

Electrochemically-triggered spatially and temporally resolved multi-component gels

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Supporting Information

Experimental Section

Chemicals: All LMWG were prepared as described previously.^[19b, 20a, 22] Deionised water was used throughout. All other chemicals were purchased from Sigma-Aldrich and used as received.

Sample Preparation: Stock solutions of LMWG (0.5 wt %, containing a final NaCl concentration of 0.1 M) at approximately pH 9 – 10 were prepared by adding dilute sodium hydroxide solution (NaOH, 1 molar equivalent of a 0.1 M solution) with stirring until fully dissolved. Upon full dissolution, the pH was lowered to ~ pH 8 using 1 M hydrochloric acid (HCl). Hydroquinone was added before beginning experiments (final concentration of 0.065 M).

Cyclic Voltammetry: All experiments were run using a Dropsens Potentiostat and a three-electrode system: the working electrode was a glassy carbon electrode; a platinum wire counter and a calomel reference electrode. Cyclic voltammetric (CV) measurements were carried out within a potential range of -0.2 to 1 V vs. a saturated calomel electrode at a scan rate of 40 mV/s. Each CV measurement consisted of one scan. For experiments using glass slides, the slides acted as the working electrode (FTO coated slides) and a printed electrode containing both the reference and counter electrodes completed the three-electrode system.

Potentiometry: For potentiometric experiments, 10 mL LMWG solutions were used, with either of the three-electrode systems mentioned above. The desired current was set and was run for 1000 s, unless stated otherwise. For the glassy carbon electrode set-up, gel growth

was monitored by taking images in 10 second increments (of the 1000 s period) using an Infinity 2-1C colour USB2 camera. The electrochemical cell and camera were mounted using clamps and backlit using LED torches. The images collected were processed using custom written Labview code capable of processing a series of images in batch mode. Essentially, the gel area was enhanced through subtraction of a background image and the resulting image subjected to a threshold procedure. Horizontal slices of the gel (1 pixel high) were taken and approximated as disc of gel. The sum of all slices of the visible gel is taken as the volume of the gel. Images were calibrated using the width of electrode. For pK_a vs lag time experiments, images were taken every 1 s and were manually analysed to pinpoint the time at which gelation began.

Rheological Measurements: Rheological measurements were made on an Anton Paar Physica MCR101 rheometer using parallel plates geometry with a 25 mm sandblasted plate. The gels were removed from the FTO-coated slide and transferred directly on to the plate using a microspatula. Frequency scans were performed from 1 rad s^{-1} to 100 rad s^{-1} under a strain of 0.5 %. The shear moduli (storage modulus G' and loss modulus G'') were measured at a frequency of 10 rad s^{-1} . All shear moduli measured were within the linear viscoelastic (LVE) region for the gels measured. Strain scans were performed from 0.1% to 100% under a frequency of 10 rad s^{-1} .

NMR Studies: LMWG solutions were prepared as previously described but using D_2O , NaOD and DCl in place of water, NaOH and HCl, respectively. Gels were prepared using potentiometric methods on FTO-coated glass slides before being transferred to NMR tubes. Gels were stirred to form a liquid before being pipetted into an NMR tube. An ethanol standard was added. NMR spectra were recorded using a Bruker DPX-400 spectrometer operating at 400 MHz for 1H .

Scanning electron microscopy: SEM images were recorded using a Hitachi S-4800 FE-SEM at 3 kV. Glass coverslips were stuck onto aluminium SEM stubs using carbon sticky tabs (Agar Scientific) and an aliquot of gel sample was then placed onto the surface of the glass (using a microspatula) and left to dry overnight. The samples were gold coated for 2 minutes at 30 μ A using a sputter-coater (EMITECH K550X) prior to imaging.

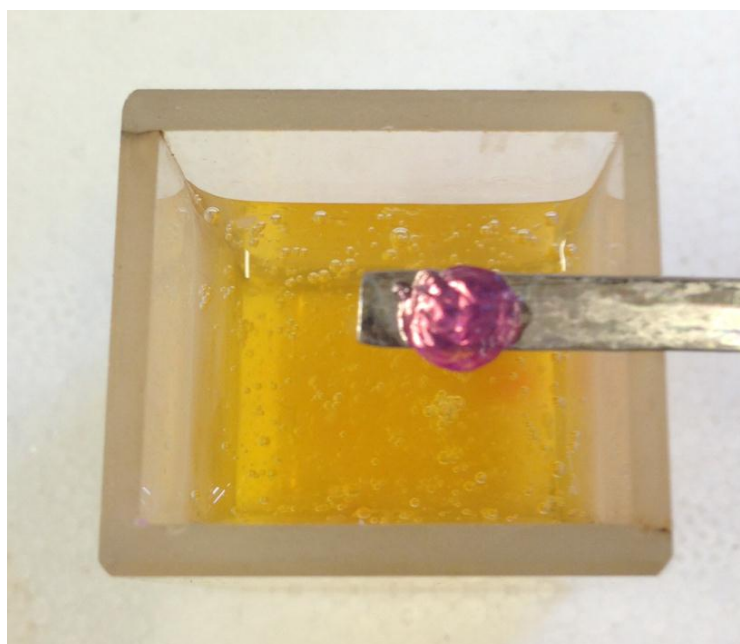


Figure S1 Photograph of gel grown on a glassy carbon electrode, dyed with Methyl Red. The gel was removed from the electrode using a spatula.

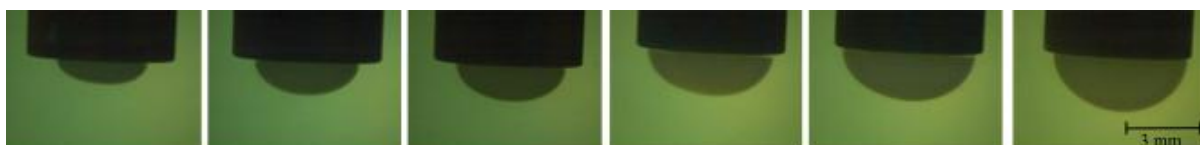


Figure S2 Photographs of gels of LMWG **1** grown on glassy carbon electrodes at different currents: (from left to right) 5 μ A, 10 μ A, 30 μ A, 40 μ A and 50 μ A. All gels were grown for 1000 s.

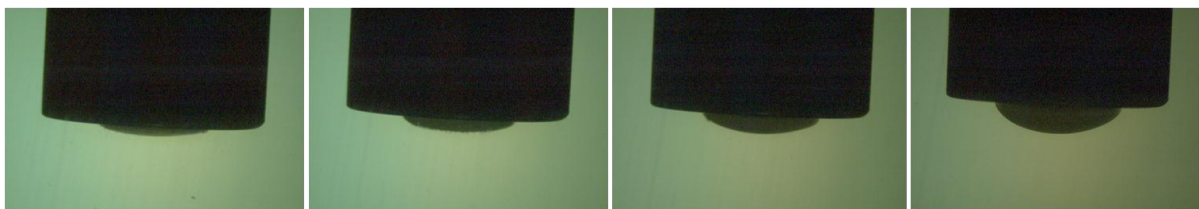


Figure S3 Photographs of gels of LMWG **2** grown on glassy carbon electrodes at different currents: (from left to right) 20 μA , 30 μA , 40 μA , 50 μA . All gels were grown for 1000 s.

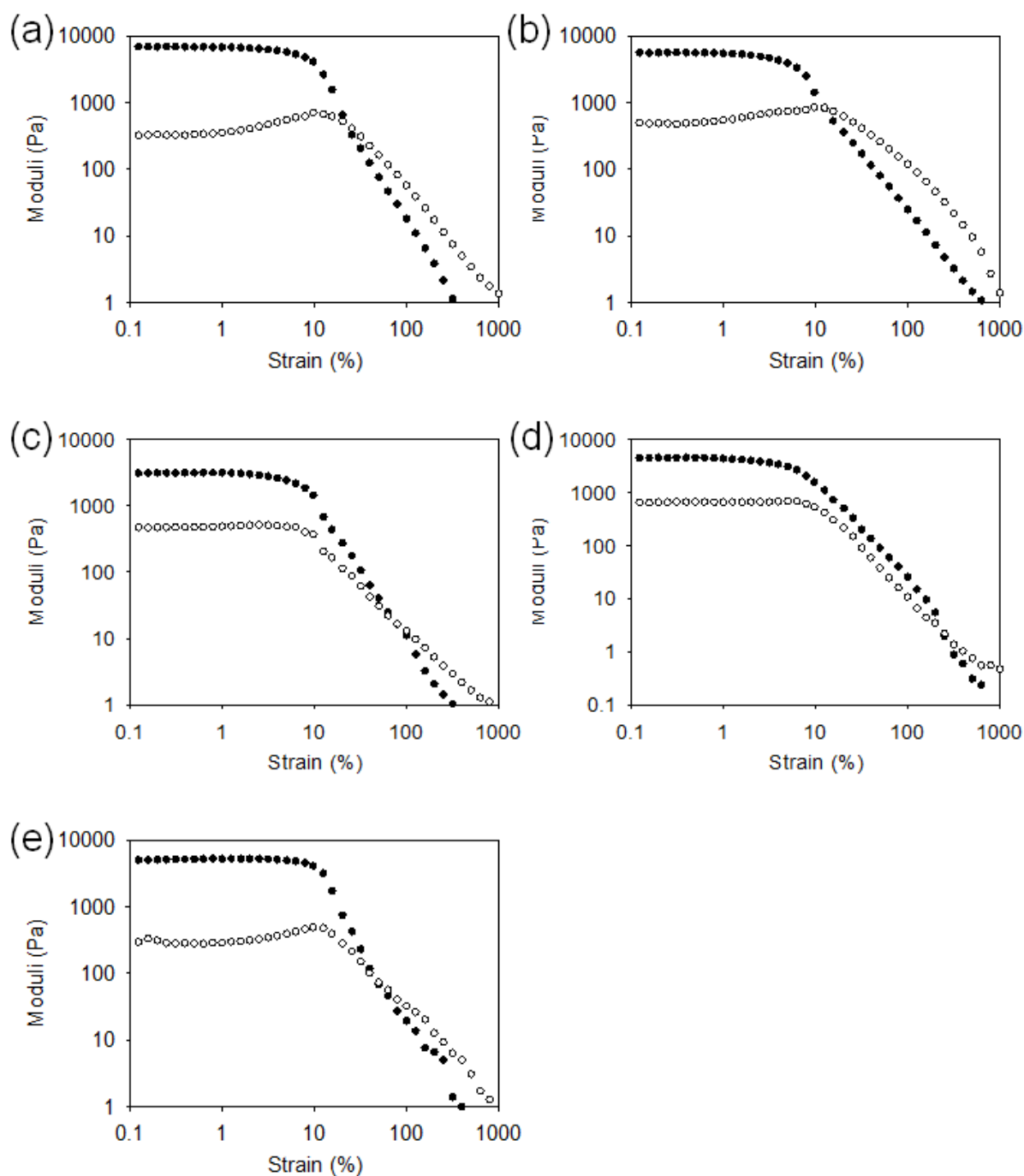


Figure S4 Strain sweeps for hydrogels prepared from different LMWG prepared on an ITO glass slide (using a current of 1000 μ A for 1000 s). Gelators: (a) gelator **1**, (b) gelator **2**, (a) gelator **4**, (b) gelator **5**, (a) gelator **6**. Note gels formed from LMWG **3** were too weak to remove and measure. In all cases, (\bullet) represents G' and (\circ) represents G'' .

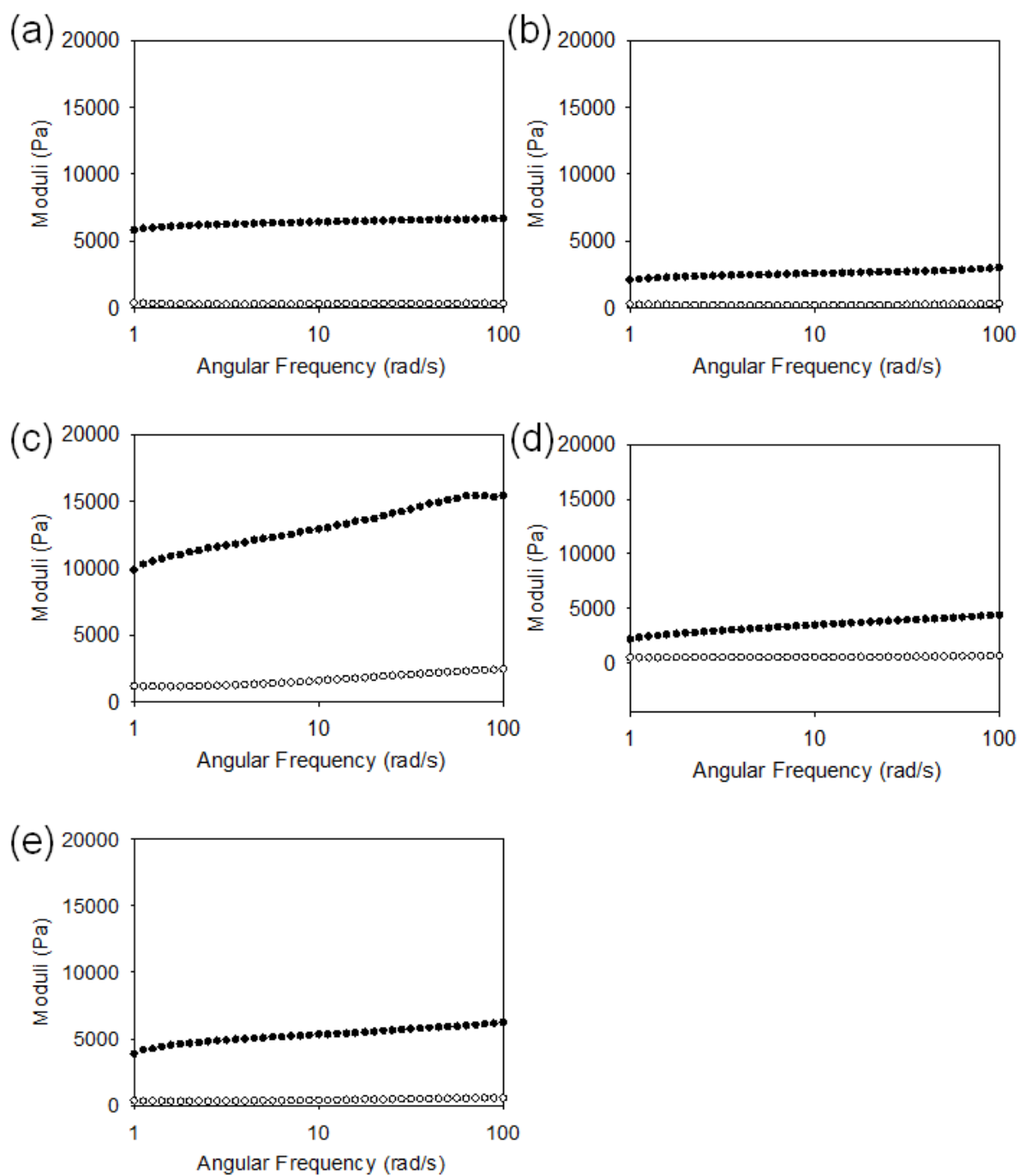


Figure S5 Frequency sweeps for hydrogels prepared from different LMWG prepared on an ITO glass slide (using a current of 1000 μA for 1000 s). Data collected at a strain of 0.5 %. Gelators: (a) gelator 1, (b) gelator 2, (a) gelator 4, (b) gelator 5, (a) gelator 6. Note gels formed from LMWG 3 were too weak to remove and measure. In all cases, (\bullet) represents G' and (\circ) represents G'' .

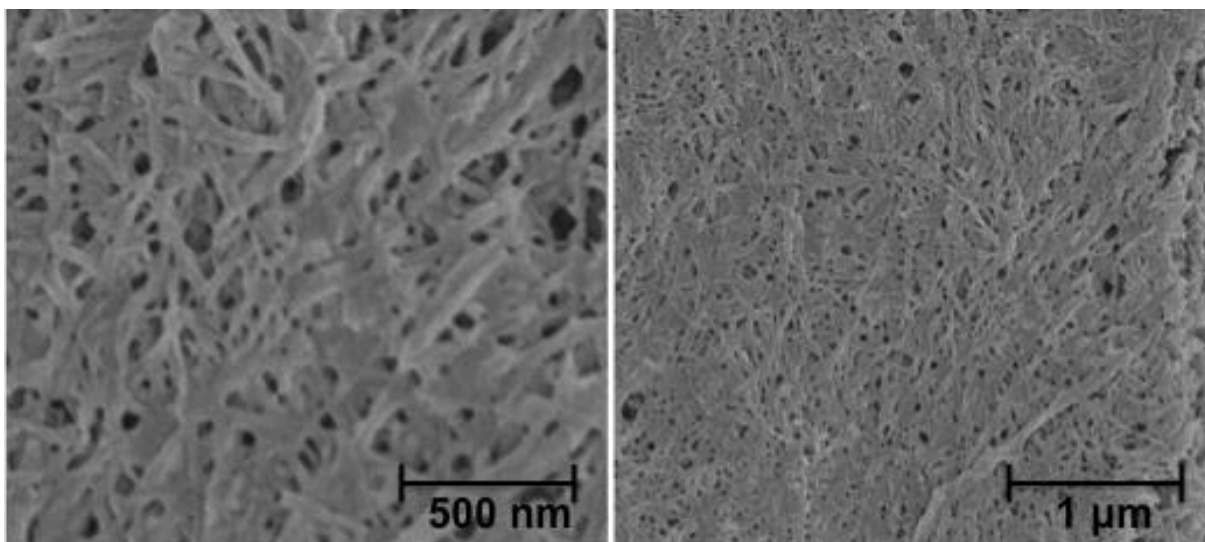


Figure S6 SEM of gels formed using **1** grown on a FTO-coated glass slide at a current of 2000 μA for 1000 s.

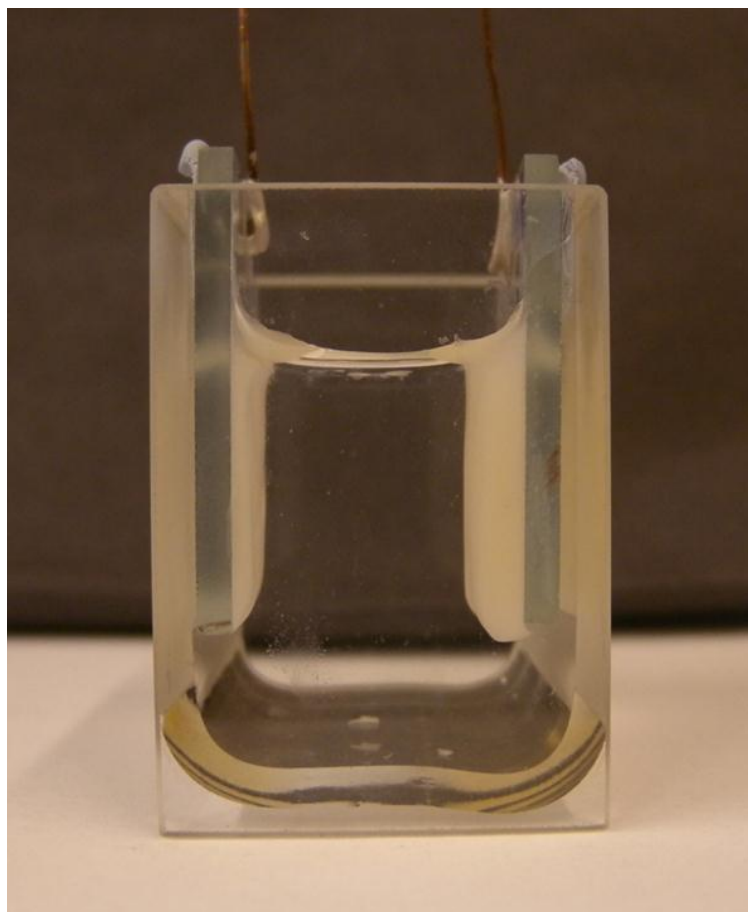


Figure S7 Two gels of different thickness grown using **1** in parallel on two conductive glass slides at (left) 1250 for 100 s and (right) 2000 μA for 300 s.

Current (μA) ^a	Time (s)	G' (Pa)	G'' (Pa)	pH
644	1000	4600	300	3.9
1288	800	6500	500	3.2
1932	800	8000	600	2.9

Table S1. Rheological properties of gels grown on glass slides at different rates by varying the current. The gel thicknesses were controlled and hence the time taken for gel formation are different. ^a Currents used have the same current densities as that of 10 μA , 20 μA and 30 μA respectively on the smaller glassy carbon electrodes.