

Gels and Networks

Many systems consist of 3 dimensional network structures.

These are often known as gels when 2 phases/ components are present.

We have already come across network structures in the case of rubbers – which are chemically crosslinked to form a network.

For these we saw the mechanical properties depended on the crosslink density.

Inorganic glasses can be thought of as consisting of a tetrahedrally bonded network, with a very high 'crosslink' density.

Epoxy resins are another example of a network structure: here a chemical reaction between the two components leads to the network, and the crosslink density can be controlled by the specific chemistry.

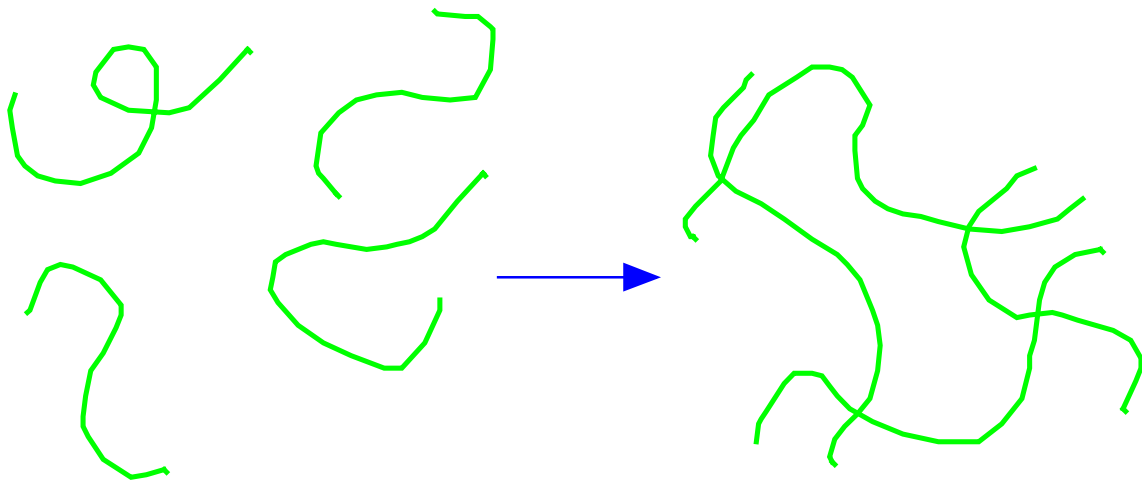
Many polymers can form gels in solution e.g. gelatin (a protein) to form 'table jelly'.

In this case the water is incorporated into the structure.

Many other foodstuffs exist as gels: yogurt, cheese.

For vegetarians gels may be made from agar (a polysaccharide from seaweed), which is also frequently used as a growth medium by microbiologists.

All these systems have in common the ability to form a network.



A gel will have a finite shear modulus – unlike a liquid.

This is a useful operational definition for identifying when gelation has occurred.

In practice measuring this can be a non-trivial problem.

Gels and network structures can vary greatly in their mechanical properties:

- **Epoxies are hard**
- **Jelly is pretty soft!**

There are many different processes by which gelation can occur, and these can be reversible or irreversible.

Irreversible processes usually arise from chemical processes.

Reversible gelation is usually associated with physical processes.

Very often gelation leads to kinetic arrest before equilibrium is reached, and equilibrium ideas must be used with caution.

Gel Transition

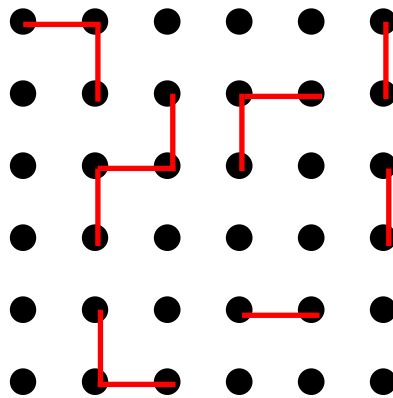
(Also known as the Sol-Gel transition, with the liquid phase being the ‘sol’)

This transition is similar to the percolation threshold, and percolation theory can be used (the same ideas as used, for instance, in studying electrical conductivity in random electrical networks).

However, because the timescales (particularly for polymers) tend to be slow and equilibrium is not usually maintained, use of such theories must be treated with caution.

Can use a lattice model, with each lattice point corresponding to individual atoms, or monomers on a polymer chain (in which case connectivity will already exist between some sites).

Construct a lattice and form bonds randomly between lattice points.



If p is the fraction of potential ‘bonds’ which have formed ($0 < p < 1$) what is the critical value p_c when a gel first forms?

The condition for gelation is that there is (for the first time) one continuous path which spans the system.

Below p_c there are only individual clusters – still in the sol phase.

Above p_c there is one 'giant molecule' in the gel phase, plus individual clusters still in the sol phase.

As p increases beyond p_c , fewer and fewer sites are not included in the gel fraction.

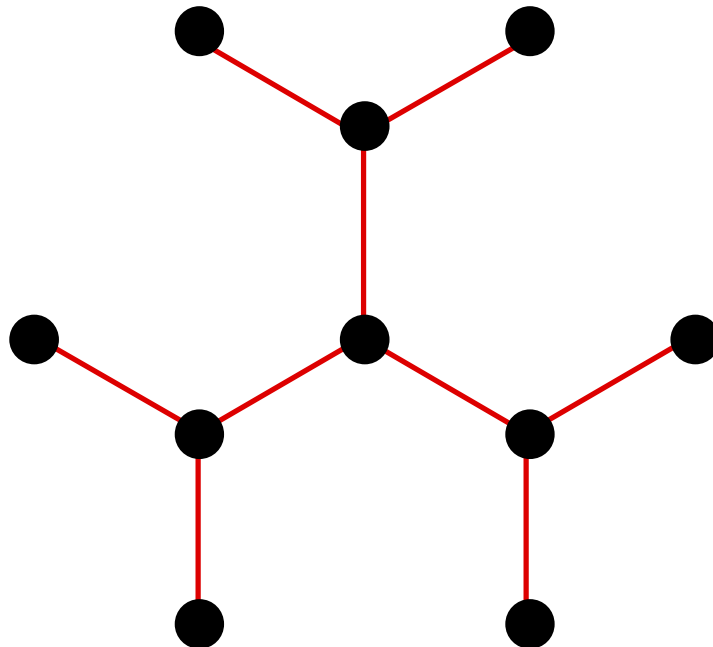
For a square lattice, $p_c = 1/2$.

Much work has been done on this via computer simulation.

This is obviously an unrealistic model for a real gelling system, but the hope is that some **properties of percolation are universal**, and thus not dependent on the specific details of the model chosen.

Flory-Stockmayer model

– percolation on a 'Cayley tree' does allow an exact (analytical) solution, although this is not generally the case.



This model neglects the possibility of closed loops.

Each monomer is assumed to link to z others (so the diagram above corresponds to $z=3$)

From each monomer $(z-1)$ new bonds can form.

The probability that a bond is made is p (i.e. the fraction of reacted bonds is p and we assume no correlation).

These bonds can form with probability $p(z-1)$

Each monomer in the n th generation will be linked to $p(z-1)$ monomers in the $(n+1)$ 'th generation.

Therefore the number of bonds N in the n th generation is:

$$N \sim [p(z-1)]^n$$

For large n , N will diverge for $p_c \geq (z-1)^{-1}$.

This defines the percolation threshold.

We find that

$p < p_c$, $N \rightarrow 0$ (all clusters still in sol fraction).
 $p > p_c$, $N \rightarrow \infty$

For $z=3$, $p_c = 1/2$, but this value is not universal.

As we approach the percolation threshold, the mean size of the clusters diverges.

Properties like the viscosity, which depend on the mean cluster size, also diverge.

For $p > p_c$, above the percolation threshold, there is an infinite cluster - a gel.

This has a finite shear modulus.

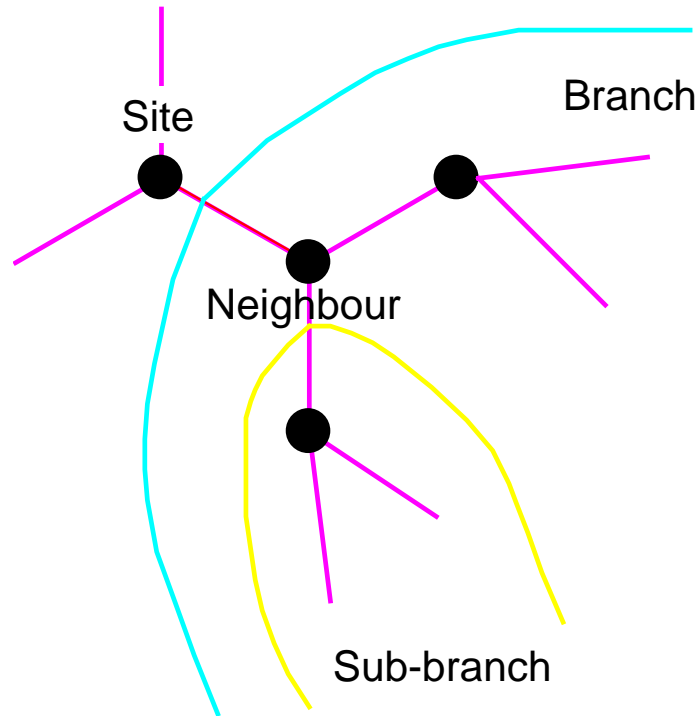
However, not all the bonds are connected to the infinite cluster.

The fraction of reacted bonds is called the gel fraction and can be calculated as follows.

The Gel Fraction in the Classical (Flory-Stockmayer) Model

Let the probability that a site is connected to infinity by a continuous path of bonds be α .

And β be the probability that the site is not connected to the infinite cluster via a particular branch.



$(z-1)$ sub branches start at neighbour.

β^{z-1} is the probability that none of neighbour's sub branches connect to infinite cluster.

Therefore the probability that a site is connected to neighbour, but not connected via that neighbour to infinity is $p\beta^{z-1}$.

Now we can write a recursive relation for β :

$$\beta = p\beta^{z-1} + (1-p)$$

↑
↑
 connected to neighbour not connected
 but not infinity to neighbour.

For the special case of $z=3$, this gives a quadratic for β which can be solved to yield

$$\beta = 1 \quad \text{or} \quad \frac{1-p}{p}$$

below threshold **above threshold.**

Hence can solve for α , the fraction of bonds connected to infinity.

$p\beta^z$ is the probability that a site is connected to a specified neighbour, but not connected to infinity.

This is equal to $(p-\alpha)$, the fraction of bonds that are reacted, but which do not form part of the infinite cluster.

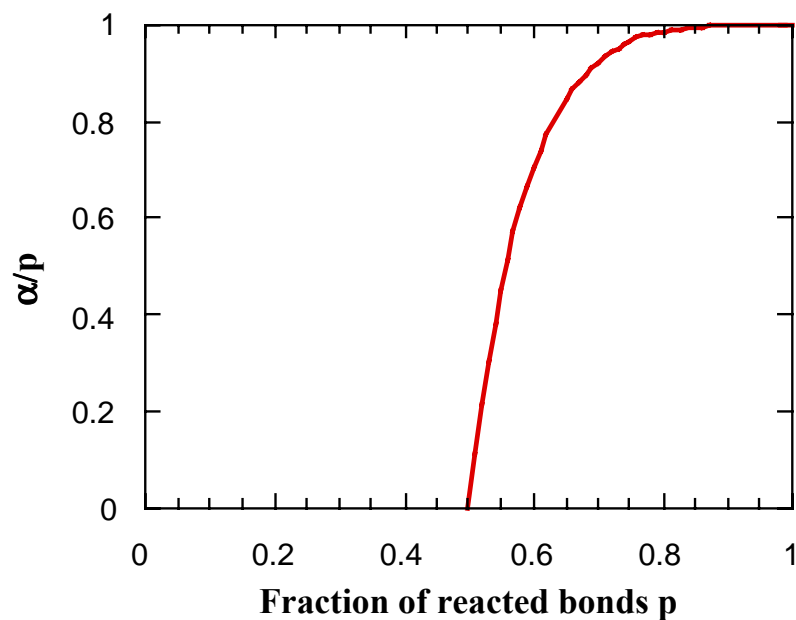
Thus $p - \alpha = p\beta^z$.

For $z=3$, and substituting for β

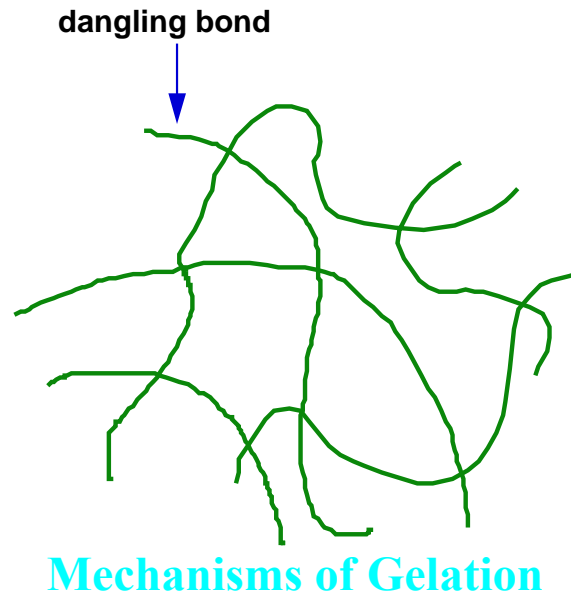
$$\frac{\alpha}{p} = 1 - \left(\frac{1-p}{p} \right)^3 \quad p > p_c$$

$$\frac{\alpha}{p} = 0 \quad \mathbf{p < p_c}$$

This function looks like:



Note we cannot use this approach to work out how gel modulus scales as we approach the critical point (from above), since the infinite cluster will have branches which are not 'elastically effective' ie dangling bonds.



There are many different mechanisms and no universal behaviour.

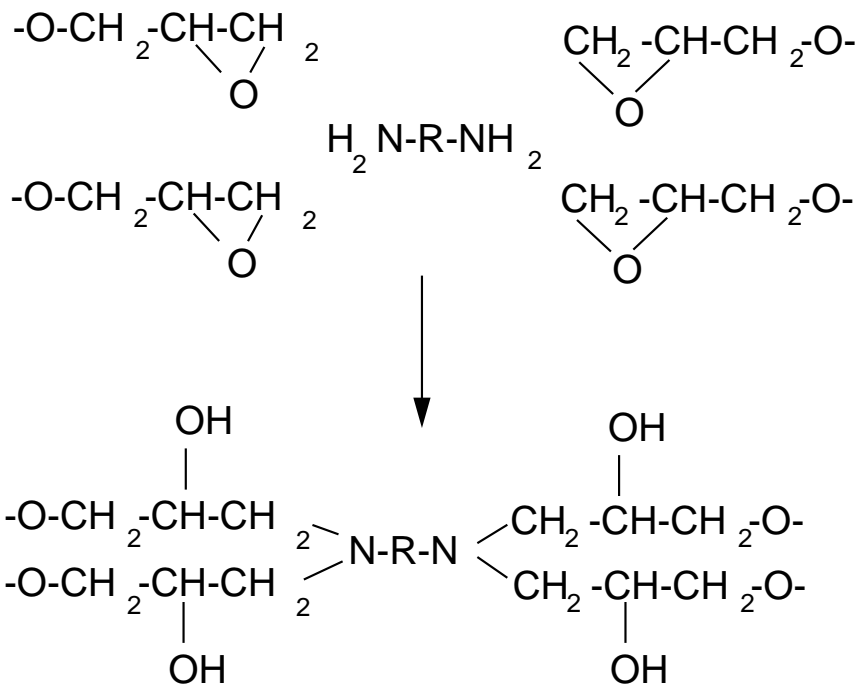
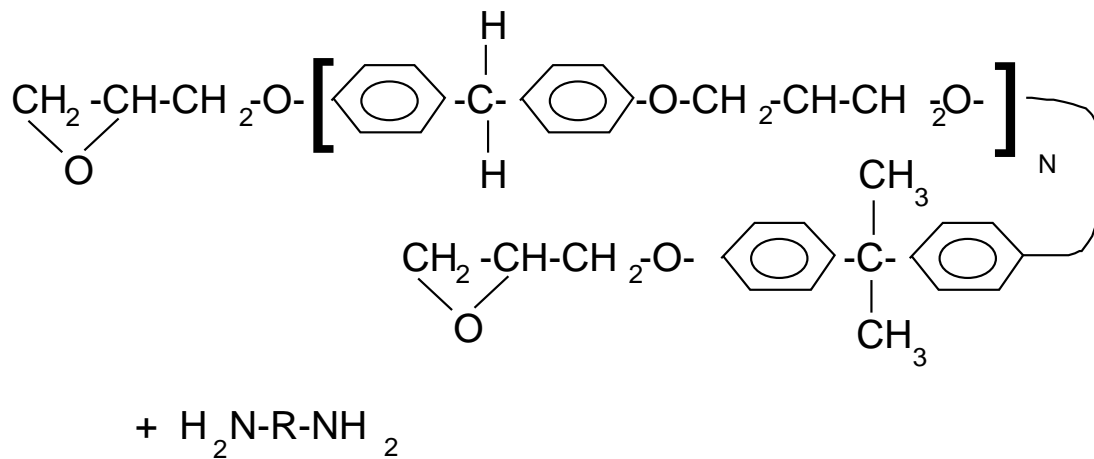
Can identify certain types of gelation:

- **Chemical Reactions**

e.g. **vulcanisation of rubber** –

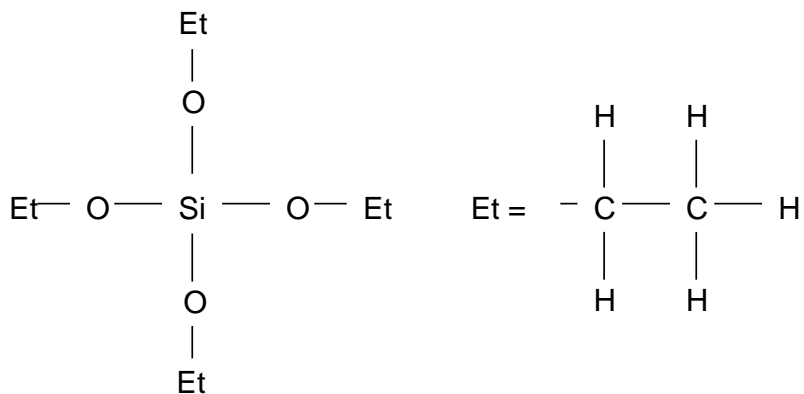
The precise chemistry of this is complex. Empirically it is found that heating natural rubber with sulphur leads to crosslinking via sulphur bridges.

The network forms as the epoxide rings open up.

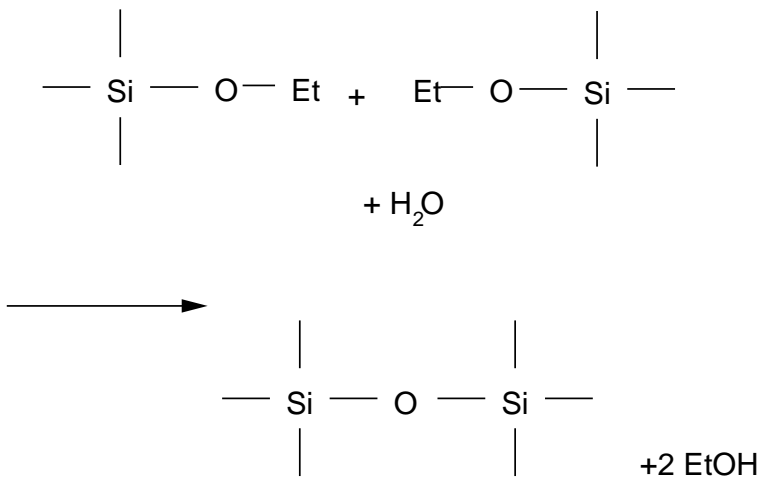


Ceramics are also often processed by a 'sol-gel' route.

In this case the network produced is 'tight' with a high crosslink density.



Tetraethoxysilane (TEOS)



The ethanol can then be washed away.

All these are irreversible processes.

Physical Processes

Physical processes tend to be reversible, often by the application of heat.

Jelly – based on gelatin

You will know from experience that

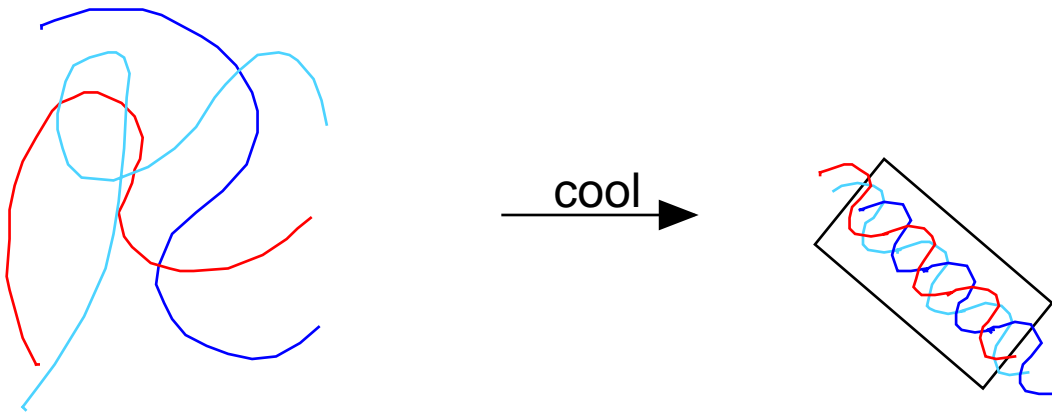
- **jelly sets upon cooling and can be remelted by heating.**
- **it is a weak gel which can flow slowly under its own weight – so a jelly mould tends to collapse.**

Jelly is basically made from gelatin – a form of denatured collagen (which is found in skin and bones).

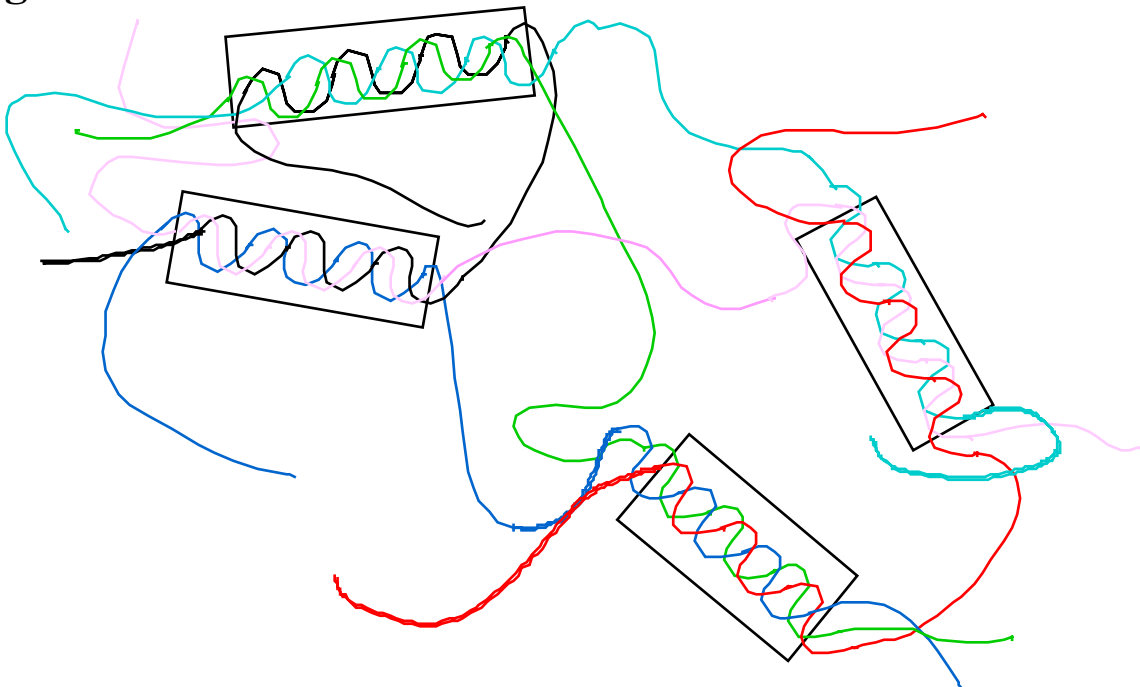
In its native state, collagen exists in a triple helical form, which is broken down to form gelatin.

When gelatin is dissolved in hot water, the molecules exist as single chains.

Upon cooling these come together, and over short sections will reform a triple helical structure (in practice this is probably bimolecular).



These triple helical regions act as 'junction zones' which take the place of the chemical crosslinks in chemical gels.



Many biopolymers form gels of this type, with regions of order forming junction zones, although they do not amount to full three-dimensional crystals.

At one point it was thought that crystals/ordered regions were the cause of formation for all reversible gels.

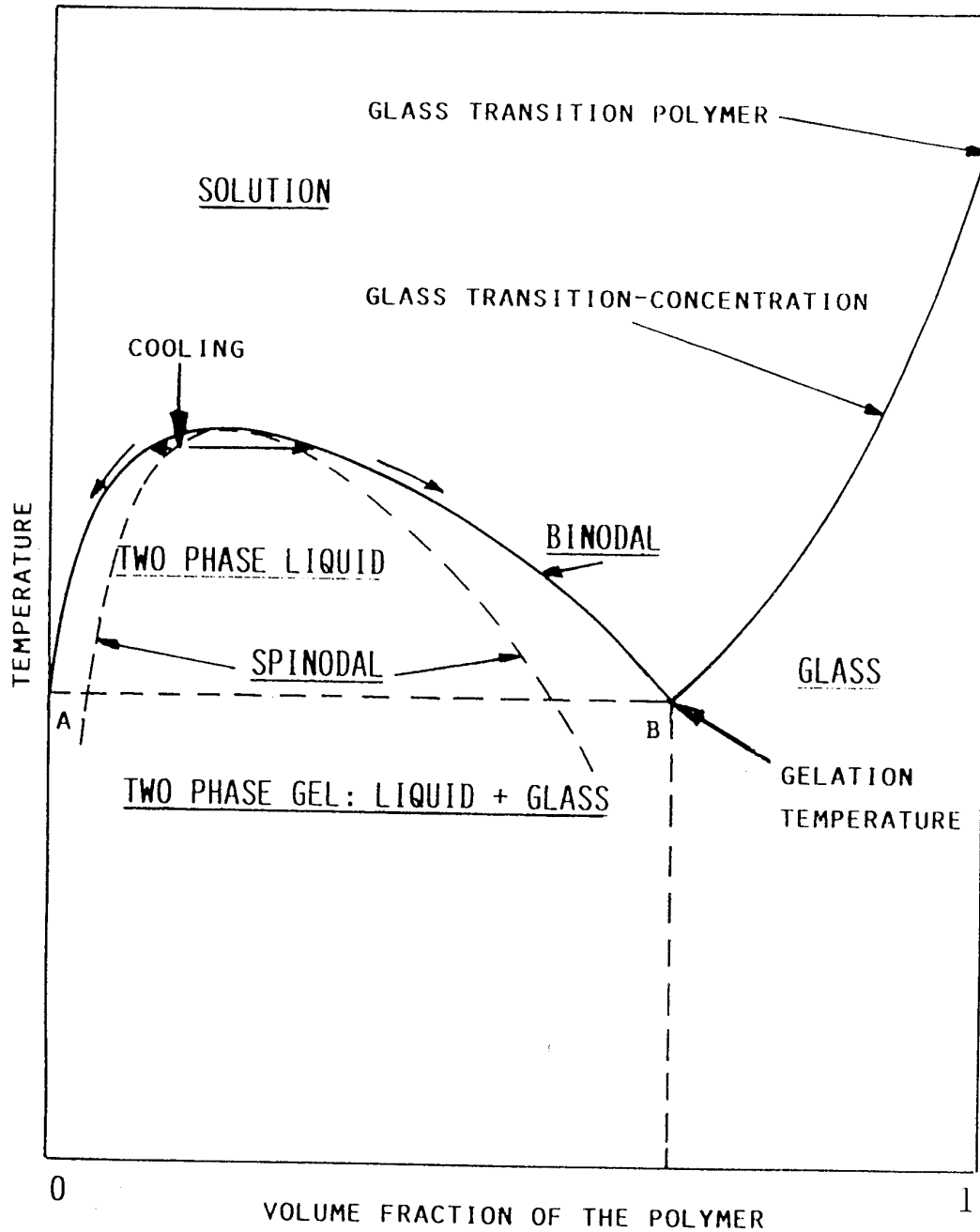
This is now known not to be true.

Atactic Polystyrene

Recall a-PS cannot crystallise.

To understand how such a system can gel, need to consider the effect of the glass transition on the phase diagram.

A gel can form at even very low v_f of polymer.



If you cool a solution of concentration c , as you cross the spinodal line 2 phases form of composition given by the coexistence curve, and in proportions given by the Lever Rule.

Cool further and T_{gel} is reached.

The phase with higher polymer fraction then forms a glass ($T_{gel}=T_g$).

As long as there is sufficient of this phase for connectivity to occur, gelation occurs.

This requirement sets a minimum polymer concentration for gelation to occur.

Precise thermal history very important in general for mechanical properties, and for gels (which are often not in thermal equilibrium anyhow), this is even more important.

In this case quench rate (cooling rate) and depth of quench (how far below the coexistence curve) matter.

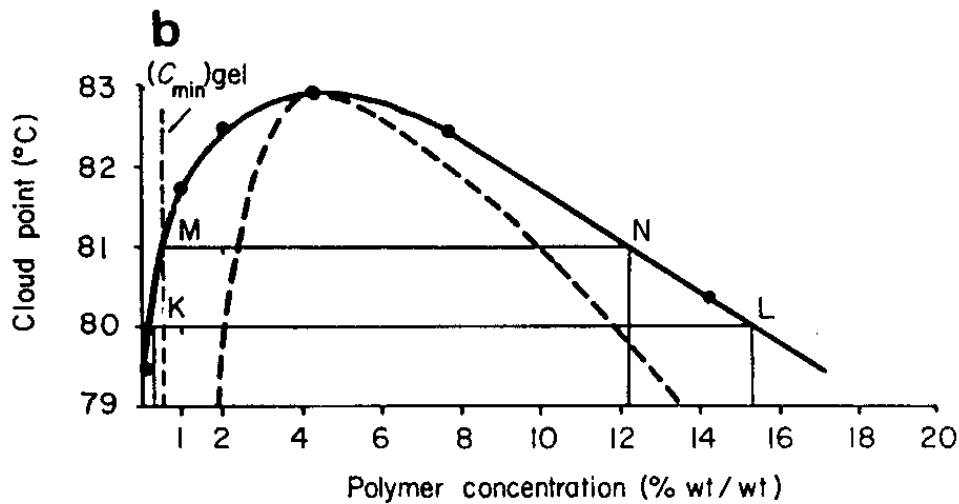


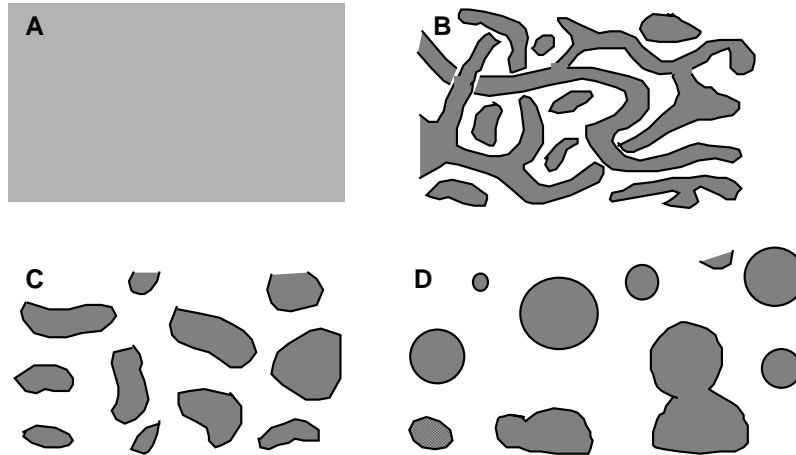
Figure 2 (a) Phase diagram for the atactic polystyrene/cyclohexanol system $M_w = 2.75 \times 10^6$ depicted in relation to the glass transition curve (the broken line is a theoretical extrapolation, see text). (b) Enlarged detail of (a) about the commensurate point. The boundary $(c_{\min})_{\text{gel}}$, and the 80 and 81°C tie lines are shown. The end points of the two tie lines drawn KL and NM, respectively, with the concentrations at 1 and 2% marked along the respective tie lines, together with the points along the coexistence curve relate to experiments described in the text. The heavy broken line represents the expected (see text) spinodal boundary

- 1% solution held at $\geq 81^\circ\text{C}$ before quenching to RT. Phase separates into 2 phases both of which can gel.
- 1% solution cooled to 80°C and held there for ~ 5 minutes before quenching. Continuous phase now cannot gel as has $c < c_{\min}$, so whole system does not gel.
- Hold this sample for long enough and can get macroscopic phase separation, and one component of this will gel.

In this case the mechanical strength is given by the hard glassy phase.

In all systems where there is **interplay of gelation and phase separation**, can have a great richness of behaviour (e.g. any system containing gelatin).

Above gelation temperature



Below gelation temperature

