Chiral Amplification Based on Sergeants and Soldiers Principle in Helically Folded Poly(naphthalenecarboxamide)

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Supporting Information

Experimental

General. ^{1}H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standards of ^{1}H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm), and the internal standards of ^{13}C NMR spectra in $CDCl_3$ was the midpoints of $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free, Kanto) was used as a dry solvent, and dehydrated toluene (Kanto) was used for azeotropically drying the monomers. 1.0 M Lithium hexamethyldisilazide (LiHMDS) in THF (Aldrich) was used as received. The M_n and M_w/M_n values of polymer were measured on a Shodex GPC-101 gel permeation chromatography (GPC) unit equipped with Shodex UV-41, Shodex RI-71S, and two Shodex KF-804L columns (bead size = 7 μm, pore size = 200 Å). THF was used as the eluent (temperature = 40 °C, flow rate = 1 mL/min), and calibration was carried out using polystyrene standards. Isolation of polyamides was carried out with a Japan Analytical Industry LC-908 recycling preparative HPLC (eluent: chloroform) using two TOSOH TSK-gel columns (2 × G2000H_{HR}). UV-vis spectra were measured on a Shimadzu UV-1800 spectrophotometer. CD spectra were measured on a JASCO J-820 spectropolarimeters using a 10 mm quartz cell. Chiral monomer **1** and achiral monomer **2** were synthesized according to our previous report.[1,2] Poly(*p*-benzamide) copolymers **5** were prepared according to the previous literature.[3]

Polymerization

The monomer **1** and **2** were copolymerized by the procedure as shown in Table 1.

Synthesis of 3c. The monomer **1** and **2** were azeotropically dehydrated with dry toluene three times and then dried under reduced pressure before use. A flask equipped with a three-way stopcock was purged with argon and then charged with 1.0 M LiHMDS in THF (0.22 mL, 0.22 mmol). The flask was cooled to –30 °C under an argon atmosphere with stirring. A solution of **1** (44.4 mg, 0.105 mmol), **2** (40.8 mg, 0.0996 mmol) and initiator (1.7 mg, 0.0080 mmol) in dry THF (0.2 mL) was cooled to –30 °C and then added at once into the flask containing LiHMDS via a syringe through the three-way stopcock in a stream of dry nitrogen. After the reaction mixture was stirred at –30 ^{o}C for 27.5 h, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified with a preparative HPLC (eluent: $CHCl_3$) using polystyrene gel columns to give **3c** (21.6 mg, 32%, M_n = 5450, M_w/M_n = 1.12) as brown viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.08 (m, Ar-*H*), 4.30-3.38 (m, -NC*H*$_2$C*H*(CH$_3$)(OC*H*$_2$C*H*$_2$)$_2$OCH$_3$ and -NC*H*$_2$C*H*$_2$(OC*H*$_2$C*H*$_2$)$_2$OCH$_3$), 3.35-3.254 (m, -OC*H*$_3$), 3.248-3.16 (m, -OC*H*$_3$), 1.31-1.12 (m, CHC*H*$_3$).

Reference

[1] Mikami, K.; Tanatani, A.; Yokoyama, A.; Yokozawa, T. *Macromolecules*, **2009**, *42*, 3849-3851.

[2] Mikami, K.; Daikuhara, H.; Kasama, J.; Yokoyama, A.; Yokozawa, T. submitted

[3] Yokoyama, A.; Inagaki, Y.; Ono, T.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.*, in press.

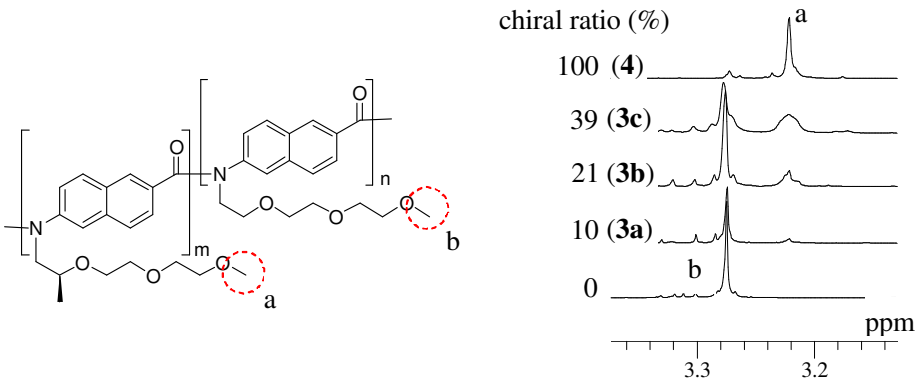


Figure S1. ^{1}H NMR spectra of chiral-achiral random copolymers after purification by HPLC in $CDCl_3$ at 25 ^{o}C to determine the chiral unit ratio in the copolymer.

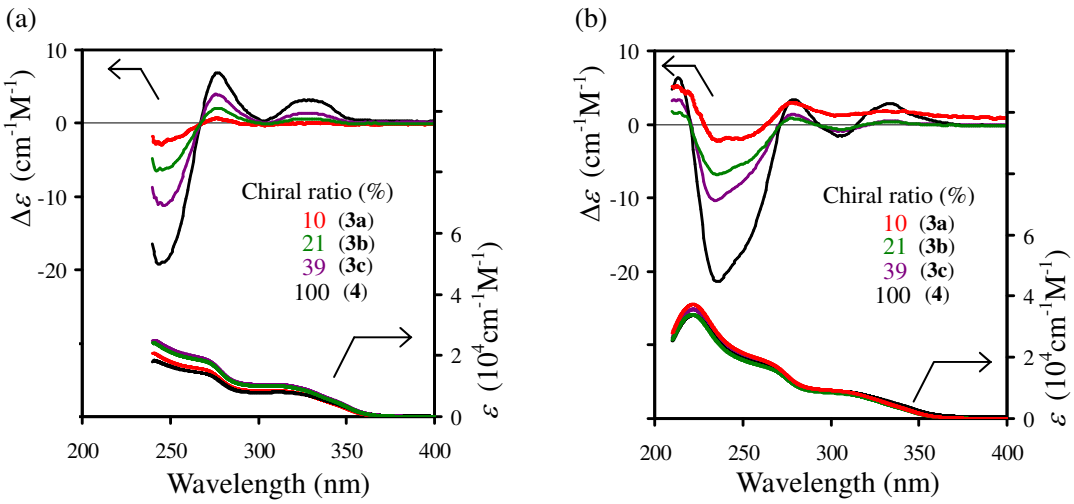


Figure S2. (a) UV and CD spectra of **3** and **4** in (a) chloroform and (b) methanol at 25 ^{o}C.

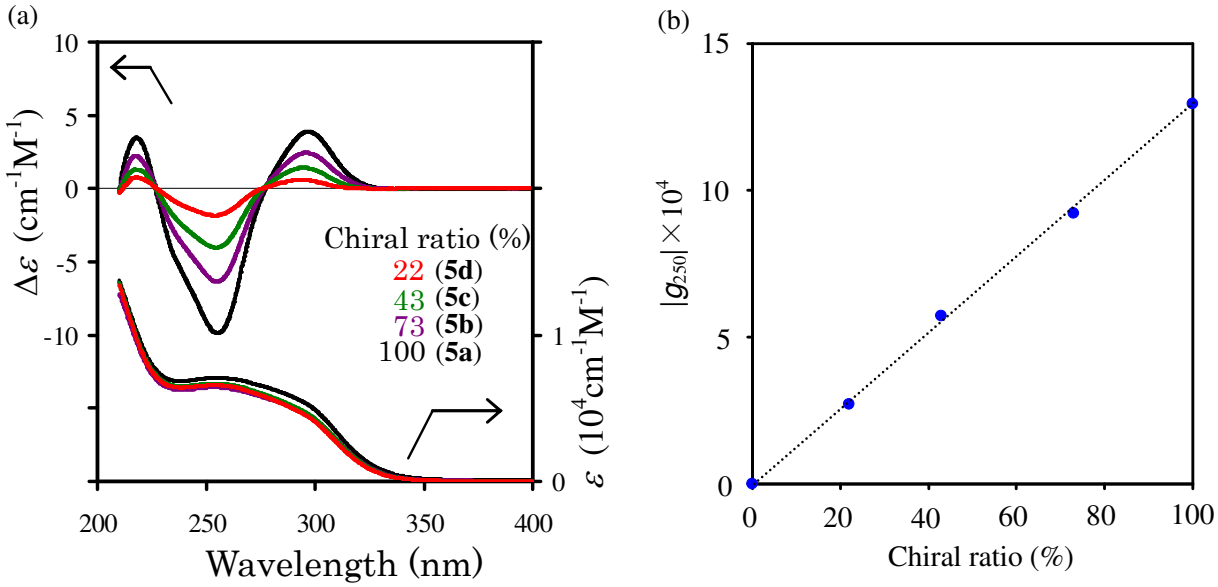
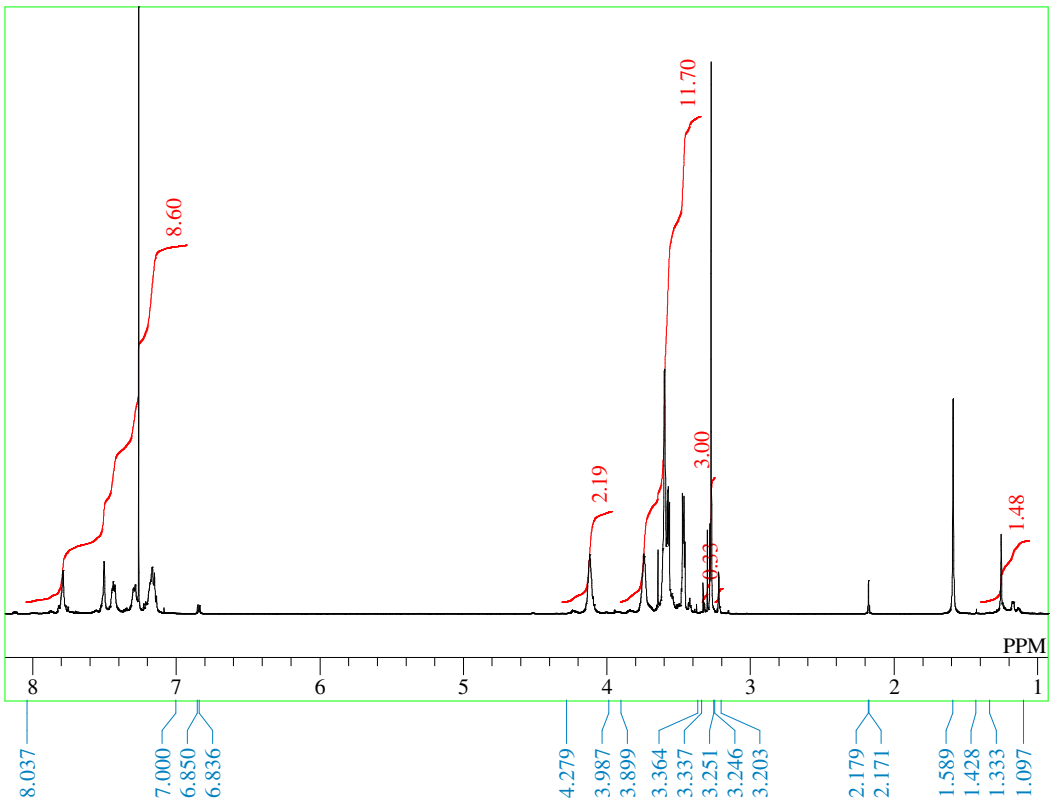
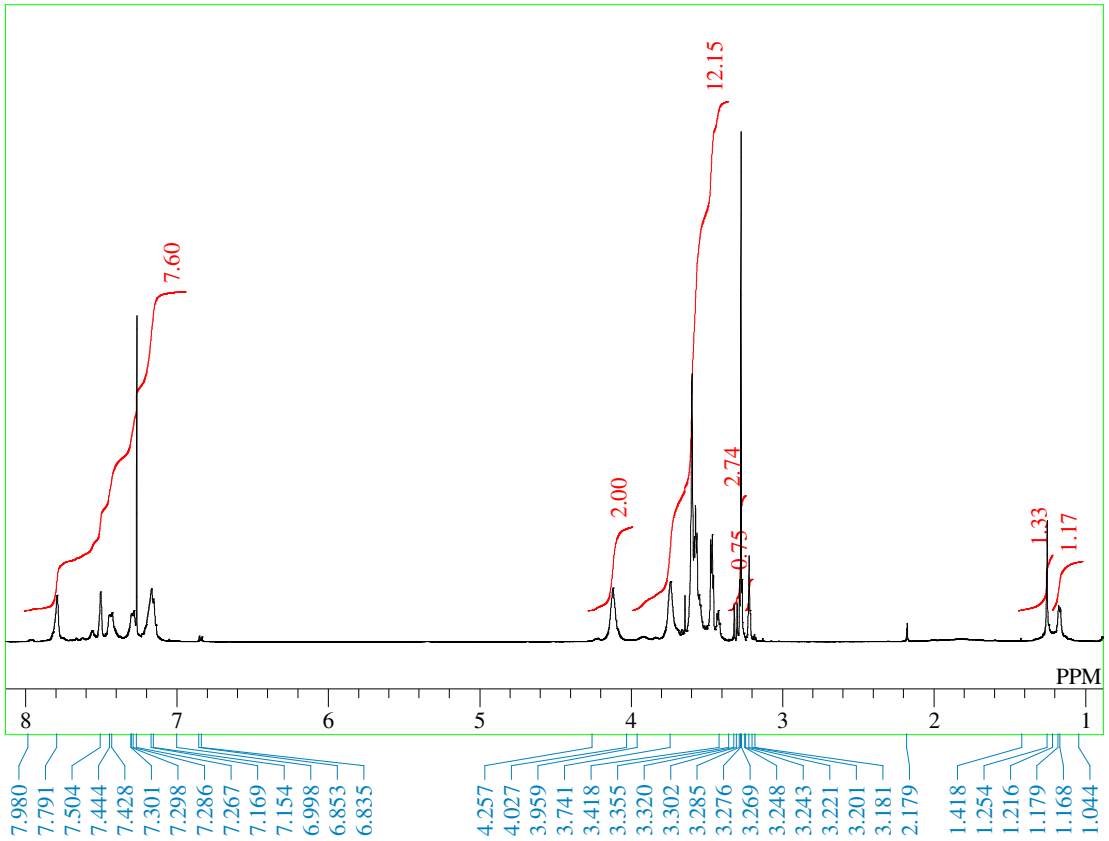


Figure S3. (a) UV and CD spectra of poly(*p*-benzamide)s (**5a** M_n = 8870, M_w/M_n = 1.08; **5b** M_n = 9200, M_w/M_n = 1.13; **5c** M_n = 8440, M_w/M_n = 1.08; **5d** M_n = 8680, M_w/M_n = 1.07) in water/methanol = 7/3 at 25 °C. (b) Plot of Kuhn dissymmetry factor (g = $\Delta\varepsilon/\varepsilon$) at 250 nm of the random copolymer in water/methanol = 7/3 (blue circle) against the chiral unit ratio. The dotted lines are meant to guide the eye.

^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3a



^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3b



^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 3c