Birefringence of a Polymeric Cholesteric Liquid Crystal Measured by Refractometry

G. V. LAIVINS and D. G. GRAY, *Pulp and Paper Research Institute of Canada, and Department of Chemistry, McGill University, Montreal, Canada H3A 2A7*

Synopsis

The Abbé refractometer provides a convenient way to measure the refractive indices and birefringence of polymeric liquid crystalline solutions. The cholesteric mesophase formed by (acetoxypropyl) cellulose and its solutions in dibutyl phthalate were examined at 26°C and 50°C. The measured refractive indices were dependent on the direction of shear when the polymer was applied to the refractometer plates. The initial shear-induced nematic-like order relaxed slowly to the equilibrium planar cholesteric structure. The refractive index for the isotropic solutions and the two refractive indices for the anisotropic solutions all varied linearly with polymer concentration, and the width of the intermediate two-phase region was readily determined. The changes in refractive index with polymer concentration and with orientation on the refractometer plate were rationalized with a simple model of the cellulosic mesophase, and an order parameter of 0.7 was estimated. The layer birefringence calculated from optical rotatory dispersion measurements of the cholesteric reflection band intensity was in good agreement with the birefringence measurements.

INTRODUCTION

The observation of birefringence with the polarizing microscope is often the easiest way to detect the anisotropic nature of liquid crystalline fluids, and birefringence can in principle be related to molecular orientation in ordered phases. The birefringences of low molar mass[1-3] and polymeric[4-7] liquid crystalline phases have been measured by refractometry. The Abbé refractometer[8] measures the critical angle for a light ray passing between two media with different refractive indices. The direction of a ray passing from some medium to the refractometer plate is governed by Snell's law, which relates the angles of incidence i and refraction r in a plane normal to the refractometer plate to the refractive indices of the medium n and the plate n_g by $n \sin i = n_g \sin r$. For $n \leq n_g$ there is a critical angle r_c given by $n_g \sin r_c = n$, below which no light emerges from the medium. The critical angle occurs for light impinging on the surface at grazing angle ($i \rightarrow 90°$). A set of axes is here defined such that the long direction of the refractometer plate is along the y axis, and the z axis is normal to the plate. Light passing through the plate is viewed in the yz plane. Thus light in the y direction enters the plate from an isotropic medium at an angle r_c which depends only on the refractive index of the medium (Fig. 1 upper sketch). In the Abbé refractometer, the critical angle corresponds to a boundary between light and dark fields in the viewing optics, which are calibrated directly in refractive index units. Abbé refractometers often contain compensating prisms which correct for the dispersion when
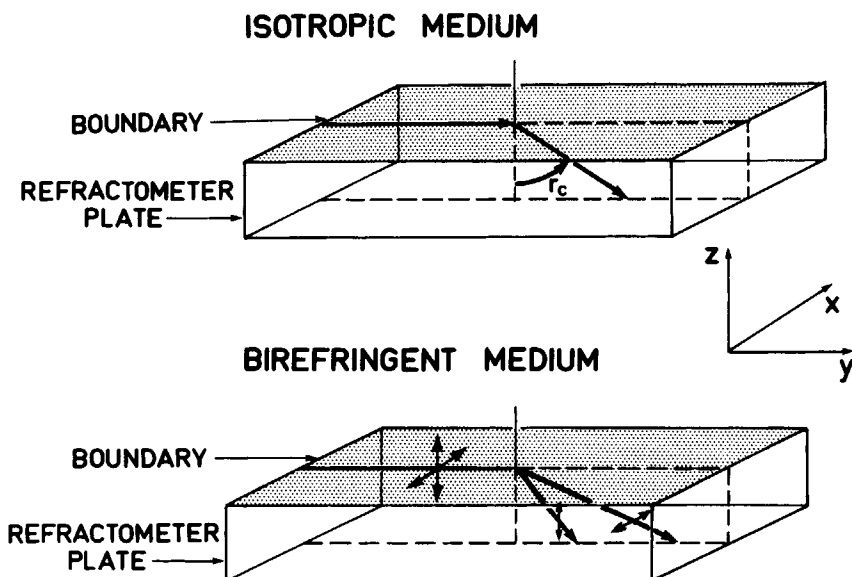
ISOTROPIC MEDIUM

BIREFRINGENT MEDIUM

Fig. 1. A light beam grazing the refractometer plate at $i \rightarrow 90°$ is refracted at the medium plate boundary (shaded region) at a critical angle r_c for an isotropic medium. For a birefringent medium with different refractive indices in the n and z directions, two critical angles will be observed (lower sketch).

illuminated with white light, and give values for n corrected to the sodium D line (589 nm).[8] All refractive indices reported here correspond to light of this wavelength.

If the medium on the Abbé plate is birefringent, then two boundaries may be visible, each corresponding to a refractive index. The position of the boundaries will depend on the birefringence of the medium, and also on its orientation with respect to the plate surface. This effect is illustrated schematically in Figure 1, lower sketch. A beam in the y direction passing through a medium with principal refractive indices n_z in the z direction and n_x in the x direction will be split into two distinct linearly polarized components with different velocities in the medium. These components will display different critical angles at the refractometer plate boundary; the component which is linearly polarized with electric vector in the xy plane gives n_x and the component which is polarized with electric vector in the yz plane gives n_z. The two components may be readily distinguished by viewing the Abbé refractometer eyepiece through a polarizing filter (Fig. 2). The observed birefringence depends on the orientation of the material on the refractometer plate; for a uniaxial material with principal axis oriented along the x direction ($n_x \neq n_y = n_z$), two lines corresponding to n_x and n_z should be visible. However, if the principal axis of the same material is oriented along the y direction (i.e., along the long dimension of the refractometer plate), then $n_y \neq n_z = n_x$ and a single line at $n_x = n_z$ should be observed. This method has been used to measure the refractive indices of oriented polymer films.[9,10]

In earlier attempts to measure the birefringence of polymer mesophases with an Abbé refractometer,[5,6] the positions of the boundaries were often
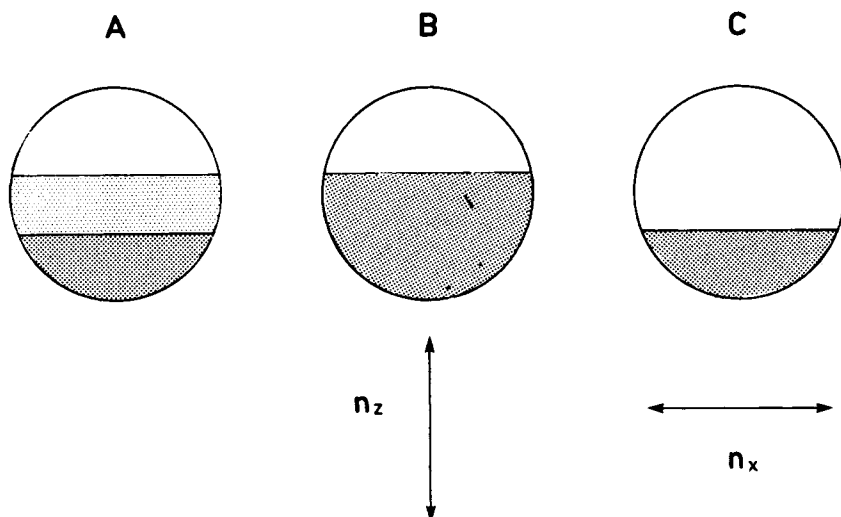
Fig. 2.   The field seen in the Abbé refractometer eyepiece for a birefringent material with the principle axis oriented in the x or z direction. (A) No polarizing filter. (B) Privileged direction of polarizer normal to the line separating the fields. (C) Privileged direction of the polarizer parallel to the line separating the fields.

indistinct, irreproducible, and time dependent, in part due to solvent evaporation from the lyotropic mesophase. In this work, a less volatile diluent was used. The refractive indices of (acetoxypropyl)cellulose-dibutyl phthalate solutions[11] were measured with an Abbé refractometer, as a function of polymer volume fraction, at 26° and 50°C. The quantitative measurements of the birefringence for anisotropic solutions are related to the molecular orientation in the ordered phase. The birefringence values, measured by refractometry, of a sheared cholesteric mesophase and an equilibrated mesophase are compared with those calculated from an optical rotatory dispersion spectrum with the de Vries equation. The order parameter of the cellulosic mesophase in a nematic-like state is estimated at both temperatures. The variation of the order parameter with the volume fraction of (acetoxypropyl)cellulose in the ordered phase of both biphasic and pure anisotropic solutions is examined.

EXPERIMENTAL

The (acetoxypropyl)cellulose was prepared and characterized as described previously.[11] Concentrated solutions of the unfractionated polymer in dibutyl phthalate (Matheson, distilled under reduced pressure) were prepared gravimetrically. The refractive indices of the solutions were measured with a Carl Zeiss Model 44159 Abbé refractometer. The concentration of the solutions on a polymer volume fraction basis varied from zero to 0.85 at 26°C, and to 1.0 at 50°C. Water from a thermostatted bath (±0.5°C) was circulated through a jacket which contained the prisms. The temperature of the water was monitored as it flowed from the jacket. No correction was made for the thermal expansion of the prisms at 50°C. Since the birefringence of a solution is the difference of two measured refractive index values no error is introduced by

omitting the correction factor. However, the individual refractive index values are ~ 0.1% too large at 50°C.

Three series of measurements (differing in the orientation of the mesophase on the refractometer plate) were made. In the first series, the prisms of the refractometer were separated and the solution was spread across the prism face. The solution was stroked repeatedly in the same direction with a microscope slide. The orientation of the solution in relation to the incident beam and the lower prism face corresponds to the x direction in Figure 1. The prisms were clamped together and the system was allowed to stand for a few minutes to allow the boundaries to develop. Two boundaries were visible in the refractometer eyepiece: the upper line (of lower refractive index) separated a light region from a greyish intermediate one; the lower line of higher refractive index separated the greyish region from a dark one. When the polarizer was placed onto the ocular with the privileged direction of the polarizer parallel to the line separating the fields of the refractometer, only the lower boundary was visible. Upon rotation of the privileged direction of the polarizer by 90°, the lower boundary disappeared and only the upper boundary between the light and intermediate regions was observed. The refractive index values corresponding to the boundaries were read from the refractometer scale.

In the second series of measurements, the solution was oriented longitudinally along the prism face by repeatedly stroking the solution from one end of the prism to the other end with a microscope slide, i.e., along the y axis of the previously defined coordinate system (Fig. 1). The upper prism was clamped into place and the system was allowed to stand for approximately 5 min. In this case, a single boundary was observed in the refractometer.

In the third series of measurements, several samples, previously oriented in the longitudinal direction, were allowed to equilibrate in the Abbé refractometer for periods of 18–24 hours. After this time, two boundaries were visible; the lower one separated the dark field from a grey one. The upper line which was indistinct separated the grey region from a light one. The fields typically observed for this equilibrated sample are compared in Figure 3 with those when the solution was initially oriented longitudinally. For a sample that had been oriented across the prism face and then allowed to stand for 18–24 hours, two boundaries were also visible. The fields observed in this latter equilibrated sample are shown and compared with those for an oriented sample in Figure 4. Note that the initial refractive indices of the samples depend on the direction of orientation, but the equilibrium values are the same in both cases.

The optical rotatory dispersion of a mesophase sample with planar texture was obtained as follows. A small quantity of an (acetoxypropyl)cellulose–dibutyl phthalate mesophase was sandwiched between two microscope cover glasses (Corning, 18 mm²). Three samples with a concentration of 0.85 and two of 0.825 on a polymer volume fraction basis were prepared. Heavy lead blocks were placed on top of each of the sandwiched samples to reduce the thickness of the viscous anisotropic solution and to ensure a uniform sample thickness. After two weeks the lead blocks were removed and the samples were allowed to equilibrate for an additional three months. The thicknesses of the coverglasses and mesophase solution were measured with a precision micrometer. The sample was mounted in the optical compartment of the

INITIAL

POLARIZER ∥   POLARIZER ⊥

n_x n_z

EQUILIBRIUM
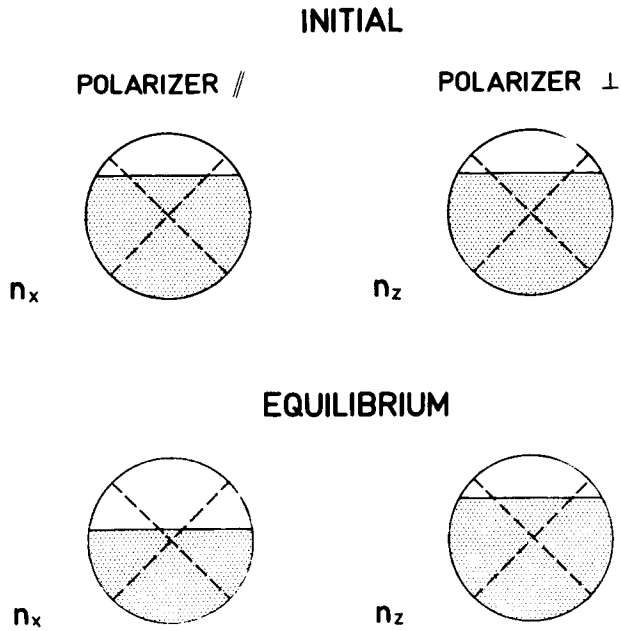
n_x n_z

Fig. 3.   The field seen in the eyepiece of the Abbé refractometer with the polarizer parallel and normal to the line separating the regions for a sample initially oriented along the refractometer plate (y direction in Fig. 1).

INITIAL

POLARIZER ∥   POLARIZER ⊥

n_x n_z

EQUILIBRIUM
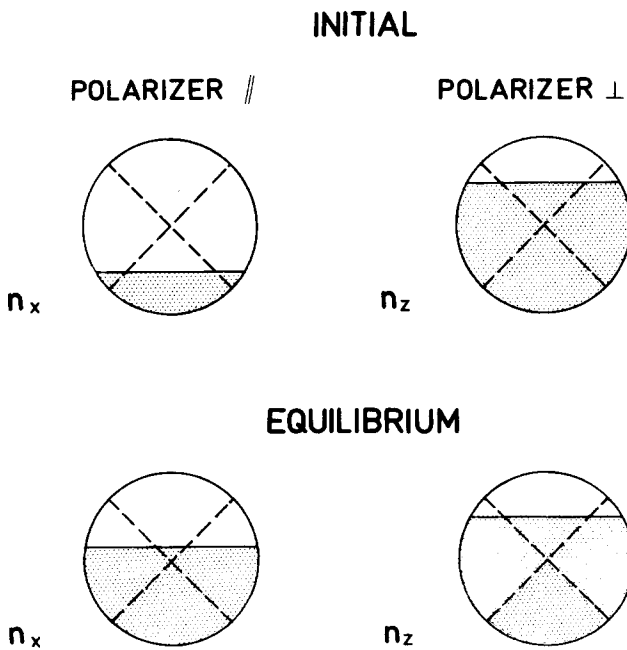
n_x n_z

Fig. 4.   The field seen in the eyepiece of the Abbé refractometer with the polarizer parallel and normal to the line separating the regions for a sample initially oriented across the refractometer plate (x direction in Fig. 1).
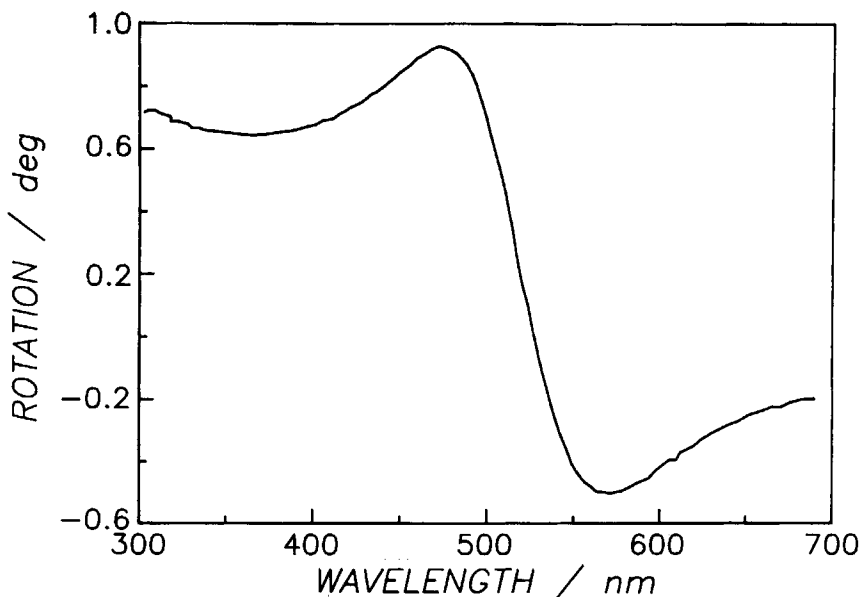
Fig. 5. The optical rotatory dispersion spectrum of a typical (acetoxypropyl)cellulose-dibutyl phthalate mesophase with reflection band in the visible wavelength range. The polymer volume fraction is 0.839 and the thickness of the sample is 0.1 μm.

Jasco ORD/UV 5 spectrophotometer, normal to the incident light beam. The spectra of the samples were recorded from 700 to 300 nm at a scan rate of 1 nm/sec. The selected full-scale setting of the optical rotation ranged from $\pm 1°$ to the maximum setting on the spectrophotometer of $\pm 2°$, depending on the thickness of the sample. The base line for the spectrum was obtained with a clean cover glass. A typical curve for the optical rotation as a function of wavelength is shown in Figure 5.

RESULTS AND DISCUSSION

Effect of Liquid Crystalline Orientation and Time

The initial positions of the boundaries observed in the refractometer depend on the direction of shearing of the mesophase on the refractometer plate (Figs. 3 and 4). An equilibrium position is reached after a number of hours. The refractive indices in the x and z directions for a series of liquid crystalline solutions are listed in Table I. The initial values for samples aligned by shear across the plate in the x direction (see Fig. 1) and the equilibrium values for the same samples are shown. The refractive indices normal to the refractometer plate do not change with time; n_z for the sheared sample and at equilibrium are the same within experimental error for each concentration. However the refractive indices across the plate, n_x, decrease markedly from the initial value to an equilibrium value. The birefringence $\Delta n_{xz} = (n_x - n_z)$ of samples oriented across the plate drops to about half of its initial value with time. However, for mesophase samples oriented along the refractometer plate in the y direction, only a single refractive index is obtained initially (Fig.

TABLE I

Measured Refractive Indices for (Acetoxypropyl)cellulose-Dibutyl Phthalate Lyomesophases

| APC Volume fraction | Temperature °C | Refractive indices | | | |
| | | Sheared[a] | | Equilibrated | |
		n_x	n_z	n_x	n_z
0.587	26	1.4818	1.4778	1.4799	1.4778
0.662	26	1.4825	1.4755	1.4805	1.4758
0.693	26	1.4818	1.4739	1.4764	1.4740
0.759	26	1.4809	1.4721	1.4764	1.4725
0.818	26	1.4810	1.4710	1.4763	1.4720
0.662	50	1.4741	1.4681	1.4703	1.4685
0.693	50	1.4739	1.4666	1.4696	1.4668
0.759	50	1.4728	1.4656	1.4690	1.4669
0.834	50	1.4728	1.4631	1.4674	1.4638
0.976	50	1.4718	1.4602	1.4672	1.4602

[a]Solution sheared across the face of the prism in the x direction.

3, upper sketch). The values for this refractive index (not listed) were equal within experimental error to the listed values for n_z. On equilibration, a second refractive index becomes evident, and the values for n_x and n_z approach those listed in Table I for the equilibrated sample after shearing in the x directions. In other words, after sufficient time the refractive index values are independent of the direction of initial orientation.

These observations can be rationalized with a naive model for cellulosic liquid crystalline solutions in which cylindrically symmetrical elements (the polymer chain segments) of refractive index n_a in the axial direction and n_t in the transverse direction are dispersed in an isotropic solvent with refractive index n_s. The fluctuations in direction along the chain may be accounted for by including an order parameter s such that the apparent chain refractive indices in the axial and transverse directions are n'_a and n'_t, respectively:

$$n'_a = (1 + 2s)n_a/3 + 2(1 - s)n_t/3$$
$$n'_t = (1 - s)n_a/3 + (2 + s)n_t/3 \tag{1}$$

The mean refractive index of the polymer, $\bar{n}_p$, is taken as

$$\bar{n}_p = (n'_a + 2n'_t)/3 \tag{2}$$

The refractive indices of binary mixtures may be estimated in a variety of ways.[12] Empirically, the specific refraction $(n - 1)/\rho$ of a substance of density ρ is often constant, and the specific refraction of a mixture is found by combining the specific refraction values for the components on a weight fraction basis. When no volume change occurs on mixing, this gives

$$n = n_1\phi_1 + n_2\phi_2 \tag{3}$$

where n_1, n_2, and ϕ_1, ϕ_2 are the main refractive indices and volume fractions of components 1 and 2, respectively. This type of additivity in principle

applies to polarizabilities rather than to refractive indices. However, in view of the low precision of the experimental results and the qualitative nature of the conclusions, the refractive indices of components with similar indices and low birefringence are combined as in the previous equations. If the refractive indices of solutions of an anisotropic polymer with an isotropic diluent can be combined similarly, then for the geometry shown in Figure 1, the refractive indices for a mesophase oriented across the refractometer plate are

$$n_x = \phi_p n'_a + (1 - \phi_p)n_s \qquad (4)$$

and

$$n_z = \phi_p n'_t + (1 - \phi_p)n_s \qquad (5)$$

where ϕ_p is the volume fraction of polymer and $(1 - \phi_p)$ is the volume fraction of solvent. Variations in order parameters with concentration are ignored for the present. The value, $\bar{n}$, for the mean refractive index of the mesophase in this orientation is given by

$$\bar{n} = (n_x + 2n_z)/3 \qquad (6)$$

If the mesophase is oriented along the plate in the y direction, a single refractive index is observed.

$$n_x = n_z = \phi_p n'_t + (1 - \phi_p)n_s \qquad (7)$$

The equilibrium state of the APC-DBP liquid crystal is a cholesteric mesophase.[13] Thin layers tend to form a planar texture, with the principal optical axis (the axis of the helicoidal structure) normal to the constraining surfaces and also normal to the long axis of the molecular chains. The refractive index normal to the refractometer plates for a planar cholesteric layer is thus

$$n_z = \phi_p n'_t + (1 - \phi_p)n_s \qquad (8)$$

The refractive index in the plane of the refractometer plate for the helicoidal cholesteric structure with no preferred surface orientation in the plane is

$$n_x = n_y = \phi_p(n'_a + n'_t)/2 + (1 - \phi_p)n_s \qquad (9)$$

In this case, the mean refractive index for the mesophase is given by

$$\bar{n} = (2n_x + n_z)/3 \qquad (10)$$

The refractive index results (Table I) are in accord with the assumption that the initial shear-oriented nematic-like orientation relaxes to the equilibrium planar cholesteric structure. At a given volume fraction of polymer, the measured n_z for sheared and equilibrium structures are the same, as required by Eqs. (5), (7), and (8). Cellulose and most cellulose derivatives display positive birefringence ($n_a \geq n_t$), so the observed n_x values are larger

than the n_z values [Eqs. (3) and (4)]. The decrease in n_x with time for the mesophase sheared in the x direction corresponds to a change from a nematic-like structure [Eq. (4)] to a cholesteric structure [Eq. (9)]. The measured birefringence $\Delta n_{xz} = n_x - n_z$ for a given value of ϕ for the equilibrium cholesteric structure [Eqs. (8) and (9)] should be half that for the mesophase oriented in the x direction [Eqs. (4) and (5)]. The results in Table I are scattered, but the mean value and standard deviation for the ratio of the two birefringence values, Δn_{xz} (equilibrated)$/\Delta n_{xz}$ (sheared), is 0.43 $\pm$ 0.13, which is within experimental error of the expected value. A further check is to calculate the mean refractive indices for the sheared samples assuming that they are nematic [Eq. (6)] and for the equilibrated samples assuming a planar cholesteric structure [Eq. (10)]. The mean refractive indices should of course be the same in both cases; the difference in mean refractive indices calculated from Eq. (6) and from Eq. (10) for the solutions listed in Table I is 0.0001 $\pm$ 0.0006.

The above explanation has been proposed for the decay in birefringence observed for (hydroxypropyl)cellulose–water mesophases[14] and is in accord with the observation that the skin of a thermotropic (hydroxypropyl)–cellulose extrudate has about twice the birefringence of the core.[15] Asada et al.[16] have followed the reforming of the cholesteric structure of aqueous (hydroxypropyl)cellulose mesophases by rheo-optical measurements of the reflection band. The results for their controlled shear conditions were explained by a reorientation and distribution of the cholesteric axes. Spreading the mesophase on the refractometer plates may cause a more severe disruption of the cholesteric structure.

MEASURED BIREFRINGENCE AND OPTICAL ROTATORY DISPERSION

According to de Vries,[17] the optical rotatory power of a planar cholesteric is given by

$$\theta = -\frac{\pi(\Delta n)^2 \lambda_0}{4\lambda^2 \bar{n}\left(1 - (\lambda/\lambda_o)^2\right)} \tag{11}$$

where θ is the optical rotation per unit length for light of wavelength λ, $\bar{n}$ is the mean refractive index, and $\Delta n = \phi_p(n'_a - n'_t)$ is the birefringence of the untwisted structure. The equation is valid for normal incidence and for wavelengths of light outside the region of total reflection at λ_o. Thus the wavelength dependence of the optical rotation may be used to estimate the local nematic layer birefringence Δn of the cholesteric structure, since λ_o and $\bar{n}$ are easily measured. The nematic-like arrangement in the cholesteric layer may be emulated by orienting the mesophase across the refractometer plates by shear in the x direction (Fig. 1). In this case, the birefringence measured by the refractometer should be equal to that calculated from optical rotation by the de Vries theory. Results for two solutions of (acetoxypropyl)cellulose in dibutyl phthalate are given in Table II. The agreement is well within the rather wide limits of experimental error.

The value for the local nematic "layer" birefringence measured by optical rotatory dispersion (ORD) on (acetoxypropyl)cellulose in acetone was signifi-

TABLE II

Comparison of Birefringence for (Acetoxypropyl)cellulose–Dibutyl Phthalate Solutions from Optical Rotatory Dispersion Measurements on Planar Cholesterics and Refractometry on Shear-Oriented Samples

APC volume fraction	Birefringence	
	ORD	Refractometry
0.818	0.0103 ± 0.001	0.0100 ± 0.001
0.843	0.0092 ± 0.001	0.0098 ± 0.001

cantly larger than the birefringence measured on the same solutions with an Abbé refractometer.[6] Subsequent comparisons for (hydroxypropyl)cellulose in water[5] and for cellulose tricarbanilate in methyl ethyl ketone[18] showed that the birefringence in the cholesteric planes measured by optical rotation was twice that measured with the Abbé refractometer. These latter observations are expected if the mesophase on the refractometer plates is in the cholesteric equilibrium arrangement, with birefringence given by Eqs. (8) and (9).

OBSERVATION OF LIQUID CRYSTALLINE PHASE SEPARATION BY REFRACTOMETRY

The critical concentrations required for liquid crystalline phase separation of polymeric mesophases have been observed by refractometry.[5,6,18-20] In these papers, the critical concentration for the formation of the liquid crystalline phase was detected by the observation of two refractive indices, but the width of the biphasic region and the magnitude of the birefringence in the anisotropic phase were in general difficult to quantify.

The refractive indices for solutions of unfractionated (acetoxypropyl)cellulose in dibutyl phthalate are shown in Figures 6 and 7. At 26°C (Fig. 6) measurements at polymer volume fractions above 0.8 were not possible because the material would not spread readily on the refractometer plates. At 50°C (Fig. 7), the diluent-free mesophase was fluid enough to allow measurements. The mesophase was oriented in the x direction across the refractometer plate. A single isotropic phase is evident at lower polymer concentrations (line segment AB on Figs. 6 and 7). At higher concentrations, two refractive indices are visible, one increasing and the other decreasing with increasing polymer concentration. Line BD and BF correspond to changes in refractive index along the shear direction and normal to the refractometer plates, respectively, with concentration for the biphasic solutions. In this region, increasing polymer concentration leads to an increase in the amount of anisotropic phase; the apparent refractive indices in this biphasic region depend on the relative amounts of the isotropic and anisotropic phases. It is sometimes difficult to detect the width of the two-phase region by polarizing microscopy, and the refractometer may provide an alternative tool for this purpose. Volume fractions corresponding to point B indicate the onset of the birefringent region (0.47 $\pm$ 0.01 at 26°C, 0.55 $\pm$ 0.01 at 50°C). Points D and F correspond to the apparent upper limit of the biphasic region (0.68 $\pm$ 0.03 at 26°C, 0.70 $\pm$ 0.01 at 50°C). The apparent insensitivity of points D and F to
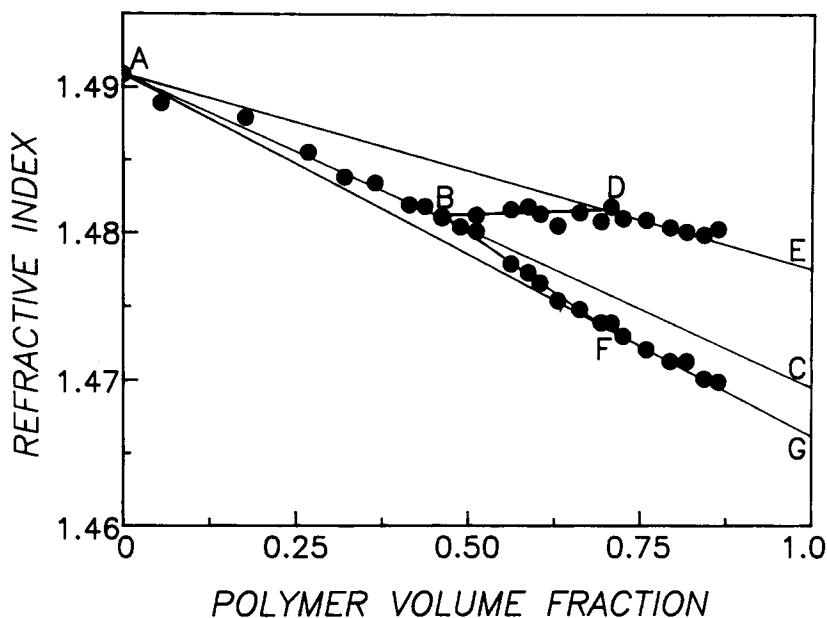
Fig. 6. The refractive index values for sheared (acetoxypropyl)cellulose-dibutyl phthalate solutions as a function of polymer volume fraction at 26°C. (See text for an explanation of letters.)
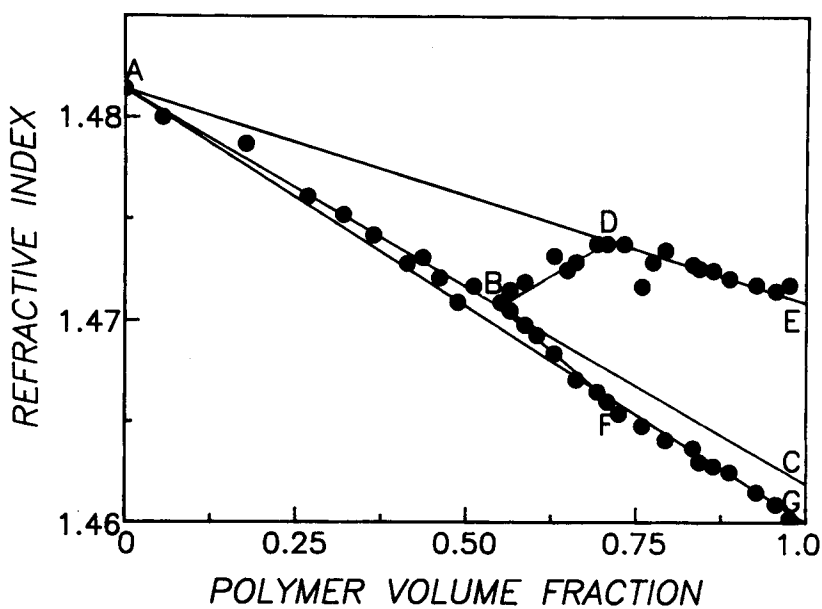

Fig. 7. The refractive index values for sheared (acetoxypropyl)cellulose-dibutyl phthalate solutions as a function of polymer volume fraction at 50°C. (See text for an explanation of letters.)

temperature is unexpected, and renders suspect the thermodynamic significance of the results for this system.

Line segments DE and FG correspond to the refractive indices of the mesophase along and across the direction of shear. The linearity of ADE and AFG is in accord with the simple model leading to Eqs. (4) and (5). The mean refractive index for the anisotropic phase, given by Eq. (6), should lie on the extension BC of the isotropic refractive index line, and the distance CE = $2(n'_a - n'_t)/3$ [Eqs. (4) and (6)] should be twice CG = $(n'_a - n'_t)/3$ [Eqs. (5) and (6)]. (For an equilibrium planar cholesteric the corresponding values for CE and CG should be $(n'_a - n'_t)/6$ and $(n'_a - n'_t)/3$, respectively). The refractive values of the APC/DBP solutions at 26°C (Fig. 6) are in reasonable agreement with this picture. Previous refractometric results for (acetoxypropyl)cellulose in acetone[6] and for (hydroxypropyl)cellulose in water and methanol[5] were measured on the equilibrium cholesteric mesophase, and the precision was lower. As in the APC/DBP system, the mean refractive index in the anisotropic phase for these latter cases was very close to the extrapolation of the line relating refractive index and volume fraction in the isotropic phase.

The APC/DBP results at 50°C show some deviation between the mean and the extrapolated isotropic refractive indices. Very marked differences in the refractive index increments in the isotropic phase and in the mesophase have been reported for cellulose tricarbanilate in methyl ethyl ketone[18] and for cellulose triacetate in trifluoroacetic acid.[20] In each case, the rate of change of the mean refractive index with polymer concentration decreases for concentrations above ϕ^i_c.

ESTIMATION OF ORDER PARAMETER

Birefringence measurements have been used to estimate the macroscopic order parameter of liquid crystals and oriented polymer fibers and films. The relationship between birefringence and orientation is not trivial.[21] Furthermore, as pointed out by Onogi, White, and Fellers,[14] the uncertainty of the side chain conformation for these cellulose derivatives prevents calculation of the birefringence for the perfectly ordered sample. The order parameter for the chain is given by

$$s = (n'_a - n'_t)/(n_a - n_t) \qquad (12)$$

(The chain birefringence $(n'_a - n'_t)$ is related to the measured birefringence Δn_{xz} of the APC-DBP mesophase by Eqs. (4) and (5), or (8) and (9), depending on the mesophase orientation.) Values for $(n_a - n_t)$ are not directly accessible for APC because a well-oriented crystalline phase has not been observed. However, if the flexible side chain and the solvent are isotropic, then the APC birefringence results only from the anisotropy of the cellulose backbone. In this case

$$(n_a - n_t) = \phi_{cell} \cdot \Delta n_{cell} = 0.016 \qquad (13)$$

where ϕ_{cell} is 0.29 the volume fraction of cellulose backbone in the APC chain, estimated from the densities and segment molar masses of cellulose and APC[13] and Δn_{cell} is 0.055, the value for a well-oriented regenerated cellulose.[22]

TABLE III

Birefringences and Order Parameters for a Series of (Acetoxypropyl)cellulose–Dibutyl Phthalate Solutions

ϕ_{cell}	Δn_{xz}		s^a	
	26°C	50°C	26°C	50°C
0.146	0	0	0	0
0.153	0.0011	0	(0.13)	0
0.168	—	0.0006	—	(0.07)
0.176	0.0040	0.0011	(0.63)	(0.12)
0.189	0.0051	0.0068	(0.51)	(0.48)
0.198	0.0070	0.0060	(0.66)	(0.57)
0.212	0.0079	0.0078	0.70	0.69
0.220	0.0065	0.0081	0.56	0.69
0.232	0.0089	0.0086	0.72	0.70
0.245	0.0100	0.0091	0.76	0.70
0.253	0.0098	0.0076	0.73	0.72
0.266	—	0.0096	—	0.68
0.278	—	0.0103	—	0.70
0.286	—	0.0106	—	0.70

[a]Values in parentheses are apparent order parameter for mixtures of isotropic and anisotropic phases.

Values for the order parameter estimated from birefringence data for the mesophase oriented across the refractometer plate are shown in Table III. No significant variation in s with polymer concentration is observed in the anisotropic region ($\phi_{cell} \geq 0.2$); the apparent decrease at lower concentration is due to the presence of the isotropic phase. Values for s of about 0.7 for semiflexible polymer chains are in accord with recent theoretical predictions.[23] It should be noted that, in common with many polymeric mesophases, cellulosic liquid crystals display a characteristic banded structure on relaxation of shear which is attributed to a zigzag of the macroscopic director about the shear direction.[24] If this phenomenon occurs on the refractometer plates, then the initial measured birefringence and the calculated order parameter may be less than the true values. Obviously, while refractometry readily gives average macroscopic birefringence values, polarizing microscopy is required to give complementary information on local orientation and disclination structure in the mesophase.

CONCLUSIONS

The refractive indices and birefringence of polymeric liquid crystalline phases may be measured readily with an Abbé refractometer. For a cholesteric system, it is possible to make measurements on either a nematic-like layer produced by shear, or on the equilibrium planar cholesteric structure. The measured birefringence in the latter case is half that for the same sample subjected to shear across the refractometer plate. The variations in refractive indices with sample orientation and with polymer concentration are rationalized by a simple model based on a birefringent cellulose core surrounded by an isotropic medium composed of side chains and solvent. The method is suitable

for polymeric mesophases of relatively low birefringence and high viscosity; changes in macroscopic orientation with time are readily followed, and the boundaries of the two-phase region may also be determined.

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