

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/or

www.warwick.ac.uk/gibsongroup

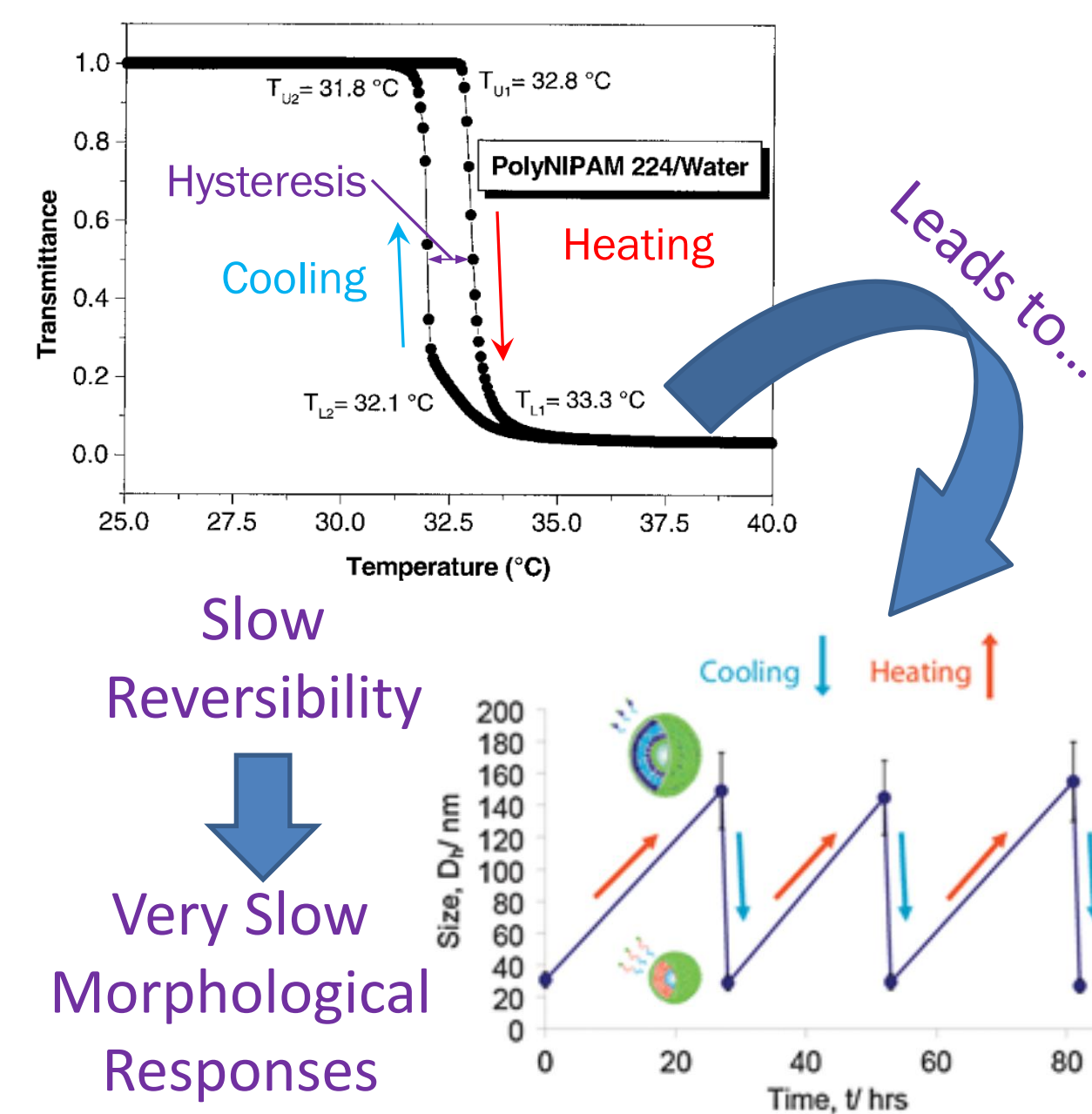


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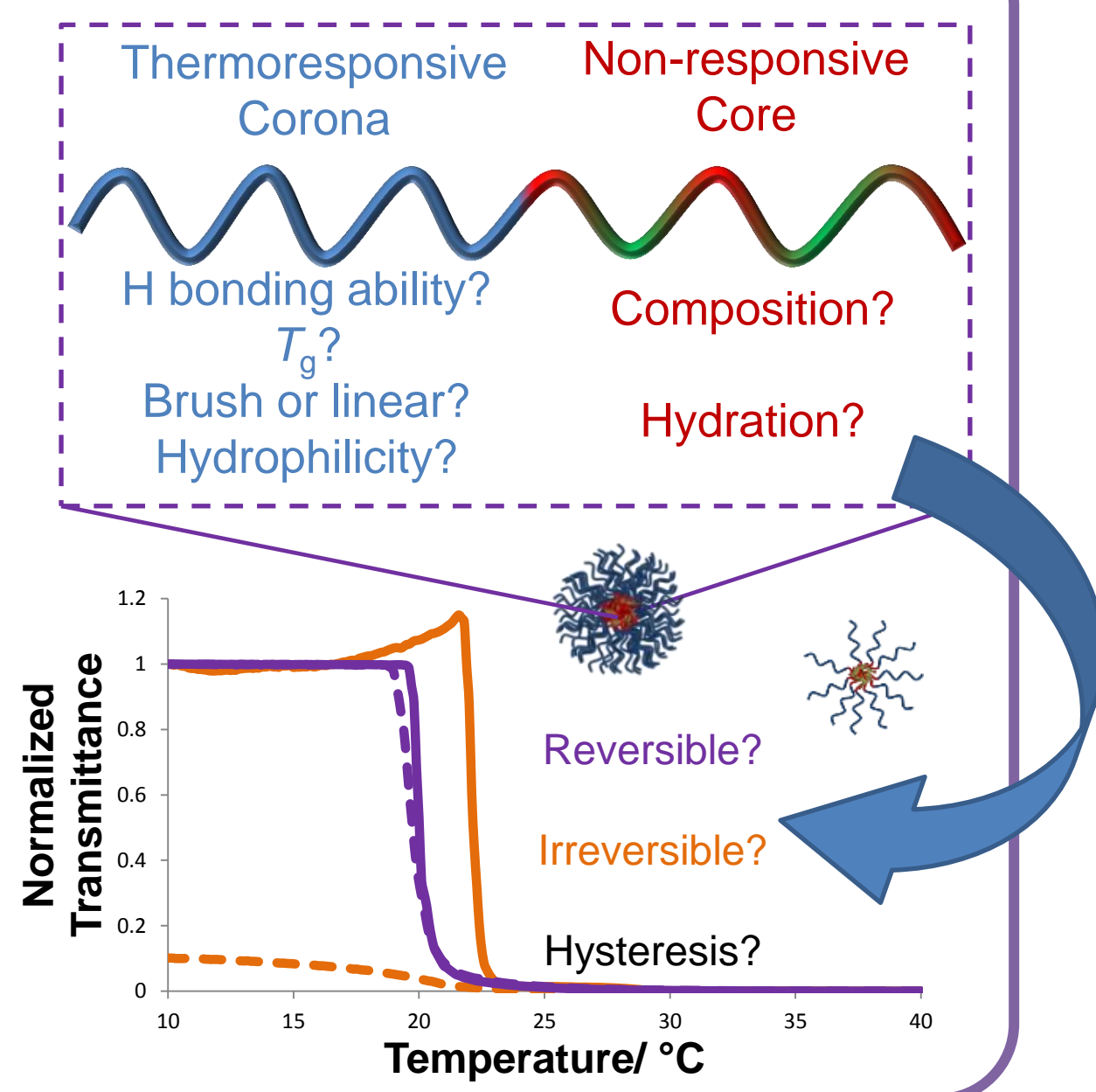
1. Background

- 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).

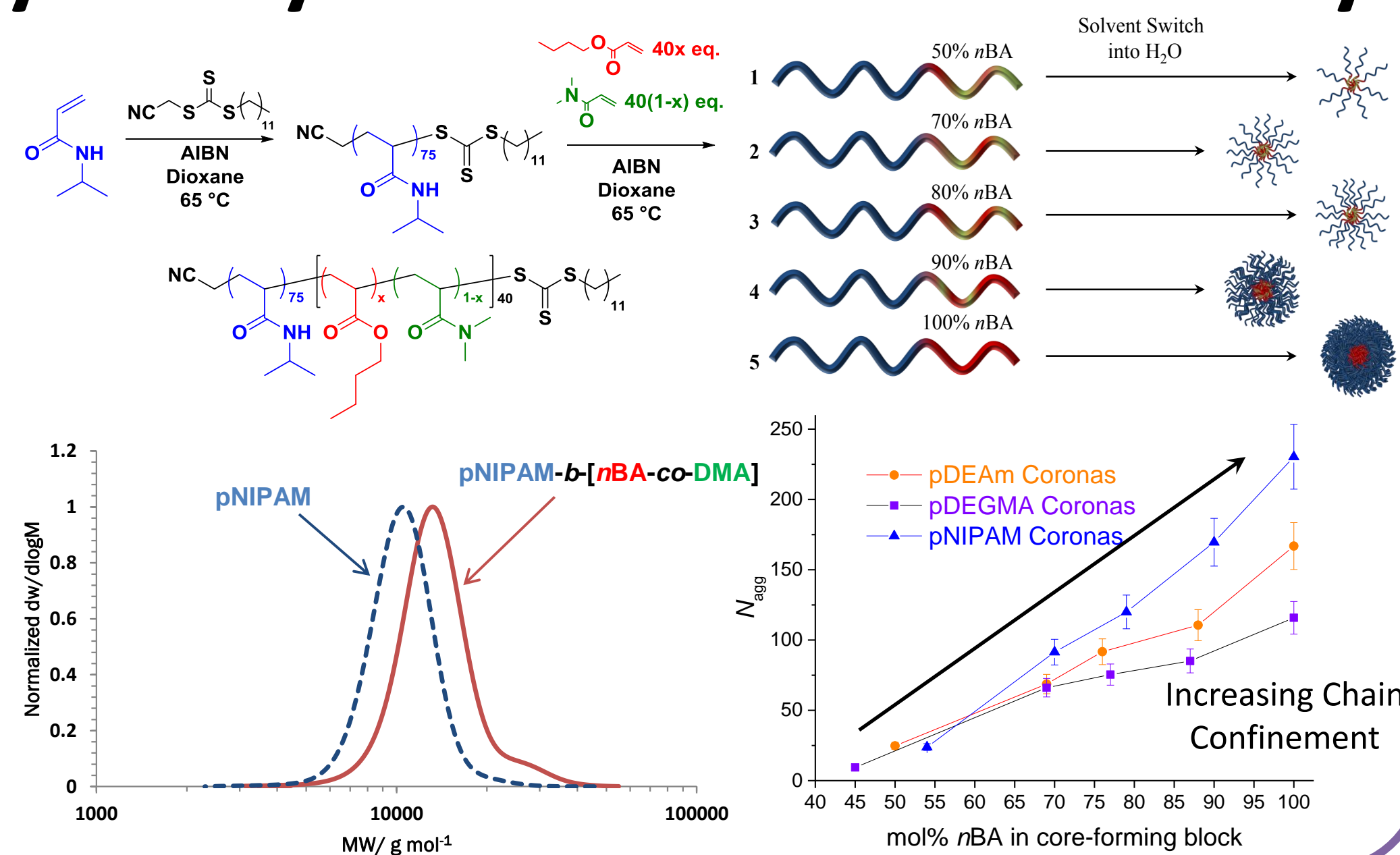


2. Block Copolymer Synthesis and Self-Assembly

- Diblock Copolymers were synthesized by RAFT polymerization.

- The copolymers were self-assembled into micelles and characterized by multi-angle SLS and DLS.

- $\uparrow nBA \rightarrow \uparrow N_{agg}$



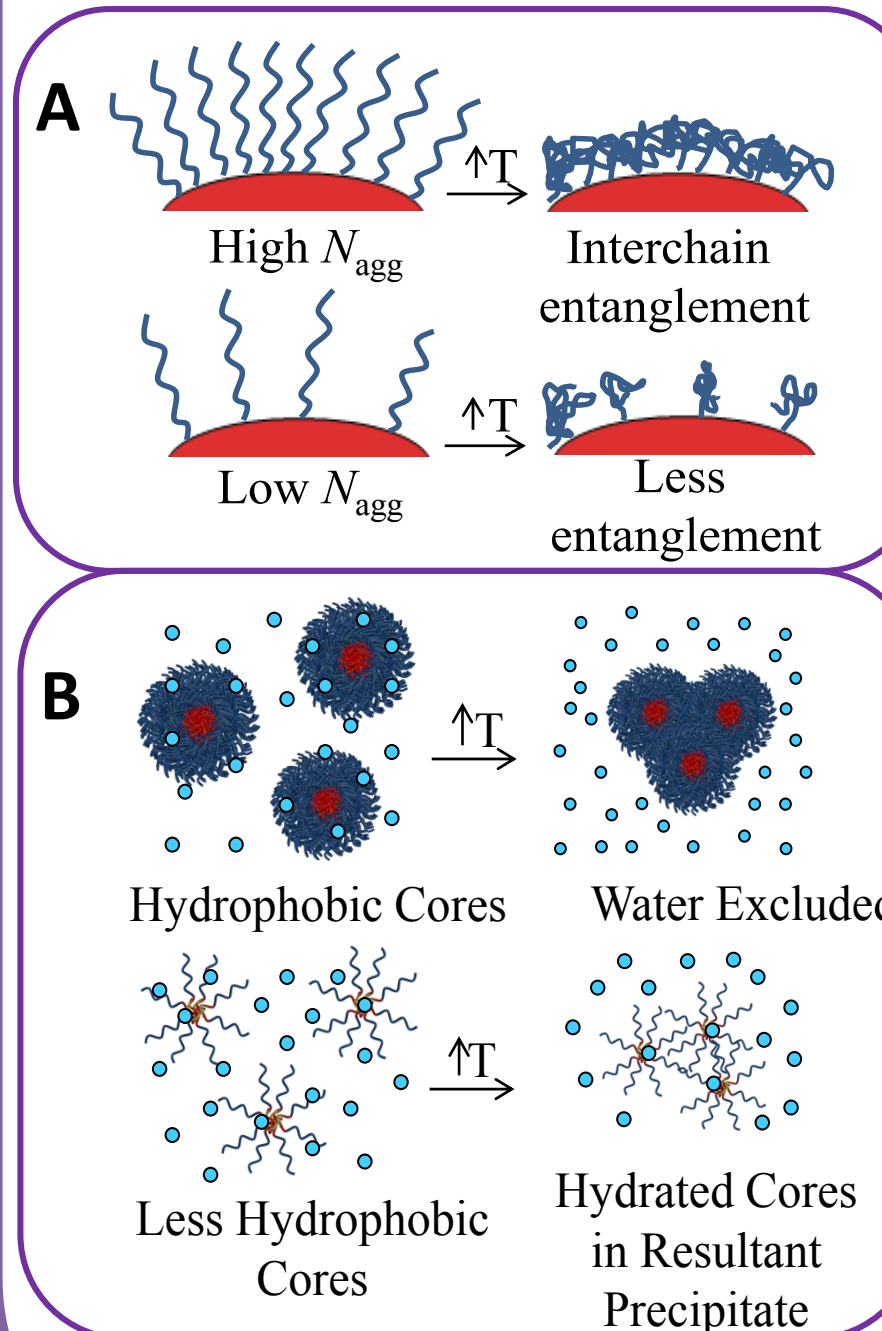
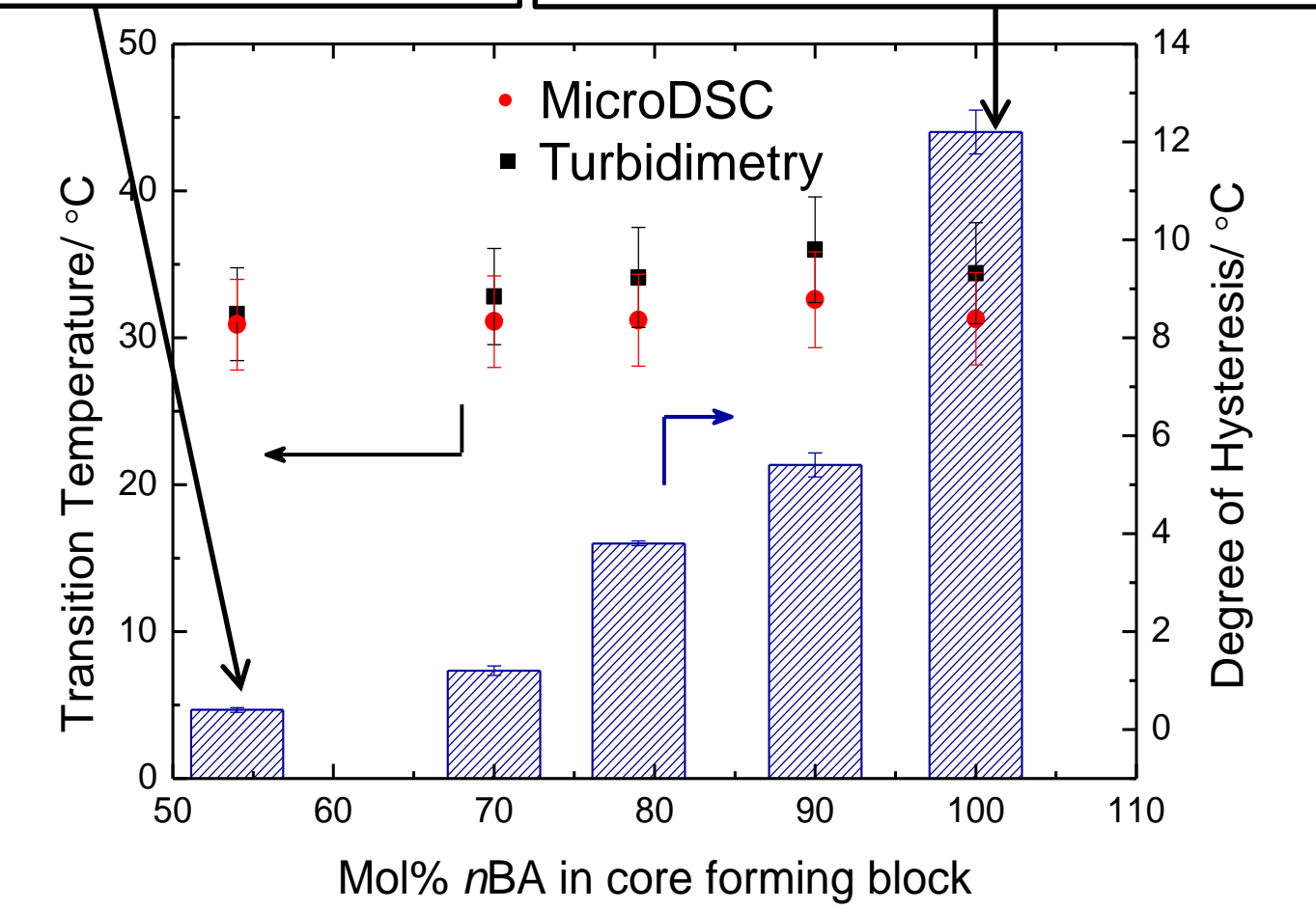
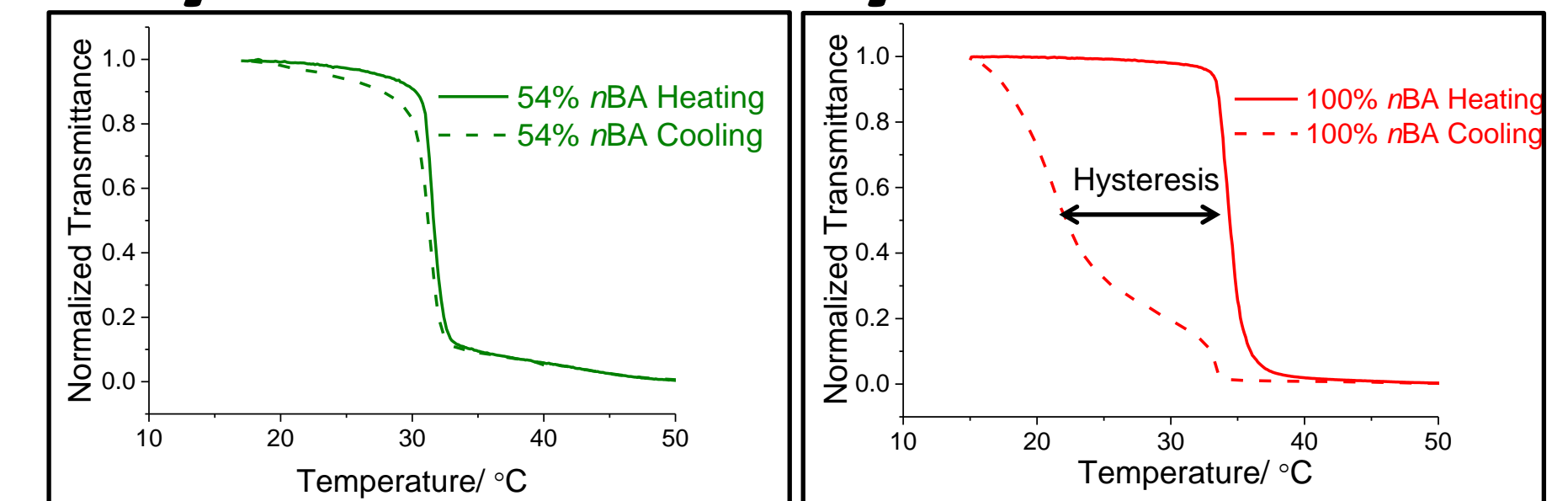
4. Hydrophobicity of the Micellar Core: The Effect of Core Hydration on Hysteresis

- The micelles' cloud point was assessed by turbidimetry.

- $\uparrow nBA$ and $\uparrow N_{agg} \rightarrow$ cloud point remained the same.

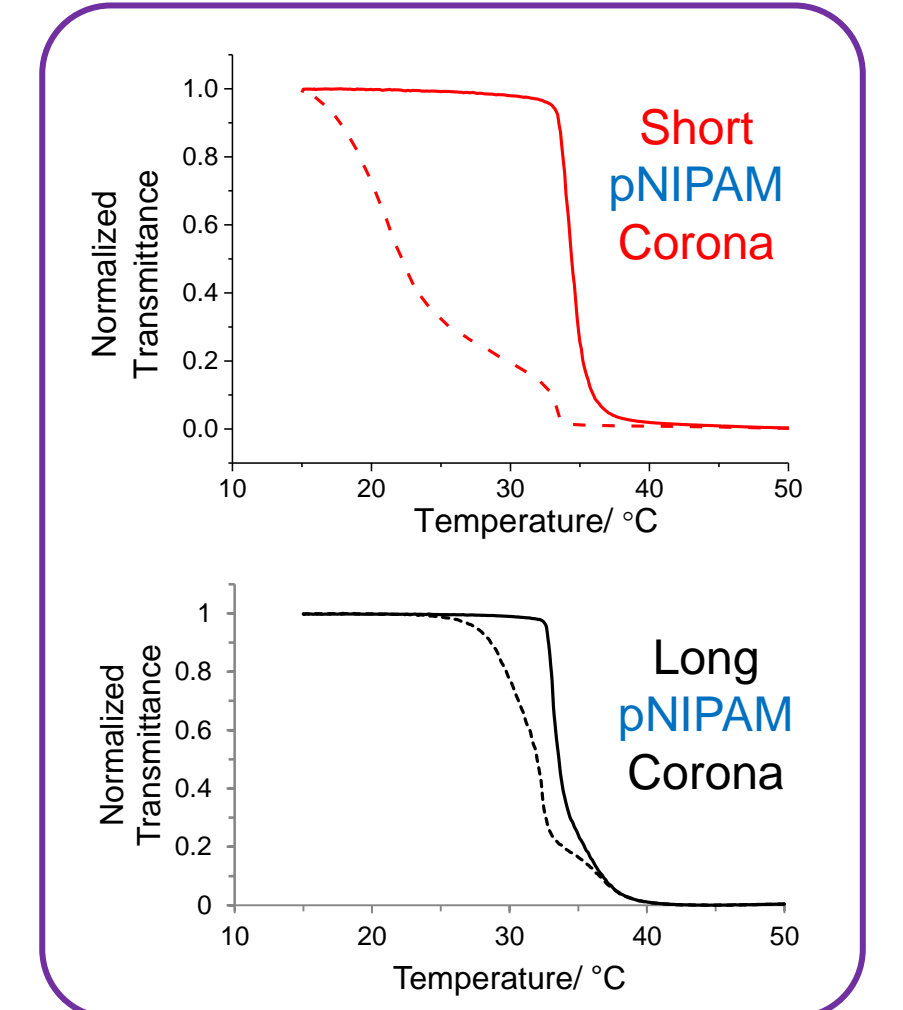
- $\uparrow nBA$ and $\uparrow N_{agg} \rightarrow \uparrow$ Hysteresis.

- 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.

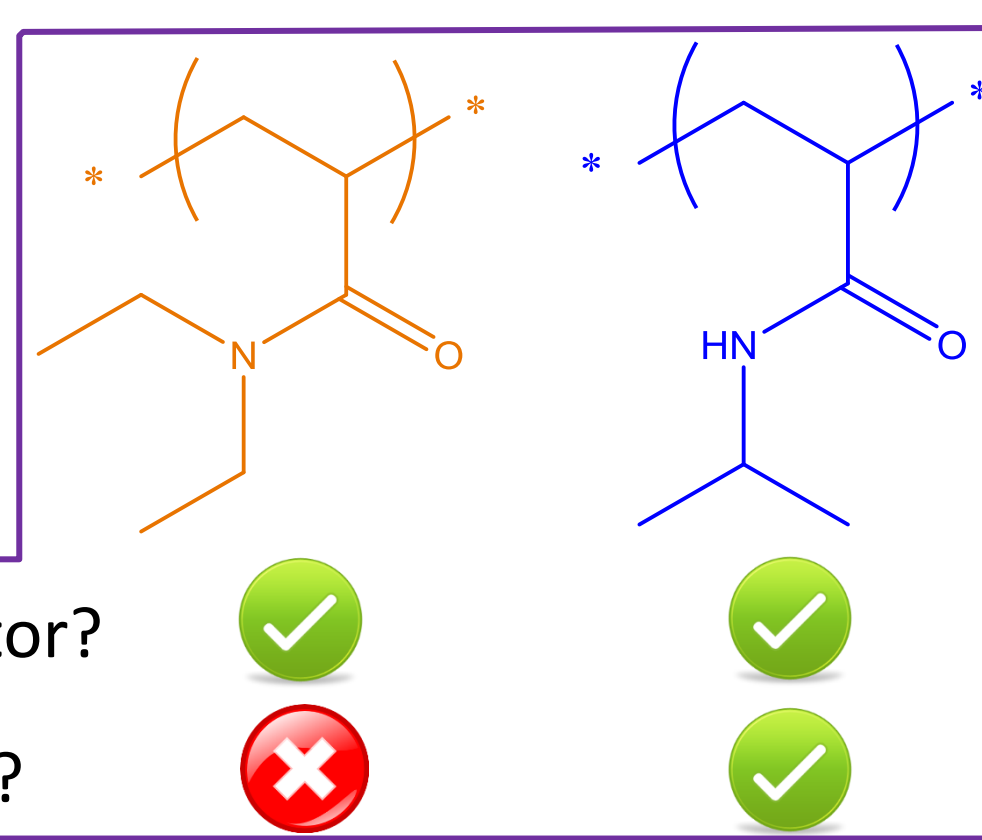
- Differences in hysteresis across the series was a result of differences in the hydration of the micellar cores.



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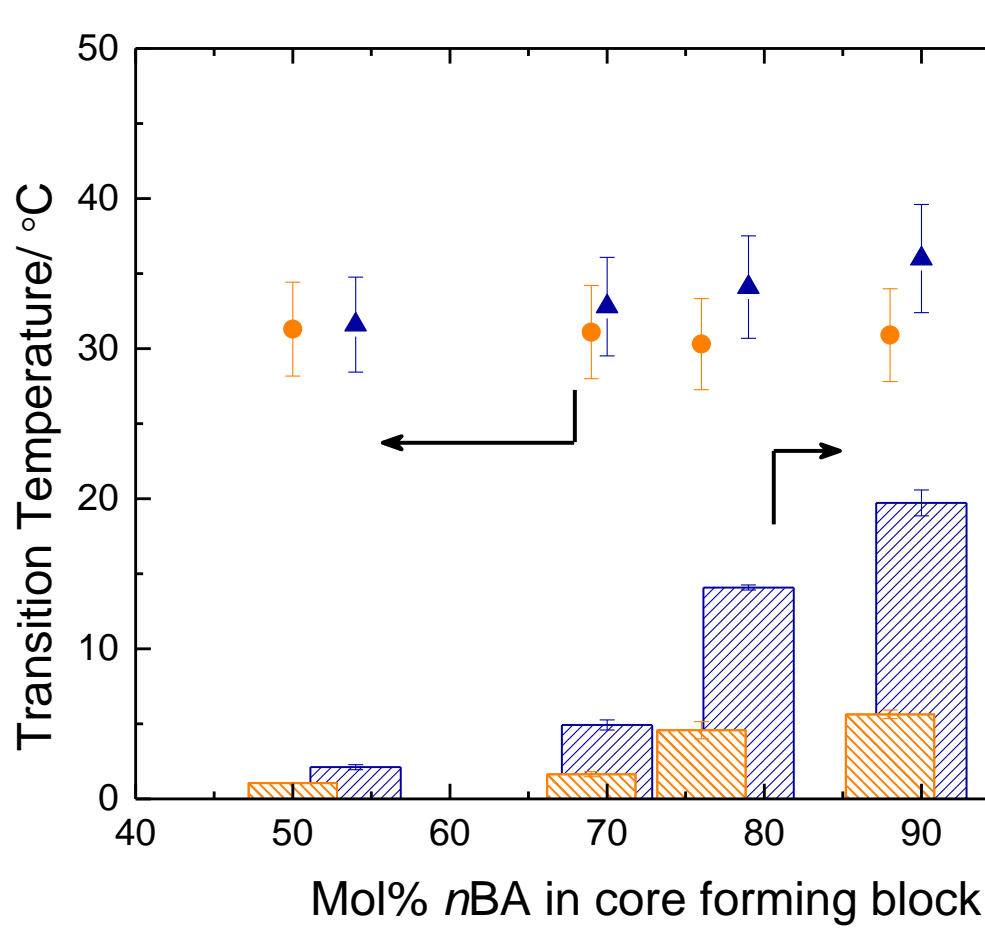
5. pDEAm vs. pNIPAM Coronas: The Effect of Hydrogen Bonding on Hysteresis

- 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.



Hydrogen bond acceptor?

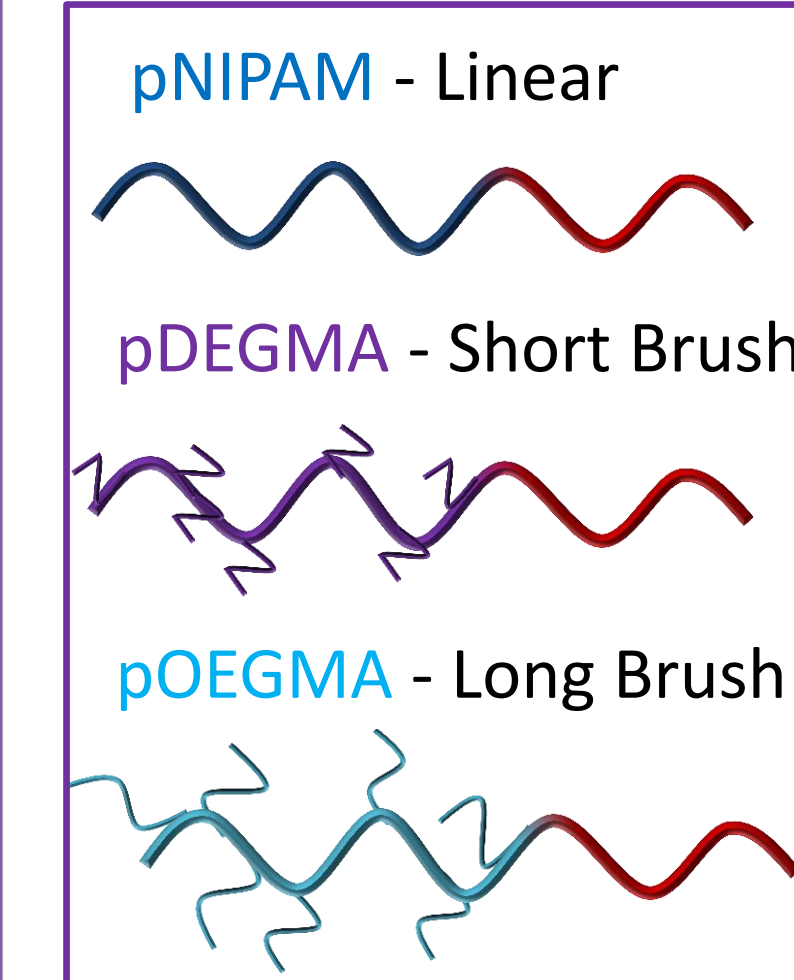
Hydrogen bond donor?



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

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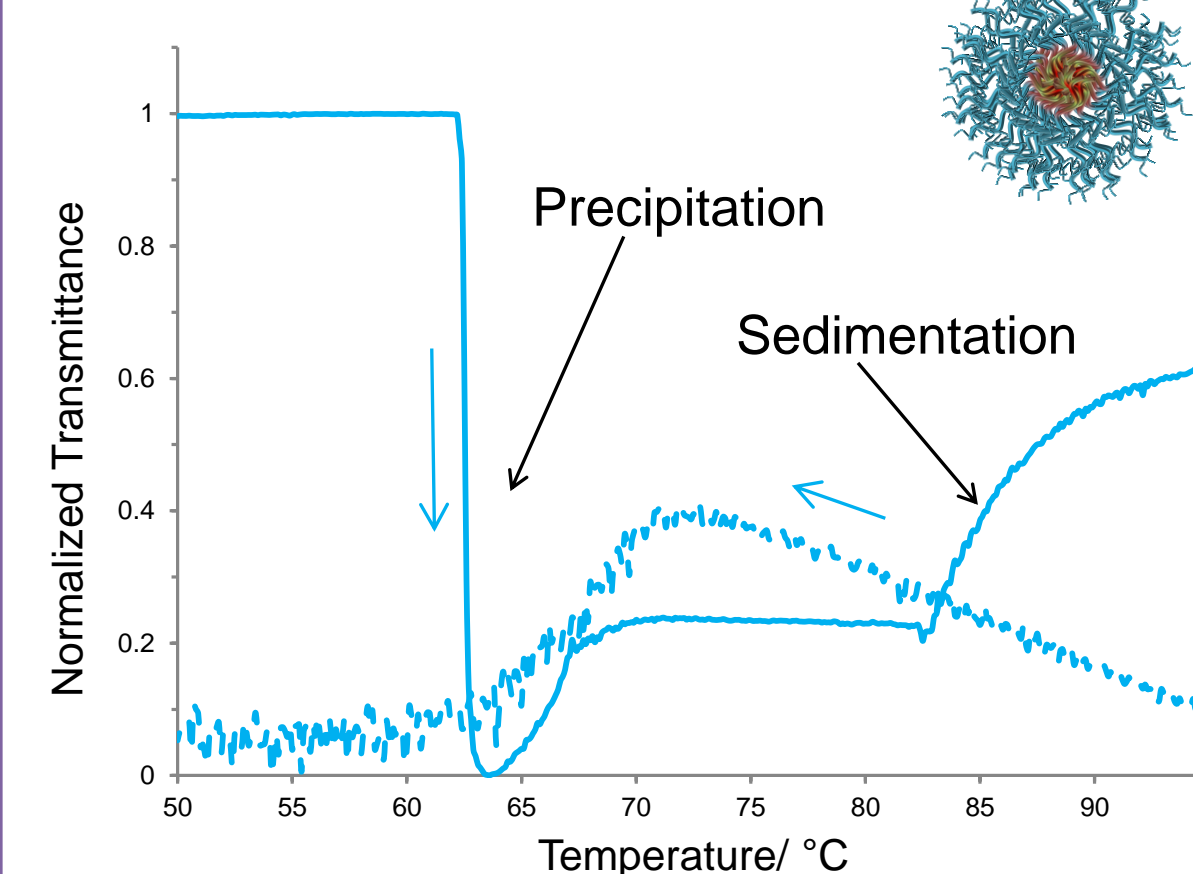
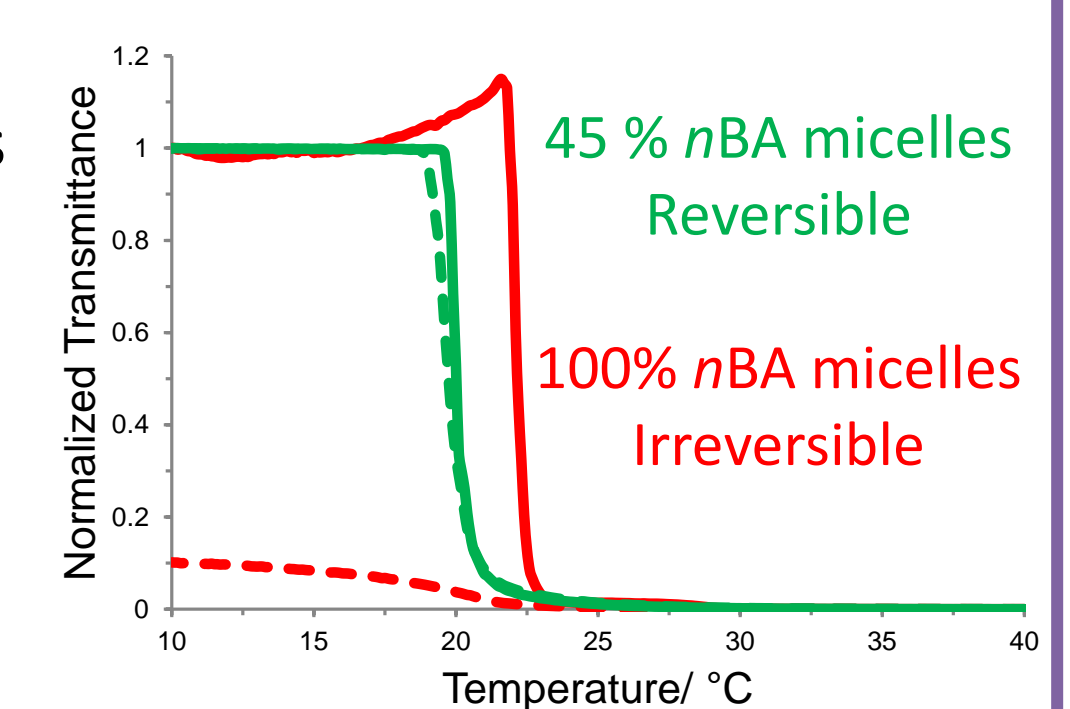
6. Linear vs. Brush-like Coronas: The Effect of Chain Confinement on Hysteresis



- 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.



- 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.

Background References

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