

From Topological Gels to Slide-Ring Materials

Yumiki Noda,¹ Yuki Hayashi,¹ Kohzo Ito²

¹Advanced Softmaterials, Incorporated, Tokatsu Techno Plaza, Kashiwanoha, Kashiwa, Chiba 277-0822, Japan

²Graduate School of Frontier Sciences, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

Correspondence to: Y. Noda (E-mail: noda@smi.jp) and K. Ito (E-mail: kohzo@k.u-tokyo.ac.jp)

ABSTRACT: A novel type of gel, called a *topological gel*, has been recently developed with a supramolecular architecture with topological characteristics. In the topological gel, polymer chains with bulky end groups are neither covalently crosslinked as in chemical gels nor attractively interacting as in physical gels but are topologically interlocked by figure-eight shaped crosslinks. Hence, these crosslinks 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*. This concept can be applied not only to gels but also to a wide variety of polymeric materials without solvents. Then, polymeric materials with movable crosslinks are referred to as *slide-ring materials* (SRMs) in a wider sense. Here, we review the synthesis, structure, physical properties, and applications of topological gels and SRMs. In particular, slide-ring elastomers show remarkable scratch-proof properties for application to coating materials for automobiles, cell phones, mobile computers, golf clubs, and so on. © 2014 The Authors Journal of Applied Polymer Science Published by Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40509.

KEYWORDS: crosslinking; elastomers; gels; supramolecular structures

Received 7 October 2013; accepted 23 December 2013

DOI: 10.1002/app.40509

INTRODUCTION

Since the discovery of crosslinking in natural rubber with sulfur in 1839 by Goodyear, the crosslinking of polymeric materials has become one of the most important topics in polymer science and technology.^{1,2} Gels are typical crosslinked materials containing solvents in a network. All gels have been classified into two categories: physical gels and chemical ones.³ Physical gels have noncovalent crosslinking junctions from ionic bonding, hydrophobic interaction, hydrogen bonding, microcrystal formation, helix formation, and so on. In general, these noncovalent crosslinks are not as stable as the covalent crosslinks in chemical gels so that physical gels show a sol–gel transition response to the temperature, pH, and solvent. On the other hand, chemical gels are more stable but have a large inhomogeneous structure; this considerably reduces their mechanical strength. In the chemical gel, long polymer chains are divided into shorter network strands of different lengths by fixed crosslinks. As a result, the tensile stress concentrates on shorter chains, thereby readily breaking down the chemical gel.

To improve the mechanical properties of gels, some novel architectures of crosslinking have been proposed so far: double network gels,⁴ nanocomposite gels,⁵ tetrapoly(ethylene glycol) gels,⁶

and so on. The double-network gel has an interpenetrating network consisting of two types of polymer components with soft and hard natures. It achieves a remarkable failure compressive stress as high as 20 MPa.⁴ Nanocomposite gels consisting of poly(*N*-isopropylacrylamide) and inorganic clay are prepared by photo-initiated free-radical polymerization in the presence of exfoliated inorganic clay in an aqueous solution and show stretchability much higher than usual chemical gels.⁵ On the other hand, tetrapoly(ethylene glycol) gels are synthesized by the combination of two well-defined symmetrical tetra-arm polymers of the same size.⁶ As a result, it yields a diamondlike polymer network with the same length of network strands; this also leads to a high elongation ratio. These new kinds of gels indicate that crosslinking drastically affects the mechanical properties.

Another novel type of gel, called a *topological gel*, has been developed with a supramolecular architecture with topological characteristics, as shown in Figure 1.⁷ The topological gel is prepared by the crosslinking of hydroxyl groups on two α -cyclodextrins (α -CDs) in different polyrotaxanes (PRs) of poly(ethylene glycol) (PEG) as a backbone. PR is a necklacelike supramolecule in which many rings are threaded onto a backbone linear chain and trapped by the capping of the chain with bulky end groups.⁸ As a result, the crosslinking junctions of the

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2014 The Authors Journal of Applied Polymer Science Published by Wiley Periodicals, Inc.

Yumiki Noda is a division manager of Business Development Division of Advanced Softmaterials, Inc., Japan. He received his M.S. degree in chemical engineering at Shizuoka University (1984) and a PhD in chemical engineering at Tokyo Institute of Technology (1998). After working as a research chemist at UBE Industries Inc., he joined Advanced Softmaterials, Inc. in 2011. He has been focusing on development of applications and market of polyrotaxane products.



Yuki Hayashi is a manager of the Technology Management Division of Advanced Softmaterials, Inc., Japan. He received his PhD in Material Engineering from Tokyo Institute of Technology in 2001. After working as a postdoctoral researcher in the National Institute of Advanced Industrial Science and Technology, Japan, and as a researcher in Fuji-film, he joined Advanced Softmaterials, Inc. in 2005. His work has been focusing on development of materials based on polyrotaxanes.



Kohzo Ito is a professor at the Graduate School of Frontier Sciences, The University of Tokyo. He received his B. E., M. E. and Ph. D. degrees in applied physics from the University of Tokyo. In 1986, he joined Research Institute of Polymers and Textiles in Tsukuba, Japan. He transferred back to The University of Tokyo in 1991. His research field includes polymer physics, soft matter physics, and supramolecular chemistry. At present, his group focuses on topological gel and slide-ring materials with freely movable cross-links. He is concurrently a director of Advanced Softmaterials Inc., which he founded to urge the application of the slide-ring materials in 2005. He has been the author of over 200 publications, including original research papers, reviews, and chapters of books, and over 50 patents. He also received The Award of the Society of Polymer Science, Japan (2006) and Grand Prize in University Corporate Relations for Creation (2006).

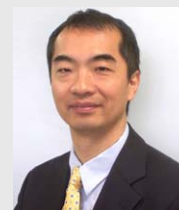


figure-eight shapes are not fixed at the PEG chains and can move freely in the polymer network. Such a polymeric material with freely movable crosslinks was theoretically considered as a sliding gel by de Gennes in 1999.⁹ In addition, the historical significance of the topological gel was reviewed through comparison of the slip-link model by Granick and Rubinstein.¹⁰ It is noteworthy that the concept of freely movable crosslinks is not limited within the topological gel containing some solvents but can also be applied to polymeric materials without solvents. Hence, polymeric materials having freely movable crosslinks are referred as to *slide-ring materials* (SRMs) in a wider sense.

Here, we review the general features, synthesis, structure, physical properties, and applications of the topological gel and SRMs. SRMs are quite different from conventional polymeric materials in that the movable crosslinks are able to relax the stress concentration based on the inhomogeneous distribution of crosslinking junctions and that SRMs have the entropy of rings strongly coupled with the entropy of strings. As a result, the mechanical properties of polymeric materials are drastically changed; this leads to remarkable scratch-proof properties. SRMs have brought about a paradigm shift in crosslinked polymeric materials since chemical crosslinking was first discovered by Goodyear.

PULLEY EFFECT AND ENTROPY OF RINGS

In SRMs, polymer chains with bulky end groups are neither covalently crosslinked as in chemical gels nor attractively inter-

acting as in physical gels but are topologically interlocked by figure-eight shaped crosslinks. Therefore, they can move freely to equalize the tension of the threading polymer chains in a manner similar to pulleys; this is called the *pulley effect*.⁷ The pulley effect is responsible for the peculiar mechanical properties of topological gels, including their extreme softness, low Young's modulus (E), J-shaped stress-strain curve, high stretchability of over 20 times in length, and huge volume swellability up to 24,000 times as much as the dry state by weight.^{11,12}

Another important feature in SRMs is that SRMs have two kinds of entropy coupled with each other by the pulley effect: the distribution entropy of rings on PR and the conformational entropy of the backbone string in PR.¹³ This is because PR consists of two topologically different components of rings and a string. These two kinds of entropy are almost independent of each other in uncrosslinked PR: rings can have arbitrary distribution, regardless of the backbone polymer conformation in PR. However, the crosslinking yields strong coupling of two kinds of entropy. All of the rings are not crosslinked in SRMs: a number of rings remain uncrosslinked. Then, these free rings have a sliding motion along an axis polymer and tend to keep random distribution in the network; this maximizes the distribution entropy of rings. When SRMs are stretched, their polymer chains are deformed to anisotropic conformation in a short timescale. This is followed by the pulley effect, in which polymer chains pass through figure-eight shaped crosslinks.

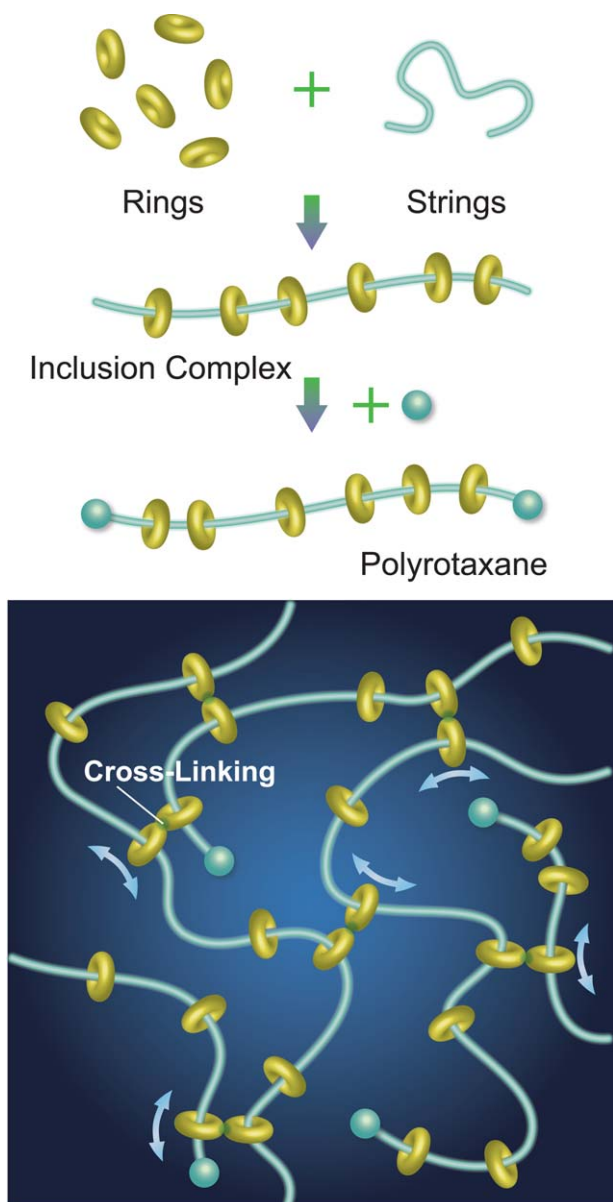


Figure 1. Schematic diagram of PR and slide-ring gel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Consequently, the pulley effect relaxes the anisotropic deformation of the polymer chains to an isotropic form. However, free rings cannot pass through crosslinks consisting of other rings of the same size, whereas axis polymer chains readily can. In other words, the pulley effect changes the length of the network strands between crosslinks, but the number of rings between the crosslinks is kept constant. As a result, the pulley effect in the deformation of SRMs yields a heterogeneous density distribution of free rings in PR, as shown in Figure 2, and reduces the distribution entropy of the free rings, which leads to a novel entropic elasticity that is completely different from rubber elasticity due to polymer conformation. This means that the topological asymmetry of ring and string bring about the exchange between two kinds of entropy by the pulley effect in SRMs unlike uncrosslinked PR. The fundamental feature of the pulley

effect with the distribution entropy of free rings is characteristic of SRMs and yields various peculiar physical properties.

SYNTHESIS AND DIVERSIFICATION OF TOPOLOGICAL GELS AND SRMS

The first topological gel was synthesized by Okumura and Ito.⁷ They used diamino-terminated PEG with a molecular weight of 20,000 as the axis of the PR because PEGs with large molecular weights form sparse inclusion complexes with α -CD. The average molecular weight of PR was determined to be 82,000 by ¹H-NMR and UV spectroscopy; this 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 PR, whereas the axis of bis(2,4-dinitrophenyl)-PEG has no hydroxyl groups. Through the intermolecular crosslinking of the α -CDs contained in the PRs, a transparent gel was obtained. Such a gel was not formed by the crosslinking of the mixture of bis(2,4-dinitrophenyl)-PEG and α -CD in the same composition as that of the same PR under the same conditions. Furthermore, we treated the topological gel with a strong base (1N NaOH) at 50°C to remove the bulky stoppers (dinitrophenyl groups) at each end of the PRs and observed a sharp liquefaction of the gel after 7 h.⁷ This indicated the first evidence of movable crosslinks; thus, the polymer network in the gel was maintained by topological restrictions and not by chemical crosslinks.

The first-synthesized topological gel enhanced the development of PR syntheses. Araki et al.¹⁴ improved the synthesis scheme of PEG-based PR with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (mediated oxidation), which results in the high-yield production and large-scale manufacturing of PR at low cost and is quite crucial for the application of SRMs. Yui and coworkers^{15,16} successfully controlled the amount of α -CDs in the PR containing PEG with a mixture of dimethyl sulfoxide and water during the inclusion complex formation. Hadziioannou et al.¹⁷ changed the time, temperature, and initial ratio of α -CD to PEG of 20,000 in molecular weight to vary the inclusion ratio.

As the details of the pulley effect were revealed, application studies have also been developed by chemical modification of the cyclic components of topological gels.¹⁸ The PR

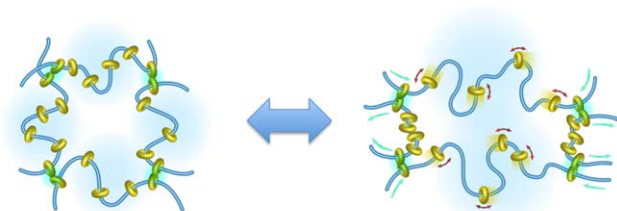


Figure 2. Entropic elasticity from the distribution entropy of the free rings. Before deformation, the free rings were distributed randomly with the highest distribution entropy. On deformation, the pulley effect changed the lengths of the network strands between crosslinks. As a result, the free rings came to be distributed heterogeneously because the free ring could not pass through the crosslinks. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modifications were analogous to those done for other oligosaccharides and polysaccharides, including cellulose, chitin, starch, and cyclodextrins (CDs). By taking an advantage of CDs that have hydroxyl groups, researchers have modified various functional groups on the cyclic component to obtain new materials with different properties, including thermoresponsive properties obtained by modification with hydrophobic groups such as methyls,¹⁹ photoresponsive large volume changes obtained by modification with azobenzene derivatives,²⁰ mesogen-modified topological gels that respond much faster than typical liquid-crystalline polymers,^{21,22} and slide-ring elastomers obtained by the crosslinking sliding graft copolymers in which CDs were modified with polycaprolactone (PCL).²³

Another important diversification of the topological gel is achieved by changes in the backbone polymer from PEG to other chains; this is, however, much more difficult than the modification of CDs. Many polymers are known to form inclusion complexes or pseudo-PR with α -, β -, and γ -CDs selectively,¹⁸ but the formation of PR with both ends capped is not easy. This is mainly because the end-capping reactions of inclusion complexes always compete against dissociation, and the end groups must be sufficiently bulky to prevent unraveling, especially in PR of γ -CD. The difficulty has been partly overcome by the capping of the same^c as a capping agent,^{24,25} the grafting of a polymer chain with long side chains,^{26,27} and so on.^{28,29} As a result, poly(dimethyl siloxane), polybutadiene, polyester, a copolymer of poly(propylene glycol) and PEG or polyethyleneimine, and others can form PR and topological gels, although it is not still easy to change the axis polymer to other chains.³⁰ In addition, the topological gel can be also diversified with cyclic molecules other than CDs, such as pillararenes,³¹ cucurbiturils,³² calixarenes,³³ and so on. Although these rings form PRs with various polymers, there have been few reports on topological gels based on them.

STRUCTURE AND PHYSICAL PROPERTIES OF TOPOLOGICAL GELS AND SRMS

Structural Analysis of PRs and Topological Gels

Topological gels and pregel PRs have been investigated by small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and quasi-elastic light scattering. The SANS profiles of sparse PRs have shown that the unmodified PR locally takes a rodlike conformation in dimethyl sulfoxide because adjacent CDs form some aggregation by strong hydrogen bonding. At higher PR concentrations, these aggregations stack hexagonally and finally yield microcrystals of CDs.³⁴ On the other hand, PRs with hydroxypropylated CDs show coiled conformations, in which the CDs are randomly distributed along PEG, because the hydrogen bonding between adjacent CDs is hindered by the hydroxypropylation of the CDs.³⁵

The chemical gel, having large inhomogeneous structures, shows an abnormal butterfly pattern, that is, prolate patterns parallel to the stretching direction in the SANS profile.³⁶ However, the topological gel shows a normal butterfly pattern, that is, prolate patterns perpendicular to the stretching direction.³⁷ The normal butterfly pattern is also observed in homogeneous polymeric materials, such as polymer films and solutions, because of the orientation of the polymer chains along the elongation or flow

direction. This means that the topological gel shows a homogeneous structure when it is elongated; this arises from the pulley effect by freely movable crosslinks.

The two-dimensional SAXS of the topological gels shows an isotropic profile in a good solvent under horizontal deformation in contrast to a vertically elliptical pattern of covalently bonded chemical gels in a good solvent under deformation.³⁸ This difference between the deformation mechanisms of the slide ring and chemical gels also verifies the pulley effect of topological gels.

The most interesting feature of PRs is that CDs in PRs can slide along a PEG backbone. The sliding motion of the CDs was confirmed by dynamic light scattering (DLS) experiments on the dissociation process of PRs.³⁹ To directly observe the dynamic behavior of a single CD in PR, Mayumi et al.⁴⁰ used a neutron spin echo technique, which could detect the dynamics on the nanometer and nanosecond scale. The neutron spin echo determined the diffusion constant of the PR to be $4 \text{ \AA}^2/\text{ns}$. This value was about one-third as small as that of free PEG without CDs. This indicated that the topological connection between the CD and PEG slowed down the local dynamics.

Mechanical Properties of SRMs

The mechanical properties of SRMs, including topological gels, are quite different from those of chemical gels. Covalently crosslinked gels exhibit S-shaped stress-strain curve. On the other hand, SRMs often show a J-shaped curve without a hysteresis loop.^{11,12} This peculiar behavior can be explained qualitatively by a free-junction model based on the pulley effect, in which three Gaussian chains at a crosslink are able to slide toward one another.^{11,12} Such J-shaped stress strain curves have also been observed in many biomaterials, such as mammalian skin, vessels, and tissues; this gives the toughness of these biomaterials. This is because the low modulus drastically reduces the energy released in a fracture, and the gradual increase in stiffness prevents elastic instability. Thus, SRMs would be promising substitutes for various types of biomaterials.

Biaxial strain testing gives us more detailed mechanical properties of the gels and elastomers. Conventional gels and elastomers with covalent crosslinks generally show a large strain coupling; for example, the elongation of materials affects the stresses on not only the vertical face to the direction of elongation but also the horizontal faces. This is because all of the chains in the network are connected, and therefore, the deformations of each chain are strongly coupled with each other. However, in the case of SRMs, the strain coupling is significantly small.⁴¹ The stress-strain behavior of topological gels at some inclusion ratio and crosslinking conditions shows good agreement with the Neo-Hookean model, which is known to describe the behaviors of ideal rubber elasticity. In addition, they show abnormally small coupling within the results of volume conservation. Thus, this behavior demonstrates a possible mechanism that can decouple the strains in different directions, that is, the pulley effect.

Sliding State and Transition

The viscoelastic profile of normal chemical gels and rubbers has no frequency dispersion and a finite equilibrium modulus (in the long-time limit) that arises from the entropic elasticity of

polymer conformation between fixed crosslinks. On the other hand, uncrosslinked entangled polymer chains show a large relaxation at the longest relaxation time and no finite equilibrium modulus like a normal liquid because the release or reptation of entangled polymers eventually relaxes the chain deformation responsible for the entropic elasticity seen in the higher frequency region. SRMs have a similar sliding motion of polymer chains at the crosslinking junction to the entangled polymer system, but axis polymer chains cannot be released completely because of the stoppers at both ends. As a result, the sliding motion yields a frequency dispersion or relaxation in the viscoelastic profile but should stop in the long-time limit; this results in another finite equilibrium modulus in the low frequency limit.^{42,43} This is called the *sliding elasticity* in the sliding state.

Normal crosslinked amorphous polymers show glassy and rubbery states, which are divided by the glass transition. SRMs should have another state called the *sliding state*, where axis polymer chains and cyclic molecules slide actively.¹³ The rubbery and sliding states are divided by the sliding transition similar to the glass transition between the glassy and rubbery states. The transition time of the sliding transition is proportional to the cube of the network strand length between crosslinks.^{43,44} This dependence is reminiscent of the tube model in the entanglement system, where the longest relaxation time is proportional to the cube of the contour polymer length. The cubic dependence on the contour length arises from the reptation of a polymer chain in the virtual tube length proportional to the contour length. On the other hand, the longest mode of the sliding motions of a polymer chain in the topological gel is restrained in the reptation in the order of the length of the network strand between the crosslinked junctions because complete release is impossible.⁴³ Consequently, the cubic dependence of the sliding relaxation time on the network strand length between crosslinks verifies the sliding motion of the polymer chains through the crosslinks in SRMs.

The sliding elasticity in the sliding state is mainly ascribed to how many free rings are restrained between the crosslinks in SRMs.⁴⁵ This means that the sliding elasticity is similar to a one-dimensional air spring, in which air molecules are confined in a one-dimensional tube. In SRMs, the sliding motion of free rings threaded to a chain is restricted within movable crosslinking junctions. A simulation study also showed that free rings behave as a one-dimensional air spring.⁴⁶ If the sliding elasticity is larger than the rubber one, the sliding transition and state should disappear because the network strand can deform more easily than form the heterogeneous density distribution of free rings by the pulley effect. The sliding transition comes from the exchange between two kinds of entropy and is not characteristic of uncrosslinked PR but of SRMs, including topological gels.

Swelling Properties of Topological Gels

The strain-driven volume change is a general property of gels being a semi-open system where the solvent can flow in and out of gels. Gels that are fully swollen in solvents show further swelling when a constant tensile strain is imposed externally. Further swelling is induced by a force to increase the conforma-

tional entropy (i.e., to reduce the anisotropy in conformation) of the deformed networks. This behavior is described by the equilibrium (osmotic) Poisson's ratio (μ_∞). Normal chemical gels show that μ_∞ is independent of strain, which is well explained by the Flory–Rehner model.⁴⁰ However, μ_∞ for topological gels with sufficiently low crosslinking densities depends on the strain (λ); μ_∞ increases with λ in the regime of λ less than a critical strain λ_c whereas μ_∞ levels off in the region $\lambda > \lambda_c$.⁴⁷ The peculiar λ -dependent μ_∞ under moderate elongation is attributed to a functional characteristic of movable crosslinks, the pulley effect, which can vary the network topology under imposed deformation so that the conformational entropy can be maximized. The leveling-off behavior of μ_∞ at high elongation is explained by the suppression of the pulley effect caused by high stacking and/or the localization of crosslinked cyclic molecules at the chain ends. These results indicate that the crosslinks in the topological gels move nonaffinely, and the number of CDs in PR, the inclusion ratio, influences how the crosslinks slide along the network strands in a nonaffine manner in response to imposed deformation.

Penetration Flow Properties of Topological Gel Membranes

The steady-state flow velocity of fluids through conventional porous membranes is linearly proportional to the imposed pressure (p); this is well known as Darcy's law. This behavior was also observed for various polymer gel-based membranes. The proportionality constant between the flow velocity of fluids and p is related to the friction coefficient (f) between the gel network and fluid, and f is independent of p for membranes based on classical gels. However, topological gels demonstrate a peculiar p dependence of f , where f sharply varies between two different values within a narrow p range.⁴⁸ This characteristic p effect on fluid permeation is a novel physical property that

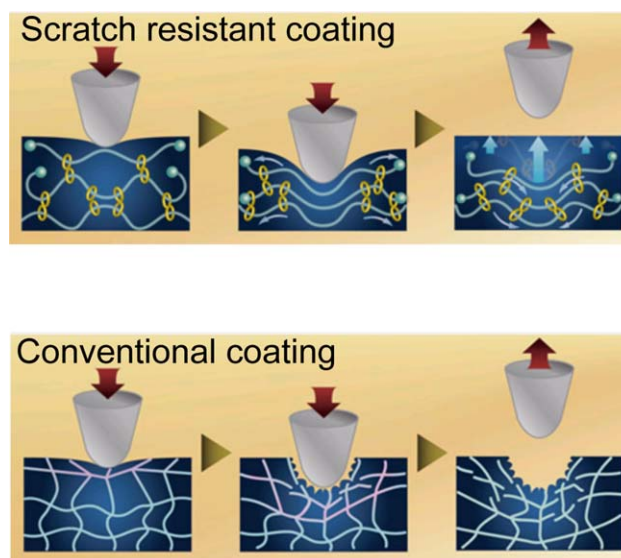


Figure 3. Schematic image of scratch recovery. Even with a high degree of crosslinking, the movable crosslinks maintained the flexibility and elasticity of the coated layer, and this caused the scratch-healing properties. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

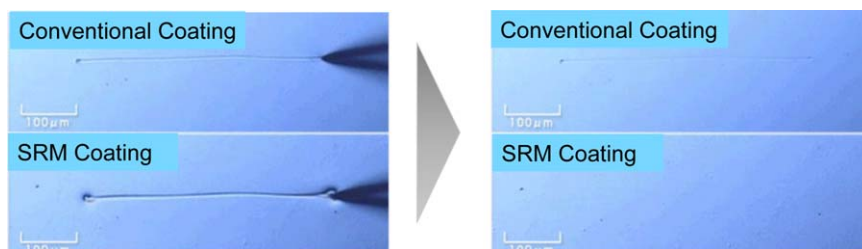


Figure 4. Self-recovery test of scratching. The self-recovery properties in a 15 μm thick SRM coating were confirmed by scratch testing with a sharp needle. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results from the slidability of the crosslinks. It indicates that topological gels are promising polymer membrane materials that enable the on–off control of fluid permeation by p . This indicates that the mesh size is changeable by external stimuli in the topological gel because of slidable crosslinks; this is quite different from normal chemical gels with fixed mesh sizes.

APPLICATIONS OF SRMS

The movable crosslinks of SRMs can be applied to elastomers without solvent when PR modified with PCL, a sliding graft copolymer, is crosslinked with other polymers, such as acrylate polymers, polyurethanes, and so on. As PR is crosslinked with other generic polymeric materials (figure-nine shaped crosslinks), the unique properties of the topological gel can be transferred and added to the properties of these materials. The movable crosslinking points are used for the pulley effect; this equalizes the tensions among polymers. When the crosslinking junction slides along the axis polymer backbone, the chain length of a network strand between the crosslinks changes. Then, uncrosslinked free rings show an air suspension effect (sliding elasticity) that attempts to retain appropriate distances, especially when the mutual distance between rings is compressed due to the deformation of the polymer. Because of these effects, SRMs have the special properties of low E' , small compression set, small stress relaxation, and a large loss tangent in the viscoelastic profile in a wide frequency range; this has not been seen in traditional elastomers.

A PR modified with PCL has already been produced industrially and is commercially available a decade after the appearance of the topological gel. The application field of this novel material spreads rapidly. They are, for example, scratch-resistant coatings, vibration-proof and sound-proof insulation materials for sound speakers, highly abrasive polishing media, dielectric actuators, pressure sensitive adhesives, and so on.

In scratch-resistant coatings, PCL-modified PR is used in combination with suitable isocyanates and polyols; this enables a high crosslink density while keeping the glass-transition temperature low. This is quite an important concept in the formulation and achievement of scratch-resistant properties on the coated surface. Because of the high elasticity and flexibility of SRM coatings, the material is able to change back to its original shape after the application of force and fill the gap in the surface, as schematically shown in Figure 3. Small damage can thus be repaired in a matter of seconds, as shown in Figure 4. It turned out that in addition to scratch-resistant properties, SRM coatings show strong adhesion to the substrates, which prevents

crack and peel off from the substrates. It should also be noted that these properties are less dependent on the surrounding temperature. The development of SRM coating was originally begun for automotive top coat use, although it has been applied to mobile devices, their accessories, and so on. In a recent study, UV-curable scratch resistant coatings were also developed.

In addition to scratch-resistant properties, the SRM coating increases the loss tangent, especially in the high (>8 kHz) frequency range, as shown in Figure 5.⁴⁹ When it is applied to a speaker cone, it enables the reduction of unnecessary vibrations of the cone, and this results in the achievement of clear and smooth sound. This technology is also of practical use.

Because PCL-modified PR can be easily incorporated into polyurethane, a wide variety of applications in coatings, adhesives, sealants, and elastomers (typical applications of the polyurethane industry) are under development. Pressure-sensitive adhesives for liquid-crystalline displays (LCDs) are typical examples. Because each molecular component in an LCD has different coefficients of thermal expansion, stress based on thermal expansion mismatching occurs among the components in use. This may cause a light leak, which deteriorates the quality of the display. To prevent this problem, a stress-relaxation, pressure-sensitive adhesive is used to assemble LCD panels. For this kind of pressure-sensitive adhesive, large stress-relaxation and high adhesion properties are required at the same time, but it is not easy to make these two properties compatible with each

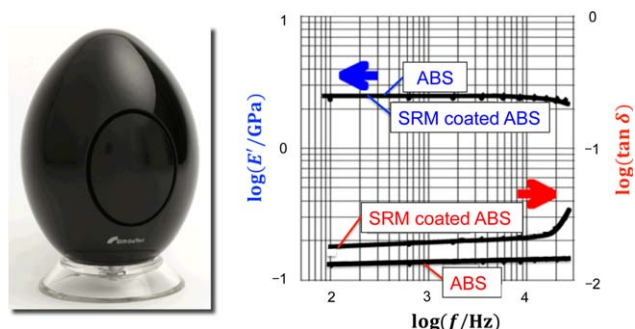


Figure 5. Egg-shaped speaker with a cone with an SRM-coated acrylonitrile-butadiene-styrene (ABS) resin. The right figure shows the difference between the cone with and without an SRM coating in the frequency dependence of the viscoelastic profiles. Although the SRM coating yielded no change in E' , it increased the mechanical loss tangent ($\tan \delta$), especially in a higher frequency region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

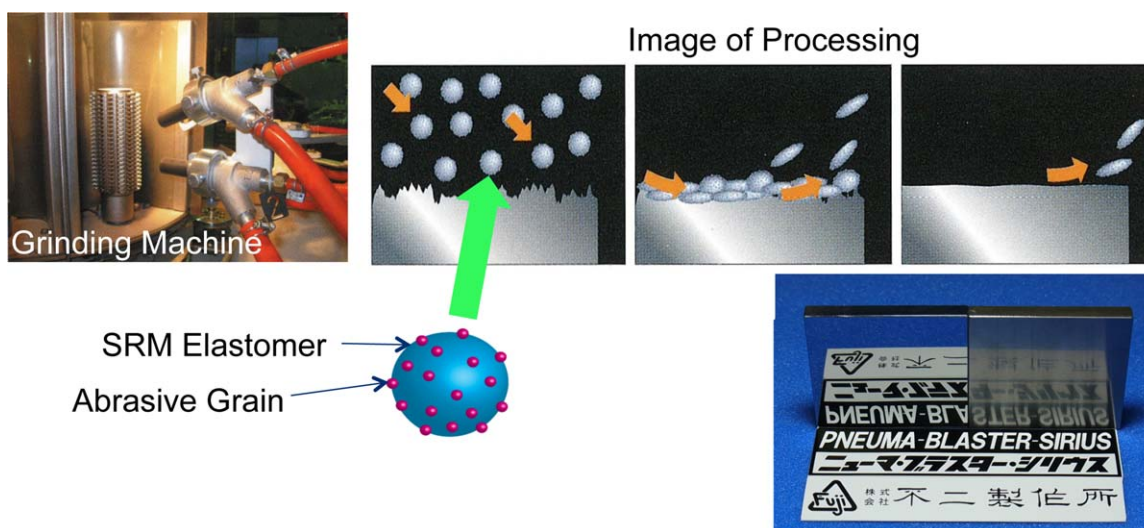


Figure 6. Highly abrasive polishing media with an abrasive supported on an SRM elastomer. The brand new polishing media could achieve a superior mirror surface finish with a processing machine that used a kind of conventional blasting known as *shot peening*. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

other. An increased amount of isocyanates crosslinker can easily improve the holding strength, but it reduces the stress relaxation dramatically. Instead of isocyanates, the addition of only a few weight percentage of PCL-modified PR enables a pressure-sensitive adhesive to realize strong adhesion without losing relaxation properties and elongation.

PCL-modified PR can also make polyurethane elastomers extremely soft with quite a low compression set, low hysteresis loss, and high transparency. SRM elastomers keep these properties, even with a high content of inorganic fillers or nanoparticles. By taking advantage of these properties, researchers have developed a couple of unique products, such as highly abrasive polishing media and dielectric actuators.

Highly abrasive polishing media have been recently developed with an SRM elastomer and abrasive, as shown in Figure 6, where the abrasive is supported on the surface of the SRM elastomer.⁵⁰ This brand new polishing media can achieve a superior mirror surface finish with a processing machine that employs a kind of conventional blasting known as *shot peening*. The polishing mechanism is explained as follows. When this polishing media is sprayed from the processing machine to the work surface, it hits the surface but does not bounce like conventional polyurethanes because of its softness, in other words, the J-shaped elasticity of SRMs, which can disperse and absorb the repulsive energy of the vertical direction from the surface at the collision. Meanwhile, the polishing media moves along the surface by residual collision energy in the horizontal direction. As a result, the polishing media uses collision energy effectively to polish the work surface. Fundamentally, any abrasive of various hardness can be supported on the surface of the SRM elastomer; thus, this technology is applicable to a wide variety of work pieces from resins to carbide or ceramics. The mirror surface finish was conventionally achieved by craftsman handwork. This new technology using an SRM elastomer will contribute to the automation of mirror-surface polishing, which is in great demand in many industries.

Various types of actuators using polymers have been proposed and developed.^{51–56} Among them, dielectric polymer actuators have recently drawn attention because of their potential high power, lightness, and energy efficiency compared to conventional actuators, such as electromagnetic motors. Dielectric polymer actuators consist of an electrically insulating elastomer and stretchable

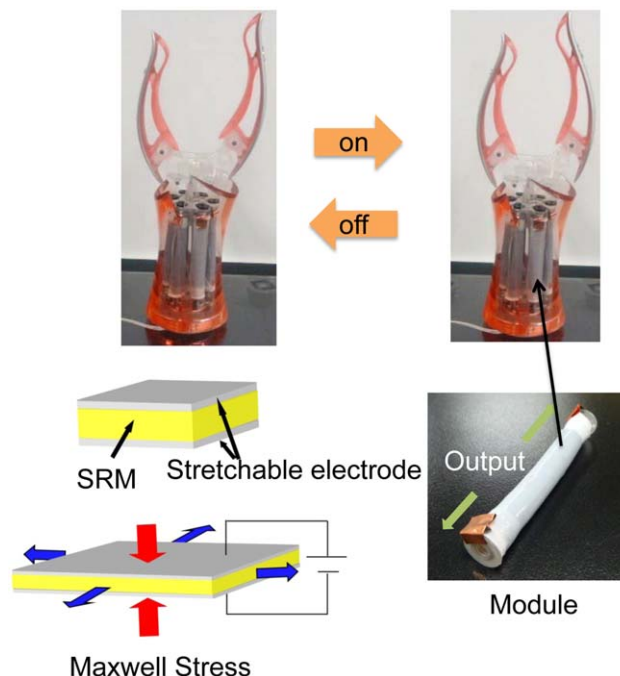


Figure 7. Dielectric polymer actuator with an SRM elastomer. An eight-roll-type actuator inside the claw-shaped artificial hand stretched simultaneously as rapidly as the voltage was induced, and this resulted in the closing of the claws. The softness of the SRM elastomer realized a large strain under a low voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrodes, as schematically shown in Figure 7, where the elastomer layer is sandwiched by the electrodes. When a voltage is applied to both electrodes, the electrodes pull each other by Coulombic forces between them. As a result, the elastomer layer is squeezed and flattened, and then, the elastomer returns to its original form when the voltage is turned off. For the elastomeric material used in this device, mechanical properties of extreme softness and low hysteresis are desired to achieve a large strain under a low voltage, a high energy efficiency, and a fast response and repeatability. Thus, the properties of SRMs, such as their J-shape elasticity, extreme softness, low hysteresis loss, and high compatibility with inorganic fillers, bring about a great advantage over conventional rubbers or elastomers in the development of dielectric polymer actuators. The SRM actuator can be used for a vibrator when an alternating-current voltage is applied. The unique characteristic will lead to lighter, smaller, quieter, more responsive, energy-efficient, and high-performance actuators in the near future.⁵⁷

As mentioned before, the topological gel shows a J-shaped stress-strain curve similar to that of biomaterials. Hence, it has great potential to be applied in biomaterials and cosmetics, such as in soft contact lenses and serum face masks, although they have not been on the market yet. On the other hand, the unique structure of PR and pseudo-PR has been intensively researched for biomedical uses so far.⁵⁸ When the bulky end of PR is cleaved *in situ*, the cyclic components are dissociated from the axis backbone. These biodegradable PRs can be used for the delivery of drugs,^{58,59} DNA,⁶⁰ and RNA.⁶¹

CONCLUSIONS

Topological gels or SRMs are a novel class of polymeric materials characterized by movable crosslinks and free rings. Their peculiar structure and physical properties are fundamentally explained by the pulley effect and the distribution entropy of rings. SRMs have been applied to self-healing coatings, vibration- and sound-insulation materials, highly abrasive polishing media, and dielectric actuators because they are extremely soft and have a strong recovery force. The novel architecture of crosslinking will create a new field in polymer science and technology.

ACKNOWLEDGMENTS

One of the authors (K.I.) thanks his colleagues, Kazuaki Kato and Koichi Mayumi, for their continuous support and gratefully acknowledges collaboration with Mitsuhiro Shibayama for the SANS measurements, Yoshiyuki Amemiya for the SAXS measurements, and Kenji Urayama for the mechanical and swelling property experiments. The authors also thank Nissan Motor Co., Ltd., NTT DOCOMO, Inc., Bifrostec, Inc., Fuji Manufacturing Co., Ltd., and Toyoda Gosei Co., Ltd., for their cooperation with applications of SRMs. This work was partially supported by Japanese Grants in Aid for Scientific Research (S; contract grant numbers 20221005 and 25220603).

REFERENCES

1. Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Oxford University Press: Oxford, **1975**.
2. Mark, J. E.; Erman, B. *Rubber Elasticity: A Molecular Primer*, 2nd ed.; Cambridge University Press: Cambridge, **2007**.
3. *Gels Handbook*; Osada, Y., Kajiwara, K., Eds.; Academic: Amsterdam, **2000**.
4. Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y. *Adv. Mater.* **2003**, *15*, 1155.
5. Haraguchi, K.; Takehisa, T. *Adv. Mater.* **2002**, *16*, 1120.
6. Sakai, T.; Matsunaga, T.; Yamamoto, Y.; Ito, C.; Yoshida, R.; Suzuki, S.; Sasaki, N.; Shibayama, M.; Chung, U. I. *Macromolecules* **2008**, *41*, 5379.
7. Okumura, Y.; Ito, K. *Adv. Mater.* **2001**, *13*, 48.
8. Harada, A.; Li, J.; Kamachi, M. *Nature* **1992**, *356*, 325.
9. de Gennes, P. G. *Phys. A* **1999**, *271*, 231.
10. Granick, S.; Rubinstein, M. *Nat. Mater.* **2004**, *3*, 586.
11. Ito, K. *Polym. J.* **2007**, *39*, 488.
12. Ito, K. *Curr. Opin. Solid State Mater. Sci.* **2010**, *14*, 28.
13. Ito, K. *Polym. J.* **2011**, *44*, 38.
14. Araki, J.; Zhao, C.; Ito, K. *Macromolecules* **2005**, *38*, 7524.
15. Oya, T.; Noguchi, M.; Yui, N. *J. Am. Chem. Soc.* **2003**, *125*, 13016.
16. Oya, T.; Utsunomiya, H.; Noguchi, M.; Yui, N. *Bioconjugate Chem.* **2005**, *16*, 62.
17. Fleury, G.; Brochon, C.; Schlatter, G.; Lapp, A.; Hadziioannou, G. *Soft Matter* **2005**, *1*, 378.
18. Araki, J.; Ito, K. *Soft Matter* **2007**, *3*, 1456.
19. Kataoka, T.; Kidowaki, M.; Zhao, C.; Minamikawa, H.; Shimizu, T.; Ito, K. *J. Phys. Chem. B* **2006**, *110*, 24377.
20. Sakai, T.; Murayama, H.; Nagano, S.; Takeoka, Y.; Kidowaki, M.; Ito, K.; Seki, T. *Adv. Mater.* **2007**, *19*, 2023.
21. Kidowaki, M.; Nakajima, T.; Araki, J.; Inomata, A.; Ishibashi, H.; Ito, K. *Macromolecules* **2007**, *40*, 6859.
22. Inomata, A.; Kidowaki, M.; Sakai, Y.; Yokoyama, H.; Ito, K. *Soft Matter* **2011**, *7*, 922.
23. Araki, J.; Kataoka, T.; Ito, K. *Soft Matter* **2008**, *4*, 245.
24. Kato, K.; Komatsu, K.; Ito, K. *Macromolecules* **2010**, *43*, 8799.
25. Yu, S.; Zhang, Y.; Wang, X.; Zhen, X.; Zhang, Z.; Wu, W.; Jiang, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 7277.
26. Yu, H.; Feng, Z.; Zhang, A.; Hou, D.; Sun, L. *Polymer* **2006**, *47*, 6066.
27. Zhang, X.; Zhu, X.; Tong, X.; Ye, L.; Zhang, A.; Feng, Z. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 5283.
28. Karaky, K.; Brochon, C.; Schlatter, G.; Hadziioannou, G. *Soft Matter* **2008**, *4*, 1165.
29. Iguchi, H.; Uchida, H.; Koyama, Y.; Takata, T. *ACS Macro Lett.* **2013**, *2*, 527.
30. Gizek, T. *J. Incl. Phenom. Macrocycl. Chem.* **2013**, *76*, 237.
31. Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.-A.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008**, *130*, 5022.
32. Freeman, W. A.; Mock, W. L.; Shih, N.-Y. *J. Am. Chem. Soc.* **1981**, *103*, 7367.
33. Gutsche, C. D. *Calixarenes*; Royal Society of Chemistry: Cambridge, **1989**.

34. Travelet, C.; Schlatter, G.; Hébraud, P.; Brochon, C.; Lapp, A.; Anokhin, D. V.; Ivanov, D. A.; Gaillard, C.; Hadziioannou, G. *Soft Matter* **2008**, *4*, 1855.
35. Mayumi, K.; Ito, K. *Polymer* **2010**, *51*, 959.
36. Zielinski, F.; Buzier, M.; Lartigue, C.; Bastide, J. *Prog. Colloid Polym. Sci.* **1997**, *90*, 115.
37. Karino, T.; Okumura, Y.; Zhao, C.; Kataoka, T.; Ito, K.; Shibayama, M. *Macromolecules* **2005**, *38*, 6161.
38. Shinohara, Y.; Kayashima, K.; Okumura, Y.; Zhao, C.; Ito, K.; Amemiya, Y. *Macromolecules* **2006**, *39*, 7386.
39. Zhao, C.; Domon, Y.; Okumura, Y.; Okabe, S.; Shibayama, M.; Ito, K. *J. Phys. Condens. Matter* **2005**, *17*, S2841.
40. Mayumi, K.; Nagao, M.; Endo, H.; Osaka, N.; Shibayama, M.; Ito, K. *Phys. B* **2009**, *404*, 2600.
41. Bitoh, Y.; Akuzawa, N.; Urayama, K.; Takigawa, T.; Kidowaki, M.; Ito, K. *Macromolecules* **2011**, *44*, 8661.
42. Fleury, G.; Schlatter, G.; Brochon, C.; Travelet, C.; Lapp, A.; Linder, P.; Hadziioannou, G. *Macromolecules* **2007**, *40*, 535.
43. Kato, K.; Ito, K. *Soft Matter* **2011**, *7*, 8737.
44. Kato, K.; Yasuda, T.; Ito, K. *Macromolecules* **2012**, *46*, 310.
45. Mayumi, K.; Tezuka, M.; Bando, A.; Ito, K. *Soft Matter* **2012**, *8*, 8179.
46. Sevick, E. M.; Williams, D. R. M. *Langmuir* **2010**, *26*, 5864.
47. Konda, A.; Mayumi, K.; Urayama, K.; Takigawa, T.; Ito, K. *Macromolecules* **2012**, *45*, 6733.
48. Katsuno, C.; Konda, A.; Urayama, K.; Takigawa, T.; Kidowaki, M.; Ito, K. *Adv. Mater.* **2013**, *25*, 4636.
49. D-Egg. Feb-15-2014. <http://www.bif-degg.jp>.
50. Fuji Manufacturing. Feb-15-2014. <http://www.fujimfg.co.jp/english/sirius.html>
51. Kaneto, M.; Kaneto, K.; Fujisue, H.; Kunifusa, M.; Takashima, W. *Smart Mater. Struct.* **2007**, *16*, S250.
52. Smela, E.; Inganäs, O.; Lundström, I. *Science* **1995**, *268*, 1735.
53. Pei, Q.; Inanäs, O. *Synth. Met.* **1993**, *55*, 3730.
54. Asaka, K.; Oguro, K. *J. Electroanal. Chem.* **2000**, *480*, 186.
55. Fukushima, T.; Asaka, K.; Kosaka, A.; Aida, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 2410.
56. Pelrine, R.; Kornbluh, R.; Pei, Q. B.; Joseph, J. *Science* **2000**, *287*, 5454.
57. Takeuchi, M. *Kobunshi* **2013**, *62*, 133.
58. Yui, Y. In *Supramolecular Polymer Chemistry*; Harada, A., Ed.; Wiley-VCH: Weinheim, **2012**; Chapter 9.
59. Liu, R.; Lai, Y. S.; He, B.; Li, Y.; Wang, G.; Chang, S.; Gu, Z. *Int. J. Nanomed.* **2012**, *7*, 5249.
60. Yamashita, A.; Yui, N.; Ooya, T.; Kano, A.; Maruyama, A.; Akita, H.; Kogure, K.; Harashima, H. *Nat. Protoc.* **2006**, *1*, 2861.
61. Kulkarni, A.; DeFrees, K.; Schuldt, R. A.; Hyun, S.-H.; Wright, K. J.; Yerneni, C. K.; VerHeul, R.; Thompson, D. H. *Mol. Pharm.* **2013**, *10*, 1299.