Microsymposia

Molecular gels formed by the self-assembly of small molecules in organic or aqueous solvents have attracted widespread attention. It is known that a common factor in all gels is the presence of a network formed by fibrous assemblies. This talk will attempt to classify molecular gels into two distinct classes based on the nature of these assemblies. In many gels, the fibers have a crystalline packing, and often the crystal structure of the fibers (in a xerogel) is identical to that of the molecules in their solid crystal. It is argued that these crystalline gels are analogous to many fibrous structures found in biology, notably the amyloid plaques that have been implicated in neurodegenerative diseases. In other gels, the fibers are completely amorphous, and in these cases, the fibers are analogous to assemblies of amphiphilic molecules such as micelles. It is further argued that these amorphous fibers are comparable to filamentous structures found in the cytoskeleton of every biological cell. Crystalline and amorphous fibers (and their gels) also show distinct properties in terms of both their structural responses (e.g., via scattering techniques) as well as in their mechanical and rheological properties.


Keywords: gel, scattering, rheology

MS.03.3

Dynamic covalent molecular gelators: in control of soft matter properties by dynamic covalent chemistry

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The self-assembly of small molecules, polymers, proteins, nanoparticles and colloids under thermodynamically equilibrium conditions has been a powerful approach for the construction of a variety of structures of nano- to micrometer dimensions, like vesicles, capsules, and nanotubes. Despite these advances, the permanent nature of these synthetic self-assembled structures does not compare well to the complex spatiotemporaneously confined self-assembly processes seen in natural systems, which for instance allow the dynamic compartmentalization of incompatible processes, responsiveness, and self-healing. It remains a challenge to develop systems in which equilibrium and kinetics of self-assembly can be independently controlled.

In our research we focus on molecular approaches which allow independent control over interaction strength and dynamics of the self-assembling building blocks [1], [2]: (i) the development of dynamic covalent gelators, leading to new supramolecular assemblies with unprecedented control of the dynamic properties, (ii) dynamic and reversible conjugated polymers, allowing easy processing in water, and (iii) dissipative self-assembly driven by a chemical fuel [3]. I will discuss the background of our approaches together with recent results, and will suggest how dynamic self-assembling systems may lead to the next generation responsive, nanostructured or self-healing materials.


Keywords: gels, gel and crystal growth, post-assembly modification

MS.03.4

The relationship between crystallisation and gel formation in low molecular weight gelators

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Crystallisation and gel formation of low molecular weight gelators (LMWGs) are inherently related as can be witnessed by many researchers the world over [1]. We shall present results on crystallisation within LMWGs and the conversion of LWMG gels into crystals. These results will help to rationalise the relationship between gel and crystal formation.

The use of the gel matrix to control crystallisation is a well known procedure. However, LMWGs have been scarcely looked at as the gel former in this crystallisation technique. We therefore aimed, and now shall present, the control of pharmaceutical polymorphism and morphology by testing a series of LWMGs [2]. Due to their reversible physical nature, in our case using anion tuning of gelation [3,4], LMWG crystallisation may represent an exciting new addition to the crystal growth tool kit.

Many researchers have noted that many LMWGs tend to convert from a gel to a crystalline material [5]. This process is often used to help determine the structure of the gel forming solid. We shall also present our take on this “phase” change and the possible applications of this phenomenon in the context of controlling crystallisation and the lack of crystallisation leading to stable gels. By influencing assembly and disassembly of the gel components, which is related to the underlying structure, the stability in relation to the gel to crystal transformation can be controlled. As a result of this knowledge, we are able to show post-assembly modification of a LMGW at the interface of the solid and liquid phases.


Keywords: supramolecular chemistry, molecular gelators, dynamic self-assembly

New insights into the polymerization and structural mechanisms of the polydiacetylene DCHD: an X-ray/MEM study

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Keywords: gels, gel and crystal growth, post-assembly modification