Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

SUPPORTING INFORMATION

Stable and Transient Self-Propagating Supramolecular Gelation

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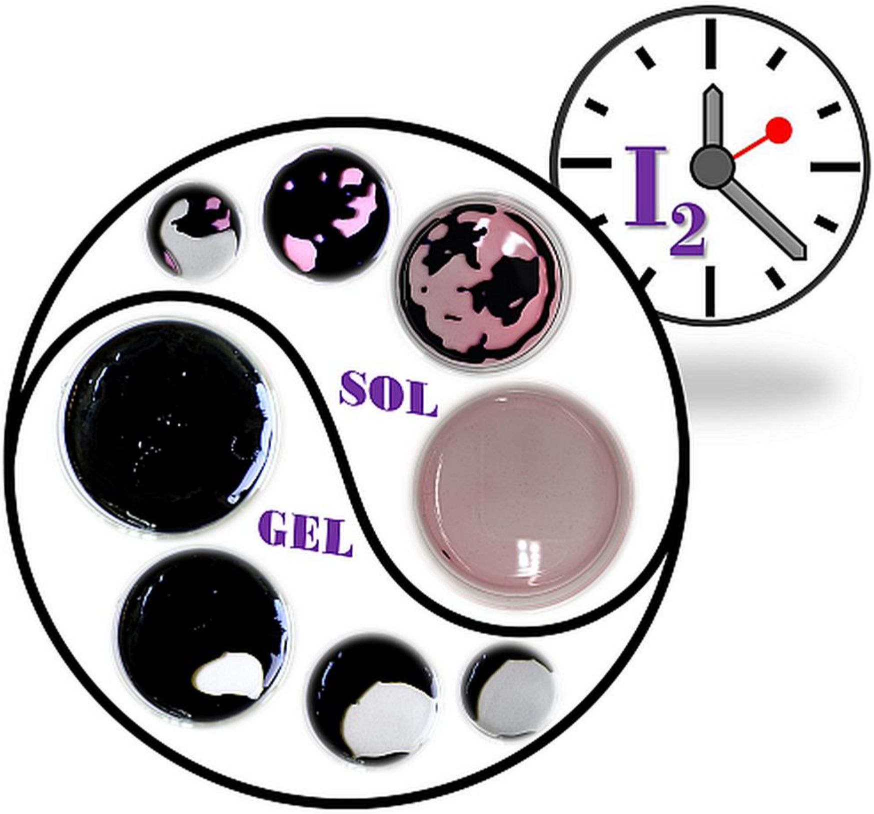

EXPERIMENTAL

Materials and Methods

Poly(vinyl alcohol) (PVA) with different molecular weights were purchased from Sigma-Aldrich (Switzerland): average M_W 130 kDa, 99+% hydrolysed (PVA 130 kDa); M_W 89–98 kDa, 99+% hydrolysed (PVA 98 kDa), average M_W 13–23 kDa, 98% hydrolysed (PVA 23 kDa). Sodium iodate $NaIO_3$ (puriss. p.a., ≥99.5%), hydroxymethanesulfinic acid monosodium salt $HOCH_2SO_2Na$ dihydrate (HMSNa), sodium bisulfate $NaHSO_4$ monohydrate (99%), δ-gluconolactone (GL, meets USP testing specifications) and bromocresol green (BG, dye content 95%) were also purchased from Sigma-Aldrich (Switzerland). Methyl yellow (MY, indicator grade) was obtained from Alfa Aesar. Water (resistivity ≥ 18 MΩ) was purified by means of a MilliQ system. Unless otherwise noted, all chemicals were of analytical or reagent grade purity, and were used as received from commercial sources.

All the experiments were performed at room temperature (23 ± 1 °C). Stock solutions of each poly(vinyl alcohol) with 7 wt% concentration (1.6 M based on the repeating unit) were prepared by dissolving the polymer in water. Dissolution was aided by warming (up to 90°C) the mixture in a water bath for 3-4 hours, then it was left under stirring at room temperature overnight. Eventually, the solution was centrifuged for 30 min at 7000 rpm to remove undissolved residues. Aqueous stock solutions were also prepared for $NaIO_3$, $NaHSO_4$ and HMSNa (**Table S1**). None of the stock solutions mentioned above was stored longer than five hours at room temperature avoiding direct light. The indicator solutions were prepared as follows. Methyl yellow MY (0.018 g) was dissolved in ethanol (8 mL), and bromocresol green BG (0.01 g) was dissolved in a 50:50 (v:v) ethanol:water mixture (8 mL).

Table S1. Composition of some stock solutions used for the experiments.

Reagent	*Concentration of stock solution (M)*	*Mass (g)*	*Volume H_2O (mL)*
$NaHSO_4$	0.05	0.069	10
$NaIO_3$	0.5 0.45	0.989 0.268	10 3
HMSNa	2.0 1.43	1.541 0.661	5 3

Self-propagating fronts triggered by the external addition of acid. The experiments were performed in Petri dishes and in graduated cylinders. The reaction mixtures were prepared by mixing 3.5 mL of PVA 7% stock solution with two drops of both MY and BG solutions (control experiments showed that the indicator mixture had no influence on the system), and 1 mL of $NaIO_3$ stock solution (0.5 or 0.45 M depending on the desired final concentration) in a 15 mL glass vial. Mixing was provided by a PTFE-coated magnetic stirring bar rotating at about 900 rpm. Then, 0.5 mL of HMSNa stock solution were added and the reaction mixture was stirred for about 1 min. Eventually, 4 mL of this reaction mixture were transferred into a Petri dish (diameter: 5 cm), or in a 5 mL graduated cylinder, and 7 µL of 0.05 M $NaHSO_4$ solution were dropped in the centre of the reaction mixture. Each experiment was repeated at least twice.

Stable gel formation. In one set of experiments sodium bisulfate $NaHSO_4$ was used as the acid source (concentrations tested: 3, 4, and 5 mM), while in another set δ-gluconolactone (GL) was used as a slow *in situ* acid generator (**Table S2**). The experimental procedure was similar in both cases, but GL was dissolved directly in 3.5 mL of the PVA 130 kDa stock solution. Then, 1 mL of iodate 0.5 M stock solution and 0.5 mL of 2 M HMSNa stock solution were added, stirred for 1 min, then 4 mL of the reaction mixture were transferred into a 5 cm-diameter Petri dish or in a graduated cylinder. The experiments were repeated at least three times.

Table S2. Concentrations of δ-gluconolactone (GL) used for stable gel formation experiments.

Final GL concentration (mM)	*Mass of GL (g)*	*Volume of the reaction mixture (mL)*
75	0.0660	5
100	0.0893	
200	0.1785	

Transient gel formation. In 5 mL of the 0.5 M $NaIO_3$ stock solution, 0.034 g of $NaHSO_4$ were dissolved (final $NaHSO_4$ concentration 0.05 M). Then, 1 mL of this iodate-bisulfate solution was added to 3.5 mL of the PVA 130 kDa stock solution, together with two drops of both MY and BG solutions (control experiments showed that the indicator mixture had no influence on the system). Eventually, 0.5 mL of the HMSNa 2 M stock solution were added, the reaction mixture was stirred for 5 s, and 4.8 mL were pipetted in a 5 cm-diameter Petri dish or in a graduated cylinder. It was not possible to make reliable rheological studies for this transient system due to its excessively short induction time. The experiment was repeated at least three times.

pH Measurements. A Hanna Instruments (USA) HI5222-02 benchtop pH-meter was used together with a HI1330B glass body combination pH microelectrode from the same company. The pH-meter was calibrated with standard buffer solutions (pH values: 1.670, 4.010, 7.010 and 10.01) before each set of analyses. The pH-electrode was cleaned after each analysis by repeated immersion in water, the excess water gently removed with hairless paper and immediately immersed in the solution to analyze. The pH-meter was interfaced with a computer through the software HI92000 – 5.0.38 (Hanna Instruments, USA) to allow continuous recording of pH values with a time interval of 1 s.

Characterisation by rotational rheometry. Rheological experiments were conducted on a MCR 302 stress-controlled rheometer from Anton Paar (Graz, Austria) at a fixed temperature of 25 °C. A PP40 (diameter = 39.969 mm) plate was used as the top geometry together with a Peltier temperature-controlled bottom plate (P-PTD 200). The gap size was set to 1 mm. The reaction mixture was pipetted into the rheometer. Due to its viscosity, the sample volume varied between 1.9 mL and 1.7 mL. These sample volumes led to a slight overfilling of the measuring gap. However, the fluid outside of the PP40 did not make a significant contribution to the measured signal. To reduce evaporation, the sample was covered with a Peltier temperature-controlled hood (H-PTD 200). The time delay after the addition of the last reagent (usually HMSNa) and before the start of the measurement was later added to each time point of the data set. Keeping this time delay as short as possible did not allow for a more precise filling of the measuring volume by varying the gap. The gelling behaviour was monitored by performing a dynamic oscillatory time sweep experiment in the linear viscoelastic region of the material. Throughout the time sweep constant oscillations at a fixed frequency of 10 rad/s were applied with a strain of 10%. Rheology data were acquired while the material was evolving into a stable gel. First data points were collected every second over a time frame of one hour, then the interval was increased to 10 s. Experimental data acquisition was stopped once the storage and loss modulus had reached a stable value. All rheological measurements were repeated three times.

The final storage modulus values are determined by fitting the G’ curves with an empirical model developed by X. Cao *et al.* (eq. S1) [1]:

$$G' = G'_{\infty}\left(1 - exp\left[-\alpha\left(t/t_{gel} - 1\right)^{\beta}\right]\right) \tag{S1}$$

The fit parameters are the final modulus (G'_{∞}), the rate of increase of G’ (α) and an exponential coefficient (β). The calculated curves match well the experimental data for times beyond the gel point $\left(t > t_{gel}\right)$.

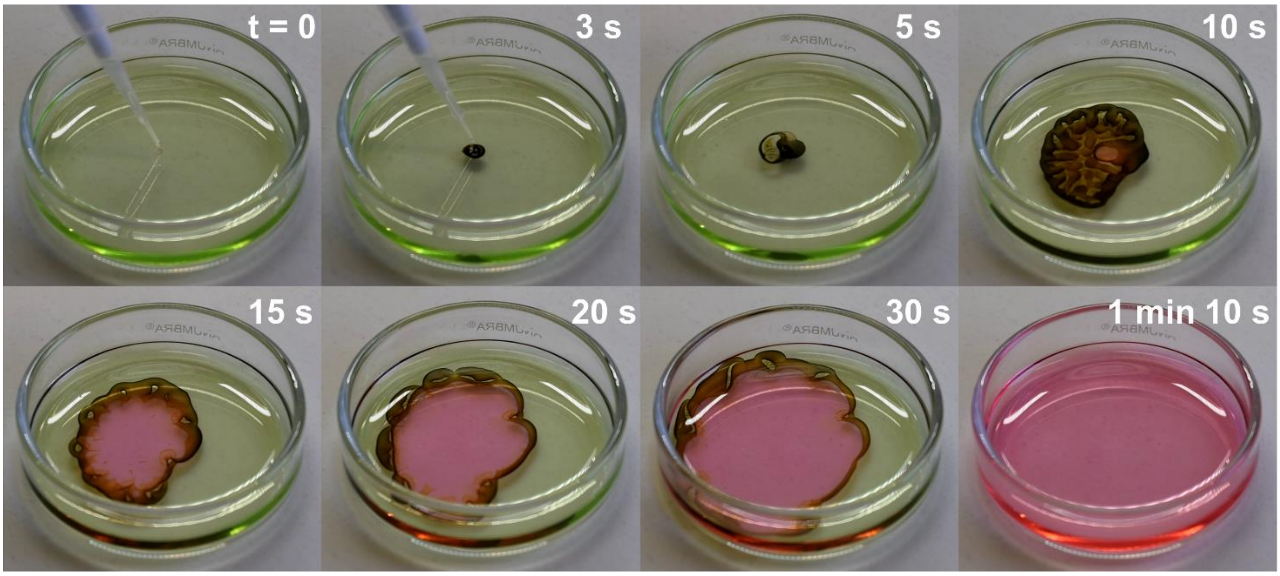

Figure S1. Front instabilities observed for the iodate-HMS-PVA system when PVA 98 kDa was used. Conditions: iodate 100 mM, HMSNa 200 mM, 5% PVA 98 kDa, mixture of MY and BG. The reaction was triggered with 7 µL of 50 mM sodium bisulfate. The diameter of the Petri dish is 2.5 cm. The snapshots were taken from **Movie S5**. *Caeteris paribus*, the behavior or PVA 23 kDa was the same as that of PVA 130 kDa. Noteworthy, the same kind of front instabilities could be observed with PVA 130 kDa and PVA 23 kDa as well, but they occurred much more rarely compared to when PVA 98 kDa was used.

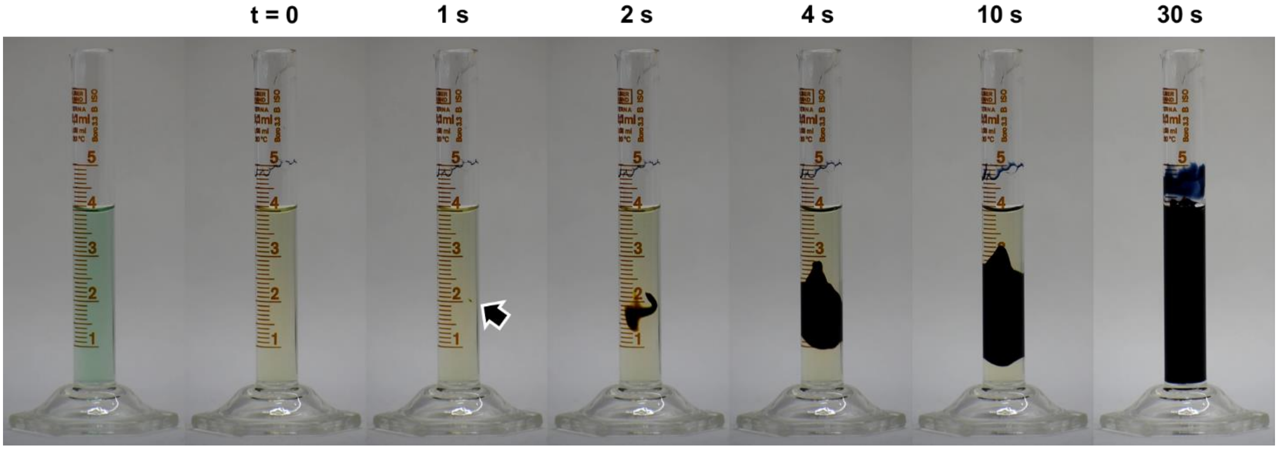

Figure S2. Stable gel formation in the iodate-HMS-PVA-GL system. The color change from light green to yellow is due to the mixture of indicators (MY-BG) and shows that, in order for the gel to form, a pH ≤ 3 must be reached, in this case thanks to the hydrolysis of δ-gluconolactone. The arrow indicates where iodine first appears.

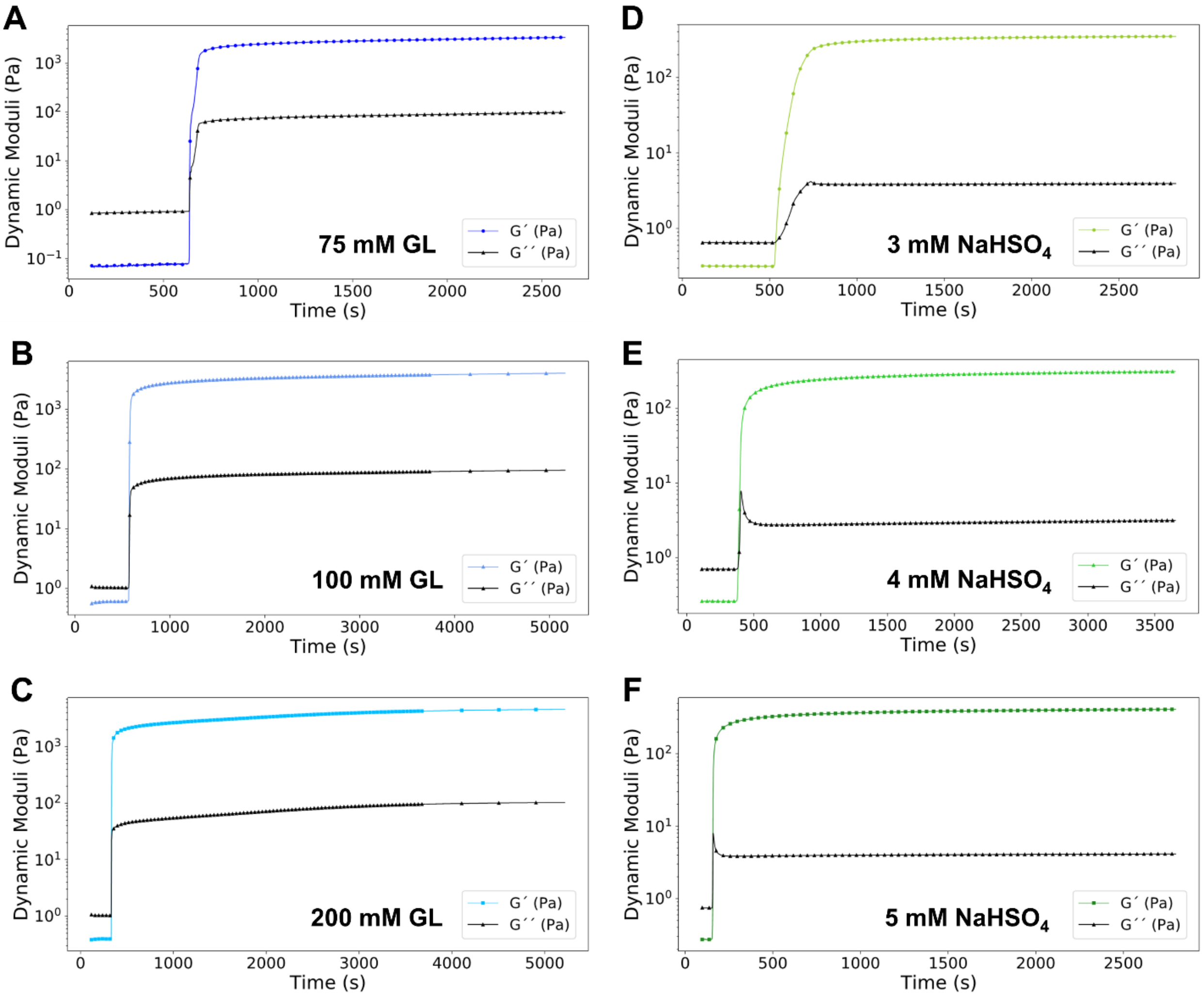

Figure S3. Complete rheology plots (G’, G’’) for the iodate-HMS-PVA systems triggered by different concentrations of (a-c) δ-gluconolactone (GL), (d-f) sodium bisulfate.

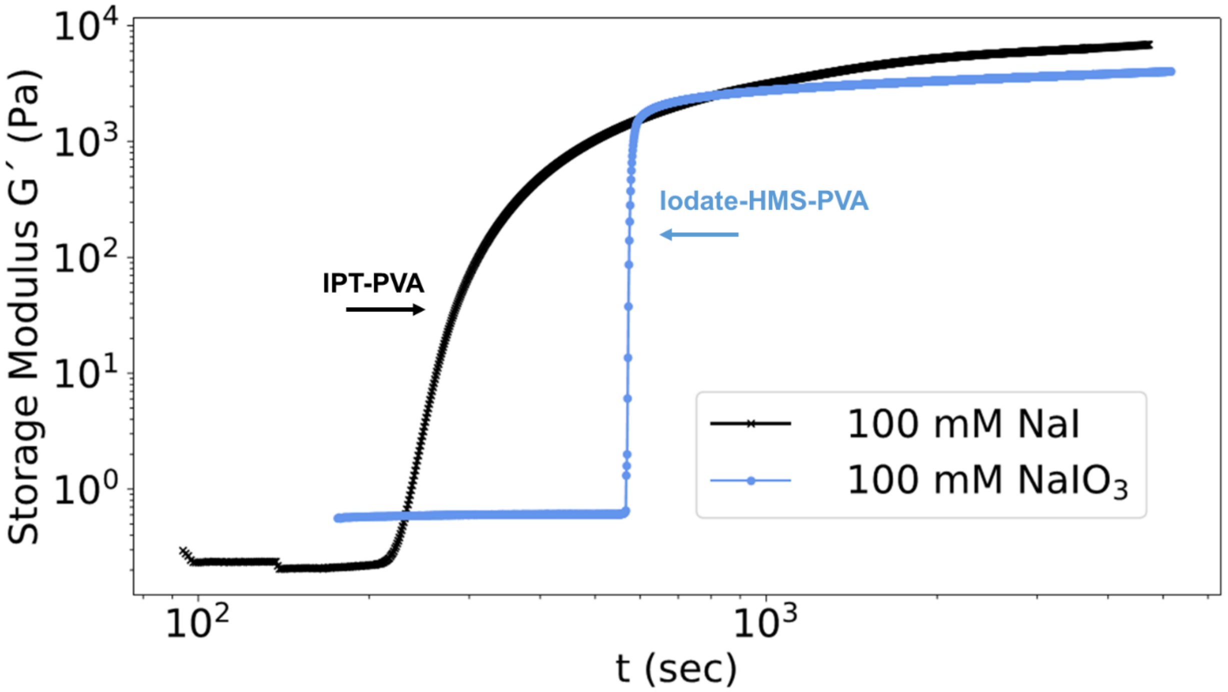

Figure S4. Effect of autocatalysis on gelation dynamics as seen by rheology. Comparison of the instantaneous gelation produced by an autocatalytic iodine clock (blue curve, iodate-HMS-GL; 100 mM iodate, 200 mM HMSNa, 100 mM GL; t_{gel} = 567 s) and the slower gelation produced by a more conventional substrate-depletive iodine clock[1] (black curve, iodide-persulfate-thiosulfate IPT; 100 mM iodide, 200 mM persulfate, 40 mM thiosulfate; t_{gel} = 247 s). For both systems PVA 130 kDa was used, with a concentration of 5%. The final mechanical modulus G’ of the gels produced is basically the same for both systems, as well as the theoretical final concentration of iodine.

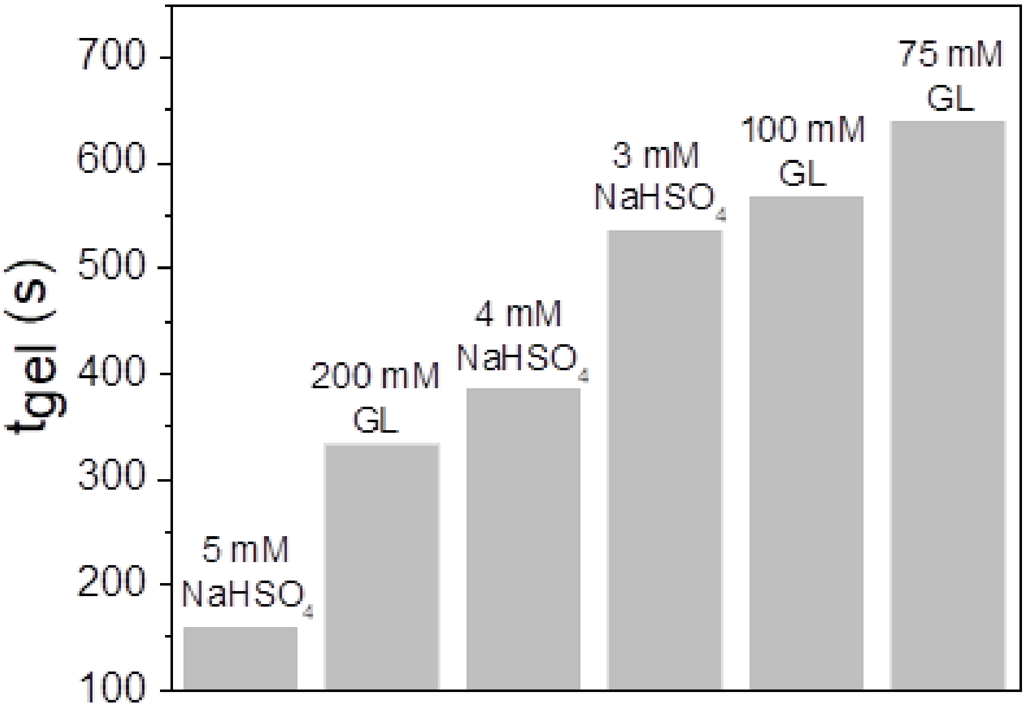

Figure S5. Gelation times t_{gel} of the iodate-HMS-PVA system for different concentrations of δ-gluconolactone GL and bisulfate $NaHSO_4$.

REFERENCES

1. S. Riedel, T. Schweizer, K. Smith-Mannschott, E. R. Dufresne and G. Panzarasa, *Soft Matter* **2021**, *17*, 1189–1193.