Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for Synthesis of a Heterotelechelic Helical Poly(methacrylamide) and its Incorporation into a Supramolecular Triblock Copolymer

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Materials and Methods

All reagents were purchased from Sigma-Aldrich, Acros Organics, TCI Chemical or Alfa Aesar and used without further purification unless otherwise mentioned. Methacryloyl chloride was distilled prior to use. 4,4'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol twice. $CDCl_3$ and dichloroethane (DCE) were dried by passing through a column packed with neutral alumina (Sorbent Tectech) prior to use.

^1H NMR spectra were recorded at 25 °C on a Bruker Avance 500 or 600 MHz spectrometer. ^{13}C NMR spectra were recorded on Bruker 150 MHz or 126 MHz spectrometers with complete proton decoupling. Chemical shifts for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are reference to residual proton in the NMR solvent ($CHCl_3$: δ 7.26). Chemical shifts for carbon are reported in ppm downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). All chemical shifts are reported as singlet (s), broad singlet (br s), doublet (d), broad doublet (br d), doublet of doublets (dd), triplet (t), broad triplet (br t), quartet (q) and unresolved multiplet (m).

Gel-permeation chromatography (GPC) characterizations were obtained from a Shimadzu pump coupled to Shimadzu UV and RI detectors with inhibitor free tetrahydrofuran (THF) as the mobile phase. The injection volume was 50 μL and the flow rate was 1 mL/min on an American Polymer Standards column set (100, 1000, 100,000 Å, linear mixed bed). The GPC instrument were calibrated using poly(styrene) standards (EasiCal, Agilent Technologies, Santa Clara, CA) and characterizations were carried out at 25 °C. M_w, M_n and $Đ$ represent weight-average molecular weight, number-average molecular weight and polydispersity, respectively.

Matrix-assisted light desorption ionization time-of-flight (MALDI-ToF) data was recorded on a Bruker UltrafleXtreme operated in the linear mode using flexAnalysis software. The matrix solution was prepared by mixing solutions of 1,8,9-anthracenetriol (dithranol, Sigma-Aldrich) in THF (20 g/L), polymer in THF (20 g/L) and sodium iodide (NaI) in acetone (20 g/L) at a volume ratio of 100 : 20 : 1. 0.5 μL of the mixture were spotted on a MALDI sample plate, air-dried and subjected to measurements.

Isothermal titration calorimetry (ITC) measurements were performed on a TA Nano ITC isothermal titration calorimeter at 25.00 °C using HPLC grade DCE. A total of 50 μL titrant was titrated into 300 μL solution in 20 additions with 150 s intervals. A baseline was obtained with pure DCE prior to sample measurements.

Viscometry measurements were carried out with a Cannon-Ubbelohde Semi-Micro viscometer (9722-G59) in a 25 °C water bath. Homopolymers, 1:1 and 1:1:1 assembled polymers were dissolved in chloroform at initial concentration of 20 g/L and were subject to dissolution by adding chloroform into the viscometer. The viscometer loaded with solution was placed vertically in the water bath and held still for five minutes for temperature equilibrium prior to each measurement. The solution was directed to the measurement bulb by applying suction at top. Measurement started by allowing the solution to move freely from the measurement bulb to the reservoir, and time required for the solution to pass the top mark and reach the bottom mark of the measurement bulb was recorded. Each measurement was least three done in triplicate.

Circular dichroism (CD) spectra were collected with a Jasco J-1500 CD spectrometer. The spectra were obtained with a quartz cuvette (l = 0.2 cm) in HPLC/UV grade dichloroethane (DCE) at 25 °C. All homopolymer samples were prepared in DCE at 10 μM. Polymer supramolecular assemblies were prepared so that the relative concentration of each homopolymer assembled in solution was equal to 10 μM.

Synthesis of benzyl 2-bromo-2-methylpropanoate (2). 4-Pyridinemethanol (0.82 g, 7.5 mmol) and triethylamine (1.6 mL, 11.5 mmol) were dissolved in a 100 mL mixture of anhydrous THF and hexanes (1/1, v/v) at 0 °C. 2-Bromopropionyl bromide (1.1 mL, 0.83 mmol) dissolved in 6 mL hexane was added dropwise over a time span of 1 hour. The mixture was warmed up to room temperature and was stirred for 2 hours. Subsequently, the mixture was quenched by adding 100 mL cold water, followed by brine wash. The dark brown organic layer was collected and dried over Na_2SO_4. After solved removal, the crude product was purified by silica column chromatography (eluent: CH_2Cl_2/acetonitrile, 10/1, v/v) to give compound **1** as a yellow oil (0.77 g, 40%). The product was stored in hexanes at 4 °C to prevent decomposition. ^{1}H NMR ($CDCl_3$) δ (ppm): 8.63 (m, 2H), 7.31 (m, 2H), 5.23 (s, 2H), 1.98 (s, 6H). ^{13}C NMR ($CDCl_3$) δ (ppm): 171.3, 149.9, 144.7, 121.7, 65.5, 55.2, 30.8. HRMS (+ESI): calculated mass for $C_{10}H_{12}BrNO_2$: 257.0051; calculated m/z: 258.0124 $(M + H)^+$; found m/z: 258.0131; difference: 2.61 ppm.

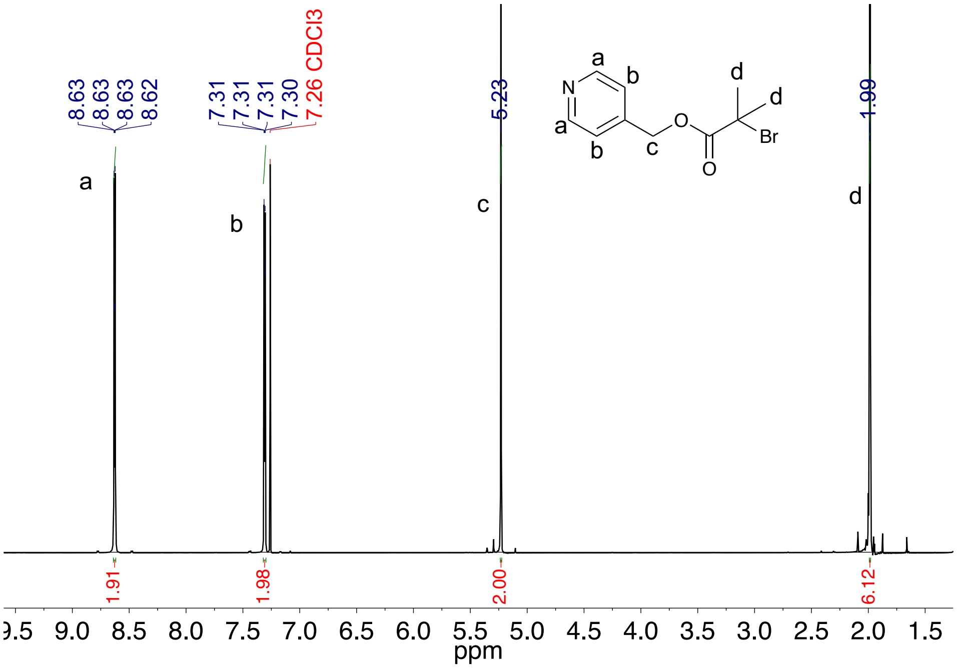

Figure S1. ^{1}H NMR spectrum of **2** ($CDCl_3$, 600MHz).

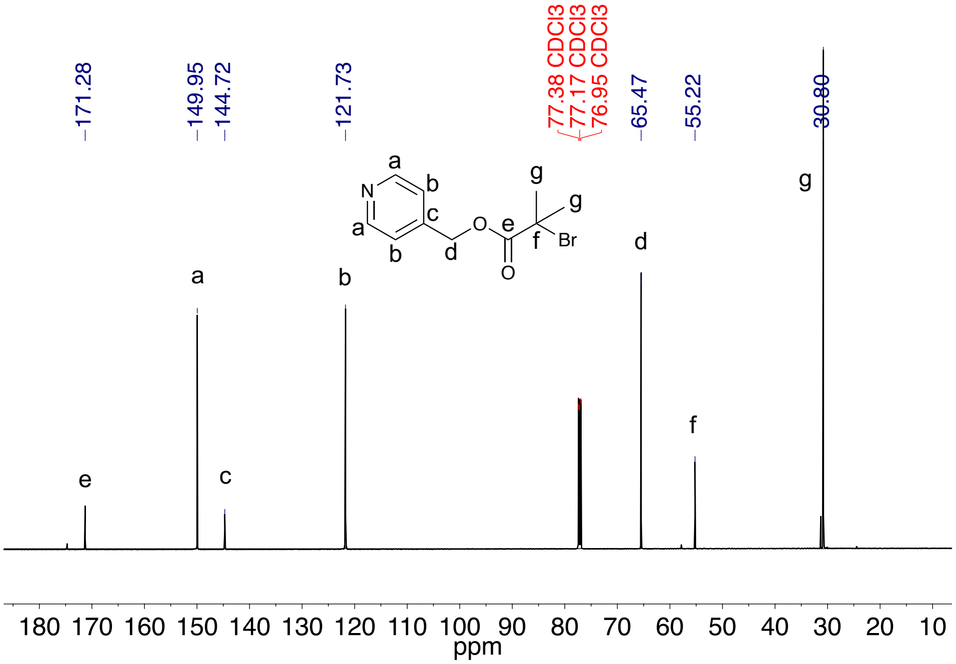

Figure S2. ^{13}C NMR spectrum of **2** ($CDCl_3$, 600MHz).

RAFT polymerization procedures. The desired amounts of monomer, Ba-CTA and AIBN were dissolved in anhydrous THF at a monomer concentration of 1 M in a Schlenk flask. Typical molar concentration was [M]: [CTA]: [I] = 100: 1: 0.1. The mixture was degassed by five freeze-pump-thaw cycles and the flask was filled with Argon. The reaction was carried out at 60 °C for 18 hours. The reaction was quenched by exposing it to air and the crude **Ba-PMAc** was purified by dialysis against acetone (MWCO = 1 kDa) for 2 days. Purified polymer was freeze dried to afford a pink foam.

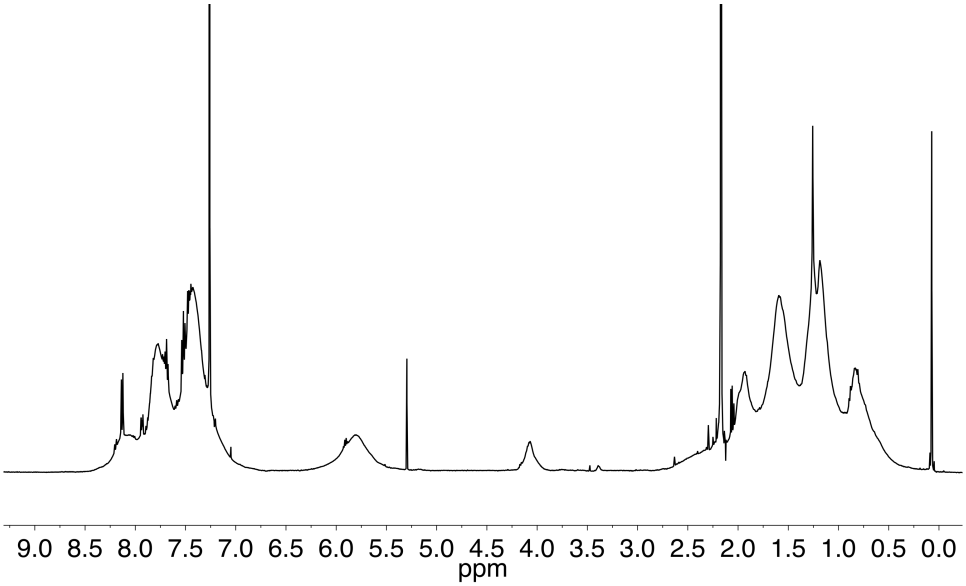

Figure S3. ^{1}H NMR spectrum of **Ba-PMAc** ($CDCl_3$, 500MHz).

Synthesis of heterotelechelic Pyr-PMAc-Ba. Compound **2,** monotelechelic **Ba-PMAc** and triethylamine were dissolved in 1.0 mL anhydrous THF in a molar ratio of 1: 2: 5. The mixture was degassed by purging argon at room temperature for 20 minutes. Hexylamine (5 eq) dissolved in 0.3 mL THF was added into the mixture dropwise. The mixture was stirred at room temperature for an additional 6 hours. Crude **Pyr-PMAc-Ba** was purified by dialysis against acetone (MWCO = 1 kDa) for 2 days. The purified polymer was freeze dried to afford a light-yellow foam.

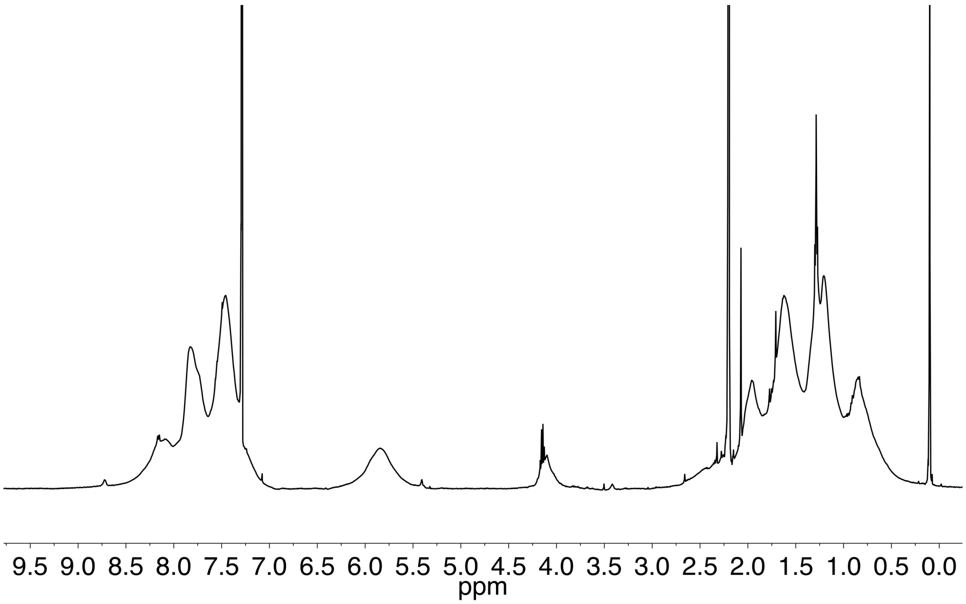

Figure S4. ^{1}H NMR spectrum of heterotelechelic **Pyr-PMAc-Ba** ($CDCl_3$, 500MHz).

ATRP and post-polymerization of Pd-Pin-PS. Styrene monomer, SCS-pincer initiator and PMDETA ligand were mixed in a Schlenk flask at a molar ratio of 500: 1: 2. The mixture was degassed by five freeze-pump-thaw cycles and the flask were backfilled with argon. Under an argon flow, a 1 molar equivalence of CuBr was added into the mixture. The flask was sealed and heated to 110 °C for 2 hours. Subsequently, the reaction was quenched by exposing to air and pouring into 20 mL anhydrous THF. Copper catalyst was removed by passing through a plug loaded with neutral alumina twice. Crude polymer was purified by dialysis against acetone.

100 mg of purified polymer were dissolved in 20 mL CH_2Cl_2/acetonitrile (1/1, v/v) under argon at room temperature. A 1.5 molar equivalence of $Pd(PhCN)_2Cl_2$ was added and the mixture was stirred for 30 minutes. A 2.5 molar equivalence of silver tetrafluoroborate ($AgBF_4$) was added and the solution was stirred for 2 hours prior to pouring into 100 mL saturated NaCl aqueous solution. The mixture was subjected to vigorous stirring overnight. Subsequently, the organic

layer was separated and dried over Na_2SO_4. Crude product was purified by dialysis against acetone (MWCO = 1 kDa) for 2 days and dried under vacuum to afford a yellow solid (quantitative yield).

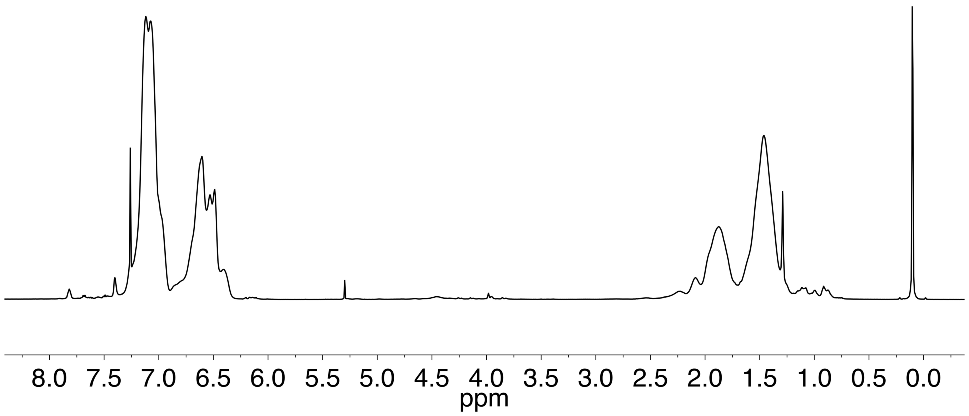

Figure S5. ^{1}H NMR spectrum of monotelechelic **Pd-Pin-PS** ($CDCl_3$, 500MHz).

Anionic polymerization of HW-PIC. Under an argon flow, 50 mL monomer were dissolved in 1.0 mL anhydrous THF in a Schlenk flask and were degassed by five freeze-pump-thaw cycles. HW-functionalized initiator ([M]: [I] = 30: 1) dissolved in 0.33 mL THF was added to the flask. The mixture was heated to 50 °C for 12 hours, followed by purification *via* precipitation in cold MeOH/H_2O (3/1 v/v) solution. The brown solid was further rinsed in acetone and the insoluble, purified polymers were filtered and dried by vacuum.

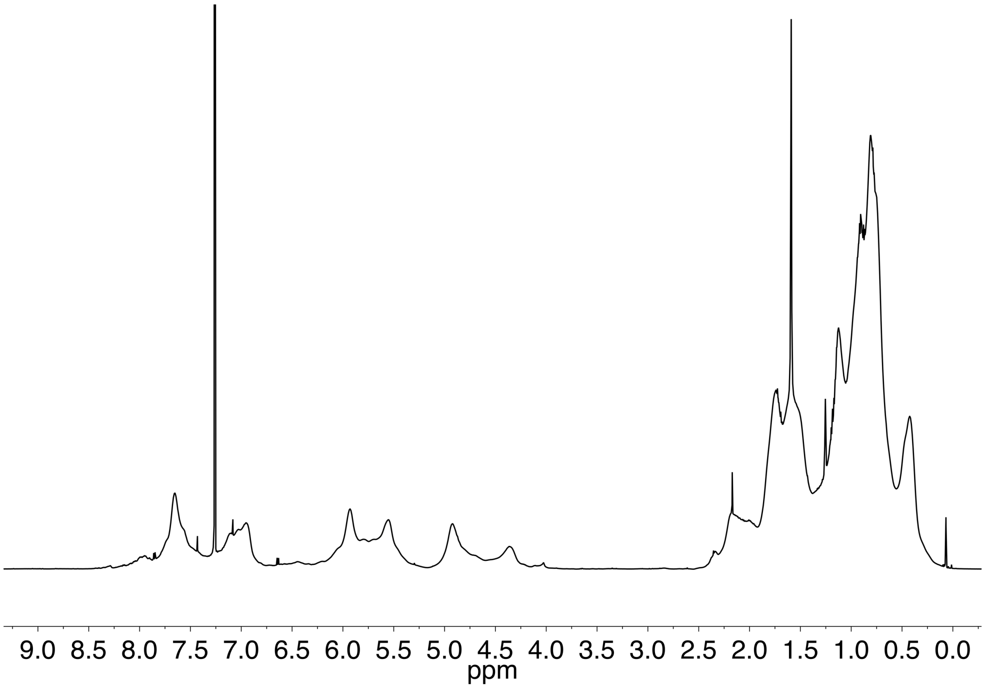

Figure S6. ^{1}H NMR spectrum of monotelechelic **HW-PIC** ($CDCl_3$, 600MHz).

GPC Characterizations of Telechelic Polymers (obtained with THF as the eluent).

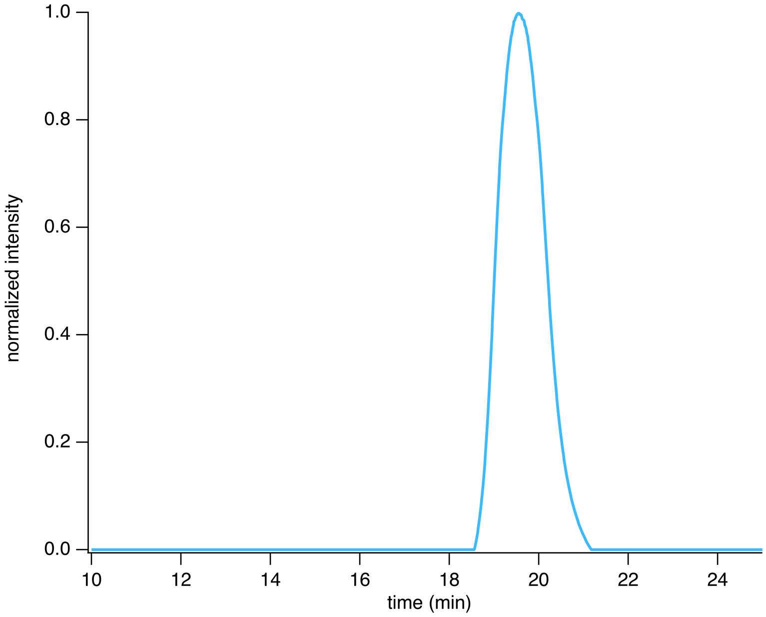

Figure S7. Normalized GPC trace for **Ba-PMAc** (M_n = 3100, $Đ$ =1.19)

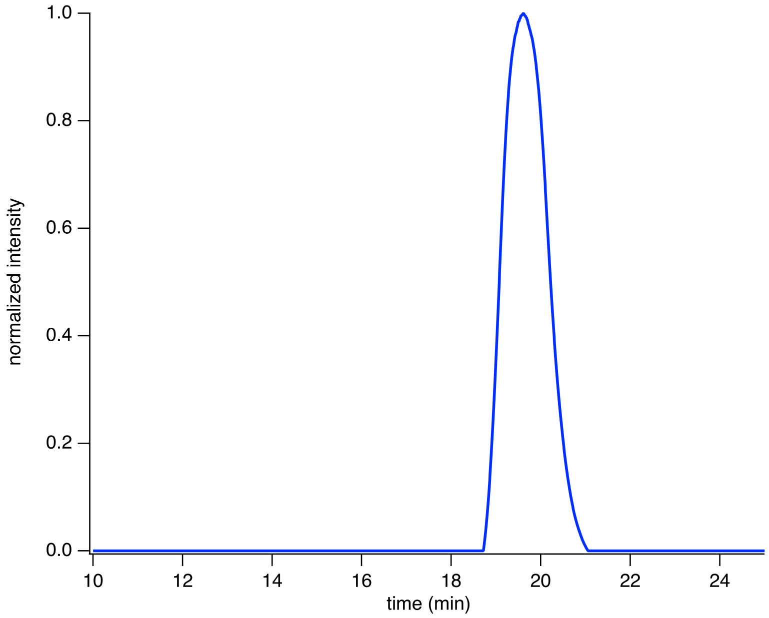

Figure S8. Normalized GPC trace for **Pyr-PMAc-Ba** (M_n = 3100, *Đ* =1.16)

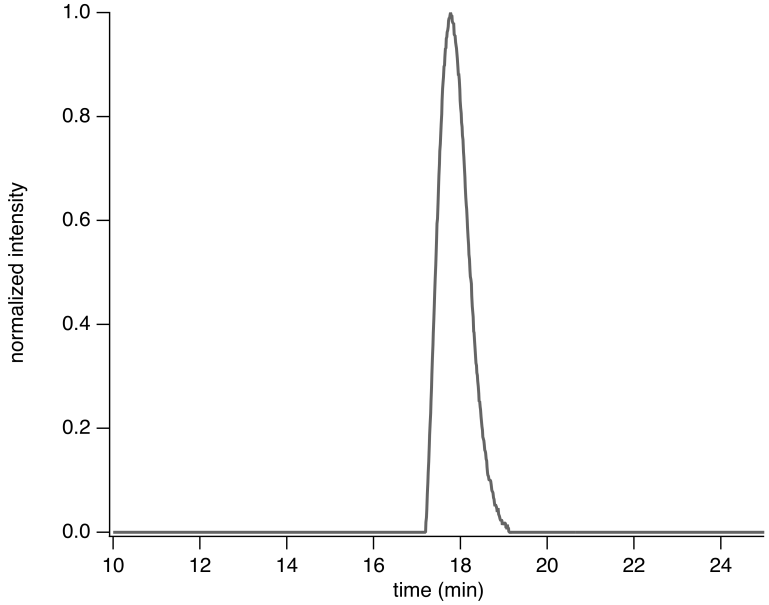

Figure S9. Normalized GPC trace for **Pd-Pin-PS** (M_n = 10100, *Đ* =1.11)

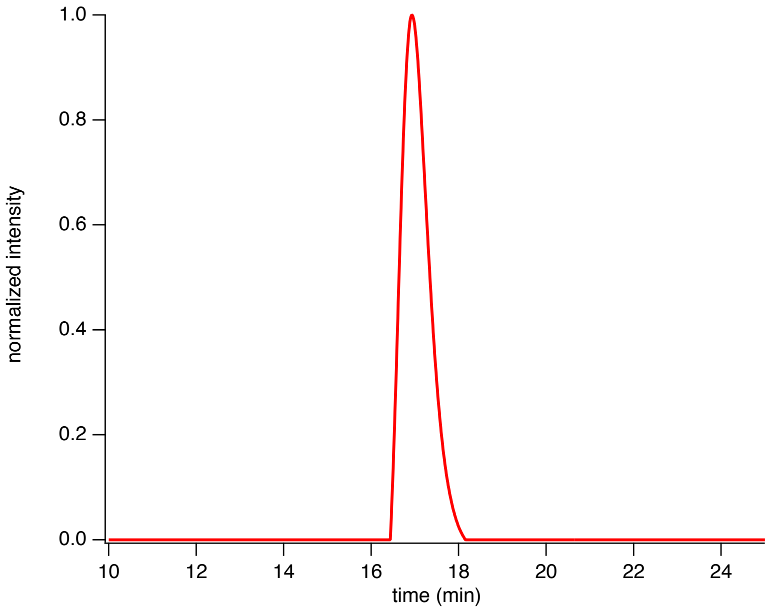

Figure S10. Normalized GPC trace for **HW-PIC** (M_n = 10200, $Đ$ =1.24)

MALDI-ToF Studies. MALDI-ToF spectra were obtained in the linear mode, and by chain ionization assisted with dithranol as matrix and NaI as the ionization agent. MALDI-ToF spectrum of monotelechelic **Ba-PMAc** underlines repetitive patterns of a groups of three peaks comprised of a charged main series (ⓑ) with two minor peaks (ⓐ and ⓒ). Each set of peaks are separated by 239 g/mol, reflecting the repeating unit of the monomer (calculated 239.32 g/mol). Peaks with the highest intensities mark the barbiturate functionalized polymers with fragmentations of the labile C-S thioester bond. This set of ions is also observed in MALDI-ToF spectrum of heterotelechelic **Pyr-PMAc-Ba** polymers. For example, an end-cleaved species with 12 repeating units $[SH\text{-}(MAc)_{12}\text{-}Ba + Na]^+$ could be found in both spectra (calculated m/z = 3361.45; m/z = 3361.277 for Figure 2, peak ②; m/z = 3361.041 for Figure S11, peak ⓑ). The second, relatively intense, minor series correlates to hydrogen ion charged, end-cleaved species while the least intense series can be assigned to the hydrogen ion charged molecular ions of **Ba-**

PMAc polymers. The **Ba-PMAc** molecular ions cannot be detected in the heterotelechelic **Pyr-PMAc-Ba** spectrum, providing evidence for complete macromolecular transformation through thiol-bromo click reaction.

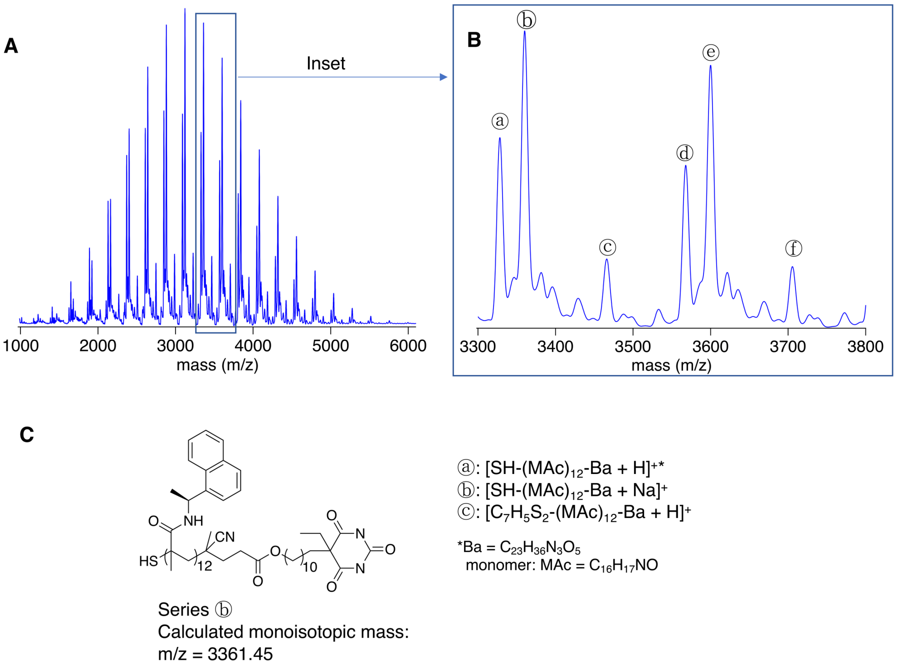

Figure S11. MALDI-ToF MS of monotelechelic **PMAc-Ba** (A) full spectrum, (B) expansion and (C) molecular structure assignments.

^{1}H NMR Titration Studies. Titration of **Pd-Pin-PS_Pyr-PMAc-Ba** into **HW-PIC** was carried out in $CDCl_3$ at 25.0 °C. Metal coordination assembled **Pd-Pin-PS_Pye-PMAc-Ba** was added into **HW-PIC** (8 mg) polymers dissolved in 0.7 mL solvent in incremental stoichiometric ratios (from 0.1 eq to 2.5 eq). HW-Ba supramolecular assembly was monitored by the shifts of HW proton and Ba proton signals. As shown in Figure S12, HW NH proton signals moved downfields (marked with red triangles and blue squares), while the broad signal of Ba NH protons (marked with orange circles) appeared and moved upfields.

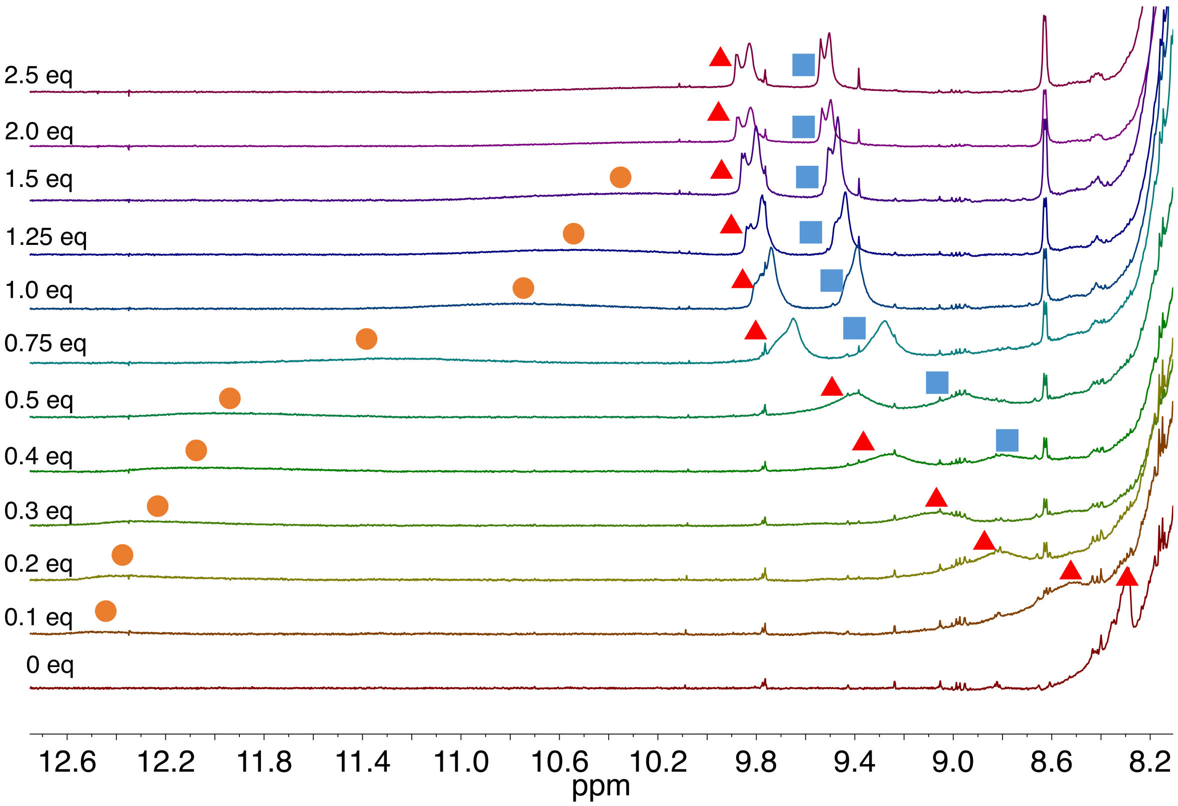

Figure S12. ^{1}H NMR spectra overlay of the titration of **Pd-Pin-PS_Pyr-PMAc-Ba** into **HW-PIC** in $CDCl_3$ at room temperature. Red triangles and blue squares mark the shift of HW proton signals and orange dots denote the broad Ba proton signals upon assembly.

ITC Titration Studies. 300 µL of 1 mM **HW-PIC** dissolved in DCE were loaded into the calorimeter. 50 µL of 10 mM **Pd-Pin-PS_Pyr-PMAc-Ba** were added by syringe in 20 equal-amount titrations after auto-calibration. The results were plotted and analyzed by NanoAnalyze software in which the association constant (K_a) was calculated using the single-site biding model (n=1). In a representative trial, K_a was calculated to be 3.44×10^4 M^{-1}.

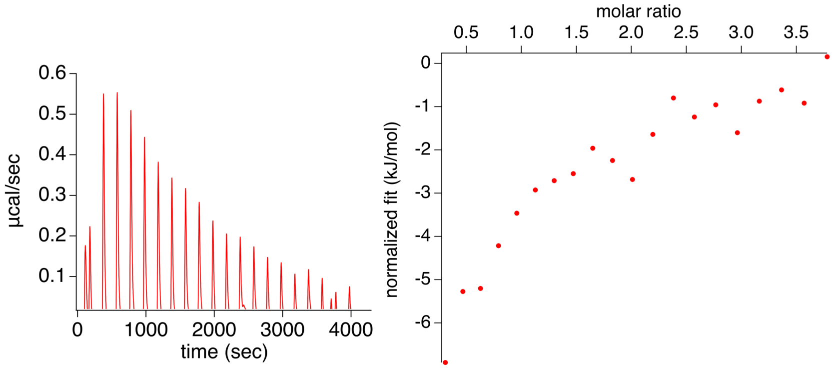

Figure S13. ITC binding isotherm and plot of the normalized fit for the titration of **HW-PIC** with **Pd-Pin-PS_Pyr-PMAc-Ba**.

Circular Dichroism (CD) Traces

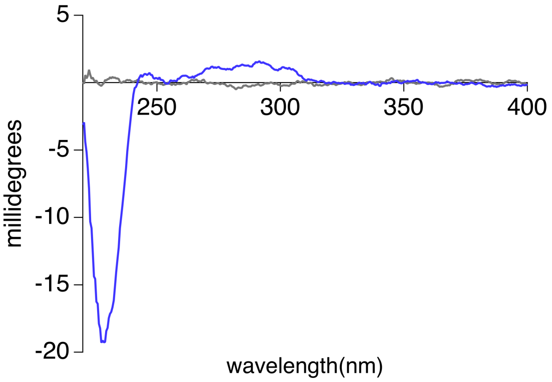

Figure S14. CD spectrum corresponding to **Pd-Pin-PS** (grey) and **Pyr-PMAc-Ba** (blue).