

UCST-driven self-assembly and crosslinking of diblock copolymer micelles

Peter J. Roth, Thomas P. Davis,* and Andrew B. Lowe*

*Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, University of New
South Wales, Kensington, Sydney, New South Wales 2052, Australia*

Electronic Supplementary Information



Experimental

Turbidity measurements were performed on a Varian Cary 300 Scan spectrophotometer equipped with a Cary temperature controller and a Peltier heating element in quartz cuvettes of 10 mm path length at a wavelength of 520 nm. Heating rates were 1°C/min for all measurements. For clear solutions (cold water; warm alcohols) the baseline was corrected to zero absorbance, A . Transmittance, $T = 10^{-A}$, was plotted against temperature and cloud points were determined at 50% transmittance or at the average of maximal and minimal transmittance for samples of which the transmittance did not decrease to $\sim 0\%$.

Synthesis

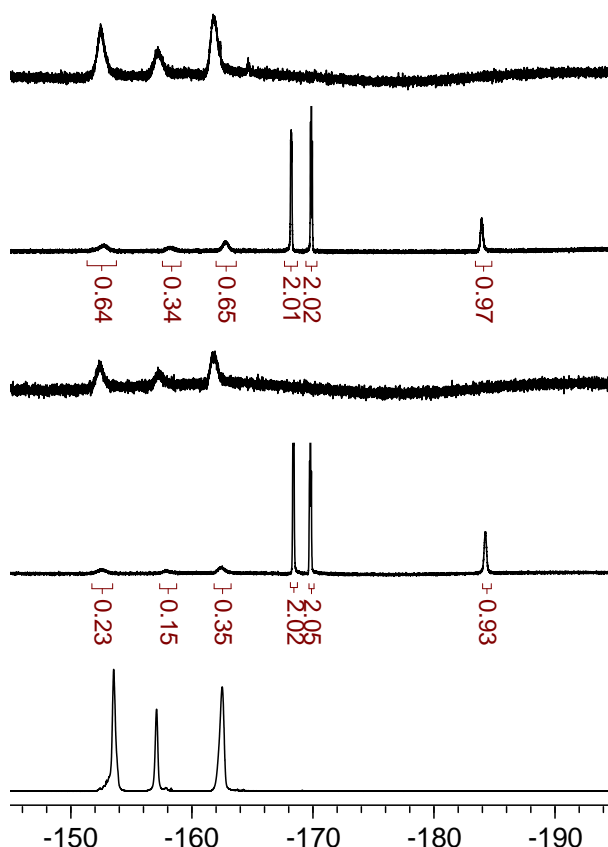


Figure S1. ^{19}F NMR spectra of

- (bottom) parent POEGMA-*b*-PPFPA, showing polymeric PFP esters;
- (second from bottom) the reaction mixture of POEGMA-*b*-PPFPA with ~ 0.95 equiv. of *N*-isopropylamine leaving $\sim 13\%$ of PFP esters intact
- (middle) POEGMA-*b*-(PNIPAM-co-PPFPA-13%) after purification by dialysis showing remaining activated ester groups
- (second from top) the reaction mixture of POEGMA-*b*-PPFPA with ~ 0.85 equiv. of *N*-isopropylamine leaving $\sim 25\%$ of PFP esters intact
- (top) POEGMA-*b*-(PNIPAM-co-PPFPA-25%) after purification by dialysis showing remaining activated ester groups

UCST values in Alcohols

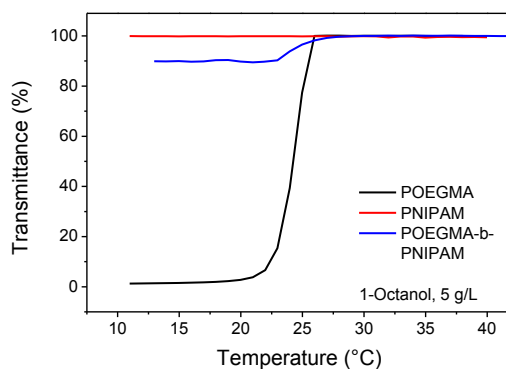


Figure S2. UV-vis turbidity measurement of POEGMA-*b*-PNIPAM in 1-Octanol (blue curve) together with cooling curves of the homo-blocks. For the diblock, the transmittance decreased only slightly due to the formation of micellar aggregates.

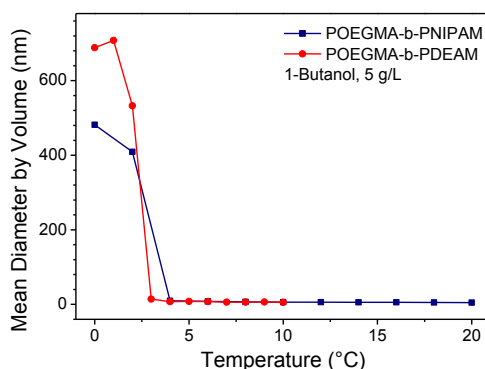


Figure S3. Mean diameter measured by DLS of diblock copolymers in 1-butanol

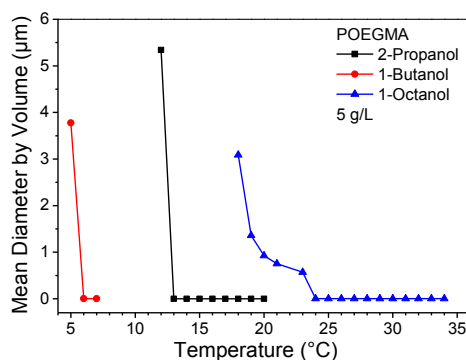


Figure S4. Temperature dependent DLS measurements of POEGMA in alcohols showing the sudden increase of size upon cooling below the cloud point due to macroscopic aggregation and precipitation. Note that the units on the y-axis are μm . The graphs end as the upper detection limit of the instrument is reached.

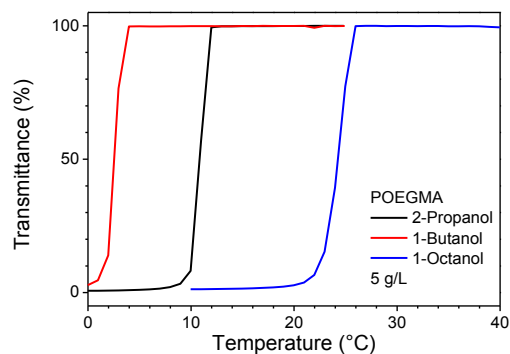
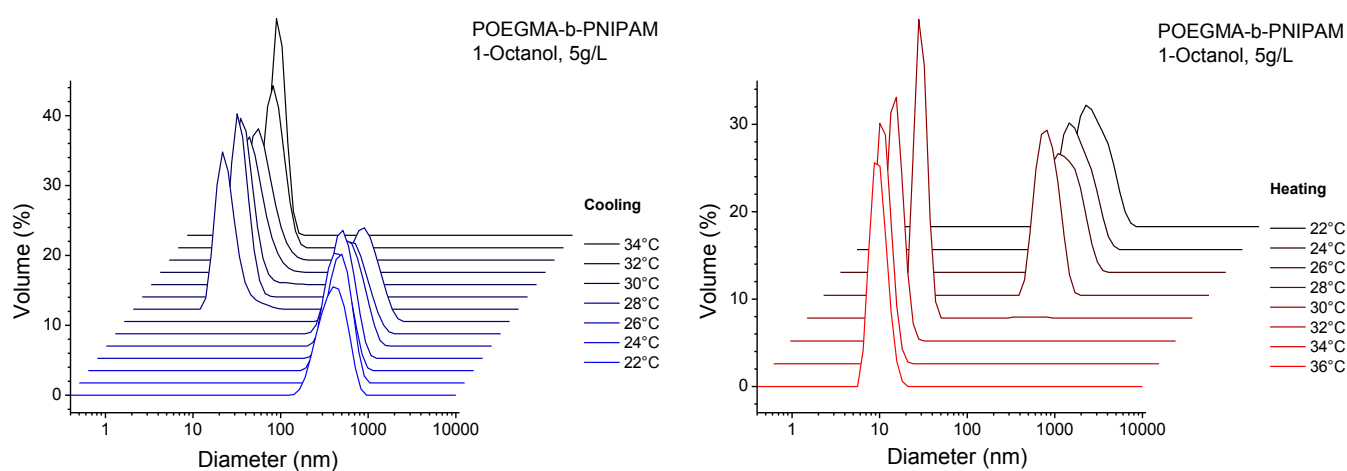


Figure S5. Turbidity curves of POEGMA in alcohols showing the sharp UCST-type transition upon cooling.

Self-Assembly in 1-Octanol



Figures S6, S7. DLS measurements of POEGMA-b-PNIPAM in 1-Octanol at a concentration of 5 g/L showing the sharp change between unimers (warm) and aggregates (cold) upon cooling (left) and heating (right).

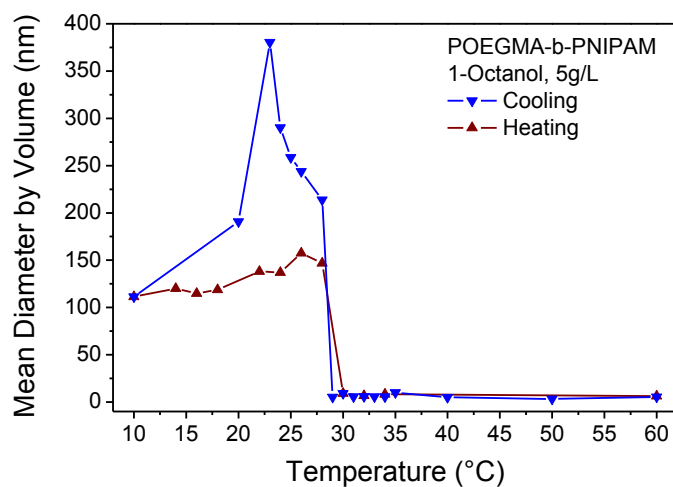


Figure S8. Change of average diameter with temperature for POEGMA-b-PNIPAM in 1-octanol. Due to high concentration of 5 g/L, larger aggregates were formed.

Crosslinking

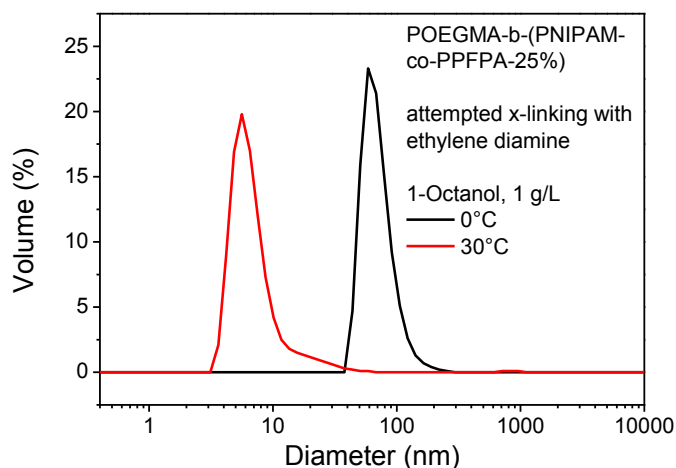


Figure S9. After attempted crosslinking of inverted micelles with PFP esters in their shell using ethylene diamine, the particles present at 0°C (black curve) were found to disintegrate into unimers when heated to 30°C (red curve; average diameter 11.13 nm; peak 5.615 nm).

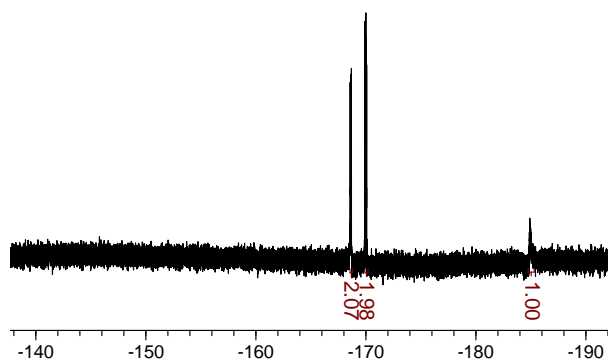


Figure S10. ^{19}F NMR spectrum of the reaction of POEGMA-*b*-(PNIPAM-co-PPFPA-25%) with 1,8-diaminooctane showing the release of free pentafluorophenol due to amide formation and crosslinking. No ester signals are seen which suggests a complete conversion of the PFP esters. However, remaining PFP esters would be expected to be attached to large crosslinked micelles; signal broadening may therefore cause ester peaks to disappear.

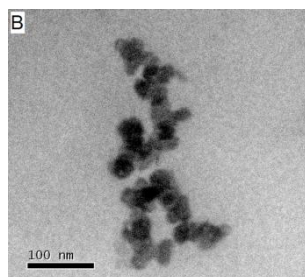


Figure S11. TEM image of (non-inverted) POEGMA core, PNIPAM shell micelles, prepared in water at 50°C, indicating the aggregation of small spherical micelles into larger aggregates

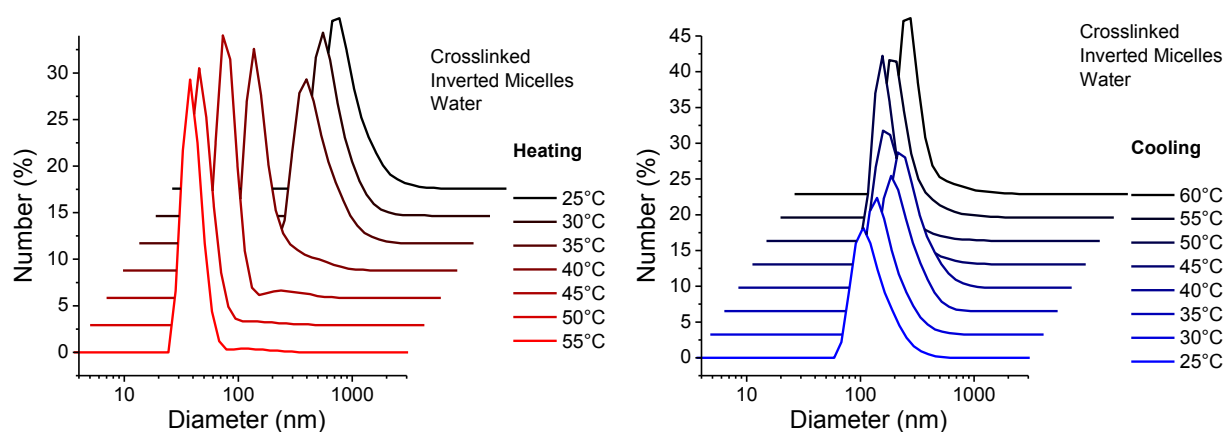


Figure S12, 13. DLS measurements of crosslinked PNIPAM shell, POEGMA core micelles in water showing the reversible collapse of the shell onto the swollen core. Left Heating, right cooling.

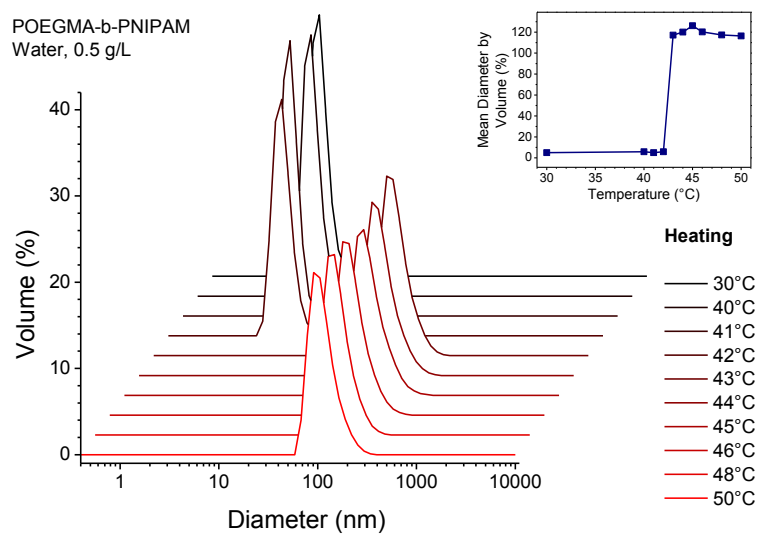


Figure S14. DLS measurements of POEGMA-b-PNIPAM in water, showing the LCST transition of the PNIPAM block at 42°C, at which self-assembly into (aggregated) micelles occurs.