

Slide-ring materials using topological supramolecular architecture

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ABSTRACT

We have recently developed a novel type of gel called *slide-ring gel* or *topological gel* 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 *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. Here 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. In particular, the slide-ring elastomer shows remarkable scratch-proof properties to be applied to coating materials for automobile, cell phone, mobile computer, fishing rod, golf club and so on.

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1. Introduction

All gels have been classified into two categories: chemical gels and physical ones [1]. Physical gels have noncovalent cross-linking junctions from ionic interaction, hydrophobic interaction, hydrogen bonding, microcrystal formation, helix formation and so on. In general, these noncovalent cross-links are not so stable 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 complicated because the recombination of cross-linking points occurs on deformation; hence, the affine deformation cannot be assumed 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.

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 solvent balances the elastic force of the chains between junction points. These cross-linked polymeric systems containing solvent are called chemical gels [1]. The swelling behavior of the chemical gels was first explained in detail by Flory and Rehner [2]. On the other hand, Tanaka discovered the volume phase transition of ionic chemical gels, in which the swelling and shrinking behaviors exhi-

bit discontinuous changes with hysteresis [3]. Then various interesting aspects of the chemical gels have been found one after the other; The kinetics of the volume phase transition [4], the frozen or fixed inhomogeneous structure [5], and the abnormally small friction behavior [6,7], a double network gel of a failure compressive stress as high as 20 MPa [8,9], and a self-oscillating gel device having a dissipative system [10].

Another recent approach for the polymer network structure has come from polyrotaxane in the supramolecular chemistry. Supramolecules and their topological characteristics have attracted considerable interest [11]. A typical example is a rotaxane, in which cyclic molecules are threaded on a single polymer chain and trapped by capping the chain with bulky end groups [12–16]. Ogi-no reported the first rotaxane using cyclodextrin (CD) as a ring molecule [17]. 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 -CD in that order [18,19]. 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 the 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) [20]: CDs mixed with PEG in

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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 [21]. In recent years, this novel architecture in supramolecular chemistry has attracted great attention as a new technique for developing functional polymeric materials [12–16,22].

The first report of a physical gel based on the polyrotaxane architecture was also presented by Harada et al. [23]: 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 polyrotaxane as the cross-linker for use in regenerative medicine [24]. 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 [25]. 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 [26]. We prepared polyrotaxane sparsely containing α -CD and subsequently cross-linked α -CDs on different polyrotaxanes as shown in Fig. 1. 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 network polymer 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 [27]. 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 [28]. Here 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 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, leading to remarkable scratch-proof properties. This may bring about a paradigm shift in the cross-linked polymeric materials since the chemical cross-linking was first discovered by Goodyear.

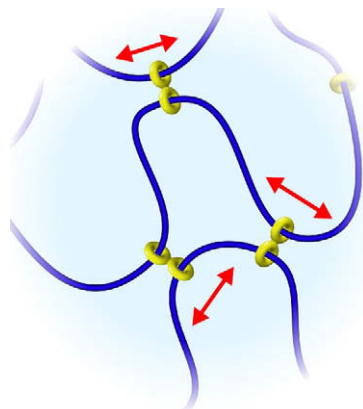


Fig. 1. Schematic diagrams of slide-ring materials with freely movable figure-of-eight cross-links acting like pulleys.

2. Synthesis of slide-ring materials

The first slide-ring material was synthesized by Okumura and Ito [26]. 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 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 determined to be 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 cross-linking 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 [26]. 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. Incidentally, the cross-linking can form the figure-of-eight junctions in a single polyrotaxane as well as between different polyrotaxanes and junctions of more than two CDs especially in high cross-linker concentration.

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 Fig. 2 [29]. 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 with 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 [30]. 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 [31]. 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.

Polyrotaxane modification is very important to obtain high-performance slide-ring materials [16]. As-prepared polyrotaxane is soluble only in a few kinds of solvents such as DMSO and sodium hydroxide (NaOHaq) since many CDs in a polyrotaxane are densely stacked forming strong hydrogen bonds with each other. The polyrotaxane modification, i.e., the preparation of various polyrotaxane derivatives replaced hydroxyl groups around CD with different functional groups such as methyl, hydroxypropyl, acetyl, carboxyl groups and so on, which hinders the hydrogen-bond

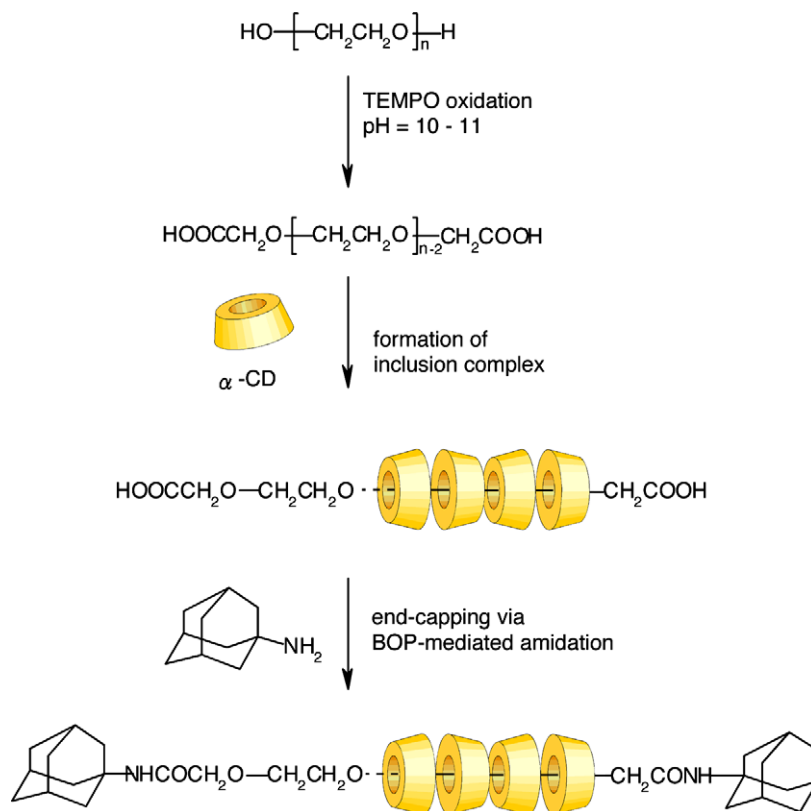


Fig. 2. The high-yield synthesis scheme of polyrotaxane of PEG and α -CD capped at both the ends with adamantane.

formation and thereby improves the solubility drastically. In addition, these functional groups yield new physical properties in polyrotaxane and slide-ring materials. For example, highly methylated polyrotaxane shows thermoreversible sol-gel transition and a slide-ring gel of carboxymethylated polyrotaxane demonstrates huge volume change depending on pH. These polyrotaxane modifications were analogous to those done for other oligosaccharides or polysaccharides, including cellulose, chitin, starch, and cyclodextrin. While molecular degradation during the modification of other polymers is problematic, the resulting damage might be limited to a slight decrease in the molecular weight of the obtained derivatives; however, this does not affect the total properties of the derivatives. On the other hand, fragmentation at any moiety in a polyrotaxane molecule always causes significant changes in the polyrotaxane structure, namely, all the scissions occurred at cyclic molecules, a linear axis, bulky end groups, and their binding moieties induce the dissociation of cyclic molecules resulting in a loss of the polyrotaxane structure. Therefore, any decomposition including hydrolytic, oxidative, thermal, and biological degradations should be strictly avoided during the polyrotaxane modifications. Typical polyrotaxane modifications were reviewed elsewhere [16].

3. Pulley effect of slide-ring materials

It is well known that the chemical gel generally has a large inhomogeneous structure due to the gelation process as schematically shown in Fig. 3, 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 concentrates on the shorter chains, thereby breaking down the chemical gel easily. To resolve this problem, we have recently developed the slide-ring gel having freely movable cross-links based on the supramolecular architecture with the

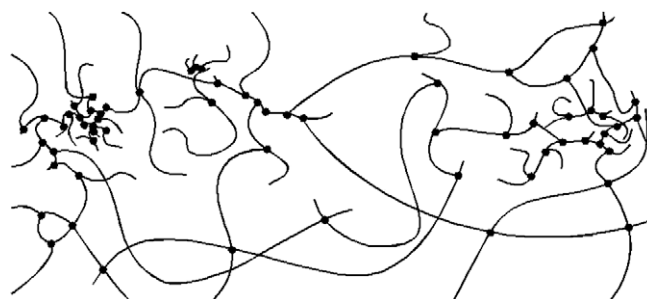


Fig. 3. Schematic diagram of chemical gels with fixed cross-linking junctions distributed inhomogeneously.

topological characteristics [26]. 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 pulley effect [26].

Fig. 4 schematically shows a comparison between the chemical and slide-ring gels on tensile deformation [26]. 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

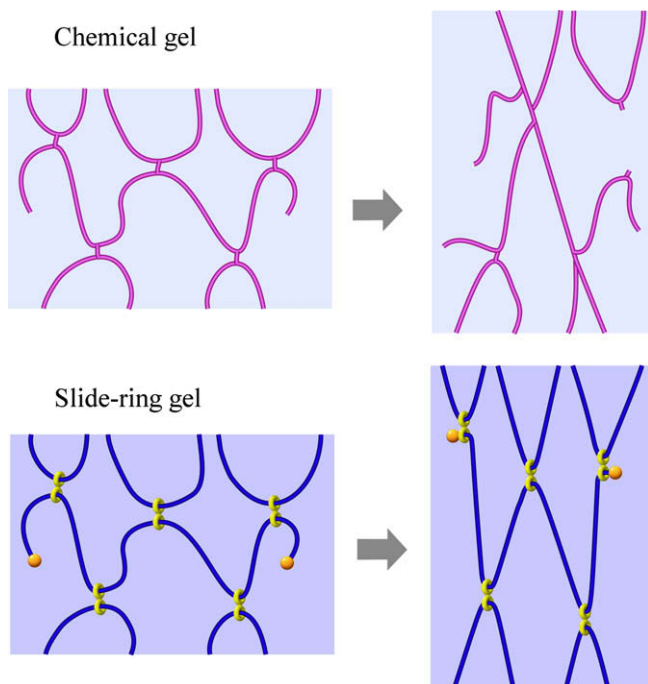


Fig. 4. Schematic comparison between chemical and slide-ring gels. The pulley effect in the slide-ring gel disperses the tension in the polymer chains automatically on tensile deformation while the tensile stress concentrates on short chains in the chemical gel.

stretchability of up to 24 times in length without hysteresis, and a large volume change of up to 24,000 times in weight. 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.

4. 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 small-angle neutron scattering (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 [32]: (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 [33]. The polymer conformation in a pregel solution is considered to be primarily responsible for the structure and properties of the slide-ring gels. Mayumi et al. found the concentration-induced conformational change in hydroxypropylated polyrotaxane (H-PR) at various concentrations from the overlap concentration c^* to the semidilute regime by SANS [34]. It was found that the persistence length of H-PR was dependent on the polymer concentration c_p , while those of PEG remained unchanged

in the same molar concentration regime. This unusual concentration dependence of polymer conformation for H-PR might indicate that CDs in H-PR could slide freely and rapidly over the whole range of PEG chains in the neighborhood of c^* but their mobility was suppressed as c_p increased due to the molecular interaction among CDs such as the hydrogen-bond formation.

Shibayama et al. also revealed a significant difference between chemical and slide-ring gels by subjecting them to SANS on uniaxial deformation [35]. It is well known that the chemical polymer gels have inherently large inhomogeneous structures due to the non-random distribution of the cross-links [5]. 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. As a result, the usual chemical gel shows an abnormal butterfly pattern [36], i.e., prolate patterns *parallel* to the stretching direction; this behavior was qualitatively explained by Onuki [37] and Panykov and Rabin [38,39]. However, the slide-ring gel shows a normal butterfly pattern, i.e., prolate patterns *perpendicular* to the stretching direction as shown in Fig. 5 [35]. 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 [40]. This indicates that the slide-ring gel shows 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 [41]. 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 exposure 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. A vertically elliptical 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 [42]. It was found that a sparse polyrotaxane including α -CDs showed the 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. 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 slide in the polymer network of the slide-ring gel, passing through the polymer chains.

5. 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 [43,44]. The physical gel shows a J-shaped stress–strain curve with large hysteresis. 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. In addition, the chemical gel shows an S-shaped stress–strain

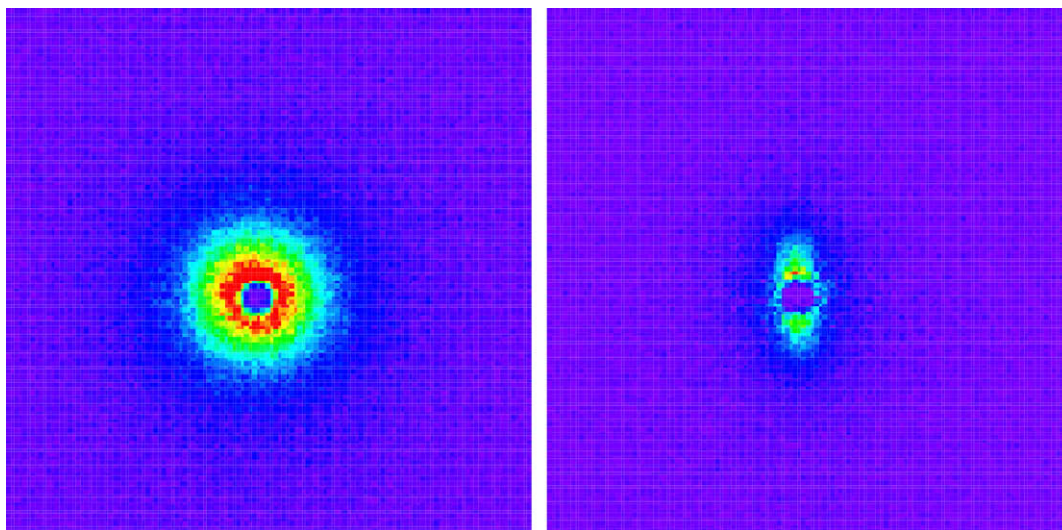


Fig. 5. SANS patterns of the slide-ring gel before (left) and after (right) uniaxial deformation 1.8 times in length in the horizontal axis. The normal butterfly pattern perpendicular to the deformed direction is clearly observed and the scattering intensity decreases with increasing extension ratio.

curve, which is well explained by the three chain model or the fixed junction model [45,46]. 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 [45,46]:

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

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 profile 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.

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 Fig. 6 [43,44]. 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

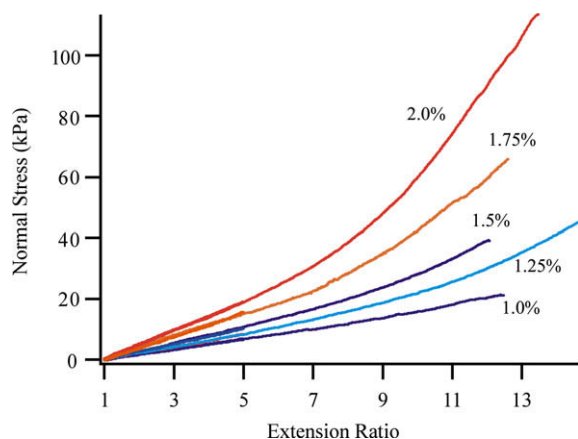


Fig. 6. Stress–strain curve of the slide-ring gel with different concentrations of cyanuric chloride as a cross-linker. The slide-ring gel shows the J-shaped stress–strain curve without hysteresis.

which three Gaussian chains are assumed to be able to slide to each other in the following manner [44].

Fig. 7 shows the comparison between the chemical and slide-ring gels with respect to the stress–strain curve in a low extension region [44]. 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 Fig. 6. The difference is also observed in the compression region [44]. 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. The stress–strain curve of the slide-ring gel depends on the cross-linking density. A slide-ring gel in high cross-linking density shows an S-shaped stress–strain curve like the chemical gel [43], but the behavior is still rather different from the chemical gel.

Many biomaterials such as mammalian skin, vessels, and tissues show J-shaped stress–strain curves, which usually provide toughness and no elastic instabilities among other advantages [47–49]. The J-shaped stress–strain curve yields the toughness

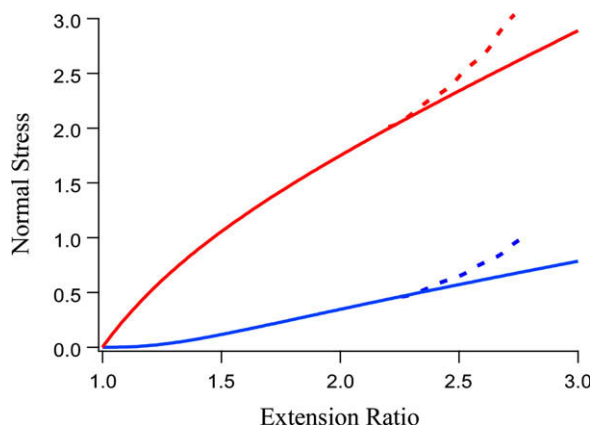


Fig. 7. The comparisons between the fixed (red) and free (blue) junction models with regard to stress–strain curves on uniaxial stretched deformation. The dotted curves reflect the deviation from the Gaussian chains.

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 [50]. 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 [33].

We have recently measured the viscoelastic properties of the slide-ring gels with DMSO or other ionic liquids [51]. 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 [52]. 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.

6. Sliding graft copolymers

We have recently developed other slide-ring materials of polyrotaxane structures by grafting some functional groups, mesogen, and polymer chains on cyclodextrins, which are called sliding graft copolymers. Kataoka et al. found thermoreversible gelation and microphase formation of aqueous solutions of a methylated polyrotaxane (MePR) [53,54]. The aqueous solutions of MePR show a lower critical solution temperature (LCST) and form an elastic gel with increasing temperature. The sol–gel transition of the MePR solutions was induced by formation and deformation of aggregates of methylated α -CDs in MePR due to hydrophobic dehydration and hydration, respectively. The X-ray diffraction (XRD) investigation revealed localization and highly ordered arrangement of methylated α -CDs along the PEG chain in the gel. The arrangement of CD molecules was also reflected by the changes in elasticity and long

relaxation behavior of the solution around the sol–gel transition. The quasi-equilibrium shear modulus of MePR solutions showed the critical phenomena against temperature. The scaling exponents measured at two different concentrations were almost equal to the values predicted by a gel percolation theory. Therefore, the heat-induced gelation of aqueous MePR solutions is well explained by a model in which clusters assembled with methylated α -CDs are gradually connected to the network as the temperature increases.

Kidowaki et al. developed a novel side-chain liquid crystalline polyrotaxane (LCPR) whose mesogenic side chains can slide and rotate on the linear backbone. To obtain the LCPR, 6-(4'-cyanobiphenyl-4'-yloxy)-hexanoyl chloride was prepared and reacted with a polyrotaxane consisting of α -CD, poly(ethylene glycol) ($M_w = 35,000$), and adamantane end groups [55]. The molecular characterization of the LCPR was performed with FT-IR, ^1H NMR, and gel permeation chromatography analysis. Its phase structures and transitions were investigated by differential scanning calorimetry, wide-angle X-ray diffraction, and polarized light microscopy experiments. The experimental results show that the LCPR has glass transition at 70 °C and mesomorphic isotropic transition at 129 °C.

Araki et al. developed a novel sliding graft copolymer, in which many linear poly- ϵ -caprolactone (PCL) side chains were bound to CD rings of a polyrotaxane, was prepared by ring-opening polymerization of ϵ -caprolactone initiated by hydroxyl groups of the polyrotaxane [56]. An amorphous, flexible, and sufficiently tough elastomer film was prepared by cross-linking the SGC—a supramolecule possessing a number of mobile side chains—with hexamethylene diisocyanate (HMDI). The slide-ring elastomer shows remarkable scratch-proof properties to be applied to coating materials for automobile, cell phone, mobile computer, fishing rod, golf club and so on [57]. It seems that the mechanical properties of the slide-ring elastomer different from conventional elastomers may yield such scratch-proof properties.

7. Concluding remarks

Since Goodyear discovered vulcanization of natural rubber 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 in polyrotaxane, 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 noncross-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 of 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. These peculiar mechanical behaviors of the slide-ring materials are similar to those of biomaterials such as mammalian skin, vessel, and tissues and may cause the remarkable scratch-proof properties. The slide-ring gel is a real example of the slip-link model, which has only been theoretically considered thus far. The concept of the pulley effect can be applied not only to gel materials such as soft contact lens and polymer bat-

teries 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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