

Universal Equation of State Describes Osmotic Pressure throughout Gelation Process

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The equation of state of the osmotic pressure for linear-polymer solutions in good solvents is universally described by a scaling function. We experimentally measure the osmotic pressure of the gelation process via osmotic deswelling. We find that the same scaling function for linear-polymer solutions also describes the osmotic pressure throughout the gelation process involving both the sol and gel states. Furthermore, we reveal that the osmotic pressure of polymer gels is universally governed by the semidilute scaling law of linear-polymer solutions.

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Flexible linear polymers in good solvents provide not only the basis of polymer physics [1,2], but also a remarkable example of the notion of universality of critical phenomena in statistical physics [2,3]. Their macroscopic collective properties are independent of the microscopic details of the system and are described by a small number of parameters, because of the great length of polymer chains. Such systems belong to the $O(n)$ -symmetric universality classes ($n = 1, 2, 3$ corresponding to the Ising, XY , and Heisenberg classes, respectively) found in many systems, ranging from those of soft and hard condensed-matter physics to high-energy physics [4]. The above linear-polymer solutions correspond to the limit of $n \rightarrow 0$ (self-avoiding walks) in three dimensions [2,4], for which the critical exponent (the excluded volume parameter) $\nu \simeq 0.588$ can be computed using three independent methods: Monte Carlo simulations [5,6], the ϵ -expansion method [7], and the conformal bootstrap method [8,9]. Furthermore, not only the critical exponents but also the asymptotic scaling functions themselves can be experimentally measured, such as the osmotic pressure [10,11] and the correlation lengths of density fluctuations [12].

We focus on the equation of state (EOS) of osmotic pressure for (electrically neutral) flexible linear polymers in good solvents, which is universally described by the following scaling function [10,11,13–16]:

$$\hat{\Pi} = f(\hat{c}), \quad (1)$$

where $\hat{\Pi} \equiv \Pi M / (cRT)$ is the reduced osmotic pressure, and $\hat{c} \equiv c/c^*$ is the reduced polymer concentration normalized by the overlap concentration $c^* \equiv 1/(A_2M)$. Here, M , R , T , and A_2 are the molar mass, gas constant, absolute temperature, and the second virial coefficient, respectively. The above definition of c^* is proportional [17] to the conventional definition of the overlap concentration $c_g^* \equiv 3M/(4\pi N_A R_g^3)$, at which the polymer chains begin to overlap to fill the space. Here, N_A

and R_g are the Avogadro constant and the gyration radius of the polymer chain, respectively.

For branched polymer solutions, it was reported that each EOS of regular star polymers with up to 18 arms exhibited only minor differences from the universal EOS (1) of linear polymers [11,17–19]. Here, $\hat{c} \equiv c/c^*$ is the only universal scaling parameter (up to multiplication by a constant) [17]. Hence, c/c_g^* is not a universal scaling

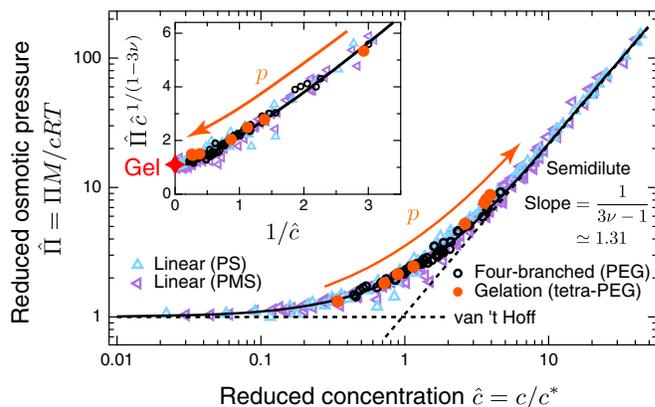


FIG. 1. Universal EOS of osmotic pressure for polymer solutions and gels in a good solvent. Main image shows the \hat{c} dependence of $\hat{\Pi}$ in a log-log plot. Inset: the \hat{c}^{-1} dependence of $\hat{\Pi} \hat{c}^{1/(1-3\nu)}$. The triangles represent two kinds of linear polymers [poly(styrene) (PS), where $M = 51\text{--}1900$ kg/mol [11], and poly(α -methylstyrene) (PMS), where $M = 70.8\text{--}1820$ kg/mol [10]] in toluene solutions. The triangles converge to the universal EOS (1) (black solid curve), which is asymptotic to the van't Hoff law ($\hat{\Pi} = 1$) as $\hat{c} \rightarrow 0$ and to the scaling law in Eq. (3) as $\hat{c} \rightarrow \infty$ (black dotted lines). The black circles represent the four-branched polymer [poly(ethylene glycol) (PEG)] solutions of $M = 10$ and 40 kg/mol. The orange-filled circles represent the sol samples that emulate the gelation process with varying degrees of connectivity ($p = 0, 0.1, \dots, 0.5$) at a constant concentration ($c = 20$ g/L). The red star in the inset corresponds to the gel samples.

parameter because $c_g^*/c^* = 3\sqrt{\pi}\Psi^*$ includes the interpenetration factor Ψ^* , which is nonuniversal for a number of arms (e.g., $\Psi^* \simeq 0.24$ and 0.44 for linear and four-branched polymer solutions, respectively [20,21]). Figure 1 demonstrates that the different kinds of linear-polymer solutions and four-branched polymer solutions converge to a universal EOS (1). In the dilute regime ($0 \leq \hat{c} < 1$), each molecular chain is isolated to sufficiently describe the universal EOS (1) through virial expansion [1],

$$\hat{\Pi} = f(\hat{c}) = 1 + \hat{c} + \gamma\hat{c}^2 + \dots \quad (\text{for } 0 \leq \hat{c} < 1), \quad (2)$$

where $\gamma \simeq 0.25$ is the dimensionless virial ratio [1,10]. In the semidilute regime ($\hat{c} > 1$), the molecular chains interpenetrate, and the universal EOS (1) is asymptotic to the semidilute scaling law [2,13]

$$\hat{\Pi} = f(\hat{c}) \simeq K\hat{c}^{(1/3\nu-1)} \quad (\text{for } \hat{c} \gg 1), \quad (3)$$

where $K \simeq 1.1$ and $1/(3\nu - 1) \simeq 1.31$ because $\nu \simeq 0.588$.

In this Letter, we experimentally investigate the osmotic pressure of polymer gels throughout the gelation process, which involves both the sol and gel states. We measured the osmotic pressure via osmotic deswelling in external polymer solutions [22–24]. Our findings are summarized in Fig. 1; the universal EOS (1) describes the osmotic pressure of both the sol (orange-filled circles) and gel (red star) states with only minor variations, although each system during the gelation process comprises highly branched polymer networks. When gelation proceeds at a constant concentration c , the average molar mass M increases and c^* decreases. Thus, both $\hat{\Pi}$ and \hat{c} continuously increase along the universal EOS (1) in the sol state. After the gelation (i.e., the sol-gel transition), because polymer gels correspond to $M \rightarrow \infty$ and $c^* \rightarrow 0$, both $\hat{\Pi}$ and \hat{c} diverge to infinity in the gel state. According to the semidilute scaling law described by Eq. (3), $\hat{\Pi} \hat{c}^{1/(1-3\nu)}$ remains constant in the gel state (red star in the inset of Fig. 1). Our findings, which elucidate the universal laws governing osmotic pressure, are not only conceptually important for statistical physics, but also practically useful for soft-matter physics. These results are essential for the applications of polymer solutions and polymer gels, which can swell by imbibing solvents.

To statically emulate the gelation process, we nonstoichiometrically tuned the mixing fractions s ($0 \leq s \leq 1/2$) of two types of precursor solutions in an AB -type polymerization system (schematics in Fig. 2). Here, s is the molar fraction of the minor precursors to all precursors. We define the connectivity p ($0 \leq p \leq 1$) as the fraction of reacted terminal functional groups, assuming the reaction is completed. By tuning s in accordance with $p = 2s$ [25,26], we can obtain a desired p . Before gelation ($0 \leq p < p_{\text{gel}}$), polymer chains crosslink to form a polydisperse mixture of highly branched polymers with increases in the average

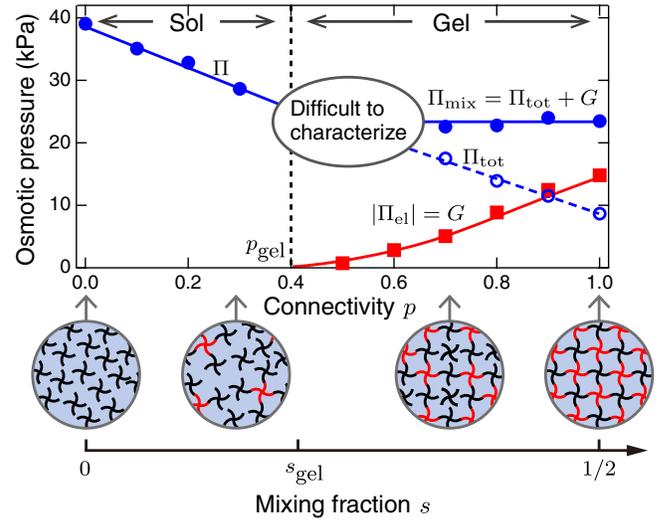


FIG. 2. Osmotic pressure of the samples emulating gelation process. The samples were prepared at a constant polymer concentration ($c = 60$ g/L) and molar mass of precursors ($M = 10$ kg/mol). By measuring Π_{tot} and G , we obtained $\Pi_{\text{mix}} = \Pi_{\text{tot}} + G$ in the gel state. As the connectivity p increases, Π and Π_{tot} decrease, and Π_{mix} remains constant (blue curves). After gelation ($p_{\text{gel}} \leq p \leq 1$), the elasticity (red curve) increases. Here, p ($0 \leq p \leq 1$) is controlled by nonstoichiometrically mixing two types of precursors in an AB -type polymerization system. Gel samples with a low connectivity ($p_{\text{gel}} \leq p < 0.7$) were difficult to characterize, because of the outflow of small polymer clusters.

molar mass M . After gelation ($p_{\text{gel}} \leq p \leq 1$), these polymer networks cross-link to complete the reaction as the elasticity increases.

Based on our findings displayed in Fig. 1, we illustrate the “nonreduced” osmotic pressure Π during the gelation process in Fig. 2. Unlike the sol state, the gel state has elastic contributions to the total swelling pressure (Π_{tot}). According to Flory and Rehner [27], Π_{tot} consists of two separate contributions as $\Pi_{\text{tot}} = \Pi_{\text{mix}} + \Pi_{\text{el}}$, where Π_{mix} and Π_{el} are the mixing and elastic contributions, respectively. We regard Π_{mix} as the osmotic pressure in the gel state, because Π_{mix} corresponds to the osmotic pressure in the sol state Π . As the connectivity p increases at a constant concentration c , Π in the sol state decreases because the chemical reaction decreases the number density of the molecules. After gelation, Π_{mix} reaches a constant; polymer gels are always in a semidilute regime with an infinite molar mass.

Materials and methods.—For the model system of AB -type polymerization in gelation, we used a tetra-arm poly (ethylene glycol) (tetra-PEG) gel that is synthesized by the AB -type cross-end coupling of two tetra-PEG units of equal size [28]. Each end of the tetra-PEG is modified with mutually reactive maleimide (tetra-PEG MA) and thiol (tetra-PEG SH). We dissolved tetra-PEG MA and tetra-PEG SH (Nippon Oil & Fat Corporation) in a phosphate-citrate

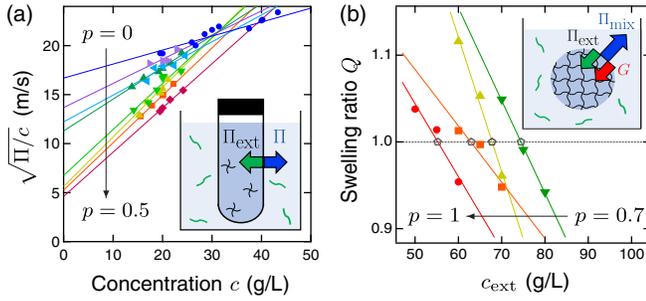


FIG. 3. Osmotic deswelling in external polymer solutions, used to measure Π and Π_{mix} , in (a) sol and (b) gel samples, respectively. For each plot, the precursors are $M = 10$ kg/mol. Each line is the least-squares fit to the data for each p . (a) Square-root plots of Π of sol samples on $c_0 = 20$ g/L for $p = 0, 0.1, 0.2, 0.25, 0.3, 0.35, 0.4,$ and 0.5 . We immersed samples with a microdialyzer in external polymer (PVP) solutions. We can determine Π , because $\Pi = \Pi_{\text{ext}}$ at equilibrium. (b) Equilibrium swelling ratio Q of gel samples on $c_0 = 60$ g/L for $p = 0.7, 0.8, 0.9,$ and 1 in the external polymer (PVP) solutions. We directly immersed samples in external solutions of various concentrations c_{ext} . We can determine Π_{mix} , because $\Pi_{\text{mix}} = \Pi_{\text{ext}} + G$ at equilibrium.

buffer with an ionic strength and pH of 200 mM and 3.8, respectively. For gelation, we mixed these solutions with equal molar masses M and equal concentrations c in various mixing fractions s . We kept each sample in an enclosed space to maintain humid conditions at room temperature ($T \simeq 298$ K) to allow completion of the reaction.

We prepared the four-branched polymer (precursor) solutions ($p = 0$) by dissolving tetra-PEG MA with molar masses of $M = 10$ and 40 kg/mol and initial concentrations $c_0 = 20$ – 120 g/L. Herein, we define the polymer concentration (c_0 and c) as the precursor weight divided by the solvent volume, rather than by the solution volume, to extend the universality of the EOS (1) to higher concentrations (see Supplemental Material, Sec. S1 [29]). We prepared the sol and gel samples that emulate the gelation process by dissolving precursors with $M = 10$ kg/mol. For $c_0 = 20$ g/L, we set $p = 2s = 0.1, 0.2, 0.25, 0.3, 0.35, 0.4,$ and 0.5 (sol samples). For $c_0 = 40, 60, 80,$ and 120 g/L, we set $p = 2s = 0.1, 0.2,$ and 0.3 (sol samples) and $0.7, 0.8, 0.9,$ and 1 (gel samples). Section S2 of the Supplemental Material describes the determination of these measurement ranges [29].

We measured the osmotic pressures in the sol samples Π , using controlled aqueous poly(vinylpyrrolidone) (PVP, K90, Sigma Aldrich) solutions, whose concentration dependence of osmotic pressure Π_{ext} was measured by Vink [31] (Supplemental Material, Sec. S3 [29]). As shown in the schematic in Fig. 3(a), each solution sample was placed in a microdialyzer (MD300, Scienova) that had a semipermeable membrane with a mesh size of 3.5 kDa. We immersed each dialyzer in an aqueous polymer (PVP) solution at a certain concentration c_{ext} with stirring.

Subsequently, each system achieved equilibrium at $\Pi = \Pi_{\text{ext}}$. (The achievement of swelling equilibrium was assured. See Supplemental Material, Sec. S4 [29].) At that time, each solution sample was changed in weight and concentration from its initial to equilibrium states, as represented by $W_0 \rightarrow W$ and $c_0 \rightarrow c$, respectively. Assuming a constant weight density and small deformation for the sample, we calculate c as $c = c_0/Q$, where $Q = W/W_0$ is the equilibrium swelling ratio. In examining the gelation process (e.g., Fig. 2), we evaluated Π of the “as-prepared” (i.e., $Q = 1$) sol samples at equal concentrations $c = c_0$ with various values of p . Measuring Q for various c_{ext} and interpolating the c_{ext} dependence of Q as a linear function, we determined c_{ext} and Π_{ext} such that each sol sample maintained its weight ($Q = 1$) and concentration ($c = c_0$).

To evaluate the parameters M and c^* from $\Pi = \Pi(c)$, which were measured at each p , we used square-root plots [1], as shown in Fig. 3(a). From the virial expansion (2), we have $\hat{\Pi} = [1 + \hat{c}/2 + (\gamma - 1/4)\hat{c}^2/2]^2 + O(\hat{c}^3)$. Together with $\gamma \simeq 1/4$ (Supplemental Material, Sec. S5 [29]) for certain few-branched polymer solutions, we have $\sqrt{\Pi}/c \simeq \sqrt{RT/M}[1 + c/(2c^*)]$ for small c/c^* . Thus, the intercept and slope of each fitting line in Fig. 3(a) give M and c^* , respectively, for each p . The obtained M and c^* values are consistent with the scaling prediction of $c^* \sim M^{1-3\nu}$ (Supplemental Material, Sec. S6 [29]).

We measured the osmotic pressure in the as-prepared gel samples Π_{mix} via osmotic deswelling. As shown in the schematic in Fig. 3(b), we immersed each gel sample directly in the external aqueous polymer (PVP) solutions of various concentrations c_{ext} , because the surfaces of the gels function as semipermeable membranes. Subsequently, each gel sample swelled or deswelled toward equilibrium at $\Pi_{\text{mix}} + \Pi_{\text{el}} = \Pi_{\text{ext}}$, changing its weight and concentration from the as-prepared to equilibrium states as represented by $W_0 \rightarrow W$ and $c_0 \rightarrow c$, respectively. The equilibrium swelling ratio $Q = W/W_0$ was measured and interpolated as a linear function of c_{ext} for each gel sample [examples are given in Fig. 3(b)]. Using the c_{ext} dependence of Q , we evaluated c_{ext} and Π_{ext} such that each gel sample maintained its weight ($Q = 1$) and concentration ($c = c_0$). (This method is the same as the above method to determine Π of the as-prepared sol samples.) Assuming $\Pi_{\text{el}} = -G$ [32], we evaluated $\Pi_{\text{mix}} = \Pi_{\text{ext}} + G$ for each as-prepared gel sample, where G is the shear modulus as measured by rheometry (Supplemental Material, Sec. S7 [29]).

Results and analysis.—The main panel in Fig. 4(a) shows the c dependence of the osmotic pressure in both the unreacted four-branched polymer solutions ($p = 0$) and the reaction-completed polymer gels ($p = 1$). The experimental results for the former and latter agree with the universal EOS (1) for linear-polymer solutions and with the semidilute scaling law $\Pi \propto c^{3\nu/(3\nu-1)}$, respectively, in

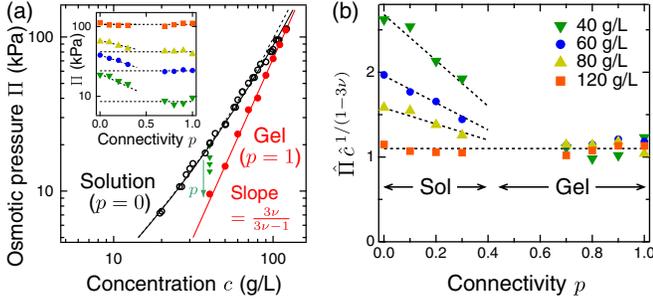


FIG. 4. Osmotic pressure during gelation process. The molar mass of precursors is $M = 10$ kg/mol, corresponding to the overlap concentration $c^* \simeq 58$ g/L at $p = 0$. (a) Osmotic pressure in the unreacted four-branched polymer solutions (black circles) and in the reaction-completed polymer gels (red-filled circles). The former and latter agree with the universal EOS (1) (black curve) and with the semidilute scaling law $\Pi \propto c^{3\nu/(3\nu-1)}$ (red line), respectively. Here, $3\nu/(3\nu-1) \simeq 2.31$ because $\nu \simeq 0.588$. The black dotted curve is the virial expansion (2) up to the third-order terms. As p increases (green triangles), Π decreases in the sol state ($0 \leq p < p_{\text{gel}}$) and remains constant in the gel state ($p_{\text{gel}} < p \leq 1$). Inset: osmotic pressure during the gelation process at a constant polymer concentration $c = c_0 = 40, 60, 80,$ and 120 g/L. The green triangles ($c = 40$ g/L) are the same as those in the main panel. The blue circles ($c = 60$ g/L) are used in Fig. 2. (b) Connectivity (p) dependence of $\hat{\Pi} \hat{c}^{1/(1-3\nu)}$. The symbols and data are the same as those in the inset of (a). In the gel state, $\hat{\Pi} \hat{c}^{1/(1-3\nu)}$ converge to the universal value $K \simeq 1.1$, which is independent of p and c .

the wide concentration range c . With an increase in c , Π in the polymer solutions (black curve) is asymptotic to Π_{mix} in the polymer gels (red line). This asymptotic relationship suggests that Π_{mix} of polymer gels is governed by the semidilute scaling law described in Eq. (3) with $K \simeq 1.1$ for polymer solutions.

The inset in Fig. 4(a) shows the p dependence of Π and Π_{mix} throughout the gelation process ($0 \leq p \leq 1$). In the sol state ($0 \leq p < p_{\text{gel}}$), Π decreases as p increases, because the average molar mass M increases. As c increases, the extent of the decrease in the osmotic pressure itself decreases. In particular, for $c = 120$ g/L, Π and Π_{mix} are constant throughout the gelation process ($0 \leq p \leq 1$), because the precursor solution is in the semidilute regime even at $p = 0$. In the gel state ($p_{\text{gel}} < p \leq 1$), Π_{mix} is constant, even when p increases. In general, the osmotic pressure is dependent and independent of the average molar mass in the dilute and semidilute regimes, respectively [2]. Thus, the constant Π_{mix} in the gel state ($p_{\text{gel}} < p \leq 1$) indicates that polymer gels are always in the semidilute regime, because of the infinite molar mass of the polymer networks.

We can interpret Π during the gelation process in the sol state ($0 \leq p < p_{\text{gel}}$) according to the universal EOS (1). By using M and c^* evaluated in Fig. 3(a) at each p , we changed the state variables (from c and Π to \hat{c} and $\hat{\Pi}$), yielding the orange-filled circles in Fig. 1. Remarkably, the

osmotic pressure of the gelation process in the sol state ($p = 0, 0.1, \dots, 0.5$) is described by the universal EOS (1) of polymer solutions, although these systems continue to form multibranching polymer clusters. Considering this finding in tandem with the semidilute scaling law observed in the gel state ($\Pi_{\text{mix}} \propto c^{3\nu/(3\nu-1)}$), it is expected that $\hat{\Pi}_{\text{mix}}$ in the gel state ($p_{\text{gel}} < p \leq 1$) conforms to the semidilute scaling law given by Eq. (3) of linear-polymer solutions [red line in Fig. 4(a)] with $K \simeq 1.1$.

Based on this expectation, we propose a universal EOS of osmotic pressure Π_{mix} for polymer gels as

$$K = \frac{\hat{\Pi}_{\text{mix}}}{\hat{c}^{1/(3\nu-1)}} \equiv \frac{M c^{*1/(3\nu-1)} \Pi_{\text{mix}}}{RT c^{3\nu/(3\nu-1)}}, \quad (4)$$

where $K \simeq 1.1$. We note that $\hat{\Pi}_{\text{mix}} \hat{c}^{1/(1-3\nu)}$ is finite, although both $\hat{c} \equiv c/c^*$ and $\hat{\Pi}_{\text{mix}} \equiv \Pi_{\text{mix}} M / (cRT)$ diverge to infinity, because gels correspond to infinite molar mass $M \rightarrow \infty$ and $c^* \rightarrow 0$. In Fig. 4(b), we demonstrate that $\hat{\Pi}_{\text{mix}} \hat{c}^{1/(1-3\nu)}$ converge to the universal value $K \simeq 1.1$, which is independent of p and c , after gelation ($p_{\text{gel}} \leq p \leq 1$). Therefore, in the inset of Fig. 1, the gel state is positioned at $(1/\hat{c}, \hat{\Pi}_{\text{mix}} \hat{c}^{1/(1-3\nu)}) \simeq (0, 1.1)$ (red star). We obtained Fig. 4(b) by setting a constant value for $M c^{*1/(3\nu-1)}$ and substituting Π and Π_{mix} [shown in the inset of Fig. 4(a)] into Eqs. (3) and (4), respectively. (Further details are given in Sec. S6 of Supplemental Material [29].) This procedure demonstrates that we can determine Π_{mix} for any polymer gel by measuring the nonuniversal parameter $M c^{*1/(3\nu-1)}$.

Concluding remarks.—We experimentally measured the osmotic pressure of polymer gels throughout the gelation process. We find that the universal EOS (1) of osmotic pressure for linear-polymer solutions describes the osmotic pressure throughout the gelation process involving both the sol and gel states (Fig. 1). In the sol state, both $\hat{\Pi}$ and \hat{c} continuously increase according to the universal EOS (1) with an increase in the average molar mass (orange-filled circles in Fig. 1). In the gel state, the osmotic pressure of the polymer gels is universally governed by the semidilute scaling law (4) [red star in Figs. 1 and 4(b)]. Here, both $\hat{\Pi}$ and \hat{c} diverge to infinity, because the gel state corresponds to the average molar mass $M \rightarrow \infty$ and the overlap concentration $c^* \rightarrow 0$. In addition, we have demonstrated that Eq. (4) enables the determination of Π_{mix} for any polymer gel by measuring a nonuniversal parameter $M c^{*1/(3\nu-1)}$.

Our results provide a new system for demonstrating universality in statistical physics because the universal EOS (1) relates to the $O(n)$ -symmetric universal classes [4]. In addition, a universal EOS and universal thermodynamics are of great interest to those studying strongly correlated fermions [33]. Our findings can stimulate research in these fields.

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