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Small-angle X-ray scattering of anisotropic gel of alginate

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Introduction

Alginate is a polysaccharide forming a gel in the presence of calcium ions. In the previous study [1], the calcium alginate gel obtained by the dialysis of an aqueous solution of sodium alginate into a calcium chloride solution was shown to be anisotropic exhibiting birefringence. In the present study, microscopic structure of the anisotropic alginate gel was studied by small-angle X-ray scattering (SAXS).

Experimental Section

Sodium alginate and calcium chloride was purchased from Wako Pure Chemical Co., Ltd. and used without further purification. The molecular weight M_v of the sample was determined to be 2.5 x 10^5 by the intrinsic viscosity measurement. Milli-Q water was used for the preparation of alginate solutions and calcium chloride solutions. An aqueous solution of sodium alginate at the concentration of 2.0 wt% was poured into a dialysis tube with the diameter of 28 mm (Sanko Junyaku Co., Ltd.) and the dialysis tube was immersed in 8 g/dL of calcium chloride solution. After the dialysis for 6 hours, the cylinder-shaped gel of calcium alginate was formed.

The small-angle X-ray scattering measurements (SAXS) were performed at temperature of 25 °C at the beam line 15A of the Photon Factory at the High Energy Acceleration Research Organization in Tsukuba, Japan. The calcium alginate gel was sliced perpendicular to the axis of the cylindrical gel to a 1mm thickness and was used as the sample for the SAXS measurements. The sample was set to the direction so that the axis of the cylindrical gel was parallel to the incident beam and the scattered beam was detected with an image intensifier coupled to a CCD camera. The SAXS measurements were performed at different points of the gel at which the distance from the center is r.

Results and Discussion

The CCD image for the scattering at the center of the gel had circular symmetry, however, the images for at off-center positions were not symmetrical. The asymmetric pattern indicates anisotropic microscopic structure of the alginate gel. In order to appreciate the scattering pattern, the scattering profiles parallel and perpendicular to the radial direction of the gel were obtained as a function of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$ by averaging the scattered intensity of the two dimensional CCD image circumferentially within the sector shape with a vertex angle of 20°. Figures 1 (a) and (b) show the scattering profiles parallel and perpendicular to the radial direction of the gel, respectively. The plots in Figure 1 (a) increase with the distance r from the center of the gel, although the plots in Figure 1 (b) are superposed with each other.

The scattering profile at the center of the gel was well represented by the broken-rod model [2] as

$$I_{br}(q) = (k_1/q)\exp(-q^2R_1^2/2) + (k_2/q)\exp(-q^2R_2^2/2) + k_3/q^2 \qquad (1)$$

where R_1 and R_2 are the cross-sectional radii of the rods. The values of R_1 and R_2 are 3 nm and 7 nm, respectively. This result suggests that there are the cross-linking regions of rod-like shape with radii distributed around several nanometers. The excess scattering intensity $I_{ex}(q) = I(q) - I_{br}(q)$ for $I(q)$ parallel to the radial direction at the off-center of the gel was represented by the stretched exponential function as

$$I_{ex} = I_0 \exp[-(q^2\Xi^2)^\beta] \qquad (2).$$

The stretched exponential function has been applied to represent the excess scattering of chemically cross-linked gels, which is enhanced by swelling from the as-prepared state and is suggested to be due to heterogeneities of gels [3]. The applicability of eq (2) to the calcium alginate gel suggests that each portion of the gel is anisotropically expanded or shrank in the gel formation process.

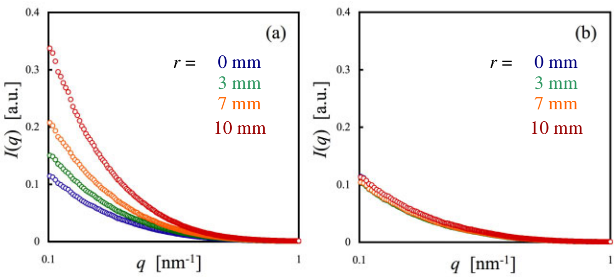

Figure 1: The scattering profiles parallel (a) and perpendicular to the radial direction of the gel, respectively. The data were obtained at the points of r = 0, 3, 7 and 10 mm from the center of the gel.

References

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