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Chiral nematic ordering of polysaccharides

D.G. Gray

Paprican and Department of Chemistry, Pulp and Paper Research Centre, McGill University, 3420 University St., Montreal, Québec, Canada H3A 2A7

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In this paper, evidence for the chiral nematic (cholesteric) self-ordering of cellulose-derived materials is reviewed. A wide range of cellulose derivatives, and some other polysaccharides, form chiral nematic phases, both in concentrated solution and in the melt. Solid films and gels retaining the chiral nematic ordering of the polymer chains may be prepared from these liquid crystalline phases. Optical and electron microscopic techniques may be used to elucidate the helicoidal structure of chiral nematic cellulosics in the liquid crystalline phase, and of the films, gels and solids prepared from such phases. Remarkably, dilute aqueous suspensions of cellulose crystallites prepared by acid degradation also show chiral nematic order; the order is preserved in dry films prepared from the suspensions. The structure of some of these samples prepared *in vitro* shows a marked resemblance to structures observed *in vivo*.

CHIRAL NEMATIC STRUCTURE

Chiral objects lack reflection symmetry; like right and left hands or enantiomeric carbon atoms chiral objects are mirror images of each other. Chiral structures abound in nature. Here, a particular helicoidal orientational order displayed by chiral nematic liquid crystalline phases is considered, and its relationship to natural structures composed of polysaccharides is indicated.

Chiral nematic order may be represented by the right- and left-handed helicoidal arrangements of small rod-like species shown in Fig. 1. Two points should be emphasized regarding chiral nematic liquid crystals: the liquid crystalline phase is *fluid* and the layers in the sketch are not real but are simply an aid in visualizing the structure. The orientation varies smoothly along the axis of the chiral nematic structure, and the orientational order is imperfect, with the rods showing a local distribution of orientation.

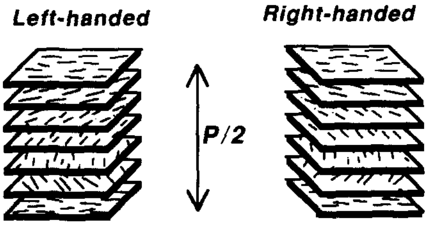

Fig. 1. Right- and left-handed chiral nematic structures consisting of short rods. *P* is the helicoidal pitch.

Derivatives of cellulose form chiral nematic phases, both in solution (lyotropic liquid crystals) (Werbowyj & Gray, 1976) and in the absence of solvent (thermotropic liquid crystals) (Tseng *et al.*, 1981). The helicoidal structure of these phases is inferred from optical and electron microscopic techniques. Other polysaccharides that have been reported to form liquid crystalline phases include derivatives of amylose (Zugenmaier & Voihsel, 1984), schizophyllan (Van & Teramoto, 1982), scleroglucan (Yanaki *et al.*, 1984) and xanthan (Maret *et al.*, 1981). Evidence for the preservation of the helicoidal organization of the liquid crystalline phase of cellulose and its derivatives in films (Bhadani & Gray, 1984) and crosslinked gels (Giasson *et al.*, 1991) has been presented. The analogy between the molecular orientation in the liquid crystalline state and the orientation of microfibrils in many biological membrane structures has been pointed out by Bouligand (1972). All of these systems show chiral nematic structure; in the case of lyotropic and thermotropic liquid crystalline phases, and of polymer glasses (films and gels derived from these phases), the oriented elements of the chiral nematic structure are the molecular chain segments. In the case of biological membranes, the chiral nematic structure is composed of oriented crystalline microfibrils embedded in a matrix. Examples include chitin fibrils in insect and crustacean cuticle (Bouligand, 1972), collagen in skeletal tissue (Bouligand & Giraud-Guille, 1985) and cellulose microfibrils in certain plant cell walls (Neville *et al.*, 1976; Roland *et al.*, 1989). An intermediate and fluid liquid crystalline phase may be involved in the formation of these chiral nematic structures. In the following section the formation of polymeric liquid crystalline phases is reviewed, with emphasis on cellulose derivatives and polysaccharides.

LIQUID CRYSTALLINE PHASE FORMATION

Polymer molecules with stiff or semi-rigid backbones are capable of forming lyotropic and thermotropic liquid crystalline phases. The polymer may adopt a helical secondary structure that results in the molecule having a rod-like shape. This is the case for certain polypeptides which possess an α-helical conformation that arises as the result of intramolecular hydrogen bonding and steric effects. Liquid crystalline rigid-rod polymers may also be composed of conformationally rigid monomer units which restrict the flexibility of the chain. These rigid monomers may be para-substituted aromatic groups as in polyamides or polyesters, or the β-linked glucopyranosic units found in cellulose and its derivatives.

Several theories of ordered phase formation relevant to this last group of polymers have been presented. Onsager (1949), using a virial approach, showed that a solution of hard, asymmetric, rod-like molecules should phase separate into two phases at a critical concentration that depends on the axial ratio of the molecule. Flory (1956) proposed a lattice theory to account for the phase separation of rigid rod-like macromolecules in solution. Ignoring intermolecular interactions other than hard-core repulsion, the critical concentration at which phase separation occurs can be expressed as:

$$V_{\mathrm{p}}^{*} \approx \frac{8}{x}\left(1 - \frac{2}{x}\right) \qquad (1)$$

where V_{p}^{*} is the critical volume fraction of the polymer and x is its axial ratio.

There are several problems associated with application of the Flory and Onsager theories to real liquid crystalline polymers. The problem that has received the most attention recently concerns the actual rigidity of the polymers. The original theoretical treatments assumed that the chains were completely rigid and rod-like, but even the most rigid polymers have some degree of flexibility at large molecular weights. To account for the semi-flexible nature of liquid crystalline polymers, the Onsager approach has been extended from rods to worm-like chains (Khokhlov & Semenov, 1981; Khokhlov & Semenov, 1982). It has been shown by Odijk (1986) that the theory of Khokhlov and Semenov can accurately predict the phase behaviour for such polymers as schizophyllan, poly(γ-benzyl L-glutamate) and DNA, although in these cases the polymers are relatively stiff with large persistence lengths. Sato and Teramoto (1990) extended Cotter's scaled particle theory and found good agreement with phase boundaries and osmotic pressures of schizophyllan and poly(hexyl isocyanate) in dichloromethane and toluene. The lattice theory of Flory (1978) has also been modified to account for chain flexibility in liquid crystalline polymers. Flory suggested that the critical concentration for mesophase formation depended on the axial ratio of the Kuhn segment, k, and not on the contour length of the chain. Therefore, semi-flexible polymers that behave as Kuhn chains can be treated in the same way as stiff polymers if the Kuhn segment length, rather than the contour length, of the polymer is used to evaluate the axial ratio.

LIQUID CRYSTALLINE CELLULOSE DERIVATIVES

In light of the apparent stiffness and extended conformation of cellulose-based polymers, it is, in retrospect, not surprising that many form liquid crystalline phases. The first published report of the formation of a liquid crystalline phase by a cellulose derivative (Werbowyj & Gray, 1976) showed that concentrated aqueous solutions of hydroxypropyl cellulose (HPC) form lyotropic mesophases that display iridescent colours over a specific concentration range. Since this initial report in 1976, many cellulose derivatives have been found to form lyotropic and thermotropic liquid crystalline phases.

The semi-flexible nature of cellulose derivatives results in these polymers having a critical concentration for mesophase formation, which is greater than that of rigid rods of the same molecular weight. The critical concentration varies with the nature of the solvent, indicating that the solvent plays a role in determining the stiffness of the cellulose backbone, but the critical concentration has been found to be unaffected by the degree of polymerization of HPC, as would be expected for a semi-flexible chain (Werbowyj & Gray, 1980; Gray, 1983). Similar results were obtained for HPC in dimethylacetamide (Conio *et al.*, 1983) and (acetoxypropyl)cellulose in dibutyl phthalate (Laivins & Gray, 1985*a*). However, these results were for polydisperse samples with chain lengths much greater than their persistence lengths. The critical concentration for cellulose acetate in trifluoroacetic acid (Navard *et al.*, 1981; Patel & Gilbert, 1983), and cellulose in *N*-methylmorpholine *N*-oxide (Chanzy & Peguy, 1980) was found to depend on the degree of polymerization. Evidently, these two polymers assume a more rigid conformation in the given solvents than HPC and its derivatives. Recent calorimetric and turbidimetric measurements on carefully fractionated and characterised HPC solutions in water (Fortin & Charlet, 1989; Robitaille *et al.*, 1991) also showed a marked dependence of critical concentration on molar mass. This work demonstrated that the 'gel phase' that separates when a *dilute* aqueous solution of HPC is heated is in fact a stable emulsion of the concentrated anisotropic phase dispersed in dilute isotropic solution.

The rigidity of cellulose derivatives in solution may be modelled by the Kratky–Porod worm-like chain, in which the chain stiffness is measured in terms of the persistence length, q, where $q = k/2$ in the limit of infinitely long chains. It has been shown that the persistence lengths for cellulose derivatives are generally 10 nm or shorter (Conio *et al.*, 1983; Krigbaum *et al.*, 1985; Laivins & Gray, 1985*a*; Bianchi *et al.*, 1986) although there are some exceptions (Mays, 1988). The predicted results of the Khokhlov–Semenov theory for some cellulose derivatives deviate significantly from the experimental data (Laivins & Gray, 1985*a*), but the theory may be more accurate for derivatives with larger persistence lengths. The Flory lattice theory has been applied quite extensively to the phase behaviour of cellulose derivatives. It has been found that the critical concentration for mesophase formation is in reasonable agreement with eqn (1) when x is taken as the Kuhn segment axial ratio of the polymer (Gray, 1983; Krigbaum *et al.*, 1985; Laivins & Gray, 1985*a*; Bianchi *et al.*, 1986; Mays, 1988), although attractive interactions may also be involved (Krigbaum *et al.*, 1985; Bianchi *et al.*, 1986).

Many cellulosics also form thermotropic liquid crystalline phases in the absence of solvent. (Acetoxypropyl)cellulose, prepared by acetylating HPC, was the first reported thermotropic (Tseng *et al.*, 1981), and a large number of other heavily substituted esters and ethers of (hydroxyalkyl)celluloses were subsequently found to form equilibrium chiral nematic phases, even at ambient temperatures (Tseng *et al.*, 1982; Bhadani & Gray, 1983; Laivins & Gray, 1985*b*; Ritcey & Gray, 1988*a*). Quantitative measurements on these systems are difficult. Chain length polydispersity, virtually unavoidable with cellulosics, must also affect the phase behaviour, especially for chains whose lengths are of the order of the persistence length or less. An unexpected biphasic region observed for a thermotropic cellulose derivative (Laivins *et al.*, 1986) was ascribed to chain length polydispersity. However, the observations might more plausibly result from the polydispersity in chain flexibility that has been demonstrated by Stupp and coworkers (Stupp *et al.*, 1988) to explain subsequent observations on other thermotropic polymer systems. Certainly, most cellulosic polymers are chemically disordered, in that there is a distribution of substituted units of different chemical compositions along the chain. The problem can be avoided experimentally by preparing either completely tri-substituted derivatives, or uniform, specifically substituted cellulose derivatives, as described above. Examination of tri-substituted ethers and esters led to the discovery that oligomers of cellulose trialkanoates form columnar thermotropic liquid crystalline phases, with properties quite different from those of the usual chiral nematic phases (Yamagishi *et al.*, 1991).

CHIRAL NEMATIC PROPERTIES OF CELLULOSE DERIVATIVES

The liquid crystalline phases of most cellulose derivatives form chiral nematic structures as a result of the chirality of the cellulose backbone. They exhibit optical properties analogous to those observed from chiral nematic mesophases of polypeptides and chiral small molecule mesogens. These optical properties have been found to be sensitive to several factors, such as the nature of the side-groups, the degree of substitution, the molecular weight of the polymer, temperature, the nature of the solvent and the polymer concentration. The optical properties of HPC mesophases were among the first to be investigated. Based on the form of the wavelength dependence of the optical rotation close to the chiral nematic reflection bands, Werbowyj and Gray (1976) observed that lyotropic mesophases of HPC in water, acetic acid and methanol have a right-handed chiral nematic twist sense (Werbowyj & Gray, 1984). HPC and its ether and ester derivatives generally form chiral nematic mesophases that have a right-handed chiral nematic twist sense, with a pitch that increases with increasing temperature and decreasing polymer concentration. This simple state of affairs might have been expected for a family of polymers that share the same chiral cellulose backbone. (The side-chain substituents are normally achiral.) However, a left-handed chiral nematic mesophase of a cellulose derivative was observed by Vogt and Zugenmaier (1985) for a solution of ethyl cellulose in glacial acetic acid. This was the first indication that the nature of the side-groups attached to the cellulose backbone can influence the chiral nematic twist sense. There have been several subsequent reports of a change in the chiral nematic twist sense that occurs with a change in the side-group substituents. Cellulose acetate in trifluoroacetic acid forms a left-handed chiral nematic mesophase which inverts to a right-handed structure when trifluoroacetate groups are added onto the polymer backbone (Ritcey & Gray, 1988*b*). The substitution of trifluoroactate groups also influenced the magnitude of the concentration dependence of the pitch. The twist sense of ethyl cellulose/chloroform mesophases is also dependent upon the nature of the side-group substitution. The acetylation of the free hydroxyl groups on ethyl cellulose can change the chiral nematic twist sense from being right-handed to left-handed, in chloroform, when a critical degree of acetylation has been reached (Guo & Gray, 1989); the pitch of the left-handed mesophases decreased with an increase in temperature whereas the right-handed mesophases showed an increase in the pitch with increasing temperature. Other modifications that have been observed to change the twist sense are the acetoacetylation of hydroxypropyl cellulose (Pawlowski *et al.*, 1987) and the substitution of a chlorine atom at the para-position of the cellulose tricarbanilate phenyl groups (Siekmeyer & Zugenmaier, 1987; Steinmeier & Zugenmaier, 1988). Further examples for (trityl)cellulose derivatives are given below. Evidently, the sign and magnitude of the pitch are quite sensitive to chain structure.

There are cases where the chiral nematic twist sense is determined by the solvent. The mesophase of ethyl cellulose in acetic acid and dichloroacetic acid changes from a left-handed to right-handed structure with a increase in the concentration of dichloroacetic acid (Zugenmaier & Haurand, 1987). In this case, it is possible that the solvent may be reacting with the polymer and therefore the change in the twist sense may be the result of a modification of ethyl cellulose. In another example, cellulose tricarbanilate was found to form a right-handed chiral nematic structure in methylpropyl ketone and a left-handed structure in diethyleneglycol monoethyl ether (Siekmeyer & Zugenmaier, 1987).

As mentioned previously, the pitch of chiral nematic mesophases of cellulose derivatives is sensitive to temperature. The usual behaviour is an increase in the pitch with an increase in temperature, although there are several examples of a decrease in the pitch with an increase in temperature. An example of a thermally induced inversion of the twist sense analogous to that observed for thermotropic polypeptides has been reported for oligomers of tri-*O*-2-(2-methoxyethoxy)ethyl cellulose (TMEC) and tri-*O*-heptyl cellulose (Yamagishi *et al.*, 1990). The pitch of TMEC increased with temperature from 80 to 106°C and then decreased with the opposite twist sense as the temperature was increased above 106°C.

The concentration of the polymer also influences the magnitude of the pitch. The usual behaviour for lyotropic mesophases of cellulose derivatives is a decrease in the pitch with an increase in the polymer concentration. However, an increase in the polymer concentration can also give an increase in the pitch (Vogt & Zugenmaier, 1985; Steinmeier & Zugenmaier, 1988). The pitch also varies as a function of the molar mass of the polymer. For thermotropic (acetoxypropyl)cellulose fractions, the short chain fraction showed the longest pitch (Ritcey & Gray, 1988*a*,*b*), and a similar trend was observed for HPC in water (Fortin & Charlet, 1989). However, Siekmeyer and Zugenmaier (1987) have reported that the pitch of a cellulose tricarbanilate/diethylene glycol monoethyl ether mesophase increases with an increase in the molar mass of the polymer.

SPECIFICALLY SUBSTITUTED CELLULOSE DERIVATIVES

The pitch and chiral nematic twist sense of mesophases of cellulose derivatives are strongly influenced by the nature of the side-group substitution and the solvent. It is not known how or why different achiral substituents on the cellulose chain or changes in the solvent can influence the chirality of these tertiary helicoidal structures. In the many studies of the liquid crystalline properties of the cellulose derivatives discussed previously, there has been little work on derivatives that have a specific substitution pattern along the cellulose backbone. It is known that the degree of side-group substitution can change the twist sense of chiral nematic mesophases of cellulose derivatives, but it is not known if the distribution of these substituents has a similar effect. Some effort has been applied to the efficient preparation of cellulose ethers; tri-*O*-alkyl cellulose (Kondo & Gray, 1992), 6-*O*-alkylcellulose (Kondo, 1993) and methyl- and ethylcelluloses with defined substitution patterns (Kondo & Gray, 1991) have been prepared. Similar methods can be used to prepare liquid crystalline derivatives containing chromophores at specific positions.

(Triphenylmethyl)cellulose or trityl cellulose is a good starting material for the preparation of specifically substituted cellulose derivatives. Trityl cellulose itself has not been found to produce a lyotropic mesophase; it is not readily soluble in common solvents, and tends to form gels when dissolved in high concentrations in polar solvents. In order to increase the solubility of tritylated cellulose in organic solvents, the free hydroxyl functionalities at positions 2 and 3 were substituted with benzyl or alkyl substituents to generate 6-*O*-trityl-2,3-*O*-benzyl cellulose or 6-*O*-trityl-2,3-*O*-alkyl cellulose derivatives.

The polymers were prepared by dissolving trityl cellulose in DMSO and adding sodium hydroxide and an alkyl iodide or benzyl chloride to the solution (Harkness & Gray, 1990*a*, *b*, *c*). The resultant polymers dissolved quite readily in organic solvents and formed lyotropic liquid crystalline phases above a critical polymer concentration. Decomposition occurred at the temperatures required to form a thermotropic mesophase (>230°C).

The optical properties of the mesophases of tritylalkyl cellulose derivatives are sensitive to the nature of the alkyl-group substitution. Several of the mesophases exhibited chiral nematic reflection bands in the visible region of the spectrum, and both left and right-handed chiral nematic structures were observed (Harkness & Gray, 1990*c*). For example, the polymer 6-*O*-trityl-2,3-*O*-pentyl cellulose was found to form a right-handed chiral nematic structure in tetrahydrofuran, whereas 6-*O*-trityl-2,3-*O*-hexyl cellulose formed a left-handed chiral nematic structure.

Replacement of the trityl group with a naphthyl chromophore allows examination of the circular dichroism in dilute solution. The trityl group was removed by treating trityl-pentyl cellulose in chloroform with gaseous hydrochloric acid (Harkness & Gray, 1991). NMR results confirmed that all of the trityl groups were removed by this process, and they also showed that most of the primary hydroxyl groups at position six were unsubstituted. The polymer 6-*O*-α-(1-methylnaphthalene)-2,3-*O*-pentyl cellulose was prepared by reacting 2-3-*O*-pentyl cellulose in dimethylacetamide with potassium t-butoxide and 1-(chloromethyl)naphthalene. This polymer formed a thermotropic right-handed chiral nematic mesophase that showed an anisotropic to isotropic phase transition in the temperature range of 90–110°C. This is in contrast to the trityl-alkyl cellulose derivatives that formed only lyotropic liquid crystalline phases. The dilute solution CD spectrum of 6-*O*-α-(1-methylnaphthalene)-2,3-*O*-pentyl cellulose suggests that the polymer may have a helical secondary structure in solution, although it is not known if or how such a secondary structure influences the chiral nematic twist sense of the mesophase.

CHIRAL NEMATIC FILMS AND GELS OF CELLULOSE DERIVATIVES

Chiral nematic liquid crystalline phases are fluid; the chiral nematic order is readily destroyed by shear, reforming when the flow ceases. The structure is of course also destroyed by dilution below the critical concentration or heating above the critical temperature for mesophase formation. The chiral nematic order of liquid crystalline phases can be trapped in cellulosic solids by a variety of techniques (Ritcey *et al.*, 1989), the simplest being casting films from a mesophase solution (Charlet and Gray, 1987). The chiral nematic order may be inferred from transmission electron microscope (TEM) images of a thin cross-section of solvent-cast films. The periodicity corresponding to half the chiral nematic pitch was clearly visible, along with some of the disclinations associated with discontinuities in the chiral nematic structure (Giasson *et al.*, 1988). The observed periodicity is apparently due to a periodic variation in thickness of the samples resulting from an artefact in microtomy (Bouligand, 1972).

The chiral nematic order may also be trapped in a solvent-swollen gel by crosslinking the orientationally ordered chains. Anisotropic gels have been prepared by crosslinking lyotropic (hydroxypropyl)cellulose liquid crystalline solutions (Suto & Tashiro, 1989; Song *et al.*, 1990), but unequivocal evidence of chiral nematic order has not been presented. Recently, the present author managed to preserve the chiral nematic order of (hydroxypropyl)cellulose solutions and films by irradiation crosslinking (Giasson *et al.*, 1991). The gels swell but do not dissolve in water. Thus the polysaccharide chains are oriented in a chiral nematic array, and the covalently bonded side-chains provide the crosslinks.

CHIRAL NEMATIC SUSPENSIONS OF CELLULOSE CRYSTALLITES

The chiral nematic arrangement of cellulose *molecular* chains in liquid crystalline solutions, melts, films and gels is thus well established. However, as mentioned above, the species displaying chiral nematic order in natural composites are polymeric microfibrils rather than individual polymer molecules. A naturally occurring fluid state incorporating chiral nematic ordering of a glucuronoxylan-stabilized suspension of cellulose microfibrils has been observed in quince seed mucilage (Willison & Abeyesekera, 1988; Reis *et al.*, 1991). This phenomenon has been reproduced *in vitro* (Revol *et al.*, 1992), starting from cellulose fibers from a variety of sources. For example, treatment of a low-yield bleached kraft wood pulp with 65% sulfuric acid at 70°C for 30 min, followed by washing to neutrality and ultrasonic dispersion, gave a stable colloidal suspension of cellulose microcrystallites with lengths ~ 100 nm and widths of ~ 5 nm. At concentrations of ~ 3%, the suspensions separated on standing into an upper isotropic phase and a lower anisotropic phase. The anisotropic phase showed the fingerprint lines characteristic of a chiral nematic phase (Fig. 2). Furthermore, the chiral nematic structure of the suspensions was preserved on careful drying, to give a film of 'paper' in which the cellulose crystallites are arranged in chiral nematic order. Transmission electron microscope images of oblique sections through this film show the arced pattern characteristic of a chiral nematic arrangement of microfibrils (Bouligand, 1972). The images of the film are virtually identical to electron microscopic images of sections of certain plant cell walls (Roland *et al.*, 1989) and other biological composites.

The formation of the ordered phase in these suspensions is attributed to the well-known entropically driven self-orientation of rod-like species above some critical concentration to give nematic order (Onsager, 1949; Flory, 1956). More surprising is the observation that the suspensions display chiral nematic order; the source of the chiral interactions between the crystallites is not obvious, as the distance separating the crystallites in the dilute suspensions must be much larger than that separating cellulose molecules in the liquid crystalline phases of cellulose derivatives. A similar behaviour has also been observed for suspensions of chitin microfibrils. The suspensions might be expected to have unusual rheological and optical properties, and provide precursors to solid films with novel oriented structures.

CONCLUSIONS

The chiral properties of cellulose are expressed at several levels. The asymmetry at the molecular level (the chiral centres in sugars and the chiral helical molecular conformation of the polysaccharide chains) must govern the chiral nematic structure observed in liquid crystalline solutions and melts. The constituents of these liquid crystalline phases, and the solids and gels derived from them, are molecularly dispersed. However, a variety of chiral structures is also observed where the elements are not individual polysaccharide

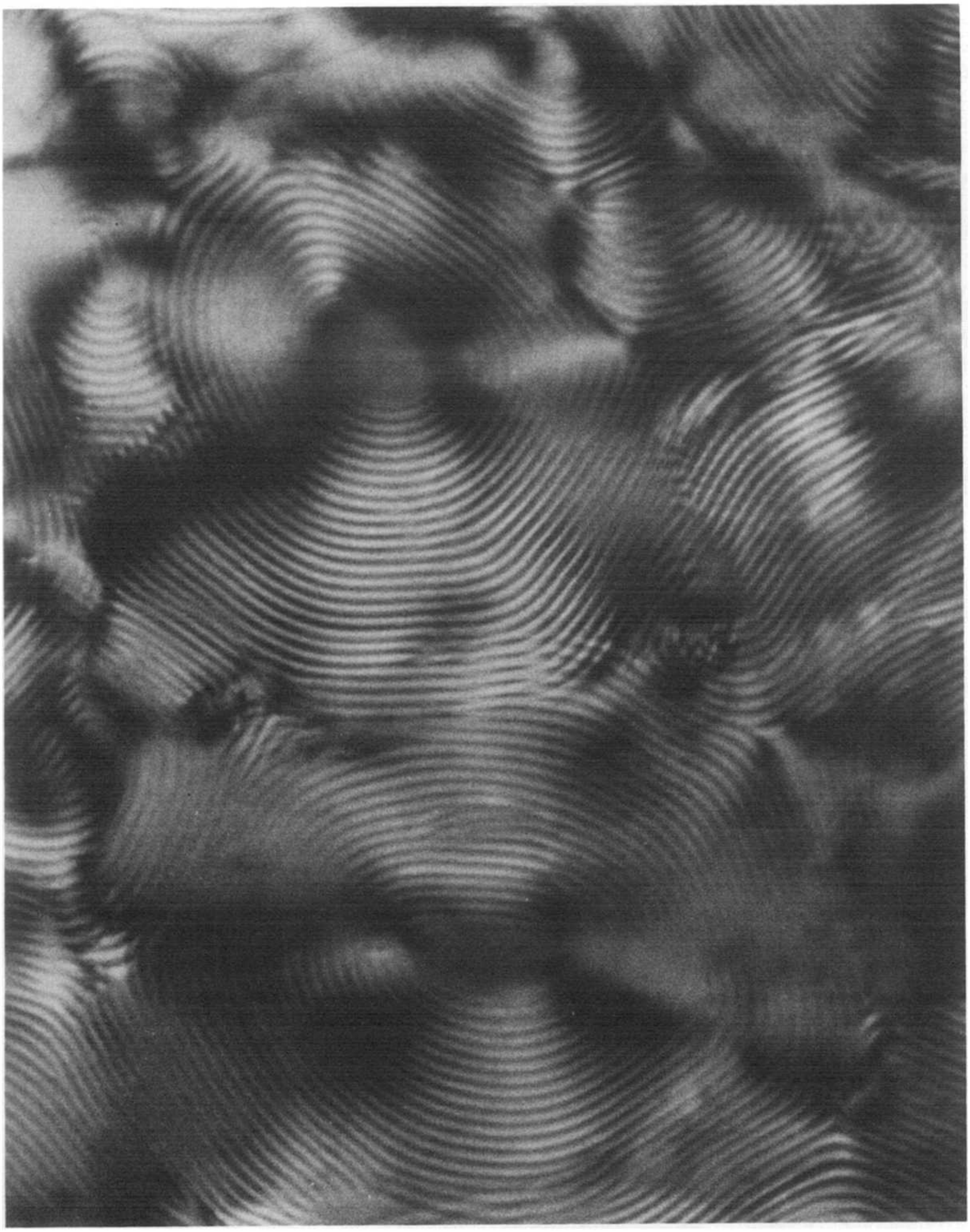

Fig. 2. Optical micrograph (crossed polars) of anisotropic phase prepared from a 3% aqueous suspension of cellulose crystallites by acid degradation and ultrasonication of a softwood kraft woodpulp. The periodic lines, characteristic of chiral nematic texture have a spacing of about 15 μm, corresponding to half the chiral nematic pitch.

molecules, as in the case of 'true' liquid crystalline phases; the individual oriented elements in this case are crystalline microfibrils or crystallites made up of many individual chain molecules. The chirality of these elements is expressed at a higher morphological level. For example, the organisation of cellulose microfibrils within some plant cell walls is chiral nematic, and a more characteristic and technologically important case is the right-handed helical arrangement of microfibrils in the secondary wall of most woody plants (Meylan and Butterfield, 1978). This structure can even lead to the observation of chiral macroscopic properties in paper sheets (Gray, 1989). The observation of chiral nematic order in dilute colloidal suspensions of crystallites made from cellulose and chitin provides a link between the molecular and the macroscopic observations, but the quantitative relationships between the chirality at different levels of structure are not fully understood.

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