

Temperature Dependence of Polymer Network Diffusion

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The swelling dynamics of polymer gels are characterized by the (collective) diffusion coefficient D of the polymer network. Here, we measure the temperature dependence of D of polymer gels with controlled homogeneous network structures using dynamic light scattering. An evaluation of the diffusion coefficient at the gelation point D_{gel} and the increase therein as the gelation proceeds $\Delta D \equiv D - D_{\text{gel}}$ indicates that ΔD is a linear function of the absolute temperature with a significantly large negative constant term. This feature is formally identical to the recently discovered “negative energy elasticity” [Y. Yoshikawa *et al.* *Phys. Rev. X* **11**, 011045 (2021)], demonstrating a nontrivial similarity between the statics and dynamics of polymer networks.

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The entropy elasticity of rubberlike solids (e.g., rubbers and polymer gels) and Brownian motion are described by formally analogous equations as both originate from thermal fluctuations. In rubberlike solids, the shear modulus G is conventionally considered to be proportional to the absolute temperature T , such that $G = nk_B T$ for an affine network model [1]. Here, n is the number density of elastically effective strands, and k_B is the Boltzmann constant. Similarly, the Einstein relation [2] indicates that the (self) diffusion coefficient of Brownian motion D_s is described as $D_s = \mu k_B T$, where μ is the mobility. This Letter reports that the investigation of the above analogy led to the discovery of a nontrivial law that describes the temperature dependence of the (collective) diffusion coefficient D of a polymer network in a solvent, which characterizes the swelling dynamics of a polymer gel. Notably, the temperature dependence of D is crucial for controlling the kinetics in applications involving sensors and actuators [3,4].

With regard to the elasticity of a polymer gel, we recently found that G is not proportional to T but is a linear function of T with a significantly large negative constant term b as $G = aT + b$ [5]. Here, the negative value of b is interpreted as “negative energy elasticity” because the first and second terms (aT and b) correspond to the entropy and internal energy contributions to G , respectively. This result disproves the conventional assertion that the gel elasticity is approximately proportional to the absolute temperature (i.e., $G \simeq aT$), similar to the rubber elasticity.

Moreover, by examining more than 50 different polymer network structures, we found [5] that G is governed by

$$G(T, c, p) = a(c, p)[T - T_0(c)], \quad (1)$$

where c is the polymer concentration and p is the network connectivity characterizing the degree of gelation progress.

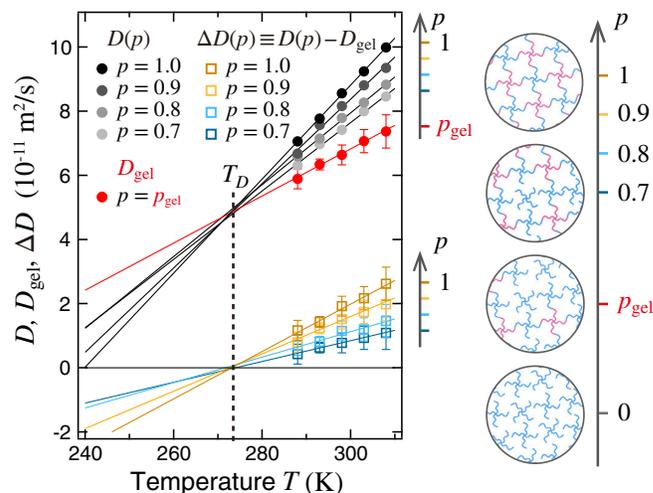


FIG. 1. Temperature (T) dependence of (collective) diffusion coefficient D and its components (D_{gel} and ΔD) in four gel samples with different network connectivities ($p = 0.7, 0.8, 0.9$, and 1.0) for a polymer concentration of $c = 60$ g/L. (see Supplemental Material, Fig. S1 for $c = 30, 90$, and 120 g/L [9].) The black and gray circles represent the experimental results of $D(T, p)$ for each sample. By extrapolating $D(T, p)$ to the gelation point ($p \rightarrow p_{\text{gel}}$), we obtained $D_{\text{gel}}(T)$ (red circles) [see Fig. 2(a)]. Then, we obtained ΔD as $\Delta D(T, p) = D(T, p) - D_{\text{gel}}(T)$ (colored squares) for each sample. The lines represent the least-squares fits of D , D_{gel} , and ΔD . We determine the temperature T_D at which ΔD does not contribute to D , i.e., $D(T_D, p) = D_{\text{gel}}(T_D)$ and $\Delta D(T_D, p) = 0$. (Schematic illustration) The gel samples were synthesized by AB-type cross-end coupling of two precursors (tetra-arm polymers) to tune p ($0 \leq p \leq 1$) after the completion of the reaction, while maintaining c .

Here, we consider the as-prepared state of the entire system consisting of gel and sol components. Because gelation is a dynamic process during which network connections are formed, we cannot precisely measure the physical properties at a certain point during gelation. To statically replicate the gelation proceed at any point, we developed a methodology that enables measurements using p as a control parameter [6,7]. This method utilizes AB -type cross-end coupling of two precursors (tetra-arm polymers) whose terminal functional groups (A and B) are mutually reactive [8] (the schematics in Fig. 1). By mixing the two precursors in stoichiometrically balanced and imbalanced ratios, we can tune p after the completion of the reaction as $p \simeq 2s$, while maintaining c . Here, p ($0 \leq p \leq 1$) is defined as the fraction of the reacted terminal functional groups to all the terminal functional groups, and s ($0 \leq s \leq 1/2$) is the molar mixing fraction of the precursors of the minor group. Using this method, we experimentally obtained Eq. (1), which implies that T_0 , which governs negative energy elasticity, is independent of p .

This Letter presents that an equation formally identical to Eq. (1) holds not only for elasticity but also for the elastic contribution of diffusion of the polymer network in a solvent. The diffusion of a network is characterized by the (collective) diffusion coefficient D [12,13] and is represented by the diffusion equation for the displacement vector of the network \mathbf{u} as

$$\frac{\partial}{\partial t} \mathbf{u} = D \nabla^2 \mathbf{u}, \quad (2)$$

where t is the time, and ∇^2 is the Laplacian operator. [For gels with a general shape, there exists an additional term proportional to $\nabla \times (\nabla \times \mathbf{u})$ in Eq. (2) [13], but it is not relevant to this study.] Figure 1 summarizes the main results. Remarkably, at a fixed c , the extrapolations of the linear fits for the T dependence of D with varying values of p intersect at a single point (that is, $[T_D, D(T_D)]$). To interpret the physical meaning of this intersection, we focus on the change in D as the gelation proceeds, that is, the p dependence of D . Throughout this Letter, we only consider gel states, that is, $p_{\text{gel}} < p < 1$, where p_{gel} represents p at the gelation point. We decompose D into two components: $D(T, c, p) = D_{\text{gel}}(T, c) + \Delta D(T, c, p)$, where we define

$$D_{\text{gel}}(T, c) \equiv \lim_{p \rightarrow p_{\text{gel}}} D(T, c, p) \quad (3)$$

and the increment from D_{gel} as gelation proceeds as

$$\Delta D(T, c, p) \equiv D(T, c, p) - D_{\text{gel}}(T, c), \quad (4)$$

which originates from the polymer network elasticity (see the section “Analysis based on the THB theory” below). As shown in Fig. 1, we find that ΔD has a form equivalent to Eq. (1) as

$$\Delta D(T, c, p) = a_D(c, p)[T - T_D(c)], \quad (5)$$

where T_D is independent of p . This property is a nontrivial feature formally identical to T_0 . We experimentally confirmed Eq. (5) for various concentrations (Supplemental Material, Fig. S1 for $c = 30, 60, 90$, and 120 g/L [9]).

We emphasize that the procedure in Eqs. (3)–(5) is not based on any assumptions or models, but instead relies only on well-defined parameters to analyze D . Many studies have investigated D of polymer gels using light scattering measurements by tuning various parameters, such as the ionization degree [14], number of pendant chains [15], polymer volume fraction [16], cross-link density [17], solvent quality [18], and temperature [12,16,18]. Notably, most studies [15–19] have assumed the Stokes-Einstein relation [$D_s = k_B T / (6\pi\eta\xi)$] with the solvent viscosity η and the correlation length ξ . However, the applicability of the Stokes-Einstein relation to polymer gels has not been strictly validated, and the meaning of ξ is unclear. In contrast, the Tanaka, Hocker, and Benedek (THB) theory [12] contains only well-defined parameters. In this Letter, we first analyze the experimental results in terms of the procedure in Eqs. (3)–(5) and then interpret our analysis based on the THB theory.

Materials and methods.—For the model polymer gel with a homogeneous network structure, we used a tetra-arm poly (ethylene glycol) (tetra-PEG) hydrogel [8], which is synthesized by AB -type cross-end coupling of two precursors: tetra-arm PEG units with molar masses of $M = 20$ kg/mol (NOF Co., Japan and XIAMEN SINOPEG BIOTECH Co., Ltd., China). Each end of the tetra-arm PEG is modified with mutually reactive maleimide (tetra-PEG-MA) and thiol (tetra-PEG-SH). All other reagents were purchased from WAKO. All the materials were used without further purification. To optimize the gelation time [20], we dissolved each precursor in a phosphate-citric acid buffer (pH 3.8), where the molar concentration was 68 and 200 mM for the dynamic light scattering (DLS) measurement and the dynamic viscoelasticity measurement, respectively. We previously confirmed that the results of the latter measurement are almost independent of the molar concentration of the buffer [5]. The polymer concentrations (c) were 30, 60, 90, and 120 g/L. We mixed the precursor solutions in different proportions of $s = 0.35, 0.40, 0.45$, and 0.50 , where $s = [\text{tetra-PEG-SH}] / ([\text{tetra-PEG-MA}] + [\text{tetra-PEG-SH}])$, to obtain gel samples with tuned p after the completion of the reaction as $p \simeq 2s$ [6]. All gel samples were used in the as-prepared state.

We measured D via DLS on an ALV/CGS-3 compact goniometer system (ALV, Langen, Germany) in the same way as in Refs. [21,22]. The gel samples were fabricated in a DLS glass tube (disposable culture tube 9830-1007 with an inner diameter of 8.4 mm; IWAKI, Japan). We measured the scattered light intensity $I(t)$ at time t at a scattering angle of $\pi/2$ at 288, 293, 298, 303, and 308 K for 600 s. Then, we

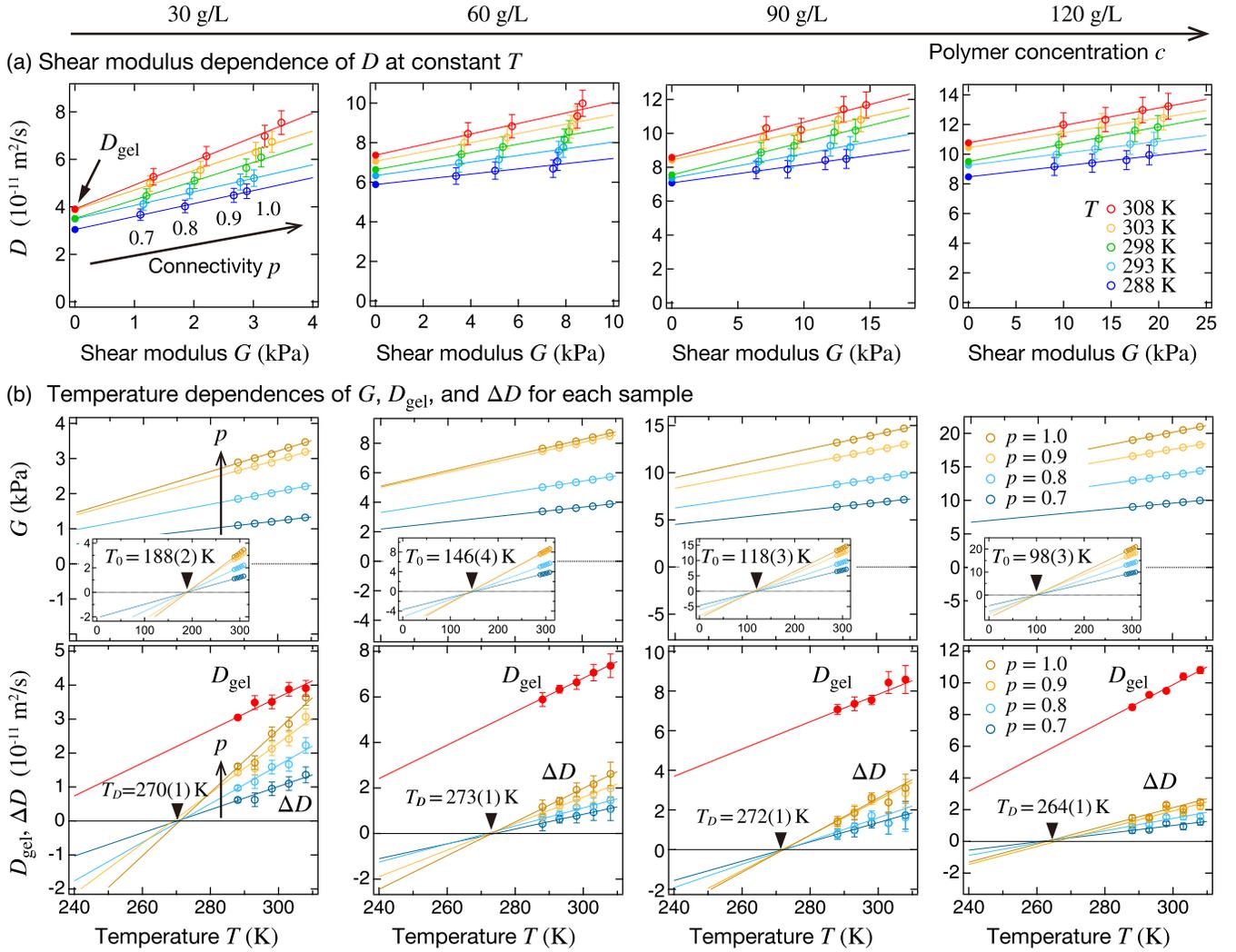


FIG. 2. Formally identical relationships governing the shear modulus G and ΔD . We synthesized the gel samples with 16 different network structures ($c = 30, 60, 90, 120$ g/L and $p = 0.7, 0.8, 0.9, 1.0$). We measured G and D at $T = 288, 293, 298, 303,$ and 308 K. The data of G are partly taken from Ref. [5]. (a) Shear modulus dependence of D at constant T . The open circles represent the experimental results, and the lines represent the least-squares fits of $D = D(G) = D_{\text{gel}} + \alpha G$. Here, $D(G = 0)$ corresponds to D_{gel} (filled circles) because of the definition in Eq. (3). (b) Temperature dependence of G (upper panels) and D_{gel} and $\Delta D \equiv D - D_{\text{gel}}$ (lower panels). Insets in the upper panels depict the same results in different ranges of T . The open circles represent the experimental results, and the lines represent the least-squares fits of the T dependences of G , D_{gel} , and ΔD . All extrapolations of $G = G(T)$ and $\Delta D = \Delta D(T)$ with the same c pass through T_0 and T_D on the T axis, leading to Eqs. (1) and (5), respectively. The value of T_0 or T_D in each graph represents the average of the four samples with different p , and the values in parentheses represent the standard deviation.

evaluated the autocorrelation functions $g^{(2)}(\tau) \equiv \langle I(0)I(\tau) \rangle / \langle I(0) \rangle^2$ for the delay time $\tau \simeq 0.01$ – 0.1 ms, corresponding to the concentration fluctuation of the polymer network [8,12]. Here, $\langle \dots \rangle$ denotes the time average. Using $g^{(2)}(\tau)$ with the partial heterodyne model [23–25], we evaluate D , details of which appear in Sec. S1 of Supplemental Material [9].

We measured the (static) shear modulus G using a dynamic shear rheometer (MCR302, Anton Paar, Austria) in the same way as in Ref. [5]. The mixed solutions of tetra-PEG-MA and tetra-PEG-SH were poured into the interstice of the double cylinder of the rheometer. The time courses of

the storage modulus G' and loss modulus G'' were measured at 298 K with the applied shear strain γ of 2.0% and the angular frequency ω of 31 rad/s. After G' reached the equilibrium, we measured the ω dependences of G' and G'' at 288, 293, 298, 303, and 308 K. Here, we varied ω from 0.63 to 63 rad/s with $\gamma = 1.0\%$, which guarantees linear elasticity. As G' was independent of ω in this region (Supplemental Material, Fig. S3 [9]), we considered G' at $\omega = 31$ rad/s and $\gamma = 1.0\%$ as G .

Results and analysis.—We analyze the experimental results in terms of the procedure in Eqs. (3)–(5). Figure 2(a) demonstrates that D is a nearly linear function of G for all

values of c and T . Here, G is controlled by tuning p [5–7,26]; G is an increasing continuous function of p , and $G \rightarrow 0$ for $p \rightarrow p_{\text{gel}}$. Based on the linearity and definitions of Eqs. (3) and (4), we determined $D_{\text{gel}}(T, c)$ by extrapolating the D – G relations to $G \rightarrow 0$ (corresponding to $p \rightarrow p_{\text{gel}}$) and $\Delta D(T, c, p) \equiv D(T, c, p) - D_{\text{gel}}(T, c) = \alpha(T, c)G(T, c, p)$, where $\alpha(T, c)$ is the slope.

Figure 2(b) depicts the T dependence of G , D_{gel} , and ΔD . Each of G and ΔD is a linear function of T with a significantly large negative constant term. The extrapolations of ΔD for each value of c converge at $T = T_D$ on the T axis. This unexpected law is described by Eq. (5), which is formally identical to Eq. (1) for G (meaning negative energy elasticity [6]). We also confirmed these results for similar gels with $M = 10$ kg/mol (Supplemental Material, Fig. S4 [9]). We note that the actual value of D would not follow the extrapolations at low T away from the measured T because the coexisting solvent (water) freezes at $T \simeq 273$ K. Despite the similarity in the forms of Eqs. (1) and (5), T_D is significantly larger than T_0 . The implication of this difference is discussed in the next section.

Analysis based on the THB theory.—We interpret our experimental results based on the THB theory [12], which shows that $D = [K + (4/3)G]/f$ in Eq. (2) for $p > p_{\text{gel}}$. Here, $K \equiv c\partial\Pi/\partial c$ is the osmotic bulk modulus, $\Pi = \Pi_{\text{mix}} + \Pi_{\text{el}}$ is the total swelling pressure (Π_{mix} and Π_{el} are the mixing and elastic contributions, respectively), and f is the friction coefficient (per unit volume) between the polymer and the solvent. We cannot directly compare our experimental results with $D = [K + (4/3)G]/f$ because $K = K_{\text{mix}} + K_{\text{el}}$ consists of both the polymer-solvent mixing contribution ($K_{\text{mix}} \equiv c\partial\Pi_{\text{mix}}/\partial c$) and elastic contribution ($K_{\text{el}} \equiv c\partial\Pi_{\text{el}}/\partial c$). Assuming that (i) $\Pi_{\text{el}} = -G$ [26], (ii) the scaling law $G \sim c^\beta$ during the swelling [27], and (iii) $f(T, c, p) \simeq f(T, c)$ (the water permeation experiments [28,29] confirm that the p dependence of f is quite weak), we can derive [21,22]

$$D(T, c, p) \simeq \frac{K_{\text{mix}}(T, c)}{f(T, c)} + (4/3 - \beta) \frac{G(T, c, p)}{f(T, c)}, \quad (6)$$

where β ranges from $1/3$ to $(9\nu - 4)/(9\nu - 3) \simeq 0.563$ depending on the polymer concentration of the gel. Here, $\nu \simeq 0.5876$ is the universal critical exponent for polymer solutions (or the self-avoiding walk) [30–32]. In the gel state ($p > p_{\text{gel}}$), K_{mix} and Π_{mix} are independent of p (see Fig. 2 in Ref. [26]). Equation (6) indicates that D is a linear function of G with increasing p , which is consistent with Fig. 2(a). Substituting Eq. (6) into Eq. (3), we have $D_{\text{gel}} \simeq K_{\text{mix}}/f$ because $G(T, c, p_{\text{gel}}) = 0$. Also, combining Eqs. (4) and (6), we obtain $\Delta D \simeq (4/3 - \beta)G/f$. Thus, D_{gel} and ΔD largely correspond to the mixing and elastic contributions to D , respectively.

Using Eq. (6) with assuming $\beta \simeq 0.563$ (i.e., $4/3 - \beta \simeq 0.770$) based on Ref. [22], we evaluate f and K_{mix}

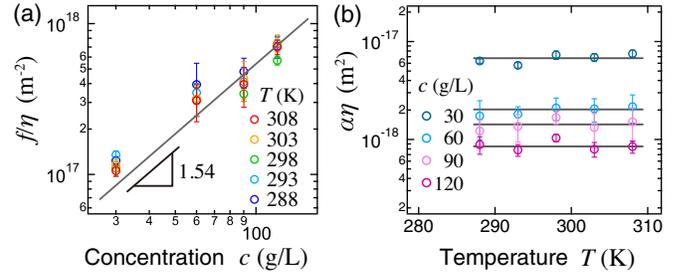


FIG. 3. (a) Log-log plots of the c dependence of f/η , indicating $f/\eta \sim c^{2\nu/(3\nu-1)} \simeq c^{1.54}$ for $\nu \simeq 0.5876$. Here, each friction coefficient between the polymer and the solvent f is obtained from the linear fits in Fig. 2(a) by assuming Eq. (6) and $\beta \simeq 0.563$. (b) Log plots of the T dependence of $\alpha\eta$. The viscosity of the solvent (water) η is taken from Ref. [35]. The solid lines serve as a guide to the eye.

from the slopes $[(4/3 - \beta)/f]$ and ordinate intercepts (K_{mix}/f) of the linear fits in Fig. 2(a) [21,22]. Figure 3(a) shows that the obtained values of f are consistent with the scaling relationships for semidilute solutions in a good solvent [28] $f/\eta \sim c^{2\nu/(3\nu-1)}$, where η is the solvent viscosity. Similarly, those of K_{mix} are consistent with $K_{\text{mix}}/k_B T \sim c^{3\nu/(3\nu-1)}$ [33,34] (Supplemental Material, Fig. S5 [9]). Moreover, Fig. 3(a) indicates that f/η is almost independent of T , which was experimentally shown using poly(acrylamide) gels (Fig. 9 in Ref. [28]). Therefore, our observations and analyses are consistent with the THB theory and scaling relationships.

To elucidate the origin of Eq. (5), we focus on the temperature (T) dependence of ΔD . Inspired by the THB theory, we plot the experimentally obtained $\alpha\eta$ against T in Fig. 3(b) to show that the T dependence of $\alpha\eta$ is quite weak. Thus, we can set $\alpha\eta \simeq h(c)$ and obtain $\alpha(T, c) \simeq h(c)/\eta(T)$. From the definition of α , we have

$$\Delta D(T, c, p) = \alpha(T, c)G(T, c, p) \simeq h(c) \frac{G(T, c, p)}{\eta(T)}, \quad (7)$$

showing that the T dependence of ΔD is determined by G/η . Because the T dependence of $1/\eta$ is greater than that of G (see Supplemental Material, Fig. S6 [9]), $1/\eta$ almost determines the T dependence of ΔD . Moreover, substituting Eq. (1) into Eq. (7), we obtain Eq. (5) by neglecting the second order terms of T (see Sec. S2 of Supplemental Material [9]). Therefore, T_D is significantly larger than T_0 , and exhibits almost no concentration dependence.

Concluding remarks.—We experimentally investigated the temperature (T) dependence of the (collective) diffusion coefficient D of polymer gels. In Eqs. (3) and (4), we operationally defined D_{gel} and ΔD , which largely correspond to the mixing and elastic contributions, respectively [Eq. (6)]. As depicted in Figs. 1 and 2(b), ΔD is a linear function of T with a significantly large negative constant

term, which is formally identical to that of the shear modulus [5]. At a certain temperature T_D , ΔD vanishes, and D is independent of the network connectivity p [Eq. (5) and Figs. 1 and 2(b)]. This simple unexpected law [Eq. (5)] has not been predicted by any existing theory and can stimulate experimental and theoretical research of T_D .

Our findings demonstrate a nontrivial similarity between the statics and dynamics of polymer networks and provide new insights into the so-called diffusio-mechanical (or stress-diffusion) coupling [36–39]. Furthermore, our findings are important for controlling the swelling response time of stimuli-responsive gels, such as sensors and actuators [3,4]. This is because a temperature change of 20 K can nearly double D up to a maximum [$c = 30$ g/L with $p = 1$ in Fig. 2(a)], and this change is mainly caused by the elastic contribution ΔD , which has not been explicitly discussed [15–17,19,25] until recently [21,22].

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Correction: The previously published Fig. 2 contained errors in the T_0 values given in the upper panels of part (b) and has been replaced.