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Gelation of Oil upon Contact with Water: A Bioinspired Scheme for the Self-Repair of Oil Leaks from Underwater Tubes

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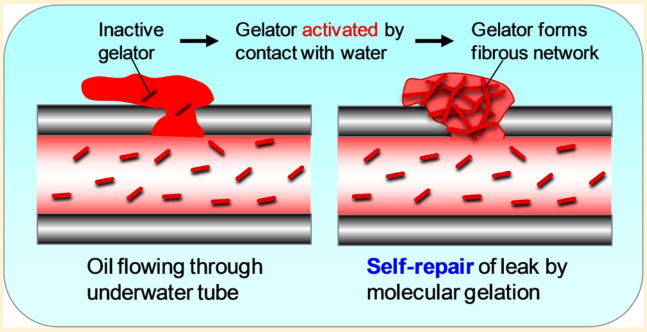
Supporting Information

ABSTRACT: Molecular organogelators convert oils into gels by forming self-assembled fibrous networks. Here, we demonstrate that such gelation can be activated by contacting the oil with an immiscible solvent (water). Our gelator is dibenzylidene sorbitol (DBS), which forms a low-viscosity sol when added to toluene containing a small amount of dimethyl sulfoxide (DMSO). Upon contact with water, DMSO partitions into the water, activating gelation of DBS in the toluene. The gel grows from the oil/water interface and slowly envelops the oil phase. We have exploited this effect for the self-repair of oil leaks from underwater tubes. When a DBS/toluene/DMSO solution flows through the tube, it forms a gel selectively at the leak point, thereby plugging the leak and restoring flow. Our approach is reminiscent of wound-sealing via blood-clotting: there also, inactive gelators in blood are activated at the wound site into a fibrous network, thereby plugging the wound and restoring blood flow.



INTRODUCTION

Synthetic small-molecules known as organogelators have the ability to self-assemble into long fibers when introduced into organic liquids (oils).[1−5] These fibers entangle and interconnect into a three-dimensional (3-D) network, thereby converting the oil into an elastic organogel.[6] Recent research into organogelators has focused on inducing gelation in response to external stimuli or environments such as temperature, redox states, pH, ultrasound, or light.[7−17] The underlying concept here is that the gelator can be toggled between two states, inactive and active. For example, in the context of light as a stimulus, the *trans* form of the gelator may be inactive in terms of its gelation ability. Upon irradiation with light, however, the gelator gets photoisomerized into its *cis* form, whereupon it becomes an active gelator.[11,16] Thus, light is used as a "switch" to activate the gelator.

In this paper, we demonstrate a new paradigm for responsive gelation: one where gelation of an oil phase is activated upon contact with an immiscible aqueous phase. The idea is illustrated in Figure 1. In the initial state (Figure 1a), i.e., when the oil alone is present, the gelator is shown as discrete molecules in the oil, i.e., the gelator is in an inactive state such that it cannot self-assemble into fibers. Next, when the oil phase is brought into contact with the water, the gelator is transformed into its active state; in turn, it begins to self-assemble into fibers (Figure 1b). A network of these fibers is initially established close to the oil/water interface (in the oil side). As time progresses, the fibers continue to form, and the gel grows to envelop the entire oil phase (Figure 1c). The mechanism by which the gelator is "switched on" by contact

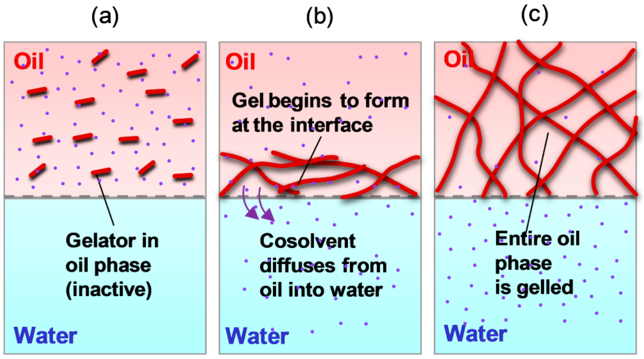


Figure 1. Concept for water-contact-induced molecular gelation of oil. Initially, in (a) the oil (a mixture of nonpolar solvents) is brought into contact with water. At this point, the gelator molecules dissolved in the oil are discrete, inactive structures. Note that the oil is immiscible with the water and the gelator does not emulsify the two. As time progresses (b), a cosolvent in the oil (shown as purple dots) diffuses into the water phase due to its greater affinity for the latter. This change in solvent composition activates the gelator in the oil phase, which then self-assembles into long fibers. Self-assembly begins at the oil/water interface and progresses upward. With further time (c), a self-assembled network of fibers envelops the entire oil phase, turning it into a gel.

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with water is detailed below. We also demonstrate a possible application of such activated gelation in the context of a flow system. Specifically, we show the spontaneous sealing of leaks (self-repair) in a tube with flowing oil, in the case where the entire tube is submerged in water. This scenario mimics the case of underwater (subsea) pipelines used to transport oil.[18−20] The analogies between the above system and the sealing of wounds in the body via the blood clotting cascade are also discussed.

■ EXPERIMENTAL SECTION

Materials. 1,3:2,4-di-*O*-benzylidene sorbitol (DBS) was obtained from Milliken Chemicals, Inc. Dimethyl sulfoxide (DMSO) was purchased from Fisher Scientific. Hydrophobic organic solvents (toluene (Tol), petrol, kerosene) and hydrophobic dyes (oil red, oil blue) were acquired from Sigma-Aldrich. All materials were used without further purification.

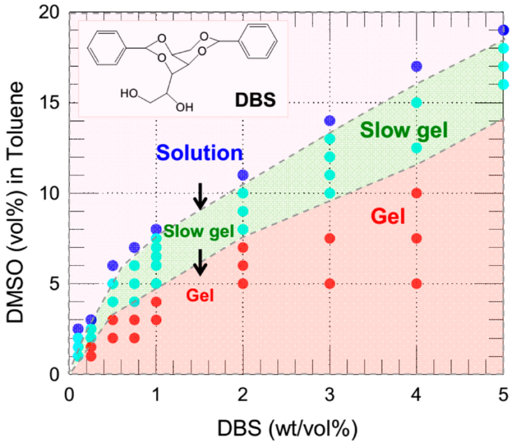
Preparation of Samples. First, the required quantity of DBS was dissolved in DMSO at room temperature. Thereafter, the required volume of hydrophobic organic solvent was added and the mixture was vortex-mixed. The vial inversion test[31] was used to infer the formation of an organogel, i.e., a sample was termed a gel if it held its own weight in the inverted vial. Gelation time was defined relative to the time when the mixture was taken off the vortex mixer ($t = 0$). If the sample was a gel in less than 1 min after this point (i.e., held its weight in the inverted vial), it was designated a "gel". If the sample took greater than 1 min to form a gel, it was designated as a "slow gel".

Rheological Studies. Rheological experiments were performed on an AR2000 stress controlled rheometer (TA Instruments). Samples were run at 25 °C on a parallel-plate geometry (25 mm diameter, 1 mm gap). Dynamic frequency spectra were obtained in the linear viscoelastic regime of each sample, as determined by dynamic strain-sweep experiments.

■ RESULTS AND DISCUSSION

Our system to demonstrate water-contact-induced gelation of oil is a very simple one. We use an inexpensive, commercially available gelator called 1,3:2,4-dibenzylidene sorbitol (DBS).[21−27] DBS is a butterfly shaped molecule with a hydroxylated center and two aromatic rings on either side (Figure 2a). It self-assembles into strong gels in a wide range of organic solvents at low concentrations (<5 wt %). Gelation has been shown to occur via a combination of hydrogen-bonding and π-stacking.[21−27] In recent studies, we and others have put forward a predictive framework for DBS gelation in various solvents using Hansen solubility parameters (HSPs).[26,27] According to this framework, the ability of DBS to form a gel or a solution (sol) in a given solvent can be rationalized by comparing the HSPs of DBS and the solvent.[28,29] The HSPs quantify the cohesive energy density δ of a species in terms of contributions from three classes of weak interactions: van der Waals or dispersive interactions (δ_D), dipole−dipole or polar interactions (δ_P), and hydrogen-bonding interactions (δ_H).[28−30] The HSPs of DBS were empirically determined to be (δ_D, δ_P, δ_H) = (17.8, 13.6, 6.4) (units of MPa$^{1/2}$).[26] Solvents that fall close to this point in 3-D Hansen space are good solvents for DBS, i.e., it is incapable of gelling these solvents. One example is DMSO that has HSPs of (18.4, 16.4, 10.2).[26] Conversely, DBS readily forms gels in solvents whose HSPs are sufficiently different from its own. Examples in this regard include *n*-alkanols, glycol ethers, and some aromatic solvents.[26] For our purpose, we chose Tol, which has HSPs of (18.0, 1.4, 2.0).

(a) Phase diagram for DBS in DMSO/Toluene mixtures



(b) Water-contact-induced DBS gelation of oil phase

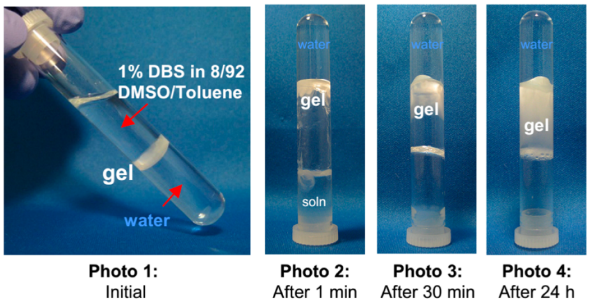


Photo 1: Initial **Photo 2:** After 1 min **Photo 3:** After 30 min **Photo 4:** After 24 h

Figure 2. Self-assembly of DBS in DMSO/Tol mixtures and the same after contact with water. (a) Phase diagram for DBS (structure shown in inset) in DMSO/Tol, as determined by vial inversion. Three distinct regions are indicated: solution or sol (pink), slow gel (green), and gel (red). (b) A sample of 1% DBS in 8/92 DMSO/Tol ("oil") is brought into contact with water (Photo 1). The water layer is at the bottom and the oil layer at the top. As time progresses, the oil layer is converted into a gel. Gelation occurs upon diffusion of DMSO from the oil to the water phase (the system moves along the arrows shown on the phase diagram). Note that the tube is shown inverted in Photos 2−4 to indicate that the oil gel is able to support the weight of the water column.

Our choice of solvents is dictated by several considerations. As noted above, DBS is highly soluble in DMSO, whereas it gels Tol. DMSO is a polar aprotic solvent, and evidently it interferes with the ability of DBS to self-assemble into fibers.[26,27] Moreover, the key features of DMSO in the present context are that (a) it is miscible with nonpolar organic liquids like Tol; and (b) it is highly soluble in water because of its strong polarity. The relevance of these aspects is shown first by Figure 2a, which is a phase diagram of DBS in DMSO/Tol mixtures. We distinguish three regions on this diagram: sol, slow gel, and gel, based on vial inversion tests.[26] That is, a sample is classified as a gel if it holds its weight in an inverted vial, whereas it is a sol if it flows upon vial inversion.[26,31] Samples were made by dissolving DBS in a given solvent mixture. In the pink region of the diagram, samples remained in the sol state at room temperature for up to several weeks. Samples in the green region were slow gels, i.e., they did not show gel-like properties immediately (i.e., within 1 min of sample preparation), but transformed into gels at some time thereafter. Finally, samples in the red region were found to be gels as soon as the sample was made (for additional details, see Supporting Information (SI), Figure S1).

Figure 2a shows that the presence of DMSO in the solvent mixture inhibits gelation. If the DMSO/Tol ratio is higher than 20/80 (v/v), no gels are formed, regardless of the DBS concentration. Conversely, in the case of Tol alone, i.e., DMSO/Tol of 0/100, DBS forms gels at very low gelator concentrations (<0.5 wt %). For the intermediate case, consider the line corresponding to 1 wt % DBS, which is the concentration used in subsequent studies for this paper. At this concentration, we obtain sols for DMSO/Tol of 8/92 or higher, slow gels between 8/92 and 5/95, and gels below 5/95. Note that gelation of DBS is known to be due to its self-assembly into long fibers, which entangle and connect into a 3-D network.[21−27] The diameter of the fibers dictates the opacity (or transparency) of the gels.[21,23] In the case of DMSO/Tol mixtures, DBS forms an opaque gel, which suggests that the fiber diameter is relatively large (>500 nm).

Next, we examined water-contact-induced gelation of DBS using a two-layer system with deionized water at the bottom and oil at the top (Figure 2b). First, 2 mL of water was placed in the test tube, followed by careful addition of 2 mL of the oil layer. Here, the "oil" is a solution of 1 wt % DBS in 8/92 DMSO/Tol. As noted above, this sample is a sol initially, i.e., prior to contacting with water. When the oil and water layers are brought into contact, a thin gel forms at the oil/water interface within a few seconds (Photo 1). Thereafter, the gel grows within the oil layer (Photo 2) and within 30 min, the entire oil layer is turned into a translucent gel (Photo 3). Note that the tube is shown inverted in the latter photos to indicate that the gel is able to support the weight of the water column above it. Dynamic rheology (SI, Figure S2) confirms the elastic nature of this gel and its elastic modulus is about 20 kPa. Over 24 h, the oil gel turns from translucent to opaque (Photo 4), which indicates the growth of thicker and longer fibers within the gel.[21,23] This gel also has a higher modulus of about 100 kPa (SI, Figure S2).

The mechanism for the above gelation is based on the higher affinity of DMSO for water relative to Tol. Calculations using the CHEMCAD software via the nonrandom two-liquid (NRTL) model show that in a DMSO/Tol/water mixture, nearly all of the DMSO will partition into the aqueous phase (assuming that the DMSO content is lower than 20/80 relative to Tol). This is consistent with the fact that DMSO is strongly polar and can therefore highly miscible with water. As a result, when the 8/92 DMSO/Tol layer is contacted with water, the DMSO diffuses into the water phase and thereby the DMSO fraction in the oil phase steadily decreases. In turn, as indicated by the phase diagram in Figure 2a, DBS undergoes self-assembly into fibrils, leading to a gel (see schematics in Figures 1b and 1c). It is important to note that DBS is a nonamphiphilic gelator, i.e., the molecule does not have a clear delineation of polar and nonpolar portions—hence, DBS does not emulsify the Tol/water mixture. Also, DBS is completely insoluble in water or in water/DMSO mixtures at low DMSO fractions.[26] Thus, the DBS remains in the oil layer and turns it into a gel. Note that the gel initially forms at the oil/water interface because this region is the first to get depleted of DMSO due to its diffusion into the water phase.

We now proceed to examine whether the above responsive self-assembly concept can be applied to the spontaneous sealing of leaks in a tube. For this experiment, we used Tygon tubing (3 mm I.D.) connected to a syringe pump. A cut was made in the tube to induce a leak. The entire tube was placed in a water bath, simulating an underwater−oil pipe (see photo in Figure S4). Oil was passed through the tube at a flow rate of 10 mL/min. In the control case, the oil was pure Tol containing a small amount (0.01 wt %) of an oil-soluble dye called "oil red". This case is depicted in Movie 1 (SI) and a still photograph from this movie is shown in Figure 3a. We observe that the oil leaks from the tube at the leak point and there is no flow beyond this point. The leaked oil collects as droplets on the surface of the water.

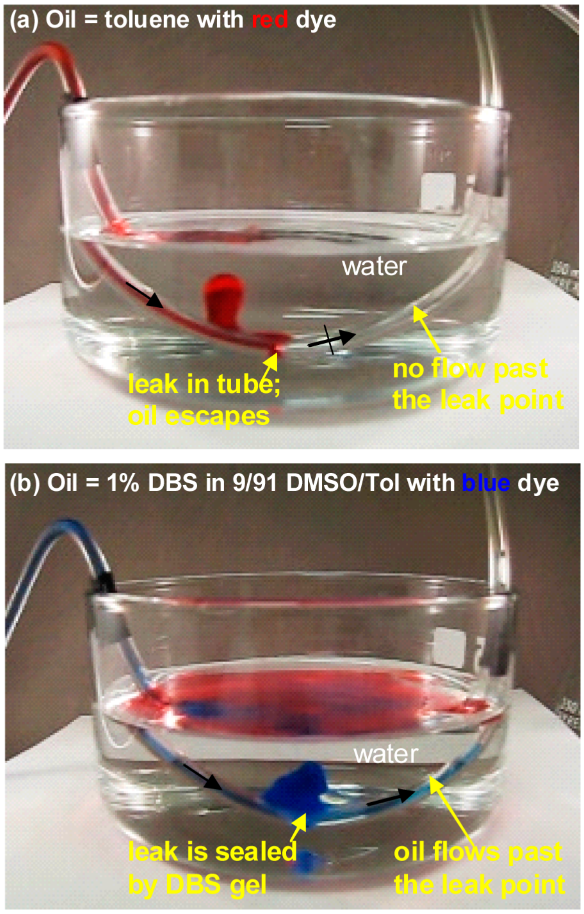


Figure 3. Self-repair of an oil leak from a tube submerged in water. (a) The control case, where oil (Tol with red dye) is passed through a Tygon tube immersed in a water bath. A cut is made in the tube to simulate a leak. At this point, the flowing oil escapes out of the tube and there is no flow past the leak point. (b) Here, the oil is a solution of 1% DBS in 9/91 DMSO/Tol, with an added blue dye. In this case, when the flowing oil reaches the leak point, a DBS gel forms at the exterior of the tube upon contact with the surrounding water. The gel seals the leak in the tube, allowing oil-flow to be restored past the leak point. The above photographs are stills from Movies 1 and 2 (SI).

Next, we substitute the pure Tol with our test sample, which is a solution of 1 wt % DBS in 9/91 DMSO/Tol. We have also added a different oil-soluble dye called "oil blue" to this sample. The experiment is depicted in Movie 2 (SI) and a still photograph from the movie is shown in Figure 3b. Note that the test oil is also a thin fluid, much like pure Tol, and it flows readily through the tube. When this oil reaches the leak point, it initially escapes out into the water. However, within a few seconds, an organogel of DBS forms around the leak point on the outside of the tube, thus plugging the leak. This gel is formed because the DMSO from the leaked oil diffuses away into the surrounding water, thus increasing the local

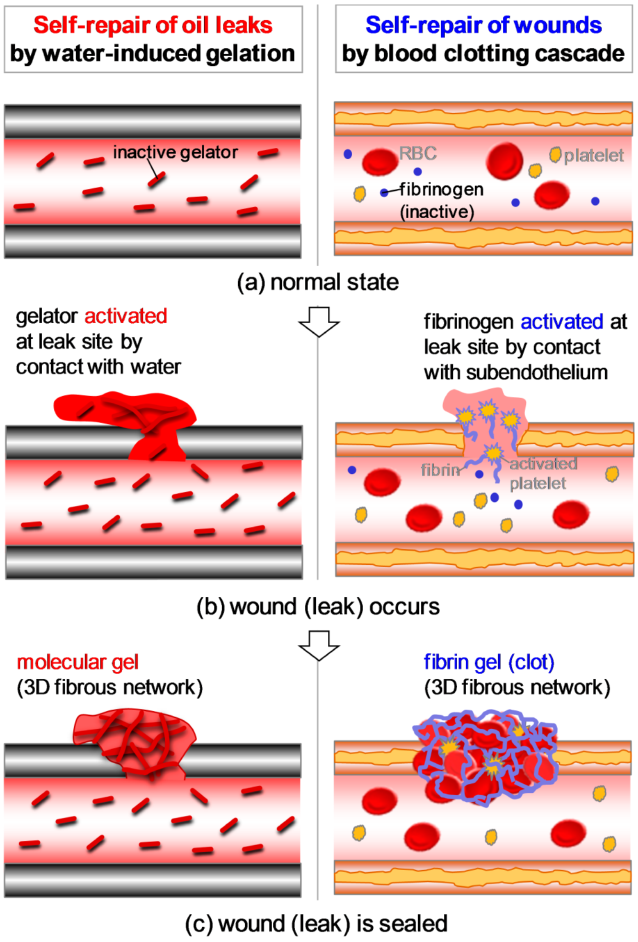


Figure 4. Analogies between self-repair of oil leaks (this study) and the self-repair of bleeding wounds in the body via the blood clotting cascade. (a) Under normal conditions, both flowing liquids have a gelator that is inactive and does not impede the flow. In blood, the gelator is the compact protein, fibrinogen. (b) When a leak occurs, the gelator is activated locally, and undergoes 1-D self-assembly into fibers. Fibrinogen is converted into insoluble fibers called fibrin. (c) The resulting fibers form a 3D network that entraps the liquid and thereby seals the leak. In the case of blood, the fibrin network constitutes the blood clot.

concentration of DBS in the oil and thereby inducing its self-assembly into fibrils. Importantly, the gel does not extend into the tube and hence it does not hinder the flow of oil. The gel forms only where the oil contacts the water, i.e., at the leak point. The net result of gel formation is that the leak is sealed, allowing the oil to continue to flow in the tube past the leak point, as shown in Figure 3b. At steady state, the leak remains plugged and flow is restored in the tube.

Our studies indicate a number of key requirements for gelation-based sealing of leaks from tubes. First, the gel strength should be high enough to form a sufficient barrier at the leak point. Second, the gel-based seal should be sufficiently thick so that it does not fall apart due to hydrostatic pressure. At the same time, the gel should not extend into the flowing oil phase because it would then slow down the flow through the tube. Can this concept be extended to other oils that are more relevant in practical contexts? We have tested kerosene and gasoline in this regard. It should be noted that DMSO is not miscible with these solvents (this can be inferred from the large difference in HSPs between that of DMSO and of these solvents).[26] To solve this problem, we added a small amount of hexanol as a cosolvent. Figure S3 (SI) shows water-contact-induced gelation of samples containing 0.5 wt % DBS in a 7/15/78 DMSO/hexanol/kerosene mixture and a 8/16/76 DMSO/hexanol/gasoline mixture. In both cases, the initial samples are low-viscosity sols, whereas they transform into gels when brought in contact with water. While these systems need to be optimized further, they are also candidates for sealing leaks in flow systems in a manner similar to Figure 3.

Finally, we draw the analogy between the leak-sealing concept used above to biological leak-sealing, i.e., to the sealing of open wounds in the body via the blood clotting cascade.[32,33] While blood clotting involves numerous species and steps, we focus on the protein fibrinogen, which is a key component in blood akin to a "gelator".[34,35] Under normal conditions, blood circulates freely in a closed loop of vessels. At this stage, fibrinogen is a compact, folded protein that is solubilized in blood plasma, and its presence as discrete spheres does not alter the viscosity of blood (Figure 4a). When a wound occurs, endothelial cells of vessels in the vicinity of the wound are damaged. At that point, the "gelator", i.e., fibrinogen, is "activated" by contact with the external environment. Activation involves the conversion (via the enzyme, thrombin) of fibrinogen into *fibrin*, which is the form capable of self-assembly.[34,35] Fibrin self-assembles into insoluble fibers (Figure 4b), which grow and entangle into a network that is able to entrap blood cells and thus prevent the loss of blood from the wound (Figure 4c). Note that the fibrin network is confined to the wound site; it does not propagate into the regions of intact blood vessels.

We can see from Figure 4 that there are several similarities to our system of leak-sealing using DBS as the gelator. First, in the initial state, when oil is freely flowing in an intact tube, DBS is inactive, i.e., present as discrete molecules. Thus, the presence of dissolved DBS at this stage does not increase the viscosity of the oil (Figure 4a). This is a key point and it illustrates why a molecular gelator is ideal for this purpose as compared to a polymeric gelator (the latter would make the oil more viscous and thereby retard the normal flow in the absence of leaks). When the leak occurs, DBS gets activated locally by contact with the external environment (i.e., water in our case). This is similar to local activation of fibrinogen at the site of a wound. Although the mechanisms involved are very different, in both cases, the gelator now becomes capable of 1-dimensional self-assembly into fibers (Figure 4b). Finally, the network of DBS fibers leads to a local gel that seals the leak, much like the case of the fibrin gel (Figure 4c). Overall, the concepts of *self-repair* and *self-healing* are inherent in both systems, i.e., in both cases, *normal fluid flow occurs in the absence of leaks, and it is only when a leak is sensed that the gelator springs into action.* We note that the terms self-repair and self-healing are usually applied in a different context for the repair of solid materials from within.[36,37] Here, the self-repair occurs at the solid/liquid interface due to the triggered self-assembly of molecules flowing in the liquid phase.

■ CONCLUSIONS

In conclusion, we have reported a simple new scheme for responsive gelation, where a gel is formed in an oily phase upon contact with an immiscible aqueous phase. The concept has been demonstrated in two ways: in a static system and in a flowing system. The underlying mechanism used here is that the self-assembly of gelators like DBS depends on the composition of the solvent.[26,27] DBS is inactive, i.e., does not form a gel, when the solvent contains sufficient DMSO. Upon contact with water, DMSO diffuses into the aqueous phase and thereby activates the self-assembly of DBS in the oil phase, leading to gelation. In static experiments, we have shown that the entire oil layer can be gelled on contact with water. In flow experiments, we have shown that DBS/oil solutions flowing through a tube immersed in water are capable of self-repair. That is, if the tube suffers a leak, the fluid spontaneously forms a gel at the leak site, allowing flow to resume in the tube. This self-repair capability is analogous to the sealing of wounds by the components in blood. We hope that our initial study will stimulate further interest in responsive gelation. The underlying concept can be generalized and extended to other gelators.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The SI contains additional figures and two movies, as described in the text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b00676.

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Notes

The authors declare no competing financial interest.

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Supporting Information for:

Gelation of Oil Upon Contact with Water: A Bioinspired Scheme for the Self-Repair of Oil Leaks from Underwater Tubes

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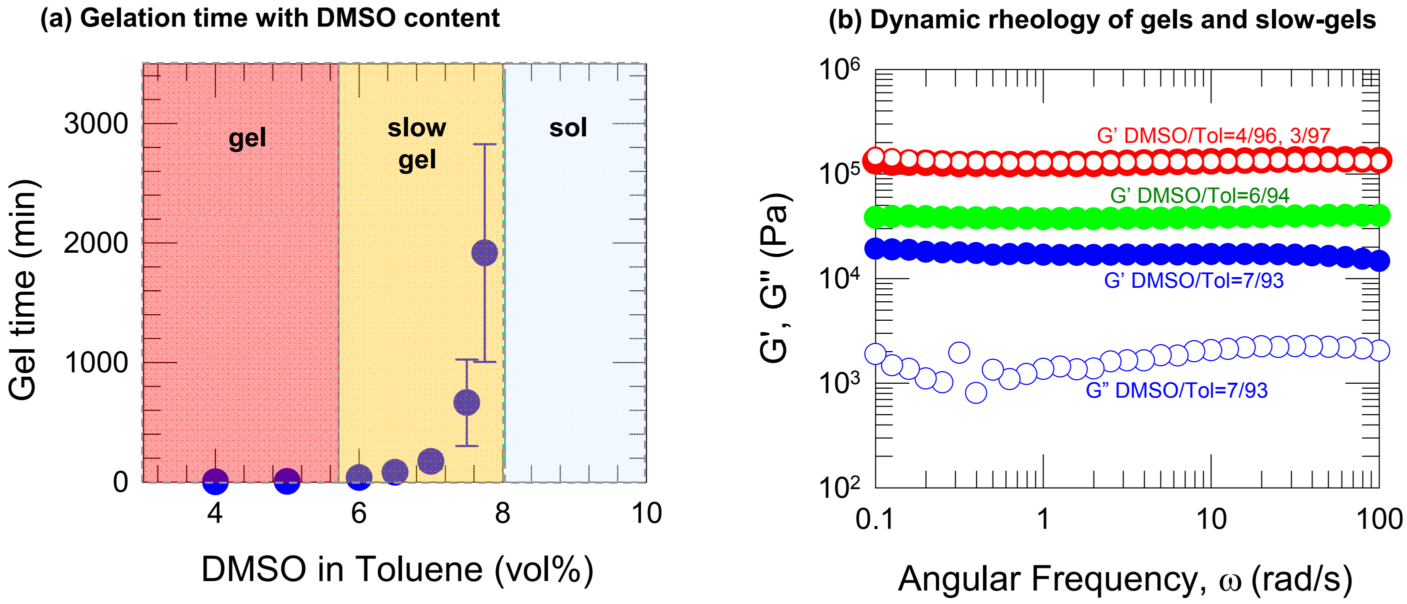
I. DBS Phase Behavior in DMSO/Tol Mixtures:

As shown in Figure 2a (main text), for the case of DBS in DMSO/Tol mixtures, the DMSO inhibits gelation. This is further shown by the data below. For 1% DBS, slow gelation was observed between the volume ratio of DMSO/Tol=6/94 and DMSO/Tol=7.75/92.25, as can be seen in Figure S1a. Note that the gelation time increases exponentially with DMSO content in the mixture. For higher DMSO, i.e., DMSO/Tol=8/92 or higher, the sample was a sol at all times (i.e., gelation time = infinity).

The gel properties are also correlated with DMSO content, as shown in Figure S1b. The data here are frequency sweeps, i.e., plots of the elastic modulus *G′* and the viscous modulus *G″* as functions of frequency. All gels show an elastic response, as expected, i.e., both *G′* and *G″* are independent of frequency and *G′* > *G″*. The value of *G′* is the gel modulus, and this value in the slow gel region increases with decreasing DMSO content. However, note that the gel moduli in the gel region are nearly identical, regardless of the DMSO content.


(a) Gelation time with DMSO content

(b) Dynamic rheology of gels and slow-gels

Figure S1. (a) Gelation time of 1% DBS in DMSO/Tol mixtures with varying vol% of DMSO. (b) Dynamic rheology of 1% DBS gels in DMSO/Tol. All samples show gel-like rheology with G' > G" (both moduli are shown for the 7/93 sample). For DMSO/Tol = 6/94 and 7/93, the samples are slow gels, whereas for DMSO content less than 6 vol%, the gels were formed instantaneously. In the case of the slow gels, the gel modulus G' decreases with increasing DMSO content. For the instant gels, G' is independent of DMSO content.

II. Water-Contact-Induced Gelation by DBS of DMSO/Tol:

In Figure 2b (main text), we showed that an “oil” of DMSO/Tol = 8/92 could be converted to a gel by bringing it into contact with an immiscible water phase. In this experiment, 2 mL of water is in contact with 2 mL of the oil layer. The oil is a sol initially. When the oil and water are contacted, a thin gel forms at the oil/water interface within a few seconds (Photo 1). Thereafter, the gel grows within the oil layer and within 30 min, the entire oil layer is turned into a translucent gel (Photos 2 and 3). Dynamic rheological data are shown below in Figure S2 for the gel in Photo 3. The The data are frequency sweeps, i.e., plots of the elastic modulus *G′* and the viscous modulus *G″* as functions of frequency. As expected, the gel shows an elastic response, i.e., both *G′* and *G″* are independent of frequency and *G′* > *G″*. The value of *G′* is the gel modulus, and it is about 20 kPa. Over 24 h, the oil gel turns from translucent to opaque (Photo 4). Dynamic rheology of the gel in Photo 4 is also shown in Figure S2. Note that the latter gel has a higher gel modulus (about 100 kPa).

(b) Water-contact-induced DBS gelation of oil phase

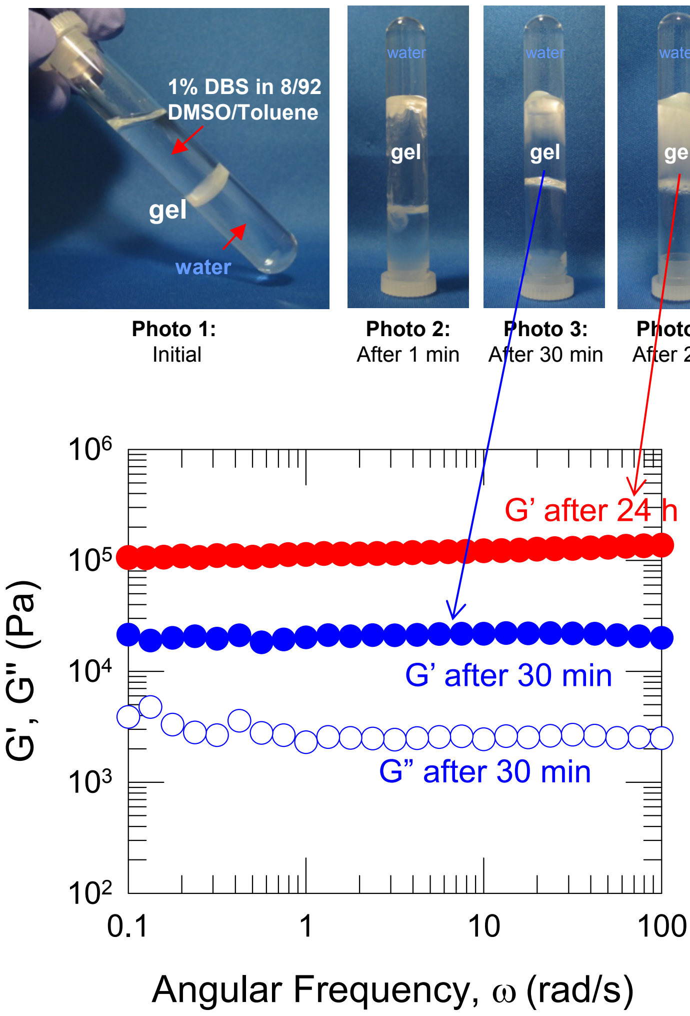


Photo 1: Initial

Photo 2: After 1 min

Photo 3: After 30 min

Photo 4: After 24 h

Figure S2. Dynamic rheology of the gels in Photo 3 and Photo 4. With time, the gel turns opaque and its modulus increases from ~ 20 kPa to 100 kPa.

III. Water-Contact-Induced Gelation by DBS of Fuel Oils:

In Figure 2b and Figure S2, the oil that was gelled was based on toluene (Tol). In Figure S3, we extend the same concept to systems where the primary component is a fuel oil (kerosene or gasoline). DMSO is not miscible with these oils and hence we use a small amount of hexanol as a compatibilizing solvent. In the photos below, each oil is a sol initially and is brought into contact with the immiscible water phase. After 1.5 h for kerosene (Photo 2) and 3 h for gasoline (Photo 4), the oil phase is completely gelled and this gel is strong enough to support the weight of the water column above it in the inverted tube.

Oil = 0.5% DBS in DMSO/Hexanol/Kerosene = 7/15/78

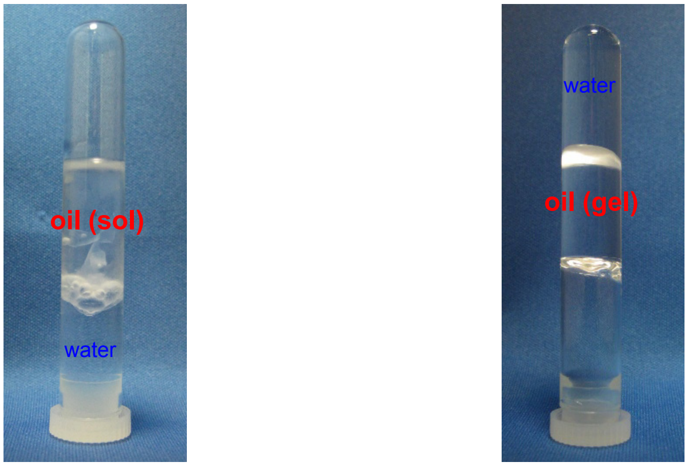


Photo 1:
After 1 min

Photo 2:
After 1.5 h

Oil = 0.5% DBS in DMSO/Hexanol/Gasoline = 8/16/76

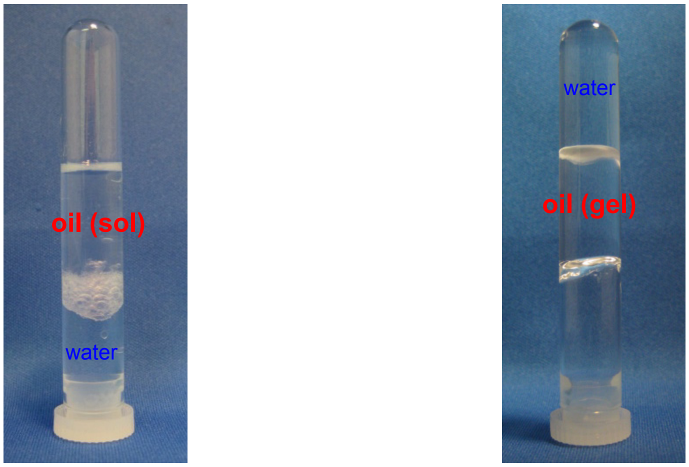


Photo 3:
After 1 min

Photo 4:
After 3 h

Figure S3. Water-contact induced gelation of oil layers containing mostly kerosene (Photos 1, 2) or gasoline (Photos 3, 4). In both cases, when the oil and water layers are brought into contact, a thin gel is formed at the interface within 1 min; however, this is not strong enough to hold its weight in the inverted tube (Photos 1 and 3). Over time (1.5 h for kerosene and 3 h for gasoline), the entire oil layer is gelled and the gel is strong enough to support its own weight as well as the weight of the water column above it in the inverted tube.

IV. Experimental Details for Demonstration of Sealing Leaks in Underwater Oil Tubes:

The experimental setup used in our studies (Figure 3 in the main text, also see Movie 1 and Movie 2) is shown below in Figure S4. A transparent and flexible Tygon tube with 3 mm I.D. is submerged in a water bath. The tube is connected to an electronic syringe pump (to the left, not seen in the photo) to flow the oil solution through the tube at a flow rate of 10 mL/min. The oil empties into the conical flask on the right. To simulate a leak, a cut was made in a portion of the tube, as shown in the inset.

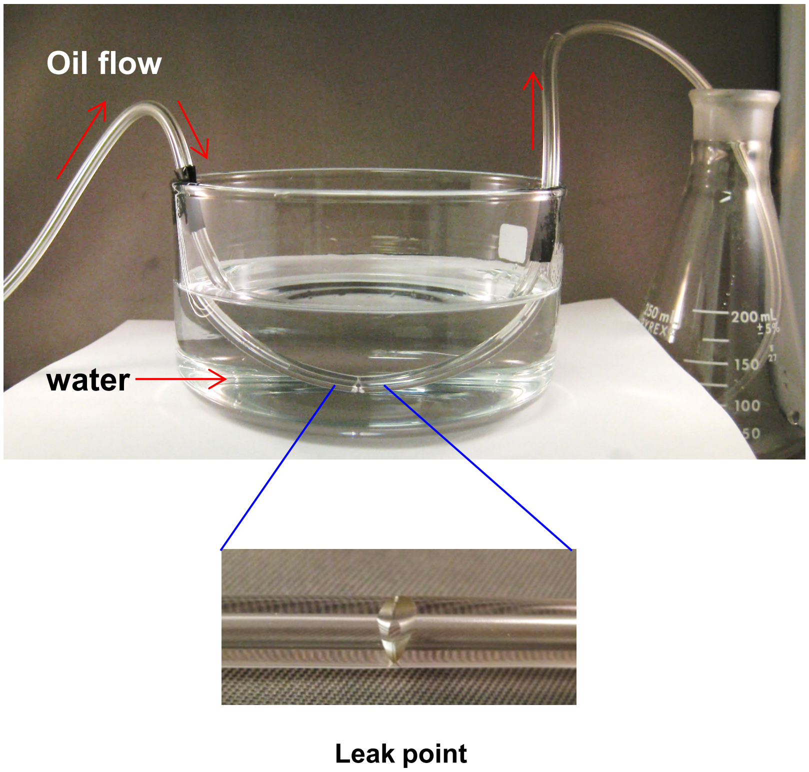


Figure S4. Experimental setup for simulating a leak from an oil-bearing tube that is submerged under water.