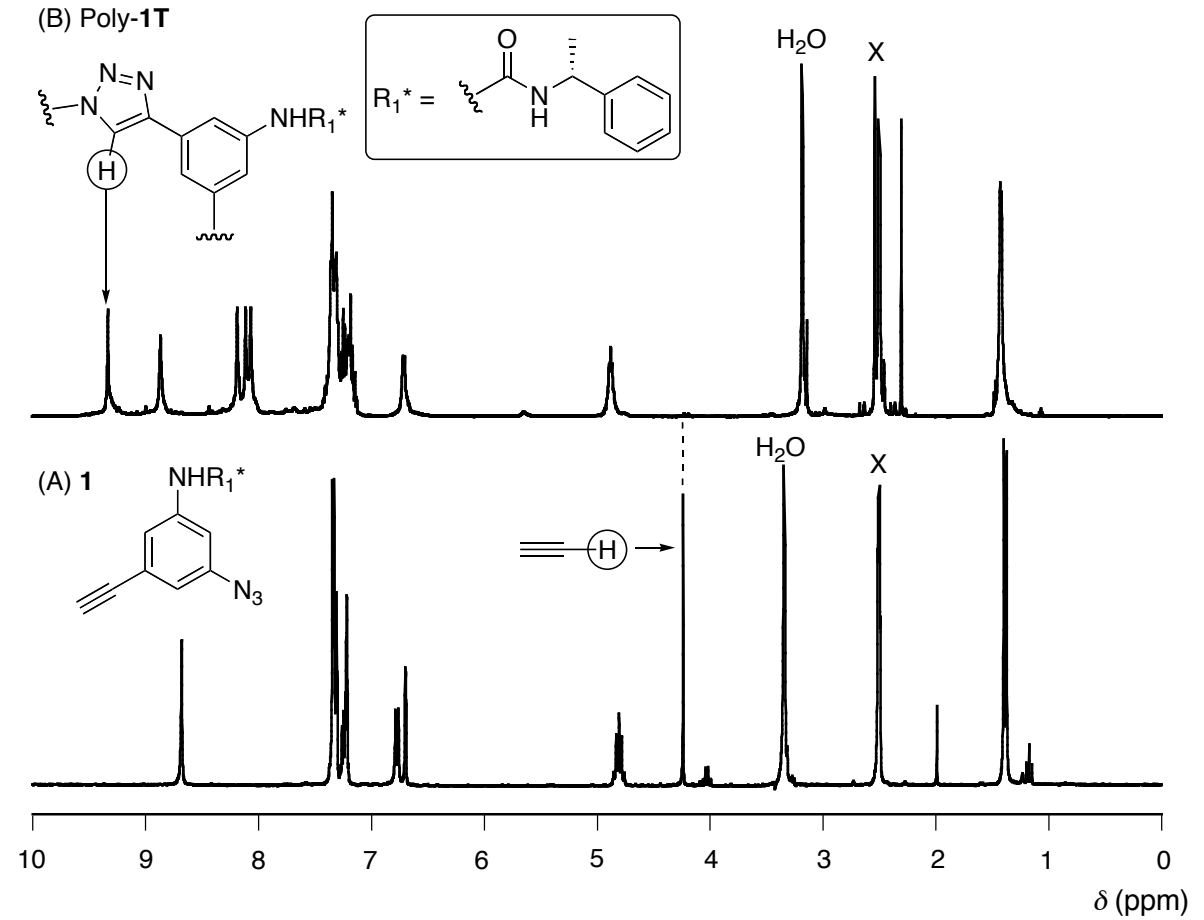



**Fig. S2** $^{1}$H NMR spectra of **1** (A) and poly-**1T** (B) in DMSO-$d_6$ at ambient temperature (26–28 °C) and 60 °C, respectively. X denotes protons from solvent.

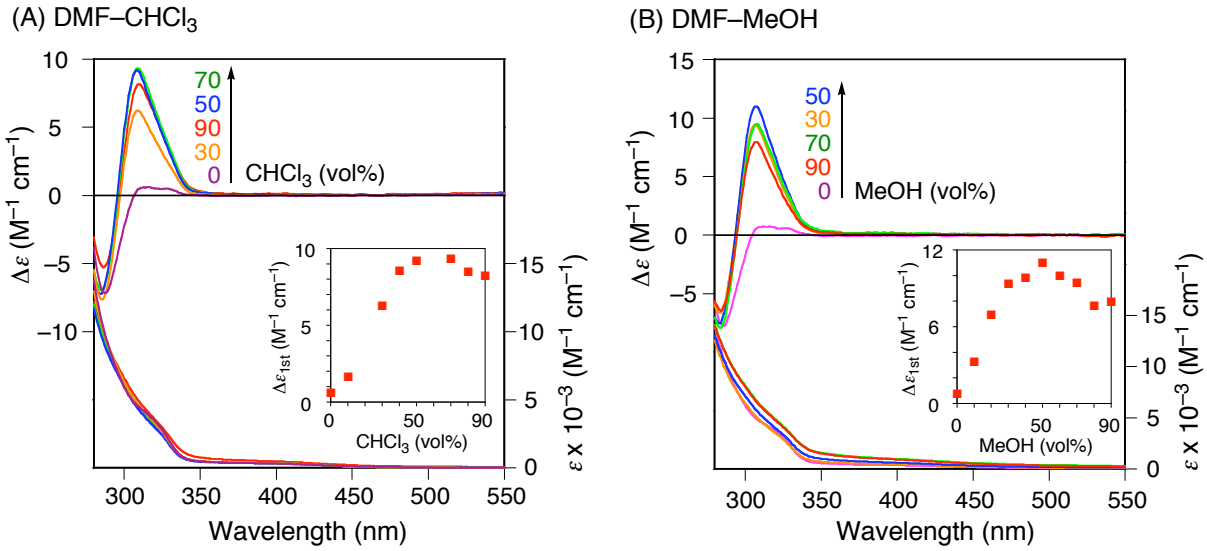



**Fig. S3** CD and absorption spectral changes of poly-**1T** in DMF–$CHCl_3$ (A) and DMF–methanol (B) mixtures at ambient temperature (26–28 °C) with a concentration of 0.2 mg/mL. Insets show plots of the CD intensity of the 1st Cotton effect ($\Delta\varepsilon_{1st}$) of poly-**1T** versus $CHCl_3$ (A) and methanol (B) contents (vol%).

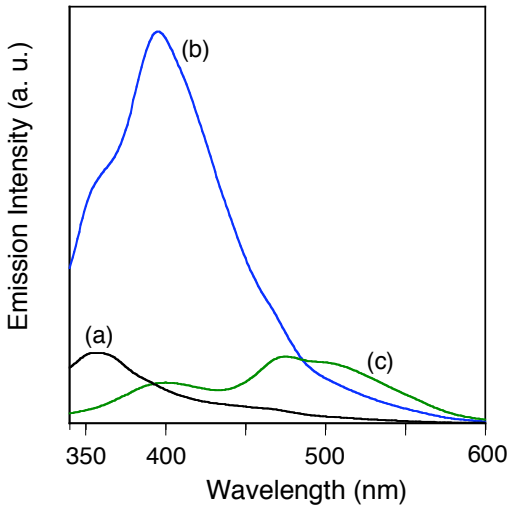



**Fig. S4** Fluorescence emission spectra (excitation wavelength = 330 nm) of **1** in DMF (a), poly-**1T** in DMF (b) and DMF–$CHCl_3$ (1/9, v/v) (c) at ambient temperature (26–28 °C). The concentrations of **1** and poly-**1T** were 0.02 mg/mL.

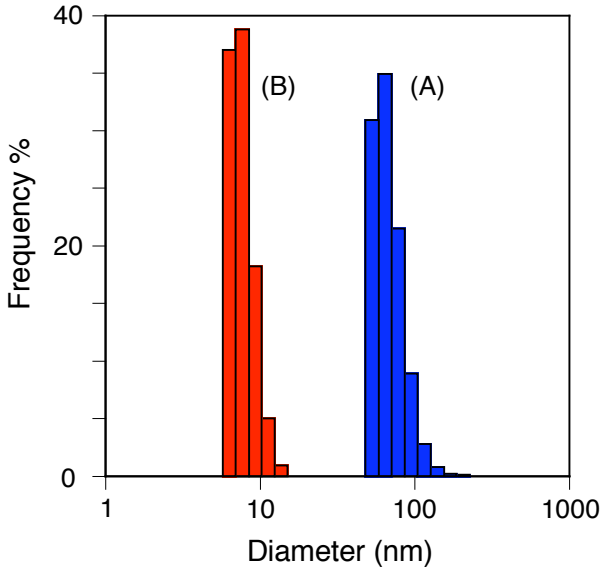



**Fig. S5** Histogram analysis of the DLS measurements of poly-**1T** in DMSO–$CHCl_3$ (3/7, v/v) (A) and DMSO (B).

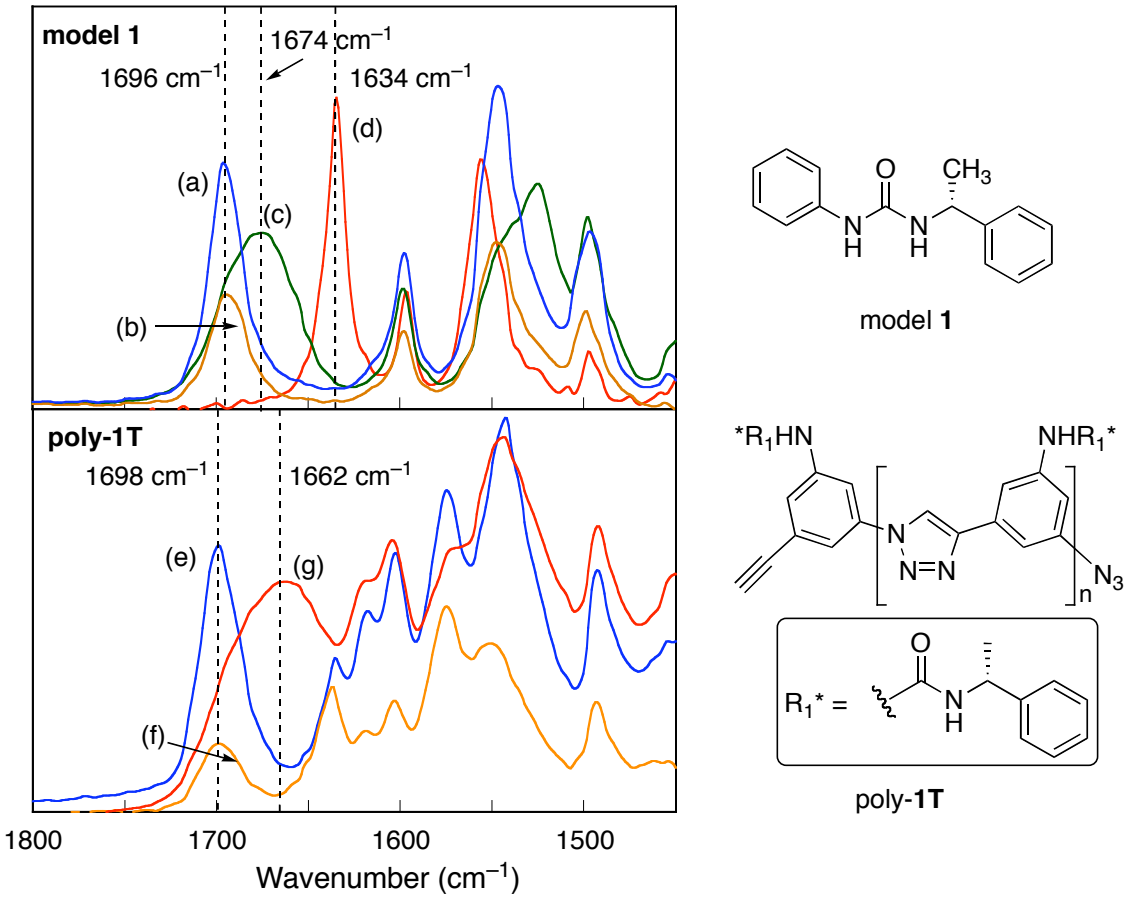



**Fig. S6** IR spectra of model **1** and poly-**1T** in DMSO (a, e), DMSO–$CHCl_3$ (1/1, v/v) (b, f), and $CHCl_3$ (c) measured in a 0.15-nm $BaF_2$ cell and in the solid state (KBr) (d, g).

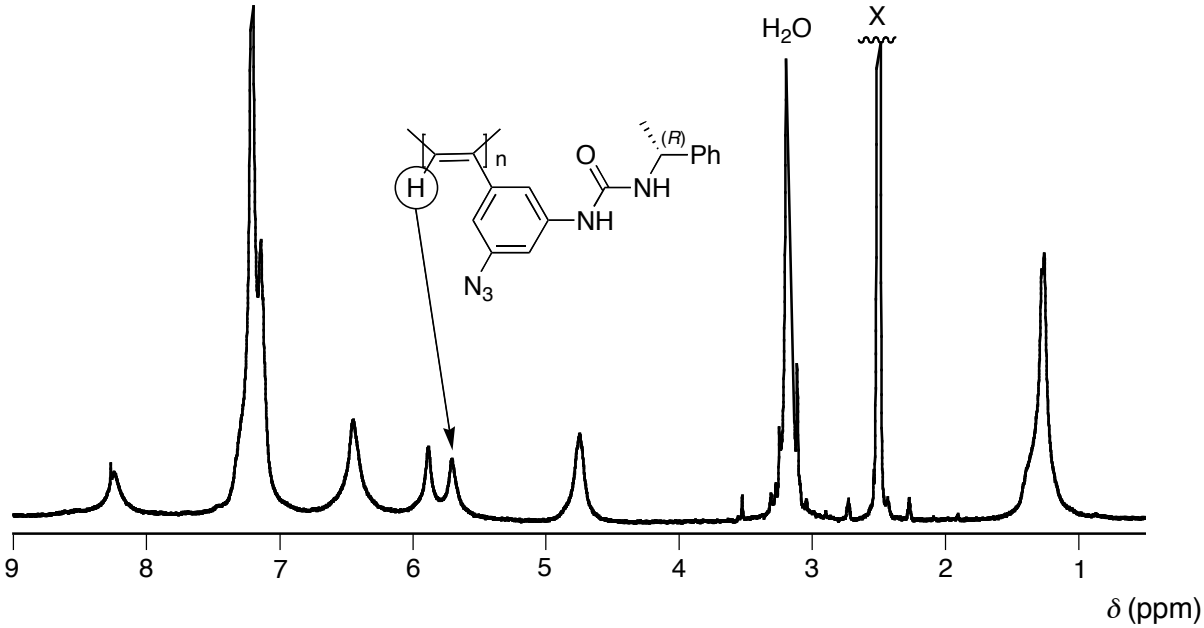



**Fig. S7** $^1$H NMR spectrum of poly-**1A** in DMSO-$d_6$ at 60 °C. X denotes protons from solvent.

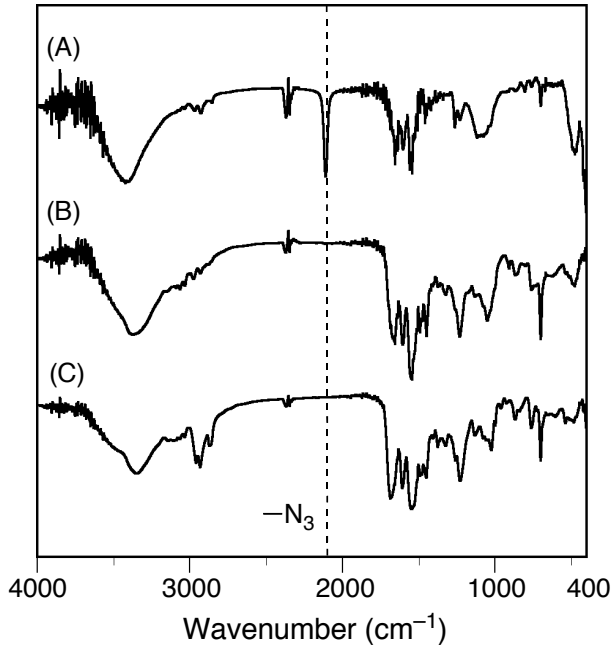



**Fig. S8** IR spectra of poly-**1A** (A), poly((*S,R*)-**4**) (B), and poly((*R,R*)-**5**) (C) (KBr).

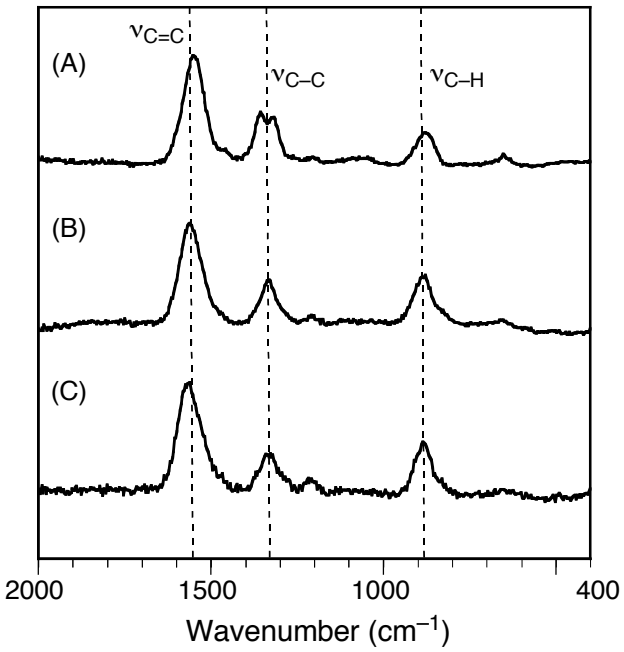
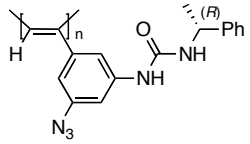


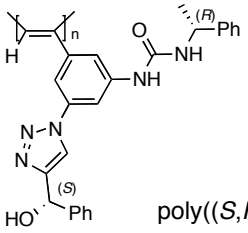

**Fig. S9** Laser Raman spectra of poly-**1A** (A), poly((*S,R*)-**4**) (B), and poly((*R,R*)-**5**) (C).

(A)



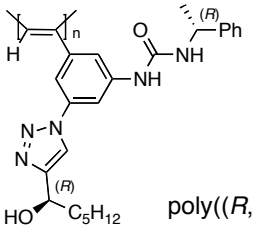
poly-**1A**

(B)



poly((*S,R*)-**4**)

(C)



poly((*R,R*)-**5**)

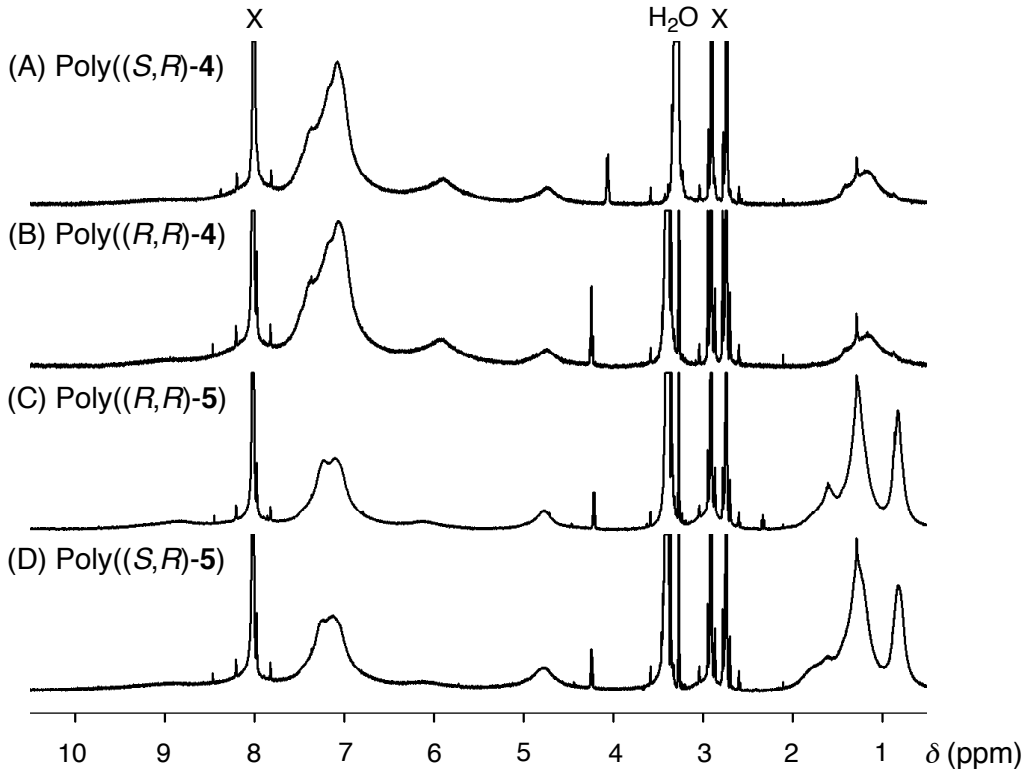



**Fig. S10** $^1$H NMR spectra of poly((*S*,*R*)-**4**) (A), poly((*R*,*R*)-**4**) (B), poly((*R*,*R*)-**5**) (C), and poly((*S*,*R*)-**5**) (D) in DMF-$d_7$ containing 100 mM LiCl at 60 °C. X denotes protons from solvent.

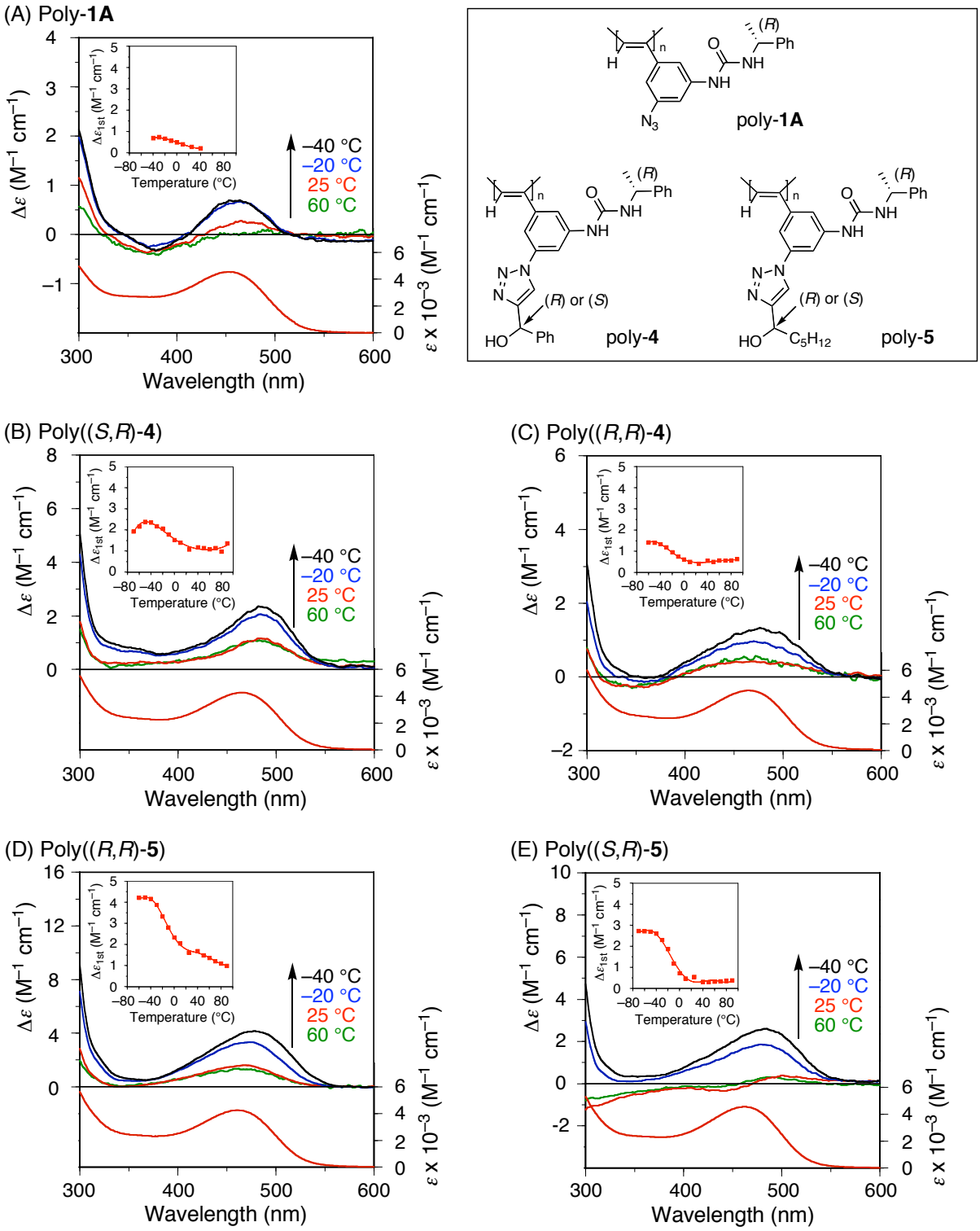



**Fig. S11** CD spectra of poly-**1A** (A), poly((*S*,*R*)-**4**) (B), poly((*R*,*R*)-**4**) (C), poly((*R*,*R*)-**5**) (D), and poly((*S*,*R*)-**5**) (E) in DMF containing 100 mM LiCl at various temperatures. Absorption spectra in DMF containing 100 mM LiCl at ambient temperature (26–28 °C) were also shown. Insets show temperature-dependent CD intensity (1st Cotton effect) changes.

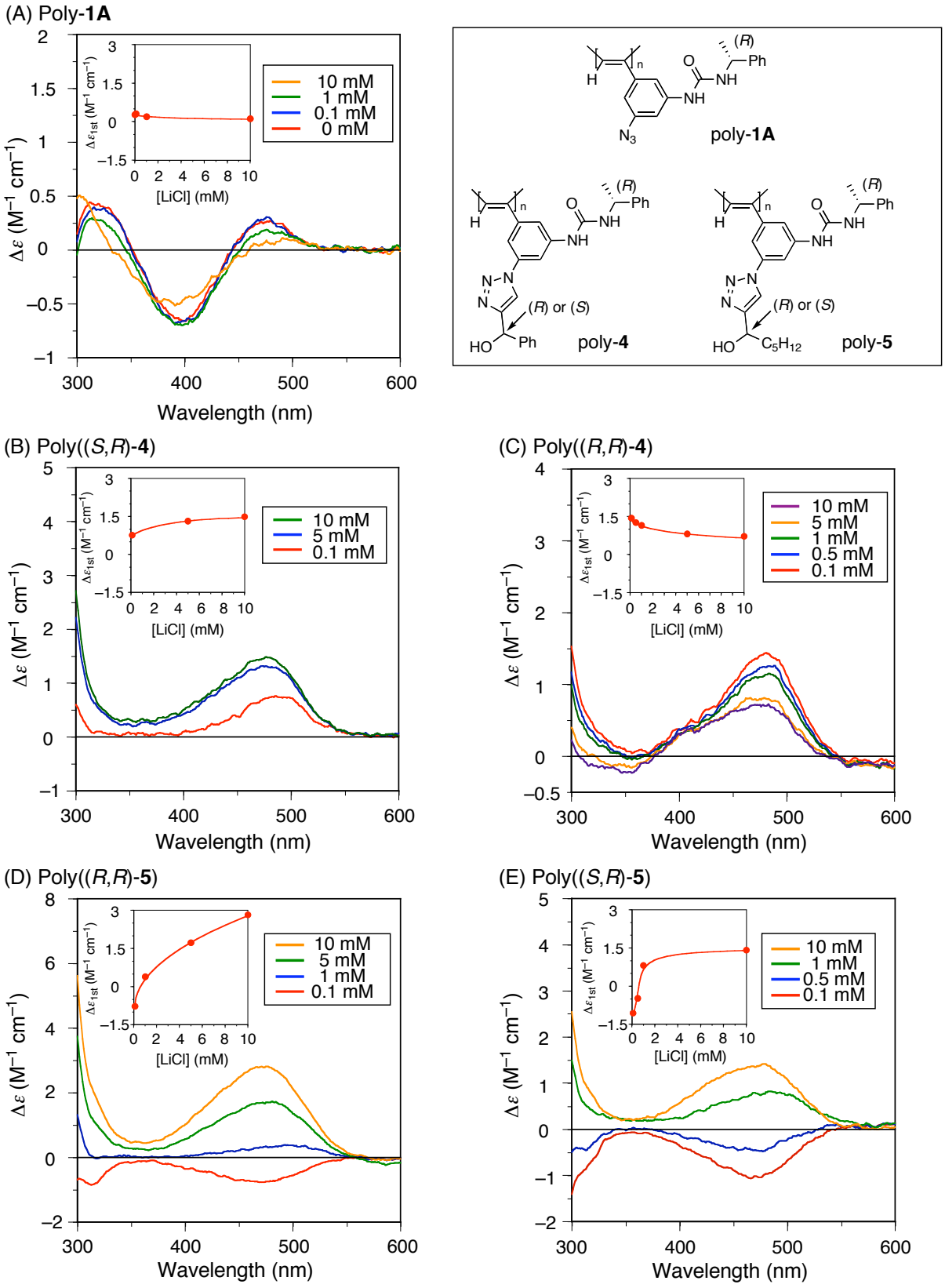



**Fig. S12** CD spectral changes of poly-**1A** (A), poly((*S*,*R*)-**4**) (B), poly((*R*,*R*)-**4**) (C), poly((*R*,*R*)-**5**) (D), and poly((*S*,*R*)-**5**) (E) in DMF at various LiCl concentrations at –10 °C. Insets show plots of the CD intensities (1st Cotton effect) versus LiCl concentration.