

## Higher order structures of gellan gum gels and the gelation mechanism

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### Introduction

A stiff polysaccharide gellan gum is known as a gelling agent. Gellan gum forms a birefringent gel at high concentration, since stiff chain polymers generally have the ability to form liquid crystal at high concentration. We have interested in such birefringent gel structures. Small angle scattering technique is the best tool for investigate the size and structure of crosslink domains within the gel.

In this study, we have discussed the gel structures and the gelation mechanism of gellan gum.

### Experimental

Sodium-type gellan gum sample NaGG-3 was used for this experiment. The weight-averaged molecular weight was  $2.17 \times 10^5$ . Degassed pure water was used for the solvent. Polymer weight fraction  $w_p$  of the gel prepared was ranging from 0.02 to 0.15. Gels were transposed into the frat cell with 1mm thickness and sealed by mica. And then samples were annealed to 90 °C, quenched to 25 °C, and kept at 25 °C for 1 week until measurements.

Small angle X-ray scattering measurements (SAXS) were performed at the BL-10C station. Time-resolved measurements with the time slice of 20 sec and the iteration of 10 were adopted for each gel sample. Excess scattering intensity  $\Delta I(q)$  was determined by the subtraction of scattering intensity of solvent from that of gels by taking account of the polymer volume fraction. Static data were obtained by the extrapolation of experimental data to time zero.

### Result and Discussion

Figure 1 demonstrates the SAXS profile for NaGG-3 gels at 25 °C. Here,  $q$  denotes the absolute value of scattering vector. Data point (unfilled circles) are shifted upward by the number A indicated in parentheses. In the sol state where  $w_p \leq 0.04057$ , both SAXS profiles follow the Lorentian curves. On the other hand, in the concentration range of  $0.05647 \leq w_p \leq 0.1028$  birefringent gels were formed. SAXS profile in this region has characteristic peaks whose  $q$  position ratio  $q_1:q_2:q_3$  to be 1:2:3 as indicated by arrows in the figure. The fact suggests the local formation of lamellar structures of gellan gum gel where the crosslink and non-crosslink domains alternately arrange. The sample with  $w_p = 0.07653$  was also subject to 90 °C preheat just before measurement. It makes the lamellar pattern obscured indicating the lamellar structure develops by time. When brittle gels are formed in the concentration range of  $w_p \geq 0.1182$ , lamellar structures are destructed and uniform gels are formed as shown in the SAXS profile.

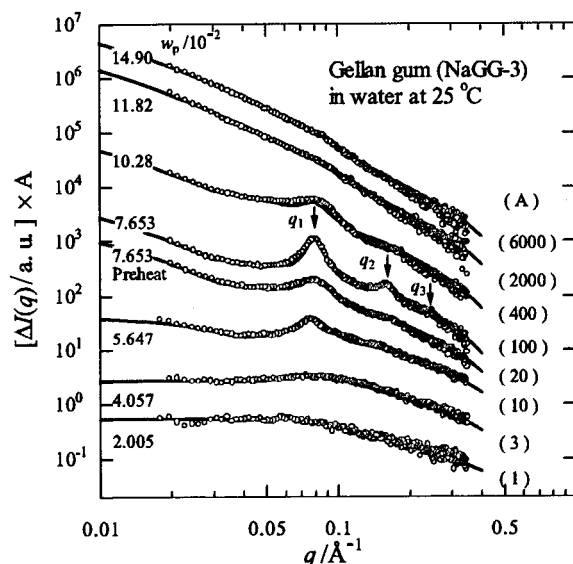


Figure 1 SAXS profiles for NaGG-3 in water at 25 °C

Solid lines for  $w_p \geq 0.05647$  are theoretical values calculated by the one dimensional paracrystal theory. We have presented the following equation

$$\Delta I(q) = \frac{\Delta I(0)}{[1 - \xi^2 q^2]} + C \frac{Z(q)}{q^2} \exp(-u^2 q^2)$$

where,  $\xi$ ,  $C$ , and  $Z(q)$  are the correlation length, arbitrary constant, and the paracrystal structure factor for the lamellar lattice model, respectively. The exponential term is the Debye-Waller temperature factor. The comparison of experimental data and the theory is fairly good. The lamellar distance estimated from this analysis to be 77 Å.

We have considered the gelation mechanism of gellan gum gels in high concentration region as follows: When the temperature is high, gellan gum chains are dispersed in solution taking the coiled conformation. On cooling, neighboring chains wind randomly at their closer point forming a discontinuous double stranded helix; *i.e.*, helix part and single coil part coexist within a chain. Here the system will be gel. Further, counterion  $\text{Na}^+$  gathers around the helix part, which accelerate the condensation of helix part, whereas strong electrostatic repulsion acts on the non-helix part. With long time, crosslink and non-crosslink domains spontaneously rearrange to the lamellar structure by the electrostatic repulsion and orientation due to the exclusion effect of stiff chains. When the polymer concentration is considerably high, such movement hardly occurs due to the entanglement effect.

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