

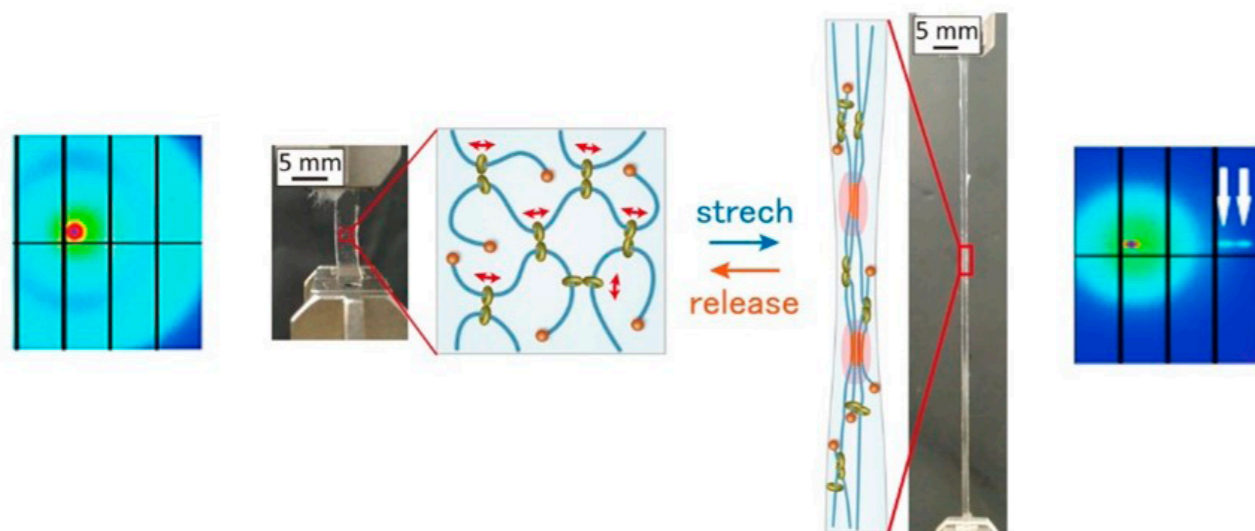
## Tough Polymer Gels Reinforced by Strain-Induced Crystallization

Recently, we have discovered that strain-induced crystallization of polymer chains occurs in slide-ring (SR) gels with slidable cross-links and simple polymer gels having homogeneous network structures. From in-situ wide-angle X-ray scattering (WAXS) experiments on the gels under repeated tensile deformation, we have found that crystalline of polymer strands in the gels forms at a large strain and destructs quickly when applied stress is reduced. The reversible strain-induced crystallization yields the high toughness and instant recoverability, which are necessary for soft actuators/sensors and artificial tendons/ligaments.

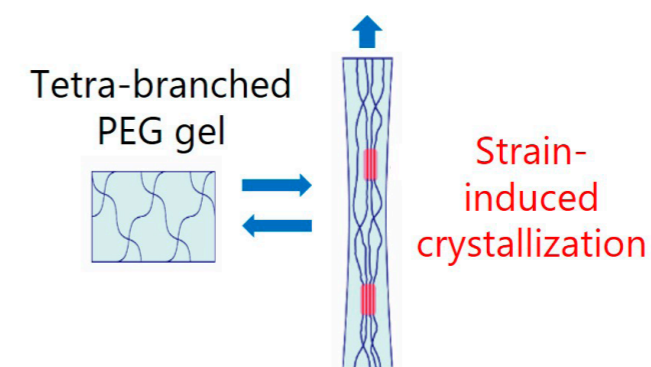
Tough polymer gels are required for various applications such as soft actuators/sensors, and artificial tendons/ligaments. For these applications, the polymer gels should show reversible mechanical responses under repeated high stress at a high frequency (ex. 1 Hz). Most tough hydrogels are reinforced by introducing sacrificial structures that can break under deformation and dissipate input energy [1, 2]. However, since the sacrificial damages cannot recover instantly, the toughness of these gels drops substantially during consecutive cyclic loadings. Recently, we have successfully developed tough and

instantly recoverable polymer gels utilizing reversible strain-induced crystallization (SIC) [3-6].

We have discovered that reversible SIC can occur in slide-ring (SR) hydrogel in which polymer chains are cross-linked by ring molecules [3]. The cross-linking points composed of ring molecules can slide along polymer chains to eliminate stress heterogeneities during deformation. The SR gel can survive at high stress (>5 MPa) and high strain (> 1000%). Also, the mechanical hysteresis under repeated cycle is quite small, and the instant recovery of extension energy between two consecutive cycles is 95 %. From



**Figure 1:** Reversible strain-induced crystallization in slide-ring hydrogels. Reproduced from Ref. 3 with permission from the American Association for the Advancement of Science.



**Figure 2:** Reversible strain-induced crystallization in Tetra-branched PEG gels.

in-situ wide-angle X-ray scattering (WAXS) experiments on the SR gel under repeated tensile deformation, we found that crystalline of PEG in the gels forms at a large strain and destructs quickly when applied stress is reduced (Fig. 1). The reversible strain-induced crystallization yields the high toughness and instant recoverability of the SR gel.

The toughening mechanism using SIC can be applied to simple polymer gels cross-linked by covalent bonds. We have found that tri-branched poly(ethylene glycol) (PEG) hydrogels show reversible SIC under cyclic stretching (Fig. 2) [4]. Furthermore, tetra-branched PEG hydrogels show SIC when PEG concentration and molecular weight between cross-links are high enough [5]. The tetra-branched PEG hydrogels can be prepared just by mixing end-functionalized tetra-PEG macromers which are commercially available. This finding leads to a simpler and low-cost fabrication process of tough and instantly recoverable gels.

The SIC of PEG chains can occur not only in hydrogels swollen with water, but also in ion gels containing salt as solvent. We have fabricated SR ion gels in which PEG chains are cross-linked by cyclodextrins (CDs) and dissolved in Li ions [6]. The SR ion gels show SIC of PEG under stretching, which results in their high crack propagation resistance and

remarkable mechanical toughness. In addition, CDs are aggregated to form a continuous hard domain, and so the SR ion gels exhibit high Young's moduli (high stiffness). High Young's modulus is important for suppressing short circuit caused by growth of Li dendrites from electrode during charge-discharge of Li ion batteries. As a result, we have successfully developed a tough and stiff gel electrolyte, which are expected to be applied for separator membranes of flexible Li ion batteries.

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### BEAMLINE

BL-10C

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