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Three Cooperative Diffusion Coefficients describing Dynamics of Polymer Gels

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Cooperative diffusion coefficient ($D_{coop}$) describes the dynamics of a polymer network in a gel, and is estimated by three independent methods. We measured three $D_{coop}$’s of a model polymer network system (Tetra-PEG gels), and obtained the experimental evidence to fundamentally understand the dynamics of polymer gels.

A hydrogel consists of a three-dimensional polymer network swollen in water. Polymer chains forming the polymer network interact with water molecules and thermally fluctuate. Because the polymer chains are cross-linked, the dynamics of polymer chains are cooperative. T. Tanaka has proposed that this cooperative motion of the polymer chains governs the swelling kinetics of polymer gels.

The cooperative diffusion of a polymer network is described based on the equation of motion for a small deformation of a unit cube in the network. When the inertial force, surface force and body force are balanced on the unit cube (Fig. 1 (a)), the displacement vector ($\mathbf{u}$) obeys the following differential equation.

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \nabla \cdot \mathbf{\sigma} - f \frac{\partial \mathbf{u}}{\partial t}$$  \hspace{1cm} (1)

where $\rho$ is the density of the network, $t$ is the time, $\mathbf{\sigma}$ is the stress tensor, and $f$ is the friction coefficient between polymer network and water. Under spherical symmetry, eq. 1 gives

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{K}{f} \frac{\partial}{\partial r} \left( \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \mathbf{u}) \right)$$  \hspace{1cm} (2)

where $K$ is the bulk modulus, $G$ is the shear modulus, and $r$ is the displacement of a point. From its similarity to the diffusion equation, eq. 2 is called the swelling equation, and the cooperative diffusion coefficient of a polymer gel ($D_{coop}$) is defined as

$$D_{coop} = \frac{K + \frac{4}{3} G}{f}$$  \hspace{1cm} (3)

The value of $f$ in eq. 3 is known to be estimated by water permeation measurements ($f_w$). In this study, we named $D_{coop}$ characterized by $f_w$ as the diffusion coefficient by water permeation ($D_{w}$).

The swelling kinetics is governed by the swelling equation (Fig. 1 (b)). By applying the initial condition that uniform stress is applied to the gel and the boundary condition that the normal stress to the gel surface is zero to eq. 2, the following solution is obtained.

$$\frac{d_n}{d_\infty} - d(t) = \frac{6}{\pi^2} \exp\left(-\frac{t}{\tau}\right)$$  \hspace{1cm} (4)

where $d_n$ is the normalized size of the gel, $d(t)$ is the diameter of the gel at time $t$, $d_\infty$ is the diameter in the initial state, $d_\infty$ is the diameter in the equilibrium state, and $\tau$ is the characteristic time of swelling. Eq. 4 well reproduced the swelling and shrinking behaviors of gels, suggesting the validity of the prediction.

The values of $d_n$ and $\tau$ are related to $D_{coop}$ as

$$D_{coop} = \frac{d_n^2}{\pi^2 \tau}$$  \hspace{1cm} (5)
In this study, we named the diffusion coefficient described by eq. 5 as the swelling diffusion coefficient ($D_{sw}$). It should be noted that $D_{sw}$ is directly estimated from a swelling measurement, independent of $D_a$.

On the other hand, the dynamics of polymer networks has been studied not only by macroscopic experiments but also by dynamic light scattering (DLS).1, 4, 5 Fluctuating polymer networks scatter the light irradiated to the gel (Fig. 1 (c)). Based on the autocorrelation function of the scattered light intensity, the diffusion coefficient is estimated. In this study, we named the diffusion coefficient measured by DLS as $D_{DLS}$. Because previous studies found that $D_{DLS}$ was identical to $D_a$ and $D_{sw}$,1,2 $D_{DLS}$ has been regarded as corresponding to $D_{coop}$.

As mentioned above, there are three independent methodologies to estimate $D_{coop}$. Many researchers have confirmed the correspondence of $D_{DLS}$ and $D_{sw}$ using neutral gels, polyelectrolyte gels, and temperature-responsive gels.3, 4, 6, 7 For example, Shibayama et al. found that the validity of the swelling equation and the correspondence of $D_{DLS}$ and $D_{sw}$ for the swelling and shrinking kinetics of chemically cross-linked polyelectrolyte poly(vinyl alcohol) gels.3, 4 On the other hand, the correspondence of $D_{DLS}$ and $D_a$ has hardly been confirmed, and the experimental evidence supporting the identity of the three $D_s$ is limited. To fully understand $D_{coop}$, a systematic investigation on the effect of network structure on these $D_s$ is vital.

In this study, we investigated three diffusion coefficients using model polymer gels with systematically tuned initial polymer volume fractions ($\phi_0$) and molecular weights between crosslinks ($M_n$) (Tetra5PEG gel). Tetra5PEG gels were formed by mixing two aqueous solutions of tetra-armed prepolymers with mutually reactive end groups (thiol (-SH) and maleimide (-MA)).8 This design enabled us to control $M_n$ and $\phi_0$ independently.9 Our previous small angle neutron scattering (SANS) measurements revealed the extremely low structural heterogeneity in Tetra5PEG gels.9-11 In addition, the relationship between the mechanical properties and network structure is well known.9 Thus, Tetra5PEG gel system is promising as a model polymer gel system. Here, we systematically tuned $M_n$ (10, 20 kg/mol; Tetra5PEG gel 10K, Tetra5PEG gel 20K) and $\phi_0$ (0.034-0.110), and investigated the effects on the three diffusion coefficients ($D_{sw}$, $D_{ao}$ and $D_{DLS}$). The correspondence between these diffusion coefficients and the conceptual cooperative diffusion coefficient was discussed.

To investigate the diffusion coefficient described by eq. 3 ($D_a$), we first measured $K$, $f_w$ and $\pi_{os}$. By the dynamic viscoelasticity measurement, the storage modulus ($G'$) and the loss modulus ($G''$) were measured. Given that $G'$ was much larger than $G''$ and independent of the frequency in the gel state, $G'$ corresponded to the shear modulus ($G$).14 Fig. 2 (a) shows the $\phi_0$-dependence of $G$. The value of $G$ increased with an increase in $\phi_0$. When we focused on Tetra5PEG gels with the same $\phi_0$, $G$ decreased with an increase in $M_n$. These results agreed well with the well-known rubber elasticity theory ($G \sim \phi_0 M_n^\alpha$) as described in our previous studies.9, 10, 12-14

Then, we investigated $K$ defined by the following equation.10

$$K = \phi_0 \frac{\partial \pi_{os}}{\partial \phi}$$ \hspace{1cm} (6)

Here, $\pi_{os}$ is the osmotic pressure. In the case of gels, $\pi_{os}$ is defined by the following equation.12

$$\pi_{os} = \pi_{sw} + \pi_{el}$$ \hspace{1cm} (7)

Here, $\pi_{el}$ is the elastic pressure that is equal to $G$, and $\pi_{sw}$ is the swelling pressure. The values of $\pi_{os}$ were measured from the swelling measurements in polyvinylpyrrolidone (PVP) solutions with various PVP concentrations ($c_{pvp}$); the osmotic pressure of the PVP solution ($\pi_{pvp}$), which completely inhibits the swelling of the hydrogel, is identical to $\pi_{os}$.13 Our previous research used a dialysis membrane to prevent PVP from penetrating into the gels.12 However, when $G$ and the swelling ratio of gel ($Q$) became large, the tension of the dialysis membrane influenced $Q$, and prevented the precise measurement of $Q$. In this case, gels were directly immersed into aqueous solutions of PVP without a dialysis membrane to avoid this imprecision. In this case, there is a possibility that PVP penetrates into the gels. To check the penetration, we compared high molecular weight PVP (1300 kg/mol) (PVP1300K) and low molecular weight PVP (29 kg/mol) (PVP29K). The $c_{pvp}$-dependence of $Q$ of Tetra5PEG gel 10K with $\phi_0 = 0.050$ is shown in Fig. S1. Based on Fig. S1, the same concentrations of PVP29K and PVP1300K restricted the swelling of a gel ($Q = 1$), suggesting that the penetration of PVP into a gel did not influence the concentration of PVP at $Q = 1$ ($c_{pvp}$). Therefore, we used PVP1300K that is considered to have more limited penetration into gels, and took the following equation that describes $\pi_{pvp}$ of PVP with a molecular weight of 28 kg/mol from the literature.12,15,16

$$\pi_{sw} = 0.878c_{pvp} + 17.25c_{pvp}^2 + 144.1c_{pvp}^2$$ \hspace{1cm} (8)

The osmotic pressure ($\pi_{os}$) of Tetra5PEG gel 10K and 20K are shown against $\phi_0$ in Fig. 2 (b). The value of $\pi_{os}$ increased with an increase in $\phi_0$. When we focused on the power law relationships between $\pi_{os}$ and $\phi_0$, all data roughly fell onto the guide line showing the theoretical prediction for good solvent in the semi-dilute region ($\pi_{os} \sim \phi_0^{1.25}$).17,18 These results suggest that $\pi_{os}$ is successfully estimated. On the other hand, a slight downward deviation from the guide line was observed in the case of Tetra5PEG gel 10K below $\phi_0 = 0.050$. This discrepancy is most likely caused by the concentration lower than the overlapping concentration of prepolymers.13

We estimated $K$ using the partial derivative of the fit function of the $\pi_{os}$-$\phi_0$ relationship with respect to $\phi_0$, based on eq. 6. The values of $f_w$ were reproduced from our previous
work, and used to estimate $D_w$ based on eq. 3. The $\phi_w$-dependence of $D_w$ is shown in Fig. 3. The values of $D_w$ were almost constant against $\phi_w$, and only showed the $M_w$-dependence. Notably, the large error bar of Tetra-PEG gel 20K with $\phi_w = 0.096$ was due to the extremely slow water permeation as mentioned in our previous paper.

Next, we investigated the diffusion coefficient measured by the swelling experiment ($D_{sw}$, eq. 5). When an as-prepared hydrogel is soaked into water, it generally swells, absorbing water. Time-evolutions of the sizes during swelling (swelling curves) are shown in Fig. 4 (a) and S2. The swelling curves of Tetra-PEG gels were well described by single exponential fittings, and sphere-shaped Tetra-PEG gels (diameter $\approx 2.6$ mm) reached the equilibrium swollen state in approximately 4 hours. Extrapolating the time to infinity in the exponential function, we estimated the values of $d_{sw}$. In Fig. 4 (b) and S3, the normalized diameters of gels ($d_{sw}$, eq. 4) are plotted against time ($t$). Each data is presented with a vertical shift ($\Delta \phi$) to avoid overlapping. The later stages of the swelling behaviors of Tetra-PEG gels were well described by eq. 4 (dotted lines in Fig. 4 (b) and S3), suggesting the validity of the swelling equation. The large error bars in the later stages reflect the small difference between $d$ and $d_{sw}$. According to the fit, we estimated the values of $\tau$.

The values of $D_{sw}$ were estimated from $d_{sw}$ and $\tau$ using eq. 5, and plotted against $\phi_w$ in Fig. 3. Although the errors were within 10%, they were not small compared to the change in $D_{sw}$. It was difficult to further decrease the errors due to experimental limitations. The value of $D_{sw}$ slightly increased with an increase in $\phi_w$ and those of different $M_w$ converged in the higher $\phi_w$ region. When we focused on the power law relationships between $D_{sw}$ and $\phi_w$ ($D_{sw} \sim \phi_w^\gamma$), Tetra-PEG gel 10K and 20K showed $\gamma = 0.37$ and 0.53, respectively.

Finally, we investigated the diffusion coefficient measured by DLS ($D_{DLS}$). Because a gel is a nonergodic matter, the scattered light intensity includes contributions from both the liquid-like dynamic fluctuation and the solid-like spatial inhomogeneity. Here, we utilized the partial heterodyne model to decompose these two components, and estimated $D_{DLS}$ as the liquid-like component.

The $\phi_w$-dependence of $D_{DLS}$ is shown in Fig. 3. The value of $D_{DLS}$ increased with an increase in $\phi_w$, and showed little $M_w$-dependence in the higher $\phi_w$ region. When we focused on the power law relationships between $D_{DLS}$ and $\phi_w$ ($D_{DLS} \sim \phi_w^\gamma$), Tetra-PEG gel 10K and 20K showed $\gamma = 0.37$ and 0.53, respectively.

To discuss the three diffusion coefficients, we introduce the scaling relationship between cooperative diffusion coefficient ($D_{coop}$) and blob size ($\xi$) proposed by de Gennes. De Gennes treated $D_{coop}$ as a simple Stokes-Einstein diffusion coefficient for a blob. When the temperature is constant, the relationship between $D_{coop}$ and $\xi$ is described by the following equation.

$$D_{coop} \sim \xi^{-\delta} \quad (9)$$

Notably, $\xi$ does not depend on $M_w$ but rather on $\phi_w$ in the semi-dilute region. Therefore, conceptually $D_{coop}$ depends only on $\phi_w$.

As shown in Figure 3, the three diffusion coefficients were divided into two types: $M_w$-dependent $D_w$ and $\phi_w$-dependent $D_{sw}$ and $D_{DLS}$. The $\phi_w$-dependence and $M_w$-independence of $D_{sw}$ and $D_{DLS}$ roughly agreed with the concept of $D_{coop}$ shown in eq. 9. Notably, the scaling is slightly lower than the theoretical prediction for semi-dilute solution of a good solvent ($D_{coop} \sim \phi_w^{0.75}$). This deviation may be caused by the crosslinking.
Fig. 5 (a) The $\phi_i$-dependence of $D_\text{sw}/D_{\text{DLS}}$ of Tetra-PEG gel with different $M_w$. (b) The relationship between $f_w$ and $f_{\text{DLS}}$ of Tetra-PEG gel with different $M_w$ ($M_w$: 10 kg/mol, circle; 20 kg/mol, triangle).

A decrease in polymer volume fraction ($\phi$) of $D_\text{sw}$ during the swelling. Based on Figure 3, one can expect that $D_\text{sw}$ decreases with swelling, and observed $D_\text{sw}$ is smaller than that in the as-prepared state. Here, we accepted the second and third hypotheses, and used $D_{\text{DLS}}$ for the further discussion. We will investigate the difference between the absolute values of $D_\text{sw}$ and $D_{\text{DLS}}$ in near future.

We then focus on $M_w$-dependent $D_\text{sw}$, which does not agree with the concept of $D_{\text{coop}}$-1. This disagreement is most likely due to $f_i$ in eq. 3, because $K$ and $G$ have clear definitions without any ambiguity. Instead of $f_w$, we can estimate a plausible $f_{\text{DLS}}$ from eq. 3 by substituting $D_{\text{coop}} = D_{\text{DLS}}$ following the above discussion. In Figure 5 (b), we plotted $f_w$ against $f_{\text{DLS}}$. Based on Tanaka’s assumption, the friction applied to water ($f_w$) is the same as the friction applied to polymer network ($f_{\text{DLS}}$) (dashed line in Figure 5 (b)); in other words, the motion of water is same as that of polymer network. However, $f_w$ was always smaller than $f_{\text{DLS}}$, and interestingly two different linear relationships between $f_w$ and $f_{\text{DLS}}$ were observed for Tetra-PEG gel 10K and 20K. These experimental observations indicate both strong correlation and essential difference between $f_w$ and $f_{\text{DLS}}$. The linear correlations indicate that the source of cooperative motion of a polymer network is the thermal motion of water molecules. On the other hand, different slopes observed in Tetra-PEG gel 10K ($f_w = 0.27$ $f_{\text{DLS}}$) and Tetra-PEG gel 20K ($f_w = 0.51$ $f_{\text{DLS}}$) indicate that the coupling of motions of the polymer network and water is influenced by crosslinking. Because the difference in motions was enhanced in more tightly crosslinked systems, it is expected that the looser the crosslinking is, the closer the motion of polymer network becomes to that of water molecules. Notably, this mismatch in motions and $f_{\text{DLS}}$-dependent swelling kinetics suggest the inapplicability of $f_w$ in eq. 3, which contradicts with Tanaka’s assumption. On the other hand, these results support Tanaka’s original idea that gel swelling is the diffusion process of a polymer network to the outer solution, and that not of water molecules to a gel.

In conclusion, we measured the cooperative diffusion coefficient ($D_{\text{coop}}$) describing the dynamics of polymer network in a gel by three methods; solvent permeation ($D_\text{sw}$), swelling experiment ($D_{\text{sw}}$) and DLS ($D_{\text{DLS}}$). By comparing these three diffusion coefficients of Tetra-PEG gels with different molecular weights between crosslinks ($M_w$) and initial polymer volume fractions ($\phi_i$), we found that $D_\text{sw}$ and $D_{\text{DLS}}$ showed the similar manners with $D_{\text{coop}}$, suggesting that $D_\text{sw}$ and $D_{\text{DLS}}$ can be considered as $D_{\text{coop}}$ in the swelling equation. In the other words, macroscopic swelling behavior is governed by microscopic concentration fluctuation. On the other hand, the behavior of $D_w$ was completely different from those of $D_\text{sw}$ and $D_{\text{DLS}}$, suggesting the inapplicability of $f_w$ in eq. 3. Swelling kinetics of gel was governed by the diffusion of polymer network to the outer solution, but not by those of water molecules. These findings will help understand the interaction between solvents and polymer networks, and the cooperative dynamics of polymer network.

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Conflicts of interest
There are no conflicts to declare.

Notes and references
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