Investigating Hysteresis in Thermoresponsive Assemblies

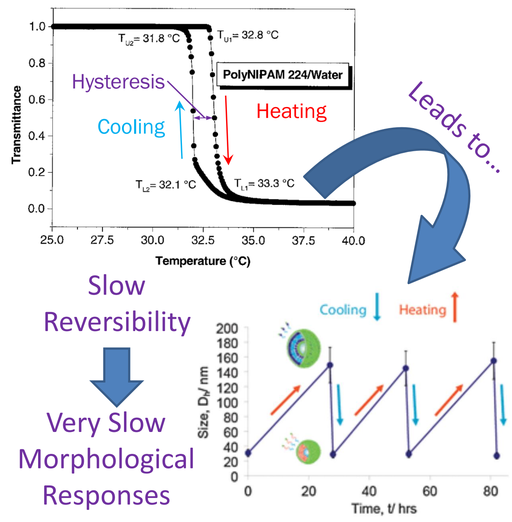
L. D. Blackman, Daniel B. Wright, Mathew P. Robin, Matthew I. Gibson and Rachel K. O'Reilly

Dept. of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

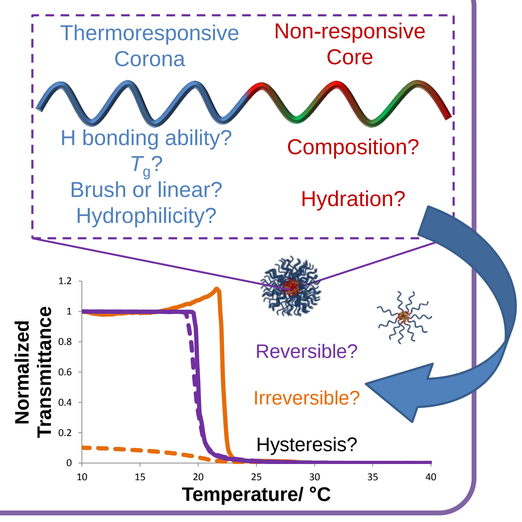
L.D.Blackman@warwick.ac.uk www.warwick.ac.uk/ror www.warwick.ac.uk/gibsongroup @LabGibson @RORGroup

1. Background

- pNIPAM is one of the most studied thermoresponsive polymers, which exhibits a lower critical solution temperature (LCST) close to body temperature.
- Some concerns exist concerning its slow reversibility (hysteresis) in certain systems.
- This hysteresis results in slow morphological responses to occur when pNIPAM is used as the responsive block.

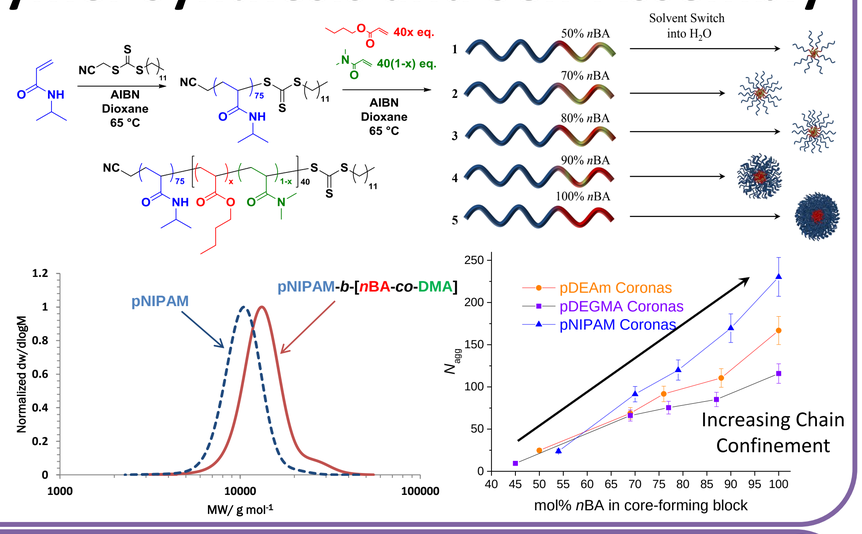


- Herein, we design micelles with tunable aggregation numbers (N_{agg}) and core hydrophobicities, in order to determine the effects of core hydration and chain confinement on thermal hysteresis. This was achieved using varying compositions of (p*n*BA-*b*-DMA) as the core block and pNIPAM as the thermoresponsive corona.
- Using the same micellar cores the effects of changing the chemistry of the corona block on thermal hysteresis was investigated. Three more distinct thermoresponsive coronas were investigated, namely (pDEAm), (pDEGMA) and (pOEGMA).



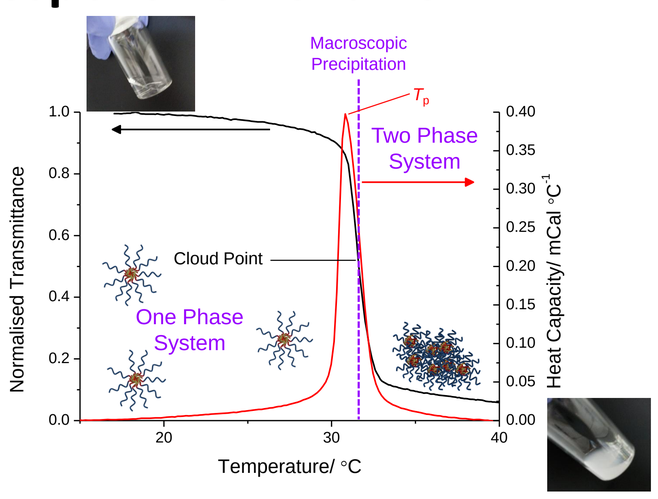
2. Block Copolymer Synthesis and Self-Assembly

- Diblock Copolymers were synthesized by RAFT polymerization.
- The copolymers were self-assembled into micelles and characterized by multi-angle SLS and DLS.
- ↑*n*BA → ↑N_{agg}.



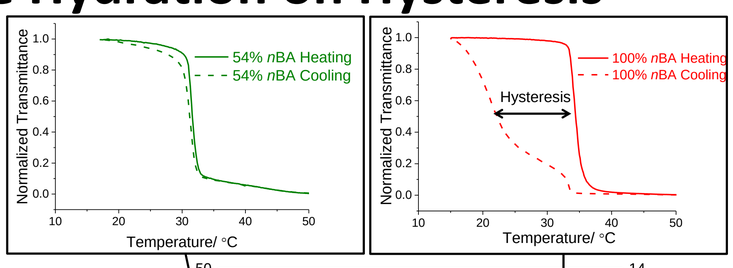
3. Assessing Thermoresponsive Behavior

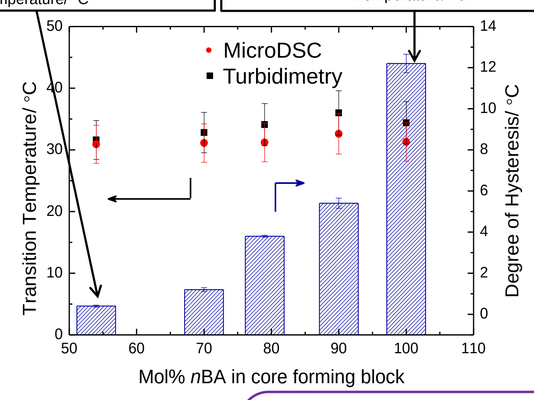
- Micelles were analyzed by variable temperature turbidimetry and microcalorimetry (microDSC).
- The cloud point transition temperature was observed by turbidimetry as a sharp decrease in the transmittance of light through the sample, as macroscopic precipitation occurred.
- The endotherm associated with the transition was observed by microDSC.

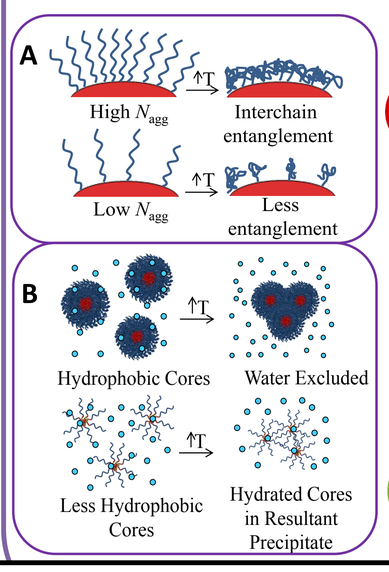


4. Hydrophobicity of the Micellar Core: The Effect of Core Hydration on Hysteresis

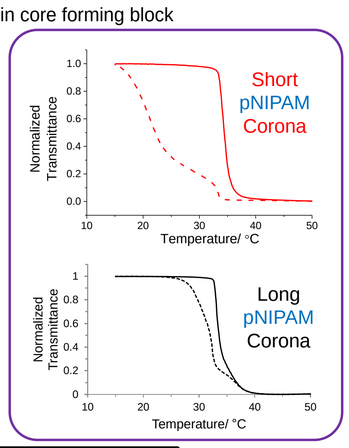
- The micelles' cloud point was assessed by turbidimetry.
- ↑*n*BA and ↑N_{agg} → cloud point remained the same.
- ↑*n*BA and ↑N_{agg} → ↑Hysteresis.
- Hysteresis caused by either an increase in chain entanglement at high N_{agg} (**A**) or a decrease in core hydration at high hydrophobicity (**B**).





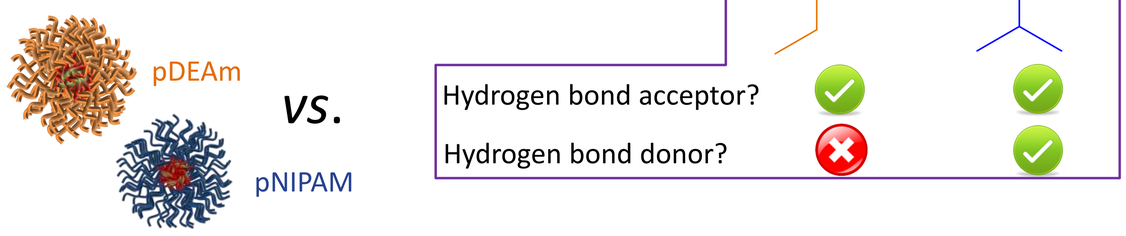


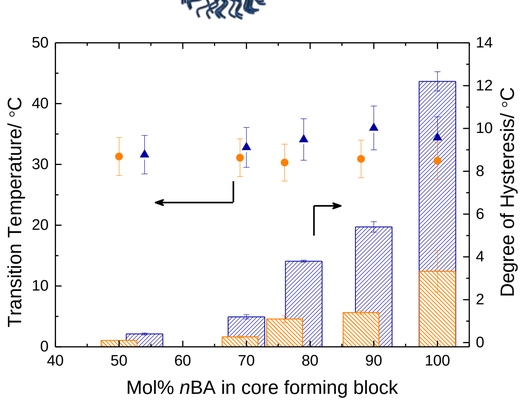
- Micelles with longer pNIPAM coronas had less hysteresis.
  - ➢ Differences in hysteresis across the series was a result of differences in the hydration of the micellar cores.



5. pDEAm *vs*. pNIPAM Coronas: The Effect of Hydrogen Bonding on Hysteresis

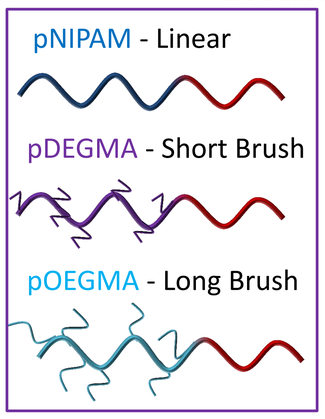
- Thermal hysteresis in pNIPAM systems has been widely attributed to pNIPAM's ability to form hydrogen bonds between polymer chains in the globular state above the transition temperature.



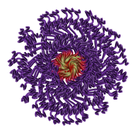


- Micelles with pDEAm coronas were investigated.
- pDEAm micelles had a lower hysteresis than the pNIPAM micelles on the whole → No polymer-polymer hydrogen bonding.
- A hysteresis was introduced in pDEAm micelles with very hydrophobic cores → Less hydrated aggregates in the globular state.

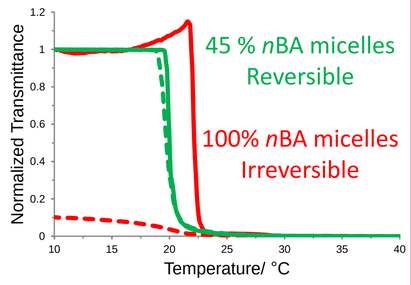
6. Linear *vs*. Brush-like Coronas: The Effect of Chain Confinement on Hysteresis

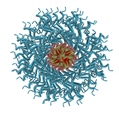


- Micelles with short (pDEGMA) and long (pOEGMA) brush side-arms were investigated.
- At low N_{agg}, the hysteresis of the pDEGMA micelles was minimal.
- At high N_{agg} pDEGMA micelles showed irreversible transitions.



pDEGMA





pOEGMA

- pOEGMA micelles also showed irreversible transitions.
- This behavior has been attributed to the increased entanglement of the brush-like chains, which prevents the rehydration of the micelles upon cooling.

Blackman, L. D.; Wright, D. B.; Robin, M. P.; Gibson, M. I.; O'Reilly, R. K. *ACS Macro Lett.* **2015**, *4*, 1210.

Blackman, L. D.; Gibson, M. I.; O'Reilly, R. K. *Manuscript in Preparation.*

Background References

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Acknowledgements

Malvern Instruments Ltd.
O'Reilly Group
Gibson Group
EPSRC Engineering and Physical Sciences Research Council
Warwick Medical School
erc European Research Council Established by the European Commission
Institute of Advanced Study IAS
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