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RESEARCH ARTICLE

Osmosis-Induced Mechanical Disintegration of Polymer Network Gels

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Abstract: A polymer network soaked in its good solvent absorbs the solvent molecules to swell up. The structurally possible swelling range of a polymer network is from its dried state to the structural swelling limit where its network strands reach their stretching limit. However, swelling of a polymer network to near its structural limit has not been realized due to the thermodynamic limitation. Here, this research succeeds in excessive swelling of polymer networks to or even beyond their structural swelling limit. For the excess swelling, dense linear polymers are repeatedly introduced inside a polymer network of interest. The linear polymers, trapped inside the polymer network, generate extremely high osmotic pressure and make the polymer network swell excessively. The resulting polymer networks, overswollen beyond their structural limit, disintegrate into microgels due to catastrophic scission of the polymer network strands, analogous to osmotic hemolysis of red blood cells in a hypotonic solution. This research is expected to contribute to osmosis-induced mechanodegradation of polymer network materials and well-controlled, swelling-based mechanochemistry.

Introduction

A polymer network immersed in its good solvent absorbs the solvent molecules to swell up. Such a swollen polymer network, called a polymer gel, is a soft and wet material composed of a solvated polymer network (gel network) and a large amount of solvent. Then, how large can a gel network swell in solvent? We adopt the simple but reasonable assumption that the structural swelling limit of a gel network is dictated by the extensibility of its network strands. Under this assumption, the structurally possible swelling range of a gel is from its dried state to the structural swelling limit where (majority of) strands of the gel network are fully stretched and reach their maximum allowable length by swelling. Nevertheless, previous research about gel swelling has been conducted only in relatively small swelling regimes.[1–10] Especially, ultimately swollen gels near their swelling limit have not been experimentally accessible due to the thermodynamic limitations. A gel has a specific swelling equilibrium in the solvent depending on its network structure and environment such as solvent species, temperature, swelling constraint, etc.[1] A gel reaches its thermodynamic swelling equilibrium when its total swelling pressure, π_{total}, reaches zero. According to the interpretation by Flory and Rehner, the swelling pressure of a gel, π_{total}, is separable into the elastic pressure, π_{el}, which works to suppress the swelling, and the osmotic pressure, π_{os}, which works to promote the swelling.[1, 6–8, 11] The elastic pressure of a gel originates from the elastic energy stored in the gel network.[8] The osmotic pressure consists of the mixing contribution, π_{mix}, which is based on the free energy of mixing of the network strands and solvent, and the ionic contribution (for ionic polymers), π_{ion}, which originates from the difference of the mobile ion concentration between inside and outside

the gel.[1, 6, 7, 12–14] When the elastic pressure and the osmotic pressure are balanced, **Equation 1** holds, and a gel reaches its swelling equilibrium;

$$\pi_{\mathrm{total}} = -\pi_{\mathrm{el}} + (\pi_{\mathrm{mix}} + \pi_{\mathrm{ion}}) = 0. \qquad \text{(Equation 1)}$$

The system is at a free energy minimum at this equilibrium, and the swelling of a gel beyond this equilibrium is thermodynamically unfavourable.

Swelling a gel network beyond its original swelling equilibrium has been realized by the molecular stent method.[15–18] In this method, dense linear polymers, called molecular stents, are introduced inside a gel of interest. A gel with introduced molecular stents is called a St gel. The presence of the molecular stent itself negligibly contributes to the elasticity unless it forms chemical crosslinking or strong physical interactions with the original gel network. On the other hand, the introduced molecular stent remarkably increases the osmotic pressure of the whole gel. Thus, this method allows control of the osmotic pressure of an entire gel, separating from the elastic pressure of the gel network. Owing to the increased osmotic pressure originating from the introduced molecular stents, a St gel immersed in its good solvent absorbs more solvent molecules and reaches another swelling equilibrium beyond the original swelling equilibrium of the sole gel network.

The molecular stent method has expanded the experimentally accessible swelling range of a gel. However, in the previous works using this method, the molecular stent was introduced to a gel only once. Consequently, only a limited concentration of the molecular stent was incorporated into a gel, which was insufficient to swell the gel to its structural limit.[15–18]

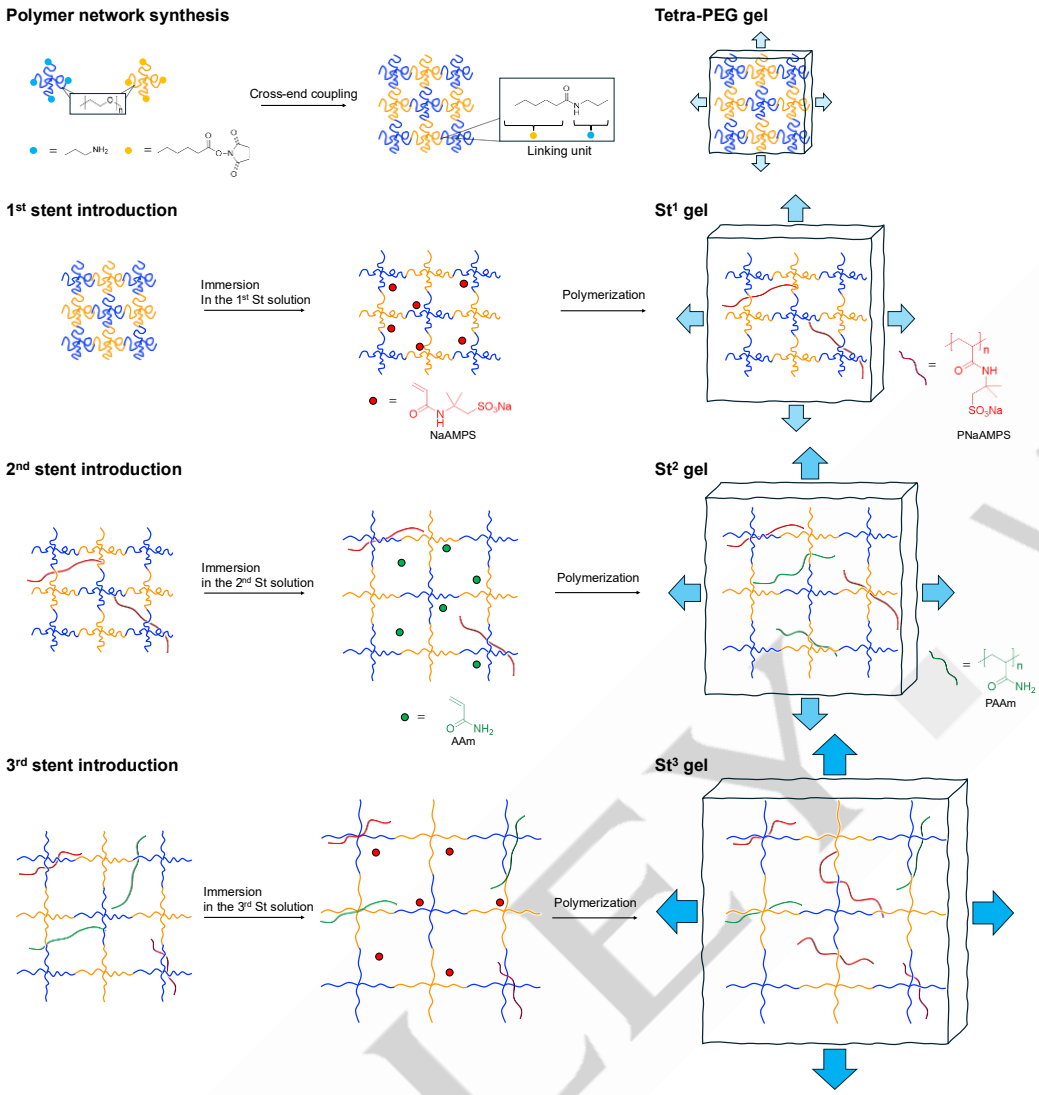
Here, this study aims to swell a gel network excessively to its structural swelling limit or even beyond the limit by the multi-step molecular stent method, where the introduction of the molecular stent is repeated several times to introduce denser molecular stents. We first systematically realized the swelling of a gel in its whole structurally possible swelling range. Moreover, we first report the “osmotic explosion” of a polymer gel overswollen beyond its structural swelling limit, which is the fragmentation of the overswollen gel network due to the catastrophic rupture of the network strands.

Results and Discussion

Achieving the structural swelling limit of the polymer network

As polymer gels of interest, we used Tetra-PEG gels with well-defined network structures to correlate the macro- and molecular-scale deformations. Tetra-PEG gels, synthesized by cross-end coupling of the 4-armed polyethylene glycols with narrow molecular weight distribution, have controlled length of the network strands as well as low spatial inhomogeneity.[19–24] Owing to its well-controlled structures, it is reasonable to assume that the macro-scale deformation of a Tetra-PEG gel network by swelling and the molecular-scale deformation of its network strands are well coupled;[25–27] if the gel swells λ_s times in length, its network strands would be also stretched approximately λ_s times. The Tetra-PEG gels with various prepolymer molecular weights and concentrations were prepared. Preparation conditions of the Tetra-PEG gels are denoted by the average molecular weight of the prepolymers, M_w, and the prepolymer concentration in the pre-gel solution relative to their overlap concentration, C^*.

Swelling of a Tetra-PEG gel far beyond its original swelling equilibrium was achieved by the multi-step molecular stent method, where the ionic and nonionic molecular stents are introduced alternately (**Scheme 1**). While a variety of polymer species can be used as molecular stents, we used poly(2-acrylamido-2-methylpropane sulfonic acid sodium salt) (PNaAMPS) and polyacrylamide (PAAm) as the ionic and nonionic molecular stents, respectively, just because they are commonly used polymers for hydrogel synthesis. We introduced ionic PNaAMPS as the 1st molecular stent, nonionic PAAm as the 2nd molecular stent, and again ionic PNaAMPS as the 3rd molecular stent into the Tetra-PEG gel of interest.[16–18] Hereafter, we denote the Tetra-PEG gels with the 1st, 2nd, and 3rd molecular stent as St^1 (PNaAMPS), St^2 (PNaAMPS/PAAm), and St^3 (PNaAMPS/PAAm/PNaAMPS) gels. This alternative introduction of the ionic and nonionic molecular stents generally increases the swelling ratio of Tetra-PEG gels more effectively than repeatedly using the ionic molecular stents (**Figure S1**). All the St gels were transparent and homogeneous in appearance, and the PNaAMPS in the St^2 gel was uniformly distributed on the cross-section of the gel (**Figure S2**), suggesting homogeneous distribution of the molecular stents inside the gels. The previous work reported negligible leakage of PNaAMPS from the St^1 gel within the experimental timescale, suggesting molecular weights of the molecular stents are sufficiently large to prevent their leakage from the St gels.[18]



Scheme 1. Schematic illustration of the multi-step molecular stent method. Swelling degree of the polymer network gel of interest increases with the number of molecular stent introductions.

Excess swelling of the Tetra-PEG gel networks

Figure 1A and B are pictures of the Tetra-PEG gels and $St^{1,2}$ gels whose prepolymer conditions are (A)10 k, C^*, (B)20 k, C^*, respectively. In both systems, the geometry of the as-prepared Tetra-PEG gels was fixed to 0.5 × 0.5 cm^2. The Tetra-PEG gels without molecular stents did not swell largely in water. On the other hand, the St^1 gels containing the molecular stent showed excessive swelling beyond the original swelling equilibrium of the sole Tetra-PEG gels. Furthermore, the St^2 gels containing denser molecular stents swelled even larger than the St^1 gels. The increase of the equilibrium swelling ratio by the molecular stent introduction is due to the large osmotic pressure of the gels originating from the molecular stents. Similar excessive swelling behaviors of the St gels were observed regardless of their prepolymer conditions (**Figures S3 and S4**).

Figure 1C shows the uniaxial swelling ratio, λ_s, of the Tetra-PEG gels and corresponding St gels. The dotted lines correspond to the structural maximum swelling ratio, λ_{max}, of each gel estimated based on the average end-to-end distance between the neighborhood cross-linking points in the as-prepared Tetra-PEG gels and contour length of the corresponding PEG network strands (**Text S1**). λ_s of the Tetra-PEG gels without molecular stents were less than 1.6, far from their structural swelling limits. On the other hand, λ_s of the St^1 gels was obviously increased, and that of the St^2 gels was increased furthermore. λ_s of both St^2 gels are quite close to their λ_{max}, which suggests that the PEG network strands inside the St^2 gels have reached their extremely elongated state. Such excessive swelling was observed in other Tetra-PEG gels with various prepolymer

conditions (Figure S4). The λ_s of the 20 k St gels tends to be larger than that of the 10 k St gels (Figure 1C and Figure S4). As explained above, an equilibrium swelling ratio of a gel is determined by the balance of its osmotic and elastic pressures. The elastic pressure generally increases with increase of the original network strand density. In this work, the as-prepared 20 k Tetra-PEG gels have lower network strand density as well as lower elastic pressure than the as-prepared 10 k Tetra-PEG gels. As a consequence, the 20 k St gels swell more than the 10 k St gels.

Young's modulus, *E*, of the gels was measured by the indentation test to estimate the stored elastic energy in the network strands. **Figure 1D** shows the relationship between the uniaxial swelling ratio and the normalized Young's modulus, E/E_0, of the swollen Tetra-PEG, St[1], and St[2] gels, where E_0 is *E* of the corresponding as-prepared Tetra-PEG gels. The dependence of E_0 on prepolymer concentration is shown in **Figure S5**. E/E_0 of the gels decreased with λ_s at the initial swelling regime and then increased at the large swelling regime. Around λ_{max}, E/E_0 of the St gels exceeded 1 although the network strands are remarkably diluted by swelling. Same tendency was observed in other Tetra-PEG gels with various prepolymer conditions (**Figure S6**).

From the modulus measurements, the elastic energy density of the gel network was estimated by extending the works of Panyukov and Rubinstein *et al.*[2, 28] According to these works, the scaling relationship for the elastic energy density, *W,* and the elastic modulus, *E*, of a gel network is given as a function of the swelling ratio λ_s as

$$W \cong E \cong \nu_e kT {\lambda_s}^2 \quad \text{(Equation 2)}$$

where ν_e is elastically effective network strand density, *k* is Boltzmann constant (1.38×10^{-21} J K^{-1}), and *T* is absolute temperature (298 K), so the value of *kT* is about 4.0×10^{-19} J. This equation indicates that the elastic energy per a network strand of a gel, $U \cong W/\nu_e$, is around $kT \times {\lambda_s}^2$. For the as-prepared Tetra-PEG gels (λ_s=1), its elastic energy per a network strand, U_0, is given by $U_0 \cong kT$. This equation is valid only in the small swelling regime where the network strands can be deemed as Hookean springs and their elastic energy is proportional to the square of the deformation ratio λ_s. Considering the large swelling regime where dependence of the elastic energy per a strand on λ_s would not be quadratic, one can generalize **Equation 2** as

$$W \cong E \cong \nu_e U(\lambda_s). \quad \text{(Equation 3)}$$

Equation 3 leads the following relationship,

$$\frac{U}{U_0} \approx \frac{E\nu_{e,0}}{E_0\nu_e} = \frac{E{\lambda_s}^3}{E_0}, \quad \text{(Equation 4)}$$

where $\nu_{e,0}$ is ν_e of an as-prepared gel with the relationship of $\nu_e = \nu_{e,0}{\lambda_s}^{-3}$. Substitution of $U_0 \cong kT$ into **Equation 4** leads the equation for rough estimation of *U* as

$$U \approx \frac{E{\lambda_s}^3 kT}{E_0}. \quad \text{(Equation 5)}$$

Figure 1E shows the relationship between the uniaxial swelling ratio, λ_s, and *U* of the gels. When the deformation of a gel is enough small, the end-to-end distance of its network strands obeys a Gaussian distribution. In this case, the network strands elastically behave as Hookean springs, and *U* is proportional to the square of λ_s. According to the previous research about swelling of Tetra-PEG gels, the proportional relationship between *U* and ${\lambda_s}^2$ was found at the low swelling regime ($\lambda_s < 3$) but nonlinear relationship was observed at $3 < \lambda_s$.[18] From Figure 1E, in the large excess swelling regime where the λ_s is almost around λ_{max}, *U* of both St gels were greatly increased with a remarkable derivation from $U \propto {\lambda_s}^2$, suggesting that the extremely elongated PEG network strands inside the St gels behave stiffly and no longer obey the Gaussian distribution. This strongly suggests that the increase of E/E_0 at large λ_s was because the effect of highly elongated PEG network strands exceeds that of the network dilution, while the decrease of E/E_0 at small λ_s is dominated by dilution of the network with swelling. Regardless of M_w of the prepolymers, the St[2] gels fabricated at lowest prepolymer concentration showed the greatest increase of *U;* 6.0×10^3 kJ mol^{-1} for 10 k, 0.86 *C** and 3.0×10^4 kJ mol^{-1} for 20 k, 0.75 *C** (**Figure S7**). This is because the PEG network strands in the gels with low prepolymer concentration are stretched more than the other St gels due to their larger swelling.

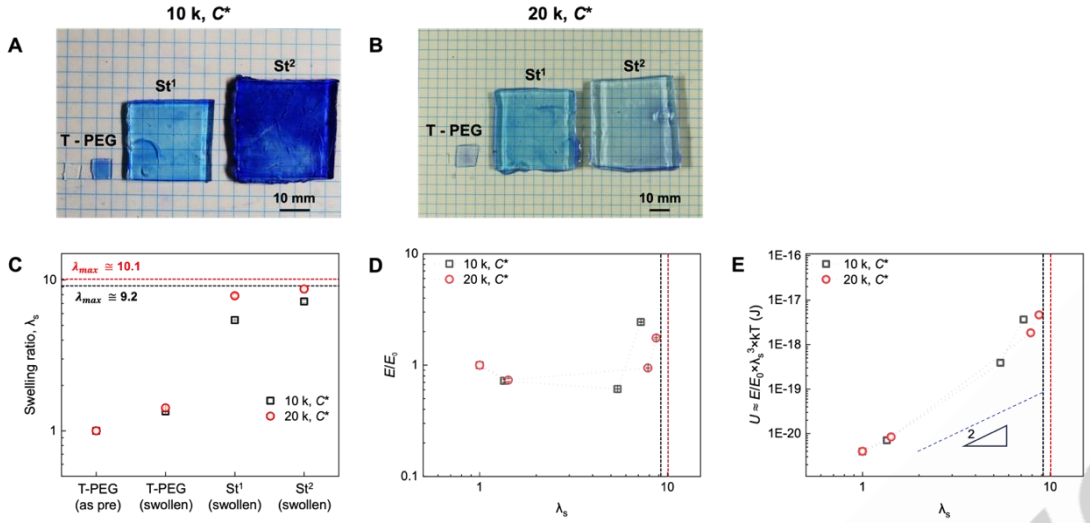


Figure 1. Excess swelling behavior and mechanical properties of the Tetra-PEG gels. a, b, Pictures of the Tetra-PEG gels and corresponding St gels, where the prepolymer condition was (**a**) 10 k, *C** and (**b**) 20 k, *C**. From the left is as-prepared Tetra-PEG, swollen Tetra-PEG, St^1, St^2 gels. The swollen gels were stained with methylene blue for visualization. **c,** Uniaxial swelling ratio, λ_s, of the Tetra-PEG gels and corresponding St^1 and St^2 gels for 10 k, *C** and 20 k, *C**. The term "as pre" stands for the as-prepared state. Black and red dotted lines show the theoretical uniaxial swelling limit based on *C** for 10 k and 20 k, respectively. **d,** Normalized elastic modulus, E/E_0, of the Tetra-PEG and St gels as a function of each their uniaxial swelling ratio, λ_s. The error bar represents mean±SD (N=3). **e,** Relationship between uniaxial swelling ratio, λ_s. and storage elastic energy per a PEG network strand, U, of the Tetra-PEG gels and corresponding St gels. Blue dotted line shows the line with a slope of 2.

Bulk disintegration of the St^3 gels

Figure 1C and E showed that the St^2 gels almost reached the structural swelling limit and stored large elastic energy in the network strands. To demonstrate the swelling of a gel beyond its structural swelling limit, the St^3 gels were prepared by introducing additional molecular stent into the St^2 gels and immersed into water. **Figure 2A** and **Movie S1** show pictures of the swelling process of the St^3 gels (10 k, *C** and 20 k, *C**) in pure water. Interestingly, the St^3 gels disintegrated in water from the surface with swelling. It means that the too-high osmotic pressure makes a gel network swell beyond its structural swelling limit, leading to the osmotic *explosion* of its network strands. After the 24 h immersion, the disintegrated St^3 gels turned into slime-like single pieces probably because the entanglement of the linear molecular stents still maintained the integrity of the material (**Figure S8**). For disentanglement of the molecular stents, the degraded St^3 gels with water were shaken gently to obtain the slurry. **Figure 2B–E** shows the optical microscope images of the exploded St^3 gels (10 k, *C** and 20 k, *C**). Numerous microgel particles, which are fragments of the St^3 gels, were observed in the slurry. The distribution of the particle size and the shape were extensive; the size of the microgels varied from a sub-mm to several mm. There are many hierarchical cracks on the surface of the microgels, suggesting the hierarchical fragmentation of the St^3 gels. The St^3 gels prepared under various conditions also showed similar osmotic explosions except for some St^3 gels (10 k, 1.4 *C** and 20 k, 0.75 *C**) (**Figure S9**). The osmotic explosion, conceptually illustrated as **Figure 2F**, is reminiscent of the osmotic hemolysis of a red blood cell in a hypotonic solution, where too much swelling of the cell induces expansion and rupture of its outer membrane. While similar osmosis-induced rupture of the *skin*, such as the split of fruits due to overwatering, are often found mainly in biosystems, osmosis-induced fragmentation of a *bulk 3D material* has rarely been reported.

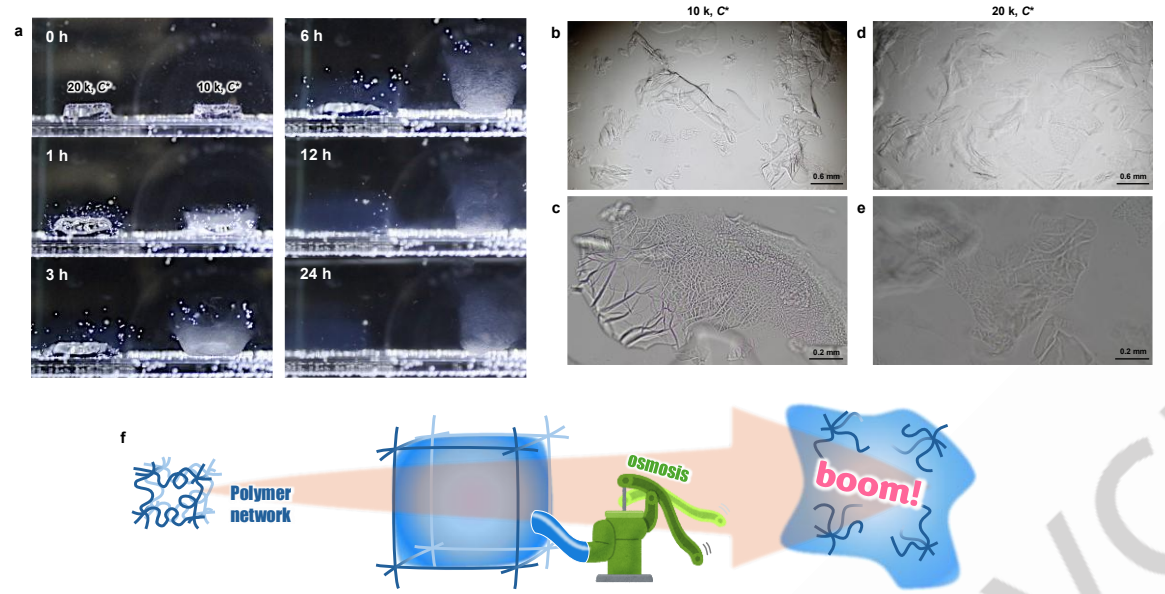


Figure 2. Osmotic explosion of the St³ gels in water. a, Pictures of the St³ gels disintegrating in water. The time on each picture corresponds to the elapsed time after the immersion in water. **b–e**, Optical microscope images of the fragmentated St³ gels: (**b, c**) 10 k, *C*** and (**d, e**) 20 k, *C**. **f**, Conceptual illustration of the osmotic explosion of a polymer network.

Discussion

As mentioned, the St³ gels were finally fragmented into microgels upon swelling. We hypothesize that the osmotic explosion of the Tetra-PEG gel networks, corresponding to rupture of the PEG network strands inside the gels, likely occurs when the elastic energy per a PEG network strand, *U*, exceeds the maximum elastic energy that single PEG network strand can withstand, denoted as U_{max}. For U_{max}, Lake and Thomas proposed an idea that U_{max} is described as the product of the bond dissociation energy of the weakest chemical bond in the main chain, U_{BDE} , and number of the bond in the main chain, *n*;[29]

$$U_{\max} = U_{\mathrm{BDE}} \times n. \qquad \text{(Equation 6)}$$

A PEG network strand inside Tetra-PEG gels consists of ethylene glycol repeating units and the linking unit containing an alkyl chain and an amide bond. The bond dissociation energies of each bond in the main chains are 364 kJ mol^{-1} (C – C bond), 331 kJ mol^{-1}(C – O bond), and 397 kJ mol^{-1} (N – C bond of amide).[30, 31] Thus, U_{BDE} of a Tetra-PEG gel network is 331 kJ mol^{-1}. Since the main chain of the single ethylene glycol unit consists of 3 covalent bonds and the linking unit consists of 9 covalent bonds (Figure 1), U_{max} of a PEG network strand inside Tetra-PEG gels is $(3 \times 331 \times n_{\mathrm{PEG}} + 9 \times 331) \times {N_{\mathrm{A}}}^{-1}$ kJ mol^{-1}, where n_{PEG} is averaged number of ethylene glycol unit in a PEG network strand, which is 112 (10 k) or 224 (20 k)[32], and N_{A} is Avogadro constant. Note that the real activation energy of the polymer scission (energy to rupture a polymer) would be lower than the above estimation because the storage elastic energy may assist the bond scission reaction and the activation energy generally decreases with an increase of the reaction timescale.[33] Thus, the estimated value can be considered as the upper limit of U_{max}.

Subsequently, we estimated *U* of the St³ gels, $U_{\mathrm{St^3}}$, and compared it with U_{max}. Although there is no stable swelling equilibrium for the St³ gels, if the strand rupture upon swelling does not occur, the St³ gels should reach the swelling equilibrium at λ_{max}. Therefore, we assume that λ_{max} is the virtual equilibrium swelling ratio of the St³ gels for the calculation. Thus, we estimated $U_{\mathrm{St^3}}$ by substitution of $\lambda_{\max} = \lambda_{\mathrm{s}}$ into **Equation 5** as

$$U_{\mathrm{St^3}} = \frac{E_{\max}{\lambda_{\max}}^3 kT}{E_0}, \qquad \text{(Equation 7)}$$

where E_{max} is elastic modulus of the St³ gels at λ_{max}. Since E_{max} is not determinable experimentally, we estimated it from the osmotic pressure. At the equilibrium swollen state of an isotropic gel, the following relationship is held;[34, 35]

$$\pi_{\mathrm{mix}} + \pi_{\mathrm{ion}} = -\pi_{\mathrm{el}} \cong \frac{E}{3}. \qquad \text{(Equation 8)}$$

This equation means that *E* of a gel at the swelling equilibrium is derivable from its osmotic pressure. The osmotic pressure of gels is often estimated by the Flory-Huggins theory based on the volume fraction of each component (**Figure S10**). We firstly estimated the osmotic pressure of the St³ gels at λ_{max} and then calculated E_{max} based on this value. The details for the calculation are described in **Texts S2 and S3**.[35] **Figure 3** summarizes the estimated *U* and U_{max} of the gels of each prepolymers condition. When the fragmentation of the

St³ gels occurs, the corresponding values of U_{St^3} are almost the same or even higher compared to U_{max} . On the other hand, in the case of the St³ gels (10 k, 1.4 *C**) that did not show fragmentation, U_{max} is one order larger than U_{St^3}.

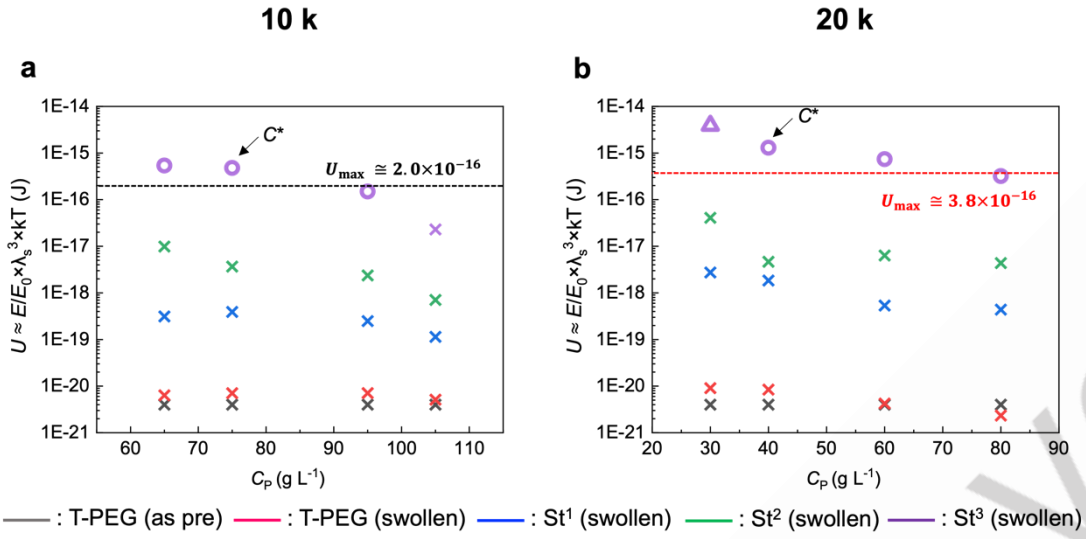


Figure 3. Estimated U and U_{max} and the occurrence of the fragmentation of the St³ gels with each prepolymers conditions. The circle and cross indicate fragmentation and no fragmentation, respectively. The triangle indicates that the St³ gels were covered by oozed molecular stent but still maintained the gel state. *C*p is prepolymer concentration, and *C** for each M_w is 75 (10 k), 40 (20 k) gL^{-1}, respectively.

For the origins of the hierarchical fragmentation, several possibilities can be proposed. One is the distribution of polymerization degree between cross-linking points. Although Tetra-PEG gels have relatively homogeneous polymer networks, there is a small distribution of polymerization degree of the network strands. Therefore, preferential scission of shorter PEG network strands would occur with swelling, leading to hierarchical crack formation on the surface. Another possible factor is the difference in the swelling rate of the gels near the surface and the inside. Since swelling of gels begins from the surface, extreme elongation and scission of network strands progress from the surface, leading to the finer cracks near the surface. Also, the oozing of the introduced molecular stent from the fracture interface should be taken into account. Since the molecular stent is a linear polymer, it gradually oozes from the original surface and the fracture interface. Although molecular stent oozing from the bulk St gels has been reported to be negligible within the experimental timescale, when the St gels are fragmented, the timescale for the diffusion of molecular stent would be extremely shorten and the molecular stent oozing from the gel fragments likely occurs within the experimental timescale.

Upon oozing the molecular stent, the local osmotic pressure of the gel near the interface decreases. Once the surface cracks are generated by swelling, oozing of the molecular stent near the crack suppresses the further swelling and nanoscale fracture of the St³ gels. For these reasons, St³ gels did not degrade to the nanoscale (molecular scale) but fragmented into microscale with many cracks. It should be noted here that the gel fragmentation in this study is different from the previously reported of swelling-induced crack propagation in gels.[36] This literature reported that the preferential swelling of a gel near the surface causes the local concentration of force at the surface defects and leads to macroscopic crack propagation from the defects, whereas it did not report bulk degradation of a gel. Our study, on the other hand, shows that excessive swelling applies enormous force to the whole gel network and disintegrates it into a microlevel.

In the case of the St³ gels (20 k, 0.75 *C**), the value of U_{St^3} is much higher than U_{max}, but the fragmentation did not occur exceptionally. Tetra-PEG gel networks prepared below *C**, including the Tetra-PEG gel network (20 k, 0.75 *C**), would have some structural defects.[24] Thus, such defects in the St³ gels (20 k, 0.75 *C**) would promote oozing of the molecular stent from them to outside, which leads to suppression of the fragmentation of the gels.

Conclusion

We succeeded in excess swelling of the gels near or beyond their structural swelling limit by the multiple introductions of the molecular stent. Near the structural swelling limit, the elastic modulus of the gels greatly increases due to the highly elongated network strands, which possibly leads development of low polymer density but stiff gels. Beyond the structural swelling limit, the overswollen gels osmotically explode into fragments

due to the rupture of the network strands, which possibly contributes to the development of polymeric materials that spontaneously degrade when disposed into water after use. This study demonstrates the power of osmotic pressure to break down molecules and materials. Just as the high pressure generated by explosives can shatter buildings (macroscopic networks), high osmotic pressure can shatter microscopic macromolecular networks. This fact shows the potential contributions of osmotic pressure to processing of materials such as osmotic milling and to environmental issues by osmotically decomposing materials at the time of disposal.

This work also implies the possibility of using swelling as a general tool to add controlled mechanical energy to the bulk polymeric materials. Typical methods to apply mechanical energy to bulk material include ultrasound or ball milling, but these methods require massive energy and the applied energy to the material is uncontrollable. The controlled extension of a polymer chain has been performed with an atomic force microscope.[37-39] Surface tension and local swelling also can induce controlled stretching of (hyper-)branched polymers.[40-42] However, these methods can only be used for a single molecule, not for bulk materials. Our multiple molecular stent method, in principle, can deform a macroscopic gel network of any chemical species to any degree by the controlled swelling. The mechanical energy accumulated to the network strands is controllable by the swelling degree and can be predicted from the bulk elastic modulus. Moreover, once sufficient amount of molecular stent is synthesized, no additional external energy supply is necessary for the fragmentation of the polymer network in solvent. We expect significant development of swelling-induced mechanochemistry by applying our multiple molecular stent method.[43]

Supporting Information

The authors have cited additional references within the Supporting Information.[49-57]

Acknowledgments

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Conflict of Interests

The authors declare no competing interests.

Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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