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Dissertation

Effect of swelling on network elasticity of hydrogel

(ゲル網目の弾性に及ぼす膨潤の効果)

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Chapter 1

General Introduction

Chapter 1 General Introduction

1.1 Overview

A hydrogel, which consists of cross-linked hydrophilic polymers and water as a solvent, is a unique material because it keeps both high water content like liquid and its shape like solid. A hydrogel has physical properties like those of living things such as flexibility and high water content. Furthermore, certain kinds of hydrogels have excellent biocompatibility [1] and stimuli-responsivity. [2, 3] Therefore, a hydrogel is expected especially as biomedical material. Recently, in addition, several kinds of strong hydrogels or tough hydrogels have been developed so that hydrogel can be used practically as load-bearing materials. [4-9] An ultra-tough double network hydrogel (DN gel) is one example of them. [8,9] A DN gel has interpenetrating network structure composed of strong polyelectrolyte gel, which is mechanically weak but swells quite large in water, as the first network and neutral gel, which is ductile but flexible, as the second network. Furthermore, a DN gel can have biocompatibility and cartilage regeneration ability by controlling its chemical species, [10] and then a DN gel is paid attention as biomedical or industrial materials like artificial cartilage.

In order to apply gels in various fields, design of the gel which has designed physical properties freely is required. To control the physical properties of gels is also important especially to develop tough hydrogel. For this purpose, it has been anticipated to clarify the relationship between structure and mechanical properties of hydrogel. The key feature of a

hydrogel is swelling. Owing to these backgrounds, to realize the correlation between structural factors and material mechanical properties of hydrogel in wide range of swelling degree is important.

However, there are several problems among previous studies. 1) Structure of target hydrogels is generally not clear and then estimated from rubber elasticity theory. Because hydrogel is generally synthesized by random copolymerization of monomer and cross-linker, its structure is quite inhomogeneous and unclear. The reason why the study about the correlation between structures and mechanical properties, especially highly swollen region, has not proceeded is because of this structural unclearness. 2) A target of previous studies was mainly middle swollen region, so there are few studies which target low swelling region or high swelling region.

As recent research, Sakai et al developed Tetra-PEG gel whose structure is clear. [6, 11] tetra-PEG gel is very effective to deal with problem 1) because this hydrogel has well-known structure. However, because Tetra-PEG gel is neutral gel and its swelling degree is small, it was impossible to verify experimentally about the effect of network elasticity in high swelling region.

Therefore, the purpose of this study is to clarify experimentally the relationship between swelling degree and elastic modulus of hydrogel whose structure is well-known and its theoretical background. To change its swelling ratio Q , we introduced linear polyelectrolytes, poly (sodium 2-acrylamido-2-methylpropane sulfonic acid) (PNaAMPS), with several concentrations into the Tetra-PEG network [12-13]. Addition of PNaAMPS increases osmotic pressure of the whole hydrogel and promotes its swelling.

Subsequently, the Tetra-PEG gel was immersed in polyethylene glycol (PEG) aqueous solutions of varied concentrations. PEG increases osmotic pressure of outside solution and therefore suppresses swelling of the network.

1.2 Outline of This Thesis

In this dissertation, I report the experimental result of the effect of ionic osmotic pressure on swelling of hydrogel by using Tetra-PEG gel, molecular stent method, and ionic osmotic pressure measurement by microelectrode technique.

In chapter 2, I explain origin of various physical properties of polymers and hydrogels. It has been said that swelling ratio of hydrogel is described by proportion between the resistance against the deformation of network, elasticity or the effect of suppression of swelling, and osmotic pressure difference, the effect of promotion of swelling. Therefore, to design swelling ratio and physical properties of hydrogel materials freely, osmotic pressure of hydrogels should be controlled without changing their network structure.

In chapter 3, I constructed the relationship between swelling ratio, network structure, and elastic modulus, physicality, of hydrogel in very wide range of swelling ratio experimentally by combining Tetra-PEG gel and molecular stent method. The structure of this gel is confirmed to be controlled very delicately. The swelling ratio of Tetra-PEG gel is widely tuned by molecular stent method, which is the method to improve the swelling ratio and osmotic pressure of hydrogel without changing the structure of hydrogel network by introducing the strong polyelectrolyte, molecular stent, into gel. This method

enables to discover the relationship between composition, swelling ratio and physical properties of a gel whose structure is well-known, and its theoretical background experimentally. As the concrete experimental method, I controlled swelling ratio, Q , of the Tetra-PEG gels by introducing the variety of concentrations of strong polyelectrolyte into gel, and immersing in water or variety of concentrations of PEG solution. PEG has the effect to suppress the swelling by increasing the osmotic pressure of outer solvent. Next, Young's modulus, E , of these hydrogel is determined by indentation test and compared to Q .

In chapter 4, I discussed the effect of ionic osmotic pressure on swelling of hydrogel experimentally and established the swelling theory of hydrogel based on the experiment by measuring the electrostatic potential by using microelectrode technique. First, I prepared Tetra-PEG gels including the various concentrations of strong polyelectrolyte, molecular stent, and measured the swelling ratio and elastic modulus by method above. Next, I determined the isolated ionic concentration in gel from the result of electrostatic potential measurement and calculated ionic osmotic pressure by van't Hoff's law. By combining this result and the relationship between swelling ratio and elastic modulus above, I described the relationship among swelling ratio, elastic modulus and ionic osmotic pressure precisely. Then, I could revisit of swelling theory of polyelectrolyte gel in existence.

In chapter 5, I summarized the entire conclusions. There have been many studies which discussed the relationship among elastic modulus, swelling ratio and ionic osmotic pressure previously in domestic and out of the state.

However, precise discussion has not been done because there are large limitations which come from heterogeneous properties of network structure of selected gels, coupling between network structure and ionic concentration, and aggregation effect of counter ions. My research enables to control the swelling ratio of the gel whose structure is well-known very widely and separate ionic osmotic pressure and structure of network, which is the problem of polyelectrolyte, by using Tetra-PEG gel and molecular stent method for the first time. Then, measuring electrostatic potential of gel enables us to estimate the effect of condensation of counter ion precisely, which is very difficult until now. These experimental methods are unique and this research has large meanings about realizing the fundamental physical properties of gels.

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Chapter 2

Backgrounds

Chapter 2 Backgrounds

2.1 A thermodynamic view of polymer material [1], [2], [3]

Polymer in solution is composed of the numerous atoms and thermally fluctuates. So, it is impossible to realize the states of all atoms completely upon deformation of polymer material. Thus, mechanical properties of polymers have been understood from their macroscopic property, i.e. thermodynamic property.

Helmholtz's free energy, F is defined as following.

$$F = U - TS \quad (2.1)$$

According to the first law of thermodynamics, the differential of internal energy, dU , is written by the sum of the differential of work, dW , and the differential of heat quantity, dQ . In quasi-static process, $dQ = TdS$, where T is absolute temperature.

$$dU = dQ + dW = TdS + dW \quad (2.2)$$

From the equations (2.1) and (2.2),

$$\begin{aligned} dF &= dU - TdS - SdT = TdS + dW - TdS - SdT \\ &= dW - SdT \end{aligned} \quad (2.3)$$

If T is constant, $SdT = 0$. The work, dW , which come from the deformation to an object, is written by the equations (2.1), (2.2), (2.3),

$$\begin{aligned} dW &= f dL = dF = dU - TdS \\ \Leftrightarrow f &= \left(\frac{\partial F}{\partial L} \right)_T = \left(\frac{\partial U}{\partial L} \right)_T - T \left(\frac{\partial S}{\partial L} \right)_T \end{aligned} \quad (2.4),$$

where f is force and L is deformation of an object.

Then, the first term of the right side of equation (2.4) is the force arisen from

the energy, whereas the second term is the force arisen from the entropy. Thus, these elasticities arisen from these forces are called energy elasticity and entropy elasticity.

In many of solids like metal or plastic, bond energy, which is a kind of potential energy, arises from chemical interactions. So, elasticity is arisen in order to be the most stable condition, which is the same as minimizing the potential energy. It means when the solid is deformed, energy elasticity is dominant. About soft matter like hydrogel or rubber, however, each molecule can move freely and the effect of its potential energy among molecules is little. In this case, elongating the network induces decrease of the degree of freedom of motion, and elasticity is arisen in order to be conditions as wide a range of conditions as possible, which is to increase entropy. Thus, when hydrogels or rubbers are deformed, entropy elasticity is dominant.

According to the second law of thermodynamics, it is known that all irreversible changes in isolated system go for the direction of increasing the entropy. By obeying this law, thermal motion of atoms or molecules goes for the most stable condition in which the number of cases the system can behave is largest. Boltzmann leaded the relationship between entropy, S , and the number of cases, Ω , by using Boltzmann constant, k_B . The dimension of Boltzmann constant is JK^{-1} , and it is found that entropy has the same dimension from this equation, too.

$$S = k_B \ln \Omega \quad (2.5)$$

It is impossible that all conditions of an enormous number of molecules is written accurately or fit a definite geometrical configuration because the

conformation of polymer chain fluctuates constantly by thermal motion. Therefore, statistical procedure which describes the properties of polymer chain with ignoring the small effects of fluctuation by picking up randomly and averaging an enormous number of molecule.

2.2 Single chain mechanics^{[2], [3], [4], [5]}

Based on the vision of random walk, the entropy of one dimensional polymer chain is calculated. First, 1-D polymer chains composed of N rigid rods whose length is a , and their direction is right or left, is taken into account. Then, if there are the right components of N_R pieces, and the left components of N_L pieces, end-to-end distance, R , is written to the following.

$$R = a(N_R - N_L) \quad (2.6)$$

The numbers of N_R and N_L are written to the following, respectively.

$$N_R = \frac{aN + R}{2a}, \quad N_L = \frac{aN - R}{2a} \quad (2.7)$$

All the number of cases, W , which polymers can deform is equal to the number of combination of picking up the N_R and N_L from N .

$$W = {}_N C_{N_R} = \frac{N!}{N_R! N_L!}$$

According to the Stirling's formula,

$$\ln n! \doteq n \ln n - n$$

From this approximation,

$$\begin{aligned} \ln W &= \ln \left(\frac{N!}{N_R! N_L!} \right) = N \ln N - N - (N_R \ln N_R - N_R) - (N_L \ln N_L - N_L) \\ &= N \ln N - N_R \ln N_R - N_L \ln N_L - N + N_R + N_L \\ &= N \ln N - N_R \ln N_R - N_L \ln N_L - N + \frac{aN + R}{2a} + \frac{aN - R}{2a} \quad (\because (2.7)) \\ &= N \ln N - N_R \ln N_R - N_L \ln N_L - N + N \end{aligned}$$

$$= N \ln N - N_R \ln N_R - N_L \ln N_L$$

From the equation (2.5),

$$\begin{aligned} S &= k_B \ln W = k_B (N \ln N - N_R \ln N_R - N_L \ln N_L) & (2.8) \\ &= k_B \left(N \ln N - \frac{aN+R}{2a} \ln \left(\frac{aN+R}{2a} \right) - \frac{aN-R}{2a} \ln \left(\frac{aN-R}{2a} \right) \right) & (\because (2.7)) \\ &= Nk_B \left(\ln N - \frac{1}{2} \left(1 + \frac{R}{aN} \right) \ln \left(\frac{aN+R}{2a} \right) - \frac{1}{2} \left(1 - \frac{R}{aN} \right) \ln \left(\frac{aN-R}{2a} \right) \right) \end{aligned}$$

Then,

$$\begin{aligned} \ln \left(1 + \frac{R}{aN} \right) &= \ln \left(\frac{aN+R}{aN} \right) = \ln \left(\frac{aN+R}{2a} \cdot \frac{2}{N} \right) = \ln \frac{2N_R}{N} = \ln 2 + \ln N_R - \ln N \\ \Leftrightarrow \ln N_R &= \ln \left(1 + \frac{R}{aN} \right) + \ln N - \ln 2 \end{aligned}$$

Also,

$$\ln \left(1 - \frac{R}{aN} \right) = \ln 2 + \ln N_L - \ln N \Leftrightarrow \ln N_L = \ln \left(1 - \frac{R}{aN} \right) + \ln N - \ln 2$$

Substituting to the equation (2.8),

$$\begin{aligned} S &= k_B \left[N \ln N - N_R \left\{ \ln \left(1 + \frac{R}{aN} \right) + \ln N - \ln 2 \right\} - N_L \left\{ \ln \left(1 - \frac{R}{aN} \right) + \ln N - \ln 2 \right\} \right] \\ &= k_B \left\{ N \ln N - N_R \ln \left(1 + \frac{R}{aN} \right) - N_L \ln \left(1 - \frac{R}{aN} \right) - (N_R + N_L) \ln N + (N_R + N_L) \ln 2 \right\} \end{aligned}$$

From the equation (2.7), because $N = N_R + N_L$,

$$\begin{aligned} S &= k_B \left\{ N \ln N - N_R \ln \left(1 + \frac{R}{aN} \right) - N_L \ln \left(1 - \frac{R}{aN} \right) - N \ln N + N \ln 2 \right\} \\ &= k_B \left\{ N \ln 2 - N_R \ln \left(1 + \frac{R}{aN} \right) - N_L \ln \left(1 - \frac{R}{aN} \right) \right\} \\ &= Nk_B \left\{ \ln 2 - \frac{N_R}{N} \ln \left(1 + \frac{R}{aN} \right) - \frac{N_L}{N} \ln \left(1 - \frac{R}{aN} \right) \right\} \\ &= Nk_B \left\{ \ln 2 - \frac{1}{2} \left(1 + \frac{R}{aN} \right) \ln \left(1 + \frac{R}{aN} \right) - \frac{1}{2} \left(1 - \frac{R}{aN} \right) \ln \left(1 - \frac{R}{aN} \right) \right\} \end{aligned}$$

Because it is assumed that $R \ll aN \Leftrightarrow \frac{R}{aN} \ll 1$, $\ln \left(1 \pm \frac{R}{aN} \right)$ can be approximated by Taylor expansion at neighborhood of $\frac{R}{aN} = 1$,

$$\ln \left(1 \pm \frac{R}{aN} \right) = \pm \frac{R}{aN} + \dots \doteq \pm \frac{R}{aN}.$$

Then,

$$\begin{aligned} S &= Nk_B \left\{ \ln 2 - \frac{1}{2} \left(1 + \frac{R}{aN} \right) \frac{R}{aN} - \frac{1}{2} \left(1 - \frac{R}{aN} \right) \cdot \left(-\frac{R}{aN} \right) \right\} \\ &= Nk_B \ln 2 - \frac{1}{2} Nk_B \left\{ \left(1 + \frac{R}{aN} \right) \frac{R}{aN} + \left(1 - \frac{R}{aN} \right) \cdot \left(-\frac{R}{aN} \right) \right\} \end{aligned}$$

$$\begin{aligned}
&= Nk_B \ln 2 - \frac{1}{2} Nk_B \cdot \frac{2R^2}{a^2 N^2} \\
&= Nk_B \ln 2 - \frac{k_B R^2}{a^2 N}
\end{aligned}$$

Therefore, the force, f , applied to the object by the entropy elasticity is written by using the equation (2.4).

$$f = -T \left(\frac{\partial S}{\partial R} \right)_T = \frac{2k_B T}{a^2 N} R$$

Because the model above is one-dimensional random walk Gaussian chain, it must be generalized to three-dimensional random walk Gaussian chain model. First, polymer chains composed of components of number of N pieces whose length is a , and its direction is selectable freely is taken into account. The number of cases, W , starting from the origin of the coordinate system to end after N steps within a volume $dR_x dR_y dR_z$ of the point with displacement vector \mathbf{R} is $W(N, \mathbf{R}) dR_x dR_y dR_z$. Because the three components of three-dimensional random walk are independent of each other, its distribution function is a product of the three one-dimensional distribution functions.

$$W(N, \mathbf{R}) dR_x dR_y dR_z = W(N, R_x) dR_x W(N, R_y) dR_y W(N, R_z) dR_z$$

The mean-square displacement of a random walk from the origin, R^2 , is equal to the mean-square end-to-end vector of a freely jointed chain with the number of monomers, N , equal to the number of steps of the walk and the monomer length, a , equal to the step size. This mean-square displacement R^2 is composed of three mean-square displacements of the three independent one-dimensional walks.

$$R^2 = R_x^2 + R_y^2 + R_z^2 = Na^2$$

The mean-square displacement along each of them must be a third of the

total.

$$R_x^2 = R_y^2 = R_z^2 = \frac{Na^2}{3}$$

The one-dimensional number of cases distribution function for the components of a random walk along each of these three axes can be obtained by substituting these mean-square displacements.

$$W(N, R_x) = \frac{\exp\left(-\frac{R_x^2}{2R_x^2}\right)}{\sqrt{2\pi R_x^2}} = \sqrt{\frac{3}{2\pi Na^2}} \exp\left(-\frac{3R_x^2}{2Na^2}\right)$$

Its distribution function for the end-to-end vector, \mathbf{R} , of an ideal linear chain of N monomers is the product of the three independent distribution functions.

$$W(N, \mathbf{R}) = \left(\frac{3}{2\pi Na^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(R_x^2 + R_y^2 + R_z^2)}{2Na^2}\right) = \left(\frac{3}{2\pi Na^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3R^2}{2Na^2}\right)$$

This probability distribution can be rewritten in the spherical coordinate system.

$$W(N, \mathbf{R}) 4\pi R^2 d\mathbf{R} = 4\pi \left(\frac{3}{2\pi Na^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3R^2}{2Na^2}\right) R^2 d\mathbf{R}$$

The entropy of an ideal chain with N monomers and end-to-end vector, \mathbf{R} , is related to the probability distribution function.

$$S(N, \mathbf{R}) = k_B \ln W = -\frac{3}{2} k_B \frac{R^2}{Na^2} + \frac{3}{2} k_B \ln\left(\frac{3}{2\pi Na^2}\right)$$

The latter terms of this equation depend only on the number of monomers, N , but not on the end-to-end vector, \mathbf{R} , and can be ignored.

$$S = -\frac{3k_B}{2Na^2} R^2$$

Therefore, the force, f , applied to the object by the entropy elasticity is written by using the equation (2.4).

$$\mathbf{f} = -T \left(\frac{\partial S}{\partial \mathbf{R}} \right)_T = \frac{3k_B T}{Na^2} \mathbf{R}$$

This 3D random-walk free-joint chain is very similar to 1D chain.

2.3 Finite extensibility effect of polymer chain^{[5], [6]}

Because the model above is supposed that segment distribution of each partial chain always obey the Gaussian distribution, it can only apply the region in which the finite extensibility of chain is not so large. Thus, it is impossible to consider a chain which is elongated close to its contour length and has non-Gaussian distribution. This finite extensibility effect should be taken into account in order to reproduce the stretching experiment of real chains. Here, I adopt two single chain elasticity models considering the finite extensibility. One is the inverse Langevin chain based on a freely-jointed chain (FJC) and the other is a worm-like chain (WLC) model.

FJC model deals with finite extensibility effect of chain statistically for the first time. This is the approach from the analogy between the relationship of applied stress and segment direction and the relationship of applied electric field and dipole direction.

Thinking about freely jointed chain whose bond number is n and which has charge $+q$ and $-q$ terminally-connected. It supposes that these segments distribution is completely random without external force and correlation between neighboring segments. When the electric field \mathbf{E} is applied against the z-axis, the force $\mathbf{f} = q\mathbf{E}$ works at positive charge whereas the force $\mathbf{f} = -q\mathbf{E}$ works at negative charge.

When the electric field E is applied, the energy chains have is proportionate to both end-to-end vector \mathbf{R} against the direction of electric field

$$U = -q\mathbf{E} \cdot \mathbf{R} = -f \cdot \mathbf{R} = -fR_1$$

R_1 is component of x_1 -axis of \mathbf{R} . Because the number of conformation z of chain obeys the Boltzmann distribution, it can be written in the following.

$$z = \exp\left(-\frac{U}{k_B T}\right) = \exp\left(\frac{fR_1}{k_B T}\right)$$

Partition function Z which corresponds to the sum of all conformation is

$$Z = \sum z = \sum \exp\left(\frac{fR_1}{k_B T}\right)$$

Because conformation whose energy state is high is energetically unstable, the probability of to be this state decreases and little contribute to partition function. If it is freely jointed chain, the number of conformation is determined by the variety of bond angle between segments of conformation.

When spherical coordinate adopts against each bond angle, Z can be rewritten in the following by using two variation angles θ and φ .

$$Z = \sum \exp\left(\frac{fR_z}{k_B T}\right) = \iint \exp\left(\frac{fR_z}{k_B T}\right) \prod_{i=1}^N \sin\theta_i d\theta_i d\varphi_i$$

Then, R_1 is rewritten in the following by using bond length a and θ .

$$R_1 = \sum_{i=1}^N a \cos \theta_i$$

By using these equations,

$$\begin{aligned} Z &= \iint \exp\left(\frac{fa}{k_B T} \sum_{i=1}^N \cos \theta_i\right) \prod_{i=1}^N \sin\theta_i d\theta_i d\varphi_i \\ &= \left[\int_0^\pi 2\pi \sin\theta_i \exp\left(\frac{fa}{k_B T} \cos\theta_i\right) d\theta_i \right]^N = \left[\frac{2\pi}{\frac{fa}{k_B T}} \left\{ \exp\left(\frac{fa}{k_B T}\right) - \exp\left(-\frac{fa}{k_B T}\right) \right\} \right]^N \\ &= \left[\frac{4\pi \sinh\left(\frac{fa}{k_B T}\right)}{\frac{fa}{k_B T}} \right]^N \end{aligned}$$

Because partition function is gotten as the function of f , Gibbs's free energy is gotten from the following relationship, $G = -k_B T \ln Z$.

$$G = -k_B N T \left[\ln \left(4\pi \sinh \left(\frac{fa}{k_B T} \right) \right) - \ln \left(\frac{fa}{k_B T} \right) \right]$$

Average end-to-end distance R is gotten as the differential of G by f .

$$\begin{aligned} R &= -\frac{\partial G}{\partial f} = \frac{\partial}{\partial f} k_B N T \left[\ln \left(4\pi \sinh \left(\frac{fa}{k_B T} \right) \right) - \ln \left(\frac{fa}{k_B T} \right) \right] \\ &= k_B N T \left\{ \frac{4\pi \cosh \left(\frac{fa}{k_B T} \right) \frac{a}{k_B T}}{4\pi \sinh \left(\frac{fa}{k_B T} \right)} - \frac{\frac{a}{k_B T}}{\frac{fa}{k_B T}} \right\} = a N \left\{ \coth \left(\frac{fa}{k_B T} \right) - \frac{1}{\frac{fa}{k_B T}} \right\} \end{aligned}$$

By rewriting $aN = R_{max}$, it is possible to connect between the proportion of deformation against the maximum finite extensibility and force by using Langevin function. By using inverse Langevin function,

$$f(\alpha) = \frac{k_B T}{b} \mathcal{L}^{-1} \left(\frac{R}{R_{max}} \right) = \frac{k_B T}{b} \mathcal{L}^{-1}(\alpha)$$

where \mathcal{L}^{-1} , f , b , R , and R_{max} are the inverse Langevin function, mean force, Kuhn length, mean end-to-end distance, and contour length, respectively, and α is R/R_{max} . This equation can be simplified by using Padé approximation as

$$f(\alpha) = \frac{k_B T}{b} \frac{\alpha(3-\alpha^2)}{1-\alpha^2} \quad (2.9)$$

The other is WLC model. This is the special case of the freely jointed chain model for very small values of the bond angle. For small values of the bond angle ($\theta \ll 1$), the $\cos \theta$ can be expanded about its value of unity at $\theta = 0$.

$$\cos \theta \cong 1 - \frac{\theta^2}{2}$$

For small θ , $\ln(1 - \theta) \cong -\theta$.

$$\ln(\cos \theta) \cong -\frac{\theta^2}{2}$$

The final relation defines as the number of main-chain bonds in a persistence segment which is the scale at which local correlations between bond vectors decay. Since θ is small, the persistence segment of the chain contains a large number of main chain bonds. And, the persistence length is the length of this persistence segment (1.1 nm).

$$l_p = -\frac{l}{\ln(\cos \theta)} = \frac{2l}{\theta^2}$$

The Flory's characteristic ratio of the worm-like chain is very large.

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta} \cong \frac{2-\frac{\theta^2}{2}}{\frac{\theta^2}{2}} \cong \frac{4}{\theta^2}$$

The mean-square end-to-end distance of the worm-like chain can be evaluated using the exponential decay of correlations between tangent vectors along the chain.

$$\begin{aligned} R^2 &= l^2 \sum_{i=1}^n \sum_{j=1}^n \langle \cos\theta_{ij} \rangle = l^2 \sum_{i=1}^n \sum_{j=1}^n (\cos\theta)^{|i-j|} \\ &= l^2 \sum_{i=1}^n \sum_{j=1}^n \exp\left(-\frac{|i-j|}{l_p} l\right) \end{aligned}$$

The summation over bonds can be changed into integration over the contour of the worm-like chain.

$$\begin{aligned} l \sum_{i=1}^N &\rightarrow \int_0^{R_{max}} du \quad \text{and} \quad l \sum_{j=1}^N \rightarrow \int_0^{R_{max}} dv \\ R^2 &= \int_0^{R_{max}} \left[\int_0^{R_{max}} \exp\left(-\frac{|u-v|}{l_p}\right) dv \right] du \\ &= \int_0^{R_{max}} \left[\left(\exp\left(-\frac{u}{l_p}\right) \int_0^u \exp\left(\frac{v}{l_p}\right) dv + \exp\left(\frac{u}{l_p}\right) \int_u^{R_{max}} \exp\left(-\frac{v}{l_p}\right) dv \right) \right] du \\ &= l_p \int_0^{R_{max}} \left[\left(\exp\left(-\frac{u}{l_p}\right) \left(\exp\left(\frac{u}{l_p}\right) - 1 \right) \right. \right. \\ &\quad \left. \left. + \exp\left(\frac{u}{l_p}\right) \left(-\exp\left(-\frac{R_{max}}{l_p}\right) + \exp\left(-\frac{u}{l_p}\right) \right) \right) \right] du \\ &= l_p \int_0^{R_{max}} \left[2 - \exp\left(-\frac{u}{l_p}\right) - \exp\left(-\frac{R_{max}}{l_p}\right) \exp\left(\frac{u}{l_p}\right) \right] du \end{aligned}$$

$$\begin{aligned}
&= l_p \left[2R_{max} + l_p \left(\exp\left(-\frac{R_{max}}{l_p}\right) - 1 \right) - l_p \exp\left(-\frac{R_{max}}{l_p}\right) \left(\exp\left(\frac{R_{max}}{l_p}\right) - 1 \right) \right] \\
&= 2l_p R_{max} - 2l_p^2 \left(1 - \exp\left(-\frac{R_{max}}{l_p}\right) \right)
\end{aligned}$$

There are two simple limits of this expression. The ideal chain limit is for worm-like chains much longer than their persistence length.

$$R^2 \cong 2l_p R_{max} \quad \text{for } R_{max} \gg l_p$$

The rod-like limit is for worm-like chains much shorter than their persistence length. The exponential can be expanded in this limit.

$$\exp\left(-\frac{R_{max}}{l_p}\right) \cong 1 - \frac{R_{max}}{l_p} + \frac{1}{2} \left(\frac{R_{max}}{l_p}\right)^2 + \dots \text{for } R_{max} \ll l_p$$

$$R^2 \cong R_{max}^2 \quad \text{for } R_{max} \ll l_p$$

In the case of the worm-like chain model, the extensional force diverges reciprocally proportional to the square of $R_{max} - R$

$$\begin{aligned}
\frac{f l_p}{2k_B T} &\cong \frac{1}{2} \left(\frac{R_{max}}{R_{max}-R}\right)^2 \quad \text{for } 1 - \frac{R}{R_{max}} \ll 1 \\
f(\alpha) &\cong \frac{k_B T}{l_p} \left\{ \frac{1}{4} \left(1 - \frac{R}{R_{max}}\right)^{-2} - \frac{1}{4} + \frac{R}{R_{max}} \right\} = \frac{k_B T}{l_p} \left\{ \frac{1}{4} (1 - \alpha)^{-2} - \frac{1}{4} + \alpha \right\}. \quad (2.10)
\end{aligned}$$

In stress-strain curve, such strain-hardening effect is shown when the finite extensibility effect appears.

In these equations, it is assumed that average end-to-end distance, R_0 , is far shorter than contour length, R_{max} , which is the maximum value R_0 can be ($R_0 \ll R_{max}$), in low swelling region, so $\alpha = \frac{R_0}{R_{max}} \ll 1$. Therefore, $1 - \alpha^2 \doteq 1$. Then, these two equations above can be changed the followings in low swelling region.

$$\begin{aligned}
f_{FJC}(\alpha) &= \frac{RT}{2l_p} \frac{\alpha(3-\alpha^2)}{1-\alpha^2} \doteq \frac{RT}{2l_p} \frac{3\alpha}{1} = \frac{3RT}{2l_p} \alpha \\
f_{WLC}(\alpha) &= \frac{RT}{l_p} \left\{ \frac{1}{4} (1 - \alpha)^{-2} - \frac{1}{4} + \alpha \right\}
\end{aligned}$$

$$\doteq \frac{RT}{l_p} \left\{ \frac{1}{4} \cdot (1)^{-2} - \frac{1}{4} + \alpha \right\} = \frac{RT}{l_p} \left\{ \frac{1}{4} - \frac{1}{4} + \alpha \right\} = \frac{RT}{l_p} \alpha$$

Because both of them can be written in Hooke's law, $f(\alpha) = k\alpha$, the nonlinear effect doesn't appear.

On the other hand in high swelling region in which appears finite extensibility effect, R_0 closes in R_{max} illimitably. So, α closes to 1. Then, thinking of the utmost limits at $\alpha \rightarrow 1$ of these equations in high swelling region,

$$\lim_{\alpha \rightarrow 1} f_{FJC}(\alpha) = \frac{RT}{2l_p} \frac{1 \cdot (3-1)}{1-1} = \frac{RT}{2l_p} \cdot \frac{2}{0} = \infty$$

$$\lim_{\alpha \rightarrow 1} f_{WLC}(\alpha) = \frac{RT}{l_p} \left\{ \frac{1}{4} (1-1)^{-2} - \frac{1}{4} + 1 \right\} = \frac{RT}{l_p} \left\{ \frac{1}{4} \cdot \frac{1}{0^2} - \frac{1}{4} + 1 \right\} = \infty$$

Because both of them approach infinity, the nonlinear effect appears.

2.4 Stress-Strain curve of hydrogel^{[2], [3]}

When it comes to thinking about rubber elastic body like hydrogel, it assumes that the N number of molecule chains forms three dimensional network structures bound by cross-linking. Classical rubber elasticity theory obeys the Gaussian chain theory based on the following assumption.

- ① Rubber is incompressible.
- ② All molecule chains are Gaussian chains of the same molecular weight.
- ③ All terminals of molecule chain bind to the network, which means without thinking of terminal.
- ④ Each molecule chain composing network obeys the Gaussian statistics.
- ⑤ Energy elasticity doesn't change by deformation.

Entropy elasticity of cross-linked polymer chain is modeled assumed to the affine deformation in which deformation of polymer chain is homothetic to deformation of entire material. Assumed to the model of cubic hydrogel whose length of each side of before deformation is L_x, L_y, L_z and they changed to $\lambda_x, \lambda_y, \lambda_z$ by uniaxial elongation deformation, the following equation is written by the assumption ① above.

$$\lambda_x \lambda_y \lambda_z = 1$$

Because of the assumption of affine deformation, end-to-end distance between polymer chains before deformation is able to be written in the following.

$$\mathbf{R}_0 = \begin{pmatrix} R_{x0} \\ R_{y0} \\ R_{z0} \end{pmatrix}$$

After deformation, it can be written in the following.

$$\mathbf{R} = \begin{pmatrix} R_x \\ R_y \\ R_z \end{pmatrix} = \begin{pmatrix} \lambda_x R_{x0} \\ \lambda_y R_{y0} \\ \lambda_z R_{z0} \end{pmatrix}$$

Then, the entire entropy change between before and after deformation can be written in the following. ν is the number of molecule chain in unit volume, network density.

$$\Delta S = S(\mathbf{R}) - S(\mathbf{R}_0) = -\frac{\nu k_B}{2} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

When the deformation is uniaxial elongation test in the direction of x-axis, the following can be written.

$$\lambda_x = \lambda, \quad \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$$

So,

$$\Delta S = -\frac{\nu k_B}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$$

Therefore, stress, σ , applied to the object by the entropy elasticity is written in the following according to the equation (2.4).

$$\sigma = -T \left(\frac{\partial S}{\partial R} \right)_T = \nu k_B T \left(\lambda - \frac{1}{\lambda^2} \right) \quad (2.11)$$

When the modulus is put to $G = \nu k_B T$, the following equation can be written.

$$\sigma = G \left(\lambda - \frac{1}{\lambda^2} \right)$$

If the deformation is small enough, $\frac{1}{\lambda^2} = 1$ can be written. So,

$$\sigma \doteq G(\lambda - 1) = G\varepsilon$$

Therefore, according to the Gaussian chain theory, it is found that stress obeys the Hooke's law if the deformation is small because it directly proportional to the strain approximately. If the deformation is large, the equation (2.11) is also called Neo-Hookean model because this relationship is changed by the finite extensibility effect of chain and so on. Although Young's modulus, E , is the physicality value defined by the simple stretching of polymer fundamentally to be exact, elastic modulus at the beginning of tensile test is used as the almost same meaning as it in this work.

2.5 Viscoelasticity^{[7], [8], [9]}

Polymer material is written as viscoelastic body, and it has both viscous property in which the work applied to the system is dissipated as the heat and elastic property in which the work is stored as the potential energy. About theoretical elastic body, certain strain arises instantaneously by applying the stress and disappears instantaneously by removing it. Such object is called Hooke elastic body and the following relationship between

stress and strain can be written. This is called Hooke's law, and G is called rigidity modulus if the strain is shear strain.

$$\sigma_1 = G\varepsilon_1 \quad (2.12)$$

About theoretical viscous body, however, certain strain arises instantaneously by applying the stress and doesn't recover by removing the stress but keeps in the constant value, and the proportional relationship between the strain velocity and stress. Such object is called Newton viscous body and the following relationship between stress and strain can be written. This is called Newton's law, and η is called viscosity.

$$\sigma_2 = \eta \frac{d\varepsilon_2}{dt} \quad (2.13)$$

Polymer substance is viscoelastic body which has both elastic and viscous properties, and can be written as the system combined them. Typical examples are Maxwell model which is modeled by combining Hooke elasticity and Newton viscosity in series or Voigt model which is modeled by combining Hooke elasticity and Newton viscosity in parallel. In these models, Hooke elasticity is shown in the spring, stress is σ_1 and strain is ε_1 and rigidity modulus is G , whereas Newton viscosity is shown in the dashpot, stress is σ_2 , strain is ε_2 , tensile viscosity is η . In Maxwell model, the same stress is applied to both spring and dashpot because they are combined in series, and total strain is sum of them. Therefore, the following relationship can be written between total stress, σ , and total strain, ε .

$$\sigma = \sigma_1 = \sigma_2 \quad (2.14)$$

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad (2.15)$$

By equations (2.12), (2.13) and (2.14),

$$\sigma = G\varepsilon_1 = \eta \frac{d\varepsilon_2}{dt}$$

By the equation (2.15),

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = \frac{1}{G} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta} \quad (2.16)$$

In Voigt model, the same strain is applied to both spring and dashpot because they are combined in parallel, and total stress is sum of them. Therefore, the following relationship can be written between total stress, σ , and total strain, ε .

$$\sigma = \sigma_1 + \sigma_2 \quad (2.17)$$

$$\varepsilon = \varepsilon_1 = \varepsilon_2 \quad (2.18)$$

By equations (2.12), (2.13), (2.17), (2.18),

$$\sigma = G\varepsilon + \eta \frac{d\varepsilon}{dt}$$

Static elasticity measurement is performed by applying unidirectional strain or stress to the sample. So, static elasticity in Maxwell model is thought that constant strain $\varepsilon = \varepsilon_0$ is applied at $t=0$ and keeps after then.

Therefore, by substituting $\frac{d\varepsilon}{dt} = 0$ to the equation (2.16),

$$\frac{1}{G} \cdot \frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\frac{d\sigma}{\sigma} = -\frac{G}{\eta} dt$$

$$\ln \sigma = -\frac{G}{\eta} t + C_1 \quad (C_1 \text{ is integration constant})$$

$$\sigma(t) = \sigma_0 \exp\left(-\frac{G}{\eta} t\right) \quad (\text{Substituting } \sigma_0 = e^{C_1})$$

In this way, stress is decreasing exponentially with time. This phenomenon is called stress relaxation and its rigidity modulus can be written in the following by the equation (2.12).

$$G(t) = \frac{\sigma(t)}{\varepsilon_0} = \frac{\sigma_0}{\varepsilon_0} \exp\left(-\frac{G}{\eta} t\right)$$

Then, substituting $\tau = \frac{\eta}{G}$, τ means the scale of velocity stress relaxes and

stress is $\frac{1}{e}$ if $t = \tau$. This τ is called relaxation time.

Dynamic elasticity measurement is performed by applying sine vibration strain or stress to the sample. So, dynamic elasticity in Maxwell model is thought that constant strain $\varepsilon(t) = \varepsilon_0 e^{i\omega t}$ is applied. Assuming that phase difference, δ , is constant strain, $\frac{\pi}{2}$, stress response then is written in the following.

$$\sigma(t) = \sigma_0 e^{i(\omega t + \delta)} = \sigma_0^* e^{i\omega t} \quad (\sigma_0^* = \sigma_0 e^{i\delta}) \quad (2.19)$$

Substitute them to the equation (2.16),

$$i\omega \varepsilon_0 e^{i\omega t} = \frac{1}{G} i\omega \sigma_0^* e^{i\omega t} + \frac{1}{\eta} \sigma_0^* e^{i\omega t}$$

$$\Leftrightarrow i\omega \varepsilon_0 = \frac{1}{G} i\omega \sigma_0^* + \frac{1}{\eta} \sigma_0^*$$

$$\Leftrightarrow \sigma_0^* = \frac{i\omega}{\frac{1}{\eta} + \frac{i\omega}{G}} \varepsilon_0 = G \frac{i\omega \frac{\eta}{G}}{1 + i\omega \frac{\eta}{G}} \varepsilon_0 = G \frac{i\omega \tau}{1 + i\omega \tau} \varepsilon_0 \quad (\tau = \frac{\eta}{G})$$

$$= G \frac{i\omega \tau (1 - i\omega \tau)}{(1 + i\omega \tau)(1 - i\omega \tau)} \varepsilon_0 = G \frac{\omega^2 \tau^2 + i\omega \tau}{1 + \omega^2 \tau^2} \varepsilon_0$$

So, according to the equation (2.19),

$$\sigma(t) = \left(\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega \tau}{1 + \omega^2 \tau^2} \right) G \varepsilon_0 e^{i\omega t} = \left(\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega \tau}{1 + \omega^2 \tau^2} \right) G \varepsilon(t)$$

Elasticity can be written in complex number if it is put to $G^* = \frac{\sigma(t)}{\varepsilon(t)}$. Therefore, this G^* is called complex modulus and its real part, G' , and imaginary part, G'' , is written in the following function of angular frequency ω .

$$G' = G \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}$$

$$G'' = G \frac{\omega \tau}{1 + \omega^2 \tau^2}$$

G' is called storage elastic modulus and shows elasticity measured. G'' is called loss elastic modulus and shows elasticity lost as heat. And, it can be written in the following.

$$G^* = G' + iG''$$

Thinking of complex plane whose horizontal axis is G' and vertical axis is G'' , because the phase difference is δ , the slope, $\tan \delta$, of coordinate $G^*(G', G'')$ on the complex plane can be written in the following.

$$\tan \delta = \frac{G''}{G'} = \frac{1}{\omega \tau}$$

$\tan \delta$ is called loss tangent and shows the fraction of modulus and viscosity because of the definition of τ . Therefore, viscous property becomes stronger with increasing $\tan \delta$, whereas the elastic property becomes stronger with decreasing $\tan \delta$.

2.6 Osmotic pressure of polymer solution^[4]

According to the mean field theory of Flory and Huggins, it is thought that polymer chains moved by random walk are existed on the lattice through the application of lattice model's vision. Then, when the proportion of lattice point occupied by monomer is ϕ , volume fraction of one-component liquid, pure water, is $1 - \phi$. If this process is isothermal process, because of (2.1)

$$\Delta F_{mix} = \Delta U_{mix} + T \Delta S_{mix} \quad (2.20)$$

According to the second law of thermodynamics, it is found that all irreversible change at isolated system goes to the direction of increasing entropy. Thermal motion of atom or molecule changes to the most stable condition in which its number of possible ways at the system increases to the most by obeying this law. Boltzmann derived the relationship (2.5) between entropy (S) and the number of possible ways at the system (Ω) by using Boltzmann's constant. (k_B) The dimension of Boltzmann's constant is JK^{-1} , and it can be realized that entropy has the same dimension due to the equation (2.5).

Then, because the number of possible ways is the situation that each lattice point in lattice model is occupied either by the chains or by the solvent molecules, the situation occupied by chains is put as Ω_A , that by solvent molecules is put as Ω_B , and the sum of both is put as Ω_{AB} .

$$\Omega_A + \Omega_B = \Omega_{AB} = n$$

n is put as the sum of the number of lattice in the system after mixing. Then,

$$\Omega_A = \varphi n$$

$$\Omega_B = (1 - \varphi) n$$

When the entropy related on the parallel displacement of chains is put as S_A and that of solvent molecules is put as S_B , each amount of change is the following.

$$\Delta S_A = S_{AB} - S_A = k_B \ln \Omega_{AB} - k_B \ln \Omega_A = k_B \ln \left(\frac{\Omega_{AB}}{\Omega_A} \right) = k_B \ln \left(\frac{1}{\varphi} \right) = -k_B \ln \varphi$$

$$\Delta S_B = S_{AB} - S_B = k_B \ln \Omega_{AB} - k_B \ln \Omega_B = k_B \ln \left(\frac{\Omega_{AB}}{\Omega_B} \right) = k_B \ln \left(\frac{1}{1 - \varphi} \right) = -k_B \ln(1 - \varphi)$$

Then, entropy change of mixing ΔS_{mix} is the following

$$\Delta S_{mix} = \frac{\varphi}{N_A} \Delta S_A + \frac{(1 - \varphi)}{N_B} \Delta S_B$$

N_A and N_B are the number of lattice occupied by chains and solvent molecules, respectively. And, because $N_A = P, N_B = 1$ in polymer solution, P is the degree of polymerization by 1mol

$$\Delta S_{mix} = \frac{\phi}{P} \Delta S_A + (1-\phi) \Delta S_B = -R \left(\frac{\phi}{P} \ln \phi + (1-\phi) \ln(1-\phi) \right) \quad (2.21)$$

Next, I'll concern about the change of internal energy by mixing. When I think about the term of internal energy that Flory-Huggins interaction parameter can be divided by interaction between monomer and monomer (χ_{MM}), between solvent and solvent (χ_{SS}), and solvent and monomer (χ_{MS}), each internal energy of monomer and solvent (U_M, U_S) is

$$U_M = \chi_{MM} \phi + \chi_{MS} (1-\phi)$$

$$U_S = \chi_{MS} \phi + \chi_{SS} (1-\phi)$$

And, the sum of them is the following.

$$\begin{aligned} U &= \frac{n}{2} [U_M \phi + U_S (1-\phi)] \\ &= \frac{n}{2} [\chi_{MM} \phi^2 + 2 \chi_{MS} \phi(1-\phi) + \chi_{SS} (1-\phi)^2] \end{aligned}$$

Then, internal energy before mixing is

$$U_0 = \frac{n}{2} [\chi_{MM} \phi + \chi_{SS} (1-\phi)]$$

So, internal energy change before and after mixing is

$$\Delta U_{mix} = \frac{U - U_0}{n} = \frac{2\chi_{MS} - \chi_{MM} - \chi_{SS}}{2} \phi(1-\phi)$$

Then, I put

$$\chi = \frac{2\chi_{MS} - \chi_{MM} - \chi_{SS}}{2RT},$$

$$\Delta U_{mix} = \chi \phi(1-\phi) RT \quad (2.22)$$

Substituting (2.21) and (2.22) to (2.20),

$$\begin{aligned} \Delta F_{mix} &= \Delta U_{mix} + T \Delta S_{mix} = \chi \phi(1-\phi) RT - RT \left(\frac{\phi}{P} \ln \phi + (1-\phi) \ln(1-\phi) \right) \\ &= RT \left[\frac{\phi}{P} \ln \phi + (1-\phi) \ln(1-\phi) + \chi \phi(1-\phi) \right] \end{aligned}$$

Then,

$$\pi_{mix} = -\frac{1}{V_1} \left(\frac{\partial \Delta F_{mix}}{\partial n_1} \right) = -\frac{1}{V_1} \left(\frac{\partial (\Delta F_{mix}/\Phi)}{\partial (1/\Phi)} \right) = \frac{\Phi^2}{V_1} \left(\frac{\partial (\Delta F_{mix}/\Phi)}{\partial \Phi} \right)$$

So,

$$\begin{aligned} \frac{\Delta F_{mix}}{\Phi} &= RT \left[\frac{\ln \Phi}{p} + \frac{1-\Phi}{\Phi} \ln(1-\Phi) + \chi(1-\Phi) \right] \\ \Leftrightarrow \frac{\partial (\Delta F_{mix}/\Phi)}{\partial \Phi} &= RT \left[\frac{1}{\Phi p} - \frac{1}{\Phi^2} \ln(1-\Phi) + \frac{1-\Phi}{\Phi} \cdot \frac{-1}{1-\Phi} - \chi \right] \\ \Leftrightarrow \Phi^2 \left(\frac{\partial (\Delta F_{mix}/\Phi)}{\partial \Phi} \right) &= RT \left[\frac{\Phi}{p} - \ln(1-\Phi) - \Phi - \chi \Phi^2 \right] \end{aligned}$$

Therefore,

$$\pi_{mix} = -\frac{RT}{V_1} \left[\ln(1-\Phi) + \left(1 - \frac{1}{p}\right) \Phi + \chi \Phi^2 \right] \quad (2.23)$$

2.7 Swelling ratio of hydrogel and elastic energy^[4]

Swelling of hydrogel and its accompanying elastic modulus change are caused by ionic osmotic pressure. So, I searched for the relationship between them. If polyelectrolyte gel immerses in pure water, the forces to counteract the difference the concentrations of network or charge between in and out of gel, π_{mix} and π_{ion} , works and gel swells by taken in water. But, elastic force, π_{el} , which works against deformation of network by swelling at the surface of gel because the conformation of network becomes unstable to be closed to finite extensibility state from random coil state by swelling in energetic term. Then, osmotic pressure of hydrogel per unit volume, π_{total} , can be given to the sum of the osmotic pressure come from mixing polymer and solvent which is described by Flory-Huggins theory, π_{mix} , osmotic pressure of elasticity of network, π_{el} , and ionic osmotic pressure of counter ion, π_{ion} , if hydrogel has charge.

$$\pi_{total} = \pi_{mix} + \pi_{el} + \pi_{ion} = \pi_{out}$$

At the equilibrium state, π_{out} is equal to 0. So, this equation is able to be written.

$$-\pi_{el} = \pi_{mix} + \pi_{ion} \quad (2.24)$$

So, it is thought that their all pressure to apply gel are matching at gel surface at the equilibrium state. π_{mix} and π_{ion} work from gel surface to outside direction when swelling whereas π_{el} works from gel surface to inside direction. Incidentally, π_{el} doesn't work in polymer solution.

Then, elastic modulus come from ionic osmotic pressure, E_{ion} , change inversely proportionate to changing the volume.

$$E_{ion} = -\frac{d\pi_{ion}}{\left(\frac{dV}{V}\right)}$$

And, volume also changes inversely proportionate to changing the ionic concentration, C_{ion} .

$$\frac{dV}{V} = \frac{d\left(\frac{1}{C_{ion}}\right)}{\left(\frac{1}{C_{ion}}\right)} = -\frac{C_{ion}}{C_{ion}^2} dC_{ion} = -\frac{dC_{ion}}{C_{ion}}$$

According to the van't Hoff's equation, ionic osmotic pressure is written by the following.

$$\pi_{ion} \text{ [J/L]} = C_{ion} \text{ [mol} \cdot \text{m}^{-3}] R \text{ [J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] T \text{ [K]} \quad (2.25)$$

So,

$$E_{ion} = -\frac{d\pi_{ion}}{\left(\frac{dV}{V}\right)} = -\frac{dC_{ion}RT}{-\frac{dC_{ion}}{C_{ion}}} = C_{ion}RT = \pi_{ion}$$

Supposed that all network contributes the elasticity, $-\pi_{el}$ is proportional to thermal energy of 1 mol times effective chain density.

$$\pi_{el} = E_{el} = -C\nu_e W \quad (2.26)$$

C is a pre-factor (in the affine network model, $C=1$, whereas in the phantom network model with four-functional cross-links, $C=0.5$ Following previous studies on tetra-PEG gels, in this study, we adopt the phantom network model.) When $\pi_{ion} = 0$, $\pi_{el} = -\pi_{mix}$ and π_{mix} is simply proportional to the concentration.

$$\pi_{mix} = -C\nu_e W_0 \quad (2.27)$$

Ionic concentration C_{ion} is calculated by the following equation.

$$\phi \doteq \frac{RT}{zF} \ln \left(\frac{C_{reference}}{C_{ion}} \right)$$

Then, ϕ means the Donnan potential, z means the number of charges of ion, and F means Faraday constant. Substituting (2.25), (2.26) and (2.27) to (2.24),

$$\frac{(W-W_0)}{RT} = \frac{C_{ion}}{C\nu_e}$$

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Chapter 3

Network elasticity of hydrogels as a function of swelling ratio

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3.1 Introduction

Hydrogels are soft and wet materials consisting of a hydrophilic polymer network surrounded by aqueous solutions. When a dried hydrogel is immersed in water, hydrophilic polymers in the hydrogel microscopically hydrate but do not dissolve owing to their cross-linked structure, resulting in a finite swelling capacity of the hydrogel. This unique swelling structure renders hydrogels promising for use as medical materials due to the similarity in terms of water content and softness between them and tissues of living organs. Although the mechanical weakness of typical synthetic hydrogels has thus far limited their application, the recent development of tough hydrogels has enabled their use as load-bearing materials. For example, a double-network hydrogel (DN gel) with an interpenetrating network structure possesses high tearing energy ($\sim 1,000 \text{ J/m}^2$) despite 90% of water content by weight, whereas typical synthetic hydrogels have considerably lower tearing energy ($\sim 10 \text{ J/m}^2$) [1, 2].

While many hydrogels put to practical use (such as contact lenses) swell moderately in water, hydrogels with a large swelling capacity lately have been in high demand. Such hydrogels, the so-called super-absorbent polymers (SAPs), are directly used in disposable diapers, deodorants, stimuli-responsive actuators, and so on. The use of highly swollen gels is also necessary for the fabrication of tough DN gels, as the brittle network strands of such highly swollen gels work as sacrificial bonds to dissipate energy and

toughen the DN gels [1]. Thus, in order to apply hydrogels widely, it is crucially important to understand the relationship between the mechanical properties of the hydrogels, such as elastic moduli, and their network parameters, especially for highly-swollen gels.

Past studies on gel swelling have established that the total osmotic pressure of a typical gel, π_{total} , is determined by three contributions: 1) mixing of polymer and solvent, π_{mix} , 2) elasticity of network strands, π_{el} , and 3) dissociated counter ions in gels, π_{ion} . Moreover, at swelling equilibrium, the total osmotic pressure of the gel is equal to that of an outside solution, π_{out} :

$$\pi_{total} = \pi_{mix} + \pi_{el} + \pi_{ion} = \pi_{out} \quad (3.1)$$

If the outside solution is a pure solvent, $\pi_{out} = 0$. For a phantom network gel without entanglements, π_{el} is given by:

$$\pi_{el} \cong -C\nu_e W = -\frac{E}{3} \quad (3.2)$$

where C is a pre-factor (in the affine network model, $C=1$, whereas in the phantom network model with four-functional cross-links, $C=0.5$), W is the average elastic energy, ν_e is the number density of elastically effective network strands, and E is the Young's modulus of the gel. Following previous studies on tetra-PEG gels, in this study, I adopt the phantom network model. When the network strands are in their relaxed state, W is in the order of RT , where R is gas constant and T is absolute temperature. Eq. (3.2) is the fundamental equation that describes how the elastic modulus of the hydrogels correlates with their network parameters.

Here, let me use swelling ratio of a gel, Q , as an index of degree of swelling. Q is defined as $Q = V/V_{\text{ref}}$, where V and V_{ref} are volumes of the gel at the state of interest and that at the reference (as-prepared) state, respectively. When Q for a gel changes as it swells or deflates, the density and average end-to-end distance of its network strands also change with Q . Thus, ν_e and W in Eq. (3.2) are functions of Q . As the swelling of a gel leads to the dilution of its network strands, ν_e is inversely proportional to Q . Classical rubber elasticity theory predicts that a polymer chain with a Gaussian end-to-end distance distribution behaves like a linear (Hookean) spring far from its stretching limit [3]. Assuming affine deformation, the change in the end-to-end distance of a network strand is a third of that in the value of Q . Thus, $W \sim Q^{2/3}$. These two relationships predict a power law of $E \sim Q^{1/3}$. This simple relationship is often yielded in experimental results when Q remains in a Gaussian regime [4, 5]. On the contrary, when the hydrogels are highly swollen, the experimental E exceeds the predicted one by this power-law, and even an increase in the value of E with that of Q is observed in some cases [4, 6]. These non-linear phenomena are caused by finite extensibility of the network strands in the highly-swollen gels.

Gaps, such as the above, in the experimental results and the theoretical research on highly swollen gels are partly owing to the difficulty of the experimental settings as follows: 1) Unclear network structure. The elastic energy stored in a gel is determined by several factors, such as the degree of polymerization of a network strand, N , and the density of an elastically effective network strand, ν_e , and so on [5]. Typical gels, however, are

synthesized simply by the random copolymerization of monomers and cross-linkers, which gives inhomogeneous and defect-rich networks. Thus, the parameters of such gels like N and ν_e cannot be determined precisely, which leads difficulty in constructing a swelling model of gels, especially in the highly swollen region. 2) Intrinsic complexity of polyelectrolytes. As expected from Eq. (3.1), a large ionic osmotic pressure π_{ion} is required to cause the hydrogels to significantly swell against network elasticity. Thus, polyelectrolyte gels with massive trapped counter ions are used in studies on highly swollen states of gels. However, polyelectrolyte gels have fixed charges in their network strands. As the electrostatic repulsion of such charges affects network strand conformation, research on the swelling of polyelectrolyte gels becomes complicated. To address 1), a Tetra-PEG gel was prepared by the end-link of four-arm star polymers with a controlled molecular weight ($M_w/M_n \sim 1.05$) [7]. Given the high reaction conversion of the end-linking reaction and the negligible entanglement or elastically ineffective loop formation, the network strand of the degree of polymerization N and the density of an elastically effective network strand ν_e , are well-defined in a Tetra-PEG gel. Systematic studies on the swelling of Tetra-PEG gels in regimes of relatively low swelling have been performed [5]. To address 2) above, the molecular stent method where a strong linear polyelectrolyte called the molecular stent is introduced to non-ionic gels (including Tetra-PEG gels) to increase their degree of swelling is developed [8-10]. High ionic osmotic pressure π_{ion} originating from dissociated counter ions of the molecular stent increases the swelling ratio of non-ionic gels. As

the network strands themselves do not have any charge, the effect of electrostatic repulsion on their conformation no longer needs to be considered.

In this chapter, my strategy is to combine Tetra-PEG gels with the molecular stent method. In an experimental method, I introduced poly(2-acrylamido-2-methylpropanesulfonic acid sodium salt) (PNaAMPS) as a strong linear polyelectrolyte to Tetra-PEG gel to cause it to swell at different ratios, Q , by immersing it in pure water or various concentrations of a PEG solution (PEG suppresses swelling by increasing outside osmotic pressure π_{out}) [9]. I then measured the Young's modulus, E , of the gels by the indentation test, and investigated the experimental relationship between Q and E . This relationship is theoretically examined by considering non-linear single-chain elasticity.

3.2 Experiments

3.2.1 Preparation of sheet-like Tetra-PEG gel

Tetra-PEG gel ($M_w = 20k$) was prepared from pre-polymer solution by cross-end coupling [7, 9]. Then, I prepared two kinds of buffer solutions and dissolved them in each. TAPEG was dissolved in phosphate buffer (pH7.4) whereas TNPEG was dissolved in citrate-phosphate buffer (pH5.8) in Falcon tube, respectively. The monomer concentration sets to the overlap concentration which has ideal polymer network without entanglement. In order to make glass mold, silicone spacer whose thickness is 2 mm was cut and put on a parallel glass plate. Pre-polymer solutions were mixed and then

injected onto this glass mold by using plastic syringe throughout the filter membrane. Then, another parallel glass plate was put on it and the mold composed of a pair of parallel glass plates was fixed and stood by two or four clips. They were kept for about half a day at room temperature until the cross-end coupling reaction was finished. I described this hydrogel composed of two pre-polymers, TAPEG and TNPEG, as Tetra-PEG (TPEG) gel.

3.2.2 Molecular stent method to improve swelling

For synthesis of linear polyelectrolyte as molecular stent, 0.3-2.5 M of sodium 2-acrylamido-2-methylpropane sulfonic acid (NaAMPS: Toagosei Co. Ltd.) was used as stent molecule [8, 9]. To start the radical polymerization, 0.1 mol% of 2-oxoglutaric acid (α -keto: Wako, Pure Chemical Industries, Ltd., Tokyo, Japan) was used as radical initiator. Next, extra-pure water was poured to dissolve them. I call this solution composed of stent monomer and radical initiator molecular stent precursor solution. TPEG gel was immersed in this molecular stent precursor solution for at least 1 day. After then, a gel was put on a parallel glass plate, another parallel glass plate was put on them, and they were wrapped by plastic wrap. Ultraviolet light (UVP lamp XX-15BLB, light intensity is below 4 mW cm^{-2}) whose wavelength is 365 nm was exposed to the glass mold from upper side of it for about 3 hours in the argon atmosphere. The argon atmosphere was used in order to remove oxygen dissolved in pre-polymer solution (desirable oxygen concentration was below 0.1 ppm). I call this gel St-TPEG gel.

3.2.3 PEG dehydration method to suppress swelling

The Tetra-PEG gel was immersed in polyethylene glycol (PEG: Wako, Pure Chemical Industries, Ltd., Tokyo, Japan) aqueous solutions of 3~33wt% whose molecular weight is 20,000 for a day. PEG increases osmotic pressure of outside solution and suppresses swelling of the network [11].

3.2.4 Determination of swelling ratio

The swelling ratio of swollen TPEG gel is calculated by using this equation, $Q (\text{mm}^3/\text{mm}^3) = (t_{\text{swollen}}/t_{\text{as-prepared state}})^3$, where t_{swollen} and $t_{\text{as-prepared state}}$ means the thickness of swollen St-TPEG gel and the as-prepared TPEG gel. [8] Each t was measured by using laser thickness meter. (Keyence Co.)

3.2.5 Indentation test

The indentation test was performed by using universal testing device (Tensilon RTC-1150A: Orientec Co.) at room temperature. The testing velocity was kept to 1 mm/min. The elastic modulus was calculated by using this equation (Hertz's equation) [12], $E = 3/4 \varepsilon_0^{-3/2} f R^{-1/2} (1 - \nu^2)$, where E , ε_0 , f , R and ν are elastic modulus (MPa), displacement (mm), force (N), radius of the jig (mm) and Poisson's ratio, respectively. In this case R was fixed to 2 mm and ν was 0.5. For calculation, I plotted ε_0 against $f^{2/3}$ and calculated the gradient of these curves at small displacement (within about 0-0.1 mm). Then, I calculated E by substituting values of this gradient and other parameters into the equation.

3.3 Results and Discussion

3.3.1 Relationship between swelling ratio and elastic modulus

Fig. 1 shows the swelling ratio of each stent concentration of St-TPEG gels in extra pure water and of Tetra-PEG gels in each concentration of PEG aqueous solutions. Although the previous research without molecular stent method reached the narrow range of swelling ratio from 0.2 to 2, I could reach the wide range of swelling ratio from 0.2 to 300 by using molecular stent method and PEG dehydration method. Fig.2 shows the swelling ratio of each stent concentration of St-TPEG gels in each concentration of PEG aqueous solution. It seems that swelling ratio increases with increasing the concentration of stent if the concentration of PEG aqueous solution is constant, whereas the swelling ratio decreases with increasing the concentration of PEG aqueous solution if the concentration of stent is constant. Fig.3 shows the plots of elastic modulus of each stent concentration of St-TPEG gels in each concentration of PEG aqueous solution. Although the comprehensible trend is not shown in elastic modulus unlike swelling ratio, elastic modulus increases with increasing PEG aqueous solution at low concentration of stent and it decreases with increasing PEG aqueous solution at high concentration of stent as a whole.

3.3.2 Comparison with the elasticity models

Fig.4 shows the plots of swelling ratio and elastic modulus of each stent concentration of St-TPEG gels in each concentration of PEG aqueous solution. According to this result, it is found that all data fit on the one

master curve not depending on the concentration of stent molecule in hydrogel and concentration of PEG aqueous solution. It insists that the elasticity of Tetra-PEG gel is controlled by only swelling ratio, i.e. the structure of network, not depending on internal stent molecules and external PEG molecules.

Next, I verified the relationship between swelling ratio and elastic modulus of Tetra-PEG gel quantitatively. According to the slope of Fig.4, it could be thought about the relationship between swelling ratio and elastic modulus of Tetra-PEG gel by dividing into two regions, i.e. low swelling region ($Q < 20$) and high swelling region ($Q > 20$). The slope of fitted graph of shrinking region is -0.37 . In high swelling region, the slope is not constant.

I will compare these relationships with classical elasticity models of hydrogels. According to the models, elastic modulus of hydrogels (E) is given by “the molar density of polymer chain (ν) multiplies elastic energy per molar density of a polymer chain multiplies 3. If network chains are able to be regarded as Gaussian chain, its elastic energy per mole is shown as RT . If this assumption is not true, however, the elastic energy possibly departs from RT . Considering the classical rubber elasticity theory, the deformation behavior of single polymer chain is able to be approximated by linear spring and its elastic energy per mole is proportionate to square of deformation ratio. The network model which concerns this effect, called Neo-Hookean model, predicts the relationship $E \sim Q^{-\frac{1}{3}}$. However, it has been known that this prediction is not applicative for gels having high swelling ratio because this model does not suppose that polymer chain has finite length and

becomes hard by full stretching. In the experiment of the St-TPEG gels, I could get the relationship $E \sim Q^{-\frac{1}{3}}$ which corresponds to classical rubber elasticity model at the low swelling region ($Q < 20$). Meanwhile, the nonlinear strain hardening which departs from classical model is found at high swelling region ($Q > 20$). This phenomenon could not be explained by the Neo-Hookean model and insists the effect of finite extensibility of polymer chains.

As I described in Chapter 2, freely-jointed chain (FJC) model and worm-like chain (WLC) model are proposed as mechanics model of polymer chain which concerns about finite extensibility effect. Then, I applied these models above to this result. FJC model could be written in (2.9)

$$f(\alpha) = \frac{RT}{b} \frac{\alpha(3-\alpha^2)}{1-\alpha^2}$$

Then, because the elastic energy of single chain ($W(R)$) is given by the following value of integral,

$$W(R) = R_{max} \int_0^\alpha f(\alpha) d\alpha = \frac{RT R_{max}}{2l_p} \left(\frac{\alpha^2}{2} - \ln(|\alpha^2 - 1|) \right)$$

$l_p = \frac{b}{2}$ is the persistence length. The reason for multiplying R_{max} is to convert the length ratio α [m/m] into displacement R [m] to calculate the energy [N · m]. Note that I adopt phantom network model ($C=0.5$ in (3.2)). So,

$$E(\alpha) = \frac{3}{2} \nu_e W = \frac{3\nu_e}{2Q} W = \frac{3\nu_e RT R_{max}}{4Ql_p} \left(\frac{\alpha^2}{2} - \ln(|\alpha^2 - 1|) \right) \quad (3.4)$$

Next, WLC model could be written in (2.10)

$$f(\alpha) = \frac{RT}{l_p} \left\{ \frac{1}{4} (1 - \alpha)^{-2} - \frac{1}{4} + \alpha \right\},$$

Then, because the elastic energy of single chain ($W(R)$) is given by the

following value of integral,

$$W(R) = R_{max} \int_0^\alpha f(\alpha) d\alpha = \frac{RT R_{max}}{4l_p} (2\alpha^2 - \alpha - (\alpha - 1)^{-1} - 1). \quad (3.5)$$

So,

$$E(\alpha) = \frac{3}{2} v_e W = \frac{3v_{e0}}{2Q} W = \frac{3v_{e0} RT R_{max}}{8Ql_p} (2\alpha^2 - \alpha - (\alpha - 1)^{-1} - 1). \quad (3.6)$$

Here, the density of Tetra-PEG pre-polymer (d) is given by the following equation.

$$d = \frac{c^* N_A}{M_w} N_A \quad (3.7)$$

where N_A means the Avogadro's number. If I assume that pre-polymers of Tetra-PEG are packed with the configuration of diamond-like lattice, the relationship between the radius of atom r and lattice constant R_0 is

$$2r = \frac{\sqrt{3}}{4} R_0 \quad (3.8)$$

The density of lattice point in unit lattice is given by the number of atoms divided by volume, and it is equal to the density of pre-polymer (d), so

$$\frac{8}{\left(\frac{\sqrt{3}}{4} R_0\right)^3} = d \Leftrightarrow R_0 = \frac{\sqrt{3}}{2} d^{-\frac{1}{3}} = \frac{\sqrt{3}}{2} \left(\frac{c^* N_A}{M_w}\right)^{-\frac{1}{3}} \quad (3.9)$$

Then, the distance between cross-lining point of network is equal to two of four Tetra-PEG branching length, so

$$\begin{aligned} R_{max} &= (\text{degree of polymerization}) \div 4 \times (\text{segment length}) \times 2 \\ &= \frac{M_w}{44.05} \div 4 \times (r_1 + 2r_2) \sin\theta \times 2 \end{aligned} \quad (3.10)$$

where r_1 , r_2 , θ mean the length of C-C single bond (0.154 nm), the length of C-O single bond (0.143 nm), the semi angle of its bond angle (54.75°), respectively. I suppose those bond length and bond angles are not changed by elongation. Because the persistence length is 0.38 nm at this conditions, the theoretical values of R_0 and R_{max} are about 8.1 nm and 82 nm by

substituting these values, respectively.

Fig.5 (a) shows the relationship between elastic modulus and swelling ratio of fitting of comparison of experimental data and freely-jointed chain model, whereas Fig.5 (b) shows relationship between elastic modulus and swelling ratio of fitting of comparison of experimental data and worm-like chain model, respectively. Two fitting curves are shown in each graph where 1) there was no fitting parameter or 2) R_0 and R_{max} were treated as fitting parameters. In the setting 1), the theoretical moduli are slightly lower than the experimental values in both FJC and WLC models, and the modulus upturn at high Q was not reproduced. Thus, some parameters must be modified. In the setting 2), the theoretical curves of both WLC and FJC models are consistent with the experimental moduli at low-swelling region. Moreover, both models qualitatively reproduce the upturn in the modulus at high-swelling region. In terms of curve shapes, however, the WLC model well reproduced the experimental results whereas the FJC model predicted a too-sharp modulus upturn. Therefore, it insists that the effect of finite extensibility could be explained by using WLC model better than FJC model. And then, the value of R_0 resulting from the fitting is about 8.9 nm, so the accuracy of this fitting is proved because it is near the theoretical value (8.1 nm). However, the value of R_{max} resulting from the fitting is about 63 nm, so the accuracy of this fitting is not proved because it departs from the theoretical value (82 nm). The reason of this is thought that the conformation of PEG I modeled is different. Although the trans-trans-trans (ttt) conformation is more stable without interaction, it is known that

trans-trans-gauche (ttg) conformation is more stable in water because oxygen atoms of PEG molecule and hydrogen atoms of water molecule interact with each other (Gauche effect). So, because the theoretical value of contour length is about 64 nm based on this conformation (ttg) and its value is near the experimental value (63 nm), it insists that the conformation of PEG in water forms trans-trans-gauche (ttg) conformation.

According to these results, it insists that the elastic modulus of Tetra-PEG gel is decided by the following elements. 1) Elastic modulus of hydrogel is given by the molar density of network chains multiplies elastic energy of polymer chains per mole. 2) Elastic energy of polymer chains per mole is described not by classical linear spring model but by WLC model concerned about finite extensibility of chain.

3.4 Conclusions

I succeeded in experimentally determining the moduli of Tetra-PEG hydrogels as a function of their swelling ratio up to a high swelling region, and theoretically explained their relationship by adopting non-linearly elastic network chains with reasonable fitting parameters. This study provides a guide for the design of hydrogel materials with a certain modulus and water content, especially at high swelling regimes. Such fully swollen hydrogels are directly used as SAPs, and are useful for the fabrication of tough DN hydrogels. Thus, this study contributes to the design of SAPs and tough DN gels with the desired degree of swelling and mechanical properties.

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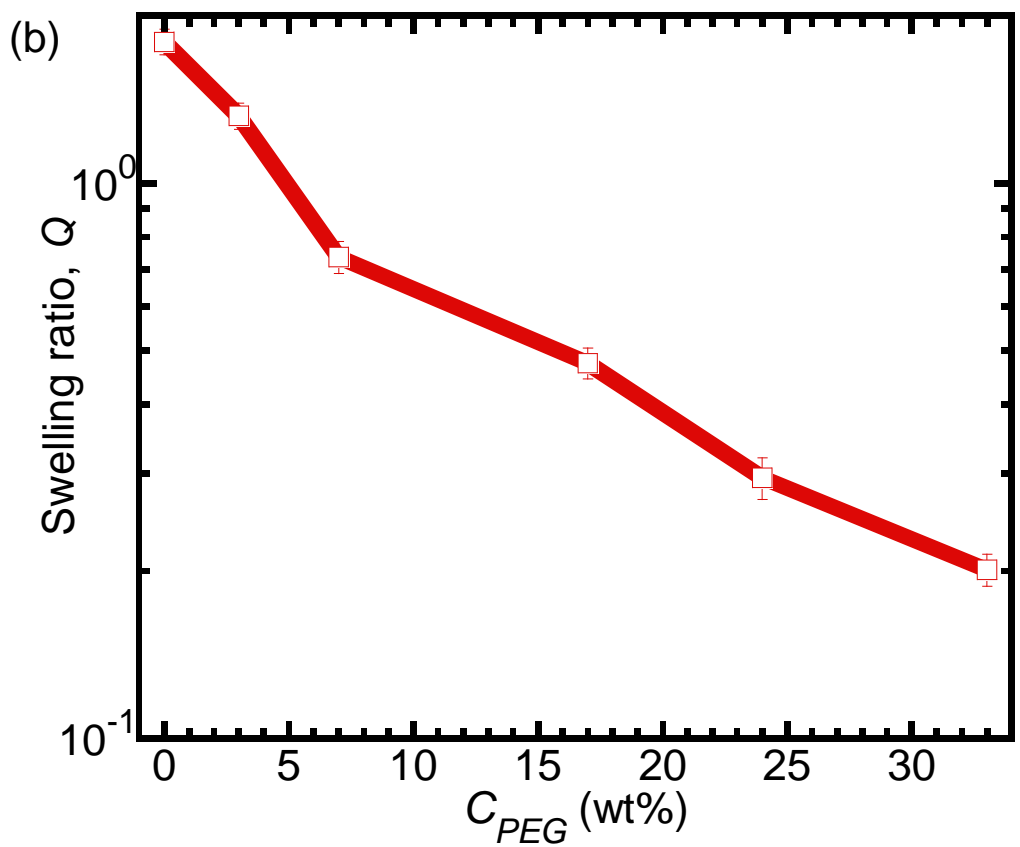
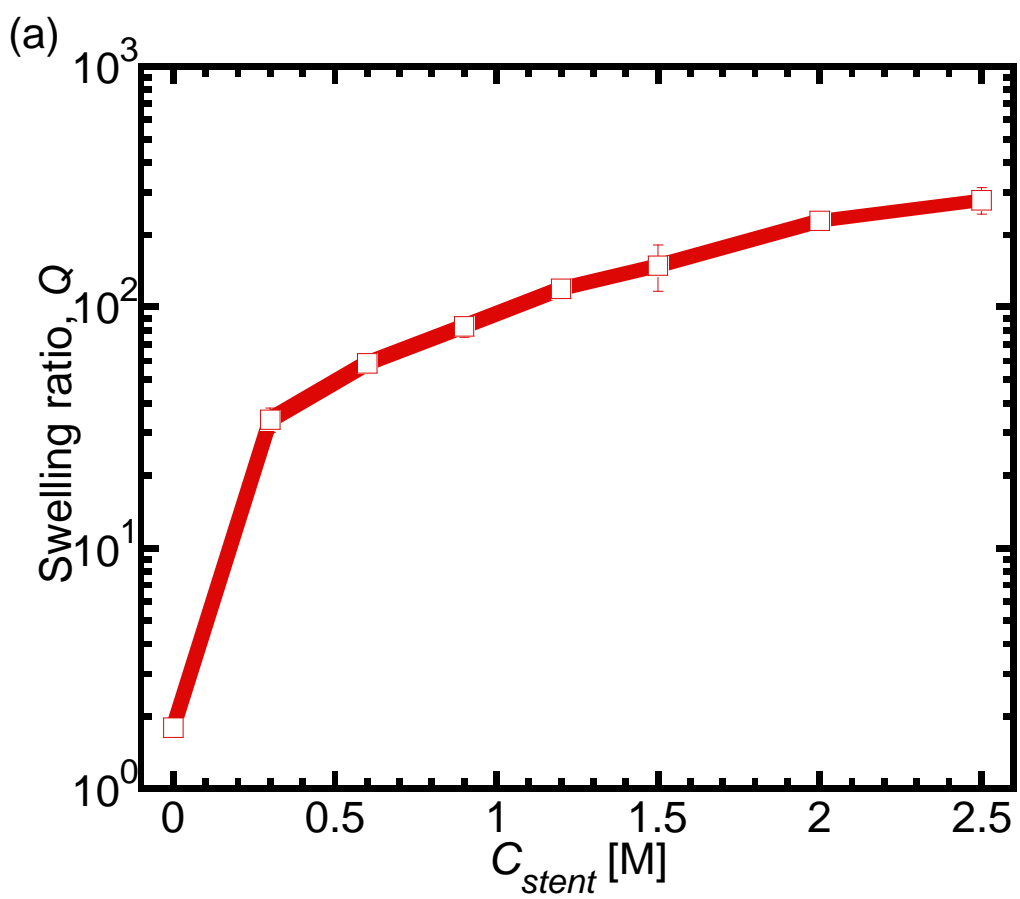


Fig.1(a) Swelling ratio, Q , of the Tetra-PEG gels swollen in pure water as a functions of feed concentration of the stent monomer, C_{stent} . (b) Q as a function of concentrations of PEG solution, C_{PEG} .

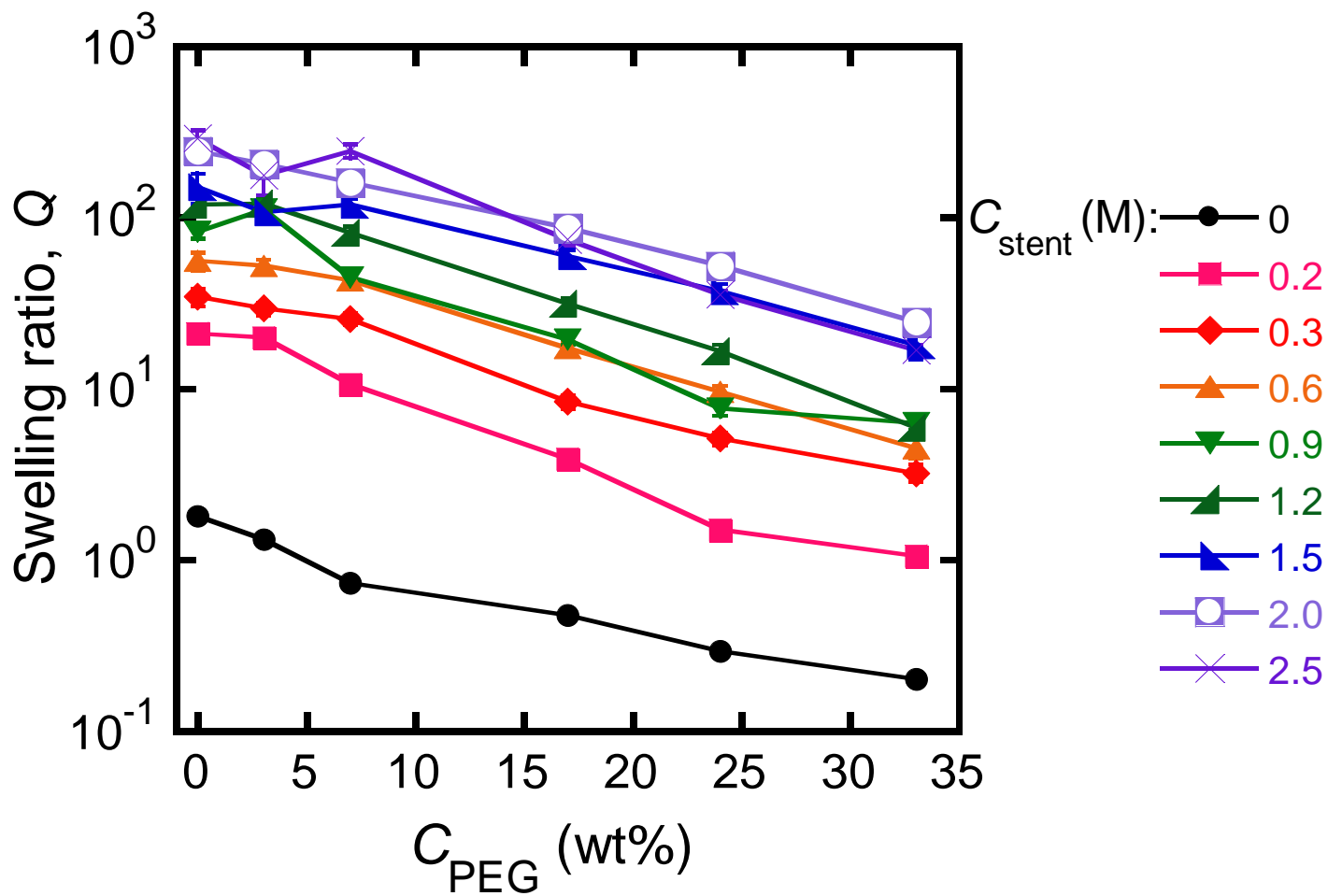


Fig.2 Swelling ratio change of different stent concentrations in each different concentrations of PEG solution.

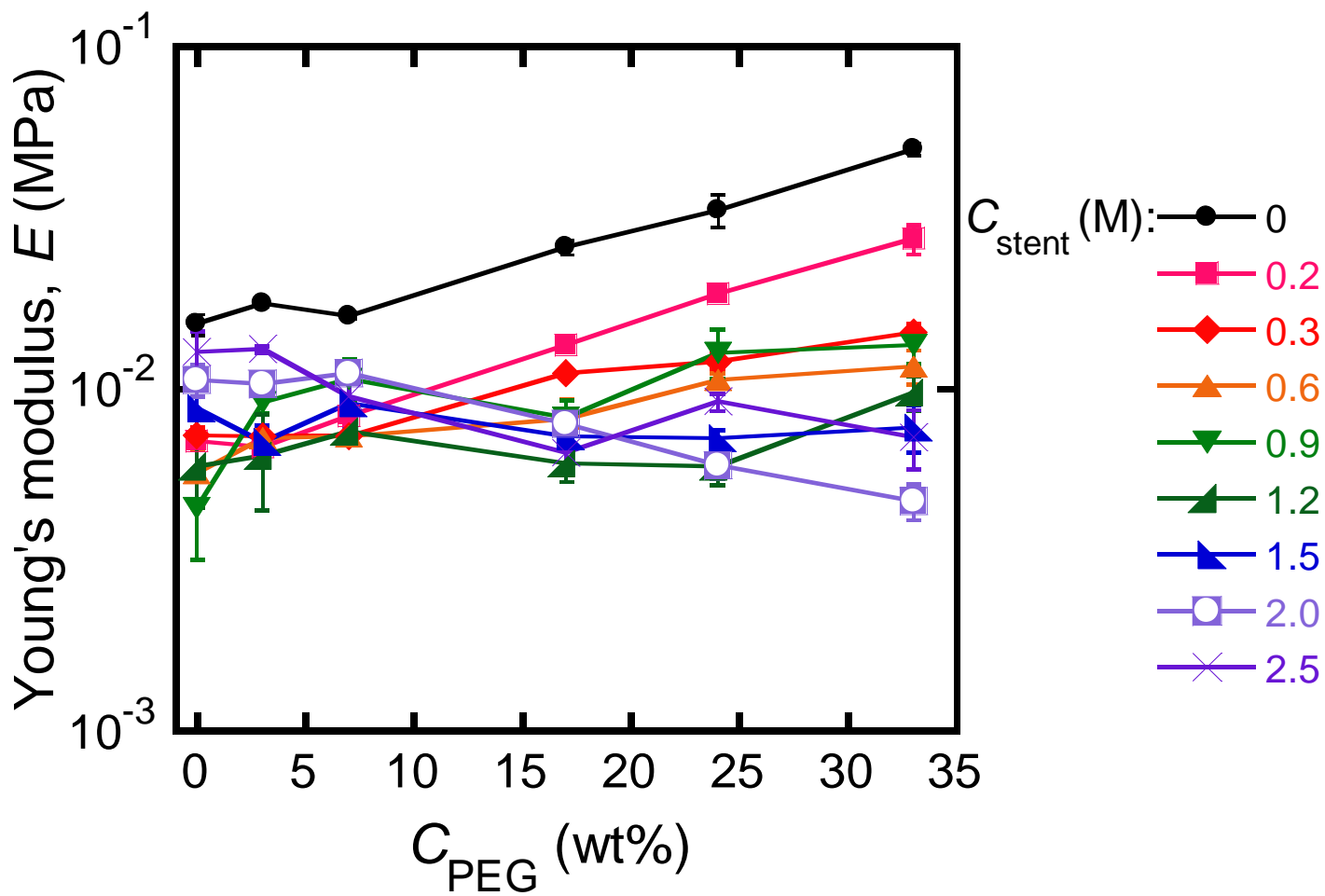


Fig.3 Elastic modulus change of different stent concentrations in each different concentrations of PEG solution.

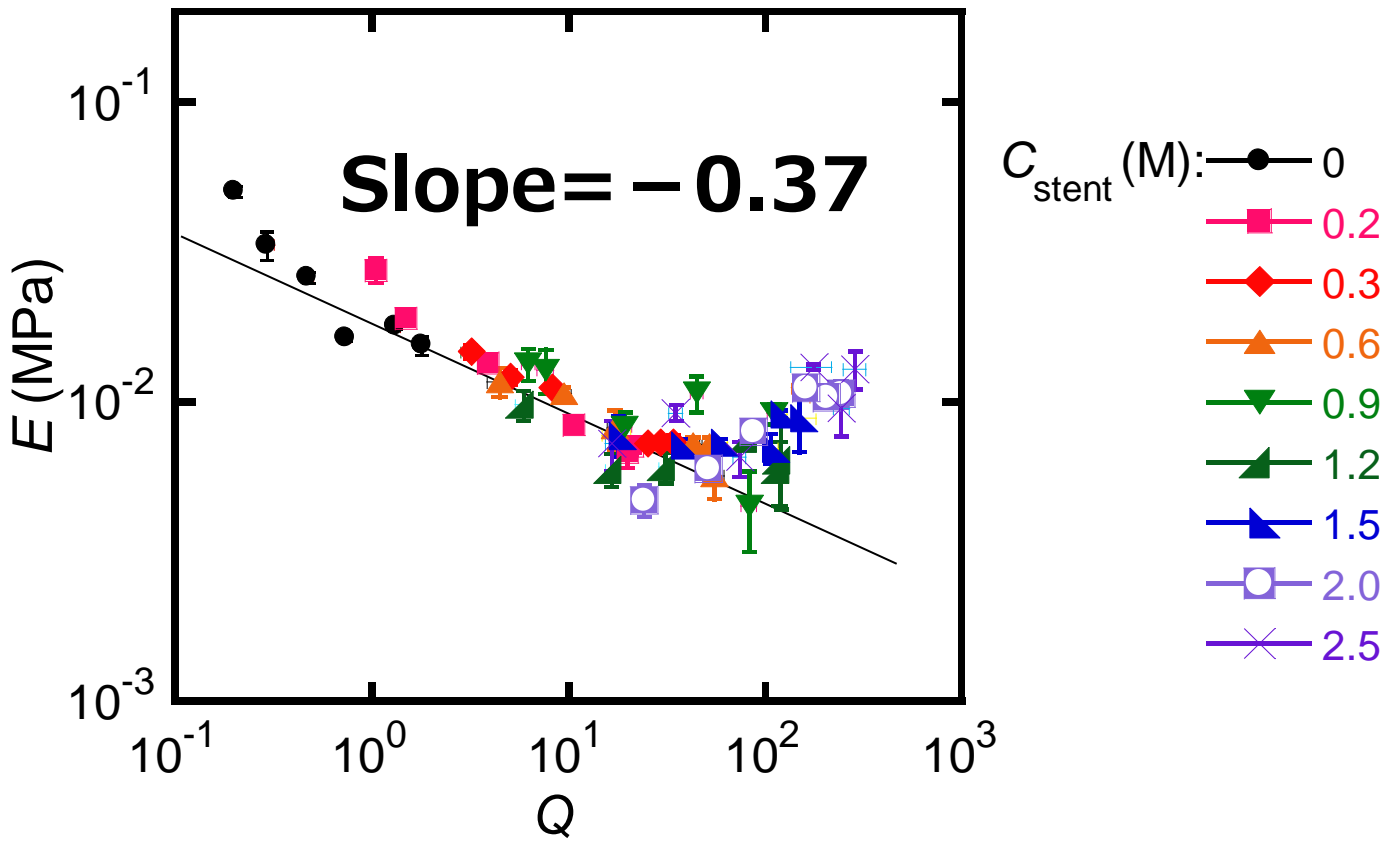


Fig.4 Relationship between elastic modulus and swelling ratio of different stent concentrations in each different concentrations of PEG solution.

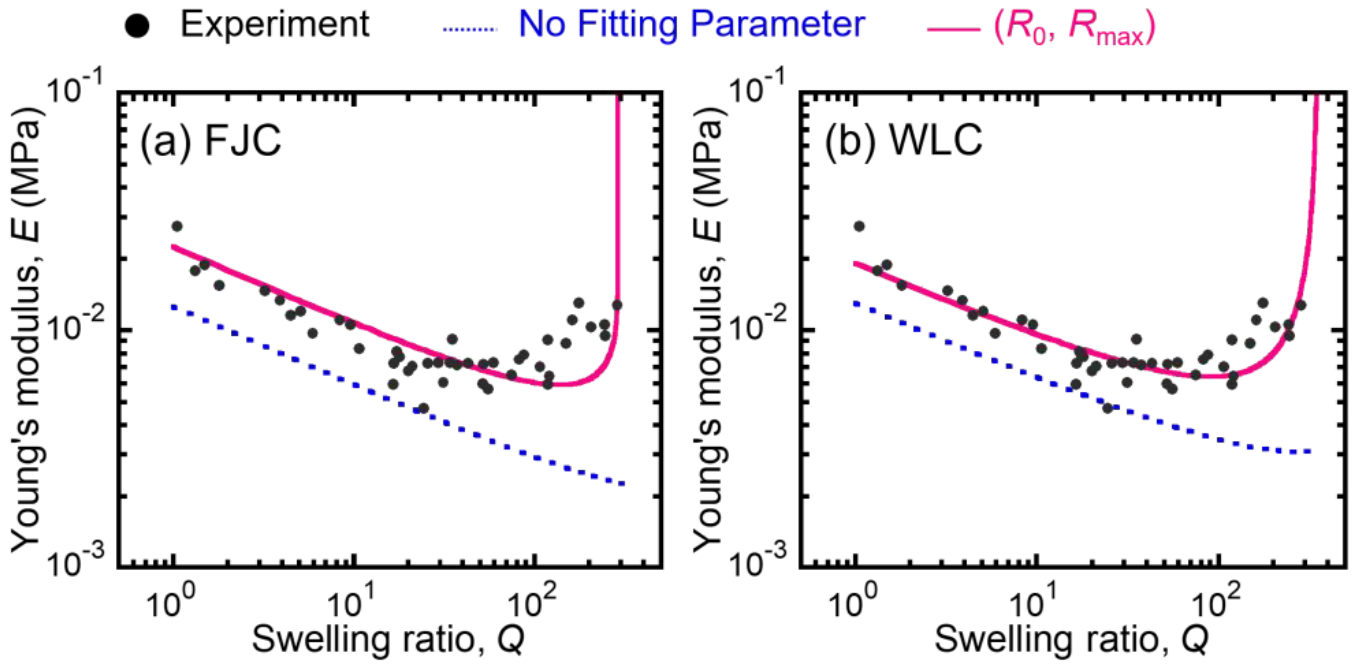


Fig.5(a) Comparison of experimental data and freely-jointed chain model's fitting of relationship between elastic modulus and swelling ratio. (b) Comparison of experimental data and worm-like chain model's fitting of relationship between elastic modulus and swelling ratio.

Chapter 4

Revisit on the effect of ionic osmotic pressure on swelling of hydrogel

Chapter 4 Revisit on the effect of ionic osmotic pressure on swelling of hydrogel

4.1 Introduction

Molecular stent method is very revolutionary in terms of controlling its swelling ratio very widely without changing network structure of hydrogel. It has been succeeded that various neutral hydrogel can be expanded to their high swelling states by this method. In previous chapter, I applied molecular stent method to swell Tetra-PEG gel ^[1] whose network structure is well-defined to high swelling region with keeping its network structure, and succeeded to discuss the relationship between swelling ratio and elastic modulus. In this chapter, I tried to discuss its relationship of other kinds of gels. In fact, some kinds of gel are used and their structures are not always clear. As the subject of industrial application of them, cell scaffolds whose purpose is to apply as sheet-like basis for culturing the cell at its surface ^[2], drug delivery system ^[3], and artificial blood vessel ^[4] and so on are tried. If the relationship between swelling ratio and elastic modulus of other gels whose structure is non-defined is discovered like Tetra-PEG gel, properties (such as modulus) of these gels can be designed easily by tuning their swelling ratio. Then, in this section, I firstly expand molecular stent method to hydrogels whose network structure is different or even unknown.

However, although such study predicts appropriate swelling ratio of a hydrogels to obtain targeted physical properties, it is not clear that how much concentration of stent molecules should be added to a gel in order to get the targeted swelling ratio. To discover the relationship between

molecular stent concentration and swelling ratio is important for preparing hydrogel whose swelling ratio and physical property are well controlled.

Thus, in this chapter I also aim to point what factor determines swelling ratio of hydrogels. Because swelling ratio of hydrogel is known to write as competition between resistance force against deformation of network (elasticity), which has the effect of suppression of swelling, and osmotic pressure of hydrogel, which is the effect of promotion of swelling^[5,6], it is required to determine both elasticity and osmotic pressure of hydrogels having various swelling ratio in order to accomplish this assignment. It is expected to discover the relationship among composition, swelling ratio and physicality of hydrogel completely and design gel materials freely if it is succeeded to discuss about the term of osmotic pressure experimentally.

As I mentioned in previous chapter, osmotic pressure of hydrogel is written in the term arisen from mixing polymer and solvent described by Flory-Huggins' theory, and the term of ionic osmotic pressure if hydrogel has charge ^[7]. A lot of verification of Flory-Huggins' theory has been already discussed by using polymer solution.^[6] Therefore, it is important to realize the effect of ionic osmotic pressure accurately for solving this assignment. However, in the case of common polyelectrolyte gels, if charge density on the network is changed to control counterion concentration, it also affects rigidity (and elasticity) of the network strands owing to repulsion of charges on the network. Therefore, it is too difficult to discuss independently osmotic pressure and elasticity of a polyelectrolyte network.

The purpose of this section is to discuss the effect of osmotic pressure in

swelling of hydrogels experimentally with molecular stent method. As the concrete experimental method, I prepared Tetra-PEG gels which include various concentrations of strong polyelectrolyte, molecular stent, and measured swelling ratio and elastic modulus as well as the previous method. Next, I determined the free ionic concentration in gel by measuring electrostatic potential and calculated ionic osmotic pressure from the equation of van't Hoff's formula. ^[8] Based on these data, I intend to review the theory of swelling of electrolyte gel in existence by describing the relationship among swelling ratio, elastic modulus and osmotic pressure on swelling of hydrogel precisely by combining this result with the relationship between swelling ratio and elastic modulus.

4.2 Experiments

4.2.1 Preparation of sheet-like Tetra-PEG gel

Tetra-PEG gel ($M_w = 10k, 20k$) was prepared from the pre-polymer solutions by cross-end coupling as well as the previous chapter. ^[1] TAPEG was dissolved in phosphate buffer (pH7.4) whereas TNPEG was dissolved in citrate-phosphate buffer (pH5.8) in Falcon tube. After the solution preparation, I waited for desired time (incubation time) to control the reactivity of the cross-end coupling and then mixed them. As end-groups of TNPEG gradually dissociates in the buffer, reaction efficiency of the coupling gradually decreases with incubation time. Incubation time was 0 min unless specially mentioned. Then, the mixed pre-polymer solutions were injected onto the glass mold by using plastic syringe throughout the filter membrane.

It was kept for about half a day at room temperature until the cross-end coupling reaction is finished. I described this hydrogel composed of two pre-polymers, TAPEG and TNPEG, as Tetra-PEG (TPEG) gel.

Tetra-PEG gels with various initial polymer concentrations, c , were prepared. The c^* means overlapping concentration which can be regarded as practical network without entanglement. If $c < c^*$ (dilute solution), chains behave as an isolated polymer. If $c > c^*$ (semi-dilute solution), chains are overlapped each other.

Bimodal Tetra-PEG gel was prepared by mixing the same molar amount of two kinds of pre-polymer which has different molecular weight (5k or 20k) with each other. The molar fraction of 20k Tetra-PEG, r , was defined by the following equation.

$$r = \frac{\text{number density of 20k Tetra-PEG prepolymer}}{\text{number density of total prepolymer}}$$

Molar fraction used in this study was written below.

TAPEG [g/mol]		TNPEG [g/mol]		20kg · mol ⁻¹ Tetra-PEG molar fraction (r)
20k [mM]	5k [mM]	20k [mM]	5k [mM]	
4	0	4	0	1
4	0	2	2	0.75
4	0	0	4	0.5
2	2	0	4	0.25
0	4	0	4	0

p -tuned Tetra-PEG gel was prepared by changing incubation time of TNPEG. The incubation times are 20 min, 80 min, and 160 min.

The polyacrylamide hydrogels, pAAM, were prepared by the random

copolymerization. An aqueous solution containing 1.0 M, 2.0 M, or 4.0 M of acrylamide, 0.5 mol% of N,N-ethylene bis-acrylamide and 0.1 mol% of 2-oxoglutaric acid in relative to the monomer concentration was poured into a reaction cell consisting of two glass plates separated by a silicone spacer of 2 mm-thick. Then the reaction cell was exposed to 365 nm UV light (UVP lamp XX-15BLB, light intensity: is below 4 mW cm^{-2}) from both sides for 8 h. All the process was performed in the argon atmosphere with oxygen concentration below 0.1 ppm.

4.2.2 Molecular stent method to improve swelling

To synthesis of linear polyelectrolyte as molecular stent, 0.3-2.5 M of sodium 2-acrylamido-2-methylpropane sulfonic acid (NaAMPS: Toagosei Co. Ltd.) as anionic stent molecule or *N*, *N*'-dimethylaminoethylacrylate (DMAEA-Q: MT Aqua Polymer, Inc.) as cationic stent molecule was used as stent molecule [9, 10]. 0.1 mol% of 2-oxoglutaric acid (α -keto: Wako, Pure Chemical Industries, Ltd., Tokyo, Japan) was used as radical initiator. These stent molecules and α -keto were dissolved in pure water. TPEG gel was immersed in this molecular stent precursor solution for at least 1 day. After then, gel was put on a parallel glass plate and another parallel glass plate was put on them and the mold was wrapped. Ultraviolet light (UVP lamp XX-15BLB, light intensity is below 4 mW cm^{-2}) whose wavelength is 365 nm was exposed to the glass mold from upper side of it for about 3 hours in the argon atmosphere (Desirable oxygen concentration was below 0.1 ppm).

4.2.3 Dehydration method to suppress swelling

The Tetra-PEG gel was immersed in three kinds of solvent. One is polyethylene glycol (PEG) aqueous solutions of 3–33wt% whose molecular weight is 20,000. Another is poly (vinyl-pyrrolidone) (PVP: Wako, Pure Chemical Industries, Ltd., Tokyo, Japan) aqueous solutions of 10~30wt% whose molecular weight is 25,000. The other is sodium chloride (NaCl: Wako, Pure Chemical Industries, Ltd., Tokyo, Japan) aqueous solutions. PEG and PVP increase osmotic pressure of outside solution and suppress swelling of the network whereas NaCl denies the ionic osmotic pressure of polyelectrolyte and suppresses swelling of the network [11].

4.2.4 Determination of swelling ratio

The swelling ratio of swollen TPEG gel is calculated by using this equation, $Q (\text{mm}^3/\text{mm}^3) = (t_{\text{swollen}}/t_{\text{as-prepared state}})^3$, where t_{swollen} and $t_{\text{as-prepared state}}$ means the thickness of swollen St-TPEG gel and the as-prepared TPEG gel. [10] Each t was measured by using laser thickness meter. (Keyence Co.)

4.2.5 Indentation test

The indentation test was performed by using universal testing device (Tensilon RTC-1150A: Orientec Co.) at room temperature. The testing velocity was kept to 1 mm/min. The elastic modulus was calculated by using this equation (Hertz's equation) [6], $E = 3/4 \varepsilon_0^{-3/2} f R^{-1/2} (1 - \nu^2)$, where E , ε_0 , f , R and ν are elastic modulus (MPa), displacement (mm), force (N), radius of the jig (mm) and Poisson's ratio, respectively. In this case R was fixed to 2 mm

and ν was 0.5. For calculation, I plotted ε_0 against $l^{2/3}$ and calculated the gradient of these curves at small displacement (within about 0-0.1 mm). Then, I calculated E by substituting values of this gradient and other parameters into the equation.

4.2.6 Microelectrode technique

Microelectrode technique was used for measuring of the electrostatic potential of the hydrogels [8]. I used two kinds of microelectrodes, working electrode and reference electrode, respectively. Working electrode was made by glass capillary tube (outer diameter 1.0 mm, inner diameter 0.78 mm, Sutter Instrument Co.). It was pulled by puller (P-1000, Sutter Instrument Co.) within 1 μm tip diameter. 3 M KCl solution was poured into it and a reversible silver/silver chloride electrode (Ag/AgCl) was inserted into it. Meanwhile, I used carbon electrode as reference electrode. Both electrodes were connected to the oscilloscope (Iwatsu, DS-4264) via high-impedance intracellular preamplifier (Model 8700 Cell Explorer, Dagan). All the measurements were done at room temperature. The inserting speed of the electrode was controlled to 395 nm/s by the micromanipulator (DMA- 1511, Narishige). Before measurement, St-TPEG gels were dialyzed in order to remove residual chemicals completely for more than 1 week. Completion of the dialyzing was checked by conductivity measurement of the solution used for dialysis with conductivity meter (FE30 KIT, Mettler-Toledo). After the completion, the gels were immersed in 10^{-5} M KCl solution and measured.

4.3 Results and Discussion

4.3.1 Relationship between elasticity and ionic concentration

Fig.1 (a) shows swelling ratio of St-TPEG gels of each stent concentration whose molecular weight is 20k in each concentration of PEG aqueous solution ($C-Q$ curve). Fig.1 (b) shows the plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_n) in each concentration of PEG solution ($E-Q$ curve). These results show that the network of Tetra-PEG gel contributes to elasticity of hydrogel, whereas stent molecule contributes to ionic osmotic pressure, and they can be separately controlled. Fig.1(c) shows the values of electrostatic potential of the St-TPEG gels of each concentration of stent molecule at each condition of PEG solution. According to this result, electrostatic potential has negative value if anionic monomer is used as stent molecule. In addition, it is found that the value of electrostatic potential seems independent from the concentration of stent molecule *in feed*. Fig.1 (d) shows the plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density. From this result, it quantitatively insists that swelling of hydrogel about this system is caused by counterions of stent molecules.

Fig.2 (a) shows the plots of $C-Q$ curve of each stent concentration of St-TPEG gels whose molecular weight is 10k in each concentration of PEG aqueous solution. Fig.2 (b) shows the plots of the normalized $E-Q$ curve in each concentration of PEG solution. Fig.2 (c) shows the values of electrostatic

potential of the St-TPEG gels of each concentration of stent molecule at each condition of them. Fig.2 (d) shows the plots of the relationship between elastic energy and normalized ionic concentration. From these results, it quantitatively insists that the physical behavior of St-TPEG gel whose molecular weight is 10k is almost the same as that of 20k's, and the relationship of elastic energy and ionic concentration does not depend on the concentrations of pre-polymers.

4.3.2 Using other kinds of stent molecule

Fig.3 (a) shows the plots of $C-Q$ curve of each stent concentration of St-TPEG gels whose stent molecule is DMAEA-Q in each concentration of PEG aqueous solution. Fig.3 (b) shows the plots of the normalized $E-Q$ curve in each concentration of PEG solution. Fig.3 (c) shows the values of electrostatic potential of the St-TPEG gels of each concentration of stent molecule at each condition of them. According to this result, electrostatic potential has positive value if cationic monomer is used as stent molecule. Fig.3 (d) shows the plots of the relationship between elastic energy and normalized ionic concentration. Although there are some large errors because of the mechanical weakness of St-TPEG gel, it quantitatively insists that the physical behavior of St-TPEG gel whose stent molecule is DMAEA-Q is similar to that of NaAMPS's, and the relationship of elastic energy and ionic concentration about this system does not depend on the kind of stent molecule from this result.

4.3.3 Immersing in other solvents

Fig.4 (a) shows the plots of $C-Q$ curve of each stent concentration of St-TPEG gels in each concentration of sodium chloride aqueous solution. Fig.4 (b) shows the plots of the normalized $E-Q$ curve in each salt concentration of sodium chloride aqueous solution. Fig.4 (c) shows the values of electrostatic potential of the St-TPEG gels of each concentration of stent molecule at each condition of them. From this graph, the more concentrations of sodium chloride solution, the less the absolute value of electrostatic potential is. Thus, it is found that ions arisen from sodium chloride solution have the effect of diminish the effect of ions arisen from stent. Fig.4 (d) shows the plots of the relationship between elastic energy and normalized ionic concentration.

Fig.5 (a) shows the plots of $C-Q$ curve of each stent concentration of St-TPEG gels in each concentration of PVP aqueous solution. Fig.5 (b) shows the plots of the normalized $E-Q$ curve in each concentration of PVP solution. Fig.5 (c) shows the values of electrostatic potential of each concentration of the St-TPEG gels of stent molecule at each condition of them.

4.3.4 Using other concentration of pre-polymers

Fig. 6 (a), (b), and (c) show the plots of $C-Q$ curve of each stent concentration of St-TPEG gels whose preparation concentration is different in each concentration of PEG aqueous solution. Fig. 6(d) shows normalized $E-Q$ curve of swelling of St-TPEG gel of c^* , dilute solution ($0.5c^*$), and semi-dilute solution ($2c^*$, $4c^*$). Although there are some errors because of the

weakness of St-TPEG gel, they are coinciding with each other to some extent. Fig.6 (e) shows the electrostatic potential of the St-TPEG gels of each preparation concentration of TPEG gel in water. The absolute value of electrostatic potential is also increasing with increasing preparation concentration. Fig.6 (f) shows the relationship between elastic energy and normalized ionic concentration. Although there are some large errors because of the weakness of St-TPEG gel, it quantitatively insists that the physical property of St-TPEG gel whose preparation concentration is different is similar to each other, and the relationship of elastic energy and ionic concentration about this system does not depend on the preparation concentration.

4.3.5 Bimodal Tetra-PEG gels

Fig. 7 (a) shows $C-Q$ curve of swelling of bimodal St-TPEG gel in water in different molar fractions. Swelling ratio is increasing with increasing molar ratio basically. Fig. 7 (b) shows normalized $E-Q$ curve of swelling of bimodal St-TPEG gel in water in different molar fractions. Fig. 7 (c) shows the electrostatic potential of bimodal St-TPEG gel in water in different molar fractions. The absolute value of electrostatic potential is also increasing with increasing molar ratio. Fig. 7 (d) shows the relationship between elastic energy and normalized ionic concentration. Although there are some large errors because of the weakness of St-TPEG gel, it quantitatively insists that the physical property of bimodal St-TPEG gel is similar to the unimodal Tetra-PEG gel's.

4.3.6 p -tuned Tetra-PEG gels

Fig. 8 (a), (b) and (c) shows $C-Q$ curve of swelling of p -tuned St-TPEG gel in water in different molar fractions. Fig. 8 (d) shows normalized $E-Q$ curve of swelling of p -tuned St-TPEG gel. Although there are some errors because of the weakness of St-TPEG gel, they are coinciding with each other to some extent. Fig.8 (e) shows the electrostatic potential of the St-TPEG gels of each preparation concentration of p -tuned St-TPEG gel in water. The absolute value of electrostatic potential decreases with increasing of incubation time. Fig. 8 (f) shows the relationship between elastic energy and normalized ionic concentration. Although there are some large errors because of the weakness of St-TPEG gel, it quantitatively insists that the physical property of p -tuned St-TPEG gel is similar to the conventional Tetra-PEG gels.

4.3.7 Comparison to polyacrylamide gel

Fig. 9 (a), (b) and (c) shows $C-Q$ curve of swelling of polyacrylamide gel in water in different molar fractions. Swelling ratio is increasing with increasing molar ratio basically. Fig. 9 (d) shows normalized $E-Q$ curve of swelling of polyacrylamide gel. Although there are some errors because of the weakness of hydrogel, they are coinciding with each other to some extent. Fig.9 (e) shows the electrostatic potential of each preparation concentration of polyacrylamide gel in water. The absolute value of electrostatic potential is also increasing with increasing preparation concentration. Fig. 9 (f) shows the relationship between elastic energy and normalized ionic concentration. Although there are some large errors because of the weakness of hydrogel, it

quantitatively insists that the physical property of pAAm gel is similar to the Tetra-PEG gel's.

4.4 Conclusions

It is succeeded to determine the ionic concentration in hydrogel by electrostatic potential measurement and evaluate the relationship with elastic modulus for the first time. Although there are many studies experimentally and theoretically in order to discuss the relationship among elasticity, swelling ratio and ionic osmotic pressure of hydrogel precisely both at domestic and abroad as previously mentioned, there is the room to discuss about its strictness because of the large restriction come from the chosen hydrogel's physical properties. In this research, I could increase the swelling ratio with keeping the advantage of well-known structure of neutral hydrogel and remove the effect on ionic osmotic pressure to the structure of network, which is the problem of polyelectrolyte, by using molecular stent method for the first time. Thus, this research is crucially important because it is succeeded to pick up only the advantages and resolve the problem of neutral hydrogel and strong polyelectrolyte.

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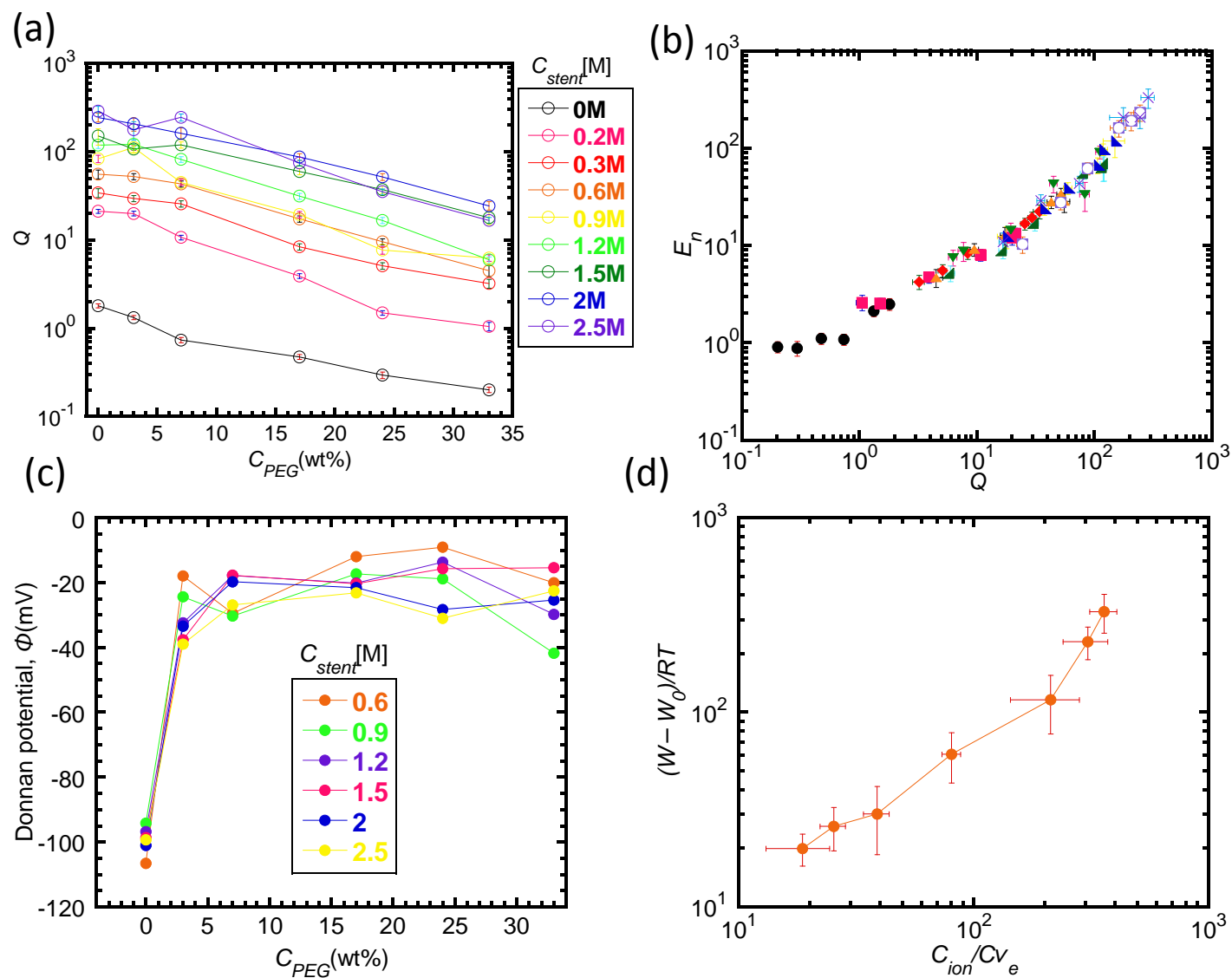


Fig.1(a) Swelling ratio of each stent concentration of St-TPEG gels whose concentrations of pre-polymer is 20k in each concentration of PEG aqueous solution. Fig.1(b) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain ($EQ/E0$) in each concentration of PEG solution. Fig.1(c) Values of electrostatic potential of each concentration of stent molecule at each condition of PEG solution. Fig.1(d) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density in water.

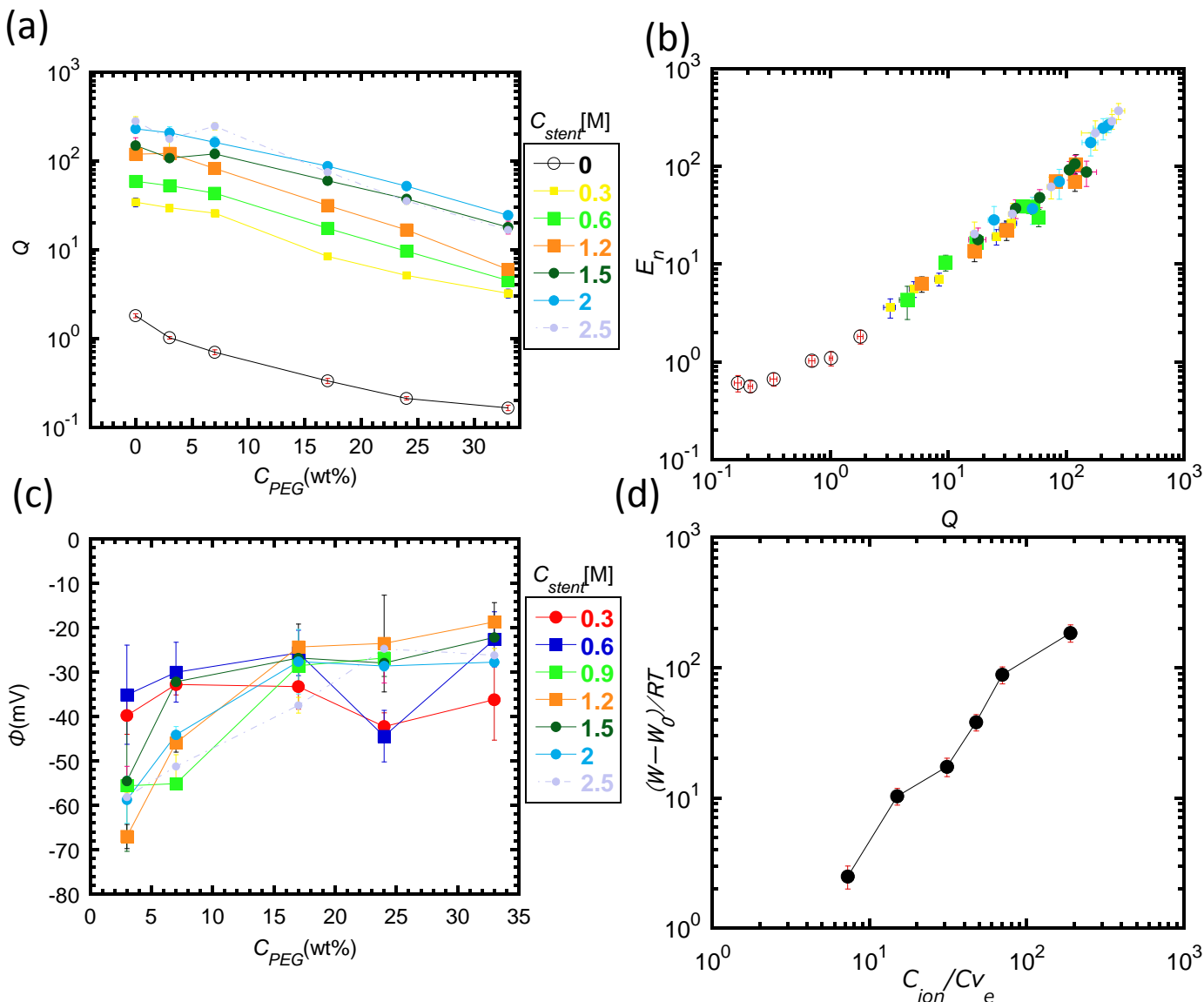


Fig.2(a) Swelling ratio of each stent concentration of St-TPEG gels whose concentrations of pre-polymer is 10k in each concentration of PEG aqueous solution. Fig.2(b) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_Q/E_0) in each concentration of PEG solution. Fig.2(c) Values of electrostatic potential of each concentration of stent molecule at each condition of PEG solution. Fig.2(d) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density in water.

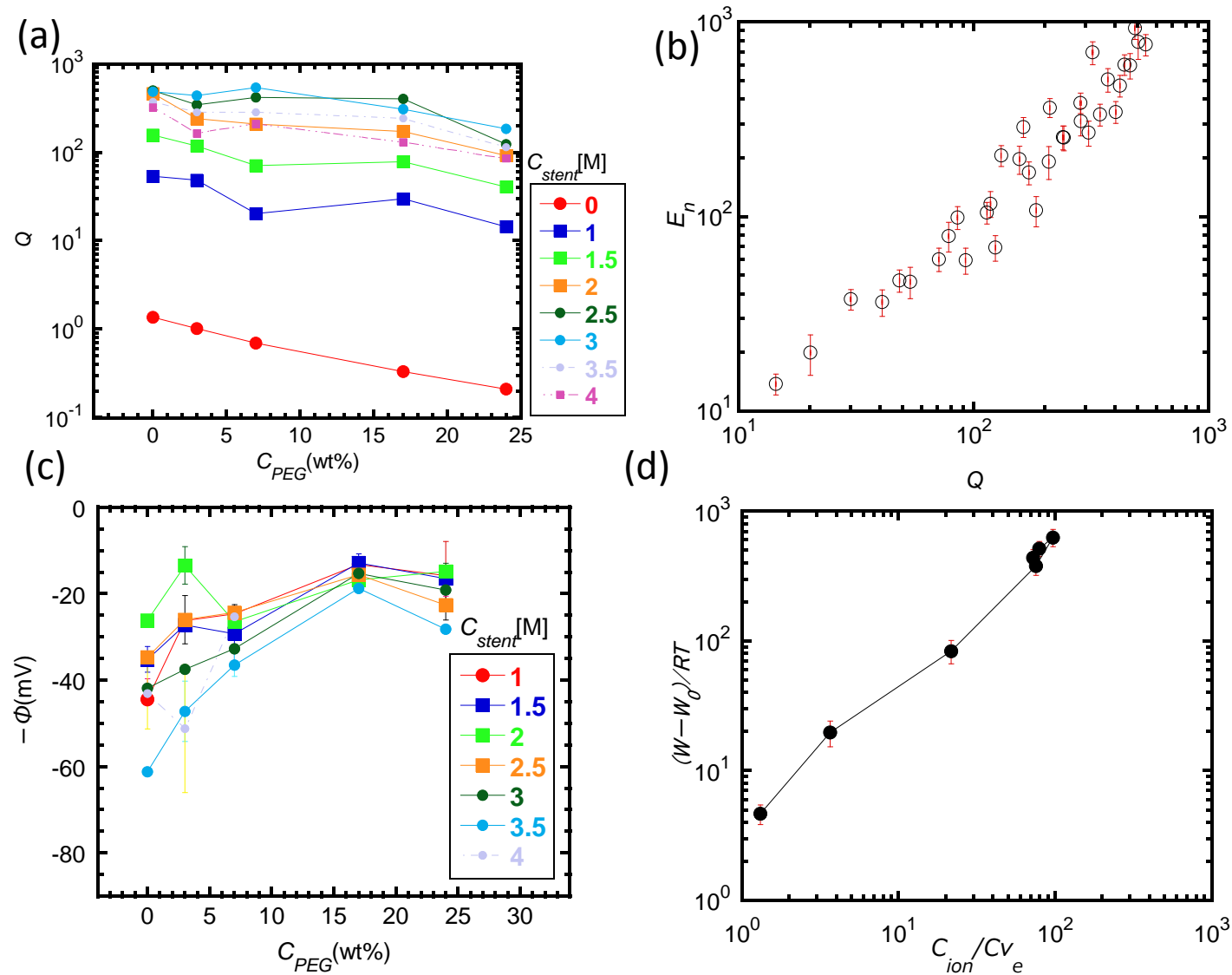


Fig.3(a) Swelling ratio of each stent concentration of St-TPEG gels whose concentrations of pre-polymer is 20k in each concentration of PEG aqueous solution. Fig.3(b) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E^n) in each concentration of PEG solution. Fig.3(c) Values of electrostatic potential of each concentration of stent molecule at each condition of PEG solution. Fig.3(d) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density in water.

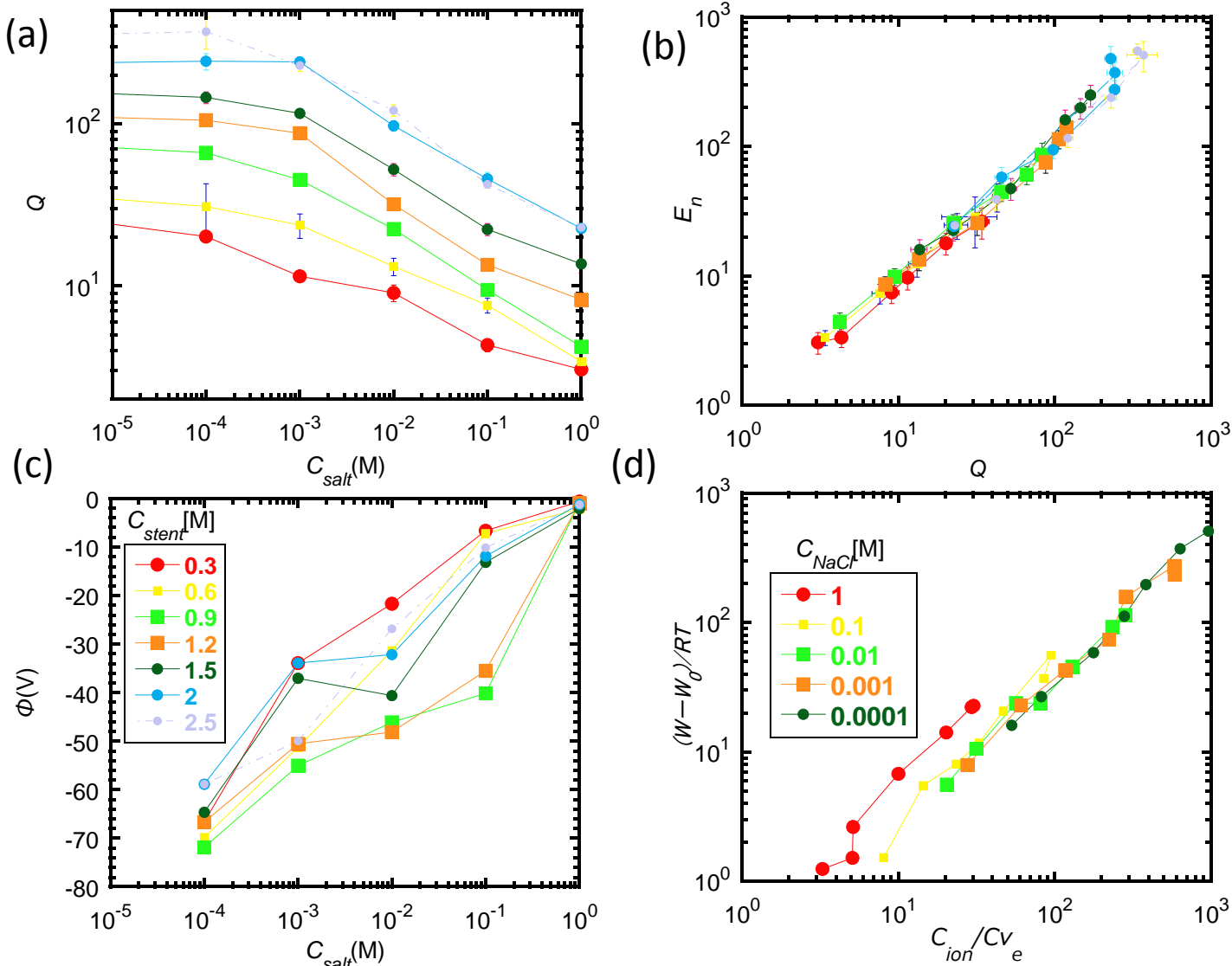


Fig.4(a) Swelling ratio of each stent concentration of St-TPEG gels whose concentrations of pre-polymer is 20k in each concentration of NaCl aqueous solution. Fig.4(b) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_n) in each concentration of NaCl aqueous solution. Fig.4(c) Values of electrostatic potential of each concentration of stent molecule at each condition of NaCl aqueous solution. Fig.4(d) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density.

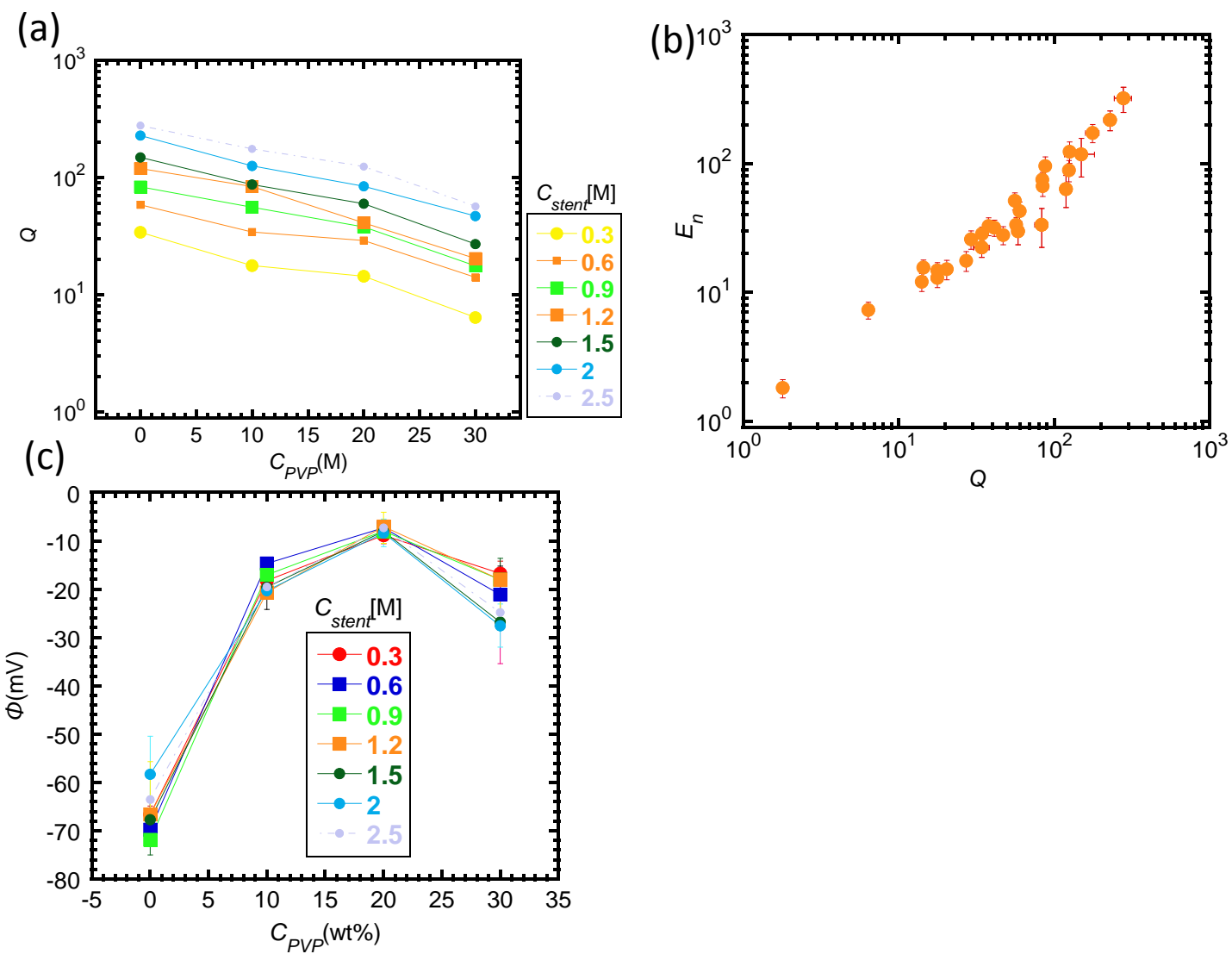


Fig.5(a) Swelling ratio of each stent concentration of St-TPEG gels whose concentrations of pre-polymer is 20k in each concentration of PVP aqueous solution. Fig.5(b) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_n) in each concentration of PVP solution. Fig.5(c) Values of electrostatic potential of each concentration of stent molecule at each condition of PVP solution.

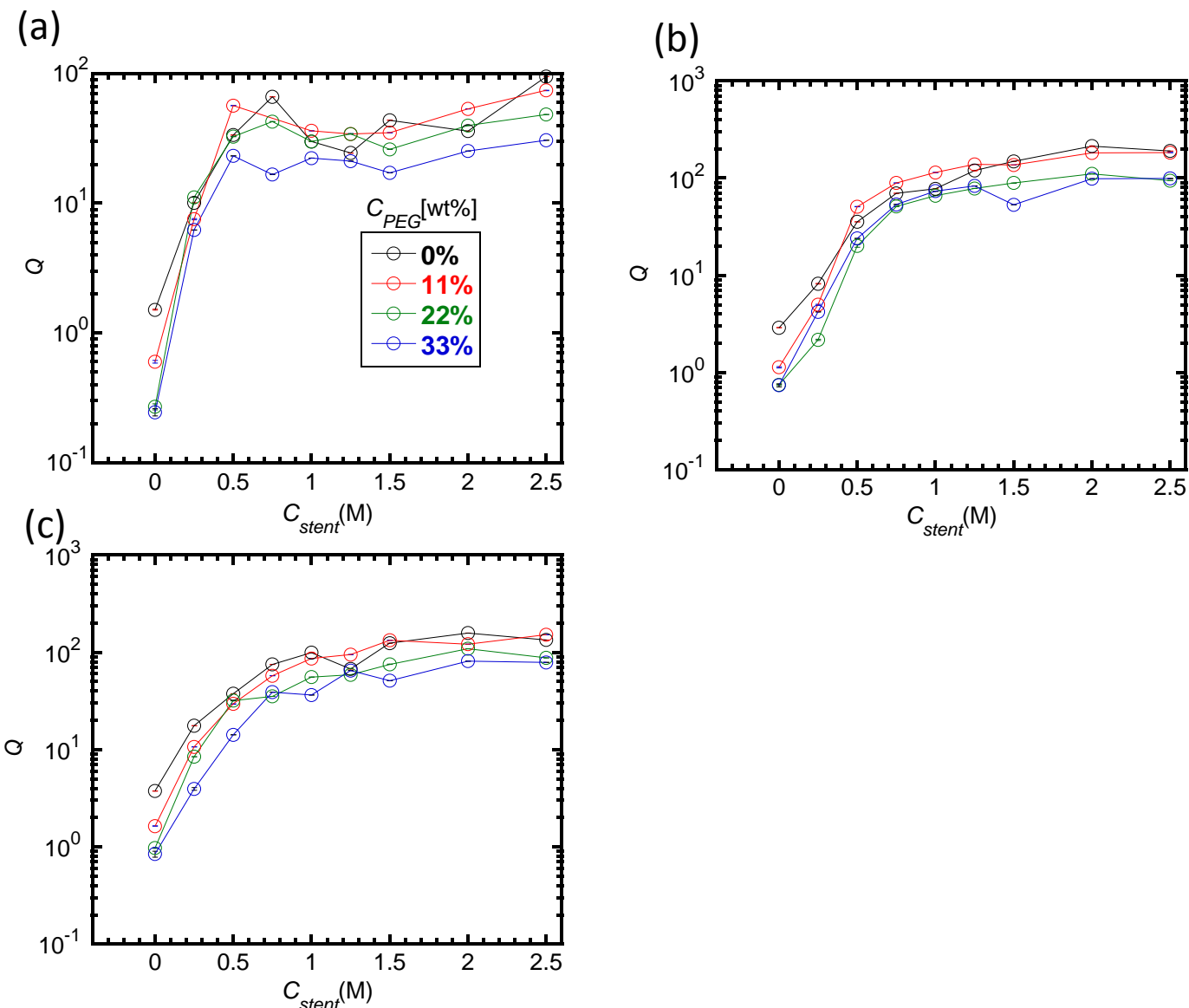


Fig.6(a) Swelling ratio of each stent concentration of St-TPEG gels whose preparation concentrations of pre-polymer is $0.5c^*$ in each concentration of PEG aqueous solution. Fig.6(b) Swelling ratio of each stent concentration of St-TPEG gels whose preparation concentrations of pre-polymer is $2c^*$ in each concentration of PEG aqueous solution. Fig.6(c) Swelling ratio of each stent concentration of St-TPEG gels whose preparation concentrations of pre-polymer is $4c^*$ in each concentration of PEG aqueous solution.

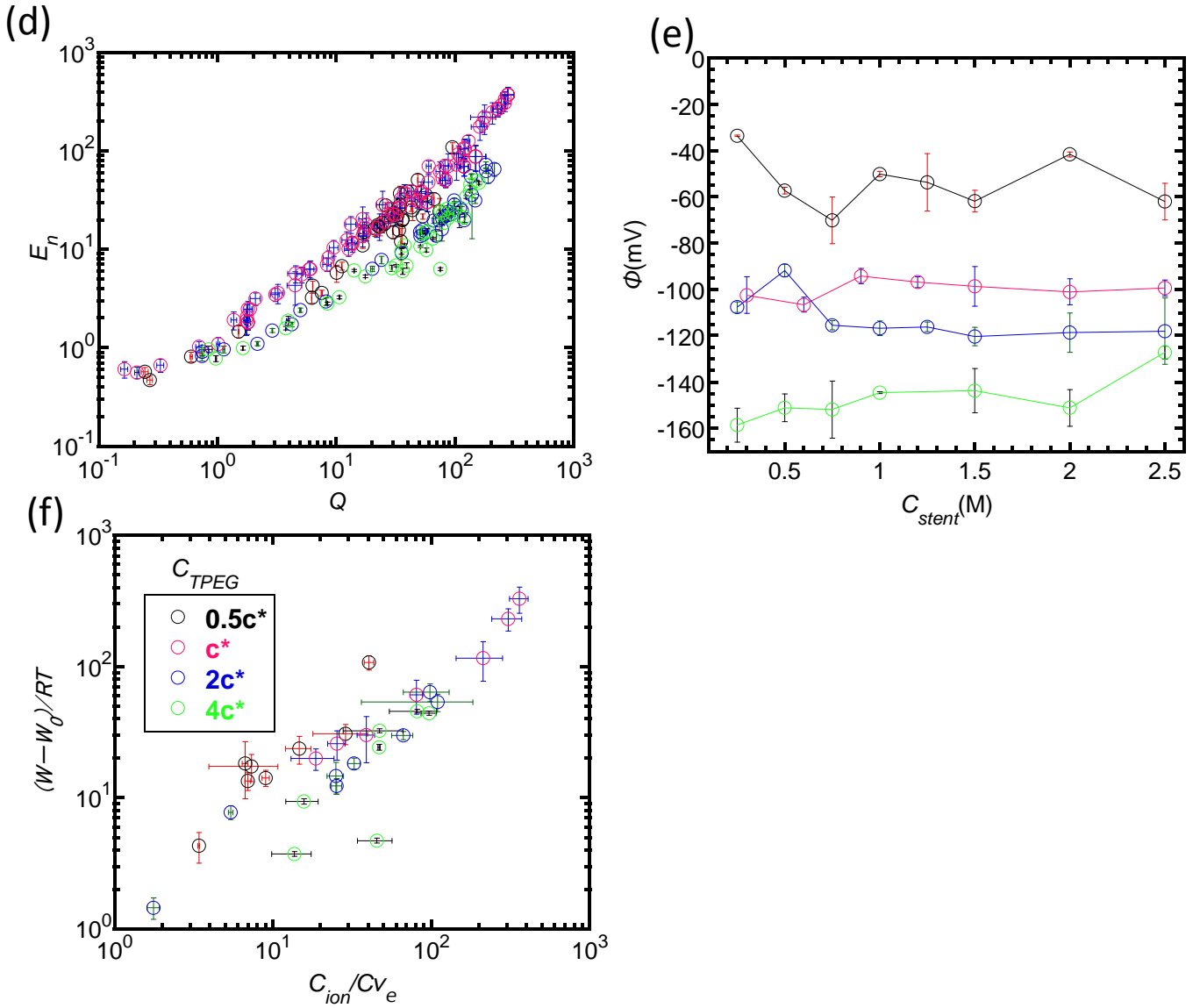


Fig.6(d) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain ($EQ/E0$) in each concentration of PEG solution. Fig.6(e) Values of electrostatic potential of each concentration of stent molecule in water. Fig.6(f) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density.

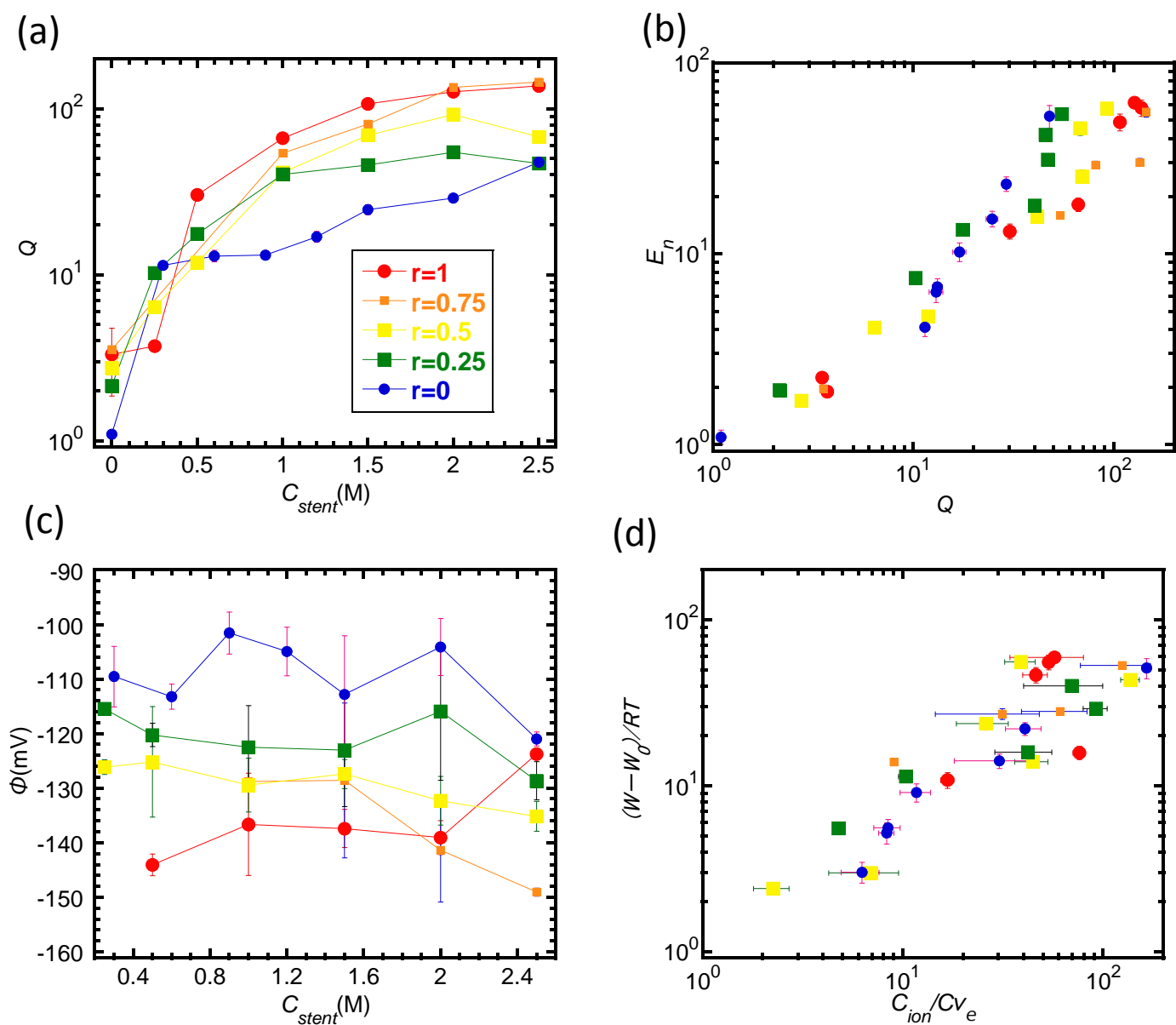


Fig.7(a) Swelling ratio of each stent concentration of St-TPEG gels whose concentrations of pre-polymer is 20k in each concentration of PEG aqueous solution. Fig.7(b) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_Q/E_0) in each concentration of PEG solution. Fig.7(c) Values of electrostatic potential of each concentration of stent molecule in water. Fig.7(d) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density.

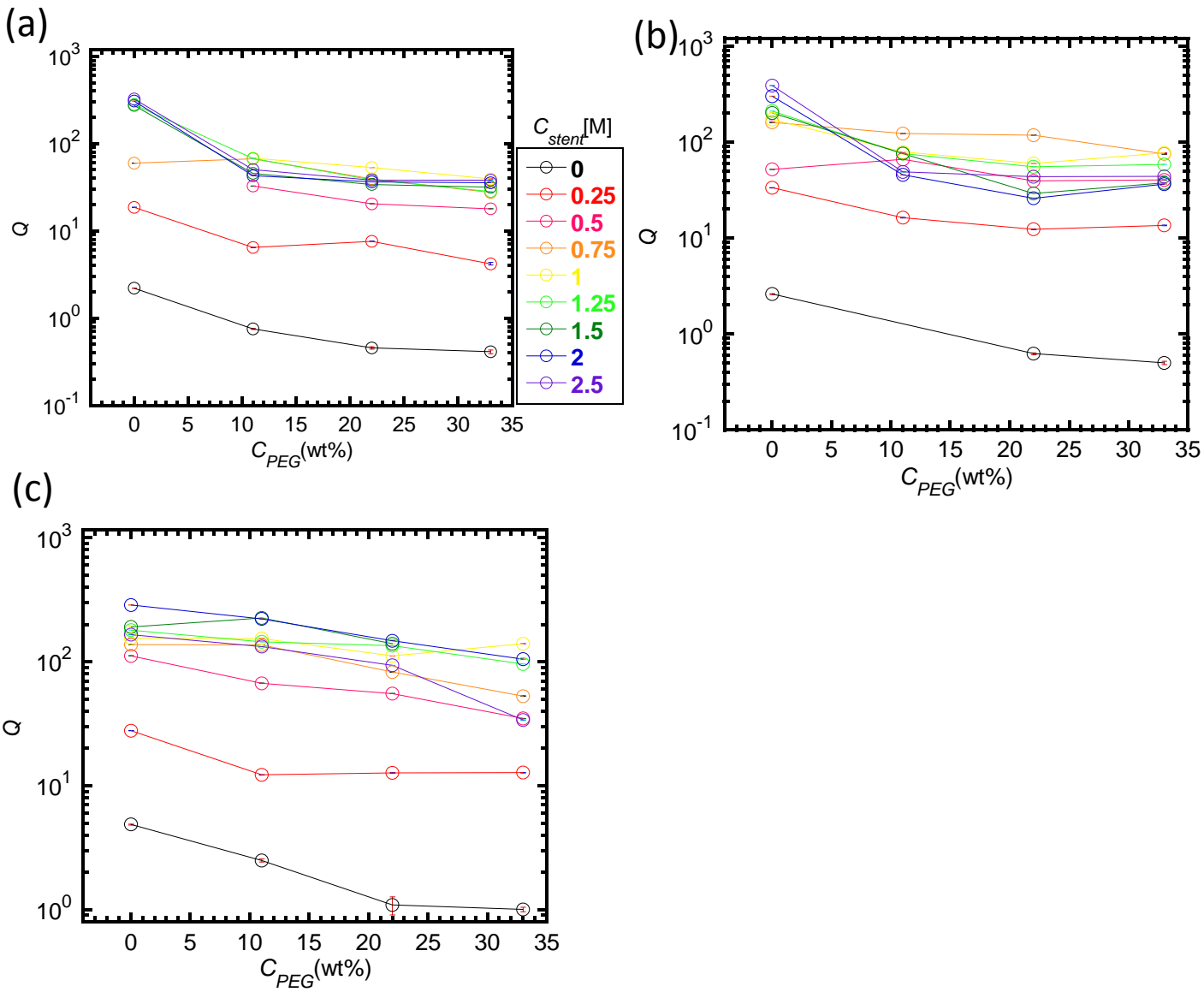


Fig.8(a) Swelling ratio of each stent concentration of p -tuned St-TPEG gels whose incubation time is 20 minutes in each concentration of PEG aqueous solution. Fig.8(b) Swelling ratio of each stent concentration of p -tuned St-TPEG gels whose incubation time is 80 minutes in each concentration of PEG aqueous solution. Fig.8(c) Swelling ratio of each stent concentration of p -tuned St-TPEG gels whose incubation time is 160 minutes in each concentration of PEG aqueous solution.

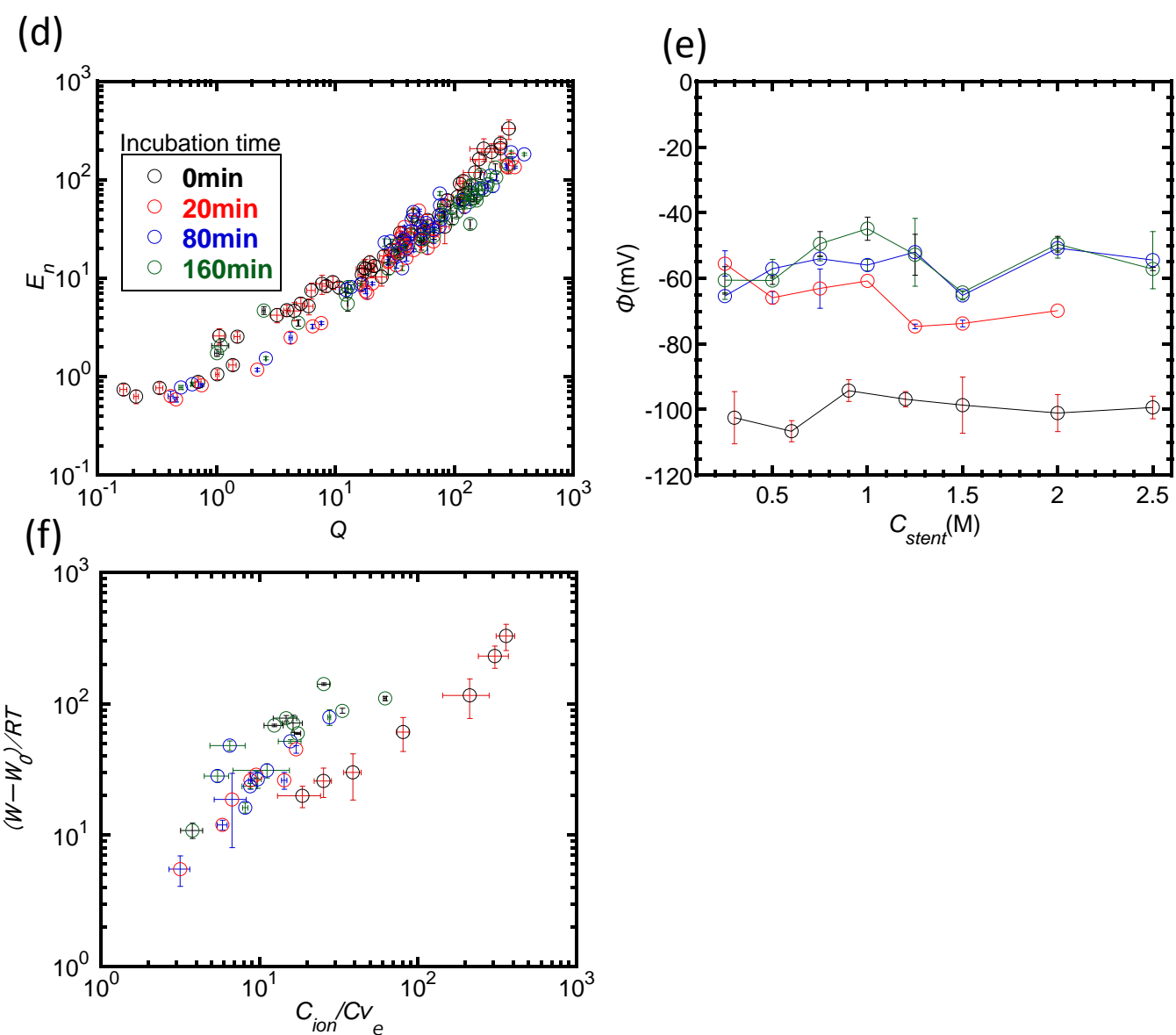


Fig.8(d) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_n) in each concentration of PEG solution. Fig.8(e) Values of electrostatic potential of each concentration of stent molecule in water. Fig.8(f) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density.

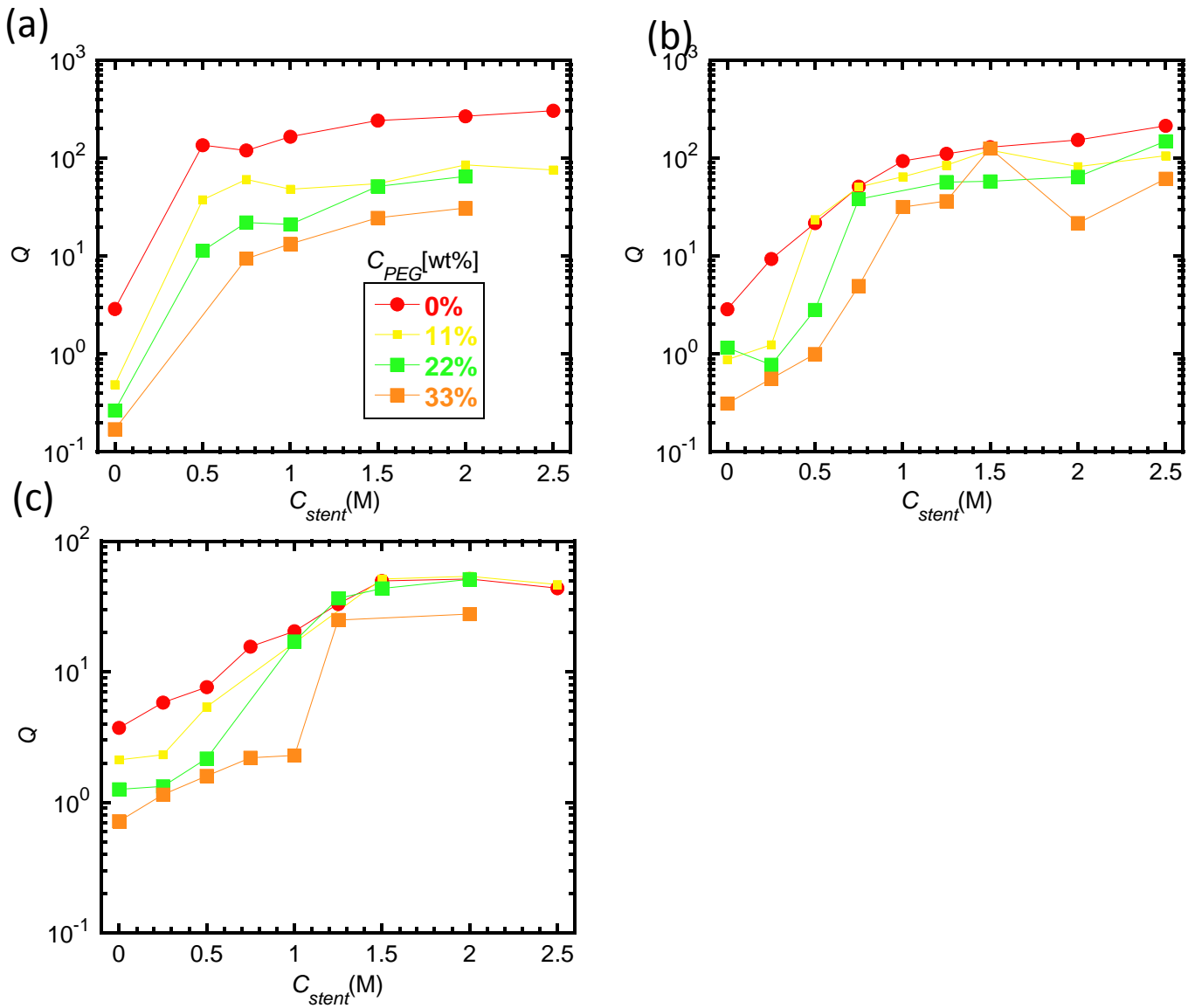


Fig.9(a) Swelling ratio of each stent concentration of pAAm gels whose monomer concentration is 4M in each concentration of PEG aqueous solution. Fig.9(b) Swelling ratio of each stent concentration of pAAm gels whose monomer concentration is 4M in each concentration of PEG aqueous solution. Fig.9(c) Swelling ratio of each stent concentration of pAAm gels whose monomer concentration is 4M in each concentration of PEG aqueous solution.

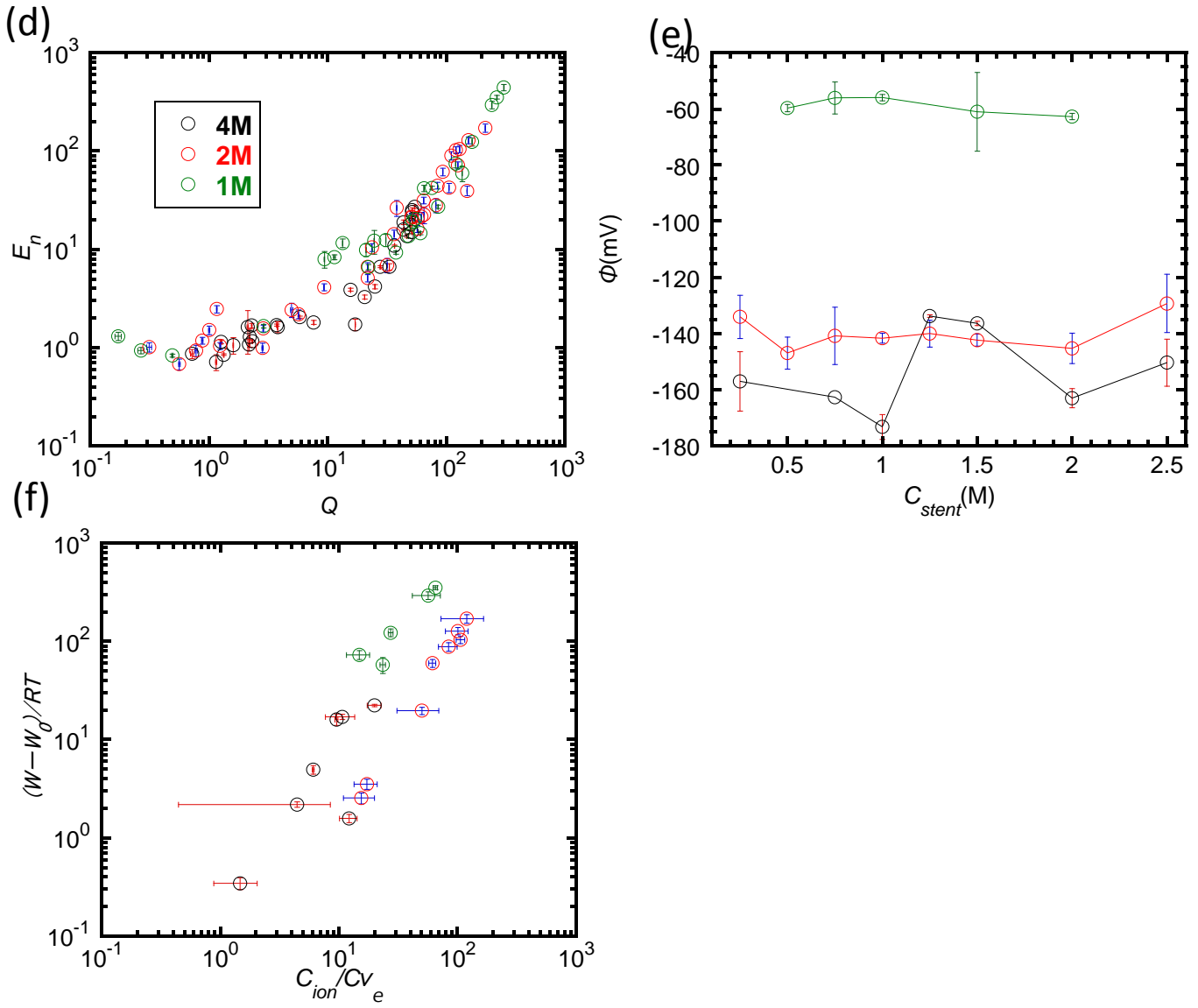


Fig.9(d) Plots of the relationship between swelling ratio (Q) and elastic energy per single polymer chain (E_n) in each concentration of PEG solution. Fig.9(e) Values of electrostatic potential of each concentration of stent molecule in water. Fig.9(f) Plots of the relationship between the changing ratio of elastic energy per single polymer chain which concerns to the osmotic pressure of mixing and ionic concentration normalized by effective network chain density.

Chapter 5

Conclusions

In chapter 3, I succeeded to obtain experimentally the relationship between swelling ratio and elastic modulus of hydrogels even in the high swollen region by increasing the swelling degree of Tetra-PEG gel by using molecular stent method. It is found that elasticity of hydrogels should be described by the elastic model which consider finite extensibility effect of network chain, not previous classical models. Based on the obtained relationship between swelling ratio and elastic modulus in high swelling region without the effect of structure change of network, it is expected that hydrogel materials which has voluntary physical properties can be designed freely by controlling its swelling ratio. Especially, design of a highly swollen hydrogel which has voluntary swelling degree and elastic modulus is expected for tuning of mechanical properties of tough DN gels consisting such hydrogel as the first network. Ultimately, it is expected that the designed hydrogel materials which has physical properties like living tissues are applied to the medical applications.

In chapter 4, I succeeded to determine dissociated ion concentration in a hydrogel by microelectrode technique and discuss the relationship between the ion concentration and its elastic energy firstly. The discovery of the relationship between ionic osmotic pressure on swelling hydrogel and the elasticity of network by this research will lead lots of development of application. For example, this research could contribute to figure out the mechanism of strong double network gel through design of swelling ratio and elasticity of the first network as I mentioned firstly. Moreover, in future it might be possible to analyze necessity of the water content and physical

properties of gel-like soft biological tissue such as cartilage in terms of swelling behavior and to design an artificial tissue which mimics properties of soft living tissue.

In terms of applications of gels, this study provides a guide for the design of hydrogel materials with a certain modulus and water content, especially at high-swelling regions. Such fully swollen hydrogels are directly useful for the fabrication of tough DN hydrogels. Based on the elasticity model, mechanical properties of a highly-swollen gel will be able to be controlled precisely. According to previous research, mechanical behavior of a DN hydrogel is mainly determined by the highly-swollen 1st network structure. Thus, this work will enable controlled mechanical behavior of DN hydrogels by controlling the 1st network structure. Such study not only provides DN hydrogels having targeted properties for specific medical and industrial applications, but also leads to further understanding of DN hydrogels.

Accomplishments

Original papers

Ken-ichi Hoshino, Tasuku Nakajima, Takahiro Matsuda, Takamasa Sakai, Jian Ping Gong, “**Network elasticity of a model hydrogel as a function of swelling ratio: From shrinking to extreme swelling states**”, *Soft Matter*, 2018, 14(47), 9693-9701

Ken-ichi Hoshino, Tasuku Nakajima, Takahiro Matsuda, Honglei Guo, Takamasa Sakai, Jian Ping Gong, “**Revisit on the effect of ionic osmotic pressure on swelling of hydrogel**”, in preparation

Ken-ichi Hoshino, Masanori Okada, Tao Lin Sun, Takayuki Nonoyama, Tasuku Nakajima, Takayuki Kurokawa, Jian Ping Gong “**Fabrication of tough hydrogel fibers from polyampholyte**”, in preparation

Presentations

○星野顕一、孫桃林、黒川孝幸、中島祐、龔劍萍、「**繊維状高靱性ゲルの創製と応用展開**」、27th Summer University in Hokkaido&2012 年度北海道高分子若手研究会、アイヌ文化センター(札幌市南区)、2012 年 8 月 31 日 ポスター

- 星野顕一、孫桃林、中島祐、黒川孝幸、龔劍萍、「両性高分子電解質を用いた高
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11 日～13 日 口頭

- 星野顕一、孫桃林、中島祐、黒川孝幸、龔劍萍、「繊維状高韌性ゲルの創製」、**ゲ
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- 星野顕一、孫桃林、中島祐、黒川孝幸、龔劍萍、「Fabrication of tough hydrogel
fibers from polyampholyte」、**IGP International Symposium**、北海道大学理学部5号
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- 星野顕一、孫桃林、野々山貴行、中島祐、黒川孝幸、龔劍萍、「繊維状高韌性ゲル
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fibers from polyampholyte」、**特別経費第一回シンポジウム**、北海道大学学術交流会
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- 岡田真典、星野顕一、孫桃林、黒川孝幸、中島祐、野々山貴行、龔劍萍、「繊維状
高韌性ゲルの創製と強度化の探究」、**第 4 回 CSJ 化学フェスタ 2014**、タワーホール船
堀(東京都江戸川区)、2014 年 10 月 14 日～16 日 ポスター **優秀ポスター発表賞**

○星野顕一、岡田真典、孫桃林、中島祐、黒川孝幸、龔劍萍、「Fabrication of tough hydrogel fibers from polyampholyte」、**The 2nd International Life-Science Symposium**、北海道大学学術交流会館、2014年10月23日 ポスター

○岡田真典、星野顕一、孫桃林、黒川孝幸、龔劍萍、「高韌性ゲルの繊維化」、**2015年度帝人21世紀フォーラム**、平成27年1月10日～11日 ポスター

○星野顕一、岡田真典、孫桃林、野々山貴行、中島祐、黒川孝幸、龔劍萍、「両性電解質高分子を用いた繊維状高韌性ゲルの創製」、**高分子学会2014年度北海道支部冬季研究発表会**、北海道大学学術交流会館(札幌市北区)、平成27年1月26日(月) 口頭

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