The North American Membrane Society (NAMS) 2021

Colorado, August-September 2021

Re-thinking polyamide thin film formation: how interfacial destabilization dictates film morphology

Adi Ben Zvi[1], Ines Nulens[2], Ivo Vankelecom[2], Guy Z. Ramon[1]

1 *Civil & Environmental Engineering, Technion – Israel Institute of Technology*

2 *Bioscience Engineering, KU Leuven, Belgium*

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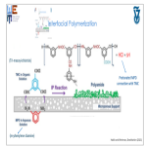
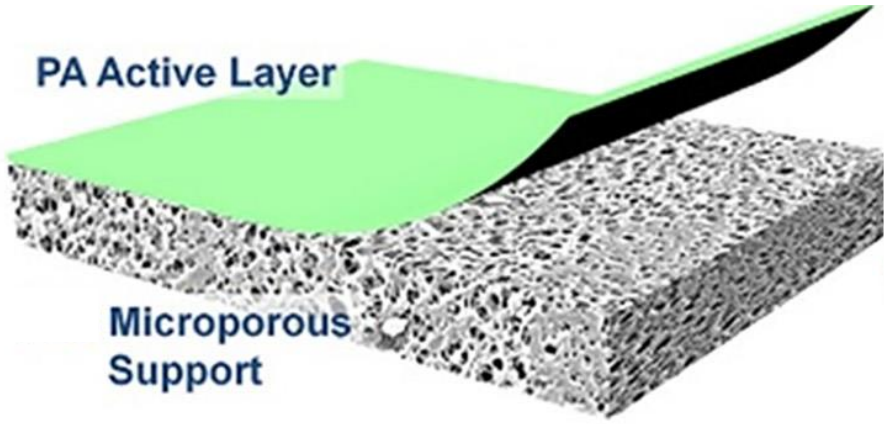
Introduction

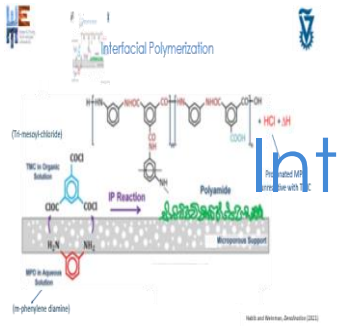
Thin Film Composite (TFC) Membranes

- TFC polyamide (PA) membranes first synthesized in late 70s by Cadotte et al.
- State-of-the-art desalination by reverse osmosis (RO) **>99% rejection**
- A thin (<250nm) PA selective layer on top of a porous support
- Fabricated via a rapid, exothermic, polycondensation reaction:

  interfacial polymerization 



Habib and Weinman, *Desalination* (2021)



Interfacial Polymerization

(Tri-mesoyl-chloride)

(m-phenylene diamine)

Protonated MPD unreactive with TMC

Habib and Weinman, *Desalination* (2021)

The Problem

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

TEM
SEM
AFM

Contradicting trends

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The Problem

Synthesis — Morphology — Performance

pH
Solvents
Time
Additives
Temperature
Support free
Monomers
Spray coating
Layer by layer

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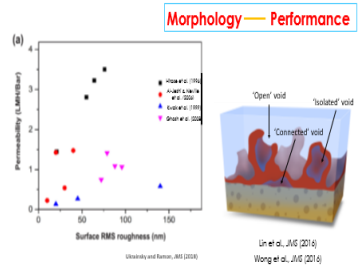
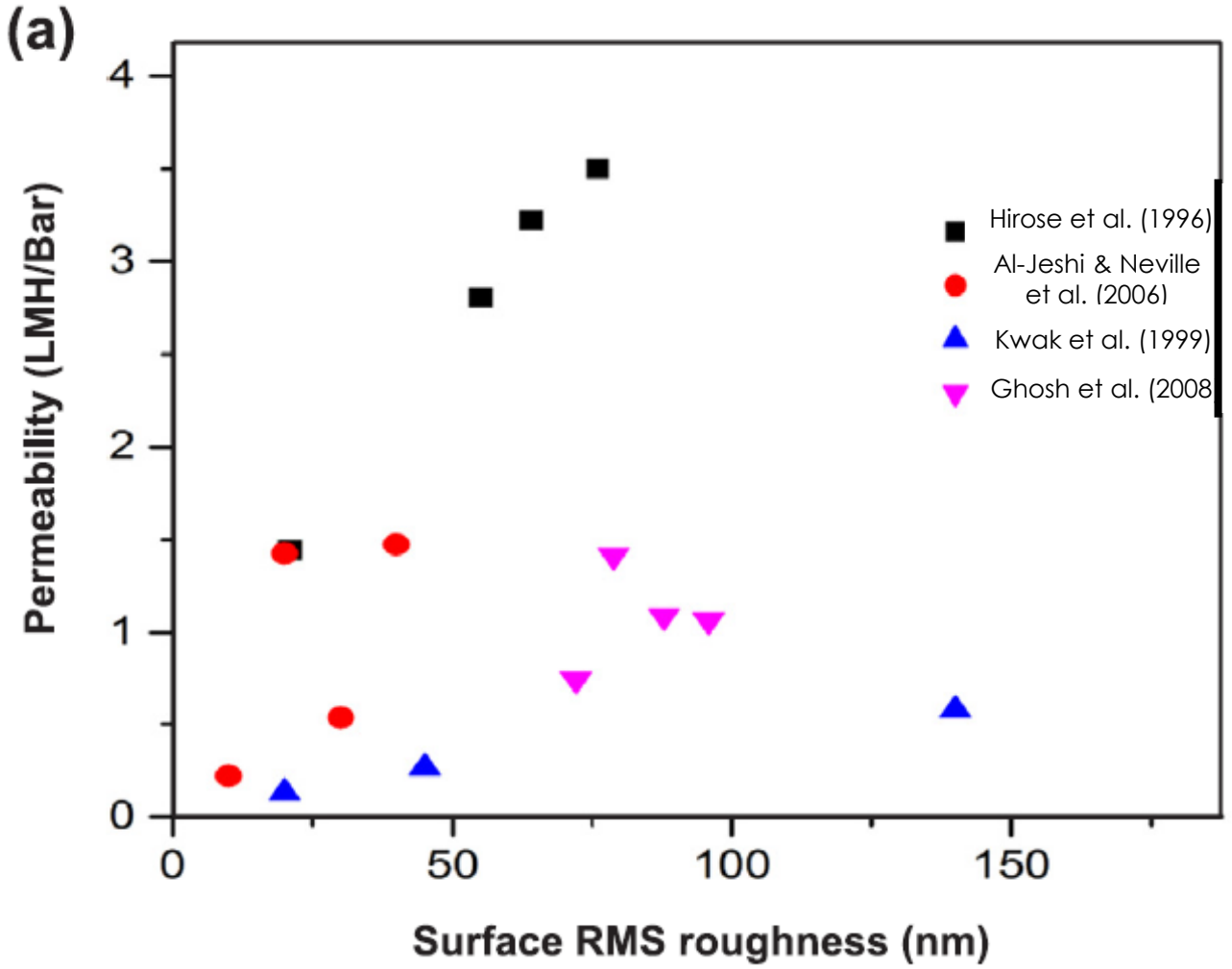
AFM

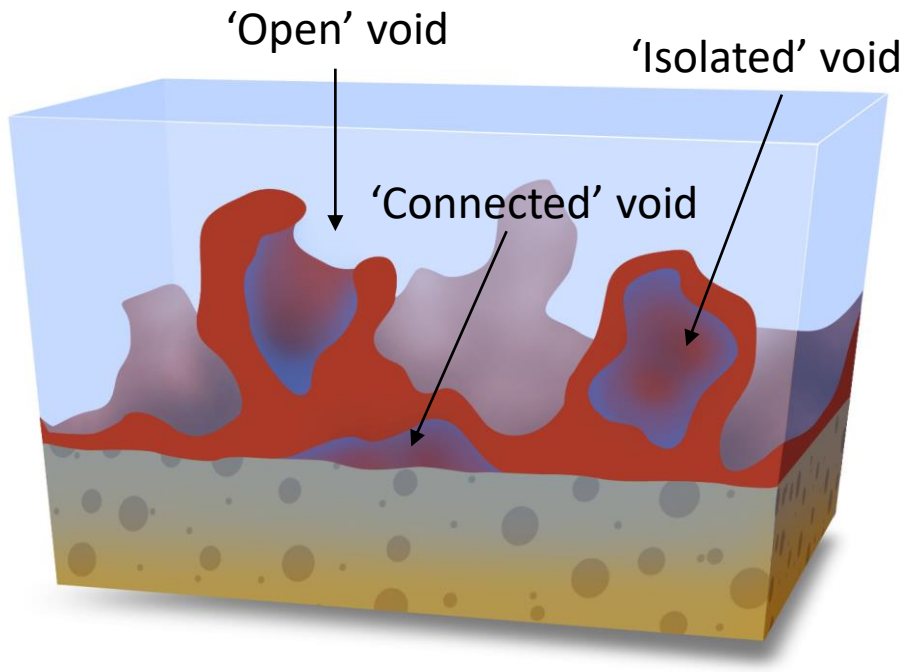
Contradicting trends



Morphology — Performance



Ukrainsky and Ramon, *JMS* (2018)



Lin et al., *JMS* (2016)

Wong et al., *JMS* (2016)

The Problem

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

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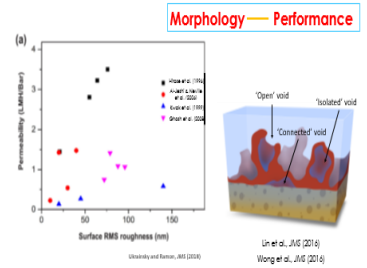
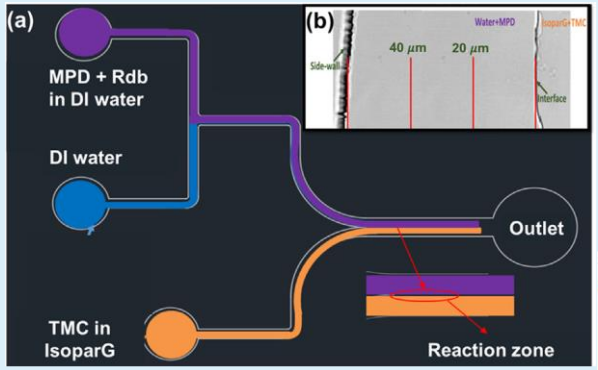


In-situ monitoring



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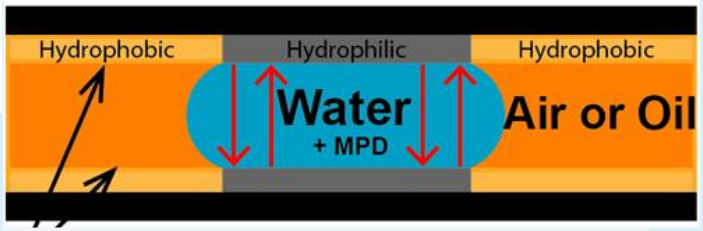
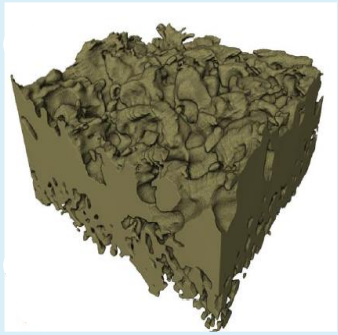


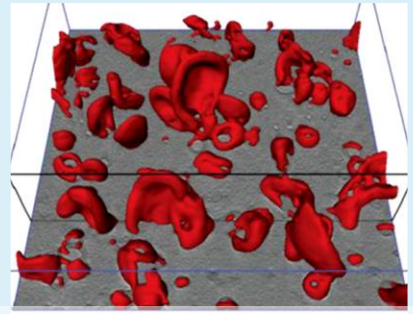
Nowbahar et al., *J. Am. Chem. Soc.* (2018)

Electron-Microscope (**EM**) **Tomography**



Culp et al., Science (2021)

3D image



Song et al. *Appl. Mater. Interfaces* (2019)

Our Approach

Synthesis —— **Morphology**

pH
Solvents
Time
Additives
Temperature
Monomers
Support free
Spray coating
Layer by layer

→ **Physical attributes**

→ **System's stability**

→ **Film morphology**

Example:

Co-solvent →

- Solubility
- Diffusion
- Viscosity
- Interfacial tension

→ ?

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Synthesis —— **Morphology**

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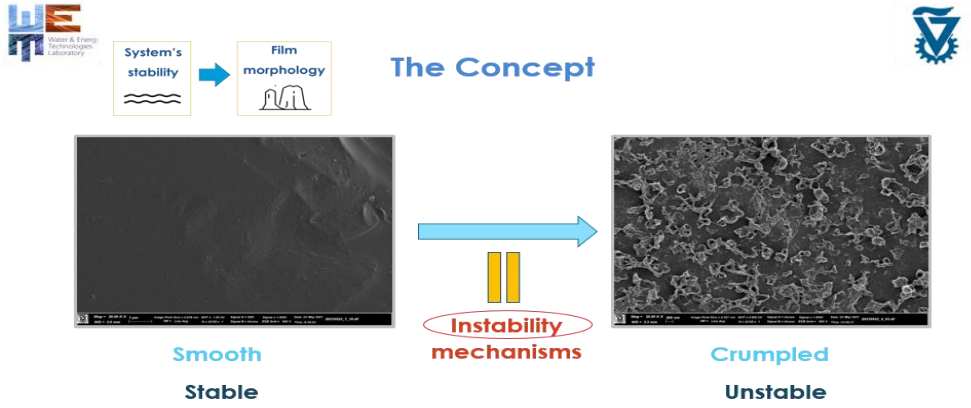

Example:

Co-solvent

- Solubility
- Diffusion
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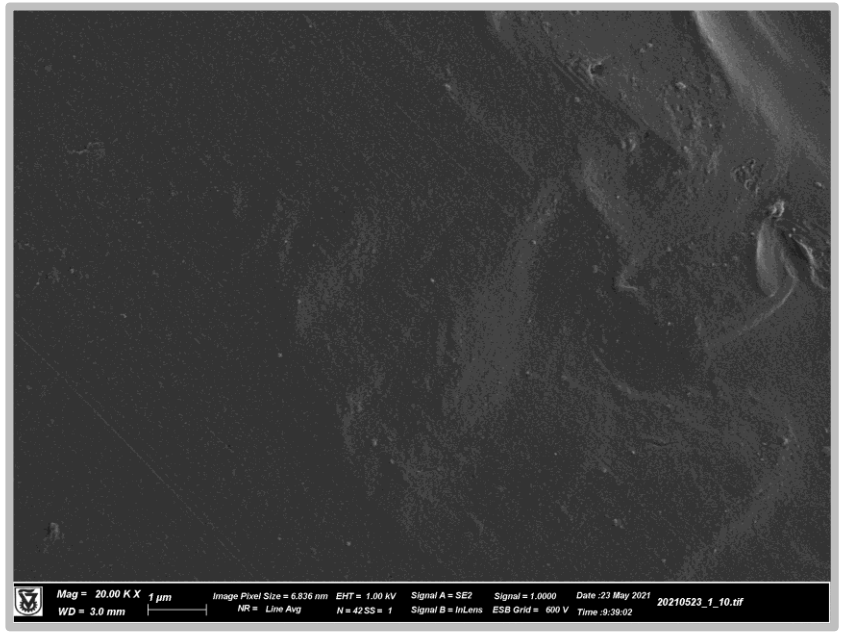
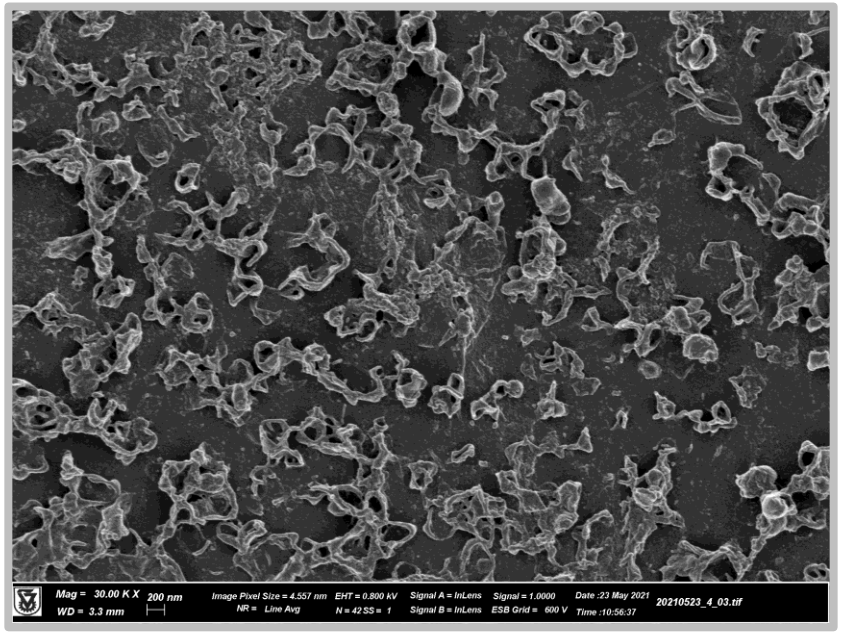
System's stability

Film morphology

The Concept



Instability mechanisms



Smooth

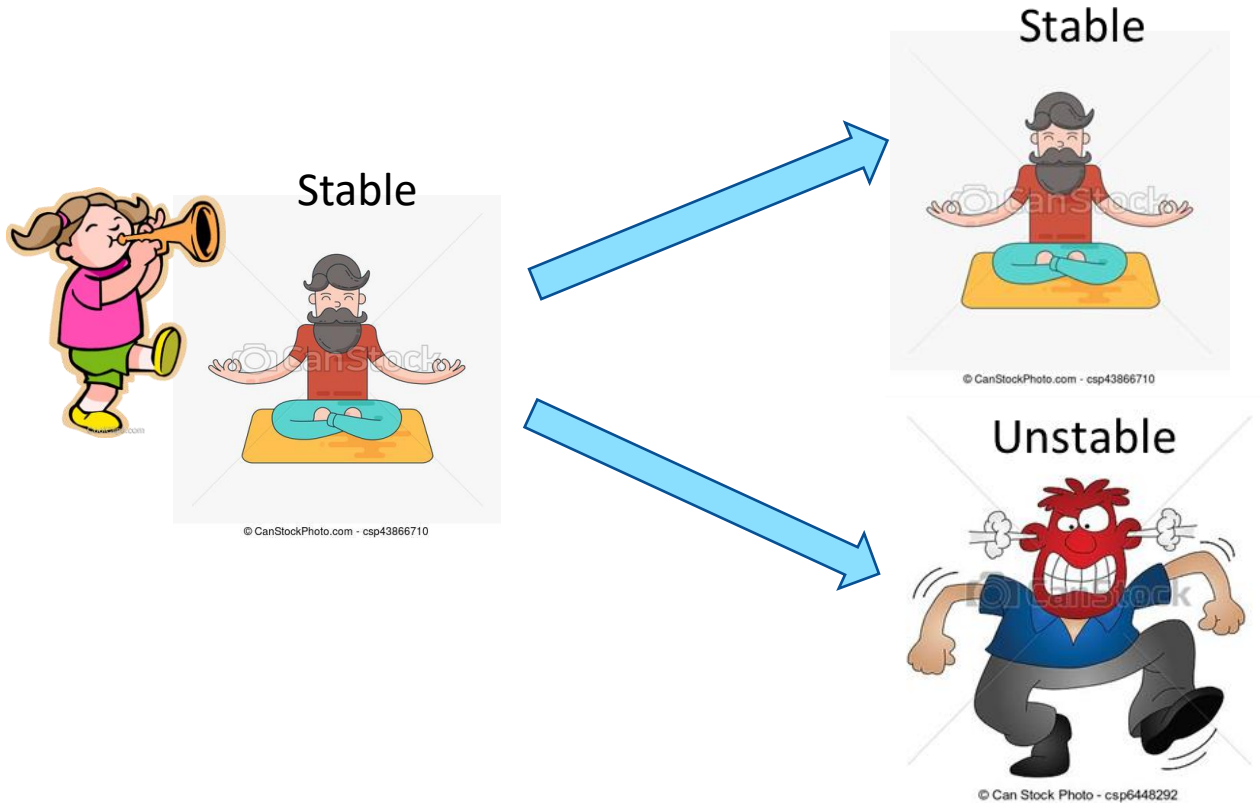
Stable

Crumpled

Unstable

Instability

The **inability** of a system to **sustain** itself against small **perturbations**.



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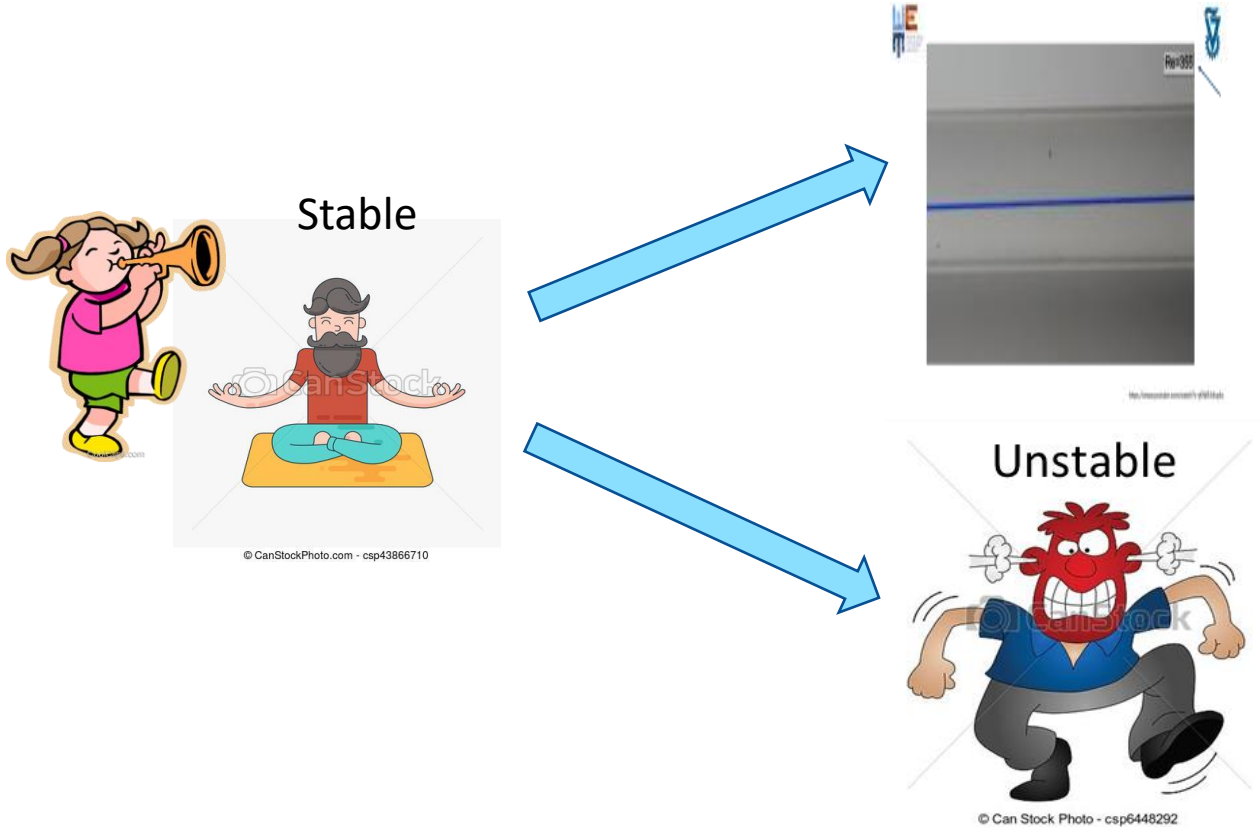
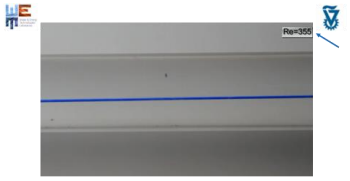


Transition from **stable** to **unstable**: e.g., laminar to turbulent flow



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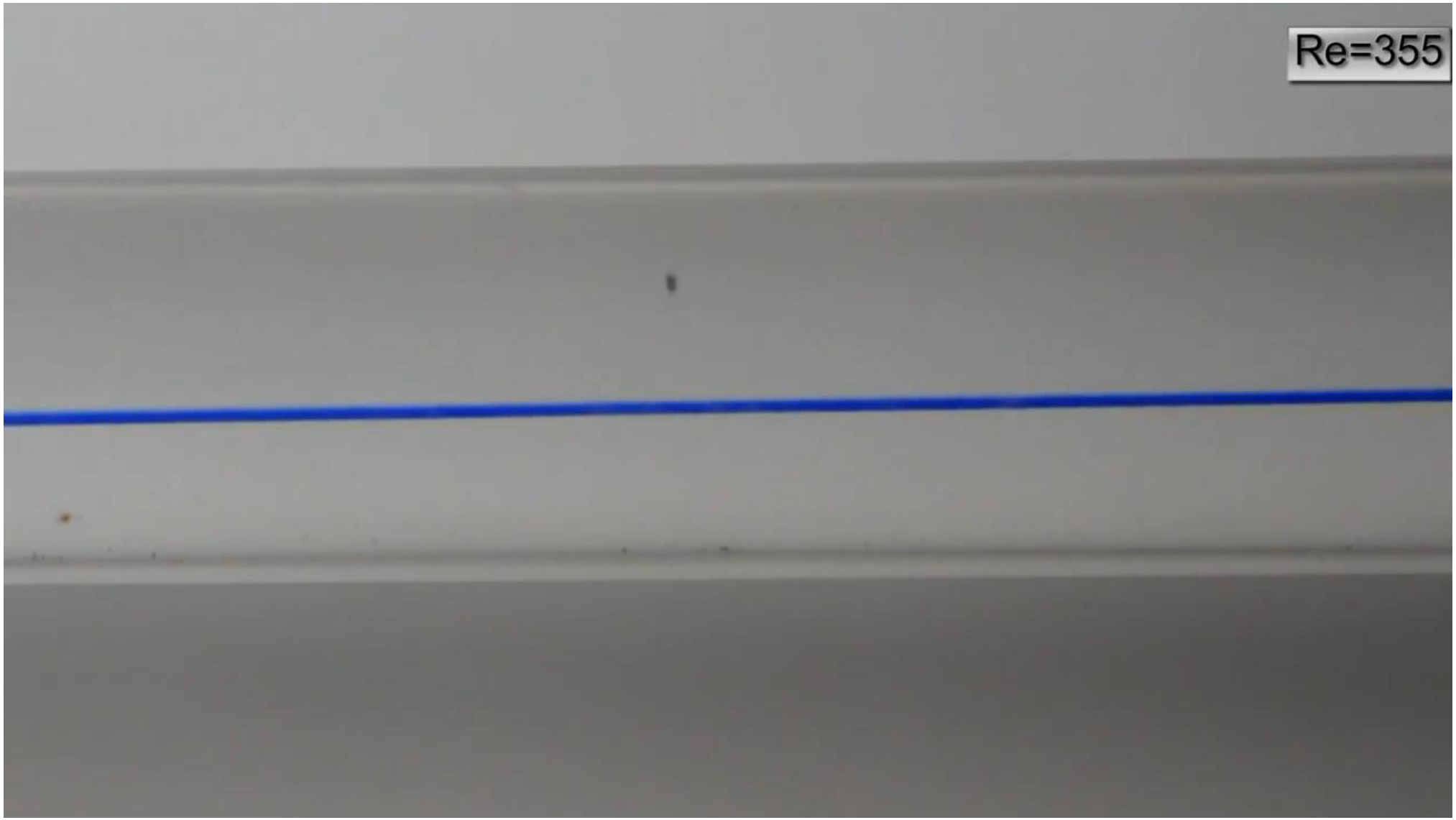
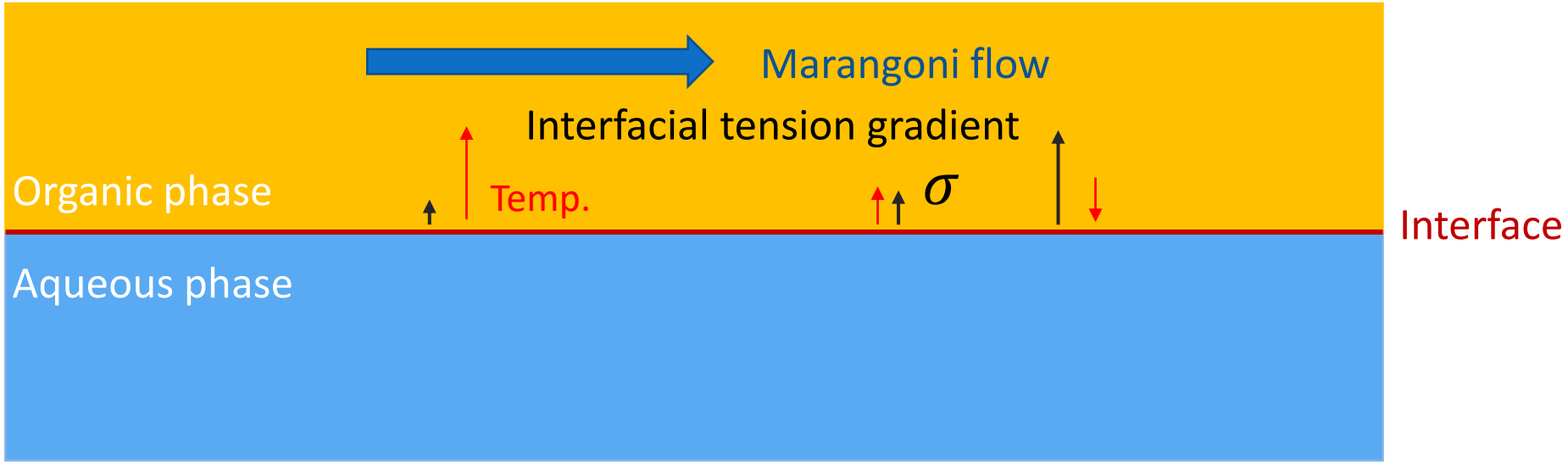


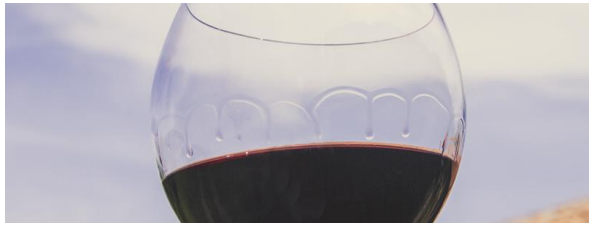
https://www.youtube.com/watch?v=y0WRJtXvpSo

Interfacial Stability - Classical Binary System



Gradients in interfacial tension drive a flow:

Marangoni flow



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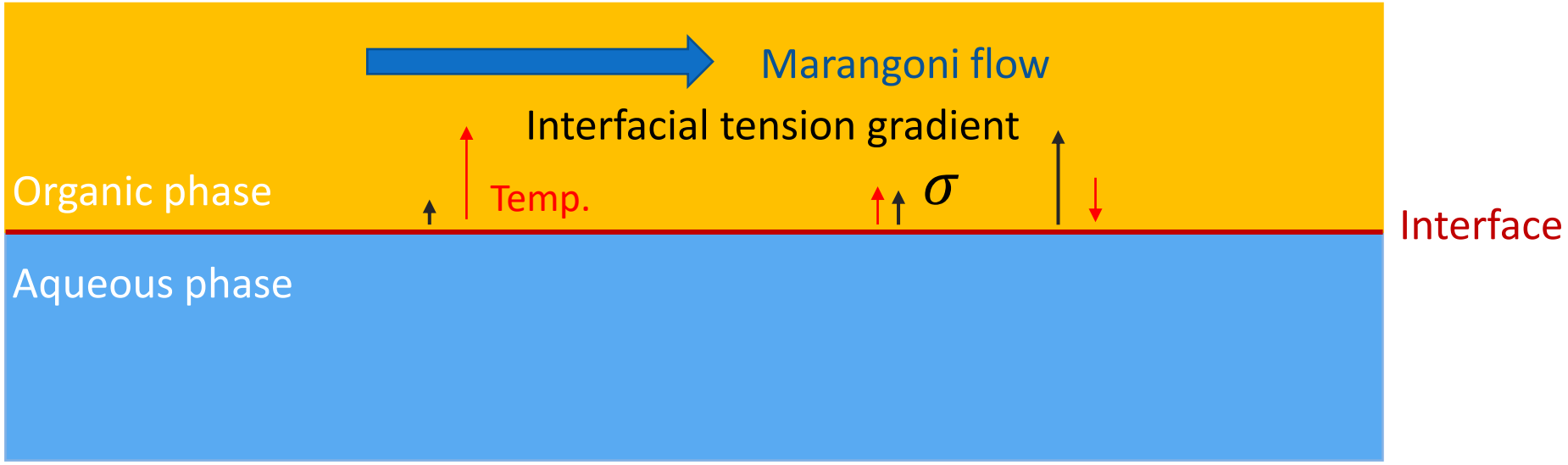

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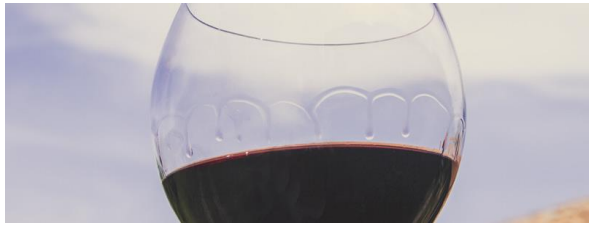

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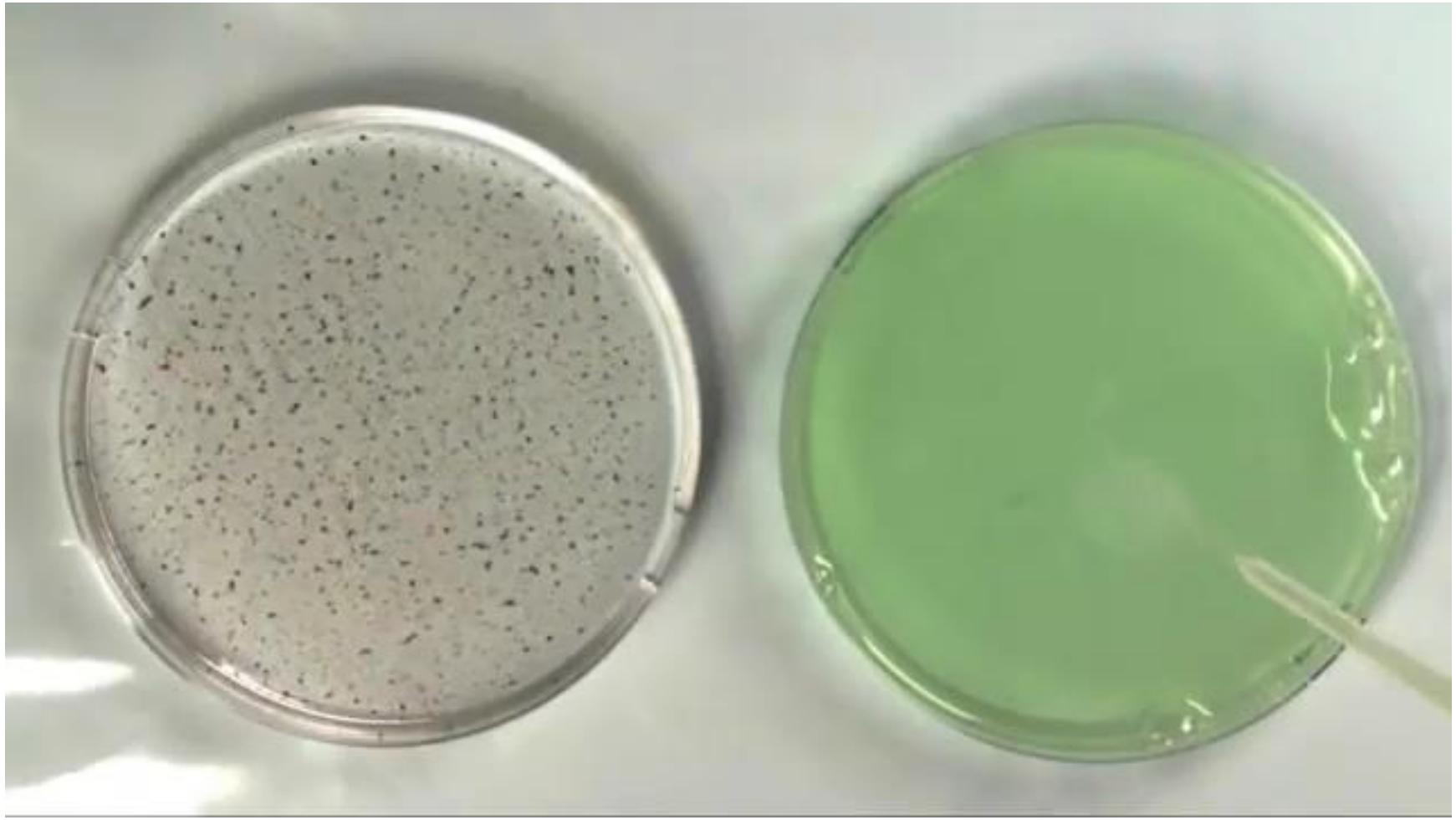

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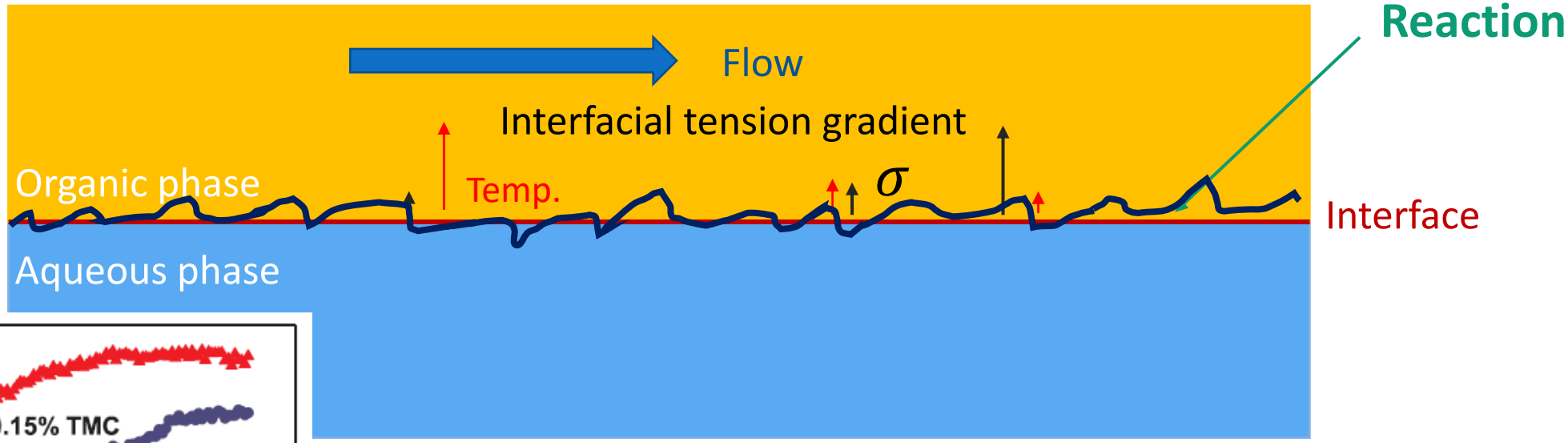
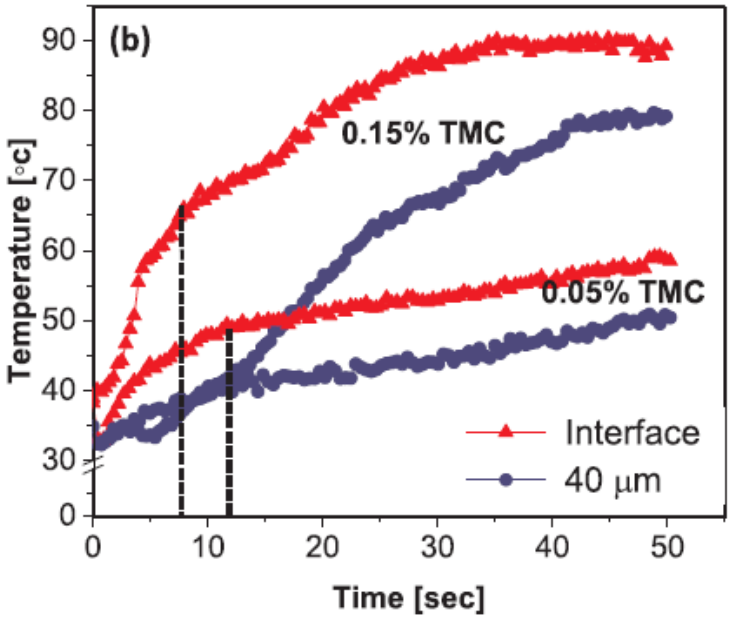
IP system

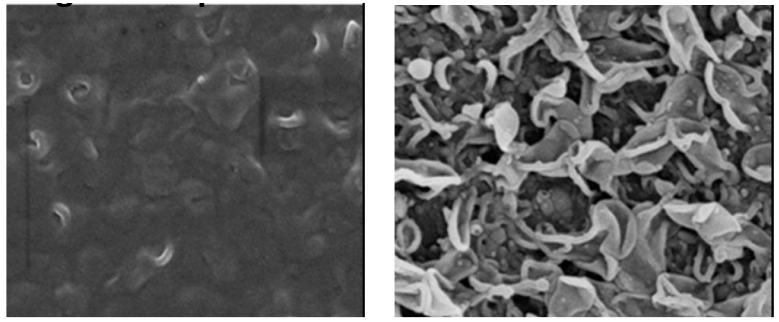




Ukrainsky and Ramon, *JMS* (2018)

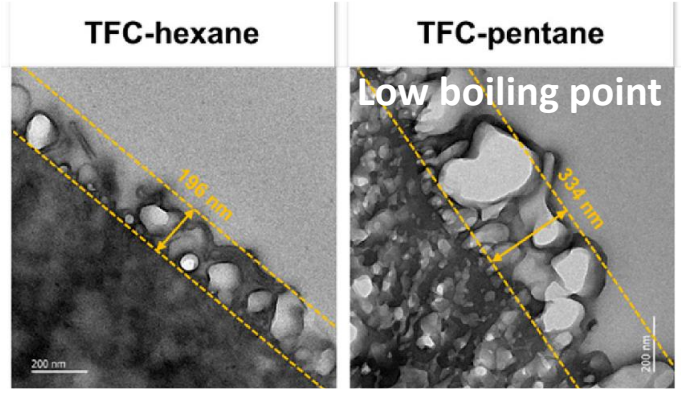
Nanobubbling

No soluble gasses **With soluble gasses**



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

Vaporization



Peng et al., *JMS* (2021)

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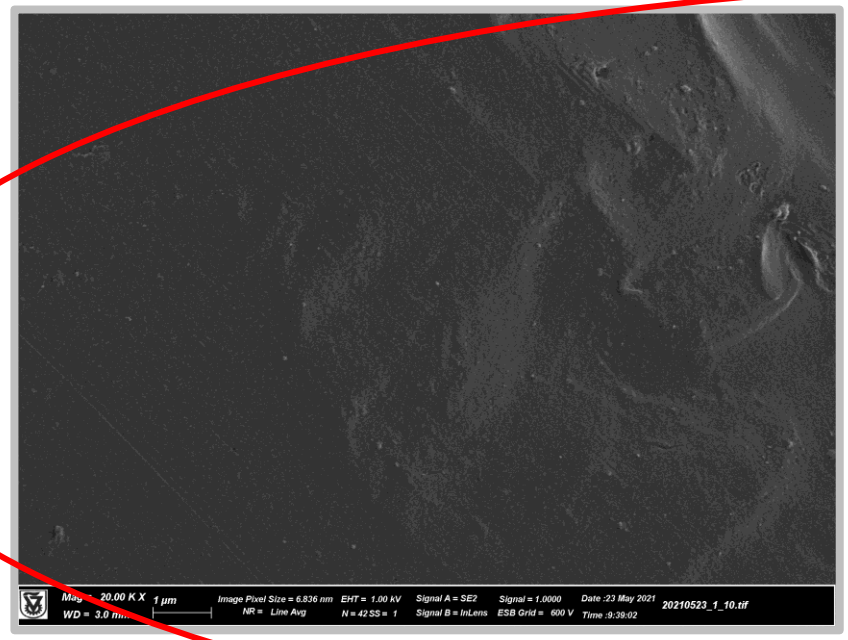
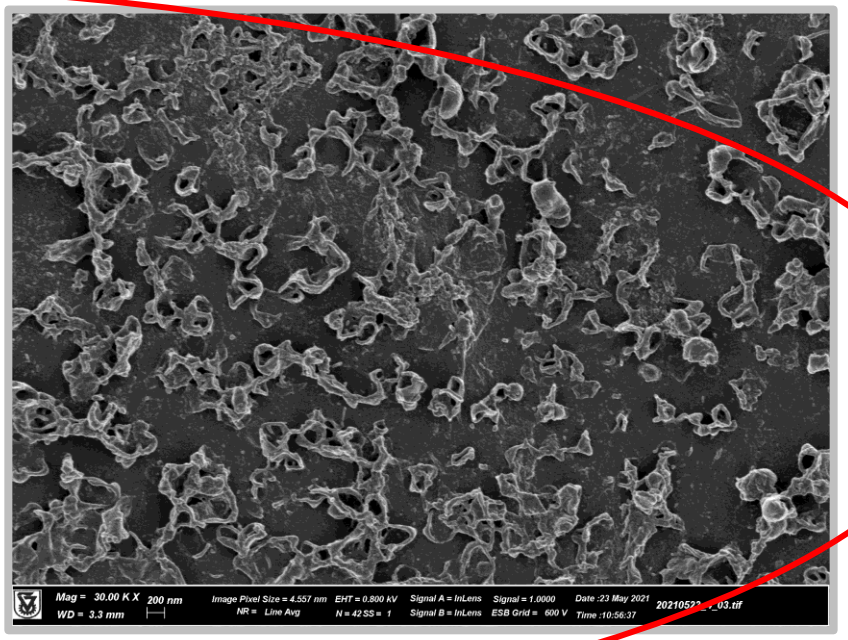
The Concept





Instability mechanisms

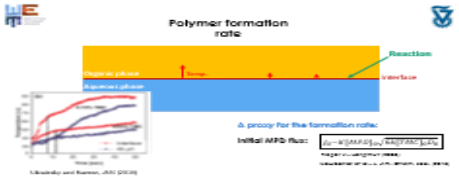
Smooth

Stable

Crumpled

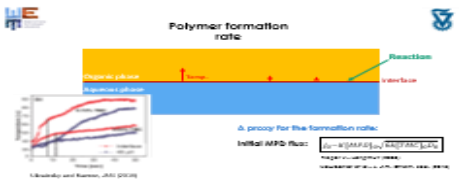
Unstable

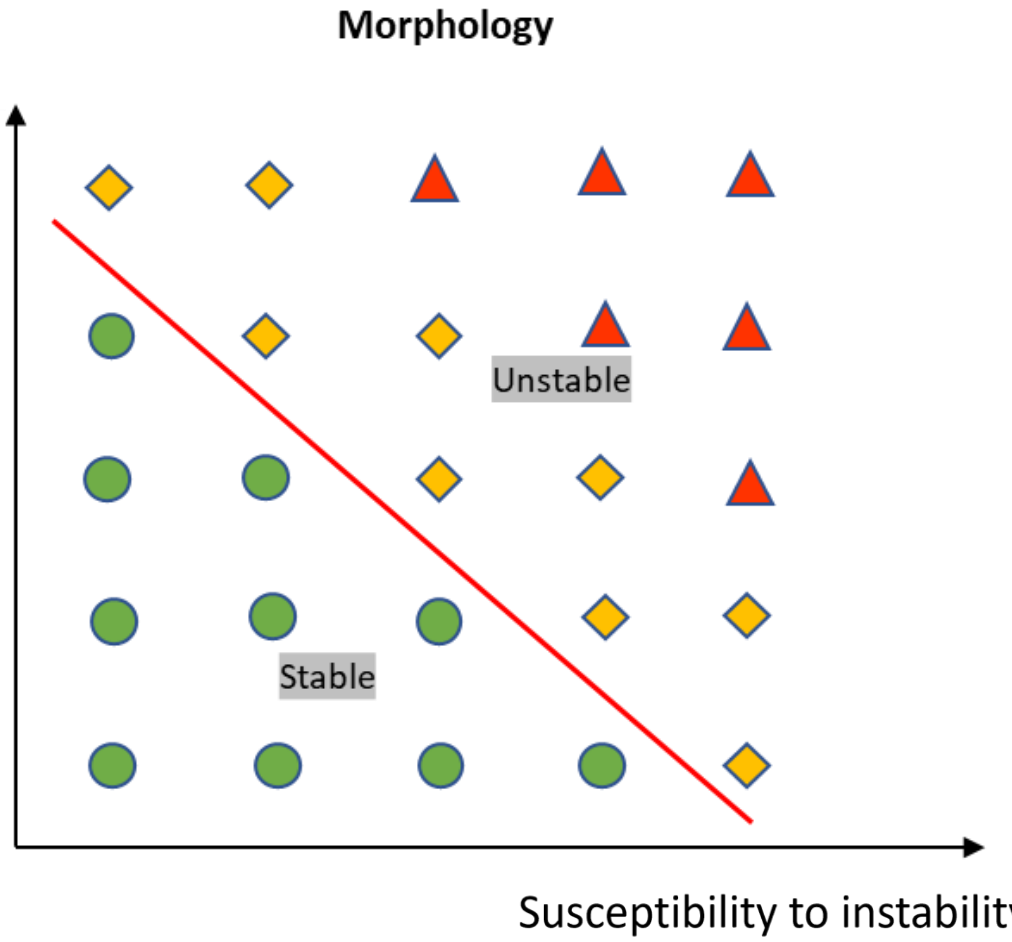
A **'phase diagram'** of **synthesis-morphology** relations in IP

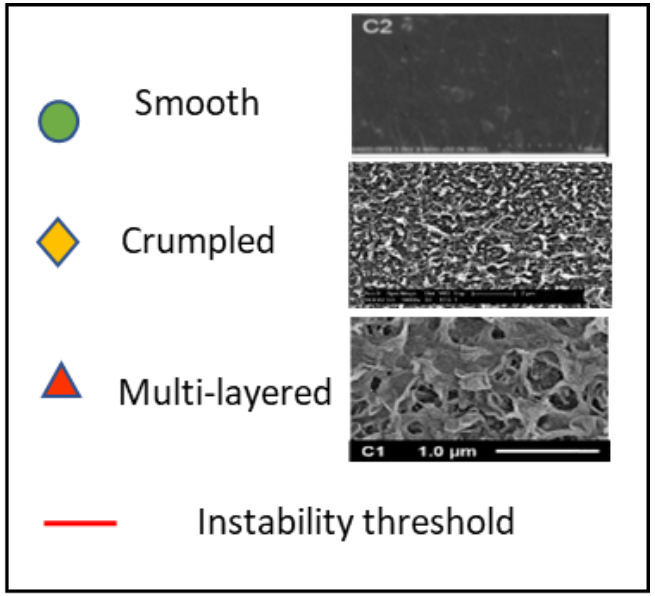


Susceptibility to instability

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







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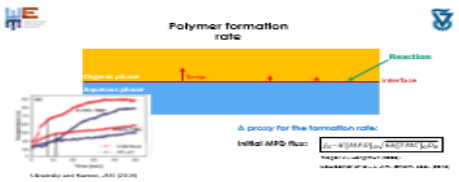
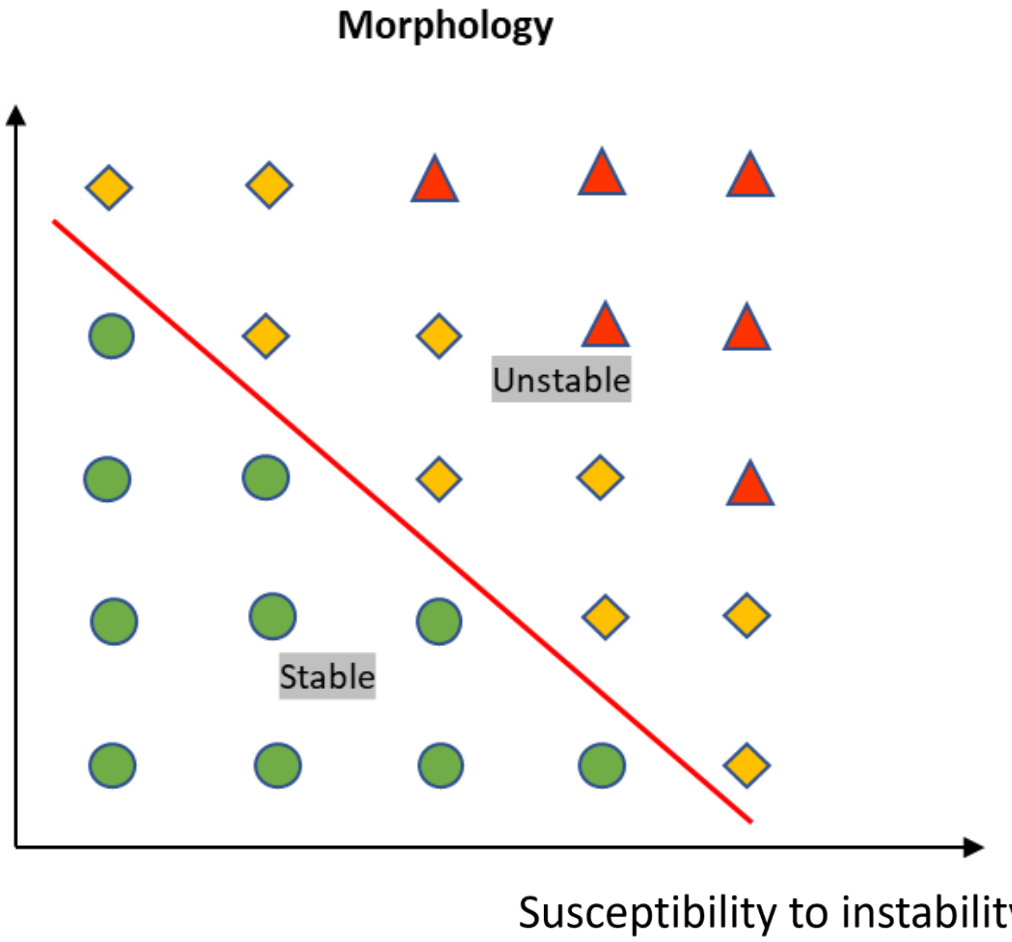
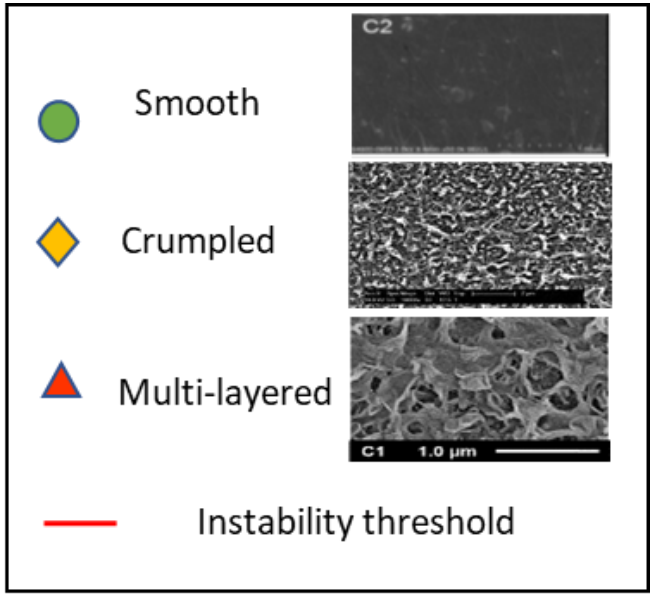
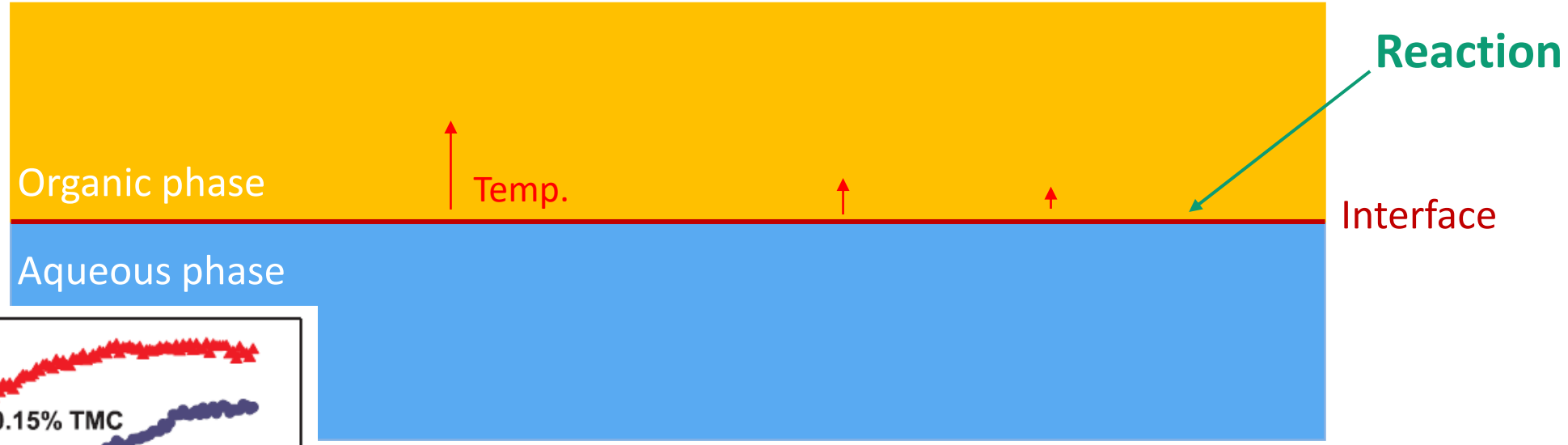
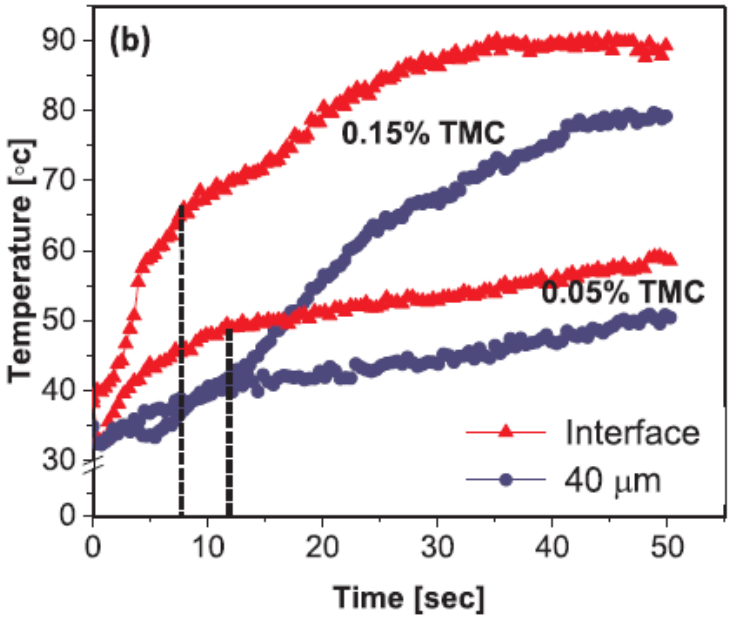






Polymer formation rate





Ukrainsky and Ramon, *JMS* (2018)

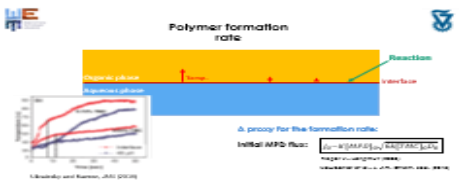
A proxy for the formation rate:

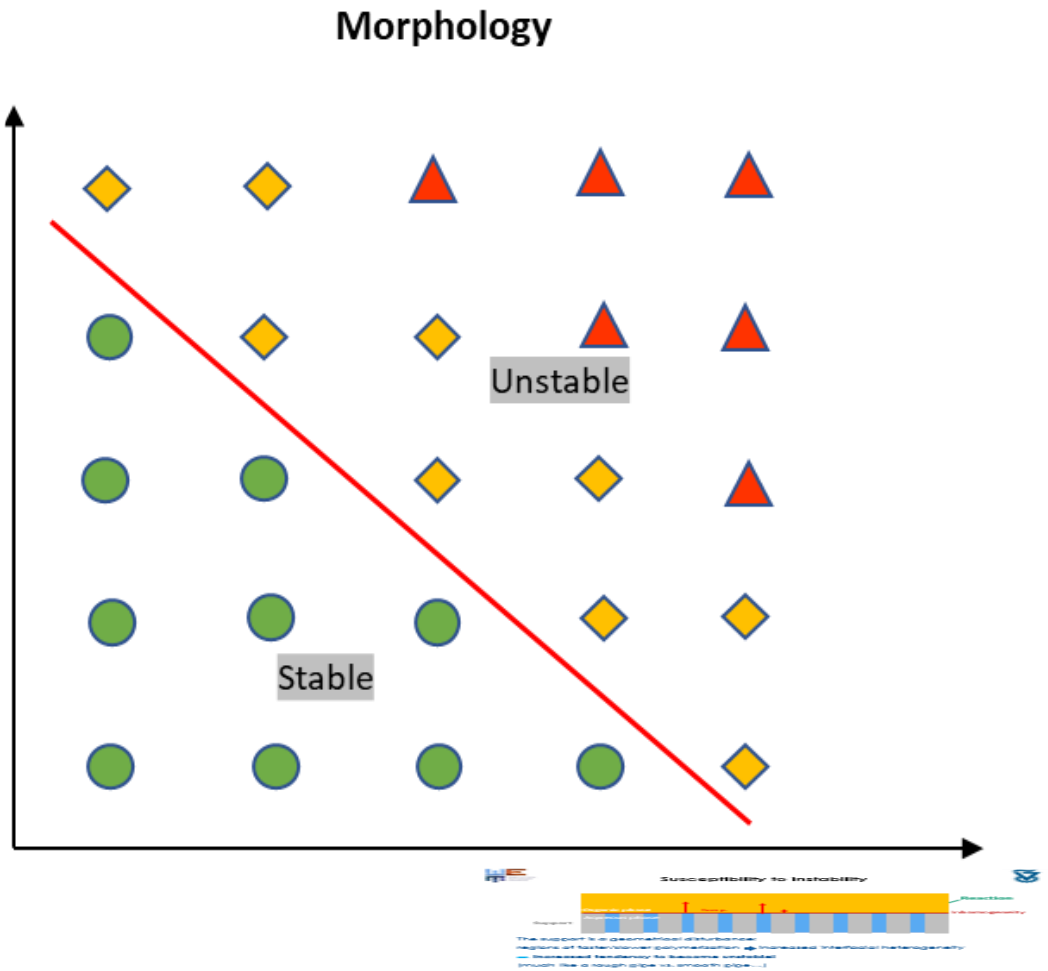
Initial MPD flux: $$J_0 \sim K[MPD]_0\sqrt{6k[TMC]_0 D_0}$$

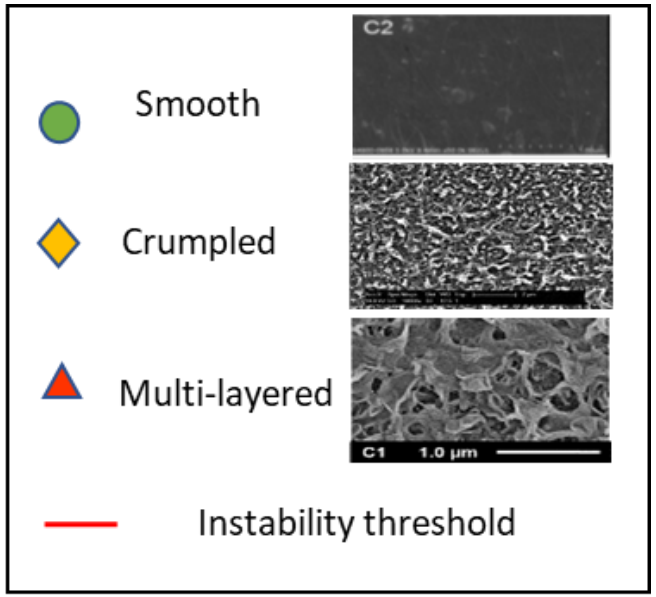
Freger V., *Langmuir* (2005)

Nowbahar et al., *J. Am. Chem. Soc.* (2018)

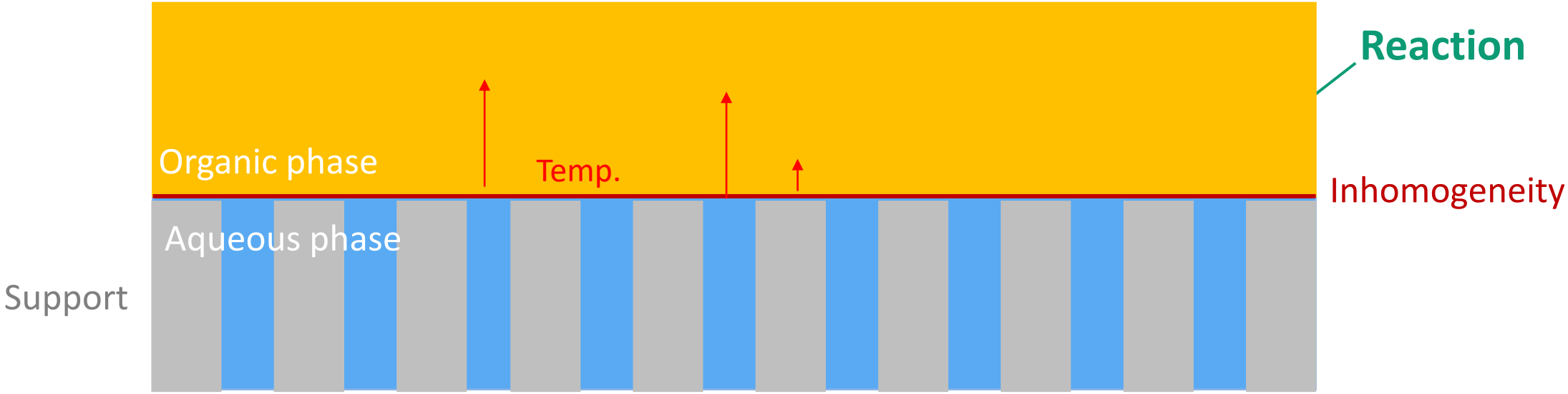
A '**phase diagram**' of **synthesis-morphology** relations in IP







Susceptibility to instability



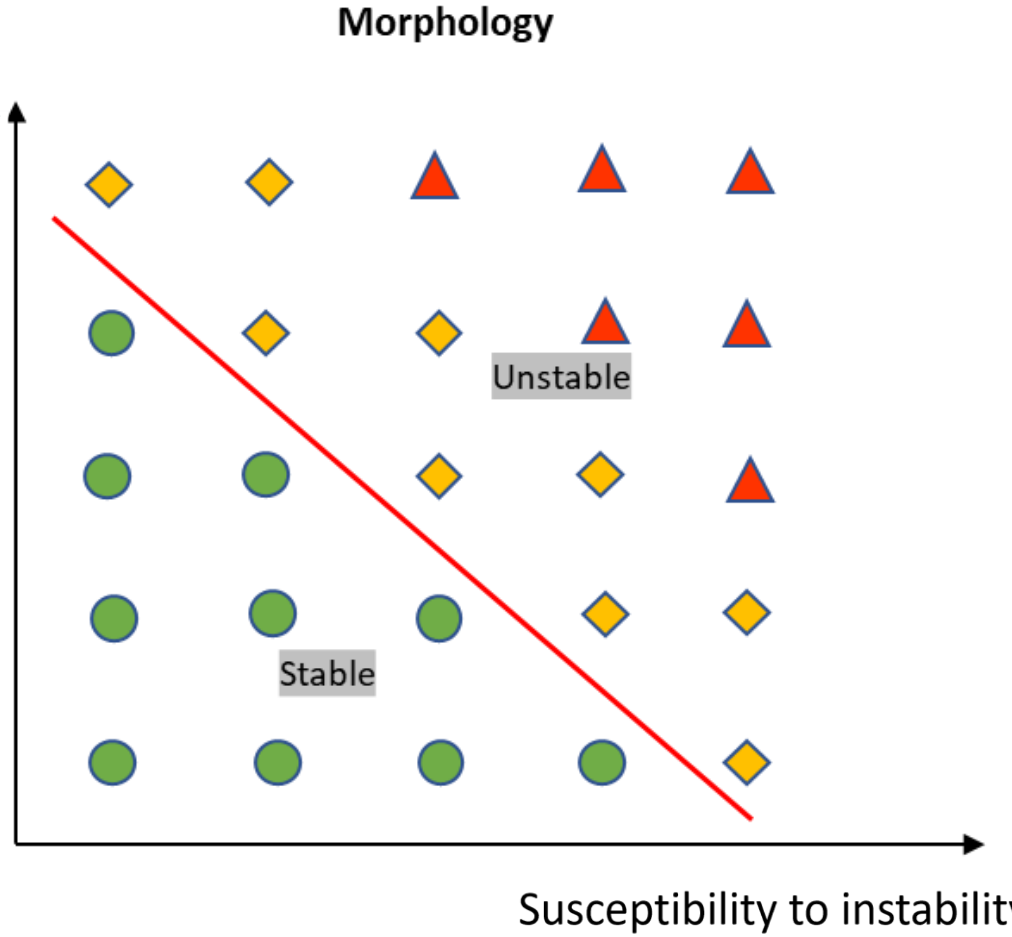
The support is a geometrical disturbance:

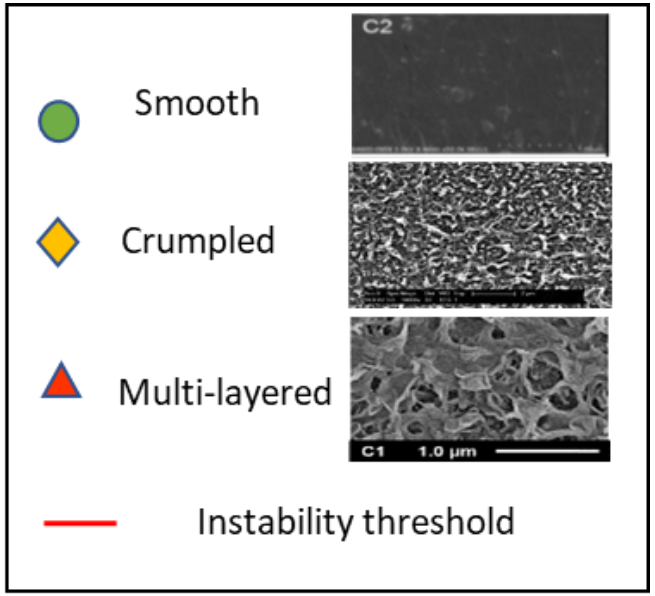
regions of faster/slower polymerization ➡ increased interfacial heterogeneity

⇒ **increased tendency to become unstable!**

(much like a rough pipe vs. smooth pipe…)

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





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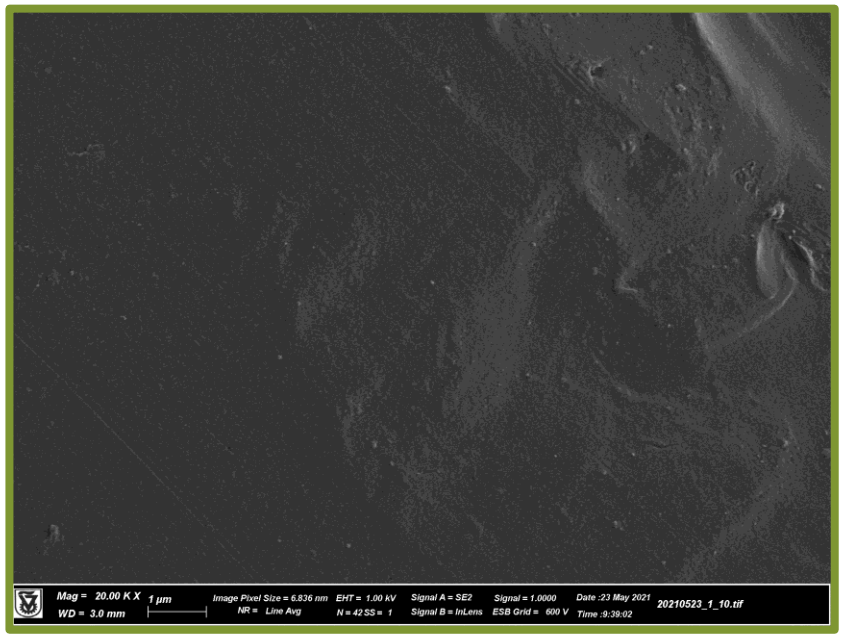
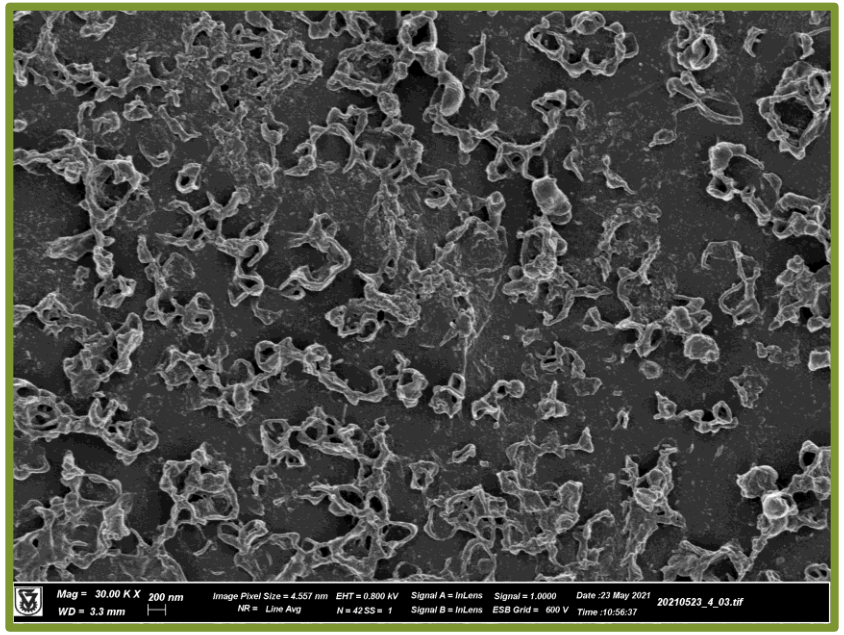
The Concept



Smooth

?

Instability mechanisms



Crumpled

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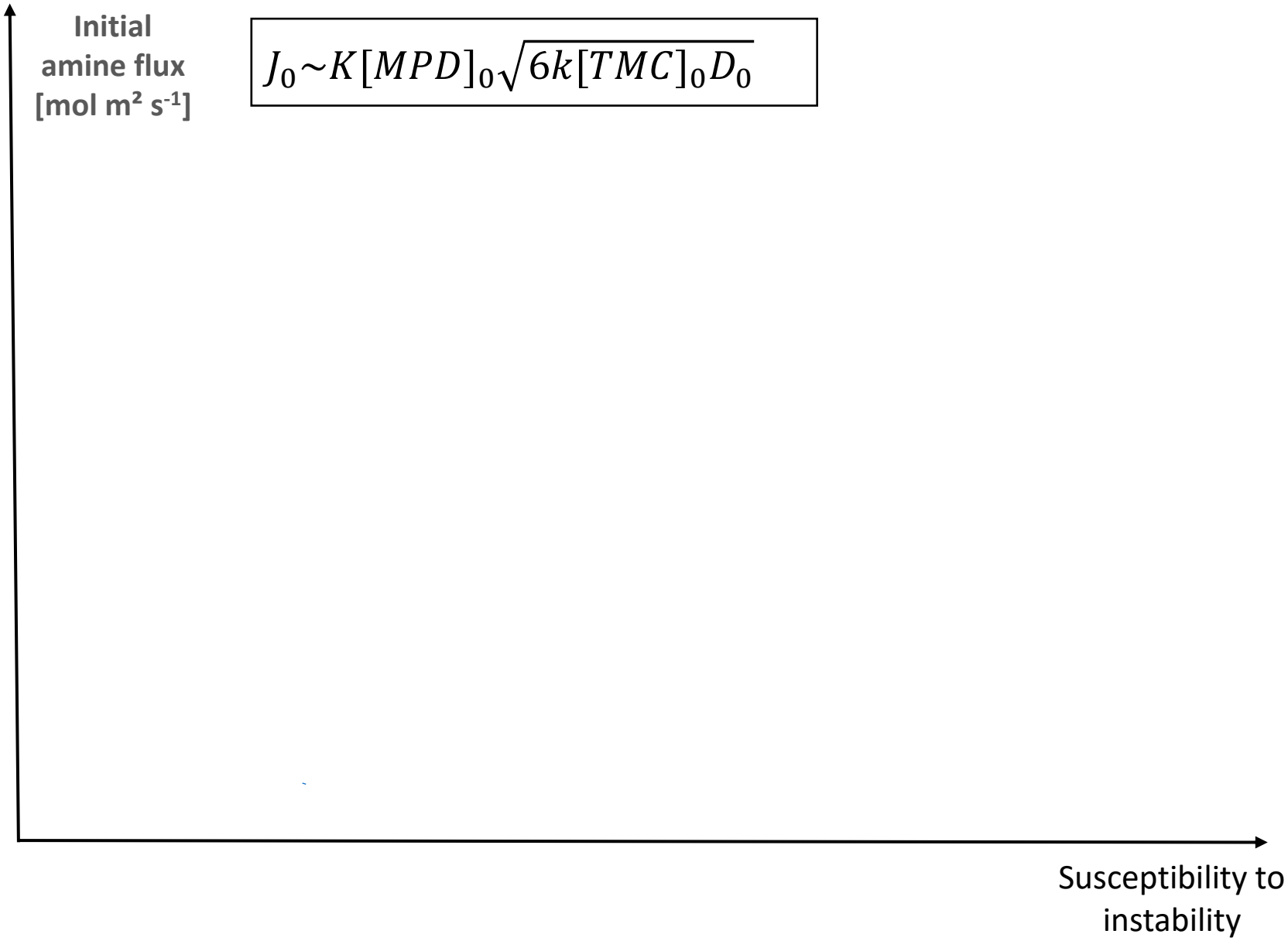
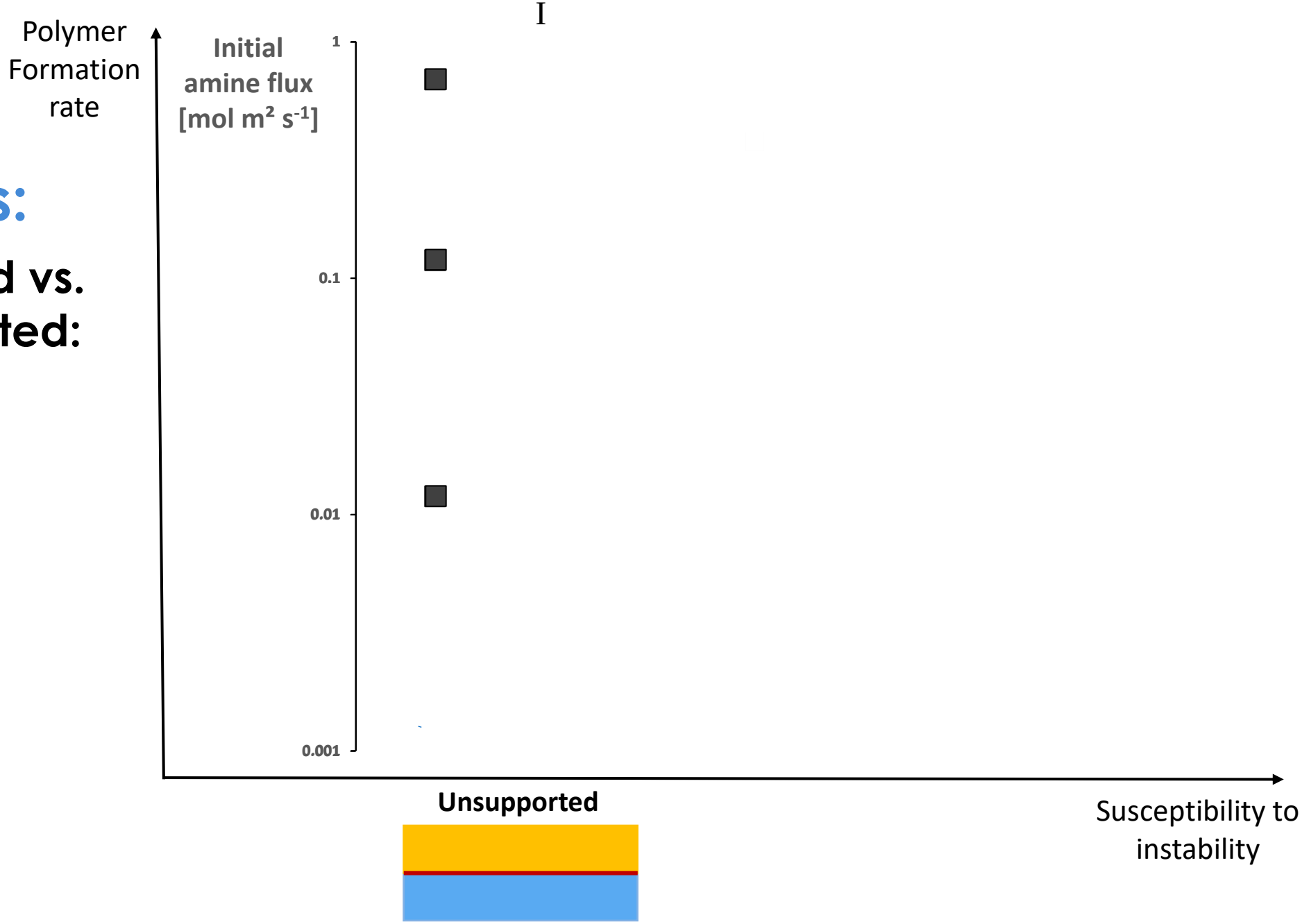
Results:

Supported vs. unsupported:



Results:

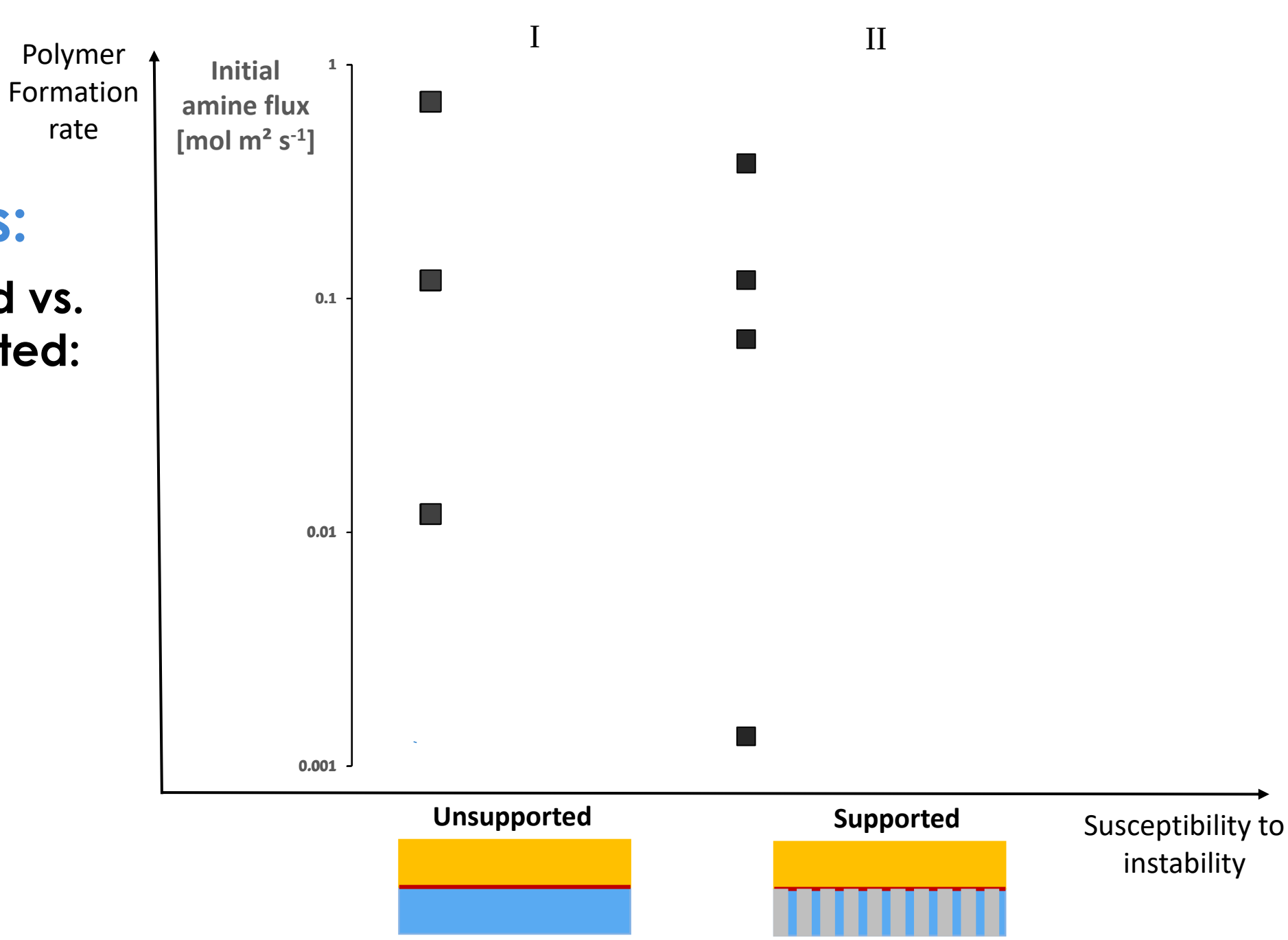
Supported vs. unsupported:



Ma et al., *Environ. Sci. Technol. Lett.* (2018), Hermans et al. *React. Funct. Polym.(2015), Jiang et al. Adv. Mater.(2018), Xu et al. JMS (2017)*

Results:

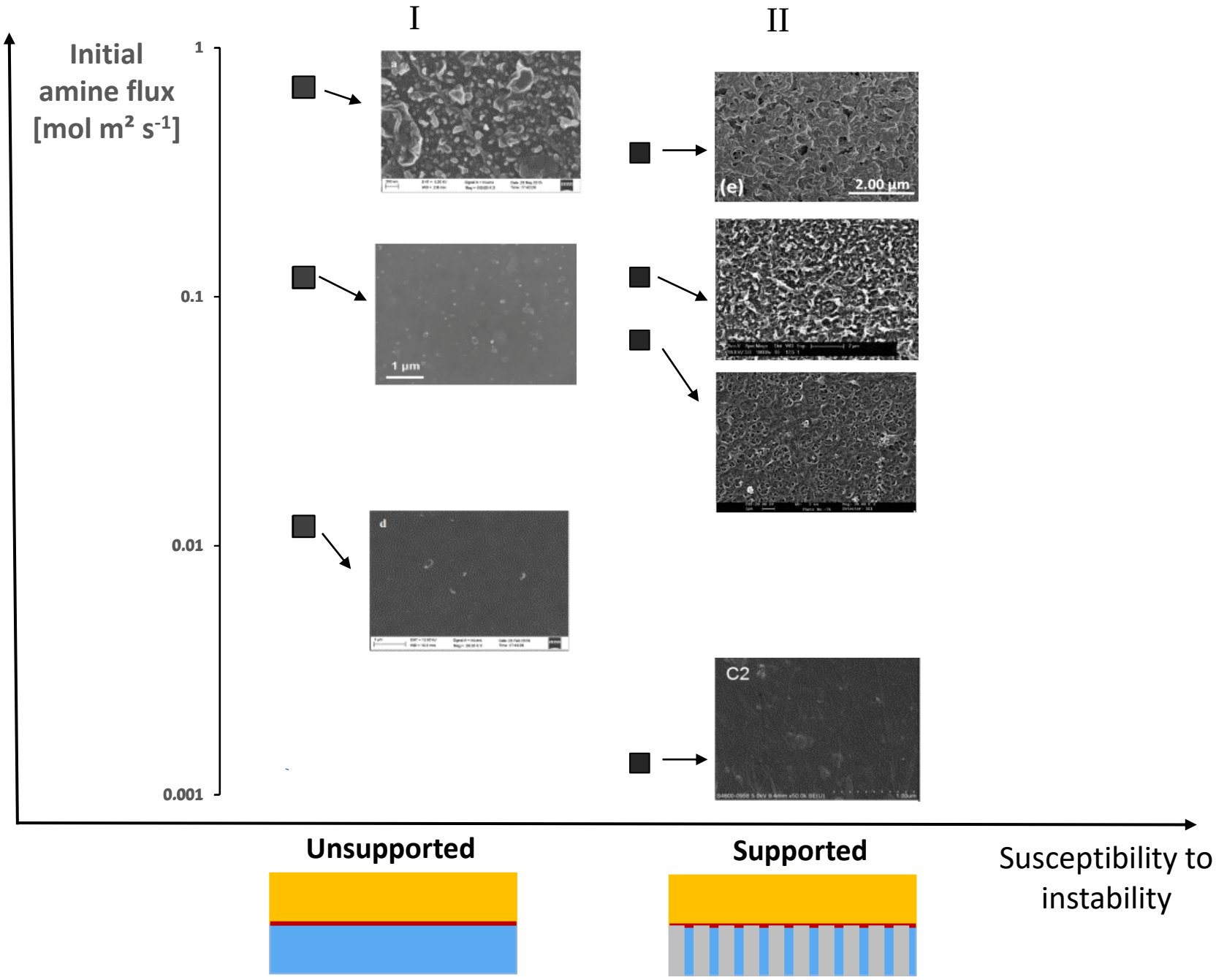
Supported vs. unsupported:



Ma et al., *Environ. Sci. Technol. Lett.* (2018), Hermans et al. *React. Funct. Polym.(2015), Jiang et al. Adv. Mater.(2018), Xu et al. JMS (2017)*

Results:

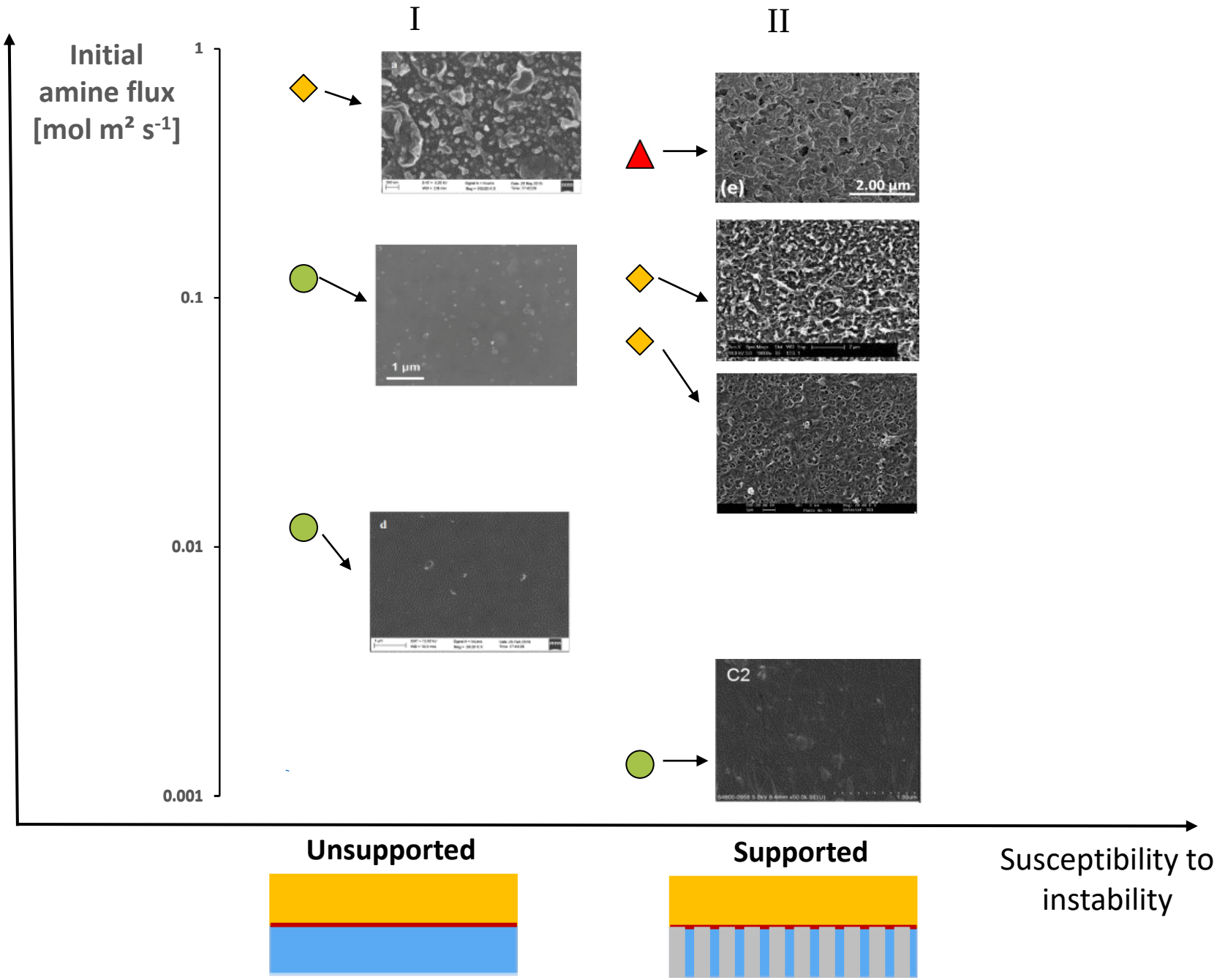
Supported vs. unsupported:



Ma et al., *Environ. Sci. Technol. Lett.* (2018), Hermans et al. *React. Funct. Polym.(2015), Jiang et al. Adv. Mater.(2018), Xu et al. JMS (2017)*

Results:

Supported vs. unsupported:



Ma et al., *Environ. Sci. Technol. Lett.* (2018), Hermans et al. *React. Funct. Polym.(2015), Jiang et al. Adv. Mater.(2018), Xu et al. JMS (2017)*

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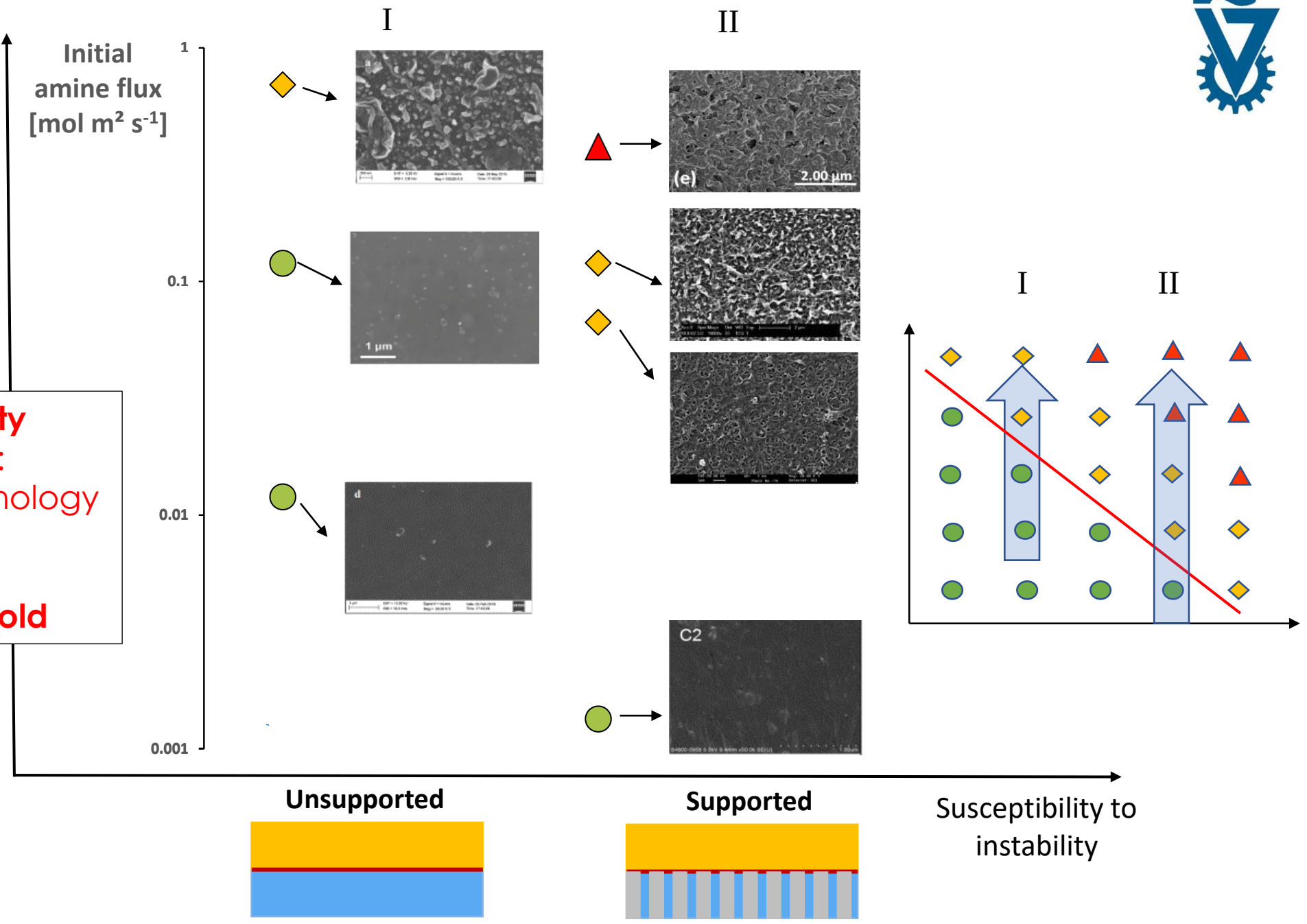
Results:

Supported vs. unsupported:

- **Increased susceptibility** and/or **formation rate**: more **crumpled** morphology
- Higher susceptibility: **lower instability threshold**



Ma et al., *Environ. Sci. Technol. Lett.* (2018), Hermans et al. *React. Funct. Polym.(2015), Jiang et al. Adv. Mater.(2018), Xu et al. JMS (2017)*

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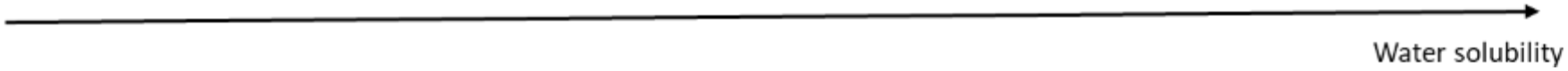
Results: Variations in the organic phase

100% Hexane	25 wt% Benzene	50 wt% Benzene	75 wt% Benzene	100 wt% Benzene



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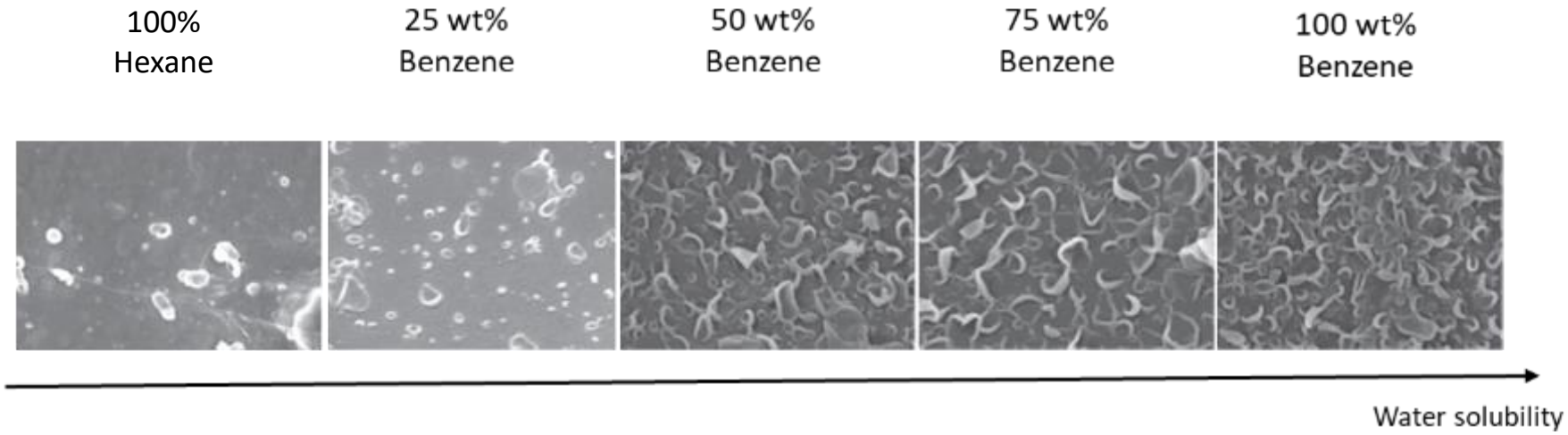
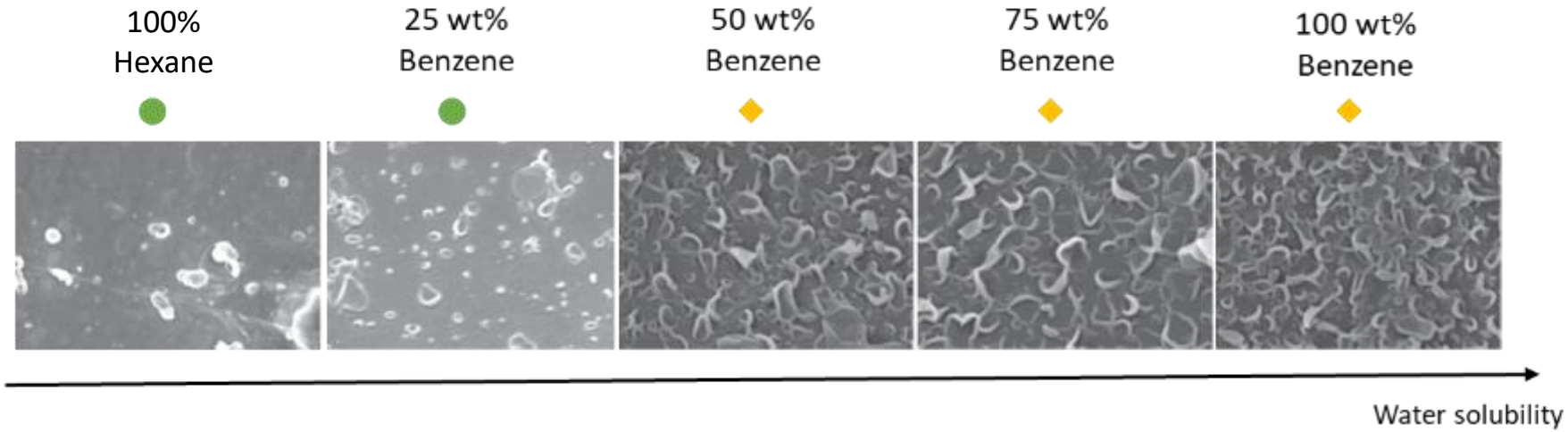
Results: Variations in the organic phase

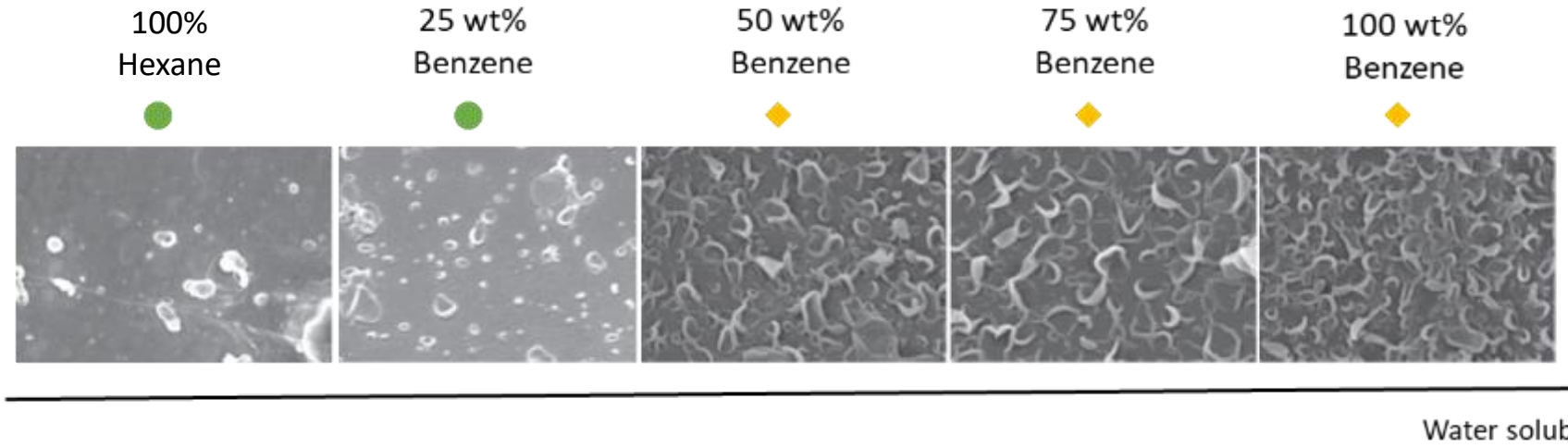


Results: Variations in the organic phase



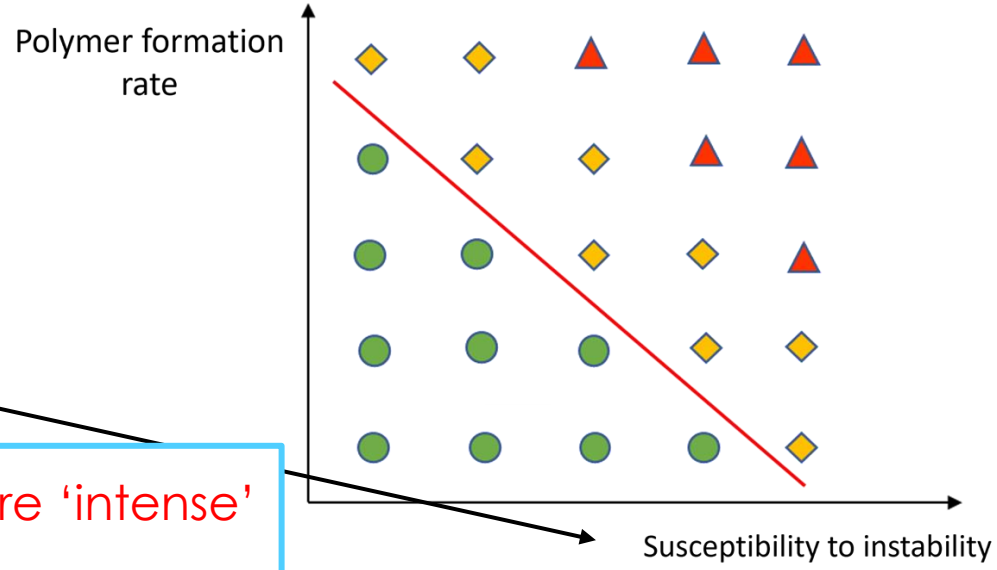
Wang et al., *Macromol Chem and Phys* (2019)

Results: Variations in the organic phase



Physical attributes

- MPD diffusion ↑
- MPD partitioning ↑
- Interfacial tension ↓



- As the water solubility increases the morphology is more 'intense'
- Adding a solvent increases both axis of the 'phase diagram'

Wang et al., *Macromol Chem and Phys* (2019)

Conclusions

- Concept of linking **stability** to **morphology** via a '**phase diagram**' was demonstrated.
- Transition from **smooth** to **crumpled** film outcome of **'stable'** to **'unstable'** state.
- **Increasing** 'polymer formation rate' and/or 'susceptibility to instability' results **in more crumpled PA** film **morphology**.
- Recast data from literature corresponds well with our framework.

Future work:

- **Experimental Design:** varying specific **physical attributes** to study effect on **morphology**.
- **Theoretical quantification:** to provide insight on **instability sensitivity** to various **physical attributes**.
- **Performance?**

Acknowledgements

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BARD

GIF
German-Israeli Foundation for Scientific Research and Development

GTEP
Grand Technion Energy Program
תוכנית האנרגיה ע"ש גרנד

ISRAEL SCIENCE FOUNDATION

RBNI
The Russell Berrie Nanotechnology Institute
Technion - Israel Institute of Technology

BSF
United States – Israel Binational Science Foundation

רשות המים

Thank you for Listening ☺