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Cholesteric Order in Aqueous Solutions of the Polysaccharide Xanthan

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Summary

Measurements of birefringence, optical rotation and laser light diffraction show that aqueous solutions of the polyelectrolytic polysaccharide Xanthan at a concentration of 7.5 % (vol/vol) have long range order very similar to cholesteric liquid crystals. The cholesteric screw is left handed implying a rod-like conformation and right handed helicity of individual molecules. The cholesteric phase separates from a less concentrated isotropic solution and spherolites are formed.

It is well known that rodlike macromolecules in solution undergo a transition from an isotropic state to a state of partial long range orientational order (usually called "lyotropic liquid-crystalline") at a critical concentration. Examples comprise viruses (BERNAL and FANKUCHEN, 1941), α-helical polypeptides (ROBINSON, 1955, 1958), nucleic acids (SENECHAL et al. 1980) and cellulose derivatives (ATKINS et al. 1980 ; BEHDA et al. 1980; TSUTSUI and TANAKA 1980; WERKOURYJ and GRAY 1979; WERKOURYI and GRAY 1976; SAMUELS 1969). In many cases a thermodynamic model of a gas of rods (ONSAGER 1949, FLORY 1956, KHOKHLOV 1980) describes fairly well the main features observed, i.e. phase separation and inverse proportionality between critical concentration (when given as mass per volume) and rod length. The peculiar optical properties of liquid crystals - as described by DE VRIES (1951) and recently summarized (KELKER and HATZ 1980) - can be used to characterize the long range organization of the anisotropic solution. It has been demonstrated this way that α-helical polypeptides and double-helical nucleic acids form optically active and birefringent cholesteric like phases, as also do hydroxypropylcelluloses (TSUTSUI and TANAKA 1980).

The chemical structure of Xanthan has been given by JANSSON et al. (1975); the polymeric backbone is a β(1→4) D-glucose chain

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as in cellulose and adopts in aqueous solution a rigid conformation above a critical ionic strength of about 10^{-2} N at room temperature (RINAUDO and MILAS 1978). This ordered conformation was confirmed (MILAS and RINAUDO 1979, MILAS and RINAUDO 1981) recently by optical rotatory power experiments ; it also depends on the molecular weight (MILAS and RINAUDO, 1981). X-ray work by MOORHOUSE et al. (MOORHOUSE et al. 1977) on dry fibers has demonstrated that Xanthan in the solid state is a right-handed high pitch (5_1) helix. A similar conformation is currently assumed to exist also in solution.

A lyotropic phase of Xanthan including phase separation was recently observed (RINAUDO et al. 1979, 1981) to exist when the helical conformation is established and above a critical concentration which varies like M_w^{-1}, M_w being the molecular weight. This phase is further described in this note, with emphasis on its optical properties. The Xanthan used was partially hydrolyzed enzymatically resulting in $M_w \approx 140000$ corresponding to a mean length of the helix of about 1400 Å. At room temperature and without added salt, above a critical concentration of about 35 g/l phase separation takes place within several hours and is then easily observable with a low magnification microscope between crossed polarisers.

Fig. 1 shows the birefringence pattern of the more concentrated bottom phase confined in a 1 cm wide quartz cell having an optical path of 1 mm. Regions of regularly spaced parallel bright and dark lines are separated from homogeneous regions the apparent colour of the latter being contineously changed through the visible on rotation of one polariser. This pattern is typical for cholesteric liquid crystals: The optically anisotropic (birefringent) rod like molecules are parallel within planes containing their long axis; consecutive planes are parallel, the molecular axis, however, is slightly twisting resulting in a long range helical structure with the cholesteric axis normal to the planes. The optical axis is normal to the cholesteric axis and rotates around it. Hence, for a certain range of molecular optical anisotropies, concentrations and cell depths, regions of cholesteric axes normal to the light beam show a bright-dark-line-pattern, the dark-dark (or bright-bright) distance being equal to half of the cholesteric pitch. Regions of cholesteric axes parallel to the light beam show no birefringence but optical rotation (DE VRIES, 1951). The top phase (Fig. 2) is an isotropic solution of Xanthan containing spherolites which slowly sediment depending on their size. The spherolites are remarkably spherical and exhibit concentric bright-dark lines including one radial defect. These observations are very similar to those on concentrated solutions of polybenzylglutamate (ROBINSON 1955, 1958).

The distance P/2 between dark (or bright) lines in a radial direction of the spherolite is identical to that normal to the dark (or bright) layers in the bottom phase and equals 12.0 ± 0.5 µm in Fig. 1 and Fig. 2. The same distance is also found from laser light diffraction of the bottom phase (Fig. 3). Such

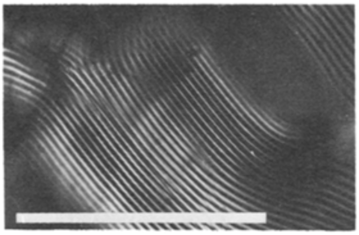

Fig. 1 - Polarization microphotograph from the bottom phase of an aqueous solution of the helical polysaccharide Xanthan confined in a 1 cm wide optical cell with 1 mm optical path. Polarizers are crossed horizontal, vertical and white light used. The white bar indicates a distance of 0.5 mm. The concentration was about 116 mg/ml or 7.5 % Vol/Vol, determined (after separation from the top phase) by weighting before and after complete evaporation of the solvent.

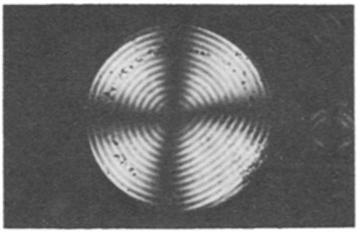

Fig. 2 - Like Fig. 1 but from the top phase showing a spherolite surrounded by a less concentrated isotropic solution.

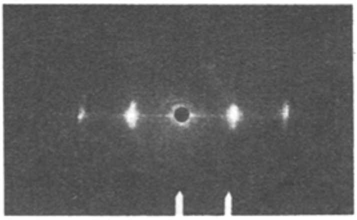

Fig. 3 - Low angle laser light diffraction pattern from a region similar to the central part of Fig. 1 but with vertical birefringence layer lines. The photograph was taken from a screen positioned 50 cm behind the sample and a He-Ne-laser (λ = 0.633 µm beam diameter about 1.5 mm) polarized along the layer lines was used. The distance (of 2.65 cm) between the white vertical marks on the screen corresponds to a periodicity of 12 µm in first order.

diffraction cannot be observed for light polarized normal to the lines, indicating that the long range periodicity does not originate from periodic variations of the particle's concentration, but rather of their orientation. A cholesteric arrangement of birefringent rods agrees with this observation, the optical periodicity being identical to half the cholesteric pitch P. There is, however, weak higher order diffraction (Fig. 3) not expected for a cholesteric structure, when considered as a contineous phase of regularly twisted anisotropic particles much smaller than optical wavelengths. Since enhanced higher order diffraction was observed from regions near the walls, we believe that some distortions due to wall effects are mainly responsible for this effect.

The birefringence of spherolites and bottom phase was determined quantitatively: By using, in the polarization microscope, monochromatic light of a sodium lamp and inserting a $\lambda/4$-waveplate or a birefringence compensator, it was found that the refractive index of the bright layers is smaller for light polarized normal to it then parallel to it for both spherolites and bottom phase: the birefringence is negative with respect to the normal of the layers. The absolute value of the birefringence was deduced from the wavelength-dependence of the optical rotation in the uniformlycoloured regions of the bottom phase. As shown in Fig. 4 the rotation is right-handed and the angle of rotation Θ is proportional to λ^{-2}. This agrees very well with DE VRIES' relation (1951) which can be written, for our geometry and $\lambda^2/P^2 << 1$, as

$$\Theta = - \frac{\pi}{4} \frac{P}{\lambda^2} \cdot \Delta n^2 \qquad (1)$$

$\Delta n = n_{\parallel} - n_{\perp}$ being the birefringence of the locally nematic (or untwisted) phase with respect to the nematic director. From the slope of Θ vs. λ^{-2} (Fig. 4) using eq. (1) and $P = 24$ µm we obtain $|\Delta n| = 2.9 \cdot 10^{-3}$ at a concentration $c = 116$ mg/ml. Anticipating a cholesteric structure we deduce a birefringence $\Delta n/c = + 2.5 \cdot 10^{-5}$ mg^{-1}ml for a completely oriented (nematic) solution of Xanthan with respect to the long axis of the rodlike molecules.

The negative sign in eq. (1) indicates that the sense of the optical rotation is opposite to the sense of the cholesteric helix (DE VRIES, 1951). Note that this is so only for $\lambda/P<1$ and DE VRIES' theory shows that polarization and cholesteric helix rotate in the same sense for $\lambda/P>1$. Therefore our data are consistent with a left-handed cholesteric structure in the bottom phase of Xanthan solutions. Since the Xanthan molecules very probably adopt a high pitch right-handed helical conformation, our observations confirm the idea proposed and outlined previously (SENECHAL et al. 1980) that in concentrated lyotropic solutions the helical surface segments of neighbouring molecules tend to align parallel thereby producing the cholesteric twist between the molecular long axes, the sense of the twist being related to the sense of the molecular helix.

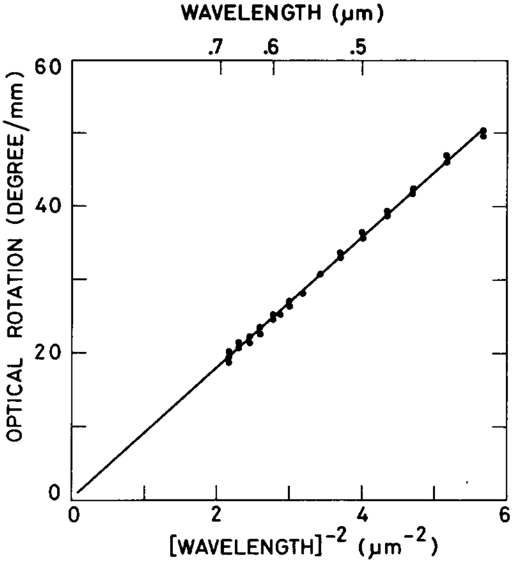

Fig. 4 - Wavelength dependence of the angle of rotation (Θ) of linearly polarized light from homogeneous regions such as the one shown in the upper right part of Fig. 1. In these regions the cholesteric axis is oriented along the light beam. A polarization microscope was used combined with a low resolution prism monochromator. The straight line results from a best linear fit through the data points and agrees with the theory by DE VRIES (1951), (see text). λ^2/P^2 is smaller than 10^{-3} in the visible.

The top phase is an isotropic solution containing spherolites which have a structure - on a local scale - very similar to the cholesteric structure of the bottom phase. However, the spherical shape of the spherolites, resulting probably from surface tension between the isotropic and anisotropic solution, implies the existence of defects, because a spherical structure with radial cholesteric axes everywhere is topolocially impossible. The elegant structure proposed by FRANK and PRICE (ROBINSON 1958) for spherolites found in solutions of polybenzylglutamate is consistent with the optical properties reported here.

An extended study of the lyotropic phase of Xanthan including measurements of the concentrations in top and bottom phase, respectively, of the cholesteric pitch and magnetic orientation-effects at various concentrations, ionic strengths and temperatures is in progress.

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