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## Supporting Information

### **Polystyrene-*block*-Polyisocyanide Copolymer: From Polymerization- induced Chiral Self-assembly to Circularly Polarized Light Emission and Enantiomer Separation**

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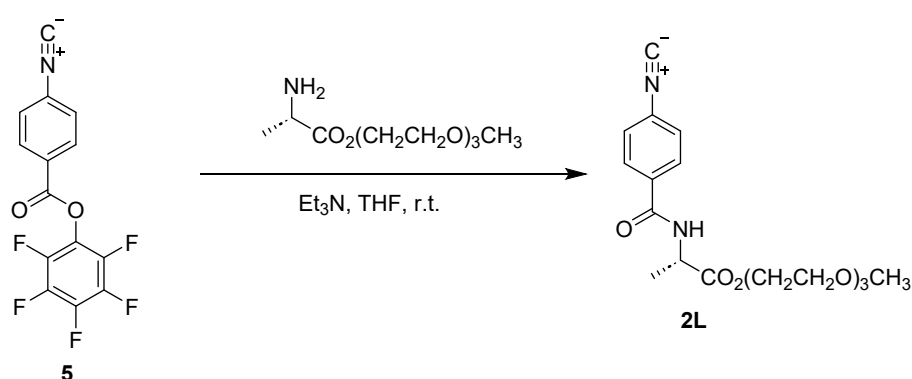
## General considerations

$^1\text{H}$  Nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz and  $^{13}\text{C}$  NMR spectra at 125 MHz on Bruker spectrometers. Chemical shifts are expressed in delta ( $\delta$ ) in parts per million (ppm) from tetramethylsilane (TMS) downwards using residual proton solvent as an internal standard. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40°C). A series of three linear Styragel HR0.5, Styragel HR3 and Styragel HR4 were used. The number average molar mass ( $M_n$ ) and its dispersity ( $D$ ) values were reported with reference to the polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. Fourier transform infrared (FT-IR) spectra were recorded at 25°C on a FT-IR instrument (VERTEX 80V) using KBr pressure plates. Absorption spectra were recorded on UNIC 4802 UV/vis double beam spectrophotometer in a 1.0 mm quartz cell at 25°C. Circular dichroism (CD) spectra were obtained in a 1.0 cm or 1.0 mm quartz cell using a JASCO J1500 spectropolarimeter. Emission spectra were recorded on Hitachi F-4600 fluorescence spectrophotometer. The circularly polarized luminescence (CPL) spectra using a JASCO CPL-300 spectrometer at room temperature. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). Relevant images were taken using a transmission electron microscope 2100 (TEM). Dynamic light scattering (DLS) was recorded using a Nano-ZS 90 Zetasizer of Malvern (UK) instrument. Thermogravimetric analysis (TGA) tests were carried out using a TGA 550 (Waters Corporation) in a nitrogen atmosphere, with a heating rate of 10°C/min, at temperatures ranging from 25°C to 800°C. The TGA tests were carried out using the TGA 550. Differential Scanning Calorimetry (DSC) measurements were performed on a Differential Scanning Calorimeter (Q20). Atomic force microscopy (AFM) measurements were performed using a BRUKER ICON-XR microscope (Oxford Instruments) under ambient conditions. The samples were imaged in tapping mode using rectangular silicon cantilevers with a spring constant of 26 N m<sup>-1</sup>, a resonance frequency ranging from 62 to 120 kHz, and a tip curvature radius of less than 10 nm, yielding both topographic and phase images of the nanostructured assemblies. TEM observations were conducted on a JEM-2100F microscope operating at an accelerating voltage of 200 kV. All solvents are from Sinopharm. Co. Ltd. and

were purified according to standard procedures before use. High-performance liquid chromatography (HPLC) was performed on a WU FENG liquid chromatograph using chiral columns (OZ-H, AS-H, and OD-H). The mobile phase was a mixture of chromatographically pure n-hexane and isopropanol. All chemicals were purchased from Energy Chemical and Titan Technology Exploration Platform Chemicals Ltd. and were used as received without further purification. No further purification is required unless otherwise stated. Toluene for polymerizations were further dried over sodium benzophenone ketyl, distilled onto lithium aluminum hydride under nitrogen, and distilled under high vacuum just before use. Styrene purification can be achieved through vacuum distillation at 70°C, which effectively separates the compound from its polymerization inhibitor. Pentafluorophenol isocyanide compound were prepared in the same way as reported in the literature.<sup>1</sup> Phenyl isocyanide compounds **2L** and **2D** were prepared according to literatures reported by our group previously.<sup>2</sup> Phenyl isocyanide compounds **3** were prepared according to literatures reported by our group previously.<sup>3</sup> Phenyl isocyanide compounds **4L** and **4D** were prepared according to literatures reported by our group previously.<sup>4</sup>

## Synthetic procedure

### Scheme S1. Synthesis of compound **2**.



*Synthesis of compound **2L***: The compound **2L** was first prepared according to Scheme S1. Compound **2L** were prepared from the reaction of **5L** with pentafluorophenol isocyanide. A round bottom flask was charged with pentafluorophenol isocyanide (2.50 g, 6.40 mmol), compound **5L** (1.50 g, 6.40 mmol),  $\text{Et}_3\text{N}$  (0.43 mL, 3.12 mmol) and anhydrous THF (60 mL).

After the resulting mixture was stirred at room temperature for 1 h, the solvent was removed by evaporation under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed successively with H<sub>2</sub>O (20 mL), saturated aqueous NaHCO<sub>3</sub> (20 mL), brine (20 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, the solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography using petroleum ether/ethyl acetate (v/v = 1/1) as eluent to afford compound **2L** as a light-yellow oil (1.78 g, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ 7.86(d, *J* = 8.0 Hz, 2H, ArH), 7.45 (d, *J* = 8.0 Hz, 2H, ArH), 6.94–6.92 (m, 1H, NHCO), 4.85–4.78 (m, 1H, CH<sub>3</sub>CH), 4.32–4.32 (m, 2H, OCH<sub>2</sub>), 3.70–3.52 (m, 10H, OCH<sub>2</sub>), 3.31 (s, 3H, OCH<sub>3</sub>), 1.50 (d, *J* = 8.0 Hz, 3H, CH<sub>3</sub>).

*Synthesis of compound 2D*: Compound **2D** was prepared under the same synthetic procedure to that of **2L**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25°C): δ 7.85 (d, *J* = 8.0 Hz, 2H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.05–7.03 (m, 1H, NHCO), 4.81–4.77 (m, 1H, CH<sub>3</sub>CH), 4.36–4.32 (m, 2H, OCH<sub>2</sub>), 3.73–3.53 (m, 10H, OCH<sub>2</sub>), 3.35 (s, 3H, OCH<sub>3</sub>), 1.51 (d, *J* = 8.0 Hz, 3H, CH<sub>3</sub>).

*Synthesis of poly-1<sub>m</sub>*: Taking poly-**1<sub>m</sub>** as an example, alkyne-Pd (II) catalyst (4.8 mg, 0.0096 mmol) were dissolved in treated styrene (200.0 mg, 1.92 mmol) under an N<sub>2</sub> atmosphere. The reaction solution was stirred at 105°C for 12 h. The polymerized solution was concentrated and precipitated into a large volume of cooled methanol. After centrifugal drying, a white flocculent solid was obtained (138 mg, 69%). SEC: *M<sub>n</sub>* = 31.2 kg/mol, *D* = 1.24. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.24–6.29 (br, ArH), 1.98–1.70 (br, CH of poly-**1<sub>m</sub>** main chain), 1.64–1.24 (br, CH<sub>2</sub> of poly-**1<sub>m</sub>** main chain). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 3030 (ν<sub>C-H</sub>), 2927 (ν<sub>C-H</sub>).

*Synthesis of poly(1<sub>200</sub>-b-2L<sub>100</sub>)*: Taking poly(**1<sub>200</sub>-b-2L<sub>100</sub>**) as an example, poly-**1<sub>m</sub>** (50.0 mg, *M<sub>n</sub>* = 31.2 kg/mol, *D* = 1.24) and compound **2L** (58 mg, 0.16 mmol) were dissolved in retorted toluene under an N<sub>2</sub> atmosphere. The reaction solution was stirred at 105°C for 12 h. The polymerized solution was concentrated and precipitated into a large volume of cooled *n*-hexane. After centrifugal drying, a yellow solid was obtained (91 mg, 81%). SEC: *M<sub>n</sub>* = 72.9 kg/mol, *D* = 1.26. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.12–6.30 (br, ArH), 4.55–3.94 (br, CH), 3.65–3.22 (br, CH<sub>3</sub> and OCH<sub>2</sub>), 1.89–1.35 (br, CH<sub>3</sub> and poly-**1<sub>m</sub>** main chain). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 2910 (ν<sub>C-H</sub>), 2875 (ν<sub>C-H</sub>), 1741 (ν<sub>C=O</sub>), 1602 (ν<sub>C=N</sub>).

*Synthesis of poly(1<sub>200</sub>-b-2D<sub>100</sub>)*: Polymer poly(**1<sub>200</sub>-b-2D<sub>100</sub>**) was prepared under the same synthetic procedure to that of poly(**1<sub>200</sub>-b-2L<sub>100</sub>**). SEC: *M<sub>n</sub>* = 74.2 kg/mol, *D* = 1.19. <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>):  $\delta$  7.21–6.20 (br, ArH), 4.22–3.86 (br, CH), 3.74–3.04 (br, CH<sub>3</sub> and OCH<sub>2</sub>), 2.23–0.60 (br, CH<sub>3</sub> and poly-**1**<sub>m</sub> main chain). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 2924 ( $\nu_{\text{C-H}}$ ), 2882 ( $\nu_{\text{C-H}}$ ), 1743 ( $\nu_{\text{C=O}}$ ), 1600 ( $\nu_{\text{C=N}}$ ).

*Synthesis of poly(**1**<sub>m</sub>-b-**3**<sub>n</sub>):* Polymer poly(**1**<sub>200</sub>-b-**3**<sub>100</sub>) was prepared under the same synthetic procedure to that of poly(**1**<sub>200</sub>-b-**2**<sub>L</sub><sub>100</sub>). SEC:  $M_n = 76.8$  kg/mol,  $D = 1.20$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.20–6.20 (br, ArH), 4.49–3.88 (br, CH), 3.77–3.13 (br, CH<sub>3</sub> and OCH<sub>2</sub>), 2.30–1.04 (br, CH<sub>3</sub> and poly-**1**<sub>m</sub> main chain). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 2923 ( $\nu_{\text{C-H}}$ ), 2851 ( $\nu_{\text{C-H}}$ ), 1746 ( $\nu_{\text{C=O}}$ ), 1600 ( $\nu_{\text{C=N}}$ ).

*Synthesis of poly(**1**<sub>m</sub>-b-**4**<sub>L</sub><sub>n</sub>):* Polymer poly(**1**<sub>200</sub>-b-**4**<sub>L</sub><sub>100</sub>) was prepared under the same synthetic procedure to that of poly(**1**<sub>200</sub>-b-**2**<sub>L</sub><sub>100</sub>). SEC:  $M_n = 71.5$  kg/mol,  $D = 1.21$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.22–6.30 (br, ArH), 4.90–4.25 (br, CH), 3.53–3.25 (br, CH<sub>2</sub>), 2.31–0.40 (br, CH<sub>2</sub>, CH<sub>3</sub> and poly-**1**<sub>m</sub> main chain). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 2922 ( $\nu_{\text{C-H}}$ ), 2850 ( $\nu_{\text{C-H}}$ ), 1750 ( $\nu_{\text{C=O}}$ ), 1600 ( $\nu_{\text{C=N}}$ ).

*Synthesis of poly(**1**<sub>m</sub>-b-**4**<sub>D</sub><sub>n</sub>):* Polymer poly(**1**<sub>200</sub>-b-**4**<sub>D</sub><sub>100</sub>) was prepared under the same synthetic procedure to that of poly(**1**<sub>200</sub>-b-**2**<sub>L</sub><sub>100</sub>). SEC:  $M_n = 72.2$  kg/mol,  $D = 1.18$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.19–6.22 (br, 9H, ArH), 4.88–4.37 (br, 1H, CH), 4.37–3.67 (br, 2H, CH<sub>2</sub>), 2.30–0.67 (br, 22H, CH<sub>2</sub>, CH<sub>3</sub> and poly-**1**<sub>m</sub> main chain). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 2926 ( $\nu_{\text{C-H}}$ ), 2855 ( $\nu_{\text{C-H}}$ ), 1746 ( $\nu_{\text{C=O}}$ ), 1601 ( $\nu_{\text{C=N}}$ ).

*Synthesis of poly-**2**<sub>L</sub><sub>n</sub>:* Taking poly-**2**<sub>L</sub><sub>100</sub> as an example, compound **2**<sub>L</sub> (100.0 mg, 0.36 mmol), alkyne-Pd(II) catalyst (1.8 mg, 0.0036 mmol) were dissolved in anhydrous THF under an N<sub>2</sub> atmosphere. The reaction solution was stirred at 55°C for 12 h. The polymerized solution was concentrated and precipitated into a large volume of cooled n-hexane. After centrifugal drying, a yellow flocculent solid was obtained (87.1 mg, 85%). SEC:  $M_n = 41.7$  kg/mol,  $D = 1.17$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.12–6.30 (br, ArH), 4.55–3.94 (br, CH), 3.65–3.22 (br, CH<sub>3</sub> and OCH<sub>2</sub>), 1.89–1.35 (br, CH<sub>3</sub>). FT-IR (KBr, 25°C, cm<sup>-1</sup>): 2910 ( $\nu_{\text{C-H}}$ ), 2875 ( $\nu_{\text{C-H}}$ ), 1741 ( $\nu_{\text{C=O}}$ ), 1602 ( $\nu_{\text{C=N}}$ ).

*Synthesis of poly(**1**<sub>m</sub>-b-**2**<sub>L</sub><sub>n</sub>) membranes:* 100 mg poly(**1**<sub>m</sub>-b-**2**<sub>L</sub><sub>n</sub>) was dissolved in 2 mL chloroform. Pour the solution into a 20×20×2 mm polytetrafluoroethylene mold and let it sit

overnight to allow the solvent to evaporate. After evaporation, soak the film in n-hexane for 12 hours. The film is then ready for use.

*Recycling experiment of poly(**1**<sub>m</sub>-b-**2L**<sub>n</sub>) membranes:* First, n-hexane is chosen as the washing solvent because it readily dissolves the analytes but does not dissolve the polymer membrane. The used membrane is placed in a clean container, and sufficient hexane is added to rinse its surface repeatedly. This process is repeated until the analytes are completely eluted. To verify the cleaning efficiency, a small piece of the rinsed membrane is cut off and dissolved in a good solvent (CH<sub>2</sub>Cl<sub>2</sub>) that can fully dissolve the membrane. The resulting solution is then analyzed by <sup>1</sup>H NMR spectrum. If no characteristic signals of the analytes are observed in the spectrum, the analytes have been completely removed, and the membrane can be reused. Following this procedure, the membrane can be effectively recovered and reused.

*Kinetic study for the block copolymerization:* Poly-**1**<sub>m</sub> (50.0 mg), compound **2L** (63.0 mg, 0.23 mmol) and internal standard polystyrene (PSt, *M*<sub>n</sub> = 4.2 kg/mol, *D* = 1.02, 5.0 mg) were dissolved in retorted toluene under an N<sub>2</sub> atmosphere. The solution was continuously stirred at 105°C under a nitrogen atmosphere, and aliquots were periodically sampled at fixed time intervals for size exclusion chromatography (SEC) analysis. The conversion rate of compound **2L** was determined by correlating the molecular weight of the resulting polymer with the linear calibration curve.

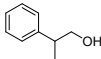

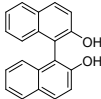
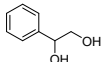
*Emission and CPL analyses.* Put the THF solution of PS-*b*-PPI (*c* = 0.2 mg/mL) into a fluorescent cuvette (optical path length = 1.0 cm) with a volume of about 3 mL at 25°C, and the cuvette was installed into Hitachi F-4600 fluorescence spectrophotometer or JASCO CPL-300 spectrometer. The fluorescence and CPL spectrum of the solution was monitored at 25°C in the range of emission wavelength between 400 and 750 nm, excited by UV light at 364 nm. A drop-coated films prepared on a quartz substrate (Daico MFG, USQ-grade) from a THF solution of the polymers (ca. 40 mg/mL) was used for solid-state spectral measurements. A scanning rate of 100 nm/min, an excitation slit width of 3000 μm, a monitoring slit width of 3000 μm.

**Table S1.** Tensile test results of PS-*b*-PPI copolymer membranes<sup>[a]</sup>

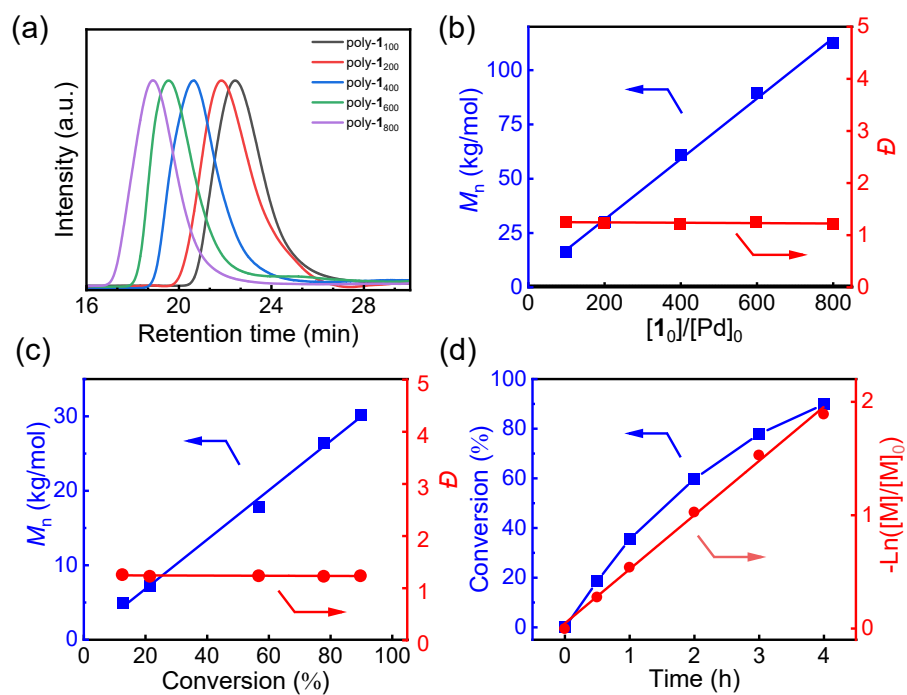
Run	Polymer	Stress (MPa)	Strain (%)
1	poly- <b>1</b> <sub>200</sub>	5.5 ± 0.4	1.2 ± 0.1
2	poly( <b>1</b> <sub>200</sub> - <i>b</i> - <b>2L</b> <sub>20</sub> )	7.7 ± 0.5	1.1 ± 0.1
3	poly( <b>1</b> <sub>200</sub> - <i>b</i> - <b>2L</b> <sub>40</sub> )	9.3 ± 0.6	1.0 ± 0.1
4	poly( <b>1</b> <sub>200</sub> - <i>b</i> - <b>2L</b> <sub>60</sub> )	11.7 ± 0.7	1.1 ± 0.1
5	poly( <b>1</b> <sub>200</sub> - <i>b</i> - <b>2L</b> <sub>80</sub> )	12.0 ± 0.8	0.9 ± 0.1
6	poly( <b>1</b> <sub>200</sub> - <i>b</i> - <b>2L</b> <sub>100</sub> )	13.7 ± 1.0	0.6 ± 0.04
7	poly( <b>1</b> <sub>200</sub> - <i>b</i> - <b>2L</b> <sub>120</sub> )	16.2 ± 1.1	0.6 ± 0.1
8	poly( <b>1</b> <sub>100</sub> - <i>b</i> - <b>2L</b> <sub>100</sub> )	17.2 ± 1.2	0.5 ± 0.04
9	poly( <b>1</b> <sub>400</sub> - <i>b</i> - <b>2L</b> <sub>100</sub> )	11.8 ± 0.9	0.9 ± 0.1
10	poly( <b>1</b> <sub>600</sub> - <i>b</i> - <b>2L</b> <sub>100</sub> )	9.8 ± 0.7	1.4 ± 0.1
11	poly( <b>1</b> <sub>800</sub> - <i>b</i> - <b>2L</b> <sub>100</sub> )	10.0 ± 0.8	1.8 ± 0.2

<sup>[a]</sup>All tensile tests were repeated three times, and the results are presented as mean ± standard deviation (SD).

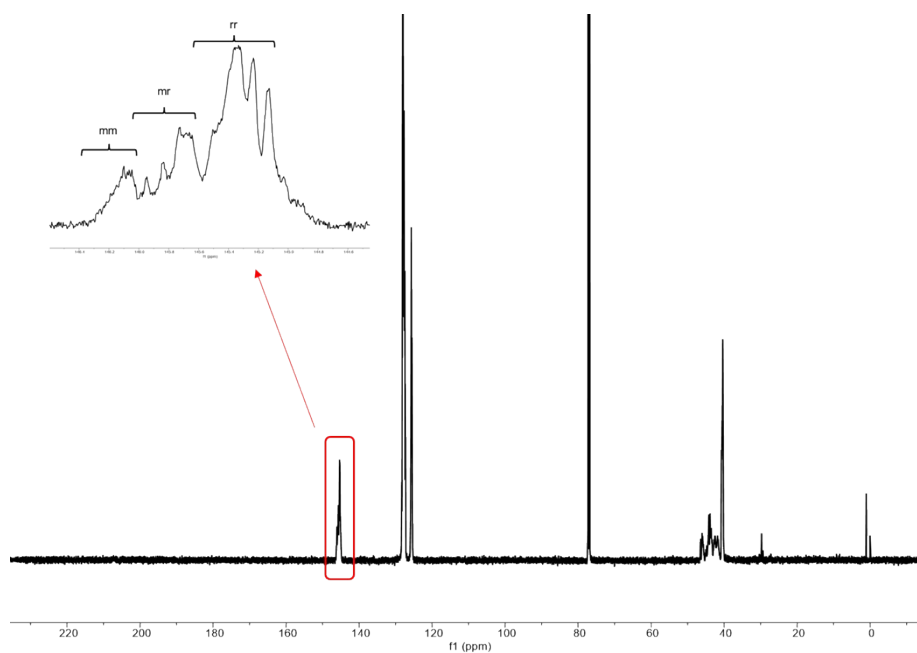
**Table S2.** Chiral Resolution using Membranes of PS-*b*-PPI<sup>[a]</sup>

Racemates	Structure	Time	<i>ee</i> <sup>[b]</sup>
<b>4a</b> <sup>[c]</sup>		20 min	96% ± 2%
<b>4b</b> <sup>[c]</sup>		10 min	69% ± 2%
<b>4c</b> <sup>[d]</sup>		20 min	42% ± 3%
<b>4d</b> <sup>[e]</sup>		12 min	29% ± 2%

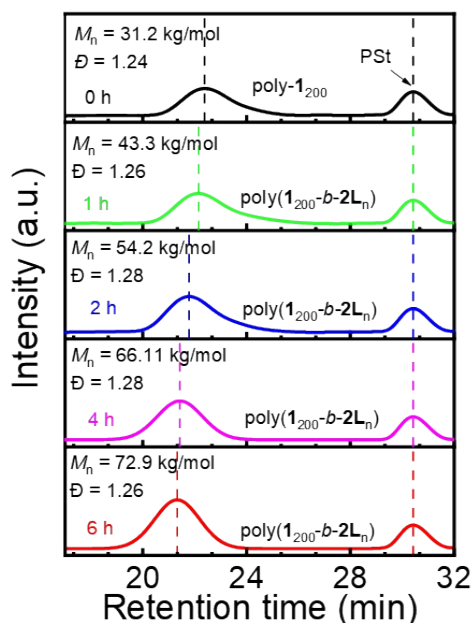
<sup>[a]</sup>The polymers were synthesized according to Scheme 1 in the main text. <sup>[b]</sup>Determined by HPLC analysis of the filtration solution. <sup>[c]</sup>Daicel Chiralpak OZ-H, *n*-hexane/*i*PrOH = 95/5, 1.0 mL/min, 254 nm, T = 25 °C. <sup>[d]</sup>Daicel Chiralpak AS-H, *n*-hexane/*i*PrOH = 95/5, 1.0 mL/min, 254 nm, T = 25 °C. <sup>[e]</sup>Daicel Chiralpak OD-H, *n*-hexane/*i*PrOH = 90/10, 1.0 mL/min, 254 nm, T = 25 °C.



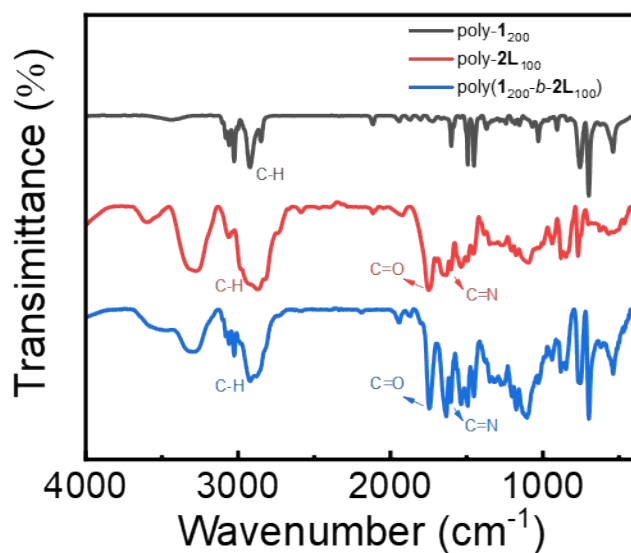
**Fig. S1.** (a) SEC curves for the polymerization of **1** initiated by the alkyne-Pd(II) catalyst at different **1**-to-Pd(II) ratios. (b) Plots of  $M_n$  and  $\bar{D}$  of poly-**1**<sub>*m*</sub> vs. the **1**-to-Pd(II) ratios. (c) Plots of  $M_n$  and  $\bar{D}$  of poly-**1**<sub>*m*</sub> vs. the conversion of **1**. (d) Plots of conversion and  $-\ln([M]/[M]_0)$  values vs. the polymerization time.



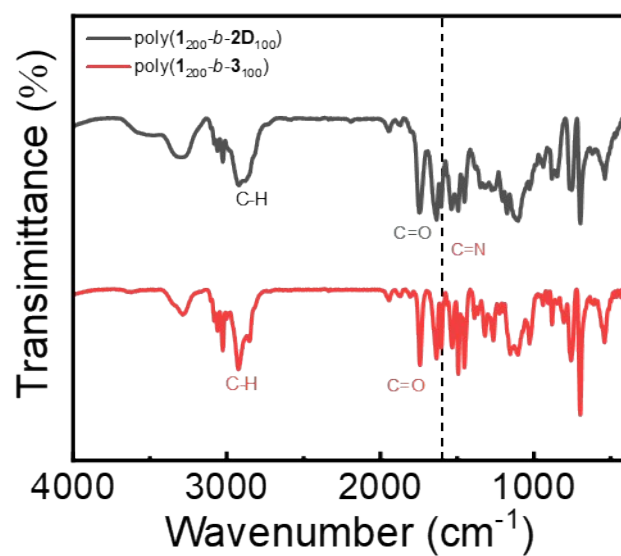
**Fig. S2.**  $^{13}\text{C}$  NMR spectrum of the poly- $\mathbf{1}_{200}$  ( $\text{CDCl}_3$ , 125 MHz).



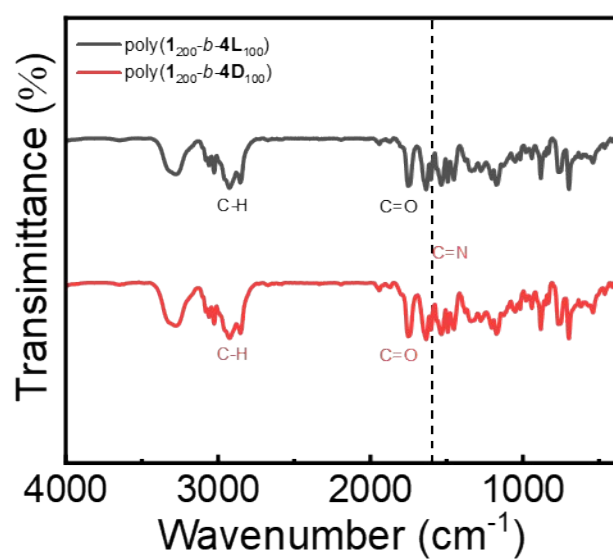
**Fig. S3.** Time-dependent SEC for the copolymerization of  $\mathbf{2L}$  catalyzed by Pd(II)-terminated poly- $\mathbf{1}_{200}$ .



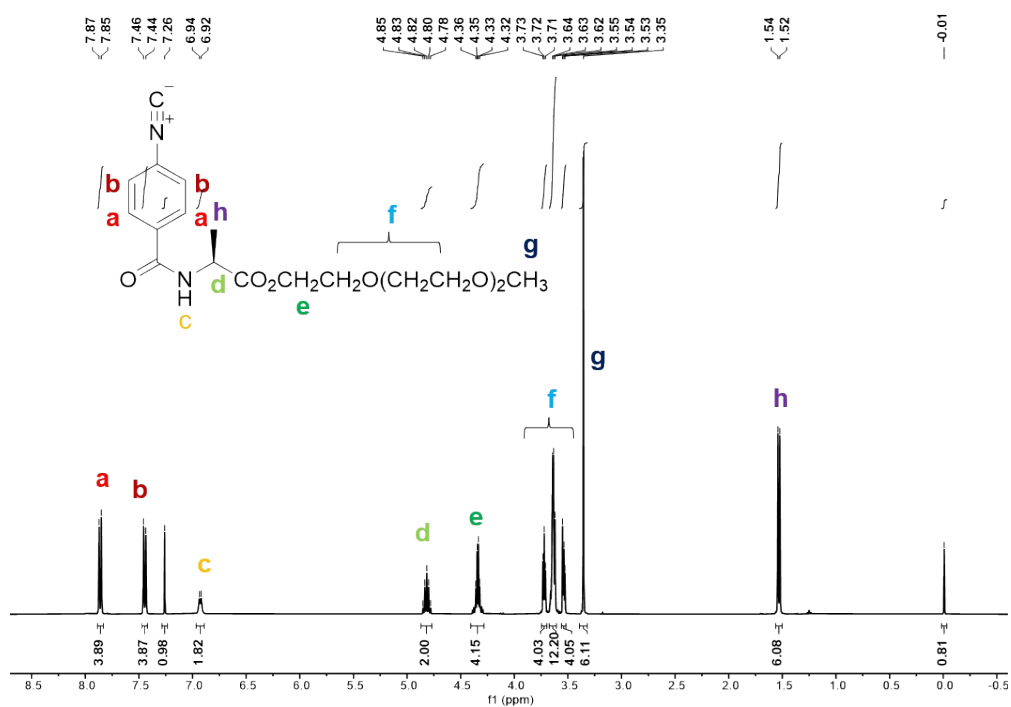
**Fig. S4.** FT-IR spectrum of poly- $\mathbf{1}_{200}$ , poly- $\mathbf{2L}_{100}$  and poly( $\mathbf{1}_{200}$ - $b$ - $\mathbf{2L}_{100}$ ).



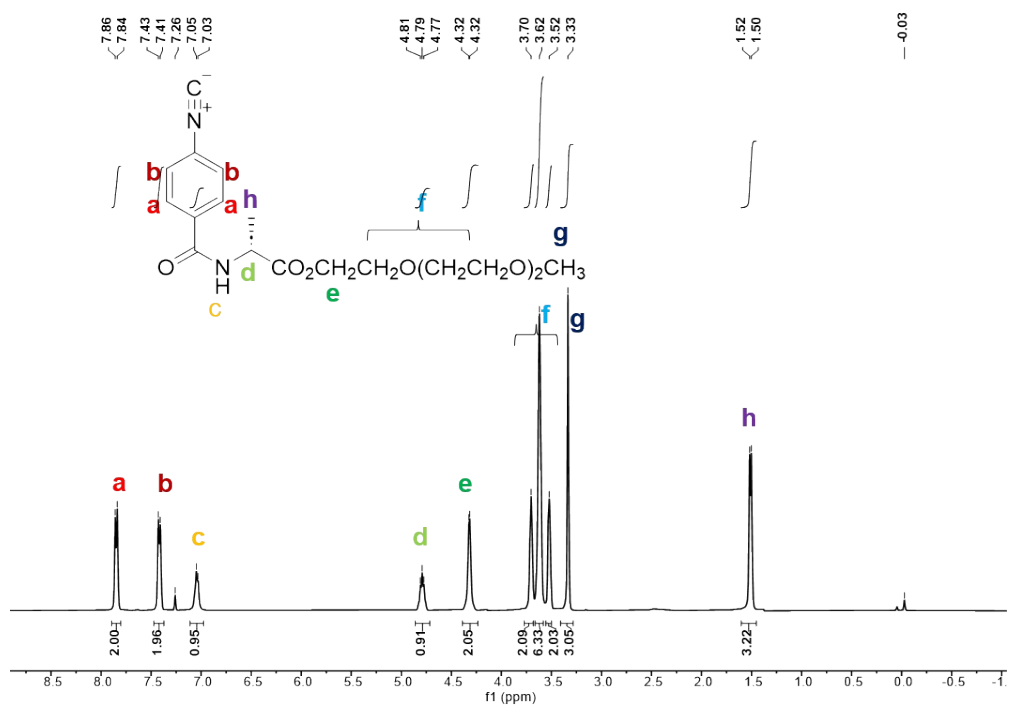
**Fig. S5.** FT-IR spectrum of poly(1<sub>200</sub>-b-2D<sub>100</sub>) and poly(1<sub>200</sub>-b-3<sub>100</sub>).



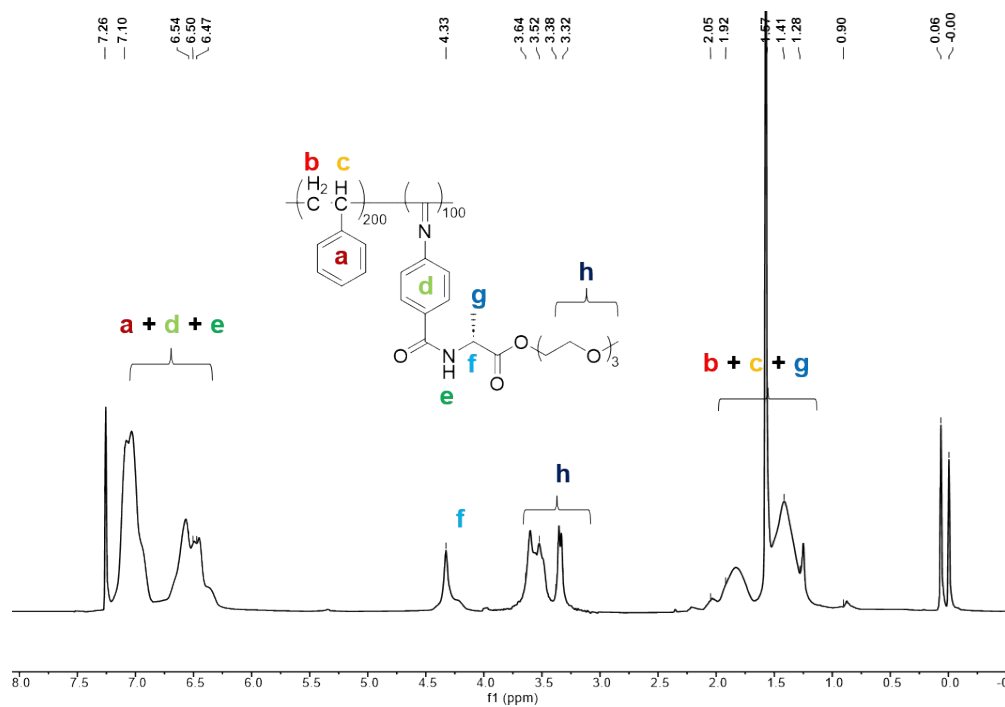
**Fig. S6.** FT-IR spectrum of poly(1<sub>200</sub>-b-4L<sub>100</sub>) and poly(1<sub>200</sub>-b-4D<sub>100</sub>).



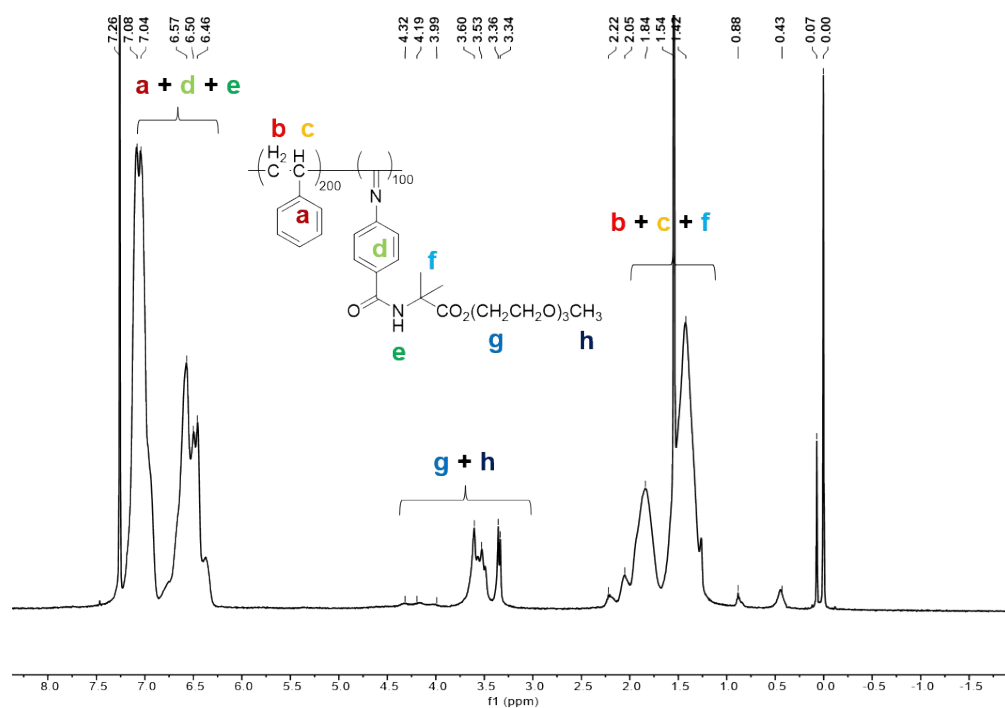
**Fig. S7.** <sup>1</sup>H NMR spectrum of the compound **2L** measured in CDCl<sub>3</sub> at room temperature.



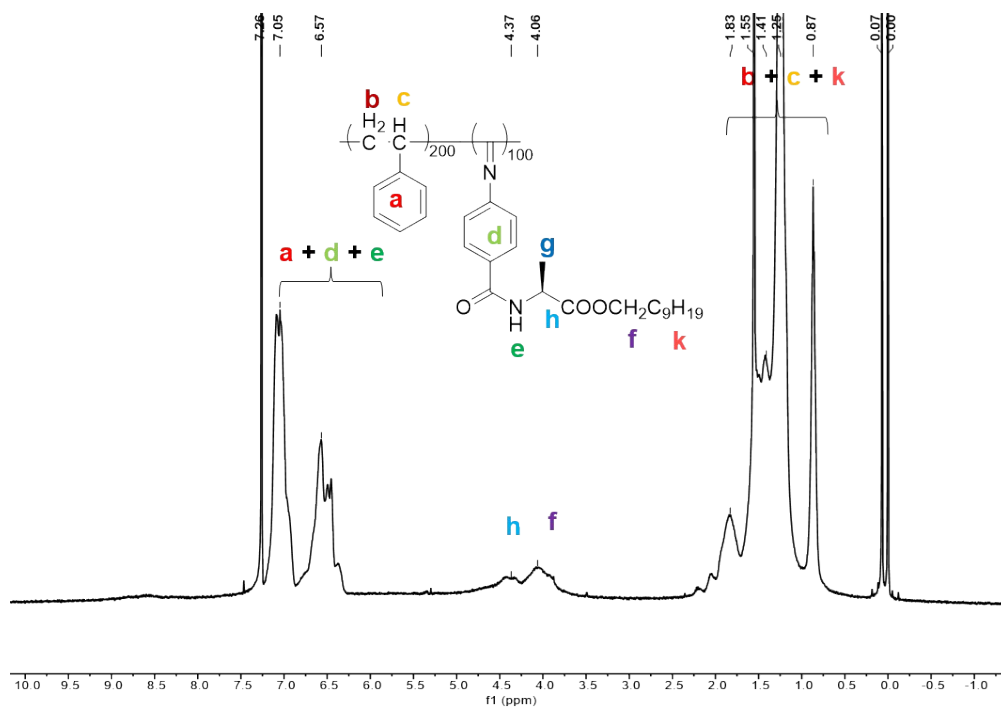
**Fig. S8.** <sup>1</sup>H NMR spectrum of the compound **2D** measured in CDCl<sub>3</sub> at room temperature.



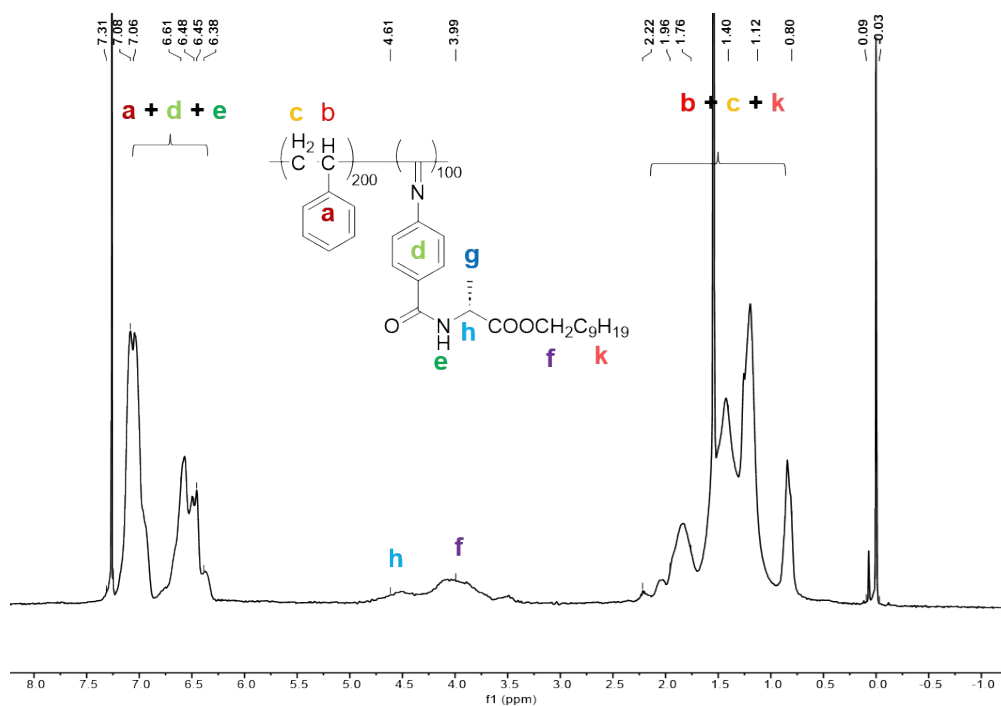
**Fig. S9.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-2D<sub>100</sub>) measured in CDCl<sub>3</sub> at room temperature.



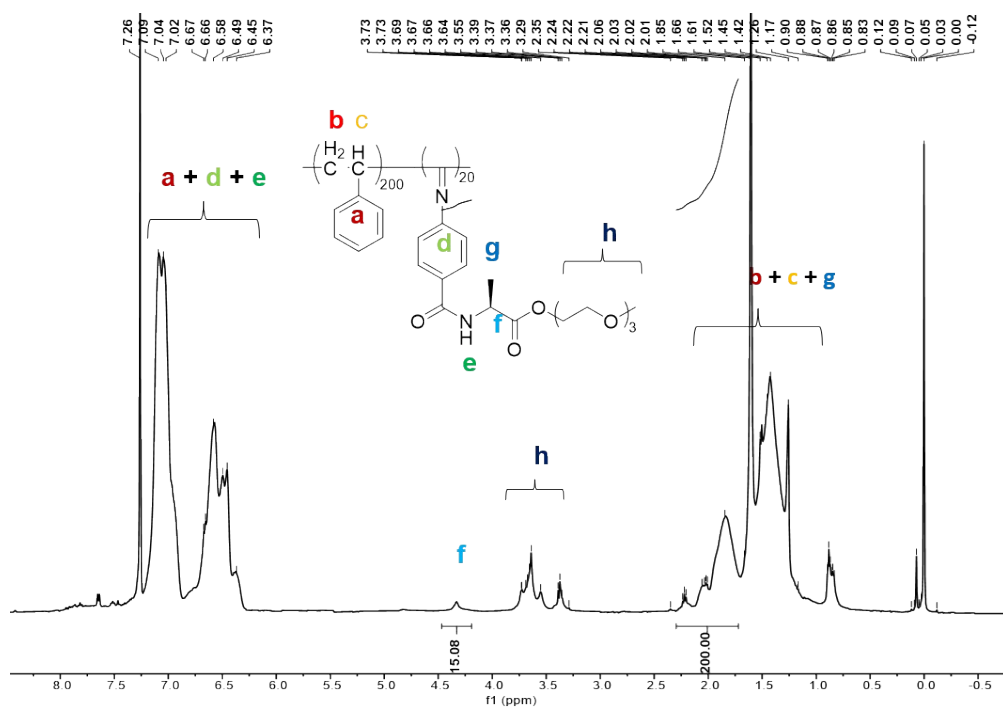
**Fig.S10.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-3<sub>100</sub>) measured in CDCl<sub>3</sub> at room temperature.



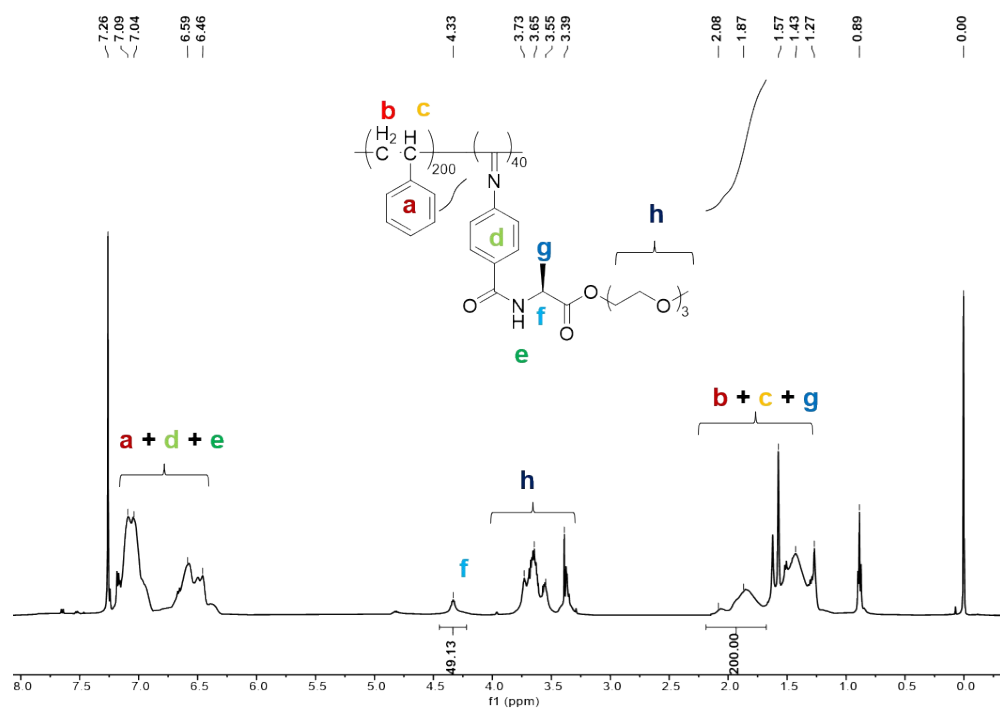
**Fig. S11.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-4L<sub>100</sub>) measured in CDCl<sub>3</sub> at room temperature.



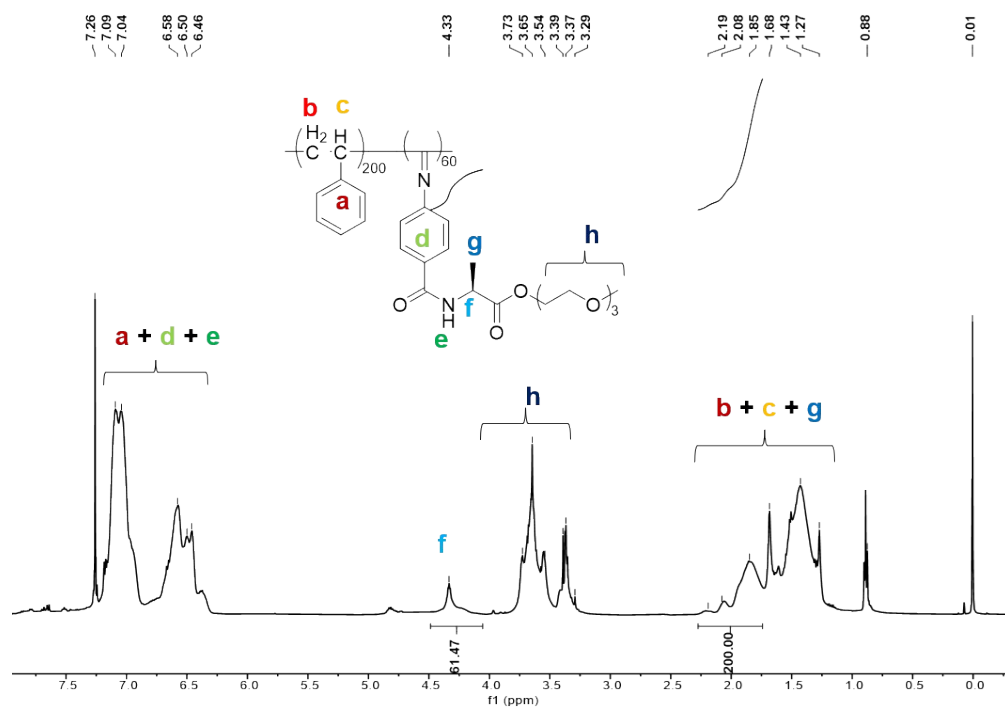
**Fig. S12.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-4D<sub>100</sub>) measured in CDCl<sub>3</sub> at room temperature.



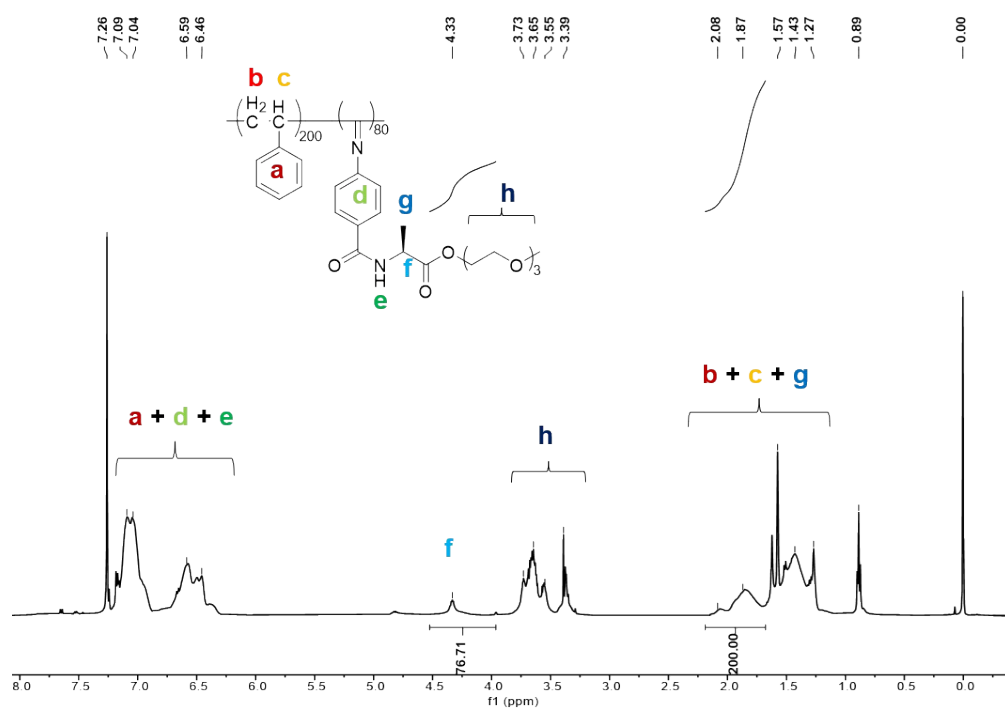
**Fig. S13.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-2L<sub>20</sub>) measured in CDCl<sub>3</sub> at room temperature.



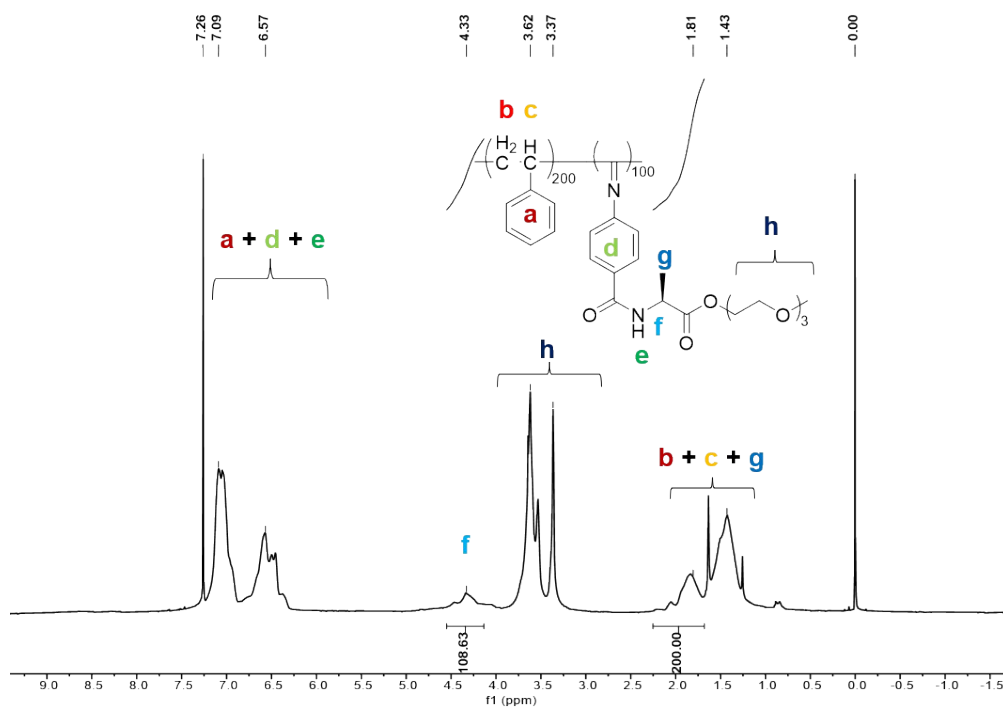
**Fig. S14.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-2L<sub>40</sub>) measured in CDCl<sub>3</sub> at room temperature.



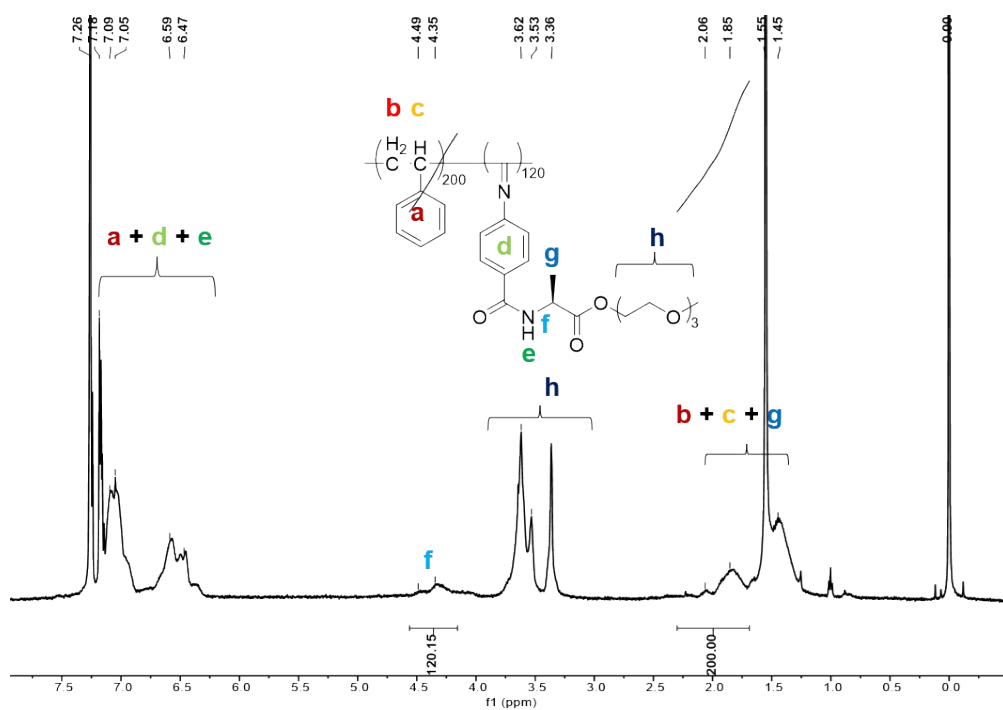
**Fig. S15.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-2L<sub>60</sub>) measured in CDCl<sub>3</sub> at room temperature.



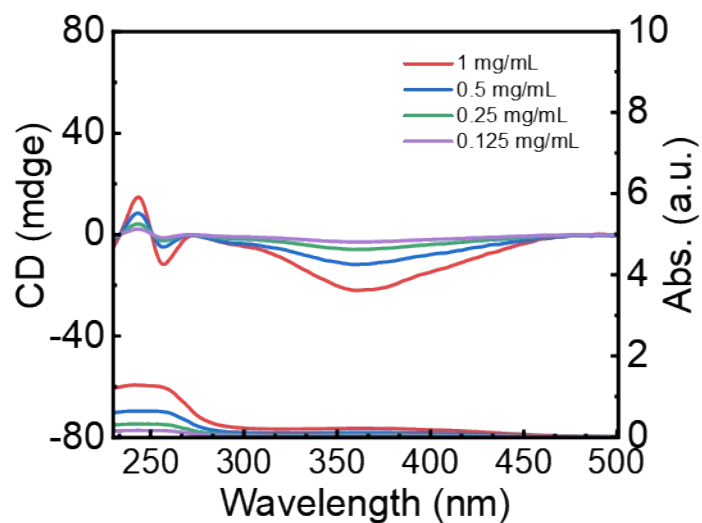
**Fig. S16.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-b-2L<sub>80</sub>) measured in CDCl<sub>3</sub> at room temperature.



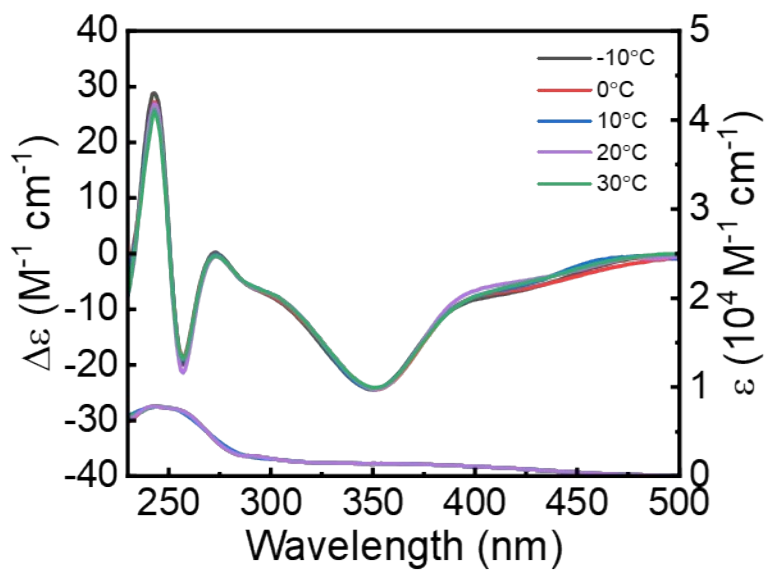
**Fig. S17.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-*b*-2L<sub>100</sub>) measured in CDCl<sub>3</sub> at room temperature.



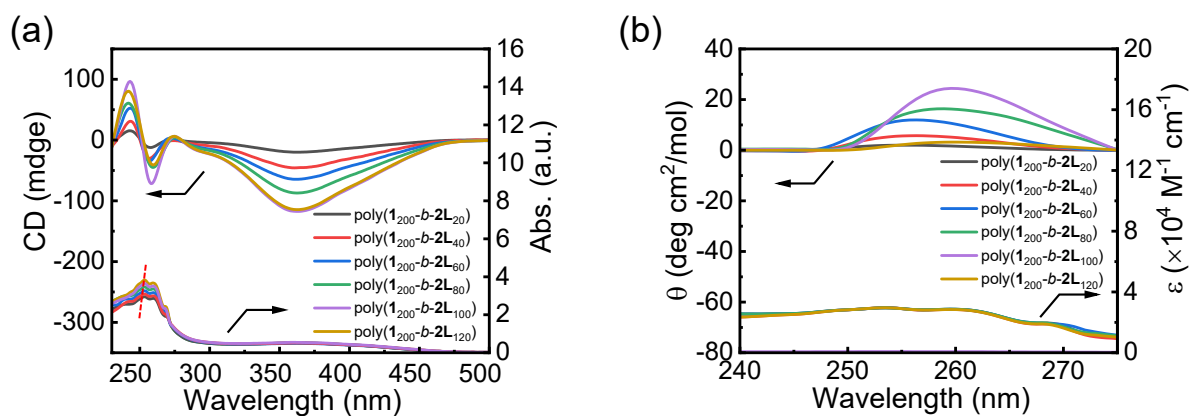
**Fig. S18.** <sup>1</sup>H NMR spectrum of the block copolymer poly(1<sub>200</sub>-*b*-2L<sub>120</sub>) measured in CDCl<sub>3</sub> at room temperature.



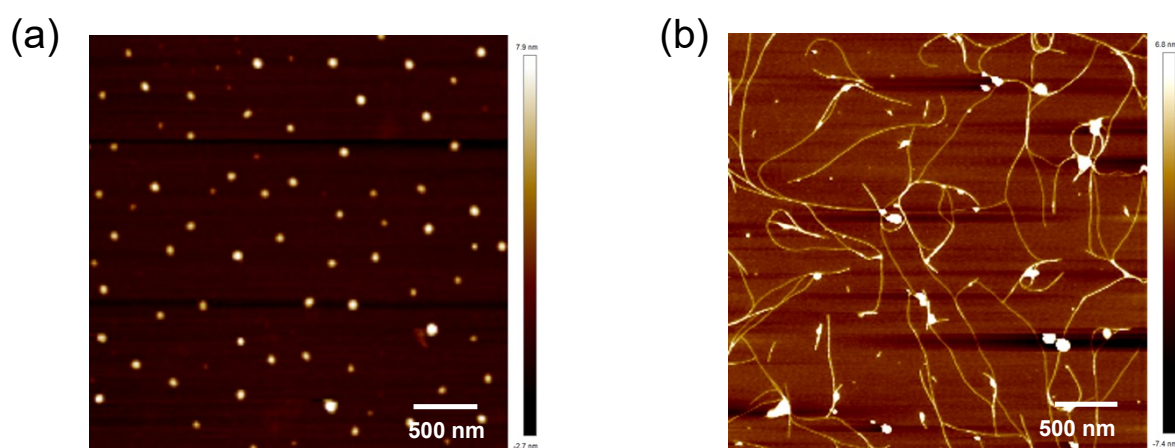
**Fig. S19.** CD and UV-vis spectra of poly( $1_{200}$ - $b$ - $2L_{100}$ ) measured in  $\text{CHCl}_3$  at different concentrations.



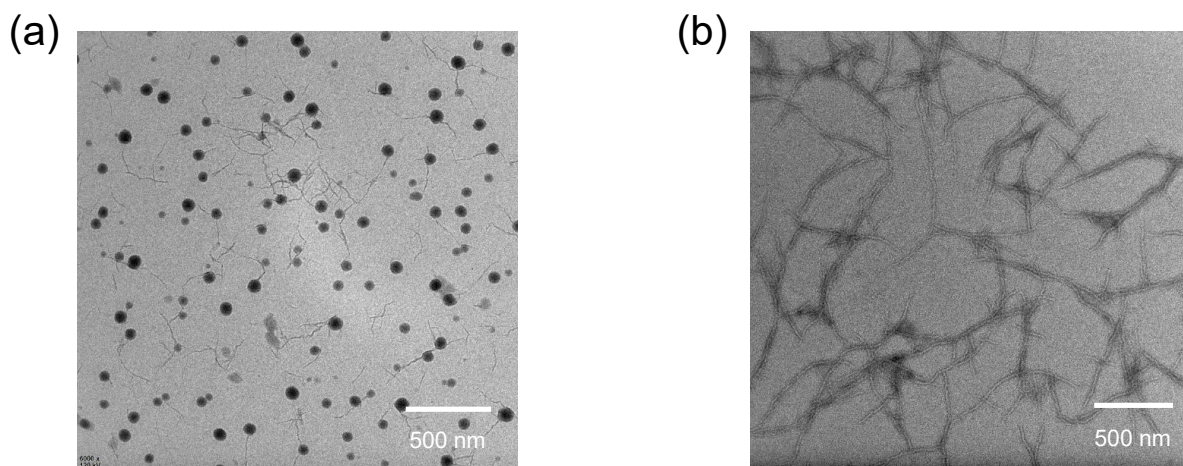
**Fig. S20.** CD and UV-vis spectra of poly( $1_{200}$ - $b$ - $2L_{100}$ ) measured in  $\text{CHCl}_3$  at different temperature.



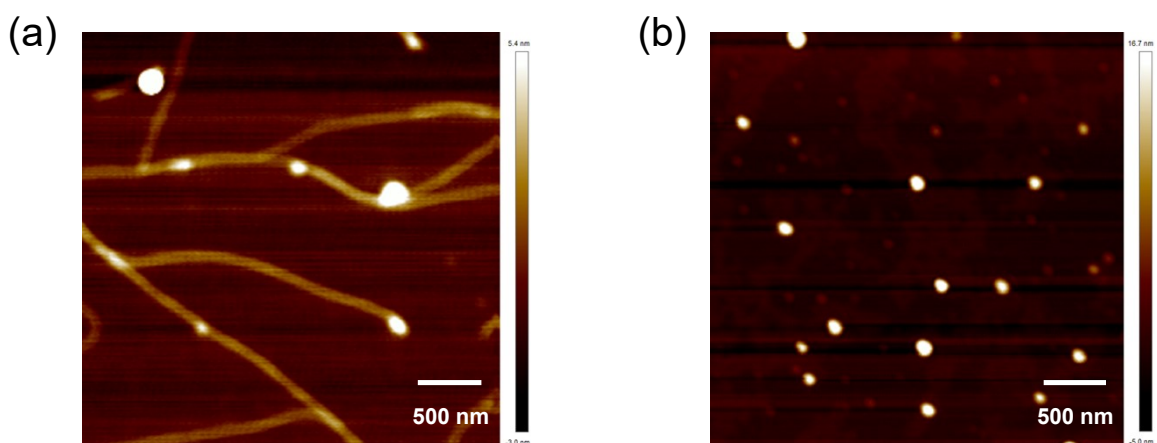
**Fig. S21.** (a) CD and UV-vis spectra of poly( $1_{200}$ - $b$ - $2L_n$ )s with different PPI lengths. (b) CD and UV-vis spectra of poly( $1_{200}$ - $b$ - $2L_n$ )s copolymers with the contribution of the PPI segment eliminated ( $c = 3.0$  mg/mL,  $\text{CHCl}_3$ ,  $25$  °C).



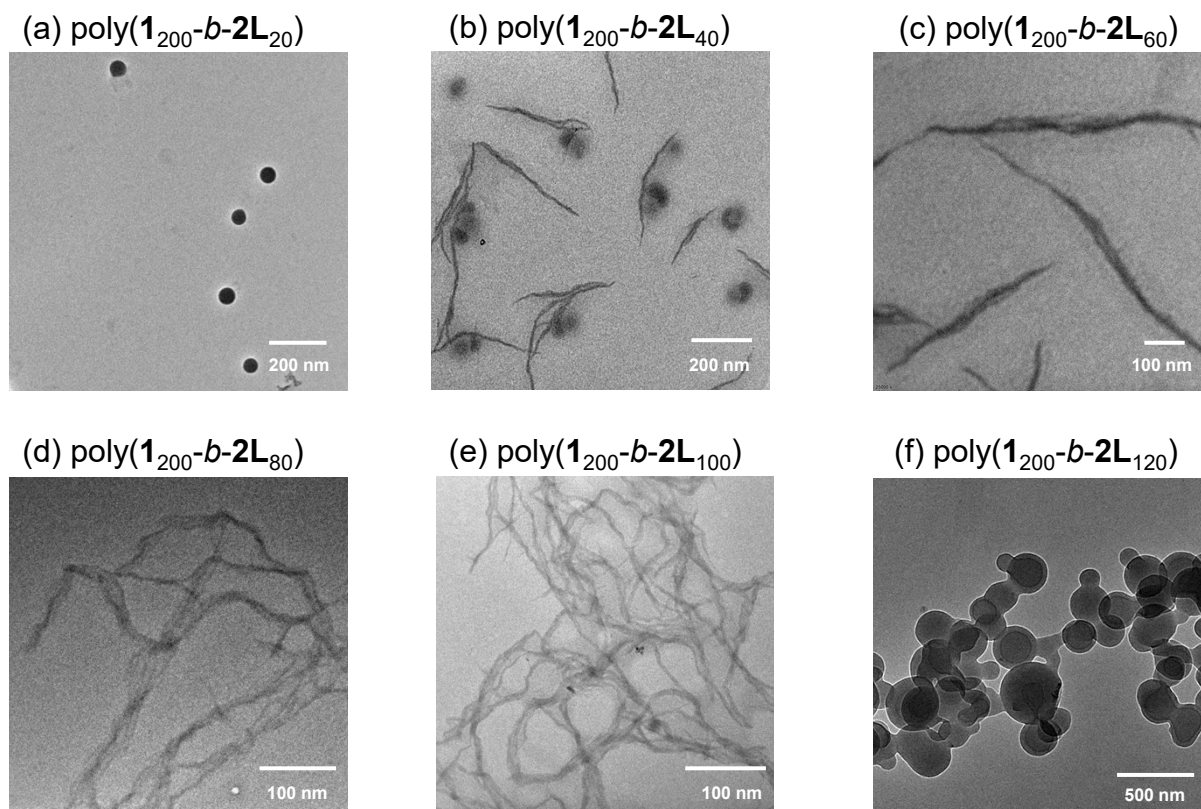
**Fig. S22.** AFM images of (a) poly( $1_{200}$ - $b$ - $2L_{20}$ ) and (b) poly( $1_{200}$ - $b$ - $2L_{80}$ ). Scale bar = 500 nm.



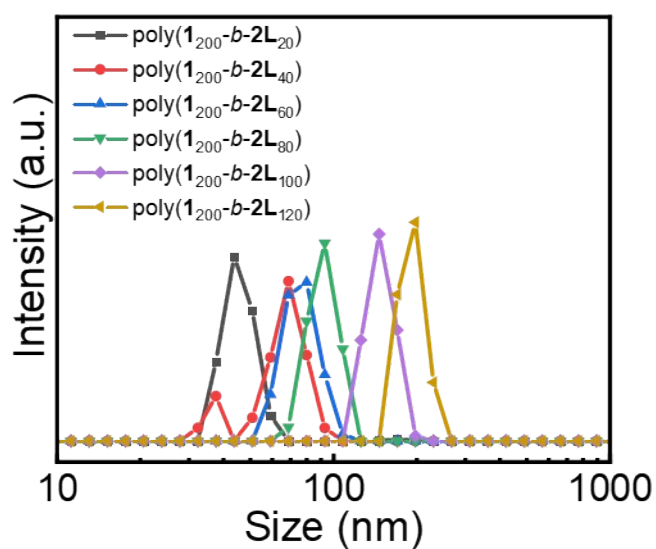
**Fig. S23.** TEM images of (a) poly( $1_{200}$ - $b$ - $2L_{40}$ ) and (b) poly( $1_{200}$ - $b$ - $2L_{80}$ ). Scale bar = 500 nm.



**Fig. S24.** AFM images of (a) poly( $1_{400}$ - $b$ - $2L_{100}$ ) and (b) poly( $1_{600}$ - $b$ - $2L_{100}$ ).



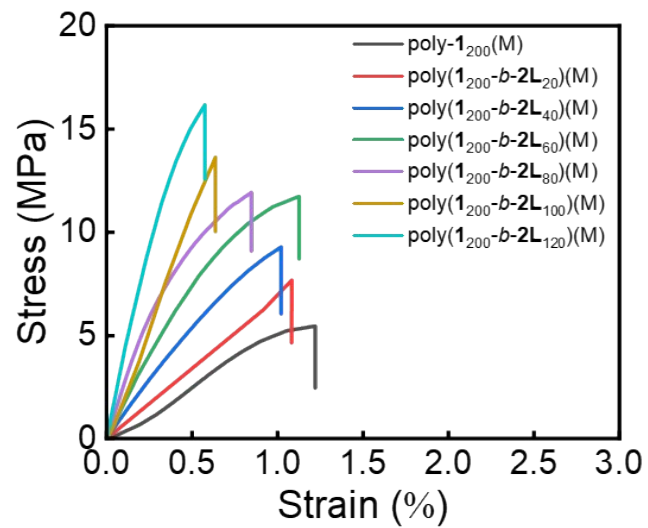
**Fig. S25.** TEM images (a)  $\text{poly}(1_{200}\text{-}b\text{-}2L_{20})$ , (b)  $\text{poly}(1_{200}\text{-}b\text{-}2L_{40})$ , (c)  $\text{poly}(1_{200}\text{-}b\text{-}2L_{60})$ , (d)  $\text{poly}(1_{200}\text{-}b\text{-}2L_{80})$ , and (e)  $\text{poly}(1_{200}\text{-}b\text{-}2L_{100})$ , and (f)  $\text{poly}(1_{200}\text{-}b\text{-}2L_{120})$ .



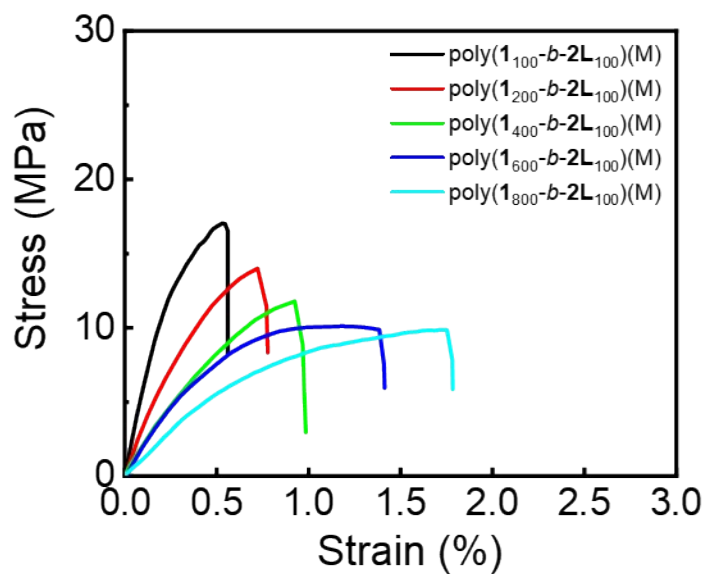
**Fig. S26.** DLS curves of  $\text{poly}(1_{200}\text{-}b\text{-}2L_n)$  measured in  $\text{CHCl}_3$  with different DP.



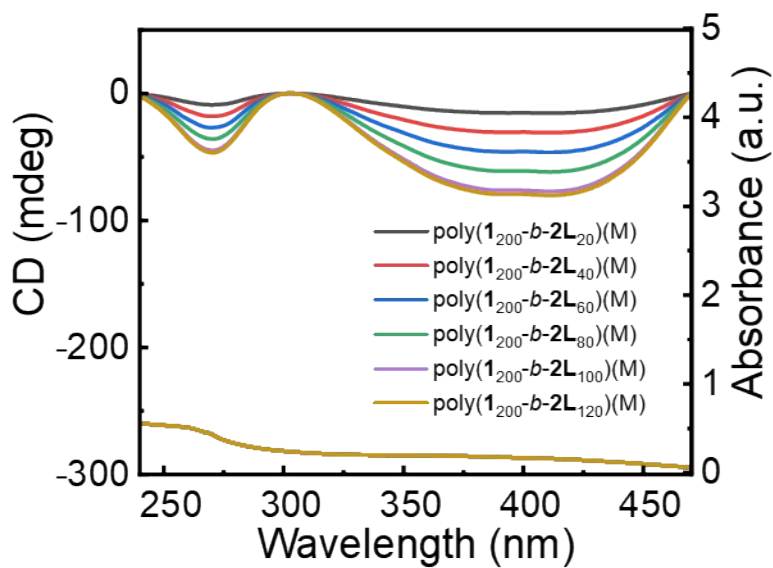
**Fig. S27.** PS-*b*-PPI membrane picture of formed by poly( $1_{200}$ -*b*- $2L_{100}$ ). Films were prepared by solvent casting from a polymer solution in a PTFE mold.



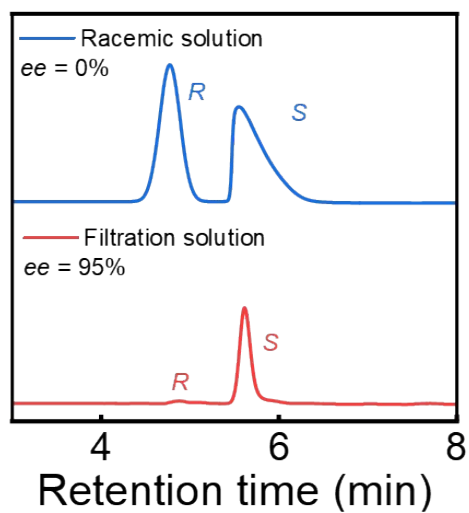
**Fig. S28.** Stress-strain curves of the poly( $1_{200}$ -*b*- $2L_n$ ) membranes. Poly- $1_{200}$ (M) refers to membranes cast from poly- $1_{200}$ .



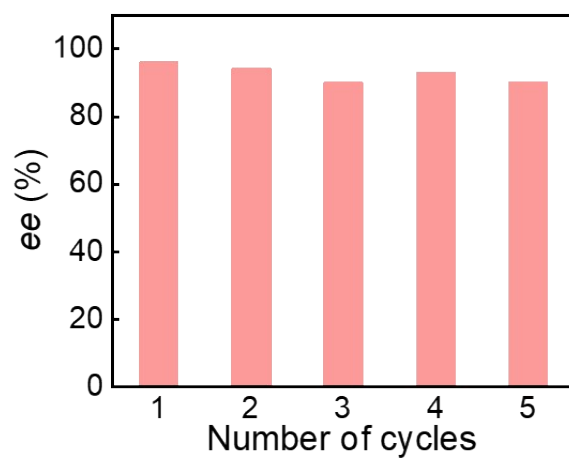
**Fig. S29.** Stress-strain curves of the poly( $1_n$ - $b$ - $2L_{100}$ ) membranes. “M” refers to the membrane.



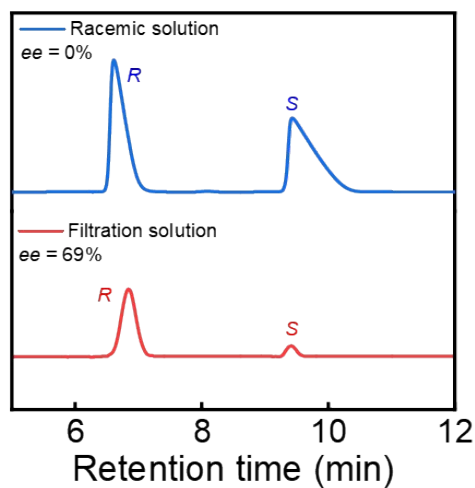
**Fig. S30.** CD and UV-vis spectra of poly( $1_{200}$ - $b$ - $2L_n$ ) membranes measured.



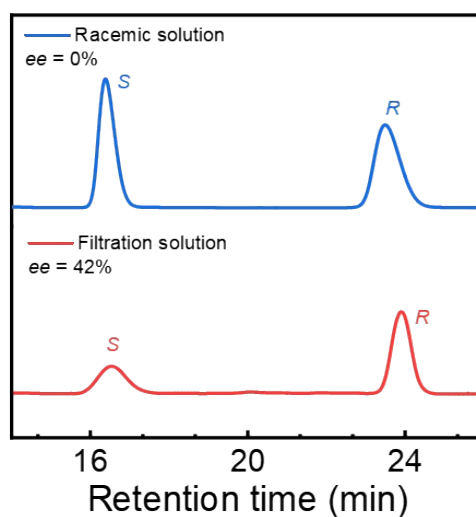
**Fig. S31.** In the presence of poly( $1_{200}$ - $b$ - $2D_{100}$ ) membrane, HPLC chromatogram of **4a** racemic solution and filtration solution.



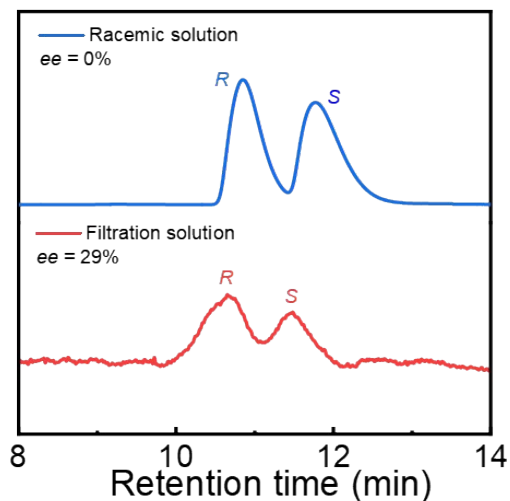
**Fig. S32.** Poly( $1_{200}$ - $b$ - $2L_{100}$ ) membrane after five “dissolution-precipitation” cycles.



**Fig. S33.** In the presence of poly( $1_{200}$ - $b$ - $2L_{100}$ ) membrane, HPLC chromatogram of **4b** racemic solution and filtration solution.



**Fig. S34.** In the presence of poly( $1_{200}$ - $b$ - $2L_{100}$ ) membrane, HPLC chromatogram of **4c** racemic solution and filtration solution.



**Fig. S35.** In the presence of poly( $1_{200}$ - $b$ - $2L_{100}$ ) membrane, HPLC chromatogram of **4d** racemic solution and filtration solution.

### References

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- 2 L. Xu, C. Wang, Y. X. Li, X. H. Xu, L. Zhou, N. Liu and Z.-Q. Wu., *Angew. Chem. Int. Ed.*, 2020, **59**, 16675–16682.
- 3 X. Song, Y.-X. Li, L. Zhou, N. Liu and Z.-Q. Wu., *Macromolecules*, 2022, **55**, 4441–4449.
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