Gelators

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A Sugar-Based Gelator for Marine Oil-Spill Recovery

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Abstract: *Marine oil spills constitute an environmental disaster with severe adverse effects on the economy and ecosystem. Phase-selective organogelators (PSOGs), molecules that can congeal oil selectively from oil–water mixtures, have been proposed to be useful for oil-spill recovery. However, a major drawback lies in the mode of application of the PSOG to an oil spill spread over a large area. The proposed method of using carrier solvents is impractical for various reasons. Direct application of the PSOG as a solid, although it would be ideal, is unknown, presumably owing to poor dispersion of the solid through the oil. We have designed five cheap and easy-to-make glucose-derived PSOGs that disperse in the oil phase uniformly when applied as a fine powder. These gelators were shown to selectively congeal many oils, including crude oil, from oil–water mixtures to form stable gels, which is an essential property for efficient oil-spill recovery. We have demonstrated that these PSOGs can be applied aerially as a solid powder onto a mixture of crude oil and sea water and the congealed oil can then be scooped out. Our innovative mode of application and low cost of the PSOG offers a practical solution to oil-spill recovery.*

Marine oil spills, which occur as a result of accidents during oil drilling in the sea or oil shipping (accounts for a third of global maritime trade), as well as natural causes such as volcanic eruption in the sea bed, is a serious environmental problem with severe adverse consequences for the marine ecosystem.[1] There is a lot of interest in developing new methods for marine oil-spill recovery.[1b,c,2] One of the emerging ideas for oil-spill recovery is selective gelation of the oil phase by using phase-selective organogelators (PSOGs).[3] In most lab-scale demonstrations, a low-polarity distilled petroleum fraction has been used. Although these excellent demonstrations are sufficient for a proof-of-concept, they are far from reality since natural crude oil is a complex mixture of several polar and nonpolar organic compounds and minerals and hence its gelation properties can be very different from a distilled nonpolar fraction. Another cause for concern is associated with the mode of application of PSOGs. All previous demonstrations have necessitated the use of a carrier solvent for uniform distribution of the gelator. Initially, water miscible non-gelling solvents were used as the carrier solvent, and these are destined to diffuse into the bulk water.[3a–c,4] Later, concerns regarding pollution of the sea by these carrier solvents led us and others to use water-immiscible gelling solvents as the carrier solvents, which are destined to congeal along with the oil.[3f,5] Two major drawbacks that preclude the practical application of this method arise from the poor solubility of gelators in gelling solvents, which necessitates large amounts of carrier solvent, and maintenance of the solution under hot conditions to avoid gelation of the carrier solvent before application. These inconveniences caused by the use of carrier solvents mean that a novel practical method for applying PSOGs for oil-spill recovery is needed. An ideal solution to this problem would be one in which the gelator can be applied directly as a solid. In line with our interest in gels and their applications,[6,7] we report a glucose-derived PSOG that can be applied directly as a solid without a carrier solvent, and a practical method for oil-spill recovery that makes use of a low-molecular-mass organogelator (LMOG; Figure 1).

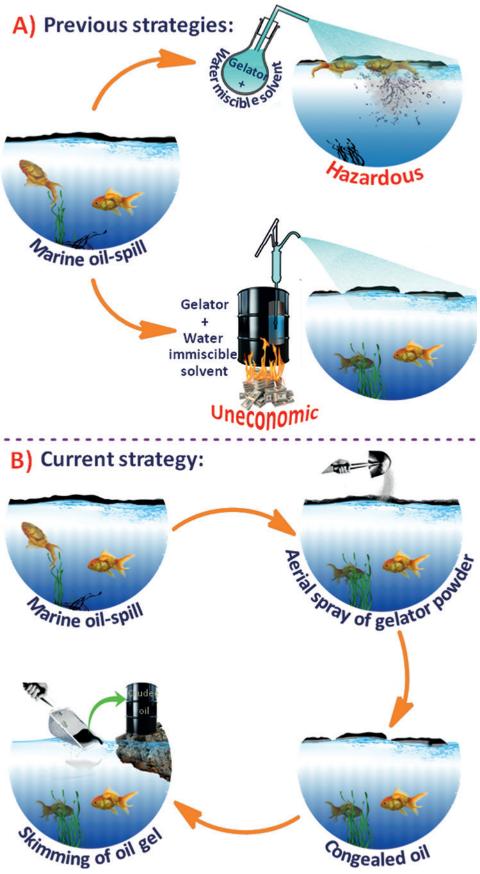

Figure 1. A) The disadvantages of marine oil-spill recovery by using PSOGs with carrier solvents. B) The proposed marine oil-spill recovery by using a gelator powder.

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For cost-effective oil-spill recovery, the PSOG should be an easily available, very cheap, nontoxic, and biodegradable oil solidifier that can congeal the oil phase very efficiently and selectively. Many alkyl 4,6-*O*-benzylidene-glycopyranosides are known organogelators of nonpolar solvents.[8,9] Both the benzylidene group and diol motifs are important structural features for gelation; the vicinal diol motif is essential for hydrogen-bond-mediated self-assembly and the benzylidene group for rigidity (conformational pre-organization). However none of these alkyl 4,6-*O*-benzylidene-glucopyranosides are known to be phase-selective gelators, presumably owing to the partial solubility of these derivatives in water. We envisioned that one of the strategies to convert them in to phase-selective gelators would be to make them more hydrophobic by modifying structural features that are not crucial for gelation, such that they become water-insoluble but still congeal oils. For this, modification at the anomeric position is presumed. We decided to use more hydrophobic thioalkyl or thioaryl motifs in place of the O-alkyl motif at the anomeric position. In order to check the feasibility, we synthesized compounds **1**–**5** (Figure 2) from cheaply available D-glucose by following straightforward reported procedures (Scheme S1 in the Supporting Information).[10]

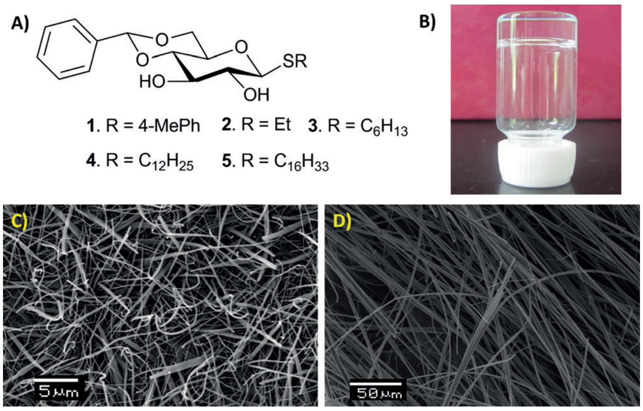

Figure 2. A) Chemical structures of gelators **1**–**5**. B) Transparent gel (stable to inversion) of gelator **1** in benzene at 0.5 wt%. C, D) SEM Images of xerogels made from a benzene gel (0.9 wt%, wt/v) of gelator **1** (C) and a benzene gel (1.25 wt%, wt/v) of gelator **2** (D). Scale bars: 5 μm and 50 μm, respectiveley.

We tested the gelation ability of diols **1**–**5** in different solvents. All of these diols form gels in nonpolar liquids such as silicon oil, pump oil, and diesel. To our satisfaction, the modification of the compounds did not compromise their gelation ability despite structural changes at the anomeric position. The critical gel concentration (CGC) values of these gelators were measured (Table S1 in the Supporting Information). It was observed that the gelation ability increased with increasing length of the thioalkyl chain. This may be attributable to an increased contribution from hydrophobic or van der Waal's interaction in the self-assembly process. Although compound **2**, which has a small alkyl chain, congealed aromatic solvents, **3**–**5** were soluble in aromatic solvents. It is worthy of note that compounds **3**–**5** took more time to congeal crude oil and its higher-boiling fractions (diesel, petrol, kerosene). This is not surprising in light of the competing solubilizing effect of the aromatic components present in these oils; crude oil and its fractions are known to contain aromatic constituents. It is interesting to note that gelators **1** and **2** are both supergelators of crude oil, with CGC values of 0.5 wt% and 0.6 wt% respectively, which is a desirable property for efficient oil-spill recovery. Since gelators **1** and **2** congealed crude oil more efficiently than the other gelators, these two were chosen for detailed studies. The stabilities of the gels formed by gelators **1**–**5** in various solvents were measured by measuring their sol–gel transition temperatures (T_{gel}; Table S1 in the Supporting Information). The gels formed by **1** and **2** showed good thermal stability and were stable for several months at ambient conditions.

A comparison of the IR spectra of gelators **1** and **2** in the self-assembled state (solution in gelling solvent) and dissociated state (solution in non-gelling solvent) suggest that intermolecular hydrogen bonding is the primary interaction for self-assembly. The O−H stretching appeared at a lower wave number in the self-assembled state (gel) than in the dissociated state (Figures S2, S3 in the Supporting Information). In addition, concentration-dependent ^{1}H NMR titration (Figures S4, S5) of the gelators in a gelling solvent confirmed the involvement of intermolecular hydrogen bonding in the self-assembly (gelation), as was evident from the down-field shift of OH signals with concentration. The higher gelation ability of gelator **1** (0.5 wt%) than gelator **2** can be attributed to the presence of a thiotolyl group in gelator **1**, which can engage in additional interactions such as π–π stacking or C−H⋯π interactions. Scanning electron microscopy (SEM) analysis (Figure 2 and Figure S8 in the Supporting Information) of the xerogels made from benzene gels of **1** and **2** revealed that these gelators form an entangled fibrous network in their gels.

We carried out rheology analysis to understand the strength and stability of the gels formed by gelators **1** and **2** (Figure 3 and Figures S6, S7 in the Supporting Information).

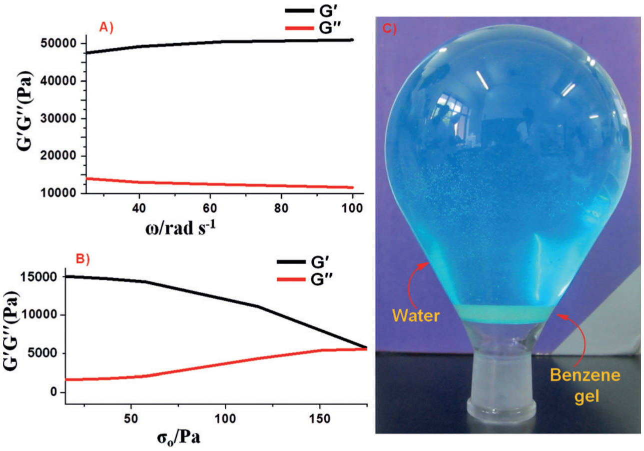

Figure 3. A, B) Rheological data for gels made in benzene with 2 wt% (wt/v) of gelator **1**. A) Frequency sweep (*ω*) and B) stress sweep (σ_0) are shown. C) A 5 wt% (wt/v) benzene gel (10 g) of gelator **1** holding the weight of 1 L of water in an inverted round-bottomed flask (copper sulfate was added to the water for better visualization).

As representative examples, a 2 wt % benzene gel of **1** and 5 wt % benzene gel of **2** were used for rheological studies. In the frequency-sweep mode, the storage modulus (elastic modulus) was always much higher than the loss modulus (viscous modulus) and both these moduli are frequency-independent, as expected of strong gels. The value of G' (elasticity modulus) is very high ($\approx$47 000 Pa for gels of **1**), which is indicative of high strength (stiffness) of the gel. In the stress-sweep mode, the plot of G' and G'' against stress amplitude (σ_o) suggests high yield stress (more than 100 Pa) for the gel, which suggests that the gel can withstand high pressure. The benzene gel of **2** showed similar rheological data (Figure S7 in the Supporting Information). We also demonstrated the gel strength in terms of the weight-holding capacity of the gels (Figure 3 c and Figure S10 in the Supporting Information). For instance, 10 g of a 5 wt % benzene gel of **1** formed at the neck of an inverted RB flask could hold 1000 g of water above it against gravity (Figure 3 c).

Having established the ability of gelators **1** and **2** to form strong and stable gels in nonpolar liquids and crude oil, we examined the gelation ability of these compounds in a biphasic system of oil and water. It was gratifying to note that both gelators could selectively congeal the oil phase without affecting the water phase. Although the biphasic CGC (BCGC) values were slightly higher than the corresponding CGC values (See Table S1 in the Supporting Information), gelator **1** also congeals the solvent at a lower weight % than gelator **2** in a biphasic system. Since gelator **1** showed a better BCGC for hydrocarbons and crude oil, we used it for oil-spill recovery. Although it is easy to congeal nonpolar liquids by applying **1** in carrier solvent, the requirement for a large volume of carrier solvent and even more of the gelator, as well as the need to keep the gelator solution under hot conditions, make this method uneconomical and impractical for real-life use. This prompted us to apply the solid gelator in finely pulverized solid form.

The main hurdle with the powder dispersion approach is discontinuous gelation owing to poor diffusion of gelator molecules through the oil phase. For instance, dicyclohexylidene mannitol, a PSOG we reported earlier,[3f] could not form an efficient continuous and uniform gel when applied as a solid powder in oil–water mixture. This is due to the gelation of only the surface of the gelator particles, which protects the solid core of the gelator from dissolution and diffusion. To our great satisfaction, gelator **1** was able to congeal all the benzene from a benzene–water (15:200, v/v) mixture when the gelator was spread as a fine powder (Figure 4 and Video S1 in the Supporting Information). The benzene layer was thickened in less than an hour and could be skimmed off with a sieved scoop (Figure 4 and Video S1). Similarly, gelator **1** could congeal the whole diesel layer from a biphasic mixture of diesel and water. The gel thus formed was strong enough to scoop with a spatula (Figure S15 in the Supporting Information).

Next, we turned our attention towards the recovery of crude oil from a biphasic mixture. For this, we recreated a realistic scenario by pouring crude oil over the surface of sea water (oil/water = 20:200, v/v) in a glass bath (Figure 5 and Video S2 in the Supporting information). Powdered gelator **1** was then dispersed over the surface. The solution was kept under gentle stirring. After some time, the crude oil layer had stopped swirling but not the water layer, which confirmed gelation of the oil layer. Compared to benzene and diesel, crude oil required longer to form a gel that is strong enough to be skimmed off. Gelator **1** could also congeal crude oil when the water was still (Video S2), thus suggesting that the gelator can easily diffuse through the oil phase even under stagnant conditions.

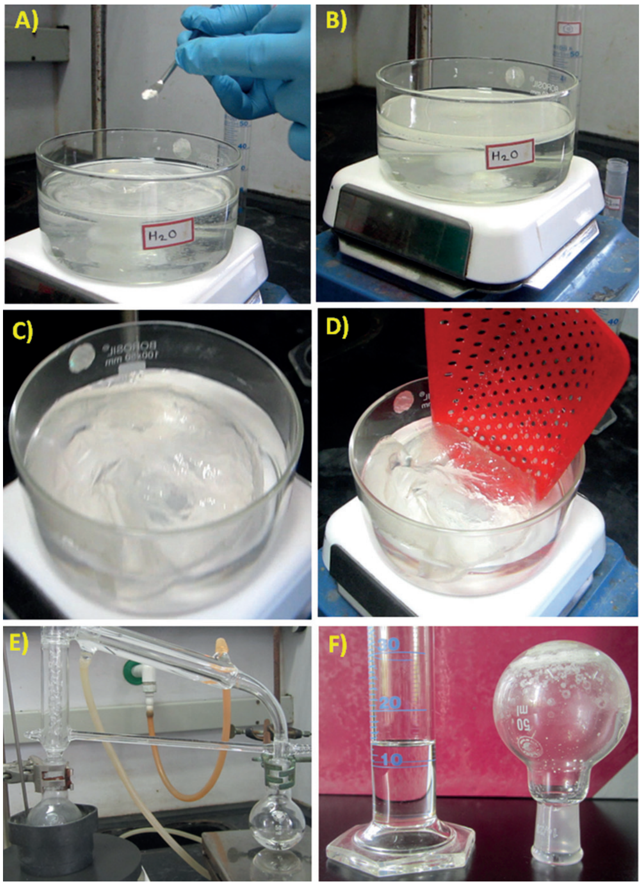

Figure 4. A) Powdered gelator **1** (150 mg) was spread over a benzene–water mixture (15 mL:200 mL). B) The mixture was allowed to congeal. C) Gelation of the benzene layer after 45 min. D) Removal of the benzene gel with a sieved scoop. E) Recovery of benzene by distillation. F) Recovered benzene and gelator.

In case of refined volatile petrochemicals like benzene, diesel, and petrol, the oil and gelator can be separated from the congealed (recovered) oil by simple distillation and so the gelator could be reused for several cycles of oil-spill recovery. The recovered crude oil gel can be fractionated by distillation just like normal crude oil (Video S3). Since crude oil contains a complex mixture of many non-volatile components and heavy-metal ions, recovery of the gelator from congealed crude oil is difficult. Hence it is very important to have a gelator with a very low CGC for crude oil. Since the gelator reported here meets the required gelation ability, with a CGC value of 0.5 wt % for crude oil, this may be practically viable method for marine oil-spill recovery.

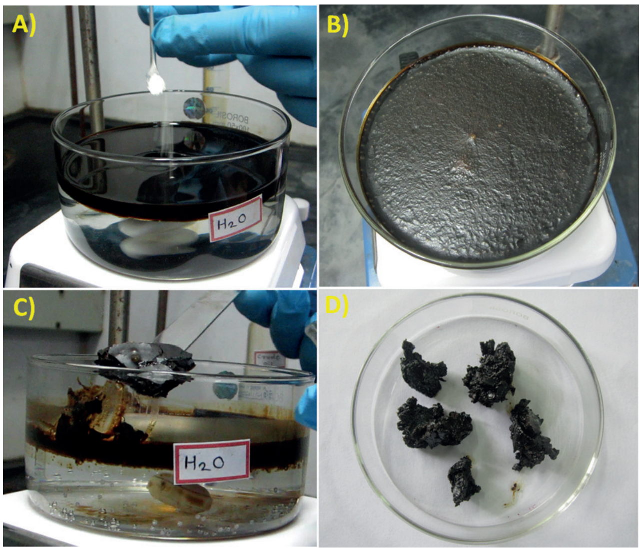

Figure 5. A) Spreading of gelator **1** powder (1 wt %, wt/v) over a layer of crude oil on water. B) Gelation of the crude-oil layer. C) The crude-oil gel was removed with a spatula. D) The removed crude-oil gel.

In conclusion, although LMOGs have been proposed for marine oil-spill recovery, the requirement for a carrier solvent limits their practical implementation. By addressing the problems associated with oil-spill recovery, we have demonstrated a practical method for oil-spill recovery that makes use of an LMOG that can be applied in the solid form. The gelator is very cheaply available and can be made from D-glucose. Furthermore, the amount of gelator required for gelation is very low. We hope that this method can be extended for practical applications by aerial spraying of the gelator powder followed by oil recovery.

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Keywords: hydrogen bonding · gelators · oil-spill recovery · phase-selective organogelators · self-assembly

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