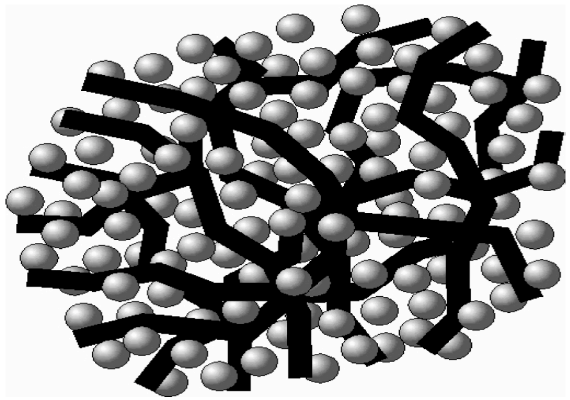
Gels

i) What is a gel?

ii) Types of gels

- Chemical gels
- Physical gels

iv) Relation to other *liquid-solid* transitions



A gel?

A gel is a gel, as long as one cannot prove that it is not a gel

K. te Nijenhuis

A gel?

> *A gel is a gel, as long as one cannot prove that it is not a gel*
>
> K. te Nijenhuis

Can we make any useful definition?

⇒ Solid-like properties - *sustain shear stress*
network spanning the system

⇒ Undergoes liquid - solid transition - *gelation*

⇒ Heterogeneous - *multi component systems*
dynamics on different time scales
multiple length scales

Example - gelatine

Gelatine: Formed from *collagen*, a protein “found” in animals. When collagen is heated, it breaks down into the *protein gelatin*.

Gelatine swells in water ⇒ *polymer solution (liquid)*

At low T gelatine+water forms a solid ⇒ *a gel*
water is trapped in a loose polymer network structure

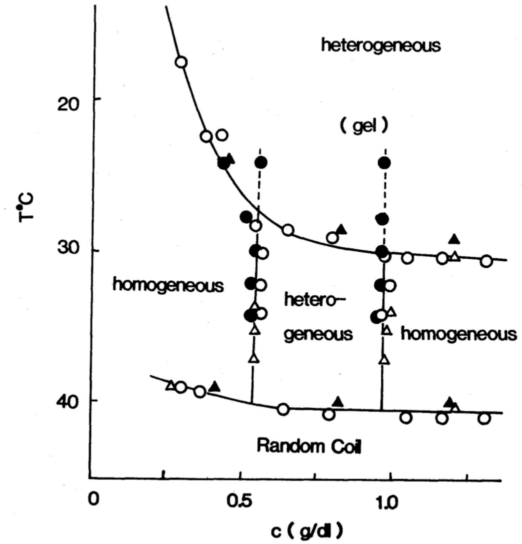
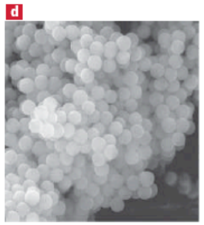


FIG. 7. Phase Diagram for Gelatin Solution.
○, $1/p$; ●, $[\alpha]_{405}$; △, η_{sp}/c; ▲, c/i_{90}.

Agric. Biol. Chem., 47, 1711 (1983)

Applications

Food



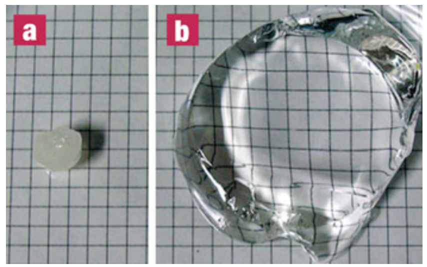
Pharmaceuticals

Batteries and fuel cells

Epoxy resins

Araldite 2000-serien i patroner

Disposable napkins



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K. te Nijenhuis

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⇒ Solid-like properties - *sustain shear stress*
network spanning the system

⇒ Undergoes liquid - solid transition - ***gelation***

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dynamics on different time scales
multiple length scales

Gelation or sol-gel transition

At the gelation point an infinite cluster is created that spans the whole system.

Macroscopic properties changes abruptly
$\Rightarrow$ from liquid-like to solid-like.

Gelation can be described as a bond percolation transition

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⇒ from liquid-like to solid-like.

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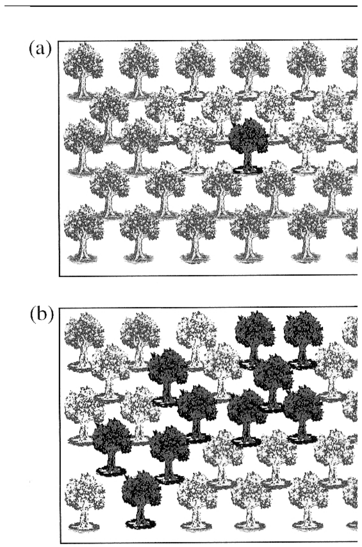
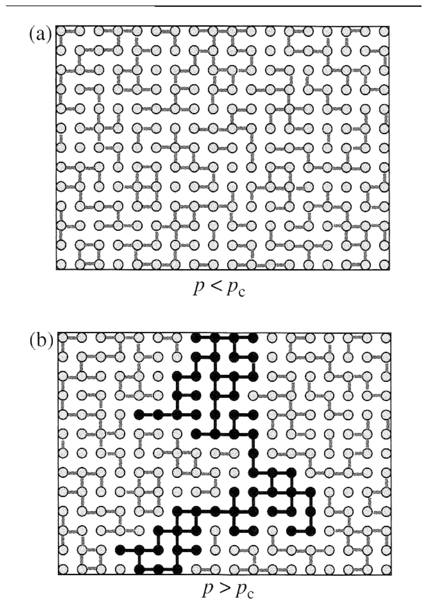
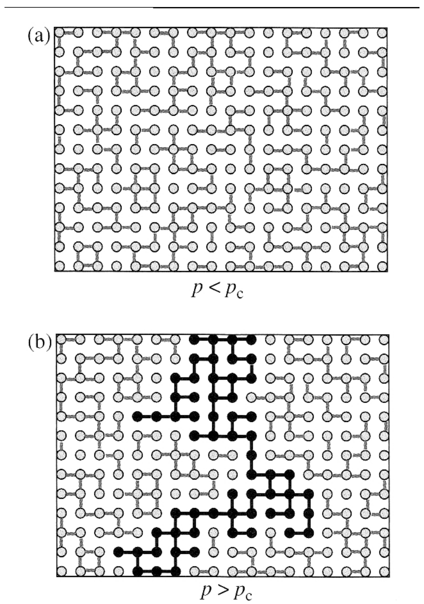


Fig. 6.10
Spreading of a disease in an orchard.



Percolation theory



Gelation can be described as a connectivity transition - *bond percolation problem*

p - probability of bond to neighbour

$p < p_c$ - sol

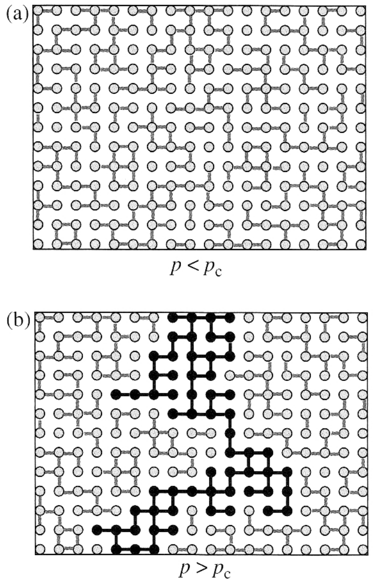
$p > p_c$ - gel

In general the problem has not an analytical solution

triangular lattice $p_c \approx 0.347$

square lattice $p_c \approx 0.5$

The gel-fraction



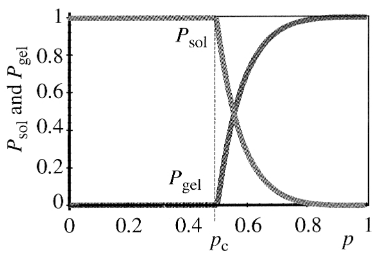


Fig. 6.15
Mean-field prediction of sol and gel fractions for functionality $f = 3$.

P_{gel} fraction of sites in the system spanning clusters
(gel fraction)

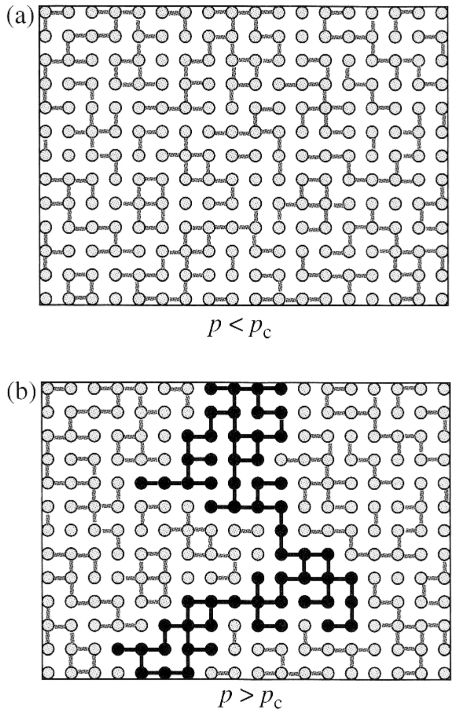
P_{sol} fraction of sites in finite clusters
(sol fraction)

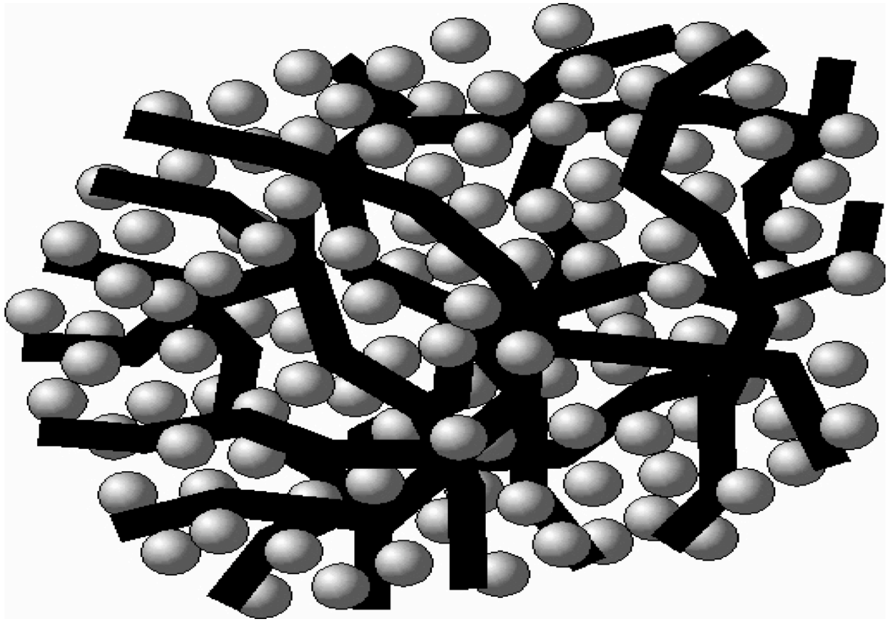
$p \leq p_c$ $\quad P_{sol}=1$ and $P_{gel}=0$

$p \geq p_c$ $\quad P_{sol}<1$ and $P_{gel}> 0$

Gelation is a continuous transition

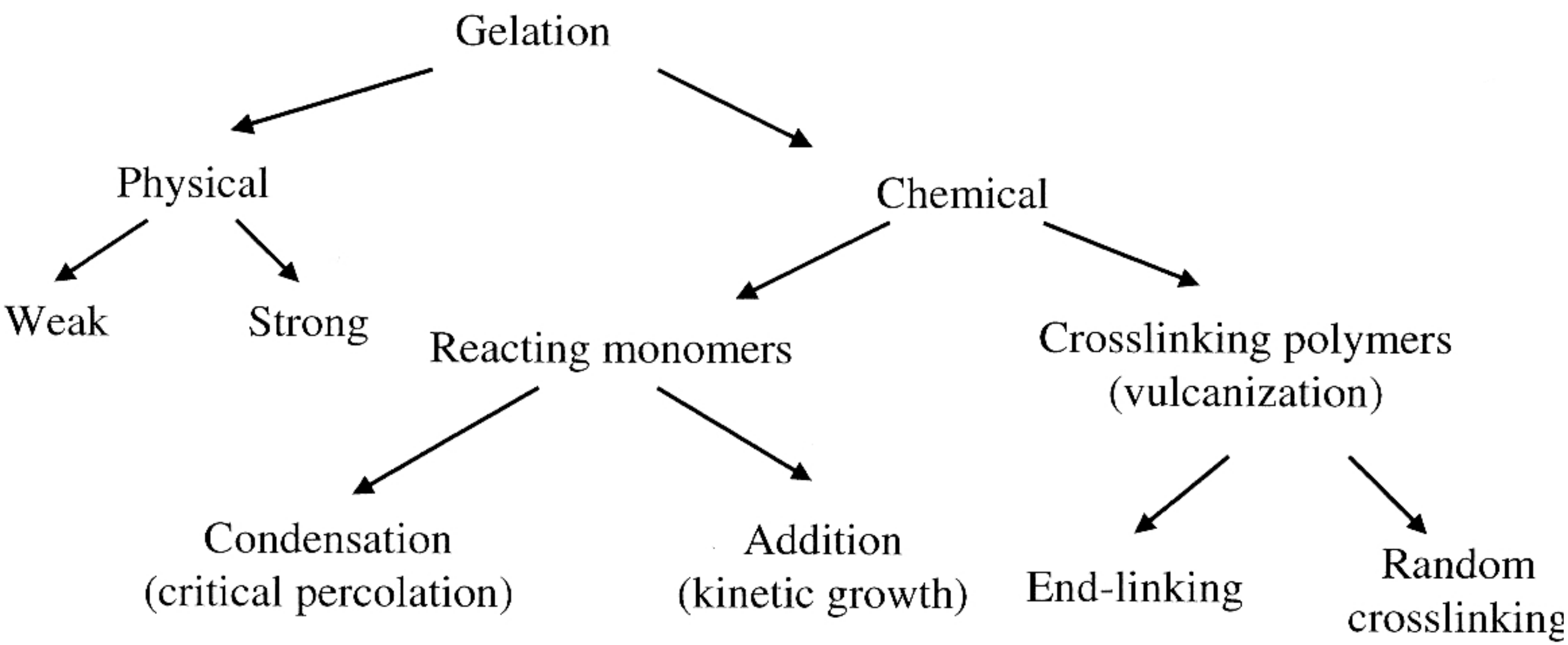
Gel





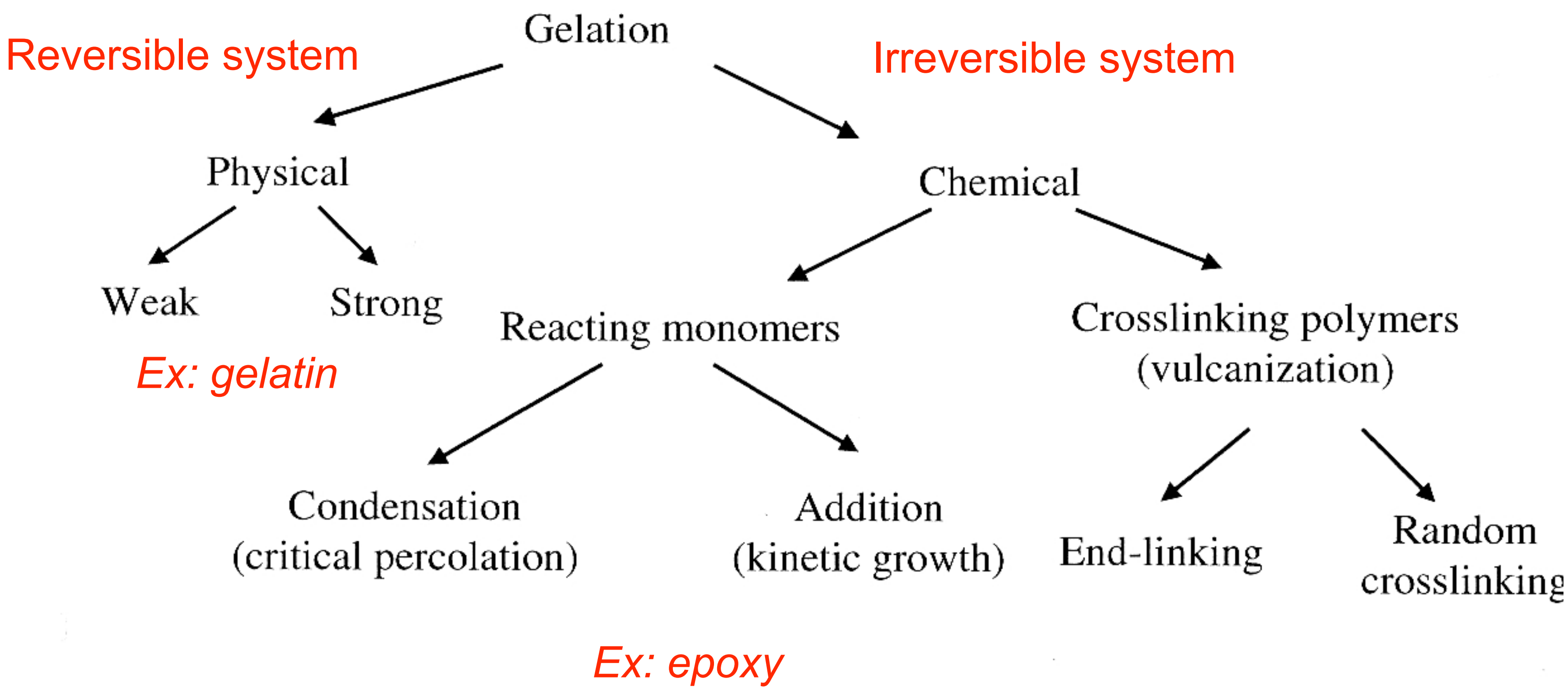
Heterogeneous system: immobile network + mobile solvent

The family of gels



From Rubinstein & Colby: Polymer Physics

The family of gels

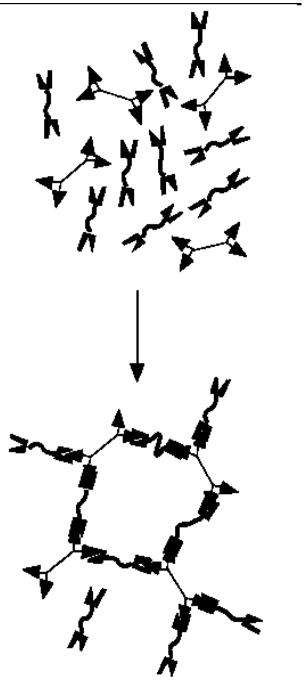


From Rubinstein & Colby: Polymer Physics

Chemical gels

Creating network by *chemical* cross links - covalent bonds

Reacting monomers:
Thermosetting resins with monomers
and hardener (epoxy)



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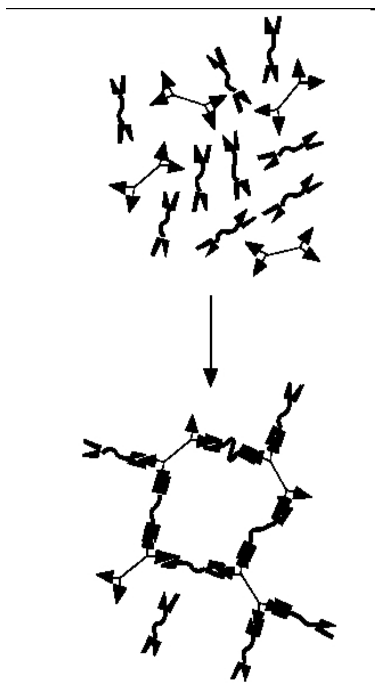

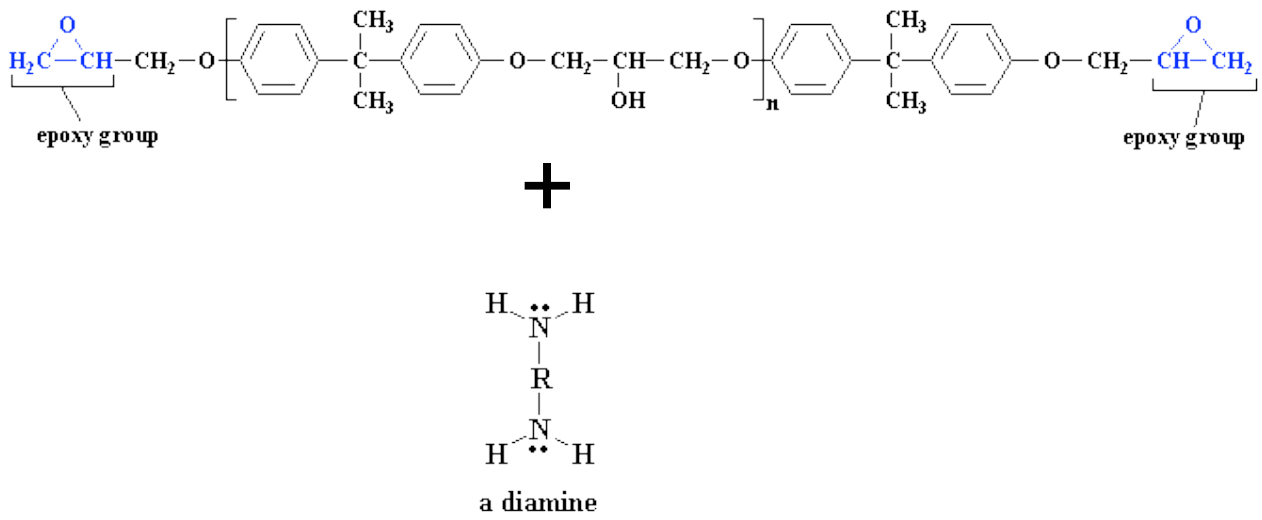

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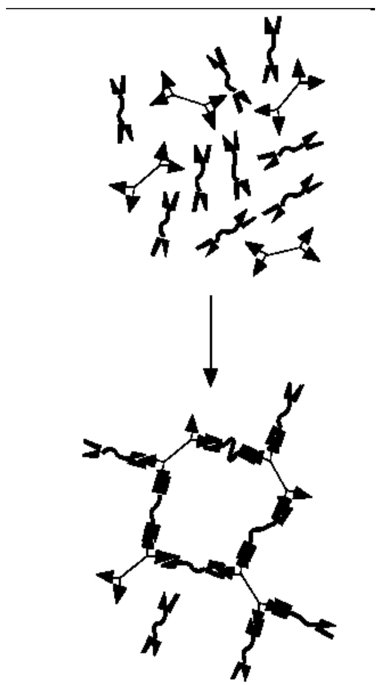

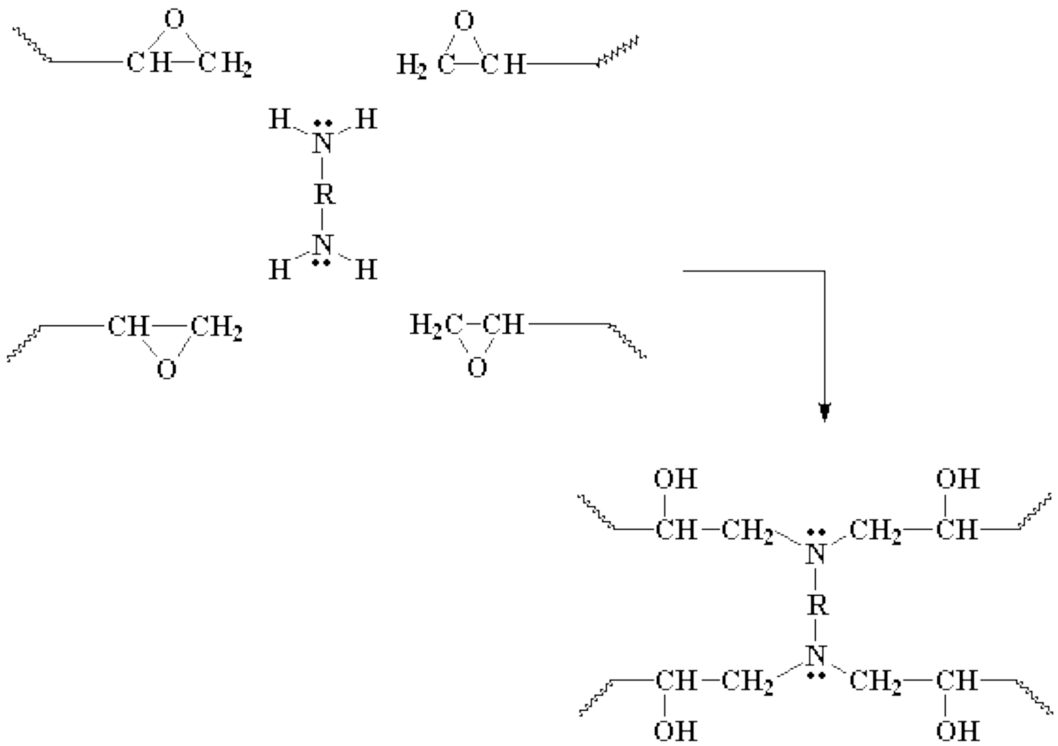

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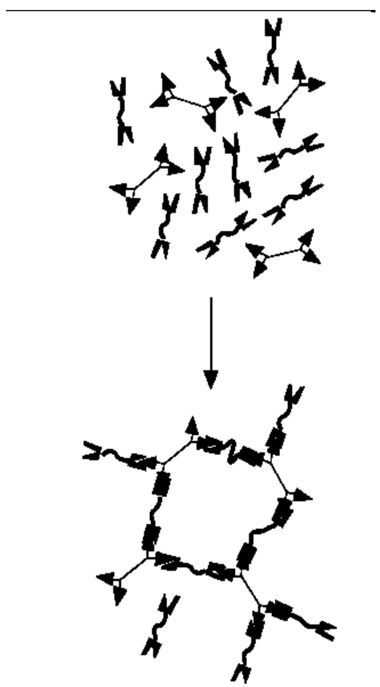

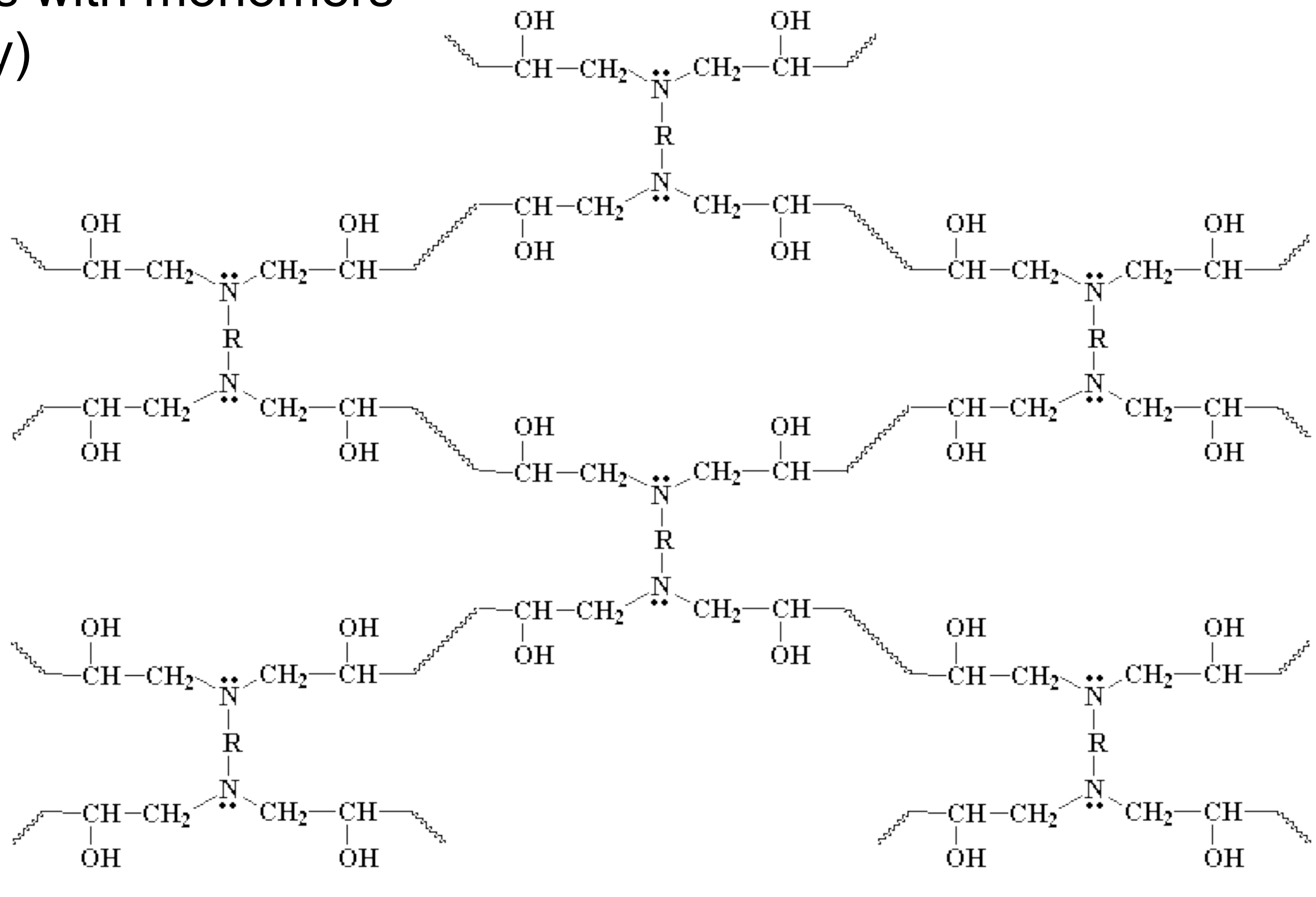

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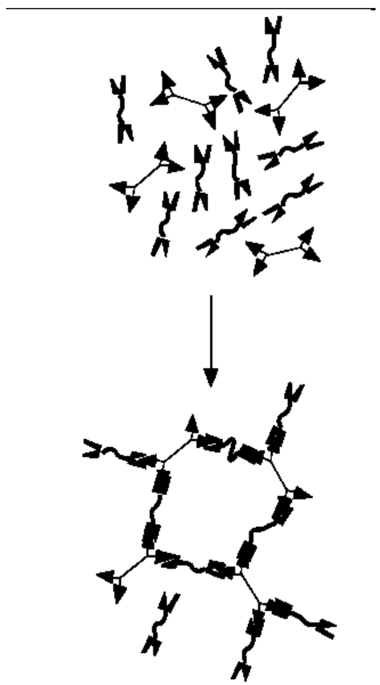
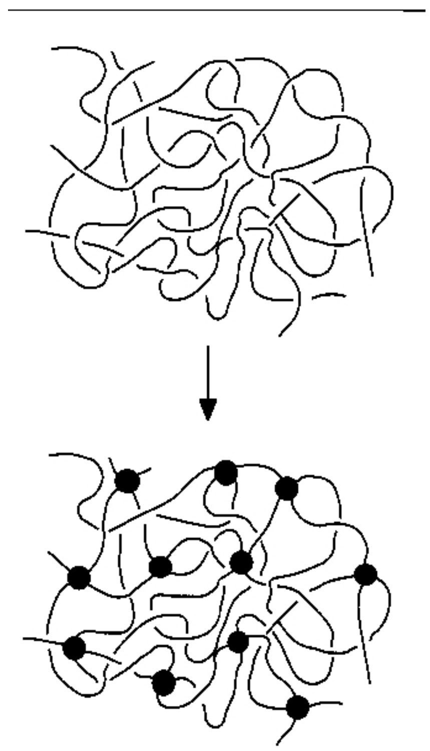


Cross-linking long polymer chains,
e.g vulcanised rubber



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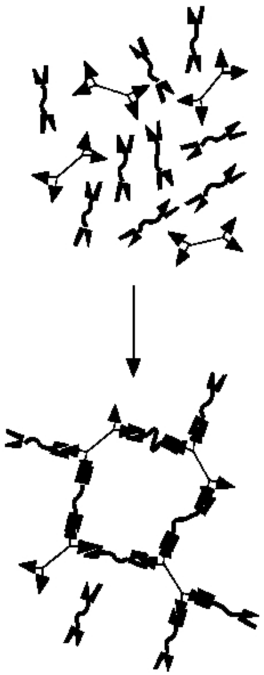
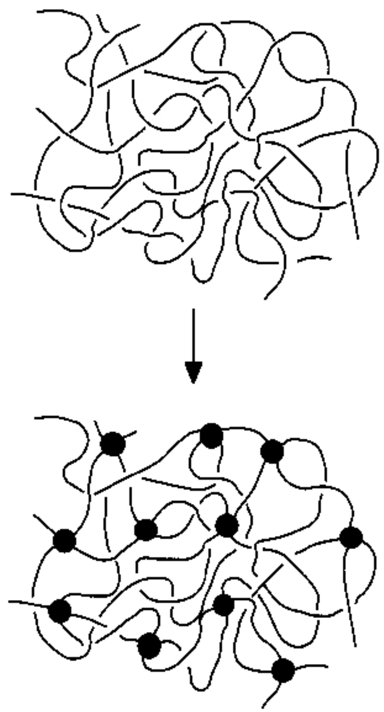


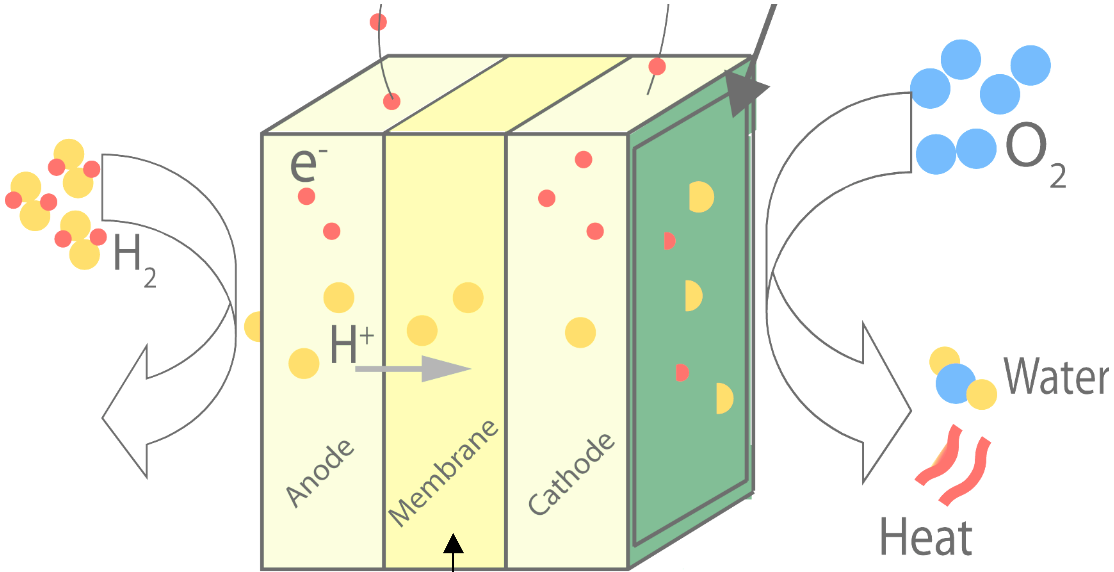
Short stiff segments/
High cross link density

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

rigid gel/glassy

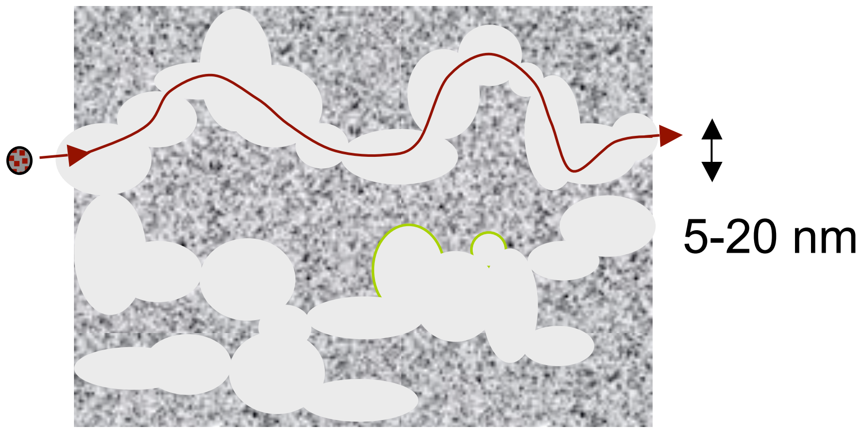


Example I: Fuel cell membranes



Polymer gel membrane

Combine mechanical stability of polymer with conductivity of a liquid phase



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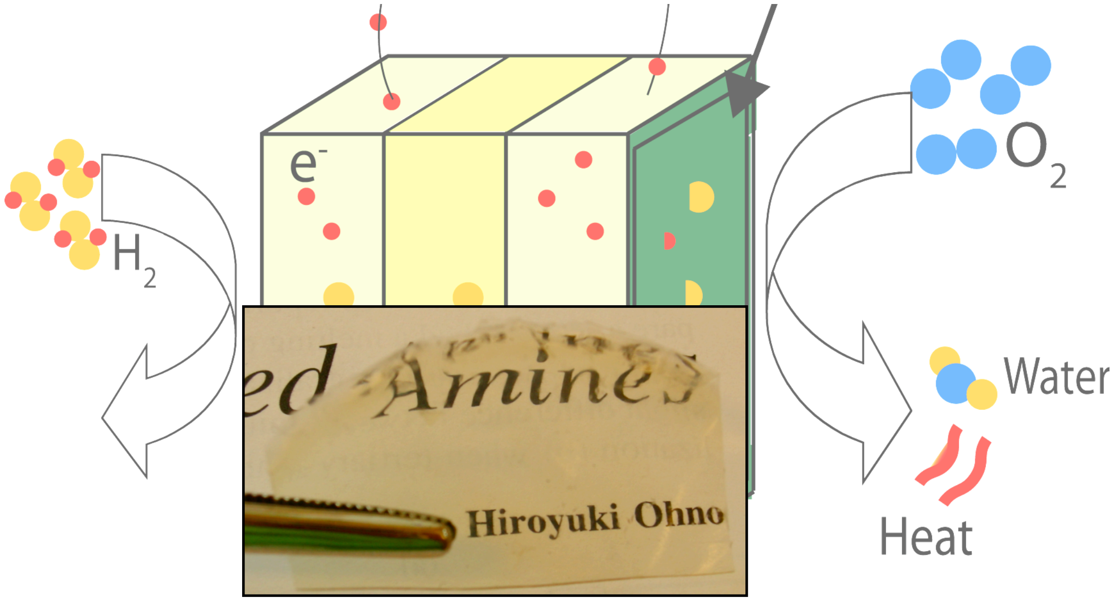
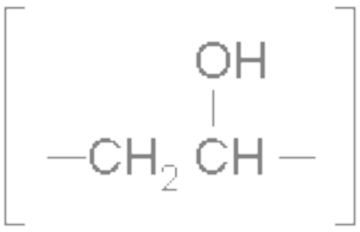
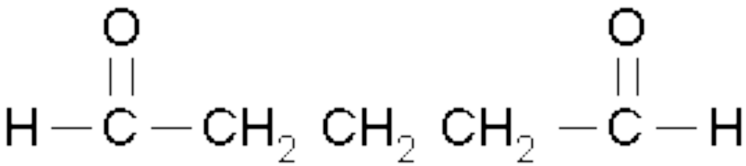


Polymer gel membrane
Combine mechanical stability of polymer with conductivity of a liquid phase

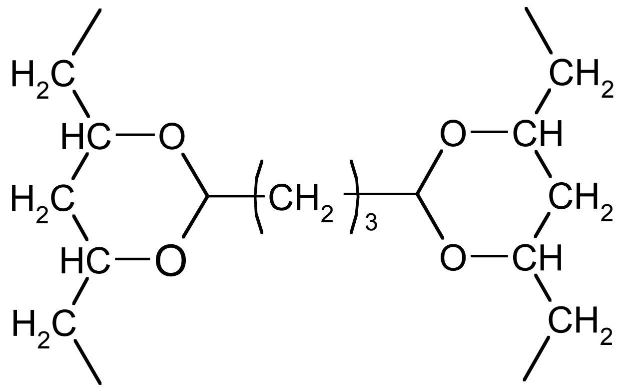
Chemical gel:
Cross-linked polymer +
acidic solution ($H_2O+H_2SO_4$)



PVA = poly(vinyl alcohol)



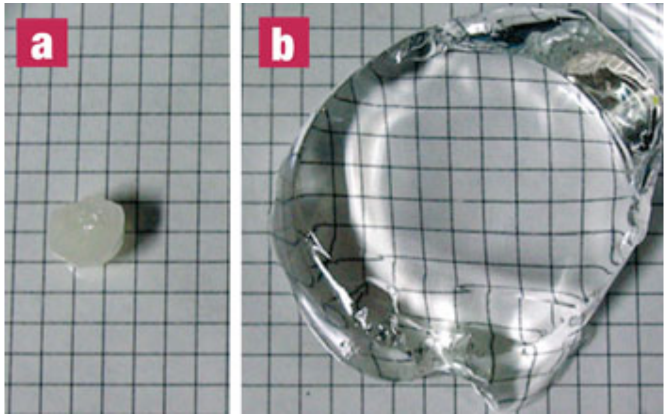
GLA (glutaraldehyde) = Pentane-1,5-dial



Example II: Superabsorbents

Superabsorbent - a gel that can swell >100 x weight

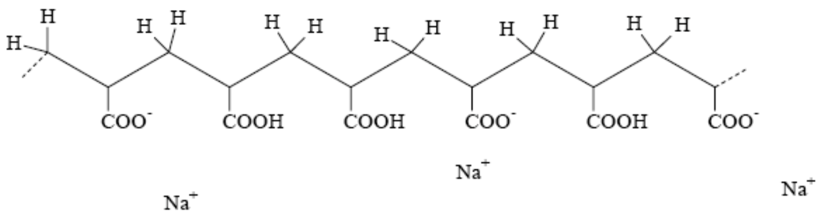
$$q_W = \frac{W_s}{W_d}$$

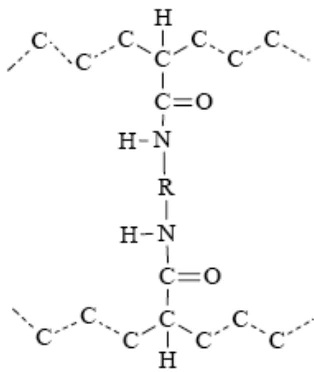


Nature Materials June 2007, 429

Volume change a balance between osmotic pressure and elasticity

Polyelectrolyte gels - control swelling by salt concentration

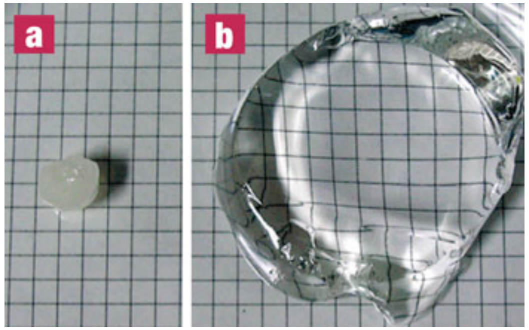


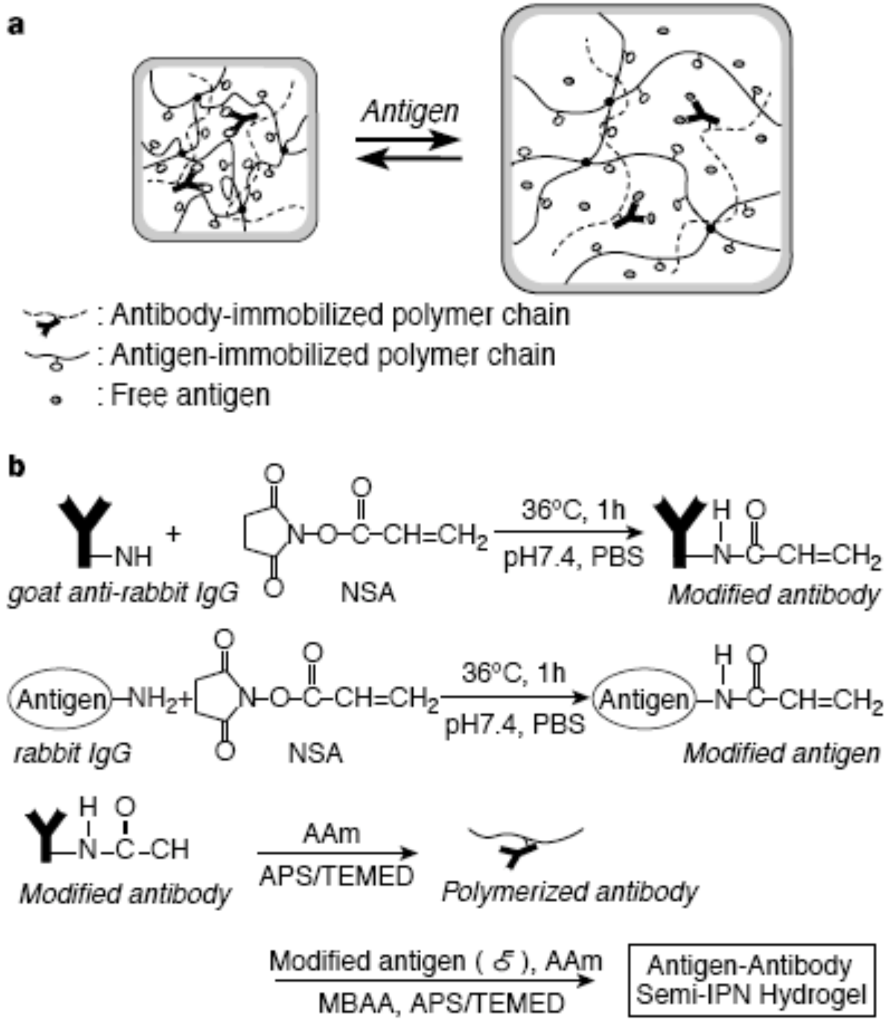


Example II: Superabsorbents

Superabsorbent - a gel that can swell >100 x weight

Antigen responsive - control swelling by presence of a specific protein





Nature 399, 766 (1999)

Example II: Superabsorbents

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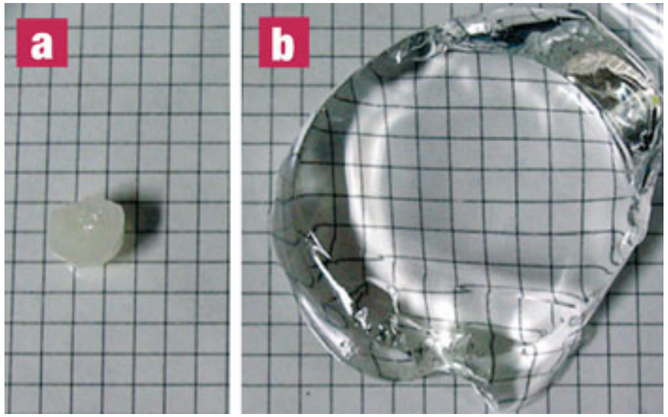


Nature Materials June 2007, 429

Volume change a balance between osmotic pressure and elasticity

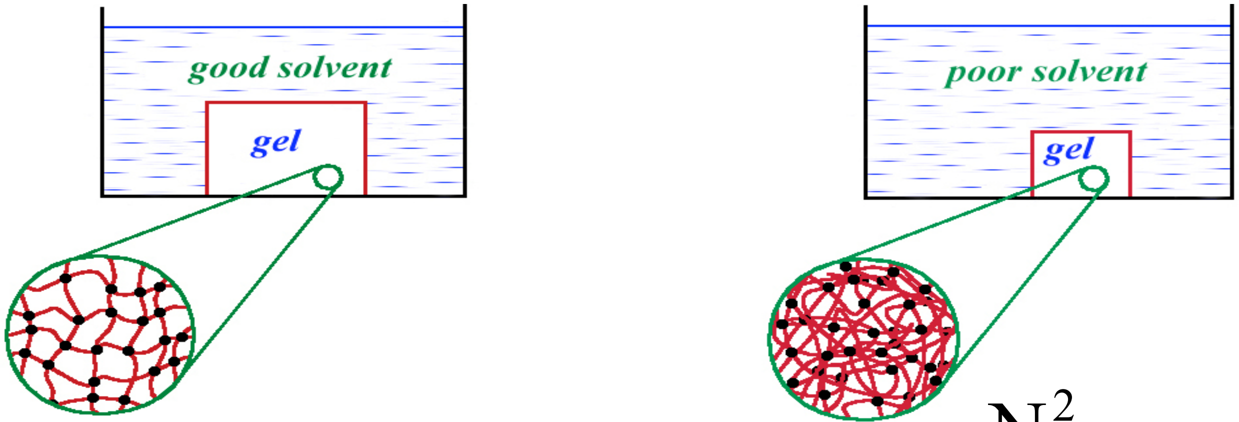
Polyelectrolyte gels - control swelling by salt concentration

Antigen responsive - control swelling by presence of protein

Lipophilic absorbent - swelling in non-polar solvent (oils)

….

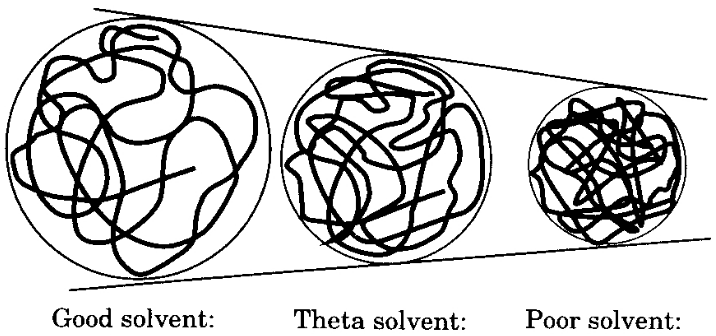
Swelling an analogue to coil-globule transition



$$F_{rep} + \Delta U_{int} = k_b T\nu(1-2\chi)\frac{N^2}{R^3}$$

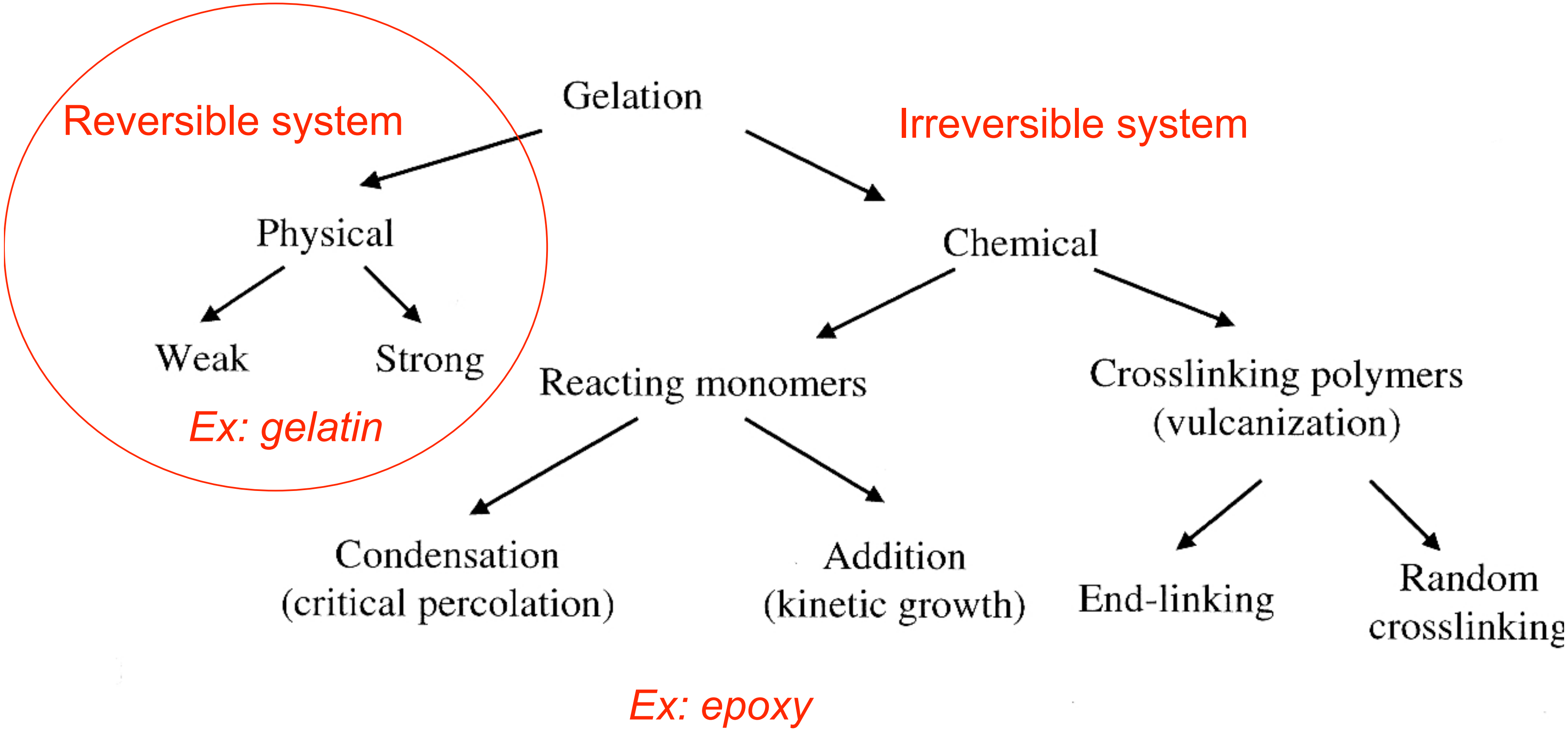
χ =1/2 and the two energies cancel and we have a "theta solvent" with pure random walk conformation!

χ <1/2 the coil is swollen (A good solvent)



χ >1/2 the coil forms a globule (A bad or poor solvent)

The family of gels



From Rubinstein & Colby: Polymer Physics

Physical gels

Creating network by *physical* cross links

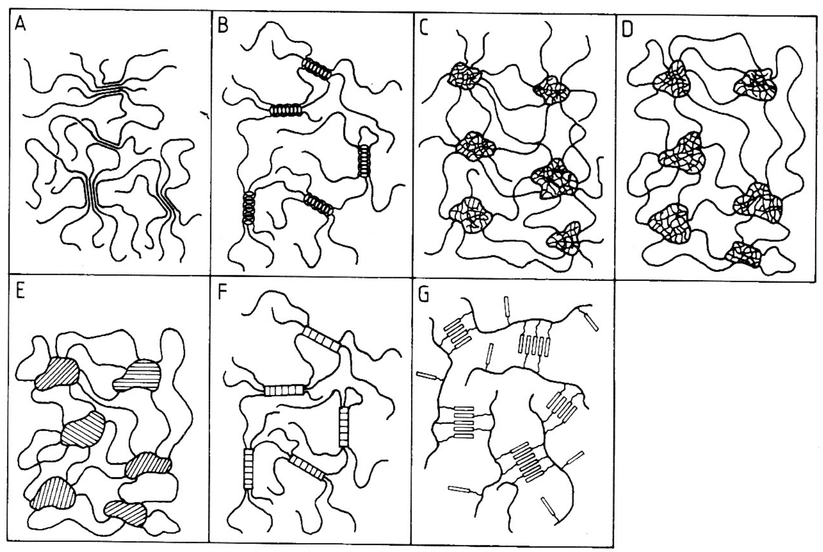


Fig. 3A–F. Schematic view of various kinds of Flory's type 3 gels: **A** PVC/plasticizer; **B** aqueous gelatin; **C** atactic PS in CS_2; **D** triblock copolymer SBS in tetradecane; **E** PO-EO-PO triblock copolymer in water; **F** s-PMMA and i-PMMA in toluene; **G** dissolved SCLCP

Te Nijenhuis, Thermoreversible Networks

Reversible cross-links

⇒ micellar crystallites

⇒ helix formation

⇒ glassy entaglements

⇒ micro-phse separation

⇒ hydrogen or ionic bonds

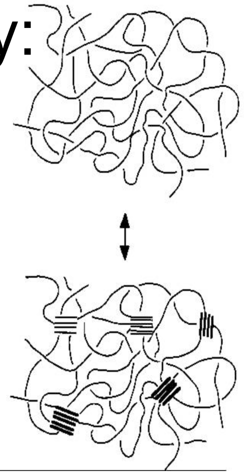
Gelation induced by:

⇒ temperature

⇒ pH

⇒ salt concentration

⇒ …

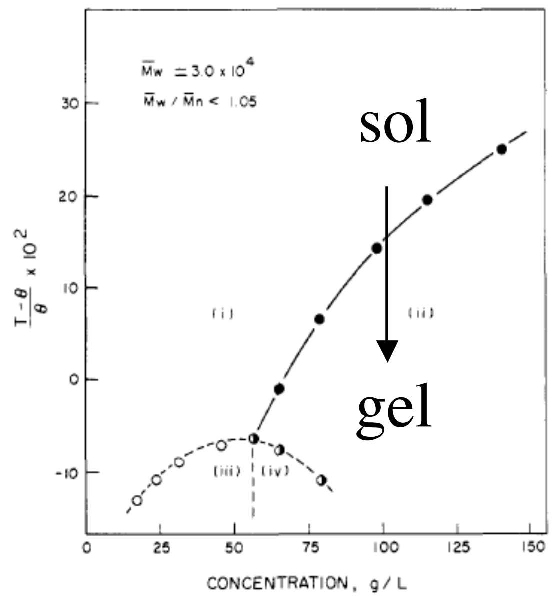


Thermoreversible gelation

Reversible transition from liquid-like to solid-like behavior
Found for a large range of macromolecular systems, biological as well as synthetic polymers (polymer solutions)

Gelation mechanism?

- *crystalline cross links*
- *entanglement*
- *phase separation*
- *aggregation/jamming*
- …

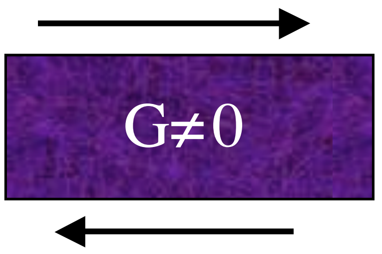


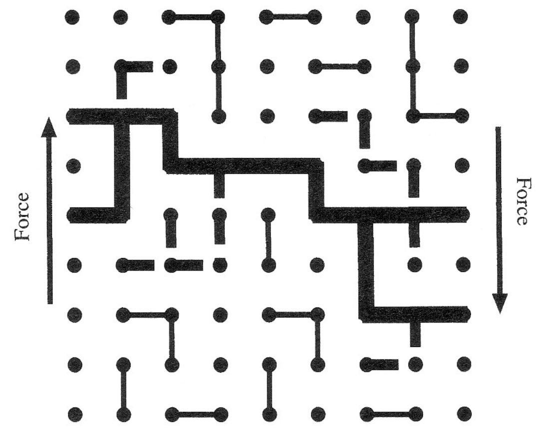
Measuring the gel-point

Rheology experiment

Transition from liquid-like to solid-like behavior

⇒ development of a shear modulus (ω=*0*)

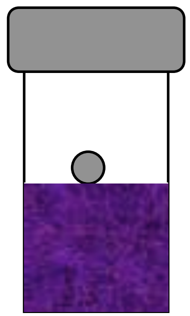




Easy in the lab method

⇒ Falling ball

⇒ TTT (tilt-test-tube)



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Rheology experiment

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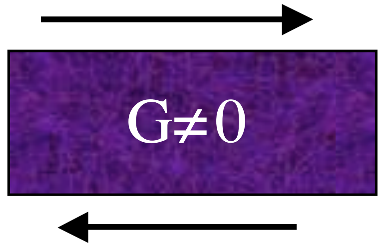

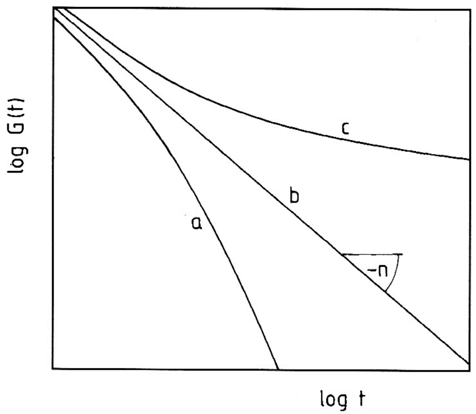

Fig. 4. Double logarithmic plot of the relaxation shear modulus vs time for a crosslinking system; *curve a* – before the gel point; *curve b* – at the gel point; *curve c* – after the gel point

Te Nijenhuis, Thermoreversible Networks

Winter-Chambon method

At the gel-point

$$G(t) = St^{-n}$$

Example - gelatine

Gelatine: Formed from *collagen*, a protein “found” in animals. When collagen is heated, it breaks down into the *protein gelatin*.

A thermoreversible system - gelatine+water

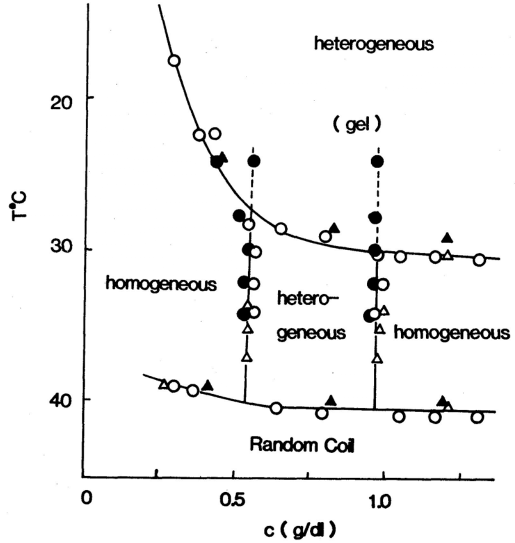

FIG. 7. Phase Diagram for Gelatin Solution.
○, $1/p$; ●, $[\alpha]_{405}$; △, η_{sp}/c; ▲, c/i_{90}.

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A thermoreversible system - gleatine+water

Crosslinks from helix formation

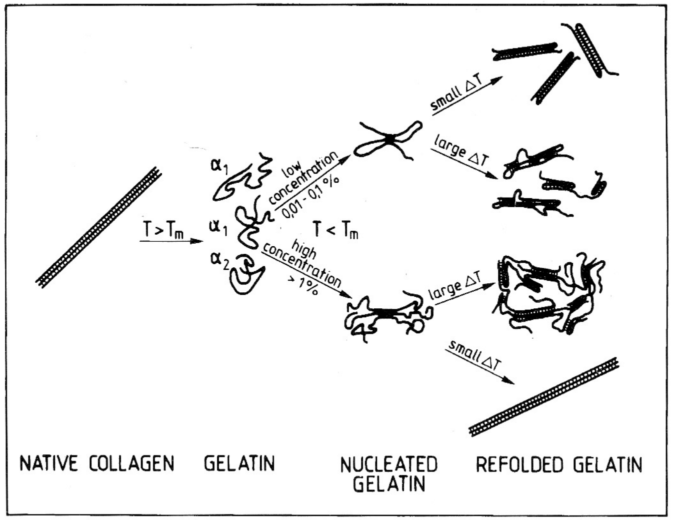


Fig. 172. Schematic view of the renaturation process of gelatin. Reproduced from Biochemistry [Ref. 460] by the courtesy of The American Chemical Society

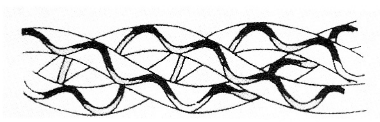
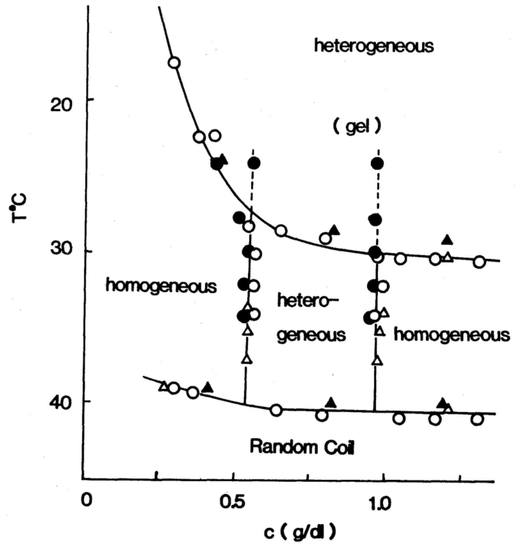


Fig. 6.4 Collagen molecules in their native conformation. Each chain is a left-handed helix; the three chains assemble to form a right-handed superhelix.



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Te Nijenhuis, Thermoreversible Networks

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A thermoreversible system - gleatine+water

Crosslinks from helix formation

Time dependence of gleation

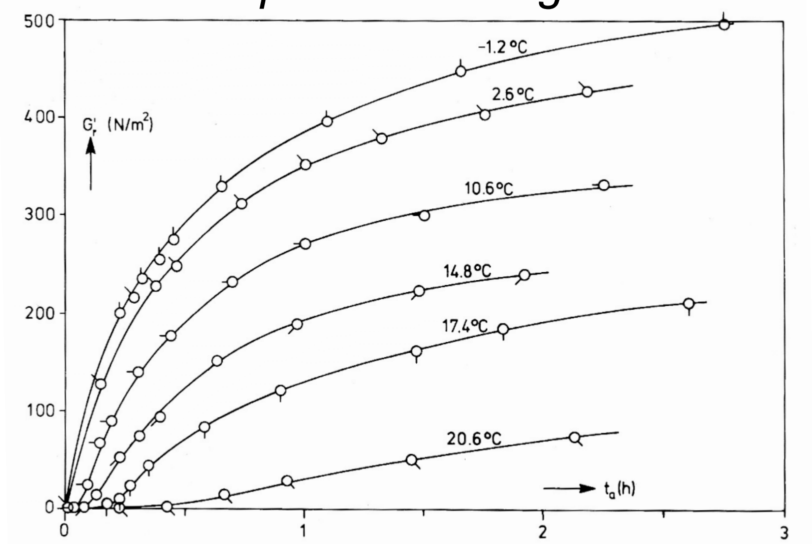


Fig. 173. Storage modulus of aqueous 1.95 wt% gelatin ($\bar{M}_w$ = 70 kg/mol) vs ageing time for several ageing temperatures; angular frequency ω = 0.393 rad/s. Reproduced from Colloid Polym Sci [Ref. 23] by the courtesy of Steinkopff Verlag Darmstadt, FRG

Te Nijenhuis, Thermoreversible Networks

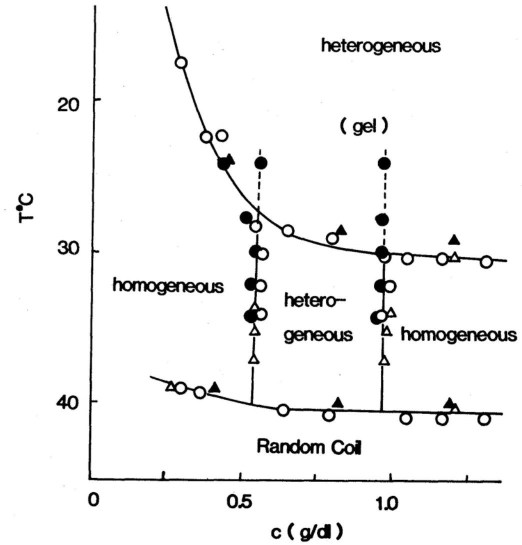
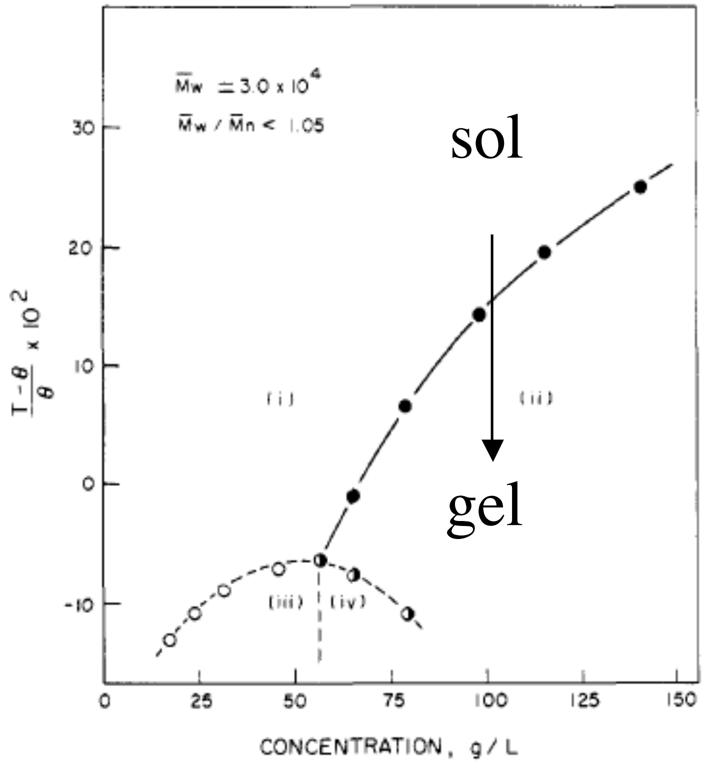


FIG. 7. Phase Diagram for Gelatin Solution.
○, $1/p$; ●, $[\alpha]_{405}$; △, η_{sp}/c; ▲, c/i_{90}.

Gelation and phase separation



Phase diagram for aPS/toluene

Gelation by phase separation

For polymer solutions we can form

- homogeneous gels
- heterogeneous gels (phase separated)

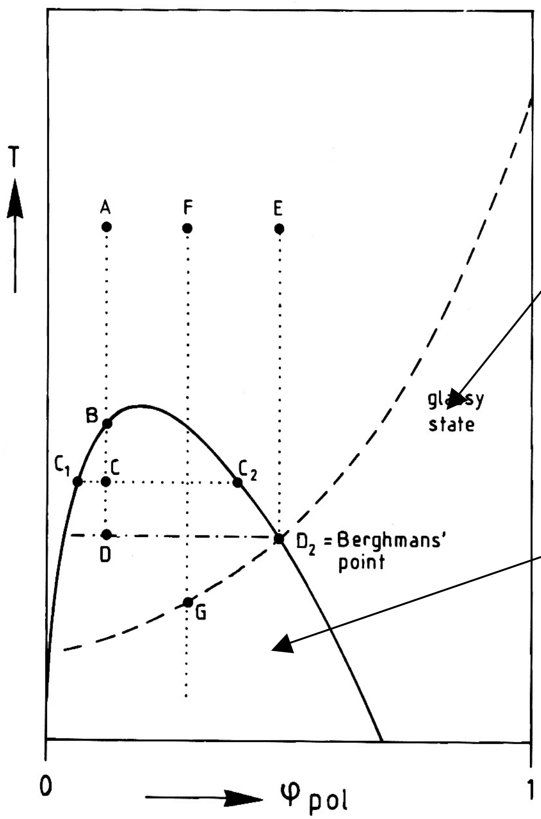


Fig. 84. Phase diagram, shown schematically, of solutions of monodisperse polymer for which the glass transition curve (----) crosses the binodal boundary curve

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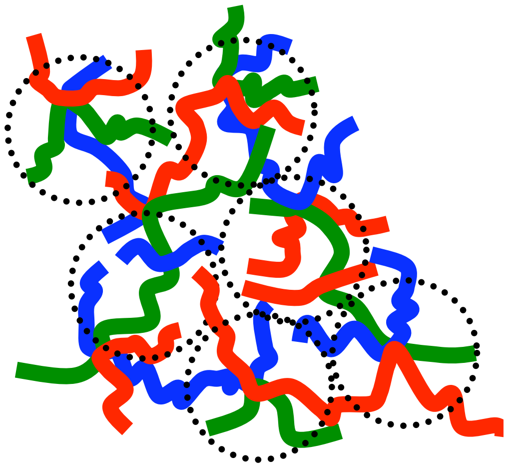
Homogeneous gel

freezing in entanglement



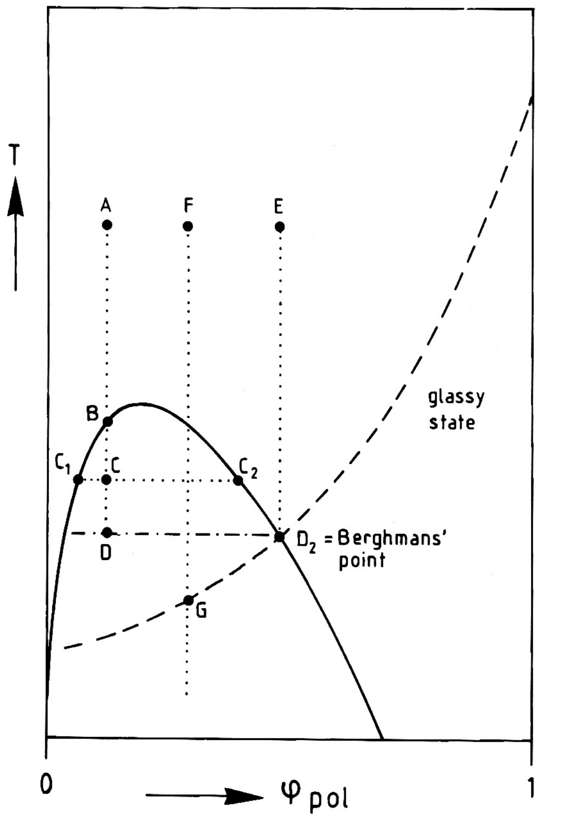
Heterogeneous gel

Phase separation & freezing in of structures

Gelation by phase separation

For polymer solutions we can form

- homogeneous gels
- heterogeneous gels (phase separated)



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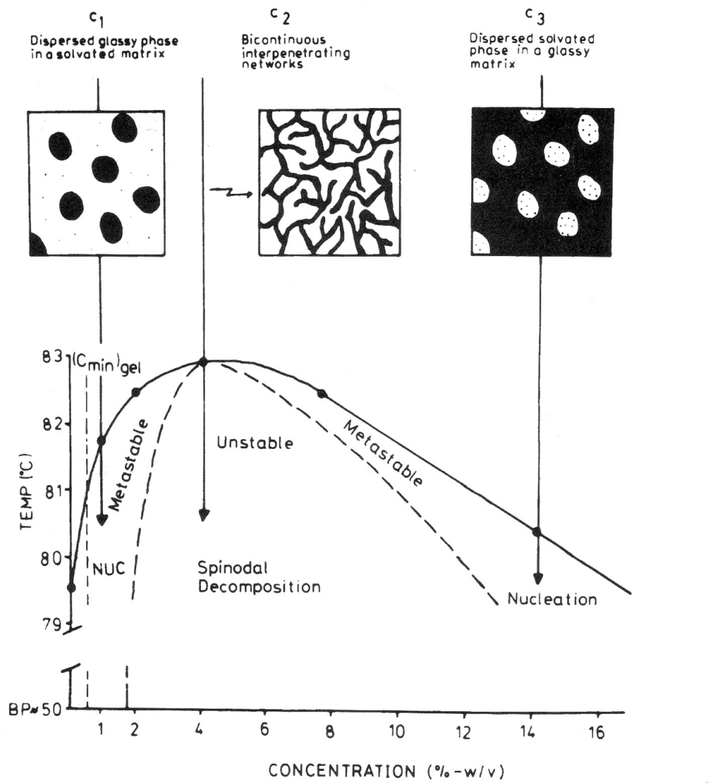

Fig. 86. Detail of Upper Critical Temperature phase diagram of aPS ($\bar{M}_w$ = 2750 kg/mol) in cyclohexanol, including expected variation in (gel) morphology with concentration. Reproduced from Makromol Chem [Ref. 276] by the courtesy of the authors and of Hüthig & Wepf Verlag Publishers, Zug, Switzerland

Gelation by phase separation

For polymer solutions we can form

- homogeneous gels
- heterogeneous gels (phase separated)

Creating different textures in the material

⇒ important for e.g taste

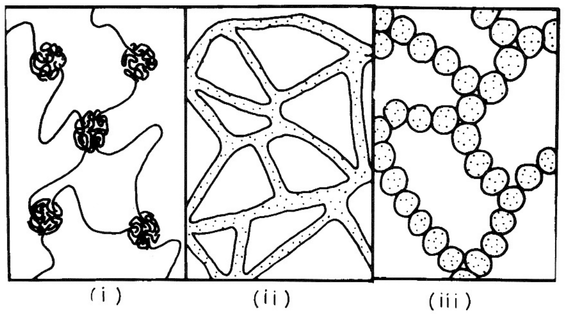

Fig. 88i–iii. Schematic illustration of the three classes of gels: **i** molecularly connected; **ii** phase connected (continuous); **iii** phase connected (adhesive). Reproduced from Makromol Chem [Ref. 276] by the courtesy of the authors and of Hüthig & Wepf Verlag Publishers, Zug, Switzerland

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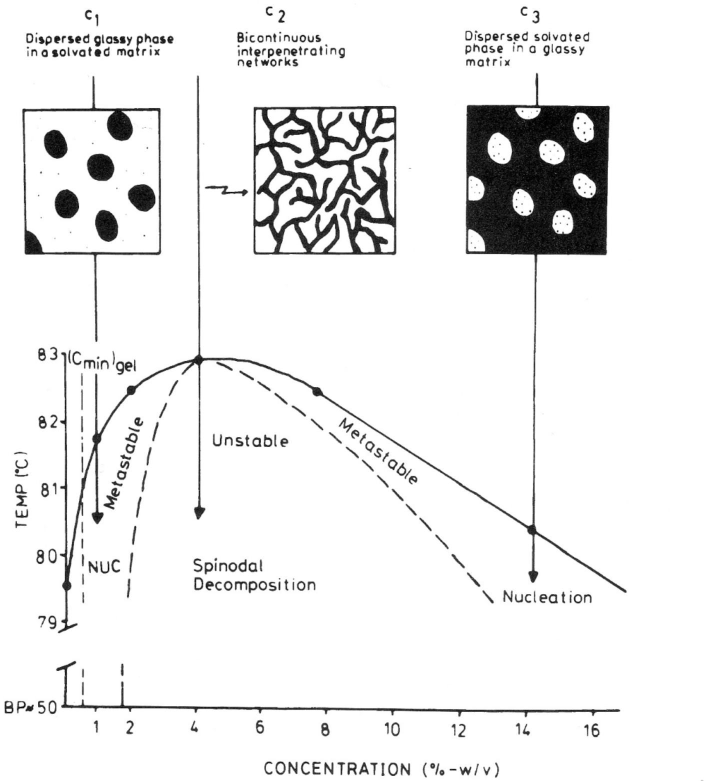
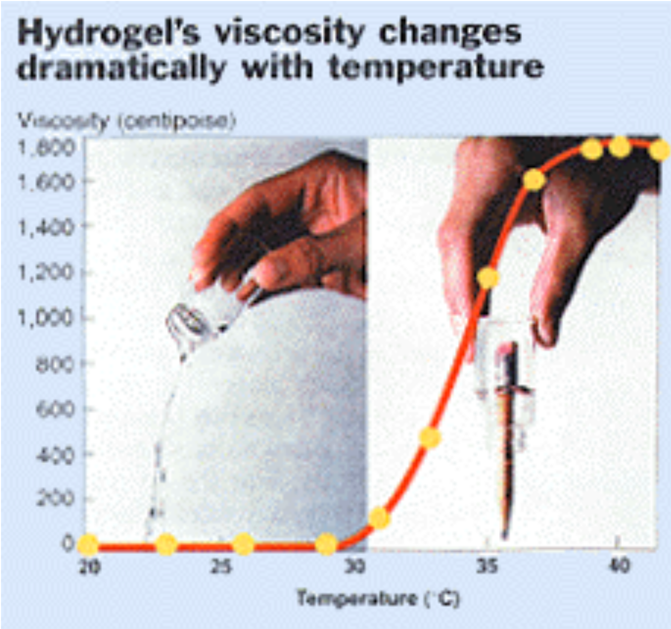
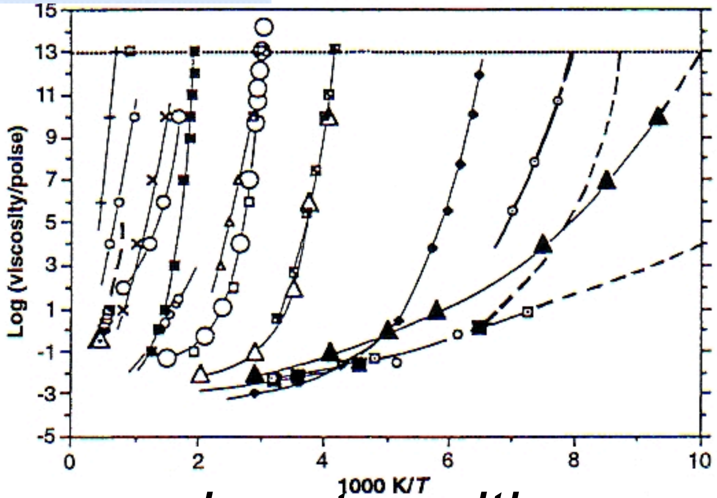


Fig. 86. Detail of Upper Critical Temperature phase diagram of aPS ($\bar{M}_w$ = 2750 kg/mol) in cyclohexanol, including expected variation in (gel) morphology with concentration. Reproduced from Makromol Chem [Ref. 276] by the courtesy of the authors and of Hüthig & Wepf Verlag Publishers, Zug, Switzerland

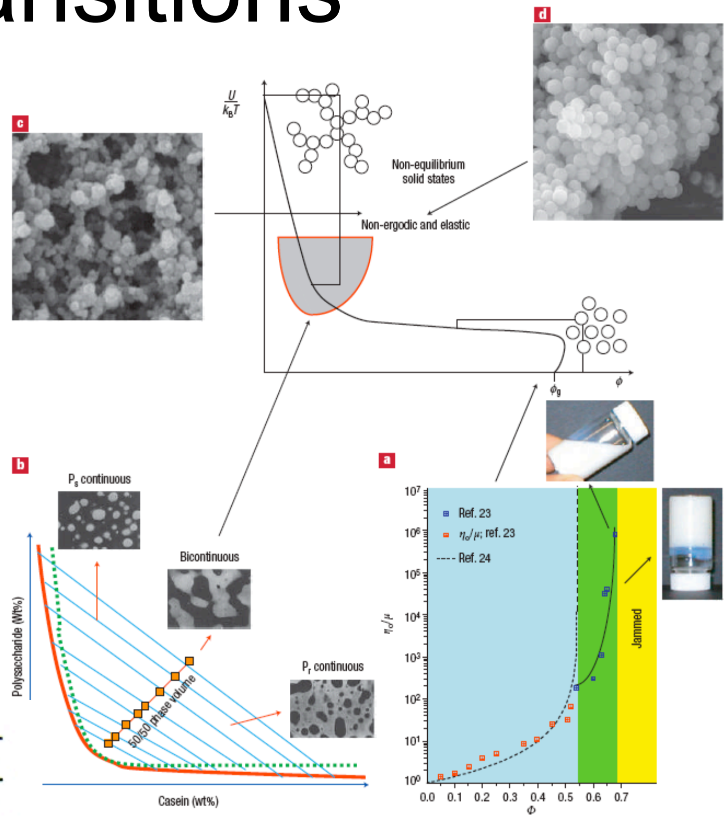
Solid - liquid transitions

gelation





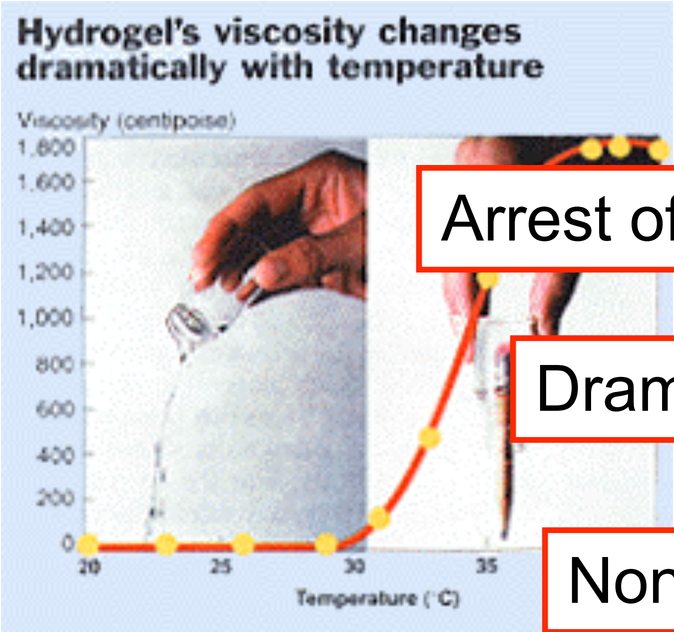
glass transition

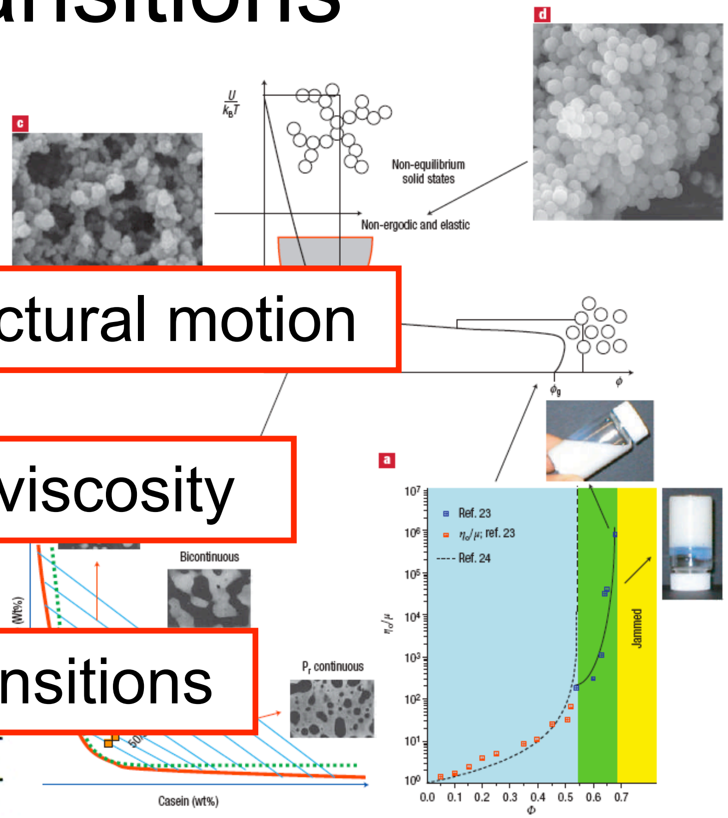


colloidal aggregation

Solid - liquid transitions

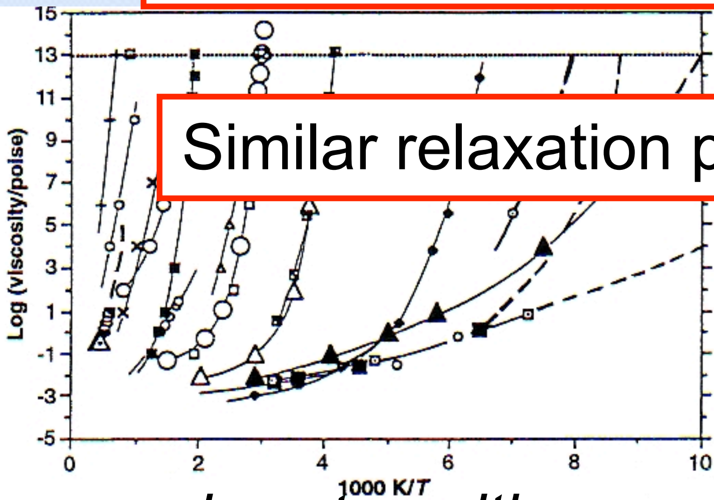
gelation





- Arrest of molecular/structural motion
- Dramatic change in viscosity
- Non-equilibrium transitions
- Similar relaxation patterns

lloidal aggregation



glass transition

Jamming?

A unifying picture of glass formation, gelation and colloidal aggregation?

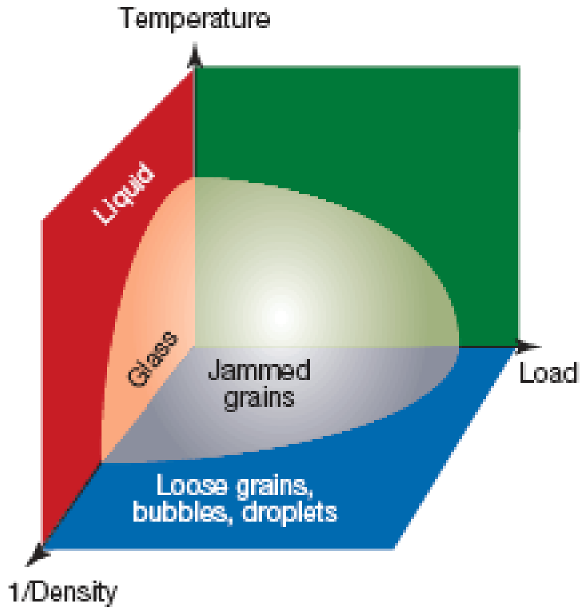
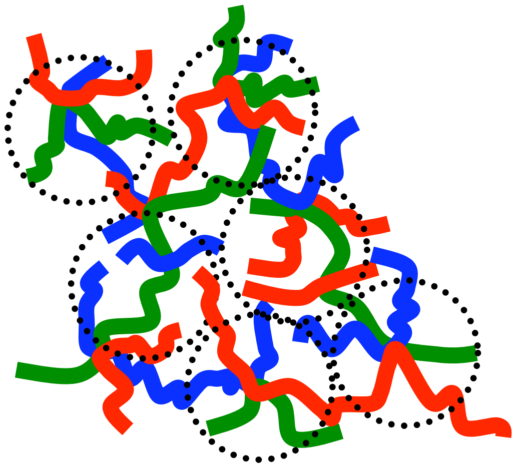


Figure 1 The jamming phase diagram proposed by Liu and Nagel[2].

Weitz, Nature 411, 774 (2001)



Next lecture

Thursday 4/10 8.00

⇒ Experimental techniques for soft matter