Metal-coordination: Using one of nature's tricks to control soft material mechanics

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Abstract

Growing evidence supports a critical role of dynamic metal-coordination crosslinking in soft biological material properties such as self-healing and underwater adhesion[1]. Using bio-inspired metal-coordinating polymers, initial efforts to mimic these properties have shown promise[2]. Here we demonstrate how bio-inspired aqueous polymer network mechanics can be easily controlled via metal-coordination crosslink dynamics; metal ion-based crosslink stability control allows aqueous polymer network relaxation times to be finely tuned over several orders of magnitude. In addition to further biological material insights, our demonstration of this compositional scaling mechanism should provide inspiration for new polymer material property-control designs.

As a result of hundreds of millions of years of molecular evolution in aqueous environments, nature today presents us with macromolecular building blocks that in water can self-assemble into materials with extraordinary physical properties [3, 4]. Synthetic polymers can to some extent mimic this behavior, but typically in lower dielectric solvents that allow for structurally simple inter-molecular bonding motifs [5-9]. For advanced polymer material applications in aqueous environments, water-compatible dynamic bonding chemistry is required, and molecular structures adapted to optimize dynamic crosslinking in biological materials have offered inspiration [10]. However, while bio-inspired polymer design is an increasingly popular strategy in advanced polymer materials engineering [11-14], most bio-molecular crosslink structures remain challenging to mimic for the molecular engineer. Inspired instead by structurally simple biochemical adaptations recently demonstrated to play a vital role in the unique mechanical properties of marine biological loadbearing materials [1], we have found that metal-catechol coordination complexes (see Figure 1a) offer a macromolecular dynamic crosslinking mechanism that is easy to mimic, functional in water and highly tunable. In particular, inspired by the iron-binding catechol-rich proteins secreted during self-

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assembly of the self-healing mussel holdfast threads [15], we recently demonstrated how dilute low viscosity

aqueous solutions of catechol-modified polyethylene-glycol (PEG) polymers and $FeCl_3$ changes to strong

visco-elastic fluids following a basic pH jump due to instant Fe^{3+}-catechol coordination crosslinking[2]. The

coordination-crosslinked polymer networks display elastic moduli approaching covalently crosslinked

hydrogels under high strain rates but with self-healing after failure. Evidence suggests however, that

several metals in addition to iron are utilized by marine and terrestrial invertebrates to control the

mechanical properties of secreted catechol-rich polymeric materials via coordination-based crosslinking [16-18]. Using vanadium, iron and aluminum salts and simple catechol-modified PEG polymers, we demonstrate

here that metal-ion identity provides remarkable control over hydrophilic metal-coordinating polymer

mechanics by dictating crosslink dynamics; at constant pH the relaxation time of aqueous polymer

networks can be tuned across several orders of magnitude controlled only by the identity of the

coordinating metal ion. Metal-ion controlled hydrophilic polymer coordinate crosslinking therefore offers a

novel dynamic crosslink mechanism needed to advance functional polymer applications in aqueous

environments.

Following the same overall protocol (see Figure 1 and methods for details) VCl_3, $FeCl_3$, or

$AlCl_3$ salts were used in establishing polymer networks with catechol:metal ratios of 3:1, 15 %(w/w)

catechol-modified PEG polymer (cPEG) and pH 8 to imitate pH conditions in typical oceanic environments.

V- and Fe-samples displayed UV-Vis absorption typical of tris-catechol-V and bis-catechol-Fe coordination

(see Figure 2a), in agreement with their blue and purple colors, respectively [2, 19]. Al-samples absorbed

poorly suggesting at most weak, if any, catechol-Al coordination within the polymer network. In the low

energy region of resonance Raman spectra, catechol-metal bonds exhibit a characteristic vibrational band

by which bidentate coordination can be distinguished from monodentate based on the presence of a

distinct charge transfer (CT) peak at ~530cm^{-1} [20]. The relative intensity of the CT band was previously used

to identify tris-catechol-metal complexation in the mussel thread cuticle [1] and the pH-induced transition

between mono-, bis- and tris-complexes in catechol-Fe polymer networks [2]. In the present study, we

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observe that catechol-V coordinate polymer networks at pH 8 have a strong and well-defined CT band in the resonance Raman spectrum suggestive of tris-complexation (see Figure 2b). The CT band in catechol-Fe coordinate polymer networks at pH 8, however, is weak and poorly defined, consistent with bis-complexation and in contrast with the spectrum of catechol-Fe coordination at pH 12. Hence, our data imply that by using V^{3+} as the coordinating metal at pH 8, a larger degree of tris-complexation is achieved than when using Fe^{3+} at the same pH (see Figure 1a). Al-catechol polymer networks at pH 8 produced no significant resonance Raman signal above polymer background, again suggesting little to no catechol-Al coordination (see Figure 2b).

To assess the influence of the different metal-catechol coordinate crosslink dynamics on polymer network mechanics, we measured the loss tangent tan δ – which is defined as the ratio of the viscous (loss) modulus to the elastic (storage) modulus – of each network under small amplitude oscillatory shear deformation (see Figure 3a). Because the mechanical properties of a transient polymer network depend on the average stability of the crosslinks in the network, identifying the critical cross-over oscillatory frequency ω_c at which the network is equally fluid- and solid-like (i.e. where tan $\delta(\omega_c)$ = 1) provides a measure of its characteristic relaxation time, $\tau_c \sim 1/\omega_c$. Changes in network crosslink dynamics will be reflected in shifts in the value of τ_c [7, 21]. For example, previous studies utilizing pH to increase crosslink stability via shifts from bis- to tris-catechol-Fe coordination accordingly reported a 10-fold increase in polymer network τ_c [2]. Here, we demonstrate that simply replacing Fe as the coordinating metal with V at constant pH 8 induces equivalent transitions in crosslink stoichiometry (see Figure 2), and a similar increase in network relaxation time as illustrated by the 10-fold rise in τ_c (see Figure 3a). In agreement with the weak Al-catechol interactions suggested by spectroscopy, the more fluid-like Al-catechol coordinate polymer networks display a characteristic relaxation time that is about 5-fold lower than for Fe-catechol.

When characterizing viscoelasticity of physically entangled polymer networks, temperature is traditionally used as an external factor to tune the network dynamics. If oscillatory shear data from

different temperatures can be shifted onto a viscoelastic master curve in a 'time-temperature' superposition, it serves as evidence that the relaxation mechanisms in the network all scale similarly with thermal energy and that the material is 'thermorheologically simple' [22]. Hence, if the distinct mechanics of different metal-catechol crosslinked polymer networks are indeed determined by unique dynamics of their coordinate crosslinks, we should be able to perform an analogous 'time-metal' superposition. To test this hypothesis, a fractional Maxwell model was first used to fit the phase angle data for Al-catechol polymer networks (see note in supplementary information and Jaishankar *et al* [23] for details). By analogy with standard time-temperature superposition, we next rescaled the corresponding tan δ data from the V- and Fe-catechol polymer networks using the independently determined values of $\omega_{c,V}$ and $\omega_{c,Fe}$ to test if their rheological properties would collapse onto the same master curve (see Figure 3b). We found that, with the exception of the Fe-catechol polymer networks at long time scales and low frequencies (discussed further below), the viscoelastic behavior of all three networks indeed followed the same fractional Maxwell form. This finding suggests that switching the coordinating metal ion identity does not induce any phase transitions or supramolecular structural changes in the polymer networks [24], in support of the hypothesis that their diverse mechanical properties are determined primarily by variations in the metal-catechol bonding dynamics [25].

In conclusion, metal-catechol coordination crosslinking offers intrinsic control over hydrophilic polymer material mechanics. In catechol-modified PEG polymer networks at pH 8, V appears to induce tris-coordination, whereas Fe induces primarily bis-coordination (see Figure 1). This difference in coordinate crosslink stoichiometry results in 10-fold higher stability of V-catechol polymer networks compared to Fe-catechol and therefore significantly more solid-like properties (i.e. tan $\delta \ll 1$) for the frequency and temperature range tested in this study (see Figure 3a). Although our spectroscopy data suggest that Al does not induce strong coordinate bonding with PEG-catechol at the typical marine pH used here (see Figure 2), Al-catechol polymer networks are significantly more elastic than cPEG networks with no metal salt (see images in Figure 1c). Hence, the non-transition metal character of trivalent Al^{3+} appears to

induce weaker non-coordinate Al-catechol interactions of perhaps more purely electrostatic nature. The different crosslink stabilities induced by V and Fe are intriguing when one considers the utilization of these metals in ascidian wound plugs and mussel threads, respectively [1, 18]. Although we recognize that the comparison between our catechol-modified PEG-polymer networks and biological materials is an over-simplification, at oceanic pH ≈ 8 the lower stability of bis-catechol-Fe coordinate crosslinks could offer enhanced dissipation in the mussel thread while the more stable tris-catechol-V coordination could provide more immediate solid-like properties to wound plugs. The use of non-reducing conditions in our experiments (and in nature), however, should not be overlooked [15]. Fe^{3+}-driven catechol oxidation appears to introduce a small fraction of covalent crosslinks in the Fe-catechol polymer networks (see supplementary Figure S2 and Barret *et al* [26] for details) whose permanent contribution to network elasticity could explain the deviation of the Fe-catechol polymer network from the time-metal coordination master curve at low frequencies (see Figure 3b). Furthermore, the blue color of V-catechol polymer networks (see Figure 2a) suggests a conversion from V^{3+}- to V^{4+}-tris-catechol coordinate complexes [19, 27] which could also potentially lead to slow, redox-driven covalent crosslinks forming in these networks over longer time. Metal redox-catalyzed covalent crosslinking is well known from metalloenzymatic activity, yet its impact on the kinetics of coordinate crosslinking in biological materials has up until recently received little attention [26, 28, 29]. However, conversions from purely coordinate to permanent covalently crosslinked materials could play a functional role in ascidian wound plugs as well as in future medical adhesives and sealants, where a gradual shift from a self-healing viscoelastic network to a chemically cured elastic solid is desirable. Finally, the time-metal coordination master curve developed here demonstrates that as a crosslinking mechanism, metal-coordination provides the opportunity to tune viscoelastic properties of hydrophilic polymer materials over several orders of magnitude purely by the simple choice of coordinating metal ion identity. While it remains speculative whether this versatile control over bulk material mechanics via crosslink dynamics has been a selective driving force integrating this crosslinking mechanism into biological materials

design, our demonstration should serve as inspiration for future design of synthetic polymer materials intended for applications in aqueous environments.

Methods

Synthesis of cPEG. cPEG polymer was synthesized using a 4-arm PEG amine core of MW 10,000 g/mol, as previously reported [30].

Gel protocol. The above described cPEG polymer was used for all gel experiments. Freeze-dried aliquots of the polymer stored under argon or N_2 at -20 °C, were equilibrated to room temperature for 1 hour prior to use and before opening sample vial to prevent water condensation on the sample. A typical 400 µl metal-catechol crosslinked gel was made as follows: **1)** Polymer solution was prepared by dissolving 80 mg polymer in 200 µl unbuffered Milli-Q water to a starting concentration of ~30% (w/w). **2)** The polymer solution was mixed with 1/3 final volume of 80 mM of either VCl_3, $FeCl_3$ or $AlCl_3 \bullet 6H_2O$ (Sigma, St. Louis, MO). **3)** Gels were established by adding 1/6 final volume of NaOH (Sigma, St. Louis, MO) at a concentration adjusted to induce a final pH 8 of the gels. This resulted in instant gelation and color development. **4)** The gel was physically mixed until a homogenous color and physical state was established (~30 sec). Samples were tested in the rheometer after 30min of relaxation in airtight containers to prevent dehydration. The final concentration of cPEG in all gels was thereby ~15% (w/w) with a final molar ratio of dopa to metal of 3:1. This corresponds to ~0.15% (w/w) of V and Fe and to ~ 0.07% (w/w) of Al in the final gels. The pH of gels was measured using a pH-meter with a flat surface electrode designed for solids, semi-solids and liquids (FieldScout SoilStik pH Meter, Spectrum Technologies, Plainfield, Illinois).

Spectroscopy. Absorbance of gels was measured at the 30min time point holding the gel between two cover slips and placing them directly in the light path of a UV-visible light spectrophotometer (Perkin Elmer, Waltham, MA). For Raman spectroscopic studies, a continuous laser beam was focused on the samples through a confocal Raman microscope (CRM200, WITec, Ulm, Germany) equipped with a piezo-scanner (P-500, Physik Instrumente, Karlsruhe, Germany). The diode-pumped 785 nm near infra-red (NIR) laser

excitation (Toptica Photonics AG, Graefelfing, Germany) was used in combination with a 20× microscope objective (Nikon, NA = 0.4). The spectra were acquired using an air-cooled CCD (DU401A-DR-DD, Andor, Belfast, North Ireland) behind a grating (300 g mm^{-1}) spectrograph (Acton, Princeton Instruments Inc., Trenton, NJ, USA) with a spectral resolution of 6 cm^{-1}. Because the samples were sensitive to burning by the laser beam, a laser power of between 10-20 mW, combined with a short integration time of 0.2 s was used for all measurements. The ScanCtrlSpectroscopyPlus software (version 1.38, Witec) was used for measurement setup and spectral processing. Each collected spectra consisted of 60 accumulations of a 0.2 s integration time. For each sample, three spectra were collected from different regions and averaged. Averaged spectra were smoothed with a Savitzky-Golay smoothing filter, and a 2nd order polynomial background was subtracted from the smoothed spectra.

Rheology. The mechanical properties of the hydrogels were tested using a rheometer (Anton Paar, Ashland, VA) with parallel plate geometry (50 mm diameter rotating top plate). All tests were done at the 30min time point after gel initiation. Oscillatory shear testing of gels as a function of frequency was performed at constant 1% strain (linear viscoelastic regime 0 - ~60% strain) while measuring storage modulus (G') and loss modulus (G'') (see representative data below). Water loss during testing was negligible due to typical gap distances between parallel plates of <1mm and typical test time of <30 min. All tests were performed at 20 °C.

Author Contributions

N.H.-A. and K.Y.C.L. designed research; N.H.-A., M.J.H., D.E.F. and G.D., performed research; D.E.F., L.H. and

P.B.M. contributed new reagents/analytic tools; N.H.-A., A.J., M.J.H., D.E.F., G.D., G.H.M., P.B.M. and

K.Y.C.L. analyzed data and N.H.-A., A.J., M.J.H., D.E.F., G.D., G.H.M., P.B.M. and K.Y.C.L. wrote the paper.

Conflict of Interest Statement

The authors declare no competing financial interests.

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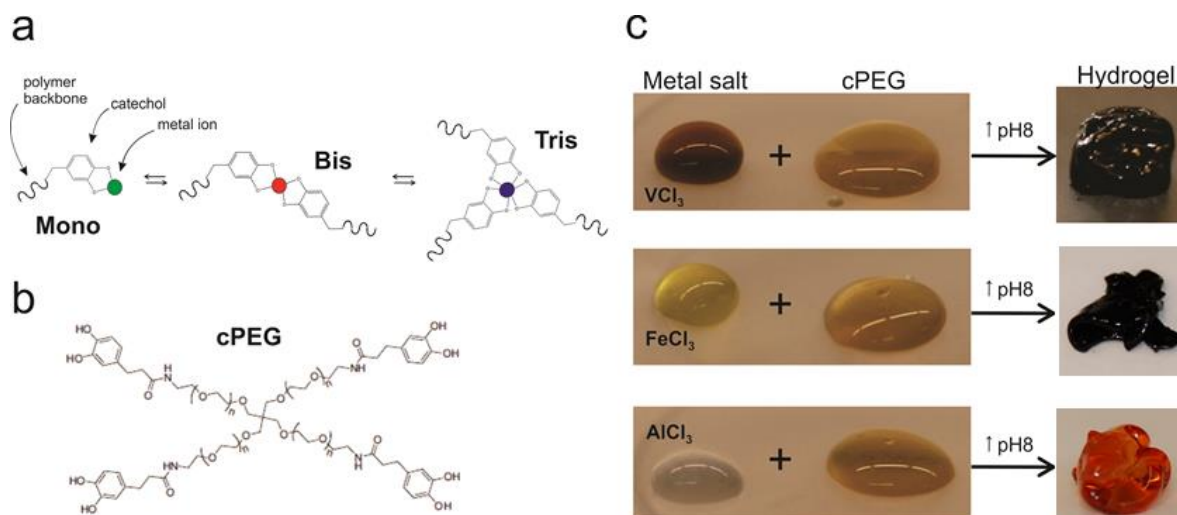
Figure 1. Metal-catechol coordination polymer networks. (a) Dynamic metal-catechol coordination complexes explored as polymer crosslinks. Order of coordinate complex stability is: tris>bis>mono (no crosslinking). **(b)** The catechol-modified polyethylene-glycol polymer (cPEG, 10 kDa PEG core) used to establish samples. **(c)** Sample fabrication. Three different trivalent metal ion cross-linkers were used to establish three different polymer networks. All networks were established with catechol:metal ratio of 3:1, 15 %(w/w) cPEG polymer and pH 8.
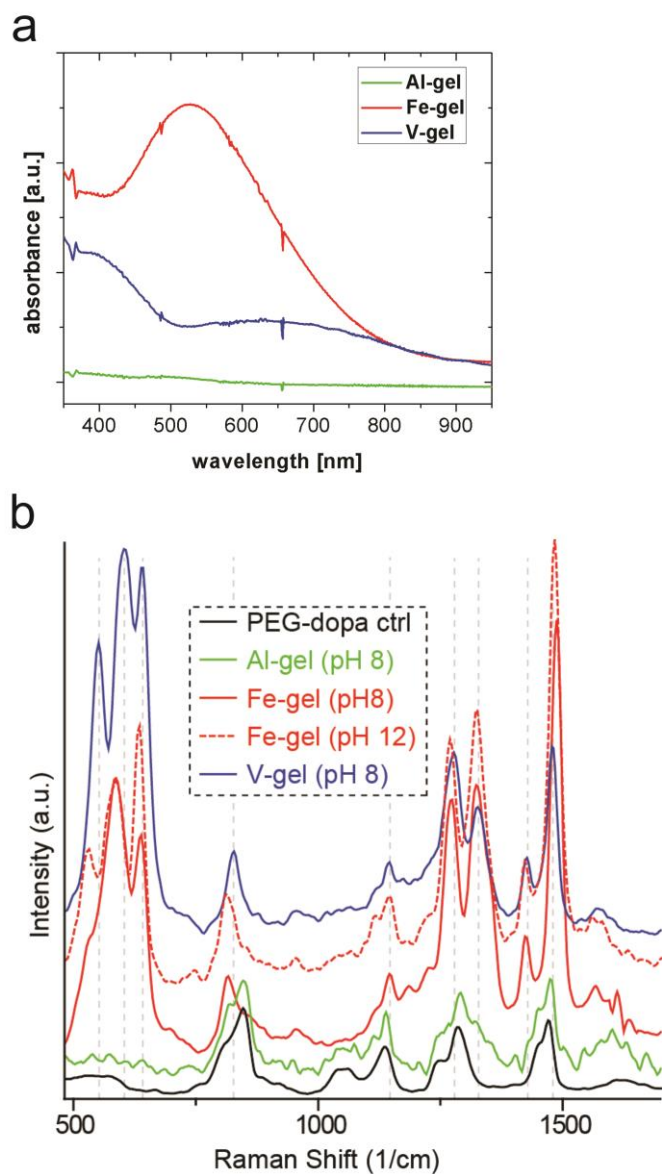
Figure 2. Spectroscopic properties of metal-catechol crosslinked polymer networks. (a) UV-Vis absorption. Fe-catechol network absorption is characteristic of mostly bis-catechol-Fe coordination (peak ~525nm), V-catechol networks absorb in agreement with tris-catechol-V coordination bonding (broad peak at 600-700nm and ~395nm) while only weak absorption is observed in Al-catechol networks. **(b)** Resonance Raman spectroscopy. The V- and Fe-catechol polymer networks show dominant resonance peaks characteristic of catechol-metal coordination arising from the metal-oxygen interaction (490–696 cm^{-1}) and catechol ring vibrations (1,190–1,519 cm^{-1}). Al-catechol polymer networks give no resonance signal above the polymer background. Also shown for comparison is the Raman spectrum for Fe-catechol polymer

networks at pH 12. Note the CT peak ~530cm^{-1} present in V-catechol polymer networks (and Fe-catechol polymer networks at pH 12).
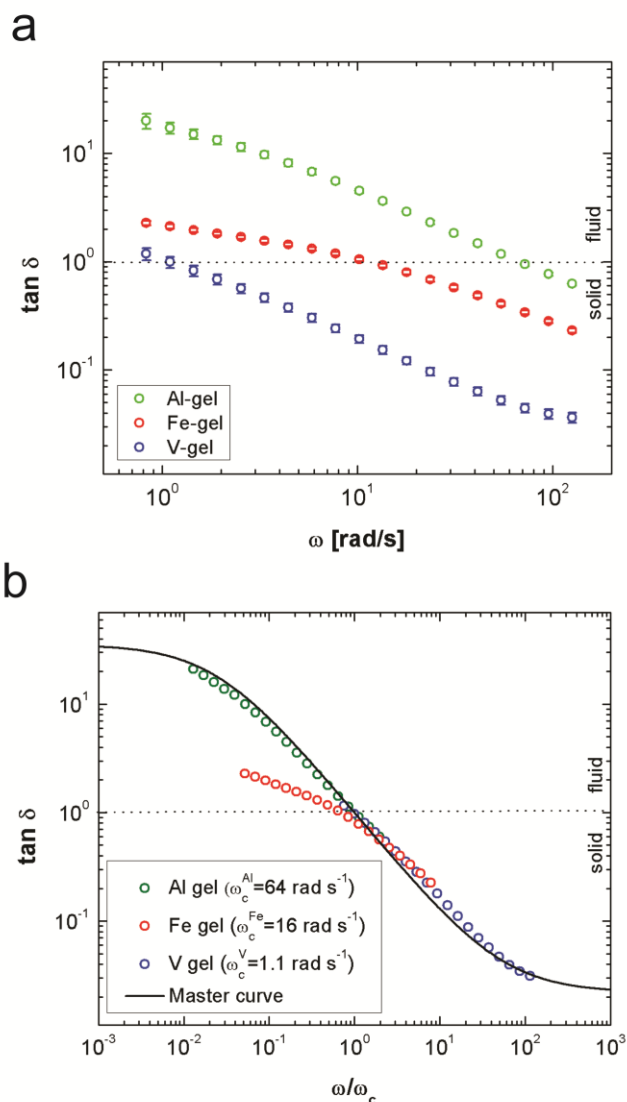

Figure 3. Mechanical properties of metal-catechol crosslinked polymer networks. (a) Linear viscoelastic properties. The loss tangent tan δ of the three different metal-catechol coordination crosslinked networks as a function of small amplitude oscillatory shear frequency (ω) is shown. The dynamically crosslinked polymer networks display increasing values of tan δ with decreasing ω as a result of decreasing numbers of elastically-active crosslinks contributing to the network. The critical cross-over oscillatory frequency ω_c at which the network is equally fluid- and solid-like is defined by tan $\delta(\omega_c) = 1$. For each data point (mean) N = 4. Error bars represent one standard deviation. See supplementary Figure S1 for loss modulus (G'') and

storage modulus (G') raw data. **(b)** Time-metal coordination superposition. With polymer network mechanics dictated by coordinate crosslink dynamics as determined by each metal ion, we can shift tan δ curves for all polymer networks onto one master curve by using their individual crossover frequency ω_c as scaling factors. The broad spectral distribution of characteristic time scales in the network is consistent with a fractional Maxwell model description as indicated by the solid line. The specific deviation of the data for Fe-catechol polymer networks in the low frequency regime (tan δ > 1) is due to unique covalent bonding (see supplementary Figure S2), which increases the network elasticity and causes these networks to be structurally different at long times (see text for details).