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Structural analysis of the Slide-ring gel by SAXS

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Introduction

Slide-ring gel (Topological gel)[1](see Fig. 1) is a new type of gel synthesized by cross-linking ⟨-cyclodextrins (⟨-CDs) contained in the sparse polyrotaxanes in solution. It consists of polymer chains with bulky end groups which are topologically interlocked by figure-of-eight cross-links of ⟨-CDs. In the slide-ring gel, it is assumed that the polymer chains freely pass through the cross-links acting like pulleys, which would results in equalizing the nanoscopic heterogeneity in structure and stress. We call this “pulley effect”.

In this study, we have measured small-angle X-ray scattering (SAXS) of slide-ring gel to investigate and confirm the “pulley effect”. It is known that the usual chemical gels which are cross-linked by covalent bond shows so-called “abnormal butterfly pattern”, in which the scattering intensity increases in a stretched direction, when they are stretched uniaxially. This indicates that the heterogeneities of uniaxially stretched chemical gels increase along the stretched direction.

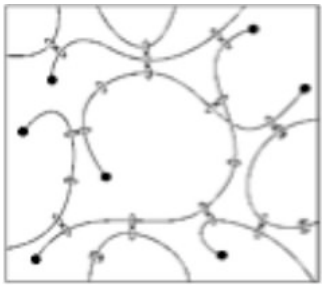

Fig. 1: The Slide-ring gel containing the figure-of-eight cross-links which slide on the polymer chain.[1]

Experimental section

SAXS measurements were conducted at the BL-15A of Photon Factory at KEK in Tsukuba, Japan. The properties of the X-ray and optical system were as follows. The wavelength was 1.5 Å. The beam size at the sample stage was 1.2 × 1.8 mm. The diameter of the beam stop placed behind 1,200 mm back from the sample was 8 mm. And a two-dimensional CCD-based X-ray detector coupled with beryllium-windowed X-ray image-intensifier (Be-XRII) was employed.

Slide-ring gels were synthesized from polyrotaxanes composed of polyethyleneglycol (MW=35,000) and ⟨-cyclodextrins. They were negatively ionized by means of cross-linking between ⟨-CDs with cyanuric chloride, so sodium chloride aqueous solution and sodium hydroxide aqueous solution became the poor solvent and the good solvent, respectively. SAXS measurements of the slide-ring gels swollen in several solvents from poor to good solvent (volume was limited to that at cross-linking) were carried out under the state of undeformed and uniaxially stretched (stretched ratio was 1.5) to the horizontal direction at room temperature.

Results and Discussion

Fig. 2 shows the two-dimensional SAXS patterns from the slide-ring gels.

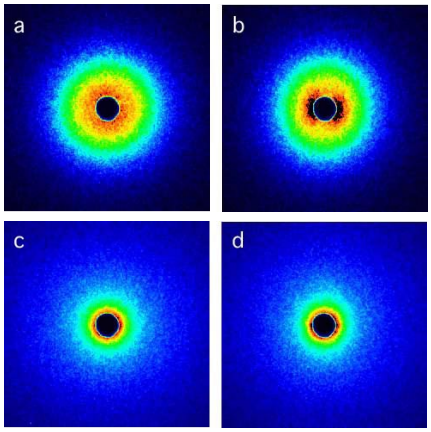

Fig. 2: Two-dimensional SAXS pattern from the slide-ring gels: (a) (b) swollen in 0.1 mol/L NaCl aqueous solution, (c) (d) in 0.1 N NaOH aqueous solution, and the left is under undeformed, the right under stretched horizontally.

In the case of poor solvent, the pattern under uniaxially stretched showed the abnormal butterfly pattern, on the other hand, in the case of good solvent, we observed almost isotropic pattern even under stretched.

Considering these results, we propose that the CDs aggregated in poor solvent so that the pulley effect became ineffective, while in good solvent the CDs homodisperse in order to maintain their homogeneous due to the Pulley effect.

Conclusion

We performed SAXS of the slide-ring gel in order to observe the pulley effect. In the present work, we obtained the static information of it. The time-resolved SAXS measurement may provide a clue to the dynamics of the pulley effect, and is in progress.

Reference

[1] Y. Okumura, K. Ito, Adv. Mater. 13, 485 (2001).

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