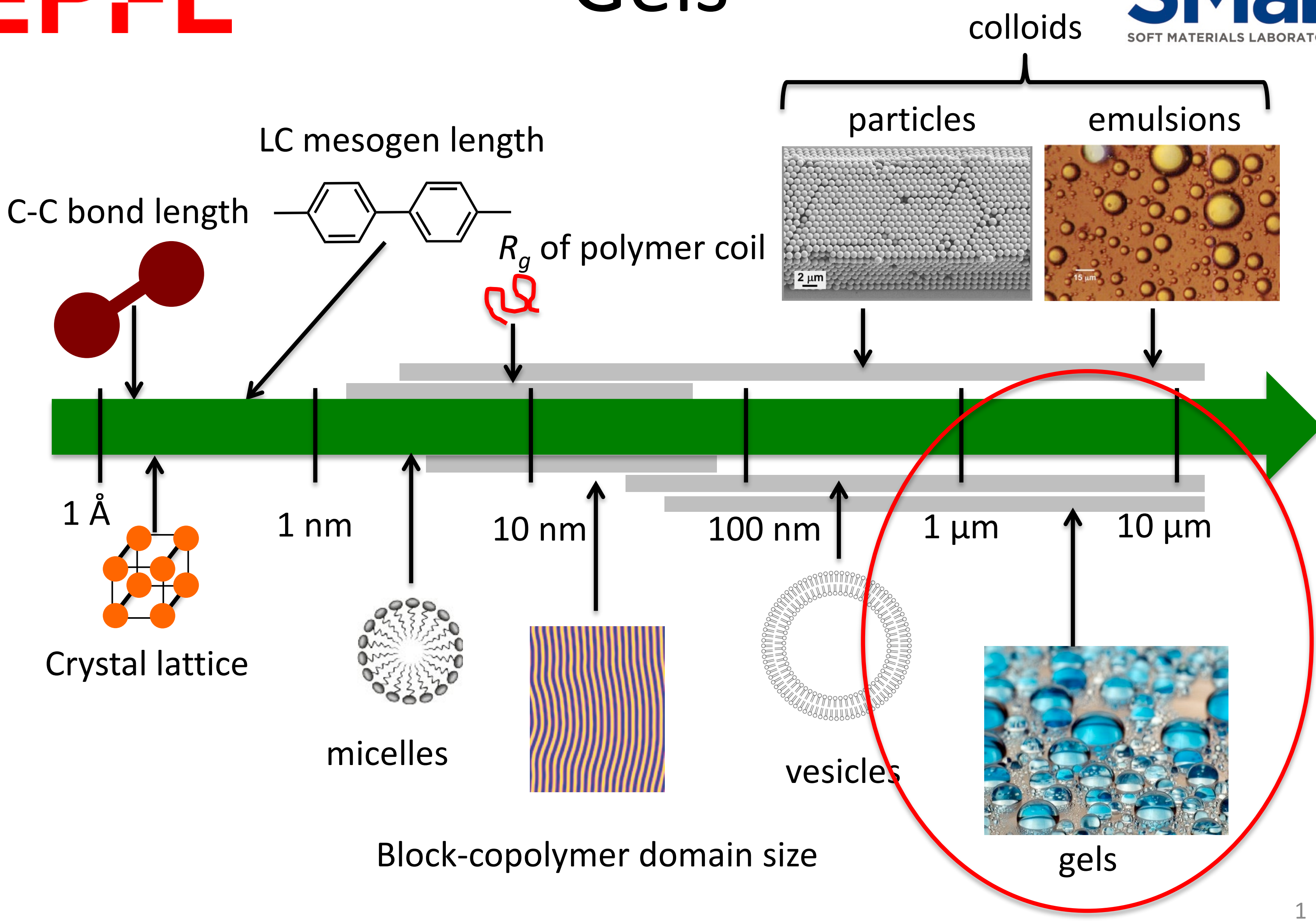
Gels



colloids
particles
emulsions
LC mesogen length
C-C bond length
R_g of polymer coil
2 µm
1 Å
1 nm
10 nm
100 nm
1 µm
10 µm
Crystal lattice
micelles
vesicles
gels
Block-copolymer domain size

Soft Matter Exam

Soft matter exam: Tuesday, **28.01.2025 from 9.15-12.15 in BC01**
If you have questions: Please come to my office on **Thursday, 23.01.2025 between 9 and 11 am in MXC 230**

You are allowed to bring a summary of maximum 10 sheets and a pocket calculator that cannot connect to the internet.

To best prepare for the exam, please make sure that you master the exercises. In addition, I put a collection of exam questions with solutions on Moodle.

Grading: challenge counts for 25% of the grade
written exam counts for 75% of the grade

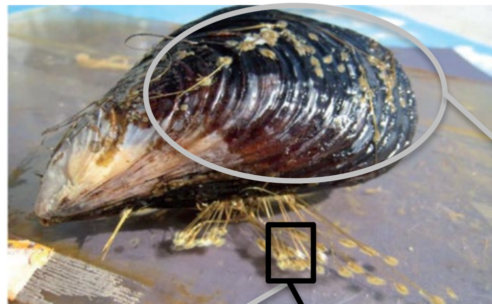
Challenges

12.12.2024: Groups 6, 7, 8, 9, 10, 12
19.12.2024: Groups 14, 16, 20, 23, 25, 11

Presentation:
Maximum 10 min + 5 min questions, each team member must present a part

Note that there is NO report to be handed in.

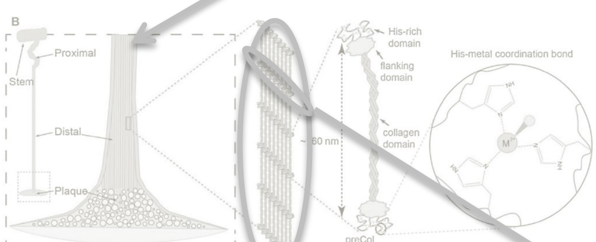
Course outline



Introduction

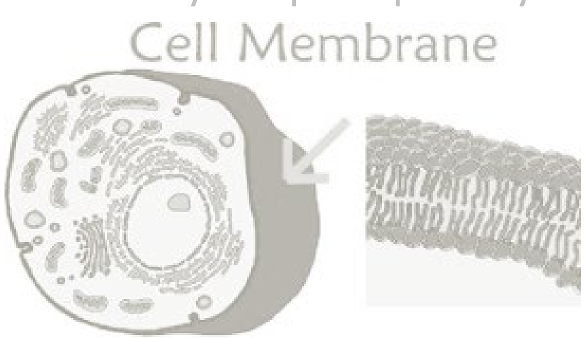
Ordered materials

Thermotropic liquid crystals



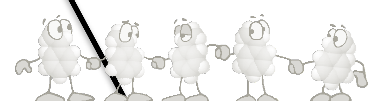
E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

Lyotropic liquid crystals

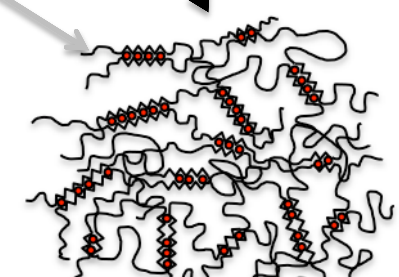


Disordered materials

Polymers

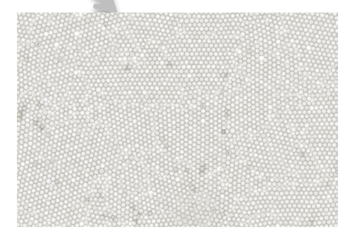


Gels



Colloids

Nanoparticles



Emulsions

Outline

- Introduction
- Gelation
- Sol-gel processes in inorganic materials
- Covalently linked hydrogels
  - Swelling
  - Deformation
- Ionically linked hydrogels
- Polyelectrolyte gels
- Responsive gels
- Microgels

Outline

- Introduction
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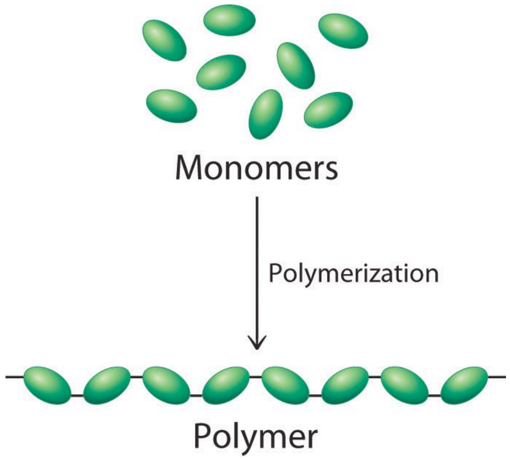
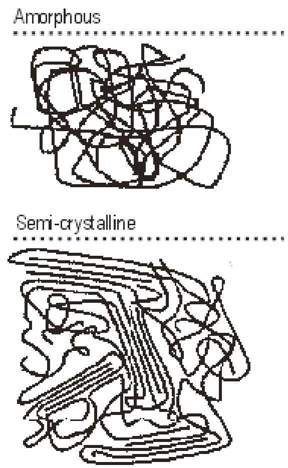
Polymers

How to make polymers



How do they arrange?

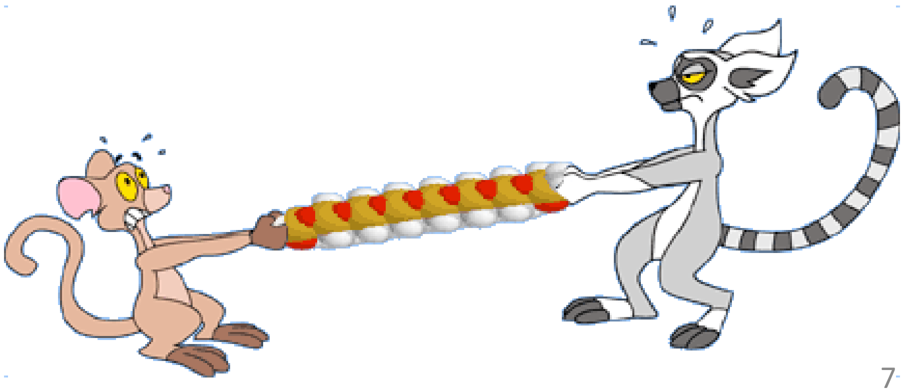


How can we make gels?

1. Polymer chemistry and macromolecular engineering: Prof. Harm-Anton Klok

2. Organic electronic materials: Holger Frauenrath

How does the structure influence their properties?



Gels

Gels are composed of subunits that are linked together to form a crosslinked network, which mechanically behaves like a solid.

- Gels are structurally disordered.
- Even though gels contain high concentrations of liquids, they mechanically behave as a solid (G’>G’’).

Gel types

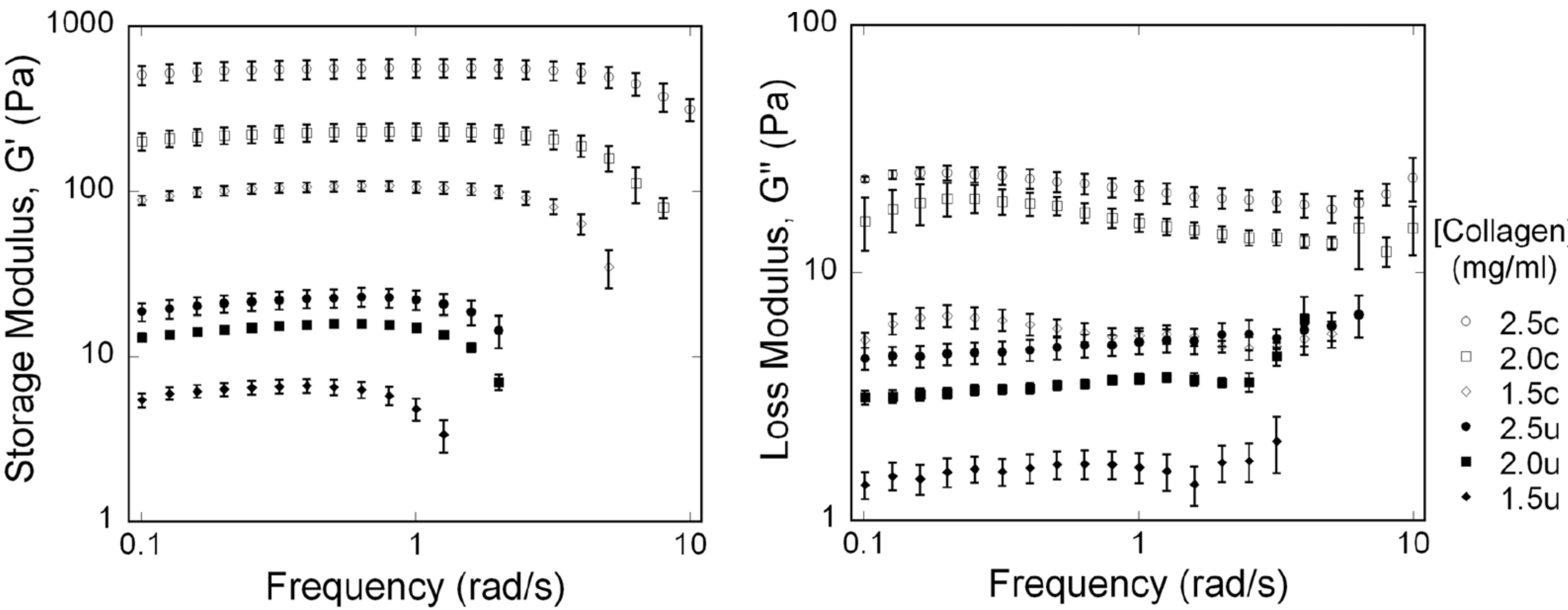
Hydrogels:
contain a high fraction of water

Organogels:
contain a high fraction of oil

Aerogels:
contain a high fraction of air

Gels

- Gels have a storage modulus G’ which displays a pronounced plateau, that lasts over an extended frequency range.
- In this plateau: G’>>G’’.
  G’ describes the elastic properties.
  G’’ describes the viscous properties.



Julias, M., et al., Biomedical Engineering Online, 2008. **7**

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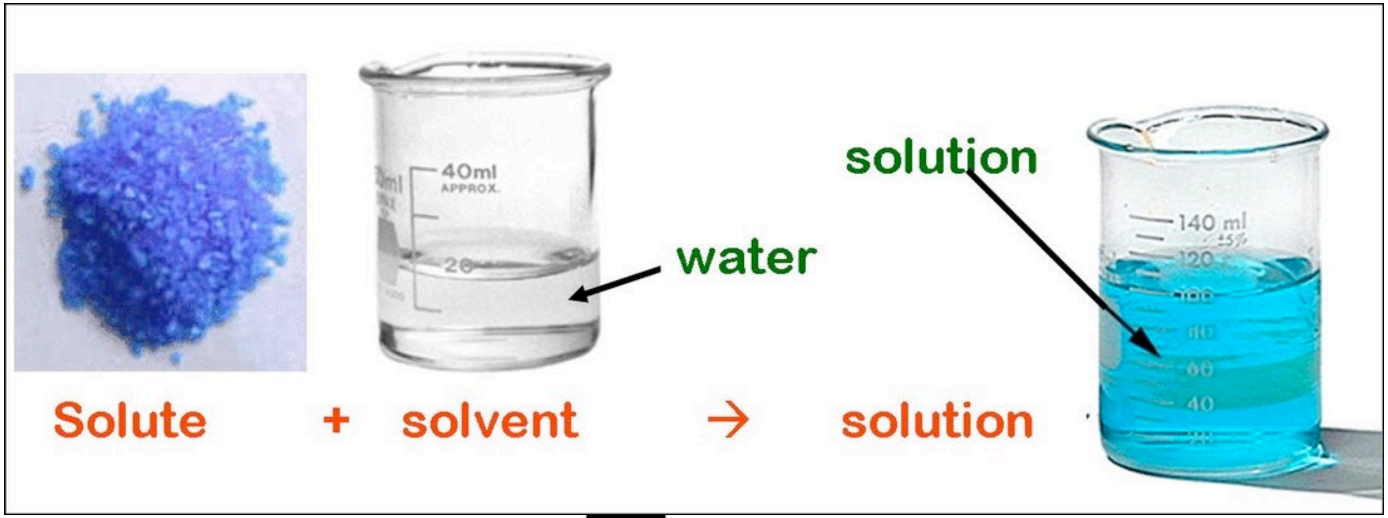
Gelation

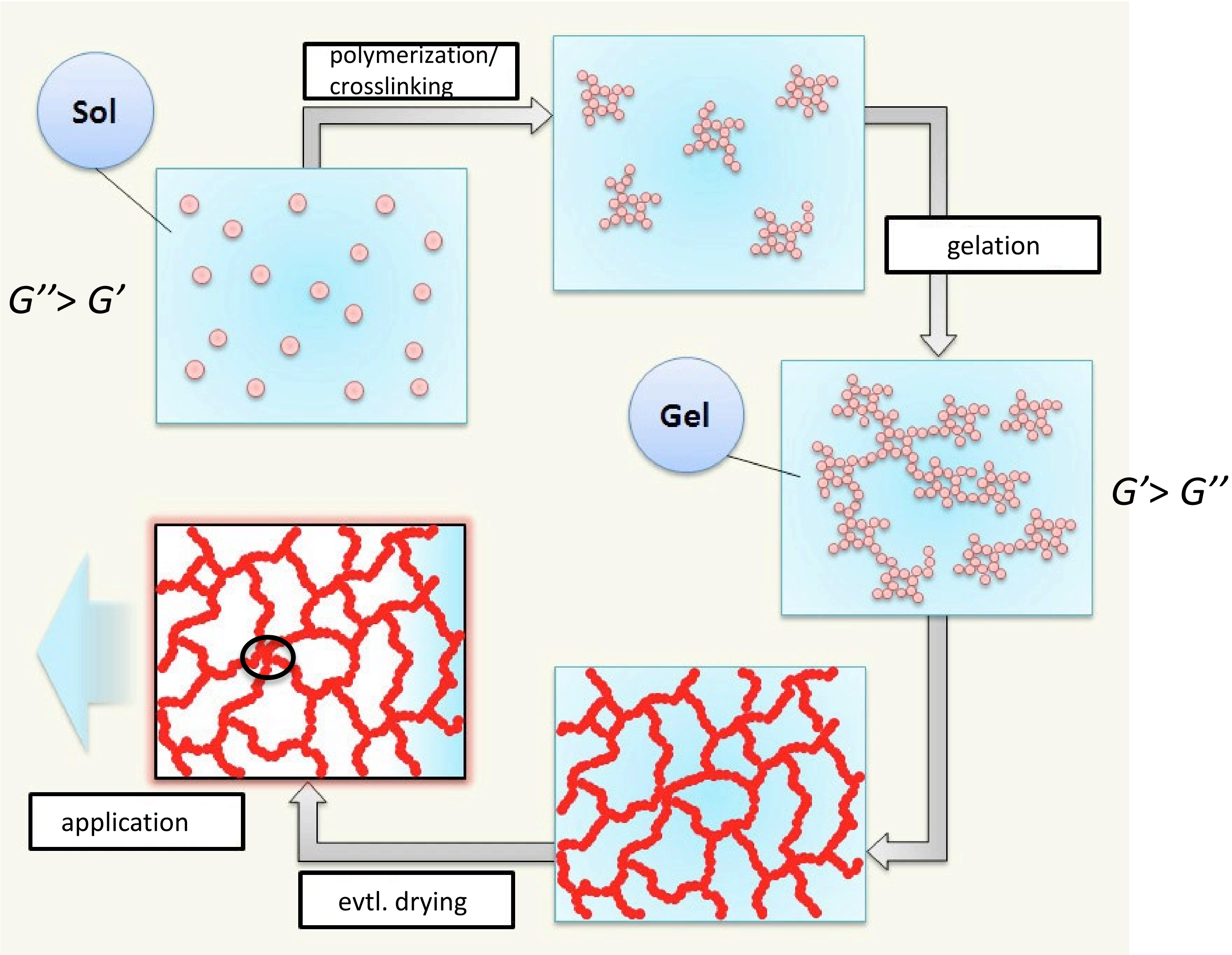
+

Gelation



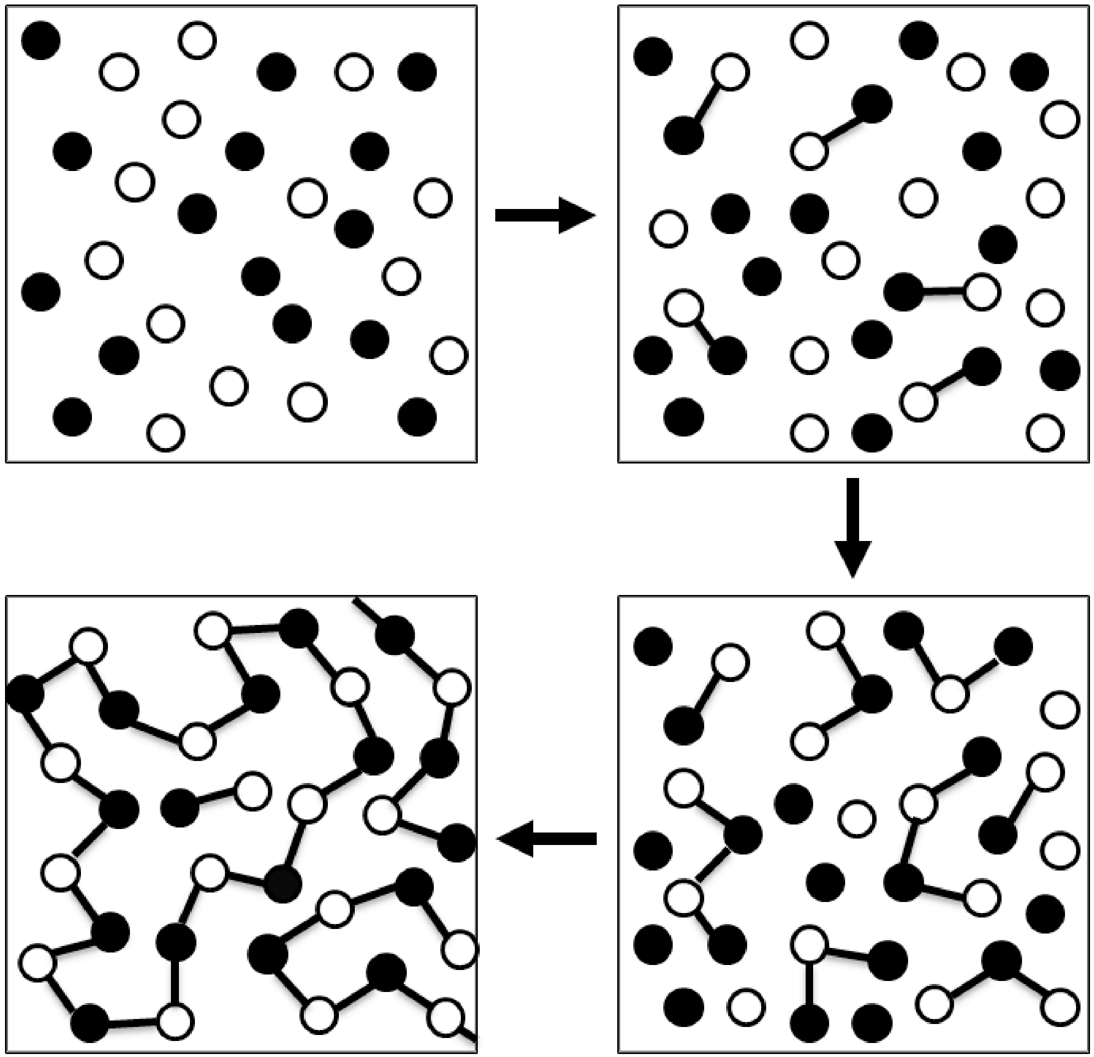
How can we transform a solution into a gel?

Sol-gel process



https://commons.wikimedia.org/wiki/File:SolGel.jpg

Analogy: Step growth polymerization

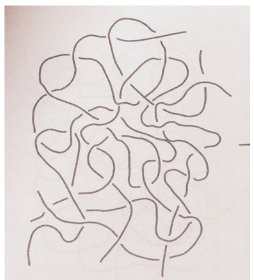


http://www.polymerdatabase.com/polymer%20chemistry/Stepgrowth%20Polymerization.html

Gelation

Physically crosslinked gels

Polymers are entangled but there are no covalent crosslinks.



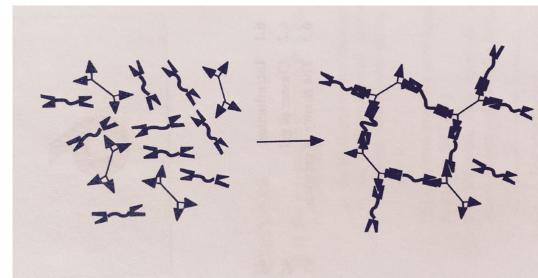
Example: gelatin

Polymers can be physically linked through the following interactions:

- H-bonding
- VdW interactions
- complexations
- entanglements

Chemically crosslinked gels

Polymers are covalently crosslinked.



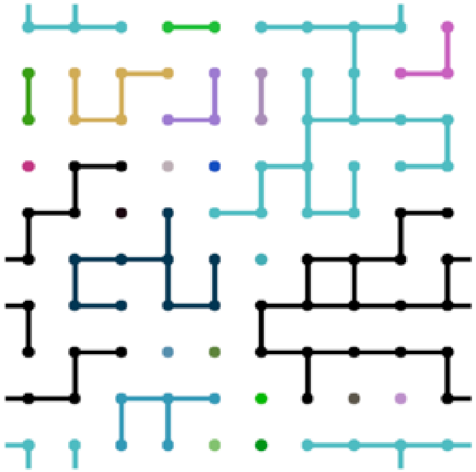
Example 1: rubber

Example 2: epoxy resigns

Gelation

sol

gel



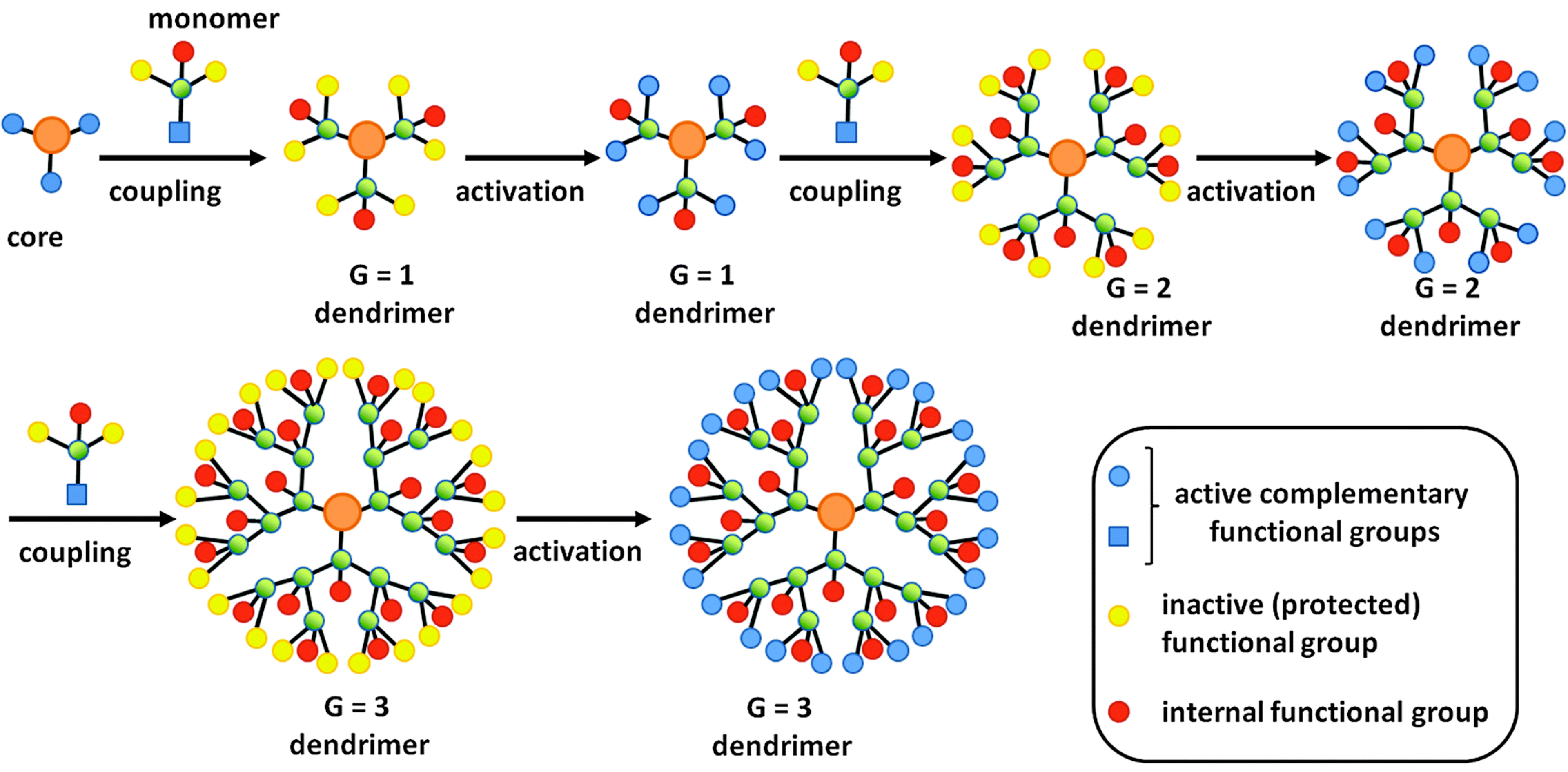
$$N \approx [f(z-1)]^n$$

$$f_c = \frac{1}{z-1}$$

N: number of bonds [-]
f: probability that a bond is formed [-]
f_c: percolation threshold [-]
z: number of neighboring points [-]
n: number of generation [-]

if $f < f_c$ $N \to 0$ as $n \to \infty$ sol
if $f > f_c$ $N \to \infty$ as $n \to \infty$ gel (fraction)

Definition of the term “generation” in polymers



M. Sowinska and Z. Urbanczyk-Lipkowska, *New Journal of Chemistry*, 2014, **38**, 2168-2203.

You have a trifunctional monomer that you would like to convert into a gel. What is the percolation threshold?

A. $f_c = 1$
B. $f_c = 1/2$
C. $f_c = 1/3$
D. $f_c = 1/4$

Assuming f = 0.1, how many generations of trifunctional monomers would you have to link until you form a network with 1000 bonds?

A. 10
B. 100
C. 1000
D. 10000
E. This system will never from a covalently crosslinked gel

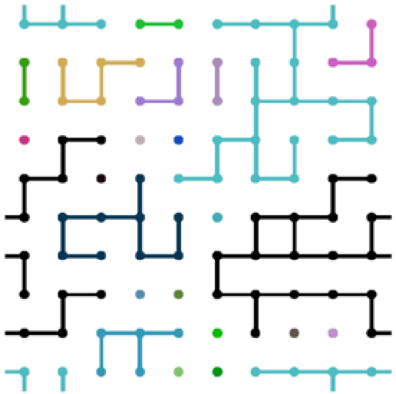
You have a bifunctional monomer that you would like to convert into a gel. What is its percolation threshold?

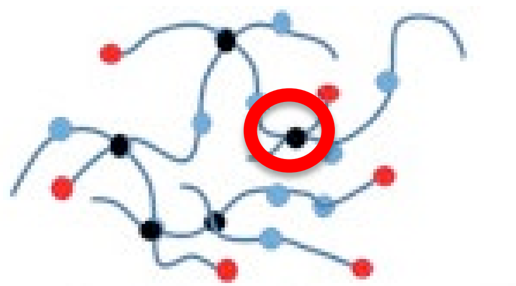
A. 1
B. 1/2
C. 1/3
D. 1/4

What would you do to form a chemically crosslinked gel with a bifunctional monomer?

A. let it react for a long time
B. increase the reaction temperature
C. mix it with tri- or multi-functional monomers
D. decrease the initiator concentration
E. stir more vigorously

Gelation





P. Polanowski, J. K. Jeszka, K. Krysiak and K. Matyjaszewski, *Polymer*, 2015, **79**, 171-178.

What is the probability that none of the neighbor's sub-branches is connected to percolating network?

$$Q^{z-1}$$

What is the probability that the cluster is connected to a neighbor but not to the percolating network?

$$fQ^{z-1}$$

What is the probability that a cluster is NOT connected to the percolating network?

$$Q = 1 - f + fQ^{z-1}$$

probability that a site is not connected to its neighbor

site is connected to neighbor but the neighbor is not connected to the percolating network.

P: Probability that a site is connected to percolating network [-]
Q: Probability that site is not connected to percolating network through one specific site [-]
z: number of neighboring points[-]

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Sol-gel process for inorganic materials

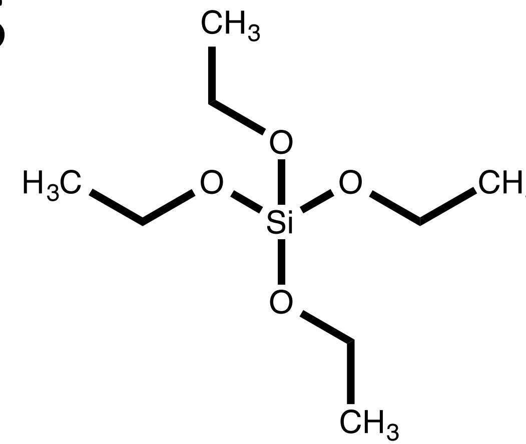
Example: Production of a SiO_2 gel.

Sol: liquid (G' < G'') *Gel:* elastic (G' > G'')

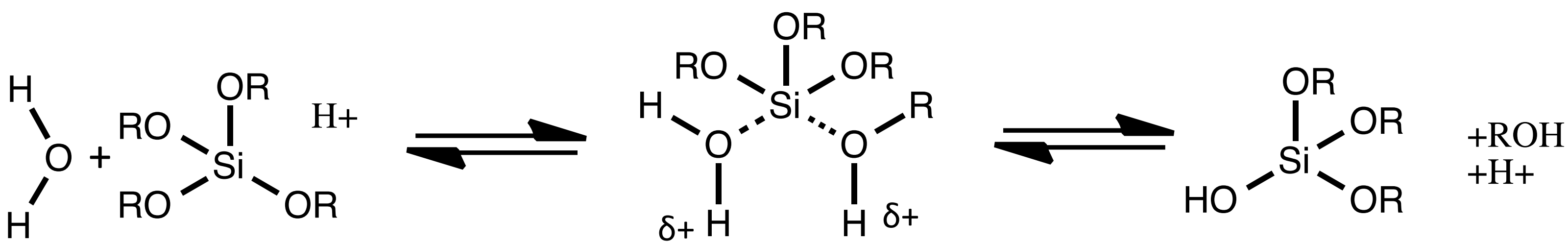
hydrolysis	$Si(OR)_4 + nH_2O \rightarrow Si(OR)_{4-n}(OH)_n + n(OR)$
condensation	$X_3SiOH + HOSiX'_3 \rightarrow X_3Si\text{-}O\text{-}SiX'_3 + H_2O$ or $X_3SiOR + HOSiX'_3 \rightarrow X_3Si\text{-}O\text{-}SiX'_3 + ROH$
gelation	spanning cluster formation
drying	loss of water
densification	thermal treatment

Hydrolysis

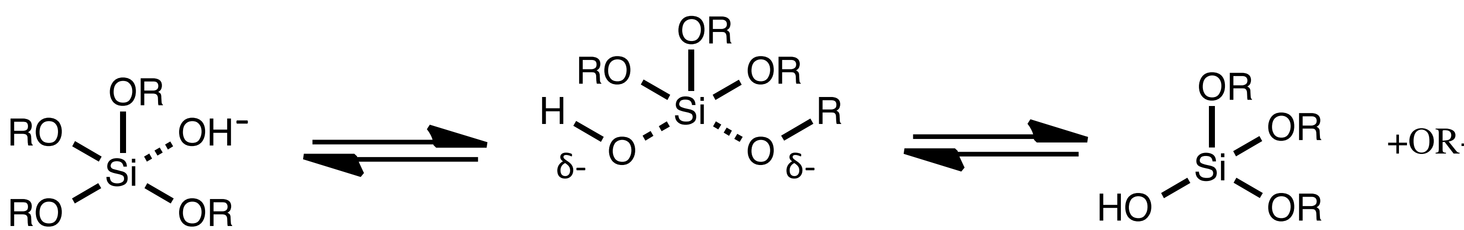
Precursor: tetraethoxy siloxane (TEOS)



acid catalyzed



base catalyzed



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gelation	spanning cluster formation
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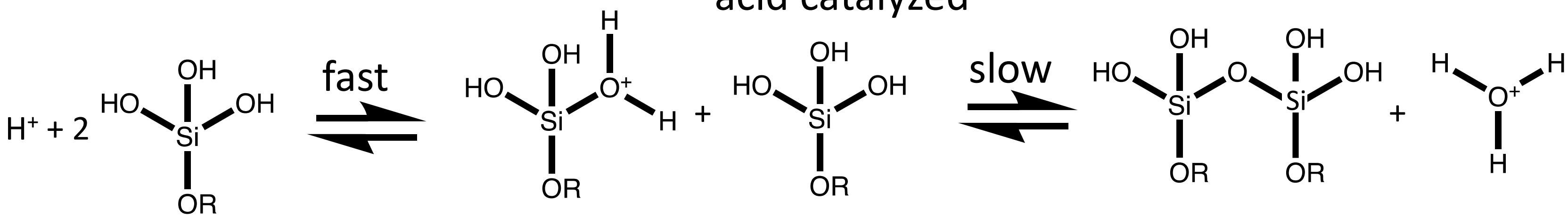
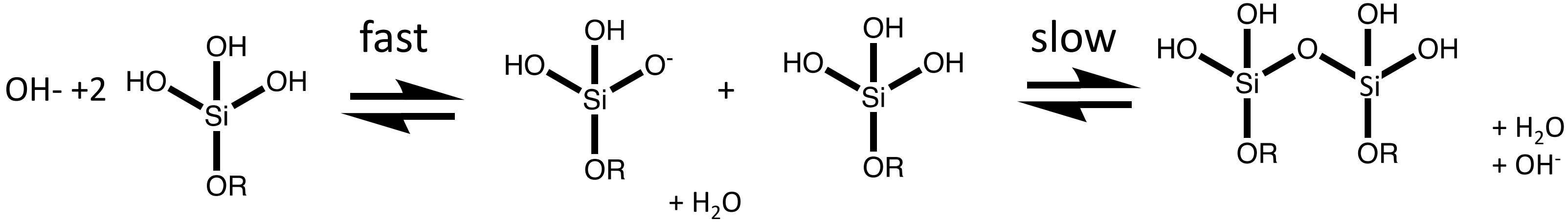
Condensation

acid catalyzed



base catalyzed



Which statement is correct if the reaction is base catalyzed?

A. $(OR)_3SiOH$ condenses faster than $(OR)_2Si(OH)_2$ which condenses faster than $(OR)Si(OH)_3$
B. $(OR)_2Si(OH)_2$ condenses fastest.
C. $(OR)Si(OH)_3$ condenses faster than $(OR)_2Si(OH)_2$ which condenses faster than $(OR)_3SiOH$

Which statement is correct if the reaction is acid catalyzed?

A. $(OR)_3SiOH$ condenses faster than $(OR)_2Si(OH)_2$ which condenses faster than $(OR)Si(OH)_3$
B. $(OR)_2Si(OH)_2$ condenses fastest.
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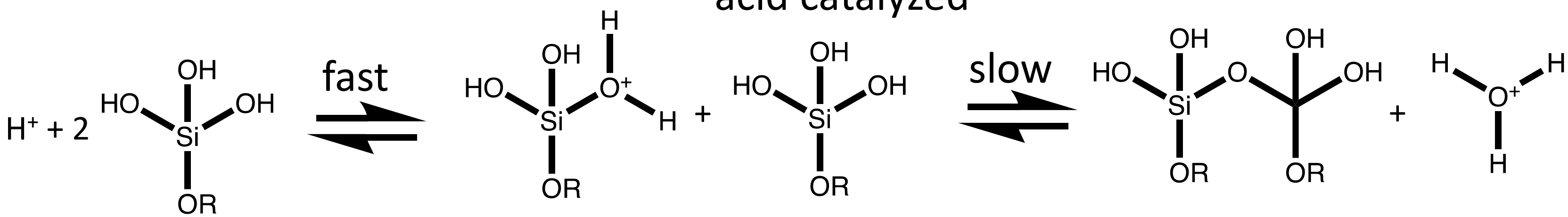
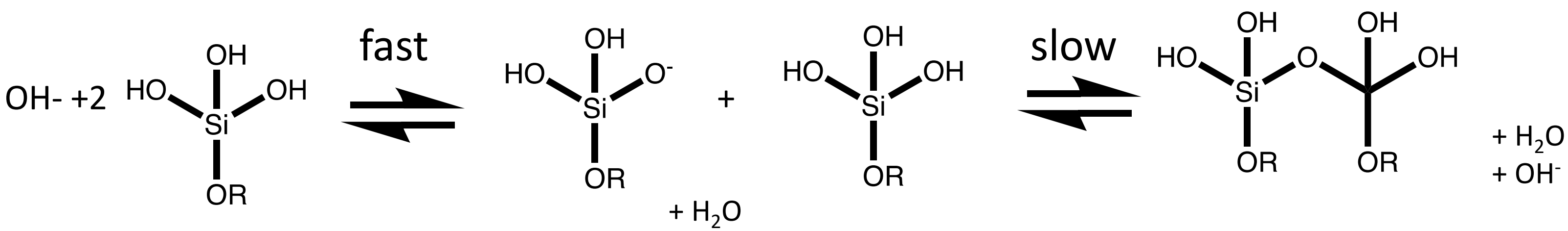
Condensation

acid catalyzed



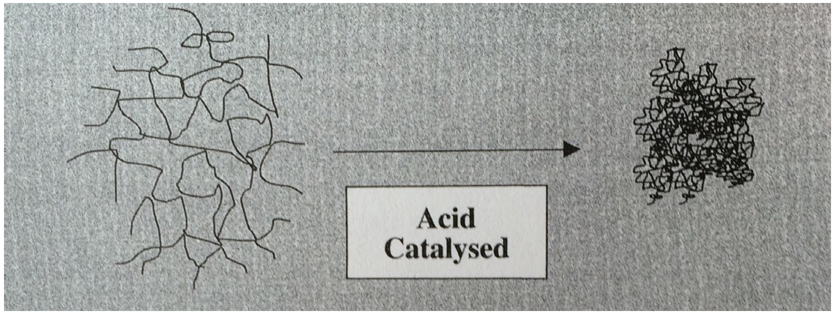
base catalyzed



Kinetics of condensation

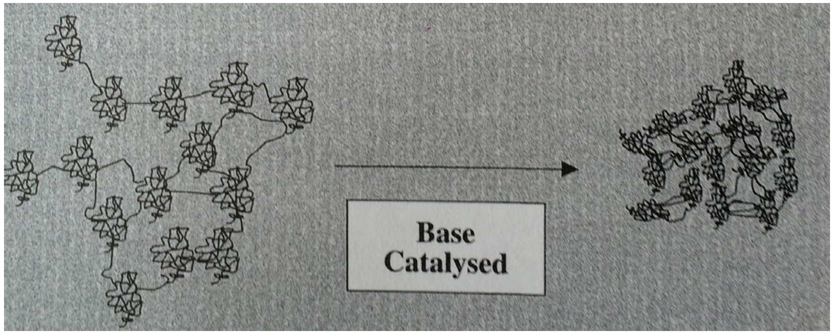
Acid catalyzed

Reaction kinetics: $(OR)_3SiOH$ condenses faster than $(OR)_2Si(OH)_2$ which condenses faster than $(OR)Si(OH)_3$.



Base catalyzed

Reaction kinetics: $(OR)_3SiOH$ condenses slower than $(OR)_2Si(OH)_2$ which condenses slower than $(OR)Si(OH)_3$.



J. D. Wright and N. A. J. M. Sommerdijk, *Sol-Gel Materials Chemistry and Applications*, CRC Press, 2001.

Sol-gel process for inorganic materials

Example: Production of a SiO_2 gel.

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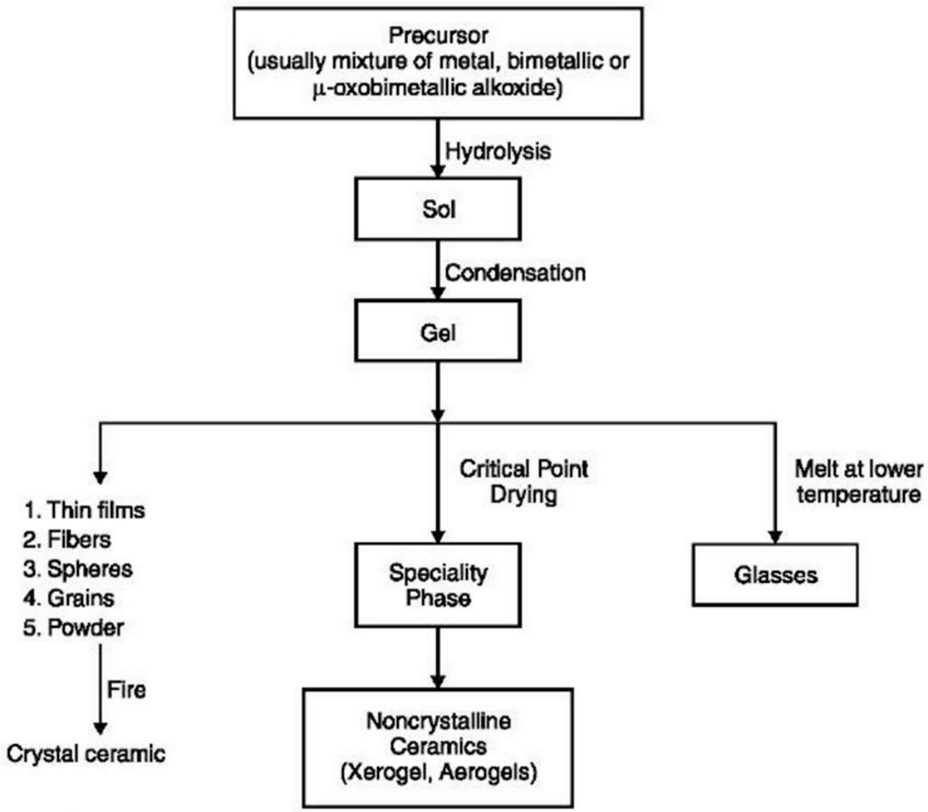
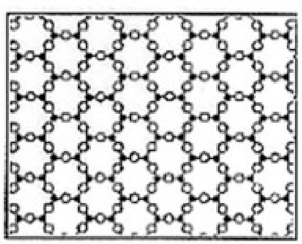
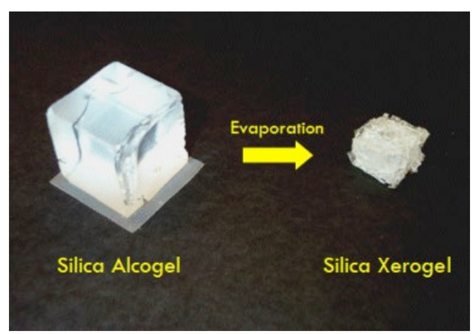
gelation	spanning cluster formation
drying	loss of water
densification	thermal treatment

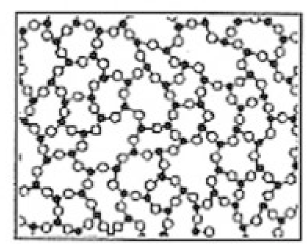
Drying/densification



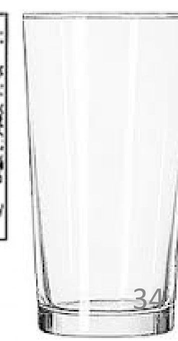


quartz





glass

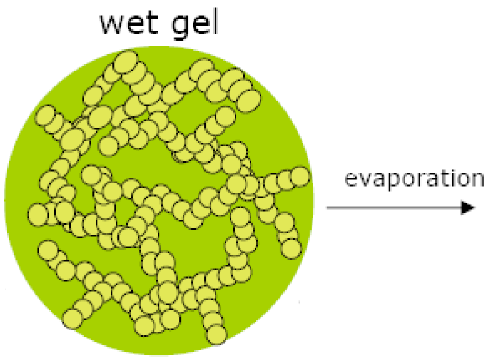


If you have a hydrogel and you dry it under ambient conditions, you obtain a dense solid and not an aerogel. Why is that the case?

A. The network is too weak and spontaneously collapses if kept in air.
B. The network disassembles into individual clusters during the drying process.
C. The surface tension of the drying fluid pulls together the network such that a dense solid forms.

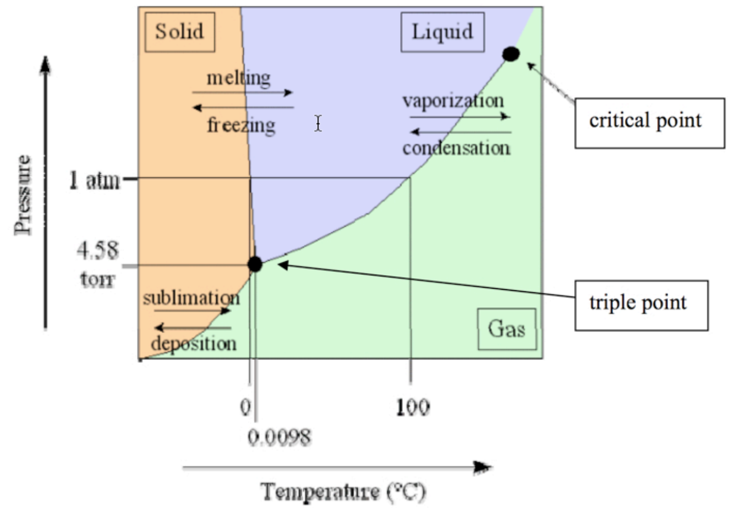
Drying/densification

drying under atmospheric conditions



http://www.centexbel.be/solgel-treatment

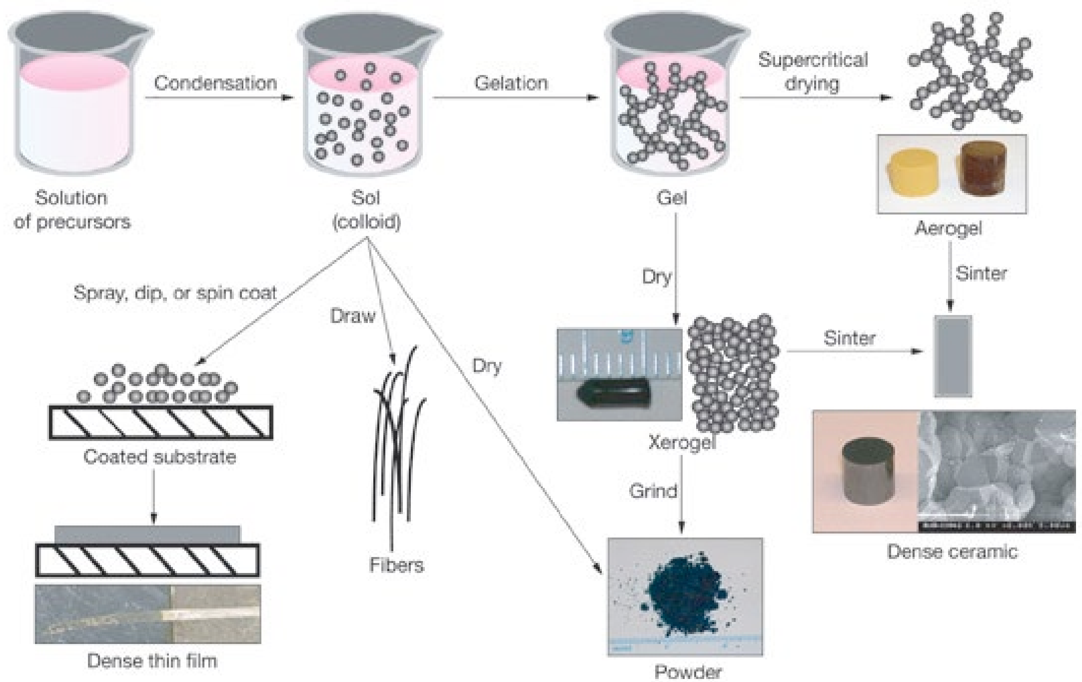
freeze drying/critical point



1. freezing

2. subliming ice

Sol-gel processes



https://str.llnl.gov/

Advantages

- Low reaction temperatures
- It is often easy to obtain precursors with a high purity
- It is easy to generate porous materials

Disadvantages

- Precursors are expensive
- The process is time consuming
- Materials shrink when they are dried and densified

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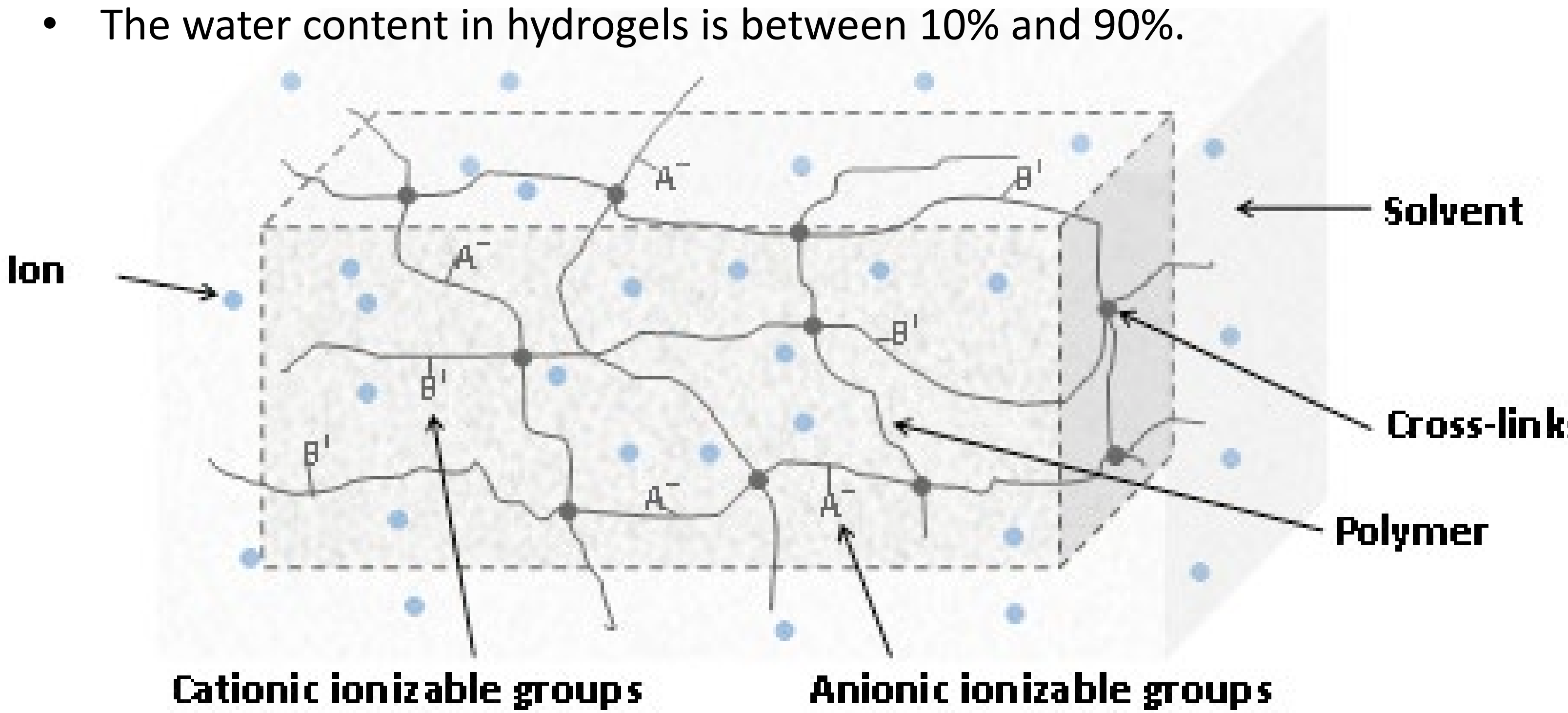
Hydrogels

- Hydrogels are loosely crosslinked, highly hydrated three-dimensional polymeric networks.
- The water content in hydrogels is between 10% and 90%.



If a hydrogel is mixed with a solvent, it swells.

The swelling is a result of an osmotic pressure Δp.

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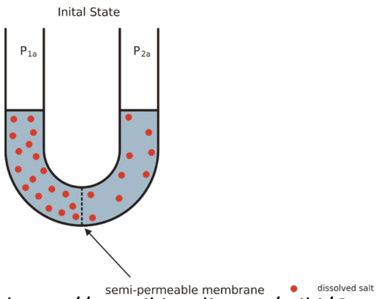
What causes a hydrogel to swell?

What causes the swelling of hydrogels?

Osmotic pressure

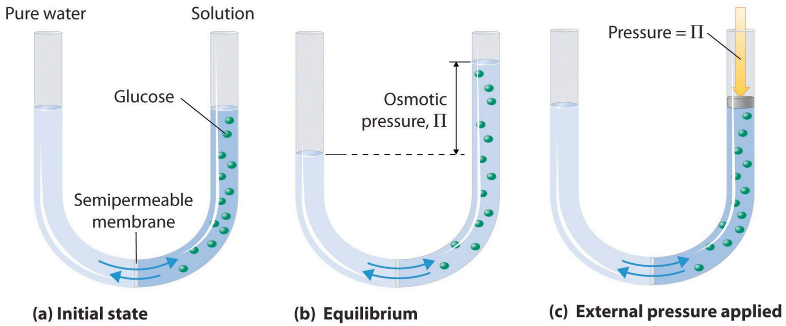
What is the osmotic pressure?

Osmosis is the diffusion of a fluid through a semipermeable membrane.



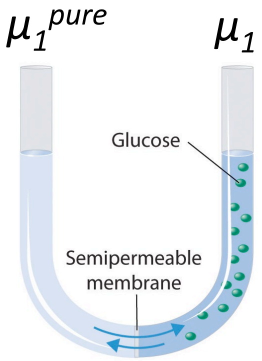
https://en.wikipedia.org/wiki/Osmosis

The osmotic pressure is the pressure difference needed to stop the flow through a semipermeable membrane.



http://2012books.lardbucket.org/books/principles-of-general-chemistry-v1.0/s17-05-colligative-properties-of-solu.html

Swelling of hydrogels



In equilibrium:

μ: chemical potential [J/molecule]
$\Delta\mu$: excess chemical potential [J/molecule]
v_s: volume of a solvent molecule [m^3]

$$\mu_1^{pure}(p,T) = \mu_1(p+\Delta p,T)$$

$$\mu_1^{pure}(p+\Delta p,T) = \mu_1(p,T) + \Delta\mu_1$$

$$\mu_1^{pure}(p+\Delta p,T) = \mu_1(p,T) + \int_p^{p+\Delta p} \frac{\partial \mu_1}{\partial p'} dp' = \mu_1(p,T) + v_s \Delta p$$

Gibbs Duhem: $$N d\mu = -S dT + V dp$$

$$\Delta p = -\frac{\Delta\mu_1}{v_s} = -\frac{\mu_1 - \mu_1^{pure}}{v_s}$$

➔ An increase in $\Delta\mu_1$ results in an increase in the osmotic pressure.

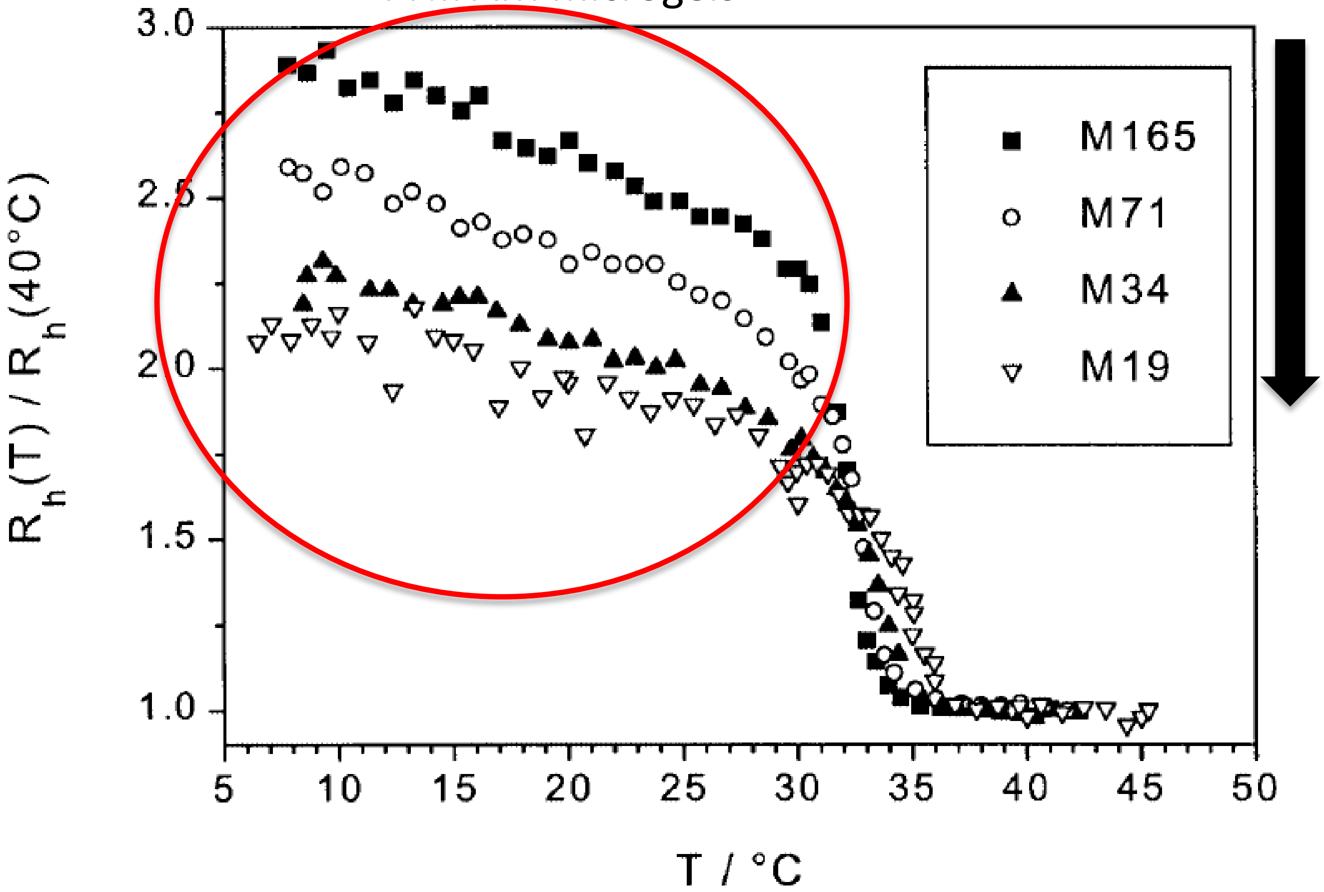
Swelling of hydrogels

http://sites.psu.edu/energyfromwater/technologies/hex/

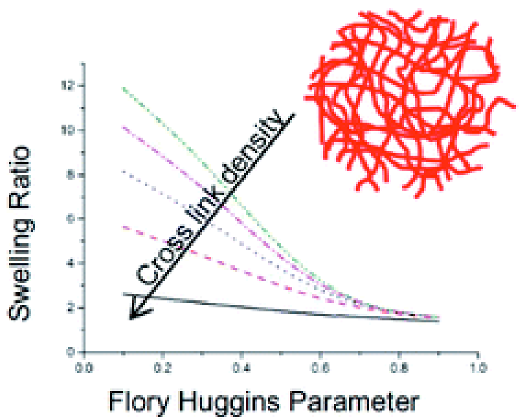
Swelling

The hydrogel swells until the force exerted by the osmotic pressure on the hydrogel equals the force required to further stretch polymers contained in the hydrogel.

PNIPAM microgels



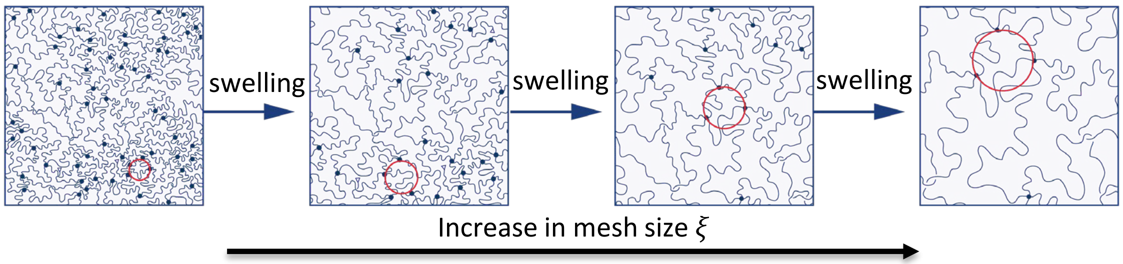
crosslinking density increases



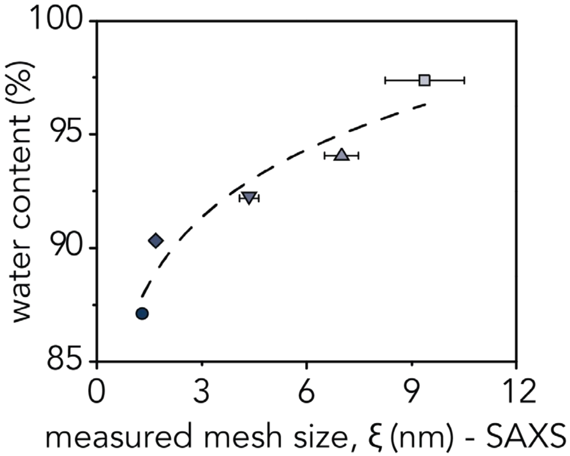
J. A. Bonham, M. A. Faers and J. S. van Duijneveldt, *Soft Matter*, 2014, **10**, 9384-9398

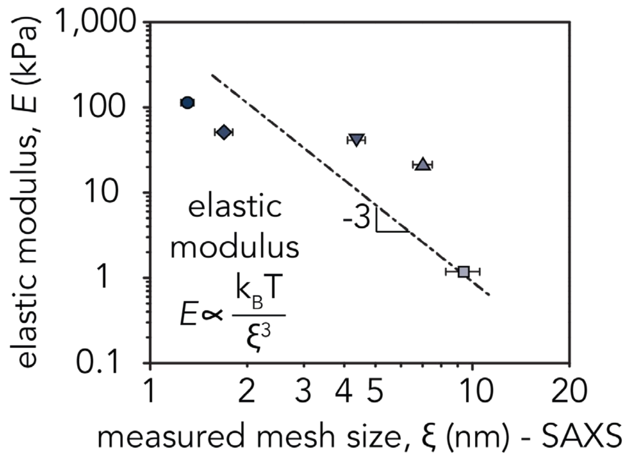
Senff, H.; Richtering, W. *Colloid Polym Sci* **2000,** *278* (9), 830-840

Influence of swelling on gel properties

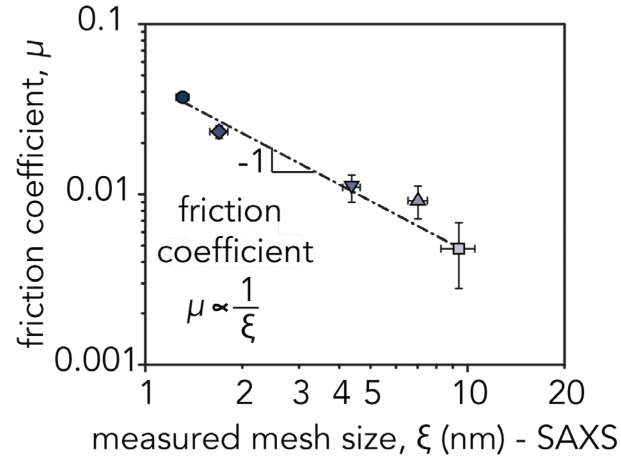


Mesh size, modulus, and friction can be tuned by controlling swelling





P.-G. de Gennes, *Scaling Concepts in Polymer Physics,* 1979.

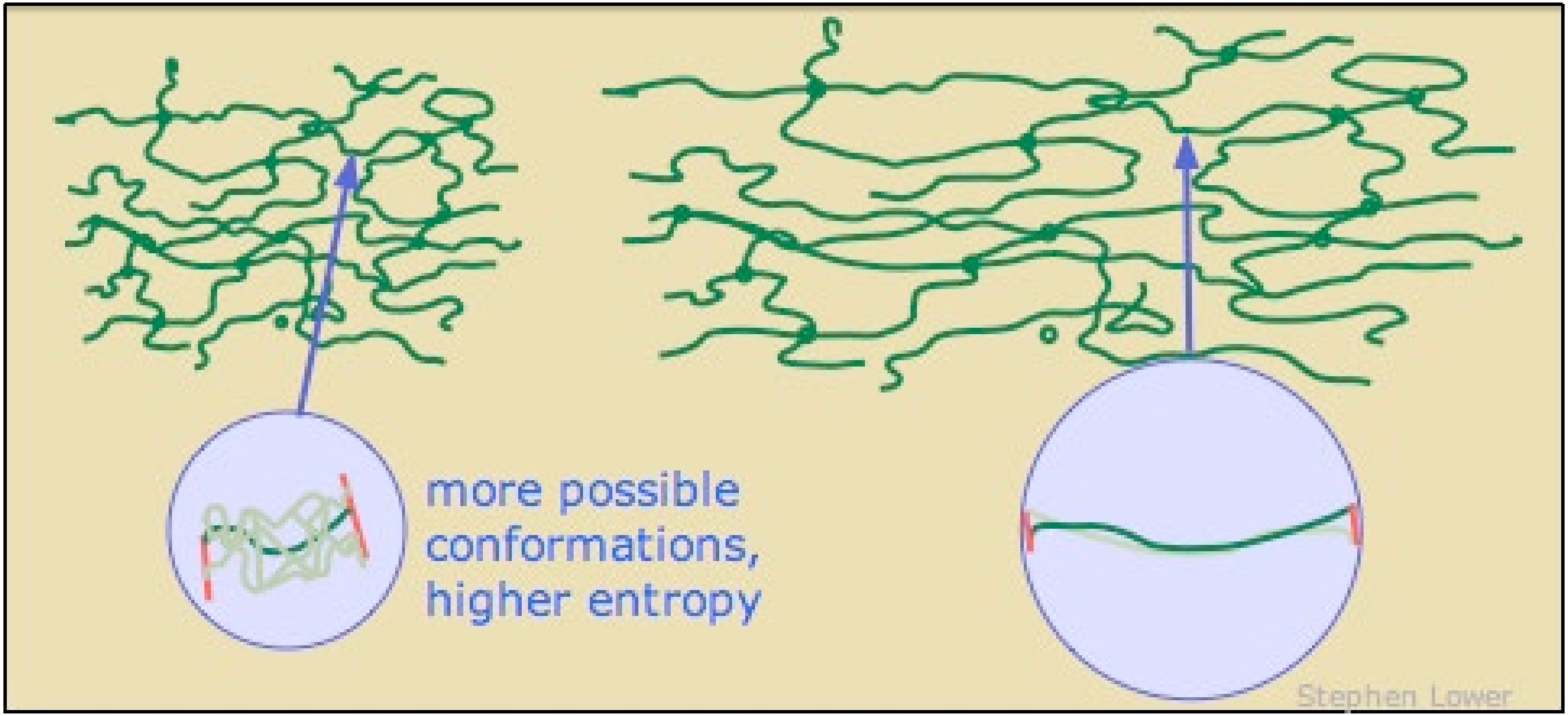


J.M. Urueña, A. Pitenis, *et al.*, *Biotribology,* **1-2,** 2015.

Outline

- Introduction
- Gelation
- Sol-gel processes in inorganic materials
- Covalently linked hydrogels
  - Swelling
  - Deformation
- Ionically linked hydrogels
- Polyelectrolyte gels
- Responsive gels
- Microgels

Deformation of gels



https://chem.libretexts.org/Textbook_Maps/General_Chemistry_Textbook_Maps

Deformation of gels

Free energy

$$F = -TS$$

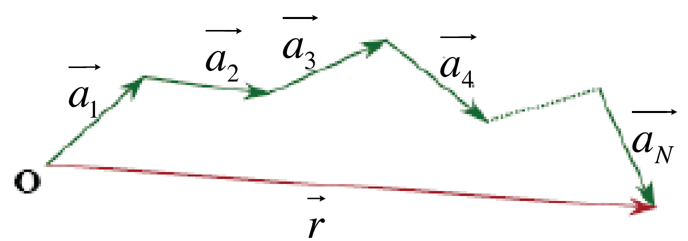
$$S = k_B \ln(P)$$

P: probability distribution function [-]
F: free energy [J]
T: temperature [K]
N: number of segments in polymer chain [-]

What is the probability to find a segment at a distance $\vec{r}$ from the origin?

Gaussian distribution:

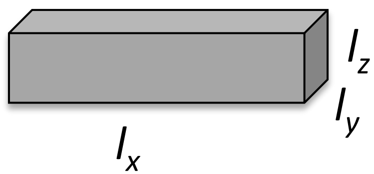
$$P(\vec{r}, N) = \left(\frac{2\pi N a^2}{3}\right)^{-\frac{3}{2}} \exp\left(-\frac{3\vec{r}^2}{2Na^2}\right)$$



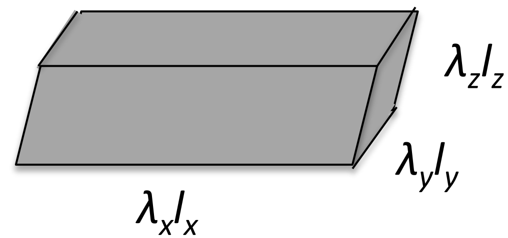
$$F(\vec{r}) = \frac{3k_B T \vec{r}^2}{2Na^2} + const$$

Deformation of hydrogels

before deformation:



after deformation:



$$r_0^2 = l_x^2 + l_y^2 + l_z^2$$

$$r_1^2 = \lambda_x^2 l_x^2 + \lambda_y^2 l_y^2 + \lambda_z^2 l_z^2$$

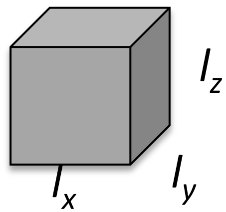
$$\Delta F(\vec{r}) = \frac{3k_B T\left(\Delta\vec{r}\right)^2}{2Na^2} \approx -T\Delta S \quad \Rightarrow$$

for a strand:

$$\Delta S = -\frac{3k_B}{2Na^2}\left[\left(\lambda_x^2 - 1\right)l_x^2 + \left(\lambda_y^2 - 1\right)l_y^2 + \left(\lambda_z^2 - 1\right)l_z^2\right]$$

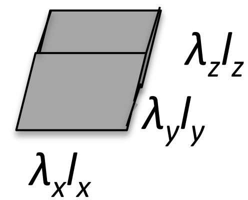
Example of deformation of hydrogels

Before deformation:



$$r_0^2 = l_x^2 + l_y^2 + l_z^2$$

After deformation:



$$r_1^2 = \lambda_x^2 l_x^2 + \lambda_y^2 l_y^2 + \lambda_z^2 l_z^2$$

If a volume contains *n* strands the change in the entropy is:

$$\left\langle l_x^2 \right\rangle = \left\langle l_y^2 \right\rangle = \left\langle l_z^2 \right\rangle = \frac{Na^2}{3} \quad \Rightarrow \quad \Delta S_{vol} = -\frac{nk_B}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

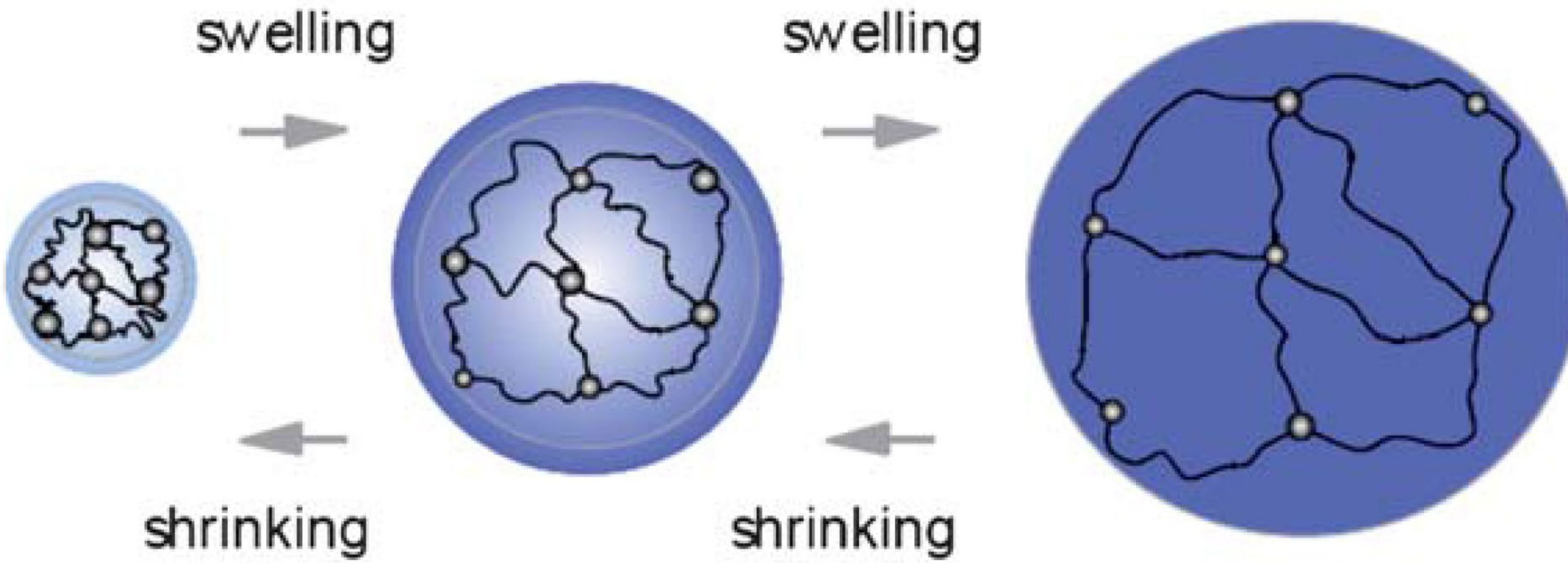
Example: An incompressible rubber is elongated along the x-direction.

$$\lambda_x = \lambda$$

$$\lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$$

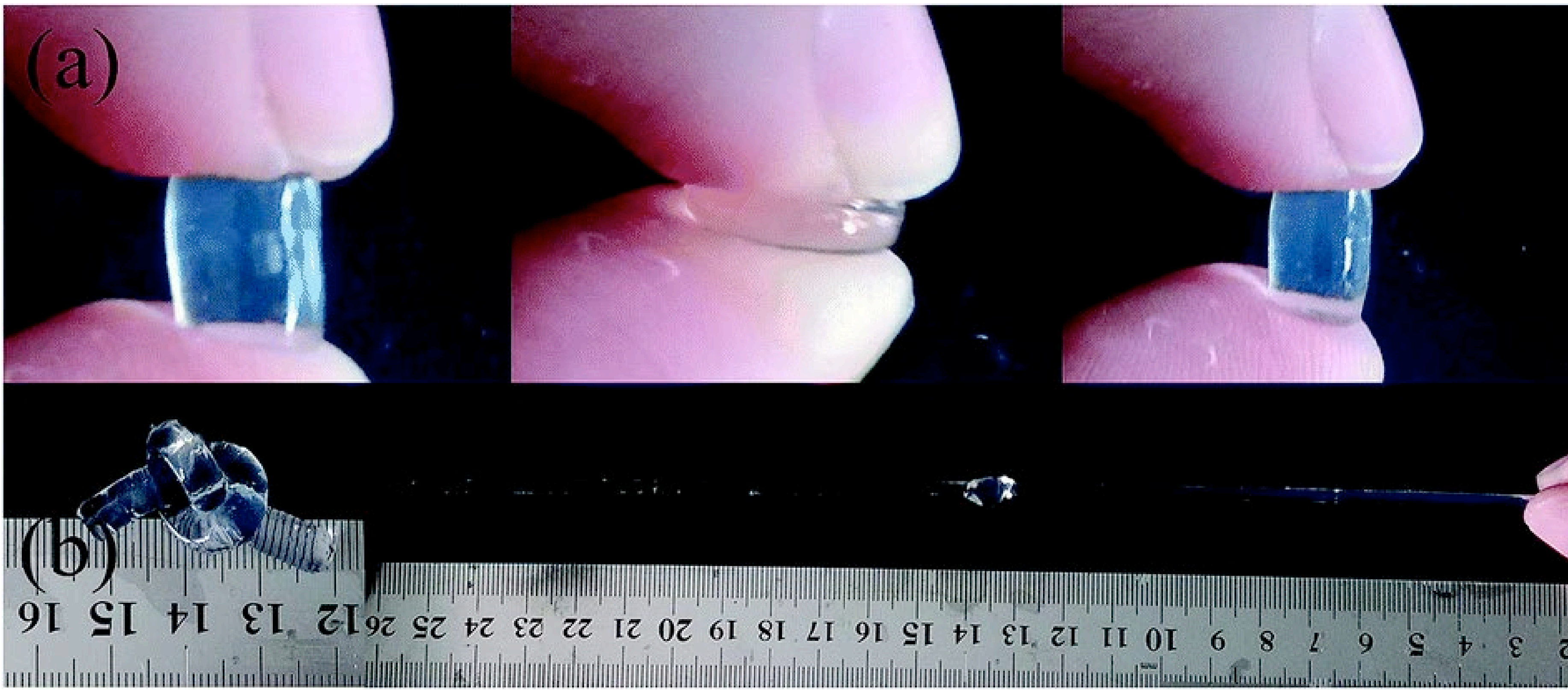
$$\Rightarrow \quad \Delta S_{vol} = -\frac{nk_B}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right) \quad \Rightarrow \quad \Delta F_{vol} = \frac{nk_B T}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$$

Swelling of hydrogels



Yang, Q.; Adrus, N.; Tomicki, F.; Ulbricht, M. *Journal of Materials Chemistry* **2011**, *21*, 2783

Deformation of hydrogels



Lin, Y.; Li, G. *Journal of Materials Chemistry B* **2014**, *2*, 6878.

Shear modulus

$$\tau = \frac{dF}{d\varepsilon}$$

with $\Delta F_{vol} = \frac{nk_BT}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$ and $\lambda = \varepsilon + 1$

$$\tau = nk_BT\left[(1+\varepsilon) - \frac{1}{(1+\varepsilon)^2}\right]$$

ε: strain [-]
γ: shear strain [-]
τ: tensile stress [Pa]
F: Helmholtz free energy [J]
G: shear modulus [Pa]
M_x: average molecular weight between crosslinks [g/mol]
ρ: density [kg/m^3]

Hydrogels usually display non-Hookean stress/strain behavior

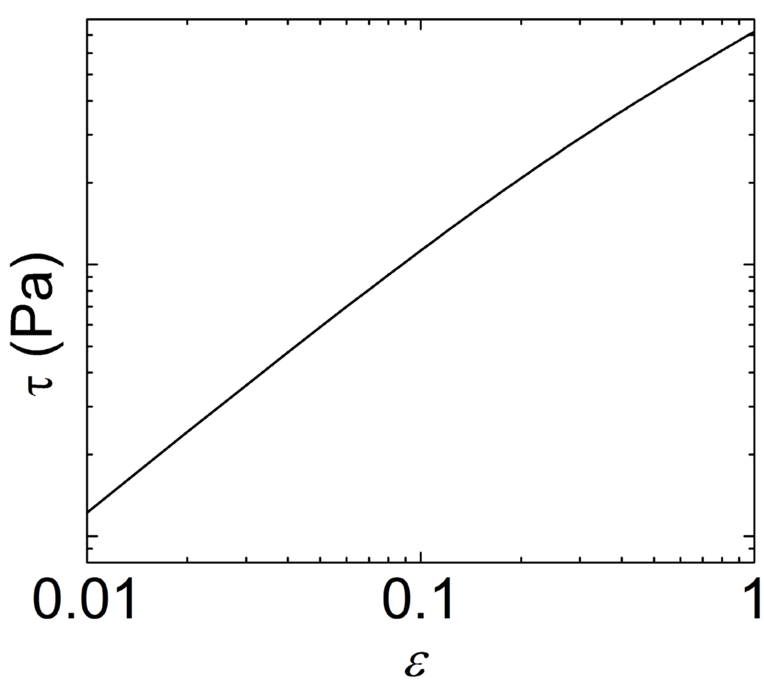
But for small strains:

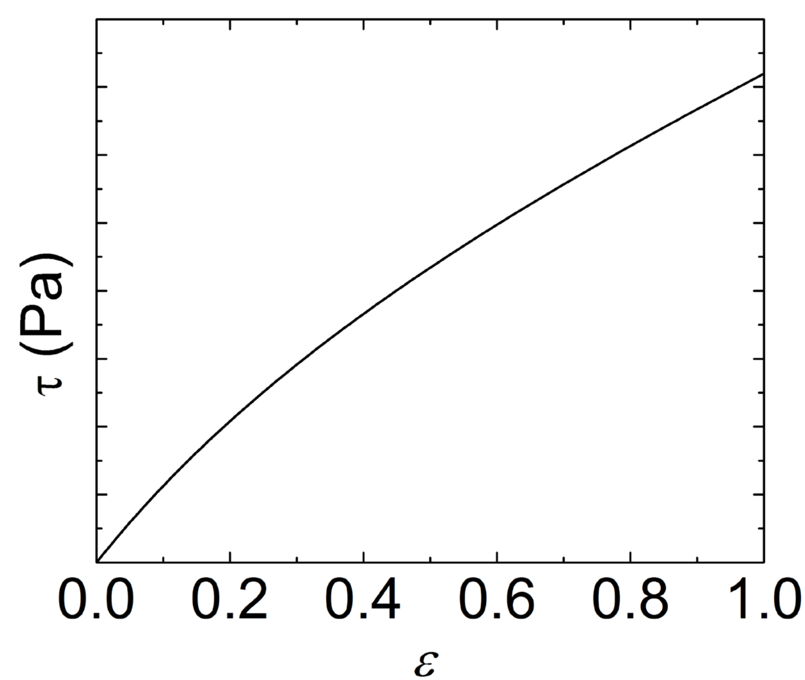
$$\tau \approx nk_BT\varepsilon$$

with $\tau = G\gamma$

$G = nk_BT$ or $G = \frac{\rho RT}{M_x}$

Stress-strain behavior of hydrogels





For small strains:

$$\tau \approx nk_B T\varepsilon$$

with $\tau = G\gamma$

$$G = nk_B T \quad \text{or} \quad G = \frac{\rho RT}{M_x}$$

$$\tau = nk_B T\left[(1+\varepsilon) - \frac{1}{(1+\varepsilon)^2}\right]$$

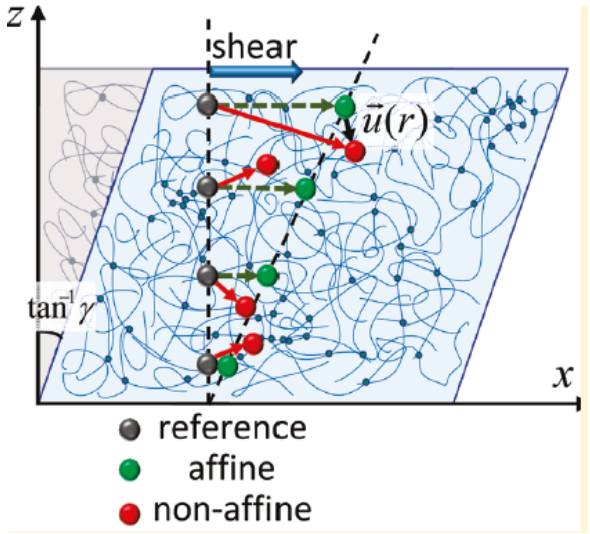
Shear modulus, G

Deformation

Affine deformation: The relative deformation of each polymer chain is equal to the relative deformation of the entire polymer network.

http://www.chemistry.ucla.edu/directory/levine-alexander-j

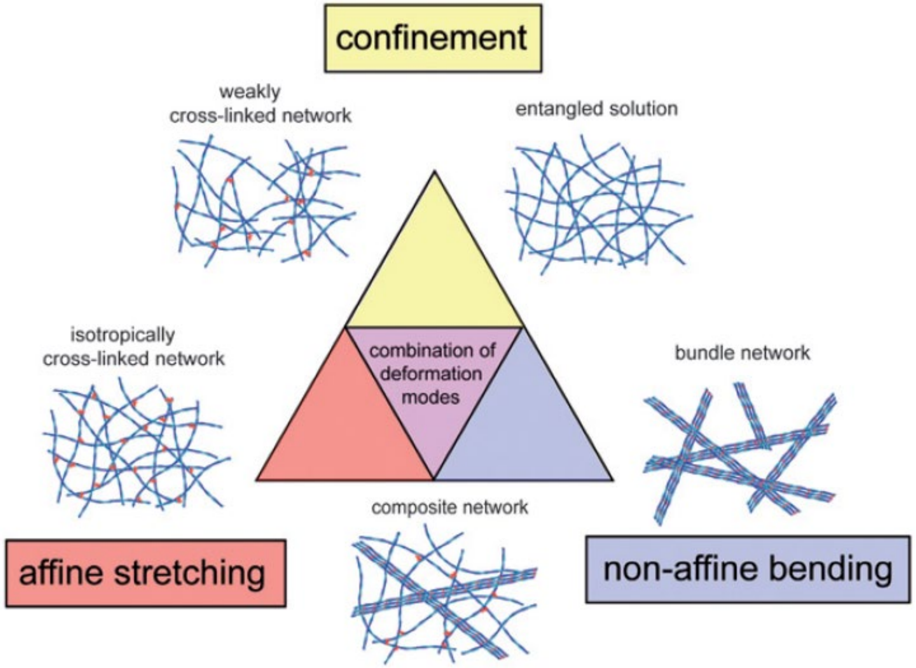
The deformation of networks with a high density of chemical crosslinks is affine.
The deformation of some composites is affine.

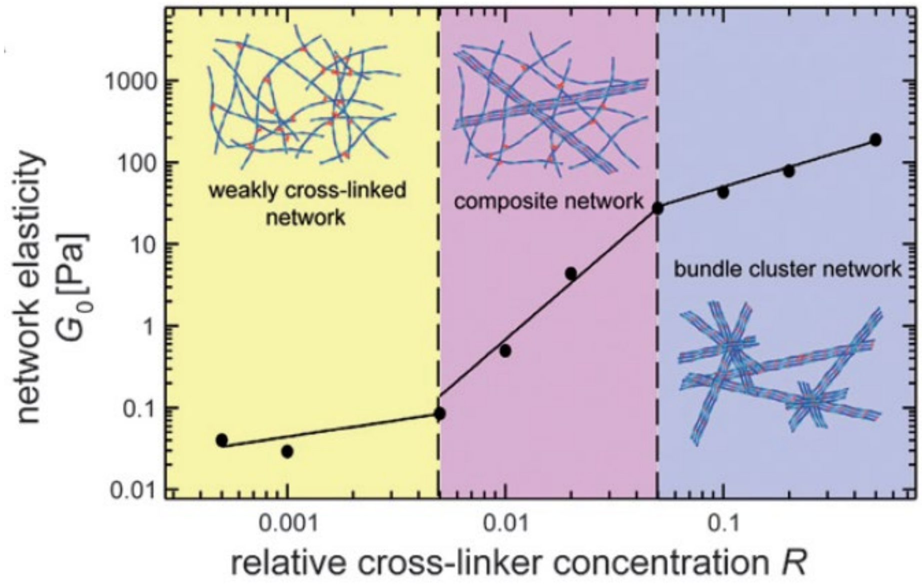


Basu, A., et al., Macromolecules, 2011. **44**(6): p. 1671-1679.

Materials that have a low density of chemical crosslinks can display an non-affine deformation.

Deformation

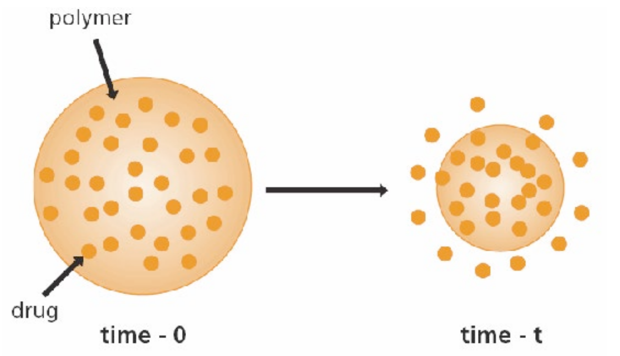




O. Lieleg, M. Claessens and A. R. Bausch, *Soft Matter*, 2010, **6**, 218-225

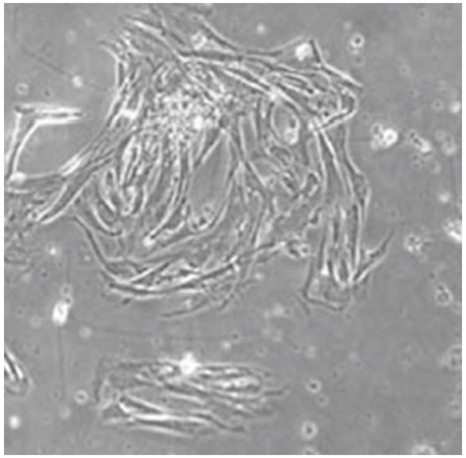
Applications of hydrogels

Drug delivery

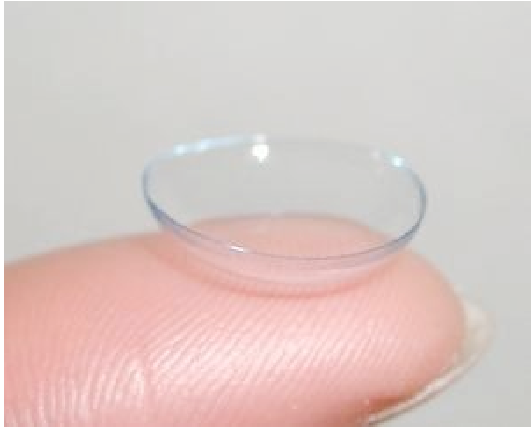


Wound healing

Tissue engineering

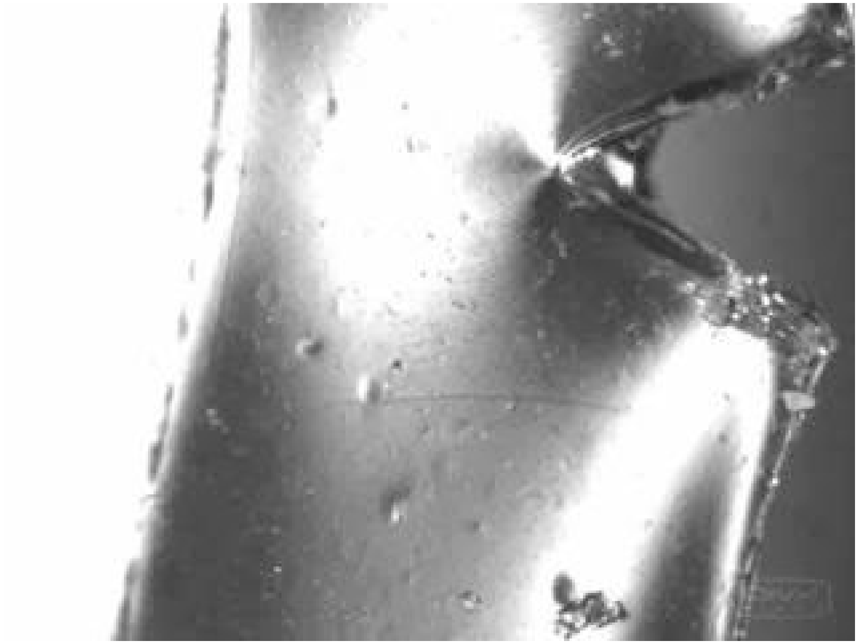


Contact lens

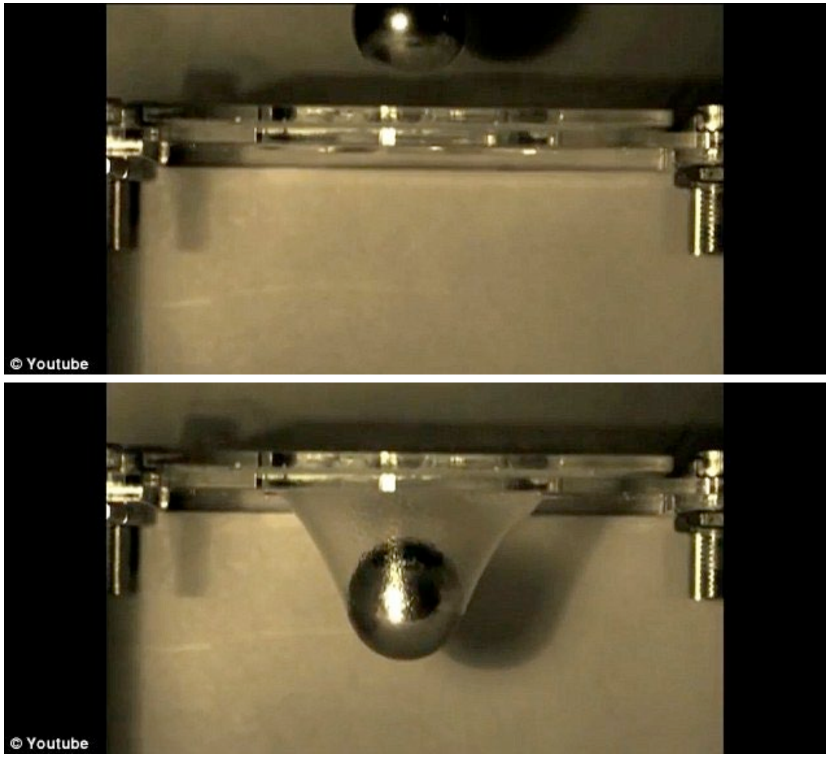


Food

Mechanical properties of hydrogels



https://www.simm.espci.fr/spip.php?article250&lang=fr



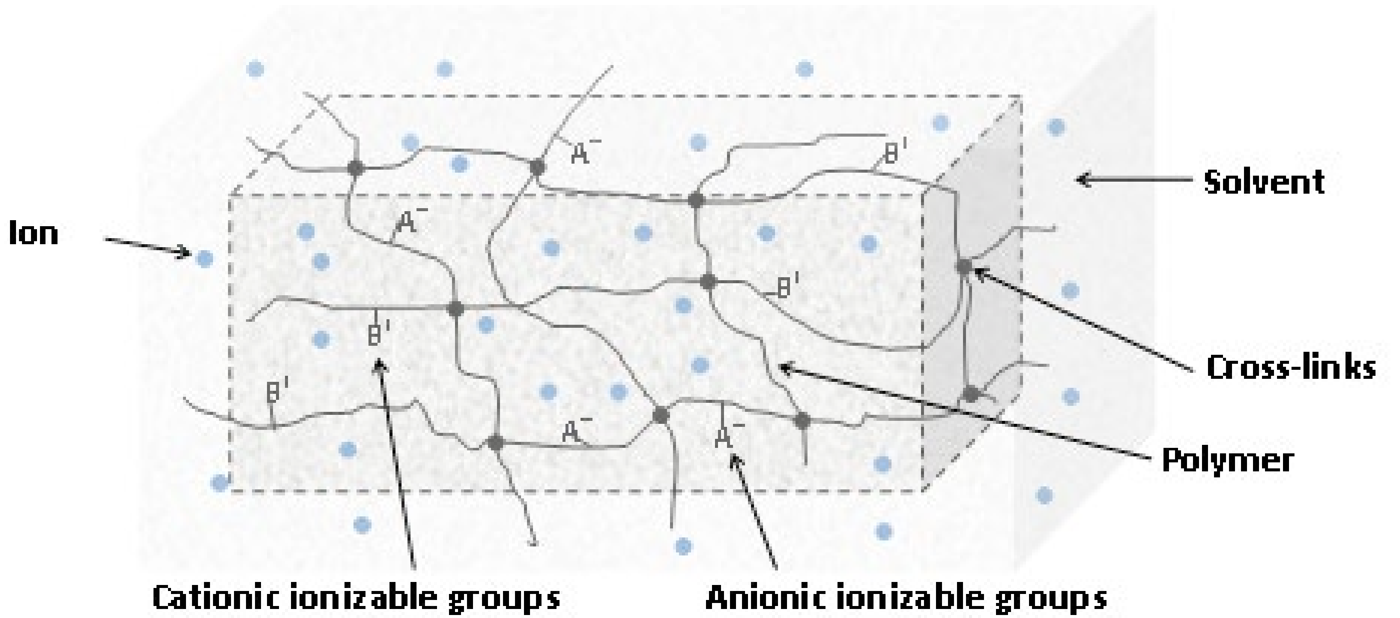
J. Y. Sun, X. H. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak and Z. G. Suo, *Nature*, 2012, **489**, 133-136.

https://www.youtube.com/watch?v=j9XBQNnVdtE

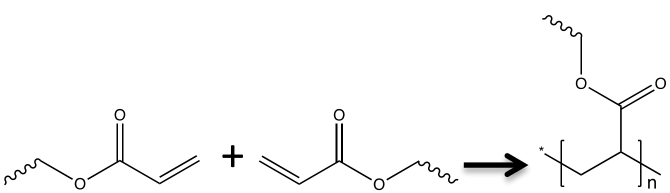
Why is the gel on the right side much more elastic?

A. It has a higher crosslink density.
B. It is made of polymers with a higher molecular weight.
C. The polymers contain a covalent and reversible crosslinks.
D. The polymers are gelled through covalent crosslinks.
E. The gel is made of a mixture of thermosets and thermoplasts.

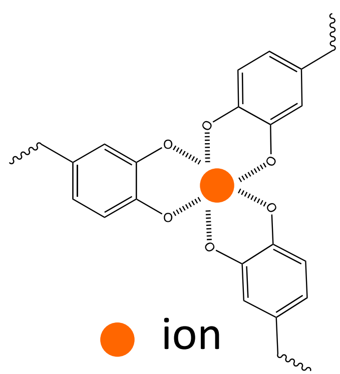
Crosslinking of hydrogels



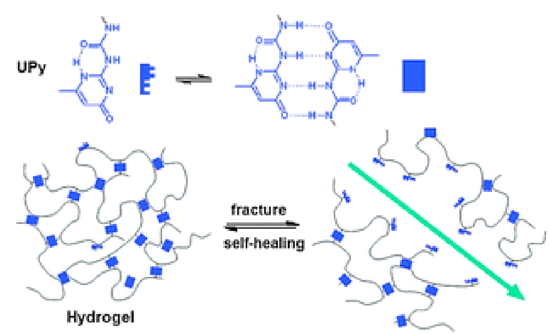
covalent links



ionic links



hydrogen bond links



J. X. Cui and A. del Campo, *Chem. Commun.*, 2012, **48**, 9302-9304.

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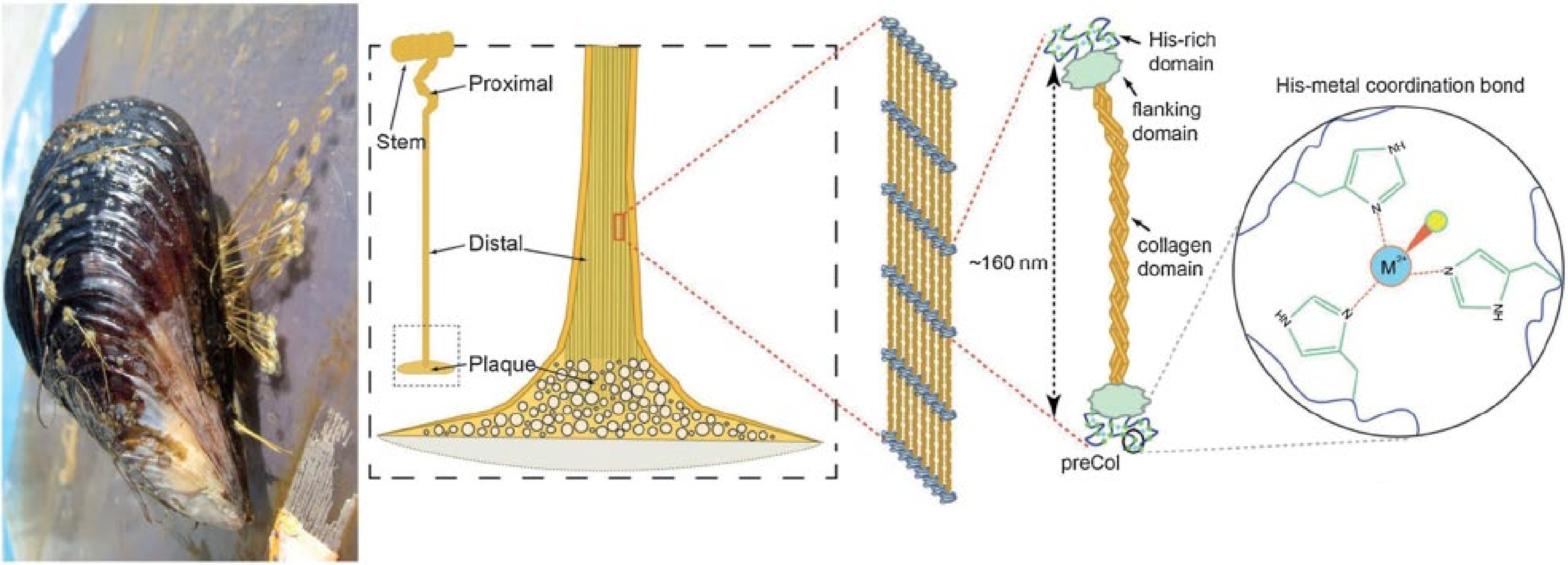
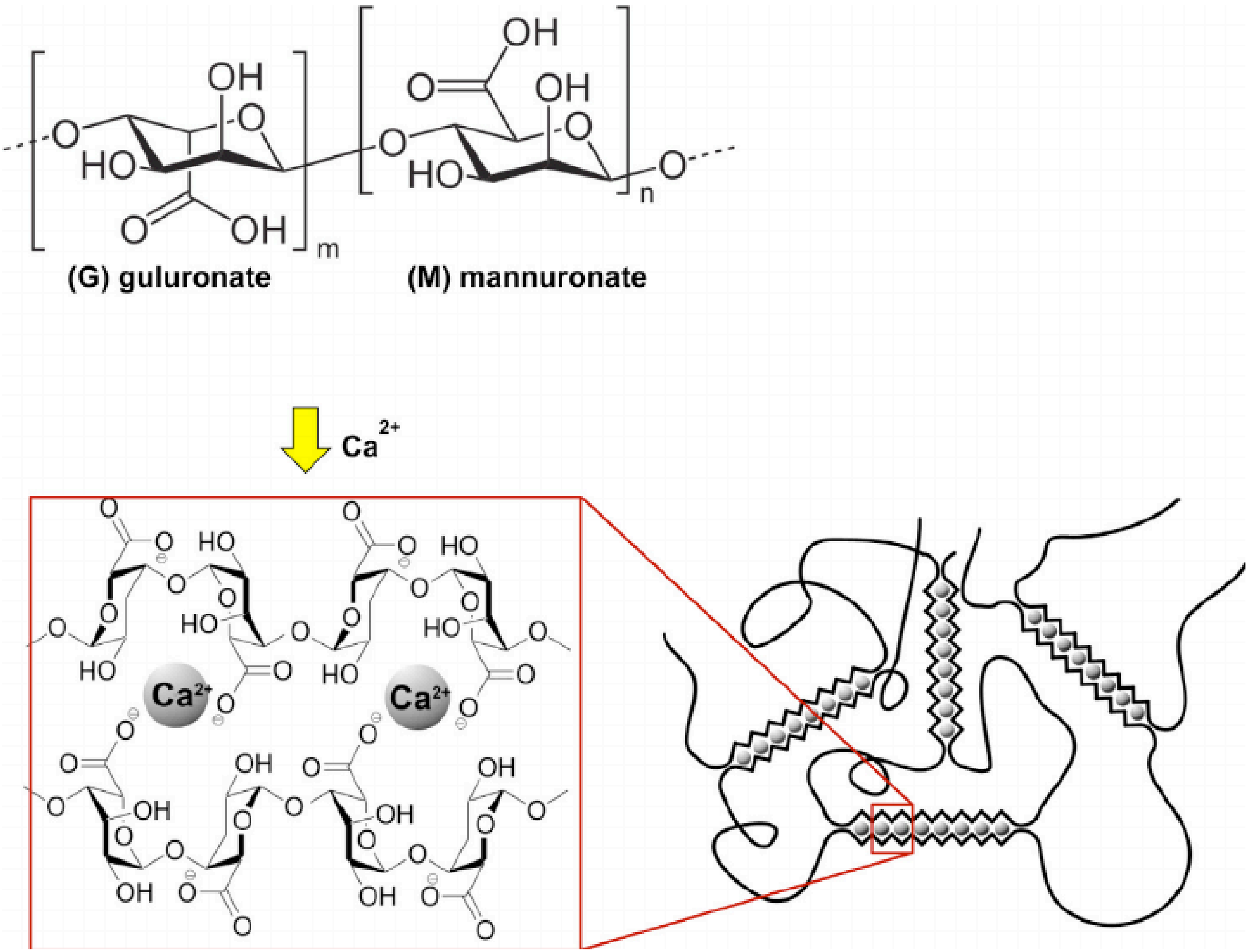
Ionically crosslinked hydrogels



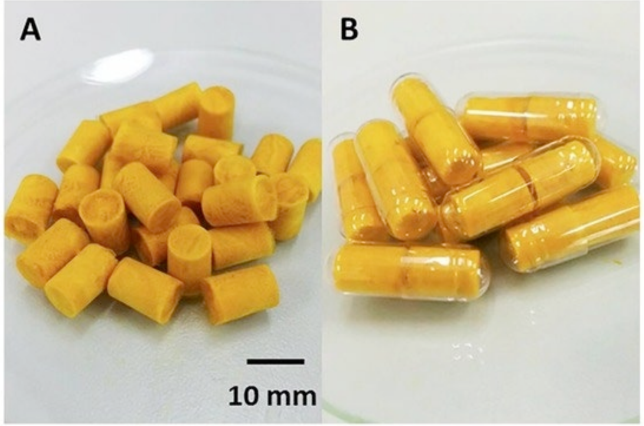
E. Degtyar, M. J. Harrington, Y. Politi and P. Fratzl, *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

Ionically crosslinked hydrogel: Alginate

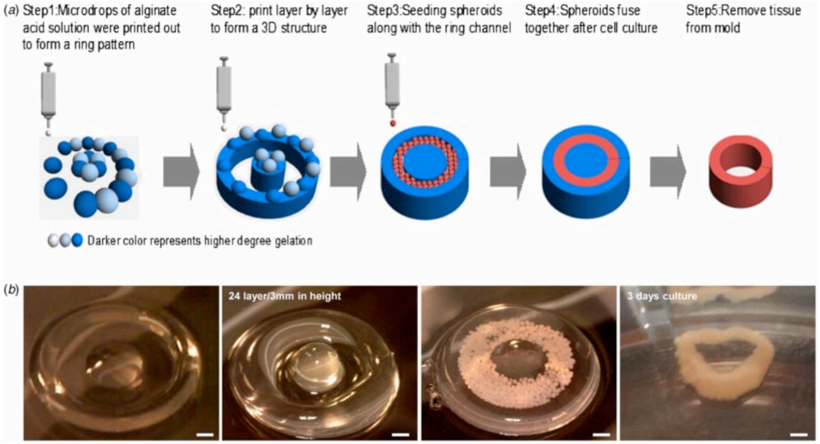


M. Bruchet and A. Melman, *Carbohydrate Polymers*, 2015, **131**, 57-64.

Alginate

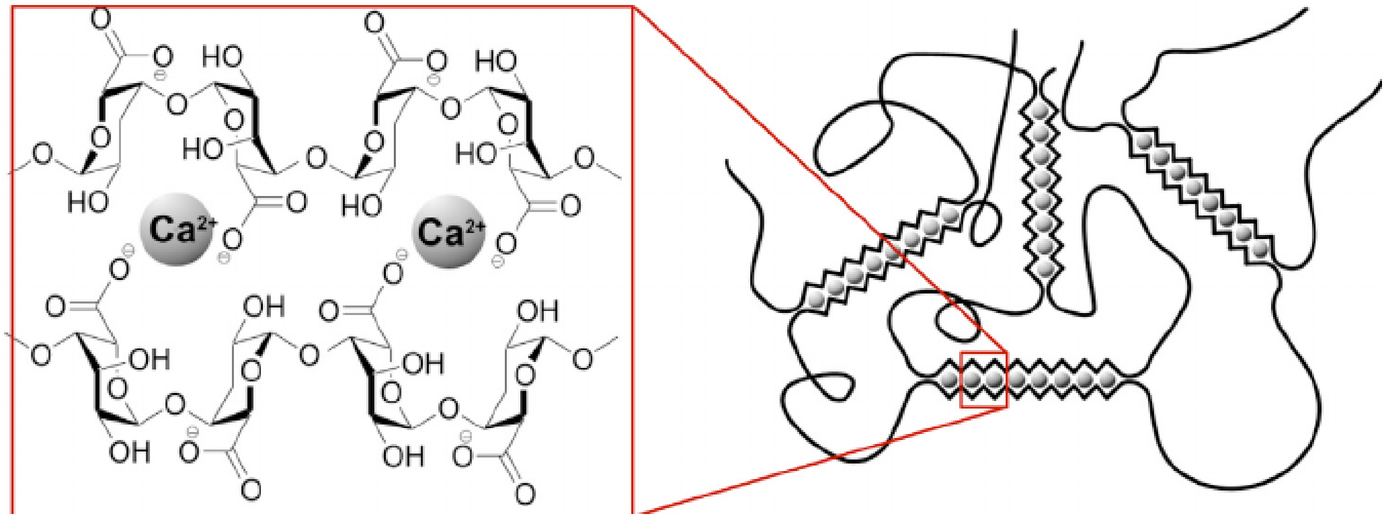


A. Petchsomrit, N. Sermkaew and R. Wiwattanapatapee, *Scientia Pharmaceutica*, 2017, **85**, 11.



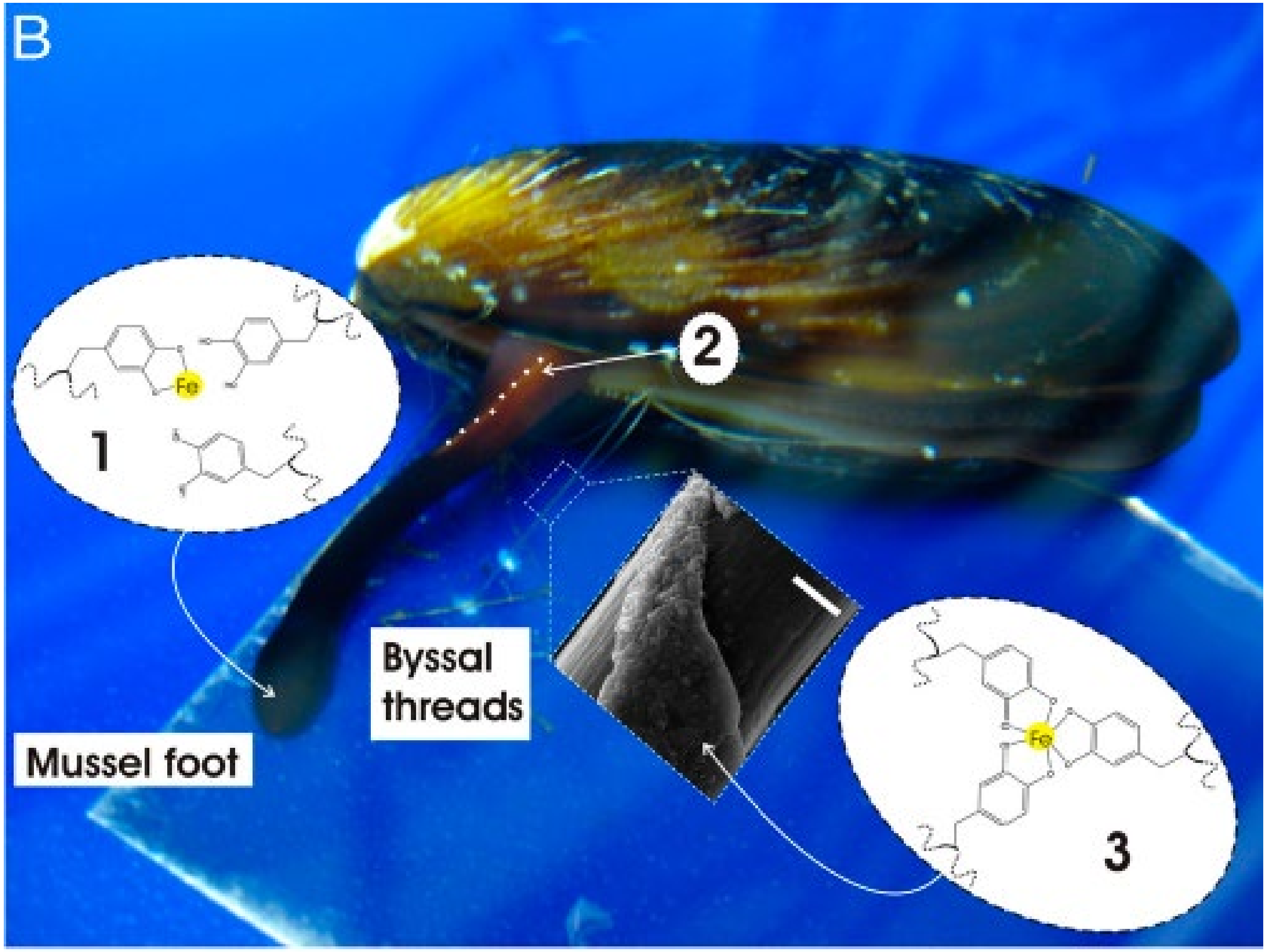
Y. Tan, D. J. Richards, T. C. Trusk, R. P. Visconti, M. J. Yost, M. S. Kindy, C. J. Drake, W. S. Argraves, R. R. Markwald and Y. Mei, *Biofabrication*, 2014, **6**.

Ionically crosslinked hydrogels



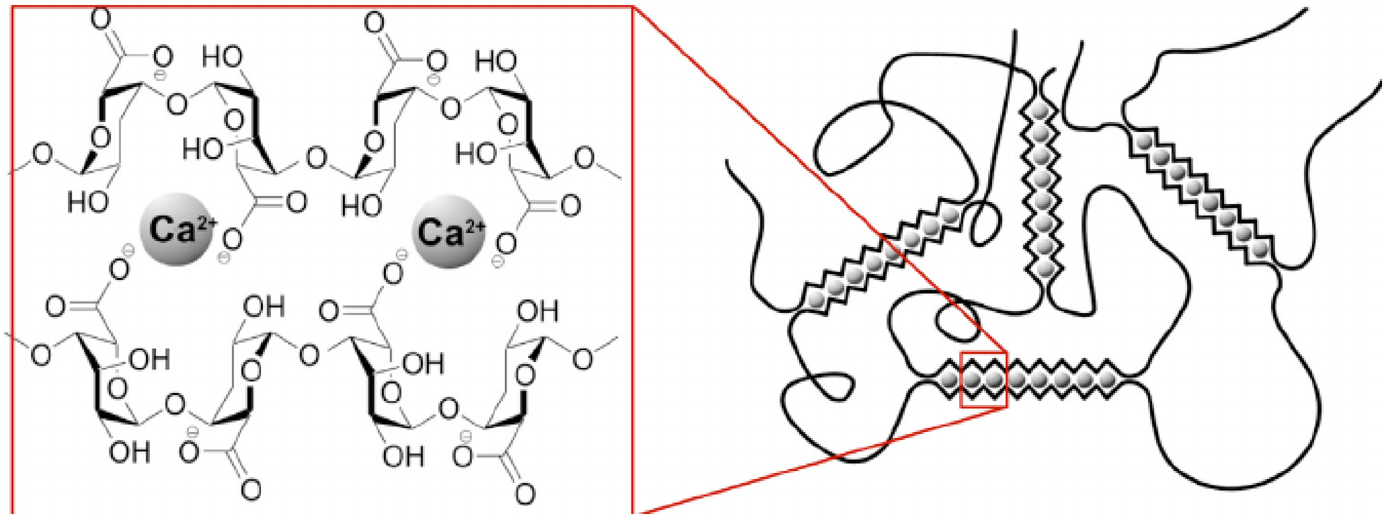
M. Bruchet and A. Melman, *Carbohydrate Polymers*, 2015, **131**, 57-64.

Catechol-crosslinked hydrogels

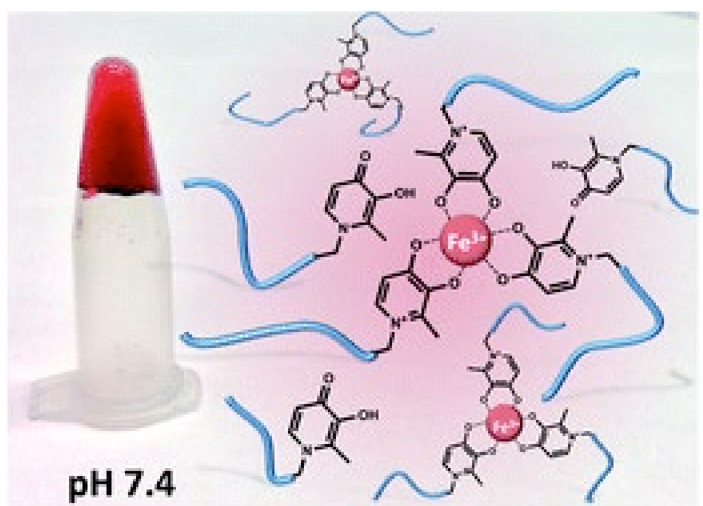


N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee and J. H. Waite, *PNAS*, 2011, **108**, 2651-2655.

Ionically crosslinked hydrogels

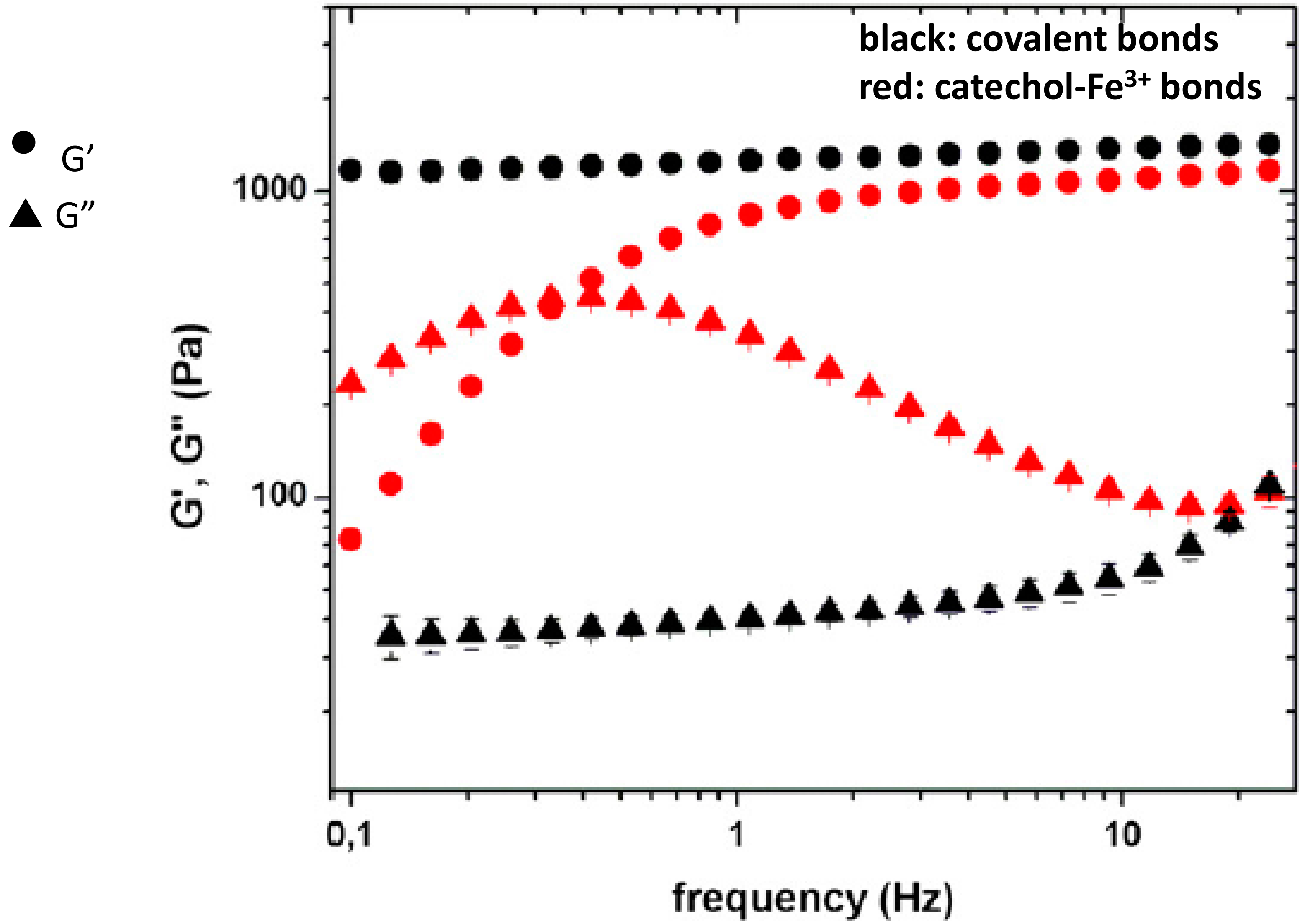


M. Bruchet and A. Melman, *Carbohydrate Polymers*, 2015, **131**, 57-64.



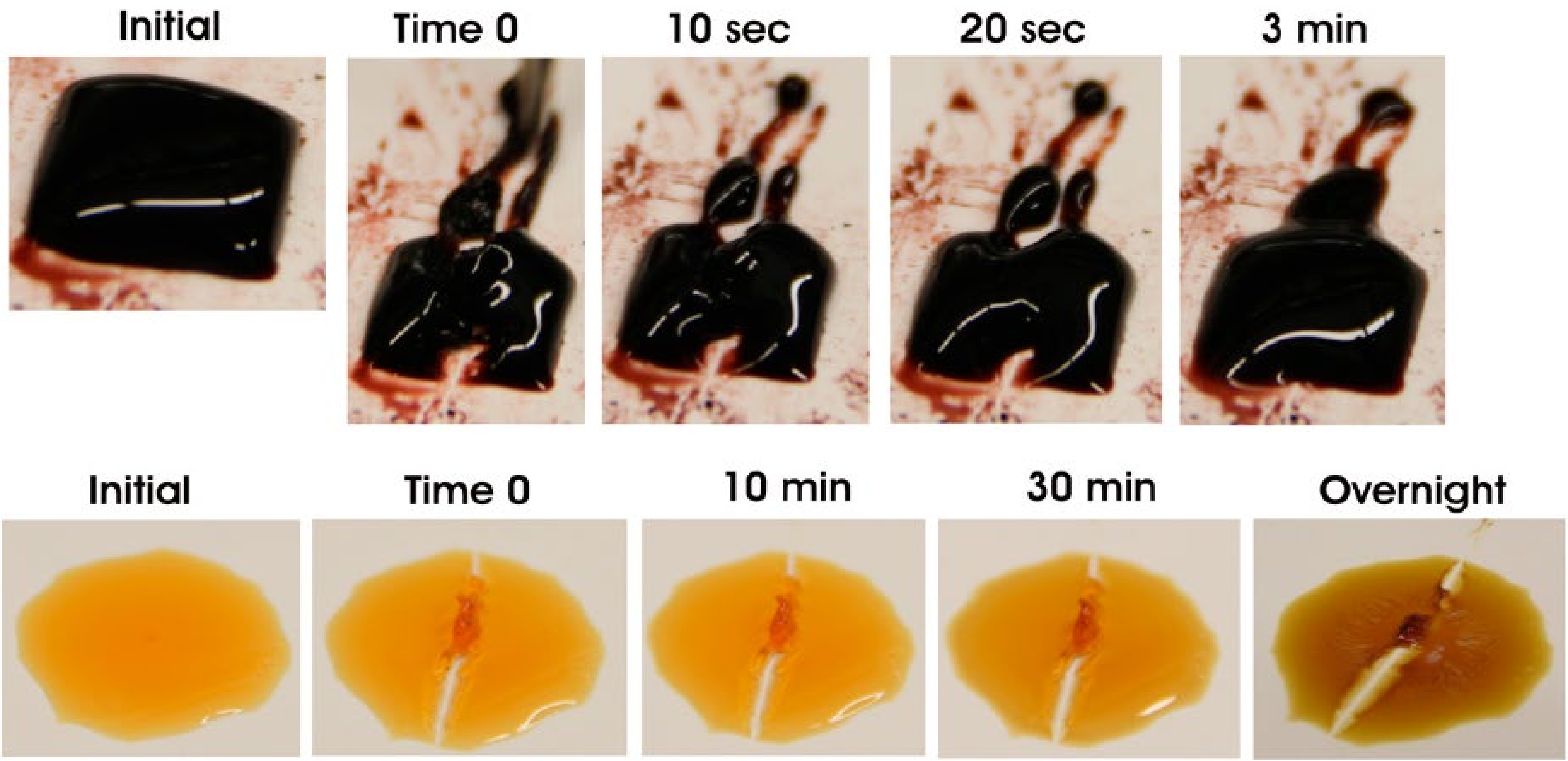
M. S. Menyo, C. J. Hawker and J. H. Waite, *Soft Matter*, 2013, **9**, 10314-10323.

Mechanical properties



N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee and J. H. Waite, *PNAS*, 2011, **108**, 2651-2655.

Self-healing properties

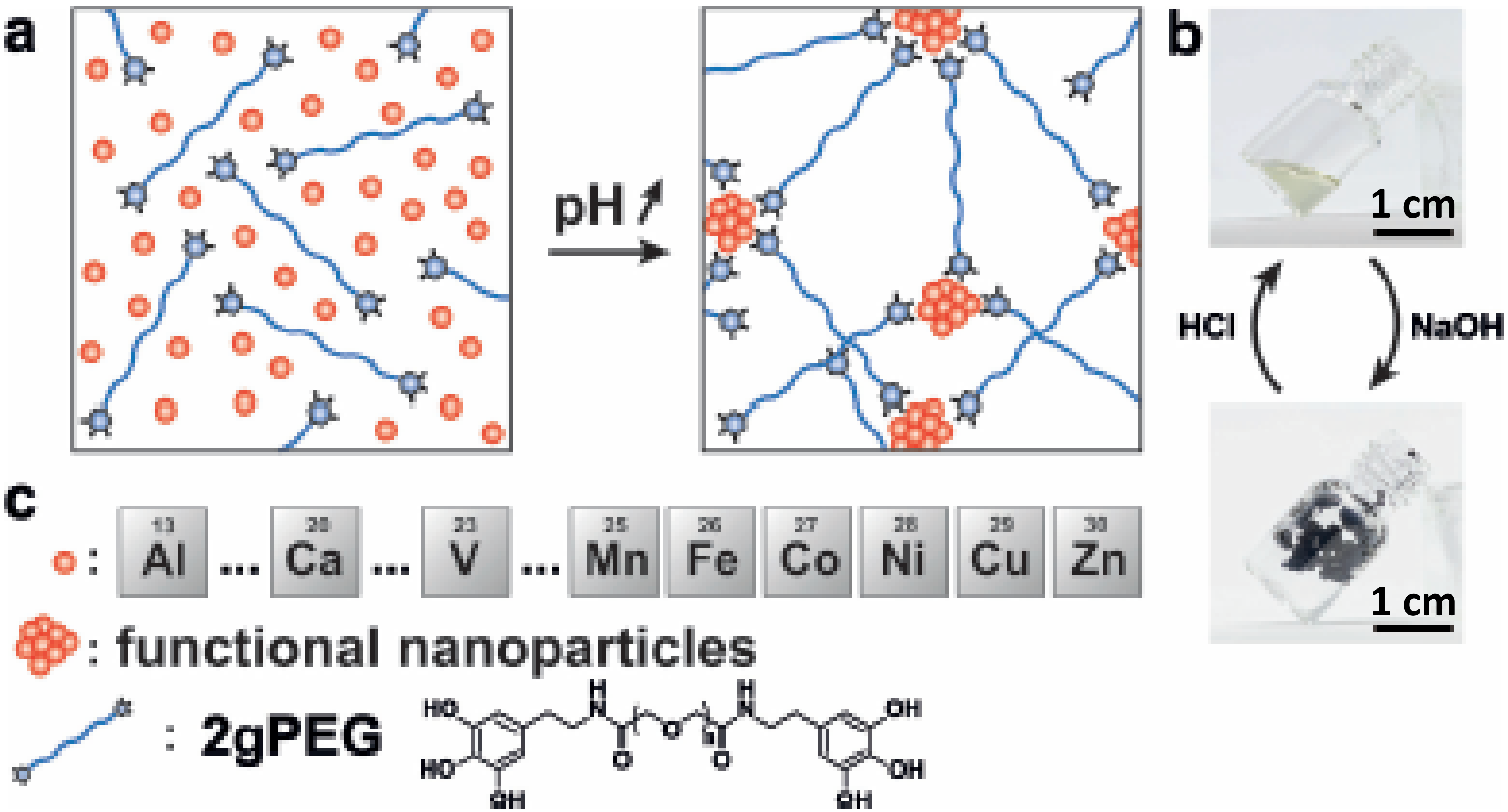


N. Holten-Andersen, M. J. Harrington, H. Birkedal, B. P. Lee, P. B. Messersmith, K. Y. C. Lee and J. H. Waite, *PNAS*, 2011, **108**, 2651-2655.

Why does the red hydrogel self-heal?

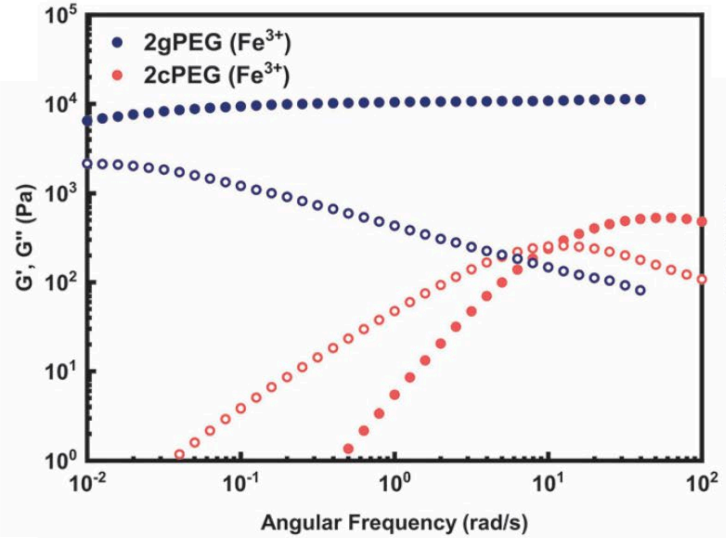
A. It is gelled through covalent bonds.
B. It is gelled through ionic bonds.
C. It has a high crosslink density.
D. It is made of low molecular weight polymers that have a high mobility.

Influence of ions



A. Charlet, V. Lutz-Bueno, R. Mezzenga, E. Amstad, *Nanoscale* **2021**, *13*, 4073, DOI: 10.1039/D0NR08351H

Influence of ions



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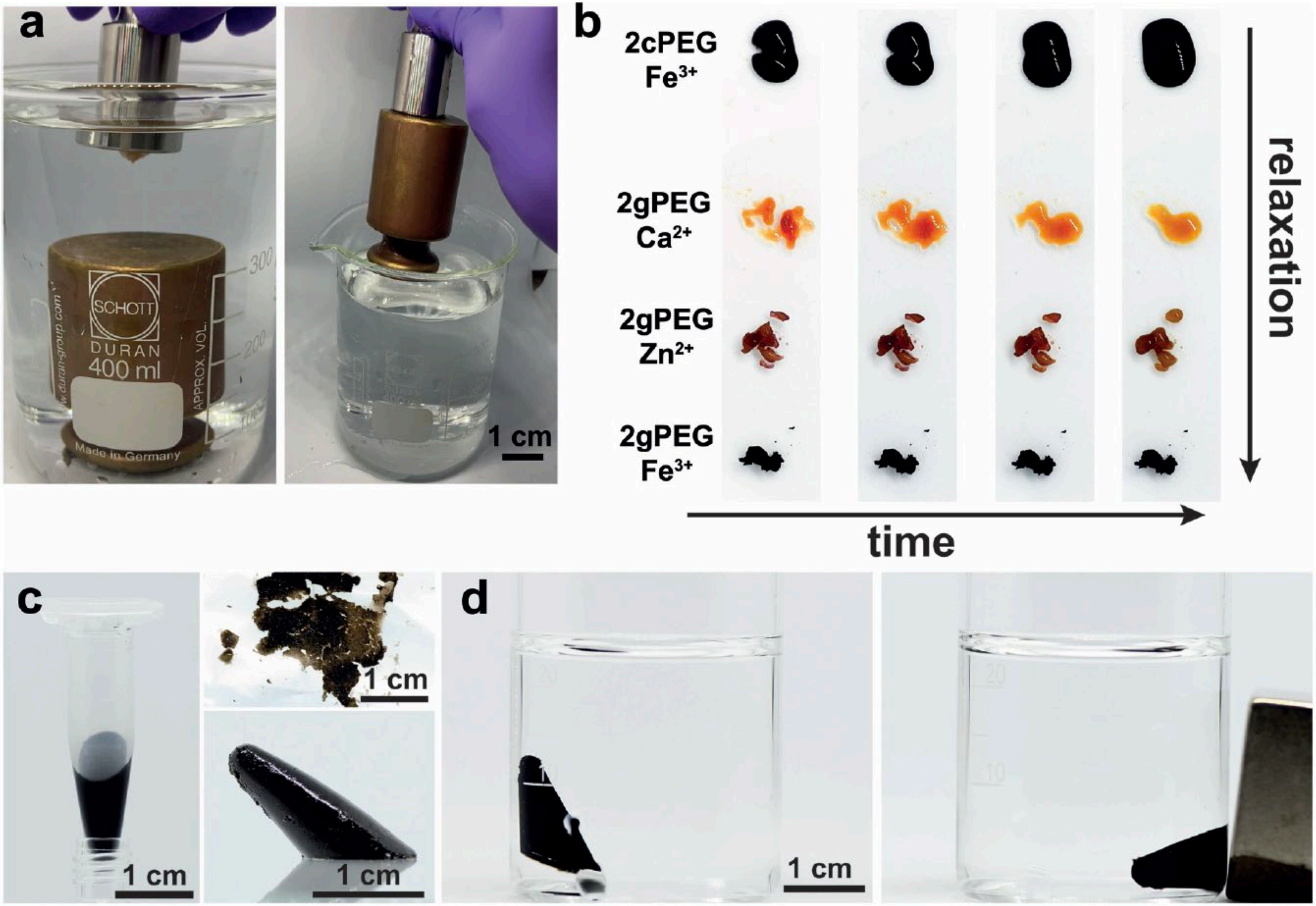
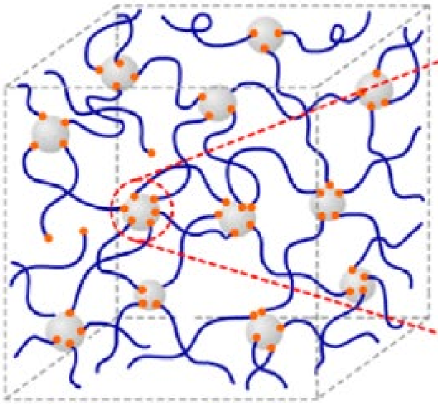


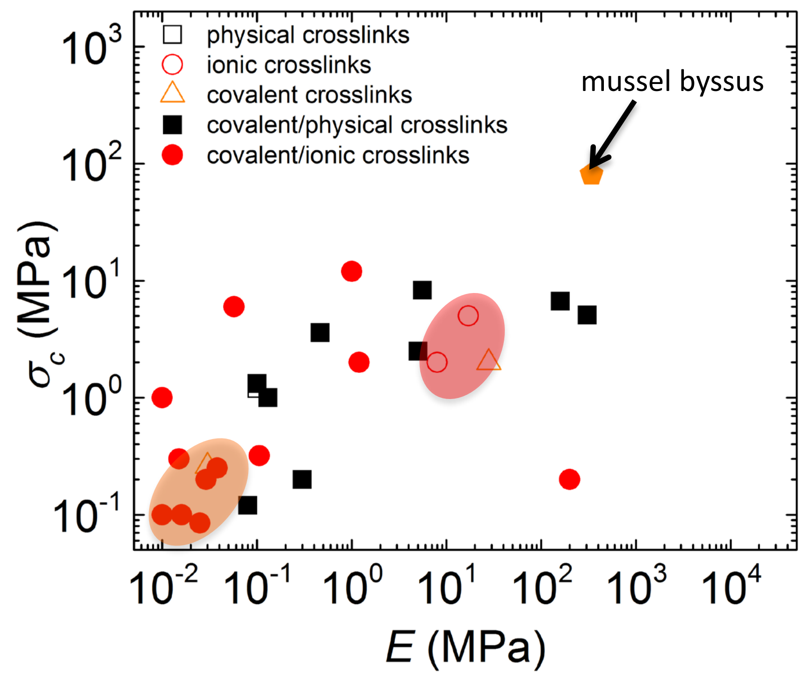
A. Charlet, V. Lutz-Bueno, R. Mezzenga, E. Amstad, *Nanoscale* **2021**, *13*, 4073, DOI: 10.1039/D0NR08351H

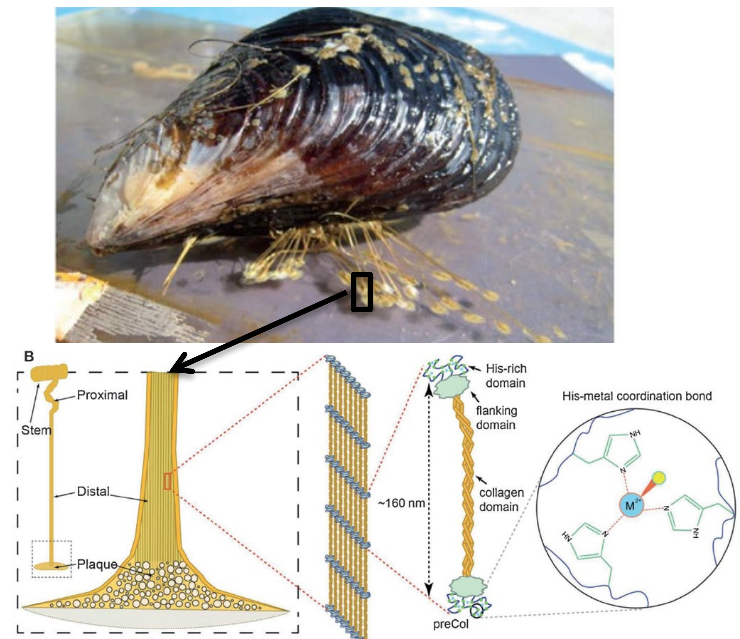
Tuning time scales of viscoelastic properties



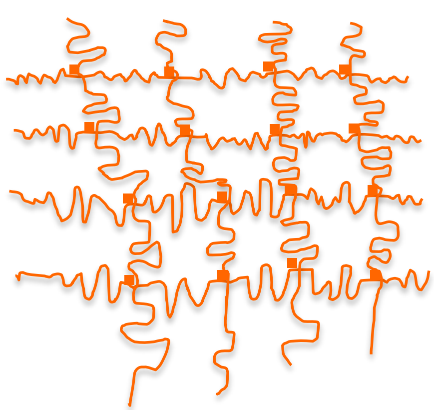
Q. C. Li, D. G. Barret, P. B. Messersmith and N. Holten-Andersen, *Acs Nano*, 2016, **10**, 1317-1324.

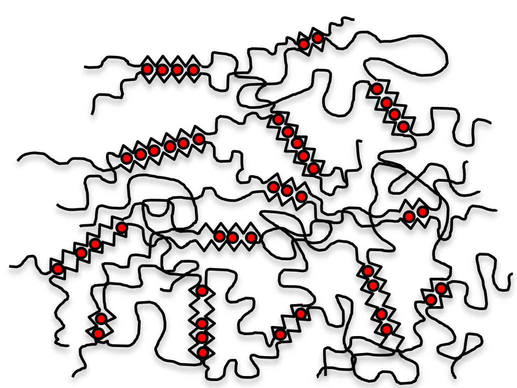
Mechanical properties of hydrogels

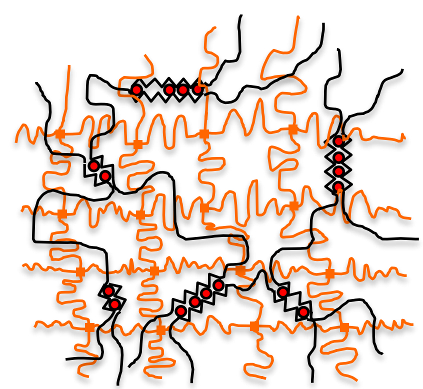




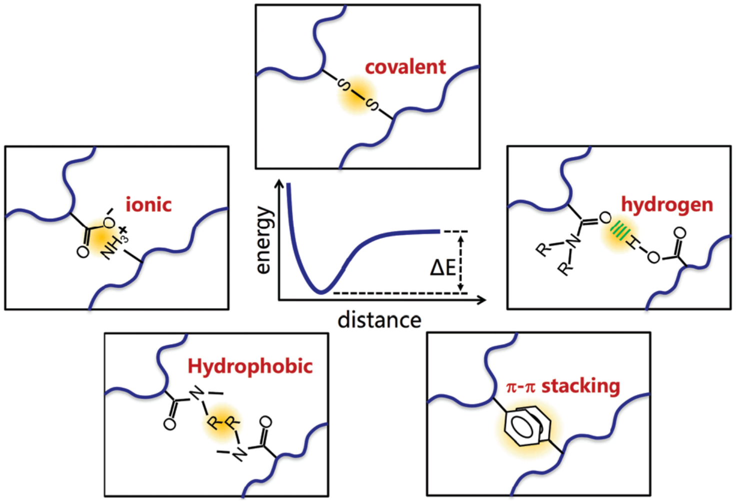
E. Degtyar, et al., *Angew. Chem. Int. Ed.*, 2014, **53**, 12026-12044

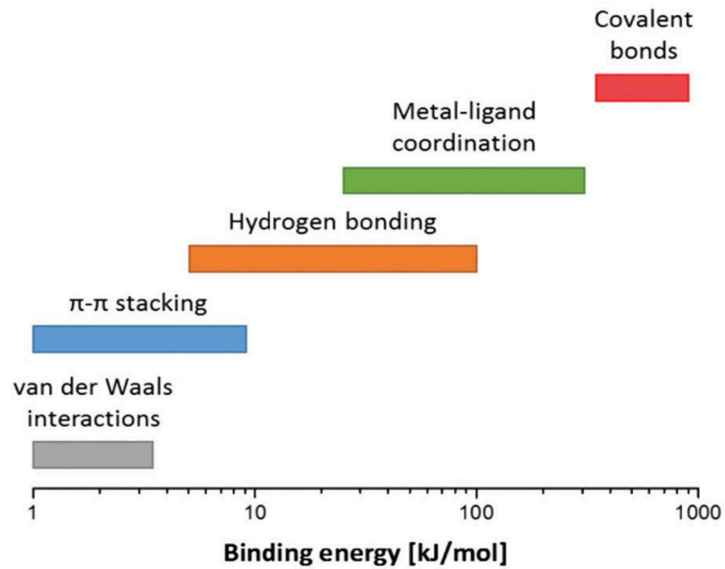


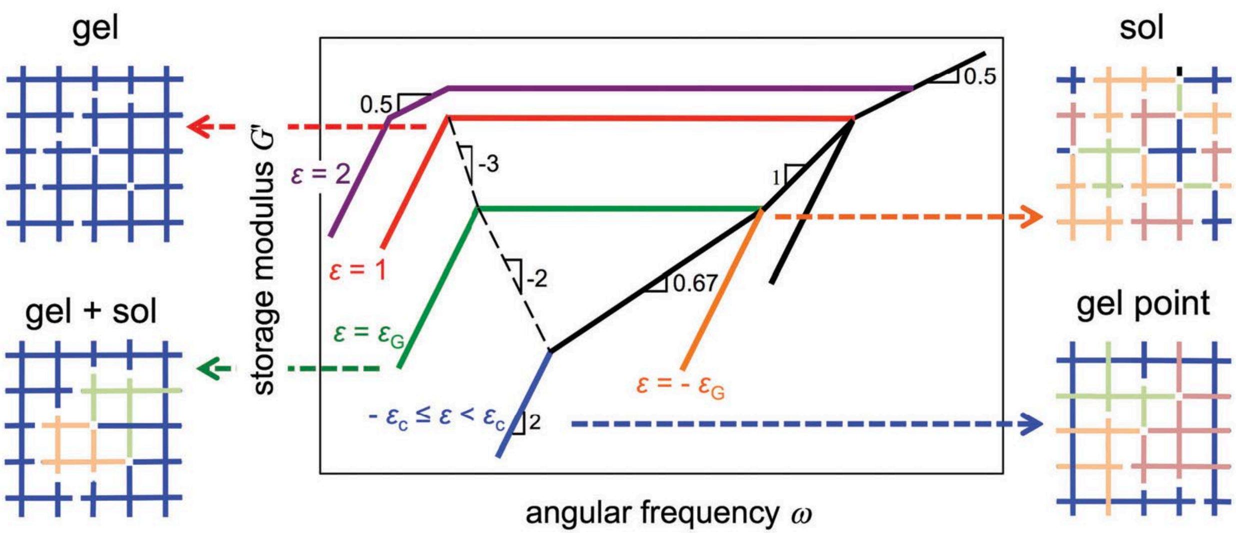




Supramolecular interactions in gels







Z. Zhang, Q. Chen, and R.H. Colby, Soft Matter **14**, 2961 (2018)

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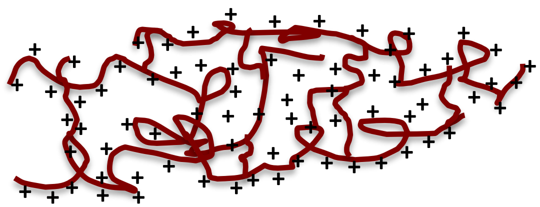
- Microgels

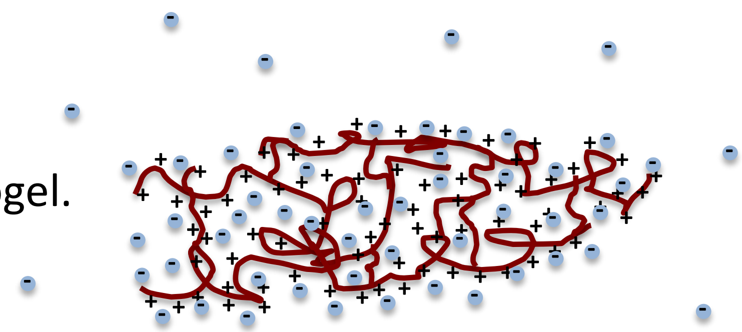
Polyelectrolytes

Polyelectrolytes are polymers that can dissociate charges if dispersed in a polar media. Hence, they are **charged polymers.**



Counter-ions must be associated with polyelectrolytes because macroscopically, we must have charge neutrality.

Counter-ions preferentially go into the hydrogel.



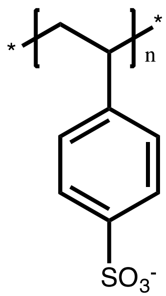
If the counter-ion concentration inside the hydrogel is higher than in the surrounding, an osmotic pressure exists.

The osmotic pressure drives the swelling of hydrogels until it equals the stress needed to further stretch the polymer chains.

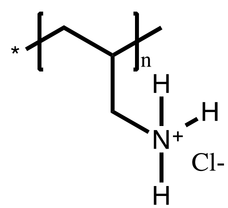
Types of polyelectrolytes

Strong polyelectrolytes:
Polymers are charged over a wide pH range.

Examples:



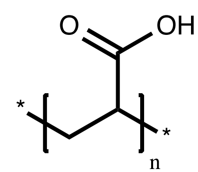
poly(styrene sulfonate) (PSS)



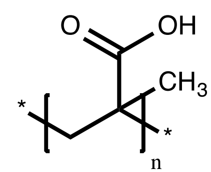
poly(allylamine hydrochloride) (PAH)

Weak polyelectrolytes:
Polymers are only charged over a limited pH range.

Examples:

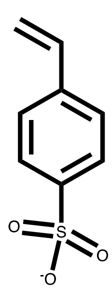


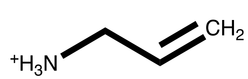
poly(acrylic acid) (PAA)

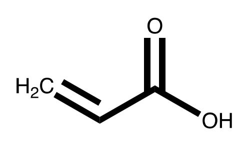


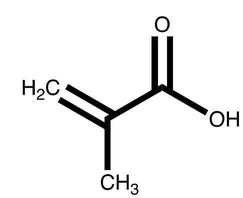
poly(methacrylic acid) (PMAA)

monomers



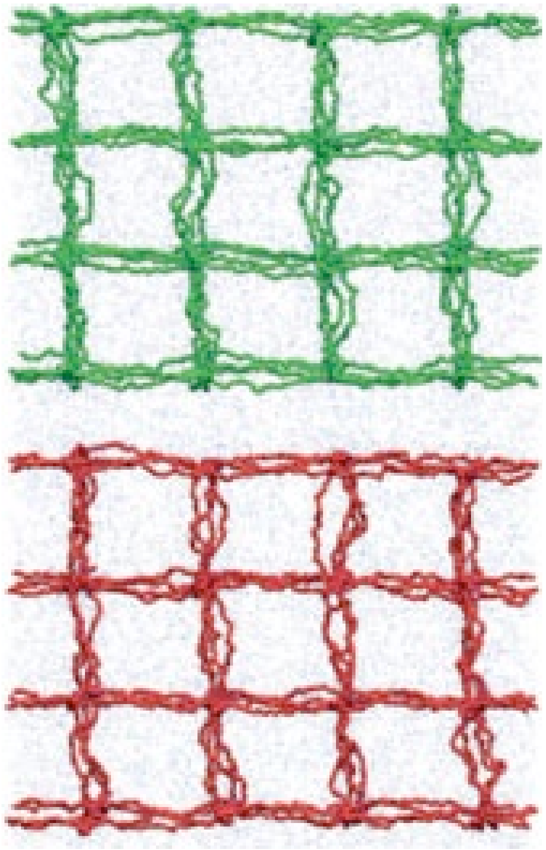






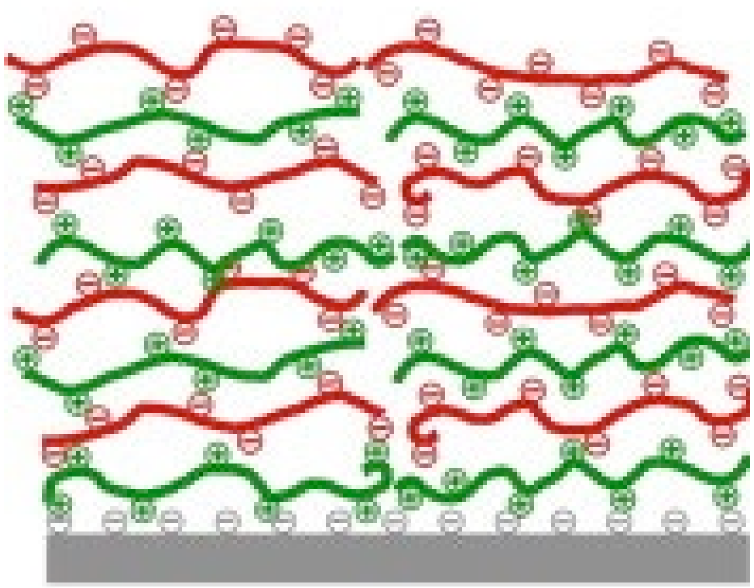
Polyelectrolyte hydrogels

covalently linked hydrogels



Erbas, A., Olvera de la Cruz, M. "Energy Conversion in Polyelectrolyte Hydrogels" ACS Macro Lett 8, 2015, 857–861.

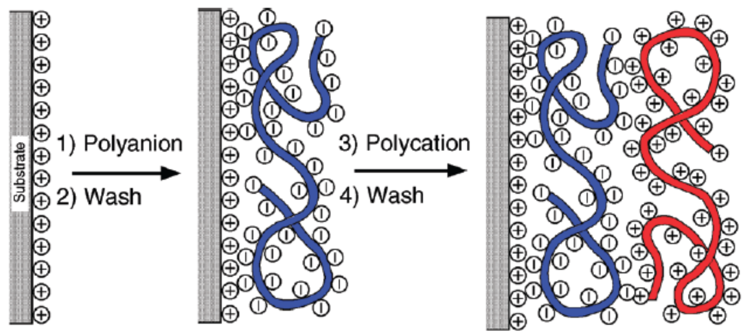
polyelectrolyte multilayers



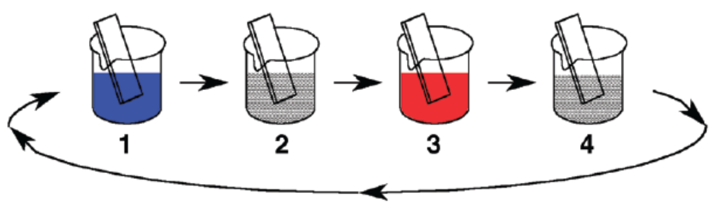
Das, B. P.; Tsianou, M. *Adv. Colloid Interface Sc* , 2017

Assembly of PEMs

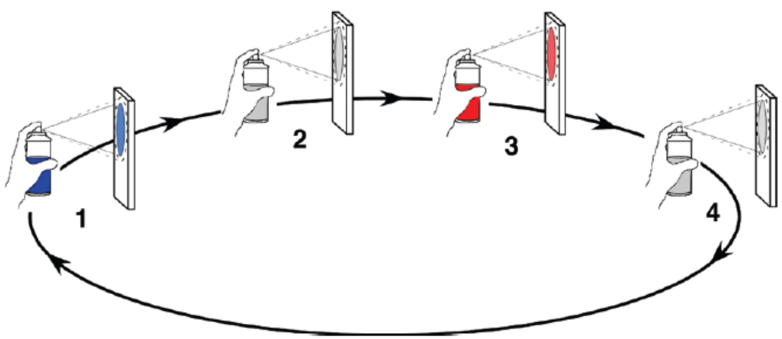
PEM: Polyelectrolyte multilayers



dipping



spraying

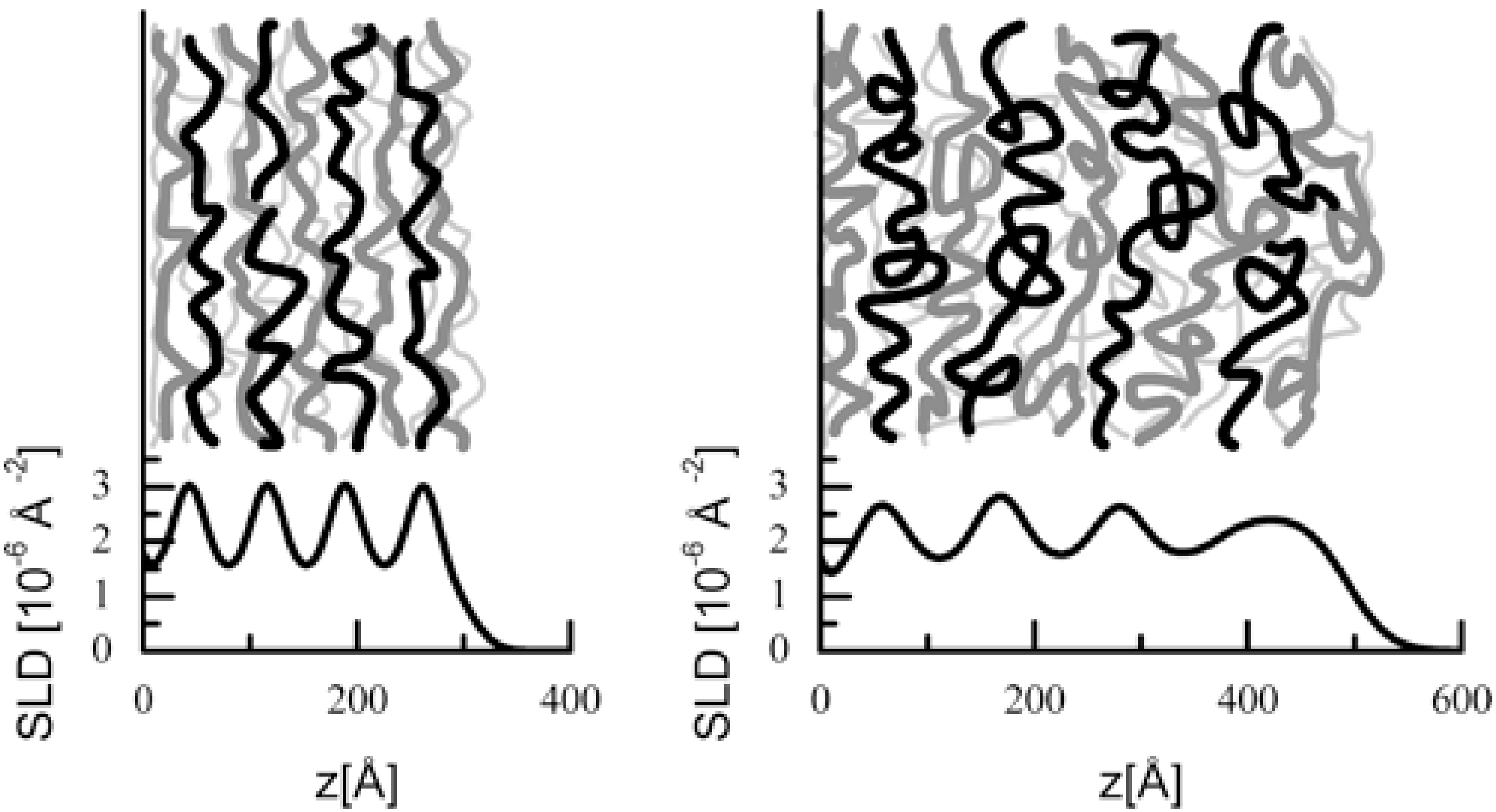


Assembly conditions:

- Longer assembly times lead to more reproducible results.
- Between the deposition of each layer, the PEMs must be thoroughly washed until the polymer solution is diluted 10^6-fold.

Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, Second Edition, Edited by Gero Decher and Joseph B. Schlenoff. 2012 Wiley-VCH Verlag GmbH & Co. KGaA.

Structure of polyelectrolyte multilayers



Gopinadhan, M.; Ahrens, H.; Günther, J.-U.; Steitz, R.; Helm, C. A., *Macromolecules* **2005,** *38* (12), 5228-5235

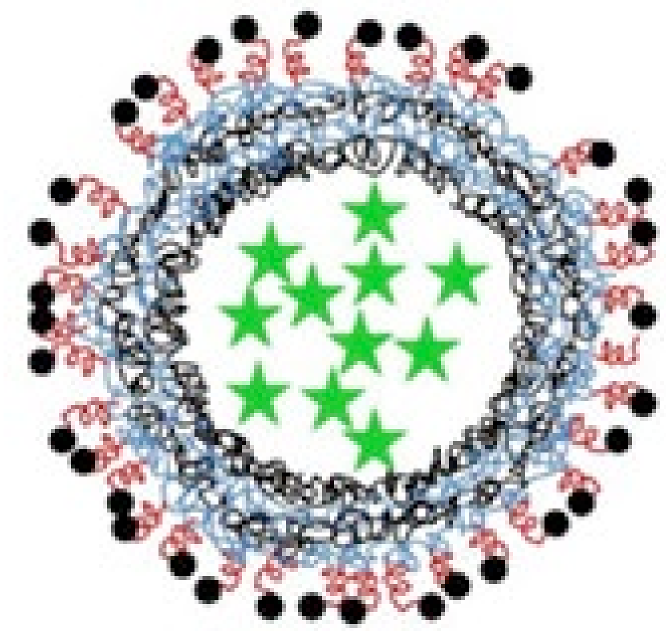
- Low temperature
- Low salt concentrations

- High temperature
- High salt concentrations

Applications of PEMs

Capsules

Capsules whose shells are made of PEMs have a very low permeability for charged substances.



S. Carregal Romero, et al. *Frontiers in Pharmacology* **3** (2012)

DNA:

DNAs are biological polyelectrolytes.

http://thetechjournal.com

Applications of polyelectrolytes

Diapers

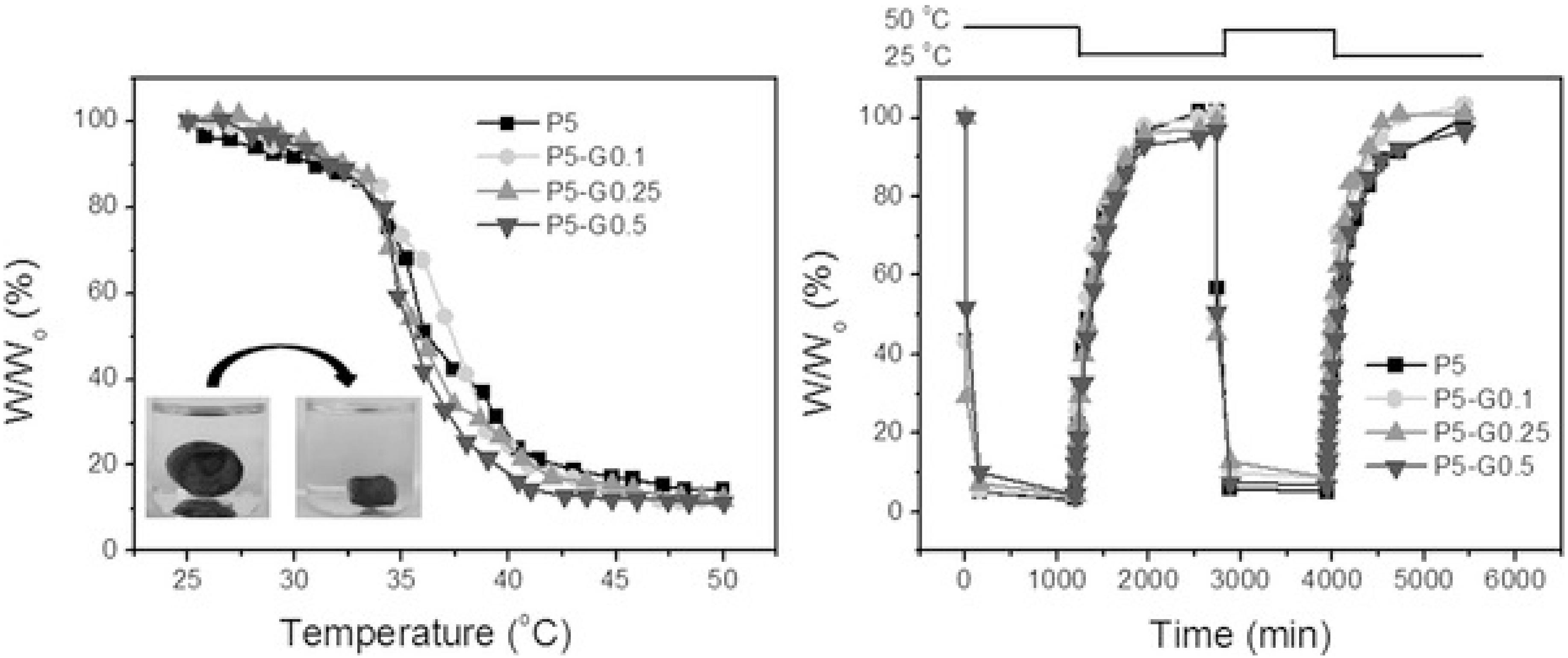
Toilet paper

Polyelectrolytes are able to absorb water in quantities several 100 times of their dry mass. Therefore, they are so-called superabsorbers.

Outline

- Introduction
- Gelation
- Sol-gel processes in inorganic materials
- Covalently linked hydrogels
  - Swelling
  - Deformation
- Ionically linked hydrogels
- Polyelectrolyte gels
- Responsive gels
- Microgels

Swelling of hydrogels



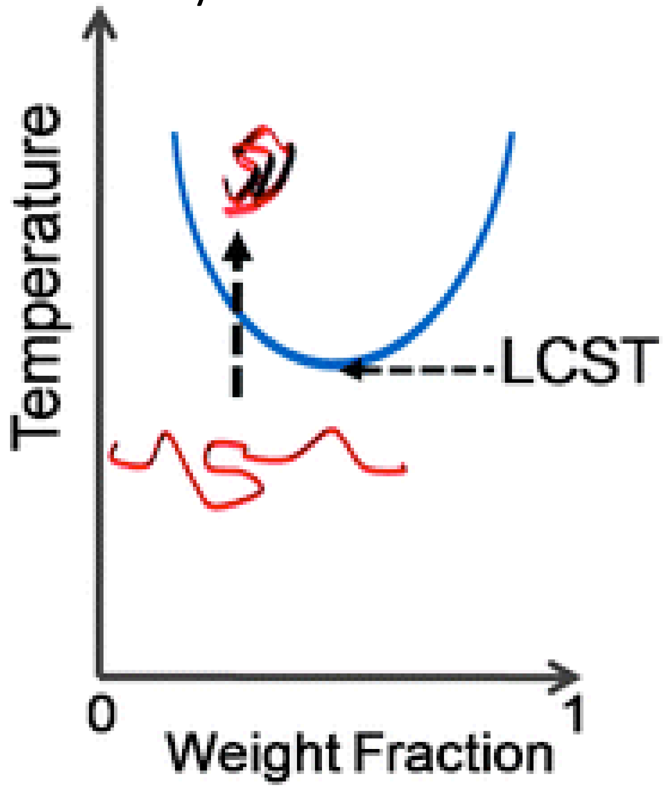
L. Qiu, D. Y. Liu, Y. F. Wang, C. Cheng, K. Zhou, J. Ding, V. T. Truong and D. Li, *Adv. Mater.*, 2014, **26**, 3333-+

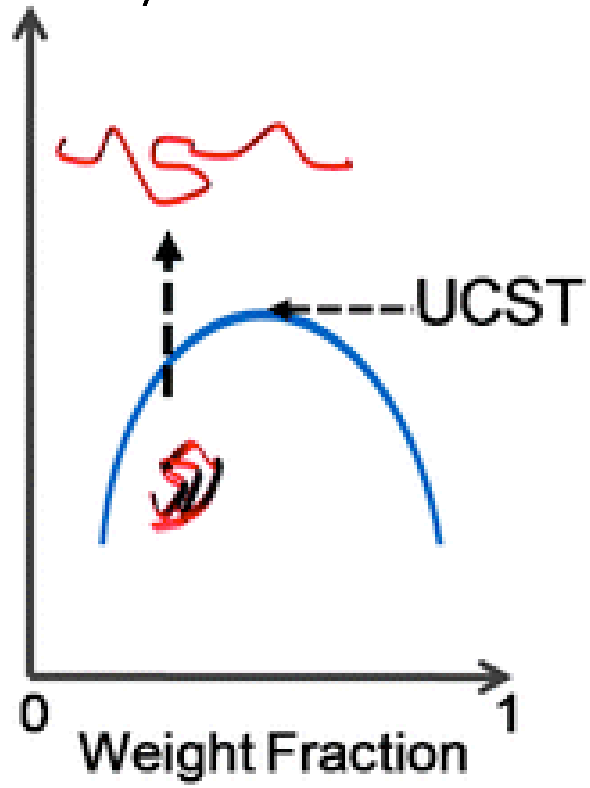
Temperature-responsive hydrogels

There are two different types of temperature responsive polymers:

Polymers with a **lower critical solution temperature (LCST)** are hydrated at T < LCST.

Polymers with an **upper critical solution temperature (UCST)** are hydrated at T > UCST:



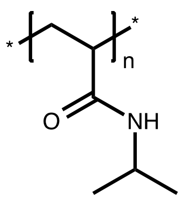


M. I. Gibson, R. K. O'Reilly. *Chemical Society Reviews* **42**, 7204 (2013)

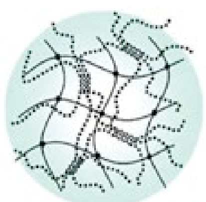
Temperature-responsive hydrogels

Example of a polymer with a LCST:

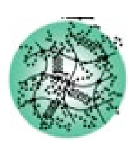
poly(N-isopropylacrylamide) (PNIPAM)



T < LCST



T > LCST

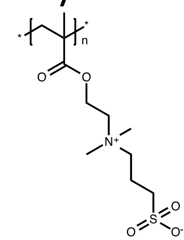


Imran, A. B.; et al. *Polym J* **2010,** *42* (11), 839-851.

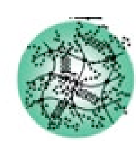
- At *T* < LCST: H-bonds between water molecules and PNIPAM form and solubilize the polymer.
- At *T* > LCST: H-bonds between water molecules and PNIPAM molecules are too weak compared to $k_B T$. The system minimizes interactions of water molecules with polymers such that the polymer collapses. The system collapses to maximize the **enthalpy**.

Example of a polymer with an UCST:

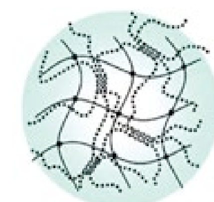
2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl) ammonium hydroxide (PMEDSAH)



T < UCST

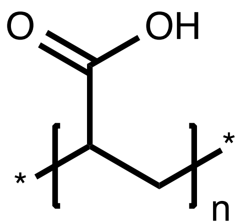


T > UCST



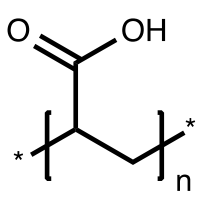
- At *T* < UCST: Ionic interactions within the polymers are strong and prevent swelling of the hydrogel.
- At *T* > UCST: Ionic interactions become weaker relative to $k_B T$ such that the hydrogel can swell to maximize the **entropy** of the system.

pH-responsive hydrogels



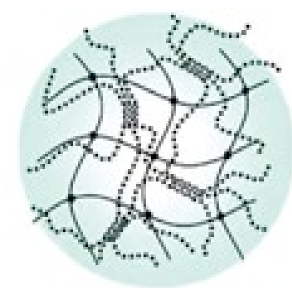
Example: poly(acrylic acid) (PAA)

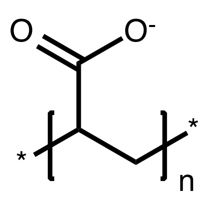
pH < pK_a



At pH < pK_a: PAA is uncharged and is poorly soluble in water.

pH > pK_a

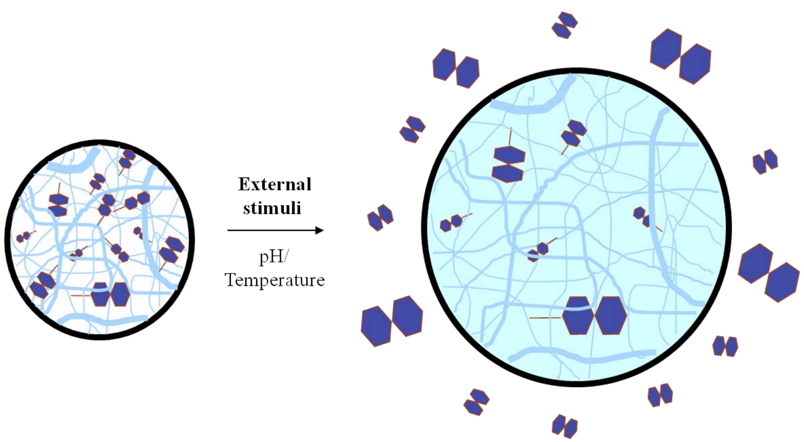




At pH > pK_a: PAA is charged and becomes soluble in water.

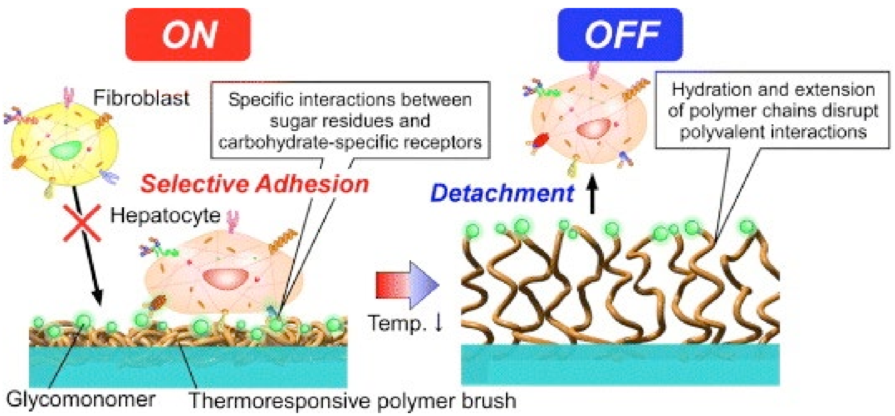
Responsive hydrogels: Applications

Controlled release of active ingredients



P. Ferreira, J. F. J. Coelho, J. F. Almeida, M. H. Gil, *Photocrosslinkable Polymers for Biomedical Applications*. Biomedical Engineering - Frontiers and Challenges (2011).

Tissue engineering/surface modification



I. Naokazu, et al., *Science and Technology of Advanced Materials* **13**, (2012).

Outline

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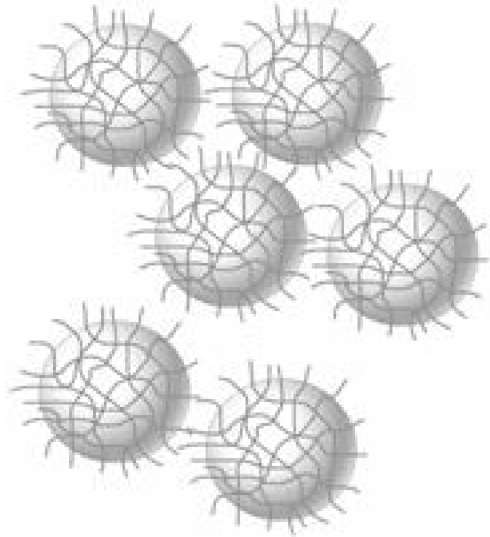
- Ionically linked hydrogels
- Polyelectrolyte gels
- Responsive gels
- Microgels

Microgels

Microgels are microparticles made of a polymeric gel.

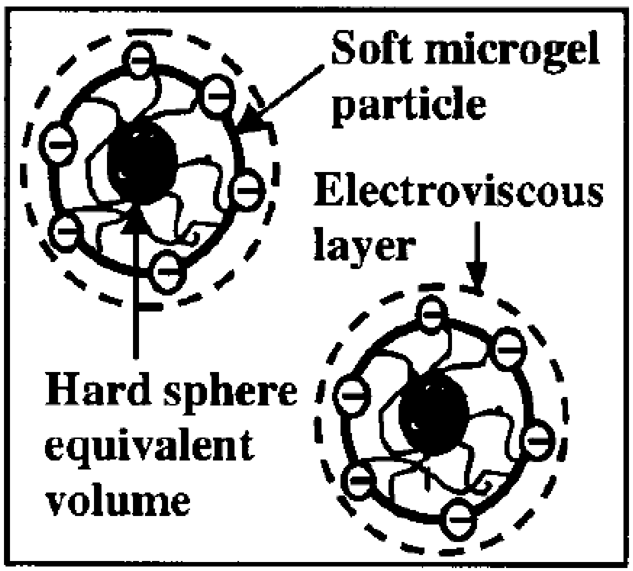
- Microgels are dispersed in a solvent.
- Microgels are swollen by the solvent.
- Microgels have a stable structure. They are either chemically crosslinked or have strong physical crosslinks.



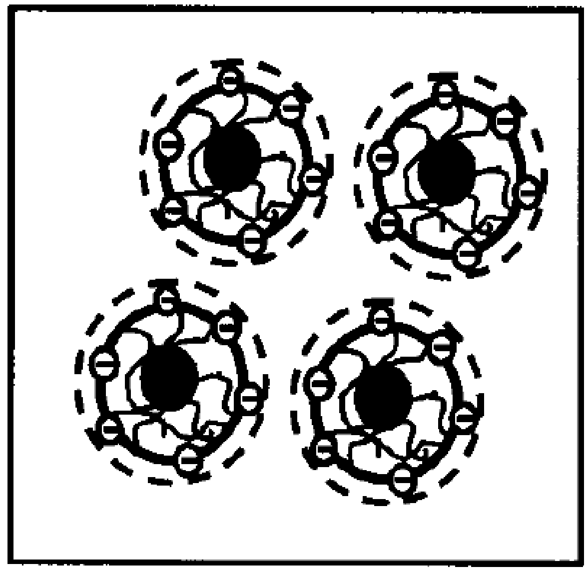
Microgels

The influence of the microgel concentration on their conformation.

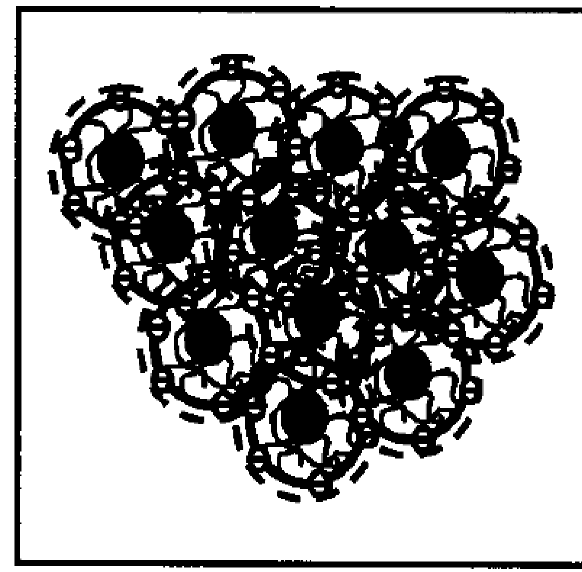
Dilute regime:
Microgels have a high water content.



Semi-dilute regime:
Microgels have an intermediate water content.



Concentrated regime:
Microgels have a low water content.



Tan, B. H.; Tam, K. C.; Lam, Y. C.; Tan, C. B. *Journal of Rheology (1978-present)* **2004,** *48* (4), 915-926

Microgels

The influence of the microgel concentration on their conformation.

Dilute regime **Concentrated regime**

$d_{av} \approx 20\ \mu m$

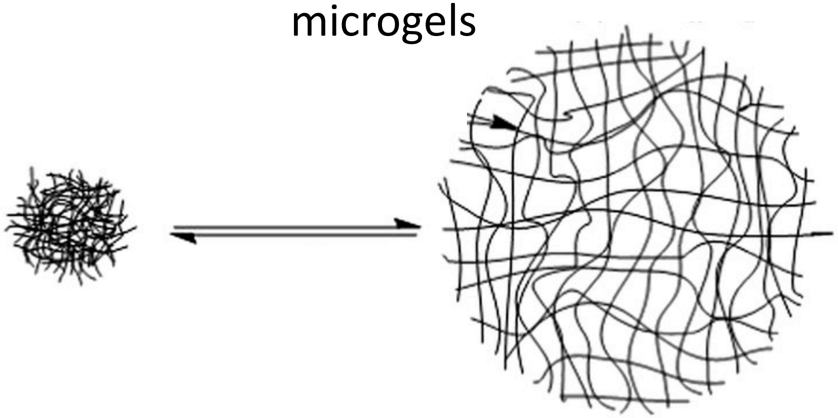
$d_{av} \approx 150\ \mu m$

Φ: 20 40 60 80

M. Kessler *et al.*, Macromolecular Rapid Communications **43**, 2200196 (2022)

Does size matter?

microgels



J. A. Bonham, M. A. Faers and J. S. van Duijneveldt, *Soft Matter*, 2014, **10**, 9384-9398

bulk hydrogels

Which hydrogel swells fastest?

A. Microgels
B. Bulk hydrogels
C. Hydrogels processed into mm-sized fibers
D. All hydrogels swell equally quickly.

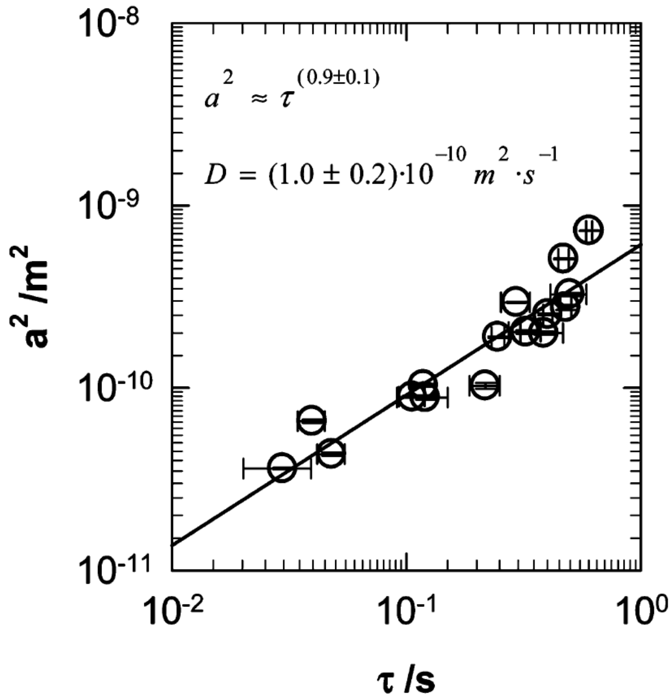
Swelling of microgels

Microgels swell much faster than bulk hydrogels.

The diffusion distance for water molecules is much shorter.

$$\tau = \frac{r^2}{\Pi^2 D}$$

τ: characteristic swelling time [s]
r: radius of microgel particle [m]
D: diffusion constant in gel [m^2/s]
a: equilibrium radius of hydrogel [m]



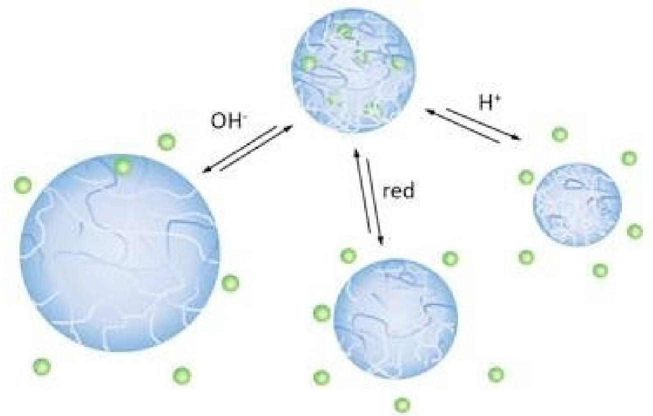
Suárez, I. J.; Fernández-Nieves, A.; Márquez, M. *The Journal of Physical Chemistry B* **2006,** *110* (51), 25729-25733

Swelling of microgels

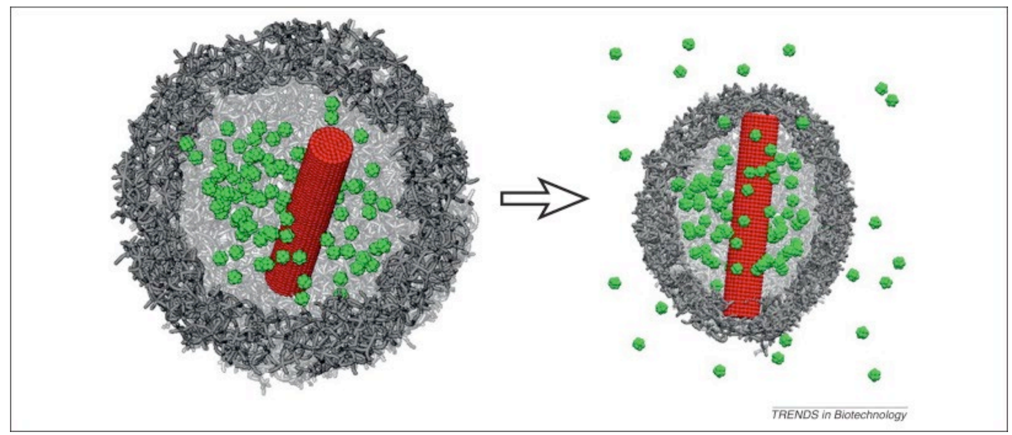
Movie taken by Matteo Hirsch

Microgels as delivery vehicles

Example: Triggered release of encapsulants



http://www.ipc.rwth-aachen.de/groups/ipc-rwth/ak-boeker/research/research-interests.html

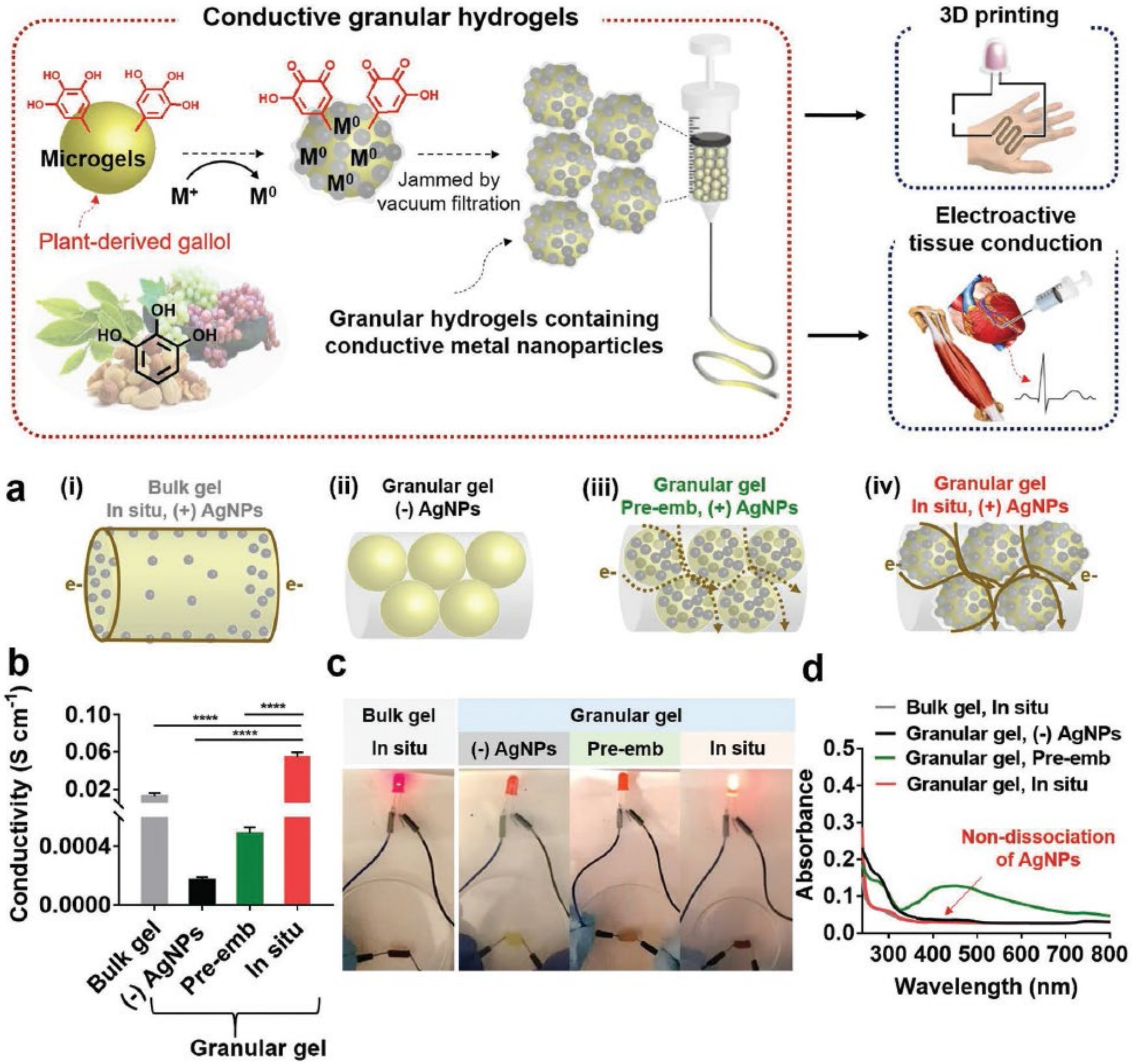


Z. G. Mills, W. Mao and A. Alexeev, *Trends in Biotechnology*, 2013, **31**, 426-434.

Capsules can be designed to release encapsulants when swollen. In this case, the higher mobility of encapsulants in the swollen state increases diffusion kinetics.

Capsules can be designed to release encapsulants when collapsed. In this case, diffusion is driven by the osmotic pressure difference.

Application:
3D printing of microgels



Shin, M.; *et al. Advanced Science* **2019**, *6* (20), 1901229