Self-Degrading Molecular Organogels: Self-Assembled Gels Programmed to Spontaneously Liquefy after a Set Time

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Abstract: Gels are used widely in the oilfield. For example, during oil recovery, organogels are pumped underground into fractures within oil-bearing rock, so as to block fluid flow. However, after several days, the gels must be degraded (liquefied) to enable oil extraction through the fractures. To degrade gels, 'degrading agents' as well as external stimuli have been examined. Here, a concept is demonstrated that avoids external agents and stimuli: *self-degrading organogels* via the self-assembly of molecular gelators. The gels are (a) extremely robust (free-standing solids) at time $t = 0$ and (b) degrade spontaneously into sols after a set time $t = t_{degr}$ that can be minutes, hours, or days. These properties are achieved by combining two readily available molecules — the organogelator (1,3:2,4)-dibenzylidene sorbitol (DBS) and an acid (e.g., hydrochloric acid, HCl) — in an organic solvent. DBS self-assembles into nanoscale fibrils, which connect into a 3-D network, thereby gelling the solvent. The acid type and concentration set the value of t_{degr} at a given temperature. Degradation occurs because the acid slowly hydrolyses the acetals on DBS, thereby converting DBS into molecules that cannot form fibrils. DBS gels with a pre-programmed 'degradation clock' can be made with both polar and non-polar organic solvents. The concept can be a game-changer for oil recovery as it promises to make it safer, more efficient, and sustainable.

Introduction

Gels are an intriguing class of soft materials that are an integral part of our everyday lives.[1,2] Common items that we encounter routinely, including desserts like gelatin (Jell-O), consumer products like toothpaste, and pharmaceutical products like soft capsules are in the gel state — where the material exhibits solid-like (elastic) properties despite containing a high fraction of liquid.[2] Gels are typically created by introducing a gelling agent (gelator) into a liquid.[3-9] The gelator forms a three-dimensional (3-D) network throughout the volume, entrapping the liquid within it via capillary forces. Gelators can include polymers (long chains), which can be crosslinked into a network;[3-5] colloidal particles that cluster into a network;[6] and small organic molecules (molecular weight < 5000 Da) that self-assemble into long fibrils and thereby into a fibrillar network.[7-9] The latter will be the particular focus of the present study. The resulting gels are termed 'molecular gels' and they can be formed in water (hydrogels) or organic liquids (organogels).

In typical cases where gels are used, the gel state is critical for the success of the application or product. However, there are instances where it is advantageous for the gel to transform into a liquid of low viscosity (i.e., a sol) after a certain period. Three such cases are illustrated in Figure 1. First, consider a gel that encapsulates a solute or payload within its matrix (Figure 1A). In some cases, delivery of the solute may require the gel to be degraded. Second, consider a gel that is being used as a fluidic valve (Figure 1B), with the solid gel blocking the gravity-driven flow of a liquid (i.e., the valve is closed). Subsequently, for the valve to be opened and the liquid to flow out, the gel must get transformed into a sol. Third, a variation of a valve is shown, where the gel is used to divert fluid flow (Figure 1C). In this case, the gel is placed in a side channel and blocks the entry of fluid into this channel. Thereby, all the fluid flows only through other channels. The scenario shown by Figure 1C is relevant during the extraction of oil from deep underground.[10,11] Here, the blocking gel is introduced into fractures in oil-bearing rock and must stay in place for a period of days or weeks. After this time, it is important for the gel to get degraded, thereby allowing oil to be extracted (this application is discussed further later in the paper).

Faced with the challenges depicted by Figure 1, researchers have resorted to a few broad strategies. First, degradable gels have been developed that respond to external stimuli like temperature[12,13] or light[14]. For instance, the gel may be induced to degrade when exposed to UV light or when heated above a critical temperature. However, applying the relevant stimulus may be impractical in many scenarios, such as in an oilfield where the gel may be located in fractures several thousand feet underground. The second possibility is to use chemicals as 'degrading agents' to convert gels to sols. In this scenario, the gel is intact until it is contacted with the degrading moieties, which can include acids,[15] bases,[16] or enzymes[17]. Degrading agents are widely used in oilfield applications, but they too can be problematic. One issue is that a solution of the degrading agent may only make contact with the *exterior* of the gel and thus the degradation may be confined to a small portion of the gel. In other words, the gel, being a solid, cannot be easily mixed with an external liquid. Also, if the degrading agent is a harsh chemical, it may cause undesired effects on the environment surrounding the gel. Thus, degrading agents may not be deployable in many cases.

The concept explored in this paper is that of *self-degrading* gels, which will degrade even if left undisturbed under ambient conditions,

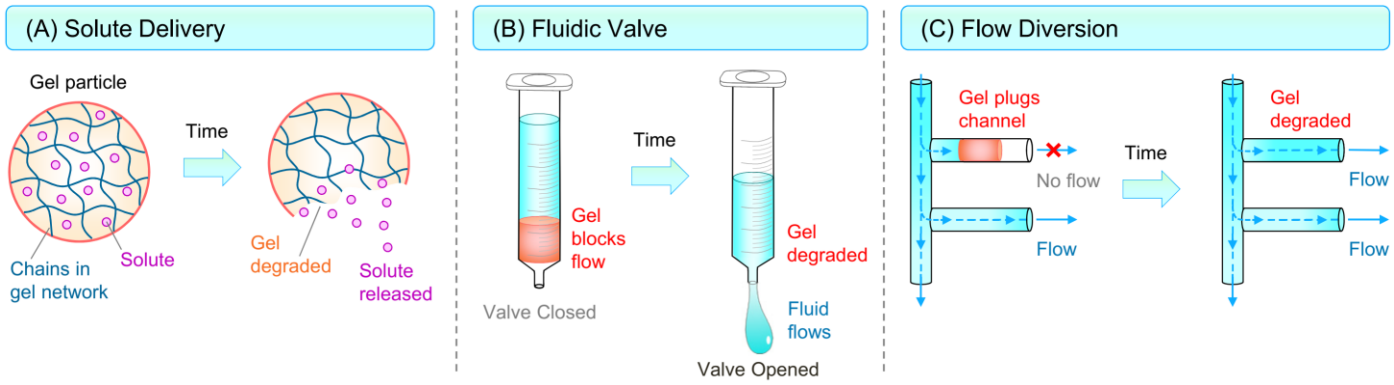

Figure 1. Self-degrading gels and their applications. The gels spontaneously transform into thin sols after a set time ($t = t_{degr}$). (A) A self-degrading gel particle releases encapsulated solute once the gel dissolves at $t = t_{degr}$. (B) In a fluidic valve, the downward flow of fluid is blocked as long as the gel at the bottom is intact. After $t = t_{degr}$, the gel liquefies and the valve opens. (C) The gel plugs the side channel and thus diverts flow away from this channel. After $t = t_{degr}$, the gel degrades, allowing flow to occur through the channel.

i.e., without contact with either external stimuli or chemicals in the external medium. The key variable that dictates the degradation will then be *time*. In other words, the time t after which the gel degrades, i.e., $t = t_{degr}$, is *programmed* into the initial gel via the composition. This is indicated in Figure 1 for each of the three cases. For instance, in Figure 1B, over the duration that the gel is intact ($t < t_{degr}$) the valve will be closed, but once $t = t_{degr}$ is reached, the gel will dissolve (i.e., convert to a sol) and the valve will open.

Our goal in this work is to make a self-degrading *molecular* gel, rather than one using polymers. After a polymeric gel degrades,[18-24] the residue will still be long chains and the solution will remain viscous. However, after a molecular gel degrades, only the small gelator molecules will remain, i.e., the degradation will be *complete* and the solution will thus have a very low viscosity. Moreover, because molecular gels form fibrils via non-covalent bonds, the gels will be *shear-thinning*, i.e., shear will break the bonds and transform the gels into a flowing liquid. Hence, the gels can be pumped down an oil well or injected into a cavity using a syringe. Polymer gels held by covalent bonds will splinter into pieces when sheared rather than shear-thin.

To our knowledge, molecular gels with the ability to self-degrade have not been reported thus far. Here, we report for the first time a class of self-degrading organogels based on the self-assembly of small gelator molecules. The gels are (a) extremely strong and robust at the initial state, i.e., at time $t = 0$, the gel modulus G' is > 10,000 Pa; and (b) they are able to degrade spontaneously into thin sols ($G' \sim 0$) after a pre-determined period of time when left undisturbed. The degradation time t_{degr} can be set to be minutes, hours, or days at a given temperature. We make these gels using the organogelator (1,3:2,4)-dibenzylidene sorbitol (DBS).[25-30] DBS is a derivative of the sugar-alcohol sorbitol and forms robust gels in a range of organic liquids, including both polar and non-polar ones. Gelation occurs because DBS self-assembles into nanoscale fibrils, which connect to form a 3-D network.[25,29] We will show that the key to self-degradation is to incorporate an acid (e.g., hydrochloric acid, HCl) into the DBS gel. The choice of acid and its concentration sets the kinetics of gel degradation and thereby the t_{degr} at a given temperature. We use NMR and mass spectrometry to pinpoint the degradation mechanism, which involves slow conversion of DBS into small molecules that cannot self-assemble. Self-degrading DBS gels are low-cost and environmentally benign. We have devised a way to prepare the gels easily in large quantities (> 1000 L) at room temperature. The use of these gels could be a game-changer for oil recovery, which could be done in a safer, more efficient and sustainable manner (due to reduced consumption of drilling fluids; see later in the paper). The concept shown here could also facilitate delivery applications in the pharmaceutical, cosmetics, and agrochemical industries.

Results and Discussion

DBS Gel Synthesis and Characterization. We first discuss how we make molecular gels of DBS in different organic solvents. The structure of DBS (Figure 2) shows that it is a butterfly-shaped molecule with two aromatic rings on either side and a central rigid ring that contains hydroxyl (–OH) groups. Conventionally, gels of DBS,[25,29] as with other molecular gels,[7-9] are made by heat, which is depicted in Figure S1A. DBS powder is added to the solvent and the mixture is heated to a high temperature (> 100°C),[25,29] whereupon the powder dissolves in the solvent and forms a thin, transparent sol. In this state, DBS molecules are either unaggregated or in small clusters. The sol is then slowly cooled to room temperature, and over that time (which can be a few hours), DBS molecules self-assemble into long nano-fibrils by non-covalent bonds: specifically hydrogen-bonding (of the –OH groups) and pi-pi stacking of the aromatic rings.[25,29] These nano-fibrils entangle with each other, forming a 3-D network, and accordingly, the sol transforms into a gel.

The above conventional method for synthesizing DBS gels (or any similar molecular gel) has its limitations due to the necessity for high heat followed by slow cooling. This method is both energy-intensive and time-consuming. In oilfield applications, gels will have to be prepared in the field at remote locations. Bulky heaters will be needed to achieve the high temperatures required, and these will also have to be transported to the field location. Heating large volumes of

Figure 2. DBS organogels and their preparation by a simple new method at room temperature. The structure of DBS is shown in the box. To make the gel, a stock solution of 15% DBS in DMSO is first prepared by simply mixing the two at room temperature. (A) The oil to be gelled is then taken in a vial (here it is 2 g butanol). The stock solution (0.14 g) is added such that the DBS concentration in the mixture becomes 1%. (B) The sample is then mixed by hand or using a vortex mixer for a few seconds. (C) Right afterward, the sample becomes an organogel due to the self-assembly of DBS into a nanofibrillar network. This method to form DBS gels is simple, quick and does not require heat. It is also shown by Movie S1.

liquids on an operating platform imposes safety concerns as well as higher costs. To avoid these issues, we have devised a novel and much simpler route for making DBS gels, which is shown by Figure 2. This route eliminates the need for heating and is entirely done at room temperature.

First, we dissolve DBS in dimethyl sulfoxide (DMSO). DMSO is known to be chemically similar to DBS. For example, in a previous study we showed that DBS and DMSO have very close solubility parameters.[29] Due to the chemical similarity, DBS does not gel DMSO and instead, it readily dissolves (up to 25% by weight) in DMSO without the need for heat. We can just add DBS powder to DMSO and gently stir the mixture to obtain a clear solution. Here, we prepare a stock solution of 15% DBS in DMSO. We then add measured quantities of this stock solution to the organic solvent to be gelled. In Figure 2, the solvent is butanol. DBS is an efficient gelator of this solvent, with just 0.25 to 1% of DBS enough to form a gel. This is because DBS and butanol are chemically dissimilar, i.e., their solubility parameters are far apart.[29] To make the gel, we add 0.14 g of the DBS stock solution to 2 g of butanol in the vial (to achieve a DBS concentration of 1%) (Figure 2A). The resulting mixture is gently mixed, either by hand or using a vortex mixer (Figure 2B). Within seconds after the mixing is complete, we have a uniform and robust gel of 1% DBS in butanol. A photo of this gel holding its weight in an inverted vial is shown in Figure 2C — note the bluish tinge of the gel, which is due to light scattering from the DBS nano-fibrils.[25,29]

The above method of gel synthesis is simpler, faster, more convenient, and requires much less input of energy than the conventional method. Starting from the preparation of the stock solution, the entire process takes *just 10 min at room temperature* (the steps in Figure 2 are further shown by Movie S1). This is a significant reduction in synthesis time compared to the conventional route, which can take hours for heating and cooling (see also Figure S1). We will show presently that DBS gels made by the two routes are nearly identical. Our method can also be extended to any other class of molecular gels. The one requirement is to know the solvent in which the gelator readily forms a thin solution (similar to DMSO in the case of DBS). The identity of such a solvent may either be known from experimental studies with the gelator or could be identified *a priori* from estimations of solubility parameters.[8,29]

The nanostructure and rheology of the 1% DBS gel in butanol are presented in Figure 3. A representative image of the nanostructure from transmission electron microscopy (TEM) is shown in Figure 3B. As expected, a network of nano-fibrils is found in the gel, with the fibrils ranging in diameter from 5 to 50 nm. This is consistent with previous reports of the nanostructure in DBS gels.[25-28] Next, the dynamic rheological response of the gel is shown in Figure 3C. This is a plot of the elastic (G') and viscous (G'') moduli as functions of the angular frequency ω. The rheology is that expected of a gel: i.e., G' surpasses G'' by an order of magnitude and both moduli are independent of ω.[31,32] The frequency-independence of the moduli indicates that the network does not relax, i.e., the bonds between DBS molecules in the network are durable and do not dissipate over time. Gels can be characterized by their value of G', which is the gel modulus. For the 1% DBS gel, G' is ~ 20,000 Pa, indicating a robust gel. Figure S2 plots G' and G'' vs. ω for the same DBS gel prepared using our simple (no-heat) method and the conventional (heat) method. The moduli are close for both the samples, indicating that the gels are comparable. Note that a very small amount of DMSO (from the stock solution) still remains in the butanol gel prepared by our simple method, but this DMSO does not have any appreciable effect on the gel rheology. For the rest of the studies in this paper, we will employ the simple method for making our gels.

We emphasize that DBS gels are remarkably strong and robust. In fact, we are not aware of any molecular gels that exhibit similar strength at gelator loadings of just 1% by weight. This point is underscored by the photos in Figure 3A of the 1% DBS gel in butanol. We show that the gel can be taken out of the vial and held between one's fingers (A1) or placed on the countertop (A2). These observations indicate that the gel has ample rigidity — i.e., a

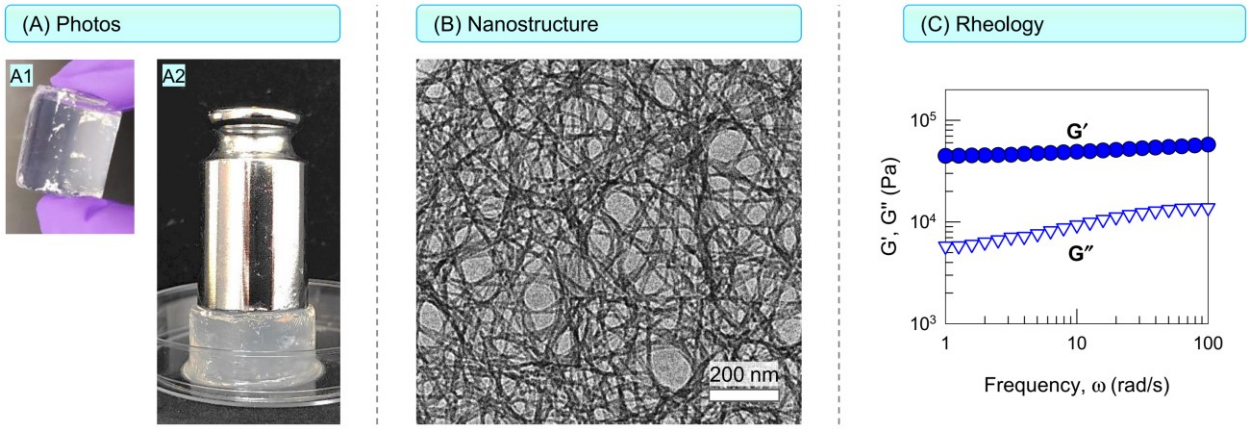

Figure 3. Photos, nanostructure, and rheology of a typical DBS gel. The gel is composed of 1% DBS in butanol. (A) Photos reveal that the gel is a free-standing solid that can support a weight of 100 g on top of it. (B) The nanostructure of the gel is shown via a TEM micrograph and it reveals a dense network of nano-fibrils. (C) Dynamic rheological data on the gel are shown in a plot of the elastic (G') and viscous (G'') moduli as functions of the angular frequency ω. The sample exhibits the expected rheology of a gel (i.e., $G' > G''$, G' independent of ω).

sufficiently high gel modulus G' — to be a free-standing solid.[31,32] Most molecular gels, on the other hand, have a paste-like consistency (akin to ketchup).[7-9] While paste-like gels can hold their weight in inverted vials, they cannot be removed out of the vials and manipulated as discrete solids. Moreover, Photo A2 further highlights the strength of the DBS gel on the countertop: on top of the gel weighing just 5 g, we place a 100 g steel weight — and the gel is able to withstand and support this load. Even free-standing polymer gels (e.g., gelatin gel desserts) will collapse under such a load.[31,32] Thus, DBS gels are indeed very strong. At the same time, they are also shear-thinning, i.e., they transform into flowable liquids when sheared.[25,29] We will return to this point later in the paper.

Self-Degradation of DBS Gels. DBS organogels are very stable, remaining intact and unchanged over long periods (more than a year) under ambient conditions. They withstand contact with strong bases (e.g., sodium hydroxide, NaOH), powerful oxidizing agents (e.g., potassium permanganate, $KMnO_4$), or reducing agents (e.g. sodium thiosulfate, $Na_2S_2O_3$) without any signs of degradation. For example, Figure S3 shows a DBS gel in hexanol at the bottom of three vials. Above this gel, we add 5 g of 1 M $KMnO_4$, $Na_2S_2O_3$, and NaOH respectively, in the three vials. After two weeks, the gel in each vial is unchanged in appearance and rheology from its initial state. However, our investigations revealed that strong acids did have an effect on DBS gels, causing their gradual transformation into thin sols. The degradation was slow enough that we could harness it for spontaneous self-degradation — where an initially robust DBS gel degrades over time.

The degradation of DBS gels can be accomplished with various kinds of acids and with gels formed in a variety of organic solvents. First, we will consider the simplest case of a *polar* organic solvent in which an *aqueous acid* such as hydrochloric acid (HCl) can be dissolved. DBS is well-known to gel a variety of polar solvents, including ethylene glycol (EG), polyethylene glycol (PEG), and aliphatic alcohols like butanol and hexanol. Note that the gel in Figures 2 and 3 was that of DBS in butanol. As a model system for this study, we have chosen a PEG of molecular weight 200 Da. This PEG is non-volatile and miscible with water, making it a convenient solvent for our work. Moreover, PEGs are biocompatible solvents that are used in drug and vaccine formulations and even as electrolytes for rechargeable batteries.[27,28] Hence, self-degrading gels of PEG could be of wide interest.

Initial results demonstrating self-degradation of PEG-based gels are shown visually in Figure 4A. We first combined PEG with aqueous HCl (1 M) in an 80/20 weight ratio. The combined liquids formed a homogeneous solution. We then converted this solution into an organogel using 2% DBS through our simple no-heat method. This gel was then left undisturbed and monitored over time at room temperature. The sample was placed in an inverted vial, which allows us to assess whether it is in the gel state. Initially, at $t = 0$, the gel holds its weight upon vial inversion (A1), indicating that the gel modulus is high and its yield stress exceeds gravity.[29,31] Note also the bluish tinge of the gel. Around the 20 h mark, we begin to see some visual differences (A2): the gel is still intact and holding its weight, but it is noticeably less bluish. The same trend is evident at the 30 h mark (A3) as the gel appears rather colorless. The loss of bluish tinge indicates weaker scattering of light, and it implies that either there are fewer nano-fibrils in the gel or the fibrils are smaller in diameter or length.[33] At the 40 h mark (A4), we see a reduction in the gel volume at the top of the inverted vial. This clearly means that some of the gel has degraded — and indeed this degraded gel has converted to a thin sol, which collects at the bottom of the vial (not evident in the photo because its volume is small). At the 50 h mark (A5), there is a further reduction in the gel volume. Finally, after 60 h (A6), all the remaining gel has converted to a sol and now this clear liquid has sufficient volume to be seen at the bottom of the vial.

Figure 4A shows that the gel spontaneously degrades over a period of 60 h. Importantly, in the initial stages (over the first 20 h), the gel is strong and indistinguishable from a regular non-degrading DBS gel. But over the next 40 h, the gel slowly liquefies until at the end, we have a clear, homogeneous sol. During the intermediate

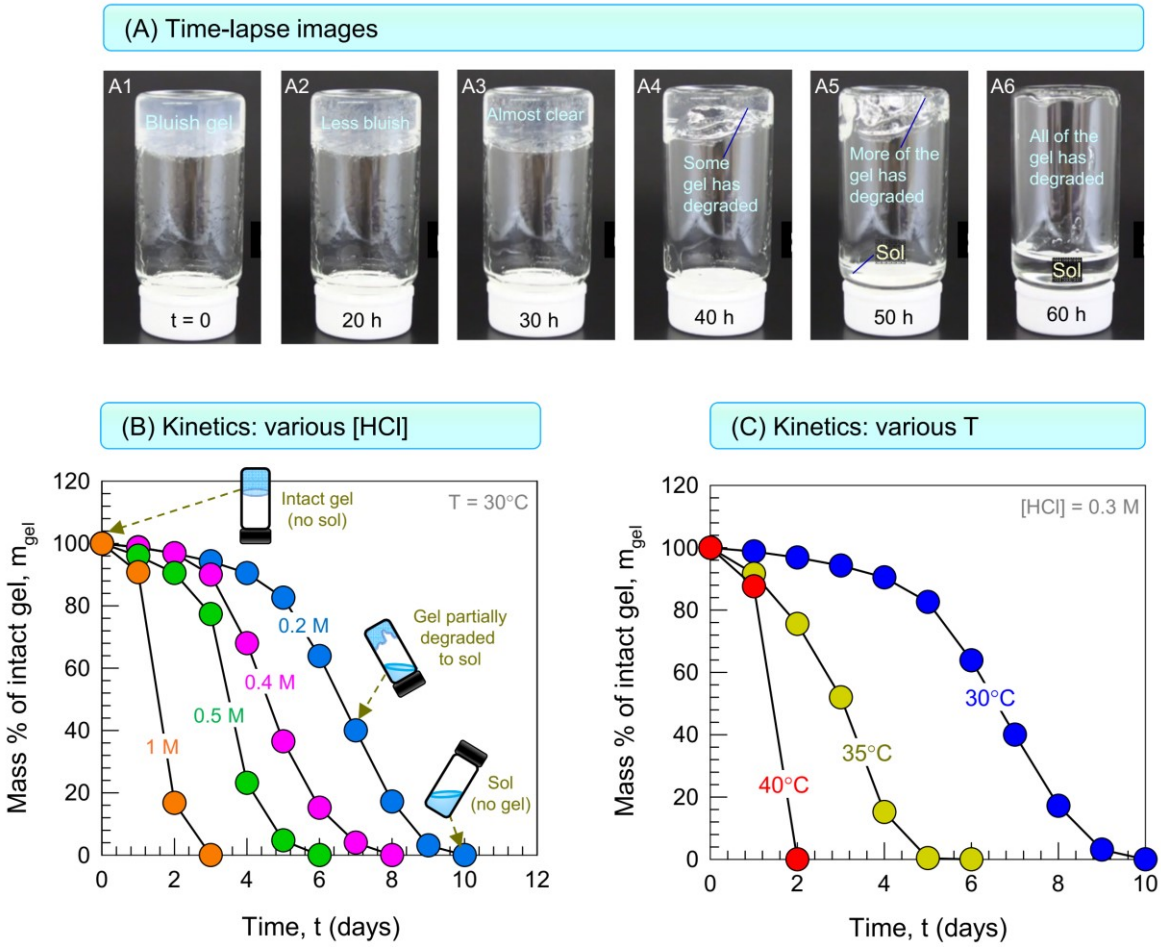

Figure 4. Self-degradation of DBS gels over time. (A) Time-lapse images showing the self-degradation of a gel over 60 h at room temperature. The gel is made with 2% DBS in a 80/20 mixture of PEG and acidic water (1 M HCl). With increasing time *t*, the gel liquefies and the mass fraction of intact gel (m_{gel}) at the top of the inverted vial decreases with *t*. By the end of the 60 h period, the gel has completely liquefied to a sol, i.e., m_{gel} drops to zero. (B) Plots of m_{gel} vs. *t* for varying [HCl] (0.2 to 1 M) at a constant temperature *T* of 30°C. (C) Plots of m_{gel} vs. *t* for varying *T* (30 to 40°C) at a fixed [HCl} of 0.3 M.

stages (40 to 60 h), the intact gel coexists with the sol. We can thus measure the mass fraction of intact gel (m_{gel}) over time *t* to monitor the kinetics of gel degradation. Details on how we do these measurements are discussed in the Experimental Section. The key variables that impact the rate of degradation are: (a) the acid concentration; (b) the acid amount (weight fraction); and (c) the temperature. We focus on (a) and (c) while keeping the acid weight fraction at 20%, i.e., a 80/20 mixture of PEG/acidic water. One reason for this is that DBS is insoluble in water on its own and thus the weight fraction of acid cannot be increased indefinitely.

First, we discuss the effect of acid concentration (Figure 4B). The data are for 2% DBS gels in 80/20 PEG/acid, with the molarity of the acid (HCl) ranging from [HCl] = 0.3 to 1 M. The temperature was held constant at 30°C. Figure 4B shows that m_{gel} drops from 100% (all gel) to 0% (all sol) over a period of days for each acid concentration, with a faster decrease at higher [HCl]. All curves exhibit an inverse-sigmoidal shape, with an initial lag in m_{gel} followed by a sharp drop and eventually a plateau at zero. The degradation time t_{degr} can be defined as the time for the gel to degrade completely (i.e., when m_{gel} = 0) or the time at the mid-point of the sigmoidal curve (i.e., when m_{gel} = 50%). In either case, t_{degr} decreases as [HCl] increases. For example, if [HCl] = 0.3 M, t_{degr} (for m_{gel} = 0) is 10 days, whereas t_{degr} is reduced to just 3 days when [HCl] = 1 M.

Next, we discuss the effect of temperature *T* on gel degradation (Figure 4C). We prepared gels of 2% DBS in 80/20 PEG/acid ([HCl] = 0.3 M). The gels were then subjected to different *T*: 30°C, 35°C, and 40°C, and in each case, we measured m_{gel} over time. As before, m_{gel} gradually decays to zero over a span of several days, with all curves having an inverse-sigmoidal shape. The higher the *T*, the faster the decay. This can be quantified via the decrease in t_{degr} (for m_{gel} = 0) as *T* increases. Specifically, t_{degr} decreases from 10 days at 30°C to 6 days at 35°C and further to 2 days at 40°C. Similar decrease in t_{degr} with *T* is reported in Figure S4 for a lower acid concentration ([HCl] = 0.2 M); note that; when the acid concentration is lower, at any given *T*, the degradation takes a longer time, in line with Figure 4B. Incidentally, we have also tried higher temperatures: for [HCl] = 0.3 M at 70°C, the gel degrades in just 2 h (data not shown).

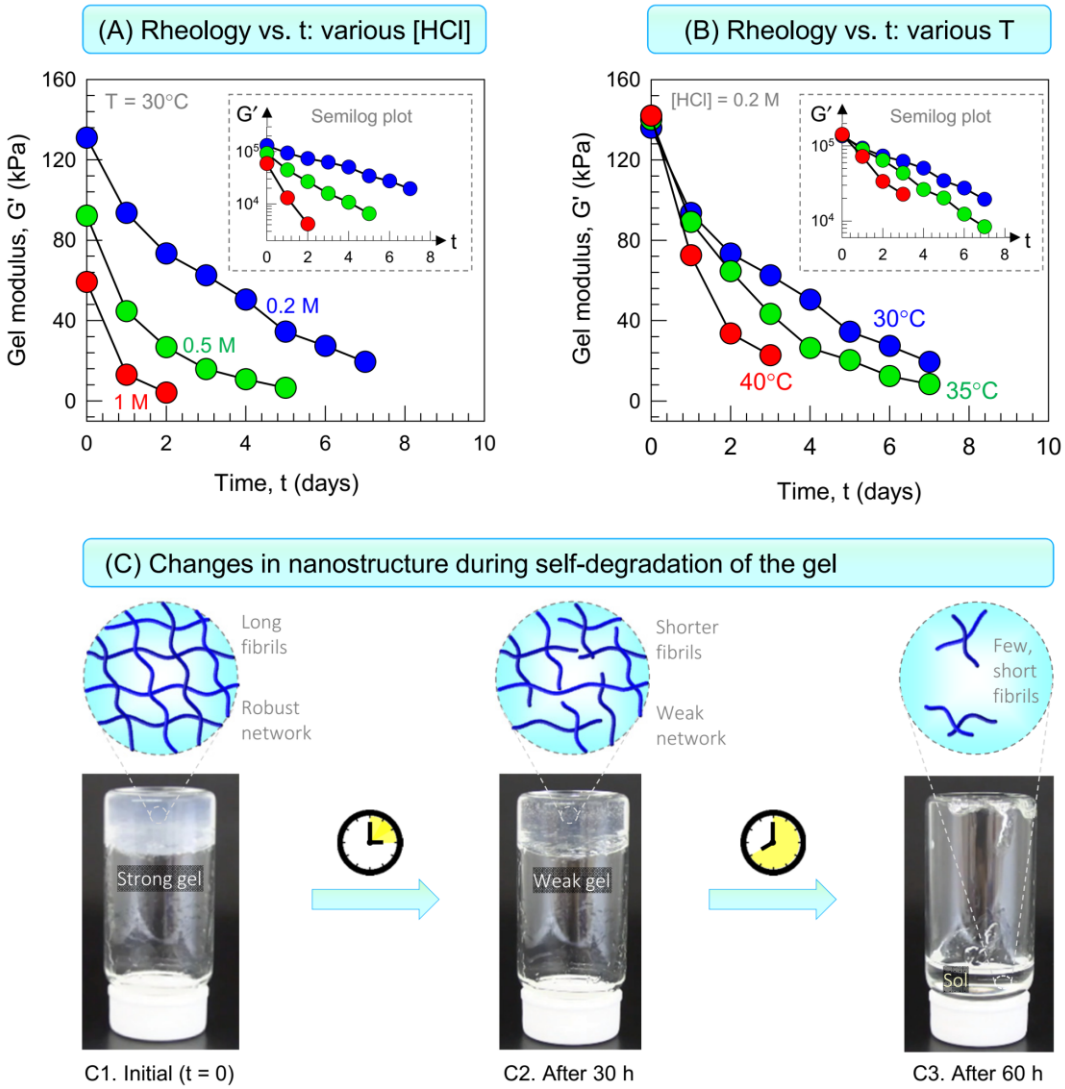

Figure 5. Changes in rheology and nanostructure during the self-degradation of DBS gels over time. The intact portion of the gel remaining at a given time *t* is studied by dynamic rheology and the gel modulus *G′* is extracted and plotted vs. *t*. Gel compositions are same as in Figure 4. (A) Plots of *G′* vs. *t* for different [HCl] at a constant temperature *T* of 30°C. (B) Plots of *G′* vs. *t* for different *T* at a fixed [HCl] of 0.2 M. The plots show an exponential decrease in *G′* over time. Consistent with the exponential decay, semilog plots (insets) of the data fall on straight lines. (C) Based on the rheology, the nanostructure of the gel is postulated to change as depicted. As the gel degrades, some of the DBS nano-fibrils disappear and thereby the network becomes less dense and hence weaker (i.e., *G′* drops). Eventually, only short fibrils remain (i.e., the network ceases to exist) and the gel becomes a sol.

As the gel spontaneously degrades, how does its rheology change? To probe this, we conducted dynamic rheology on the intact portion of the gel at different time points as it underwent degradation. From the data, the gel modulus *G′* is plotted vs. *t* in Figure 5. The experiments were done in two ways, much like those in the previous figure. First, we held the temperature constant at 30°C and varied the acid content. The data in Figure 5A are for 2% DBS gels in 80/20 PEG/acid, with the [HCl] ranging from 0.2 to 1 M. The acid sets the initial value of *G′* — the more the acid, the lower this *G′*. Thereafter, *G′* decays exponentially, and the decay is also faster at higher acid content. The exponential nature of the decay is shown clearly by the semilog plot in the inset, where the *G′* axis is on a log scale while *t* is on a linear scale. The straight lines on this plot confirm the exponential form of the decay and the slope of the line is steeper when the [HCl] is higher. We also measured the rheology at various *T* while holding [HCl] constant. The data for 2% DBS gels in 80/20 PEG/0.2 M [HCl] at three *T* are shown in Figure 5B. Note that the initial gel modulus *G′* is insensitive to *T* — thus, all three curves start from the same value of *G′*. However, the decay in *G′* is faster at higher *T*, and this is evident from the inset semilog plot, where a steeper slope is observed at higher *T*.

Collectively, the data in Figures 4 and 5 reveal the nanostructural transition depicted in Figure 5C. As DBS reacts with the acid, we can hypothesize that the molecule is being transformed to a form that cannot assemble into nano-fibrils. It is well-known that the *G′* of DBS gels increases with DBS concentration *c* in a power-law with a slope around 2, i.e., $G' \sim c^2$.[27,29] This is also reflected in our own data;

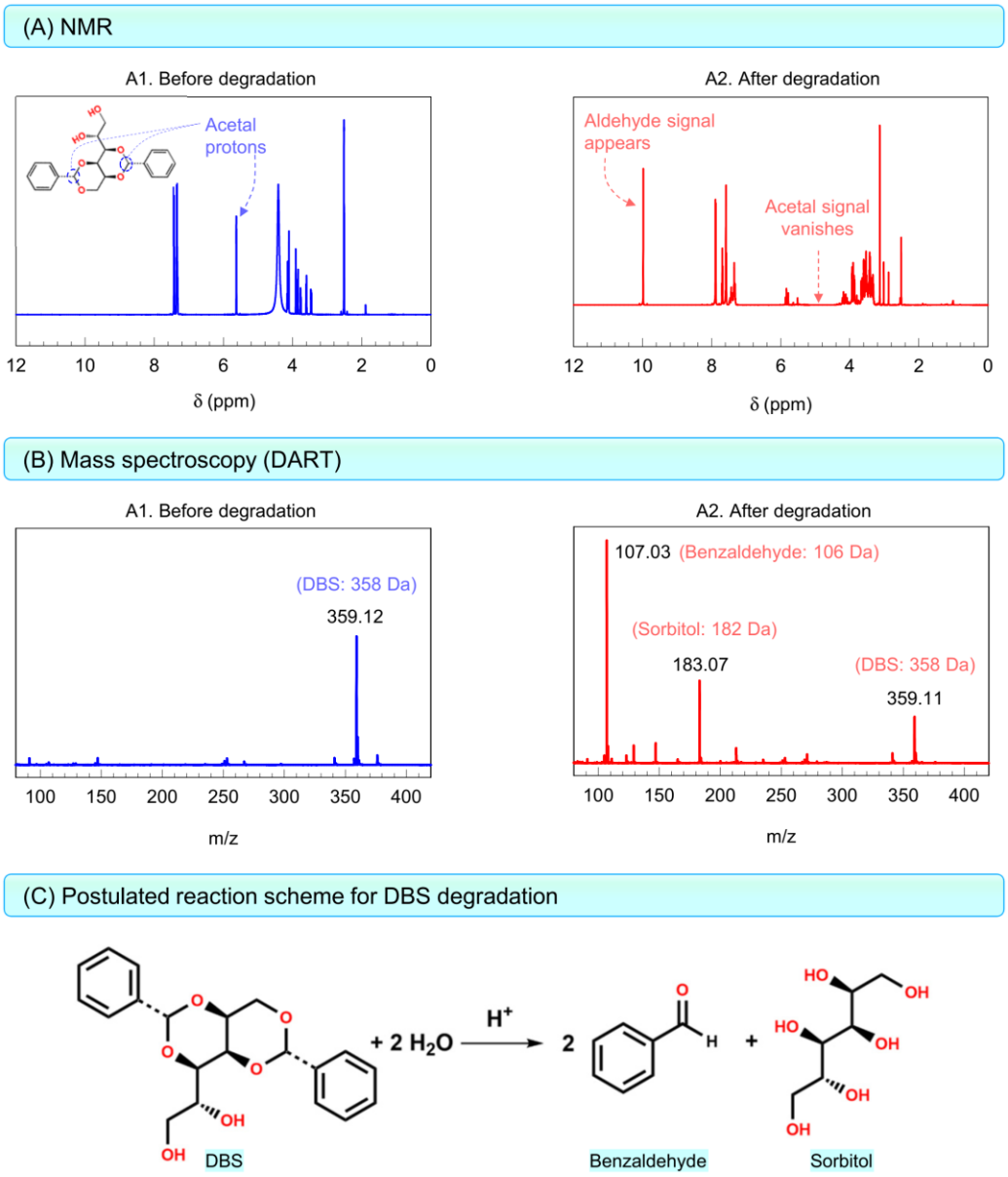

Figure 6. Deciphering the mechanism for self-degradation of acid-containing DBS gels. (A) ^{1}H NMR spectra of 1% DBS in 95/5 d-DMSO/1 M HCl in D_2O. The initial (undegraded) sample shows signals corresponding to the acetal protons whereas in the degraded sample, the acetal signals vanish and an aldehyde signal appears. (B) Mass spectroscopy (DART) of a 2% DBS gel in 80/20 PEG/0.3 M HCl. Before degradation, a DBS peak is seen. After degradation, additional peaks corresponding to benzaldelhyde and sorbitol appear. (C) The data imply the reaction scheme shown, where the acetals in DBS are slowly hydrolyzed in the presence of the acid, leading to the formation of benzaldehyde and sorbitol.

see Figure S5. Thus, the decrease in G' with t reflects a lowering of the DBS concentration that is part of the fibrillar network. This is shown in Panel C2 of Figure 5 as a network that is less dense than the initial network in Panel C1 (in other words, the mesh size ξ of the network increases with t). Note also that, during the initial period of the degradation, although G' drops with t, the gel has sufficient integrity to entrap all the solvent and retain its weight in the inverted vial. This explains why we see the 'lag phase' in the m_{gel} vs. t plots in Figures 4B and 4C. During this lag period, m_{gel} is close to 100%, i.e., there is negligible sol fraction coexisting with the intact gel. As G' drops further with t, a point is finally reached when the fibrillar network no longer spans the sample volume, and at that stage, some of the gel converts to a viscous sol. The sol fraction keeps growing with t until at the end, only the sol is left behind. In the sol, we expect to find only small fibrillar clusters, as shown in Panel C3.

Mechanism for Self-Degradation. What exactly is the chemical reaction between DBS and acid? Why does this reaction lead to gel degradation? To elucidate the mechanism, we turned to Nuclear Magnetic Resonance (NMR) spectroscopy and Mass Spectrometry (MS). First, we present data from ^{1}H NMR in Figure 6A. We analyzed two samples, each containing 1% DBS in 95/5 DMSO/HCl. The DMSO was deuterated (DMSO-d6) and the acid (1 M HCl) was also prepared using deuterated water (D_2O). One sample was analyzed right after preparation (before the DBS degraded), while the other sample was incubated at 40°C for a week before analysis (to

allow the DBS to degrade). The NMR spectra reveal significant differences between the two samples. Notably, the signals corresponding to the acetal protons of DBS are present in the initial sample (A1), but these signals vanish in the degraded sample (A2). In the latter, a new signal indicative of an aldehyde proton emerges. This observation suggests that the acid hydrolyzes the two acetal groups in DBS to form a product containing an aldehyde. We will show presently that this product is benzaldehyde.

To further investigate the degradation products, the DBS samples were subjected to MS, specifically via the Direct Analysis in Real Time (DART) technique.[34] In this technique, the sample is ionized by the addition of a proton, resulting in a +1 charge and an increase in the mass of the molecule by one. Thus, the mass-to-charge ratio (m/z) corresponds to the molecular weight (MW) of the species plus one. DART was used on a 2% DBS gel in 80/20 PEG/0.3 M [HCl] before and after degradation (Figure 6B). The DART spectrum of the initial gel (B1) primarily exhibits a single peak at 359, corresponding to the MW (+1) of DBS. In the spectrum of the degraded sample (B2), one peak still corresponds to unreacted DBS at 359, but two other peaks are observed at 183 and 107. These must be the reaction products and their MWs must then be 182 and 106. Such products can be accounted for by the reaction scheme shown in Figure 6C. Here, hydrolysis of DBS is catalyzed by the acid, resulting in the formation of benzaldehyde (MW = 182) and sorbitol (MW = 106). Thus, our studies conclusively prove that the self-degradation of the gel is due to the acid-induced hydrolysis of the acetal groups on DBS. Such hydrolysis is well-known and is documented in textbooks.[35,36]

We can also explicitly make the connection between the reaction scheme in Figure 6C and the nanostructural transition in Figure 5C. The key point is that the reaction products, benzaldehyde and sorbitol, cannot assemble into nano-fibrils. As noted earlier, DBS self-assembles into fibrils through non-covalent interactions: a combination of hydrogen-bonding of the hydroxyls and pi-pi stacking of the aromatic rings. Removal of either the hydroxyls or the aromatic rings from a DBS molecule would eliminate its ability to associate with its neighbors. In other words, the hydrolysis of DBS will remove molecules from the fibrils, which will either create gaps or breaks in the fibrils or make the fibrils shorter. The net result would be to make the fibrillar network less dense over time, as shown in Figure 6C, which explains the drop in G' with t and the eventual transition of the gel to a sol.

Additional evidence supporting the proposed reaction mechanism is shown in Figure S6. Here, we combine 5 g of DBS powder with 5 g of 2 M HCl in water. Note that DBS is insoluble in water and so the powder initially sits atop the acidic solution (Photo 1 in Figure S6A). With time (over a few days), the DBS powder disappears, leaving two immiscible liquid phases: a top oily phase and a bottom aqueous phase (Photo 2 in Figure S6A). NMR analysis (Figure S6B) confirms that the top layer is benzaldehyde, which has limited solubility in water. The other reaction product, sorbitol, is water-soluble and partitions into the aqueous phase. Thus, the observations in Figure S6 are again consistent with the reaction in Figure 6C.

Applications for Self-Degrading Gels. Self-degrading DBS gels could be useful in a range of scenarios and we now explore a couple of the possibilities indicated by Figure 1. The first is a valve that opens after a set time (Figure 7). For this, we start with a gel of 2% DBS in 80/20 PEG/acid (3 M). The acid molarity is kept high so that the gel degrades at room temperature in a reasonably short time, i.e., in ~ 12 h. 5 mL of this gel is introduced into an open syringe at t = 0. The bottom end of this syringe (below the gel) has an orifice with a diameter of 2 mm. Because the gel (dyed blue) is solid, it does not flow out of the orifice when the syringe is vertical (Figure 7A). Next, in the headspace above the gel, we add 8 mL of mineral oil (dyed red). Although the oil is a liquid, it cannot flow out of the syringe because its path is blocked by the gel (Figure 7A). As long as the gel maintains its structural integrity, this situation will continue, meaning that the valve with remain closed. We leave the syringe undisturbed at room temperature and monitor it. By the 12 h mark, the gel is degraded considerably. A few minutes before this mark, a small amount of sol (i.e., liquefied gel) is seen to drop down into the beaker (Figure 7B). Just a few minutes later, the entire gel is liquefied and flows out of the orifice (Figure 7C). In turn, the red liquid is no longer blocked (i.e., the valve is now opened) and this liquid flows out too. The experiment in Figure 7 is also shown as a movie in Movie S2. On the whole, using the self-degrading DBS gel, we have demonstrated a valve that remains closed for the first 12 h and thereafter spontaneously opens. Such a valve could be integrated into a variety of devices for timed delivery of fluids and thereby of solutes in them (e.g., agrochemicals or cosmetics).

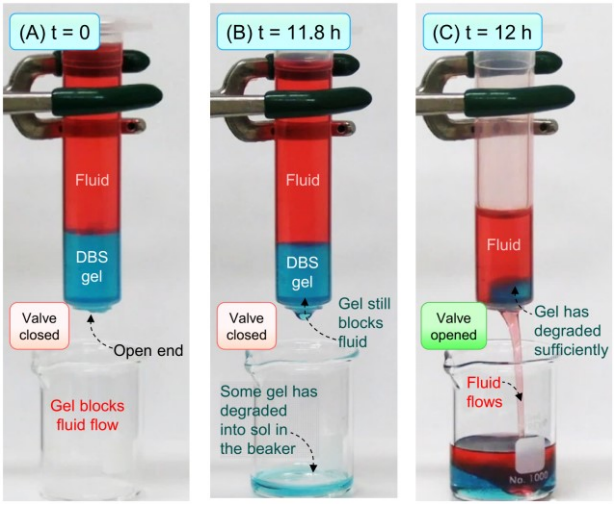

Figure 7. Valve based on a self-degrading DBS gel that opens after a set time. (A) At t = 0, a gel of 2% DBS in 80/20 PEG/3 M HCl is placed at the bottom of a syringe with an open end, and 8 mL of mineral oil is added above the gel. The gel blocks the flow of the oil. (B) After 11.8 h, a small amount of degraded gel is observed in the beaker. (C) At the 12 h mark, the gel has degraded sufficiently so that the valve opens and the red fluid flows into the beaker. This experiment is also shown by Movie S2.

Our second demonstration shows how a self-degrading gel could be used as a flow-diverting agent for a set time (Figure 8). For our demonstration, we use a plastic tube with a closed bottom end and an open side channel (Figure 8A). Details on how this setup was made are given in the Experimental Section. Initially, when mineral oil is introduced from the top into the vertical tube, it flows through the side channel and drips out. Thus, in this initial 'control' state, the side

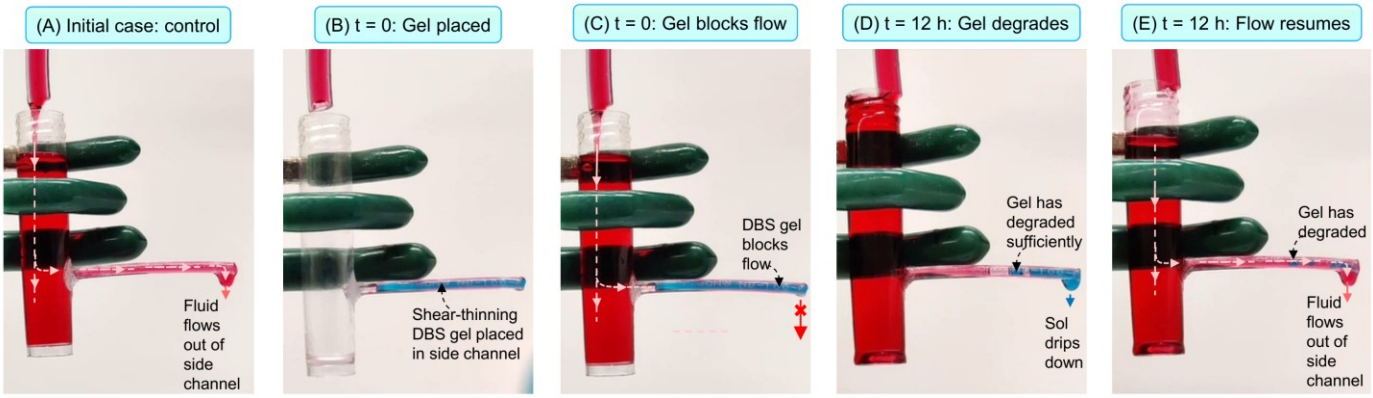

Figure 8. Flow diversion for a set time using a self-degrading DBS gel. (A) The setup involves a vertical main tube with a side channel. When fluid (mineral oil) is introduced from the top, it flows out of the side channel. (B) A gel of 2% DBS in 80/20 PEG/3 M HCl is injected into the side channel. (C) When fluid is now added to the tube, it cannot flow through the side channel because of the blocking gel. Thus, the gel diverts flow away from this channel. (C) At the 12 h mark, the gel is sufficiently degraded to a sol, which is forced out of the channel by the hydrostatic pressure of the fluid. (D) As a result, the block in the channel is removed, and fluid flows out through it. The entire process is shown by Movie S3.

channel is *open*. We then introduce the self-degrading DBS gel into the side channel. The gel composition is the same as in Figure 7: it is made with 2% DBS in 80/20 PEG/acid (3 M), and it is designed to self-degrade in ~ 12 h.

To place the DBS gel in the side channel, we exploit its shear-thinning rheology, which is shown in Figure S7. First, under steady-shear (Figure S7A), the gel does not flow (i.e., its viscosity η is infinite) at shear stresses below its yield stress (σ_y). Beyond σ_y, η drops rapidly with increasing shear-stress, i.e., the sample shear-thins. Likewise, under dynamic rheology (Figure S7B), G' and G'' are constant (with $G' > G''$) within the linear viscoelastic regime at low stresses. At high stresses, the moduli drop with stress and G'' overtakes G', indicating that the sample is now more viscous than elastic. Shear-thinning arises because the gel network is formed via weak, non-covalent bonds. When sheared, these bonds break and the network is disrupted, which is why the sample flows. Once the shear is stopped, the bonds re-form and the network is recovered, i.e., the sample reverts to a gel state.

Figure S7C probes the breakdown and recovery of structure in the gel through dynamic rheology over three time zones. First, Zone 1 characterizes the initial rheology of the gel in the linear regime (i.e., at a low stress of 10 Pa): the gel has an elastic response, with $G' > G''$ and G' having a value of 30,000 Pa. Next in Zone 2, we apply high oscillatory shear at a stress of 300 Pa for 2 min. In Zone 2, $G'' > G'$, indicating that the structure is broken and the gel has been liquefied. Then, we stop this high shear and immediately switch back to the low stress of 10 Pa in Zone 3. Within 30 s, the sample reverts to being a gel and we recover the gel-like rheology ($G' > G''$). Note also that G' attains a value close to its initial value of 30,000 Pa. We then break the structure again in Zone 4 (300 Pa) and monitor the recovery once more in Zone 5 (10 Pa). Again, we observe the fast reversion to the gel state. In practical terms, this means that if a DBS gel is sheared (e.g., by a vortex-mixer or a high-shear mixer), it will convert into a pourable liquid. This is further shown by the photos in Figure S7D. Once the shear is stopped, the gel state revovers very quickly.

The shear-thinning rheology allows us to take the above DBS gel (dyed blue) and liquefy it by imposing high shear. The liquid can thus be loaded into a syringe and we inject it into the side channel. Within seconds, the liquid sets into a gel in the channel (Figure 8B). With this gel in place, we introduce mineral oil into the tube from the top. Now, the oil cannot flow out through the side channel because the gel acts as a plug and blocks the flow (Figure 8C) — so, the channel is in a *closed* state. After 12 h at room temperature, the DBS gel self-degrades, and in the process, it liquefies (Figure 8D). The hydrostatic pressure of the red liquid column then activates the flow of this liquefied gel and blue liquid drips out of the side channel. In turn, because there is no longer a blocking gel, the side channel now flips from a *closed* to an *open* state. As a result, the red liquid also follows suit and flows out of the side channel. To summarize Figure 8, the presence of intact DBS gel in a side channel diverts the flow away from that channel. Once the gel self-degrades, flow through that channel resumes.

The relevance of the above scenario during oil extraction will now be discussed (see Figure S8). A well-known problem in this regard is termed '*lost circulation*' (Figure S8A). To extract oil from an underground rock formation, a well has to be drilled down from ground level. During the drilling operation, a 'drilling fluid' is sent down a borehole through a drill pipe. This fluid serves multiple purposes: it lubricates the drill bit and stabilizes borehole walls with hydrostatic pressure. Also, the fluid exits through nozzles in the drill bit and recycles back to the surface, thereby carrying rock cuttings with it. The returning fluid is filtered and recirculated. Fluid can, however, be lost from the circulation if it seeps into fractures in the oil-rich rock. Such fluid loss is a problem: it constitutes a waste of resources as well as risks to the environment and to the safety of the drilling operation. Thus, the oilfield industry has been urgently seeking solutions to this vexing problem.

A potential remedy involves using a gel (such as our DBS gel) to plug the fractures (Figure S8B). First, the gel is pumped down the well: note that it will flow when sheared due to its shear-thinning nature. Once the gel enters the fractures it will quickly recover to the

gel state. Due to its high modulus, it will plug the fracture. Next, the drilling fluid is pumped down. Because the gel plugs the fractures, fluid loss to the fractures will be prevented. The drilling operation can then be completed without any 'lost circulation'. This is exactly analogous to our demonstration in Figure 8A-C where the gel plug in the side channel blocked the flow of the red fluid through this channel.

Next, we come to the stage where a *self-degrading* gel is truly advantageous. If the fractures in the rock are permeable, then oil (and also gas) can be extracted through these same fractures (Figure S8C). However, the gel is blocking the flow of oil and so this gel will need to be degraded. Our DBS gel offers a solution that avoids the need for any degrading agents or stimuli.[37] We can design the gel to self-degrade slowly, i.e., over a period of days to even weeks, allowing enough time to complete the drilling of the well. By that time, if the gel has mostly degraded (Figure S8C), then the fractures will be unblocked and oil can then be extracted through the fractures and up to the surface level through the well. Note that, in a given oil drilling operation, the degradation time of the gel will have to be chosen based on (a) the temperatures expected in the rock formation at the desired depth, and (b) how long the drilling will take, which can range from days to even weeks.

Drilling fluids used in oil extraction (often called 'drilling muds') can be based on either polar or nonpolar liquids. Examples of the latter are mineral oil (or other aliphatic hydrocarbons) and toluene (or other aromatic hydrocarbons). We can formulate self-degrading DBS organogels with such nonpolar liquids as well. To induce such gels to degrade, aqueous acid (such as HCl, acetic acid, formic acid, etc.) can be incorporated as droplets, i.e., as an emulsion, in the nonpolar matrix. Figure S9 shows an example of such an 'emulsion gel' using mineral oil as the nonpolar solvent. Acid (1 M HCl) is emulsified into the gel at a 5 wt% concentration. The gel was made by the simple method from Figure 2. First, the aqueous acid was added to the oil and then the DBS stock solution in DMSO was added, followed by vortex mixing. Right away, a stable emulsion gel is obtained (Figure S9A). No other surfactant or stabilizer is needed to create the emulsion. Optical microscopy shows that the gel contains stable aqueous droplets (with diameters of 5 to 50 μm). The gel is turbid due to the microscale droplets. It is robust and retains its weight in the inverted vial. Over a period of days at room temperature, the gel self-degrades (Figure S9B, S9C). By day 12, the degradation is complete and the entire sample has transformed into a sol. Thus, the concept shown in this paper of a self-degrading DBS gel can be applied to a variety of liquid matrices, both polar and nonpolar.

Conclusions

We have presented the first examples of self-degrading molecular organogels using DBS as the gelator. DBS readily self-assembles into a 3-D network of nanoscale fibrils in a variety of organic solvents, thereby converting the liquids into robust, free-standing gels. The incorporation of an acid such as HCl into the gel makes the gel degrade spontaneously over time into a sol. Because the rate of degradation is slow, the initial gel is strong and robust depsite having the degrading agent embedded in it. The degradation time t_{degr} of the gels can be tailored, ranging from hours to days to weeks, depending on the acid concentration and the external temperature. Self-degradation occurs because the acid hydrolyzes DBS into benzaldehyde and sorbitol. These hydrolysis products lack the ability to self-assemble into fibrils, and thereby the gel gradually transforms into a thin solution. We have highlighted the utility of DBS-based self-degrading gels for applications in time-activated valves (i.e., valves that open after a set time) and as flow diverting agents that block flow through specific channels for a set time. The latter application is highly relevant for oil drilling operations, where these self-degrading gels present a novel solution to the long-standing problem of 'lost circulation'.

Experimental Section

Materials. DBS was purchased from Alfa Chemistry. DMSO was obtained from Alfa Aesar. All other chemicals were from Sigma-Aldrich, including the solvents butanol, hexanol, ethylene glycol, polyethylene glycol (PEG, 200 Da), and hydrochloric acid (HCl).

Gel Preparation. DBS gels were typically prepared using the simple method discussed under Figure 2 and Figure S1B. The gelling solution (15% w/w DBS in DMSO) was added to the solvent of interest (e.g., butanol, hexanol, or PEG), followed by hand-shaking or vortex-mixing for 30 s. At the end of this process, a robust gel of DBS in the solvent was obtained. For comparison, the conventional method (Figure S1A) was also used to make DBS gels. In that case, DBS powder was added to the solvent, followed by heating the mixture up to > 100°C. Within about an hour, the DBS dissolved in the solvent, giving a sol. As this sol was cooled to room temperature, it transformed into a gel.

Degradation Studies. For the studies described in Figures 4 and 5, the following protocol was used. First, a given gel, e.g., of 2% DBS in a 80/20 mixture of PEG and acidic water (HCl of a given molarity) was made in a 20 mL glass vial. The vial was broken and the gel cylinder (2.5 cm diameter and 5 cm height) was taken out. This gel was then placed vertically in a larger glass bottle (100 mL volume, with a base of 6 cm diameter). The bottle was capped and then placed upright in a water bath, with the water level reaching three-quarters up to the top of the bottle (leaving the cap untouched). The temperature of the water bath was controlled by an immersion heater (Julabo).

As the gel in the bottle degraded, some of the gel transformed into a sol, and this sol remained at the bottom of the bottle. To measure the mass of intact gel at any given time, the gel-cylinder was taken out of the bottle and weighed. Thereafter, it was promptly returned to the bottle for the rest of the experiment. The above protocol was repeated for gels of different composition and for different temperatures (data in Figure 4). For the rheological studies during gel degradation (Figure 5), at a given time point, a thin slice of the gel was cut from the cylinder and was characterized by rheology. The rest of the gel-cylinder was returned to the bottle as before.

Rheology. Rheological experiments were performed on an AR2000 stress-controlled rheometer (TA Instruments). Samples were run on a parallel plate geometry (20 mm diameter). Dynamic frequency

spectra were conducted in the linear viscoelastic regime of the samples, as determined previously from dynamic stress sweeps. In addition, steady-shear rheology (viscosity vs. shear-stress, Figure S7A) as well as time-sweeps to study the recovery of structure after shear (Figure S7C) were also conducted.

Transmission Electron Microscopy (TEM). TEM was conducted on a JEOL JEM 2100 microscope at 100 keV. The gel of 1% DBS in butanol was formed on carbon/Formvar-coated copper grids using our simple method (Figure 2). The grids were then dried at room temperature. The dried grids were then stained with a 1% aqueous solution of uranyl acetate (UA) (from Sigma-Aldrich). The grids were air-dried before imaging.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR spectra were recorded on either a 600 MHz Bruker Advance III NMR spectrometer equipped with a room temperature TXI probe or a 800 MHz Bruker Advance III HD NMR spectrometer equipped with a Cryo-QCI probe at a sample temperature of 298.2 K. The data shown in Figure 6 are for 1% DBS in a 95/5 mixture of deuterated-DMSO/1 M HCl in D_2O.

DART-MS. A time-of-flight mass spectrometer (JEOL AccuTOF), equipped with a direct analysis in real time (DART) ion source, was used. Mass spectra were acquired at a rate of one spectrum per second, with a mass/charge (m/z) range of 50–600. An inverted melting point capillary was used to introduce the sample (gel or sol) into the DART source region. The DART ion source was operated in the positive mode with helium gas. The glow discharge needle potential was set at 3.5 kV and the grid voltage was 250 V.

Valve Experiment. For the experiment in Figure 7, the DBS gel was formed at the bottom of a 10 mL syringe. After the gel was formed, a 2 mm orifice (hole) was made at the syringe's end using a razor blade. 8 mL of red-dyed mineral oil was added into the headspace above the gel within the syringe. The setup was monitored until the gel degraded, as shown in the figure.

Flow-Diversion Experiment. For the experiment in Figure 8, two transparent plastic tubes were connected together. The larger tube (5.5 cm length, 1 cm diameter) was closed at one end. A small hole was created in the side-wall of this tube, and the smaller tube (3.5 cm length, 2 mm diameter) was inserted into this hole and affixed using epoxy resin. Thereby, the small tube became a side branch from the large tube. The DBS gel was used to block flow through this side channel for a duration of time until it degraded.

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Supporting Information: The SI includes a PDF file that has the following figures:

Fig. S1: Comparing methods to make DBS gels.
Fig. S2: Rheology of DBS gels made by the two methods.
Fig. S3: Stability of DBS gels to strong chemicals.
Fig. S4: More data on self-degradation at different temperatures.
Fig. S5: Rheology of DBS gels vs. DBS concentration.
Fig. S6: Confirming the mechanism for DBS gel self-degradation.
Fig. S7: Shear-thinning of DBS gels and their recovery after shear.
Fig. S8: Self-degrading gels and lost circulation in the oilfield.
Fig. S9: Self-degrading DBS emulsion gels in nonpolar liquids.

In addition, the SI contains Movies S1, S2, and S3, which accompany Figures 2, 7, and 8 in the text, respectively:

Movie S1: Simple method to prepare DBS gels.
Movie S2: Gel-based valve that opens after a set time.
Movie S3: Gel-based flow diversion for a set time.

Declaration of Interests: Authors have filed a patent application (US 20230279282A1 / WO 2023164561 A1) to commercially protect this technology.

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