Supporting Information for

Mechano-Responsive Polymer Solutions Based on CO_2 Supersaturation: Shaking-induced Phase Transitions and Self-Assembly or Dissociation of Polymeric Nanoparticles

Peter J. Roth,* Jing Yang Quek, Yicheng Zhu, Bianca M. Blunden, and Andrew B. Lowe*

Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering, UNSW Australia,
University of New South Wales, Kensington, Sydney, NSW 2052, Australia
Email: P.Roth@unsw.edu.au (P.J.R)

Experimental Section

Methods. Optical photographs were taken with a Sony alpha 350; contrast was corrected and images were cropped in Adobe Lightroom software.

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 with a cooling rate of 1 °C/min. For clear solutions the baseline was corrected to zero absorbance, A. Transmittance, $T = 10^{-A}$, was plotted against temperature and cloud points were determined at $T = 50$ %.

pH values were measured on a Mettler Toledo SevenCompact instrument after calibration on standard solutions according to the manufacturer's specifications.

Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano ZS at a scattering angle of 173 ° and were analyzed by Malvern Zetasizer Software version 6.20.

Transmission electron microscopy (TEM) was conducted on a Jeol 1400 instrument with an accelerating voltage of 100 kV. Two drops of polymer solutions were dropped onto a carbon coated copper grid sitting on a filter paper before drying the grid overnight.

Size exclusion chromatography (SEC) in dimethylacetamine (DMAc) was performed on a Shimadzu system with four 300×7.8 mm^2 linear phenogel columns (10^5, 10^4, 10^3 and 500 Å) operating at a flow rate of 1 mL/min. The system was calibrated with a series of narrow molar mass distribution polystyrene (PS) standards with molar masses ranging from 0.58–1820 kg/mol.

Materials. All reagents were purchased from Sigma-Aldrich and were used as received unless stated otherwise. 2-(Dimethylamino)ethylmethacrylate, DMAEMA, was passed through basic Al_2O_3 to remove inhibitors. Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol and stored at –24 °C. Soda water was regular drinking quality carbonated natural mineral water produced in Australia containing 40 mg/L sodium, < 0.1 mg/L fluoride[1] with a measured pH of 4.35.

Synthesis. Poly[2-(dimethylamino)ethylmethacrylate], **pDMAEMA**, was synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization. Monomer DMAEMA (2.8 g, 17.8 mmol, 300 equiv), solvent acetonitrile (4 mL), RAFT agent 2-cyano-2-propyl benzodithioate (13.1 mg, 0.059 mmol, 1 equiv), and initiator AIBN (1.0 mg, 0.0059 mmol, 0.1 equiv.) were mixed in a flask which was subsequently purged with nitrogen for 20 min and placed into a preheated oil bath (70 °C) for 20 h. Polymerization was stopped by quenching the reaction in liquid nitrogen. A sample (100 μL) was withdrawn, diluted with $CDCl_3$ (550 μL), and analysed by ^{1}H NMR spectroscopy which indicated a monomer conversion of 67 % by comparison of the signal at $\delta = 4.20$ ppm (t, 2 H of monomer) with the signal at $\delta = 4.00$ ppm (2 H of polymer). The polymer was isolated as a pink powder (1.75 g, 63 %) by two precipitations into diethyl ether–hexane (2:3) followed by drying in vacuum. $M_{\mathrm{n,\ theor.}}$ (from conversion) = 31.8 kg/mol, $M_{\mathrm{n,SEC}} = 22.3$ kg/mol (DMac, polystyrene standard), $Đ_{\mathrm{M}} = M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}} = 1.14$. ^{1}H NMR ($D_2O$, 300 MHz), δ/ppm = 4.11 ($–OC\underline{H}_2CH_2–$), 2.67 ($–OCH_2C\underline{H}_2–$), 2.27 ($–N(C\underline{H}_3)_2$), 2.04 (backbone $–C\underline{H}_2C(CH_3)R–$), 1.08, 0.90 (backbone $–CH_2C(C\underline{H}_3)R–$).

Poly(4-vinyl-1*H*-imidazole),**p4VIm**, with $M_n = 14.3$ kg/mol and low polydispersity was synthesized by RAFT polymerization using 2-(((dodecylthio)-carbonothioyl)thio)-2-methylpropanoic acid as chain transfer agent as described elsewhere.[2]

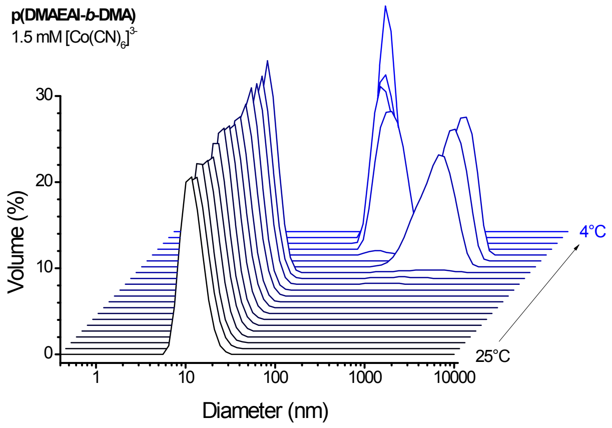
Poly(*N*-acryloyl histamine), **pNAHist**, with $M_n = 4.8$ kg/mol and $Đ_{\mathrm{M}} = M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}} = 1.15$ was synthesised by postpolymerization modification of poly(pentafluorophenyl acrylate) with histamine in the presence of *S*-methyl methane thiosulfonate, as described elsewhere.[3]

Likewise, poly(*N*-acryloyl histamine-*block*-dimethylacrylamide), **p(NAHist-*b*-DMA)**, consisting of approximately 28 repeat units of pNAHist and 34 repeat units of DMA with $M_n = 8.2$ kg/mol and $Đ_{\mathrm{M}} = M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}} = 1.20$ was synthesised by postpolymerization modification of poly(pentafluorophenyl acrylate-*block*-dimethylacrylamide) with histamine in the presence of *S*-methyl methane thiosulfonate.[3]

Poly[(dimethylaminoethyl 2-acrylamido isobutyramide)-*block*-dimethylacrylamide], **p(DMAEAI-*b*-DMA)** with a molar composition of 54 mol% DMAEAAI repeat units and 46 mol% DMA repeat units, $M_{n,SEC} = 27.3$ kg/mol (polystyrene standard) and $Đ_{\mathrm{M}} = M_{\mathrm{w,SEC}}/M_{\mathrm{n,SEC}} = 1.19$ was prepared by postpolymerization modification of poly[(2-vinyl-4,4-dimethylazlactone-*block*-dimethylacrylamide] prepared by RAFT polymerisation with dimethylaminoethylamine as described elsewhere.[4]

*UCST behaviour of p(DMAEAI-*b*-DMA) in the presence of cobaltate ions.*

The diblock copolymer p(DMAEAI-*b*-DMA) self-assembled into micellar aggregates in acidic soda water when trivalent cobaltate ions where added, due to a crosslinking of the protonated amine groups with cobaltate rendering the pDMAEAI block insoluble. Heating to 50 °C did not change the aggregates suggesting the absence of a UCST transition below this temperature. After shaking the pH increased which reduced the amount of crosslinking causing dissolution of aggregates. At this higher pH value, however, the pDMAEAI block showed UCST behaviour in water: cooling of the solution caused re-formation of micellar aggregates. This observation is in agreement with literature on the UCST transition of the sister polymer pDMAEMA in the presence of cobaltate which decreases with increasing pH.[5] In our case, the UCST transition within the p(DMAEAI-*b*-DMA) diblock copolymer was observed by DLS. Upon cooling from 25 °C to 4 °C, the (volume-average) diameter suddenly increased drastically around 10 °C above 1000 nm, then, upon further cooling, decreased to a value of 100.56 ± 2.93 nm with low dispersity (see Figure). We previously observed a similar behaviour during the formation of micelles driven by the UCST of poly[oligo(ethylene glycol) methyl ether methacrylate] in alcohols. The stage of large aggregates was attributed to the gradual nature of UCST transitions in which ill-defined aggregates form which then, at lower temperature, form defined nano-objects as the entire thermoresponsive block becomes solvophobic.[6, 7]



References

1. K. Mills, S. Falconer and C. Cook, *Australian Dental Journal*, 2010, **55**, 411-416.
2. B. M. Blunden, A. Rawal, H. Lu and M. H. Stenzel, *Macromolecules*, 2014, **47**, 1646-1655.
3. J. Y. Quek, P. J. Roth, R. A. Evans, T. P. Davis and A. B. Lowe, *Journal of Polymer Science Part A: Polymer Chemistry*, 2013, **51**, 394-404.
4. J. Y. Quek, Y. Zhu, P. J. Roth, T. P. Davis and A. B. Lowe, *Macromolecules*, 2013, **46**, 7290-7302.
5. F. A. Plamper, A. Schmalz and A. H. E. Müller, *Journal of the American Chemical Society*, 2007, **129**, 14538-14539.
6. P. J. Roth, T. P. Davis and A. B. Lowe, *Macromolecules*, 2012, **45**, 3221-3230.
7. P. J. Roth, T. P. Davis and A. B. Lowe, *Polymer Chemistry*, 2012, **3**, 2228-2235.