Supplementary Information (SI) for Polymer Chemistry.

Supporting information

Living Polymerization of an Amphiphilic Helical Aramid Diblock Copolymer

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Materials and instrumentation

Materials

Aniline, anhydrous pyridine, anhydrous potassium carbonate, anhydrous tris(o-tolyl)phosphine and Pd on carbon (10 wt.% loading) were purchased from Sigma Aldrich and used without further purification. Dry dichloromethane, dry chloroform, dry N,N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAc) and 1M iodine monochloride solution in dichloromethane were purchased from Acros Organics and used without further purification. 2,4-Difluoro-5-nitrobenzoic acid was purchased from Fluorochem. Rest of the reagents and solvents were purchased from Sigma-Aldrich or Acros Organics and used without further purification. Methyl 2,4-dihydroxy-5-nitrobenzoate and 15-bromo-2,5,8,11-tetraoxapentadecane were synthesized according to our previous report.[1] Deuterated solvents (CDCl3 and DMSO-d6) were purchased from Cambridge Isotope Laboratories, Inc. Polymerization was performed in flame-dried glassware under argon atmosphere. Polysterene latex spheres (PCS control L100) with 100 nm diameter were purchased from Beckman Coulter Inc.

Instrumentation

All ^{1}H NMR, ^{13}C NMR, ^{31}P and ^{19}F NMR spectra were recorded on either a Bruker Avance III 300 MHz or a Bruker Avance III 400 MHz FT NMR spectrometer. Chemical shifts were given in ppm relative to the residual solvent peak (CDCl3: 7.27 for ^{1}H; CDCl3: 77.16 for ^{13}C; DMSO-d_6: 2.50 for ^{1}H; DMSO-d_6: 39.51 for ^{13}C). HR-MS (ESI+) mass spectra were measured on a Bruker FTMS 4.7T BioAPEX II and a Dionex Ultimate 3000 UHPLC system (ThermoFischer Scientifics, Germering, Germany) connected to a QExactive MS with a heated ESI source (ThermoFisher Scientific, Bremen, Germany); onflow injection of 1 μL sample (c = ca. 50 μg mL−1 in the indicated solvent) with an XRS auto-sampler (CTC, Zwingen, Switzerland); flow rate 120 μL min−1; ESI: spray voltage 3.0 kV, capillary temperature 280 °C, sheath gas 30 L min−1, aux gas 8 L min−1, s-lens RF level 55.0, aux gas temperature 250 °C (N2); full scan MS in the alternating (+)/(−)-ESI mode; mass ranges 80–1'200 m/z, 133–2'000 m/z, or 200–3'000 m/z at 70'000 resolution (full width half-maximum); automatic gain control (AGC) target of 3.00·106; maximum allowed ion transfer time (IT) 30 ms; mass calibration to <2 ppm accuracy with Pierce® ESI calibration solns. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (SEC) with DMF as eluent. The DMF SEC system is an automated Agilent 1260 Infinity II HPLC system equipped with one Agilent PolarGel M guard column (particle size = 8 µm) and two Agilent PolarGel M columns (ID = 7.5 mm, L = 300 mm, particle size = 8 µm). Signals were recorded by an interferometric refractometer (Agilent 1260 series). Samples were measured using DMF + 0.05M LiBr as the eluent at 60 °C and a flow rate of 1.0 mL/min. The DMF SEC systems were calibrated with weight poly(styrene) standards in a range from $10^3$to 3×10^6 Da. The polymers were purified by JAI LC-9130 recycling GPC with $CHCl_3$ as the eluent. The system consisted of two linear Jaigel-2H and Jaigel-1H columns. Signal detection was performed with a UV 600 Next detector. All polymer samples were filtered through a PTFE syringe membrane filter (0.45 µm pore size, VWR) prior to injection. Slow additions of the monomers into the reaction mixtures were conducted using a syringe pump (World Precision Instruments, SP100iZ) equipped with a BD syringe and a needle measuring 0.8 mm in diameter.

AFM sample preparation

The polymer was solubilized in HPLC grade water. For SEM and AFM imaging, a drop of 5 µL was deposited onto a silicon wafer (Siltronix, Archamps, France) and air-dried over a period of 12 hours before imaging and measurement.

AFM measurement

AFM images were taken with the use of a Park NX10 instrument (Park Systems Corp., Suwon, Korea), equipped with Smart Scan software version 1.0 RTM. All measurements were performed in an acoustic enclosure (JPK Instruments AG, Berlin, Germany) equipped with antivibration table (e-Stable mini, Kurashicki Kako Co., LTD, Okayama, Japan). Tips used for imaging were TAP300AL-G (Budget Sensors, Sofia, Bulgaria) with declared tip radius of less than 10 nm. All images were taken in tapping mode, scanning rate of 0.5± 0.3 Hz and with imaging size of 1024x1024 or 2048x2048 pixels. Raw data was elaborated with the use of XEI software (Park Systems). Height profiles were obtained with the Gwyddion software.

Multi-angle depolarized epolarized dynamic light scattering DDLS

Multi-angle DDLS was performed with a light scattering goniometer (CGS-8F, ALV Langen, Germany), equipped with a solid-state laser (Coherent Verdi V5, 532 nm wavelength) with single-mode fiber detection optics (OZ from GMP, Zurich, Switzerland), and ALV 7004 correlators (ALV, Langen, Germany). Polarizer filters were set in vertical-horizontal mode. Measurements consisted of 5 accumulations of 20s and were performed in triplicate. The sample concentration was 3 mg/mL in water and the measurement temperature was set as 25°C, with measured angles in the range between 56.0° and 132.5°. Decay rates were extracted from the autocorrelation curves using the 2nd order cumulant analysis.[2] Translational diffusion coefficient D_t and rotational diffusion coefficient D_r were extracted from the linear fit of the plot of decay rate as a function of q^2, with the magnitude of the scattering vector q calculated as Eq.1.

$$q = \frac{4\pi n}{\lambda} sin(\frac{\theta}{2}) \qquad \text{(Eq.1)}$$

Where n is the refractive index of the medium (water), λ is the wavelength of the laser source and θ is the scattering angle.

The Broersma relations for rod-like particles[3] were used to estimate the length and diameter of the particles, by solving the system of equations for D_t and D_r (Eq. 2 and 3) using the experimentally obtained diffusion coefficients as inputs. SciPy package[4] was used to find a numerical solution.

$$D_t = \frac{k_b T}{3\pi\eta L}(\delta - \frac{\gamma_\perp + \gamma_\parallel}{2}) \qquad \text{(Eq.2)}$$

$$D_r = \frac{3k_b T}{\pi\eta L^3}(\delta - \xi) \qquad \text{(Eq.3)}$$

Where k_b is the Boltzmann's constant, T is the absolute temperature, η is the viscosity of the solvent, L is the cylinder length, and:

$$\delta = \ln\left(\frac{2L}{D}\right) \qquad \text{(Eq.4)}$$

$$\gamma_\perp = -0.193 + \frac{0.15}{\delta} + \frac{8.1}{\delta^2} - \frac{18}{\delta^3} + \frac{9}{\delta^4} \qquad \text{(Eq.5)}$$

$$\gamma_\parallel = 0.807 + \frac{0.15}{\delta} + \frac{13.5}{\delta^2} - \frac{37}{\delta^3} + \frac{22}{\delta^4} \qquad \text{(Eq.6)}$$

$$\xi = 1.14 + \frac{0.2}{\delta} + \frac{16}{\delta^2} - \frac{63}{\delta^3} + \frac{62}{\delta^4} \qquad \text{(Eq.7)}$$

Where D is the diameter of the cylinder.

Small angle X-ray scattering (SAXS)

SAXS measurements were performed at the Austrian SAXS beamline at ELETTRA (Trieste, Italy). An X-ray wavelength of 0.154 nm (8 keV) and a sample-to-detector distance of 906.18 mm were used, resulting in a q-range from $0.08 < q < 74.^{-1}$, where $q = 4\pi / \lambda \sin(\theta/2)$, with λ being the wavelength and θ the scattering angle. The 2D SAXS patterns were acquired using a 2D Pilatus3 1M detector (Dectris Ltd, Baden, Switzerland; area 169 x 179 mm^2 with a pixel size of 172 x 172 μm^2), radially integrated into the one-dimensional scattering function *I(q).* Measurements were carried out in 4 repetitions of 15s each, and the average of the repetitions was used. No beam damage was observed between repetitions. A concentration of 3 mg/ml in water was used. A background sample containing water was also measured from which the sample I(q) curve was subtracted.

The model was fitted with a core-shell cylinder model[5] using SasView 5.0.6 software. The core-shell cylinder model is indicated in Eq.8-12:

$$I(q,\alpha) = \frac{scale}{V_s} F^2(q,\alpha)\sin(\alpha) + background \qquad \text{(Eq.8)}$$

$$F(q,\alpha) = (\rho_{core} - \rho_{shell})V_c \frac{\sin\left(q\frac{1}{2}L\cos(\alpha)\right)}{q\frac{1}{2}L\cos(\alpha)} \frac{2J_1(q\,R\sin(\alpha))}{q\,R\sin(\alpha)} + \qquad \text{(Eq.9)}$$

$$(\rho_{shell} - \rho_{solvent})V_s \frac{\sin\left(q(\frac{1}{2}L + T)\cos(\alpha)\right)}{q(\frac{1}{2}L + T)\cos(\alpha)} \frac{2J_1(q\,(R+T)\sin(\alpha))}{q\,(R+T)\sin(\alpha)}$$

$$V_s = \pi(R+T)^2(L+2T) \qquad \text{(Eq.10)}$$

$$V_c = \pi R^2 L \qquad \text{(Eq.11)}$$

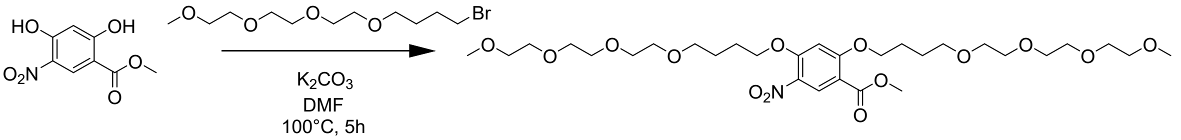
Where α is the angle between the cylinder axis and the vector *q*, *L* corresponds to the length of the cylinder and *R* to the radius of the core, V_s is the total volume of the cylinder while V_c is the volume of the core of the cylinder. The thickness of the shell is represented by *T*. The electron densities of the core, shell and solvent are represented by ρ_{core}, ρ_{shell} and $\rho_{solvent}$ respectively. To allow for better fit stability, their values were arbitrarily set $\rho_{core} = \rho_{solvent} - 5$ and $\rho_{shell} = \rho_{solvent} + 5$. J_1 is the Bessel function of first order. *background* is an additive constant which was set as 0.02. To account for cylinders at all orientations in solution, the form factor is integrated from 0 to 90° as shown in Eq. 12.

$$F^2(q) = \int_0^{\frac{\pi}{2}} F^2(q,\alpha)\sin(\alpha)d\alpha \qquad \text{(Eq.12)}$$

Supplemental experimental procedures

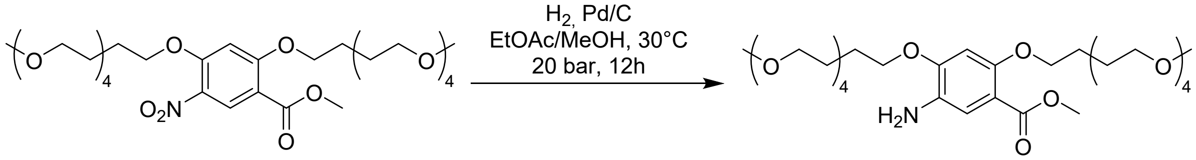
Synthesis of monomers

Synthesis of methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-nitrobenzoate



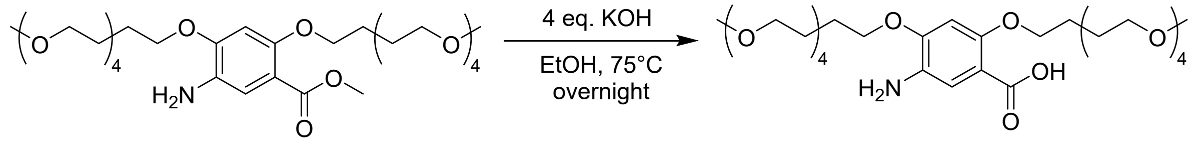
Methyl 2,4-dihydroxy-5-nitrobenzoate (5.00 g, 1 Eq, 23.5 mmol), 15-bromo-2,5,8,11-tetraoxapentadecane (18.2 g, 2.6 Eq, 61.0 mmol) and potassium carbonate (19.5 g, 6 Eq, 141 mmol) were mixed in dry DMF (70 mL) and heated at 100 °C for 6 h. The excess potassium carbonate was filtrated and washed with DCM. The solvents were removed under reduced pressure. The crude residue was extracted 3x with DCM. The combined organic layers were washed with water and brine, dried over Mg_2SO_4 and concentrated. The crude product was purified using reverse phase Isolera (MeCN:H_2O gradient) and afforded a yellow oil (7.75 g, 51%). ^{1}H NMR (400 MHz, DICHLOROMETHANE-*d*$_2$) δ ppm 8.52 (s, 1 H), 6.53 (s, 1 H), 4.17 (dt, *J*=19.84, 6.28 Hz, 4 H), 3.84 (s, 3 H), 3.45 - 3.62 (m, 28 H), 3.27 - 3.41 (m, 6 H), 1.89 - 2.04 (m, 4 H), 1.74 - 1.89 (m, 4 H). ^{13}C NMR (101 MHz, DICHLOROMETHANE-*d*$_2$) δ ppm 164.69, 164.37, 158.15, 132.29, 131.50, 112.25, 98.73, 72.46, 71.13, 71.07, 70.94, 70.67, 70.45, 70.05, 59.15, 52.40, 26.61, 26.41, 26.36

Synthesis of methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-aminobenzoate



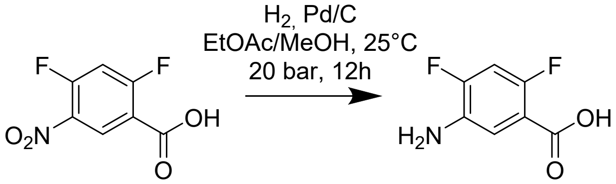
Methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-nitrobenzoate (1.00 g, 1 Eq, 1.54 mmol) was dissolved in a MeOH and ethyl acetate mixture (90:10). Pd/C (10 wt % loading) (0.1 g, 10 wt %) was added and the mixture was stirred and hydrogenated for 12h at 30°C under H_2 atmosphere (20 bar). The crude mixture was filtered through Celite®545 and the filtrate was concentrated under reduced pressure to afford the pure product as a black oil (quantitative). ^{1}H NMR (400 MHz, DICHLOROMETHANE-*d*$_2$) δ ppm 7.16 (s, 1 H), 6.46 (s, 1 H), 4.05 (t, *J*=6.30 Hz, 2 H), 3.96 (t, *J*=6.17 Hz, 2 H), 3.75 - 3.81 (m, 3 H), 3.45 - 3.64 (m, 28 H), 3.33 (s, 6 H), 1.71 - 1.96 (m, 8 H). ^{13}C NMR (101 MHz, DICHLOROMETHANE-*d*$_2$) δ ppm 166.86, 153.63, 151.36, 130.72, 117.34, 112.88, 100.66, 72.47, 71.71, 71.42, 71.26, 71.11, 71.07, 71.01, 70.94, 70.75, 70.66, 68.90, 62.94, 59.15, 54.55, 54.27, 53.73, 53.46, 51.86, 30.66, 27.11, 26.90, 26.84, 26.58. ESI-HRMS m/z (M+H)$^+$: calculated 620.36, found 620.3622.

Synthesis of methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-aminobenzoic acid **5**



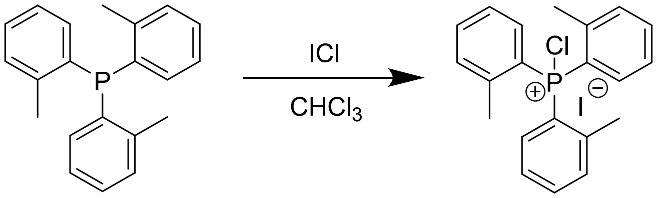
Methyl 2,4-bis((2,5,8,11-tetraoxapentadecan-15-yl)oxy)-5-aminobenzoate (3.7 g, 1 Eq, 6 mmol) and potassium hydroxide (1.3 g, 4 Eq, 23.84 mmol) were mixed in ethanol (60 mL), stirred and heated to reflux at 85°C overnight. The solvent was removed under reduced pressure and water was added. The solution was neutralized (pH = 6) with diluted HCl and then extracted three times with DCM. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography using DCM:MeOH as the eluent (gradually from 100:0 to 92:8) to afford the pure desired product **5** as a brown oil (2.16 g, 60%). ^{1}H NMR (400 MHz, CHLOROFORM-*d*) d ppm 7.48 (s, 1 H), 6.47 (s, 1 H), 4.20 (t, *J*=6.60 Hz, 2 H), 4.08 (t, *J*=6.30 Hz, 2 H), 3.50 - 3.74 (m, 30 H), 3.37 (d, *J*=2.08 Hz, 6 H), 1.86 - 2.04 (m, 4 H), 1.70 - 1.86 (m, 4 H). ESI-HRMS m/z $(M+H)^+$: calculated 606.34, found 606.3473.

Synthesis of 5-amino-2,4-difluorobenzoic acid **7**



2,4-Difluoro-5-nitrobenzoic acid (5.00 g, 1 Eq, 24.6 mmol) was dissolved in a MeOH and ethyl acetate mixture (90:10). Pd/C (10 wt % loading) (0.5 g, 10 wt %) was added and the mixture was stirred and hydrogenated for 12h at 25°C under H_2 atmosphere (20 bar). The crude mixture was filtered through Celite®545 and the filtrate was concentrated under reduced pressure to afford the pure product as a beige solid (quantitative). ^{1}H NMR (400 MHz, DMSO-d_6) d ppm 7.27 (dd, *J*=10.15, 7.46 Hz, 1 H), 7.10 (t, *J*=10.94 Hz, 1 H), 5.21 (br. s., 2 H). ^{19}F NMR (377 MHz, DMSO-d_6) d ppm -122.86 (s, 1 F), -124.03 (s, 1 F). ^{19}F NMR (377 MHz, CHLOROFORM-*d*) d ppm -118.11 (s, 1 F), -119.28 (s, 1 F). ^{13}C NMR (75 MHz, DMSO-d_6) d ppm 164.88, 153.90, 150.62, 133.06, 117.58, 115.24, 104.79. ESI-HRMS m/z $(M+H)^+$: calculated 174.04, found 174.03614.

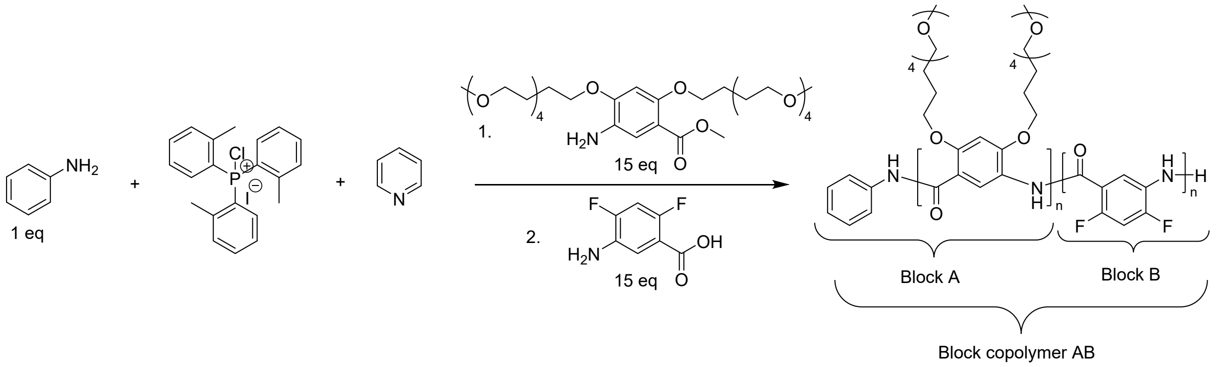
Synthesis of reagent chlorotri-o-tolylphosphonium iodide **PHOS3**



A 50 mL Schlenk flask containing a magnetic stirrer is backfilled with argon 3x. A solution of iodine chloride (1.6 g, 9.9 mL, 1 molar, 1 Eq, 9.9 mmol) in chloroform and 10 mL of dry chloroform are added to the flask. Tri-o-tolylphosphane (3.0 g, 1 Eq, 9.9 mmol) is dissolved in 10 mL of dry chloroform and added slowly (4 mL/h) to the flask with a syringe pump. The solvent is evaporated through the Schlenk line into trappers cooled with liquid nitrogen. Dry pentane (20 mL) is added to the flask to wash the reagent then removed through the Schlenk line. The content of the flask is kept under inert atmosphere. ^{31}P-NMR (400 MHz, CHLOROFORM-d) δ ppm 63.73.

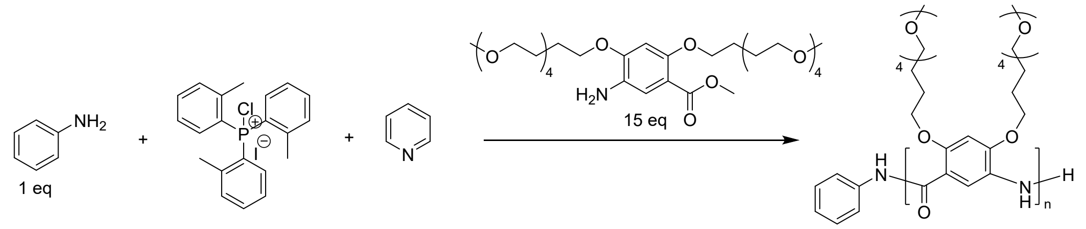
Polymerization protocols

Polymerization of diblock copolymer **AB**



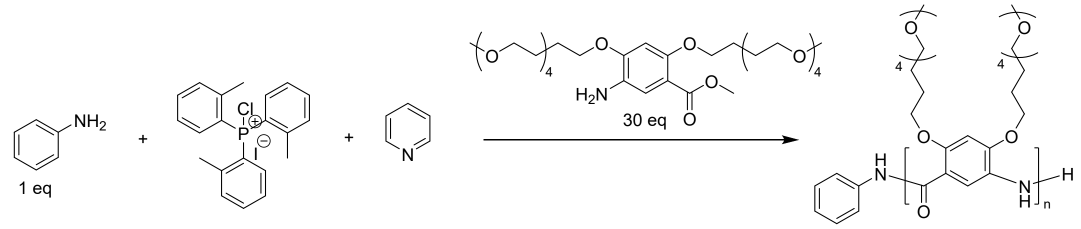
Chlorotri-o-tolylphosphonium iodide **PHOS3** (702 mg, 50 Eq, 1.50 mmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 5.60 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (713 mg, 0.73 mL, 300 Eq, 9.02 mmol) and aniline (2.80 mg, 1 Eq, 30.1 µmol) in 0.1 mL of dry DCM and dry DMAc (3:2) mixture were added to the solution under stirring. In different Schlenk flasks, **5** (273 mg, 15 Eq, 451 µmol) and **7** (78.1 mg, 15 Eq, 451 µmol) were evacuated and backfilled with argon three times. A solution (0.29 M) of **5** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.1 mL/h). Once the addition of **5** was completed, a solution (0.29 M) of **7** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture, also by using a syringe pump (0.1 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude polymer was purified by recycling gel permeation chromatography (chloroform) to afford the purified block copolymer diblock copolymer **AB**. ^{19}F NMR (377 MHz, CHLOROFORM-*d*) δ ppm -117.12, -123.77. ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm -112.39, -112.68.

Polymerization of homopolymer **P1**



Chlorotri-o-tolylphosphonium iodide **PHOS3** (376 mg, 50 Eq, 805 µmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 1.15 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (178 mg, 0.182 mL, 150 Eq, 2.25 mmol) and aniline (1.40 mg, 1 Eq, 30.1 µmol) in 0.1 mL of dry DCM and dry DMAc (3:2) mixture were added to the solution under stirring. In a Schlenk flask, **5** (137 mg, 15 Eq, 225 µmol) was evacuated and backfilled with argon three times. A solution (0.29 M) of **5** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.1 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude polymer was purified by recycling gel permeation chromatography (chloroform) to afford the purified polymer **P1**.

Polymerization of homopolymer **P2**



Chlorotri-o-tolylphosphonium iodide **PHOS3** (176 mg, 25 Eq, 376 µmol) was introduced into a Schlenk flask under inert atmosphere and dissolved in 2.46 mL of dry DCM and dry DMAc (3:2) mixture. Dry pyridine (382 mg, 0.39 mL, 300 Eq, 4.83 mmol) and aniline (1.50 mg, 1 Eq, 16.1 µmol) in 0.1 mL of dry DCM and dry DMAc (3:2) mixture were added to the solution under stirring. In a Schlenk flask, **5** (293 mg, 15 Eq, 483 µmol) was evacuated and backfilled with argon three times. A solution (0.29 M) of **5** in dry DCM and dry DMAc (3:2) mixture was added dropwise to the reaction mixture at RT using a syringe pump (0.1 mL/h). The reaction was quenched with a 1 N HCl solution and extracted with DCM three times. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude polymer was purified by recycling gel permeation chromatography (DMF) to afford the purified polymer **P2**.

SEC (DMF) elugrams

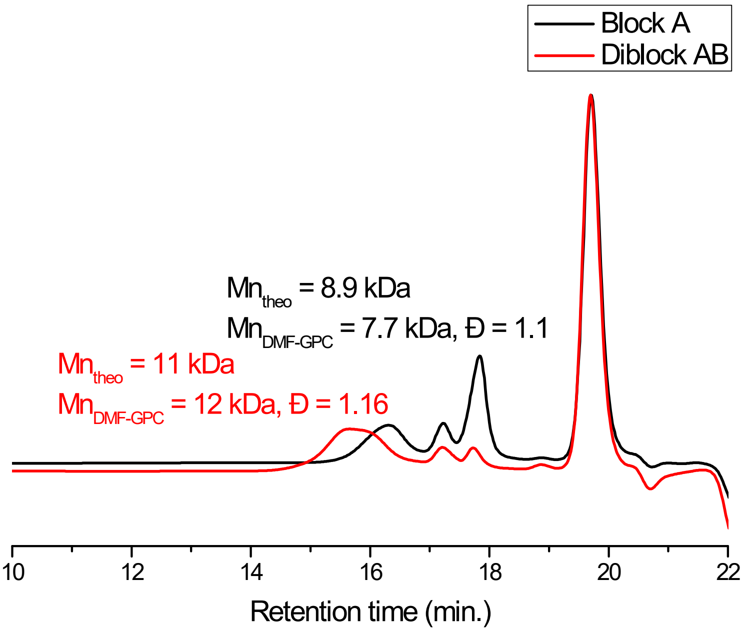


***Figure S1**. GPC (DMF) trace of crude polymer block A (black) and crude diblock AB (red).*

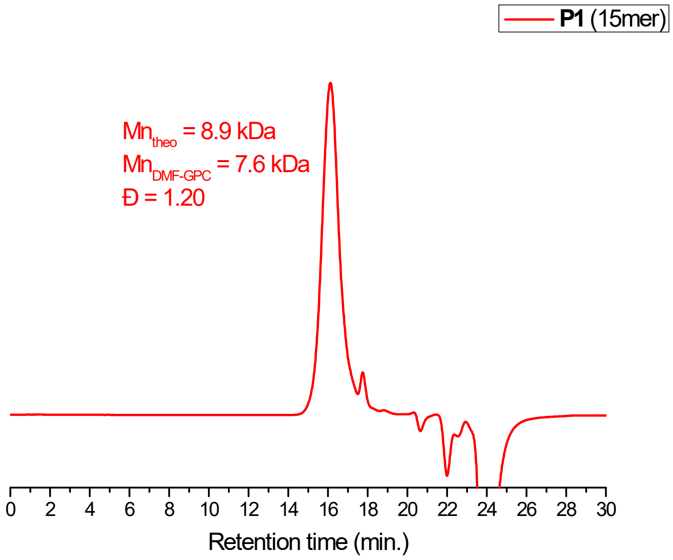


Figure S2. *GPC (DMF) trace of purified homopolymer **P1**.*

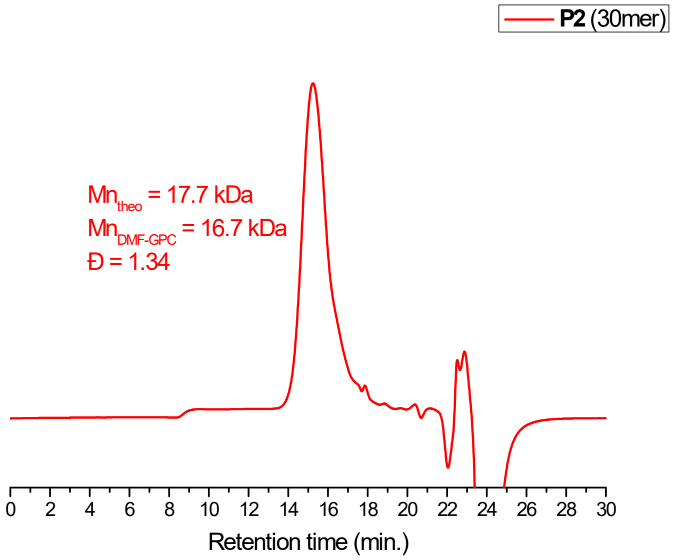


Figure S3. *GPC (DMF) trace of homopolymer **P2**.*

NMR spectra of monomers and of polymers

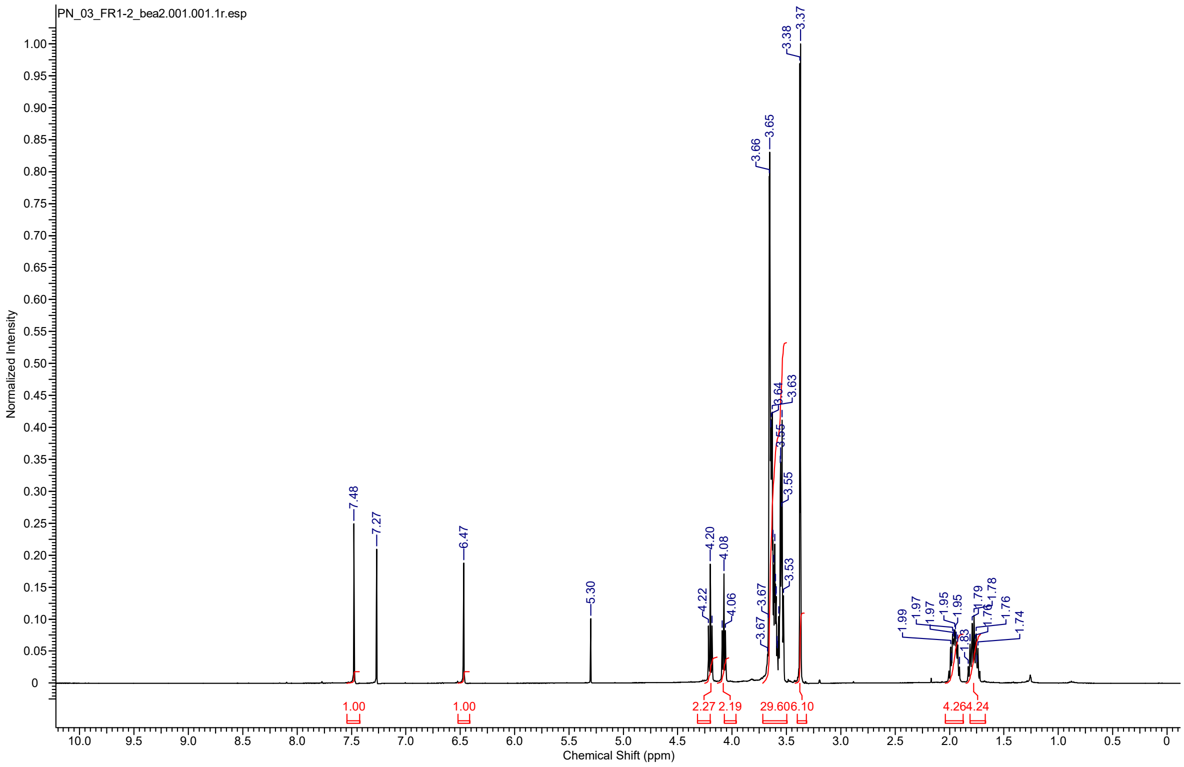


Figure S4. *^{1}H NMR spectrum (400 MHz, $CDCl_3$) of monomer **5**.*

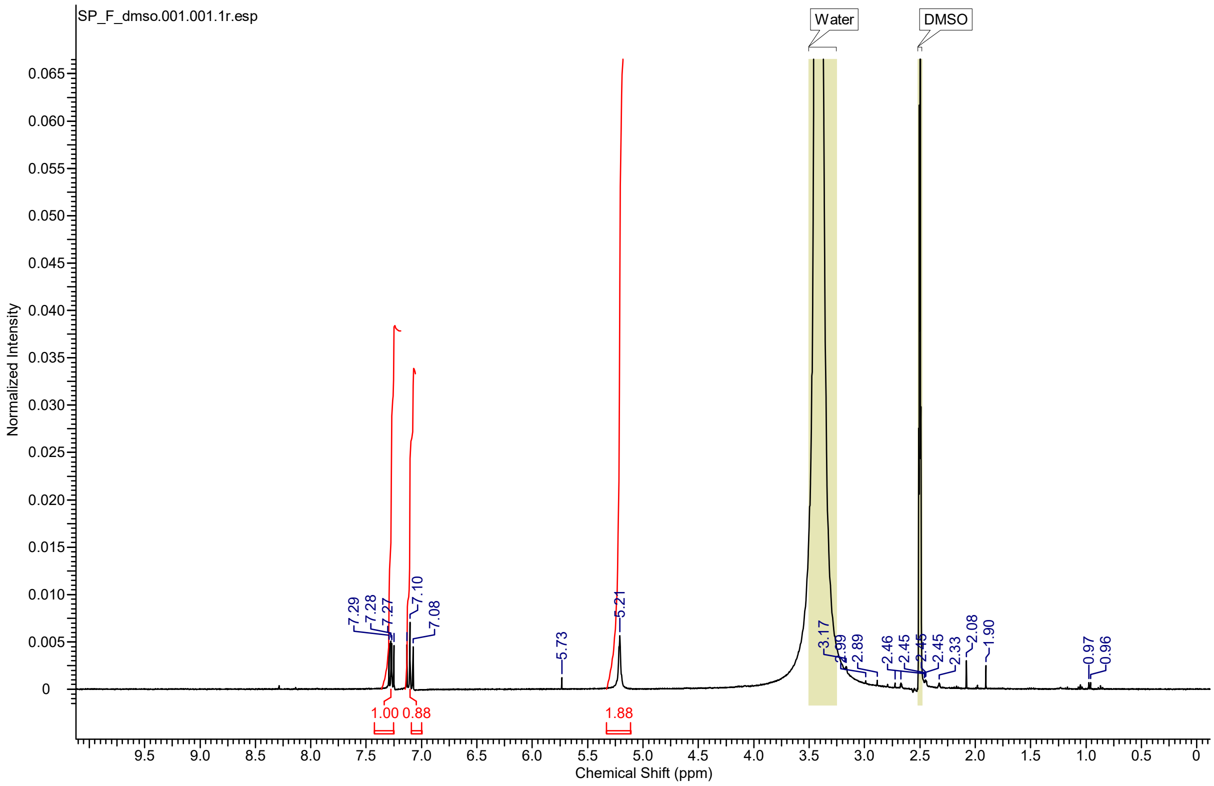


Figure S5. *^{1}H NMR spectrum (400 MHz, DMSO-d_6) of monomer **7**.*

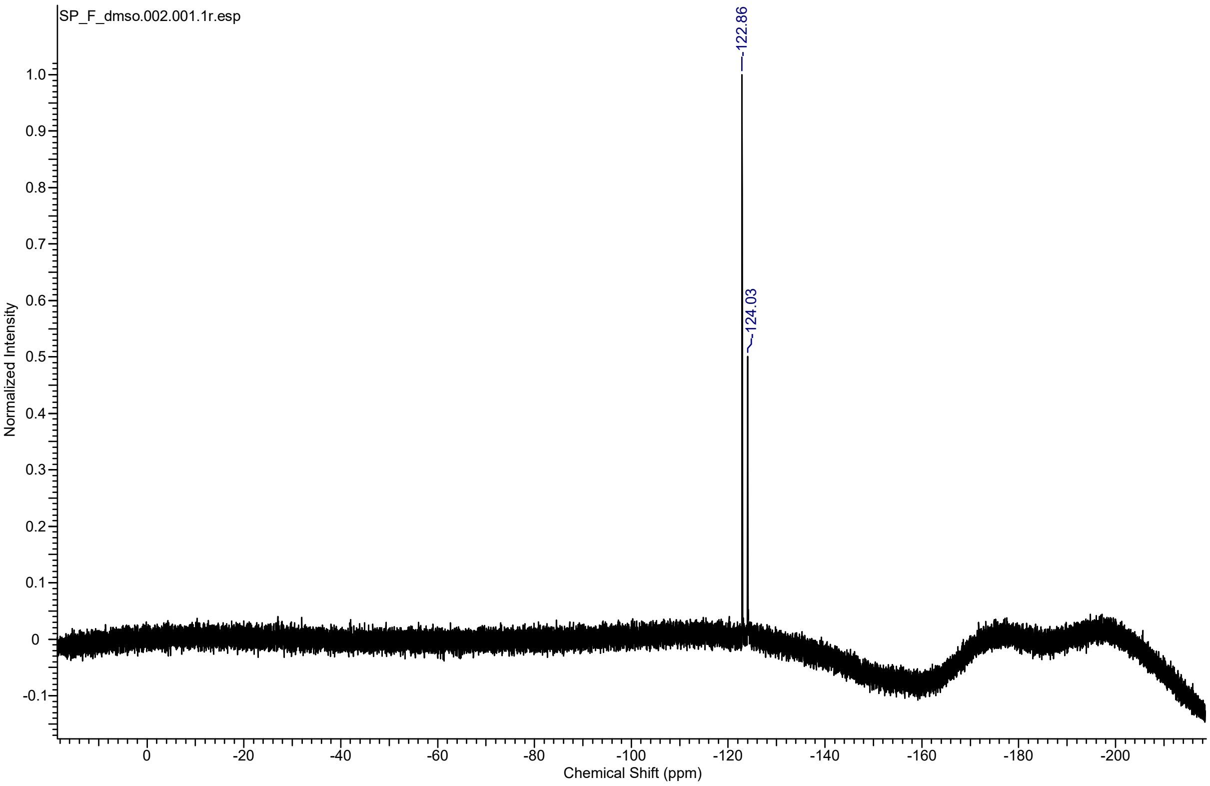


Figure S6. *^{19}F NMR spectrum (400 MHz, DMSO-d_6) of monomer **7**.*

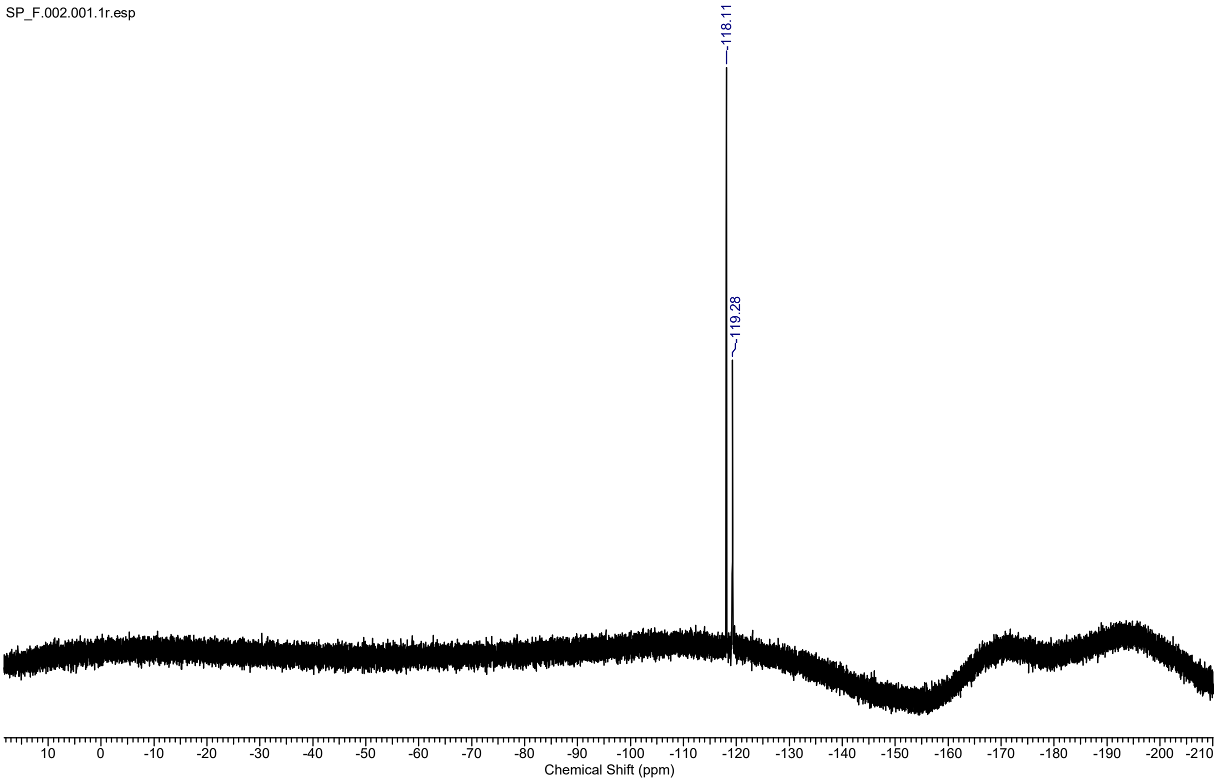


Figure S7. *^{19}F NMR spectrum (400 MHz, $CDCl_3$ + 1 drop of pyridine) of monomer **7**.*

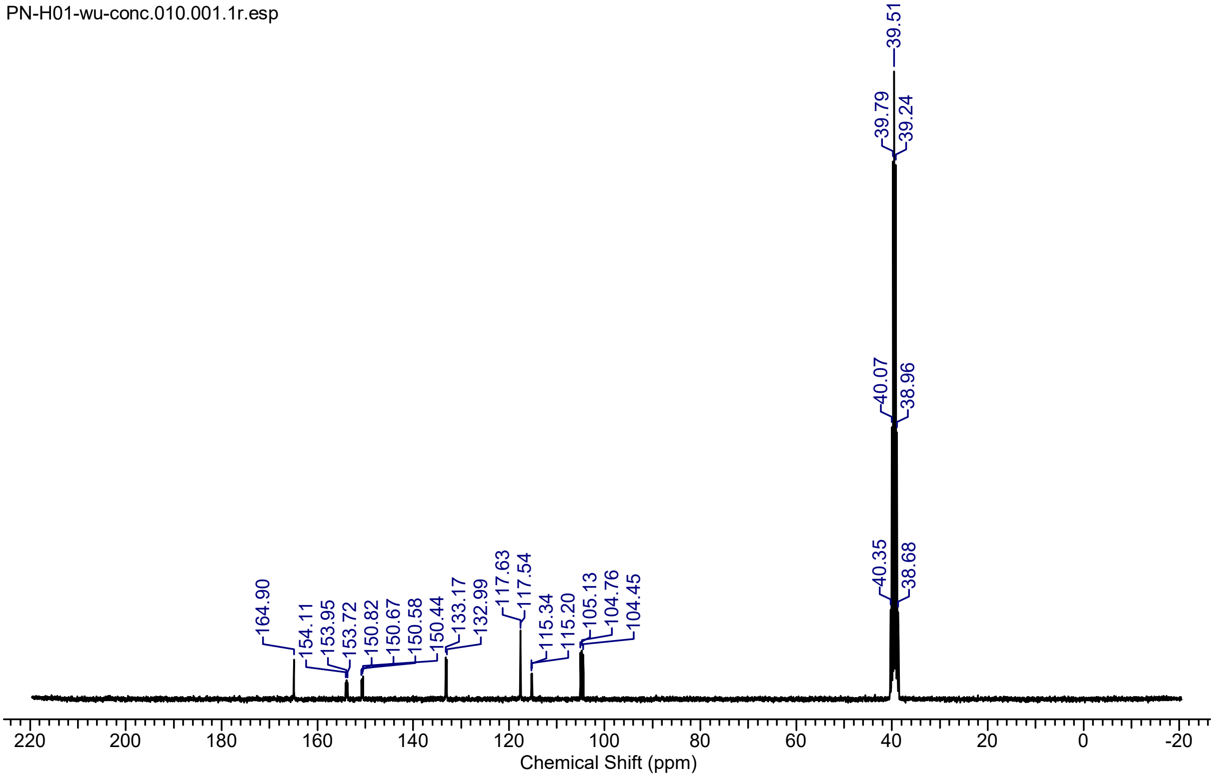


Figure S8. ^{13}C NMR spectrum (300 MHz, DMSO-d_6) of monomer ***7***.

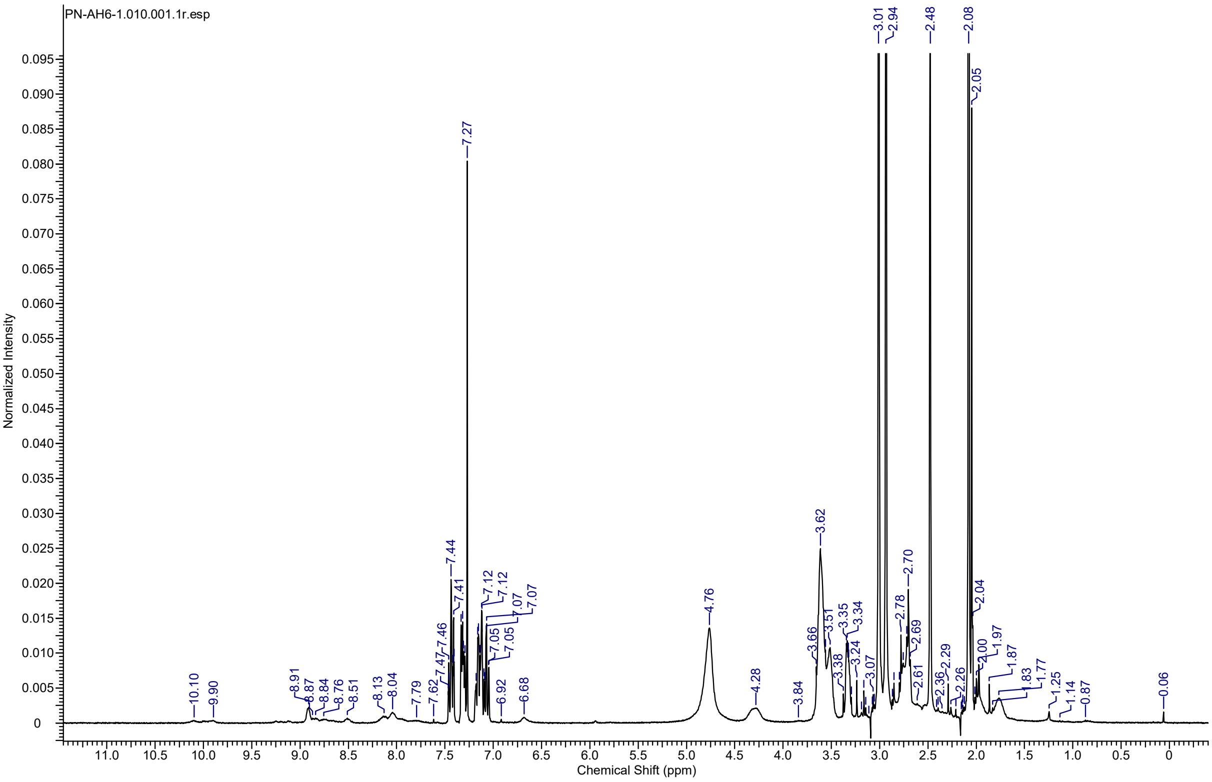


Figure S9. ^{1}H NMR spectrum (300 MHz, CDCl$_3$) of crude polymer block A.

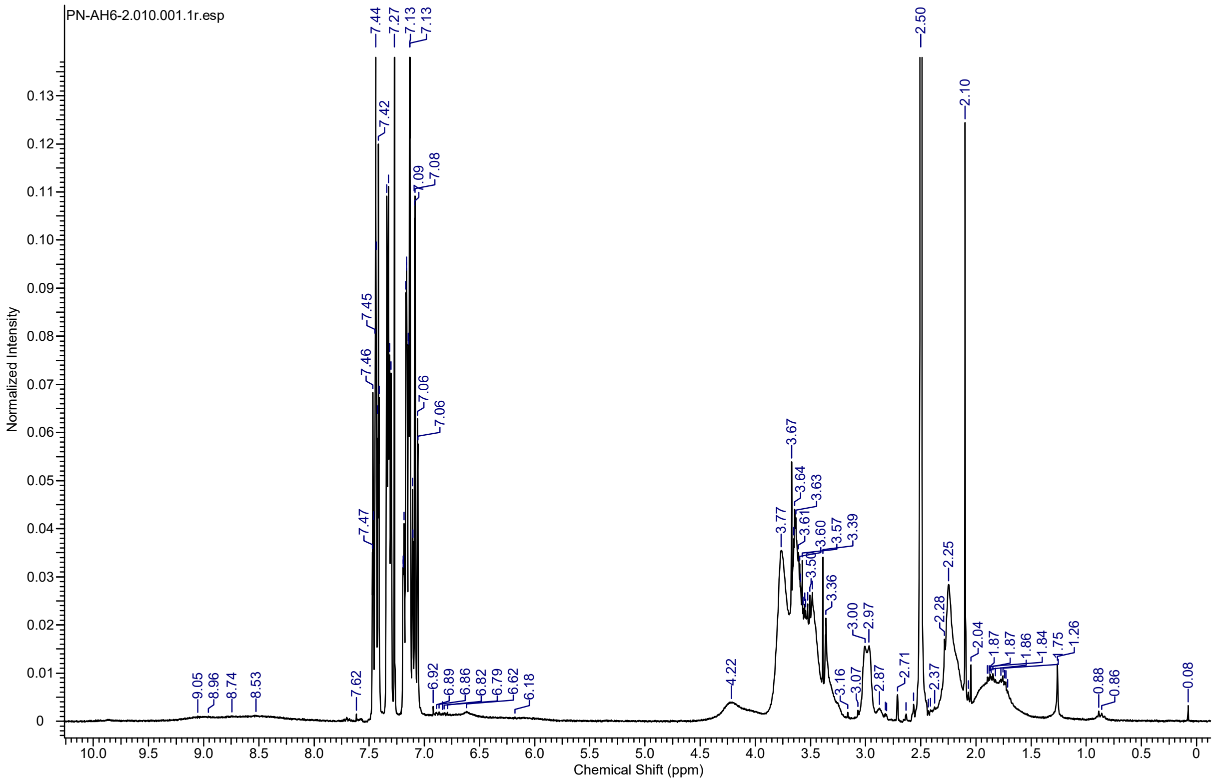


Figure S10. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of crude diblock copolymer **AB**.*

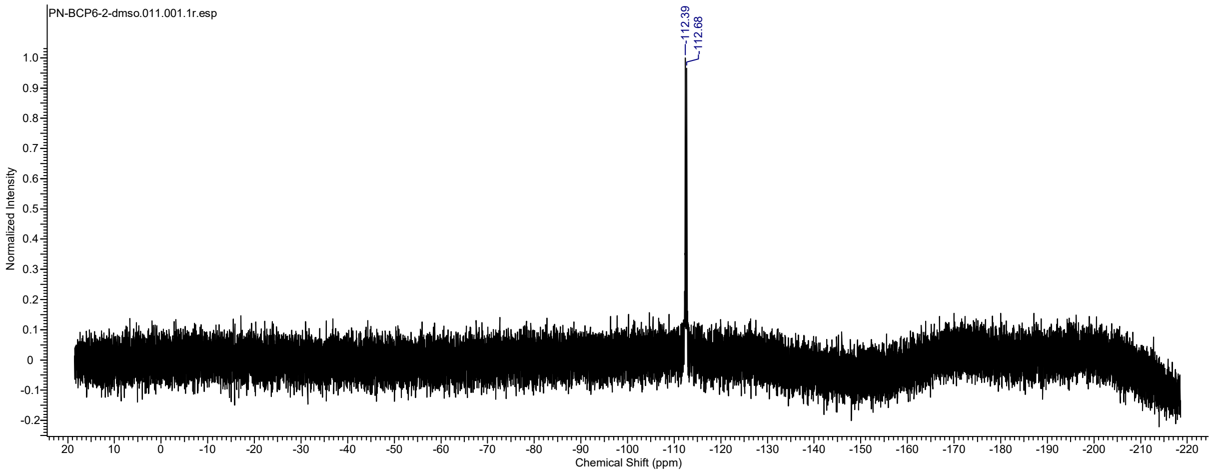


Figure S11. *^{19}F NMR spectrum (300 MHz, DMSO-d_6) of crude diblock copolymer **AB**.*

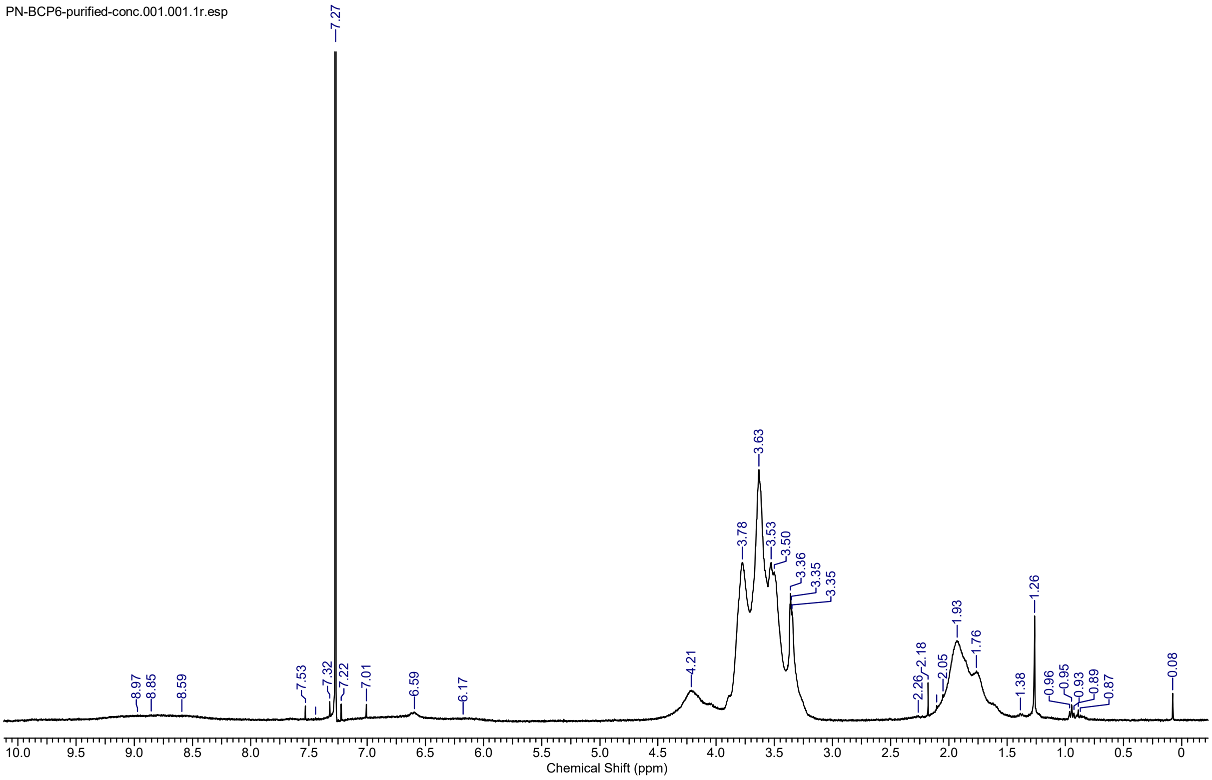


Figure S12. *^{1}H NMR spectrum (400 MHz, CDCl$_3$) of purified diblock copolymer* ***AB****.*

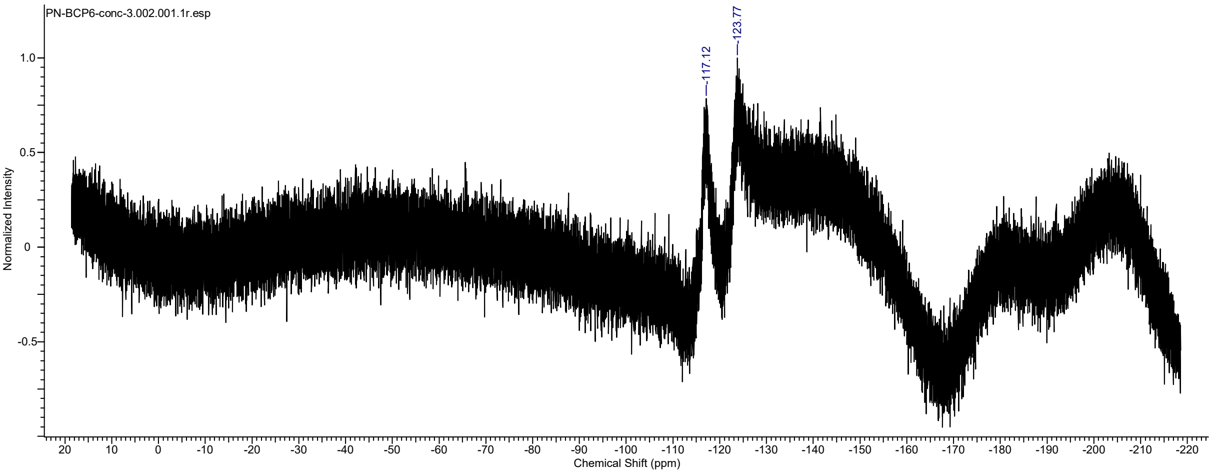


Figure S13. *^{19}F NMR spectrum (400 MHz, CDCl$_3$) of purified diblock copolymer* ***AB****.*

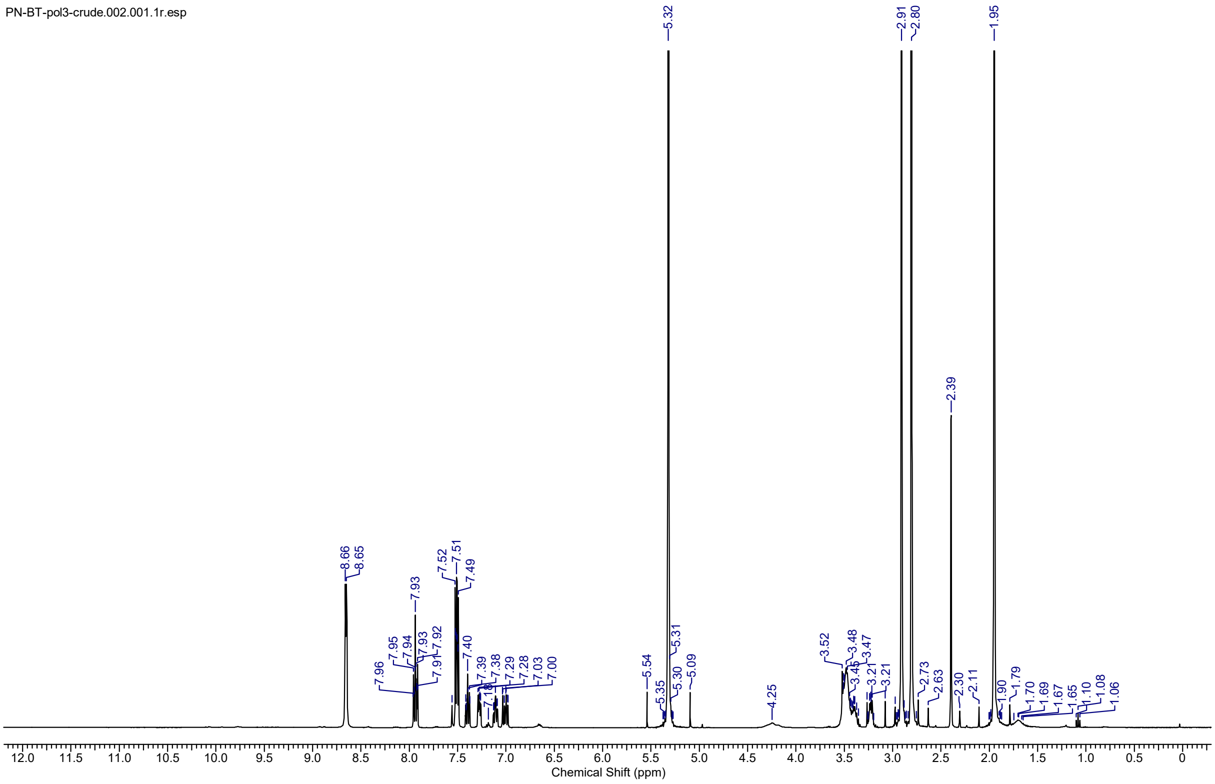


Figure S14. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of crude homopolymer ***P1***.

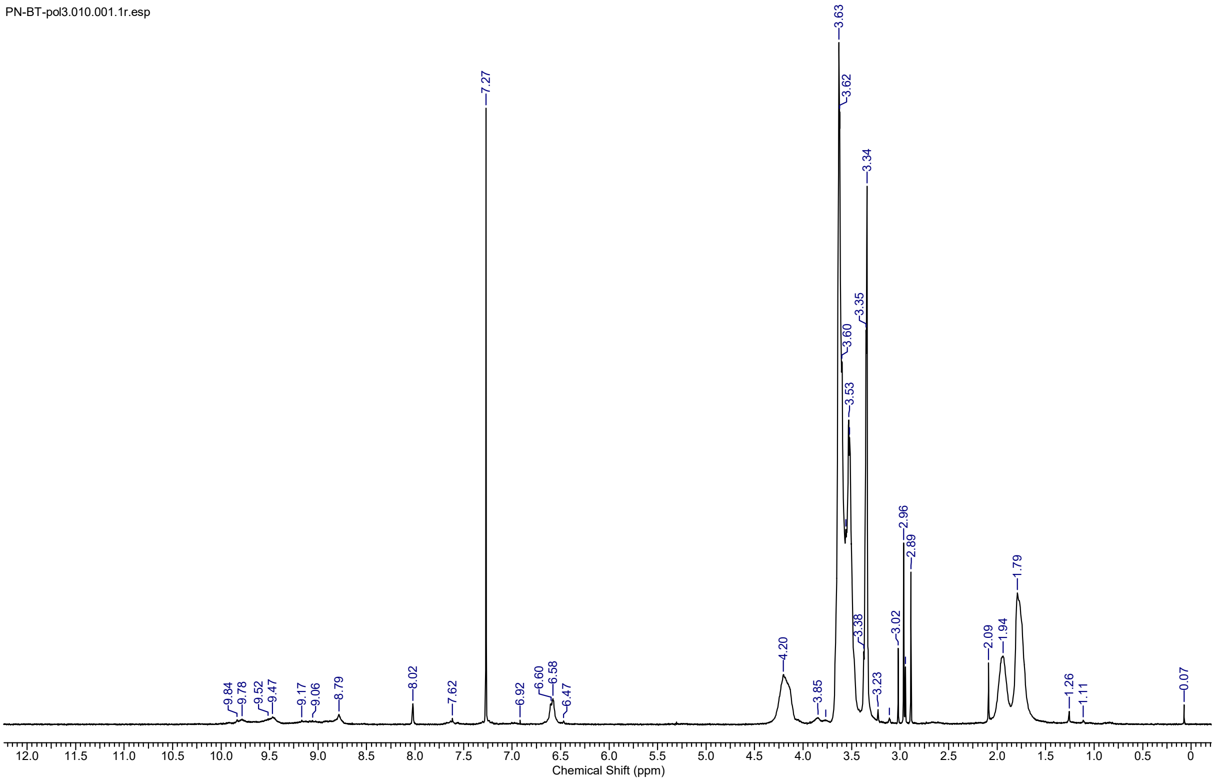


Figure S15. ^1H NMR spectrum (300 MHz, $CDCl_3$) of purified homopolymer ***P1***.

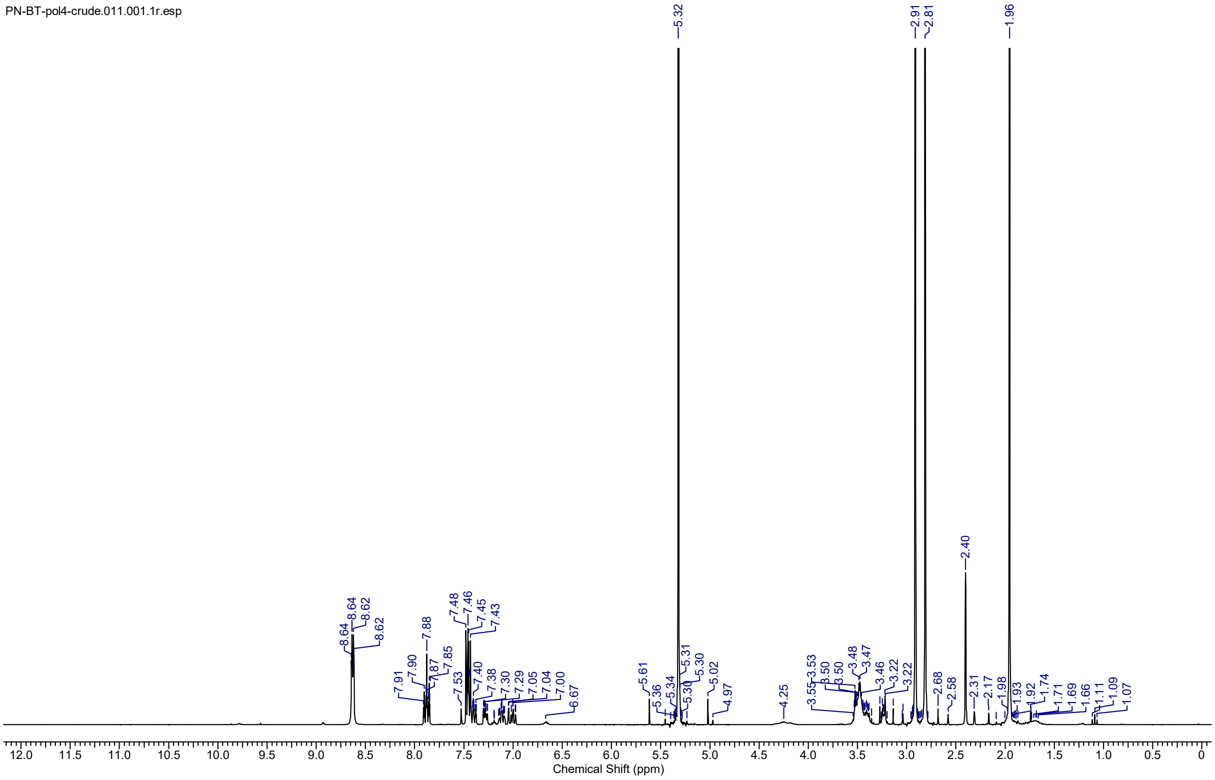


Figure S16. *^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of crude homopolymer **P2**.*

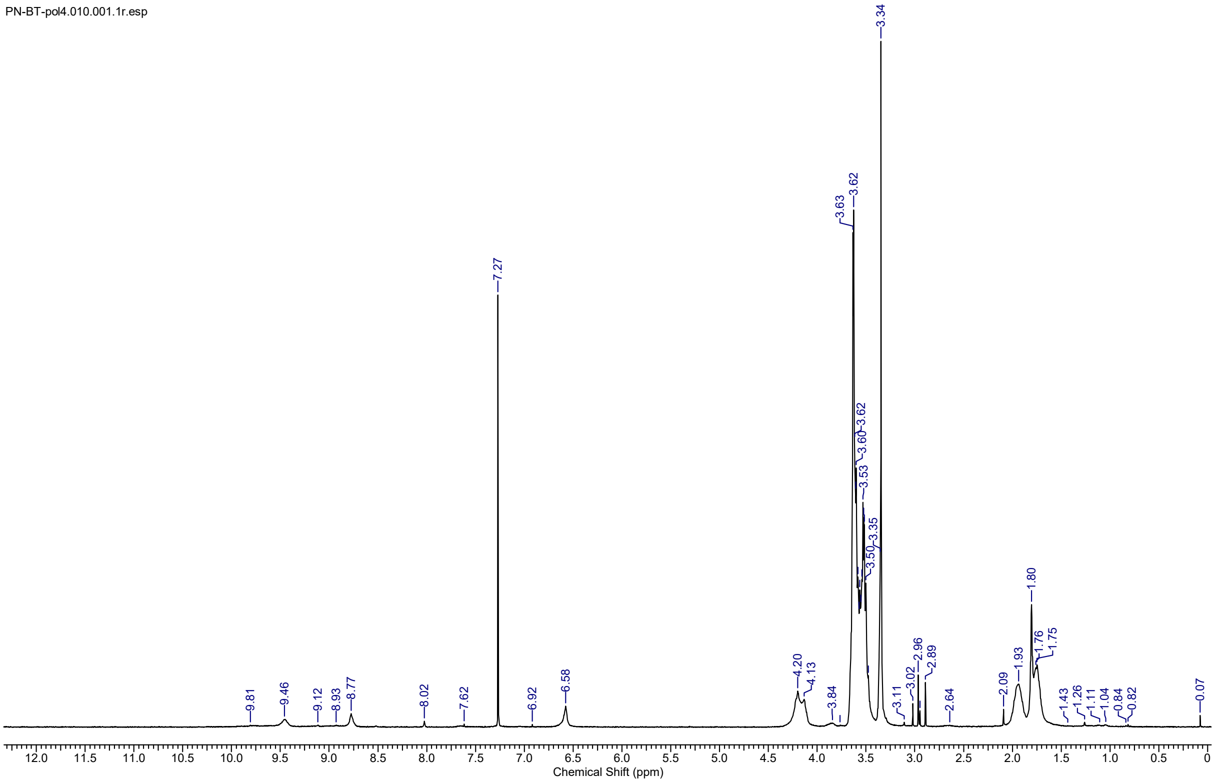


Figure S17. *^{1}H NMR spectrum (300 MHz, $CDCl_3$) of purified homopolymer **P2**.*

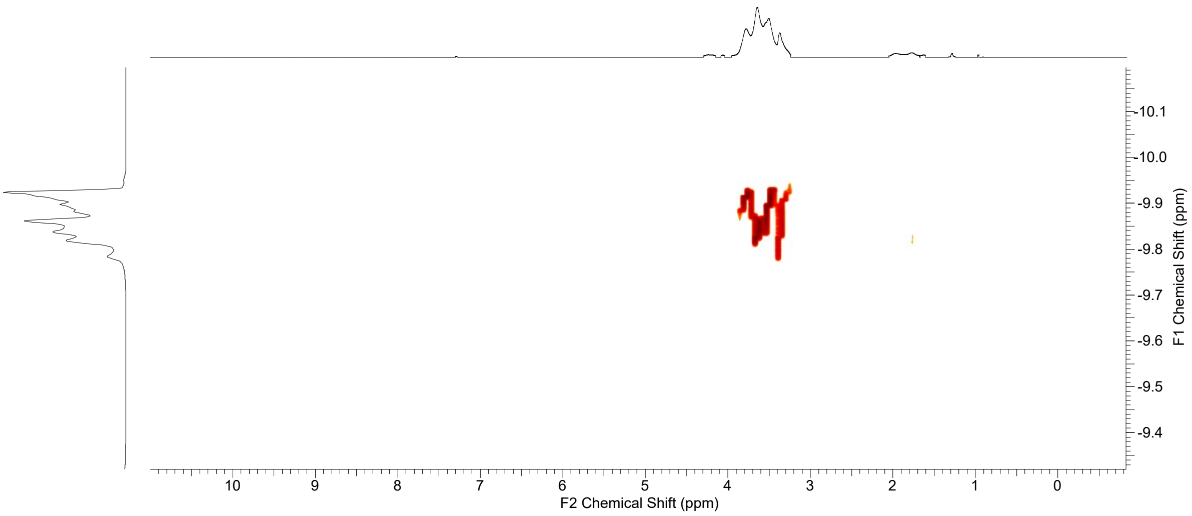


Figure S18. *DOSY spectrum (400 MHz, $CDCl_3$) of purified diblock copolymer* ***AB****.*

High-resolution mass spectrum (HR-MS) of monomer **7**

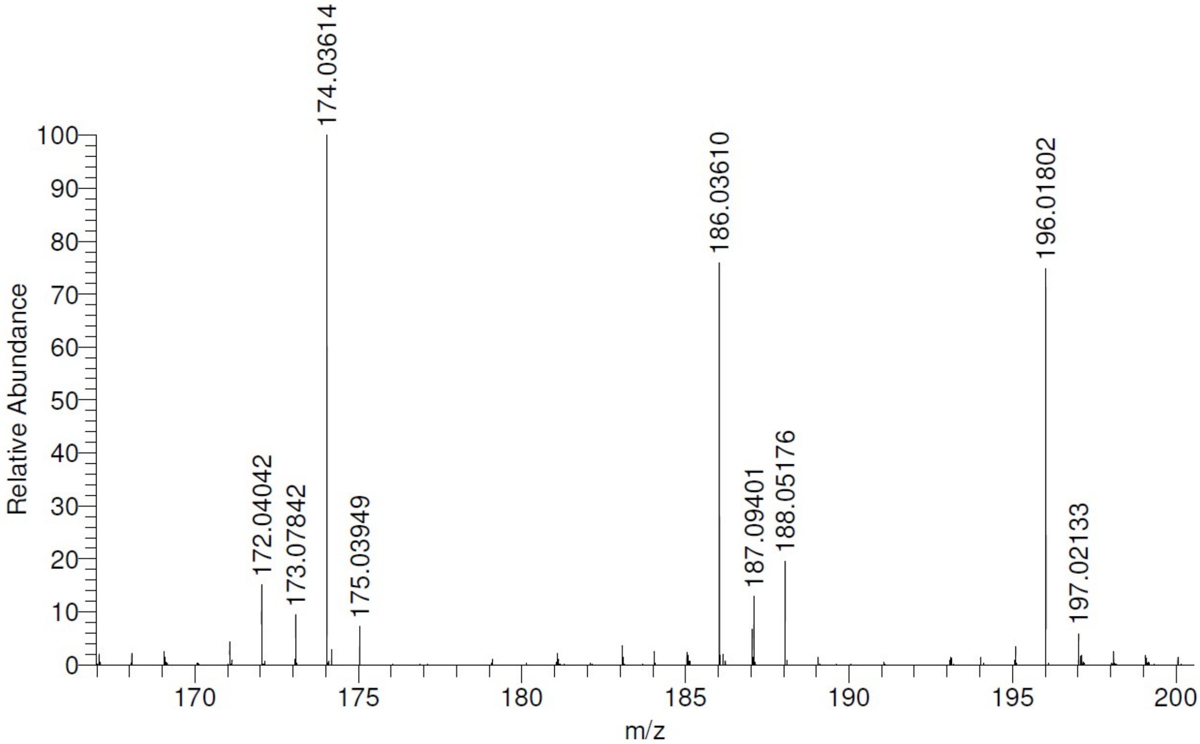
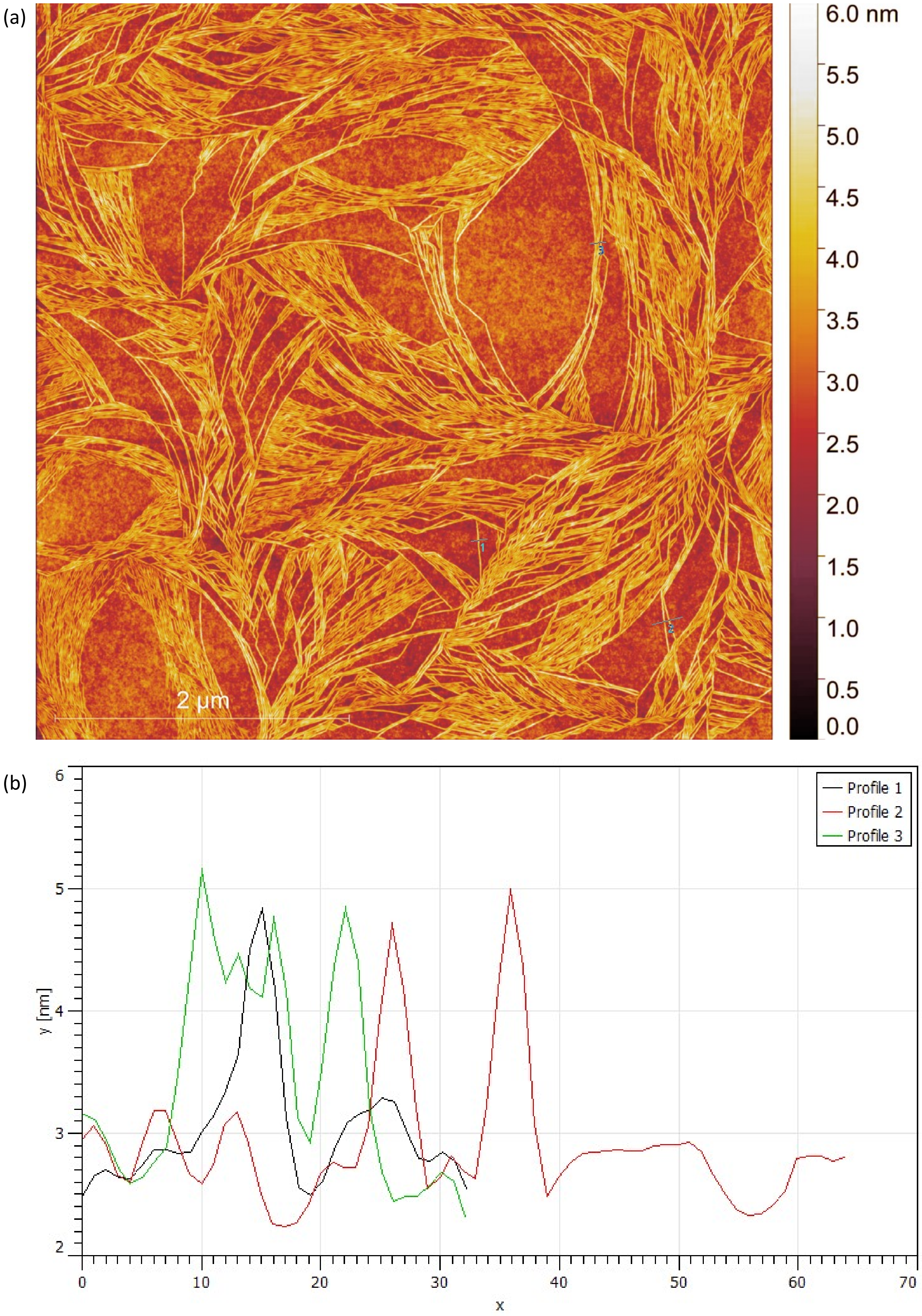


Figure S19. *HR-MS spectrum of monomer **7** in MeOH.*

AFM images of DIBLOCK COPOLYMER AB



(c)

	h [nm]
Profile 1	2.2128
Profile 2	2.1680
	2.1864
Profile 3	1.5902
	1.0584
	2.1334

Figure S20. *(a) AFM image of diblock copolymer AB at a sample concentration of 2 mg/L in water. (b) Height profiles were measured across 3 different strands or group of strands and compiled in the table (c) above. Bilateral minimum background mode was used to determine the height profile. Because of the known systemic errors associated with the AFM technique, exact strand lengths were not measured.*

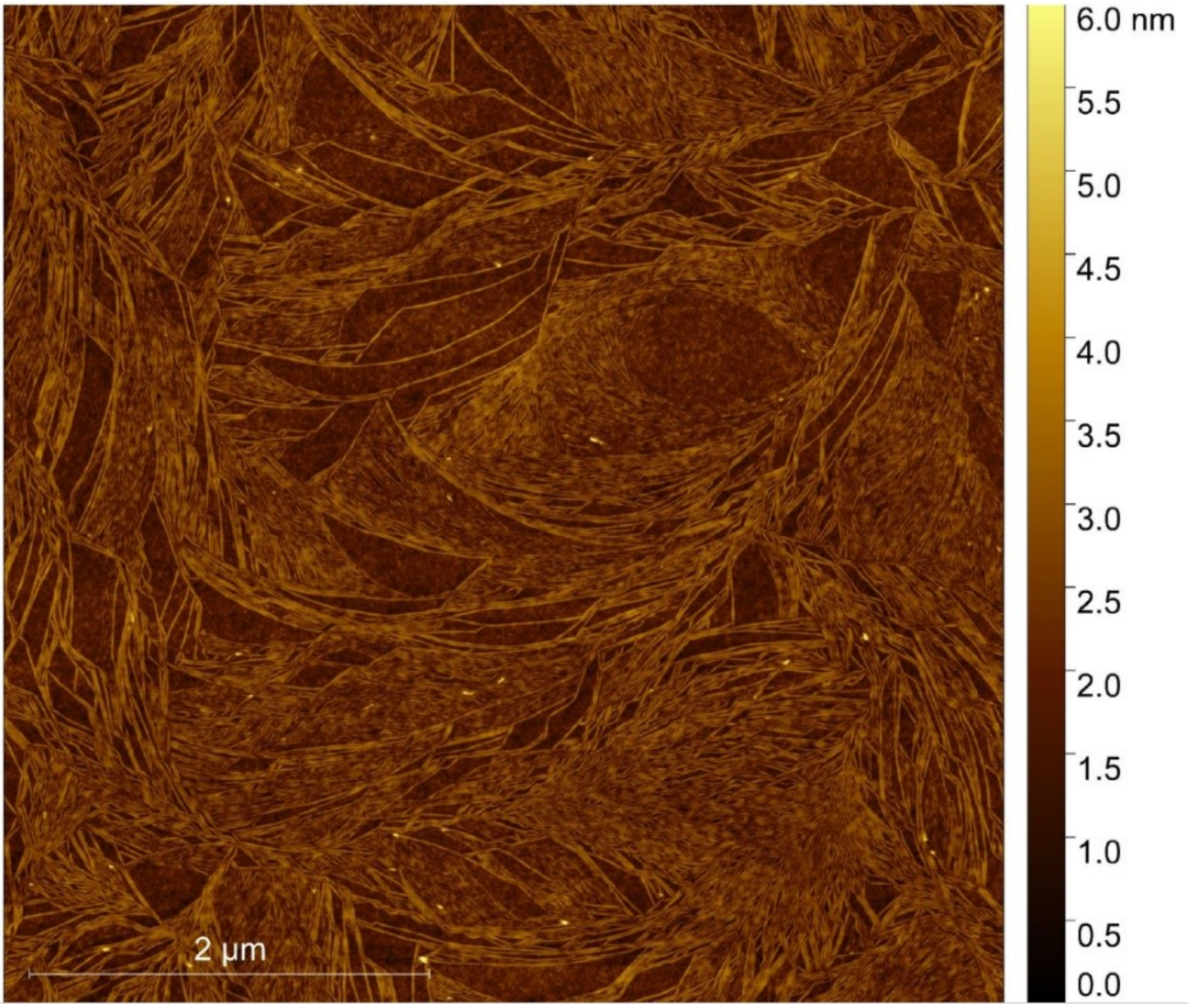
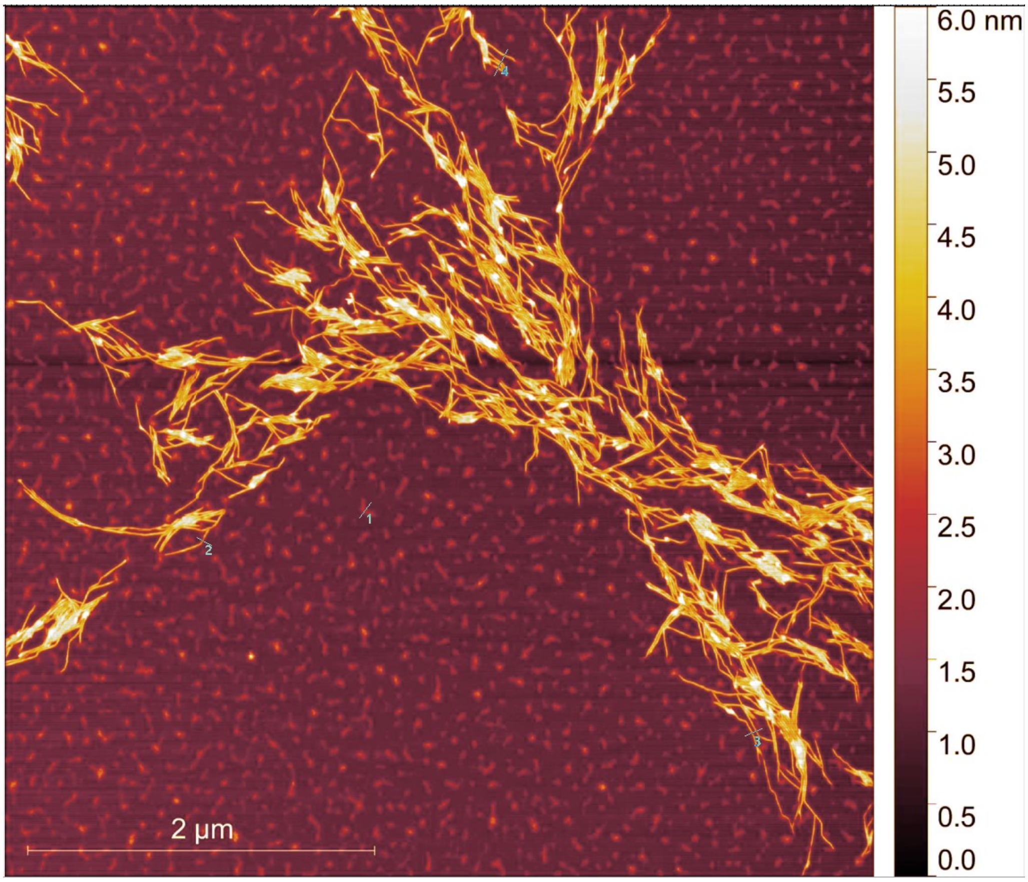
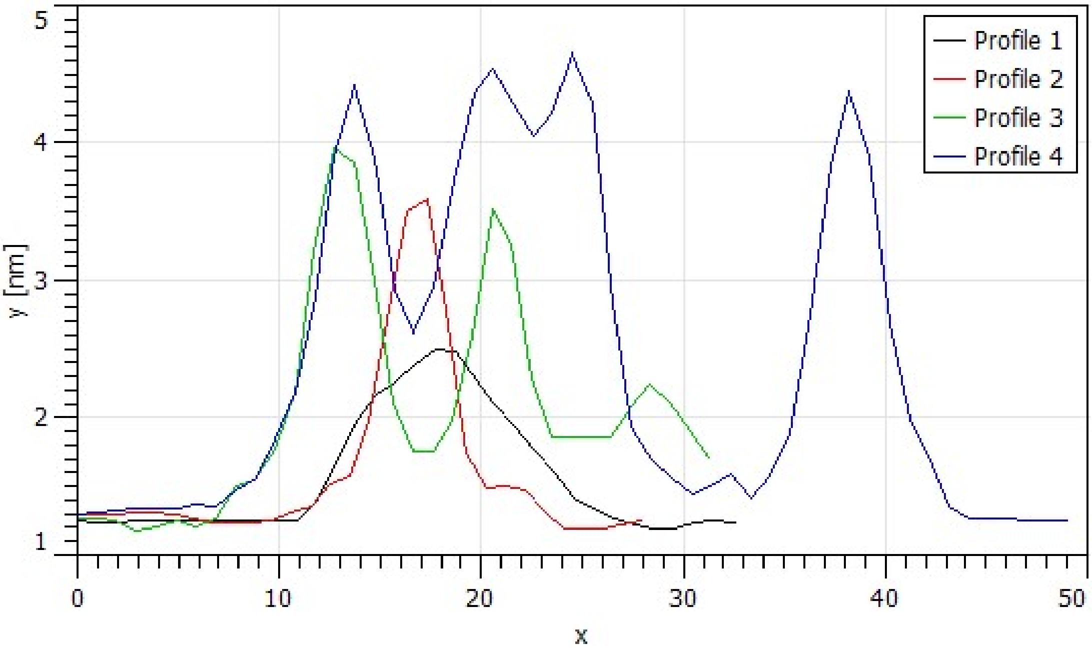


Figure S21. *AFM image of diblock copolymer AB at a sample concentration of 2 mg/L in water.*

(a)



(b)



	h [nm]
Profile 1	1.2669
Profile 2	0.0453
	2.3665

(c)

Profile 3	2.5055
	1.7074
Profile 4	2.4408
	1.1998
	1.8889
	3.0114

Figure S22. *(a) AFM image of diblock copolymer AB at a sample concentration of 4 mg/L in water. (b) Height profiles were measured across 3 different strands or group of strands and compiled in the table (c) above. Bilateral minimum background mode was used to determine the height profile. Because of the known inaccuracies associated with the AFM technique, exact strand lengths were not measured.*

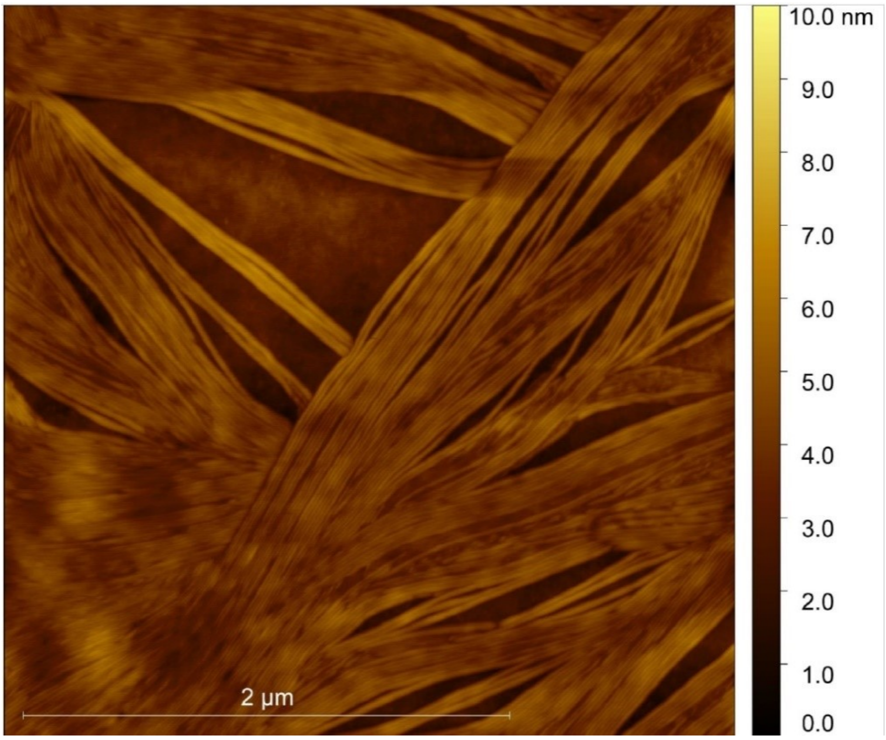


Figure S23. *AFM image of diblock copolymer AB at a sample concentration of 6 mg/L in water.*

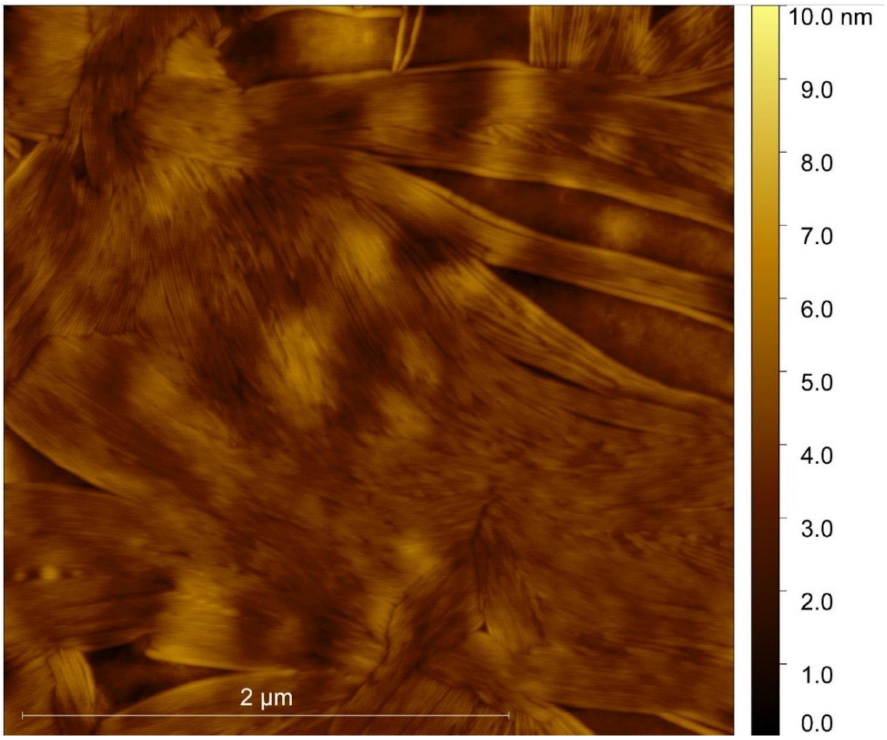


Figure S24. *AFM image of diblock copolymer AB at a sample concentration of 6 mg/L in water.*

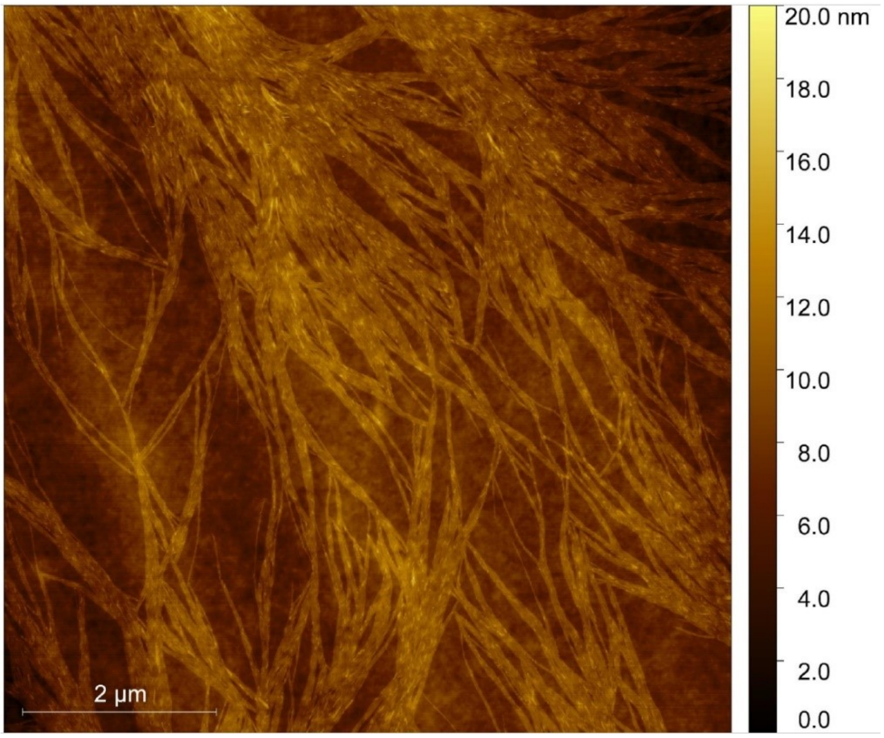


Figure S25. *AFM image of diblock copolymer AB at a sample concentration of 5 mg/mL in water.*

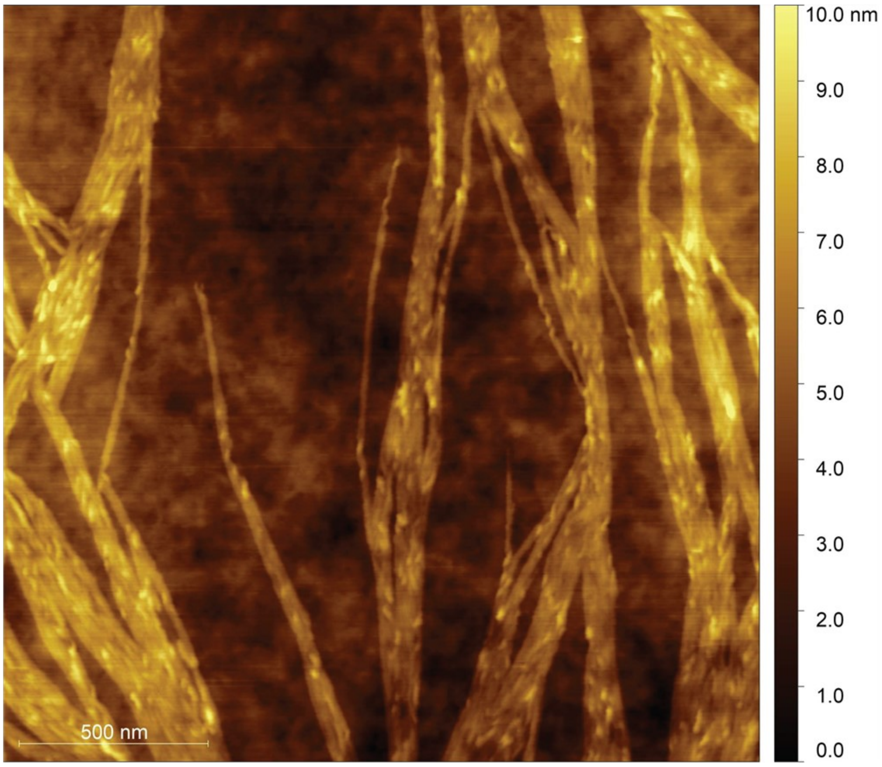


Figure S26. *AFM image of diblock copolymer AB at a sample concentration of 5 mg/mL in water.*

SAXS

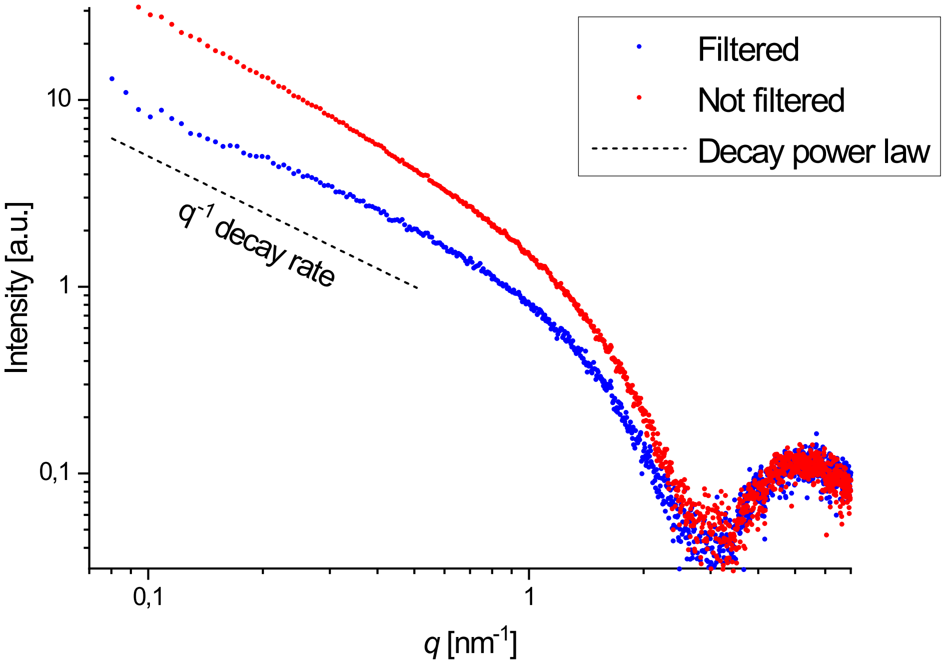


Figure S27. *SAXS scattering curves of diblock copolymer AB at a sample concentration of 5 mg/mL in water.*

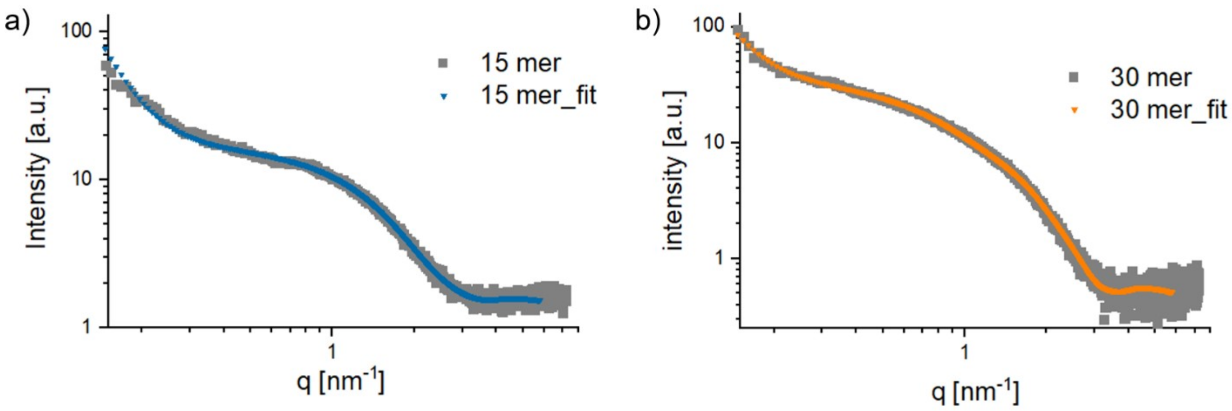


Figure S28. *SAXS scattering curves of homopolymers* ***P1*** *(a) and* ***P2*** *(b) at a sample concentration of 10 mg/mL in water.*

DLS

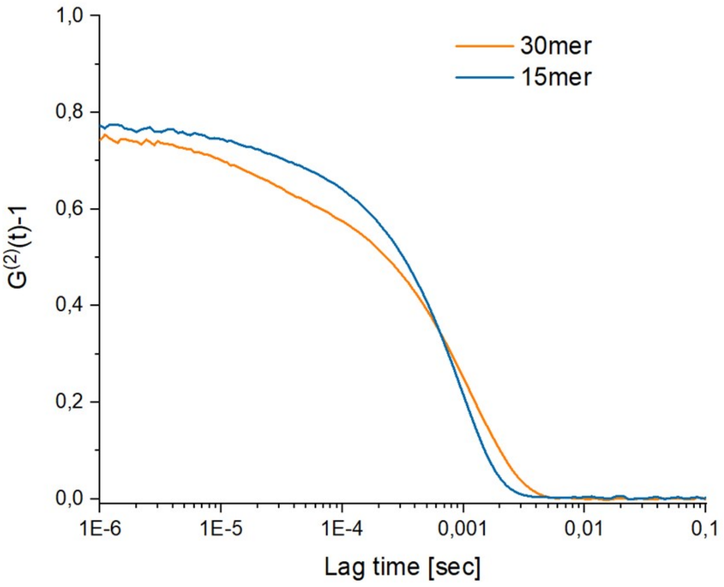


Figure S29*. DLS measurements of polymers* ***P1*** *and* ***P2*** *in water (3 mg/mL).*

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