Structural development of sodium-form gellan gum gels on cooling

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Introduction

In the previous report, PF Activity Report, 18B, 139 (2000), we presented local lamellar structures of gellan gum gels in high concentration regions. In this study, we have investigated the structural change accompanied by the gelation process of gellan gum on cooling. A time-resolved SAXS measurement using the synchrotron radiation X-ray is the best tool for the observation of structural change with the time scale of second order.

Experimental

Two fractionated sodium-form gellan gum samples (NaGG), F-8-2 with M_v = 32000 and F-9 with M_v = 18000, were chosen for this study. Here, M_v represents the viscosity average molecular weight. The weight fraction of NaGG in the gel was adjusted to 0.06 for both gels in where the lamellar structure was formed at 25 °C. A solution in the sol state was quenched manually by turning a valve connecting two water circular baths controlled at 90 °C and 23 °C in parallel. Time resolved SAXS measurements with a time slice of 5 sec and a frame number of 30 were performed on the SAXES apparatus in BL-10C station. Measurements were started at t = 15, 90, and 180 sec. Here, time t was counted when the temperature decreased after the quenching operation.

Results and Discussion

Figure 1 demonstrates the result of excess scattering intensity $I(q)$ for NaGG sample F-8-2 on cooling. Here q denotes the magnitude of scattering vector. In the sol state, $T > 33$ °C, SAXS profiles almost overlap as drawn by two solid lines. It suggests that gellan gum chains are molecularly dispersing in the solvent, although the presence of a tiny amount of aggregate is observed as an enhanced low angle scattering intensity. When the temperature decreases below T_g = 32 °C, $I(q)$ monotonically increases by time and further lamellar peaks begin to appear. We regarded T_g as the gel formation temperature and it was small *c.a.* 15 °C from the melting point of the gel. The thermal hysteresis of gellan gum gel can be explained by the structural difference between the transient gel with weakly ordered and enough matured gel with highly ordered. The peak position q_m for all $I(q)$ takes the same value of 0.081 Å^{-1} obtained for the gel ripen for 1 week which is shown by the bold solid line. It means that the lamellar structure with the same repeating distance is already formed even at the early stage of the gellan gum gelation process. The same behavior was also observed for the sample F-9.

To clarify the structural development of lamellar gels, the ratio of $I(q)$ for gels to that for sol at q_m, $A(t)$, was calculated. Intensities for gels were corrected taking the melting of gel due to the exposure of strong X-ray into account. In Figure 2, $A(t)$ for both gels are plotted against t. It is clearly seen that there are two stages in the gelation process of gellan gum. Values of $A(t)$ for both samples drastically increase in the early stage and then gradually approaches to some value in the next stage. It suggests that gellan gum chains in solution condense as aggregates or microgels that pile up further until it forms a macrogel. Consequently, the concentration fluctuation of gellan gum drastically enlarges in the early stage. In the second stage, the increment of concentration fluctuation stagnates and ordering to the lamellar structure progresses slowly. The results are fairly compared with the double exponential type equation with four adjustable parameters of A_i and k_i:

$$A(t) = 1 + A_1\exp[k_1(t-t_g)] + A_2\exp[k_2(t-t_g)] \qquad (1)$$

The second and the third terms correspond to the early and the second stage, respectively.

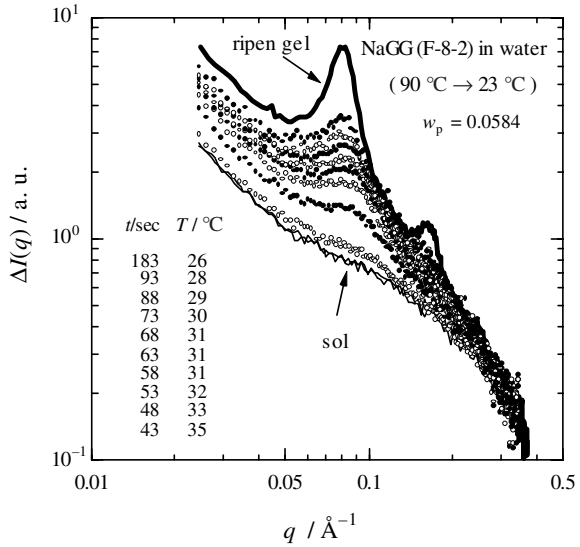

Figure 1. SAXS profiles for NaGG (F-8-2) on cooling.

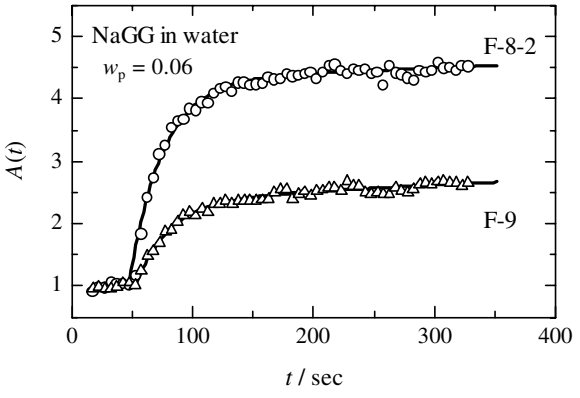

Figure 2. Lamellar peak intensity increment by the gelatin. Solid lines are calculated by Eq. (1).

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