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Ionic Liquid Microemullsions, Templates for Directing Morphology of Cellulose Biopolymer Nanoparticles

August 19, 2015

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Outline

- Background on Cellulose and Ionic Liquids
- Materials and Methods
- Results: Designing an IL/Cellulose μemulsion
- Results: Light Scattering Studies
- Conclusions to Date and Future Work

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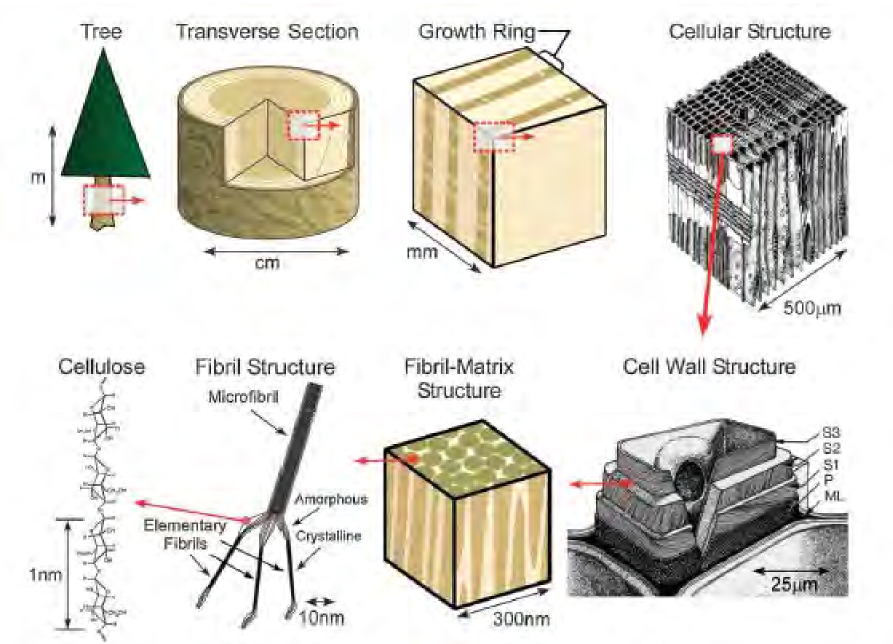
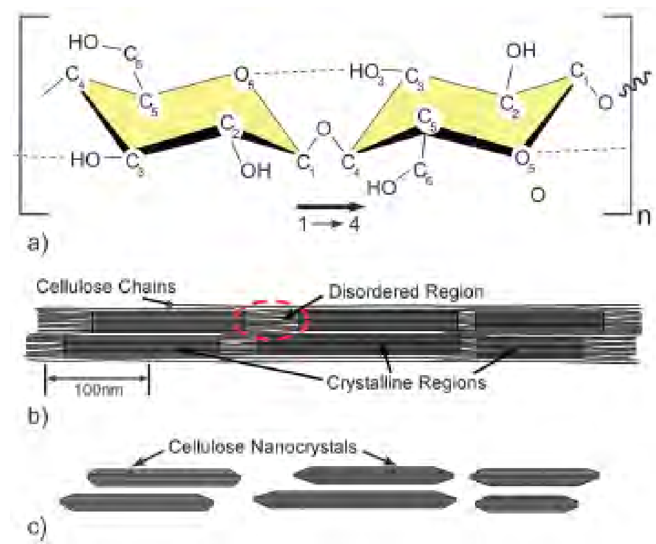
Introduction to nano Cellulose

Cellulose is the most abundant natural polymer on Earth

- Inexpensive
- Chemically stable
- Nontoxic
- Biodegradable
- Modifiable

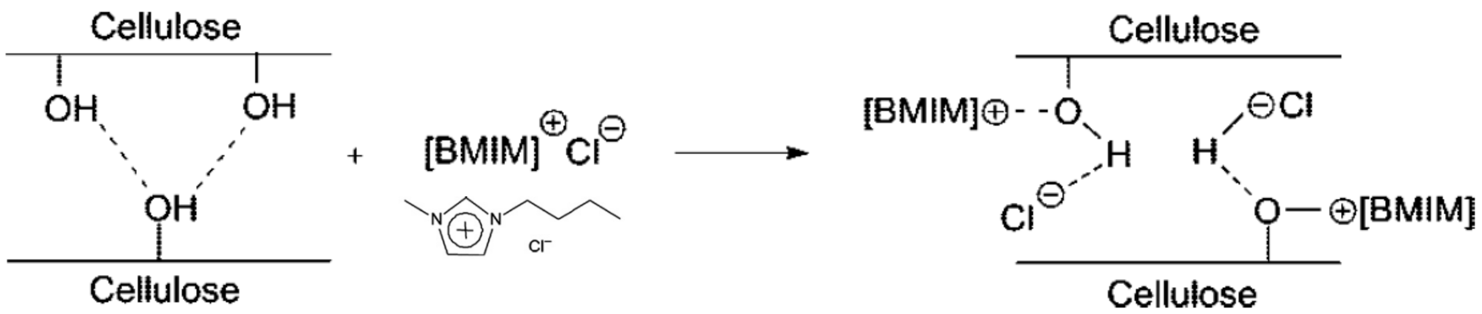
INSOLUBLE





ILs can Dissolve Cellulose

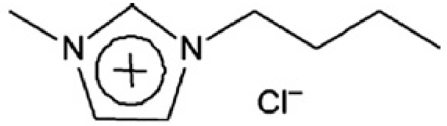
- Cellulose is intra and inter-molecularly connected by hydrogen bonds, and is insoluble in water and most organic solvents
- Solvent dissolution is necessary in multistep processes
- Drastic conditions such as the viscose method are used for the dissolution of cellulose
- ILs form electron donor-acceptor complexes with hydroxyl groups of cellulose resulting in separation and dissolution



A. Pinkert et al. / Chem. Rev. 2009, 109, 6712–6728

Introduction to microemulsions

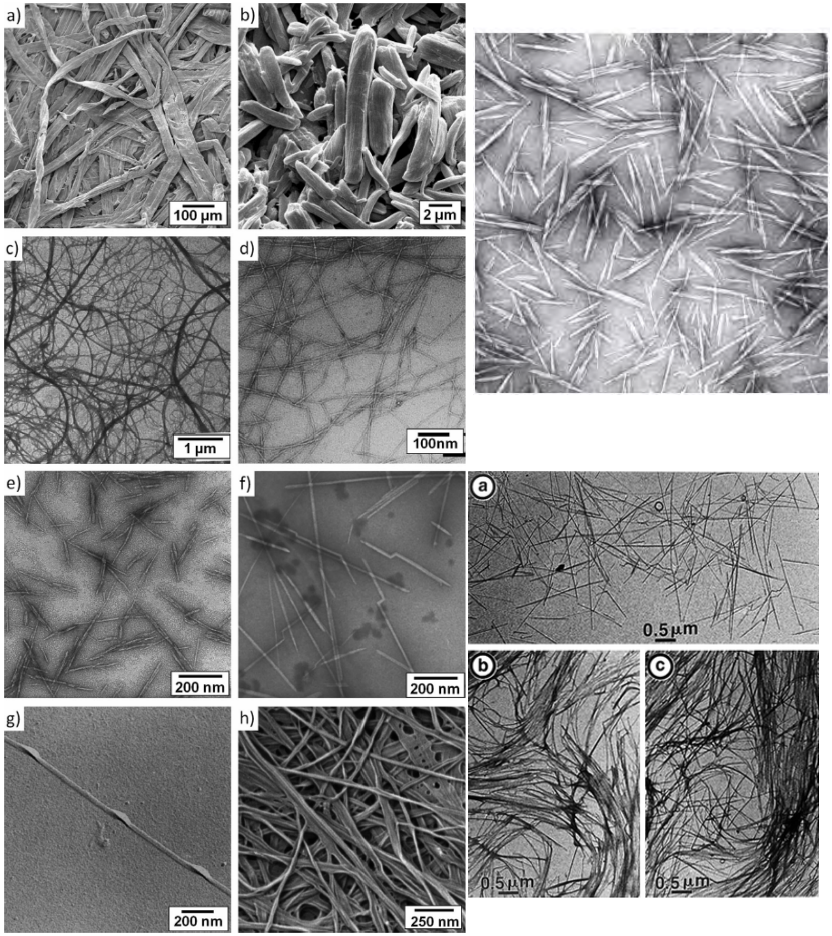
- Microemulsions are transparent, isotropic, and thermodynamically stable dispersions of two immiscible liquids stabilized by surfactant.
- Applications in chemical reactions and materials syntheses with some peculiar advantages.
- Recently, ILs have replaced water and/or traditional organic solvents to prepare novel IL-based microemulsions
- Similar to "classic" microemulsions, gradual substructural transition from microdroplets to a bicontinuous structure spans the single-phase microemulsion region.



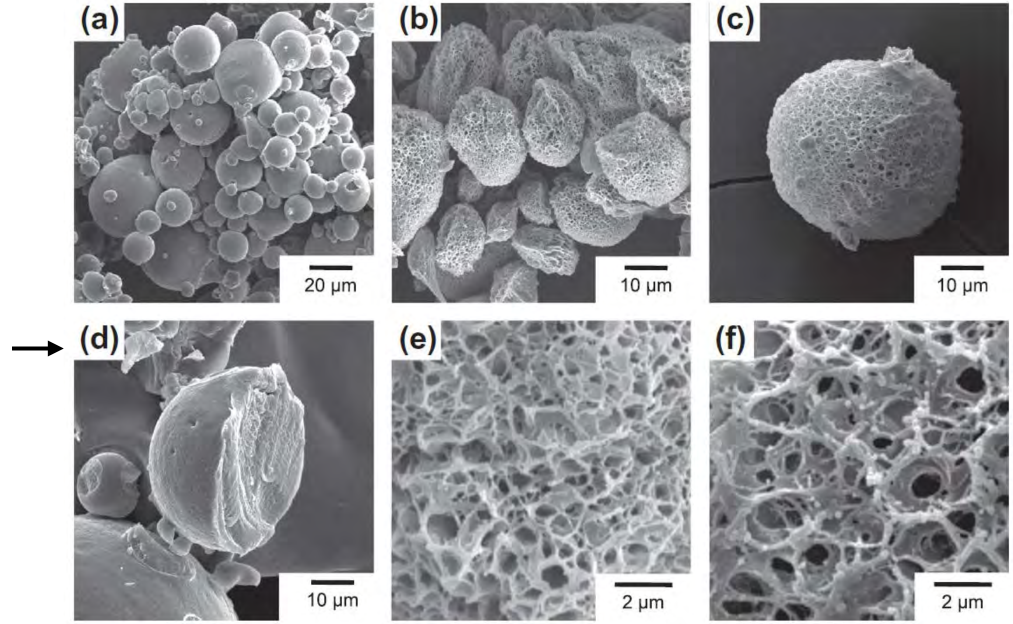
1-Butyl-3-methylimidazolium chloride ([bmim][Cl])

MP ≈ 70 °C

Cellulose Nanoparticles



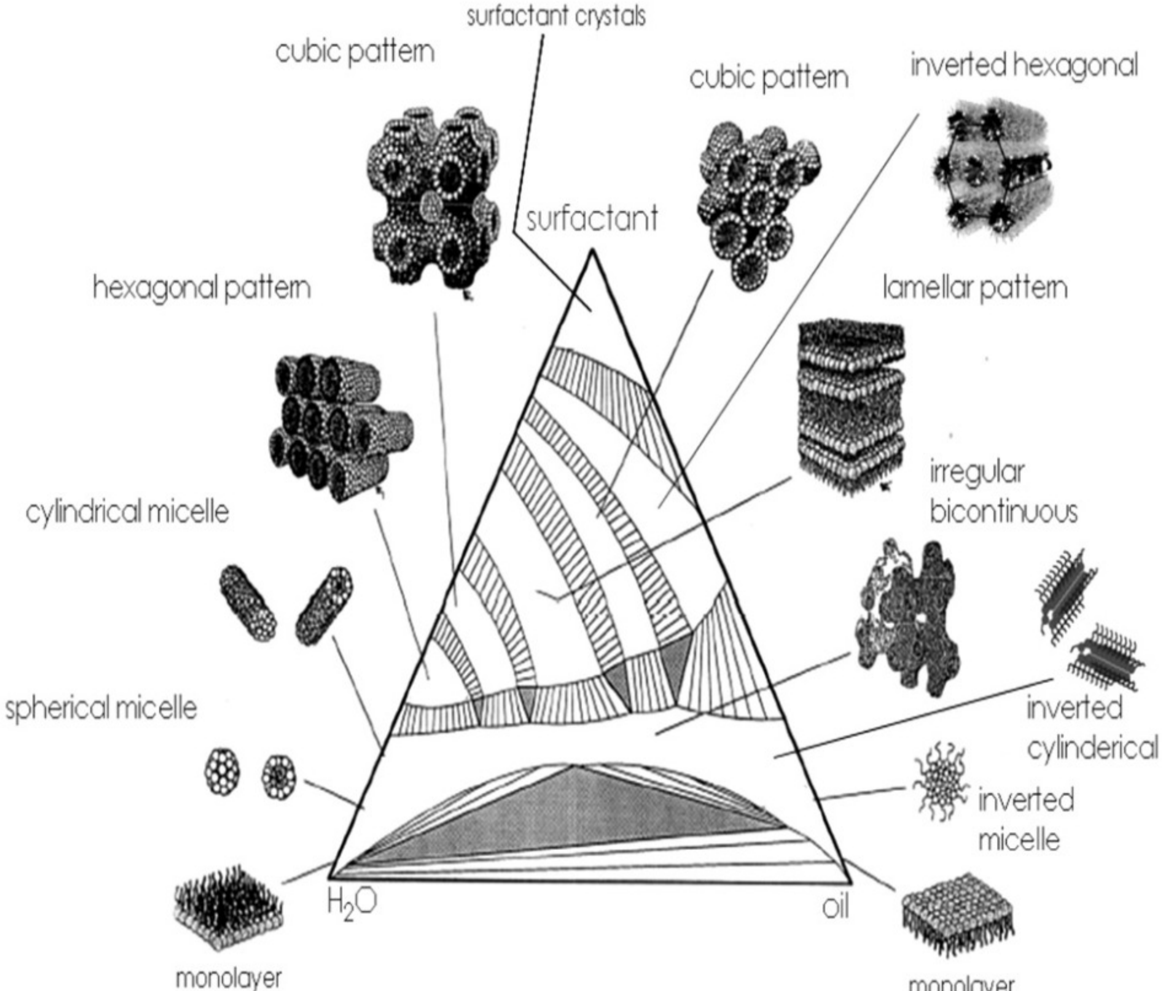
Typical Nanocellulose Morphologies



T. Suzuki et al. / Journal of Colloid and Interface Science 418 (2014) 126–131

Emulsion Directed Cellulose Morphology
(NOT nanocellulose)

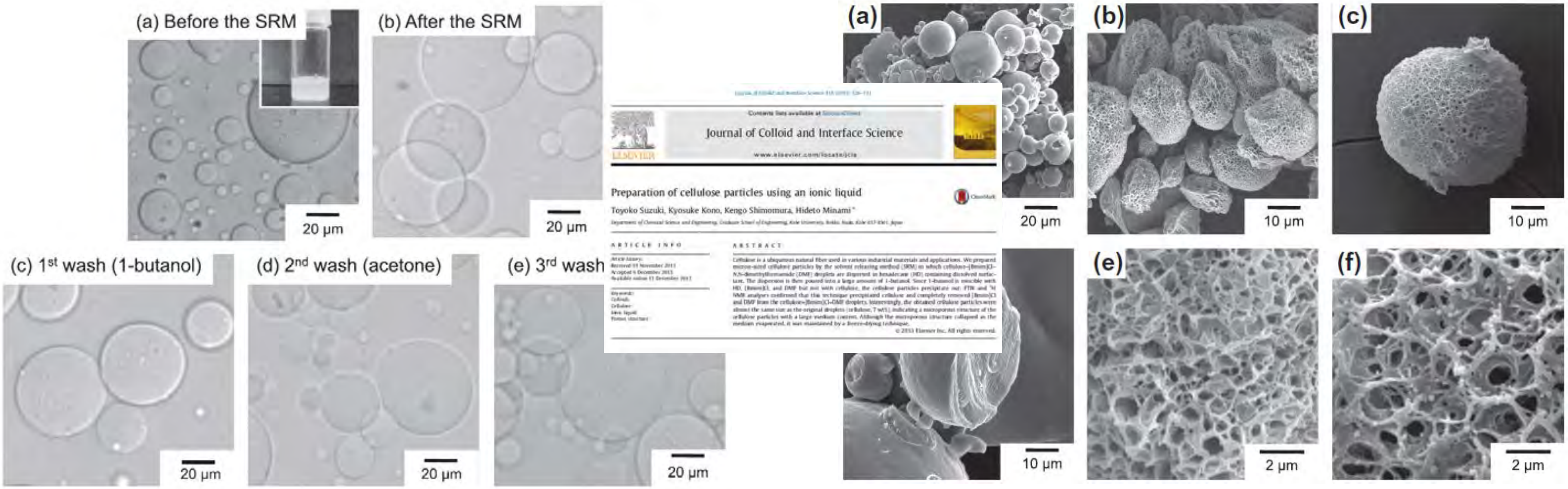
µEmulsion Structure Control



V. Singh et al. / Asian J Pharm 2013;7:1-7

- Microemulsions are thermodynamically stable, clear, colloidal dispersions immiscible liquids, stabilized by surfactant.
- Microemulsions typically have a droplet diametesr of approximately 100 nm or less.
- Can be tuned to have cylindrical shapes or several bicontinuous structures

Related Work: ILs and Cellulose



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Micron-sized cellulose particles prepared by the "solvent releasing method" (SRM). Preciptated from Cellulose–[Bmim]Cl–N,N-dimethylformamide (DMF) droplets dispersed in hexadecane (HD) containing dissolved surfactant.

Q: Can cellulose particle size and morphology be precisely controlled by creating a true IL-Cellulose microemulsion?

Materials & Methods

Microemulsion: Quasi-Ternary phase diagram constructed with BmimCl/Span80/Tween20/Sunflower Oil. Warm emulsion technique adapted at 50 °C, for reduced viscosity.

Cellulose Solution: 10 % wt. Microcyrstalline cellulose (Sigma Aldrich) dissolved in 10 % wt. DMF:BmimCl solution, for reduced viscosity

Particle Formation: Two methods explored.

Frozen phase centrifugation followed by solvent removal

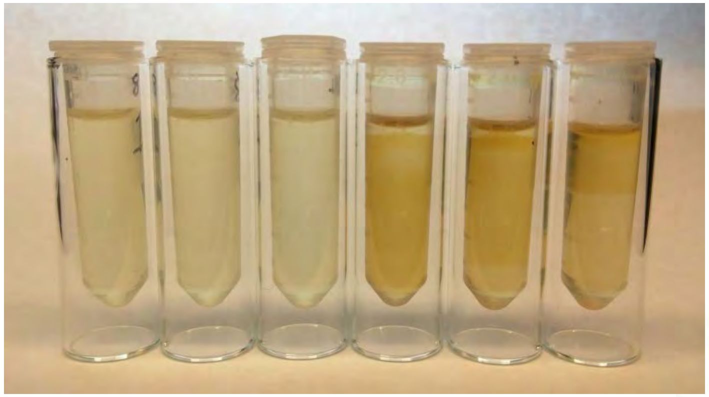
Anti-Solvent preciptation

Analysis: Direct observation (OM/SEM), Particle Surface contrast (interferometry), time-resolved small angle laser light scattering.

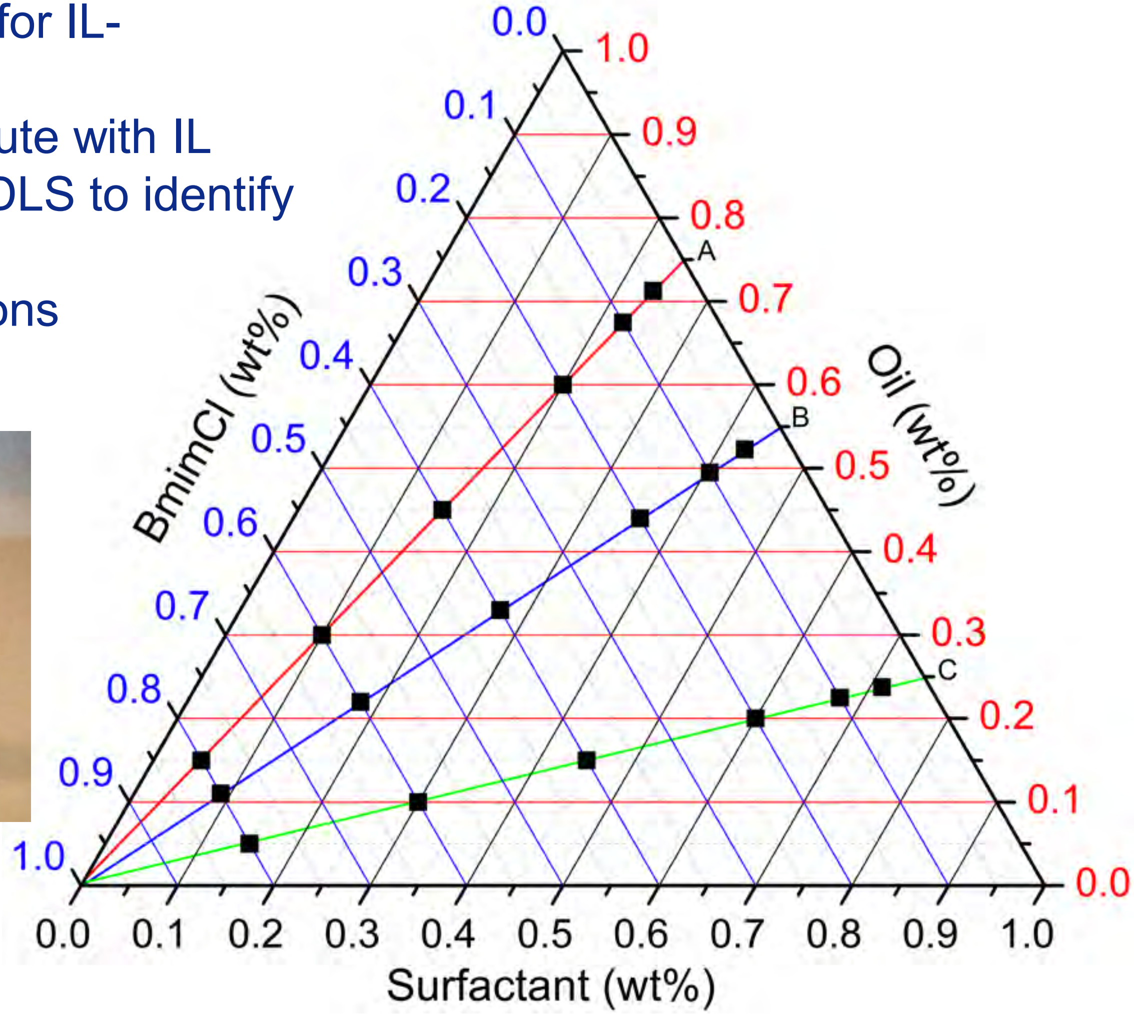
1. Particles cast of surface
2. Size, formation and growth vs antisolvent addition
3. Particle morphology and its relationship to processing

Exploring the Phase Diagram

- Establishing phase diagram for IL-cellulose μE
- Start with fixed ratios and dilute with IL
- Use visual observation and DLS to identify phases
- Repeat with Cellulose solutions

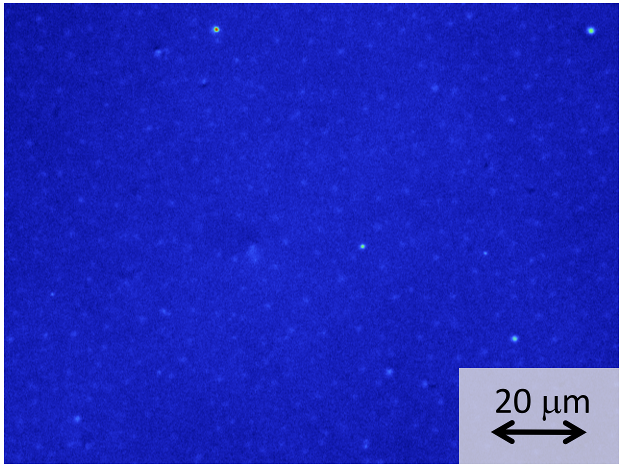


Dilution Line C: Showing Phase transition from a single isotropic phase (1- 3) through a 3 phase region (4 & 5) to 2 phases (6).

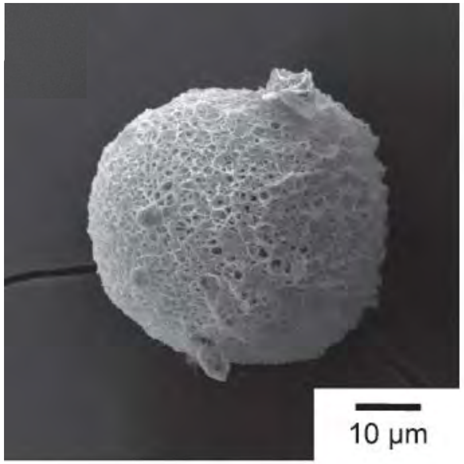


Particle Size Results

- Dynamic Light Scattering measures the hydrodynamic radius of μE as well as particles in solution
- Particles deposited on Si wafer can be measured with Interferometer and SEM



Nanoparticle measurements by Interferometer



SEM of Cellulose Particle

T. Suzuki et al. / Journal of Colloid and Interface Science 418 (2014) 126–131

number	water, wt %	TX-100, wt %	$bmimPF_6$, wt %	R	D_h, nm
1	83.7	15.0	1.1	0.17	8.3
2	78.1	20.3	1.6	0.17	8.5
3	71.8	26.2	2.0	0.17	9.0
4	83.3	15.1	1.6	0.24	12.6
5	77.1	20.7	2.2	0.24	12.8
6	70.5	26.7	2.8	0.24	11.9
7	81.5	15.7	2.8	0.41	18.9
8	74.8	21.4	3.8	0.41	18.3
9	68.9	26.4	4.7	0.41	17.9

Representative results μE size measurements by DLS

Y. Gao et al. / Langmuir 2005, 21, 5681-5684

Conclusions

- Recent work suggests microemulsions can be used to control cellulose particle morphology.
- Size can be controlled by the adjustment of solvent/surfactant ratios.
- Interferometry may be a useful tool for particle charaterization

Future Work

- Continued study of IL-Cellulose microemulsion formulation and phase structures
  - Conductivity and SAXS measurments
  - Study the final particle morphology vs microemulsion structure
- Studies of the solubility of cellulose in different ILs, ie. changing anions (acetate) or alkyl chains
- Measuring the crystallinity of nanocellulose particles using Xray diffractometry (XRD)
- Continued work on particle recovery methods
- Nanoparticle functionalization via known cellulose chemistry