Semidilute Principle for Gels

Naoyuki Sakumichi, Takashi Yasuda, and Takamasa Sakai

Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan.

(Dated: December 12, 2022)

Polymer gels such as jellies and soft contact lenses are soft solids consisting of three-dimensional polymer networks swollen with a large amount of solvent. For approximately 80 years, the swelling of polymer gels has been described using the Flory–Huggins mean-field theory. However, this theory is problematic when applied to polymer gels with large solvent contents owing to the significant fluctuations in polymer concentration. In this study, we experimentally demonstrate the superiority of the semidilute scaling law over the mean-field theory for predicting the swelling of polymer gels. Using the semidilute scaling law, we experimentally determine the universal critical exponent \( \nu \) of the self-avoiding walk via swelling experiments on polymer gels. The experimentally obtained value \( \nu \approx 0.589 \) is consistent with the previously reported value of \( \nu \approx 0.588 \), which was obtained by precise numerical calculations. Furthermore, we theoretically derive and experimentally demonstrate a scaling law that governs the equilibrium concentrations. This scaling law contradicts the predictions made by de Gennes’ \( c^* \) theorem. A major deficiency of the \( c^* \) theorem is that the network elasticity, which depends on the as-prepared state, is neglected. These findings reveal that the semidilute scaling law is a fundamental principle for accurately predicting and controlling the equilibrium swelling of polymer gels.

I. INTRODUCTION

The swelling of polymer networks by absorption of surrounding solvent is a ubiquitous phenomenon [1, 2]; for example, it is used in water-absorbent materials in disposable diapers and portable toilets. Here, polymer networks swollen with a large amount of solvent are called polymer gels, such as jellies and soft contact lenses. As-prepared polymer gels after fabrication are generally not in an equilibrium swollen state and swell when immersed in a solvent. Revealing the governing law for the swelling of polymer gels has long been an important issue [3, 4], and considerable studies have been conducted to predict the equilibrium swollen state (e.g., the liquid content in swollen polymer gels) [4–21]. This is because it is essential for a fundamental understanding of polymer gels and their applications. For example, in practical biomedical applications such as drug delivery [22], adhesion barriers [23], and artificial vitreous humor [24], understanding the swelling behavior of polymer gels is essential because the liquid content significantly influences the softness and mass diffusivity of polymer gels in the external environment.

According to Flory and Rehner [4], the swelling equilibrium of (electrically neutral) polymer gels in good solvents is determined by the balance between the elastic (\( \Pi_{el} \)) and mixing (\( \Pi_{mix} \)) contributions in the total swelling pressure of polymer gels [Fig. 1(a)]:

\[
\Pi_{tot} = \Pi_{mix} + \Pi_{el},
\]

The elastic contribution satisfies \( \Pi_{el} = -G_0(c/c_0)^{1/3}, \) [21, 25] because uniform swelling reduces the density of the polymer network. Here, \( G_0 \) is the shear modulus in the as-prepared state, and \( c_0 \) and \( c \) are the polymer mass concentrations in the as-prepared and equilibrium states, respectively. Therefore, we consider the expression for \( \Pi_{mix} \).

A conventional approach to describe \( \Pi_{mix} \) in Eq. (1) is the Flory–Huggins (FH) mean-field theory, which was originally developed for polymer solutions [26–28]. The FH mean-field theory is applicable to concentrated polymer systems such as non-dilute polymer solutions and polymer blends with small concentration fluctuations [29], because it uses the mean-field approximation. Thus, its application to dilute systems, including polymer gels with low polymer volume fractions (typically less than 0.1), is problematic, as pointed out by Flory himself†. However, in numerous subsequent studies, the FH theory has been inappropriately applied to polymer gels containing a large amount of solvent [5–8], resulting in significant inconsistencies in the reported polymer–solvent interaction parameters [30–33].

Another well-known claim, de Gennes’ \( c^* \) theorem [2], asserts that the polymer concentration \( c_{eq} \) of a polymer gel in the equilibrium swollen state is proportional to the overlap concentration \( c^* \) of a group of polymer chains in a good solvent. Notably, this so-called \( c^* \) “theorem” is not a mathematical theorem but only a physical conjecture that requires experimental validation. This

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* These authors contributed equally: N. Sakumichi, T. Yasuda
† Correspondence should be addressed to N. Sakumichi or T. Sakai: sakumichi@gel.t.u-tokyo.ac.jp; sakai@gel.t.u-tokyo.ac.jp

† Regarding the limitations of the FH mean-field theory, Flory stated, “Of importance here is the realization that the theory as developed so far is inappropriate, generally speaking, for dilute polymer solutions” on p. 505 in Ref. [1].
conjecture follows from the assumption that subchains (chains between adjacent crosslinks) in an equilibrium swollen network of a polymer gel disinterpenetrate, i.e., subchains do not interpenetrate each other and remain in contact at the overlap threshold. Here, polymer gels are considered as a set of closely packed polymer chains sealed together by crosslinks, similar to polymer solutions at the overlap threshold $c^*$. Several experimental observations have supported this conjecture, revealing similarities in the scaling relations between polymer gels and semidilute solutions [9–11]. However, subsequent systematic measurements of the elastic modulus of gels contradict the disinterpenetration of the swollen network chains assumed in this conjecture [8, 12, 13]. Hence, the $c^*$ theorem, although seemingly plausible, remains controversial.

In this study, we measure $\Pi_{\text{mix}}$ of chemically crosslinked polymer gels with precisely controlled homogeneous network structures [34] throughout the quasistatic swelling process from the as-prepared to equilibrium state [Fig. 1(b)], using the osmotic deswelling method proposed in 1940s [35] and developed in the 1980s [36]. Consequently, we successfully demonstrate that the semidilute scaling law of polymer solutions [2, 37] governs $\Pi_{\text{mix}}$ of polymer gels in Eq. (1). Furthermore, by assuming the semidilute scaling law as the fundamental principle for polymer gels, we theoretically derive and experimentally validate the following three arguments. First, the semidilute scaling law is superior to the FH mean-field theory in accurately predicting the equilibrium state of polymer gels throughout the quasistatic swelling process. Second, swelling experiments of polymer gels provide a novel method for experimentally determining the overlap threshold $c^*$. Hence, $c^*$ is measured from a gel taken out from the solvent. Third, we experimentally evaluated $\Pi_{\text{mix}}$ through the quasistatic swelling process, from the as-prepared to equilibrium swollen states in a pure solvent. A gel after fabrication is called the as-prepared state, where the volume is $V_0$. Upon immersing into a pure solvent, the as-prepared gel swells because its osmotic pressure ($\Pi_c = \Pi_{\text{mix}} + \Pi_{\text{el}} > 0$) is larger than the osmotic pressure outside ($\Pi_{\text{ext}} = 0$). After a few days, the gel reaches the equilibrium swollen state at which $\Pi_{\text{tot}} = 0$, changing its volume ($V_0 \rightarrow V_{\text{eq}}$) and polymer mass concentration ($c_0 \rightarrow c_{\text{eq}}$).

II. FLORY–HUGGINS MEAN-FIELD THEORY AND SEMIDILUTE SCALING LAW OF $\Pi_{\text{mix}}$

To determine the law governing $\Pi_{\text{mix}}$ of polymer gels, we experimentally evaluated $\Pi_{\text{mix}}$ throughout the quasistatic swelling process, from the as-prepared to equilibrium swollen states, via osmotic deswelling [35, 36, 44]. As shown in Fig. 1(b), we immerse a gel sample in an external polymer solution with a certain external osmotic pressure $\Pi_{\text{ext}}$. The equilibrium condition is $\Pi_{\text{tot}} = \Pi_{\text{ext}}$, at which the osmotic pressure inside and outside the gel is equivalent. Especially, $\Pi_{\text{ext}} = 0$ for a pure solvent, as shown in Fig. 1(a). Hence, by gradually tuning $\Pi_{\text{ext}}$.
with the controlled aqueous polymer solutions [43], we can evaluate $\Pi_{\text{mix}}$ as

$$\Pi_{\text{mix}} = \Pi_{\text{ext}} + G_0 \left( \frac{c}{c_0} \right)^{1/3}, \quad (2)$$

where $G_0$ and $c$ can be experimentally measured. We assume Eq. (2) throughout this study. In this study, we consider only the equilibrium states of the polymer gels in external polymer solutions, such as the as-prepared ($Q = 1$ and $\Pi_{\text{ext}} > 0$), swelling ($Q > 1$ and $\Pi_{\text{ext}} > 0$), and equilibrium swollen ($Q > 1$ and $\Pi_{\text{ext}} = 0$) states. Here, $Q \equiv V/V_0$ is the volume swelling ratio [see Fig. 1(b)].

In a solution with sufficiently long polymer chains, the Flory–Huggins (FH) mean-field theory [26–28] predicts that

$$\Pi_{\text{mix}} = -\frac{k_B T}{v} \left[ \phi + \ln (1 - \phi) + \chi \phi^2 \right], \quad (3)$$

where $k_B$, $T$, $v$, and $\phi$ are the Boltzmann constant, absolute temperature, volume of solvent molecules, and polymer volume fraction, respectively. The FH interaction parameter $\chi$ quantifies the energies of the interactions between the polymer units and the solvent molecules per lattice site as follows: $\chi \equiv z (\epsilon_{\text{pp}} + \epsilon_{\text{ss}} - 2\epsilon_{\text{ps}})/(2k_B T)$, where $z$ is the coordination number of the lattice, and $\epsilon_{\text{pp}}$, $\epsilon_{\text{ss}}$, and $\epsilon_{\text{ps}}$ are the polymer–polymer, solvent–solvent, and polymer–solvent interaction energies, respectively. Although the FH theory is applicable only to concentrated polymer solutions [29], it has been inappropriately applied to polymer gels containing a large amount of solvent, by suitably adjusting $\chi$ [5–8]. Consequently, significant inconsistencies in $\chi$ were reported in previous studies, although $\chi$ should be constant for the same polymer–solvent system and temperature [45, 46]. For example, $\chi = 0.426$ for the poly(ethylene glycol) (PEG) hydrogel [30] and $\chi = 0.366$, 0.441, and 0.465 for the aqueous PEG solution with the molar masses $M = 4.6$ [31], 10 [32], and 33 kg/mol [33], respectively, were reported at $T = 298$ K, using $v = 18 \times 10^{-6}$ m$^3$/mol.

By contrast, we propose that the semidilute scaling law of polymer solutions [2, 37] governs $\Pi_{\text{mix}}$ in polymer gels, based on a recent observation [44]. In Ref. [44], it was observed that a universal osmotic equation of state of polymer solutions [2, 37, 47–49] describes $\Pi_{\text{mix}}$ throughout the gelation process. For polymer solutions, the semidilute scaling law is expressed as $\Pi_{\text{mix}} M / (cN_A k_B T) = K (c/c^*)^{1/(3\nu - 1)}$, where $K \approx 1.1$ is the universal constant for the semidilute polymer solutions, $N_A$ is the Avogadro constant, $c^*$ is the overlap concentration, and $\nu \approx 0.588$ is the universal critical exponent of the SAW [38–42]. However, for polymer gels, $c^* \to 0$ and $c/c^* \to \infty$ [44], because the molar mass of a polymer network is infinite. Thus, we introduce the regulator $M_{\text{seg}}$ to propose the following semidilute scaling law:

$$\frac{\Pi_{\text{mix}}}{nk_B T} = K \left( \frac{n}{n_{\text{seg}}^*} \right)^{\nu - 1}, \quad (4)$$

as a fundamental principle for polymer networks that contain a large amount of solvent. Here, both sides of Eq. (4) are dimensionless; $n \equiv c N_A / M_{\text{seg}}$ is the number density of a “segment” of polymers, where $M_{\text{seg}}$ is the molar mass of the segment. In this study, we use $M_{\text{seg}} = 44 \times 10^{-3}$ kg/mol, which is the molar mass of an ethylene glycol unit as a segment. In Eq. (4), $n_{\text{seg}}^*$ is a parameter that depends on $T$ and the type of polymer network and solvent considered. We determined $n_{\text{seg}}^*$ by adjusting to the experimental data. This procedure is similar to the determination of $\chi$ in the FH mean-field theory from the experimental data.

Notably, a few pioneering studies [11, 16–20] attempted to describe the equilibrium swelling of polymer gels using the semidilute scaling law such as $\Pi_{\text{mix}} \sim \phi^{3/4}$. However, they did not focus on demonstrating the superiority of the semidilute scaling law over the FH mean-field theory, owing to the limited accuracy of the gel experiments and the lack of theoretical comprehension of polymer gels. By contrast, in this study, we experimentally demonstrate the superiority of Eq. (4) over the FH mean-field theory [Eq. (3)] in terms of predicting the equilibrium state of polymer gels throughout the quasistatic swelling process. We verify the superiority of the semidilute scaling law using precisely controlled homogeneous networks [34] and a different definition of the polymer mass concentration [44] that enables us to extend the universality of the osmotic equation of state of polymer solutions.

### III. MATERIALS AND METHODS

#### A. Fabrication of model gels

As a model system to examine the quasistatic swelling process of chemically crosslinked polymer gels, we used a tetra-branched PEG hydrogel [34], synthesized via the AB-type cross-end coupling of two prepolymer (tetrarm PEG) units of equal size. Each end of the tetra-arm PEG was modified with a mutually reactive maleimide (tetra-PEG MA) and thiol (tetra-PEG SH). We dissolved tetra-PEG MA and tetra-PEG SH (NOF Co., Japan & XIAMEN SINOPEG BIOTECH Co., Ltd., China) in phosphate citrate buffer with an ionic strength of 100 mM and a pH of 3.8. For gelation, we mixed these two solutions with equal molar masses $M$ for equal prepolymer mass concentrations $c_0$ at various mixing fractions $s$. Here, $s$ is the molar fraction of the minor prepolymer (tetra-PEG SH) to all prepolymer ($0 \leq s \leq 1/2$). By tuning $s$, the desired connectivity $p$ can be obtained in accordance with $p = 2s [50, 51]$, where $p$ is defined as the fraction of reacted terminal functional groups to all
term $b$ in a narrow temperature ($T$) range. This finding contradicts the conventional models that assume $G_0$ is approximately proportional to the absolute temperature $T$.

We measured $G_0$ of each as-prepared gel sample using dynamic viscoelasticity measurement. Immediately after mixing the tetra-PEG MA and tetra-PEG SH aqueous solutions for 60 seconds, the resulting solutions were poured into the gap of the double cylinder of a dynamic shear rheometer (MCR 301 and 302, Anton Paar, Graz, Austria). Then, we cyclically sheared the samples in the gap between the inner cylinder and the outer cup at 298 K for $6 \times 10^4$ seconds, yielding the time course of the storage modulus $G'$. The applied frequency and strain were 1 Hz and 1%, respectively. After $G'$ reached equilibrium, which corresponded to the completion of the chemical reaction of the MA and SH functional groups, we determined $G'$ at 1 Hz as the (equilibrium) shear modulus $G_0$. We provide the experimental results in Appendix A.

**IV. SEMIDILUTE SCALING LAW FOR $\Pi_{\text{mix}}$**

We investigated whether the FH theory or the semidilute scaling law is more accurate in describing $\Pi_{\text{mix}}$ throughout the quasistatic swelling process. Figure 2 shows the polymer mass concentration ($c$) dependence of $\Pi_{\text{mix}}$ for all samples considered in this study, involving the as-prepared, swelling (and deswelling, described in Appendix D), and equilibrium swollen states. In addition, it shows the FH theory [Eq. (3)] with the previously reported value of $\chi = 0.426$ [30] and the semidilute scaling law [Eq. (4)] with the one-parameter least-square fit of $n_{\text{seg}}^c$ to the data of the as-prepared state. The best-fit parameter, $n_{\text{seg}}^c = 3.80(8) \times 10^{28}$ m$^{-3}$, is obtained from $\Pi_{\text{mix}}$ of the polymer gels and is approximately identical to that of the prepolymer solutions in the semidilute regime [44] (see Appendix E). Here, the number in parentheses is the standard deviation in the last digits. All the samples (i.e., as-prepared, swelling, deswelling, and equilibrium swollen states with various network conditions of $p$, $c_0$, and $M$) conform to the semidilute scaling law with an exponent of $3\nu/(3\nu - 1) \approx 2.31$ over a wide concentration range. The semidilute scaling law is universal for a large variety of chemically different polymer networks and solvents, as shown in Appendix F using the data available from previous studies [9, 13–15, 17]. Further, the FH theory fails to describe $\Pi_{\text{mix}}$ for low concentrations. This result is consistent with the fact that the FH theory is justified at high concentrations because it is a mean-field theory. Notably, the difference in $\Pi_{\text{mix}}$ at low concentrations leads to large deviations in the prediction of the equilibrium volume swelling ratio $Q_\text{eq} \equiv V_\text{eq}/V_0$ in the equilibrium swollen state (see Sec. V).
Assuming that the semidilute scaling law [Eq. (4)] is a fundamental principle governing $\Pi_{\text{mix}}$ in polymer gels, we can experimentally determine the universal critical exponent $\nu$ of the SAW [2, 38, 39] from the data of the $c$ dependence of $\Pi_{\text{mix}}$ in Fig. 2. From the two-parameter [68] $\{\beta \equiv 1/(3\nu - 1)\}$ and $n_{\text{seg}}^*$ least-square fit to all the data in Fig. 2 with Eq. (4), we obtain the best-fit parameter set as $n_{\text{seg}}^* = 3.73(23) \times 10^{28}$ m$^{-3}$ and $\beta = 1.302(20)$. This result corresponds to $\nu = 0.5893(38)$, which is consistent with the previously reported values $\nu = 0.5875970(4)$ and $\nu = 0.5874(3)$ obtained from Monte Carlo calculations [40] and the $\epsilon$ expansion method [41], respectively. In addition, the obtained value $\nu \approx 0.589$ is comparable to the previous experimental results of $\nu = 0.583(3)$ [56], $2\nu = 1.17$ [57], $2\nu = 1.16$ [58], and $2\nu = 1.19(1)$ [59], which were measured by the molar-mass dependence of the gyration radius in dilute polymer solutions with light scattering. These results are summarized in Table I. Notably, our approach of determining $\nu$ using $\Pi_{\text{mix}}$ of the polymer gels offers advantages over that of polymer solutions [56–59] in terms of the polydispersity effect. Moreover, the overlap threshold is negligible, because polymer gels comprise infinite polymer networks in the semidilute regime. Therefore, we conclude that measuring the polymer mass concentration dependence of $\Pi_{\text{mix}}$ of polymer gels provides a new method to experimentally determine the universal critical exponent $\nu$ of the SAW.

\section*{V. PREDICTION OF THE QUASISTATIC SWELLING PROCESS}

Figure 3 demonstrates that Eq. (1) together with the semidilute scaling law [Eq. (4)], rather than the FH mean-field theory [Eq. (3)], accurately predicts the experimental value of the volume swelling ratio $Q \equiv V/V_0$ throughout the quasistatic swelling process (blue arrow). The explicit forms of these equations and the typical changes in $\Pi_{\text{mix}}$ and $\Pi_{\text{ext}}$ are provided in Appendix G. As shown in Fig. 2, $\Pi_{\text{mix}}$ estimated by the FH theory and that by the semidilute scaling law are in agreement at high mass concentrations. Thus, at high mass concentrations (corresponding to $Q \approx 1$), the predictions of $Q$ using the FH theory and semidilute scaling law are consistent. By contrast, $\Pi_{\text{mix}}$ estimated by the FH theory and that by the semidilute scaling law predict different values in the low mass concentrations, which correspond to low $\Pi_{\text{ext}}$ in Fig. 3. Although the difference in $\Pi_{\text{mix}}$ in Fig. 2 is small, the difference in $Q$ in Fig. 3 is significantly large. The deviation of the FH theory from the experimental value of $Q$ in the low $\Pi_{\text{ext}}$ range may be attributed to the increase in spatial concentration fluctuations at low concentrations, which increases the deviation from the mean-field approximation.

\begin{table}[h]
\centering
\begin{tabular}{l c}
\hline
References & Method \\
\hline
Ref. [40] & Monte Carlo simulations  $\nu = 0.5875970(4)$ \\
Ref. [41] & $\epsilon$-expansion at order $\epsilon^6$  $\nu = 0.5874(3)$ \\
Ref. [42] & Conformational bootstrap $\nu = 0.5877(12)$ \\
Ref. [56] & Light scattering of solutions  $\nu = 0.583(3)$ \\
Ref. [57] & Light scattering of solutions  $2\nu \approx 1.17$ \\
Ref. [58] & Light scattering of solutions  $2\nu \approx 1.16$ \\
Ref. [59] & Light scattering of solutions  $2\nu = 1.19(1)$ \\
This study & Swelling experiments of gels  $\nu \approx 0.589$ \\
\hline
\end{tabular}
\caption{Universal critical exponent $\nu$ of self-avoiding walks evaluated by different methods.}
\end{table}
The swelling ratio of polymer gels and polymer solutions is approximately identical (see Appendix E), whereas previously reported values of the FH interaction parameters $\chi$ for polymer gels and polymer solutions exhibit significant inconsistencies [30–33]. Thus, by measuring $n_{\text{seg}}^*$ from the polymer solutions, we can determine $\Pi_{\text{mix}}^2$ and accurately predict the equilibrium swelling ratio of polymer gels. Conversely, by measuring $n_{\text{seg}}^*$ from $\Pi_{\text{mix}}$ of the polymer gels, we can determine the osmotic equation of state of the prepolymer solutions [2, 37, 47–49]. However, applying the FH theory to $\Pi_{\text{mix}}$ of (dilute) polymer gels does not yield an accurate $\chi$. These results indicate that the semidilute scaling law is superior to the FH theory in terms of predicting the entire quasistatic swelling process of polymer gels.

FIG. 3. Volume swelling ratio ($Q$) throughout the quasistatic swelling process. We measured $Q$ by gradually tuning $\Pi_{\text{ext}}$ (schematic). The blue circles are the experimental results with $M = 40$ kg/mol for $c_0 = 120$ g/L at $p = 0.6$. The black dashed and solid curves are the predictions from Eq. (1) using the FH theory [Eq. (3)] with $\chi = 0.426$ [30] and $v = 18 \times 10^{-4}$ m$^3$/mol and the semidilute scaling law [Eq. (4)] with $n_{\text{seg}}^* = 3.80 \times 10^{28}$ m$^{-3}$ and $\nu = 0.588$, respectively. In these predictions, we use the polymer mass concentration $c_0$ and experimentally measured shear modulus $G_0$ at the as-prepared state ($Q = 1$). For the equilibrium swollen state in a pure solvent ($\Pi_{\text{ext}} = 0$), the experimental result, semidilute scaling law, and FH theory predictions are $Q = 6.47, 6.99$, and 9.98, respectively.

The superiority of the semidilute scaling law is also established by the experimental result that $n_{\text{seg}}^*$ for the polymer gels and prepolymer solutions are approximately identical (see Appendix E), whereas previously reported values of the FH interaction parameters $\chi$ for polymer gels and polymer solutions exhibit significant inconsistencies [30–33]. Thus, by measuring $n_{\text{seg}}^*$ from the polymer solutions, we can determine $\Pi_{\text{mix}}^2$ and accurately predict the equilibrium swelling ratio of polymer gels. Conversely, by measuring $n_{\text{seg}}^*$ from $\Pi_{\text{mix}}$ of the polymer gels, we can determine the osmotic equation of state of the prepolymer solutions [2, 37, 47–49]. However, applying the FH theory to $\Pi_{\text{mix}}$ of (dilute) polymer gels does not yield an accurate $\chi$. These results indicate that the semidilute scaling law is superior to the FH theory in terms of predicting the entire quasistatic swelling process of polymer gels.

VI. SCALING LAW FOR EQUILIBRIUM CONCENTRATION BEYOND DE GENNES’ $c^*$ THEOREM

Based on the experimental results, we propose a scaling law that predicts $c_{\text{eq}}$ (i.e., the polymer mass concentration at $\Pi_{\text{tot}} = 0$), while contradicting the predictions made by the $c^*$ theorem. The semidilute scaling law [Eq. (4)] together with Eq. (1) and $\Pi_{\text{tot}} = 0$ yields

\[ n_{\text{eq}} = n_{\text{seg}}^* X_0^{(9\nu-3)/(6\nu+1)}, \]

where $X_0 \equiv G_0/(Kn_{\text{seg}}^* n_0^{1/3} k_B T)$ is a dimensionless parameter determined by the parameters of the as-prepared state ($G_0$ and $n_0$). Figure 5 shows that the equilibrium concentrations ($c_{\text{eq}}$) in Figs. 3 and 4 are governed by Eq. (5) rather than by the $c^*$ theorem. Each gel swells toward the equilibrium swollen state from the as-prepared state at a constant $X_0$ (black arrows). All gels swollen in a pure solvent (filled symbols) with various network conditions of $p$, $c_0$, and $M$ exhibit the scaling law of Eq. (5) with an exponent of 0.506, whereas the $c^*$ theorem fails to predict the $G_0$ and $c_0$ depen-
The present results also clarify the inaccuracy of the interpretation of the experimental results that had affirmed the \( c^* \) theorem. The scaling relation of Young’s modulus \( E = 3G \sim c^{3\nu}/(3\nu - 1) \) in the equilibrium swollen state serves as the experimental evidence of the \( c^* \) theorem. However, this observation is only a necessary condition for the \( c^* \) theorem, not a sufficient condition. This observation is a consequence of the semidilute scaling law \[ E \sim \Pi_{eq} \sim c^{3\nu}/(3\nu - 1) \] in the equilibrium swollen state \( \Pi_{eq} = 0 \), as shown in Fig. 2. A major deficiency of the \( c^* \) theorem is that the network elastic contribution \( \Pi_{el} \), which depends on the as-prepared state, is neglected in determining the equilibrium concentrations of the polymer gels, assuming complete disinterpenetration of the subchains in a swollen network. By contrast, Eq. (5) includes the elastic contribution, as follows: \( \Pi_{el} = -G_0 (c/c_0)^{1/3} \). This can be used to predict the equilibrium concentrations of polymer gels in a pure solvent as the scaling law of the one-parameter \( X_0 \). Our results reveal the scaling law governing \( c_{eq} \) by (i) assuming the semidilute scaling law, rather than the FH mean-field theory, governs \( \Pi_{mix} \); (ii) changing the definition of the polymer mass concentration to extend the universality of the semidilute scaling law to higher concentrations; and (iii) using experimentally measured \( G_0 \) in the as-prepared state for determining the network elastic contributions \( \Pi_{el} \) of the swollen polymer gels, considering the negative energetic elasticity [52–55].

![Graph](image)

**FIG. 5.** Semidilute scaling law (black solid line) for determining the equilibrium concentrations [Eq. (5)]. The open circles are the polymer mass concentrations of polymer gels at the as-prepared state \( (Q = 1) \). The dimensionless parameter \( X_0 \equiv G_0/(K_n^{*2/3}n_01/3k_BT) \) at the as-prepared state determines the equilibrium concentrations \( c_{eq} \) (filled circles) of polymer gels in a pure solvent \( (\Pi_{ext} = 0) \) with \( n_{seg}^* = 3.80 \times 10^28 \text{ m}^{-3} \).

The experimental data are the same as those in Figs. 3 and 4. De Gennes’ \( c^* \) theorem predicts that \( c_{eq} \) is constant (gray dashed lines) for each \( M \); this fails to explain the dependence of \( c_{eq} \) on the as-prepared states \( (c_0 \) and \( G_0) \). To plot the gray dashed lines, we use \( c_{eq} = 58.5, 34.4, \) and \( 20.3 \text{ g/L} \) for \( M = 10, 20, \) and \( 40 \text{ kg/mol} \), respectively. Here, \( 58.5 \text{ g/L} \) is the overlap concentration \( c^* \) of prepolymer solutions with \( M = 10 \text{ kg/mol} \) [44]. Moreover, \( 34.4 \) and \( 20.3 \text{ g/L} \) is calculated from \( c^* \sim M^{1-3\nu} \) in the polymer solutions.

The scaling law [Eq. (5)] is considered a general law that can be applied not only to the present gel but also to other polymer gels that are electrically neutral binary mixtures in good solvents. Moreover, the semidilute principle, which has been established for electrically neutral gels, is expected to be a firm basis for the prediction of swelling of charged polymer gels such as living organisms. Because Eq. (1) is a sum of \( \Pi_{mix} \) and \( \Pi_{el} \) without any cross-correlations [21, 60–62], the semidilute principle for electrically neutral gels can be extended to charged gels by simply adding an excess pressure term to account for electric charge. Therefore, the semidilute principle facilitates fundamental understanding of polymer gels, and will find broader applications in fields such as life science [22, 63], biomaterials [23, 24], petroleum extraction [64, 65], and cooking [66].
ACKNOWLEDGMENTS

We would like to thank Nobu C. Shirai for the useful comments. This work was supported by the Japan Society for the Promotion of Science (JSPS) through the Grants-in-Aid for Early Career Scientists Grant No. 19K14672 to N.S., Scientific Research (B) Grant No. 22H01187 to N.S., JSPS Research Fellows Grant No. 20224177 to T.Y., and Scientific Research (A) Grant No. 21H04688 to T.S., and Transformative Research Area Grant No. 20H05733 to T.S. This work was also supported by the Japan Science and Technology Agency (JST) CREST Grant No. JPMJCR1992 to T.S.

AUTHOR CONTRIBUTIONS

N.S., T.Y., and T.S. conceived, designed, and discussed the research. N.S. developed the theoretical framework. T.Y. designed and performed the experiments. N.S. and T.Y. analyzed and interpreted the results and wrote the manuscript. T.S. supervised the whole research.

Appendix A: Measured shear modulus at the as-prepared state

Figures 6(a) and (b) show the dependence of $G_0$ on the polymer concentration ($c$) and connectivity ($p$), respectively. In addition, to obtain the results shown in Fig. 2 (samples corresponding to the green and blue filled circles), we measured $G_0 = 40.0$, 67.2, and 92.3 kPa for $c_0 = 200$, 300, and 400 g/L, respectively, with $M = 20$ kg/mol at $p = 1$, and $G_0 = 2.1$ kPa for $c_0 = 120$ g/L with $M = 40$ kg/mol at $p = 0.6$, which is not shown in Fig. 6. For a low $c_0$ or low $p$, swelling experiments cannot be performed, because gels lose their shape and weight owing to their low elasticity.

Appendix B: Equilibrium state in swelling experiments and its verification

We evaluated the polymer mass concentration $c$ at the equilibrium states in the swelling experiments as

$$c = \frac{c_0}{Q + (Q - 1)c_0/\rho_{PEG}}, \quad (B1)$$

where the volume swelling ratio $Q \equiv V/V_0$ is calculated as

$$Q = \frac{W}{W_0} + \left(\frac{W}{W_0} - 1\right)\frac{(\rho_{PEG}/\rho_{water} - 1)c_0}{\rho_{PEG} + c_0}, \quad (B2)$$

using experimentally measured $W_0$ and $W$. Here, $\rho_{PEG} \simeq 1129$ kg/m$^3$ and $\rho_{water} \simeq 1000$ kg/m$^3$ are the polymer (PEG) and solvent densities, respectively. Further, we estimated the amount of polymeric clusters slightly leaked from the gel samples with $p < 1$, to evaluate $c$ of the gels immersed in the solvents with a high accuracy (see Appendix C). Notably, we define the polymer mass concentrations ($c_0$, $c$, and $c_{eq}$) as the prepolymer weight divided by the solvent volume, rather than the solution volume, to extend the universality of the semidilute scaling law [Eq. (4)] to higher concentrations. (Further details are provided in Sec. S1 in the Supplemental Material in Ref. [44].) Similarly, to calculate $\Pi_{mix}$ in the FH mean-field theory given by Eq. (3), we evaluate the polymer volume fraction $\phi$ as

$$\phi = \frac{c_0/\rho_{PEG}}{Q(1 + c_0/\rho_{PEG})}. \quad (B3)$$

FIG. 7. Time courses of swelling ratio in the (a) swelling and (b) deswelling experiments. The sample conditions for (a) and (b) are the same as those for Fig. 3 (blue circles) and Fig. 9 (yellow diamonds), respectively. Horizontal black lines indicate equilibrium swelling ratio. (a) We set $c_{ext} = 0, 40, 80, \text{and } 120$ g/L for the gel samples with $M = 40$ kg/mol for $c_0 = 120$ g/L at $p = 0.6$. For $c_{ext} = 0$ (blue symbols), the three representative experiments agreed with each other. (b) We set $c_{ext} = 40, 80, \text{and } 160$ g/L for the gel samples with $M = 10$ kg/mol for $c_0 = 50$ g/L at $p = 1$. 

FIG. 6. Dependence of shear modulus at the as-prepared state on polymer mass concentration and connectivity. (a) Dependence of $G_0$ on the polymer concentration $c_0 = 10$ – 120 g/L with the molar mass $M = 10$ and 40 kg/mol at $p = 1$. (b) Dependence of $G_0$ on the connectivity $p = 2s = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$, and 1 for the various polymer concentration $c_0 = 40$ – 120 g/L with molar mass $M = 10$ kg/mol.
We ensure that each gel sample reached equilibrium in the swelling experiments, as evidenced by the swelling and deswelling processes of the polymer gels to the equilibrium state illustrated in Figs. 7(a) and (b), respectively. To reach equilibrium (horizontal black lines), approximately one week was required. Here, we determined that the equilibrium was reached when the volume swelling ratio Q remained constant for two or three days. We performed three swelling experiments under the same conditions [blue symbols in Fig. 7(a) for \( c_{\text{ext}} \) = 0] to confirm the reproducibility of the time course of Q.

**Appendix C: Leakage of polymeric clusters from gels fabricated at a low connectivity**

We evaluate the amount of leakage of polymeric clusters from each gel sample fabricated at a connectivity \( p \) such that \( p_{\text{gel}} < p < 1 \) (stoichiometrically imbalanced mixing). Here, \( p_{\text{gel}} \) is the connectivity at gel point. Upon immersing a gel sample (fabricated at \( p \)) in solvents, the unreacted terminal functional groups yield polymeric clusters that are unconnected to the gel network. Thus, the polymer mass of the gel samples decreases from pre-immersion (\( \mathcal{M}_0 \)) to post-immersion (\( \mathcal{M}_0^{\text{im}} \)). The polymer mass concentration at pre-immersion is \( c_0 \equiv \mathcal{M}_0/V_0 \), where \( V_0 \) is the volume of the gel sample. Assuming that the semidilute scaling law [Eq. (4)] holds, we can estimate the polymer mass concentration at post-immersion \( c_0^{\text{im}} \equiv \mathcal{M}_0^{\text{im}}/V_0 \) as

\[
c_0^{\text{im}}(c_0, p) = c_0 \cdot \left[ \frac{\Pi_{\text{mix}}(p)}{\Pi_{\text{mix}}(1)} \right]^{3n-1}, \tag{C1}
\]

where \( \Pi_{\text{mix}}(p) \) is the mixing contribution of the osmotic pressure of the gel sample (\( p_{\text{gel}} < p \leq 1 \)) and \( \Pi_{\text{mix}}(1) \) is that of the as-prepared gel sample fabricated at \( p = 1 \).

| \( p \) (g/L) | 0 | 0.6 | 0.7 | 0.8 | 0.9 | 1 | 20 | 40 | 60 | 80 | 120 | 100 | 120 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| \( \Pi_{\text{mix}} \) (kPa) | 67.4 | 68.9 | 70.1 | 72.2 | 72.3 | 110.5 | 116.1 |
| \( c_0^{\text{im}} \) (g/L) | 97.0 | 97.9 | 98.7 | 99.7 | 100 | 117.4 | 120 |

By using Eq. (C1) and measuring the connectivity (\( p \)) dependence of \( \Pi_{\text{mix}} \) of the gel samples in the as-prepared state, we estimated the amount of leakage of polymeric clusters. Figure 8(a) shows the interpolation of \( c_{\text{ext}} \), which yields \( Q = 1 \) for each gel sample with \( M = 10 \) kg/mol for \( c_0 = 100 \) g/L at \( p = 0.6, 0.7, \ldots, 1.0 \) (gray pentagons). Thus, we determined \( \Pi_{\text{mix}} \) of each as-prepared gel sample as \( \Pi_{\text{mix}} = \Pi_{\text{ext}} + G_0 \). Figure 8(b) shows the connectivity (\( p \)) dependence of \( \Pi_{\text{mix}} \) evaluated using the data in Fig. 8(a). As \( p \) decreases, \( \Pi_{\text{mix}} \) also decreases because of the increase in the amount of leakage of the polymeric clusters (schematic in Fig. 8(b)).

Table II shows \( c_0^{\text{im}} \) of the gel samples in the as-prepared state with \( M = 10 \) kg/mol for \( c_0 = 100 \) g/L and with \( M = 40 \) kg/mol for \( c_0 = 120 \) g/L. The decreasing rate is \( 1 - c_0^{\text{im}}/c_0 \approx 0.025-0.030 \) for these samples at \( p = 0.6 \). The obtained \( c_0^{\text{im}} \) was used in Fig. 2 to evaluate the qua-

**FIG. 8.** Estimated decrease in polymer mass concentration of polymer gels in the as-prepared state due to the leakage of polymeric (PEG) clusters. (a) Volume swelling ratio \( Q \) and (b) \( \Pi_{\text{mix}} \) of gel samples for the connectivity \( p = 2s = 0.6, 0.7, 0.8, 0.9, 1 \) at the equilibrium state in the external polymer (PVP) solutions. The molar mass and mass concentration of the prepolymer solutions were \( M = 10 \) kg/mol and \( c_0 = 100 \) g/L, respectively. (a) By interpolating \( c_{\text{ext}} \) that yields \( Q = 1 \) for each gel sample (gray pentagons), we can determine \( \Pi_{\text{mix}} \) for each as-prepared gel sample, as \( \Pi_{\text{mix}} = \Pi_{\text{ext}} + G_0 \). (b) We evaluated each \( \Pi_{\text{mix}} \) using the data in (a). As \( p \) decreases, \( \Pi_{\text{mix}} \) also decreases owing to the increase in the leakage of the polymeric clusters.

**FIG. 9.** Swelling ratio throughout the quasistatic deswelling process. We measured \( Q \) by gradually tuning \( \Pi_{\text{ext}} \). The yellow diamonds are the experimental results with \( M = 10 \) kg/mol for \( c_0 = 50 \) g/L at \( p = 1 \). The black solid and dashed curves are the predictions using the FH theory [Eq. (G2)] with \( \chi = 0.426 \) [30] and \( \nu = 18 \times 10^{-6} \text{m}^2/\text{mol} \) and the semidilute scaling law [Eq. (G1) with \( n_{\text{Hg}} = 3.80 \times 10^{28} \text{m}^{-3} \) and \( \nu = 0.588 \)], respectively. In these predictions, we use the polymer concentration \( c_0 \) and experimentally measured shear modulus \( G_0 \) at the as-prepared state (\( Q = 1 \)).
sistic swelling process (blue circles) and various connectivities (light blue circles). We also used the evaluated \( c_{0}^1 \) to predict \( Q \) and \( c_{eq} \) in Figs 3, 4, and 5.

Appendix D: Deswelling experiments

In Fig 9, we demonstrate that the semidilute scaling law, rather than FH mean-field theory, accurately predicts the volume swelling ratio \( Q = V/V_0 \) in the quasistatic deswelling process. Although polymer gels generally swell because \( \Pi_{\text{tot}} = \Pi_{\text{mix}} + \Pi_{\text{el}} > 0 \) in the as-prepared state, we can quasistatically deswell the polymer gels by gradually increasing \( \Pi_{\text{ext}} \) from the as-prepared state via osmotic deswelling \([35, 36]\). For the quasistatic deswelling process (yellow arrow), the semidilute scaling law accurately predicts the experimental result \( Q \) under the present experimental conditions \( Q > 0.4 \) and \( c < 120 \text{ g/L} \), whereas the FH mean-field theory fails to predict \( Q \) around \( Q = 1 \). This result supports the superiority of the semidilute scaling law over the FH mean-field theory for \( \Pi_{\text{mix}} \) of polymer gels. However, we note that there is a limitation of the semidilute scaling law for \( \Pi_{\text{mix}} \) in the quasistatic deswelling process because polymer gels will be beyond the semidilute regime at a significantly lower \( Q \).

Appendix E: Comparison of osmotic pressure of polymer gels and prepolymer solutions

To evaluate the consistency of \( n_{\text{seg}}^* \) in Eq. (4), we experimentally compared the polymer concentration \( c \) dependence of \( \Pi_{\text{mix}} \) in Fig. 2 with that of the unreacted prepolymer solutions \( (p = 0) \) \([44]\). Figure 10 demonstrates that \( \Pi_{\text{mix}} \) of the polymer gels exhibits the semidilute scaling law \( [\text{Eq. (4)}] \) with an exponent of \( 3\nu/3\nu - 1 \approx 2.31 \). By contrast, the prepolymer solutions obey the universal osmotic equation of state (green dashed curves) \([2, 37, 47–49]\), because prepolymers have finite molar mass and in the dilute regime \( (c < c^*) \) for a low \( c \). Notably, for a high \( c \), \( \Pi_{\text{mix}} \) of prepolymer solutions (green dashed curves) is asymptotic to the semidilute scaling law of polymer gels (black solid line). The \( \Pi_{\text{mix}} \) of polymer gels is approximately identical to that of prepolymer solutions in the semidilute regime \( (c \gg c^*) \). Thus, the semidilute scaling law \( [\text{Eq. (4)}] \) for polymer gels is nothing but that for prepolymer solutions. Based on this result, we can determine \( n_{\text{seg}}^* \) in Eq. (4) by measuring the osmotic equation of state of the prepolymer solutions.
FIG. 12. Decrease in $\Pi_{\text{mix}}$ and $|\Pi_{\text{el}}| = G_0(c/c_0)^{1/3}$ (red curve) associated with swelling. We obtained $\Pi_{\text{mix}}$ under the FH mean-field theory (black dashed curve) and semidilute scaling law (black solid curve) from Eqs. (3) and (4), respectively. Here, we used $c$ and $\phi$ obtained from Eqs. (B1) and (B3). We set the as-prepared conditions of $c_0$ and $G_0$ identical to those for the blue circles in Fig. 3. The FH interaction parameter $\chi \approx 0.439$ was adjusted at the as-prepared state ($Q = 1$), which is the constant value during swelling. The intersection points (black filled and unfilled circles) of $\Pi_{\text{mix}}$ and $|\Pi_{\text{el}}|$ indicate the predictions of $Q$ at the equilibrium swollen state in a pure solvent ($\Pi_{\text{tot}} = 0$).

Appendix G: Comparison of the two equilibrium swelling equations

We theoretically compare two equations [Eq. (1)] using the FH mean-field theory [Eq. (3)] and semidilute scaling law [Eq. (4)] for $\Pi_{\text{mix}}$, to show that a small difference in $\Pi_{\text{mix}}$ leads to a large difference in predicting the equilibrium volume swelling ratio $Q_{\text{eq}}$ in the equilibrium swollen state. We obtain two equilibrium equations with a certain $\Pi_{\text{ext}}$ as follows:

$$nk_BTK\left(\frac{n}{n_{\text{seg}}^*}\right)^{1/3} - G_0\left(\frac{c}{c_0}\right)^{1/3} = \Pi_{\text{ext}}, \quad (G1)$$

using the semidilute scaling law for $\Pi_{\text{mix}}$, where $K = 1.1$ and $n = cN_A/M_{\text{seg}}$ with $M_{\text{seg}} = 44 \times 10^{-3}$ kg/mol for the ethylene glycol unit, and

$$-\frac{kT}{v}\left[\phi + \ln(1 - \phi) + \chi\phi^2\right] - G_0\left(\frac{c}{c_0}\right)^{1/3} = \Pi_{\text{ext}}, \quad (G2)$$

using the FH theory for $\Pi_{\text{mix}}$, where $v = 18 \times 10^{-6}$ m$^3$/mol for aqueous solvents. In equations (G1) and (G2), the volume swelling ratio $Q$ can be predicted using the experimentally measured $G_0$ and Eqs. (B2), (B1) and (B3) for $Q$, $c$ and $\phi$.

Figure 12 shows the typical change in $\Pi_{\text{mix}}$ under the Flory–Huggins (FH) mean-field theory (black dashed curve), $\Pi_{\text{mix}}$ under the semidilute scaling law (black solid curve), and $|\Pi_{\text{el}}| = G_0(c/c_0)^{1/3}$ (red solid curve) throughout the swelling process. As $Q$ increases, $\Pi_{\text{mix}}$ of the FH mean-field theory becomes larger than that of the semidilute scaling law. The intersection points of $\Pi_{\text{mix}}$ and $|\Pi_{\text{el}}|$ indicate the prediction of $Q$ under the equilibrium swollen state in a pure solvent ($\Pi_{\text{tot}} = 0$). The FH mean-field theory predicts higher $Q$ than the semidilute scaling law.

Appendix F: Semidilute scaling law for $\Pi_{\text{mix}}$ in previous studies

Figure 11 shows the polymer mass concentration dependence of $\Pi_{\text{mix}}$ in this study (gray open circles) and previous studies (filled symbols) [9, 13–15, 17] and demonstrates that the semidilute scaling law [Eq. (4)] is universal for a large variety of chemically different polymer networks and solvents within the experimental error. Here, we used $G = E/3$ measured at the equilibrium swollen state to evaluate $\Pi_{\text{mix}} = G$ at the equilibrium concentration $c_{\text{eq}}$ in previous studies. Notably, we define $c_{\text{eq}}$ of previous studies as the prepolymer weight divided by the solvent volume, as used in this study. The main panel in Figure 11 demonstrates the universality of the semidilute scaling law by the horizontal shift of the polymer mass concentration ($c$ to $\tilde{c} = (A'/A)^{(3\nu-1)/3\nu} c$). Here, we denote $\Pi_{\text{mix}} = A\tilde{c}^{3\nu/(3\nu-1)}$ for this study and $\Pi_{\text{mix}} = A'\tilde{c}^{3\nu/(3\nu-1)}$ for each previous study, as shown in the inset in Figure 11.
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