Solvent and Ca^{2+} triggered robust and fast stress generation by ultrathin triple-network hydrogels

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ABSTRACT

Solvent-triggered isometric stress generation of an ultrathin and tough triple-network (TN) hydrogel was systematically studied as functions of the pre-strain and ethanol/water mixture solvent. The obtained results along with the solvent-induced changes in the volume and modulus of the hydrogel were further analyzed with emphasis on clarifying the stress generation mechanism of the TN gel. Ca^{2+}-triggered stress generation of the gel was also preliminarily explored. High stress generation of 0.4 MPa was obtained within tens of seconds at the low pre-strain of 25% by alternating water and ethanol. Both negative and positive stress generation of the gel were achieved just by changing the composition of the ethanol/water mixture solvent. Mechanism analysis indicates that, modulus change of the gel is the dominant reason for their solvent-triggered high and fast stress generation. In the case of the Ca^{2+}-triggered stress generation of the gel, it is also attributed to the modulus change induced by the physical cross-linking of Ca^{2+} between the negatively charged first network chains of the TN hydrogel.

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1. Introduction

In the past couple of decades, many researches in artificial-muscles have been performed, mainly focusing on the materials that are "strong and flexible", "smart responsive to stimuli", and "fast and high force output", mimicking the energy-conversion functions observed in natural muscles [1–4]. Polymer hydrogels, which are soft, wet, and show stimuli-response capability, have drawn great attention as artificial muscles since 1990s [5–14]. Actuation of polymer gels are usually based on the volume changes in response to a wide range of stimuli, such as light, temperature, pH, solvent, antibody–antigen interaction, and chemical oscillation [5–10]. Contraction, motion, and bending of polymer hydrogels driven by electric field provide alternative approaches to chemical ones for energy conversion [11–14]. However, most of the studies on artificial muscles based on hydrogels did not continue later on. This is because several obstacles associated with the extensive use of gel-based artificial muscles, could not be solved. Among them, the weak mechanical strength and slow response are the two main issues.

In the early 2000s, several approaches were invented to develop hydrogels with high strength and toughness [15–17]. These studies have dramatically changed the common understanding that a hydrogel was a mechanically weak material, and thus greatly promote the potential use of this material, especially as the load-bearing soft tissues such as artificial muscles. Among these works, double network (DN) principle offers bulk polymer hydrogels with mechanical strength (fracture stress $\sigma_b > 1$ MPa) and

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toughness (fractural energy $\sim 10^3$ J/m^2) as high as that of real cartilage [18].

Thus, the remaining main key issue is to address the slow response rate of those artificial-muscle systems based on bulk polymer gels. As the double network hydrogels, containing *c.a.* 90 wt% of water, are elastic materials when the deformation rate is not extremely fast, the isometric stress generation of these hydrogels is based on volume change driven by the environmental stimuli. Accordingly, the response kinetics of the gel is governed by the solvent diffusion, and the response time τ is related to the characteristic size of the specimen h and the collective diffusion constant D_c as [19]

$$\tau = h^2/(\pi^2 D_c). \tag{1}$$

Thus, one of the approaches to increase the response time is to use tough ultrathin film hydrogels and/or gel fibers. The D_c of a typical hydrogel is in the order of 10^{-10} m^2/s. So the response time of a gel film with 100 μm in thickness is in the order of 10 s.

However, it is a difficult task to synthesize thin and tough double network film hydrogels. Different from common interpenetrated network (IPN) polymer materials, the double network hydrogels that possess high strength and toughness have a contrasting network structure. The first network is rigid and brittle, and the second network is soft and highly stretchable. Because of this specific structure requirement, the first network is too brittle to manipulate with a decreased thickness during synthesis. We have developed a three-step polymerization method to synthesize the thin and tough film hydrogels with triple network (TN) structure based on the tough DN gel principle [20–22]. (This gel was called as DN gel in the cited literatures. Since virtually it has a triple network structure, we call it as TN gel in this paper.) Using this method, we have synthesized tough TN hydrogels with the thickness of 30 $\sim$ 100 μm. Under a certain pre-strain, these hydrogels could be triggered by ethanol, a poor solvent to PAAm network, and gave a high muscle-level stress output of 0.25 MPa with a response time of $\sim$10 s [20].

In this work, we present a systematic investigation on the isometric stress generation of an ultrathin film TN gel of 100 μm in thickness triggered by ethanol/water mixture solvent. From the changes in both the volume and Young's modulus, the stress generation mechanism of the gel is clarified. Human and animal muscles were featured as their ability to execute mechanical-related actions and energy conversion through Ca^{2+} signal-induced robust and fast contraction [23]. To mimic this mechanism, Ca^{2+} response of the system was also explored.

2. Results and discussion

The triple-network (TN) hydrogel used in this work consists of poly(2-acrylamido-2-methylpropane-sulfonic acid) (PAMPS) as the first network, polyacrylamide (PAAm) as the second and the third network. This strong and tough ultrathin TN hydrogel was prepared at the optimized conditions using the formulation shown in the caption of Fig. 1. The procedures to synthesize and optimize the structure of the sample are the same as reported [20]. The

final thickness of the TN hydrogel in water was 100 $\pm$ 10 μm and the water content was about 93 wt%.

The experimental setup for stress generation is shown in Fig. 1a. The setup involves a solution system which is applied to trigger the volume contraction or expansion of the gel, and a load cell which is used to measure the isometric contractile stress of the TN gel. The tensile stress–strain curve of the gel measured with a commercial test machine (Tensilon RT-1150A, Orientec Co.) is shown in Fig. 1b. Here the stress σ is defined as the tensile force F divided by the initial cross section area S_0 of the sample in water, $\sigma = F/S_0$, and the strain ε as the length change (L–L_0) in relative to the initial length L_0 in water, $\varepsilon = (L–L_0)/L_0$. L stands for the current length at tensile force F in various solvents.

The gel shows an yielding at about 300% strain in similarity to conventional DN hydrogels. Fig. 1c presents the cyclic changes in the isometric stress of the TN gel alternately triggered by water and EtOH under the pre-strain of 25%, 75%, and 250%. The initial stress (σ_0) of the TN gel in water increases rapidly with the increase of the applied pre-strain, in accordance with that presented by the part of the stress–strain curve before yielding (Fig. 1b). Reversible stress change of the TN gel in response to the solvent change is observed under all of the applied pre-strain. With the exchange of water to ethanol, the stress decreases first and then increases rapidly to an equilibrium value. The reverse process also shows similar response. Moreover, the increment amplitude from the initial stress plateau (σ_0) to the higher stress plateau (σ_p) decreases with increasing the applied pre-strain. Setting here σ_0 as the base line, the "contractile stress", $\Delta\sigma = \sigma_p - \sigma_0$, was calculated and shown in Fig. 1d as a function of the applied pre-strain. Nonlinear dependence of $\Delta\sigma$ on the pre-strain is observed. $\Delta\sigma$ decreases from 0.4 to 0.1 MPa with the increase of the pre-strain from ε_{pre} = 25% to 250%, implying a strong stress generation of the TN gel at low pre-strain. Our tensile hysteresis measurement on bulk DN gels has shown that the PAMPS network starts to rupture when the strain exceeds 50%, and fractures persistently with the increase of strain [24]. Therefore, the decrease of the contractile stress with the pre-strain should be attributed to the softening of the gel due to internal fracture of the PAMPS network.

Fig. 2a shows the cyclic change in the isometric stress of the TN gel alternately triggered by water and 50% EtOH (EtOH-50) at a pre-strain of 100%. For comparison, the behavior alternately triggered in water and pure EtOH is also included in the figure. Each cycle can be well reproduced without obvious loss in stress. In the EtOH-50, the gel shows a low isometric stress in comparison with that in water, which is contrary to what has occurred in the pure EtOH. This result suggests a great adjustability in the isometric stress of the TN gel from contractile response (increase in stress) to relax response (decrease in stress) with the change of solvent composition. More systematic results are shown in Fig. 2b, which presents the contractile stress as a function of EtOH content. When the EtOH content is not very high, the contractile stress $\Delta\sigma$ shows a negative value, and $\Delta\sigma$ decreases and then increases with the increase in the EtOH content. The minimal
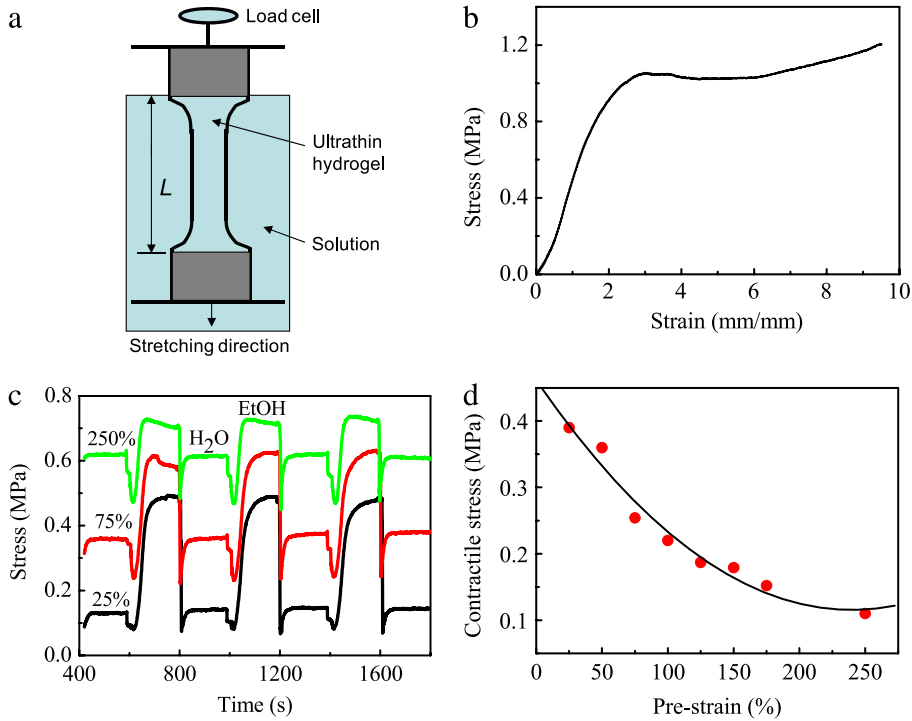
Fig. 1. (a) Illustration of the experimental setup for the stress generation test of the ultrathin film TN gel of 100 μm thickness. (b) Stress–strain curve of the gel in distilled water. (c) Response of the isometric stress of the gel periodically triggered by water and EtOH under different pre-strain. The percentages shown in the figure are values of pre-strain applied. (d) The isometric contractile stress of the TN gel as a function of the pre-strain applied. The gel was in a dumbbell shape (length 51 mm, width 4 mm, gauge length 20 mm). The strain loading velocity was 60 mm/min. The formulation of the gel precursor solution: First network, 1 M 2-acrylamido-2-methylpropane-sulfonic acid (AMPS) monomer, 0.04 M N, N'-methylenebis(acrylamide) crosslinking agent, and 0.001 M 2-oxoglutaric acid (OA) initiator; Second network, 4 M acrylamide (AAm)/0.001 M OA/0.08 M NaCl; Third network, 2 M AAm/0.001 M OA.

contractile stress $\Delta\sigma$ is at the 50% EtOH content. With further increase in the EtOH content, $\Delta\sigma$ increases, and becomes positive when EtOH content is higher than 90%. So, by controlling the EtOH content, the contractile stress $\Delta\sigma$ of the TN gel can be tuned in a wide range from -0.24 to 0.25 MPa, the latter is comparable to $0.1 \sim 0.8$ MPa of the natural muscles [25]. Furthermore, the isometric stress spectrum triggered by a sequence of solvents is shown in Fig. 2c. Corresponding to the result in Fig. 2b, similar distribution of the isometric stress is obtainable, which further confirms the sequential adjustability of the stress of the system. In general, each cyclic trigger can be achieved within several tens of seconds according to Fig. 2a, c. Although such response time of our present TN gel system is three orders of magnitude longer that those demonstrated for the natural muscles of several tens to hundreds of milliseconds [26,27], the further improvement is expected to be accomplished by fabricating thinner tough gels with a thickness of $\sim$10 μm.

What causes this adjustability in the isometric stress of TN gels? To clarify its mechanism, the solvent-induced changes in the volume and Young's modulus of the TN gel were investigated at their free-standing state. In comparison with water, EtOH is a very poor solvent to PAAm network. When being immersed in the water/EtOH mixture solvents, the free standing TN gel deswells greatly as presented in the inset of Fig. 3a. The contraction ratio, $\Delta\varepsilon$ was calculated as $\Delta\varepsilon = [(L_0 - L_x)/L_0] \times 100\%$. Here L_0 and L_x are

the free-standing length of the TN gel in water and in EtOH-x (x means the weight percent of ethanol), respectively. As shown in Fig. 3a, the gel deswells in all of the solvent composition, showing a maximum $\Delta\varepsilon = 35\%$ at the EtOH content of 70%, which is about one-third higher than that in pure EtOH. It suggests that the negative contractile stress ($\Delta\sigma < 0$) in mixture solvent with EtOH less than 90% in Fig. 2b is not directly attributed to the deswelling behavior in the mixture solvents. It should be noted that the decrease in $\Delta\varepsilon$ when the EtOH content is higher than 70% may be due to the fast freezing of PAMPS and PAAm chains in EtOH, especially in pure EtOH, which prevents a persistent collapse of the networks to their equilibrium state.

Young's modulus, E_{EtOH-x}, of the TN gel in the various EtOH-x solvents is shown in Fig. 3b. With the increase in the EtOH content, E_{EtOH-x} decreases gradually and reaches a minimum of 0.14 MPa at $x = 50$, and then increases slowly until $x = 80$. Further increase in EtOH content brings about an abrupt increase in modulus, and E_{EtOH-x} finally increases to 178 MPa at $x = 100$. Comparing with Fig. 2b, we found that the variation trend between E_{EtOH-x} and $\Delta\sigma$ is very similar, both of which attain a minimum at the EtOH content of 50%. This result clearly demonstrates that solvent-triggered isometric stress generation of the TN gel results from the change of its modulus induced by the solvents. Young's modulus of the gel in water is dominated by the elasticity of the highly stretched PAMPS chains that are much rigid than Gaussian chains [28]. Deswelling of the gel in mixture solvent relaxes the stretched PAMPS chains
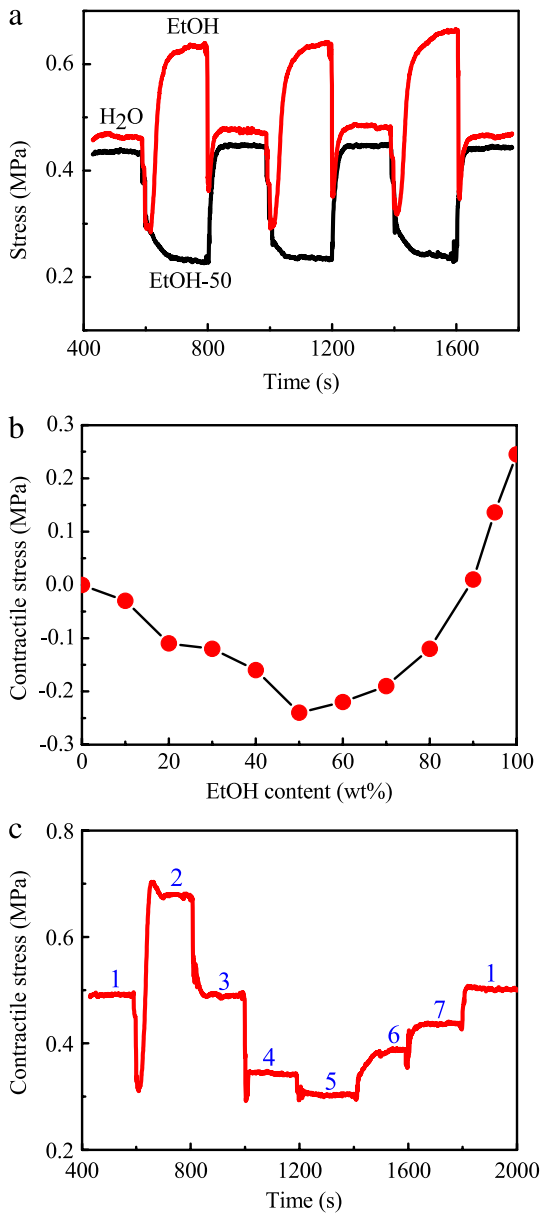
Fig. 2. (a) Response in the isometric stress of the TN gel periodically triggered by water and EtOH-*x* (*x* = 50, 100). (b) The contractile stress of the TN gel as a function of the EtOH content. (c) Sequential response in the isometric stress of the TN gel respectively triggered by water (1), EtOH (2), EtOH-90 (3), EtOH-70 (4), EtOH-50 (5), EtOH-30 (6), and EtOH-10 (7). The pre-strain for all the samples was set at 100%.

Fig. 3. The size contraction ratio $\Delta\varepsilon$ (a) and Young's modulus (b) of the ultrathin TN gel at the free-standing state as a function of the EtOH content in the applied solvents. The inset in (a) presents the typical appearances of the TN gel in EtOH, EtOH-80, and water, respectively. The modulus of the samples measured in EtOH-90 and pure EtOH is not shown because they are larger than 100 MPa. (c) Contractile stress at a pre-strain $\varepsilon_{\text{pre}} = 1$ calculated from Eq. (4). For comparison, the experimental result of Fig. 2b is also shown in (c).

and therefore softens the gel. On the other hand, molecular interaction between PAAm polymer chains in the poor solvent of EtOH contributes to the effective physical crosslinking, and therefore hardens the gel. According to the data of $E_{\text{EtOH-}x}$ in Fig. 3b, the former effect on the modulus of the TN gel is dominant when $x < 50$, while the latter effect is dominant when $x > 50$. The very high modulus E_{EtOH} of 178 MPa, which is more than two orders in the magnitude larger than $E_{\text{water}} = 0.31$ MPa, indicates that the polymer networks are frozen in pure EtOH.
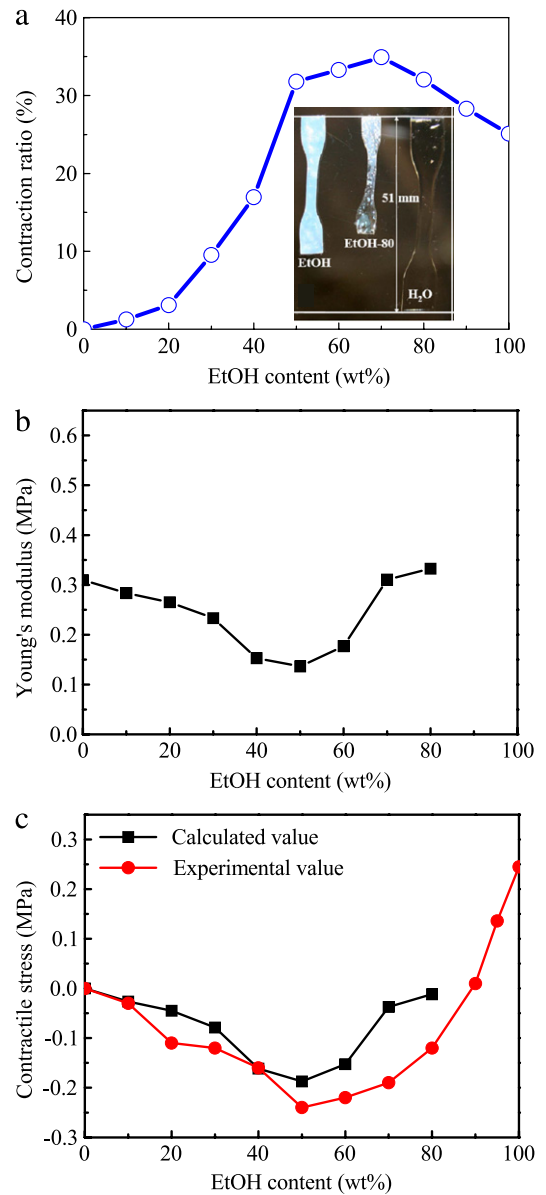
Next, we discuss more quantitatively on the contribution of modulus to the contractile stress. Assuming that the deformation of the gel is in elastic range, the isometric stress in water, σ_0, and in EtOH-*x*, σ_p, can be related to the pre-strain ε_{pre} applied and contraction ratio $\Delta\varepsilon$ in the poor solvent EtOH-*x*. Noting that the nominal σ_p was recorded as tensile force divided by the initial cross section area of the gel in water regardless of contraction in poor solvents, we therefore have

$$\sigma_0 = E_{\text{water}}\varepsilon_{\text{pre}} \tag{2}$$

$$\sigma_p = (1 - \Delta\varepsilon)^2 E_{\text{EtOH-}x}(\varepsilon_{\text{pre}} + \Delta\varepsilon)/(1 - \Delta\varepsilon)$$
$$= E_{\text{EtOH-}x}(\varepsilon_{\text{pre}} + \Delta\varepsilon)(1 - \Delta\varepsilon). \tag{3}$$

Therefore, the contractile stress

$$\Delta\sigma = \sigma_p - \sigma_0$$
$$= [E_{\text{EtOH-}x}(1 + \Delta\varepsilon/\varepsilon_{\text{pre}})(1 - \Delta\varepsilon) - E_{\text{water}}]\varepsilon_{\text{pre}}. \tag{4}$$

When the size contraction ratio $\Delta\varepsilon$ is small in comparison with the pre-strain applied ($\Delta\varepsilon/\varepsilon_{\text{pre}} \ll 1$), and also much smaller than 100% ($\Delta\varepsilon \ll 1$), the contractile stress is dominated by the modulus change and approximately,

$$\Delta\sigma \simeq (E_{\text{EtOH-}x} - E_{\text{water}})\varepsilon_{\text{pre}}. \tag{5}$$

Eq. (5) suggests that when the size contraction effect is negligible, the contractile stress at a designated pre-strain is simply determined by the modulus change induced by solvent exchange.

The physical quantities $\Delta\varepsilon$, E_{water}, and $E_{\text{EtOH-}x}$ can be determined by using bulk TN gel. Both the calculated (according to Eq. (4)) and experimental values of $\Delta\sigma$ were shown in Fig. 3c, which are well consistent with each other in the range of EtOH content less than 80%. However, we found that the calculated positive value of $\Delta\sigma$ is much higher than the observation when the EtOH content is higher than 80% (data not shown). This suggests that when the EtOH content is very high, the gel is in plastic state and the linear elastic assumption at a large strain $\varepsilon_{\text{pre}} = 1$ may be not true for the TN gel in the high rigid state.

According to the result of Fig. 3b that shows softening of the gel in the EtOH/water mixture ($x < 90$), the initial sharp drop and then the rapid increase of the stress in Fig. 1c, in response to the solvent exchange from water to pure EtOH, is attributed to the finite solvent exchange time. At the very beginning of the solvent alternation, it causes a transient EtOH/water mixture on/near the surface of the gel and thereby leads to softening of the gel. With the increase of the solvent exchange time, the EtOH/water mixture changes to pure EtOH and thereby leads to hardening of gel.

The solvent-triggered stress change of the TN gel is a diffusion-controlled process, and the dynamics of the stress response follows an exponential relationship with a characteristic time τ.

$$\ln\frac{\sigma_{\max} - \sigma_t}{\sigma_{\max} - \sigma_0} = -\frac{t - t_0}{\tau}. \tag{6}$$

Here, $\sigma_{\max}$, σ_0 and σ_t are the maximum stress, the stress at $t = t_0$ that the solvent is exchanged and the stress at time t of the TN gel, respectively. Analysis using Eq. (6) shows that the characteristic time of stress increase and decrease in response to solvent exchange between water and EtOH is in the order of 10 s, in agreement with the characteristic time for solvent diffusion estimated from Eq. (1).

Since the TN gel carries negative charges in its first network (PAMPS), we can also use Ca^{2+} ions to generate contractile stress. Ca^{2+} will form an ionic bridge between sulfonic groups SO_3^- of the PAMPS network, and increase the modulus. Fig. 4a shows the contractile stress of the TN gel induced by ion stimuli in 0.5 M $CaCl_2$ aqueous solution at 100% pre-strain. Within the response time of ~30 s, reproducible $\Delta\sigma$ of 0.03 MPa is observed for the
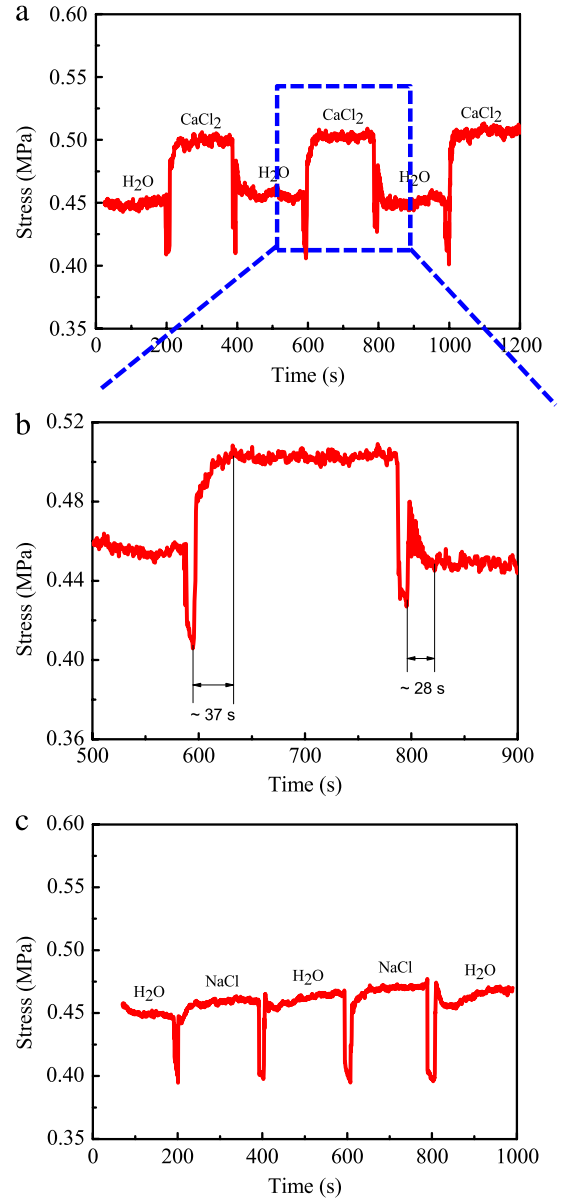

Fig. 4. Response in the isometric stress of the TN gel periodically and alternately triggered by water and 0.5 M $CaCl_2$ (a) or 0.75 M NaCl (c) aqueous solutions. For clarity, (b) shows the partial enlargement of (a). The pre-strain was set at 100%.

TN gel in the $CaCl_2$ solution. In this case, the ion-induced contraction of the gel length was $\Delta\varepsilon = 3.7\%$ and the gel modulus was increased by a factor of 1.2 ($E_{CaCl_2}/E^{\text{water}} = 1.2$) to $E_{CaCl_2} = 0.36$ MPa. This result indicates that the electrostatic interaction between the Ca^{2+} ions and the SO_3^- groups of the PAMPS is strong enough to overwhelm the high osmotic pressure of the PAAm network and cause size and modulus change of the gel. It should be pointed out that the contractile stress is hardly observed when the same experiment was performed in 0.75 M NaCl aqueous solution (Fig. 4c). This result indicates that the electrostatic shielding effect of the salt ions is negligible to the TN gel. This indicates that the swelling of the TN gel is governed

by the osmotic pressure of the neutral second and third networks, surpassing the osmotic pressure generated by the counter ions of the charged first network. It should be mentioned that the pulse-like negative peaks of $\Delta\varepsilon$ in Fig. 4a, c were artifact induced by the exchange of the solvents. At present, although the Ca^{2+}-induced contractile stress and response time of the TN gel are inferior to those of the natural muscles, its response to Ca^{2+} stimulus enables us to design soft and wet artificial muscles more approaching the true function of the natural ones.

3. Conclusions

The ultrathin TN gel exhibits robust and fast solvent-triggered stress generation, resembling muscle-like behavior. High stress generation of 0.4 MPa was obtained within several tens of seconds at the low pre-strain of 25% by alternating water and ethanol. At the pre-strain of 100%, both negative and positive contractile stress of the TN gel were well adjustable by changing the composition of the ethanol/water mixture solvents, over a wide range of $-0.24 \sim 0.25$ MPa. The mechanism of the stress generation of the TN gel in the ethanol/water mixture solvents is attributed to the solvent-induced change in its modulus. Besides organic solvent-responsive capability, the inorganic ion Ca^{2+}-responsive capability of the TN gel was also confirmed, which suggests the TN gel is multi-responsive to the external stimuli. The contractile stress of 0.03 MPa could be obtained in ~30 s when the TN gel was triggered in 0.5 M $CaCl_2$ aqueous solution, induced by the cross-linking effect of Ca^{2+} on the negatively charged PAMPS network. The present TN gel system exhibits a comparable contractile stress with $0.1 \sim 0.8$ MPa of the natural muscles. Although the response time is still much slow in comparison with $10 \sim 100$ ms of the natural muscles [29], it provides us a new avenue to fabricate soft and wet artificial muscles more approaching the natural ones.

Acknowledgment

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