Small-Angle X-Ray Scattering Study on Deformation Mechanism of Highly Stretchable Hydrogels Using Polyrotaxane Cross-linkers

Extremely stretchable and tough hydrogels are fabricated by incorporating a small amount of polyrotaxane cross-linker into polymer networks. Polyrotaxane is a necklace-like supramolecular assembly in which cyclic molecules are threaded on an axial linear chain, and the cyclic molecules can slide along the axial chain. By cross-linking cyclic molecules in polyrotaxanes with polymer networks, we can introduce slidable cross-links in the gels. The sliding motion of the cyclic molecules in the gels homogenizes the network structure, remarkably improving stretchability and toughness. We have performed small-angle X-ray scattering (SAXS) experiments on the gels containing polyrotaxane cross-linkers under deformation to characterize the homogeneity of the polymer network.

Hydrogels, which are polymer networks swollen in water, have been expected to be used as biomaterials such as artificial skin, artificial vessels, and joint prostheses because of their high biocompatibility. However, one of the problems for such biological applications is that conventional hydrogels are quite brittle. To improve the mechanical strength of hydrogels, various chemical designs of polymer networks have been proposed in the last two decades [1]. One promising strategy to toughen the gels is to connect polymer chains by slidable cross-links. Okumura and Ito developed a novel type of advanced polymer gel, called a “slide-ring (SR) gel” [2, 3]. SR gel is prepared from polyrotaxane (PR), which is a necklace-like molecule composed of an axial polymer chain and cyclic molecules. By cross-linking the cyclic molecules on different PRs, the linear polymers are interlocked by figure-of-eight cross-links composed of cyclic molecules. The cross-links can slide along the polymer chains to equalize the internal stress in SR gels just like pulleys. Due to the mobility of the cross-links, SR gels demonstrate remarkable properties such as high extensibility and a great degree of swelling.

Recently, Imran et al. reported that introducing slidable cross-links into conventional chemical gels changes drastically the mechanical toughness [4]. *N*-Isopropylacrylamide (NIPA) hydrogel is a well-known thermoresponsive gel that changes in volume in response to temperature. To improve the low mechanical strength of NIPA hydrogels, NIPA and sodium acrylic acid (AAcNa) monomers are polymerized by polyrotaxane cross-linkers in which cyclic molecules contain vinyl groups. The NIPA-AAcNa-PR hydrogels with slidable cross-linking points show excellent stretchability and toughness compared with conventional NIPA gels (Fig. 1). The mechanical toughness is thought to result from the mobility of the ring molecules like SR gels.

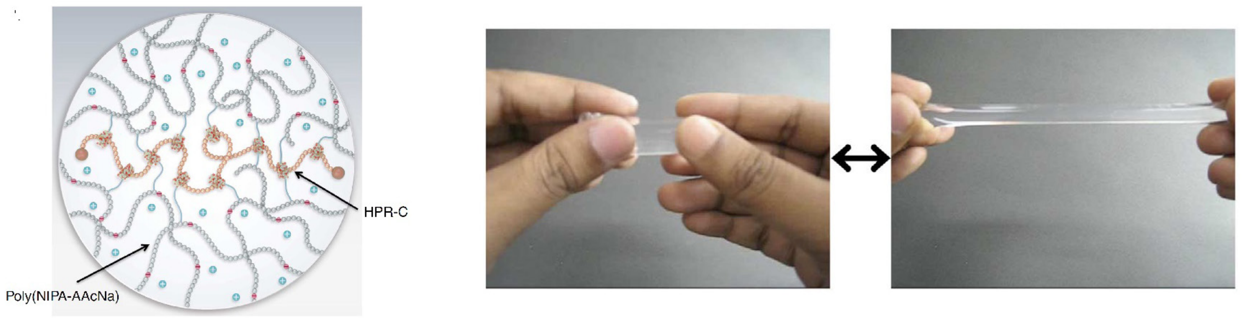

Figure 1: Schematic view of highly stretchable hydrogel containing polyrotaxane cross-linkers and photograph of deformed state of the gel. The figure was reproduced from ref. 4.

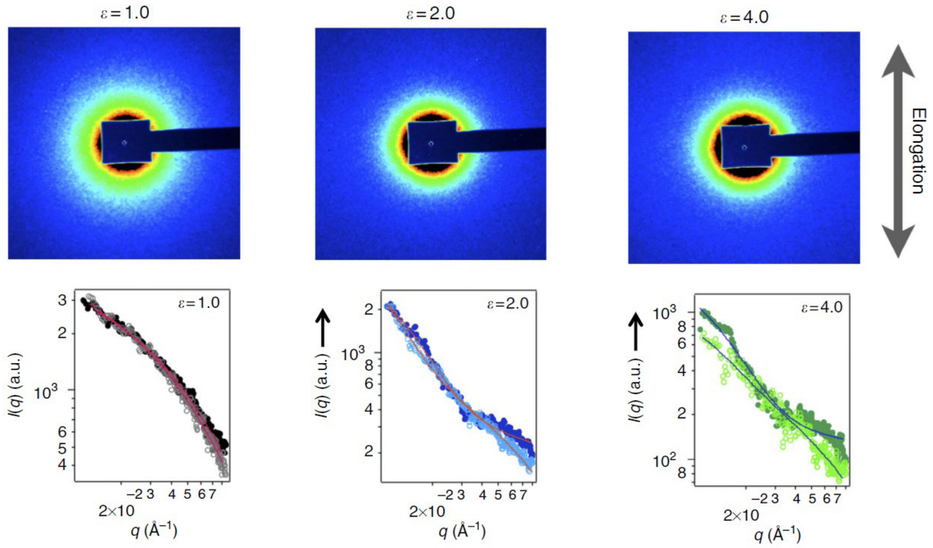

Figure 2: 2-D SAXS patterns and sector average of the 2-D patterns (open circles: the direction parallel to the elongation, closed circles: the direction perpendicular to the elongation) for the highly stretchable gels with polyrotaxane under deformation. ε is the stretching ratio. The figure was reproduced from ref. 4.

To confirm the pulley effect of the movable cross-links in the NIPA-AAcNa-PR hydrogels, we performed small-angle X-ray scattering (SAXS) experiments on deformed gels. When the conventional chemical gels are deformed, the inhomogeneity of the network structure is enhanced; the inhomogeneous structure has been observed by SAXS and small-angle neutron scattering (SANS) [1]. The two-dimensional (2D) X-ray or neutron scattering patterns of deformed chemical gels are elongated in the stretching direction. The anisotropic scattering patterns, called abnormal butterfly patterns, originate from the inhomogeneous network structure [1]. Figure 2 (top) shows 2D SAXS patterns of the NIPA-AAcNa-PR hydrogels under uniaxial deformation (stretching ratio ε = 1, 2, 4). The SAXS pattern of the hydrogel remains isotropic at high deformation ratios, which is consistent with the results for SR gels in a good solvent [3]. The isotropic SAXS patterns indicate that the mobility of the ring molecules in the PR cross-linkers suppresses the inhomogeneity of the network structure. We quantitatively evaluated the SAXS patterns by calculating the sector average of the intensity in the directions parallel and perpendicular to the stretching. Figure 2 (bottom) shows the sector-averaged scattering profiles of the hydrogel at elongation ratios ε = 1–4 in each direction. We can fit the scattering functions with the sum of two functions: a Lorentzian function that describes polymer concentration fluctuation, and a squared Lorentzian function that corresponds to excess scattering from spatial inhomogeneity. The correlation length ξ and Ξ for the Lorentzian and squared Lorentzian function remains almost constant for all deformation ratios, which suggests that the NIPA-AAcNa-PR hydrogels have a more homogenous structure than conventional chemical gels. Thus, the SAXS results prove that the movable cross-links in the gels homogenize the polymer network structure.

Using a small amount of polyrotaxane as a cross-linker in a polymer network leads to dramatic changes in the toughness. This method can be applied to various polymer networks to improve their mechanical strength. Developing hydrogels with good mechanical performance in a simple way at low cost will enable new applications of hydrogels in the fields of drug delivery systems, tissue engineering, and biomaterials.

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BEAMLINES

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