

Supporting Information

Synthesis of poly(3-hexylthiophene)-*block*-poly(phenylisocyanide) copolymers and their self-assembly in solution

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Contents

1. General consideration.....	2
2. Synthesis of intermediates and isocyanide monomer 5.....	3
3. Living polymerization procedures and self-assembly process.....	5
4. Typical procedure for solution assembly of poly(1 ₂₀ - <i>b</i> -5 _n).....	6
5. NMR spectrum of compound 2.....	8
6. NMR spectrum of compound 3.....	9
7. NMR spectrum of compound 4.....	10
8. NMR spectrum of monomer 5.....	11
9. NMR spectrum of diblock copolymers.....	12
10. Time-dependent SEC analyses.....	14
11. TGA curves and DSC curves of polymer and diblock copolymers.....	14
12. AFM images of assembled poly(1 ₂₀ - <i>b</i> -5 ₁₅₀) diblock copolymer.....	15
13. SEM images of poly(1 ₂₀ - <i>b</i> -5 _n) diblock copolymers.....	15
14. DLS curves of poly(1 ₂₀ - <i>b</i> -5 _n) diblock copolymers.....	16
15. UV-vis absorption spectra of poly(1 ₂₀ - <i>b</i> -5 _n) diblock copolymers.....	16
16. Polarized optical micrograph (POM) of poly(1 ₂₀ - <i>b</i> -5 ₁₅₀).....	17
References.....	18

1. General consideration

All materials used in this study were characterized by ^1H NMR and ^{13}C NMR spectra recorded at Bruker 400 MHz spectrometer with CDCl_3 solvent and the chemical shifts were referenced to the residual signal of CDCl_3 (δ 7.26 ppm), ^2H NMR spectra were measured at 400 MHz and 300 K (61 MHz ^2H frequency). The molecular weight (M_n) and M_w/M_n of P3HT block copolymers were determined by SEC (Waters 2414) using RI detectors, which is calibrated by polystyrene standards with THF at a flow rate of 0.8 mL/min. FT-IR spectra were recorded on PerkinElmer Spectrum BX FT-IR system at 25 °C. CD and UV-vis spectra were recorded on JASCO J1500 and UNIC 4802 UV/vis double beam spectrophotometers in a 1.0 cm quartz cell at 25 °C. Fluorescence spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer. The slitwidths were set at 5.0 nm. The optical rotations were measured in THF at 25 °C using a 10.0 cm quartz cell on a WZZ-2B polarimeter. Melting points were obtained with a Mel-Temp apparatus and are uncorrected. Atomic force microscope (AFM) was performed on a Cypher S microscope (Oxford Instruments, Asylum Research). Transmission electron microscopy (TEM) observations were conducted on a JEM-2100F electron microscope operating at an acceleration voltage of 200 kV. The field emission scanning electron microscope (FESEM) maps were obtained on the extreme high-resolution (XHR) Thermo Scientific Verios G4 UC microscope equipped with an Ultim Max 170 (Oxford, UK) detector to detect the elemental distribution. Dynamic light scattering (DLS) measurements were carried on a Nano-ZS90 Zetasizer of Malvern (UK) instrument, all data were averaged over threetime measurements. Optical Polarizing Microscopy (POM) fully characterized the phase structures of all compounds by polarizing microscope (DYP-606).

All starting materials were obtained commercially and used as received without further purification otherwise denoted. THF was distilled from sodium/benzophenone, and dichloromethane (DCM) was freshly distilled over calcium hydride prior to use. The Ni(II) complex and monomer **5**, and homopolymers poly-**1**₂₀, and copolymers poly(**1**₂₀-*b*-**5**_n) were prepared according to the similar procedures reported by us previously. ¹ Val-based isocyanide monomer **5** was synthesized according to Scheme 1 using a new modified synthesis route.

2. Synthesis of intermediates and isocyanide monomer 5

Synthesis of *L*-valine phenylpropylester 2

A suspension of *L*-valine (20.0 g, 171 mmol, 1.00 eq.), 3-phenyl-1-propanol (24.4 g, 179 mmol, 1.05 eq.) and *p*-toluenesulfonic acid monohydrate (36.0 g, 188 mmol, 1.10 eq.) in 500 mL of toluene was refluxed for 10 h in a Dean-Stark water trap until the expected amount of water and a clear brown solution was formed. The solvent was removed under reduced pressure; the residue was taken up with DCM and washed with saturated NaHCO₃ solution and water to get the free base. The aqueous phases were extracted with DCM and the combined organic phases were dried over MgSO₄ and concentrated in vacuo to obtain crude **2** as a brown oil (35.3 g, 88%) which was used for the next step without further purification. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.29 - 7.25 (m, 2H), 7.20 - 7.16 (m, 3H), 4.16 - 4.11 (m, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.08 - 1.92 (m, 3H), 1.46 (s, 1H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 175.5, 141.0, 128.4, 128.4, 128.4, 126.0, 64.0, 59.9, 32.2, 32.1, 30.2, 19.3, 17.2.

Synthesis of 4-aminobenzoyl-*L*-valine phenylpropylester 3

L-Valine phenylpropylester **2** (1.41 g, 6 mmol) was dissolved in 30 mL THF and cooled to 0 °C, triethylamine (2.6 mL, 18.2 mmol) was added, and the reaction was stirred 0.5 h. and subsequently 4-aminobenzoic acid (0.82 g, 6 mmol), 1-hydroxybenzotriazole (HOBt, 0.9 g, 6.6 mmol), N-[3-(dimethylamino) propyl]propylidamide hydrochloride (EDCI, 1.34 g, 7 mmol) were added. The reaction mixture was stirred at 25 °C for 10 h until the substrates were completely consumed as indicated by thin layer chromatography (TLC) analysis. The reaction solution was washed with brine water, the organic layer was collected and dried over anhydrous Na₂SO₄, and concentrated to dryness. The residues were purified by silica gel column chromatography using petroleum ether-ethyl acetate as eluent to afford a white solid (1.8 g, yield: 84%). M. p. = 132.3-133.0 °C. [α]_D²⁰ = +35.3 (*c* 0.10, in CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.65 - 7.63 (m, 2H), 7.30 - 7.25 (m, 2H), 7.21 - 7.16 (m, 3H), 6.67 - 6.64 (m, 2H), 6.49 (d, *J* = 8.5 Hz, 1H), 4.77 (dd, *J* = 8.6, 4.9 Hz, 1H), 4.20 - 4.18 (m, 2H), 4.01 (s, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.28 - 2.23 (m, 1H), 2.04 - 1.95 (m, 2H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.5, 167.0, 149.8, 140.9, 128.8, 128.5, 128.4, 126.1, 123.6, 114.1, 64.6, 57.2, 32.1, 31.7, 30.2, 19.0, 18.0.

Synthesis of 4-formaminobenzoyl-*L*-valine phenylpropylester 4

After a mixture of formic acid (14.12 mL, 10.2 mmol) and acetic anhydride (0.76 mL, 8.04 mmol) was stirred at room temperature for 1 h. 4-Aminobenzoyl *L*-valine phenylpropylester **3** (1.7 g, 4.79 mmol) in ethyl acetate (50 mL) was added to the mixture. The dispersion solution was stirred 12 h and then quenched by water (30 mL). To the solution was added ethyl acetate (50 mL), the organic layer was washed two times with brine, and then dried over anhydrous Na₂SO₄. After the solvent was removed under reduced pressure, the residues were purified by silica gel column chromatography using petroleum ether -ethyl acetate (2:1, v/v) as eluent to afford a white solid (1.39 g, yield: 76%). M. p. = 147.8 - 148.1 °C. [α]₂₀ D = +52.9 (*c* 0.10, in CHCl₃). ¹H NMR (400 MHz, CDCl₃) rotamer, δ (ppm) 8.80 (s, 0.42 H), 8.42 (s, 0.64 H), 7.95 (s, 0.4 H), 7.83 - 7.78 (m, 2H), 7.65 - 7.58 (m, 2H), 7.31 - 7.20 (m, 2H), 7.23 - 7.11 (m, 4H), 6.63 (d, *J* = 8.6 Hz, 1H), 4.78 (dd, *J* = 8.6, 4.8 Hz, 1H), 4.20 - 4.17 (m, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.31 - 2.26 (m, 1H), 2.04 - 1.96 (m, 2H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 172.3, 166.5, 166.2, 161.5, 158.9, 140.8, 140.0, 139.8, 130.6, 130.1, 129.0, 128.5, 128.4, 128.2, 126.1, 126.0, 119.4, 117.7, 64.8, 64.7, 57.5, 32.1, 31.6, 30.1, 19.0, 18.0.

Synthesis of 4-isocyanobenzoyl-*L*-valine phenylpropylester monomer **5**

Under the nitrogen atmosphere, 4-formaminobenzoyl-*L*-valine phenylpropylester **4** (0.8 g, 2.1 mmol) was dissolved in 20 mL dry DCM, and cooled to 0 °C. Then triethylamine (Et₃N, 0.75 mL, 5.5 mmol, 2.5 eq.) was added and stirred, over a period of 1 h, a solution of triphosgene (BTC, 443 mg, 1.5 mmol) in 10 mL dry DCM was added dropwise maintaining the temperature at 0 °C. after a few minutes the reaction temperature was raised to room temperature. The mixture was stirred for an additional 3 h until complete conversion, monitored by TLC. The reaction was quenched by addition 10 mL of a saturated NaHCO₃ aqueous solution. The phases were separated and the aqueous phase was extracted with DCM while the combined organic phases were washed with brine. Then the organic phase was dried over Na₂SO₄, filtered, and concentrated. Purification on flash column chromatography (petroleum ether/EtOAc = 4/1) afforded 4-isocyanobenzoyl-*L*-valine phenylpropylester monomer **5** as a white solid (0.62 g, yield: 81%). M. p. = 75.5 - 76.5 °C. [α]₂₀ D = +46.9 (*c* 0.10, in CHCl₃). ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.86 - 7.83 (m, 2H), 7.84 - 7.83 (m, 2H), 7.47 - 7.45 (m, 2H), 7.31 - 7.27 (m, 3H), 6.61 (d, *J* = 8.5 Hz, 1H), 4.77 (dd, *J* = 8.5, 4.7 Hz, 1H), 4.23 - 4.17 (m, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.33 - 2.25 (m, 1H), 2.04 - 1.97 (m, 2H),

1.03 (d, $J = 6.9$ Hz, 3H), 1.00 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 172.0, 166.8, 165.5, 140.7, 135.0, 128.5, 128.3, 128.3, 126.7, 126.1, 64.9, 57.6, 32.1, 31.6, 30.1, 19.0, 17.9.

3. Living polymerization procedures of block copolymers

The variety of P3HT-based BCPs have been commonly prepared from 2,5-dibromo-3-hexylthiophene and isopropylmagnesium chloride *via* Grignard metathesis polymerization using $\text{Ni}(\text{dppp})\text{Cl}_2$ (dppp=1,3-bis(diphenylphosphanyl)propane) as a single catalyst,² and a reactive Ni(II) terminated P3HT residues thus can initiate block copolymerization of phenyl isocyanide with Val-based solvophilic side chain in a controlled manner to afford P3HT-*b*-poly(arylisocyanide) block copolymers.³

Taking poly(1₂₀-b-5₁₅₀) as an example: 10 mL oven-dried Schlenk flask equipped with a stir bar was charged with 2,5-dibromo-3-hexylthiophene (65 mg, 0.20 mmol) and dry THF (2.0 mL). After a solution of isopropylmagnesium chloride (2.0 M solution in THF, 0.10 mL, 0.20 mmol) was added *via* a syringe under nitrogen atmosphere, the resulting mixture was subsequently stirred at 25 °C for 2 h. $\text{Ni}(\text{dppp})\text{Cl}_2$ (5.4 mg, 0.01 mmol, $[\text{monomer}]_0/[\text{Ni}(\text{dppp})\text{Cl}_2]_0 = 20$) was then added to the reaction mixture. After 1 h, SEC analyses indicated monomer **1** was almost completely consumed. The *in-situ* generated Ni(II)-terminated P3HT (poly-**1**₂₀, $M_n = 7.96$ kDa, $M_w/M_n = 1.22$) was treated with monomer **5** (80.0 mg, 0.22 mmol) in THF. The initial feed ratio of isocyanide monomer **5** to Ni(II)-catalyst was 150 ($[\mathbf{5}]_0/[\text{Ni}]_0 = 150$). The reaction flask was then stirred for 5 h at 25 °C, and the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum, afford poly(**1**₂₀-*b*-**5**₁₅₀) as a deep purple solid (130 mg, 86% yield). SEC: $M_n = 35.1$ kDa, $M_w/M_n = 1.12$. ^1H NMR (400 MHz, CDCl_3) δ (ppm) 7.81 (br, 1H, CONH), 7.11 -7.04 (br, aromatic), 6.98 (s, thiophene ArH), 4.33 -3.55 (br, -NHCH and -OCH₂-), 2.81 - 2.79 (br, thiophene-CH₂), 2.33 - 2.21 (br, CH₂-Ph and (CH₃)₂CH-), 1.90 - 0.52 (br, CH₂- and CH₃-). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 171.6, 141.4, 128.3, 125.9, 63.7, 32.1, 31.7, 30.5, 29.5, 29.2, 22.6, 19.2, 14.1. UV/Vis (THF): $\lambda_{\text{max}} = 390$ nm. FT-IR (cm^{-1}): 2910 ($\nu_{\text{C-H}}$), 2865 ($\nu_{\text{C-H}}$), 1735 ($\nu_{\text{NHC=O}}$), 1630 ($\nu_{\text{OC=O}}$), 1600 ($\nu_{\text{C=N}}$).

Kinetic study for the block copolymerization: Under N₂ atmosphere, a solution of the *in-situ* generated Ni(II)-terminated poly-**1**₂₀ was added to the mixture of monomer **5** and internal standard polystyrene. The solution was stirred at ambient temperature and was followed by measuring SEC

of the aliquots taking out from the reaction solution at appropriate time intervals. The conversion of monomer **5** was calculated based on the peak area of unreacted **5** relative to that of the internal PSt standard on the basis of the linear calibration curve. The M_n and M_w/M_n were estimated by SEC and reported as equivalent to PSt standards. Time-dependent SEC was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C), and a series of two linear TSK gel GMHHR-H columns were used (THF, 0.8 mL/min, 40 °C).

4. Typical procedure for solution assembly of poly(1**₂₀-**b**-**5**_n)**

Intermolecular interaction of the chain-extended π -conjugated PPI may drive the generated supramolecular structure of P3HT-based BCPs in the non-selective solvent. With six diblock copolymers of poly(**1**₂₀-**b**-**5**_n) on hand, self-assembly of the poly(**1**₂₀-**b**-**5**_n) samples were prepared by solvent casting in THF at ambient temperature. These aggregates were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), dynamic light scattering (DLS), ultraviolet–visible (UV-vis) spectroscopy and circular dichroism (CD) spectroscopy analyses.

Self-assembled sample preparation for AFM and TEM observation: Stock solutions of poly(**1**₂₀-**b**-**5**₃₀), poly(**1**₂₀-**b**-**5**₅₀), poly(**1**₂₀-**b**-**5**₈₀), poly(**1**₂₀-**b**-**5**₁₀₀), poly(**1**₂₀-**b**-**5**₁₅₀), and poly(**1**₂₀-**b**-**5**₂₀₀) in dry THF (0.5 mg/mL) were prepared, and were casted for 2 h to at ambient temperature. Samples for AFM measurements were prepared by casting 20 μ L aliquots of the stock solutions of the copolymers onto freshly cleaved silicon wafers and after 30 minutes the excess of solution was removed with blotting paper. Subsequently, the substrate was dried under nitrogen flow for several minutes. AFM were performed at room temperature in a dry state using Cypher S microscope (Oxford Instruments). Both topographic and phase images of assemblies of different nanostructures were obtained in Tapping Mode using rectangular silicon cantilever with a spring constant of 26 N m^{-1} , a resonance frequency lying in the 62-120 kHz range and a radius of curvature of less than 10 nm. Measurement of length and width of the nanofibers were taken using the section Particle Analysis tool provided with the AFM software (Asylum Research).

TEM investigations were performed under a way similar to AFM. A drop of the solution (20 μ L) was placed on a copper grid for 1 min and then blotted with filter paper to remove excess solution. TEM observations were carried out on a JEM-2100F operating at 200 kV accelerating voltage.

Emission and CPL analyses: Taking the photoluminescence (PL) and circularly polarized luminescence (CPL) spectra of poly(**1**₂₀-*b*-**5**₁₀₀) as an example. Put the THF solution of poly(**1**₂₀-*b*-**5**₁₀₀) ($c = 0.1$ 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, excited by UV light at 390 nm. A drop-coated films prepared on a quartz substrate (Daico MFG, USQ-grade) from a THF solution of the copolymers (ca. 40 mg mL⁻¹) 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.

5. NMR spectrum of compound 2

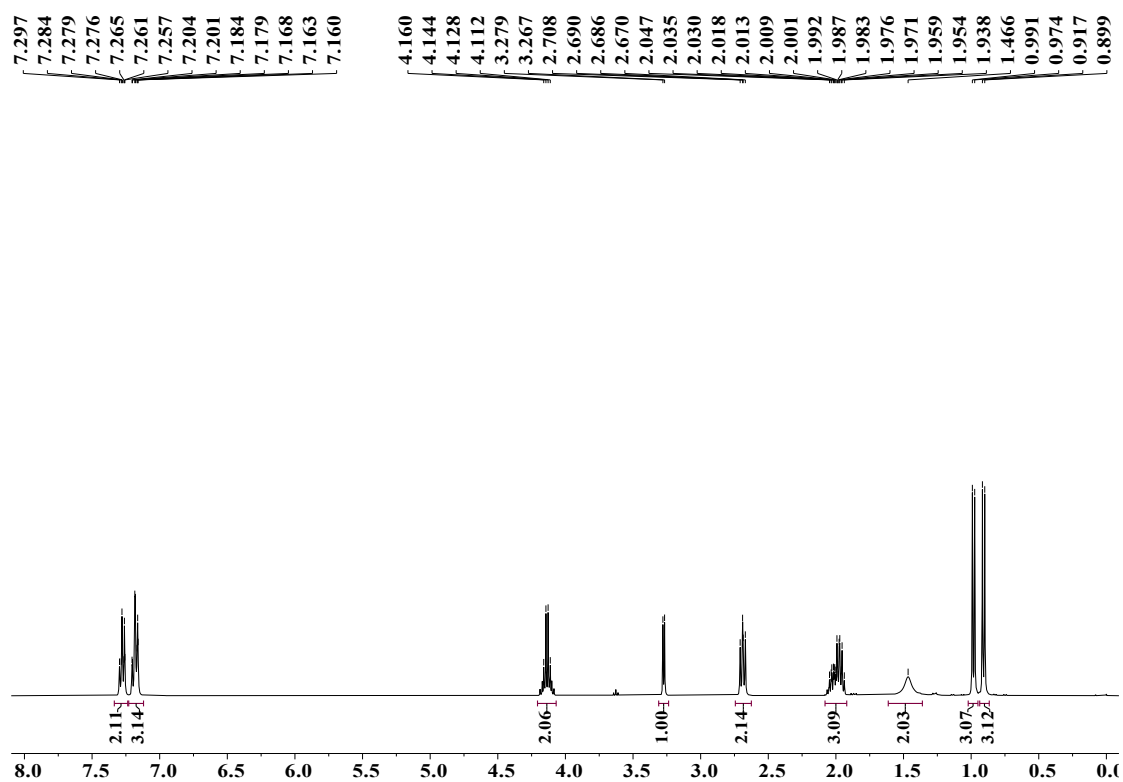


Fig. S1. ^1H NMR (400 MHz, CDCl_3) spectrum of compound 2.

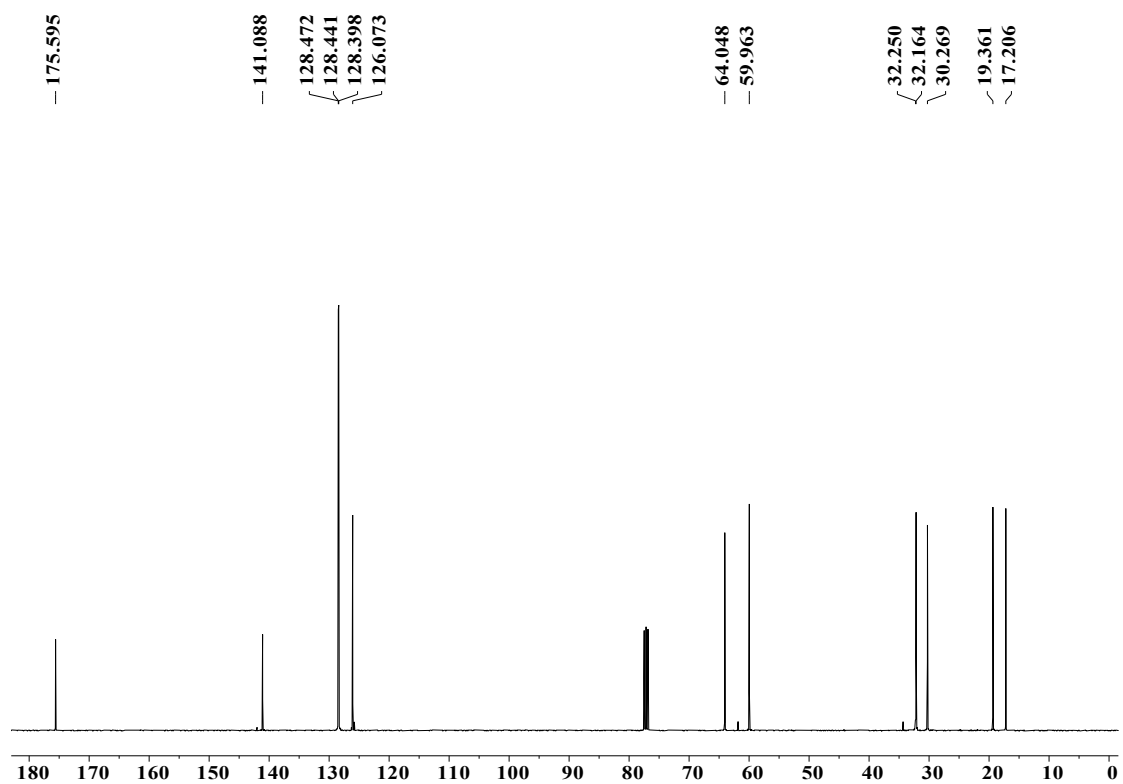


Fig. S2. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound 2.

6. NMR spectrum of compound 3

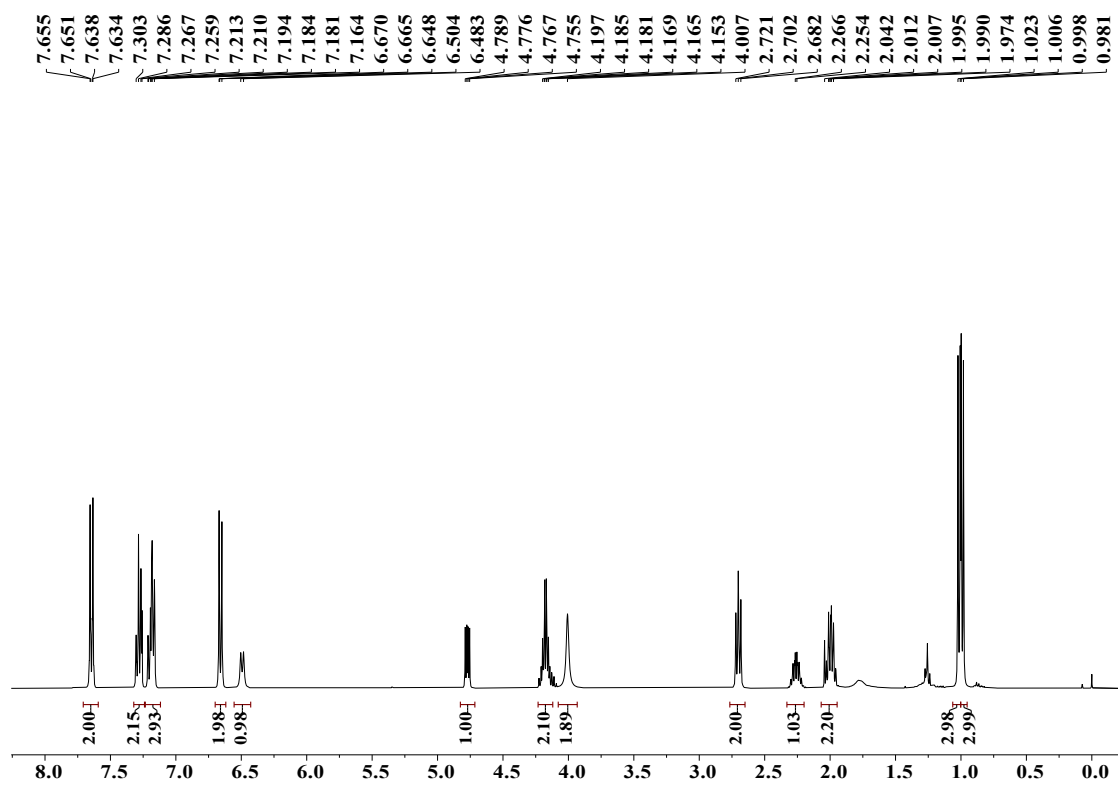


Fig. S3. ^1H NMR (400 MHz, CDCl_3) spectrum of compound 3.

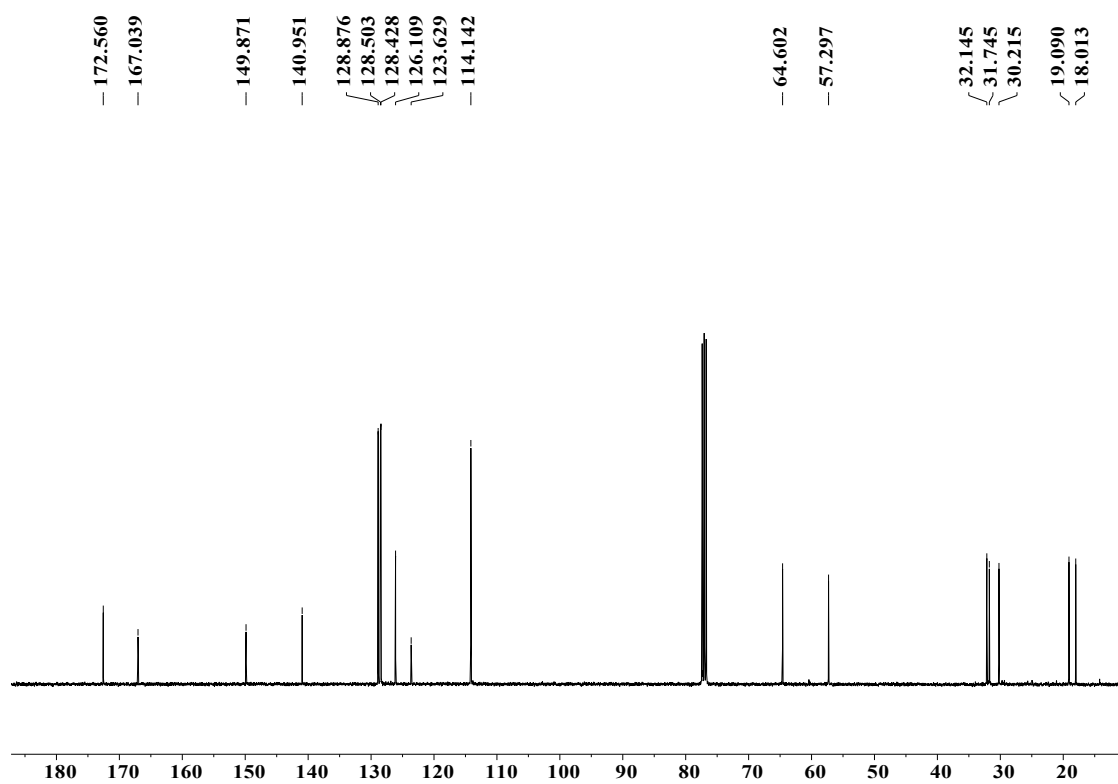


Fig. S4. ^{13}C NMR (100 MHz, CDCl_3) spectrum of compound 3.

7. NMR spectrum of compound 4

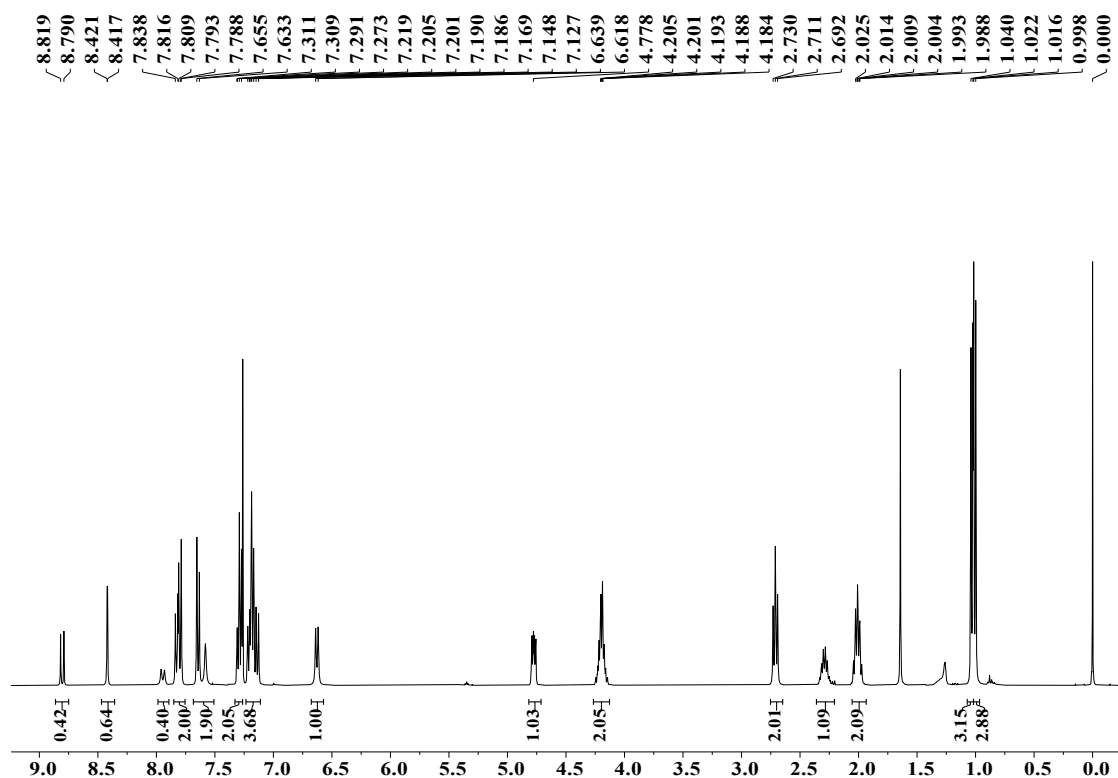


Fig. S5. ¹H NMR (400 MHz, CDCl₃) spectrum of compound 4.

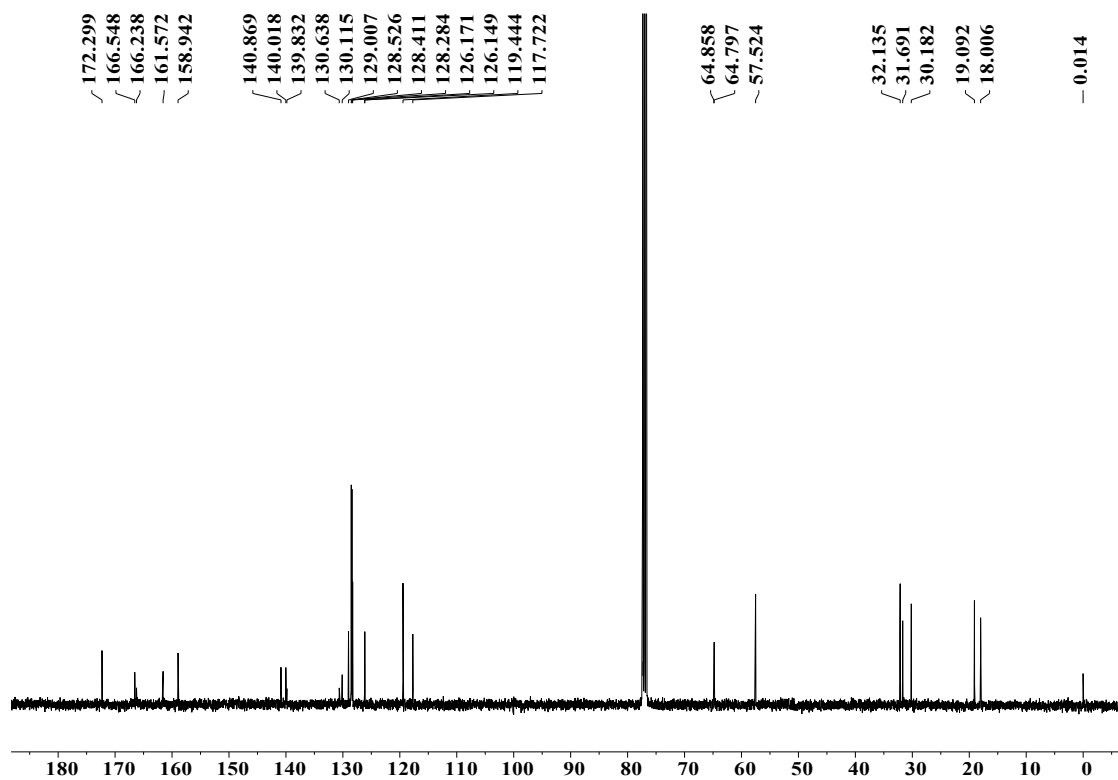


Fig. S6. ¹³C NMR (100 MHz, CDCl₃) spectrum of compound 4.

8. NMR spectrum of monomer 5

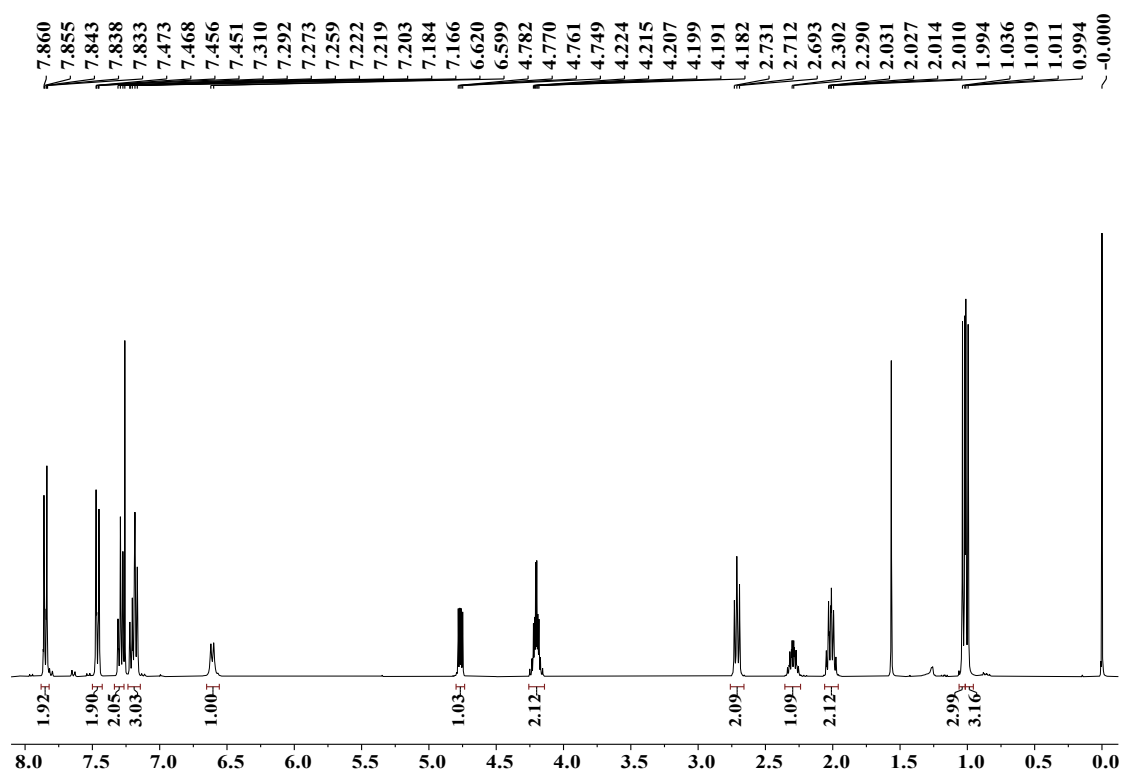


Fig. S7. ^1H NMR (400 MHz, CDCl_3) spectrum of monomer 5.

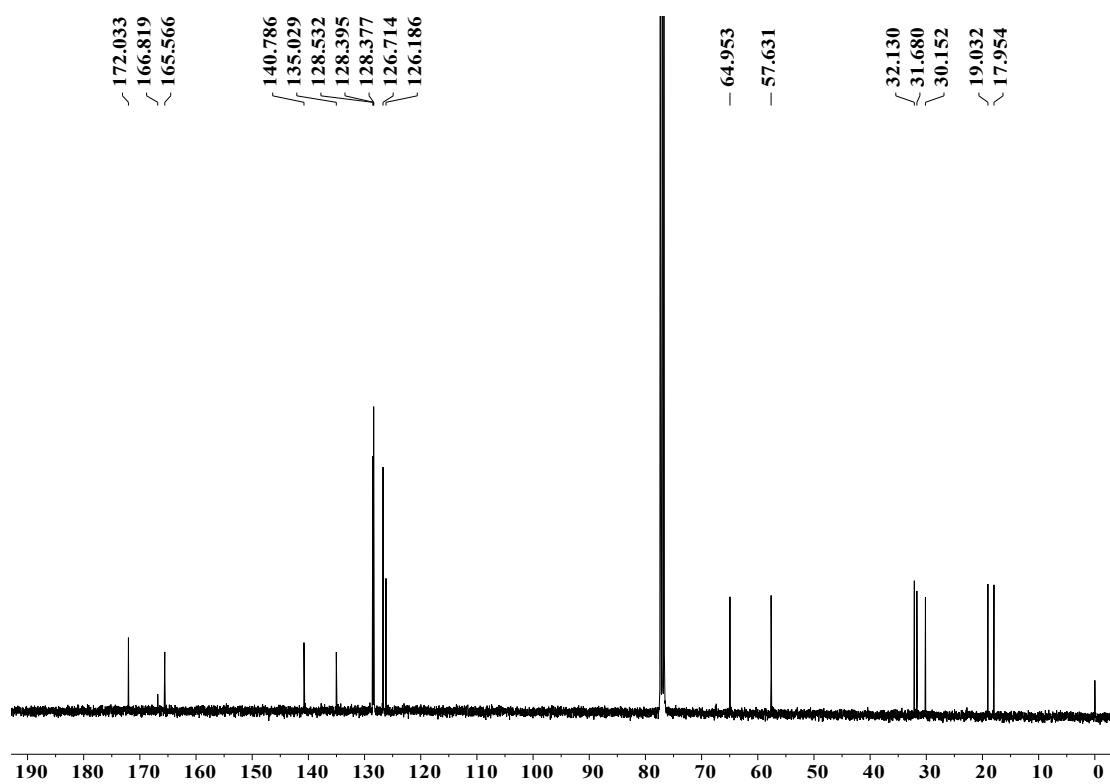


Fig. S8. ^{13}C NMR (100 MHz, CDCl_3) spectrum of monomer 5.

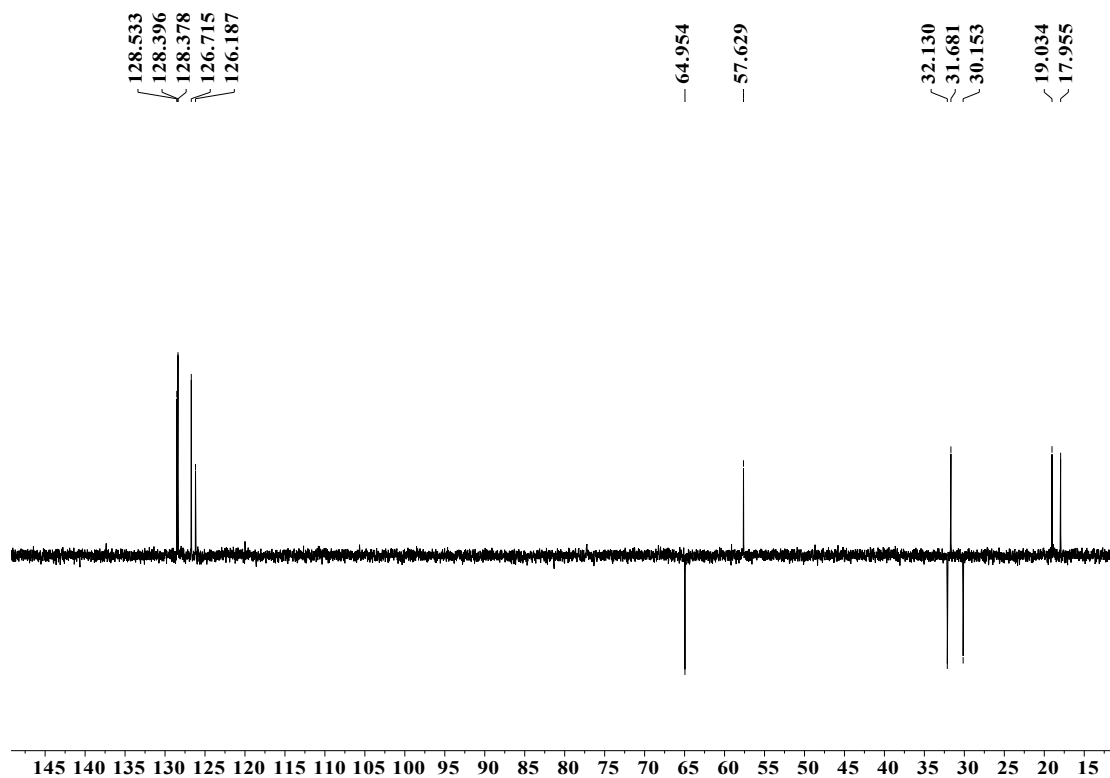


Fig. S9. DEPT 135 ^{13}C NMR (100 MHz, CDCl_3) spectrum of monomer **5**.

9. NMR spectrum of diblock copolymers

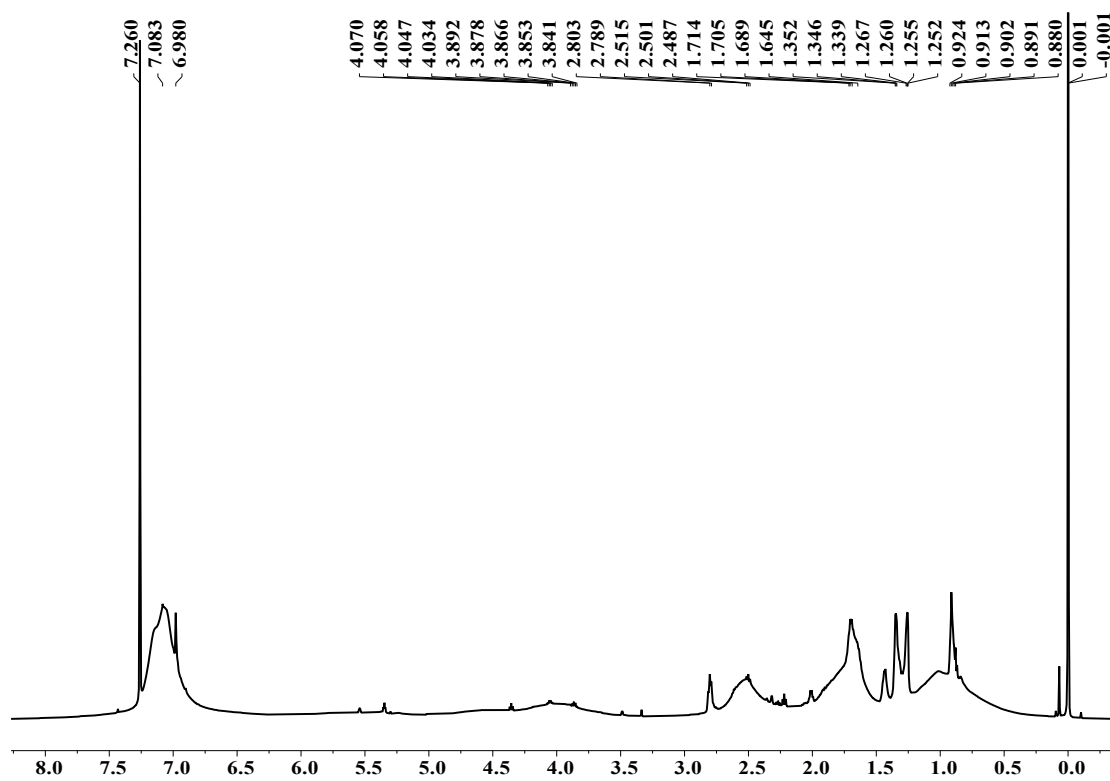


Fig. S10. ^1H NMR (400 MHz, CDCl_3) spectrum of diblock copolymer **poly(1₂₀-b-5₁₅₀)**.

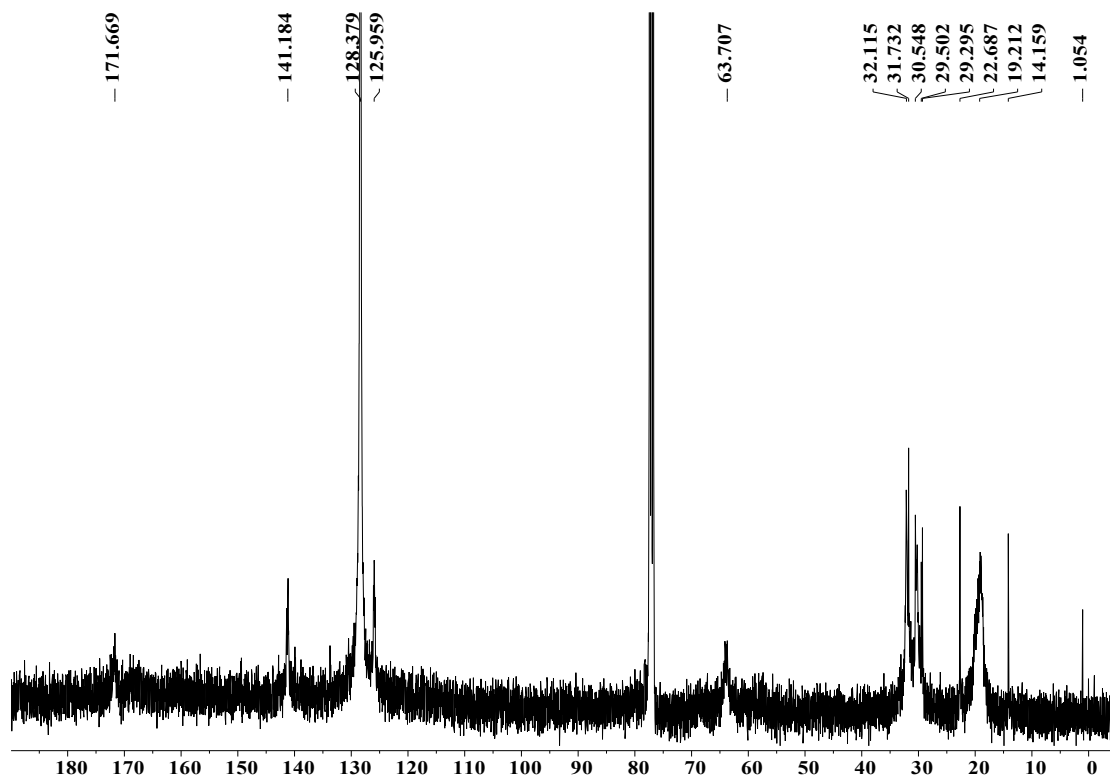


Fig. S11. ^{13}C NMR (100 MHz, CDCl_3) spectrum of diblock copolymer $\text{poly}(1_{20}\text{-}b\text{-}5_{150})$.

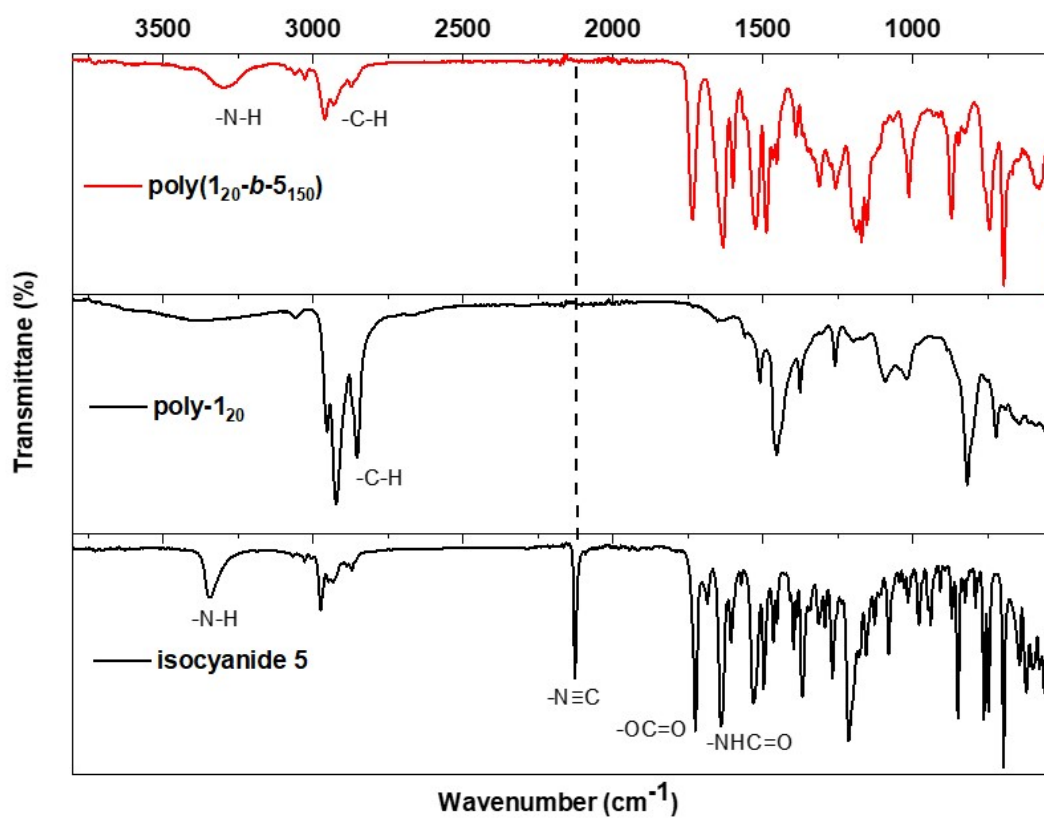


Fig. S12. FT-IR spectrum of diblock copolymer $\text{poly}(1_{20}\text{-}b\text{-}5_{150})$.

10. Time-dependent SEC analyses

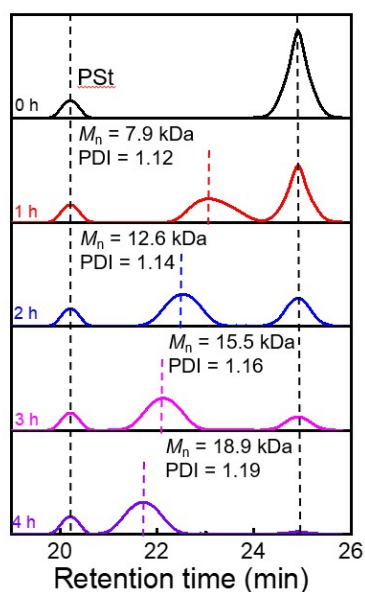


Fig. S13. Time-dependent SEC for Ni(dppp)Cl-catalyzed **5** polymerization ($[\mathbf{5}]_0/[\text{Ni}]_0 = 100$, THF, 55 °C) using polystyrene (PSt) as the internal standard.

11. TGA curves and DSC curves of polymer and diblock copolymers

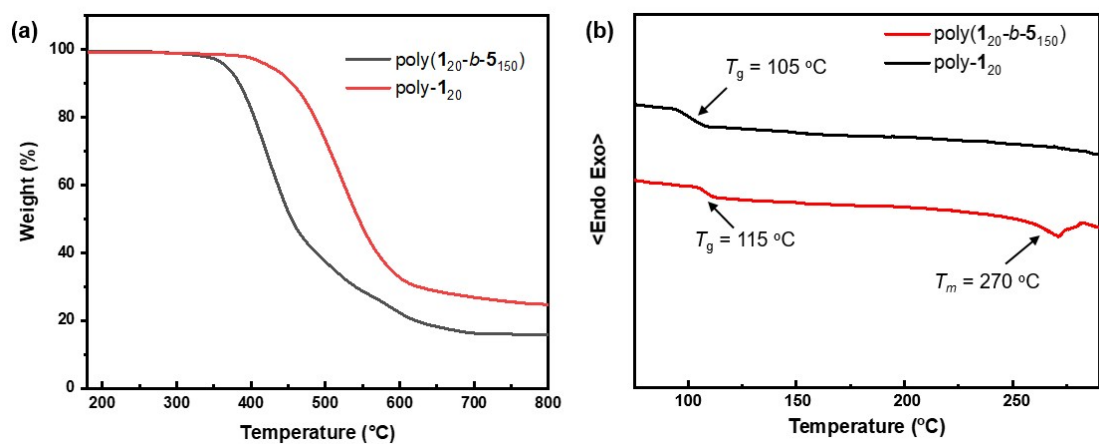


Fig. S14. (a) TGA curves of poly-**1**₂₀ and poly(**1**₂₀-*b*-**5**₁₅₀). (b) DSC curves of poly-**1**₂₀ and poly(**1**₂₀-*b*-**5**₁₅₀) (recorded under nitrogen atmosphere at a heating rate of 10 °C/min).

12. AFM images of assembled poly(1_{20} - b - 5_{150}) diblock copolymer

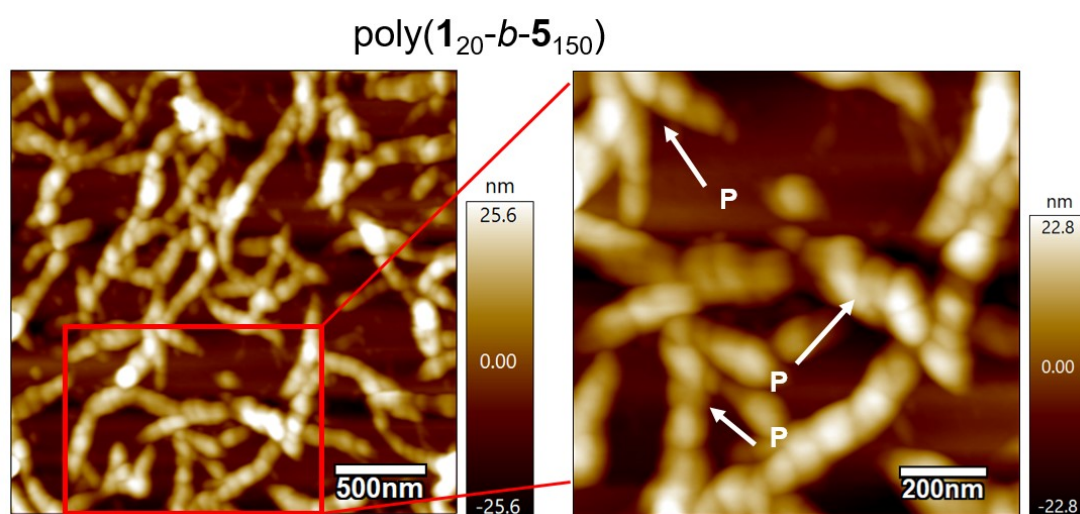


Fig. S15. AFM images of assembled poly(1_{20} - b - 5_{150}) diblock copolymer casted from THF solution (0.5 mg/mL).

13. SEM images of poly(1_{20} - b - 5_n) diblock copolymers

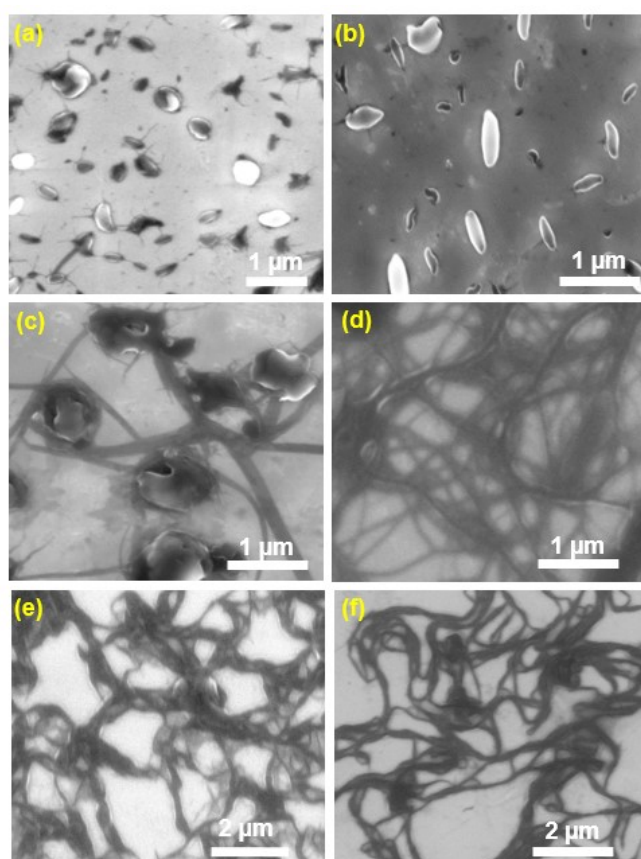


Fig. S16. FESEM images (a-f) of poly(1_{20} - b - 5_n) diblock copolymers micelles obtained in THF at 0.1 mg/mL, where $n=30$ (a), 50 (b), 80 (c), 100 (d), 150 (e) and 200 (f).

14. DLS curves of poly(1_{20} - b - 5_n) diblock copolymers

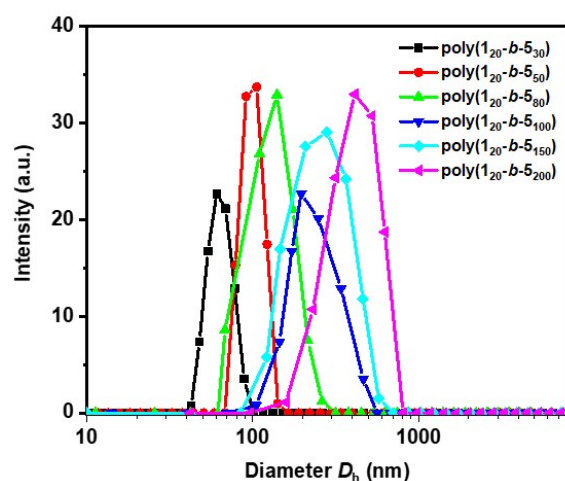


Fig. S17. DLS curves of poly(1_{20} - b - 5_n) diblock copolymers with different degrees of polymerization measured in THF ($c = 0.2$ mg/mL).

15. UV-vis absorption spectra of poly(1_{20} - b - 5_n) diblock copolymers

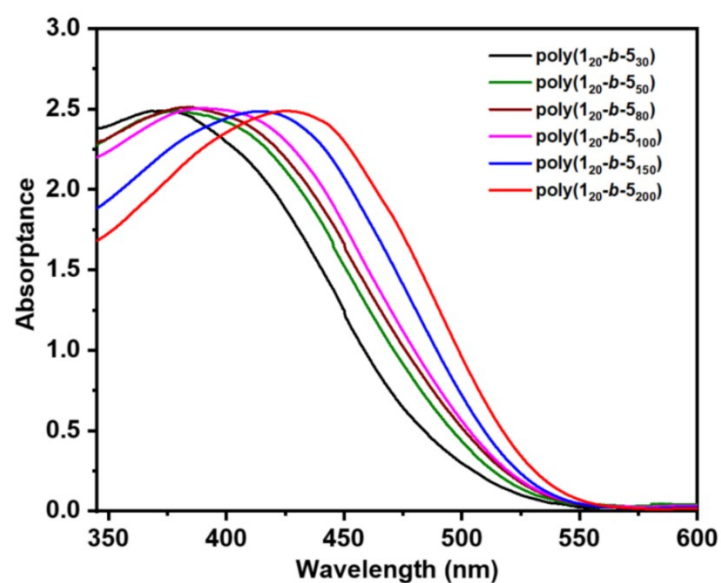


Fig. S18. UV-vis absorption spectra of poly(1_{20} - b - 5_n) diblock copolymers in THF ($c = 0.1$ mg/mL).

16. Polarized optical micrograph (POM) of poly(1_{20} - b - 5_{150})

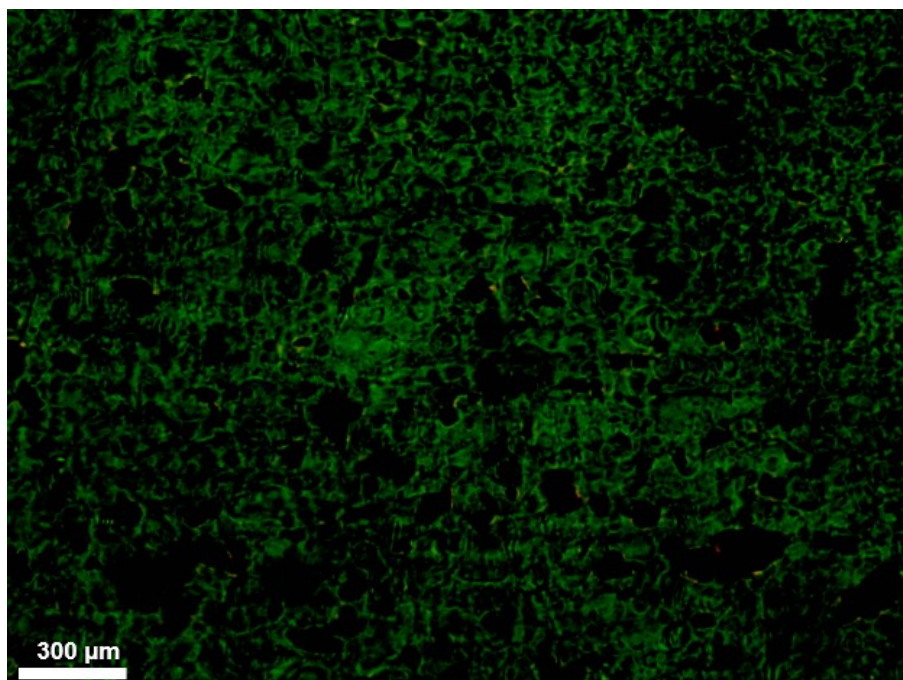


Fig. S19. POM of a lyotropic liquid crystalline phase of poly(1_{20} - b - 5_{150}) in CH_2Cl_2 solution (*ca.* 12.0 wt %) taken at room temperature.

References

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