CHEMISTRY LETTERS, pp. 601-604, 1993.

An Observation of the Electric Birefringence Signal of κ-Carrageenan Gel

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Electric birefringence signal of κ-carrageenan gel was measured for the first time. The signal was found to consist of two processes, which correspond to the orientational motion of the junction zone and the deformation of the whole network structure of the gel.

Recently, much interest has been focused on the thermoreversible gel of polysaccharides because of its physicochemical aspect of the gelation mechanism and the application as intelligent materials. Sol-gel transition of κ-carrageenan has been studied extensively as a model of polysaccharide gel.[1-3] However, there are few reports concerning the network structure of the gel because of the lack of appropriate method.

In this study, we have applied the electric birefringence method to investigate the network structure of polysaccharide gel. So far, the electric birefringence method has been mainly used for properties of polymer solutions,[4-6] but its application to gel has never been examined. We report here the preliminary results of the electric birefringence measurements of κ-carrageenan gel, whose results reflect the information of network structure of gel.

κ-Carrageenan, extracted from *Eucheuma cottonii*, was supplied from Mitsubishi Rayon, Co. Ltd. (Tokyo). The sample was dissolved in distilled water to prepare the 0.5% (wt/wt) solution. Electric birefringence was measured using an apparatus constructed in our laboratory.[7,8] The Kerr cell,[7] which contained the sample solution, was cooled to 7 °C to make a gel. When the rectangular electric pulse was applied to the cell, the electric birefringence signal from the gel was observed.

Figure 1(a) shows a typical electric birefringence signal of κ-carrageenan gel at a low electric field strength. When the rectangular electric pulse is applied, the signal rises, and reaches a steady-state. After the electric field is terminated, the signal decays to the baseline. The signal profile is similar to those obtained for the molecularly dispersed polymer solution,[9-11] where each

anisotropic polymer molecule can rotate to orient toward the electric field direction. The similarity of these signal profiles let us conclude that some anisotropic segments are also present in the gel structure, which are able to orient by the electric field. These segments may be the junction zones forming the gel network structure.[12,13]

When the electric field was raised above a threshold strength, the signal profile dramatically changed (Fig. 2(a)). In this case, the signal continually increased and the steady-state value was not obtained, even when the electric pulse with longer pulse width was applied. Both the rise and decay portions of the signal in Fig. 2(a) appear to consist of two steps. The decay portions of both signals in Figs. 1 and 2 were then decomboluted. The decay portion of the electric birefringence signal is generally expressed by the multi-exponential terms characterized by their different relaxation times τ_i and respective contributions A_i;[4]

$$\Delta n(t)/\Delta n_0 = \Sigma A_i \exp(-t/\tau_i) , \qquad (1)$$

where, Δn_0 is the value of the electric birefringence just before the applied electric field was terminated. If only one exponential term contributes to the signal, the logarithmic plot of $\Delta n(t)/\Delta n_0$ *versus* time should be linear. This relation is appropriate in the case of low field strength as shown in Fig. 1(b). The relaxation time, which was calculated from the slope, is 64 μs. On the other hand, the logarithmic plot of the decay portion at higher field strength is not linear as shown in Fig. 2(b), indicating that the additional exponential term with different relaxation time should be involved. Consequently, the "peeling"

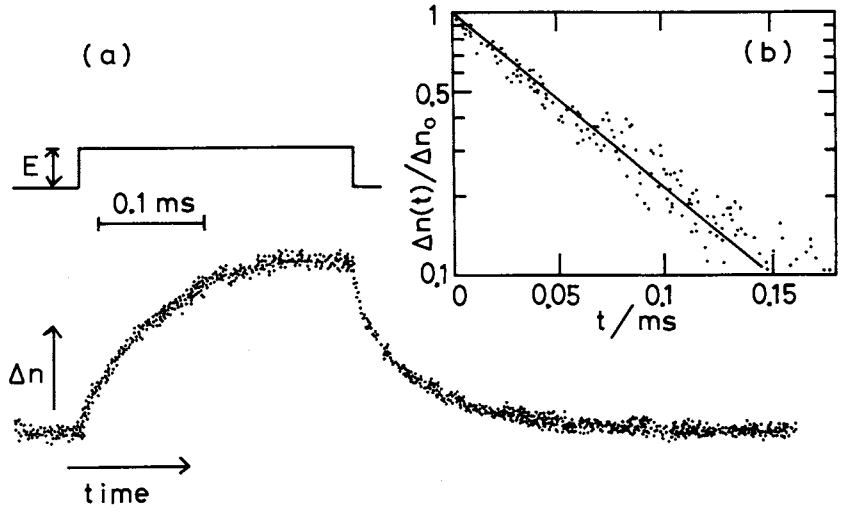

Fig. 1. (a) A typical electric birefringence signal of κ-carrageenan gel at a low electric pulse field. Electric field strength is 0.6 kV/cm. The solution concentration is 0.5% wt/wt. (b) The logarithmic plot of the normalized decay signal *versus* time.

method is applied to obtain the relaxation times and their relative contributions.[14] At the long time region in Fig. 2(b), the plots of $\log(\Delta n(t)/\Delta n_0)$ *vs.* t are approximately linear with lower slope. This slope gives a longer relaxation time τ_{long} and its extrapolation to zero time gives its relative contribution A_{long}. The values subtracted the A_{long} component from the total decay curve are also plotted in the same figure. Those values are approximated by a linear line and, therefore, the other exponential term with shorter relaxation time τ_{short} and its contribution A_{short} can be obtained by its slope and intercept. The obtained values of the relaxation times and their contributions are τ_{short} = 203 μs and A_{short} = 0.365, and τ_{long} = 13.5 ms and A_{long} = 0.635, respectively. This shorter relaxation time (203 μs) is roughly comparable with the one (64 μs) obtained at the low electric field strength. This indicates that the component with shorter relaxation time should be ascribed to the same process, that is, the orientational motion of the junction zones in gel network structure. While, at present, the slow process with longer relaxation time can not be identified exactly. By considering that this process appears only when the higher electric field is applied and its relaxation time is abnormally long comparing to that of ordinal segment orientation, the process is possibly caused by deformation of the whole network structure of the gel after the orientational process of the junction zone segments. X-Ray fibre diffraction study suggests that the junction zone may be characterized by a bundle of some helical carrageenan chains with diameter of 12 Å/chain.[12] The number of helical chains aggregated in the bundle structure is not known

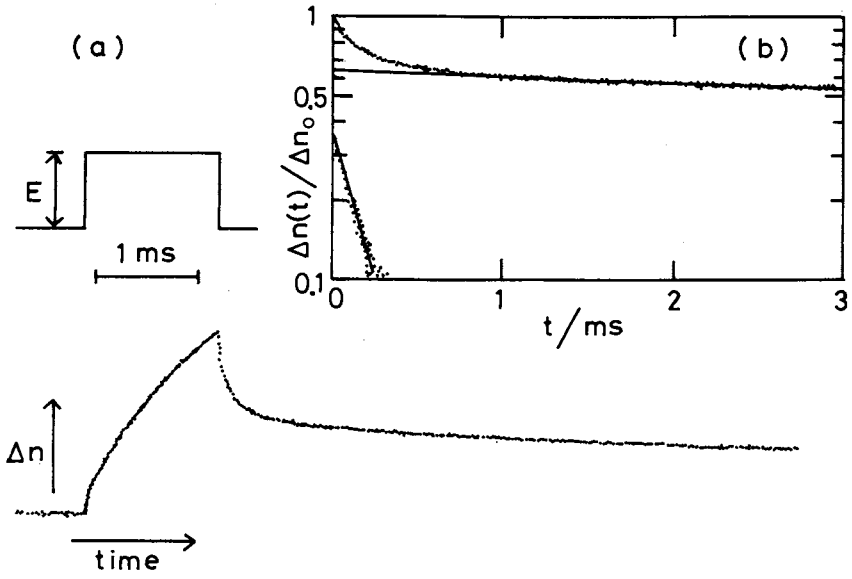

Fig. 2. (a) A typical electric birefringence signal of κ-carrageenan gel at a higher electric pulse field. Electric field strength is 1.3 kV/cm. The solution concentration is 0.5% wt/wt. (b) The logarithmic plot of the normalized decay signal and the subtracted values *versus* time. (see text)

presicely. Supposing that the diameter of the bundle structure is in the range of 12-100 Å, the length of the junction zone can be roughly estimated by using the Broersma's equation[15] with the value of relaxation time 64 μs to be in the range of 1200-1600 Å.

In conclusion, this work indicates the possibility of the electric birefringence method to investigate the network structure of gel. More detailed investigation both on the field strength and concentration dependence are now under investigation.

This work was in part supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 03805083). We also thank Daicel Chemical Co., Ltd. for financial support.

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(Received December 14, 1992)