

Partitioning law of polymer chains into flexible polymer networks

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The equilibrium partitioning of linear polymer chains into flexible polymer networks is governed by intricate entropic constraints arising from the configurational degrees of freedom of both chains and networks; however, a quantitative understanding remains elusive. Using model hydrogels with precisely defined network structures, we experimentally demonstrate a universal law governing the partitioning of linear polymers into flexible polymer networks. We establish a label-free contactless method to measure the partition ratio, based on the increase in the osmotic pressure induced by the partitioning of the external polymer chains. Moreover, we reveal a universal law in which the partition ratio is determined solely by R_g/l_{cycle} , where R_g is the gyration radius of the polymer chain and $l_{\text{cycle}} \equiv \xi^{-1/3}$ is the characteristic mesh size of the network, defined by the cycle rank ξ , i.e., the number density of elastically effective cycles.

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I. INTRODUCTION

Solute partitioning in polymer gels is governed by complex physical and chemical interactions between solutes and the polymer network. Polymer gels are a unique class of materials in which a solvent-swollen polymer network facilitates solute exchange with the external environment. The equilibrium concentration ratio of the solutes between the gel (ϕ_{int}) and an external solution (ϕ_{ext}), defined as the partition ratio $K \equiv \phi_{\text{int}}/\phi_{\text{ext}}$, depends on the interactions between the solutes and the polymer network [1–14]. Typically, K decreases with increasing solute size, similar to behavior in rigid, static porous media [15–18]. Such size-dependent partitioning plays a critical role in applications ranging from membrane separation and size-exclusion chromatography [19] to regulation of solute distribution in biological systems such as membrane-bound organelles and biomolecular condensates [20,21].

Despite its importance, the microscopic mechanism governing network-dependent variations in K has remained elusive. According to the Nernst distribution law [22,23], which is a fundamental principle in physical chemistry [24], the partition ratio should be concentration-independent in the dilute regime, allowing for the definition of a constant partition ratio K_0 . Descriptions of K_0 often rely on obstacle models such as the Ogston model [1–9]. The Ogston model characterizes the network as a set of rigid rods; however, the rod size

depends on network concentration and does not correspond to the actual fiber radius of polymer chains [3,4]. Moreover, experimentally measured K frequently varies with solute concentrations in gels [5], contradicting the Nernst distribution law, which predicts constant K_0 . A thermodynamic approach [10] based on osmotic equilibrium has also been applied to analyze K ; however, it has not provided a quantitative explanation.

These theoretical inconsistencies reflect the experimental challenges involved in accurate measurements of K . First, polymer gels typically exhibit significant structural and spatial inhomogeneity [25], resulting in nonuniform solute distributions. Second, measurements using fluorescently labeled solutes [3,4,6–9] are susceptible to unintended chemical interactions and molecular aggregation, leading to systematic deviations in the measured values, particularly under conditions far from the ideal dilute regime. Moreover, these factors may interact synergistically, further complicating the accurate determination of partition ratios.

In this article, we develop an unlabeled, contactless method for measuring the partition ratio K to overcome these experimental challenges. Using the physical laws governing osmotic pressure in polymer gels [10,26–28], we establish a scaling relationship between osmotic pressure and total polymer concentration, enabling accurate determination of the partitioned polymer concentration through measurements of the equilibrium swelling ratio [Fig. 1(a)]. Model gel systems formed from star-shaped polymers [29] provide an ideal platform for such measurements [30–33] because they permit precise tuning of the network structure. Here, the use of chemically identical PEG for both the solute and the network eliminates specific interactions (e.g., χ -parameter effects or preferential adsorption), allowing us to isolate the purely geometrical and topological constraints governing partitioning.

We systematically investigate the partitioning behavior of polymer chains in model gels across a broad range of polymer

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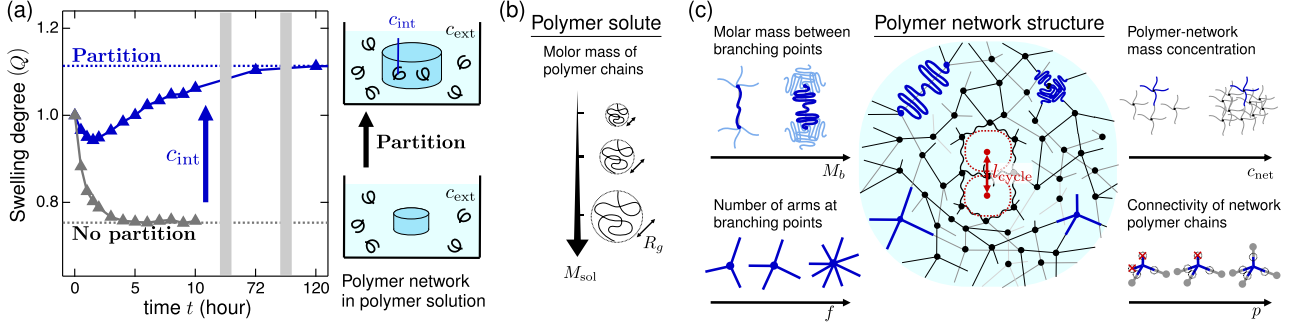


FIG. 1. Evaluation of partition ratio K of polymer chains into polymer gels with controlled network structures. (a) Time evolution of the swelling ratio in polymer gels immersed in external polymer solutions with concentration c_{ext} , induced by increasing the internal concentration of partitioned polymer chains c_{int} . When external polymer chains do not partition into the gel ($c_{\text{int}} \approx 0$), the gel deswells to reach equilibrium (gray dashed line). In contrast, when external polymer chains partition into the gel ($c_{\text{int}} > 0$), the osmotic pressure increases with c_{int} [Eq. (2)], causing the gel to swell further until reaching equilibrium (blue dashed line). (b) Control of solute size by varying the molar mass of polymer chains M_{sol} to have different gyration radii R_g . (c) Polymer network structures with different network cycle lengths l_{cycle} determined by the molar mass between branching points M_b , polymer-network mass concentration c_{net} , number of arms at branching points f , and network connectivity p .

solute sizes and network structures [Figs. 1(b) and 1(c)]. Our findings demonstrate that the Nernst distribution law holds for model gels in the dilute regime, with the experimentally measured partition ratio K becoming constant ($K = K_0$). Furthermore, by examining the characteristic length scales (mesh sizes) of the polymer network for various densities and topologies, we reveal that K_0 is governed by a universal law based on the ratio of the solute gyration radius (R_g) to the network cycle length (l_{cycle}), deviating significantly from the predictions of the Ogston model.

II. THEORY OF EQUILIBRIUM SWELLING IN POLYMER GELS

We consider the equilibrium swelling of polymer gels immersed in external solutions, both with and without solute partitioning. First, we review the osmotic equilibrium of polymer gels in external polymer solutions, assuming negligible partitioning into the gel [10,26–28]. Throughout this study, we adopt the polymer mass concentration c , defined as the polymer mass per unit volume of solvent [27], to describe the equilibrium swelling of polymer gels. The volume fraction ϕ is given by $\phi = c/(\rho_p + c)$, where ρ_p is the mass density of the polymer. When a polymer gel is immersed in an external solution with mass concentration c_{ext} that exerts osmotic pressure Π_{ext} , the gel reaches equilibrium by adjusting its weight ($W_0 \rightarrow W_{\text{eq}}$) and polymer-network mass concentration ($c_{\text{net},0} \rightarrow c_{\text{net}}$). Osmotic equilibrium occurs when the internal osmotic pressure, composed of the polymer-solvent mixing contribution (Π_{mix}) and the network elastic contribution (Π_{el}), balances the external osmotic pressure (Π_{ext}):

$$\Pi_{\text{mix}} + \Pi_{\text{el}} = \Pi_{\text{ext}}. \quad (1)$$

For gels with sufficient polymer-solvent miscibility, Π_{mix} follows the semidilute scaling law, $\Pi_{\text{mix}} \propto c_{\text{net}}^{3\nu/(3\nu-1)}$ [27,28,34,35], where $\nu \approx 0.588$ is the critical exponent for self-avoiding walks in three dimensions [26,36]. The prefactor depends on the polymer-solvent interactions and temperature. The elastic contribution is given by

$\Pi_{\text{el}} = -G_0(c_{\text{net}}/c_{\text{net},0})^{1/3}$ [37,38], where G_0 is the shear modulus of the gel in its as-prepared state. Using Eq. (1), when $c_{\text{net},0}$, G_0 , and the prefactor of Π_{mix} are known, we can determine equilibrium c_{net} from Π_{ext} without direct measurements. Alternatively, c_{net} can be calculated directly from the equilibrium mass swelling ratio defined as $Q_{\text{eq}} = W_{\text{eq}}/W_0 = (c_{\text{net},0}/c_{\text{net}})(\rho_s + c_{\text{net}})/(\rho_s + c_{\text{net},0})$, where ρ_s is the mass density of a pure solvent. In this study, we use $\rho_p \approx 1129 \text{ kg/m}^3$ and $\rho_s \approx 997 \text{ kg/m}^3$ for polymers [poly(ethylene glycol)] and aqueous solvents [39], respectively.

Next, we extend the osmotic equilibrium described by Eq. (1) to systems in which the external polymer solutes partition into the polymer gel. In this case, the polymer solutes entering the gel increase Π_{mix} . When the solute consists of polymer chains chemically identical to those forming the network, both the network polymer (with mass concentration c_{net}) and the partitioned polymer chains (with mass concentration c_{int}) contribute to the mixing term as

$$\Pi_{\text{mix}} = A(c_{\text{net}} + c_{\text{int}})^{3\nu/(3\nu-1)}, \quad (2)$$

where the total polymer mass concentration $c = c_{\text{net}} + c_{\text{int}}$ determines Π_{mix} using the scaling law applied in the absence of partitioning. Equation (2) indicates that regardless of their origin (network or partitioned chains), the polymer segments contribute equally to Π_{mix} .

Below, we experimentally validate Eq. (2), rather than an (incorrect) alternative additive decomposition:

$$\Pi_{\text{mix}} = \Pi_{\text{mix}}^{(\text{net})} + \Pi_{\text{mix}}^{(\text{int})}, \quad (3)$$

where $\Pi_{\text{mix}}^{(\text{net})} \propto c_{\text{net}}^{3\nu/(3\nu-1)}$ and $\Pi_{\text{mix}}^{(\text{int})} \propto c_{\text{int}}^{3\nu/(3\nu-1)}$ are the mixing contributions from the network and partitioned chains, respectively. Our results demonstrate that Eq. (2) provides the correct description, confirming that osmotic pressure arises from the collective interactions of all polymer segments rather than from the separate contributions of distinct polymer populations.

III. MATERIALS AND METHODS

We used polymer gels with precisely controllable network structures [29] as model systems to investigate the network partitioning law. We synthesized star polymer networks through the end-to-end polymerization of two types of star polymers with mutually reactive terminal functional groups, enabling precise control of the molar mass between branching points (M_b), network connectivity (p), branching number (f), and polymer-network mass concentration ($c_{\text{net},0}$). We dissolved each star polymer [poly(ethylene glycol), PEG] with either maleimide (MA) or thiol (SH) terminal functional groups (Xiamen Sinopeg Biotech Co., Ltd., China) in an aqueous citrate-phosphate buffer at pH 3.4–3.8 with an ionic strength of 0.1 M for $c_{\text{net},0} = 30, 60$, and 90 g/L. For gelation, we mixed these two solutions with equal molar masses of the precursors $M_{\text{pre}} = 10, 20$, and 40 kg/mol and identical arm numbers ($f = 3, 4$, and 8) at a volume mixing fraction s ($0 \leq s \leq 1/2$). This allowed systematic variation of $M_b = 2M_{\text{pre}}/f$ and $p = 2s$ [40], where p is the fraction of reacted to total terminal functional groups ($0 \leq p \leq 1$). We poured each mixed solution into a disk-shaped mold (10 mm diameter, 2 mm height), and maintained the samples at a temperature of $T = 298$ K for 1–3 days to ensure reaction completion.

We immersed each gel sample in an excess external aqueous linear-PEG solution with a controlled concentration c_{ext} and osmotic pressure Π_{ext} . We prepared these external PEG solutions with molar masses $M_{\text{sol}} = 5, 10$, and 20 kg/mol (Xiamen Sinopeg Biotech Co., Ltd., China), exhibiting narrow molar mass distributions $M_w/M_n < 1.05$, for $c_{\text{ext}} = 10$ –120 g/L dissolved in deionized water. We determined Π_{ext} using the established osmotic equation of state for linear-PEG solutions [41–43] [detailed in Supplemental Material (SM) [44], Sec. S1]. After confirming equilibrium (see SM [44], Sec. S2), we measured the weight change of each gel sample ($W_0 \rightarrow W_{\text{eq}}$) using an electronic scale. We verified that buffer salts initially present in the gel do not measurably affect partitioning and swelling in linear-PEG solutions (detailed in SM [44], Sec. S3).

IV. OSMOTIC PRESSURE IN GELS CONTAINING PARTITIONED POLYMER CHAINS

To verify Eq. (2), we directly quantified c_{int} by drying the gels to remove the solvent and measuring the dry weight $W_{\text{dry}} = W_{\text{net}} + W_{\text{int}}$, where W_{net} and W_{int} are the weights of the network and partitioned chains, respectively. We prepared cylindrical gel samples (5.3 mm diameter, 4.8 mm height), equilibrated them in external PEG solutions, and vacuum-dried them at $T = 333$ K for at least 6 h. We used a thermogravimetric analyzer (DTG-60H, SHIMADZU, Japan) to accurately measure W_{dry} (see SM [44], Sec. S4 for detailed results). Because $W_{\text{net}} = W_0[c_{\text{net},0}/(\rho_s + c_{\text{net},0})]$ remained constant during swelling and deswelling, we calculated $c_{\text{net}} = \rho_s W_{\text{net}}/(W_{\text{eq}} - W_{\text{dry}})$ and $c_{\text{int}} = \rho_s(W_{\text{dry}} - W_{\text{net}})/(W_{\text{eq}} - W_{\text{dry}})$.

We demonstrate that Eq. (2), rather than Eq. (3), governs Π_{mix} in polymer gels containing partitioned polymer chains. By directly measuring the internal polymer concentration (c_{int}) via drying, we calculate $\Pi_{\text{mix}} = \Pi_{\text{ext}} - \Pi_{\text{el}}$ for the total polymer concentration $c = c_{\text{net}} + c_{\text{int}}$. To evaluate Π_{el} , we

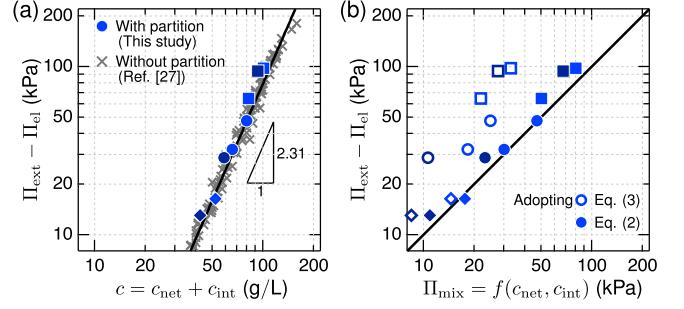


FIG. 2. Experimental verification of Π_{mix} in polymer gels containing partitioned polymer chains. (a) Semidilute scaling law [Eq. (2), black solid line] governing $\Pi_{\text{mix}} = \Pi_{\text{ext}} - \Pi_{\text{el}}$ in polymer gels with (blue filled symbols) and without (gray crosses) partitioned chains [27,28]. (b) Comparison between measured $\Pi_{\text{mix}} = \Pi_{\text{ext}} - \Pi_{\text{el}}$ and calculated Π_{mix} using Eqs. (2) and (3) (filled and open symbols, respectively).

used the previously measured shear modulus G_0 [45] (detailed in SM [44], Sec. S5). As shown in Fig. 2(a), Eq. (2) (black solid line) accurately describes the measured Π_{mix} in gels containing partitioned polymer chains (blue filled symbols). The prefactor $A \approx 1.9$ was obtained from these plots and agrees with the value previously reported for gels without partitioning (gray crosses) in aqueous PEG systems at $T = 298$ K [27,28]. By contrast, Fig. 2(b) reveals that the experimentally determined Π_{mix} deviates significantly from predictions using Eq. (3) (open symbols), whereas calculations using Eq. (2) (filled symbols) agree well with experiment. This agreement enables the evaluation of c_{int} using Eqs. (1) and (2).

V. NERNST DISTRIBUTION LAW FOR POLYMER CHAIN PARTITIONING INTO POLYMER NETWORKS

We systematically measured the equilibrium swelling ratio Q_{eq} for various molar masses of the polymer solute (M_{sol}) and network structures characterized by M_b , $c_{\text{net},0}$, p , and f . Our results demonstrate that the Nernst distribution law ($K \approx K_0$) holds for polymer chain partitioning in polymer networks. As shown in Fig. 3(a), Q_{eq} decreases with increasing c_{ext} and M_{sol} (all other data are presented in SM [44], Sec. S2). Using Eqs. (1) and (2), we evaluated ϕ_{int} . Figure 3(b) shows that ϕ_{int} is directly proportional to ϕ_{ext} in the dilute-concentration regime (black solid lines), indicating a constant partition ratio $K_0 = \phi_{\text{int}}/\phi_{\text{ext}}$, which is consistent with the Nernst distribution law [23]. Notably, when ϕ_{ext} exceeds a critical threshold ($\phi_{\text{ext}}/\phi_{\text{ext}}^* > 1$), this relationship breaks down as higher-order concentration terms become significant ($K > K_0$), with ϕ_{ext}^* decreasing as M_{sol} increases (detailed in SM [44], Sec. S1).

VI. UNIVERSAL LAW OF CONSTANT PARTITION RATIO FOR POLYMER CHAIN PARTITIONING INTO POLYMER NETWORKS

We reveal a universal law governing K_0 for polymer chain partitioning into polymer networks. To identify the characteristic length scale governing partitioning, we examine three candidates: the mean distance between branching points $l_{\text{branch}} (= n^{-1/3})$, between elastically effective junction points

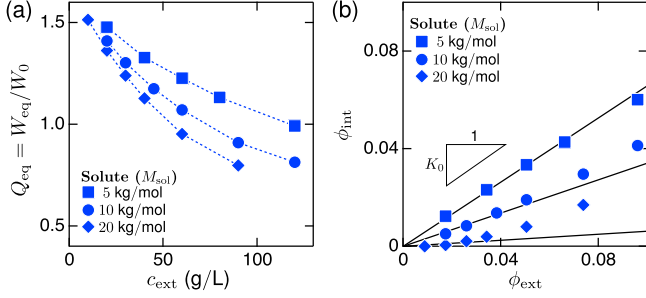


FIG. 3. Evaluation of constant partition ratio K_0 demonstrating the Nernst distribution law ($K \approx K_0$). Typical results for $M_{\text{sol}} = 5, 10$, and 20 kg/mol (squares, circles, and diamonds, respectively) partitioning into polymer networks with identical conditions: $M_{\text{pre}} = 20$ kg/mol for $c_{\text{net},0} = 60$ g/L at $s = 0.5$ and $f = 4$. (a) Dependence of equilibrium swelling ratio $Q_{\text{eq}} = W_{\text{eq}}/W_0$ on c_{ext} . As c_{ext} increases, Π_{ext} increases and Q_{eq} decreases according to Eq. (1). (b) Dependence of ϕ_{int} on ϕ_{ext} , where ϕ_{int} are evaluated using Eqs. (1) and (2). We determine the constant partition ratio $K_0 = \phi_{\text{int}}/\phi_{\text{ext}}$ (black solid line) using data from the dilute-concentration regime ($\phi_{\text{ext}}/\phi_{\text{ext}}^* < 1$), where partitioned linear polymers are isolated; see SM [44], Sec. S1 for ϕ_{ext}^* .

$l_{\text{junction}} (= \mu^{-1/3})$, and between the centroids of elastically effective cycles $l_{\text{cycle}} (= \xi^{-1/3})$. Here, n , μ , and ξ are the number densities of total precursors, elastically effective junction points, and elastically effective cycles (cycle rank), respectively, calculated via the Bethe approximation [40,46,47] (see Appendix B).

Figure 4 shows the measured K_0 values plotted against the dimensionless ratio R_g/l_{cycle} . We find that the universal partitioning law

$$K_0 = \exp[-4(R_g/l_{\text{cycle}})^2] \quad (4)$$

accurately describes all data over a wide range of polymer solute sizes and network structures. By contrast, l_{branch} and l_{junction} fail to collapse the data for networks with varying f and p , except for the data with $f = 4$ and $p = 1$, for which $l_{\text{branch}} = l_{\text{junction}} = l_{\text{cycle}}$ (see Fig. 7 in Appendix C). Using the functional form $K_0 = \exp[-4(R_g/l)^2]$ with $l = l_{\text{branch}}, l_{\text{junction}}$, or l_{cycle} , the root-mean-squared deviations between measured and predicted K_0 for the remaining data are 0.24, 0.22, and less than 0.1, respectively, confirming that the cycle length is the governing parameter (Fig. 7).

We also compared our results with the conventional Ogston model [1–9], which predicts $K_0 = e^{-\phi_{\text{excl}}}$ based on the excluded volume fraction ϕ_{excl} of the network for the solute. The measured K_0 values systematically exceed the predictions of the Ogston model (see Fig. 6 in Appendix A). This discrepancy arises because the Ogston model treats polymer networks as rigid rodlike obstacles, thereby neglecting network topology.

To rationalize the universal law in Eq. (4), we propose a cycle-based model (Fig. 5). We consider a volume element of size $\sim l_{\text{cycle}}^3$ associated with a single elastically effective cycle in the network [Fig. 5(a)]. The center of a guest chain (i.e., a partitioned polymer chain) with gyration radius R_g is sterically excluded from a toruslike region with tube radius R_g and volume $\sim R_g^2 l_{\text{cycle}}$ surrounding the cycle [Fig. 5(b)].

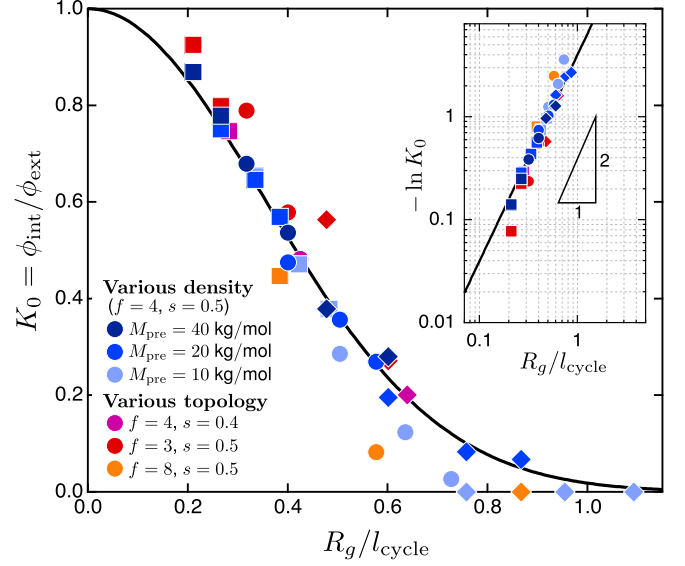


FIG. 4. Universal law governing constant partition ratio K_0 of polymer chains in polymer networks. We systematically varied polymer network structures by tuning network density with $M_{\text{pre}} (= fM_b/2) = 10, 20$, and 40 kg/mol for $c_{\text{net},0} = 30, 60$, and 90 g/L, network topology with $f = 3, 4$, and 8 (red, blue, and orange symbols) at $p = 0.8$ and 1.0 (purple and blue symbols), and polymer solute size with $M_{\text{sol}} = 5, 10$, and 20 kg/mol (squares, circles, and diamonds). All K_0 values follow Eq. (4) (black solid curve) as a function of the ratio between the gyration radius of the polymer solute and the cycle length R_g/l_{cycle} . Inset: Log-log plot showing $-\ln K_0 \propto (R_g/l_{\text{cycle}})^2$ [Eq. (4)], except for $K_0 = 0$.

According to the Poisson distribution, the probability of partitioning corresponds to the zero-encounter probability, $P(0) = e^{-(n)}$, where the mean number of encounters with obstructing cycles is $\langle n \rangle \propto R_g^2/l_{\text{cycle}}^2$. Setting $K_0 = P(0)$ [1] yields $\ln K_0 \sim -(R_g/l_{\text{cycle}})^2$, recovering the functional form of Eq. (4). In the dilute regime, the chemical-potential difference of the solute between the gel and the external solution ($\Delta\mu$) determines the partition ratio via $K_0 = \exp(-\Delta\mu/k_B T)$. Our model shows $\Delta\mu \propto k_B T (R_g/l_{\text{cycle}})^2$ from an entropic confinement penalty imposed by the network topology,

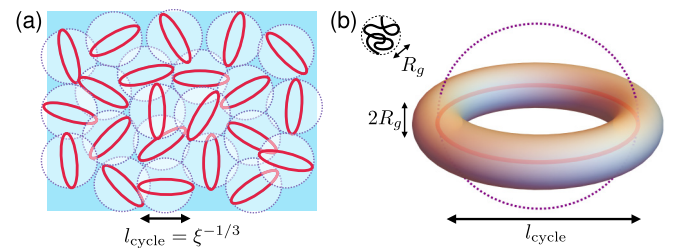


FIG. 5. Cycle-based model for the partitioning of polymer chains into polymer networks. (a) Schematic of a polymer network composed of elastically effective cycles (red circles), each associated with a representative volume element of size $\sim l_{\text{cycle}}^3$ (blue dashed circles). (b) Steric exclusion around a single cycle: the center of a guest polymer chain with gyration radius R_g is excluded from a toruslike region (gray shaded) with tube radius R_g surrounding the cycle within a volume element of size $\sim l_{\text{cycle}}^3$.

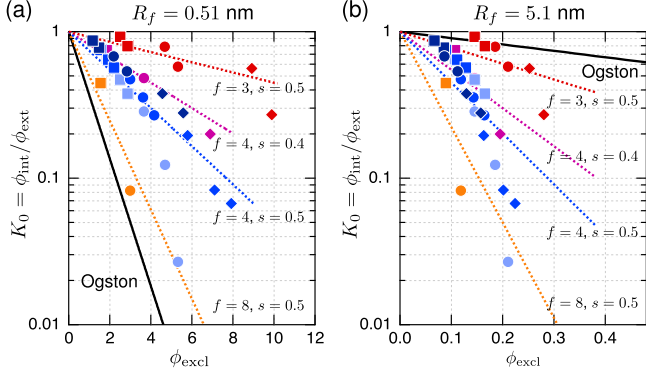


FIG. 6. Comparison of the measured constant partition ratio K_0 with the conventional Ogston model [1,2]. The black solid line represents the prediction of the Ogston model as a function of the excluded volume fraction ϕ_{excl} , revealing an inconsistency with the measured K_0 values (colored symbols). In panel (a), the cross-sectional radius of the PEG chain is set to $R_f = 0.51$ nm based on the literature [4], while in panel (b), it is set to $R_f = 5.1$ nm (ten times the literature value) to evaluate the model sensitivity in calculating ϕ_{excl} .

thereby extending the thermodynamic treatment [10] to explicitly include topological constraints. This framework is analogous to the Casassa model for partitioning in rigid porous media [11,15]; in our model, elastically effective cycles impose conformational constraints on guest chains. Thus, elastically effective cycles serve as the fundamental structural units governing partitioning in polymer networks.

VII. CONCLUDING REMARKS

We experimentally investigated the partitioning of polymer chains into polymer networks for various solute sizes and network structures (Fig. 1). By extending the semidilute scaling law [Eq. (2)] to gels containing partitioned chains (Fig. 2), we systematically measured the partition ratio K using osmotic equilibrium and demonstrated that the Nernst distribution law holds with a constant K_0 (Fig. 3). The obtained K_0 is inconsistent with the predictions of the conventional Ogston model (Fig. 6) and instead follows the universal partitioning law [Eq. (4)] (Fig. 4).

These findings establish l_{cycle} as the characteristic length scale governing partitioning in gel networks (Figs. 4 and 7). Notably, the same length scale (l_{cycle}) also governs scaling properties of elastic modulus [40,45,48,49], fracture behavior [50,51], and particulate gel mechanics [52]. By extending this framework to partitioning, our work provides a unified physical description that connects the mechanical and partitioning properties of polymer networks through their topology. By using a chemically identical PEG-PEG system, we isolated the steric exclusion arising purely from topological constraints. This approach extends classical partitioning theories for rigid porous media, such as the Casassa model [15], to flexible polymer networks. In practical systems, chemical interactions between solutes and networks will introduce additional contributions that can be treated as corrections to this topological baseline. This framework offers predictive insights into solute behavior in diverse network environments, with broad implications for biological systems [20], drug delivery [53], and polymer separation technologies [19].

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DATA AVAILABILITY

The data supporting this study's findings are available within the article and its Supplemental Material [44].

APPENDIX A: COMPARISON OF MEASURED K_0 WITH THE CONVENTIONAL OGSTON MODEL

We compare our experimentally determined K_0 values with the prediction of the conventional Ogston model $K_0 = e^{-\phi_{\text{excl}}}$, where $\phi_{\text{excl}} = \phi_{\text{net}}(1 + R_g/R_f)^2$ [1–9]. Here, R_f is the

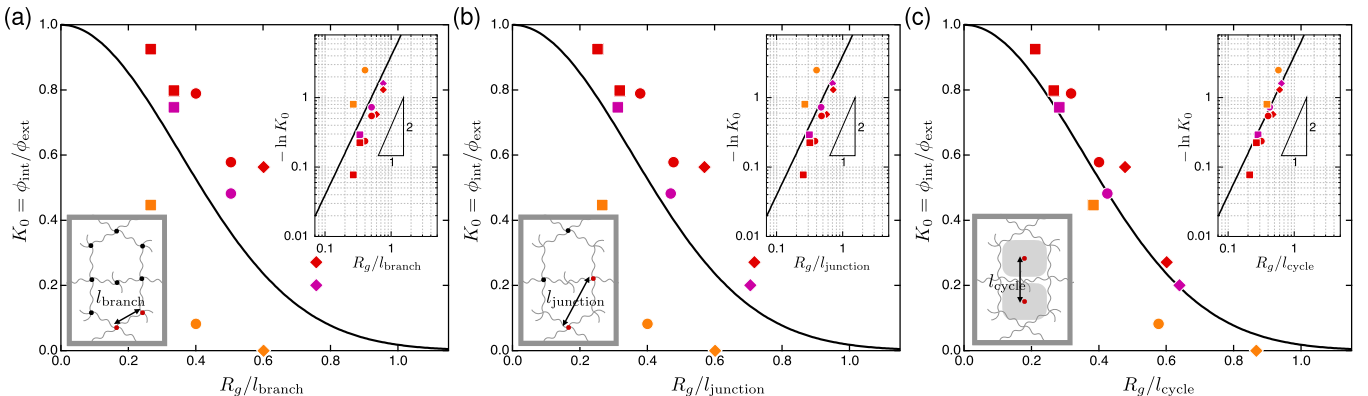


FIG. 7. The partition ratio K_0 for polymer gels with various network topologies (different f and p) plotted against alternative characteristic length scales: (a) R_g/l_{branch} , (b) R_g/l_{junction} , and (c) R_g/l_{cycle} . The K_0 values are identical to those in Fig. 4.

cross-sectional radius of the network strands, and the solute gyration radius R_g follows the scaling law $R_g \propto M_{\text{sol}}^\nu$ [54].

Figure 6 plots K_0 against ϕ_{excl} using (a) $R_f = 0.51$ nm from the literature [4] and (b) $R_f = 5.1$ nm, a value ten times larger, to test model sensitivity, comparing the measured K_0 values in this study (colored symbols) with the prediction of the Ogston model (black solid line). The measured K_0 values vary significantly depending on the network structure (colored dashed lines) and systematically exceed the model predictions in Fig. 6(a). While increasing R_f in Fig. 6(b) shifts the prediction of the Ogston model toward higher K_0 values, the model fails to capture the structural dependence of the measured K_0 . These results demonstrate that the Ogston model is inadequate for describing the partitioning of polymer chains into flexible polymer networks, regardless of the choice of R_f .

APPENDIX B: CALCULATION OF LENGTH SCALES OF THE POLYMER NETWORK USING THE BETHE APPROXIMATION

We evaluate the characteristic length scales (mesh sizes) of the polymer network by using the Bethe approximation for star polymer networks [46,47]: the distances between (i) branching points l_{branch} , (ii) elastically effective junction points l_{junction} , and (iii) centroids of elastically effective cycles l_{cycle} . Consider an AB -type polymerization system formed by mixing f -functional precursors with terminal functional groups A and B at a molar fraction $s : (1-s)$. We define p_A ($0 < p_A \leq 1$) and p_B ($0 < p_B \leq 1$) as the fractions of reacted A - and B -terminal functional groups, respectively. The overall conversion is $p \equiv sp_A + (1-s)p_B$, and the stoichiometric balance $sp_A = (1-s)p_B$ yields $p_A = p/(2s)$ and $p_B = p/[2(1-s)]$. Within the Bethe approximation, let Q_A and Q_B be the fractions of A - and B -terminal functional groups not connected to the infinite network, respectively. These fractions satisfy the following coupled equations:

$$\begin{aligned} Q_A &= p_A Q_B^{f-1} + 1 - p_A, \\ Q_B &= p_B Q_A^{f-1} + 1 - p_B. \end{aligned} \quad (\text{B1})$$

By solving Eq. (B1) for the nontrivial (unique) solutions within the range $0 \leq Q_A < 1$ and $0 \leq Q_B < 1$, we obtain Q_A and Q_B . Let $X_A^{(n)} = \binom{f}{n} Q_A^{f-n} (1-Q_A)^n$ and $X_B^{(n)} = \binom{f}{n} Q_B^{f-n} (1-Q_B)^n$ be the fractions of precursors forming n -functional elastically effective junction points, where $\binom{f}{n} = f!/[n!(f-n)!]$ is the binomial coefficient. The numbers of elastically effective chains $\hat{\nu}$ and junction points $\hat{\mu}$ per

TABLE I. Elastically effective network structure parameters per precursor as functions of functionality f and mixing fraction s under the Bethe approximation: chains $\hat{\nu}$, junction points $\hat{\mu}$, and cycles $\hat{\xi}$.

f	s	$\hat{\nu}$	$\hat{\mu}$	$\hat{\xi}$
3	0.5	1.5	1	0.5
4	0.5	2	1	1
4	0.4	1.36	0.75	0.61
8	0.5	4	1	3

precursor are given by

$$\begin{aligned} \hat{\nu} &= \frac{1}{2} \left[s \sum_{n=3}^f n X_A^{(n)} + (1-s) \sum_{n=3}^f n X_B^{(n)} \right], \\ \hat{\mu} &= s \sum_{n=3}^f X_A^{(n)} + (1-s) \sum_{n=3}^f X_B^{(n)}. \end{aligned} \quad (\text{B2})$$

The number of elastically effective cycles per precursor is then $\hat{\xi} = \hat{\nu} - \hat{\mu}$. Table I summarizes the calculated values of $\hat{\nu}$, $\hat{\mu}$, and $\hat{\xi}$ for the gels used in this study.

The characteristic length scales are calculated as follows: $l_{\text{branch}} = n^{-1/3}$, where $n = c_{\text{net},0} N_A / M_{\text{pre}}$ is the number density of total precursors and N_A is the Avogadro constant. Similarly, $l_{\text{junction}} = \mu^{-1/3}$ and $l_{\text{cycle}} = \xi^{-1/3}$, where $\mu = \hat{\mu}n$ and $\xi = \hat{\xi}n$ are the number densities of elastically effective junction points and cycles, respectively.

APPENDIX C: IDENTIFICATION OF THE LENGTH SCALE GOVERNING PARTITIONING

We demonstrate that l_{cycle} , rather than l_{branch} or l_{junction} , is the critical parameter for observing the universal partitioning law Eq. (4). As shown in Table I, $l_{\text{cycle}} [= (\hat{\xi}n)^{-1/3}]$ varies independently of $l_{\text{branch}} (= n^{-1/3})$ and $l_{\text{junction}} [= (\hat{\mu}n)^{-1/3}]$ when the network topology changes with f and p (see SM [44], Sec. S2 for the values of l_{branch} , l_{junction} , and l_{cycle} for all experimental conditions). Note that $l_{\text{cycle}} = l_{\text{branch}} = l_{\text{junction}}$ for $f = 4$ and $s = 0.5$ because $\hat{\xi} = \hat{\mu} = 1$. Figure 7 shows the measured K_0 values for various network topologies (purple, red, and orange symbols) as functions of R_g/l_{branch} , R_g/l_{junction} , and R_g/l_{cycle} , respectively. In Figs. 7(a) and 7(b), the measured K_0 values do not collapse onto a single curve and show significant variation with changes in f and p when using R_g/l_{branch} or R_g/l_{junction} as the scaling parameter, which is inconsistent with the universal scaling relation Eq. (4) demonstrated in Fig. 4 (black solid curve). In contrast, as shown in Fig. 7(c), the measured K_0 values agree well with the universal scaling relation when using R_g/l_{cycle} . These findings confirm that l_{cycle} is the length scale governing polymer chain partitioning into polymer networks.

- [1] A. G. Ogston, The spaces in a uniform random suspension of fibres, *Trans. Faraday Soc.* **54**, 1754 (1958).
- [2] T. C. Laurent and J. Killander, A theory of gel filtration and its experimental verification, *J. Chromatogr. A* **14**, 317 (1964).

- [3] J. C. Williams, L. A. Mark, and S. Eichholtz, Partition and permeation of dextran in polyacrylamide gel, *Biophys. J.* **75**, 493 (1998).
- [4] V. Hagel, T. Haraszti, and H. Boehm, Diffusion and interaction in PEG-DA hydrogels, *Biointerphases* **8**, 36 (2013).

- [5] J. E. Schnitzer, Analysis of steric partition behavior of molecules in membranes using statistical physics. Application to gel chromatography and electrophoresis, *Biophys. J.* **54**, 1065 (1988).
- [6] E. M. Johnson, D. A. Berk, R. K. Jain, and W. M. Deen, Diffusion and partitioning of proteins in charged agarose gels, *Biophys. J.* **68**, 1561 (1995).
- [7] J. Tong and J. L. Anderson, Partitioning and diffusion of proteins and linear polymers in polyacrylamide gels, *Biophys. J.* **70**, 1505 (1996).
- [8] C. Kotsmar, T. Sells, N. Taylor, D. E. Liu, J. M. Prausnitz, and C. J. Radke, Aqueous solute partitioning and mesh size in HEMA/MAA hydrogels, *Macromolecules* **45**, 9177 (2012).
- [9] N. R. Richbourg and N. A. Peppas, Solute diffusion and partitioning in multi-arm poly(ethylene glycol) hydrogels, *J. Mater. Chem. B* **11**, 377 (2023).
- [10] F. Horkay and M. Zrinyi, Studies on mechanical and swelling behavior of polymer networks on the basis of the scaling concept. 6. Gels immersed in polymer solutions, *J. Macromol. Sci. B* **25**, 307 (1986).
- [11] M. Kremer, E. Pothmann, T. Roessler, J. Baker, A. Yee, H. Blanch, and J. M. Prausnitz, Pore-size distributions of cationic polyacrylamide hydrogels varying in initial monomer concentration and cross-linker/monomer ratio, *Macromolecules* **27**, 2965 (1994).
- [12] S. H. Gehrke, J. P. Fisher, M. Palasis, and M. E. Lund, Factors determining hydrogel permeability, *Ann. N. Y. Acad. Sci.* **831**, 179 (1997).
- [13] S. Tsonchev, R. D. Coalson, and A. Duncan, Partitioning of a polymer chain between a confining cavity and a gel, *Phys. Rev. E* **76**, 041804 (2007).
- [14] J. J. F. Sleeboom, P. Voudouris, M. T. J. J. M. Punter, F. J. Aangenendt, D. Florea, P. van der Schoot, and H. M. Wyss, Compression and reswelling of microgel particles after an osmotic shock, *Phys. Rev. Lett.* **119**, 098001 (2017).
- [15] E. F. Casassa, Equilibrium distribution of flexible polymer chains between a macroscopic solution phase and small voids, *J. Polym. Sci. B Polym. Lett.* **5**, 773 (1967).
- [16] J. C. Giddings, E. Kucera, C. P. Russell, and M. N. Myers, Statistical theory for the equilibrium distribution of rigid molecules in inert porous networks. Exclusion chromatography, *J. Phys. Chem.* **72**, 4397 (1968).
- [17] M. Doi, Equilibrium partition coefficient of macromolecules between random porous network and bulk liquid, *J. Chem. Soc. Faraday Trans. 2* **71**, 1720 (1975).
- [18] I. Teraoka, Polymer solutions in confining geometries, *Prog. Polym. Sci.* **21**, 89 (1996).
- [19] A. A. Gorbunov, L. Ya. Solovyova, and V. A. Pasechnik, Fundamentals of the theory and practice of polymer gel-permeation chromatography as a method of chromatographic porosimetry, *J. Chromatogr. A* **448**, 307 (1988).
- [20] K. Sugano *et al.*, Coexistence of passive and carrier-mediated processes in drug transport, *Nat. Rev. Drug Discov.* **9**, 597 (2010).
- [21] M. T. Wei, S. Elbaum-Garfinkle, A. S. Holehouse, C. C. H. Chen, M. Feric, C. B. Arnold, R. D. Priestley, R. V. Pappu, and C. P. Brangwynne, Phase behaviour of disordered proteins underlying low density and high permeability of liquid organelles, *Nat. Chem.* **9**, 1118 (2017).
- [22] M. Berthelot and E. Jungfleisch, On the law which governs the distribution of a substance between two solvents, *Ann. Chim. Phys.* **26**, 396 (1872).
- [23] W. Nernst, Distribution of a substance between two solvents and between solvent and vapor, *Z. Phys. Chem.* **8**, 110 (1891).
- [24] P. Atkins and J. de Paula, *Elements of Physical Chemistry* (Oxford University Press, New York, NY, 2013).
- [25] M. Shibayama, Spatial inhomogeneity and dynamic fluctuations of polymer gels, *Macromol. Chem. Phys.* **199**, 1 (1998).
- [26] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1953).
- [27] T. Yasuda, N. Sakumichi, U. Chung, and T. Sakai, Universal equation of state describes osmotic pressure throughout gelation process, *Phys. Rev. Lett.* **125**, 267801 (2020).
- [28] N. Sakumichi, T. Yasuda, and T. Sakai, Semidilute principle for gels, [arXiv:2210.15275](https://arxiv.org/abs/2210.15275).
- [29] T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, R. Yoshida, S. Suzuki, N. Sasaki, M. Shibayama, and U. Chung, Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers, *Macromolecules* **41**, 5379 (2008).
- [30] X. Li, K. Khairulina, U. Chung, and T. Sakai, Migration behavior of rodlike dsDNA under electric field in homogeneous polymer networks, *Macromolecules* **46**, 8657 (2013).
- [31] X. Li, K. Khairulina, U. Chung, and T. Sakai, Electrophoretic mobility of double-stranded DNA in polymer solutions and gels with tuned structures, *Macromolecules* **47**, 3582 (2014).
- [32] T. Fujiyabu, X. Li, M. Shibayama, U. Chung, and T. Sakai, Permeation of water through hydrogels with controlled network structure, *Macromolecules* **50**, 9411 (2017).
- [33] T. Fujiyabu, X. Li, U. Chung, and T. Sakai, Diffusion behavior of water molecules in hydrogels with controlled network structure, *Macromolecules* **52**, 1923 (2019).
- [34] J. des Cloizeaux, The Lagrangian theory of polymer solutions at intermediate concentrations, *J. Phys. (Paris)* **36**, 281 (1975).
- [35] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).
- [36] A. Pelissetto and E. Vicari, Critical phenomena and renormalization-group theory, *Phys. Rep.* **368**, 549 (2002).
- [37] H. M. James and E. Guth, Simple presentation of network theory of rubber, with a discussion of other theories, *J. Polym. Sci.* **4**, 153 (1949).
- [38] F. Horkay, I. Tasaki, and P. J. Bassar, Osmotic swelling of polyacrylate hydrogels in physiological salt solutions, *Biomacromolecules* **1**, 84 (2000).
- [39] G. S. Kell, Density, thermal expansivity, and compressibility of liquid water from 0° to 150°C: Correlations and tables for atmospheric pressure and saturation reviewed and expressed on 1968 temperature scale, *J. Chem. Eng. Data* **20**, 97 (1975).
- [40] Y. Yoshikawa, N. Sakumichi, U. Chung, and T. Sakai, Connectivity dependence of gelation and elasticity in AB-type polymerization: An experimental comparison of the dynamic process and stoichiometrically imbalanced mixing, *Soft Matter* **15**, 5017 (2019).
- [41] I. Noda, N. Kato, T. Kitano, and M. Nagasawa, Thermodynamic properties of moderately concentrated solutions of linear polymers, *Macromolecules* **14**, 668 (1981).
- [42] Y. Higo, N. Ueno, and I. Noda, Osmotic pressure of semidilute solutions of branched polymers, *Polym. J.* **15**, 367 (1983).

- [43] T. Yasuda, M. Ino, T. Sakai, and N. Sakumichi, Universal-ity of osmotic equation of state in star polymer solutions, [arXiv:2302.13669](https://arxiv.org/abs/2302.13669).
- [44] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/vvg5-dhy2> for experimental details and additional analyses.
- [45] Y. Yoshikawa, N. Sakumichi, U. Chung, and T. Sakai, Negative energy elasticity in a rubberlike gel, *Phys. Rev. X* **11**, 011045 (2021).
- [46] C. W. Macosko and D. R. Miller, A new derivation of average molecular weights of nonlinear polymers, *Macromolecules* **9**, 199 (1976).
- [47] D. R. Miller and C. W. Macosko, A new derivation of post gel properties of network polymers, *Macromolecules* **9**, 206 (1976).
- [48] M. Lang, On the elasticity of polymer model networks containing finite loops, *Macromolecules* **52**, 6266 (2019).
- [49] N. Sakumichi, Y. Yoshikawa, and T. Sakai, Linear elasticity of polymer gels in terms of negative energy elasticity, *Polym. J.* **53**, 1293 (2021).
- [50] Y. Masubuchi, Y. Doi, T. Ishida, N. Sakumichi, T. Sakai, K. Mayumi, K. Satoh, and T. Uneyama, Phantom-chain simulations for the effect of node functionality on the fracture of star-polymer networks, *Macromolecules* **56**, 9359 (2023).
- [51] Y. Masubuchi, Phantom chain simulations for fracture of end-linking networks, *Polymer* **297**, 126880 (2024).
- [52] M. Bantawa, B. Keshavarz, M. Geri, M. Bouzid, T. Divoux, G. H. McKinley, and E. Del Gado, The hidden hierarchical nature of soft particulate gels, *Nat. Phys.* **19**, 1178 (2023).
- [53] J. Li and D. J. Mooney, Designing hydrogels for controlled drug delivery, *Nat. Rev. Mater.* **1**, 16071 (2016).
- [54] S. Kawaguchi, G. Imai, J. Suzuki, A. Miyahara, T. Kitano, and K. Ito, Aqueous solution properties of oligo- and poly(ethylene oxide) by static light scattering and intrinsic viscosity, *Polymer* **38**, 2885 (1997).