Ordering in aqueous schizophyllan solutions

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Schizophyllan is an extra-cellular linear β-1,3-D-glucan with one α-6-1-linked glucose residue per three main chain glucose residues. The schizophyllan solution has unique and characteristic solution properties different from other biopolymer solutions. This thesis treats or deals with the schizophyllan-water interface, particularly the order-disorder transition. This thesis is summarized as follows.

The order-disorder transition was treated by using the general theory for the linear cooperative transition. The agreement between the theory and experimental data was satisfactory, when the theory took into account the polydispersity effects. In frozen state, schizophyllan solutions have unfrozen bound water of 11.34 molecules per schizophyllan repeat unit below the melting point. It is noted that unfrozen water is different from structured water forming the ordered structure, because structured water is frozen. Excess heat capacities provide the enthalpy level of 3.61 kJmol^{-1}at the melting for unfrozen bound water. This means that unfrozen bound water exists at 57% above the heat of fusion of water, and is considerably ordered.

Schizophyllan solutions have four different water structures, which have inherent relaxation times and exist in specific amounts around the triple helix. These relaxation times are independent of the polymer concentration. This means that these water structures form specific phases, although not realized by clear interfaces. In the frozen state, three relaxation modes were found, but one of the relaxation modes disappeared below -30°C. Therefore, this relaxation mode is due to the partial melting and the others are due to unfrozen bound water.

The cholesteric pitch of aqueous schizophyllan solutions strongly depends on the order-disorder transition and these data are treated by the modern theory for lyotropic cholesteric liquid crystals. The chiral interaction parameters $\lambda\Delta$ and δ^* change remarkably in the transition. This is because the transition is concerned with the conformational change in the vicinity of the triple helix, thus changing $\lambda\Delta$ and δ^*. The chiral interactions between hard cores are amplified by the concentration and then lead to a remarkable change of the cholesteric pitches.