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# Dynamics of hydrogels with a variable ratio of permanent and transient crosslinks: constitutive model and its molecular interpretation

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1 **Dynamics of hydrogels with a variable ratio of permanent**  
2 **and transient crosslinks: constitutive model and its**  
3 **molecular interpretation**

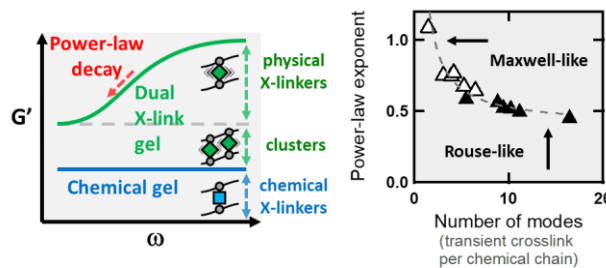
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## Abstract

1  
2 Mechanical reinforcement of hydrogels is important to gel science. “Dual crosslink” hydrogels  
3 with chemical and transient crosslinks can exhibit improved mechanical properties compared  
4 to the corresponding chemically crosslinked gels. Here we use model dual poly(vinyl alcohol)  
5 crosslink gels with a variable ratio of chemical and transient crosslinks to study how this ratio  
6 affects chain dynamics. Torsion and tensile test results are well described by a constitutive  
7 model with only four parameters. The characteristic time of network relaxation (corresponding  
8 to the peak of the loss modulus) increases with decreasing transient crosslinker concentration.  
9 The characteristic time distribution gradually changes from Maxwell-like to Rouse-like  
10 relaxation. These results imply that the Rouse mode of the chains between crosslinks controls  
11 transient network dynamics. Our work provides a molecular interpretation of network dynamics  
12 and guide optimization of the crosslinking ratios in dual crosslink gels.

13

# 1. Introduction

To overcome the brittleness of conventional chemical hydrogels for applications requiring mechanical toughness, various strategies of mechanical reinforcement have been reported since 2001.<sup>1-4</sup> Among them, the concept of sacrificial bonds to dissipate strain energy and prevent stress concentration to the crack tip was found promising. After the pioneering works of Gong and her coworkers on “double network” hydrogels using irreversible covalent bond breaking in the interpenetrated networks,<sup>3,5</sup> use of reversible breaking of noncovalent bonds which can break and reform has become popular and various examples of such dissipative hydrogels having different noncovalent interactions as reversible crosslinks have been reported in the last decades.<sup>6-10</sup> Reversible dissociation/reassociation of the crosslinks can provide self-recovering properties to the networks, attracting the attention of material scientists.<sup>11-13</sup>

Though their specific time-dependent mechanical properties are of interest from a rheological point of view, quantitative studies have been less reported. The two main parameters investigated in our study are the concentration of elastically active crosslinks, which determines the modulus, and the lifetime of the transient crosslinks, which controls the network relaxation time. While it is feasible to tailor transient crosslinks at the molecular scale by choosing their concentration and their lifetime by picking various types of interactions, it is more difficult to quantitatively correlate molecular parameters to macromolecular properties such as the distribution of chain relaxation times. In addition, it is a challenge to design and synthesize a simple model dissipative gel system and to develop constitutive models able to quantitatively describe the mechanical behaviors under small and large deformations with different loading histories by taking into account the transient bond dynamics, with as few parameters as possible. Narita, Creton and their coworkers have developed a simple model dynamic hydrogel based on poly(vinyl alcohol), PVA, having simultaneously chemical and physical crosslinks.<sup>14-17</sup>

1 Starting from a PVA chemical gel crosslinked by glutaraldehyde, a “dual crosslink” PVA  
2 hydrogel is prepared by immersing the chemical gel into a solution of borax to incorporate  
3 borate ions acting as physical crosslinkers. When the stretch rate is sufficiently small compared  
4 to the characteristic relaxation time of the transient crosslinks, it was demonstrated that  
5 incorporation of the transient crosslinks to the chemical network improves the fracture  
6 resistance of the gel compared to the corresponding chemical gel. The dynamics of the PVA  
7 dual crosslink gel has a well-defined main relaxation time determined from the peak of the loss  
8 modulus, stemming from the physical bond dissociation. Using the PVA dual crosslink  
9 hydrogel, some rheological features such as additivity of the physical crosslinks and chemical  
10 crosslinks (equivalent to the corresponding chemical gel) in terms of the moduli, as well as  
11 separability of the strain rate-dependent stress into a time-dependent term and a strain-  
12 dependent term (expressed as a neo-Hookean model), have been experimentally demonstrated  
13 (for certain loading histories).<sup>14,15</sup>

14 Hui and Long proposed a 3D finite strain constitutive model for the PVA dual crosslink gel.<sup>18-</sup>  
15 <sup>20</sup> A simplified description of the dynamics of the transient physical crosslinks with breaking  
16 and healing times, taking into account the steady-state behavior of the transient physical  
17 crosslinks, can fit both uniaxial tensile tests and torsion tests in shear rheometry. Using only  
18 four physically grounded parameters, the model can fit and predict very well various  
19 loading/unloading behaviors at different stretch rates. The model was successfully used to  
20 model the propagation of a crack in the PVA dual crosslink gel.<sup>17,21</sup>

21 In these previous works, the mechanical properties of the PVA dual crosslink gel were  
22 intensively studied at one preparation condition at a fixed chemical and physical crosslinkers  
23 concentrations, optimized for high toughness. The constitutive model has been applied to the  
24 same optimized gel. It is however interesting to investigate the effects of the two main  
25 parameters controlling transient crosslinks, their concentration and the relaxation time. The

1 effect of the relaxation time was investigated as a function of the temperature for the optimized  
2 gel.<sup>22</sup> The validity of the model and the applicability of time-temperature superposition were  
3 confirmed. Here we report the influence of the relative ratio of chemical and physical crosslinks  
4 on the rheological properties. We investigate a series of PVA dual crosslink gels with different  
5 ratios of permanent and transient crosslinks. All gels are characterized by uniaxial tensile tests  
6 and torsion tests and the validity of the constitutive model is tested by fitting both tensile and  
7 torsion results with the same set of two parameters for the moduli and another two for the  
8 characteristic time. More importantly, analyzing the crosslinker concentration dependence of  
9 the parameters also helps us to understand their physical significance. A goal of this paper is  
10 to provide molecular interpretations of the model parameters.

## 1 **2. Experimental Section**

### 2 **2.1. Sample preparation**

3 PVA dual crosslink gel samples at different chemical and physical crosslinking ratios were  
4 prepared by using the procedure described previously.<sup>15,16</sup> Briefly, PVA chemical gels were  
5 first prepared by cross-linking PVA (molecular weight: 89,000–98,000, degree of  
6 hydrolyzation: 99 %) in aqueous solutions with the chemical crosslinker glutaraldehyde, GA,  
7 at pH =1.9. The PVA concentration was kept constant at 12 wt% for all the gels tested. We  
8 used two GA concentrations in the feed, 5.5 and 16.5 mM, corresponding to crosslinking ratio  
9 in the feed,  $C_{GA} = 0.2$  and 0.6 mol% (molar ratio to the monomer units of PVA). After the  
10 overnight crosslinking reaction, the obtained PVA chemical gels were used for measurements  
11 as prepared. PVA dual crosslink gels were then prepared by incorporating borate ions, physical  
12 crosslinkers, to the chemical gels. In this process the chemical gels were washed with a large  
13 amount of water to a neutral pH. The swollen chemical gels were then immersed in aqueous  
14 solutions of sodium tetraborate decahydrate (borax) for 3 days. The borax concentration in the  
15 solution,  $C_{borax}$ , varied from 1 to 50 mM. The volume of the borax solution was 20 times that  
16 of the chemical gels. By dissolution of tetraborate, borate ions are formed, which are able to  
17 form complexes with diols on the PVA chains. To quantitatively study the effects of the  
18 physical crosslinking ratio, it is crucial to compare gels with different crosslinking ratios at the  
19 same PVA concentration. It should be noted that the complexation of borate ions induces both  
20 deswelling (due to crosslinking) and swelling (due to the introduction of charges to the neutral  
21 gel). The swelling ratio was controlled by addition of NaCl to the system: the electrostatic  
22 interactions are screened and the gels deswell to the same PVA concentration as that of the  
23 corresponding chemical gel. For each GA and borax concentration, the optimal NaCl  
24 concentration was determined and varied from 90 to 460 mM.<sup>16</sup>

## 1 **2.2. Mechanical tests**

### 2 *2.2.1. Tensile tests*

3 Stress relaxation in uniaxial tensile tests was performed on an Instron 5565 tensile tester with a  
4 10 N load cell. Samples of dual crosslink gels as well as chemical gels in a rectangular shape  
5 with 5 mm width, 1.5 mm thickness, and 20 mm gauge length (length between clamps) were  
6 stretched to  $\lambda_0 = 1.1$  at a constant stretch rate of  $0.1 \text{ s}^{-1}$ , then stress relaxation was recorded. We  
7 kept the samples in paraffin oil during all the tests to prevent them from drying.

### 8 *2.2.2. Torsion tests*

9 To characterize the linear viscoelastic properties of the dual crosslink gels and the chemical  
10 gels, small strain oscillatory shear measurements were performed on a parallel plate geometry  
11 having roughened surfaces (25 mm in diameter) with an ARES LS1 rheometer (TA  
12 instruments). The sample thickness was 1.5 mm. Frequency sweep tests with a dynamic range  
13 varying from 0.1 to 100 rad/s were carried out at 25 °C within the linear viscoelasticity regime  
14 (0.8 – 1 % strain).

15



## 1 **3. Continuum theory**

### 2 **3.1. Model description**

3 Here we briefly describe the latest version of the rate-dependent finite three-dimensional  
4 continuum theory validated in the Gaussian chain regime for stretch lower than about 2, with a  
5 PVA dual crosslink gel having a chemical crosslinking ratio of 0.2 mol% prepared with  $C_{\text{borax}}$   
6 of 1 mM.<sup>20,22</sup> This model was developed with the following key assumptions. (1) The chemical  
7 crosslinks are assumed to be unbreakable (fracture is not considered) while the physical  
8 crosslinks are assumed to undergo a time-dependent breaking and reforming (healing) process.  
9 The dual crosslink gel network consists of permanent chains attached to chemical crosslinks  
10 and transient chains attached to physical crosslinks. The strain energy of the network is thus  
11 the sum of that of the permanent and transient chains. (2) The physical bonds' breaking and  
12 reforming process reaches a dynamic equilibrium soon after the gel is synthesized. In other  
13 word, there is a thermodynamic equilibrium between "closed" transient crosslinks (elastically  
14 active) and "open" crosslinks. Thus, the molar fraction of breaking crosslinks and healed  
15 crosslinks per unit time are equal and independent of time (steady state assumption). This  
16 breaking (healing) rate is denoted by  $\bar{\gamma}_{\infty}$  ( $\text{s}^{-1}$ ). (3) The stress sustained by a transient chain is  
17 instantaneously relaxed when it breaks; after a temporary chain is reattached, it is in the relaxed  
18 state immediately and carries no strain energy. The reattached temporary chain experiences the  
19 deformation history from its birth at time  $\tau$  (s) to the current time  $t$  (s). (4) Macroscopically the  
20 gel is incompressible and isotropic. For both permanent and transient chains, the Neo-Hookean  
21 model (Gaussian chains) is used to specify the strain energy of a chain under deformation. (5)  
22 We assume that the rates of chain breaking and healing are independent of the imposed strain  
23 history as observed by experiments.<sup>15</sup>

1 Assuming that before loading ( $t < 0$ ), the physical crosslinks have reached a state of dynamic  
 2 equilibrium in which the healing rate is equal to the breaking rate, i.e.,  $\bar{\gamma}_\infty$ , the nominal stress  $\sigma$   
 3 (Pa) in a uniaxial tension test with stretch ratio  $\lambda(t)$  is:

$$\sigma = \mu\rho \left( \lambda(t) - \frac{1}{\lambda^2(t)} \right) + \mu n(t) \left( \lambda(t) - \frac{1}{\lambda^2(t)} \right) \quad (\text{eq.1})$$

$$+ \mu\bar{\gamma}_\infty \int_0^t \Phi_B \left( \frac{t-\tau}{t_B} \right) \left( \frac{\lambda(t)}{\lambda^2(\tau)} - \frac{\lambda(\tau)}{\lambda^2(t)} \right) d\tau.$$

4 Equation (1) means that the stress is the sum of three terms: (i) the stress carried by the  
 5 permanent network (the first term of the right side), (ii) the stress carried by the transient chains  
 6 existing from  $t = 0$  (the second term) and survives to the current time, (iii) and the stress carried  
 7 by healed transient chains (the third term with the integral).

8 The use of neo-Hookean model means that the stress in the permanent network is  
 9  $\mu\rho \left( \lambda(t) - \frac{1}{\lambda^2(t)} \right)$ , where  $\mu$  (Pa) is the small strain shear modulus,  $\rho$  is the molar fraction of the  
 10 permanent chains relative to the total number of chains. Since both the transient and permanent  
 11 networks obey Gaussian chain statistics (i.e., neo-Hookean model) the stress carried by the  
 12 transient chains has the same dependence on the stretch ratio except in this case  $\rho$  is replaced  
 13 by the molar fraction of the transient crosslinks, which are attached at  $t = 0$  and survive to the  
 14 current time  $t > 0$ ,  $n(t)$ .  $n(t)$  is<sup>19,20</sup>

$$n(t) = \bar{\gamma}_\infty \int_{-\infty}^0 \Phi_B \left( \frac{t-\tau}{t_B} \right) d\tau = \bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \left[ 1 + (\alpha_B - 1) \frac{t}{t_B} \right]^{\frac{2-\alpha_B}{1-\alpha_B}}, \quad (\text{eq.2})$$

15 where  $\bar{\gamma}_\infty$  ( $s^{-1}$ ) and  $\Phi_B$  are given by

$$\bar{\gamma}_\infty = \frac{1 - \rho}{t_H + \frac{t_B}{2 - \alpha_B}}, \quad (\text{eq.3})$$

$$\phi_B\left(\frac{t-\tau}{t_B}\right) = \left[1 + (\alpha_B - 1) \frac{t-\tau}{t_B}\right]^{\frac{1}{1-\alpha_B}}. \quad (\text{eq.4})$$

1  $\bar{\gamma}_\infty$  ( $\text{s}^{-1}$ ) is a function of the characteristic transient bond breaking time  $t_B$  (s) and the  
 2 characteristic transient bond healing time  $t_H$  (s). Its physical signification can be better  
 3 explained by shear modulus expression shown later in this section.  $\phi_B(t-\tau)$  is called the  
 4 survivability function which denotes the fraction of chains that are born at  $\tau$  and survive till the  
 5 current time  $t > \tau$ . Eg.4 can be obtained by solving a simple breaking model,  $d\phi_B/dt =$   
 6  $-\phi_B^{\alpha_B}/t_B$ , where  $1 < \alpha_B < 2$  is a dimensionless material constant that specifies the average  
 7 survival time of a physical bond, to statistically describe the spectrum of the relaxation time  
 8 related to the transient physical bond breaking. This second term represent the stress relaxation  
 9 due to the breaking of the physical bonds attached at  $t = 0$ .

10 The third term expresses the recovery of stress by healing of the broken bonds. We assume that  
 11 the transient chain healed at  $t = \tau$  does not carry stress, starts to obey the same survivability  
 12 function  $\phi_B$ , and has a different reference configuration from the original chain. This results in  
 13 a different stretch dependent term  $\lambda(t) \cdot \lambda^{-2}(\tau) - \lambda(\tau) \cdot \lambda^{-2}(t)$ .

14 The theory also predicts the dynamic shear modulus in linear viscoelastic regime with the same  
 15 set of parameters.<sup>19,22</sup> The complex modulus  $G^*(\omega)$  is written as:

$$G^*(\omega) = \mu \left\{ \rho + \bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \left[ 1 - \frac{2 - \alpha_B}{\alpha_B - 1} \cdot I(\omega) \right] \right\} \quad (\text{eq.5})$$

16 with

$$I(\omega) = \int_0^\infty \exp\left(-i \frac{\omega t_B}{\alpha_B - 1} u\right) (1 + u)^{-\frac{1}{\alpha_B - 1}} \cdot du \quad (\text{eq.6})$$

17 The integral  $I(\omega)$  which is a function of the angular frequency  $\omega$ , is numerically evaluated. And  
 18 the expressions for  $G'(\omega)$  and  $G''(\omega)$  are given as:

$$G'(\omega) = \text{Re}[G^*(\omega)]$$

$$= \mu\rho + \mu\bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \left[ 1 - \frac{2 - \alpha_B}{\alpha_B - 1} \int_0^\infty \cos\left(\frac{\omega t_B}{\alpha_B - 1} u\right) (1 + u)^{\frac{-1}{\alpha_B - 1}} du \right] \quad (\text{eq.7})$$

$$G''(\omega) = \text{Im}[G^*(\omega)]$$

$$= \mu\bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \left[ \frac{2 - \alpha_B}{\alpha_B - 1} \int_0^\infty \sin\left(\frac{\omega t_B}{\alpha_B - 1} u\right) (1 + u)^{\frac{-1}{\alpha_B - 1}} du \right] \quad (\text{eq.8})$$

1 From **eq.7** the low frequency limit is:

$$G'(\omega \rightarrow 0)$$

$$= G_0 = \mu\rho + \left[ \frac{\mu(1 - \rho)t_B}{(2 - \alpha_B)t_H + t_B} \Gamma\left(\frac{2\alpha_B - 3}{\alpha_B - 1}\right) \cos\left(\frac{2 - \alpha_B}{2(\alpha_B - 1)} \pi\right) \right] \left(\frac{t_B \omega}{\alpha_B - 1}\right)^{\frac{2 - \alpha_B}{\alpha_B - 1}}$$

$$\sim \mu\rho \quad (\text{eq.9})$$

2 In the low frequency limit, the transient chains fully relax, and the modulus corresponds to that  
3 of the permanent chains.

4 In the high frequency limit, we have:

$$G'(\omega \rightarrow \infty) = G_\infty$$

$$= \mu\rho + \frac{\mu(1 - \rho)t_B}{(2 - \alpha_B)t_H + t_B} \left[ 1 - \frac{(2 - \alpha_B)(\alpha_B - 1)}{t_B^2} \frac{1}{\omega^2} \right]$$

$$= \mu\rho + \mu(1 - \rho) \frac{\frac{t_B}{2 - \alpha_B}}{t_H + \frac{t_B}{2 - \alpha_B}}$$

$$= \mu\rho + \mu\bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \quad (\text{eq.10})$$

5 In the high frequency limit, both permanent crosslinks and closed transient crosslinks additively  
6 contribute to the elasticity, thus the modulus corresponding to the closed transient crosslinks is

7 written as  $G'_{\text{closed}} = \mu\bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B}$ . The fraction of closed transient crosslinks to the total

1 crosslinks is written as  $\rho_{closed} = \bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$ , since  $G'_{closed} = \mu\rho_{closed}$ . It should be noted that  
2 the fraction of the (total) transient crosslinks is  $1 - \rho$ , which is equal to  $\bar{\gamma}_{\infty} \left( t_H + \frac{t_B}{2-\alpha_B} \right) =$   
3  $\bar{\gamma}_{\infty} t_H + \rho_{closed}$  by **eq.3**. Thus, the fraction of the open transient crosslinks,  $\rho_{open}$ , is  $\rho_{open} =$   
4  $\bar{\gamma}_{\infty} t_H$ .

5 **Eq.8** shows that  $G''(\omega)$  is concave downward, thus the value of time,  $\tau_X = 1/\omega_X$  corresponding  
6 to the maximum, which traditionally used in the interpretation of linear rheological experiments  
7 to define the relaxation time, is a reasonable characteristic time of the dissipation of the system.  
8 Its value can be analytically calculated as a function of the model parameters (the derivation is  
9 given in Supporting Information):

$$\tau_X = \frac{t_B}{(\alpha_B - 1) \cdot f\left(\frac{2-\alpha_B}{\alpha_B-1}\right)} \quad (\text{eq.11})$$

10 where  $f$  is a dimensionless function of  $\frac{2-\alpha_B}{\alpha_B-1}$ . Therefore,  $\tau_X$  is proportional to  $t_B$ , with a  
11 coefficient which is a function of only  $\alpha_B$ . For  $0.1 \leq \frac{2-\alpha_B}{\alpha_B-1} \leq 0.9$ ,  $f\left(\frac{2-\alpha_B}{\alpha_B-1}\right)$  can be well  
12 approximated by a linear function,  $f\left(\frac{2-\alpha_B}{\alpha_B-1}\right) = -0.053 + 0.802\frac{2-\alpha_B}{\alpha_B-1}$ .

13 The five material parameters,  $\mu$  (Pa),  $\rho$ ,  $t_B$  (s),  $t_H$  (s) and  $\alpha_B$ , can be reduced to the following  
14 four parameters, which have plausible rheological significance:  $\mu\rho$  (Pa),  $\mu\bar{\gamma}_{\infty}$  (Pa s<sup>-1</sup>),  $t_B$  (s) and  
15  $\alpha_B$ .  $\mu\rho$  and  $\mu\bar{\gamma}_{\infty}$  represent the modulus (in the form of  $\mu\bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$ ) for the chemical and the  
16 transient networks respectively, and their crosslinker concentration dependence will be  
17 discussed in section 4.2.  $t_B$  and  $\alpha_B$  control the characteristic relaxation time of the network.  
18 Their dependences on the crosslinker concentrations and physical interpretation are discussed  
19 in section 4.3.

## 20 **3.2. Parameter determination by fitting**

1 The experiments reported in this work are performed in the linear regime where the strains are  
2 small. This is the regime of focus in this paper. The four parameters were determined by fitting  
3 the experimental data of both the tensile and torsion tests using the equations governing each  
4 test. A set of parameters fitting both tests was found. Determination of the parameters was  
5 done by fitting the data of a tensile stress relaxation test, and the parameters were fine-tuned to  
6 match the rheology data. Details of the fitting procedure can be found in the reference.<sup>20</sup> Briefly,  
7 from a single tensile stress relaxation test, consisting of a rapid stretching to  $\lambda = \lambda_0$  and  
8 relaxation,  $\mu\rho$  and  $\alpha_B$  were determined from the relaxation part. Since the healed transient  
9 chains do not carry stress during relaxation, **eq.1** is simplified to:

$$\begin{aligned} \sigma(t) &= \mu\rho(\lambda_0 - \lambda_0^{-2}) + \mu n(t)(\lambda_0 - \lambda_0^{-2}) & \text{(eq.12)} \\ &= \sigma_\infty + (\lambda_0 - \lambda_0^{-2}) \cdot \mu\bar{\gamma}_\infty \frac{t_B}{2 - \alpha_B} \left[ 1 + (\alpha_B - 1) \frac{t}{t_B} \right]^{-\frac{2 - \alpha_B}{\alpha_B - 1}} \end{aligned}$$

10 where  $\sigma_\infty$  is the stress at long times, from which the value of  $\mu\rho$  is determined as  $\mu\rho =$   
11  $\sigma_\infty/(\lambda_0 - \lambda_0^{-2})$ . For  $t \gg t_B$ , one finds from **eq.12**  $\sigma(t) - \sigma_\infty \sim t^{-\frac{2 - \alpha_B}{\alpha_B - 1}}$ . This allows us to  
12 determine  $\alpha_B$  from the slope of the logarithmic plot of stress versus time.  $t_B$  and  $\mu\bar{\gamma}_\infty$  were  
13 determined by fitting the rapid stretching part of the stress-strain curve with **eq.1**. Next, we  
14 fitted the torsion data.  $G'(\omega)$  and  $G''(\omega)$  were fitted using **eq.7** and **eq.8** to fine-tune the  
15 parameters. The value of  $t_B$  was accurately determined by this fine-tuning, thanks to the peak  
16 position in  $G''$  which is sensitive to the value of  $t_B$  (**eq.11**).

17 As noted in our previous work,<sup>16</sup> the moduli from the torsion tests are lower than those predicted  
18 from the parameters by the tensile tests by a factor of about 2. This discrepancy is believed to  
19 arise from the fact that the torsion test is performed in a parallel plate geometry (not in the cone  
20 plate geometry) where pre-compression is applied, and this is not accounted for in our equations  
21 (**eq.7** and **eq.8**).<sup>19</sup>

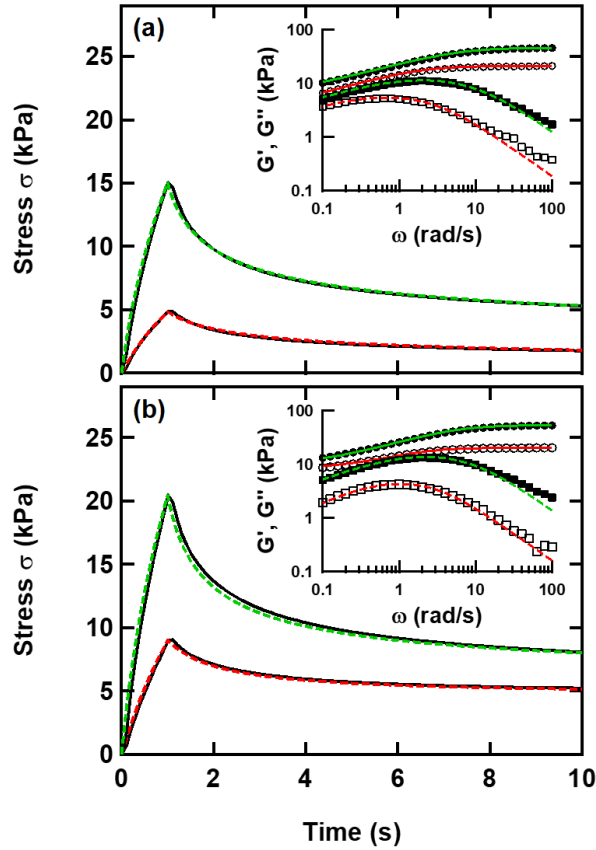
## 4. Results and Discussion

### 4.1. Fitted material parameters

A set of the fitting parameters for both the tensile and torsion tests was determined and summarized in **Table I**. Comparison between fitting curves calculated with these parameters and the experimental results of the tensile stress relaxation and the torsion frequency sweep tests are shown in **Figures 1** for four dual crosslink gels as example. In Supporting Information one can find comparisons for all the dual crosslink gels tested in this work for both tests, up to 100 s in stress relaxation tests (**Figures S2 – S5**). The model agrees well with the experimental results for all samples tested, and one set of the parameters for each dual crosslink gel can reasonably fit both tensile and torsion tests. This result indicates the validity of the model for a wide range of crosslinking ratios.

**Table I.** Four reduced fitting parameters and the shift factor for moduli.

$C_{GA}$ (mol%)	$C_{borax}$ (mM)	$\mu\bar{\gamma}_{\infty}$ (kPa s <sup>-1</sup> )	$\mu\rho$ (kPa)	$t_B$ (s)	$\alpha_B$	Shift factor
<b>0.2</b>	<b>1</b>	20.9	2.41	0.367	1.64	0.90
	<b>3</b>	77.7	3.24	0.213	1.69	0.34
	<b>5</b>	125	6.73	0.174	1.66	0.47
	<b>10</b>	263	7.82	0.110	1.67	0.48
	<b>20</b>	452	9.55	0.0734	1.66	0.29
	<b>50</b>	1240	34.9	0.0572	1.63	0.20
<b>0.6</b>	<b>1</b>	33.7	17.2	0.393	1.48	0.48
	<b>3</b>	106	19.1	0.238	1.57	0.54
	<b>5</b>	155	19.7	0.213	1.57	0.37
	<b>10</b>	340	20.9	0.130	1.60	0.41
	<b>20</b>	578	21.0	0.0916	1.61	0.43
	<b>50</b>	1020	38.4	0.0683	1.57	0.39



1  
2 **Figure 1.** Comparison of the model prediction with the experimental results for the tensile  
3 relaxation tests. Uniaxial tensile stress as a function of time for dual crosslink gels with a chemical  
4 crosslinker concentration of (a) 0.2 and (b) 0.6 mol%. Results for two borax concentrations are  
5 shown, 1 mM (red) and 10 mM (green). Solid curves: experiments. Dashed curves: model prediction.  
6 Inset: Comparison of the model prediction with the experimental results for the small amplitude  
7 shear torsion tests. Viscoelastic moduli as a function of angular frequency for dual crosslink gels  
8 with a chemical crosslinker concentration of (a) 0.2 and (b) 0.6 mol%. Results for two borax  
9 concentrations are shown, 1 mM (red lines, open symbols) and 10 mM (green lines, filled symbols).  
10 Solid curves and circles:  $G'$ . Dashed curves and squares:  $G''$ .

11 We emphasize that by fitting both tensile and torsion data, we were able to obtain reasonably  
12 accurate material parameters, for the following reasons. By fitting the tensile tests, from the  
13 stress relaxation part, the values of  $\mu\rho$  and  $\alpha_B$  can be accurately determined, while those of  $t_B$   
14 and  $\mu\bar{\gamma}_\infty$ , are less accurately found (the product of them is accurately found). This is due to the  
15 relatively low amount of broken and healed transient bonds during the rapid loading phase of  
16 the relaxation test where  $\dot{\lambda}$  is high but the final stretch ratio  $\lambda_0$  is low. By fitting the torsion

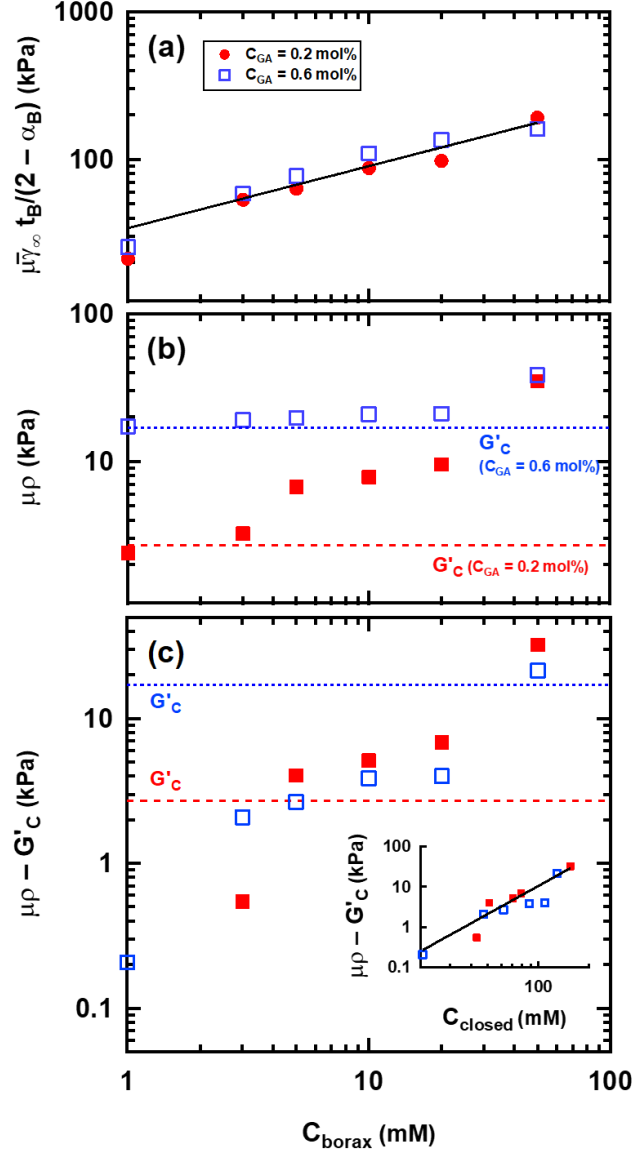


1 tests, the values of  $t_B$  can be accurately determined from the peak of  $G''$ . However, the values  
 2 of  $\mu\rho$  and  $\mu\bar{\gamma}_\infty$  are less accurately measured due to the precompression applied in the parallel  
 3 plate geometry. The values of the shift factor used to adjust the discrepancy in the absolute  
 4 values of the moduli in the tensile tests and rheology tests are also shown in **Table I**. The  
 5 values of  $\mu\rho$  and  $\mu\bar{\gamma}_\infty$ , which fitted well the tensile tests data, were multiplied by this factor to  
 6 fit the torsion test data. The average value of these shift factors is 0.45. The dispersion of the  
 7 shift factor is large since for each gel the measurement is different, and the normal force  
 8 relaxation of the pre-compressed sample is difficult to control.

## 9 **4.2. Modulus ( $\mu\rho$ and $\mu\bar{\gamma}_\infty$ )**

### 10 **4.2.1. Elastically active crosslinker populations**

11 In this section we study the relation between the crosslinker concentrations and the two  
 12 parameters,  $\mu\rho$  and  $\mu\bar{\gamma}_\infty$ . We use the glutaraldehyde concentration in the feed,  $C_{GA}$  in mol%,  
 13 and the borax concentration in the feed in the preparation solution,  $C_{borax}$  in mM, as  
 14 experimental parameters of the chemical and physical crosslinkers concentrations, respectively.  
 15 First we investigate  $\mu\bar{\gamma}_\infty$ . The contribution of the closed transient crosslinks to the elastic  
 16 modulus is given by  $G'_{closed} = \mu\bar{\gamma}_\infty \cdot \frac{t_B}{2-\alpha_B}$ , which is a measurable rheological quantity of the  
 17 system (recall  $G'_{closed}$  is the contribution of the physical crosslinks to the elastic modulus at high  
 18 frequency  $\omega \rightarrow \infty$ , see **eq.10**). Here we evaluate this reduced parameter  $\mu\bar{\gamma}_\infty \cdot \frac{t_B}{2-\alpha_B}$  without  
 19 discussing separately the four parameters of which it is composed ( $\mu$ ,  $\bar{\gamma}_\infty$ ,  $t_B$  and  $\alpha_B$ ). The  
 20 dependence of  $G'_{closed}$  on the borax concentration  $C_{borax}$  are plotted in **Figure 2a**. They increase  
 21 with borax concentration, and practically no chemical crosslinker concentration dependence is  
 22 found. A power-law fitting curve is shown in the figure: the exponent is found to be about 0.5,  
 23 i.e.,  $G'_{closed} \propto C_{borax}^{0.5}$ .



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**Figure 2.** (a) Borax concentration dependence of  $G'_{closed} = \mu\bar{\gamma}_{\infty} \frac{t_B}{2 - \alpha_B}$  (Modulus contribution from closed transient crosslinks). The solid line is a power-law fit with an exponent of 0.51. (b) The borax concentration dependence of  $\mu\rho$ . The dashed lines indicate the elastic modulus of the corresponding chemical gels. (c) The value of  $G'_{slow} = \mu\rho - G'_c$  as a function of the borax concentration  $C_{borax}$  in feed. Inset: the elastically active closed physical crosslinker concentration  $C_{closed}$ . The solid line is a linear fit with an exponent of 2.3. The filled red circles represent the dual crosslink gel for  $C_{GA} = 0.2$  mol%, open blue circles for  $C_{GA} = 0.6$  mol%.

9 For a more quantitative discussion, we estimate *the molar concentration of the elastically active*  
 10 *transient physical crosslinks*,  $C_{closed}$ , from the elastic modulus  $G'_{closed}$ . The elastic modulus is  
 11 proportional to the molar concentration of elastically active chain and is written as  $G'_{closed} =$

1  $\frac{1}{2} C_{\text{closed}} \cdot RT$ , where  $R$  is the gas constant and  $T$  is the absolute temperature. The factor 1/2  
 2 indicates that each crosslinker is tetrafunctional and crosslinks two chains. In this relation  
 3  $C_{\text{closed}}$  has mol/m<sup>3</sup> as unit, and is recalculated in mM. We found values between 17 and 155  
 4 mM with the same  $C_{\text{borax}}$  dependence as  $G'_{\text{closed}}$ .<sup>23</sup>  
 5 Next we study the dependence on the borax concentration of the time-independent reduced  
 6 parameter  $\mu\rho$ . Recall that  $\mu\rho$  corresponds to the elastic modulus at zero frequency ( $t \gg t_B$ )  
 7 (**eq.10**). We performed tensile stress relaxation test up to 100 s for  $t_B$  lower than 1 s. The  
 8 physical model of the dual crosslink gel assumes that the transient crosslinks dissociate and the  
 9 chains fully relax at low frequency, thus the value of  $\mu\rho$  is expected to be the same as the  
 10 modulus of the chemical gel used to prepare the dual crosslink gels, and therefore should be  
 11 independent of the borax concentration in the feed,  $C_{\text{borax}}$ .  
 12 **Figure 2b** shows the borax concentration dependence of  $\mu\rho$ . For both chemical crosslinking  
 13 ratios, the values of the elastic modulus  $G'_C$  for the corresponding chemical gels (measured  
 14 independently with the chemical gel samples) are indicated by the dashed lines. For the gels  
 15 with  $C_{\text{GA}} = 0.2$  mol%, at low borax concentrations we find fitted values of  $\mu\rho$  close to that of  
 16 the chemical gel (2.7 kPa), then they increase with increasing borax concentration. At  $C_{\text{borax}} =$   
 17 50 mM,  $\mu\rho$  reaches 25 kPa. For gels with  $C_{\text{GA}} = 0.6$  mol%, at borax concentrations below 20  
 18 mM the values of  $\mu\rho$  are comparable to that of the chemical gel (17 kPa), then they increase to  
 19 30 kPa for  $C_{\text{borax}} = 50$  mM. These results indicate that at the lower frequency experimentally  
 20 investigated, the modulus of the dual crosslink gels matches with that of the chemical gels only  
 21 at sufficiently low borax concentration. *This result suggests that at high borax concentrations*  
 22 *the physical crosslinkers increase  $\mu\rho$ , forming a second population of elastically active physical*  
 23 *crosslinkers with a much longer lifetime than that corresponding to  $G'_{\text{closed}}$ .* This second

1 population is rheologically indistinguishable from the chemical crosslinks within the window  
2 of observation times explored here.

3 The modulus due to the presence of this longer lived population of physical crosslinks can be  
4 determined by subtracting *the elastic modulus of the corresponding chemical gel*  $G'_C$  from the  
5 fitted value of  $\mu\rho$  for each dual crosslink gels assuming that additivity holds for this population.  
6 The result is shown in **Figure 2c**. Even though the eventual errors of this subtraction between  
7 the data from two separate rheological measurements can be large, one can still see that the  
8 values of  $G'_{\text{slow}} = \mu\rho - G'_C$  increase with borax concentration  $C_{\text{borax}}$ , and no clear effect of the  
9 degree of chemical crosslinking is found. This result suggests that the presence of the  
10 permanent crosslinks does not influence the formation of this slower population at the studied  
11 crosslinking ratios. The values of  $G'_{\text{slow}}$  (0.1 – 30 kPa) are comparable to (or lower than) those  
12 of  $G'_C$  (3 or 17 kPa). Finally, these values of modulus due to slow physical crosslinks are also  
13 lower than those of the closed physical crosslinks (21 – 190 kPa, as shown in **Figure 2a**).

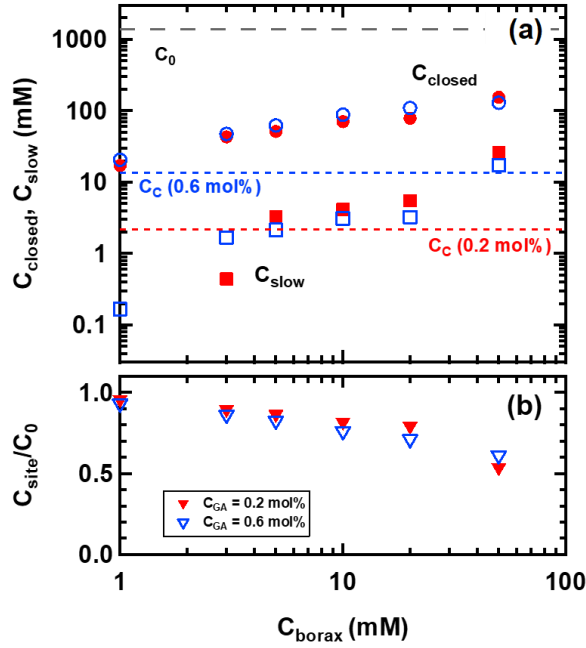
14 To better characterize the origin of this long lived population of physical crosslinks, the values  
15 of  $G'_{\text{slow}} = \mu\rho - G'_C$  are plotted in the inset of **Figure 2c** as a function of the concentration of  
16 elastically active chains due to physical crosslinkers which dissociate within the experimental  
17 time scale,  $C_{\text{closed}}$ . The values of  $G'_{\text{slow}}$  increase with  $C_{\text{closed}}$  with a power-law exponent of about  
18 2.3. This power-law exponent suggests that the origin of this slow population is due to  
19 clustering of two (or more) physical crosslinkers.

20 In the case of binding of mobile crosslinkers which can diffuse in the network and bind on the  
21 chains, the binding potential can entropically and enthalpically vary depending on the position  
22 relative to the existing physical and chemical crosslinkers. Binding to a site very close to an  
23 existing crosslinker is preferred, as the local polymer concentration is higher. This clustering  
24 is also expected to bring an entropic gain for polymer chains.<sup>24</sup> The lifetime of a cluster made  
25 of several physical bonds should be longer than that of a single bond, as it is necessary to break

1 all the bonds for the chain to relax. Clustering involving a chemical crosslink and physical  
2 crosslinks might occur. However, it is difficult to rheologically detect such clusters, since they  
3 are not distinguishable from a simple chemical crosslink in the linear regime. Furthermore, we  
4 expect the concentration of clusters near a chemical crosslink to be very low since the  
5 concentration of the chemical crosslinks itself,  $C_C$ , estimated from the value of  $G'_C$ , is also very  
6 low compared to  $C_{\text{closed}}$ . The values of  $C_C$  are estimated to be 2 and 14 mM for  $C_{GA}$  of 0.2 and  
7 0.6 mol%.

8 The slower population can be an important factor in determining gel failure under large  
9 deformation. Previously it was shown that the stretch at break of the dual crosslink gels is very  
10 sensitive to the chemical and physical crosslinking ratios, and decreases with increasing  
11 chemical and physical crosslinking ratio.<sup>16</sup> This is presumably due to the increase in the amount  
12 of the slower population which is expected to behave similarly to permanent crosslinks which  
13 enhance the brittleness.

14 The concentrations of the three different elastically *active* components are summarized here.  
15 The concentrations of permanent chemical crosslinks ( $C_C$ ), and of the two populations of  
16 transient physical crosslinks, the fast one ( $C_{\text{closed}}$ ) and slow one ( $C_{\text{slow}}$ ), were estimated from the  
17 corresponding modulus and are plotted as a function of the borax concentration in the feed  $C_{\text{borax}}$   
18 in **Figure 3a**. At all borax concentrations  $C_{\text{borax}}$  tested here, the values of  $C_{\text{closed}}$  are higher than  
19 those of  $C_{\text{slow}}$  and  $C_C$ , indicating that the time-dependent elasticity of the dual crosslink gels is  
20 still governed by the transient crosslinks. At high  $C_{\text{borax}}$ , the difference between  $C_{\text{closed}}$  and  $C_{\text{slow}}$   
21 becomes smaller.



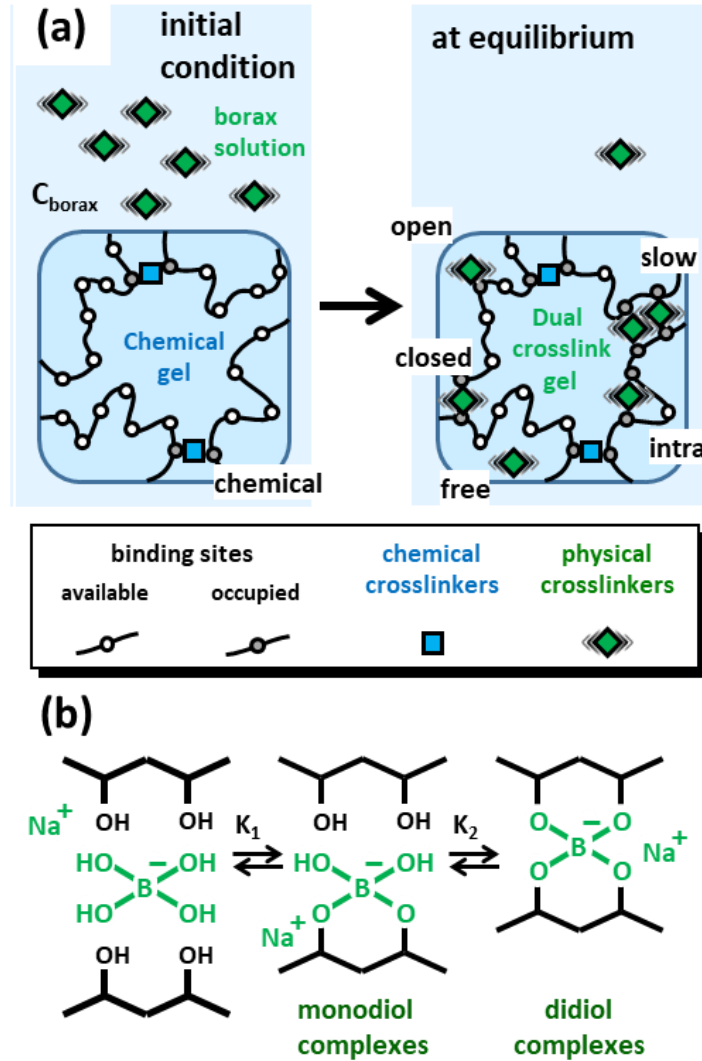
1  
2 **Figure 3.** The borax concentrations dependence of the two populations of the transient physical  
3 crosslinks: the fast one  $C_{\text{closed}}$  (circles) and the slow one  $C_{\text{slow}}$  (squares). The red symbols are for  
4  $C_{\text{GA}} = 0.2 \text{ mol\%}$ , blue ones for  $C_{\text{GA}} = 0.6 \text{ mol\%}$ . Dashed lines: red for  $C_c$  for  $C_{\text{GA}} = 0.2 \text{ mol\%}$ , blue  
5 for  $C_c$  for  $C_{\text{GA}} = 0.6 \text{ mol\%}$ , gray for the total concentration of the binding site,  $C_0$  (see the text).

#### 6 4.2.2. Elastically inactive crosslinker populations

7 In the previous subsection, we have shown that there are three populations of elastically active  
8 crosslinkers, and that their concentration can be estimated from the corresponding elastic  
9 modulus. The correspondence between the elastic modulus and the model parameters,  $\mu\rho$  and  
10  $\mu\bar{\gamma}_{\infty}$ , was also demonstrated. In our steady state model, we assume that there is a  
11 thermodynamic equilibrium between the elastically active closed crosslinks and the elastically  
12 *inactive* open crosslinks. This equilibrium depends on the physical chemistry of the dynamic  
13 bonds used as transient crosslinks. In this subsection, we discuss the open crosslinks and other  
14 elastically inactive populations of the transient crosslinks. As seen later in this subsection, the  
15 concentration of available binding sites is an important parameter influencing the dynamics of  
16 the breaking/healing of the transient crosslinks and we now attempt to approximately evaluate

1 it. This argument will be useful to better comprehend the dynamics  
2 developed in the next section 4.3.

3 The complexation of borate ions with diol binding sites (two neighboring hydroxyl groups) on  
4 the PVA chains has two binding equilibria as borate ions can interact with one or two diol  
5 binding sites as illustrated in **Figure 4**. At equilibrium, the borate ions can take three states. (1)  
6 “Free” borate ions in the gel and in the solution which do not interact with PVA chains, their  
7 concentration is defined as  $C_{\text{free}}$  (mol/L). (2) Borate ions which complex with one diol binding  
8 site (monodiol complexation), do not crosslink chains. This state corresponds to “open”  
9 crosslink (with the concentration of  $C_{\text{open}}$ ), as it readily forms a closed crosslink with an  
10 available diol binding site. (3) Borate ions complexing with two diol binding sites (didiol  
11 complexation) can be further classified into three different states which are not  
12 thermodynamically distinguishable. (3a) The borate ions in didiol complexes can be *intra-*  
13 chain didiol complexes ( $C_{\text{intra}}$ ), and these complexes are elastically *inactive*. (3b) They can be  
14 also inter-chain didiol complexes which serve as “closed” crosslinks ( $C_{\text{closed}}$ ), thus elastically  
15 *active*. Finally, (3c) they can also form a cluster of the didiol complexes behaving as a slow  
16 population of the crosslink ( $C_{\text{slow}}$ ), considered as elastically *active*.

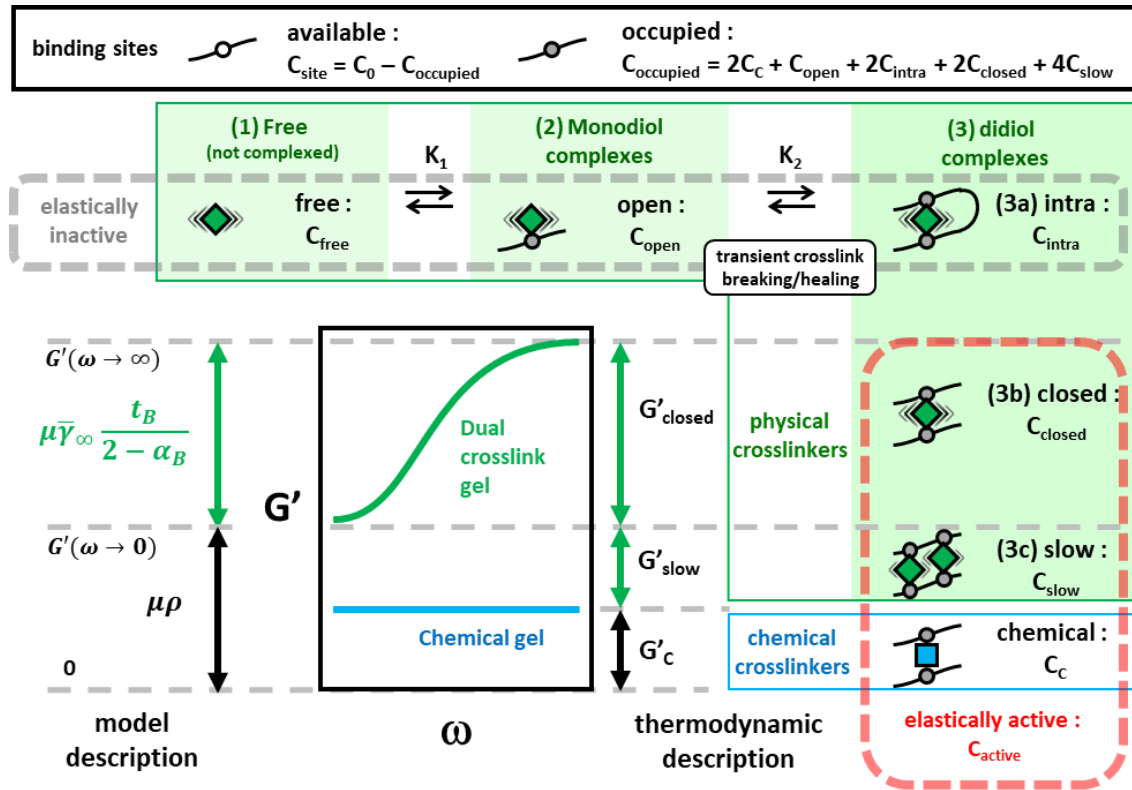


1  
 2 **Figure 4.** (a) Schematic illustrations of transient crosslinker incorporation into the chemical gel. (b)  
 3 Binding equilibria of the borate ion and diols on PVA chains.

4 The two binding constants,  $K_1$  and  $K_2$  (L/mol), are written as  $K_1 = \frac{C_{\text{open}}}{C_{\text{free}} \cdot C_{\text{site}}}$  and  $K_2 = \frac{C_{\text{di}}}{C_{\text{open}} \cdot C_{\text{site}}}$ ,  
 5 where  $C_{\text{site}}$  is the concentration of available binding sites on the PVA chains, and  $C_{\text{di}} = C_{\text{intra}} +$   
 6  $C_{\text{closed}} + C_{\text{slow}}$ . In **Figure 5** we schematically illustrated in green these five different populations  
 7 of physical crosslinkers (borate ions), as well as chemical crosslinks (in blue) and didiol binding  
 8 sites on the PVA chains. For the elastically active populations (3b, 3c and the chemical  
 9 crosslinks), the correspondence with  $G'(\omega)$  and the model parameters are also shown. The  
 10 dynamics of the transient crosslink breaking/healing are described by the second equilibrium



- 1 (i.e., by the binding constant  $K_2$ ), which depends on the three concentrations,  $C_{di}$ ,  $C_{open}$  and  $C_{site}$ .
- 2 Here we attempt to estimate them as quantitatively as possible.



3

4 **Figure 5.** Classification of the different species involved in the binding equilibria of borate ion-diol

5 complexation, and their concentration. Correspondence between the model description and the

6 thermodynamic description of the elastic modulus.

7 *Didiol complex concentration.* Contrary to  $C_{closed}$  and  $C_{slow}$ , which are concentrations of the

8 elastically active populations, it is experimentally difficult to determine the concentration of the

9 rheologically undetectable intrachain crosslink,  $C_{intra}$ . In dilute solutions intrachain

10 crosslinking is favored, while in semi-dilute solutions and gels the amount of the interchain

11 crosslinks increases. Since intrachain crosslinking involves the formation of a loop on the

12 polymer chain, chain rigidity is a factor controlling the size of the loop. Pezron et al.<sup>25-27</sup>

13 estimated the ratio of interchain to intrachain crosslinks as a function of the polymer

14 concentration, by correlating the sizes of the blob and the loop formed by intrachain crosslink.

15 Applying their theory to our system with a fixed PVA concentration of 12 wt%, the ratio of

16 inter- to intra-chain crosslink is estimated to be about 1.7. In the following, we use this value,

1 thus  $C_{\text{intra}} = (C_{\text{closed}} + C_{\text{slow}})/1.7$ . It should be noted that for our systems the PVA chains are  
2 integrated into the percolated chemical network, thus the chains between crosslinks might have  
3 lower deformability to form a loop than the chains in solution, and  $C_{\text{intra}}$  could be lower than  
4 this estimate.

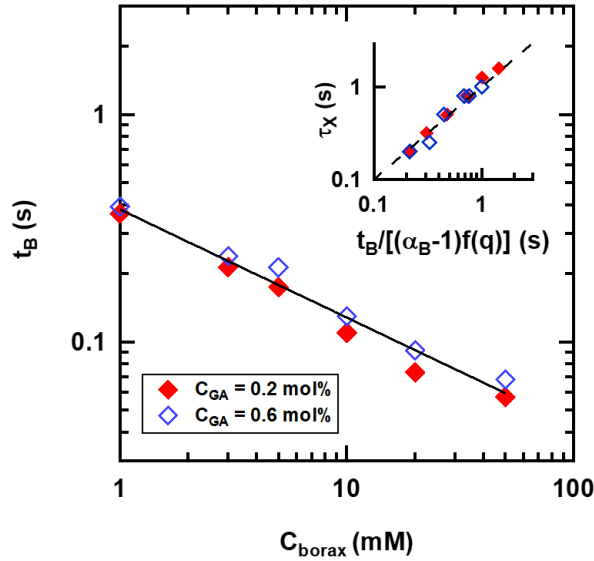
5 *Monodiol complex (open crosslink) concentration.* For solutions with relatively low PVA  
6 concentrations (without chemical crosslinks),  $^{11}\text{B}$  NMR spectroscopy has been used to  
7 determine the concentrations of different states of borate ions.<sup>28,29</sup> The results indicate that  
8 monodiol complexes, corresponding to open transient crosslinks have much weaker signals  
9 than the didiol complexes (closed transient crosslinks), as the binding equilibrium is toward the  
10 didiol complexes, or  $C_{\text{closed}} \gg C_{\text{open}}$ . We will further discuss  $C_{\text{open}}$  in the next section. We did  
11 not perform NMR measurements of our chemically crosslinked systems with relatively higher  
12 PVA concentration, due to difficulties in sample preparation.

13 *Available binding site concentration.* The total concentration of binding sites is estimated to  
14 be  $C_0 = 1.36 \text{ M}$ ,<sup>30</sup> which is shown as a black dashed line in **Figure 3a**. The concentration of  
15 occupied binding sites can be determined from that of the chemical crosslinks and the bound  
16 borate ions in monodiol and didiol complexes, thus  $C_C$ ,  $C_{\text{open}}$ ,  $C_{\text{closed}}$ ,  $C_{\text{intra}}$  and  $C_{\text{slow}}$ .  
17 Specifically, the concentration of the occupied sites can be written as  $C_{\text{occupied}} = 2C_C + C_{\text{open}} +$   
18  $2C_{\text{closed}} + 2C_{\text{intra}} + 4C_{\text{slow}}$ , where the numerical factors 1, 2 or 4 in this equation indicate the  
19 number of binding sites for the different binding mechanisms and assumes a cluster of 2 didiol  
20 complexes. The concentration of available binding sites  $C_{\text{site}}$  is  $C_{\text{site}} = C_0 - C_{\text{occupied}}$ . The values  
21 of  $C_{\text{site}}$  are estimated by inputting into this equation the values of these different concentrations  
22 (rheologically determined:  $C_C$ ,  $C_{\text{closed}}$ ,  $C_{\text{slow}}$ ; estimated from  $C_{\text{closed}}$  and  $C_{\text{slow}}$ :  $C_{\text{intra}}$ ;  $C_{\text{open}}$  is  
23 ignored since  $C_{\text{open}} \ll C_{\text{closed}}$ ). In **Figure 3b**  $C_{\text{site}}/C_0$  is plotted as a function of the borax  
24 concentration  $C_{\text{borax}}$ .  $C_{\text{site}}/C_0$  decreases with  $C_{\text{borax}}$ , and for the gel with the highest degree of  
25 binding,  $C_{\text{site}}/C_0$  is estimated to be about 0.54 ( $C_{\text{site}}$  is about 0.73 M). Therefore, although the

1 concentration of the elastically inactive populations may not be quantitatively very accurate we  
2 can still conclude that the saturation of binding sites does not occur in the studied conditions:  
3 there are plenty of available binding sites. Note that  $K_2 \cdot C_{\text{site}} = \frac{C_{\text{di}}}{C_{\text{open}}}$ , thus close to the binding  
4 saturation, with decreasing  $C_{\text{site}}$ ,  $C_{\text{di}}$  relatively decreases and the dynamics of the transient  
5 crosslink breaking/healing can be very different.

### 6 **4.3. Characteristic time ( $t_B$ and $\alpha_B$ )**

7 In this section we investigate the effect of the crosslinking ratio on the characteristic relaxation  
8 time of the dual crosslink gels, by focusing on the two parameters,  $t_B$  and  $\alpha_B$ .  $t_B$  is the  
9 characteristic transient bond breaking time and is proportional to the rheologically directly  
10 measurable relaxation time  $\tau_X$  of the peak position of  $G''$  (section 3.1, **eq.11**) with a coefficient  
11 depending only on  $\alpha_B$ . In the inset of **Figure 6**, this proportionality is shown. The values of  
12 the coefficient,  $1/[(\alpha_B - 1) \cdot f(q)]$ , vary between 2.5 and 4.7. The concentration dependence  
13 of  $\alpha_B$  will be discussed later in this section. As seen in the inset of **Figure 1** (and **Figure S2**),  
14 the position of the peak depends on the chemical crosslinker concentration: gels with  $C_{\text{borax}} =$   
15 10 mM (filled symbol, green curves) show the peak at higher frequency than the gels with  $C_{\text{borax}}$   
16 = 1 mM (open symbols, red curves). **Figure 6** shows that fitted values of  $t_B$  obtained from the  
17 rheological curves decrease with increasing borax concentration  $C_{\text{borax}}$ , and do not show any  
18 obvious chemical crosslinking ratio dependence. The value of  $t_B$  is found to approximately  
19 scale as  $t_B \sim C_{\text{borax}}^{-0.48}$ . Thus, for this system, the bond breaking time decreases with increasing  
20 physical crosslinker concentration.



1

2 **Figure 6.** The values of  $t_B$  as a function of the borax concentration  $C_{\text{borax}}$ . Red diamonds:  $C_{\text{GA}} =$   
 3 0.2 mol%; blue diamonds:  $C_{\text{GA}} = 0.6$  mol%. The solid line is a power-law fit with an exponent of -  
 4 0.48. Inset: the network relaxation time at the peak of  $G''$ ,  $\tau_X$ , as a function of  $t_B$  (see eq.11).

#### 5 **4.3.1 Molecular interpretation: theoretical framework**

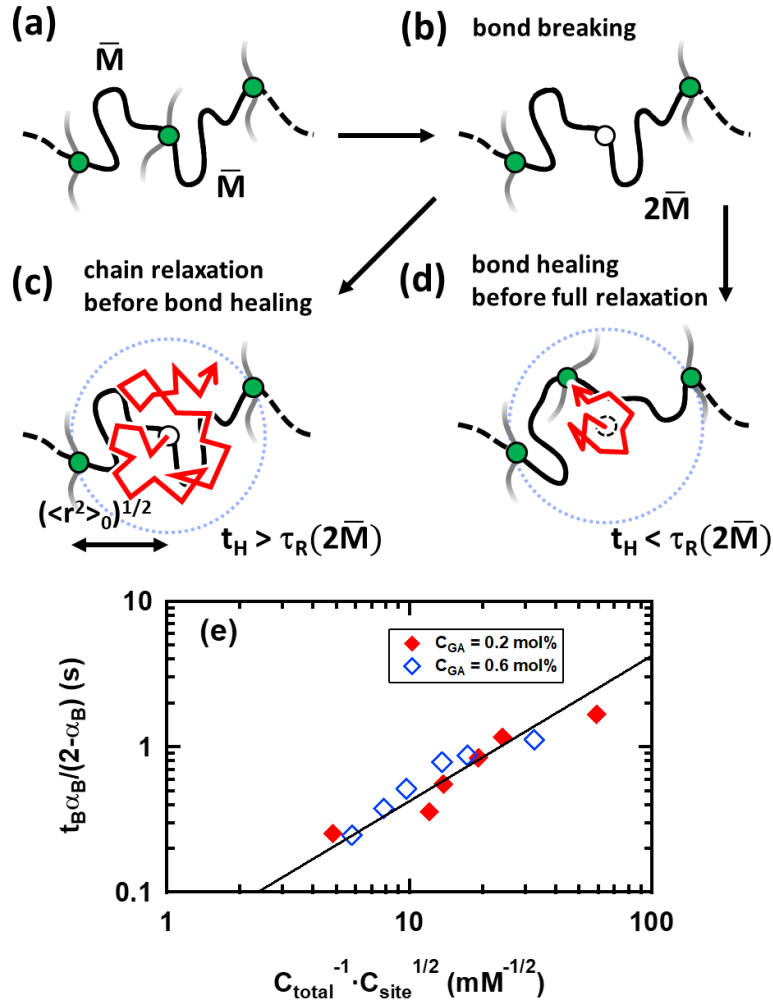
6 We now attempt to interpret this concentration ( $C_{\text{borax}}$ ) dependence from a macromolecular  
 7 point of view, by considering the chain relaxation dynamics as a function of transient bond  
 8 breaking and healing times following the argument of Indei and Takimoto for associative  
 9 polymers.<sup>31</sup>

10 In a dual crosslink network prepared from a percolated chemical network by incorporating  
 11 additional transient crosslinks, each transient crosslink is located on a part of a chain between  
 12 two other crosslinks which can be permanent or transient, and are elastically active during the  
 13 bond breaking time scale considered here. In **Figure 7a** this chain is indicated in black and the  
 14 average Kuhn segment number between two adjacent crosslinks is defined as  $\bar{M}$ . When the  
 15 transient crosslink breaks with a characteristic breaking time  $t_b$ , a subchain having  $2\bar{M}$  segments  
 16 is released and starts to relax (**Figure 7b**). We will discuss the relation between this molecular  
 17 parameter  $t_b$  and the model parameter  $t_B$  later in this section. The mean square displacement,  
 18 MSD, of the open transient bond on this subchain (after its release) is approximately:<sup>32</sup>

$$MSD \sim \langle \Delta r^2 \rangle_0 \left( \frac{t}{\tau_R} \right)^{\frac{1}{2}} \quad \text{for } t < \tau_R \quad (\text{eq.13i})$$

$$MSD \sim \langle \Delta r^2 \rangle_0 \quad \text{for } t > \tau_R \quad (\text{eq.13ii})$$

- 1 where  $\langle \Delta r^2 \rangle_0$  is the mean square length of the subchain, and  $\tau_R$  is the Rouse relaxation time of
- 2 a subchain having the segment number of  $2\bar{M}$ .



3  
4 **Figure 7.** (a) – (d) Schematic illustrations of relaxation of a subchain after bond breaking in  
5 competition with bond healing. (e)  $\tau_X$  as a function of  $C_{\text{total}}^{-1} \cdot C_{\text{site}}^{1/2}$ . Red diamonds:  $C_{GA} = 0.2$  mol%;  
6 blue diamonds:  $C_{GA} = 0.6$  mol%. The solid line is a linear fit.

- 7 Next we include bond healing in the argument: the open transient crosslink can reattach with
- 8 an available binding site nearby, and its characteristic time is  $t_h$ . Since the transient crosslink

1 can move while it is open (starting at  $t = 0$ ), the subchain can fully relax if  $t < t_h$ . Thus, we can  
 2 rewrite **eq.13** by replacing  $t$  with  $t_h$ :

$$MSD \sim \langle \Delta r^2 \rangle_0 \left( \frac{t_h}{\tau_R} \right)^{\frac{1}{2}} \quad \text{for } t_h < \tau_R \quad \text{(eq.14i)}$$

$$MSD \sim \langle \Delta r^2 \rangle_0 \quad \text{for } t_h > \tau_R \quad \text{(eq.14ii)}$$

3 For the case of  $t_h > \tau_R$ , the subchain can fully relax before the transient crosslink reattaches  
 4 (**Figure 7c**), thus the MSD of the open transient crosslink can reach its maximum value,  $\langle \Delta r^2 \rangle_0$ .

5 On the contrary, for  $t_h < \tau_R$ , the transient crosslink reattaches before the chain fully relaxes  
 6 (**Figure 7d**), thus the value of MSD is lower than that for  $t_h > \tau_R$ . Bond healing can occur in  
 7 multiple steps (number of step:  $n_{\text{step}}$ ) when  $t_h < \tau_R$ , until the subchain fully relaxes and its  
 8 equilibrium is reached, thus  $MSD \cdot n_{\text{step}} \sim \langle \Delta r^2 \rangle_0$ .

9 The network relaxation time  $\tau_X$  can also be interpreted as the time required for the subchain to  
 10 reach its equilibrium state during which the transient crosslink breaks in single or multiple steps,  
 11 thus it is written as

$$\tau_X \sim n_{\text{step}} \cdot t_b \sim \frac{\langle \Delta r^2 \rangle_0}{MSD} \cdot t_b \quad \text{(eq.15)}$$

12 In summary, our analysis shows that

$$\tau_X \sim \left( \frac{\tau_R}{t_h} \right)^{\frac{1}{2}} \cdot t_b \quad \text{for } t_h < \tau_R \quad \text{(eq.16i)}$$

$$\tau_X \sim t_b \quad \text{for } t_h > \tau_R \quad \text{(eq.16ii)}$$

### 13 4.3.2 Molecular interpretation: Experimental data

14 The physical crosslinker concentration dependences of  $t_h$  and  $\tau_R$  are now studied. The Rouse  
 15 relaxation time of the subchain having the Kuhn segment number of  $2\bar{M}$  is written as  $\tau_R = \tau_0 \cdot$   
 16  $(2\bar{M})^2$ , where  $\tau_0$  is the relaxation time of the Kuhn segment. Since  $\bar{M}$  is inversely proportional

1 to the crosslinking ratio,  $\tau_R$  scales with the concentration of the total elastically active crosslinks,

2  $C_{\text{active}} = C_{\text{closed}} + C_{\text{slow}} + C_C$ , as

$$\tau_R \sim C_{\text{active}}^{-2} \quad (\text{eq.16iii})$$

3  $C_{\text{active}}$  is estimated from the elastic moduli, and found to be between 19 and 183 mM, For

4 simplification, we have ignored the influence of loops made by the intrachain crosslinks on the

5 chain dynamics. Bond healing requires an available binding site on the polymer, thus the bond

6 reassociation time  $t_h$  is inversely proportional to its concentration, i.e.,

$$t_h \sim C_{\text{site}}^{-1} \quad (\text{eq.16iv})$$

7 where  $C_{\text{site}} = C_0 - 2C_C - C_{\text{open}} - 2C_{\text{closed}} - 2C_{\text{intra}} - 4C_{\text{slow}}$ , as shown in the subsection 4.2.2. As

8 discussed previously, we assume  $C_{\text{open}} \ll C_{\text{closed}} < C_0$ , thus we ignore  $C_{\text{open}}$ .  $C_{\text{site}}$  varies between

9 1.3 and 0.73 M. From **eq.16i,iii,iv**,  $\tau_X$  is expected to scale as  $\tau_X \sim C_{\text{active}}^{-1} \cdot C_{\text{site}}^{1/2}$ . In **Figure 7e**,

10 the values of  $\tau_X$ , are plotted as a function of  $C_{\text{active}}^{-1} \cdot C_{\text{site}}^{1/2}$ . The solid line corresponds to a

11 linear fit, suggesting that the scaling corresponding to **eq.16i** holds. Even at lower values of  $\tau_X$ ,

12 we did not observe a regime corresponding to **eq.16ii**. The absence of this regime shows that

13 in the studied conditions, the relaxation time of the network equals  $n_{\text{step}} \cdot t_b$ , with  $n_{\text{step}} > 1$  and  $\tau_R >$

14  $t_h$ .

15 Here we compare the constitutive model parameters ( $t_B$  and  $t_H$ ) with the molecular parameters

16 ( $t_b$  and  $t_h$ ). According to the definition,  $t_H$  is identical to  $t_h$ . From **eq.11** and **eq.15**, we have

17  $\tau_X \sim t_B \sim n_{\text{step}} \cdot t_b$ . Thus we conclude that the decrease in  $t_B$  with increase in  $C_{\text{borax}}$  shown in

18 **Figure 6** is due to the decrease in  $n_{\text{step}}$ , as a consequence of the decrease in  $C_{\text{site}}$  and of the

19 increase in  $C_{\text{active}}$ . Since  $n_{\text{step}} > 1$ , it is necessary to slightly modify one of the assumptions of

20 the model described in section 3.1 to meet the argument above. The assumption (3) should be

21 rewritten as “(3’) the stress sustained by a transient chain is relaxed with a Rouse relaxation

22 time after single or multiple transient bond breaking steps, as a function of the healing time of

1 the crosslink. A fully relaxed temporary detached chain can be reattached without carrying  
 2 strain energy, and experiences the deformation history from its birth at time  $\tau$  (s) to the current  
 3 time  $t$  (s).” The equations are identical and consistent with the argument.

4 Let us roughly estimate the order of the three characteristic times,  $\tau_R$ ,  $t_b$ , and  $t_h$ . From the value  
 5 of the plateau modulus at high frequency  $G' = k_B T / \xi^3$ , the size of the Gaussian subchain,  $\xi$ , is  
 6 determined. Then the number of Kuhn segment  $\bar{M}$  is determined from  $\xi = b_K \bar{M}^{1/2}$ , with the  
 7 Kuhn segment size of  $b_K$ . The Rouse relaxation time  $\tau_R$  is written as  $\tau_R = \tau_0 \cdot (2\bar{M})^2$ . We  
 8 used the viscosity of water,  $\eta_s = 0.00089$  Pa s,  $b_K = 0.62$  nm,<sup>33</sup> thus  $\tau_0 = \eta_s b_K^3 / k_B T = 5.2 \times$   
 9  $10^{-11}$  s. The values of  $\tau_R$  for the dual crosslink gels studied here are estimated to be between  
 10  $1 \times 10^{-6}$  and  $7 \times 10^{-8}$  s.

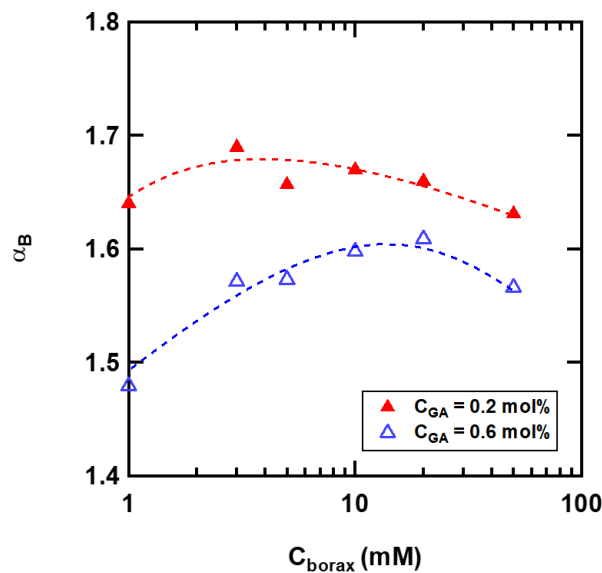
11 The values of  $t_b$  and  $t_h$  cannot be determined from the analysis above. Still, from **eq.15** and  
 12 **eq.16i**, we can estimate the highest values of  $t_h$  and  $t_b$ , as well as the lowest value of  $n_{\text{step}}$ .  
 13 Specifically, since  $t_h < \tau_R$ ,  $t_b < \tau_X$ , **eq.15** and **eq.16i**, imply  $\tau_X / t_b \sim n_{\text{step}} = (\tau_R / t_h)^{1/2}$ . Since  $t_b < \tau_X$ ,  
 14 we assume the highest value of  $t_b$  is close to the lowest value of  $\tau_X$  measured, about 0.2 s. With  
 15  $t_b = 0.2$  s, we find the values of  $n_{\text{step}}$  between 1 and 8 for the different crosslinking ratios. Since  
 16  $n_{\text{step}} = (\tau_R / t_h)^{1/2}$ , we can approximately estimate  $t_h$  from the values of  $\tau_R$ , and we find the values  
 17 of  $t_h$  is between  $1 \times 10^{-8}$  and  $8 \times 10^{-8}$  s. This very fast healing time might be due to the presence  
 18 of binding site in the vicinity of the closed crosslink. In fact, practically any part of the PVA  
 19 chain can be a binding site, and a dissociated crosslink can be immediately captured by a  
 20 neighboring binding site.

21 From the thermodynamic argument,<sup>34</sup> we have  $\frac{t_b}{t_h} = \frac{C_{\text{di}}}{C_{\text{open}}}$ . Thus the ratio of the two  
 22 characteristic time corresponds to the ratio of the closed and open crosslinks. For the largest  
 23 value of  $t_b = 0.2$ , the ratio  $t_b / t_h$  varies between  $3 \times 10^6$  and  $2 \times 10^7$ , indicating that  $t_b \gg t_h$  and  
 24  $C_{\text{closed}} \approx C_{\text{di}} \gg C_{\text{open}}$ . And when  $t_b$  is smaller, then this ratio becomes larger.



### 1 4.3.3. Molecular interpretation of $\alpha_B$

2 The values of  $\alpha_B$  are plotted as a function of the borax concentration in **Figure 8**. For the gels  
3 with the chemical crosslinking ratio of  $C_{GA} = 0.6$  mol%, the values of  $\alpha_B$  are found between  
4 1.48 and 1.61, they first increase with  $C_{borax}$  then decrease. The maximum is at  $C_{borax} \sim 20$  mM.  
5 For gels with  $C_{GA} = 0.2$  mol%, the values of  $\alpha_B$  are found between 1.63 and 1.69, higher than  
6 those for the gel with  $C_{GA} = 0.6$  mol%. Though the variation is small, they peak around  $C_{borax}$   
7 = 3 mM.

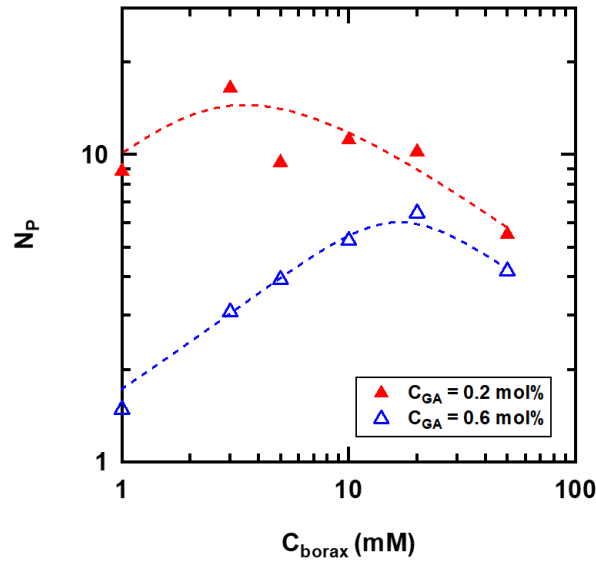


8

9 **Figure 8.** The values of  $\alpha_B$  as a function of the borax concentration. Red triangles:  $C_{GA} = 0.2$  mol%;  
10 blue triangles:  $C_{GA} = 0.6$  mol%. The dashed curves are guide for the eye.

11 The material parameter  $\alpha_B$  describes the spectrum of relaxation times of the transient strands.  
12 As shown in 4.3.1, the relaxation time  $\tau_X$  depends on the subchain length, or on the crosslinking  
13 ratio. Thus it is expected that the spectrum of the relaxation times can be expressed as a function  
14 of the number of relaxation modes due to the distribution of the subchain length in the dual  
15 crosslink network. First, we find the slowest relaxation modes (longest chain). It is reasonable  
16 to take the Rouse mode of a primary chain between the two neighboring permanent crosslinks  
17 as the slowest mode, since we first prepare a permanent chemical network then we add transient

1 crosslinks. When the transient crosslinks are added to the primary chain, the primary chain is  
 2 divided into subchains, having shorter Rouse relaxation times. We define a parameter  $N_P$ , the  
 3 number of the transient crosslinks per primary chain, as the ratio of  $\rho_{closed} = \bar{\gamma}_{\infty} \cdot \frac{t_B}{2-\alpha_B}$  to  $\rho$ ,  
 4 which signifies the ratio of the transient closed physical crosslinks to the permanent crosslink  
 5 including the chemical crosslinks and the slow population of the physical crosslinks which do  
 6 not break at the time scale of the measurement, thus behave similarly to the permanent  
 7 crosslinks.



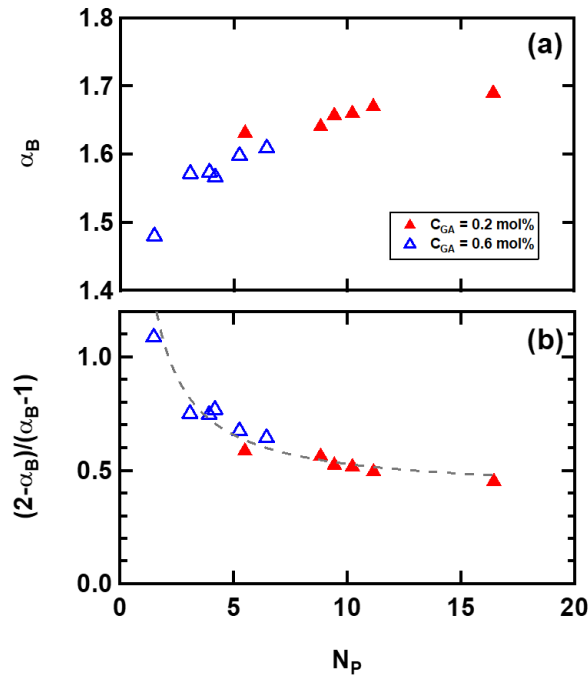
8

9 **Figure 9.** Number of the elastically active transient physical crosslinks per non transient crosslinks  
 10 as a function of the borax concentration. Filled red triangles:  $C_{GA} = 0.2$  mol%; open blue triangles:  
 11  $C_{GA} = 0.6$  mol%. The dashed curves are guide for the eye.

12 The values of  $N_P = \rho_{closed}/\rho$  are plotted as a function of  $C_{borax}$  in **Figure 9**. At low  $C_{borax}$ ,  $N_P$   
 13 increases with  $C_{borax}$  as the increase in  $\rho_{closed}$  is dominant, while at high  $C_{borax}$  it decreases with  
 14  $C_{borax}$  since the increase in  $\rho$  is dominant due to the increase in the slow population of the  
 15 physical crosslinks, giving a maximum. The position of the maximum is determined by the  
 16 value of  $G'_C$ : for gels with the lower chemical crosslinking ratio ( $C_{GA} = 0.2$  mol%) the peak is  
 17 found at a lower  $C_{borax}$  (about 0.3 mM), while for the gels with  $C_{GA} = 0.6$  mol% the peak is at  
 18 about 20 mM. The values of  $N_P$  range between 5.5 and 16 for  $C_{GA} = 0.2$  mol%, and between

1 1.5 and 6.4 for  $C_{GA} = 0.6$  mol%, indicating that it is experimentally difficult to increase the  
 2 value by more than 20 in this system.

3 One can notice resemblance between the  $C_{borax}$  dependence of  $\alpha_B$  and that of  $N_P$  shown in  
 4 **Figure 8** and **Figure 9**, suggesting that  $\alpha_B$  scales with  $N_P$ . **Figure 10a** shows  $\alpha_B$  as a function  
 5 of  $N_P$  for both chemical crosslinking ratios. We clearly see a consistent trend for the two  
 6 chemical crosslinker concentrations:  $\alpha_B$  increases with  $N_P$ . This result indicates that the  
 7 physical meaning of the parameter  $\alpha_B$  is related to the number of the relaxation modes of a  
 8 chain.



9

10 **Figure 10.** The values of (a)  $\alpha_B$  and (b)  $(2 - \alpha_B)/(\alpha_B - 1)$  as a function of  $N_P$ . Filled red triangles:  
 11  $C_{GA} = 0.2$  mol%; open blue triangles:  $C_{GA} = 0.6$  mol%. The dashed curve is an empirical relation

12 
$$\frac{2-\alpha_B}{\alpha_B-1} = \frac{1.28}{N_P} + 0.40$$
 (see the text).

13 To further quantify the rheological significance of  $\alpha_B$ , we estimate the dependence of  $\frac{2-\alpha_B}{\alpha_B-1}$  on

14  $N_P$ . We consider the value of  $\frac{2-\alpha_B}{\alpha_B-1}$  as a criterion to understand the rheological signification of

15  $\alpha_B$ : in tensile relaxation tests, the power-law behavior  $\sigma(t) - \sigma_\infty \sim t^{-\frac{2-\alpha_B}{\alpha_B-1}}$  is found from **eq.12**,

1 and in torsion tests, we find a power-law behavior  $G' - \mu\rho \sim \omega^{\frac{2-\alpha_B}{\alpha_B-1}}$  from **eq.9**. The values of  
2  $\frac{2-\alpha_B}{\alpha_B-1}$  are plotted as a function of  $N_P$  in **Figure 10b**. They range between 1.09 and 0.45 and  
3 decreases with  $N_P$ . This result suggests that with increasing number of transient crosslinkers  
4 and hence relaxation modes, the dynamics of the system gradually move from a Maxwell-like  
5 behavior with  $\frac{2-\alpha_B}{\alpha_B-1} = 1$  to a Rouse-like behavior with  $\frac{2-\alpha_B}{\alpha_B-1} = 0.5$ . It suggests also that the  
6 value of  $\alpha_B$  can be determined from the rheologically measurable value of  $N_P =$   
7  $\left(\mu\bar{\gamma}_\infty \cdot \frac{t_B}{2-\alpha_B}\right)/\mu\rho = [G'(\omega \rightarrow \infty) - G'(\omega \rightarrow 0)]/G'(\omega \rightarrow 0)$ . By fitting the data in **Figure**  
8 **10b**, we propose an empirical relation:

$$\frac{2-\alpha_B}{\alpha_B-1} = \frac{1.28}{N_P} + 0.40, \quad (\text{eq.17})$$

9 which is shown in the figure as a gray dashed curve. The value of  $\frac{2-\alpha_B}{\alpha_B-1}$  goes to 0.4 at  $N_P \gg 1$ ,  
10 this value is slightly lower than what is expected for the Rouse mode. The two factors (1.28  
11 and 0.40) should be intrinsic to this system. Universality of this relation needs to be further  
12 confirmed with different dual crosslink networks.

13 It should be noted that it is difficult to observe this Rouse-like mode in associative polymer  
14 solutions (physical gels) with small numbers of stickers (small  $N_P$ ), due to the terminal flow.  
15 In fact, this Rouse-like mode should occur between the relaxation times due to the transient  
16 crosslink breaking  $\tau_X$  and the terminal time  $\tau_{\text{terminal}}$ , where  $\tau_{\text{terminal}}$  scales as  $\tau_{\text{terminal}} \sim \tau_X \cdot N_P^2$ .<sup>31</sup>  
17 Thus, for small  $N_P$ , the terminal flow occurs immediately after the transient bond breaking and  
18 the Maxwell type rheological response is obtained. In the case of the dual crosslink systems,  
19 the terminal flow is suppressed by the permanent chemical crosslinks, thus the dynamics of the  
20 gels with a small number of transient crosslinks can be measured and studied.

## 5. Conclusions

In this paper, the dynamics of the PVA-borax dual crosslink hydrogels as a function of the chemical and physical crosslinker concentrations were studied. The constitutive theory which predicts the stress-strain behaviors in both tensile and torsion tests, was used to determine a set of four reduced parameters fitting both tests. The validity of the theory for the PVA dual crosslink gels at various crosslinking ratios was confirmed. To systematically describe the network dynamics and to provide molecular interpretation of the model parameters, we discussed the crosslinkers concentration dependences of the elastic modulus, the characteristic relaxation time and its distribution.

Evidently the main contribution of the transient crosslinkers is the time-dependent elastic population having the elastic modulus of  $\mu\bar{\gamma}_{\infty} \frac{t_B}{2-\alpha_B}$ , with a large dissipation. With increasing crosslinker concentration, this modulus increases. Besides this transient population of the elasticity which was expected, we found a second population of longer lived elastically active chains, measured as part of the low frequency modulus,  $\mu\rho$ , but higher than the modulus of the corresponding chemical gel. This additional long live population of crosslinks increases with transient crosslinker concentration and had not been previously identified for the PVA dual crosslink gel. We speculate that these long live crosslinks are due to clustering of mobile transient crosslinkers which can bind to any part of the chain. This result suggests that the dissipative properties of the dual crosslink gels do not proportionally increase with the transient crosslinker concentrations, and formation of such slower population needs to be considered.

It is noteworthy that the concentration of transient crosslinks can influence the relaxation time. We found that the network relaxation time  $\tau_X$  obtained from the peak of  $G''$  increases with decreasing borax concentration. This crosslinker concentration dependence was interpreted to

1 be a consequence of an imperfect relaxation of the subchain due to bond reassociation faster  
2 than the chain relaxation: before full relaxation of a chain, multiple transient crosslink breaking  
3 and healing occur, increasing the apparent relaxation time  $\tau_x$ . The average length of the  
4 subchain between two physical crosslinks is thus a parameter as it determines the Rouse  
5 relaxation time.

6 The scaling analysis with eq.16i,iii,iv suggests that the network relaxation time is inversely  
7 proportional to the concentration of the elastically active crosslinks and to the square root of  
8 the concentration of available binding sites. The studied dual crosslink gels have plenty of  
9 binding sites for the mobile transient crosslinkers on the chains, and at the studied conditions  
10 where the binding is far below the saturation, the binding site concentration remains high. This  
11 results in a fast bond healing time and very low open transient crosslinker concentration. Thus  
12 the dynamics are governed by the change in the total active crosslinker concentration, or by the  
13 Rouse relaxation time.

14 Networks with less binding sites in fixed positions along the chain can be developed, by  
15 copolymerizing monomers with and without ligand, for example. Such networks have a lower  
16 binding site concentration and saturation can be easily achieved. Close to the saturation the  
17 available binding site concentration decreases and concentration of open crosslinks and the  
18 bond healing time would increase, resulting in crosslinking ratio dependences of the network  
19 dynamics different from the current system. Systematic comparative studies are necessary for  
20 complete understanding.

21 The distribution of the apparent relaxation times, expressed in the theory as the exponent  $\alpha_B$ ,  
22 corresponds to the distribution of the Rouse relaxation time. We showed that the exponent  $\alpha_B$   
23 is a function of the number of the relaxation modes on a permanent chain having transient  
24 crosslinks, expressed as the ratio of the high frequency modulus and the low frequency modulus,

1  $N_P = \left( \mu \bar{\gamma}_\infty \cdot \frac{t_B}{2 - \alpha_B} \right) / \mu \rho = [G'(\omega \rightarrow \infty) - G'(\omega \rightarrow 0)] / G'(\omega \rightarrow 0)$ . We believe that the simple  
2 relation between  $\alpha_B$  and  $N_P$  expressed by eq.17 also proves that the Rouse dynamics of the  
3 subchains determine the network relaxation. This result suggests also that the number of the  
4 fitting parameter of the constitutive model can be reduced to three, as  $\alpha_B$  is a function of the  
5 other three parameters.

6

## 7 **Supporting Information**

8 Derivation of Equation 11. Fitting curves for tensile and torsion tests for all the dual crosslink  
9 gels tested in this work.

10

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15

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7 of the volume of the solution to that of the chemical gel is 20 and the gel volume was kept constant,  
8 thus borate ion can be concentrated in the gel and  $C_{\text{closed}}$  can be larger than  $C_{\text{borax}}$ , up to about 20  
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18 by intrachain crosslink, interchain crosslinking should become favored. Thus the ratio of interchain  
19 crosslinks to intrachain crosslinks,  $R_{\text{inter/intra}}$ , scales with the blob size  $\xi$  as  $R_{\text{inter/intra}} \approx \xi_1/\xi$ . Since  $\xi$   
20 varies with the polymer concentration  $C$  as  $\xi \sim C^{-5/4}$ , we have  $R_{\text{inter/intra}} \approx (C/C_1)^{5/4}$ . Pezron et al.  
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12 healing rate constant. The binding constant  $K_2$  ( $M^{-1}$ ) is equivalent to the ratio of the healing rate  
13 constant to the breaking rate constant,  $K_2 = \frac{k_{\text{heal}}}{k_{\text{break}}}$ . Since we can define the breaking time  $t_B$  as  
14  $t_b = \frac{1}{k_B}$ , and the healing time  $t_H$  as  $t_H = \frac{1}{k_H \cdot C_{\text{site}}}$ , we have  $\frac{t_B}{t_H} = \frac{k_H \cdot C_{\text{site}}}{k_B} = K_2 \cdot C_{\text{site}} = \frac{C_{\text{di}}}{C_{\text{open}}}$ .
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