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Synthesis and Fracture Process Analysis of Double Network Hydrogels with a Well-Defined First Network

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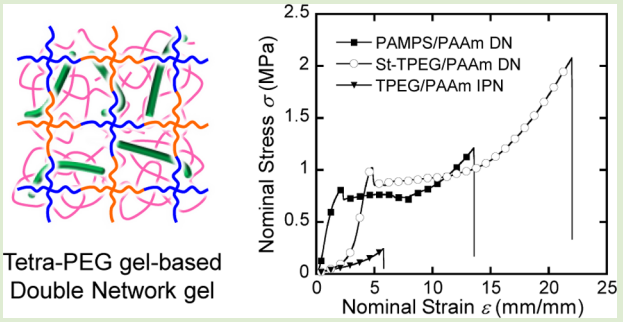
ABSTRACT: To investigate the effect of inhomogeneity in the first network on the enormously high toughness of double network (DN) gels, we fabricated DN gels with a nearly homogeneous first network structure (named St-TPEG/PAAm DN gels) based on tetra-PEG (TPEG) gels via a molecular stent method. The St-TPEG/PAAm DN gels also show excellent mechanical properties and yielding-like phenomena comparable to conventional DN gels. This result demonstrates that the inhomogeneity within the first network is not essential for the specific toughening mechanism of DN gels. On the other hand, the St-TPEG/PAAm DN gels and conventional DN gels undergo substantially different fracture processes before the yielding point. This suggests the importance of a "homogenization process" for the yielding of DN gels. Since the St-TPEG/PAAm DN gels consist of a well-defined first network, they may serve as model DN gels in the future for further studies on fracture processes of DN gels.



Double network hydrogels (DN gels) are extremely tough interpenetrating network (IPN) hydrogels consisting of a densely cross-linked, highly swollen, and brittle polyelectrolyte first network and a sparsely cross-linked, condensed, and ductile neutral second network.[1] Tough DN gels show yielding and mechanical hysteresis during tensile deformation, similar to the Mullins effect of rubbers.[2,3] Extensive studies have revealed that the high toughness of DN gels is derived from internal fracture of the first network during large deformation.[4] As DN gels consist of the brittle first and ductile second networks, at a crack tip where stress is concentrated the former breaks first, and then the latter starts to deform. At that time, due to contrasting structures and strong entanglement of the two networks, the first network breaks into fragment in a broad zone (~100 μm in width), while the second network stretches a lot with keeping its network structure.[5−7] As much energy is dissipated during this process, the energy required for crack propagation (toughness) in DN gels increases enormously. This internal fracture of the first network can be visualized as large and irreversible mechanical hysteresis during uniaxial elongation.[2,8] Considering this toughening mechanism, it is easily imagined that the structure of the first network is crucial for the internal fracture process and therefore the toughness of the DN gels. In fact, if the first network is too soft and ductile, internal fracture does not occur, and the sample shows no yielding and distinctly low toughness.[9]

In most cases, the first network of tough DN gels is synthesized by random copolymerization of monomer and cross-linker. Thus, it contains, intrinsically, mesh-size level inhomogeneity due to the large distribution of the polymer chain lengths between the next-neighboring cross-linking points.[10−12] The effect of such first network inhomogeneity to the mechanical properties of DN gels has been analyzed both experimentally and theoretically. For example, if the first network is synthesized with poor solvent, it contains extensive inhomogeneity, and the DN gels show a distinct necking phenomenon.[13] If void structure on the micrometer scale is introduced to the first network, the toughness of the DN gels remarkably increases.[14] The role of such inhomogeneity in the fracture process of DN gels has been discussed with cyclic tensile testing and model fitting.[8,15] Some theoretical models were established considering the chain length distribution of the first network.[16,17] These studies show that a certain level of inhomogeneity within the first network increases the toughness of DN gels. These results seem to suggest that the large inhomogeneity is responsible for the occurrence of the internal fracture and, therefore, is essential for the specific toughening mechanism of DN gels.[8,12]

To clarify the role of inhomogeneity, we tried to fabricate DN gels with the nearly homogeneous first network and analyze their mechanical properties. Two difficulties of this study are how to synthesize a homogeneous network and how

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to make it highly swollen in aqueous solution. We solved these difficulties by using two novel solutions: utilization of tetra-PEG gels and the molecular stent method.[9,18] Tetra-PEG (TPEG) gels are synthesized by A−B-type cross-end coupling of two tetra-arm poly(ethylene glycol) (tetra-PEG) units that have amine (TAPEG) and activated ester (TNPEG) terminal groups, respectively.[18] Several experimental results have suggested that TPEG gels have nearly ideal network structure, such as low molecular weight distribution between cross-linking points, negligible entanglement, and negligible elastically ineffective loop formation.[19−24] However, as TPEG gels are neutral and not in a highly swollen state in water, TPEG gels cannot be directly used as the first network of tough DN gels. To overcome this problem, the molecular stent method, which is the technique to synthesize neutral first network-based tough DN gels, was also used together.[9] In this technique, linear, strong polyelectrolyte chains or ionic micelles (molecular stent) are introduced to neutral gels. As the overall osmotic pressure is increased by this process, the swelling degree of gels remarkably increases. As a result, network chains of neutral gels are stretched to the extended conformation, like those of polyelectrolyte gels, and such swollen gels can be used as the first network for tough DN gels. In this study, we applied the molecular stent method to TPEG gels to develop highly swollen gels with nearly homogeneous chain length, which are suitable for the first network of tough DN gels with a well-defined first network structure. In this paper, such TPEG gel-based DN gels are called "homogeneous DN gels" because of the nearly homogeneous molecular weight of the first network chains.

The synthesis scheme of the DN gels with a homogeneous first network is shown in Figure 1. First, the first network TPEG gel with nearly ideal network structure was synthesized. Second, strong polyelectrolyte linear chains (molecular stent), poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), were polymerized in the presence of the TPEG gels. The TPEG gel containing the molecular stent (St-TPEG gel) increased in volume substantially when it was immersed in the precursor solution of the second network. Finally, the second network neutral polyacrylamide (PAAm) gel was synthesized in the presence of the St-TPEG gel. Mechanical properties of the resulting St-TPEG/PAAm DN gel were measured in the as-prepared state. The detailed synthesis method is shown in the Experimental Section.

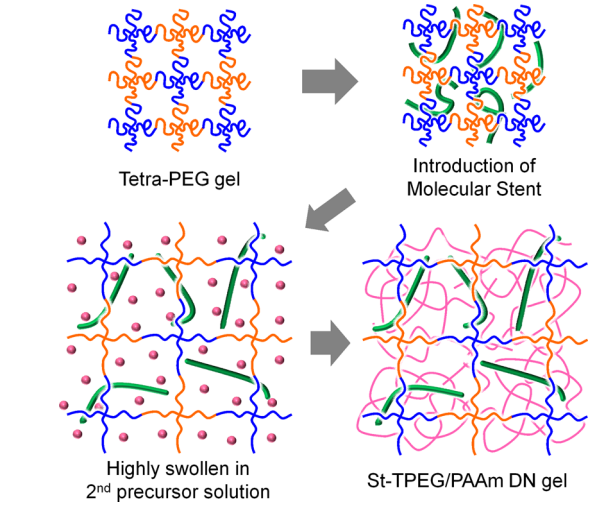

Figure 1. Synthesis scheme of the double network hydrogels from the first network with homogeneous chain length. First, the first network tetra-PEG (TPEG) gel with well-defined network structure was synthesized. Second, linear polyelectrolytes (molecular stent, green) were synthesized within the TPEG gel to increase the overall osmotic pressure and swelling degree of the gel. Finally, the second network PAAm (pink) was synthesized within the highly swollen TPEG gel.

Figure 2 shows the uniaxial stress−strain curves of the conventional PAMPS/PAAm DN gel, the St-TPEG/PAAm DN gel (with molecular stent), and the TPEG/PAAm IPN gel (without molecular stent). In this figure, the data of the St-TPEG/PAAm DN gel with 0.6 M molecular stent (in the as-prepared state) were shown because this composition leads to the most excellent mechanical robustness of the TPEG-based DN gel. We succeeded in synthesizing the strong and tough DN gel with a homogeneous first network by combining the tetra-PEG gel and molecular stent method. The St-TPEG/PAAm DN gel contained 81 wt % water and showed high fracture stress of 2 MPa, high fracture strain of 2200%, and, most importantly, a yielding-like phenomenon like conventional DN gels. One major difference between these DN gels is the much smaller initial modulus of the St-TPEG/PAAm DN gel. This indicates that the tetra-PEG network in the St-TPEG/PAAm DN is less stretched and relatively soft, whereas the PAMPS network in the PAMPS/PAAm DN is almost fully stretched and stiff. In contrast to the St-DN gel, the TPEG/PAAm IPN gel (synthesized without molecular stent) was much weaker than the DN gels. The excellent mechanical properties of the St-TPEG/PAAm DN gel suggest that the first network inhomogeneity itself is not the origin of high strength/toughness of DN gels.

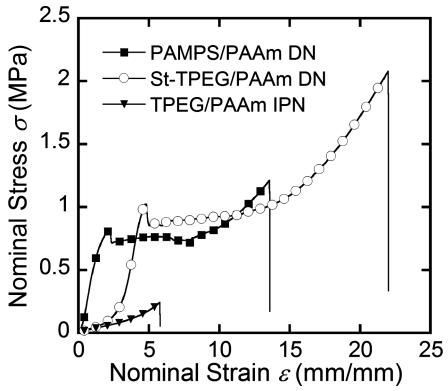

Figure 2. Nominal stress−strain curves of the PAMPS/PAAm DN, the St-TPEG/PAAm DN (with 0.6 M molecular stent), and the TPEG/PAAm IPN (without molecular stent) gels. Tensile velocity was fixed at 100 mm/min. These gels contained 80 wt %, 81 wt %, and 77 wt % of water, respectively.

Subsequently, cyclic tensile testing, which is a facile way to analyze internal fracture processes of DN gels, was performed on the PAMPS/PAAm and the St-TPEG/PAAm DN gels. The amount of the first network fractured can be quantitatively analyzed from dissipated energy or a decrease of elastic modulus, during the test.[8,15] Following our recent report,[15] the stress−strain curves of the DN gels are divided into three regions, which are prenecking (before the yielding point), necking (stress plateau), and hardening (after necking) regions. In the case of conventional DN gels, the internal fracture occurs as follows. In the prenecking region, a little internal fracture

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occurs with homogeneous deformation. In the necking region, a constricted region is formed on the sample, and "catastrophic internal fracture" accompanied by sample shape transition occurs at the interface between un-necked and constricted parts. In the hardening region, gel deformation becomes homogeneous again, and a large amount of internal fracture continuously occurs. The cyclic loading curves of the PAMPS/PAAm and St-TPEG/PAAm DN gels are shown in Figure 3.

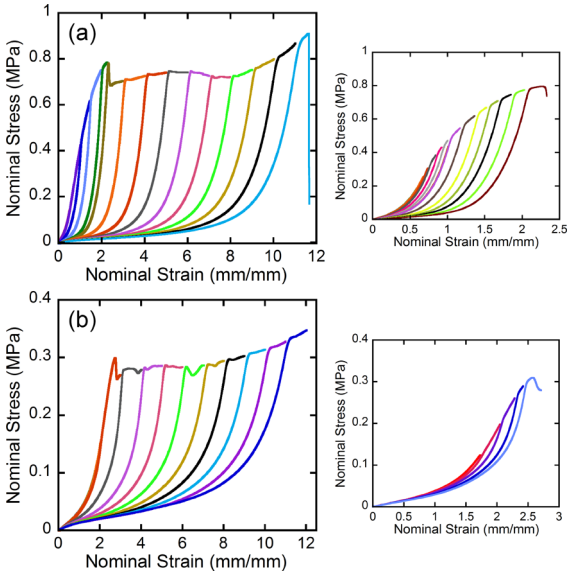

Figure 3. Cyclic loading curves of (a) the PAMPS/PAAm DN gel and (b) the St-TPEG/PAAm DN gel (1.0 M molecular stent). The large figures on the left are those of the overall fracture process, and the small figures on the right are those in the prenecking region. Tensile velocity was fixed at 100 mm/min. The St-TPEG/PAAm DN gel contained 81 wt % of water.

Here, the results of St-TPEG/PAAm gel synthesized with 1.0 M molecular stent were shown for its similar yield strain with that of PAMPS/PAAm DN gel, which makes experimental results of the two DN gels easily comparable. Beyond the yielding point (necking and hardening regions), both of the DN gels showed large mechanical hysteresis, which indicates the occurrence of large amounts of internal fracture. Our previous study has suggested that the internal fracture in these regions is the dominant overall energy dissipation process, which affects the strength/toughness of DN gels.[15] Thus, the result shown in Figure 2 indicates the similarity of the toughening mechanism of inhomogeneous and homogeneous DN gels. In contrast, in the prenecking region, the two DN gels showed substantially different mechanical hysteresis. The PAMPS/PAAm DN gel showed relatively large hysteresis even before the yielding point. It indicates the existence of some internal fracture of the first network.[15] On the other hand, the St-TPEG/PAAm DN gel showed very small hysteresis in this region. This means that the internal fracture of the first network hardly occurred in the relatively homogeneous system. Figure 4 shows the normalized Young's modulus, E, of the DN gels after experiencing a certain maximum strain ε_{max}. In the prenecking region, E of the PAMPS/PAAm DN gel remarkably decreased with ε_{max}, but that of the St-TPEG/PAAm DN gel was almost insensitive to ε_{max}. This result quantitatively indicates negligible internal

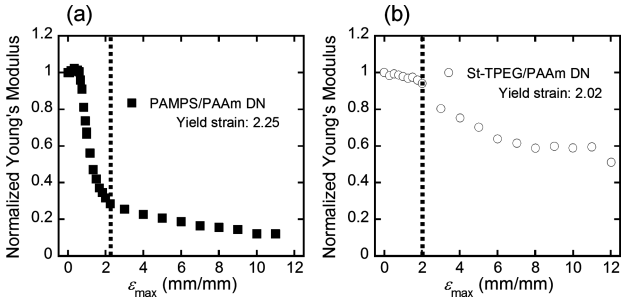

Figure 4. Normalized Young's modulus E of (a) the PAMPS/PAAm and (b) the St-TPEG/PAAm DN gels after experiencing a certain maximum strain ε_{max}. The dashed lines indicate the yield strain of each gel. Normalization was performed by dividing raw Young's moduli with those of the virgin ($\varepsilon_{max} = 0$) samples.

fracture of the St-TPEG/PAAm DN gel in the prenecking region.

Here, we discuss the effect of chain length distribution (inhomogeneity) on the internal fracture process of DN gels in the prenecking region, in other words, the condition for the occurrence of necking (yielding) beyond which global fracture of the first network occurs by catastrophic internal fracture. When strain is applied to the PAMPS/PAAm DN gel, the shortest chains in the first network break first due to stress concentration. Similarly, with an increase in strain, the shortest first network chain at that time breaks in order of chain length. As a result, the chain length distribution of the remaining ones becomes narrow. Thus, the first network gradually becomes homogeneous with an increase in strain.[15] We call the above-mentioned process the "homogenization process". The certain amount of internal fracture in the prenecking region of PAMPS/PAAm DN gels indicates that the yielding occurs only after the first network reaches a certain homogeneous level. In contrast, only slight preinternal fracture is required for yielding of the St-TPEG/PAAm DN gels. This is because the initial first network structure of these DN gels is already nearly homogeneous. On the basis of these facts, we have reached the conclusion that for the occurrence of catastrophic internal fracture the first network structure must be nearly homogeneous. This conclusion is easily understandable. When the chain length distribution is large, the shortest chains break first no matter where they are located. Such fracture does not lead to global internal fracture. When the chain length distribution becomes narrower to a certain level, the chains behind the largest internal crack always break first due to stress concentration, which leads to catastrophic internal crack propagation and global yielding.

The above arguments indicate that inhomogeneity is not essential for the specific toughening mechanism of DN gels. Beware that it does not mean that the inhomogeneity of the first network is not important. The inhomogeneity of the first network should affect the mechanical balance between the first network and the second network. A large inhomogeneity of the first network leads to a low yielding stress, which makes the catastrophic internal fracture occur easily.[13,14]

Lastly, it should be noted that the first network of the St-TPEG/PAAm DN gels is not completely homogeneous, and it also contains some inhomogeneity, as confirmed by slight mechanical hysteresis in the prenecking region. This is probably due to molecular weight distribution (although it is extremely small) and incomplete reaction between two tetra-PEGs.

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In conclusion, we succeeded in the fabrication of tough St-TPEG/PAAm DN gels with TPEG gel-based homogeneous first network. We found that the homogeneous DN gel showed essentially the same toughening behavior as that of the conventional DN gel with a very inhomogeneous first network. Thus, we conclude that the first network inhomogeneity is not essential for the specific toughening mechanism of the DN gels. Since the St-TPEG/PAAm DN gels consist of a first network with a well-defined structure, they may serve as a better model system in the future for further studying the fracture process and toughening mechanisms of DN gels. In addition, different from the conventional DN hydrogels that have modulus degradation even at small deformation, the homogeneous St-TPEG/PAAm DN gels are stable and show negligible modulus change before yielding, which is important in practical applications.

EXPERIMENTAL SECTION

Synthesis of the First Network. Tetraamine-terminated PEG (TAPEG) and Tetra-NHS-glutarate-terminated PEG (TNPEG) (NOF Corporation) were used as received. The average molecular weight of each tetraarm-PEG was 10 kg/mol. The tetra-PEG (TPEG) gels were synthesized as reported.[20] Briefly, equal amounts of 100 mg/mL of TAPEG solution of phosphate buffer (pH 7.4) and TNPEG solution of phosphate-citric acid buffer (pH 5.8) were mixed together, poured into the glass mold, and kept for 12 h at room temperature. TPEG gels were then immersed in the molecular stent precursor solution containing 0.6 or 1.0 M 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and 0.1 mol % of 2-oxoglutaric acid as photoinitiator for 3 days. After immersion, 365 nm UV was irradiated for 3 h to synthesize linear PAMPS within TPEG gels. Such TPEG gels containing PAMPS are called St-TPEG gels. The PAMPS gels were synthesized separately by 365 nm UV irradiation to 1 M AMPS, 4 mol % of *N*,*N*′-methylenebisacrylamide (MBAA) as cross-linker, and 1 mol % of 2-oxoglutaric acid as initiator aqueous solution for 6 h.

Synthesis of the Second Network. The St-TPEG, the TPEG, and the PAMPS gels were immersed in the second network precursor solution containing 2 M acrylamide (AAm), 0.02 mol % of MBAA, and 0.01 mol % of 2-oxoglutaric acid for 1 day. By immersion, the St-TPEG gels containing 0.6 and 1.0 M molecular stent (St-TPEG gel) increased in volume by about 24 times and 97 times, respectively. After immersion, 365 nm UV was irradiated for 7 h to synthesize the second PAAm network within the St-TPEG, the TPEG, and the PAMPS gels; then finally the St-TPEG/PAAm DN, the TPEG/PAAm IPN, and the PAMPS/PAAm DN gels were obtained.

Measurements. Uniaxial tensile tests were performed on dumbbell-shaped gels with a Tensilon RTC-1310A (Orientec Co.) tensile tester. Cyclic tensile tests were also performed on the same samples as reported.[15] First, samples were elongated to a certain strain and unloaded. Then they were elongated again to higher strain and unloaded. This process was repeated until sample fracture occurred. ε_{max} is defined as the maximum strain that the sample experienced. All the measurements were performed on as-prepared gels.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. *Adv. Mater.* **2003**, *15*, 1155−1159.
(2) Na, Y.-H.; Tanaka, Y.; Kawauchi, Y.; Furukawa, H.; Sumiyoshi, T.; Gong, J. P.; Osada, Y. *Macromolecules* **2006**, *39*, 4641−4645.
(3) Mullins, L. *Rubber Chem. Technol.* **1948**, *21*, 281−300.
(4) Gong, J. P. *Soft Matter* **2010**, *6*, 2583−2590.
(5) Huang, M.; Furukawa, H.; Tanaka, Y.; Nakajima, T.; Osada, Y.; Gong, J. P. *Macromolecules* **2007**, *40*, 6658−6664.
(6) Yu, Q. M.; Tanaka, Y.; Kurokawa, T.; Furukawa, H.; Gong, J. P. *Macromolecules* **2009**, *42*, 3852−3855.
(7) Tanaka, Y.; Kawauchi, Y.; Kurokawa, T.; Furukawa, H.; Okajima, T.; Gong, J. P. *Macromol. Rapid Commun.* **2008**, *29*, 1514−1520.
(8) Webber, R.; Creton, C.; Brown, H. R.; Gong, J. P. *Macromolecules* **2007**, *40*, 2919−2927.
(9) Nakajima, T.; Sato, H.; Zhao, Y.; Kawahara, S.; Kurokawa, T.; Sugahara, K.; Gong, J. P. *Adv. Funct. Mater.* **2012**, *22*, 4426−4432.
(10) Bastide, J.; Leibler, L. *Macromolecules* **1988**, *21*, 2647−2649.
(11) Shibayama, M. *Macromol. Chem. Phys.* **1998**, *199*, 1−30.
(12) Na, Y.-H.; Kurokawa, T.; Katsuyama, Y.; Tsukeshiba, H.; Gong, J. P.; Osada, Y.; Okabe, S.; Karino, T.; Shibayama, M. *Macromolecules* **2004**, *37*, 5370−5374.
(13) Kawauchi, Y.; Tanaka, Y.; Furukawa, H.; Kurokawa, T.; Nakajima, T.; Osada, Y.; Gong, J. P. *J. Phys. Conf. Ser.* **2009**, *184*, 012016.
(14) Nakajima, T.; Furukawa, H.; Tanaka, Y.; Kurokawa, T.; Gong, J. P. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 1246−1254.
(15) Nakajima, T.; Kurokawa, T.; Ahmed, S.; Wu, W.-L.; Gong, J. P. *Soft Matter* **2013**, *9*, 1955−1966.
(16) Wang, X.; Hong, W. *Soft Matter* **2011**, *7*, 8576−8581.
(17) Zhao, X. H. *J. Mech. Phys. Solids* **2012**, *60*, 319−332.
(18) Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U.-I. *Macromolecules* **2008**, *41*, 5379−5384.
(19) Matsunaga, T.; Sakai, T.; Akagi, Y.; Chung, U.-I.; Shibayama, M. *Macromolecules* **2009**, *42*, 1344−1351.
(20) Matsunaga, T.; Sakai, T.; Akagi, Y.; Chung, U.-I.; Shibayama, M. *Macromolecules* **2009**, *42*, 6245−6252.
(21) Akagi, Y.; Katashima, T.; Katsumoto, Y.; Fujii, F.; Matsunaga, T.; Chung, U.-I.; Shibayama, M.; Sakai, T. *Macromolecules* **2011**, *44*, 5817−5821.
(22) Lange, F.; Schwenke, K.; Kurakazu, M.; Akagi, Y.; Chung, U.-I.; Lane, M.; Sommer, J.; Sakai, T.; Saalwachter, K. *Macromolecules* **2011**, *44*, 9666−9674.
(23) Nishi, K.; Chijiishi, M.; Katsumoto, Y.; Nakao, T.; Fujii, K.; Chung, U.-I.; Noguchi, H.; Sakai, T.; Shibayama, M. *J. Chem. Phys.* **2012**, *137*, 224903.
(24) Akagi, Y.; Gong, J. P.; Chung, U.-I.; Sakai, T. *Macromolecules* **2013**, *46*, 1035−1040.