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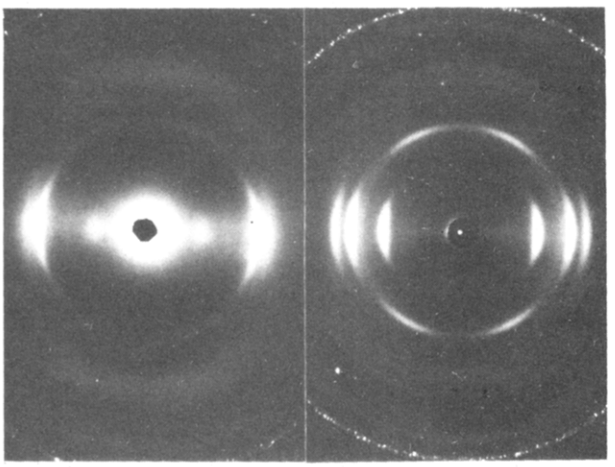

a b

Figure 1. X-ray diffraction patterns of the oriented chitosan A films: (a) before annealing at 75% relative humidity; (b) after annealing in water at 200 °C, under vacuum.

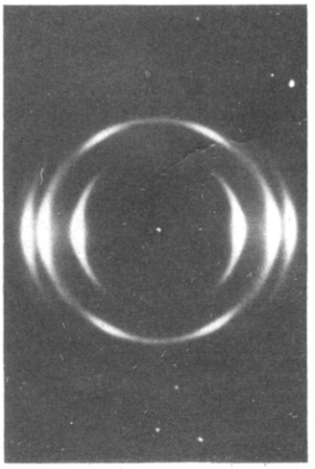

Figure 2. Fiber pattern of the oriented chitosan B film after annealing in water at 200 °C, under vacuum.

A New Polymorph of Chitosan

Chitosan, the N-deacetylation product of chitin, is a promising biomass for industrial purposes and is under intensive investigation for this application.[1] However, only a few studies on the molecular conformation of chitosan have been reported. The first X-ray fiber diagram was published by Clark and Smith in 1937.[2] They obtained an X-ray diffraction pattern from a chitosan fiber prepared by deacetylating the naturally oriented chitin fiber of lobster tendon: we call this sample "tendon chitosan". Each reflection spot of the pattern was well separated but somewhat diffuse because of the low crystallinity of the chitosan. The unit cell was determined to be orthorhombic with a = 8.9, b = 17.0, and c (fiber axis) = 10.25 Å. Darmon and Rudall[3] suggested that the lattice showed the same symmetry as the unit cell of α-chitin.

Recently, two other polymorphs have been obtained by Samuels[4] from chitosan films prepared from formic acid solutions. The unit cells of these polymorphs were orthorhombic with a = 7.76, b = 10.91, and c (fiber axis) = 10.30 Å and a = 4.4, b = 10.0, and c = 10.3 Å, respectively.

The possibility of fruitful X-ray diffraction analysis is solely dependent on the sample crystallinity. Recently, annealing in a solvent, usually water, at high temperature was found to be effective in improving the crystallinity of several polysaccharides: (1→3)-β-D-glucan,[5] (1→3)-α-D-glucan[6] and its acetyl derivative,[7] Lichenan,[8] Konjac glucomannan and its acetate,[9] and (1→3)-α-D-mannan.[10] We report a new chitosan polymorph induced by annealing and publish the clearest fiber pattern of any obtained hitherto. On the basis of this pattern, we propose a chitosan conformation.

A chitosan powder (sample A) was prepared from the chitin of crab shell, *Chionecetes opilio* O. Fabricus, by sodium hydroxide deacetylation.[11] The degree of deacetylation was measured by elemental analysis to be 99.5%, and the reduced viscosity, $\eta_{sp}C^{-1}$, in 0.2 M acetic acid was 5.5 L g^{-1} at a chitosan concentration of 5 mg L^{-1} at 30 °C. Another chitosan powder (sample B) having no acetyl group and $\eta_{sp}C^{-1}$ of 4.0 L g^{-1} at 5 mg L^{-1} was also prepared from the same crab shell chitin by repeating the deacetylation procedure. Each chitosan powder was prepared as a 0.2 M acetic acid solution (c 0.3 g L^{-1}), deposited onto a poly(ethylene terephthalate) film, and allowed to evaporate. The film thus prepared was immersed in 1 M aqueous NaOH for 30 min to make an acetate-free chitosan film. After washing with water, a strip of the film was stretched to three times its original length in water at 95 °C. The film prepared from sample A was well oriented but of low crystallinity (Figure 1a). The same film annealed in water at 190 °C or more in a closed bomb, with the film length kept constant, was of higher crystallinity (Figure 1b). The X-ray diffraction patterns were recorded by using a flat-film camera with a Rigaku Geigerflex X-ray diffractometer employing Ni-filtered Cu Kα radiation generated at 40 kV and 15 mA.

The stretched chitosan film before annealing (Figure 1a) showed a pattern similar to that from the tendon chitosan reported by Clark and Smith[2] except for the presence of a very weak equatorial reflection having a d spacing of 5.90 Å, which corresponded to the (120) reflection of the annealed chitosan. The fiber pattern was observed when the film was exposed to X-rays at 75% relative humidity. However, when irradiated under vacuum, the film showed a very diffuse diffraction pattern. That this change was brought about by changing the relative humidity indicates that the unit cell has water molecules, as suggested by Averbach.[12]

On the other hand, the fiber pattern of the annealed chitosan A film (Figure 1b) did not show any variation even when the relative humidity was changed from 0 to 100%: the same fiber pattern was obtained under vacuum even when the annealed film was dried under vacuum at 110 °C for 7 h. From the sharpness of each reflection, it is clear

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Table I
Observed Spacings and Intensities for the Annealed Chitosan

hkl	spacings, Å: calcd	spacings, Å: obsd	intensities (obsd)[a]
120	5.83	5.83	VS
200	4.12	4.17	VS
040	4.12		
220	3.69	3.72	VS
140	3.69		
320	2.61	2.64	M
160	2.61		
101	6.46	6.50	VW
021	6.46		
121	5.08	5.01	VW
221	3.47	3.48	M
141	3.47		
241	2.81	2.80	W
301	2.66	2.62	M
061	2.66		
311	2.62		
002	5.20	5.22	VW[b]
102	4.40	4.37	VS
022	4.40		
122	3.88	3.86	M
202	3.23	3.19	W
042	3.23		
212	3.17		
222	3.01	2.98	W
142	3.01		
242	2.54	2.54	W
013	3.39	3.40	VW[b]
103	3.19	3.17	M
023	3.19		
113	3.14		
123	2.96	2.98	M
203	2.65	2.62	VW
043	2.65		
213	2.62		
223	2.52	2.51	W
143	2.52		
104	2.48	2.47	M
024	2.48		
114	2.45		
124	2.37	2.37	VW
034	2.35		

[a] Abbreviations: VS, very strong; M, medium; W, weak, VW, very weak. [b] Observed by tilting each corresponded θ value.

that our annealed chitosan film has the highest crystallinity of any reported hitherto.

Figure 2 shows the fiber pattern of the annealed chitosan film prepared from the chitosan powder having no acetyl groups (sample B). The lesser orientation compared to sample A (Figure 1b) may be due to lower molecular weight because sample B was prepared by more rigorous sodium hydroxide deacetylation than sample A and has a lower solution viscosity. The fiber pattern is similar to that of the annealed sample A (Figure 1b), but it is interesting that a weak equatorial reflection having a d spacing of 9.4 Å was not observed in the annealed film of sample B (Figure 2). The reflection seems to have a d spacing similar to that of the very strong (020) reflection in chitosan tendon[2] and also that of the unannealed chitosan film (Figure 1a). It is probable that a small amount of the crystallinity of the unannealed chitosan film remains in the annealed chitosan A but not in the annealed B film. The intensities of four reflections in the annealed chitosan A were also different from those of B: the intensity of the equatorial reflection having a d spacing of 4.62 Å in A is medium, but none in B; the first layer's 4.56-Å reflection is weak in A, but none in B; the second layer's 5.22-Å reflection is very weak in A, but is observable only by tilting in B; and the third layer's 3.40-Å reflection is medium in A, but is observable only by tilting in B (Table I). As mentioned above, chitosan A seems to have a higher molecular weight than B. That is, the crystallinity in the unannealed chitosan A did not disappear completely under annealing and may be due to its decreased molecular mobility. For the same reason, the annealed chitosan A may have imperfections in crystalline structure. Therefore, the equatorial reflections having d spacings of 9.4 and 4.62 Å and the first layer's 4.56-Å reflection were ignored, and the intensities of all reflections observed in B were employed in this study.

Table II
Crystal Data for the Annealed Chitosan

crystal system	orthorhombic
lattice parameters	
a, Å	8.24
b, Å	16.48
c (fiber axis), Å	10.39
ρ(obsd), g cm^{-3}	1.44
no. of glucosamine residues	8
ρ(calcd), g cm^{-3}	1.52
no. of chains	4
helix parameters[a]	
n	2
h, Å	5.20

[a] n = number of glucosamine residues per turn. h = advance per residue along the helix axis.

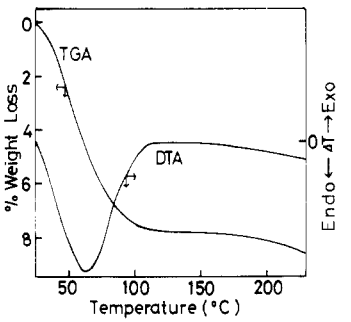

Figure 3. Thermogravimetry (TGA) and differential thermal analysis (DTA) curves on chitosan A powder annealed in water at 200 °C.

All 22 visible diffraction spots could be indexed with an orthorhombic unit cell with a = 8.24, b = 16.48, and c (fiber axis) = 10.39 Å (Tables I and II). The fiber axis length is similar to those observed for all other chitosan unit cells and also the chitin cells, indicating that the chitosan molecule in the present unit cell also has a twofold helical conformation.

The crystalline density calculated with eight glucosamine residues per cell, ρ_{calcd} = 1.52 g cm^{-3}, is in reasonable agreement with the experimental density, ρ_{obsd} = 1.44 g cm^{-3}, which was measured by the flotation method in a carbon tetrachloride–m-xylene solution at 25 °C. It is believed that there is no water molecule in the unit cell because there was no observed change in the X-ray fiber pattern with changing relative humidity.

The absence of a water molecule in the unit cell was verified by the following thermal analyses. An annealed chitosan powder was prepared by a procedure similar to that for the annealed film of chitosan A. Chitosan A powder was dissolved as a 0.2 M solution in aqueous acetic acid, neutralized with 1 M NaOH, precipitated by adding methyl alcohol, washed with water, annealed in water at 200 °C, washed with methyl alcohol, and dried in air. The powder thus prepared showed a powder pattern corre-

sponding to that of the annealed film of chitosan A (Figure 1b). Figure 3 shows the thermal analyses on the annealed chitosan powder. The thermogravimetry (TGA) and the differential thermal analysis (DTA) were carried out with a Rigaku Thermoflex in the range 25–230 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. With increasing temperature, the weight of the powder decreased rapidly until ca. 110 °C, slowly in the range 110–160 °C, and then very gradually. The DTA shows a strong endotherm until 110 °C, practically no change in the range 110–160 °C, and an endotherm at higher temperature; the latter reaction may due to a partial decomposition of the chitosan. These results indicate that all water molecules included in the annealed chitosan powder are removed at 110 °C. Therefore, an X-ray analysis was done with the annealed chitosan powder having no water molecules. Immediately after drying under vacuum at 110 °C for 7 h, the annealed chitosan powder was X-rayed under vacuum. The resultant powder pattern was just the same as that of the undried powder. Furthermore, the fiber pattern of the annealed chitosan A film (Figure 1b) did not change under the same conditions of drying the film as for the annealed chitosan powder. From these results, it is clear that the unit cell does not have any water molecules. The calculated density, 1.52 g cm^{-3}, is lower than that of cellulose (around 1.62 g cm^{-3}). This may be due to the presence of the primary amino group in chitosan.

Averbach[12] reported that chitosan appears to have an atomic arrangement similar to that of chitin. The position of the (020) peak (c is the fiber axis) depended on the water content and was lowered on drying at 134 °C. It was postulated that water molecules are loosely bound between the chitosan chains along the [010] direction.

In contrast, our annealed chitosan showed no (020) reflection and had a strong (120) reflection which was not observed in the tendon chitosan and was very weak in our chitosan film before annealing. With increasing annealing temperature, the intensity of the former reflection, which was strong before annealing (Figure 1a), decreased and that of the latter increased. Except for this, both chitosans showed similar equatorial reflections. As with (1→3)-α-D-glucan and other polysaccharides,[5–10] it is difficult to consider that annealing produced any drastic change in the chain packing of chitosan since the chitosan film did not show any appreciable change during annealing even though this is an irreversible process. Furthermore, the a- and b-axis lengths of our annealed chitosan are a little smaller than those of the tendon chitosan.[2]

These observations lead to the following proposal on the chitosan conformation in the present new polymorph. There seems to be only a small difference in chain packing between the tendon chitosan cell and our annealed cell, that is, the presence or absence of water molecules. Upon removal of loosely bound water molecules between the chains along the [010] direction in the tendon chitosan, new interchain hydrogen bonds may be formed. The present new polymorph of chitosan is energetically more stable than that of the tendon chitosan. Further analysis is under way.

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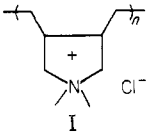
Chloride Ion Conductivity in a Plasticized Quaternary Ammonium Polymer

Solvent-free polymer electrolytes[1,2] have generated much interest owing to their possible use in high energy density batteries. Most research in this area has focused on alkali metal ion conduction in solid electrolytes formed by alkali metal salts and poly(ethylene oxide)[3] or poly(propylene oxide).[2] Although cation transport has been substantiated by use of reversible cation electrodes, i.e., alkali metals,[4–6] intercalates,[1] and sodium amalgam,[7] charge transport by anions may be substantial.[5,6] Here we report the first studies of fast anion conduction in solid polymer electrolytes, poly(diallyldimethylammonium chloride) (I, DDAC) plasticized with poly(ethylene glycol) (II, PEG; average MW = 300). In these anhydrous electrolytes, the positive charge is anchored in the polymer backbone. Thus the dc electrical properties displayed by these conductors are clearly attributable to the anion.



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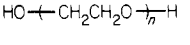

n ~ 6

II

An important motivating factor for the use of DDAC is that the positive quaternary nitrogen is surrounded by four alkyl groups, thus separating the opposite charges and reducing tight ion pairing. Tight ion pairing has been shown to significantly reduce the mobility of charge carriers in solid polymer electrolytes.[8]

Use of plasticizers in polymers is known to increase polymer chain flexibility, increase free volume, and decrease the glass transition temperature, T_g. These changes are also known to increase ionic conductivity in solid electrolytes.[9,10] Therefore, the present research was designed to investigate the possibility that plasticizers might increase the ionic conductivity of the polyelectrolyte DDAC.

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