



Title	Creep Behavior and Delayed Fracture of Tough Polyampholyte Hydrogels by Tensile Test
Author(s)	Karobi, Sadia Nazneen; Sun, Tao Lin; Kurokawa, Takayuki; Luo, Feng; Nakajima, Tasuku; Nonoyama, Takayuki; Gong, Jian Ping
Citation	Macromolecules, 49(15), 5630-5636 <a href="https://doi.org/10.1021/acs.macromol.6b01016">https://doi.org/10.1021/acs.macromol.6b01016</a>
Issue Date	2016-08-09
Doc URL	<a href="http://hdl.handle.net/2115/66863">http://hdl.handle.net/2115/66863</a>
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Macromolecules, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see <a href="http://pubs.acs.org/doi/abs/10.1021/acs.macromol.6b01016">http://pubs.acs.org/doi/abs/10.1021/acs.macromol.6b01016</a> .
Type	article (author version)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	Manuscript-sun-macromolecules.pdf



[Instructions for use](#)

# Creep Behavior and Delayed Fracture of Tough Polyampholyte Hydrogels

## by Tensile Test

Sadia Nazneen Karobi<sup>1,+</sup>, Tao Lin Sun<sup>2,3,+</sup>, Takayuki Kurokawa<sup>2,3</sup>, Feng Luo<sup>2</sup>, Tasuku Nakajima<sup>2,3</sup>, Takayuki Nonoyama<sup>2,3</sup>, Jian Ping Gong<sup>2,3\*</sup>

<sup>1</sup>Graduate School of Life Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>2</sup>Faculty of Advanced Life Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>3</sup>Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan

\*E-mail: [gong@mail.sci.hokudai.ac.jp](mailto:gong@mail.sci.hokudai.ac.jp)

+ The two authors are equally contributed.

### Abstract

Polyampholyte (PA) hydrogels are a new class of tough and self-healing supramolecular hydrogels that have a potential as load-bearing soft materials. Studying on the creep behavior of these hydrogels and understanding the molecular mechanism are important for prediction of life time of the materials. In the present work, we study the creep rupture dynamics of the PA hydrogels with and without chemical cross-linking, in certain observation time window. We have found that, above some critical loading stress both physical and lightly chemically crosslinked hydrogels undergo creep rupture while moderately chemically crosslinked hydrogel resists creep flow. To elucidate the molecular mechanism, we have further compared the creep behaviors of the physical and lightly chemically crosslinked samples. The creep rate of the samples decreases with the creep time, following a power law relation, regardless of the loading stress variation. The fracture time of both of these hydrogels exponentially decreases with the increase of the loading stress, following the same master curve at high loading stress region, while the behavior of

the two samples becomes different in the low loading stress region. We have explained the delayed fracture dynamics at high loading stress region in terms of relatively weak strong bond rupture mechanism.

## **1. Introduction**

Load-bearing soft materials are necessary not only for tissue engineering but also for different bio-medical applications, drug delivery systems etc.<sup>1,2</sup> Hydrogels, three-dimensional networks composed of crosslinked macromolecules and abundant water, belong to soft & wet material. Based on some similarities to biological tissues, for example their soft and hydrated form, hydrogels have drawn a great attention as synthetic equivalents for use in biological systems. However, the scope of hydrogel applications is often severely limited by their mechanical weakness and brittleness. Invention of the tough double network hydrogel and revealing of its toughening mechanism have found a general solution to develop tough hydrogels, that is, to introduce into the hydrogels sacrificial bonds that rupture during sample deformation.<sup>3-5</sup> The sacrificial bonds effectively dissipate energy and impart toughness of the hydrogels. Based on this sacrificial bonds mechanism, many tough hydrogel materials as well as elastomers have been fabricated using either chemical bonds,<sup>6-8</sup> or physical bonds, such as ionic bonds,<sup>9-11</sup> hydrogen bonds,<sup>12</sup> hydrophobic bonds.<sup>13-15</sup> The hydrogels with physical sacrificial bonds have shown multifarious unique properties like fatigue resistance, shape-memory effect, shock absorption capability, self-healing and self-recovery, along with the high toughness.<sup>10-13,15</sup> For the real application of various tough hydrogels as potential load-bearing soft materials, it is essential to know the long term time-dependent mechanical behavior of the materials.

Systematic study on the creep behaviors of the hydrogels under a constant load is one of the most essential approaches for the understanding of the fracture mechanism and prediction of life time of the materials. In our present article, we study creep rupture dynamics of tough and self-healing polyampholyte (PA) hydrogels recently developed.<sup>10,16</sup> Such PA hydrogels were synthesized from radical copolymerization of oppositely charged ionic monomers around zero-net charge composition at very high concentration without or with a slight chemical cross-linking. For example, the P(NaSS-*co*-MPTC) physical hydrogels, copolymerized from 2.1 M total monomers solution of sodium *p*-styrenesulfonate (NaSS) and 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC), exhibit high strength (tensile fracture stress  $\sigma_b = 1.8$  MPa), high extensibility (tensile fracture strain  $\epsilon_b = 7.4$ ), and high toughness (tearing energies  $T = 4000$  J/m<sup>2</sup>).<sup>10</sup> These values are ranked among the highest level of soft materials, either synthetic such as tough DN hydrogels, filled rubbers, or natural, such as cartilages.<sup>17</sup>

The excellent mechanical performances of the PA hydrogels are the results of formation of multiple ionic bonds, both inter- and intra-chains, whereupon the topological entanglement and/or chemical cross-linking of the polymer chains substantially stabilize the ionic bonding.<sup>10,16</sup> Owing to the random distribution, the ionic bonds have a wide range of bond strength. The strong bonds work as permanent cross-linker, imparting the elasticity of the hydrogel. The weak bonds are fragile and they break under stress, serving as reversible sacrificial bonds. Upon rupture of the weak bonds, the globule polymer chain becomes unfolded, serving as hidden length.<sup>18</sup> These two processes dissipate energy and impart toughness to the hydrogel, in analogy to that of bone toughening in which Ca<sup>2+</sup> ion rupture

and protein unfolding dissipate energy.<sup>19</sup> Due to the dynamic nature of the ionic bonds, the PA hydrogels are strongly viscoelastic, exhibiting a broad dynamic mechanical spectra.<sup>10</sup>

In this study, we study the creep behaviors of the PA hydrogels using P(NaSS-*co*-MPTC) gels as a model system by tensile test. Both physical PA gel without any chemical cross-linking (denoted as p-PA gel) and chemical PA gel that is slightly crosslinked by chemical cross-linker (denoted as c-PA gel) are used. The chemical cross-linking is expected to prevent the flow of the polymer chains and thus to delay the rupture of the PA hydrogels. To the authors' knowledge, most of the creep experiments have been performed on mechanically weak hydrogels by shearing test using rheometer or compression test.<sup>20-22</sup> The high toughness of the PA hydrogels permits us to study on the creep behavior of the material by tensile test. We believe that, this investigation will help for designing long-term load bearing soft materials for tissue engineering and different bio-medical applications.

## **2. Experimental**

### ***2.1 Materials***

Commercially available anionic monomer, sodium *p*-styrenesulfonate (NaSS); cationic monomer, 3-(methacryloylamino)propyl-trimethylammonium chloride (MPTC); cross-linker, N,N'-methylenebis(acrylamide) (MBAA); UV initiator,  $\alpha$ -ketoglutaric acid, were all purchased from Wako Pure Chemical Industries, Ltd. and used as received. Millipore de-ionized water is used in all of the experiments.

### ***2.2 Synthesis of PA hydrogels***

PA hydrogels were synthesized by free radical random co-polymerization from precursor aqueous solution containing total ionic monomer concentration  $C_m$  ( $=[\text{NaSS}] + [\text{MPTC}]$ ) of 2.3 M with the mole fraction of anionic monomer  $f$  ( $=[\text{NaSS}]/C_m$ ) of 0.52, according to the method described in our previous reports.<sup>10</sup> 0.1 mol%  $\alpha$ -ketoglutaric acid (in relative to  $C_m$ ) as the initiator, 0, 0.01 and 0.1 mol% MBAA as the chemical cross-linker were added in the solution for the polymerization. For simplicity, physical gel without chemical cross-linker is denoted as p-PA gel, and chemical crosslinked gels with 0.01 and 0.1 mol% MBAA are denoted as c-PA1 and c-PA2, respectively. The polymerization was carried out in argon atmosphere in which the oxygen concentration was less than 0.1 ppm by irradiating with 365 nm UV light (light intensity  $\sim 4 \text{ mW/cm}^2$ ) from both sides for 8 hours. The reaction cell was made by two parallel glass plates (10 cm $\times$ 10 cm) separated by a 1.5 mm thick silicone spacer. After polymerization, the hydrogels were immersed in a large amount of water for 1 week to reach equilibrium, and the water was changed every day. During this process, the hydrogels shrank due to the formation of ion bonds between the opposite charges on the polymer and their mobile counter ions were dialyzed from the hydrogels. After reaching the equilibrium state in water, the hydrogels thickness changed from 1.5 mm in the as-prepared state to 1.38-1.43 mm in water, depending on the cross-linker concentration.

## ***2.3 Characterization of hydrogels***

### ***2.3.1 Water content measurement***

The water content of the samples was measured using the moisture balance (Moisture balance; MOC-120H, SHIMADZU Co.), where the weight change of samples was monitored during the drying process. Water was gradually evaporated from the hydrogel at an elevated temperature from 30 to 120 °C until the weight change of samples no longer change. Water content  $C$  (wt%) is defined as the ratio percentage between the weight of water in gel to the total weight of the gel.

### ***2.3.2 Tensile test***

The tensile test was carried out on dumbbell-shaped samples with the standard JIS-K6251-7 size (12 mm in gauge length ( $L_0$ )  $\times$  2 mm in width ( $w$ )) using a commercial tensile tester (Tensilon RTC-1310A, Orientec Co.). The tensile deformation was performed at a stretch velocity  $v = 200$  mm/min, which gives the stretch rate  $\dot{\epsilon} = v/L_0$  of  $0.28 \text{ s}^{-1}$ . The nominal stress  $\sigma$  was estimated from the stretch force divided by the cross-section area of the un-deformed sample. The strain  $\epsilon$  was estimated from the clamp displacement divided by  $L_0$ . The deformation ratio  $\lambda$  was obtained from the ratio of stretching length  $L = L_0 + vt$  and the initial length  $L_0$ , where  $t$  is the stretching time. The yield stress was obtained at which the tangent modulus  $d\sigma/d\epsilon$  changes at the greatest rate with respect to the increasing strain. To prevent the water evaporating from hydrogels, all of the measurements were performed in a water bath made from a transparent box at about 25 °C except specified.

### ***2.3.3 Creep and creep recovery tests***

The creep test was carried out on dumbbell-shaped samples using with the dimensions of  $L$ -8 mm,  $w$ -2 mm by using the tensile mode of a commercial tensile tester (Shimadzu Tensile Tester). The cut sample was adjusted between the clamps by using both-sided adhesive tape to prevent from the sample slippage. The initial distance  $L_0$  between the two clamps of the tester was 6 mm. The sample experienced a jump of tensile stress  $\sigma_0$ , and the stress was held a constant for 36 hours except the sample failure occurred before 36 h. Here,  $\sigma_0$  is the nominal stress calculated from the stretch force divided by the cross-section area of the un-deformed sample. A short loading time before reaching  $\sigma_0$  should be performed so that the influence of loading history on the creep behavior of the gel can be minimized. We have confirmed that the loading strain rate from 0.01 to 1.0  $s^{-1}$  at the early stage of the experiment has little influence on the subsequent creep behavior (Figure S1). Therefore, for all the creep experimental, a given strain rate of 0.28  $s^{-1}$  was performed before reaching a described  $\sigma_0$ .

The clamp displacement was recorded with a sampling interval of 1 sec, 5 sec, and 10 min; consequently, the time profile of the nominal strain  $\varepsilon_c$  that is estimated from the clamp displacement divided by  $L_0$  was recorded. The failure time  $t_f$  and failure strain  $\varepsilon_f$  at which the onset of the macroscopic crack start to grow was recorded. The strain rate,  $\dot{\varepsilon}_c = d\varepsilon_c/dt$ , was calculated from strain-time curves. To reduce the noise of strain rate, the strain-time curves were smoothed based on Savitzky-Golay filter method in the origin 9.0 software before calculating the strain rate, where 10 ~ 2000 data points were used for getting the smoothing curve for the differentiation of each data point. To prevent the water evaporating

from hydrogels, all of the measurements were performed in a plastic box connecting with a humidity control system (~ 95 % humidity) during the entire course of the experiment.

Creep recovery test were conducted by applying a constant stress  $\sigma_0$  (= 0.1 MPa) to a sample for a fixed time (3 hours or 10 hours), and then the stress was removed to allow the sample to recover at a zero stress for a fixed time period (4 hours). The strain evolution was continuously monitored during the recovery process.

### **3. Results**

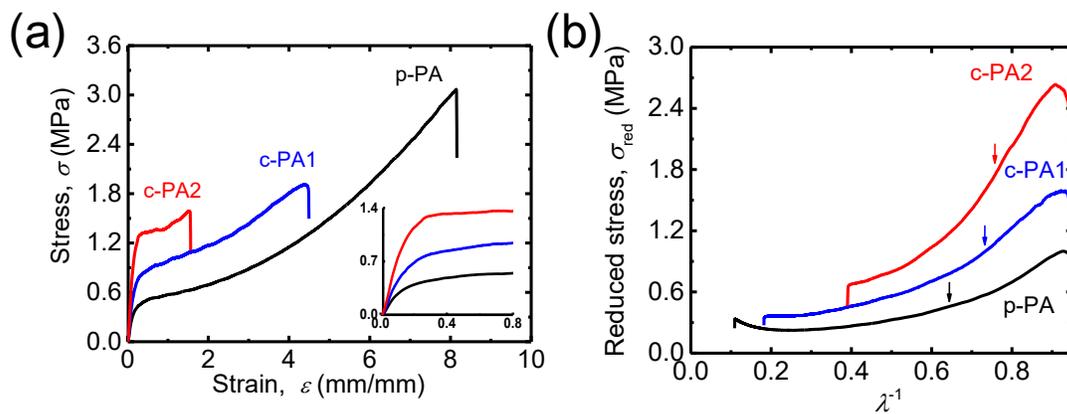
#### **3.1 Tensile behaviors of the PA hydrogels**

PA hydrogels are a unique system with randomly dispersed cationic and anionic repeat groups on the polymers, and these opposite charges form ionic bonds of a wide distribution of strength through inter-chain and intra-chain complexation.<sup>10,18</sup> The inter-chain ionic bonding serves as physical cross-linking to increase the modulus of the hydrogels. Previous studies have shown that the mechanical toughness of the PA hydrogels is strongly dependent on the concentration of the precursor monomer solution for the polymerization. When the concentration was higher than 1.5 M, very tough physical PA gels were formed, even without any chemical crosslinking. At such high concentration, the polymers formed are topological entangled, which favors inter-chain complexation. Presence of a small amount of chemical cross-linker stabilizes the ionic bonds formation, as revealed by the substantial increase of the stiffness and the yield stress but the decrease of fracture stress and extensibility of the sample.<sup>23</sup> **Figure 1a** shows the tensile behavior of polyampholyte

hydrogels with different amount of chemical cross-linker density, denoted as p-PA (0 %), c-PA1 (0.01 mol%), and c-PA2 (0.1 mol%), at a stretching strain rate of  $0.28 \text{ s}^{-1}$ . The corresponding physical properties of PA gels are summarized in **Table 1**. All of the three samples show almost the same water content, independent of the chemical cross-linker density. However, the stiffness and yielding stress substantially increase but the extensibility of the samples decreases with the chemical cross-linker density when compared at the same strain rate. To find the role of chemical cross-linker on the chain extensibility of PA gels, Mooney-Rivlin plot of the stress-strain data ( $\sigma$  vs.  $\epsilon$ ), in which the reduced stress,  $\sigma_{red} = \sigma/(\lambda-\lambda^{-2})$ , is plotted against the stretching ratio,  $\lambda=\epsilon+1$ , is shown in **Figure 1b**. At small stretching ratio, the reduced stress shows a high peak value. The chemically crosslinked c-PA1 gel and c-PA2 gel show much higher peak of reduced stress than that of the physical p-PA gel, which clearly shows that the shear modulus at small stretching is enhanced by chemical cross-linking. At the observing strain rate of  $0.28 \text{ s}^{-1}$ , all of the samples exhibit substantial strain softening even before yielding, indicating that the rupture of weak bonds that have very short association time in comparison with the inverse of the strain rate has already occurred before the yield point. However, only the p-PA gel, which has a much large deformability, shows a slight strain hardening at large stretching ratio. Considering the flexible nature of the polyampholyte chains, the strain-hardening might be ascribed to the finite extensibility effect of the chains bridged by the ionic bonds. However, as the PA gels have complicated meso-scale structure, other molecular mechanisms may not be excluded.<sup>24,25</sup> It should be noticed that the tensile behaviors of the PA gels strongly depends on the loading strain rate.<sup>18</sup>

**Table 1** Water content and mechanical properties of polyampholyte hydrogels measured by tensile test at a strain rate of  $0.28\text{s}^{-1}$ .

Sample	Cross-linker (mol%)	Water content (wt%)	Peak of reduced stress (MPa)	Yielding stress (MPa)	Fracture strain	Fracture stress (MPa)
p-PA	0	$51\pm 1$	1.0	0.51	8.14	3.06
c-PA1	0.01	$57\pm 2$	1.6	0.81	4.39	1.91
c-PA2	0.1	$62\pm 4$	2.6	1.30	1.54	1.59

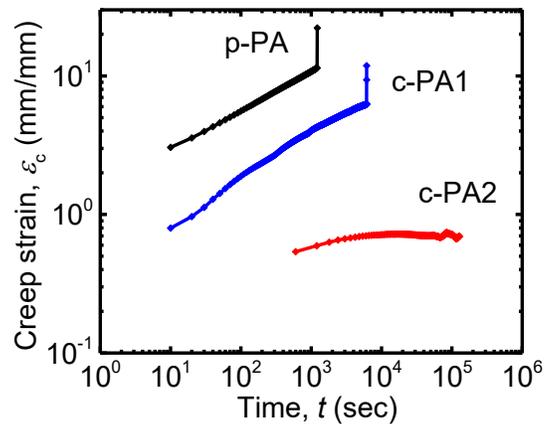


**Figure 1** (a) Comparison of tensile stress-strain curves of p-PA gel, c-PA1 and c-PA2 gel; (b) Mooney-Rivlin plot of the stress-strain curves. The arrows correspond to the yielding points of samples determined from (a). The inset in (a) is the amplified stress-strain behavior at small deformation.

### 3.2 Creep deformation behavior of PA hydrogels

As the chain mobility strongly depends on the molecular structure (the strength of ionic bonds, the trapped entanglements, and the chemical cross-linking density) and the external stimulation (loading stress), we study the effect of step loading stress on the creep behavior of polyampholyte hydrogels with and without chemical cross-linking.

### 3.2.1 Effect of chemical cross-linkers

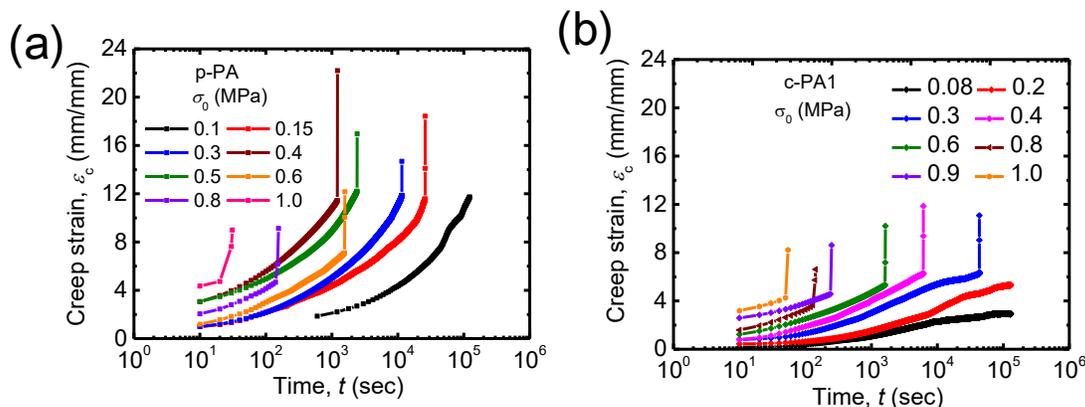


**Figure 2.** Log-log plot of creep strain  $\varepsilon_c$  and creep time  $t$  of p-PA gel, c-PA1, and c-PA2 gel under a constant step stress  $\sigma_0$  ( $= 0.4$  MPa).

**Figure 2** shows the creep deformation behaviors of polyampholyte hydrogels for p-PA, c-PA1 gel, and PA2 gel under a constant step stress  $\sigma_0$  ( $= 0.4$  MPa). For tracking the nominal strain for the creep process, we reset the recorded time at the beginning of creep process to 0. For the p-PA gel, the creep strain  $\varepsilon_c$  slowly grows with time  $t$  at first, and then at a well-defined time  $t_f$ , it suddenly accelerates. This time  $t_f$  corresponds to the starting of the macroscopic crack growth and is named as the failure time. The corresponding strain at

failure is denoted as  $\varepsilon_f$ . Addition of a small amount of chemical cross-linker (0.01 mol%) in c-PA1 gel suppresses the growth of creep strain, and delays the fracture. As a result, the c-PA1 gel shows a smaller failure strain  $\varepsilon_f$  and a longer failure time  $t_f$  than those of the p-PA gel. Increase of the chemical cross-linker to 0.1 mol% remarkably prevents the creep. In fact, the sample c-PA2 shows negligible creep in the observation time window. Thus, 0.1 mol% chemical cross-linking not only prevents the creep flow but also stabilizes the ion bonds to delay the creep at a moderate stress level. These results indicate that the substantial creep of the PA gels is due to the breaking of the ionic bonds of inter-chains, and not due to the breaking of the covalent bonds of the polymer chain. From the practical point of view, certain amount of chemical cross-linking is required to improve the long-term performance of the PA hydrogels.

### 3.2.2 Effect of step loading stress



**Figure 3** Creep deformation  $\varepsilon_c$  vs. time  $t$  of p-PA gel (a) and c-PA1 gel (b) with various step loading stress  $\sigma_0$ . The abrupt increase of the creep strain corresponds to the sample

rupture. The p-PA gel does not fracture at  $\sigma_0 = 0.1$  MPa while the c-PA1 gel does not rupture at  $\sigma_0 = 0.08$  MPa and 0.2 MPa in the observation time window of 36 h.

As the c-PA2 sample shows negligible creep under a loading stress  $\sigma_0 = 0.4$  MPa, we further focus on the creep of p-PA and c-PA1 samples under varied stress  $\sigma_0$ , as shown in **Figure 3a** and **3b**, respectively. The creep deformation behavior strongly depends on the loading stress. Both the p-PA gel and the c-PA1 gel show a critical stress below which no failure occurs in the observation time window of 36 h. The c-PA1 gel has a higher critical stress (0.2 MPa) than that of the p-PA gel (0.1 MPa). For a better comparison, the loading stress dependences of failure time and failure strain for the two samples are summarized in **Figure 4a** and **Figure 4b**, respectively.

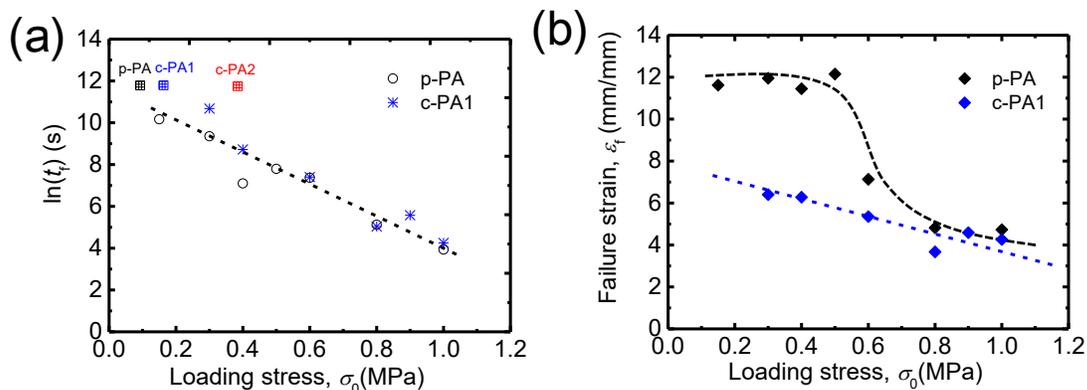
It has been found that the correlation between the failure time and the loading stress for some soft glassy systems follows a power-law relation, known as Basquin's law.<sup>26,27</sup> On the other hand, for some gel systems the failure time follows an exponential relation with the loading stress.<sup>22,28,29</sup> Comparing with the power-law relation, as shown in **Figure S2**, the exponential relation gives a better fitting to our results. As shown in **Figure 4a**, the logarithm of the failure time is observed to decrease linearly with increase of loading stress. This indicates that the creep rupture of PA system is governed by the thermally activated process with an energy barrier related to the breaking of ionic bonds that provide the cross-linking in the network structure.<sup>22,28,29</sup> **Figure 4a** shows that the two gels follow the same master curve for the loading stress above 0.4 MPa. This result indicates that the ionic bonds responsible for the creep in this stress range have the same bond strength, independent of

the chemical cross-linking. This master curve is not hold for small stress region. In fact, as shown in **Figure 3**, no creep failure occurs below the critical loading stress (0.1 MPa and 0.2 MPa for p-PA and c-PA1, respectively) in observation time window of 36 h. If we plot these data at 36 h in **Figure 4a**, one can argue that for a loading stress below the critical value, if the samples also rupture at a longer time than 36 h, the failure time will not fall on the same master line for the large stress region, but will follow another line with a steeper slope. Furthermore, the chemically crosslinked c-PA samples might have a steeper slope than that of the p-PA sample in the low loading stress region. The two distinct exponential regimes of delayed fracture time with applied stress was previously observed in colloid system and have been explained by heterogeneous and multiscale structure.<sup>22,28,29</sup> So the deviation of the data from the single master curve at low stress range also suggests the heterogeneous structure of the PA gels.

Both samples show decreasing tendency in failure strain with increasing loading stress (**Figure 4b**). At small loading stress from 0.15 to 0.5 MPa, the p-PA gel shows a plateau of failure strain  $\epsilon_f$ , much larger than that of the c-PA1 gel. At high loading stress from 0.8 to 1.0 MPa, the failure strains of the two samples overlap. These results are roughly in consistent with the stress dependence of the failure time.

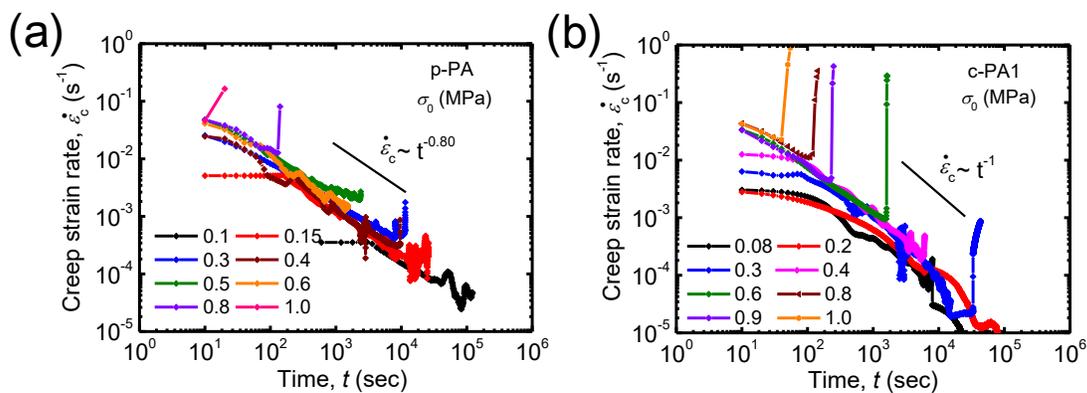
It is attempting to correlate the different creep behaviors between at small and at large loading stress (**Figure 4**) with the yielding stress of the tensile data (**Figure 1a**). However, the tensile curve and the yielding stress of the samples are strongly dependent on the strain

rate, which makes it difficult to compare the loading stress with the yielding stress since the creep occurs at very different strain rate.



**Figure 4.** Loading stress  $\sigma_0$  dependences of failure time  $t_f$  (a) and failure strain  $\epsilon_f$  (b) of the creep test. The square lattice symbols in **Figure 4a** stand for the samples that do not fracture in the observation time window of 36 h.

### 3.3. Origin of the delayed fracture in PA hydrogels

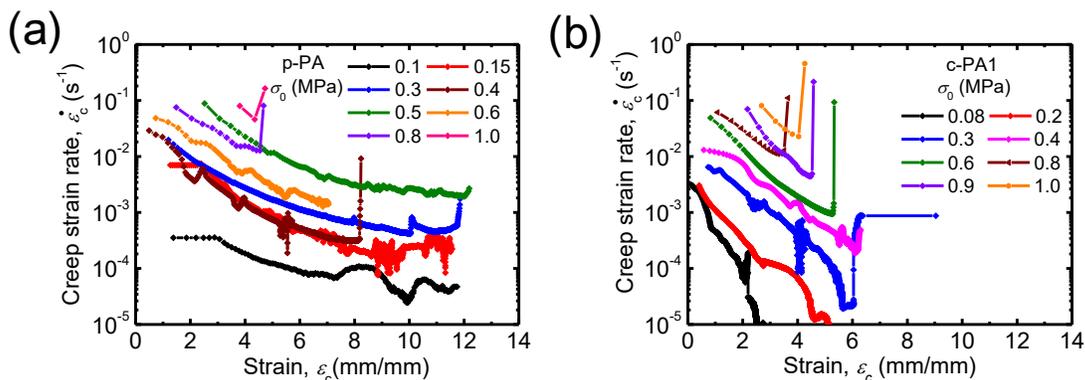


**Figure 5** The creep strain rate with respect to time at various loading stress  $\sigma_0$  for p-PA gel (a) and c-PA1 gel (b).

Commonly, a fracture is interpreted as a phenomenon occurring when bonds are loaded with a force greater than they can bear: bonds then break one after another.<sup>30</sup> For the delayed fracture, it can be understood by the thermally activated process.<sup>22,28,29</sup> The applied stress lowers the activation energy barrier of bond breakage, increases the bond dissociation rate and consequently, and facilitates nucleation and subcritical growth of micro-cracks.<sup>30</sup> The comparison of strain rate of physical and chemical gels gives us important information on the molecular origin of delayed fracture in the PA gels.

**Figure 5** shows the logarithmic plots of strain rate,  $\dot{\epsilon}_c = d\epsilon_c/dt$ , with respect to creep time,  $t$ , for p-PA gel and c-PA1 gel. Although the creep strain increases with time, the strain rate decreases with time for both samples. Under the same loading stress, p-PA gel shows the higher creep strain rate than that of c-PA1 gel, suggesting that the slight chemical cross-linking of the gel not only enhances the density of the physical cross-linking but also substantially influence the ionic bond strength which determines the creep dynamics of the hydrogels. Similar to the Andrade creep law at the primary regime,<sup>31</sup> both two samples show that, the creep strain rate follows a master curve with the negative power law relation to time,  $\dot{\epsilon}_c \sim t^\alpha$  for different loading stress. The p-PA gel ( $\alpha \sim -0.72$ ,  $R=0.97$ ) exhibits a smaller exponent value than that of the c-PA1 gel ( $\alpha \sim -1.1$ ,  $R=0.90$ ), indicating that slight chemical cross-linking has some effect to retard the creep. The power law exponent -0.72 in

p-PA gel is the same as the observation in bio-hydrogels that are also physically cross-linked hydrogel system.<sup>26</sup>

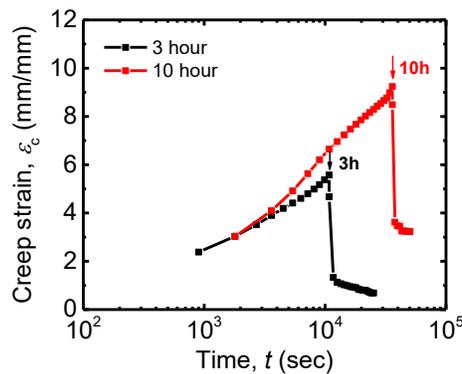


**Figure 6.** Creep strain rate with respect to creep strain at various loading stress  $\sigma_0$  for p-PA gel (a) and c-PA1 gel (b).

The decreasing in the creep strain rate with time might stem from the strain hardening effect. To discuss this possibility, the creep strain rate,  $d\epsilon_c/dt$ , is plotted in respect to creep strain,  $\epsilon_c$ , for various loading stress, as shown in **Figure 6**. Very different behaviors are observed for p-PA gel and c-PA1 gel. In the case of p-PA gel, the creep strain rate decreases with the increasing of creep strain at first, and then approaches to steady values before fracture, for data performed at relatively small loading stress. The former can be understood by the increase in the strain hardening effect of polymer chains, while the latter can be understood as their chain slippage at a steady velocity, before the fracture. This may explain why a plateau of fracture strain is observed at small stress (**Figure 4b**). On the other hand, the c-PA1 gel shows a more rapid decrease in the strain rate with the increase of the creep strain and the sample breaks abruptly without showing plateau region of strain rate.

These results indicate that the additional chemical cross-linking enhances the strain hardening effect and the constraints of chemical cross-linking prevent the chain from slippage or flow.

### 3.4 Creep recovery behavior



**Figure 7** Creep recovery test of p-PA gel. After a creep time of 3 hours or 10 hours (indicated by arrows) by a tensile stress  $\sigma_0 = 0.1$  MPa, the stress was removed and the sample was allowed to relax for 4 hours. Recovery in the deformation of the sample was observed. The un-overlapped parts at the two creep curves are due to the samples variabilities.

To study the role of reversible ionic bonds on the creep behavior of p-PA gels, creep recovery test was performed at a tensile stress  $\sigma_0 = 0.1$  MPa. **Figure 3** tells that at this stress, the sample did not show failure even for 36 h creep test. As shown in **Figure 7**, the strain increases with the creep time during the step loading region. However, once the load was removed, a large part of the strain decreased immediately, which was followed by a

gradual decrease of strain for a prolonged time. Comparing with the result of 3 hour creep that shows a tendency towards full recovery after 4 hours, the result of 10 hour creep shows a level off of strain around the 4 hours recovery time. This indicates that the creep deformation is due to the breaking of the ionic bonds, and the broken bonds at large creep strain do not reform (self-heal) with the bonds of the neighboring chains so that the corresponding creep deformation becomes elastic, while the bonds broken at small strain reform with bonds of the neighboring chains so that the corresponding creep deformation becomes viscoelastic. The result at 10 hour indicates that some permanent creep might exist for long creep time even before the macroscopic sample failures.

#### 4. Discussions

As the creep rupture of PA gel system is governed by the thermally activated process of the ionic bonds, the linear relation between the logarithm of the failure time,  $\ln t_f$ , and the loading stress,  $\sigma_0$ , shown in **Figure 4a** can be described by the Eyring theory,<sup>32</sup>

$$t_f = t_0 \exp \left( \frac{E_a - \sigma_0 V}{k_B T} \right) \quad (1)$$

Where,  $E_a$  is the activation energy for the transition from one state to another,  $V$  is the free volume and  $t_0$  is the characteristic time for chain segment motion. The  $E_a$  here can be interpreted as the dissociation energy of the multiple ionic bonds in hydrated environment, while the  $V$  is the volume of ionic bonds structure. By fitting the experimental data of **Figure 4a** using equation (1), one obtains  $V = 30.8 \text{ nm}^3$ . This free volume  $V$  is larger than those of the typical solid glassy polymer systems determined from the similar creep test.<sup>32</sup>

The characteristic length calculated from the free volume  $V$  is around 3.13 nm. This length can be understood as the size of the ionic bonds responsible for the creep in the observation condition. As the length of  $\sim 3$  nm is far larger than the monomer size of the polymer, it reflects the multiple bonds structure of the PA gels.

The extrapolation of the master curve to the zero loading stress in **Figure 4a** gives a fracture time  $t_{f,\sigma=0}$  ( $=1.7 \times 10^5$  s). The time thus obtained can be understood as the bond life time for the bonds that account for the creep of the master curve. This argument can be confirmed by comparing with the dynamic mechanical spectra of the sample. According to our previous work, the physical P(NaSS-co-MPTC) gel shows a  $\tan\delta$  minimum around the frequency  $\omega \sim 5 \times 10^{-6}$  Hz, which is the onset of the relaxation of the strong bonds.<sup>10</sup> This frequency is found to be well related to  $t_{f,\sigma=0}$  through the relation  $t_{f,\sigma=0} = 1/(2\pi\omega)$ . This suggests that the failure time of the creep test at relatively high loading stress is related to the relaxation of the strong bonds with life time in the order of  $\sim 10^5$  s.

As discussed in the previous section, below the critical loading stress, the failure time, if could be measured, will deviate from the straight line shown in **Figure 4a**, which suggests that the logarithm of the failure time at small loading stress region (below the critical loading stress) will follow another master curve that is located above the master curve observed in **Figure 4a**, and the master curve at small stress region might have a steeper slope than that of large loading stress region. Moreover, the c-PA1 sample might have a larger slope than that of the p-PA sample in the low loading stress region. According to the Eyring theory, such behaviors could be related to an associated structure with a longer life

time (higher activation energy) and larger free volume than that observed in the high loading stress region, that is, more strong ionic bonds with a larger characteristic structure.

These discussions tell that, the delayed fracture at large loading stress is governed by relatively weak strong bonds, having a life time of  $10^5$  s and a characteristic structure length scale of  $\sim 3$  nm. At small loading stress range, below the critical stress, the delayed fracture is dominated by more strong bonds, having a life time longer than  $10^5$  s, and is out of the observation time range of the current experiment. The p-PA gel and c-PA1 gel all follow the same master curve at high loading stress region, which gives the same activation energy  $E_a$  and free volume  $V$ . This indicates that the chemical cross-linking does not influence the relatively weak strong bonds. As a result, the p-PA gel and c-PA1 gel only show the creep difference in the small loading stress region, which is governed by the dynamics of strong bonds with very long life time. Systematic studies on the creep behavior at small loading stress are necessary in future.

It should be mentioned that the so-called weak bonds of the PA gels, having a bond exchange time in the order of seconds, as determined by the dynamic rheological measurement, do not contribute to the creep behaviors in the experimental window of this study.<sup>10</sup> They are expected to make contribution only at very high loading stress.

## **Conclusions**

The creep of PA gels under a stress of sub-MPa is observed. Addition of slight amount of chemical cross-linker (c-PA1, 0.01mol%) to the PA hydrogel only changes the creep behavior at small load stress while the creep can be prevented by moderate chemical cross-

linking (c-PA2, 0.1 mol%). The creep strain rate of the PA gels follows the power law relation with time,  $\dot{\varepsilon}_c \sim t^\alpha$ , independent of the loading stress. The exponent  $\alpha$  is -0.72 for the physical p-PA gel and -1.1 for the chemically crosslinked c-PA1 gel. The decrease of the creep strain rate with time is due to finite chain extensibility effect, which is more remarkable for the chemically crosslinked sample.

While the creep rupture time and strain at small stress region differs for physical PA gel and slightly crosslinked PA gel, the same creep rupture behavior is observed for the two gels at large stress region. Critical stresses, which depend on the chemical crosslinking, are observed for the creep rupture. The different creep rupture regimes with the applied stress reveal that the PA gels have heterogeneous, multi-scale structure, and chemical crosslinking only influences the strong bonds of large structure. At large stress region, the failure time decreases exponentially with the increase of the applied tensile stress, for both types of gels, indicating the thermally activated bond breaking mechanism. According to the Eyring theory, the life time and characteristic structure length of these bonds are estimated as  $\sim 10^5$  s and  $\sim 3$  nm, respectively. These bonds can be associated to the relatively strong ionic bonds discussed in our previous work.<sup>10</sup>

### **Supporting Information**

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Figure S1 shows the loading strain rate on the creep behavior of p-PA gels under a constant step stress  $\sigma_0$  (= 0.10 MPa)

Figure S2 shows log-log plot of the failure time vs loading stress for p-PA gel and c-PA1 gel.

### Acknowledgments

This research was financially supported by Grant-in-Aid for Scientific Research (S) (No. 124225006) from the Japan Society for the Promotion of Science (JSPS). This research was also funded by ImpACT Program of Council for Science, Technology and Innovation (Cabinet Office, Government of Japan).

### References

- (1) Moutos, F. T.; Freed, L. E.; Guilak, F. A biomimetic three-dimensional woven composite scaffold for functional tissue engineering of cartilage. *Nat. Mater.* **2007**, *6* (2), 162–167.
- (2) Drury, J. L.; Mooney, D. J. Hydrogels for tissue engineering: scaffold design variables and applications. *Biomaterials.* **2003**, *24* (24), 4337–4351.
- (3) Webber, R. E.; Creton, C.; Brown, H. R.; Gong, J. P. Large strain hysteresis and mullins effect of tough double-network hydrogels. *Macromolecules* **2007**, *40* (8), 2919–2927.
- (4) Tanaka, Y.; Kuwabara, R.; Na, Y.-H.; Kurokawa, T.; Gong, J. P.; Osada, Y. Determination of fracture energy of high strength double network hydrogels. *J. Phys. Chem. B* **2005**, *109* (23), 11559–11562.

- (5) Gong, J. P. Why are double network hydrogels so tough? *Soft Matter* **2010**, *6* (12), 2583-2590.
- (6) Nakajima, T.; Sato, H.; Zhao, Y.; Kawahara, S.; Kurokawa, T.; Sugahara, K.; Gong, J. P. A universal molecular stent method to toughen any hydrogels based on double network concept. *Adv. Funct. Mater.* **2012**, *22* (21), 4426–4432.
- (7) Ducrot, E.; Chen, Y.; Bulters, M.; Sijbesma, R. P.; Creton, C. Toughening elastomers with sacrificial bonds and watching them break. *Science* **2014**, *344* (6180), 186–189.
- (8) Hu, J.; Kurokawa, T.; Nakajima, T.; Sun, T. L.; Suekama, T.; Wu, Z. L.; Liang, S. M.; Gong, J. P. High fracture efficiency and stress concentration phenomenon for microgel-reinforced hydrogels based on double-network principle. *Macromolecules* **2012**, *45* (23), 9445–9451.
- (9) Mayumi, K.; Marcellan, A.; Ducouret, G.; Creton, C.; Narita, T. Stress-strain relationship of highly stretchable dual cross-link gels: separability of strain and time effect. *ACS Macro Lett.* **2013**, *2* (12), 1065–1068.
- (10) Sun, T. L.; Kurokawa, T.; Kuroda, S.; Ihsan, A. B.; Akasaki, T.; Sato, K.; Haque, M. A.; Nakajima, T.; Gong, J. P. Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity. *Nat. Mater.* **2013**, *12* (10), 932–937.
- (11) Sun, J.-Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. Highly stretchable and tough hydrogels. *Nature* **2012**, *489*

(7414), 133–136.

- (12) Guo, M.; Pitet, L. M.; Wyss, H. M.; Vos, M.; Dankers, P. Y. W.; Meijer, E. W. Tough stimuli-responsive supramolecular hydrogels with hydrogen-bonding network junctions. *J. Am. Chem. Soc.* **2014**, *136* (19), 6969–6977.
- (13) Haque, M. A.; Kurokawa, T.; Kamita, G.; Gong, J. P. Lamellar bilayers as reversible sacrificial bonds to toughen hydrogel: hysteresis, self-recovery, fatigue resistance, and crack blunting. *Macromolecules* **2011**, *44* (22), 8916–8924.
- (14) Jiang, G.; Liu, C.; Liu, X.; Zhang, G.; Yang, M.; Chen, Q.; Liu, F. Self-healing mechanism and mechanical behavior of hydrophobic association hydrogels with high mechanical strength. *J. Macromol. Sci. Part A* **2010**, *47* (4), 335–342.
- (15) Tuncaboylu, D. C.; Sari, M.; Oppermann, W.; Okay, O. Tough and self-healing hydrogels formed via hydrophobic interactions. *Macromolecules* **2011**, *44* (12), 4997–5005.
- (16) Ihsan, A. B.; Sun, T. L.; Kuroda, S.; Haque, M. A.; Kurokawa, T.; Nakajima, T.; Gong, J. P. A phase diagram of neutral polyampholyte - from solution to tough hydrogel. *J. Mater. Chem. B* **2013**, *1* (36), 4555–4562.
- (17) Naficy, S.; Brown, H. R.; Razal, J. M.; Spinks, G. M.; Whitten, P. G. Progress toward robust polymer hydrogels. *Aust. J. Chem.* **2011**, *64* (8) 1007–1025.
- (18) Sun, T. L.; Luo, F.; Kurokawa, T.; Karobi, S. N.; Nakajima, T.; Gong, J. P.

- Molecular structure of self-healing polyampholyte hydrogels analyzed from tensile behaviors. *Soft Matter* **2015**, *11*(48), 9355–9366.
- (19) Fantner, G. E.; Hassenkam, T.; Kindt, J. H.; Weaver, J. C.; Birkedal, H.; Pechenik, L.; Cutroni, J. A.; Cidade, G. A. G.; Stucky, G. D.; Morse, D. E.; Hansma, P. K. Sacrificial bonds and hidden length dissipate energy as mineralized fibrils separate during bone fracture. *Nat. Mater.* **2005**, *4* (8), 612–616.
- (20) Choi, J.; Bodugoz-Senturk, H.; Kung, H. J.; Malhi, A. S.; Muratoglu, O. K. Effects of solvent dehydration on creep resistance of poly(vinyl alcohol) hydrogel. *Biomaterials* **2007**, *28* (5), 772–780.
- (21) Skrzyszewska, P. J.; Sprakel, J.; de Wolf, F. A.; Fokkink, R.; Cohen Stuart, M. A.; van der Gucht, J. Fracture and self-healing in a well-defined self-assembled polymer network. *Macromolecules* **2010**, *43* (7), 3542–3548.
- (22) Sprakel, J.; Lindström, S. B.; Kodger, T. E.; Weitz, D. A. Stress enhancement in the delayed yielding of colloidal gels. *Phys. Rev. Lett.* **2011**, *106* (24), 248303.
- (23) Ihsan, A. B.; Sun, T. L.; Kurokawa, T.; Karobi, S. N.; Nakajima, T.; Nonoyama, T.; Roy, C. K.; Luo, F.; Gong, J. P. Self-healing behaviors of tough polyampholyte hydrogels. *Macromolecules* **2016**, *49* (11), 4245–4252.
- (24) Storm, C.; Pastore, J. J.; MacKintosh, F.; Lubensky, T.; Jamney, P. A. Nonlinear elasticity in biological gels. *Nature* **2005**, *435*(May), 191–194.

- (25) Carrillo, J.-M. Y.; MacKintosh, F. C.; Dobrynin, A. V. Nonlinear elasticity: from single chain to networks and gels. *Macromolecules* **2013**, *46* (9), 3679–3692.
- (26) Leocmach, M.; Perge, C.; Divoux, T.; Manneville, S. Creep and fracture of a protein gel under stress. *Phys. Rev. Lett.* **2014**, *113* (3), 038303.
- (27) Bauer, T.; Oberdisse, J.; Ramos, L. Collective rearrangement at the onset of flow of a polycrystalline hexagonal columnar phase. *Phys. Rev. Lett.* **2006**, *97* (25), 258303.
- (28) Brenner, T.; Matsukawa, S.; Nishinari, K.; Johannsson, R. Failure in a soft gel: delayed failure and the dynamic yield stress. *J. Nonnewton. Fluid Mech.* **2013**, *196*, 1–7.
- (29) Gibaud, T.; Frelat, D.; Manneville, S. Heterogeneous yielding dynamics of a colloidal gel. *Soft Matter* **2010**, *6* (15), 3482–3488.
- (30) Wang, X.; Hong, W. Delayed fracture in gels. *Soft Matter* **2012**, *8* (31), 8171–8178.
- (31) Nechad, H.; Helmstetter, A.; El Guerjouma, R.; Sornette, D. Creep ruptures in heterogeneous materials. *Phys. Rev. Lett.* **2005**, *94* (4), 045501.
- (32) Vanel, L.; Ciliberto, S.; Cortet, P.-P.; Santucci, S. Time-dependent rupture and slow crack growth: elastic and viscoplastic dynamics. *J. Phys. D. Appl. Phys.* **2009**, *42* (21), 214007.

## Table of Contents Graphic

### Creep Behavior and Delayed Fracture of Tough Polyampholyte Hydrogels

#### by Tensile Test

Sadia Nazneen Karobi<sup>1,+</sup>, Tao Lin Sun<sup>2,3,+</sup>, Takayuki Kurokawa<sup>2,3</sup>, Feng Luo<sup>2</sup>, Tasuku Nakajima<sup>2,3</sup>, Takayuki Nonoyama<sup>2,3</sup>, Jian Ping Gong<sup>2,3\*</sup>

<sup>1</sup>Graduate School of Life Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>2</sup>Faculty of Advanced Life Science, Hokkaido University, Sapporo 060-0810, Japan

<sup>3</sup>Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, Japan

\*E-mail: [gong@mail.sci.hokudai.ac.jp](mailto:gong@mail.sci.hokudai.ac.jp)

+ The two authors are equally contributed.

