Nonionic Star Polymers with Upper Critical Solution Temperature in Aqueous Solutions

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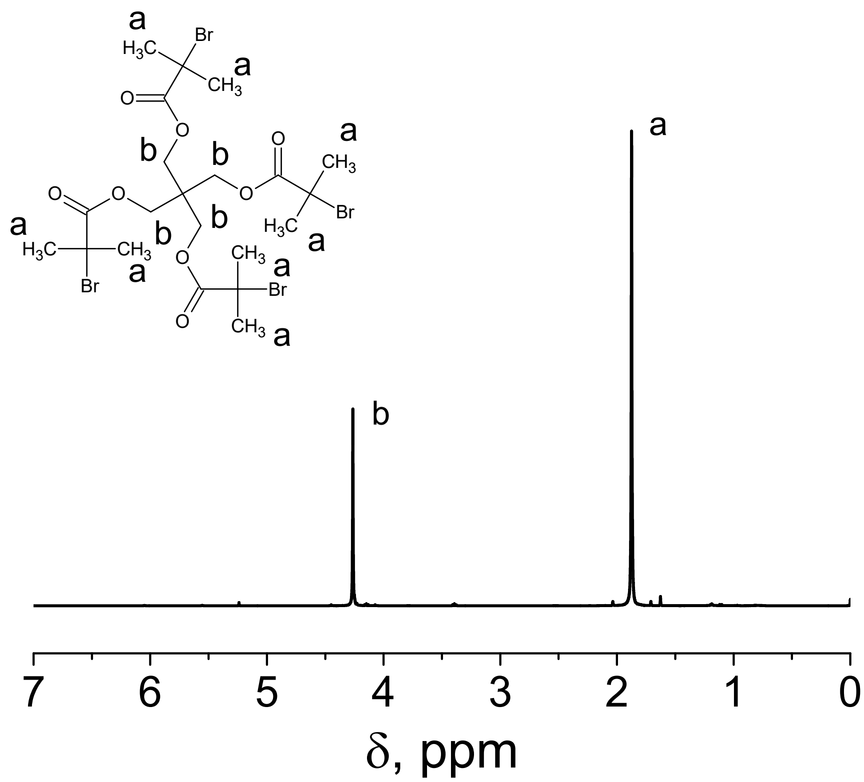

Fig. S1. ^{1}H NMR spectrum of pentaerythritol tetrakis(2-bromoisobutyrate) in $CDCl_3$.

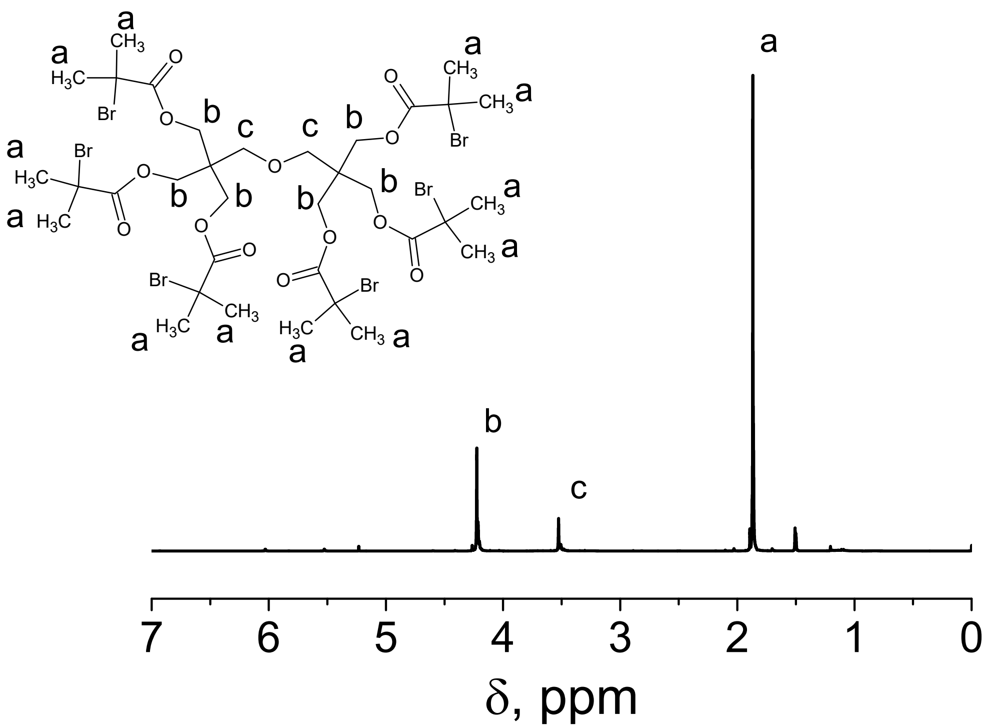

Fig. S2. ^1H NMR spectrum of dipentaerythritol hexakis(2-bromoisobutyrate) in $CDCl_3$.

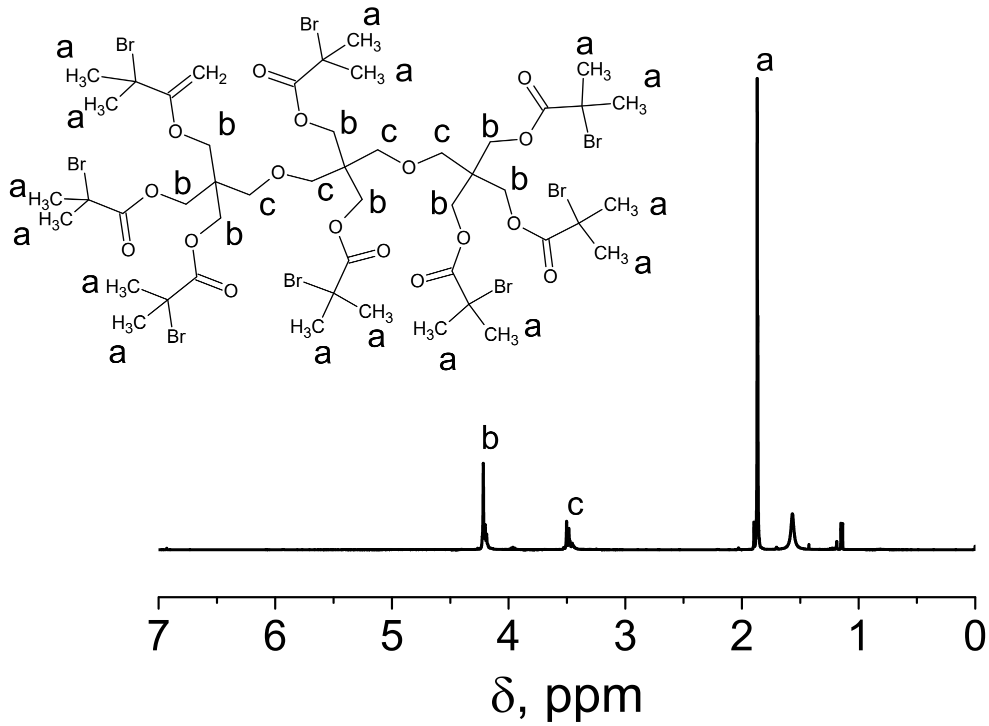

Fig. S3. ^{1}H NMR spectrum of tripentaerythritol octakis(2-bromoisobutyrate) in $CDCl_3$.

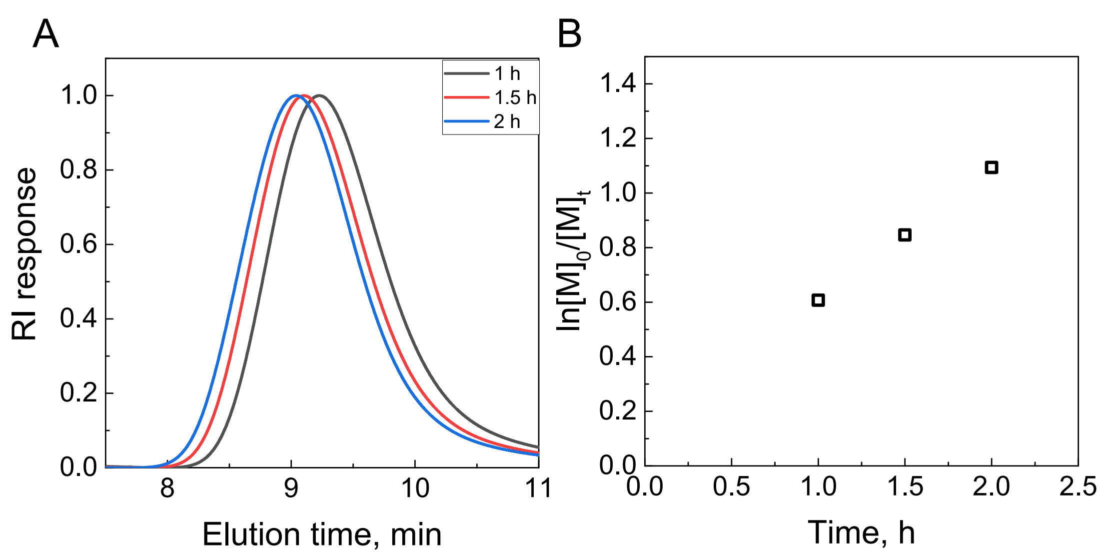

Fig. S4. GPC traces (A) and time evolution of $\ln[M]_0/[M]_t$ (B) during synthesis of linear BOC PAMA via ARGET ATRP polymerization of 2-BOC AMA using a linear ATRP initiator.

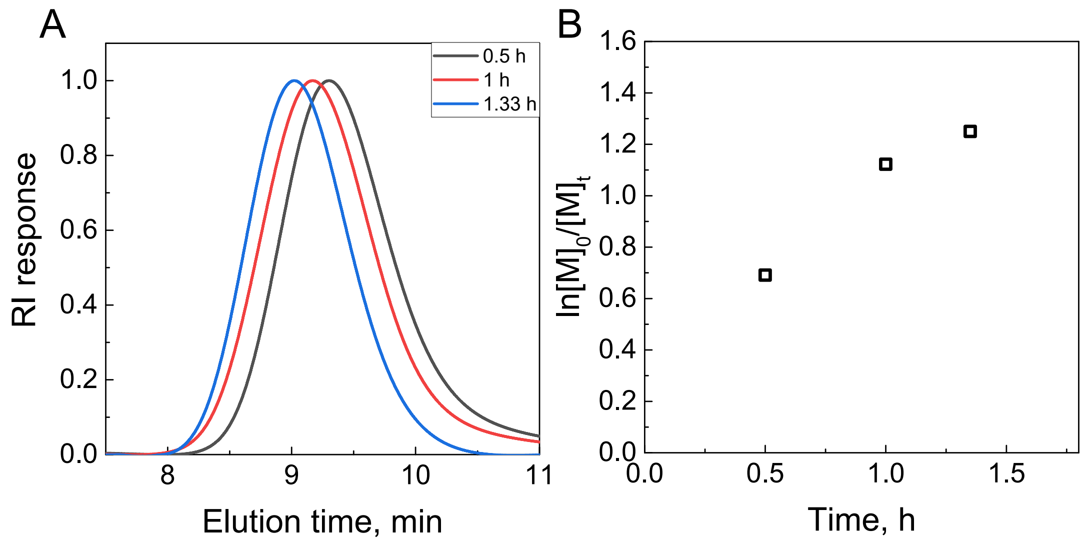

Fig. S5. GPC traces (A) and time evolution of ln$[M]_0/[M]_t$ (B) during synthesis of 6-arm BOC PAMA via ARGET ATRP polymerization of 2-BOC AMA using a 6-arm ATRP initiator.

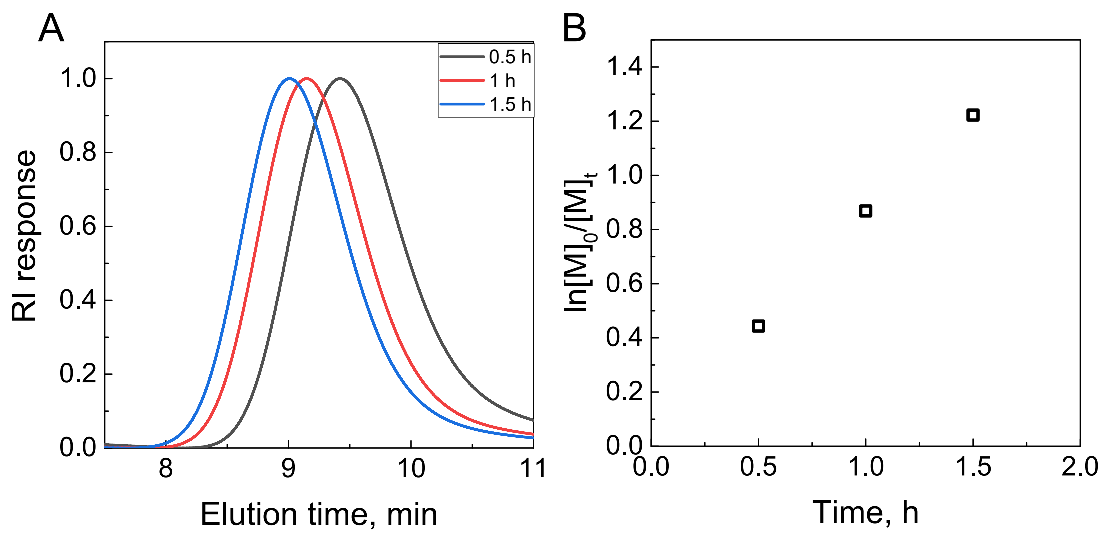

Fig. S6. GPC traces (A) and time evolution of ln$[M]_0/[M]_t$ (B) during synthesis of 8-arm BOC PAMA via ARGET ATRP polymerization of 2-BOC AMA using an 8-arm ATRP initiator.

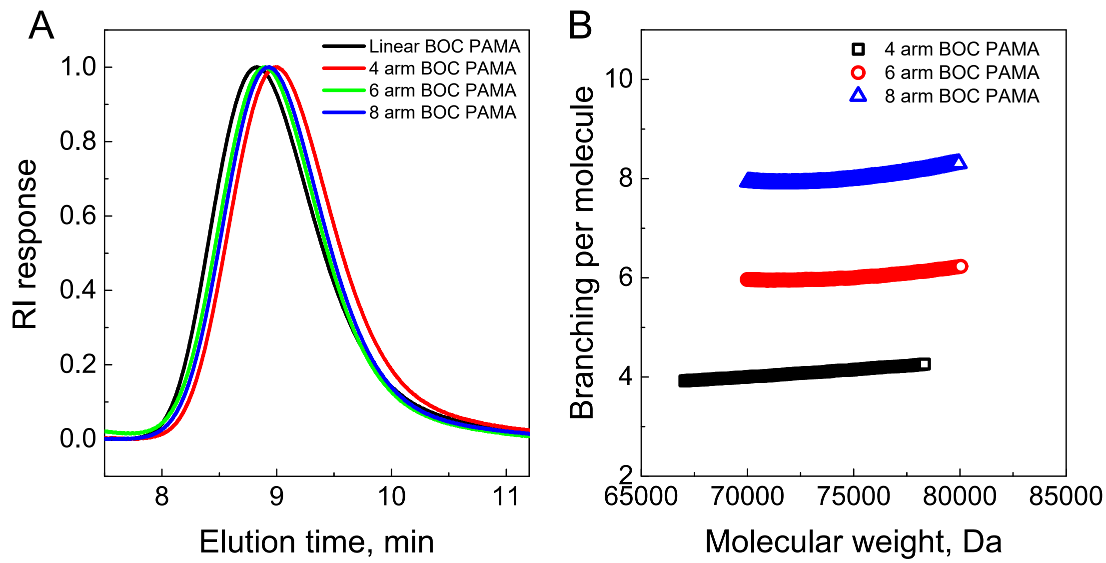

Fig. S7. (A) GPC traces of linear, 4-, 6-, and 8-arm BOC PAMAs in DMF (flow rate 0.2 ml/min) as monitored by a RI detector. (B) Branching per molecule for 4-, 6-, and 8-arm BOC PAMAs based on the viscosity measurements performed using a Wyatt Viscostar III detector.

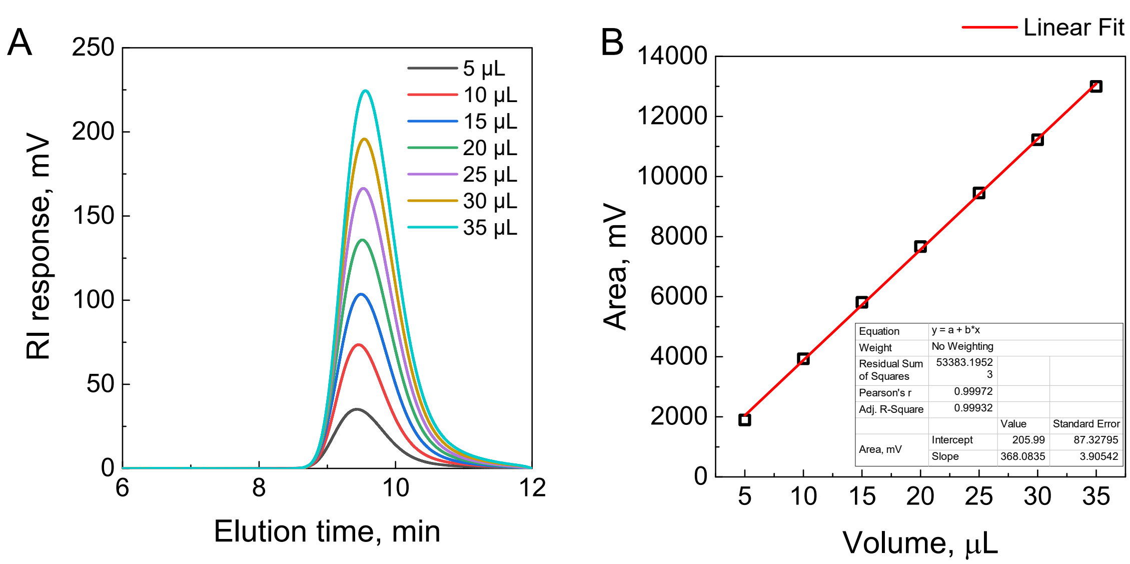

Fig. S8. Calibration of the detector response. (A) GPC traces of polystyrene solutions in DMF (flow rate 0.2 ml/min) with different injection volumes as monitored by a RI detector. (B) RI response as a function of injection volume for polystyrene.

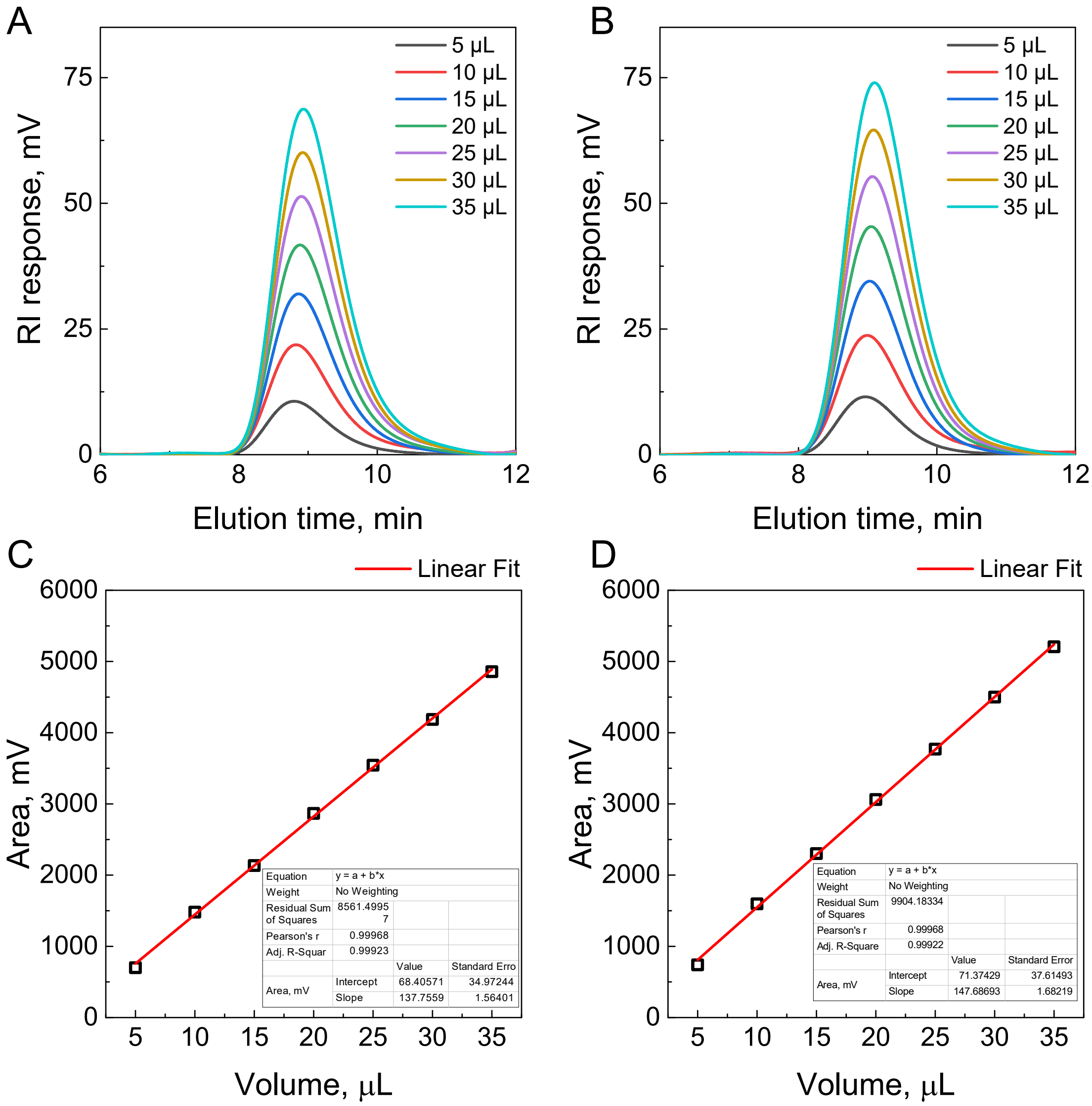

Fig. S9. GPC traces of linear (A) and 4-arm (B) BOC PAMAs in DMF (flow rate 0.2 ml/min) at different injection volumes as monitored by a RI detector, and the corresponding RI responses as a function of injection volume for linear (C) and 4-arm (D) BOC PAMAs.

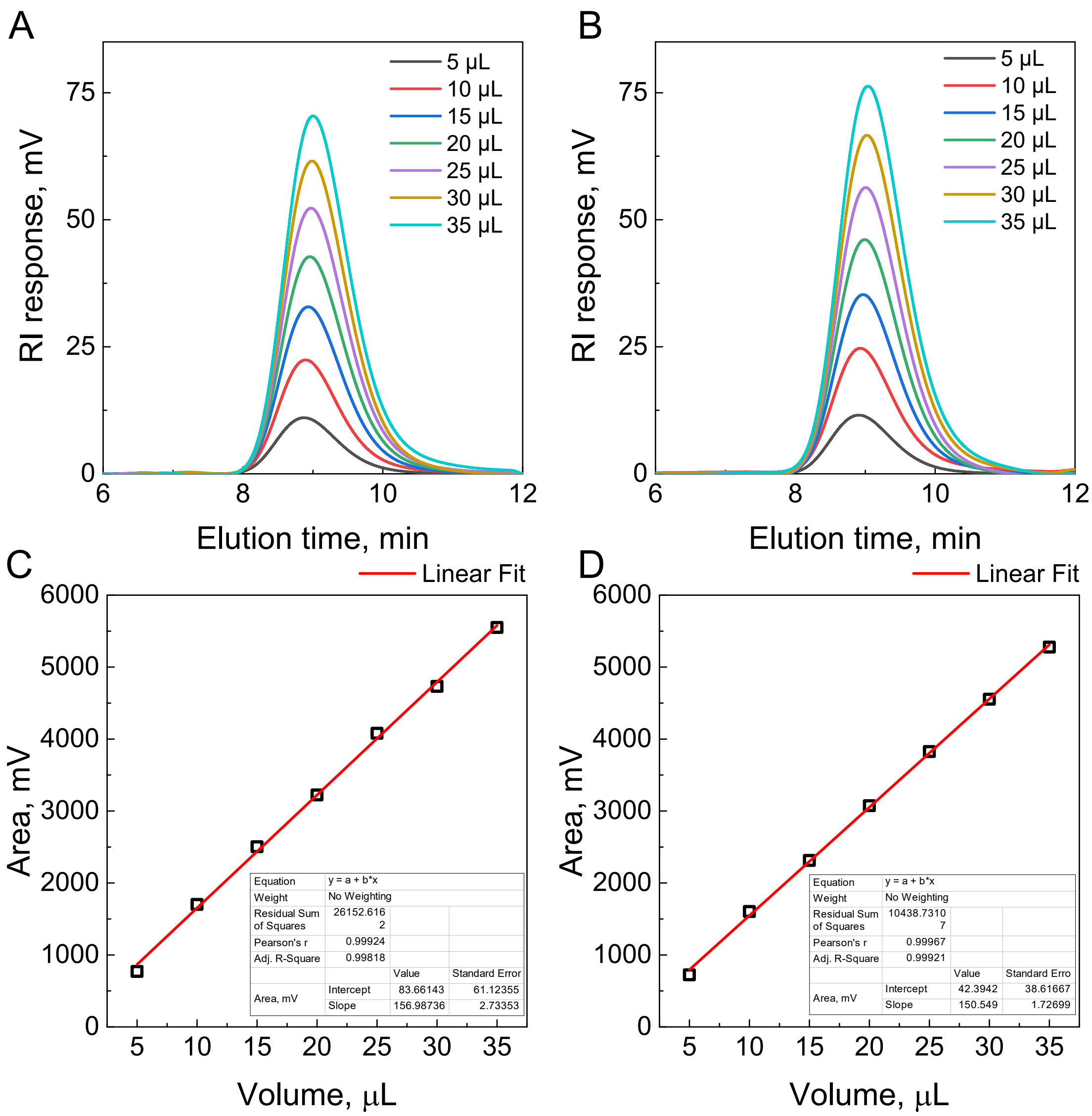

Fig. S10. GPC traces of 6-arm (A) and 8-arm (B) BOC PAMAs in DMF (flow rate 0.2 ml/min) at different injection volumes as monitored by a RI detector and the corresponding RI responses as a function of injection volume for 6-arm (C) and 8-arm (D) BOC PAMAs.

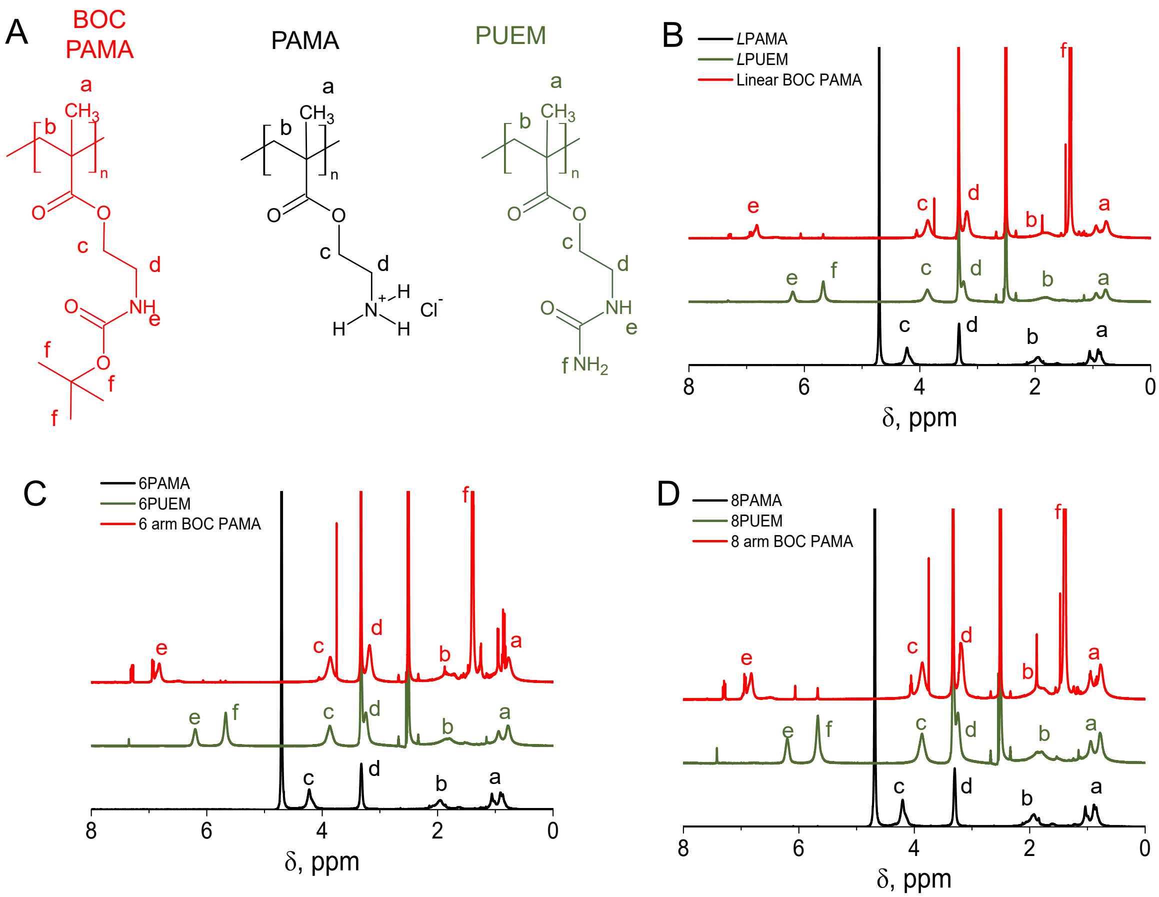

Fig. S11. Chemical structures of BOC PAMA, PAMA and PUEM (A), and [1]H NMR spectra of linear (B) 6-arm (C) and 8-arm (D) BOC PAMAs (d_6-DMSO), PAMAs (D_2O) and PUEMs (d_6-DMSO).

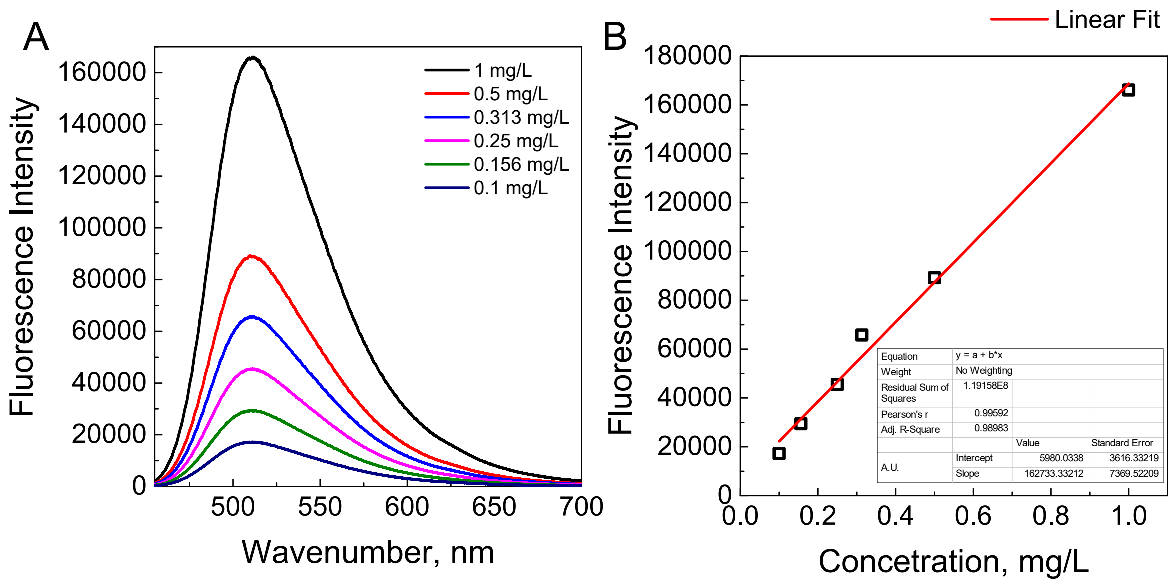

Fig. S12. Fluorescence spectra ($\lambda_{ex} = 445$ nm) of proflavine solutions at different concentrations (A) and the resultant calibration curve (B). The solution pH was adjusted to 6.

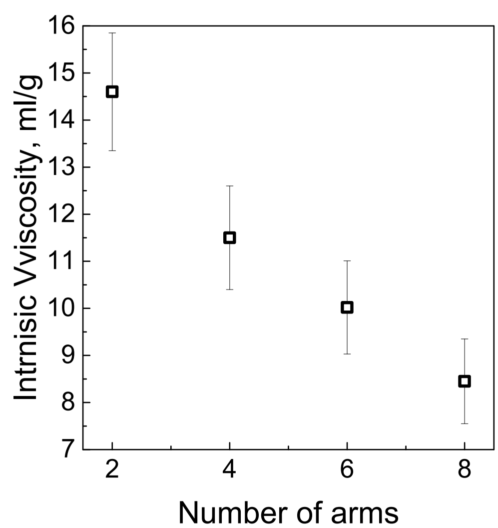

Fig. S13. Intrinsic viscosity of PUEMs as a function of number of arms.

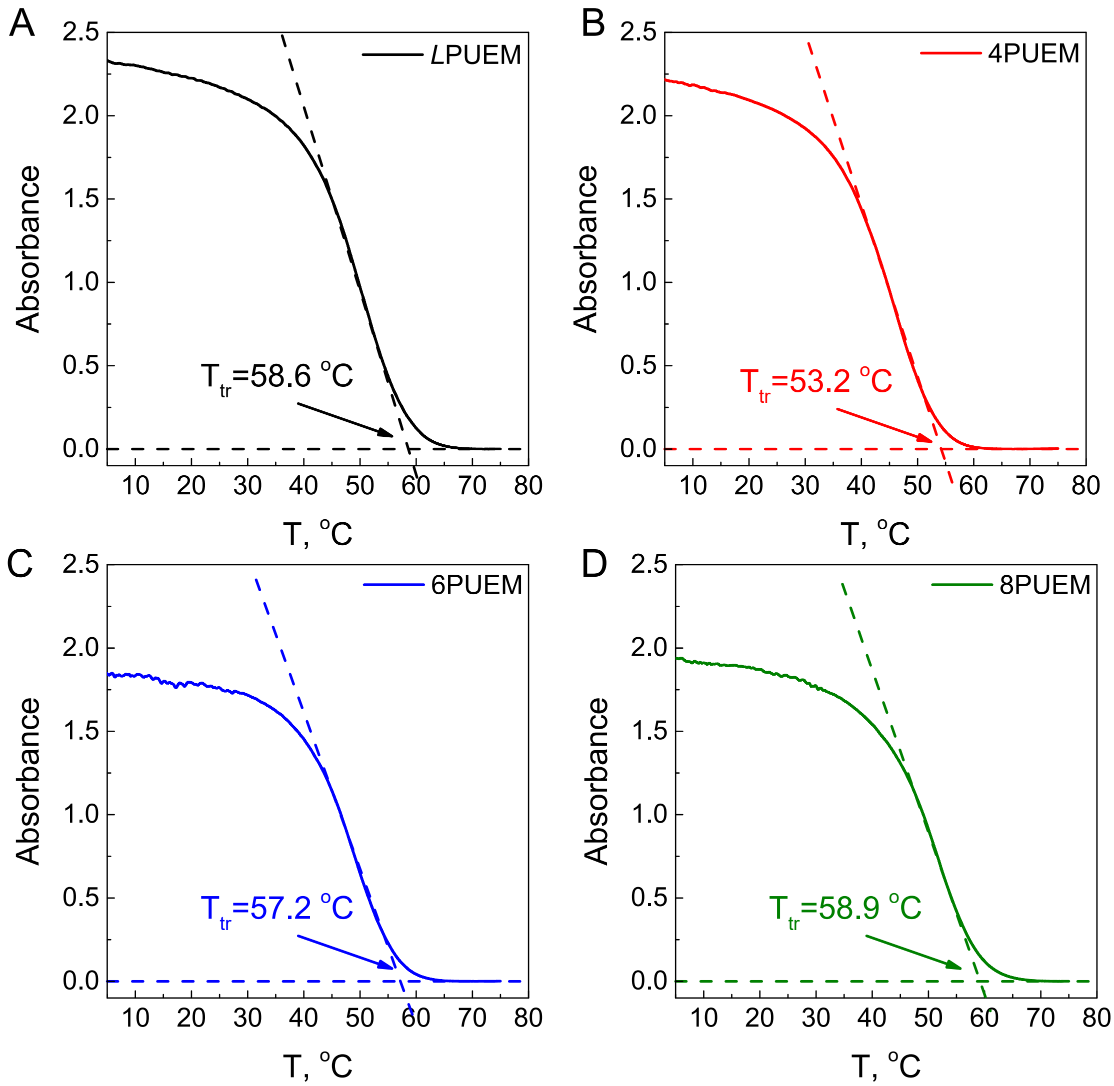

Fig. S14. Determination of transition temperature from the turbidity measurements of 1.0 mg/mL aqueous solutions of *L*PUEM (A), 4PUEM (B), 6PUEM (C) and 8PUEM (D) at 620 nm at a cooling rate of 0.5 ˚C/min.

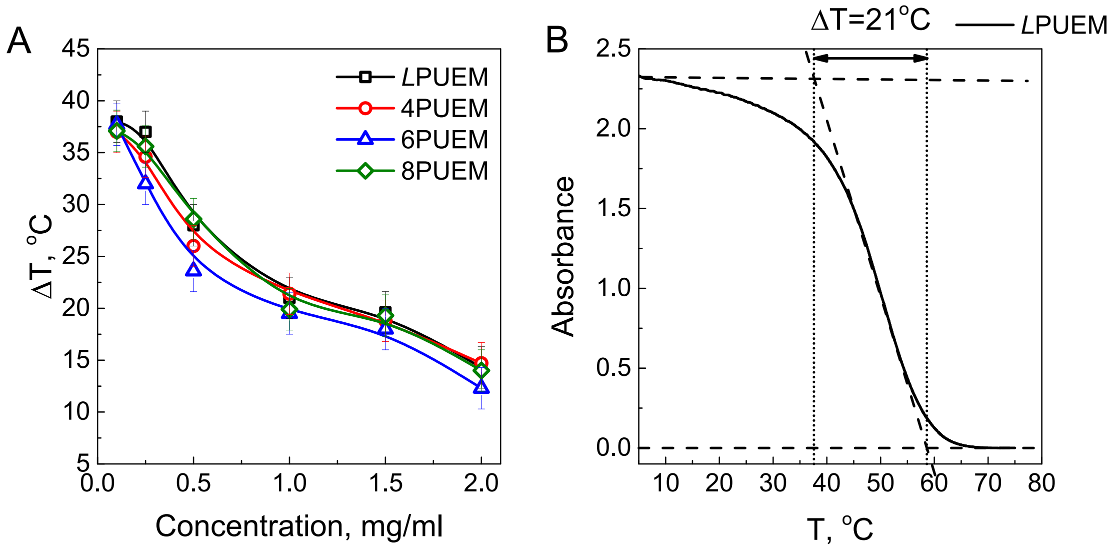

Fig. S15. (A) The effect of polymer concentration on the phase transition window (ΔT) for *L*PUEM (squares), 4PUEM (circles), 6PUEM (triangles) and 8PUEM (diamonds). (B) An example of determination of ΔT from the turbidity measurements for 1.0 mg/mL aqueous solutions of *L*PUEM at 620 nm at a cooling rate of 0.5 ˚C/min.

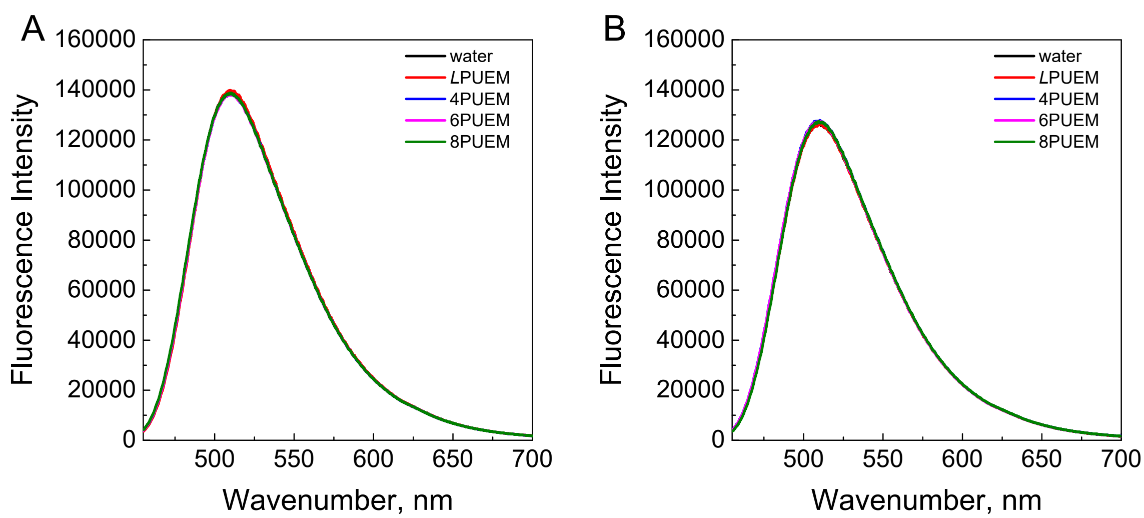

Fig. S16. Fluorescence emission spectra (λ_{ex}=445 nm) of proflavine in the presence of 0.5 mg/ml (A) and 2 mg/ml (B) solutions of linear, 4-, 6- and 8-arm PUEMs above UCST transition. Temperature was 65 ^{o}C for 0.5 mg/ml solutions and 75 ^{o}C for 2 mg/ml solutions. All solutions were adjusted to pH 6.

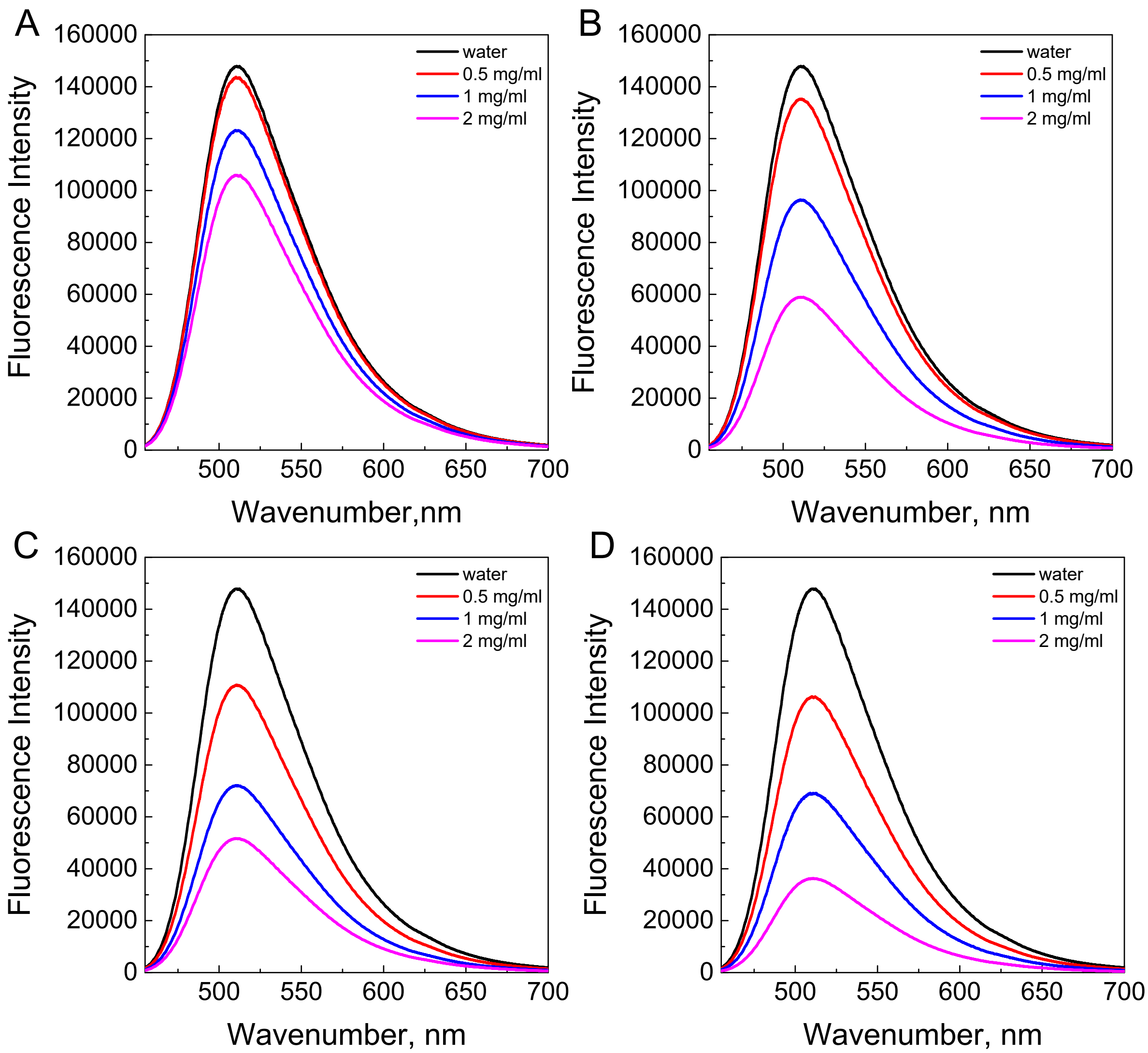

Fig. S17. Fluorescence emission spectra (λ_{ex}=445 nm) of proflavine supernatant solution after centrifugation of 0.5, 1 and 2 mg/ml solutions of linear (A), 4-arm (B), 6-arm (C), and 8-arm PUEMs (D) at 5 ^{o}C. All solutions were adjusted to pH 6.

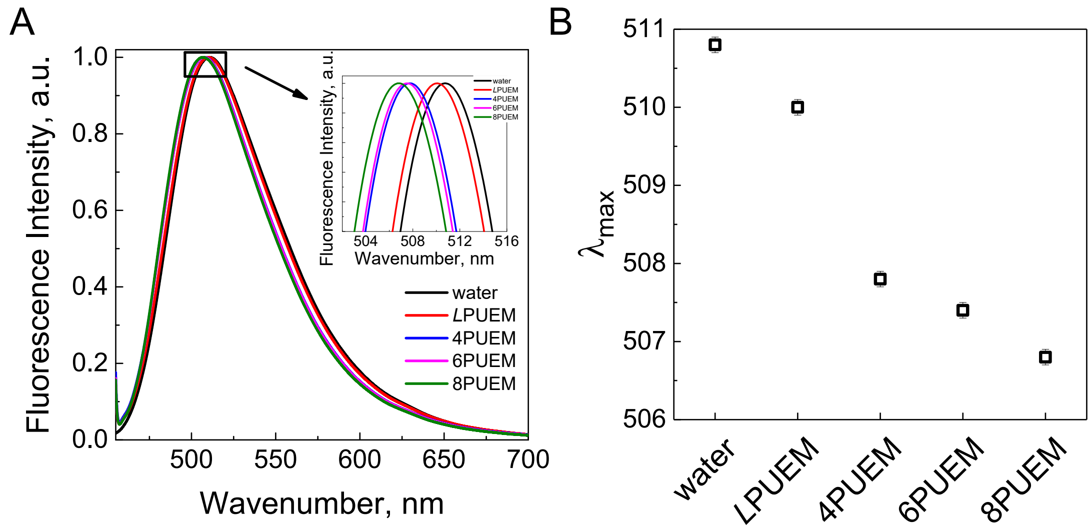

Fig. S18. (A) Fluorescence emission spectra (λ_{ex} = 445 nm) of proflavine in water or 2 mg/ml aqueous solutions of linear, 4-, 6- and 8-arm PUEMs at 5 ^{o}C. (B) Wavelength at the maximum of fluorescent emission of proflavine below the PUEM transition temperature. All solutions were adjusted to pH 6.

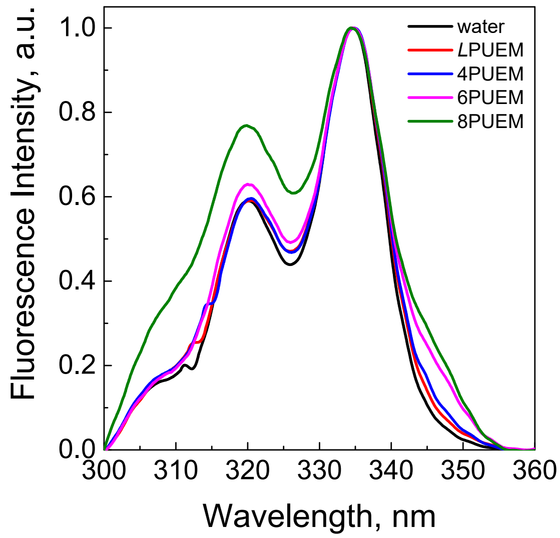

Fig. S19. Fluorescence excitation spectra of pyrene in aqueous solutions at 75 ^{o}C in the absence and presence of the UCST polymers. Polymer concentrations were 1 mg/ml. All solutions were adjusted to pH 6.