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Organogels

Soft Optical Devices from Self-Healing Gels Formed by Oil and Sugar-Based Organogelators**

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Dedicated to Professor M. V. George

Polymeric gels have attracted much attention because of their application in cosmetics, medicine,[1] the food industry, controlled release,[2] the development of smart materials, and so forth. Recently the focus has shifted to supramolecular gels formed by self-assembly of small monomeric species through noncovalent interactions, owing to the reversibility of their formation and their degradability, homogeneity, and tunability, which make them superior to polymeric gels.[3] Different classes of low-molecular-weight organogelators (LMWOs) that can congeal a variety of organic solvents have been reported.[3b,4] However, there are only limited examples of harvesting function from these novel materials.[5–17] Exploration of novel functions from these soft materials continues to be a challenging and exciting task. Herein we report two supergelators that can congeal oils and hydrocarbon solvents to give strong, self-supporting, and highly transparent gels with self-healing properties. We also demonstrate novel applications of these transparent oil gels for making soft optical devices.

Carbohydrates and other polyhydroxy compounds partially decorated with hydrophobic moieties were found to be one class of cheap and easy-to-synthesize LMWOs.[18] As the partial protection of carbohydrates as cyclic ketal derivatives not only imparts amphiphilicity but also assists in preorganization by restricting the conformational freedom for self-assembly, ketal derivatives of many carbohydrates have been exploited as organogelators.[18a,19] We have reported the gelation ability of cyclitols with bidirectionally oriented hydroxy groups flanked by hydrophobic ketal moieties.[20] As part of our continued interest in these lines, we have designed and synthesized two mannitol-based diols (**1** and **2**; see Figure 1 and the Supporting Information) flanked by two ketal moieties.

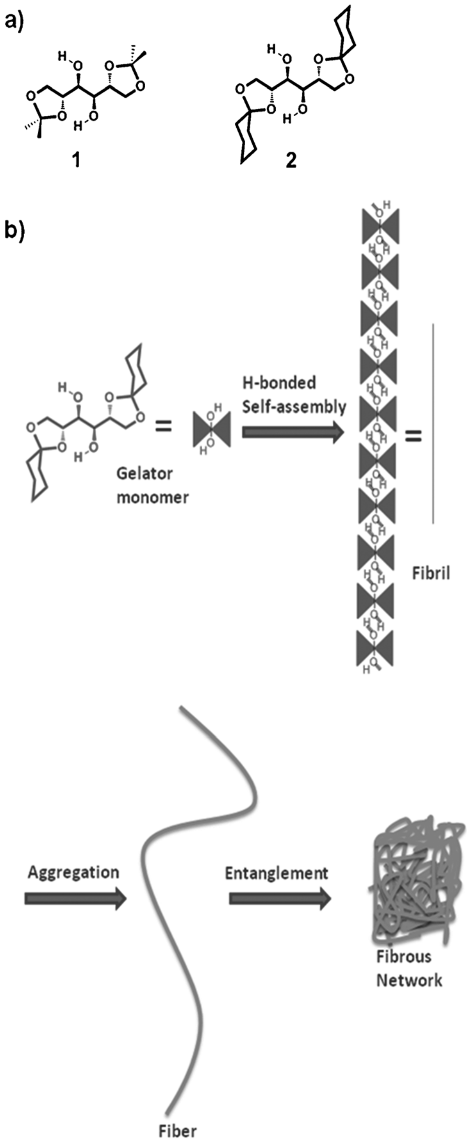

Figure 1. a) Structures of gelators **1** and **2**. b) Mechanism of gelation by diols **1** and **2** in nonpolar solvents.

Both the diols **1** and **2** formed gels with hydrocarbon solvents. While **1** formed translucent gels with lower alkane solvents and transparent gels with higher alkanes, aromatic hydrocarbon solvents, and edible oils, diol **2** formed transparent gels with all these solvents (Table S1 in the Supporting Information). Interestingly, **1** and **2** formed gels with alkane solvents at very low concentrations with critical gel concentrations (CGCs) as low as 0.2 wt%, elevating them to the category of supergelators. Also, these alkane gels showed high

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gel–sol transition temperatures indicative of the high strength of these gels. In nonpolar solvents, the hydroxy groups facilitate self-assembly of **1** and **2** along one direction (Figure 1) to form fibrils, and these fibrils on aggregation form fibers, which entangle to form 3D fibrous spaghetti-like networks immobilizing the solvent via capillary force.[21] In a nonpolar medium, the contribution of hydrophobic moieties towards self-assembly will be very minimal, but the hydrophobic interaction with the nonpolar solvent would prevent the gelator from precipitation. Gelation experiments with solvents and oils that can compete for hydrogen bonding resulted either in weaker gels or in clear solutions, thus supporting the role of intermolecular hydrogen bonding in the gelation process (see the Supporting Information). Also, mannitol derivatives lacking either the diol unit or the diketal motifs (**3**–**5**, see the Supporting Information) failed to congeal any of the solvents tested, thus showing the importance of the combination of these moieties for gelation.

Concentration-dependent titration monitored by ^{1}H NMR spectroscopy provided concrete evidence for the role of hydrogen bonding in self-assembly of **1** and **2**. The hydroxy proton signals of both **1** and **2** shifted gradually downfield with a gradual increase in concentration, thus supporting the self-assembly through intermolecular hydrogen bonding (Figure S2 in the Supporting Information). FTIR spectroscopy gave additional evidence for the hydrogen-bonded self-assembly of gelator molecules. The FTIR spectrum of **1** in chloroform, where it does not form a gel, showed the OH stretching signal as a broad signal peaking around 3564 cm^{-1}, suggesting that no hydrogen-bonded aggregation occurs in a nongelling solvent. However, FTIR spectra of benzene gel of **1** and xerogel of **1** made from its benzene gel showed signals with OH stretching frequencies of 3288 and 3275 cm^{-1}, respectively, confirming the involvement of intermolecular hydrogen bonding in the gelation process. Similar results were also obtained for **2** (Figure S3 in the Supporting Information). Powder XRD of xerogel made from benzene gel of **2** showed a sharp peak at $2\theta = 2.01336°$, suggesting a periodic arrangement in the gel fibers. The morphologies of these gels were probed using various microscopic techniques. AFM scanning of thin layers of xerogels made by dropcasting dilute solutions of gelators in heptane, a gelling solvent, revealed their fibrillar morphologies. While **1** showed bundles of long fibers, **2** showed a fibrous entangled network (Figure 2a,b and Figure S5 in the Supporting Information). Scanning electron microscopy (SEM) images of xerogels of **1** and **2** made from their gels in different solvents showed different textures. As with AFM, **1** showed bundles of long fibers and **2** showed a fibrous network (Figure 2c,d and Figure S4 in the Supporting Information).

The gels formed by **1** and **2** with oils at concentrations as low as 0.2 wt% are sufficiently strong that they are stable for months without losing their transparency, volume, and shape. The gel can be molded into any self-supporting geometrical shape using appropriate molds. Also, these gels can be sliced into various geometrical shapes with a razor. More interestingly, these gels showed remarkable self-healing properties. When a block of gel was cut into two pieces and then joined together, the pieces merged into a continuous block. This

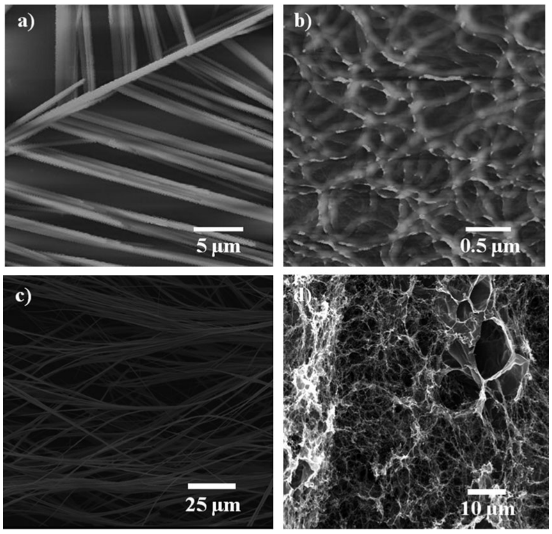

Figure 2. a) AFM image of the heptane gel of **1**. b) AFM image of the heptane gel of **2**. c) SEM image of the benzene gel of **1**. d) SEM image of the cyclohexane gel of **2**.

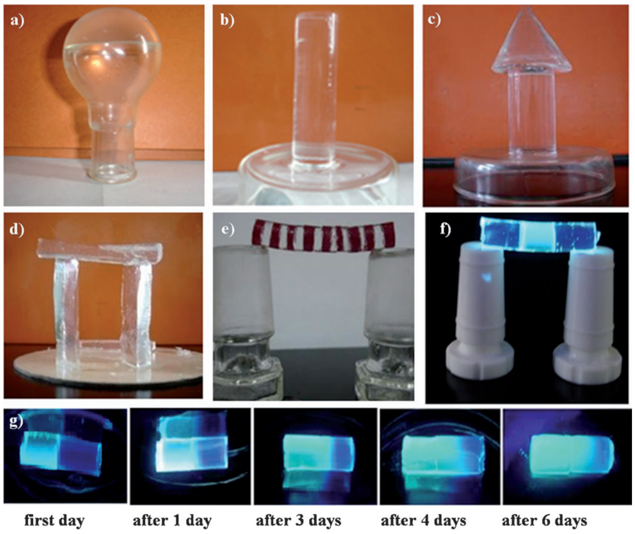

Figure 3. a) The massive amount of gel made from **1** in pump oil (0.23 wt%) in a 100 mL round-bottom flask is stable to inversion. b) A gel cylinder of diameter 2.9 cm and height 9 cm made from paraffin oil gel of **1** (0.3 wt%). c) A gel tower made by fusing a cylinder of 2.9 cm(d) × 6 cm(h) and a cone of height 4 cm and diameter 5.5 cm made from silicone oil gel of **2** (1 wt%). d) A gel bridge made from three gel bars cut out from a bigger block of gel made of **1** in pump oil (0.23 wt%). e) A 5 cm(h) × 1 cm(d) cylinder made from 17 small gel discs by the alternate fusion of PTCA-doped (PTCA = perylene-3,4,9,10-tetracarboxylic acid anhydride) and undoped gel discs of approximate thickness 3 mm suspended on two glass stoppers of 5.5 cm height. Both undoped and doped gels were made from **2** in pump oil (1 wt%). f) A gel cylinder of length 4.6 cm and diameter 1.2 cm made by the fusion of a pyrene-doped gel piece with two undoped gel pieces. The photograph was taken after exposing the gel to UV light. Both undoped and doped gels were made from **2** in pump oil at 1 wt%. g) A pyrene-doped gel fused to an undoped gel, both made of **2** in pump oil at 1 wt% concentration. The pyrene moved across the fusion interface slowly, thus demonstrating the exchange of dissolved matter. Similar motion of free gelator molecules would allow the growth of fibers across the interface or the connection of two fibers across the interface, and such dynamics would help in self-healing.

fusion could be taken in hand or suspended in air just by holding one side. Also, several small blocks of gels could be joined together to form a stable self-supporting bar (Figure 3). Although similar healing properties of a blend of polymeric gelator and clay were demonstrated recently,[22] such self-healing properties in supramolecular gels are very scarce.[23] This remarkable healing power allowed us to make various complex geometrical objects by fusing several pieces. The fusion of a pyrene-doped gel with an undoped gel established the diffusion of pyrene to the undoped piece, thus suggesting the dynamic exchange of dissolved molecules across the fusion interface. Since there will be a dynamic equilibrium between free dissolved gelators and the self-assembled gelators (fibers) in the gel (continuous formation of new fibers and dissociation of old fibers), such movement of free gelator molecules across the interface would allow the growth of fibers across the fusion interface or connection of broken fibers across the interface, thus facilitating the self-healing process (Figure 3, see the Supporting Information).

Interestingly, gels of **1** and **2** in higher hydrocarbon solvents and oils showed remarkably high transmittance in the visible region (see the Supporting Information) and weak transmittance in the UV region, thus suggesting that these can be used for applications where selective UV filtering is required (e.g. UV-protective goggles, skin creams). These gels have refractive indices (see the Supporting Information) similar to that of glass ($n \approx 1.5$). Excellent light transmittance, thermal reversibility, moldability, glasslike refractive indices, and the self-healing nature of these gels constitute a unique blend of properties that can be exploited for making soft optical devices. To explore these possibilities, we made different optical devices using the paraffin oil gel of **2**, such as a planoconvex lens, a double convex lens, a prism, gel plates, and cubes (Figure 4). The double convex lens was made by combining two planoconvex lenses by exploiting the self-healing power these gels. The lens could be handled gently, the focal length could be determined by conventional methods, and the lens could be used to magnify objects just like any normal glass lens. Similarly, a prism made out of these gels refracted white light into its components (Figure 4b).

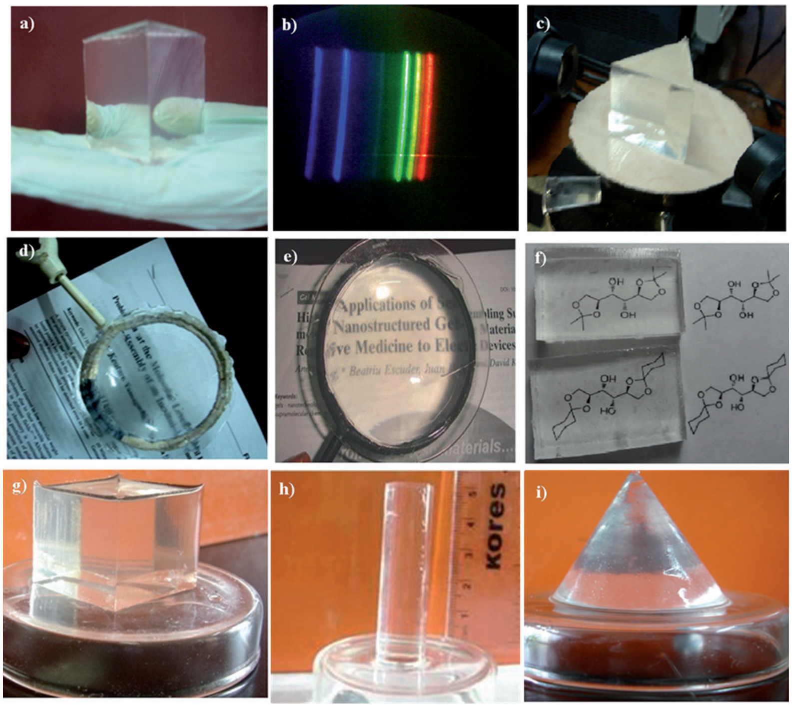

Figure 4. a) A gel prism made from pump oil gel of **2**. b) The diffraction pattern observed using the gel prism. c) The gel prism mounted on a spectrometer table. d) The double convex gel lens made from the pump oil gel of **2** supported on a metallic ring. e) A planoconvex lens made from paraffin oil gel of **2**. f) View of the structure of the gelators through their paraffin oil gels. g) A gel cube of size 8 cm×8 cm×8 cm. h) Gel cylinder of diameter 2.9 cm and height 5 cm. i) Gel cone of diameter 6 cm and height 8 cm.

As soft optical devices are shatter-free, they are convenient in terms of safety, handling, and so forth and are desirable in applications such as making eye-protecting devices. Although polymer-based gels have been proposed to be useful for making optical devices,[24] ours is the first report of noncovalent-polymer-based optical devices, which has additional properties such as reversibility and flexibility. Also, the gels' self-healing properties make them functionally scratch-free. Furthermore, these easy-to-handle, strong, and highly transparent oil gels could substitute the inconvenient liquid oil drops in oil immersion microscopy and oil condensers in differential interference contrast microscopy, as they have refractive indices similar to that of glass.

In conclusion, we have designed and synthesized two organogelators that can be made in one simple step from cheaply available D-mannitol, which can gelate nonpolar solvents and oils. By ^{1}H NMR and FTIR spectroscopy techniques we have established that intermolecular hydrogen bonding is the primary driving force for this gelation process. As these oil gels are strong, highly transparent, self-healing, and have glass-like refractive indices, we have exploited them for making soft optical devices. High visible-light transmittance and low UV transmittance of these gels is also exciting for developing optical devices with UV-filtering abilities. The thermal reversibility of these supramolecular polymers makes them attractive for developing flexible optical devices (e.g. lenses with changing focal lengths). Furthermore, as these gels are nontoxic and environmentally friendly, they have advantages over conventional non-biodegradable polymers.

Experimental Section

2: 1,1-dimethoxycyclohexane (6.3 g, 44 mmol) and *p*-toluenesulfonic acid (0.4 g, 2 mmol) were added to a suspension of D-mannitol (4 g, 22 mmol) in dry DMF (100 mL). The resulting mixture was stirred at 60 °C for 1 h. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and neutralized by addition of triethylamine (2 mL). The solvents were evaporated under reduced pressure on a rotary evaporator, and the residue was extracted with ethylacetate. The organic phase was washed with water, dried over $MgSO_4$, filtered, and concentrated. The crude material thus obtained was purified by column chromatography using petroleum ether/ethyl acetate (6:4 v/v) as the eluent to obtain diol **2** as a white solid (4.8 g, 63 %).

Gelation test: 10 mg compound was dissolved in 500 μL solvent in a test tube by heating, and the solution was allowed to cool to room temperature. A sample was classified as a gel if it was stable to inversion of the test tube.

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