

Electronic Supplementary Information

Complex Thermoresponsive Behavior of Diblock Polyacrylamides

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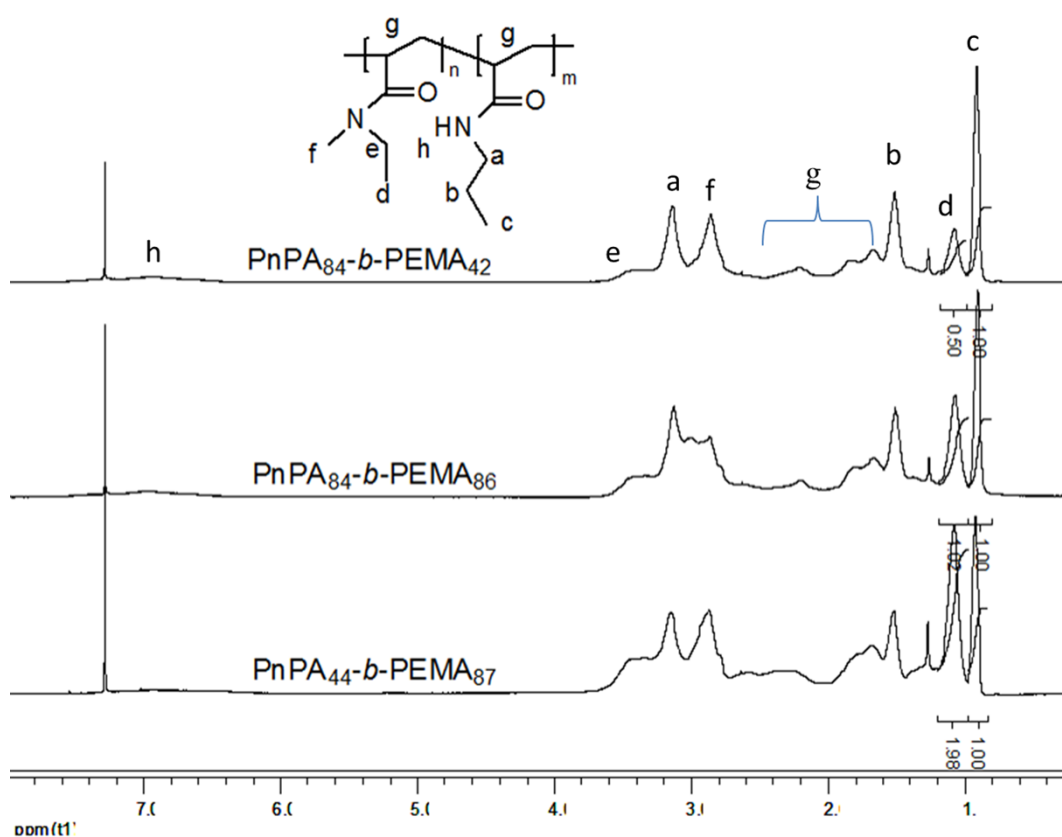


Fig. S1 ¹H NMR spectra of PnPA-*b*-PEMA in CDCl₃ and the integrations of the related peaks.

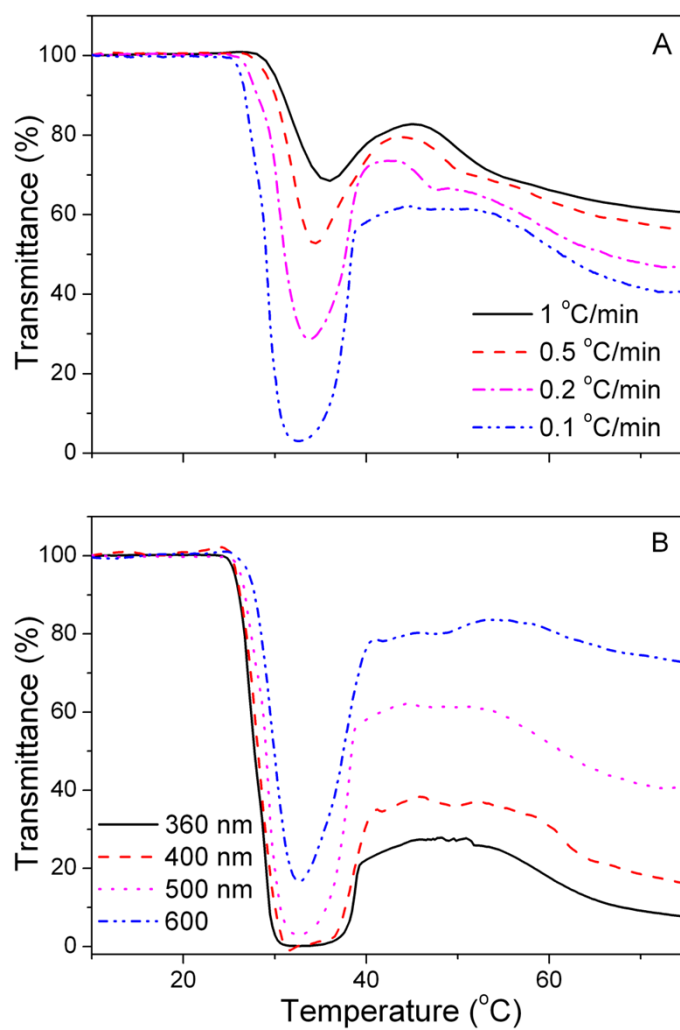


Fig. S2 Transmittance versus temperature plots of aqueous solution of PnPA₈₄-*b*-PEMA₄₂ (5 g/L) (A) at different heating rates observed at a wavelength of 500 nm, and (B) at a heating rate of 0.1 °C/min observed at different wavelengths.

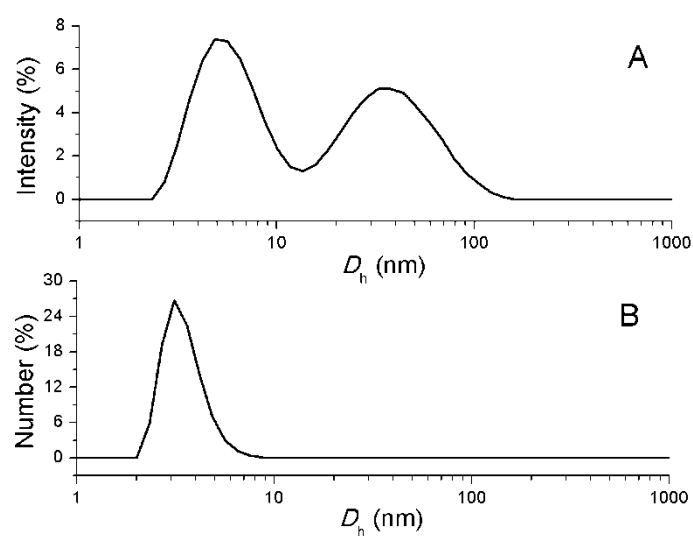


Fig. S3 (A) Intensity-average and (B) number-average size distributions of PnPA₈₄-*b*-PEMA₄₂ (5 g/L at 20 °C).

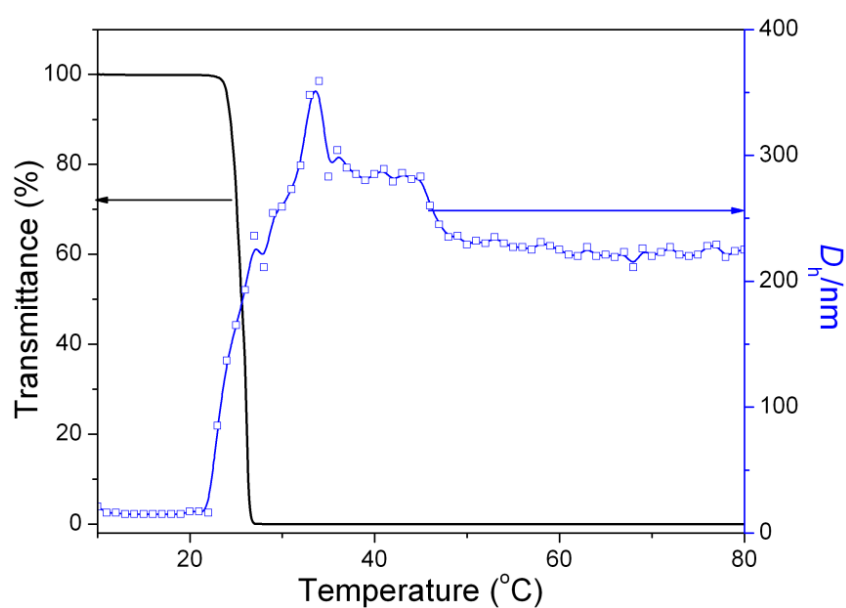


Fig. S4 Comparison of intensity-average size distribution (D_h) and transmittance of PnPA₈₄-*b*-PEMA₄₂ as a function of temperature at concentrations of 10 g/L

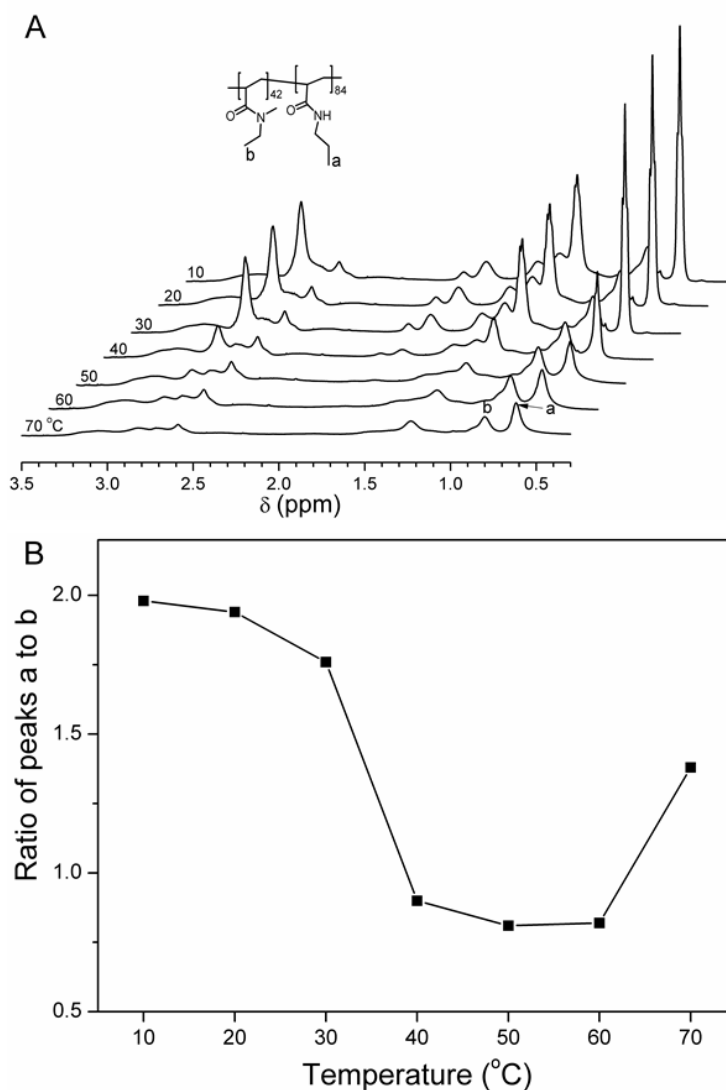


Fig. S5 (A) ^1H NMR spectra of $\text{PnPA}_{84}\text{-}b\text{-PEMA}_{42}$ recorded at different temperatures in D_2O . (B) The integration ratio of peaks *a* to *b* in the spectra as a function of temperature. The spectra were taken for each 10 °C interval equilibrated for 10 min. At low temperatures the peak ratio of *a/b* is similar to that obtained in CDCl_3 (1.98), indicating both blocks of the polymer are soluble in D_2O and the polymer exist as unimers. At 30 °C, the peaks of the PnPA block start to broaden and the peak ratio of *a/b* (1.75) begins to decrease sharply from 1.76 to 0.90, indicating the collapse of PnPA block and the loose clusters may be formed. Further dehydration of the PnPA block occurs in the temperature range of 30-40 °C. The peak ratio *a/b* remains stable afterward until about 70 °C, when peaks *a* and *b* both show reduced intensity due to the collapse of the PEMA block, leading to a higher peak ratio of *a/b* (1.38).

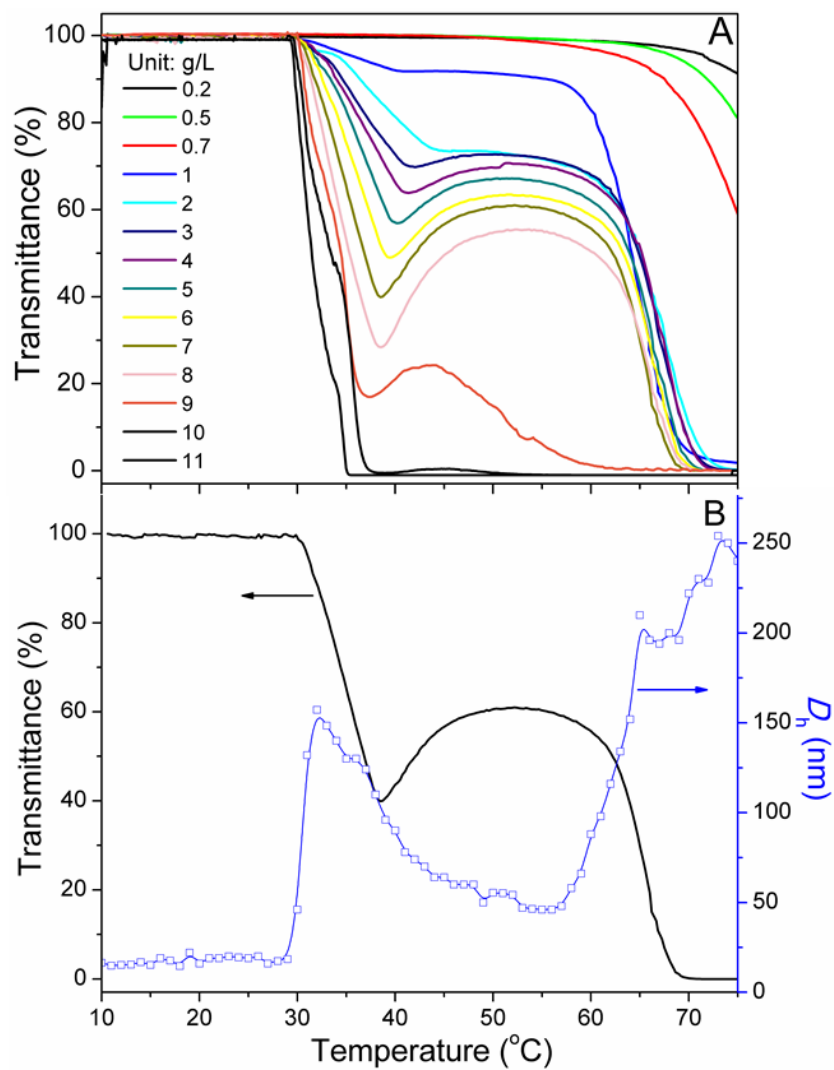


Fig. S6 Transmittance of aqueous solutions of PnPA₄₄-*b*-PEMA₈₇ as a function of temperature observed at 500 nm with a heating rate of 0.1 °C/min. (A) at different concentrations, (B) comparison of hydrodynamic diameters (D_h) and transmittance of PnPA₄₄-*b*-PEMA₈₇ in water (7 g/L) as a function of temperature.

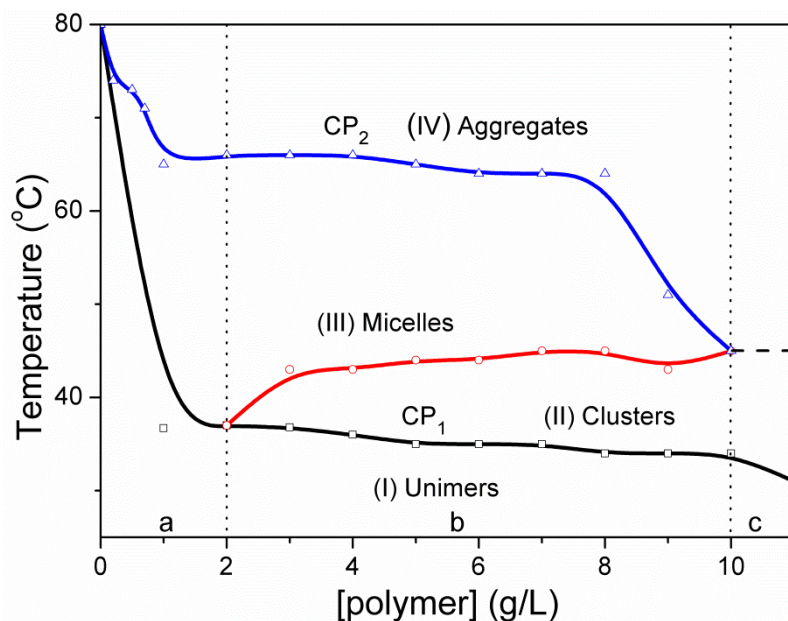


Fig. S7 Concentration-temperature phase diagram of PnPA₄₄-*b*-PEMA₈₇. Low concentration range a: The unimers change to micelles and then to aggregates; Medium concentration range b: The unimers transform into micelles, then clusters and finally aggregates; High concentration range c: The unimers transform into clusters and into aggregates with increasing temperature. The concentration and temperature scales are approximate and serve as a general trend.

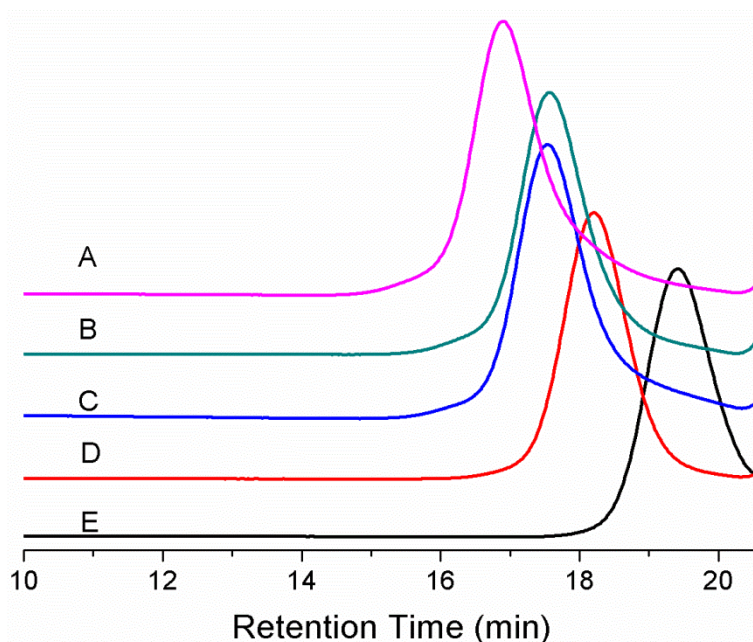


Fig. S8 SEC traces of block copolymers and homopolymer (A) PnPA₈₄-*b*-PEMA₈₆ (B) PnPA₈₄-*b*-PEMA₄₂ (C) PnPA₄₄-*b*-PEMA₈₇ (D) PnPA₈₄ (E) PnPA₄₄. DMF was used as the mobile phase with a flow rate of 1.0 mL/min at 50 °C and with PMMA standards.