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Fine Structure and Optical Properties of Cholesteric Films Prepared from Cellulose 4-Methylphenyl Urethane/*N*-Vinyl Pyrrolidinone Solutions

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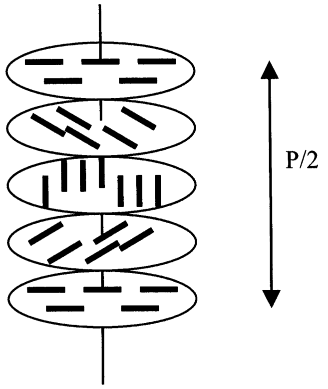
ABSTRACT: Solutions of 4-methylphenylurethane of cellulose in *N*-vinyl pyrrolidinone have been investigated, and a cholesteric mesophase was found above a concentration of 35 wt % of polymer. The selective reflection of light from the cholesteric solutions lies in the visible region of the spectrum and moves from blue toward red with increasing temperature. After photopolymerization of these solutions, solid opalescent films, which conserve the cholesteric order of the lyotropic phase, can be prepared. The fine structure of these colored films has been investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). In the fractured surfaces of the films, a periodic lamellar structure, which may arise from the helically twisted structure of the cholesteric mesophase, is observed. The periodicity of the lamellar structure is in good agreement with the calculated value of half a pitch of the cholesteric helix.

Introduction

Many cellulose derivatives form lyotropic cholesteric liquid crystalline phases in a variety of solvents.[1−4] The structure of a cholesteric liquid crystal is generally represented by the model shown in Scheme 1. At small distances, the ordering of the rod-shaped molecules is similar to the nematic ordering, and in each layer the molecules are predominantly oriented along a director. However, the cholesteric structure differs from the nematic structure in the arrangement of the rod-shape molecule layers. In the former structure, the presence of a chiral center causes the director to turn by a small angle on going from one layer to the next one, so that a supermolecular structure with helical ordering appears. In this type of liquid crystals, selective reflection of light can be observed when the pitch of the cholesteric helix coincides with the wavelength of light. Since the reflection conditions vary with the angle between the cholesteric helix and the incident light, different reflection colors can be seen depending on the observation angle, and the solutions appear to be iridescent. De Vries demonstrated that, for an incident angle of 90°, the pitch P and the wavelength of the reflected light λ_0 are related by the following equation: $\lambda_0 = nP$, where n is the average refractive index.[5]

A widely investigated cellulose derivative is the phenylurethane of cellulose (cellulose tricarbanilate), which forms excellent lyotropic cholesteric liquid crystalline phases in ketones, ethers, and glycols.[4,6−8] Depending on the solvent, left-handed and right-handed helicoidal liquid crystal structures have been identified for this derivative.[4,8] Furthermore, with changing solvent, different dependencies of the pitch of the cholesteric helix with temperature and concentration have been observed.[4,8] Recently, a range of substituted phenylurethanes of cellulose has been investigated. For these materials, it was observed that the handedness of the supermolecular cholesteric structures depends strongly on the position of the substituent at the phenyl ring (*meta* or *para*) and less on the kind of substituent (methyl, chloro, or fluoro).[9] For partially substituted derivatives, the optical properties depend also on the site of substitution in the glucose residues.[9] Despite the accumulated experimental data, the conformation of the molecules of cellulose derivatives in the lyotropic phase remains unknown. Studies of cellulose derivatives in the solid state have shown that the molecules form rodlike helices, which are always left-handed.[8] In contrast with this, in the lyotropic state the supermolecular structures may be left- or right-handed, depending on the solvent, and the arrangement of the cellulose molecules to form the supermolecular structure is not clear. It is evident from the experimental data that polymer−solvent interactions play an important role, but current theoretical studies cannot explain the experimental results.

Scheme 1. Schematic Arrangement of the Molecules in the Cholesteric Mesophase (*P* Pitch of the Helix)



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When the cholesteric liquid crystalline phase is prepared using a monomer as a polymerizable solvent, solid opalescent films, which conserve the selective reflection of the liquid crystalline phase, can be obtained by photopolymerization. Possible applications of these materials are in information display and storage devices,[10] and as components of security papers, decorative films, and pigments.[11,12]

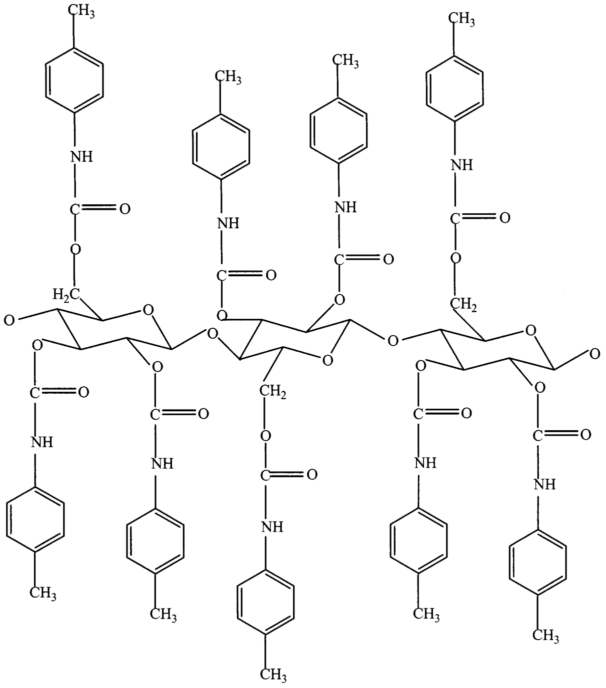
Considerable efforts have been made to prepare materials that incorporate the liquid crystalline properties of cellulose derivatives in a polymerizable matrix. For example, Jiang and Huang reported the formation of opalescent films by the photocuring of liquid crystalline solutions of ethylcyanoethylcellulose in acrylic acid,[13−17] while Müller et al. described the preparation of composites which retain the cholesteric structure from lyotropic solutions of 3-chlorophenylurethane of cellulose in diethylene glycol dimethacrylate.[18,19] The work on ethylcyanoethylcellulose/poly(acrylic acid) composites has shown formation of lamellar structures after photopolymerization of liquid crystalline solutions. These structures are reminiscent of the textures found in cholesteric liquid crystals although the latter arise from the periodicity of molecular orientation as against density differences. Similar periodic lamellae have been observed in other cholesteric liquid crystalline systems by transmission electron microscopy (TEM).[20−23] While many reports have highlighted correlations between cholesteric phases and development of lamellar periodicity, the origin of the contrast causing the structures observed by TEM has been subject of debate.[23] It has been pointed out that direct investigations of solid surfaces using atomic force microscopy (AFM) offer a more reliable tool compared to TEM to probe correlations between lamellar structure and cholesteric order.[24]

In this work, we present a study of the optical properties of liquid crystalline solutions of 4-methylphenylurethane of cellulose in *N*-vinyl pyrrolidinone (NVP) and of composites prepared by photopolymerization of the solutions. A study on a similar system, i.e., a phenylurethane of cellulose in methyl acrylate and methyl methacrylate, was recently reported by us.[25] However, in that work, we were interested in the mechanical behavior of the composites and the degree of homogeneity of the samples as a function of composition. Here, our aim is to gain a clearer picture of the internal structure of the composites using both SEM and AFM measurements. The resolution of the AFM is superior to previous work and provides a guide to the substructure. Despite the limitations of the TEM measurements that have been addressed by several authors,[23] few studies have been conducted using AFM. The few reports of AFM measurements on cholesteric liquid crystalline systems have dealt with microtomed surfaces which are subject to artifact formation. Our AFM measurements were carried out on fracture surfaces and this provides a more realistic picture of the internal structure.

Experimental Section

Materials. 4-Methylphenylurethane of cellulose (4-MPC, Scheme 2) was produced using a heterogeneous method.[26] Low molecular weight cellulose was first prepared by dispersing 30 g of cellulose acetate (Aldrich, $M_n = 30\,000$) in a solution of sodium hydroxide (30 g) in methanol (1.5 L) for 2 h. The dispersion was neutralized with glacial acetic acid, filtered, and dried at 80 °C for 24 h in vacuo. The completeness of the deacetylation reaction was checked by IR spectroscopy. For the synthesis of 4-MPC, dry low molecular weight cellulose powder (5 g) was soaked in distilled pyridine (200 mL) overnight under a nitrogen atmosphere, then 25 g of 4-methylphenyl isocyanate (Aldrich) was added dropwise, and the mixture was refluxed at 110 °C. A clear brown viscous solution was produced, and after being stirred for 6 h, the clear solution was poured into a 1:1 mixture of methanol−water. The raw product was purified by two reprecipitations from an acetone solution into methanol. After drying in a vacuum for 12 h, the product was extracted in a Soxhlet apparatus over methanol for 1 day to remove impurities soluble in methanol. Then, the product was dissolved in acetone, centrifuged to remove solid impurities, and precipitated in methanol to produce a white fibrous powder. The powder was dried in vacuo at 80 °C overnight and then submitted for elemental analysis.

Scheme 2. 4-Methylphenylurethane of Cellulose



Elemental Analysis. Cellulose derivatives were analyzed for elemental composition using a Control Equipment Corp. 440 elemental analyzer. The degree of substitution (DS) was derived by comparing experimental values of elemental analysis results with theoretical values of elemental composition, determined over the full degree of substitution range (0−3). The DS was determined from the percentage of nitrogen, as nitrogen had the largest change in percentage composition over the degree of substitution range. The 4-methylphenylurethane prepared was found to have a degree of substitution of 2.8.

Composite Preparation. Solutions were prepared from 0 to 50 wt % 4-methylphenylurethane of cellulose in NVP. All solutions had 1% photoinitiator added (Daro Cur 1173-Ciba Speciality Chemicals) and were left to homogenize for 1 week at room temperature in the dark. The viscous solutions were spread into a custom-built cell and polymerized under a UV lamp (3400 μW/cm^3 at 360 nm) for 30 min. To investigate the influence of the ordering of the liquid crystal on the morphology of the composites obtained by photopolymerization, two films were prepared from each solution. Half of each solution was polymerized immediately after placing it into the polymerization cell, and the second half of the solution 12 h later. During this time, the polymerization cell was kept in the dark, at room temperature.

Measurements. The solutions were analyzed using an Olympus BH-2 polarizing optical microscope. The average refractive index, *n*, of the solutions was measured at room temperature with an Abbé refractometer. UV−vis spectra were recorded using a Shimadzu 160A spectrophotometer with a custom-built temperature controller. The morphology and

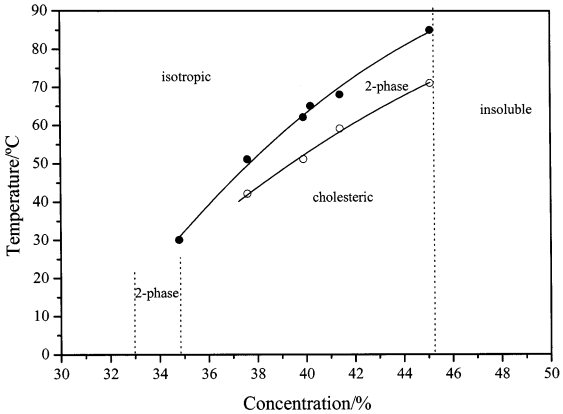


Figure 1. Clearing temperatures as a function of composition determined from polarization microscope observations. The isotropic, cholesteric, and biphasic phase regions are indicated.

Table 1. Reflection Wavelengths, Average Refractive Index, and Pitch at Room Temperature for Different Concentrations

concentration, %	wavelength, λ_0/nm	refractive index, *n*	pitch, P/nm
38.9	449	1.549	290
41.6	436	1.553	281
43.8	464	1.554	299

structure of the composites was investigated by scanning electron microscopy (SEM), using a Hitachi S-2700 microscope operating at 10 KV. For the SEM study, the films were cryofractured, in directions perpendicular and tangential to the composite film surface. The fractured surface was covered with a thin layer of gold using a gold sputterer. The magnification of the SEM was calibrated with latex particles with a known diameter of 0.137 ± 0.016 μm (Agar Scientific). Further investigations on the structure of the composites were carried out using atomic force microscopy (AFM). The AFM images were taken in air using a Digital Instruments 3100 NanoScope microscope. The microscope was operated in the taping mode. For the AFM study, the films were cryofractured as for the SEM study, but gold coating was not required.

Results and Discussion

Polymer Solutions. Phase Behavior. Clear isotropic solutions are formed for concentrations below 33 wt % polymer at room temperature, while a completely anisotropic solution is obtained for concentrations above 35 wt % polymer. These anisotropic systems exhibit oily streaks when viewed under the optical microscope indicative of a cholesteric structure. For concentrations greater than or equal to 45 wt % polymer, homogeneous solutions could not be prepared. The liquid crystalline samples in the concentration range 35−45 wt % polymer reflect visible light and exhibit an intense blue coloration, which is independent of concentration and can be observed at room temperature. As shown in Figure 1, the clearing temperatures of the anisotropic solutions increase with increasing 4-MPC content.[27] There is a two-phase region between the cholesteric and the isotropic region, characterized by a blurred schlieren texture, when viewed under the microscope.

UV−Vis Spectroscopy. The selective reflection wavelength of the liquid crystalline solutions may be determined from the minimum of the UV−vis transmission curves. Table 1 shows the reflection wavelengths determined as a function of composition, together with the pitch of the cholesteric mesophases, which was calculated using the De Vries equation. Both λ_0 and the pitch are independent of concentration.

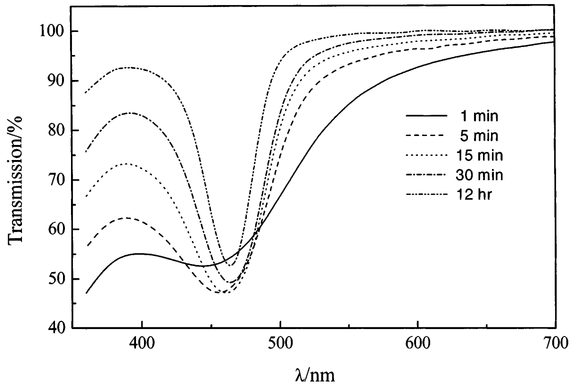


Figure 2. UV−vis spectra of a cholesteric solution containing 43.8% 4-MPC as a function of time.

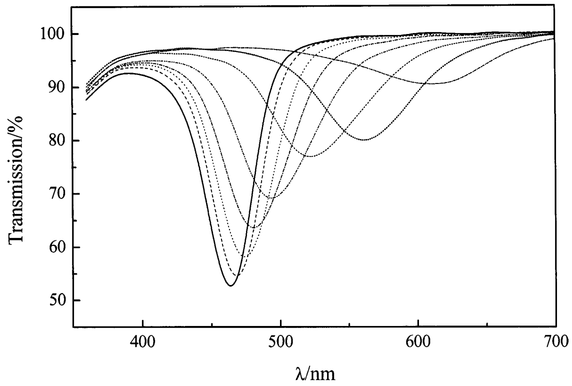


Figure 3. UV−vis spectra of a cholesteric solution containing 43.8% 4-MPC as a function of temperature. From left to right the temperatures at which the spectra were collected are 18, 24, 29, 40, 48, 60, 68, and 79 °C.

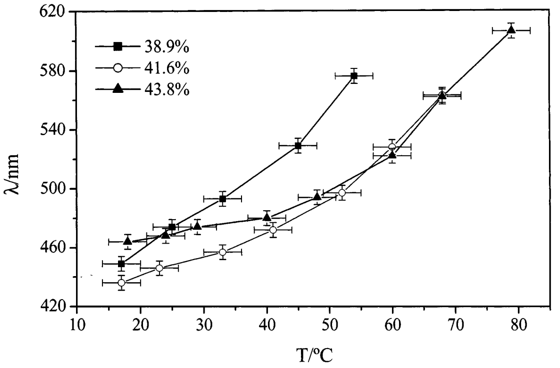


Figure 4. Reflection wavelengths, λ_0, as a function of temperature for several compositions.

A key point in the preparation of cholesteric films is the degree of ordering of the cholesteric phase in the solution prior to the polymerization. As the solutions are highly viscous, reaching a good degree of ordering requires a long aging time. To evaluate this, UV−vis measurements were carried out, at room temperature, as a function of time after the lyotropic solutions were placed into the UV−vis cells. Figure 2 shows the UV−vis spectra collected for a solution with 43.8% 4-MPC. This solution reflects light at ca. 460 nm, and the UV−vis peak becomes narrower with increasing time. All solutions studied exhibit a similar behavior. As discussed by Werbowyj et al.,[28] a narrow reflection band can only be obtained when there is a good alignment of the cholesteric phase in the planar texture. If the sample has a polydomain structure, where the helicoidal axes are directed at all angles within the sample, transmis-

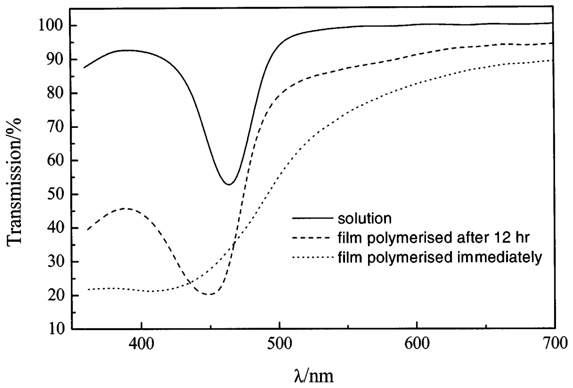


Figure 5. UV−vis spectra at room temperature, of a solution with 43.8% 4-MPC and composites prepared from this solution.

sion measurements will show reflection at a range of wavelengths around λ_0, rather than a sharp peak at λ_0. Therefore, we can conclude that in our system the alignment of the cholesteric phase improves with time, and that a reasonably good alignment is achieved after 12 h.

The behavior of the solutions was also investigated as a function of temperature. These measurements were carried out 24 h after the solutions were placed in the UV cells. As shown in Figure 3 for a solution with 43.8 wt % 4-MPC, the reflection peak broadens with increasing temperature, and at a critical temperature, which rises with increasing 4-MPC content, it disappears. The critical temperature determined here correlates well to the clearing temperature determined by optical microscopy (Figure 1). It can also be observed that the wavelength of the selective reflection increases with increasing temperature. Plots of the reflection wavelength (λ_0) as a function of temperature are not linear (Figure 4). The pitch, which can be calculated from the values of λ_0 and the average refractive index, also rises as the temperature increases, indicating an expansion of the packing along the helical axis with increasing thermal motion of the system. Although several dependencies of the pitch on temperature have been proposed for lyotropic phases of cellulose derivatives,[7] caution must be taken in the interpretation of these results, as the temperature dependence of the refractive index has been ignored and data for λ_0 are available only in a relatively narrow range of temperatures.

Composites. UV−Vis Spectroscopy. Upon polymerization, the samples remained clear and no sign of phase separation could be observed. Moreover, the films exhibit similar coloration to the initial solutions, suggesting that the cholesteric order of the solutions has been conserved in the composites. Figure 5 shows the UV−vis transmission curves of composites together with the solution prior to photopolymerization. It can be observed that the composites exhibit a selective reflection band comparable to that of the solution, although the selective reflection of the composites is shifted to slightly shorter wavelengths. A small shift has been

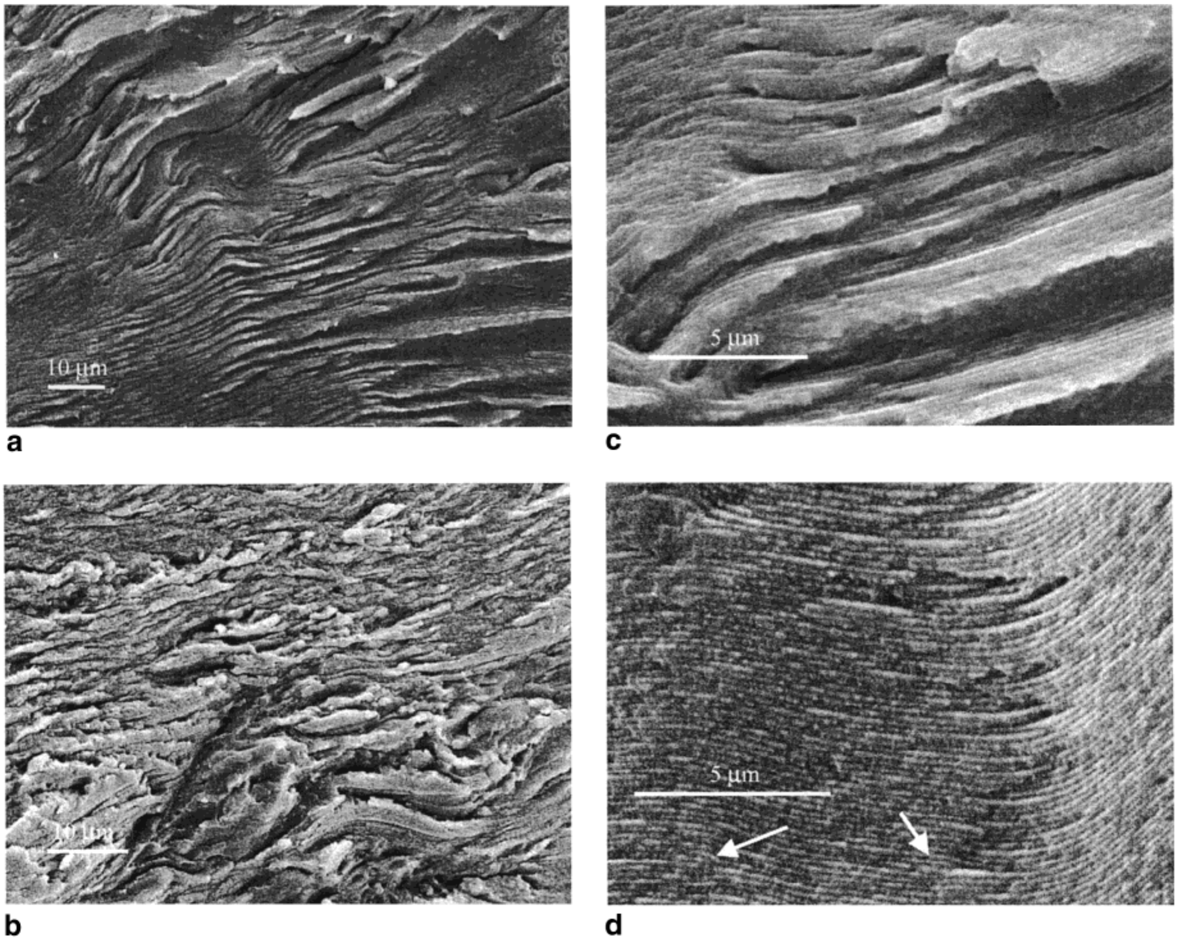


Figure 6. SEM micrographs of composites fractured normal to the composite film surface with (a) 43.8% 4-MPC, polymerized after 12 h in the cell, magnification 700×; (b) 43.8% 4-MPC, polymerized immediately, magnification 1000×; (c) 43.8% 4-MPC, polymerized after 12 h in the cell, magnification 4000×; and (d) a different area of part c, magnification 5000×.

reported in other systems,[29] and is attributed to volume shrinkage during polymerization.

The reflection peak becomes very broad when the film is polymerized immediately after placing the solution in the polymerization cell. This is in agreement with our observations on the optical behavior of the solutions as a function of time. A narrow reflection band requires a good alignment of the cholesteric phase, which is achieved when the solution is allowed to order in the cell for several hours before polymerization.

SEM. The SEM study was carried out only on films prepared from anisotropic solutions. At low magnifications, the films fractured in a direction perpendicular to the composite surface exhibit a layered structure (Figure 6a), with the layers roughly parallel to the external surface. The morphologies of films polymerized immediately (Figure 6b) and after 12 h (Figure 6a) in the polymerization cell are similar, but the layered structures of the latter are more regular. The correlation between the broadening of the reflection peak in the UV−vis spectra and the irregularity of the structure observed by SEM suggests that the layered structure of the composites is related to the supermolecular structure of the cholesteric liquid crystalline solutions. At higher magnifications, the fractured surface exhibits a periodic striation (Figure 6c), similar to those observed previously in other cholesteric liquid crystalline systems studied by transmission electron microscopy (TEM).[20−23] Costello et al. reported the observation of periodicity in one direction in TEM images of a thermotropic cholesteric liquid crystal (a mixture of chiral 4-cyano-4′-(2-methyl)butylbiphenyl with a number of nonchiral cyanobiphenyls), while they observed periodicity in two directions for the corresponding blue phase.[20] A periodic microstructure was also observed by Boudet et al. in thermotropic side-chain liquid crystals[23] and by Giasson et al. in a study of cross-linked cholesteric films of hydroxypropylcellulose.[2,21] Finally, a periodic structure was also found in a study of ethylcyanoethylcellulose/poly(acrylic acid) composites,[22,13] prepared by photopolymerization of cholesteric solutions. All these authors have found a good correlation between the periodicity of the structure and the value of half the pitch of the cholesteric mesophase. To explain this correlation, it has been proposed that the periodic striation is caused by the presence of lamellae normal to the fractured surface. This lamellar structure, which produces the periodic striation, may arise from the helically twisted structure of the cholesteric mesophase. The periodic direction of striation is parallel to the axial direction of the cholesteric helix and the striation is parallel to the layers of ordered molecular chains (Scheme 3).

The periodicity of the striations in our system was established by taking 10 distance measurements in each micrograph and calculating an average value. This value was corrected with a calibration of the magnification of the microscope. For the composite prepared from the solution with 43.8 wt % 4-MPC, the distance between the periodic striations is 140 ± 30 nm. This value is comparable to that of half the pitch, $P/2$, of the cholesteric mesophase, which can be calculated using the De Vries equation (Table 1) and is 150 nm for this composition. This agreement supports the idea of a relationship between the periodic striations and the structure of the cholesteric mesophase. Further support is given by the presence of some defects in the periodic striations observed in the SEM micrographs. For example, in Figure 6d, some pairs of disclinations are indicated by arrows. These defects have also been observed in cholesteric liquid crystalline solutions by optical microscopy and therefore their presence in the fine structure of the composites corroborates the idea that the periodic striations reflect structural features of the cholesteric liquid crystals.

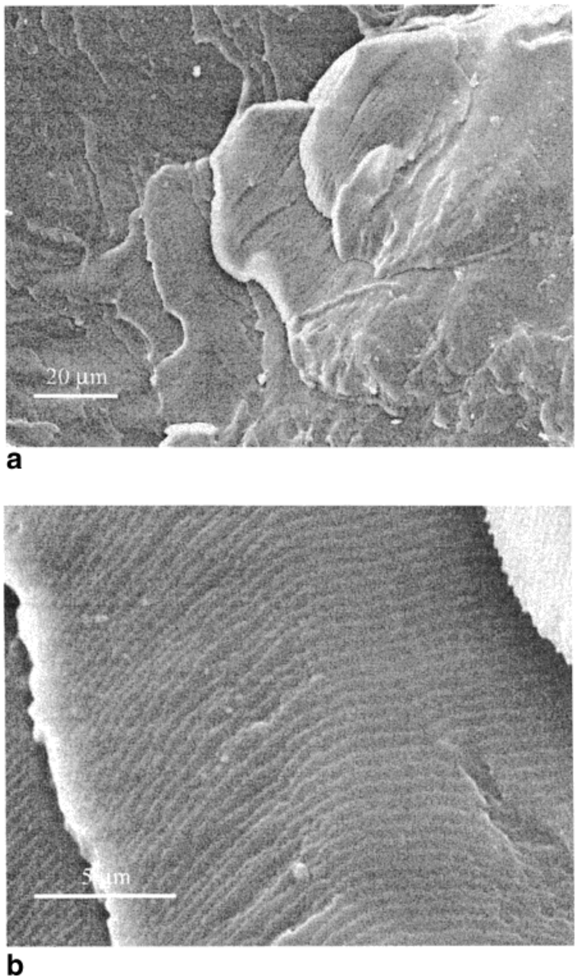
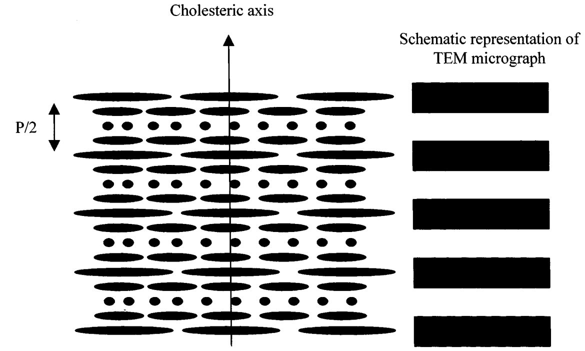


Figure 7. SEM micrographs of a composite with 43.8% 4-MPC fractured tangential to the composite film surface with (a) magnification 500× and (b) magnification 3500×.

Scheme 3. Proposed Correspondence Between the Molecular Oeientation in the Cholesteric Phases and the Periodic Structure Observed in TEM[23]



When the films are fractured in a direction tangential to the composite film surface, a layered structure is also observed at low magnifications (Figure 7a), while at higher magnifications periodic striations, caused by the lamellae, are evident (Figure 7b). In this orientation, the lamellae are parallel to the external surface, and

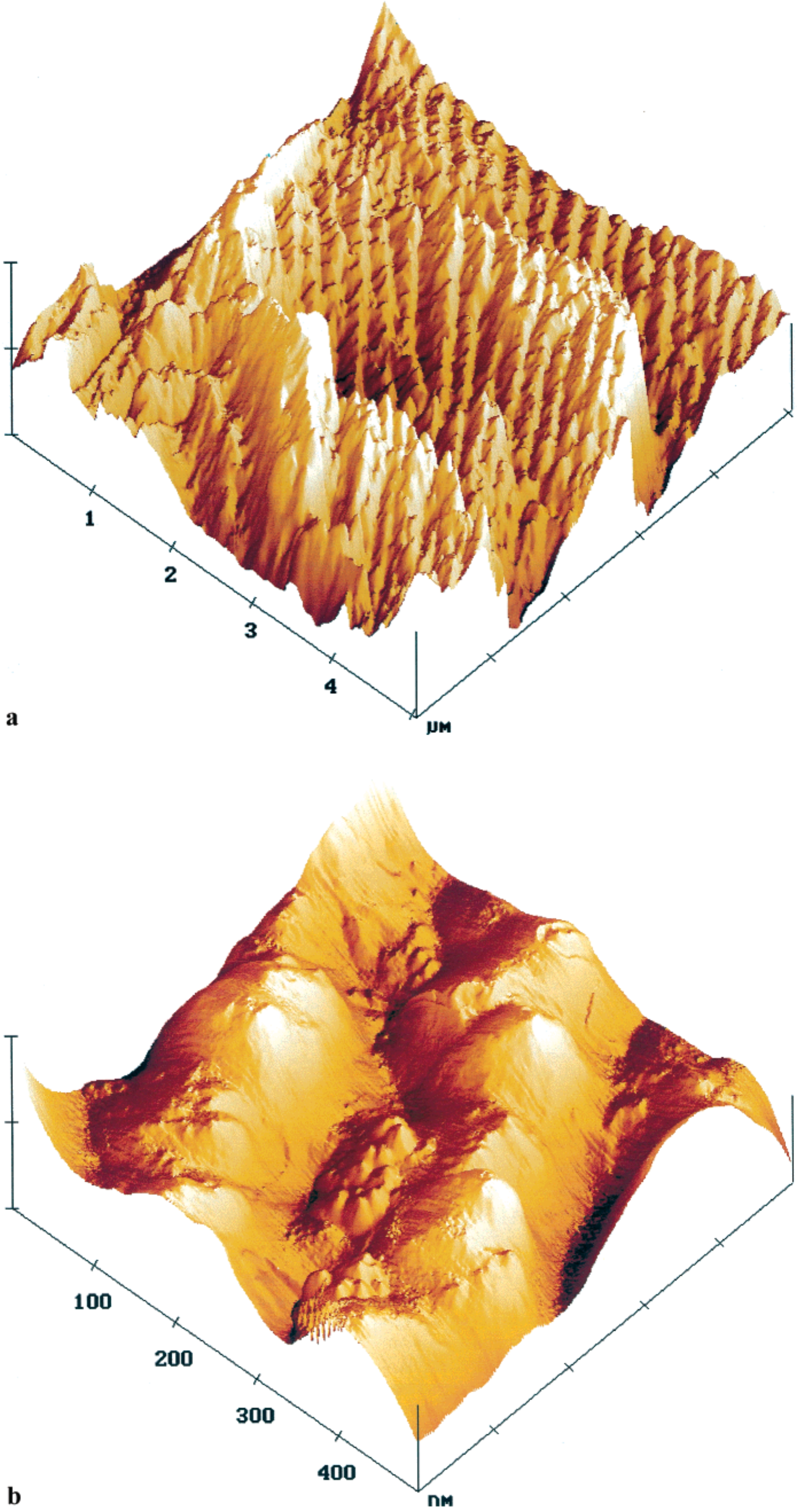


Figure 8. AFM image of a composite with 43.8% 4-MPC fractured normal to the composite film surface: (a) 4.5 × 4.5 μm; (b) 0.5 × 0.5 μm.

therefore they resemble steps. The striations in the tangential orientation are less regular and the periodicity of the striations is larger than that of films fractured normal to the composite surface.

AFM. To gain further insight into the structure of the composites, an AFM study was carried out on composites prepared from anisotropic solutions. Figure 8a shows a 4.5 × 4.5 μm 3-dimensional surface image of the fracture surface of a composite film normal to the external surface. The lamellae can be clearly observed, crossing the image from the lower corner to the upper corner. Similar features have been observed in thermotropic cholesteric liquid crystals[23] and composites prepared from lyotropic liquid crystals[22] by TEM and AFM. Height profile analysis of the AFM images obtained for the 4-MPC composites indicates that the periodicity of the lamellae is ca. 200 nm, comparable to the values obtained from the SEM micrographs. The peak-to-valley height is in the range 30−70 nm.

AFM images (Figure 8b) show that the lamellar surface is not smooth, but uneven and irregular. When the images are viewed in two dimensions, the irregularities in the surface could be described as small particles, and this has been interpreted by Huang et al.[22] as being caused by a microphase separation which occurred when the composites were prepared by photopolymerization. However in the 3-dimensional images obtained for the 4-MPC composites, there is no clear evidence of small particles, and the irregularities on the lamella surfaces do not show any periodicity or characteristic size, in contrast with the results of Huang et al.[22] The detailed arrangement of the two polymers present in our system cannot be determined from the measurements carried out, and microphase separation cannot be excluded as electron microscopy provides a poor contrast between polymers. A preliminary study of phenylurethane of cellulose/polymethyl acrylate composites, prepared by photopolymerization of cholesteric mesophases, has been carried out by small-angle neutron scattering (SANS).[30] These composites exhibit a large scattering, independent of composition, which is likely to arise from the presence of microvoids, and therefore the homogeneity of these films could not be fully established. Dynamical mechanical thermal analysis (DMTA) data indicate that the phenylurethane of cellulose/polymethyl acrylate composites may not be fully homogeneous.[25] Thus, one possibility is that the particle-like structure, whose ends are shown protruding from the layers in Figure 8b, represent a series of domains. These domains comprise the bundles of 4-MPC in liquid crystal alignment coated and cemented together in the layered structure by the PVP. Further studies of the 4-MPC/NVP composites and analogous systems will be required to establish the structure at the molecular level.

Conclusions

4-MPC solutions in NVP form cholesteric mesophases above a concentration of 35 wt % polymer. Composites that conserve the cholesteric order may be prepared by photopolymerization of these solutions. These composites exhibit a selective reflection of light similar to that of the solutions. The microstructure and morphology of the composites appears to reflect structural features of the cholesteric liquid crystals. The composites could be described as made of lamellae with a thickness of half a pitch of the cholesteric helix. These lamellae are oriented parallel to the external surface of the composite. Although AFM and SEM measurements have provided useful information about the microstructure, it is still unclear precisely how the two polymers cellulose 4-methylphenylurethane and poly(vinylpyrrolidone) are arranged in the lamellae.

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