Molecular Gels

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Flexible Optics: Recent Developments in Molecular Gels

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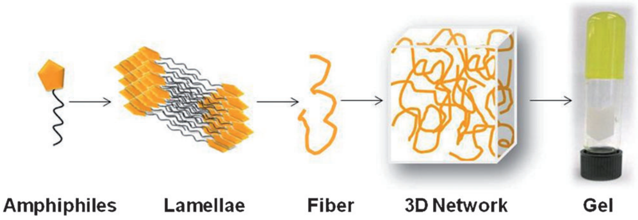
Self-assembly is an attractive bottom-up strategy for the development of the next generation of functional soft matter.[1] Molecular gels (MGs) are one class of such soft material that has garnered much attention from scientists in diverse research areas. MGs are solid-like viscoelastic materials comprising a large pool of liquid (water or organic liquid) immobilized by very small amount of nonpolymeric low-molecular-weight amphiphiles.[2] The solvent-immobilization properties of such amphiphiles stems from their propensity to hierarchically self-assemble at the nanoscale through weak intermolecular interactions to form a microscale three-dimensional (3D) network. Within this network, the solvent molecules are entrapped, resulting in the formation of a coherent gel (Scheme 1). Such gels are of particular interest owing to their nonpolymeric nature, gel-to-sol reversibility, ability to form high-aspect-ratio assemblies, and biocompatibility.

Through systematic tailoring of the amphiphile structure, the MGs can be imparted with diverse functional properties. Consequently, unlike polymeric gels, MGs have been used as smart materials in a wide spectrum of applications in, for example, drug delivery, energy, food, tribology, and electronics.[3–5] Despite these possibilities their practical potential beyond biomedical applications has not been realized until recently. Several factors such as the multistep schemes for gelator synthesis, energy-intensive gelation steps, and low gel strengths have been the principal constraints to the full exploitation of MGs for high-volume industrial applications. However, owing to comprehensive efforts by the gel researchers over the last decade, current research has to overcome the limitations and MGs can be designed efficiently for desired bulk-scale applications.



Scheme 1. Schematic representation of hierarchical self-assembly of amphiphiles in gelation processes.

Recently, John and co-workers have developed inexpensive, eco-friendly sugar gelators that can selectively gel the oil phase from an oil–water mixture at room temperature.[6] The use of a room-temperature phase-selective gel system can be a promising approach for the treatment of oil spills. In another interesting application in the catalysis of organic reactions, the catalytic sites are present on the self-assembled network of the MG and in the liquid pool.[7] Utilization of MGs in catalysis facilitates the fine-tuning of catalyst performance, which is otherwise difficult with conventional heterogeneous catalysts. In yet another study, Yamanaka and co-workers developed hydrogels from urea/sugar-conjugated amphiphiles, which could be efficiently employed as the base in gel electrophoresis.[8] Because of the simple extraction process and unique separation pattern possible with such MGs, this new method can replace classical agarose-based gel electrophoresis techniques. Likewise, MGs have been used for developing light-harvesting materials, electronic devices, electrolytic gels for batteries, and many other smart materials.[3–5]

Interestingly, in more recently published work of Sureshan et al. several limitations of MGs are circumvented to enable their usage in niche applications in photonics.[9] They have described the synthesis of simple sugar-based amphiphiles for the development of "soft" optical devices, further broadening the span of MG applications. Specifically, the amphiphiles were diketal derivatives of mannitol, that is, the diol part was flanked by ketal motifs on both ends (Figure 1 A). A one-step synthesis with relatively simple purification was employed, thereby ensuring its scalability. The amphiphiles were found to be super organogelators with an average minimum gelation concentration of less than 0.5 wt %. Routine heat-induced gelation schemes—heating

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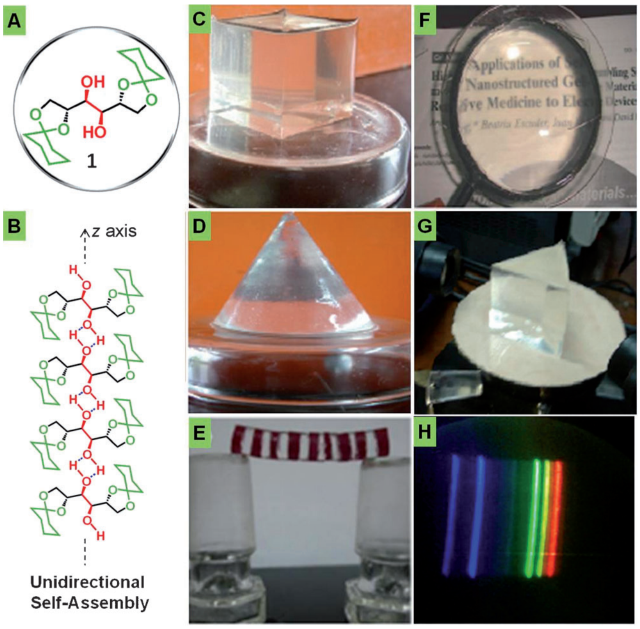

Figure 1. A) Structural formula of gelator **1**, from which organogels and optical devices were developed. B) Unidirectional arrangement of **1** in an organic solvent. C,D) A self-standing cube and cone made from pump oil gel. E) A self-supporting gel cylinder made by fusing 17 different pump oil gel discs. The alternate discs were doped with perylenetetracarboxylic anhydride for better visualization. F) A plano-convex lens made from paraffin oil gel. G,H) A prism made from paraffin oil gel and the diffraction pattern observed after refraction of white light.

the mixture of amphiphile and solvent to form the sol and cooling the sol to room temperature—were adopted to produce gels. These amphiphiles tend to self-organize and form a fibrillar network, which in turn immobilizes the organic liquids (Scheme 1). Two types of intermolecular forces—hydrophobic interactions and hydrogen bonding, existing between the respective ketal and diol motifs—synergistically contribute towards an efficient self-assembly pattern (Figure 1B). The contribution of both interactions towards gelation was thoroughly studied using spectroscopic analytical methods and by systematic alteration of the amphiphilic structure.

The most interesting aspect of this gelator system, in particular the cyclohexane ketal derivative of mannitol, **1**), was its propensity to form organogels with remarkable strength, high elasticity, and self-healing properties. The combination of such properties was difficult to achieve with earlier MG systems. The strength and elasticity of the organogels was displayed by molding the gels in numerous self- self-supporting shapes (Figure 1C,D). The enhanced strength of these gels can be attributed to restricted conformational freedom and very high intermolecular interaction affinity. Such features induce a highly ordered and aligned arrangement of amphiphiles in the self-assembled structures, which in turn minimizes packing defects and increases the cohesive strength of the network. The self-healing property was demonstrated by fusing several blocks of gel to develop a self-supporting continuous bar (Figure 1E). The dynamic equilibrium between free (dissolved) and aligned (self-assembled) amphiphilies coupled with their high affinity for each other appears to enhance the self-healing properties of these gels. Similar design concepts—molecules with conformational restrictions and interaction affinity—have also been recently deployed to develop strong and self-healing gels. Aida et al. utilized the very high affinity of positively charged third-generation dendrimers towards anions to develop self-supporting hydrogels.[10] Thus, the current study demonstrates that such design concepts indeed play a key role in gelation and should be taken into account in the future in the design new molecular gelators.

Not only do **1**-based organogels exhibit extraordinary mechanical properties, but formed with long-chain hydrocarbons as solvent they are transparent and show high transmittance in the visible region with glass-like refractive indices ($n \approx 1.5$). These gels display a unique combination of properties which was exploited to conceptually develop soft optical devices such as flexible lenses and prisms which showed potential in their ability to magnify objects and refract white light, respectively (Figure 1F–H). It has been hypothesized that the soft nature and self-healing properties of such gels may render the devices shatter- and scratch-free. Their self-healing properties, scratch resistance, and glass-like refractive index make these systems highly attractive for eye protection and even for intraocular lenses.

Although in the work of Sureshan and co-workers only macroscopic optical elements such as lenses and prisms are demonstrated, the real advantage of their research might lie in the realization of low-cost microphotonic structures. A good candidate in this context is the class of metamaterials with negative or near-zero dielectric constants. The bottom-up approach generally practiced in MG development will allow scientists to engineer the optical properties of materials by embedding these soft materials with nanoparticles (quantum dots or metal nanoparticles) or liquid-crystal molecules. The latter approach will even render these structures to be tunable in their optical response. Thus, the use of MGs presents an entirely new direction for the fabrication of microphotonic systems. Furthermore, the low-cost, bottom-up nature of this fabrication technique makes it much more attractive than the fabrication-equipment-intensive approaches currently in use.

In conclusion, the current research not only introduces MGs to optics but also affirms the fact that MGs are indeed amenable to new areas beyond their traditional biomedical applications. It also illustrates the key structural considerations required for developing self-supporting MGs. However, this nascent approach requires further validation. This work should stimulate the development of novel MG-based smart materials with desired functionalities.

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