

An unusual state of matter

Intermediate States

ROMAN LUBORADZKIInstitute of Physical Chemistry, Warsaw
Polish Academy of Sciences
romek@ichf.edu.pl

At school we are taught that matter exists in three states: gas, liquid, and solid. Meanwhile even a cursory glance at the world around us suggests that things are not really all that simple, that there must be some intermediate state between a liquid and a solid

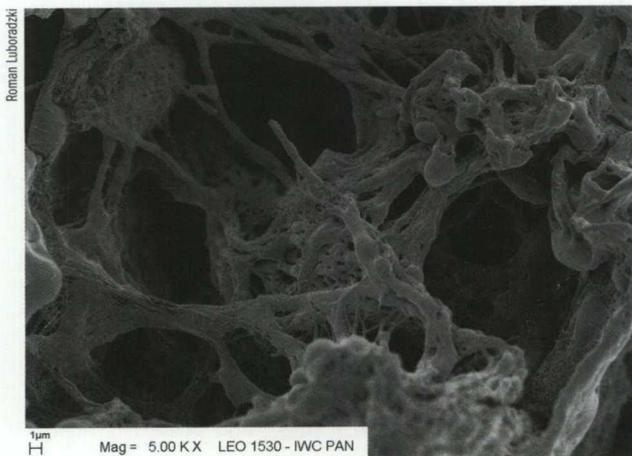
The name of the “liquid crystals” used inside our computer screens alone suggests they are situated somewhere in between a liquid and a crystal. Another concept that defines such an intermediate state of matter is that of a “gel” – although admittedly here we are entering a realm where definitions can be vague.

Everyone knows what a gel is...

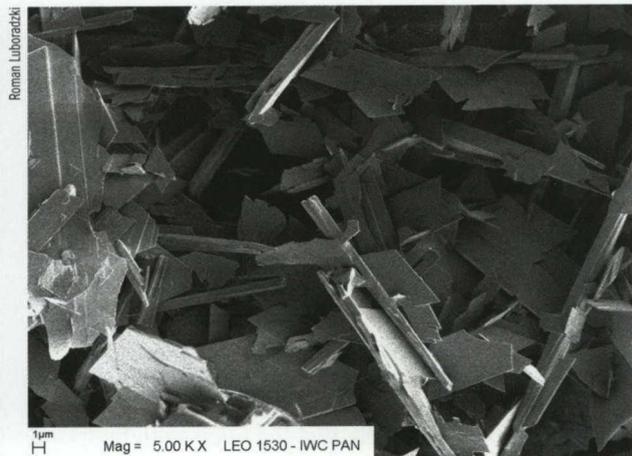
The first problem encountered in the study of gels is indeed one of definition. Quoting the opening statement of a paper by Prof. Ben Feringa published in 2000 in the leading chemistry journal *Angewandte Chemie*, “Everyone knows what a gel is...”, would certainly resolve the prob-

lem deftly – yet it would also mean simply ducking the issue. Therefore we will define a gel as a system comprising at least two ingredients, where each ingredient forms a separate continuous phase spanning the entire volume of the gel. One of the ingredients, known as the gelling agent, creates a solid, branched, porous network spanning a liquid – the other gel ingredient – thus immobilizing it. From a chemical perspective gels may be formed by a variety of systems. The liquid phase is frequently water (such gels are called aquagels), although it may also be alcohol or another organic solvent. This phase may be removed by drying the gel, thus leading to the formation of xerogels (aerogels).

The fundamental classification of gels is based on the type of interactions responsible for the formation of a rigid network, or the type of gelling factor. We differentiate between chemical gels, where the molecules of the gelling agent form covalent bonds, and physical gels, where the gelling agent molecules form much weaker molecular interactions. Chemical gels include cross-linked polymers, silicone gels, and gels based on metal oxides, and their formation is an irreversible process. Physical gels, on the other hand, may be formed by very different substances, from large protein molecules to small sugars comprising a dozen or so atoms. Molecular interactions within them depend on the type of the gelling agent. They may be hydrogen bonds, π - π interactions, solvophobic and other effects, and crucially they are weak enough for the



Shown here and on the following photographs: images obtained using a scanning electron microscope (SEM) showing xerogels (gels following the removal of solvent)



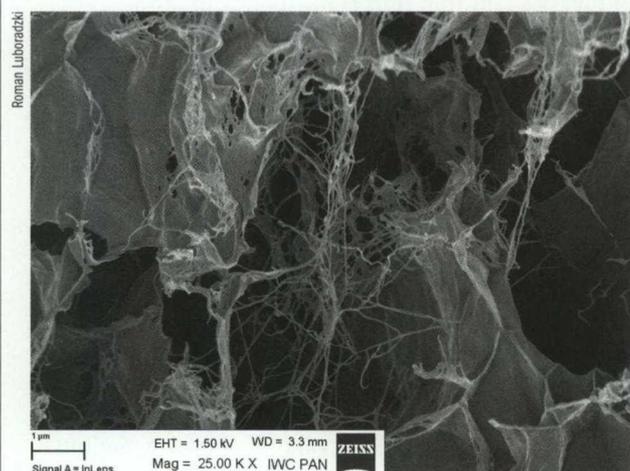
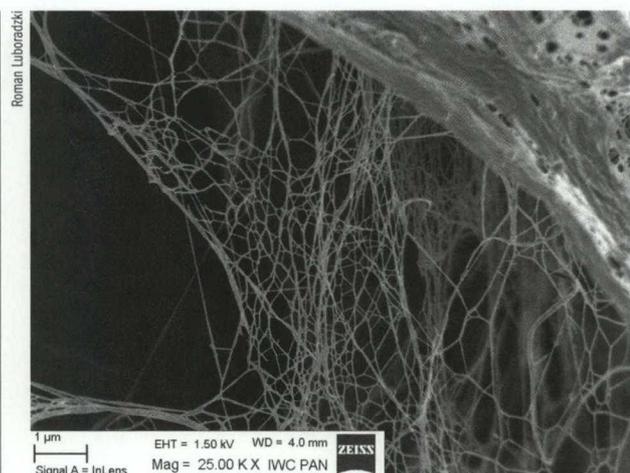
Physical gels, i.e. those where small or very small particles of a given substance are able to immobilize relatively large quantities of the solvent, are particularly interesting

formation of physical gels to be reversible. The reverse transition of gels into sols is usually brought about by a gradual increase of temperature. On a macroscopic scale gels are characterized by distinctive mechanical, optical, as well as sound-transmission properties. However, due to the variety of substances that may form gels and the interactions responsible for their formation, the boundaries between gels and other states classified as soft matter (complex fluids) are frequently unclear.

Unusual structures

How small can the molecules of a gelling agent be? The really small ones may contain no more than a dozen or so atoms. This poses a question, one that does not apply just to gel formation but is in fact one of the fundamental problems in chemistry: How do small molecules organize into larger structures which may additionally serve functions that were not present in the original building-blocks? As well as its value for fundamental research, a better answer to this question would bring huge practical applications. For example, it would make it possible for gelling agents to be tailor-designed for specific applications, thus saving time and money spent on searching for them at random.

But this is not a simple matter, and it appears that we are still some way from ever developing a computer program able to take the drawing of a given chemical compound as input and predict if it will have gelling properties or which gels it will work in. This does not mean we are doomed to keep searching at random, however. The starting point in formulating an answer to the above question could be provided by images of xerogels (dried gels), obtained using transmission electronic microscopy (TEM) or scanning electronic microscopy (SEM), in the majority of cases showing a network of interwoven strands ranging in thickness from a few nanometers to several hundred nanometers. The formation of such strands, usually resulting from the cooling of a hot, concentrated solution of gelling factor, of course involves strongly anisotropic growth (fast in one direction while slow in the others) and that, in turn, leads to various molecular interactions. Gelling agents based on urea derivatives are a classic example of this. Known crystalline structures of those compounds show molecules forming hydrogen-bond chains, with much weaker van der Waals forces occurring between them. The capacity for the molecules to become packed together in this manner implies fast growth in the direction determined by the formation of the hydrogen bonds, and effectively it may lead to the formation of the previously mentioned strands and the emergence of gelling abilities. All this taken together suggests a research methodology: observing the crystalline structures of potential (as well as existing) gelling agents and analyzing the molecular interactions within them.



An important characteristic of physical gels is their relatively poor durability, that is their ability to revert back to sols. In some case this “weakness” turns into an advantage: for example, if the glue used in self-adhesive Post-It notes were much stronger, they would certainly not be of much practical use

Despite its basis in a very simple idea, this “crystallography approach” does work surprising well - in certain cases it allows us to explain the specific appearance of the strands (for example, if they are reminiscent of twisted threads, crystallography explains why they twist clockwise or anticlockwise) or why the gelification of moist solvents proceeds differently from dry ones. It may even inspire us to design ever more complex systems containing not one but two gelling agents (two-component gels). And lastly, it may be a source of personal satisfaction: as X-ray crystallography was the present author’s own first specialization, I am particularly pleased that X-ray structural analysis is proving to be so useful. ■

Further reading:

- Weiss R.G., Terech P. (2005). *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*. Dordrecht: Springer.
- Fages F., Araki K. (2005). *Low molecular mass gelators: design, self-assembly, function*. Berlin: Springer.