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Theory and experiments on elasticity of topological gels

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最近、物理ゲルでも化学ゲルでもない新しい種類のゲル「トポロジカルゲル」が注目を集めている。トポロジカルゲルは伸長時に極めて柔らかい初期弾性を示すことが見出されている。我々はトポロジカルゲルの特徴である「線状高分子が架橋点を自由に通り抜ける」効果（滑車効果）に着目し、化学ゲルの３chainモデルに基づく弾性理論を拡張して、トポロジカルゲルの伸張弾性理論を得た。トポロジカルゲル特有の極端に柔らかい非線形弾性を理論的に再現することに成功した。また貧溶媒中での硬い弾性は滑車効果の消失に起因することを見出した。

1 Topological gel

Polymer gels, three-dimensional network of polymer chains, are classified into chemical and physical gels. However, we have recently developed 'topological gel' or 'slide-ring gel' with a novel kind of cross-linking junctions using cyclic molecules [1]. In the topological gel, the polymer chains with bulky end groups are neither covalently cross-linked like chemical gels nor attractively interacted like physical gels, but are topologically interlocked by figure-of-eight cross-links. The polymer chains in topological gel pass through the figure-of-eight cross-links like pulleys to equalize their tensions cooperatively. We call these functions 'pulley effect' [1]. In this study, we confirm the pulley effect of the figure-of-eight cross-links through mechanical properties of the topological gel by the stress-strain behavior.

2. MATERIALS

We use polyrotaxane (PR) consisting of α-cyclodextrin (α-CD) and poly(ethylene glycol) (PEG), in which α-CDs are threaded on a single PEG chain and are trapped by capping the chain with bulky end groups. In this case, PEG chain with large molecular weight (MW=100,000 or 500,000) is used to form polyrotaxane sparsely populated with α-CDs,

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because PEG with larger molecular weight forms sparse inclusion complexes with α-cyclodextrin (α-CD).

3. Modified 3 chain model for topological gel

It is well known that the uniaxial tensile deformation of usual chemical gels provides the concave-down stress-strain curve in the low elongation region, given by

$$\sigma = 3\nu kT\left(\lambda - \lambda^{-2}\right) \qquad (1)$$

where ν is the number density of cross-links, λ the elongation ratio, kT the thermal energy. However, the stress-strain curves of the topological gel largely deviate from eq. 1 (Fig. 1): the curves for the samples of lower cross-linking density are substantially concave up without hysteresis loop in the low elongation region.

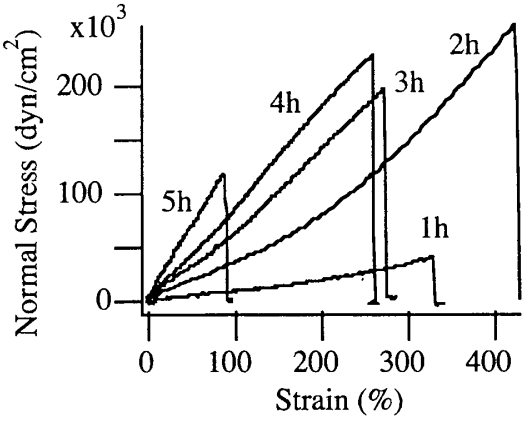

Figure 1: Stress-strain curve of topological gels in the gelation process.

A simple way to describe the elasticity of gels is provided by the three chain model using chains x, y, z with constant N segments in the x-, y-, z-directions, respectively. On uniaxial tensile deformation in the z-direction, the stress-strain behavior is in general given by

$$\sigma = \nu R_0\left(f_z - \lambda^{-1.5} f_{xy}\right) \qquad (2)$$

where f_z and f_{xy} represent the tensions of the chain z and of the chain x or y, respectively. When we employ the Gaussian chain, the classical stress-strain curve of the chemical gels is characterized by eq. 1. In order to explain the unique stress-strain curve of the topological gel, we modify the three chain model, where the three chains can slide to each other. This model provides the boundary condition that the extension forces of three chains should be equal. Therefore, eq. 1 is modified from the condition $f_z = f_{xy} \equiv f_s(\lambda)$ as

$$\sigma_{topo} = \nu R_0 f_s\left(1 - \lambda^{-1.5}\right). \qquad (3)$$

To describe a polymer tension more rigorously, we adopted an approximate form of the entropic force obtained from a self-avoiding walk (SAW) chain.

As a result, the modified model gives us good agreements between the experimental and theoretical results. These indicate that the unique stress-strain curves of the topological gel are explained by the modified three chain model, and the pulley effect enables all chains in the network to behave as a hypothetical single chain just like a thread in knitting or stocking.

Reference

1) Okumura. Y. ; Ito, K. *Adv. Mater.* **13** (2001) 485.