Electronic Supplementary Information for:

Enantioseparation on poly(phenyl isocyanide)s with macromolecular helicity memory as chiral stationary phases for HPLC

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Contents

1. Instruments

The NMR spectra were measured using a Varian VXR-500S spectrometer (Varian, Palo Alto, CA) operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C using tetramethylsilane (TMS) for CDCl$_3$ as the internal standard. The IR spectra were recorded on a JASCO FT/IR-680 spectrometer (JASCO, Tokyo, Japan). Elemental analyses were performed by the Nagoya University Analytical Laboratory in School of Agriculture. The absorption and CD spectra were obtained in a 1.0-mm quartz cell at 25 °C using a JASCO V570 spectrophotometer and a JASCO J820 spectropolarimeter, respectively. The polymer concentration was calculated on the basis of the monomer units and was 1.0 mg mL^{-1}. The optical rotations were measured in a 2-cm quartz cell on a JASCO P-1030 polarimeter. The size exclusion chromatography (SEC) was performed using a JASCO PU-2080 liquid chromatograph equipped with a UV-visible (JASCO UV-2070) detector and a Tosoh TSKgel Multipore H$_{XL}$-M SEC column (Tosoh, Tokyo, Japan), and chloroform was used as the eluent at the flow rate of 1.0 mL min^{-1}. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh). The high performance liquid chromatography (HPLC) experiments were performed on a JASCO PU-2080 Plus liquid chromatograph equipped with Multi UV-Vis (JASCO MD-2010 Plus) and polarimetric detectors (JASCO OR-2090 Plus, Hg–Xe without filter) at room temperature. A solution of racemate was injected into the chromatographic system using a Rheodyne Model 7725i injector (20 μL loop). The thermogravimetric (TG) analyses were conducted on a SEIKO EXSTAR6000 TG/DTA 6200 (Seiko Instruments Inc., Chiba, Japan) under a heating rate of 10 °C min^{-1} in a nitrogen flow of 200 mL min^{-1}.

2. Materials

Anhydrous tetrahydrofuran (THF), methanol, chloroform, dichloromethane, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) (water content < 0.005%) were purchased from Wako (Osaka, Japan) and stored under dry nitrogen. 4-Nitrobenzoic acid and palladium 10% activated carbon were purchased from Aldrich (Milwaukee, WI). *p*-Dodecylaniline (**2**), ethyl 4-aminobenzoate (**4–Et**) and aniline (**5**) were obtained from Wako (Osaka, Japan). 12-Aminododecanoic acid methyl ester,[S1] 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM)[S2] and optically active right- and left-handed helical poly(4-carboxyphenyl isocyanide)s with macromolecular helicity memory (*P*-poly-**1**–**H**(+) and *M*-poly-**1**–**H**(–), respectively)[S3] were prepared as previously reported. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(4-

carboxyphenyl isocyanide) (poly-**1**–**H**) were 8.23×10^4 and 5.40, respectively, as its ethyl esters determined by SEC with polystyrene standards using chloroform as the eluent at a flow rate of 1.0 mL min^{-1}. The solvents used in the chromatographic experiments were of HPLC grade. The racemates were commercially available or were prepared by the usual methods.[S4] Porous spherical (3-aminopropyl)-triethoxy silanized silica gel (Daiso gel SP-1000-7-APSL, A-silica) with a mean particle size of 7 μm and a mean pore diameter of 100 nm was kindly supplied from Daicel Chemical Industries (Tokyo, Japan).

3. Synthesis of Poly(phenyl isocyanide)s with Macromolecular Helicity Memory

Synthesis of 3–Me. The synthesis of **3**–**Me** was carried out according to Scheme S1. DMT-MM (1.81 g, 6.54 mmol) was added to a solution of 4-nitrobenzoic acid (0.801 g, 4.79 mmol) and 12-aminododecanoic acid methyl ester (1.00 g, 4.36 mmol) in anhydrous THF (35 mL). The reaction mixture was stirred at room temperature under a dry nitrogen atmosphere. After 15 h, the solvent was removed by evaporation. The residue was dissolved in chloroform (50 mL), and the solution was washed with aqueous NaHCO$_3$ (50 mL), water (50 mL), aqueous HCl (1 M, 50 mL), water (50 mL) and brine (50 mL), and then dried over anhydrous MgSO$_4$. After filtration, the solvent was removed by evaporation, and the residue was purified by column chromatography (SiO$_2$, chloroform / methanol = 95 / 5) to give the product **6** in 85% yield (1.54 g). This was subjected to the next reaction without further purification.

The product **6** (1.00 g) was dissolved in dichloromethane (17 mL), and to this was added palladium 10% activated carbon (0.27 g). The mixture was stirred at room temperature for 18 h under an atmosphere of H$_2$. After filtrating off by celite, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (NH$_2$–SiO$_2$, chloroform) to give **3**–**Me** (510 mg, 52% based on 12-aminododecanoic acid methyl ester) as a white solid. Mp: 88.8–89.3 °C. IR (KBr, cm^{-1}): 3415 ($\nu_{\text{N-H}}$), 3324 ($\nu_{\text{N-H}}$), 1722 ($\nu_{\text{C=O}}$ ester), 1621 (amide I), 1534 (amide II). ^{1}H NMR (CDCl$_3$, rt, 500 MHz): δ 1.26–1.37 (m, CH$_2$, 14H), 1.55–1.63 (m, CH$_2$, 4H), 2.30 (t, J = 7.6 Hz, CH$_2$, 2H), 3.41 (q, J = 7.2 Hz, CH$_2$, 2H), 3.67 (s, CH$_3$, 3H), 3.96 (br, NH, 2H), 5.96 (br, NH, 1H), 6.66 (d, J = 8.8 Hz, aromatic, 2H), 7.59 (d, J = 8.8 Hz, aromatic, 2H). ^{13}C NMR (CDCl$_3$, rt, 125 MHz): δ 25.2, 27.2, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 30.0, 34.3, 40.2, 51.7, 114.4, 124.7, 128.8, 149.6, 167.4, 174.6. Anal. Calcd (%) for C$_{20}$H$_{32}$N$_2$O$_3$: C, 68.93; H, 9.26; N, 8.04. Found: C, 68.77; H, 9.20; N, 8.05.
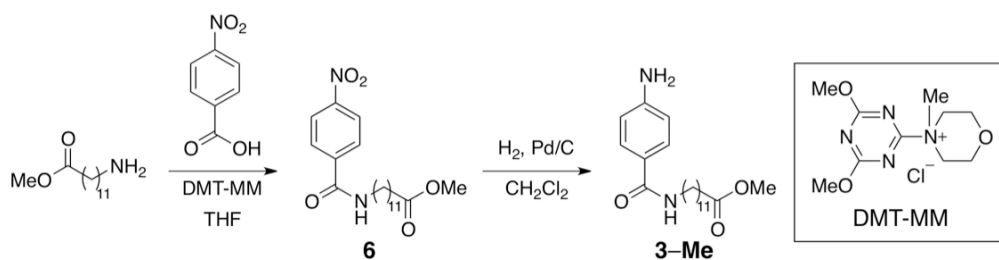
Scheme S1 Synthesis of **3–Me**.

Preparation of *P*-poly(2-*co*-3–Me)(+) and *M*-poly(2-*co*-3–Me)(–). These polymers were prepared according to Scheme S2. DMT-MM (1.51 g, 5.76 mmol) was added to a solution of *P*-poly-**1**–**H**(+) (203 mg, 1.38 mmol) and **2** (286 mg, 1.09 mmol) in DMSO (20 mL) and degassed water (4 mL). The reaction mixture was stirred at room temperature. After 14 h, the resulting polymer was precipitated into a large amount of methanol (500 mL), collected by centrifugation, washed with methanol (70 mL × 3), and dried in vacuo at room temperature. The recovered polymer was then allowed to react with **3**–**Me** (145 mg, 0.416 mmol) in the presence of DMT-MM (381 mg, 1.38 mmol) in THF (40 mL). After stirring at room temperature for 12 h, the resulting polymer was precipitated into a large amount of methanol (500 mL), collected by centrifugation, washed with methanol (70 mL × 3), and then dried in vacuo at room temperature overnight. The obtained polymer contained a small amount of the unreacted carboxy pendant groups, and therefore, the reaction was repeated using the recovered polymer with **2** (184 mg, 0.703 mmol) in the presence DMT-MM for 12 h and then with a mixture of **3**–**Me** (145 mg, 0.416 mmol) and **2** (108 mg, 0.413 mmol) for 10 h to complete the modification of the carboxy pendant groups, yielding *P*-poly(2-*co*-3–Me)(+) (466 mg, 85%). In the same way, *M*-poly(2-*co*-3–Me)(–) was prepared in 72% yield. The *P*-poly(2-*co*-3–Me)(+) and *M*-poly(2-*co*-3–Me)(–) were found to contain 7.4 mol% and 6.8 mol% of **3**–**Me** residues, respectively, as the pendant group to each monomer unit estimated by their ^{1}H NMR spectra. These values were in agreement with those estimated by elemental analyses. The obtained polymers (*P*-poly(2-*co*-3–Me)(+) and *M*-poly(2-*co*-3–Me)(–)) were then annealed in chloroform (1.0 mg mL^{-1}) under reflux for 10 days (Fig. S1a). A fully substituted *P*-poly-**2**(+) was also prepared to investigate its liquid crystallinity (see Fig. S3A).

Spectroscopic data of *P*-poly(2-*co*-3–Me)(+): IR (KBr, cm^{-1}): 3285 (ν_{N-H}), 1643 (amide I), 1523 (amide II). ^{1}H NMR (CDCl$_3$, 30 °C, 500 MHz): δ 0.86 (br, CH$_3$, 2.78H), 1.26 (br, CH$_2$, 17.7H), 1.54 (br, CH$_2$, 2.15H), 2.28 (br, CH$_2$, 0.15H), 2.54 (br, CH$_2$, 1.85H), 3.64 (s, CH$_3$, 0.22H), 3.30–4.20 (br, CH$_2$, 0.15H), 4.60–8.60 (br, aromatic and NH, 8.07H), 9.40–10.80 (br,

NH, 1H). $[\alpha]_D^{20}$ 1547 (c 0.1, chloroform). Anal. Calcd (%) for $(C_{26}H_{34}N_2O)_{92.6}(C_{28}H_{35}N_3O_4)_{7.4}$: C, 79.11; H, 8.65; N, 7.32. Found: C, 78.94; H, 8.69; N, 7.35.

Spectroscopic data of M-poly(**2**-co-**3**–**Me**)(–): IR (KBr, cm^{-1}): 3292 (ν_{N-H}), 1643 (amide I), 1523 (amide II). ^{1}H NMR (CDCl$_3$, 30 °C, 500 MHz): δ 0.86 (br, CH$_3$, 2.80H), 1.26 (br, CH$_2$, 17.7H), 1.53 (br, CH$_2$, 2.14H), 2.28 (br, CH$_2$, 0.14H), 2.55 (br, CH$_2$, 1.86H), 3.64 (s, CH$_3$, 0.20H), 3.30–4.10 (br, CH$_2$, 0.14H), 4.60–8.60 (br, aromatic and NH, 8.07H), 9.40–10.80 (br, NH, 1H). $[\alpha]_D^{20}$ –1513 (c 0.1, chloroform). Anal. Calcd (%) for $(C_{26}H_{34}N_2O)_{93.2}(C_{28}H_{35}N_3O_4)_{6.8}$: C, 79.17; H, 8.66; N, 7.31. Found: C, 78.95; H, 8.51; N, 7.35.
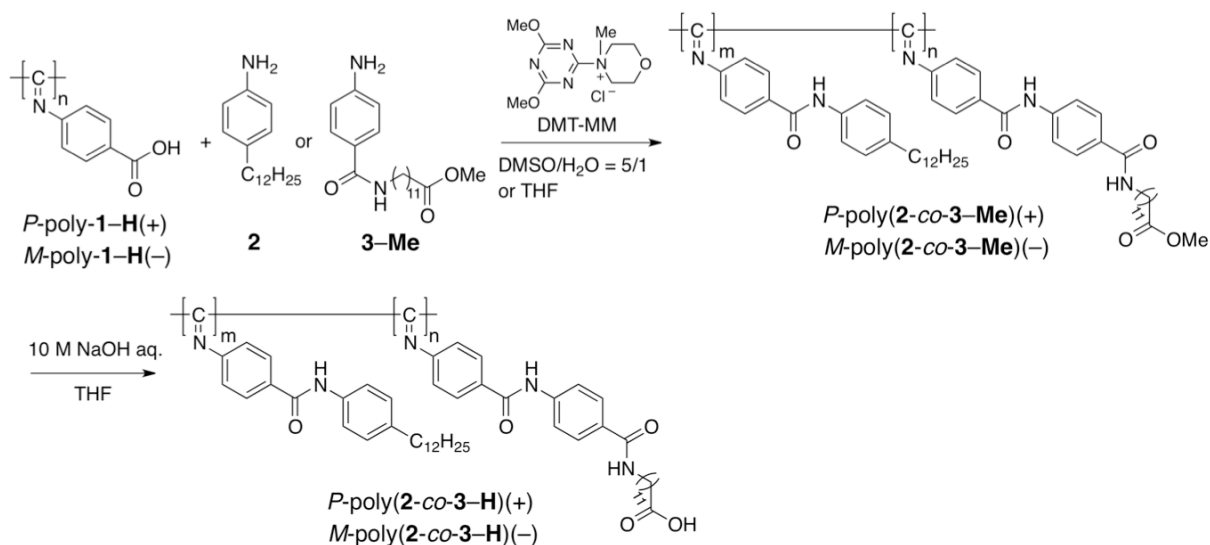
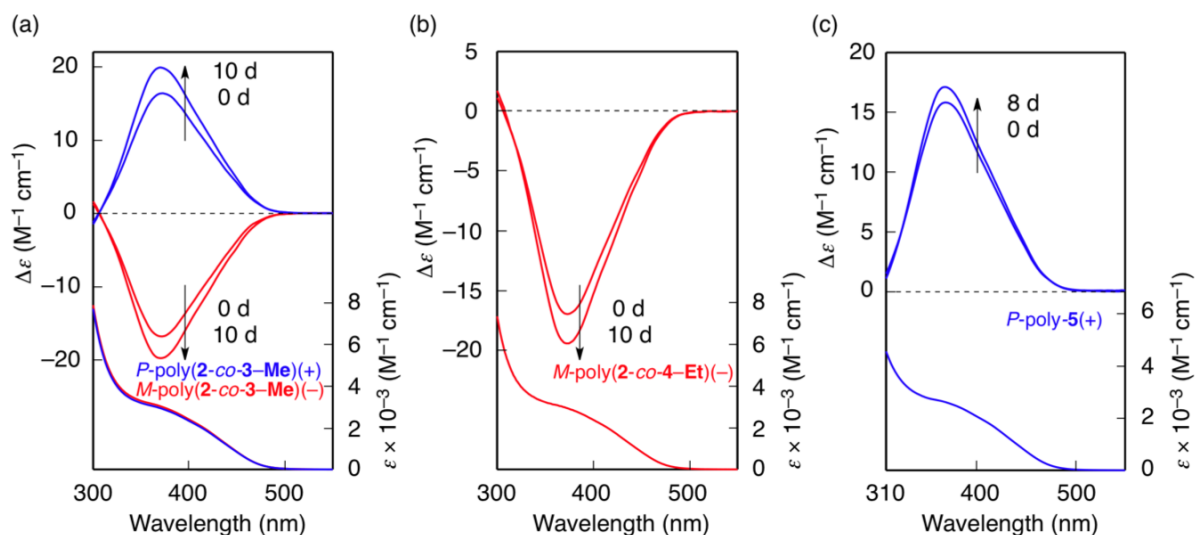**Scheme S2** Preparation of P-poly(**2**-co-**3**–**H**)(+) and M-poly(**2**-co-**3**–**H**)(–).

Fig. S1 CD and absorption spectra of *P*-poly(**2**-*co*-**3**–**Me**)(+), *M*-poly(**2**-*co*-**3**–**Me**)(–) (a), *M*-poly(**2**-*co*-**4**–**Et**)(–) (b) and *P*-poly-**5**(+) (c) before and after annealing in chloroform under reflux for 10 days (a and b) and 8 days (c), measured at 25 °C in chloroform (1.0 mg mL^{-1}).

Preparation of *P*-poly(2-*co*-3–H)(+) and *M*-poly(2-*co*-3–H)(–). *P*-poly(**2**-*co*-**3**–**Me**)(+) (300 mg, 0.763 mmol) was dissolved in THF (30 mL) containing aqueous NaOH (10 M, 6 mL), and the mixture was stirred at 55 °C. After 2 days, the resulting polymer was precipitated into a large amount of methanol (500 mL), collected by centrifugation, washed with aqueous HCl (2 M, 70 mL) and methanol (70 mL × 3), and dried in vacuo, yielding *P*-poly(**2**-*co*-**3**–**H**)(+) (260 mg, 86%). In the same way, *M*-poly(**2**-*co*-**3**–**H**)(–) was prepared in 84% yield.

Spectroscopic data of *P*-poly(**2**-*co*-**3**–**H**)(+): IR (KBr, cm^{-1}): 3283 (v_{N-H}), 1642 (amide I), 1517 (amide II). ^{1}H NMR (CDCl$_3$, 30 °C, 500 MHz): δ 0.86 (br, CH$_3$, 2.78H), 1.26 (br, CH$_2$, 17.7H), 1.54 (br, CH$_2$, 2.15H), 2.28 (br, CH$_2$, 0.15H), 2.54 (br, CH$_2$, 1.85H), 3.30–4.20 (br, CH$_2$, 0.15H), 4.60–8.60 (br, aromatic and NH, 8.07H), 9.40–10.80 (br, NH, 1H). [α]$_D^{20}$ 1605 (*c* 0.1, chloroform). Anal. Calcd (%) for (C$_{26}$H$_{34}$N$_2$O)$_{92.6}$(C$_{27}$H$_{33}$N$_3$O$_4$)$_{7.4}$: C, 79.09; H, 8.64; N, 7.34. Found: C, 79.10; H, 8.61; N, 7.12.

Spectroscopic data of *M*-poly(**2**-*co*-**3**–**H**)(–): IR (KBr, cm^{-1}): 3284 (v_{N-H}), 1641 (amide I), 1517 (amide II). ^{1}H NMR (CDCl$_3$, 30 °C, 500 MHz): δ 0.86 (br, CH$_3$, 2.80H), 1.26 (br, CH$_2$, 17.7H), 1.53 (br, CH$_2$, 2.14H), 2.28 (br, CH$_2$, 0.14H), 2.55 (br, CH$_2$, 1.86H), 3.30–4.10 (br, CH$_2$, 0.14H), 4.60–8.60 (br, aromatic and NH, 8.07H), 9.40–10.80 (br, NH, 1H). [α]$_D^{20}$ –1604 (*c* 0.1, chloroform). Anal. Calcd (%) for (C$_{26}$H$_{34}$N$_2$O)$_{93.2}$(C$_{27}$H$_{33}$N$_3$O$_4$)$_{6.8}$: C, 79.16; H, 8.65; N, 7.32. Found: C, 79.01; H, 8.80; N, 7.33.

Preparation of *M*-poly(2-*co*-4–Me)(–). The compound was prepared according to Scheme S3. DMT-MM (754 mg, 2.72 mmol) was added to a solution of *M*-poly-**1**–**H**(–) (200 mg, 1.36 mmol) and **2** (338 mg, 1.29 mmol) in DMSO (20 mL) and degassed water (4 mL), and the mixture was stirred at room temperature. After 18 h, the resulting polymer was precipitated into a large amount of methanol (500 mL), collected by centrifugation, washed with methanol (70 mL × 3), and dried in vacuo at room temperature. The recovered polymer was allowed to react with **4**–**Et** (10.6 mg, 0.0642 mmol) in the presence of DMT-MM (354 mg, 1.28 mmol) in THF (20 mL). After stirring at room temperature for 18 h, the resulting polymer was precipitated into a large amount of methanol (400 mL), collected by centrifugation, washed with methanol (70 mL × 3), and then dried in vacuo at room temperature overnight. The obtained polymer contained a small amount of the unreacted carboxy pendant groups, and therefore, the reaction was repeated using the recovered polymer with **2** (669 mg, 2.56 mmol) in the presence of DMT-MM (708 mg, 2.56 mmol) in THF (20 mL), yielding *M*-poly(**2**-*co*-**4**–**Et**)(–) (452 mg, 86%). The obtained polymer (*M*-poly(**2**-*co*-**4**–**Et**)(–)) was then annealed in chloroform (1.0 mg mL^{-1}) under reflux for 10 days (Fig. S1b).

M-poly(**2**-*co*-**4**–**Et**)(–) (341 mg, 0.884 mmol) was dissolved in THF (12 mL) containing aqueous NaOH (10 M, 85 μL) and the mixture was stirred at room temperature. After 2 days, the resulting polymer was precipitated into a large amount of methanol (240 mL), collected by centrifugation, washed with aqueous HCl (2 M, 70 mL) and methanol (70 mL × 3), and dried in vacuo, affording *M*-poly(**2**-*co*-**4**–**H**)(–) (317 mg, 93%). The resulting *M*-poly(**2**-*co*-**4**–**H**)(–) (280 mg, 0.729 mmol) was then treated with diazomethane in diethyl ether to convert the carboxy groups into the methyl esters, yielding *M*-poly(**2**-*co*-**4**–**Me**)(–) (274 mg, 97%). The ^{1}H NMR spectrum of *M*-poly(**2**-*co*-**4**–**Me**)(–) was almost identical to that of *M*-poly-**2**(–), because the content of the **4**–**Me** residues of *M*-poly(**2**-*co*-**4**–**Me**)(–) was too small to determine by ^{1}H NMR, and therefore, it was assumed to be equal to the amount of **4**–**Et** in the feed (5 mol%). The CD and absorption spectra of *M*-poly(**2**-*co*-**4**–**Me**)(–) measured in chloroform are shown in Fig. S2.

Spectroscopic data of *M*-poly(**2**-*co*-**4**–**Me**)(–): IR (KBr, cm^{-1}): 3284 (v_{N-H}), 1640 (amide I), 1523 (amide II). ^{1}H NMR (CDCl$_3$, 30 °C, 500 MHz): δ 0.86 (br, CH$_3$, 3H), 1.25 (br, CH$_2$, 18H), 1.52 (br, CH$_2$, 2H), 2.54 (br, CH$_2$, 2H), 4.60–8.40 (br, aromatic, 8H), 9.40–11.00 (br, NH, 1H). $[\alpha]_D^{20}$ –1525 (*c* 0.1, chloroform). Anal. Calcd (%) for (C$_{26}$H$_{34}$N$_2$O)$_{95}$(C$_{16}$H$_{12}$N$_2$O$_3$)$_5$: C, 79.54; H, 8.61; N, 7.28. Found: C, 79.57; H, 8.50; N, 7.07.
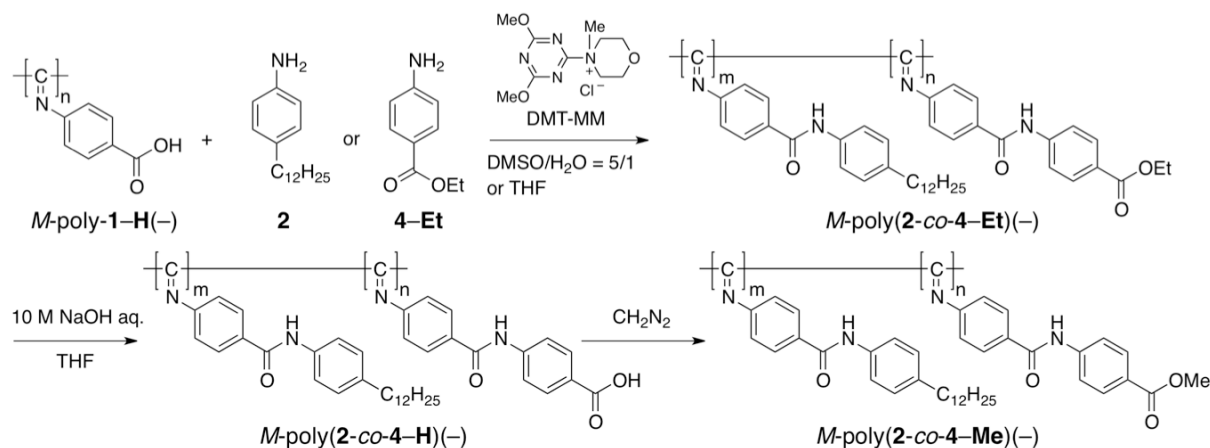
Scheme S3 Preparation of *M*-poly(**2**-*co*-**4**–**Me**)(–).
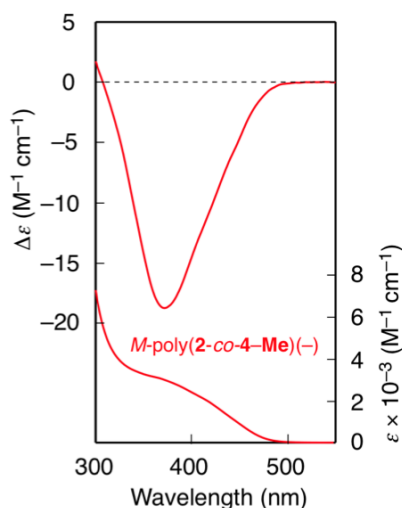
Fig. S2 CD and absorption spectra of *M*-poly(**2**-*co*-**4**–**Me**)(–) in chloroform (1.0 mg mL^{-1}) at 25 °C.

Preparation of *P*-poly-5(+). This polymer was prepared according to Scheme S4. DMT-MM (823 mg, 2.97 mmol) was added to a solution of *P*-poly-**1**–**H**(+) (221 mg, 1.50 mmol) and **5** (286 mg, 3.07 mmol) in DMSO (23 mL) and degassed water (4.6 mL), and the reaction mixture was stirred at room temperature. After 16 h, the resulting polymer was precipitated into a large amount of methanol (500 mL), collected by centrifugation, washed with methanol (70 mL × 3), and dried in vacuo at room temperature overnight. The reaction of the recovered polymer was repeated with **5** (286 mg, 3.07 mmol) in the presence of DMT-MM (824 mg, 2.98 mmol) in DMF (25 mL) for 16 h, yielding *P*-poly-**5**(+) (289 mg, 87%). The obtained polymer (*P*-poly-**5** (+)) was then annealed in chloroform (1.0 mg mL^{-1}) under reflux for 8 days (Fig. S1c).

Spectroscopic data of P-poly-**5**(+): IR (KBr, cm^{-1}): 3291 (ν_{N-H}), 1647 (amide I), 1528 (amide II). ^{1}H NMR (CDCl$_3$, 30 °C, 500 MHz): δ 4.60–9.00 (br, aromatic, 8H), 9.40–10.80 (br, NH, 1H). [α]$_D^{20}$ 2574 (c 0.1, chloroform). Anal. Calcd (%) for (C$_{14}$H$_{10}$N$_2$O)$_n$: C, 75.66; H, 4.54; N, 12.60. Found: C, 75.46; H, 4.67; N, 12.67.
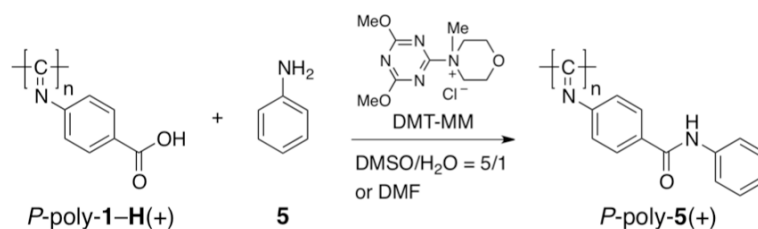
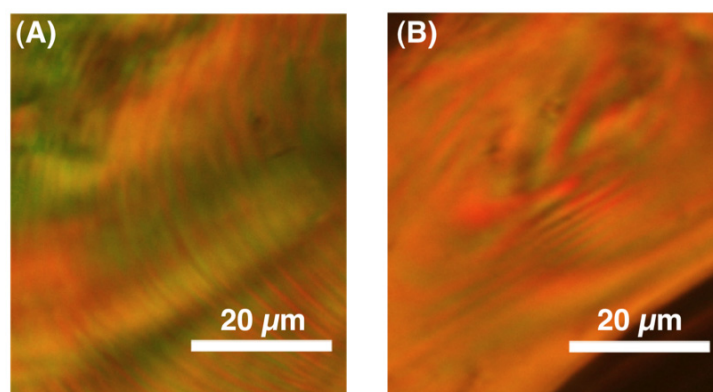

Scheme S4 Preparation of P-poly-**5**(+).

Fig. S3 Polarized optical micrographs of cholesteric LC phases of P-poly-**2**(+) (A) and P-poly-**5**(+) (B) in chloroform.

4. Immobilization of P-Poly(**2**-*co*-**3**–H)(+) and M-Poly(**2**-*co*-**3**–H)(–) on Silica Gel (Fig. 2)

A-Silica (840 mg) was dispersed in a solution of P-poly(**2**-*co*-**3**–H)(+) (210 mg, 0.532 mmol) in THF (12 mL). After evaporating the solvent, the residue was dispersed in pyridine (6.0 mL), and DMT-MM (80.0 mg, 0.289 mmol) was added to the suspended solution. After stirring at room temperature for 19 h, the resulting silica gel was collected by filtration, washed with THF (300 mL) and methanol (300 mL), and dried in vacuo at room temperature overnight. The silica gel was then treated with diazomethane in diethyl ether to convert the remaining carboxy groups of P-poly(**2**-*co*-**3**–H)(+) into the methyl esters at room temperature. The P-poly(**2**-*co*-**3**–H)(+)-bound silica gel (P-poly(**2**-*co*-**3**–Si)(+)) thus obtained was collected by filtration, washed with THF (300 mL) and methanol (300 mL), and dried in vacuo at room temperature overnight (1.00 g). The content of P-poly(**2**-*co*-**3**–H)(+) chemically bonded to silica gel was estimated by TG analysis and was 9.6 wt%. In the same way, M-poly(**2**-*co*-**3**–

H)(–) was chemically bonded to silica gel (*M*-poly(**2**-*co*-**3**–**Si**)(–)), and its content was estimated to be 10.6 wt%.

5. Preparation of Chiral Columns

Preparation of Coated-Type Column Packing Materials. A typical experimental procedure is described below. *M*-poly(**2**-*co*-**4**–**Me**)(–) dissolved in THF was coated on the A-silica according to the previously reported method,[S5] and the solvent was evaporated under reduced pressure. The weight ratio of *M*-poly(**2**-*co*-**4**–**Me**)(–) to silica gel was ca. 20 : 80.

Preparation of Chiral Columns. Each column packing material was packed into a stainless-steel tube (25 cm × 0.20 cm (i.d.)) by conventional high-pressure slurry packing technique using a Chemco Slurry-Packing Apparatus Model 124A (Chemco, Osaka, Japan).[S6] The plate numbers of the columns were 1200–2200 for benzene with hexane–2-propanol (90 : 10) as the eluent at a flow rate of 0.1 mL min^{-1}. The dead time (t_0) was estimated using 1,3,5-tri-*tert*-butylbenzene as the nonretained compound.[S7]

6. Supporting References

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S6   Y. Okamoto, M. Kawashima and K. Hatada, *J. Chromatogr., A*, 1986, **363**, 173–186.

S7   H. Koller, K.-H. Rimböck and A. Mannschreck, *J. Chromatogr., A*, 1983, **282**, 89–94.