Materials Science

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Structural Study on Pulley Effect of Slide-Ring Gel by Small-Angle X-ray Scattering

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Introduction

Slide-ring gel [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 (Fig. 1). One of the remarkable characteristics of the slide-ring gel is "pulley effect", where the polymer chains freely pass through the cross-links acting like pulleys. When the gel is stretched, it is assumed that the nanoscopic heterogeneity in structure and stress is equalized due to the pulley effect. In this study, we investigated the pulley effect by small-angle x-ray scattering (SAXS) of the slide-ring gel under various solvent conditions.

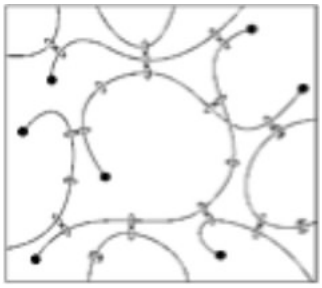

Fig. 1: Schematic view of slide-ring gel. The gel contains the figure-of-eight crosslinks that slide along the polymer chain [1].

Experimental

The sample used was synthesized from polyrotaxanes composed of polyethyleneglycol (MW = 35,000) and cyclodextrins (CDs). They were negatively ionized by means of cross-linking between CDs with cyanuric chloride. Therefore NaCl aqueous solution and NaOH aqueous solution were the poor solvent and the good solvent, respectively.

Experiments were performed at BL-15A. The X-ray wavelength was 1.50 A. An X-ray Image Intensifier coupled X-ray CCD detector [2] was used as a detector. The sample-to-detector distance was around 1800 mm and the SAXS images of 0.08 $nm^{-1} < q < 0.8$ nm^{-1} were recorded, where q is the scattering vector. The exposure time for each image was 1 s. By changing the ratio of NaCl and NaOH in the solvent, we measured how the structure of gel varies depending on the solvent.

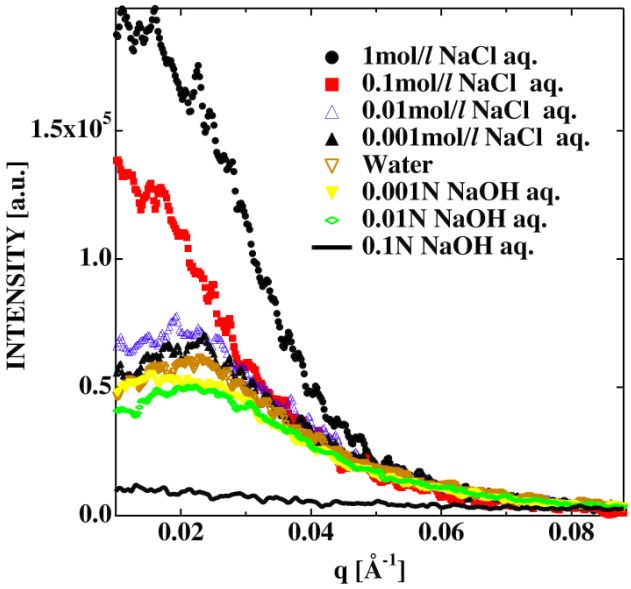

Fig. 2: SAXS intensity profiles of the slide-ring gel.

Results & Discussion

Figure 2 shows the SAXS intensity profiles of the slide-ring gel with different solvents. When the solvent is 0.1 N NaOH aq., no scattering intensity peak was observed. As the fraction of NaOH reduces, the scattering intensity increases and the scattering intensity peak appears. This indicates that the gel forms phase separation structure that has a correlation length of around 30-50 nm. Because the CDs interact with the solvent more strongly than the polymer chains, the CDs aggregate under poor solvent. It is thought that the aggregation makes the pulley effect ineffective.

References

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