In situ assessment of cellulose reactivity kinetics with DSC heat of dissolution and heat-controlled cross-polarized microscopy

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Motivation

- Regenerated cellulose production, e.g., manufacturing man-made cellulosic fibers and membranes, requires the dissolution of cellulose into a solvent and subsequent precipitation in an antisolvent to produce the desired product.
- Various methods are applied for increasing cellulose reactivity and dissolution.

Background

Cellulose dissolution depends on cellulose feedstock and solvent properties.

Each solvent has a *temperature range* where the dissolution occurs; e.g., NaOH/water, <0 °C.

Controlling the cellulose–solvent system temperature enables dynamic reaction kinetics analysis.

Two complementary methods

Temperature-controlled cross-polarized microscopy – image luminance over time

DSC heat of dissolution

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DSC heat of dissolution

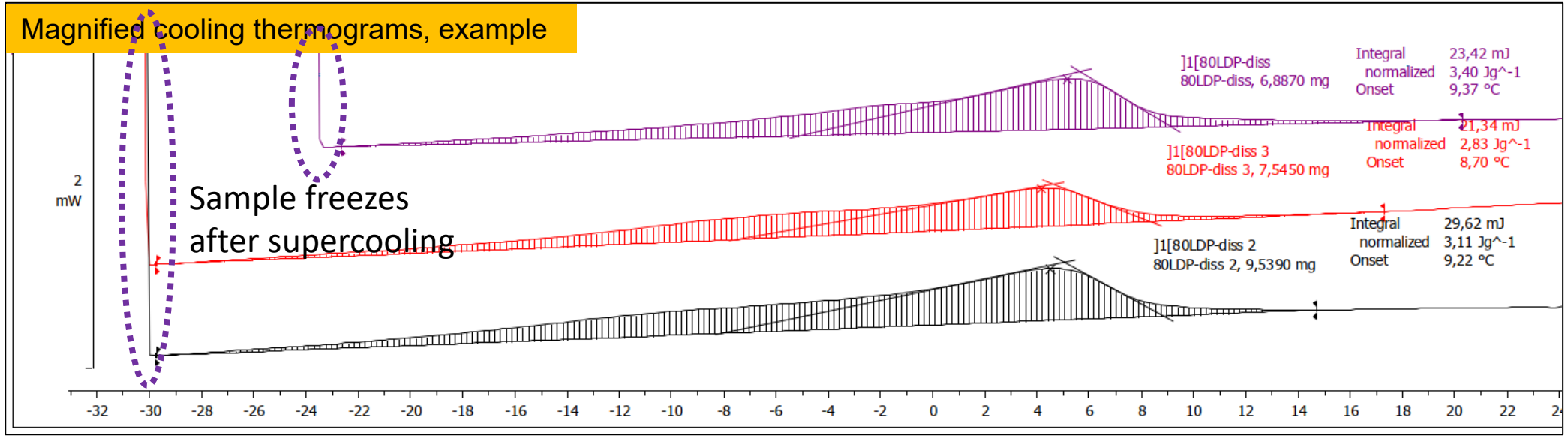
- Cellulose dissolution is a thermodynamic event, driven by entropy: at certain conditions, the dissolved state is more favored.
- As cellulose dissolves, it releases heat to its environment. This exothermic event that can be detected with a calorimeter.

Materials

- Pulp samples with varying cellulose molecular weight were prepared by acid hydrolysis (0.5 M H_2SO_4) for varying lengths of time
- Pulp degree of polymerization was calculated from limiting viscosity values (SCAN-CM 15:99)
- NaOH/ZnO solvent was prepared

DSC methodology

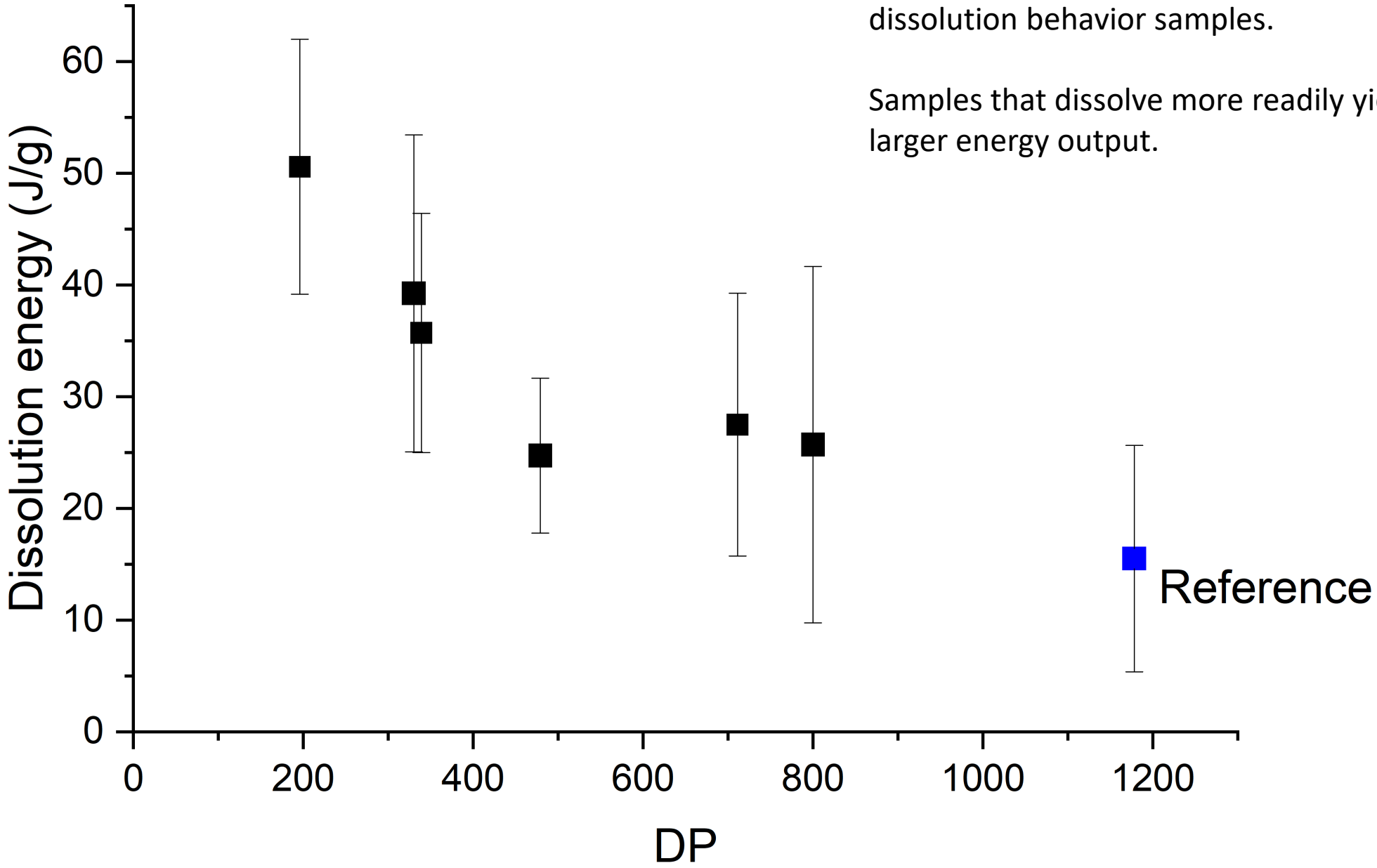
- Cellulose sample was mixed with NaOH/ZnO solvent in a DSC pan.
  - 7.0 wt% cellulose, 7.8 wt% NaOH, 1.3 wt% ZnO
- Pan was sealed and DSC program was run, dropping sample temperature at -10 °C/min
- Below 10 °C, exothermic peaks were detected
- Dissolution enthalpy was calculated by was integrating peak area
- Divided by the cellulose sample mass, energy per gram of pulp (J/g).



DSC, results

Varying sample degree of polymerization (DP) with hydrolysis ➔ different dissolution behavior samples.

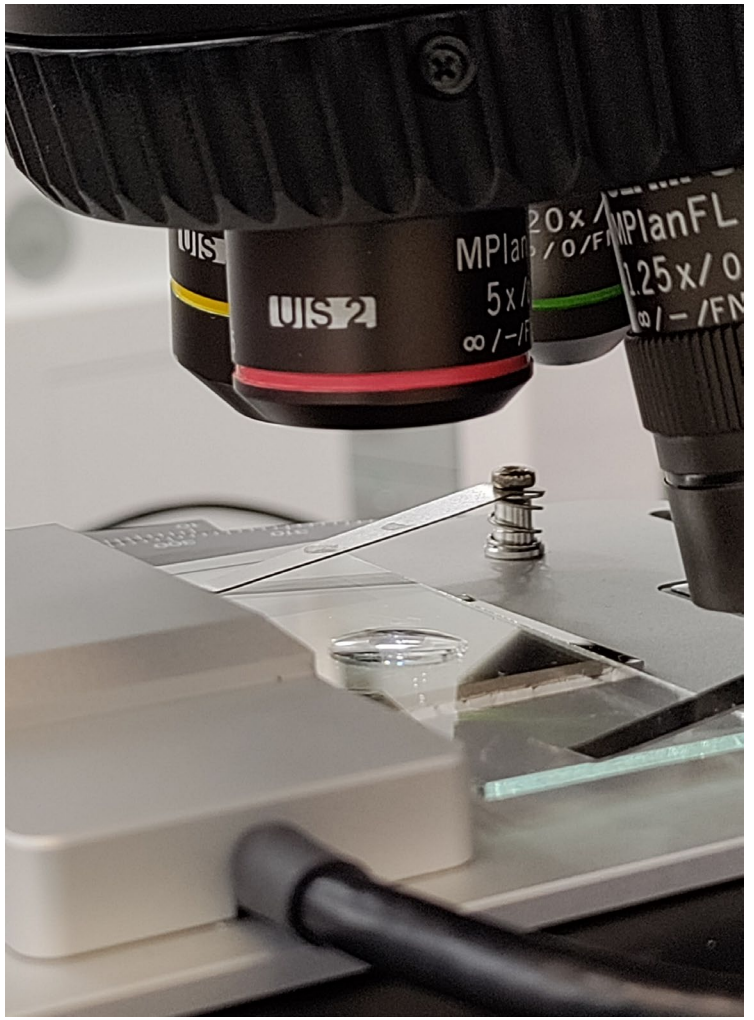
Samples that dissolve more readily yield larger energy output.



Cross-polarized light microscopy

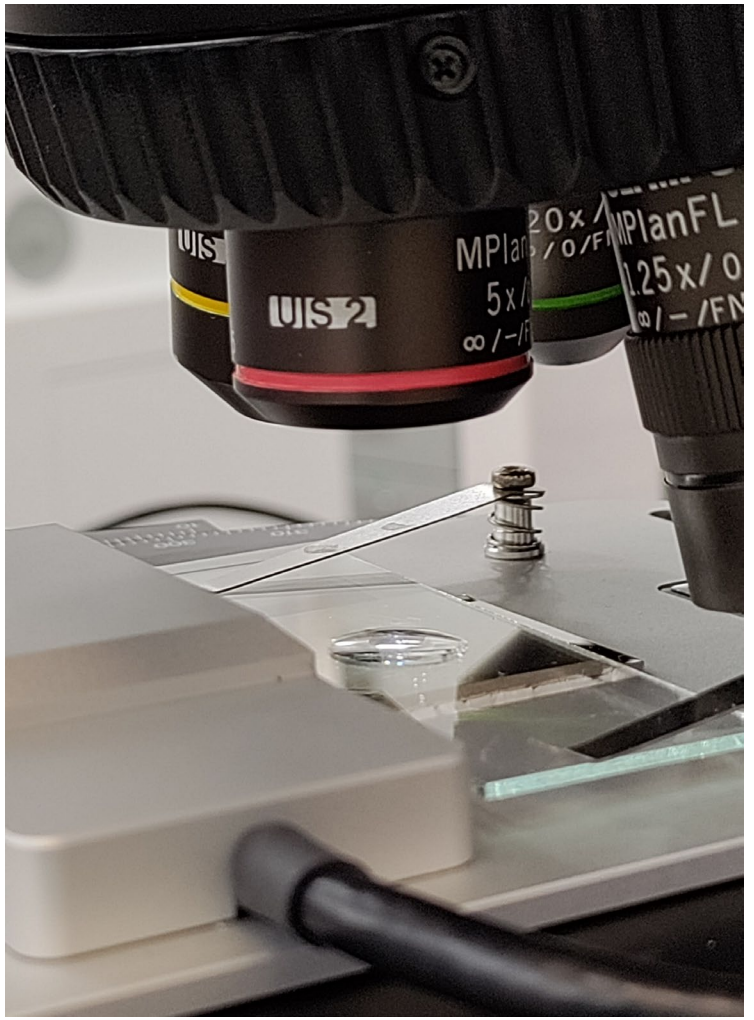
Cross-polarized light microscopy

- Dissolution of cellulose in NaOH/water occurs in a narrow temperature range.
- During microscopy, by changing the temperature with the aid of a temperature-controlled stage, the dissolution can be visualized in real time.

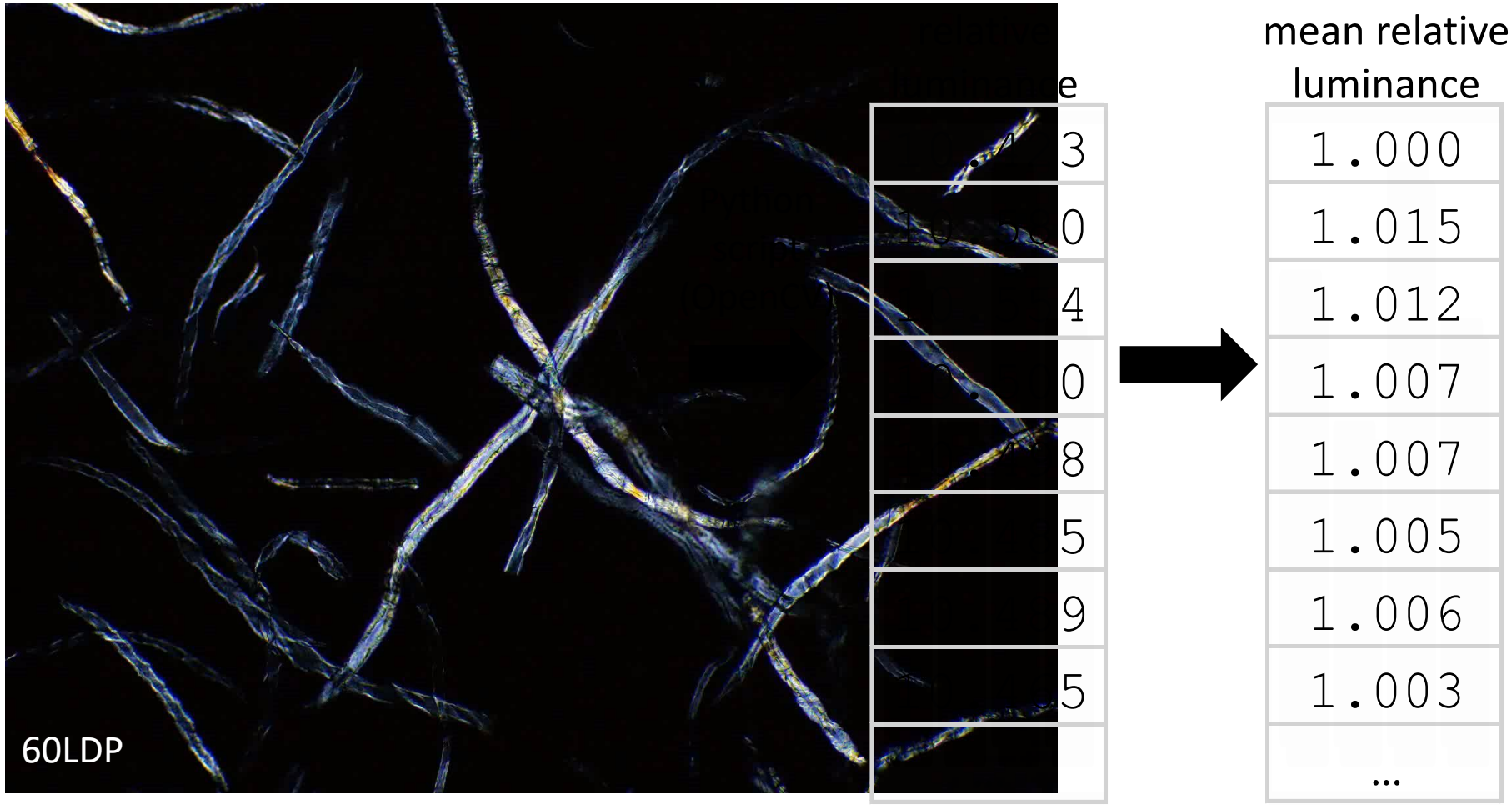


Cross-polarized light microscopy

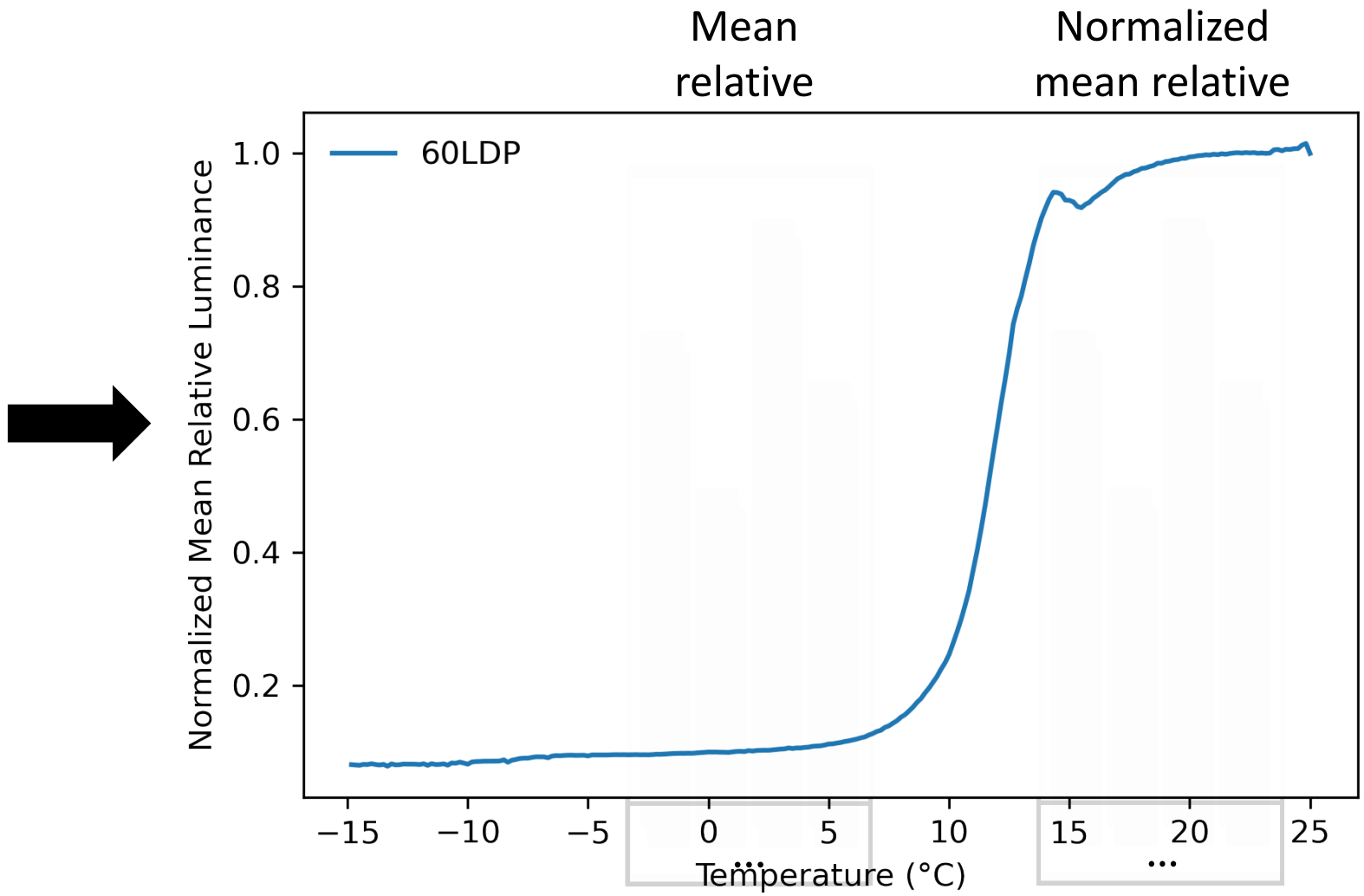
- Crystalline cellulose has *birefringent* domains that are visible under cross-polarized light.
- As cellulose dissolves, the birefringence dissipates, and the total luminance starts to decrease.

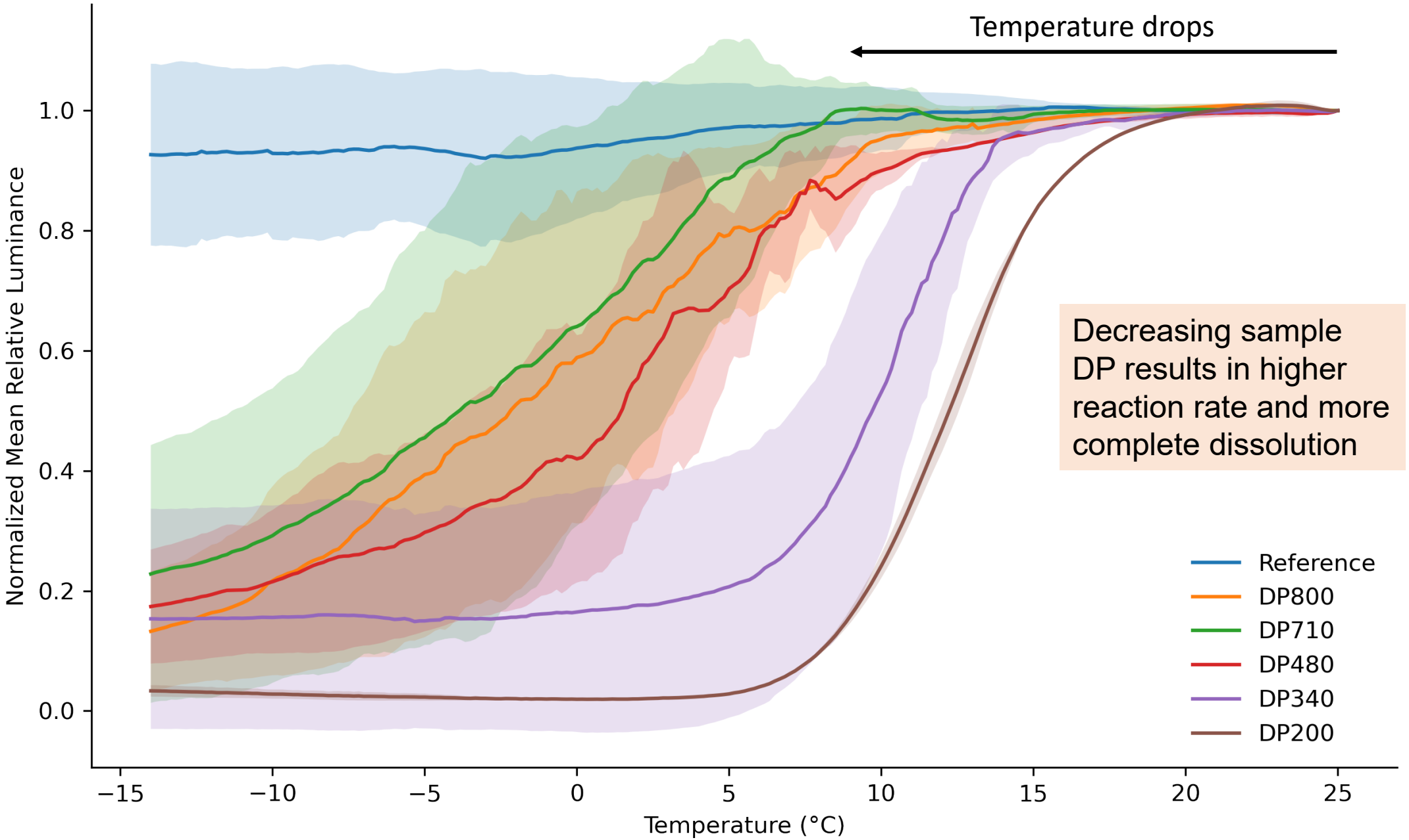


Video file converted frame by frame to relative luminance values



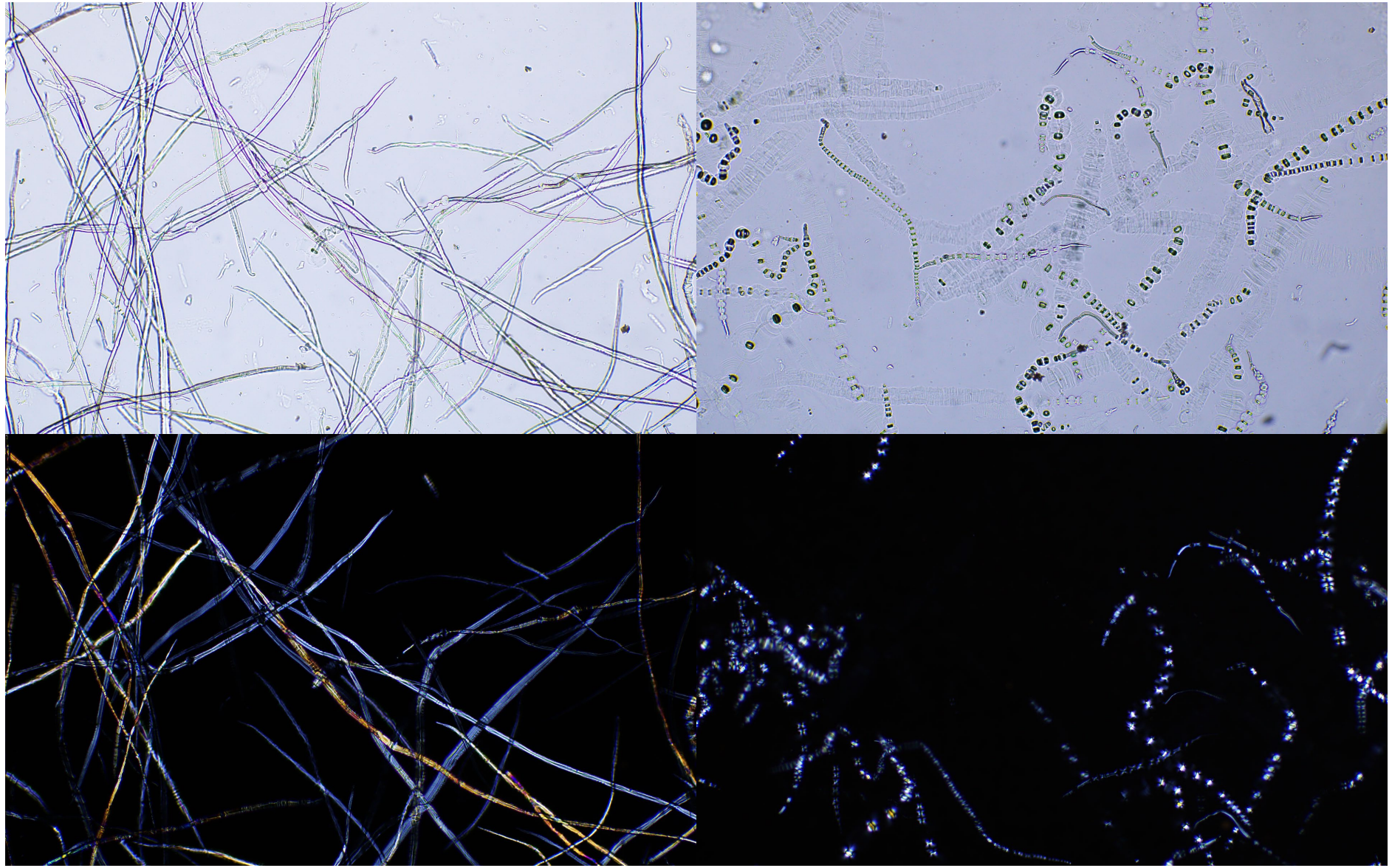
Relative luminance values plotted against system temperature




Temperature drops
Normalized Mean Relative Luminance
1.0
0.8
0.6
0.4
0.2
0.0
−15
−10
−5
0
5
10
15
20
25
Temperature (°C)
Decreasing sample DP results in higher reaction rate and more complete dissolution
Reference
DP800
DP710
DP480
DP340
DP200

DP800

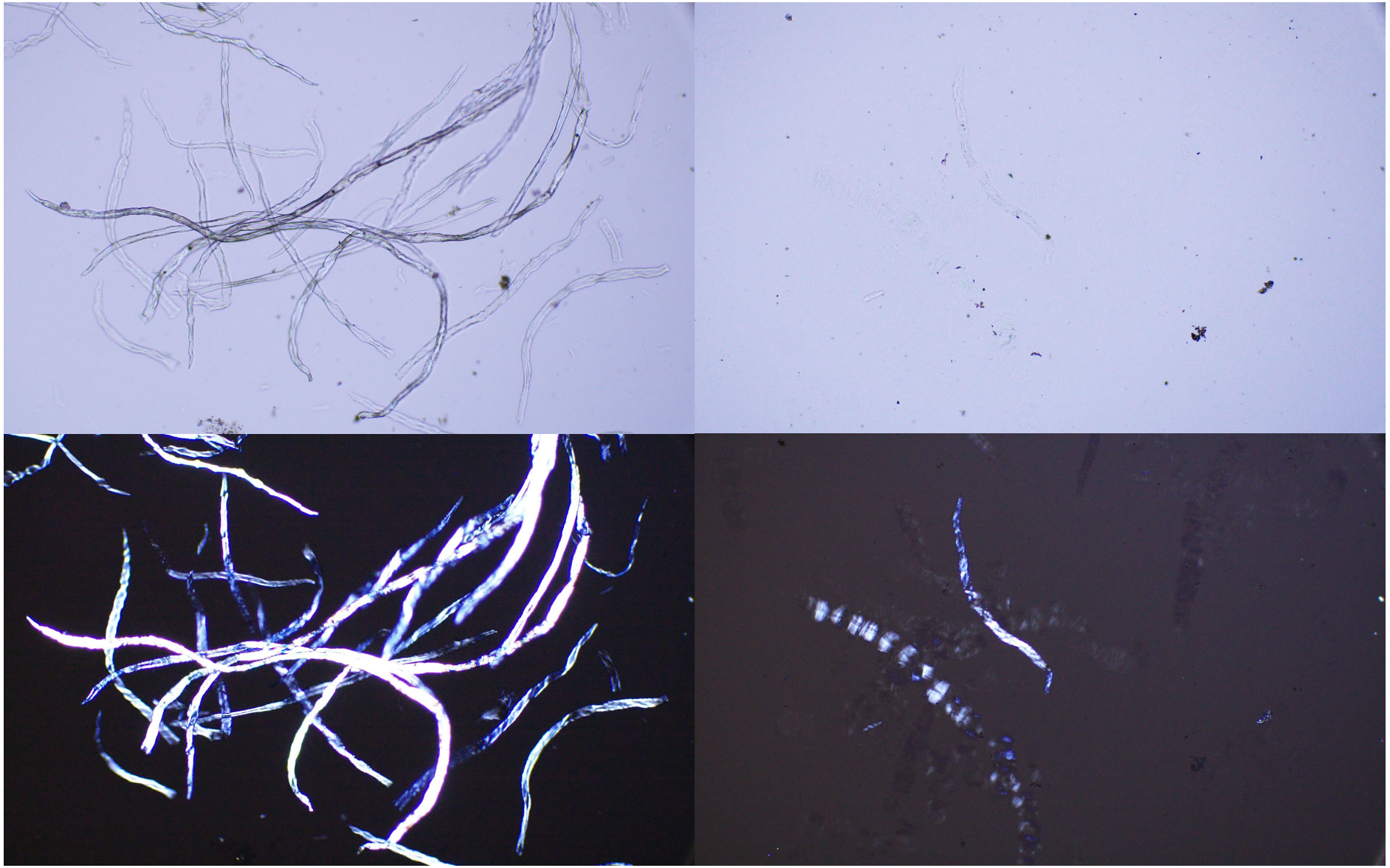
Before dissolution



After dissolution

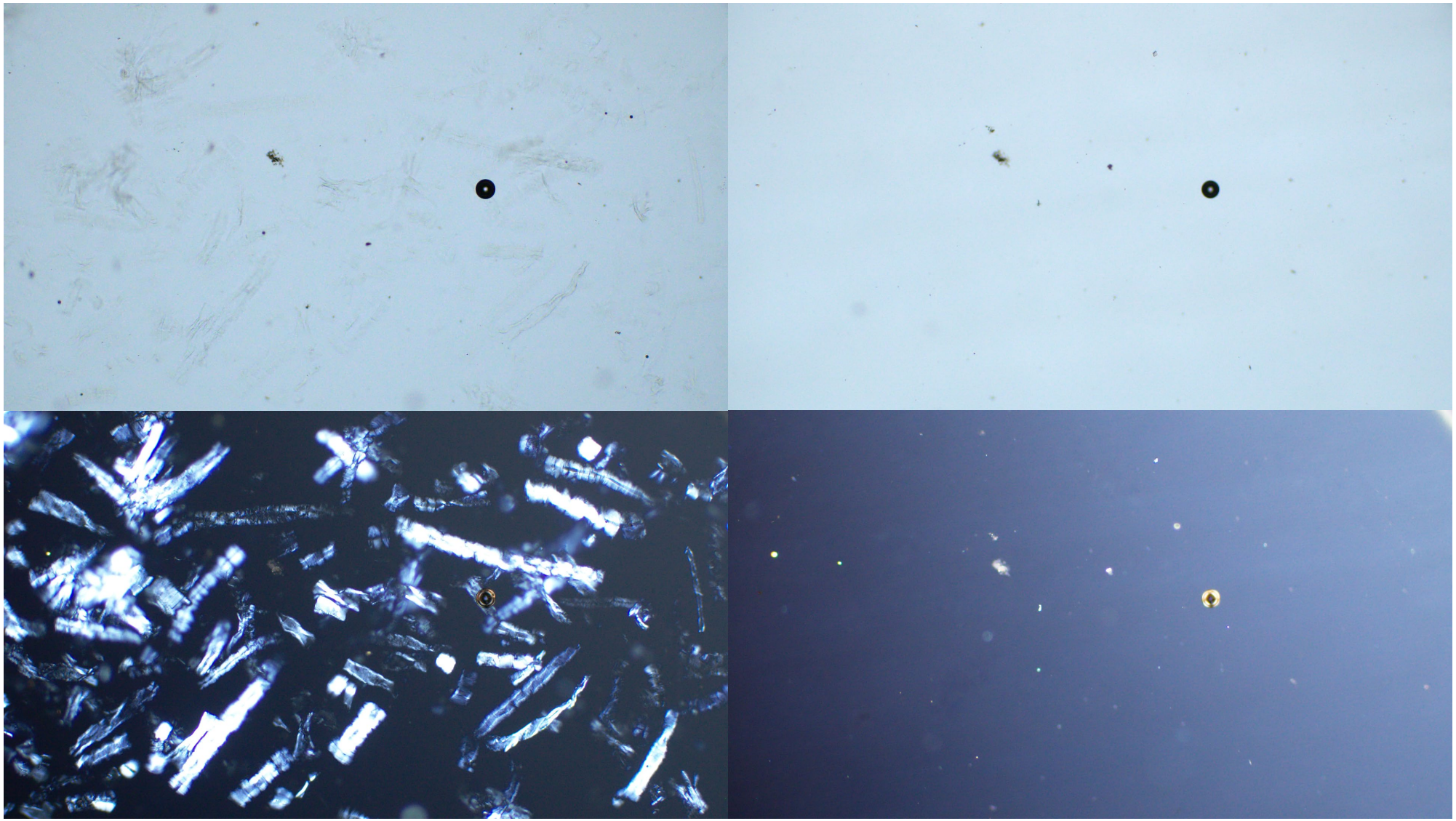
DP340

Before dissolution



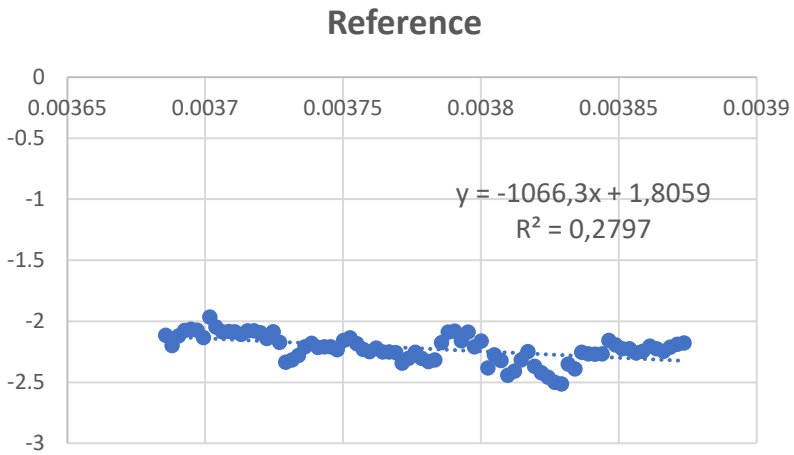
After dissolution

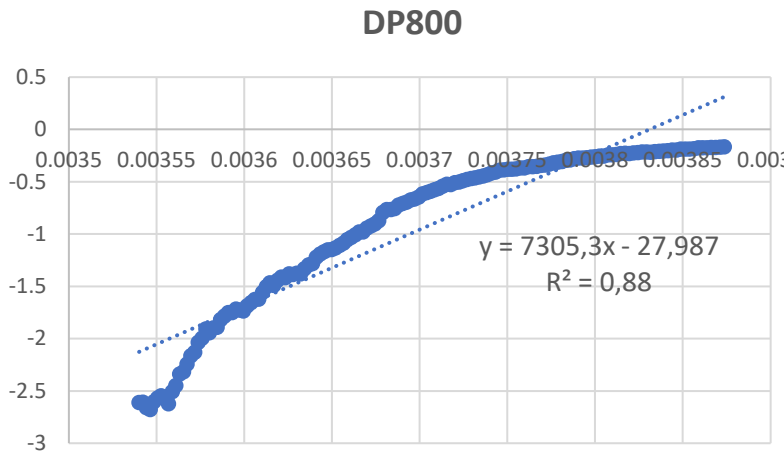
DP200
Before
dissolution

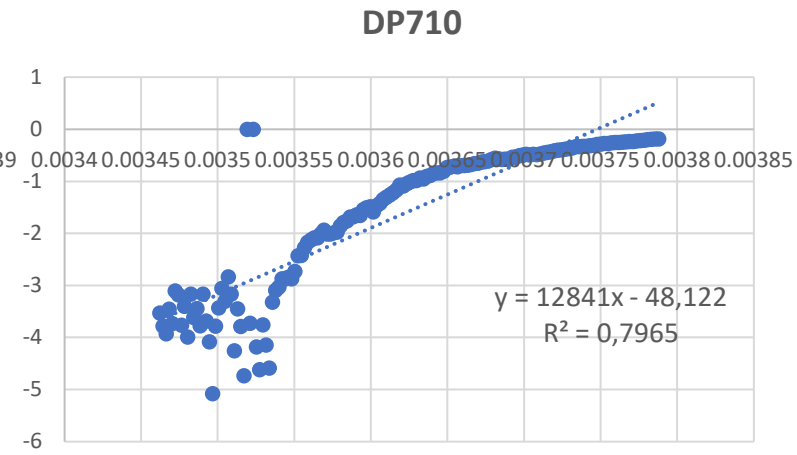


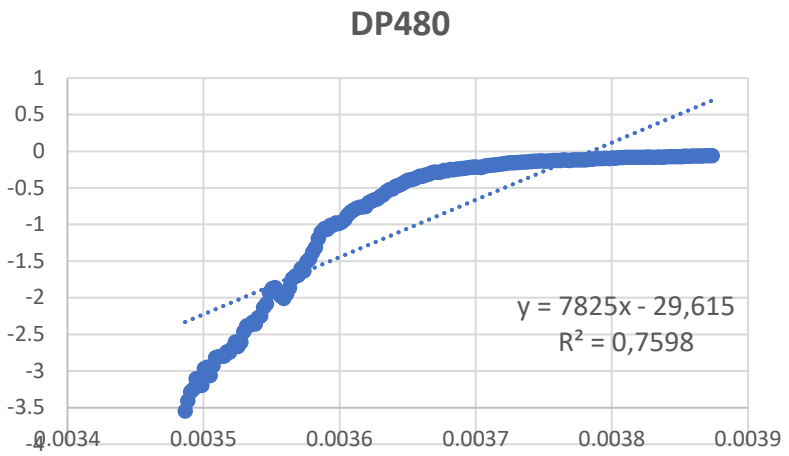
After
dissolution

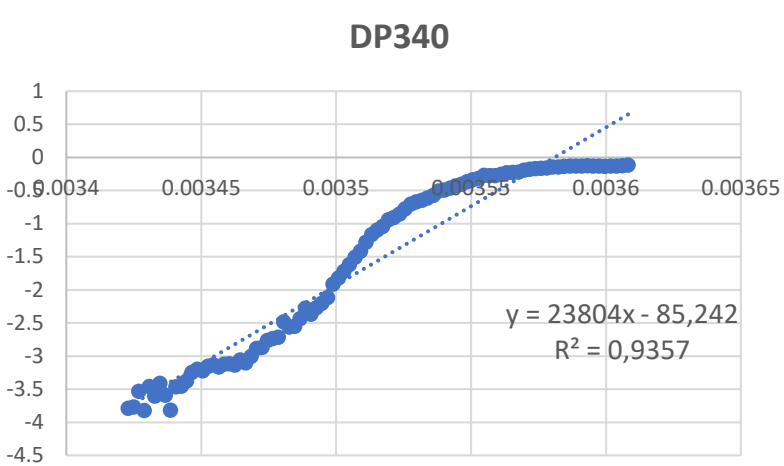
Arrhenius plots *(slide to be finalized)*

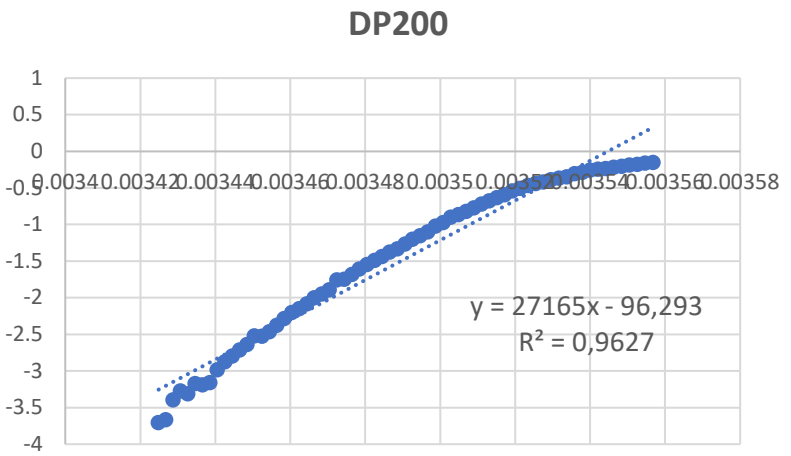












Conclusions

- DSC may be utilized in real-time dissolution studies
  - Swelling, dissolution ➔ Both are exothermic reactions
- Microscopy relevant tool for assessing both reactivity kinetics and dissolution mode
  - Dissolution visualized in real-time
  - Full dissolution or only loss of birefringence? ➔ Further studies needed
- Methods useful for various solvents,
  - e.g., NaOH/water,
  - ionic liquids

Upcoming research

- Effect of alkaline pretreatments on cellulose dissolution

- Visualization of additive effect on dissolution kinetics in NaOH/water solvents
  - No additives, urea, ZnO, urea & ZnO together

References

- *To be finalized*

Thank you!