Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Facile Synthesis and Chiral Recognition of Block and Star Copolymers Containing Stereoregular Helical Poly(phenyl isocyanide) and Polyethylene Glycol Blocks

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General consideration.

The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 600 or 400 MHz spectrometer {H}. Mass spectrometry were recorded on ACQUITY UPLC LCT Premier XE. Elemental analysis were recorded on Vario EL c. Size exclusion chromatography (SEC) was performed on Waters 1515 pump and Waters 2414 differential refractive index (RI) detector (set at 40 °C) using a series of linear Styragel HR1, HR2 and HR4 columns. Molecular weight (M_n) and its polydispersity (M_w/M_n) data are reported relative to polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.3 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets. UV-vis spectra were performed on a UNIC 4802 UV/VIS double beam spectrophotometer in 1.0 cm length quartz cell. Circular dichroism (CD) spectra were obtained in a 1.0 mm quartz cell at 25 °C using a JASCO J1500 spectropolarimeter. The polymer concentration was calculated on the basis of the monomer units and was 0.20 mg/mL. Emission spectra were recorded on Hitachi F-4600 fluorescence spectrophotometer. Dynamic light scattering (DLS) was recorded using a Nano-ZS 90 Zetasizer of Malvern (UK) instrument. All samples were filtered with syringe filters (0.8 μm pore size, Cellulose Acetate filter media) prior to the measurements, and all data were averaged over three time measurements. Samples for atomic force microscopy (AFM) measurements were prepared by drop casting solutions of polymer onto pre-cleaned silicon wafers or mica placed. AFM images were acquired in tapping mode with a Digital Instruments Dimension 3100 Scanning Probe Microscope, 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. Scanning electron microscopy (SEM) was performed on a SU8020 operating at 5.0 kV accelerating voltage.

All solvents were obtained from Sinopharm. Co. Ltd., and were purified by the standard procedures before use otherwise denoted. 5-Trimethylsilyl-4-prntyn-1-ol, 4-ethynylbenzoic acid, 4-dimethylaminopyridine (DMAP), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI), terakis(triphenylphosphine)palladium(0), copper(I) chloride, copper(I) iodide, tetrabutylammonium fluoride (TBAF), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 5-(prop-2-yn-1-yloxy)isophthalic acid, MA-poly-**2**$_m$s and BA-poly-**2**$_m$s were purchased from Aladdin and Sigma-Aldrich. Co. Ltd., and were used as received without further purification otherwise denoted. Phenyl isocyanide monomers **1a**,[1] **1L**, **1D**,[2] dansyl modified L- and D-phenylalanine (L- or D-DNSP),[3] were prepared according to the literatures and the structures were confirmed by ^{1}H NMR. All the polymerizations was carried out in a dry glass ampule under a dry nitrogen atmosphere.

Synthesis of MA-poly-1$_m$s:

Synthesis of ***3***. 5-Trimethylsilyl-4-prntyn-1-ol (2.98 mL, 16.42 mmol) was added to a mixture of 4-ethynylbenzoic acid (2.00 g, 13.68 mmol), EDCI (3.28 g, 16.42 mmol) and DMAP (0.84 g, 6.84 mmol) in dichloromethane (50 mL) via a syringe. The resulting solution was stirred at room temperature for 3 h, and quenched by water. The organic layer was washed with sodium bicarbonate (10 mL × 3) and brine (10 mL × 3), dried over anhydrous Na_2SO_4 and concentrated to dryness. The isolated residue was further purified by silica gel chromatography (eluent: *n*-hexane/ethyl acetate = 50/1, v/v) to give **3** as a white solid (3.50 g, 90% yield). M.p.: 39.8−42.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.99−7.97 (m, 2H, aromatic), 7.56−7.53 (m, 2H, aromatic), 4.40 (t, J = 9.6 Hz, 2H, CO_2CH_2), 3.23 (s, 1H, HC≡C), 2.41 (t, J = 10.8 Hz, 2H, $CO_2CH_2CH_2C\underline{H_2}$), 2.02−1.95 (m, 2H, $CO_2CH_2C\underline{H_2}$), 0.14 (t, J = 4.8 Hz, 9H, TMS). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 165.87, 132.15, 130.33, 129.55, 126.85, 105.71, 85.57, 82.89, 80.24, 63.97, 27.90, 16.88, 0.19. MS m/z calcd for $C_{17}H_{20}O_2Si$ $[M+H]^+$: 285.1326. Found: 285.1304. Anal. Calcd

(%) for $C_{17}H_{20}O_2Si$: C, 71.79; H, 7.09. Found (%): C, 71.82; H, 7.28. FT-IR (KBr, cm^{-1}): 3263 ($\nu_{C\text{-}H}$), 2976 ($\nu_{C\text{–}H}$), 2960 ($\nu_{C\text{–}H}$), 2898 ($\nu_{C\text{–}H}$), 2174 ($\nu_{C\equiv C}$), 2108 ($\nu_{C\equiv C}$), 1702 ($\nu_{C=O}$).

Synthesis of **4**: Under dry nitrogen atmosphere and keep in dark place, compound **3** (1.00 g, 3.52 mmol) was treated with *trans*-bis(triethylphosphine)palladium(II) dichloride (1.59 g, 3.86 mmol) in the presence of copper(I) chloride (0.34 g, 1.75 mmol) as catalyst in 30 mL of diethylamine and dichloromethane (v/v = 1/1). The mixture was stirred at room temperature for 1 h. After the solvent was removed by evaporation under reduced pressure, the residue was purified by chromatography (eluent: *n*-hexane/ethyl acetate = 40/1, v/v) to afford **4** (1.67 g, 72% yield) as a light yellow solid. M.p.: 55.6−57.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.91−7.89 (m, 2H, aromatic), 7.29−7.26 (m, 2H, aromatic), 4.38 (t, J = 9.6 Hz, 2H, CO_2CH_2), 2.40 (t, J = 10.2 Hz, 2H, $CO_2CH_2CH_2C\underline{H_2}$), 2.01–1.94 (m, 14H, $CO_2CH_2C\underline{H_2}$ and $PC\underline{H_2}CH_3$), 1.25–1.17 (m, 18H, $PCH_2C\underline{H_3}$), 0.14 (t, J = 5.4 Hz, 9H, TMS). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.44, 132.70, 130.55, 129.53, 127.03, 106.80, 105.88, 101.87, 85.43, 63.60, 28.01, 16.90, 15.52, 8.45, 0.21. MS m/z calcd for $C_{29}H_{49}ClO_2P_2PdSi$ $[M+H]^+$: 662.1749; Found: $C_{29}H_{49}ClO_2P_2PdSi$, 662.1767. Anal. Calcd (%) for $C_{29}H_{49}ClO_2P_2PdSi$: C, 52.65; H, 7.47. Found (%): C, 52.71; H, 7.51. FT-IR (KBr, cm^{-1}): 2964 ($\nu_{C\text{–}H}$), 2935 ($\nu_{C\text{–}H}$), 2877 ($\nu_{C\text{–}H}$), 2175 ($\nu_{C\equiv C}$), 2113 ($\nu_{C\equiv C}$), 1715 ($\nu_{C=O}$).

Synthesis of **5**: To a solution of **4** (1.30 g, 1.96 mmol) in dry THF (20 mL) under dry nitrogen atmosphere, a solution of TBAF (2.57 g, 9.82 mmol) in THF (10 mL) was added via a syringe. After the mixture stirred at 0 °C for 0.5 h, the reaction solution was removed by evaporation under reduced pressure. Then dichloromethane (30 mL) was added and the organic phase was washed with H_2O (15 mL × 3) and brine (15 mL × 3), dried over anhydrous Na_2SO_4 and concentrated to dryness. The isolated residue was further purified by silica gel chromatography (eluent: *n*-hexane/ethyl acetate = 20/1, v/v) to afford **5** (1.06 g, 92%

yield) as a light yellow solid. M.p.: 44.8−45.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.91−7.89 (m, 2H, aromatic), 7.29−7.27 (m, 2H, aromatic), 4.40 (t, J = 9.6 Hz, 2H, CO_2CH_2), 2.39−2.35 (m, 2H, $CO_2CH_2CH_2C\underline{H_2}$), 2.02–1.94 (m, 15H, HC≡C, $CO_2CH_2C\underline{H_2}$ and $PC\underline{H_2}CH_3$)), 1.25−1.17 (m, 18H, $PCH_2C\underline{H_3}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 166.41, 132.74, 130.53, 129.51, 126.98, 106.79, 101.93, 83.14, 69.18, 63.41, 27.84, 15.53, 8.43. MS m/z calcd for $C_{26}H_{41}O_2P_2Pd$ [M–Cl]$^+$: 553.1617; Found: $C_{26}H_{41}O_2P_2Pd$ [M–Cl]$^+$, 553.1505. Anal. Calcd (%) for $C_{26}H_{41}ClO_2P_2Pd$: C, 52.98; H, 7.01. Found (%): C, 52.91; H, 7.06. FT-IR (KBr, cm^{-1}): 3295 ($\nu_{C\text{-}H}$), 2967 ($\nu_{C\text{–}H}$), 2935 ($\nu_{C\text{–}H}$), 2877 ($\nu_{C\text{–}H}$), 2115 ($\nu_{C\equiv C}$), 1715 ($\nu_{C=O}$).

*Synthesis of MA-poly-**1a**$_{100}$*: A 10 mL oven-dried flask was charged with monomer **1a** (0.11 g, 3.32 μmol), THF (1.64 mL) and a stir bar. To this stirring solution was added a solution of **5** in THF via a microsyringe at room temperature. The concentrations of monomer **1a** and initiator **5** were 0.2 and 0.002 M, respectively ([**1a**]$_0$/[**2**]$_0$ = 100). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 9 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight afforded MA-poly-**1a**$_{100}$ as a yellow solid (0.10 g, 92% yield). SEC: M_n = 26.9 kDa, M_w/M_n = 1.21. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.31 (br, aromatic), 5.73 (br, aromatic), 4.04–3.82 (br, OCH_2), 1.63–0.85 (br, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C\text{–}H}$), 2925 ($\nu_{C\text{–}H}$), 2853 ($\nu_{C\text{–}H}$), 2112 ($\nu_{C\equiv C}$), 1721 ($\nu_{C=O}$), 1599 ($\nu_{C=N}$).

Polymerization of **1L** and **1D** was performed in a similar way to monomer **1a**. The characterization data for poly-**1L**$_{100}$ and poly-**1D**$_{100}$ were showed below.

*Poly-**1L**$_{100}$*: SEC: M_n = 27.1 kDa, M_w/M_n = 1.22. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.66–6.95 (br, aromatic), 5.93–5.56 (br, aromatic), 4.92–4.35 (br, OCH), 1.26–0.42 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C\text{–}H}$), 2927 ($\nu_{C\text{–}H}$), 2869 ($\nu_{C\text{–}H}$), 2121 ($\nu_{C\equiv C}$), 1722 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$).

*Poly-**1D**$_{100}$*: SEC: M_n = 26.8 kDa, M_w/M_n = 1.23. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 7.65–6.94 (br, aromatic), 5.92–5.55 (br, aromatic), 4.91–4.35 (br, OCH), 1.85–0.41 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2954 ($\nu_{C\text{–}H}$), 2929 ($\nu_{C\text{–}H}$), 2869 ($\nu_{C\text{–}H}$), 2121 ($\nu_{C\equiv C}$), 1716 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$).

Synthesis of helix-coil and helix-coil-helix block copolymers:

*Synthesis of poly(**1a**$_{100}$-b-**2**$_{45}$).* A 100 mL oven-dried, three-neck flask equipped with a stir bar was evacuated and purged with N_2 three times prior to addition of any reagents. MA-poly-**1a**$_{100}$ (100.0 mg, SEC: M_n = 26.9 kDa, M_w/M_n = 1.21) and MA-poly-**2**$_{45}$ (66.5 mg, SEC: M_n = 2.0 kDa, M_w/M_n = 1.15) were dissolved in THF and added to the purged flask via a syringe under a constant N_2 flow. DBU (1.98 μL, 13.30 μmol) was then added to the stirring mixture followed by CuI (0.17 mg, 0.67 μmol) and the stirring reaction mixture was heated to 40 °C in a preheated oil bath for 24 h. Upon cooling to room temperature, the solution was concentrated slightly and precipitated into methanol. The solid was isolated via filtration and dried under vacuum at room temperature, afford poly(**1a**$_{100}$-*b*-**2**$_{45}$) as a yellow solid (121.1 mg, 73% yield). SEC: M_n = 30.2 kDa, M_w/M_n = 1.35. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.01 (s, CH of triazole), 7.31 (br, aromatic), 5.73 (br, aromatic), 4.05–3.82 (br, CO_2CH_2), 3.64–3.38 (br, OCH_2 of PEG), 1.62–0.85 (br, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C\text{–}H}$), 2925 ($\nu_{C\text{–}H}$), 2853 ($\nu_{C\text{–}H}$), 1717 ($\nu_{C=O}$), 1603 ($\nu_{C=N}$).

The diblock copolymer poly(**1L**$_{100}$-*b*-**2**$_{45}$) and poly(**1D**$_{100}$-*b*-**2**$_{45}$) were prepared followed the same procedure described above by using BA-poly-**2**$_{45}$, MA-poly-**1L**$_{100}$, and MA-poly-**1D**$_{100}$, respectively. The characteristic data are showed below.

*Poly(**1L**$_{100}$-b-**2**$_{45}$)*: 79% yield. SEC: M_n = 29.7 kDa, M_w/M_n = 1.30. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C):

δ 8.01 (s, CH of triazole), 7.66–6.97 (br, aromatic), 5.94–5.56 (br, aromatic), 4.93–4.37 (br, OCH), 3.65–3.50 (br, OCH_2 of PEG), 1.86–0.44 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C–H}$), 2927 ($\nu_{C–H}$), 2871 ($\nu_{C–H}$), 1717 ($\nu_{C=O}$), 1603 ($\nu_{C=N}$).

*Poly(**1D**$_{100}$-b-**2**$_{45}$)*: 76% yield. SEC: M_n = 29.9 kDa, M_w/M_n = 1.33. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.02 (s, CH of triazole), 7.68–7.03 (br, aromatic), 5.93–5.57 (br, aromatic), 4.92–4.35 (br, OCH), 3.64–3.48 (br, OCH_2 of PEG), 1.85–0.41 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2957 ($\nu_{C–H}$), 2927 ($\nu_{C–H}$), 2871 ($\nu_{C–H}$), 1722 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$).

The triblock copolymer poly(**1a**$_{100}$-*b*-**2**$_{45}$-*b*-**1a**$_{100}$), poly(**1L**$_{100}$-*b*-**2**$_{45}$-*b*-**1L**$_{100}$), and poly(**1D**$_{100}$-*b*-**2**$_{45}$-*b*-**1D**$_{100}$) were prepared followed the similar procedure described above using the BA-poly-**2**$_{45}$ instead of MA-poly-**2**$_{45}$. The characteristic data are displayed below.

*Poly(**1a**$_{100}$-b-**2**$_{45}$-b-**1a**$_{100}$)*: 78% yield. SEC: M_n = 58.7 kDa, M_w/M_n = 1.42. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.01 (s, CH of triazole), 7.31 (br, aromatic), 5.74 (br, aromatic), 4.06–3.84 (br, CO_2CH_2), 3.64–3.40 (br, OCH_2 of PEG), 1.68–0.85 (br, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C–H}$), 2924 ($\nu_{C–H}$), 2853 ($\nu_{C–H}$), 1720 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

*Poly(**1L**$_{100}$-b-**2**$_{45}$-b-**1L**$_{100}$)*: 76% yield. SEC: M_n = 51.1 kDa, M_w/M_n = 1.69. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.01 (s, CH of triazole), 7.65–6.94 (br, aromatic), 5.92–5.56 (br, aromatic), 4.91–4.35 (br, CO_2CH), 3.74–3.53 (br, OCH_2 of PEG), 2.18–0.43 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C–H}$), 2927 ($\nu_{C–H}$), 2871 ($\nu_{C–H}$), 1717 ($\nu_{C=O}$), 1601 ($\nu_{C=N}$).

*Poly(**1D**$_{100}$-b-**2**$_{45}$-b-**1D**$_{100}$)*: 77% yield. SEC: M_n = 50.8 kDa, M_w/M_n = 1.61. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.02 (s, CH of triazole), 7.65–6.95 (br, aromatic), 5.94–5.57 (br, aromatic), 4.95–4.39 (br, CO_2CH), 3.65–3.49 (br, OCH_2 of PEG), 2.19–0.45 (br, CH, CH_2 and CH_3). FT-IR (cm^{-1}): 2955 ($\nu_{C–H}$), 2927 ($\nu_{C–H}$), 2866 ($\nu_{C–H}$), 1716 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

Synthesis of BA-poly-1_ms:

Synthesis of ***6***: 5-Trimethylsilyl-4-prntyn-1-ol (3.42 g, 21.90 mmol) was added to a mixture of 5-(prop-2-yn-1-yloxy)isophthalic acid (4.00 g, 18.21 mmol), EDCI (4.19 g, 21.91 mmol) and DMAP (1.34 g, 10.90 mmol) in dichloromethane (80 mL) via a syringe. The resulting solution was stirred at room temperature for 3 h and quenched by water. The organic layer was washed with sodium bicarbonate (10 mL × 3) and brine (10 mL × 3), dried over anhydrous Na_2SO_4 and concentrated to dryness. The isolated residue was further purified by silica gel chromatography (eluent: *n*-hexane/ethyl acetate = 40/1, v/v) to give **6** as a white solid (3.50 g, 90% yield). M.p.: 46.3−47.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.30 (s, 1H, aromatic), 7.83 (s, 2H, aromatic), 4.78 (d, J = 2.4 Hz, 2H, HC≡C$\underline{H_2}$), 4.44 (t, J = 6.6 Hz, 4H, CO_2CH_2), 2.56 (s, 1H, HC≡C), 2.42 (t, J = 7.2 Hz, 4H, $CO_2CH_2CH_2C\underline{H_2}$), 2.02–1.98 (m, 4H, $CO_2CH_2C\underline{H_2}CH_2$), 0.14 (s, 18H, TMS). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 165.50, 157.63, 132.14, 123.89, 120.42, 105.63, 85.68, 77.70, 76.51, 64.25, 56.42, 27.89, 16.83, 0.21. MS m/z calcd for $C_{27}H_{36}O_5Si_2$ $[M+H]^+$: 497.2163; Found: $C_{27}H_{36}O_5Si_2$, 497.2195. Anal. Calcd (%) for $C_{27}H_{36}O_5Si_2$: C, 65.28; H, 7.31. Found (%): C, 65.33; H, 7.27. FT-IR (KBr, cm^{-1}): 3265 ($\nu_{C–H}$), 2975 ($\nu_{C–H}$), 2960 ($\nu_{C–H}$), 2896 ($\nu_{C–H}$), 2175 ($\nu_{C≡C}$), 2110 ($\nu_{C≡C}$), 1703($\nu_{C=O}$).

Synthesis of ***7***: Under dry nitrogen atmosphere and keep in dark place, compound **6** (1.00 g, 6.03 mmol) was treated with *trans*-bis(triethylphosphine)palladium(II) dichloride (2.74 g, 6.65 mmol) in the presence of copper(I) chloride (0.64 g, 3.32 mmol) as catalyst in 20 mL of diethylamine and dichloromethane (v/v =1/1). The mixture was stirred at room temperature for 1 h. After the solvents were removed by evaporation under reduced pressure, the residue was purified by silica gel chromatography (eluent: *n*-

hexane/ethyl acetate = 25/1, v/v) to give **7** as a light yellow oil (3.83 g, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.23 (s, 1H, aromatic), 7.82 (s, 2H, aromatic), 4.82 (s, 2H, $PhOC\underline{H_2}$), 4.42 (t, J = 6.6 Hz, 4H, CO_2CH_2), 2.41 (t, J = 7.2 Hz, 4H, $CO_2CH_2CH_2C\underline{H_2}$), 2.02–1.97 (m, 4H, $CO_2CH_2C\underline{H_2}$), 1.84–1.81 (m, 12H, $PC\underline{H_2}CH_3$), 1.12–1.07 (m,18H, $PCH_2C\underline{H_3}$), 0.15 (s, 18H, TMS). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 164.73, 157.35, 130.83, 122.90, 120.67, 105.62, 85.71, 64.19, 58.49, 27.97, 15.40, 15.22, 8.35, 0.23. MS m/z calcd for $C_{39}H_{65}ClO_5P_2PdSi_2$ $[M+H]^+$: 874.2987; Found: $C_{39}H_{65}ClO_5P_2PdSi_2$, 874.2942. Anal. Calcd (%) for $C_{39}H_{65}ClO_5P_2PdSi_2$: C, 53.63; H, 7.50. Found (%): C, 53.58; H, 7.48. FT-IR (KBr, cm^{-1}): 2956 (ν_{C-H}), 2924 (ν_{C-H}), 2856 (ν_{C-H}), 2175 ($\nu_{C\equiv C}$), 2134 ($\nu_{C\equiv C}$), 1728 ($\nu_{C=O}$).

Synthesis of ***8***: To a solution of **7** (3.00 g, 3.48 mmol) in dry THF (60 mL) under dry nitrogen atmosphere, a solution of TBAF (4.48 g, 17.15 mmol) in THF (10 mL) was added via a syringe. After the mixture was stirred at 0 °C for 0.5 h, the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane and the organic phase was washed with H_2O (15 mL × 3) and brine (15 mL × 3). The organic layer was dried over Na_2SO_4. After filtration and evaporation, the resulting crude product was purified by column chromatography (eluent: *n*-hexane/ethyl acetate = 20/1, v/v) to afford **8** as a light yellow oil (2.48 g, 93% yield). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.25 (s, 1H, aromatic), 7.83 (s, 2H, aromatic), 4.82 (s, 2H, $PhOC\underline{H_2}$), 4.45 (t, J = 6.0 Hz, 4H, $CO_2C\underline{H_2}$), 2.40–2.38 (m, 4H, $CO_2CH_2CH_2C\underline{H_2}$), 2.06–2.01 (m, 6H, $CO_2CH_2C\underline{H_2}$ and $HC\equiv C$), 1.85–1.82 (m, 12H, $PC\underline{H_2}CH_3$), 1.13–1.08 (m, 18H, $PCH_2C\underline{H_3}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 165.62, 158.24, 131.69, 122.83, 120.63, 99.33, 93.73, 82.91, 69.34, 63.89, 58.37, 27.67, 15.31, 15.12, 8.26. MS m/z calcd for $C_{33}H_{49}ClO_5P_2Pd$ $[M+H]^+$: 728.1823, Found: $C_{33}H_{49}ClO_5P_2Pd$, 728.1792. Anal. Calcd (%) for $C_{33}H_{49}ClO_5P_2Pd$: C, 54.33; H, 6.77.

Found (%): C, 54.29; H, 6.65. FT-IR (KBr, cm^{-1}): 3288 ($\nu_{\mathrm{C-H}}$), 2964 ($\nu_{\mathrm{C-H}}$), 2935 ($\nu_{\mathrm{C-H}}$), 2876 ($\nu_{\mathrm{C-H}}$), 2130 ($\nu_{\mathrm{C\equiv C}}$), 1717 ($\nu_{\mathrm{C=O}}$).

*Synthesis of BA-poly-**1a**$_{100}$*: A 10 mL oven-dried flask was charged with monomer **1a** (100.0 mg, 0.35 mmol), THF (1.75 mL) and a stir bar. To this stirring solution was added a solution of **8** in THF via a microsyringe at ambient temperature. The concentrations of monomer **1a** and initiator **8** were 0.2 and 0.002 M, respectively ([**1a**]$_0$/[**8**]$_0$=100). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 11 h. After cooled to room temperature, the polymerization solution was precipitated into a large amount of methanol, collected by centrifugation, and dried in vacuum at room temperature overnight afford BA-poly-**1a**$_{100}$ as a yellow solid (92.0 mg, 92% yield). SEC: M_n = 27.4 kDa, M_w/M_n = 1.22. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ 7.34 (br, aromatic), 5.77 (br, aromatic), 4.07–3.86 (br, OCH$_2$), 1.52–0.87 (br, CH$_2$ and CH$_3$). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{\mathrm{C-H}}$), 2928 ($\nu_{\mathrm{C-H}}$), 2868 ($\nu_{\mathrm{C-H}}$), 2118 ($\nu_{\mathrm{C\equiv C}}$), 1717 ($\nu_{\mathrm{C=O}}$), 1603 ($\nu_{\mathrm{C=N}}$).

Polymerization of **1L** and **1D** using Pd(II) initiator **8** were performed followed the similar procedure. The characterization data for BA-poly-**1L**$_{100}$ and BA-poly-**1D**$_{100}$ were showed below.

*BA-poly-**1L**$_{100}$*: SEC: M_n = 24.9 kDa, M_w/M_n = 1.20. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ 7.65–6.96 (br, aromatic), 5.92–5.56 (br, aromatic), 4.90–4.37 (br, OCH), 2.18–0.42 (br, CH, CH$_2$ and CH$_3$). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{\mathrm{C-H}}$), 2927 ($\nu_{\mathrm{C-H}}$), 2869 ($\nu_{\mathrm{C-H}}$), 2122 ($\nu_{\mathrm{C\equiv C}}$), 1719 ($\nu_{\mathrm{C=O}}$), 1601 ($\nu_{\mathrm{C=N}}$).

*BA-poly-**1D**$_{100}$*: SEC: M_n = 26.2 kDa, M_w/M_n = 1.23. ^{1}H NMR (600 MHz, CDCl$_3$, 25 °C): δ 7.68–7.03 (br, aromatic), 5.95–5.60 (br, aromatic), 4.95–4.40 (br, OCH), 2.18–0.47 (br, CH, CH$_2$ and CH$_3$). FT-IR (KBr, cm^{-1}): 2957 ($\nu_{\mathrm{C-H}}$), 2927 ($\nu_{\mathrm{C-H}}$), 2869 ($\nu_{\mathrm{C-H}}$), 2120 ($\nu_{\mathrm{C\equiv C}}$), 1718 ($\nu_{\mathrm{C=O}}$), 1599 ($\nu_{\mathrm{C=N}}$).

Synthesis of helix-(coil)$_2$ star polymers:

The synthetic procedure for helix-(coil)$_2$ miktoarm star polymers was similar to those of AB and ABA. The characterization data for poly(**1a**$_{100}$-*b*-(**2**$_{45}$)$_2$), poly(**1L**$_{100}$-*b*-(**2**$_{45}$)$_2$) and poly(**1D**$_{100}$-*b*-(**2**$_{45}$)$_2$) were showed below.

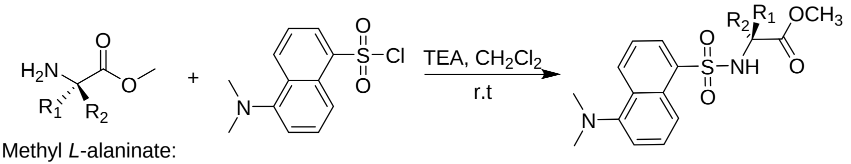
*Poly(**1a**$_{100}$-b-(**2**$_{45}$)$_2$)*: 78% yield. SEC: M_n = 32.6 kDa, M_w/M_n = 1.31. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.01 (s, CH of triazole), 7.31 (br, aromatic), 5.74 (br, aromatic), 4.04–3.82 (br, CO_2CH_2), 3.64–3.38 (br, OCH_2 of PEG), 1.59–0.85 (br, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2955 ($\nu_{C–H}$), 2928 ($\nu_{C–H}$), 2868 ($\nu_{C–H}$), 1716 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

*Poly(**1L**$_{100}$-b-(**2**$_{45}$)$_2$)*: 76% yield. SEC: M_n = 29.1 kDa, M_w/M_n = 1.43. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.00 (s, CH of triazole), 7.66–6.99 (br, aromatic), 5.94–5.58 (br, aromatic), 4.94–4.37 (br, CO_2CH), 3.64–3.37 (br, OCH_2 of PEG), 2.21–0.45 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2953 ($\nu_{C–H}$), 2927 ($\nu_{C–H}$), 2868 ($\nu_{C–H}$), 1715 ($\nu_{C=O}$), 1597 ($\nu_{C=N}$).

*Poly(**1D**$_{100}$-b-(**2**$_{45}$)$_2$)*: 77% yield. SEC: M_n = 29.8 kDa, M_w/M_n = 1.39. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ 8.01 (s, CH of triazole), 7.66–6.95 (br, aromatic), 5.93–5.55 (br, aromatic), 4.92–4.35 (br, CO_2CH), 3.64–3.48 (br, OCH_2 of PEG), 2.17–0.42 (br, CH, CH_2 and CH_3). FT-IR (KBr, cm^{-1}): 2953 ($\nu_{C–H}$), 2920 ($\nu_{C–H}$), 2871 ($\nu_{C–H}$), 1719 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$).

Synthesis of D/L-Ala-DNSP

Scheme S1. Synthesis of D/L-Ala-DNSP



Methyl *L*-alaninate: $R_1 = CH_3$, $R_2 = H$
Methyl *D*-alaninate: $R_1 = H$, $R_2 = CH_3$

L-Ala-DNSP, $R_1 = CH_3$, $R_2 = H$
D-Ala-DNSP, $R_1 = H$, $R_2 = CH_3$

Synthesis of ***L-Ala-DNSP****:* Dansyl chloride (2.74 g, 10.19 mmol) was added dropwise to a solution of methyl *L*-alaninate (1.05 g, 10.19 mmol) and TEA (1.23 g, 12.23 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After the mixture was stirred for 12 hour at room temperature, the resulting solution was washed with water (30 mL), brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: *n*-hexane/ethyl acetate = 5/1, v/v) to give L-Ala-DNSP (2.77 g, 81% yield). Mp: 109.1–111.7 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.55−7.18 (m, 7H, aromatic and NH), 4.01−3.94 (m, 1H, $CHCO_2$), 3.34 (s, 3H, CO_2CH_3), 2.88 (s, 6H, NCH_3), 1.31–1.29 (d, J = 7.2 Hz, 3H, $CHC\underline{H_3}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 172.41, 152.05, 134.77, 131.88, 130.84, 129.79, 129.75, 128.59, 127.18, 123.24, 118.94, 115.40, 52.47, 51.82, 45.55, 19.80. $[\alpha]^{25}_D$ –596.2 (c = 0.1, $CHCl_3$). MS m/z calcd for $C_{16}H_{20}N_2O_4S$ $[M + H]^+$: 337.1144, Found: $C_{16}H_{20}N_2O_4S$, 337.1220. Anal. Calcd (%) for $C_{16}H_{20}N_2O_4S$: C, 57.13; H, 5.99. Found (%): C, 57.19; H, 6.01. FT-IR (KBr, cm^{-1}): 2951 ($\nu_{C–H}$), 2840 ($\nu_{C–H}$), 2783 ($\nu_{C–H}$), 1743 ($\nu_{C=O}$).

D-Ala-DNSP was prepared under the same synthetic procedure to that of **L-Ala-DNSP** described above, and the characterization data are displayed below.

D-Ala-DNSP: Mp: 110.5–112.3 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.55−7.18 (m, 7H, aromatic and NH), 4.01−3.94 (m, 1H, $CHCO_2$), 3.34 (s, 3H, CO_2CH_3), 2.88 (s, 6H, NCH_3), 1.31–1.29 (d, J = 7.2 Hz, 3H, $CHC\underline{H_3}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 172.44, 152.08, 130.87, 129.78, 128.62, 127.21, 123.27, 118.97, 115.43, 52.50, 51.85, 45.58, 19.83. $[\alpha]^{25}_D$ +600.6 (c = 0.1, $CHCl_3$). MS m/z calcd for

$C_{16}H_{20}N_2O_4S$ [M + H]$^+$: 337.1144, Found: $C_{16}H_{20}N_2O_4S$, 337.1222. Anal. Calcd (%) for $C_{16}H_{20}N_2O_4S$: C, 57.13; H, 5.99. Found (%): C, 57.17; H, 5.97. FT-IR (KBr, cm^{-1}): 2945 ($\nu_{C–H}$), 2846 ($\nu_{C–H}$), 2788 ($\nu_{C–H}$), 1743 ($\nu_{C=O}$).

AFM and SEM observations: All samples reported were prepared by passing dilute copolymer solutions through 0.45 μm PTFE syringe filters and dropped onto a clear, precleaned silicon wafers. Taking poly(**1L**$_{100}$-*b*-**2**$_{450}$) as an example, the copolymer (1.00 mg) was first dissolved in THF (0.40 mL) and then added water (2.00 mL) dropwise under high speed stirring. THF was removed by dialysis against deionized water with slow stirring for two days. Sample preparation through filtration and then drop onto the silicon wafer. After the sample was slowly dried in air, it was subjected to AFM and SEM observations.

Critical aggregation concentration (CAC): The CACs of the amphiphilic block and star copolymers were determined by fluorimetry method with pyrene as fluorescent probe.[4] Taking poly(**1L**$_{100}$-*b*-**2**$_{450}$) as an example, a flask equipped with a stir bar was filled with poly(**1L**$_{100}$-*b*-**2**$_{450}$) (10.00 mg) and THF (1.00 mL). Water (5.00 mL) was added by the injection pump at the rate of 2.5 mL h^{-1}. After the addition, THF was removed by dialysis against deionized water with slow stirring for two days. The resulting solution was dilution and transfer into screw bottle with pyrene solution of acetone ($c = 3 \times 10^{-5}$ M), the acetone have been evaporated. After ultrasonication for a short while, the solutions were monitored by fluorescence spectrometer.

Chiral recognition: Taking poly(**1L**$_{100}$-*b*-**2**$_{450}$) as an example, poly(**1L**$_{100}$-*b*-**2**$_{450}$) (2.00 mg) was dissolved in THF (0.50 mL) at room temperature. To this high speed stirring solution, water (4.00 mL) was added dropwise, then L- or D-DNSP (1.00 mg) was added. After ultrasonication for a short while, the suspensions containing DNSP and copolymer were monitored by fluorescence spectrometer.

References

(1) Wu, Z.-Q.; Ono, R. J.; Chen Z.; Bielawski, C. W. Synthesis of poly(3-alkylthiophene)-*block*-poly(arylisocyanide): two sequential, mechanistically distinct polymerizations using a single catalyst. *J. Am. Chem. Soc*. **2010**, *132,* 14000.

(2) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. Screw-sense-selective polymerization of aryl isocyanides initiated by a Pd-Pt μ-ethynediyl dinuclear complex: a novel method for the synthesis of single-handed helical poly(isocyanide)s with the block copolymerization technique. *Chem.–Eur. J.* **2000**, *6,* 983.

(3) Zhang, L.; Jin, Q.; Lv, K.; Qin, L.; Liu, M. Enantioselective recognition of a fluorescencelabeled phenylalanine by self-assembled chiral nanostructures. *Chem. Commun*. **2015**, *51*, 4234.

(4) Pioge, S.; Fontaine, L.; Gaillard, C.; Nicol, E.; Pascual, S. Self-Assembling Properties of Well-Defined Poly(ethylene oxide)-*b*-poly (ethyl acrylate) Diblock Copolymers. *Macromolecules* **2009**, *42*, 4262.

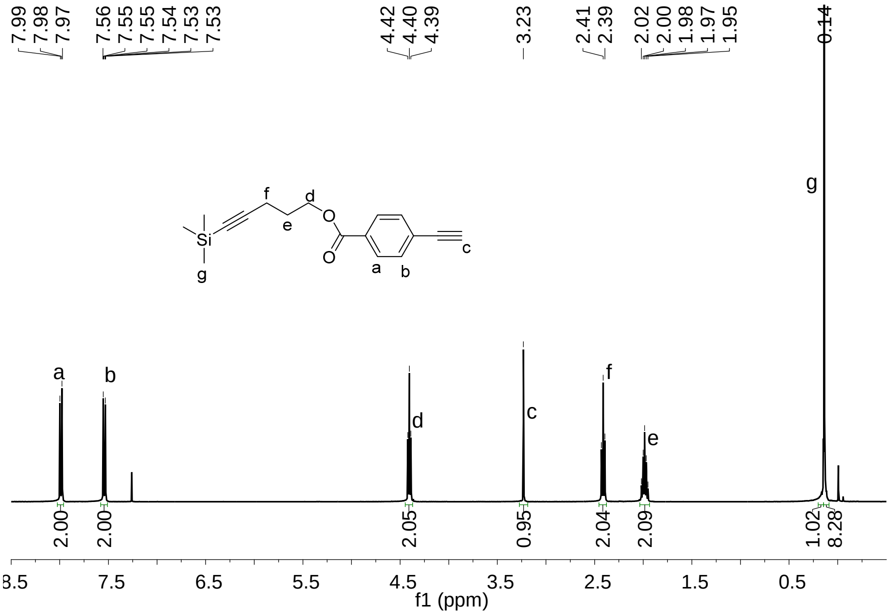


Figure S1. ^{1}H NMR (600 MHz) spectrum of **3** measured in $CDCl_3$ at 25 °C.

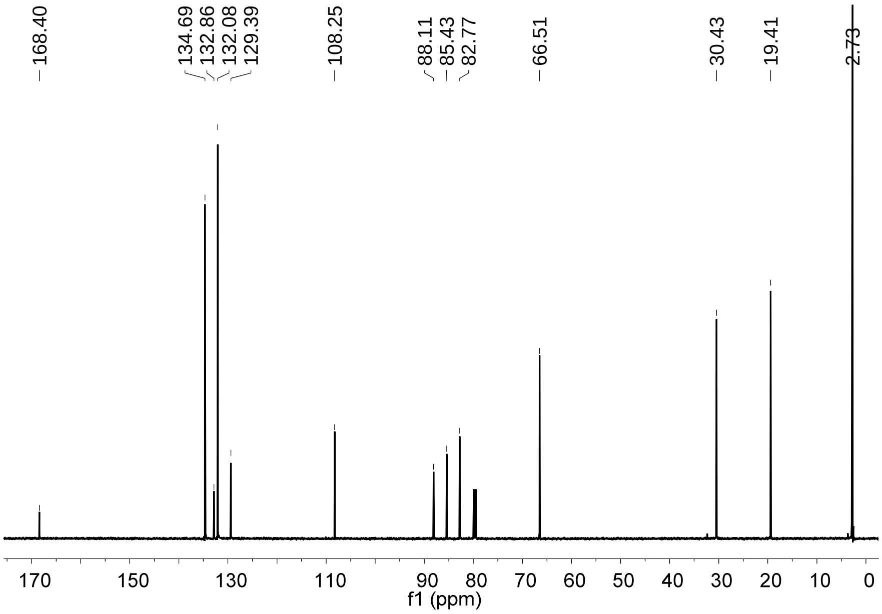


Figure S2. ^{13}C NMR (150 MHz) spectrum of **3** measured in $CDCl_3$ at 25 °C.

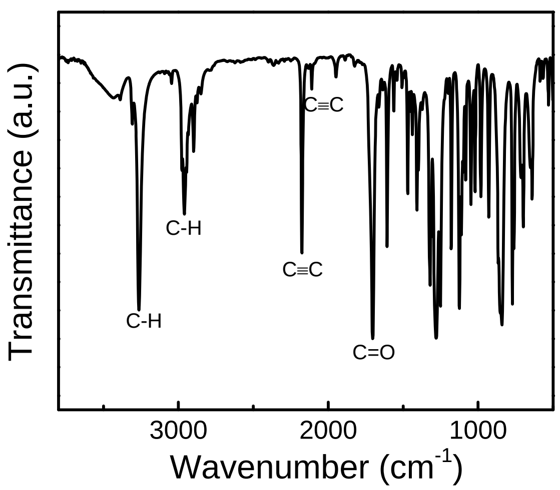


Figure S3. FT-IR spectrum of **3** measured at 25 °C using KBr pellets.

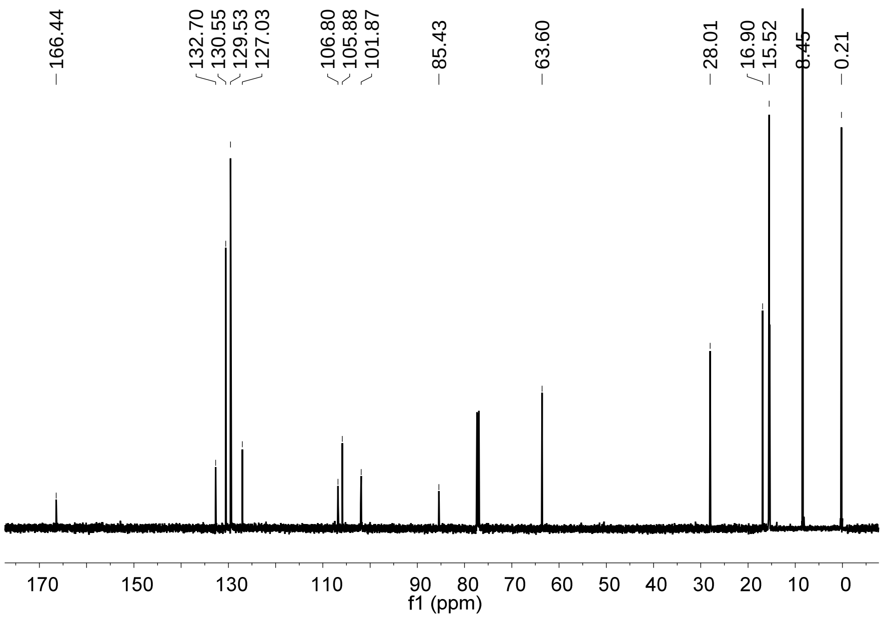


Figure S4. ^{13}C NMR (150 MHz) spectrum of **4** measured in CDCl$_3$ at 25 °C.

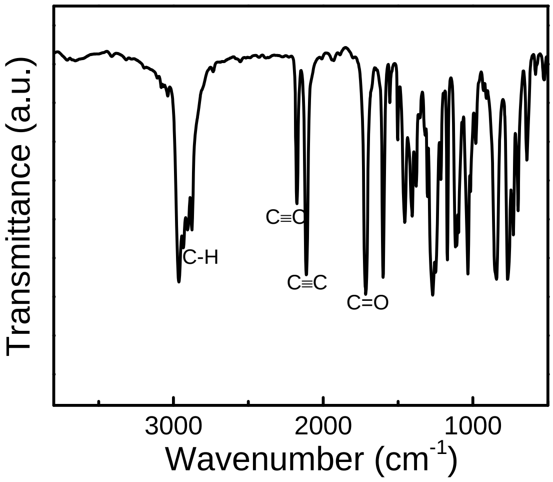


Figure S5. FT-IR spectrum of **4** measured at 25 °C using KBr pellets.

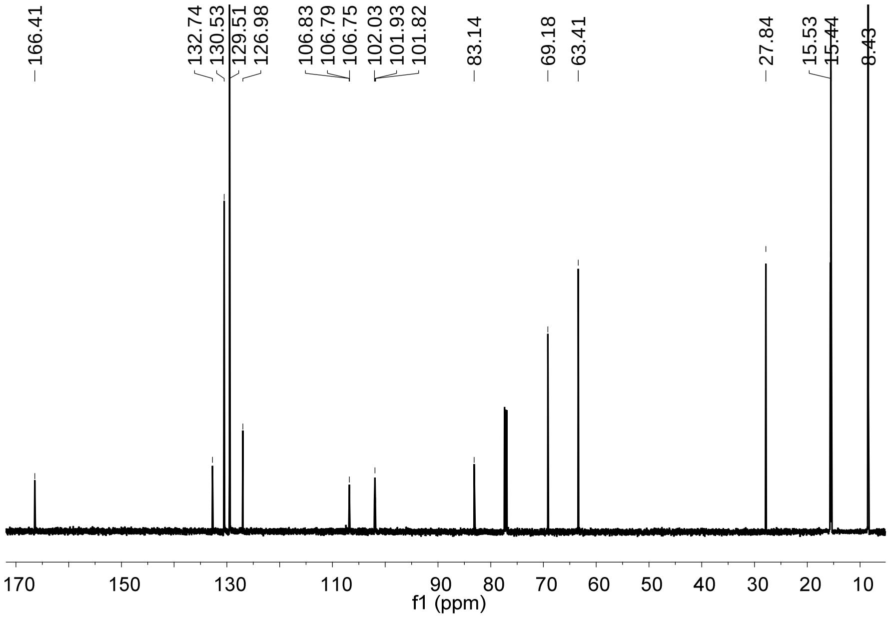


Figure S6. ^{13}C NMR (150 MHz) spectrum of **5** measured in $CDCl_3$ at 25 °C.

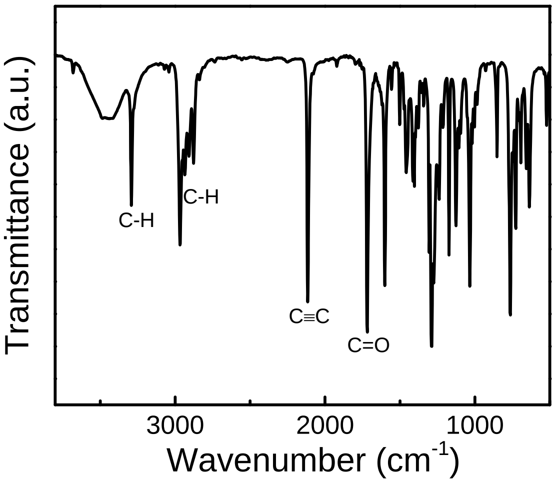


Figure S7. FT-IR spectrum of **5** measured at 25 °C using KBr pellets.

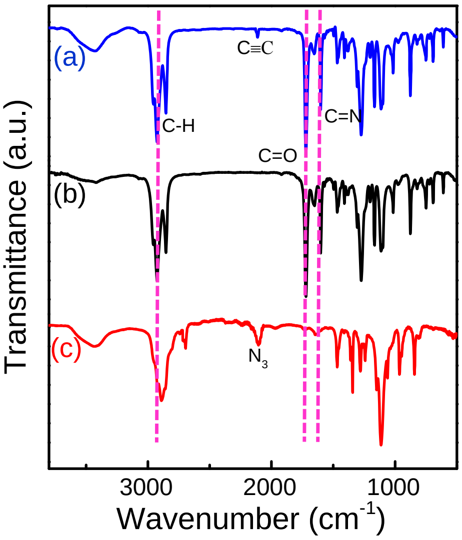


Figure S8. FT-IR spectra of the alkyne end-functionalized helical MA-poly-$\mathbf{1a}_{100}$ (a), helix-coil diblock copolymer of poly($\mathbf{1a}_{100}$-*b*-$\mathbf{2}_{45}$) (b), and random coil homopolymer poly-$\mathbf{2}_{45}$ (c) measured at 25 °C using KBr pellets.

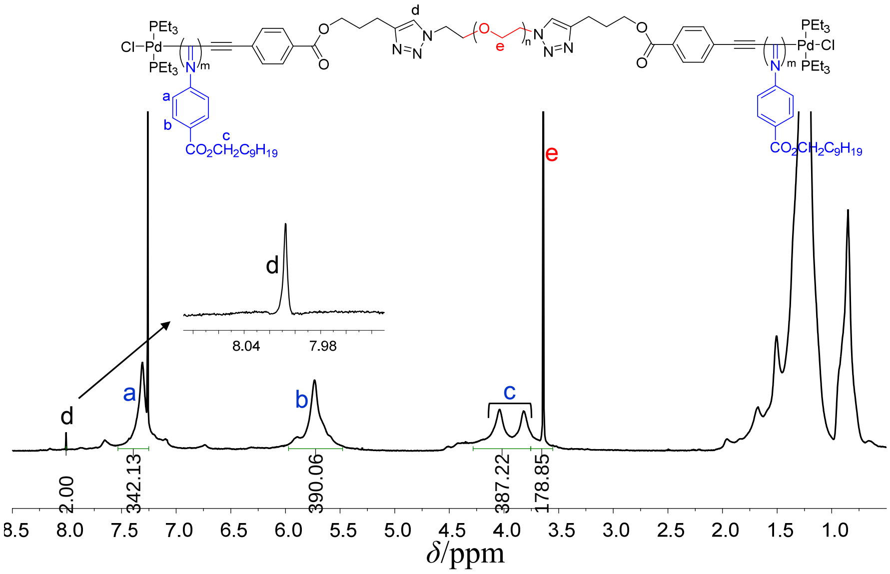


Figure S9. ^{1}H NMR (600 MHz) spectrum of triblock copolymer poly(**1a**$_{100}$-*b*-**2**$_{45}$-*b*-**1a**$_{100}$) measured in $CDCl_3$ at 25 °C.

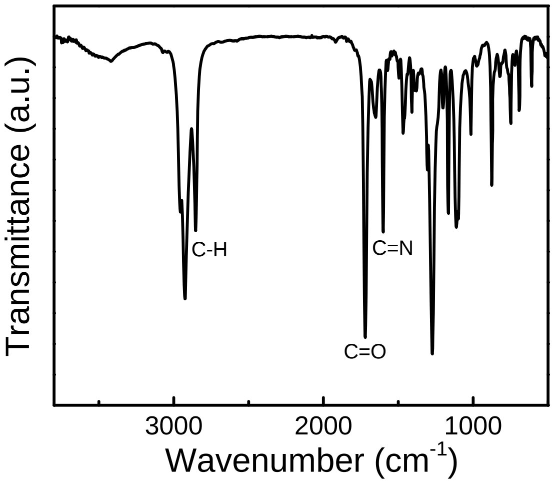


Figure S10. FT-IR spectrum of poly(**1a**$_{100}$-*b*-**2**$_{45}$-*b*-**1a**$_{100}$) measured at 25 °C using KBr pellets.

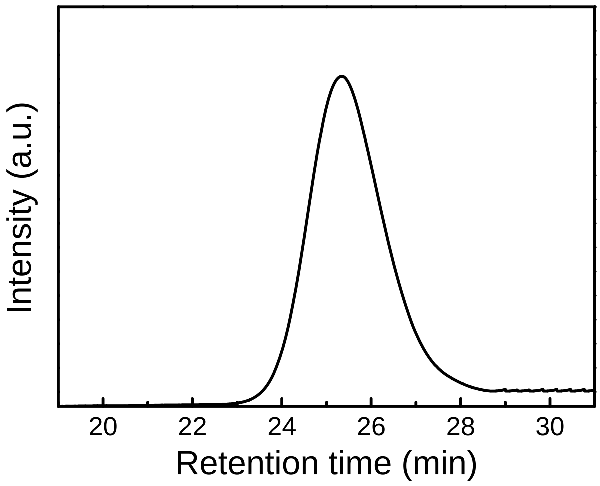


Figure S11. Size exclusion chromatograms of MA-poly-**1L**$_{100}$. SEC condition: eluent = THF, temperature = 40 °C.

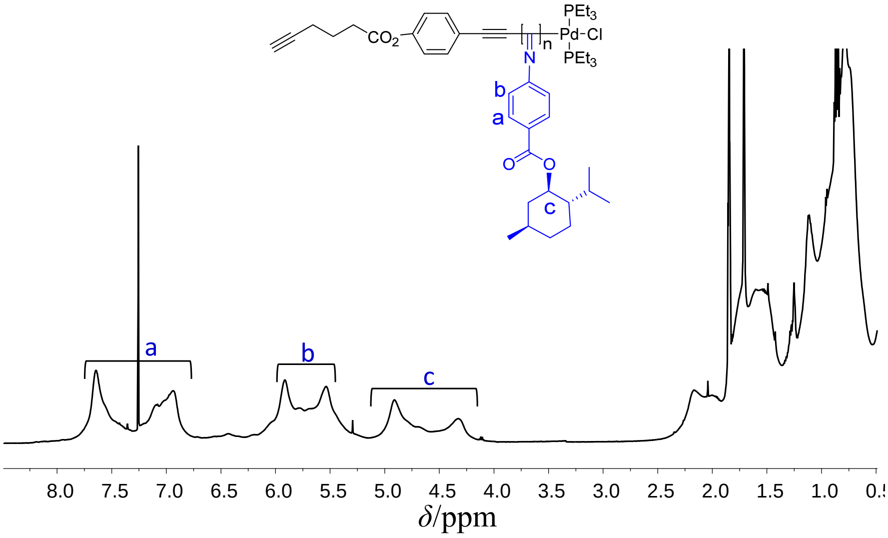


Figure S12. ^{1}H NMR (600 MHz) of MA-poly-**1L**$_{100}$ measured in $CDCl_3$ at 25 °C.

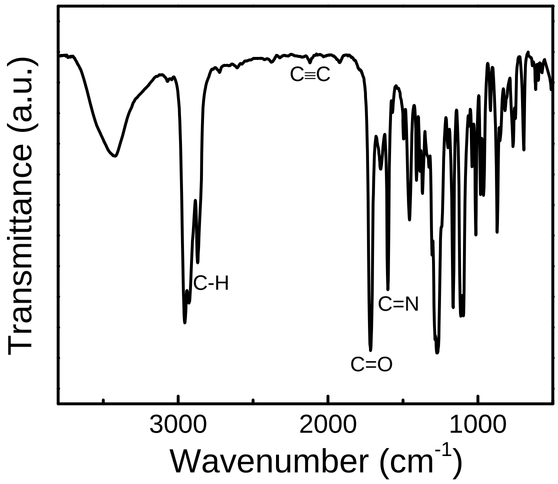


Figure S13. FT-IR spectrum of MA-poly-**1L**$_{100}$ measured at 25 °C using KBr pellets.

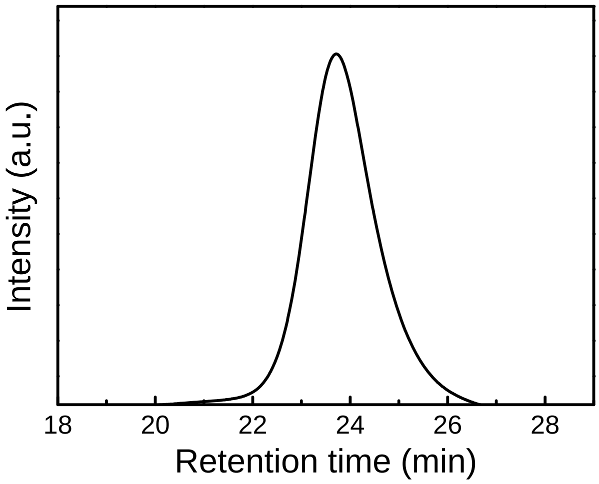


Figure S14. Size exclusion chromatograms of MA-poly-**1D**$_{100}$. SEC condition: eluent = THF, temperature = 40 °C.

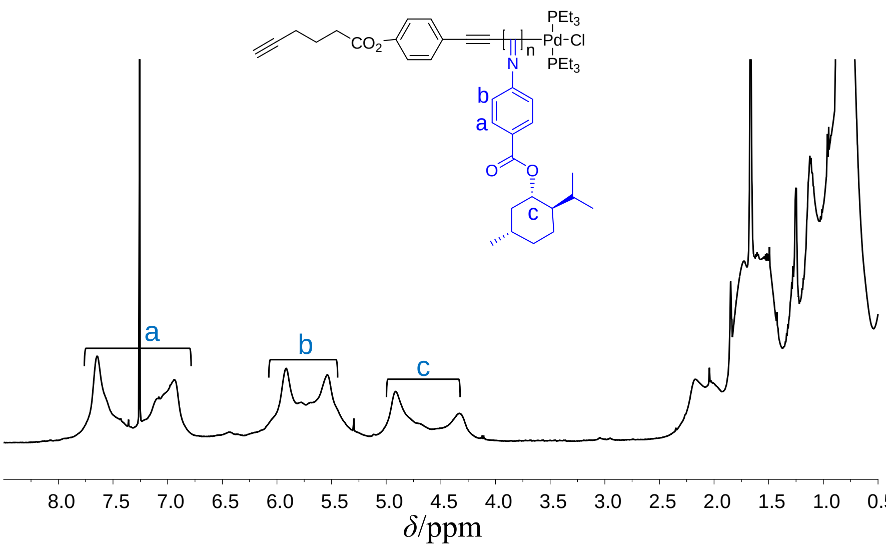


Figure S15. ^{1}H NMR (600 MHz) of MA-poly-**1D**$_{100}$ measured in CDCl$_3$ at 25 °C.

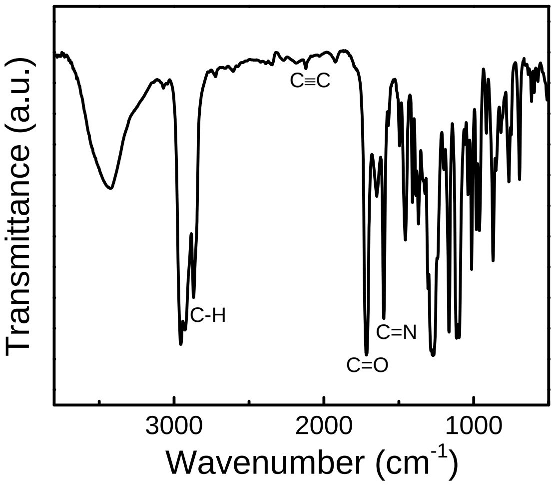


Figure S16. FT-IR spectrum of MA-poly-**1D**$_{100}$ measured at 25 °C using KBr pellets.

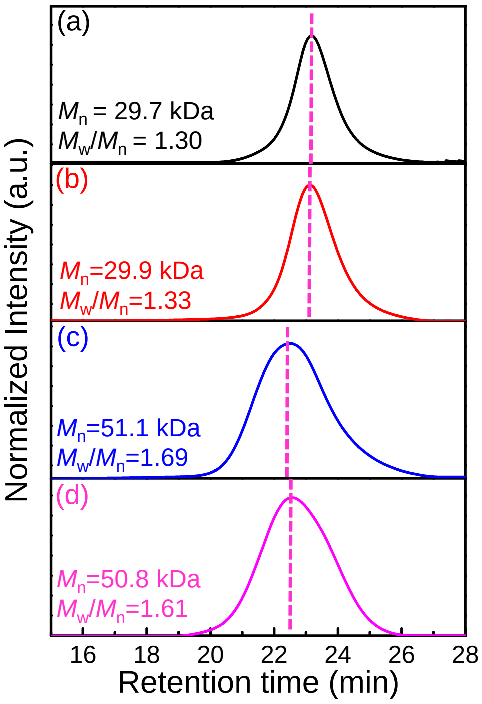


Figure S17. Size exclusion chromatograms of poly($\mathbf{1L}_{100}$-*b*-$\mathbf{2}_{45}$) (a) poly($\mathbf{1D}_{100}$-*b*-$\mathbf{2}_{45}$) (b) poly($\mathbf{1L}_{100}$-*b*-$\mathbf{2}_{45}$-*b*-$\mathbf{1L}_{100}$) (c) and poly($\mathbf{1D}_{100}$-*b*-$\mathbf{2}_{45}$-*b*-$\mathbf{1D}_{100}$) (d). SEC condition: eluent = THF, temperature = 40 °C.

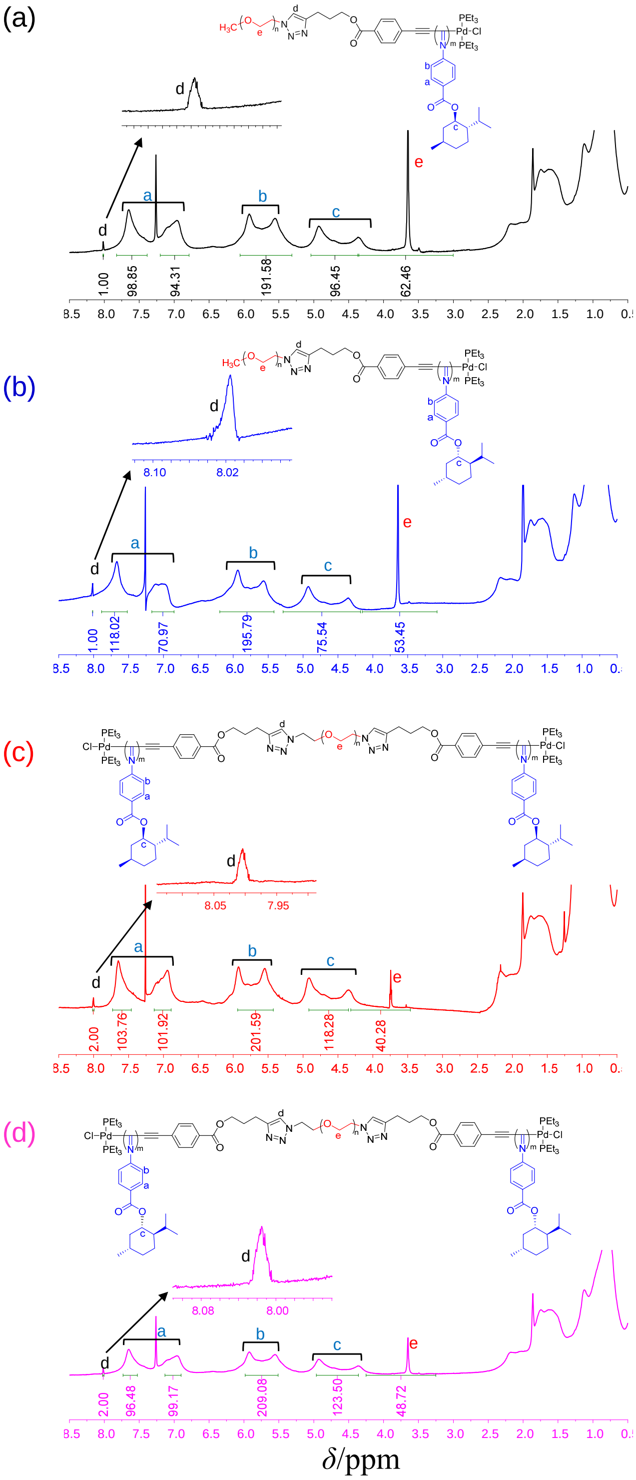


Figure S18. ^{1}H NMR (600 MHz) spectrum of poly(**1L**$_{100}$-*b*-**2**$_{45}$) (a) poly(**1D**$_{100}$-*b*-**2**$_{45}$) (b) poly(**1L**$_{100}$-*b*-**2**$_{45}$-*b*-**1L**$_{100}$) (c) and poly(**1D**$_{100}$-*b*-**2**$_{45}$-*b*-**1D**$_{100}$) (d) measured in CDCl$_3$ at 25 °C.

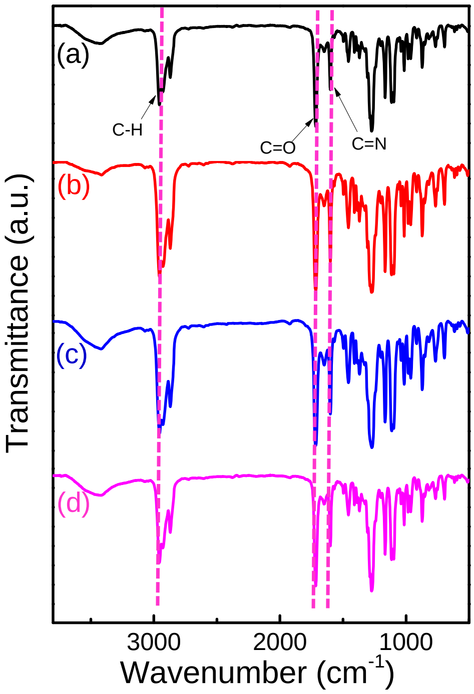


Figure S19. FT-IR spectrum of poly(**1L**$_{100}$-*b*-**2**$_{45}$) (a), poly(**1D**$_{100}$-*b*-**2**$_{45}$) (b), poly(**1L**$_{100}$-*b*-**2**$_{45}$-*b*-**1L**$_{100}$) (c), and poly(**1D**$_{100}$-*b*-**2**$_{45}$-*b*-**1D**$_{100}$) (d) measured at 25 °C using KBr pellets.

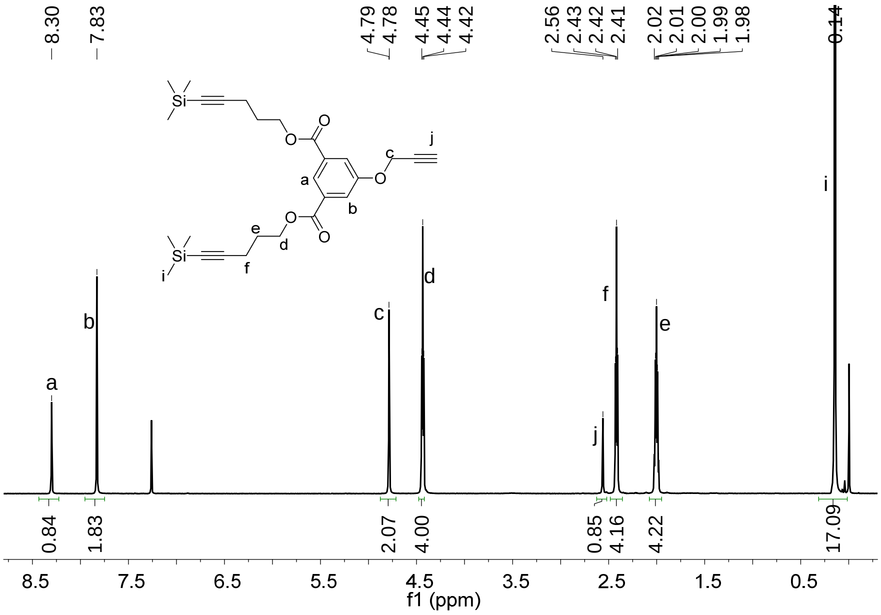


Figure S20. ^{1}H NMR (600 MHz) spectrum of **6** measured in $CDCl_3$ at 25 °C.

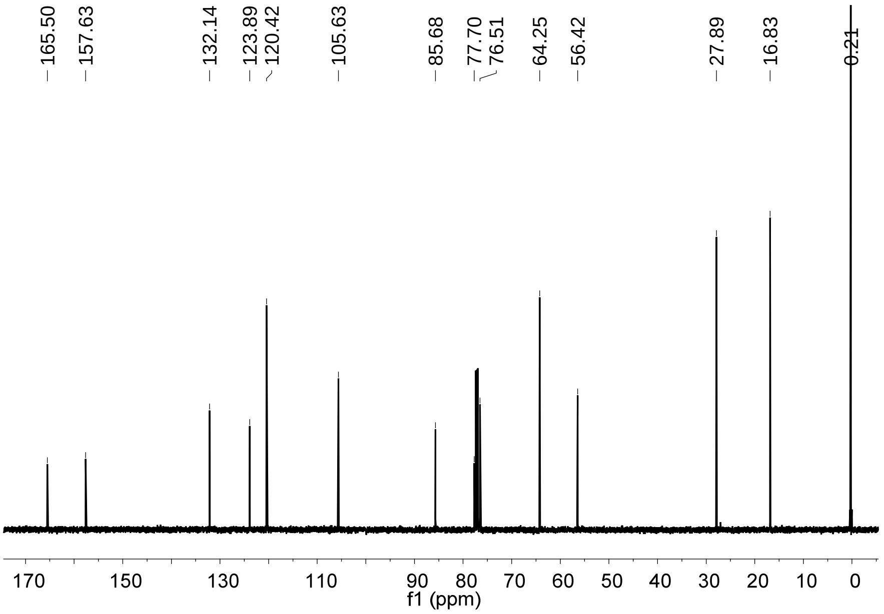


Figure S21. ^{13}C NMR (150 MHz) spectrum of **6** measured in $CDCl_3$ at 25 °C.

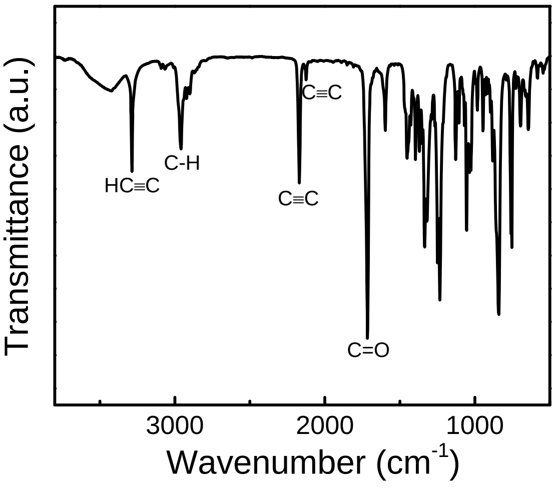


Figure S22. FT-IR spectrum of **6** measured at 25 °C using KBr pellets.

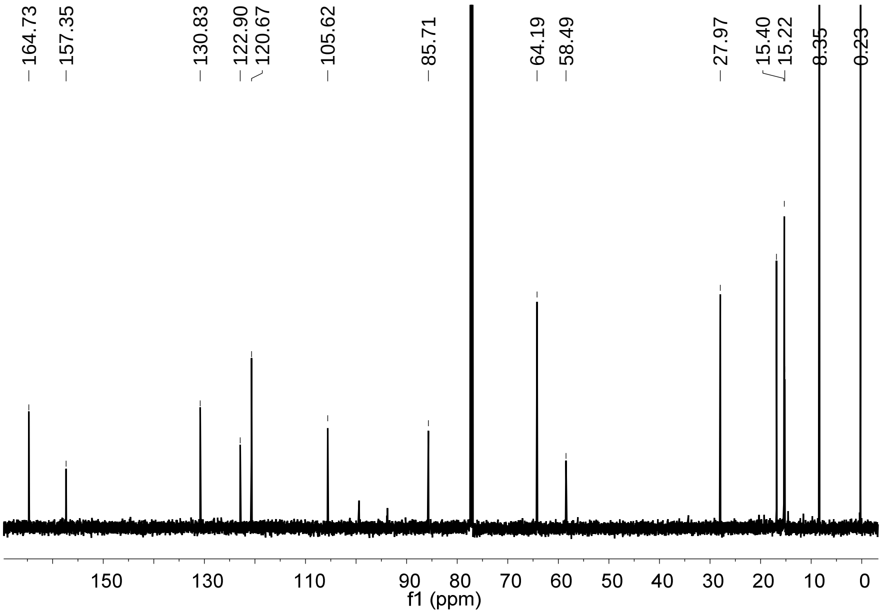


Figure S23. ^{13}C NMR (150 MHz) spectrum of **7** measured in $CDCl_3$ at 25 °C.

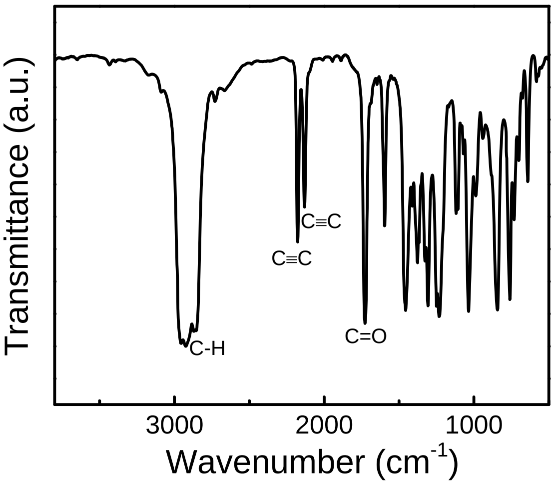


Figure S24. FT-IR spectrum of **7** measured at 25 °C using KBr pellets.

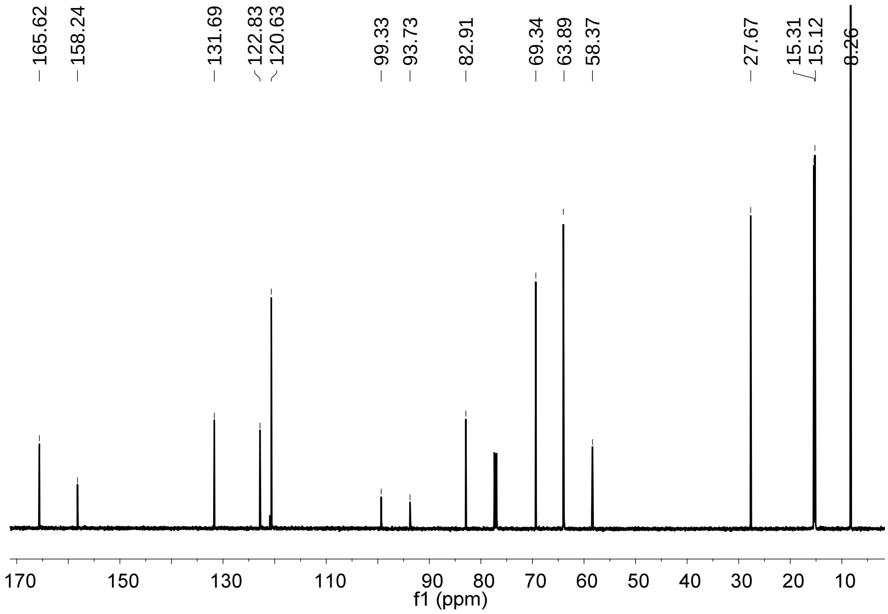


Figure S25. ^{13}C NMR (150 MHz) spectrum of the Pd(II) initiator **8** measured in $CDCl_3$ at 25 °C.

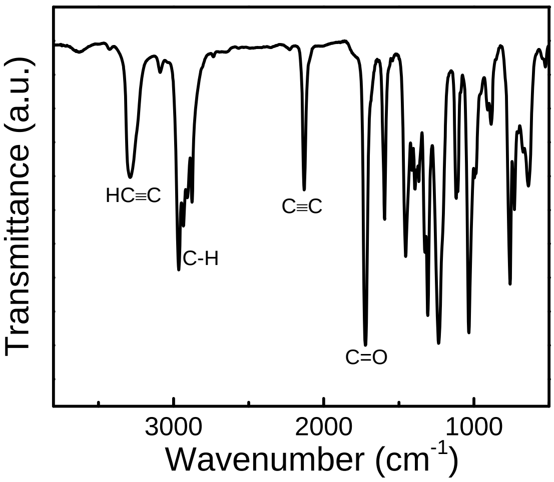


Figure S26. FT-IR spectrum of the Pd(II) initiator **8** measured at 25 °C using KBr pellets.

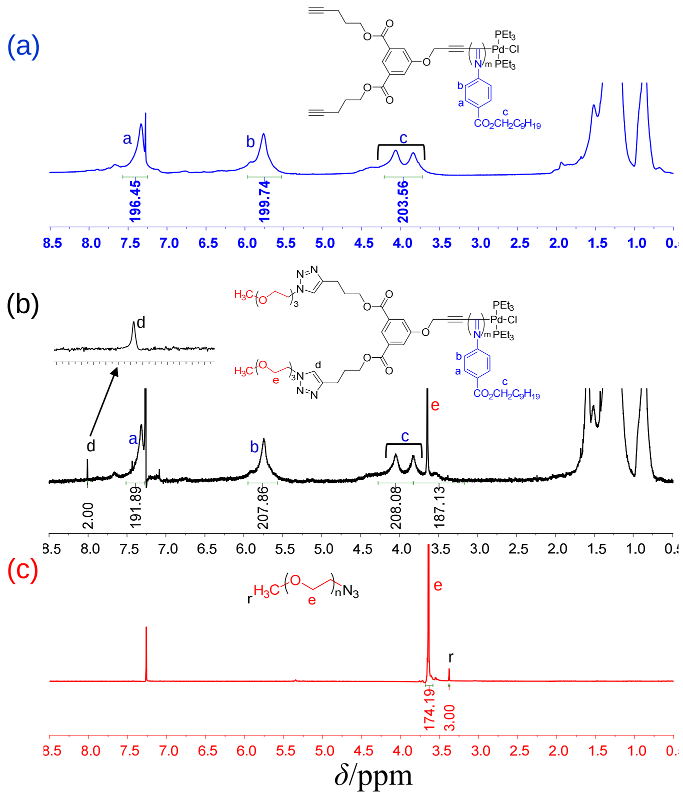


Figure S27. ^{1}H NMR (600 MHz) spectrum of BA-poly-**1a**$_{100}$ (a), poly(**1a**$_{100}$-*b*-(**2**$_{45}$)$_2$ (b), and MA-poly-**2**$_{45}$ (c) measured in $CDCl_3$ at 25 °C.

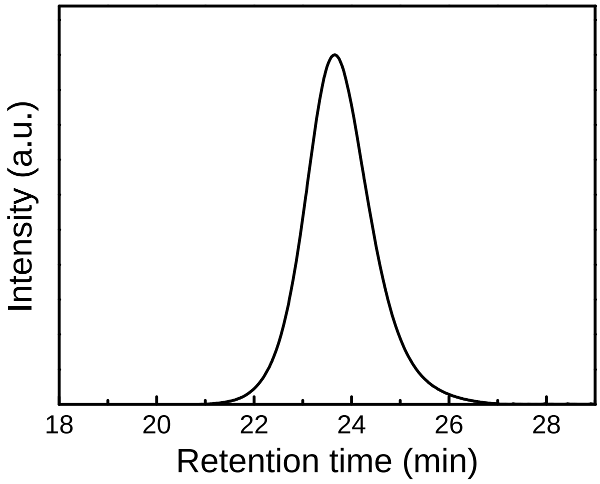


Figure S28. Size exclusion chromatograms of BA-poly-**1L**$_{100}$. SEC condition: eluent = THF, temperature = 40 °C.

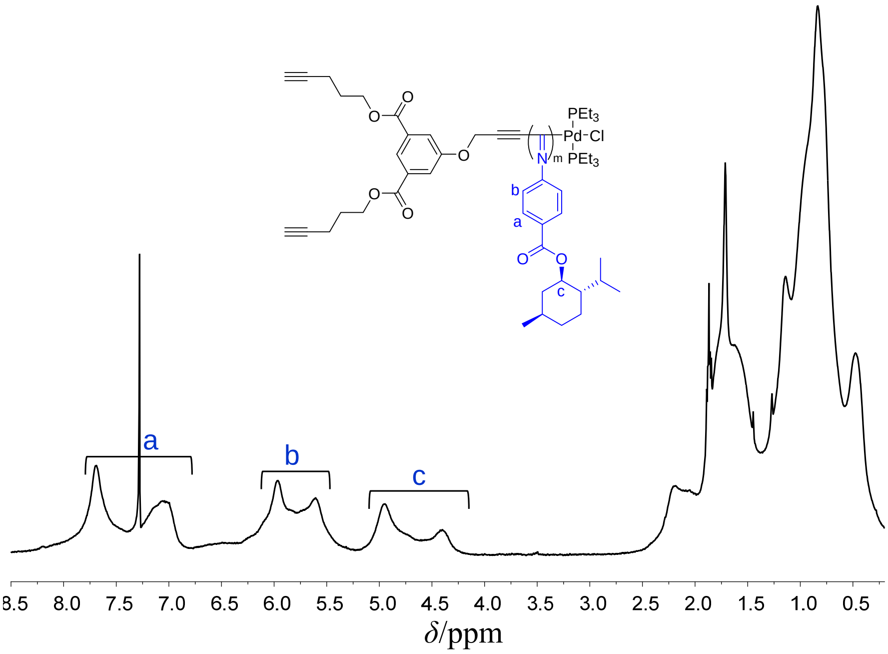


Figure S29. ^{1}H NMR (600 MHz) of BA-poly-**1L**$_{100}$ measured in $CDCl_3$ at 25 °C.

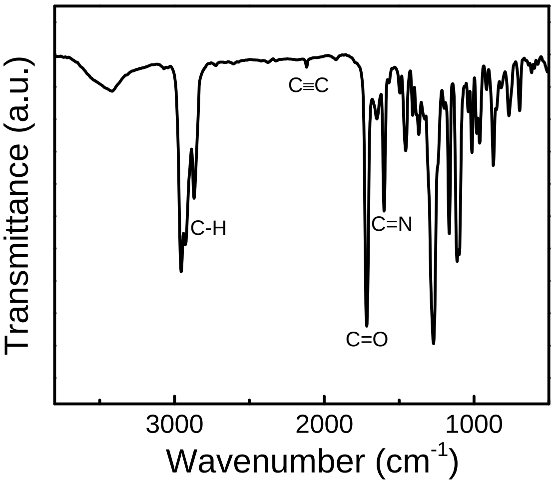


Figure S30. FT-IR spectra of BA-poly-**1L**$_{100}$ measured at 25 °C using KBr pellets.

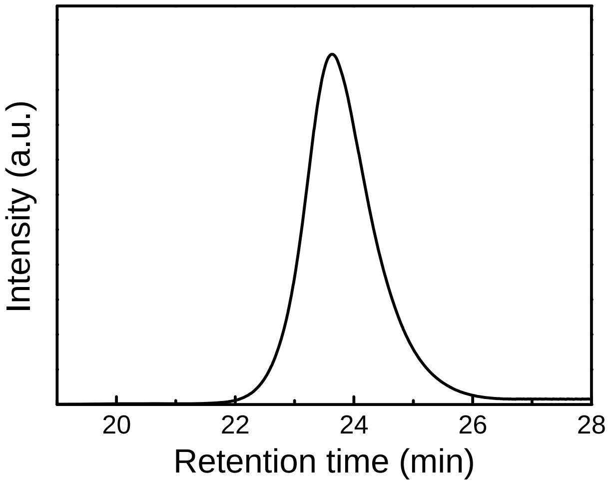


Figure S31. Size exclusion chromatograms of BA-poly-**1D**$_{100}$. SEC condition: eluent = THF, temperature = 40 °C.

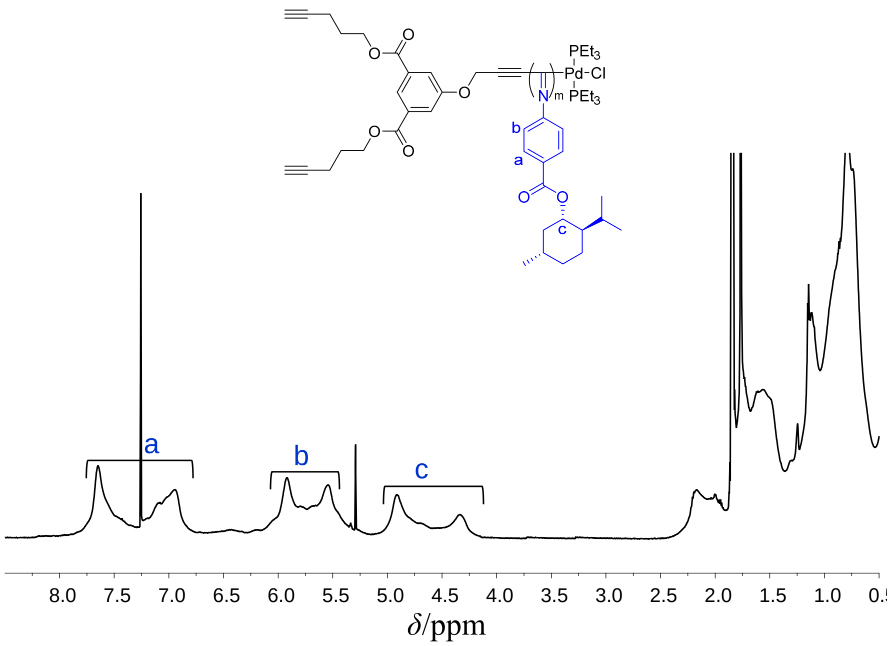


Figure S32. ^{1}H NMR (600 MHz) of BA-poly-**1D**$_{100}$ measured in $CDCl_3$ at 25 °C.

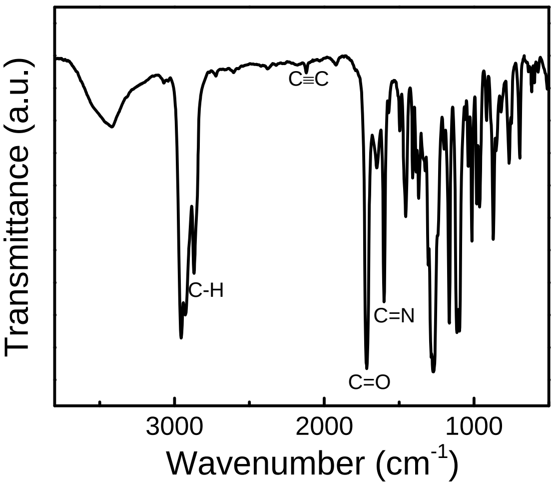


Figure S33. FT-IR spectrum of BA-poly-**1D**$_{100}$ measured at 25 °C using KBr pellets.

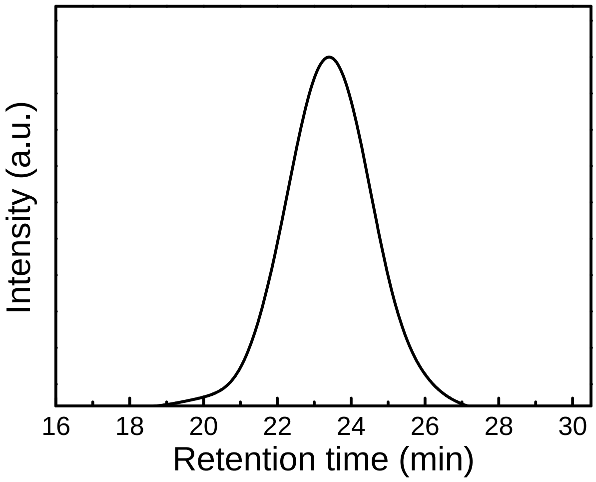


Figure S34. SEC chromatograms of helix-(coil)$_2$ miktoarm star polymer poly(**1L**$_{100}$-*b*-(**2**$_{45}$)$_2$). SEC condition: eluent = THF, temperature = 40 °C.

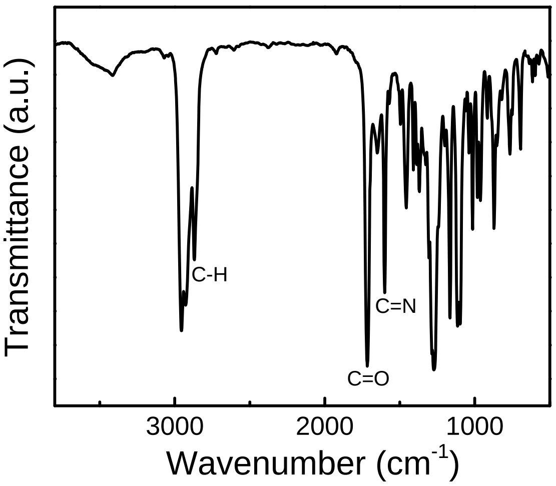


Figure S35. FT-IR spectrum of helix-(coil)$_2$ miktoarm star polymer poly(**1L**$_{100}$-*b*-(**2**$_{45}$)$_2$) measured at 25 °C using KBr pellets.

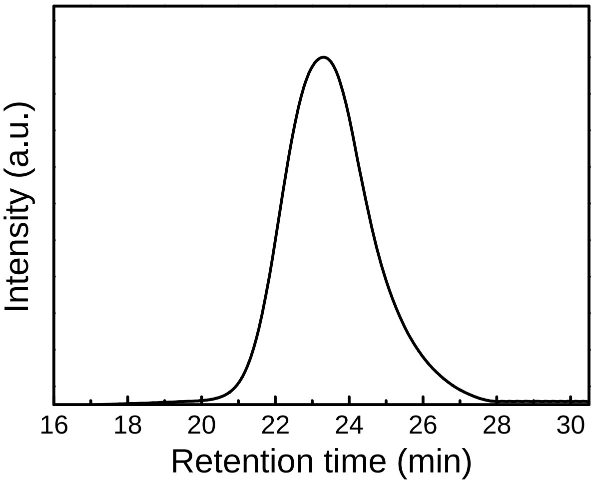


Figure S36. SEC chromatograms of helix-(coil)$_2$ miktoarm star polymer poly(**1D**$_{100}$-*b*-(**2**$_{45}$)$_2$). SEC condition: eluent = THF, temperature = 40 °C.

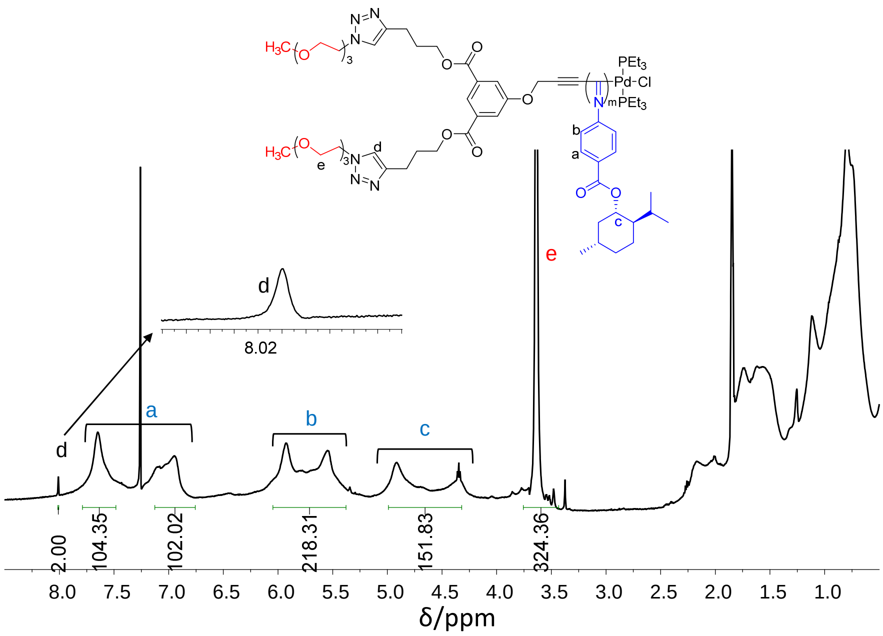


Figure S37. ^{1}H NMR (600 MHz) spectrum of helix-(coil)$_2$ miktoarm star polymer poly(**1D**$_{100}$-*b*-(**2**$_{45}$)$_2$) measured in $CDCl_3$ at 25 °C.

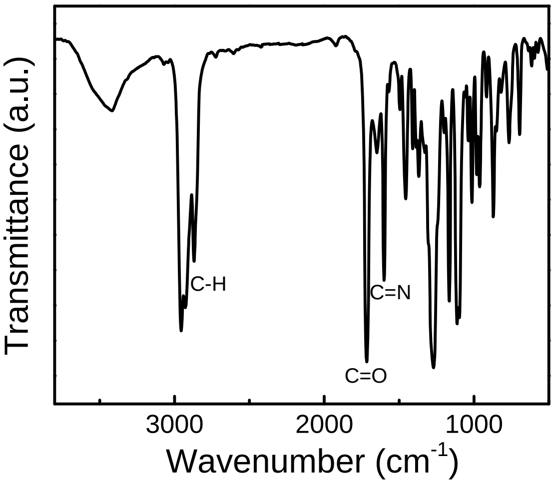


Figure S38. FT-IR spectrum of helix-(coil)$_2$ miktoarm star polymer poly(**1D**$_{100}$-*b*-(**2**$_{45}$)$_2$) measured at 25 °C using KBr pellets.

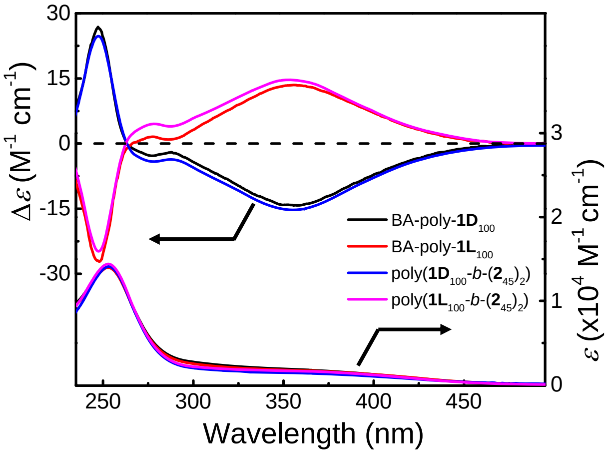


Figure S39. CD and UV-vis spectra of BA-poly-**1L**$_{100}$, BA-poly-**1D**$_{100}$ homopolymers and miktoarm star polymer poly(**1L**$_{100}$-*b*-(**2**$_{45}$)$_2$) and poly(**1D**$_{100}$-*b*-(**2**$_{45}$)$_2$) measured in THF at 25 °C (*c* = 0.20 mg/mL).

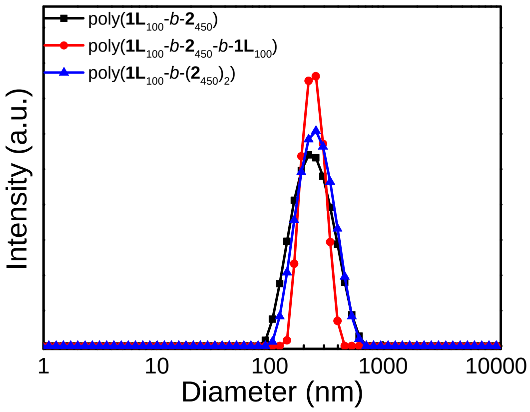


Figure 40. The DLS curves for diblock copolymer poly(**1L**$_{100}$-*b*-**2**$_{450}$), triblock copolymer poly(**1L**$_{100}$-*b*-**2**$_{450}$-*b*-**1L**$_{100}$), and miktoarm star polymer poly(**1L**$_{100}$-*b*-(**2**$_{450}$)$_2$) at different time.

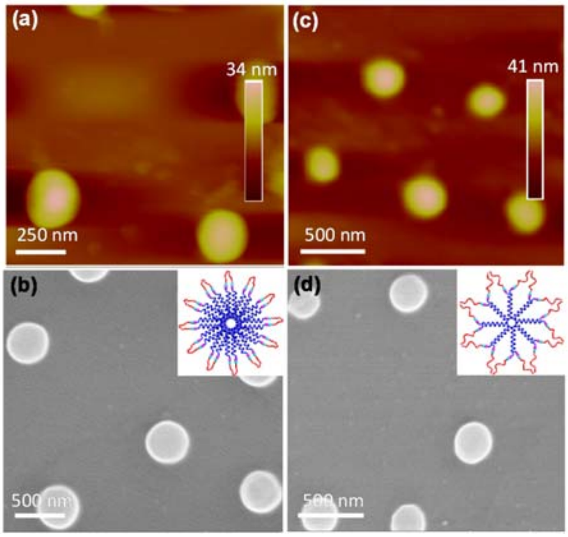


Figure S41. AFM height images (a, c) and SEM images (b, d) of the supramolecular structures self-assembled from the triblock copolymer poly(**1L**$_{100}$-*b*-**2**$_{450}$-*b*-**1L**$_{100}$) (a, b) and the miktoarm arm star polymer poly(**1L**$_{100}$-*b*-(**2**$_{450}$)$_2$) (c, d) in H_2O (0.5 mg/mL) at 25 °C.

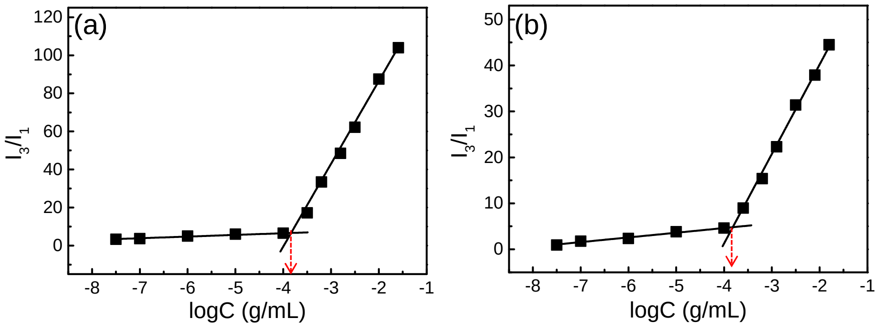


Figure S42. Plots of the emission ratio of I_3/I_1 (I_{385}/I_{374}) versus the polymer concentration (logarithmic scale) for triblock copolymer poly(**1L**$_{100}$-*b*-**2**$_{450}$-*b*-**1L**$_{100}$) (a) and the miktoarm arm star polymer poly(**1L**$_{100}$-*b*-(**2**$_{450}$)$_2$) (b) in water at 25 °C with the presence of pyrene ($c = 3.0 \times 10^{-5}$ M).

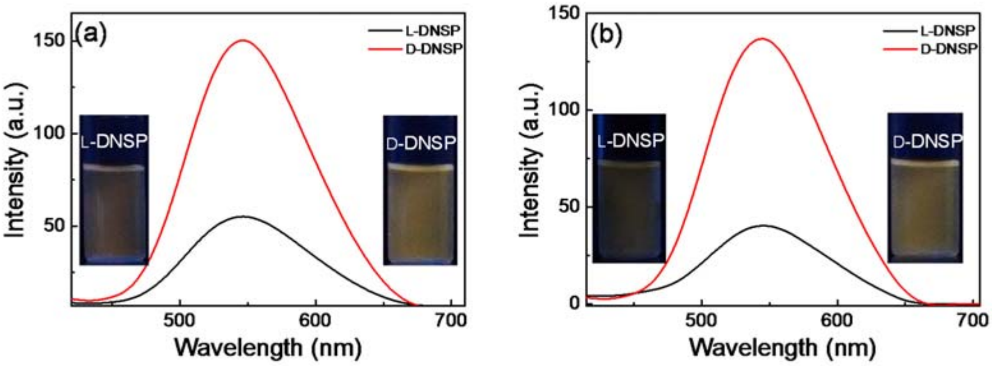


Figure S43. The emission spectra of the L- and D-DNSP encapsulated aggregates of helix-coil diblock copolymer poly(**1**L$_{100}$-*b*-**2**$_{450}$) (a) and the helix-coil-helix triblock copolymer poly(**1**L$_{100}$-*b*-**2**$_{450}$-*b*-**1**L$_{100}$) (b) measured in water at 25 °C (λ_{exc} = 390 nm). Inserts are the photographs of the respective solutions under UV light of 365 nm.

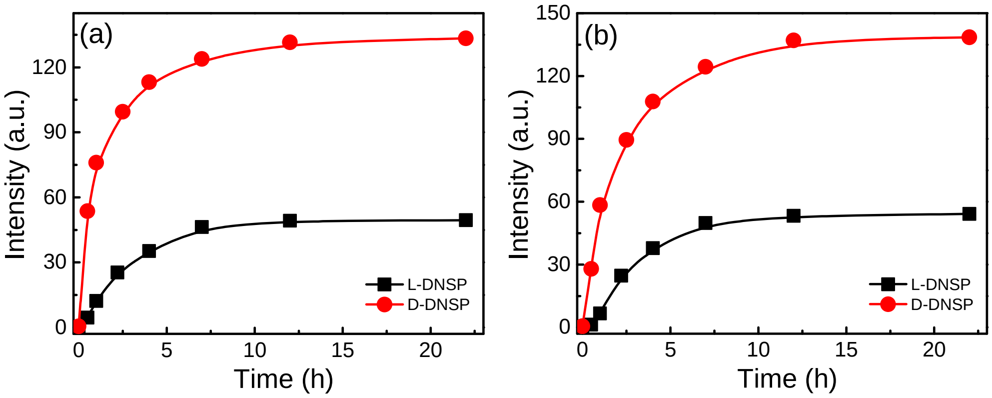


Figure S44. Time-dependent emission at 548 nm of L- and D-DNSP encapsulation into helix-coil diblock copolymer poly(**1**L$_{100}$-*b*-**2**$_{450}$) (a) and helix-coil-helix triblock copolymer poly(**1**L$_{100}$-*b*-**2**$_{450}$-*b*-**1**L$_{100}$) (b) in water at 25 °C.

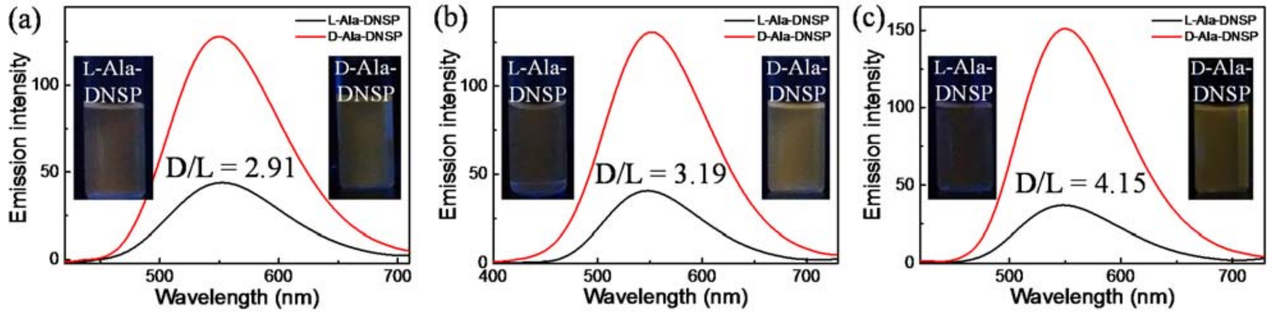


Figure S45. The emission spectra of the L- and D-Ala-DNSP encapsulated aggregates of helix-coil diblock copolymer poly($\mathbf{1L}_{100}$-*b*-$\mathbf{2}_{450}$) (a), helix-coil-helix triblock copolymer poly($\mathbf{1L}_{100}$-*b*-$\mathbf{2}_{450}$-*b*-$\mathbf{1L}_{100}$) (b), and helix-(coil)$_2$ miktoarm star poly($\mathbf{1L}_{100}$-*b*-($\mathbf{2}_{450}$)$_2$) (c) measured in water at 25 °C (λ_{exc} = 390 nm). Inserts are the photographs of the respective solutions under UV light of 365 nm.

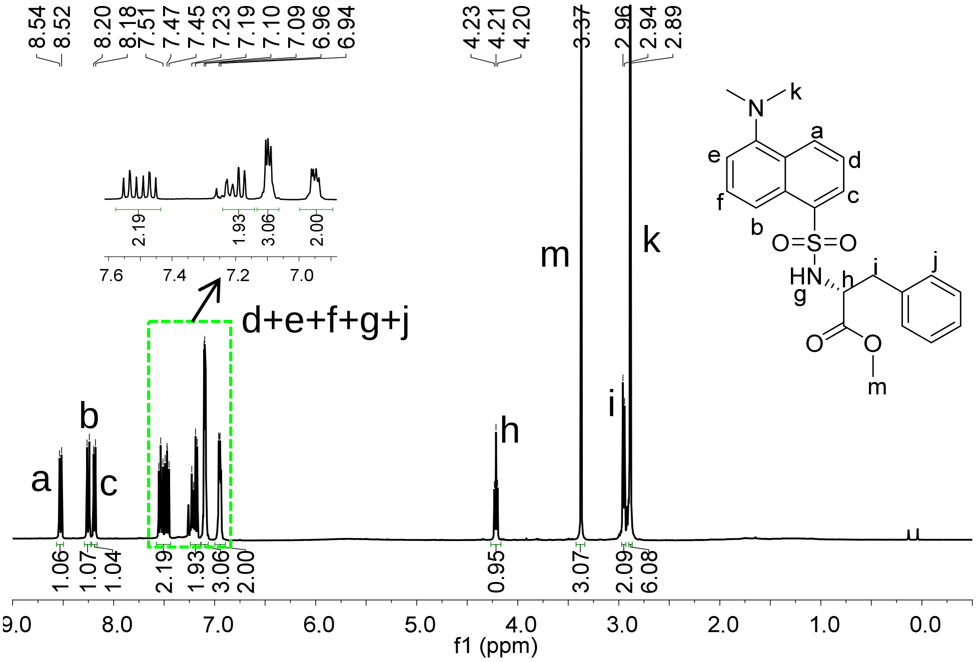


Figure S46. ^{1}H NMR (400 MHz) spectrum of L-Phe-DNSP measured in $CDCl_3$ at 25 °C.

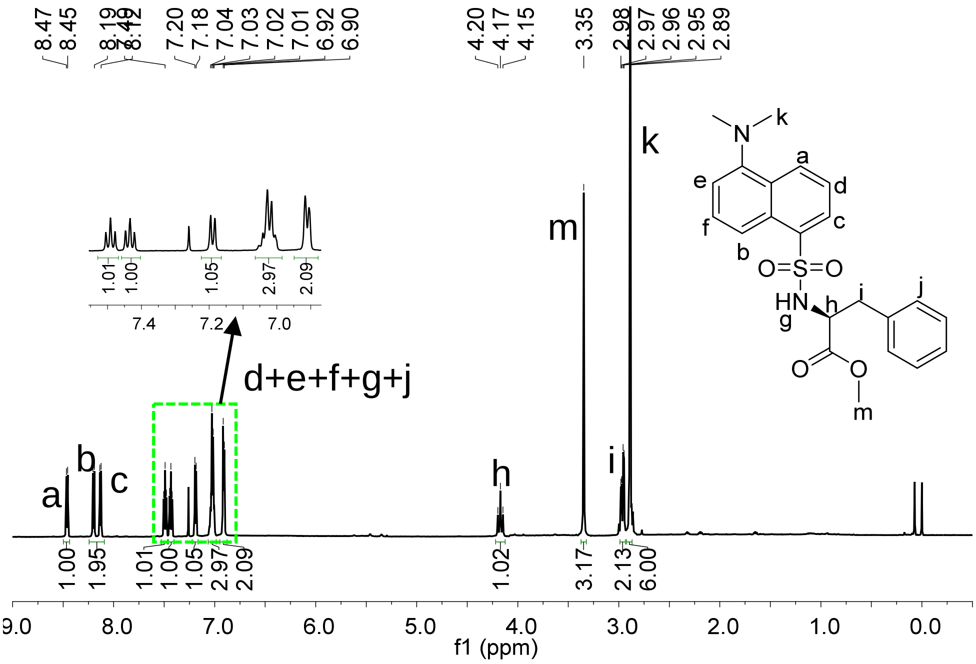


Figure S47. ${}^{1}H$ NMR (400 MHz) spectrum of D-Phe-DNSP measured in $CDCl_3$ at 25 °C.

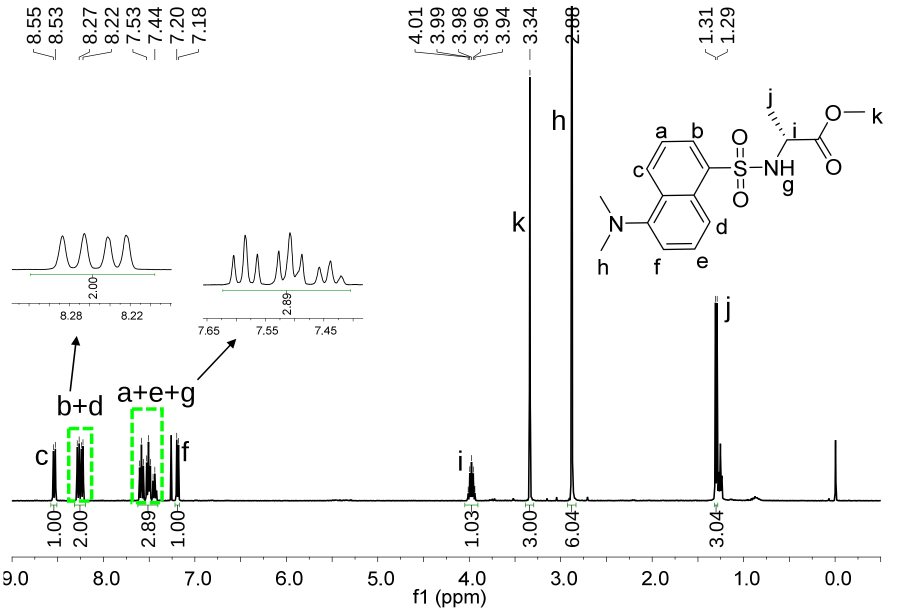


Figure S48. ${}^{1}H$ NMR (400 MHz) spectrum of L-Ala-DNSP measured in $CDCl_3$ at 25 °C.

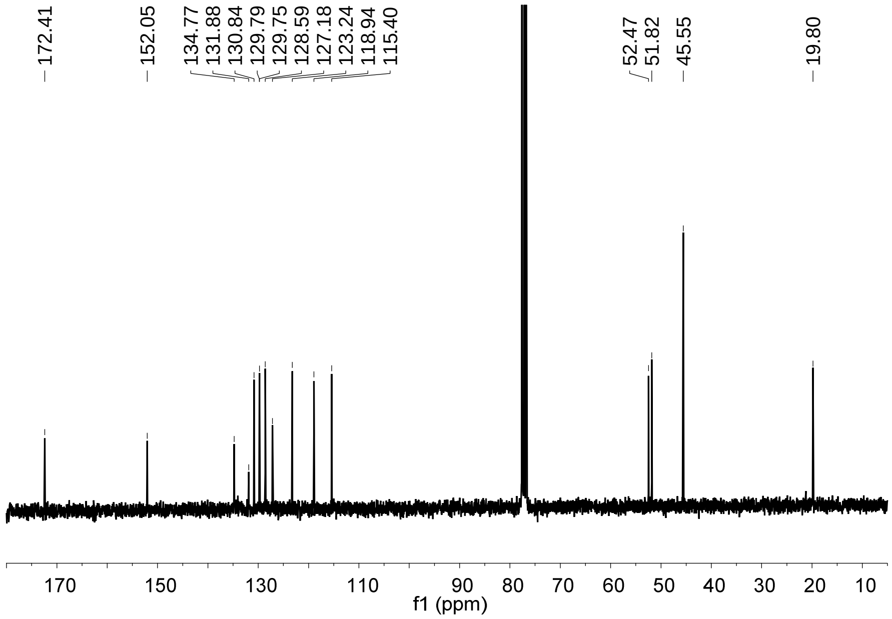


Figure S49. ^{13}C NMR (100 MHz) spectrum of L-Ala-DNSP measured in $CDCl_3$ at 25 °C.

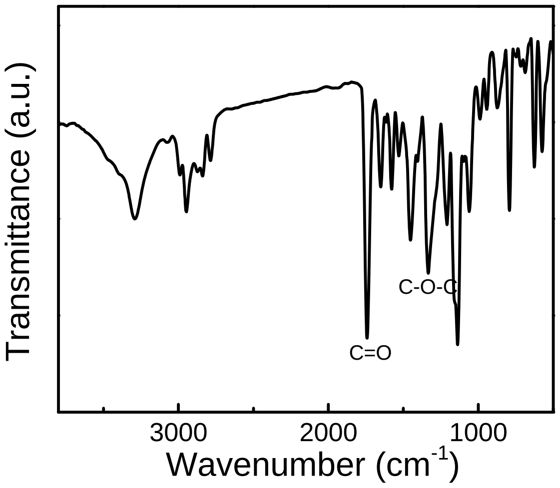


Figure S50. FT-IR spectrum of L-Ala-DNSP measured at 25 °C using KBr pellets.

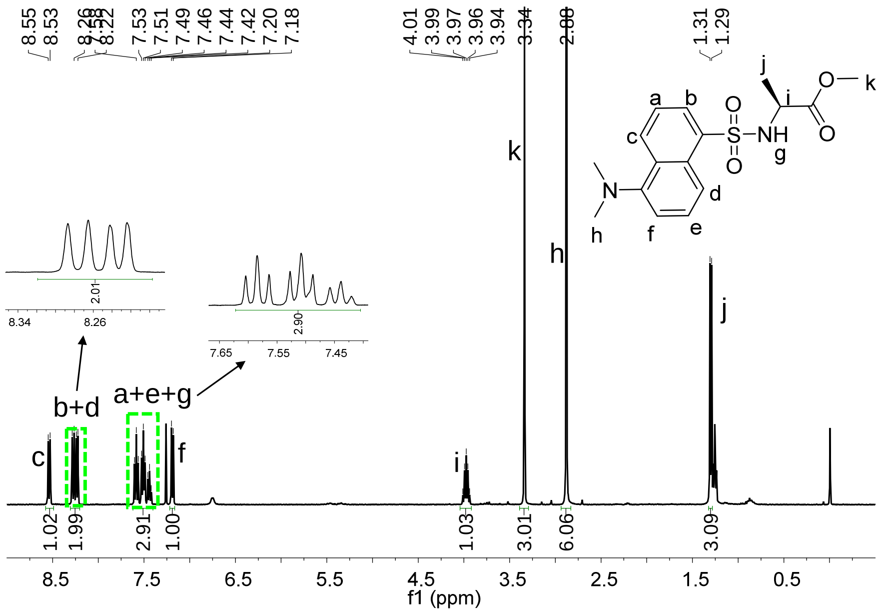


Figure S51. ^{1}H NMR (400 MHz) spectrum of D-Ala-DNSP measured in $CDCl_3$ at 25 °C.

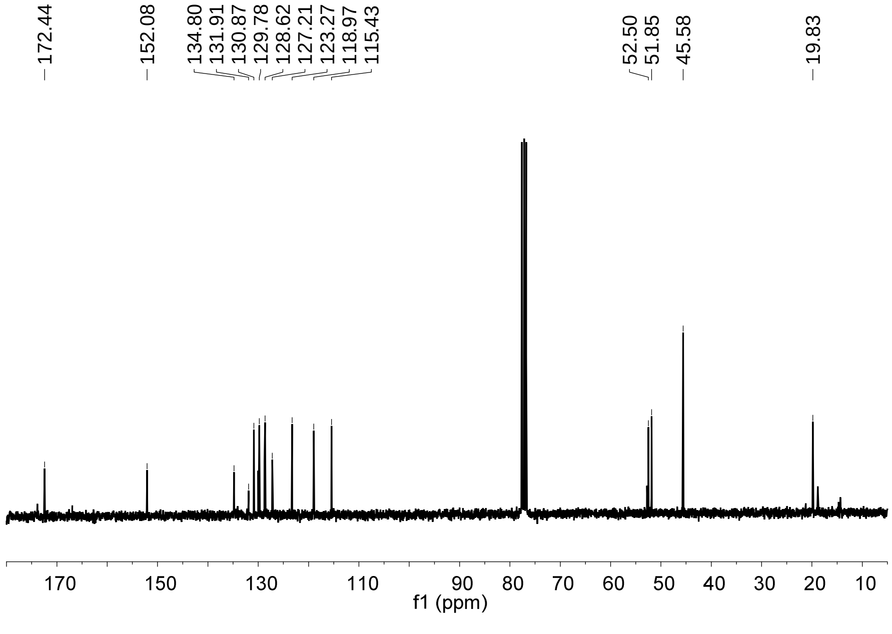


Figure S52. ^{13}C NMR (100 MHz) spectrum of D-Ala-DNSP measured in $CDCl_3$ at 25 °C.

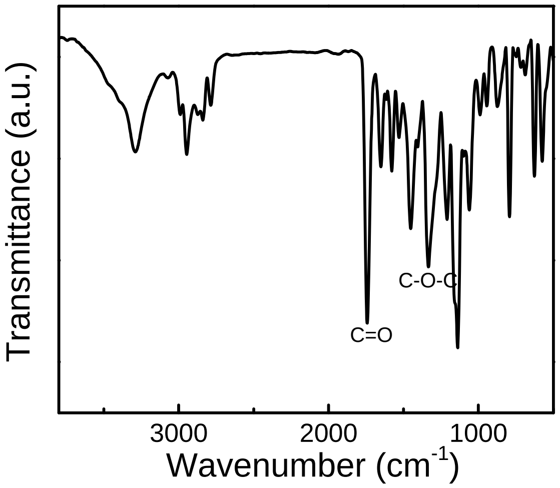


Figure S53. FT-IR spectrum of D-Ala-DNSP measured at 25 °C using KBr pellets.