



Three Cooperative Diffusion Coefficients describing Dynamics of Polymer Gels

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-02-2018-001357.R1
Article Type:	Communication

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Three Cooperative Diffusion Coefficients describing Dynamics of Polymer Gels

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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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.^{1,2}

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.¹ 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.

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

where ρ is the density of the network, t is the time, σ is the stress tensor, and f is the friction coefficient between polymer network and water. Under spherical symmetry, eq. 1 gives

$$\frac{\partial \mathbf{u}}{\partial t} = \frac{K + \frac{4}{3}G}{f} \frac{\partial}{\partial r} \left\{ \frac{1}{r^2} \left[\frac{\partial}{\partial r} (r^2 \mathbf{u}) \right] \right\} \quad (2)$$

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*,³ and the cooperative diffusion coefficient of a polymer gel (D_{coop}) is defined as

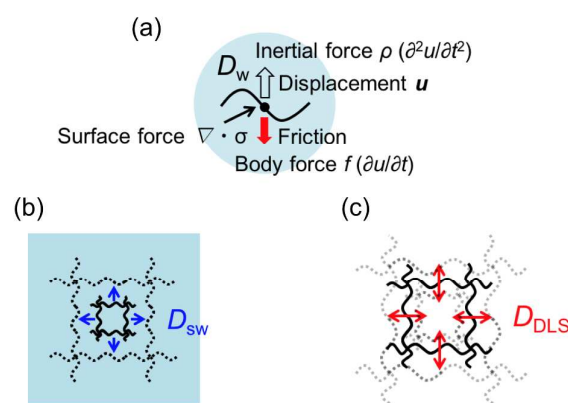


Fig. 1 Schematic illustrations of the dynamics of a polymer network represented by (a) diffusion coefficient by water permeation (D_w), (b) diffusion coefficient by swelling experiment (D_{sw}), and (c) diffusion coefficient by DLS experiment (D_{DLS})

$$D_{\text{coop}} = \frac{K + \frac{4}{3}G}{f} \quad (3)$$

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)).² 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.

$$d_n = \frac{d_\infty - d(t)}{d_\infty - d_0} = \frac{6}{\pi^2} \exp\left(-\frac{t}{\tau}\right) \quad (4)$$

where d_n is the normalized size of the gel, $d(t)$ is the diameter of the gel at time t , d_0 is the diameter in the initial state, d_∞ is the diameter in the equilibrium state, and τ is the characteristic time of swelling. Eq. 4 well reproduced the swelling and shrinking behaviors of gels, suggesting the validity of the prediction.²⁻⁴

The values of d_∞ and τ are related to D_{coop} as

$$D_{\text{coop}} = \frac{d_\infty^2}{\pi^2 \tau} \quad (5)$$

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† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

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_w .

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_w 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_w 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 three D s is vital.

In this study, we investigated three diffusion coefficients using model polymer gels with systematically tuned initial polymer volume fractions (ϕ_0) and molecular weights between crosslinks (M_w) (Tetra-PEG gel). Tetra-PEG 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_w and ϕ_0 independently.⁹ Our previous small angle neutron scattering (SANS) measurements revealed the extremely low structural heterogeneity in Tetra-PEG gels.⁹⁻¹¹ In addition, the relationship between the mechanical properties and network structure is well known.⁹ Thus, Tetra-PEG gel system is promising as a model polymer gel system. Here, we systematically tuned M_w (10, 20 kg/mol; Tetra-PEG gel 10k, Tetra-PEG gel 20K) and ϕ_0 (0.034-0.110), and investigated the effects on the three diffusion coefficients (D_w , D_{sw} 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_w), we first measured K , G and f_w . 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 ϕ_0 -dependence of G . The value of G increased with an increase in ϕ_0 . When we focused on Tetra-PEG gels with the same ϕ_0 , G decreased with an increase in M_w . These results agreed well with the well-known rubber elasticity theory ($G \sim \phi_0 M_w^{-1}$) as described in our previous studies.^{9, 10, 12-14}

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

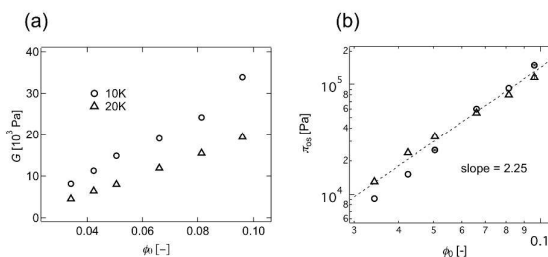


Fig. 2 The ϕ_0 -dependence of G (a) and π_{os} (b) of Tetra-PEG gels with different M_w (M_w : 10 kg/mol, circle; 20 kg/mol, triangle)

$$K = \phi \frac{\partial \pi_{os}}{\partial \phi} \quad (6)$$

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

$$\pi_{os} = \pi_{sw} + \pi_{el} \quad (7)$$

Here, π_{el} is the elastic pressure that is equal to G , and π_{sw} is the swelling pressure. The values of π_{sw} were measured from the swelling measurements in polyvinylpyrrolidone (PVP) solutions with various PVP concentrations (c_{pvp}); the osmotic pressure of the PVP solution (π_{pvp}), which completely inhibits the swelling of the hydrogel, is identical to π_{sw} .¹⁵ 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 study, 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 Tetra-PEG 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 π_{pvp} of PVP with a molecular weight of 28 kg/mol from the literature.^{12, 15, 16}

$$\pi_{sw} = 0.878c'_{pvp} + 17.25c'^2_{pvp} + 144.1c'^3_{pvp} \quad (8)$$

The osmotic pressure (π_{os}) of Tetra-PEG gel 10K and 20K are shown against ϕ_0 in Fig. 2 (b). The value of π_{os} increased with an increase in ϕ_0 . When we focused on the power law relationships between π_{os} and ϕ_0 , all data roughly fell onto the guide line showing the theoretical prediction for good solvent in the semi-dilute region ($\pi_{os} \sim \phi_0^{2.25}$).^{17, 18} These results suggest that π_{os} is successfully estimated. On the other hand, a slight downward deviation from the guide line was observed in the case of Tetra-PEG 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 π_{os} - ϕ_0 relationship with respect to ϕ_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. 3.¹⁹ The ϕ_0 -dependence of D_w is shown in Fig. 3. The values of D_w were almost constant against

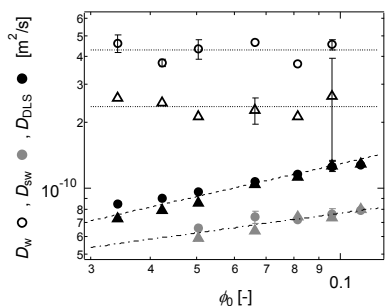


Fig. 3 The ϕ_0 -dependences of D_w (white symbols), D_{DLS} (black symbols) and D_{sw} (gray symbols) of Tetra-PEG gel with different M_w (M_w : 10 kg/mol, circle; 20 kg/mol, triangle).

ϕ_0 , and only showed the M_w -dependence. Notably, the large error bar of Tetra-PEG gel 20K with $\phi_0 = 0.096$ was due to the extremely slow water permeation as mentioned in our previous paper.¹⁹

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 ≈ 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_∞ . In Fig. 4 (b) and S3, the normalized diameters of gels (d_n , eq. 4) are plotted against time (t). Each data is presented with a vertical shift (Δd) 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*.² The large error bars in the later stages reflect the small difference between d and d_∞ . According to the fit, we estimated the values of τ .

The values of D_{sw} were estimated from d_∞ and τ using eq. 5, and plotted against ϕ_0 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 ϕ_0 , and those of different M_w converged in the higher ϕ_0 region. When we focused on the power law relationships between D_{sw} and ϕ_0 ($D_{sw} \sim \phi_0^x$), Tetra-PEG gel 10K and 20K showed $x = 0.22$ and 0.40 , 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.⁴

The ϕ_0 -dependence of D_{DLS} is shown in Fig. 3. The value of D_{DLS} increased with an increase in ϕ_0 , and showed little M_w -

dependence in the higher ϕ_0 region. When we focused on the power law relationships between D_{DLS} and ϕ_0 ($D_{DLS} \sim \phi_0^y$), Tetra-PEG gel 10K and 20K showed $y = 0.37$ and 0.53 , respectively.

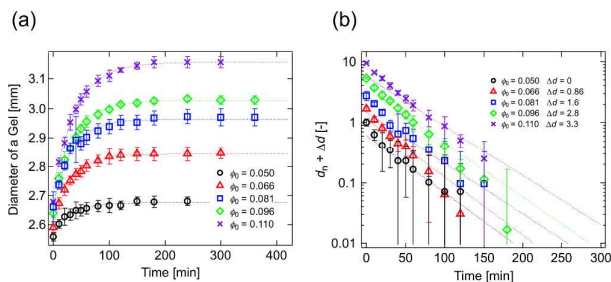


Fig. 4 (a) The typical swelling curves of Tetra-PEG gel 10K (b) The typical time courses of d_n during the swelling experiments for Tetra-PEG gel 10K (ϕ_0 : 0.050, circle; 0.066, triangle; 0.081, square; 0.096, diamond; 0.110, cross)

To discuss the three diffusion coefficients, we introduce the scaling relationship between cooperative diffusion coefficient (D_{coop}) and blob size (ξ) proposed by de Gennes.¹⁷ 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 ξ is described by the following equation.

$$D_{coop} \sim \xi^{-1} \quad (9)$$

Notably, ξ does not depend on M_w but rather on ϕ_0 in the semi-dilute region. Therefore, conceptually D_{coop} depends only on ϕ_0 .

As shown in Figure 3, the three diffusion coefficients were divided into two types: M_w -dependent D_w and ϕ_0 -dependent D_{sw} and D_{DLS} . The ϕ_0 -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 ($D_{coop} \sim \phi_0^{0.75}$). This deviation may be caused by the crosslinking.

To check the similarity of D_{sw} and D_{DLS} , we plotted D_{sw}/D_{DLS} against ϕ_0 in Figure 5 (a). As shown in the Figure, D_{sw}/D_{DLS} was nearly constant (≈ 0.64) over the whole experimental range, suggesting that D_{sw} strongly corresponds to D_{DLS} . In other words, the macroscopic swelling behavior is correlated to the microscopic fluctuation of a polymer network. The difference in absolute values between D_{sw} and D_{DLS} may possibly originate from the following three points. First is the difference in the motions described by D_{sw} and D_{DLS} ; D_{sw} describes the translational diffusion, while D_{DLS} describes the thermal fluctuation (Figure 1 (b) and (c)). Second is the inapplicability of eq. 4 and 5 due to the larger swelling ratio of Tetra-PEG gels (1.14-2.13) compared to previous studies (1.24). Third is the

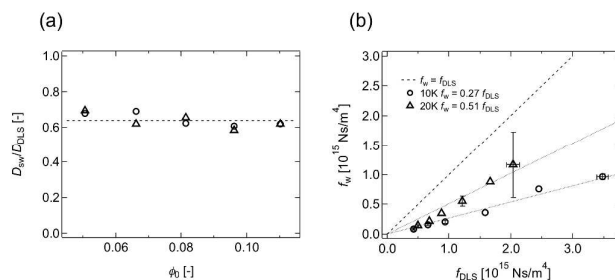


Fig. 5 (a) The ϕ_0 -dependence of D_{sw}/D_{DLS} of Tetra-PEG gel with different M_w (b) The relationship between f_w and f_{DLS} of Tetra-PEG gel with different M_w (M_w : 10 kg/mol, circle; 20 kg/mol, triangle).

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

We then focus on M_w -dependent D_w , which does not agree with the concept of D_{coop} .¹ This disagreement is most likely due to f in eq. 3, because K and G have clear definitions without any ambiguity. Instead of f_w , we can estimate a plausible f (f_{DLS}) from eq. 3 by substituting $D_{coop} = D_{DLS}$ following the above discussion. In Figure 5 (b), we plotted f_w against f_{DLS} . Based on Tanaka's assumption, the friction applied to water (f_w) is the same as the friction applied to polymer network (f_{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_{DLS} , and interestingly two different linear relationships between f_w and f_{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_{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 ($f_w = 0.27 f_{DLS}$) and Tetra-PEG gel 20K ($f_w = 0.51 f_{DLS}$) 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_{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 not that of water molecules to a gel.

In conclusion, we measured the cooperative diffusion coefficient (D_{coop}) describing the dynamics of polymer network in a gel by three methods; solvent permeation (D_w), swelling experiment (D_{sw}) and DLS (D_{DLS}). By comparing these three diffusion coefficients of Tetra-PEG gels with different molecular weights between crosslinks (M_w) and initial polymer volume fractions (ϕ_0), we found that D_{sw} and D_{DLS} showed the similar manners with D_{coop} , suggesting that D_{sw} and D_{DLS} can be considered as D_{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_{sw} and D_{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.

This work was supported by the Japan Society for the Promotion of Science (JSPS) through the Grants-in-Aid for the Graduate Program for Leaders in Life Innovation (GPLLI), the International Core Research Center for Nanobio, Core-to-Core Program A. Advanced Research Networks, and the Grants-in-Aid for Young Scientists (A) Grant Number 23700555 to TS, and Scientific Research (S) Grant Number 16746899 to UC. This work was also supported by the Japan Science and Technology Agency (JST) through the Center of Innovation program (to UC), and PREST (to TS).

Conflicts of interest

There are no conflicts to declare.

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