# Investigating Hysteresis in Thermoresponsive Assemblies

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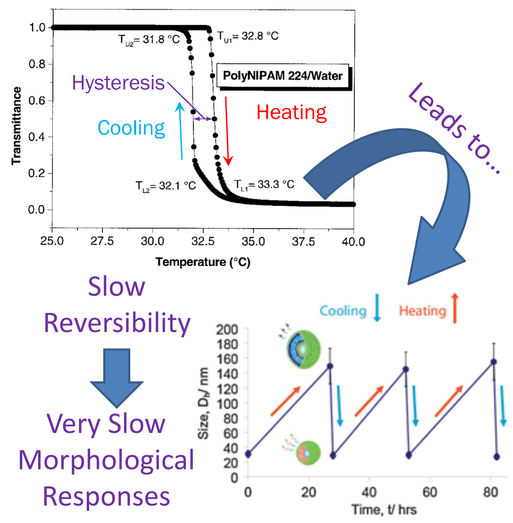
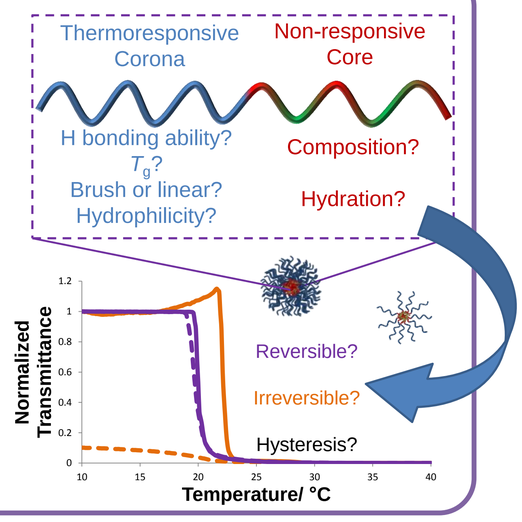
## 1. Background

- 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.

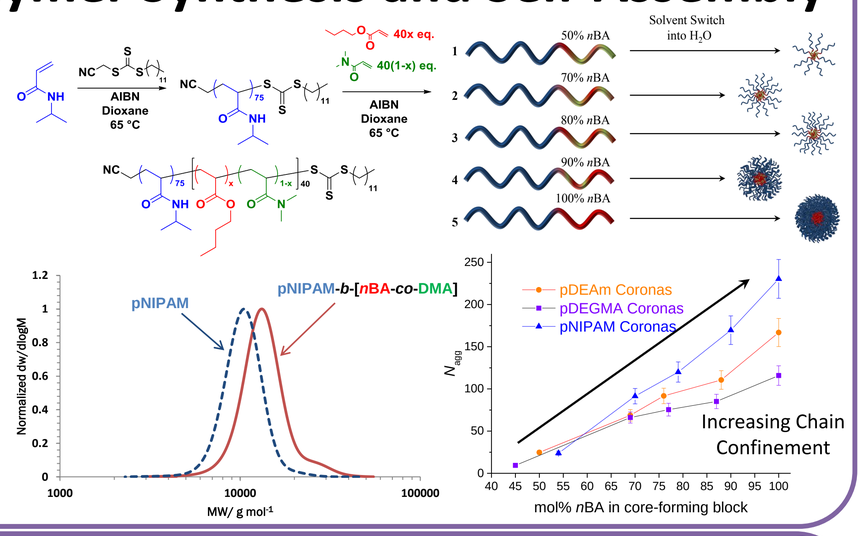



- Herein, we design micelles with tunable aggregation numbers ($N_{agg}$) and core hydrophobicities, in order to determine the effects of core hydration and chain confinement on thermal hysteresis. This was achieved using varying compositions of (p*n*BA-*b*-DMA) as the core block and pNIPAM as the thermoresponsive 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).



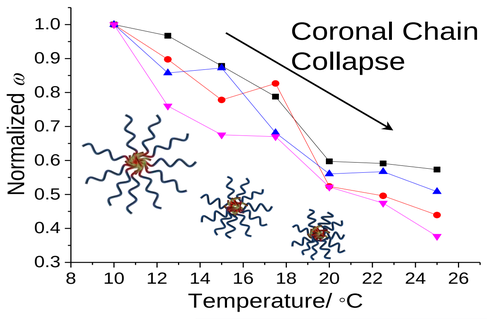

## 2. Block Copolymer Synthesis and Self-Assembly

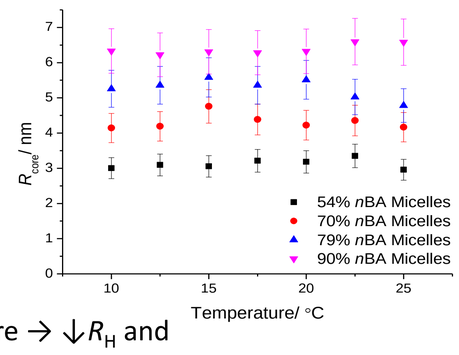
- Diblock Copolymers were synthesized by RAFT polymerization.
- The copolymers were self-assembled into micelles and characterized by multi-angle SLS and DLS.
- ↑*n*BA → ↑$N_{agg}$.




## 3. Variable Temperature Multi-Angle SLS and DLS

- Micelles with pNIPAM coronas were analyzed by multi-angle SLS and DLS at various temperatures below the thermal transition temperature.
- ↑Temperature → $N_{agg}$ and $R_{core}$ remain the same.

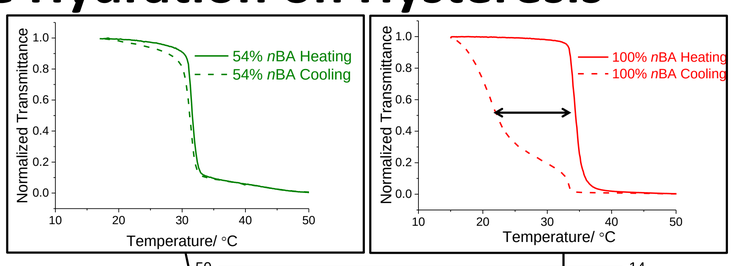


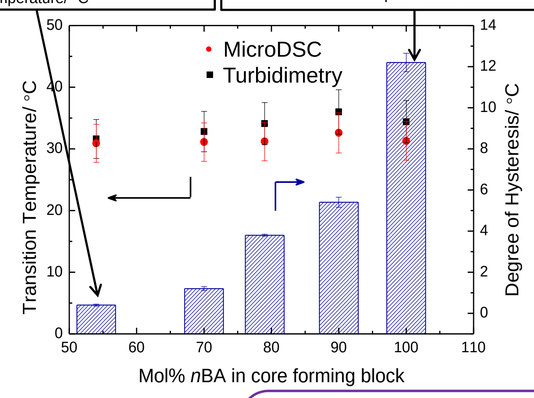



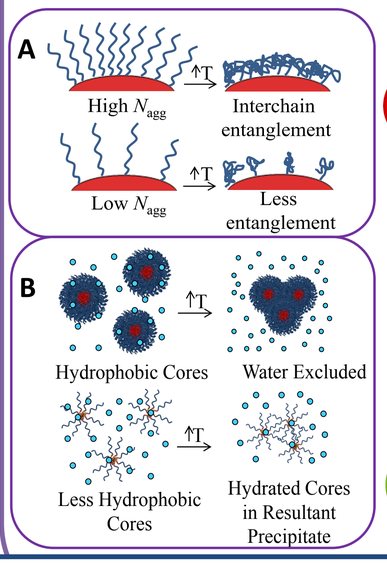

- ↑Temperature → ↓$R_H$ and ↓corona stretching parameter ($\omega$)
- This occurred at temperatures well below the cloud point

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

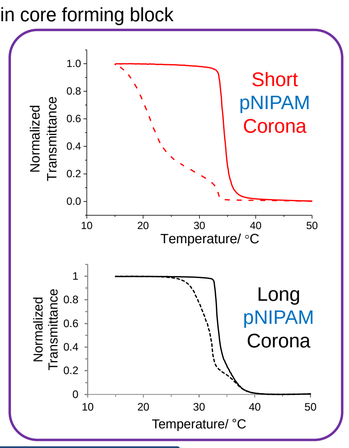
- The micelles cloud point was assessed.
- ↑*n*BA and ↑$N_{agg}$ → cloud point remained the same.
- ↑*n*BA and ↑$N_{agg}$ → ↑Hysteresis.
- Hysteresis caused by either an increase in chain entanglement at high $N_{agg}$ (**A**) or a decrease in core hydration at high hydrophobicity (**B**).



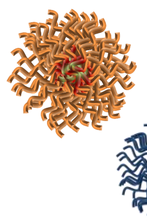

- Micelles with longer pNIPAM coronas had less hysteresis.
- Differences in hysteresis across the series was a result of differences in the hydration of the micellar cores.

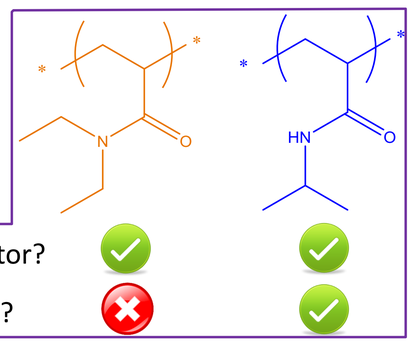



Blackman, L. D.; Wright, D. B.; Robin, M. P.; Gibson, M. I.; O'Reilly, R. K. *ACS Macro Letters* **2015**, 1210.

## 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.



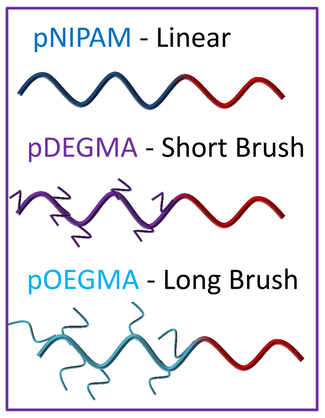





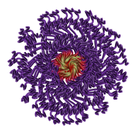


- Micelles with pDEAm coronas were investigated.
- pDEAm micelles had a lower hysteresis than the pNIPAM micelles on the whole → no polymer-polymer H bonding.
- A hysteresis was introduced in pDEAm micelles with very hydrophobic cores.

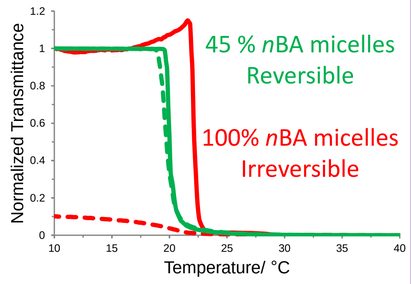
## 6. Linear *vs*. Brush-like Coronas: The Effect of Chain Confinement on Hysteresis

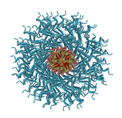



- Micelles with short (pDEGMA) and long (pOEGMA) brush side-arms were investigated.
- At low $N_{agg}$, the hysteresis of the pDEGMA micelles was minimal.
- At high $N_{agg}$ pDEGMA micelles showed irreversible transitions.



pDEGMA



pOEGMA




- pOEGMA micelles also showed irreversible transisitons.
- 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.; Gibson, M. I.; O'Reilly, R. K. *Manuscript in Preparation.*

*Background References*

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