Cutting-Edge Science of Cyclodextrin

Review

Slide-Ring Materials Using Cyclodextrin

Kohzo Ito

Graduate School of Frontier Sciences, The University of Tokyo;
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We have recently synthesized slide-ring materials using cyclodextrin by cross-linking polyrotaxanes, a typical supramolecule. The slide-ring materials have polymer chains with bulky end groups topologically interlocked by figure-of-eight shaped junctions. This indicates that the cross-links can pass through the polymer chains similar to pulleys to relax the tension of the backbone polymer chains. The slide-ring materials also differ from conventional polymers in that the entropy of rings affects the elasticity. As a result, the slide-ring materials show quite small Young’s modulus not proportional to the cross-linking density. This concept can be applied to a wide variety of polymeric materials as well as gels. In particular, the slide-ring materials show remarkable scratch-proof properties for coating materials for automobiles, cell phones, mobile computers, and so on. Further current applications include vibration-proof insulation materials for sound speakers, highly abrasive polishing media, dielectric actuators, and so on.

Key words cyclodextrin; polymer; polyrotaxane; supramolecule; gel

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides: α-, β-, or γ-CDs have six, seven, or eight glucose units of 0.44, 0.58, or 0.74 nm in inner diameter, respectively.1,2) CDs show high biosafety and biocompatibility for pharmaceutical use, 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, watersoluble CDs tend to include small hydrophobic molecules such as drugs in their cavities, which is called inclusion complex formation. As a result, CDs have been used to improve the water solubility of drugs in the pharmaceutical industry. On the other hand, CDs can include a polymer chain as well as small molecules. 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)3): CDs mixed with PEG in water were threaded onto a PEG self-assembly. Subsequently, both ends of the pseudo-polyrotaxane were capped with bulky groups to form polyrotaxane (PR) in 1992.4)

We have recently developed supramolecular cross-linking structure based on the PR architecture as shown in Fig. 1.5) We prepared PR sparsely containing α-CD and subsequently cross-linked α-CDs on different PRs. 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 slide-ring materials.6) Such a polymeric material with freely movable cross-links was theoretically proposed as a sliding gel by de Gennes in 1999.7) In addition, Granick and Rubinstein reviewed the historical significance of the slide-ring materials...
or gels compared to the slip-link model. In this review, we provide an overview of the slide-ring materials using CDs. 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 Goodyear discovered the cross-linking of natural rubber.

2. Pulley Effect and Entropy of Rings

The slide-ring materials have polymer chains topologically interlocked by figure-of-eight junctions. Therefore, they can move freely to relax the tension of the backbone polymer chains similar to pulleys, which is called the pulley effect. The pulley effect yields peculiar mechanical properties of the slide-ring materials such as extreme softness or low Young’s modulus, J-shaped stress–strain curve, high stretchability over 20 times in length, huge volume swellability up to 24000 times as much as the dry state by weight. Another important feature in the slide-ring materials is the entropy of rings. The slide-ring materials have two kinds of entropy coupled with each other by the pulley effect: the distribution entropy of rings on PR and conformational entropy of the backbone string in PR. These two kinds of entropy behave almost independently of each other in PRs when they are not cross-linked. This is because rings can have an arbitrary distribution irrespective of the axis chain conformation. In the slide-ring materials, however, the two kinds of entropy are strongly coupled with each other by the pulley effect as shown in Fig. 2. On tensile deformation, axis polymer chains in the slide-ring materials are deformed to anisotropic conformation in a short-time scale, followed by the pulley effect that they pass through figure-of-eight shaped cross-links. However, uncross-linked free rings cannot pass through figure-of-eight cross-links. This means that the pulley effect changes the length of network strands between cross-links but the number of rings between cross-links is kept constant. Consequently, the pulley effect yields heterogeneous distribution of free rings, which leads to the entropic elasticity. In other words, the topological asymmetry of ring and string exchanges two kinds of entropy by the pulley effect in the slide-ring materials.

3. Diversification of Slide-Ring Materials

Chemical modifications to the cyclic components of PRs have been performed to give the slide-ring materials new functions as well as to improve the solubility of PR. Different functional groups are introduced on CDs to obtain new slide-ring materials with various properties such as thermoresponsive behavior, photo-responsive volume changes, mesogen-modified slide-ring gels, and sliding graft copolymers in which CDs are modified with polycaprolactone. Most PRs have been synthesized using PEG as an axis polymer chain, although many other polymers are known to form inclusion complexes or pseudo-PR with α-, β-, and γ-CDs selectively. However, it is difficult to form PR with both the ends capped in almost all of them since the end-capping reactions of inclusion complexes always compete against the dissociation. The problem was partly overcome by capping the same CD as a capping agent, grafting a polymer chain with long side chains, and so on. Consequently, poly(dimethyl siloxane), polybutadiene, and a copolymer of poly(propylene glycol) and PEG can form PR and slide-ring gels.

4. Structure and Physical Properties

The nano- and meso-scopic structures of slide-ring materials and PRs have been investigated by small-angle neutron scattering (SANS), small-angel X-ray scattering (SAXS), and quasi-elastic light scattering (QELS). The structural analysis demonstrates that PR in dimethyl sulfoxide takes a rodlike conformation because of the strong hydrogen bonding between adjacent CDs. As PR concentration increases, these aggregations stack hexagonally to form columnar microcrystals of PRs. When hydroxyl groups on CDs in PR are modified, on the other hand, the conformation of PR changed from rodlike to a coiled one, where CDs are randomly distributed along PEG. This is mainly because the hydrogen bonding between adjacent CDs is hindered by the modification.

The SANS profile of the chemical gel shows prolate patterns parallel to the stretching direction, which is called an abnormal butterfly pattern. Meanwhile, the slide-ring gel indicates prolate patterns perpendicular to the stretching direction, i.e., a normal butterfly pattern as shown in Fig. 3. The normal butterfly pattern is also seen in polymer films and solutions because of the orientation of the polymer chains along the elongation or flow direction. This means that the slide-ring gel has a homogeneous structure on tensile deformation, which is ascribable to the pulley effect by freely movable cross-links.

The mechanical properties of slide-ring materials are quite different from the usual polymeric materials. Polymeric materials with covalent cross-links such as chemical gels show the S-shaped stress–strain curve while the slide-ring gel exhibits a J-shaped curve without hysteresis loop. This difference was explained by the free junction model based on the pulley effect. The J-shaped curves yield the toughness.
of materials and are seen in many biomaterials such as mammalian skin, vessels and tissues. The J-shaped curve gives us low modulus drastically decreasing the energy released in a fracture. This means that the slide-ring materials would be promising for various biomaterials.

The biaxial strain testing gives us information on more detailed mechanical properties of polymeric materials. Covalently cross-linked polymeric materials such as chemical gels and elastomers generally exhibit a large strain-coupling: when they are stretched, the stresses are yielded on the horizontal face as well as the vertical one to the elongated direction. This reflects that all chains in a network are connected with each other. However, the slide-ring gels have negligibly small strain-coupling and Neo-Hookean stress–strain behavior similar to ideal rubber elasticity. This may be because the pulley effect can decouple the strains in different directions.

Usual chemical gels and elastomers have the viscoelastic profile of no frequency dispersion and the equilibrium modulus from the entropic elasticity of polymer conformation. Meanwhile, the viscoelastic profile of the slide-ring gel exhibits a frequency dispersion or relaxation, i.e., the sliding transition as shown in Fig. 4. The transition time of the sliding transition increases with the cube of the polymer length between cross-links. This dependence reflects the sliding motion of polymer chains through cross-links, i.e., the reptation of backbone polymer chains in the order of the length of a network strand between cross-linked junctions. The slide-ring materials have Young’s modulus due to how many free rings are included. This is similar to a one-dimensional tube, in which air molecules are confined. The molecular simulation suggests that free rings behave as a one-dimensional air spring.

The solvent permeation properties are also different between the slide-ring gel and usual ones. The conventional chemical and physical gels show that the steady-state flow velocity of fluids is proportional to the induced pressure as well as conventional porous membranes, which is called Darcy’s law. This means that the classical gel has the constant friction coefficient between gel network and fluid independently of the pressure. On the other hand, the slide-ring gel indicates a drastic increase of the friction at a pressure threshold as shown in Fig. 5. This suggests that the induced pressure changes the network size in the slide-ring gel due to the movable cross-links. In other words, the slide-ring gel shows the on-off control of fluid permeation induced by the pressure.
5. Application of Slide-Ring Materials

When PR is modified with polycaprolactone and cross-linked with other polymers such as acrylate polymers, polyurethanes, and so on, the unique mechanical properties of the movable cross-links can be applied to elastomers and resins in the solid state. Here the cross-linking points yield the pulley effect to relax the tensions among polymers. If the cross-links and free rings slide along the axis polymer chain, the chain length of a network strand between cross-linking junctions changes and uncross-linked free rings have the air spring effect. As a result, the slide-ring materials show low Young’s modulus, small compression set, and small stress relaxation.

The slide-ring materials can be used for scratch-proof coatings and finishes.32 Small damage in the slide-ring materials is repaired in a matter of seconds since the slide-ring materials are used for dielectric materials for sound speakers, highly abrasive polishing media, and so on. The slide-ring materials are also used for dielectric actuator due to extreme softness even in a high content of inorganic nanoparticles and high dielectric constant, which leads to the large strain under low voltage.

6. Conclusion

Slide-ring materials are a novel class of polymeric materials characterized by movable cross-links, which yield the pulley effect and strong coupling between two kinds of entropy of rings and strings. They show various peculiar physical properties quite different from usual polymeric materials such as low Young’s modulus, the sliding transition, J-shaped stress–strain curves and so on. The slide-ring materials are applied to self-healing coatings, vibration insulation materials, highly abrasive polishing media, and dielectric actuators. The novel architecture of cross-linking will create a new field in polymer science and technology.

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References