Aligning Self-Assembled Gelators by Drying under Shear

Emily R. Draper,[a] Oleksandr O. Mykhaylyk[b] and Dave J. Adams[a],*

[a] Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD, U.K.

[b] Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

*Email: d.j.adams@liverpool.ac.uk

SUPPORTING INFORMATION

Instruments and Procedures

Preparation of LMWG Solutions

The gelator was added to 2 mL of water with an equimolar amount of sodium hydroxide (0.1 M, aqueous) to a concentration of 5 mg/mL. The solution was stirred until all the gelator was dissolved.

Hydrogel Formation

A pH switch method was used to form the hydrogels. Solutions were prepared as above. The solution was then transferred to a vial containing 5 mg/mL of glucono-δ-lactone (GdL) and shaken gently. The sample was then left to stand overnight to allow gelation to occur. For gels formed on the rheometer under shear the solution was prepared as above, but instead of leaving overnight it was transferred onto the bottom plate of the rheometer and the geometry lowered on top.

Rheological Measurements

Dynamic rheological and viscosity measurements were performed using an Anton Paar Physica MCR101 and MCR301 rheometer. A cone and plate measuring system was used to perform viscosity measurements and gelling under shear. A parallel plate measuring system was used for time sweeps. For time sweeps and gelling under constant shear, the gels were prepared in a vial and transferred onto the bottom plate. All experiments were performed at 25 °C.

Gelling under shear and shear aligning: Shear aligning experiments were performed using a 25 mm cone geometry with a piece of glass secured to the bottom plate. A constant shear rate of 10 s^{-1} was applied to the samples and a viscosity measurement recorded every 30 seconds. For shear aligned solutions these measurements were done for 16 hours. For shear aligned gels this was done for between 2 and 3 hours.

Time sweeps: Time sweeps were performed with a 50 mm plate with a plate gap of 0.8 mm. Tests were performed at an angular frequency of 10 rad s^{-1} and with a strain of 0.5 %. The top plate was flooded with mineral oil to prevent the sample from drying.

Rheo-Optics: Measurements were performed at the University of Sheffield using a prototype mechano-optical rheometer (Anton Paar Physica MCR301 coupled with SIPLI technique) designed together with Anton Paar. The shear experiments were performed using a 25 mm torsional parallel plate with a gap distance of 0.2 mm, angular speed of 1.6 rad s^{-1} (maximum shear rate of 100 s^{-1}) and a duration of the shear pulse 30 seconds. A total of 320 frames were taken at 0.2 seconds per frame. A halogen lamp (white light source) was used for the sample illumination.

pH Measurements

A FC200 pH probe (HANNA instruments) with a 6 mm x 10 mm conical tip was used for pH measurements. The stated accuracy of the pH measurements is ±0.1. For pH measurement during gelation pH was recorded every minute until a gel was formed. The temperature was maintained at 25 °C during the titration by using a circulating water bath.

Optical Microscopy under Cross-Polarised Light

Optical microscope images were collected using a Nikon Eclipse LV100 microscope with a Nikon TU Plan ELWD 50x/0.60 lens attached to an Infinity2-1C camera, with both polariser on. Samples for optical microscopy were prepared on glass microscope slides and allowed to dry for 24 hours before imaging.

Photoconductivity Measurements

Photoconductivity measurements were performed using a Palmsens^3 Potentiostat operating in a two electrode configuration in the absence of a supporting electrolyte. A 365 nm LED (LedEngin Inc, LZ1-10U600) with a light source powered by a TTi QL564P power supply operating at 1.0 W was also used as a light supply. Linear sweep measurements were recorded from -4 V to 4 V at a scan rate of 0.05 V/s and a preconditioning step at 0.002 V for 2 seconds. Xerogels were prepared *via* the pH switch method as previously described. Once the gels were formed approximately the same volume of each gel could be placed onto a glass slide between two silver electrodes spaced 3 mm apart. The silver electrodes were made using silver paste which attached copper wires to the glass slide. The gel was then allowed to dry in air

overnight to form a xerogels, shown in Fig. SX. Epoxy resin glue was placed over the silver electrodes. Again, this was left to dry overnight.

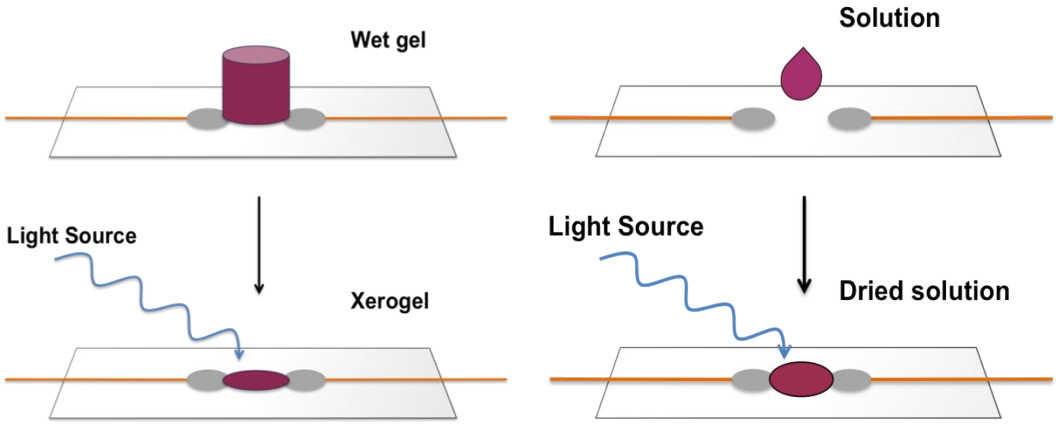

Figure S1. Experimental set up for measuring the photoconductivity of xerogels and dried solutions.

The counter and reference electrode clips were connected to one copper wire and the working on the other copper wire to make a two-electrode experiment. Dried solutions at pH 10 were prepared as previously mentioned but placed between the copper wires on the glass slide. For 'on-off' experiments, a cover was placed over the lamp for 'off' and then removed for 'on'.

For directional dependence measurements silver electrodes were placed 3 mm apart with and against the alignment of the samples, this was determined using the optical microscope to place the electrodes. For not aligned samples electrodes were places left and right of the sample and at the top and the bottom of the sample as shown below and in the Fig. S1 and S2.

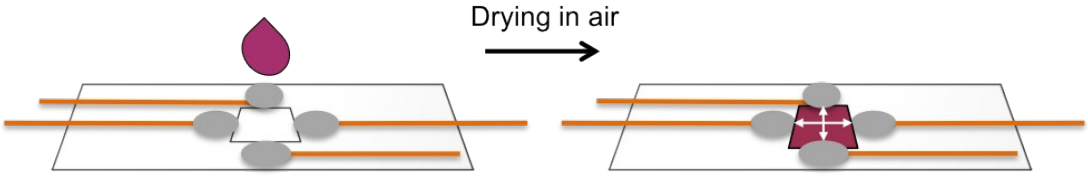

Figure S2. Experimental set up of conductivity of aligned samples. Silver electrodes are placed on all sides of the sample. Arrows indicate the direction of the measurement taken.

Profilometry

Profilometry measurements were carried out using an Ambios XP-200 profilometer. Samples were prepared using a mask, or by cutting the sample with a scalpel to get a clean edge.

Spin Coating

The spin coater used was a Laurell Technologies Corporation WS-650 Series Spin Processor. Spin coating was performed using 50 μL of solution **1** at various concentrations on glass cut to size. Samples were span at 800-10,000 rpm for 30-60 seconds.

UV-Vis Absorption Measurements

Solution UV-Vis absorption data was measured using a Thermo Scientific Nanodrop 2000/2000c spectrophotometer. The spectrophotometer was used in cuvette mode were samples were prepared in PMMA plastic cuvettes with a pathlength of 1.0 cm. Aqueous samples were prepared at high pH using equimolar amounts of 0.1 M aqueous NaOH solution to gelator and made up to 2 mL with distilled water. A concentration of 5 mg/mL of a gelator was used for aqueous solutions and a dilution series was made for a calibration curve. To investigate whether absolute amount of material had an effect on conductivity a series of samples were prepared and the conductivity measured. The sample was then re-dissolved in high pH water and the UV-vis absorption measured and the concentration determined from the calibration curve.

Scanning Electron Microscopy and Image Analysis

SEM images were obtained using a Hitachi S-4800 FE-SEM. Dried gels and solutions were prepared as above. A small section of the slide was cut and stuck onto aluminum SEM stubs using carbon tabs. Images were collected in deceleration mode. Images were analyzed using the image analysis software ImageJ, with the plugin OrientationJ.

Supplementary Figures

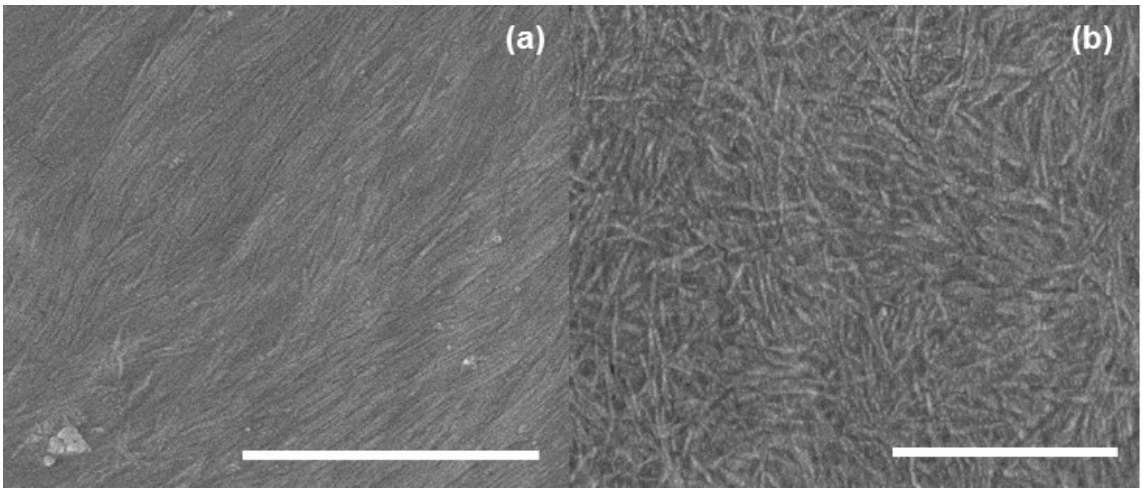

Figure S3. SEM images of (left) dried solution of 1 showing worm-like micelles and (right) xerogel-**1** showing entangled fibres. In both cases, the scale bar is 1 μm.

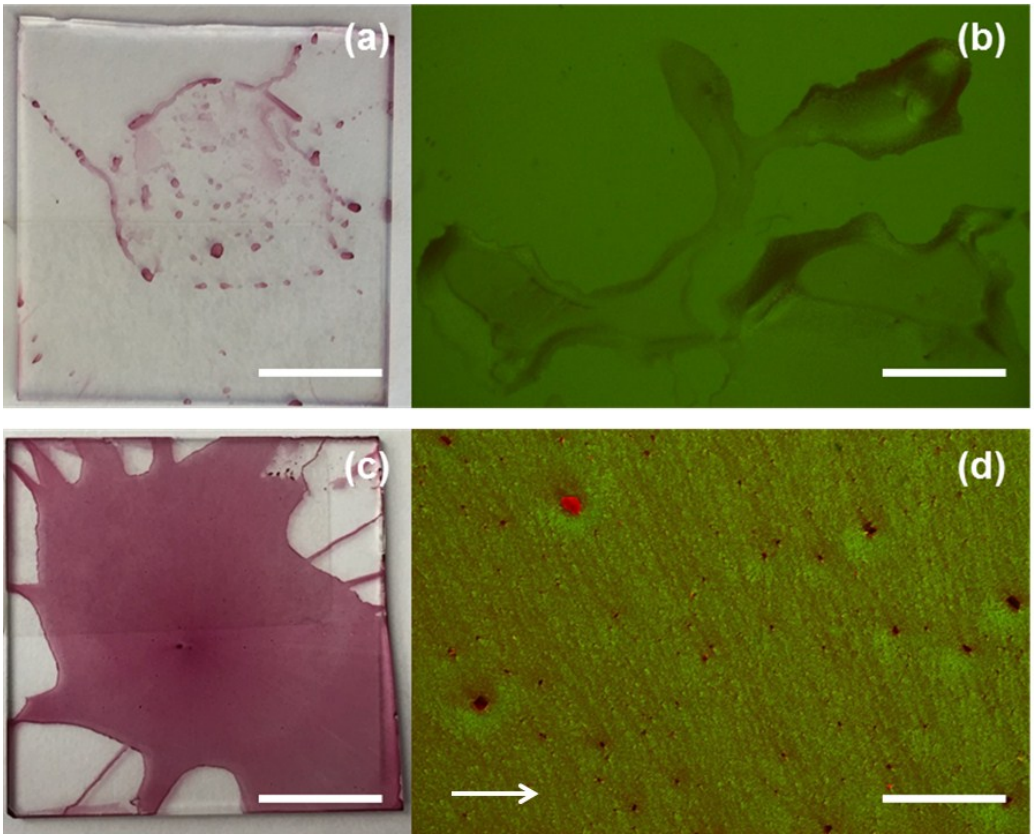

Figure S4. Photographs of spin coated films of solution of **1** (a) at 5 mg/mL (c) at 50 mg/mL. Scale bar represents 1 cm. Spin coated films microscope images under cross-polarised light (b) at 5 mg/mL and (d) at 50 mg/mL. Scale bar represent 0.5 mm. Spin coating was performed at 1800 rpm for 30 seconds. The arrow in (d) shows the orientation of the polars on the polarized light image (PLI).

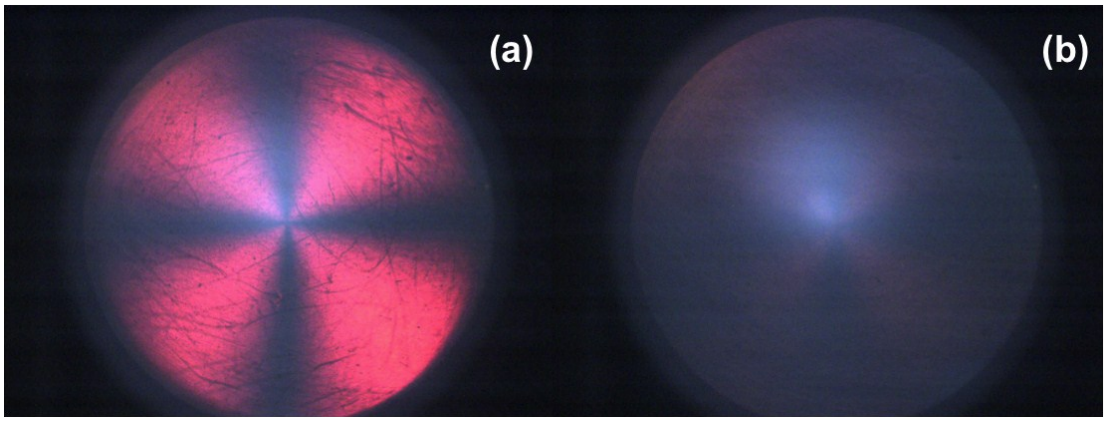

Figure S5. Polarised light images (PLIs) of solutions of **1** in water at pH 9 under shear using a 25 mm parallel disks rotating at angular speed of 1.6 rad s^{-1} with (a) a 0.2 mm gap distance and (b) a 0.5 mm gap.

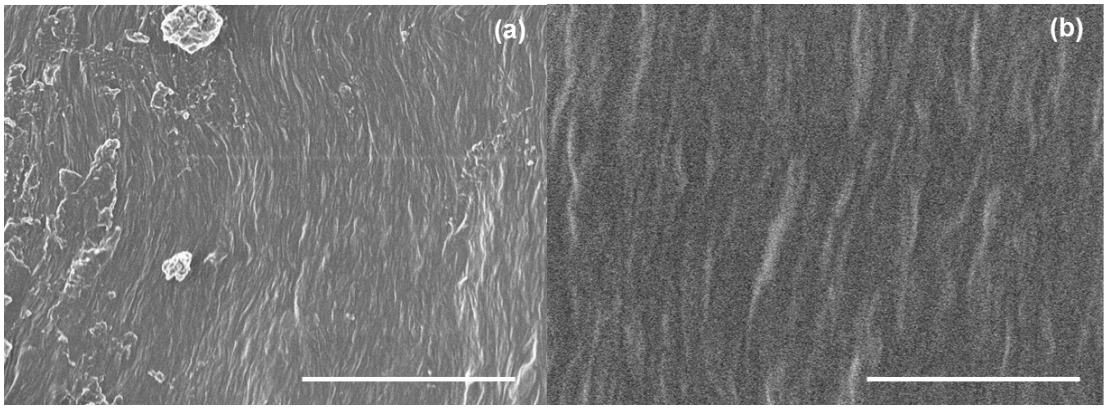

Figure S6. Representative SEM image of a dried aligned solution The scale bar in (a) represents 5 μm and (b) 1 μm.

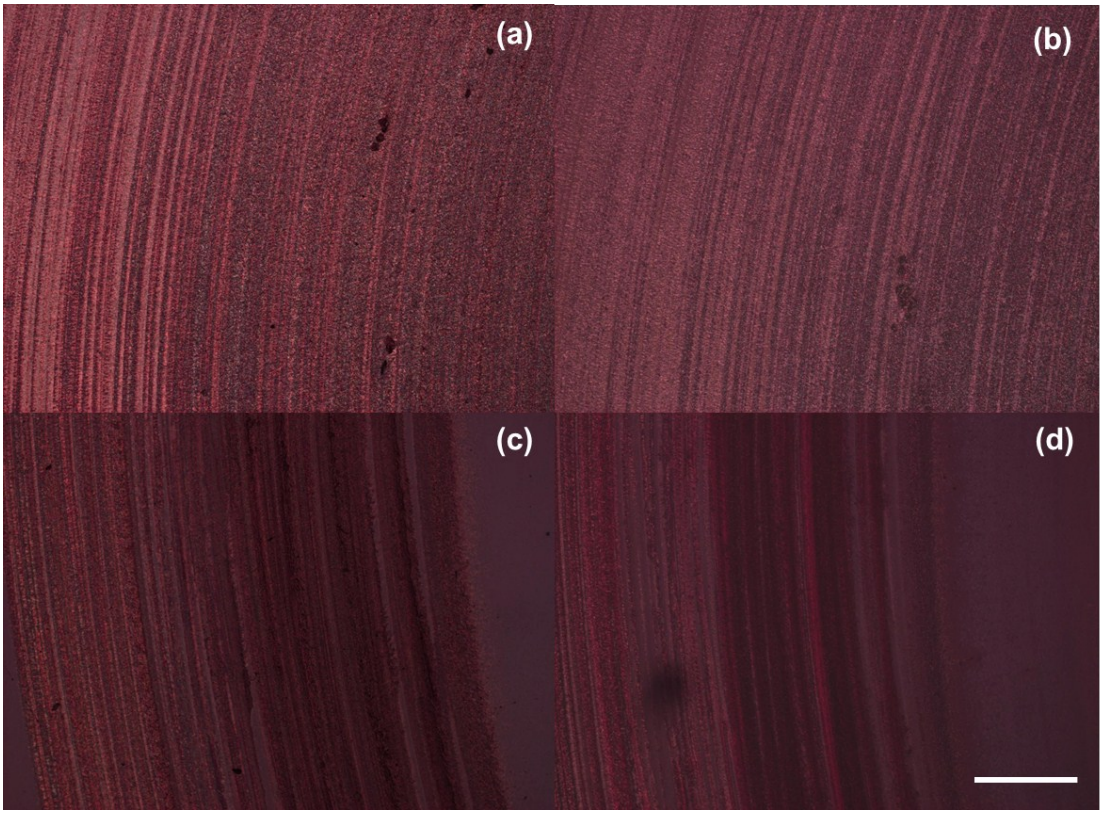

Figure S7. Images showing the top and bottom of the glass slide for the aligned dried samples showing that the alignment is consistent throughout the depth of the sample. The samples were prepared on microscope slides as described above and imaged from both sides of the slide. (a) shows the top of the sample of the dried solution. (b) shows the bottom of the sample of the dried solution. (c) shows the top of the sample of the dried gel. (d) shows the bottom of the sample of the dried gel. The scale bar represents 400 μm in each case.

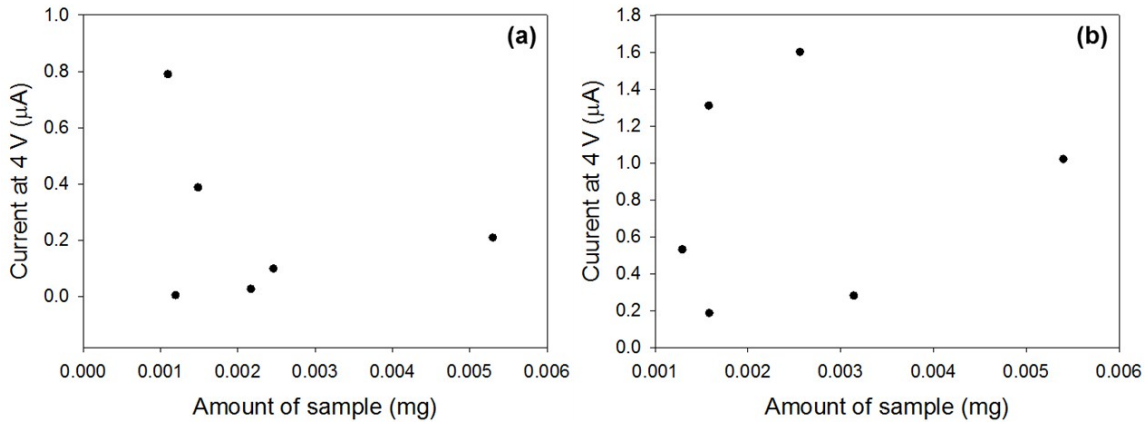

Figure S8. Current at 4 V under 365 nm LED compared to the concentration of sample between the silver electrodes for dried solution of **1** (a) against alignment and (b) with alignment.

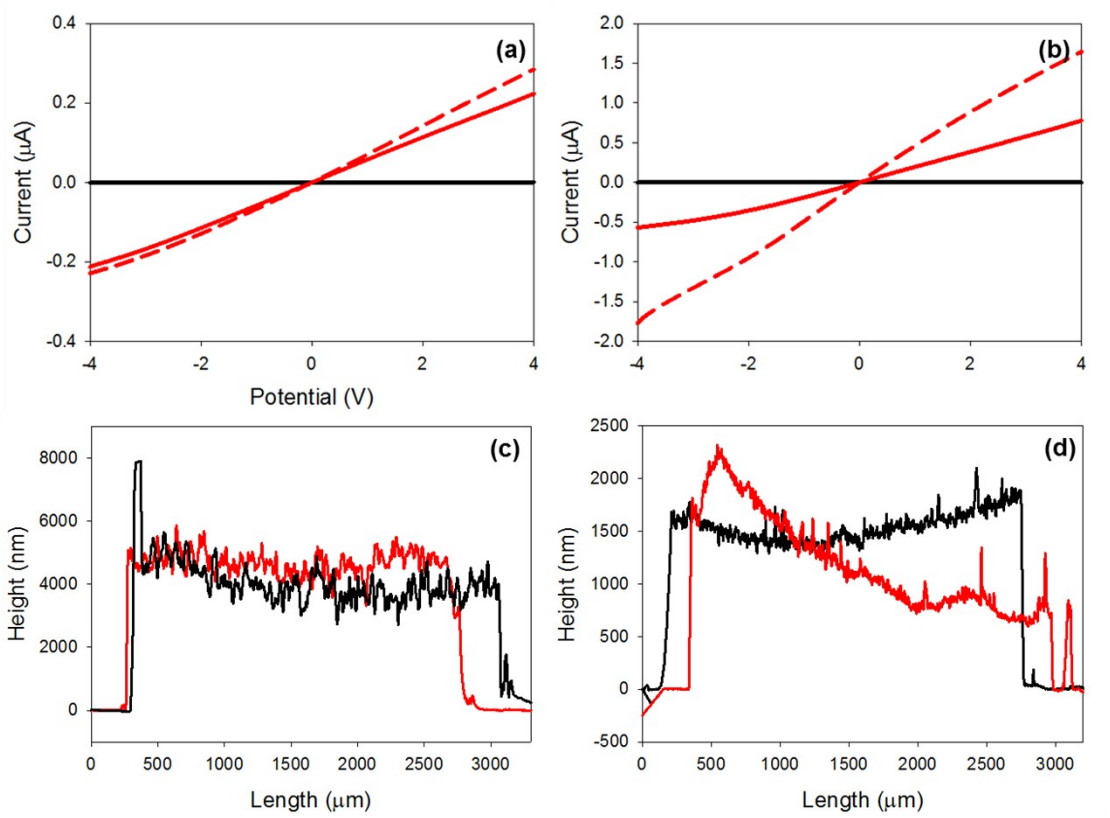

Figure S9. Photoconductivity of (a) xerogel-**1**, solid black line is measured in the dark, dashed red line is measured from left to right and solid red line is measured from top to bottom and (b) dried solution of 1, solid line is measured in the dark, dashed red line is measured with the alignment and solid read line against the alignment. Profilometry measurements of (c) xerogel-1, left to right (red) and top to bottom (black) and (d) dried solution of **1**, black data is with alignment and red data is against alignment.

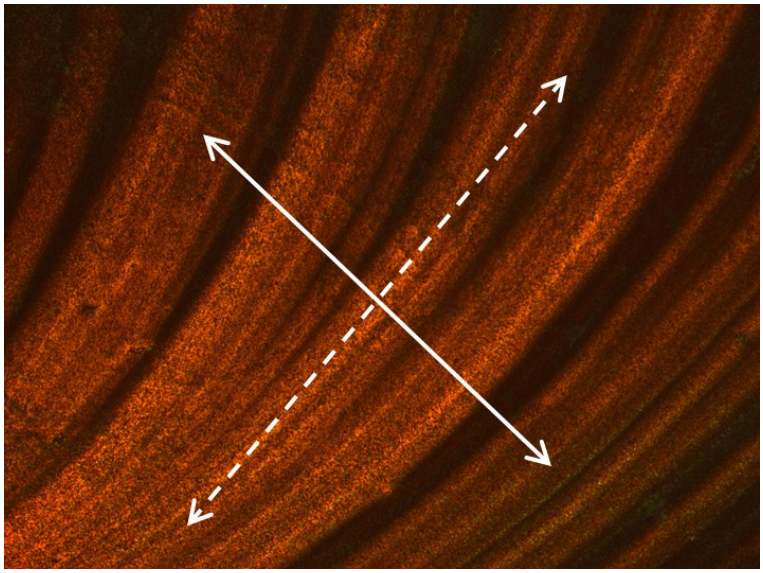

Figure S10. Optical microscope image showing the direction in which the measurements were recorded for the dried solutions, aligned via a coffee-ring effect. The dashed line is along the alignment and the solid line against the alignment.

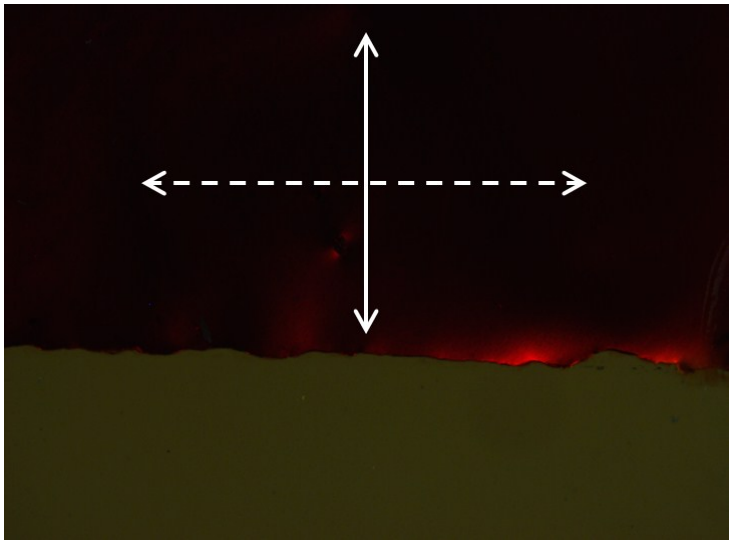

Figure S11. Optical microscope image showing the direction in which the measurements were recorded for the xerogels dried without a shear step.

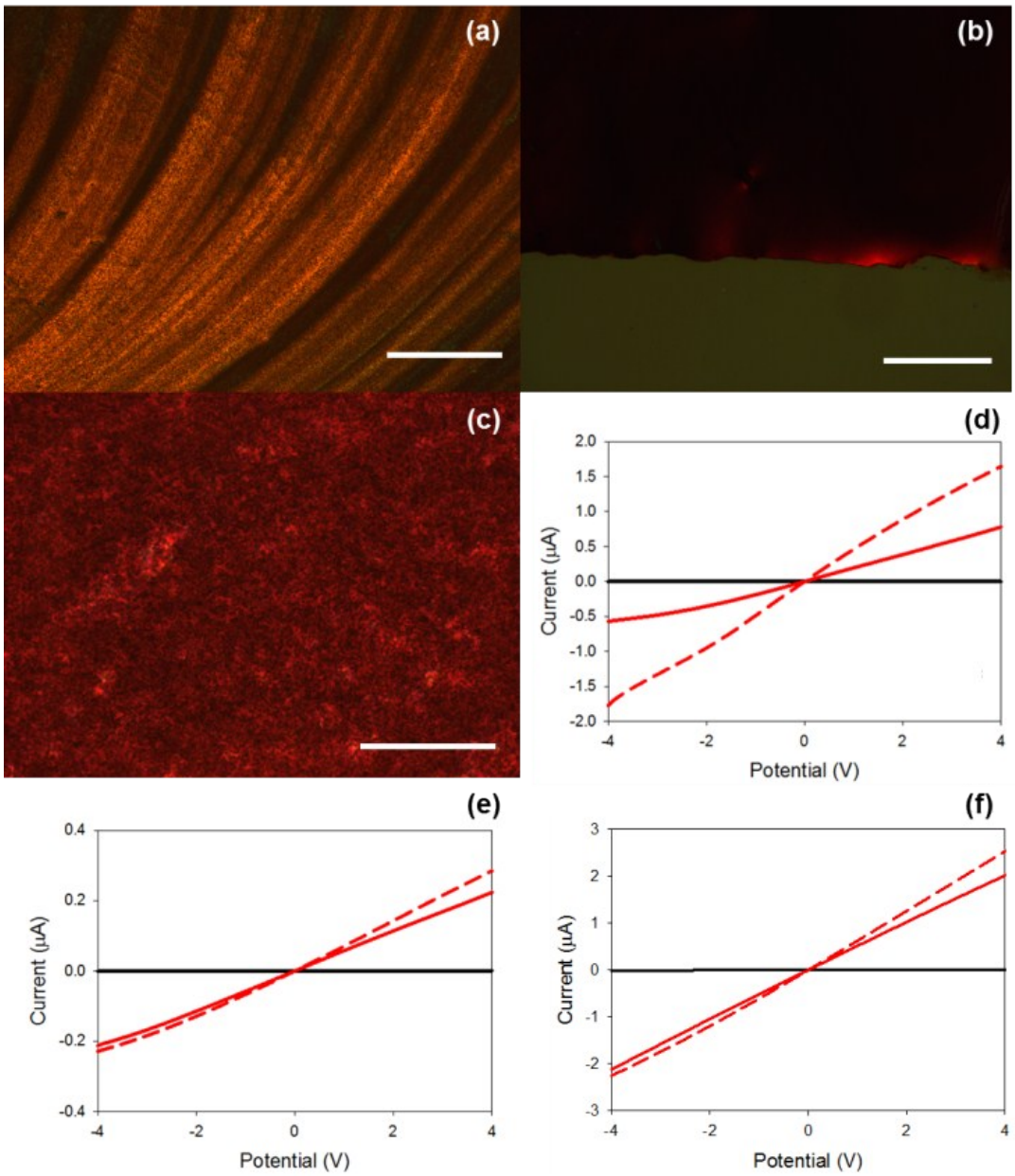

Figure S12. Microscope images taken under cross-polarised light of (a) dried solution of **1**; (b) xerogel-**1**; (c) solution of **1** dried in a square mask to remove alignment. In all cases, the scale bar represents 50 μ m. (d), (e), and (f) show the photoresponse of (a), (b), and (c) respectively. Black data is taken in the dark, red data is under illumination using a 365 nm light. The dashed red data are measurements recorded from left to right of the sample and solid red data recorded from the top to the bottom of the sample.

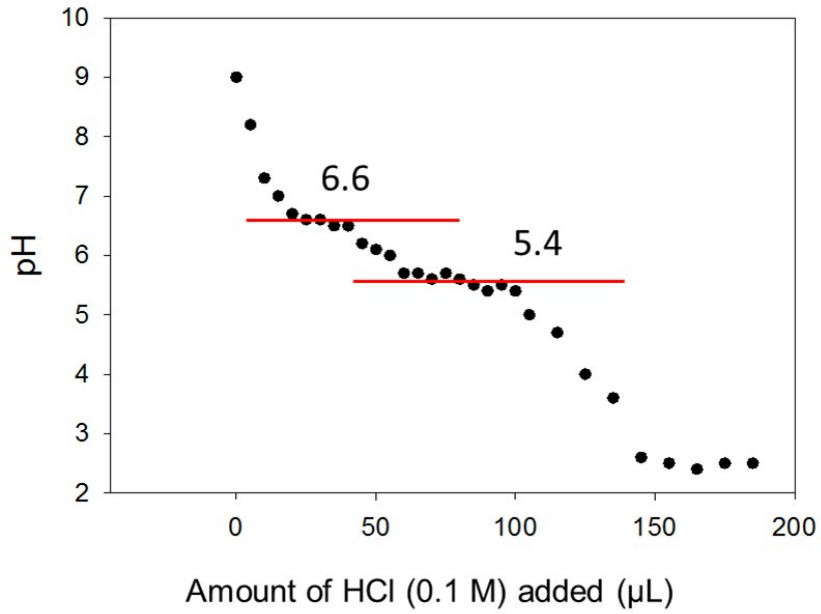

Figure S13. Decrease in pH for a solution of **1** after addition of HCl (0.1 M). Plateaus show the two pK_as of the gelator.

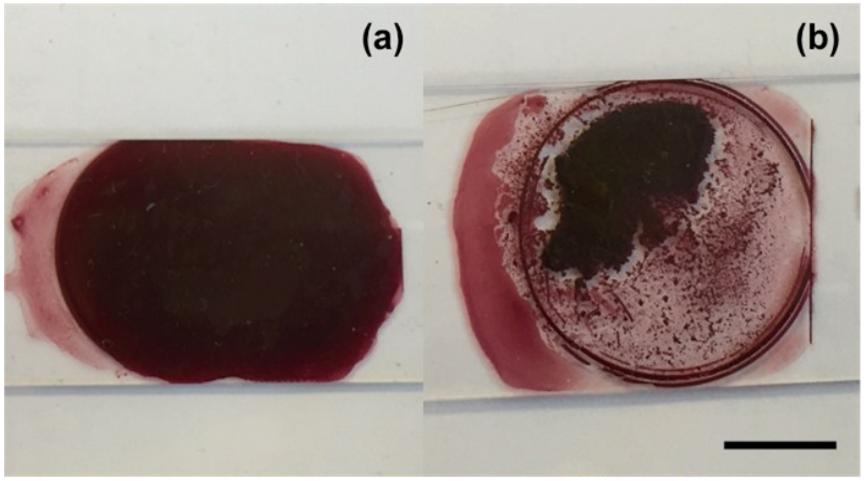

Figure S14. Photographs of shear aligned xerogel-**1** after shearing for (a) 1 hour 30 minutes and (b) 4 hours using a 25 mm cone at 10 rad/s. Scale bar represents 1 cm.

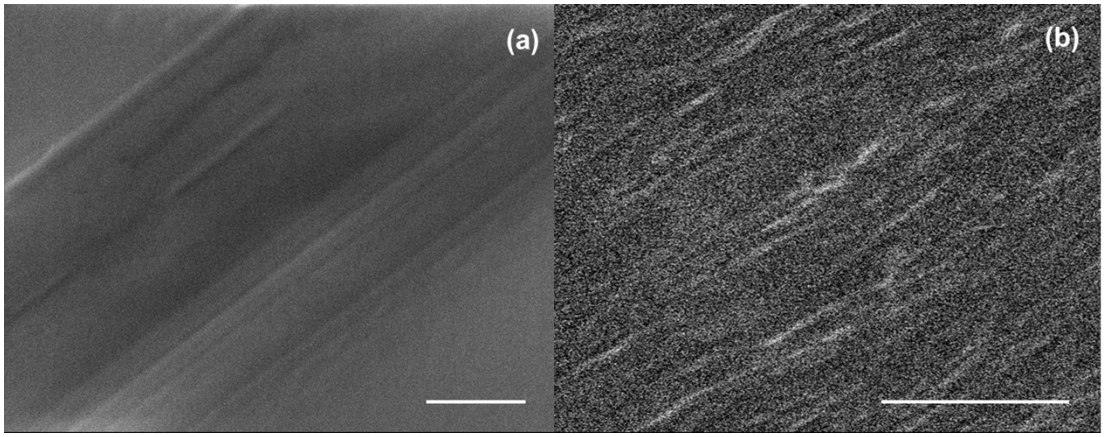

Figure S15. Representative SEM image of a dried aligned solution. The scale bar in (a) represents 10 μm and (b) 1 μm.

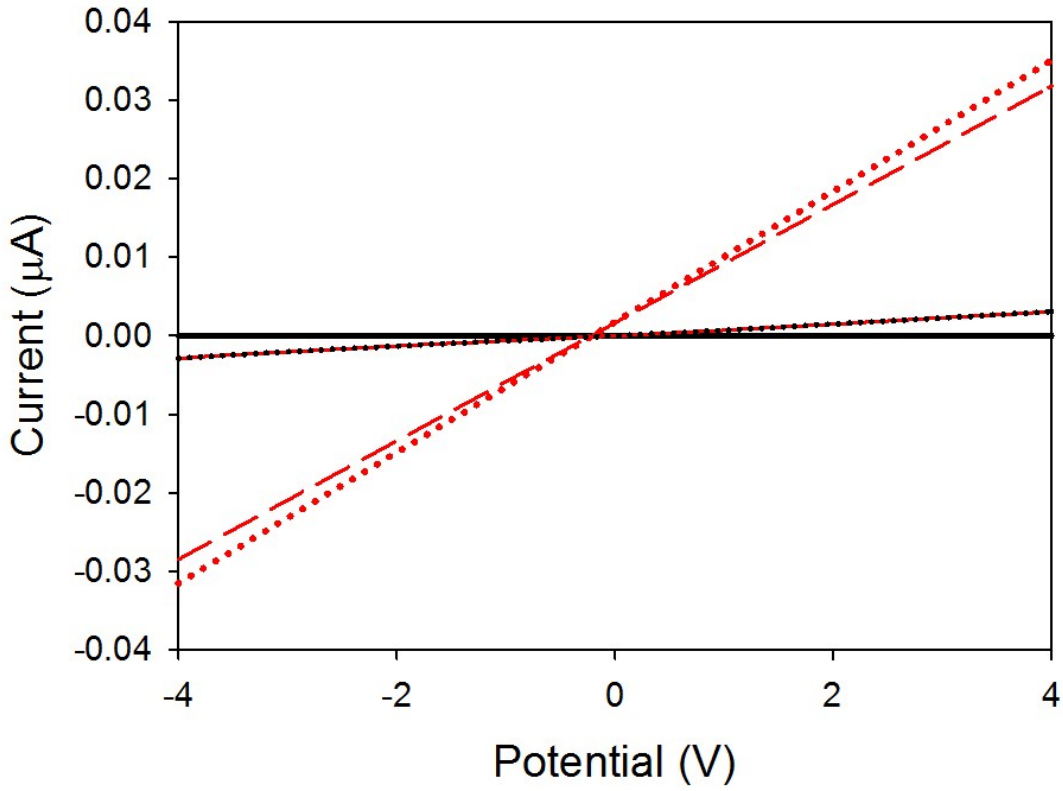

Figure S16. Photoresponse data for an aligned gel sample measured with alignment initially (dashed line) and 6 months later (dotted line), and against alignment initially (red solid line) and 6 months later (black dotted line). Solid black line the dark measurement.