Negative energy elasticity in a rubber-like gel

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Rubber elasticity is the archetype of the entropic force emerging from the second law of thermodynamics; numerous experimental and theoretical studies on natural and synthetic rubbers have shown that the elasticity originates mostly from entropy change with deformation. Similarly, polymer gels containing a large amount of solvent have also been postulated that the shear modulus \( G \), which is a kind of modulus of elasticity, is approximately equivalent to the entropy contribution \( G_S \), but this has yet to be verified experimentally. In this study, we measure the temperature dependence of the shear modulus \( G \) in a rubber-like (hyperelastic) polymer gel whose polymer volume fraction is at most 0.1. As a result, we find that the energy contribution \( G_E \) can be a significant negative value, reaching up to double the shear modulus \( G \) (i.e., \( |G_E| \approx 2G \)), although the shear modulus of stable materials is generally bound to be positive. We further argue that the energy contribution \( G_E \) is governed by a vanishing temperature that is a universal function of the normalized polymer concentration, and \( G_E \) vanishes when the solvent is removed. Our findings highlight the essential difference between rubber elasticity and gel elasticity, which were previously thought to be the same, and push an established field of gel elasticity into a new direction.

I. INTRODUCTION

Rubbers and rubber-like polymer gels are composed of network structures formed by crosslinking polymer chains and have very different elastic properties than hard solids such as metals and ceramics: soft, high elongation, and exhibiting the Gough-Joule effect. This difference stems from the difference in the origin of elasticity. The elastic properties of hard solids are explained by energy elasticity, which originates from internal energy change resulting mainly from changes in their bond angles and bond lengths. On the other hand, the anomalous elastic properties of rubbers and rubber-like polymer gels are explained by entropy elasticity, which originates from entropy change resulting mainly from changes in the conformation of polymer chains [1–3].

We can experimentally determine the entropy contribution \( \sigma_S \) and the energy contributions \( \sigma_E \) by measuring the (shear) stress \( \sigma \) as a function of temperature \( T \) in a constant-volume condition [1,3] (the van’t Hoff isochore [4]). We consider an incompressible elastomer and give an external (shear) strain \( \gamma \). In an isothermal process, the corresponding stress \( \sigma = \sigma(T, \gamma) \) is related to the Helmholtz free energy density \( f = f(T, \gamma) \) as \( \sigma = \partial f / \partial \gamma \). On the basis of \( f = e - Ts \), where \( e \) is the internal energy density and \( s \) is the entropy density, we can separate the entropy contribution \( \sigma_S \) and the energy contribution \( \sigma_E \) to the stress \( \sigma = \sigma_S + \sigma_E \) as \( \sigma_S \equiv -T \partial s / \partial \gamma \) and \( \sigma_E \equiv \partial e / \partial \gamma \). According to the Maxwell relation

\[
\partial s / \partial T = -\partial \sigma / \partial T, \quad \sigma_S(T, \gamma) = T \frac{\partial \sigma}{\partial T}(T, \gamma). \tag{1}
\]

By using Eq. (1), we can determine \( \sigma_S \) by measuring the \( T \) dependence of \( \sigma \) when \( \gamma \) is fixed. Then, we can obtain \( \sigma_E \) as \( \sigma_E = \sigma - \sigma_S \).

Similarly, we can experimentally determine the entropy contribution \( G_S \) and the energy contributions \( G_E \) by measuring the shear modulus \( G \) as a function of temperature \( T \) in a constant-volume condition. Here, the shear modulus is defined by

\[
G(T) \equiv \left. \frac{\partial \sigma}{\partial \gamma}(T, \gamma) \right|_{\gamma=0} = \left. \frac{\partial^2 f}{\partial \gamma^2}(T, \gamma) \right|_{\gamma=0}. \tag{2}
\]

The entropy and energy contributions to the shear modulus are defined by

\[
G_S(T) \equiv \left. \frac{\partial \sigma_S}{\partial \gamma}(T, \gamma) \right|_{\gamma=0} = -T \left. \frac{\partial^2 s}{\partial \gamma^2}(T, \gamma) \right|_{\gamma=0}, \tag{3}
\]

and

\[
G_E(T) \equiv \left. \frac{\partial \sigma_E}{\partial \gamma}(T, \gamma) \right|_{\gamma=0} = \left. \frac{\partial^2 e}{\partial \gamma^2}(T, \gamma) \right|_{\gamma=0}, \tag{4}
\]

respectively. In the same manner as Eq. (1), we can determine the entropy and the energy contributions as

\[
G_S(T) = T \frac{dG}{dT}(T), \tag{5}
\]

\[
G_E(T) = G(T) - G_S(T), \tag{6}
\]

by measuring the \( T \) dependence of \( G \). Since \( G \) is a material constant, it is better to use \( G \) rather than \( \sigma \) to discuss entropy and energy elasticities. However, many

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studies for rubber elasticity have used $\sigma$ due to the difficulty in accurately measuring $G$.

Figure 1 demonstrates how to determine $\sigma_S$ and $\sigma_E$ from experimental data ($\sigma(T)$) for natural rubber (Fig. 1(a)) and polymer gel (Fig. 1(b)). Both are commonly highly stretchable as a result of network structures formed by chemically crosslinked polymer chains. As shown in Fig. 1(a), it was confirmed that $\sigma \simeq \sigma_S$ in the case of natural and synthetic rubbers by numerous experimental [5-9] and theoretical [10, 11] studies; $|\sigma_E|$ was less than a quarter of $\sigma$. Thus, the elasticity of rubber-like (i.e., hyperelastic) polymer materials has been widely considered to be described primarily as entropy elasticity [1, 3]. For example, in polymer gels containing a large amount of solvent, $\sigma \simeq \sigma_S$ has also been postulated [12-15]; nevertheless, no experimental verification has been conducted.

In this study, to examine this conventional postulation, we measure the temperature dependence of the shear stress and the shear modulus in a tetra-functional hydrogel (tetra-PEG gel) [16], as a model rubber-like polymer gel whose crosslinked structure does not change (i.e., a so-called chemical gel or a covalently bonded gel). Remarkably, we find that $\sigma_E$ can be a negative value as large as $\sigma$, i.e., $|\sigma_E| \sim \sigma$ (Fig. 1(b)). This means that $G_E$ can be a negative value as large as $G$, although the shear modulus of stable materials is generally bound to be positive. We further argue that $G_E$ is governed by a vanishing temperature that is a universal function of the normalized polymer concentration, and $G_E$ vanishes when the solvent is removed. Our findings would stimulate a re-examination of a vast amount of research on gel elasticity.

This paper is organized as follows. In Sec. II we explain the materials and methods. In Sec. III we show basic properties of gel elasticity. In Sec. IV we analyze our experimental results and validate the existence of a universal function that governs the energy contribution of gel elasticity. In Sec. V we propose a possible molecular interpretation of negative energy elasticity. In Sec. VI we summarize the main results of this paper. The details of the comparison between our experimental results and the phantom network model are described in the appendix D to avoid digressing from the main subject.

II. MATERIALS AND METHODS

A. Fabrication of tetra-PEG gels

For a model rubber-like polymer gel, we used tetra-PEG gel [16], which is highly stretchable and has homogeneous network structure. As shown in Fig. 2, tetra-PEG gel is synthesized by AB-type cross-end coupling of two kinds of precursors: tetra-armed poly(ethylene glycol) (PEG) chains whose terminal functional groups (A and B) are mutually reactive.
PEG-MA) and tetra-thiol-terminated poly(ethylene glycol) (tetra-PEG-SH) with molar masses \( M = 10, 20 \) (NOF Co., Japan), and 40 (XIAMEN SINOPEG BIOTECH Co., Ltd., China) kg/mol. The precursors (tetra-PEG-MA and tetra-PEG-SH) were each dissolved in phosphate-citrate buffer whose molar concentration and pH were 200 mM and 3.8, respectively. Here, the experimental results of the shear modulus \( G \) did not depend on molar concentration and pH. To control the connectivity \( p \) after completion of the chemical reaction, we nonstoichiometrically mixed the two kinds of precursor solutions with equal molar mass \( M \) and precursor concentration \( c \) (see Appendix C). The weight fraction of tetra-PEG-MA to all precursors was \( q_w = 0.50, 0.55, 0.60, \) and 0.65. We set \( c = 30, 60, 90, \) and 120 g/L. Here, in this paper, we define \( c \) as the precursor weight divided by the solvent volume (not the solution volume).

### B. Measurement of shear modulus

We measure the shear modulus \( G \) using the dynamic shear rheometer (MCR301 and MCR302, Anton Paar, Austria), as shown in Fig. 3(a). Immediately after mixing the two kinds of precursor solutions, we poured the resulting solutions into the gap within the double cylinder of the dynamic shear rheometer. Then, we measured the time courses of the storage modulus \( G' \) and loss modulus \( G'' \) at 298 K with the applied strain 1%. After \( G' \) reached equilibrium, which means completion of the chemical reaction between maleimide and thiol, we measured the temperature \( (T) \) dependence of \( G' \) from \( T = 298 \) to 278 K and then from 278 to 298 K. There was almost no hysteresis for the down and up temperature scan. In all samples, the obtained \( G' \) is independent of the frequency \( (\omega/2\pi) \) below 10 Hz, and the loss tangent \( \tan \delta = G''/G' \) is at most \( 10^{-2} \) at 1 Hz, as shown in Fig. 3(b). Thus, we regard \( G' \) at 1 Hz as the (static) shear modulus \( G \) given by \( G = \lim_{\omega \rightarrow 0} G'(\omega) \).

The rheological measurement described above allows us to satisfy a constant-volume condition necessary to determine the entropy and energy contributions \( (\sigma_S, \sigma_E, G_S, G_E) \). The factors that contribute to volume change are shear deformation and temperature change. First, shear deformation can suppress volume change caused by a decrease in internal pressure [11, 17]. Second, setting 278 K \( \leq T \leq 298 \) K guarantees a negligible volume change for the following three reasons: (i) if \( T < 273 \) K, the water freezes; (ii) if \( T \) considerably exceeds 298 K, the gel shrinks due to the large elastic contribution to the osmotic pressure [17]; (iii) the gel hardly thermally expands because it contains a large amount of water as a solvent. A detailed quantitative analysis is given in Appendix A. The relative volume change due to temperature change within 278 K \( \leq T \leq 298 \) K is of the order of \( 10^{-3} \), and the relative volume change due to shear deformation is negligible in comparison.

### III. BASIC PROPERTIES OF GEL ELASTICITY

Figure 4(a) shows the \( T \) dependence of \( \sigma \) under fixed strain \( \gamma \) for a polymer gel and demonstrates the following two facts. First, \( \sigma \) is an ideally linear function of \( T \) within the measured range. Thus, we regard the slope of the linear fitting of the \( \sigma-T \) relation as \( \partial \sigma/\partial T \) in Eq. (1). Second, all linear extrapolations of \( \sigma = \sigma(T) \) for \( \gamma \leq 140\% \) (solid gray lines) pass through the one point \((T_0)\) on the \( T \) axis. We call this proper temperature \( T_0 \) the “vanishing temperature”. We emphasize that the “actual” stress \( \sigma \) does not follow the extrapolation lines (solid gray lines) at low temperatures away from the measured temperature \((<278 \) K) and certainly does not vanish at \( T_0 \). We extrapolate the \( \sigma-T \) relation just to calculate the energy and entropy contributions of \( \sigma \).

The polymer gel (tetra-PEG gel) is an ideal rubber-like (i.e., hyperelastic) material in the sense that the stress–strain relation (the black symbols in Fig. 4(b)) exhibits a wide range of linear elasticity \( (\gamma \lesssim 140\%) \). Thus, the (shear) modulus \( G \), which is defined in Eq. (2), describes the elasticity of the polymer gel. This ideal linear elasticity of the polymer gel implies that the volume is certainly constant under shear deformation and is an advantage for investigating elasticity compared to natural and synthetic rubbers.
FIG. 4. Polymer gel exhibiting a wide range of linear elasticity under shear deformation.
(a) Temperature ($T$) dependence of (shear) stress $\sigma$ under fixed (shear) strain $\gamma$ ($1, 20, 40, 60, 80, 100, 120, 140, 160, 180\%$) within $278 \text{K} \leq T \leq 298 \text{K}$. The data for $\gamma = 60\%$ correspond to Fig. 1(b). The straight lines are obtained from a least-squares fit and are extrapolated to $T = 0 \text{K}$. Within the measured range, $\sigma$ is a nearly linear function of $T$ at each $\gamma$ (inset). The gray solid extrapolation lines ($\gamma \leq 140\%$) pass through the vanishing temperature $T_0$ on the $T$ axis.
(b) Stress ($\sigma$)–strain ($\gamma$) curve (black symbols) with $\sigma_S$ (blue symbols) and $\sigma_E$ (red symbols). The data are extracted from Fig. 1(a) at $T = 288 \text{K}$. The $\sigma$, $\sigma_S$ and $\sigma_E$ show linear elasticity over a wide range up to $\gamma = 140\%$. The linearity of $\sigma_S$ and $\sigma_E$ to $\gamma$ corresponds to the $\gamma$-independence of $T_0$.

The blue and red symbols in Fig. 1(b) show $\sigma_S$ and $\sigma_E$, respectively, calculated from Eq. (1) and $\sigma(T)$ in Fig. 1(a). Figure 1(b) (and Fig. 1(a) above) demonstrates that $\sigma_E$ is comparable to $\sigma$ and that $\sigma_S$ and $\sigma_E$ are also linear with respect to $\gamma$ for a wide range of the strain ($\gamma \lesssim 140\%$). Thus, the entropy and energy contributions to the shear modulus ($G_S$ and $G_E$, Eqs. (3) and (4)) describe the entropy and the energy elasticities, respectively.

IV. UNIVERSAL FUNCTION THAT GOVERNS ENERGY ELASTICITY

A. Vanishing temperature

To investigate the relationship between the negative energy elasticity of the polymer gel and the microscopic structure of the polymer network, we independently and systematically control three parameters of the precursors: the molar mass $M$, the concentration $c$, and the connectivity $p$ (see Sec. 3A). Here, $p$ ($0 \leq p \leq 1$) is defined as the fraction of the reacted terminal functional groups and is controlled by mixing two kinds of precursors nonstoichiometrically (see Appendix C). In the polymer network after completion of the chemical reaction, $c$ and $M$ correspond to the polymer (network) concentration and double the molecular weight between crosslinks, respectively.

From the experimental results shown in Fig. 5(a), we find two features: (i) $G$ is a nearly linear function of $T$ in the measured range, and (ii) the vanishing temperature $T_0$ is independent of $p$. These features indicate that

$$G(T, M, c, p) = a(M, c, p) \left[ T - T_0(M, c) \right],$$

where we introduce a prefactor $a = a(M, c, p)$. According to Eq. (7), in the measured range, the entropy contribution

$$G_S(T, M, c, p) = a(M, c, p)T,$$

is a linear function of $T$, and the energy contribution

$$G_E(T, M, c, p) = -a(M, c, p)T_0(M, c),$$

is independent of $T$ and governed by $T_0$.

By analyzing the systematic results shown in Fig. 5(a), we reveal a law governing $T_0$. Figure 5(b) demonstrates that all the results at different values of $M$ and $c$ collapse onto a single master curve, which means

$$T_0(M, c) = T_0 \left( \frac{c}{c^*} \right).$$

Here, $c^* = c^*(M)$ is the normalization factor chosen to construct the master curve. It is notable that $c^*(M)$ is in close agreement with the overlap concentration of the precursors $c^*_{\text{vis}}(M)$ obtained by a viscosity measurement 14. Here, the overlap parameter $c/c^*_{\text{vis}}$ determines the dilute ($c/c^*_{\text{vis}} < 1$) and semidilute ($c/c^*_{\text{vis}} > 1$) regimes of polymer concentration $c$. This agreement and Eq. (10) invoke the osmotic pressure in the polymer solution, which is represented by a universal function of $c/c^*_{\text{vis}}$ in the dilute ($c/c^*_{\text{vis}} < 1$) and semidilute ($c/c^*_{\text{vis}} > 1$) regimes 18. We note that the maximum polymer volume fraction in this study is about 0.1, and it is unclear whether Eq. (10) holds at higher polymer concentration ($c/c^*_{\text{vis}} \gg 1$).
FIG. 5. The existence of a universal function that governs the energy contribution of gel elasticity.

(a) Temperature ($T$) dependence of the shear modulus $G$. We obtain each gray line from a least-squares fit of each sample that is characterized by the three parameters of the precursors: the molar mass $M$, the concentration $c$ and the connectivity $p$. All gray lines that have the same $M$ and $c$ pass through a vanishing temperature $T_0$ on the $T$ axis, which leads to Eq. \( (1) \). The value of $T_0$ in each graph is the average over the four samples with different values of $p$, and the values in parentheses represent the standard deviation.

(b), (c) The normalized concentration ($c/c^*$) dependence of $T_0$. We set $c^* = 80, 60, 40$, and $30$ g/L for $M = 5, 10, 20$, and $40$ kg/mol, respectively, to construct the master curve. The orange triangles, blue diamonds, red circles and black squares represent $M = 5, 10, 20$, and $40$ kg/mol, respectively. Each filled symbol represents the average of four samples taken from (a). Additionally, each open symbol represents the value of one equal weight mixing sample ($p = 1$). Log-log (b) and linear (b, inset) plots of $c/c^*$ vs $T_0$ demonstrate the scaling law $T_0 \sim (c/c^*)^{-1/3}$ in the dilute regime ($c/c^* < 1$). A linear plot of the inverse normalized concentration ($c/c^*$)$^{-1}$ vs $T_0$ (c) demonstrates that $T_0$ becomes nearly zero in the dense limit ($c/c^* \rightarrow 0$). This result agrees with $|G_E| \ll G_S$ for rubber elasticity given in previous studies \[ \text{Ref. } \]

(d) Connectivity $p$ and $c/c^*$ dependence of $g$. We obtain the contour plot from data points (white circles) that represent samples shown in (a). The sol-gel transition line (gray thick line) is the interpolation of data (black crosses) taken from Ref. \[ \text{Ref. } \].
We consider the dilute and dense regimes. In the dilute regime \( (c/c^* < 1) \), we find a scaling law
\[
T_0 \sim \left( \frac{c}{c^*} \right)^{-1/3},
\]
as shown in Fig. 5(b). Since \( c^{-1/3} \) seems to be proportional to the linear distance between crosslinks \( l \), we have \( T_0 \sim l \). This fact is important in conjecturing the molecular interpretation of negative energy elasticity (see Sec. V) below. If \( T_0 \) follows the scaling law in Eq. (11) below the measured \( c/c^* \) range, \( T_0 \) reaches the measured temperature \( (T \gtrsim 280 \textnormal{ K}) \) at \( c/c^* \sim 0.12 \). Thus, if \( c < 0.12c^* \), tetra-PEG gels are expected to be mechanically unstable because \( G < 0 \). This expectation is consistent with a previous study that reported that tetra-PEG gels cannot be formed below \( c/c^* \sim 0.1 \) around 300 K.

In the dense regime \( (c/c^* \gg 1) \), Fig. 5(c) shows that as \( (c/c^*)^{-1} \rightarrow 0 \), which means that the solvent is removed, \( T_0 \) tends to decrease to nearly zero. This result agrees with previous studies on natural and synthetic rubbers without solvent; the absolute value of the energy contribution \( (aT_0) \) is much smaller than the value of the entropy contribution \( (aT) \). In other words, this result suggests that the presence of solvent is the origin of energy elasticity in the polymer gels, as discussed below (Sec. V).

**B. Prefactor of shear modulus**

Using dimensional analysis, we determine the functional form of \( a = a(p,M,c) \). Since \( a \) has the same dimension as \( cR/M \), the dimensionless combination is \( g \equiv cM/(cR) \), where \( R \) is the gas constant. Then, \( g \) depends on the dimensionless parameters composed of \( p, M \) and \( c \), i.e., \( g = g(p,c/c^*) \). Figure 5(d) validates this dimensional analysis. Substituting \( g = g(p,c/c^*) \) and Eq. (10) into Eq. (7), we have
\[
G(T,M,c,p) = \frac{cR}{M} g \left( p, \frac{c}{c^*} \right) \left[ T - T_0 \left( \frac{c}{c^*} \right) \right].
\]

Although \( g(p,c/c^*) \) and \( T_0(c/c^*) \) depend on the kinds of polymer chains and solvents that constitute polymer gels, Eq. (12) generally represents \( G \) in homogeneous polymer gels. For example, Fig. 5(c) gives \( T_0(c/c^*) \) for the tetra-PEG gel. Since the measured region is limited to 278 K \( \leq T \leq 298 \textnormal{ K} \), it does not necessarily mean that Eq. (12) is applicable for other \( T \) regions.

The behavior of the contour lines of \( g(p,c,c^*) \) in Fig. 5(d) is consistent with recent experiments on the polymer gels for the dilute \( (c/c^* < 1) \) and semidilute \( (c/c^* > 1) \) regimes. In the dilute regime \( (c/c^* < 1) \), Fig. 5(d) shows that the contour lines of \( g(p,c,c^*) \) are nearly parallel to the sol-gel transition line \( T^* \) corresponding to \( g(p,c,c^*) = 0 \). Thus, the contour lines are consistent with previous experiments [19, 20]. There seems to be no theory (e.g., percolation theories and mean-field theories) that quantitatively explains the dependence of \( g \) on \( c/c^* \). The behavior of \( g(p,c,c^*) \) is qualitatively considered to be caused by elastically ineffective connections such as intramolecular bonds and loops [15, 20, 21].

In the semidilute regime \( (c/c^* > 1) \), Fig 5(d) shows that \( g \) is almost independent of \( c/c^* \), and we find \( g(p,c,c^*) \sim 2.4 \xi(p) \) from the experimental data (see Appendix D). Here, the number per precursor of elastically effective cycles \( \xi(p) \) satisfies \( 0 \leq \xi(p) \leq 1 \) and is calculated using the Bethe approximation [22, 23]. Equation (12) with \( g(p,c,c^*) \sim 2.4 \xi(p) \) leads to \( G(p) \sim \xi(p) \), which is consistent with previous experiments [24, 21]. We remark that the entropy contribution obtained in our study, \( G_S = cRg(p)T/M \), is 2.4 times as large as \( G_S^{\text{phm}} = cR\xi(p)T/M \), which is predicted by the phantom network model [3, 25].

**V. MICROSCOPIC ORIGIN OF NEGATIVE ENERGY ELASTICITY**

Figure 6 reveals that the conformational energy change cannot explain the microscopic origin of negative
energy elasticity in a rubber-like gel. Previous studies on a rubber has shown that $\sigma_E/\sigma = T_0 \frac{1}{c^*} \ln (r^2/l)$, where $(r^2)_0$ is the unperturbed mean-square end-to-end distance. This equation is interpreted through the rotational isomeric state (RIS) model in relation to conformational energy. For example, the RIS model explains that the experimentally determined small and positive energy contribution in the PEG rubber is $\sigma_E/\sigma = 0.07 \pm 0.01$ from the conformational change around the C-C bond (Fig. 7(a)). However, this result is considerably different from our result, as shown in Fig. 6 $\sigma_E/\sigma$ for tetra-PEG gel is large and negative ($\sigma_E/\sigma = G_E/G = -1.81 \pm 0.04$ at the maximum) and has the strong dependence on $c$. Thus, we suggest that the internal energy change with deformation originates mainly from some kind of intermolecular (i.e., polymer-polymer, solvent-polymer, and solvent-solvent) interactions. In addition, since the components remain constant, the Flory-Huggins theory (and the $\chi$ parameter) cannot explain the interaction energy change with deformation. Therefore, we need a new molecular interpretation of negative energy elasticity.

We propose a possible molecular interpretation of negative energy elasticity in a rubber-like gel (Fig. 7(b)); the negative $G_E/G$ value in the gel and the scaling law in Eq. (11) originate from the fact that the stretching of a polymer chain increases the number of solvent molecules attractively interacting with the polymer chains. The top of Fig. 7(b) shows a single polymer chain (blue curve) between crosslinks (red points) in the dilute regime ($c/c^* < 1$), where most of the chains are isolated. We define the territory of a polymer chain as the region containing solvent molecules that interact with the chain and assume that the territory is roughly described as a cylinder shape (light blue region) with radius $r$ and height $l$. As shown in the bottom of Fig. 7(b), when the polymer chain is mechanically stretched at the stretch ratio $\lambda$, the territory increases, i.e., an increase in the number of solvent molecules interacting with the chain. Here, the solvent molecules come in from outside the original (i.e., undeformed) territory. Under small deformation, the radius $r$ remains nearly constant because the length of a chain in the direction perpendicular to the stretching direction does not change. Assuming that the total energy of the solvent-polymer interaction per chain is proportional to the volume of the territory, the solvent-polymer interaction energies at undeformed and deformed chains are proportional to $r^2l$ and $r^2l\lambda$, respectively. Thus, when a single polymer chain is stretched, the change in the total energy of the solvent-polymer interaction is proportional to $r^2l(\lambda - 1)$. Therefore, the energy elasticity of the gel ($G_E \sim T_0$) is proportional to the linear distance between crosslinks $l$, i.e., $T_0 \sim l$. Supposing $l \sim c^{-1/3}$, we have $T_0 \sim c^{-1/3}$, which is consistent with the scaling law in Eq. (11) for a fixed $M$ (and a fixed $c^*(M)$).

The proposed molecular interpretation is also consistent with the experimental results in semidilute and dense regimes. In the semidilute regime ($c/c^* \gg 1$), the territories (light blue regions in Fig. 7(b)) overlap with each other. Thus, the dependence of $T_0$ on $c$ falls below the scaling law ($T_0 \sim c^{-1/3}$) as shown in Fig. 7(b). In the dense regime ($c/c^* \ll 1$), the solvent diminishes, and the effect of the solvent-polymer interaction on energy elasticity becomes negligible compared to that of the conformational energy change (Fig. 7(a)), which is consistent with the results shown in Figs. 5(c) and 6.

Although the proposed molecular interpretation appears to explain the experimental results well, further investigations are needed as this study only performed macroscopic measurements. For example, molecular-scale experiments (such as light scattering and single-chain experiments) and numerical simulations (such as molecular dynamics simulations) will better reveal the microscopic origin of the negative energy
VI. CONCLUDING REMARKS

In conclusion, we have discovered that the energy contribution to shear modulus ($G_E$), which is negligible in rubbers, can be a significant negative value in rubber-like polymer gels containing a large amount of solvents (the polymer volume fraction $\lesssim 0.1$). Further systematic experiments with various network structures have revealed that the shear modulus $G$ is simply described by Eq. (12), and $G_E$ is governed by a vanishing temperature $T_0$ that is a universal function of the normalized polymer concentration $c/c^*$. The vanishing temperature $T_0$ exhibits a scaling law of $T_0 \sim (c/c^*)^{-1/3}$ in the dilute regime ($c/c^* < 1$). Based on this scaling law, we have suggested the microscopic origin of negative energy elasticity: it emerges from the interaction between the polymer chain and the solvent, as shown in Fig. 7(b). To establish this origin from a molecular description and to verify whether our findings are universal in other polymer gels, further studies are needed.

Our findings have essential implications for past research on gel elasticity, which was previously thought to be the same as rubber elasticity. For example, in the previous paper using tetra-PEG gels [14], $G \approx G_S$, i.e., $G_E \approx 0$, was assumed, and the dependence of the shear modulus $G$ on the polymer-concentration $c$ was interpreted as the crossover between the phantom [3, 24] and affine [1] network models. However, our results (Figs. 3(b) and 3(c) and Eq. (12)) point out that the above assumption is invalid, and “the crossover” does not mean the phantom-affine crossover but originates from the dependence of $T_0$ on $c$. As this example shows, our study provides a new perspective on gel elasticity and urges re-examinations of a vast amount of previous research on gel elasticity.

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AUTHOR CONTRIBUTIONS

T.S. planned and supervised the whole project. Y.Y. designed and performed the experiments. N.S. developed the theoretical framework. U.C. contributed to discussions throughout the project. Y.Y. and N.S. analyzed and interpreted the results and wrote the manuscript.

Appendix A: Volume change due to temperature change and shear deformation

To demonstrate that the experiment in this study was conducted with a negligible volume change, we evaluate the relative volume change (i.e., the volume strain) due to temperature change and shear deformation. First, we evaluate the relative volume change of tetra-PEG gels with a change of temperature in free thermal expansion at 1 atm. The densities of the tetra-PEG gels are considered to be equal to the densities of the aqueous PEG solution with the corresponding same polymer concentration $c$. According to Ref. [28], the densities of aqueous PEG solutions at a temperature $T = 277$ K ($\rho(277K)$) and at a temperature $T = 298$ K ($\rho(298K)$) can be calculated by the following formulae:

$$ \rho(277K)/(g/cm^3) = 1.0000 + 0.19820w, $$
$$ \rho(298K)/(g/cm^3) = 0.99707 + 0.17441w, $$
respectively. Here, $w = c/(c + 997.07\text{~(g/L)})$ is the mass fraction of PEG. In this study, experiments were conducted in the temperature range of 278 K to 298 K. However, to use literature values, we compare densities in a slightly wider temperature range (277 K and 298 K). Also, in this study, $w$ at each sample is independent of $T$ because all the samples are prepared at $T = 298$ K. The relative volume change caused by a decrease in temperature from 298 K to 278 K at 1 atm is given as

$$ \frac{\Delta V}{V} = \frac{V(298K) - V(277K)}{V(298K)} = 1 - \frac{\rho(298K)}{\rho(277K)}, $$

where $V(277K)$ and $V(298K)$ are the volumes at 277 K and 298 K, respectively. By using Eqs. (A1) and (A2), we obtain $\Delta V/V \sim 10^{-3}$ as summarized in Table I. Here, $m \sim n$ means the quantities $m$ and $n$ have the same order of magnitude.

Second, we show that the relative volume change caused by the Poynting effect (i.e., the normal stress difference $\gamma \simeq G \gamma^2$ under shear deformation) is negligible. The relative volume change is written as

$$ \frac{\Delta V_{\text{Poy}}}{V} = \frac{N_1}{K} \simeq \frac{G \gamma^2}{K} < 2 \times 10^{-10}, $$

where the applied strain is $\gamma = 0.01$, and the shear and bulk moduli are $G < 40$ kPa and $K > 2$ GPa, respectively. Thus, the volume change due to the Poynting effect is negligible.
effect is negligible than the volume change due to the free thermal expansion ($\Delta V/V \sim 10^{-3}$). Similarly, other volume changes associated with internal pressure changes during shear deformation are negligible because of a sufficiently large bulk modulus ($K > 2$ GPa).

Summary, the free thermal expansion is dominant in the relative volume change, but negligible ($\Delta V/V \sim 10^{-3}$). Thus, we conclude that the experimental condition can be regarded as a constant-volume condition. We give a detailed estimation of the contribution to entropy elasticity by the small volume change in Appendix B.

### Appendix B: Contribution to Entropy Elasticity by Small Volume Changes

In this appendix, we demonstrate that the small volume change due to temperature change (i.e., $\Delta V/V \sim 10^{-3}$ calculated in Appendix A) has a negligible effect on the analysis of entropy elasticity. We consider a compressible elastic body with an external pressure $P$ and an external shear strain $\gamma$. The derivative of the Helmholtz free energy $F$ for a compressible elastic body with an external shear strain $\gamma$ is given by [29]

$$dF = -SdT - PdV + V\sigma d\gamma. \tag{B1}$$

We consider a situation where the only parameters that can be controlled (with constant external pressure $P$) are temperature $T$ and an external shear strain $\gamma$. The infinitesimal volume change is

$$dV = V(T, \gamma)\alpha(T, \gamma)dT + \frac{\partial V(T, \gamma)}{\partial \gamma}d\gamma, \tag{B2}$$

where

$$\alpha(T, \gamma) = \frac{1}{V(T, \gamma)} \frac{\partial V(T, \gamma)}{\partial T} \tag{B3}$$

is a thermal expansion coefficient [29]. Substituting Eq. (B2) into Eq. (B1), we have

$$dF = -(S + PV\alpha)dT + \left(V\sigma - P\frac{\partial V}{\partial \gamma}\right)d\gamma. \tag{B4}$$

Here and hereafter, we omit the variables $(T, \gamma)$, because all physical quantities are bivariate functions of $(T, \gamma)$. By considering $\partial^2 F/\partial T \partial \gamma$, we have the Maxwell relation:

$$-\frac{\partial}{\partial \gamma} \left(S + PV\alpha\right) = \frac{\partial}{\partial T} \left(V\sigma - P\frac{\partial V}{\partial \gamma}\right). \tag{B5}$$

By using $\partial V/\partial T = V\alpha$ and $\partial P/\partial \gamma = 0$ (because $P$ is a constant), Eq. (B5) is rewritten as

$$-\frac{\partial S}{\partial \gamma} = \frac{\partial}{\partial T} \left(V\sigma - PV\alpha\right) + \frac{\partial}{\partial \gamma} \left(PV\alpha\right) + \frac{\partial^2 V}{\partial T \partial \gamma} + P\frac{\partial}{\partial \gamma} \left(V\alpha\right) \tag{B6}$$

$$= V\frac{\partial \sigma}{\partial T} + V\alpha \sigma. \tag{B7}$$

Therefore, the entropy contribution to the stress is

$$\sigma_s(T, \gamma) = -T \frac{\partial S}{\partial \gamma}(T, \gamma) = T \frac{\partial \sigma}{\partial T}(T, \gamma) + T\alpha \sigma. \tag{B7}$$

In Eq. (B7), an additional term $T\alpha \sigma$ is added to Eq. (1), as a result of taking into account the volume change.

We compare $T\alpha \sigma$ with $T\partial \sigma/\partial T$ in Eq. (B7). The ratio is

$$\frac{T\alpha \sigma}{T \frac{\partial \sigma}{\partial T}} \sim \alpha \Delta T \frac{\sigma}{\Delta \sigma} \sim 10^{-2}, \tag{B8}$$

where $\alpha \Delta T \sim \Delta V/V \sim 10^{-3}$ (see Appendix A) and $\sigma/\Delta \sigma \sim 10$ (see Fig. 4a). Here, $m \sim n$ means the quantities $m$ and $n$ have the same order of magnitude. Equation (B8) shows that the additional term $T\alpha \sigma$ caused by the volume change only affects the entropy elasticity by a few percent.

We note that the negligible effect of volume change on the temperature dependence of the shear stress (and shear modulus) of the gel is consistent with the absence of thermoelastic inversion, as shown in Fig. 4a). Here, the thermoelastic inversion is an inversion of the temperature dependence of stress in the low strain region caused by thermal expansion, and observed in various synthetic and natural rubbers [1, 5].

### Appendix C: Control of the connectivity

To obtain tetra-PEG gels with different values of connectivity $p$ after completion of the chemical reaction, we nonstoichiometrically mixed the two kinds of precursor solutions in weight fractions of tetra-PEG-MA to all precursors $q_w$. Here, $p$ ($0 \leq p \leq 1$) is the fraction of the reacted maleimide and thiol groups. Assuming that almost all the minor terminal groups react, we have [21]

$$p = \begin{cases} 2q_{w, \text{MA}} & \text{for } 0 \leq q \leq 1/2, \\ 2(1-q) q_{w, \text{SH}} & \text{for } 1/2 \leq q \leq 1. \end{cases} \tag{C1}$$
The dimensionless structural parameters $\nu$, $\mu$, and $\xi$ cannot be experimentally observed but can be theoretically estimated as a function of connectivity $p$ by using the Bethe approximation \[D2\] (also called the tree approximation \[D1\] and the mean-field approximation \[D3\]). The number per precursor of the elastically effective cycles $\xi$ is obtained by $\xi = \nu - \mu$, where $\nu$ and $\mu$ are the numbers per precursor of elastically effective chains and crosslinks, respectively. Here, the elastically effective chain is defined as the chain whose both ends connect to crosslinks.

FIG. 8. Comparison between the experimentally obtained $g = g(p,c/c^*)$ (defined in Eq. \[12\]) and the dimensionless structure parameter $\xi = \nu - \mu$. Here, $\nu$ and $\mu$ are the numbers per precursor of elastically effective chains and crosslinks, respectively. We calculate $\nu$, $\mu$, and $\xi$ using the the Bethe approximation with $p$ estimated from Eq. \[C1\]. We determine $g$ from the data in Fig. 5a with Eq. \[12\]. Each symbol represents one sample that is characterized by the molar mass $M$, the concentration $c$, and the connectivity $p$. The blue diamonds, red circles and black squares represent diamonds, red circles and black squares represent $20, 10$, and $20$ kg/mol, respectively. The green line represents $g = 2.4 \xi$. The four blue diamonds enclosed by the gray curve represents the samples with the lowest normalized polymer concentrations ($c/c^* \approx 0.5$) in this experiment. They deviate from the green line because they have many elastically ineffective connections such as the intramolecular bonds and loops \[D4\], which causes overestimation of $\xi$.

where $p_{MA}$ and $p_{SH}$ are the terminal functionalization fractions of tetra-PEG-MA and tetra-PEG-SH, respectively. Here, $q$ is the molar fraction of tetra-PEG-MA to all precursors and is determined from $q_w$ with consideration of the molecular weight distributions and functionalities of the precursors. Further details of this method are described in Ref. \[D4\].

Appendix D: Bethe approximation to calculate the structural parameters

We compare $\xi(p) = \nu(p) - \mu(p)$ with $g = g(p,c/c^*)$ defined in Eq. \[12\]. Figure 8 shows $g(p,c/c^*) \approx 2.4 \xi(p)$. In the semi-dilute regime $(c/c^* > 1)$, it was reported \[D4\] that the $p$ dependence of $G$ is well reproduced by $G(p) \sim \xi(p)$. Equation \[12\] with $g(p,c/c^*) \approx 2.4 \xi(p)$ leads to $G(p) \sim \xi(p)$ \[D4\]. However, the entropy contribution obtained in this study, $G_S = cR\xi(p)T/M$, is $2.4$ times as large as $G_S^{\text{phantom}} = cR\xi(p)T/M$ that is predicted by the phantom network model \[D3\].

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