Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

for

Nucleobase-Functionalized Acrylic ABA Triblock Copolymers and Supramolecular Blends

Keren Zhang,[a] Motohiro Aiba,[b] Gregory B. Fahs,[a] Amanda G. Hudson,[a] William D. Chiang,[a] Robert B. Moore,[a] Mitsuru Ueda,[b] and Timothy E. Long[a]*

[a] Department of Chemistry, Macromolecules and Interfaces Institute

Virginia Tech, Blacksburg, VA 24061, USA

[b] Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Analytical Methods. WAXD were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-rays with a wavelength of 0.154 nm (Cu Kα). Scattering from a silver behenate standard was used to calibrate the sample-to-detector distance. For WAXD, the sample-to-detector distance was 80.0 mm. WAXD two-dimensional diffraction patterns were obtained using an image plate, with an exposure time of 2 hours. All WAXD data were analyzed using the SAXSGUI software package to obtain azimuthal averaged WAXD intensity versus 2θ profiles, where θ is one half of the scattering angle. WAXD profiles were vertically shifted to facilitate a comparison of the peak positions.

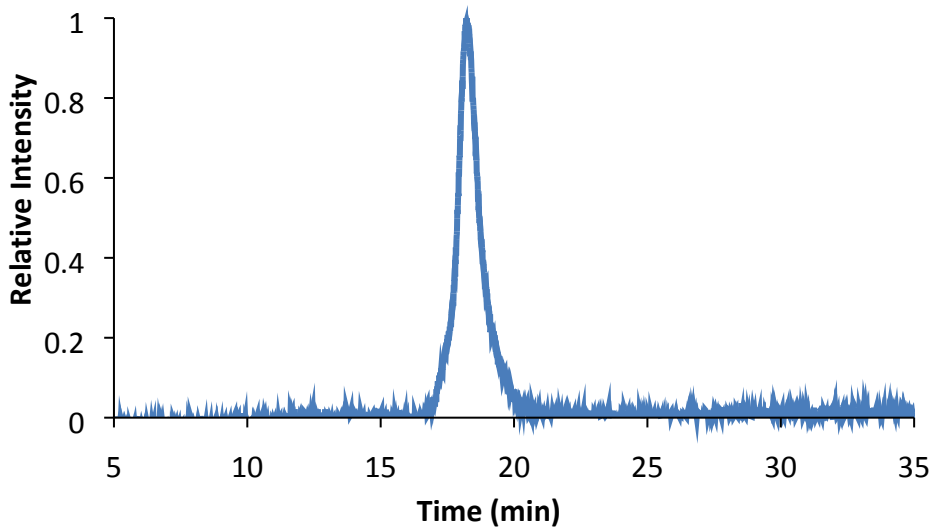

Figure S1. SEC trace of poly(*n*BA) difunctional macro-initiator.

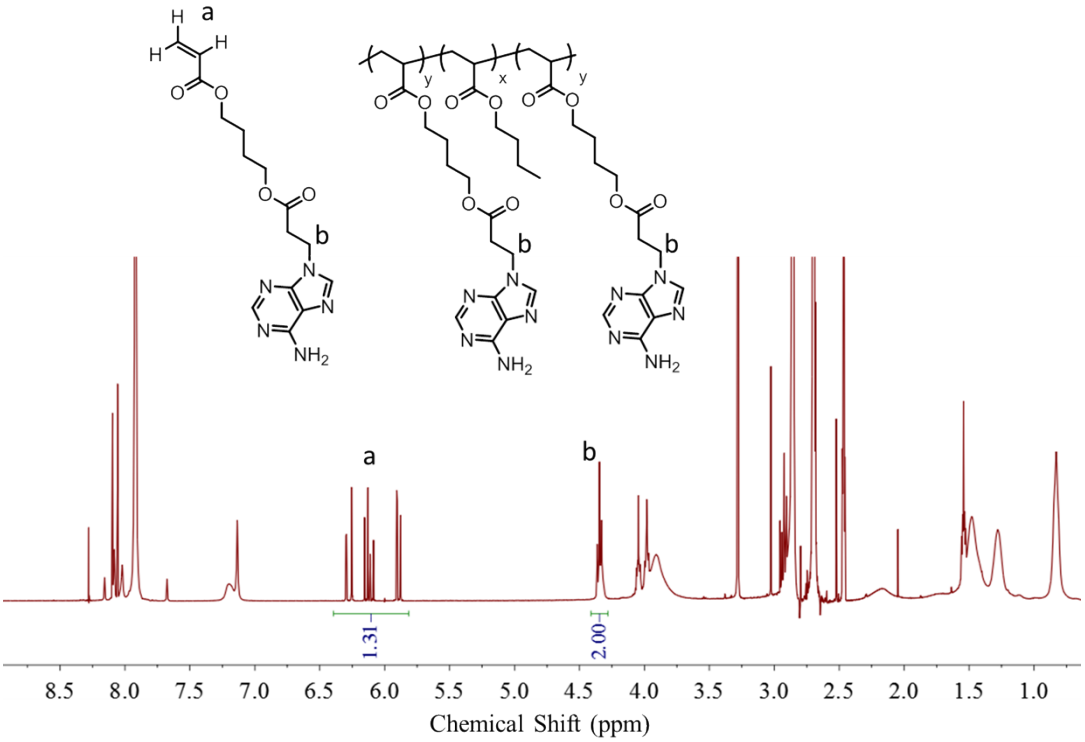

Figure S2. ^{1}H NMR spectrum of reaction mixture after 2nd RAFT polymerization step of adenine block. The integrations of peak a and b were used to calculate conversion.

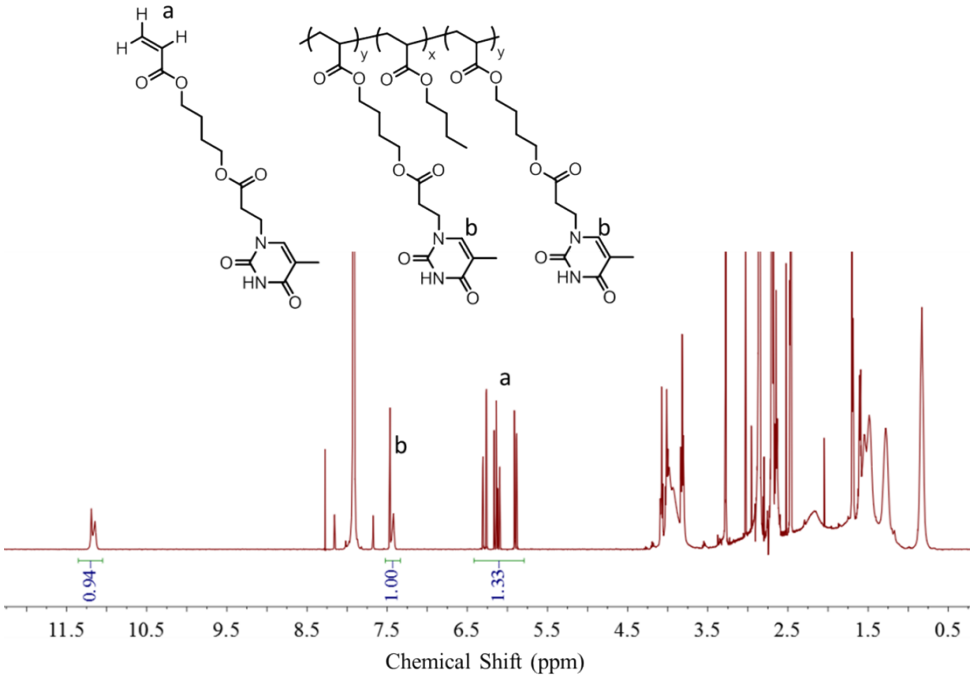

Figure S3. [1]H NMR spectrum of reaction mixture after 2[nd] RAFT polymerization step of thymine block. The integrations of peak a and b were used to calculate conversion.

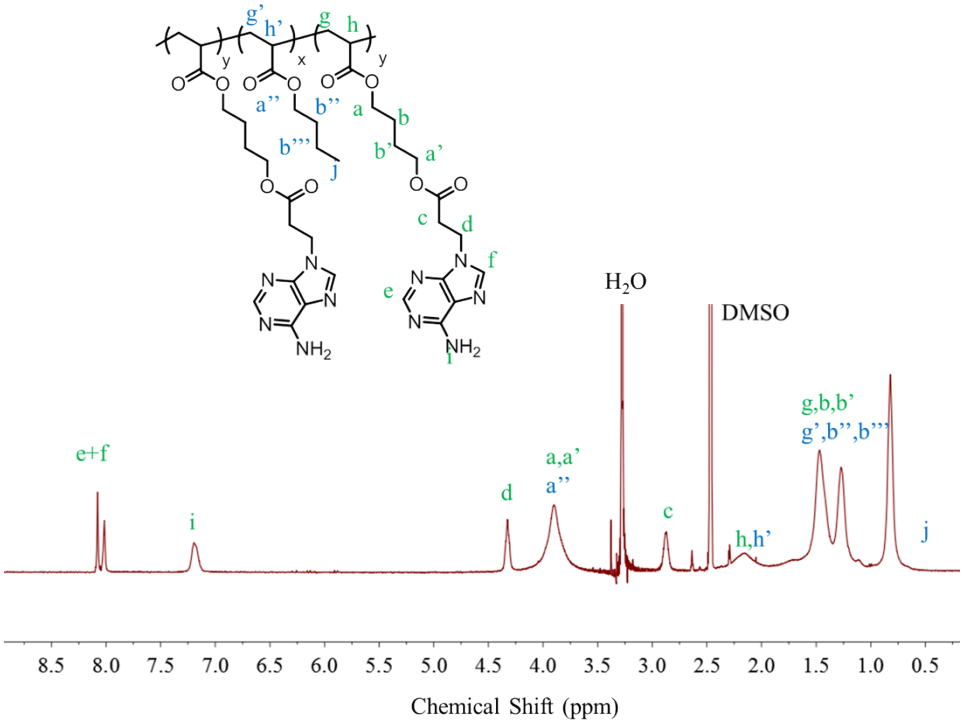

Figure S4. [1]H NMR spectrum of poly(AdA-*b*-*n*BA-*b*-AdA) with 19 mol% adenine.

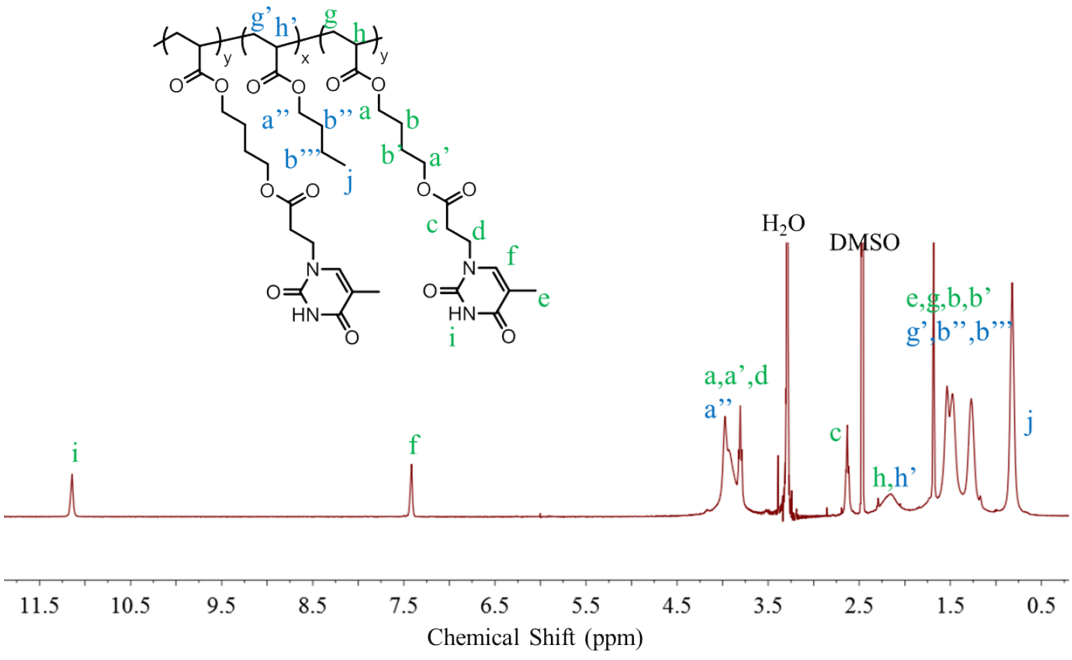

Figure S5. [1]H NMR spectrum of poly(ThA-*b*-*n*BA-*b*-ThA) with 21 mol% thymine.

Table S1. DP and molecular weight from ^{1}H NMR spectrums. All data were based on the second RAFT polymerization step in Scheme 1, polymerization of AdA/ThA external block with P*n*BA macro-CTA. Conversion refers to the AdA/ThA monomer conversion. DP refers to the degree of polymerization for the nucleobase-functionalized block. DP_1 was calculated from ^{1}H NMR spectroscopic analysis of the reaction mixture immediately after polymerization through a comparison of monomer conversion and targeted molecular weight from feed. DP_2 was calculated from ^{1}H NMR spectroscopic analysis of the purified copolymers, using the ratio of nucleobase-functionalized block to P*n*BA internal block.

	Conversion	Targeted Mn at 100% conversion	DP_1	(Nucleobase:*n*BA) ratio of pure copolymer	DP_2	Average DP	Molecular weight	Total molecular weight
poly(AdA-*b*-*n*BA-*b*-AdA)	56%	50.1 kDa	84.5	4.3:1	81.3	83	27.6 kDa	72.4 kDa
poly(ThA-*b*-*n*BA-*b*-ThA)	56%	53.0 kDa	91.1	3.7:1	94.6	93	30.1 kDa	74.9 kDa

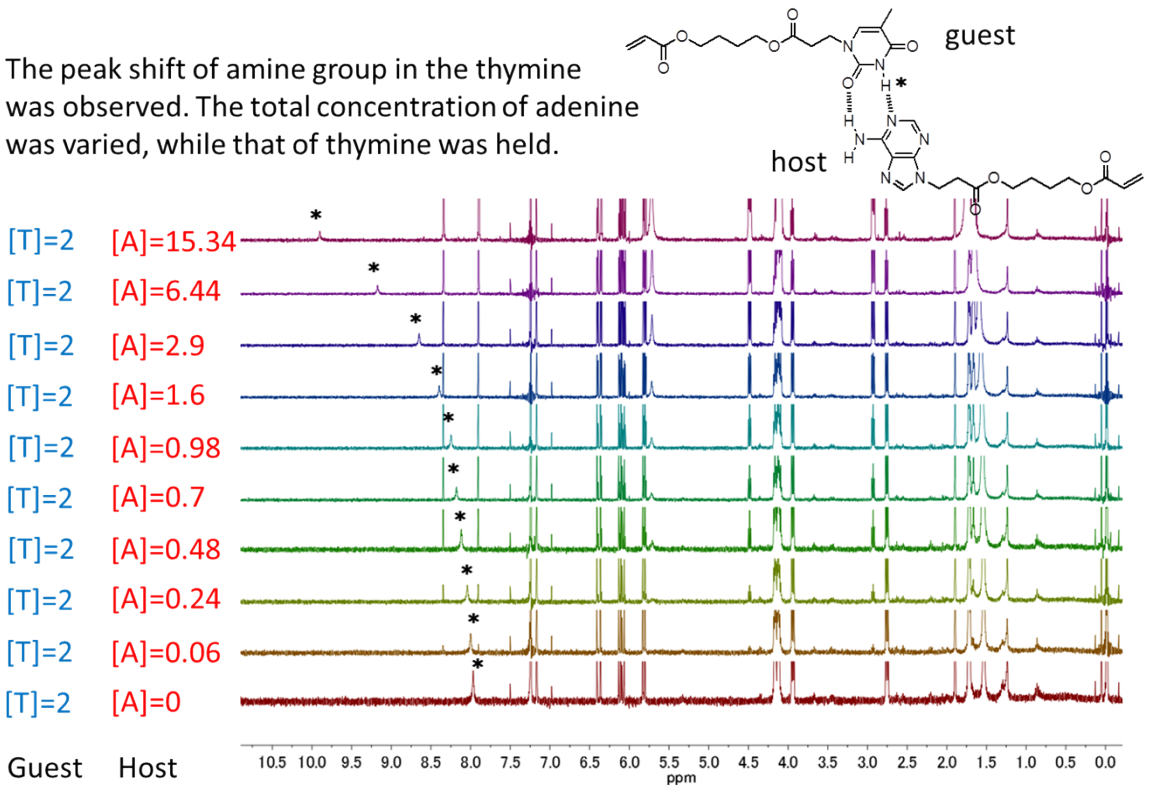

Figure S6. [1]H NMR spectrum overlay of titration experiment with constant ThA concentration of 2 M and increasing AdA concentration from 0 M to 15.34 M.

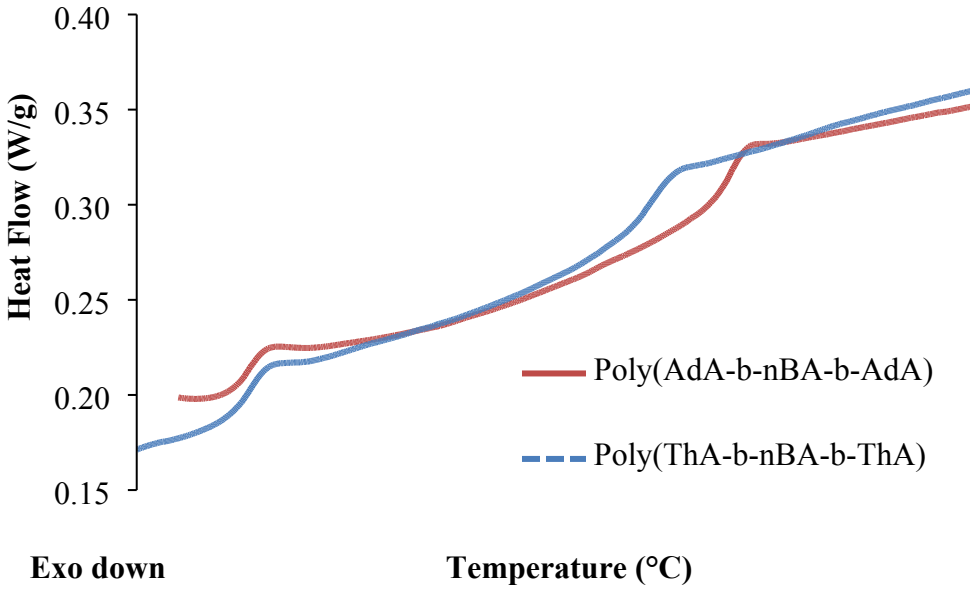

Figure S7. DSC 2nd heat of poly(ThA-*b*-*n*BA-*b*-ThA) and poly(AdA-*b*-*n*BA-*b*-AdA).

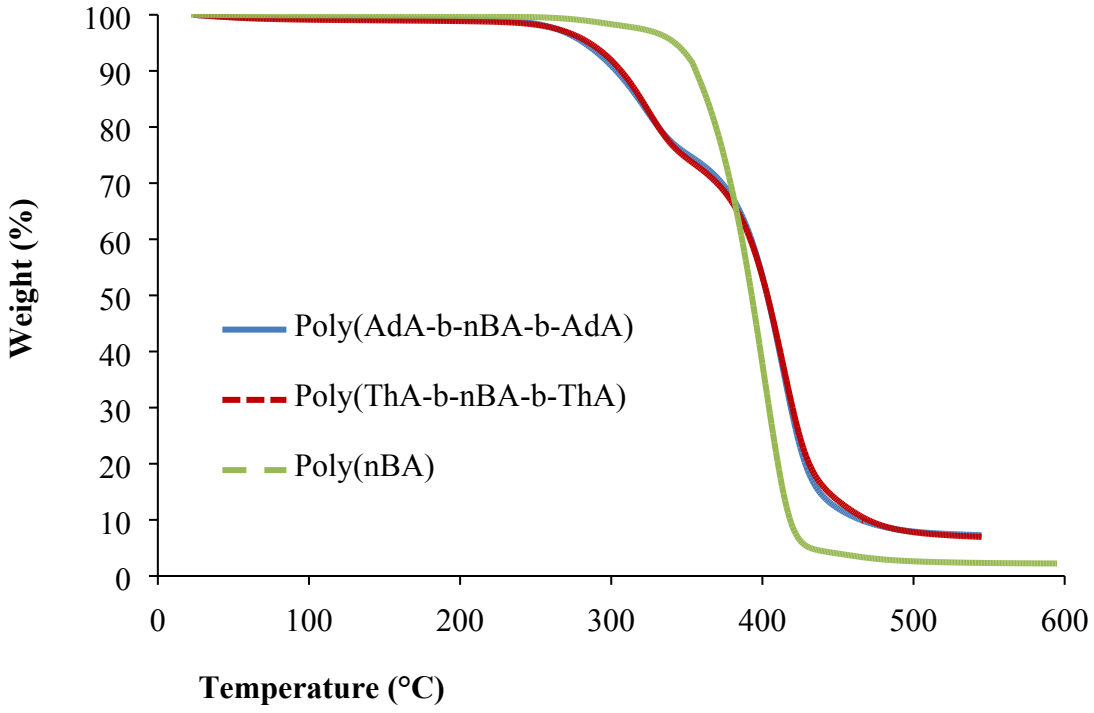

Figure S8. TGA traces of poly(ThA-*b*-*n*BA-*b*-ThA), poly(AdA-*b*-*n*BA-*b*-AdA), and poly(*n*BA).

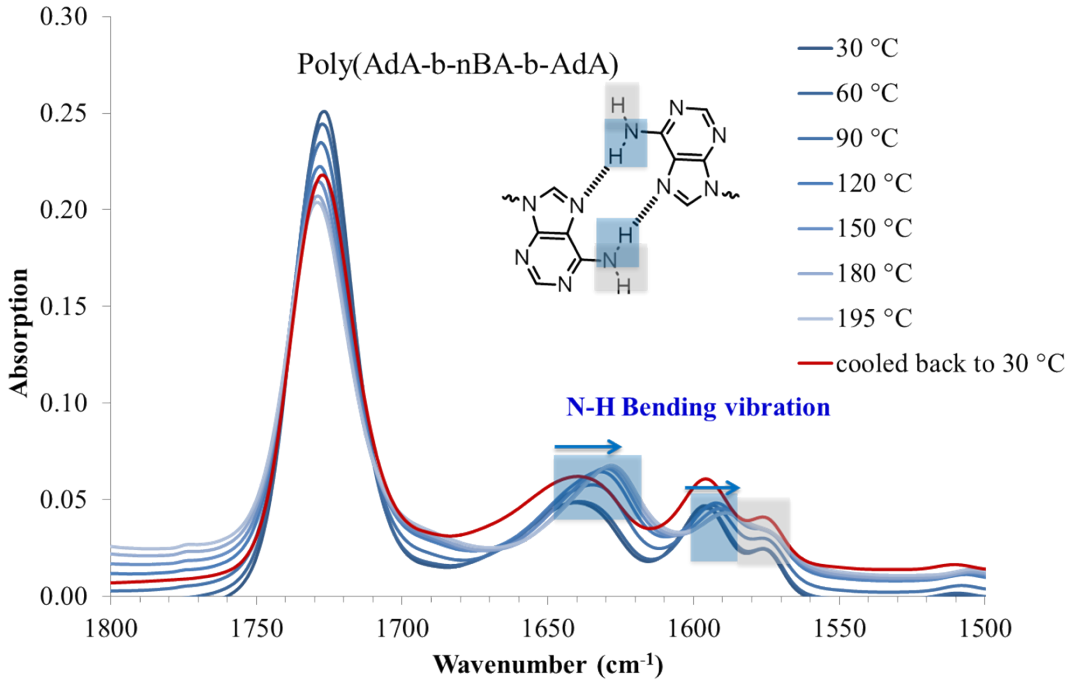

Figure S9. Variable temperature FT-IR spectra in the 1500-1800 cm^{-1} region of poly(AdA-*b*-*n*BA-*b*-AdA).

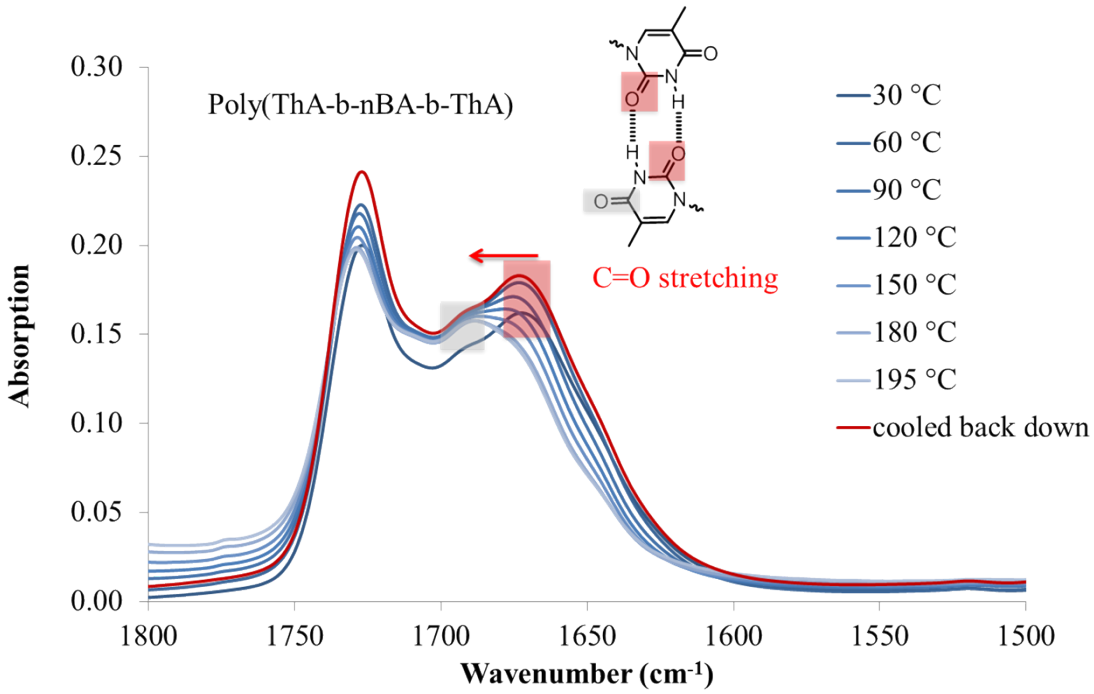

Figure S10. Variable temperature FT-IR spectra in the 1500-1800 cm^{-1} region of poly(ThA-*b*-*n*BA-*b*-ThA).

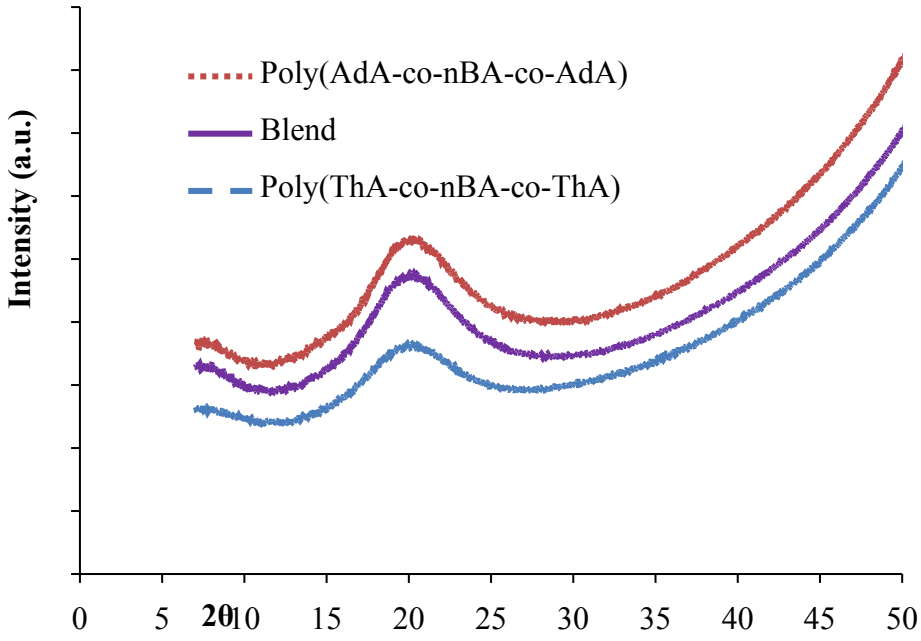

Figure S11. WAXD of solution-cast nucleobase-functionalized triblock copolymers and their blend. For clarity, data were shifted vertically by arbitrary factors.