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Scrolling for Gels

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Gels are extremely useful materials. We all come into contact with gels every day, but probably give them little thought. To form a gel, a network must be formed immobilizes the solvent, such that the material that is mainly a liquid behaves as a solid. Many gels are formed from entangled or cross-linked polymers and the design rules here are relatively well understood.

A different method of forming gels is to use low molecular weight gelators (LMWG).[1] As the name suggests, in this case the network is formed from small molecules that self-assemble. The molecules assemble into long structures such as fibers which are typically a few nanometers in width, but microns in length. These fibers entangle, branch and/or cross-link to form the network that immobilizes the solvent.

These gels are extremely interesting. They differ in properties from polymer gels where the cross-links are permanent; for example, being held together by non-covalent interactions, they are often reversible. These gels are being widely investigated for a range of applications, from biomaterials to optoelectronics.[2-4] A major issue however is that there are limited design rules for which molecules will self-assemble in the right manner and which will not. This means that most LMWG are found by accident or by a simple chemical permutation around an already known structure. However, even this latter approach often fails. This means that if a LMWG with the desired properties is accidentally found, all is well, but it is much more difficult to design for a specific application from first principles.[1,5]

To try and address this, a number of approaches have been taken. Perhaps the most common is to simply build a large library and hope that one molecule has the correct properties. Some success has been found using solvent parameters to post-rationalise why some molecules are effective and some are not.[6] Another common approach is to examine the crystal structures of the LMWG, preferably from the solvent that is to be gelled (although this is rarely possible), or less preferably from another solvent. It can also be informative to examine the crystal structures of molecules that are not effective LMWG. From all of the structures, it is common to try and link specific interactions to the success or failure of the molecule as a gelator. A final approach is to use a computational approach to understand the efficacy of a gelator. Despite all these approaches, it is probably fair to say that there is still a significant way to go in terms of understanding such that the field can rationally design gelators a priori.

The paper by Jones et al. tackles this issue head on.[7] A combined crystallographic and atomistic approach has been used to understand the intermolecular interactions in bis(urea)s and their ability to form gels. Comparing the crystal structures and the gelation ability of a small library of bis(urea)s showed that only one molecule was able to form gels in a number of solvents. However, all of the bis(ureas) showed the same underlying tendency to form lamellar crystals. Here, as is the case here, it is worth pointing out that many gels are formed by heating the potential LMWG in a solvent and then allowing the solution to cool. This is clearly similar to what would be done if one wished to recrystallize a molecule and there are clear conceptual links between gelation are crystallization. Indeed, gelation has been referred to as failed crystallization![1] Indeed, crystals also formed directly from some of the gels. Really interestingly, the metastability of the gels depended on the size of the container in which the gel was formed. This time dependence presumably shows that there is a low barrier between the assembly in the gel phase and that in the crystal phase.

There is always a question as to whether the crystal form can be linked to the gel phase. The gel phase here appears to be non-crystalline. However, the easy transition from the gel to crystal however presumably implies that there are close similarities in packing. Jones et al. hypothesized that lamellar structures are formed first, and that either gels or crystals grow from these lamellae. Using a molecular dynamics (MD) approach, the folding and scrolling of lamellae was investigated. Interestingly, scrolling is not accompanied by an increase in hydrogen bonding, implying that non-directional polar interactions and van der Waals are instead the major contributors. The authors link the scrolling of lamellae to the formation of fibrils that ultimately lead to a gel. Hence, scrolling and stacking of the lamellae result in gelation or crystallization respectively and hence the relative rates of each determine the outcome (Figure 1).

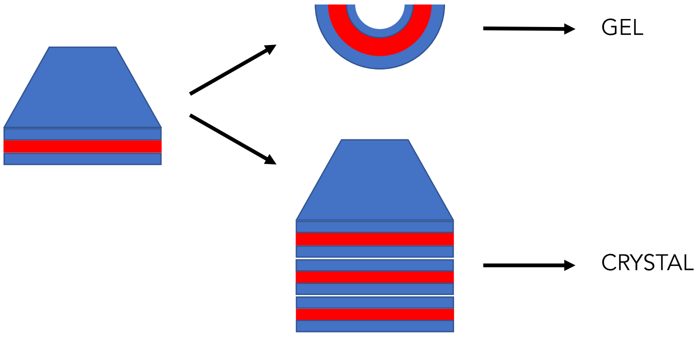

Figure 1. Scrolling (top) or stacking (bottom) of lamellae leads to gels or crystals respectively,

If scrolling leads to gelation, what drives scrolling? The authors suggest that this is driven by structural asymmetry. If the faces of the lamellae are symmetrically equivalent, there is no driving force for curvature. The MD simulations imply that the bending and scrolling arises in case where one face of the lamellae contracts more than the other, and can be related to the packing in the bis(urea)s. For these systems, the gel fibers observed are relatively uniform in width, and the MD simulations suggest that this is due to there being an optimum number of lamellae in a scrolled structure.

This work therefore brings together a combined experimental and computational approach to give new insights into the world of LMWG. Rather than trying to link simply the molecular structures to the ability to form a gel, the authors suggest instead that gelation results from how lamellae stack, with scrolling being a pre-requisite for the formation of the necessary fibrils that lead the gel network. This work offers therefore a new insight into why gels form rather than crystals, and suggests that it may be possible to predict gelation from crystallographic data. If this could be shown to be relevant to other classes of LMWG, it could be that we are getting close to understanding why gels form and answering key questions such as why do closely related molecules exhibit such differing ability to gel.

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