

Universal Equation of State of Osmotic Pressure for Polymer Gels

Takashi Yasuda¹, Naoyuki Sakumichi¹, and Takamasa Sakai¹

¹Department of Bioengineering, The University of Tokyo, Bunkyo-ku, Japan

ABSTRACT

Polymer gels are soft solids consisting of three-dimensional polymer networks with predominantly liquid content. The polymer networks is dissolved in the solvents and thus have the osmotic pressure while being a viscoelastic solid. Examining the precisely controlled polymer gels with various network structures, we successfully decompose the elastic contribution to the osmotic pressure and experimentally reveal that the osmotic pressure throughout the gelation process is described by the universal osmotic equation of state of polymer solutions. Furthermore, we find that the semidilute scaling law of polymer solutions, including the critical exponent of self-avoiding walks, universally governs polymer gels. Our findings demonstrate that the semidilute scaling law is a fundamental principle for governing the osmotic pressure of polymer gels.

INTRODUCTION

The osmotic pressure is a kind of colligative property that exhibits a law independent of the type of substance. For dilute solutions, it is widely known that the osmotic pressure obeys the van 't Hoff law, which is analogous to the ideal gas law. However, because of the significant excluded volume of polymer chains, the osmotic pressure in polymer gels is not described through the van 't Hoff law^{1,2}.

On the other hand, for solutions of linear polymer chains, the elaborate studies in the 1970-80s^{3,4} have revealed that the osmotic pressure for the dilute to semidilute regime in good solvents is described by the universal equation of state (EOS): $\hat{\Pi} = f_{\Pi}(\hat{c})$. Here, $\hat{\Pi} \equiv \Pi M/(cRT)$ is the reduced osmotic pressure and $\hat{c} \equiv c/c^*$ is the reduced polymer mass concentration c normalized by overlap concentration $c^* \equiv 1/(A_2M)$, where M is the molar mass, R is the gas constant, T is the absolute temperature, and A_2 is the second virial coefficient. In the dilute regime ($0 \leq \hat{c} < 1$), each molecular chain is isolated to sufficiently describe the universal EOS through virial expansion:

$$\hat{\Pi} = 1 + \hat{c} + \gamma \hat{c}^2 + \cdots, \quad (1)$$

where $\gamma \approx 0.25$ is the dimensionless virial ratio⁵. In the semidilute regime ($\hat{c} > 1$), the molecular chains interpenetrate, and the universal EOS is asymptotic to the semidilute scaling law⁶:

$$\hat{\Pi} = K \hat{c}^{\frac{1}{3\nu-1}}, \quad (2)$$

where $K \approx 1.1$ is the universal constant and $1/(3\nu - 1) \approx 1.31$ because of the excluded volume parameter $\nu \approx 0.588$ for good solvents⁵. Here, ν is also known as the universal critical exponent of the self-avoiding-walk universality class⁷.

In this study, we experimentally reveal that the osmotic pressure throughout the gelation process (i.e., polymer chains in solutions are crosslinked to form the infinite polymer networks) is described by the universal EOS of polymer solutions¹. Furthermore, we find that the semidilute scaling law of polymer solutions [Eq. 2], including the critical exponent of self-avoiding walks, universally governs polymer gels^{1,2}.

RESULTS AND ANALYSIS

To investigate the governing law of osmotic pressure in polymer gels, we experimentally measured the osmotic pressure throughout the gelation process via membrane osmometry¹. Here, we statically reproduced the gelation process to measure the osmotic pressure by using *AB*-type polymerization system⁸. Moreover, we decompose the elastic contribution Π_{el} to the measured osmotic pressure Π to evaluate the mixing contribution $\Pi_{mix} = \Pi - \Pi_{el}$ in polymer gels. Here, we measured the shear modulus G_0 of polymer gels at the as-prepared state via dynamic viscoelasticity measurement to evaluate the elastic contribution $\Pi_{el} = -G_0$.

Figure 1(a) shows Π , Π_{el} and Π_{mix} during the gelation process. Unlike the sol state ($0 \leq p < p_{gel}$, where p is the network connectivity and p_{gel} is the gelation point), the gel state ($p_{gel} < p \leq 1$) has elastic contributions Π_{el} to the osmotic pressure Π . As the connectivity p increases at a constant c , Π in the sol state decreases because of the increase of M (blue solid line). After gelation, Π_{mix} reaches a constant (blue solid line); polymer gels are always in a semidilute regime with an infinite M . On the other hand, Π decreases (blue dotted line) and Π_{el} increases (red solid curve) as p increases in gel state.

We demonstrate that the decrease of Π in the sol state and the constant Π_{mix} in gel state in **Fig. 1(a)** is described through the universal EOS of polymer solutions^{3,4} and the semidilute scaling law⁵ [Eq. 2], respectively. To change the state variable ($c \rightarrow \hat{c}$ and $\Pi \rightarrow \hat{\Pi}$), we evaluate M and c^* for each p in the sol state, using the square root plot⁵ $\sqrt{\Pi/c} \simeq \sqrt{RT/M[1 + c/(2c^*)]}$ for small c/c^* . The obtained M and c values are consistent with the scaling prediction of $c^* \sim M^{1-3\nu}$.

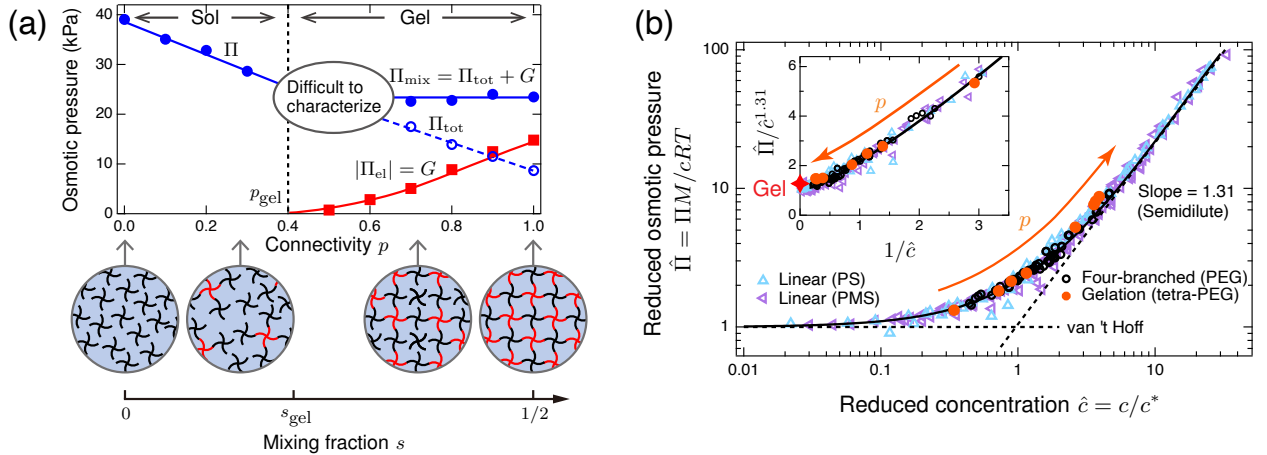


Figure 1: (a) Osmotic pressure and (b) universal equation of state during gelation process¹.

Figure 1(b) shows the universal EOS (black solid curve) in the linear polymer solutions^{3,4} (light blue and purple open triangles), in the prepolymer solutions ($p = 0$) (black open circles), and during the gelation process in the sol state (orange filled circles). With the increase of M and decrease of c^* as p increases, the osmotic pressure during gelation process in the sol state is described by the same universal laws as for the polymer solutions.

On the other hand, in the gel state, $\hat{\Pi} \rightarrow \infty$ and $\hat{c} \rightarrow \infty$ because $M \rightarrow \infty$ and $c^* \rightarrow 0$. However, we can consider $\hat{\Pi}_{\text{mix}} \hat{c}^{1/(1-3\nu)}$ for the gel state, using the obtained scaling relation $c^* \sim M^{1-3\nu}$ for the sol state. The inset in **Fig. 1(b)** demonstrate that $\hat{\Pi} \hat{c}^{1/(1-3\nu)}$ during the gelation process in the sol state (orange filled circles) and in the gel state (red stars) converge to the universal value $K \approx 1.1$, which is independent of M , c , and p . Thus, Π_{mix} of the polymer gels is universally governed by the semidilute scaling law of polymer solutions [Eq. 2]. Therefore, the osmotic pressure throughout the gelation process is described by the universal EOS of polymer solutions.

REFERENCES

1. Yasuda T., Sakumichi N., Chung U., and Sakai T. Universal equation of state describes osmotic pressure throughout gelation process. *Phys. Rev. Lett.* **2020**, 125, 267801.
2. Sakumichi N., Yasuda T., and Sakai T. Semidilute principle for gels. arXiv:2210.15275.
3. Noda I., Kato N., Kitano T., and Nagasawa M. Thermodynamic properties of moderately concentrated solutions of linear polymers. *Macromolecules* **1981**, 14, 668-676.
4. Higo Y., Ueno N., and Noda I. Osmotic pressure of semidilute solutions of branched polymers. *Polym. J.* **1983**, 15, 367-375.
5. Flory P.J. *Principle of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
6. Des Cloizeaux J. The Lagrangian theory of polymer solutions at intermediate concentrations. *J. Phys. (Paris)* **1975**, 36, 281-291.
7. Pelissetto A., and Vicari E. Critical phenomena and renormalization-group theory. *Phys. Rep.* **2002**, 368, 549-727.
8. Sakai T., Matsunaga Y., Yamamoto Y., Ito C., Yoshida R., Suzuki S., Sasaki N., Shibayama M., and Chung U. Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. *Macromolecules* **2008**, 41, 5379-5384.