Effect of Host-Guest Interaction on Swelling Behavior and Equilibrium Swollen State of Host-Guest Gel

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A Host-Guest gel is a supramolecular network formed by the dynamic crosslinking between β-cyclodextrin and adamantane molecules, and has a novel tough and self-healing properties. In our previous study, we showed that this gel has a topological permanent crosslinking in addition to the dynamic crosslinking, and these two types of crosslinking brings a unique swelling property such as attaining an equilibrium swollen state. In the present study, we examined the swelling behavior and equilibrium swollen states of the Host-Guest gel. The analysis of the swelling process revealed the dynamic crosslinking hardly affect the diffusion on polymer chain under the swelling process. On the other hand, analysis of the equilibrium swollen state with and without a competitor of Guest molecule showed that the dynamic crosslinkings can trap the entanglements of polymer chains even in the equilibrium state because the dynamic crosslinkings are anchored by the permanent crosslinkings and consequently stored in the equilibrium state. These results indicate that the swelling properties of the Host-Guest gels are dominated by both dynamic and permanent crosslinkings in the network.

Key Words: Polymer gel / Supramolecular network / Host-Guest interaction / Swelling behavior / Equilibrium swollen state

1. INTRODUCTION

Material design aiming for toughening and prolonging the life of polymeric materials has attracted much attention over the years to realize an environmentally sustainable society. As one of them, there is an approach by introducing non-covalent bonds to polymeric materials, such as hydrogen bonds1, 2), ionic interactions3, 4), metal coordination5), and so on. Among these intermolecular interactions, Harada et al. reported that an intermolecular specific interaction called “Host-Guest interaction” is very effective to improve mechanical properties in addition to impart the self-healing property6, 7). This Host-Guest interaction is a specific hydrophobic interaction between a host cyclic cyclodextrin molecule and a guest hydrophobic molecule. The cyclodextrin molecule has a hydrophilic surface on its outer side and a hydrophobic cavity on its inner side, thus they can form the stable inclusion complex by inclusion of a hydrophobic molecule inside a cavity, especially in water. The gel in which this inclusion complex is designed to work as a physical crosslinking is called “Host-Guest gel”. In addition to showing very flexible and tough mechanical properties, this Host-Guest gel has been reported to exhibit self-healing properties and stimulus responsiveness depending on the combination of a host molecule and a guest molecule, and now is anticipated as a new environmentally harmonized material for sustainable society. Figure 1 shows a schematic illustration of the Host-Guest gel. The cyclodextrin and the hydrophobic molecules introduced into the polymer side chain are under the thermally equilibrium state in which dissociation and reassociation are repeated inside the network.

Fig. 1 Schematic illustration of the Host-Guest gel examined in this research.
This Host-Guest gel swells against various types of solvents and reaches equilibrium swollen state like ordinary permanent networks. A physically crosslinked gel consisting only of ordinary physical crosslinking finally dissolves because the equilibrium state is inclined in the direction of crosslinkings dissociation in a good solvent. Thus, the Host-Guest gel has specific swelling characteristics, such as an equilibrium swollen state, which is not characteristic for networks having only physical crosslinkings of the inclusion complex.

In our previous study, we revealed the relationship between the specific physical properties and network structure of the Host-Guest gel, especially from the viscoelastic approach. We experimentally demonstrated that the Host-Guest gel contains two kinds of crosslinking points. One is a physical crosslinking due to the “Host-Guest crosslinking” introduced according to molecular design. The Host-Guest crosslinking acts as a sticker in the network, thereby increasing the friction coefficient of the polymer chain and retarding the Rouse relaxation mode of network strands. The other crosslinking is a topological crosslinking derived from the “rotaxane structure” formed by penetration of the main chain polymer constituting the network into the cavities of the side chain cyclodextrin. This rotaxane structure works as a permanent but movable topological crosslinking for the main chains, and this permanent crosslinking is attributed to the molecular origin of a specific swelling characteristic capable of achieving an equilibrium swollen state even in a good solvent. Thus, these two types of crosslinkings make the Host-Guest gel a unique gel. In the previous study, we mainly focused on the relationship between mechanical properties and network structure. However, details of the swelling behavior of this complicated network and also role of the Host-Guest crosslinking in the network structure under its equilibrium swollen state remain unclear. In this research, we focus on the swelling behavior of the Host-Guest gel and the network structure in the equilibrium swollen state, and discuss the diffusion behavior of the polymer strand in the swelling process and how the equilibrium state is affected by the Host-Guest interaction.

2. EXPERIMENTAL

2.1 Sample Preparation

Host-Guest gel samples were prepared following to the previous studies, 6-acrylamido-β-cyclodextrin (βCD-AAm) as a host monomer and adamantane acrylamide (Ad-AAm) as a guest monomer were added into distilled water in an equimolar ratio, and the mixture was stirred in an oil bath at 90 °C for 3 hours to allow forming a Host-Guest inclusion complex. This procedure is necessary because Ad-AAm is insoluble in water due to its high hydrophobicity while the Host-Guest inclusion complex is soluble in water. The obtained complex solution was air-cooled at room temperature and then filtered using a 0.8 μm cellulose acetate filter to remove insoluble portion of Ad-AAm. This inclusion complex solution including excess amount of βCD-AAm was used as a crosslinking agent solution. Concentration of βCD-AAm and Ad-AAm was determined by NMR measurement and details were discussed in our previous study. After adding Acrylamide as a main chain monomer to the above crosslinking agent solution and adding Ammonium persulfate (APS) and N, N, N′, N”-tetramethylethylenediamine (TEMED) as initiators, a pre-gel solution was prepared. Total monomer, APS, and TEMED concentrations were fixed at 2.0 mol kg⁻¹, 0.020 mol kg⁻¹, and 0.020 mol kg⁻¹, respectively and the feed concentration Cᵢ of inclusion complex (crosslinking agent) was varied between 0.020-0.050 mol kg⁻¹. The pre-gel solution was poured into a 1 mm thick mold and gelled to prepare a sample for dynamic viscoelasticity measurement. Similarly, a pre-gel solution was poured into a capillary having an inner diameter of 1 mm and gelled to prepare a cylindrical gel, which was used for swelling experiment. The gelation reaction was carried out at 25 °C for 12 hours or more, and the reaction was finished completely in any of the measurements.

2.2 Swelling observation

A cylindrical Host-Guest gel with a diameter of approximately 1 mm was swollen in distilled water at 25 °C and its diameter change was monitored with an optical microscope (ECLIPS E 400, NIKON). From the gel diameter at equilibrium swollen state, dₒ, and the polymer volume fraction at as prepared state φₒ, the swelling ratio and the polymer volume fraction at equilibrium swelling were determined.

The Host-Guest gels at the equilibrium swollen state in distilled water were transferred into an aqueous host competitor solution in which βCD-AAm was dissolved, and the swelling process under competitor was observed. From the change in diameter, the polymer volume fraction at equilibrium swollen state in the competitor aqueous solution φₑ was determined. The concentration of host competitor was varied between 4.0 × 10⁻⁴ – 4.0 × 10⁻² mol kg⁻¹.

2.3 Dynamic oscillatory measurement

Dynamic viscoelastic measurements were performed using a stress-controlled rheometer (MCR 302, Anton Paar). For the measurement, a parallel disk type fixtures with a
diameter of 25 mm and 12 mm were used. Frequency sweep measurements were carried out at 25 °C in the range of angular frequency $\omega = 100 - 0.1$ s$^{-1}$. The measurements were carried out beforehand confirming that the magnitude of the strain in the frequency sweep measurement was sufficiently small and did not exceed the linear region.

3. RESULTS AND DISCUSSION

3.1 Analysis of Swelling Process

Figure 2 (A) shows the time dependence of the gel diameter in the swelling process of the Host-Guest gel with $C_c = 0.040$ mol kg$^{-1}$. Here, $d(t)$ is the diameter of gel in cylindrical shape at time $t$, and $d_0$ is the diameter at the onset of swelling at $t = 0$. The gel diameter increased with increasing time and reached the equilibrium swollen state. According to Tanaka et al., the swelling behavior of a polymer gel is determined by cooperative diffusion of network strands and solvent molecules.$^9, 10$). When the spherical gel swells in a solvent after the time has passed sufficiently, the swelling speed $d_n$ of the gel is approximately given by the following equation;

$$d_n = \frac{d(t) - d_e}{d_e - d_0} \approx \frac{6}{\pi^2} \exp\left(-\frac{1}{\tau} t\right)$$

(1)

where $d_0$ is the gel diameter in the initial state, $d(t)$ is the diameter at time $t$, and $d_e$ is the gel diameter at the equilibrium swollen state. Figure 2 (B) shows a semilogarithmic plot of the time dependence of $d_n$ for the Host-Guest gels with various $C_c$. The results of fitting by Eq. (1) in the long time region are also shown with black dotted lines. A single relaxation process over a long time region was observed for each of a Host-Guest gel, and the experimental values and fitting results show good agreement. From this fitting, the apparent relaxation time $\tau$ of the cylindrical gels can be determined.

The relaxation time in a swelling process of a polymer gel depends on the diameter $d_e$ and swelling ratio in the case of a cylindrical gel, and it also depends on the cooperative diffusion coefficient $D$ of the network strand. Therefore, comparison should be made with $D$ instead of $\tau$. The coefficient $D$ in the cylindrical gel is estimated by the following equation from $\tau$ in the swelling process$^{10-12}$.

$$D = \frac{3\pi^2 d_e^2}{68\tau}$$

(2)

Figure 3 shows the $C_c$ dependence of $D$ calculated from the relaxation time $\tau$ and the gel diameter $d_e$ obtained from fittings by Eq. (1). $D$ was slightly larger at $C_c = 0.050$ mol kg$^{-1}$, but became almost constant ($\sim 2.2 \times 10^{-7}$ cm$^2$ s$^{-1}$) at any concentrations. This average value is consistent with the order of diffusion coefficient ($10^{-8} - 10^{-7}$ cm$^2$ s$^{-1}$) in the swelling/shrinking process of general polymer gels$^{13}$, and also in accordance with the coefficient ($\sim 3 \times 10^{-7}$ cm$^2$ s$^{-1}$) for the chemically crosslinked acrylamide gel reported by Tanaka et al.$^9$. 

![Graph showing the Cc dependence of D](image1)

![Graph showing the time dependence of d_n and fitting curves](image2)
These results indicate that $D$ of the Host-Guest gel in the swelling process is hardly affected by the Host-Guest interaction although the Rouse mode of the gel is significantly delayed by the Host-Guest interaction. This result could be interpreted as follows. As we have reported in our previous study, the Host-Guest gel includes a “rotaxane structure” formed by penetration of a polymer main chain into a cyclodextrin cavity. This rotaxane structure is considered to act as a mobile but permanent crosslinking. This frozen crosslinking is expected to change the temporary Host-Guest crosslinkings into the permanent crosslinkings through increasing the probability of reassociation in equilibrium state between the same host guest pair from zero to no zero value. Thus, the Host-Guest crosslinking is anchored and stored by the permanent crosslinking. The “rotaxane structure” crosslinking causes also insoluble entanglements. These permanent crosslinkings support the equilibrium elastic modulus of the gel. According to Li and Tanaka, $D$ in the swelling process of polymer gel can be related to the moduli as $D = (K + 4G/3)/\zeta$, where $K$ is the bulk modulus associated with the osmotic pressure, $G$ is the network shear modulus and $\zeta$ is the friction coefficient of the network strand. Herein, $D$ is rewritten as $D \approx K/\zeta$ because $K$ is much larger than $G$. In the temperature range of measurement (~25°C), the rate of dissociation and reassociation of the Host-Guest crosslinking is sufficiently fast. Therefore in the time scale of the polymer strands under the swelling process, the Host-Guest crosslinking itself would has almost no effect for the bulk modulus because the whole network structure composed mainly of trapped entanglements are essentially unvaried at $C_e > 0.02$ mol kg$^{-1}$. Furthermore, viscoelastic measurements revealed that the Rouse mode of network strands was significantly delayed by the sticker, but relaxation similar to the usual entanglement system was observed after the sticker relaxation. When the dissociation and reassociation time scale of the Host-Guest complex is sufficiently fast, the Host-Guest crosslinking does not act as a sticker and has no role to change the friction coefficient of the network strand $\zeta$ significantly in the swelling process. Therefore, $D$ does not depend on the concentration of the Host-Guest crosslinking.

### 3.2 Linear viscoelasticity as prepared and in equilibrium swollen states

Figure 4 shows the viscoelastic spectra of the Host-Guest gels with $C_e = 0.040$ mol kg$^{-1}$ at as prepared and in equilibrium swollen states. Similarly to the previous study, the weak relaxation mode from the Rouse relaxation ($G' \sim G'' \sim \omega^{0.5}$) on the high frequency side of the rubbery plateau region were observed for both the samples. The frequency dependence of the moduli did not almost change in the entire frequency range and only the relaxation strength decreased due to swelling. We have demonstrated that the most of elastic modulus at as prepared state can be attributed to entanglements, not to the Host-Guest crosslinking. The contribution of the rotaxane structure and Host-Guest crosslinking is estimated to be negligibly small to the elastic modulus in the measuring temperature range of Fig. 4. Since the concentration of the network strand is decreased during the swelling process, the entanglement density and therefore the rubbery plateau modulus would be decreased. As a result, only the relaxation strength decreased. On the other hand, the frequency dependence of relaxation spectrum itself did not change, which indicated the relaxation time of each relaxation mode had not changed. In ordinary polymer solutions, the relaxation time of Rouse mode is fundamentally insensitive to polymer concentration. In other words, at the equilibrium swollen state in distilled water, these results suggest that not all of the crosslinkings dissociate like a normal physically crosslinked gel but maintain a certain equilibrium state. Therefore, the frequency dependence of the relaxation spectrum of the whole system did not change, only the relaxation intensity was considered to be reduced.

### 3.3 Equilibrium swollen state under host competitors

Figure 5 shows the host competitor concentration $C_{H\text{ost}}$ dependence of the polymer volume fractions at the equilibrium swollen state $\varphi_{e2}$ under coexistence of host competitor for
the Host-Guest gel with $C_c = 0.040$ mol kg$^{-1}$. The result of $\phi_{e2}$ with $C_{\text{Host}} = 0$ corresponds to the result in distilled water containing no competitor. With the increase in $C_{\text{Host}}$, $\phi_{e2}$ decreased, but did not depend on $C_{\text{Host}}$ and kept a constant value over a certain $C_{\text{Host}}$.

The equilibrium swollen state of the polymer gel is generally determined by Flory-Rhener’s equation\(^{17}\). In this equation, the equilibrium swollen state is determined by the competition between the mixing energy and the elastic energy of the network and is described using the following equation;

$$\nu_i \left[ 2\phi_0 - \left( \frac{\phi}{\phi_0} \right)^{1/3} \right] = \ln(1 - \phi) + \phi + \chi \phi^2 \quad (3)$$

where $\phi_0$ and $\phi$ represent the polymer volume fractions in the reference state and the equilibrium swollen state, $\nu$ is the effective network chain density, $\nu_i$ is the unit volume of the solvent, $\chi$ is the chi parameter of the network chain. When the guest molecules were capped with the introduction of the competitive agent, the affinity between the solvent and the network strand could be increased by suppressing the hydrophobicity. In short, the degree of swelling is increased with reduction of the apparent $\chi$. On the other hand, even at the equilibrium swollen state in distilled water, the network is not dissolved due to the rotaxane structure and maintains a constant local concentration, so that the Host-Guest complex cannot be completely dissociated by anchoring of the permanent crosslinkings and would contribute a certain portion of equilibrium modulus by trapping the entanglements. We note that this is consistent with the fact that the Rouse relaxation is delayed to the same extent as the preparation state even in the equilibrium swollen state, which is shown by the viscoelastic measurement. In summary, the swelling in the competitive agent simultaneously is controlled by the two effects of decreasing $\chi$ due to capping guest molecules and eliminating entanglements accompanying elimination of Host-Guest crosslinking. We emphasis that some portion of the Host-Guest crosslinking can contribute to the equilibrium elastic modulus. This kind of role of temporary crosslinking is completely different from that assumed in the pioneer theory for temporary networks, in which all the temporal crosslinking relaxes its stress.

Next, we discuss more details of the Host-Guest interaction in swelling state. Since $\phi_{e2}$ decreased exponentially with respect to $C_{\text{Host}}$, fitting was performed using the following equation;

$$\phi_{e2} = \phi_{\text{pla}} + A \exp\left( - \left( \frac{C_{\text{Host}}}{C_0} \right)^B \right) \quad (4)$$

where $\phi_{\text{pla}}, A, B,$ and $C$ are fitting parameters. $\phi_{\text{pla}}$ corresponds to the polymer volume fraction of the Host-Guest gel when it does not depend on $C_{\text{Host}}$. The fitting result to Eq. 4 is also

![Image](image-url)
shown in Fig. 5 (A) with black dotted lines. The $C_{\text{swell}}$ dependence of $\varphi_{\text{pla}}$ could be described well by Eq. (4). Therefore, the same fitting analysis was performed for gels with various $C_{\text{c}}$, and $C_{\text{c}}$ dependence of $\varphi_{\text{pla}}$ was obtained. The result is shown in Fig. 5 (B). $\varphi_{\text{pla}}$ increased with increasing $C_{\text{c}}$, showing an approximately proportional relationship. In the state where the polymer volume no longer changes with the competitor concentration, we consider that all the Host-Guest crosslinkings are dissociated and all of the guest molecules are capped. Further assuming that the osmotic pressure of the competitor solution hardly changes, the modulus would be derived from entanglements trapped by the permanent crosslinking which is not depending on the Host-Guest crosslinking and entanglement. These results suggest that the number of rotaxane structure also increases with increasing $C_{\text{c}}$. This topological permanent crosslinking dominates the equilibrium swollen state in the absence of the effect of the Host-Guest crosslinking.

Figure 6 shows the result of the frequency sweep measurement at the equilibrium swollen state in the host competitor solution of $C_{\text{Host}} = 0.020$ mol kg$^{-1}$ for the Host-Guest gel with $C_{\text{c}} = 0.040$ mol kg$^{-1}$. $G'$ was almost constant independent of the frequency and showed a viscoelasticity spectrum like a chemically crosslinked gel. When the Host-Guest crosslinking are all capped by the competitor, the Rouse mode is not delayed and the entanglement trapped by the Host-Guest crosslinking is also reduced. In the equilibrium swollen state, all the crosslinkings other than the rotaxane structure are lost, which results in the similar behavior to a chemically crosslinked gel.

4. CONCLUSION

We investigated the effect of the Host-Guest interaction on the swelling properties of the Host-Guest gel having both the physical crosslinking and topological permanent crosslinking. The results are summarized as follows; (1) the diffusion coefficient of the Host-Guest gel in the swelling process is hardly affected by the Host-Guest interaction; (2) the viscoelastic spectra are unchanged before and after the swelling, indicating that the Host-Guest crosslinking is stored and can support the stress when the gel is at equilibrium swollen state; (3) when all the Host-Guest crosslinkings are capped by introducing host competitors, the Rouse relaxation is not retarded anymore and the entanglements trapped by the Host-Guest crosslinkings dissociate, which results in the behavior like the chemically crosslinked gels. These characteristic swelling properties are considered to be unique to the Host-Guest gels having two types of crosslinking derived from one molecular design.

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