

## Supplementary Information

for

### Nucleobase-Functionalized ABC Triblock Copolymers: Self-assembly of Supramolecular Architectures

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**Materials.** *n*-Butyl acrylate (*n*BA, 99+%) was purchased from Aldrich and passed through neutral alumina columns before use.  $\alpha,\alpha'$ -Azobis(isobutyronitrile) (AIBN, Fluka, 99%) was recrystallized from methanol. 1,4-Butanediol diacrylate (Alfa Aesar, 99%) was used without further purification. Adenine (A, 99%), thymine (T, 99%), triethylamine (TEA, 99%), potassium carbonate (99%), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%), and 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%) were purchased from Aldrich and used without further purification. Hexane (HPLC grade), chloroform (CHCl<sub>3</sub>, HPLC), tetrahydrofuran (THF, HPLC grade), *N,N*-dimethylsulfoxide (DMSO, HPLC grade) and *N,N*-dimethylformamide (DMF, HPLC grade, anhydrous) were purchased from Fisher Scientific and used as received.

**Analytical Methods.** <sup>1</sup>H NMR spectra were collected in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> on a Varian INOVA spectrometer operating at 400 MHz at 23 °C. Differential scanning calorimetry (DSC) was performed under a nitrogen flush of 50 mL/min at a heating rate of 10 °C/min on a TA instruments Q1000 DSC, which was calibrated using indium (mp = 156.60 °C) and zinc (mp = 419.47 °C) standards. Glass transition temperatures were measured as the midpoint of the

transition in the second heating scan. DMA was conducted on a TA Instruments Q800 in tension mode at a frequency of 1 Hz, an oscillatory amplitude of 8  $\mu\text{m}$ , and a static force of 0.01 N. The temperature ramp was 3  $^{\circ}\text{C}/\text{min}$ . The glass transition temperature ( $T_g$ ) was determined at the peak maximum of the  $\tan \delta$  curve.

SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu  $K\alpha$ ). The sample-to-detector distance was 1600 mm, and  $q$ -range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 2 hours. All the SAXS data were analyzed using the SAXSGUI software package to obtain radially integrated SAXS intensity versus scattering vector  $q$ , where  $q = (4\pi/\lambda)\sin(\theta)$ ,  $\theta$  is one half of the scattering angle and  $\lambda$  is the wavelength of X-ray.

**Polymerization of poly(ThA) macro-CTA.** ThA (5.0 g, 15.4 mmol), AIBN (4.1 mg, 25  $\mu\text{mol}$ ), CPDT (79.5 mg, 0.25 mmol), and DMF (29 g, 15 wt%) were charged into a single-neck Schlenk flask and subjected to four cycles of freeze-pump-thaw and subsequent refilling with argon. The flask was then sealed and thermostated at 65  $^{\circ}\text{C}$  for 3 h. The copolymer was isolated from precipitation into methanol and dried under vacuum at room temperature for 24 h. The monomer: initiator: CTA ratio was 616:1:10. End group analysis using  $^1\text{H}$  NMR revealed molecular weight  $M_n=9.4$  kDa. Conversion was 58%.

**Chain extension of poly(ThA) with  $n\text{BA}$ .** Typical synthesis of poly(ThA- $b$ - $n\text{BA}$ ) was conducted as follows.  $n\text{BA}$  (1.6 mg, 12.2 mmol), AIBN (0.3 mg, 2.0  $\mu\text{mol}$ ), poly(ThA) macro-CTA (225 mg, 24.0  $\mu\text{mol}$ ), and DMF (7.1 g, 20 wt%) were charged into a single-neck Schlenk

flask and subjected to four cycles of freeze-pump-thaw and subsequent refilling with argon. The flask was then sealed and thermostated at 65 °C for 3 h. The copolymer was isolated from precipitation into methanol water mixture and dried under vacuum at room temperature for 24 h. The monomer: initiator: CTA ratio was 6100:1:10. <sup>1</sup>H NMR revealed molecular weight of poly(ThA-*b-n*BA)  $M_n$ = 9.4 and 19.3 kDa for each block, with a conversion of 29%.

**Chain extension of poly(ThA-*b-n*BA) with AdA.** Typical synthesis of poly(ThA-*b-n*BA-*b*-AdA) was conducted as follows. AdA (466.2 mg, 1.4 mmol), AIBN (0.4 mg, 2.3 μmol), poly(ThA-*b-n*BA) macro-CTA (669 mg, 23.3 μmol), and DMF (4.5 g, 20 wt%) were charged into a single-neck Schlenk flask and subjected to four cycles of freeze-pump-thaw and subsequent refilling with argon. The flask was then sealed and thermostated at 65 °C for 3 h. The copolymer was isolated from precipitation into methanol water mixture and dried under vacuum at room temperature for 24 h. The monomer: initiator: CTA ratio was 609:1:10. <sup>1</sup>H NMR revealed molecular weight of poly(ThA-*b-n*BA-*b*-AdA)  $M_n$ = 9.4-19.3-6.8 kDa, with a conversion of 33%.

**Solution cast copolymer films preparation.** Solution cast: PTBA copolymers were dissolved in DMSO (2 solid wt%) at 50 °C for 18 h and casted to a Teflon mold. The mold was placed at 80 °C for 48 h to slowly evaporate the DMSO. The dried copolymer film was then annealed in vacuum at 120 °C for 48 h.

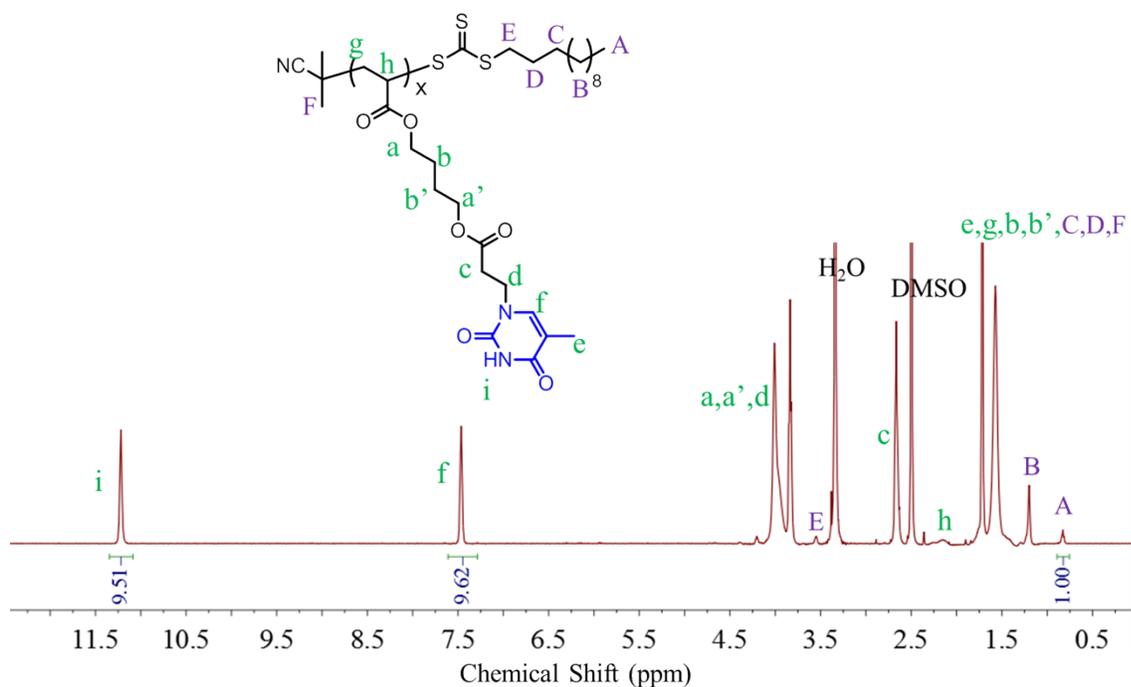


Figure S1.  $^1\text{H}$  NMR spectrum of poly(ThA) macro-CTA and end group analysis for determining molecular weight.

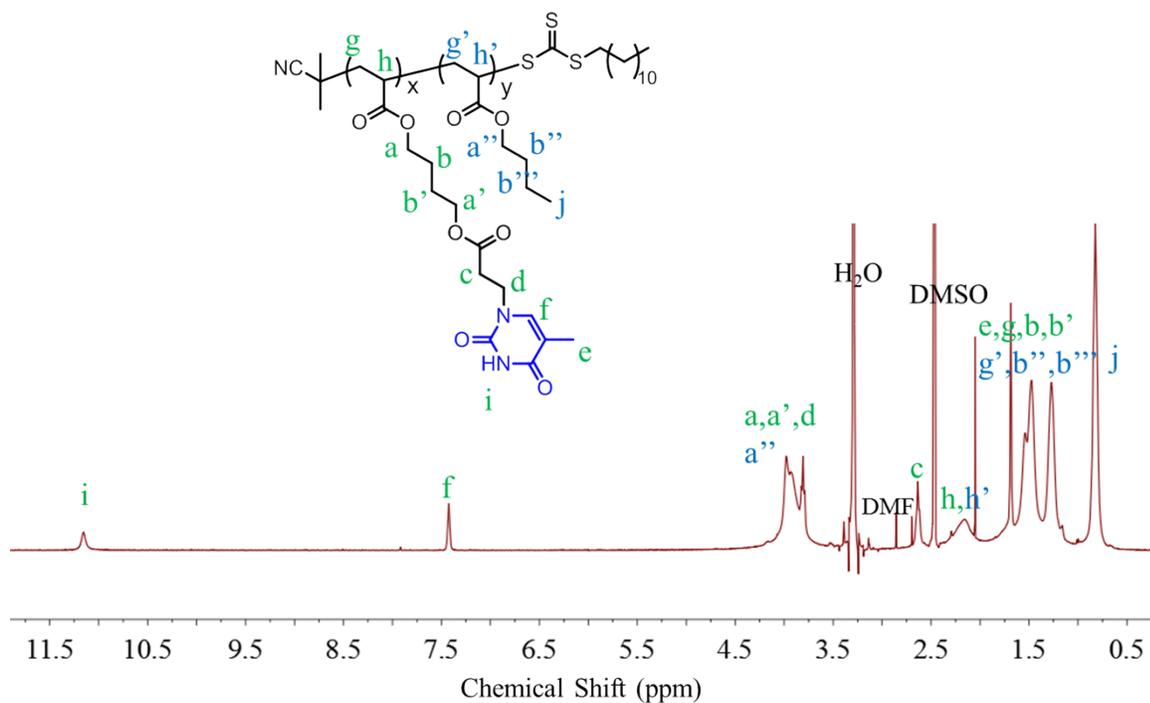


Figure S2.  $^1\text{H}$  NMR spectrum of poly(ThA-*b*-*n*BA) diblock copolymer macro-CTA.

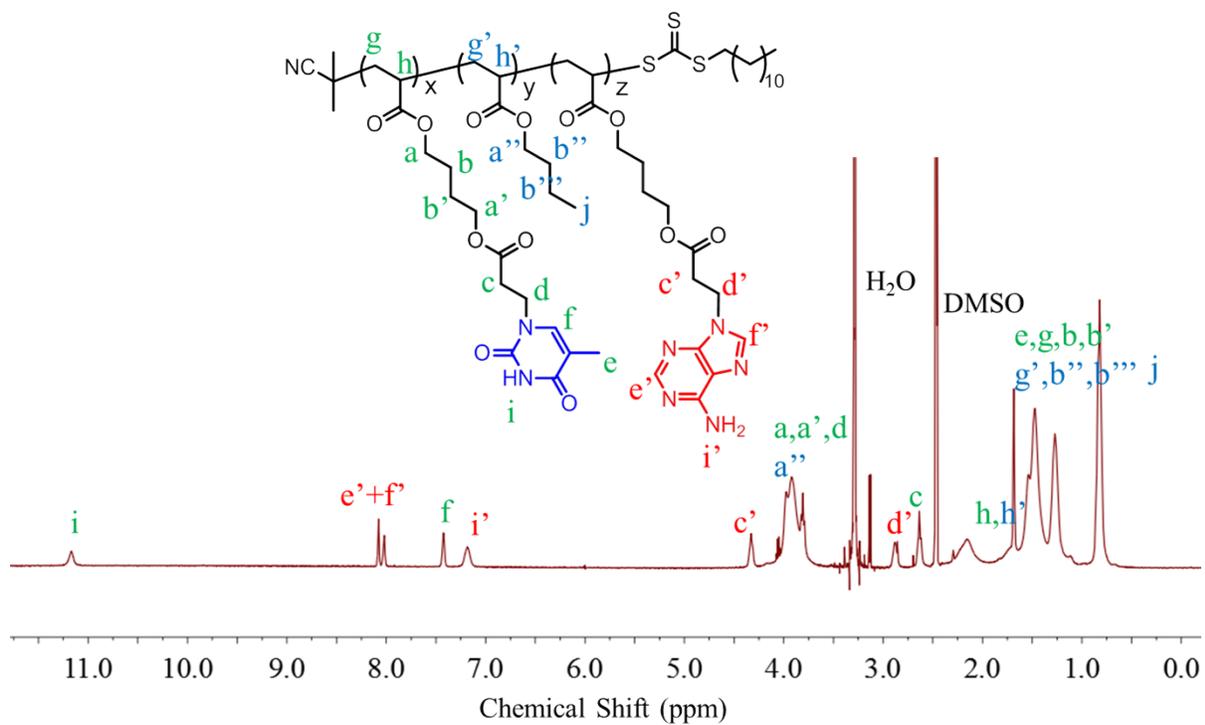


Figure S3. <sup>1</sup>H NMR spectrum of poly(ThA-*b*-*n*BA-*b*-AdA) triblock copolymer.

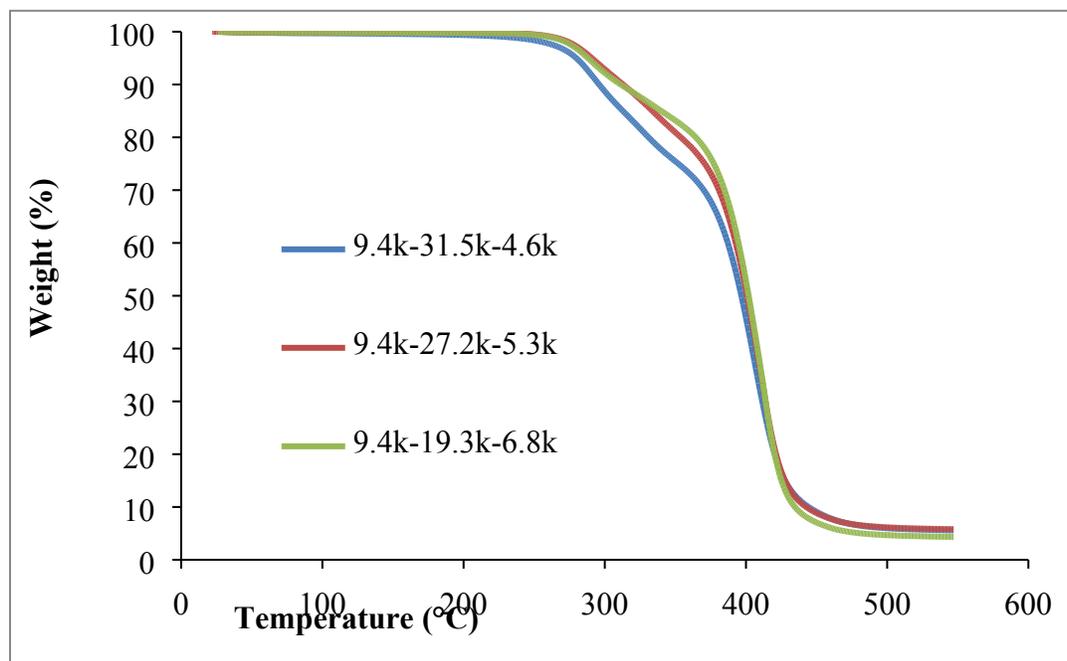


Figure S4. TGA profiles of poly(ThA-*b*-*n*BA-*b*-AdA) triblock copolymers.