Towards better understanding of **synthesis-morphology-performance in polyamide membranes:** Visualization under controlled reaction conditions

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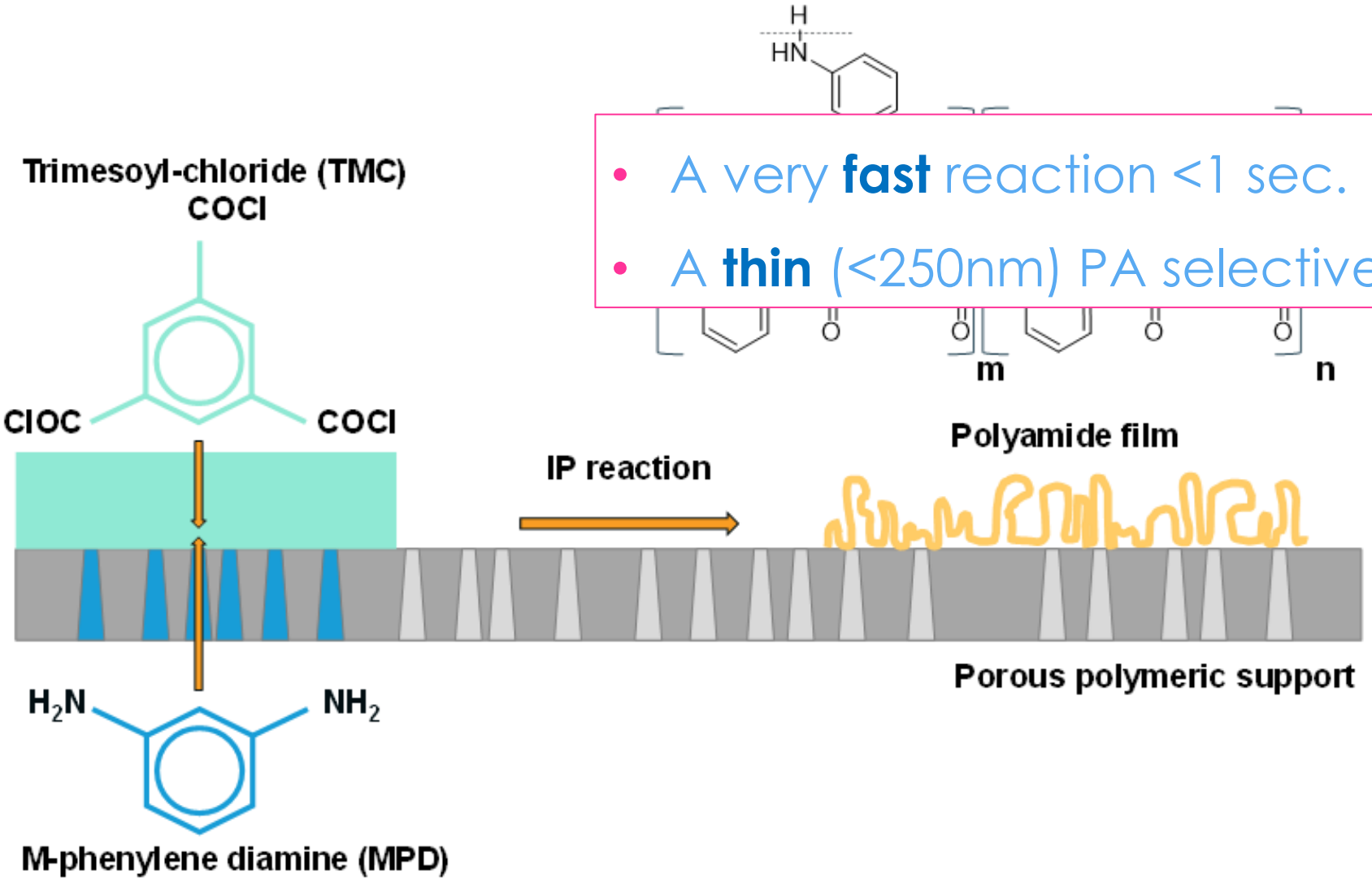
2 Nano-science and Nano-Technology program, Technion – Israel Institute of Technology

Water & Energy Technologies Laboratory

Interfacial Polymerization (IP)

- A very **fast** reaction <1 sec.
- A **thin** (<250nm) PA selective layer



Nulens and Ben Zvi et al., *JMS* (2022)

Desalination by RO

The product of IP:

Crumpled polyamide film

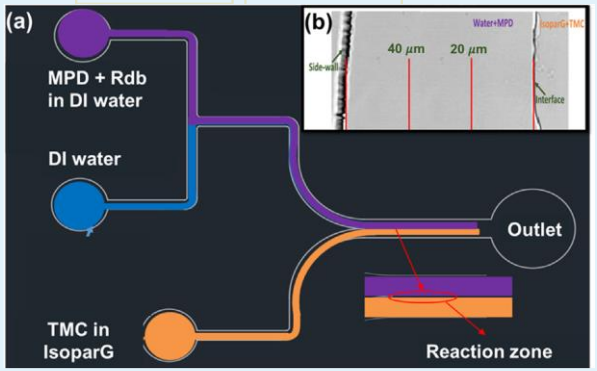
Synthesis — ? — Morphology — ? — Performance

pH Solvents Time

Controlling reaction conditions

+

In-situ monitoring



Ukrainsky and Ramon, *JMS* (2018)

Contradicting trends

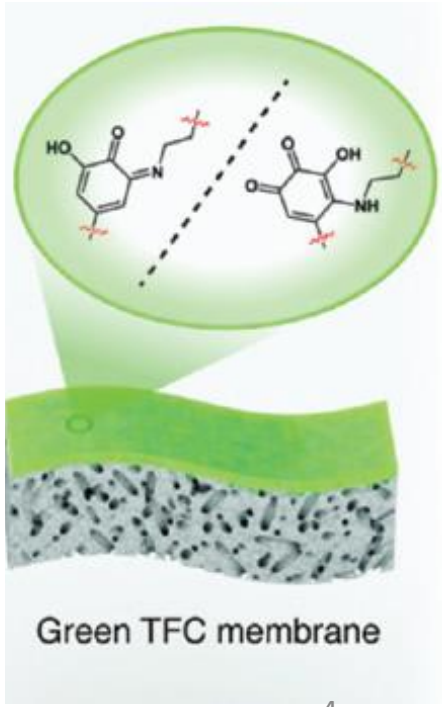
Motivation

Synthesis — ? — **Morphology** — ? — **Performance**

Why?

⇩

- ✓ Improve existing membranes
- ✓ Move towards ‘green materials’

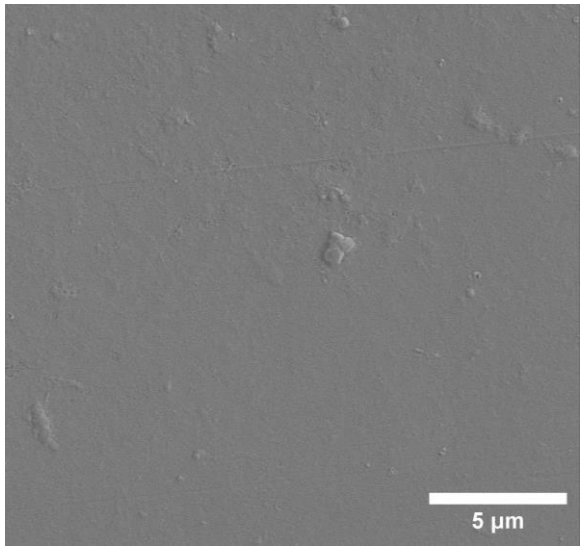


Park et al., Green Chem. 2021

Synthesis — Morphology

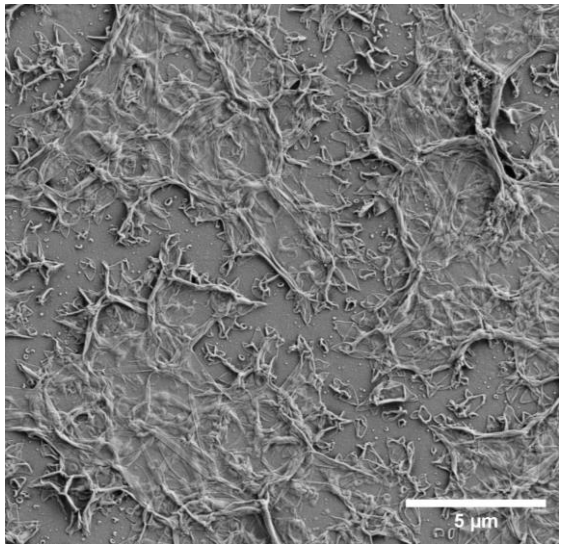
Instability

The Concept

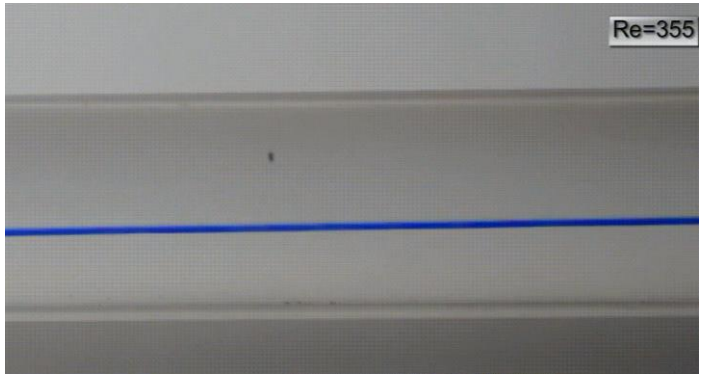


Smooth= Stable

Instability mechanisms



Crumpled= Unstable

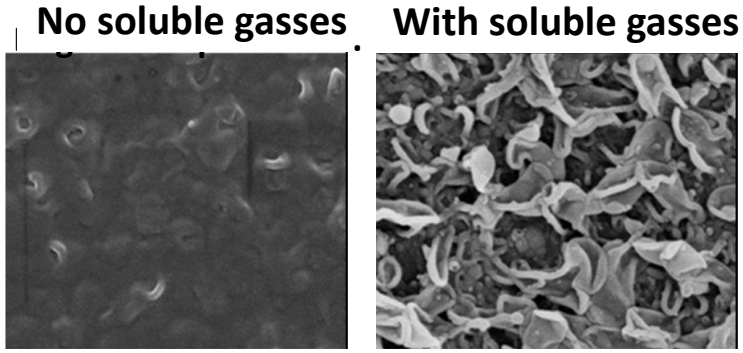


https://www.youtube.com/watch?v=y0WRJtXvpSo

Nulens and Ben Zvi et al., *JMS* (2022)

Instability mechanisms

During IP



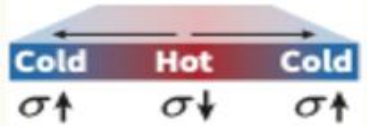
Ma et al., *Environ. Sci. Technol. Lett.* (2018)

Bubble formation

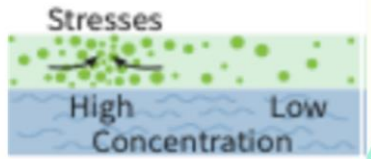
Elastic crumpling

Hydrodynamic instability

Thermo-capillarity

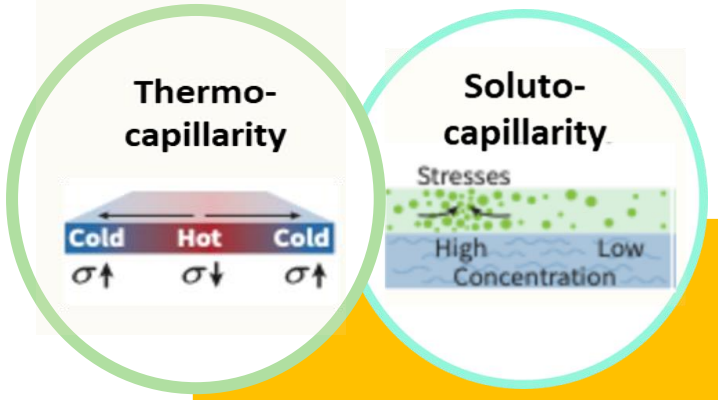


Soluto-capillarity

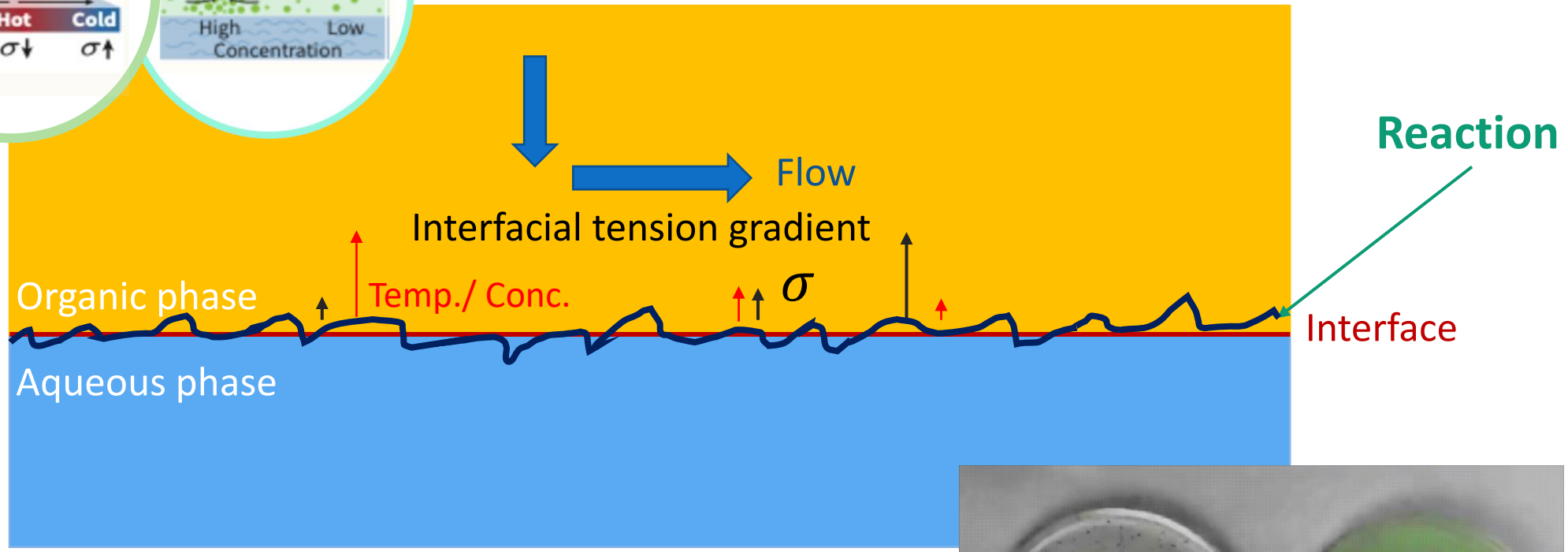


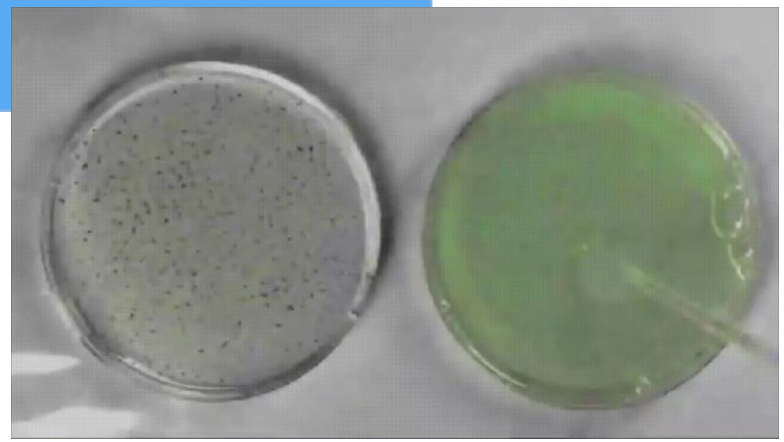
Freger and Ramon, *Prog. Polym. Sci.* (2021)

Hydrodynamic instability



IP system





Gradients in interfacial tension drive a flow: **Marangoni flow**

https://www.youtube.com/watch?v=y0WRJtXvpSo

Instability mechanisms

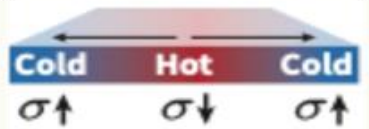
During IP

Hydrodynamic instability

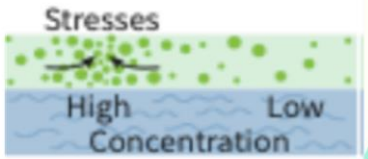
Bubble formation

Elastic crumpling

Thermo-capillarity

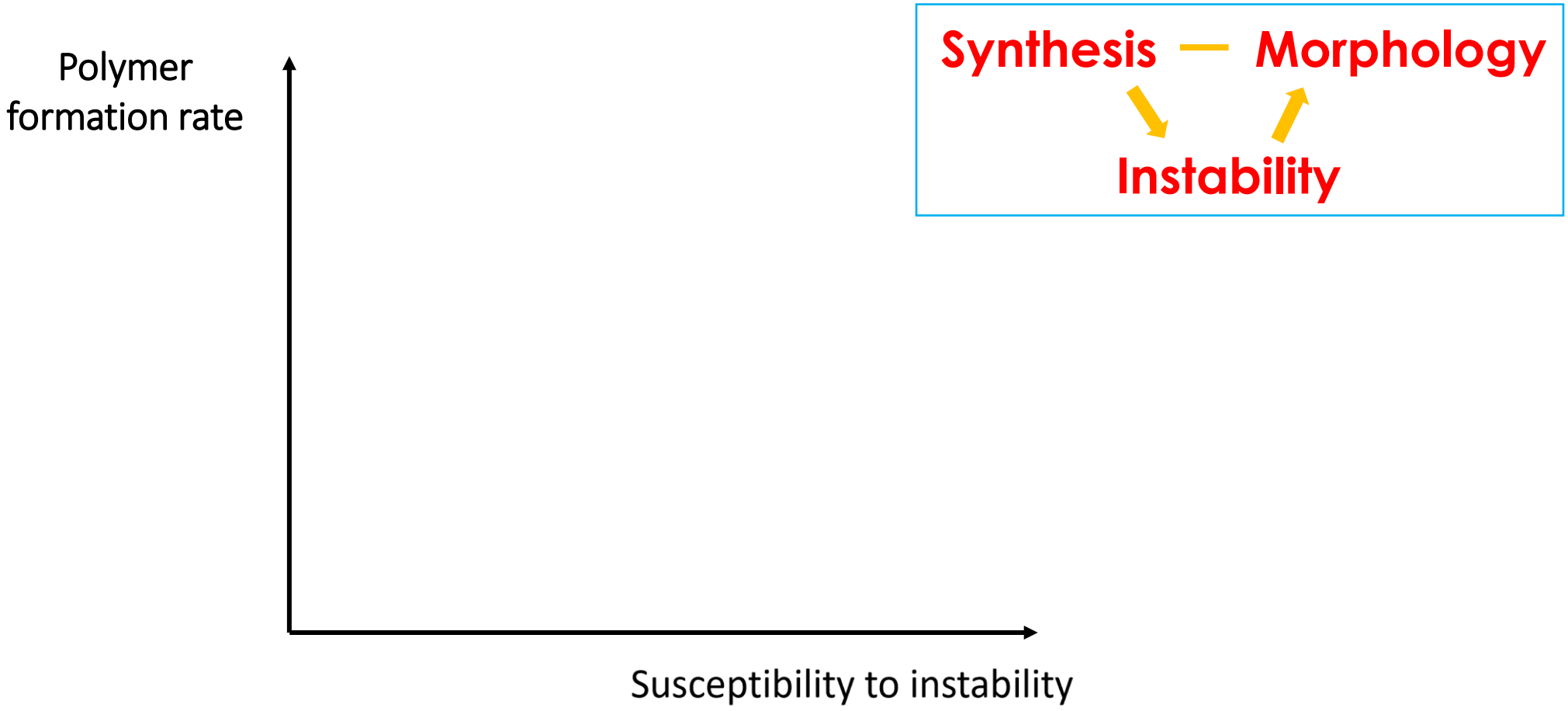


Soluto-capillarity

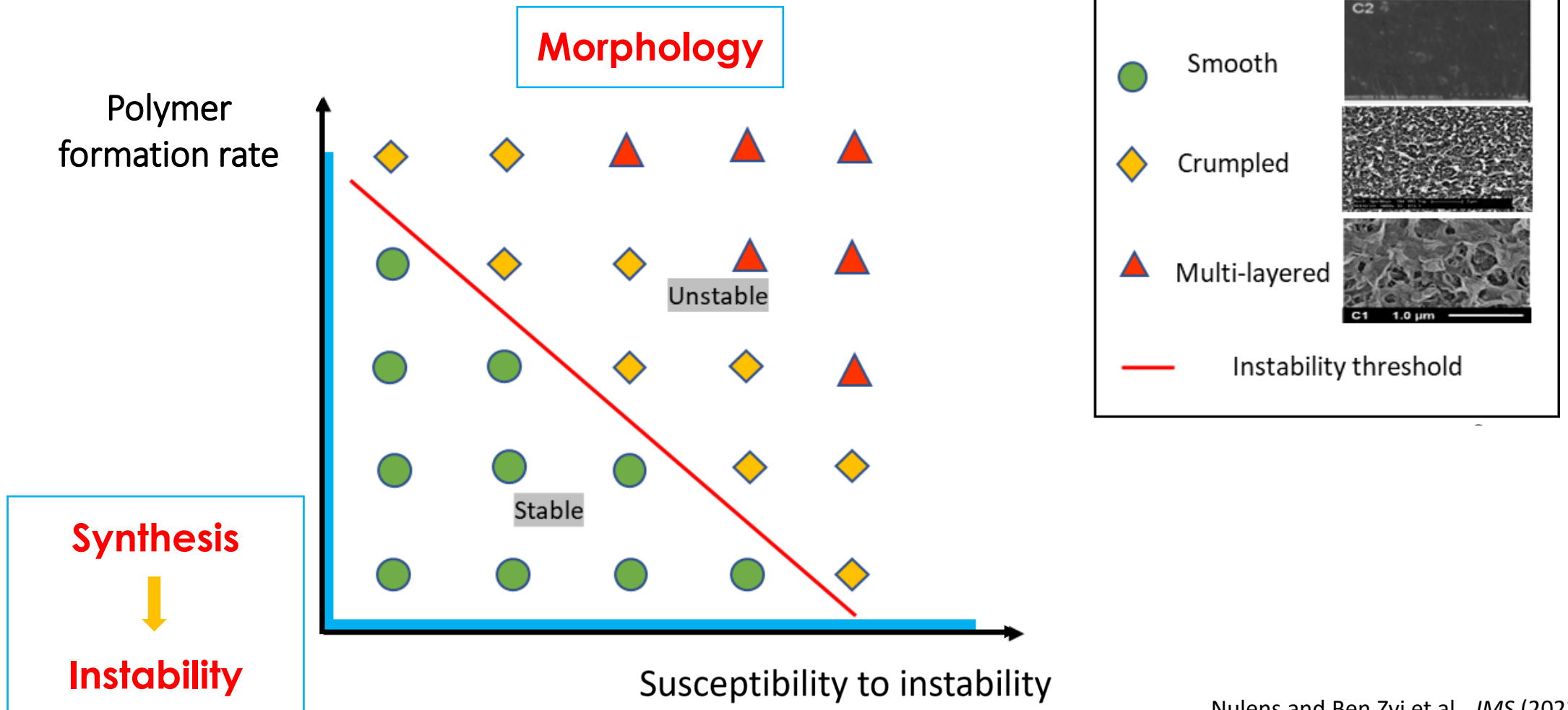


Freger and Ramon, *Prog. Polym. Sci.* (2021)

A ‘**phase diagram**’ of **synthesis-morphology** relations in IP

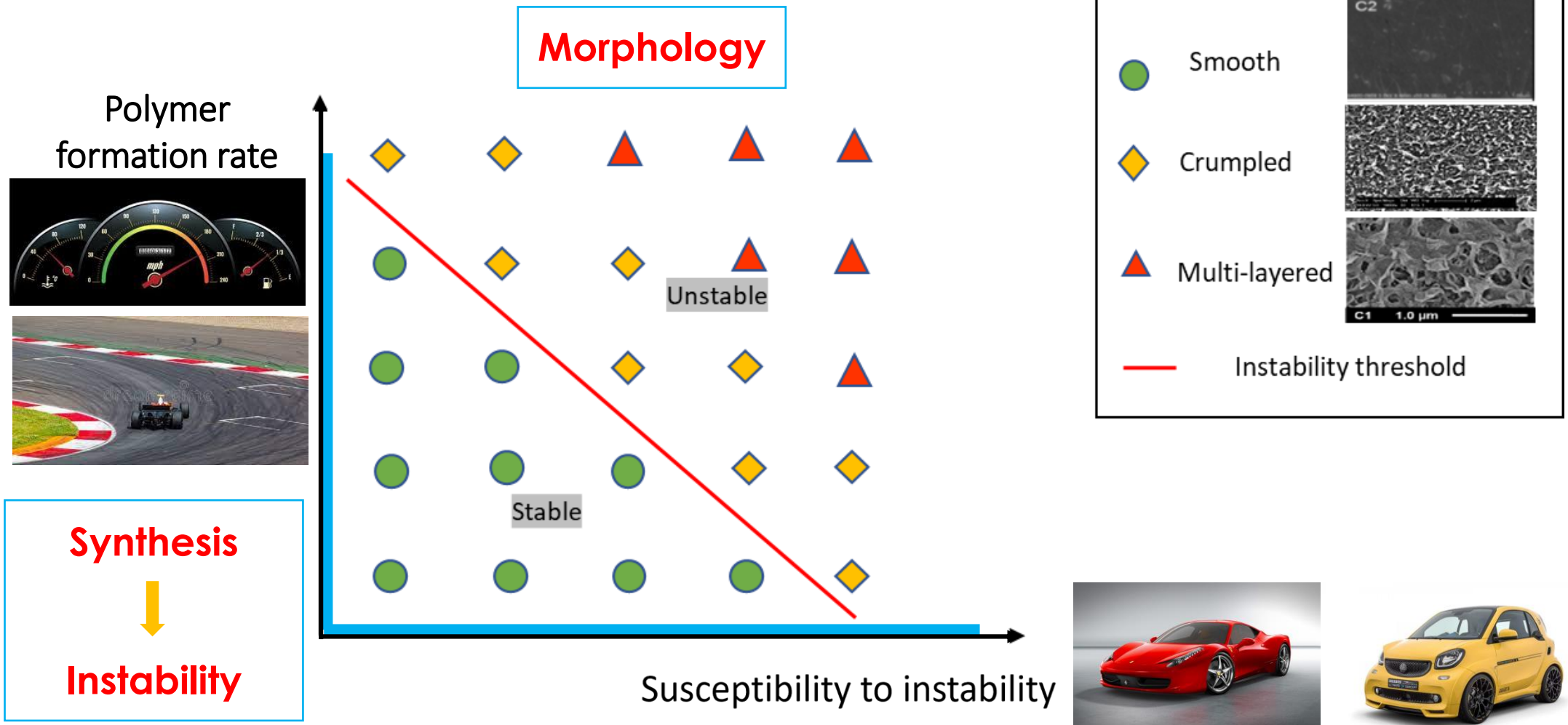


A '**phase diagram**' of **synthesis-morphology** relations in IP



Nulens and Ben Zvi et al., *JMS* (2022)

A ‘**phase diagram**’ of **synthesis-morphology** relations in IP



A '**phase diagram**' of **synthesis-morphology** relations in IP

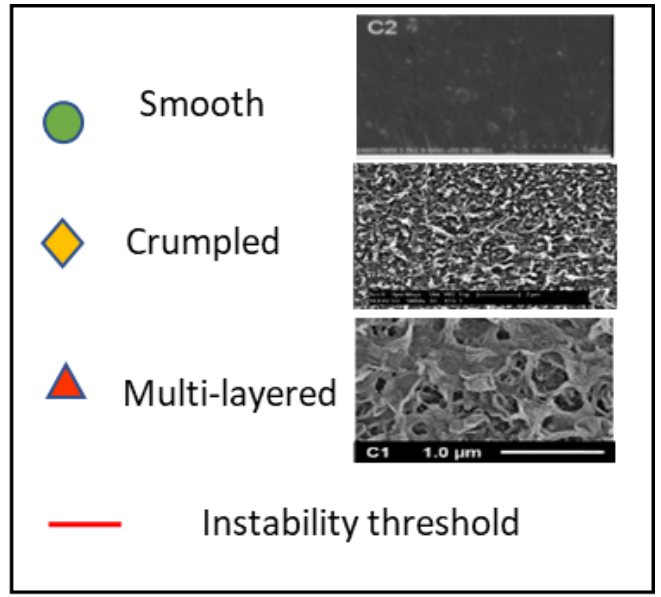
Morphology ✓

Polymer formation rate

Unstable

Stable

Susceptibility to instability



?

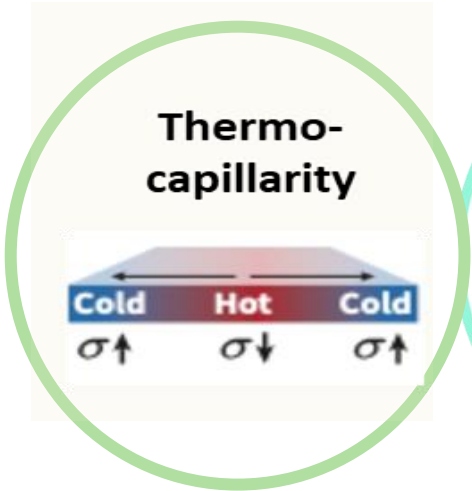
Synthesis ↓ **Instability**

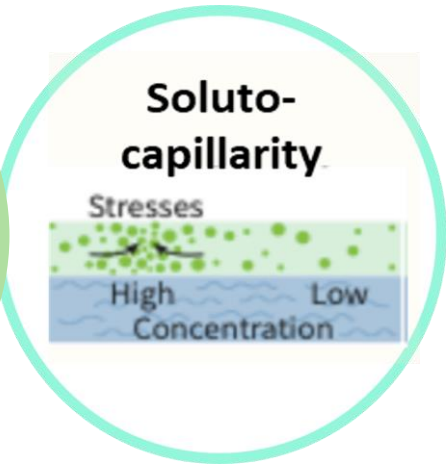
Nulens and Ben Zvi et al., *JMS* (2022)

Instability mechanisms

During IP

Hydrodynamic instability=
flow in IP system

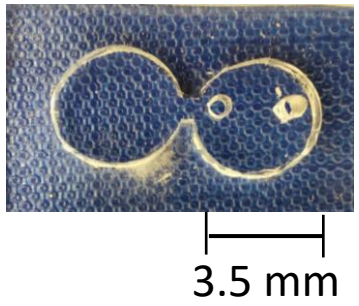




Freger and Ramon, *Prog. Polym. Sci.* (2021)

How can we observe a flow in IP ?

Microfluidic device



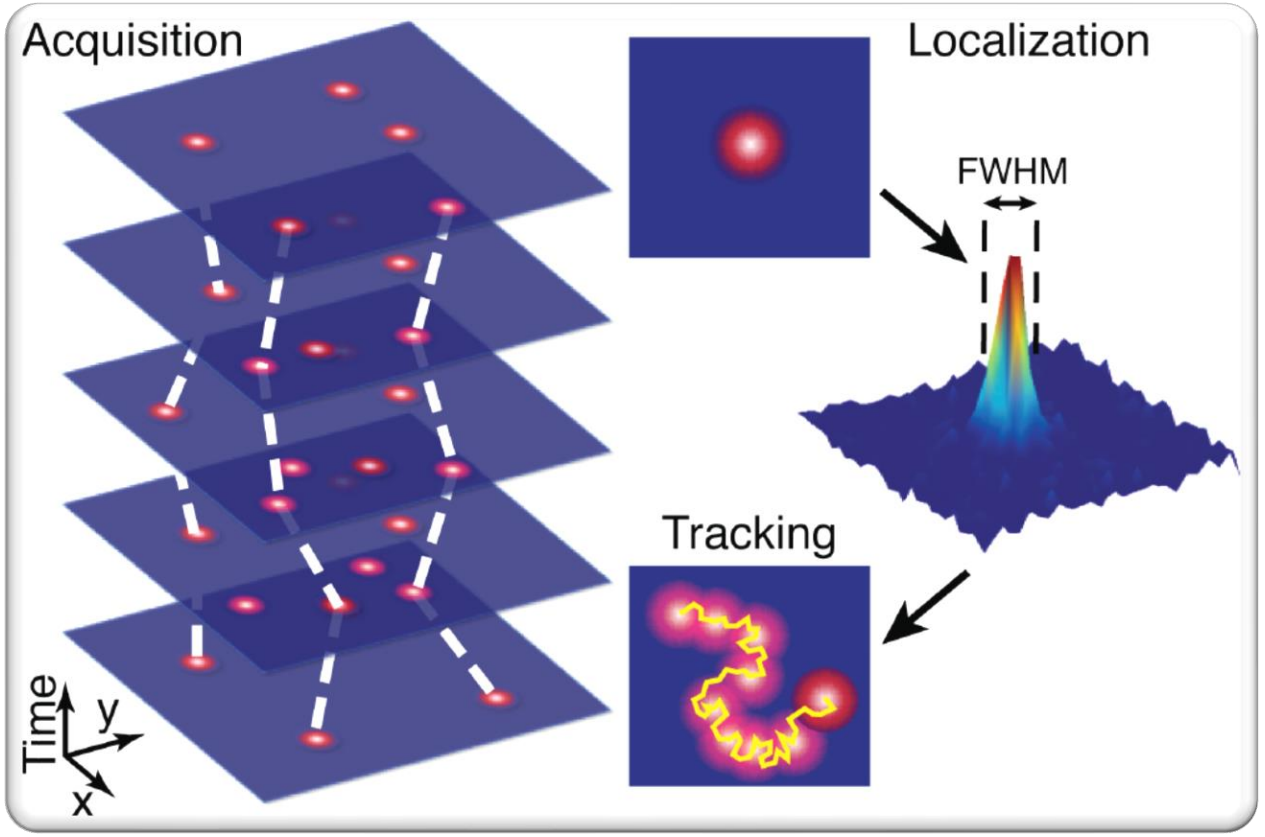
Confocal Microscopy

Videos of 2D image over time
~39 frames/sec

Aqueous phase: fluorescent particles (1µm) + MPD

Organic phase: Isopar-G + TMC

Particle Tracking



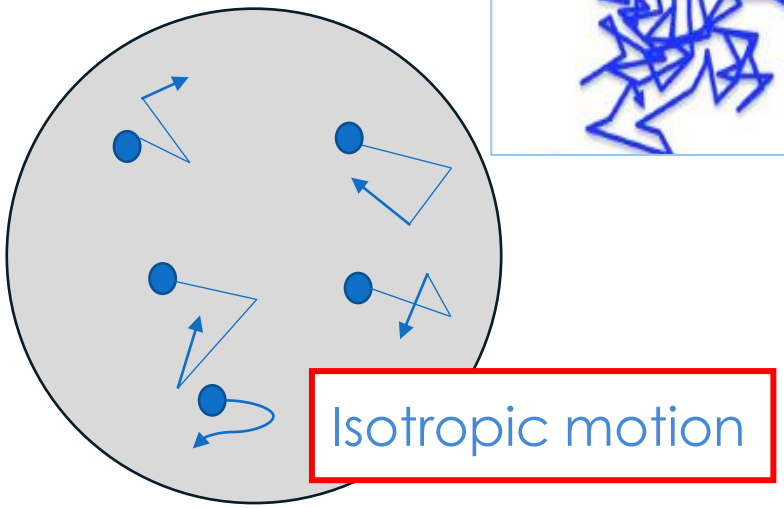
Manzo et al., Rep. on Prog. in Phys. (2015)

- Acquisition of the displacement using confocal microscopy
- Tracking particles using TrackMate plugin, Fiji (Meijering et al., Meth. Enzymol. (2012))

What do we expect to see?

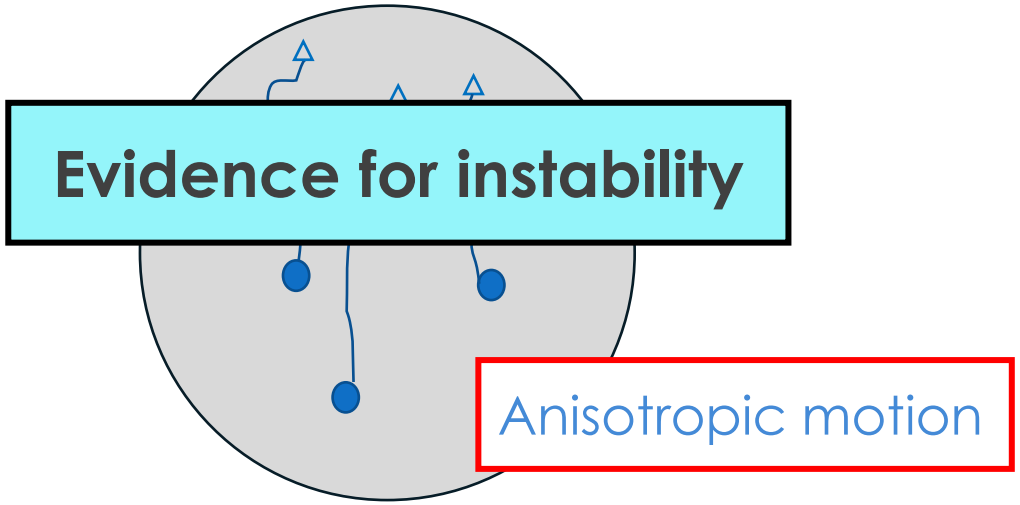
Random motion (Brownian)

Trajectories:



- No bulk flow.
- The motion is thermal-driven.

Directed motion



- Particles act as tracers that move with the bulk.
- **Brownian + bulk directed motion**

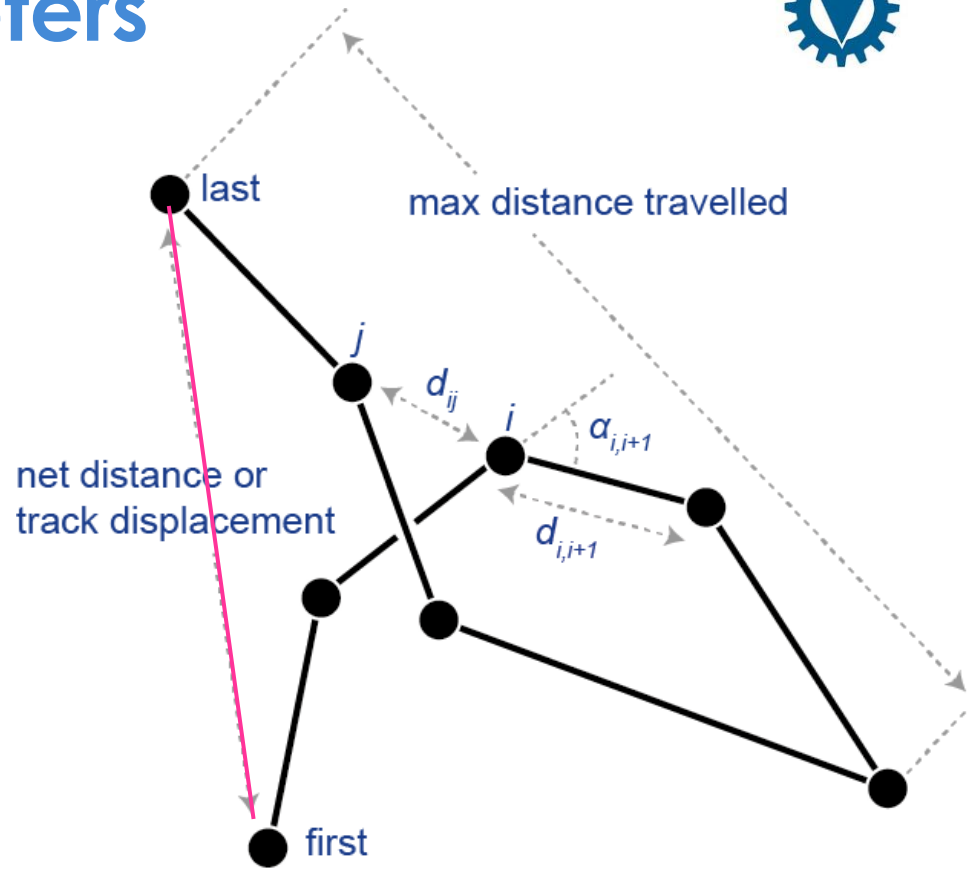
Motion Parameters

1. **Linearity =** $\frac{\text{net distance}}{\text{total distance travelled}}$

$0 < \text{Linearity} < 1$

"Confined" movement~ Brownian motion

Directed motion



total distance travelled = $\sum d_{i,i+1}$

max distance travelled = Max d_{ij}

mean directional change = $1/N \sum \alpha_{i,i+1}$

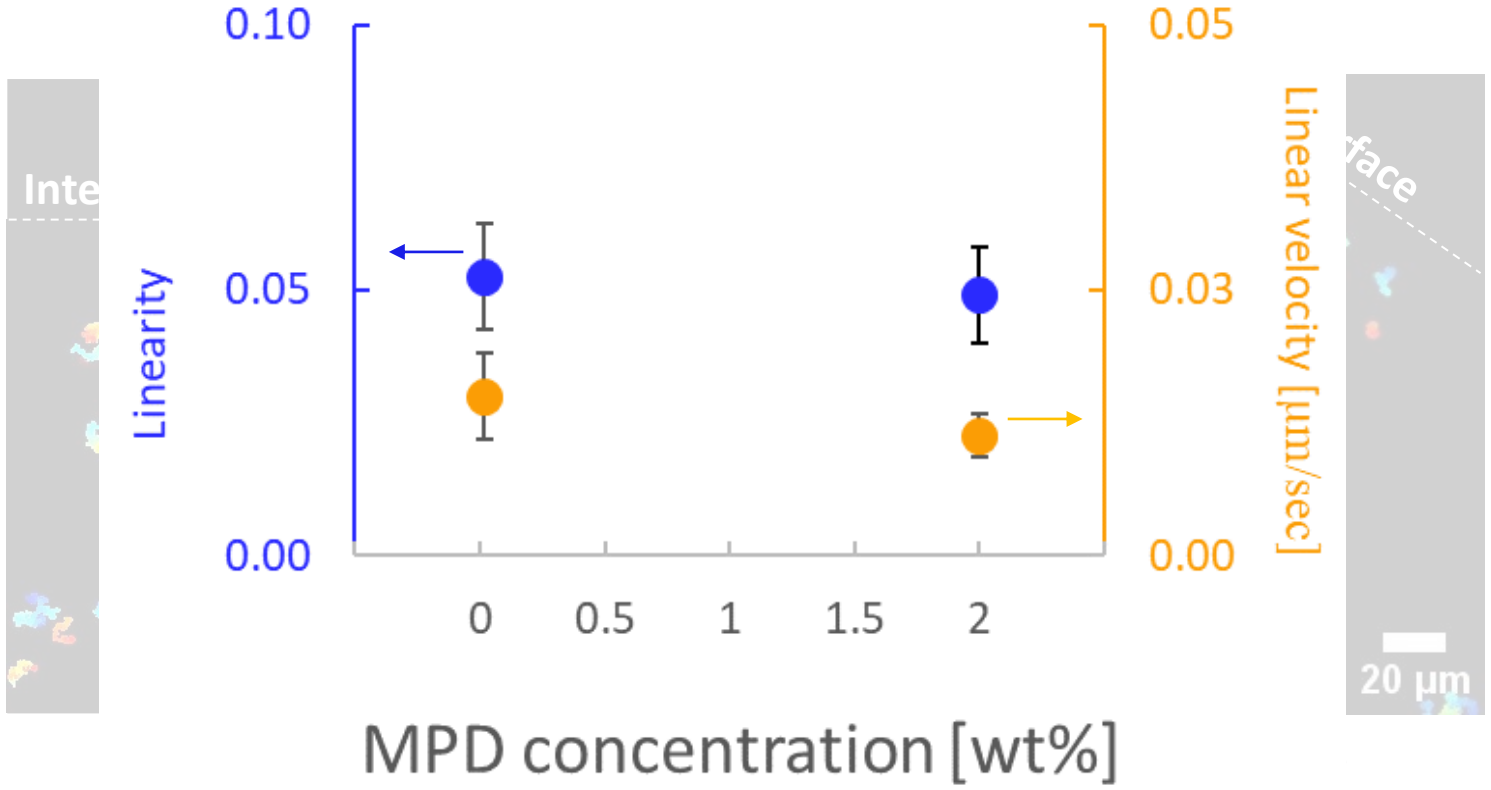
2. **Linear speed=** $\frac{\text{net distance}}{\text{total track time}}$

Meijering et al., Meth. Enzymol. (2012)

Results

Blank = No reaction

Increasing MPD concentration

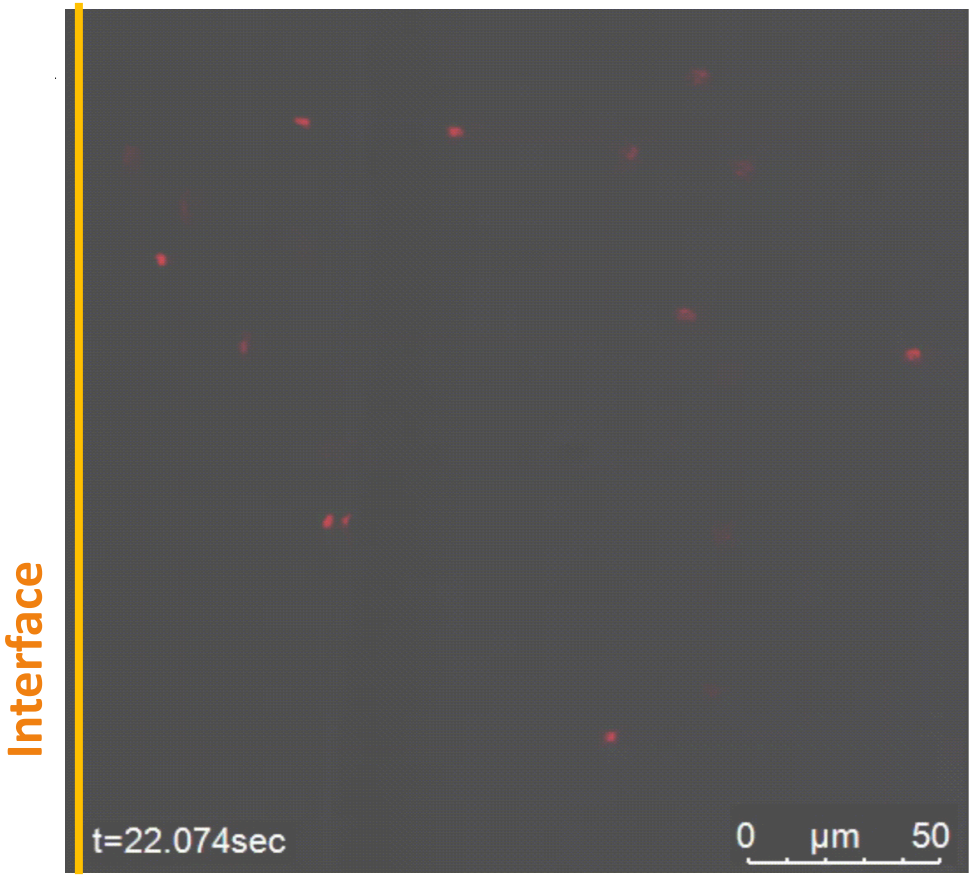


'Brownian like' motion without an IP reaction when MPD diffusion increases

In-situ Imaging:
Increasing monomers concentrations

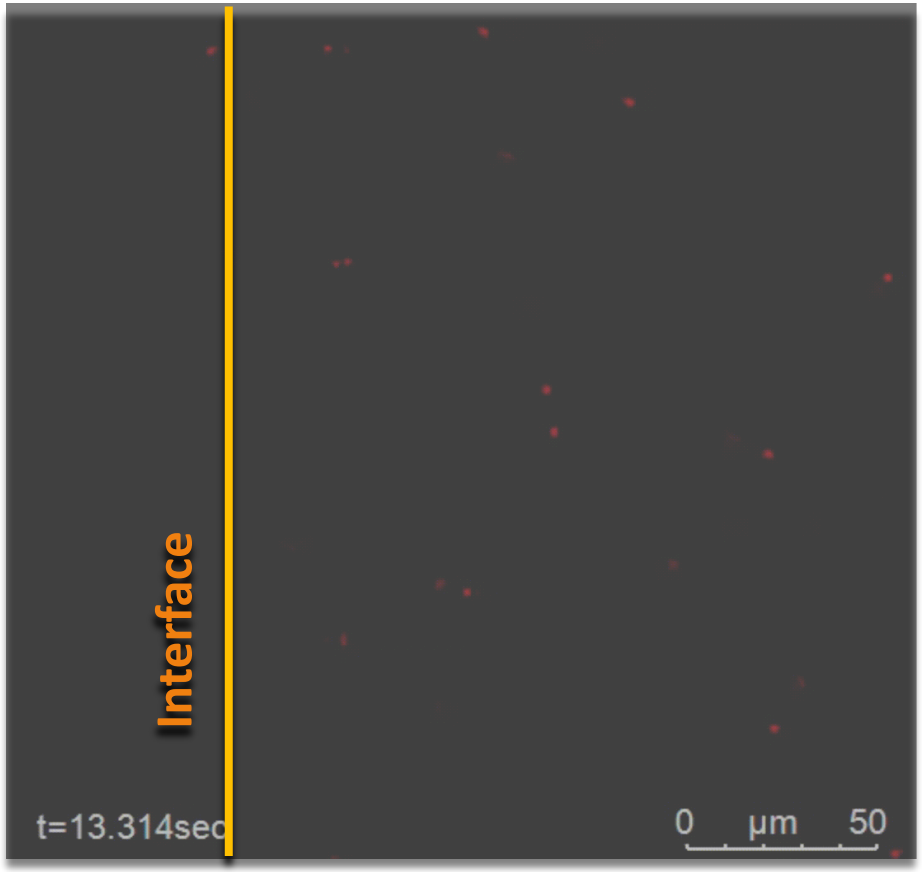
Low concentrations:

0.02% MPD; 0.001% TMC

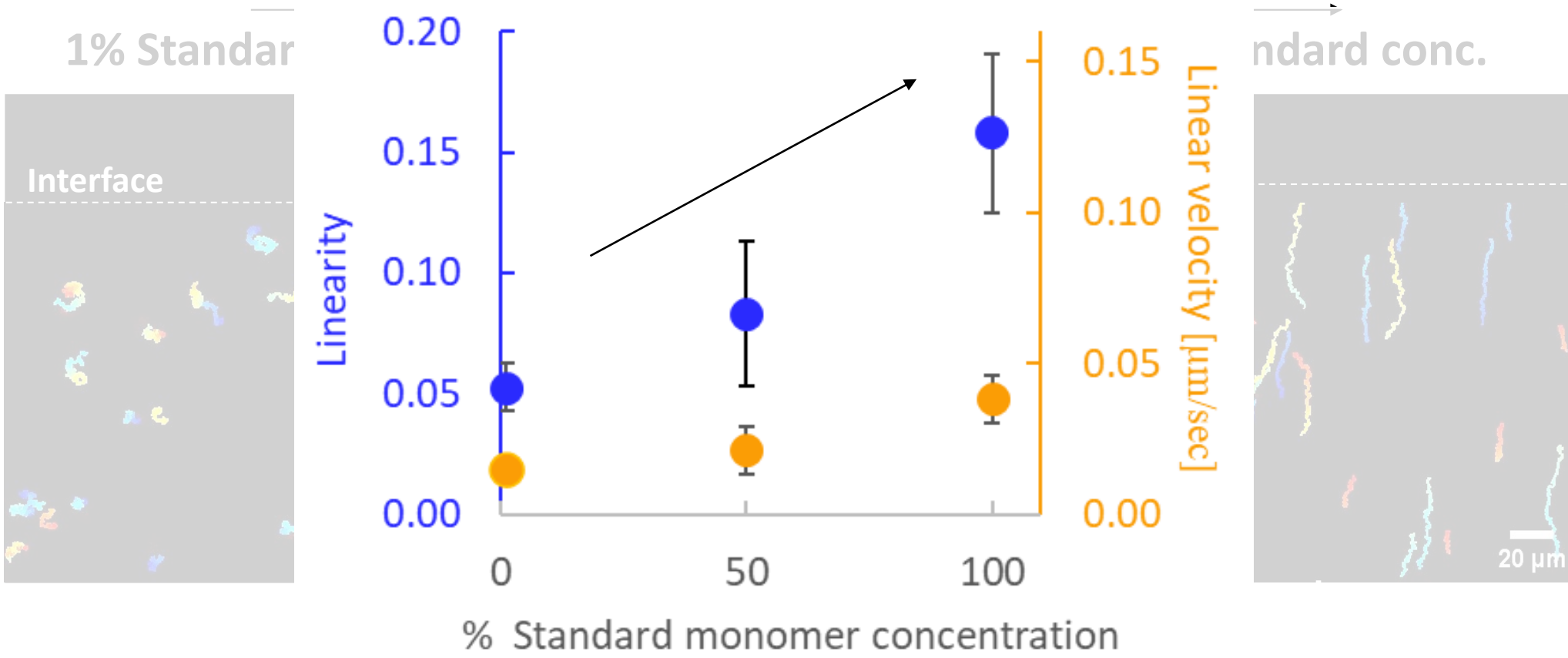


Standard concentrations:

2% MPD; 0.1% TMC

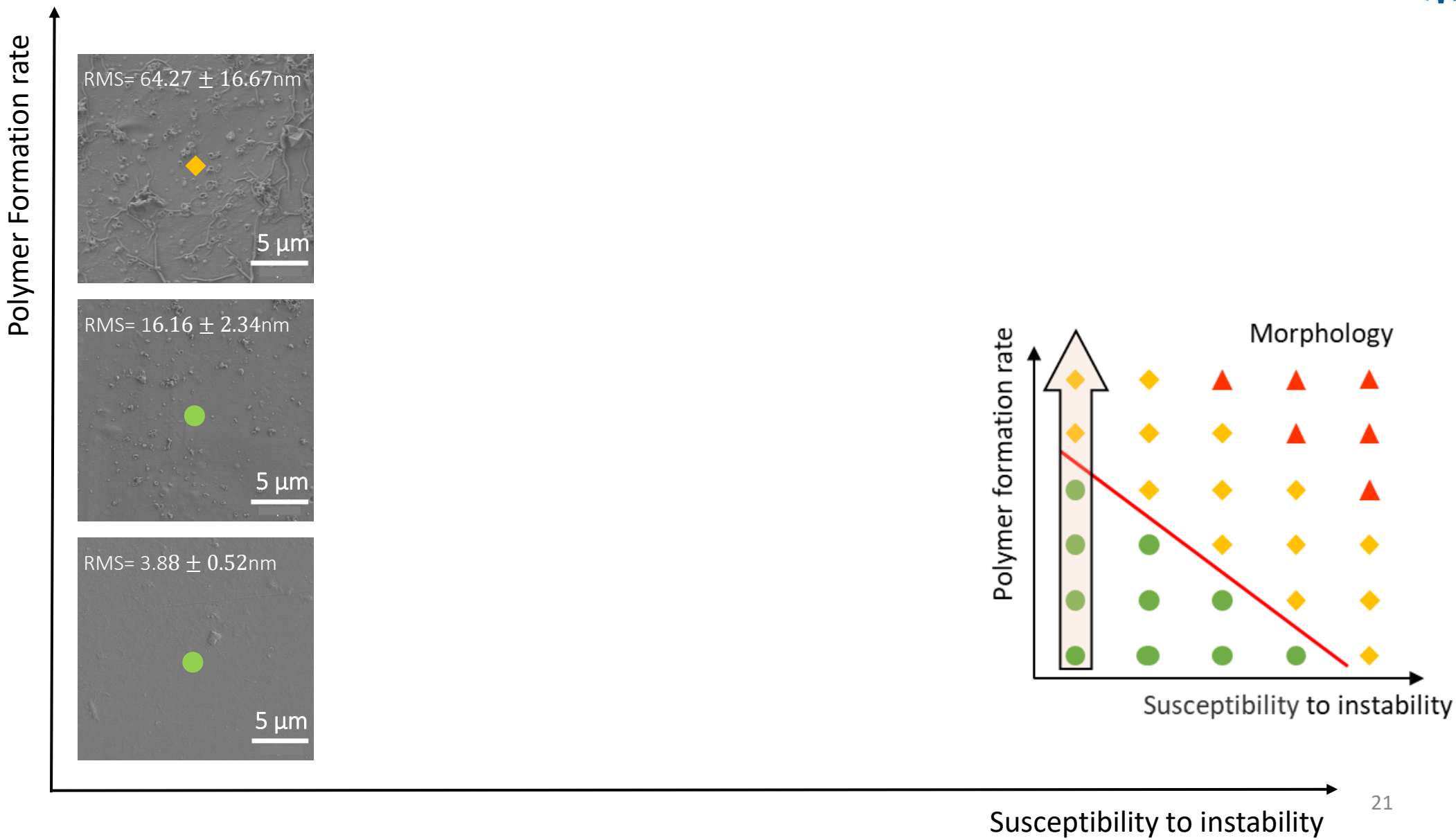


Increasing monomers concentrations



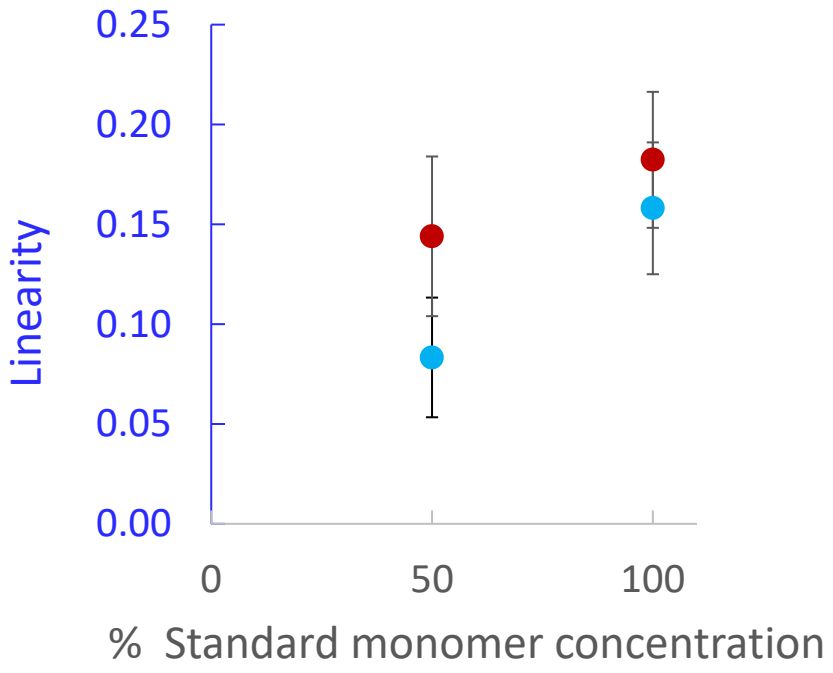
- Very low concentration: 'Brownian like' motion
- Increasing concentration more directed motion towards the interface

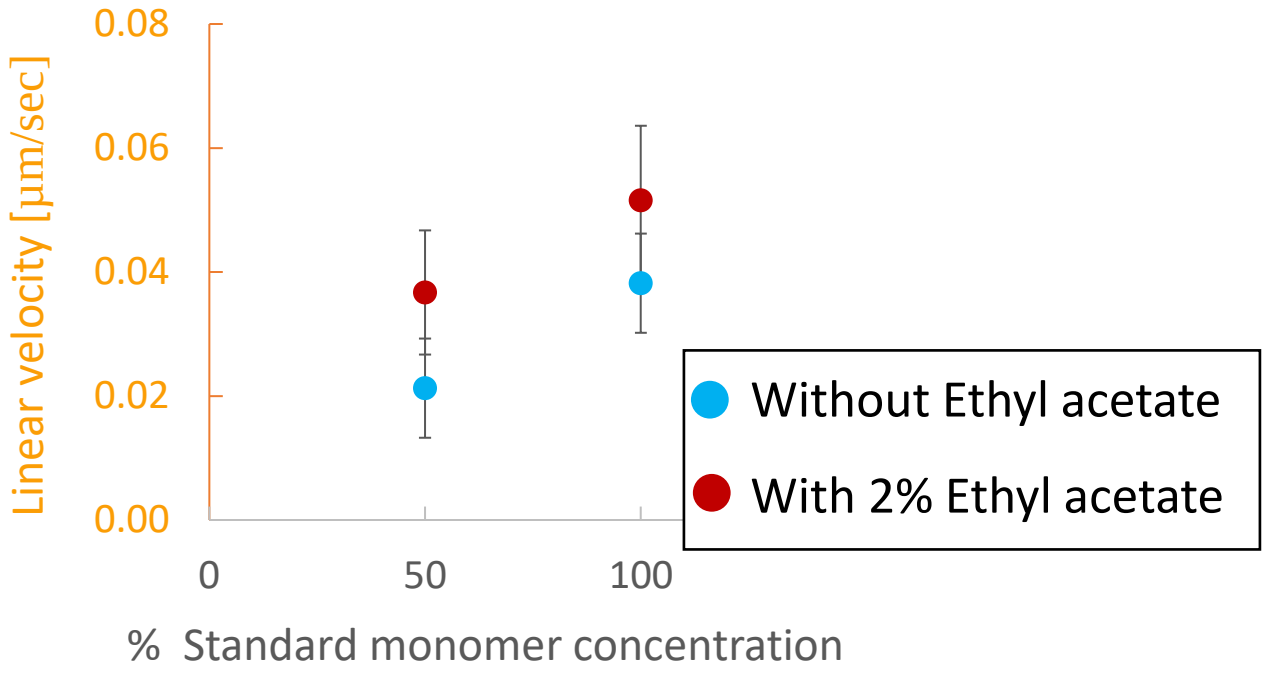
Instability-Morphology



A co-solvent + Increasing monomers concentrations

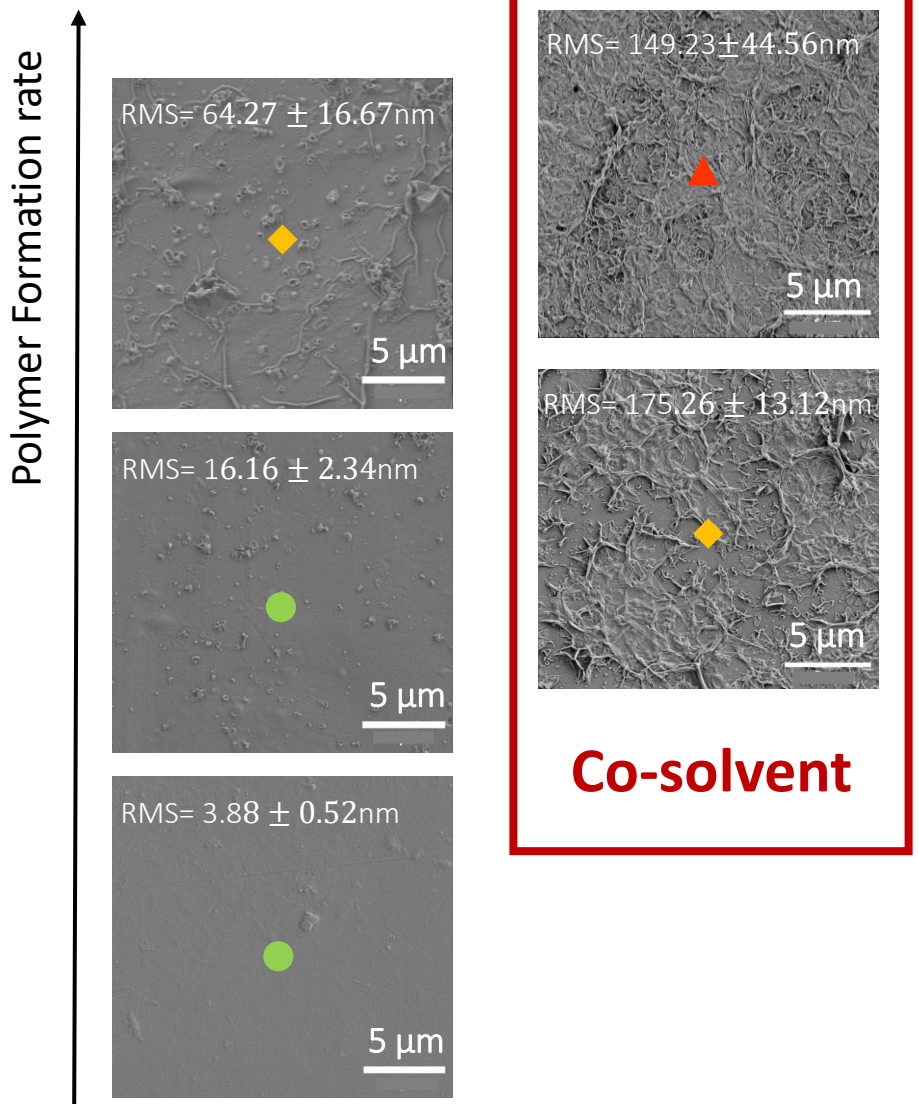
MPD diffusion ↑ | MPD partitioning ↑ | Interfacial tension ↓

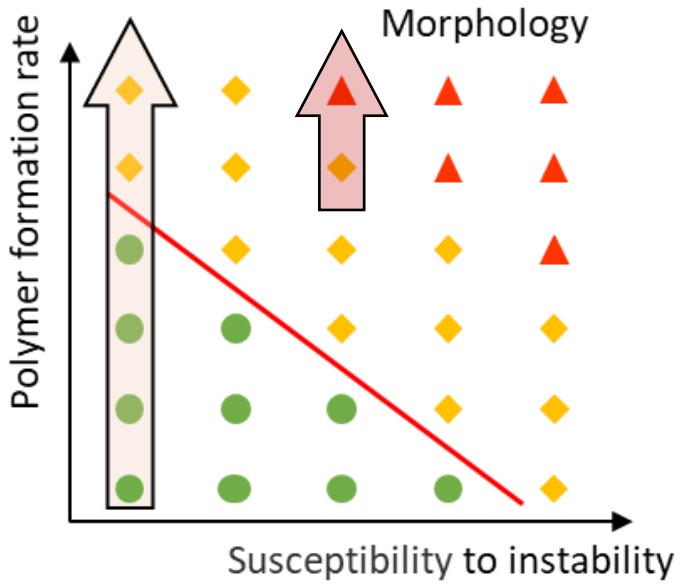




- Adding a co-solvent increasing directionality and speed of motion.
- Stronger effect in lower monomer concentrations.

Instability-Morphology

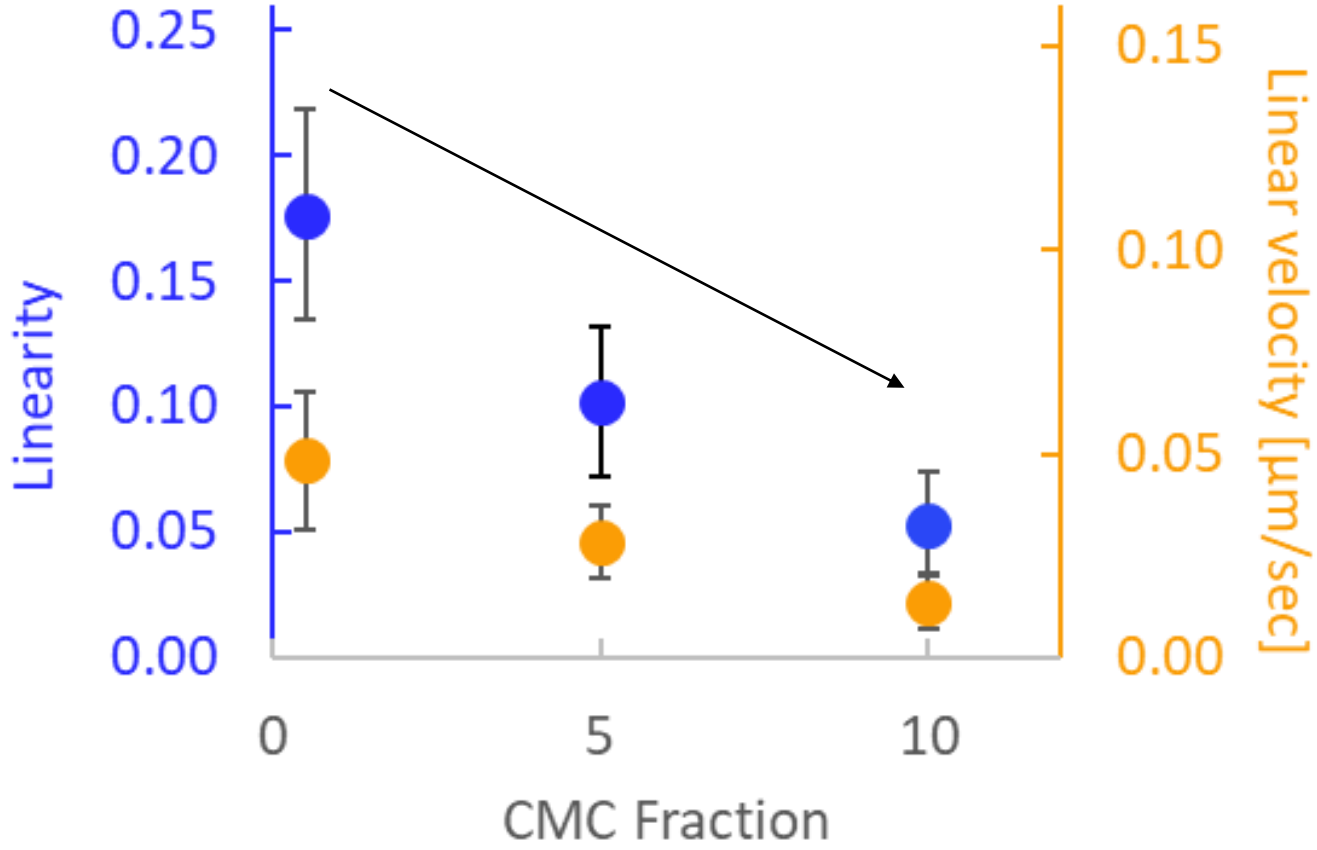




Increasing surfactant concentration

Interfacial tension ↓

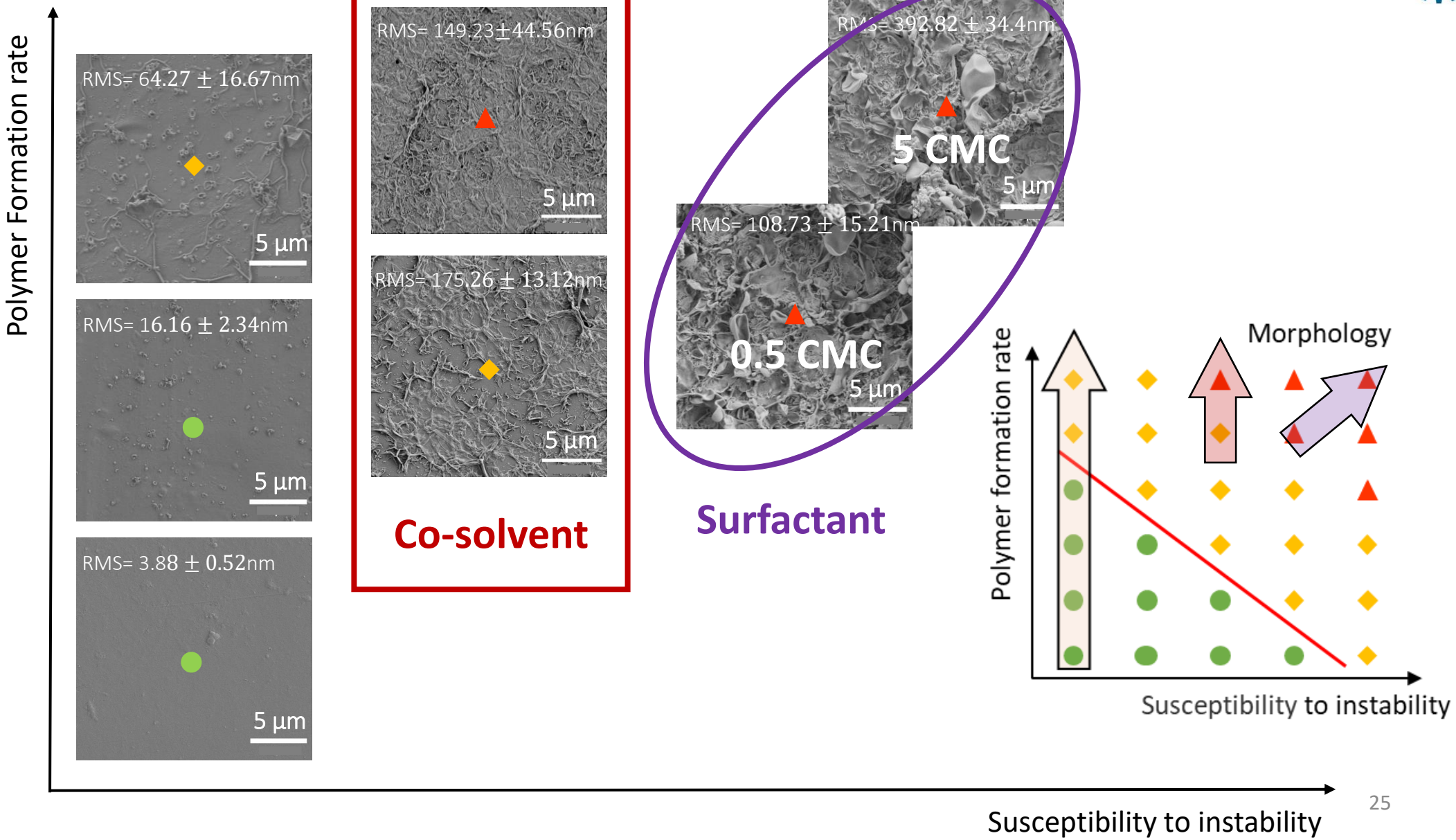
0.5 CMC



C SDS

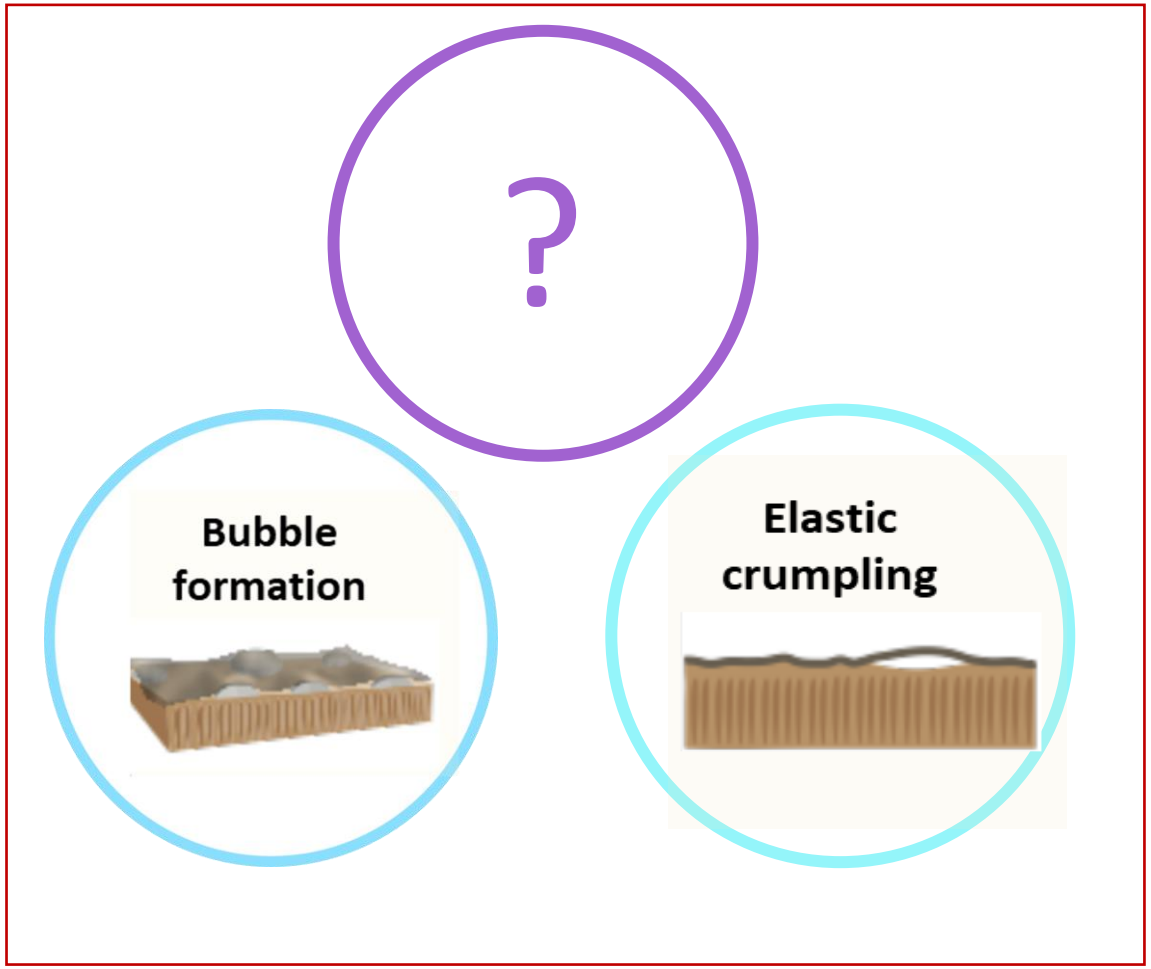
Above the CMC: 'Brownian like' motion

Instability-Morphology

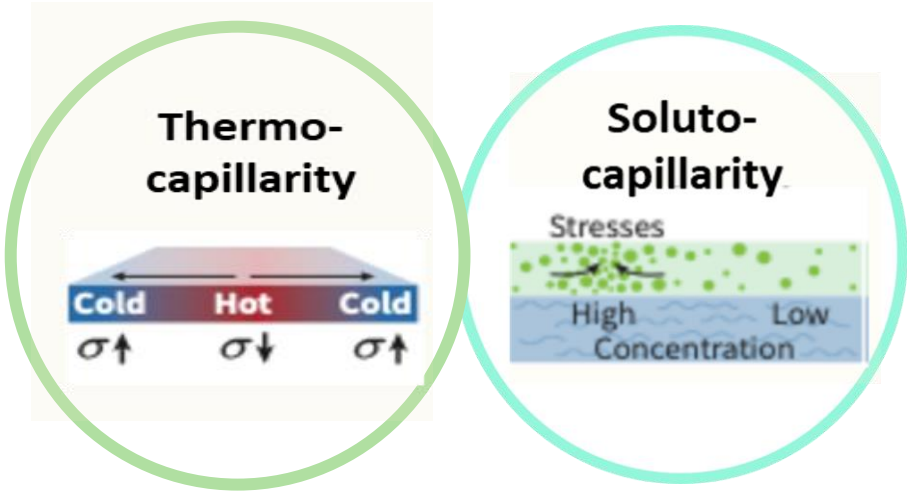


Instability mechanisms

During IP



Hydrodynamic instability=
flow in IP system



Freger and Ramon, *Prog. Polym. Sci.* (2021)

Conclusions

	Increasing **monomer concentrations**	Adding a **co-solvent**	Adding a **surfactant**
Synthesis			
Instability	More directed motion	More directed motion	Below CMC - More directed motion Above CMC – 'Brownian like' motion
Morphology	More crumpled morphology	More crumpled morphology	Muti-layered morphology

Tracking particles provides us with new insights about IP

Acknowledgements

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קרן קימת לישראל
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