polymer papers

The cholesteric nature of cellulose triacetate solutions

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Solutions of cellulose triacetate (CTA) in trifluoroacetic acid (TFA) become liquid crystalline above a certain critical concentration. Using the techniques of spectrophotometry, wide-angle light scattering and circular dichroism we have shown that the mesophase formed is cholesteric. We have measured its pitch, which depends on polymer concentration, and shown that the cholesteric structure is right-handed. Measurements of optical activity and the optical effects of shear and magnetic fields are also described and discussed.

Keywords Cellulose triacetate liquid crystals; polymer mesophase; macromolecular mesophase; liquid crystal polymer; polymer cholesteric

INTRODUCTION

Many kinds of macromolecule or polymer are known to form liquid crystals in certain solvents. The general requirements are that the polymer chain should be fairly rigid and that the concentration should exceed a certain critical value. Under these conditions rod macromolecules can readily form a nematic state, where the long axes of the rods are closely parallel over macroscopic regions of the solution. The long axes of the rods then define the director $\vec{n}$ of the mesophase.

Chiral macromolecules generally form a chiral (i.e. a cholesteric) mesophase. The mesophase chirality originates from the assymetry of the interactions between chiral macromolecules. Thus the short-range order is nematic but there is a long-range twisting of the nematic structure in a regular manner along a helicoidal axis $\vec{N}$ which is orthogonal with $\vec{n}$. Most biological polymers have been found to form cholesteric solutions. Using optical techniques, previous studies have been made of some polypeptides and some cellulose derivatives, discussed below.

The polypeptides (e.g. polybenzyl glutamate PBLG) form cholesteric liquid crystals with a large pitch (1–100 μm) which can be seen as a finger-print pattern by using a polarizing microscope[1,2] and is readily measurable. Hence the effect of electric[3] or magnetic[4] fields on the pitch can be studied. The dielectric and magnetic anisotropy of PBLG is such that the long axis of the macromolecular rod prefers to orient parallel to the direction of an applied field. Hence a cholesteric–nematic transition can be induced at a certain critical field, or magnitude related to the twist elastic constant of the cholesteric phase[5,6].

The cellulose and cellulose derivatives, e.g. hydroxypropyl cellulose dissolved in water[7] or organic solvents[8], are found to be cholesteric with a smaller pitch (0.3–10 μm) than most polypeptides. The pitch generally depends on the nature of the solvent, the concentration of polymer and the temperature. Cellulose acetate, butyrate, ethyl cellulose and cellulose triacetate have been reported to form cholesteric solutions with a spherulitic texture[9]. Cellulose itself dissolves in trifluoroacetic acid–chlorinated alkane mixtures and was found to adopt a cholesteric structure although the pitch was not measured[10].

Cellulose acetate forms anisotropic solutions in various solvents[11–14]. In a recent paper, Patel and Gilbert[14] found that the pitch was about 10 μm for a trifluoracetic acid–dichloromethane solvent mixture but they did not measure the pitch in the pure trifluoroacetic acid (TFA).

In this paper, liquid crystalline solutions of cellulose triacetate (CTA) dissolved in trifluoroacetic acid are studied by several optical techniques; spectrophotometry, polarimetry, light scattering and optical microscopy.

EXPERIMENTAL

Materials

Cellulose triacetate, with $72\,000 < M_w < 74\,000$ and a degree of substitution of about 2.9 was obtained from Fluka AG. The trifluoroacetic acid, also from Fluka AG, and the CTA were used without further purification. The polymer was dried for 12 h at 100°C before dissolution, which was done by shaking the CTA and TFA at room temperature for a time dependent on concentration (1 to 4 h) and occasionally stirring. Bubbles were removed by centrifuging for about 30 min at 500 g. Polymer concentrations (c) are quoted as g of dry polymer per 100 ml of solvent. The critical concentration at which liquid crystallinity occurs we denote by c^{**}.

Techniques

Measurements of apparent optical absorption between wavelengths of 500 and 710 nm were made using 1 cm cells

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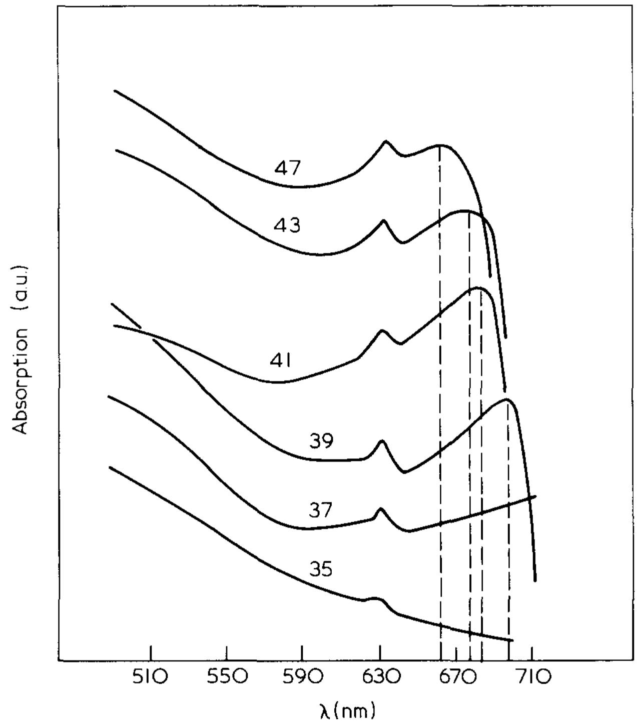

Figure 1 Optical extinction (arbitrary units) *versus* free space wavelength for CTA/TFA liquid crystalline solutions. Numbers on curves refer to concentration in g per 100 ml

with a Unican SP1800 spectrophotometer. As the attenuation of light by liquid crystals is mostly due to scattering, the term apparent absorption is used in this paper to denote optical extinction.

Specific rotation $[\alpha]$ was measured at a wavelength of 546 nm using a Bendix NPL type 143 polarimeter. The optical rotation is defined conventionally by

$$[\alpha]=\frac{100(\alpha-\alpha_0)}{zc}$$

where α and α_0 are the rotation in degrees of the solution and solvent respectively. z is the path length in dm and c is the polymer concentration as defined above.

Circular dichroism (c.d.) measurements were made with a Jasco J 40cs Recording Spectrophotometer, using 50 μm path length cells.

Wide angle light scattering (WALS) measurements were made using a Sofica Photogoniodiffusometer type M42000 at a wavelength of 546 nm.

Optical microscopy measurements were made with a Swift microscope with the usual polarization accessories.

RESULTS AND DISCUSSION

Below the critical concentration (c^{**}), found to be 34 g/100 ml at room temperature, the CTA/TFA solutions were transparent liquids. Above c^{**} the solutions appeared turbid and scattered light strongly, showing irridescent colours when viewed in white light. As the angle of scattering increased, the dominant colours were red until 50°, yellow until 75°, green until 30°, blue until 110° and violet for large angles. This behaviour is typical of cholesteric liquid crystals, whether they be small molecule thermotropic phases[15] or polymer solutions[7]. For nematics, the turbidity is usually ascribed to orientation fluctuations of the director $\vec{n}$. In cholesterics $\vec{n}$ changes in a regular helical way along another axis $\vec{N}$. The turbidity in cholesterics can be thus due to orientation fluctuations in both $\vec{n}$ and $\vec{N}$. The irridescent colours are usually ascribed to light scattering which has a strong wavelength dependence, from fluctuations in $\vec{n}$ and/or $\vec{N}$. The strong wavelength dependence originates from the ordered structure of the cholesteric and can be regarded as Bragg reflections from the pitch of the helix traced out by $\vec{n}$. The helical pitch $P=2L$, where L is the distance along $\vec{N}$ between two adjacent layers with directors $\vec{n}$ and $-\vec{n}$. (There is no physical distinction between these layers.)

Using a 1 cm square glass cell, anisotropic solutions were studied with white and laser light. Although one scattering colour was dominant at a given angle using white incident light, others were present, showing different orientations of $\vec{N}$. Using a near-monochromatic, parallel and small diameter laser beam, inhomogenous scattering was observed along the path of the beam, which appeared to consist of irregularly spaced dots. These intensity fluctuations at constant wavelength again suggest the presence of fluctuations in $\vec{N}$ over sub-mm distances.

Above a polymer concentration of about 45 g/100 ml, the single anisotropic phase separated (after centrifugation) into a gell-like white phase lying above an anisotropic solution and therefore of lower density. The densities of TFA and CTA are 1490 and 1340 kg m^{-3}, respectively. Thus the gel was more concentrated with polymer than the anisotropic solution, the values being about 58 g/100 ml and 44 g/100 ml, respectively.

This behaviour differs from that reported by Patel and Gilbert[14] who detected, using optical microscopy, a biphasic interval of concentration of about 6% for $c>c^{**}$. This difference will be discussed in a forthcoming paper[16].

Spectrophotometry

As previously discussed, a cholesteric phase is an optically anisotropic medium where the optic axis ($\vec{n}$) rotates along the $\vec{N}$ axis, the pitch P determining the spatial period. Bragg diffraction may be used to approximately describe the coherent scattering from such a periodic system, the Bragg equation then being

$$P\sin\theta=\frac{m\lambda}{\bar{n}},$$

where m is an integer, 2θ is the angle between the incident and the scattered light, λ is the free-space wavelength and $\bar{n}$ is the average refractive index of the medium. In spectrophotometry, the optical extinction of the sample is determined over a range of wavelengths by measuring the intensity of the light transmitted by a sample. Because of the Bragg scattering an extinction edge is found (*Figure 1*). Because $\sin\theta \leqslant 1$ it follows from the Bragg equation that light of wavelength exceeding $\frac{Pn}{m}$ is not coherently scattered and therefore suffers little attenuation. For $\lambda<\frac{Pn}{m}$ the Bragg equation shows that coherent scattering will occur. Because of random orientations of $\vec{N}$ in the sample and due to the influence of $\sin\theta$ in the Bragg formula the extinction curve is expected to be an increasing function of the wavelength until $\sin\theta=1$, when a sudden decrease of extinction is predicted at a wavelength $\lambda^*=\frac{Pn}{m}$. *Figure 1* shows that this is not exactly

Table 1 Summary of experimental results for CTA/TFA solutions. The pitch was determined from spectrophotometric measurements. The refractive index ($\bar{n}$) data is from ref. 17. c is the concentration in g ml^{-1} of solvent

c (g ml^{-1})	$\bar{n}$	Pitch (nm)	[α] (deg dm^{-1} g^{-1} ml)
0.35			−249
0.37			−396
0.39	1.3441	522	−440
0.40		519	
0.41	1.3464	510	−446
0.43	1.3478	506	−232
0.47		496	

the case, and we attribute the finite gradient at the extinction edge to orientational fluctuations in $\vec{n}$. The sample was in a 1 cm square cell with faces normal to the incident beam. The spectra show two peaks; one at 630 nm due to the solvent and another, near the extinction edge, which we have taken to define λ^*. This latter peak was present only in the anisotropic solution, which is strong evidence for the existence of the cholesteric phase at $c > 0.34$ g ml^{-1}. Values of the pitch P are shown in *Table 1*, assuming $m = 1$[15]. Average refractive index values $\bar{n}$ were taken from ref 17. *Table 1* shows that P decreases with increasing concentration as is usual for lyotropic polymer liquid crystals. Similar behaviour was found for PBLG in dioxane[18] and hydroxypropyl cellulose (HPC) in water[18,19] where the pitch was related to the volume concentration of polymer φ_2 by $P = K\varphi_2{}^a$ where K and a were constant for a given polymer–solvent pair. For PBLG/dioxane $a = -2$ and for HPC/water $a = -3$. The data in *Table 1* gave $a = -0.3$ for CTA/TFA solutions.

Wide-angle light scattering (WALS)

Because of the fluctuations of $\vec{N}$ as discussed in the above section, a liquid crystalline sample may be regarded as analogous to a powder sample in X-ray scattering, where coherent scattering occurs from the material within a crystallite of size considerably larger than a wavelength, but the crystallites have a random orientation of crystal axes within the sample. Thus when illuminated with monochromatic light, a cholesteric region will only scatter strongly (coherently) if there is an angle of θ between $\vec{n}$ and the incident light direction such that $P \sin\theta = \frac{m\lambda}{n}$ where the symbols have been defined in the previous section. In this Bragg formula, the usual scattering angle $= 2\theta$. The angular dependence of the scattered intensity was measured with the Sofica instrument using an anisotropic 41 g/100 ml solution. The result is shown in *Figure 2*. As in X-ray scattering by powders, we assume the intensity maximum is at the Bragg angle, giving $\theta = 51.4°$. With $m = 1$, $\lambda = 546$ nm and $\bar{n}$ taken from ref 17, the cholesteric pitch is 519 ± 5 nm. This compares well with 510 ± 4 nm found spectrophotometrically. As in X-ray diffraction, the width of the intensity peak is able to give useful information about the size of the region of the scatterer over which coherent scattering occurs. In the optical region, the Scherrer X-ray equation may be written

$$l \approx \frac{\lambda}{n\,\Delta\theta \cos\theta}$$

where l is a size characteristic of the coherent scattering region and $\Delta\theta$ is the width of the scattering peak at half-height. The intensity in *Figure 2* is not symmetrical and is superimposed on a large background intensity baseline. By allowing for the variation of the incoherently scattered baseline as shown in *Figure 2*, $\Delta\theta$ was estimated to be about 4 degrees which gives $l \approx 8$ μm using the Scherrer equation. If l is regarded as the distance over which $\vec{N}$ is closely rectilinear and $P \approx 0.5$ μm as previously found then the direction of the cholesteric helix persists over about 16 turns.

Polarimetry

A cholesteric structure, with a pitch commensurate with the optical wavelength, interacts strongly with circularly polarized light. The fundamental effect it has on a transmitted light beam may be described by two complex refractive indices n_R and n_L, for right and left-handed circularly polarized light, respectively. In practice it is usual to describe the cholesteric structure by the specific rotation [α] which is proportional to the difference between the indices of refraction for left (L) and right (R) circularly polarized light, and the circular dichrosim

$$\Delta\varepsilon = \varepsilon_L - \varepsilon_R = \frac{1}{[M]z}\log_{10}\left(\frac{I_R}{I_L}\right),$$

where ε is the molar extinction, $[M]$ is the molar concentration in moles of polymer per ml of solvent, z is the path length in cm and I_R and I_L are the transmitted intensities for right and left-handed circularly polarized light. It can be shown that $[\alpha] \propto Re(n_L - n_R)$ and $\Delta\varepsilon \propto Im(n_L - n_R)$, where Re and Im denote the real and imaginary parts, respectively.

A circular dichroism (c.d.) spectrum (*Figure 3*) was recorded with 43 g/100 ml anisotropic solution in a 10 mm glass cell. A strong c.d. peak was found at a free-space wavelength of 694 nm. The theory of c.d. in cholesterics[15] shows that $\Delta\varepsilon$ is a maximum when the wavelength in the sample is equal to the cholesteric pitch P. Thus $P = \frac{\lambda}{n}$ and our data gives $P = 515$ nm. This compares closely with our previous result of 514 nm found spectrophotometrically. *Figure 3* shows that $\varepsilon_L > \varepsilon_R$ (positive Cotton effect) which is evidence[15] for a right-handed cholesteric structure. The peak value of $\Delta\varepsilon$ is large, 4200 cm^2 mol^{-1}, typical of a cholesteric structure.

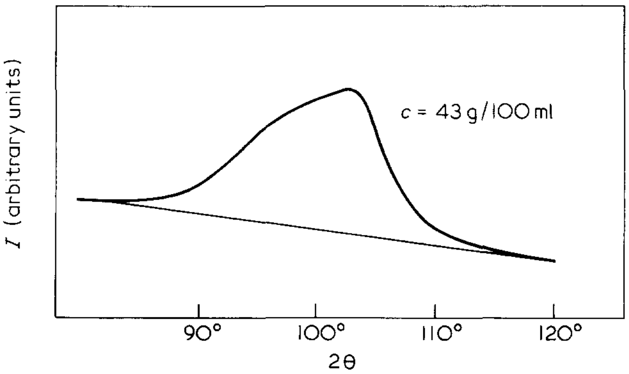

Figure 2 Intensity (arbitrary units) of scattered light *versus* scattering angle for a 0.41 g ml^{-1} CTA/TFA liquid crystalline solution. The straight line is the assumed background intensity variation

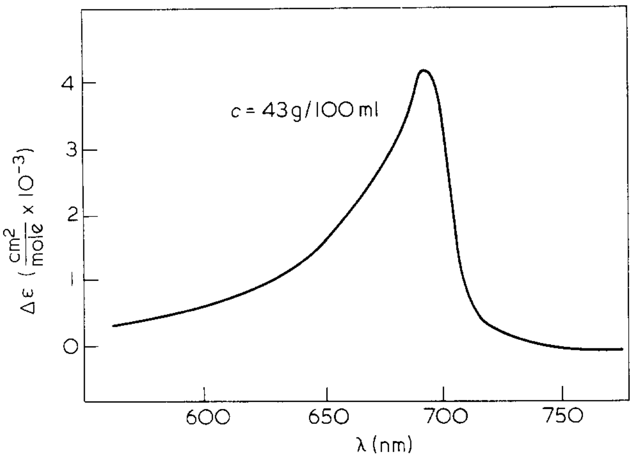

Figure 3 Circular dichroism $\epsilon_L - \epsilon_R$ *versus* free-space wavelength for a liquid crystalline 0.43 g ml^{-1} CTA/TFA solution

The large value of $\Delta\varepsilon$ implies that there will be a correspondingly large value of the specific rotation $[\alpha]$. This was measured using a 0.1 mm path length cell at $\lambda = 546$ nm over a range of concentrations greater than 34 g/100 ml. *Table 1* shows the results; large and negative values of $[\alpha]$. Negative values of $[\alpha]$ were expected because the measurement wavelength is smaller than that at the c.d. maximum. A larger than expected ($\approx \pm 50\%$) variation between individual $[\alpha]$ values of the same concentration was found: the values of $[\alpha]$ at any one concentration shown in *Table 2* are the mean of several determinations. Because $[\alpha]$ depends on the angle between $\vec{N}$ and the light propagation direction, we surmise that the observed variation in $[\alpha]$ values originates from the fluctuations of the average direction of $\vec{N}$ from one sample to another. This is to be expected when the correlation distance l (≈ 8 μm from our previous results) is not negligibly small compared with the path length (100 μm) of the cell. Despite these fluctuations, $[\alpha]$ in *Table 1* increases with concentration except for the 0.43 g ml^{-1} solution which was very viscous and for which the cell filling process could have caused a permanent orientation of $\vec{N}$. The decrease in pitch with increasing concentration shown in *Table 1* explains the decrease in $[\alpha]$ with increasing concentration through the de Vries equation[20],

$$\alpha(\lambda) = \frac{-\pi \Delta n^2 \lambda_0}{4\bar{n}\lambda^2 \left[1 - \left(\frac{\lambda}{\lambda_0}\right)^2\right]}.$$

In the above equation, λ is the wavelength at which α is measured, λ_0 is the wavelength where $\alpha(\lambda)$ changes sign and Δn is the birefringence of the layers, which in the de Vries theory are rotated about the $\vec{N}$ axis to form the cholesteric phase. Identifying λ_0 with $\bar{n}P$, the above equation explains (at $\lambda < \lambda_0$) the sign of $[\alpha]$ and the decrease of $[\alpha]$, through P, with the concentration.

The de Vries equation gives $\Delta n \approx 0.003$, much lower than the values ($0.07 < \Delta n < 0.04$) reported for cellulose[21]. This is to be expected as the de Vries equation was derived for light propagating parallel to $\vec{N}$ and our sample consisted of regions where $\vec{N}$ was randomly orientated. Secondly, the CTA chain is not a perfectly rigid rod and fluctuations in $\vec{n}$ will reduce the layer birefringence.

Shear-induced birefringence

When examined using a microscope with crossed polarizers the anisotropic solutions of CTA/TFA showed some structure but on average only a small depolarization and brightening of the field of view. On applying a small shear to a solution between the two slides, a large intensity change occurred. The intensity change was negligible when the shear direction was parallel to the polarizer axes and a maximum when at ±45° to these axes, showing the effect to be due to shear birefringence rather than optical rotation induced by shear. We infer that the shear flow induced a temporary cholesteric–nematic transition. On stopping the shear, the birefringence decreased slowly with time, compared with the apparently instantaneous disappearance shown by the isotropic solutions, which showed a much weaker flow birefringence. Replacing the microscope eye-piece with a photomultiplier, the intensity was recorded as a function of time. Taking the zero of shear-induced intensity as the quiescent slightly depolarized intensity normally observed between crossed polarizers with no shear, then the intensity decay was closely described by the expression

$$I(t) = I(0)e^{-\frac{t}{\tau}}$$

where $I(0)$ is the intensity transmitted immediately before shear stopped and τ is a relaxation time characteristic of the anisotropic solution. In view of the proposed mechanism for the birefringence, τ is a measure of the time taken for the shear-induced nematic state to re-form to its natural cholesteric state. For $c = 41$ g/100 ml τ was ~ 65 s, compared with < 0.2 s for isotropic solutions of similar viscosity. Presumably τ depends on the competition between structuring and randomising forces, i.e. the twist elastic constant K_{22} and Brownian motion as measured by kT, where k is Boltzmann's constant and T the Kelvin temperature. K_{22} is small for lyotropic polypeptide solutions[22] and if similar for CTA/TFA could explain the large magnitude of τ.

Magnetic field effects

As discussed previously, the mode of orientation of polypeptides in applied magnetic fields is such that a cholesteric–nematic transition is observed at large enough applied fields. This transition was not found for anisotropic CTA/TFA solutions using spectrophotometry (field up to 2 Tesla) and circular dichroism (field up to 1.1 Tesla). Thus either the molecular diamagnetic anisotropy is negative so that the molecular length prefers to lie transverse to the applied field, or it is weakly positive and the fields used were not large enough. The magnetic field induced birefringence of isotropic solutions was studied in an attempt to decide between these alternatives but the birefringence was too weak to provide a conclusive result. Thus we infer that, (unless the optical anisotropy of the molecule is near zero), the diamagnetic anisotropy is very small compared with that of the polypeptides, where, e.g., the magnetic birefringence in isotropic PBLG is easily measurable[23].

CONCLUSION

The cholesteric nature of liquid crystalline solutions of cellulose triacetate in trifluoroacetic acid has been unambiguously shown.

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