Assembling polymers at interfaces for encapsulation

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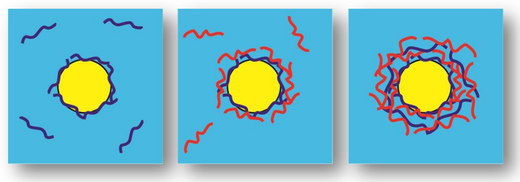
Context and Goal

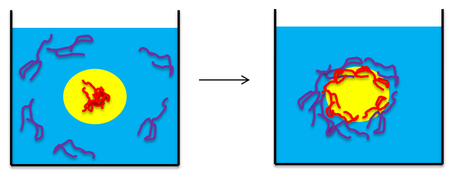
- Polymer capsules are used to protect and deliver active species. Polymer capsules are often obtained by interfacial polymerization at the oil/water interface, raising toxicity issues because of unreacted monomers
- Our goal is to design and produce capsules obtained from polymer assembly at the oil-water interface. We aim at rationalizing their design with respect to their mechanical and permeability. We wish to produce and characterize this capsules using microfluidics.

2 types of capsules

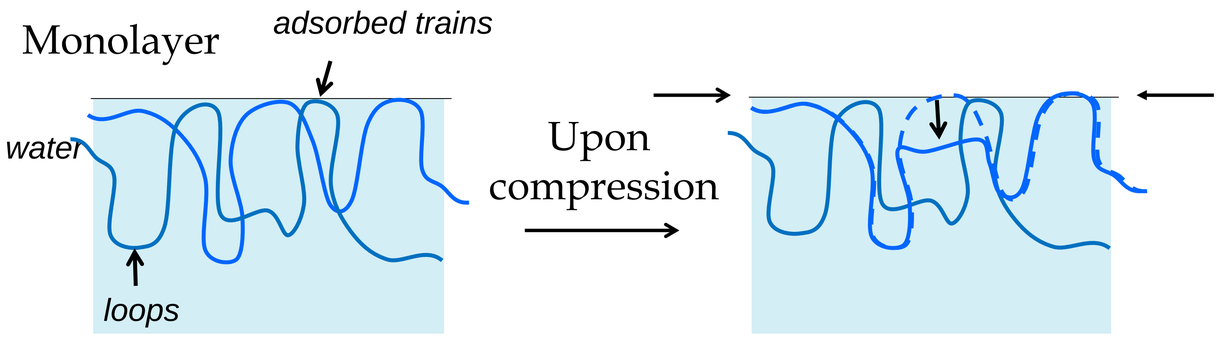
- Layer-by-layer assembly of polymers on oil droplets



- Coacervation at interfaces



Polymer dynamics at liquid interfaces



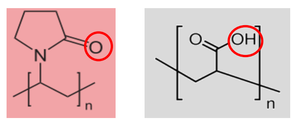
Hydrogen-bonded LbL system

Key parameters

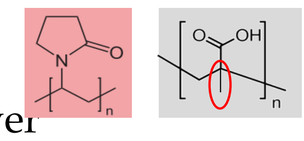
- Anchoring energy with the interface
- Interaction between the polymers

Couple used

- Hydrogen bonds only:
  PVP + PAA

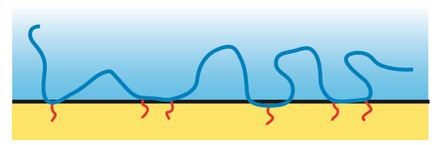


- Hydrogen bonds and hydrophobic interaction
  PVP + PAA



- Anchoring energy of the first layer

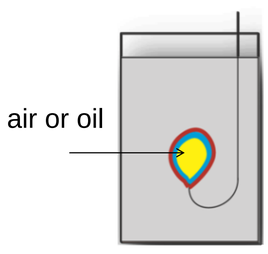
PAA**α**$C_{\mathbf{n}}$, **α** % of hydrophobic anchors of size **n**



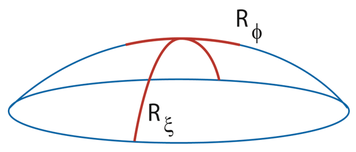
Interfacial rheology study

Pendant drop method :

1. Assembling the multilayer on a pendant drop

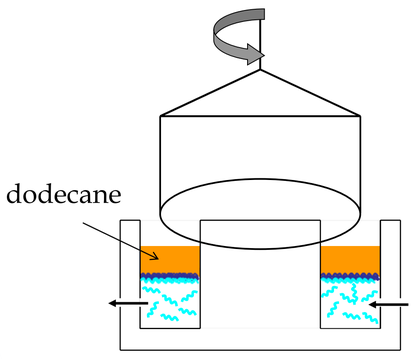


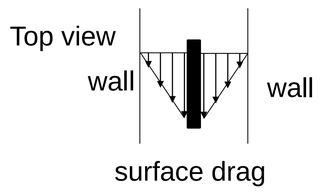
2. Compression of the droplets and pressure measurement to obtain interfacial tension as a function of area



$$\Delta P_{apex} = \frac{2\,T_{apex}}{R_{apex}}$$

Surface shear rheology:

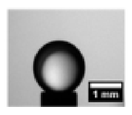




$$|G| = \frac{\sigma_s}{\gamma_s}$$

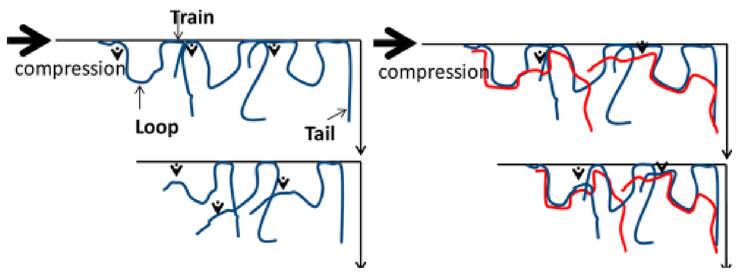
Results

The strength of interactions between the polymer layers enables to tune the dynamics of the chains in the multilayer.

PAA/PVP Weak interactions	PMAA/PVP Strong interactions	
High compressibility Low shear modulus	**Low compressibility High shear modulus**	
Slow and fast compression	**Slow compression**	**Fast compression**
		
No wrinkle	No wrinkle	Wrinkles

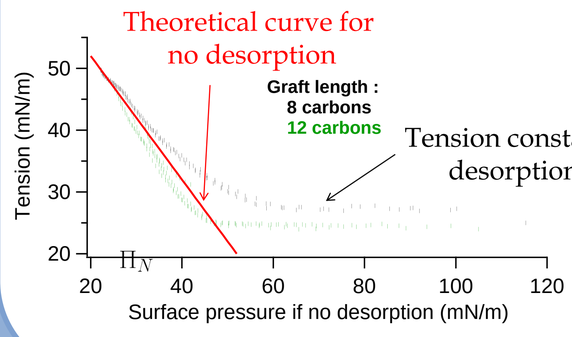
Stronger interaction lead to

→ Larger life time of physical bonds between the layers
→ Higher number of physical links : tighter network, G' ↑
→ Expulsion of monomers upon compression is more difficult



Le Tirilly et al, ACS *MacroLetters*, 2015

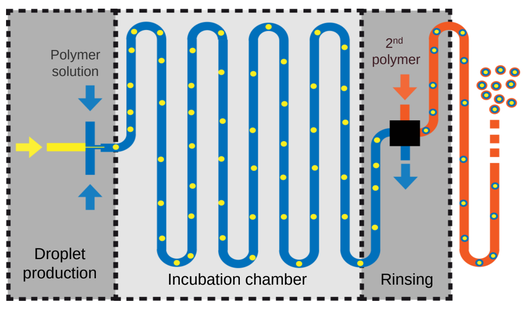
The anchoring energy of the first layer (PAA%Cn) enables to control the adsorption-desorption dynamics

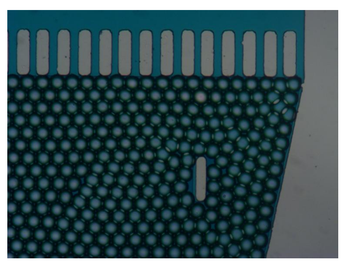


Tri-layer PAA1C12/PVP/PAA
Droplet stretches because of low interfacial tension and low shear modulus

Microfluidic study

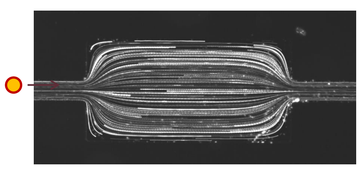
Production of monodisperse capsules

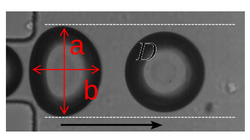




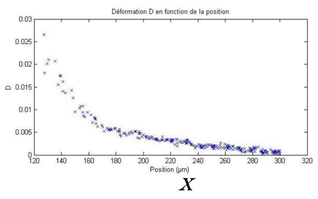
~ 20 µm

Online characterization of mechanics in constrictions





$$D = \frac{a-b}{a+b}$$



Conclusion

We have developped a toolbox to control and measure the dynamics and mechanics of polymer assemblies at liquid interfaces