# Direct Observation of Sol−Gel Conversion: The Role of the Solvent in Organogel Formation

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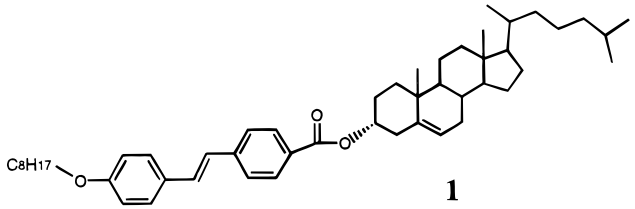
The unique ability of low-molecular-weight gelators to immobilize various organic fluids has led to much recent research.[1] The diversity of nanostructures provided by these gels make them excellent platforms for sensors,[2,3] templates for the synthesis of materials,[4−6] and media for electrochemistry[7,8] and biological science.[9,10] Many gels consist of three-dimensional networks in which helical fibrils trap large amounts of organic solvents; however, the mechanism of organogel formation remains ambiguous. The role of the organic solvent in determining the gel properties is a central question. It is clear that a given gelator can gel certain solvents, and that the specific solvent strongly influences the physical properties of the gel.[1,11] However, it has been shown that the enthalpies of gel formation are largely independent of solvent for a wide range, but strongly dependent on gelator structure.[12] It has been suggested that the solvent is entrapped between microcrystals of the gelator by capillary forces.[13] Herein, we address these questions by monitoring the sol−gel phase transition process via atomic force microscopy (AFM). We show gel formation is initiated by a change in the gelator−solvent interaction, resulting in dewetting of sol phase from a solid support. The results indicate direct participation of the organic solvents in the formation of fibers.

Many gelators exhibit a moderate affinity for solvent molecules and a tendency to self-assemble or aggregate. Cholesterol derivatives have been found to be efficient gelators presumably due to the tendency to form one-dimensional stacks of the steroid units, and it suggested this is the primary driving force for gelation.[11,12] We have used a gelator containing a cholesterol tethered to a *trans*-stilbene (**1**). Recently[14] we reported that this compound gels several organic solvents. The spectroscopic "signature" from the stilbene absorption and fluorescence indicates that the stilbene is aggregated; however, the aggregation state and level appear different from aggregates where the stilbene aggregation is the primary self-assembly process. Although several imaging techniques have been used to observe gels,[1,6] atomic force microscopy is extremely attractive since the gels can be examined under ambient conditions.




**1**

Samples were prepared by spreading a heated mixture of **1** and 1-octanol (at a weight ratio of 1.6:100) onto a freshly cleaved surface of highly oriented pyrolytic graphite (HOPG). As the sol phase was cooled to room temperature under ambient conditions, the sample was placed in the AFM chamber for imaging. AFM measurements were tapping mode to minimize damage of the soft surface by the single-crystal silicon probe.

A series of time transient images were acquired to monitor the sol to gel phase transition, as shown in Figure 1. The structures are typical of the entire surface. The gelation started from a solution homogeneously dispersed onto the hydrophobic HOPG substrate (Figure 1a). As gel formation commenced, the solution dewetted from the surface, forming circular and elongated droplets, leaving exposed substrate (Figure 1b). According to Young's equation, the contact angle of a liquid on a solid surface is determined by the balance between the cohesive force within the liquid and the adhesive force between the solid and liquid. Since the HOPG surface is unchanged, the predominant contribution to the gelation-induced dewetting must arise from a change in the cohesive force. This implies that gelator−solvent interaction is enhanced during gel formation, and the influence of solvent and gelator are both important at the initial stage of the gelation process.[15] It is also evident that fine fibers, with average length of 250 ± 5 nm and width as thin as 6.5 ± 0.5 nm, started to form at this stage. We infer that the elongation of the droplets was directed by the one-dimensionally developed fibers.

Upon further development (Figure 1c), fine fibers became dominant at the expense of the sol-phase droplets, forming condensed islands. The one-dimensional growth of individual fibers suggests continuous stacking of the gelator molecules, which may facilitate the sol−gel phase transition. Note that the height of the condensed island (125 nm)[16] in Figure 1c is about twice as high as that of the sol droplets (73 nm) in Figure 1(b); the sol−gel transition is accompanied by a two-dimensional condensation as well as an expansion in the third dimension. Further condensation allowed combination of neighboring fine fibers into thicker ones, as shown in Figure 1d. The width of the fibers here ranges from 6 to 25 nm, suggesting one thick fiber is composed of up to four fine fibers. The time span between Figure 1d and Figure 1e was only 3 min; however, during this time bundles of expanded fibers formed from the short fur-like fibrils. The fiber bundles are 100 to 500 nm in width (Figure 1e). At the

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(15) Note that the dewetting of the solution on HOPG surface furnished a way to probe the variation of the gelator−solvent interaction, which should similarly occur during the gelling of a bulk solution of the mixture.
(16) Refer to the highest position relative to the blank areas in the image. The height of the feature was measured from the image in height mode, which was simultaneously acquired with the image in amplitude mode. The heights in the subsequent text were measured under the same condition.

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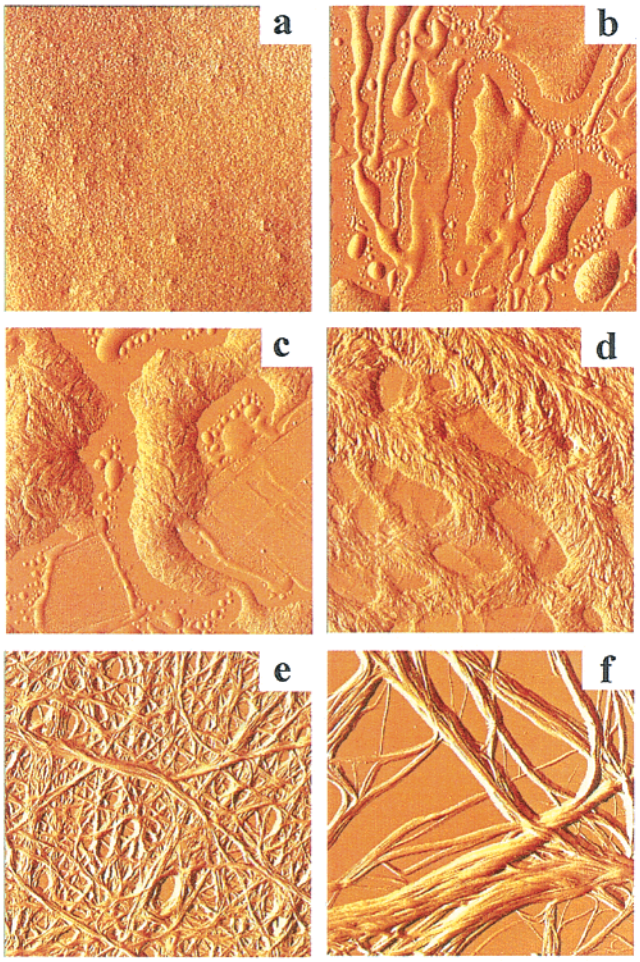


**Figure 1.** Time transient AFM images (in amplitude mode) of sol−gel phase transition. Images were acquired after the heated sol-phase solution (1.6%) was cooled to room temperature for (a) 0, (b) 10, (c) 15, (d) 18, (e) 21, and (f) 31 min. The scale of all the images is 12 × 12 $\mu$m.

center of the image, it is evident that neighboring fiber bundles continued twisting to form broader and more condensed ones. The fibers in the final image of Figure 1f are as broad as 1.5 $\mu$m, and it took 10 min for the transition from Figure 1e to Figure 1f. The rigid network is very stable below the phase transition temperature (60 °C). The height of the features (526 nm) in Figure 1f is six times higher than the height of the sol-phase droplets in Figure 1b. Little volume change occurs during gel formation in cylindrical tubes. Since the gels are independent of the substrate, this leads to the conclusion that bulk solvent in the sol-phase was trapped and condensed by the gel-phase fibers to develop a three-dimensional fibril network. However, it remains unclear where the solvents locate in the network.

To address this question, a fibril bundle was cut by the AFM tip by increasing the driving amplitude to 503 mV. The cross-section was then imaged at a normal driving amplitude of 64 mV. The high resolution image of the cross-section (Figure 2a) shows that the fiber bundles consist of tens of unit fibers, and more importantly, the cross-section suggests a fluidized surface, remarkably different from the rigid side walls of the fibers. This observation indicates that solvent molecules are involved inside the bundles, either within the unit fibers or in "channels" between them. A zoom-in image in Figure 2b resolves individual unit fibers. The corresponding height cross section (lower panel) displays a uniform width of 6.2 ± 0.5 nm for a single unit fiber, and a separation of 5.0 ± 0.5 nm between neighboring ones. The width is consistent with the fibers measured in Figure 1b,c, confirming that fiber bundles result from assembly of unit fibers initially formed (Figure 1b). Assuming that the fibers contain

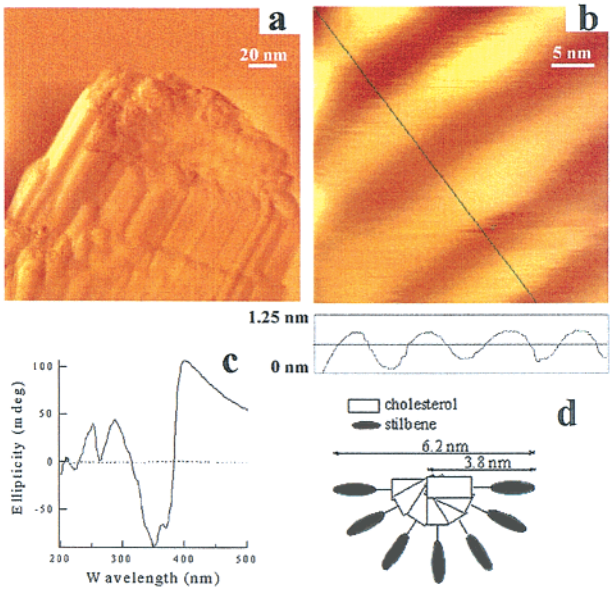


**Figure 2.** (a) The cross-section of a fibril bundle (in amplitude mode) as formed at the last stage (Figure 1f) of sol−gel phase transition. (b) High-resolution image (in height mode) illustrating uniform single unit fibers with a width of 6.2 ± 0.5 nm, and separation between neighboring fibers of 5.0 ± 0.5 nm. (c) Circular dichroism spectra of sol (dash line) and gel (solid line) for 1.5% **1** in octanol, as a helical stacking model of the **1** molecules in a unit fiber. (d) Possible helical stacking model of the 7 molecules in a unit fiber.

stacked gelator molecules and solvent molecules fill the separation areas between the fibers, we can make an estimation of the solvent distribution within the gel. Using the density of octanol (0.827) and the molecular weights of **1** and octanol of 721 and 130, respectively, it can be calculated that a 1 nm segment of a "unit fiber" from a 1.6% gel contains 1.6 gelator molecules and approximately 159 octanol molecules (30%) inside the fiber with the remaining 382 solvent molecules (70%) in the space between the fibers. This suggests that 30% of the solvent molecules contribute to the fiber formation, reinforcing the idea of strong gelator−solvent interactions within the gel. It is consistent with the finding that the stilbene can photoisomerize within the gel whereas crystalline *trans*-stilbene derivatives generally do not isomerize. This is also consistent with the observation that a particular gelator can only gel selected solvents. Since the other 70% of solvent molecules are simply trapped between the fibers, it seems possible that another solvent might replace this part of mixture provided it does not dissolve the gelator molecules. The successful gelation of a mixture containing 30% octanol and 70% hexane (which alone is not gelled) by as low as 1% **1** supports this assumption. From molecular modeling, the length of **1** is estimated as 3.8 nm. The width of 6.2 nm for a single unit fiber suggests an aggregation model of **1** molecules as illustrated in Figure 2d, with 1.4 nm overlap of two cholesterol moieties at the center region and the stilbene chromophores extending out analogous to that proposed by Shinkai et al.[12] The one-dimensional helical stacking should provide the driving force to form the unit fibers. The chirality of the features was identified by the circular dichroism (CD) spectra for the gel as shown in Figure 2c, suggesting the stilbene units are organized a chiral array (Figure 2d). The idea that occasional association ("velcro"-like) between stilbenes extending out from adjacent stacks provides the adhesion linking unit fibers is reinforced by the previous reported evidence for stilbene aggregation (not possible within a single stack) in the gels but not the sols.[14]

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