

## Supporting Information

# Self-Assembly and Fluorescent Emission of UV-responsive Azobenzene-Containing Helical Poly(Phenyl Isocyanide) Copolymers

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## General consideration

All the  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were recorded using a Bruker 600 MHz spectrometer operated in the Fourier Transform mode. 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 two linear TSK gel GMHHR-H columns. The  $M_n$  and  $M_w/M_n$  values were reported relative to the polystyrene standards. The eluent was tetrahydrofuran (THF) at a flow rate of 0.8 mL/min. FT-IR spectra were recorded on Perkin-Elmer Spectrum BX FT-IR system using KBr pellets at 25 °C. Circular dichroism (CD) spectra were performed on JASCO J1500 using 10.0 or 1.0 mm quartz cells. Absorption spectra were recorded on UNIC 4802 UV/vis double beam spectrophotometer using 10.0 or 1.0 mm quartz cell at 25 °C. Fluorescence spectra were recorded using a Hitachi F-4600 fluorescence spectrophotometer. The slit widths were set at 5.0 nm. Dynamic light scattering (DLS) measurements were carried on a Nano-ZS90 Zetasizer of Malvern (UK) instrument, all data were averaged over three time measurements. Transmission electron microscopy (TEM) observations were conducted on a JEM-2100F electron microscope operating at an acceleration voltage of 200 kV. The samples for TEM observation were prepared by casting the corresponding solutions of polymers onto copper mesh grids and drying in air at room temperature. The UV light irradiation was conducted by a UV LED irradiator (UVATA, wavelength = 365 nm), while the visible light irradiation was performed through a Vis LED irradiator (CCS, wavelength = 500 nm).

All solvents were purchased from Sinopharm. Co. Ltd., and were purified by the standard procedures before use. All chemicals were obtained from Aladdin, Sinopharm, and Sigma-Aldrich Chemical Co. Ltd., and were used as received without further purification otherwise denoted. The phenyl alkyne-Pd(II) complex,<sup>1</sup> pentafluorophenol isocyanide,<sup>2</sup> and oligo polyethylene glycol group-functionalized phenyl isocyanide (monomer 2)<sup>3</sup> were prepared according to the literatures.

**Synthesis of Azo-C<sub>6</sub>-OH.** To a 100 mL round-bottom flask equipped with a magnetic stir bar was added 4-(phenylazo)phenol (5.50 g, 27.78 mmol), 6-chloro-1-hexanol (5.67

g, 41.66 mmol),  $K_2CO_3$  (5.75 g, 41.66 mmol) and a trace amount of KI were added in DMF (100 mL). The reaction was allowed to proceed in  $N_2$  atmosphere. After the solution was stirred for 12 hours at  $90^\circ C$ , the reaction mixture was poured into a large amount of deionized water, and then extracted with chloroform. The organic phase was collected and anhydrous  $MgSO_4$  were added into the chloroform solution. After being stirred overnight, the chloroform solution was collected after filtration. The crude product was received from rota-evaporation. The final product Azo- $C_6$ -OH was obtained after recrystallization in ethanol and dried completely in vacuum at room temperature (7.87 g, 95% yield).  $^1H$  NMR (600 MHz,  $CDCl_3$ ,  $25^\circ C$ ):  $\delta_H$  (ppm) = 7.84-7.92 (m, 4H, - $CH$ - of azobenzene group), 7.48 (m, 2H, - $CH$ - of azobenzene group), 7.42 (t, 1H, - $CH$ - of azobenzene group), 6.98 (d, 2H, - $CH$ - of azobenzene group), 4.05 (t, 2H, - $CH_2$ -O- next to azobenzene group), 3.66 (t, 2H, - $CH_2$ -OH), 1.83 (m, 2H, -Ph-O- $CH_2$ - $CH_2$ -), 1.61 (m, 2H, - $CH_2$ - $CH_2$ -OH), 1.37-1.55 (m, 4H, - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ -OH).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ,  $25^\circ C$ ):  $\delta_C$  (ppm) = 161.62, 152.76, 146.86, 130.29, 129.00, 124.73, 122.51, 114.68, 68.18, 62.82, 32.63, 29.14, 25.85, 25.52.

**Synthesis of AzoPI (monomer 1).** To a 100 mL round-bottom flask equipped with a magnetic stir bar was added Azo- $C_6$ -OH (0.43 g, 1.44 mmol), pentafluorophenol isocyanide monomer (0.41 g, 1.31 mmol), DMAP (0.32 g, 2.62 mmol), and TEA (4 mL) in anhydrous THF (50 mL). The reaction was allowed to proceed in  $N_2$  atmosphere. After the solution was stirred for 5 h at  $25^\circ C$ , the solvent was removed by evaporation under reduced pressure. The residue was purified by column chromatography using petroleum ether/ ethyl acetate (8:1, v/v) as the eluent (0.56 g, 91% yield).  $^1H$  NMR (600 MHz,  $CDCl_3$ ,  $25^\circ C$ ):  $\delta_H$  (ppm) = 8.07 (d, 2H, - $CH$ - of phenyl group), 7.82-7.91 (m, 4H, - $CH$ - of azobenzene group), 7.49 (d, 2H, - $CH$ - of azobenzene group), 7.38-7.46 (m, 3H, - $CH$ - of phenyl and azobenzene groups), 6.96 (d, 2H, - $CH$ - of azobenzene group), 4.35 (t, 2H, - $CH_2$ -O- next to phenyl group), 4.07 (t, 2H, - $CH_2$ -O- next to azobenzene group), 1.72-1.92 (m, 4H, - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ -O-), 1.13-1.36 (m, 4H, - $CH_2$ - $CH_2$ - $CH_2$ - $CH_2$ -O-).  $^{13}C$  NMR (600 MHz,  $CDCl_3$ ,  $25^\circ C$ ):  $\delta_C$  (ppm) = 165.02, 161.52, 152.76, 146.91, 131.21, 130.78, 130.31,

129.00, 126.42, 124.71, 122.52, 114.65, 68.05, 65.51, 29.05, 28.58, 25.77, 25.74.

**Typical polymerization procedure for poly-1<sub>n</sub>.** The polymerization procedure is given below taking poly-1<sub>40</sub> as an example. A 10 mL oven-dried flask was charged with monomer **1** (213.39 mg, 0.50 mmol), phenyl alkyne-Pd(II) initiator (6.35 mg 0.0125 mmol), dry THF (2.5 mL) and a stir bar. The concentrations of monomer **1** and Pd(II) initiator were 0.2 and 0.005 M respectively ( $[1]_0/[Pd]_0 = 40$ ). The reaction flask was then immersed into an oil bath at 55 °C and stirred for 12 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 poly-1<sub>40</sub> as a yellow solid (195.8 mg, 89% yield). SEC:  $M_n = 14.1$  kDa,  $M_w/M_n = 1.19$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta_H$  (ppm) = 7.66-7.92 (br, -CH- of azobenzene group), 7.29-7.51 (br, -CH- of phenyl group), 6.47-7.06 (br, -CH- of azobenzene group), 5.57-6.06 (br, -CH- of phenyl group), 3.48-4.61 (br, -OCH<sub>2</sub>-), 0.95-2.04 (br, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). FT-IR (KBr, 25 °C, cm<sup>-1</sup>): 2936 ( $\nu_{C-H}$ ), 2865 ( $\nu_{C-H}$ ), 1717 ( $\nu_{C=O}$ ), 1601 ( $\nu_{C=N}$ ).

**Typical polymerization procedure for poly(1<sub>40</sub>-b-2<sub>m</sub>).** The polymerization procedure is given below taking poly(1<sub>40</sub>-b-2<sub>40</sub>) as an example. Into a 10 mL reaction tube with magnetic stirring bar was added poly-1<sub>40</sub> (40.0 mg,  $2.836 \times 10^{-3}$  mmol), monomer **2** (46.0 mg, 0.113 mmol) and dry THF (1.2 mL) under nitrogen. The reaction solution was kept stirring for 18 h at 55 °C. After that, the mixture was precipitated into a large amount of diethyl ether, and the precipitated solid was collected by centrifugation. The isolated poly(1<sub>40</sub>-b-2<sub>40</sub>) was washed with diethyl ether several times. After dried in vacuum at room temperature overnight, poly(1<sub>40</sub>-b-2<sub>40</sub>) was obtained as a brown solid (75.9 mg, 88% yield). SEC:  $M_n = 27.1$  kDa,  $M_w/M_n = 1.17$ . <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta_H$  (ppm) = 8.55 (br, -NH-), 7.58-7.94 (br, -CH- of azobenzene group), 7.27-7.49 (br, -CH- of phenyl group), 6.33-7.04 (br, -CH- of azobenzene and phenyl groups), 5.43-6.18 (br, -CH- of phenyl group), 3.92-4.83 (br, -OCH<sub>2</sub>- from poly-1<sub>40</sub> block and -CH(CH<sub>3</sub>)NH- from poly-2<sub>40</sub> block and), 2.98-3.88 (br, -CH<sub>2</sub>- of oligo polyethylene glycol group), 0.96-2.06 (br, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-). FT-IR (KBr, 25 °C, cm<sup>-1</sup>):

<sup>1</sup>): 3260 ( $\nu_{\text{N-H}}$ ), 2936 ( $\nu_{\text{C-H}}$ ), 2865 ( $\nu_{\text{C-H}}$ ), 1746 ( $\nu_{\text{C=O}}$ ), 1717 ( $\nu_{\text{C=O}}$ ), 1627 ( $\nu_{\text{C=N}}$ ), 1601 ( $\nu_{\text{C=N}}$ ).

***Self-assembly of amphiphilic poly(1<sub>40</sub>-b-2<sub>n</sub>) copolymers in aqueous solutions.*** The self-assembly of poly(1<sub>40</sub>-b-2<sub>m</sub>) copolymers was conducted by dissolving the copolymer in THF and then dialyzing against deionized water. Taking poly(1<sub>40</sub>-b-2<sub>40</sub>) as an example, 10 mg of the copolymer was firstly dissolved in 10 mL of THF. Then, deionized water was added into the solution at a rate of 1 mL/h under vigorous stirring until the solution changed from transparent to translucent. Then the solution was subsequently dialyzed against deionized water for 72 h (dialysis membrane, molecular weight cut-off: 14 000 g/mol) at room temperature. After being diluted with deionized water and equilibrated at room temperature for 48 h, the self-assemblies of poly(1<sub>40</sub>-b-2<sub>40</sub>) in aqueous solutions were obtained.

***Critical aggregation concentration (CAC) measurement of poly(1<sub>40</sub>-b-2<sub>n</sub>) copolymers.*** The CACs of poly(1<sub>40</sub>-b-2<sub>m</sub>) copolymers in aqueous solutions were measured using pyrene as a fluorescent probe. Taking poly(1<sub>40</sub>-b-2<sub>40</sub>) as an example, the CAC measurement for poly(1<sub>40</sub>-b-2<sub>40</sub>) was performed as follows. Pyrene (5.1 mg) was dissolved in 15 mL of acetone and then 10  $\mu\text{L}$  of the solution was added into each cuvette. The acetone was allowed to evaporate. Then 2.0 mL of poly(1<sub>40</sub>-b-2<sub>40</sub>) aqueous solutions with concentrations ranging from 0.488 to 250 mg/L were added into the pyrene-containing cuvette separately. Upon sonication for 10 min, the solutions were kept at room temperature and equilibrated for 24 h before fluorescent emission measurements with an excitation wavelength of 335 nm. The emission spectra were recorded in the 340-600 nm wavelength range. For each spectrum obtained, the intensity ratio of the first and third peaks,  $I_1/I_3$ , was calculated. The CAC was estimated as the concentration at which  $I_1/I_3$  began to drop, indicating that polymer aggregation occurred.

## References

(1) Y.-X. Xue, Y.-Y. Zhu, L.-M. Gao, X.-Y. He, N. Liu, W.-Y. Zhang, J. Yin, Y. Ding,

H. Zhou, Z.-Q. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 4706-4713.

(2) J. Yin, L. Xu, X. Han, L. Zhou, C. Li and Z.-Q. Wu, *Polym. Chem.*, 2017, **8**, 545-556.

(3) Y. Chen, Z.-H. Zhang, X. Han, J. Yin and Z.-Q. Wu, *Macromolecules*, 2016, **49**, 7718-7727.

**Table S1.** Results for the synthesis of poly-**1**<sub>n</sub>s using phenyl alkyne-Pd(II) as the initiator in THF at 55 °C<sup>a</sup>.

| run | polymer | $M_n$ (Da) <sup>b</sup> | $M_w/M_n$ <sup>b</sup> | Yield <sup>c</sup> (%) |
|-----|---------|-------------------------|------------------------|------------------------|
|-----|---------|-------------------------|------------------------|------------------------|

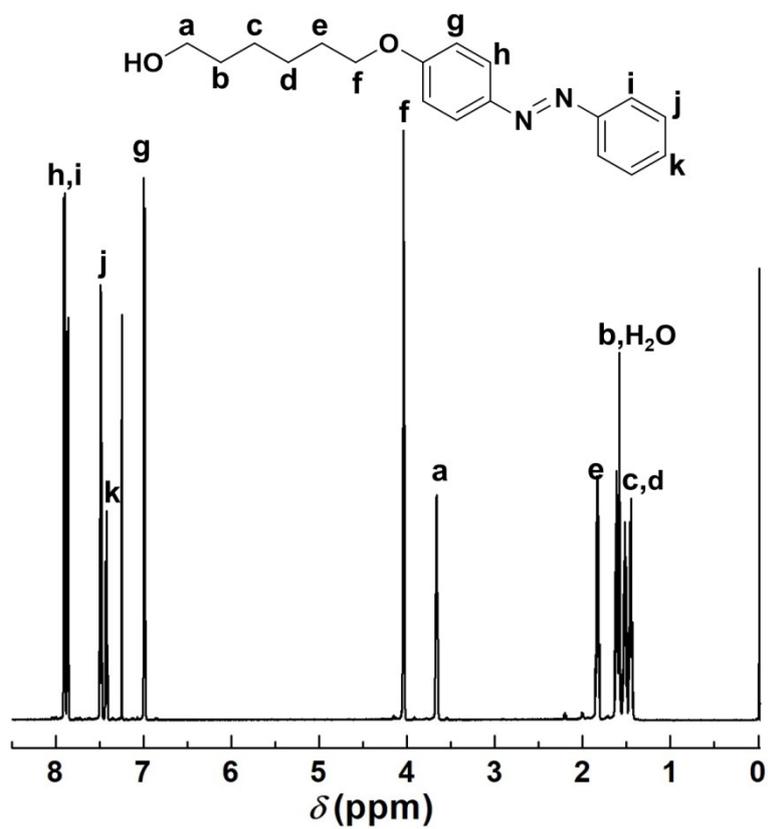
|   |                               |                    |      |    |
|---|-------------------------------|--------------------|------|----|
| 1 | poly- <b>1</b> <sub>20</sub>  | $7.40 \times 10^3$ | 1.13 | 87 |
| 2 | poly- <b>1</b> <sub>40</sub>  | $1.41 \times 10^4$ | 1.19 | 89 |
| 3 | poly- <b>1</b> <sub>60</sub>  | $2.10 \times 10^4$ | 1.14 | 87 |
| 4 | poly- <b>1</b> <sub>80</sub>  | $2.88 \times 10^4$ | 1.15 | 88 |
| 5 | poly- <b>1</b> <sub>100</sub> | $3.58 \times 10^4$ | 1.11 | 89 |

<sup>a</sup>The polymers were synthesized according to Scheme 1b in the main text. <sup>b</sup>The  $M_n$  and  $M_w/M_n$  data were determined by SEC and reported as equivalent to standard polystyrene. <sup>c</sup>Isolated yield.

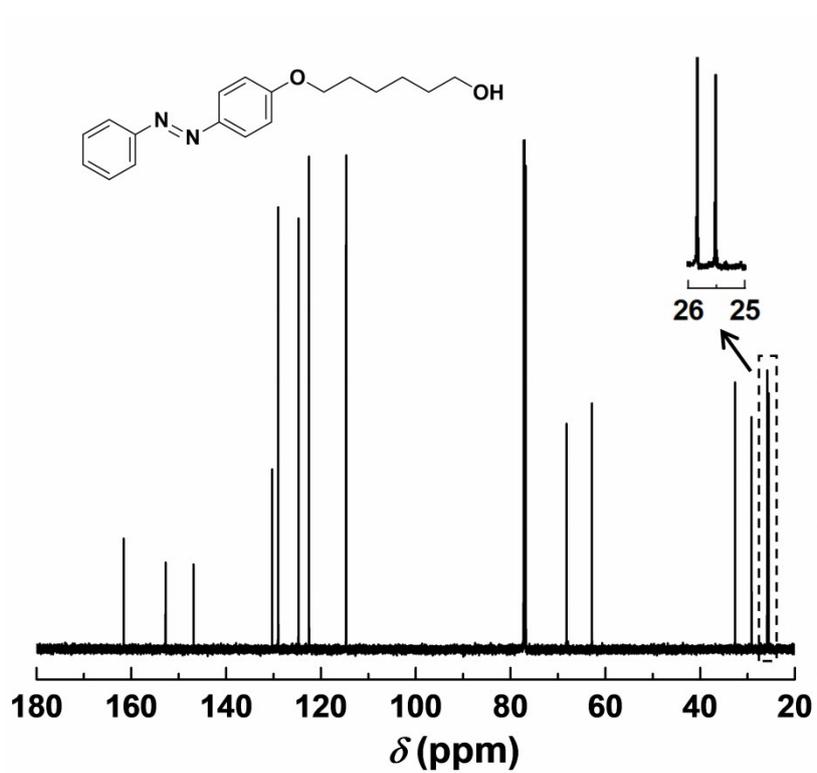
**Table S2.** Results for the synthesis of poly(**1**<sub>40</sub>-*b*-**2**<sub>m</sub>) copolymers using poly-**1**<sub>40</sub> as the initiator in THF at 55 °C<sup>a</sup>.

| run | Polymer  | $M_n$ (Da) <sup>b</sup> | $M_w/M_n$ <sup>b</sup> | Yield <sup>c</sup> (%) |
|-----|--|-------------------------|------------------------|------------------------|
| 1   | poly( <b>1</b> <sub>40</sub> - <i>b</i> - <b>2</b> <sub>20</sub> ) | $2.08 \times 10^4$      | 1.15                   | 89                     |
| 2   | poly( <b>1</b> <sub>40</sub> - <i>b</i> - <b>2</b> <sub>40</sub> ) | $2.71 \times 10^4$      | 1.17                   | 88                     |
| 3   | poly( <b>1</b> <sub>40</sub> - <i>b</i> - <b>2</b> <sub>80</sub> ) | $4.16 \times 10^4$      | 1.18                   | 86                     |

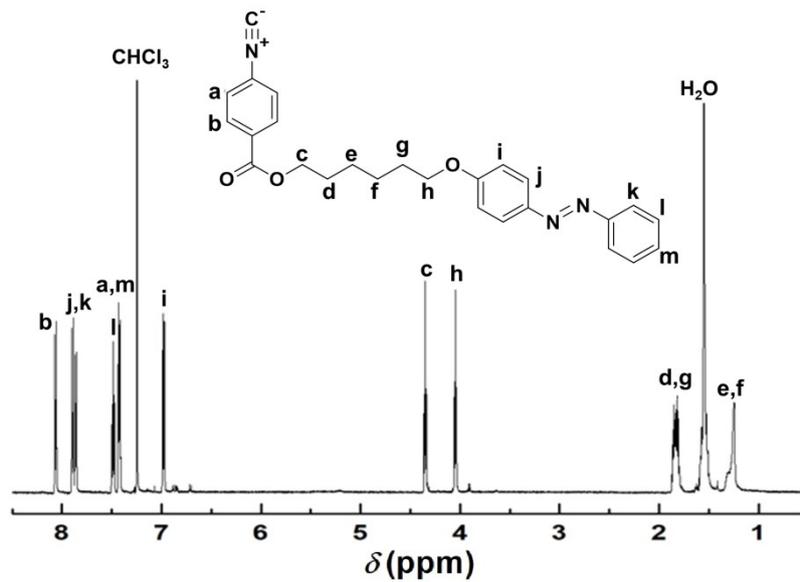
<sup>a</sup>The polymers were synthesized according to Scheme 1b in the main text. <sup>b</sup>The  $M_n$  and  $M_w/M_n$  data were determined by SEC and reported as equivalent to standard polystyrene. <sup>c</sup>Isolated yield.



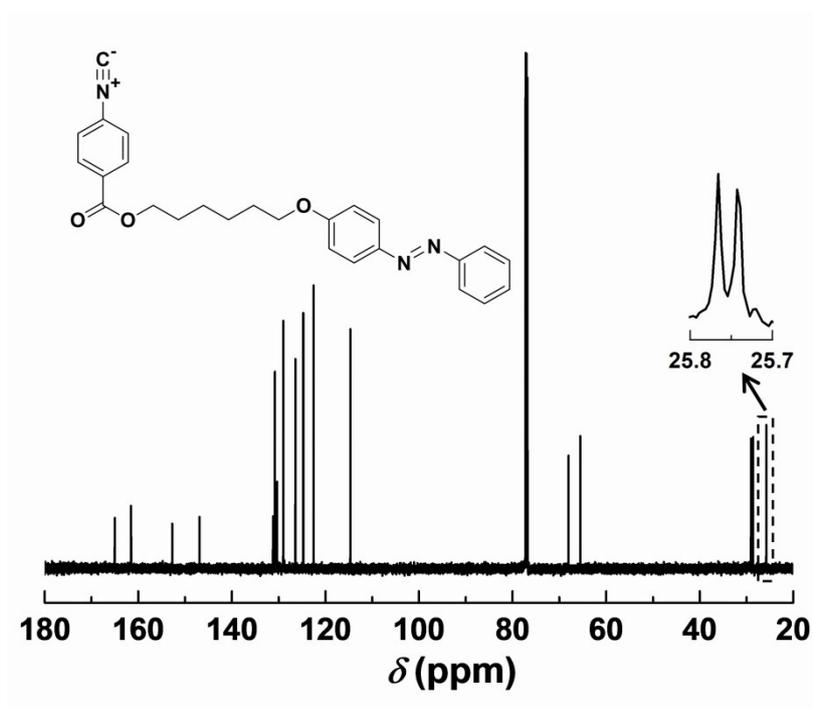
**Figure S1.** <sup>1</sup>H NMR spectrum of the Azo-C<sub>6</sub>-OH measured in CDCl<sub>3</sub> at 25 °C.



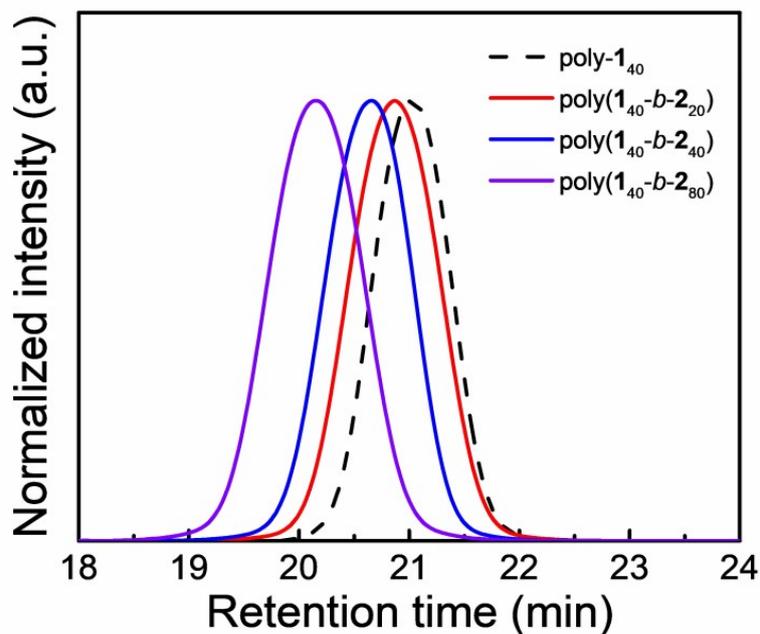
**Figure S2.** <sup>13</sup>C NMR spectrum of the Azo-C<sub>6</sub>-OH measured in CDCl<sub>3</sub> at 25 °C.



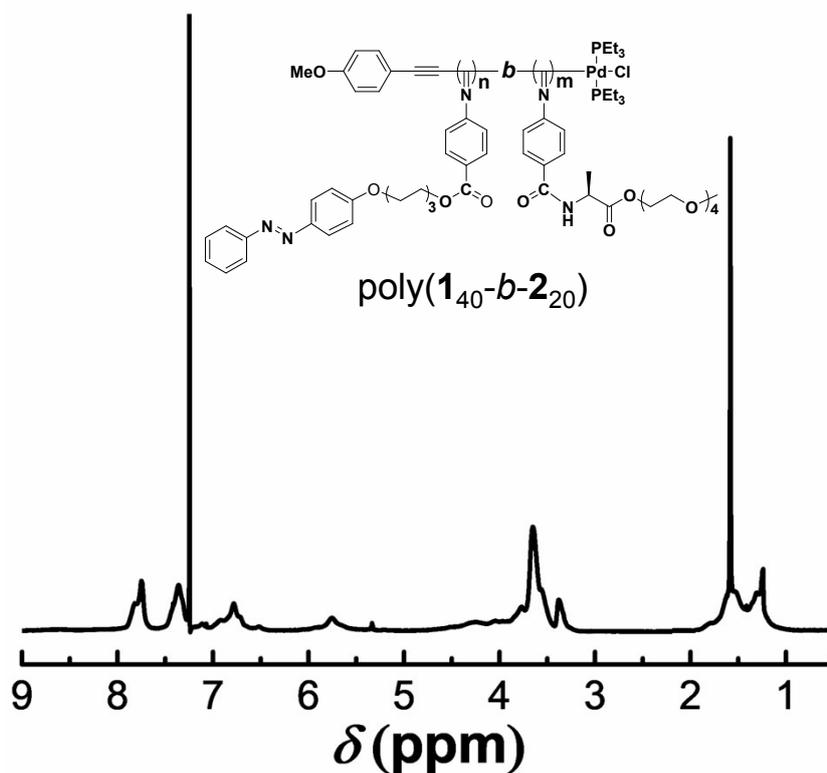
**Figure S3.**  $^1\text{H}$  NMR spectrum of the monomer **1** measured in  $\text{CDCl}_3$  at 25 °C.



**Figure S4.**  $^{13}\text{C}$  NMR spectrum of the monomer **1** measured in  $\text{CDCl}_3$  at 25 °C.



**Figure S5.** Size exclusion chromatograms of poly( $1_{40}$ - $b$ - $2_m$ ) copolymers prepared from the polymerization of monomer **2** using the poly- $1_{40}$  as the macroinitiator with different initial feed ratios of monomer to initiator. SEC condition: eluent = THF, temperature = 40 °C.



**Figure S6.**  $^1\text{H}$  NMR spectrum of poly( $1_{40}$ - $b$ - $2_{20}$ ) measured in  $\text{CDCl}_3$  at 25 °C.

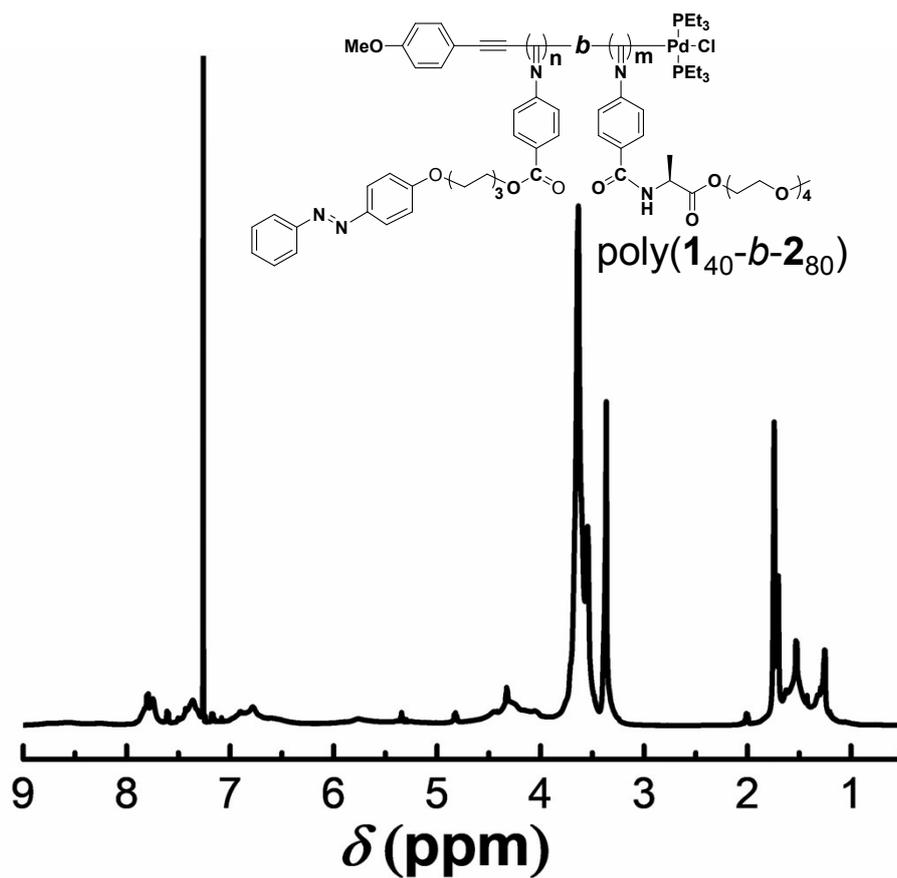


Figure S7. <sup>1</sup>H NMR spectrum of poly(1<sub>40</sub>-b-2<sub>80</sub>) measured in CDCl<sub>3</sub> at 25 °C.

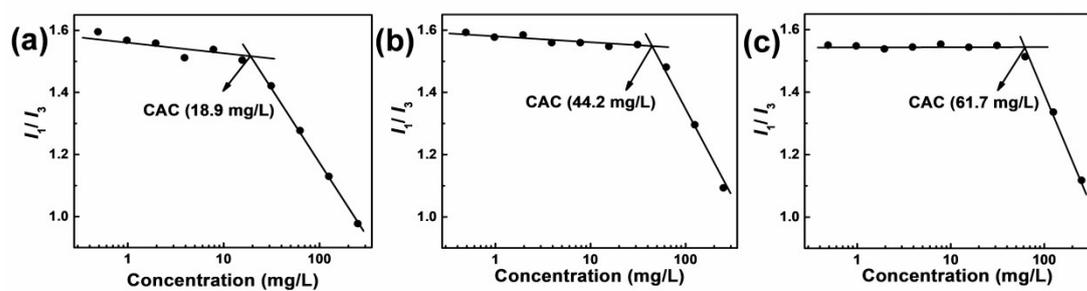


Figure S8. CAC of the (a) poly(1<sub>40</sub>-b-2<sub>20</sub>), (b) poly(1<sub>40</sub>-b-2<sub>40</sub>), and (c) poly(1<sub>40</sub>-b-2<sub>80</sub>).