Supramolecular double-networks based on microgels with reversible covalent interactions

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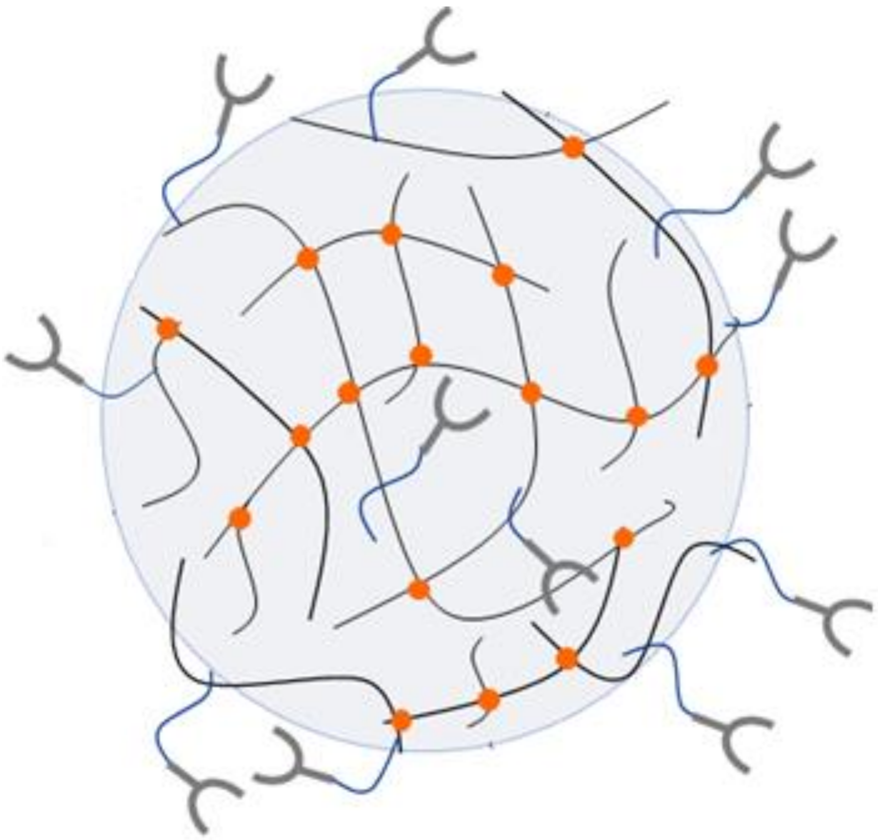
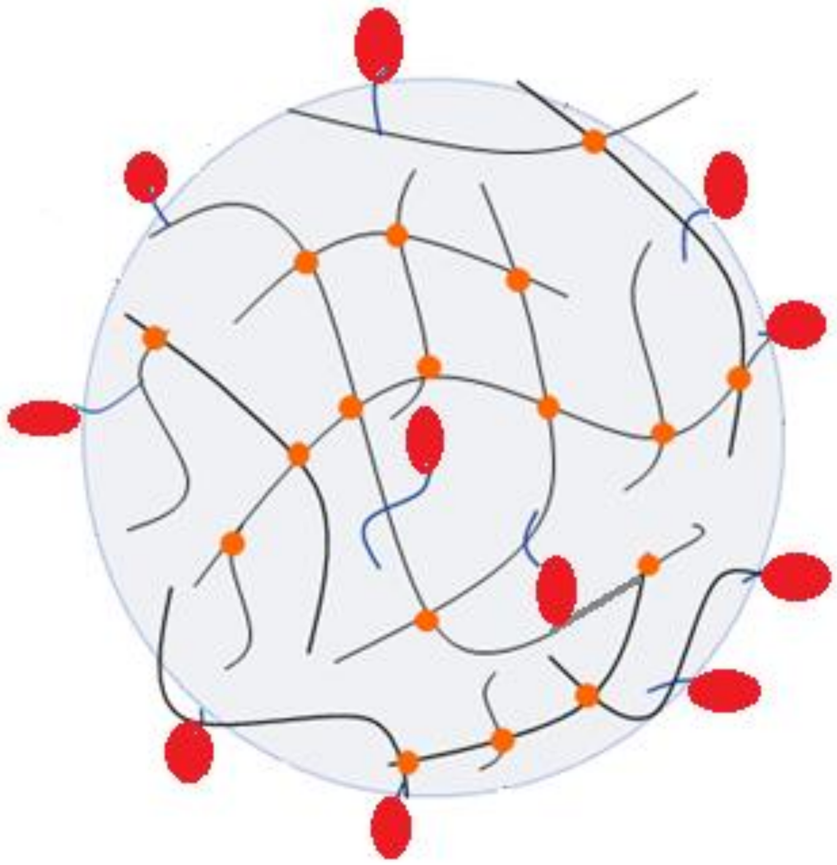
DSM Meeting - January 2019

Objective

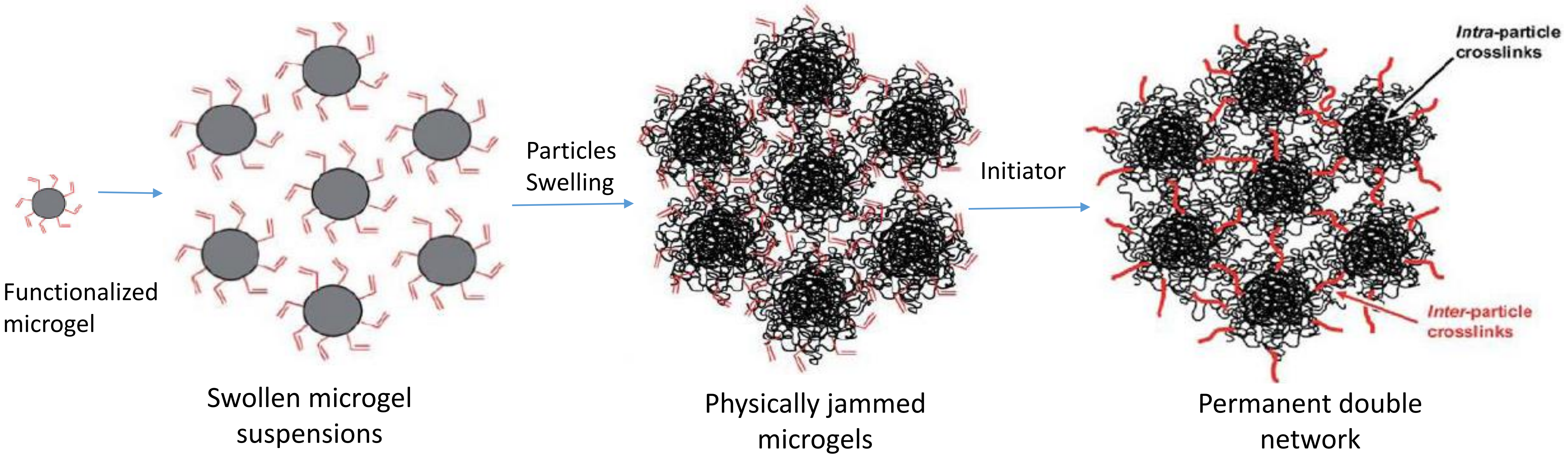
Supramolecular networks from building blocks interacting through complementary reversible covalent bonds





Building block: polymer network

The state of art: permanent network



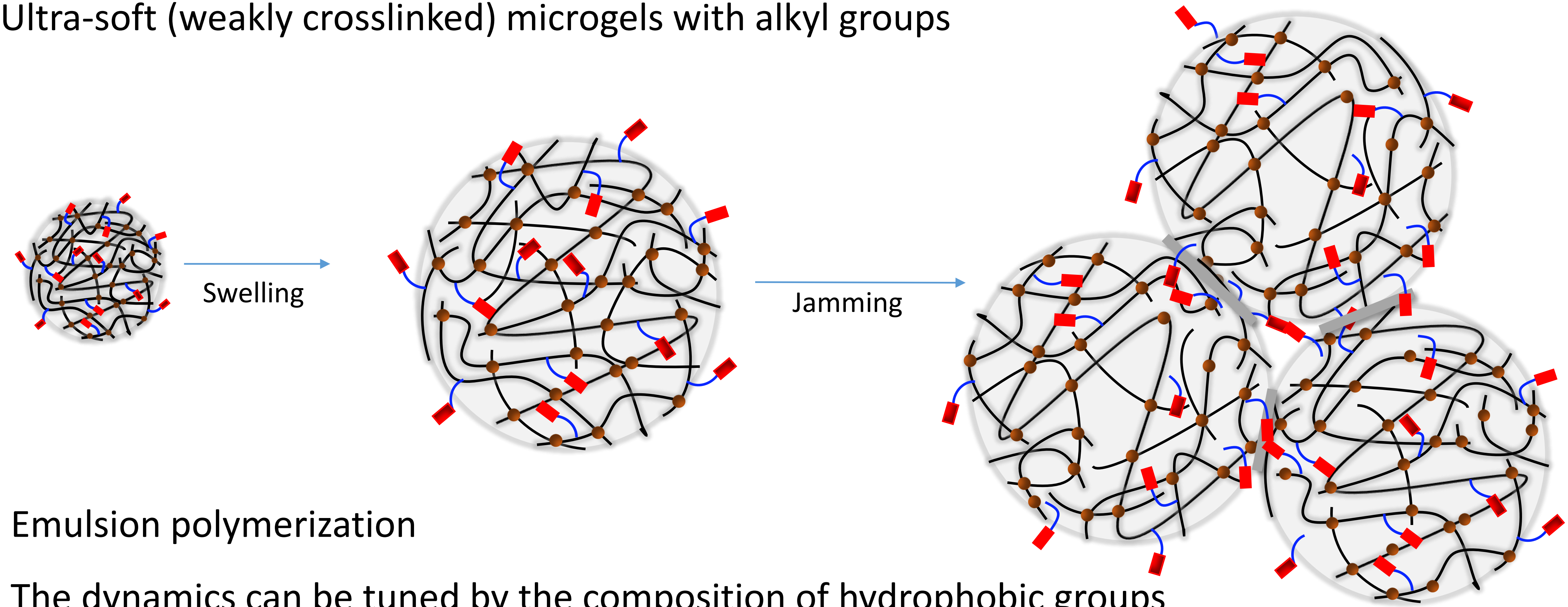
Covalent bonds using vinyl groups

Applications: injectable fluid for soft tissue repair

R. Liu et al., *Tuning the swelling and mechanical properties of pH-responsive doubly crosslinked microgels using particle composition*, Soft Matter, **7**, 9297 (2011)

Associative microgels with hydrophobic interactions

Ultra-soft (weakly crosslinked) microgels with alkyl groups



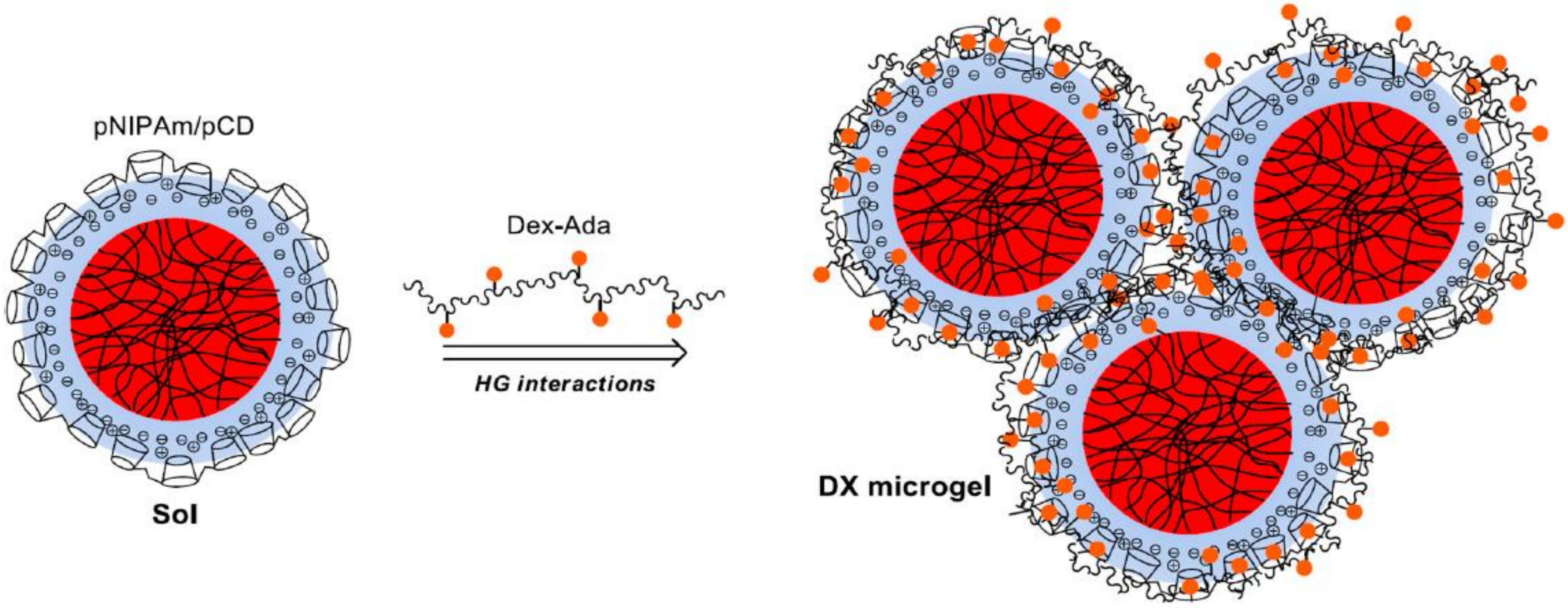
Emulsion polymerization

The dynamics can be tuned by the composition of hydrophobic groups

Applications: additives for rheology control

Mattiello, M. (2018). *Structure and dynamics of dense suspensions of soft colloids with tunable short-range attraction*. ESPCI Paris.

Reversible double-network



Building blocks of pNIPAm/cyclodextrin core-shell complex

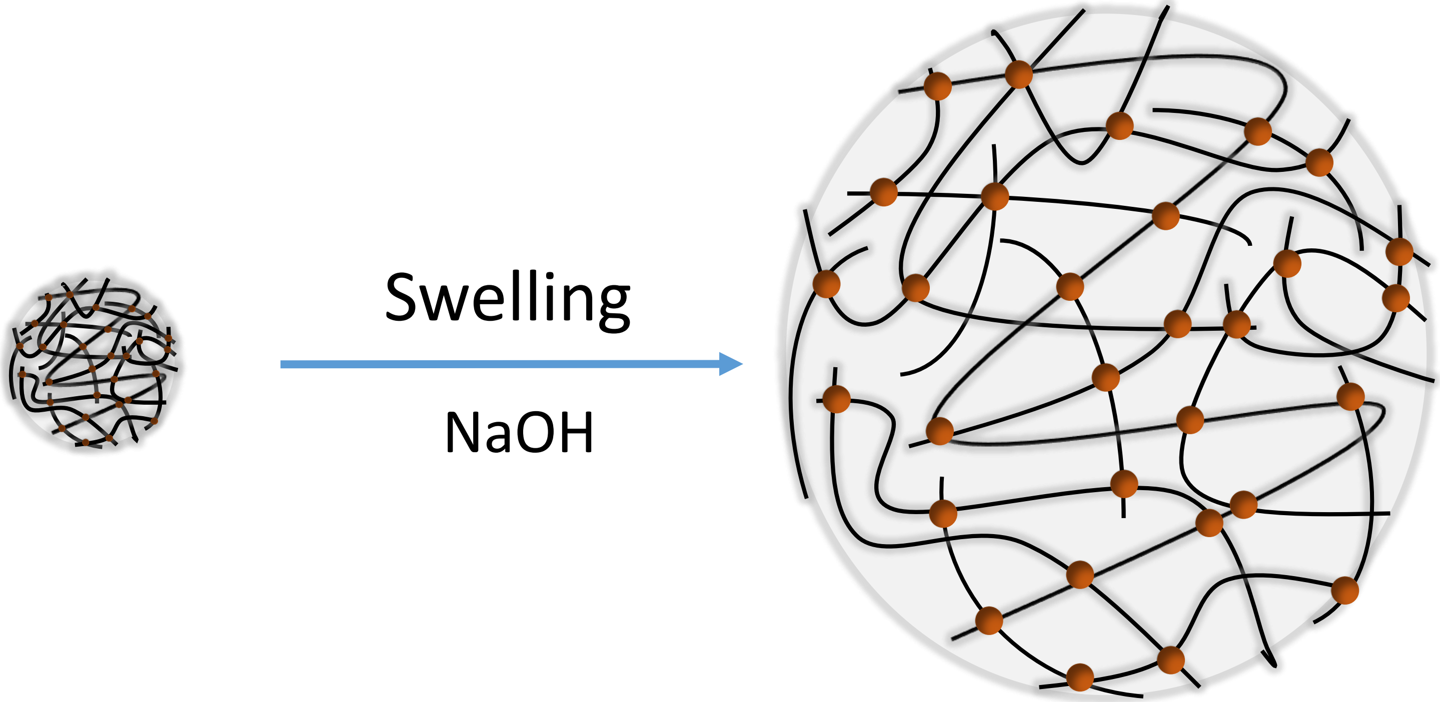
Noncovalent bonds with adamantane-substituted dextrans

Host-guest interactions

Antoniuk I. et al., *Supramolecular Hydrogel Based on pNIPAm Microgels Connected via Host–Guest Interactions*. Polymers (2018)

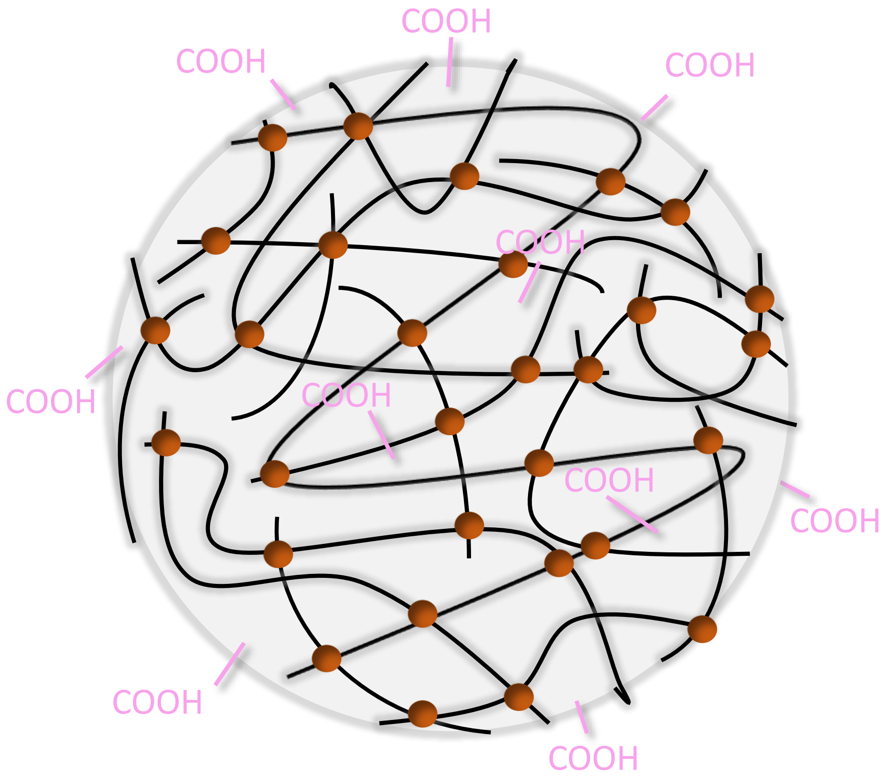
Road map: 1st step

POLYELECTROLYTE MICROGELS | FUNCTIONALIZED MICROGELS | DOUBLE NETWORK



- Characterization of microgels
- Training in laboratory techniques
- Learning and practicing rheology and DLS

Repulsive microgels



Ionization of COOH → osmotic pressure

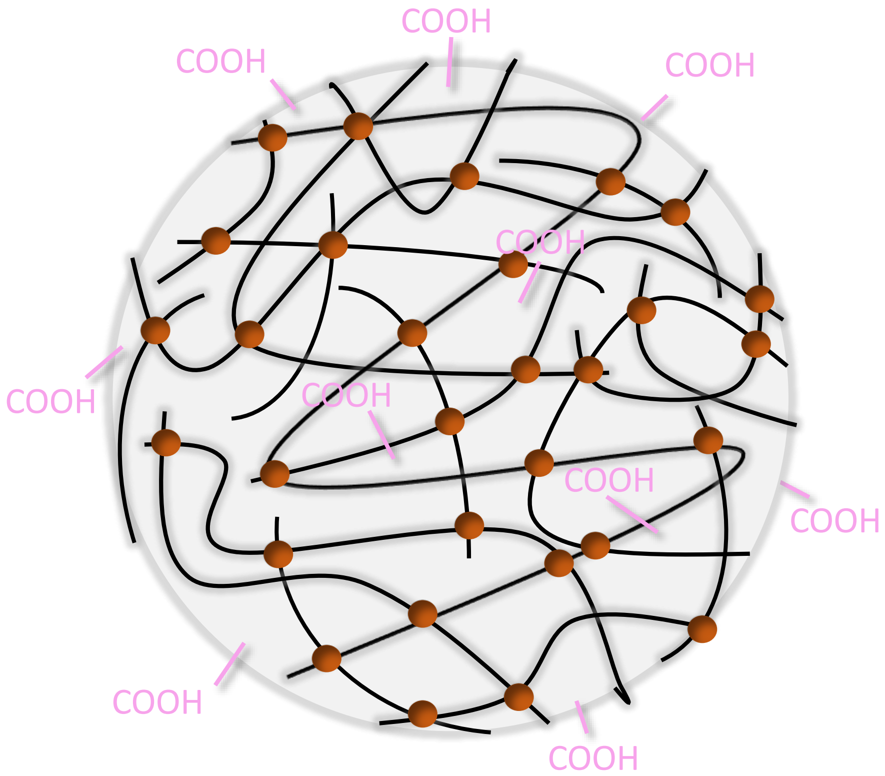
Poly(ethyl-acrylate-co-methacrylicacid)

Trimethylolpropane triacrylate crosslinks

EA (%mol)	MAA (%mol)	TPMTA (%mol)
59.5	39.7	0.8

Microgels synthetized by COATEX

Repulsive microgels



Ionization of COOH → osmotic pressure

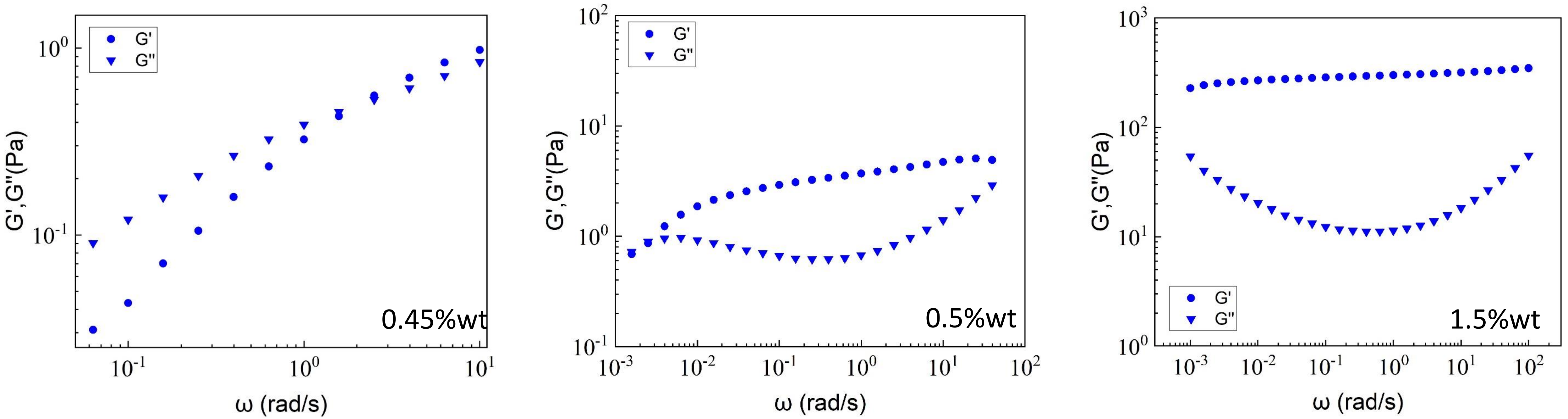
Poly(ethyl-acrylate-co-methacrylicacid)

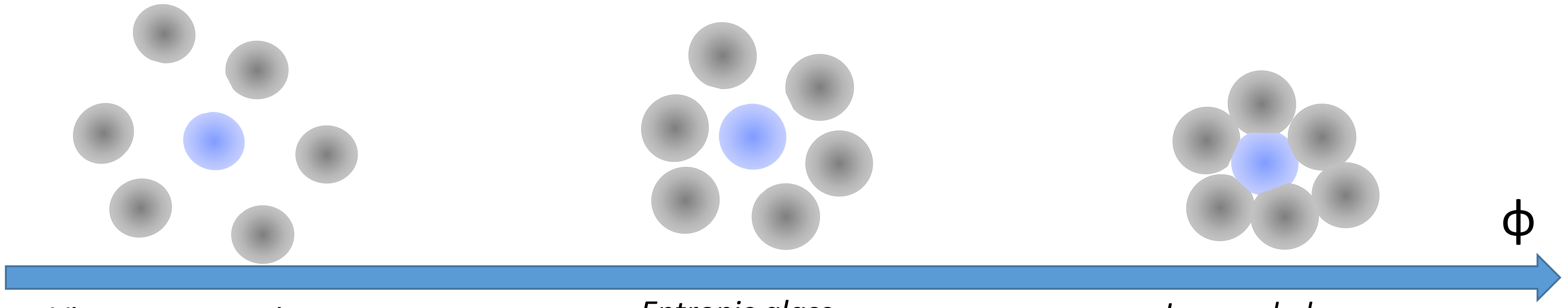
Trimethylolpropane triacrylate crosslinks

EA (%mol)	MAA (%mol)	TPMTA (%mol)	R_h collapsed state (nm)	R_h max swelling (nm)
59.5	39.7	0.8	58 $\pm$ 2	237 $\pm$ 2

Microgels synthetized by COATEX

Linear rheology of repulsive microgels





Viscous suspension

Entropic glass
Weak solid-like regime

Jammed glass
Strong solid like regime

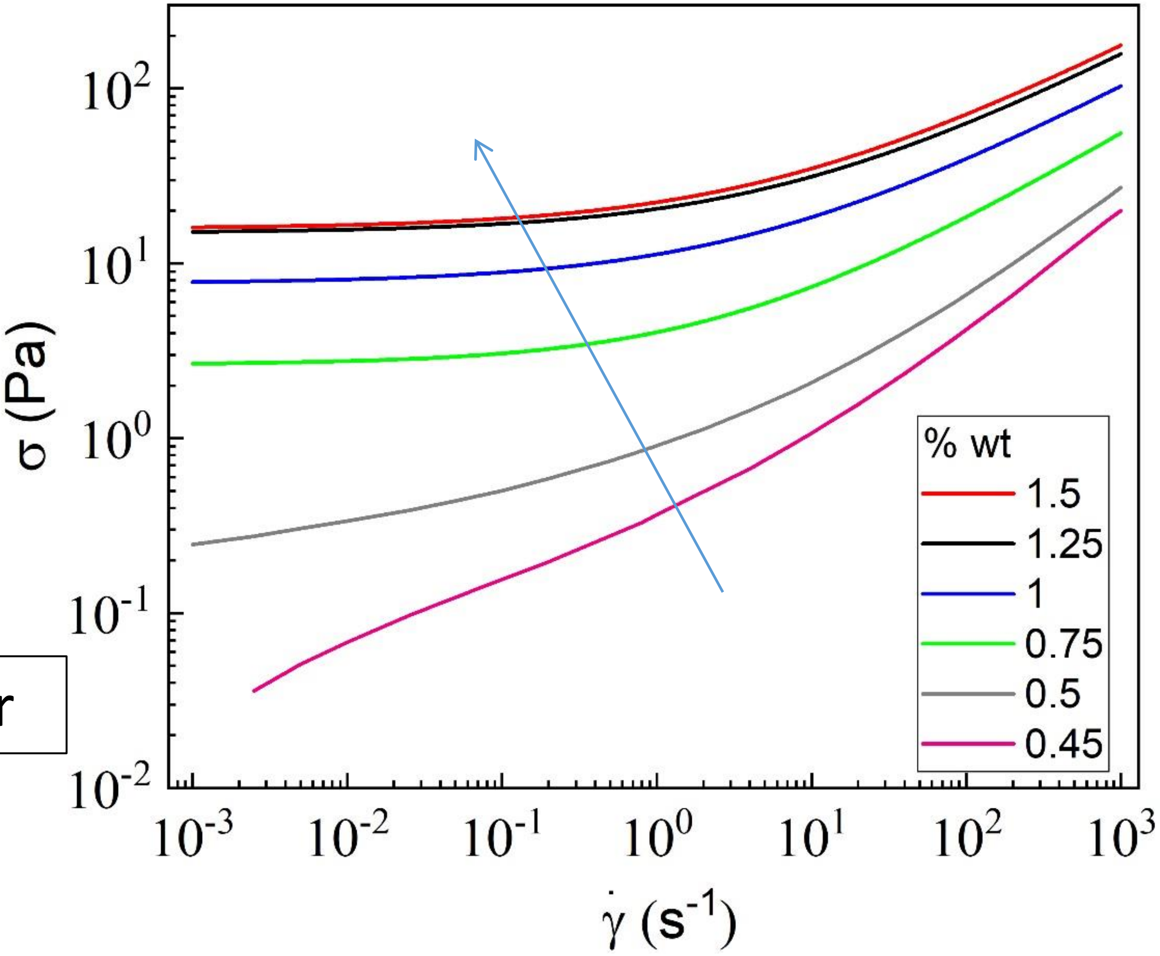
Pellet C, Cloitre M., The glass and jamming transition of soft polyelectrolyte microgel suspensions. Soft Matter, **12**, 3710 (2016)

Non linear rheology: flow curves

Jammed

Glass

Terminal behavior

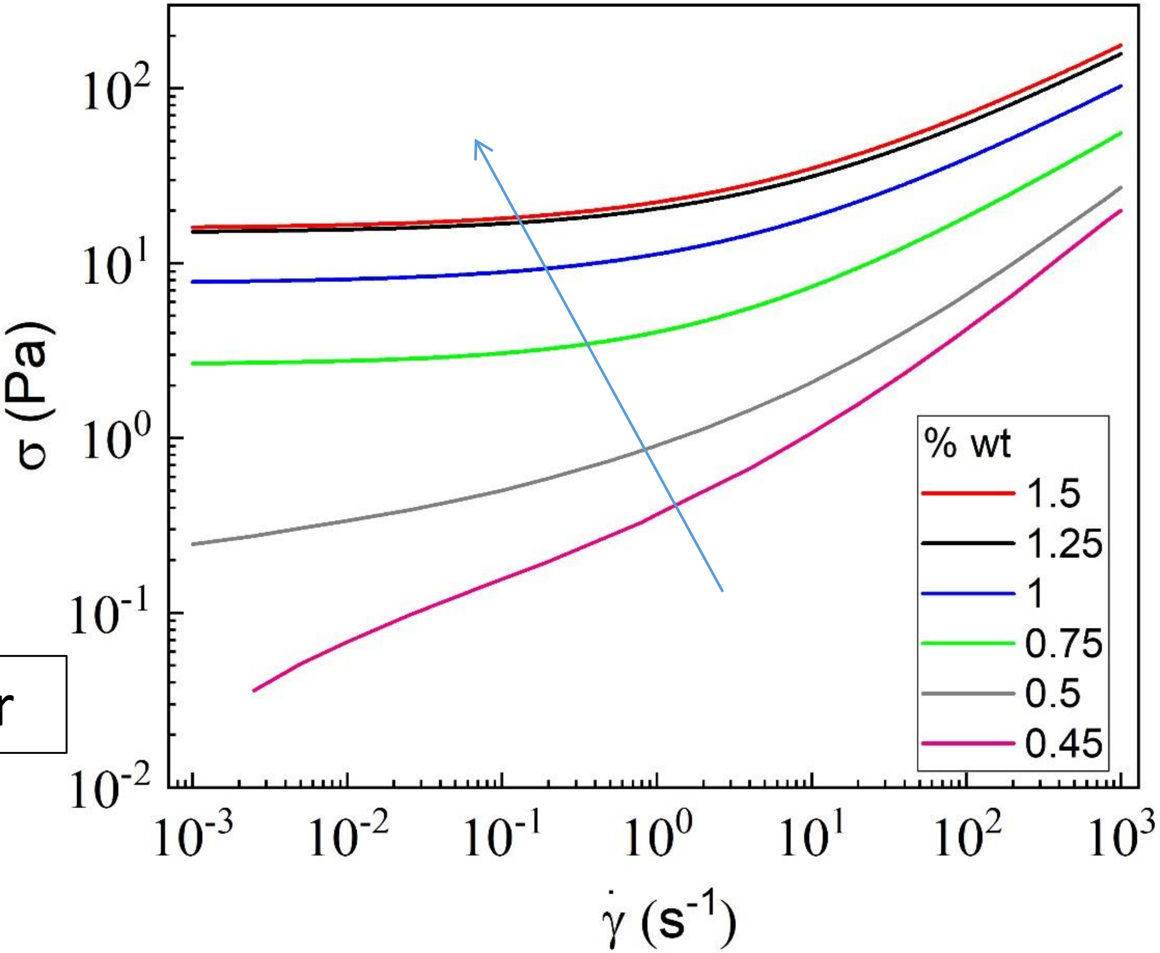


Non linear rheology: flow curves

Jammed

Glass

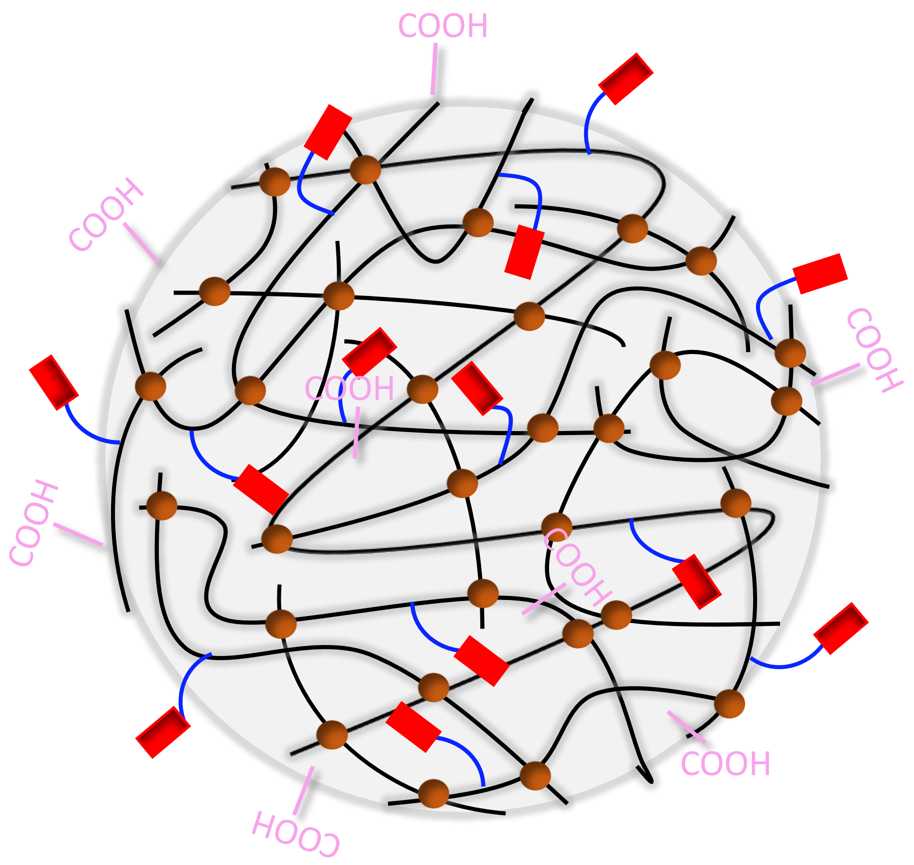
Terminal behavior



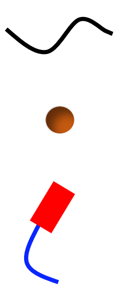
Jammed glass regime: stress plateau+power law

Fitted to Herschel Bulkley equation: $\sigma = \sigma_y + k\dot{\gamma}^n$ n < 0.5

Associative microgels



Hydrophobically modified microgels



Poly(ethyl-acrylate-co-methyl metacrylate)

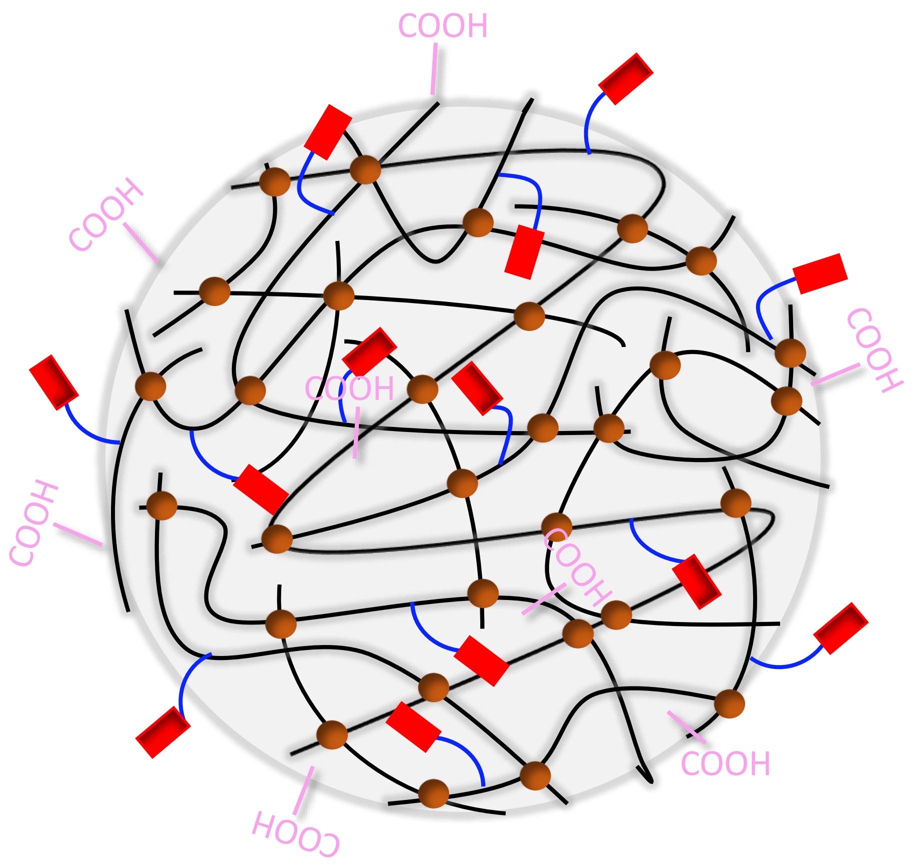
Trimethylolpropane triacrylate crosslinks

Sticker

EA (%mol)	MMA (%mol)	TPMTA (%mol)	Sticker formula
59.4	39.6	1	$-C_{22}H_{45}$

Microgels synthetized by COATEX

Associative microgels



Hydrophobically modified microgels

Poly(ethyl-acrylate-co-methyl metacrylate)

Trimethylolpropane triacrylate crosslinks

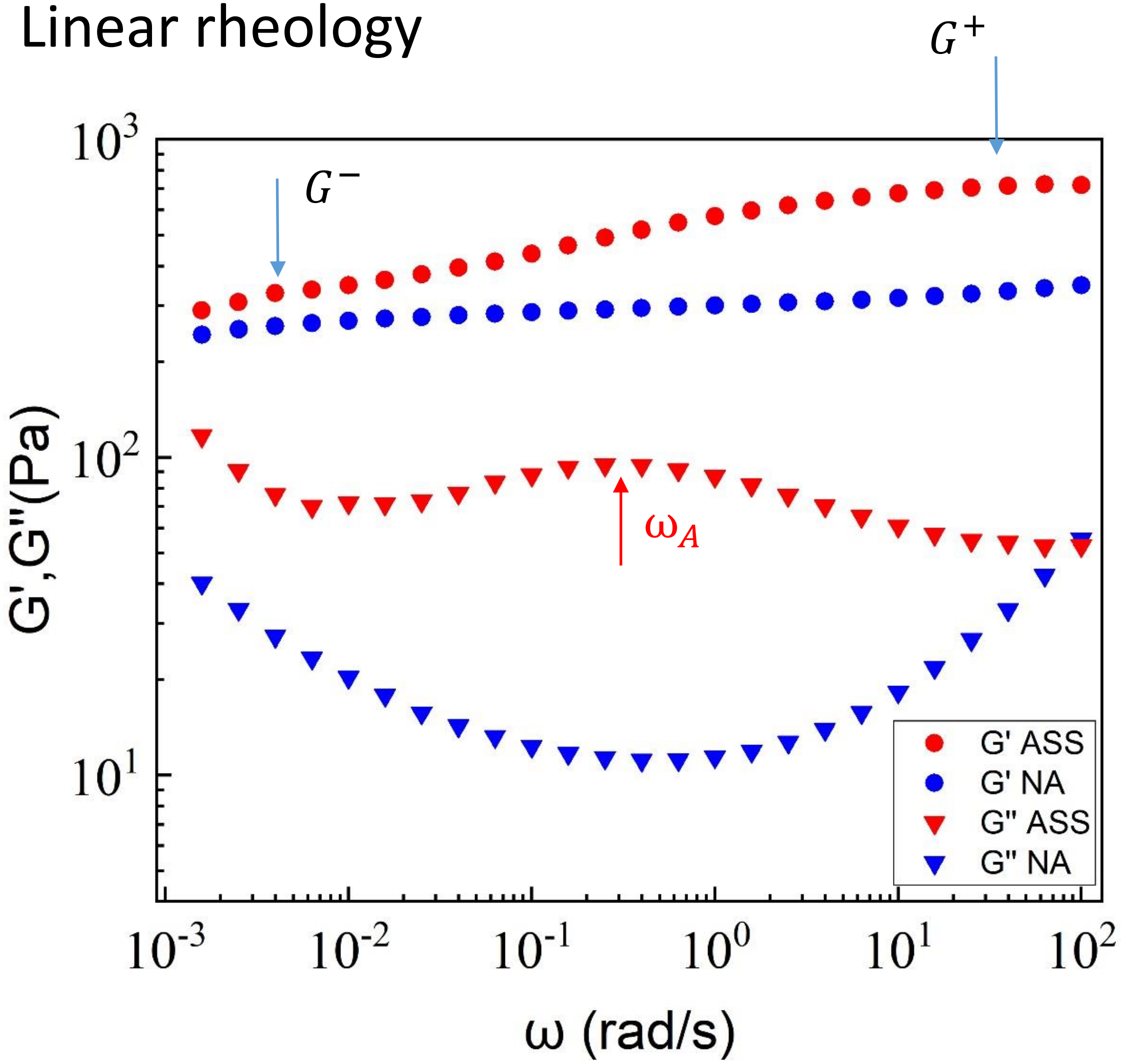
Sticker { Alkyl chain (associative part) / Polyethilene oxide (spacer)

EA (%mol)	MMA (%mol)	TPMTA (%mol)	Sticker formula
59.4	39.6	1	$-C_{22}H_{45}$

Microgels synthetized by COATEX

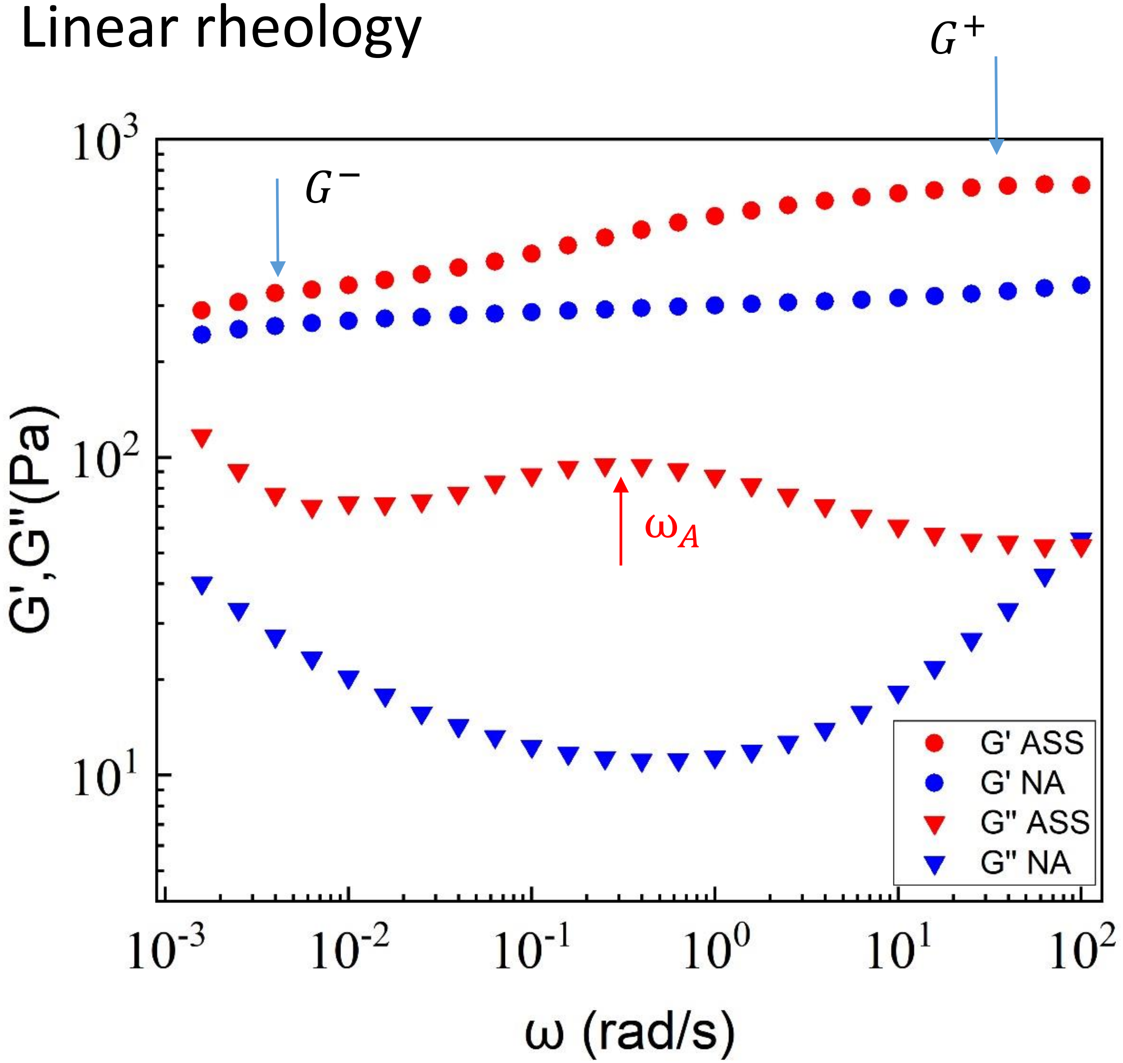
Repulsive VS associative microgels in solid-like regim

Linear rheology



Repulsive VS associative microgels in solid-like regim

Linear rheology

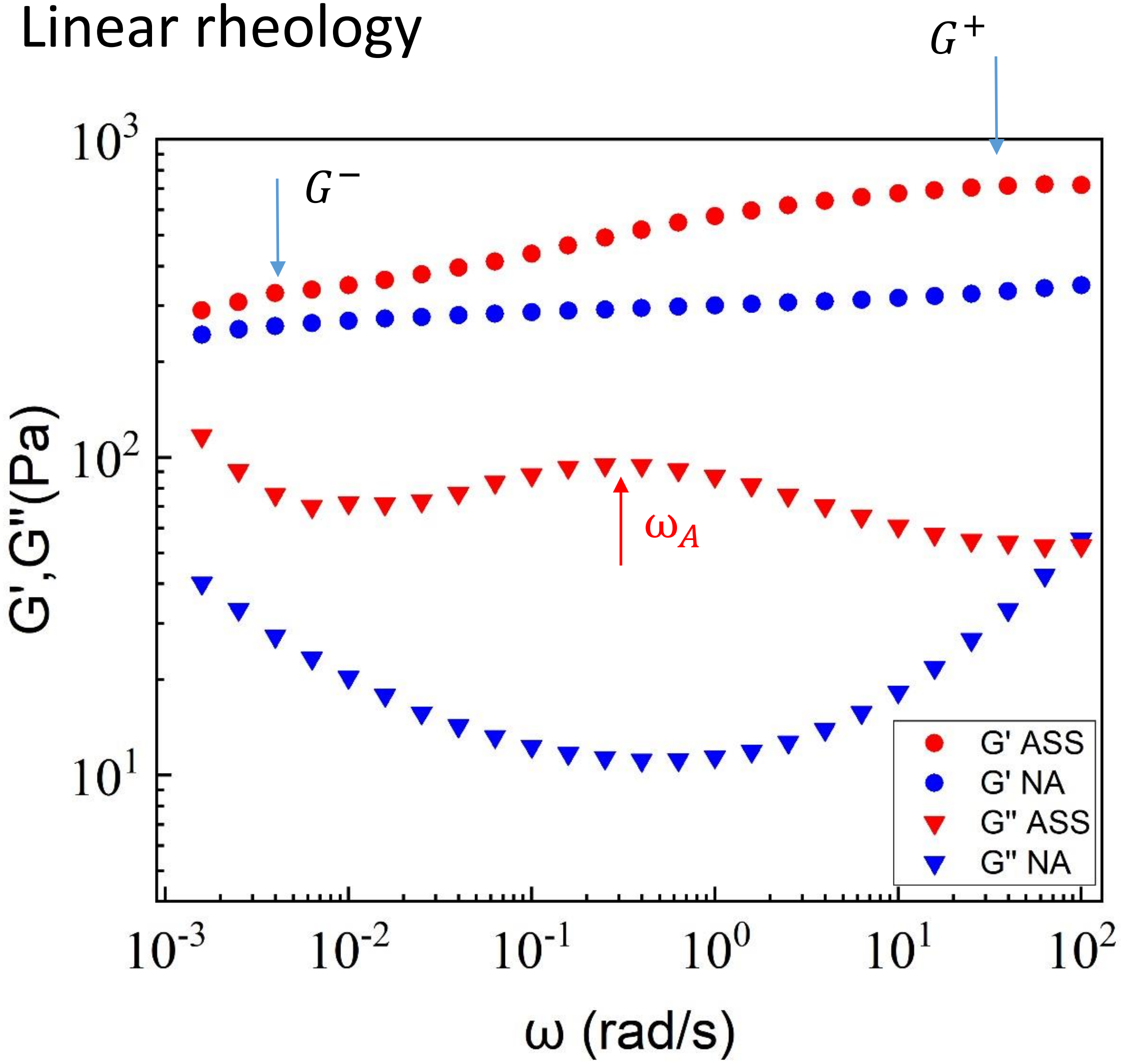


Association contributes to elasticity at high frequency

ω_A relaxation frequency of the cage

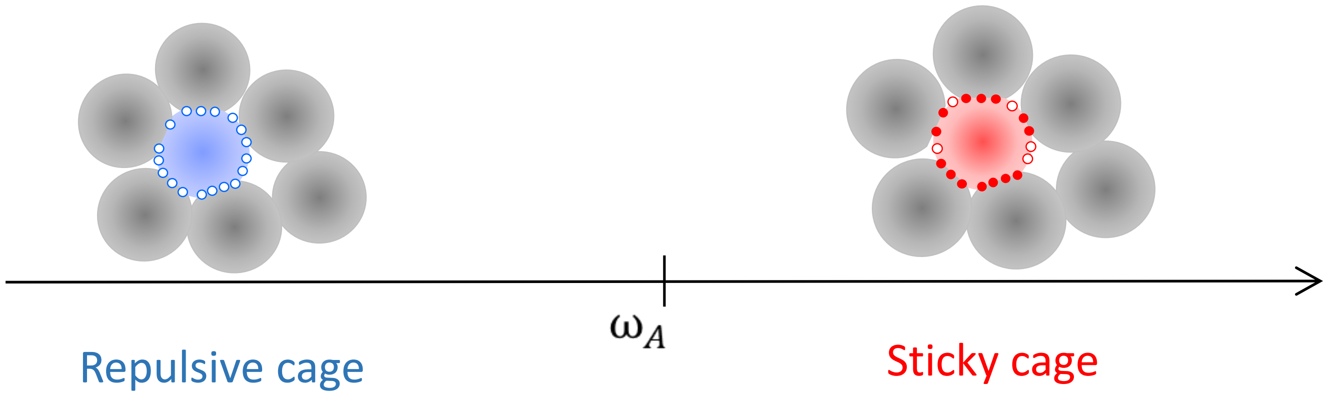
Repulsive VS associative microgels in solid-like regim

Linear rheology



ω_A relaxation frequency of the cage

Association contributes to elasticity at high frequency

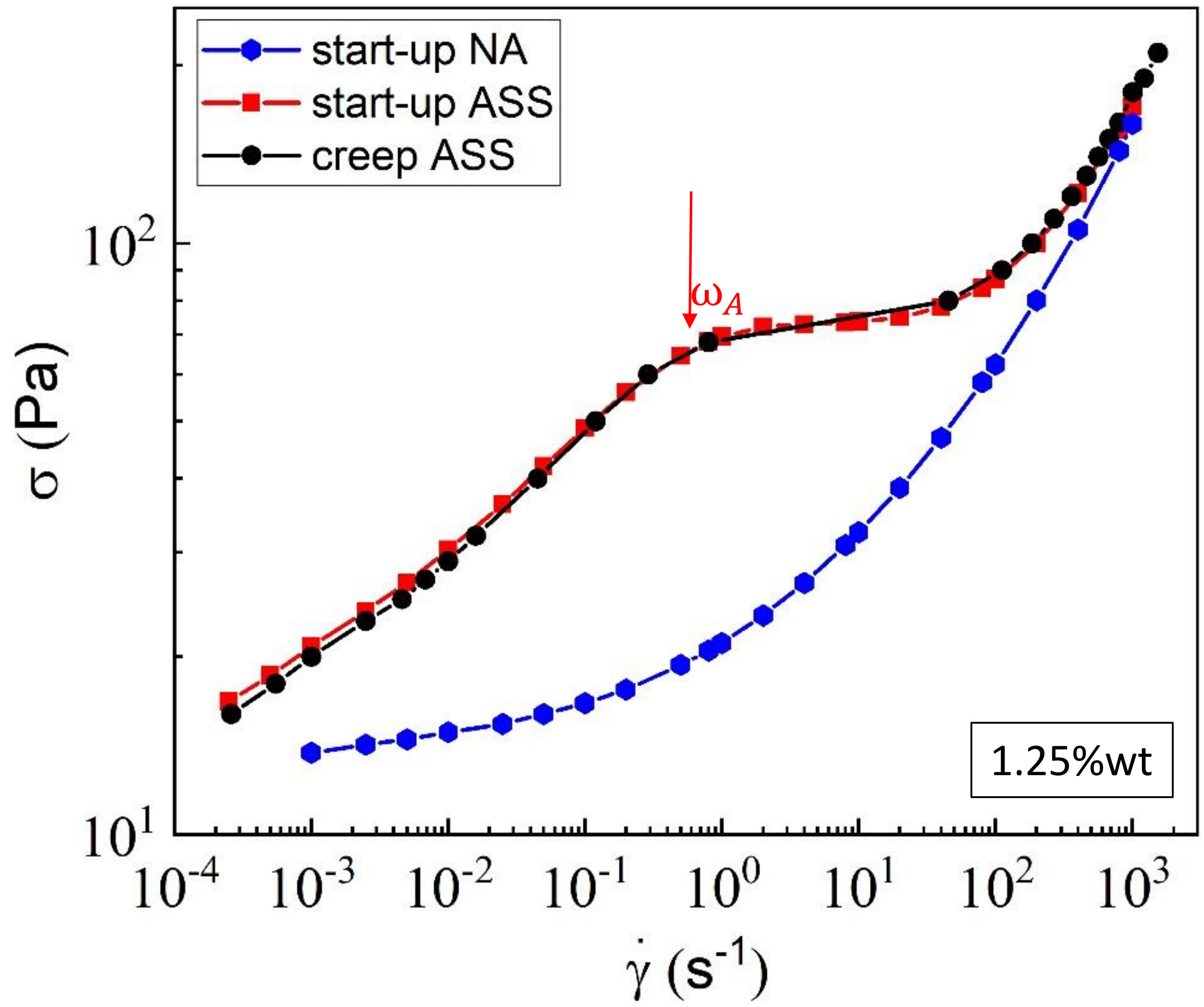


ω_A depends on the activation energy of association

$$\omega_A = \omega_0 \, e^{-E/RT}$$

Repulsive VS associative microgels in solid-like regim

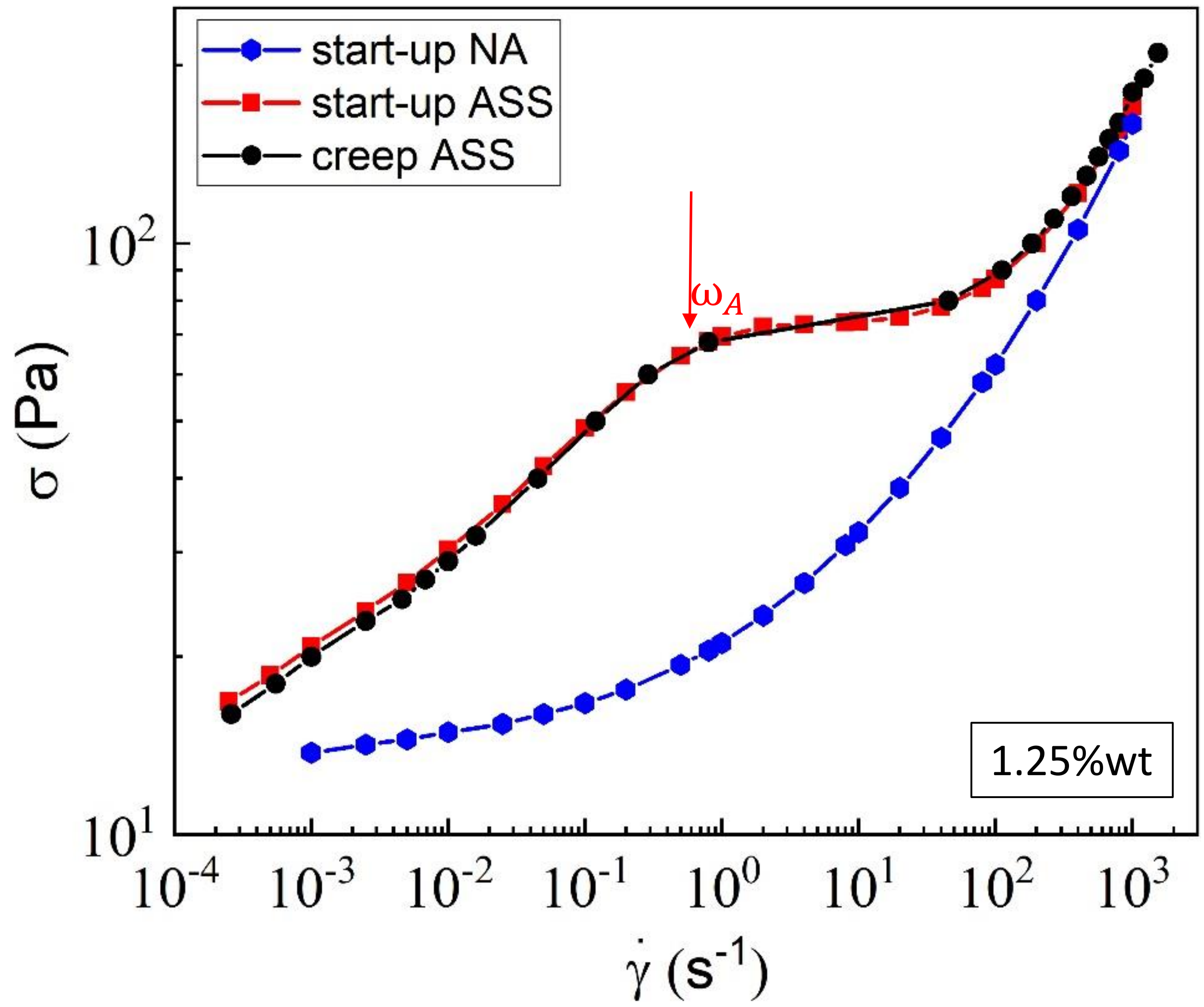
Non linear rheology



$\dot{\gamma} = \omega_A$ marks the onset of the plateau

Repulsive VS associative microgels in solid-like regim

Non linear rheology

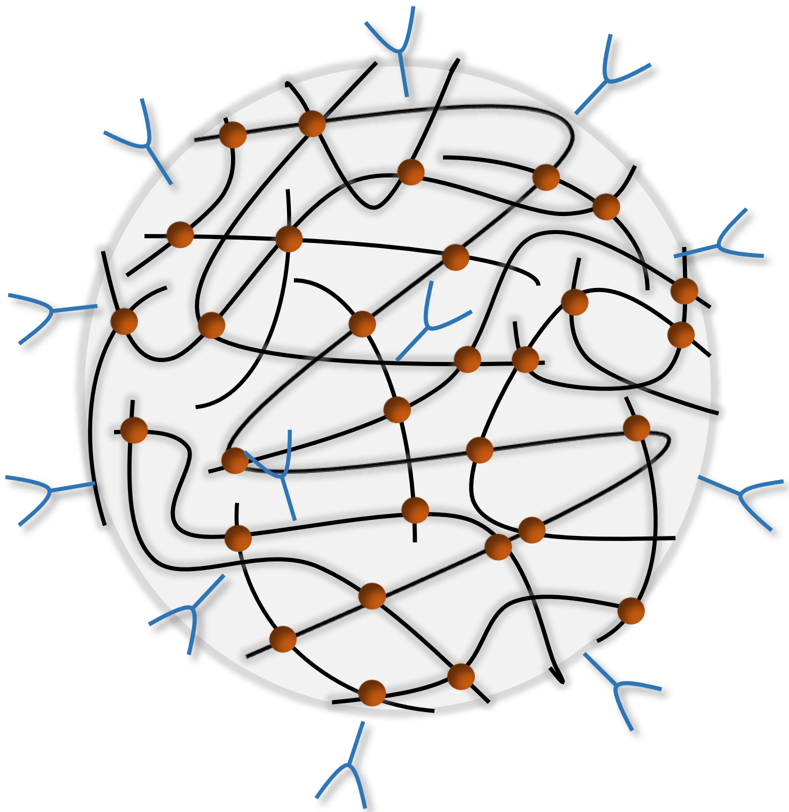


$\dot{\gamma} = \omega_A$ marks the onset of the plateau

- Presence of plateau region
- Shear banding
- Association causes flow heterogeneous

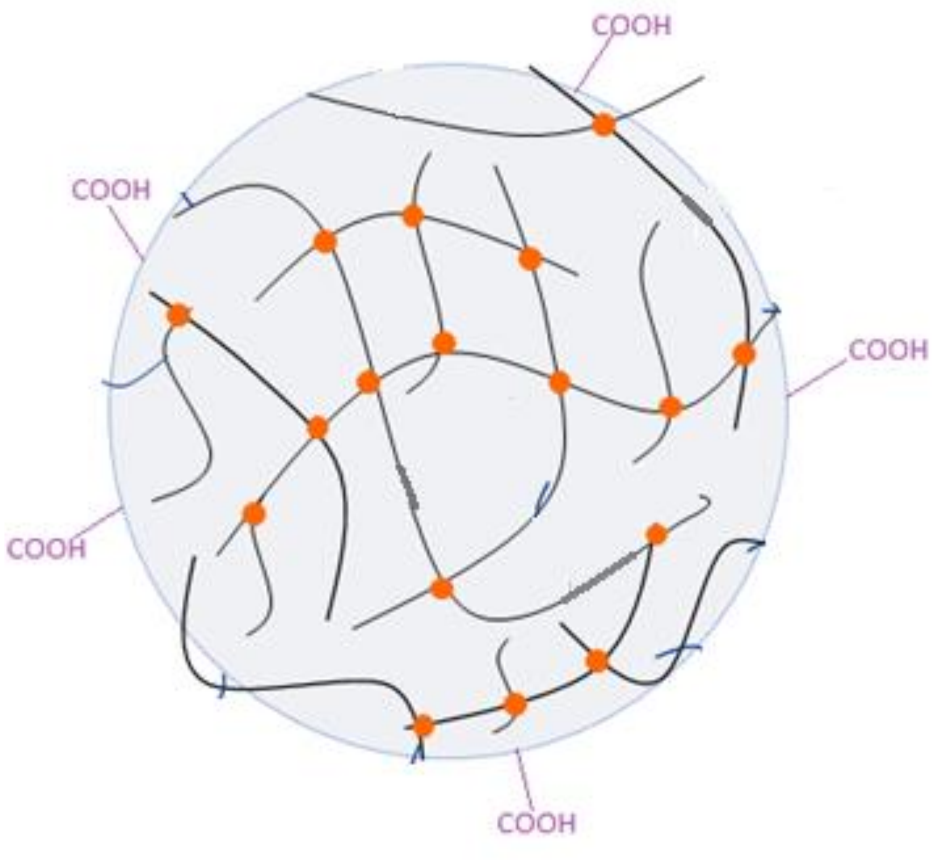
Road map: 2nd step

POLYELECTROLYTE MICROGELS | **FUNCTIONALIZED MICROGELS** | DOUBLE NETWORK

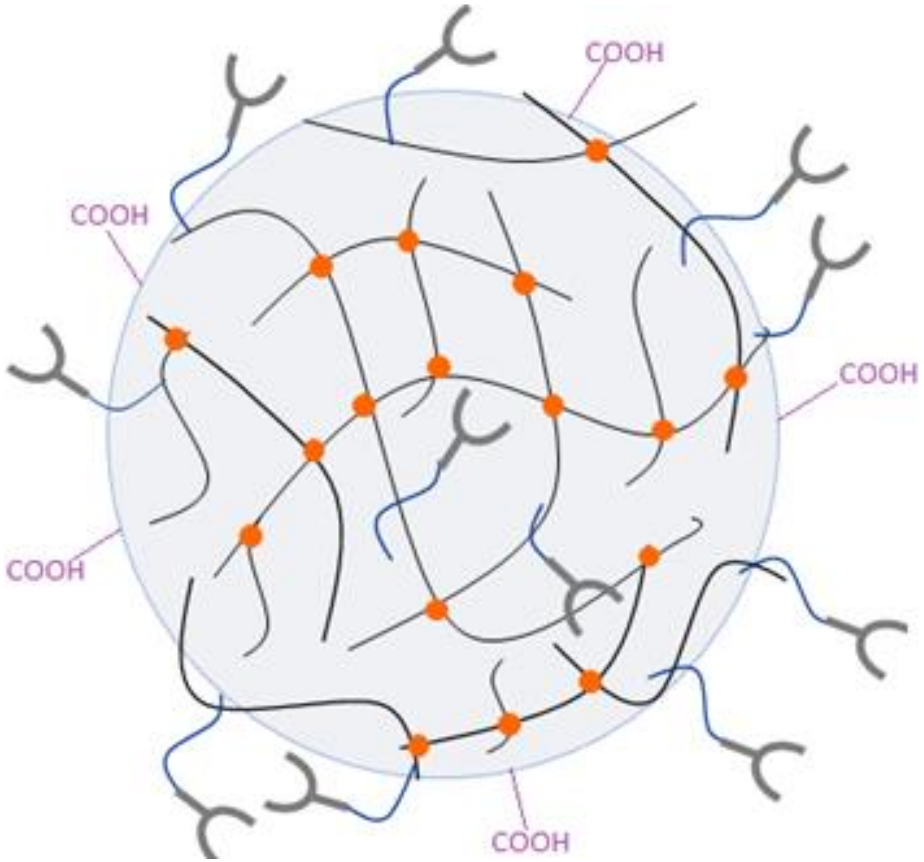


- Microgels grafted by radical polymerization
- Different covalent reactions possible

Functionalization



Boronic acid
pH=5
EDC (activated agent)
Room temperature

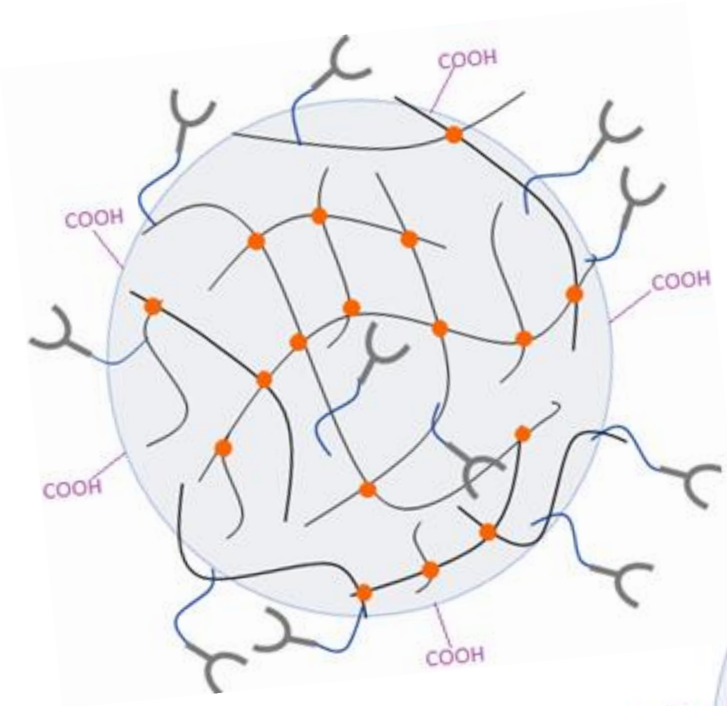


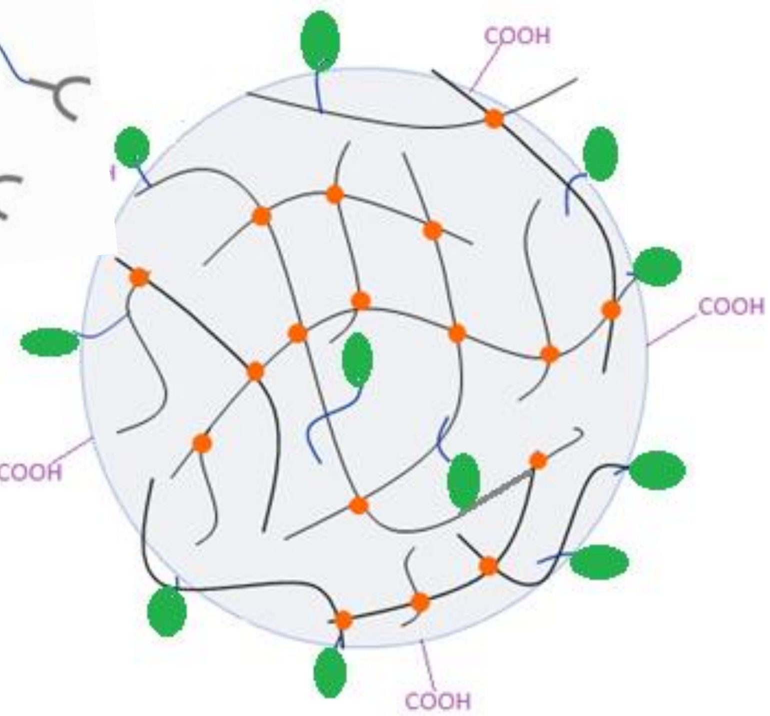
Other possible reactions: amine / aldehyde

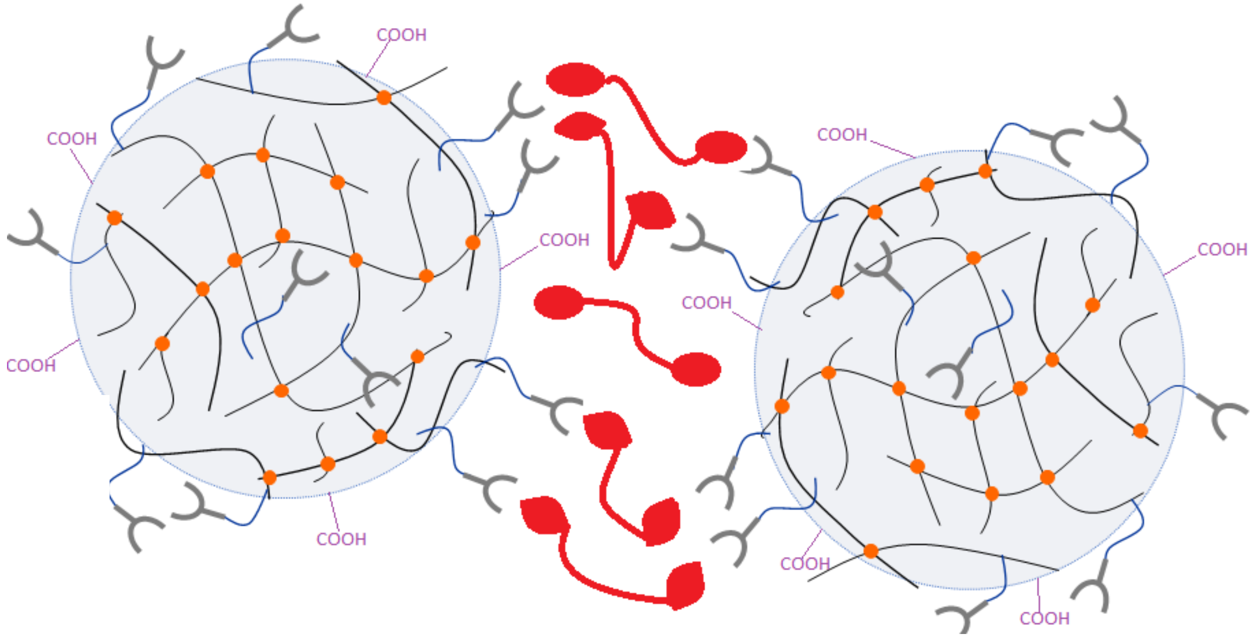
Fournier, M. R. (2016). *Polymères associatif par interaction covalente réversible diol-acide boronique*. ESPCI Paris

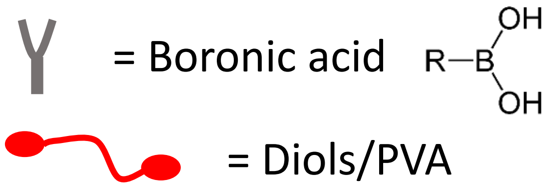
Road map: 3rd step

POLYELECTROLYTE MICROGELS → FUNCTIONALIZED MICROGELS → DOUBLE NETWORK









Outlooks

Parameters

pH $\longrightarrow$ changes the equilibrium of the reaction of the boronic acid

Mixture of functionalized microgels with different size and different chemistry

Objective

Formulation of mixtures

Mechanical properties relevant to applications

Dynamics and rheology

THANK YOU FOR
YOUR ATTENTION