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Examination of the Theories of Rubber Elasticity Using an Ideal Polymer Network

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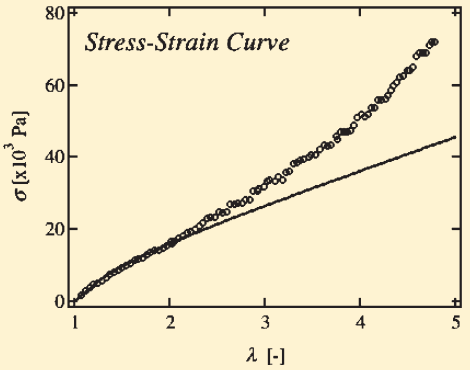
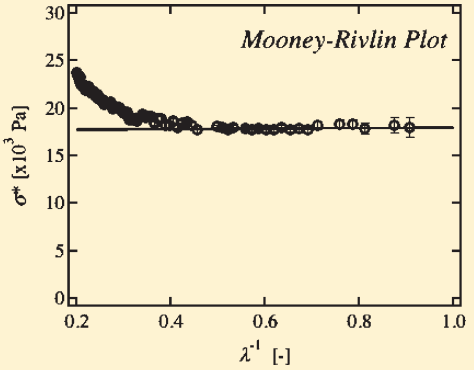
Supporting Information

ABSTRACT:





We evaluate the homogeneity of Tetra-PEG gel and examine the models predicting rubber elasticity. Infrared spectroscopy revealed the near absence of dangling chains. Concentration dependence of the number of elastically effective chains revealed the near absence of elastically ineffective loops and the validity of the phantom network model. These data suggest that Tetra-PEG gel is close to an ideal polymer network and that the phantom network model is the true model describing the contribution of the chemical cross-link to the rubber elasticity of a swollen polymer network.

INTRODUCTION

Polymeric materials are indispensable in our life. In spite of such importance, a basic understanding of the molecular model of polymeric materials, especially with regard to the rubber elasticity of polymer networks, has never been fully established. This is partially because polymer networks inherently have a substantial number of inhomogeneities in their structures, including connectivity (dangling chains, elastically ineffective loops), topological (trapped entanglement), and spatial (inhomogeneous distribution of polymer segments) inhomogeneities.[1] Because of the lack of universal methods controlling these inhomogeneities, we have no universal design guide for fabricating the polymeric materials with required mechanical properties. In addition, the determination of the true model describing the rubber elasticity of polymer networks with intrinsic parameters remains to be achieved.[2−5] This is because of the absence of an "ideal polymer network", that is, one free from any inhomogeneities. Thus, it is one of the ultimate goals in the research field of polymer science to realize an "ideal polymer network".

Recently, we succeeded in forming a near-ideal polymer network known as Tetra-PEG gel,[6] which is formed by A−B type cross-end coupling of two tetra-arm poly(ethylene glycol) (PEG) units that have mutually reactive amine (TAPEG) and activated ester (TCPEG) terminal groups (Tetra-PEG units). Previous analyses demonstrated that Tetra-PEG gel is free from spatial inhomogeneities and is a possible candidate for an ideal polymer network.[7,8] Owing to its homogeneity, it has high transparency (∼100%), high deformability (∼900%), and high breaking strength (∼30 MPa).[9]

In this paper, we tried to determine which model would best predict the contribution of the chemical cross-link to rubber elasticity using Tetra-PEG gel. First, we reevaluated and confirmed the homogeneities of Tetra-PEG gel, and we then compared the elasticity of Tetra-PEG gel with theoretical predictions.

EXPERIMENTAL PROCEDURE

Synthesis of Tetra-PEG Modules. Tetra-amine-terminated PEG (TAPEG) and tetra-NHS-glutarate-terminated PEG (TNPEG) were

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prepared from tetrahydroxyl-terminated PEG (THPEG) having equal arm lengths. Here, NHS stands for *N*-hydroxysuccinimide. The details of TAPEG and TNPEG preparation were reported previously.[6] The molecular weights (M_w) of TAPEG and TNPEG were matched to each other (M_w = 20 kg/mol).

Characterization of Tetra-PEG Modules. The molecular weight (M_w) and the functionality of a Tetra-PEG module were estimated by ^{1}H NMR measurements. ^{1}H NMR spectra were obtained on a JEOL JNM-AL (300 MHz) or JEOL Alpha series (500 MHz) spectrometer with tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent. The polydispersity was determined using a gel permeation chromatography (TOSOH HLC-8220) system equipped with two TSK gel columns (G4000HHR and G3000HHR). The columns were eluted with DMF containing lithium chloride (10 mM) with a flow rate of 0.8 mL/min at 40 °C. The molecular weights were calibrated with poly(ethylene glycol) standards (Polymer Laboratories, Ltd., Church Station, UK).

Fabrication of Tetra-PEG Gels. Constant amounts of TAPEG and TNPEG (40−140 mg/mL) were dissolved in phosphate buffer (pH 7.4) and phosphate−citric acid buffer (pH 5.8), respectively. The corresponding initial polymer volume fractions, φ_0, were in the range between 3.40×10^{-2} and 1.10×10^{-1} (mass density = 1.129 g/cm^3). To control the reaction rate, we adjusted the ionic strengths of the buffers to be 50 mM for lower polymer concentrations (40−80 mg/mL) and 100 mM for higher polymer concentrations (100−140 mg/mL). Two solutions were mixed, and the resulting solution was poured into the mold. We allowed at least 12 h for the completion of the reaction before the following experiment was performed.

Infrared (IR) Measurement. Tetra-PEG gels were prepared as cylinder shapes (height: 10 mm; diameter: 20 mm). Prepared gel samples were soaked in H_2O for 3 days at room temperature and then dried. Dried gel samples were cut into thin films (thickness: 20 μm) using a Microtome (SM2000R, Leica). IR spectra of dried gel samples were obtained at 25°C by using a IR spectrophotometer equipped with a MCT detector (Nicolet 6700 FT/IR, Thermo Scientific), in which 128 scans were coadded at a resolution of 4 cm^{-1} for samples. More than two samples were tested for each network concentration.

Stretching Measurement. The stretching measurement was carried out on the dumbbell-shaped films using a mechanical testing apparatus (Rheo Meter: CR-500DX-SII, Sun Scientific Co.) at a cross-head speed of 0.1 mm/s. The gel samples were used in the as-prepared state. Each specimen was stretched and released repeatedly two times, and the reproducibility of the results was confirmed. More than 10 samples were tested for each network concentration, and the observed moduli were arithmetically averaged.

RESULTS AND DISCUSSION

Reaction Efficiency (*p*): IR Measurement. Generally, it is difficult to estimate the conversion of a gelation reaction (p). NMR measurements do not work well in gel systems because NMR spectra become broadened for gels. An example of the NMR spectrum of Tetra-PEG gel is shown in Supporting Information Figure 1. It was difficult to estimate p from this NMR spectrum. One of the most conventional methods to estimate p is to use the theory of treelike structures, in which we can estimate p from the sol fraction.[10,11] However, it is widely known that this method underestimates p, especially in a dilute system.[12,13] In our previous study, we measured the sol fraction and estimated $p \sim 0.75$, which was smaller than those of other polymer network systems.[2,11] We tried to directly revaluate the p using IR spectroscopy, as IR spectra are not affected by the topological structure of a polymer network. Figure 1a shows an

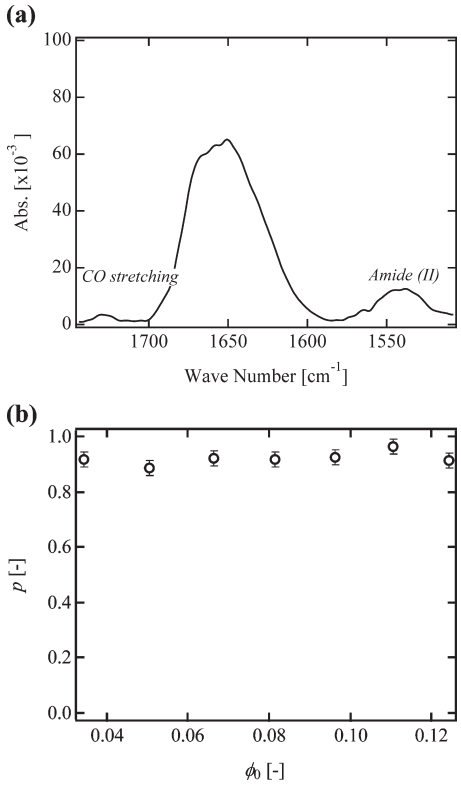

Figure 1. (a) IR spectrum of dried Tetra-PEG gel (φ_0 = 0.096). (b) Reaction efficiency (p) as a function of initial polymer fraction (φ_0).

example of an IR spectrum (φ_0 = 0.096). The reaction conversion was estimated from the peak area of CO stretching (1725 cm^{-1}) and that of amide (II) (1545 cm^{-1}) as follows:

$$p = \frac{S_{\mathrm{amide(II)}}}{S_{\mathrm{amide(II)}} + 1.36 S_{\mathrm{CO}}} \quad (1)$$

where $S_{\mathrm{amide(II)}}$ and S_{CO} are the peak area of amide(II) and CO stretching, respectively. The ratio of the molar absorbance coefficient of CO stretching to amide(II) was estimated to be 1.00:1.36 in advance (Supporting Information Figure 2). The variation of p against φ_0 is shown in Figure 1b. The value of p was almost constant and was close to 0.9, which was extremely high, given that the functionality of the terminal conversion ratio was around 0.95. These results suggest the near absence of dangling chains in Tetra-PEG gel and the molecular weight between neighboring cross-links being $\sim 1 \times 10^4$ g/mol.

Trapped Entanglements: Mooney−Rivlin Plotting. We next focused on the models predicting the stress−strain relationship of polymer networks. In the original theory of rubber elasticity proposed by Flory, the relationship between nominal stress (σ) and nominal strain (λ) of rubbery materials is given by[14]

$$\sigma = G(\lambda - \lambda^{-2}) \quad (2)$$

where G is the elastic modulus. The material, the stress−strain relationship of which is represented by eq 2, is called the incompressible neo-Hookean material. When σ^* ($= \sigma / (\lambda - \lambda^{-2})$) is plotted against λ^{-1} (Mooney−Rivlin plot), eq 2 is shown as a flat line. Note that the The Flory theory does not take into account of trapped entanglement. As a result, σ^* in a Mooney-Rivlin plot is independent of λ^{-1}.

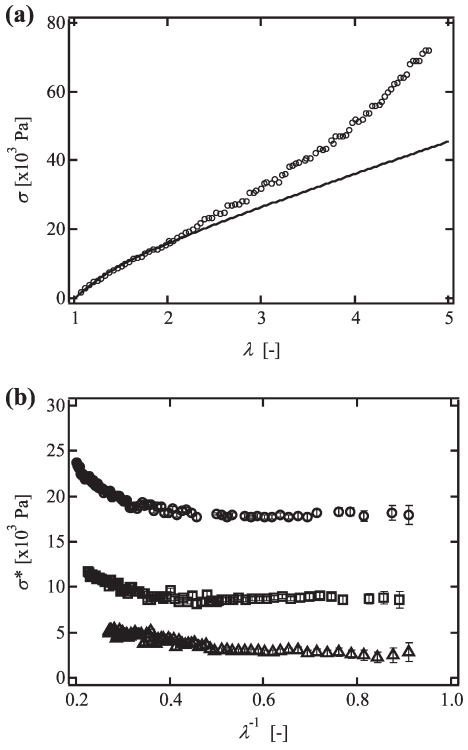

Figure 2. (a) Stress−strain relationship of Tetra-PEG gel ($\varphi_0 = 0.066$). The solid line is the fitting result of eq 2. (b) Mooney−Rivlin plot of Tetra-PEG gel. Circles: $\varphi_0 = 0.034$; squares: $\varphi_0 = 0.066$; triangles; $\varphi_0 = 0.096$.

The stress−strain relationship of Tetra-PEG gel ($\varphi_0 = 0.066$) is shown in Figure 2a. The solid line is the fitting result of eq 2 for the low strain region ($1 < \lambda < 1.2$). Surprisingly, the relationship between σ and λ was well described by eq 2 in a wide range ($1 < \lambda < 2$), showing the incompressible neo-Hookean material behavior, and then deviated upward from the prediction of eq 2. It should be noted that the stress−strain relationship of conventional polymer networks fabricated so far deviates downward from the prediction of eq 2 because of the presence of trapped entanglements. As a typical stress−strain relationship, the result of natural rubber is shown in Supporting Information Figure 3. The correspondence with eq 2 suggests the near absence of trapped entanglements in Tetra-PEG gel. This correspondence is also clearly shown in the Mooney−Rivlin plot (Figure 2b); σ^* did not depend on λ ($G = 0$) in the range $0.5 < \lambda^{-1} < 1$. As far as we know, the λ-independent σ^* was previously observed only in a model network system, in which the degree of polymerization between neighboring cross-links was extremely small ($\approx$12)[15] and equilibrium-swollen polymer networks.[16] Therefore, this is the first observation of λ-independence of σ^* in polymer networks in as-prepared state.

The Mooney−Rivlin plot of natural rubber shows the strong upturns in the ranges $\lambda^{-1} < 0.2$ and $0.5 < \lambda^{-1} < 1$ due to strain-induced crystallization and trapped entanglements, respectively (Supporting Information Figure 4). It is noteworthy that there was little effect of trapped entanglements for Tetra-PEG gels, of which the initial polymer fraction (φ_0) was far above the critical overlapping concentration of Tetra-PEG units ($\varphi^* \approx 0.04$). The near absence of trapped entanglements was attributed to the impenetrable spherelike behavior of Tetra-PEG units above the φ^* previously shown in small-angle neutron scattering (SANS) measurements.[7] At this stage, we can treat Tetra-PEG gel as a polymer network that is practically free from spatial inhomogeneities, dangling chains, and trapped entanglements; only the contribution of elastically ineffective loops (EIL), in which chains are connected to the macroscopic body but do not deform with the macroscopic body, needs to be investigated.

Elastically Effective Chains. Many models predicting the contribution of trapped entanglements to rubber elasticity have been proposed.[4,17−25] However, in general, it is difficult to evaluate the model describing the contribution of trapped entanglements because the stress−strain relationship obtained from experiments inevitably contains the contributions of both trapped entanglements and chemical cross-links, which cannot be separated. The determination of the model predicting the contribution of chemical cross-links is also difficult for the same reason. To evaluate the models describing rubber elasticity, we should first evaluate the model predicting the contribution of chemical cross-links using an ideal polymer network free from any inhomogeneities. Therefore, we tried to evaluate the EIL of Tetra-PEG gel and verified the validity of models predicting the contribution of chemical cross-links to rubber elasticity.

There are three conventional models describing the contribution of chemical cross-links to rubber elasticity. First, in the affine network model, which is the original model proposed by Flory, G is given by[14]

$$G_{\mathrm{Af}} = \nu RT \tag{3}$$

where ν is a molar concentration of elastically effective chains (EEC), R is the gas constant, and T is the absolute temperature. EEC is defined as the chains both ends of which are connected to the active cross-links. The affine network model assumes that cross-links are firmly connected to the elastic body, and EECs deform in the same manner with the macroscopic body.

James and Guth proposed the phantom network model, in which G is given by[26]

$$G_{\mathrm{Ph}} = \left(1 - \frac{2}{f}\right)\nu RT = (\nu - \mu)RT = \xi RT \tag{4}$$

where f is the functionality of cross-links, μ is the molar concentration of chemical cross-links, and ξ is a molar concentration of an independent circuit in the network. The phantom network model assumes that cross-links fluctuate, and EECs are loosely connected to the elastic body and deform less than the macroscopic body.

A third model is the junction affine network model, which predicts the intermediate value as follows:[20,27]

$$G_{\mathrm{JA}} = (\nu - h\mu)RT \tag{5}$$

where h is a constant indicating the thermal fluctuation of chemical cross-links. In these models, the values of ν and ξ are calculated from p according to the theory of treelike structures.[10,28]

We estimated the molar concentration of elastic elements in Tetra-PEG gel (ν_{el}) defined by

$$G = \nu_{\mathrm{el}} RT \tag{6}$$

The variation of ν, ξ, and ν_{el} against φ_0 is shown in Figure 3.

ν and ξ calculated from p increased linearly with an increase in φ_0, reflecting the constant p. In addition, ν_{el} estimated from G also increased linearly with an increase in φ_0. ξ and ν_{el} corresponded well with each other and were approximately half

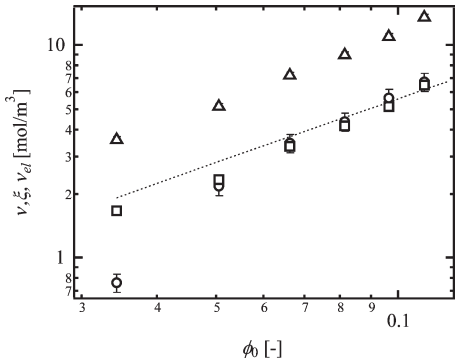

Figure 3. The value of ν_{el} (circles) estimated from the stretching measurement as well as ν (triangles) and ξ (squares) estimated from the reaction efficiency (p) as a function of φ_0. The dashed line is the guide showing the relationship $\nu \sim \varphi_0$.

of ν. This result is easily expected for the perfect 4-functional network ($f = 4$) according to eqs 3 and 4, i.e., $\xi = \nu/2$. Here, we discuss the remaining inhomogeneity in Tetra-PEG gel, the EIL. Because EIL do not bear the load, the presence of EIL decreases the ν_{el} from the theoretical prediction (ν or ξ). To account for the experimental results, we made the following two hypotheses: (i) Tetra-PEG gel is free from EIL, and its elasticity is well described by the phantom network model, and (ii) Tetra-PEG gel has a large amount of EIL, and its elasticity is described by the affine network model or the junction affine network model. In principle, EIL increase with a decrease in φ_0, especially near the φ^*, because the probability of intramolecular reaction increases with a decrease in φ_0.[29] Therefore, if a large amount of EIL exists in the network, ν_{el} should deviate downward from ν or ξ with a decrease in φ_0. In contrast, the experimental result shows the correspondence between ν_{el} and ξ in the wide range ($0.05 < \varphi_0 < 0.11$). The downward deviation of ν_{el} from ξ was observed only around and below φ^* ($\approx$0.04), suggesting the loop formation. These data strongly suggest the validity of hypothesis (i). The near absence of EIL may be attributed to the A−B type cross-to-end coupling, eliminating the self-biting reaction. Again, these data strongly suggest the near absence of EIL in the semidilute condition ($0.05 < \varphi_0 < 0.11$) and the validity of the phantom network model.

CONCLUSION

The results are summarized as follows: (1) in Tetra-PEG gel, there were only a few dangling chains, trapped entanglements, and elastically ineffective loops; (2) the elasticity of Tetra-PEG gel was well described by the phantom network model. Taken together, these conclusions indicate that Tetra-PEG gel is close to an ideal polymer network and that the phantom network model is the model describing the contribution of chemical cross-links to rubber elasticity. It should be noted that these results were obtained from highly swollen polymer networks in dilute or semidilute regions. In dilute or semidilute regions, the interactions between polymer chains become weaker than those in concentrated regions. Therefore, the phantom network theory may not be applicable for the elasticity of concentrated polymer networks.

To examine the models of rubber elasticity in a concentrated region, we need to overcome at least two problems. First, the polymer networks prepared in a concentrated region tend to have a large amount of trapped entanglements. We need to develop a novel method to avoid the formation of trapped entanglements. Second, although we can prepare the concentrated polymer networks free from entanglements by shrinking the Tetra-PEG gel formed in semidilute regions, such polymer networks have the supercoiled network structure. We need to understand the effect of the supercoiling on rubber elasticity. This effect will be reported in a forthcoming paper.

In this paper, we for the first time confirmed the validity of the phantom network model using a near-ideal polymer network. These data also suggest that the theory of rubber elasticity based on the phantom network model correctly describes the contribution of chemical cross-links to the rubber elasticity of swollen polymer networks. Further investigation on the contribution of trapped entanglements will determine the true theory of rubber elasticity of swollen polymer networks.

ASSOCIATED CONTENT

Supporting Information. NMR spectra of Tetra-PEG gel, IR spectrum of tetra-amide-terminated PEG and tetra-COOH-terminated PEG, stress−strain curve of natural rubber, and Mooney−Rivlin plot of stress−strain curve of natural rubber; experimental procedures of NMR spectra, IR measurement, and stretching measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Author Contributions

[⊥]These authors contributed equally to this work.

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