

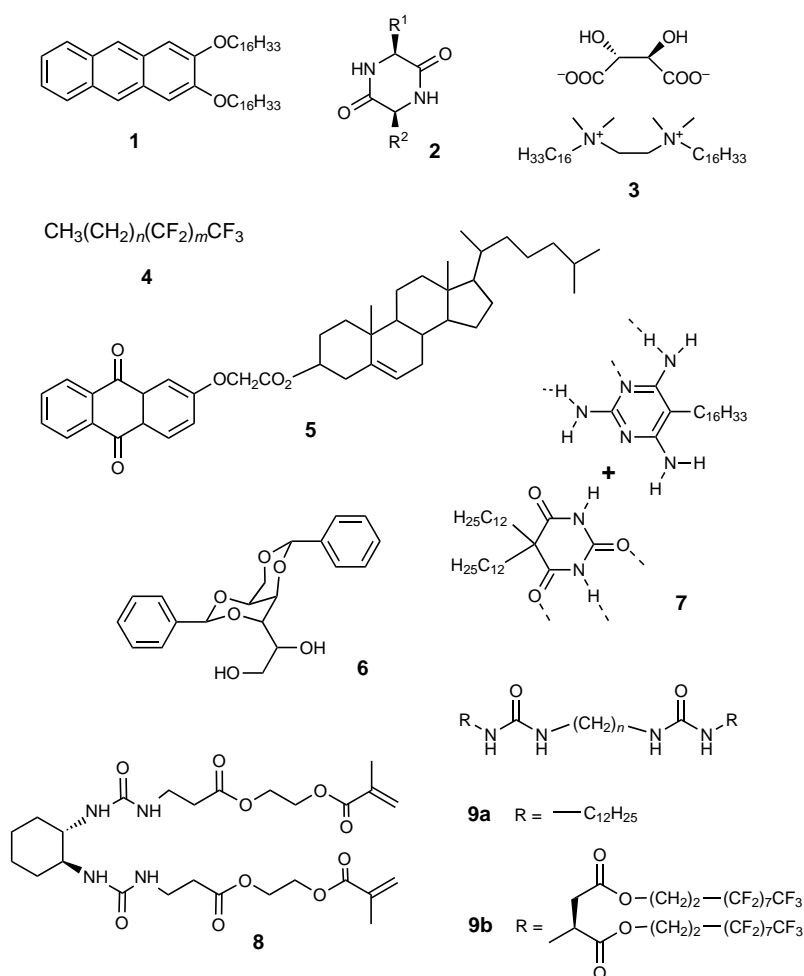
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## New Functional Materials Based on Self-Assembling Organogels: From Serendipity towards Design\*\*

Jan H. van Esch\* and Ben L. Feringa

Everyone knows what a gel is, but from a scientific point of view the term gel encompasses chemically very diverse systems. Gel systems formed by, for instance, dilute solutions of polymers, proteins, and inorganic substances like silica or clays in water and organic solvents have been well studied and are widely used in, for example, photographic, cosmetics, food, and petroleum industries.<sup>[1]</sup> In recent years there has been a rapidly growing interest in low molecular weight gelling agents, which is motivated not only by the many potential applications of gels, but also by the fact that these systems exhibit striking properties with respect to self-assembly phenomena (Scheme 1).<sup>[2, 3]</sup>

These “organogels” have in common with other gel systems that the gelling agent forms a continuous three-dimensional entangled network in the solvent, thereby preventing the liquid from flowing.<sup>[4]</sup> In contrast to their macromolecular and inorganic counterparts, the network structure formed by low molecular weight organogelators is held together solely by noncovalent forces, including hydrogen bonding,  $\pi$  stacking, and solvophobic effects (Figure 1). The self-



Scheme 1. Examples of low molecular weight gelling agents, illustrating the enormous structural diversity among organogelators.

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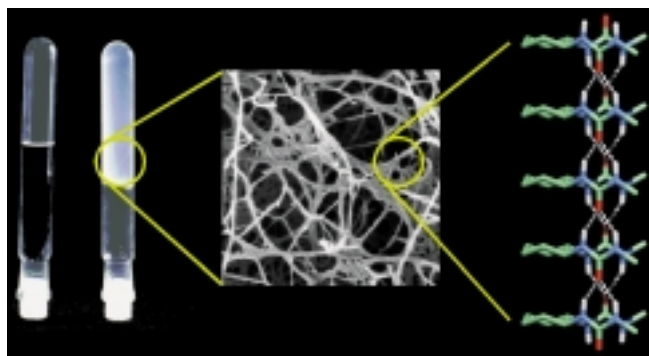


Figure 1. Organic gelling agents self-assemble into one-dimensional fibers (left) and finally an entangled network (middle), which causes gelation of the liquid (right).

assembly process starting from a single molecule to fibers and ultimately an entangled network structure is thus completely reversible, and at the same time also highly efficient as most organogelators already form gels at concentrations well below 1 wt %.

The second distinct feature of organogels is that the network filaments consist of well-ordered arrays of molecules up to micrometer lengths, and different filament architectures like tapes, rods, fibers, sheets, and cylinders have been reported. Although the formation of organogels from small organic molecules is an excellent example of a supramolecular self-assembly process, most organogelators have been found by serendipity rather than design, and many aspects of organogels are still poorly understood. The control of gelation phenomena induced by small molecules and the design of new gelling agents are therefore challenging goals leading to a new area of fascinating organic materials, and it has only been recently that a number of successes have been reported.

In a recent paper in *Science*, Beckman, Hamilton, and co-workers reported on new microcellular organic materials which have been prepared by supercritical drying of organogels in CO<sub>2</sub>.<sup>[5]</sup> The most remarkable feature of this system is that except for the organogelator and CO<sub>2</sub>, no other compounds or cosolvents are involved, resulting in a single-step, very clean, and environmentally friendly method to create these materials. The essence of this work is that the authors succeeded in the design of organic gelling agents for CO<sub>2</sub>, that is, compounds that strongly associate and form an entangled network structure at lower temperature or pressure, but would dissolve upon increasing the temperature or pressure. For this purpose gelling agents were developed in which urea groups, to achieve association through multiple hydrogen bonding, are combined with groups showing affinity for CO<sub>2</sub> to increase the solubility, in this particular case perfluoroalkanes (e.g. **9b**, Scheme 1).

The results of this very basic design are remarkable. The compounds dissolve very well in supercritical CO<sub>2</sub> at higher temperatures and pressures, but upon cooling the solution turns into an opaque gel. Moreover, upon removal of the solvent by simply lowering the pressure, the network structure is preserved and a highly porous and self-supporting monolithic foam is obtained (Figure 2). The foams combine an

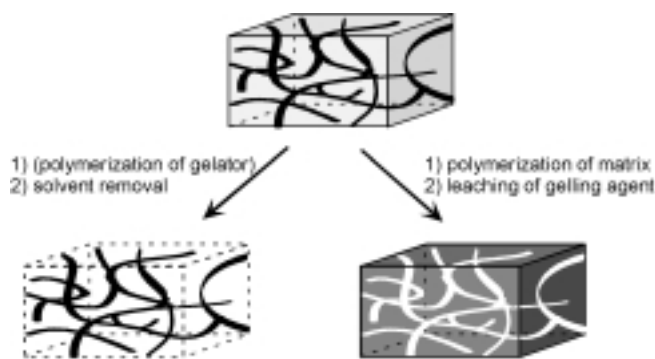


Figure 2. Preparation of organic aerogels (left) and porous membranes (right) from organogels.

extraordinary low density (<5% of the bulk density of the organogelators) with a submicrometer cellular size, properties which could not be obtained with traditional polymers in combination with CO<sub>2</sub> as foaming agent. These organic analogues of silicate aerogels are therefore highly interesting materials for application in separation processes as well as for use as novel low dielectric or insulating materials and as support for catalysts.

The design of novel gelling agents as reported by Beckman, Hamilton et al.<sup>[5]</sup> is, however, not without precedent. Other research groups including those of Terech, Hanabusa, Weiss, Shinkai, and Boden as well as our group all made significant contributions towards the design of novel gelling agents and the understanding of the gelation phenomena.<sup>[2, 6]</sup> Important guidelines for the design of novel gelling agents that emerged from these studies are: 1) the presence of strong self-complementary and unidirectional intermolecular interactions to enforce one-dimensional self-assembly; 2) control of fiber–solvent interfacial energy to control solubility and to prevent crystallization; and 3) some factor to induce fiber cross-linking for network formation.

Most new gelling agents that resulted from these studies are based on peptides or carbohydrates because of the strength and high directionality of hydrogen-bond interactions. Especially cyclic dipeptides and bis-urea-based gelling agents appeared to be very efficient gelling agents and combine easy accessibility with a wide solvent scope, and in the case of the bis-urea gelling agents it was shown that the supramolecular architecture can be controlled by the spacer between the urea groups.<sup>[6e, 7, 8]</sup> The hydrogen bonding core of these cyclic dipeptides and bis-ureas provide a “gelating scaffold” which can easily be functionalized without loss of gelation ability. For example, we reported some years ago that the polymerizable bis-urea **8** (Scheme 1) is a potent gelling agent for apolar solvents.<sup>[8b]</sup> After photopolymerization of benzene gels and removal of the solvent by freeze-drying, an organic aerogel was obtained with very similar characteristics with respect to density and cellular size as that reported by Beckman, Hamilton et al.<sup>[5]</sup>

Another exciting development is the use of organogelators as template for the preparation of nanostructured materials. First Möller<sup>[9]</sup> and later also Weiss<sup>[10]</sup> and Nolte<sup>[11]</sup> prepared membranes with nanosized pores by the gel–template–leaching process, taking advantage of the distinct feature of

organogelators to *reversibly* form elongated fibers with well-defined dimensions and geometry. In the gel–template–leaching process, gels of various gelling agents are prepared in polymerizable solvents like methacrylates or styrene in the presence of a cross-linking agent. After polymerization of the matrix, the organic gelling agent is removed again by extraction with a proper solvent (Figure 2). In this way the organogel fiber network is “imprinted” in the cross-linked polymer matrix, resulting in porous membranes with channels of submicrometer and in some cases even nanometer dimensions.

Although this method holds great promises, the preservation of the original fiber morphology in the polymer network is often rather poor, which is most likely due to the flexible nature of the cross-linked polymers used. This drawback was recently overcome by Shinkai and co-workers, who used gels formed by chiral organogelators as a template to control the morphology of silica formed by a concurrent inorganic sol–gel process.<sup>[12]</sup> After removal of the organic template by calcination, hollow fibers and, under carefully controlled conditions, even helical silica fibers with a single screw sense were obtained. It should be noted that the organic gel network only acts as a template when it bears a significant fraction of cationic groups, indicating the necessity of strong interactions between the organic template network and the growing inorganic silica gel.

The regular arrangement of organic gelling agents in the network filaments has also been exploited as a framework for the spatial organization of covalently attached functional groups, for example fullerene derivatives or other conjugated moieties. It has been shown that this strategy can be very successful for improving collective properties like electron conductivity.<sup>[13]</sup>

A completely different but very appealing issue in gel research is the development of “smart” or “responsive” gel systems.<sup>[14]</sup> Pioneering work on smart polymer gels which could reversibly swell or shrink upon exposure to some chemical or physical triggering event has been carried out by Tanaka.<sup>[4b]</sup> Recently, the Tanaka-group developed a novel gel system which can bind guest molecules by multiple-point noncovalent interactions.<sup>[15]</sup> Most interestingly, swelling of the gel induced by a temperature change increases the distance between the individual interaction points. As a result the binding changes from a multiple-point to a single-point interaction, and the affinity decreases by more than one order of magnitude. It is foreseen that this principle can be applied for controlled drug-release systems, and gels can be designed to respond to other triggers like solvent polarity or pH value as well.

It should be emphasized that organogels are very attractive systems for the design of novel responsive gels, because their formation is completely reversible. Here the challenge is to couple the self-assembly process to a chemical or physical trigger (Figure 3). Having the feature of reversibility in mind, Aggeli et al. designed various peptide-based gelling agents which self-assemble into extended  $\beta$ -sheet tapes and which, depending on the polarity of the solvents, entangle to form gels.<sup>[6d]</sup> To make gel systems that are responsive to pH value some basic amino acids have been incorporated in the

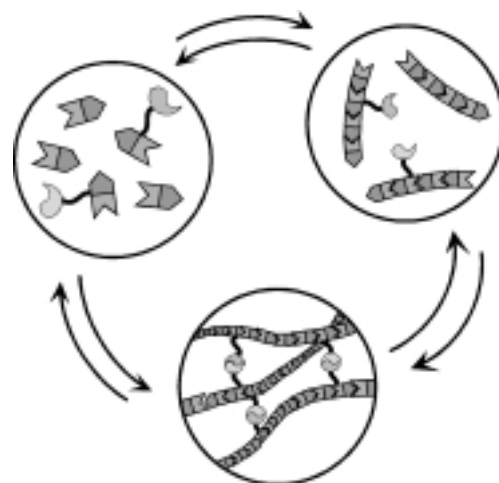


Figure 3. Cartoon of switchable organogels, showing the different levels at which switching might affect the viscoelastic properties.

peptide, and indeed it was found that a change in pH triggers the reversible transition from the gel state to a solution. Gels of other peptides respond to shear by a change of their viscoelastic properties. Shinkai and co-workers have demonstrated already some years ago by using an azobenzene-steroid-based gel system that it is possible to switch by irradiation with UV and visible light from solution to the gel state and back,<sup>[16a]</sup> and two other recent publications indicate that also host–guest interactions can be employed to control the structure or stability of organogels.<sup>[16]</sup>

In conclusion, within a very short period organogels have developed from a chemical and physical curiosity to a highly promising new area of research. Their well-defined structure, the coexistence of these highly ordered fibers with a liquid phase, the large interfacial area, and the possibility to entrap solutes within the network pores make organogels very attractive materials for membrane and separation technology, catalysis, or drug delivery.

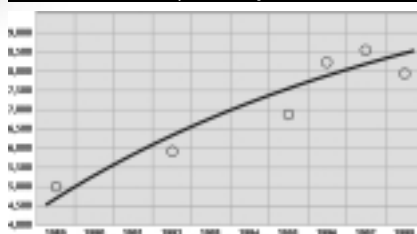
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