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FORMATION OF LIQUID-CRYSTALLINE PHASES BY TWO PHENYLALKANOYL ESTERS OF *O*-(HYDROXYPROPYL)CELLULOSE AND THE (3-CHLOROPHENYL)URETHANE OF CELLULOSE

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ABSTRACT

Thermotropic and lyotropic liquid-crystalline phases were produced from three newly synthesized cellulose derivatives, namely the phenylacetate and 3-phenylpropionate of *O*-(hydroxypropyl)cellulose, and the (3-chlorophenyl)-urethane of cellulose. The liquid-crystalline phases were characterized with regard to the shape of the molecular chains, helicoidal cholesteric structure (pitch and order parameter), refractive indices, optical behaviour, and textures in the polarizing microscope. The cellulosic-chain direction in thermotropic liquid crystals having banded textures was shown to lie perpendicular to the bands, and a positive birefringence was demonstrated for a cholesteric liquid-crystalline phase.

INTRODUCTION

O-(Hydroxypropyl)cellulose (HPC) and many derivatives thereof exhibit lyotropic and thermotropic liquid-crystalline phases[1]. HPC has been used to produce a large variety of derivatives, and is preferred over cellulose for this purpose because of its better solubility. The products are obtained in high yields and high degrees of substitution. The aliphatic esters of HPC have been thoroughly investigated by Gray *et al.*[2], who detected thermotropic mesophases in unfractionated samples below the clearing temperature of *ca.* 160°, and observed lyotropic cholesteric phases in acetone. The cholesteric phases have been investigated mainly with regard to the pitch of their helicoidal structures.

EXPERIMENTAL

Phenylalkanoyl esters of *O*-(hydroxypropyl)cellulose were produced for a study of the liquid-crystalline, thermotropic behaviour of cellulose derivatives as follows: HPC (3 g) was dissolved in pyridine (25 mL) at room temperature, and acid chloride (5 mL) was added to a clear solution in portions of $^1/_3$ under constant stirring. After a reaction time of *ca.* 3 hours at room temperature, the viscous

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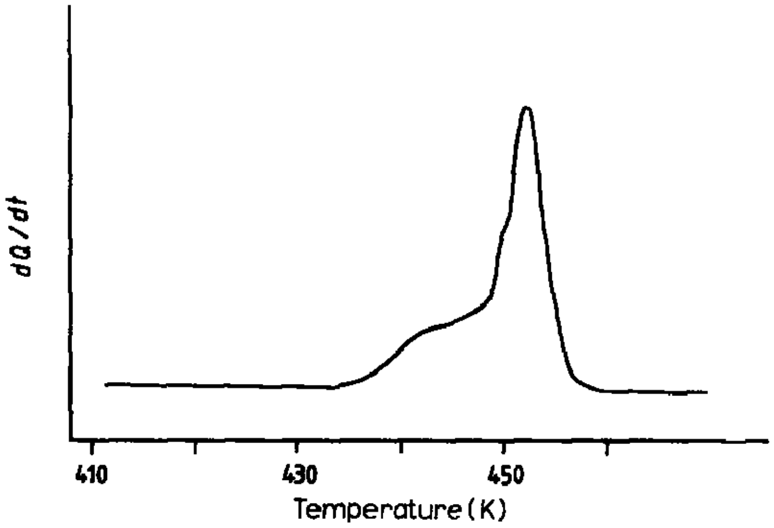

Fig. 1. Thermogram (DSC) obtained by heating 5 mg of PPC at 10 K/min.

reaction mixture was poured into water. The esters precipitated as a white, tough substance and were then further purified by dissolving and reprecipitating several times from acetone–water, a process which did not, however, change the aforementioned character of the substance. Phenylacetyl chloride and 3-phenylpropionyl chloride were used as the acylating agents.

The (3-chlorophenyl)urethane of cellulose was synthesized for the extension of our study to lyotropic, liquid-crystalline cellulose derivatives: cellulose (1 g) was suspended in pyridine (20 mL) and swollen for 30 min at 80° and then 3-chlorophenyl isocyanate (5 mL) was added dropwise under stirring. After 12 h the reaction mixture was poured into methanol (500 mL) and the precipitated product extracted by filtration. It was then twice redissolved and reprecipitated in dichloromethane–methanol. The white end product was dried *in vacuo*.

Degree of substitution (d.s.) was determined qualitatively by infrared analysis: the d.s. was found to be higher than 2.9 for all derivatives synthesized. It is known that the reaction of cellulose with phenyl isocyanate is nondegradative[3]. The starting material for the (3-chlorophenyl) urethane (Avicel) has $\overline{\mathrm{d.p.}}$ ~120 and should remain the same for 3-ClPC. The commercial HPC has $\overline{\mathrm{d.p.}}$ ~315.

RESULTS AND DISCUSSION

Thermotropic liquid-crystalline behavior. — The phenylacetate (PAC) and 3-phenylpropionate (PPC) of HPC were easily obtained as tough, highly viscous materials that can be drawn into fibres. Comparable anisotropic textures were observed in the polarizing microscope for both cellulose derivatives. The textures disappeared for PAC at *ca.* 440 K and for PPC at *ca.* 450 K on heating the samples at 10 K/min and reappeared at temperatures ~10 K lower when the samples were cooled. A transition into the isotropic phase was present for PPC in the thermogram of a differential scanning (DSC) experiment where the heating rate was 10 K/min (Fig. 1). The relatively sharp peak at 452 K is preceded by two shoulders, the origin of which is not known at present.

Fibres drawn from either PAC or PPC showed the so-called banded textures

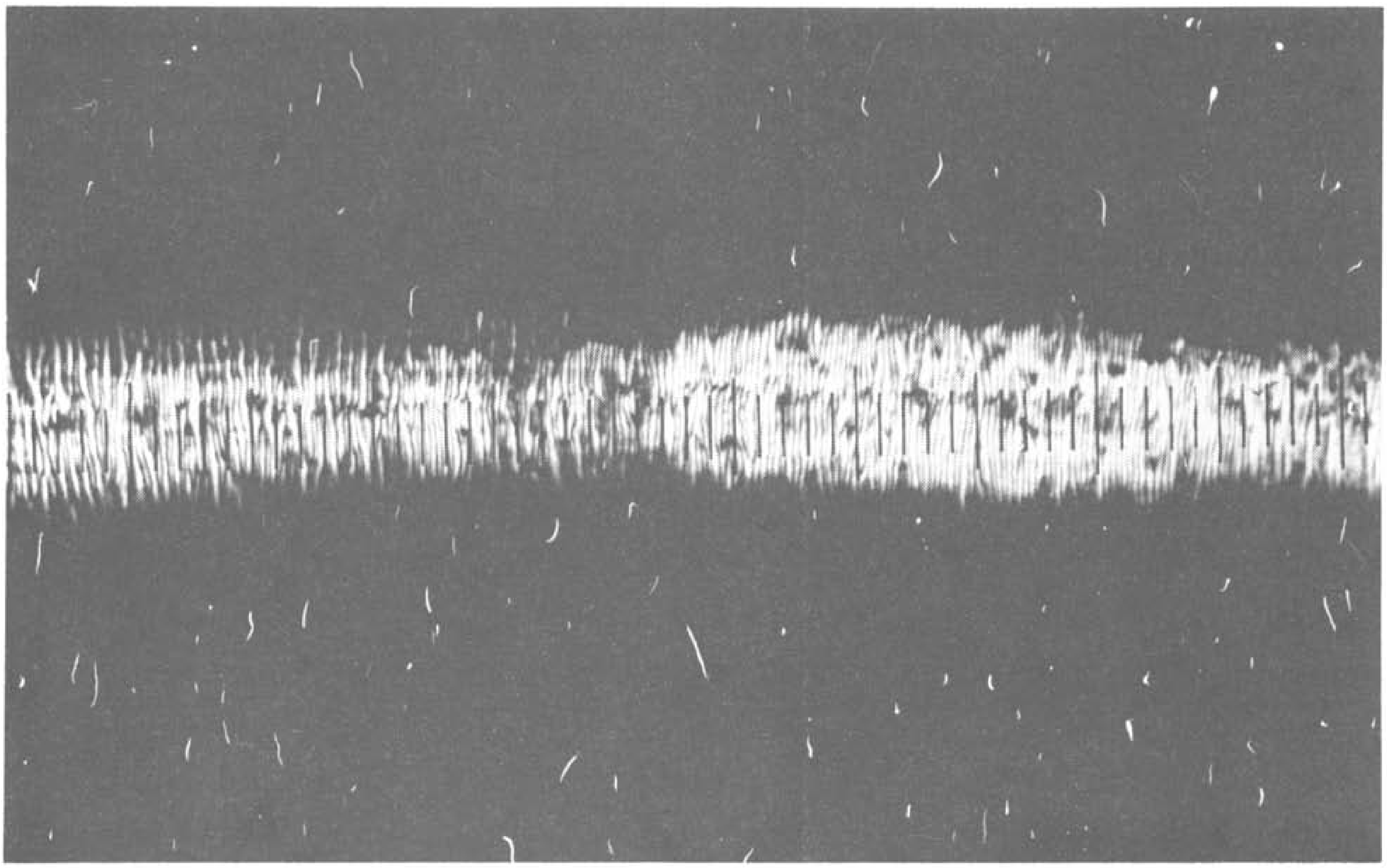

Fig. 2. Banded texture of a fibre of PPC under the polarizing microscope. The distance between the small scale-marks is 0.04 mm.

under the polarizing microscope (Fig. 2). Banded structures are observed on sheared HPC liquid crystals and represent a structural and morphological feature of sheared or drawn liquid crystalline polymers[4]. This optical anisotropy in the

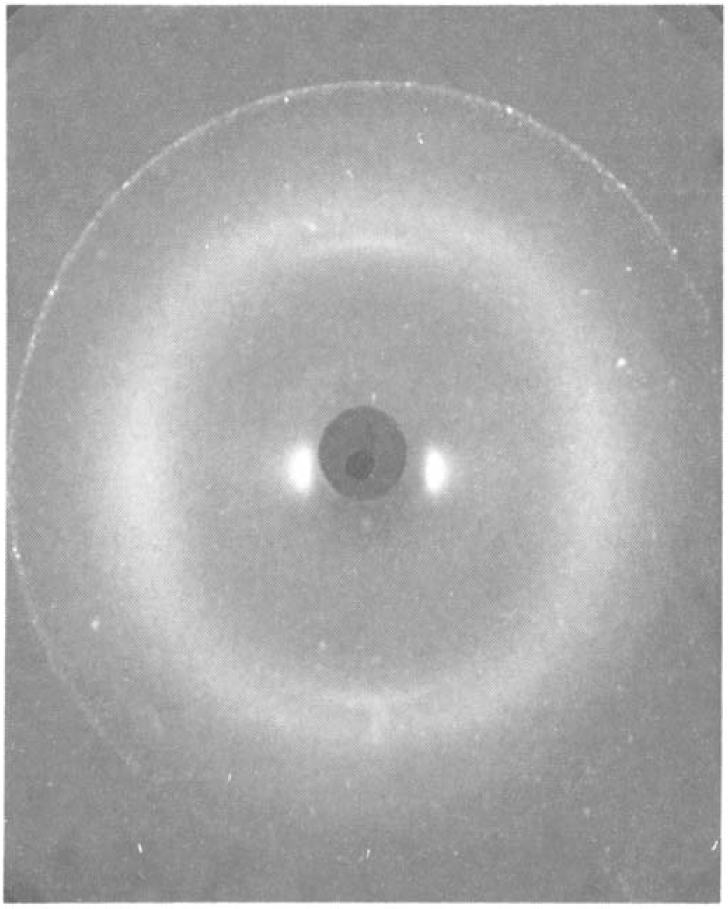

Fig. 3. X-ray fibre pattern of the sample of PPC shown in Fig. 2. The fibre axis is vertical. The sharp ring originates from the calibration material, CaF_2.

polarizing microscope can be explained by a periodic discontinuity along the shear direction, caused by stress relaxation after extension[4].

An X-ray pattern of a fibre of PPC having a banded texture is very informative (Fig. 3), despite the fact that only two pairs of reflections and a broad ring having the *d*-spacing of the average van der Waals distances are recognizable. The fibre axis is unaxial, with the ordered polymer chains almost perfectly aligned along it and lying perpendicular to the bands of the texture. The meridional reflection at $d = 5.02$ Å represents the rise per residue in cellulosics and suggests a rod-like conformation[6]. The *d*-spacings range from 5.15 to 5.25 Å for sheet-like conformations. The equatorial reflection at $d = 16$ Å is caused by the packing of the chains and may correspond to the diameter of a single chain, as shown[7] for the comparable X-ray diagram of CTC II. There is little tilting of the cellulosic-chains, as shown by the small arcing of the reflections. The breadth of the equatorial reflections is indicative of scattering from a non-crystalline structure. A diffuse, broad ring showing almost no preferred orientation represents an isotropic distribution of contacts of atoms at approximately van der Waals distances, and may be related to a disorder of the substituents of the cellulose chains. The absence of layer lines on the X-ray diagram indicates a lack of correlation between chains.

When the interpretation of the X-ray pattern of PPC is considered in conjunction with the texture seen in the polarizing microscope, the evidence for a thermotropic, nematic, liquid-crystalline phase is unequivocal. The same conclusion can be drawn for PAC, which exhibits a similar X-ray and texture pattern. However, the strong equatorial reflections in the X-ray diagram, which are not given by normal nematic phases, require us to assume the formation of clusters in the liquid-crystalline phase.

Lyotropic liquid-crystalline phases. — The newly synthesized (3-chlorophenyl)urethane of cellulose (3-ClPC) exhibited lyotropic liquid-crystalline phases in various solvents at high concentrations, and provided new insights into the structural features of cholesteric phases. For more than 30 years it has been known that polymers may form liquid-crystalline phases if certain conditions are met. Cellulose and cellulose derivatives in various solvents are examples of excellent model systems for comparison of experimental results with theoretical predictions for lyotropic liquid-crystalline phases. Highly concentrated solutions having mesophase behaviour have been obtained with *O*-(hydroxypropyl)cellulose (HPC), *O*-ethylcellulose (EC), and cellulose tricarbanilate (CTC). We found that 3-ClPC forms cholesteric phases in diethylene glycol monoethyl ether (DEME), ethyl methyl ketone (MEK), and 2-pentanone (2-P), and made extensive use of DEME, which because of its high boiling temperature is most suitable for investigations of the lyotropic mesophase. The mesophase concentration can be kept almost constant over a long period of time, even at elevated temperatures. This solvent was also successfully used in studies[5] with CTC.

Polarizing-microscopic studies. Highly concentrated solutions of 3-ClPC in DEME (50–90%) showed green to red iridescence. Optically anisotropic textures

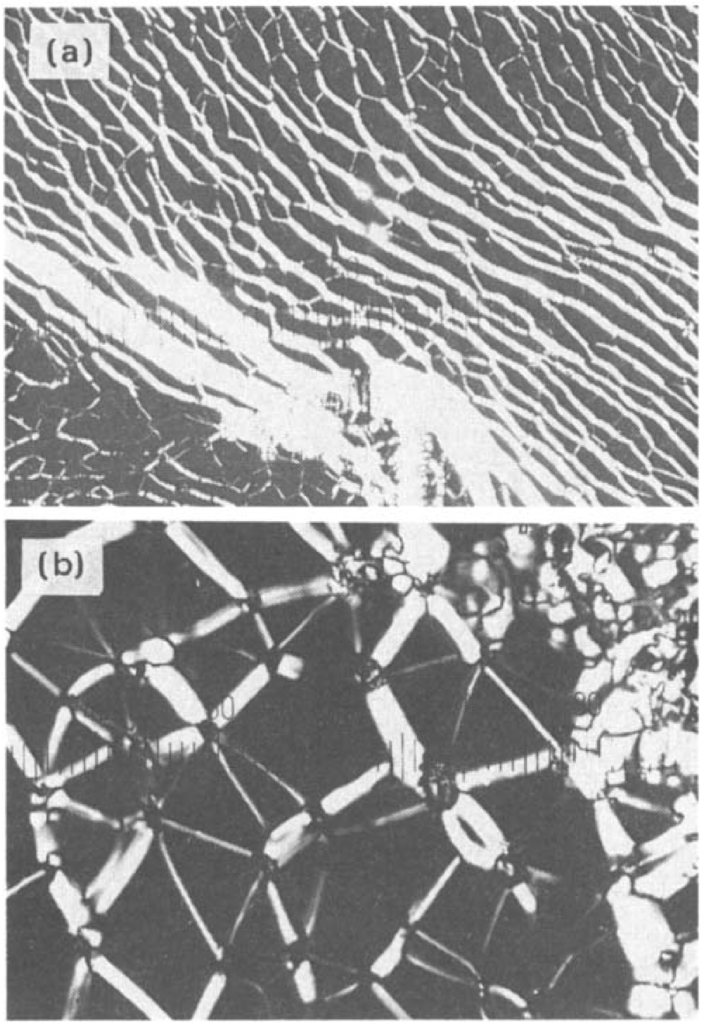

Fig. 4. Texture of the system 3-ClPC–DEME in the polarizing microscope with crossed polarizers at room temperature: (a) oily-streak texture for a concentration of 0.7 g/mL (distance between the small scale-marks, 0.04 mm); (b) enlarged section of (a).

were observed in the polarizing microscope with crossed polarizers when the anisotropic solutions were prepared between two glass plates. Examples are presented in Figs. 4 and 5. The observed textures are characteristic of cholesteric phases, and have also been found[8] for the system CTC/MEK. Crystalline spherulites having positive optical character appeared when the solvent slowly evaporated.

Birefringence. The model for cholesteric phases consists of twisted nematic sheets for which the uniaxial optical axis lies parallel to the axis of the helicoidal structure. Two refractive indices are normally observed in the anisotropic phases, n_0 the index for the ordinary ray, n_e that for the extraordinary ray. The refractive indices depend on the structure of the material and are a function of such features of a cholesteric phase as the pitch of the helicoidal structure, which in its turn varies with changes in temperature, concentration, solvent, *etc.*

Figure 6 gives the concentration and temperature dependence of the refractive indices for the system 3-ClPC–DEME. They were determined in the anisotropic phase on surface-aligned samples with a refractometer. Solutions having concentrations (c) smaller than 0.5 g/mL showed one isotropic refractive index at room temperature. Anisotropic solutions with $c > 0.5$ g/mL were positively birefringent with $n_e > n_0$. This unusual result for a cholesteric phase is supported by conoscopic observations in the polarizing microscope and will be discussed later.

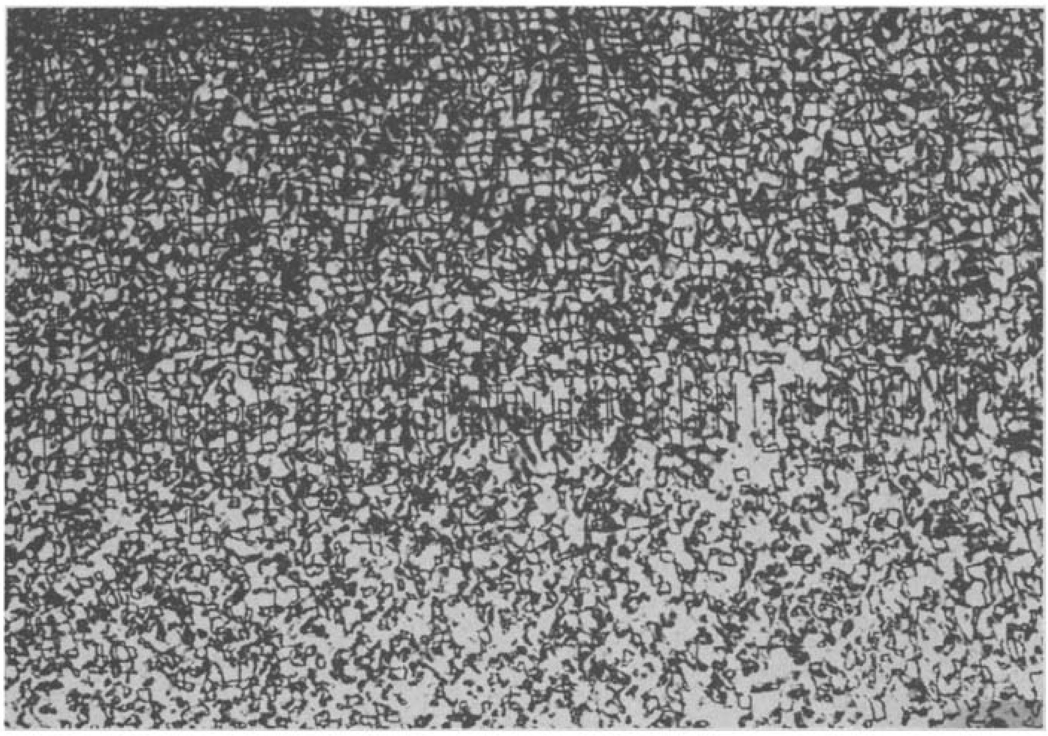

Fig. 5 Texture of 3 ClPC–DEME at a concentration >0.8 g/mL. Distance between small scale-marks, 0.04 mm.

The refractive index increment d*n*/d*c* is constant and equal to 0.14 in the isotropic phase (Fig. 6a), and it changes to 0.06 for d*n*/d*c* and 0.08 for dn_e/dc in the anisotropic phase. Samples having concentrations >0.9 g/mL were highly viscous and inhomogeneous, and an accurate determination of their refractive indices was not possible.

At low temperatures a constant birefringence was observed (Fig. 6b). The birefringence then became smaller with increasing temperature. It is not clear from Fig. 6b if a discontinuity in refractive indices is present at the clearing temperature (cholesteric–isotropic T_c) which would signify a first order transition. Such a phase transition should be accompanied by a change in enthalpy (ΔH) in a DSC experiment. However, a caloric effect has not been detected, and the character of the phase transition remains undetermined; the DSC instrument may not be sensitive enough for the measurement of a small ΔH.

Order parameter. The average deviation from an ideal parallel orientation of all molecular axes can be described for liquid crystals by the order parameter S, where

$$S = 1/2\,(3\cos^2\delta - 1), \qquad (1)$$

and δ is the angle between the molecular axes and a director. The order parameter was determined by Vogt[7] for various cellulose-derivative systems using a method of Haller *et al.*[9], in which temperature-dependent birefringence measurements are evaluated with respect to the anisotropic molecular polarizability and correlated with S.

Figure 7 gives the order parameter as a function of the reduced temperature T^* for a sample of 0.7 g/mL 3-ClPC–DEME ($T^* = T/T_c$; $T_c = 46°$ for this concen-

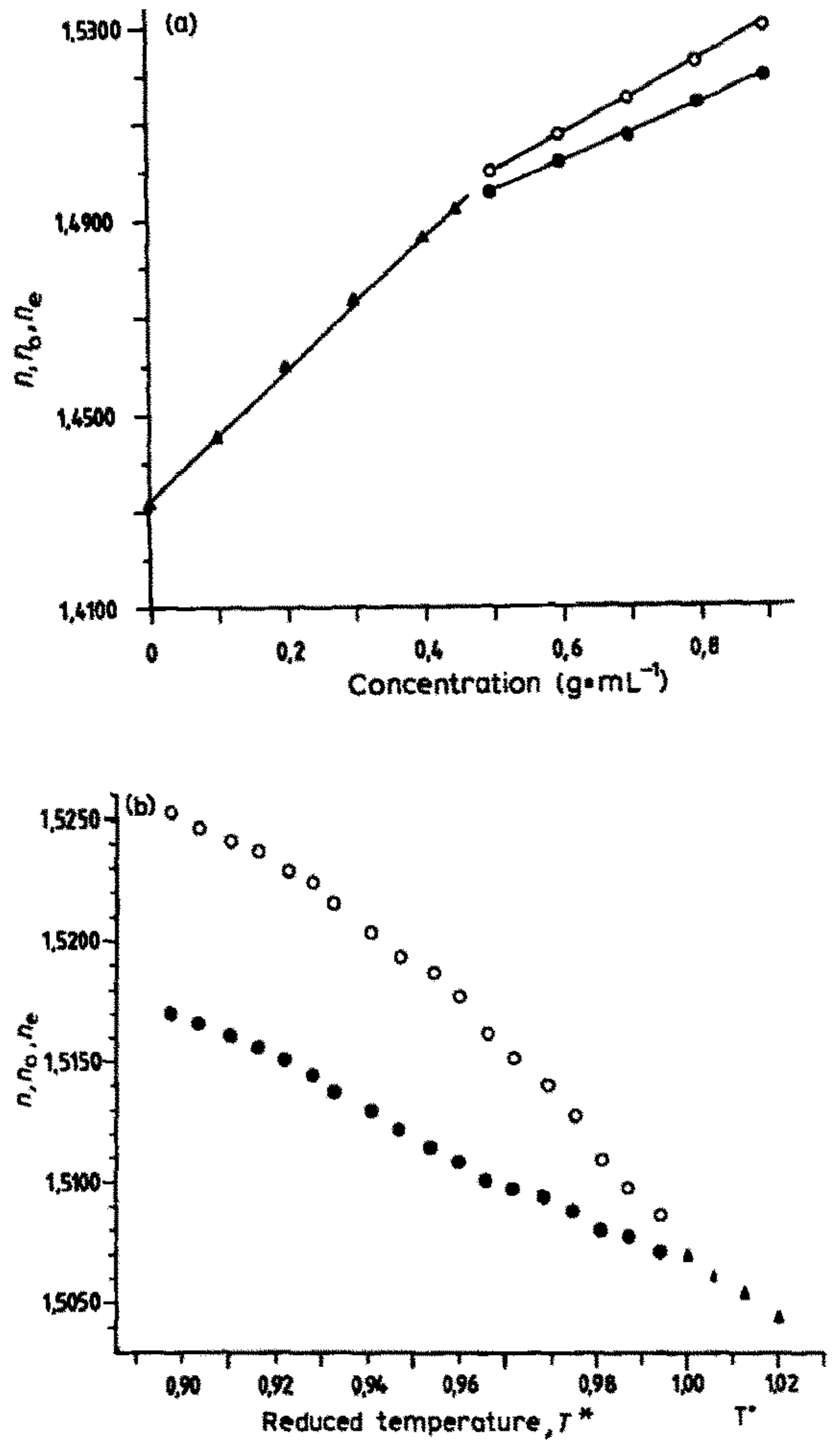

Fig. 6. Refractive indices (n ▲; n_o ●; n_e ○) of the system 3-ClPC–DEME as function of (a) concentration (room temperature) and (b) reduced temperature, T^* (= T/T_c where T_c, the clearing temperature = 324 K for c = 0.8 g/mL).

tration). The value of S is relatively large (0.7) at 22° and for a time it continuously decreases with increasing temperature, then it discontinuously drops to zero in a small step at T_c = 46°. A similar dependence of S was obtained for the system ethylcellulose–glacial acetic acid, in contrast to fractionated cellulose tricarbanilate–ethyl methyl ketone, where S is still much larger[10] at T_c.

Conoscopic observations. Observations in the conoscopic light-convergent mode were carried out in the polarizing microscope with crossed polarizers. The optical axis of the cholesteric phase lay parallel to the axis of the microscope in surface-aligned samples. The optical behaviour of the liquid-crystalline phase can be studied in such an experiment. The positive optical sign of the birefringence, established through refractive-index measurements, was confirmed for 3-ClPC–

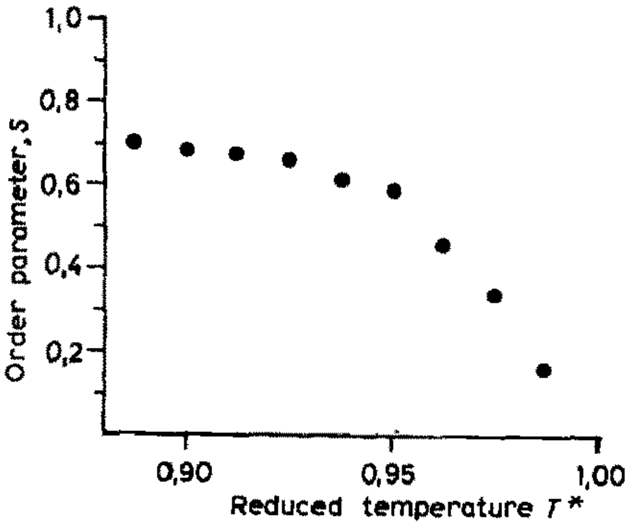

Fig. 7. Order parameter S as a function of reduced temperature, T^*, for a surface-aligned sample of 3-ClPC–DEME at 0.7 g/mL).

DEME by the distribution of colour observed with an accessory plate in the light path. Fig. 8 shows a pattern given in the conoscopic observation mode by a 0.7 g/mL sample of 3-ClPC–DEME. The cross in this figure remained unchanged when the sample was rotated, and thus signifies the presence of a uni-axial optic axis. However, another sample of the same derivative at the same concentration, prepared from a different batch of Avicel, provided the two different patterns of Fig. 9 before and after a 45° rotation of the sample. The suggested biaxial axis was confirmed by the detection of three refractive indices for a surface-aligned sample in the refractometer (Fig. 10). The two patterns of Fig. 9 are found regularly for cholesteric phases of various cellulose derivatives, but were difficult to interpret since only two refractive indices had been detected[5,7,11].

Pitch. The cholesteric structure of a system can be characterized by the pitch and handedness of the twisted nematic sheets, which form a helicoidal structure. The determination of the size and to some extent the handedness were performed on surface-aligned samples by three independent methods: 1, transmission spectroscopy (u.v.-v.i.s.); 2, optical rotatory dispersion (ORD) measurement; 3, the Grandjean line method.

According to theoretical considerations of de Vries[12], right-handed circularly

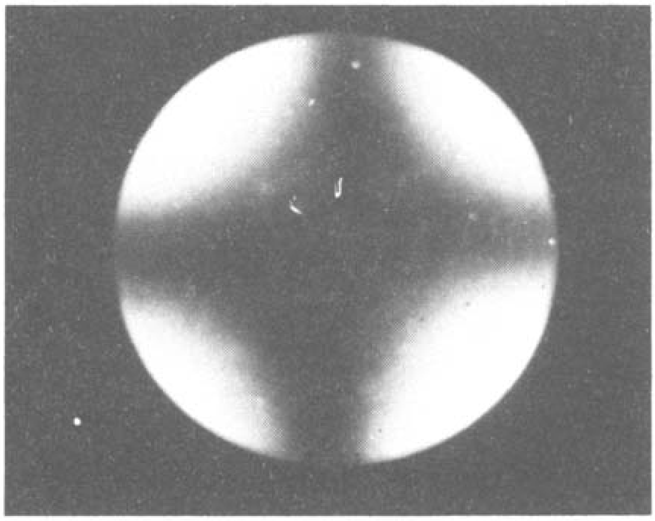

Fig. 8. Conoscopic observation of a sample of 3-ClPC–DEME at 0.7 g/mL, uniaxially surface-aligned.

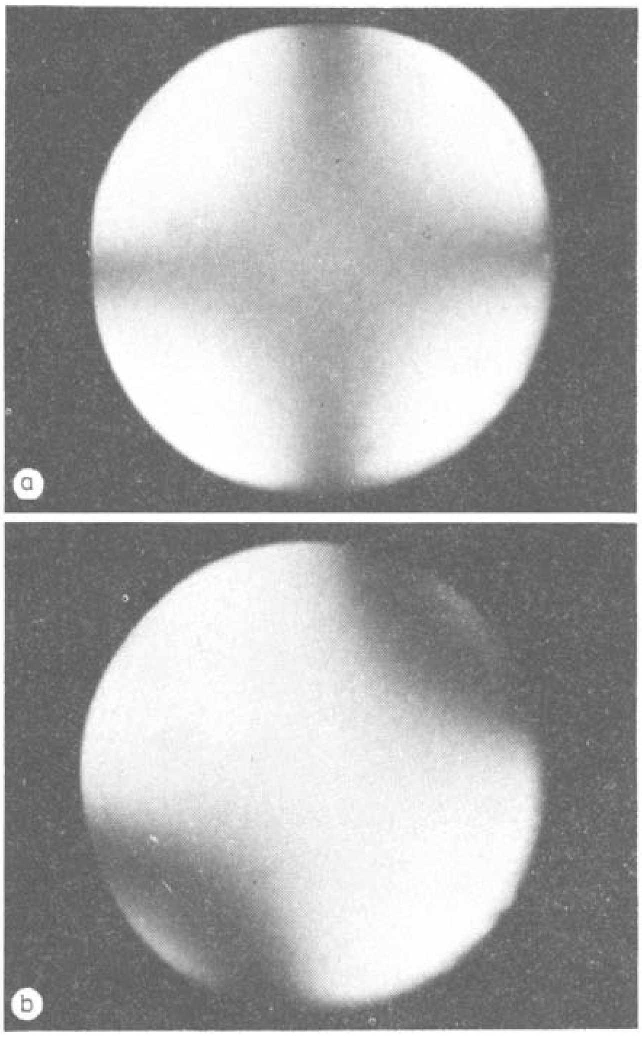

Fig. 9. Conoscopic observation of a sample of 3-ClPC–DEME from a different batch of cellulose, 0.7 g/mL, biaxially surface-aligned: (a) rotation 0°, (b) sample rotated 45° between crossed polarizers.

polarized light is reflected by a right-handed helicoidal structure at a selective wavelength λ_0. The same holds for left-handed circularly polarized light at left-handed helicoidal structures. The selective wavelength is related to the pitch p by

$$\lambda_0 = \bar{n} \cdot p, \tag{2}$$

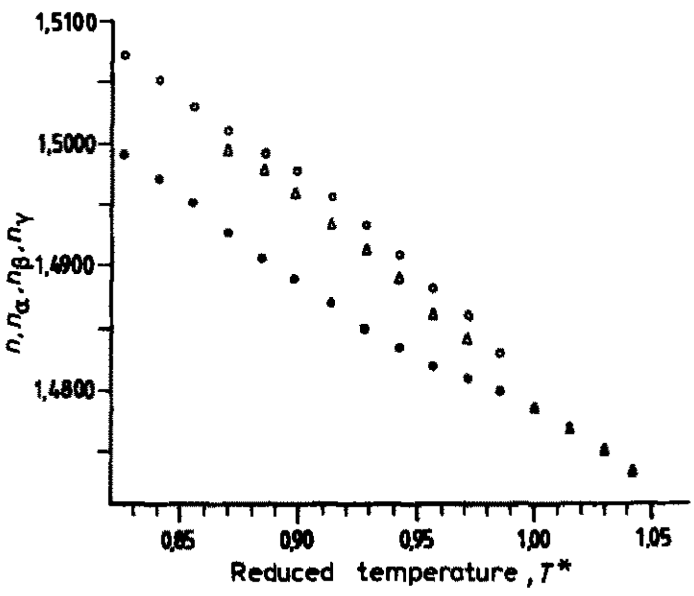

Fig. 10. Refractive indices (n ▲, n_α ●, n_β △, n_γ ○) of the sample of Fig. 12 as a function of reduced temperature, T^*.

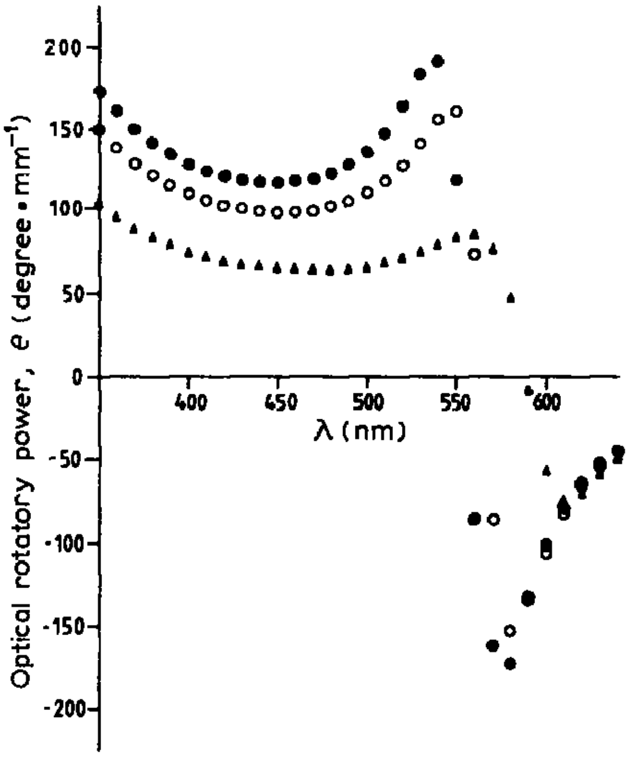

Fig. 11. Optical rotatory power θ as a function of wavelength, λ, 3-ClPC–DEME at 0.8 g/mL at various temperatures: 25° ●●, 30° ○○, 35° ▲▲.

where $\bar{n}$ is the mean nematic refractive index. This effect is observable in the transmission spectra, by a peak because a circular component of the incident light at λ_0 will be attenuated by a helicoidal structure of a certain pitch. In optical rotatory measurements a singularity is present at λ_0. The optical rotatory dispersion can be described by a relationship developed by de Vries.

Our investigations were carried out on samples prepared between two quartz plates, which were rubbed in one direction to ensure proper surface alignment. The two plates were kept at a constant distance with a 50 μm spacer. Figure 11 shows the observed optical rotatory power θ as a function of the wavelength of light λ at different temperatures for the system 0.7 g/mL 3-ClPC–DEME. The size of the pitch of the helicoidal structure was determined from λ_0, the wavelength for which $\theta = 0$, using eq. (*2*) with $\bar{n}$ taken from Fig. 6b. A right-handed helicoidal structure exhibits a positive θ for $\lambda < \lambda_0$ and corresponds to a positive sign of the pitch p.

The results of the determination of the pitch are summarized as a function of temperature in Fig. 12. The values obtained by the two described methods agreed within 1%. A sharp break in the slope is observed at 30°, corresponding to a break in the plot of refractive indices *vs.* temperature (Fig. 6b).

A direct and independent determination of the pitch is provided by the Grandjean line method. The liquid-crystalline sample is placed between a lens and a glass plate (Fig. 13), and rings are observed through the polarizing microscope with polarizers crossed. An unperturbed helicoidal structure having its optical axis parallel to the light rays can only develop where the distance between lens and glass plate corresponds to an integral multiple of $p/2$. The boundaries between ordered and disordered structures are then observed as concentric rings (Fig. 14),

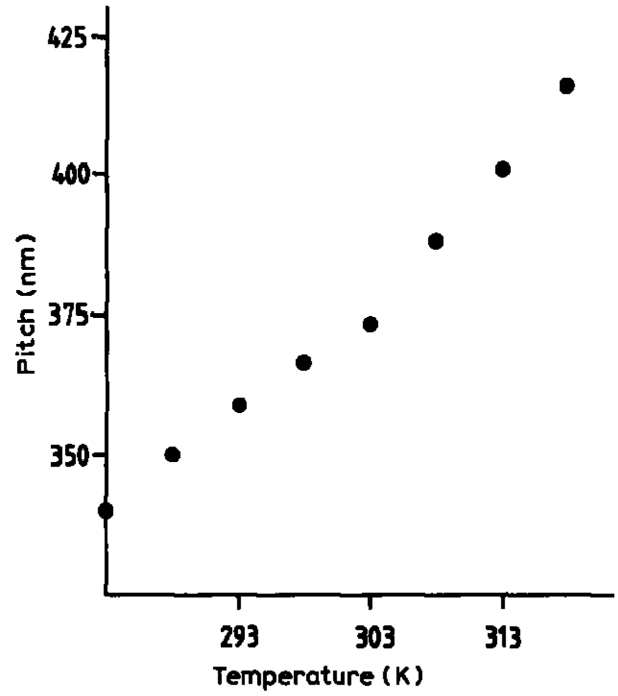

Fig. 12. Pitch of the helicoidal cholesteric structure of 3-ClPC–DEME at 0.7 g/mL as a function of temperature, determined by transmission spectroscopy or the ORD method.

and serve for an evaluation of the pitch of cellulose-derivative systems[13].

The view shown in Fig. 14a clearly demonstrated, through different colours and an uneven shape, that the innermost 2 or 3 rings should not be used in determining the pitch. At least 20 orders of Grandjean lines were observed for 0.7 g/mL 3-ClPC–DEME at 25° (Fig. 14b), and a value of $p = 380 \pm 20$ nm was calculated from a number of measurements. This compares well with the value $p = 366$ nm found by the ORD method.

Figure 15 shows the pitch as a function of concentration. The value increases with increasing concentration, a result very similar to the one published for liquid-crystalline cellulose tricarbanilate[13]. However, CTC in other solvents may show decreasing pitch with increasing concentration. This behaviour cannot be explained at the present.

X-ray investigations. X-ray scattering experiments were performed on dry 3-ClPC fibres and on cholesteric solutions in DEME. The X-ray diagram of a dry fibre drawn in hot air was comparable with that of a dry fibre of cellulose tricarbanilate. A relatively sharp equatorial reflection was observed at $d = 20$ Å and a meridional reflection at $d = 5.1$ Å. Layer lines were not observed. The inter-

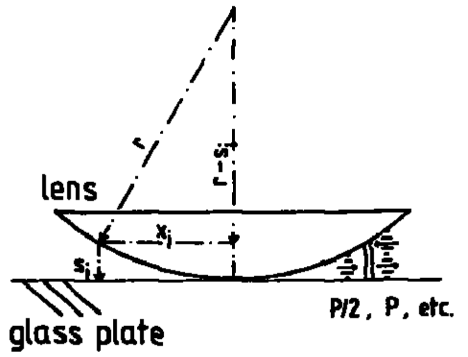

Fig. 13. Experimental set-up for the observation of Grandjean lines. Symbols: r, radius of lens; x_i, radius of observed ring i; s_i, thickness of sample at x_i.

pretation of this pattern follows the ideas evaluated for CTC. The ordered, rod-like molecular chains are poorly correlated along the drawing direction or fibre axis. They are laterally packed with a regular spacing of 20 Å. The relatively sharp reflection with d = 18.3 Å in a Debye–Scherrer pattern of lyotropic liquid crystals of 3-ClPC–DEME may be due to a different type of lateral packing of the ordered chains. A similar decrease of observed d-spacing in lyotropic liquid crystals as compared to dry fibres was found for some CTC–solvent combinations.

CONCLUSIONS

A strong influence of solvent on the size of the pitch was observed for lyotropic liquid-crystalline preparations of 3-ClPC when butanone (MEK) or 2-

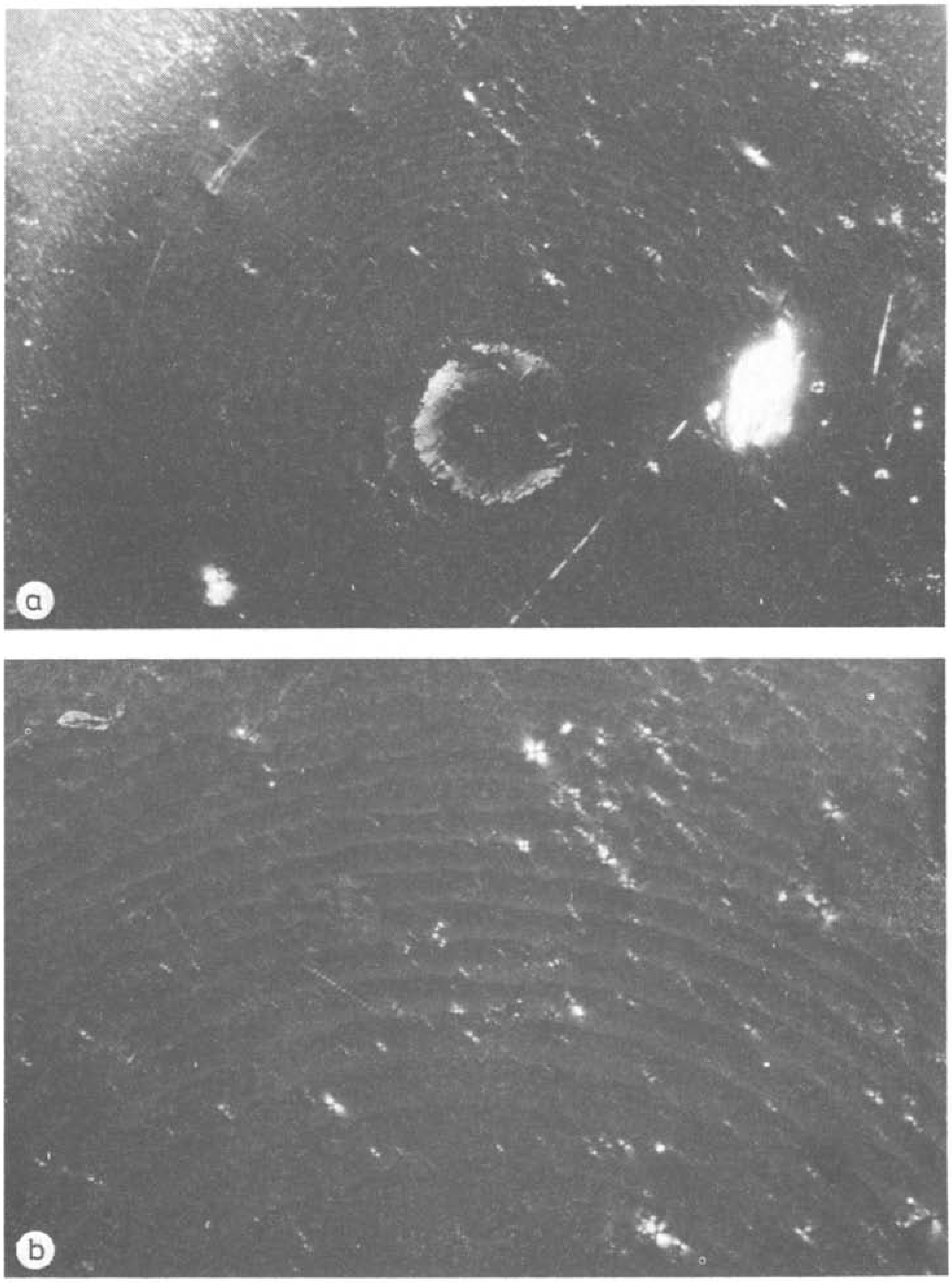

Fig. 14. (a) Grandjean lines observed through a polarizing microscope with crossed polarizers for 3-ClPC–DEME at 0.7 g/mL; (b) enlarged section of (a).

pentanone (2-P) were compared with diethylene glycal monoethyl ether (DEME). The behaviour of liquid-crystalline phases of 3-ClPC closely resembles that of CTC, which was investigated in an earlier study[14]. Both cellulose derivatives exhibit lyotropic cholesteric phases having an unusual positive birefringence and a positive slope of plots of pitch as a function of concentration. However, a break in the curve of $p(T)$ has not been detected in the CTC–solvent combinations. If the chlorine in ClPC is placed in the 4 position of the phenyl ring, cholesteric liquid-crystalline phases are not observed in the solvents DEME, MEK, or 2-P.

The structural features of cellulose-derivative chains are quite similar in lyotropic and thermotropic liquid-crystalline phases as revealed by their X-ray patterns. Rod-like chains have to be assumed which form clusters showing packing reflections in the X-ray diagrams of the order of the diameter of the rods. A similar type of packing has to be assumed for the dry fibres of CTC and 3-ClPC, whose X-ray patterns compare well with those of the liquid-crystalline phases.

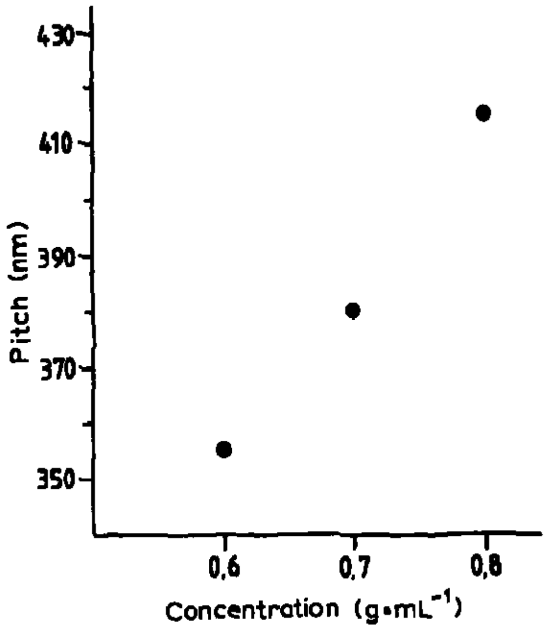

Fig. 15. Pitch as a function of concentration for 3-ClPC–DEME at 25° determined by the Grandjean line method.

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