Supramolecular Crosslinked Hydrogels: Similarities and Differences with Chemically Crosslinked Networks

Sandrine Laquerbe, Cédric Lorthioir[b], Tetsuharu Narita[a], Christophe Meyer[c], Guylaine Ducouret[a], Patrick Perrin[a], Nicolas Sanson[a]

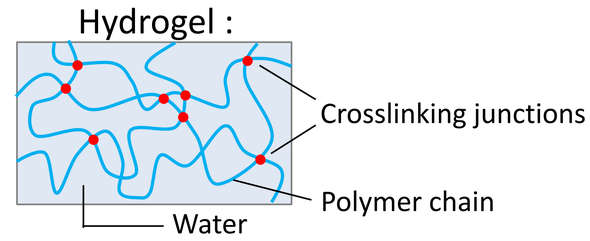
[a] *Soft Matter Sciences and Engineering, ESPCI Paris, PSL University, Sorbonne Université, CNRS, F-75005 Paris, France.*
[b] *Sorbonne Université, CNRS, Collège de France, Laboratoire de Chimie de la Matière Condensée de Paris, LCMCP, F-75005 Paris, France.*
[c] *Equipe Chimie Moléculaire et Catalyse, Unité Chimie Moléculaire, Macromoléculaire, Matériaux (C3M)-UMR 7167 ESPCI Paris, CNRS, PSL University, F-75005 Paris, France.*

Objectives

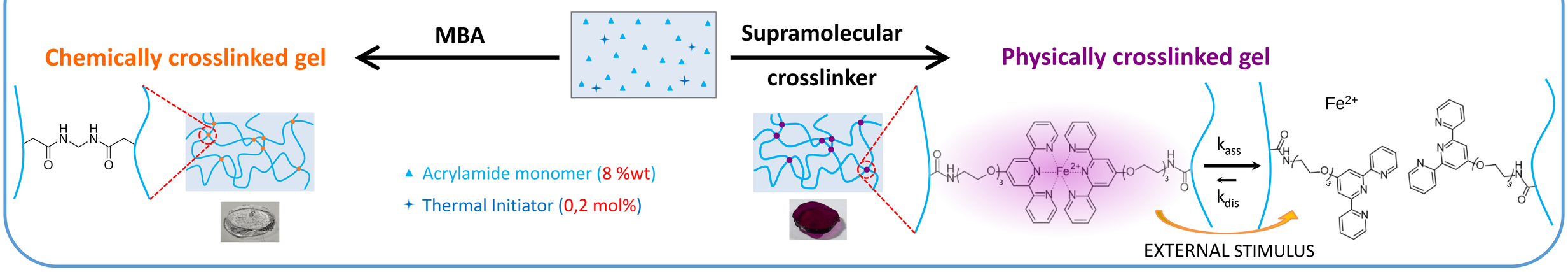
- Prepare dual gels by mixing permanent (= chemical) and non-permanent (= supramolecular) crosslinks

⇨ Modulation of gel properties (mechanical, rheological…)

⇨ Stimuli-responsive materials with controlled structure (oxidant, pH…)

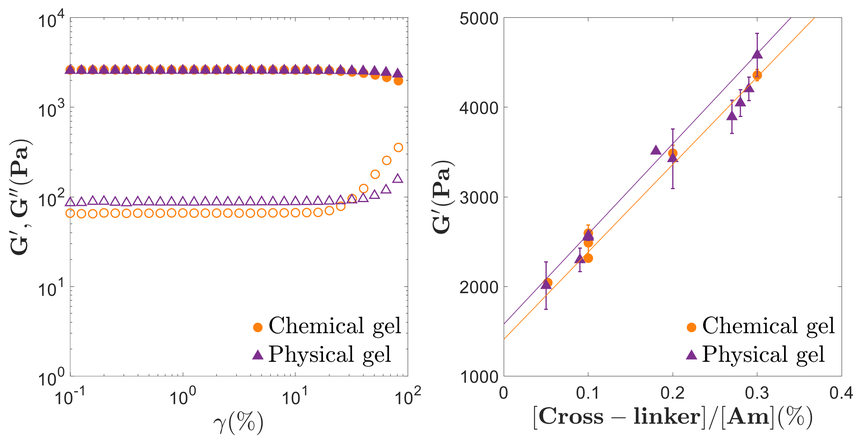


Gel Synthesis



Similarities between chemical and physical gel

In network structure (rheology)



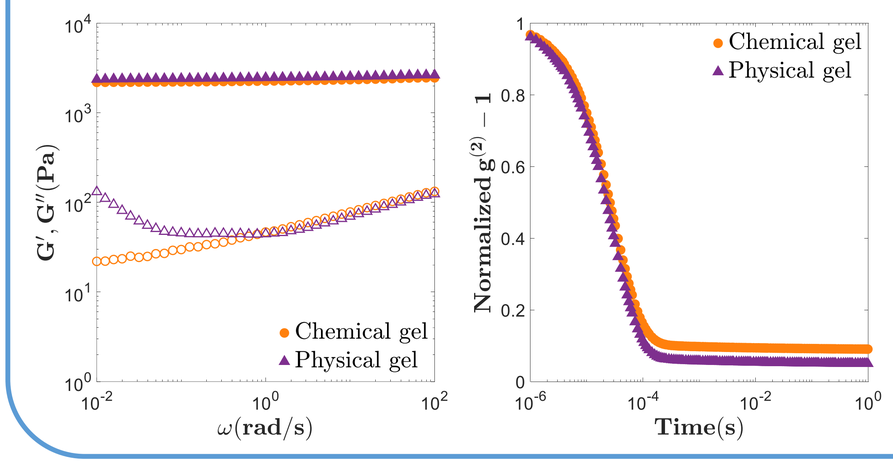
- **Model for ideal networks:**

$$G' = G'_e + a\frac{[crosslinker]}{[monomer]}$$

Entanglements : Linear pAm solution : $G' \sim 1300\ Pa\ > G''$

Crosslinking efficiency : ~40 % for both gels (similar to literature on chemical pAm gels)

In dynamics (Dynamic Light Scattering, rheology)



- No cross-over between G' and G''
- A unique decorrelation for both gels at the same decorrelation time

⇨ In the supramolecular gel, **dynamics are slower than the observation time**

Supramolecular gel behaves similarly to a chemically crosslinked network

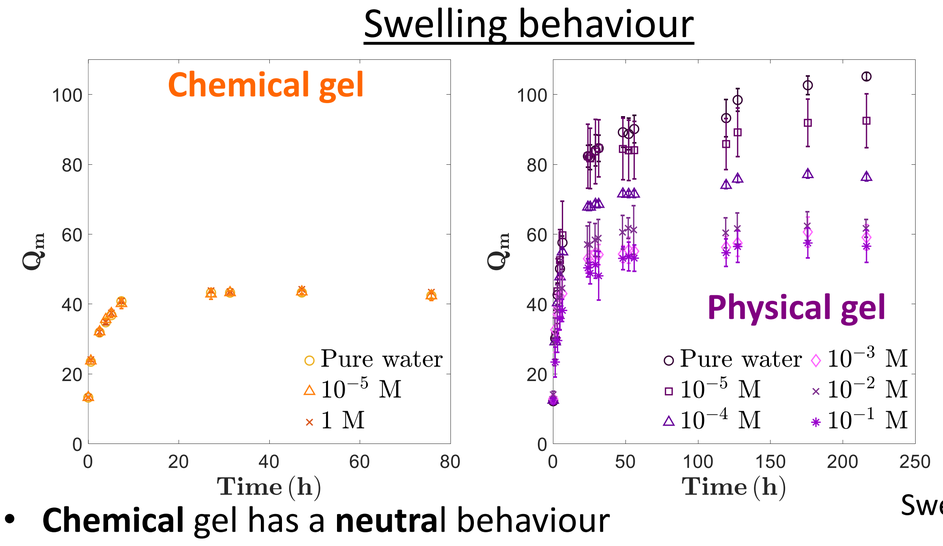
Bis-complex formation constants:

- $\beta_2 > 10^{16}\ L^2.mol^{-2}$
- $k_{diss} = 1{,}6.10^{-7}\ s^{-1}$

Rubinstein, Colby *Polymer Physics*
Journal of The Chemical Society, 1962, pp 341-350
Journal of Materials Chemistry, 2012, 22, 21366

Differences between chemical and physical gel

Swelling behaviour

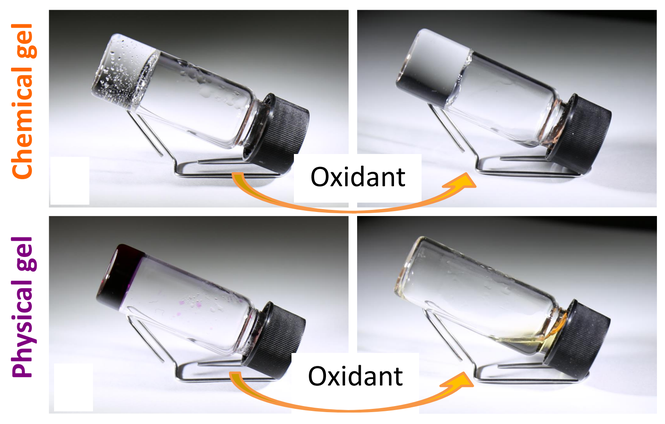


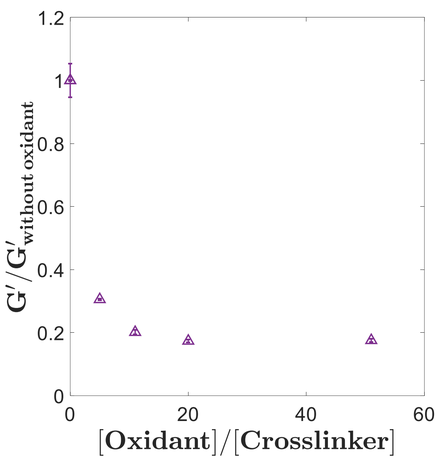
- **Chemical** gel has a **neutra**l behaviour
- **Physical** gel shows a **polyelectrolyte** behaviour

Swelling ratio :

$$Q_m = \frac{m_{gel}(t)}{m^0_{polymer}}$$

Stimuli-responsive gels





- **Gel-to-sol transition** thanks to an oxidant
- **Controlled tuning of mechanical properties**

Conclusions

One-pot synthesis of a supramolecular gel with:

- **Structure and dynamics similar to chemical networks** at investigated observation time ($\sim 10^{-6}s - 10^{2}s$)
- But a **polyelectrolyte** behaviour and a dormant **stimuli-responsiveness**

Outlooks

- Better understanding of gel structure via **Double Quanta NMR,**
- **Reversibly transform** physical gels to solution thanks to **electrochemistry,**
- Study of dual gels by **mixing both types of crosslinker** through a one-pot synthesis.