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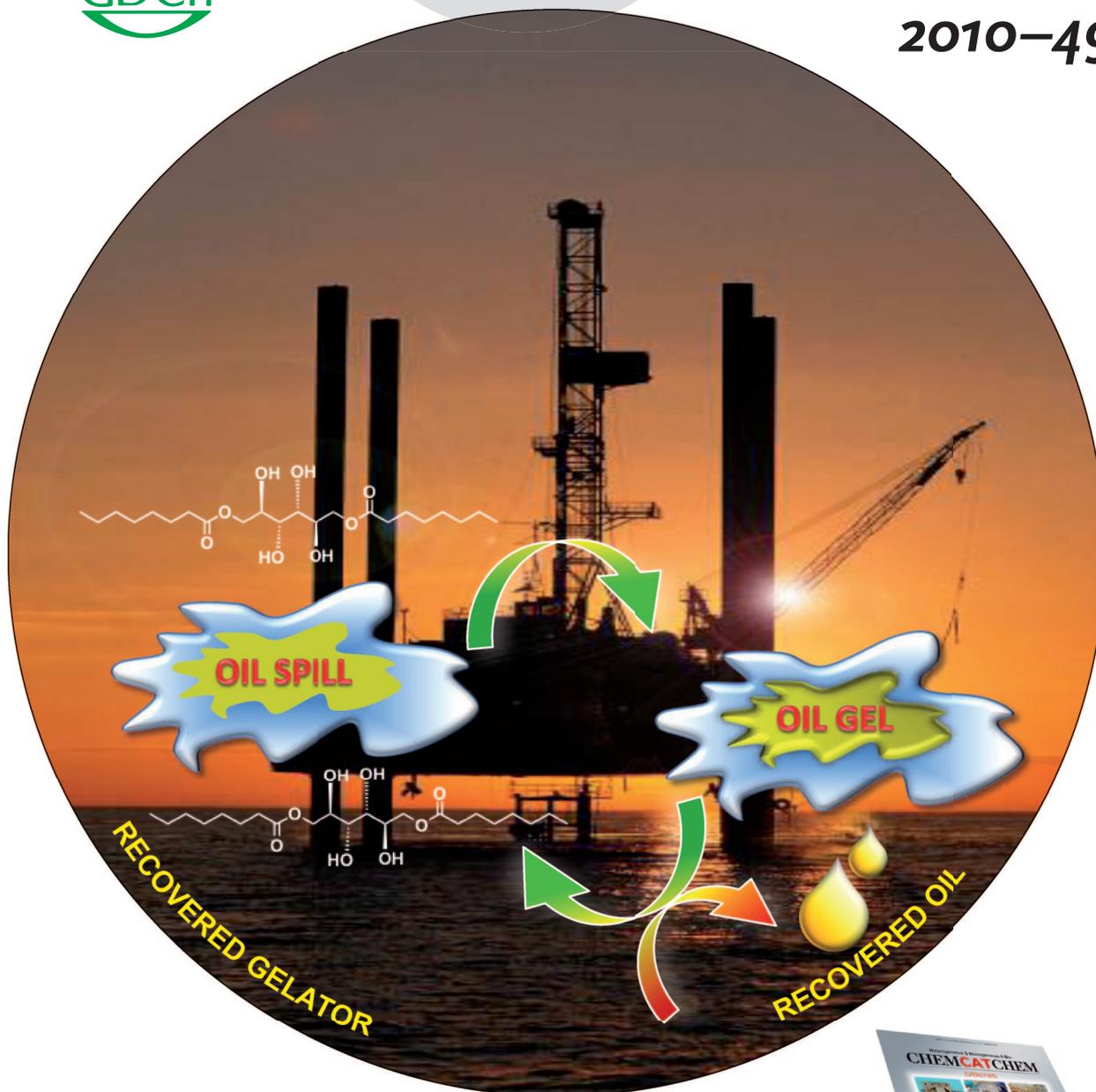
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**Semiconductor Gas Sensors**

A. Teleki et al.

**Highlights: Carbon Monoxide Detection • Carbon Nanotubes as Nanopores • Insulin Synthesis**

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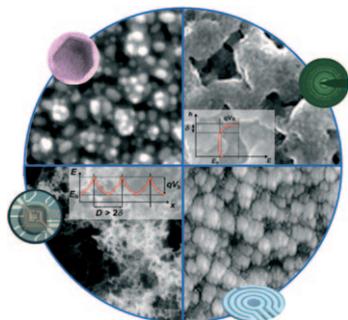
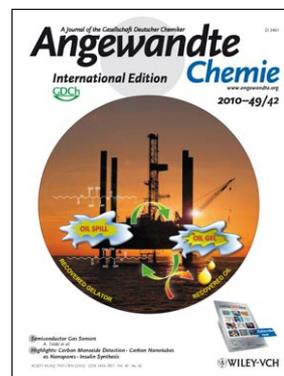


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## Cover Picture

**Swapnil R. Jadhav, Praveen Kumar Vemula, Rakesh Kumar, Srinivasa R. Raghavan, and George John\***

*In the near future* molecular gels may serve in the ecologically sound cleanup of oil spills. In their Communication on page 7695 ff., G. John and co-workers describe how newly developed sugar alcohol gelators can be used for the unprecedented phase-selective gelation of various crude-oil fractions from oil–water mixtures at room temperature. The gels facilitate both the containment and the reclamation of oil.

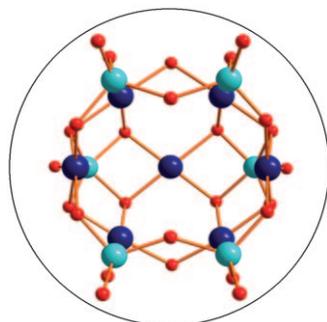
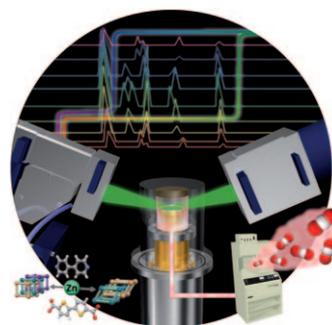


### **Gas Sensors**

A. Teleki et al. describe in their Review on page 7632 ff. the synthesis and deposition methods for the preparation of gas sensors based on metal oxide semiconductors. They also discuss the synthesis of highly porous semiconductor films through new aerosol techniques.

### **Coordination Polymers**

In their Communication on page 7660 ff., R. Matsuda, S. Kitagawa, and co-workers tune the structural flexibility and sorption behavior of 3D porous coordination polymers by changing the degree of interpenetration.



### **Mixed-Valent POMs**

In their Communication on page 7807 ff. U. Kortz et al. present the bowl-shaped polyoxometalate (POM)  $[\text{Pd}^{\text{II}}_7\text{V}^{\text{V}}_6\text{O}_{24}(\text{OH})_2]^{6-}$ , which maintains its solution structure in the gas phase.

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

Swapnil R. Jadhav, Praveen Kumar Vemula, Rakesh Kumar, Srinivasa R. Raghavan, and George John\*

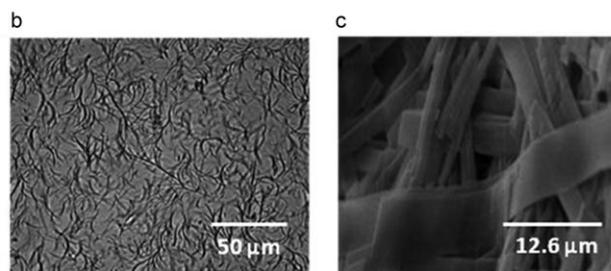
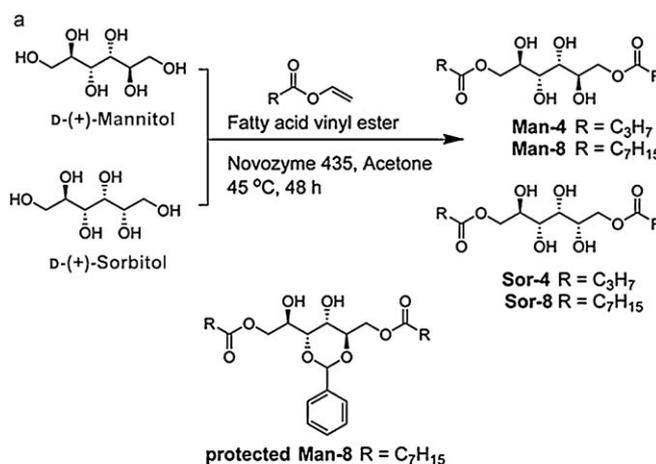
The world has witnessed several marine oil spills, including the recent one caused by the blowout of an oil well in the Gulf of Mexico.<sup>[1]</sup> Such oil spills cause irrecoverable damage to the environment and the ecosystem.<sup>[2]</sup> There is clearly a need for materials to contain oil spills and reclaim the oil. Current materials for this purpose are classified as dispersants, sorbents, and solidifiers.<sup>[3]</sup> Typically, dispersants emulsify the oil,<sup>[4]</sup> sorbents are solid powders that absorb the oil,<sup>[5]</sup> and solidifiers are usually polymeric materials that gel the oil layer.<sup>[6]</sup> 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.<sup>[7,8]</sup> 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.<sup>[9–12]</sup> Above the minimum gelation concentration (MGC), the fibers become entangled into a network, thereby converting the liquid into a coherent gel.<sup>[13–15]</sup> 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  $T_{\text{gel}}$  (gel-to-sol transition temperature) and reverted to the gel state by cooling below  $T_{\text{gel}}$ . 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,<sup>[7]</sup> with amino acid amphiphiles. Molecular gelators based on naturally occurring compounds<sup>[16,17]</sup> including closed-chain sugars have been synthesized previously; however, gelators based on open-chain sugars (sugar alcohols) remain almost unexplored.<sup>[18–20]</sup> 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 benzylidene-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 regioselective 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,

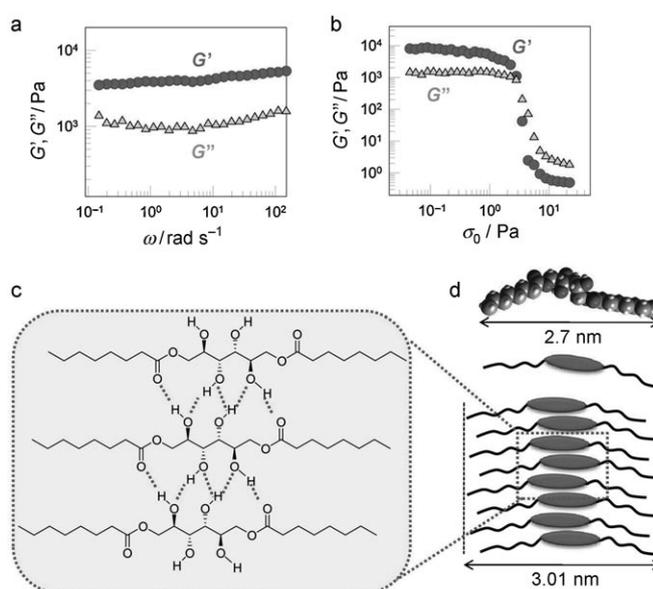
**Table 1:** Gelation abilities (MGC values in % wt/v) of sugar amphiphiles **Man-4**, **Man-8**, **Sor-4**, and **Sor-8** in various organic liquids and oils.<sup>[a]</sup>

Liquid or oil	<b>Man-4</b>	<b>Man-8</b>	<b>Sor-4</b>	<b>Sor-8</b>
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 <sup>[b]</sup>	–	G (2.5)	–	G (3.5)

[a] Values in parenthesis are minimum gelation concentration of gelator (% wt/v, mg/100  $\mu$ L). 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.

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  $T_{\text{gel}}$  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  $T_{\text{gel}}$  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.

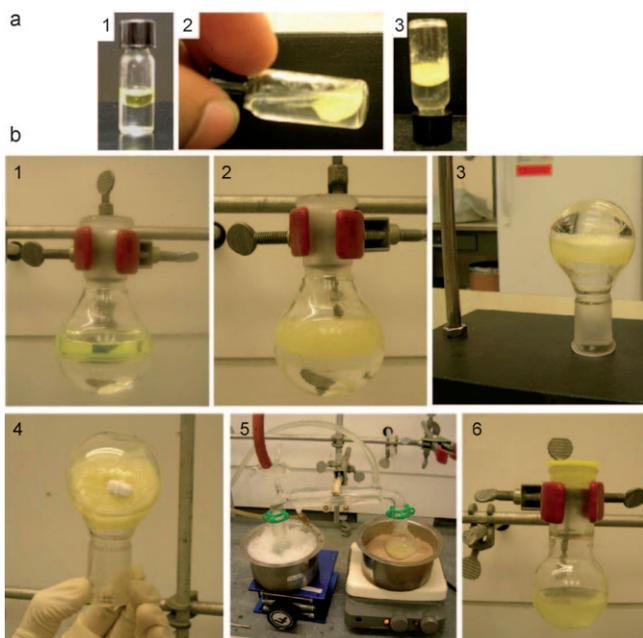
The strength of the organogels was then studied by rheology. Figure 2 a shows the frequency response of a gel of



**Figure 2.** Dynamic rheology of diesel gel and a model for self-assembly of amphiphiles. a) Frequency sweep ( $\omega$ ) and b) stress sweep ( $\sigma_0$ ) 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**.

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  $\sigma_0$  for the same sample. The stress amplitude  $\sigma_0$  at which a sharp decrease in moduli occurs is the yield stress of the gel, and its value ( $\approx 30$  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<sub>2</sub> 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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**Keywords:** biocatalysis · molecular gelators · oil pollution · self-assembly · solidifiers

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Supporting Information

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

*Swapnil R. Jadhav, Praveen Kumar Vemula, Rakesh Kumar, Srinivasa R. Raghavan, and  
George John\**

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## **Experimental Section**

**Materials.** Mannitol, sorbitol, molecular sieves (4, 8 and 12 mesh) and phosphomolybdic acid were purchased from Acros Chemicals (Fisher Scientific Company, Suwanee, GA.). The Novozyme 435 [Lipase B from *Candida antarctica*, (CALB)] and Lipolase 100L was obtained as a gift from Novozymes through Brenntag North America. Benzaldehyde was purchased from Alfa Aesar (Fisher Scientific Company, Suwanee, GA.). Vinyl esters of fatty acids were bought from TCI America (Portland, OR). Flash column chromatography was performed on silica gel H (200-300 mesh). Analytical thin layer chromatography (TLC) was performed on glass plates pre-coated with a 0.25 mm thickness of silica gel. The developed TLC plates were visualized by staining with ethanolic phosphomolybdic acid (PMA).

**Enzyme catalytic method for regioselective esterification of open chain sugars:** Novozyme 435 (0.35 g) was added to a mixture of mannitol (0.546 g, 3 mmol), vinyl esters (9 mmol; vinyl butyrate and vinyl caprylate) and activated molecular sieves (10 g) in dry acetone (40 mL). The reaction mixtures were shook at 200 rpm in an incubator shaker at 45 °C for 48 hr. After the completion of reaction (monitored by TLC), reaction mixtures were filtered and solvent was removed in rotary evaporator. The obtained crude products were purified by silica gel flash chromatography using chloroform: methanol (9:1) as an eluent. All products were obtained as white solids. The yields were above 70% for all the reaction.

### **Characterization of Sugar Esters.**

**Mannitol dibutyrate (Man-4).**  $^1\text{H}$  NMR (500MHz, DMSO- $d_6$ ):  $\delta$  3.33-4.79 (m, 12H), 2.29 (t, 4H), 1.52 (sextet, 4H), 0.86 (t, 6H);  $^{13}\text{C}$  NMR (75MHz, DMSO- $d_6$ ):  $\delta$  173.86, 69.67, 68.81, 67.57, 36.6, 18.8, 14.01. EI-MS  $m/z$   $[\text{M}+2\text{Na}]^+$  = 365.6. Anal. Calcd. for  $\text{C}_{14}\text{H}_{26}\text{O}_8$ : C, 52.16; H, 8.13; O, 39.71. Found: C, 52.00; H, 8.10; O, 39.91.

**Mannitol dioctanoate (Man-8).**  $^1\text{H}$  NMR (500MHz, DMSO- $d_6$ ):  $\delta$  3.33-4.79 (m, 12H), 2.29 (t, 4H), 1.52 (m, 4H), 1.25 (m, 16H), 0.86 (t, 6H);  $^{13}\text{C}$  NMR (75MHz, DMSO- $d_6$ ):  $\delta$  173.86, 69.67, 68.81, 67.57, 34.24, 31.84, 29.15, 25.16, 22.77, 14.65. EI-MS  $m/z$   $[\text{M}+\text{Na}]^+$  = 457.29. Anal. Calcd. for  $\text{C}_{22}\text{H}_{42}\text{O}_8$ : C, 60.80; H, 9.74; O, 29.45. Found: C, 60.85; H, 9.72; O, 29.49.

**Sorbitol dibutyrate (Sor-4).**  $^1\text{H}$  NMR (500MHz, DMSO- $d_6$ ):  $\delta$  3.33-4.91 (m, 12H), 2.29 (t, 4H), 1.52 (sextet, 4H), 0.86 (t, 6H);  $^{13}\text{C}$  NMR (75MHz, DMSO- $d_6$ ):  $\delta$  175.12, 174.71, 73.15, 72.74, 70.58, 69.16, 66.03, 65.86, 36.6, 18.8, 14.25. EI-MS  $m/z$   $[\text{M}+2\text{Na}]^+ = 366.3$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{26}\text{O}_8$ : C, 52.16; H, 8.13; O, 39.71. Found: C, 52.18; H, 8.11; O, 39.74.

**Sorbitol dioctanoate (Sor-8).**  $^1\text{H}$  NMR (500MHz, DMSO- $d_6$ ):  $\delta$  3.33-4.91 (m, 12H), 2.29 (t, 4H), 1.52 (m, 4H), 1.25 (m, 16H), 0.86 (t, 6H);  $^{13}\text{C}$  NMR (75MHz,  $\text{CDCl}_3$ )  $\delta$  175.12, 174.71, 73.15, 72.74, 70.58, 69.16, 66.03, 65.86, 34.38, 31.85, 29.29, 29.12, 25.08, 22.78, 14.25. EI-MS  $m/z$   $[\text{M}+\text{Na}]^+ = 457.29$ . Anal. Calcd. for  $\text{C}_{22}\text{H}_{42}\text{O}_8$ : C, 60.80; H, 9.74; O, 29.45. Found: C, 60.73; H, 9.75; O, 29.48.

**Synthesis of Man-8-protected** (Benzylidene derivative of Man-8): A mixture of Man-8 (0.308 g, 0.7 mmol), benzaldehyde (0.106 g, 0.1 mL, 1mmol) and concentrated sulfuric acid (10  $\mu\text{L}$ , catalytic amount) was added to a dry dichloromethane (1.5 mL). The reaction mixture was stirred at room temperature for 15 minutes. The reaction mixture was analyzed by TLC for completion of the reaction, later filtered and concentrated. The obtained crude products were purified by silica gel flash chromatography (prior to usage, silica gel was washed with methanol and dried overnight) using dichloromethane as an eluent. The chromatography afforded 0.339 g of product (92 %) as white solid.

$^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.45 (m, 1H), 7.38 (m, 4H), 5.9 (s, 1H), 3.9-4.5 (m, 8H), 3.5 (s, 2H), 2.37 (t, 4H), 1.64 (m, 4H), 1.29 (m, 16H), 0.88 (t, 6H). EI-MS  $m/z$   $[\text{M}]^+ = 522.6$ .

## **Gelation and Gel Characterization**

**Gelation method for MGs.** Typically, gelator (0.1-3 mg) in required solvent (0.1-1mL) was heated until the solid was completely dissolved. The resulting solution was slowly allowed to cool to room temperature, and gelation was visually observed. A gel sample was obtained that exhibited no gravitational flow in inverted tube. All gels obtained are thermally reversible. Above their gelation temperature, the gels dissolved in the solvent, but could be returned to their original gel state upon cooling.

**Gel-sol melting temperature ( $T_g$ ).** Gel melting temperature was determined by typical tube inversion method.<sup>[1,2]</sup> In a 2 mL scintillation vial gel was prepared as described above; the vial was immersed in the oil-bath 'upside down' and slowly heated. The temperature at which the viscous gel melted down was recorded as  $T_{gel}$ .

[1] F. M. Menger, K. L. Caran, *J. Am. Chem. Soc.* **2000**, *122*, 11679-11691.

[2] P. K. Vemula, G. John, *Chem. Commun.* **2006**, 2218-2220.

**Optical microscopy studies.** A standard glass slide containing a small portion of gel was mounted on Leica DM LB2 microscope stage and the phase changes were observed with 10x PH1 phase contrast objective.

**Morphological studies of the gel structure (SEM).** A Small amount of gel was placed on carbon-tape attached aluminum grid and allowed to dry overnight under ambient condition. Later, the sample was coated with thin-layer of gold (50 nm) using sputtering machine and directly imaged under Zeiss DSM 940 thermionic electron microscope.

**Infra-red (IR) spectroscopy.** IR spectroscopic analysis of the gel was performed using Nicolet 380 FT-IR spectrophotometer in ATR mode, while the liquid samples were sandwiched between NaCl plates.

**X-ray diffraction studies.** A small portion of a gel sample was transferred in a sample holder and immediately the reflectance was measured. The XRD measurement was performed on

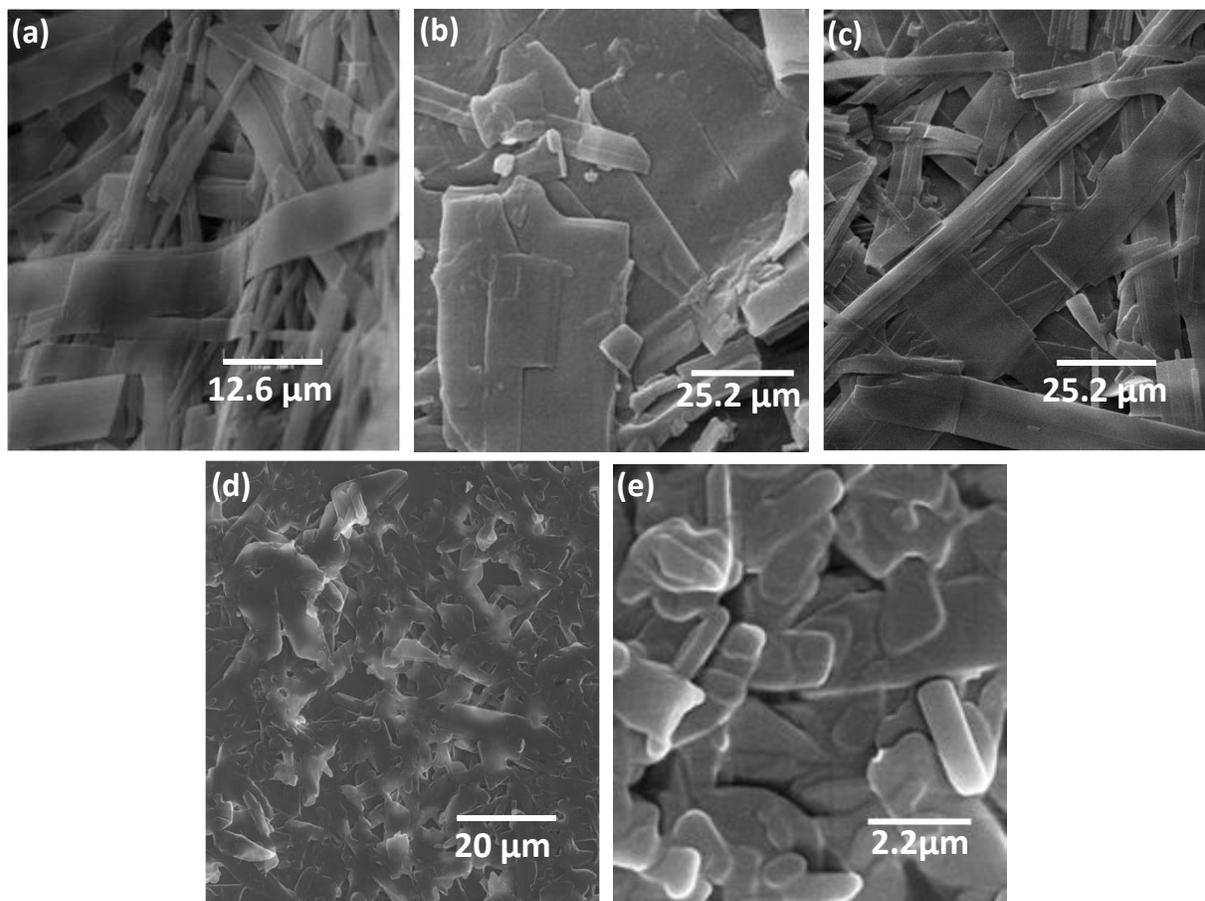
PANalytical X'Pert PRO with MPD PW 3040/60 generator S/N DY 2974 and monochromatic Cu-Co radiation (45 kV, 40 A).

**Rheological studies of diesel-gels.** Rheological studies were performed on AR 2000 rheometer equipped with a cone and plate arrangement [ $1^{\circ} 58' 47''$  angle and 40mm diameter with a truncation gap of 47  $\mu\text{m}$ ]. All the gels were prepared at 5% wt/v and allowed to set for 3 hours. A small portion of set gel was placed on the smooth plate of a rheometer and the cone- plate geometry was lowered to its truncation gap, and the gel was allowed to equilibrate for 10 minutes before starting the experiment. Measurements were performed in frequency sweep (0.01-10Hz) with either 0.01 or 0.1% strain and strain sweep (0.01%- 100%) modes at a constant frequency of 1Hz. Experiments were repeated twice.

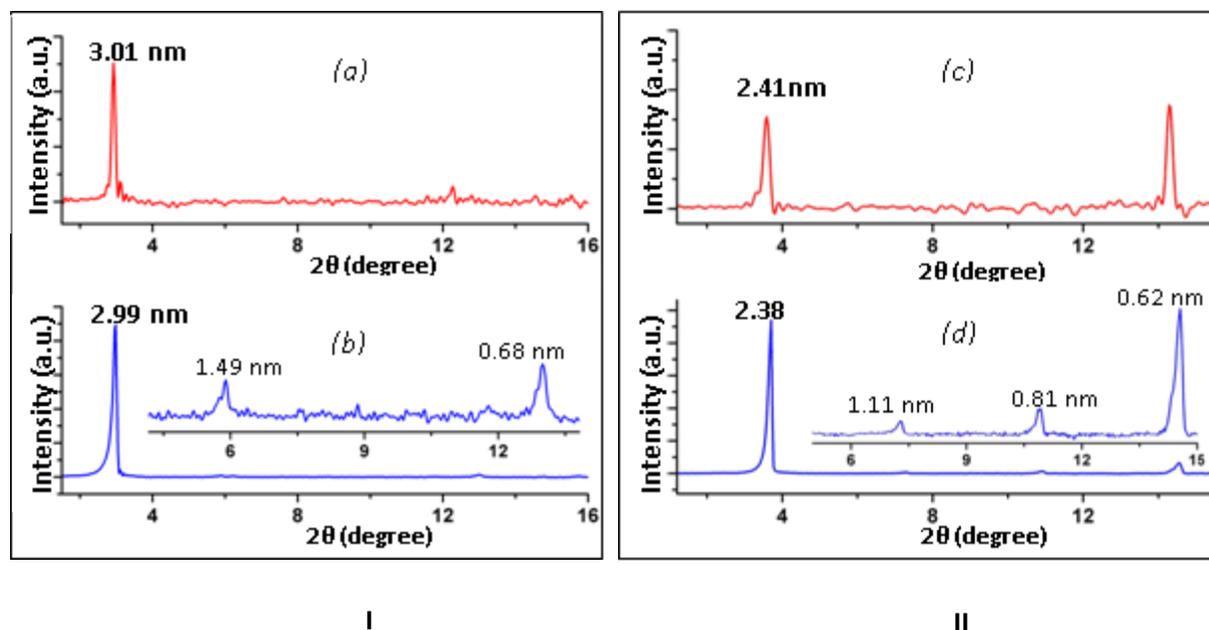
**Table S1.** The gel-sol melting temperature ( $T_{gel}$ ) of **Man-8** and **Sor-8**

Gels	$T_{gel}$ (°C)	
	<b>Man-8</b>	<b>Sor-8</b>
Cyclohexane	97-99	49-52
Toluene	80-83	38-40
Benzene	82-84	42-43
Coconut Oil	106-108	38-41
Canola Oil	109-111	42-43
Olive Oil	110-112	41-43
Soyabean Oil	101-103	43-45
Grape Seed Oil	110-111	51-53
Mineral Oil	120-125	63-69
Paraffin Oil	110-120	60-65
Diesel	102-105	56-59

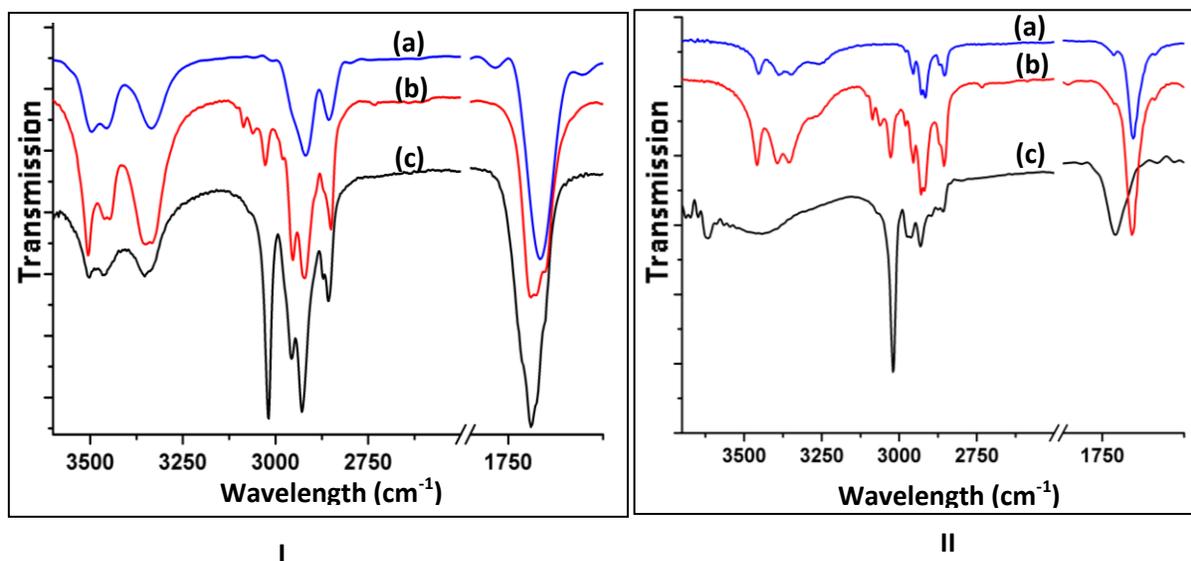
**Table S1.** The gel-to-sol transition temperature ( $T_{gel}$ ) for all the gels was determined at the concentration of 5 % (wt/v) using tube inversion method. Depending on the organic liquid, the  $T_{gel}$  values were found to be in the range of 82-125°C for **Man-8** gels and 38-69 °C for **Sor-8** gels. **Man-8** gels exhibited higher  $T_{gel}$  values compared to corresponding **Sor-8** gels, which indicates that **Man-8** gels are thermally more stable than **Sor-8** gels.



**Figure S1.** SEM images Open chain sugar gels. (a) **Man-8**-toluene gel, (b) **Man-8**-cyclohexanol, (c) **Man-8**-ethylacetate gel, (d) **Sor-8**-toluene gel, and (e) **Sor-8**-cyclohexane gel. In above all experiments, gelator concentration was 2.5% (wt/v).

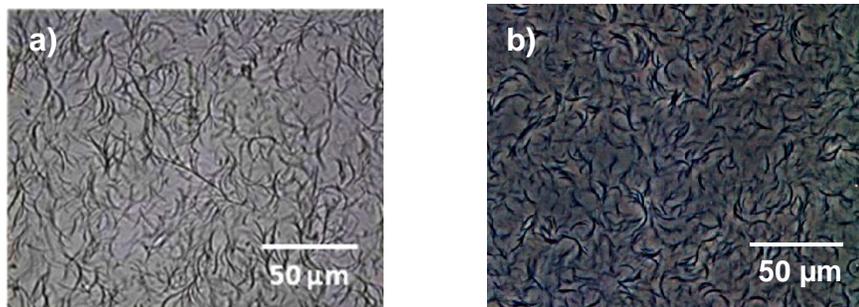


**Figure S2. I.** (a) X-ray diffraction (XRD) pattern of **Man-8**-toluene gel (b) XRD pattern of **Man-8** powder with an inset of showing the magnified region from  $2\theta = 6-13^\circ$ . **II.** (c) XRD pattern of **Sor-8**-toluene gel (d) XRD pattern of **Sor-8** powder with an inset of showing the magnified region from  $2\theta = 6-16^\circ$ . Clearly, the XRD pattern for the sugar amphiphiles is characterized by reflection peaks, and the obtained spacings ( $d$ ) follow the ratio of 1:1/2:1/3. Thus, it can be inferred that in crystalline state, the sugar amphiphiles stack together to produce lamellar structures with periodicity of 2.96 and 2.38 nm respectively. In native gels of the two sugar amphiphiles, the long  $d$ -spacing was found to be independent of the nature of organic liquid and similar to that found in the corresponding crystalline solids; for **Man-8** gels it was approximately 3.01nm and **Sor-8** gels it was approximately 2.41 nm.

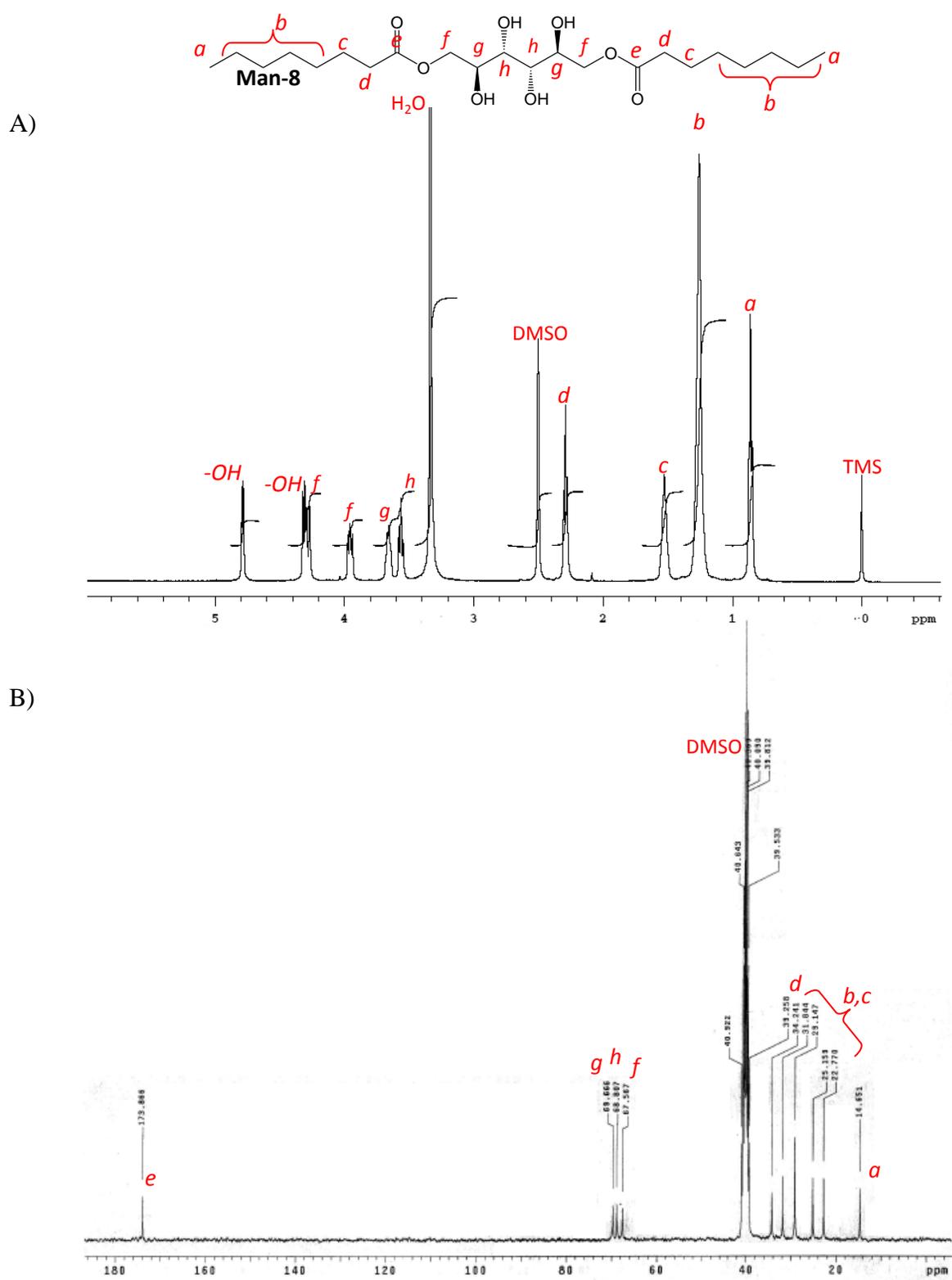


**Figure S3. I.** FTIR spectra of (a) **Man-8** solid (b) **Man-8** toluene gel and (c) **Man-8** in toluene (isotropic solution). **II.** FTIR spectra of (a) **Sor-8** solid (b) **Sor-8** toluene gel and (c) **Sor-8** in toluene (isotropic solution). When the isotropic solution was cooled to form gel state, the distinct shift was observed in the carbonyl groups' wavenumbers (from  $1720\text{ cm}^{-1}$  to  $1709\text{ cm}^{-1}$  for **Man-8** gelators and from  $1730\text{ cm}^{-1}$  to  $1704\text{ cm}^{-1}$  for **Sor-8** gelators) and in the hydroxyl groups' wavenumbers; thus confirming the participation of carbonyl and hydroxyl groups of sugar moieties in hydrogen bonding.

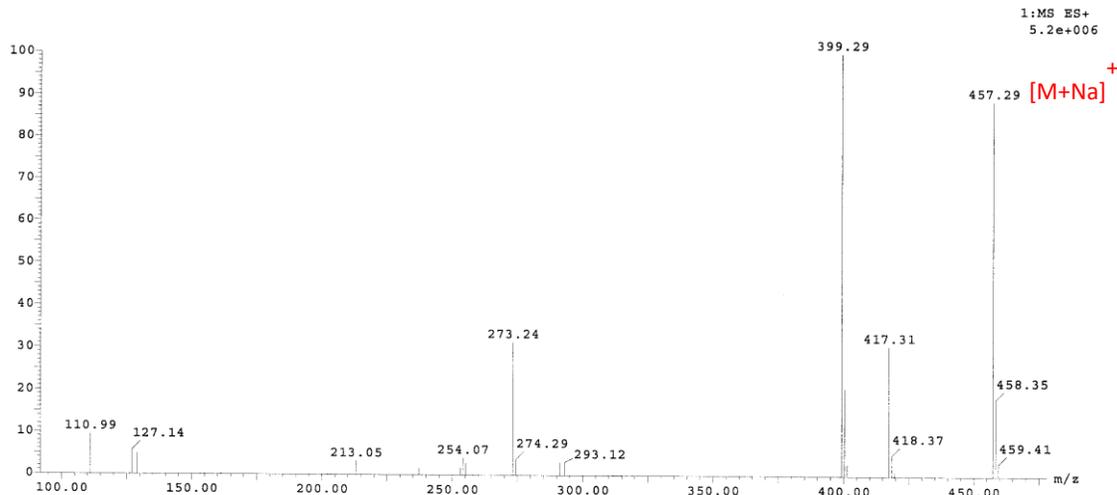
Methods Characterization	Convention heating- cooling method	Aliquot Method
Optical Microscopy	Micrometer long Fiber	Micrometer long Fiber
$T_{gel}$ ( $^{\circ}C$ )	102-105	100-104
D-spacing from XRD (nm)	2.99	2.98



**Figure S4. I.** Characterization data of diesel gel of **Man-8** obtained from two methods, conventional heating-cooling and aliquot method. **II.** Optical images of diesel gel obtained by a) heating-cooling method and b) aliquot method.



A)



B)

**ATLANTIC MICROLAB, INC.**

Sample No. Man-8

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PROFESSOR/SUPERVISOR: Prof. George John  
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Company / School The City College of New York  
Address MR 1024, Chemistry Department  
City College of New York  
160 Convent Avenue, NY, NY-10031  
NAME Swapnil R Jadhav DATE 21 JAN 2010

Element	Theory	Found	
CHO	434.564		
C		60.85	
H		9.72	
O		29.49	

Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
Elements Present: <u>C<sub>22</sub>H<sub>42</sub>O<sub>8</sub></u>	
Analyze for: <u>CHO</u>	
Hygroscopic <input type="checkbox"/>	Explosive <input type="checkbox"/>
M.P. _____	B.P. _____
To be dried: Yes <input type="checkbox"/> No <input checked="" type="checkbox"/>	
Temp. _____	Vac. _____ Time _____
FAX Service <input type="checkbox"/>	FAX Phone # _____
Rush Service <input checked="" type="checkbox"/>	(SEE CURRENT PRICE LIST)
Phone Service <input type="checkbox"/>	Phone No. _____

Man-8 Molecular Formula:  $C_{22}H_{42}O_8$   
 Calcd. % C, H & O = 60.80, 9.74 & 29.45  
 Found % C, H & O = 60.75, 9.72 & 29.49

**Figure S5. A.** EI-MS spectrum and **B.** Elemental analysis data of Man-8.

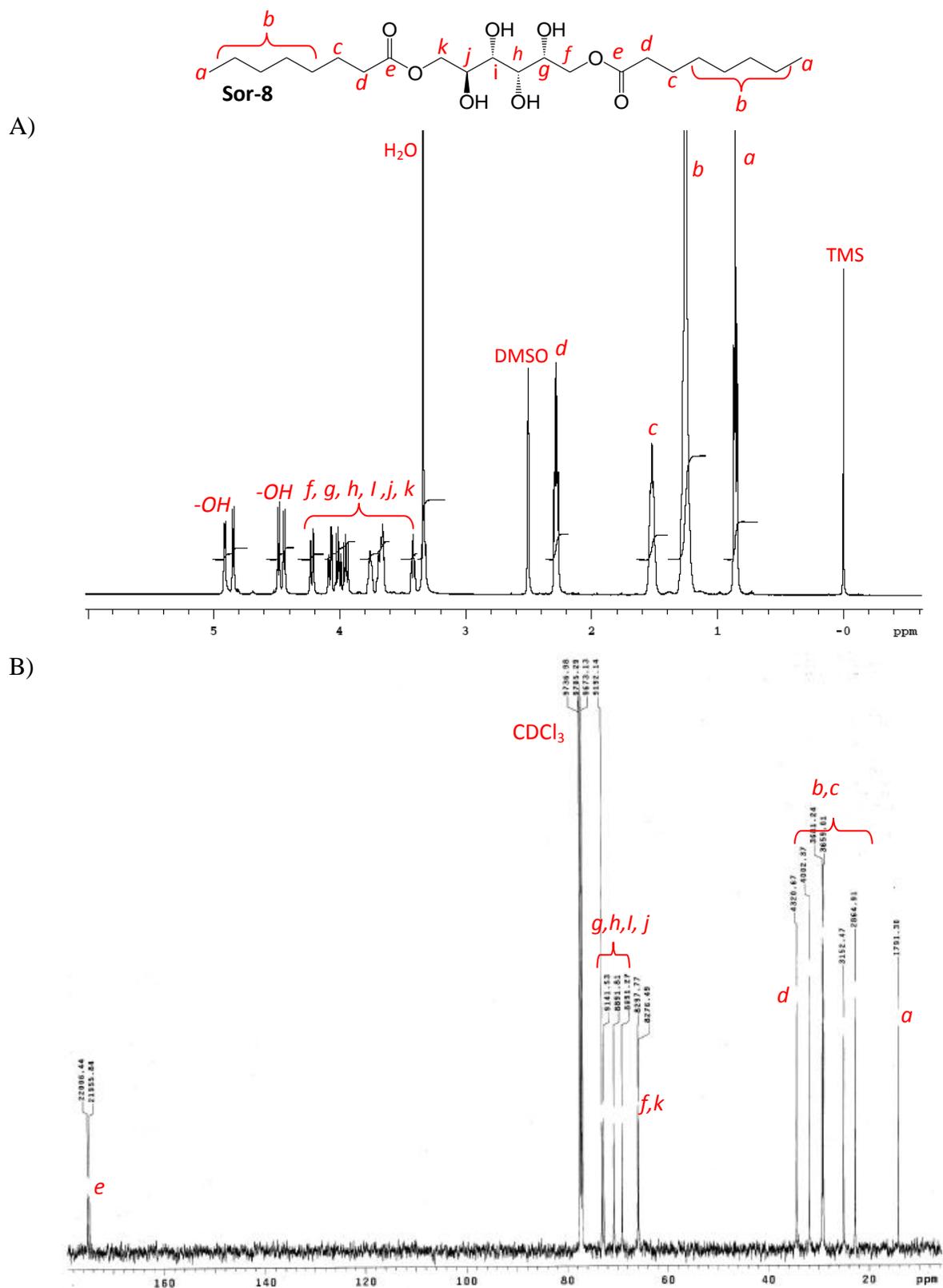
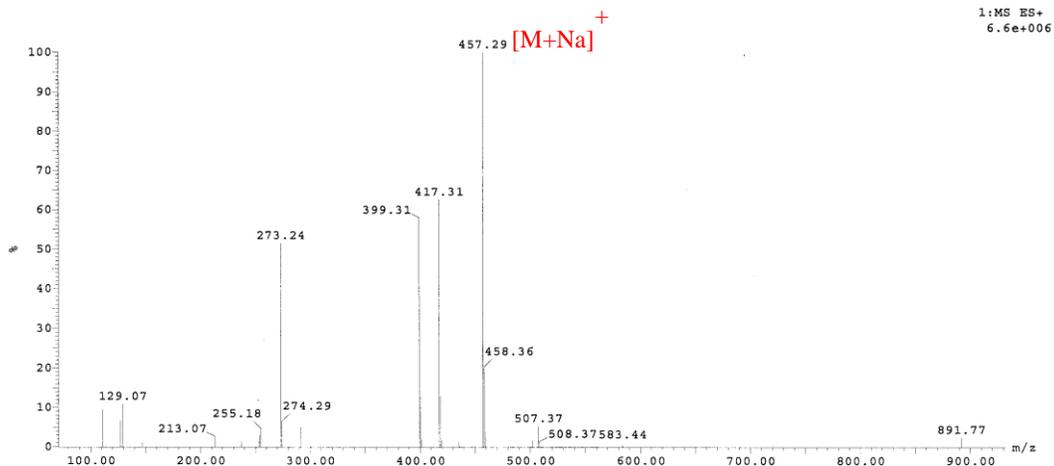


Figure S6. A.  $^1\text{H}$ -NMR spectrum and B.  $^{13}\text{C}$ -NMR spectrum of Sor-8

A)



B)

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160 Convent Avenue NY NY-10031

NAME: Swapnil R. Jadhav DATE: 21 Jan 2010

Element	Theory	Found	Single <input checked="" type="checkbox"/>	Duplicate <input type="checkbox"/>
CHO	434.564			
C		60.73		
H		9.75		
O		29.48		

Elements Present: C<sub>22</sub>H<sub>42</sub>O<sub>8</sub>  
Analyze for: CHO  
Hygroscopic  Explosive   
M.P. \_\_\_\_\_ B.P. \_\_\_\_\_  
To be dried: Yes  No   
Temp. \_\_\_\_\_ Vac. \_\_\_\_\_ Time \_\_\_\_\_  
FAX Service   
FAX Phone # \_\_\_\_\_  
Rush Service  (SEE CURRENT PRICE LIST)  
Phone Service   
Phone No. \_\_\_\_\_

Sor-8 Molecular Formula:  $C_{22}H_{42}O_8$   
 Calcd. % C, H & O = 60.80, 9.74 & 29.45  
 Found % C, H & O = 60.73, 9.75 & 29.48

Figure S7. A. EI-MS spectrum and B. Elemental analysis data of Sor-8.