

Novel Cross-Linking Concept of Polymer Network: Synthesis, Structure, and Properties of Slide-Ring Gels with Freely Movable Junctions

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ABSTRACT: We have recently developed a novel type of gel called the *slide-ring gel* or *topological gel* that is different from physical and chemical gels by using the supramolecular architecture with topological characteristics. In this gel, polymer chains with bulky end groups exhibit neither covalently cross-links as in chemical gels nor attractive interactions as in physical gels but are topologically interlocked by figure-of-eight cross-links. Hence, these cross-links can pass along the polymer chains freely to equalize the tension of the threading polymer chains similarly to pulleys; this is called the *pulley effect*. The slide-ring gel is a new cross-linking concept for the polymer network as well as a real example of a slip-link model or sliding gel, which was previously considered only theoretically. In this study, we review the synthesis, structure, and mechanical properties of the slide-ring gels with freely movable cross-linking junctions based primarily on our recent studies. The pulley effect of the slide-ring gels has been recently confirmed by mechanical measurements, small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), quasi-elastic light scattering (QELS), etc. This concept can be applied to not only gels but also to a wide variety of polymeric materials without solvents. [doi:10.1295/polymj.PJ2006239]

KEY WORDS Slide-Ring Gel / Pulley Effect / Polyrotaxane / Cross-Link / Stress-Strain Curve / Small Angle Scattering /

Since the discovery of cross-linking in natural rubber with sulfur in 1839 by Goodyear, the cross-linking of polymeric materials has become one of the most important topics in polymer science and technology.^{1,2} Uncross-linked natural rubbers or elastomers inherently resemble liquids with regard to their flow behavior, although they exhibit viscoelastic properties based on the entanglement of polymer chains. If cross-linked, they behave like solids to maintain their shape against deformation above the glass temperature. Thus far, the unique mechanical behavior of cross-linked polymeric materials has been investigated by many researchers. Kuhn and Mark assumed the affine deformation of cross-linking junction points and a Gaussian random chain between cross-links in order to explain the stress-strain curves of the cross-linked polymeric materials; this is called the fixed junction model.^{2,3} Since then, this simple assumption has been reconsidered by Guth and James,⁴ Flory,⁵ Edwards⁶ and so on. For example, Guth and James took into account the fluctuation of the cross-linking junctions, which is referred to as the phantom network model.⁴ However, some experimental results obtained from small-angle neutron scattering (SANS) supported the affine deformation of the fixed junction model rather than the phantom network model.^{7,8}

Another important factor of rubber elasticity arises from the entanglement effect.^{9–11} Edwards *et al.* proposed the slip-link model in which the chain can slip at a trapped entanglement depending on the elongation.¹² Such an entanglement reduces the conformational entropy of the chains somewhat but not as much as the reduction caused by chemical cross-links; hence, it affects the rubber elasticity. The slip-link model is now widely used in computer simulations of the viscoelastic behavior for uncross-linked and cross-linked polymeric materials. It is well known that the entanglement effect is described effectively by the tube model or reptation model developed by de Gennes,⁹ Edwards, and Doi¹⁰ in the 1970s, in which each chain is assumed to move along the tube due to constraints imposed by surrounding chains.

When cross-linked polymeric materials are immersed in a good solvent, they absorb the liquid solvent until the swelling force associated with the mixing entropy between the chains and the solvent balances the elastic force of the chains between junction points. These cross-linked polymeric systems containing the solvent are called chemical gels.¹³ The swelling behavior of the chemical gels was explained in detail by Flory and Rehner.⁵ On the other hand, Tanaka discovered the volume phase transition

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of the chemical gels, in which the swelling and shrinking behaviors exhibit discontinuous profiles with hysteresis.^{14,15} This novel discovery regarding the cross-linked polymeric materials has attracted considerable interest from researchers in the field of polymer science. As a result, some interesting aspects of the chemical gels have been discovered one after the other; these aspects include the kinetics of the volume phase transition by Tanaka and Fillmore,¹⁶ the frozen or fixed inhomogeneous structure of the chemical gels by Shibayama,¹⁷ and the abnormally small friction behavior of gels by Gong and Osada.^{18–24} In addition, various new types of gels have been developed thus far. For example, Gong and Osada developed a double network gel having a high modulus up to the sub-megapascal range with a failure compressive stress as high as 20 MPa.^{25–30} The double network gel has both soft and hard components so as to avoid fracture as in the case of biomaterials. Furthermore, Yoshida incorporated a dissipative system into gels to realize a self-oscillating gel device^{31–34} and also reported comb-type grafted hydrogels showing a rapid de-swelling response to temperature changes.^{35,36}

All gels are classified into two categories: chemical gels and physical gels.¹³ Physical gels have noncovalent cross-linking junctions arising due to ionic interaction, hydrophobic interaction, hydrogen bonding, microcrystal formation, helix formation and so on. In general, these noncovalent cross-links are not as strong as the covalent cross-links in chemical gels, and the physical gels show a sol-gel transition response to temperature, pH, and solvent. The mechanical behavior of the physical gels is complex because the recombination of cross-linking points occurs on deformation; hence, the affine deformation is not validated in the physical gel. The recombination causes hysteresis in the stress-strain curve of the physical gel, which means that it cannot regain its original shape from the deformed one as quickly as the chemical gel. Haraguchi *et al.* have recently developed a novel type of gel called the nano-composite gel, which has clay as the cross-linking junction.^{39,40} Polymer chains of *N*-isopropyl acrylamide strongly absorb onto the clay surface at both ends, thus bridging different clays. Surprisingly, the nano-composite gel shows high stretchability up to 10 times its original length. This suggests that the structures of the cross-linking junctions play an important role in determining the mechanical properties of polymeric materials.

Another recently approach for the polymer network structure has been developed using polyrotaxane in the supramolecular chemistry. Supramolecules and their topological characteristics have attracted considerable interest.^{41–43} A typical example is that of rotaxanes, in which cyclic molecules are threaded on a sin-

gle polymer chain and trapped by capping the chain with bulky end groups.^{44–48} Ogino reported the first rotaxane using cyclodextrin (CD) as the ring molecule.⁴⁹ CDs are cyclic oligosaccharides comprising six, seven, or eight glucose units with inner diameters of 0.44, 0.58, or 0.74 nm, respectively, that are called α -, β -, or γ -CDs in that order.^{41,50,51} As compared to other cyclic molecules, CDs are readily available in both high purities and large quantities and can be modified with various functional groups. The most important feature of CDs is their amphiphilic property: CDs have hydrophobic inside and hydrophilic outside. Therefore, water-soluble CDs tend to include small hydrophobic molecules in their cavities, which is called the inclusion complex formation. In 1990, Harada and Kamachi reported the first synthesis of pseudo-polyrotaxane in which many α -CD molecules are threaded on a single polymer chain of polyethylene glycol (PEG):⁵² CDs mixed with PEG in water were threaded onto a PEG self-assembly. Subsequently, in 1992, both the ends of the pseudo-polyrotaxane were capped with bulky groups to form polyrotaxane.⁵³ In recent years, this novel architecture in supramolecular chemistry has attracted great attention as a new technique for developing functional polymeric materials.^{44–48,54–73}

The first report of a physical gel based on the polyrotaxane architecture was also presented by Harada *et al.*:⁵⁴ When α -CDs were mixed with long PEG chains at a high concentration in water, sol-gel transition occurred due to hydrogen bonding between the α -CDs threaded on the PEG chains in different pseudo-polyrotaxanes. In addition, Yui and coworkers formed some hydrogels using biodegradable CD polyrotaxane⁵⁶ as the cross-linker for use in regenerative medicine.⁶¹ The biodegradable polyrotaxane has a hydrolysis part, namely, an ester bond between a bulky end group and the polymer axis. Consequently, the erosion time of the biodegradable hydrogel strongly depends on its polyrotaxane content. Furthermore, Takata *et al.* synthesized recyclable cross-linked polyrotaxane gels: topologically networked polyrotaxane capable of undergoing reversible assembly and disassembly based on the concept of dynamic covalent bond chemistry.^{45,48,73} They cross-linked poly(crown ether)s with dumb-bell-shaped axle molecules, which show a reversible cleavage of the disulfide bond. As a result, a novel reversible cross-linking/decross-linking system that could recycle networked polymeric materials was realized.

We have recently developed another cross-linking structure based on the polyrotaxane architecture.⁶⁸ We prepared polyrotaxane sparsely containing α -CD and subsequently cross-linked α -CDs on different polyrotaxanes. As a result, the cross-linking junctions

of the figure-of-eight shapes are not fixed at the PEG chains and can move freely in the polymer network. We refer to this new cross-linked polymer network as a *slide-ring material*. Such a polymeric material with freely movable cross-links was theoretically considered as a sliding gel by de Gennes in 1999.⁷⁴ In addition, the historical significance of the slide-ring materials or gels was reviewed comparing them with the slip-link model by Granick and Rubinstein.⁷⁵ In this study, we provide an overview of the general features, synthesis, structure, and mechanical properties of the slide-ring gels. It is noteworthy that the concept of freely movable cross-links is not limited to within the slide-ring gel containing some solvents but can also be applied to slide-ring polymeric materials without solvents. As mentioned later, it is clear that the freely movable cross-link drastically changes the mechanical properties of polymeric materials. This may bring about a paradigm shift in the cross-linked polymeric materials since they were first discovered by Goodyear.

PULLY EFFECT OF SLIDE-RING MATERIALS

As mentioned earlier, all gels are categorized into physical and chemical gels according to their network junctions.¹³ The physical gel has noncovalent cross-links so that it can be easily liquefied at high temperature or in a good solvent. On the other hand, the chemical gel with covalent cross-links is more stable than the physical gel, and therefore, it is used in many applications such as soft contact lens and so on. However, the chemical gel generally has a large inhomogeneous structure due to the gelation process, which considerably reduces the mechanical strength. In the chemical gel, long polymer chains are divided into shorter pieces of different lengths by fixed cross-links. As a result, the tensile stress is concentrated on the shortest chains, thereby breaking down the chemical gel easily.

To resolve this problem of the chemical gels, we have recently developed the slide-ring gel having freely movable cross-links based on the supramolecular architecture and the topological characteristics, as mentioned earlier (Figure 1).⁶⁸ In the slide-ring gel, the polymer chains with bulky end groups exhibit neither covalently cross-links as in chemical gels nor attractive interactions as physical gels but are topologically interlocked by figure-of-eight cross-links. Therefore, the figure-eight-shaped cross-links can pass along the polymer chains freely in order to equalize the tension of the threading polymer chains in a manner similar to pulleys; this is called the *pulley effect*.⁶⁸

Figure 2 schematically shows a comparison between the chemical and slide-ring gels on tensile de-

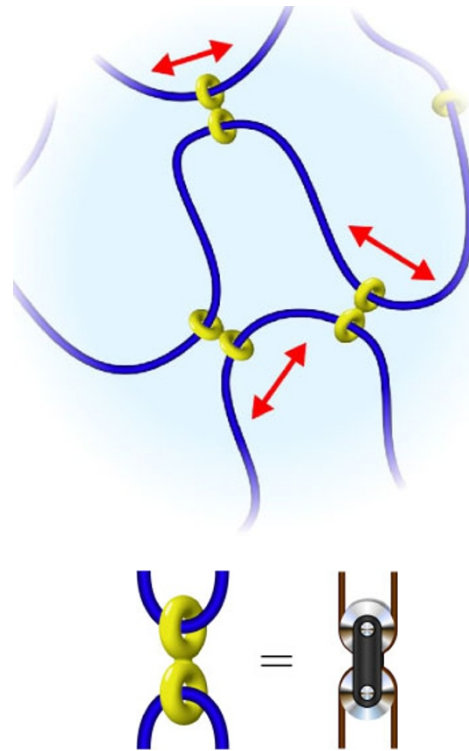


Figure 1. Schematic diagrams of slide-ring materials with freely movable figure-of-eight crosslinks acting like pulleys.

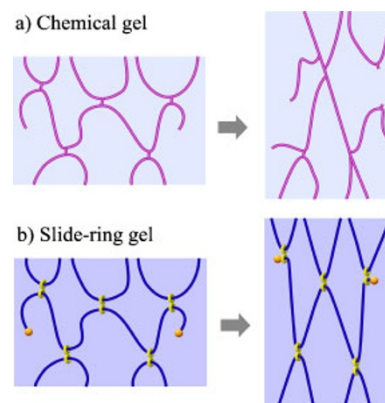


Figure 2. Schematic comparison between chemical and slide-ring gels. The pulley effect in the slide-ring gel disperses the tension in the polymer chains automatically on tensile deformation while the tensile stress concentrates on short chains in the chemical gel.

formation.⁶⁸ The polymer chains in the chemical gel are gradually broken due to the heterogeneous polymer length between the fixed cross-links. On the other hand, the polymer chain in the slide-ring gel can pass through the figure-of-eight cross-links acting as pulleys. It is noteworthy that the equalization of tension can occur not only in a single polymer chain but also among adjacent polymers interlocked by the figure-of-eight cross-links. As a result, the slide-ring gel shows a high stretchability of up to 24 times in length, and a large volume change of up to 24,000 times in weight.

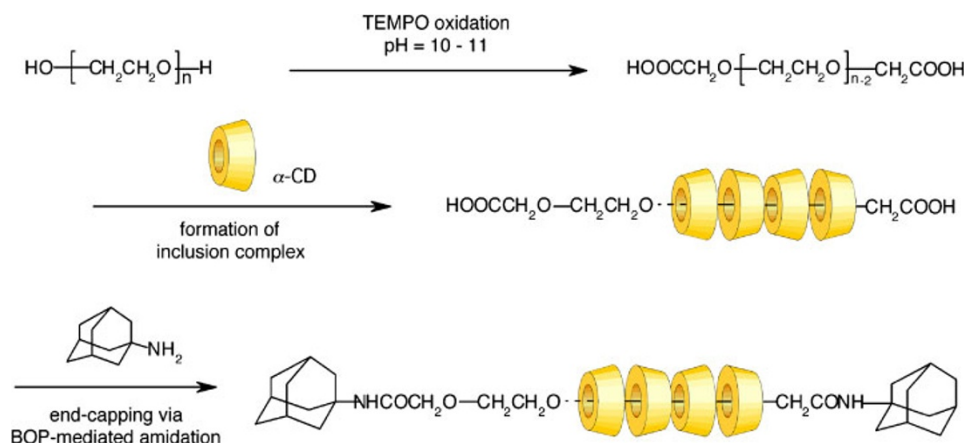


Figure 3. The high-yield synthesis scheme of polyrotaxane of PEG and α -CD capped at both the ends with adamantane.

Furthermore, the pulley effect is expected to yield various unique properties of the slide-ring gel that are different from the chemical gel, as mentioned later.

SYNTHESIS OF SLIDE-RING MATERIALS

The first slide-ring gel was synthesized by Okumura and Ito.⁶⁸ We used diamino-terminated PEG (PEG-DAT) with a molecular weight of 20,000 as the axis of the polyrotaxane because PEGs having larger molecular weights form sparse inclusion complexes with α -CD. The average molecular weight of the polyrotaxane was determined to be 82,000 by ^1H nuclear magnetic resonance (NMR) and ultraviolet spectroscopy, which indicated that 64 α -CD units were captured in the polymer chain. The polymer chain can hold a maximum of about 230 α -CD units if the α -CDs are densely packed; the inclusion ratio is equal to 28%. There are more than a thousand hydroxyl groups on the α -CDs contained in the polyrotaxane, while the axis of bis(2,4-dinitrophenyl)-PEG (PEG-DNB2) has no hydroxyl groups. By intermolecular cross-linking of the α -CDs contained in the polyrotaxanes, a transparent gel was obtained. Such a gel was not formed by the cross-linking of the mixture of PEG-DNB2 and α -CD in the same composition as that of the polyrotaxane under the same conditions. Furthermore, we treated the slide-ring gel with a strong base (1 N NaOH) at 50 °C so as to remove the bulky stoppers (dinitrophenyl groups) at each end of the polyrotaxanes and observed a sharp liquefaction of the gel after 7 h.⁶⁸ This indicates the first evidence of the movable cross-links; thus, the polymer network in the gel is maintained by the topological restrictions and not by the chemical cross-links.

Araki and Ito have recently developed a new method for the synthesis of sparse polyrotaxane with a minimum number of reagents and an easy, one-step, high-yield preparation method for PEG-COOH of

any molecular weight with a high degree of modification by using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) mediated oxidation, as shown in Figure 3.⁷⁶ TEMPO oxidation yields a carboxyl content of higher than 95% in PEG-COOH by the conversion of the terminal hydroxyl groups. The preparation of the polyrotaxane from PEG-COOH was further investigated by comparing it to that from PEG-DAT. The PEG-based yield of the combination of PEG-COOH and 1-adamantanamine used as a capping agent ranged from 91% to 98%, which is much higher than that of PEG-DAT. These novel improvements result in the high-yield production of polyrotaxanes at low cost and can potentially be applied for large-scale manufacture of polyrotaxanes that can be used in prospective applications.

Yui *et al.* have controlled the amount of α -CDs in the polyrotaxanes containing PEG by using a mixture of dimethyl sulfoxide (DMSO) and water during the inclusion complex formation.^{70,72} The solvent has a significant influence on the inclusion ratio of α -CDs in the polyrotaxanes. Recently, Hadziioannou *et al.* changed the time, temperature, and initial ratio of α -CD to PEG having a molecular weight of 20,000 and indicated that the inclusion ratio varied from 3 to 125.⁷⁷ It was found that very sparse pseudo-polyrotaxanes were formed at a high temperature, while the threaded α -CD acted like a nuclei with a favorable driving force for the final inclusion complex at a lower temperature.

SCATTERING STUDIES OF SLIDE-RING GELS

The slide-ring gels have remarkable physical properties such as high extensibility. In order to elucidate the physical picture and properties, slide-ring gels and pregel solutions were investigated by SANS, small-angle X-ray scattering (SAXS), and quasi-elastic light scattering (QELS).

Shibayama *et al.* measured the SANS of sparse polyrotaxanes and investigated sol-gel transition using solvents of deuterated DMSO (d-DMSO) or deuterated sodium hydroxide (NaODaq) and revealed the following results.⁷⁸ (1) The polyrotaxane chains show rod-like conformations in d-DMSO and behave as Gaussian chains in NaODaq. (2) The degree of inhomogeneity of the slide-ring gel in NaODaq has a minimum around the sol-gel transition whereas that in d-DMSO increases monotonically with the cross-linker concentration. (3) The scattering intensity of the slide-ring gel in NaODaq can be described by a Lorentz function, while that in d-DMSO is given by the sum of a squared Lorentz function and a scattering function for a rod. These differences were ascribed to the stacking behavior of α -CDs in polyrotaxanes. Hadziioannou *et al.* also demonstrated the rod-like conformation of polyrotaxanes in d-DMSO.⁷⁹ The polymer conformation in a pregel solution is considered to be primarily responsible for the structure and properties of the slide-ring gels.⁷⁹

Shibayama *et al.* also revealed a significant difference between the behavior of chemical gels and that of slide-ring gels by subjecting them to SANS on uniaxial deformation.⁸⁰ It is well known that the chemical polymer gels have inherently large inhomogeneous structures due to the non-random distribution of the cross-links.¹⁷ These inhomogeneities usually increase with the swelling or deformation since the cross-linking junctions are permanently fixed on the polymer chains and the gel cannot adjust its cross-link distribution or polymer length in the network when its environment changes.¹⁷ As a result, the usual chemical gel shows an abnormal butterfly pattern,^{81–87} *i.e.*, prolate patterns *parallel* to the stretching direction; this behavior was qualitatively explained by Onuki⁸⁸ and Panykov and Rabin.^{89,90} However, the slide-ring gel shows a normal butterfly pattern, *i.e.*, prolate patterns *perpendicular* to the stretching direction as shown in Figure 4.⁸⁰ To the best of our knowledge, this is the first study to report that cross-linked polymer gels exhibit the normal butterfly pattern. The normal butterfly pattern is also observed in homogeneous polymeric materials such as polymer films and solutions due to the orientation of the polymer chains along the elongation or flow direction.⁹¹ This indicates that the slide-ring gel shows a homogeneous structure when it is elongated. It is considered that this definite difference between the slide-ring and chemical gels arises from the pulley effect.

Amemiya *et al.* performed SAXS of the slide-ring gels, focusing on the structure of the movable cross-links.⁹² The main advantage of SAXS over SANS is that the exposure time is shorter due to the high brilliance of synchrotron radiation X-rays. The short ex-

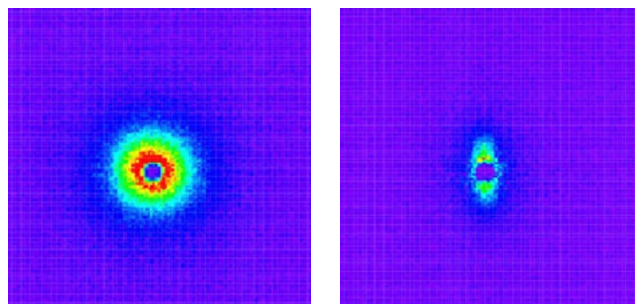


Figure 4. SANS patterns of the slide-ring gel before (left) and after (right) uniaxial deformation 1.8 times in length in the horizontal axis. The normal butterfly pattern perpendicular to the deformed direction is clearly observed and the scattering intensity decreases with increasing extension ratio.

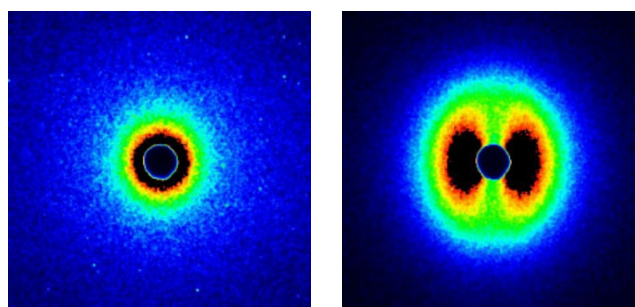


Figure 5. SAXS patterns of the slide-ring gels with NaOH (left) and NaCl (right) aqueous solvents on uniaxial deformation 2 times in length in the horizontal axis. The left figure demonstrates almost the uniform pattern while the right shows the abnormal butterfly one parallel to the deformed direction. The figure-of-eight crosslinking junctions are sparsely distributed in the gel with NaOH solvent and can move freely in the polymer network (smooth pulley) while the junctions form aggregation in the gel with NaCl solvent and cannot pass through the polymer chains freely (rusty pulley).

posure time makes it possible to study the structure of gels in various types of evaporable solvents. The SAXS results showed that in a poor solvent, the sliding cross-links form aggregates that prevent the pulley effect, while the polymer chains freely pass through the cross-links acting as pulleys in a good solvent as shown in Figure 5. A vertically elliptic pattern was observed in the two-dimensional SAXS profiles of covalent-bonded chemical gels in a good solvent under uniaxial horizontal deformation, while an isotropic profile was observed for the slide-ring gels in a good solvent under deformation. This difference between the deformation mechanisms of the slide-ring and chemical gels verified the pulley effect of the slide-ring gels.

We investigated the sliding modes of cyclic molecules in polyrotaxanes and those of cross-linking junctions in the slide-ring gel by QELS.⁹³ It was found that a sparse polyrotaxane including α -CDs showed the

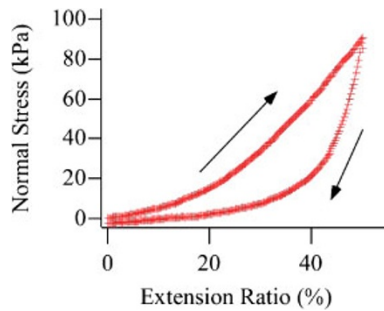


Figure 6. Stress-strain curve of konjak used as a physical gel. The physical gel shows concave stress-strain curve with large hysteresis.

sliding mode in a solution in addition to the self and cooperative diffusion modes whereas the sliding mode was not observed in a dense polyrotaxane including α -CDs. After the gelation of the sparse polyrotaxane, the self-diffusion mode of the polyrotaxane disappeared, but the sliding mode was still observed. This indicates that the figure-of-eight cross-links in the slide-ring gel slide in the polymer network, passing through the polymer chains. The diffusion constant of α -CD in the sliding mode was two orders of magnitude smaller than that in free diffusion, which may be caused by the trans-gauche transformation of the PEG chain.

MECHANICAL PROPERTIES OF SLIDE-RING GELS

The mechanical properties of the slide-ring gel are quite different from those of conventional physical and chemical gels.⁹⁴ The physical gel shows a J-shaped stress-strain curve with large hysteresis, as shown in Figure 6. The large hysteresis is caused by recombination among noncovalent cross-links in a polymer network on deformation. On the other hand, the chemical gel shows no hysteresis since it exhibits stable covalent cross-links without recombination on deformation, as shown in Figure 7. In addition, the chemical gel shows an S-shaped stress-strain curve similar to that of cross-linked natural rubber, which is well explained by the three chain model or the fixed junction model. In the fixed junction model, assuming the affine deformation of the junction points and the additivity of the individual conformational entropies of the three Gaussian chains, we can obtain the dependence of the normal stress σ on the extension ratio λ for a uniaxial deformation using the following well-known expression:^{1,2}

$$\sigma = \nu kT(\lambda - \lambda^{-2}) \quad (1)$$

where ν is the cross-linking density; k , the Boltzmann constant; and T , the temperature. The stress-strain curve of the chemical gel shows a concave-down pro-

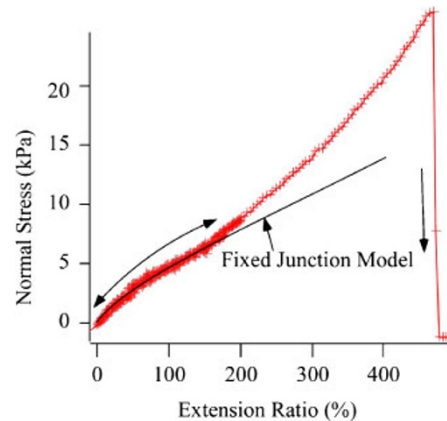


Figure 7. Stress-strain curve of poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) gel. The chemical gel shows the S-shaped stress strain curve without hysteresis. The stress-strain behavior in low extension ratio is well described by the fixed junction model.

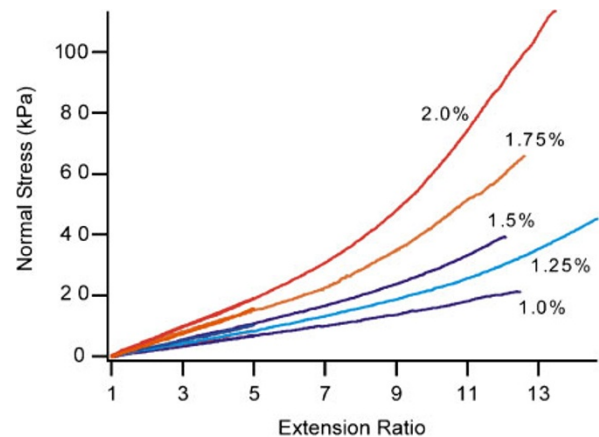


Figure 8. Stress-strain curve of the slide-ring gel with different concentrations of cyanuric chloride as a cross-linker. The slide-ring gel shows the J-shaped stress-strain curve without hysteresis.

file in the low extension region, which is well-fitted by eq 1, while it shows a concave-up profile with deviation from eq 1 in the high extension region because of non-Gaussian behavior or the stretching effect. As a result, the chemical gel shows the S-shaped stress-strain curve in Figure 7.

The slide-ring gel exhibited a J-shaped curve different from the chemical gel; furthermore, it showed no hysteresis loop in contrast to the physical gel, as shown in Figure 8.⁹⁴ This behavior can be explained in a qualitative way by the modified three chain model or the free junction model corresponding to the pulley effect, in which three Gaussian chains are assumed to be able to slide toward each other in the following manner. Let us consider that three chains in the x -, y -, and z -directions have N_x , N_y , and N_z segments, respectively, and displacement lengths R_x , R_y and R_z in that order, where the total chain length $3N$ is constant:

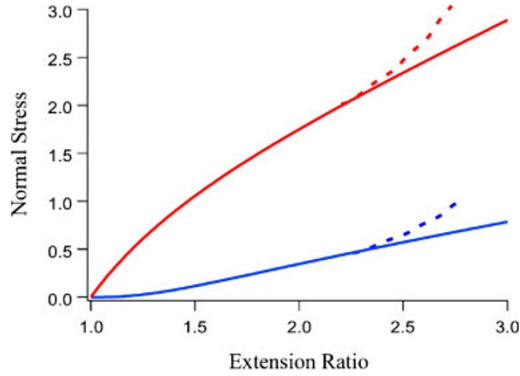


Figure 9. The comparisons between the fixed (red or upper) and free (blue or lower) junction models with regard to stress-strain curves on uniaxial stretched deformation. The dotted curves reflect the deviation from the Gaussian chains.

$$N_x + N_y + N_z = 3N \quad (2)$$

Then, the probability W is given by:

$$W(N_x, N_y, N_z; R_x, R_y, R_z) = \left(\frac{3}{2\pi b^2}\right)^{9/2} (N_x N_y N_z)^{-3/2} \times \exp\left[-\frac{3}{2b^2} \left(\frac{R_x^2}{N_x} + \frac{R_y^2}{N_y} + \frac{R_z^2}{N_z}\right)\right] \quad (3)$$

where b is the segment length. If the gel is deformed uniaxially in the z -direction, R_x , R_y , and R_z are related to the λ as $R_x = R_y = R_0/\sqrt{\lambda}$ and $R_z = \lambda R_0$, where $R_0 = \sqrt{N}b$ is the displacement at equilibrium. Therefore, the entropy is written as:

$$S(N_x, N_y, N_z; \lambda) = -\frac{3k}{2} \left[\ln(N_x N_y N_z) + \frac{N}{\lambda N_x} + \frac{N}{\lambda N_y} + \frac{\lambda^2 N}{N_z} \right] + \frac{9k}{2} \ln\left(\frac{3}{2\pi b^2}\right) \quad (4)$$

Here, we maximize the entropy with respect to N_x , N_y , and N_z as $\partial S/\partial N_x = \partial S/\partial N_y = 0$, which leads to $N_x = N_y$, and $N_z(\lambda)$ as a function of λ obtained by solving the following equation:

$$\frac{1}{N_z} - \frac{\lambda^2 N}{N_z^2} = \frac{2}{3N - N_z} - \frac{4N}{\lambda(3N - N_z)^2} \quad (5)$$

Then, the total free energy is given by:

$$F(\lambda) = \frac{n}{2} kTV \left[\ln \frac{N_z(3N - N_z)^2}{4} + N \left(\frac{\lambda^2}{N_z} + \frac{4}{\lambda(3N - N_z)} \right) \right] \quad (6)$$

As a result, the normal stress σ can be expressed as $\sigma(\lambda) = \partial F(\lambda)/\partial(\lambda V)$ where n and V are the total number of chain segments between the cross-links and the total volume of the gel, respectively.

Figure 9 shows the comparison between the chemical and slide-ring gels with respect to the stress-strain

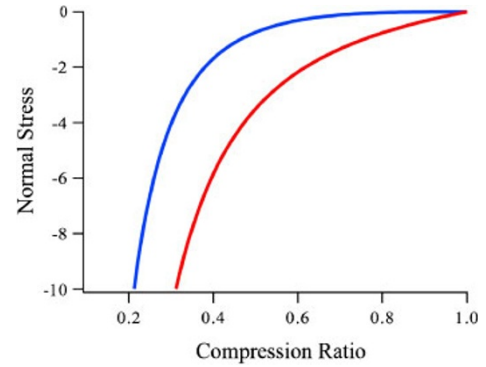


Figure 10. The comparisons between the fixed (red or lower) and free (blue or upper) junction models with regard to stress-strain curves on uniaxial compressed deformation.

curve in a low extension region. The chemical gel shows the concave-down stress-strain curve, as mentioned earlier, while the slide-ring gel exhibits the concave-up curve, which agrees qualitatively with the J-shaped experimental results, as shown in Figure 8. The difference is also observed in the compression region, as shown in Figure 10. The free junction model indicates that the slide-ring material shows a significantly small amount of normal stress at a low compression ratio, and the normal stress increases drastically with the compression ratio below $\lambda \approx 0.4$. On the other hand, the fixed junction model shows that the normal stress increases gradually with compression. It is noted that this difference is not limited only to within the gel materials but should be observed in the cross-linked polymeric materials without solvents. Consequently, the inherent pulley effect arising from freely movable cross-links provides significantly different mechanical properties from the fixed cross-linking junctions.⁹⁵

Next, we consider the biaxial deformation of the cross-linked polymeric materials and balloon inflation. In the fixed junction model, the dependence of the surface tension γ on the extension ratio λ is given by:⁹⁶

$$\gamma = \frac{nkT}{A} (1 - \lambda^{-6}) \quad (7)$$

where A denotes the unstretched cross-section area in the initial state before inflation. Then, the pressure p in a spherical balloon is given by:

$$p = \frac{3nk_B T}{V_0} \left(\frac{1}{\lambda} - \frac{1}{\lambda^7} \right) \quad (8)$$

where V_0 is the volume of the spherical balloon in the initial state before inflation. This has a maximum at $\lambda = 7^{1/6} \approx 1.383$, as shown in Figure 12, which was verified experimentally.⁹⁷ However, similar to the stress-strain curve, as mentioned earlier, the actual p - λ profile turns upwards, thereby deviating from

eq 8 in the high extension region over $\lambda \approx 2.5$ because of the non-Gaussian behavior or stretching effect. As a result, a cylindrical balloon exhibits a bistable state, called *elastic instability*, in which the swollen and shrunken parts coexist in the balloon. This elastic instability is also observed in the generation of bubbles during foam production and the development of aneurysms in arteries in the human body.

The free junction model provides a significantly different p - λ profile. If the gel is deformed biaxially in the x and y -directions, R_x , R_y and R_z are related to the extension ratio λ as $R_x = R_y = \lambda R_0$ and $R_z = R_0/\lambda^2$. Therefore, the entropy is written as:

$$S(N_x, N_y, N_z; \lambda) = -\frac{3k}{2} \left[\ln(N_x N_y N_z) + \frac{\lambda^2 N}{N_x} + \frac{\lambda^2 N}{N_x} + \frac{N}{\lambda^4 N_z} \right] + \frac{9k}{2} \ln\left(\frac{3}{2\pi b^2}\right) \quad (9)$$

By maximizing the entropy with respect to N_x , N_y , and N_z as $\partial S/\partial N_x = \partial S/\partial N_y = 0$, we have $N_x = N_y$ and $N_z(\lambda)$ as a function of λ obtained by solving the following equation:

$$\frac{1}{N_z} - \frac{N}{\lambda^4 N_z^2} = \frac{2}{3N - N_z} - \frac{4\lambda^2 N}{(3N - N_z)^2} \quad (10)$$

Then, the total free energy is given by:

$$F(\lambda) = \frac{n}{2} kTV \left[\ln \frac{N_z(3N - N_z)^2}{4} + N \left(\frac{1}{\lambda^4 N_z} + \frac{4\lambda^2}{3N - N_z} \right) \right] \quad (11)$$

In addition, the surface tension γ and balloon pressure p are calculated as:

$$\gamma = \frac{1}{A} \frac{dF}{d\lambda^2} \quad (12)$$

$$p = \frac{2}{3\lambda^2 V_0} \frac{dF}{d\lambda} \quad (13)$$

Figures 11 and 12 show the comparisons between the free and fixed junction models with regard to the dependence of γ and p , respectively, on λ . As λ increases, p in the free junction model has a maximum at $\lambda \approx 2.132$ and then decreases slightly and gradually; however, the actual p - λ profile turns upwards in the high extension region over $\lambda \approx 2.5$ because of the non-Gaussian behavior or stretching effect, as mentioned earlier. It is thus clear that the free junction model provides no elastic instability that may cause aneurysms. Hence, the slide-ring materials with freely movable cross-links are more favorable for use in artificial arteries than fixed cross-linking materials.

Many biomaterials such as mammalian skin, vessels, and tissues show J-shaped stress-strain curves,

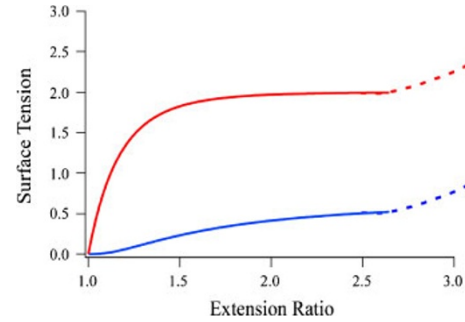


Figure 11. The comparisons between the fixed (red or upper) and free (blue or lower) junction models with regard to surface tension on biaxial deformation. The dotted curves reflect the deviation from the Gaussian chains.

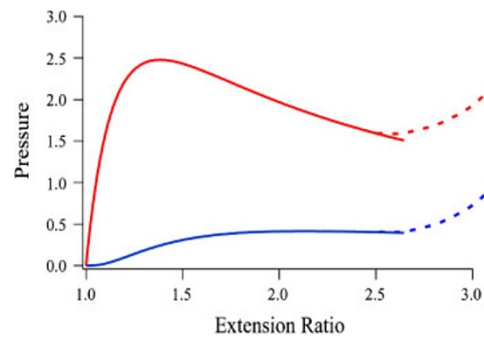


Figure 12. The comparisons between the fixed (red or upper) and free (blue or lower) junction models with regard to pressure in a spherical balloon on inflation. The dotted curves reflect the deviation from the Gaussian chains.

which usually provide toughness and no elastic instabilities among other advantages.^{98–100} The J-shaped stress-strain curve yields the toughness because its low shear modulus drastically reduces the energy released in the fracture, driving crack propagation. In addition, the material becomes stiffer as the extension ratio approaches to the fracture point. The slide-ring materials show J-shaped stress-strain curves that are similar to the curves shown by biomaterials such as mammalian skin, vessels, and tissues. This indicates that the slide-ring materials are suitable for use as substitutes for various types of biomaterials. If artificial arteries are made of the slide-ring materials, they may fit better with the native ones than fixed cross-linked materials.

Hadziioannou *et al.* have recently reported the viscoelastic properties of slide-ring gels and found two relaxation modes, which were ascribed to the sliding of α -CD rings on the PEG chain.¹⁰¹ Then, based on the viscoelastic behaviors of slide-ring gels in DMSO or water, they indicated that the slide-ring gel with water contained highly cross-linked chemical and physical domains with short flexible chains, while the network in the DMSO had long rigid chains

because of low cross-link density and the presence of long α -CDs transient tubes. This is consistent with the experimental results of SANS and SAXS, as mentioned earlier. The long α -CDs transient tubes in DMSO also caused a difference in the relaxation time. Furthermore, they have reported systematic data to verify the suggestions by SANS and viscoelastic measurements.⁷⁹

We have recently measured the viscoelastic properties of the slide-ring gels with DMSO or other ionic liquids.¹⁰² Our results obtained for the slide-ring gels with DMSO or other ionic liquids showed a plateau without apparent relaxations even for the polyrotaxane with high molecular weight and highly viscous solvents. This discrepancy from the previous results by Hadziioannou *et al.* may be due to the difference in the solvent used because the ionic liquids and DMSO are good solvents for polyrotaxanes whereas water is not. We also reported that the elastic modulus of the slide-ring gels with water was an order of magnitude larger than that of the slide-ring gels with DMSO or other ionic liquids, and that in the modulus decreased gradually to half its original value with a decrease in frequency from 100 to 0.1 rad/s. These results suggested that the CD molecules in the slide-ring gel with water formed aggregations.

Koga and Tanaka performed a molecular simulation of Brownian dynamics by using a simple model of polymer networks with tri-functional sliding junctions in order to study the elastic properties of the slide-ring gel in comparison with those of conventional chemical gels.¹⁰³ The J-shaped stress-strain curve was obtained, and the mobility and distribution of the sliding junctions along the polymer chains drastically changed with deformation. They also observed that the uniaxial deformation formed aggregations of the sliding junctions with a decrease in the number of elastically effective chains.

CONCLUDING REMARKS

For a long time, since its discovery by Goodyear in 1839, cross-linking was considered to be fixed at the polymer chains. The rubber elasticity at a low extension ratio is well explained by the fixed junction model by assuming the affine deformation of the network with fixed junction points and the entropy change in the Gaussian chains. We have recently discovered a new type of material that exhibits freely movable cross-linking, *i.e.*, slide-ring materials. These materials are formed by the cross-linking of only cyclic molecules, which are sparsely threaded on a linear polymer chain. Because the cross-linking junction can move in the polymer network, the structure and properties of the polymeric materials are drastically

different from conventional cross-linked or non-cross-linked materials. This phenomenon is called the pulley effect. It was observed from the SANS and SAXS studies that the slide-ring gels exhibited the normal butterfly pattern on uniaxial deformation that is different from the abnormal butterfly pattern exhibited by the chemical gels with fixed junctions. The mechanical behaviors of the slide-ring materials were well explained by the free junction model taking into account the pulley effect. The slide-ring materials show the J-shaped stress strain curve that is different from the S-shaped curve shown by the polymeric materials with fixed junctions such as cross-linked rubbers and chemical gels. Furthermore, they have no elastic instability, in contrast to usual cross-linked polymeric materials. These mechanical behaviors of the slide-ring materials are similar to those of biomaterials such as mammalian skin, vessel, and tissues. The slide-ring gel is a real example of the slip-link model, which has only been theoretically considered thus far, and it can be regarded as the third cross-linking concept after the conventional chemical and physical concepts, where the polymer network is interlocked by topological restrictions. The concept of the pulley effect can be applied not only to gel materials such as soft contact lens and polymer batteries but also to polymeric materials without solvent such as paint, textiles, films, and so on. This is important not only for the development of high-performance gels but also as a new framework for general polymeric materials.

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