

Electronic Supplementary Information

Temporal viscosity modulations driven by a pH sensitive polymer coupled to a pH-shifting chemical reaction

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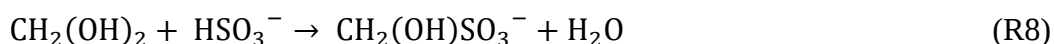
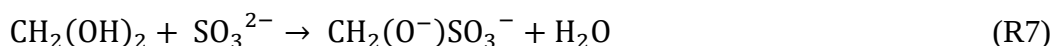
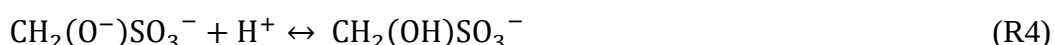
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Chemical reactions of the systems considered.

The original chemical reactions as in references [17, 18, 19] read for the FS case:



For the FSG reaction two new reactions need to be added:



where GL = Gluconolactone, GA = Gluconic Acid and G^- = Gluconate.

Let us now consider the differences introduced by the actual system in the main text. Here, we consider the equilibrium displacement produced by the acidic environment generated after the PAA

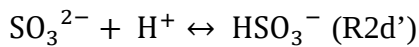
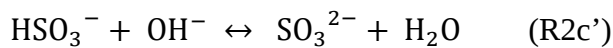
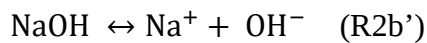
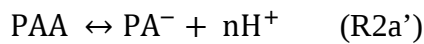
dissociation in H₂O. In this sense, the presence of HSO₃⁻, necessary in the original recipe, is provided by the SO₃²⁻ and the H⁺ released by the PAA. (eq. 1 and 2). The remaining equations remain unaltered.

Thus, reaction (R2) is replaced by the following two reactions in the FS-PAA and FSG-PAA systems:



where PAA = Poly(acrylic acid) and PA⁻ = Poly(acrylate) ion

It is also possible to propose an analogous model for the FBS-PAA reaction. In this case, SO₃²⁻ would be generated by the addition of NaOH in combination with HSO₃⁻ and reaction (R2) is now substituted by the following 4 reactions:



FS-PAA with bisulfite and sodium hydroxide (FBS-PAA)

Another possible route to couple the PAA polymer with the FS reaction is by replacing the sulfite from the previously explained FS-PAA system by bisulfite and sodium hydroxide (hereafter so-called FBS-PAA). Due the acidic character of the polymer, the bisulfite requires the presence of sodium hydroxide to obtain enough sulfite for producing the clock behavior. In Fig.S1a we compare the temporal pH evolution for both recipes by using for the FS-PAA system, sulfite [SO₃²⁻]₀ = 0.0684 M, [Formaldehyde]₀ = 0.0653 M and for the FBS-PAA system, [HSO₃⁻]₀ = 0.0684 M, [NaOH]₀ = 0.0921 M and [Formaldehyde]₀ = 0.098 M. In both experiments [PAA]₀ = 0.4386 wt %. Both curves exhibit a similar transition of pH and viscosity in time (figure 4a), the initial and final pH values being nearly the same. The induction times are slightly shifted one from each other, i.e. the induction time of the bisulfite reaction is mildly delayed with regard to that of the sulfite reaction.

As can be seen in Fig.S1c, the viscosity values for the bisulfite reaction for all shear rates between 10 s⁻¹ and 1000 s⁻¹ are significantly smaller compared to those of the sulfite reaction.

Fig.S1b shows the viscosity and the pH as a function of time for the reaction with bisulfite. In this case, the viscosity behaves in a similar way than in the bisulfite case. However, even if the pH and viscosity curves match in shape, the viscosity jump between the initial and final state are considerably smaller in comparison with the original recipe. As can be seen in the results, this procedure was effective for reproducing the dynamics of the reaction, but it has negative effects on the resulting dynamic viscosity. This result also suggests that a polybasic polymer should be used (instead of a polyacid polymer) to enhance the viscosity jumps once we have replaced the sulfite in the FS system.

Up to now we have shown the versatility of the FS-PAA system with two different examples where, depending on the initial chemical reagents, the overall reaction may have a better affinity to the polymer. In the forthcoming section we will limit ourselves to the case where the bisulfite is omitted (only FS-PAA reaction) as this recipe displays larger jumps in the viscosity.

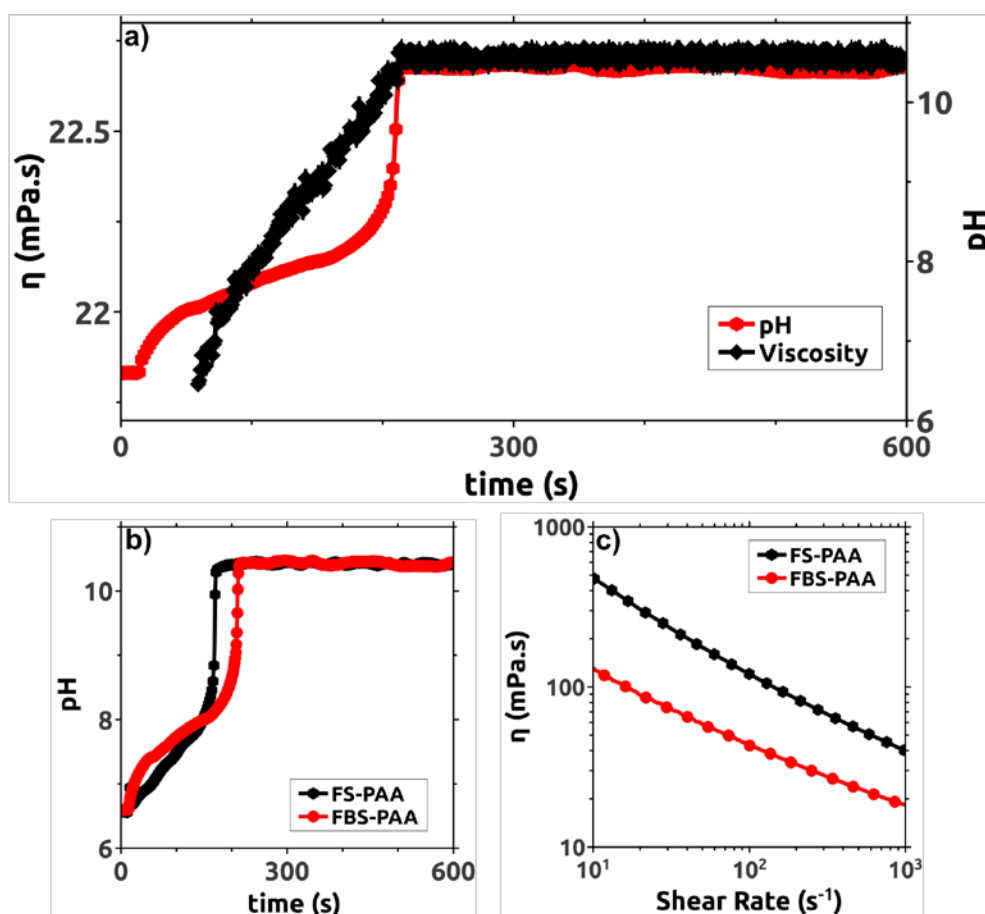


Figure S1: Comparison of FS-PAA and FBS-PAA reaction dynamics. For the sulfite reaction: $[SO_3^{2-}] = 0.0684$ M, $[Formaldehyde]_0 = 0.0653$ M. For the modified reaction with bisulfite: $[HSO_3^-]_0 = 0.0684$ M, $[NaOH]_0 = 0.0921$ M and $[Formaldehyde]_0 = 0.0933$ M. In all cases $[PAA]_0 = 0.4386$ wt %. a) Viscosity and pH temporal evolution for the FBS-PAA reaction. All viscosity measurements were performed fixing the shear rate at $500\ s^{-1}$. b) pH as a function of time compared for the FS-PAA and FBS-PAA reactions. c) Viscosity as a function of shear rate for both reactions.

PAA short chain

Fig.S2 shows an analogous analysis for the FS-PAA reaction, but replacing the PAA-4 10^6 g/mol by another one with shorter length chains (PAA-4.5 10^5 g/mol). In this case, the polymer dissociation and rheology completely differ from the PAA-4 10^6 g/mol case (Figure 1 of the main text). As can be observed in Fig.S2a, by fixing the sulfite and formaldehyde initial concentrations, the maximum pH and viscosity differences are obtained for concentrations of $[PAA-4.5 \ 10^5 \text{ g/mol}]_0$ in the interval [0-1] wt %. For higher concentration values, there is no significant difference between the initial and final states.

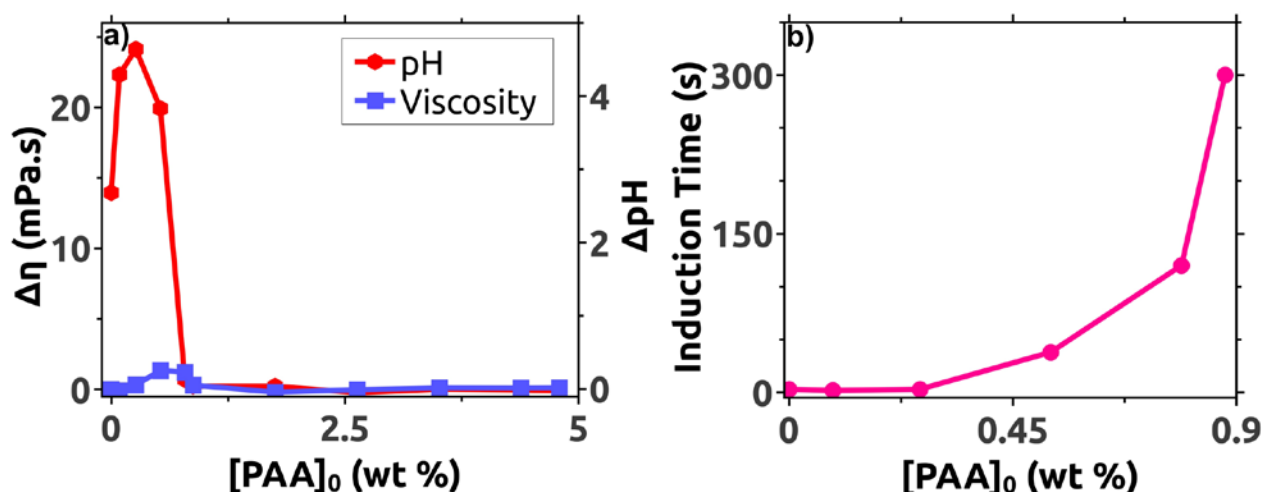


Figure S2: FS-PAA reaction replacing the PAA-4 10^6 g/mol by PAA-4.5 10^5 g/mol. For these experiments $[SO_3^{2-}]_0 = 0.0684$ M and $[Formaldehyde]_0 = 0.0933$ M. The shear rate and the temperature were fixed at 500 s^{-1} and 23°C , respectively. a) Comparison between pH and viscosity difference between the initial and final values. b) Induction time variation by increasing the polymer concentration.

Although the maximum pH difference is comparable with that obtained with the larger polymer, the maximum viscosity difference is much lower. Please note that the viscosity axis in figure S2a was set using the same range compared to figure 2 column b (in the main text) for better comparison. This result was expected as the polymer length chain is much shorter and its final concentration in solution (once the clock is observed) is much lower. Despite this, the viscosity changes, confirming the coupling between the reaction and the polymer. Fig.S2b shows how the induction time increases by increasing the polymer concentration, in an analogous way as the system with the larger polymer. For $[PAA-4.5 \ 10^5 \text{ g/mol}]$ concentrations above 0.8 wt %, there is no possibility to measure the induction time because there is no clock behavior.

Considerations about polymer overlap concentration

It is important to demonstrate that the increment in the viscosity observed in Fig. 2b1 is not produced due to the polymer overlap concentration (c^*). In order to show this, we will introduce here two different analyses for supporting our considerations.

Firstly, it is important to understand how the polymer is related with c^* . Particularly for the PAA, the overlap concentration will be not a single value but will depend also on the dissociation which, at the same time, is related with the pH of the solution. For concentrations above c^* , the rheological behavior of the solution will be affected by the interaction between polymer molecules and, as a consequence, the elastic property will be augmented increasing the viscosity. According to [23], c^* can be estimated as:

$$c^* = \frac{Mw}{R_g^3 N_A} \quad (1)$$

Where Mw is the molecular weight, R_g is the radius of gyration and N_A is the Avogadro number.

Thus, c^* will be inversely proportional to the length of the polymer molecule. However, for PAA molecules, R_g will vary depending on the dissociation degree of the polymer which, in turn, will depend on the pH of the solution [20]. Nevertheless, for higher pH values, the ionic strength provided by the sodium ions (already dissolved in the solution) will quench the electrostatic repulsion produced by the carboxylic groups [20]. This would prevent a fully elongation of the PAA molecules [20] which can be translated as a low R_g value, and therefore the viscosity of the solution will be much lower compared to a solution of PAA in pure water. Despite this, c^* can be estimated by the method described in [24]. For the PAA-4 10^6 g/mol, we obtained a concentration $c^* \cong 2.64$ wt % which is far from those values used in this work (up to 0.5 wt %, which corresponds to the stock solution).

Analogously, the same procedure can be used to estimate c^* for the short length polymer (PAA-4.5 10^5 g/mol). In this case, we have obtained a $c^* \cong 8.33$ wt %, which indicates that our range of concentrations (figure S2a) is one order of magnitude below the overlap concentration c^* .

Secondly, and as a complementary analysis to support our previous calculations, we have also measured the first normal stress difference (N_1), which is useful to observe the elastic property of a non-Newtonian polymer solution. We analyzed the most concentrated solutions used for each polymer and compared them with control solutions of PAA and NaOH. Results are in the figure S3.

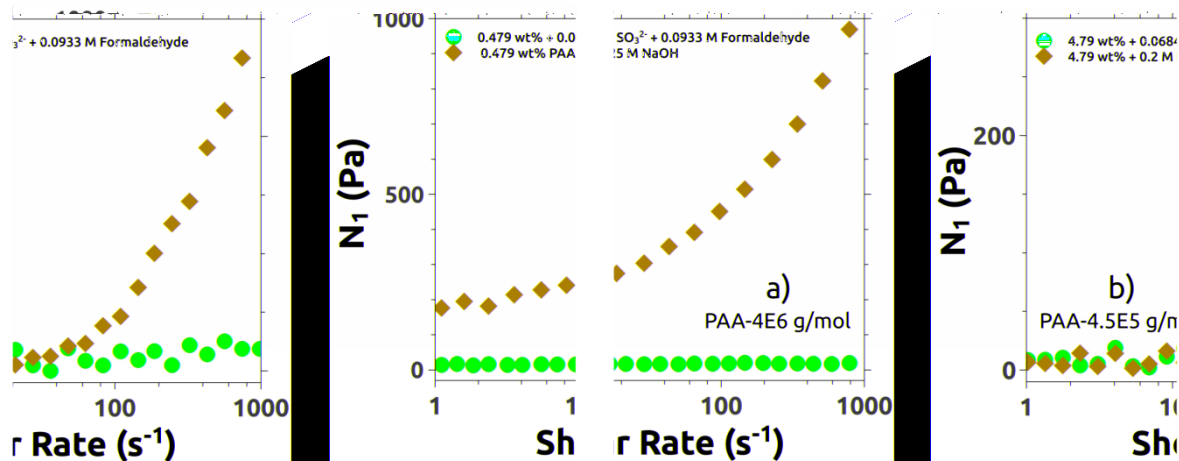


Figure S3 Measurement of the first normal stress difference N_1 for large chain (PAA-4 10^6 g/mol) and short chain (PAA-4.5 $\times 10^6$ g/mol) polymers. a) N_1 measured for the more viscous solution (0.479 wt %) used in the main analysis (blue dots) and compared with a control solution of PAA (long chain) and NaOH (green diamonds curve). b) N_1 measured for the most viscous solution (4.79 wt %) used for the complementary analysis (supp. Info, blue dots) compared with a control solution of PAA (short chain) and NaOH (green diamonds curve).

In the figure S3 it is possible to see the differences between two solutions expected to be the most elastic that appeared in the figures 2b1 and S2a compared with PAA control solutions. In figure S3a), the control solution (green diamonds curve) exhibits a strong increase in normal stress. This is expected since a 4 10^6 g/mol 0.47 wt% PAA solution gelifies for a broad range of NaOH concentrations [8] due the extension of the polymer chain. As was discussed before, the PAA dissociation increases the radius of gyration R_g and in consequence, an overlapping scenario is reached. However, the blue dotted curve shows that there was no measurable normal stress found for the shear rate used in our previous measurements (500 s^{-1}). In this case, even with the same polymer concentration, the presence of sodium ions provided by the SO_3^{2-} solution quenched the electrostatic repulsion impeding the elongation of the PAA molecules. This quenching effect produces a decrement in the elastic property and therefore no overlap occurs at the analyzed concentration. A similar situation can be observed in figure S3b), where the normal stress of the control solution (green diamonds curve) increases for shear rates around 100 s^{-1} , while the blue dotted curve does not exhibit any appreciable normal stress in the range of studied shear rates, due to the same quenching effect observed in figure S3a). As these results were obtained for the most viscous (and also expected, elastic) solutions, this conclusion can be extended to the rest of values measured in figure 2 and S2. These results strengthen our previous conclusions and guarantee that our experiments were done with concentrations below c^* .