

# Molecular Design of Tunable Biomimetic Polymeric Thin Films

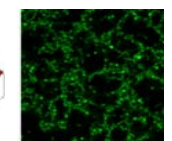
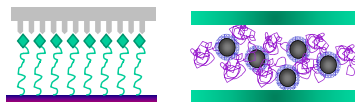
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## Polymeric Thin Films for Coating, Adhesion and Lubrication



## Molecular Design of Tunable Bio-inspired Interfaces

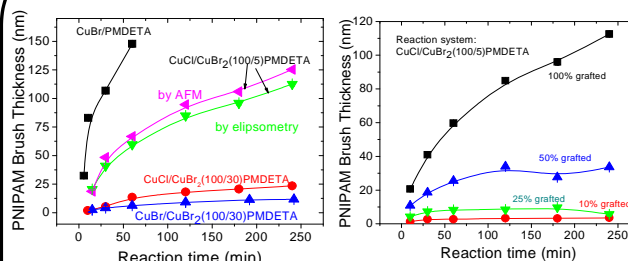


Polymer brush Hydrogel-polymer

### Objectives

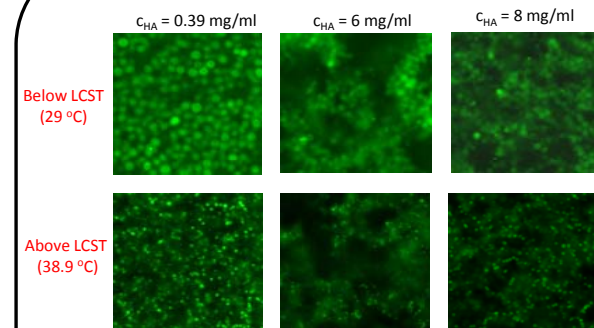
- Synthesis of smooth stimuli-responsive polymer thin films:** PNIPAM brush-like interfaces of controllable interfacial properties
- Colloidal reinforced biocompatible polymeric thin films:** Hyaluronic acid biopolymers added with hydrogel particles
- Structure and dynamics of proteins at polymer interfaces:** Single-molecule spectroscopy and imaging approach

## Control of growth and graft density of PNIPAM brushes



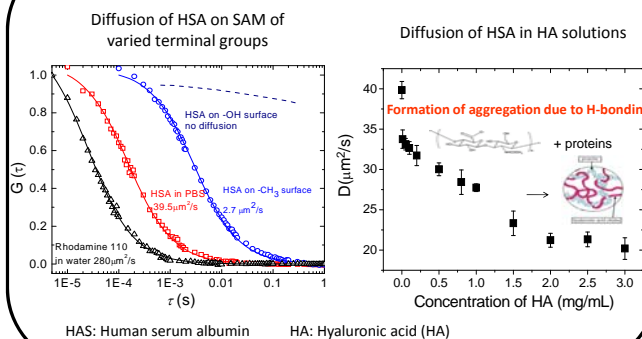
- Controllable ATRP reaction kinetics for PNIPAM brush growth
- PNIPAM graft density is varied by varying the mixture ratio of  $-CH_3$  terminated inert spacer and  $-Br$  terminated initiator upon LB deposition

## Control of hydrogel-biopolymer gelation

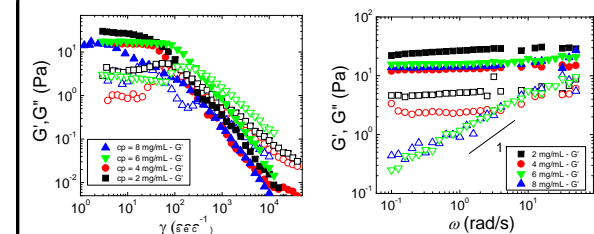


- Emergence of discernable fractal clusters at  $c_p = 6$  mg/ml
- No evident change in structure above LCST for high polymer concentrations
- Glass-like arrest observed for  $c_p < 1$  mg/ml below the LCST while ergodic fluid phase exists above LCST

## Protein interaction with surfaces and biopolymer solutions



## Viscoelasticity of hybrid hydrogel-polymer thin films

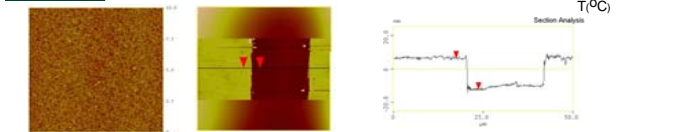
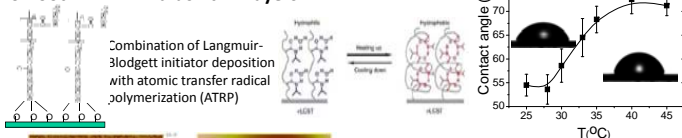


- Characteristic behavior of "soft glassy materials"
- Low frequency plateau in  $G'$
- Shear thinning is evident at high shear rate and broad peak in  $G''$  signifies structural relaxation
- Little difference in magnitude of  $G'$  and  $G''$  above 2 mg/ml

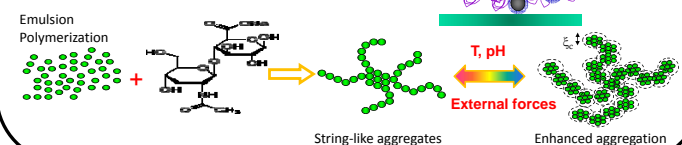
## System Employed: Poly(N-isopropylacrylamide) (PNIPAM)-Based

PNIPAM: Lower Critical Solubility Temperature (LCST) close to body temperature  
Stimuli-responsive, Biocompatible, High water content...

### Smooth PNIPAM brush thin layers

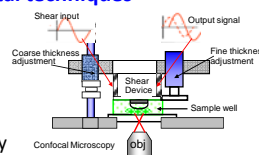


### PNIPAM hydrogel-biopolymer hybrid thin films

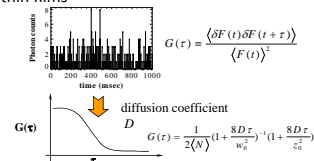
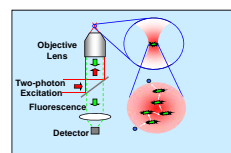


## Experimental techniques

- Confocal Micron-Gap Rheometer:**
  - Single-particle imaging
  - In-situ interfacial friction measurement



- Fluorescence Correlation Spectroscopy**
  - Single-molecule spectroscopy
  - In-situ measurement of confined thin films



## Summary

- Successful synthesis of molecularly smooth stimuli-responsive PNIPAM brush layers of controllable thickness and graft density
- Strong effect of surface hydrophobicity on surface diffusion of HSA protein
- Protein-polymer aggregation due to H-bonds and hydrophobic interaction with a strong dependence of polymer additive concentration
- Ongoing work** on macromolecular dynamics:
  - Effect of environmental stimuli (T, pH, ionic strength) on protein-PNIPAM interactions.
  - Effect of PNIPAM brush thickness, grafting density, end-functionality, etc.

## Acknowledgments

3M non-tenured faculty award

