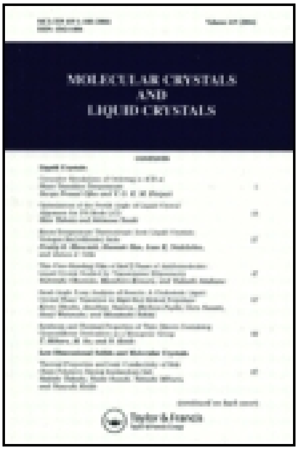

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Cholesteric Structure and Order-Disorder Transition in Aqueous Solutions of Schizophyllan, a Triple-Helical Polysaccharide

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Cholesteric Structure and Order-Disorder Transition in Aqueous Solutions of Schizophyllan, a Triple-Helical Polysaccharide

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Cholesteric pitch ($P=2\pi/q_c$) was measured for aqueous solutions of a triple-helical polysaccharide schizophyllan as a function of temperature (T), concentration (c) and molecular weight (M_v). q_c was substantially independent of M_v but changed with T and c. At higher temperatures, $q_c$changed monotonously with T but showed a sudden decrease around 7–18°C on lowering T, which was due to the order-disorder transition of aqueous schizophyllan.. The concentration dependence of q_c for D_2O solutions in the high temperature disordered state is the same as that for H_2O solutions, and interpreted theoretically using the threaded effective freely jointed chain model. On temperature jump experiments, q_c did not follow immediately T, but changed with the time elapsed. The relaxation time τ_{ch} was less than a few minutes. Since the conformation of the triple helix follows T much faster than τ_{ch}, this relaxation comes from rotational diffusion of the triple helix.

Keywords: Cholesteric pitch; rodlike polymer; liquid crystal; polysaccharide; temperature jump

1. INTRODUCTION

Schizophyllan is a β-1,3-D-glucan produced by fungus schizophyllan commune. Norisuye and collaborators[1] discovered that it exists in water as a triple helix with three polysaccharide chains held together by hydrogen bonds and one glucose residue per each three main chain glucose residues directing outward the helix core. In water the triple helix is very rigid and intact. It has been shown however aqueous schizophyllan undergoes an order-disorder transition depending remarkably on solvent and molecular weight.[2,] At low temperatures an ordered structure is formed around the helix core of side chains and nearby water molecules, which is destroyed as the temperature is raised. The transition is highly cooperative as judged from the remarkable molecular weight dependence, but little dependent on concentration, indicating the microscopic structure surrounding the helix is determined by temperature (in D_2O than H_2O) irrespective of concentration. An aqueous solution forms a cholesteric mesophase at higher concentrations due to the chirality of the helix3 and its cholesteric pitch, a macroscopic property, changes with the order-disorder transition, a microscopic structure. This reveals a clear correspondence between the microscopic structure and cholesteric pitch, a macroscopic property. It has been found the microscopic structure follows quickly the temperature but the macroscopic property, cholesteric pitch, is delayed behind the temperature change. The present study discusses this structural correspondence and dynamic feature in detail with the results on solutions of schizophyllan in H_2O and D_2O.

2. EXPERIMENTAL RESULTS

2.1 Order-disorder transition in H_2O and D_2O

Figure 1 shows plots of [α] against temperature for aqueous solutions (H_2O, ca. 1wt%) of schizophyllan of different molecular weight (M_v=viscosity-average molecular weight), exhibiting the transition between 3 and 8℃. The transition was also detected by excess heat capacity (ΔC_g), as shown in Figure 2; the transition temperature T_C is around 18℃ for the higher molecular weight sample.

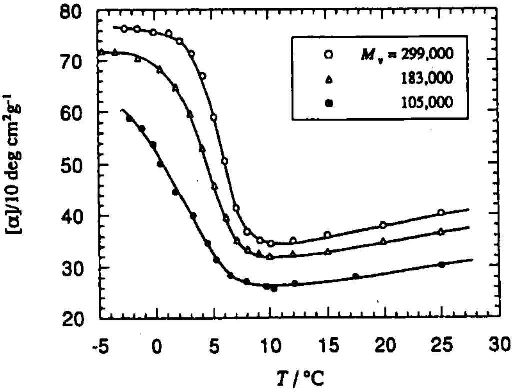

Figure 1. Order-disorder transition in schizophyllan-H_2O (1wt%)

These results confirm the previous finding[2] that T_C is about 12℃ higher in D_2O than H_2O but depends slightly on concentration. Figure 3 shows the temperature dependence of cholesteric wavenumber q_c for D_2O and H_2O solutions ($q_c = 2\pi/P$; P = cholesteric pitch). In both solutions, q_c changes drastically in the transition region, following closely the structure changes detected by optical rotation(OR) and heat capacity as shown in Figures 1 and 2. It is shown that q_c changes linearly with $1/T$ at high temperatures in the disordered region. Figure 4 shows the concentration dependence of cholesteric wavenumber q_c schizophyllan-H2O and –D2O solutions at 25℃. The data points for the two solvents form a single composite curve, exhibiting no isotope effect and molecular weight dependence. This behavior of q_c in the disordered region is essentially the same as usual

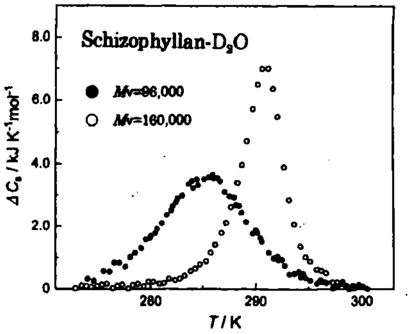

Figure 2. Excess heat capacity of schizophyllan-D_2O solutions.

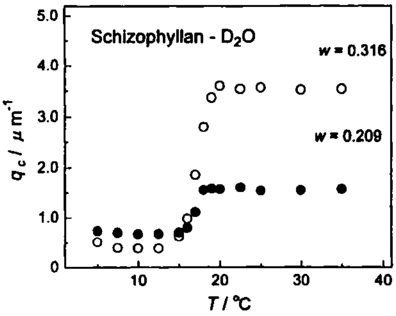

Figure 3a. Cholesteric wavenumber of schizophyllan-D_2O solutions.

polymer cholesteric solutions.[4]

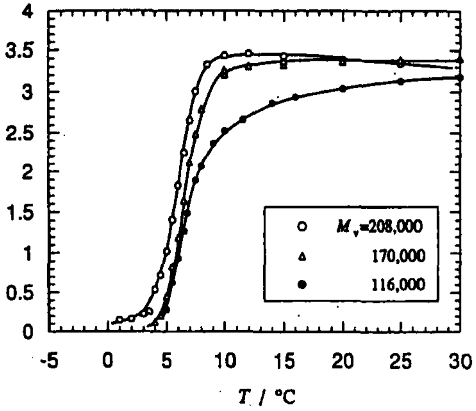

Figure 3b. Schizophyllan-H_2O

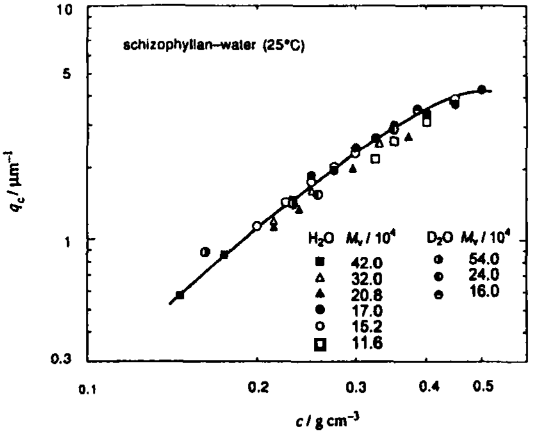

Figure 4. Concentration dependence of cholesteric wavenumber for schizophyllan-H_2O and schizophyllan-H_2O; solid curve, theoretical values.[4]

2.2 Temperature jump experiments

When the temperature of a solution was changed suddenly, q_c did not follow it immediately. Figure 5 illustrates the time courses $q_m(t)$ of cholesteric pitch for the raising (25℃→80℃) and cooling (80℃→25℃) for a solution of sample S21(Mv=208,000) (c=0.225). In either case, the transient cholesteric wavenumber $q_m(t)$ changes rapidly in the initial stage and tends to level off to the equilibrium value q_c, where t is the time elapsed after the temperature jump. In both cases, initial course is expressed by a single exponential decay of the correlation time τ_{ch}:

$$q_m(t) = q_o + [q_m(0) - q_c]\exp(-t/\tau_{ch}) \tag{1}$$

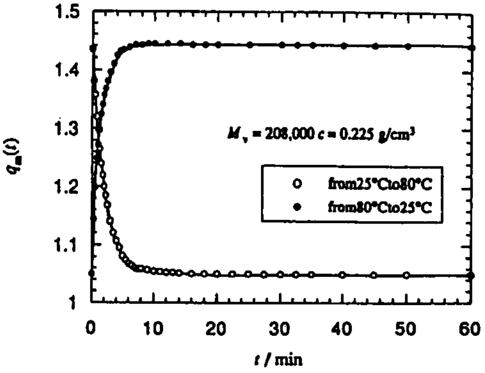

Figure 5. Transient cholesteric wavenumber on temperature jumps.

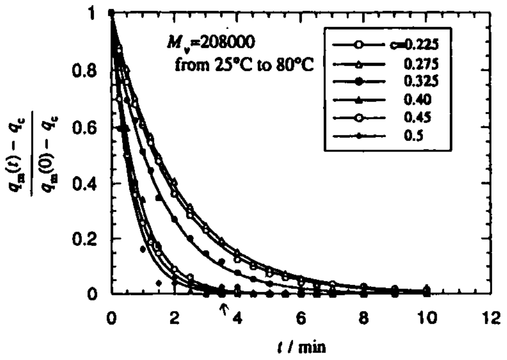

Figure 6. Time course of $q_m(t)$ on heating. Curves, fitting to eq. (1)

Figure 6 summarizes the results from the raising (25℃→80℃) experiments for this samples, where the curves represent the values fitted to eq. (1). Similar results were obtained from cooling experiments but at lower concentrations. All the results were fitted to eq. (1) to estimate relaxation time τ_{ch}. Figure 7 shows the relaxation time data as functions of *c*. It is seen that τ_{ch} decreases with *c* and is lower on raising than on cooling. Figure 8 shows the results on three different samples on cooling from 80℃ to 25℃, where $q_m(t)$ is expressed by a sum of two exponential decays ($\tau_{ch'}$ and $\tau_{ch}{}^*$). The shorter relaxation time $\tau_{ch'}$ behaves similarly to τ_{ch} as in Figure 7(smaller symbols). On the

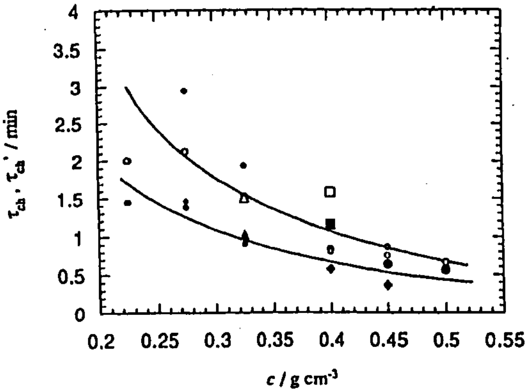

Figure 7. Relaxation times τ_{ch} and τ_{ch}' for the fast process on heating and cooling. Smaller symbols, complicated relaxation.

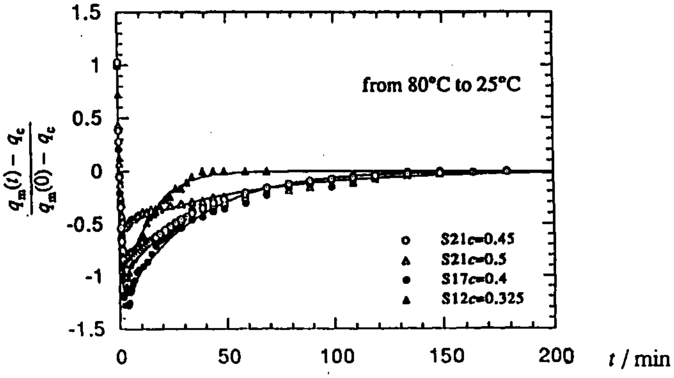

Figure 8. Complicated relaxations of $q_m(t)$ on cooling.

other hand the slower relaxation time τ_{ch}^* increases with c as seen in Figure 9. It is remarked that in the transition region, a temperature jump as small as 2°C is enough to induce a significant change in q_c.

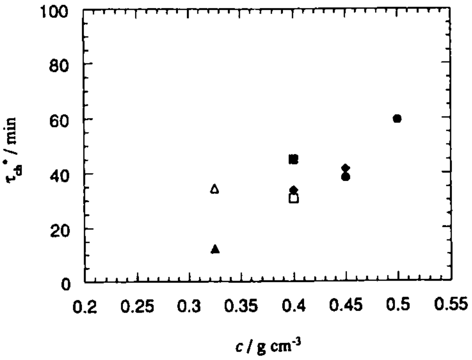

Figure 9. Concentration dependence of τ_{ch}^* for the slower relaxation.

3. DISCUSSION

3.1 Static Aspects

We have derived a theoretical expression for qc assuming that threaded equivalent freely jointed chain with the segment length κ interact each other with the dispersion energy of Osipov:[5]

$$q_c = [6S^2/\kappa^2 I_2(S)]\ [\lambda\ \Delta + \delta^*/H_A(\phi)] \qquad (2)$$

where λ (of the order of unity) and δ^* are numerical coefficients and S and ϕ are the orientational order parameter (nematic) and volume fraction of the polymer, respectively, Δ is the depth of the thread and $I_2(S)$ is a known function of S.[4] The solid curve in Figure 4 represents the theoretical values for q_c calculated with $\lambda\ \Delta = -0.0581$ and $\delta^* = 0.162$., which fits all the data points closely. This is consistent with the fact that q_c in the disordered state resembles those for usual polymer cholesteric solutions. On the other hand, as seen in Figures 3, q_c in the ordered state is much lower than that in the disordered state discussed above. Since the front factor of eq. (2) is considered to be insensitive to temperature, this difference is ascribed to the second factor. The following is a tentative explanation of this difference. In the disordered state, the side chains of schizophyllan triple helix form a deep groove with larger attractive energy. In the ordered state, this groove is filled with ordered water molecules and the triple helical rod becomes more smooth, reducing both $\lambda\ \Delta$ and δ^*. A more quantitative answer for $\lambda\ \Delta$ and δ^* will be obtained by analyzing q_c *vs* c data in this temperature region according to eq. (2).

3.2 Dynamic Aspects

As shown in Section 2.2, transient cholesteric wavenumber $q_m(t)$ does not follow the temperature change immediately, but is expressed by eq. (1). Observations of a multi-domain cholesteric phase by polarization microscopy showed that on the temperature jump the cholesteric pitch changed toward the equilibrium value but the orientation of the domains was almost unchanged. A theoretical consideration of this behavior is attempted using a continuum theory approach. Here we assume that a cholesteric specimen is divided into sub-domains with plains perpendicular to the cholesteric axis separated by a characteristic length l_{ch}. In each sub-domain the triple helical molecules undergo rotational diffusion to approach step by step to the new equilibrium orientation. Eventually the system comes close to the equilibrium state except for some defects in the boundary regions. Thus the rotational diffusion is the rate determining process for the transition from one orientation state (characterized by one value of q_c) to the other. The defects are eventually absorbed into the bulk phase, leaving some discontinuities as their traces. From this idea an equation for τ_{ch} in terms of l_{ch} is derived, predicting a linear correlation of τ_{ch} with l_{ch}^2. From the observed τ_{ch}, l_{ch} is found to be in the range between 1 to 4 μm and 0.62 and 2 μm, for the heating and cooling, respectively. On heating l_{ch} is nearly equal to the starting pitch, whereas on cooling l_{ch} is about 1/3 of the starting pitch. It is reasonable that l_{ch} is of the order of P. In this case there is an overshoot followed by the fast and slow relaxations. No molecular mechanism is as yet elucidated.

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