Importance of Entanglement between First and Second Components in High-Strength Double Network Gels

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ABSTRACT: The double network (DN) gels, composed of a minor component, chemically cross-linked polyelectrolyte (first network), and the major one, linear neutral polymer (second network), exhibit anomalously high mechanical strengths. In this study, adopting the concentration of the second polymer as the experimental parameter, we investigate the relation between the mechanical strength and the dynamics of polymer concentration fluctuation. The former is measured by compression and tearing tests; the latter is measured by a special dynamic light scattering technique (called SMILS) suitable for polymer gels. The mechanical strength is enhanced when the concentration is so high that the second polymer chains strongly entangle each other. The main finding of SMILS is that the diffusion constant of the concentration fluctuation of the second polymer is increased by the existence of the first network despite the minority of the first component ($<^1/_{10}$ in monomer ratio to the second component). This indicates that there is entanglement also between the first and the second polymers. The inter-species entanglement and inhomogeneities of the first network suggested in our previous study [*Macromolecules* **2004**, *37*, 5370] give support to the crack model concerned with yielding around the crack tip, which explains the high mechanical strength.

1. Introduction

In order to realize practical use of polymer gels, such as artificial tissues and flexible machine parts, we need to make a great improvement in their mechanical strength. However, the gels are a dilute system; conventional gels show very low mechanical strength,[1] compared with rubbers. In addition, polymer gels inevitably contain frozen inhomogeneities due to the concentration fluctuation during gelation processes.[2] The inhomogeneities mainly work as mechanical defects; it is well-known that chemically cross-linked gels with turbidity, often observed at high cross-linker concentrations and indicating the existence of strong inhomogeneities, are very easy to break.

Recently, some different approaches to improve the strength of gels have been proposed.[3,4] One of the successful cases is a remarkable development of topological gels,[3] which are cross-linked with figure-of-eight molecules slidable along the linear chains. Because of the movable cross-link structure, the position of each polymer chain can be adjusted in response to external deformation; topological gels should be free from the stress concentration caused by the frozen inhomogeneities. In fact, topological gels can sustain large strain and stress compared with the usual chemical gels. Another successful case is nanocomposite gels,[4] cross-linked with clay particles on which the linear chains can adsorb. It is proposed that for nanocomposite gels, the frozen inhomogeneities are suppressed even at high cross-linker (i.e., the clay) densities and that this property affects the high mechanical strength.

Our group has also realized another novel high-strength gels[5] by introducing a double network (DN) structure inside the gels, i.e., reinforcing a tightly cross-linked rigid gel (first network) with mutually entangled flexible long polymers (second network) penetrating in the first network. Among various combinations of hydrophilic polymers,[5] the best combination in our past study is poly(2-acrylamido-2-methylpropanesulfonic acid), PAMPS, as the first network and poly(acrylamide), PAAm, as the second network. A DN gel synthesized at an adequate composition, despite the approximately 90 wt % water content, shows anomalously high compressional fracture stresses of $\sigma \sim 40$ MPa and fracture energy of $G \sim 700$ J/m^2. The high mechanical strength of DN gels contrasts with the weakness of the corresponding pure PAMPS gel, $\sigma \sim 0.2$ MPa and $G \sim 1$J/m^2, and with the slackness of the corresponding bare PAAm linear chains that behave as a sticky sol (i.e., it is not able to retain any definitive shape under gravity). DN gels can be regarded as a kind of IPN (interpenetrating polymer network) in a limiting condition that the two components have extremely asymmetrical mechanical properties. Interestingly, as for bulk mechanical property, the existence of the second PAAm is hidden with the rigid first PAMPS network (e.g., Young's modulus of a DN gel is almost the same as that of the corresponding PAMPS gel), the effect of PAAm arises as the anomalously high resistance for fracture. Further interestingly, the fracture energy G hardly depends on crack velocity V (described below), suggesting the high strength is not merely a consequence of the usual viscoelasticiy of the second PAAm.

In order to sublimate the empirical recipe for DN gels into a principal for the design of various high-strength gels, we carried out a series of fundamental studies,[5−7] where the composition of the first PAMPS network was fixed, while molecular weight and cross-linking density of the second network were varied. Mechanical measurements revealed the following conditions required to accomplish the anomalously high mechanical strength:

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(P1) The molar ratio of PAAm (for the second network) to PAMPS (for the first network) should fall at least into a range of several to a few decades.[5]

(P2) The second network should not contain substantial chemical cross-linkage. The DN gels with the anomalous high strength are obtained only when the first PAMPS is highly cross-linked and the second PAAm is without chemical cross-linkage or slightly cross-linked (the role of the slight cross-linkage is probably to increase effective molecular weight of the PAAm chains, rather than to make percolated PAAm networks). The fracture energy G decreases with the cross-linking density of the second network.[6]

(P3) For DN gels with uncross-linked second PAAm, the molecular weight M_w of PAAm should be higher than a critical value falling in a range of 10^5-10^6.[7]

These previous results indicate that the second PAAm should be in highly entangled states to exhibit the anomalously high mechanical strength.

(P4) In addition, G very weakly depends on the crack velocity V.[6]

We emphasis that the above four results cannot be explained by the well-known mechanisms to enhance the fracture energy G of the soft polymer systems, i.e., chain stretching[8] and sliding[9] in the vicinity of the crack tip and bulk viscoelasticity.[10] For example, if the chain stretching effect of PAAm dominates the fracture energy, G is around 10 J/m^2, 1−2 orders of magnitude less than the experimental value of tough DN gels.[6,7] The chain sliding mechanism is also inconsistent with the previous result (P4) because, according to the mechanism, G should be roughly proportional to V.[9] The bulk viscoelasticity effect cannot work well, because the polyelectrolyte nature of the first network provides large elastic modulus to DN gels and tan δ in rheological measurements remains at small values, of a few percent (on the order of 0.01) for a frequency range of 0.1−100 Hz.[6]

On the other hand, dynamic light scattering measurements on DN gels[11] show the existence of an uncommon slow relaxation mode. To explain this result, we proposed a "void model", where the first PAMPS network contains voidlike structures while the second PAAm chain undergoes slow concentration fluctuation. In connection with this, a scaling theory based on a heterogeneous structural model was proposed to explain the anomalous high strength of DN gels.[12] The theory, however, does not make a concrete consideration on what kind of isotropic heterogeneity can enhance the mechanical strength. Thus, it is impossible to compare the theoretical prediction with the experiment in detail.

Very recently, we have started to vary the structure of the first PAMPS network by changing the composition and the gelation method, and we have found a new kind of DN gel showing a necking phenomenon.[13] That is, on tensile tests on the gels, yielding deformation occurs in a part of the sample, and a "neck" (narrowing zone) appears and grows up with further elongation. During the neck propagation, a plateau region appears in the loading curve. The plateau value of the tensile stress does not depends much on the stretching rate. After the neck propagation, the gel becomes fairly soft (but not sol) and sustains large elongations (up to an elongation ratio of $\lambda \sim 20$). It is probable that the first heterogeneous network breaks into small clusters during the necking deformation and the clusters play a role of cross-linker of the second PAAm chains. The necking phenomenon can be regarded as a damage accumulation of the first network and suggests a new fascinating hypothesis for the anomalous toughness of the original (former) DN gels:[13] if the softened zone is formed in a mesoscale region around the crack tip (Figure 1), it should cause remarkable energy dissipation, resulting in enhancement of the fracture energy. An advantage of the hypothesis is that it does not conflict with the previous result (P4). Further, as described later (in the Discussion), it is also compatible with the main result of the present study, i.e., the existence of effective entanglement between the first PAMPS and the second PAAm.

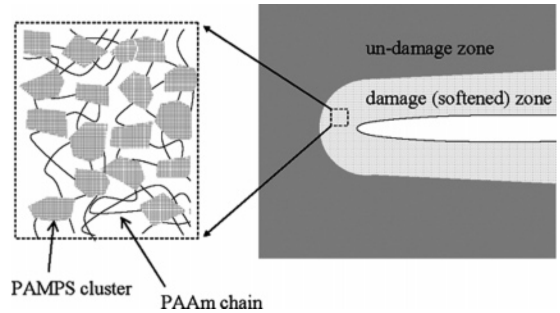

Figure 1. Schematic representation of the localized softening mechanism for the anomalous high mechanical strength of DN gels proposed in ref 13.

In the present study, we return to the former structure of the first network that produces DN gels without necking (on the macroscopic scale), and investigate the effect of the concentration of the second PAAm, C_{PAAm}, maintaining average molecular weight at a constant value. The present study is complementary to the previous study,[7] in which the effect of molecular weight was investigated at a constant C_{PAAm}. In addition, we present experimental results of dynamic light scattering (DLS) measurement carried out with a special apparatus suitable for inhomogeneous gels.[14] (The specialized DLS technique is called "SMILS".) The aim of SMILS measurement is to investigate structural feature of DN gels from behavior of dominant relaxation modes. The present experimental results indicate that the anomalous high mechanical strength of DN gels is closely related to the entanglement among the polymer chains in the system. In the Discussion, we further consider the effect of the entanglement in DN gels in the context of proposed fracture mechanisms.

2. Experiments

Sample Preparation. The detailed synthesis protocol of DN gels was described in ref 5; hence, we briefly explain the essential point. All the first PAMPS gels were synthesized from a common aqueous solution containing AMPS monomer, cross-linker of *N,N′*-methylenebis(acrylamide) (MBAA), and radical initiator of ketoglutaric acid at the following composition: AMPS 1 M, MBAA 4 mol %, and ketoglutaric acid 0.1 mol % (the molar percentages are with respective to the AMPS monomer). After the gelation reaction was completed (the reaction was induced by ultraviolet irradiation), the first PAMPS gels were then soaked in precursor solutions for the second PAAm network, containing AAm monomer and ketoglutaric acid (without MBAA). Two series of PAAm solutions were prepared. For one series, the PAAm concentration was systematically changed and the molar percentage of ketoglutaric acid (with respect to the AAm monomer) was kept at 0.1 mol %. For the other series, the PAAm concentration was changed and the molar percentage of ketoglutaric acid was kept at 0.01 mol %. After the swelling equilibrium was reached, the gels were exposed with ultraviolet irradiation to activate the polymerization reaction of the AAm. We regard the AAm concentration of the immersion solutions as the concentration C_{PAAm} of PAAm chains in the finished DN gels; this can be justified by the following facts: (i) the volume of the PAMPS gels increases up to about 10 times during the immersion (the AMPS concentration of the PAMPS gels shrank to about 0.1 M), that is, the concentration of AAm in the immersed gels is close to that of the surrounding solutions; (ii) the reaction efficiency of AAm is very high. The rough estimations of the molecular weight of PAAm, M_w, are 5.6×10^5 g/mol for the former series and 1.0×10^7 g/mol for the latter series. (These values were evaluated by GPC measurements on the two-component polymer solutions of PAMPS and PAAm, synthesized from solutions of AAm monomer and pre-existing PAMPS chains at compositions corresponding to DN gels.[7])

Mechanical Strength Measurement. Compressional fracture stress σ and fracture energy G were measured in the same manner as in ref 6. The measurement of σ was performed on cylindrical (5 mm in thickness and 9 mm in diameter) gels; the compression rate is 0.1/min. The fracture energy G was measured by tearing tests on trouser-shaped samples (5 mm in thickness (along the crack front line), 30 mm in length (with 20 mm initial "legs"), and 7.5 mm in width); the tearing velocity was 500 mm/min.

Scanning Microscopic Light Scattering. Quantitative determination of the minute network size was performed with the scanning microscopic light scattering (SMILS) system.[14,15] SMILS was recently developed for the minute characterization of network structure in inhomogeneous polymer gels. Conventional light scattering systems are hardly used to quantitatively characterize the network structure in chemically cross-linked polymer gels since static inhomogeneities that are inevitably memorized in chemically cross-linked polymer gels sometimes cause undesired large scattering intensity due to interference, which prevents the exact quantative characterization. However, SMILS enables us to scan and measure at many different positions in an inhomogeneous gel, in order to rigorously determine a time- and space-averaged, i.e., ensemble-averaged, (auto-) correlation function of fluctuating concentration in the gel. By analyzing the determined ensemble-averaged function, it is possible to quantitatively characterize the relaxation-time distribution of polymer gels, which is related to their network structure. Here, we take the advantage of SMILS to investigate the inner structure of DN gels based on the dynamics of polymer concentration fluctuation in DN gels. DN gel samples for SMILS were prepared in sample tubes of 10 mm inner diameter and were observed in as-prepared state at 30 °C. For each sample, the measurement was carried out on 50 positions spaced 100 μm apart. According to the procedure in ref 14, we calculated the space and time-average of the data on light scattering signal, and obtained the ensemble-averaged dynamic structure factor, $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau)$, by a formulas proposed in ref 14. Since $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau)$ of most samples showed two-step relaxation behavior (the details are described in the next section), we carried out further data analysis as follows: we assumed a superposition of two logarithmic Gaussian distributions (LGD) as the fitting function for the relaxation time distribution $P_{\mathrm{en}}(\tau_R)$ for $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau)$

$$P_{\mathrm{en}}(\tau_R) = A_{\mathrm{fast}} \exp\left[-\frac{(\ln \tau_R - \ln \tau_{\mathrm{fast}})^2}{2{\sigma_{\mathrm{fast}}}^2}\right] + A_{\mathrm{slow}} \exp\left[-\frac{(\ln \tau_R - \ln \tau_{\mathrm{slow}})^2}{2{\sigma_{\mathrm{slow}}}^2}\right] \quad (1)$$

where τ_{fast} and τ_{slow} are characteristic relaxation times, A_{fast} and A_{slow} are the amplitudes, and σ_{fast} and σ_{slow} are the logarithmic peak widths for the fast and slow modes, respectively. Then, $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau)$ can be approximately expressed by a superposition of many exponential functions[14]

$$\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau) = N \sum_{i=1}^{n} P_{\mathrm{en}}(\tau_{R,i}) \exp\left[-\frac{\tau}{\tau_{R,i}}\right] \quad (2)$$

where $\{\tau_{R,i}\}$ is a geometric progression expressed as $\tau_{R,i} = \tau_{R,\min}(\tau_{R,\max}/\tau_{R,\min})^{(i-1)/n}$ ($i = 1, 2, ..., n$), and N is a normalized factor defined as $N = (1/n)\ln(\tau_{R,\max}/\tau_{R,\min})$. By using eq 2, the nonlinear least fitting of $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau)$ to the right-hand side of eq 2 was performed, where six parameters, τ_{fast}, τ_{slow}, A_{fast}, A_{slow}, σ_{fast}, and σ_{slow}, in eq 1 were treated as fitting parameters. The fitting was performed with $\tau_{R,\min} = 10^{-6}$ s and $\tau_{R,\max} = 10^0$ s, and $n = 40$ for all cases. These six parameters were then determined by the requirement of minimize the following residual

$$\Omega = \left\{\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(\tau) - \int P_{\mathrm{en}}(\tau_R) \exp\left[-\frac{\tau}{\tau_R}\right] d\left(\frac{1}{\tau_R}\right)\right\}^2 \quad (3)$$

Then, the area of each peak was determined by $S_i = \sqrt{2\pi}\sigma_i A_i$, (subscript i is "fast" or "slow"), where S_i satisfies $S_{\mathrm{fast}} + S_{\mathrm{slow}} = 1$. The "LGD scheme" can also be extended for multiple relaxation cases.

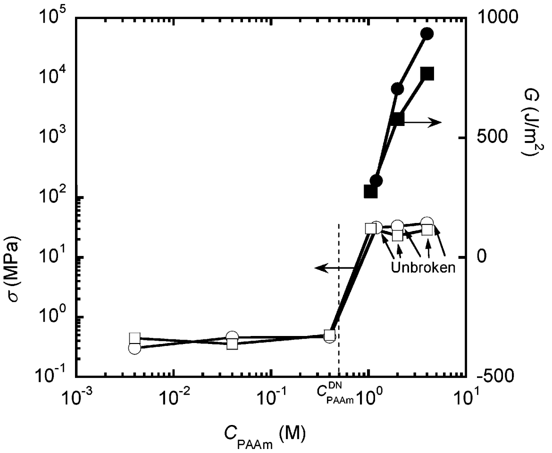

Figure 2. Fracture stress σ and the fracture energy G of as-prepared DN gels, as a function of the second linear PAAm concentration C_{PAAm}: (□, ■) σ and G for $M_w = 5.6 \times 10^5$, (○, ●) σ and G for $M_w = 1.0 \times 10^7$. Tearing velocity for G measurement: 500 mm/min.

3. Results

Mechanical Strength. In the compression test, the Young modulus determined from the initial slope of S−S curve is almost independent of C_{PAAm} and also almost the same as that for the pure PAMPS gel swollen in water. On the other hand, the mechanical strength drastically increases above a critical value of C_{PAAm}. Figure 2 shows C_{PAAm} (the PAAm concentration) dependence of the compressive fracture stress, σ, and the fracture energy, G. For $C_{\mathrm{PAAm}} \leq 0.4$ M, σ is about 0.5 MPa, this is close to the value for the pure PAMPS gel used as the first network of DN gels. Thus, in this region of C_{PAAm}, the existence of the second PAAm has no effect on the mechanical strength of DN gels. On the other hand, above $C_{\mathrm{PAAm}} \approx 0.5$ M, σ begins to increase, and for $C_{\mathrm{PAAm}} \geq 1.0$ M the gels become anomalously tough: they do not break even at quite large compression strains above 90% (indicated in Figure 2). We assign the value of $C_{\mathrm{PAAm}} = 0.5$ M as the characteristic concentration $C_{\mathrm{PAAm}}^{\mathrm{DN}}$ for the enhancement of the mechanical strength. For $C_{\mathrm{PAAm}} > C_{\mathrm{PAAm}}^{\mathrm{DN}}$, the tearing measurement is feasible; the measured fracture energy G steeply increases with C_{PAAm}. It should be noticed that there is no remarkable difference in the mechanical strength between the samples with $M_w = 5.6 \times 10^5$ and those with $M_w = 1.0 \times 10^7$. This indicates that the molecular weight M_w of the second polymer does not directly affect the mechanical strength provide it is sufficiently large (see the previous result (P3) mentioned in the Introduction).

SMILS Measurement on DN Gels. We present, in Figure 3 and Figure 4, results of SMILS on DN gels. Figure 3a shows representative data on the dynamic correlation function measured with different scattering vector q, where the ensemble-averaged dynamic component of the structure factor $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}$ is plotted as a function of $q^2\tau$. The data of $\Delta\mathscr{G}_{\mathrm{en}}^{(1)}(q^2\tau)$ measured at different scattering vectors fall onto a single curve showing a two-step

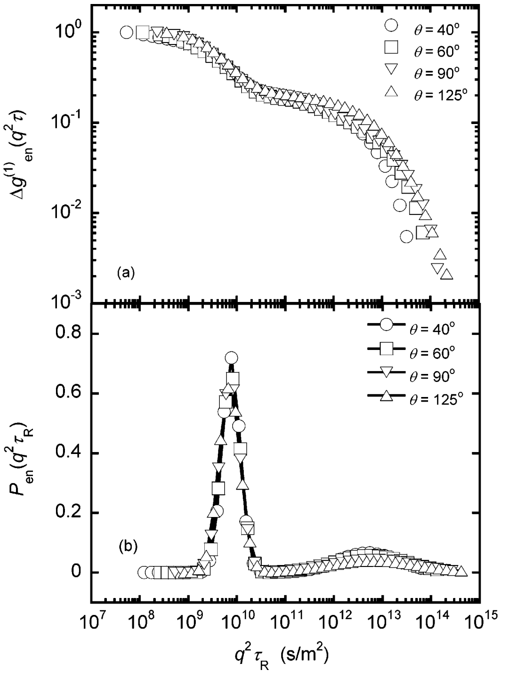

Figure 3. (a) q^2-scaled correlation function $\Delta g_{en}(q^2\tau)$ and (b) the q^2-scaled relaxation-time distribution $P_{en}(q^2\tau_R)$ for as-prepared DN gels with second linear PAAm molecular weight at $M_w = 1.0 \times 10^7$, $C_{PAAm} = 2$ M in preparation. The symbols indicate different scattering angles.

relaxation, indicating the existence of two relaxation modes (referred as "fast mode" and "slow mode") coming from translational diffusion dynamics. The existence of the two modes is consistent with our previous study.[11] Figure 3b shows the corresponding relaxation time distribution $P_{en}(\tau_R)$ and their fitting curve determined by the LGD scheme. With an usual formula from the theory of Brownian motion, $D = 1/(q^2\tau_R)$, we can estimate the typical values of the diffusion constant for the both modes from the peak positions in Figure 3b; for the fast mode, $D_{fast} = 1.6 \times 10^{-10}$ m^2/s, and for the slow mode, $D_{slow} = 3.2 \times 10^{-13}$ m^2/s. The broadness of the peaks can be characterized by the variance, $2\sigma_{fast} = 0.94$ and $2\sigma_{slow} = 4.0$, indicating the relaxation time distribution of the slow mode ranges over about 4 decades. The diffusion constant and the peak broadness are evaluated on other samples.

Figure 4a shows a comparison of the dynamic structure factor with different C_{PAAm}. The slow mode obviously gets indistinctive with increasing C_{PAAm} as seen in Figure 4a, and at the highest C_{PAAm}, 4 M, it completely disappears. Figure 4b shows the relaxation time distribution $P_{en}(\tau_R)$ calculated from $g^{(1)}_{en}(\tau)$ by LGD scheme. The position of the fast mode peak is insensitive to C_{PAAm}. The slow mode peak is suppressed with increasing C_{PAAm}, correspondingly, the height of the fast mode peak increases with C_{PAAm} ($P_{en}(\tau_R)$ is normalized so that the sum of both peak areas is one). It should be noticed that the mechanical strength and the relative area of the slow mode peak S_{slow} depend on C_{PAAm} in the opposite way; in particular, the toughest sample shows no slow mode. On the other hand, the dependence of S_{fast} on C_{PAAm} is very similar to that of G as shown in Figure 4c. A clear correlation between S_{fast} and G can be seen also in Figure 4d. Thus, we mainly focus on the fast mode in the following section, and compare the mode with relaxation modes of corresponding polymer solutions of linear PAAm (and solution of linear PAAm and linear PAMPS) to speculate the structural feature in DN gels.

SMILS Measurement on PAAm Solutions. In this part, we present SMILS results on PAAm *polymer* solutions (and a two component solution of PAAm and PAMPS described later), and compare them with SMILS results and the mechanical strength of DN gels. The linear PAAm solutions were prepared with varying C_{PAAm} from 4×10^{-4} to 2 M, in the same manner as the second network of DN gels (except for the absence of the preexisting PAMPS). It is noted that the highest C_{PAAm} for PAAm solution was set at 2 M although this concentration is lower than the highest C_{PAAm} for DN gels. It is because PAAm solution prepared at high PAAm concentration becomes too viscous to get rid of the small bubbles emerged in preparation. The relaxation time distribution is shown in Figure 5a. We have one main peak of the fast mode (and a very weak peak of the slow mode). The diffusion coefficient D was determined from the sets of peak positions, which were measured at different scattering angles for each samples, and plotted as a function of C_{PAAm} in Figure 5b. For comparison, we also plot the D_{fast} of DN gels in the same figure. (For DN gels with much lower C_{PAAm} than 1 M, the DLS signal is always hindered by the abnormal excess static scattering due to the inhomogeneities of first PAMPS network.) The D of the PAAm solutions increases with C_{PAAm}. There is a bending point in the $D - C_{PAAm}$ relation around $C_{PAAm} = 2 \times 10^{-3}$ M, which corresponds to the crossover concentration C^*_{PAAm} from dilute to semidilute polymer solutions.[17] Around C^*_{PAAm}, the dominant dynamics of the system is switched from the translation motion of independent polymer chains (below C^*_{PAAm}) to the cooperative motion of the overlapping chains (above C^*_{PAAm}); below we use the notation D_{coop} to refer to the diffusion constant above C^*_{PAAm}.

Comparing Figures 2−5, we find out the following three essential points. First, the critical concentration of toughness, C_{DN}, is much larger than C^*_{PAAm}, $C_{DN}/C^*_{PAAm} \sim 50$. (This result is well consistent with the previous results.[7]) The concentration a few tens times higher than C^*_{PAAm} corresponds with the higher critical concentration of the entanglement, that is the boundary between the semidiluted and concentrated regions.[17]

(E1) That is the effect of PAAm chains emerges in the regime of C_{PAAm} where the chains remarkably entangle each other.

Second, D_{coop} for PAAm solutions increases toward D_{fast} of DN gels with increasing C_{PAAm}. At the highest C_{PAAm} for PAAm solutions ($C_{PAAm} \sim 2$ M), D_{coop} becomes close to D_{fast}, where $D_{coop} \approx 0.6 \times D_{fast}$. It is noted that these concentrations are several tens larger than concentration of the PAMPS (~0.1 M), and the pure PAMPS gels corresponding to the first network makes no definite DLS signal, due to the strong static scattering.

(E2) From the above observations, it is pretty certain that the fast mode of DN gels comes from the concentration fluctuation of the PAAm chains.

Third, D_{coop} becomes clost to D_{fast}, however D_{coop} seems always lower than D_{fast}, in the high C_{PAAm} region below 4 M. Perhaps, at 4 M of C_{PAAm}, D_{coop} becomes similar to D_{fast}, although the D_{coop} of the 4 M PAAm solution was not observed in the present study due to its difficulity of treatment as mentioned above. However, for the higest C_{PAAm} for PAAm solutions in the present study ($C_{PAAm} \sim 2$ M), there is a quantitative difference between D_{fast} ($\approx 1.6 \times 10^{-10}$ m^2/s) and D_{coop} ($\approx 1 \times 10^{-10}$ m^2/s). The meaning of this difference is important. Also, it is worth noting that the value of D_{fast} corresponds quite well to the ceiling value of D_{coop} for PAAm gels, which is accomplished in the very high C_{PAAm} (~7 M) region of PAAm gels in a previous study.[14] Furthermore, the other kind of PAAm solution containging linear PAMPS chains (called "DN solution") shows no increase of D_{coop} at 2 M of C_{PAAm}, as shown in Figure 5b.

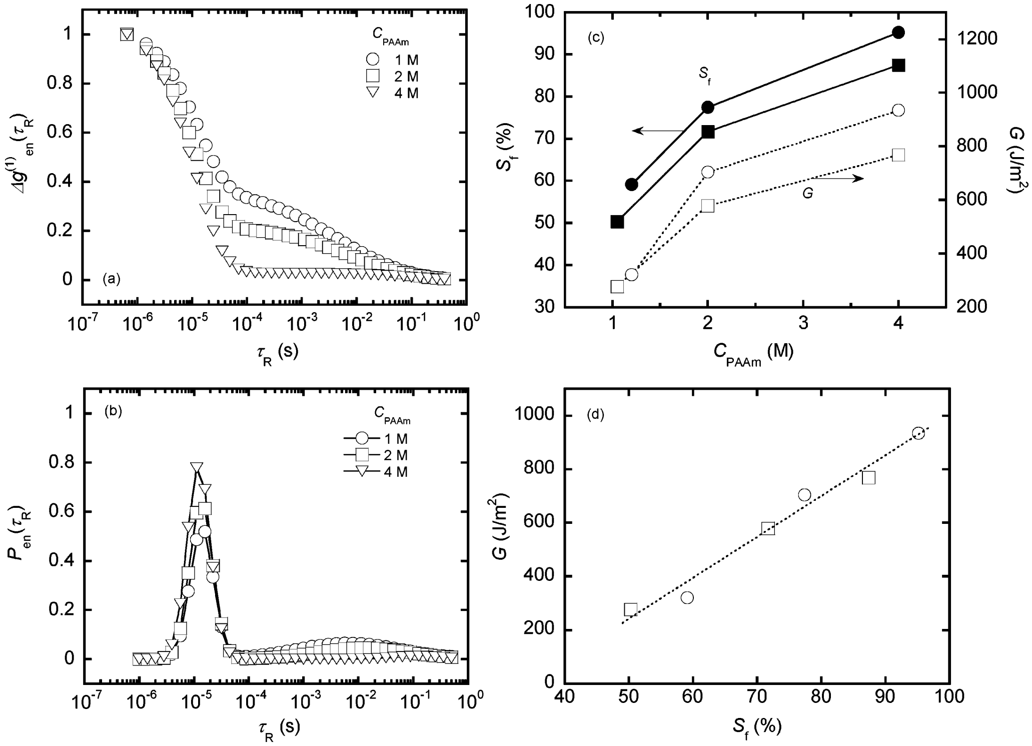

Figure 4. (a) Ensemble-averaged correlation function $\Delta g_{\rm en}(\tau)$ and (b) relaxation-time distribution function $P_{\rm en}(\tau_R)$ for as-prepared DN gels at various second linear PAAm concentrations for $M_w = 1.0 \times 10^7$. The scattering angle is 90°. (c) The fracture energy G and the area of fast mode S_f for as-prepared DN gels, as a function of PAAm polymer concentration $C_{\rm PAAm}$: (■, □) S_f and G for $M_w = 5.6 \times 10^5$, (●, ○) S_f and G for $M_w = 1.0 \times 10^7$. (d) G as a function of S_f: (□) $M_w = 5.6 \times 10^5$, (○) $M_w = 1.0 \times 10^7$. The dashed line is guide to the eye.

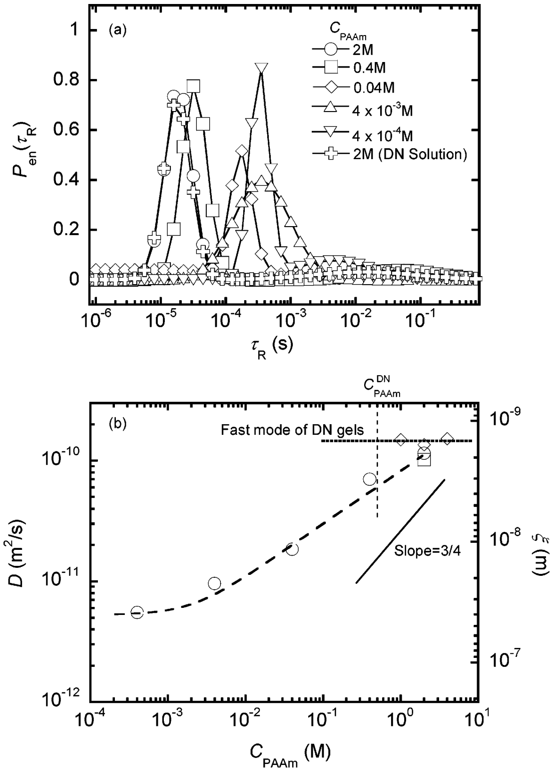

Figure 5. (a) Ensemble-averaged relaxation-time distribution function $P_{\rm en}(\tau_R)$ for linear PAAm and DP solutions for $M_w = 1.0 \times 10^7$. The scattering angle is 90°. (b) Diffusion coefficient D (left) and characteristic size ξ (right) for PAAm, DN solutions and DN gels, as a function of PAAm polymer concentration $C_{\rm PAAm}$: (○) PAAm and (□) DN solutions for $M_w = 1.0 \times 10^7$ and (◇) the fast mode of DN gels.

(E3) From the above observations, the fluctuation dynamics of the second PAAm is influenced by the sparse but the stiff and percolated PAMPS network.

4. Discussion

The experimental finding (E3) shows the existence of some effective interaction between PAMPS and PAAm components. A possible interpretation for the interaction is an inter-species (i.e., PAMPS−PAAm) topological constraint: in DN gels, the PAMPS network plays the role of "skeleton" for the second mutually entangled PAAm chains. Thus, there exists an entanglement between PAMPS and PAAm. In this situation, thermally induced strain of PAMPS network causes the concentraion fluctuation of PAAm component, giving a distinct DLS signal in SMILS for high $C_{\rm PAAm}$ (for pure PAMPS gels or DN gels with low $C_{\rm PAAm}$, the DLS signal is undetectable). In other words, the fluctuation dynamics of both PAMPS and PAAm components are tightly coupled by the inter-species entanglement for high $C_{\rm PAAm}$.

On the basis of the above interpretation, we can explain the reason why $D_{\rm fast}$ for DN gels is substantially larger than $D_{\rm coop}$ for PAAm solutions even in the high $C_{\rm PAAm}$ region around 2 M. In the normal linear polymer solutions, the cooperative diffusion is concerned with the decay of the concentration fluctuation of the polymer; the driving force of the decay is the spatial gradient of osmotic pressure, and the resistance is the friction between polymer and solvent, i.e., PAAm and water in our present case; the cooperative diffusion constant is given by $D_{\rm coop} = K_{\rm os}/\zeta$,[16] where $K_{\rm os}$ is the osmotic compression modulus of PAAm and ζ is the inverse of the permeability constant of water through PAAm. For the case of DN gels, $K_{\rm os}$ should be replaced by the effective modulus of $K_{\rm os} + K_{\rm el}$, where added term $K_{\rm el}$ comes from *elastic* deformation of the first PAMPS network. On the other hand, ζ should be almost the same for the PAAm solutions and for the DN gels, because PAMPS is minor component and ζ is determined by $C_{\rm PAAm}$. This leads to a value of $D_{\rm fast}$ higher than $D_{\rm coop}$. On the basis of this physical picture, we can also explain why $D_{\rm coop}$ of the DN sol is almost

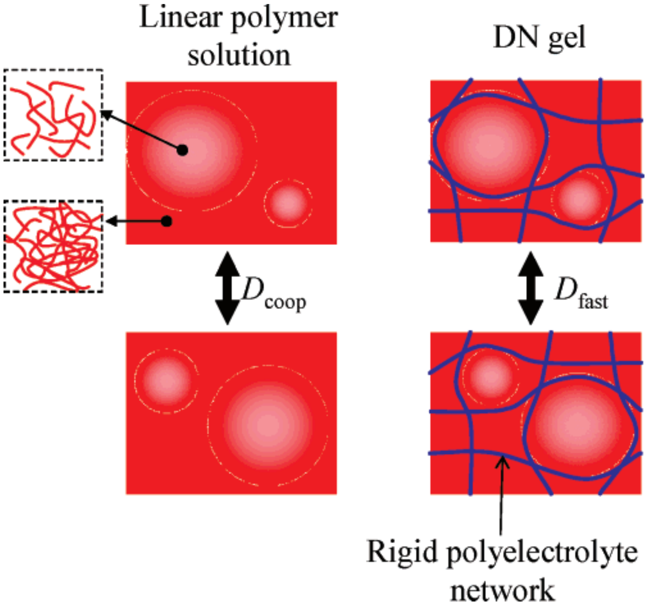

Figure 6. Schematic illustrations of diffusion dynamics in semidilute linear polymer and double-network gels. In semidilute solution, polymer chains are entangled with themselves. The polymer concentration fluctuation of entangled polymer chains is caused by their cooperative diffusion process. On the other hand, in the double-network gels, the major component is the second linear polymer chains, which are entangled not only with themselves but also with the minor component of the first chemically cross-linked rigid polyelectrolyte network. The polymer concentration fluctuation of the major component is coupled with the fluctuating motion of the rigid network. Thus, the apparent cooperative diffusion process of entangled linear polymer chains in double-network gels is to be relatively faster than that in usual semidilute polymer solutions, even if they are at the same polymer concentration.

the same as that of the pure PAAm solution: without cross-linking, the PAMPS component cannot store the elastic energy.

It is certain that $K_{\rm el}$ (from PAMPS) dominates $K_{\rm os}$ (from PAAm), because the PAMPS skeleton is so rigid that the Young modulus of pure PAMPS gel is almost the same as that of the DN gels even for high $C_{\rm PAAm}$. This is a consequence from the polyelectrolyte nature of PAMPS. We may regard the PAAm component as "superabundant and shaggy probe" to detect the concentration fluctuation of the PAMPS network in DN gels in dynamic light scattering observation, as illustrated in Figure 6.

The experimental finding (E1) shows that entanglement is essential for the enhancement of the mechanical strength. As considered above, there are two kinds of entanglement: PAAm–PAAm entanglement and PAMPS–PAAm entanglement. Which is more essential for the anomalously high mechanical strength? We speculate that the PAAm–PAAm entanglement plays a secondary role from the following reasons. (a) If the PAAm–PAAm entanglement worked as the permanent cross-links, addition of the chemical cross-linking to the second PAAm network should facilitate or at least could not seriously disturb the effect of enhancing the mechanical strength. In fact, the addition of a small amount of the chemical cross-linker (MBAA) drastically reduces the mechanical strength to the level of usual PAAm gels (see (P4)). (b) There is a possibility that the PAAm–PAAm entanglement is concerned with a large dissipation due to chain sliding or chain pulling-out. However, these mechanisms are inconsistent with the fact that observed fracture energy is quite insensitive to the crack velocity (see (P4)).

On the other hand, the PAMPS–PAAm entanglement is compatible with the localized softening mechanism proposed in ref 13, because the force transmission from PAAm to PAMPS is indispensable for the mesoscale softened zone to be produced (see Figure 1). (We will make a further description on the connection between the localized softening and structural feature in the last part of this section.)

A remaining problem is the origin of the slow mode. Our interpretation is as follows. The radical polymerization of PAAm with pre-existing PAMPS produces a larger amount of short PAAm chains than that without PAMPS; and the short chains can diffuse in the system, getting past the obstacle of PAMPS and long PAAm chains. This diffusion corresponds to the slow mode. The mode is expected to be slow due to the friction with the obstacle, to have a wide distribution of characteristic time due to the molecular weight distribution of PAAm and inhomogeneities of PAMPS, and to be indistinct (and frozen) for higher $C_{\rm PAAm}$ due to the crowding effect. These three inferences are consistent with the observed behavior of the slow mode.

Before concluding, we address the relation between the present results and our previous studies.[11] In the previous paper,[11] the cross-linking density y of the second PAAm was chosen as experimental parameter, and relaxation time distribution $P(\tau)$ and mechanical strength (fracture stress σ) were measured on DN gels of which the second PAAm chains have lower average molecular weight and a wider molecular weight distribution than the present study. The main findings were as follows:[11] (i) $P(\tau)$ showed broadly distributed peaks of the slow mode when y is zero and the peaks shrunk to disappear with increasing y; (ii) the fracture stress showed a similar dependence on the cross-linking density. We proposed, based on point i, an inhomogeneious structural model that the first PAMPS network contains void-like regions where PAAm chains fluctuate as in usual solutions, producing the slow mode. We also speculated that the finding in point ii indicates that the high mechanical strength of DN gels is caused by dissipation concerned with the slow mode. The latter speculation is denied by the present study in which molecular weight of PAAm chain is larger than in the previous study:[11] as described above, the increase of $C_{\rm PAAm}$ (of un-cross-linked and longer PAAm) results in the increase of the mechanical strength but in the decrease of the slow mode signal; the strongest sample shows no slow mode peak. From the previous and the present studies, we can picture the following structural feature of the tough DN gels: (1) the first PAMPS network is fairy inhomogeneous (containing void regions) and (2) PAMPS and PAAm are strongly entangled with each other. This feature is compatible with the localized softening mechanism (depicted in Figure 1) that assumes that the fragmentation of PAMPS network occurs around the crack tip (corresponding to point 1) and the resultant PAMPS clusters are connected with PAAm chains (corresponding to point 2). Thus, we stress the localized softening mechanism as a potential hypothesis at present.

5. Summary and Conclusion

We have systematically investigated how the mechanical strength and the fluctuation dynamics of DN gels change, depending on the second PAAm concentration $C_{\rm PAAm}$. The mechanical strength is enhanced only when $C_{\rm PAAm}$ is so high that the PAAm chains strongly entangle each other. On the other hand, the relaxation time distribution of the fluctuation shows the existence of two diffusion modes, the fast and slow modes. The fast mode is the counterpart of the cooperative diffusion mode in the usual polymer solutions. However, the diffusion constant of the fast mode $D_{\rm fast}$, almost independent of $C_{\rm PAAm}$ and substantially larger than the cooperative diffusion constant $D_{\rm coop}$, seems to be dominated by the PAMPS skeleton. This indicates the existence of strong entanglement between PAMPS and PAAm in the high C_{PAAm} regime. Such entanglement is consistent with our hypothesis that the anomalous high strength comes from the local softening (i.e., the damage accumulation of the first network) of DN gels.

An essential feature of DN gels is that it consists of two kinds of polymers with asymmetrical mechanical properties. The difference between D_{fast} and D_{coop} can be attributed to this nature of DN gels. In the field of polymer physics, much attention has been paid on dynamics of binary systems consisting of components with extremely asymmetrical properties.[18,19] Beside the problem of fracture, DN gels present an interesting example in such a line of studies.

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