True Chemical Structure of Double Network Hydrogels

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ABSTRACT: We elucidate why the anomalous high strength of double network gels is obtained when the second network is polymerized without any cross-linkers. We have synthesized *truly independent*-DN gels (named "*t*-DN" gels), which do not have any covalent bonds between the first and the second networks, and showed that the *t*-DN gels cannot be toughened by the un-cross-linked second network. It means that the high strength of usual DN gels without the cross-linker of the second network is actually achieved by the inter*connection* between the two networks through covalent bonds (so usual DN gels were named "*c*-DN" gels). Further, we found that the *t*-DN gels become stronger than the *c*-DN gels when the second network is loosely cross-linked. As the *t*-DN gels have a more simple structure than the *c*-DN gels, we expect that the toughening mechanism of DN gels will be clarified by studying the *t*-DN gels in the future.

1. Introduction

Living organs work with fantastic functions in soft and wet gel-like state. Thus, hydrogels attract much attention as excellent wet materials, suitable for making artificial organs for medical treatments. Conventional hydrogels, however, are too brittle to be applied to such applications. Recently, remarkable progresses have been achieved in increasing the toughness of hydrogels by several approaches, such as slide ring gels, nanocomposite gels, double network (DN) gels, and click gels.[1−4]

Among them, the DN gels, developed by our group, show the anomalously high mechanical strength and toughness.[3] The DN gels are interpenetrating network (IPN) hydrogels, consisting of poly(2-acrylamido-2-methylpropanesulfonic acid) gels (PAMPS gels, rigid and brittle) as the first network and polyacrylamide gels (PAAm gels, soft and ductile) as the second network. Although the fracture energy G of the PAMPS gels is about 1 J/m^2 and G of the PAAm gels is about 10 J/m^2, G of the DN gels becomes anomalously high about 1000 J/m^2 at its maximum, which is 100−1000 times higher than the primary gels. Inspired by the DN gels, the strengthening of hydrogels by IPN structure is also investigated in some other systems. Myung et al. have created the poly(ethylene oxide)/poly(acrylic acid) IPN hydrogels exhibiting large tensile fracture stress,[5] and Weng et al. have synthesized the modified-hyaluronan/poly(*N,N*′-dimethylacrylamide) IPN hydrogels with both excellent mechanical properties and suitability for cell cultivation.[6]

We have found that the modified DN gels show a kind of necking phenomenon in tensile test.[2] Further, the DN gels that do not show necking exhibit a significant hysteresis during the uniaxial tension and compression.[7,8] On the basis of these findings, Brown and Tanaka (one of the authors) proposed, independently, similar models to explain the fracture process and the high fracture energy of the DN gels[9,10] during the deformation process; the wide range of first brittle PAMPS network breaks into small clusters, costing large fracture energy, and the clusters play a role of multifunctional cross-linker of the second ductile PAAm chains. In the tearing test, the width of the zone where PAMPS network is completely broken, called the "softened zone", is assumed ∼100 μm.[10] As proof of the formation of the softened zone, after the tearing test, significant reduction of elastic modulus was observed on the fracture surfaces.[11] The classical Lake−Thomas theory predicts that the ideal fracture energy G_c of cross-linked polymer systems can be calculated by $G_c = \rho n U$, where ρ is the area density of polymer chains on fracture surfaces, U is a bond dissociation energy, and n is the average number of monomer units between cross-linkers.[12] This equation means that when a general cross-linked polymeric material is broken, only the polymer chains located at a crack tip are cut off. On the contrary, the fracture behavior of the DN gels, forming the thick softened zone, is distinctly unusual. We guess that, for the breakage of wide range of the brittle first PAMPS network, the elongation of flexible second PAAm plays a role to transfer the force to far from a crack tip.

Although these models can explain the anomalous high strength of the DN gels, there are still unsolved problems. One of them is that the DN gels become the strongest when the second component, PAAm, is polymerized without the presence of any cross-linkers, rather than with cross-linkers.[13] On the basis of the common knowledge, this result does not make sense. Figure 1 shows the schematic illustrations on how the fracture mechanism of DN gels is changed by the presence or absence of cross-linking points in the second network. Linear PAAm chains in the gel likely do not sustain the load and transfer the force as linear chains are dragged out of PAMPS network during the deformation. In fact, in the case of hyaluronan/poly(*N,N*′-dimethylacrylamide) IPN gels, a little amount of cross-linker is required in the second polymerization for the high strength, different from PAMPS/PAAm DN gels.[6] So it is a puzzle how the force is transferred via un-cross-linked linear PAAm and how the linear PAAm sustains the force.

In order to understand this curious phenomenon, we have to consider some interaction between the first PAMPS network and the second PAAm chains. Several possible interactions have been proposed. One is the entanglement of PAAm to PAMPS. By dynamic light scattering we have found that the strength of the DN gels increases as the entanglement between the networks increases.[14] The other is the molecular association. Wu et al. found, by small-angle neutron scattering and viscosity measurement, that PAMPS and PAAm prefer each other, rather than solvent water.[15−17] On the other hand, Brown proposed the supposition that the fracture process of the first network induced the cross-linking reaction between the two networks.[9] Additionally, it cannot be denied that chain transfer reaction, occurred during the second network polymerization, connects the two

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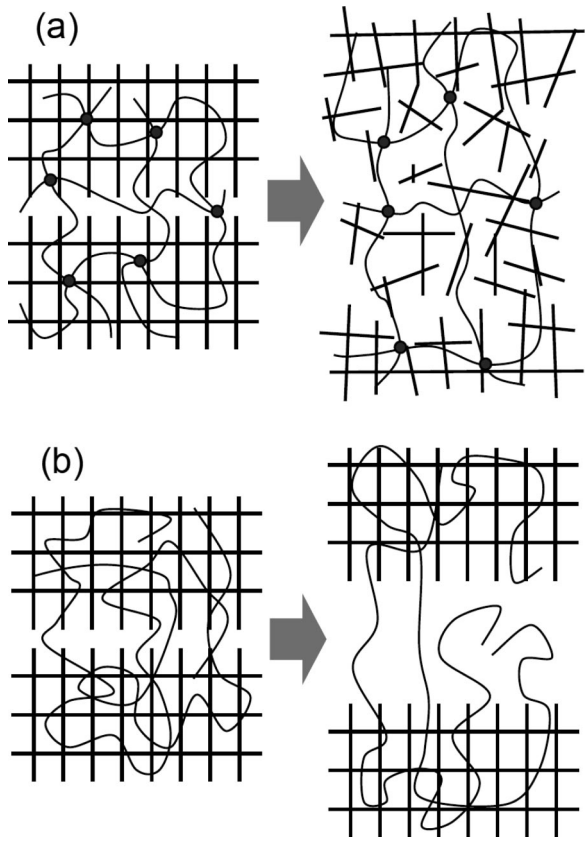

Figure 1. Two different scenarios for the formation of the softened zone around a crack. Solid mesh denotes PAMPS network, curved lines denote PAAm chains, and filled circles denote cross-linking points of PAAm. (a) If PAAm is chemically cross-linked, cross-linking points play as anchors; so the force can be transferred to PAMPS network far from a crack by elongation of PAAm network. As a result, a wide range of PAMPS network is broken. (b) On the contrary, linear PAAm chains do not transfer the force likely. Probably they are only dragged out from PAMPS network by stretching.

networks. However, these explanations look still not sufficient to understand the anomalously high strength of the DN gels without the cross-linker of the second PAAm network.

Thus, here we put forward another scenario that (i) when the first PAMPS gels are synthesized, divinyl-cross-linker *N,N′*-methylenebis(acrylamide) (MBAA) is sometimes reacted only on one side and unreacted double bonds were still remained in the first PAMPS gels; (ii) when the second PAAm is synthesized in the first PAMPS gels, AAm and the remained double bonds are copolymerized and then the second PAAm is chemically cross-linked with the first PAMPS gels. In this scenario, usual DN gels have inter-cross-linked (*connected*) double network structure (so named "*c*-DN" gels). If we make all the remained double bonds in the first PAMPS network inert before the second polymerization of AAm, PAAm will become un-cross-linked with the first PAMPS network; then the strength of the DN gel will fall down. Thus, in this article, we report some simple experiments to check this scenario. We tried to synthesize *truly independent*-DN gels (named "*t*-DN" gels), which do not have any covalent bonds between the first and the second networks, and investigate their mechanical strength.

2. Experimental Section

2.1. Materials. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was recrystallized from methanol, *N,N′*-methylenebis(acrylamide) (MBAA) was recrystallized from ethanol, 2-oxoglutaric acid was used as received, and acrylamide was recrystallized from chloroform.

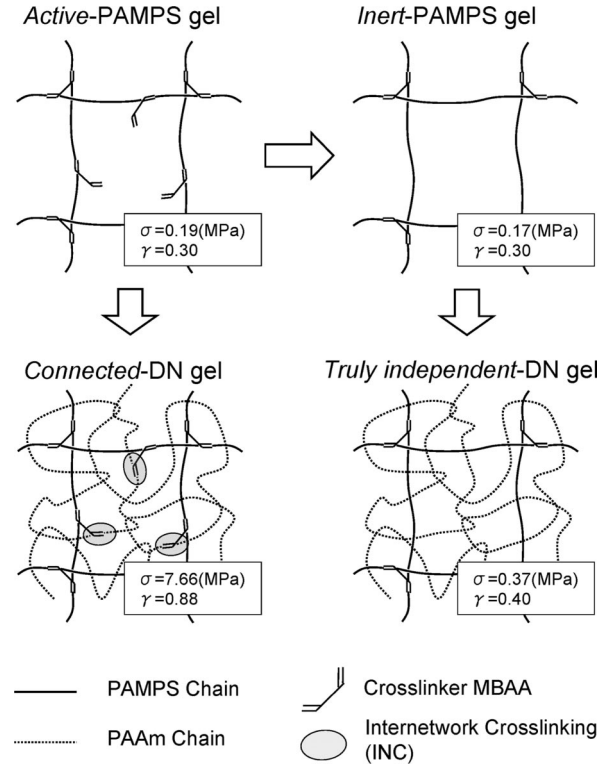

Figure 2. Chemical structures and the mechanical properties of *active*-PAMPS gels, *inert*-PAMPS gels, *connected*-DN gels, and *truly independent*-DN gels. The fracture stress σ and the fracture strain γ are measured by a compressive test.

2.2. Gel Preparation. Both *t*- and *c*-DN gels were prepared by two-step free-radical polymerization.[3] The preparation routes and chemical structures of both the DN gels are shown in Figure 2. The first network *active*-PAMPS gels (named "*a*-PAMPS" gels) were synthesized from aqueous solution containing 1 M AMPS as monomer, 4 mol % MBAA as cross-linker, and 0.01−5 mol % 2-oxoglutaric acid as UV initiator (the molar percentages are relative to the monomer). To perform the polymerization, the solution was purged in an argon atmosphere to remove dissolved oxygen, and then it was irradiated with UV light (365 nm) for at least 7 h.

After the first polymerization, some of *a*-PAMPS gels were immersed in a large amount of 0.1 M 2-oxoglutaric acid aqueous solution for at least 1 day until they absorbed this initiator solution enough. Through 365 nm UV irradiation for 10 h, sufficient radicals were generated and almost all of the unreacted double bonds remained in PAMPS gels reacted to form inert group. Thus, *inert*-PAMPS gels were prepared (named "*i*-PAMPS" gels).

Both the *a*- and *i*- PAMPS gels were then immersed in aqueous solution of 2 M AAm, 0.01 mol % 2-oxoglutaric acid, and 0−0.3 mol % MBAA. After the concentration of the solution in the gels came to equilibrium, the polymerization was performed again by 365 nm UV irradiation for at least 8 h. The *c*- and *t*-DN gels were synthesized from the *a*- and *i*-PAMPS gels, respectively. Synthesized DN gels were immersed in large amount of pure water at least for 5 days to remove residual unreacted reagents. All photopolymerizations were performed under an argon blanket, in which the oxygen concentration was less than 0.1 ppm.

2.3. Mechanical Strength Measurements. The fracture stress σ, the fracture strain γ, and the Young's moduli E of prepared gels were determined by the compressive stress−strain test,[13] which was performed on cylindrical gels (4.5 mm in thickness and 9 mm in diameter) with a commercial test machine (Tensilon RTC-1150A, Orientec Co.). The compression rate was fixed at 0.1 min^{-1}. The fracture energy G was measured by tearing test with the commercial machine on trousers-shaped samples (4.6 mm in thickness, 50 mm in length with an initial notch of 20 mm, and 7.5 mm in width), standardized as JIS-K6252 1/2 size.[14,18−20] G, defined as the energy

required to create a unit area of fracture surface in a sample gel, was calculated by $G = F_{ave}/w$,[20] where F_{ave} is the average tearing resistance force and w is the width of the gel. All the samples were measured at a constant tearing rate (velocity) V of 4.2×10^{-3} m/s (250 mm/min). It is noted that we have found the G dependency on the tearing velocity of DN gels is quite weak, and this tendency is constant even if the cross-linker density of the second network was changed;[12,14] thus, we consider that the fracture energy is determined definitely at a constant tearing rate for the present study. It also should be noted that in our previous papers[7,14,18,19] G was calculated by the different expression of $G = F_{ave}/(2w)$. The reason for the modification is that the present expression $G = F_{ave}/w$ is adequate for our testing machine in which only one arm of the tearing sample is pulled (the other arm is fixed). That is, the crack velocity is a half of the pulling velocity V_p for the asymmetrical loading, $V = (1/2)V_p$; the work done to the sample per unit time $\dot{W}$ is given by $\dot{W} = F_{ave}V_p$, and the rate $\dot{A}$ of increasing the *pair of* fracture surfaces area is $\dot{A} = 2wV$; thus $G \equiv \dot{W}/\dot{A} = F_{ave}/w$.[21]

3. Results and Discussion

3.1. Effect of the Internetwork Cross-Linking between the First and Second Networks. Comparing the mechanical properties shown in Figure 2, both the *a*- and *i*-PAMPS gels (initiator concentration: 0.1 mol %) are very weak, fractured at low stress and strain (σ is $\sim$ 0.2 MPa and γ is $\sim$0.3). This is a typical behavior of common brittle polyelectrolyte gels. The quite similar mechanical properties of both the *a*- and *i*-PAMPS gels mean that the structures of both are not so different. However, after the second polymerization of PAAm in both gels, the mechanical properties of the *c*- and *t*-DN gels, made respectively from the *a*- and *i*-PAMPS gels, become quite different. The *c*-DN gels show anomalously high strength comparing to PAMPS gels; σ of the *c*-DN gels is 7.66 MPa, which is 40 times larger than before, and γ is 0.88, which is 3 times larger than before. On the other hand, the mechanical properties of the *t*-DN gels are not enhanced at all after the second polymerization; σ of the *t*-DN gel is 0.37 MPa, which remains much smaller than the *c*-DN gel.

Here, we try elucidating these results by the various assumptions described in the Introduction. If one of the previous assumptions, such as the entanglement, the molecular interaction, or the cross-linking reaction induced by the fracture or chain transfer reaction during second polymerization, is the main factor of the toughening by un-cross-linked second network, both the *c*- and *t*-DN gels must be strengthened by the second polymerization because they should affect both type of DN gels similarly. However, the *t*-DN gels are actually quite weak in contrast with the tough *c*-DN gels; consequently, the experimental results cannot be explained by only these assumptions. On the contrary, they can be explained easily by our new assumption. That is, when the *c*-DN gels are synthesized from the *a*-PAMPS gels, the covalent bonds are formed between the two networks via the remained double bonds of MBAA in *a*-PAMPS gels; as a result, the second PAAm forms the "network" structure via the PAMPS network and can sustain force; thus, the *c*-DN gels exhibit an extremely high strength. On the other hand, in the case of *t*-DN gels, synthesized from *i*-PAMPS gels, the covalent bonds between the two networks are not formed because no residual double bonds exist in *i*-PAMPS gels; therefore, the *t*-DN gels are not toughened at all by the un-cross-linked second network.

As explained above, these results straightforwardly imply that the interpenetrated linear PAAm without any cross-linking does not strengthen PAMPS gels at all. On the other hand, PAAm in the *c*-DN gels is not linear in actual; the second PAAm in the *c*-DN gels is no doubt chemically inter-cross-linked with the first network PAMPS gels through the remained double bonds of MBAA. It is noted that the structure of the *c*-DN gels is neither semi-IPN gel nor full-IPN gel; it should be called semi-ICN (inter-cross-linked network) gel.

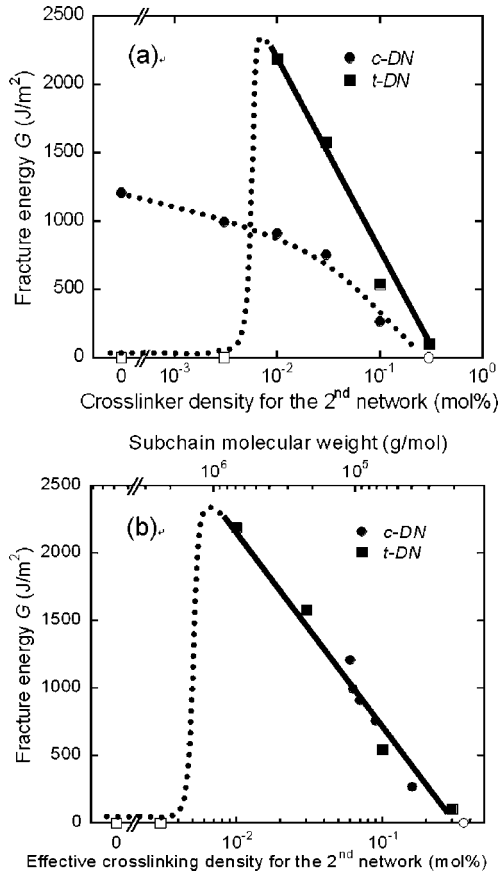

Figure 3. Fracture energy G of *connected*-DN (*c*-DN) gels and *truly independent*-DN (*t*-DN) gels as a function of (a) the cross-linker density of the second network and (b) the effective cross-linking density of the second network. Open symbols indicate too weak samples to be measured by tearing test. Solid straight lines are the fitted curve to the experimental equation as described in the text.

3.2. Effect of the Cross-Linking Density of the Second Network. In the last paragraph, the importance of the cross-linkage of the second network for the toughness of DN gels was confirmed. On the basis of this result, we come into another idea that *i*-PAMPS gels may be strengthened by polymerizing AAm in the presence of the cross-linker, MBAA, to form a truly independent double network. Figure 3a shows the fracture energy G of the *t*- and *c*-DN gels with the second network PAAm polymerized in the presence of various amount of cross-linker densities. In the case of *c*-DN gels, G has the highest value $\sim$1200 J/m^2 when the cross-linker density of the second network PAAm gels is zero,[18] and G decreases monotonically as the cross-linker density increased. On the contrary, in the case of the *t*-DN gels, G takes too small value to be measured when the cross-linker density is less than 0.01 mol %. However, as the cross-linker density increases over a critical value $C^*_{\text{2nd cross-linker}}$ about 0.01 mol %, G suddenly shows the maximum value $\sim$2200 J/m^2, which is about 2 times larger than the highest G of the *c*-DN gels. This extraordinarily large G is the highest of hydrogels as far as we know. (It is noted that in tensile test some *t*-DN gels deformed largely. Thus, it is sometimes difficult to determine the exact value of G compared to other cases.) The critical value $C^*_{\text{2nd cross-linker}}$ probably means the minimum cross-linking density necessary to synthesize substantial PAAm gels; if the cross-linker density is below $C^*_{\text{2nd cross-linker}}$, the second PAAm network cannot form the substantial gels; as a consequence, G shows quite lower values.

Above the critical cross-linker density $C^*_{\text{2nd cross-linker}}$, the G of the *t*-DN gels decreases as the cross-linker density increases, and the G can be fitted to the following experimental equation as shown in Figure 3a:

$$G = -759 - 1477 \log(C^{t\text{-DN}}_{\text{2nd cross-linker}}) \quad (1)$$

where $C_{\text{2nd cross-linker}}$ [mol %] is the cross-linker density of the second network in feed in the *t*-DN gels. Summarizing the results, it is confirmed that in spite of a large structural difference between conventional chemical cross-linkage and INC, they operate similarly as cross-linking points of the second network and effectively enhance the toughness of DN gels; additionally, the less cross-linker is used, the larger G of the *t*-DN gels becomes.

Here, on the basis of this theory that the cross-linking by forming INC points and by forming independent PAAm network play the same role in the mechanical toughness of DN gels, we also apply eq 1 for estimating the equivalent density of INC, C_{INC}, for *c*-DN gel. That is

$$G = -759 - 1477 \log(C^{c\text{-DN}}_{\text{2nd cross-linker}} + C_{\text{INC}}) \quad (2)$$

For the first network prepared in the same conditions, C_{INC} should be independent of $C^{c\text{-DN}}_{\text{2nd cross-linker}}$. By substituting the G and $C^{c\text{-DN}}_{\text{2nd cross-linker}}$ of the five *c*-DN gels shown in Figure 3a into eq 2, C_{INC} were calculated. Expect for the case of $C^{c\text{-DN}}_{\text{2nd cross-linker}} = 0.1$ mol %; C_{INC} estimated from eq 2 shows the almost same value of 0.059 ± 0.007 mol %, regardless the change in the cross-linker density of the second network. This determined value is convenient to estimate the amount of the effective cross-linking density of the *c*-DN gels; it is roughly calculated by "the cross-linker density of the second PAAm network in feed + 0.06 [mol %]". By using this estimation scheme, we replotted the fracture energy G of both the *c*-DN and *t*-DN gels as functions of the effective cross-linking density in both DN gels, as shown in Figure 3b. It is confirmed that both the G can be fitted to the same straight line of eq 1.

In conclusion, the *t*-DN gels are able to be toughened by the cross-linked second network, and an optimal second network cross-linker density of 0.01 mol % is observed to toughen the *t*-DN gels. Above this optimal value, the toughness of the *t*-DN gels decreases with the increase in the second cross-linker density. In *c*-DN gels, PAAm forms internetwork cross-linking through residual double bonds existing in PAMPS network, which serves as an equivalent cross-linking as that in *t*-DN gels for PAAm. The equivalent cross-linking density by the INC is estimated as 0.06 mol % for the *c*-DN gels of which the PAMPS is synthesized at an initiator concentration of 0.1 mol %. This equivalent cross-linking density is about 6 times larger than the optimal cross-linking density of the strongest *t*-DN gels. So the *c*-DN gels in the present conditions are weaker than the *t*-DN gels.

3.3. Effect of the Initiator Concentration for the First Network Polymerization. As just mentioned above, the optimized *t*-DN gel was stronger than the *c*-DN gels because the latter has too many internetwork (between the first and second networks) cross-linking (INC) points. If the INC density can be controlled, *c*-DN gels as tough as the optimized *t*-DN gel might be synthesized. We guess the INC density can be controlled by the concentration of the initiator in the first network polymerization. According to the radical polymerization theory, the excess initiator that is not used for the radical polymerization of PAMPS gels will attack the unreacted double bonds of cross-linker MBAA in the gels to make the bonds inert. Thus, the more initiator we used, the less unreacted double bonds remained in the *a*-PAMPS gels and the less INC density in the *c*-DN gels.

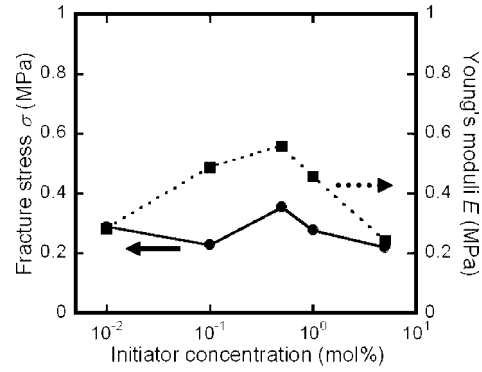

Figure 4. Compressive fracture stress σ and Young's moduli E of *active*-PAMPS (*a*-PAMPS) gels as a function of the initiator concentration.

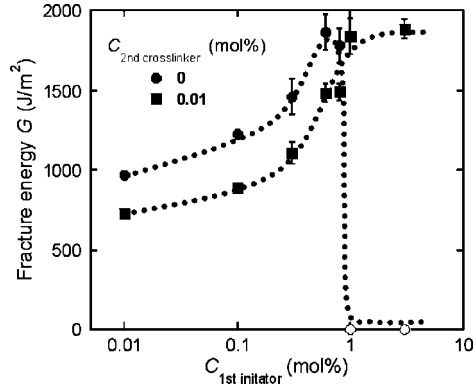

Figure 5. Fracture energy G of *connected*-DN (*c*-DN) gels as a function of the initiator concentration of the first network. The cross-linker density in feed of the second network is 0 or 0.01 mol %. Open symbols indicate too weak samples to be measured by the tearing test.

However, when a large amount of initiator is used for preparation of gels, not only the density of residual double bonds but also the network structure of gels may change. Hence, at first, in order to assess the influence of the network structure changing, the mechanical properties of the first network PAMPS gels were observed. Figure 4 shows the fracture stress σ and Young's moduli E of the *active*-PAMPS gels prepared with various initiator concentration. The fracture stress of the gels is almost independent of the initiator concentration. On the other hand, the Young's modulus shows the broad peak related to the initiator concentration. Excess initiators lead to the formation of dangling chains and the lack of initiators tends to disturb the figuration of entire network, so the optimum initiator concentration for the Young's moduli exists, and it is 0.5 mol % in this system.

We synthesized and measured the two kinds of *c*-DN gels: one was without any second cross-linker ($C_{\text{2nd cross-linker}}$: 0 mol %), and another was with the lowest critical amount of second cross-linker ($C_{\text{2nd cross-linker}}$: 0.01 mol %). Figure 5 shows the fracture energy G of the *c*-DN gels with various initiator concentrations for the synthesis of the first network PAMPS gels. In the case of $C_{\text{2nd cross-linker}} = 0.01$ mol %, G increases simply with the increment of initiator concentration and shows the constant value when the initiator concentration reaches more than 1 mol %. On the other hand, in the case of $C_{\text{2nd cross-linker}} = 0$ mol %, G similarly increases at first with the increment of initiator; however, when the initiator concentration reaches 1 mol %, G decreases so steeply that they cannot be measured. It looks there is no relationship between these behaviors of G and the properties of the first network gels shown in Figure 4, and the results are rather inconsistent with our prediction. The more

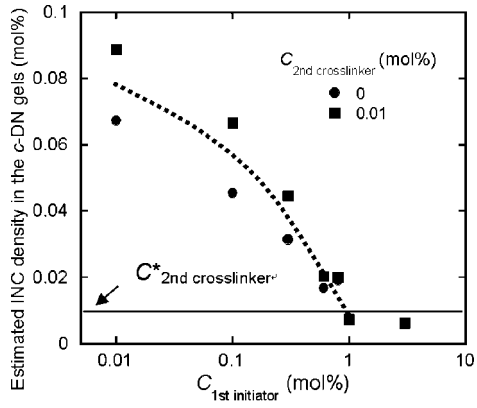

Figure 6. Estimation of the internetwork cross-linking (INC) density in the *connected*-DN (*c*-DN) gels against the initiator concentration for the first network polymerization, calculated from the fracture energy of the *c*-DN gels consisting of not cross-linked (●) or loosely cross-linked (■) second network referred to Figure 5 by eq 1. The solid line indicates the lowest critical cross-linker density of the second network, $C^*_{\text{2nd cross-linker}}$, for the *truly independent*-DN (*t*-DN) gels.

initiators are infused, the less residual double bonds are formed, so *G* increases straightforwardly with the initiator concentration at first. In addition, it is easily predicted that the double bonds practically disappear when the concentration of initiator reaches the critical value. In this study, this critical value can be assumed as 1 mol % as the behavior of *G* switched significantly at this point. When more initiators are used, there is only a few or no remained INC in the gels. Hence, *G* of the DN gels without second cross-linker decreases steeply due to shortage of INC, whereas *G* of the DN gels with 0.01 mol % second cross-linker retains the same value because the effective cross-linking density of PAAm becomes equal to the initial cross-linker density (0.01 mol %).

Finally, *G* of the strongest *c*-DN gel reaches ~1900 J/m^2, which is almost the same as the value of the optimized *t*-DN gel. Based on the results shown in Figure 5, the optimal initiator concentration for the first network is 0.6 mol % for preparing the strongest *c*-DN gels without the cross-linker for the second network. It is a kind of magic initiator concentration for preparing the strongest *c*-DN gels conveniently.

3.4. Estimation of the Internetwork Cross-Linking Density in the DN Gels. The results shown in Figure 5 also imply that the INC points between the first and the second networks in the *c*-DN gels decrease as the initiator concentration for the first network increases; in addition, almost all the INC points of the *c*-DN gels are extinct by using more than 1 mol % of the initiator. Here, we try to estimate the density of INC for various initiator concentrations from Figure 5 by adopting eq 2 once again.

Figure 6 shows the estimated C_{INC} as a function of the initiator concentration for synthesizing the first network. There are two sets of data. One is estimated from *G* of the *c*-DN gels without cross-linker for the second network ($C^{\text{c-DN}}_{\text{2nd cross-linker}} = 0$ mol %). The other is estimated from *G* of the *c*-DN gels with the lowest critical amount of the second cross-linker ($C^{\text{c-DN}}_{\text{2nd cross-linker}} = 0.01$ mol %). As shown in Figure 6, in both cases, the estimated C_{INC} decreases as the initiator concentration increases. When the first initiator is 0.1 mol %, which is the same condition for the results shown in Figures 2 and 3, the estimated C_{INC} becomes ~0.06 mol %. It is consistent with the results in Figure 3b. When the initiator concentration is higher than 1 mol %, the estimated C_{INC} becomes lower than 0.01 mol %. It is also consistent with the results shown in Figure 5. That is, when the INC density is lower than the lowest critical value $C^*_{\text{2nd cross-linker}} = 0.01$ mol %, the second PAAm cannot form substantial network; hence, the *c*-DN gels become quite weak.

It should be emphasized again that the *t*-DN gels can be possibly prepared by using a sufficient amount of the initiator for the preparation of the first network. However, the excess amount of the initiator also affects the polymerization and the number of dangling chains of the first network probably increases. With these careful considerations, this technique with the excess initiator is useful to prepare the *t*-DN gels. Also, it is why there is an optimal initiator concentration for the first network for preparing the strongest *c*-DN gels without the cross-linker for the second network, as mentioned above.

Finally, we should mention the direct identification of C═C double bonds in the *a*-PAMPS gels or the covalent bonds of the INC points between the two networks of the *c*-DN gels, which is crucially important for this study. We have struggled to identify the unreacted double bonds or INC points by using various available methods, such as NMR, FT-IR, Raman spectroscopy, DLS, and UV/vis measurements; however, any definite evidence could not be obtained because of their weak signal. Based on the present results, the density of unreacted double bonds in the *a*-PAMPS gels is estimated as 0.08−0 mol %, depending on the initiator concentration in synthesizing the PAMPS gels (Figure 6). Therefore, even for the maximum case of 0.08 mol %, it corresponds to a relative concentration of 8×10^{-4} to PAAm that is the main component of the DN gels, and an absolute concentration of 1.6×10^{-3} M, as can be calculated from $8 \times 10^{-4} \times 2$ M (of AAm). This low concentration is probably the reason why we could not directly recognize the signal from the residual double bond by spectroscopy. Nevertheless, we believe that the presence of the unreacted double bonds in the *a*-PAMPS gels is well revealed by many consistent results obtained in the present study. These facts have essentially answered our puzzle on why the *c*-DN gels with the second network polymerized in the absence of the second cross-linker shows the highest strength. Additionally, we continue this study to obtain direct evidence of the unreacted double bonds and hope that it will be shown in the future.

4. Conclusion

We have created the *t*-DN gels having truly independent double network structure and revealed the true chemical structure of the *c*-DN gels. We found that in the *c*-DN gels the second network synthesized without the cross-linker is actually connected to the first network by copolymerizing with the unreacted cross-linker of the first network, which forms internetwork cross-linking (INC) points. This structure explains the anomalously high strength of the *c*-DN gels without adding any cross-linkers for the second network. That is, the force applied to the DN gel is transferred to from the first network to the second one through this interconnected structure. On the other hand, the *t*-DN gels, which consist of two truly independent and interpenetrated network structures, also show a high toughness when the cross-linker density of the second network is just above the lowest critical and optimal value $C^*_{\text{2nd cross-linker}}$. Furthermore, we established an empirical relationship between *G* and the cross-linker density of the second network. The *G* of the *c*-DN gel can also be expressed by this relationship by substituting the cross-linker density with an effective value. This result indicates that the INC in the *c*-DN gels and the cross-linking of PAAm in the *t*-DN gels have the similar effect on the force transfer during the fracture process of the DN gels. As the *t*-DN gels have a more simple structure than that of the *c*-DN gels, we expect that the toughening mechanism of anomalously strong DN gels will be clarified by studying the *t*-DN gels.

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References and Notes

(1) Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 485.
(2) Haraguchi, K.; Takeshita, T. *Adv. Mater.* **2002**, *14*, 1121.
(3) Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. *Adv. Mater.* **2003**, *15*, 1155.
(4) Malkoch, M.; Vestberg, R.; Gupta, N.; Mespouille, L.; Dubois, P.; Mason, A.; Hedrick, J.; Liao, Q.; Frank, C.; Kingsbury, K.; Hawker, C. *Chem. Commun.* **2006**, *26*, 2774.
(5) Myung, D.; Koh, W.; Ko, J.; Hu, Y.; Carrasco, M.; Noolandi, J.; Ta, C. N.; Frank, C. W. *Polymer* **2007**, *48*, 5376.
(6) Weng, L.; Gouldstone, A.; Wu, Y.; Chen, W. *Biomaterials* **2008**, *29*, 2153.
(7) Na, Y.-H.; Tanaka, Y.; Kawauchi, Y.; Furukawa, H.; Sumiyoshi, T.; Gong, J. P.; Osada, Y. *Macromolecules* **2006**, *39*, 4641.
(8) Webber, R.; Creton, C.; Brown, H. R.; Gong, J. P. *Macromolecules* **2007**, *40*, 2917.
(9) Brown, H. R. *Macromolecules* **2007**, *40*, 3815.
(10) Tanaka, Y. *Europhys. Lett.* **2007**, *78*, Art. No. 56005.
(11) Tanaka, Y.; Kawauchi, Y.; Kurokawa, T.; Furukawa, H.; Okajima, T.; Gong, J. P. *Macromol. Rapid Commun.* **2008**, *29*, 1514.
(12) Lake, G. J.; Thomas, A. G. *Proc. R. Soc. London* **1967**, *300*, 108.
(13) Na, Y.-H.; Kurokawa, T.; Katsuyama, Y.; Tsukeshiba, H.; Gong, J. P.; Osada, Y.; Okabe, S.; Karino, T.; Shibayama, M. *Macromolecules* **2004**, *37*, 5370.
(14) Huang, M.; Furukawa, H.; Tanaka, Y.; Nakajima, T.; Osada, Y.; Gong, J. P. *Macromolecules* **2007**, *40*, 6658.
(15) Tominaga, T.; Tirumala, V. R.; Lin, E. K.; Gong, J. P.; Furukawa, H.; Wu, W. L. *Polymer* **2007**, *48*, 7449.
(16) Tominaga, T.; Tirumala, V. R.; Lin, E. K.; Gong, J. P.; Wu, W. L. *J. Phys. Chem. B* **2007**, *112*, 3903.
(17) Tirumala, V. J.; Tominaga, T.; Lee, S.; Butler, P. D.; Lin, E. K.; Gong, J. P.; Wu, W. L. *J. Phys. Chem. B* **2007**, *112*, 8024.
(18) Tanaka, Y.; Kuwabara, R.; Na, Y.-H.; Kurokawa, T.; Gong, J. P.; Osada, Y. *J. Phys. Chem. B* **2005**, *109*, 11559.
(19) Tsukeshiba, H.; Huang, M.; Na, Y.-H.; Kurokawa, T.; Kuwabara, R.; Tanaka, Y.; Furukawa, H.; Osada, Y.; Gong, J. P. *J. Phys. Chem. B* **2005**, *109*, 16304.
(20) Furukawa, H.; Kuwabara, R.; Tanaka, Y.; Kurokawa, T.; Na, Y.-H.; Osada, Y.; Gong, J. P. *Macromolecules* **2008**, *48*, 7173.
(21) Anderton, G. E.; Treloar, L. R. G. *J. Mater. Sci.* **1971**, *6*, 562.

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