The Effect of Micellisation on the Thermoresponsive Behaviour of Polymeric Assemblies

@RORgroup @LabGibson

L.D.Blackman@warwick.ac.uk

Lewis D. Blackman, *Daniel B. Wright, Mathew P. Robin, Matthew I. Gibson and Rachel K. O'Reilly*

Department of Chemistry, University of Warwick, Coventry, UK

1. Background

- Thermoresponsive self-assemblies have shown potential for a wide range of applications.
- Poly(*N*-isopropyl acrylamide) (pNIPAM) is one of the most widely studied thermoresponsive polymers and shows a lower critical solution temperature (LCST) close to body temperature (≈32 °C).
- One limitation of pNIPAM is that it exhibits slow reversibility (hysteresis) upon cooling in certain systems.
- This phenomenon is not fully understood and numerous reports show seemingly contradictory data.

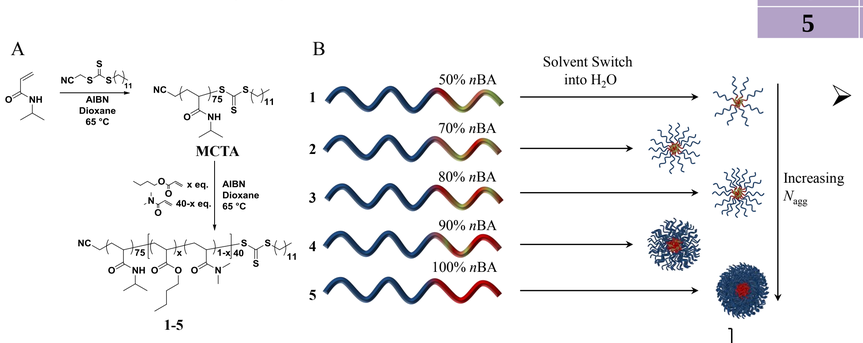
2. Aims and Objectives

- To synthesise a series of micelles with thermoresponsive pNIPAM coronas and varying core hydrophobicity by copolymerising varying amounts of a hydrophilic monomer (dimethyl acrylamide, DMA) into the core-forming hydrophobic block composed of poly(*n*-butyl acrylate) (*n*BA).
- To study the macroscopic and nanoscale behaviour using a combination of variable temperature DLS and SLS, tubidimetry and microcalorimetry in order to understand how these behaviours change with small changes in the micellar structure.

3. Polymer Synthesis and Micelle Preparation

- pNIPAM-*b*-p(*n*BA-*co*-DMA) diblock copolymers were synthesised by RAFT polymerisation from a pNIPAM macroCTA (**MCTA**) to yield polymers with varying mol % of a hydrophobic monomer (*n*BA) in the second block (**1**-**5**).

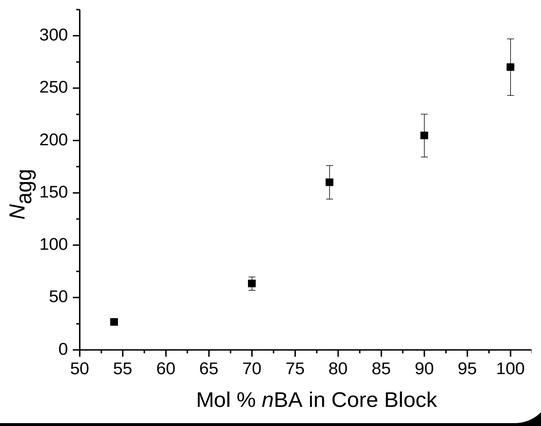
Polymer	Monomer Feed Ratio	Mol % *n*BA in core block	$Đ_M$
MCTA	N/A	N/A	1.07
1	1:1	54	1.10
2	7:3	70	1.11
3	4:1	79	1.10
4	9:1	90	1.11
5	1:0	100	1.11



- The diblock copolymers were self-assembled into micelles in aqueous solution using a solvent switch technique.

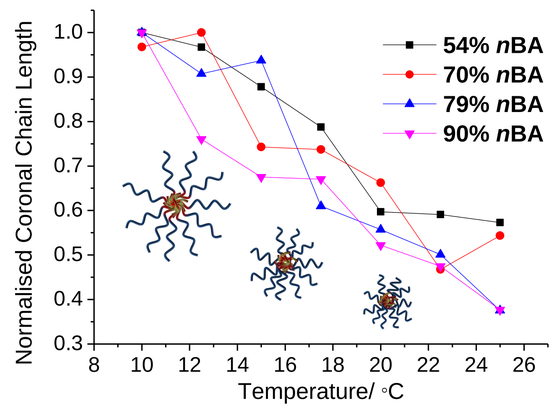
- The micelles were analysed by multi-angle dynamic and static light scattering (DLS and SLS) at 20 °C and were shown to have increasing N_{agg} values with mol % *n*BA in the core-forming block.

Mol % *n*BA in core block	R_H/ nm	R_{core}/ nm
54	9.3	3.7
70	14.0	4.9
79	16.5	7.0
90	14.9	7.3
100	19.8	8.1

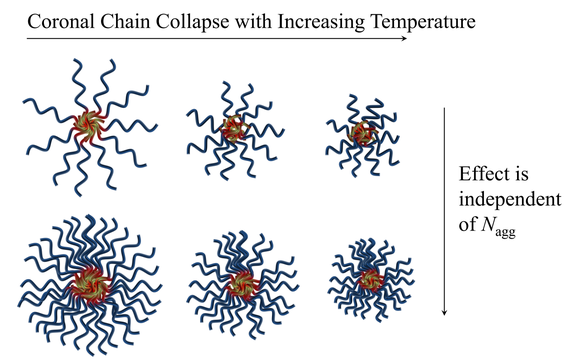


4. Variable Temperature DLS and SLS

- The micelles were analysed by multi-angle DLS and SLS at temperatures ranging from 10-25 °C.
- Partial Zimm analysis revealed the core radii, which when combined with R_H from DLS, allowed the coronal chain length across the temperature range to be calculated.

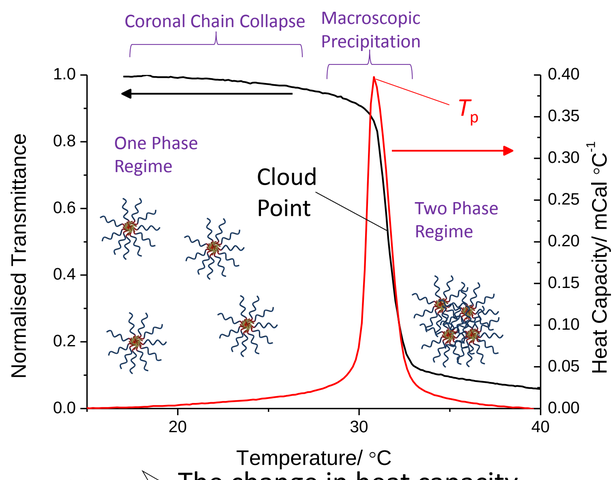


- The pNIPAM chains began to respond by collapsing at temperatures well below the known LCST.
- The trend in the coronal chain collapse was independent of N_{agg} in the regime investigated.

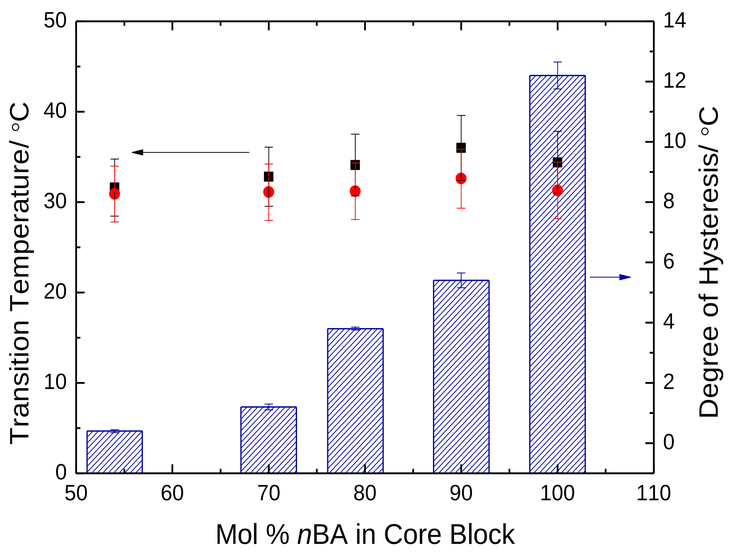


5. Microcalorimetry and Turbidimetry Analysis

- The micelles were heated above the LCST of pNIPAM and the change in turbidity was measured.
- Macroscopic precipitation of the micelles lead to a decrease in the transmitted light.
- The cloud point (the temperature at which the transmittance reaches half of the original transmittance at T<<LCST) was shown to be independent of N_{agg} when heating the sample.



- The change in heat capacity with varying temperature, measured by microcalorimetry, also showed the same transition temperature for all the micellar systems studied.
- The thermal hysteresis, (the difference between the cloud points from turbidimetry obtained from heating and cooling the sample) was shown to increase with increasing core hydrophobicity.
- Micelles with higher N_{agg} took longer to resuspend upon cooling.



Left axis: Phase transitions observed by variable temperature techniques at 1 mg/mL with 10% error bars. Black squares represent cloud points determined by turbidimetry. Red circles represent T_p values determined by microcalorimetry. Right axis: Degree of hysteresis observed by turbidimetry analysis. Error bars are standard deviation over 3 repeats.

6. Conclusions

- Micelles of tunable N_{agg} were synthesised by controlling the ratio of hydrophobic to hydrophilic monomer in the core-forming block of well-defined amphiphilic diblock copolymers.
- Collapse of the pNIPAM coronal chains was observed by variable temperature light scattering prior to the cloud point, however the degree of coronal collapse over the temperature range investigated was not dictated by N_{agg}.
- The transition temperatures observed by turbidimetry and microcalorimetry were independent of N_{agg}. However, the thermal hysteresis showed a positive correlation with core hydrophobicity, and therefore N_{agg}.

- This was attributed to either intraparticle chain entanglement at high N_{agg} (A) or a decrease in the hydration of the micelle cores, leading to more dehydrated precipitates for micelles composed of more hydrophobic polymers (B). Additional work is being carried out to investigate these theories further.
- These results demonstrate that consideration of the macroscopic and molecular behaviour of responsive polymers at both the unimer and particle level must be considered for real-world applications.

7. Acknowledgements

We thank EPSRC, BP and the IAS for financial support. We also thank Malvern Instruments Ltd. for use of their microcalorimetry facilities.

8. References

1. Gibson, M. I.; O'Reilly, R. K. *Chem. Soc. Rev.* **2013**, *42*, 7204-7213.
2. Charbonneau, C.; De Souza Lima, M. M.; Chassenieux, C.; Colombani, O.; Nicolai, T. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3955-3964.
3. Nuopponen, M.; Ojala, J.; Tenhu, H. *Polymer* **2004**, *45*, 3643-3650.
4. Wright, D. B.; Patterson, J. P.; Pitto-Barry, A.; Cotanda, P.; Chassenieux, C.; Colombani, O.; O'Reilly, R. K. *Polym. Chem.* **2015**, *DOI: 10.1039/C4PY01782J*.

WARWICK THE UNIVERSITY OF WARWICK

EPSRC Engineering and Physical Sciences Research Council

bp

Institute of Advanced Study IAS