SUPPORTING INFORMATION

Supramolecular Gel Formation Controlled by an Iodine Clock

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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 thiosulfate (99%) and ammonium persulfate (98%) were purchased from Sigma-Aldrich (Switzerland). Methyl-β-cyclodextrin (average M_W 1310 Da, mβCD) was purchased from Acros Organics (Germany) and sodium iodide (99+%) was obtained from Fisher Scientific (UK). Unless otherwise noted, all chemicals were of analytical or reagent grade purity and were used as received from commercial sources. Water was purified by means of a MilliQ system (resistivity ≥ 18 MΩ).

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. Stock solutions were also prepared for sodium iodide, sodium thiosulfate and ammonium persulfate (Table S1). Stock solutions were stored for no longer than five hours at room temperature (23 ± 1°C) avoiding direct light.

Typical experimental protocols

Gel formation: All samples were prepared at room temperature (23 ± 1°C) by mixing in a 15 mL glass vial 3.5 mL PVA stock solution with 0.5 mL NaI and 0.5 mL $Na_2S_2O_3$ stock solution, respectively. Mixing was provided by a PTFE-coated magnetic stirring bar rotating at about 900 rpm. Brief sonication in an ultrasonic bath was used to remove air bubbles when necessary. Then, 0.5 mL $(NH_4)_2S_2O_8$ stock solution was added and the reaction mixture was stirred for exactly 1 min before being loaded into the rheometer or used otherwise.

Gel dissolution: For the dissolution experiments, 0.1 M solutions of $Na_2S_2O_3$ or CH_3-β-cyclodextrin were prepared by dissolving 0.655 g $Na_2S_2O_3$ or 0.081 g CH_3-β-cyclodextrin in 5 mL water, respectively. To prepare the gel samples, aliquots of 0.2 mL of the reaction mixture (prepared as described above) were transferred in test-tubes (40 x 8 mm ∅) and left to gel for 25 min. The resulting piece of gel was then transferred into the solution of interest (sodium thiosulfate, CH_3-β-cyclodextrin, water) and left undisturbed until it was fully dissolved or, when water was used, for 24 h.

Table S1. Summary of the stock solutions used for the experiments.

Reagent	Concentration of the stock solution (M)	Mass of reagent (g) dissolved in 5 mL water
Sodium iodide NaI	0.25	0.187
	0.5	0.375
	0.75	0.562
	1.0	0.750
Sodium thiosulfate $Na_2S_2O_3$	0.2	0.158
	0.4	0.327
	0.6	0.474
	0.8	0.654
Ammonium persulfate $(NH_4)_2S_2O_8$	2	2.28
Methyl-β-cyclodextrin	0.025	0.164
	0.05	0.328
	0.075	0.491
	0.1	0.655

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 stock solutions were mixed as described under *Gel formation*, then the reaction mixture was pipetted into the rheometer. Due to the high viscosity of the PVA 130 kDa, the sample volume varied between 1.9 mL and 1.7 mL. For samples prepared with PVA 89-98 kDa and 13-23 kDa, the sample volume could be reduced to 1.7 - 1.6 mL. All 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 of typically 90 - 200 s between the addition of the ammonium persulfate stock solution and 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 $\left(t > t_{gel}\right)$.

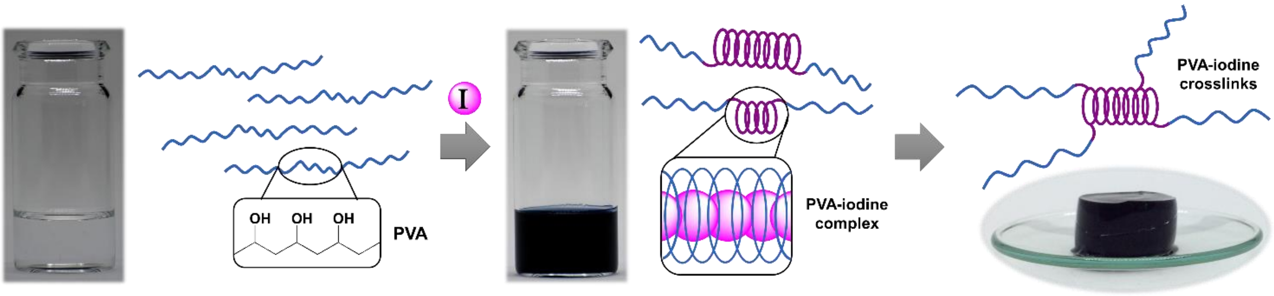


Figure S1. Simplified representation of the PVA-iodine gel formation.

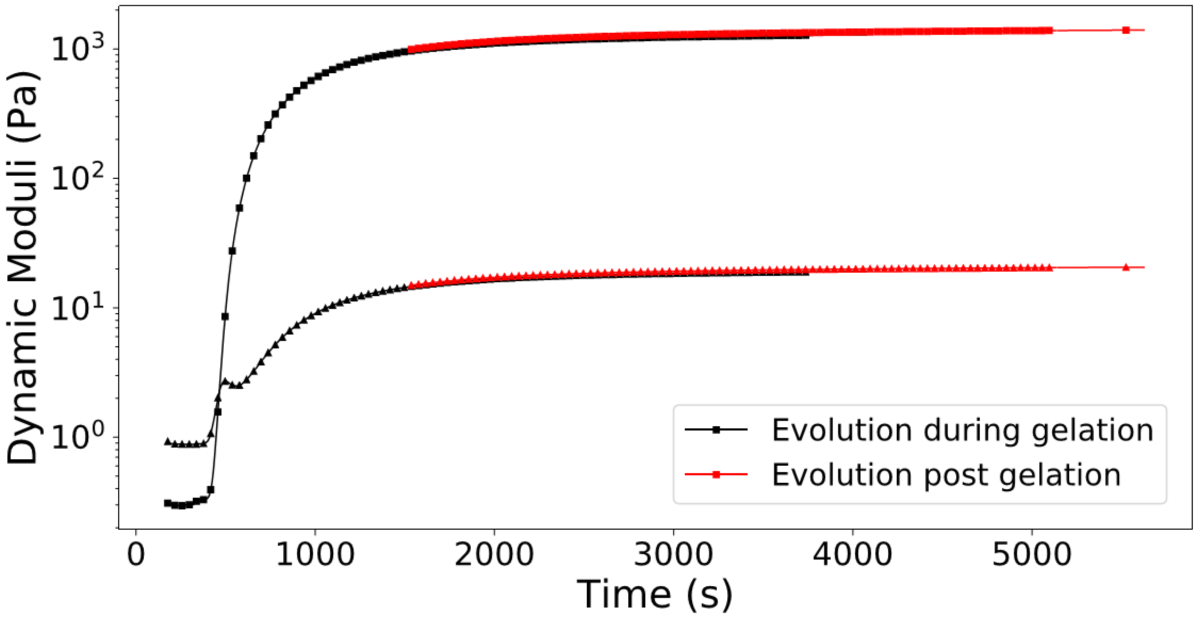


Figure S2. Proof that the rheometry measurements do not influence gelation nor the mechanical properties of a typical PVA-iodine gel ([NaI] = 50 mM, [$Na_2S_2O_3$] = 40 mM, [$(NH_4)_2S_2O_8$] = 200 mM, 5% PVA 130 kDa). The value of G’ measured for a gel allowed to form inside the rheometer before being analyzed is the same as that measured for a gel in the usual conditions.

WINTER-CHAMBON ANALYSIS OF THE IPT-PVA SOL-GEL TRANSITION

The state of matter between the sol and the gel state is termed a *critical gel*. It is characterized by G' = G'' over a range of frequencies. Since in the dynamic time sweep experiments only $\omega = 10$ rad s^{-1} was tested, a series of frequency sweep experiments has to be performed to get a multifrequency picture of the sol-gel transition. This method was pionieered by H. Winter and F. Chambon [2]. To perform this method, the duration of one frequency sweep Δt_{FS} should be substantially shorter than the mutation time λ_{mu} characterizing the speed of gelation around the cross-over point (eq. S2):

$$\Delta t_{FS} \ll \lambda_{mu} \qquad \text{(S2)}$$

$$\lambda_{mu} = \left[\frac{1}{G}\frac{\partial G}{\partial t}\right]^{-1} \qquad \text{(S3)}$$

In eq. S3, G is the mechanical modulus (G' or G'') which changes faster during gelation, usually G'.

A critical gel is characterized by a self-similar structure, *i.e.* relaxation phenomena are the same on different length scales. Below a characteristic relaxation time λ_0, this property is lost and relaxation occurs on smaller length scales. To probe the critical gel character of a sample, test frequencies ω should therefore fulfil the condition in eq. S4:

$$\omega < \frac{1}{\lambda_0} \qquad \text{(S4)}$$

We tried the Winter-Chambon analysis only on one gel composition ([NaI] = 50 mM, [$Na_2S_2O_3$] = 40 mM, [$(NH_4)_2S_2O_8$] = 200 mM, 5% PVA 130 kDa), since the condition in eq. S2 could not be fulfilled by other samples. For a frequency sweep $\omega \in$ (3.16, 10, 31.6, 100, 316 rad s^{-1}) at a strain amplitude γ_0 = 10%, Δt_{FS} is about 54 s. Mutation times for G' at the five frequencies are shown in **Figure S3a**. Except for $\omega = 316$ rad s^{-1}, the condition in eq. S2 is not fulfilled, the gelation reaction is too fast. If the different frequency sweeps are plotted, as in **Figure S3b**, one should see a transition G' < G'' for short times, G' = G'' at the gelation point and G' > G'' beyond. But in **Figure S3b** G' = G'' cannot be seen, because the structure of the gel is evolving too fast during the one frequency sweep at the gelation point. However, when plotting G', G'' of the different frequencies against time, one obtains **Figure S3c**, where the critical gel behavior is clearly revealed *i.e.* for $t \approx 410$ s, G' = G'' for all $\omega \in$ (3.16, 10, 31.6, 100 rad s^{-1}). For $\omega = 316$ rad s^{-1}, G' = G'' is at 800 s. This different behaviour is explained by $\omega > 1/\lambda_0$ *i.e.* the higher frequency probes the gel structure at different length scales than the lower frequencies. From **Figure S3c** we can therefore say $\lambda_0 < 10$ ms.

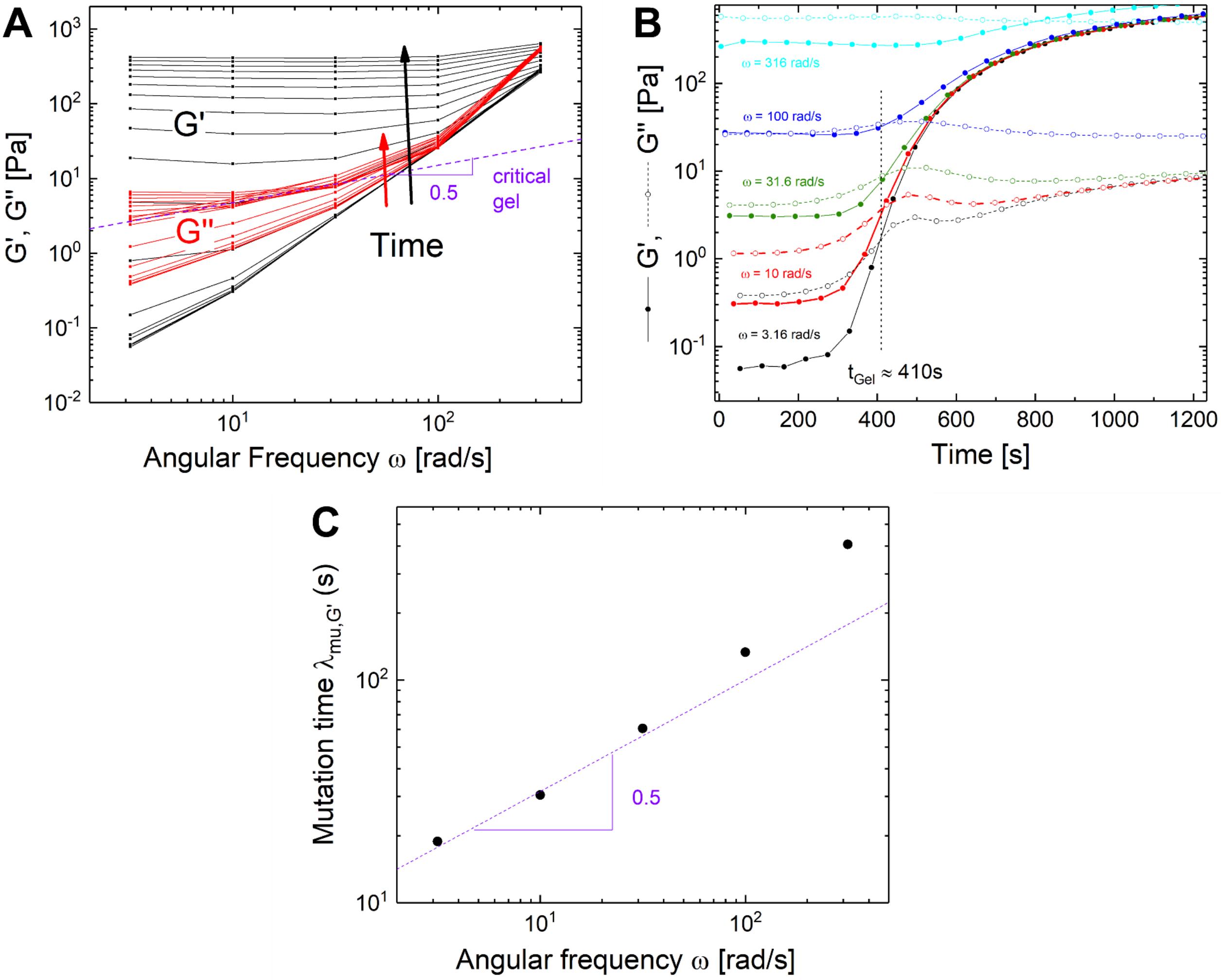
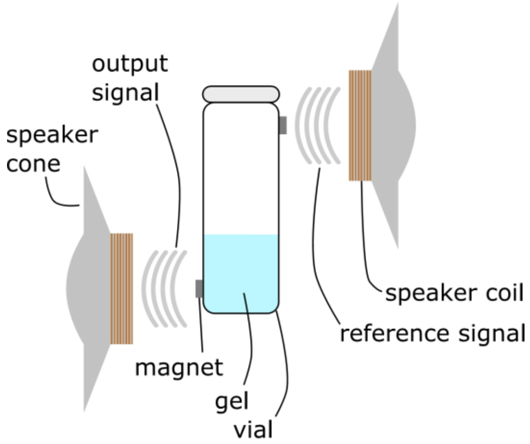


Figure S3. Winter-Chambon analysis of the sol-gel transition in a typical IPT-PVA system ([NaI] = 50 mM, [$Na_2S_2O_3$] = 40 mM, [$(NH_4)_2S_2O_8$] = 200 mM, 5% PVA 130 kDa). (a) Frequency sweeps at γ_0 = 10% measured every 54 s. (b) Data from Figure S3a plotted against time. (c) Mutation time calculated for G’ from data in Figure S3b.

INVESTIGATION OF GELATION DYNAMICS BY ACOUSTIC RESONANCE SPECTROSCOPY

We use acoustic resonance spectroscopy (ARS) as a non-destructive, impedance-based measurement method to excite and detect vibrational modes in a gel sample [3]. In particular, the lower frequency vibrational modes provide information on the gel's stiffness. Compared to rheometry or compression-based testing, ARS does not require direct contact between a probe and the sample, thereby providing insights into the progression of the gel's stiffness over time without actually touching the gel. Moreover, it allows to measure the sample over much longer times (tens of hours). However, as the models underpinning the vibrational modes in acoustic resonance spectroscopy in our lab-made set-up are not yet as well established as other modulus measurement methods, the resulting data provide a qualitative, rather than quantitative, understanding of the gel evolution over time.

The experimental setup used to perform ARS measurements is depicted in **Scheme S1**. A 30 mL glass vial is prepared by attaching two small magnets on its sides, one is placed near the top of the vial and the other on the opposite side near the bottom of the vial. The vial is then filled with 10 mL of the gelation mixture, closed, and suspended via rubber bands behind a speaker cone. A second speaker cone is placed on the other side of the vial, opposite to the first, and its inductor is aligned with the lower magnet on the vial. The first speaker cone's inductor is aligned with the magnet affixed near the top of the vial. The first speaker produces a reference signal, thereby exerting forces on its neighboring magnet (and thereby the vial) via its inductor. In response, the gel vibrates with an amplitude dependent on its stiffness. This vibration affects the movement of the vial, changing the impedance of the second speaker, which is reflected in the voltage measured across its inductor. The larger the movement induced in the gel by the first speaker cone, the greater the voltage measured across the second speaker cone, indicating vibrational modes as we sweep through a range of frequencies.



Scheme S1. Schematic representation of the experimental setup for the ARS measurements.

Samples were prepared and mounted in the ARS set-up before the clock's induction time, allowing measurements to commence prior to the formation of the PVA-iodine gel. We performed frequency sweeps in 0.25 Hz increments from 10 Hz to 200 Hz in two phases. During the first hour of measurements, sweeps were performed every 2 minutes, with a 30 ms interval between frequencies. The second phase of measurement consisted of a slower sweep with 100 ms between frequencies, providing better resolution. These measurements were performed once per hour for 14 hours. A total of 45 frequency sweeps were performed. **Figure S4** shows selected frequency sweeps, illustrating the progression of the gelation for varying sodium iodide NaI concentrations. The lightest curve reflects the first measurement after the sample was suspended in the instrument. Subsequent (darker) curves were taken at 11 min, 22 min, 33 min, 161 min, 623 min, and 855 min, respectively, after the start of measurement. **Figure S4a** shows frequencies sweeps for a sample with an iodide concentration of 25 mM. In this case, according to ARS, either no gel is formed or the gel is to dissipative to generate eigenmodes measurable by our system. The peak near 40 Hz, as well as that near 100 Hz, are both modes of the system and do not reflect eigenfrequencies of the sample. However, by doubling the iodide concentration to 50 mM, we begin to see peaks associated with a vibrating gel (**Figure S4b**). **Figures S4c,d** show that as we continue to increase the iodide concentration (respectively from 75 mM to 100 mM), the gel forms more quickly and, in their final state, are stiffer than those samples with lower iodide concentrations, in accordance with the rheometry data. However, ARS data suggest that the gels are still evolving hours after their formation, a detail which could not be appreciated from the rheological studies. The reasons for such behavior are not yet clear and could deserve dedicated investigations.

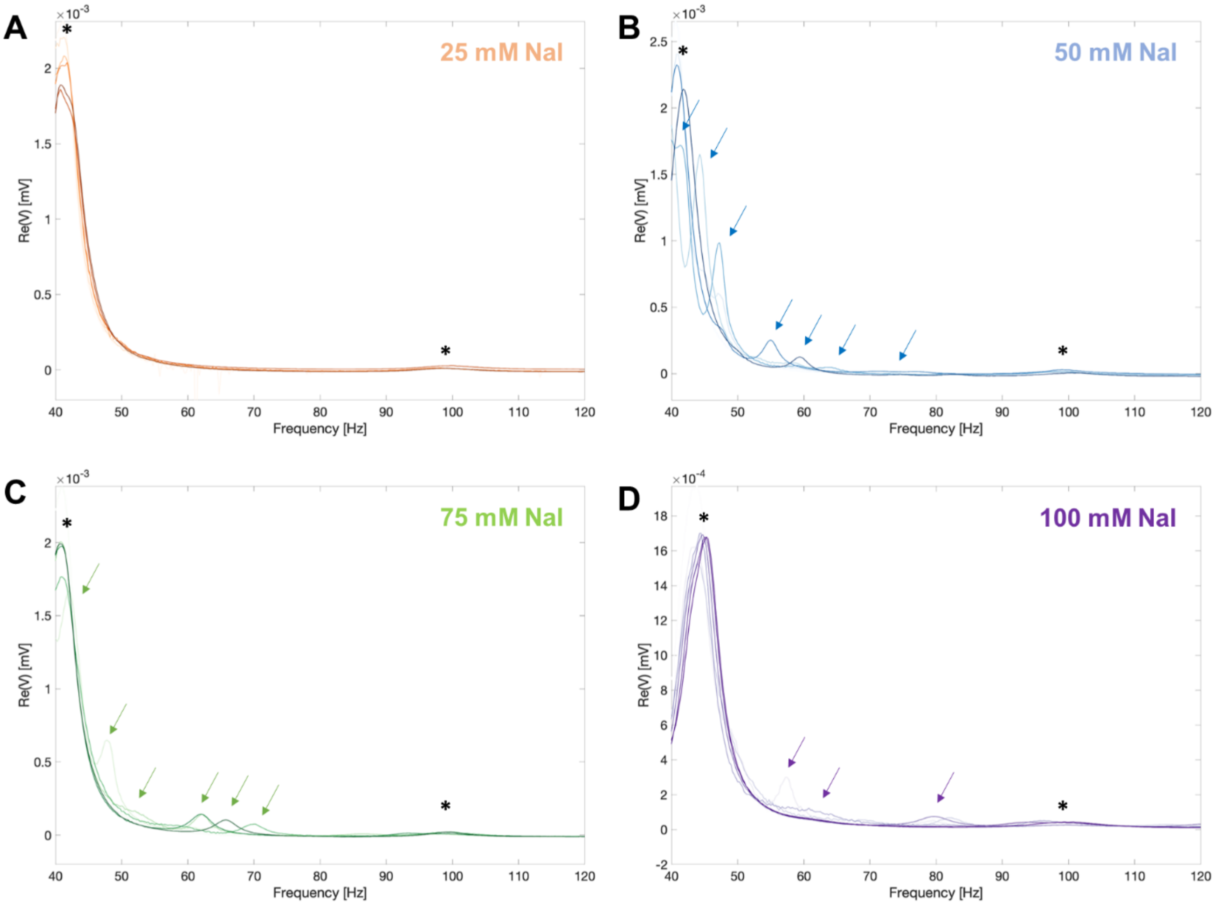


Figure S4 Selected frequency sweeps, illustrating the progression of gelation, for varying sodium iodide NaI concentrations: (a) 25 mM, (b) 50 mM, (c) 75 mM, (d) 100 mM. The system peaks at ~45 Hz and ~ 100 Hz, originating from our ARS set-up, are identified with asterisks while the peaks originating from the sample with arrows. Both samples with 50 mM and 75 mM NaI show a clear progression of stiffness, as the sample peaks move towards the right over time.

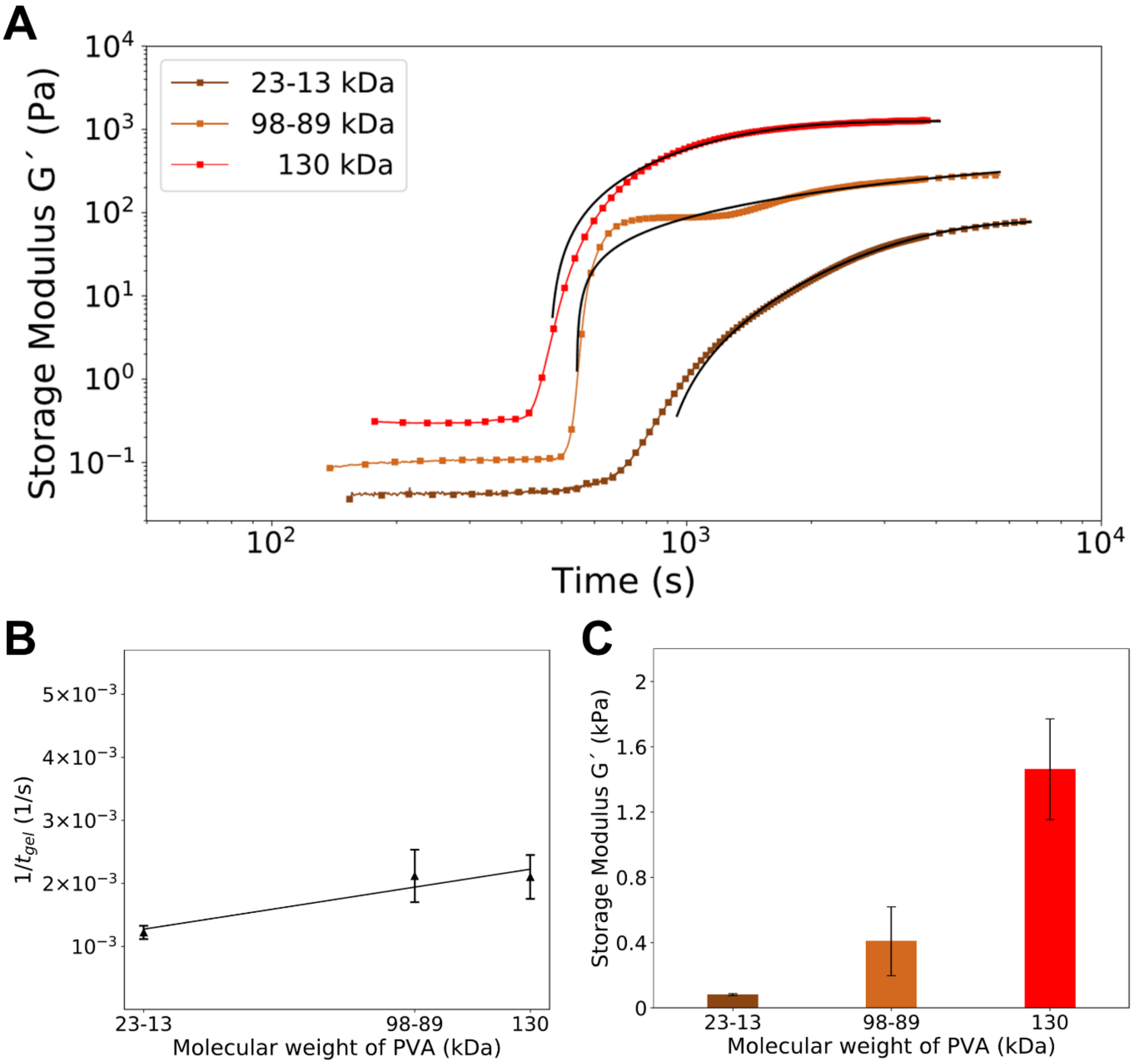


Figure S5. Effect of PVA molecular weight on gelation time and mechanical properties of the gel. [NaI] = 50 mM, [$Na_2S_2O_3$] = 40 mM, [$(NH_4)_2S_2O_8$] = 200 mM, 5% PVA. It is known from the literature that the PVA-iodine interaction is sensitive to the molecular weight of the polymer chains, and that longer chains assume more easily the shape necessary to form the supramolecular complex [4,5].

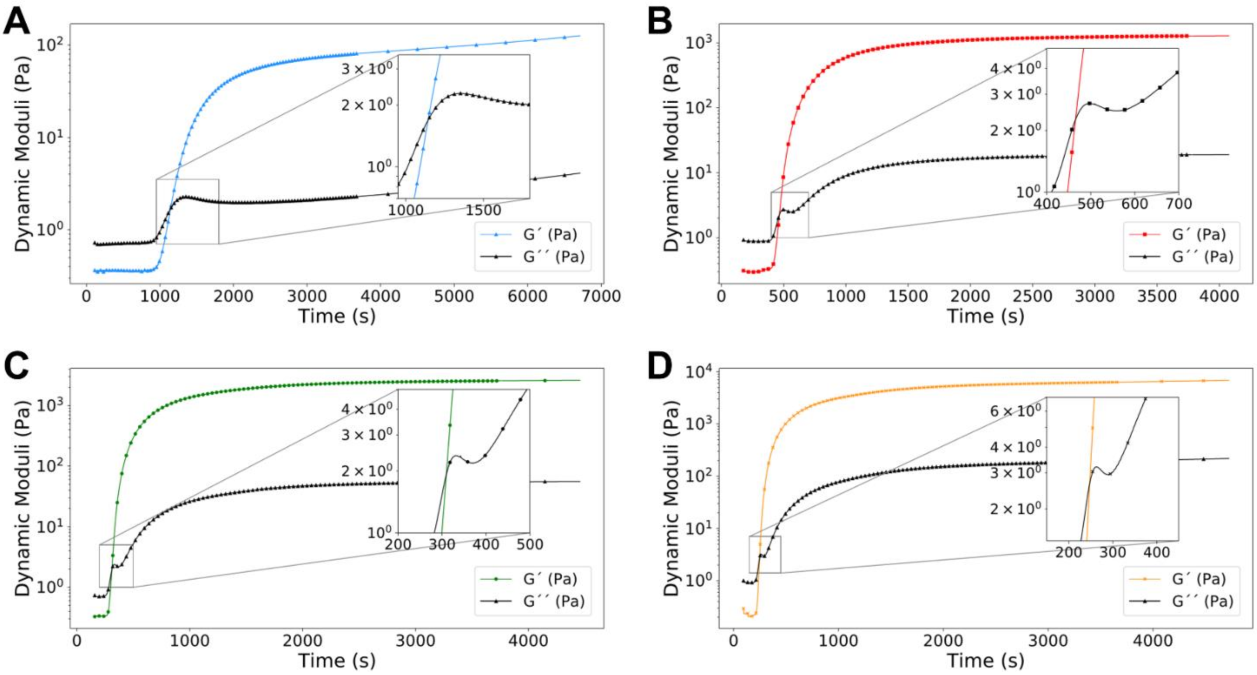


Figure S6. Impact of the iodide NaI concentration on the rheological properties of the IPT-PVA system: [NaI] = 25 mM (a), 50 mM (b), 75 mM (c), 100 mM (d). [$Na_2S_2O_3$] = 40 mM, [$(NH_4)_2S_2O_8$] = 200 mM, 5% PVA 130 kDa.

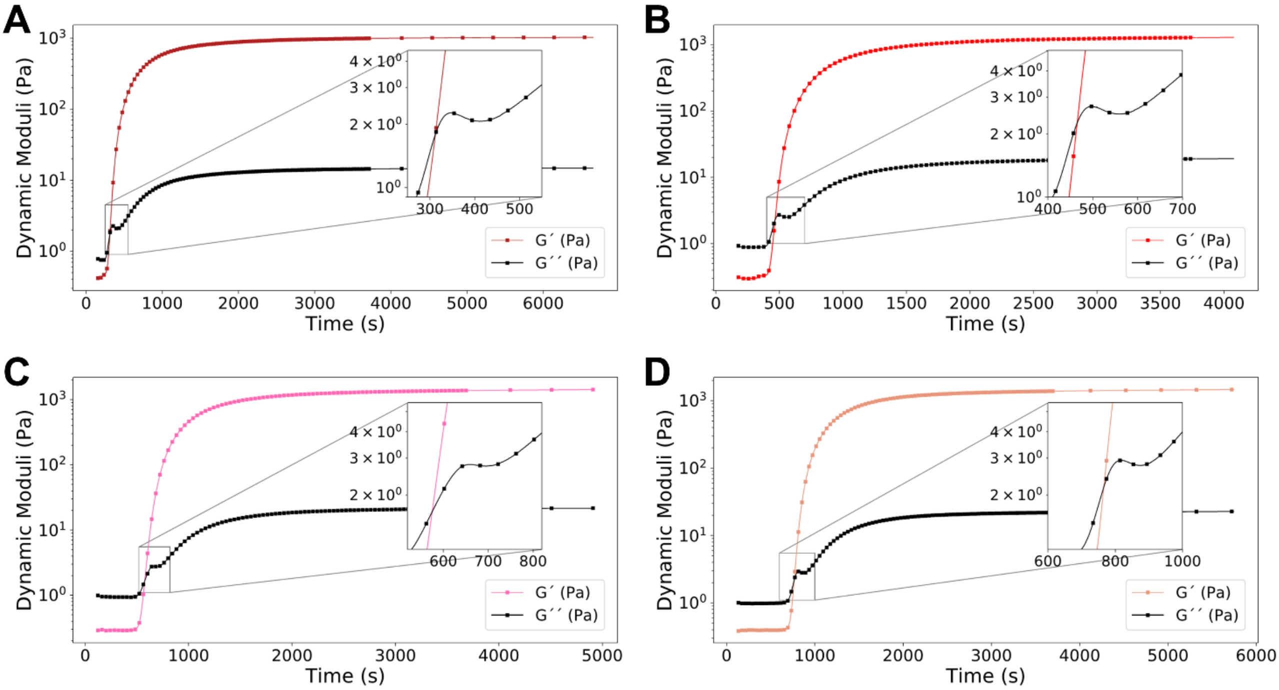


Figure S7. Impact of the thiosulfate $Na_2S_2O_3$ concentration on the rheological properties of the IPT-PVA system: $[Na_2S_2O_3]$ = 20 mM (a), 40 mM (b), 60 mM (c), 80 mM (d). [NaI] = 50 mM, $[(NH_4)_2S_2O_8]$ = 200 mM, 5% PVA 130 kDa.

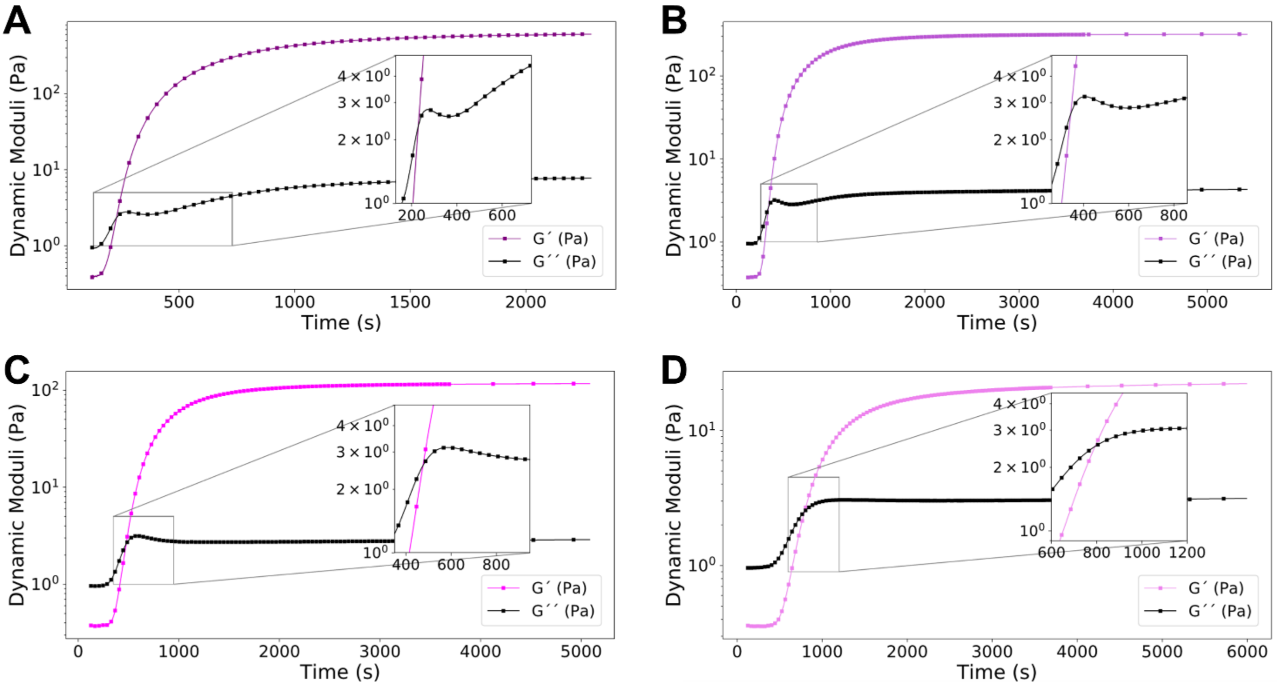


Figure S8. Rheology plots for the system iodide-persulfate-mβCD (methyl-β-cyclodextrin) with different concentrations of the latter: [mβCD] = 2.5 mM (a), 5 mM (b), 7.5 mM (c), 10 mM (d). [NaI] = 50 mM, [$(NH_4)_2S_2O_8$] = 200 mM, 5% PVA 130 kDa.

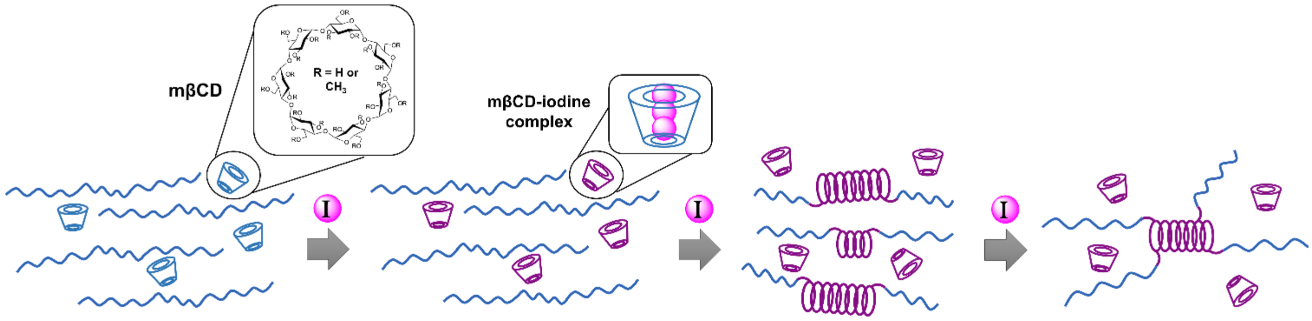


Figure S9. Simplified representation of the iodide-persulfate-mβCD-PVA system.

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