Supporting Information for

Synthesis of Conjugated Diblock Copolymers: Two Mechanistically Distinct, Sequential Living Polymerizations Using a Single Catalyst

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General Considerations. All solvents were purchased from Fisher Scientific and used without further purification unless otherwise noted. All other chemicals were purchased from Aldrich, Alfa Aesar, or Fisher, and were used as received. 2,5-Dibromo-3-hexylthiophene (**1**),[1] *t*-butyl 4-isocyanobenzoate (**4**),[2] 1-isocyanohexadecane (**6**),[3] *N*-dodecyl-2,5-dibromopyrrole (**9**),[4] 2,5-bis(hexyloxy)phenylene (**10**),[5] 2-(2-methoxyethoxy)ethyl 4-aminobenzoate (**11**)[6] and poly-**2**[7] were prepared according to literature procedures. The monomer 2-(2-methoxyethoxy)ethyl 4-isocyanobenzoate (**3**) was prepared according to Scheme S1. A regioregular poly(3-hexylthiophene) (M_n = 8.17 kDa, PDI = 1.30) was synthesized according to literature procedure.[1] THF was dried over 3 Å molecular sieves and deoxygenated using a Vacuum Atmospheres Company solvent purification system. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Varian 300, 400, or 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units and expressed in parts per million (ppm) downfield from tetramethylsilane using the residual solvent as an internal standard. For ^{1}H NMR: CDCl$_3$, 7.26 ppm. For ^{13}C NMR: CDCl$_3$, 77.16 ppm. Coupling constants (J) are expressed in hertz. Size exclusion chromatography (SEC) was performed at room temperature on either: (1) a home-built system equipped with a Waters Model 510 HPLC pump, two fluorinated polystyrene columns (IMBHW-3078 and I-MBLMW-3078) arranged in series, and a Waters 486 Tunable Absorbance Detector (λ = 450 nm) or (2) a Viscotek GPCmax system equipped with two fluorinated polystyrene columns (I-MBHMW-3078 and I-MBLMW-3078) thermostatted to 24 °C and arranged in series, a Viscotek VE 3580 Refractive Index (RI) detector, and a Viscotek 2600 Photodiode Array detector (λ = 460 nm). Molecular weight and polydispersity data are reported relative to polystyrene standards in tetrahydrofuran (THF). IR spectra were recorded using Perkin-Elmer Spectrum BX FT-IR system in KBr

matrices. UV–vis spectra were recorded using a Perkin Elmer Instruments Lambda 35 spectrometer. Microanalyses were performed by Midwest Microlabs, LLC (Indianapolis, IN). Melting points were obtained with a Mel-Temp apparatus and are uncorrected. High resolution mass spectra (HRMS) were obtained with a VG analytical ZAB2-E instrument (ESI or CI). Samples for atomic force microscopy (AFM) measurements were prepared by drop casting $CHCl_3$ solutions of the polymer onto pre-cleaned silicon wafers and placed in covered Petri dishes to slow the evaporation process. AFM images were acquired in tapping mode with an Asylum MFP-3D AFM/SPM, performed at room temperature in air using standard silicon cantilevers with a nominal spring constant of 50 N/m and resonance frequency of ~300 kHz. The images were acquired at a scan frequency of 1 Hz in 1×1 μm^2 or 0.5×0.5 μm^2 areas. Differential scanning calorimetry (DSC) was performed using a Mettler-Toledo DSC823e under an atmosphere of nitrogen at a heating/cooling rate of 20 °C min^{-1} or 10 °C min^{-1}. Transmission electron microscopy (TEM) was performed in bright-field mode with a TECNAI Spirit Biotwin at 80 kV accelerating voltage. Samples for TEM measurements were prepared by one of two methods: (1) samples were diluted with equal volume of 1 wt% aqueous solution of phosphotungstic acid stain and cast onto copper mesh grids; or (2) samples were cast onto lacy carbon grids that were pretreated with a 0.25 mg mL^{-1} aqueous dispersion of graphene oxide (GO).[8] Micrographs were collected at 100,000× magnification. XPS spectra were recorded using a commercial X-ray photoelectron spectrometer (Kratos Axis Ultra), utilizing a monochromated Al-K X-ray source (1486.5 eV), hydrid optics and a multi-channel plate and delay line detector coupled to a hemispherical analyzer. The photoelectrons take-off angle was normal to the surface of the sample and 15°, 26°, 38°, 45°, or 52º with respect to the X-ray beam. All spectra were recorded using a single sweep and an aperture slot of 300×700 μm, and high resolution spectra for each element were collected with a pass energy of 20 eV, while surveys were collected using 80 eV pass energy. The pressure measured in the analysis chamber was typically 4×10^{-9} Torr during data acquisition. Samples for dynamic light scattering (DLS) were measured in aqueous media. The custom-built DLS instrument consisted of a Brookhaven Instruments Limited (Worcestershire, U.K.) system, a model BI-9000AT digital correlator, a model EMI-9865 photomultiplier, and a model 17 mW He-Ne laser (NSG America, SELFOC micro-lens, 1.8 mm diameter, 0.25 pitch) operated at 632.8 nm. Measurements were performed at 20 °C. Prior to analysis, solutions were filtered through a 0.45 μm Millex GV PVDF membrane filter (Millipore Corp., Medford, MA) to remove dust particles. Scattered light was collected at a fixed angle of 90°. The digital correlator was operated with 522 ratio spaced channels, an initial delay of 2 μs, a final delay of 100 ms, and a duration of 3 min. A photomultiplier aperture was used and the incident laser intensity was adjusted to obtain a photon counting of between 200 and 300 kcps. Only data in which the measured and calculated baselines of the intensity autocorrelation function agreed to within 0.1% were used to calculate particle sizes. The calculations of the particle size distributions and distribution averages were performed with the ISDA software package (Brookhaven Instruments), which employed single exponential fitting, cumulants analysis, and non-negatively constrained least-squares (CONTIN) particle size distribution analysis routines. The number average particle diameters (*Davg*) and standard deviations were generated from the analysis of a minimum of 150 particles from at least three different micrographs. All measurements were made in triplicate.

Scheme S1. Synthesis of 2-(2-methoxyethoxy)ethyl 4-isocyanobenzoate (**3**)
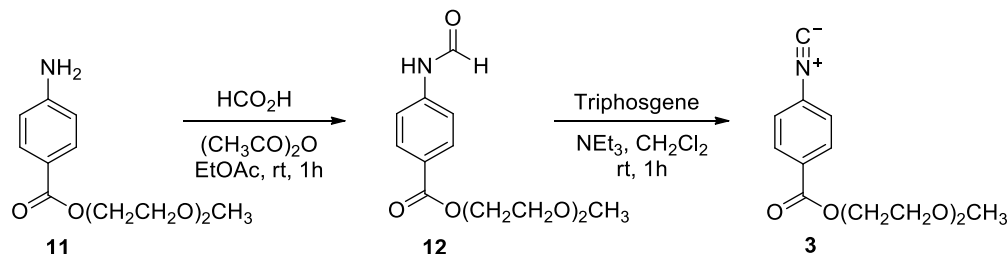
2-(2-methoxyethoxy)ethyl 4-formamidobenzoate (12). After a mixture of formic acid (1.08 mL, 28.7 mmol) and acetic anhydride (0.543 mL, 5.74 mmol) was stirred at room temperature for 1 h under argon, a solution of **7** (1.37 g, 5.74 mmol) in dry ethyl acetate (50 mL) was added to the aforementioned mixture at 0 °C. The resulting mixture was stirred at 0 °C for 30 min, and then at room temperature for 30 min. Ethyl acetate (50 mL) was added to the solution and the resulting mixture was filtered. The filtrate was washed with H_2O (100 mL) and brine (100 mL), and then dried over anhydrous $MgSO_4$. After the residual solvent was removed by evaporation, the crude product was purified by column chromatography (SiO_2; 1:1 hexanes: ethyl acetate, v/v) to afford the desired product as a clear oil (1.15 g, 75% yield). IR (KBr, cm^{-1}): 3274 (ν_{N-H}), 1704 ($\nu_{C=O}$ ester), 1603 ($\nu_{C=O}$ amide). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.38 (s, OCH$_3$, 3H), 3.56–3.59 (m, OCH$_2$, 2H), 3.38–3.72 (m, OCH$_2$, 2H), 3.82–3.85 (m, OCH$_2$, 2H), 3.45–4.45 (m, OCH$_2$, 2H), 7.11 (d, J = 8.7 Hz, 0.6 H, NH), 7.55–7.62 (m, 1.2H, NH and Ar), 7.75–7.92 (m, 0.4 H, Ar), 7.95–8.12 (m, 2.4 H, Ar), 8.25–8.50 (m, 1.0 H, Ar and CHO), 8.84 (d. J = 11.4 Hz, 0.4 H, CHO). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 59.16, 64.17, 69.41, 70.66, 72.01, 117.22, 119.13, 126.05, 126.60, 131.11, 131.79, 141.11, 141.29, 159.25, 161.87, 165.86, 166.06. HRMS m/z calcd for C$_{13}$H$_{18}$NO$_5$ [M+H]$^+$: 268.1185; Found: 268.1186. Anal. Calcd (%) for C$_{13}$H$_{17}$NO$_5$ (268.12): C, 58.42; H, 6.41; N, 5.24; Found (%): C, 58.21; H, 6.45; N, 5.22.
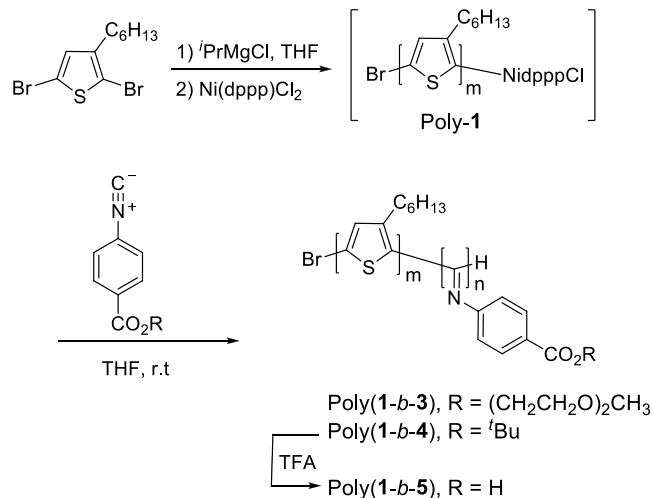
2-(2-methoxyethoxy)ethyl 4-isocyanobenzoate (3). Triethylamine (1.05 mL, 7.48 mmol) was added to a solution of **12** (1.0 g, 3.75 mmol) in dry CH$_2$Cl$_2$ (50 mL). After the reaction mixture was stirred at 0 °C for 10 min under argon, a solution of triphosgene (677 mg, 2.27 mmol) in CH$_2$Cl$_2$ (50 mL) was added dropwise to the mixture *via* syringe. The resulting mixture was stirred at room temperature for 1 h and then additional CH$_2$Cl$_2$ (150 mL) was added. After filtration, the resulting solution was washed with aqueous NaHCO$_3$ (100 mL; 10 wt% NaHCO$_3$) and then dried over anhydrous MgSO$_4$. After the residual solvent was removed by evaporation, the crude product was purified by column chromatography (SiO$_2$; 2 : 1 hexane : ethyl acetate, v/v) to afford the desired product as a clear liquid (654 mg, 70% yield). IR (KBr, cm^{-1}): 2124 (ν_{CN}), 1724 ($\nu_{C=O}$ ester). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.38 (s, CH$_3$, 3H), 3.55-3.58 (m, CH$_2$, 2H), 3.68-3.70 (m, CH$_2$, 2H), 3.82-3.85 (m, CH2, 2H), 4.48-4.51 (m, CH$_2$, 2H), 7.44 (d, J = 6.6 Hz, Ar, 2H), 8.10 (d. J = 6.6 Hz, Ar, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 59.26, 64.76, 69.25, 70.74, 72.05, 126.57, 131.06, 131.12, 165.13, 167.12. HRMS m/z calcd for C$_{13}$H$_{16}$NO$_4$ [M+H]$^+$: 250.1079; Found: 250.1078. Anal. Calcd (%) for C$_{13}$H$_{15}$NO$_4$ (249.10): C, 62.64; H, 6.07; N, 5.62; Found (%): C, 62.56; H, 6.21; N, 5.58.

Scheme S2. Synthesis of poly(**1**-*b*-**2**), poly(**7**-*b*-**2**) and poly(**8**-*b*-**2**)
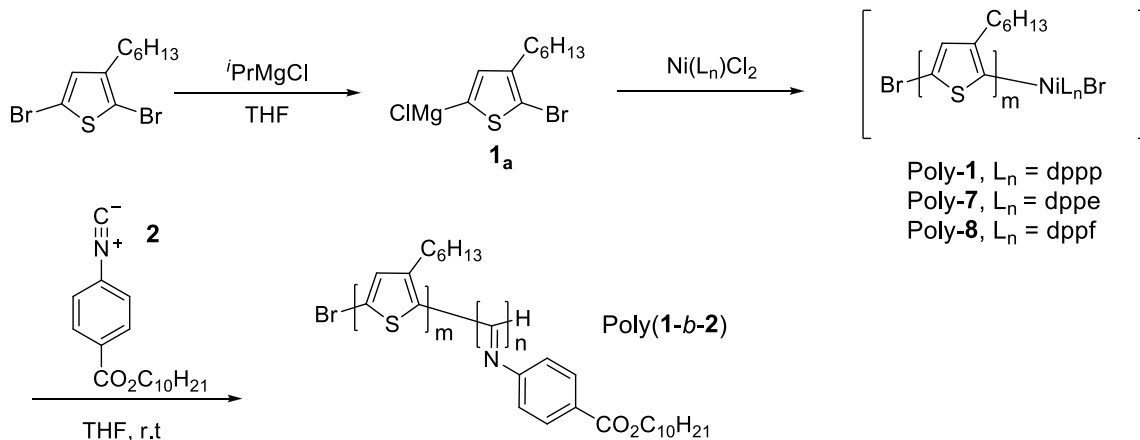
Representative Copolymerization Procedure: Poly(1-*b*-2), Poly(7-*b*-2) and Poly(8-*b*-2). Following a previously reported procedure,[7] a 50 mL oven-dried Schlenk flask was charged with 2,5-dibromo-3-hexylthiophene (0.15 g, 0.47 mmol), dry THF (2.0 mL), and a stir bar. After adding isopropylmagnesium chloride (0.23 mL, 2.0 M solution in THF), the resulting mixture was placed in an oil bath thermostatted to 50 °C for 2 h. Upon cooling to room temperature, dry THF (6.0 mL) and Ni(dppp)Cl$_2$ (10.2 mg, 0.019 mmol) (dppp = 1,3-bis(diphenylphosphino)propane) were added to the reaction mixture, and the polymerization progress was monitored by SEC until the molecular weight of poly-**1** ceased to increase. SEC analysis of an aliquot removed from the reaction mixture showed that the polymer prepared in situ exhibited the following characteristics: M_n = 3572 Da, M_w/M_n = 1.28. Under nitrogen, **2** (108 mg, 0.38 mmol) was then added to the reaction mixture. After the reaction mixture was stirred at room temperature for 1 h, 30 mL of methanol was poured into the reaction flask, which caused a dark-purple solid to precipitate. The solid was then isolated *via* filtration, and then washed with excess methanol and hexanes to remove residual metal salts, unreacted monomer and oligomers. The resulting purple solid was then dried under vacuum to afford 141 mg (76% yield, two steps) of the desired block copolymer poly(**1**-*b*-**2**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.84–1.71 (br, CH$_2$ and CH$_3$), 2.80–2.81 (br, thiophene CH$_2$) 3.56–4.49 (br, OCH$_2$), 5.34–6.31 (br, Ph), 6.97–7.01 (s, thiophene ArH), 7.15–7.40 (br, Ph).

Scheme S3. Synthesis of poly(**1**-*b*-**3**), poly(**1**-*b*-**4**) and poly(**1**-*b*-**5**)

Poly(**1**-*b*-**3**), R = $(CH_2CH_2O)_2CH_3$
Poly(**1**-*b*-**4**), R = ^tBu
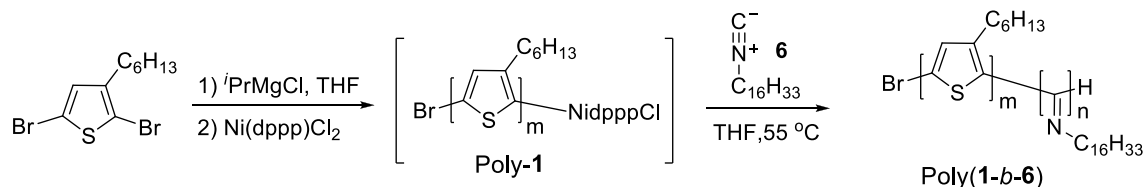Poly(**1**-*b*-**5**), R = H

Representative Copolymerization Procedure: Poly(1-*b*-3) and Poly(1-*b*-4). Following a previously reported procedure,[7] a 25 mL oven-dried flask was charged with 2,5-dibromo-3-hexylthiophene (0.15 g, 0.47 mmol), dry THF (4.5 mL), and a stir bar. After adding isopropylmagnesium chloride (0.48 mL, 1.0 M solution in THF), the resulting mixture was placed in an oil bath thermostatted to 50 °C for 2 h. Upon cooling to ambient temperature, Ni(dppp)Cl$_2$ (7.3 mg, 0.013 mmol) (dppp = 1,3-bis(diphenylphosphino)propane) was added to the reaction mixture, and the polymerization progress was monitored by SEC until the molecular weight of **1** ceased to increase. SEC analysis of an aliquot removed from the reaction mixture showed that the polymer prepared in situ exhibited the following characteristics: M_n = 5802 Da, M_w/M_n = 1.24. Under nitrogen, **3** (70 mg, 0.28 mmol) was then added to the reaction solution. After the reaction mixture was stirred at room temperature for 1 h, 30 mL of methanol was poured into the reaction flask, which caused a dark-purple solid to precipitate. The solid was then isolated *via* filtration, and washed with excess methanol and hexanes to remove residual metal salts, unreacted monomer and oligomers. The resulting purple solid was then dried under vacuum to afford 113 mg (78% yield, two steps) of the desired block copolymer poly(**1**-*b*-**3**). ¹H NMR (CDCl$_3$, 400 MHz): δ 0.83–0.97 (br, CH$_3$), 1.19–1.49 (br, CH$_2$), 1.58–1.76 (br, CH$_2$), 2.66–2.88 (br, CH$_2$), 3.13–3.99 (br, OCH$_2$), 4.11–4.64 (br, CO$_2$CH$_2$), 5.08–6.44 (br, aromatic), 6.86–7.10 (br, thiophene), 7.36–8.36 (br, aromatic). Poly(**1**-*b*-**4**) was prepared in a similar manner to poly(**1**-*b*-**3**). 233 mg (86% yield) ¹H NMR (CDCl$_3$, 400 MHz): δ 0.79–0.98 (br, CH$_3$), 1.13–1.83 (br, CH$_2$), 2.69–2.87 (br, CH$_2$), 4.86–6.29 (br, aromatic), 6.74–8.14 (br, aromatic).

Representative Procedure for the Synthesis of Poly(1-*b*-5). After dissolving poly(**1**-*b*-**4**) (15 mg, 2.46 μmol) in THF (10 mL), trifluoacetic acid (0.20 mL, 33 mmol) was added. The reaction mixture was allowed to stir at room temperature for 24 h, after which the solvent was removed under reduced pressure. The resulting crude solid was then washed with cold hexanes and dried under reduced pressure to afford the desired product (12 mg, 80% yield). ¹H NMR (CDCl$_3$, 400 MHz): δ 0.84–0.98 (br, CH$_3$), 1.13–1.83 (br, CH$_2$), 2.69–2.87 (br, CH$_2$), 4.86–6.29 (br, aromatic), 6.74–8.14 (br, aromatic).

Scheme S4. Synthesis of poly(**1**-*b*-**6**)

Representative Copolymerization Procedure: Poly(1-*b*-6). A 25 mL oven-dried flask was charged with 2,5-dibromo-3-hexylthiophene (0.14 g, 0.43 mmol), dry THF (4.5 mL) and a stir bar. After adding isopropylmagnesium chloride (0.45 mL, 1.0 M solution in THF), the resulting mixture was placed in an oil bath thermostatted to 50 °C for 2 h. Upon cooling to ambient temperature, Ni(dppp)Cl$_2$ (4.8 mg, 0.0089 mmol) (dppp = 1,3-bis(diphenylphosphino)propane) was added to the reaction mixture, and the polymerization progress was monitored by SEC until the molecular weight of **1** ceased to increase. SEC analysis of an aliquot removed from the reaction mixture showed that the polymer prepared in situ exhibited the following characteristics: M_n = 8329 Da, M_w/M_n = 1.33. Under nitrogen, **6** (68 mg, 0.27 mmol) was then added to the reaction mixture. After heating to 50 °C and stirring overnight, 30 mL of methanol was poured into the reaction flask, which caused a dark-purple solid to precipitate. The solid was then isolated *via* filtration, and washed with excess methanol and hexanes to remove residual metal salts, unreacted monomer and oligomers. The resulting purple solid was then dried under vacuum to afford 90 mg (65% yield, two steps) of the desired block copolymer poly(**1**-*b*-**6**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.82–0.95 (br, CH$_3$), 1.09–1.48 (br, CH$_2$), 1.64–1.76 (br, CH$_2$), 2.60–2.95 (br, CH$_2$), 3.04–3.67 (br, C=NCH$_2$), 6.94–7.01 (br, aromatic).

**Scheme S5.** Synthesis of poly(**9**-*b*-**2**) and poly(**10**-*b*-**2**)
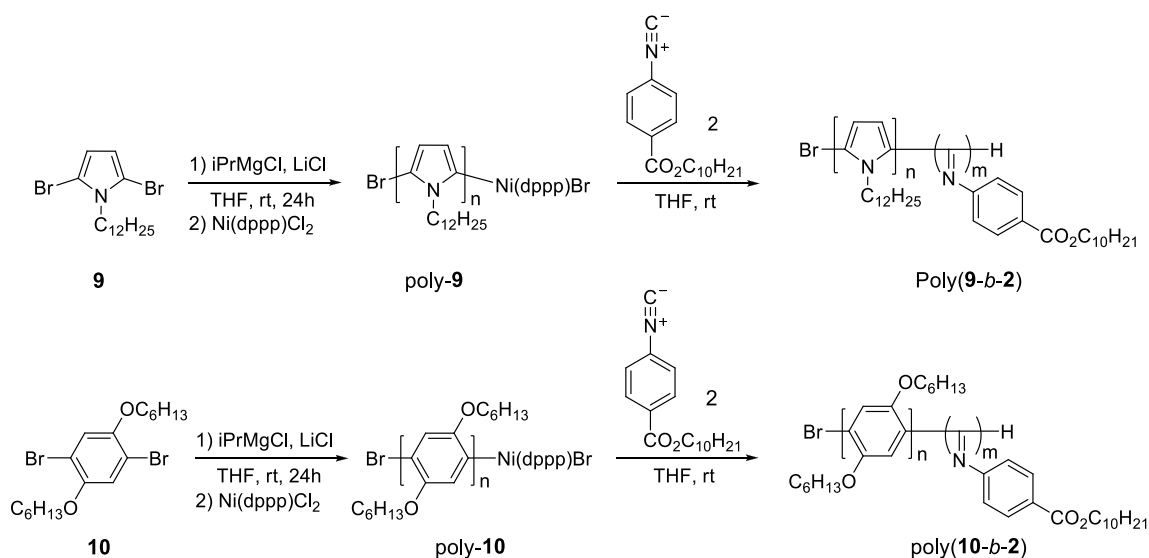
Representative polymerization Procedure of Poly(9-*b*-2) and Poly(10-*b*-2). A 10 mL oven-dried flask containing anhydrous lithium chloride (32.1 mg, 0.76 mmol) was heated under reduced pressure, and then cooled to room temperature under a nitrogen atmosphere. Monomer **9** (0.300 g, 0.76 mmol) was then added to the flask, and the atmosphere in the flask was replaced with nitrogen. THF (5.0 mL) was added via syringe, and the mixture was stirred at room temperature. Isopropylmagnesium chloride (1.0 M solution in THF, 0.76 mL, 0.76 mmol) was then added via syringe, and the mixture was stirred at room temperature for 24 h. To this mixture was added Ni(dppp)Cl$_2$ (7.8 mg, 0.015 mmol), and the polymerization progress was monitored by SEC until the molecular weight of poly-**9** ceased to increase. SEC analysis of an aliquot removed from the reaction mixture showed that the polymer prepared in situ exhibited the following characteristics: M_n = 7329 Da, M_w/M_n = 1.27. Under nitrogen, **2** (85 mg, 0.30 mmol) was then added to the reaction solution. After the reaction mixture was stirred at room temperature for 1 h, 30 mL of methanol was poured into the reaction flask, which caused a dark-purple solid to precipitate. The solid was then isolated *via* filtration, and washed with excess methanol and hexanes to remove residual metal salts, unreacted monomer and oligomers. The resulting purple solid was then dried under vacuum to afford 222 mg (85% yield, two steps) of the desired block copolymer poly(**9**-*b*-**2**). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.73–1.66 (br, CH$_2$, CH$_3$), 3.36–3.92 (br, CH$_2$N), 4.00–4.65 (br, OCH$_2$), 5.59–6.95 (br, Aromatic), 7.34–8.32 (br, Aromatic). Poly(**10**-*b*-**2**) was prepared in a similar manner to that of poly(**9**-*b*-**2**). 236 mg (72% yield) ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.62–2.13 (br, CH$_2$, and CH$_3$), 3.50–4.64 (br, OCH$_2$, and CO$_2$CH$_2$), 5.24–6.22 (br, aromatic), 6.75–7.12 (br, aromatic), 7.34–8.06 (br, aromatic).

Synthesis of the Poly-4 and Poly-6 Homopolymers. *t*-Butyl 4-isocyanobenzoate (**4**), (30 mg, 0.15 mmol) was placed in an oven dried two-neck flask, which was then evacuated on a vacuum line and refilled with dry N$_2$. After this vacuum–refill procedure was repeated three times, dry CH$_2$Cl$_2$ (3.0 mL) was added with a syringe. After complete

dissolution of the monomer, a solution of $NiCl_2 \cdot 6H_2O$ in dry methanol (0.05 M, 0.30 mL, 0.015 mmol) was added, and the mixture stirred under N_2 atmosphere at room temperature for 6 h. The polymer was isolated by precipitation from excess methanol, collected by centrifugation, and then dried under reduced pressure at room temperature to afford poly-**6** as a yellow solid (20 mg, 67% yield). SEC: $M_n = 19.0$ kDa, PDI = 1.30. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 1.04–2.01 (br, CH$_3$), 4.95–6.34 (br, aromatic), 6.51–7.95 (br, aromatic). Poly-**6** was prepared in a similar manner as poly-**4**. Yield: 70%. SEC: $M_n = 4.4$ kDa, PDI = 1.60. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 0.74–0.85 (br, CH$_3$), 1.00–1.72 (br, CH$_2$), 2.86–3.83 (br, NCH$_2$).
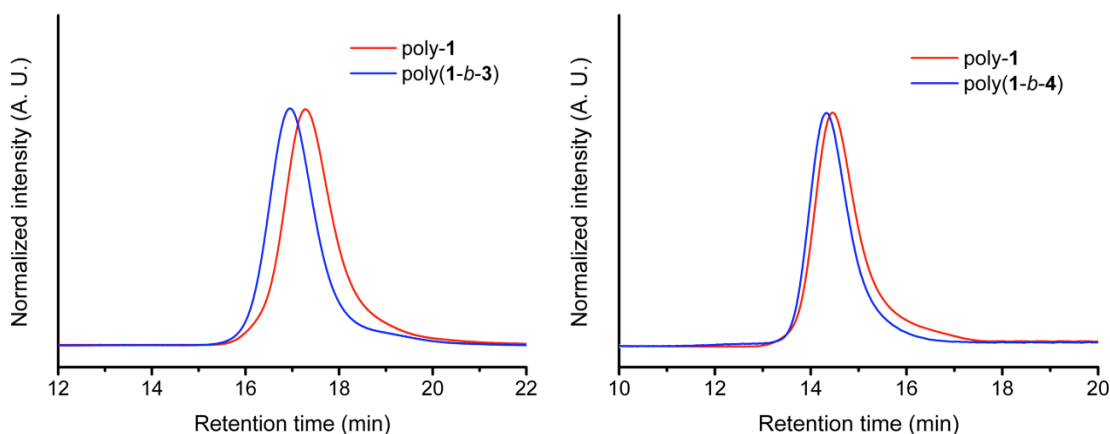
Figure S1. Left: size exclusion chromatograms of macroinitiator poly-**1** ($M_n = 5.80$ kDa, $M_w/M_n = 1.24$, red) and its respective block copolymer poly(**1**-*b*-**3**) ($M_n = 8.80$ kDa, $M_w/M_n = 1.19$, blue); Right: size exclusion chromatograms of macroinitiator poly-**1** ($M_n = 11.2$ kDa, $M_w/M_n = 1.32$, red) and its respective block copolymer poly(**1**-*b*-**4**) ($M_n = 13.2$ kDa, $M_w/M_n = 1.17$, blue).
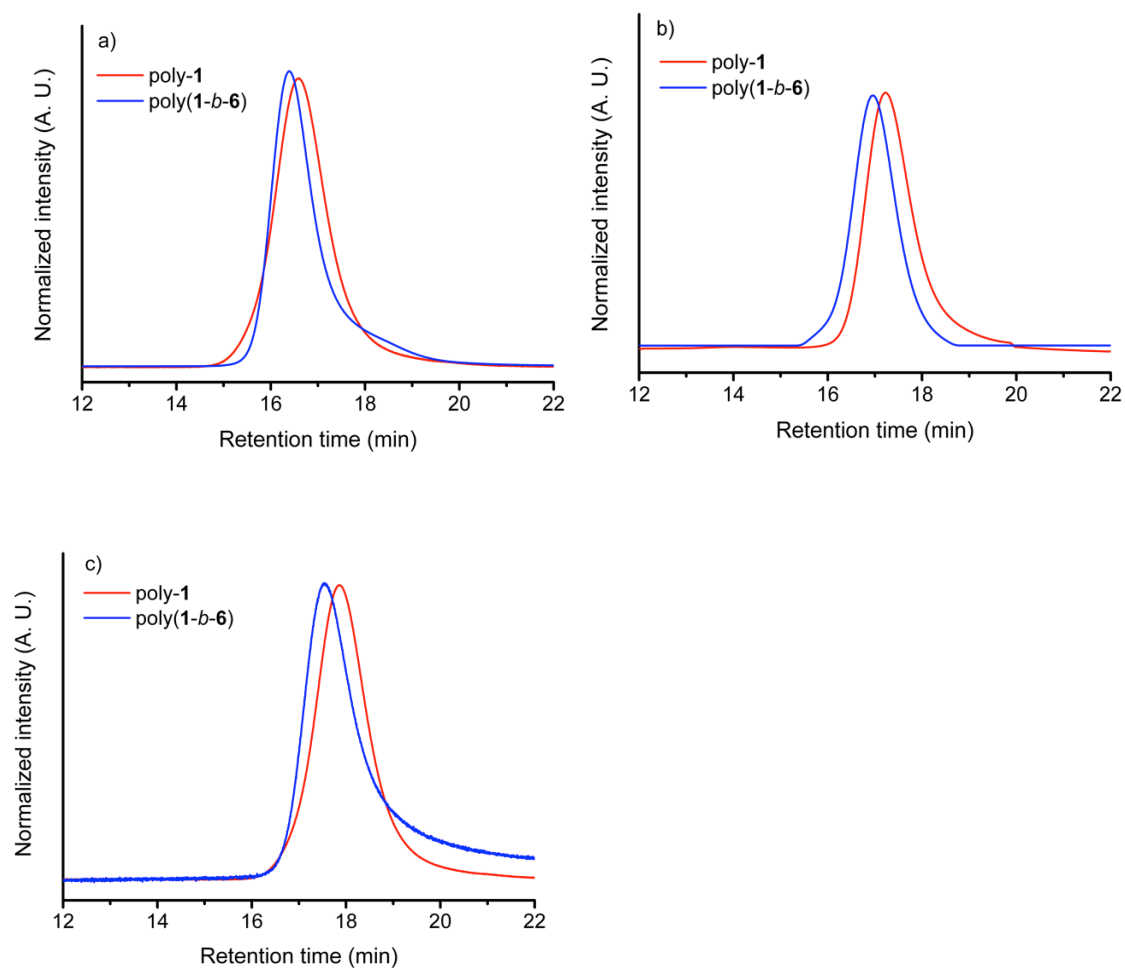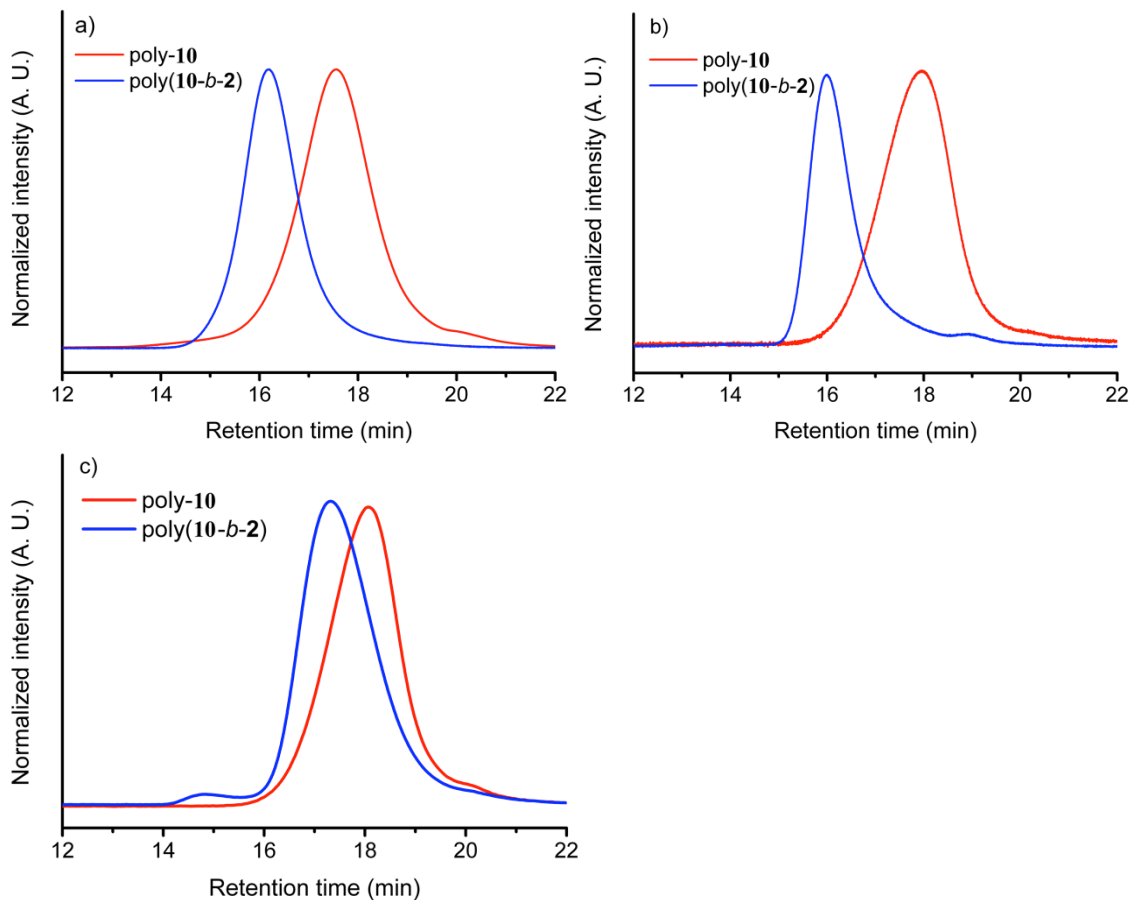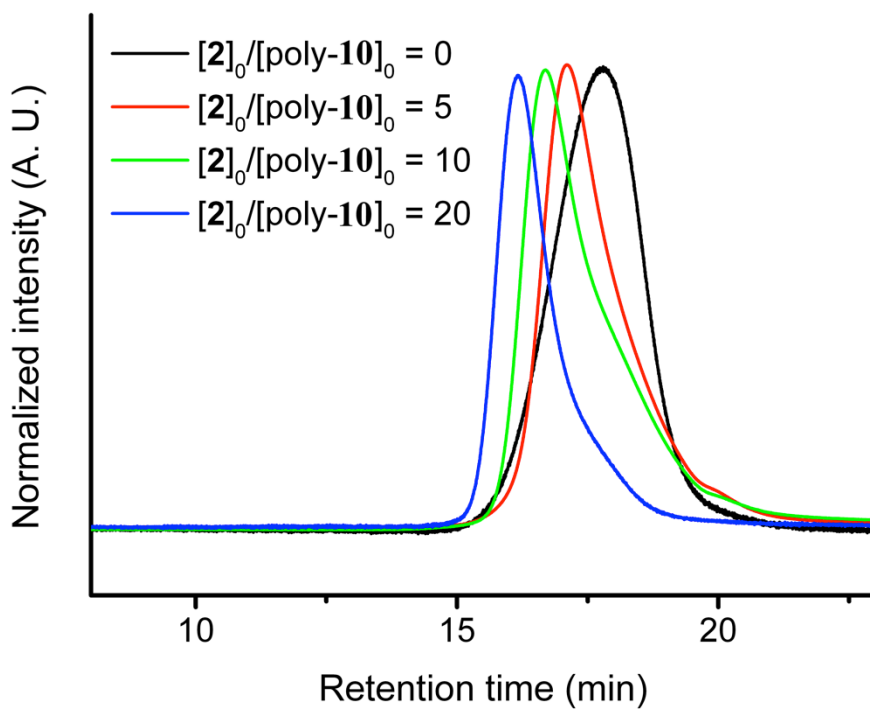
Figure S2. Size exclusion chromatograms of macroinitiator poly-**1** (red) and its respective block copolymer poly(**1**-*b*-**6**) (blue); a) poly-**1** ($M_n = 8.33$ kDa, $M_w/M_n = 1.23$), poly(**1**-*b*-**6**) ($M_n = 10.1$ kDa, $M_w/M_n = 1.22$); b) poly-**1** ($M_n = 5.85$ kDa, $M_w/M_n = 1.16$), poly(**1**-*b*-**6**) ($M_n = 8.39$ kDa, $M_w/M_n = 1.38$); c) poly-**1** ($M_n = 3.88$ kDa, $M_w/M_n = 1.25$), poly(**1**-*b*-**6**) ($M_n = 4.26$ kDa, $M_w/M_n = 1.20$).
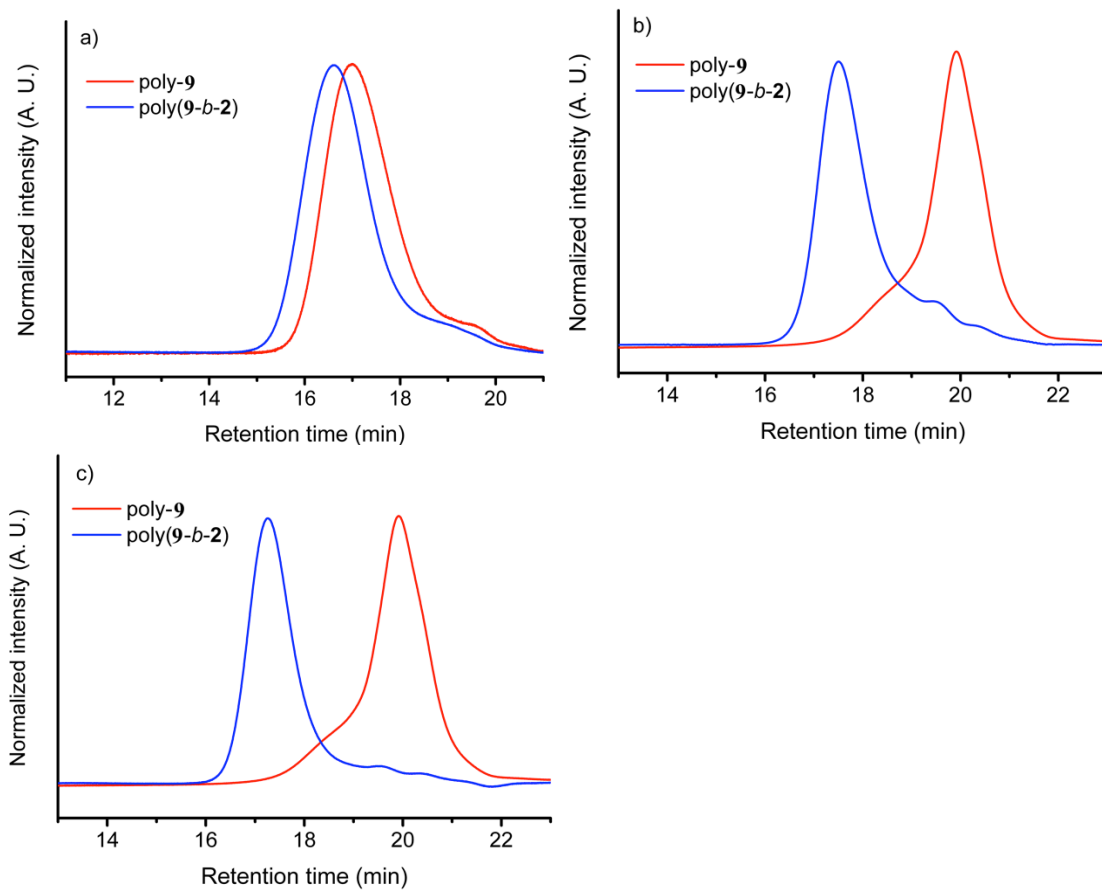
Figure S3. Size exclusion chromatograms of macroinitiator poly-**9** (red) and its respective block copolymer poly(**9**-*b*-**2**) (blue); a) poly-**9** (M_n = 4.64 kDa, M_w/M_n = 1.23), poly(**9**-*b*-**2**) (M_n = 6.34 kDa, M_w/M_n = 1.22); b) poly-**9** (M_n = 1.05 kDa, M_w/M_n = 1.16), poly(**9**-*b*-**2**) (M_n = 4.05 kDa, M_w/M_n = 1.21); c) poly-**9** (M_n = 1.05 kDa, M_w/M_n = 1.16), poly(**9**-*b*-**2**) (M_n = 6.02 kDa, M_w/M_n = 1.23).
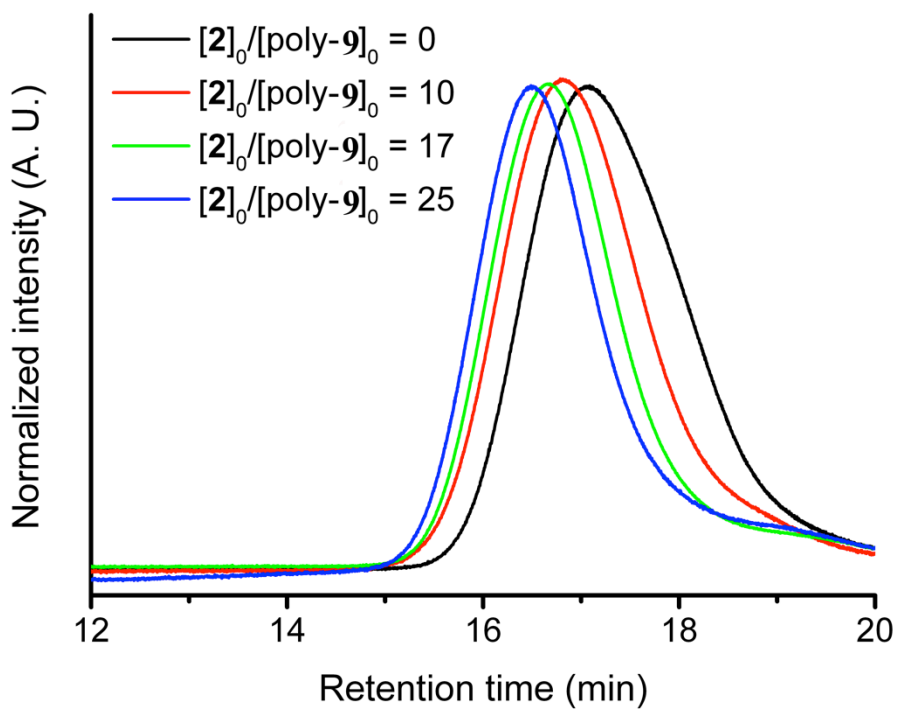
Figure S4. Size exclusion chromatograms of poly(**9**-*b*-**2**) synthesized using different feed ratios of **2** to macroinitiator poly-**9** ($M_n = 6.78$ kDa, $M_w/M_n = 1.33$).

Figure S5. Size exclusion chromatograms of macroinitiator poly-**10** (red) and its respective block copolymers poly(**10**-*b*-**2**) (blue); a) poly-**10** (M_n = 5.71 kDa, M_w/M_n = 1.36), poly(**10**-*b*-**2**) (M_n = 12.2 kDa, M_w/M_n = 1.36); b) poly-**10** (M_n = 4.50 kDa, M_w/M_n = 135), poly(**10**-*b*-**2**) (M_n = 15.3 kDa, M_w/M_n = 1.16); c) poly-**10** (M_n = 4.04 kDa, M_w/M_n = 1.35), poly(**10**-*b*-**2**) (M_n = 5.51 kDa, M_w/M_n = 1.27).

Figure S6. Size exclusion chromatograms of poly(**10**-*b*-**2**) synthesized using different feed ratios of **2** to macroinitiator poly-**10** (M_n = 5.26 kDa, M_w/M_n = 1.39).
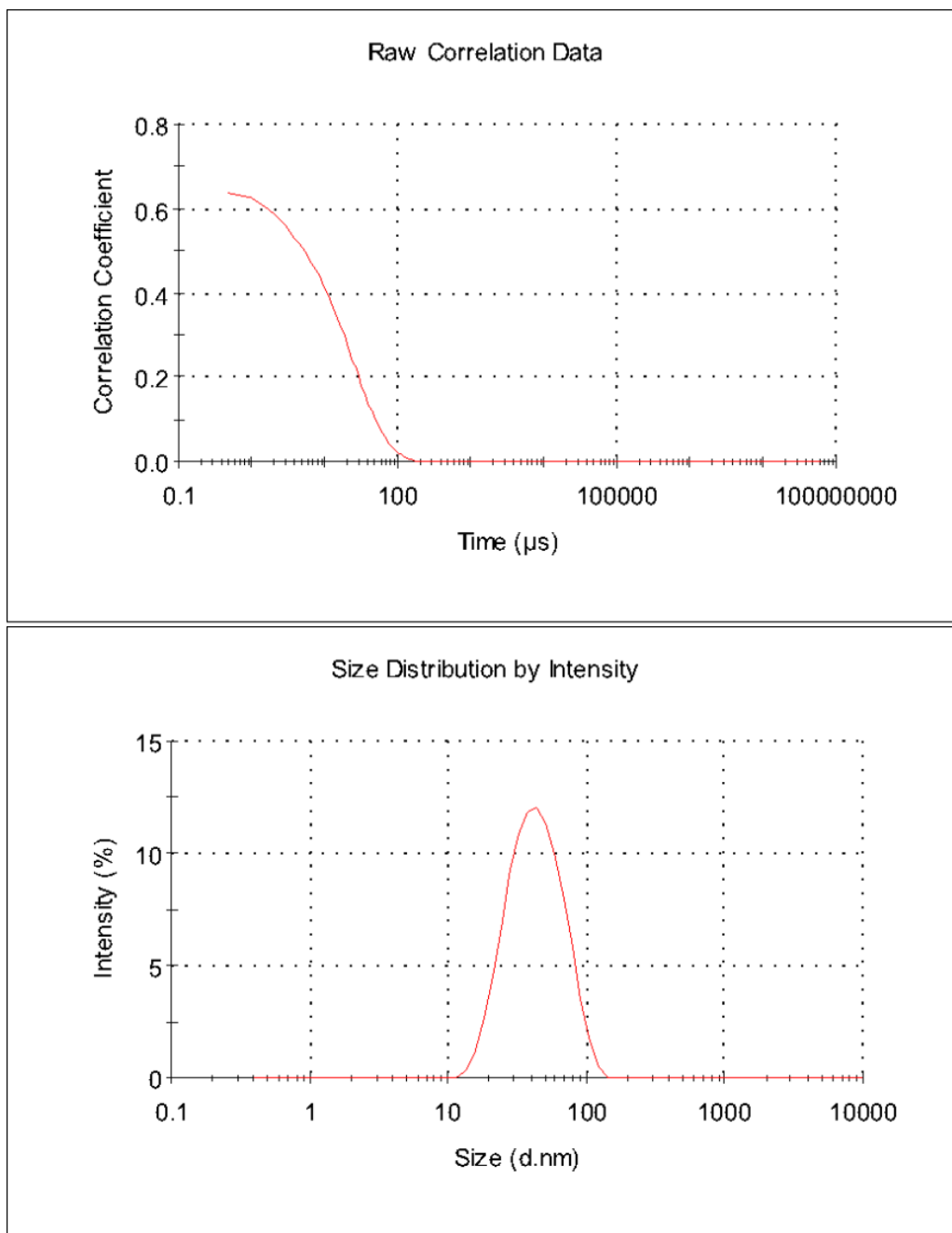
Figure S7. DLS data of nanoparticles formed from block copolymer poly(**1**-*b*-**3**) in THF and methanol (1/1, v/v) at 25 °C. The hydrodynamic diameter was determined to be 41 +/- 4 nm.
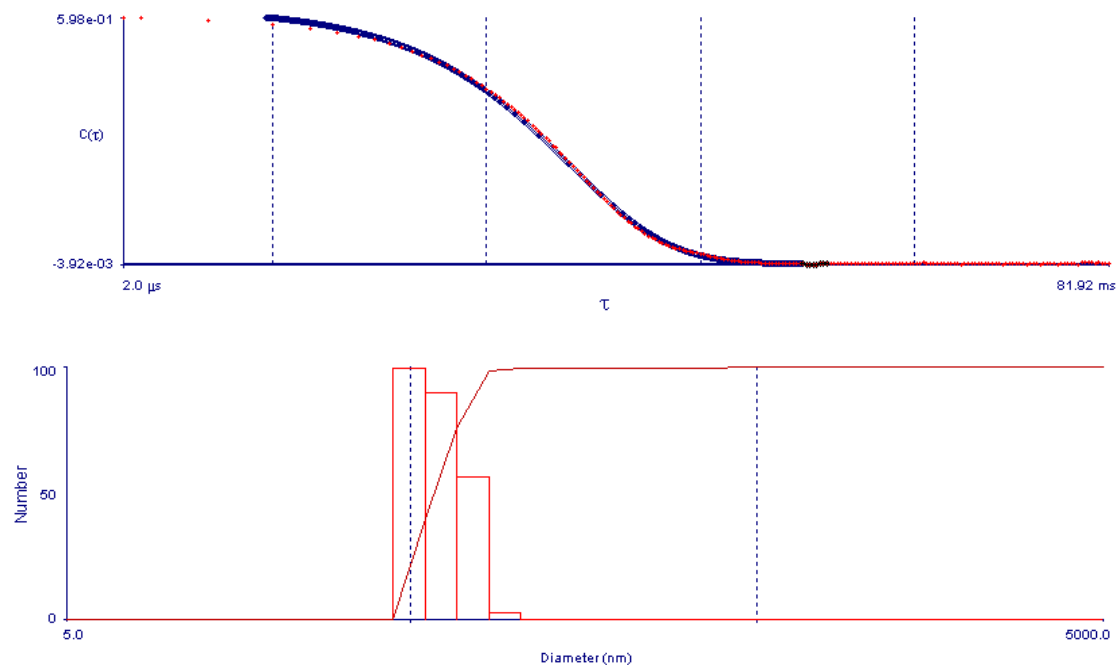
Figure S8. DLS data of nanoparticles formed from block copolymer poly(**1**-*b*-**5**) in water. The hydrodynamic diameter was determined to be 89 +/- 6 nm.
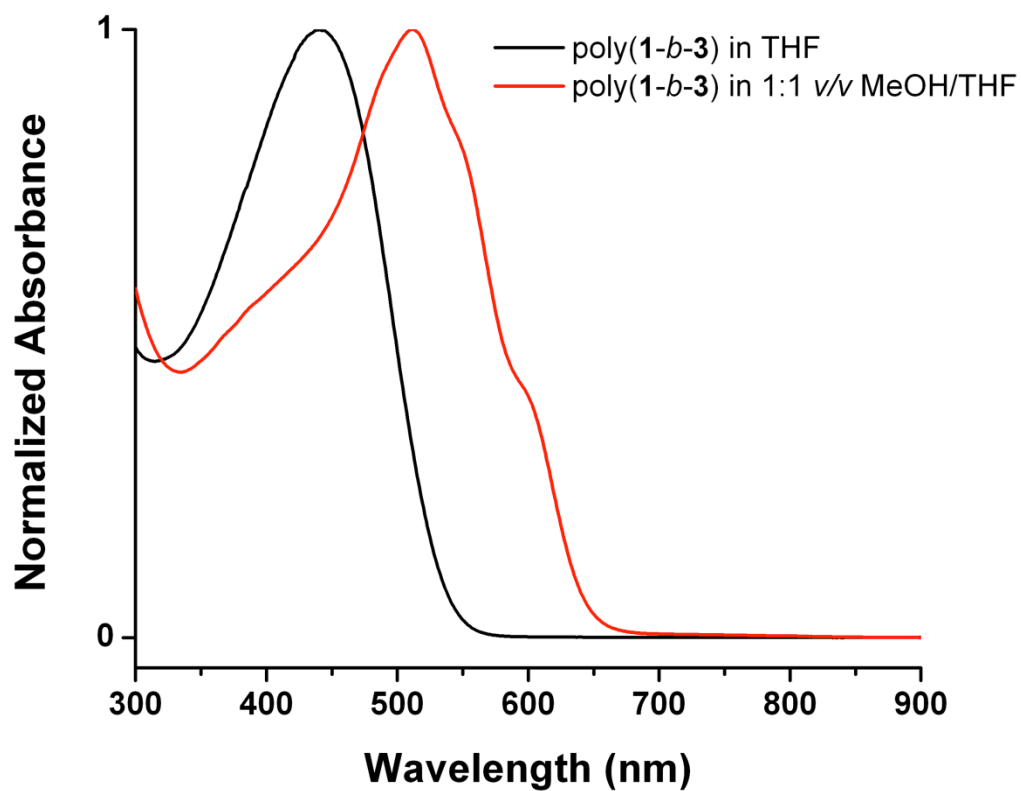
Figure S9. UV-vis spectra of poly(**1**-*b*-**3)** (entry 1 in Table 1) in THF before (black) and after (red) the addition of an equal volume of methanol at 25 °C.
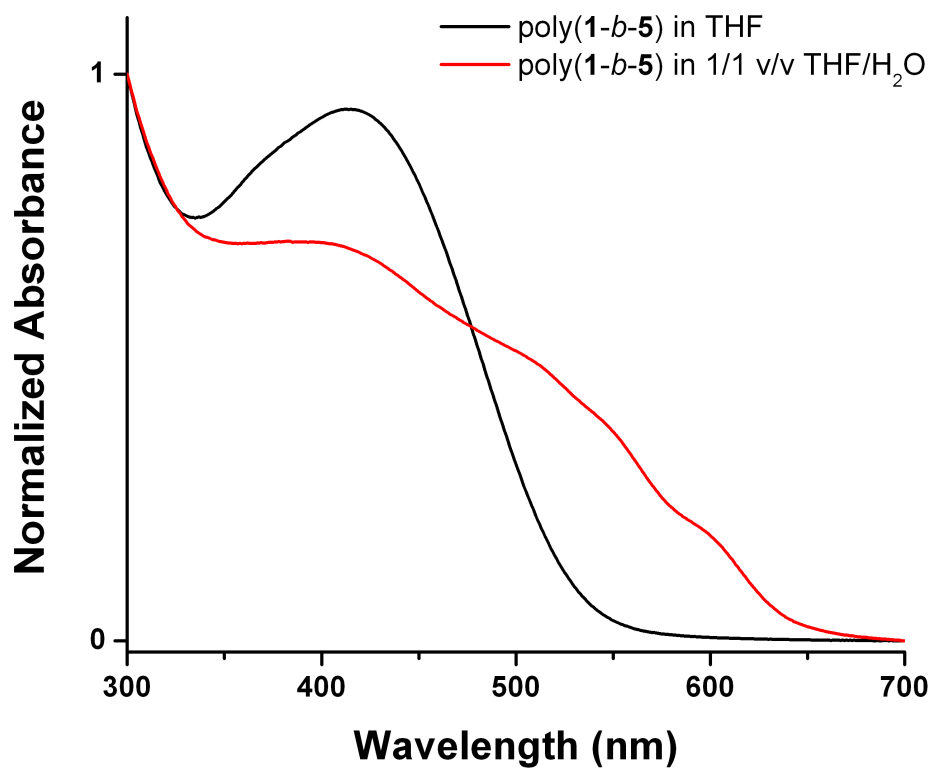
Figure S10. UV-vis spectra of poly(**1**-*b*-**5**) (entry 1 in Table 1) in THF before (black) and after (red) the addition of an equal volume of water at 25 °C.
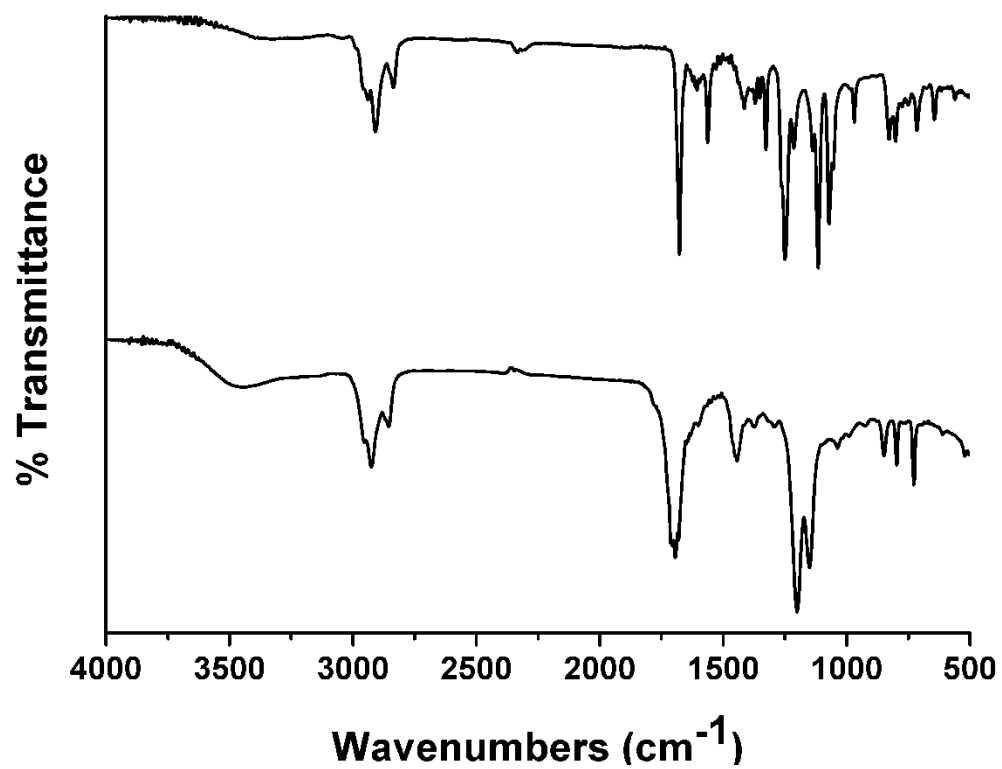
***Figure* S11.** IR spectra of poly(**1**-*b*-**4**) (top spectrum) and the resulting poly(**1**-*b*-**5**) (bottom spectrum) after deprotection.
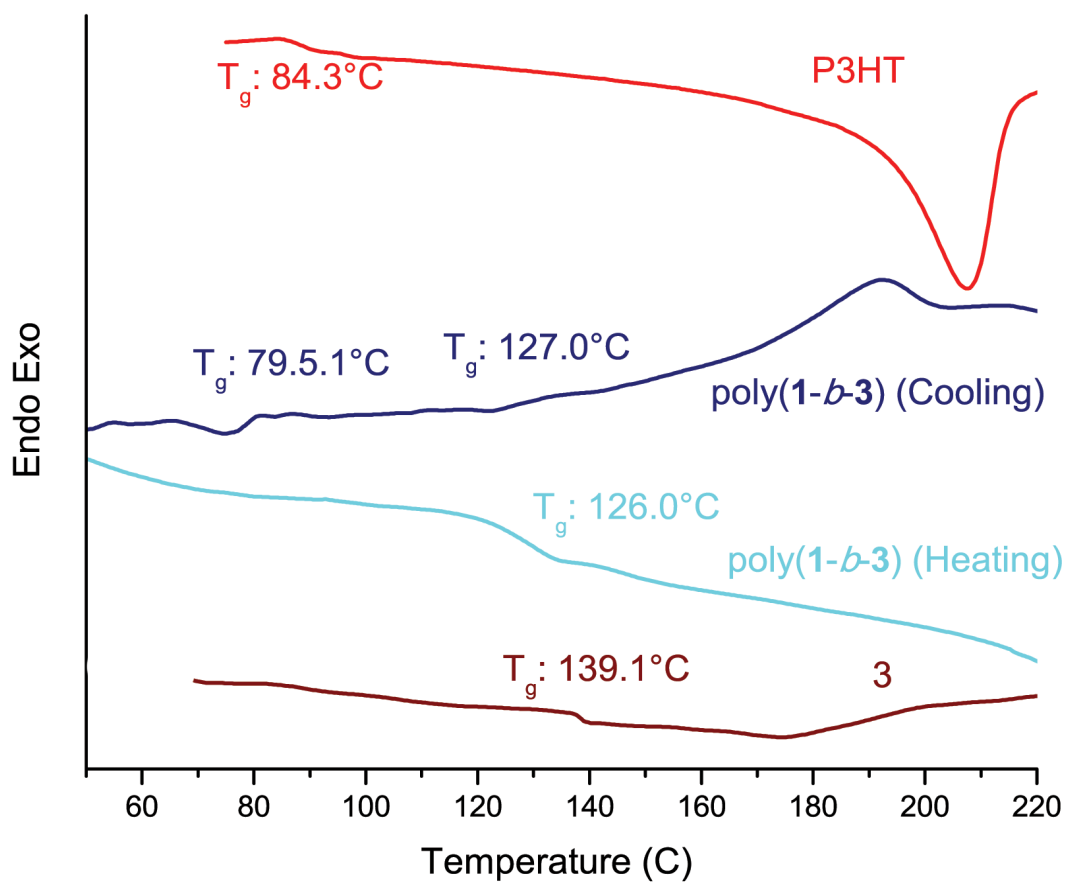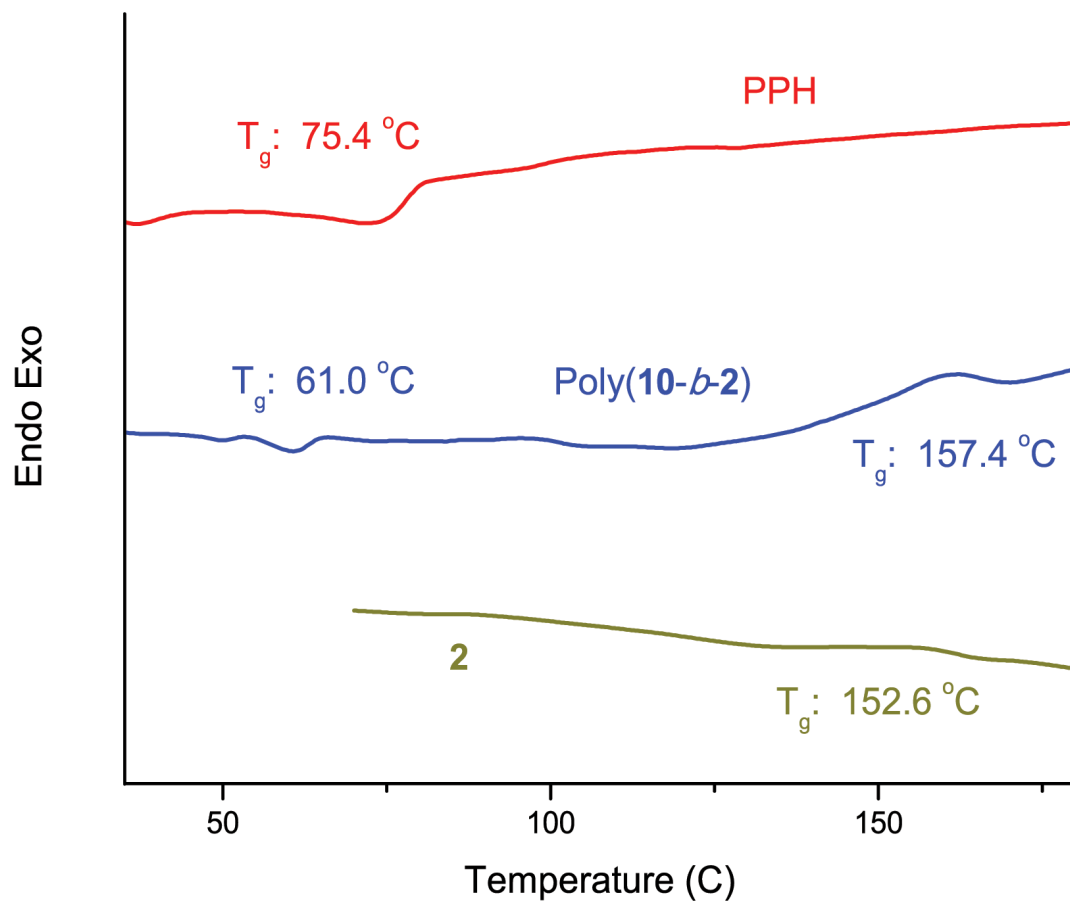
***Figure* S12.** DSC thermograms of (top) P3HT (M_n = 8.2 kDa), (middle) poly(**1**-*b*-**3**) (M_n = 15.9 kDa) and (bottom) a homopolymer of **3** (M_n = 32 kDa) (rate = 20 °C min^{-1}).
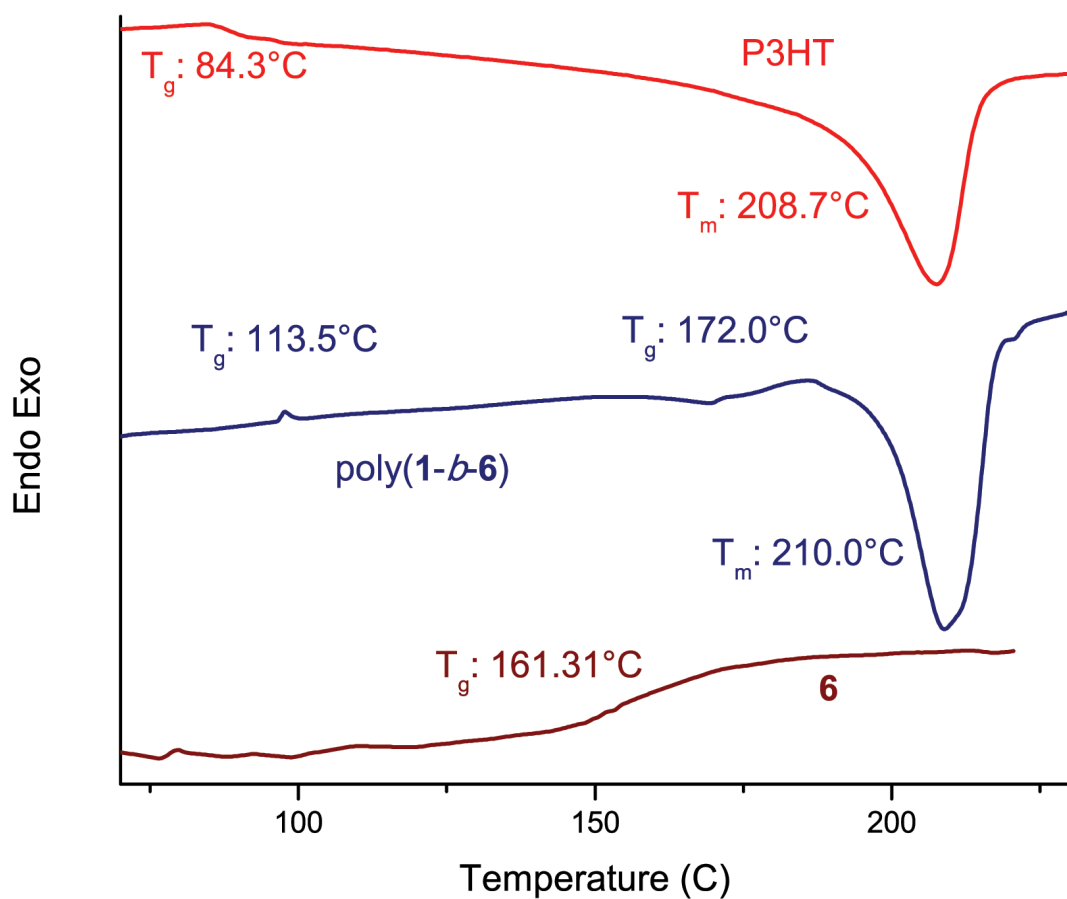
Figure S13. DSC thermograms of (top) P3HT (M_n = 8.2 kDa), (middle) poly(**1**-*b*-**6**) (M_n = 11.3 kDa) and (bottom) a homopolymer of **6** (M_n = 2.9 kDa) (rate = 20 °C min^{-1}).
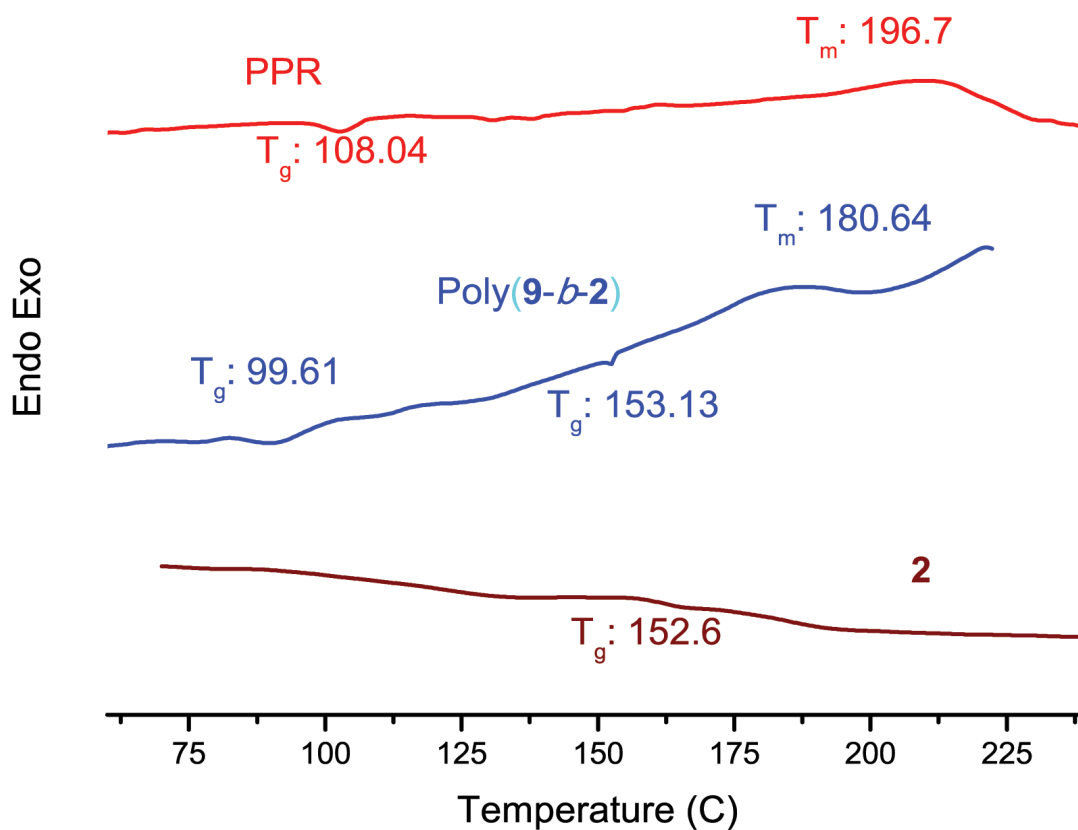
Figure S14. DSC thermograms of (top) poly-**9** (M_n = 7.7 kDa), (middle) poly(**9**-*b*-**2**) (M_n = 11.2 kDa) and (bottom) a homopolymer of **2** (M_n = 17.0 kDa) (rate = 20 °C min^{-1}).
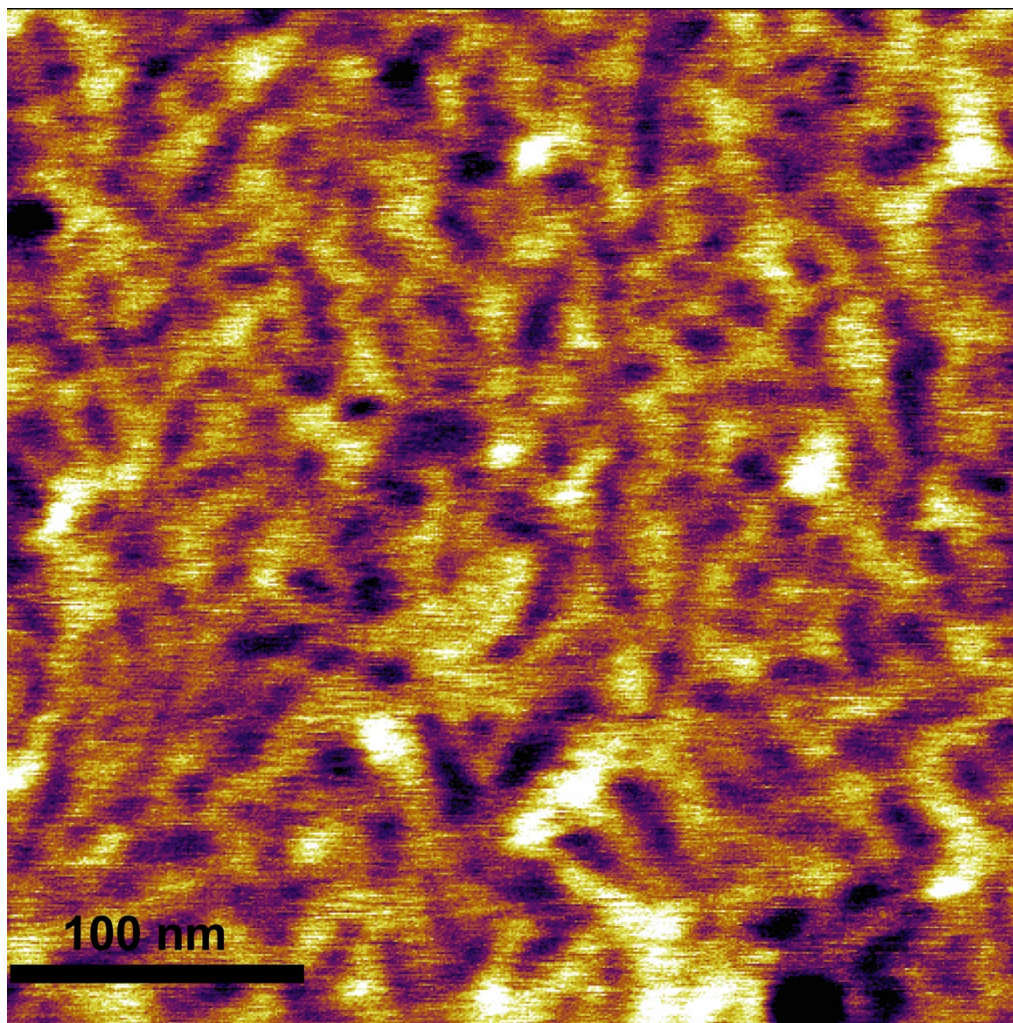
Figure S15. DSC thermograms of (top) poly-**10** (M_n = 6.2 kDa), (middle) poly(**10**-*b*-**2**) (M_n = 10.0 kDa) and (bottom) a homopolymer of **2** (M_n = 17.0 kDa) (rate = 20 °C min^{-1}).
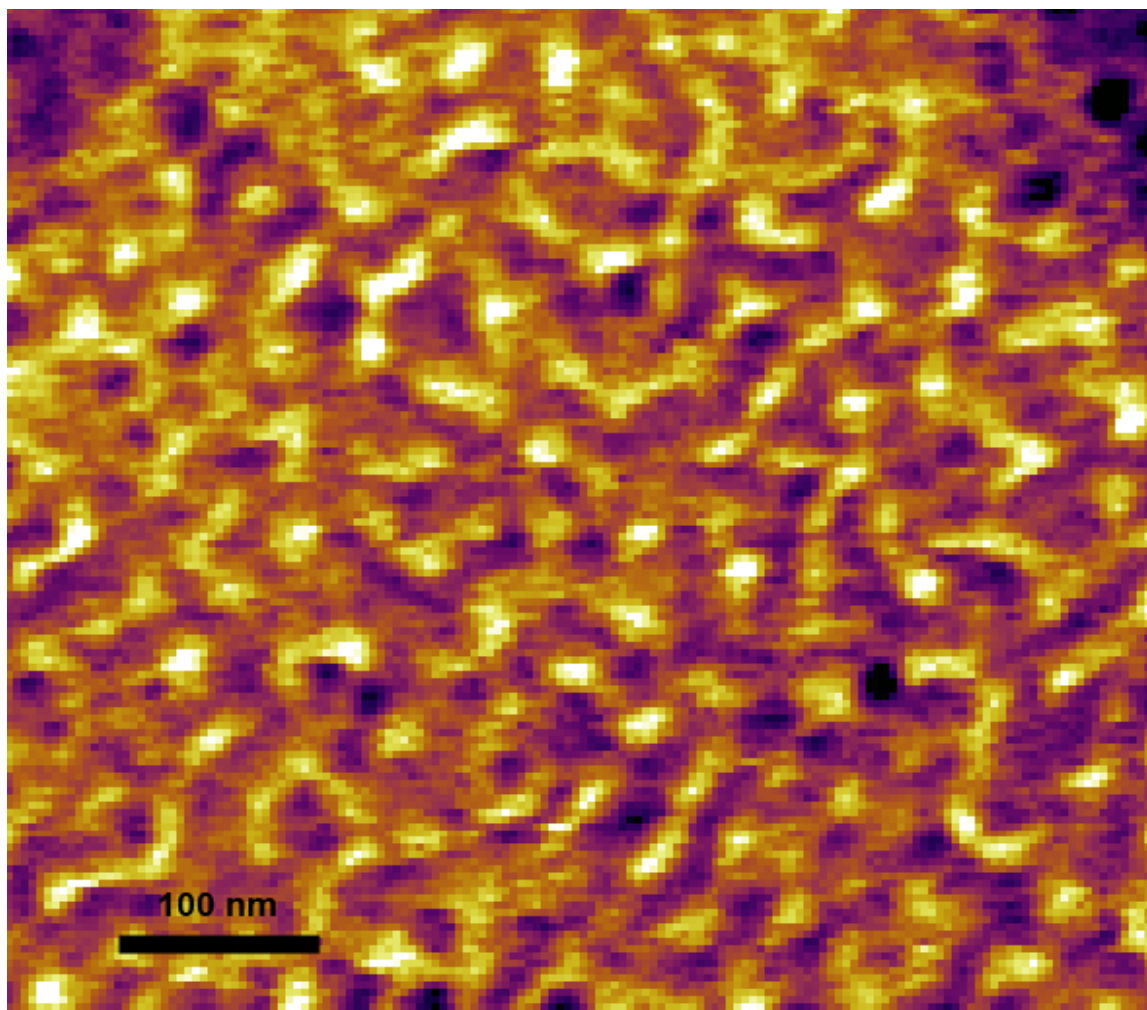
200 nm
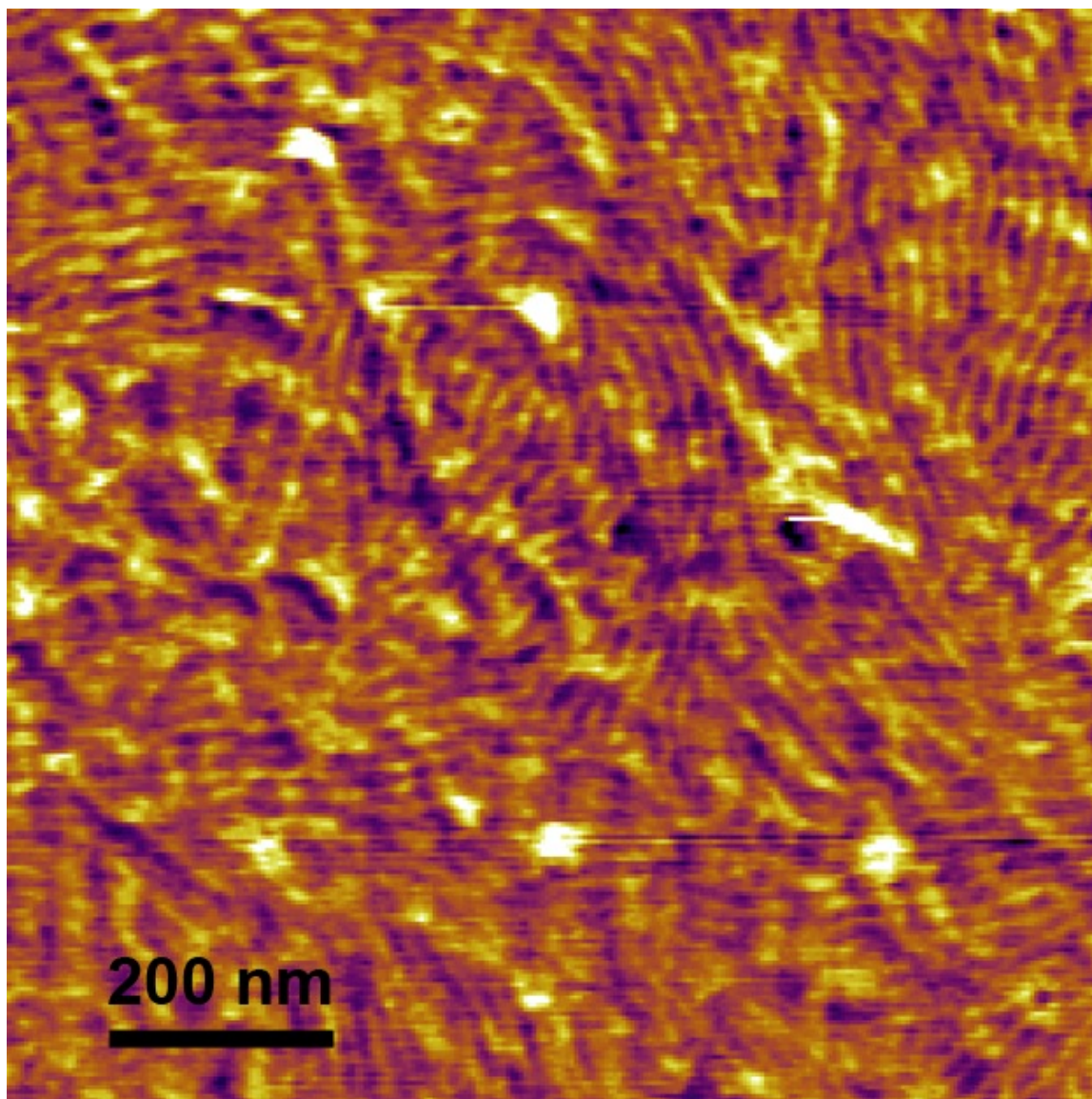
***Figure* S16.** AFM phase image of poly(**1**-*b*-**3**) (M_n = 12.3 kDa) spin-coated from $CHCl_3$ (1.4 mg mL^{-1}) onto a Si wafer.
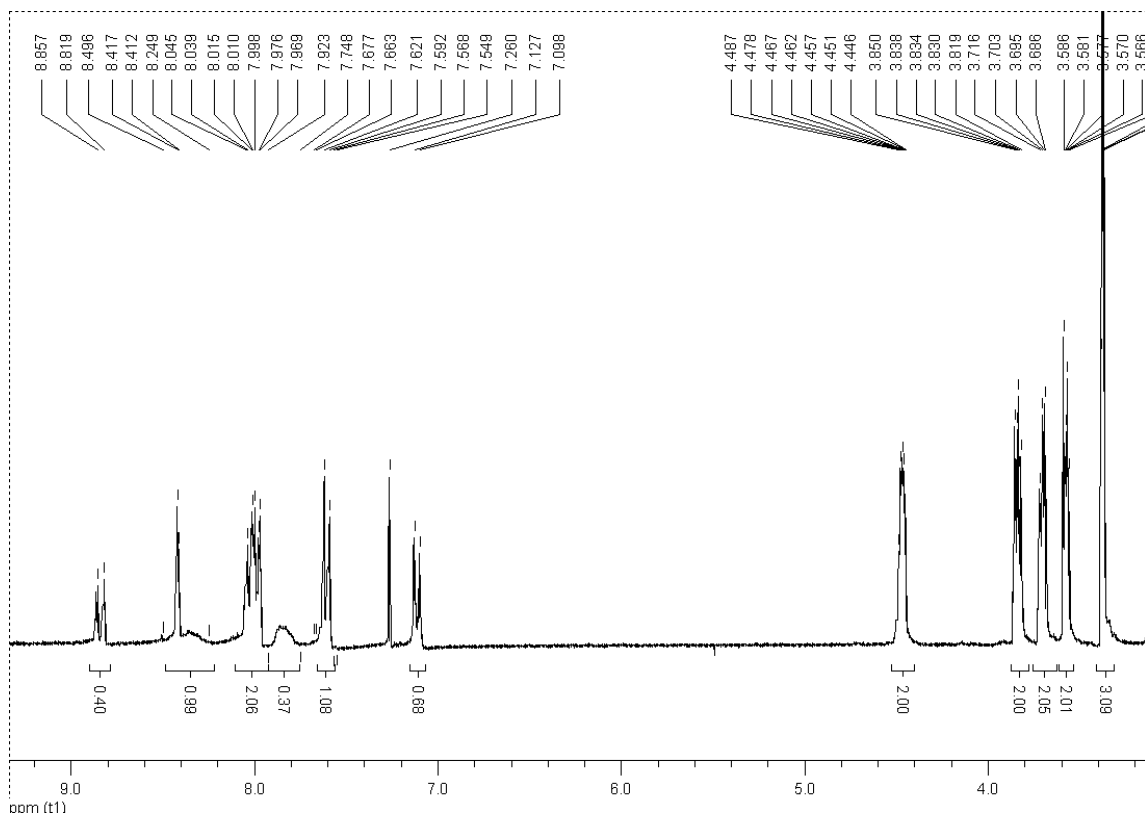
***Figure* S17.** AFM phase image of poly(**1**-*b*-**6**) (M_n = 11.3 kDa) spin-coated from $CHCl_3$ (2.5 mg mL^{-1}) onto a Si wafer.
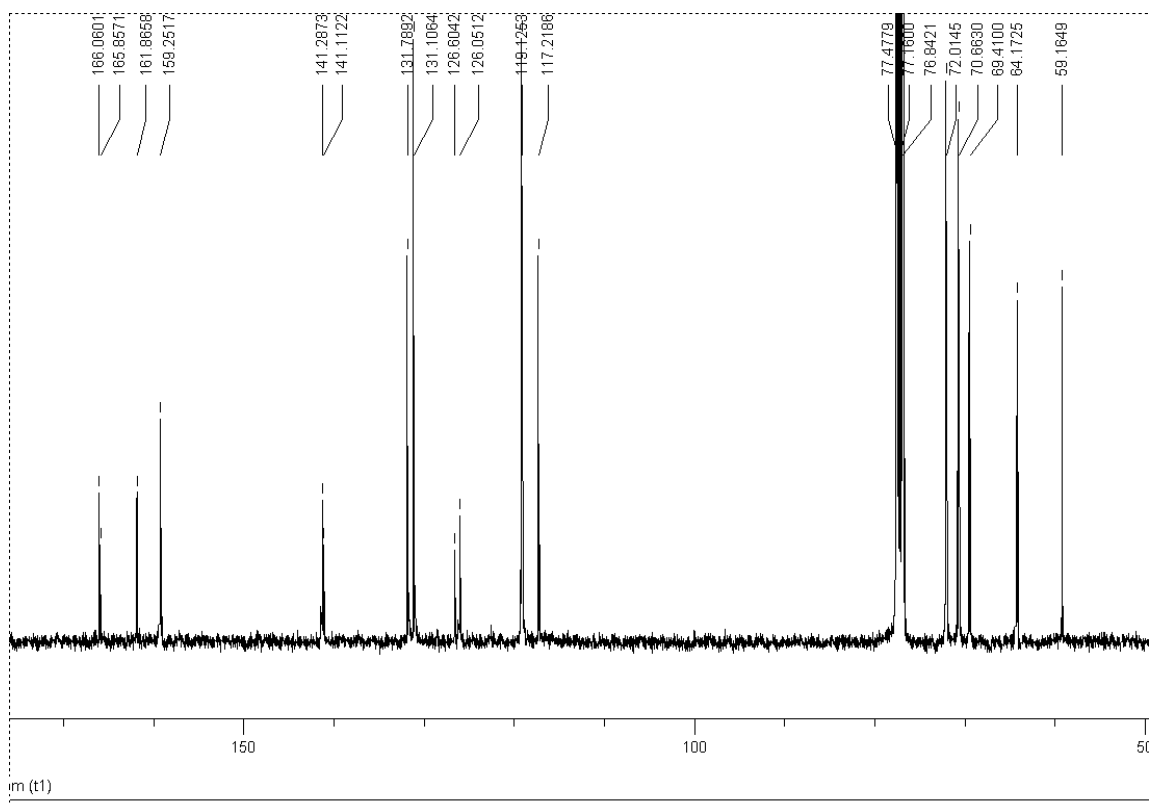
***Figure* S18.** AFM phase image of poly(**10**-*b*-**2**) (M_n = 10 kDa) spin-coated from CHCl$_3$ (10 mg mL^{-1}) onto a Si wafer.

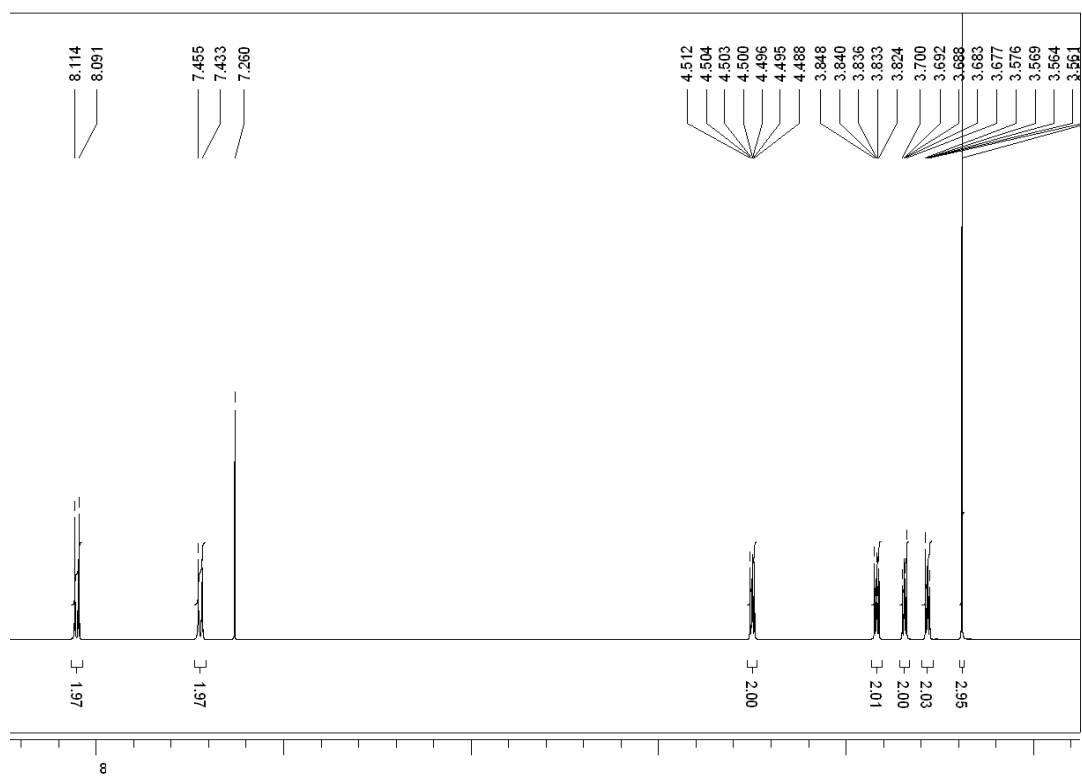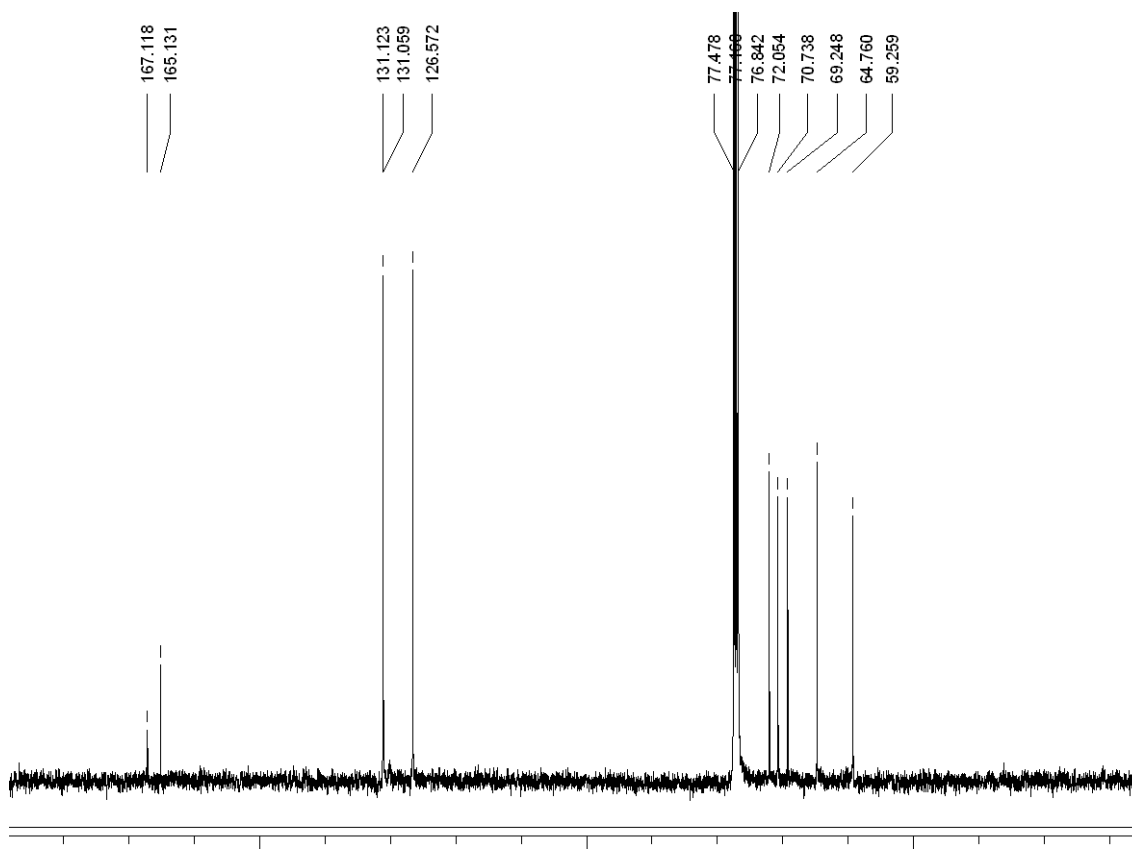***Figure* S19.** ^{1}H NMR spectrum of **12** (CDCl$_3$, 25 °C, 300 MHz).

***Figure* S20.** ^{13}C NMR spectrum of **12** (CDCl$_3$, 25 °C, 300 MHz).

Figure **S21.** ^{1}H NMR spectrum of **3** (CDCl$_3$, 25 °C, 300 MHz).

Figure **S22.** ^{13}C NMR spectrum of **3** (CDCl$_3$, 25 °C, 300 MHz).

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