Effect of Polymer Entanglement on the Toughening of Double Network Hydrogels

Hiroyuki Tsukeshiba,[†] Mei Huang,[†,‖] Yang-Ho Na,[†] Takayuki Kurokawa,[†] Rikimaru Kuwabara,[†] Yoshimi Tanaka,[‡] Hidemitsu Furukawa,[†] Yoshihito Osada,[†] and Jian Ping Gong*,[†,§]

Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan, Creative Research Initiative, Hokkaido University, Sapporo 001-0021, Japan, and SORST, JST, Sapporo 060-0810, Japan

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The mechanical strength of double network (DN) gels consisting of highly cross-linked poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) as the first component and linear polyacrylamide (PAAm) as the second component has been investigated by varying the molecular weight of the second polymer PAAm, M_w. The experimental results reveal that, for toughening of the DN gels, (1) M_w is one of the dominant parameters; (2) there is a critical value of $M_w = 10^6$ for a remarkable enhancement; (3) the fracture energy of DN gels with a M_w larger than 10^6 reaches a value as high as 10^3 J/m^2. By plotting the strength of DN gels (fracture stress σ and fracture energy G) against a characteristic parameter of $c[\eta]$, where c is the average concentration of PAAm in the DN gels and $[\eta]$ is the intrinsic viscosity of PAAm, it is found that the dramatic increase in the mechanical strength of the DN gels occurs above the region where linear PAAm chains are entangled with each other. Thus, we conclude that the entanglement between the second component PAAm plays an important role of the toughening mechanism of DN gels. This result supports the heterogeneous model, which predicts the presence of "voids" of the first network PAMPS with a size much larger than the radius of the second polymer PAAm.

1. Introduction

Hydrogels have been paid great attention as soft and wet matter[1] from various perspectives; for example, swelling properties and stimuli responsiveness have been extensively studied. In industry, superabsorbent polymer (SAP) and soft contact lenses are substantially successful examples of hydrogel applications.[1]

Recently hydrogels have become especially attractive due to the new application such as soft and wet machine,[2] lubricating material,[3] and cell scaffolds in tissue engineering.[4] Despite their high potential as smart materials, the low mechanical strength was a significant disadvantage from a practical standpoint.

Gel scientists have strived to establish a useful method to create tough gels. In several recent years, several great achievements have been made. Haraguchi et al. synthesized nanocomposite gel with a homogeneously dispersed clay sheet as a cross-linker, which shows a resistance to extension as large as 1000%;[5] Okumura and Ito have created topological gel with figure-of-eight cross-linkers which is able to slide along polymer chains and consequently to equalize the tension of polymer chains;[6] Gong et al. succeeded in creating a tough double network (DN) gel, which is a kind of interpenetrated gel prepared in the following two-step gel formation: the first step is gelation of rigid polyelectrolyte (the first network), and in the second step flexible neutral polymers (the second network) are synthesized in the first network.[7] The DN gels, containing 90% water, exhibit compressive fracture strength of more than 20 MPa and a rather high Young's modulus (ca. 0.1 MPa).

It was clarified that the toughening of the DN gels is realized when the first network is a highly cross-linked polyelectrolyte gel and the second network consists of weakly cross-linked or even un-cross-linked neutral polymers. In addition, the mono-molar ratio of the second to the first network should be a few dozen.[7] For example, the fracture energy G of a DN gel, consisting of poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) as the first network and poly(acrylamide) (PAAm) as the second network (PAMPS/PAAm DN gels), reaches a value as high as 10^3 J/m^2, when it is synthesized in an optimized condition. The value is much larger than the fracture energy of individual PAAm gel (ca. 10 J/m^2) and PAMPS gel (ca. 0.1 J/m^2).[8−10]

The remarkable enhancement of the DN gels cannot be explained in terms of existing theories proposed for different mechanisms enhancing the fracture energy G of the soft polymeric systems, such as Lake−Thomas theory[11] and de Gennes theory.[12] For example, if the fracture energy is estimated by the Lake−Thomas theory, G is around 10 J/m^2, two orders less than the experimental value of tough DN gels.[8]

A rheological characterization of the DN gels shows that the bulk response of the DN gels to an applied shear deformation is nearly elastic within a strain amplitude of 0.1% in a frequency range from 10^{-2} to 10 Hz. This should be attributed to the large amount of water (90 wt %) contained in the PAMPS/PAAm DN gels.

The DN gels are highly transparent in a wavelength of 300−800 nm, indicating no phase separation between the two polymer components. Dynamic light scattering (DLS) measurement showed that slow modes, probably corresponding with the Rouse mode of the PAAm solution, exists in the tough PAMPS/PAAm DN gels with a low or non-cross-linked density of PAAm.[13] To permit a Rouse-like motion of the second component in the

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* To whom correspondence should be addressed.
† Graduate School of Science, Hokkaido University.
‖ On leave from Institute of Pharmaceutical Engineering, Zhejiang University, Hangzhou 310027, China.
‡ Creative Research Initiative, Hokkaido University.
§ JST.

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highly cross-linked first network, voids with a size ξ_{void} much larger than the average mesh size of the first network, ξ, are expected to exist in the first PAMPS network. These results suggest that the large "voids", filled with viscoelastic PAAm, play an important role for the enhancement of G.

We consider that a key to elucidating the toughness of the DN gels is its dependence on the molecular weight M_w of the PAAm chains, because M_w affects entanglement between PAAm and PAMPS and between PAAm, and then the entanglement leads dissipative processes resistant to crack growth. For example, if the enhancement of the G is due to the chain sliding of PAAm in PAMPS network, the relative size of the PAAm chain to the average mesh size of PAMPS, ξ, would be crucial; on the contrary, if the voids play a role of crack stopper, the relative size of the PAAm chain to the voids would be important for the enhancement.

In this study, we have prepared PAMPS/PAAm DN gels with different molecular weight M_w of the second PAAm polymer (the gels have un-cross-linked second networks), while keeping the structure of the first PAMPS network constant, and investigate the effect of M_w on the fracture strength σ and fracture energy G of the DN gels.

2. Experimental Section

To investigate the effect of M_w on the mechanical strength, it is necessary to control M_w. M_w in the DN gels can be changed by adjusting the amount of the initiator I in the second polymerization; however, determination of it is impossible. Hence, the following strategy is made. We prepare a series of PAAm solution with the same compositions as the second networks and a series of two-component polymer solutions of PAMPS and PAAm (PAMPS + PAAm) by polymerizing AAm in PAMPS solutions and determine the relationship between $M_w(I)$ and the amount of the initiator I for the each series of solutions by GPC measurement. If $M_w(I)$ for PAAm and for PAMPS + PAAm solutions fall onto a common behavior (this is actually the case as seen in Figure 2), we judge that the existence of PAMS chains does not disturb the distribution of the molecular weight of PAAm and apply $M_w(I)$ for PAAm solutions to that of the DN gels. The detailed procedures for our experiment are described in the following subsections.

(2.1) Materials. Acrylamide (AAm) was recrystallized from chloroform and dried prior to use. 2-Acrylamido-2-methylpropanesulfonic acid (AMPS) was recrystallized from boiling methanol and dried under vacuum prior to use. N,N'-Methylenebis(acrylamide) as cross-linker (MBAA) was recrystallized from ethanol. 2-Oxoglutaric acid as initiator was purchased from Aldrich and used as received. Poly(acrylamide) (PAAm, $M_w =$ 12 000, 80 000, 600 000, 5 000 000, 9 000 000) used as standard polymer for GPC analysis was obtained from Polysciences Inc (Warrington, PA). Milli-Q treated distilled water was used to prepare all aqueous solutions.

(2.2) Synthesis of Linear Polymer. *(2.2.a) Synthesis of Linear PAMPS.* Polymerization of AMPS was carried out in the same conditions as that of PAMPS hydrogels, without cross-linker. The PAMPS compound was obtained by freeze-drying after being dialyzed against deionized water for a week in order to remove unreacted monomer and other ions. This PAMPS is used to prepare the solutions for gel permeation chromatography (GPC) measurement.

(2.2.b) Synthesis of Linear PAAm. Solutions of 2 M AAm monomer containing various amounts of initiator ($I = 0.005-2$ mol %) were prepared with Milli-Q water. Then the sample solution was polymerized by the UV irradiation. The poly-

merized PAAm solution was directly used for GPC analysis without any purification.

For comparison, PAAm is also polymerized from the AAm solutions in the presence of 20.7 wt % PAMPS linear polymer. The concentration of PAMPS corresponds to that of PAMPS gel used as the first network of DN gel, which has a swelling degree of 50, about 0.1 M AMPS concentration.

(2.3) GPC Analysis. M_w of PAAm was determined by GPC measurement using a HITACHI L-7110 pump and a HITACHI 7490 RI detector, using a method the same as in a previous study.[14,15] The GPC pump was equipped with a HITACHI L-7200 autosampler and controlled by a computer with the Millennium Chromatography Manager. The sample solution (20 μL) of 0.1$-$0.2 wt % in concentration was injected and delivered through a Φ4 mm $\times$ 30 mm reversed-phase guard column and a reverse-phase Shodex KB-806 column with a size of Φ4.6 mm $\times$ 300 mm. The column temperature was set as 40.0 °C, and 0.1 M NaNO$_3$ was used as elution solvent (flow rate = 0.3 mL/min). All HPLC samples were prepared with elution solvent, and standard PAAm compounds were used for calibration.

(2.4) Synthesis of the DN Gels. The DN gels were synthesized by a two-step sequential network formation technique following the previous reports.[7] As the first step, PAMPS gel is polymerized from 1 M AMPS aqueous solution containing 4 mol % cross-linker of MBAA and 0.1 mol % initiator of 2-oxoglutaric acid (both relative to AMPS). Photoinitiated polymerization was carried out at room temperature under exposure to a UV lamp for 10 h. The polymerized PAMPS gel was immersed into 2 M AAm aqueous solution containing various amount of initiator I for at least 1 day. After the swollen PAMPS gel was then taken out from AAm aqueous solution, the second polymerization of AAm was carried out in the first network under the same experimental condition as before. The volume change of DN gels is very small from the as-prepared state after swelling in water.

(2.5) Elemental Analysis. To evaluate the amount of PAA chains that get out from the DN gels during the swelling treatment, the contents of nitrogen, N, and sulfur, S, of the gels were determined by elemental analysis (MT-6 CHN CORDER, Yanaco Co., and DX-500, Dionex Co.), and the molar ratio of AAm to AMPS was estimated from the results. (The amount of MBAA is small and neglected.)

(2.6) Mechanical Measurements. The mechanical strength of the DN gels was evaluated by a combination of compression test and tearing test. The compression test, determining the compressive fracture stress, can be used whether the sample gel is brittle or tough. However, the data for tough gels include large errors, because the breaking point could not be precisely detected due to high compressive deformations. On the other hand, although the tear test determining the fracture energy G cannot be carried out for brittle gels, it can present a quantitative evaluation for the mechanical strength of tough DN gels.

(2.6.a) Compression Test for Determining Fracture Stress. The compressive stress$-$strain measurements were performed on the DN gels swollen in water for 7 days, using a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.) with the original attachments (made by ARAI SEISAKUSYO).[7] A cylindrical gel sample of 9 mm diameter and 5 mm thickness was set on the lower plate and compressed by the upper plate of the attachment, which was connected to a load cell, at a strain of 10% thickness/min. The strain ratio, γ, is defined by $\Delta L/L$, where L is the initial thickness of the sample and ΔL is the change of the thickness. Young's modulus was calculated from the stress$-$strain curve in a strain range of $0 < \gamma < 0.1$. Fracture
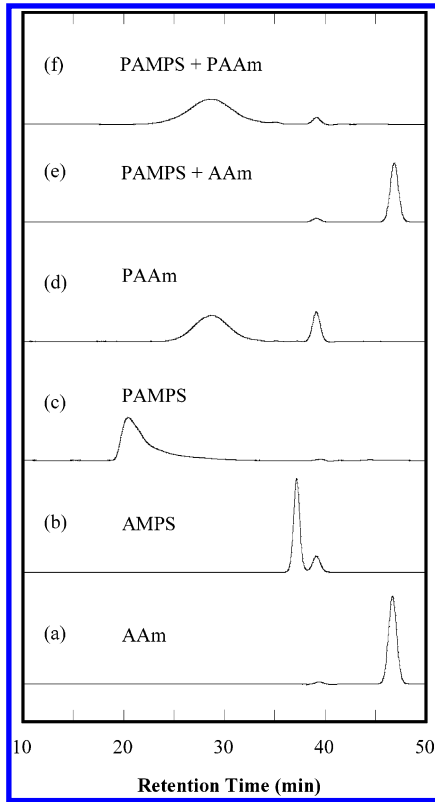
Figure 1. Retention times of solutions containing AAm (a), AMPS (b), PAMPS (c), PAAm (d), PAMPS + AAm (e), and PAMPS + PAAm (f). The elution curve of d represents the sample from the mixture of 0.1 M PAMPS and 2 M AAm, while f corresponds to the sample in which 2 M AAm was polymerized in solution containing 0.5 mol % initiator and 0.1 M PAMPS. The concentrations of AAm (a), AMPS (b), PAMPS (c), PAAm (d), PAMPS + AAm (e), and PAMPS + PAAm (f) solutions were diluted to 0.765, 0.705, 1.312, 4.630, 5.464, and 5.40 mg/mL, respectively, for GPC analysis.

stress σ was determined as the stress at which visible cracks appear in the samples. Data of σ is the average for at least five measurements.

(2.6.b) Tear Test for Determining Fracture Energy. The tear test for the DN gels[8] was carried out using a commercial test machine (Tensilon RTC-1150A, Orientec). Gels were cut in a trouser-shape, which is standardized JIS-K6252 $^1/_2$ size ($w = 5-5.5$ mm; $d = 7.5$ mm; $L = 30$ mm; initial notch = 20 mm), with a gel cutting machine (Dumb Bell Co., Ltd.). The two arms of a test piece were cramped and pulled apart at a constant velocity of 500 mm/min, and the tearing force was recorded. Fracture energy, G, defined as the energy required to create a unit area of fracture surface, is calculated by the following equation,

$$G = \frac{F_{av}}{2w}$$

where F_{av} is the average tearing force and w is the width of the gels.

3. Results

(3.1) Molecular Weight of PAAm. Parts a−f of Figure 1 show the retention times of solutions containing AAm, AMPS, PAMPS, PAAm, PAMPS + AAm, and PAMPS + PAAm, respectively. The notation of PAMPS + AAm represents the two-components solution with 0.1 M PAMPS and 2 M AAm, while PAMPS + PAAm represents a two-components solution
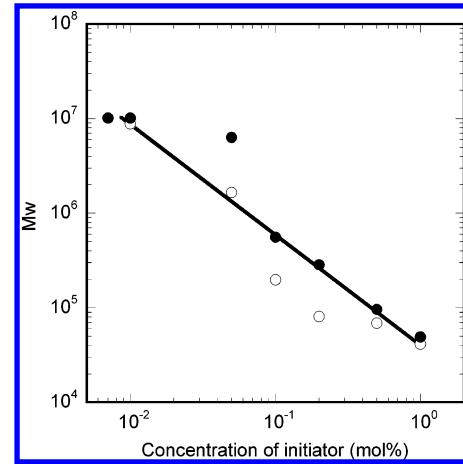

Figure 2. Relationship between the initiator concentration and the molecular weight of PAAm (M_W) polymerized in water (●) and in 0.1 M PAMPS linear polymer (○).

TABLE 1: Summarized Experimental Data of Molecular Weight (M_w), Polydispersity M_w/M_n, the Contour Length L_c (nm), the Equivalent Random Coil Diameter d_η (nm), the Intrinsic Viscosity $[\eta]$ (cm^3/G) of PAAm, and the Molar Ratio R of AAm to AMPS in the DN Gels

$M_w(I)$	M_w/M_n	$[\eta]$ (cm^3/g)	L_c (nm)	d_η (nm)	R (mol/mol)
2.0×10^4	1.7	1.87×10^1	7.30×10^1	7.78×10^0	4.9
1.8×10^5	2.7	8.06×10^1	6.33×10^2	2.63×10^1	5.0
8.8×10^5	3.0	2.32×10^2	3.10×10^3	6.36×10^1	11.5
1.4×10^6	3.9	3.15×10^2	4.92×10^3	8.22×10^1	15
3.4×10^6	6.1	5.69×10^2	1.20×10^4	1.34×10^2	18
5.2×10^6	6.6	7.55×10^2	1.83×10^4	1.70×10^2	19.5
5.2×10^6	7.1	7.55×10^2	1.83×10^4	1.70×10^2	19
8.2×10^6	1.9	1.02×10^3	2.88×10^4	2.19×10^2	20

prepared by polymerizing 2 M AAm with 0.5 mol % initiator in 0.1 M PAMPS solution. The molar ratios of AAm to AMPS in PAMPS + AAm and in PAMPS + AAm solutions are 20, which is the same as that in the DN gels.

By comparing the peaks of PAMPS (Figure 1c) and PAAm (Figure 1d), we found that they are not overlapped with each other. Furthermore, since the amount of AAm is in large excess to AMPS, the peak of PAMPS in PAMPS + AAm solution is too weak to be observed (Figure 1e). Therefore, we can characterize $M_w(I)$ of PAAm polymerized with various I in PAMPS solution by GPC without worry about the effect of PAMPS. By comparing Figure 1f and Figure 1d, we found that the peaks of PAAm polymerized in the presence and absence of PAMPS are completely the same. It should be noted that the small peak at a retention time of 39 min always appears due to some system noises.

Figure 2 shows the dependence of molecular weight of PAAm on I polymerized in the presence and absence of 0.1 M PAMPS linear polymer. With the increase of I, the weight average molecular weights of linear PAAm decrease approximately in the same manner regardless of the presence or absence of PAMPS. Therefore, the influence of the PAMPS appears to be much smaller than that of the initiator concentration.

Extrapolating the above observation in the DN gels, we consider that the molecular weight $M_w(I)$ of PAAm polymerized inside the DN gels is the same as that polymerized in water. In the following discussion, $M_w(I)$ for the PAAm polymerized in water is used as $M_w(I)$ in the DN gels.

Table 1 summarizes the average $M_w(I)$, the polydispersity M_w/M_n, the intrinsic viscosity $[\eta]$, the contour length L_c, and the equivalent random coil diameter d_η of the linear PAAm in water.

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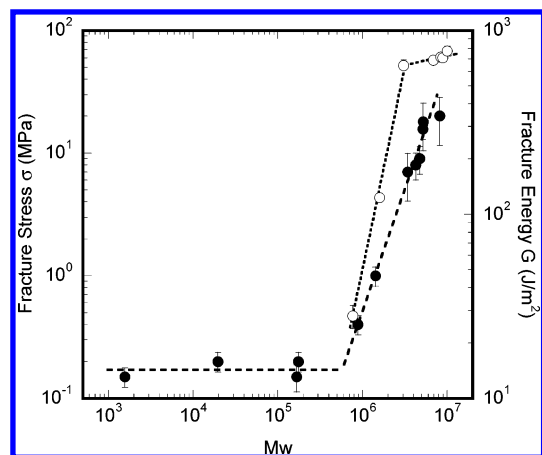*J. Phys. Chem. B, Vol. 109, No. 34, 2005* **16307**

Figure 3. Relationship between the average molecular weight of PAAm (M_w) and the compressive fracture stress (●) and fracture energy (○) of the DN gels. The dashed lines are guides for eyes.

The intrinsic viscosity $[\eta]$ (cm^3/g) is calculated by the Mark−Houwink−Sakurada equation as follows:[16]

$$[\eta] = KM_w{}^\alpha \qquad (1)$$

where $K = 2.58 \times 10^{-2}$ and $\alpha = 0.665$ are determined by GPC using standard samples. The contour length L_c (nm) is calculated by multiplying M_w with 0.25 nm/71.08, where 0.25 nm is the monomer size and 71.08 is the monomeric molecular weight of AAm, respectively. The equivalent random coil diameter d_η (nm) is calculated from[16]

$$d_\eta/nm = 1.08 \times 10^{-1}\sqrt[3]{[\eta]M_w} \qquad (2)$$

Since PAAm chains are physically trapped in the PAMPS network, they could diffuse out of the gel for a prolonged time. This would affect the mechanical strength of the gel, because the concentration of the second polymer is one of the two main parameters of the mechanical strength of DN gel.[7] So, we estimate the loss of the second PAAm by diffusion for DN gels swollen in large amounts of water for a prolonged time. Just after the second polymerization, without swelling, the molar ratio of AAm to AMPS was 20 (mol/mol), regardless of the change in initiator I for PAAm polymerization. The molar ratios of AAm to AMPS for samples swollen in water for 1 month were estimated from the results of elemental analysis, and the data are shown in Table 1. It reveals that the amount of PAAm diffused out of gels depends on M_w. High molecular weight PAAm remains inside the gel after 1 month; low molecular weight PAAm diffuses out of the gel. The cutoff is around $M_w = 10^6$.

(3.2) Mechanical Property of DN Gels. *(3.2.1) Fracture Stress.* All the samples have a Young's modulus of 0.3 (±0.04) MPa, regardless of the change in M_w of PAAm. However, the strength of the DN gels is strongly dependent on the M_w of PAAm, as shown in Figure 3. The filled circles in Figure 3 show the relationship between M_w and the compressive fracture stress σ of the DN gels. A notable increase in the strength of DN gel is observed when M_w is around a value of 10^6. On the other hand, the strength of the samples does not change when M_w is below the critical value. As mentioned above, the error of σ becomes larger for $M_w > 10^6$, i.e., for tough gels. However, we believe the behavior of σ for high M_w in Figure 3 is reliable, because it corresponds well with the behavior of the fracture energy G described below.

(3.2.2) Fracture Energy. For the gels with $M_w > 10^6$, the tear test was performed just after the second polymerization, i.e., without the swelling treatment, since the loss of PAAm by diffusion is negligible. The open circles in Figure 3 show the fracture energy G of the DN gels. We find that G increases with M_w sharply in a range of $1 \times 10^6 < M_w < 3 \times 10^6$, and above it, G saturates to a value.

By comparing the results from the two different measurements, we conclude that the strength of the DN gels strongly depends on M_w and dramatically increases with M_w in the range of $1 \times 10^6 < M_w < 3 \times 10^6$.

4. Discussion

The first network PAMPS takes an extended conformation in water due to the high osmotic ionic pressure, and the average mesh size ξ of the network is in an order of several nanometers.[17] From Table 1, it is clear that both the contour length L_c and the d_η of PAAm are much larger than the ξ of the first network PAMPS for $M_w < 10^6$, which does not show any enhancement in the mechanical strength. This indicates that the PAAm entanglement with PAMPS, which should occur even for $M_w < 10^6$, is not responsible for the toughening of the DN gels.

In the previous paper, we found, by DLS measurement, that the presence of a slow mode besides the usual gel mode (fast mode) is closely correlated with the enhancement of the strength of DN gels. Then, an inhomogeneous structure model, which consists of a PAMPS network with large "voids" and flexible PAAm polymers ("void model") has been proposed.[13] According to the model, the size of "void" (ξ_{void}) is considered to be much larger than the PAAm radius (d_η) as well as the mesh size of the first network PAMPS (ξ), at the extreme as large as several micrometer, although ξ is around several nanometers. Therefore, the PAAm in the voids may play an important role.

Supposing that the voids are relevant for the strength of the DN gel and that PAAm exists in the voids behaves as solution, we discuss a physical meaning of the critical molecular weight $M_w = 10^6$ on the basis of the theory of polymer solution. The rheological properties of a polymer solution strongly depends on the concentration of the polymer; and the concentration can be categorized into the following three regions: (1) dilute solution region, where random coils of the polymer do not come into contact with each other; (2) semidilute region, where polymer chains overlap with each other, (3) concentrated region, where polymer chains are entangled with each other. The product of the polymer concentration c (g/cm^3) and the intrinsic viscosity $[\eta]$ (cm^3/g) gives the nondimensional parameter determining which regime the polymer solution is in. In general, the condition $c[\eta] = 1$ is a criterion for the boundary between the diluted and semidiluted regions. For PAAm aqueous solution, it has been reported that $c[\eta] \approx 10$ corresponds with the boundary between the semidiluted and concentrated regions.[15]

To characterize the region of the PAAm inside the void of the DN gels that is effective for enhancing the mechanical strength of gel, we calculated the equivalent concentration of PAAm in the DN gels from Table 1 and replot Figure 3 in terms of $c[\eta]$, and the results are shown in Figure 4. In estimation of c, the loss of PAAm due to the diffusion is considered [we ignore the change of M_w: if we take account of it, the left three data (filled circles) in Figure 4 shift right; however they should stay in the foot of the "hill"; hence, the following discussion is not modified]. We have ignored the change of M_w due to the loss by diffusion, and M_w in Table 1 was used for the calculation.
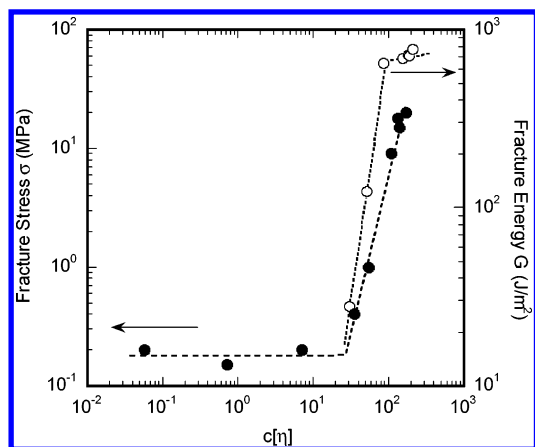
Figure 4. Strength of the DN gels against $c[\eta]$ calculated from the data in Table 1. Here, c is the concentration of the second PAAm in the DN gels taken into account of the lost by diffusion, $[\eta]$ is the intrinsic viscosity of PAAm (cm^3/g) calculated from the average molecular weight of PAAm (M_w) using eq 1.

The curves turned out to show dramatic transition in mechanical around $c[\eta] \approx 20$, which well coincides with the critical entanglement point of PAAm solution. Therefore, the drastic increase in the mechanical strength of DN gels occurs when PAAm chains are entangled with each other. This result also helps us to understand why the ratio of AAm to AMPS of the DN gels is another important criterion that influences the mechanical property. We found that the fracture energy saturates at a $c[\eta]$ value of about 100; a further increase in $c[\eta]$ does not enhance the strength.

5. Conclusions

Previous research revealed that the tough DN gels are obtained only when (1) the gel consists of polyelectrolyte gel as the first network and neutral polymer as the second network, (2) the molar ratio of the first to the second component is a few dozen, and (3) the first component is tightly cross-linked and the second one is in linear state or loosely cross-linked. From this work, not only the concentration of the second linear polymer but also (4) the molecular weight of the second linear polymer (M_w) is a prior parameter related to the mechanical strength of DN gels. When M_w is lower than 10^6, DN gels are as fragile as PAMPS single network gel, showing a $\sigma \approx 0.1$ MPa and a G less than 1 J/m^2. When $M_w > 10^6$; however, the strength of the DN gels dramatically increases and saturates at $M_w = 3 \times 10^6$, attaining values as high as $\sigma \approx 20$ MPa and $G \approx 10^3$ J/m^2.

Since the contour length L_c and the radius of the random coil d_η of PAAm linear chain having a molecular weight of $M_w > 10^6$ is much larger than the average mesh size of the first network ξ, this prominent molecular weight effect of the PAAm cannot be explained in terms of the chain sliding mechanism in the PAMPS network. According to the inhomogeneous model based on the structural analysis with DLS measurement, we found the critical molecular weight corresponding to the criteria of physical entanglement of PAAm chains with each other in the void of the first network with a size ξ_{void} much larger than the radius of the PAAm chains. Above the entanglement condition, the second PAAm is not only interpenetrated to the PAMPS network but also forms a very soft continuous network due to the physical entanglement (Figure 5).

Consequently, we consider that the provided "void" and "entanglement" probably play two major roles at the crack tip; the first is making curvature larger to prevent stress concentra-
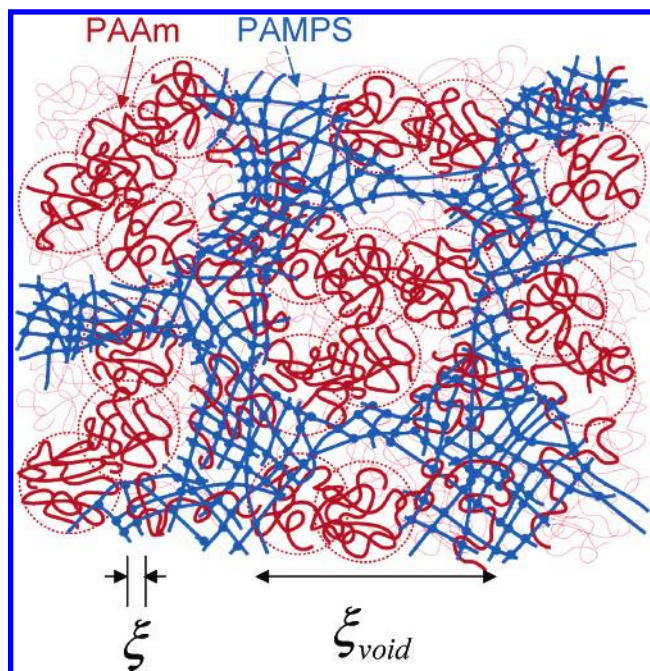

Figure 5. Inhomogeneous structure model modified from ref 13 for the tough DN gels. The first network PAMPS has a mesh size ξ of several nanometers with large "voids" of size $\xi_{void} \gg \xi$. The second component PAAm chains are in a concentrated region, and they both entangled with each other and with the PAMPS network. For clarity, only some of the PAAm chains are highlighted by bolder lines. The voids that filled with concentrated PAAm act as a "crack-stop" to enhance the mechanical strength of the DN gels.

tion, and the second is energy dispersion or resistance of fracture energy. Thus, both effects reduce stress around the leading edge of crack propagation to prevent the crack, growing to a macroscopic level. That is, the void acts as "crack stop". Generally, fracture in polymers are accompanied by various molecular processes, such as chain uncoiling, scission, and chain pullout at the interface, when two surfaces are created as a result of crack propagation. We suppose the same is true in this case, and inside the void, physically entangled PAAm plays the major part of energy-consuming process, and this process becomes effective at the entanglement condition of PAAm. This toughening mechanism gives us the tough hydrogel with high swelling degree.

Okumura has discussed the Griffith criterion for heterogeneous materials consisting of a soft phase with an elastic modulus μ_s and a hard phase with μ_h to propose an essential mechanism for the extremely large G of the DN gels.[18] The relevance of the model for the tough DN gels is under study yet.

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