Microstructure and mechanical properties of **surfactant lamellar phases added by CNM**

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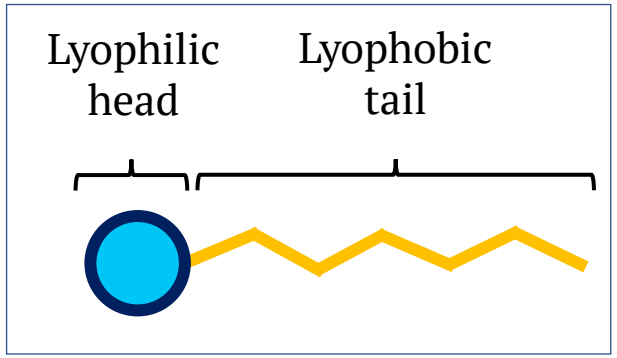
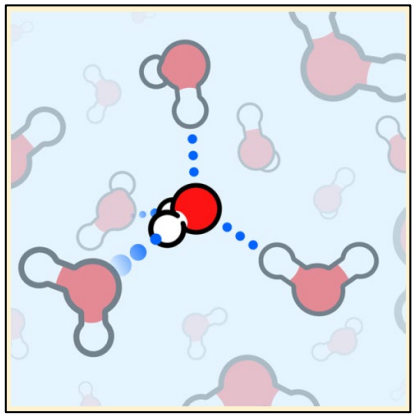
Watson Loh – Unicamp, Brazil

Lyotropic liquid crystals

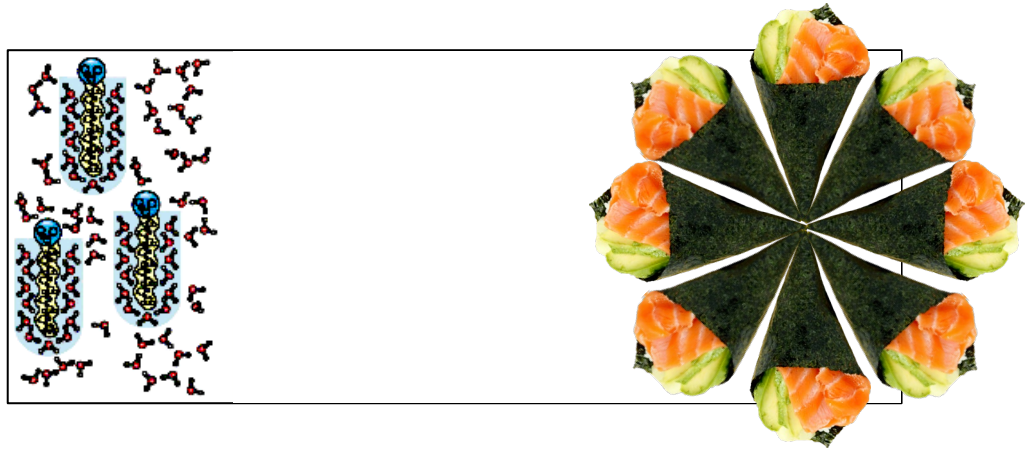
Surface active agents



Pure water @ RT



Surfactant molecules in water

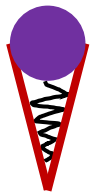


Lyotropic liquid crystals

Last talk of the session (just before lunch)

Critical packing parameter (CPP)

$$CPP = \frac{V}{al}$$



Lyotropic liquid crystals

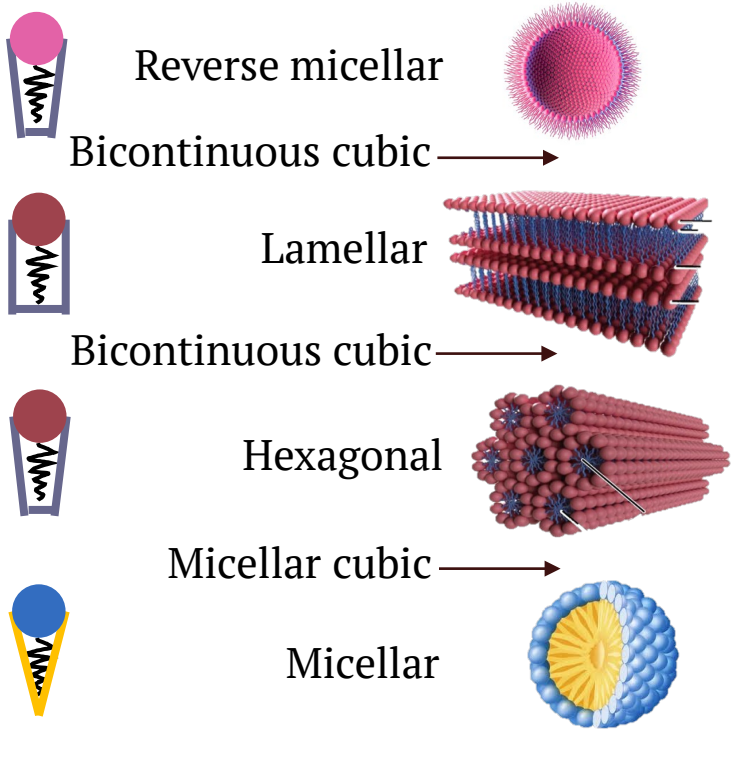
Self-assembly structure (aggregates)

$CPP > 1$

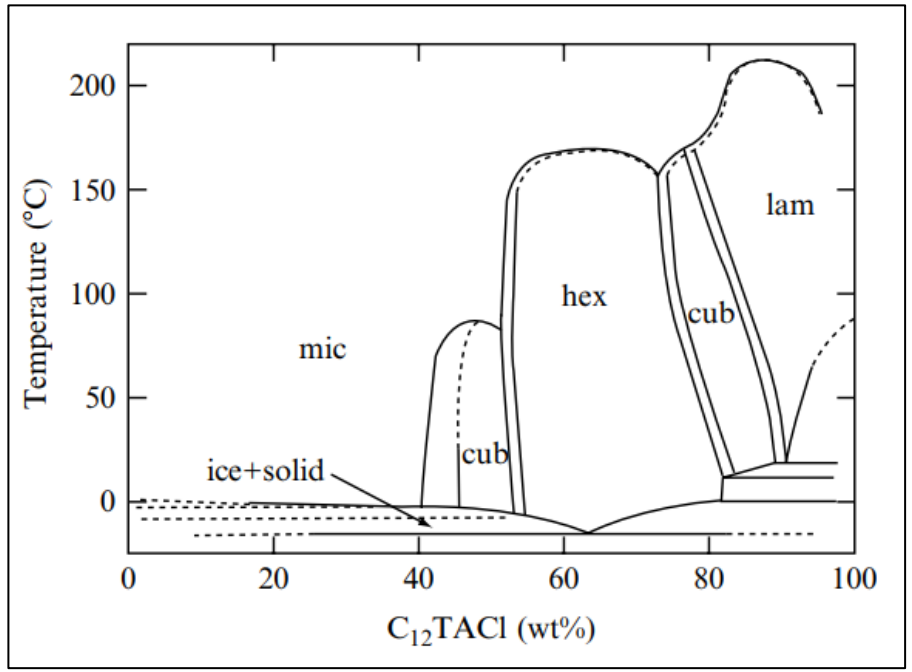
$\frac{1}{2} < CPP < 1$

$\frac{1}{3} < CPP < \frac{1}{2}$

$CPP < \frac{1}{3}$

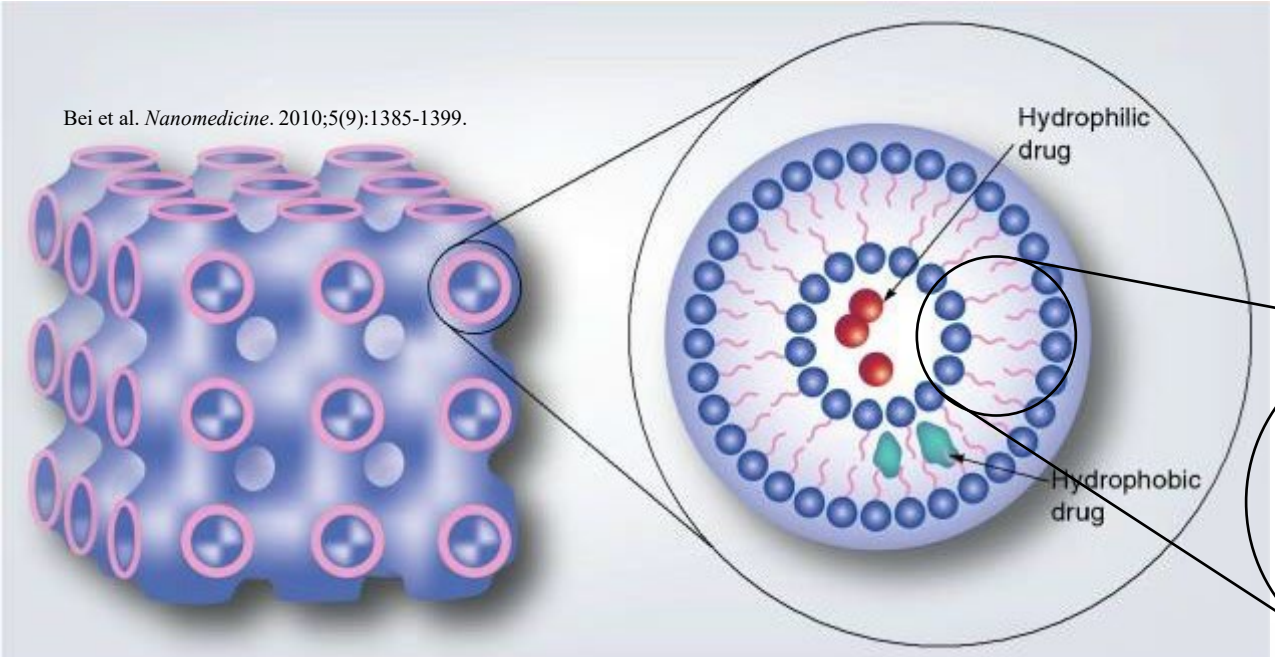


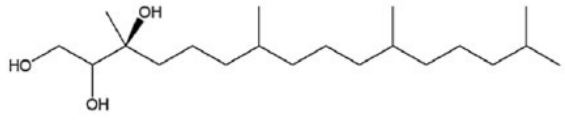
Binary phase diagram



Holmberg, Lindman et al. (2002) Surfactants and Polymers in Aqueous Solution

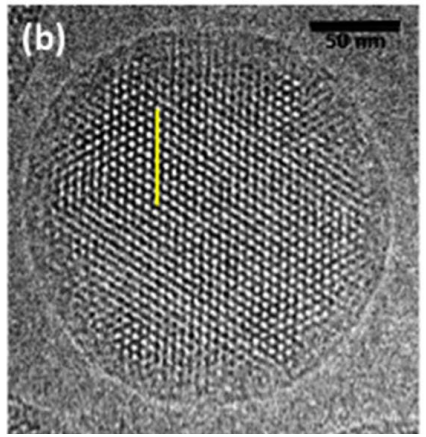
Cubosomes

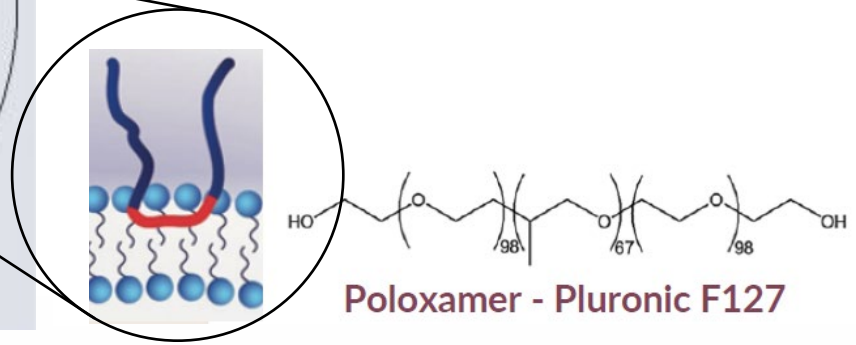




Phytantriol

3,7,11,15-tetrametil-hexadecano-1,2,3-triol



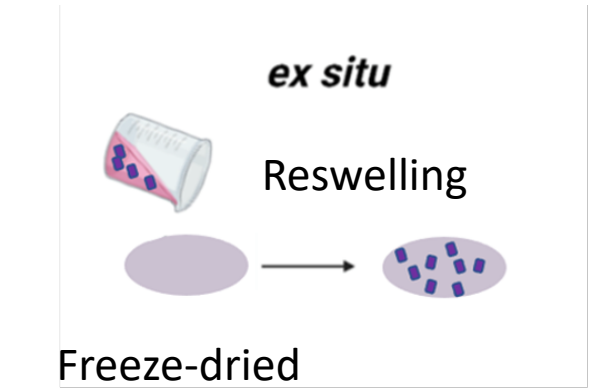


Poloxamer - Pluronic F127

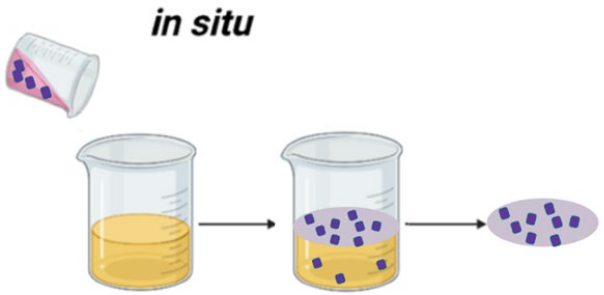
doi.org/10.1016/j.ejpb.2017.03.022

TAPPI NANO DIVISION

Cubosomes

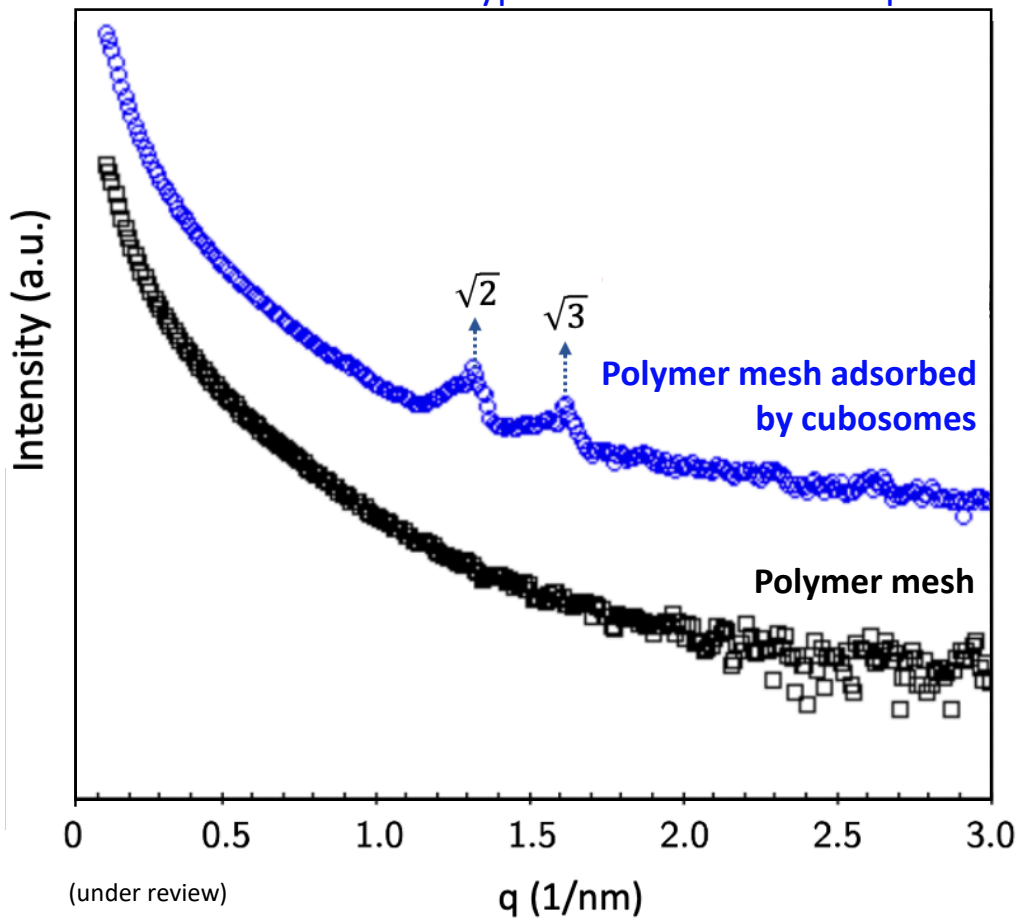


Freeze-dried
BC membrane

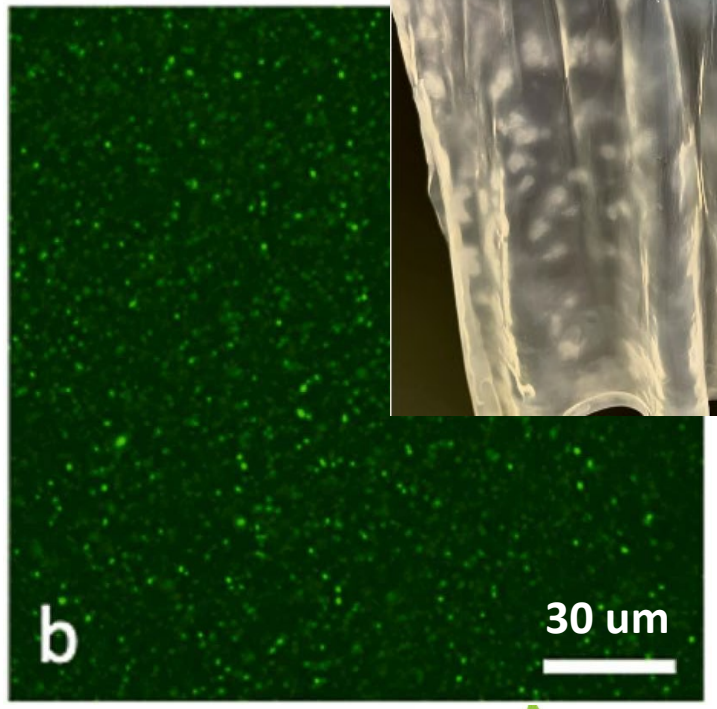


Culture medium

Pn3m-type bicontinuous cubic phase



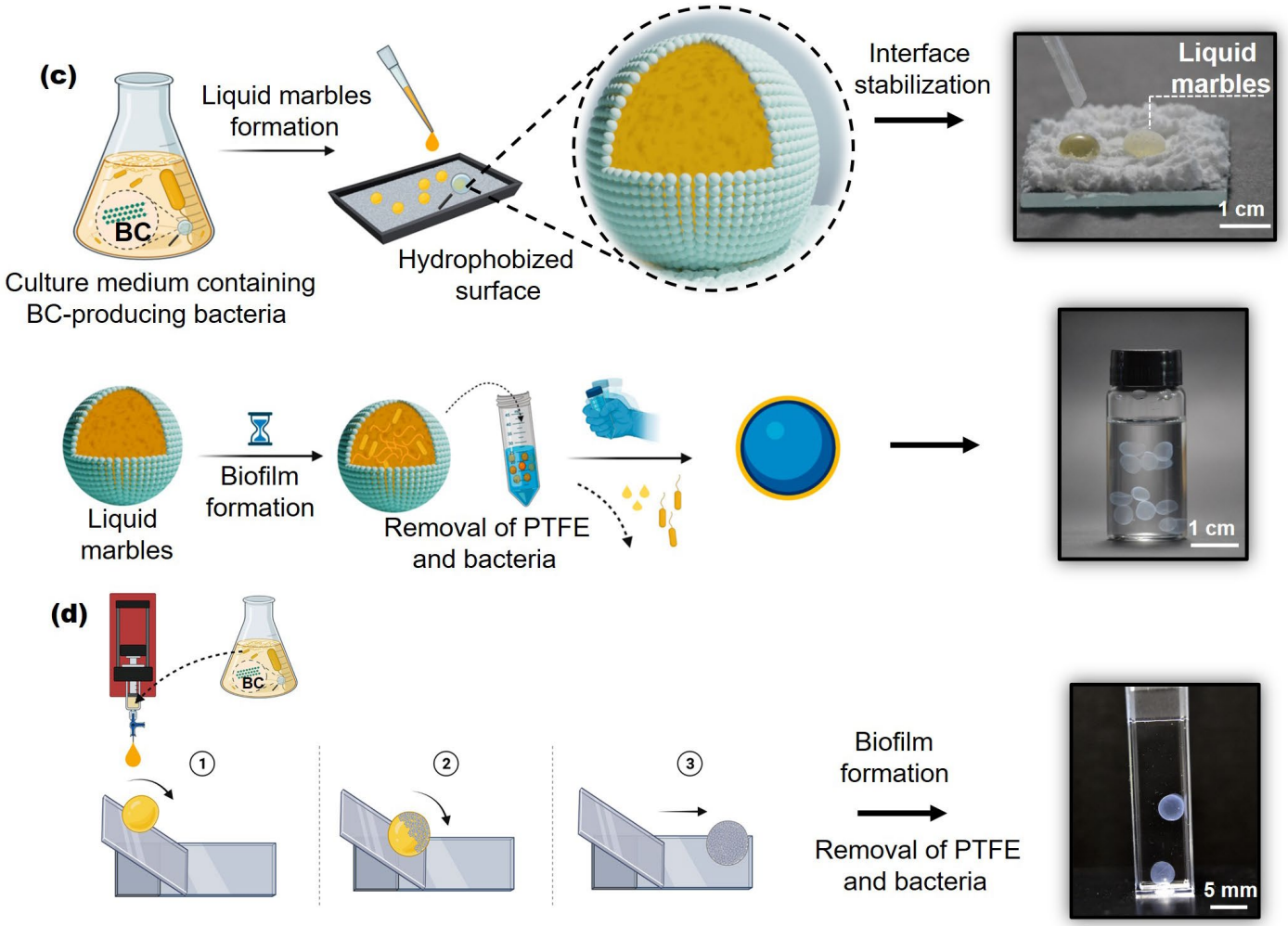
(under review)

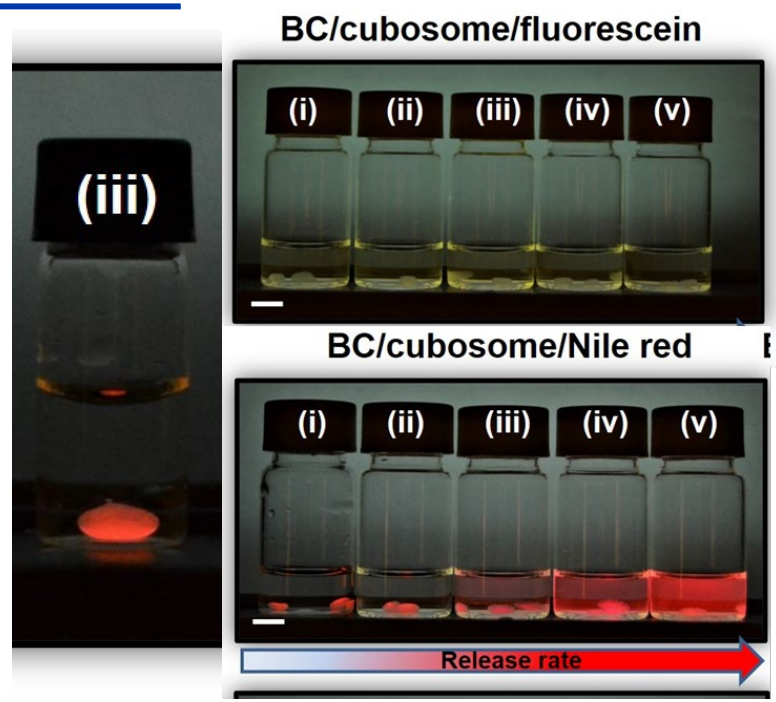


Villalva, Otoni, Loh (under review)

TAPPI NANO DIVISION

Cubosomes

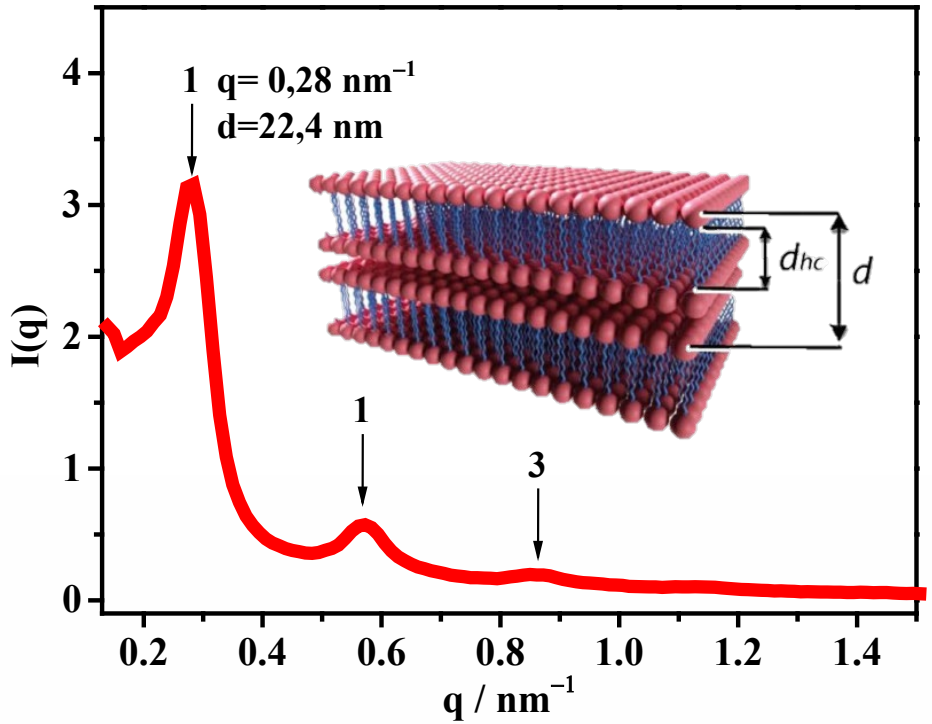




Ferreira, Otoni, Rojas et al. (under review)

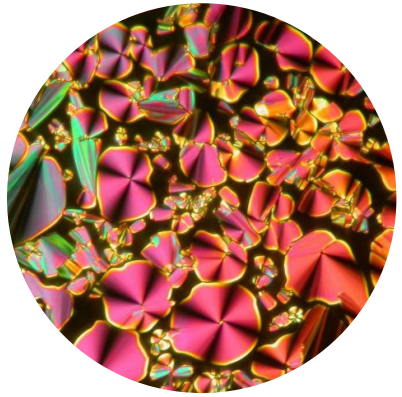
Lamellar phase

SAXS



POM

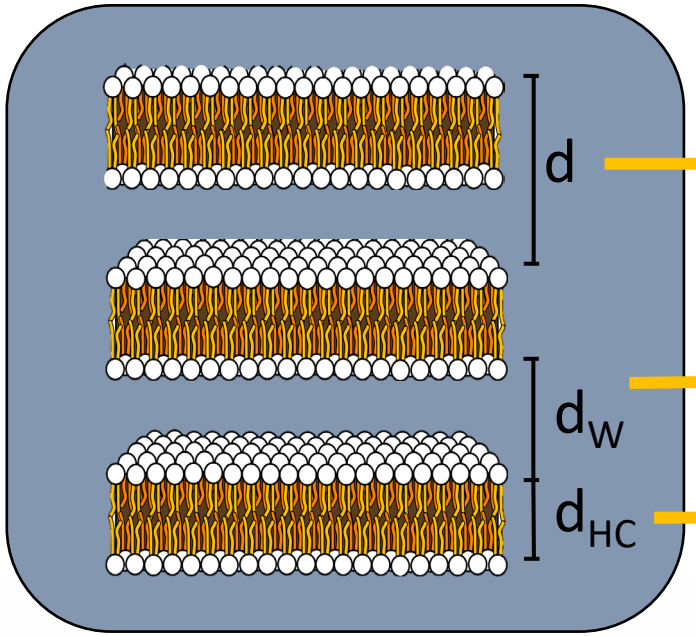
Isotropic



Lamellar

Structural parameters of the lamellar phase

$$q = \frac{2\pi}{d}$$

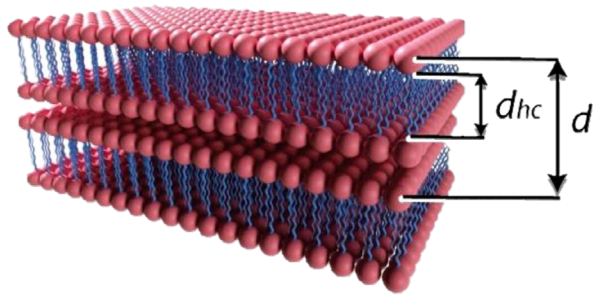


Interlamellar spacing
(Repeating distance of the bilayers)

Polar layer thickness
(aqueous domain)

Bilayer thickness
(nonpolar domain)

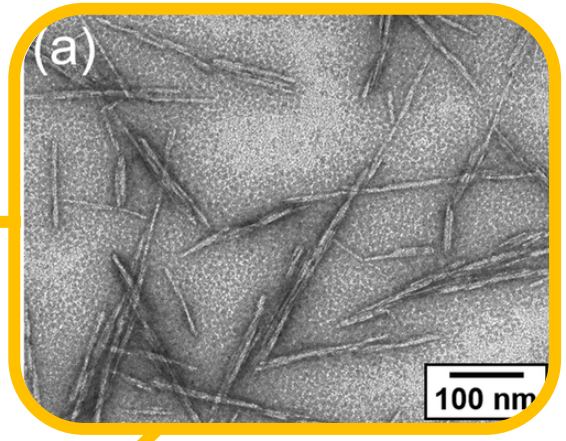
DODAC lamellar phase + nanocelluloses

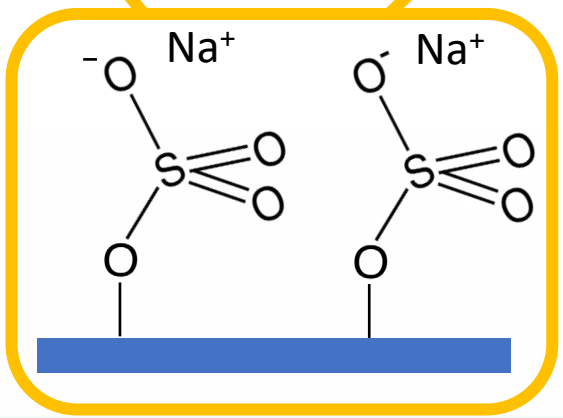


+ CNC or CNF

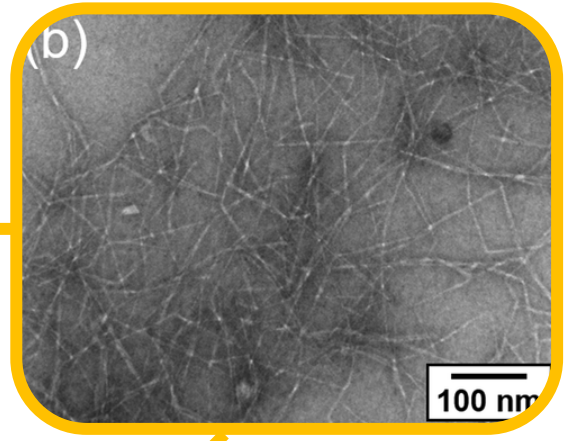
Nanocelluloses

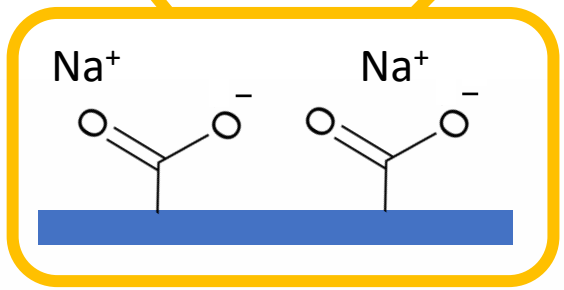
CNC
Commercial





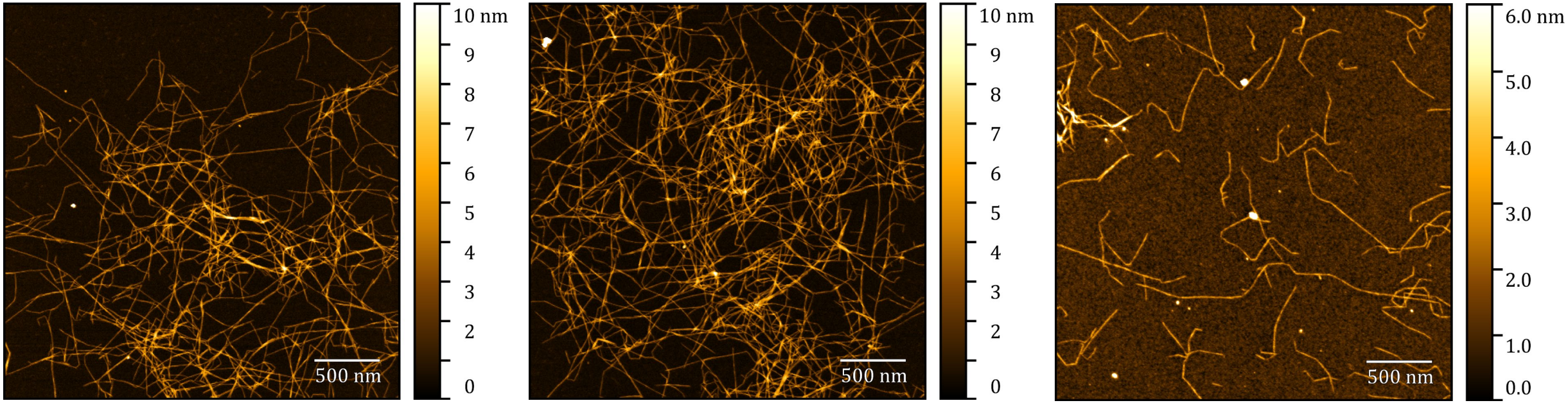
TEMPO-CNF
Lab-made





Chem. Soc. Rev. 47, 2609–2679 (2018)

TEMPO-CNF



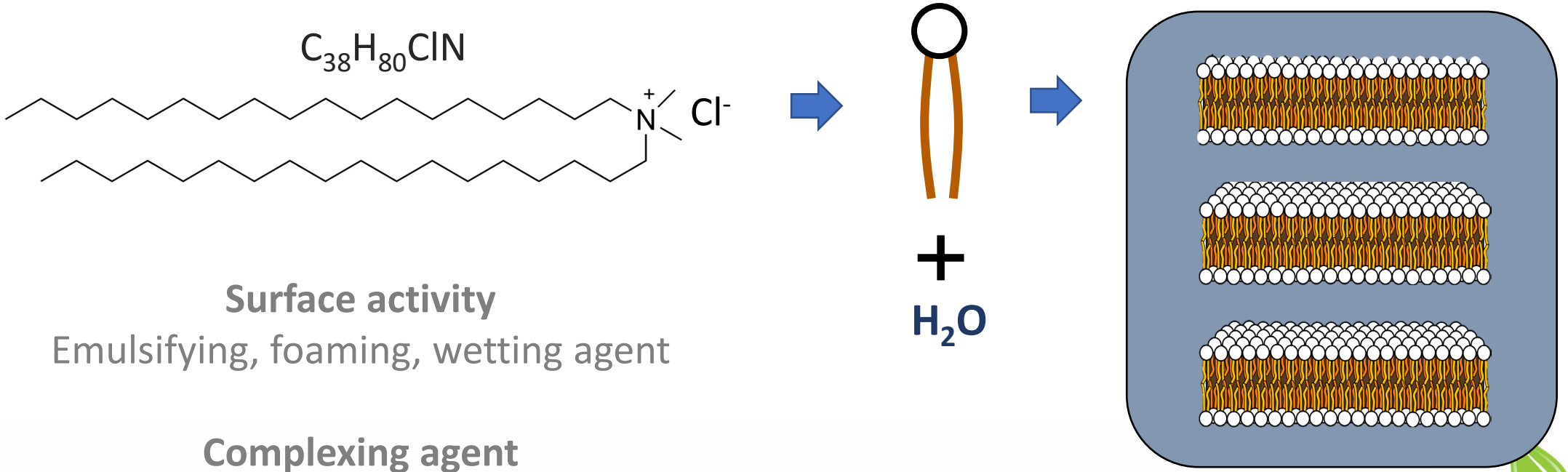
10 mg L^{-1}

Mean width (height): 1.7 nm (±0.7)

Charge density: 760 µmol g^{-1} (±80)

Armsoft E (commercial)

Composed mainly of di(hydrogenated tallow) dimethylammonium chloride in ethanol



Surface activity

Emulsifying, foaming, wetting agent

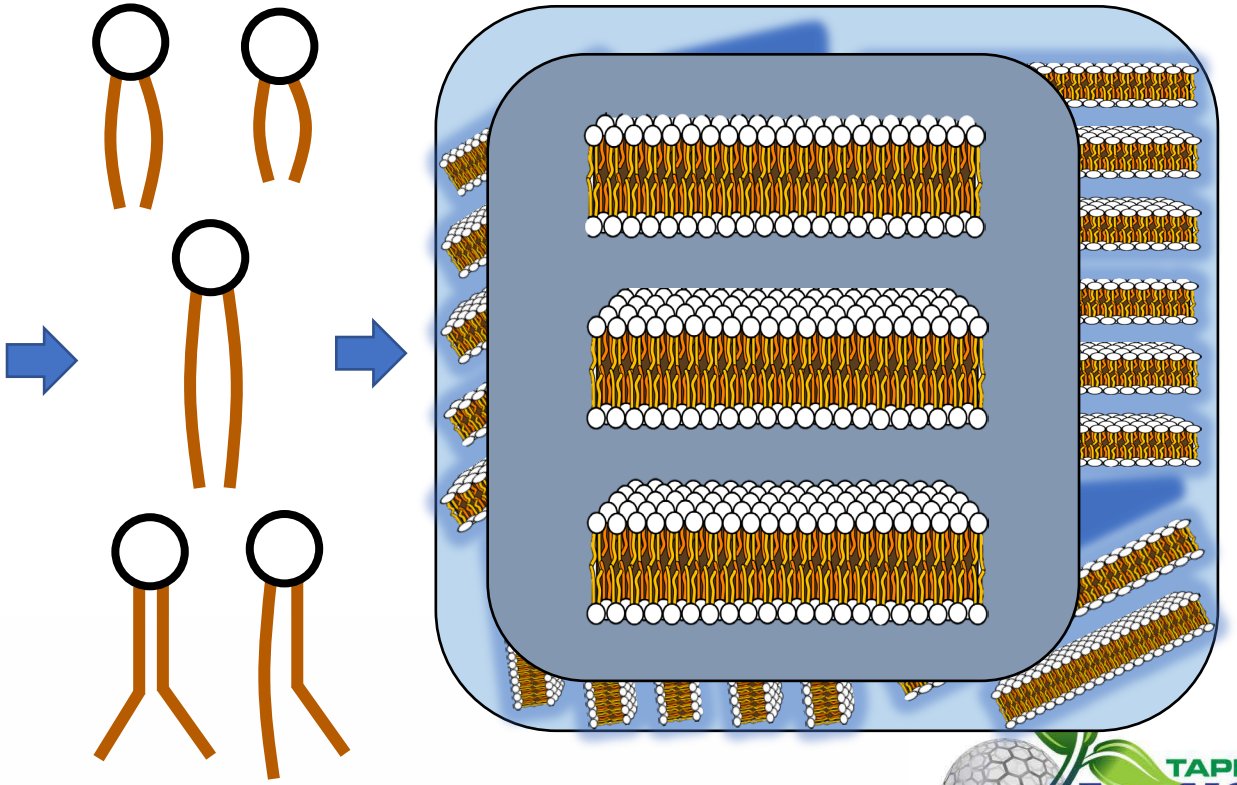
Complexing agent

Anionic species with poor water solubility
(water treatment, sugar refining etc.)

Armsoft E (commercial)

Fatty acid precursors for surfactant synthesis

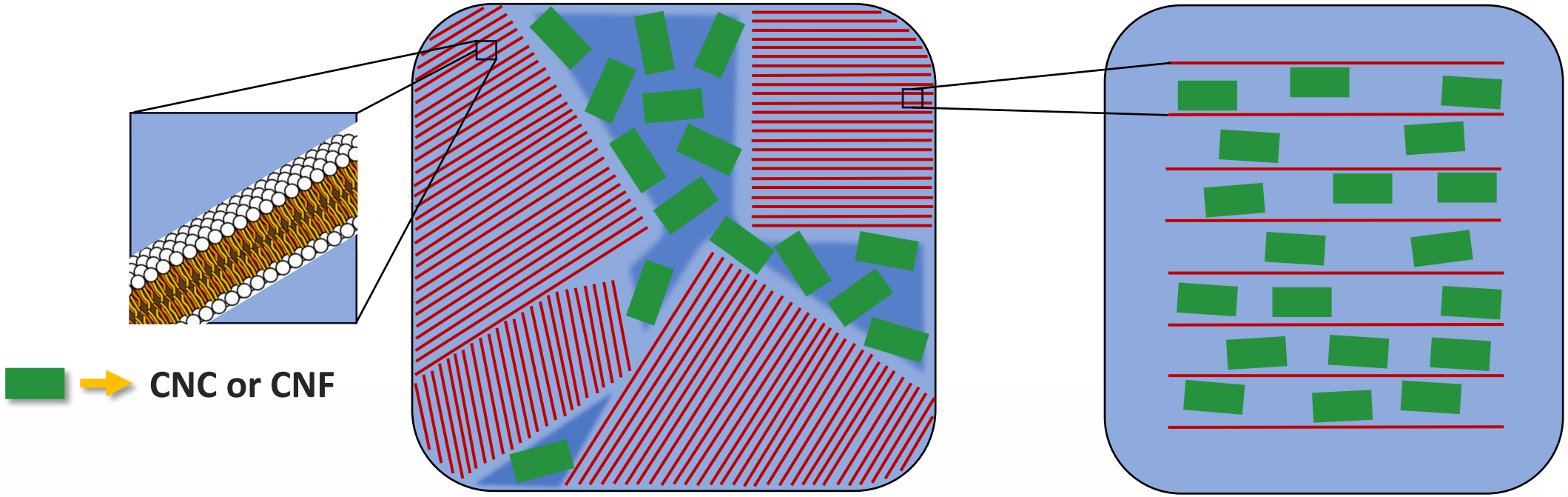
Fatty acid chain	Composition (%)
14:0	1-6
16:0	20-37
16:1	1-9
18:0	25-40
18:1	31-50
18:2	1-5



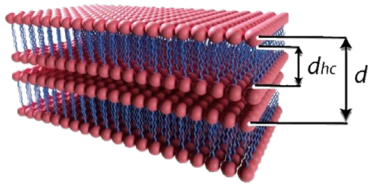
CNM whereabouts (?)

Between voids or in defect regions of the liquid crystalline phase

Confined in the aqueous space between DODAC bilayers



Sample preparation

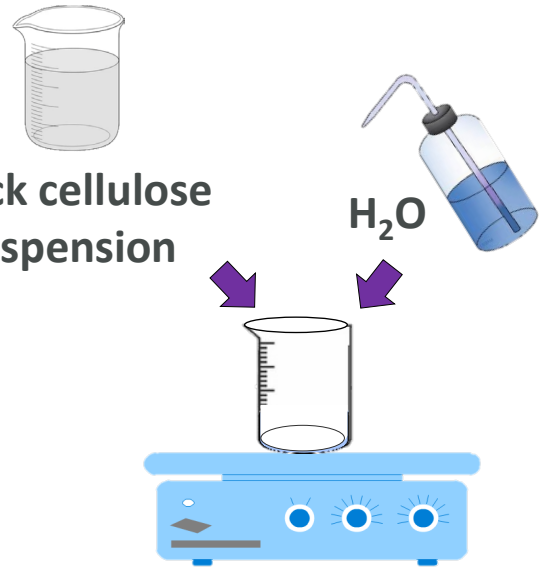


10, 30, or 50 wt% DODAC + 1 wt% CNC or 0.1 wt% CNF

1. 10% DODAC
2. 10% DODAC + 1% CNC
3. 10% DODAC + 0.1% CNF
4. 30% DODAC
5. 30% DODAC + 1% CNC
6. 30% DODAC + 0.1% CNF
7. 50% DODAC
8. 50% DODAC + 1% CNC
9. 50% DODAC + 0.1% CNF

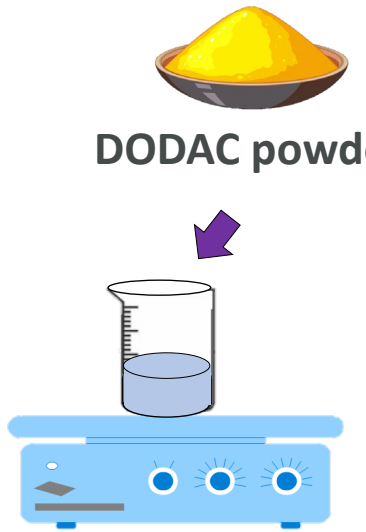
Sample preparation

1



Cellulose suspension
Mechanical stirring for 1 h

2



Slow addition of DODAC powder

3

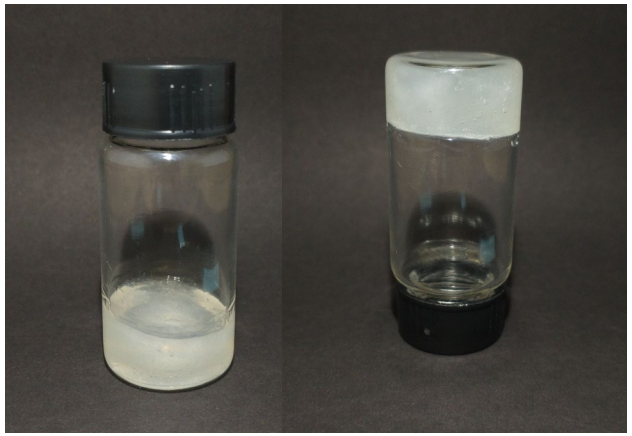
Mechanical stirring for 3 h at 40 °C

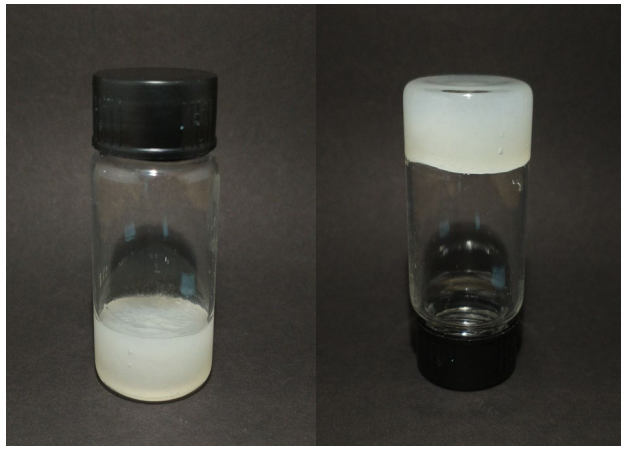
4

Air bubble removal

Macroscopic aspect

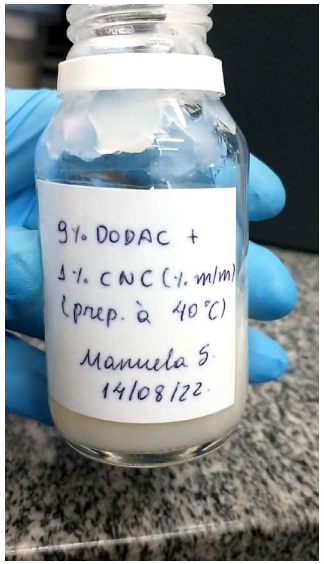
10% DODAC	10% DODAC + 1% CNC	10% DODAC + 0.1% CNF



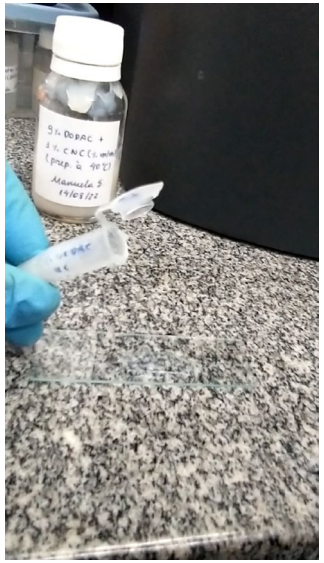


Macroscopic aspect

10% DODAC + 1% CNC

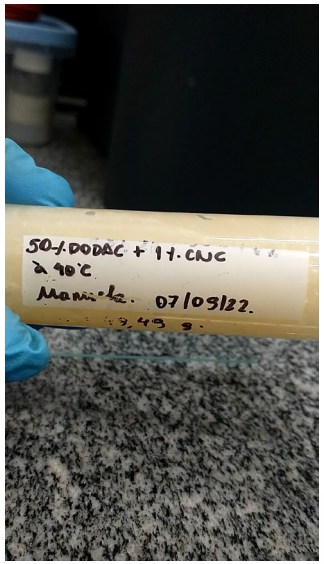


25 °C



40 °C

50% DODAC + 1% CNC

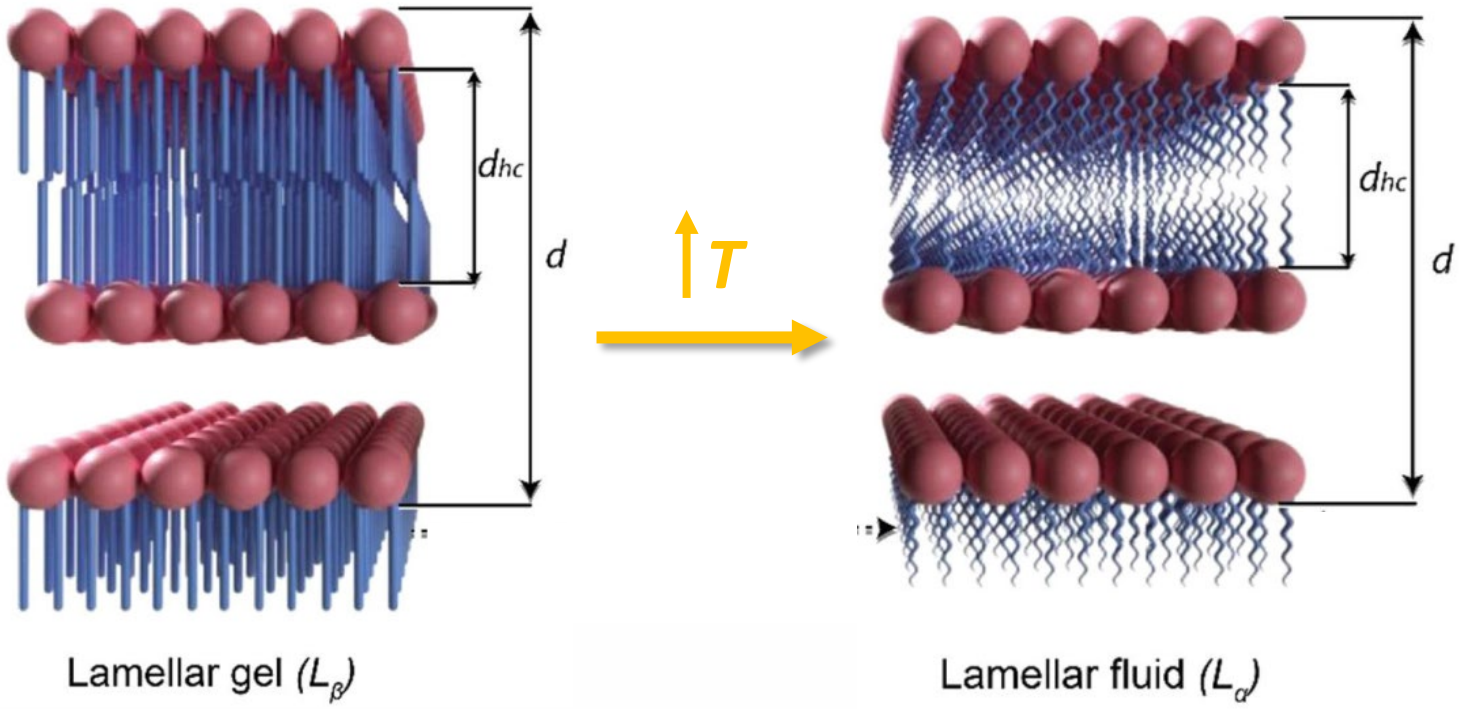


25 °C

40 °C

L_β L_α

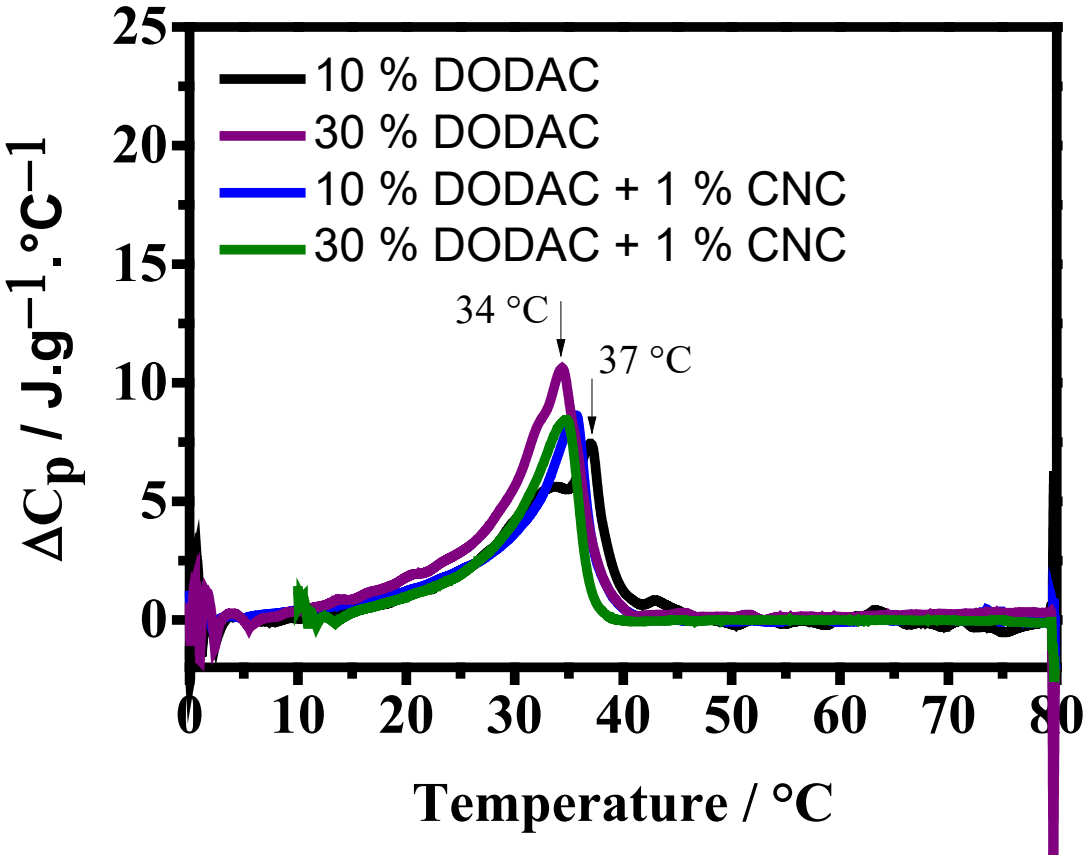
Types of lamellar phases: L_β and L_α



Ferreira, G. A. *J. Dispers. Sci. Technol.* 1–14 (2021)

DSC

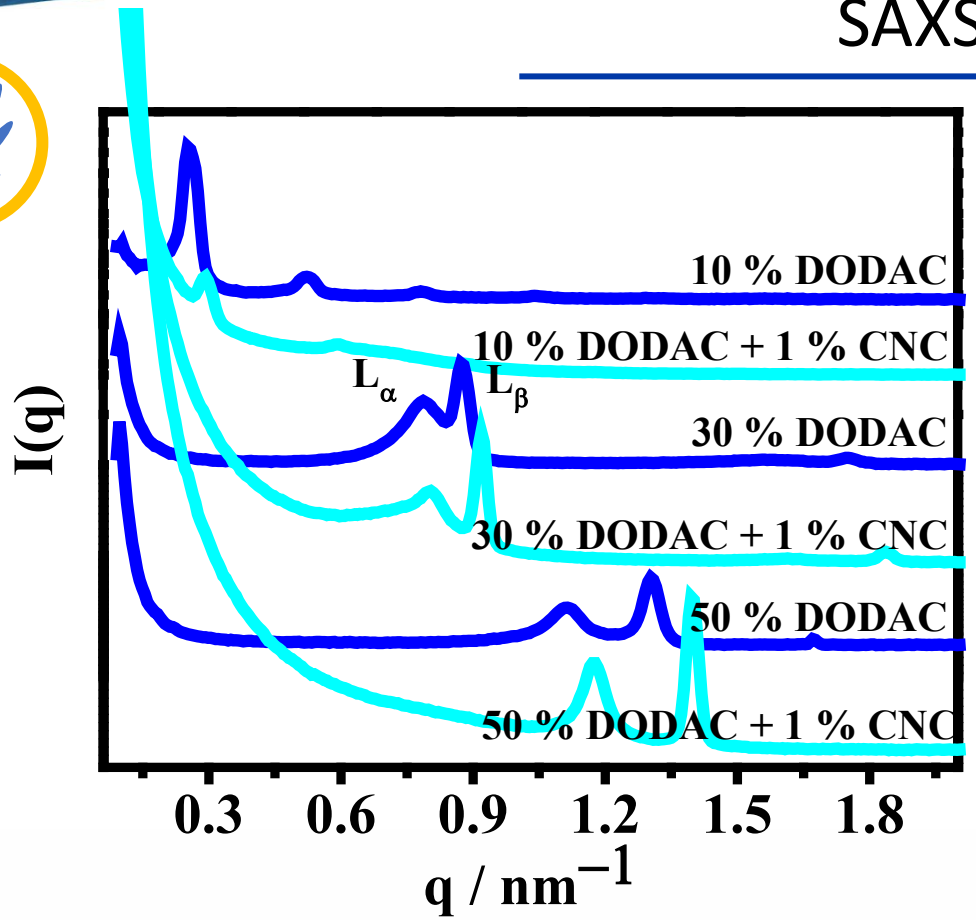
Gel-to-fluid phase transition temperature (T_m) and the transition enthalpy (ΔH)



Sample	DSC	
	Transition L_β-L_α	
	T_m / °C	ΔH / J g^{-1}
10% DODAC	37	67
10% DODAC + 1% CNC	34	74
10% DODAC + 0.1% CNF	36	74
30% DODAC	35	79
30% DODAC + 1% CNC	36	92
30% DODAC + 0.1% CNF	36	76
50% DODAC	37	84
50% DODAC + 1% CNC	36	86
50% DODAC + 0.1% CNF	36	88

(±15)

SAXS (1% CNC)

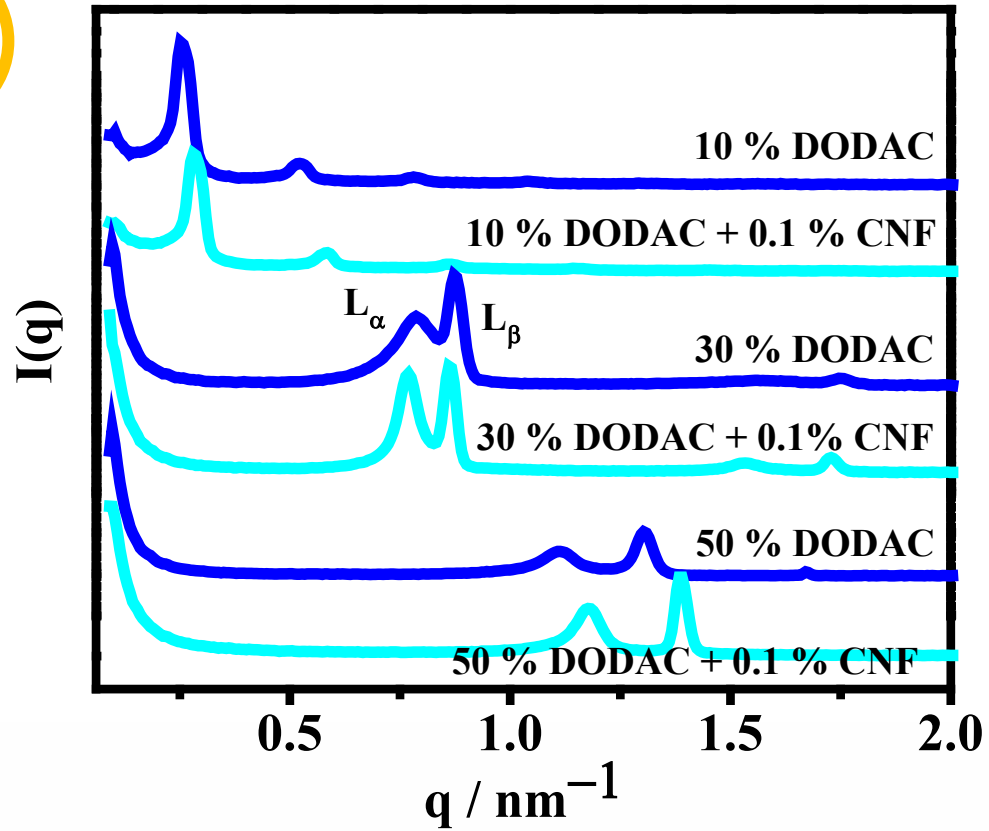


Sample	SAXS (1st peak)
	d/nm (±1)
10% DODAC	24.6
10% DODAC + 1% CNC	21.6
30% DODAC	7.9
30% DODAC + 1% CNC	7.8
50% DODAC	5.6
50% DODAC + 1% CNC	5.3

30+ wt% DODAC led to L_α e L_β phases

10 wt% DOCAC: shift to higher *q* values (lower repeating distances)

SAXS (0.1% CNF)



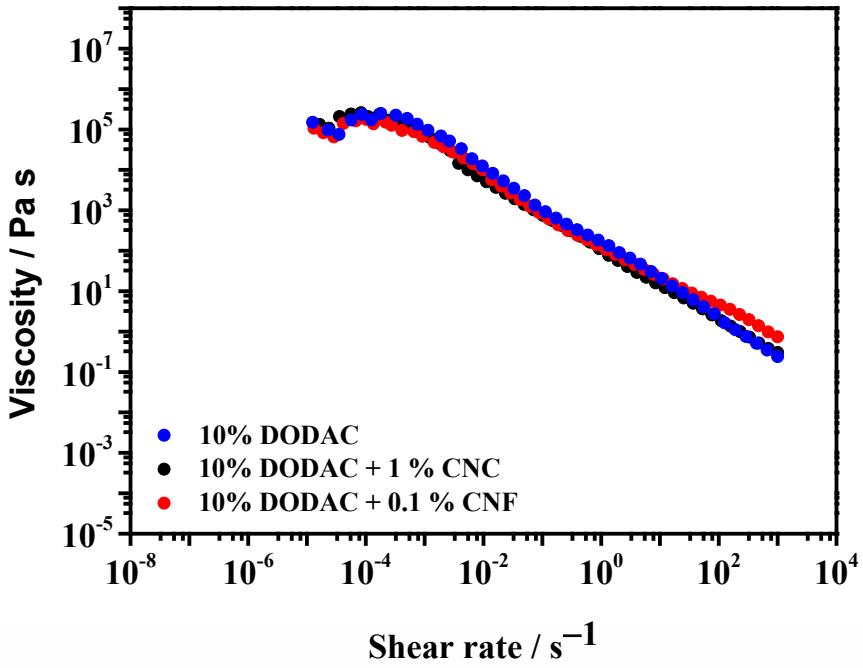
Sample	SAXS (1st peak)
	d/nm (±1)
10% DODAC	24.6
10% DODAC + 0.1% CNF	18.8
30% DODAC	7.9
30% DODAC + 0.1% CNF	7.9
50% DODAC	5.6
50% DODAC + 0.1% CNF	5.3

30+ wt% DODAC led to L_α e L_β phases

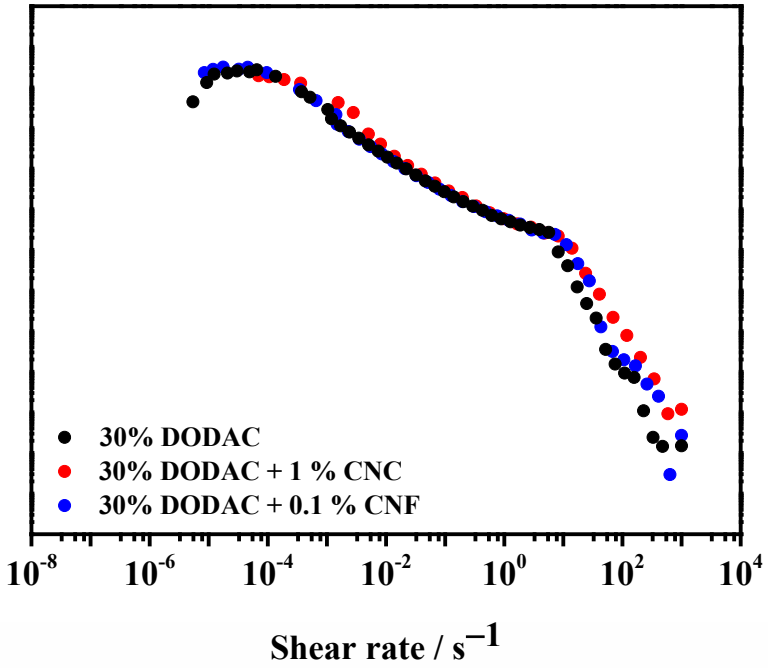
10 wt% DOCAC: shift to higher *q* values (lower repeating distances)

Flow curves

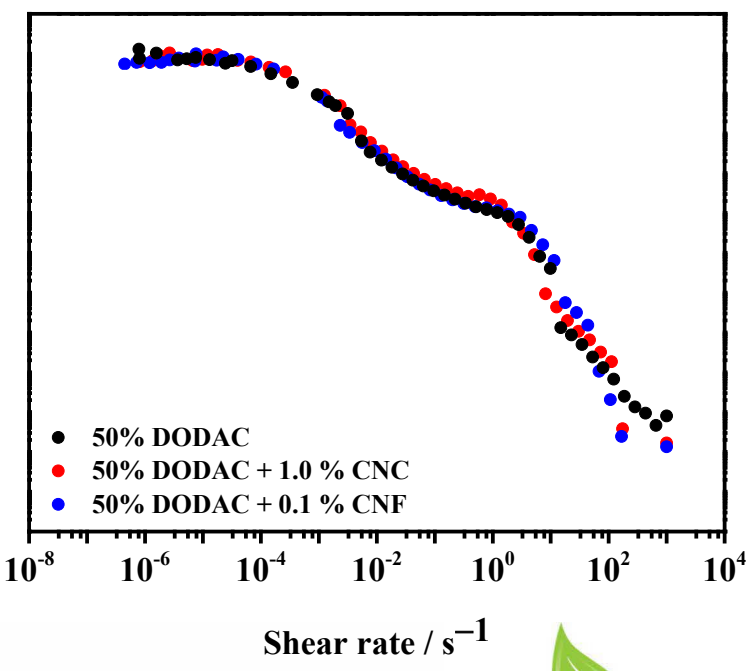
10 wt% DODAC



30 wt% DODAC



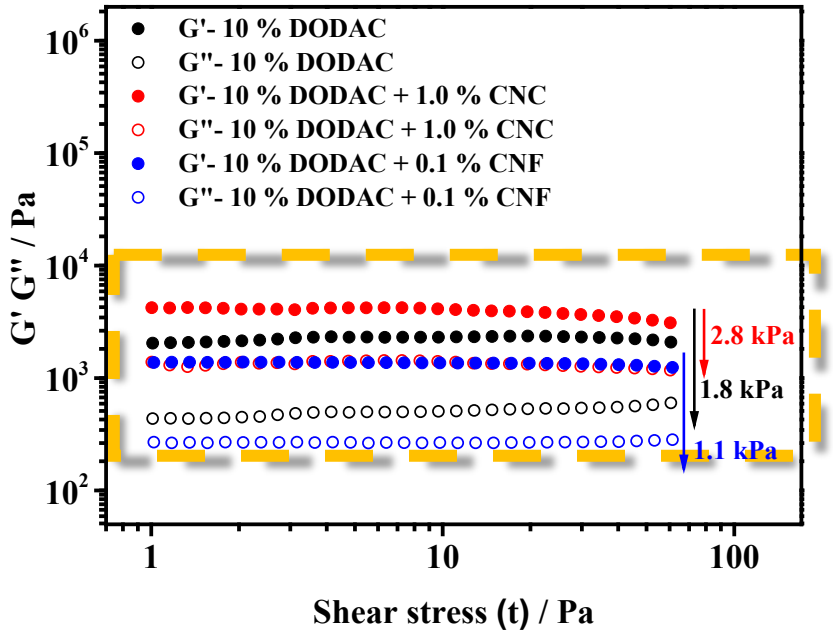
50 wt% DODAC



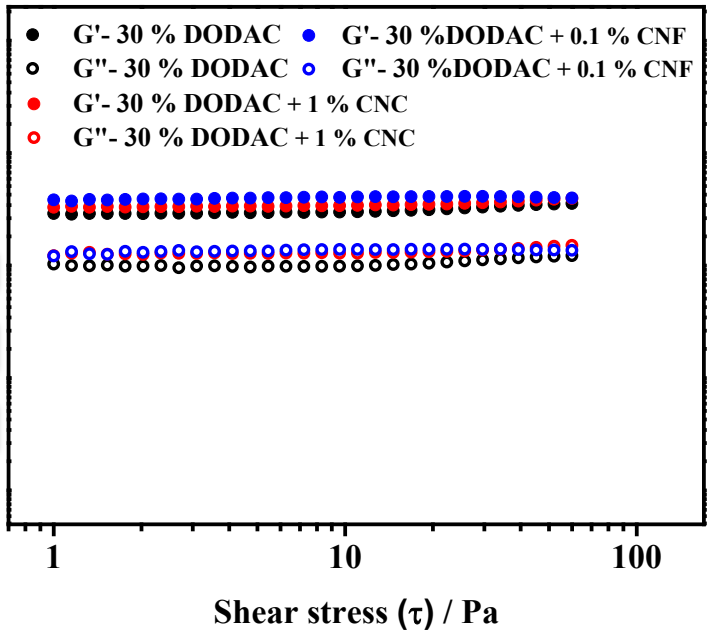
CNM did not change the **viscosity** of the lamellar phase

Amplitude sweeps

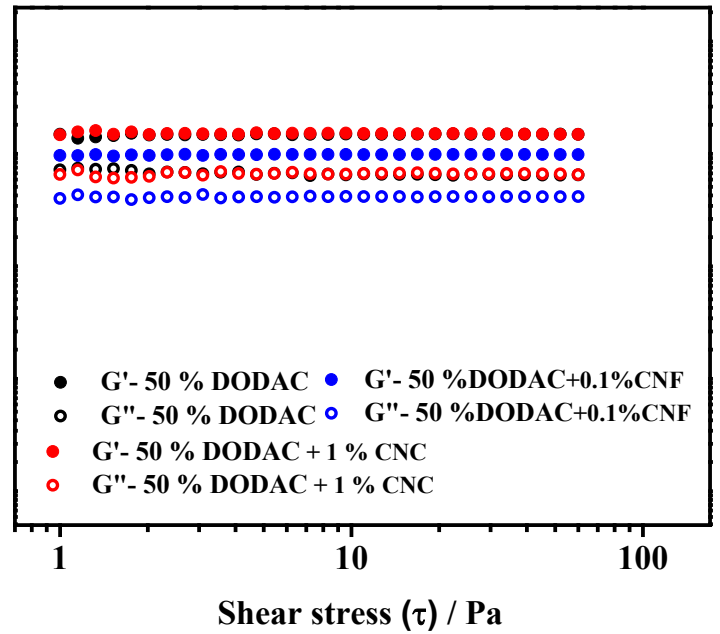
10 wt% DODAC



30 wt% DODAC



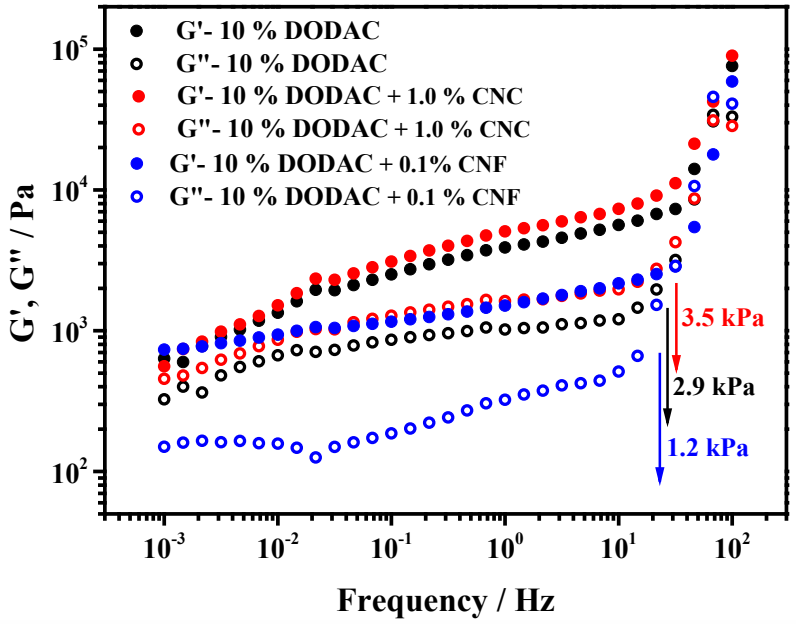
50 wt% DODAC



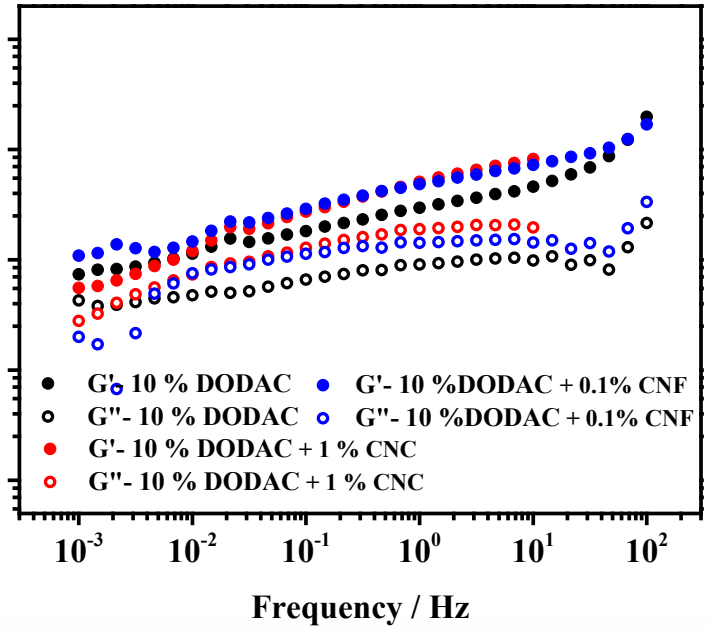
10% DODAC: CNC increased G'
CNF decreased G''

Frequency sweeps

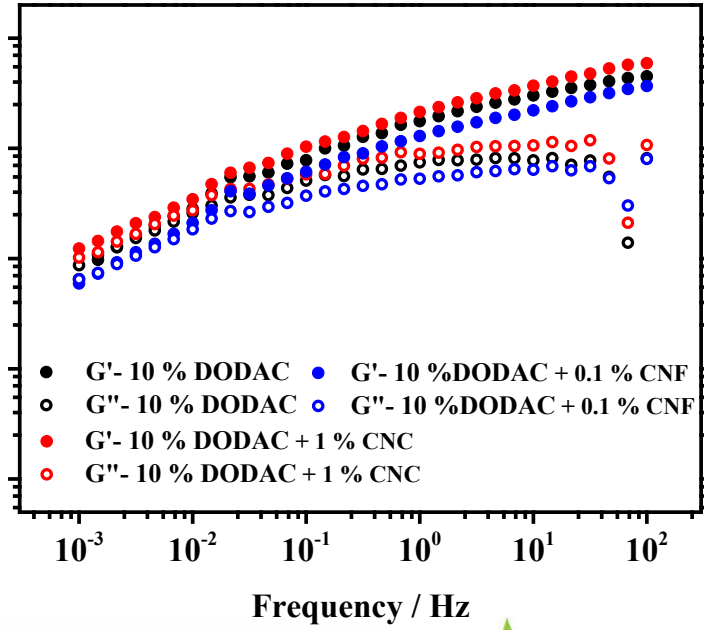
10 wt% DODAC



30 wt% DODAC



50 wt% DODAC



10% DODAC: CNC increased G'
CNF decreased G''

Conclusions

- CNM changed the lamellar microstructure and the rheology of 10% DODAC samples only
- CNM can be confined in the aqueous space between the bilayers (for 10% DODAC samples) and form microsized aggregates (CLMS)
- CNC stiffened while CNF ‘plasticized’ the gel. CNM morphology seems to play a role on the interaction with the lamellar phases.
- What’s next?
  - CNM structuring/organization (e.g., nano-IR, cryo-TEM)
  - Molecular anionic cellulose derivative (e.g., CMC)
  - Influence of surface charge density
  - Applications: lubricant (skincare)

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Thank you!

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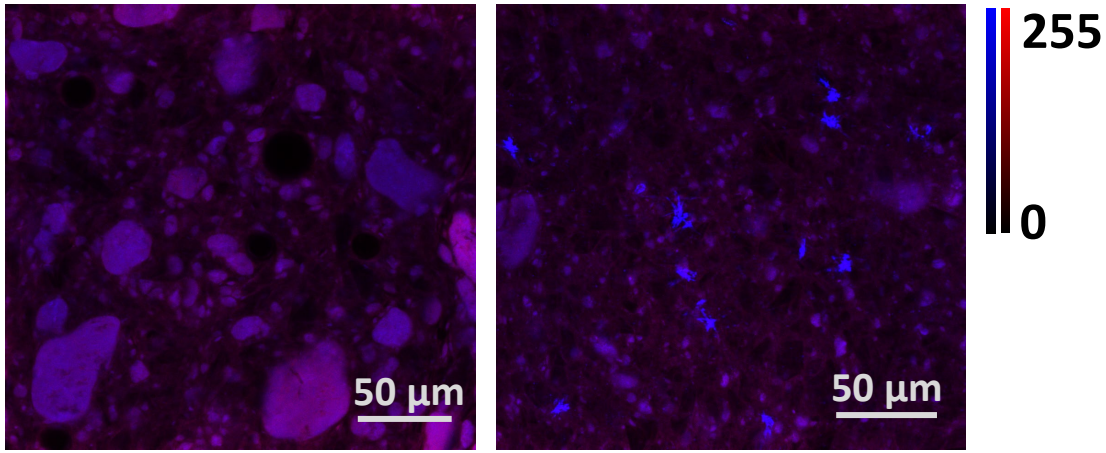
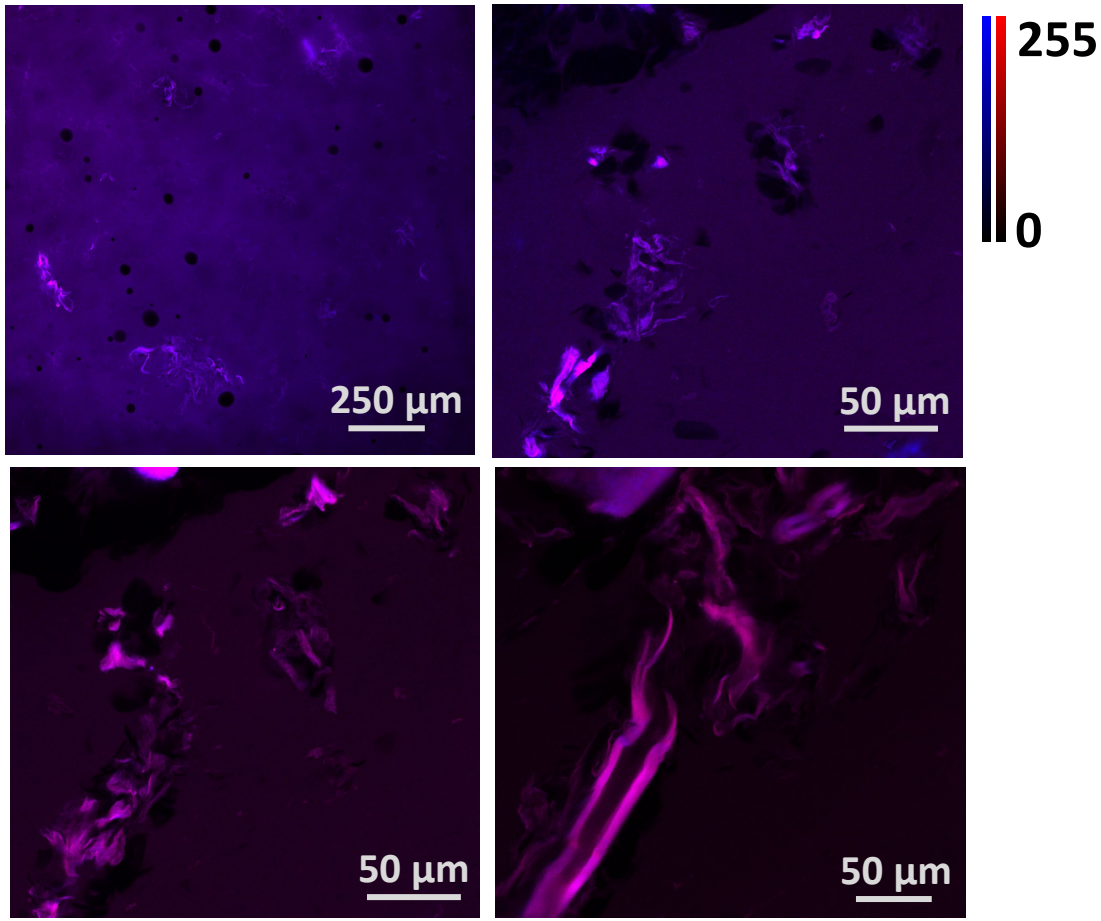
Confocal microscopy



10% DODAC + 0.1% CNC (NR / NB)



10% DODAC + 0.1% CNF (NR / NB)