

# STRUCTURATION AND RHEOLOGICAL PROPERTIES OF GELS MADE FROM GLUTEN PROTEINS

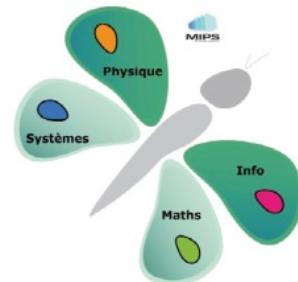
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- 3) Ingénierie des Agropolymères et Technologies Emergentes UMR 1208, INRA, 34000 Montpellier , France

FUNDING: INRA / LABEX NUMEV



# Context

Wheat, Rye, Barley



**GLUTEN**

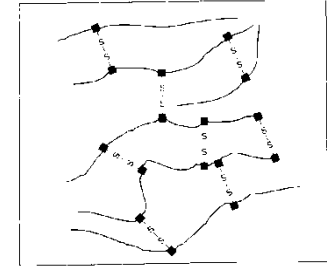
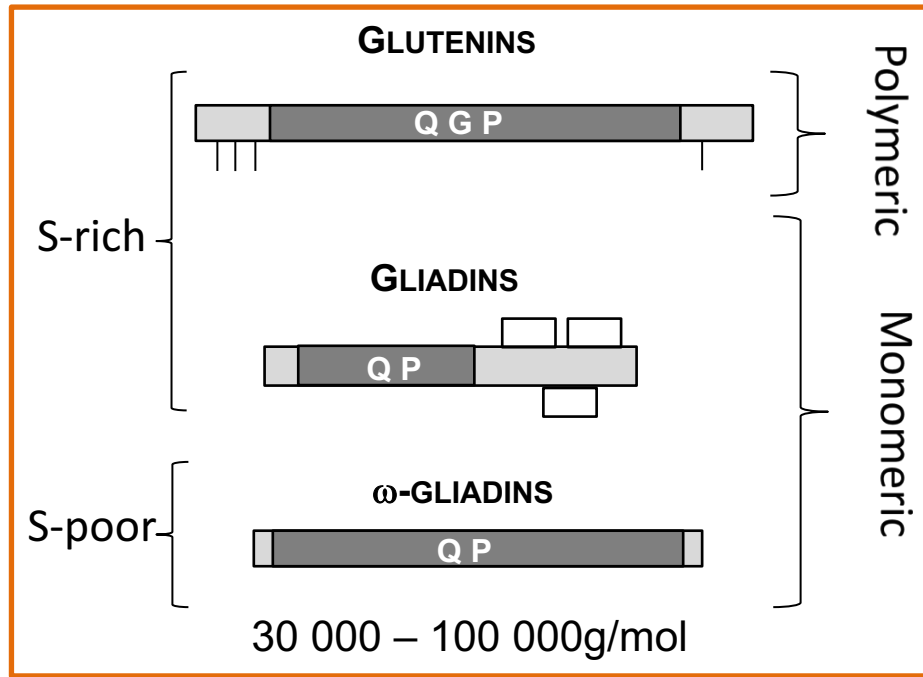
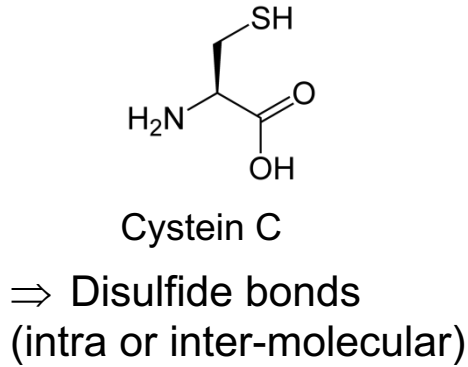
**Unique** visco-elastic network !  
Role of kneading (transient network)



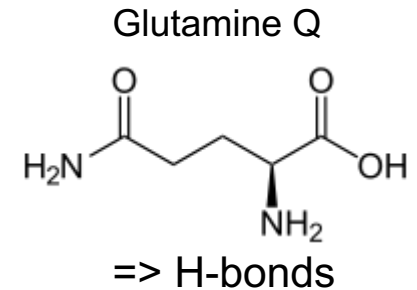
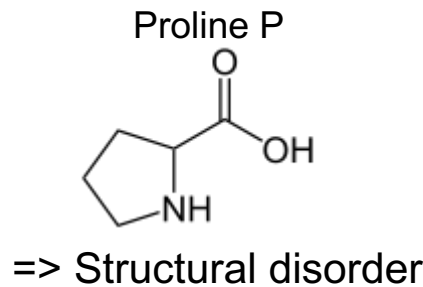
Bread with no gluten

# Gluten proteins

More than 50 proteins, classification:



  
 Repetitive domain

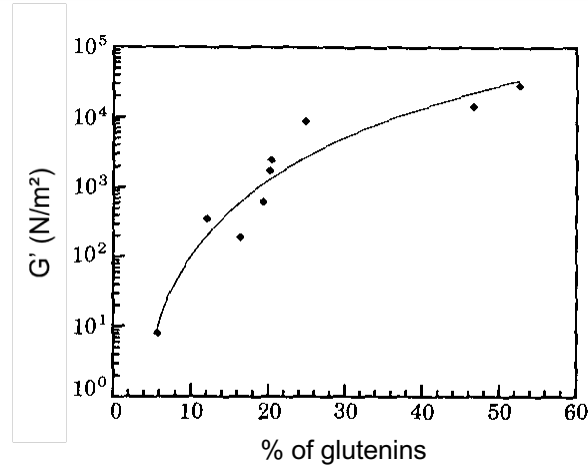


**Non soluble in water**

Prolamins: soluble in water/ethanol – acetic acid

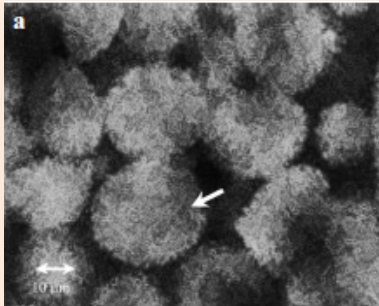
# Rheological properties: background

## GLUTENIN CONTRIBUTION TO ELASTICITY



Cornec et al, *J. Cereal Sci.* 1994

## PARTICLE GEL

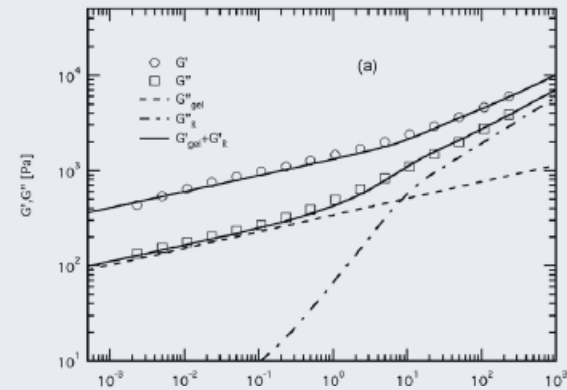


Don et al, *J. Cereal Sci.* 2003

**Glutenin macro polymer**

1.5% SDS

## POLYMERIC GEL



Ng et al, *J. Rheol.* 2008

**Critical gel**

Water

Studies performed in water: bad solvent of gluten proteins

# Outline

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## I- System

## II- Structure

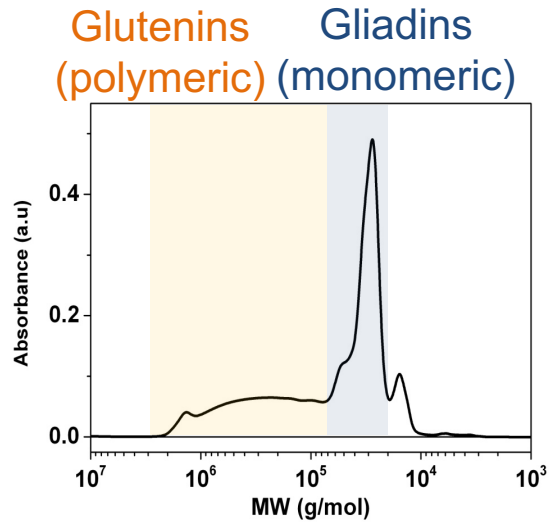
- Dilute regime
- Concentrated regime

## III- Rheology

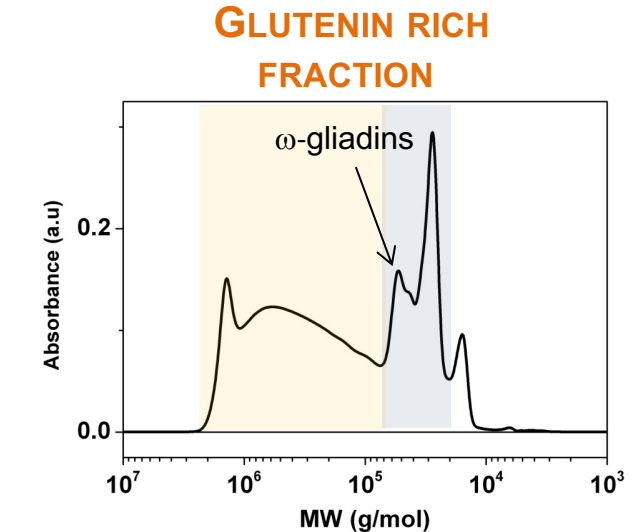
- Concentration dependence
- Ageing effect

# Model system: fraction enriched in glutenins

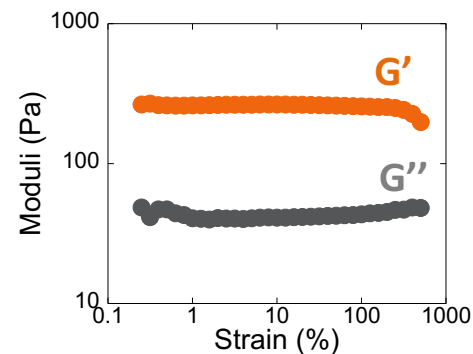
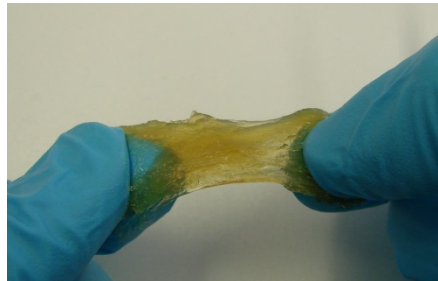
## GLUTEN SOLUBILISED IN WATER/ETHANOL (50/50)



Purification



Like a glue!



Very large linear regime.

# Outline

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## I- System

## II- Structure

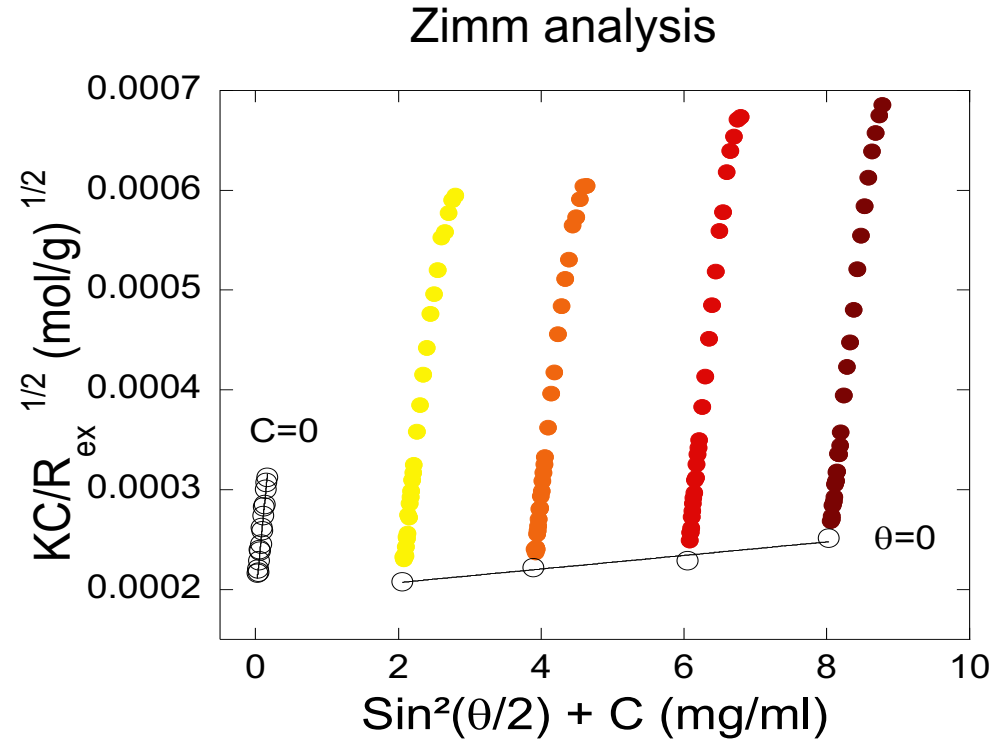
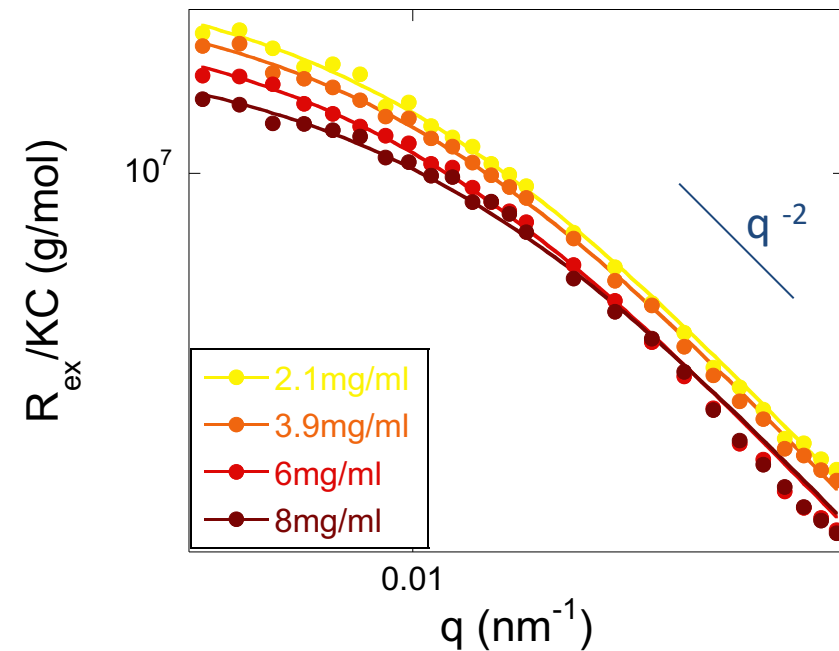
- Dilute solutions
- Concentrated regime

## III- Rheology

- Concentration dependence
- Ageing effect

# Structure in dilute solution

## STATIC LIGHT SCATTERING



Debye model => **polymeric structure**

**Very large polymeric objects:  
several proteins**

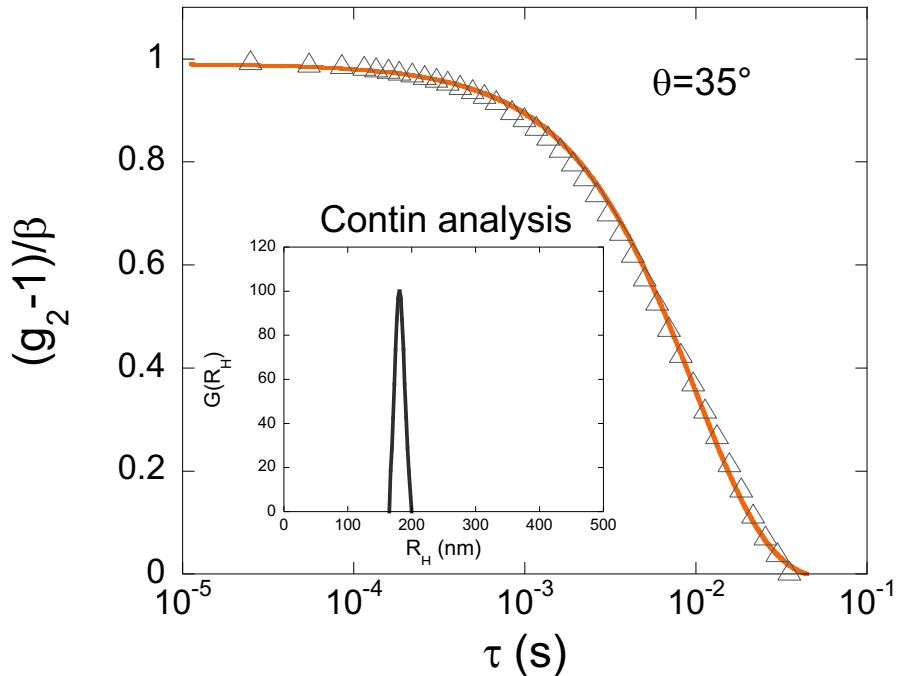
$$M_{w \text{ app}} = 27\,000\,000 \text{ g/mol}$$

$$R_{g \text{ app}} = 150 \text{ nm}$$



# Dynamics in dilute solution

## MULTI-ANGLE DYNAMIC LIGHT SCATTERING

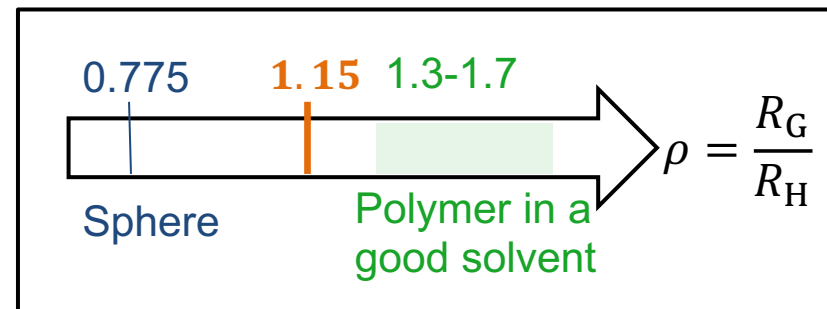
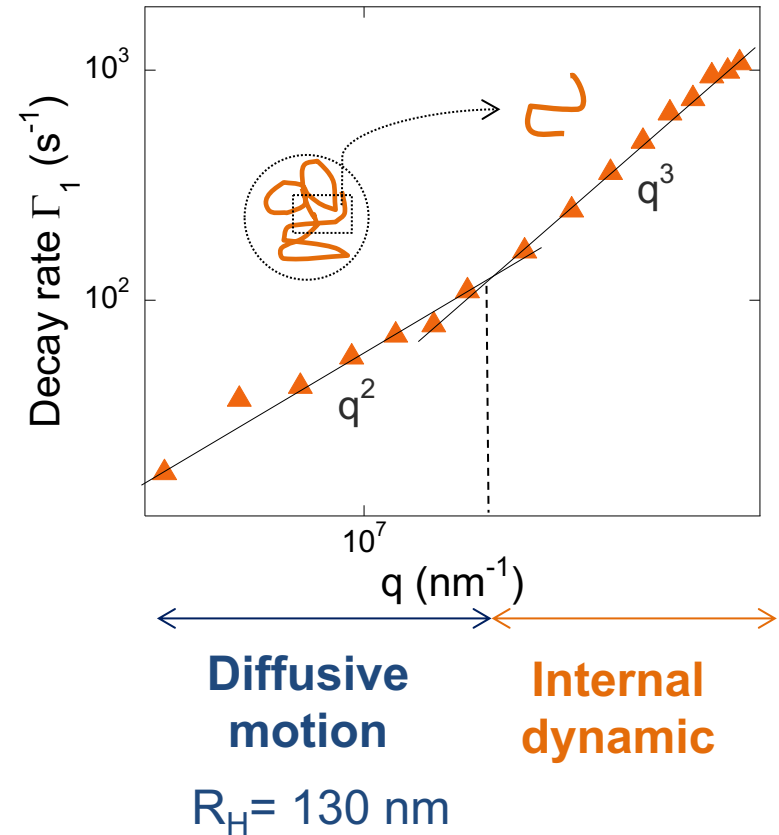


Monoexponential decay at low angles

Cumulant analysis

$$\Gamma_1 = - \lim_{t \rightarrow 0} \frac{d(g_2 - 1)}{dt}$$

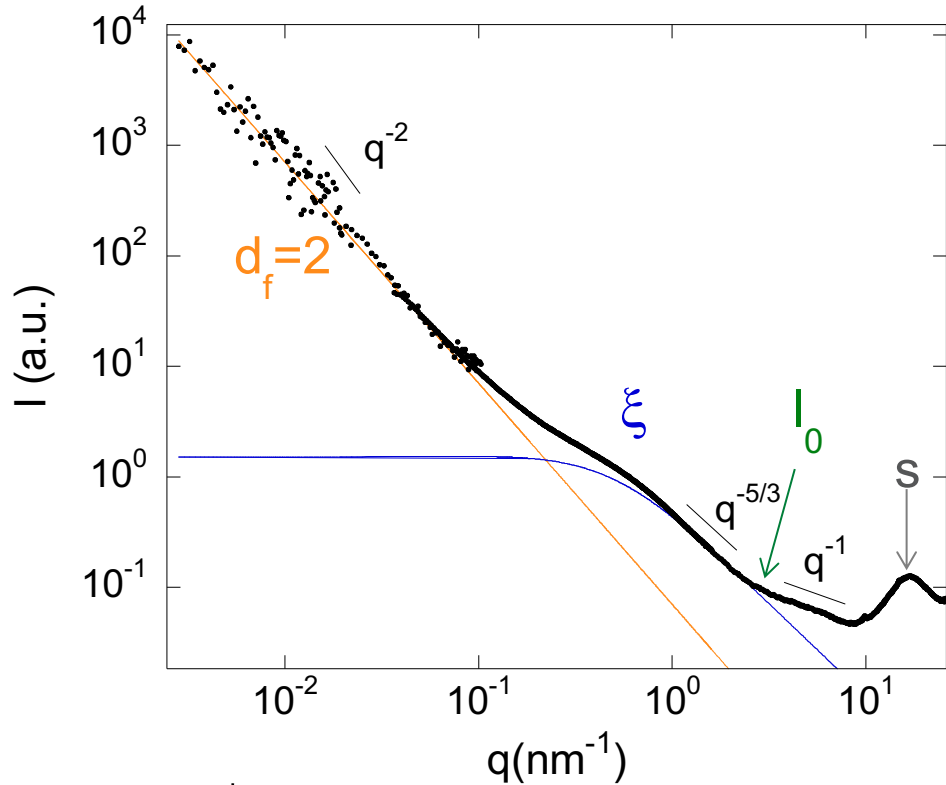
**Monodisperse objects with an internal dynamic**



**Crosslinked - Branched polymeric structure**

# Structure in concentrated systems

## STATIC X-RAY AND NEUTRON SCATTERING

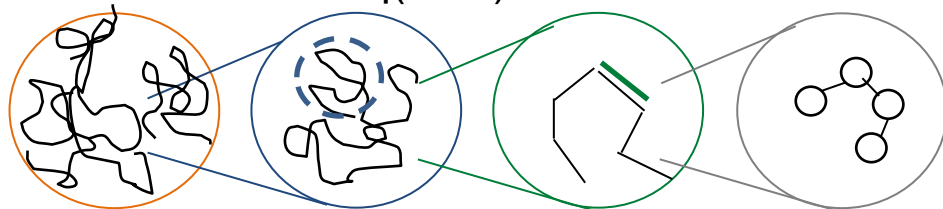


$d_f$  : fractal dimension  
(spatial concentration fluctuations)

$\xi$  : correlation length = blob size  
(time dependent concentration fluctuation)

$l_0$  : persistence length

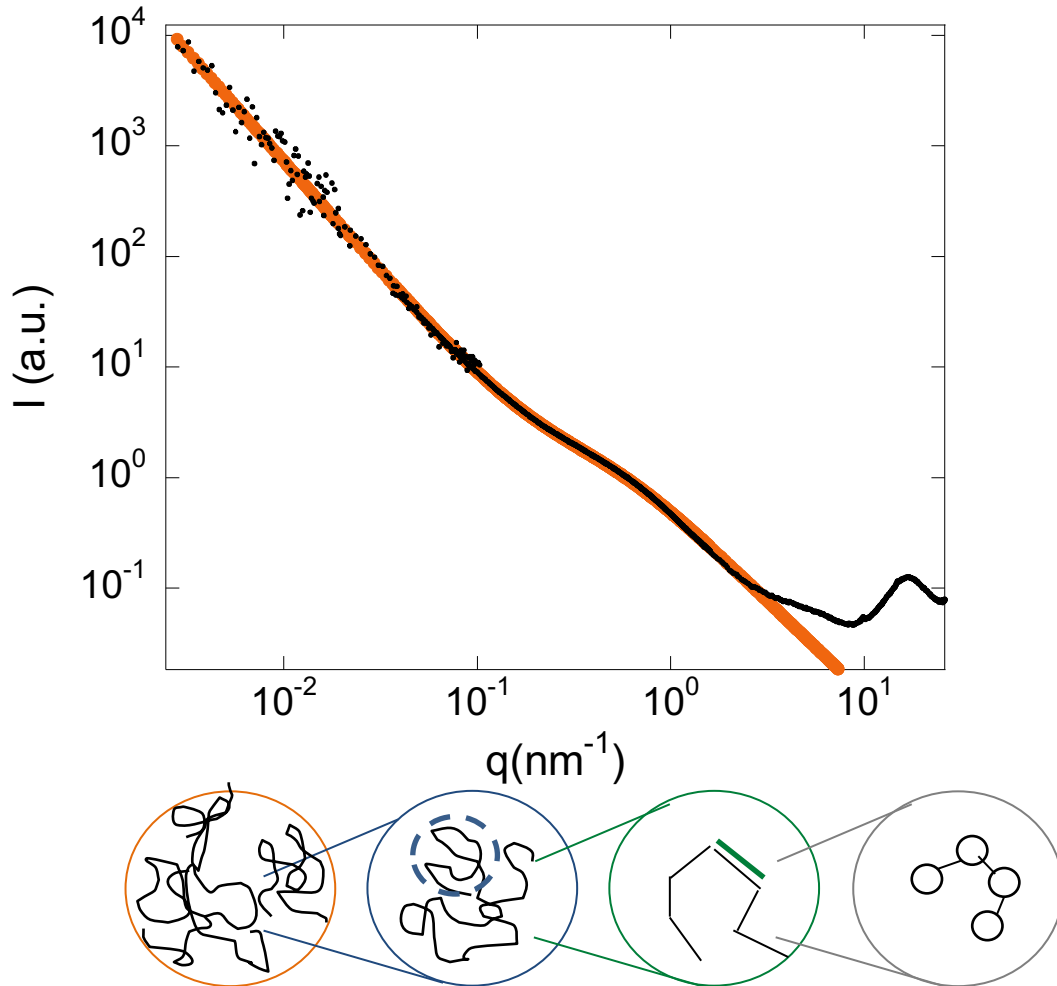
$S$ : average distance between atoms



**=> Polymeric network with a fractal organisation at larger scale**

# Structure in concentrated systems

## STATIC X-RAY AND NEUTRON SCATTERING



Model derived from polymeric gels:  
Falcao et al, *Macromolecules* 1993

$$I = a_1 \frac{(1+q\xi)^{1/3}}{(1+q^2\xi^2)} [1 + a_2 q^{-d_f}]$$

$$d_f=2 \quad \xi=f(C)$$

Semi-dilute regime of a polymer  
in a good solvent:

$$\xi = l_0 \cdot \phi^{-3/4}$$

$$l_0=0.6 \text{ nm}$$

comparable to unstructured proteins



=> Polymeric network with a fractal organisation at larger scale

# Outline

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## I- System

## II- Structure

- Dilute solutions
- Concentrated regime

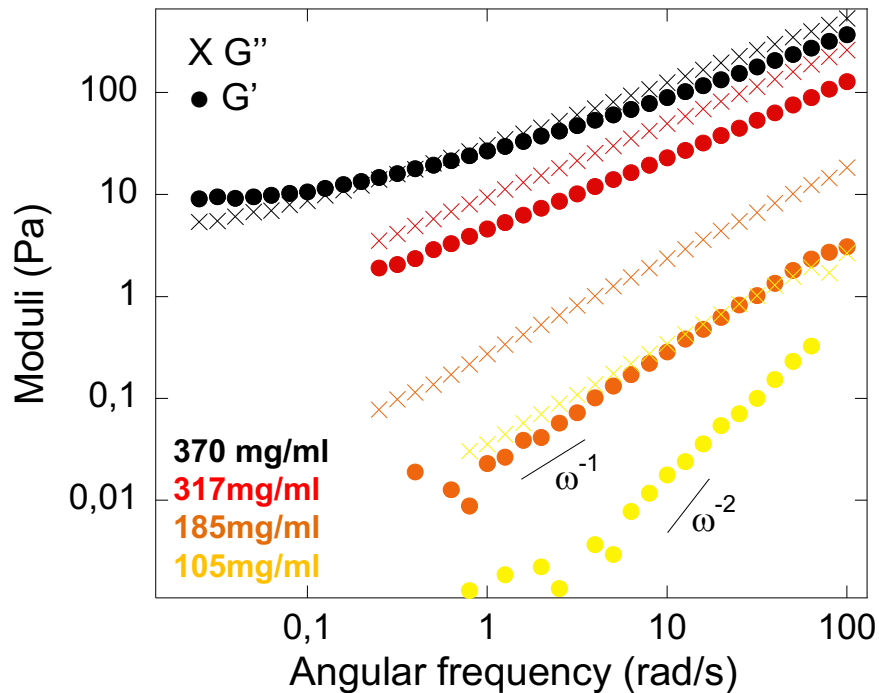
## III- Rheology

- Concentration dependence
- Ageing effect

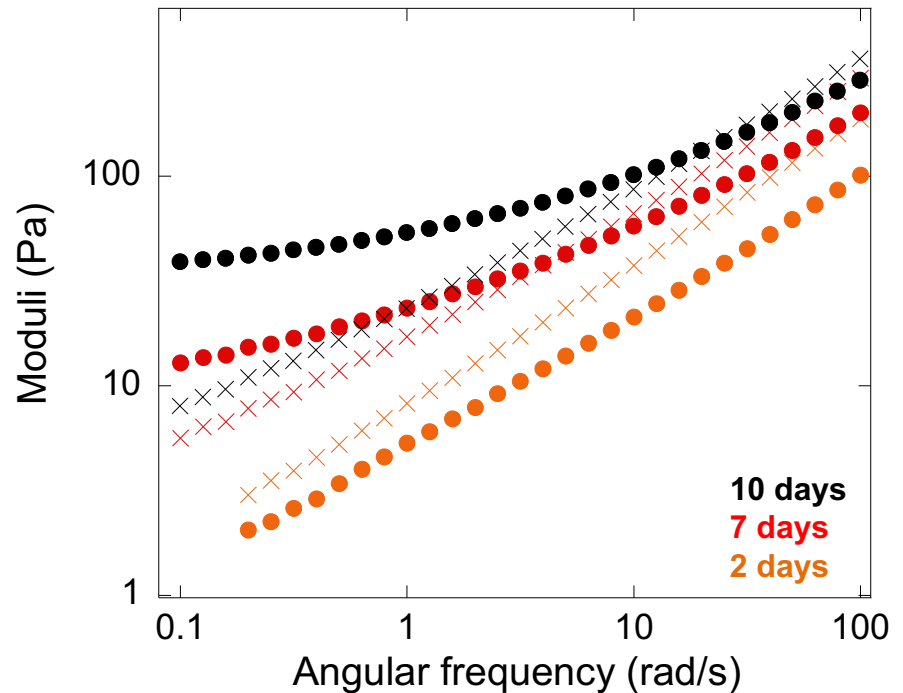
# C° and time dependent rheological properties

## LINEAR RHEOLOGY

### Concentration effect (day1)



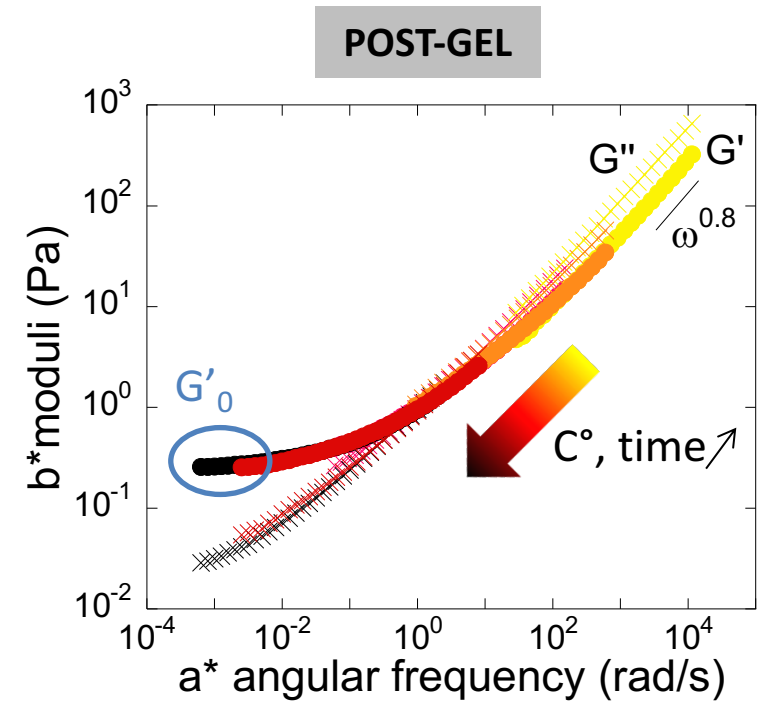
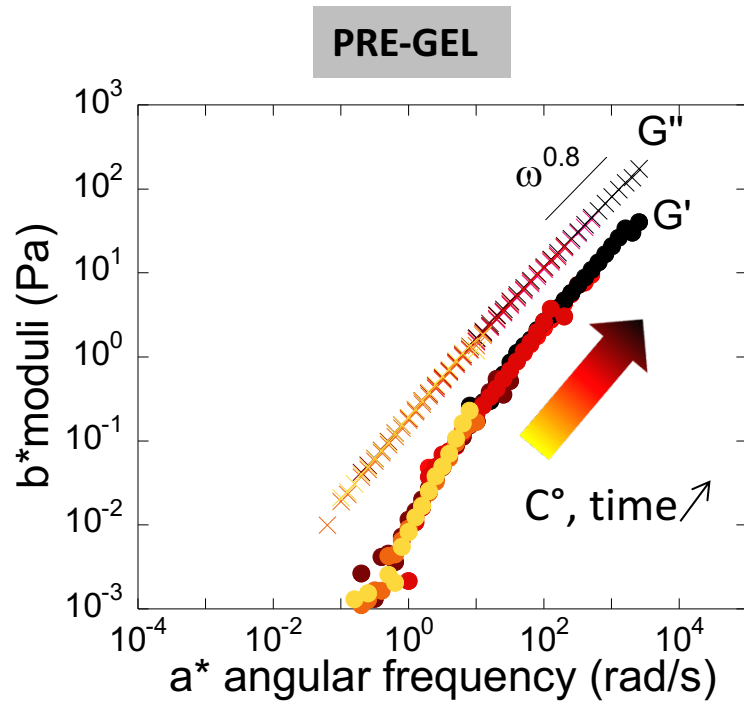
### Ageing effect (317 mg/ml)



Sol-gel transition with ageing time and concentration

# Self-similar structure below and above critical gel

## Master curves

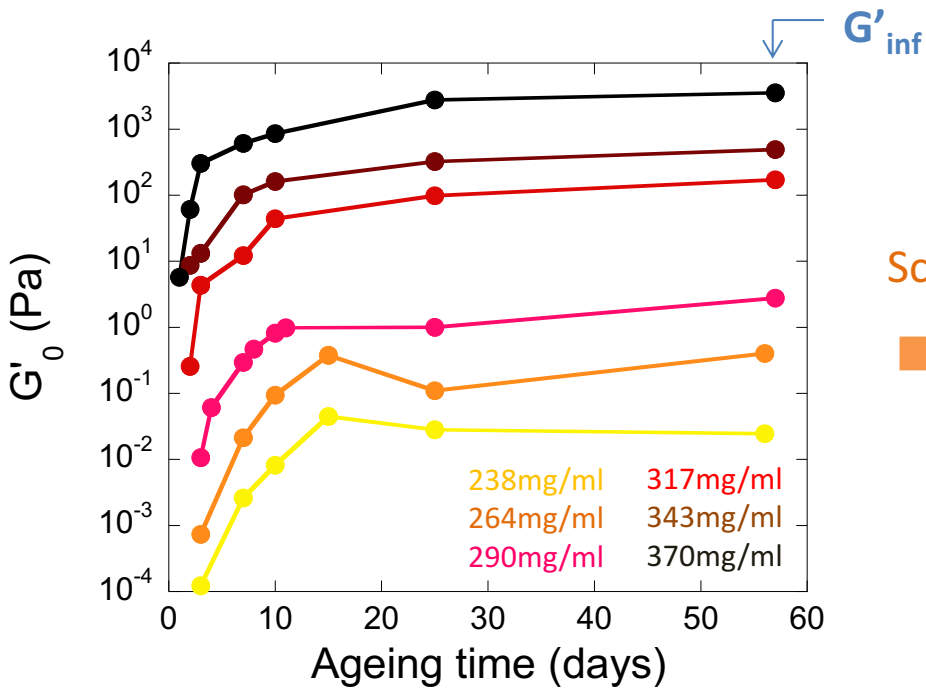


**Critical gel:  $G' \sim G'' \sim \omega^n$**  Winter–Chambon gel point criterion, 1986

$n_{\text{exp}} = 0.8 \Rightarrow$  consistent with percolation theory:  $n = 0.75$

**Time-ageing-concentration superpositions**  
**Self similar structures below and above critical gel**

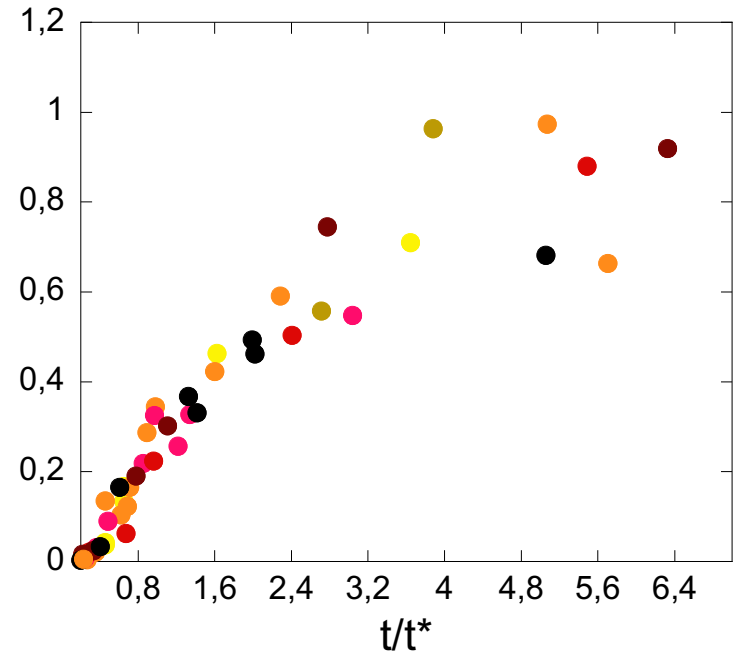
# Gelation kinetics



Scaling

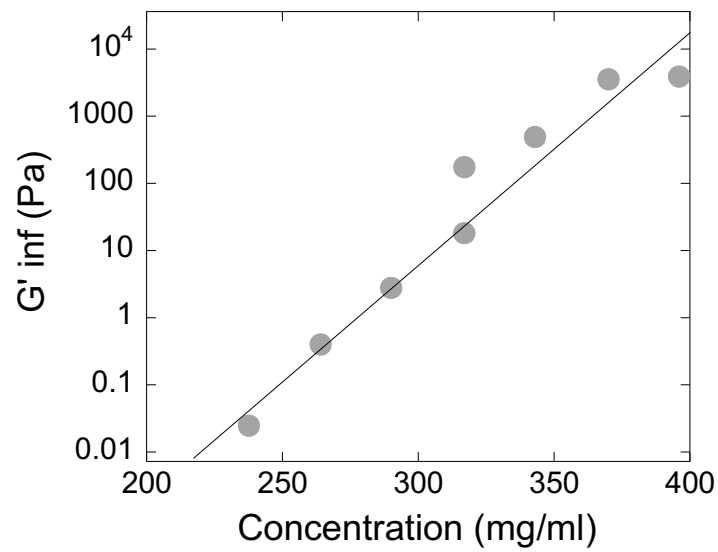
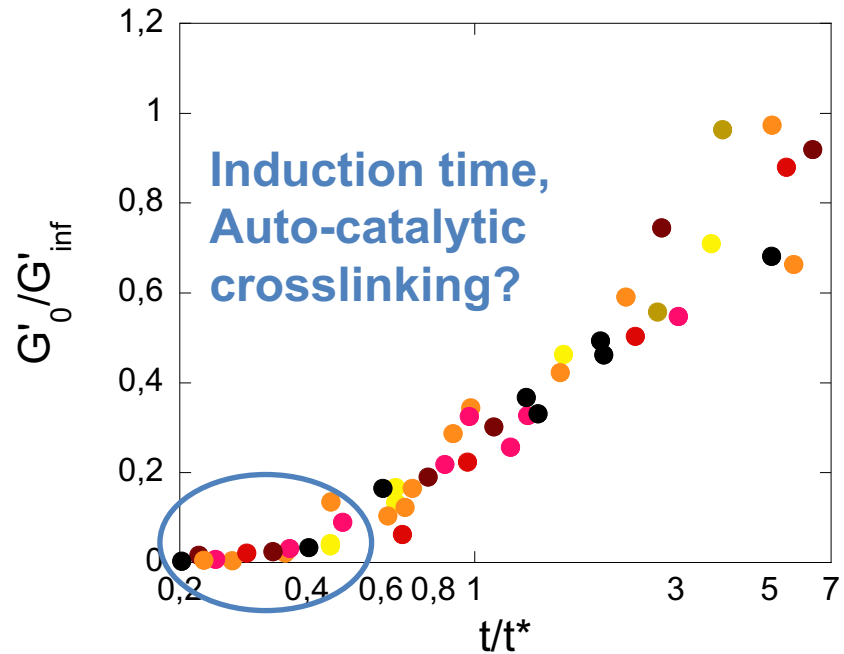
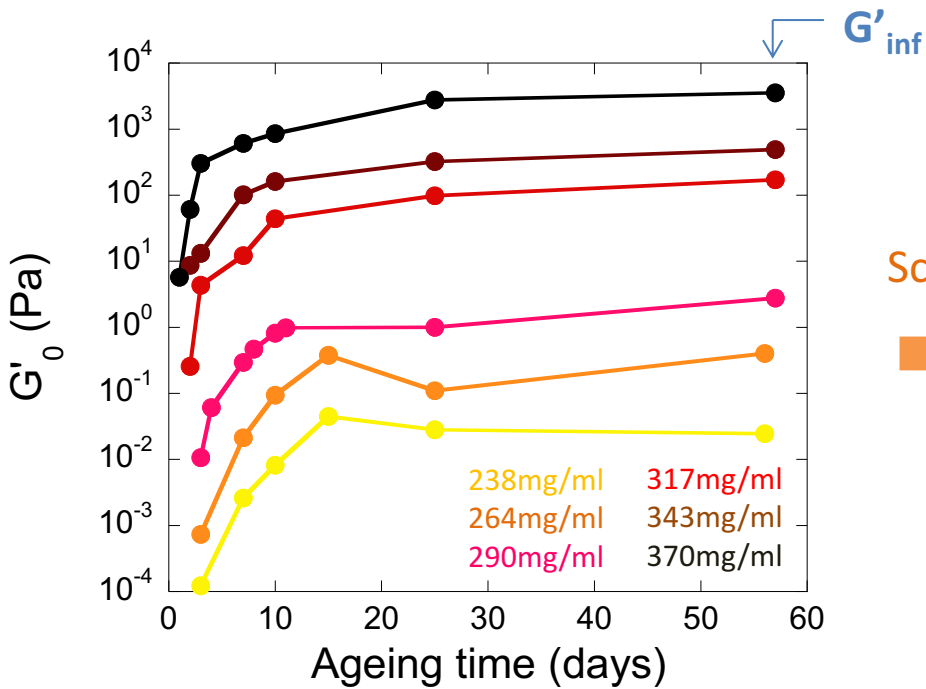


$G'_0/G'_{inf}$



- Exponential evolution: atypical - meaning?

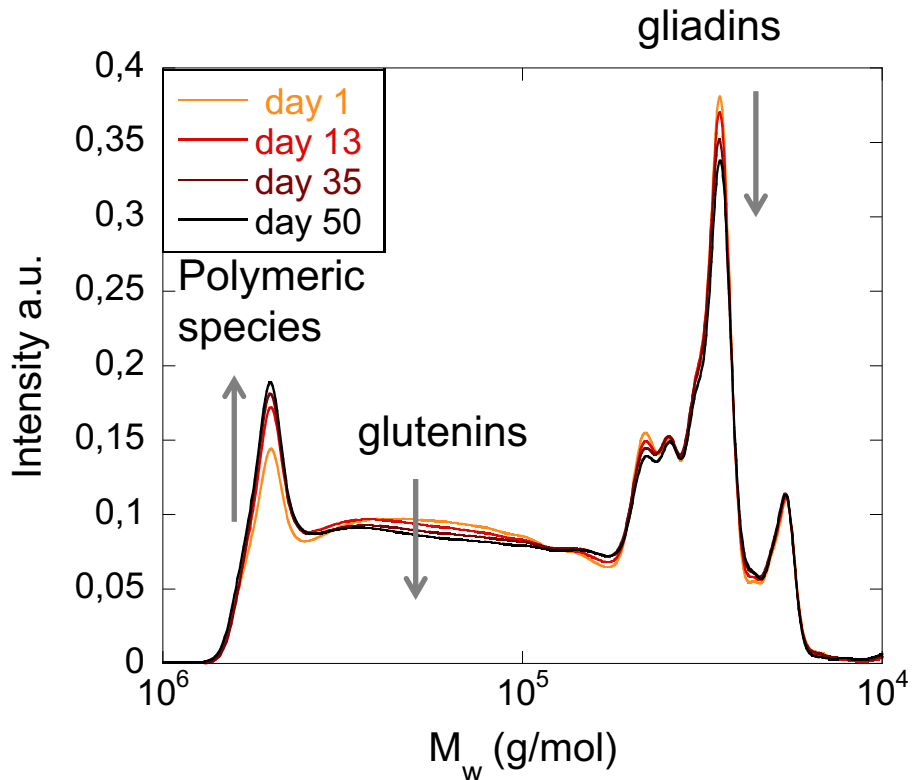
# Gelation kinetics



- Exponential evolution: atypical - meaning?

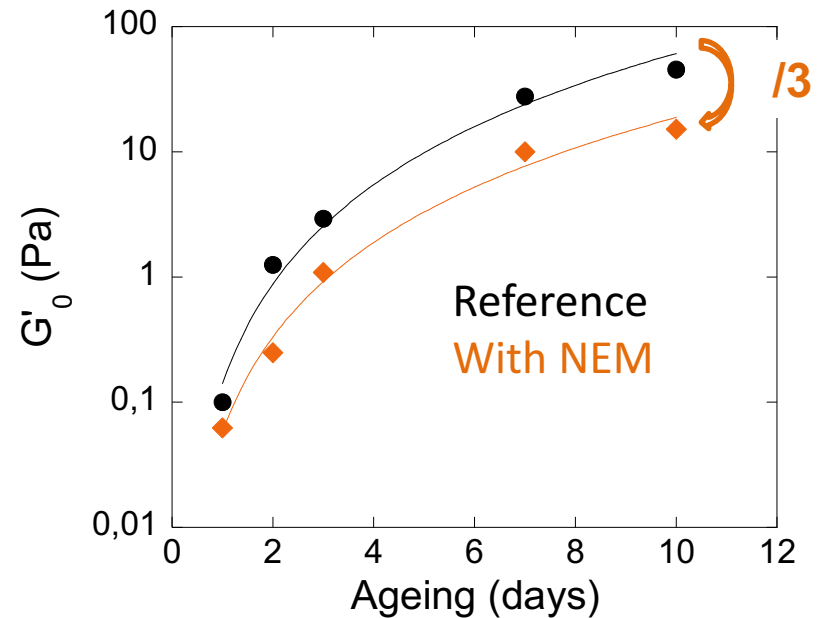
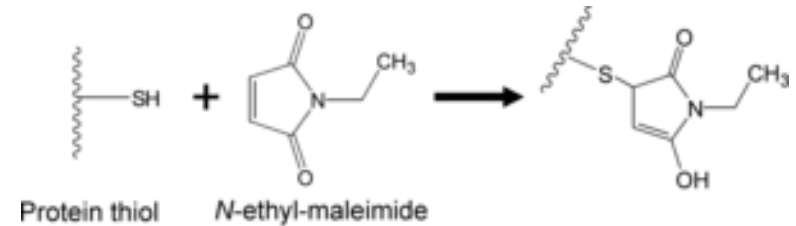


# Origin of ageing?



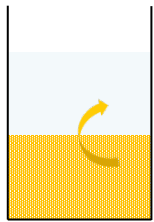
**Formation of covalent polymeric species with ageing time.**

N-Ethylmaleimide (NEM): blocks thiol groups:



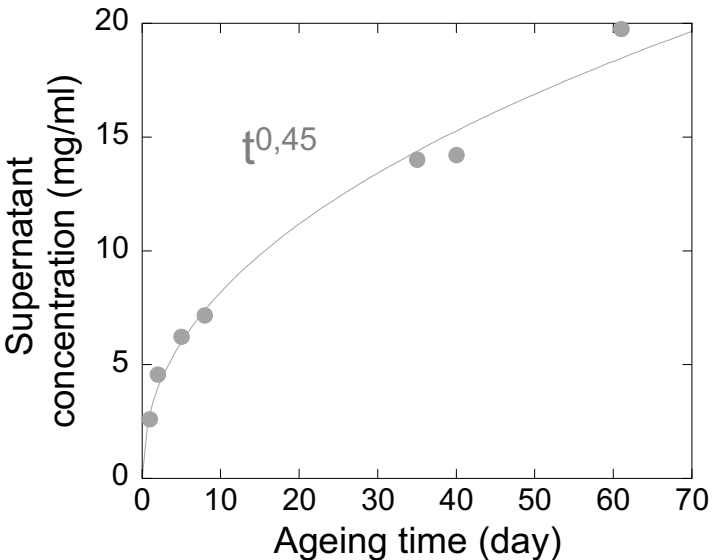
**Disulfide bond shuffling participate in ageing.**

# Origin of ageing?

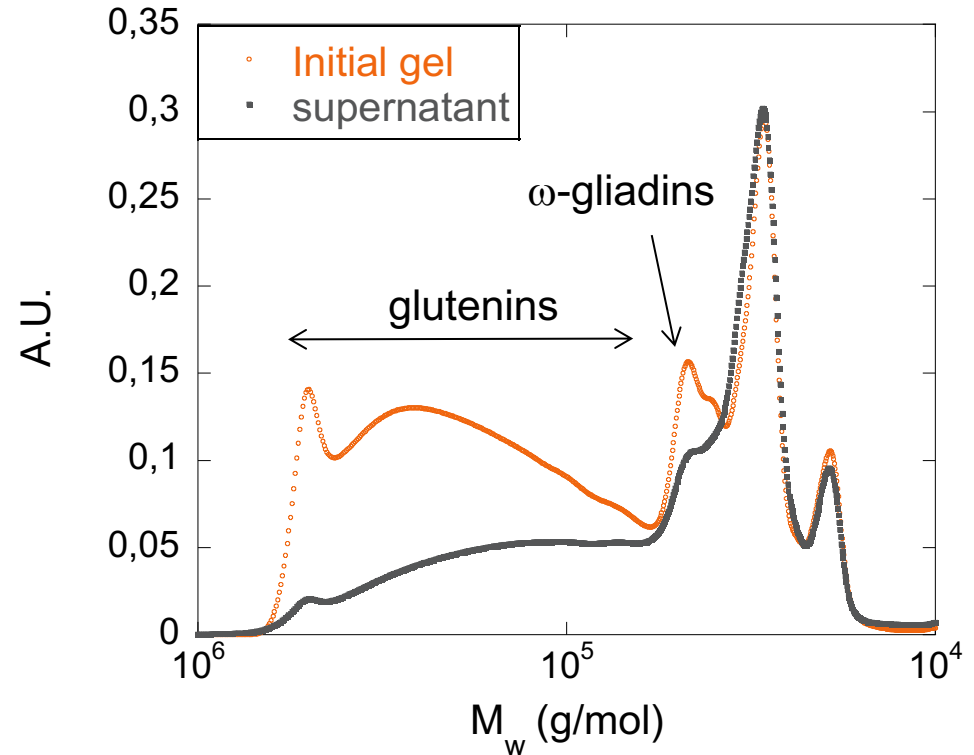


SUPERNATANT

GEL



$t^{1/2} \Rightarrow$  Fickian motion

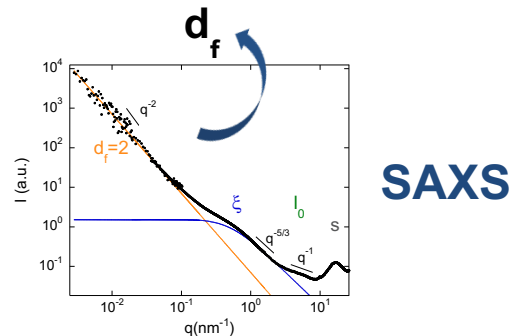
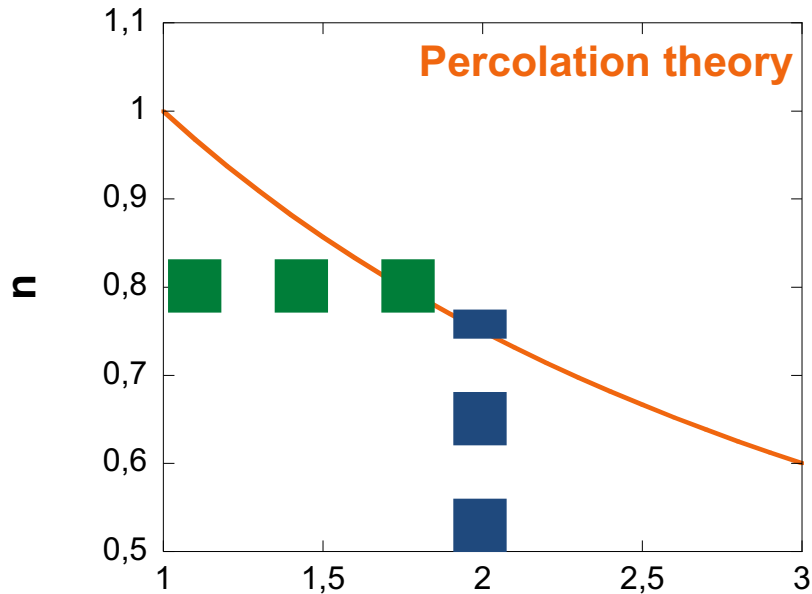
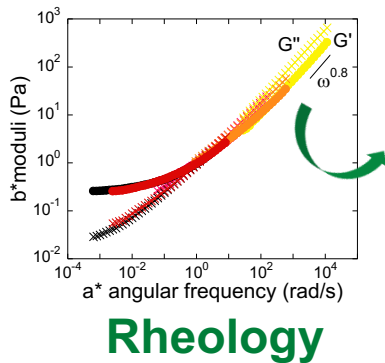


**Gel structure held by glutenins and  $\omega$ -gliadins (no cystein).  
 $\Rightarrow$  Non covalent bonds also participate in ageing.**

# Conclusions

Gluten model system in water-ethanol:

- Structure and dynamics well described by **crosslinked polymer models**.
- Time and concentration** dependent gelation.
- Covalent and non-covalent crosslinking.



# Acknowledgments

## TECHNICAL SUPPORT:

J. Bonicel (HPLC)

P. Dieudonné (SAXS)

## LARGE SCALE FACILITIES:



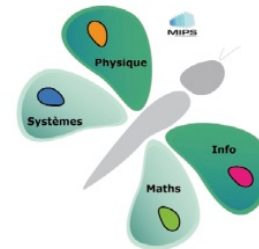
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P. Kwasniewski

M.S. Appavou

Z. Fu

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LABEX NUMEV