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Preliminary Communication. Refractive index of a sheared cholesteric polymer

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PRELIMINARY COMMUNICATION

Refractive index of a sheared cholesteric polymer

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After unwinding a cholesteric solution of a mesomorphic polymer by shear, we investigate the evolution of the refractive index. Two mechanisms with different time constants are observed, one corresponding to the cholesteric rewinding, the other to the reorientation of the cholesteric axes.

Strong interest in the optical properties of mesomorphic polymers such as cellulose derivatives has resulted in numerous experimental studies in recent years. These studies have elucidated several problems related to the cholesteric pitch. Future applications will require an understanding and subsequently control of both the equilibrium and dynamic molecular motions which result in the formation of the cholesteric structure. The pitch and the uniformity of the cholesteric organization are particularly sensitive to the molecular motions which may occur. Refractive index measurements are simple and permit a better understanding of deformation and reorganization of cholesteric polymers in solution after the application of a shear. A study made by Laivins and Gray [1] has shown that the shear obtained by translation of one of two surfaces enclosing a cholesteric sample leads to the destruction of the cholesteric and the subsequent formation of a nematic-like texture. On relaxation of the shear the cholesteric structure is restabilized in a planar cholesteric structure.

Here we discuss not only the values of the refractive index immediately following the shear and at equilibrium, but also the time dependence of the refractive index. The essential question is to understand how the planar cholesteric reorganizes after the formation of the nematic structure on shearing. The chronology of the two possibilities, rewinding and reorientation of tilted cholesteric domains, is not well known.

One of the simplest apparatus for measurements of an anisotropic refractive index is the Abbé refractometer [2-4]. The sample is placed between two parallel surfaces separated by 10-1000 μm. The refractive index is obtained by measurement of the critical angle through which a light beam parallel to the sample surfaces is refracted. Both surfaces containing the sample are shown in the upper diagram of figure 1 (*a*). The x axis corresponds to the direction of the incident light. For a non-spherical molecular geometry, as in mesomorphic phases, the observed polarizabilities may be very different parallel or perpendicular to the main direction of these molecules. For a nematic phase, different theories relate the observed birefringence (the difference between the parallel $n_\parallel$ and perpendicular $n_\perp$ components of the refractive index defined with respect to the nematic axis) to the anisotropy of the molecular polarizabilities

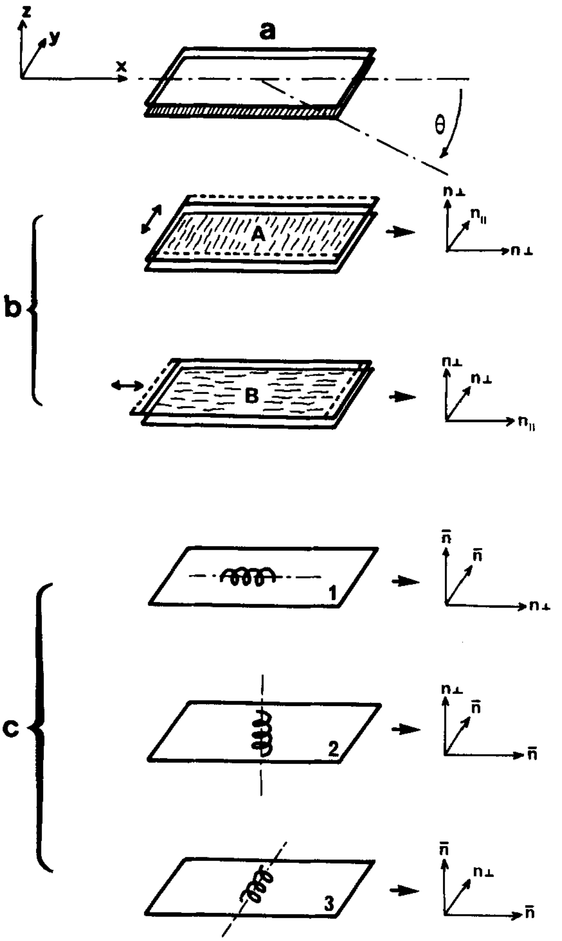

Figure 1. (*a*) Refractive index measurements: incident light in the x direction is refracted by an angle θ directly related to the refractive index of the sample. For a uniaxial birefringent medium with an optic axis not parallel to x, two angles associated with z or y polarizations are found. (*b*) Orientation of molecules along y or x is obtained (case A or B) by shearing, i.e. moving the upper slide of the sample along the y or x direction. (*c*) The cholesteric optical axis can be oriented along three main directions; c1 : x, c2 : z, c3 : y.

[5, 6]. Rigorously it is necessary to introduce the effect of the internal field resulting from interactions between neighbouring molecules [6] and that of an isotropic solvent [1] on the polarizabilities. The imperfection of phase alignment resulting from thermal fluctuations requires the use of the order parameter S [7, 8].

For a cholesteric phase two different geometries can occur [9]: for light polarized parallel to the optical cholesteric axis, the molecules are perpendicular and the measured index, n_e, will be the same as $n_\perp$ of the equivalent nematic. For light polarized perpendicular to the optic axis, the average of $n_\parallel$ and $n_\perp$ of the equivalent nematic is given (cf. figure 1 (*c*)) [9, 10] by

$$n_{0\mathrm{Ch}} = \bar{n} = \sqrt{[\tfrac{1}{2}(n_\parallel^2 + n_\perp^2)]} \simeq \frac{n_\parallel + n_\perp}{2}.$$

This approximation is sufficient for the low values of anisotropy obtained here. The anisotropy of the refractive index is defined as positive for a nematic with largest index along the optical axis ($n_{\parallel} > n_{\perp}$). The corresponding cholesteric, will have negative anisotropy because the optical axis is defined by the axis of the helicoidal superstructure and is consequently perpendicular to the nematic axis of the layers. This describes the majority of cases. However lateral groups of some mesomorphic polymers have a large polarizability and it is possible to observe the reverse case [11]: $n_{\parallel} < n_{\perp}$ and consequently $\Delta n_{\mathrm{Ch}} > 0$ and $\Delta n_{\mathrm{N}} < 0$. The refractometer, by a simple measurement of the indices n_z and n_y (cf. figure 1) just after shear assuming a nematic-like organization, allows the determination of the sign of Δn.

For cholesterics of low molar mass with the optical axis perpendicular to the walls, rheo-optical experiments [12] have shown that even for large shear the helical structure was not destroyed but was mainly tilted from the initial planar texture. In contrast studies on solutions of cholesteric cellulose derivatives, such as HPC or APC, showed that shear caused by sliding one of the two plates containing the sample easily leads to the formation of a nematic-like organization with the director parallel to the direction of shear [1] (cf. figure 1 (*b*)). Immediately after shearing in the *y* and *x* directions (cases A and B in figure 1 (*b*)) different refractive indices can be measured with the refractometer. Insertion of a polarizer in the refracted beam enables the separation and identification of the two principal refractive indices. For case A the maximum birefringence possible is observed between the *z* and *y* direction. For component case B only one is seen because $n_z = n_y = n_{\perp}$. After a long relaxation time, which depends on the viscosity of the mesomorphic solution, a stabilization occurs. The measured values of the refractive index correspond to case 2 of figure 1 (*c*). Texture studies with a polarizing microscope have confirmed that the planar structure is reformed.

For the polymers studied, anchorage energies eventually stabilize the organization in a planar cholesteric texture (cf. figure 1 (*c*), 2) however the equilibrium structure does not exclude the possibility of a preliminary molecular reorientation. A rewinding of the helicoidal superstructure with the optic axis parallel to *y* or *x* (cf. figure 1 (*c*), 1 and 3) and subsequent orientation may occur. The ability to separate and analyse the contributions of the two relaxation mechanisms (rewinding and reorientation) which reform the equilibrium planar texture is of great interest. Figures 2 (*a*–*c*) give a diagrammatic resumé of the observed variation of the refractive indices as a function of time (for the two shear directions A or B) and the analyser position by which n_z or n_y is selected. The variation of n_z does not depend on the shearing direction (A or B) as indicated in figure 2 (*a*).

The refractive index, n_z, shows an increasing haze with equilibration time following shear along the *y* axis. This haze is attributed to the presence of many optic axes as the cholesteric superstructure is rewound probably, as shown in cases 1 and 2 of figure 1 (*c*), from the nematic-like orientation during the equilibration period. Case 3 is less probable due to steric factors than the alignment of case 1. The two probable cases 1 and 2 lead to the same variation of the refractive index n_y shown in figure 2 (*c*) and so a hazy region is not observed.

The refractive index n_z shows the same evolution as during the equilibration from type A shear as indicated in figure 2 (*a*). The probable optic axes of the cholesteric superstructure are shown in cases 2 and 3 of figure 1 (*c*) (case 1 is less probable here due to steric factors than the alignment in case 3). The equilibrium refractive index value for n_y will be different when the optic axis of the cholesteric superstructure is as

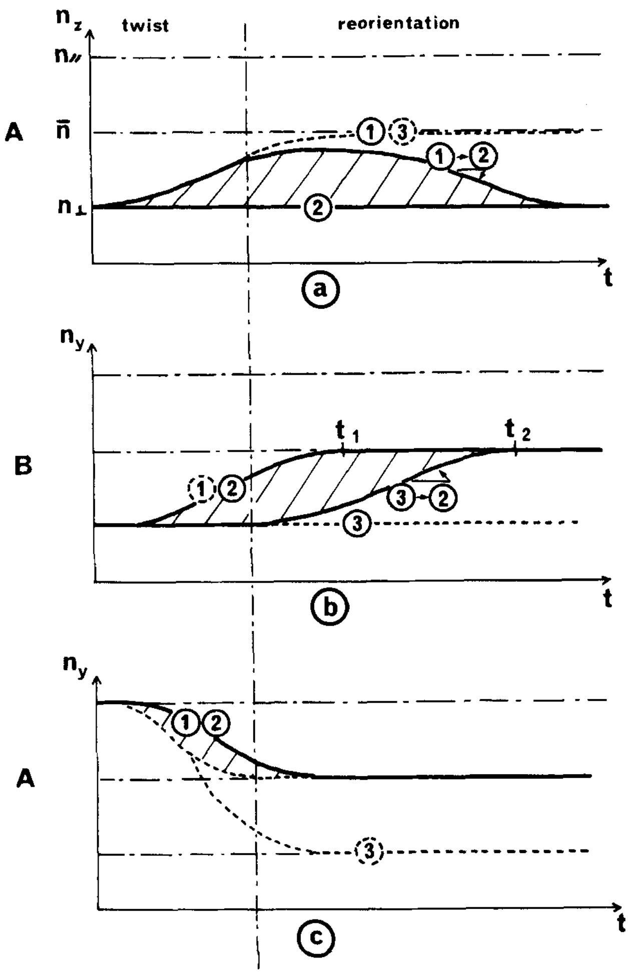

Figure 2. Prediction of the variation of the refractive indices on relaxation of the shear at $t = 0$.The different orientations of the optic axis (cf. 1, 2, 3, figure 1 (*c*)) lead to different variations of the refractive index. Surface interactions lead to a preference for the planar configuration 2. Part of the sample rewinds directly following case 2, the rest following 1 and 3, with a rapid time constant t_1 (*b*). The directions 1 and 3 reorient consequently with a time constant t_2 (*b*) (cf. text).

in case 2 or as in case 3 (cf. figure 1 (*c*)). The variation of n_y with equilibration time for each of the three cases is shown in figure 2 (*b*). Since both of the alignments for the optic axis are probable, a haze is observed in the eyepiece of the refractometer. A relatively short time constant, t_1, associated with the elastic twist energy can be assigned, as indicated in figure 2 (*b*). After a longer equilibration time the haze disappears. This disappearance occurs as the optic axes of the structure reorient into a planar texture. Long range interactions with the refractometer walls provide the driving force which causes the reorientation of the helicoidal axes into the equilibrium planar cholesteric texture. As these interactions are relatively weak and steric obstacles must be overcome the characteristic time for this reorganization is expected to be slower than for the twist reorientation.

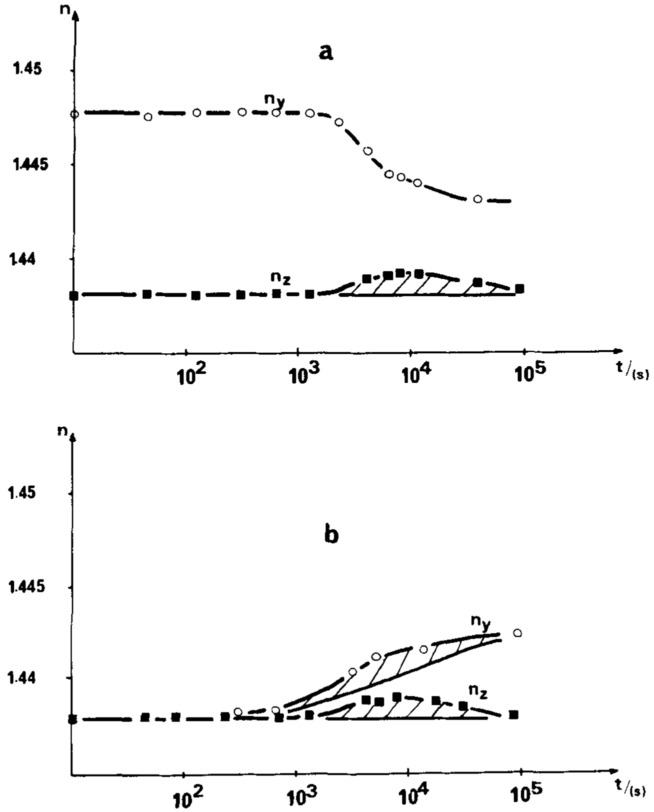

Figure 3. Experimental results obtained with 60 per cent g/g HPC (M.W. $= 10^5$) in acetic acid. (*a*) Variation of n_y and n_z with time after a shear of type A: for n_z a haze is observed in the hatched zone corresponding to (*a*), in figure 2. No haze is observed for n_y. (*b*) Variation of n_y and n_z with time after shear of type B: for n_z we observe the same variation as for case (*a*), in figure 2, for n_y, we found case (*b*), figure 2, when a haze is observed only the higher value of the refractive index is measurable with the Abbé refractometer: the lower continuous line limiting the hatched regions is indicative only.

We have obtained preliminary results using an Abbé refractometer for solutions of HPC (Aldrich) in dimethylacetamide with different concentrations, and in acetic acid. The time variation of the refractive indices obtained for a 60 per cent (g/g) solution of HPC (M.W. $= 10^5$) in acetic acid following shear along the y axis and the x axis is given in figure 3 (*a*) and (*b*), respectively. It was not possible to obtain an exact value for the minimal refractive indices during the equilibration period while the rewinding of the cholesteric superstructure occurred. A dense, broad haze which is attributed to the many orientations of the cholesteric axis was observed; the breadth of the haze is indicated by the hatched regions in figure 3.

The refractive index values are given in the table for solutions with concentrations of 60 per cent HPC in acetic acid and 75 per cent HPC in dimethyl acetamide. When the haze was visible through the eyepiece of the refractometer, the indices given correspond to the value for the upper limit of the region of haze. An increase in the equilibration time for the reformation of the planar cholesteric texture with an increase in the viscosity of the solution is indicated by the data in the table. It is noteworthy that for the 40 per cent HPC solution a divergence of the n_z index was not

The refractive indices n_y and n_z obtained on shear relaxation are given as a function of time for shear of type A and B (cf. figure 1), for different solvent concentrations and two molecular weights of HPC.

Composition of solution studied	Shear direction	Index	Equilibration time/s			
			Immediately after shear	10^2	10^4	10^5
HPC 40 per cent g/g M.W. = 10^5 in acetic acid at 27°C	A	n_y	1·4228	1·4228	1·4195	1·4195
		n_z	1·4169	1·4169	1·4169	1·4169
	B	n_y	1·4169	1·4170	1·4190	
		n_z	1·4169	1·4169	1·4169	
HPC 60 per cent g/g M.W. = 10^5 in acetic acid at 27°C	A	n_y	1·4476	1·4477	1·4440	1·4430
		n_z	1·4380	1·4383	1·4395	1·4385
	B	n_y	1·4380	1·4383	1·4420	1·4430
		n_z	1·4380	1·4384	1·4396	1·4390
HPC 75 per cent g/g M.W. = 60000 in DMAC at 22°C	A	n_y	1·4785	1·4775	1·4750	1·4745
		n_z	1·4710	1·4720	1·4725	1·4720
	B	n_y	1·4712	1·4722	1·4730	1·4735
		n_z	1·4710	1·4722	1·4722	

observed (i.e. a haze was not visible). This can be attributed to a tendency to reorganize directly as shown in figure 1 (*c*), case 2. The thickness of the sample may play an important role in the reorganization mechanism and will be studied in future work.

A great deal of information could be deduced from the variation of the refractive indices following the shear of cholesteric polymeric solutions. The relative importance and characteristic times for both the rewinding and the helicoidal structure reorientation can be obtained. The effect of parameters such as molar mass, cholesteric pitch, and sample thickness which may all alter the relative importance of surface and volume effects, remain to be studied. Viscosity modifications greatly change the characteristic times for the equilibration processes. The different types of anchorage possible with cholesteric polymers and the efficiency of the anchorage may also be studied by refractometry as outlined here.

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