Molecular Gelators

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Sugar-Derived Phase-Selective Molecular Gelators as Model Solidifiers for Oil Spills**

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The world has witnessed several marine oil spills, including the recent one caused by the blowout of an oil well in the Gulf of Mexico.[1] Such oil spills cause irrecoverable damage to the environment and the ecosystem.[2] There is clearly a need for materials to contain oil spills and reclaim the oil. Current materials for this purpose are classified as dispersants, sorbents, and solidifiers.[3] Typically, dispersants emulsify the oil,[4] sorbents are solid powders that absorb the oil,[5] and solidifiers are usually polymeric materials that gel the oil layer.[6] However, all current materials have limitations, both in containing the oil spread and in allowing recovery of the spilled oil. For example, polymeric solidifiers cannot be blended easily with viscous oils, and the recovery of oil from polymer gels is cumbersome.

An effective and ideal solidifier for oil spills must: 1) selectively and efficiently gel the oil phase in the presence of water at room temperature; 2) be synthesized easily and at low cost; 3) be environmentally benign; 4) facilitate recovery of the oil from the gel; and 5) be recyclable and reusable. Herein, we describe a new class of amphiphilic solidifiers based on derivatives of naturally occurring sugar alcohols. These amphiphiles can function as phase-selective gelators (PSGs) of the oil phase from a mixture of oil and water.[7,8] They can potentially satisfy each of the above criteria and therefore are promising model candidates for oil-spill remediation.

The PSGs are examples of molecular gelators, in other words, small molecules that self-assemble into nanoarchitectures (like fibers) in liquids.[9–12] Above the minimum gelation concentration (MGC), the fibers become entangled into a network, thereby converting the liquid into a coherent gel.[13–15] Intermolecular interactions between gelator molecules are noncovalent and hence relatively weak, for example hydrogen bonds and van der Waals interactions. Thus, molecular gels tend to be thermoreversible; that is, the gel can be liquefied by heating beyond a temperature T_{gel} (gel-to-sol transition temperature) and reverted to the gel state by cooling below T_{gel}. We exploit the thermoreversibility of gels formed by our PSGs for the recovery of gelled oil through simple distillation.

The first example of phase-selective gelation was demonstrated by Bhattacharya and Krishnan-Ghosh.[7] with amino acid amphiphiles. Molecular gelators based on naturally occurring compounds[16,17] including closed-chain sugars have been synthesized previously; however, gelators based on open-chain sugars (sugar alcohols) remain almost unexplored.[18–20] The PSGs reported here are dialkanoate derivatives of the sugar alcohols mannitol (**Man**) and sorbitol (**Sor**) (Figure 1 a). Conventional routes to such compounds involve

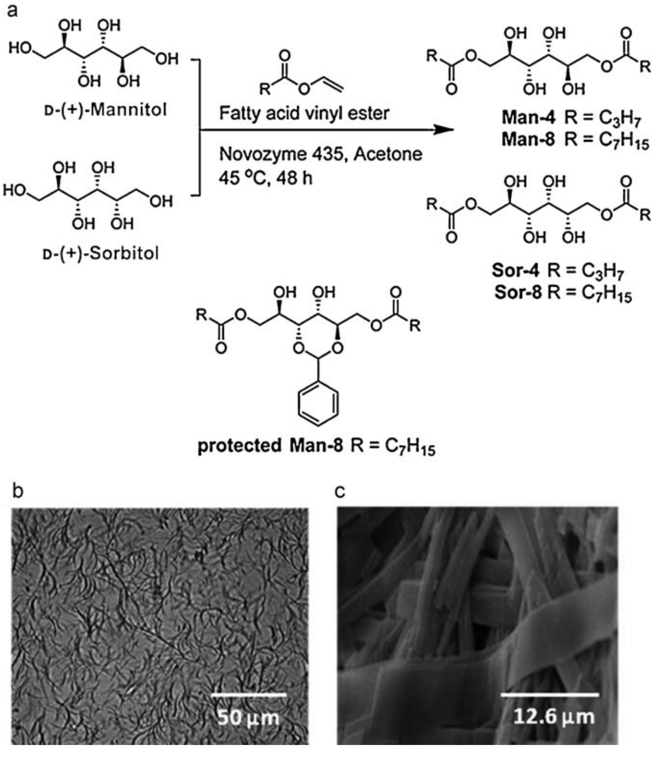

Figure 1. a) Chemical structure of open-chain sugar amphiphiles, their enzyme-mediated synthesis, and the structure of the benzylidine-protected sugar amphiphile, protected **Man-8**. b) Image of self-assembled aggregates of **Man-8** in diesel recorded with an optical polarized microscope. c) Image of a toluene gel recorded with a scanning electron microscope (SEM). (An SEM image of a diesel gel could not be obtained; it was difficult to prepare xerogels of diesel gel owing to the high boiling point of diesel.)

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multiple steps with protection and deprotection protocols. Here we prepared PSGs in a single step by employing regiospecific enzyme catalysis (see the Supporting Information for details). The ease of synthesis and the abundance of sugar alcohols in nature ensure that the PSGs are inexpensive, nontoxic, and biodegradable.

The gelling abilities of the sugar gelators are summarized in Table 1. **Man-4**, **Man-8**, **Sor-4**,and **Sor-8** gel numerous organic liquids including diesel and mineral and silicone oils, with minimum gelation concentrations (MGCs) ranging from 1.5 to 5 % wt/v. For example, **Man-8** gels diesel at 2.5 % wt/v; in other words, it immobilizes diesel to roughly 32 times its own dry weight. All gels were thermoreversible and their T_{gel} values ranged from 82–125 °C and 38–69 °C for **Man-8** and **Sor-8** (5 % wt/v), respectively (see Table S1 in the Supporting Information). They were stable for several months, indicating their temporal stability. Note that mannitol and sorbitol have similar chemical structures, except for the orientation of the hydroxy group at the C2 stereocenter (Figure 1 a). This subtle change in chirality significantly impacts gelling ability—the mannitol derivatives formed stronger gels and had higher T_{gel} values. Alkyl chain length also influences gelling ability—the MGCs of dioctanoate derivatives were much lower than those of the dibutanoates. Together, the results indicate that gelling can be modulated by altering either the hydrophilic sugar or the hydrophobic fatty acid chain of these gelators.

Table 1: Gelation abilities (MGC values in % wt/v) of sugar amphiphiles **Man-4**, **Man-8**, **Sor-4**, and **Sor-8** in various organic liquids and oils.[a]

Liquid or oil	Man-4	Man-8	Sor-4	Sor-8
coconut oil	G (4.0)	G (1.3)	G (5.0)	G (3.0)
olive oil	G (2.5)	G (1.0)	G (3.0)	G (1.5)
soybean oil	G (4.0)	G (1.3)	G (5.0)	G (3.0)
grape seed oil	G (4.0)	G (1.3)	G (5.0)	G (3.0)
canola oil	G (4.0)	G (1.0)	G (5.0)	G (3.0)
cooked sunflower oil	G (4.0)	G (1.0)	G (5.0)	G (3.0)
cyclohexane	G (3.0)	G (2.5)	G (3.0)	G (2.5)
toluene	G (2.5)	G (1.5)	G (3.0)	G (2.5)
benzene	G (2.5)	G (1.5)	G (3.25)	G (3.0)
chloroform	S	S	S	S
ethyl acetate	G (2.5)	G (2.0)	S	S
tetrahydrofuran	S	S	S	S
methanol	S	S	S	S
water	I	I	I	I
hexane	–	P	–	P
heptane	–	P	–	P
diesel	–	G (2.5)	–	G (3.5)
mineral oil	–	G (1.2)	–	G (1.5)
paraffin oil	–	G (2.0)	–	G (2.5)
pump oil	–	G (4.0)	–	G (5.0)
silicone oil	–	TG (5.0)	–	TG (5.0)
mixture of hydrocarbons[b]	–	G (2.5)	–	G (3.5)

[a] Values in parenthesis are minimum gelation concentration of gelator (% wt/v, mg/100 μL). G = opaque gel; TG = transparent gel; S = soluble; I = insoluble; P = precipitation. [b] Mixture of aliphatic (pentane, hexane, octane) and aromatic (benzene, toluene, xylene) solvents in 1:1 volume ratio.

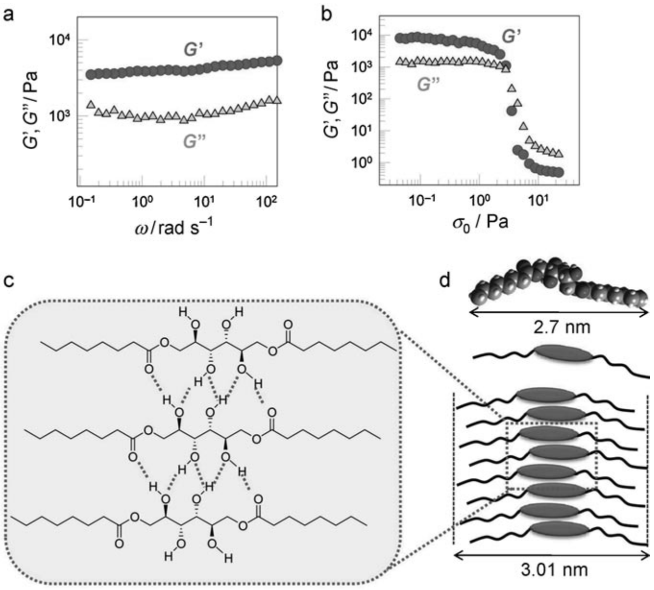

Figure 2. Dynamic rheology of diesel gel and a model for self-assembly of amphiphiles. a) Frequency sweep (ω) and b) stress sweep (σ_0) of 5 % wt/v **Man-8** gel in diesel. c) Possible hydrogen-bonding network in **Man-8** amphiphiles with schematic representation of postulated molecular packing model for organogels of **Man-8**. d) The energy-minimized structure of **Man-8**.

The strength of the organogels was then studied by rheology. Figure 2 a shows the frequency response of a gel of 5 % wt/v **Man-8** in diesel. The elastic modulus G' is independent of frequency and much higher than the viscous modulus G'' over the frequency range. This response is typical of gels as it shows that the sample does not relax over long time scales. The value of G' is a measure of the gel stiffness, and its value here (ca. 4000 Pa) indicates a gel of moderate strength. Figure 2 b shows a plot of the moduli G' and G'' as a function of the stress amplitude σ_0 for the same sample. The stress amplitude σ_0 at which a sharp decrease in moduli occurs is the yield stress of the gel, and its value (≈ 30 Pa) is sufficiently high for the gel to support its own weight in an inverted vial.

We then evaluated the ability of **Man-8** and **Sor-8** to phase-selectively gel oil in the presence of water. Since a required heating step in phase-selective gelation would be impractical for high-volume applications like oil-spill recovery, a room-temperature gelation protocol was formulated. First, we dissolved a high concentration of the gelator in a water-miscible solvent (ethanol). An aliquot of this solution was then added to a 1:1 mixture of oil (diesel) and water in a vial or flask. Spontaneous partitioning of the aliquot solvent into water and the gelator into the oil phase was observed; gelation of oil phase occurred while the aqueous phase was left intact. Note the photograph of an inverted vial in Figure 3 a: the oil gel is strong enough to hold not only its weight but also the weight of the aqueous solution on top (the rheology of the oil gel was identical to that in Figure 2). Such efficient phase-selective gelation was observed with many oils including diesel, gasoline, pump oil, crude-oil fractions (alkanes with $n > 9$ carbon atoms) and mixture of hydrocarbon solvents (aliphatic and aromatic), thereby indicating potential applicability to real oil-spill situations and treatment

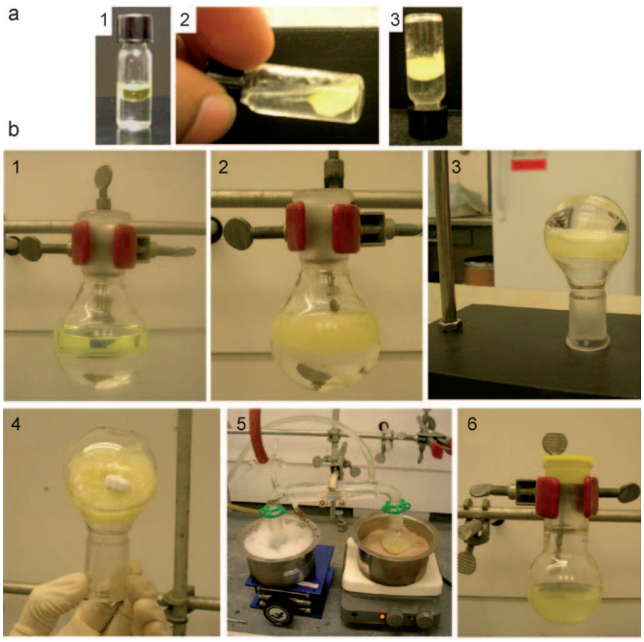

Figure 3. Phase-selective gelation and diesel recovery from a two-phase system. a) Phase-selective gelation of an organic liquid in the presence of water. If a smaller amount of gel forms it will float (picture 2); at higher concentrations of gel, the flow of water is stopped upon inversion of the vial (picture 3). b) Gelation of bulk diesel in the presence of water, and its quantitative recovery through vacuum distillation. Photographs: 1) diesel and water form a two-phase system; 2) gel forms instantaneously upon addition of gelator by syringe; 3) Owing to the strength of the diesel gel, the flow of water is stopped upon inversion of flask; 4) Diesel gel remains after removal of the bottom water layer; 5) The entrapped diesel is recovered by vacuum distillation; 6) Recovered diesel.

of refinery effluent. Importantly, even impure compounds exhibited phase-selective gelation. Also, the oil to water ratio, type of water (river water from Hudson River, New York City, USA and sea water from Cooney Island, Brooklyn, USA) and nature of the aqueous solution (acidic, basic, neutral, saturated NaCl and saturated $CaCl_2$ solution) did not alter the phase-selective gelation, which indicates the robustness of the phenomenon.

Optical and scanning electron microscope (SEM) images (Figure 1c and Figure S1 in the Supporting Information) show networks of entangled fibers in the gels. X-ray diffraction (XRD) studies (see Figure S2 in the Supporting Information) suggest that the fibers are stacks of gelator molecules with the tails tilted relative to the fiber axis (Figure 2d). Fiber assembly, in turn, is believed to be driven by intermolecular hydrogen bonding between the hydroxy groups of adjacent gelators (Figure 2c). Proof for the hydrogen bonding in the gel state comes from Fourier transform infrared spectroscopy (FTIR) (see Figure S3 in the Supporting Information). The importance of hydrogen bonding was also shown by the synthesis of a hydroxy-protected benzylidene derivative of **Man-8** (Figure 1a), which did not gel any of the oils (see the Supporting Information for synthesis and characterization). In the case of the phase-selective gelation, it is clear that the presence of water does not disrupt the hydrogen bonding of **Man-8** and **Sor-8** in the oil phase, possibly because the hydrophobic tails on either side of the sugar head ensure that the molecules remain in the nonpolar oil layer. In contrast, **Man-8** and **Sor-8** did not gel protic solvents like ethanol, presumably because these solvents compete for hydrogen bonding with the hydroxy groups on the gelators. Importantly, the properties of gels obtained by the aliquot method and by conventional heating were similar (see Figure S4 in the Supporting Information).

In the few existing examples of low-molecular-weight phase-selective oil gelators, the recovery of oil from the gels and the recycling of the gelator were not demonstrated. For application in oil remediation, these aspects must be addressed. We therefore performed gelation of diesel (20 mL) in the presence of 40 mL of water (Figure 3b). A solution of **Man-8** in ethanol was added by syringe to this mixture such that its concentration in diesel was 5% wt/v. The diesel gelled instantly, and within 1 h the gel was strong enough to bear its weight plus that of 40 mL water (see Video S1 in the Supporting Information). Subsequently, water was removed by syringe, and the gel was subjected to distillation by heating it to 125 °C (above T_{gel}), whereupon the gel liquefied and the diesel distilled off. Diesel could thus be recovered almost quantitatively. The residue in the flask was characterized by thin layer chromatography, and **Man-8** was found to be intact. Recycled **Man-8** could gel a fresh batch of diesel, confirming its reusability. Phase-selective gelation of oil was also performed on a thin layer (<1 mm) of diesel floating on a large pool of water (in a Petri dish). The resulting gel could be scooped out with a spatula, and the oil in it could again be recovered through distillation. This example mimics the real scenario of an oil spill.

In conclusion, we have demonstrated a new class of sugar-gelators that can selectively gel (solidify) the oil phase from an oil–water mixture at room temperature. Quantitative recovery of oil from the gel has been achieved through simple vacuum distillation. The gelators are easily synthesized and environmentally benign, and can be recovered and reused multiple times. We believe this is a promising approach for the containment and treatment of oil spills.

Experimental Section

Room-temperature gelation (aliquot method): An aliquot of gelator was prepared in a hydrophilic solvent (alcohols, dioxane, and tetrahydrofuran). A specific amount of prepared aliquot, capable of delivering the MGC concentration, was injected at the interface. In a typical phase-selective gelation experiment conducted at 25–30 °C, 25 mg of **Man-8** was dissolved in 400 μL of ethanol. This aliquot was injected at the interface of the diesel–water mixture (1 mL each). The mixture was allowed to set to obtain gel of only diesel phase.

Details of the synthesis, characterization, gel preparation, and gel characterization (gel melting temperature, optical microscopy, electron microscopy, XRD, IR, and rheology) are included in the Supporting Information.

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