Electric field orientation of sonicated κ-carrageenan in aqueous solution: ionic polarization of loosely bound counterions

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The electric field orientation of κ-carrageenan in aqueous solution was investigated by the reversing-pulse electric birefringence method at 633 nm and 33°C. The observed field orientation was attributed to the fast-induced polarization of the counterions (K^+ ions) in the ionized polymer domain. Since the charge density parameter ξ of non-helical and elongated κ-carrageenan is 0.66, the fast-induced ionic polarization is probably due to the counterions loosely bound by Debye–Hückel type electrostatic forces, but not due to the condensed counterions.

(Keywords: κ-carrageenan; electric birefringence; ionic polarization)

Introduction

Polyelectrolyte molecules with no permanent dipole moment can be oriented in aqueous solutions when an external electric field is applied. The main source of this orientation should be a field-induced ionic polarization of the counterions surrounding the polyion[1–5]. Many theoretical treatments have been presented to account for this polarization mechanism, yet none still seems to be complete. Some theories are based on the polarization of counterions, which are 'tightly-bound'[6,7] or simply 'bound'[8–10] to the vicinity of the polyion because of a high charge density.The tightly bound counterions are treated as 'condensed' in the counterion condensation theory, in which the condensation occurs if the charge density parameter ξ of a polyelectrolyte is larger than unity[11]. On the other hand, the simply bound counterions are not rigorously defined with respect to their binding nature. Other theories are based on the polarization of counterions which are more 'loosely bound' in the ion atmosphere by Debye–Hückel type electrostatic forces[12].

From the experimental point of view, however, no explicit discussion has been advanced on the polarization mechanism and the polarizable ions are attributed either to the condensed counterions or to loosely bound counterions in the ion atmosphere. Previous experiments of electric field orientation have been carried out mainly with synthetic polyelectrolytes[4,5,13] and polynucleotides[1,7,14]. In most cases, values of ξ are larger than unity because of the high charge density along the polyion chain; hence, the ionic polarizability has been usually interpreted as being only due to the condensed counterions.

We can clearly demonstrate here that κ-carrageenan, a stiff acidic polysaccharide with no condensed counterion (i.e. $\xi < 1$), also exhibits a large reversing-pulse electric birefringence (RPEB) signal which results from the ion atmosphere polarization of loosely bound counterions. This result is of immediate importance for a recent theoretical development of new orientation functions[6,7,12].

Experimental

As a sample polyelectrolyte, κ-carrageenan was used because it consists of regular repeating units with a large distance between charged groups (10.3 Å on average), that is, a sulphate group per disaccharide[15]. κ-Carrageenan, extracted from *Eucheuma cottonii*, was supplied by Mitsubishi Rayon Co. Ltd (Tokyo). Infra-red spectra showed a characteristic band at $850\,cm^{-1}$ which was assigned to the D-galactose 4-sulphate residue[15].

In order to obtain a stiff κ-carrageenan sample with low molecular weight and narrow molecular weight distribution, the polymer was sonicated in aqueous solution with a Tomy Seiko UR-200P sonicator at 0°C and a power level of 200 W for 2 h. The effect of irradiation time on molecular weights was examined by gel permeation chromatography (g.p.c.) with small portions of κ-carrageenan solution at 20 min intervals during irradiation. Poly(ethylene oxide) samples (Tosoh Co. Ltd, Japan) were used as standards for a calibration curve, from which the weight-average molecular weight (M_w) and the ratio of weight- to number-average molecular weights (M_w/M_n) could be calculated. *Figure 1* shows M_w and M_w/M_n at various irradiation times, as obtained from g.p.c. chromatograms. Both M_w and M_w/M_n sharply decreased in the initial stages of irradiation and then gradually approached constant values.

In the present electric birefringence study, a sample sonicated for 120 min was used; the values of M_w and M_w/M_n were 1.3×10^5 and 1.6, respectively. After exhaustively dialysing against distilled water, this sample was first converted to the acidic form through a mixed-bed ion-exchange column (Amberlite IR-120, IRA-402), and then the sample in potassium form was obtained by exact neutralization with aqueous potassium hydroxide. This carrageenan stock solution was diluted with distilled water. The concentration was determined from the dried weight.

Electric birefringence was measured at 633 nm and 33°C in aqueous solutions on an apparatus constructed

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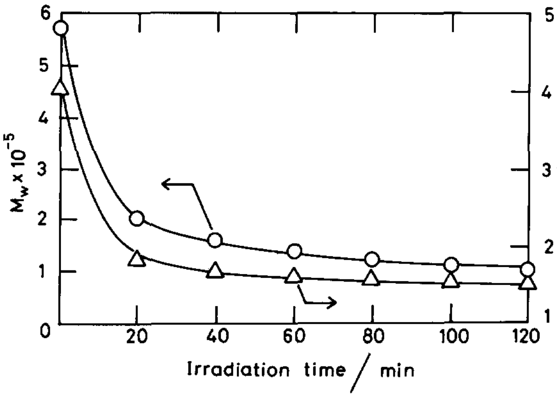

Figure 1 Dependence of M_w (○) and M_w/M_n (△) of κ-carrageenan on irradiation time. Values of M_w and M_w/M_n were estimated by the g.p.c. method. Poly(ethylene oxide) was used as a standard for the calibration curve

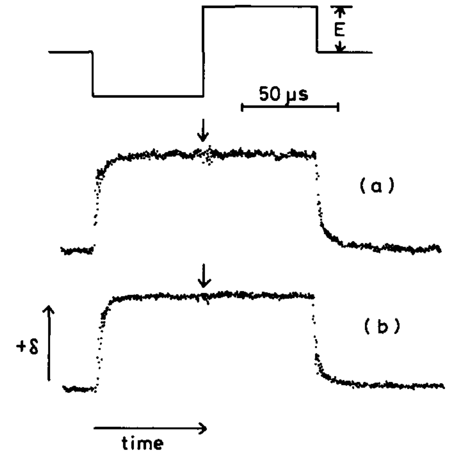

Figure 2 Typical RPEB signals, expressed by the optical phase retardation δ, of sonicated potassium κ-carrageenan in aqueous solution. The sampling time of the signal is 50 ns per word. The field strengths are (a) 2.8 kV cm^{-1} and (b) 4.6 kV cm^{-1}, respectively. The corresponding reversing-pulse electric field is also shown schematically

in our laboratory[16]. The sample concentration was 2.4 mM in terms of disaccharide unit.

Results and discussion

Figure 2 shows typical RPEB signals of sonicated κ-carrageenan at two electric field strengths. Upon reversal of the pulse field (arrows), which occurred in <200 ns, no transient extremum but random noises could be observed in both signals; one at low field (2.8 kV cm^{-1}) and the other at a relatively high field (4.6 kV cm^{-1}). A birefringence signal should show a large dip after the reversal of the pulse field if a polyion possesses a permanent dipole moment and/or a slow-induced ionic dipole moment[17]. Our results indicate that κ-carrageenan does not possess either of these electric moments but possesses only moments arising from electronic anisotropy and/or fast-induced ionic polarizability[17].

Figure 3 shows the steady-state values of electric birefringence of sonicated κ-carrageenan, which were measured at various field strengths, *E*, and plotted against the second or the first power of *E*. Morris measured the electric birefringence of κ-carrageenan by the conventional single-square-pulse method, showing that the Kerr law was obeyed in the low field strength region ($E < 2$ kV cm^{-1})[18]. From the δ *versus* E^2 plot in *Figure 3*, our sonicated sample also obeys the Kerr law in the low field region. In this case, the field dependence can possibly be analysed with the classical orientation function, which takes into account the permanent dipole moment term β ($=\mu E/kT$) and the electronic polarizability term γ ($=\Delta\alpha E^2/2kT$) as the electric moments, where *k* is the Boltzmann constant and *T* is the absolute temperature[19]. Hence, we first tried to fit our data to a theoretical curve of $\beta^2/2\gamma = 0$ ($\mu = 0$) for field strengths up to 13.3 kV cm^{-1}, to test if electronic polarizability alone would contribute to the field orientation of κ-carrageenan. The data could not be fitted to this curve but fitted best to a curve of $\beta^2/2\gamma = 4$. From this, and the result obtained from the reverse transient profile which reveals that $\beta = 0$, it can be concluded that fast-induced ionic polarizability is responsible for the field orientation of κ-carrageenan.

A good fitting of the δ *versus* E^2 plot with the parameter $\beta^2/2\gamma = 4$ indicates the contribution from a permanent-like dipole moment, if not the true permanent dipole moment, to the field orientation of κ-carrageenan. Part of the fast-induced ionic dipole moment of κ-carrageenan may be saturated at an electric field strength and may behave like a permanent moment at higher fields, as suggested for some polyelectrolytes[20–22]. In order to estimate the value of ionic polarizabilities, we attempted to fit the present data to the orientation function which was recently proposed on the basis of the saturable and unsaturable induced dipole (SUSID) orientation mechanism[23,24]. This mechanism consists of the unsaturable ionic polarizability $\Delta\alpha'$ and the saturable ionic polarizability $\Delta\sigma$, which is saturated at the critical electric field E_0 and, thereafter, behaves as a permanent-like dipole moment ($\Delta\sigma E_0$).

The best fitted theoretical curve, calculated by the SUSID orientation function, is shown in *Figure 3* by solid lines. From this curve-fitting, the following were evaluated[23,24]: $\Delta\sigma E_0 = 4.0 \times 10^{-27}$ C m, $\Delta\alpha' = 3.9 \times 10^{-33}$ F m^2, $E_0 = 4.2$ kV cm^{-1} and the optical anisotropy factor $(g_3 - g_1) = 1.76 \times 10^{-3}$. Since the fast-

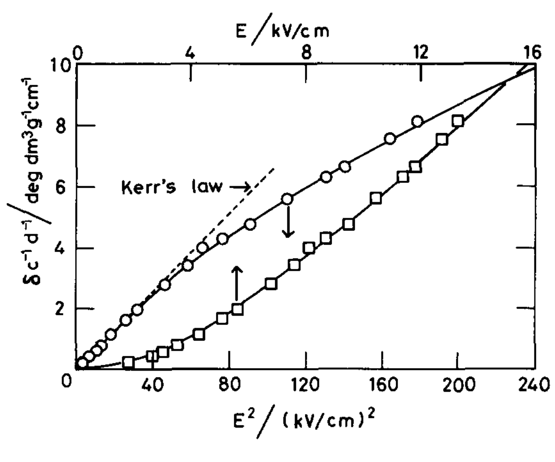

Figure 3 Field-strength dependence of the steady-state birefringence of a sonicated κ-carrageenan sample. The ordinate is expressed in terms of $\delta c^{-1} d^{-1}$ ($\Delta n = \lambda\delta/2\pi d$) where *d* is the optical path length (10 mm) of a Kerr cell, λ is the wavelength (632.8 nm) and *c* is the mass concentration (mg cm^{-3}) of κ-carrageenan. The values are plotted against *E* and E^2. The solid lines represent a SUSID theoretical curve

induced ionic polarization of κ-carrageenan would be saturated at an E_0 of 4.2 kV cm^{-1}, an RPEB signal was measured above this field strength (*Figure 2b*). No difference at the pulse reversal, however, could be observed between the signals below E_0 (*Figure 2a*) and above E_0 (*Figure 2b*). This result indicates that the fast-induced ionic polarization rapidly reverses its direction upon pulse reversal, even if the polarization is saturated above E_0.

From the values obtained above, the total ionic polarizability ($\Delta\alpha_{\text{total}} = \Delta\alpha' + \Delta\sigma$) of κ-carrageenan is estimated to be 2.2×10^{-32} F m^2. By analysing the experimental data with the classical orientation function, Stellwagen proposed the polarizability of DNA to be in the range of 10^{-30}–10^{-32} F m^2 (ref. 25). Yamaoka and Fukudome reported values of 10^{-31}–10^{-32} F m^2 for $\Delta\alpha_{\text{total}}$ of DNA[24]. Tricot *et al.*[4] measured the polarizability of poly(*N*-methyl-2-vinylpyridinium) to be 10^{-30}–10^{-32} F m^2, while Hanss *et al.*[5] estimated the value to be $(2–4) \times 10^{-30}$ F m^2 for carboxymethylcellulose. A comparison between these values and the one obtained in this study suggests that the magnitude of the polarizability of κ-carrageenan is in the lower limit, possibly because $\xi < 1$. The parameter is given as $\xi = e^2/\varepsilon kTb$, where e is the elementary electronic charge, ε is the dielectric constant of the solvent and b is the length between charges on a polyion chain. Manning's theory predicts that the counterion condenses on the polyion and suppresses the effective charge of the polyion until the charge density parameter ξ of the polyion is reduced to unity[11].

An optical rotation experiment indicates that our sample is in a non-helical conformation above 20°C[26]. The value of ξ of κ-carrageenan in the non-helical and elongated conformation was calculated to be 0.66 with $b(\text{non-helical}) = 10.3$ Å[27]. Thus, the κ-carrageenan in the non-helical conformation should have no condensed counterion according to Manning's theory. Consequently, all counterions are loosely bound to the polyion as a result of the Debye–Hückel type electrostatic interaction. This theoretical prediction leads to the conclusion that the field-induced polarization of κ-carrageenan is not due to the condensed counterions but due to the loosely bound counterions in the ion atmosphere.

In conclusion, the field orientation mechanism of κ-carrageenan was accounted for by fast-induced ionic polarization from the RPEB signal profile. This polarization originates from the counterions loosely bound to the polyion domain by Debye–Hückel type electrostatic interactions, but not from the counterions condensed to the polyion sites. It is now clear that the electrostatically bound counterions are sufficient to induce the polarization for field orientation. However, if the value of ξ is higher than 1, the condensed counterions should also be considered to produce sufficient polarization. The ι-carrageenan main chain has two sulphate groups per disaccharide residue, hence $\xi > 1$. Some comparative studies of κ- and ι-carrageenans are in progress and the results will be reported in the near future.

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