Supplementary Information (SI) for Chemical Science.
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Supporting Information for

Ultra-High Molecular Weight Polymer Synthesis via Aqueous Dispersion Polymerization

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Supporting Information:

Materials and Instrumentation

Materials

All chemicals were used as received unless otherwise noted. 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid (DDMAT) was synthesized according to previous literature.[1] *N*-Acryloylmorpholine (NAM, Sigma Aldrich, 97%), *N,N*-dimethylacrylamide (DMA, TCI Chemicals, 99%), and 1,4-dioxane (Fischer Chemical, 99%) were passed through a plug of basic alumina prior to use. Ammonium sulfate ($(NH_4)_2SO_4$, 99%) was purchased from EDM Chemicals, Inc. Water (HPLC Grade) was purchased from Fischer Chemical. *N,N*-Dimethylformamide (DMF, 99.8+%) was obtained from Thermo Scientific.

Instrumentation

NMR Spectroscopy. ^{1}H NMR spectra were recorded using a 400 MHz Bruker spectrometer. Deuterated chloroform ($CDCl_3$) and deuterium oxide (D_2O) were used as solvents. Chemical shifts (δ) are reported in ppm and the residual solvent signal served as a reference. Monomer conversion was determined using ^{1}H NMR spectroscopy performed on a Magritek Spinsolve Ultra 60 MHz benchtop spectrometer using *N,N*-dimethylformamide as an internal standard.

Size Exclusion Chromatography (SEC). Experiments were performed in *N,N*-dimethylacetamide (DMAc) with 50 mM LiCl at 50 °C at a flow rate of 1.0 mL/min (Agilent Infinity II isocratic pump, degasser, and autosampler). A ViscoGel I-series 5 µm guard column, Malvern I-MBLMW, and IMBHMW 3078 columns with an exclusion limit of 20,000 g/mol and 1.0×10^7 g/mol, respectively, were used. A refractive index detector (Wyatt Optilab T-rEX) operating at 658 nm and a light scattering detector (Wyatt miniDAWN Treos) operating at 659 nm were used. Molecular weights and dispersities were calculated with Wyatt ASTRA software using multi-angler laser light scattering data. Polymer samples were dehydrated via lyophilization and dissolved in SEC solvent at a concentration of < 3 mg/mL.

Dynamic Light Scattering (DLS). DLS was performed with a non-invasive backscatter system (Malvern Zetasizer Nano ZS) with a measuring angle at 173˚ and adjustable focus. DLS of samples was performed at 25˚C and 0.1% w/w of particles diluted with 0.5 M $(NH_4)_2SO_4$. The size distributions reported were averaged over three runs.

Transmission Electron Microscopy (TEM). TEM was performed using a Thermo Scientific Talos L120C G2 (S)TEM operating at an accelerating voltage of 120 kV. Digital images were acquired with a 4K × 4K Thermo Scientific Ceta CMOS camera and Digital Micrograph 1.93 image acquisition software (Gatan Inc., Pleasanton, CA, USA.). Samples were prepared on Electron Microscopy Sciences Formvar Carbon Film on 400 mesh nickel grids (FCF400- Ni). 6 µL of polymer particle solution (1.0 mg/mL in 0.5 M $(NH_4)_2SO_4$) was spotted on the grid for 30 s. Afterwards, solvent was wicked off with filter paper.

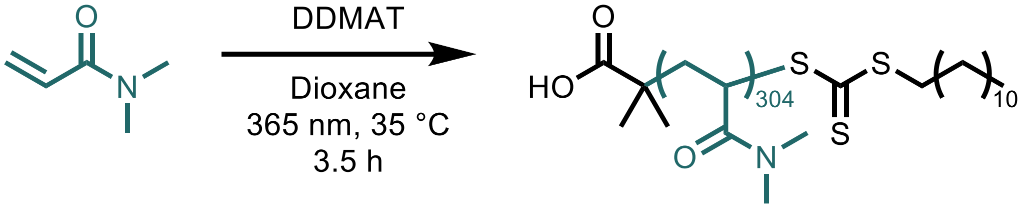
Visible Light Microscopy (VLM). VLM was performed using a Zeiss Axio Imager M2 Microscope (Carl Zeiss Microscopy LLC, White Plains, NY, USA) and visualized using Zen microscopy software (Carl Zeiss Microscopy). A drop of 0.1% w/w solution of polymer particles was placed on a glass microscope slide and lightly compressed under a thin glass slide cover prior to imaging.

Ultraviolet Light Set-Up. Photoiniferter polymerizations were stirred while being irradiated with ultraviolet light (365 nm, 3.5 mW/cm^2) from a MelodySusie nail lamp purchased from Amazon. While powered on, the lamps heated to approximately 35 °C.

Oscillatory Rheology. Viscosity measurements on native polymer particle dispersions and diluted polymer solutions were performed on a Discovery HR-2 rheometer (TA Instruments) using a 40 mm cone geometry held at a 50 µm gap. Care was taken to avoid forming and trapping bubbles beneath the geometry and water was added to the solvent trap to avoid dehydration during measurement.

Experimental Procedures

Synthesis of PDMA macroiniferters



A typical protocol for the photoiniferter polymerization of poly(*N,N*-dimethylacrylamide) (PDMA) MI_{30k} was as follows. DMA (10 g, 100.9 mmol, 400 equiv) and DDMAT (92.0 mg, 0.252 mmol, 1 equiv) were dissolved in 1,4-dioxane (24.75 mL). DMF (0.25 mL) was used as an internal standard to monitor the consumption of monomer. The solution was transferred to a 25 mL Schlenk flask with a magnetic stir bar and sparged with argon for 1 h. The flask containing the solution was then placed in a UV lamp (365 nm, 3.5 mW/cm^2) on a magnetic stir plate for 3.5 h. The UV lamp warmed to approximately 35 °C while powered on. The reaction was quenched by exposure to air (76% conversion, $M_{n,\mathrm{Theory}}$ = 30.5 kg/mol, $M_{n,\mathrm{SEC}}$ = 38.8 kg/mol, $Đ$ = 1.02). The PDMA product was then purified by precipitating the reaction solution into cold hexanes and centrifuging to yield a yellow solid. After redissolving the polymer in minimal acetone, it was precipitated into cold hexanes two more times. After the final precipitation, the PDMA was dissolved in water and lyophilized to yield the polymer product as a yellow solid.

Table S1: Molecular weight and dispersity data for macroiniferters.

Macroiniferter	$M_{n,\mathrm{Theory}}$[a] (kg/mol)	$M_{n,\mathrm{SEC}}$[b] (kg/mol)	$Đ$[b]
MI_{30k}	30.5	38.8	1.02
MI_{80k}	81.4	80.7	1.05
MI_{120k}	124.1	120.5	1.07

[a] Determined via ^{1}H NMR spectroscopy

[b] Determined by SEC equipped with a multiangle light-scattering detector.

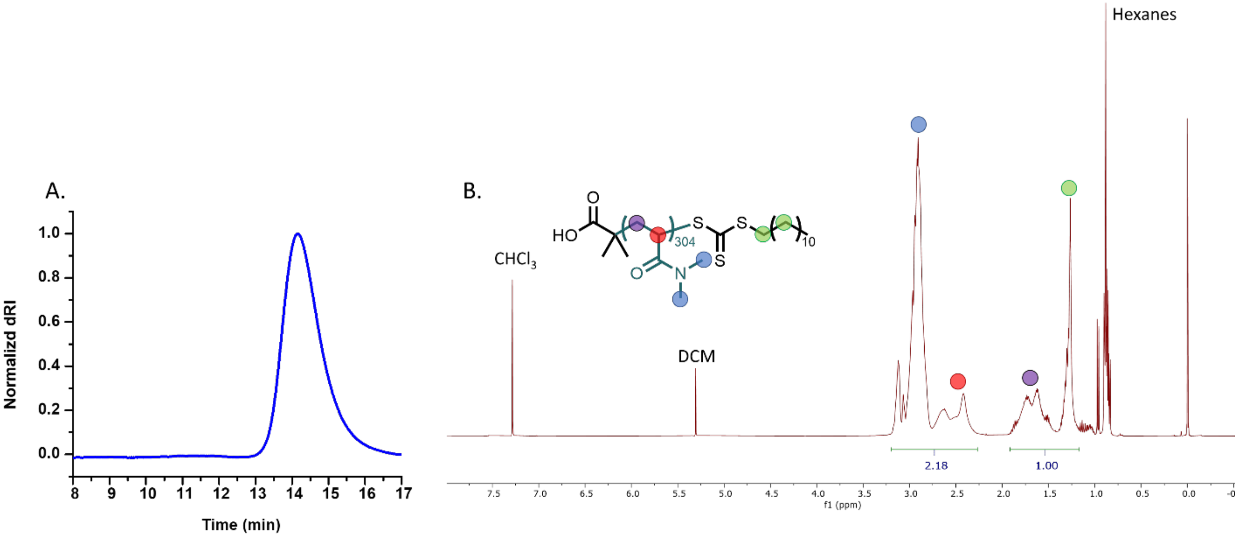


Figure S1. (A) Size-exclusion chromatogram of MI_{30k} and (B) ^{1}H NMR spectrum of MI_{30k} in $CDCl_3$.

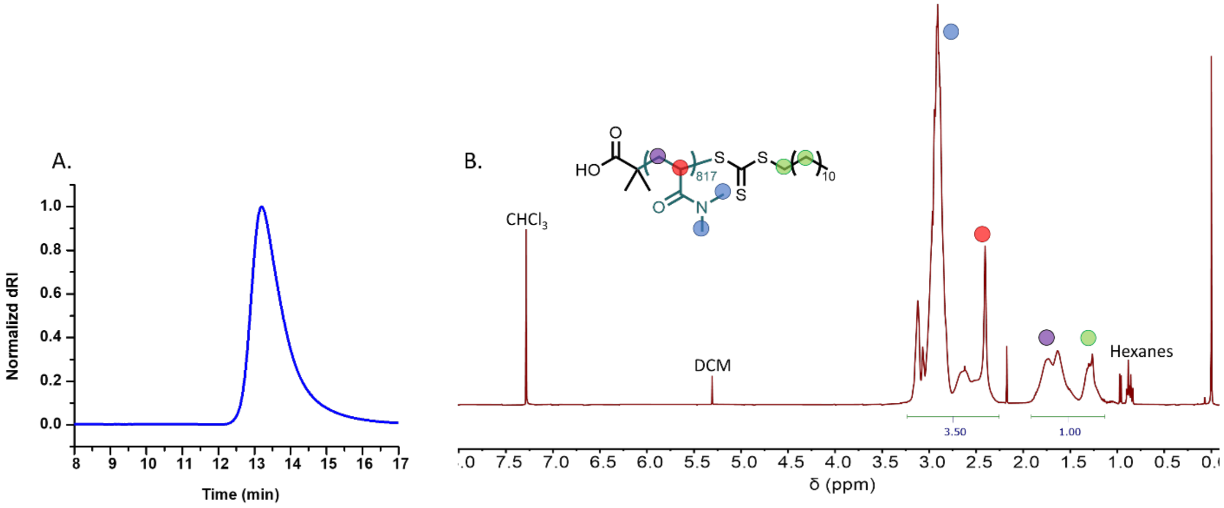


Figure S2. (A) Size-exclusion chromatogram of MI$_{80k}$ and (B) ^{1}H NMR spectrum of MI$_{80k}$ in CDCl$_3$.

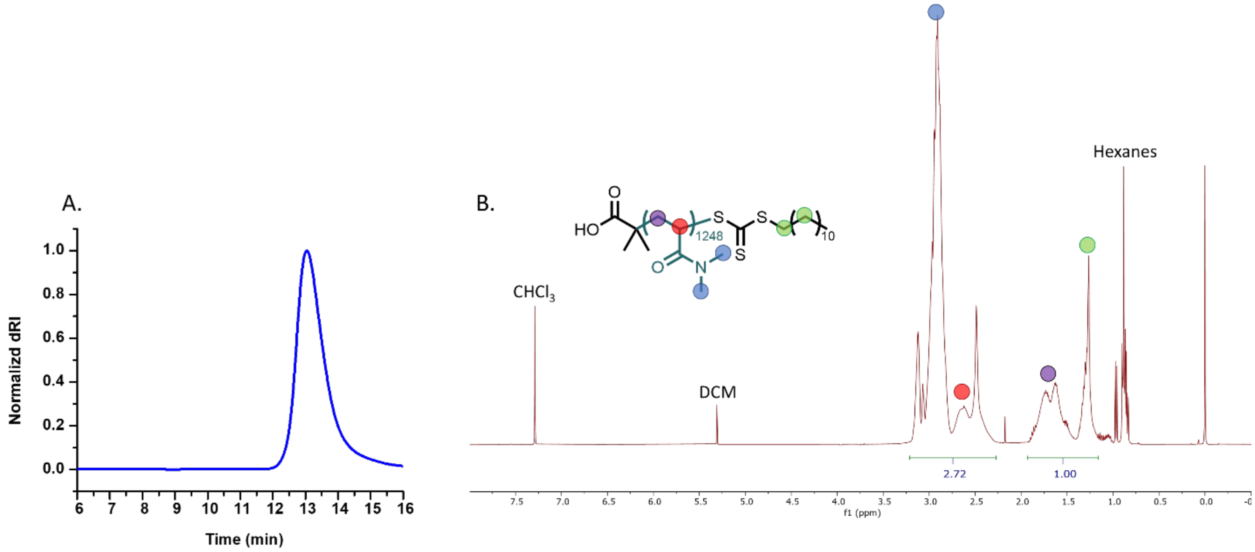
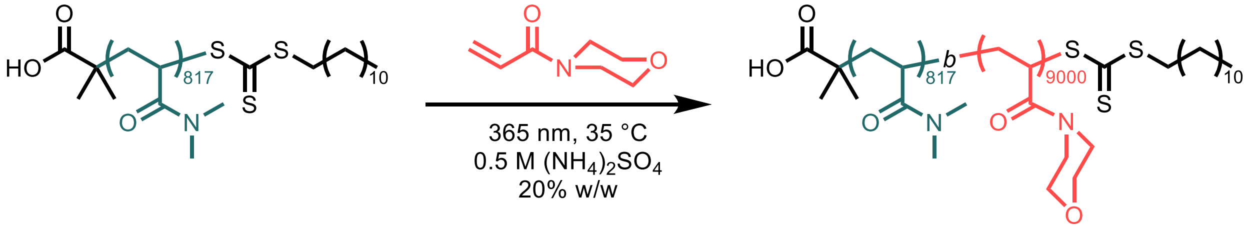


Figure S3. (A) Size-exclusion chromatogram of MI$_{120k}$ and (B) ^{1}H NMR spectrum of MI$_{120k}$ in CDCl$_3$.

Photoiniferter PISA of NAM with PDMA macroiniferters



A typical protocol for the photoiniferter PISA reaction was as follows. NAM (1000 mg, 0.819 mL, 7.08 mmol, 9000 equiv) and MI_{80k} (64.1 mg, 0.000787 mmol, 1 equiv) were dissolved in 4.1 mL of 0.5 M $(NH_4)_2SO_4$. DMF (0.15 mL) was used as an internal standard to monitor consumption of monomer. This solution was added to a scintillation vial with a magnetic stir bar, sealed with a rubber septum, and sparged with argon for 20 min. The vial containing the solution was then placed in a UV lamp (365 nm, 3.5 mW/cm^2) on a magnetic stir plate for 10 h. The UV lamp warmed to 35 °C while powered on. The reaction was quenched by exposure to air (>99% conversion, $M_{n,\text{Theory}}$ = 1350 kg/mol, $M_{n,\text{SEC}}$ = 1760 kg/mol, $Đ$ = 1.19). Particle solutions were used without purification for subsequent characterization.

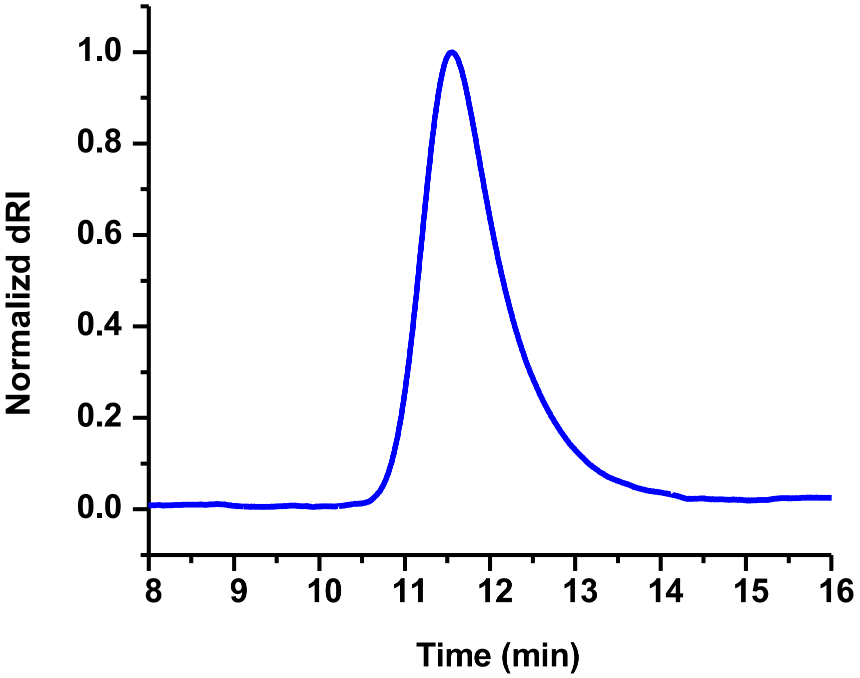


Figure S4. Size-exclusion chromatogram of $PDMA_{304}$-*b*-$PNAM_{9000}$.

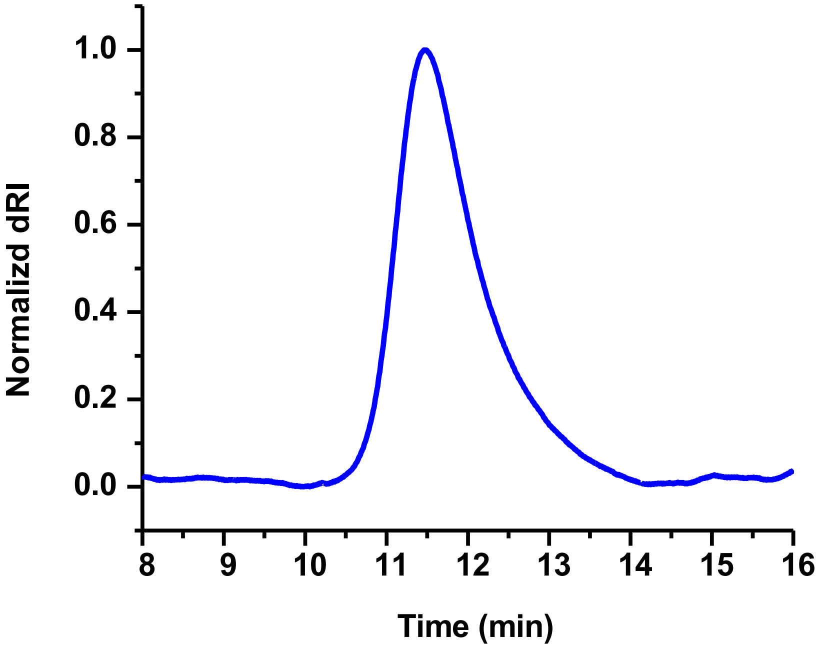


Figure S5. Size-exclusion chromatogram of $PDMA_{304}$-*b*-$PNAM_{12000}$.

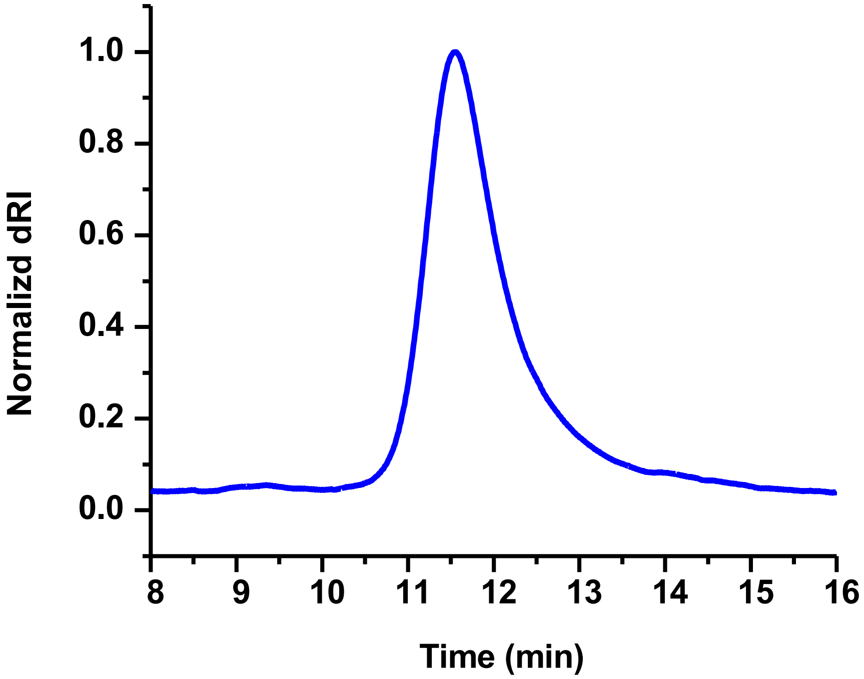


Figure S6. Size-exclusion chromatogram of $PDMA_{304}$-*b*-$PNAM_{9000}$ made without $(NH_4)SO_4$ as a control.

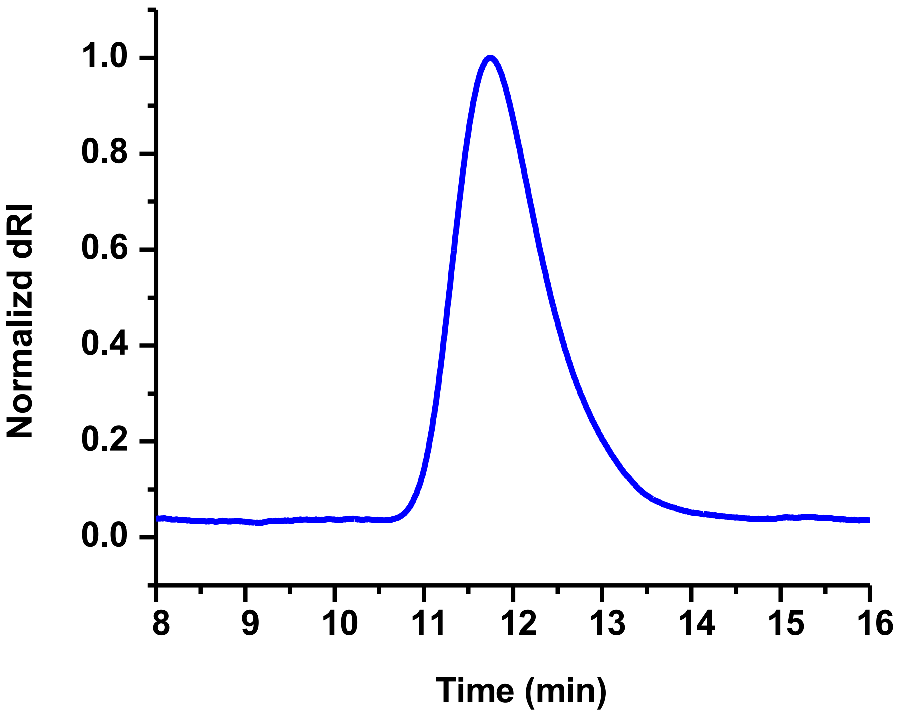


Figure S7. Size-exclusion chromatogram of PDMA$_{817}$-*b*-PNAM$_{9000}$.

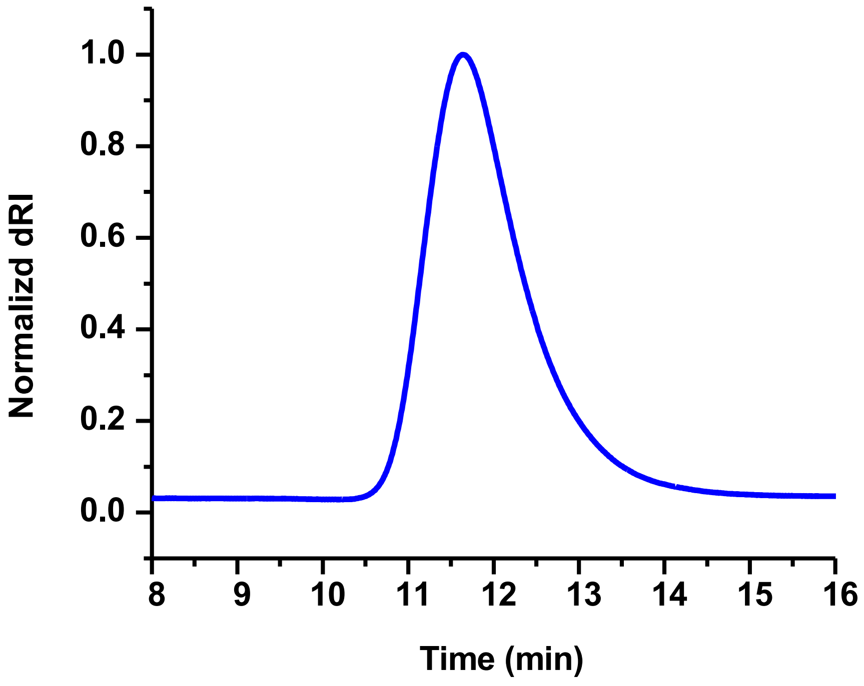


Figure S8. Size-exclusion chromatogram of PDMA$_{817}$-*b*-PNAM$_{12000}$.

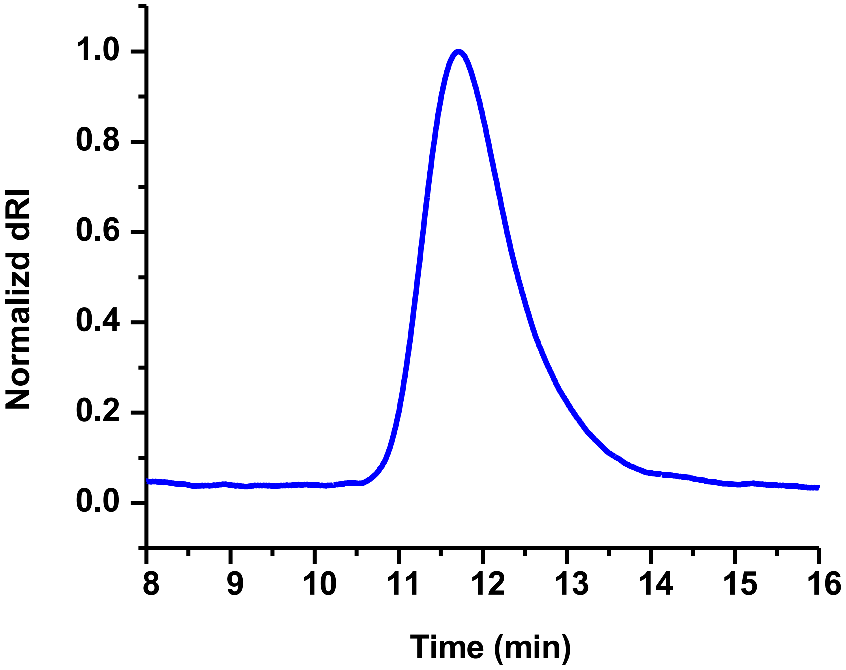


Figure S9. Size-exclusion chromatogram of PDMA$_{817}$-*b*-PNAM$_{14000}$.

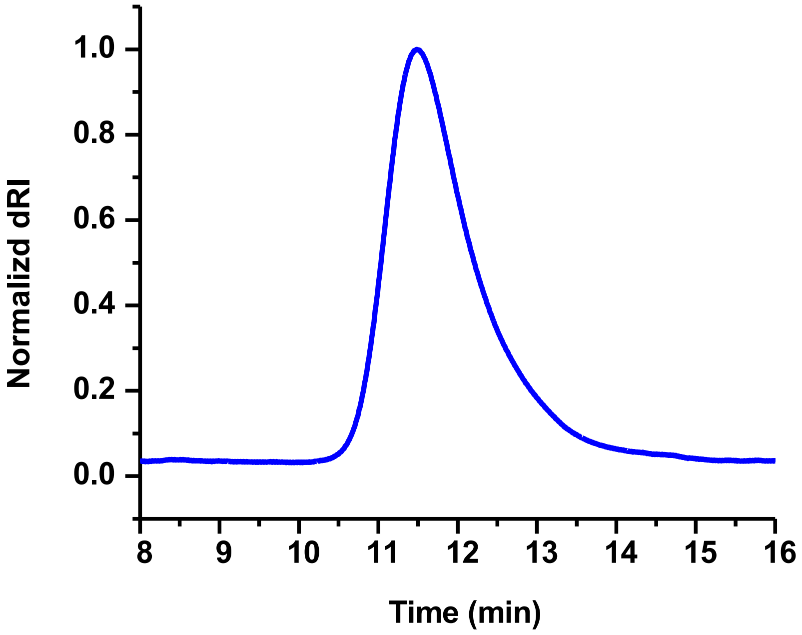


Figure S10. Size-exclusion chromatogram of PDMA$_{817}$-*b*-PNAM$_{16000}$.

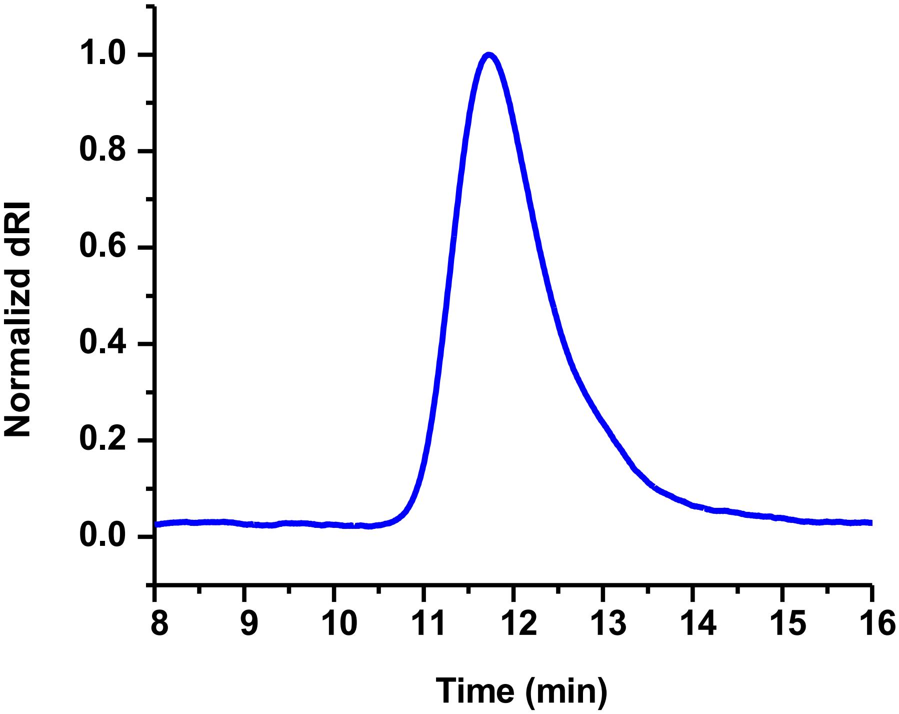


Figure S11. Size-exclusion chromatogram of $PDMA_{1248}$-*b*-$PNAM_{9000}$.

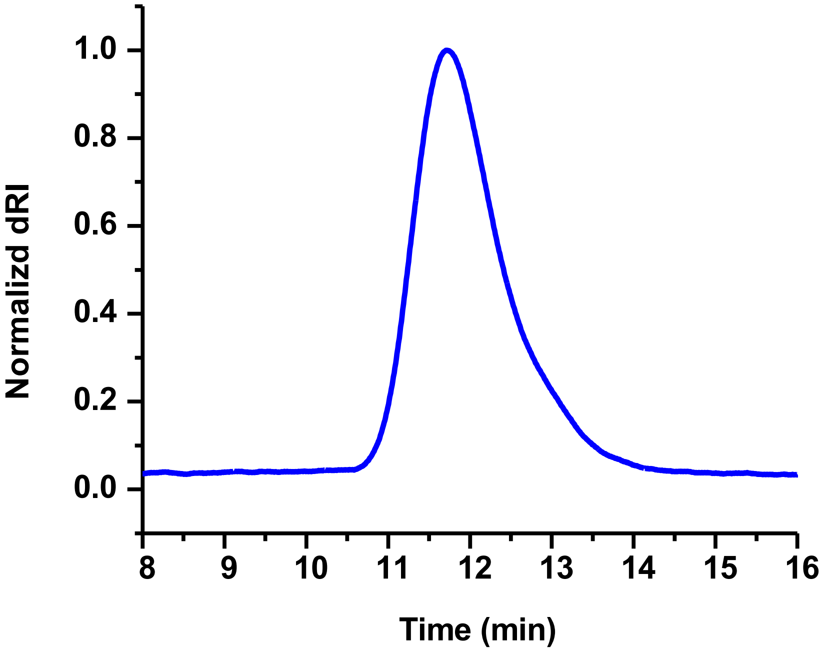


Figure S12. Size-exclusion chromatogram of $PDMA_{1248}$-*b*-$PNAM_{12000}$.

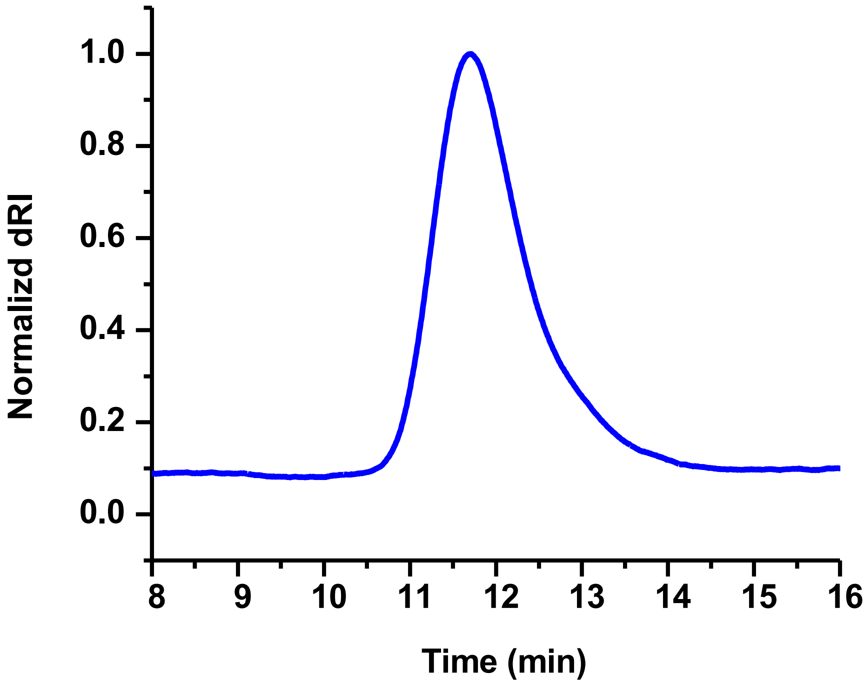


Figure S13. Size-exclusion chromatogram of PDMA$_{1248}$-*b*-PNAM$_{14000}$.

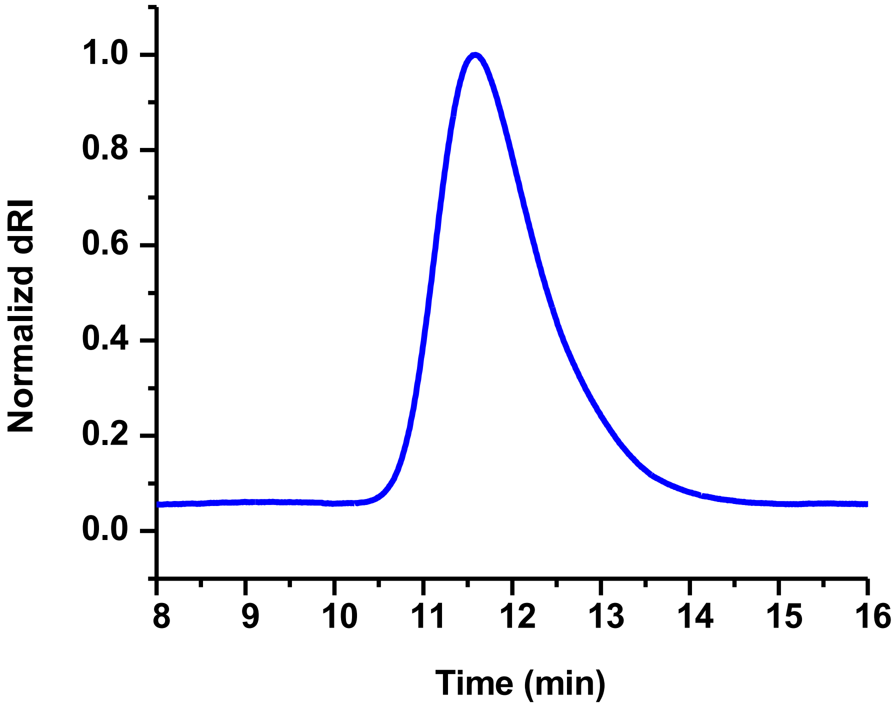


Figure S14. Size-exclusion chromatogram of PDMA$_{1248}$-*b*-PNAM$_{16000}$.

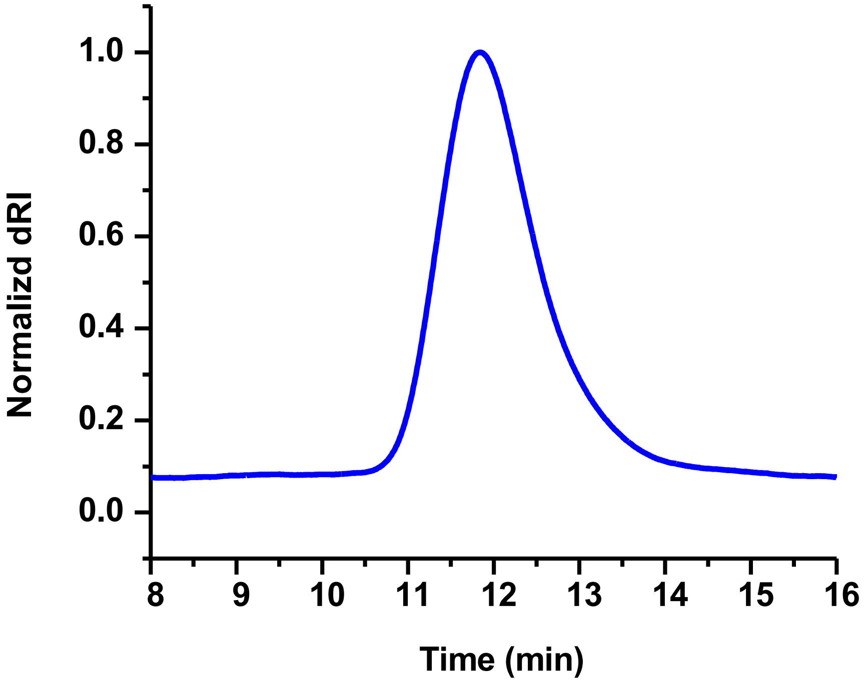


Figure S15. Size-exclusion chromatogram of PDMA$_{1248}$-*b*-PNAM$_{18000}$.

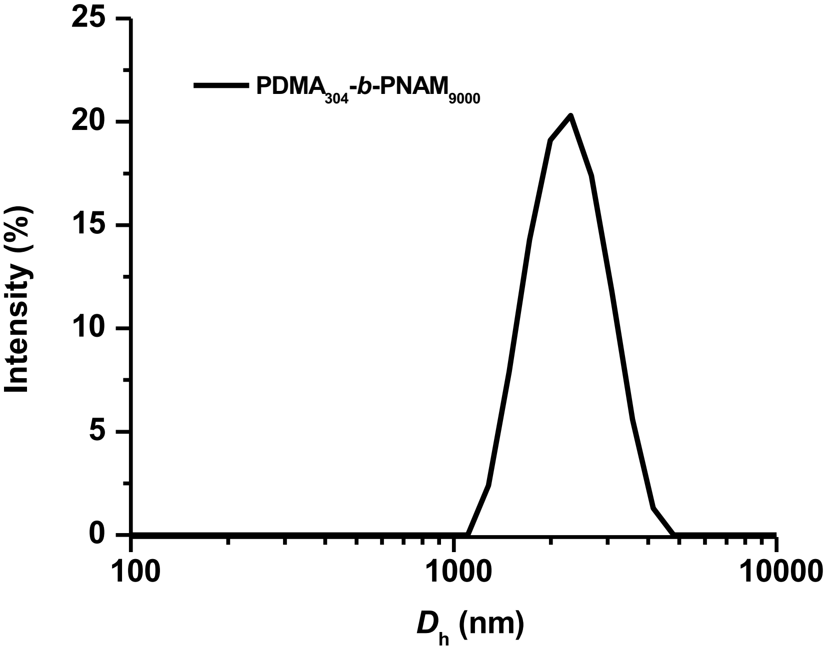


Figure S16. Dynamic light scattering (DLS) trace of PDMA$_{304}$-*b*-PNAM$_{9000}$.

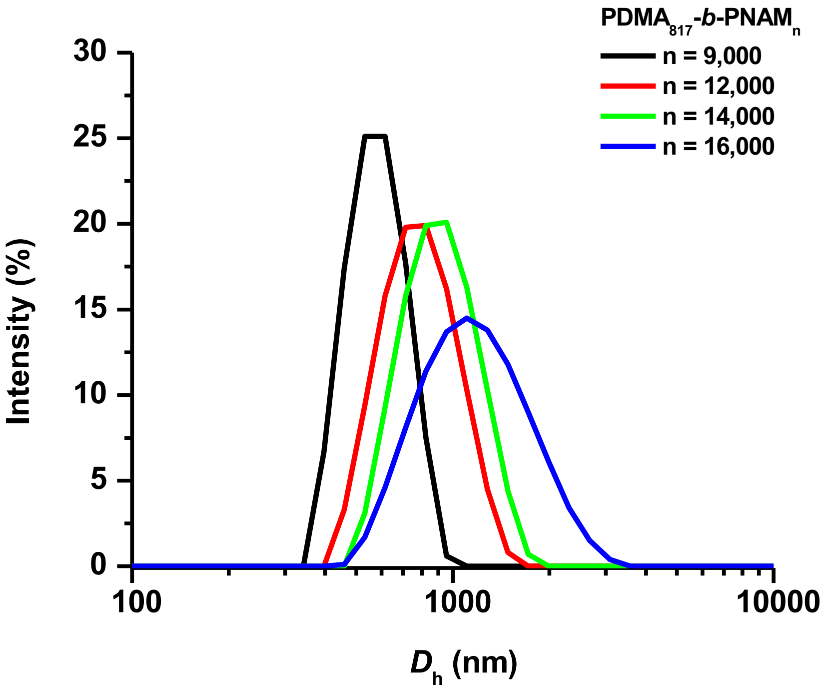


Figure S17. DLS traces of PDMA$_{817}$-*b*-PNAM$_n$, where n = 9,000 (black), 12,000 (red), 14,000 (green), and 16,000 (blue).

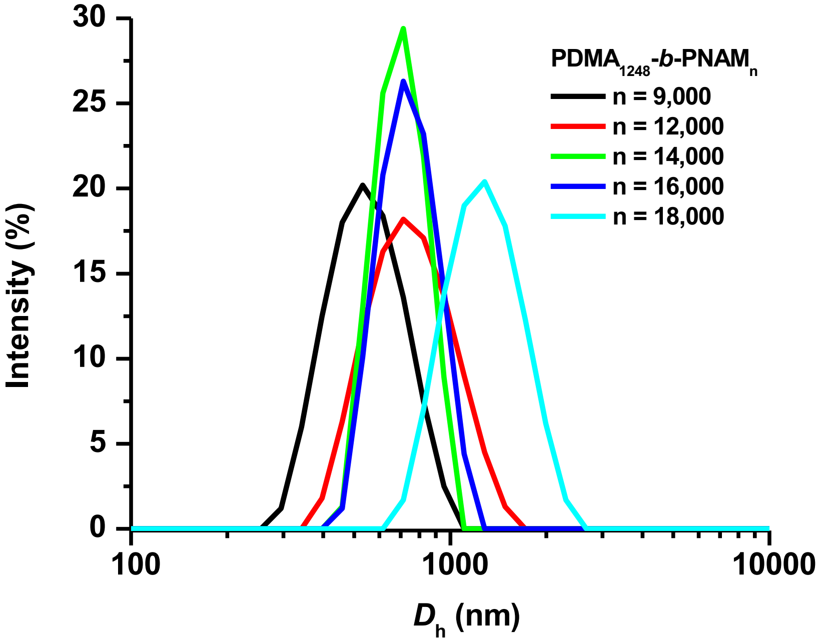


Figure S18. DLS traces of PDMA$_{1248}$-*b*-PNAM$_n$, where n = 9,000 (black), 12,000 (red), 14,000 (green), 16,000 (blue), and 18,000 (teal).

References

1. John T. Lai, Debby Filla, Ronald Shea. Functional polymers from novel carboxyl-terminated trithiocarbonates as highly efficient RAFT agents. *Macromolecules* 2002, **35**, 6754-6756.