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1 **Dual crosslink hydrogels with metal-ligand coordination bonds –**
2 **tunable dynamics and mechanics under large deformation**

3
4 **Jingwen Zhao¹, Tetsuharu Narita^{1,2*} and Costantino Creton^{1,2*}**

5
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11
12
13 **Abstract**

14
15 *Introducing additional physical and reversible crosslinks to a chemically crosslinked*
16 *hydrogel is an interesting and viable alternative to increase the toughness of a hydrogel. Yet*
17 *while in general the physical crosslink points provide dissipative mechanisms, there are still*
18 *many details that are unknown in particular on the role that physical crosslinks play on the*
19 *large strain behavior. We explore the mechanical properties in small and large strain of two*
20 *dual crosslink gels made from a random copolymer of Poly(acrylamide-co-vinylimidazole)*
21 *with a range of elastic moduli in the tens of kPa. The interaction between vinyl imidazole*
22 *groups and Metal ions (Zn^{2+} and Ni^{2+}) results in physical crosslink points and in a markedly*
23 *stretch rate dependent mechanical behavior. While a main relaxation process is clearly*
24 *visible in linear rheology and controls the small and intermediate strain properties, we find*
25 *that the strain hardening behavior at stretches of $\lambda > 4$ and the stretch at break λ_b are*

1 *controlled by an additional longer lived physical crosslinking mechanism that could be due to*
2 *a clustering of physical crosslinks..*

3

4 **Introduction**

5 Hydrogels are promising candidates for biomedical applications such as artificial organs or
6 tissue engineering thanks to their liquid-like and solid-like properties¹. However, contrary to
7 biological hydrogels such as cartilage, conventional synthetic hydrogels made by free radical
8 polymerization suffer from mechanical fragility, due to the heterogeneous network structures
9 and the lack of dissipative mechanisms². Mechanical reinforcement has become one of the
10 hottest topics of gel science in the last decades³⁻⁹. Among the different reinforcement
11 strategies, introduction of sacrificial bonds inside the gel in order to dissipate energy near the
12 crack tip has proved promising. The pioneering work of Gong⁹ in 2003 provided a good
13 solution by creating two interpenetrated networks having different properties: a low volume
14 fraction of highly crosslinked and stretched network and a high volume fraction of loosely
15 crosslinked second network. This hydrogel has a much better fracture toughness than either
16 network on its own. However, this network design strategy based on irreversible bond
17 breaking results in permanent damage in the network¹⁰, thus the same mechanical behaviors
18 of the virgin gels cannot be recovered after loading cycles.

19 A successful alternative can be the incorporation of reversible crosslinks into the network.
20 Because the reversible crosslinks serve as sacrificial bonds they can break and reform under
21 strain and hence make the propagation of a crack more energetically costly¹¹. Although the
22 detailed mechanism by which these dynamic bonds delay crack propagation may be complex,
23 it has been proposed that the presence of these additional bonds may reduce local stress

1 concentration, delaying the rupture of the chemical networks¹². As reversible bonds, various
2 non-covalent and dynamic covalent bonds can be employed, and there have been many
3 examples reported in the literature^{3, 5, 13, 14}. It should be noted that hydrogels with only
4 physical crosslinks (and possibly entanglements) may irreversibly plastically flow at long
5 time scales if the longest characteristic relaxation time is comparable to or shorter than the
6 inverse of the strain rate. Adding a small amount of chemical crosslinks to prevent the
7 terminal flow and keep the reference state of deformation is a practical solution as employed
8 in the certain number of the systems reported in the literature, especially for the networks with
9 short lived reversible bonds¹⁵⁻¹⁷.

10 Creton, Narita, and their coworkers have reported an intriguing example of such “dual
11 crosslink” hydrogels, having a small amount of permanent crosslinks and a large amount of
12 transient crosslinks¹⁸⁻²¹. Based on poly(vinyl alcohol), PVA, permanently crosslinked by
13 glutaraldehyde and transiently crosslinked by borate ions (by dynamic covalent bond), their
14 PVA dual crosslink gels exhibit time-dependent elasticity. Prepared by a simple procedure,
15 consisting of incorporating physical crosslinks by diffusion of borate ions into a previously
16 prepared chemical gel, some unique rheological features of the PVA dual crosslink gel have
17 been experimentally and theoretically characterized with the corresponding chemical gel as
18 reference.^{18, 20-26} The chemical and physical crosslinks contribute to the viscoelasticity
19 independently, and the moduli of the dual crosslink gels can be decomposed into the
20 contribution of the chemical bonds (same as that of the reference chemical gel) and that of the
21 physical bonds (not identical to a corresponding physical gel due to the suppression of the
22 terminal flow by the chemical crosslinks) (additivity)^{22, 25}. The stretch rate-dependent stress
23 can be then separated into the product of a time-dependent term (equivalent to a relaxation
24 modulus) and a strain-dependent term (expressed as a neo-Hookean model)²². This behavior

1 can be quantitatively described by a constitutive model combining large strain elasticity and
2 time-dependent sticker dynamics^{19, 23, 24} and using only four physically based parameters is
3 sufficient to fit both tensile and torsion tests results.

4 The systematic studies of the mechanical properties of the PVA dual crosslink gels over a
5 wide range of time scales and strain rates indicate the importance to study the properties at
6 different characteristic bond breaking rates as well as at very high extension^{22, 25}. Does the
7 dual crosslink gel behave similarly to the chemical gel at time scales much longer than its
8 transient bond breaking time? Or, can the strain rate be normalized by a characteristic time
9 measurable in linear rheology to obtain a universal law for the time-dependent properties? In
10 order to answer these questions, it is important to investigate the mechanical properties of
11 dual crosslink gels having a short characteristic time and/or at very slow stretch rate. The
12 relaxation time of the PVA dual crosslink gel is relatively long (of the order of 1 s) and it is
13 difficult to tune it in a physicochemical manner. It is also experimentally difficult to perform
14 time-consuming mechanical tests at very slow stretch rates, due to problems of drying or
15 poroelastic relaxation.

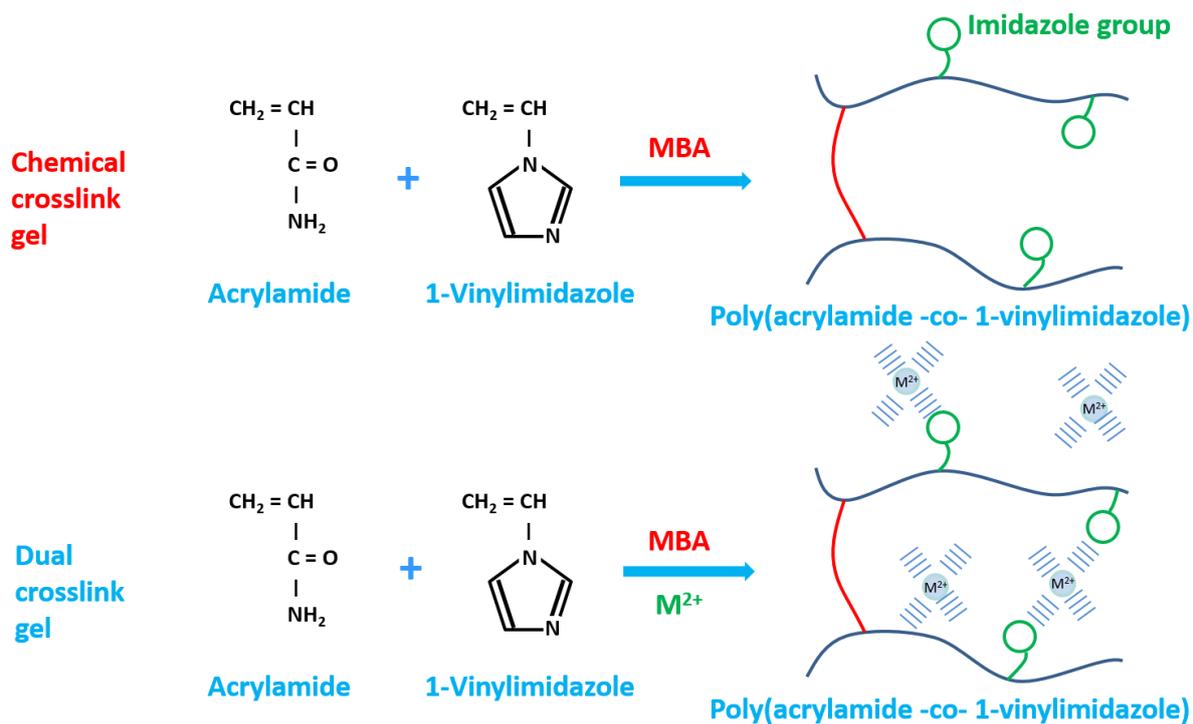
16 Metal-ligand coordination bonds can be a promising option as tunable transient crosslinks: by
17 changing metal ion species dynamics can be tuned. Various physical gels crosslinked by
18 metal-ligand coordination bonds have been reported²⁷⁻³⁰. Holten-Andersen et al. developed
19 physical gels crosslinked by catechol-Fe³⁺ complexes exhibiting pH sensitive mechanical
20 properties²⁷. Histidine-modified star PEG polymers were synthesized to mimic the histidine-
21 rich regions of the mussel byssal thread collagen²⁸. 4-arm-PEG-Histidine (4PEG-His)
22 crosslinked with metal ions was synthesized to produce hydrogels with tunable relaxation
23 times, which follow the order Ni²⁺ > Cu²⁺ > Zn²⁺.

1 More recently various tough dual crosslink hydrogels with metal-ligand coordination bonds
2 have been reported³¹⁻³³. While macroscopic tests of their toughness and self-recovery
3 properties were studied, the nonlinear mechanical properties as a function of the transient
4 bond relaxation time and the strain rate have not been systematically studied. Kean et al.
5 synthesized a series of dual crosslink *organogels* with metal-ligand coordination bonds, and
6 showed that the short-lived transient crosslinks do not increase the modulus (thus they are
7 *invisible*), while they can improve the extensibility of the network better than the long-lived
8 transient crosslinks³⁴. This intriguing observation is one of the motivations of the work we
9 report.

10 We investigate here a new dual crosslink hydrogel based on polyacrylamide, another simple
11 neutral hydrosoluble polymer, copolymerized with N-vinylimidazole. This gel possesses a
12 fast and tunable dynamics due to imidazole – metal ion coordination bonds and ingredients
13 are commercially available and readily soluble in water. Poly(acrylamide-co-vinylimidazole)
14 was synthesized by free radical copolymerization in the presence of physical crosslinkers
15 (transient metal ions, Ni²⁺ or Zn²⁺) and a chemical crosslinker (methylene bisacrylamide)
16 (**Figure 1**: Schematic presentation of the formation of the chemical gel and the dual crosslink
17 gel**Figure 2**). With this relatively easy and quick “one-pot” synthesis (simultaneous chemical
18 and physical crosslinking and polymerization), we successfully synthesized hydrogels having
19 both chemical and physical crosslinks. This simple fabrication process from inexpensive
20 readily available components sacrifices precise network and structural control but makes it
21 possible to produce the necessary amount of material samples to perform systematic
22 mechanical tests in large strain.

1 In this work we attempt to understand the relation between the macroscopic mechanical
2 properties in large strain and the dynamics of the coordination bonds over a wide dynamic
3 range.

4



1

2 **Figure 1:** Schematic presentation of the formation of the chemical gel and the dual crosslink
 3 gel

4 .

5

6

7

1 **Experimental section**

2 **Materials**

3 Acrylamide (AAm), 1-vinylimidazole (VIm), methylene bisacrylamide (MBA), potassium
4 persulfate (KPS), N,N,N',N'-Tetramethylethylenediamine (TEMED), nickel chloride, and
5 zinc chloride were purchased from Sigma Aldrich, and used as received. Milli-Q water is
6 used for the sample preparation.

7 **Sample Preparation**

8 Dual crosslink gels and the corresponding chemical gels were prepared by radical
9 polymerization. For the chemical gel, an aqueous solution containing AAm (1.8 M), VIm
10 (0.2 M), MBA (2 – 10 mM, corresponding to 0.1 – 0.5 mol% of the total monomer
11 concentration, 2 M) and KPS (6 mM) was prepared under nitrogen flow at low temperature
12 (in an ice bath). The solution was then transferred in a glovebox, and TEMED (20 mM) was
13 added to initiate radical polymerization. After the overnight reaction, the obtained P(AAm-co-
14 VIm) chemical gels were used for measurements as prepared. P(AAm-co-VIm)-M²⁺ dual
15 crosslink gels were prepared in the same procedure, by adding further NiCl₂ or ZnCl₂ in the
16 solution, the concentration of MBA was fixed at 3 mM (0.15 mol%). After the overnight
17 crosslinking reaction, the obtained P(AAm-co-VIm)-M²⁺ dual crosslink gels were used for
18 measurements as prepared.

19 **Linear viscoelastic properties**

20 The linear viscoelastic properties of the dual crosslink gels in small strain oscillatory shear
21 were characterized in a parallel plates geometry with roughened surfaces (20 mm in diameter)
22 with the ARES LS1 rheometer (TA instruments). The sample thickness was 1.5 mm.

1 Frequency sweep tests with a dynamic range varying from 0.1 to 100 rad/s were carried out at
2 25 °C within the linear viscoelasticity regime (0.2 – 0.8 % strain).

3 **Uniaxial tensile tests**

4 The large deformation behavior of the gels was investigated by uniaxial tensile test to fracture
5 and step-cycle loading – unloading tests on an Instron 5565 tensile tester with a 10 N load cell.

6 Samples were rectangular in shape with 5 mm in width, 1.5 mm in thickness, and 15 mm in
7 length L_0 (length between clamps). We kept the samples in paraffin oil during all the tests to
8 prevent them from drying following a previously published procedure¹⁸.

9

1 Results and Discussion

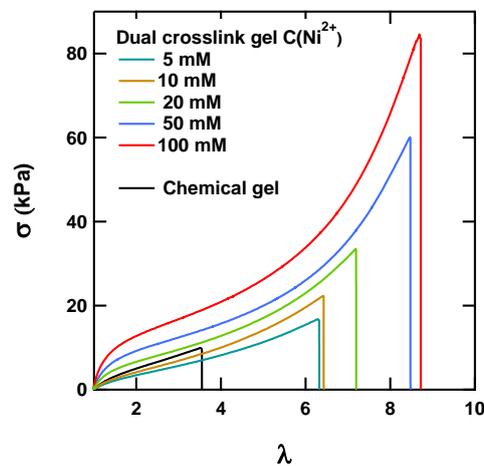
2 (1) Strength of P(AAm-co-VIm)-Ni²⁺ dual crosslink gel

3 In order to confirm that the introduction of the metal-ligand coordination bonds can improve
4 the strength of the polyacrylamide gel, we performed uniaxial stretching experiments and
5 characterized the nonlinear (large strain) behavior of the P(AAm-co-VIm)-Ni²⁺ dual crosslink
6 gels, at different Ni²⁺ concentrations (5 – 100 mM). The tensile stress σ was plotted as a
7 function of the stretch ratio λ (defined as $\lambda = L/L_0$) at the same stretch rate $\dot{\lambda} = 0.06 \text{ s}^{-1}$. The
8 results for the dual crosslink gels with different values of $[\text{Ni}^{2+}]$ and for the corresponding
9 chemical gel are shown in **Figure 2**. For all values of $[\text{Ni}^{2+}]$, the dual crosslink gels have
10 higher extensibilities than the chemical gel and the strain at break dramatically increases with
11 the introduction of physical crosslinks: with a value of λ at break λ_b varying from less than 4
12 for the chemical gel to over 6 for the dual crosslink gels. λ_b can reach to about 8.5 when the
13 concentration of the transient crosslinker $[\text{Ni}^{2+}]$ is increased to 100 mM.

14 For the values of the stress, a complex $[\text{Ni}^{2+}]$ dependence is seen. For $[\text{Ni}^{2+}] > 20 \text{ mM}$, the
15 increase of $[\text{Ni}^{2+}]$ leads to a significant increase of the stress over the whole range. The stress
16 vs. stretch curves resemble more those of a strain crystallizing rubber such as natural rubber³⁵
17 or a pressure-sensitive-adhesive³⁶: softening at intermediate strains, indicating the breakup of
18 a network structure, and strain hardening at large strain indicating finite extensibility of the
19 polymer chains. This strain hardening behavior becomes significant at $\lambda > 5$, a stretch level
20 which is not easily accessible for conventional chemical gels, or even with the PVA dual
21 crosslink gels¹⁸. For gels with low Ni²⁺ concentration (5 and 10 mM), the stress-strain curve
22 is similar to that of the chemical gel, but with much higher extensibility, with $\lambda_b > 6$. It should

1 be pointed out however that the modulus of the dual crosslink gel with $[\text{Ni}^{2+}] = 5 \text{ mM}$ is lower
2 than that of the chemical gel. We assume that this comes from the modification of radical
3 polymerization due to the presence of nickel ions which reduces the chemical crosslinking
4 density in the dual crosslink gel. For the rest of this paper we investigated the dual crosslink
5 gel with $[\text{Ni}^{2+}] = 100 \text{ mM}$, corresponding to the stoichiometric amount needed to complex the
6 ion with two imidazole ligands ($[\text{VIm}] = 200 \text{ mM}$).

7



8

9 **Figure 2:** Stress - strain curves of the dual crosslink gels with different Ni^{2+} concentrations
10 compared with the corresponding chemical gels at a stretch rate of 0.06 s^{-1} at room
11 temperature.

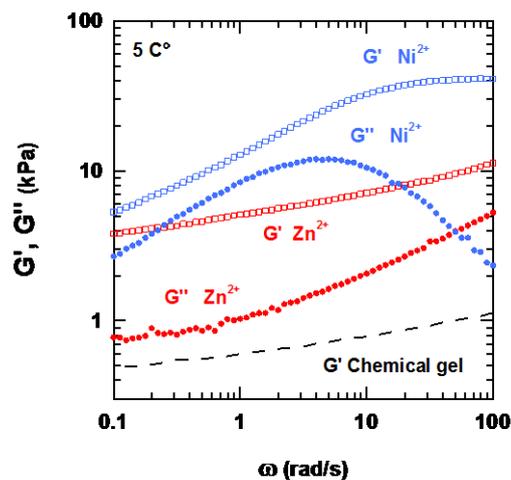
12

13 (2) Tunable dynamics: linear rheology

14 By changing the nature of the metal ions, the dynamics of the transient crosslinks and the
15 relaxation time of the dual crosslink gel can be tuned. Here, we chose Ni^{2+} and Zn^{2+} as two
16 relatively fast exchanging transient metal ions to study the tunable mechanics of dual
17 crosslink hydrogels with metal-ligand coordination.

18

1 **Figure 3** shows the dynamic moduli as a function of angular frequency for P(AAm-co-VIm)-
 2 Ni²⁺ and Zn²⁺ dual crosslink gels at 5°C and $G'(\omega)$ for the corresponding chemical gel (The
 3 value of G'' was very low (0.05 – 0.4 kPa) and is not shown)). For the Ni²⁺ based dual
 4 crosslink gel, G' increased with frequency up to an elastic plateau at $\omega > 20$ rad/s while G''
 5 showed a broad peak correlated with the rate of decrease in G' . This result indicates that the
 6 dissociation of the physical crosslinks by Imidazole-Ni²⁺ ion interactions induce a large
 7 dissipation around $\omega = 4 - 5$ rad/s. The P(AAm-co-VIm)-Zn²⁺ gel has a lower G' over the
 8 whole frequency range, and no clear elastic plateau is observed within the tested frequency
 9 window. Similarly G'' does not show a peak indicating that the dissociation kinetics of Zn²⁺ -
 10 Imidazole is much faster than that of Ni²⁺ - Imidazole and the peak of G'' is not
 11 experimentally accessible with this rheometer.



12

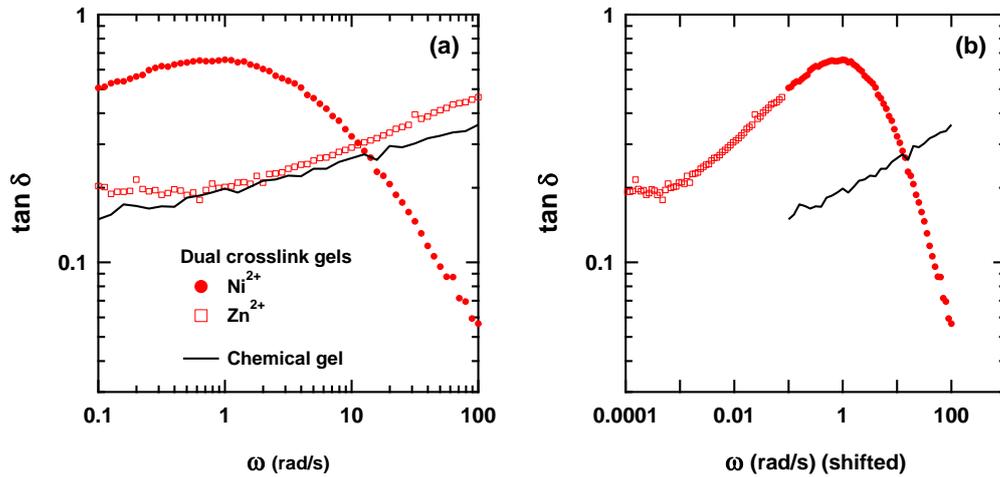
13 **Figure 3.** Angular frequency dependence of $G'(\omega)$ and $G''(\omega)$ for the P(AAm-co-VIm)-M²⁺
 14 dual crosslink gels compared with the corresponding chemical gel. [M²⁺] = 100 mM, at 5 °C.

15

16 A simple physical picture of the dual crosslink gels suggests an additive contribution of
 17 permanent and transient crosslinks to the dynamic moduli, and the dynamics of the transient

1 bonds can be characterized by a main relaxation time. Note that in principle the value of
 2 $G'(\omega)$ for these gels should approach the value of G' of the chemical gel at low frequency.
 3 However, as shown in **Figure 3** the measured values of G' are still significantly higher than
 4 that of the chemical gel even at the lowest frequency studied. This result indicates that there
 5 can be a second slower transient component in the dual crosslink gel systems.

6 In order to estimate the characteristic relaxation time of the P(AAm-co-VIm)-Zn²⁺ dual
 7 crosslink gel which does not show a peak of G'' in an accessible frequency range, we
 8 constructed a master curve of the loss tangent $\tan \delta$. **Figure 4** shows $\tan \delta(\omega)$ of the two
 9 P(AAm-co-VIm)-M²⁺ dual crosslink gels. The values of $\tan \delta(\omega)$ of the P(AAm-co-VIm)-
 10 Ni²⁺ gel show a peak at about $\omega = 1$ rad/s, while for the P(AAm-co-VIm)-Zn²⁺ $\tan \delta$ increases
 11 monotonously with ω . The P(AAm-co-VIm)-Zn²⁺ curve was horizontally shifted to
 12 successfully obtain a master curve (**Figure 4b**) so that the characteristic relaxation time of
 13 P(AAm-co-VIm)-Zn²⁺ can be estimated to be 0.56 ms.



14
 15 **Figure 4:** (a) The loss tangent $\tan \delta$ of Ni²⁺ and Zn²⁺ dual crosslink gels and the chemical gel,
 16 as a function of ω . (b) $\tan \delta$ as a function of shifted ω .

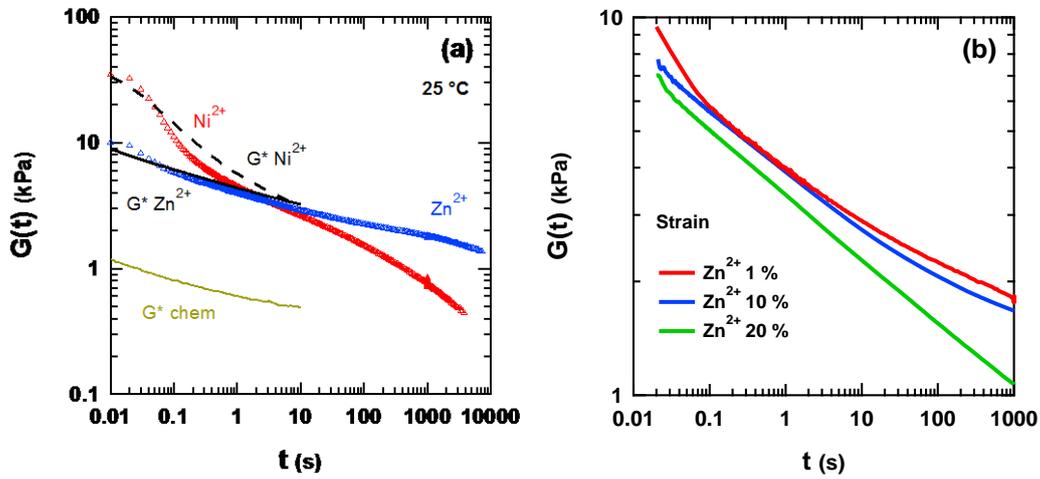
17

1 (3) Stress relaxation

2 In order to investigate the dynamics of the dual crosslink gels over a larger time window,
3 shear stress relaxation tests were performed. **Figure 5a** shows the relaxation modulus of
4 P(AAm-co-VIm)-Ni²⁺ (red) and P(AAm-co-VIm)-Zn²⁺ (blue) dual crosslink gels at a fixed
5 strain of 1 %. The relaxation modulus of the P(AAm-co-VIm)-Ni²⁺ gel shows two relaxation
6 processes at $t < 1$ s and after about 10 s. After several thousand seconds, $G(t)$ of this dual
7 crosslink gel appears to approach the value of the chemical gel. On the other hand the
8 relaxation modulus of the P(AAm-co-VIm)-Zn²⁺ gel starts from lower values than that of
9 P(AAm-co-VIm)-Ni²⁺ gels, and the following relaxation is less pronounced. Interestingly, the
10 values of the modulus of these two gels intersect with each other after about 3 s, confirming
11 the different behavior at long times. Our physical picture of the dual crosslink gels assumes
12 that the modulus of the dual crosslink gel at low frequency should be equivalent to that of the
13 corresponding chemical gel. However, even at 1000 s the dual crosslink gels do not fully relax
14 suggesting the existence of a slower relaxation mode in the dual crosslink gels.

15 The results in the frequency domain and time domain can be compared by using the Cox-
16 Merz rule. For the gel with Ni²⁺, the relaxation modulus and the dynamic modulus do not
17 match: in fact during the stress relaxation, breaking and healing of the physical crosslinks
18 occurs but the healed bonds do not carry stress, while during the dynamic measurement the
19 oscillatory deformation is continuous and the elastically active chains between healed bonds
20 carry stress. Thus the dynamic modulus is slightly higher than the relaxation modulus. For the
21 P(AAm-co-VIm)-Zn²⁺ gel, the difference between the relaxation modulus and the dynamic
22 modulus is small, due to the fast dynamics of the transient crosslinks with Zn²⁺.

1 In order to make a connection with the large strain behaviors discussed in the next section, let
 2 us check the strain dependence of the stress relaxation in shear. A shear stress relaxation was
 3 carried out for different imposed strains (1, 10 and 20 %) and results are shown in **Figure 5b**
 4 for the P(AAm-co-VIm)-Zn²⁺ gel. The relaxation modulus of the P(AAm-co-VIm)-Zn²⁺ gel
 5 decreases with increasing strain, suggesting that the slower relaxation did not satisfy the
 6 separability between the strain- and time-dependent terms of the stress. This point is further
 7 discussed in the next section.



8

9 **Figure 5.** *a)* Stress relaxation $G(t)$ as a function of time of the dual crosslink gels with Ni²⁺
 10 (red) and Zn²⁺ (blue) at 25 °C, and the dynamic modulus obtained with the Cox-Merz rule for
 11 the chemical gel (yellow line) and the dual crosslink gels with Ni²⁺ (black dotted line) and
 12 Zn²⁺ (black solid line). *b)* Shear stress relaxation modulus $G(t)$ for different imposed strains (1,
 13 10 and 20 %) for the P(AAm-co-VIm)-Zn²⁺ gel.

14

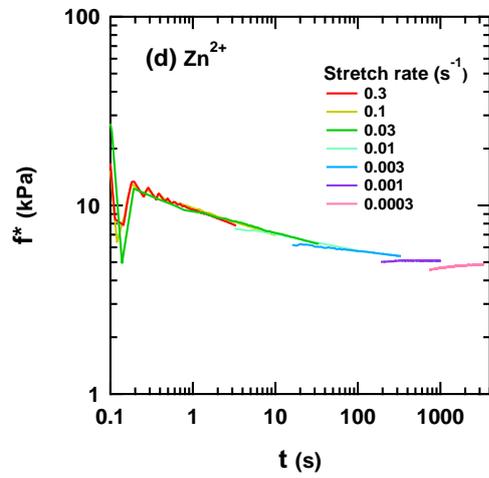
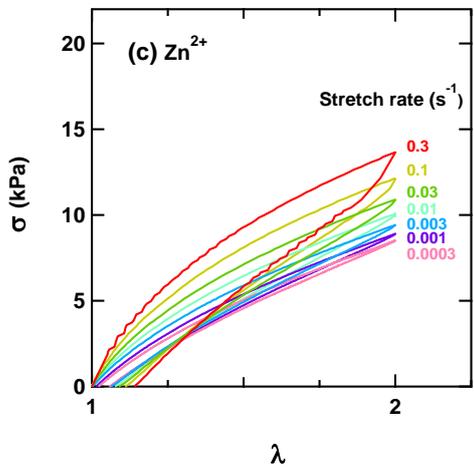
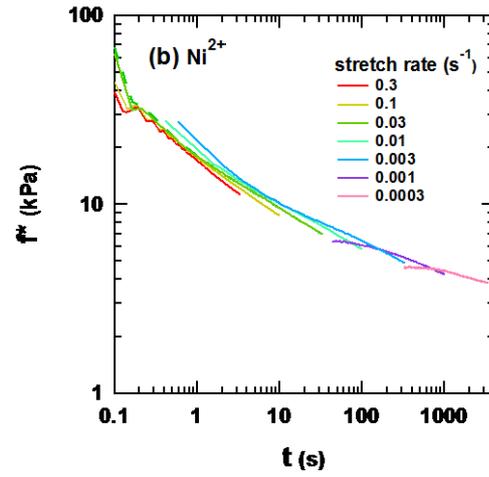
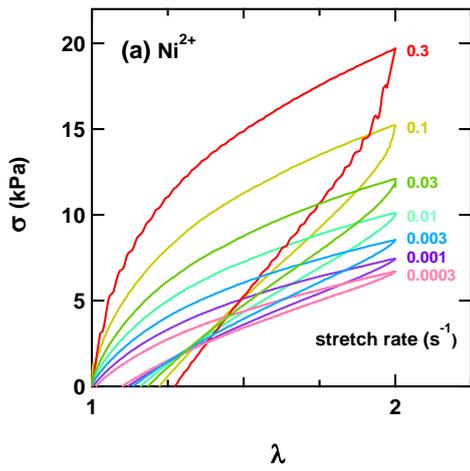
15 **(4) Intermediate strain tensile cyclic tests**

16 At intermediate deformations we carried out a series of loading and unloading cycles up to λ
 17 = 2 at seven different stretch rates (0.0003, 0.01, 0.003, 0.01, 0.03, 0.1 and 0.3 s⁻¹) on both
 18 types of dual crosslink gels to investigate the strain dependence of the modulus as well as the
 19 hysteresis (**Figure 6a, c**). These gel samples were not stretched to rupture, and the same

1 sample was stretched repeatedly at different stretch rates after a sufficiently large recovery
2 time of 30 min between each cycle.

3 Both initial modulus and hysteresis show a strong stretch rate dependence for the P(AAm-co-
4 VIm)-Ni²⁺ gel while for the P(AAm-co-VIm)-Zn²⁺ gel the dependence is weaker. At the end
5 of the unloading cycle we observed a small residual deformation increasing with stretch rate
6 due to the bending of the sample. This residual deformation disappears during the recovery
7 period.

8 This large strain behavior is now analyzed in terms of separability between the strain-
9 dependent and time-dependent component of the tensile stress. In a previous publication¹⁸ we
10 showed that for a similar system, the reduced stress $f^* = \sigma/(\lambda - \lambda^{-2})$ measured at different
11 stretch rates, plotted as a function of time formed a master curve. For these gels, for $\lambda < 2$ the
12 stress could be separated into a strain-dependent term (Neo-Hookean contribution), and a time
13 dependent term f^* (dynamics of the physical crosslinks). By using the loading part of the data
14 of **Figure 6a** and **c**, we plotted the reduced stress f^* as a function of time in **Figure 6b** and **d**
15 and a reasonable master curve was obtained for both dual crosslink gels with Ni²⁺ and Zn²⁺,
16 demonstrating the approximate separability into a strain-dependent Neo-Hookean term, and a
17 time dependent term f^* in that range of intermediate strain where only softening is observed
18 (see **Figure 2**: Stress - strain curves of the dual crosslink gels with different Ni²⁺
19 concentrations compared with the corresponding chemical gels at a stretch rate of 0.06 s⁻¹ at
20 room temperature.).



1

2

3 **Figure 6.** *a) and c)* Stress-strain curves of loading and unloading cycles with different stretch
 4 rate of dual crosslink gels with $[\text{Ni}^{2+}] = 100 \text{ mM}$ (a), $[\text{Zn}^{2+}] = 100 \text{ mM}$. *b) and d)*
 5 corresponding reduced stress from loading curves as a function of time.

6

7

1 **(5) Uniaxial tensile tests to fracture**

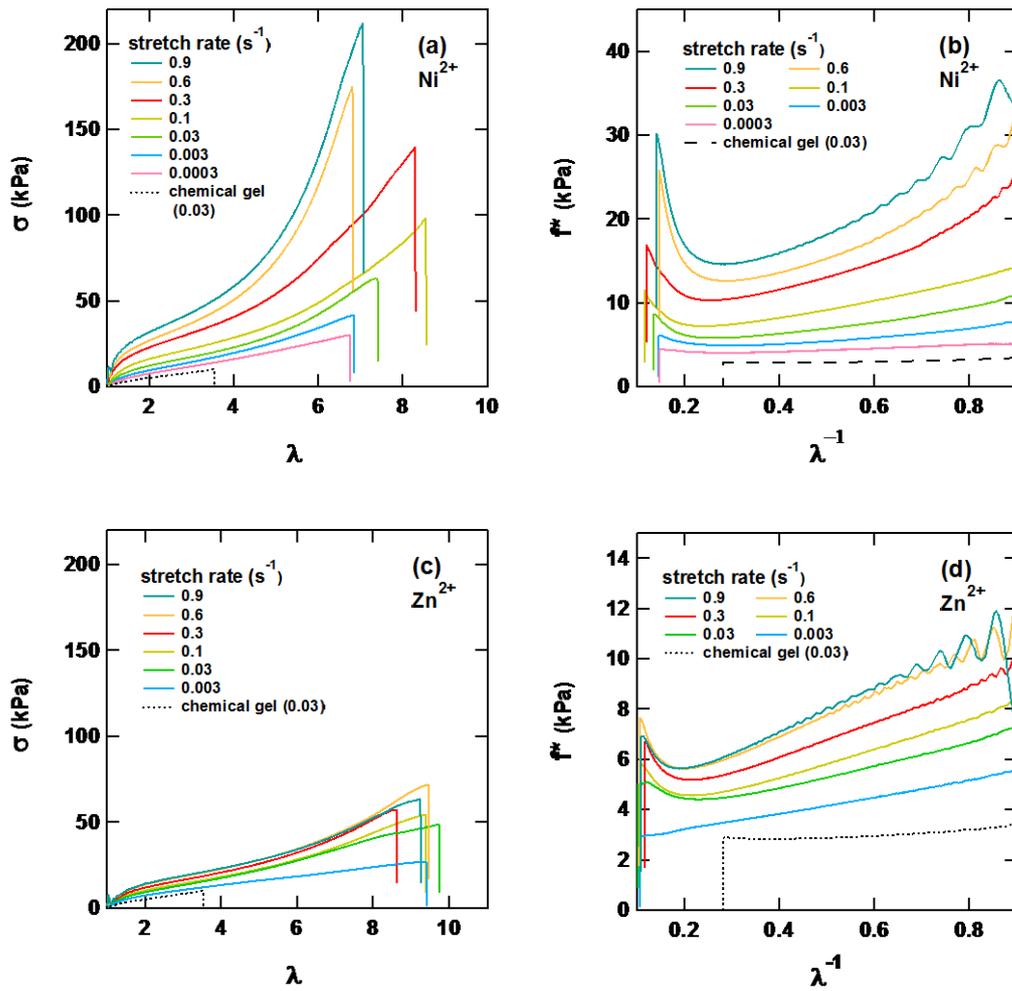
2 Tensile stress - strain curves of the dual crosslink gels with Ni^{2+} and Zn^{2+} at various stretch
3 rates $\dot{\lambda}$ (from 0.9 to 0.0003 s^{-1}) are shown in **Figure 7a, c** together with the data for the
4 corresponding chemical gel at the stretch rate $\dot{\lambda} = 0.03 \text{ s}^{-1}$. Note that the chemical gel does
5 not exhibit any particular stretch rate dependence (data not shown). It is immediately evident

6 - that the addition of the transient crosslinks significantly increases the extensibility at
7 rupture λ_b compared to that of the chemical gel and

8 - that λ_b does not show a clear stretch rate dependence for both gels.

9 For the P(AAm-co-VIm)- Ni^{2+} gel the values of λ_b were found around 6.5 – 8.5, and for the
10 P(AAm-co-VIm)- Zn^{2+} gel, they were slightly higher than that of P(AAm-co-VIm)- Ni^{2+} gel,
11 around 8.5 – 10. These results indicate that transient crosslinks, even with very fast dynamics
12 relative to the applied stretch rate, can increase the extensibility of the dual crosslink gels
13 without increasing the modulus (thus rheologically invisible) as observed previously for
14 organogels³⁴.

15 Both gels display a marked stretch rate dependent softening at intermediate strains, and a rate
16 dependent strain hardening at large strain. To further analyze the details of the stress strain
17 relationship and the contribution of the transient crosslinks, the Mooney representation of the
18 stress, classically used in rubber elasticity, was applied^{37,38}. In this representation of the data
19 the relationship between f^* and λ reveals the difference in stiffness between the sample and a
20 hypothetical material with the same initial modulus and following classical rubber elasticity. A
21 decreasing f^* indicates softening relative to rubber elasticity and an increasing f^* reveals
22 hardening.



1

2

3 **Figure 7.** Stress-strain curves of dual crosslink gels with $[\text{Ni}^{2+}] = 100 \text{ mM}$ (a), $[\text{Zn}^{2+}] = 100$
 4 mM (b), and the corresponding Mooney plots (b, d).

5

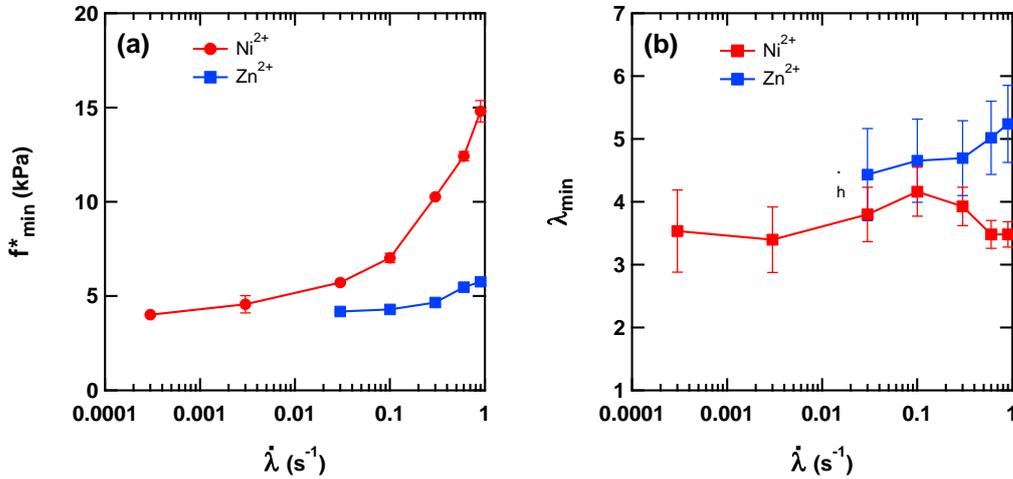
6 The reduced stress can be plotted as a function of λ^{-1} (**Figure 7b, d**). As expected, the
 7 reduced stress of the chemical gel at a stretch rate of 0.03 s^{-1} is almost independent of λ^{-1} ,
 8 which indicates that, in the absence of physical bonds and polymer entanglements, the
 9 uniaxial deformation of the chemical gel is well described by the rubber elasticity model and
 10 the constant value of the reduced stress is equivalent to its shear modulus. For dual crosslink
 11 gels, the values of reduced stress are higher than that of the chemical gel over the whole range
 12 of λ , even at very low stretch rates, which can be explained by the existence of the slow

1 components. At almost all stretch rates, a non-linear viscoelastic softening occurs in the small
2 λ region ($\lambda^{-1} > 0.3$): with increasing λ the reduced stress decreases. In the large λ region ($\lambda^{-1} <$
3 0.2), the reduced stress increases again, or a strain hardening appears relative to the Neo-
4 Hookean behavior.

5 We characterized the stretch rate dependence of the strain hardening behavior, with the values
6 of the minimum in f^* (f_{\min}^*) and those of the corresponding stretch λ_{\min}^{-1} in **Figure 8**. For
7 both gels, f_{\min}^* increases with stretch rate (**Figure 8a**). Since this increase is due to the
8 dynamics of the physical crosslinks, at slower stretching rate the physical bonds can exchange
9 more effectively and relax the stress leading to a lower value of f_{\min}^* . The values of λ_{\min} are
10 plotted as a function of $\dot{\lambda}$ in **Figure 8b**. We observed a slight stretch rate dependence of λ_{\min}
11 suggesting the existence of a second longer relaxation time. In principle if the observed strain
12 hardening is due the limiting extensibility of the chains between physical crosslinks, the value
13 of λ_{\min} should be related to the chain length between the effective crosslinks and decrease
14 with increasing f_{\min}^* . We do not see any clear correlation between the two values. If the strain
15 hardening is due to the non-Gaussian stretch of the chains between chemical crosslinks
16 (containing many transient physical crosslinks), then λ_{\min} is expected to be independent of the
17 stretch rate. One can argue that this is roughly the case (from **Figure 8b**) but the value of is
18 too small to be consistent with the crosslink density of the chemical gel. This again suggests
19 the existence of a second (slow) physical crosslinking mechanism that would always be active
20 at the investigated stretch rates.

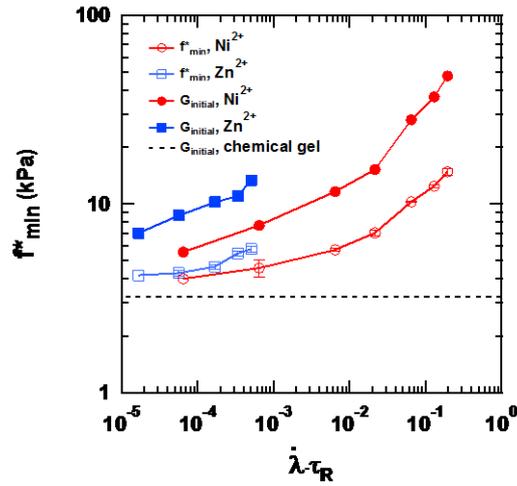
21 With the relaxation time of both gels known from linear rheology, it is possible to compare
22 these two gels by shifting horizontally the data by τ_R . To study the large strain (nonlinear)
23 properties, the minimum value of the reduced stress f_{\min}^* was plotted as a function of stretch

1 rate $\dot{\lambda}$ (**Figure 8a**). We can now replot f_{\min}^* as a function of a Weissenberg number $\dot{\lambda} \cdot \tau_R$
2 (**Figure 9**). The relatively high value of f_{\min}^* at high $\dot{\lambda} \cdot \tau_R$ represents the non-relaxed physical
3 bonds, which result in more elastic gels. At low values of $\dot{\lambda} \cdot \tau_R$, the physical bonds relax
4 completely, leading to the plateau of f_{\min}^* around 4 kPa. Theoretically, without a second
5 relaxation mechanism, this plateau should be reaching the value of the chemical gel, which is
6 not true for this system: the plateau value is still higher than that of the chemical gel (about 3
7 kPa). In Figure 9 we also replotted the values of f_{\min}^* to compare them to those of the initial
8 modulus G_{initial} as a function of stretch rate. Both small strain and large strain moduli show a
9 qualitatively similar stretch rate dependence on $\dot{\lambda} \cdot \tau_R$, however the two curves are not parallel.
10 The fact that the difference between f_{\min}^* and G_{initial} is larger at high $\dot{\lambda} \cdot \tau_R$ indicates that f_{\min}^*
11 relaxes more slowly than G_{initial} , thus that it is mostly controlled by the slower relaxation
12 mode.



13

14 **Figure 8.** The minimum value of reduced stress f_{\min}^* (a), the corresponding value of λ_{\min}^{-1} (b)
15 and λ (c) as a function of stretch rate of Ni²⁺ (red) and Zn²⁺ (blue) dual crosslink gels. Error
16 bars were calculated by increasing the value of f_{\min}^* by 0.05 kPa.



1

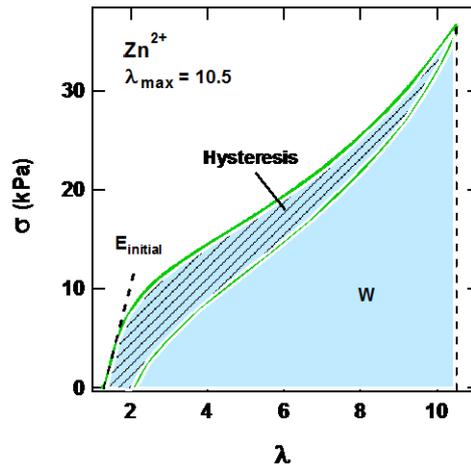
2 **Figure 9.** Modulus E and minimum value of reduced stress f_{\min}^* of Ni^{2+} (red) and Zn^{2+} (blue)
 3 dual crosslink gels as a function of $\dot{\lambda} \cdot \tau_R$.

4

5 (6) Step-cycle uniaxial tensile tests and energy dissipation

6 Loading unloading step-cycle extension tests at incremental values of strain were performed,
 7 at a constant stretch rate $\dot{\lambda} = 0.3 \text{ s}^{-1}$. 30 min of rest time was applied before each cycle and the
 8 maximum stretch was increased by $\lambda = 0.5$ for each cycle up to the sample rupture.

9 As shown in **Figure 10**. The calculation of the hysteresis (Hys), normalized hysteresis
 10 (Hys/W) and the initial modulus (E_{initial}). Erreur ! Source du renvoi introuvable., the hysteresis
 11 (Hys) of each loop can be calculated by integrating the area between the loading and
 12 unloading curves, while the normalized hysteresis (Hys/W) is the ratio of the hysteresis to the
 13 total work input which can be determined by the area under the loading curve of each loop.
 14 The initial modulus of each loop E_{initial} can be determined by fitting the loading curves at low
 15 deformation.



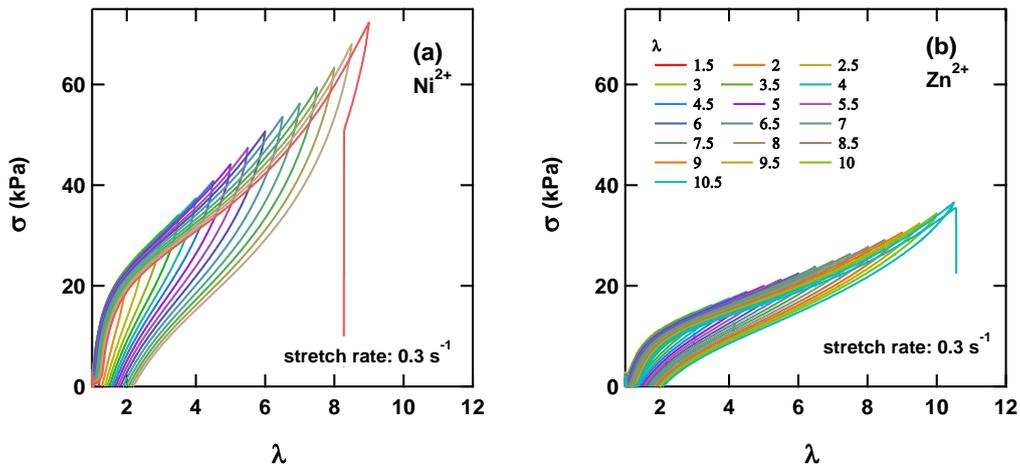
1

2 **Figure 10.** The calculation of the hysteresis (Hys), normalized hysteresis (Hys/W) and the
 3 initial modulus (E_{initial}).

4

5

6 **Figure 11.** Step-cycle extension tests of dual crosslink gels with $[\text{Ni}^{2+}] = 100 \text{ mM}$ (a), $[\text{Zn}^{2+}]$
 7 $= 100 \text{ mM}$ (b). shows the step-cycle curves of dual crosslink gels with Ni^{2+} and Zn^{2+} . These
 8 two gels show similar dissipative behaviors: the P(AAm-co-VIm)- Ni^{2+} gel has a higher
 9 modulus and lower extensibility, consistent with the tensile uniaxial stretching result and a
 10 remaining residual extension after the rest time was observed for both gels in large strain, due
 11 to permanent change in the structure.



1

2 **Figure 11.** Step-cycle extension tests of dual crosslink gels with $[\text{Ni}^{2+}] = 100 \text{ mM}$ (a), $[\text{Zn}^{2+}]$
 3 $= 100 \text{ mM}$ (b).

4

5 A few interesting features can be learned from plotting the initial modulus E and normalized
 6 hysteresis as a function of the maximum stretch λ_{max} of each loop are shown in **Figure 12**.

7 Initial modulus (a) and energy dissipation (b) and as a function of the maximum stretch λ_{max}
 8 of each loop of dual crosslink gels with $[\text{Ni}^{2+}] = 100 \text{ mM}$ (red), $[\text{Zn}^{2+}] = 100 \text{ mM}$ (blue)..

9 E_{initial} of both gels stays almost constant at small strain, then starts to decrease slightly for
 10 $\lambda_{\text{max}} > 4$. The extensibility of the corresponding chemical gel is about 4, suggesting that the

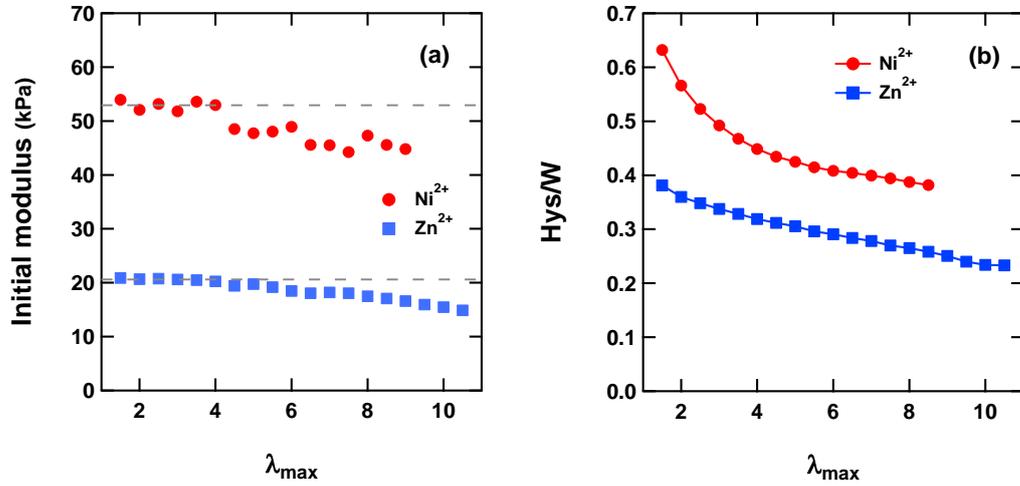
11 chemical network starts to be irreversibly and locally damaged at large strain, and that the
 12 transient crosslinks can prevent propagation of the local damages allowing further

13 deformation of the dual crosslink gels. The values of Hys/W of both gels decrease with λ_{max} ,
 14 which indicates that the gels become more elastic with increasing maximum strain.

15 Additionally a higher hysteresis represents a larger energy dissipation and it is important to
 16 assess the consistency between the large strain (nonlinear) and small strain (linear) energy

17 dissipation. Compared to the P(AAm-co-VIm)-Zn²⁺ gel, the P(AAm-co-VIm)-Ni²⁺ gel has a

- 1 significantly higher W (area under the loading curve), and also a higher normalized hysteresis
- 2 Hys/W consistent with the small strain results of **Figure 3**.



- 3
- 4 **Figure 12.** Initial modulus (a) and energy dissipation (b) and as a function of the maximum
- 5 stretch λ_{max} of each loop of dual crosslink gels with $[Ni^{2+}] = 100$ mM (red), $[Zn^{2+}] = 100$ mM
- 6 (blue).

7

1 **Conclusion**

2 In order to investigate systematically the effect of the dynamic bond exchange rate on the
3 macroscopic properties of hydrogels containing physical and chemical crosslinks, we
4 designed and synthesized P(AAm-co-VIm)-M²⁺ dual crosslink gels having a tunable
5 characteristic relaxation time in order to characterize their time-dependent mechanical
6 properties in small and large strain. These dual crosslink gels were permanently crosslinked
7 by methylene bisacrylamide and transiently crosslinked by a metal ion – imidazole ligand
8 coordination, with two different ions, Ni²⁺ and Zn²⁺, having different characteristic
9 breaking/reforming times.

10 Linear rheological measurements showed that the P(AAm-co-VIm)-M²⁺ dual crosslink gels
11 exhibit time-dependent elasticity, i.e. the $G'(\omega)$ increases with frequency and $G''(\omega)$ shows a
12 peak, due to the dissociation of the transient crosslinks followed by chain relaxation. The
13 dynamics of the dual crosslink gels can be tuned by changing the metal ions: the P(AAm-co-
14 VIm)-Zn²⁺ dual crosslink gel exhibited a much faster relaxation process than the P(AAm-co-
15 VIm)-Ni²⁺ dual crosslink gel, hence more suitable to characterize the mechanical properties at
16 very slow stretch rate (relative to the characteristic time). In addition we observed signs of
17 the existence of a slower relaxation component due to a more long-lived physical crosslinking
18 mechanism, since the elastic modulus of the dual crosslink gels did not reach to the value of
19 the corresponding chemical gel even at times of the order of 1000 s.

20 At intermediate strains ($\lambda < 2$) The P(AAm-co-VIm)-Zn²⁺ dual crosslink gel, having much
21 faster association/dissociation dynamics than that of the P(AAm-co-VIm)-Ni²⁺ dual crosslink
22 gel, exhibits a lower hysteresis in the tensile loops. Based on the strain-rate dependent tensile
23 behavior at small strain, a master curve of the reduced stress as a function of time was

1 obtained for both gels, thus in that strain range, a separability of the stress into strain-
2 dependent and time-dependent terms holds.

3 The key result at larger strain is the difference in extensibility between the dual crosslink gels
4 and the chemical gel even at stretch rates significantly slower than the inverse of the main
5 relaxation time of the gel, a situation where the stress-strain curves are nearly identical except
6 for the fracture point.

7 The stress at large strain proved to be also strongly strain-rate dependent, with in particular a
8 strongly rate dependent strain hardening at large strain. Mooney plots of the reduced stress
9 were used to characterize this strain hardening behavior and showed that the reduced stress at
10 the onset of strain hardening kept increasing with stretch rate, suggesting the existence of a
11 second relaxation time due to a longer lived physical crosslinking mechanism.

12 Finally we found that the initial elastic modulus of the gel during step-cyclic tests started to
13 decrease at values of $\lambda \sim 4$ close to the stretch a break of the chemical gel. This suggests that
14 in dual-crosslink gels, molecular damage occurs at that stage but no macroscopic crack forms
15 and propagates. This strongly supports a mechanism where the physical crosslinks are
16 actively protecting (or shielding) neighboring covalent bonds from the stress transfer
17 occurring when a chemical bond breaks, in qualitative agreement with the model recently
18 proposed by Tito et al.¹²

19

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