Supplementary information for 'Metal-coordination: Using one of natures tricks to control soft material mechanics'

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Theoretical development of Time-Metal coordination superposition master curve

As a first attempt to model the rheological behavior of the different metal-crosslinked gels, the generalized linear viscoelastic Maxwell model was used to fit the measured loss-tangent $\tan\delta = G''(\omega)/G'(\omega)$ from the small amplitude oscillatory shear (SAOS) data. However, it was found that this fit was unsatisfactory, because of the inability of the linear model to capture the power-law behavior exhibited by many gel-like materials, including the ones of interest in our present study, without incorporating a very large number of relaxation modes. We therefore employ the fractional Maxwell model, which can be most clearly interpreted in terms of a mechanical element commonly referred to as a 'springpot. Most viscoelastic constitutive models invoke mechanical analogs that employ a combination of springs which obey Hooke's law of elasticity (i.e. the stress in the element is directly proportional to the strain), and dashpots which obey Newton's law of viscosity (i.e. the stress in the element is directly proportional to the strain rate). The springpot generalizes these elements by embodying a constitutive law in which the stress in the element is directly proportional to the α-th order derivative of strain, where $0 < \alpha < 1$ [1], i.e.

$$\sigma_{\text{springpot}} = \mathbb{V}\frac{d^\alpha \gamma(t)}{dt^\alpha} \tag{1}$$

Here $\mathbb{V}$ is a material property of the gel which is best thought of as a 'quasi-property' [2] with units Pa s$^\alpha$. It is clear that we retrieve the familiar limits of a Hookean spring and a Newtonian dashpot when $\alpha = 0$ and $\alpha = 1$, respectively, and figure S1(a) below shows these limits schematically. We may now construct constitutive models using springpot elements analogous to models involving a combination of springs and dashpots. One such constitutive model is the fractional Maxwell model, which consists of two springpot elements combined in series. This model is shown schematically in 1(b) above and the constitutive equation for the fractional Maxwell model is given by [3]

$$\sigma(t) + \frac{\mathbb{V}}{\mathbb{G}}\frac{d^{\alpha-\beta}\sigma(t)}{dt^{\alpha-\beta}} = \mathbb{V}\frac{d^\alpha \gamma(t)}{dt^\alpha} \tag{2}$$

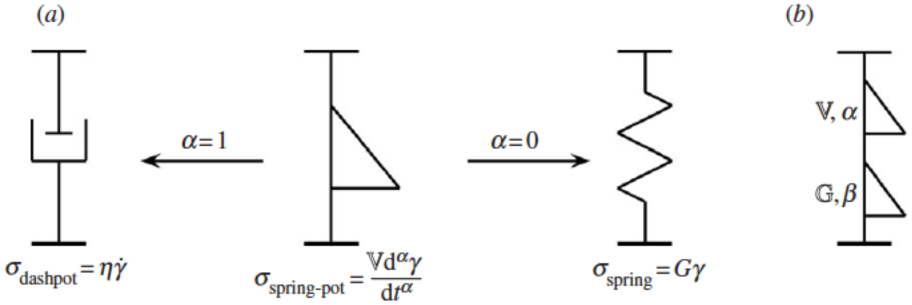


Figure S1: Schematic diagrams showing the springpot (a) and its use in the fractional Maxwell model (b).

where we take $\alpha > \beta$ without loss of generality, and $\mathbb{V}$ (units of Pa s$^{\alpha}$) and $\mathbb{G}$ (units of Pa s$^{\beta}$) are the quasi-properties of the two elements. We are interested in finding the expression for the loss-tangent $\tan\delta = G''(\omega)/G'(\omega)$ in this model, so that we may fit the linear viscoelastic data measured for the gels and quantitatively describe the rheological response of the gels in a compact way. If the gels synthesized from different metal ions are self-similar, we should be able to collapse the linear viscoelasticity data obtained from all gels onto a master curve obtained by fitting the fractional Maxwell model to the $\tan\delta(\omega)$ data for any gel. To find $\tan\delta$, we first Fourier transform the constitutive equation (2) and rearrange to obtain

$$\Gamma^*(\omega) = \frac{\mathbb{V}(i\omega)^{\alpha} \cdot \mathbb{G}(i\omega)^{\beta}}{\mathbb{V}(i\omega)^{\alpha} + \mathbb{G}(i\omega)^{\beta}} \tag{3}$$

and we have

$$\tan\delta \equiv \frac{G''}{G'} = \frac{\mathrm{Im}(G^*)}{\mathrm{Re}(G^*)} = \frac{\mathbb{G}\omega^{\beta}\sin(\pi\alpha/2) + \mathbb{V}\omega^{\alpha}\sin(\pi\beta/2)}{\mathbb{G}\omega^{\beta}\cos(\pi\alpha/2) + \mathbb{V}\omega^{\alpha}\cos(\pi\beta/2)} \tag{4}$$

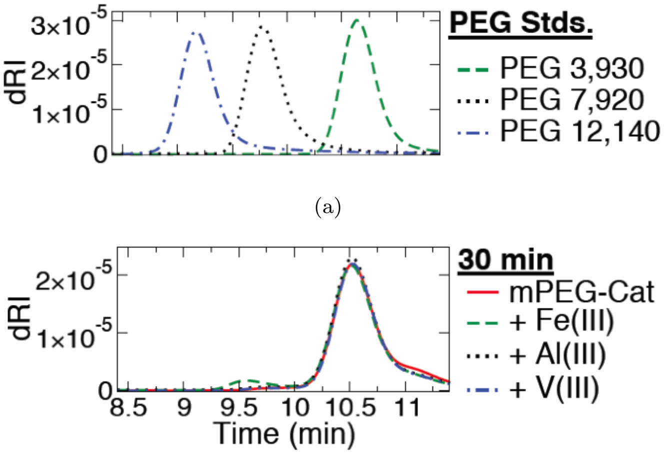
To find the crossover frequency ω_c, we solve equation (4) for the special condition when $\tan\delta = 1$ to obtain

$$\omega_c = \left[\frac{\mathbb{G}}{\mathbb{V}}\left(\frac{\sin(\pi\alpha/2) - \cos(\pi\alpha/2)}{\cos(\pi\beta/2) - sin(\pi\beta/2)}\right)\right]^{1/(\alpha-\beta)} \tag{5}$$

We now rewrite equation (4) in terms of the reduced frequency $\omega_r = \omega/\omega_c$ by combining equations (4) and (5):

$$\tan\delta = \frac{(1-\tan(\pi\beta/2))\tan(\pi\alpha/2) + \omega_r^{\alpha-\beta}(\tan(\pi\alpha/2)-1)\tan(\pi\beta/2)}{(1-\tan(\pi\beta/2)) + \omega_r^{\alpha-\beta}(\tan(\pi\alpha/2)-1)} \tag{6}$$

To generate Figure 3b in the main manuscript, we first fit the predicted loss tangent given by the fractional Maxwell model (equation (4)) to the linear viscoelastic frequency sweep data of Al gels and find $\alpha = 0.982, \beta = 0.014, \mathbb{V} =$ 406 Pa s$^{0.982}$ and $\mathbb{G} = 2.3 \times 10^4$ Pa s$^{0.014}$. With these values, the numerical value for the crossover frequency c,Al is found from equation (5) to be $\omega_{\mathrm{c,Al}} = 64$ rad s^{-1}. We now re-plot the experimental data for the dimensionless loss tangent of the Al gel versus the dimensionless reduced frequency ω_r and overlay the curve obtained from equation (6) using the values of α and β determined above. The $\tan\delta(\omega)$ data of the Fe gel and the V gel can be laterally shifted onto this same curve with shift factors that closely matches the value of ω_c obtained for each metal gel by directly fitting equation (4) to the corresponding data set (we find $\omega_{c,\mathrm{Fe}} = 16$ rad s^{-1} and $\omega_{c,\mathrm{V}} = 1.1$ rad s6−1). No vertical shift of the data is required. This result supports the assertion that the solid line in Figure 3b (obtained from equation (6) using values of α and β extracted from Al-gel data initially) is indeed a master curve. The progressive deviation of the rheological data obtained with the Fe gel for $\omega_r < 1$ is a result of a small fraction of covalent bonding of the Fe-gel (see supplementary Figure S2) that increases the elasticity of the gel (and thus reduces the loss tangent). This is explained in more detail in the main text of the paper.



(a)

(b)

Figure S2: GPC data showing the PEG standards (top) and the results of mPEG-Cat reactions (bottom) with Fe(III), Al (III) and V(III). A multimer peak ∼9.5min is increased with Fe(III) in support of Fe-induced covalent crosslinking. The multimer appears to be a dimer but its exact chemistry is currently under investigation. See Analysis of metal-induced covalent crosslinking protocol for experimental details.

One important consequence of the best fit values obtained for the material coefficients α and β (i.e. $\alpha \approx 1$, but $\alpha \neq 1$; and $\beta \approx 0$ but $\beta \neq 0$) is the presence of the bounded upper and lower plateaus for tan that can be seen in Figure 3b in the low frequency and high frequency limits, respectively. Equation (6) gives us that $\tan\delta \approx \tan(\pi\alpha/2)$ for $\omega_r \ll 1$ and $\tan\delta \approx \tan(\pi\beta/2)$ for $\omega_r \gg 1$. If α is identical to unity, there would be no low frequency plateau (i.e. the loss tangent diverges like a Newtonian fluid in the limit of low frequencies), and if $\beta = 0$ the loss tangent would approach zero as expected for an ideal elastic solid response in the limit of high frequencies.

Analysis of metal-induced covalent crosslinking protocol

mPEG-Cat (see below) was synthesized as previously reported [4]. The molecular weight was characterized by MALDI-TOF MS and found to be ∼ 5,600 g/mol. In order to replicate gel formation conditions as closely as possible, the polymer endgroup was kept constant ((200 mg/mL) × (10,000 g/mol)$^{-1}$ × (4 endgroups/polymer) = 80 mM endgroup). Therefore to make an equivalent mPEG-Cat solution a final polymer concentration of 448 mg/mL is needed (80 mM × 5,600 g/mol = 448 mg/mL). 100 mM stock solutions of $FeCl_3$, VCl_3, and $AlCl_3{\cdot}6H_2O$ were freshly prepared. The metal: mPEG-Cat ratio was set to 1:3. Initially, 1.5 mL 100 mg/mL mPEG-Cat solutions with 1:3 metal:mPEG-Cat were used to determine the amount of 1.00 M NaOH needed to be added to raise the pH to 8 for each metal studied. In this case the gel condition was not replicated exactly in order to conserve polymer. From these titration experiments, a volume of 1.00 M NaOH/ mass of mPEG-Cat could be determined for each metal for GPC experiments. 10.0 mg mPEG-Cat aliquots (1.79 mol), which had been speedvaced to remove water, were redissolved in water, as listed in the table below. 100 mM metal stock was then added. Then after 1 min, 1.00 M NaOH as listed in the table below was added, 30 min was allowed to pass, and then 978 L of GPC buffer (100 mM $NaSO_4$, 50 mM citrate, pH 3.5) was added and the sample was injected onto the GPC column within 5 min. After addition of GPC buffer, samples were at 10 mg/mL for injection on the column. The control mPEG-Cat solution was mPEG-Cat dissolved in the GPC buffer at 10 mg/mL. The GPC method employed was identical to a method that has been previously published for separation of $AgNO_3$ oxidized mPEG-Cat [5].

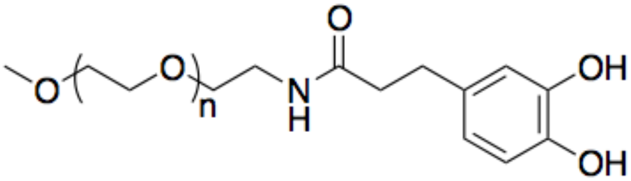


Figure S3: mPEG-Cat

	H_2O (μL)	100 mM metal (μL)	1.00 M NaOH (μL)
$FeCl_3$	12.4	5.95	3.92
$AlCl_3$	12.3	5.95	4.05
VCl_3	12.6	5.95	3.80

Figure S4: The conditions of the three different mPEG-Cat-metal reactions.

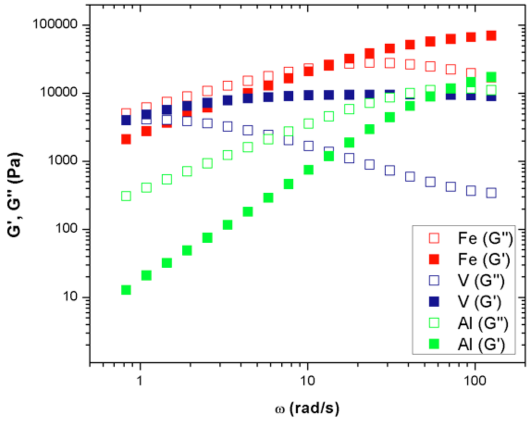


Figure S5: Example of oscillatory shear data from the different metal-catechol crosslinked gels.

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