Award No. DMR-0934115

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Solid-like Liquid Crystalline Materials

Wisconsin - Puerto Rico Partnership for Research and Education in Materials

nm mrsec University of Wisconsin-Madison

University of Wisconsin–Madison NSEC

University of Wisconsin - Madison
Madison, Wisconsin

University of Puerto Rico - Mayagüez
Mayagüez, Puerto Rico

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Host-defense
Peptide-mimetic
Foldamers and Polymers
as Antimicrobial agents

Health

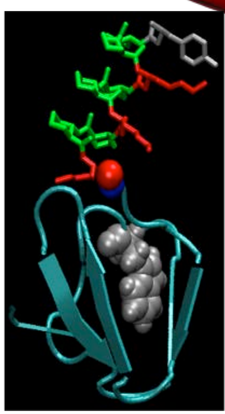
Liquid Crystalline
Elastomers and Gels
with tunable properties

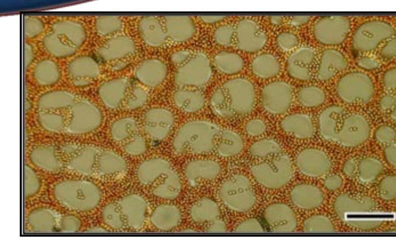
Novel Smart Materials

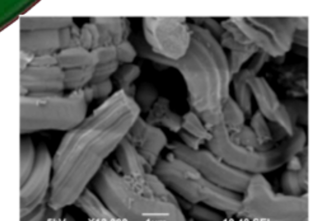
Synergistic-Coherent
Research and Education

Multifunctional
Nanoporous
Materials for
Sustainable Catalysis

Renewable Energy &
Climate Change

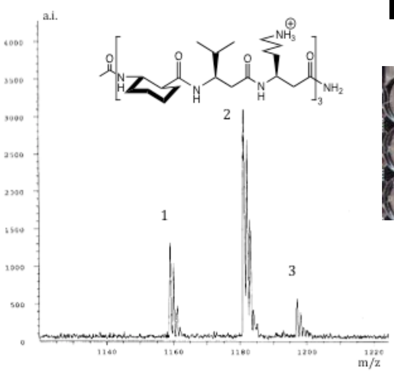






IRT 1- Host-defense peptide-mimetic foldamers as antimicrobial agents

Synthesis and characterization of antimicrobial beta-peptides at UPRM



(ACHC-V-K)$_3$

[0][beta-peptide]

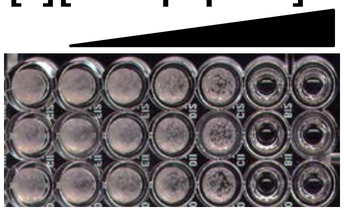
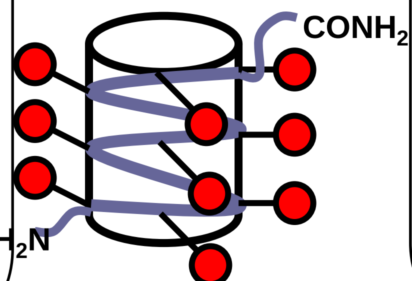


Table 1. Average Minimum Inhibitory Concentrations (MIC) against *C. albicans* and Percent Hemolysis at the Average MIC

peptide	average MIC[a] µg/mL	% hemolysis at MIC[b]
L-magainin 2 derivative	>128	48*
D-magainin 2 derivative	>128	48*
β^3Tyr-(ACHC-β^3Val-β^3Lys)$_3$ (1)	16	21
β^3Tyr-(ACHC-β^3Leu-β^3Lys)$_3$ (2)	11	73
β^3Tyr-(ACHC-β^3Phe-β^3Lys)$_3$ (3)	8	80
β^3Tyr-(β^3Val-β^3Val-β^3Lys)$_3$ (4)	69	9
β^3Tyr-(ACHC-ACHC-β^3Lys)$_3$ (5)	21	7
(ACHC-β^3Val-β^3Lys)$_3$ (6)	17	5
β^3Lys-β^3Val-β^3Val-ACHC-β^3Lys-β^3Val-ACHC-ACHC-β^3Lys (7)	>128	ND

Design of new, more selective antifungals…

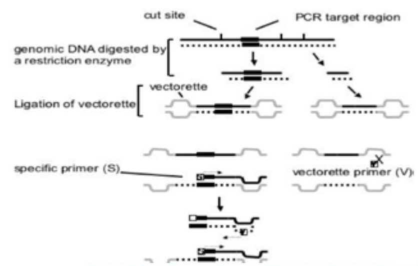
- ❖Improve transport into the cell
- ❖Targeting
- ❖Develop biomedical applications

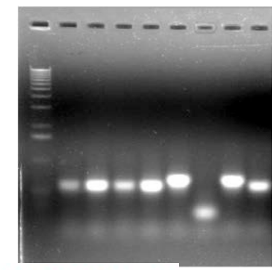


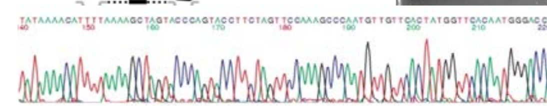
β-peptides: antimicrobial, biologically-inspired materials

MICROBE

A genetic approach for the elucidation of the mechanisms of action of antifungal β-peptides

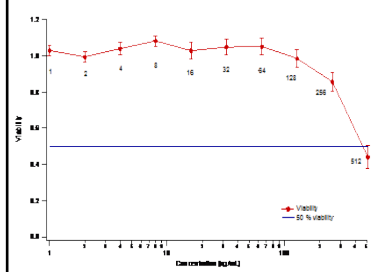


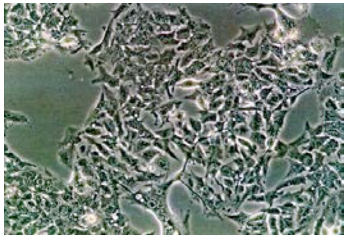




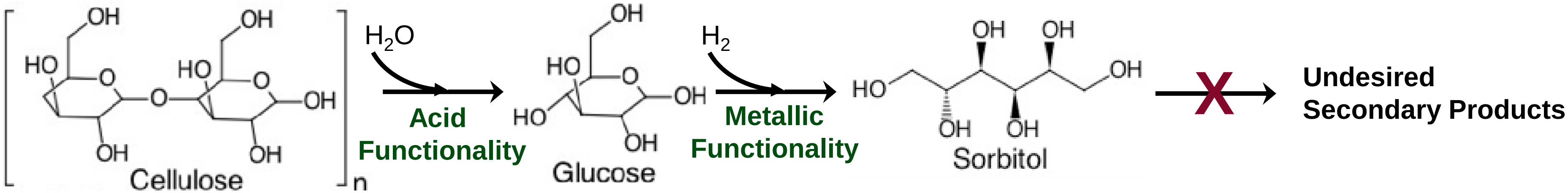
HOST

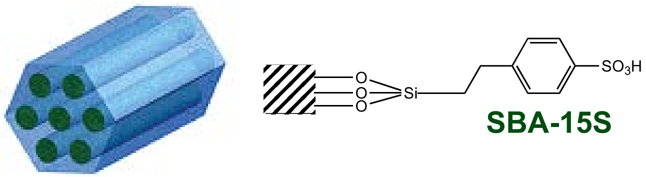
Studying toxicity of beta-peptides on liver cells





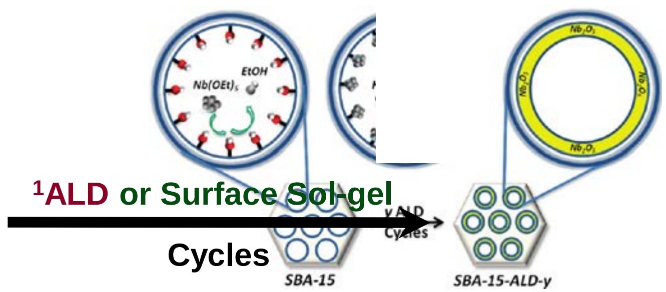
Bifunctional materials with Improved Hydrothermal Stability for the catalytic conversion of cellulose into soluble renewable feedstocks





- Activity increases with an increase in sample acidity.
- Addition of Ru controls selectivity.
- Ru/SBA-15S is more hydrothermally stable than SBA-15, but not sufficiently for industrial application.

Reyes-Luyanda, D.; Flores-Cruz, J.; Morales-Pérez, P.; Encarnación-Gómez, L.; Shi, F.; Voyles, P.; Cardona-Martínez, N., Top. Catal. 2012, 55(3), 148-161.

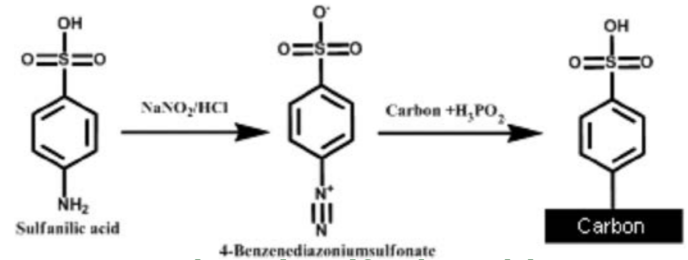


Developed Mesoporous Niobia – Silica Composite Catalysts with Improved Hydrothermal Stability

1. Pagán-Torres, Y. J.; Gallo, J. M. R.; Wang, D.; Pham, H. N.; Libera, J. A.; Marshall, C. L.; Elam, J. W.; Datye, A. K.; Dumesic, J. A., ACS Catal. 2011, 1(10), 1234-1245.

Development of Mesoporous Carbons with Acid Functionalities with Improved Thermo Solvent Stability

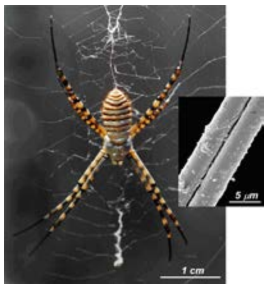
CMK-3, CMK-5, FDU-15 Mesoporous Carbons

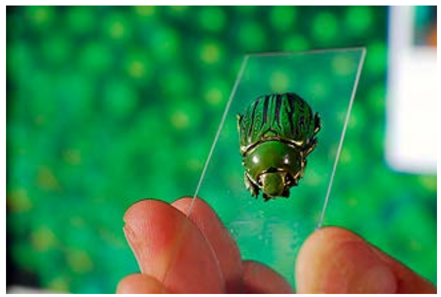


Phenyl Sulfonic Acid Functionalized Carbon

Liquid Crystalline Materials

- Anisotropic materials
- Undergo changes in ordering in response to chemical and biological stimuli
- Change properties in response to external stimuli (flow, M or E)





This is evident in the functional versatility of biological systems.

Biological Systems:
- spider silk
- slime of slugs
- chemoresponsive membranes

Synthetic Systems:
- electronics
- displays
- structural

Unresolved challenge: to design low molecular weight LC composite materials with mechanical properties that permit facile processing and integration into devices while maintaining their responsiveness to a range of stimuli.

Limitation: fluid nature of the liquid crystal

IRT 3 Objectives

The main objective is to lead a concerted **theoretical and experimental effort** for the rational design of solid-like LC systems:

- colloidal liquid crystal gels with magnetic nano and micro-particles
- chemically crosslinked liquid crystalline elastomers modified with magnetic nano and micro-particles

Which will allow us to identify the origins of experimentally observed behaviors and to design or dial-in specific thermodynamic, mechanical, and optical responses that rely on advanced molecular models of the considered materials.

Integration w/ other IRT3 Projects

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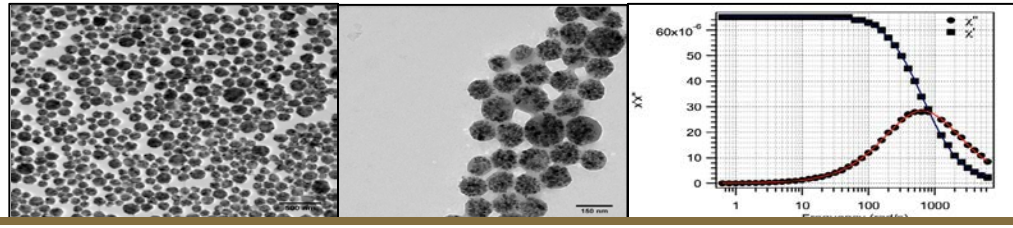
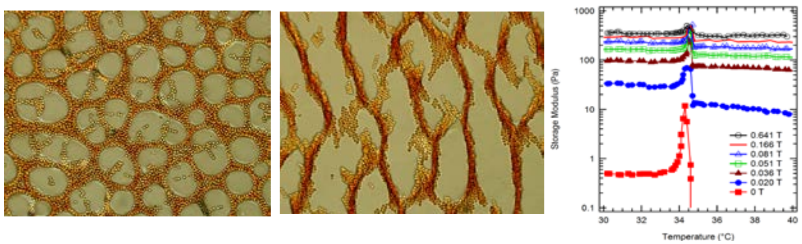
Synthesis of Magnetic Polymer Nanospheres
Edwin De la Cruz/Carlos Rinaldi



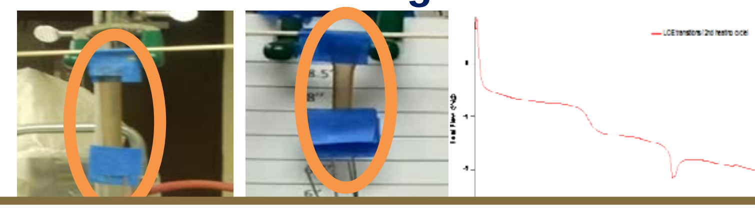
De la Cruz, worked at UW with Abbott (summer 2010)

PROVIDE

Colloid-in-Liquid Crystal Gels
Heberth Diestra/Aldo Acevedo

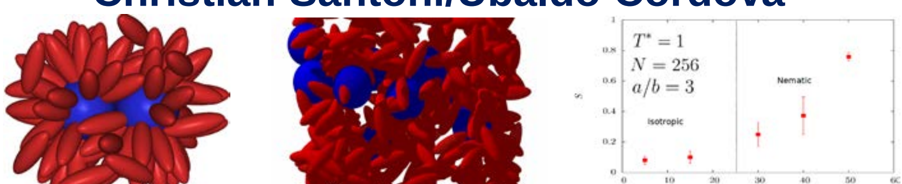


Liquid Crystal Elastomers
S. Herrera / B. Calcagno / A. Acevedo



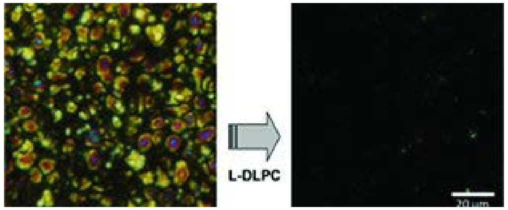
Calcagno visited UW to interact with Crone (summer 2011)

Diffusion, rheology and structure of LC suspensions via Brownian Dynamics Simulation
Christian Santoni/Ubaldo Córdova



Ubaldo visited UW to interact with de Pablo and Abbott
Santoni, worked at UW with de Pablo (summer 2012)

Surface-Driven Ordering Transitions in LC Composites
N. Abbott (UW)

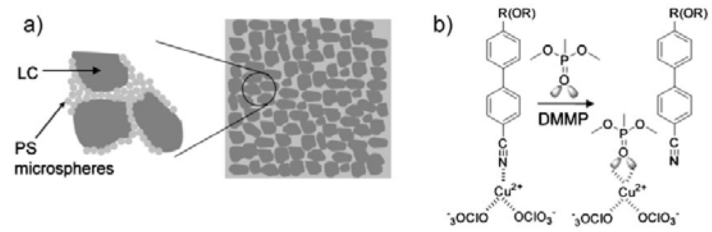


Colloid-in-Liquid Crystal Gels (CLCGs)

In 2008, Abbott's group at University of Wisconsin synthesize CLCGs with commercial polystyrene micro-particle (1µm) and the 5CB, E7, TL205 NLCs and use these soft materials as support in the cell culture of fibroblast and chemically responsive liquid crystal sensors.

Colloid-in-liquid crystal gels that support growth of

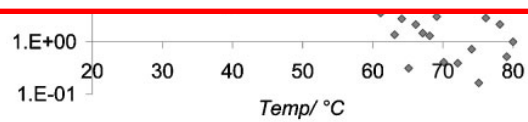
Chemically Responsive Gels

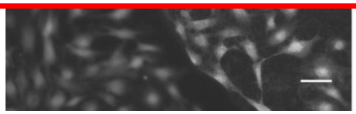


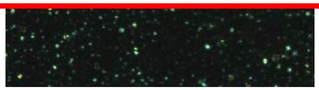
Nevertheless,

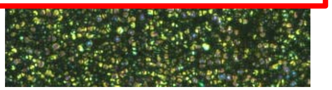
(1) The structure/orientation and mechanical properties of the substrate can control the type of cell grown.
(2) Detection in liquid interfaces require stronger materials (to support weight) and thicker (better signal and more manageable).

Can we modify CLCGs with magnetic particles to meet these criteria?









Agarwal, A.; Huang, E.; Palecek, S.; Abbott, N. L. Optically Responsive and Mechanically Tunable Colloid-In-Liquid Crystal Gels that Support Growth of Fibroblasts. Adv. Mater. 2008, 20, 4804–4809.
Pal, S. K.; Agarwal, A.; Abbott, N. L. Chemically Responsive Gels Prepared from Microspheres Dispersed in Liquid Crystals. Small 2009, 5, 2589–2596.

Rheological, Optical, and Thermal Characterization of Temperature-Induced Transitions in Liquid Crystal Ferrosuspensions

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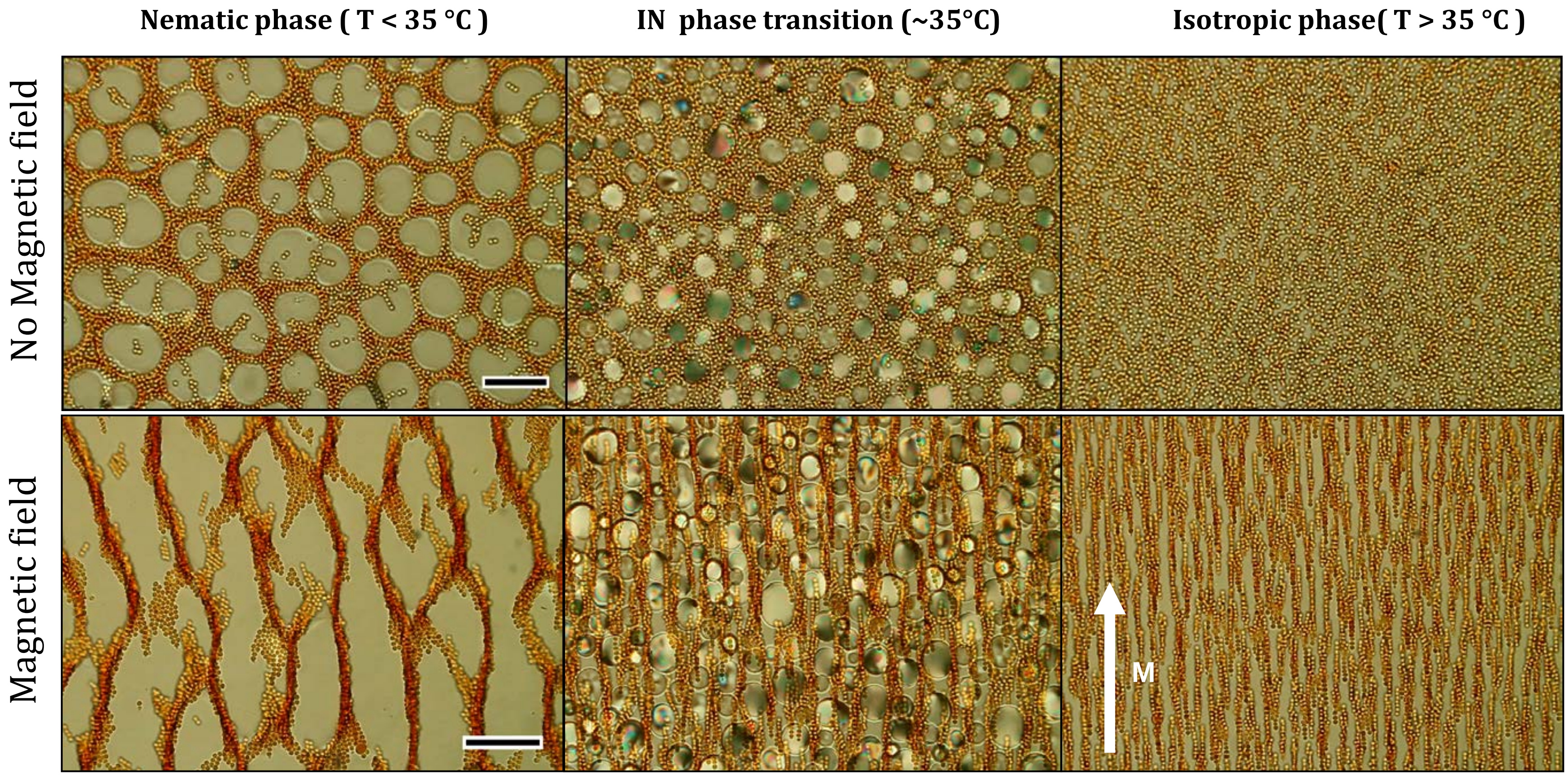
H. Diestra-Cruz, **C. Rinaldi** & **A. Acevedo**

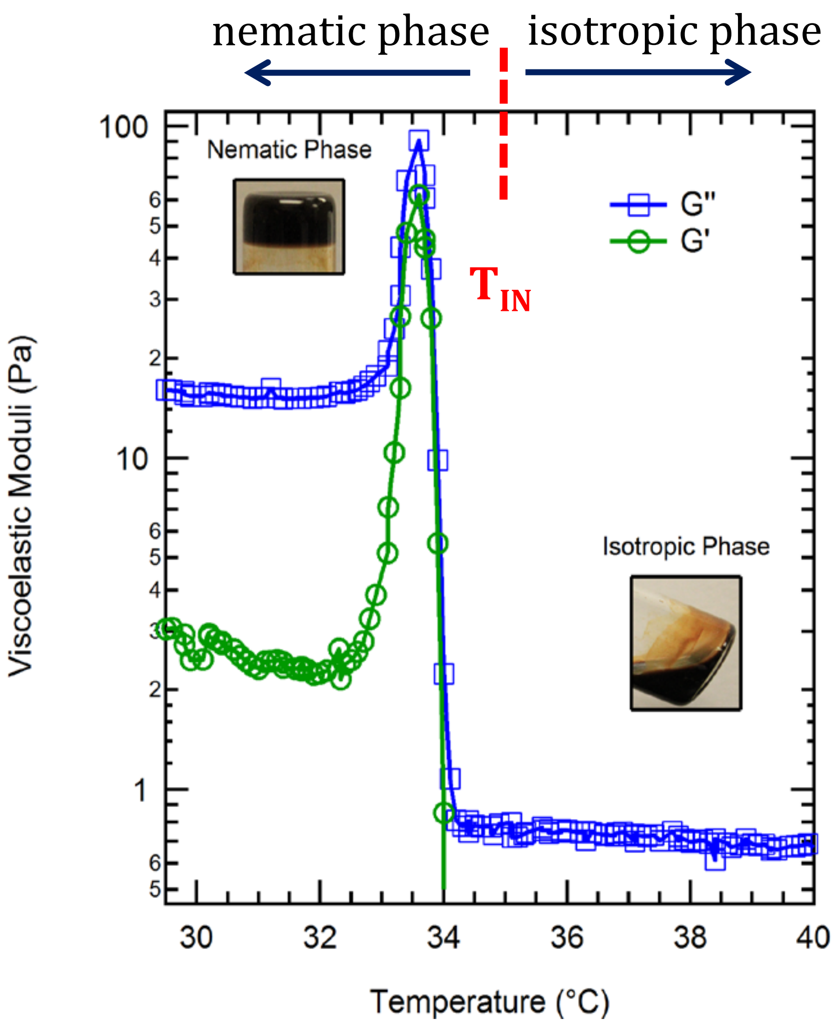
Commercial superparamagnetic microparticles (d ~ 3 μm)
Nematic liquid crystal 5CB (T_{IN} = 35°C)

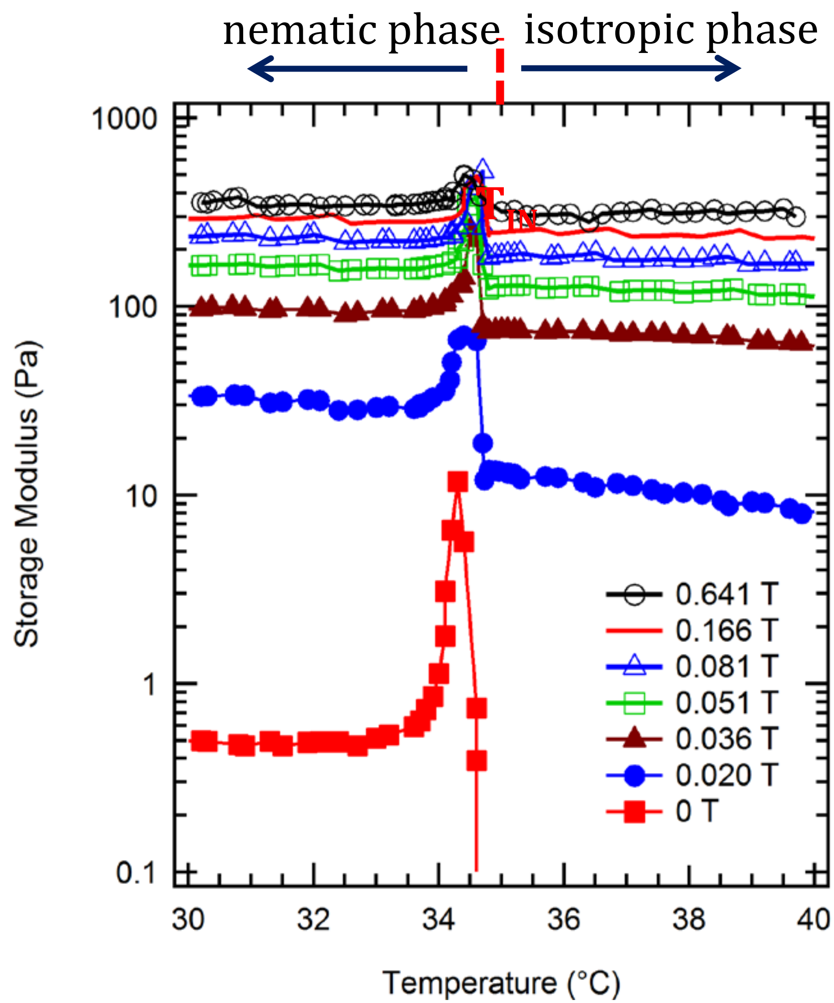
decreasing temperature ←



Network morphology in the nematic phase of a 10 wt% LCFs at magnetic field of 0 T (top) and 0.067 T (bottom). Arrow indicates the field direction. Scale bar: 50 µm.

Rheological characterization





Temperature dependence of loss (G'') and storage (G') modulus for the 20 wt% LCF at zero field (left).
Temperature dependence of the storage modulus for the 10 wt% LCF at different magnetic fields (right).

Magneto-rheological characterization

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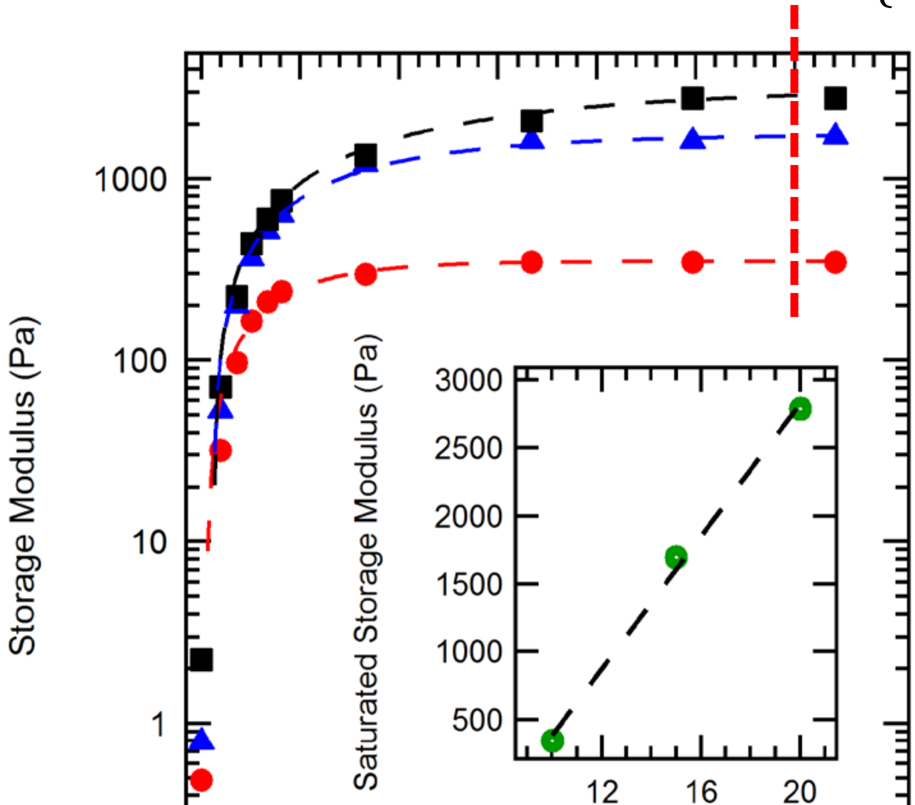
Mechanical saturation (~0.6 T)



NEMATIC PHASE

The storage modulus (G') is dependent of the magnetic field

- G' = 0.5 – 500 Pa (10 wt%)
- G' = 1 – 1500 Pa (15 wt%)
- G' = 3 – 3000 Pa (20 wt%)

G' can be controlled by external magnetic fields over several orders

JOURNAL OF APPLIED PHYSICS **111**, 07B308 (2012)

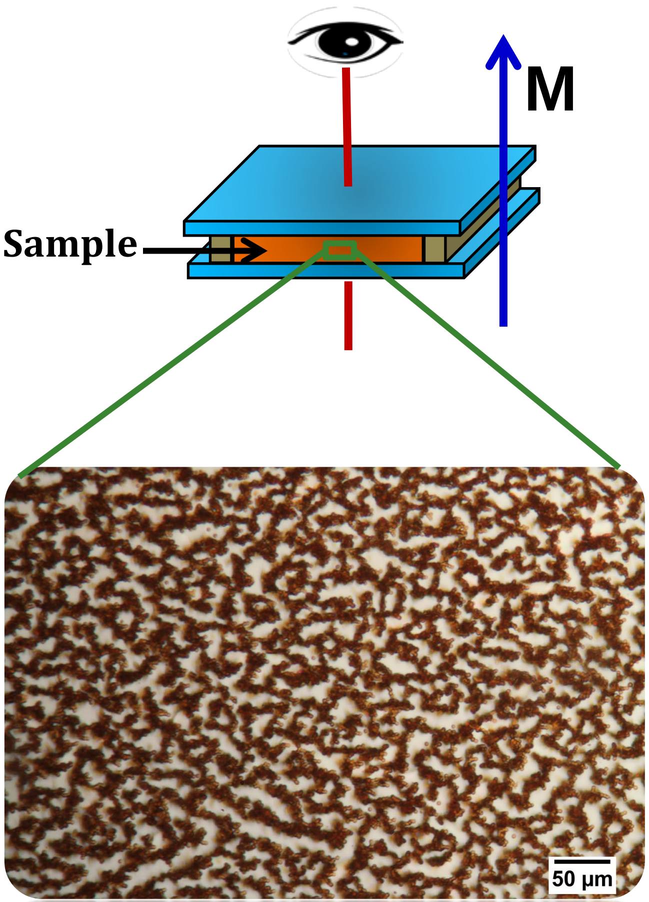
Rheological, optical, and thermal characterization of temperature-induced transitions in liquid crystal ferrosuspensions

Heberth Diestra-Cruz, Carlos Rinaldi, and Aldo Acevedo[a)]
Department of Chemical Engineering, University of Puerto Rico, Mayagüez Campus, P.O. Box 9000 Mayagüez, Puerto Rico 00681

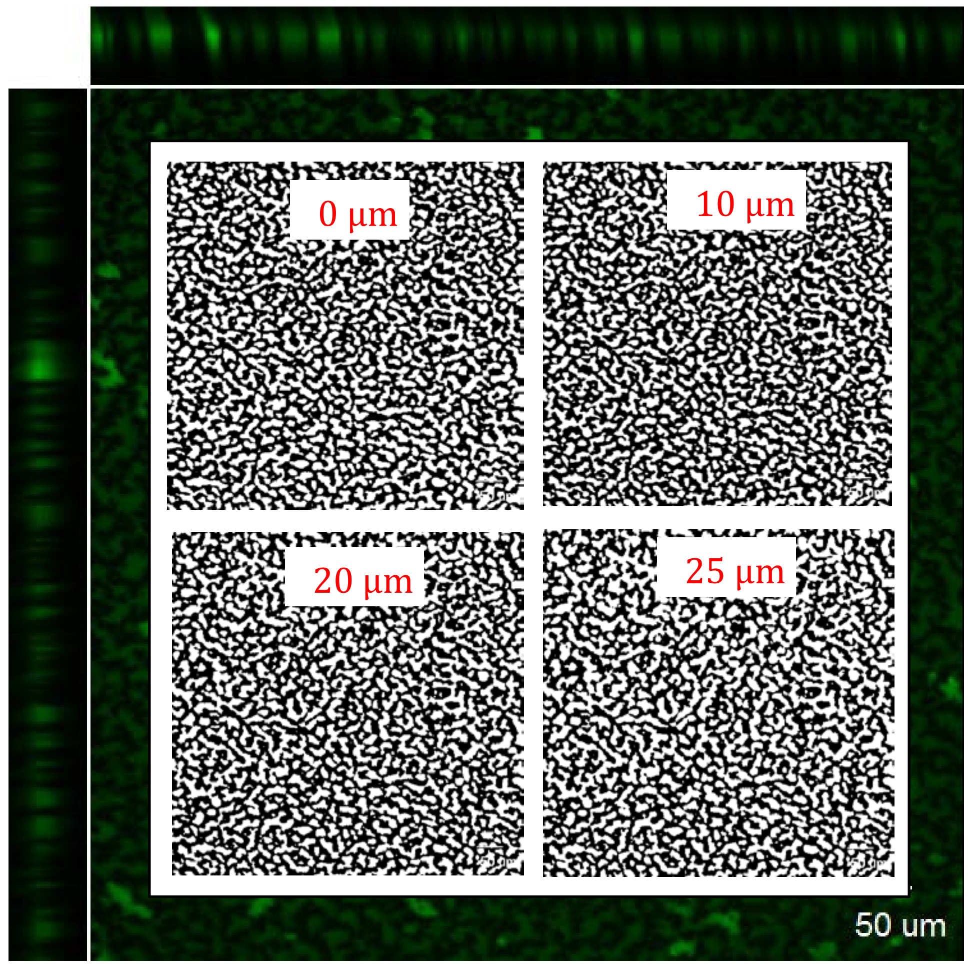
Particle structure morphology

Observations at quiescent conditions

Part. Concent. : 20 wt%
Magnetic field : 0.130 T
Sample thickness : 25 μm



CONFOCAL MICROSCOPY



The minimum Structural Similarity index was 0.90

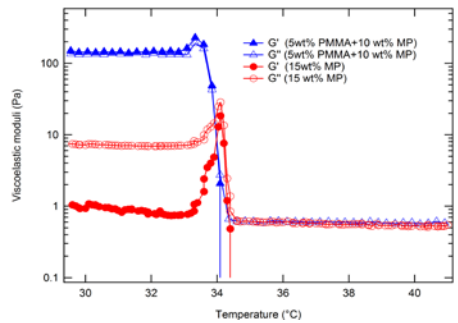
Anisotropic dye : N,N'-bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylenedicarboximide-BTBP

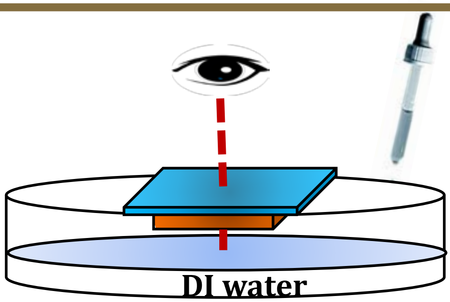
Current Efforts and Interactions

Current work:

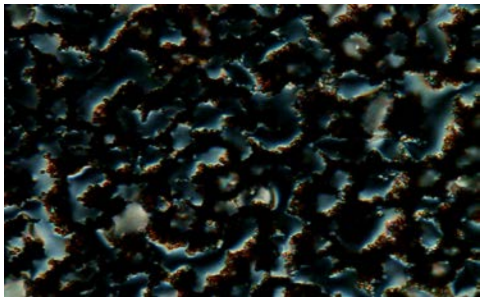
1. Determine the effects of particle size, surface chemistry and matrix on the mechanical properties.
2. Study the feasibility of using LCFs as chemical sensors.

Interactions with Abbott's research group

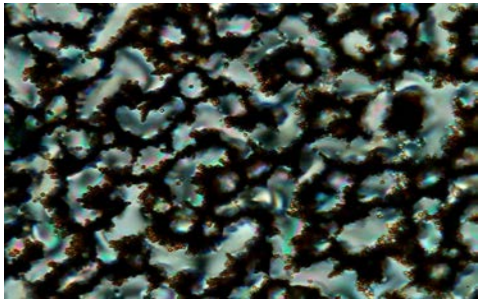




Free surface in contact with air



Free surface in contact with water



- Collaborating with Abbott to explore effect of microstructure of CLCGs on surface-driven ordering transitions.
- Heberth will be at UW during the summer perform experiments with CLCGs.

Thanks!

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?

Particle structure morphology

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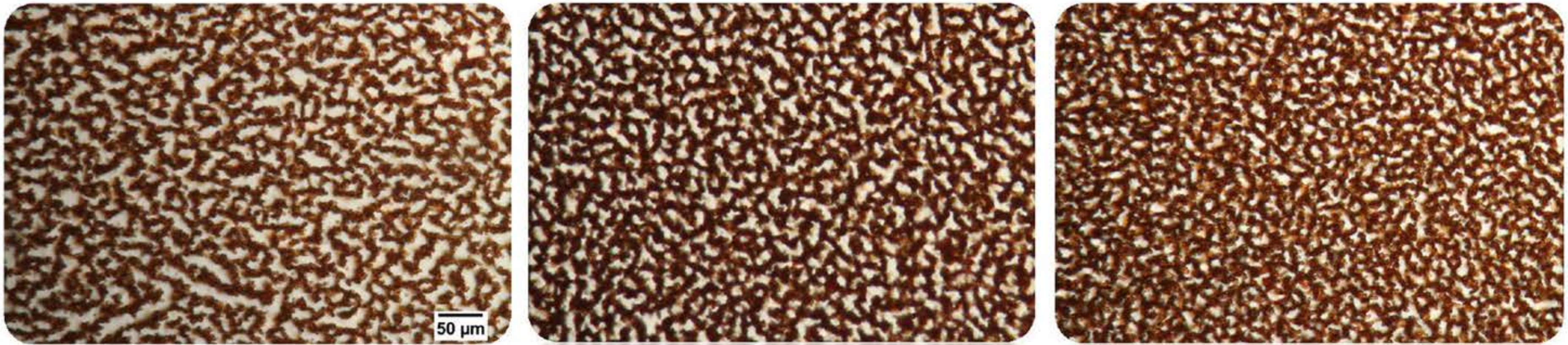
Cooling rate

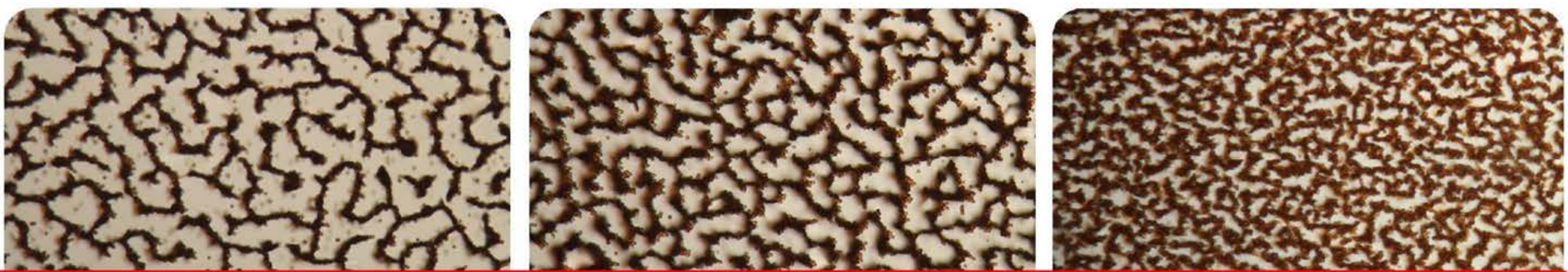


Cooling rate : 1°C/min **5°C/min** **10°C/min**

Part. Concent. : 20 wt%

Thickness : 25 µm

Particle concentration



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