Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Nanogel-like UCST Triblock Copolymer Micelles Showing Large Volume Expansion before Abrupt Dissolution

Amélie Augé, Daniel Fortin, Xia Tong and Yue Zhao*

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

Yue.zhao@usherbrooke.ca

Synthesis of 7-acryloyloxy-4-methylcoumarin (AOMC) monomer

The AOMC monomer was synthesized using method previously described[S1]. In round bottom flask, 0.1 mol 7-hydroxy-4-methylcoumarin, 0.1 mol NaOH and 550 mL EtOH were introduced. The mixture was heated at 60°C for dissolve coumarin compound. The flask was then cooled at room temperature and placed in ice bath. 0.1 mol methacryloyl chloride was added dropwise. The mixture was maintained under magnetic stirring during 90 minutes. Ice water was then added for precipitate AOMC. The white compound was filtered and washed with cold water and finally dried under vacuum. AOMC was purified by recrystallization in methanol.

Synthesis of S,S'-Bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate (BTC) chain transfer agent

The BTC chain transfer agent was synthesized following previous method[S2]. In round bottom flask placed in ice bath, 2.74 g carbon disulfide, 10.75 g chloroform, 5.23 g acetone and 241 mg tetrapropylammonium hydrogen disulfate were dissolved in 12 mL of toluene. The mixture was placed under nitrogen atmosphere. 20.16 g of NaOH aqueous solution was added dropwise and mixture was maintained at room temperature under magnetic stirring

over-night. 90 mL water was then added for dissolve the solid compound. The aqueous phase was extracted and neutralized with 12 mL of concentrated HCl solution. The brown compound formed was filtered, washed with water and dried under vacuum. The product was purified by washing in toluene/acetone mixture. After drying, the final product was yellow.

Composition of copolymers

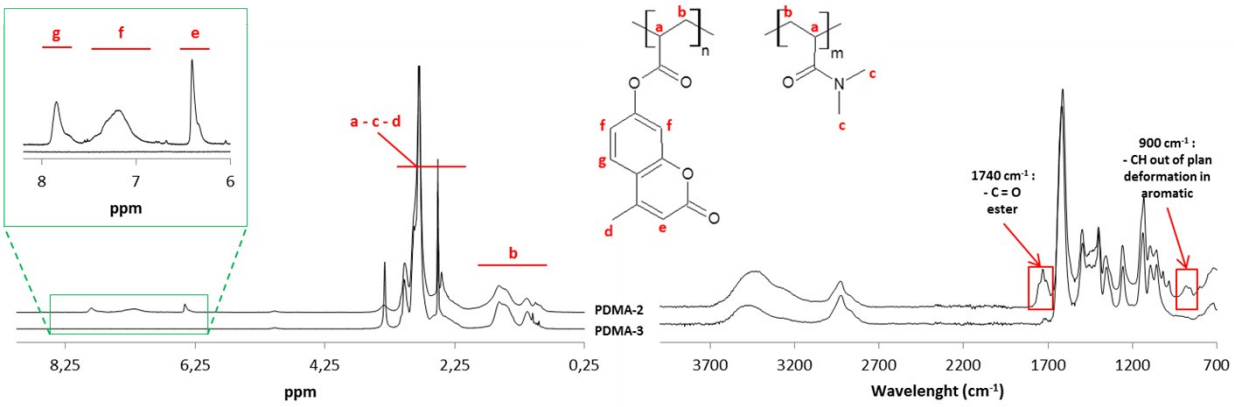

Figure S1. ^{1}H-NMR and FTIR spectrums of PDMA-2 and PDMA-3 copolymers.

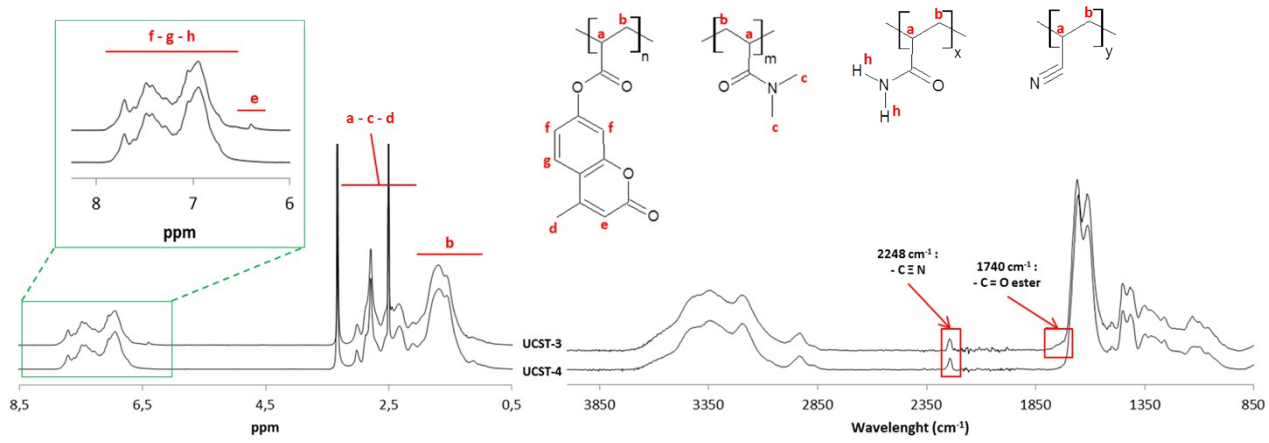

Figure S2. ^{1}H-NMR and FTIR spectrums of UCST-3 and UCST-4 copolymers.

Determination of critical micellar concentration (CMC) of UCST-3 copolymer

The CMC at 25°C for UCST-3 was determined by dynamic light scattering[S3]. Generally the pyrene method is used for CMC measurements, but in this case this method is not suitable because the copolymer contains coumarin. Indeed the wavelength of excitation and emission for pyrene and coumarin are in the same wavelength interval. Several copolymer solutions were prepared with concentration between $1{,}0.10^{-2}$ and $1{,}5.10^{-5}$ wt%. Figure 3S shows the variation of log(scattered intensity) as function of -log(concentration). We can see that log(scattered intensity) decreases linearly when the concentration decreases. This trend is consistent because the micelle concentration decreases. When the CMC value is reached, a break of slope is observed corresponding to passage from micelles to unimers form. Finally the CMC value for UCST-3 copolymer is $1{,}72.10^{-4}$ wt%.

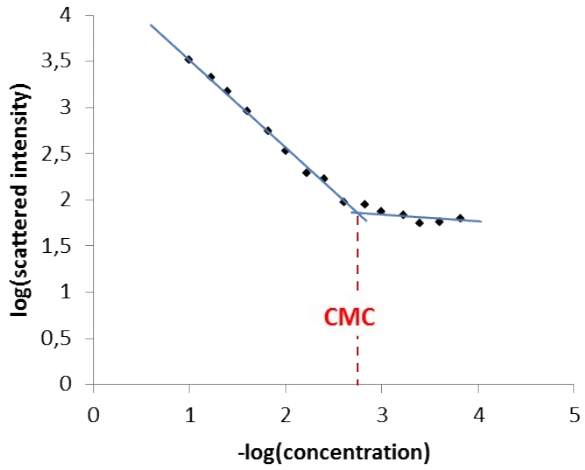

Figure S3. Determination of CMC value for UCST-3 copolymer using dynamic light scattering method.

Thermosensitive behavior of UCST-3 in water studied by dynamic light scattering

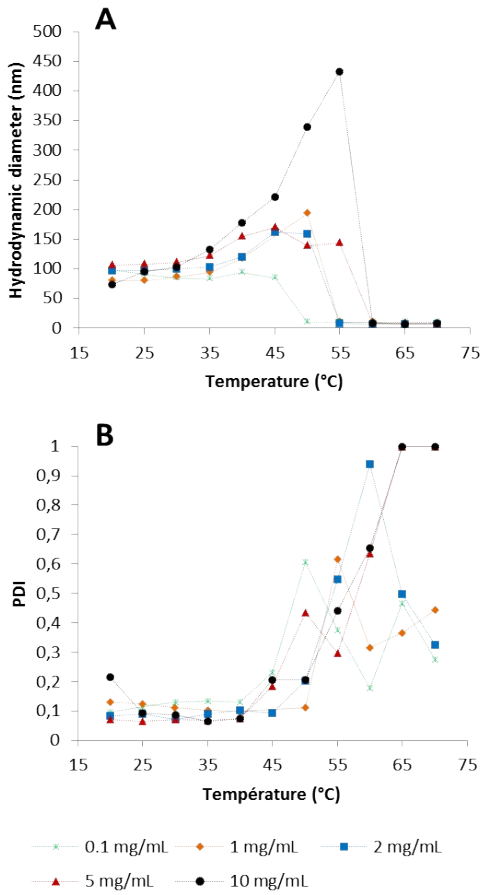

Figure S4. Variation of (a) hydrodynamic diameter and (b) polydispersity index with temperature for various concentrations of UCST-3 copolymer in water.

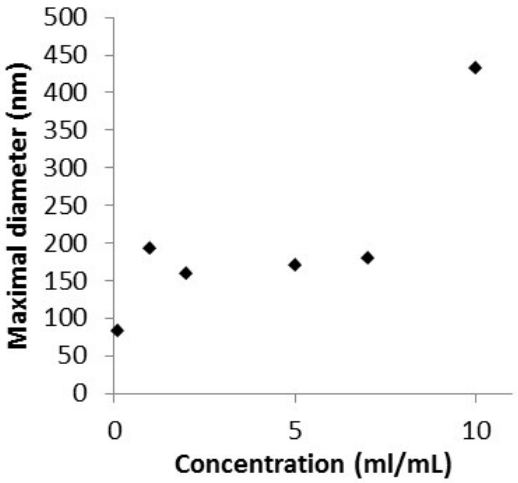

Figure S5. Variation of maximal diameter reached just before micelles dissociation as function of copolymer concentration.

Effect of solvent substitution on thermosensitive behavior of UCST-2 studied by dynamic light scattering and transmittance

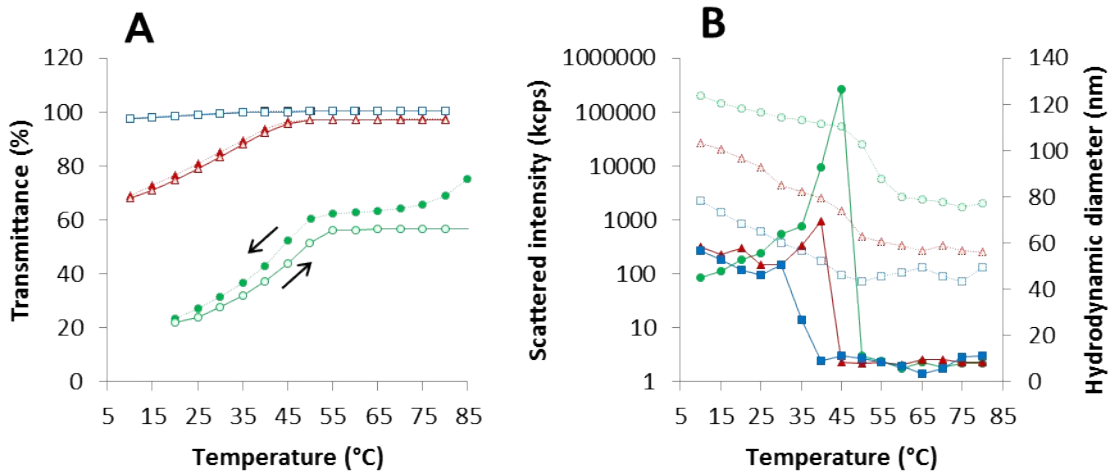

Figure S6. Variation of (a) transmittance, (b) hydrodynamic diameter and scattered intensity with temperature for UCST-2 at 0.01 wt% (circles), 0.1 wt% (square) and 1 wt% (triangle) in water. On Figure S6b, the solid lines correspond to diameter and dash lines correspond to scattered intensity.

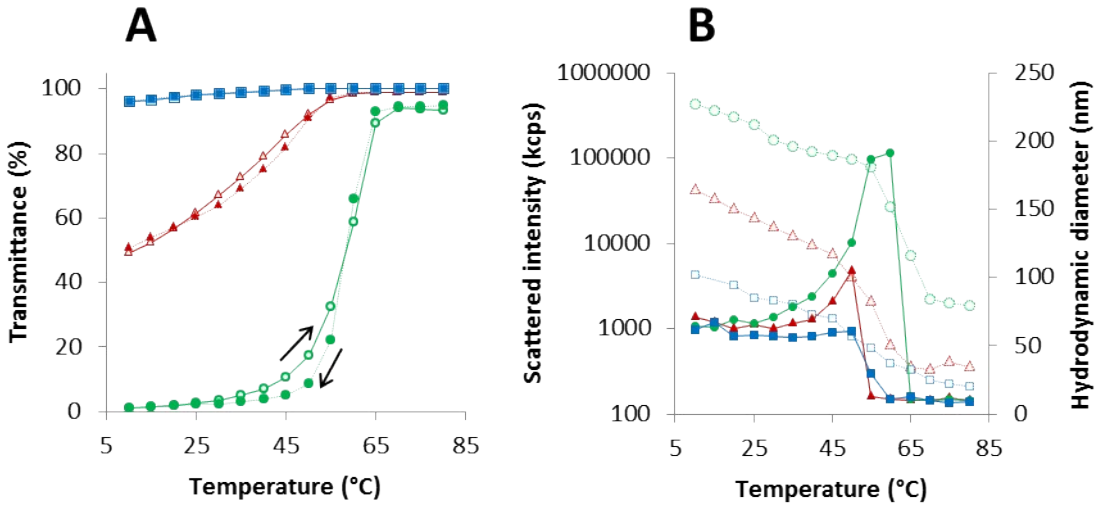

Figure S7. Variation of (a) transmittance, (b) hydrodynamic diameter and scattered intensity with temperature for UCST-2 at 0.01 wt% (circles), 0.1 wt% (square) and 1 wt% (triangle) in deuterated water. On Figure S7b, the solid lines correspond to diameter and dash lines correspond to scattered intensity.

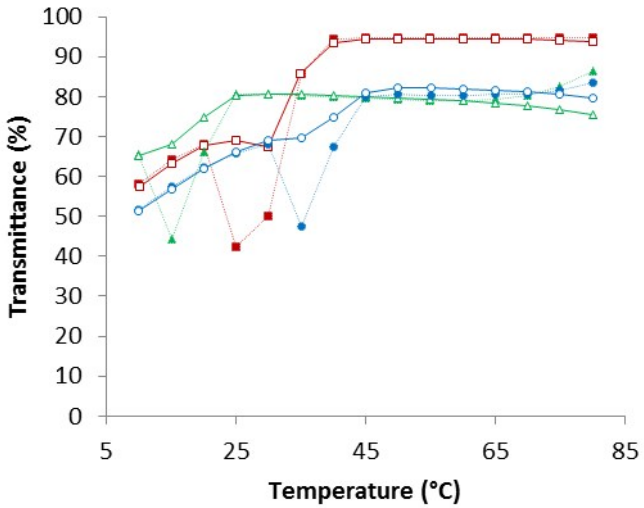

Figure S8.*: Variation of transmittance with temperature during cooling (dash lines)-heating (solid lines) process for UCST-2 at 1 wt% in 0.05 M (blue circle), 0.1 M (red square) and 0.2 M (green triangle) NaSCN aqueous solutions.*

(S1) Patel, M. G. Acrylic Copolymers Based on Coumarin Derivated: Synthesis and Characterization. *Malaysian Polym. J.* **2011**, 6 (1), 70-86.

(S2) John T. Lai; Debby Filla, A.; Shea, R. Functional Polymers from Novel Carboxyl Terminated Trithiocarbonates as Highly Efficient RAFT Agents. *Macromolecules* **2002**, 35, 6754-6756.

(S3) Topel, Ö.; Çakin, B. A.; Budana, L.; Hoda, N. Determination of Critical Micelle Concentration of Polybutadiene-block-Poly(ethyleneoxide) Diblock Copolymer by Fluorescence Spectroscopy and Dynamic Light Scattering *J. Mol. Liq.* **2013***,* 177, 40-43.