

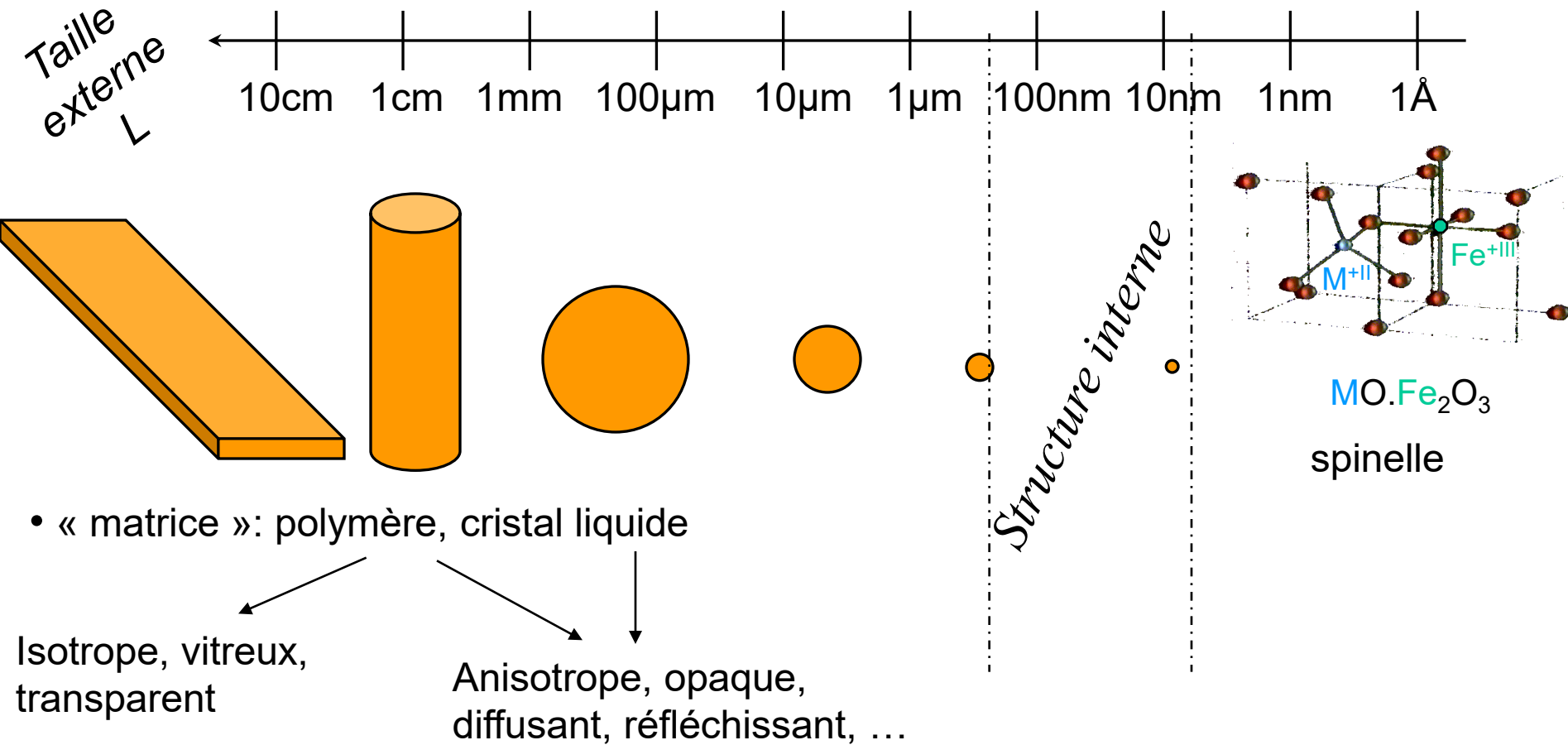


Olivier Sandre

Auto-assemblage de nanoparticules magnétiques et de
copolymères:

Gels, Minigels, Vésicules et Coacervats Magnétiques

Nanocomposites magnétiques



• charge inorganique: nanoparticules → magnétisme (aimantation) + autre propriété: biréfringence, absorption kHz-MHz (chauffage), GHz (micro-onde)-THz (visible), diffraction, diffusion (X, neutrons)...

• en plus: tensioactif, adjuvant, solvant, ...

Matériaux multi-

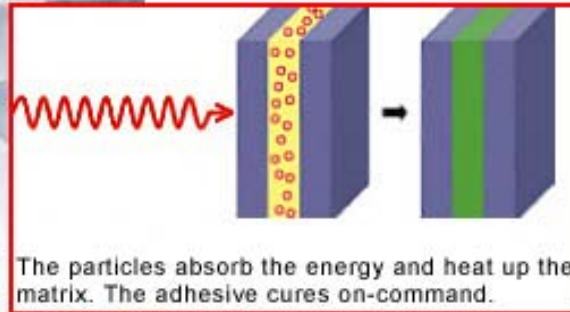
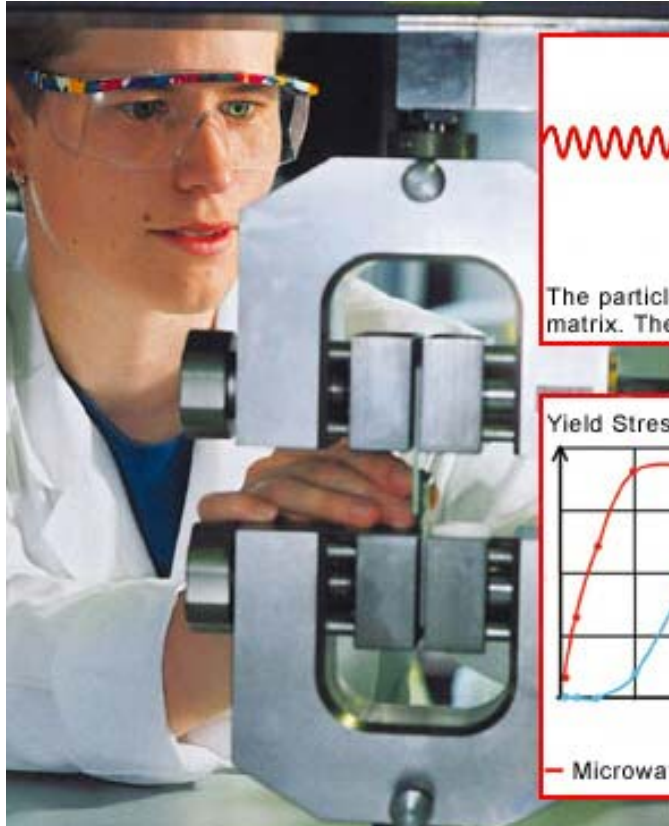
_____ -composants,

_____ -échelles,

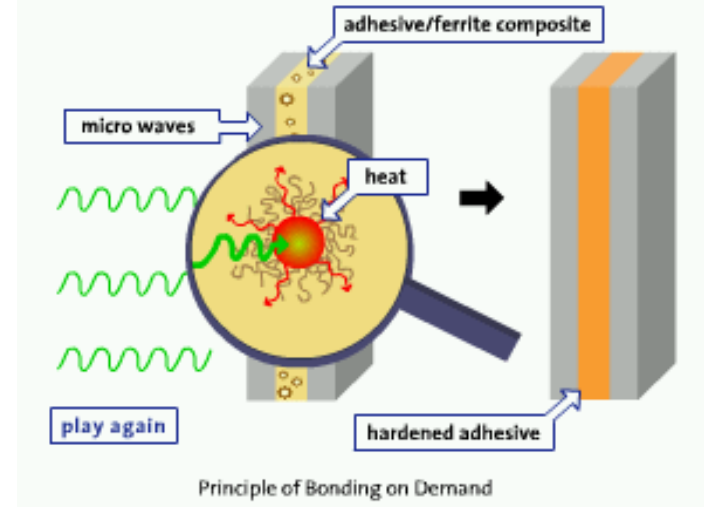
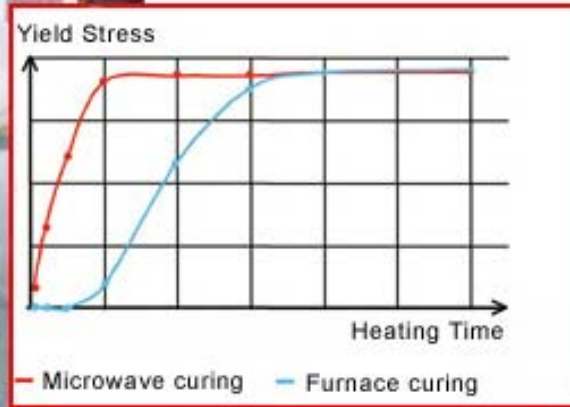
_____ -responsifs, ...

Exemple industriel (Sustech Darmstadt)

'Bond/Disbond-on-Command'



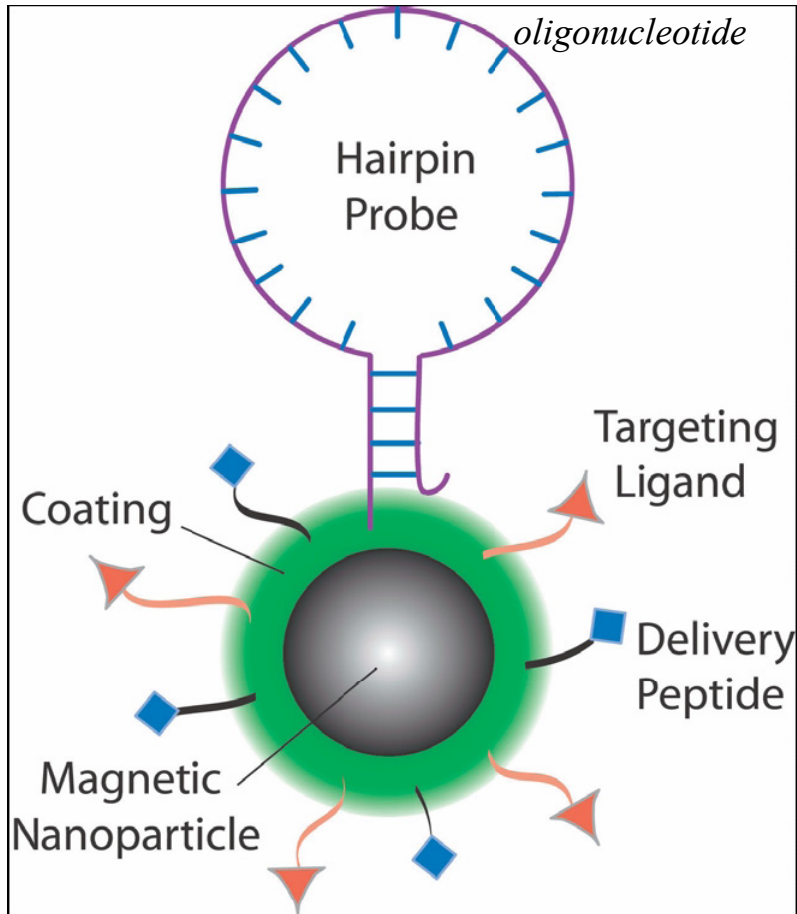
The particles absorb the energy and heat up the matrix. The adhesive cures on-command.



Principle of Bonding on Demand

Exemple de « concept » biotechnologique

Multifunctionalized Magnetic Nanoparticle



- *Imaging*

*Magnetic resonance
fluorescence*

- *Detection*

- *Diagnosis*

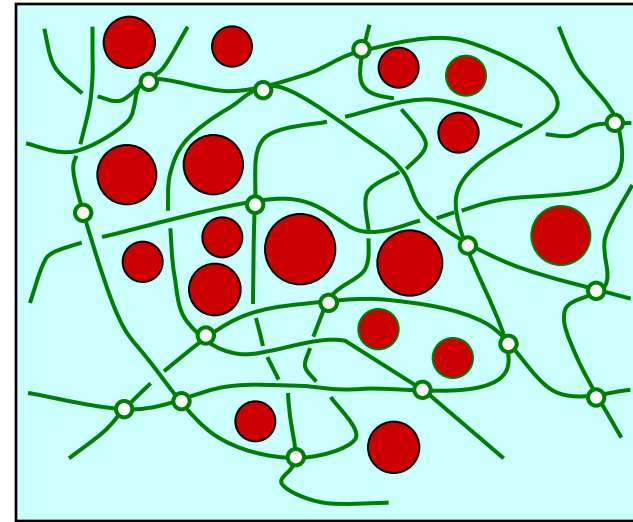
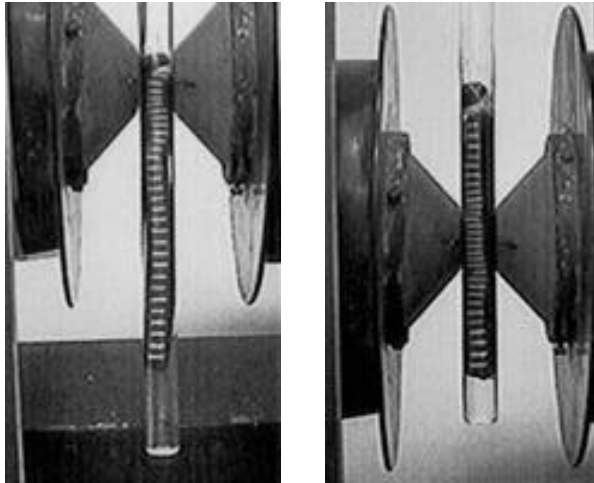
- *Therapy*

*Magnetically guided Drug delivery
Hyperthermia*

*P. Gould « Nanoparticles probe Biosystems »
Materials Today (2004)*

Ferrogels = magnetic nanoparticles trapped in hydrogels

Hydrogel: PVA / GDA, PAM / MBA, ...



Zrínyi M, Barsi L, Büki, A, *J. Chem. Phys.* **1996** 104, 8750

Mitsumata T, Ikeda K, Gong J-P, Osada Y, Szabó D, Zrínyi M, *J. Appl. Phys.* **1999** 85, 8451

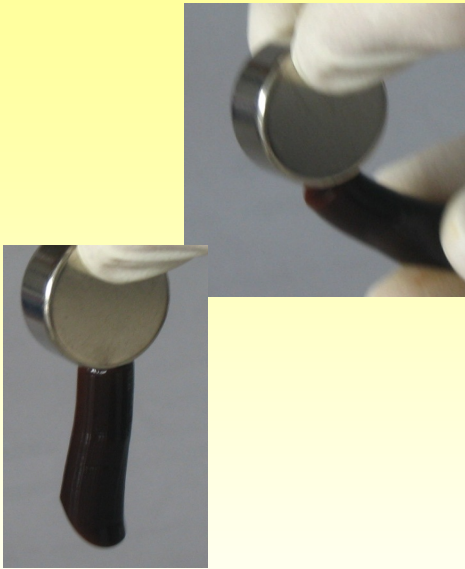
Macroscopic ferrogels :
soft magneto-elastic actuators

$\gamma\text{Fe}_2\text{O}_3$ or Fe_3O_4 nanoparticles

- Structure & dynamics at “meso” scale:
- Blocking of nanoparticles?
 - Perturbation of mesh size?
 - Aggregation state of nanoparticles?

Différentes mises en forme: Biogels Magnétiques d'Alginate

Gel Cyindrique



Actionneurs magnéto-sensibles, muscles artificiels

Film



Films emballage biodégradables, tests mécaniques

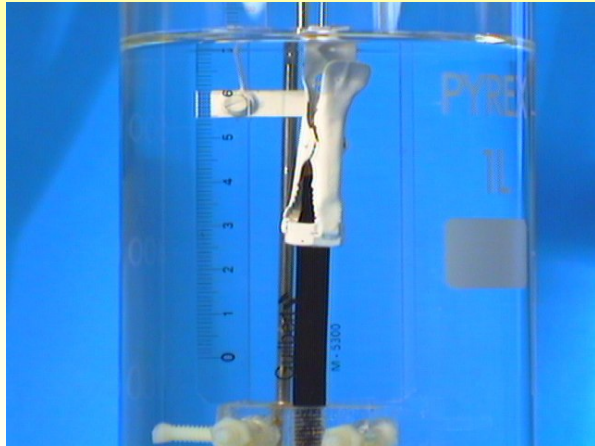
Billes millimétriques



Traitement d'eau contaminée par des métaux toxiques par séparation magnétique

Différentes mises en forme: Ferrogels polyacrylamide & dérivés

Gel cylindrique



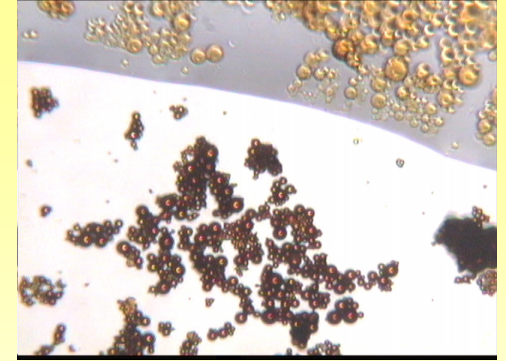
Actionneurs magnéto-sensibles, muscles artificiels

Film mince

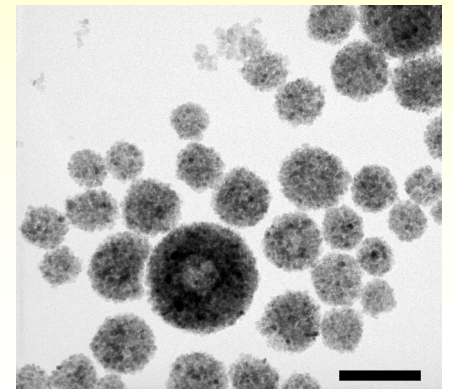


Films utilisés en diffusion des neutrons

Billes micrométriques



& sub-micrométriques



100 nm

- état de gonflement (volume) variable avec: solvant, pH, T
- cinétique de gonflement de type diffusive ($\tau \sim D / L^2$)

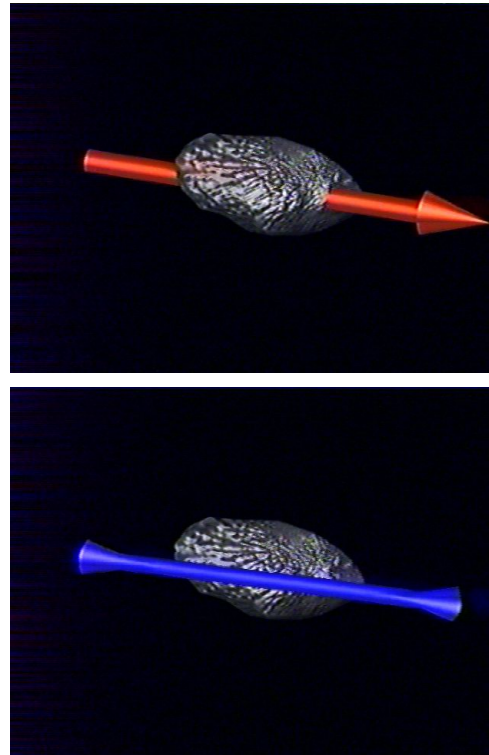
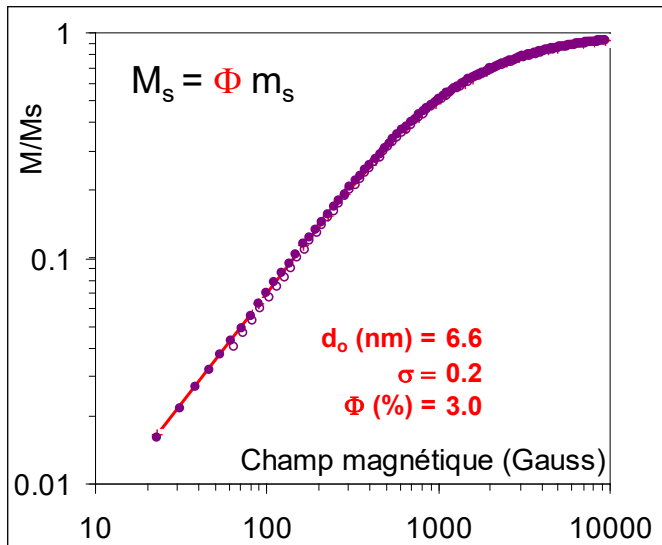
Matériau de départ : ferrofluide « vrai »

Ferrofluide: suspension de nano-particules magnétiques (solution colloïdale)
stable quelle que soit l'intensité du champ magnétique

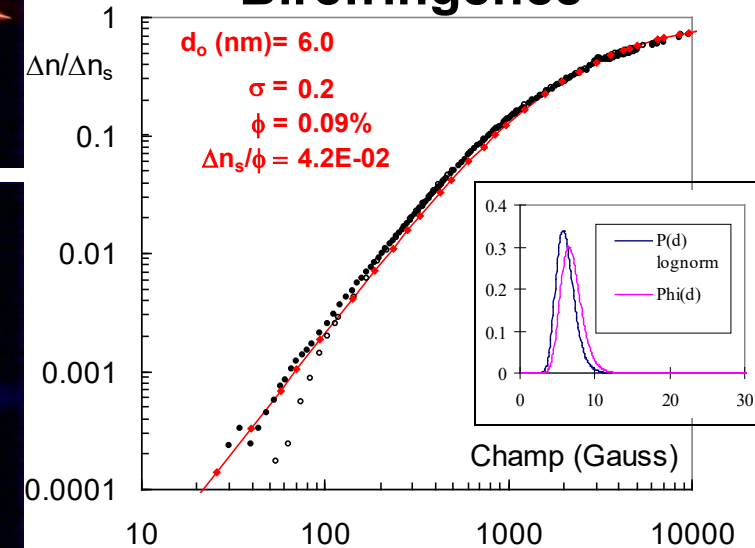
- pas d'attraction des particules par un gradient de champ B, ni de chaînage des particules par interaction dipolaire
- mais orientation progressive des particules, selon lois de Langevin:

Aimantation

$$m_s = 3,1 \cdot 10^5 \text{ A/m (SI)} \quad m_s / 4\pi = 300 \text{ G (CGS)}$$

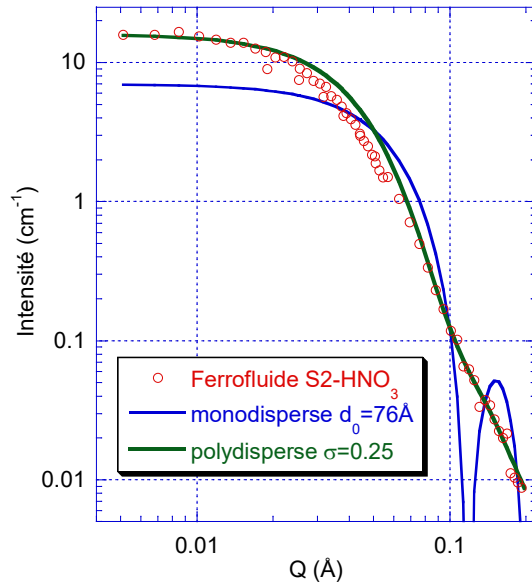
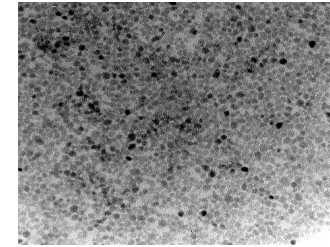
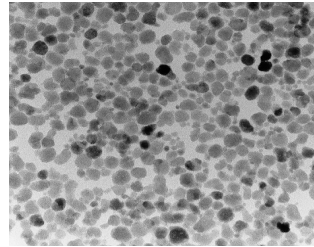


Biréfringence

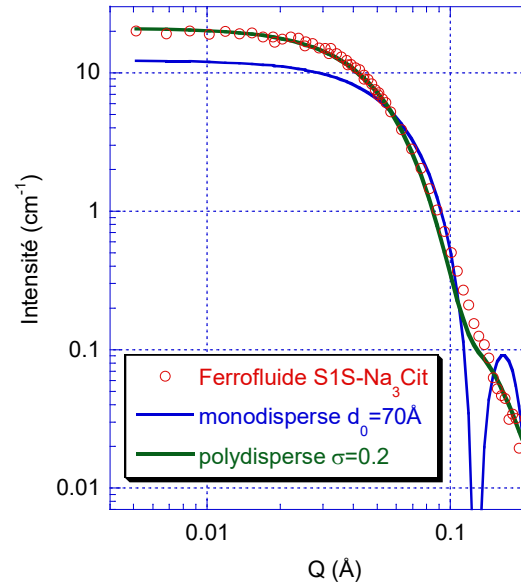


Forme des nano-particules

Exemples d'images
TEM de fractions
triées en tailles :



Ferrofluide acide (S2-HNO₃)



Ferrofluide neutre (S1S-Na₃Cit)

Facteurs de forme
expérimentaux,
ajustés par $P(q)$
théorique de sphères
pondéré par une
distribution
Log-Normale

Spectromètre PACE (LLB), expérience n°6899 (2003): O. Sandre,
F. Chécot, S. Lecommandoux R. Perzynski & J. Oberdisse

Ferrofluides ioniques

- « Procédé Massart »:

Co-précipitation alcaline de FeCl_2 et FeCl_3

→ nano-particules de magnétite Fe_3O_4

suivie d'une oxydation complète par $\text{Fe}(\text{NO}_3)_3$

→ nano-particules de maghémite $\gamma\text{-Fe}_2\text{O}_3$,
en milieu acide (HNO_3)

R. Massart *IEEE Trans. Magn.* **17** 1247 (1981)

- Charges électrostatiques de surface (PCN \approx 7)

- Polydispersité des tailles: $5\text{nm} < d < 14\text{nm}$

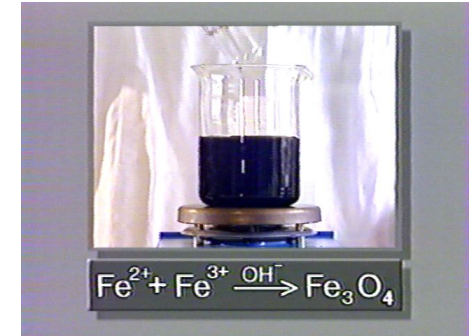
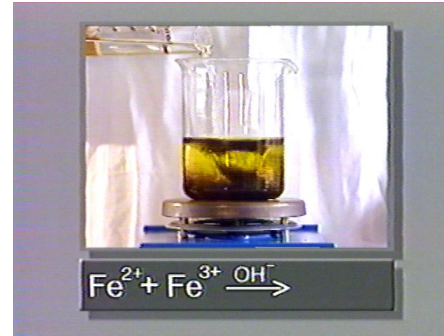
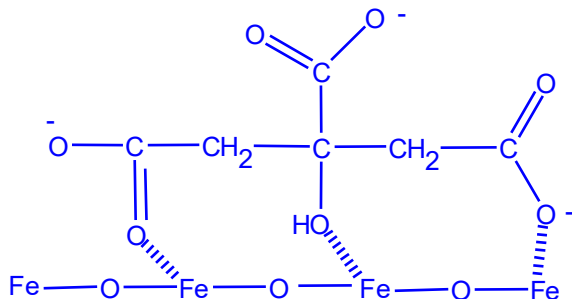
- Tri reposant sur des démixtions successives :

R. Massart, E. Dubois, V. Cabuil, E. Hasmonay
J. Magn. Mater. **149** 1 (1995)

Plusieurs traitements de surface qui assurent la stabilité colloïdale :

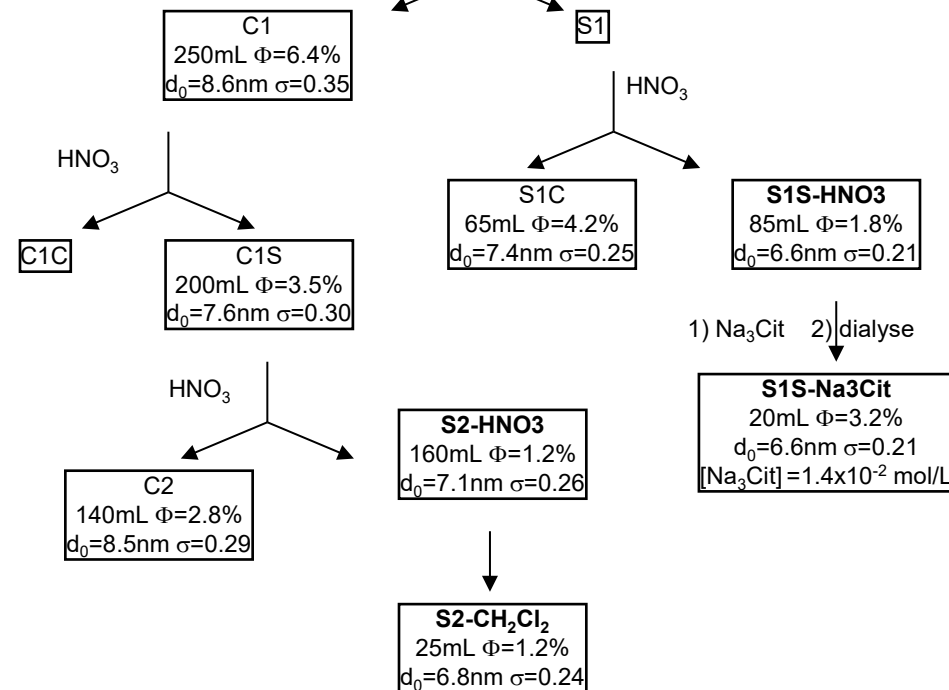
- surfactants (acide oléique, di-ester phosphorique,...) pour les solvants organiques (alcanes, chlorés,...)

- citrate de sodium en milieu aqueux neutre (pH=7.2)

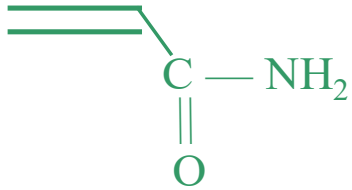


835mL ferrofluide acide DE1, $\Phi=2.5\%$
Polydisperse $d_0=7\text{nm}$ $\sigma=0.39$

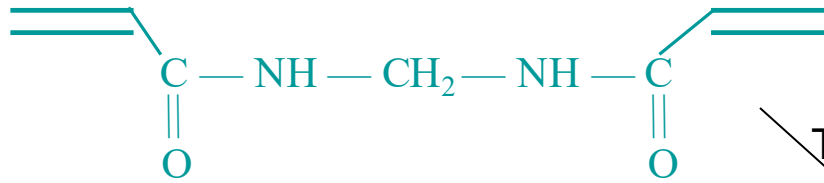
démixtion avec HNO_3 excès



Poly(acrylamide) et dérivés



Acrylamide, AM



N,N 'méthylène-bis-acrylamide, BA

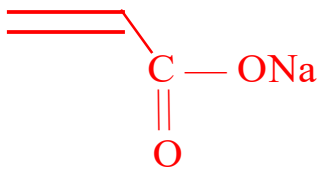
T = 70°C

$(\text{NH}_4)_2\text{S}_2\text{O}_8$
0.1 mol%

Monomère
[AM]=0.5 mol/L

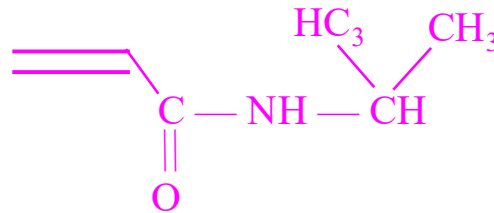
Réticulant
 $C_x = [\text{BA}] / [\text{AM}]$
= 0.5 – 2 mol%

Co-monomères:



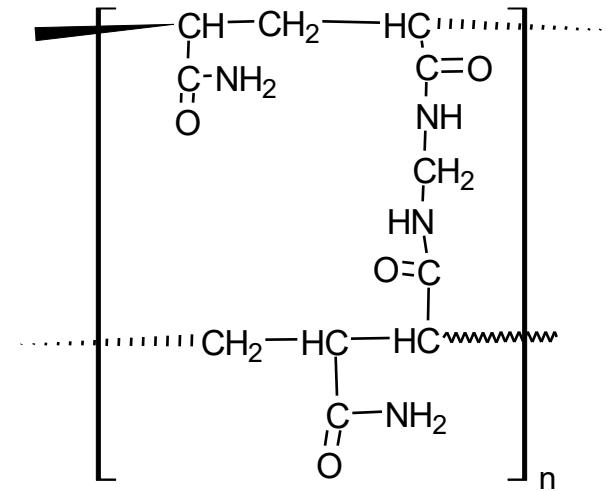
Acrylate de sodium, AS

Chargé négativement

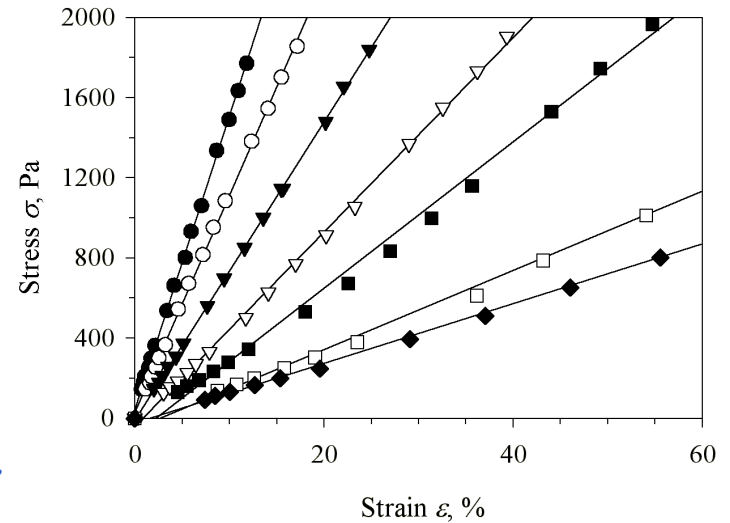
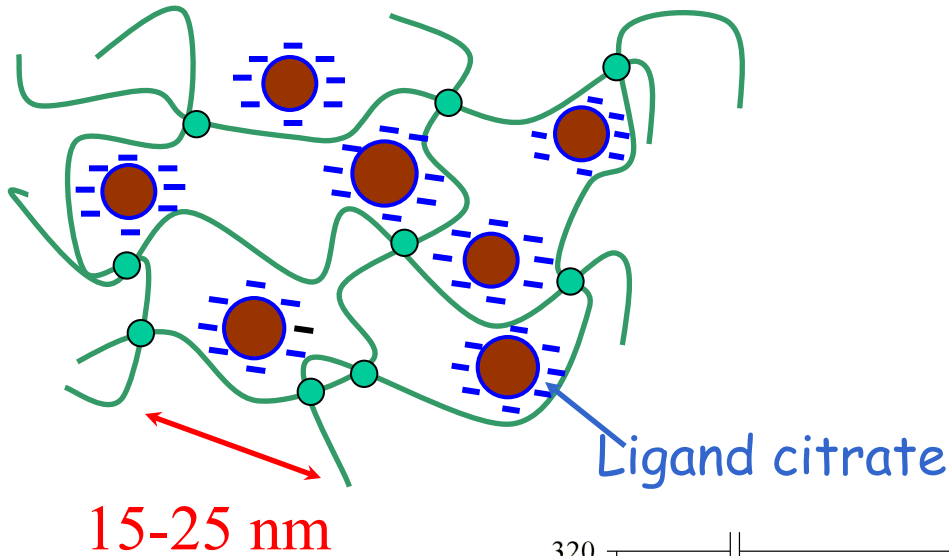


N – isopropyl acrylamide, NIPAM

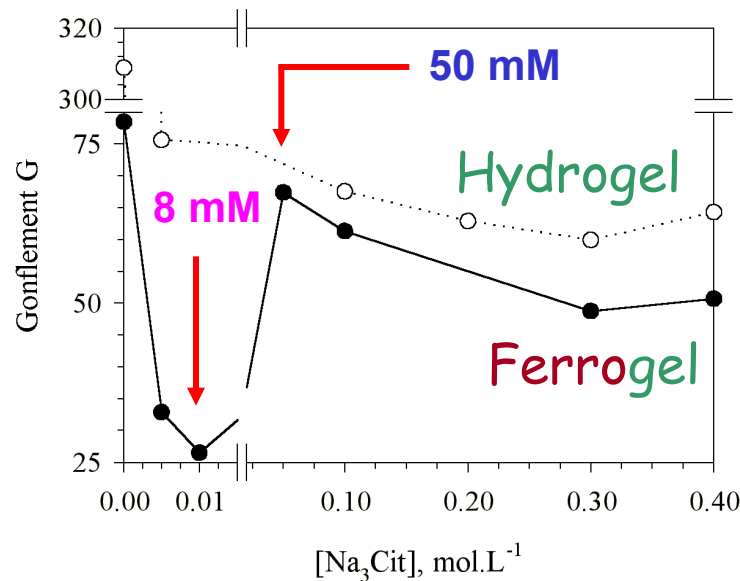
Thermosensible



Propriétés comparées des Ferrogels & des Hydrogels



$$G = \frac{m_{H_2O}}{m_{polymère}^{sec}}$$



Gonflement des gels
Minimal à basse
[citrate]

A. Galicia, O. Sandre, F. Cousin,
D. Guemghar, C. Ménager, V. Cabuil,
J. Phys. Cond. Mat. **15**,
S1379-S1402 (2003)

Swelling pressure of PAM Ferrogels

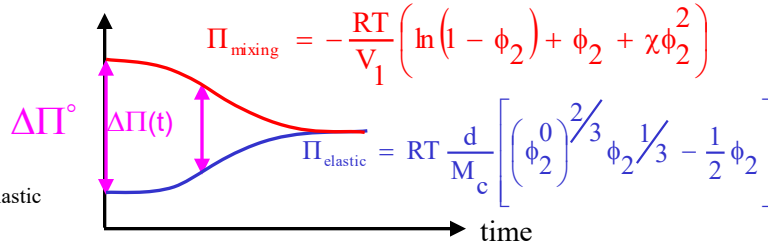
Model of swelling (Flory - Rehner)

HYDROGEL

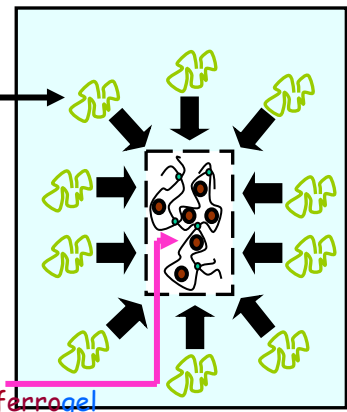
$$\Delta\Pi_{\text{swelling}} = \Pi_{\text{mixing}} - \Pi_{\text{elastic}}$$

FERROGEL

$$\Delta\Pi_{\text{swelling}} = \Pi_{\text{mixing}} - \Pi_{\text{elastic}} - \Pi_{\text{interaction}}$$

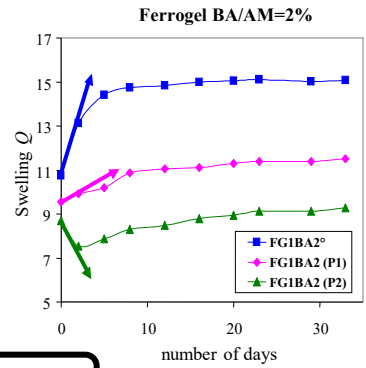
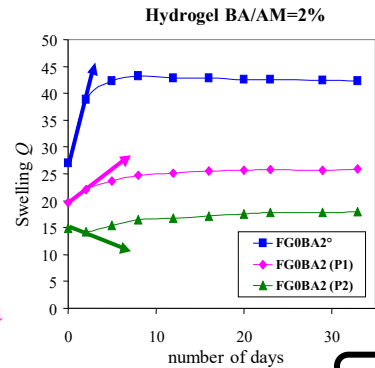


Estimate of initial Π^0



Dextran
 $M = 110,000 \text{ g/mol}$
 exerting a gauged osmotic pressure :
 $P1=1000 \text{ Pa}$
 $P2=3000 \text{ Pa}$

Hydrogel or ferrogel



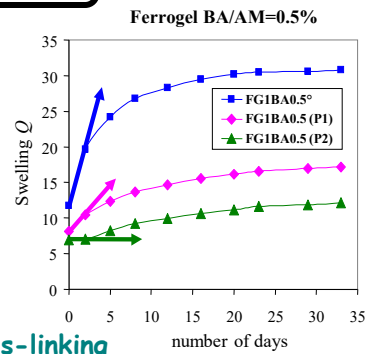
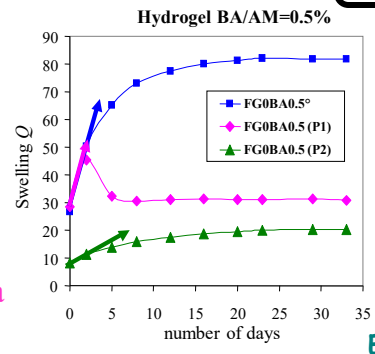
$1000 \text{ Pa} < \Delta\Pi_{\text{swelling}}^{\circ} < 3000 \text{ Pa}$

With particles
 $\Phi^0 = 1 \%$

$\Delta\Pi_{\text{swelling}}^{\circ} \leq 3000 \text{ Pa}$

Without particles

Kinetics of swelling



Effect of interactions

$\Delta\Pi_{\text{swelling}}^{\circ} > 3000 \text{ Pa}$

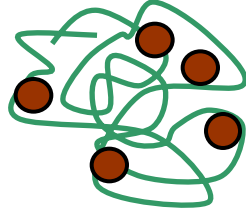
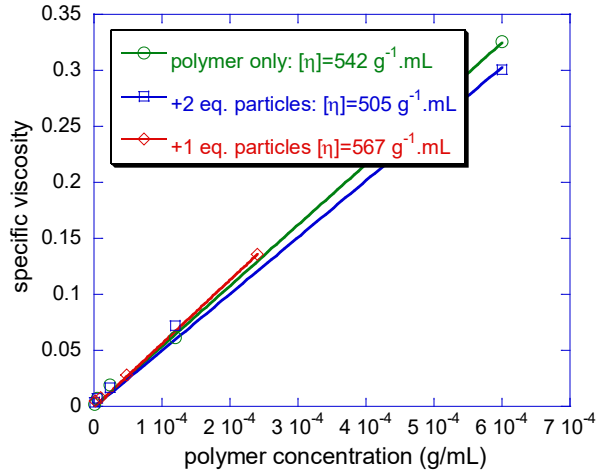
$\Delta\Pi_{\text{swelling}}^{\circ} \approx 3000 \text{ Pa}$

Effect of cross-linking

Agrégats de particules par le PAM linéaire

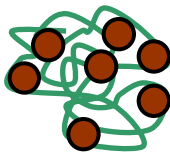
Viscosimétrie et « nano-rhéologie »

Viscosimetry at high citrate concentration [Na₃Cit] = 50mM



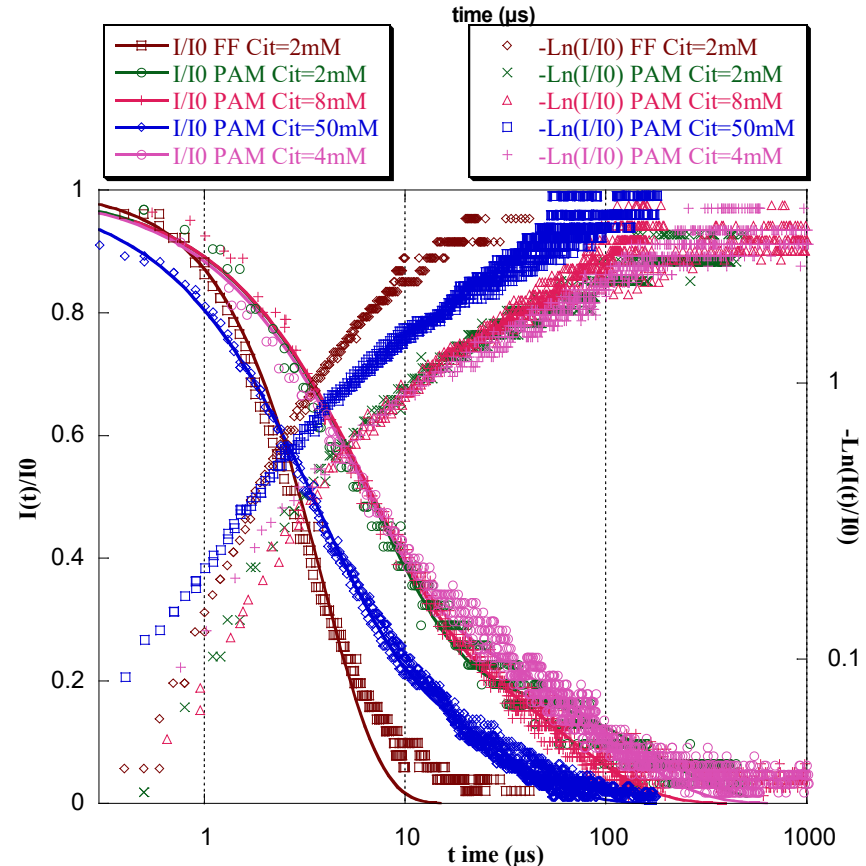
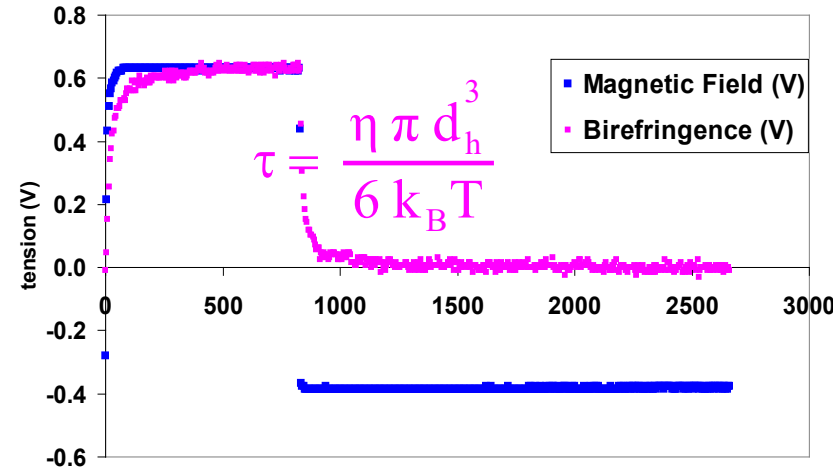
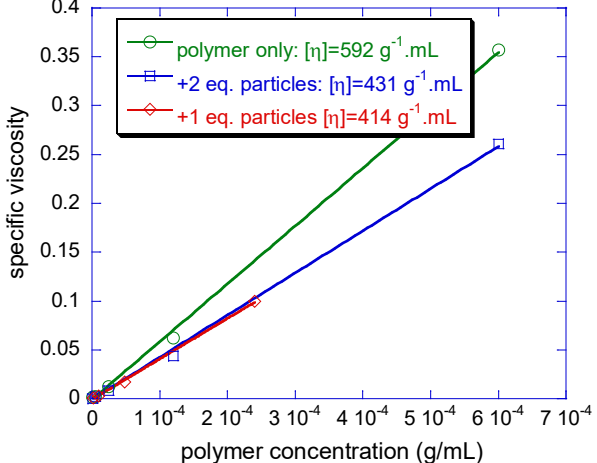
[Na₃Cit] = 50 mM
d_H = 107 nm

$$\alpha^3 = \frac{[\eta]}{[\eta]^\theta} = \left(\frac{R_{g\theta}}{R_g} \right)^3$$

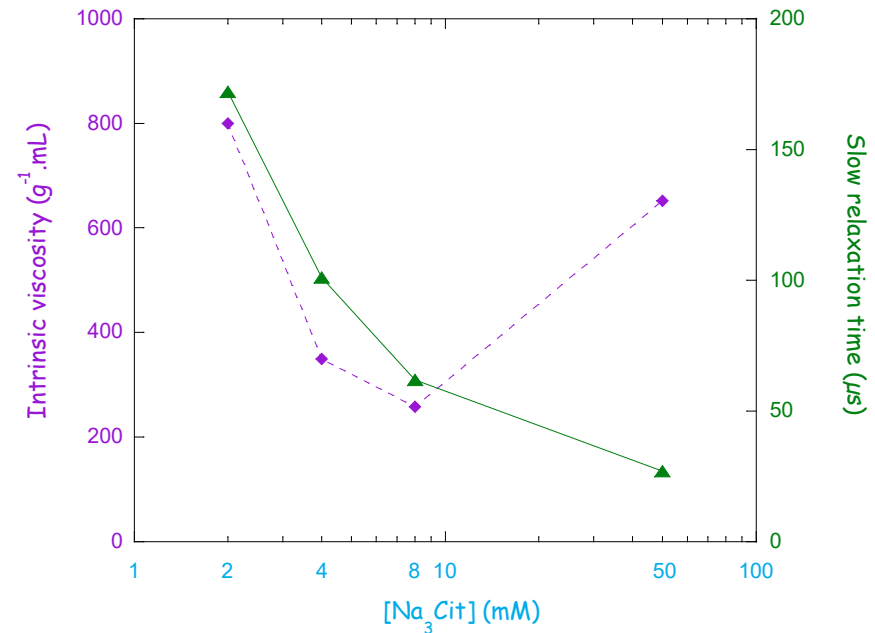
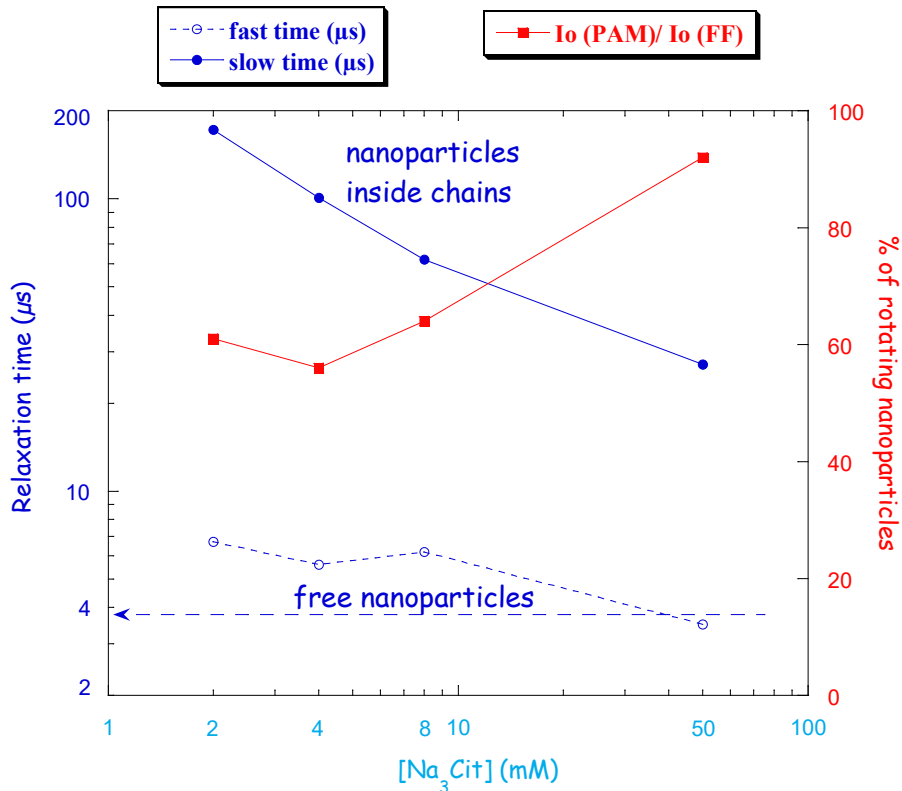


[Na₃Cit] = 8 mM
d_H = 78 nm

Viscosimetry at low citrate concentration [Na₃Cit] = 8mM



Competition between citrate desorption and PAM adsorption



• low salinity: $[\text{Na}_3\text{Cit}] \leq 8 \text{ mM}$

Intrinsic Viscosity $\propto d_h^3$

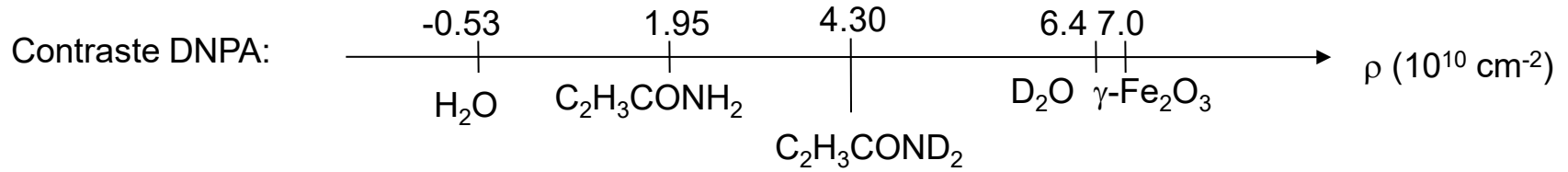
Chains decorated by nanoparticles

• high salinity: $[\text{Na}_3\text{Cit}] > 8 \text{ mM}$

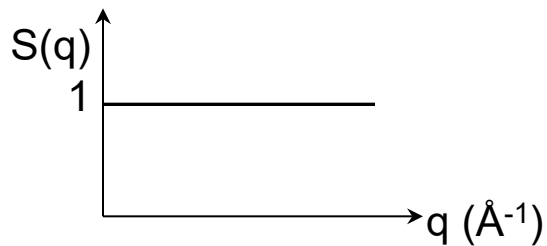
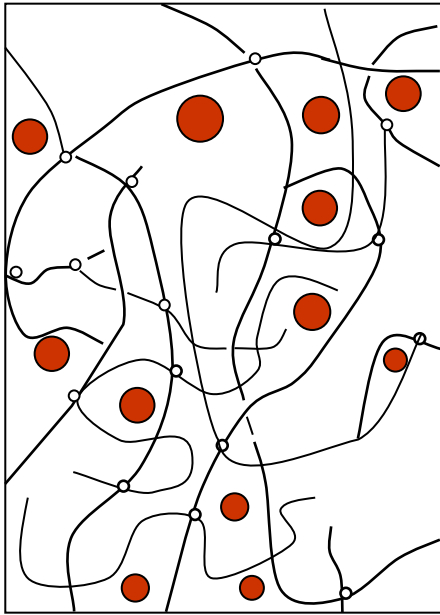
Chains weakly interacting with nanoparticles

- Slow and fast relaxation times both increase when $[\text{Na}_3\text{Cit}]$ decreases
- About 40% of nanoparticles are hampered in their rotation (below 50 mM)

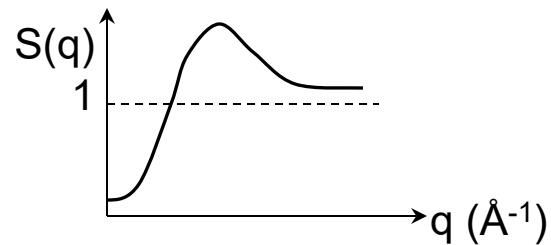
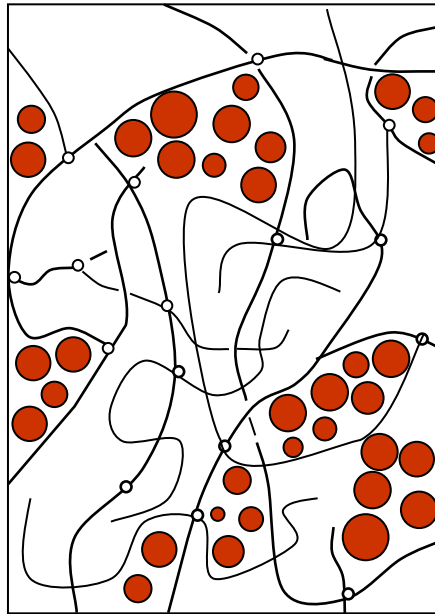
Structures internes possibles des ferrogels



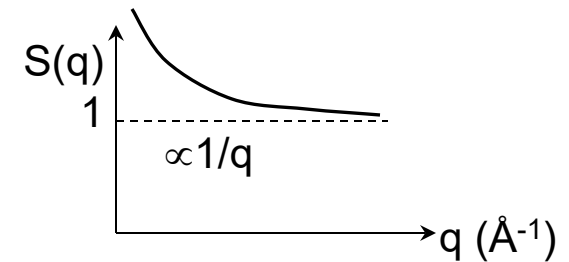
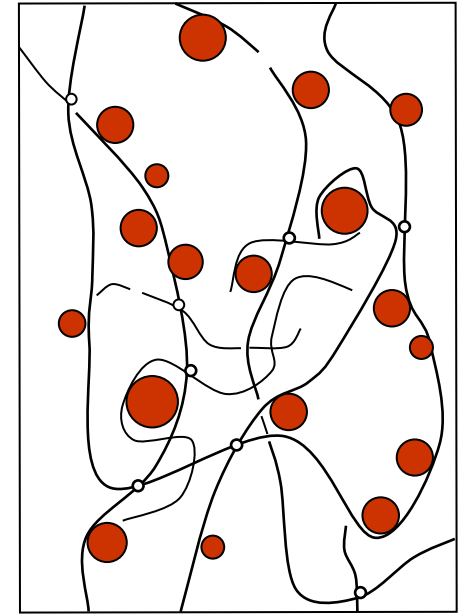
A) Répartition homogène



B) Poches liquides



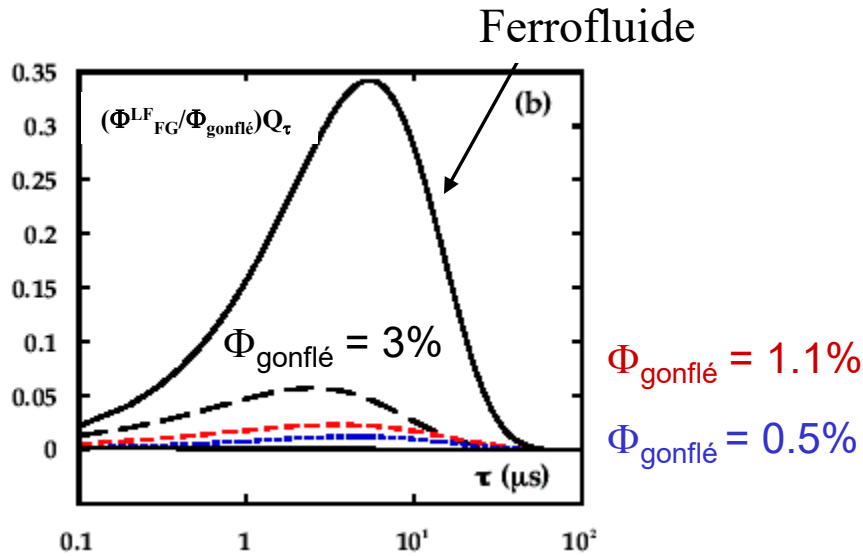
C) Chaînes décorées



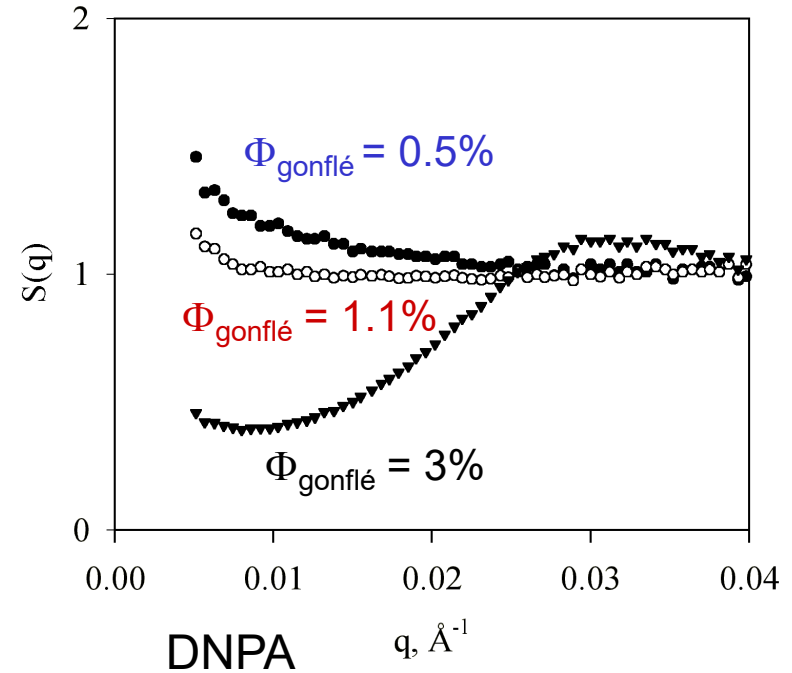
Structure d'un ferrogel peu perturbé

Réseau de PAM réticulé à $C_x=0.5$ mol%
 Particules de tailles larges ($d_0=9\text{nm}$ $\sigma=0.3$)

$$\Pi_{\text{ferrofluide}} < \Pi_{\text{hydrogel}}$$



Biréfringence dynamique



DNPA $q, \text{\AA}^{-1}$

- + de particules libres de tourner à forte Φ
- + de particules bloquées à faible Φ

- Répulsif à forte Φ
- Attractif à faible Φ

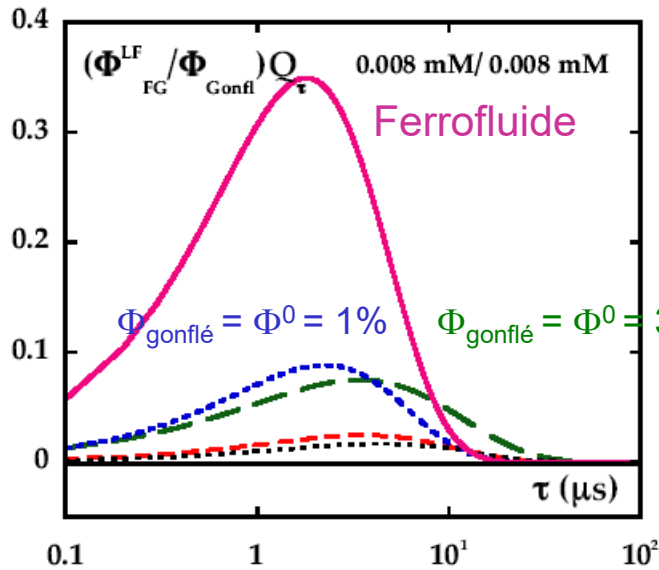
→ Coexistence de poches liquides (B) et de chaînes décorées (C)

Structure d'un ferrogel très perturbé

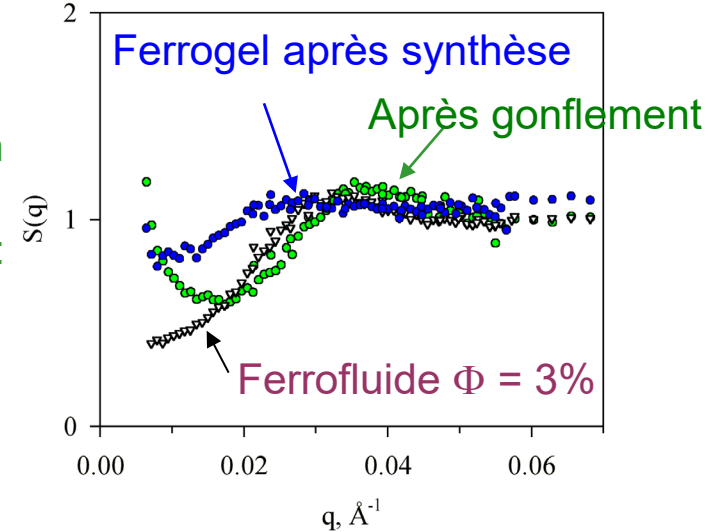
Réseau de PAM réticulé à $C_x=2$ mol%

Particules de tailles triées ($d_0=8\text{nm}$ $\sigma=0.2$)

$$\Pi_{\text{ferrofluide}} > \Pi_{\text{hydrogel}}$$

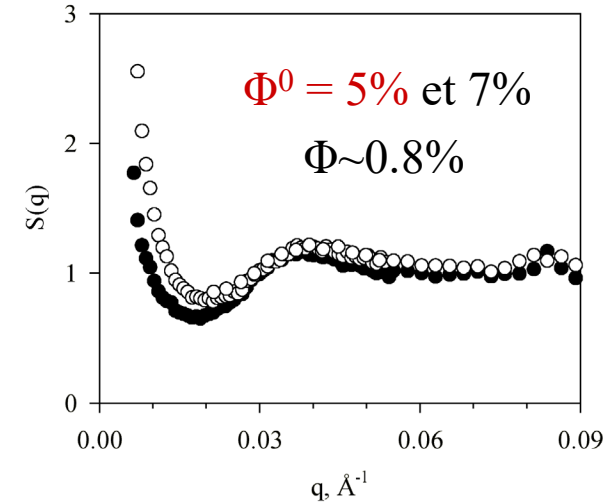


Réorganisation des particules à Φ constante :



Biréfringence dynamique

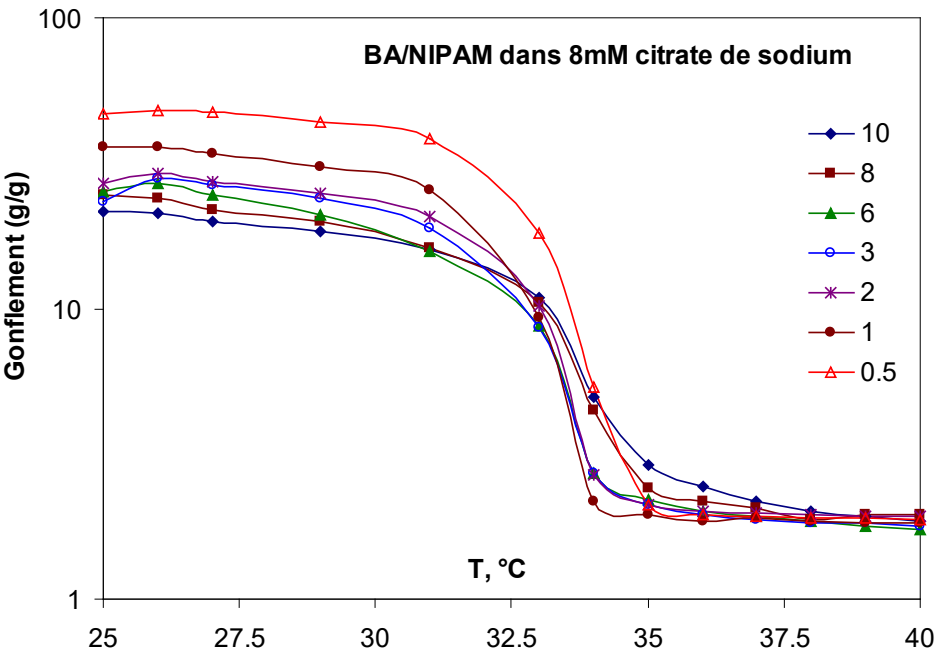
- + de particules libres de tourner à faible $\Phi^0=1$ ou 3%
- + de particules bloquées et temps caractéristiques + longs à forte Φ^0 (soit faible Φ_{gonfl} , car fort relargage)



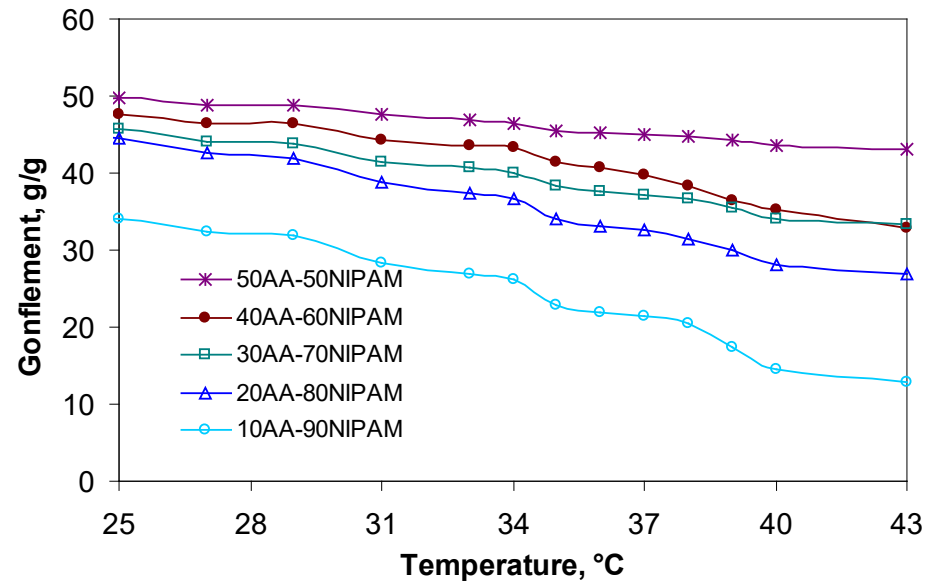
Thermogels

Poly(NIPAM) réticulé BA : transition de volume à $T_c=32^\circ\text{C}$ (LCST)
Applications bios: drug delivery contrôlé par ΔT + champs magnétique

Mais le réseau de NIPAM ne retient pas les nanoparticules magnétiques !

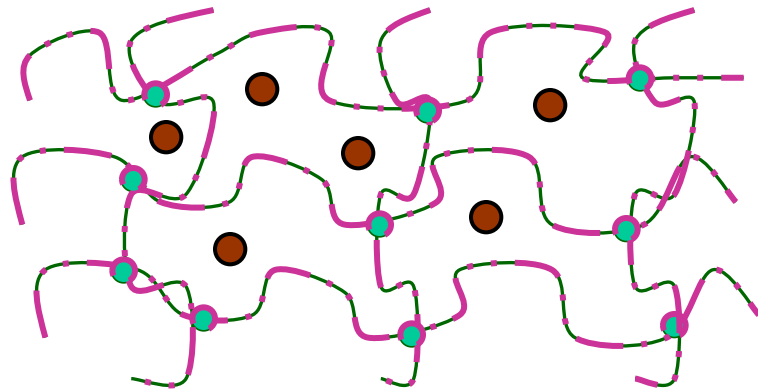


taux de réticulation C_x ?



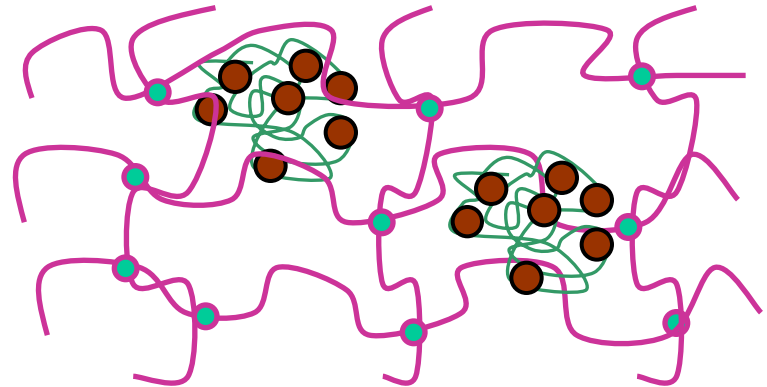
fraction AM dans un copo stat?

Réseaux mixtes NIPAM / PAM

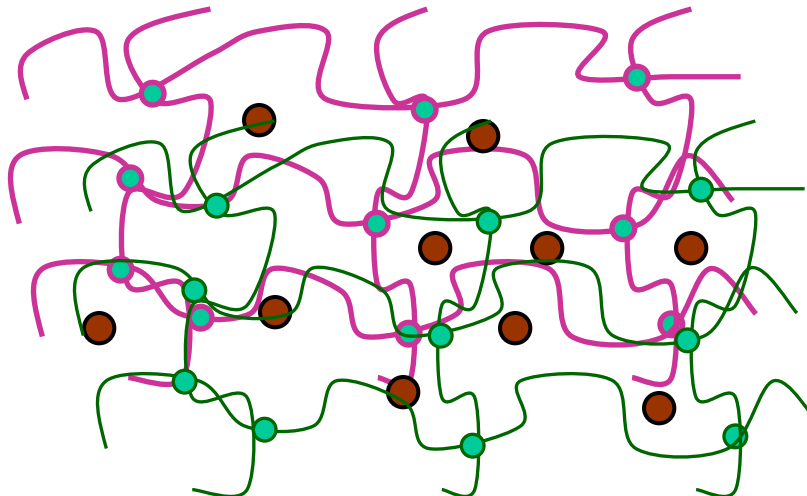


← Copolymère statistique

Réseau semi-interpénétré →



Copolymères « topologiques »

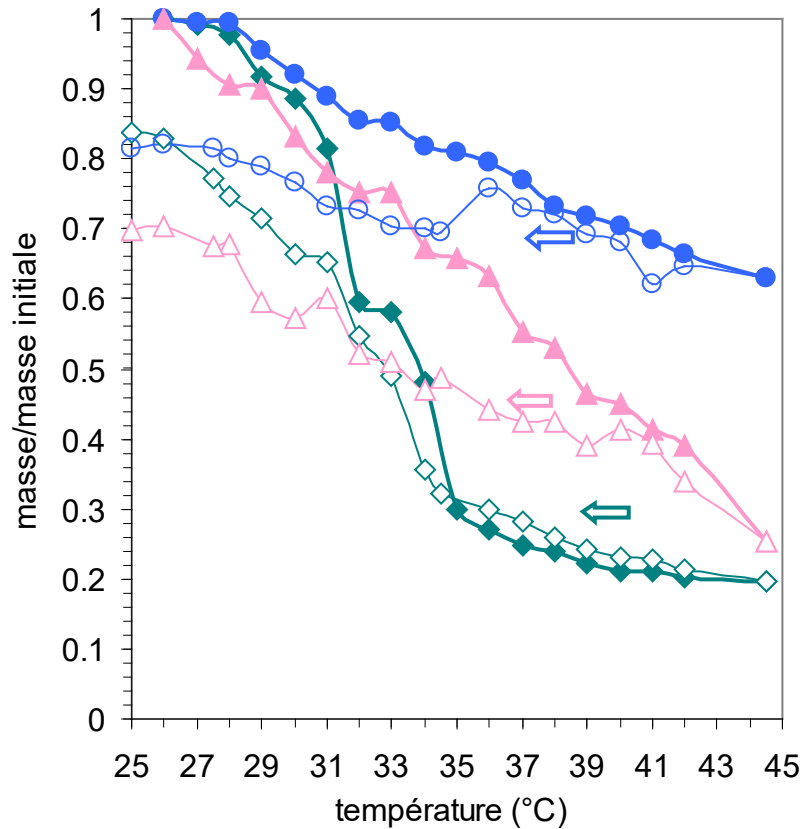


← Réseaux interpénétrés

Thermogels magnétiques: gonflement

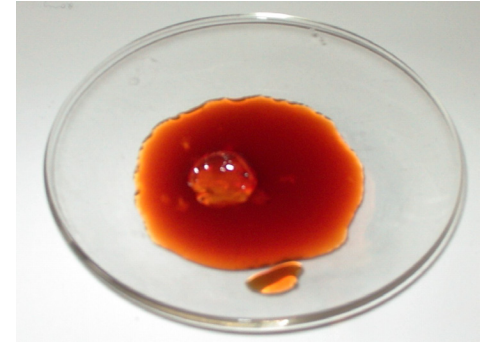
AM apporté:

- Co-monomère (statistique)
- Chaînes PAM 5,000,000

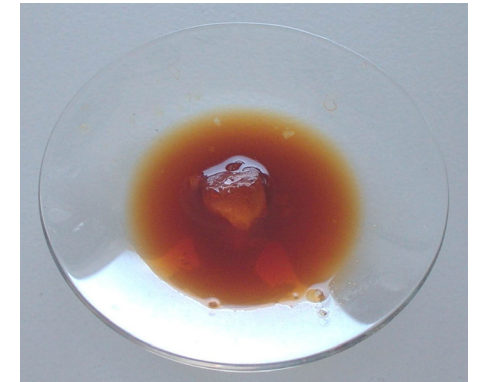


$C_x=2 \text{ mol\%}$, $\Phi^0=1\%$

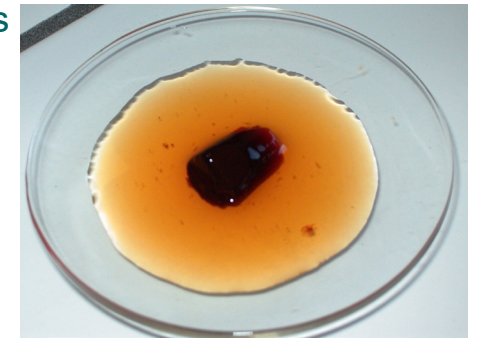
Copolymère statistique
80%NIPAM-20%AM



Copolymère statistique
90% NIPAM-10%AM

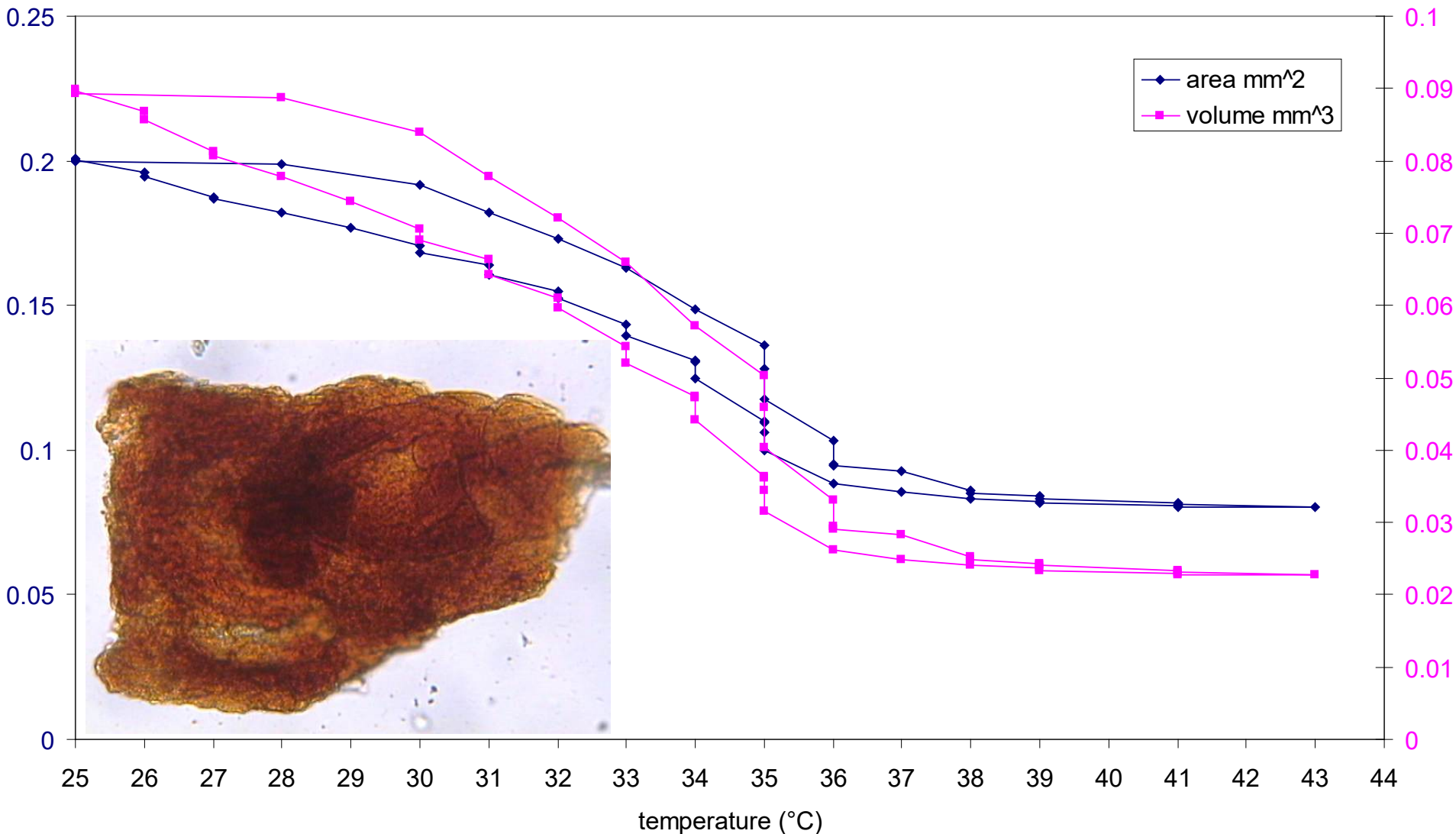


Réseaux semi-interpénétrés
90% NIPAM-10%AM

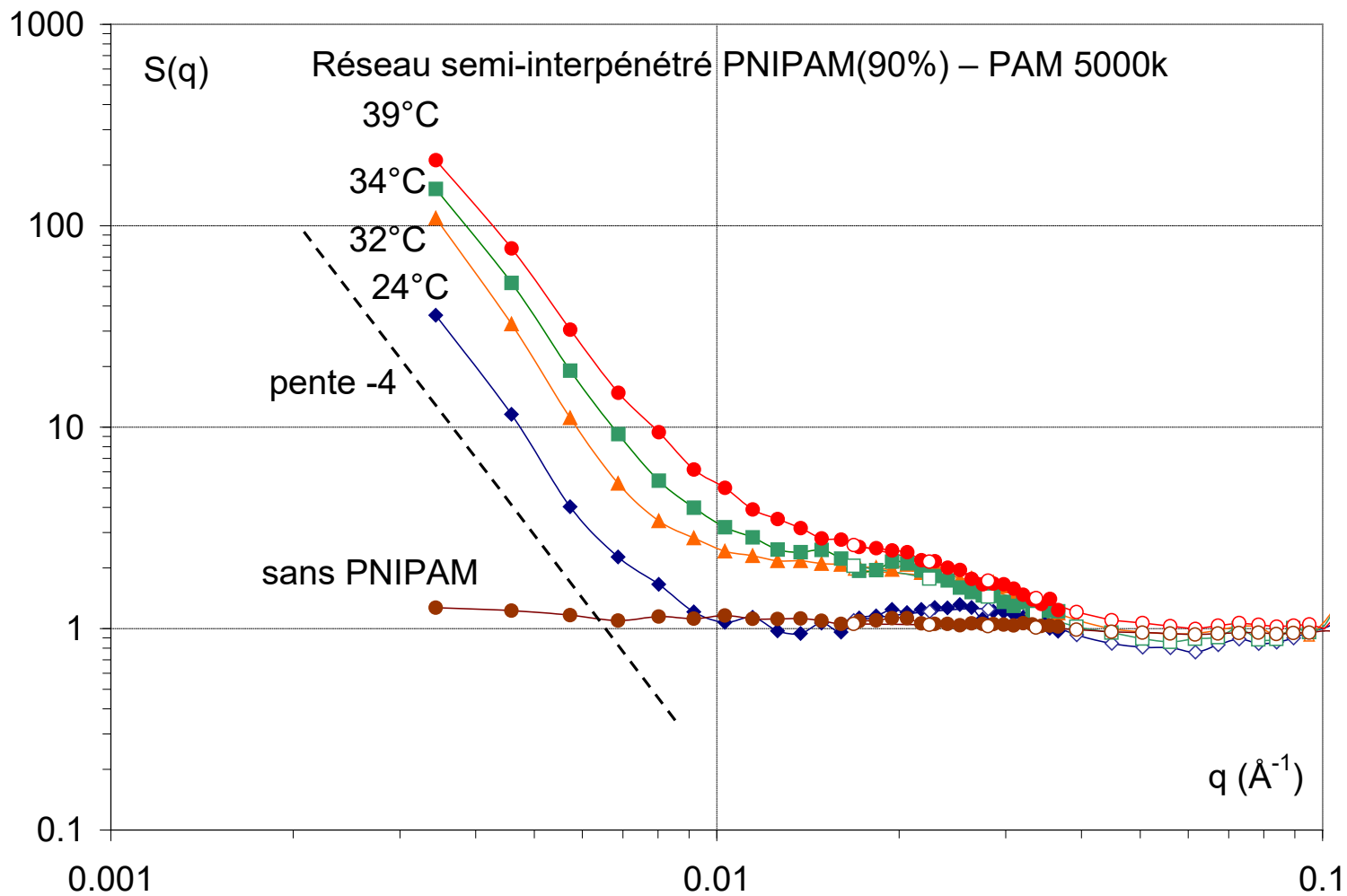


Magnetic thermosensitive microgels

First encouraging results ! (Delphine El kharrat's thesis)



Suivi de la transition par DNPA



PACE – LLB