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Relaxation Processes in sheared films of ethyl-cyanoethyl cellulose cholesteric liquid crystalline solutions

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The relaxation processes in sheared films of ethyl-cyanoethyl cellulose [(E-CE)C]/acrylic acid (AA) cholesteric liquid crystalline (LC) solutions were studied by polarizing optical microscopy (POM) and UV-Vis spectrophotometry. Under shearing normal to the helix axis and above the critical shear rate, the planar texture arrangement of the (E-CE)C/AA cholesteric LC solution was destroyed and transformed to the nematic phase. Observed by POM, the banded texture formed quickly following the cessation of the shear, but it was unstable and disappeared after several minutes. The reflection spectrum of the sheared (E-CE)C/AA cholesteric LC solution film was recorded as a function of relaxation time. It was found that the selective reflection property was lost under the shear, but the shape of the reflection spectrum recovered quickly with cessation of the shear, and the reflection peak in the spectrum became sharper with time, returning to the original form before shearing. A proposed model of the structural transformation during the relaxation was confirmed by additional optical measurement and transmission electron microscopy.

1. Introduction

The structural deformation of nematic or cholesteric liquid crystalline polymer (LCP) phases under shear is one of the most interesting topics in the field of both polymer science and liquid crystals. Many investigations of the behaviour, mechanism and rheology of sheared LCP phases have been reported. Since cholesteric LCPs have a twisting power resulting in the self-assembly of the cholesteric phase, the deformation and relaxation processes of a sheared cholesteric liquid crystalline phase are more complex than those of a nematic phase. Firstly, different deformations of the sheared cholesteric phase occur, according to the conditions between the helix axis and the shearing direction. There are three representative deformations [1], i.e. splay–bend–twist deformation when the helix axis is along the shearing direction, splay–bend deformation when the helix axis is along the velocity gradient direction [2–6], and the twist deformation when the helix axis is along the vortex axis of the shearing [7, 8]. Secondly, the rheological properties and deformation behaviour of the cholesteric phase are

markedly changed depending on different shearing histories and rates [9]. Among these three cases, the splay–bend deformation has attracted most attention, and has been investigated both experimentally and theoretically. Because of the selective reflection properties (Bragg reflection) of the cholesteric phase, the maximum wavelength of the selective reflection (λ_{\max}) is related to the pitch (P) of the cholesteric phase and can be described by the equation [10]:

$$\lambda_{\max} = nP \sin \varphi \quad (1)$$

where n is the mean refractive index of the mesophase and φ is the angle between the incident light and the ‘molecular layers’ in the cholesteric phase. Therefore, variations in the properties of sheared cholesteric phases can be studied by measuring reflection spectra; this is the rheo-optical technique [2–5]. Pochan, *et al.* [2, 3, 5] have used the technique to investigate structural responses under different shearing rates with different cholesteric systems or mixed nematic–cholesteric systems. Different textures (Grandjean, focal-conic, and homeotropic) have been formed depending on whether the experiments were conducted below or above a critical shear rate. Similarly, Asada *et al.* [4] have measured the intensity and variation of the spectra to

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interpret the mechanism of shear-induced structural changes in the cholesteric phase. They proposed that the helix axis may be oblique under a given shear rate or during the relaxation process. However, the details of the relaxation and structural transformation of sheared cholesteric liquid crystals require more investigation and experimental observation. Thus, our aim is to measure the optical properties of the lyotropic cholesteric phase of ethyl-cyanoethyl cellulose [(E-CE)C]/acrylic acid (AA) solution after a transient shearing (above the critical shear rate) by using another rheo-optical method, and to investigate and interpret the relaxation and structural transformation of the cholesteric LC phase.

(E-CE)C, which is a cellulose derivative with two different ether groups, ethyl and cyanoethyl, can form cholesteric liquid crystalline solutions in acrylic acid. When the concentration is above the critical concentration, the solutions exhibit multitexture behaviour on variation of the concentration [11]. In certain concentration regions, the (E-CE)C/AA solutions exhibit vivid colours due to selective reflection. Moreover, in a previous study, it was found that the (E-CE)C/AA cholesteric structure can be frozen in (E-CE)C/poly(acrylic acid) (PAA) composites by photopolymerizing the solvent AA [12]. After microtoming or sectioning these composites, the morphology and structure of the cholesteric phase was observed by transmission electron microscopy (TEM), [11, 12]. This is a convenient way to study structural transformation during the relaxation process of a (E-CE)C/AA cholesteric oriented solution.

In this paper, the variation in structure of oriented films of the LC solution during the relaxation process was studied *in situ* by measuring the selective reflection spectrum of the LC solution films; a model of the structural transformation during the relaxation is proposed.

2. Experimental

2.1. Materials

The (E-CE)C sample used was prepared by reaction of ethyl cellulose (from Luzhou Chemical Plant, PR China) and acrylonitrile, as described in our previous paper [13]. The degree of substitution for ethyl was about 2.1 and for cyanoethyl was about 0.33, measured by elemental analysis (CHN-O-RAPID, Heraeus, Germany). The molecular weight of (E-CE)C, M_w , measured by gel permeation chromatography (GPC) (ALC-244-GPC, Waters) and calibrated using polystyrene standards, was 1.9×10^5 , and the polydispersity index, $M_w/M_n=1.98$. Reagent grade AA was distilled in vacuum at 50°C before use. The (E-CE)C was mixed with AA plus 2 wt% (with respect to the solvent AA), benzoin ethyl ether initiator at room temperature

(about 25°C). The mixture was allowed to set for one or more weeks, and the resulting homogeneous solution was then stored in the dark until used. Solution films were sandwiched between two glass slides, giving a film thickness of about $80\ \mu\text{m}$; the films were then stored in the dark for several hours to form homogenous mesophases. The concentration of the (E-CE)C/AA cholesteric LC solutions was controlled in the region 42–56 wt%; they showed a planar texture in which the helix axis was aligned perpendicular to the film surface.

2.2. Apparatus and measurements

The experimental set-up used is similar to that reported previously by Pochan [2] and Asada [4]. However, the optical properties of the reflected light were recorded in our experiment, rather than the wavelength and intensity of the transmitted light. In addition, in their apparatus the cholesteric solutions were sheared by a rotating shear plate, whereas here the (E-CE)C/AA cholesteric LC solution films were transiently sheared by moving one of the slides at a constant speed of $3\ \text{mm s}^{-1}$, a rate which is above the critical value, and the helix axis is along the velocity gradient direction, see figure 1.

In order to investigate the variation of the direction of the helix axis, the samples were placed on a rotating sample stage with the rotation axis perpendicular to the slide surface (see figure 1). If the helix axis is perpendicular to the film surface, the angle between

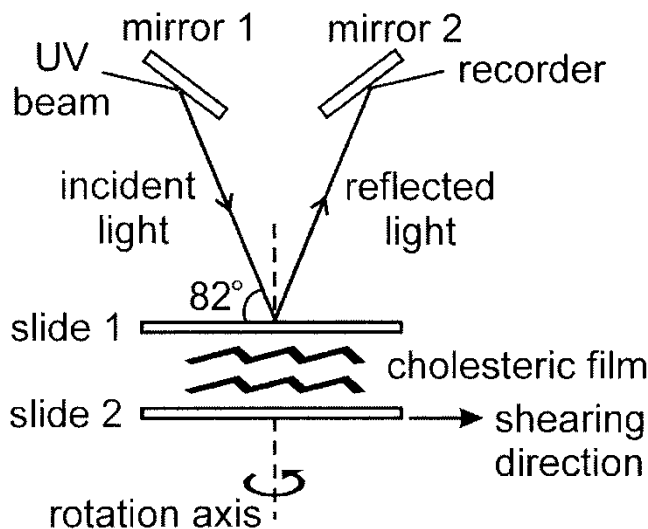


Figure 1. Experimental set-up. The position of the sample in the reflection spectra measurements, slide 1, is fixed and slide 2 is moved to obtain shearing. The sample is placed on a stage that can be rotated around the direction normal to the film surface. The fixed angle between the incident light and the film surface was 82° .

the incident light and the ‘molecular layers’ (φ) in the cholesteric phase will be fixed to 82° with different sample rotation angles. If the helix axis is oblique to the film surface, then φ will vary with the sample rotation angle, and the deviation angle between the helix axis and the rotation axis can be calculated according to the wavelength of the reflection.

The reflection spectra of the oriented solution films were recorded using a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan) during the relaxation process. The definition of the relaxation time, t_r , in this work was the period from the end of shearing to the end of the reflection spectral scanning. The morphology of the oriented film was also observed by polarized optical microscopy (POM) (Orthoplan-Pol, Leitz). The mean refractive index of the solution films was measured by an Abbe refractometer (2WA, Shanghai Optical Instrument Factory, PR China).

Since the structure of the (E-CE)C/AA solution could be frozen in the (E-CE)C/PAA composite, the sheared solution film was polymerized immediately (transferred within 5 s, from the UV-Vis spectrophotometer to the photopolymerization apparatus) after a given relaxation time. The solution film was inserted into a UV chamber equipped with a 250 W high intensity mercury arc lamp for 2 min and the (E-CE)C/PAA composite film formed, after polymerization of the AA. The distance between the lamp and the sample was 5 cm and the polymerization temperature was 0°C . Variation in the structure and morphology of the oriented solution film was studied by a transmission electron microscope (TEM) (JEM-100CX/II, Jeol, Japan) at 100 keV, after the composites film was sectioned to give ultra-thin films (60–70 nm) by an ultra-microtome (LKB-208B,

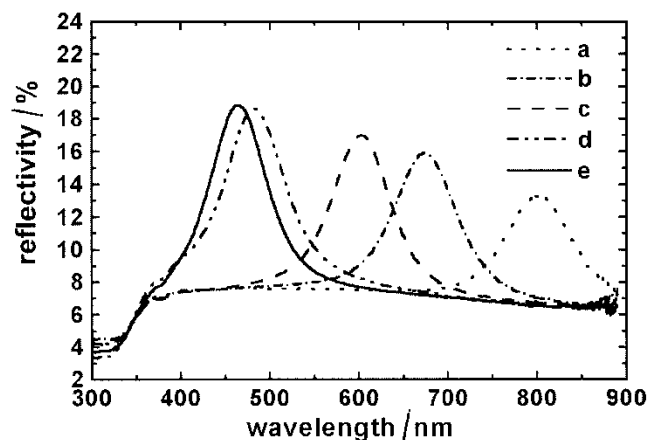


Figure 2. Reflection spectra of (E-CE)C/AA cholesteric LC solution films of different concentrations: (a) 43, (b) 46, (c) 48, (d) 50.5, (e) 51.5 wt%.

Bromma, Switzerland). The cutting direction was perpendicular to the film surface.

3. Results and discussion

3.1. Relaxation behaviour

When the concentration is in the region 42–56 wt%, the (E-CE)C/AA cholesteric LC solutions show a planar texture in which the helix axis is aligned perpendicular to the film surface. The pitch of (E-CE)C/AA cholesteric LC solutions approached the wavelength of visible light, and the solutions exhibit vivid colours due to the selective reflection of visible light. The maximum wavelength of the reflection of the cholesteric phase, λ_{max} , varies with the (E-CE)C concentration (see figure 2) and the λ_{max} shifts to shorter wavelengths with increasing in (E-CE)C concentration.

In order to compare with the rheo-optical method, the relaxation process in sheared (E-CE)C/AA solution

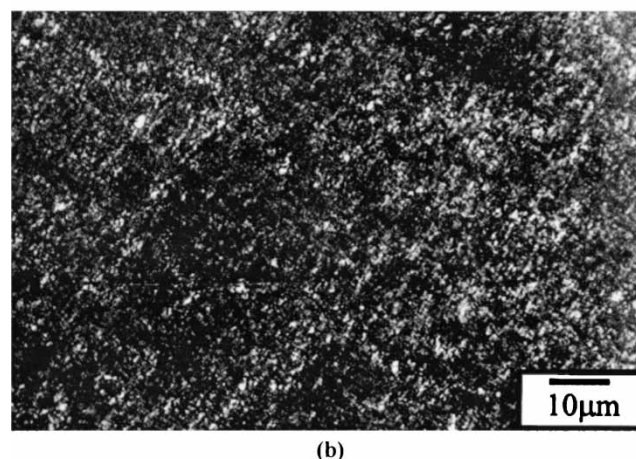
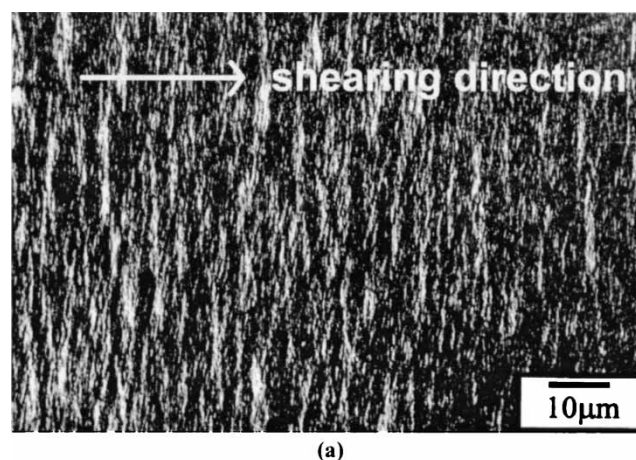


Figure 3. POM micrographs of the 51.5 wt% (E-CE)C/AA LC oriented solution film after relaxation for (a) 1, (b) 10 min.

was observed first by POM. When a strong transient shearing is applied, the (E-CE)C/AA cholesteric LC structure is destroyed and transformed to a nematic phase. The relaxation process then begins and a banded (or striped) texture is formed in a few seconds after the cessation of shearing; figure 3(a) shows the banded texture of the oriented solution film.

It can be seen from figure 3 that some periodic dark and bright bands are seen perpendicular to the shearing direction, and that the brightness and darkness of the bands varies continuously with rotation of the sheared solution film. The width of the bands is about $2\mu\text{m}$, which is larger than the pitch of the cholesteric phase (several hundred nm). A schematic representation of the orientation of polymer chains in the banded texture is shown in figure 4; it has been suggested that the polymer chains are oriented along the shearing direction in a zigzag manner [17].

Subsequent upon the relaxation process, the banded texture of the oriented solution films is unstable and it disappears after several minutes, as shown in figure 3(b). The banded texture is a commonly observable phenomenon, which results from the periodicity of the sinusoidal or zigzag packing structure; it has been found in many sheared cholesteric LCPs, such as hydroxypropylcellulose (HPC) [18–20], acetoxypolypropylcellulose (APC) [21], ethylcellulose (EC) [22], and poly(benzyl glutamate) (PBG) [23–25]. It is generally believed that the banded texture is formed due to the relaxation of oriented polymer chains after shearing in order to release energy that is stored in the polymer chains during shearing; this energy is usually thought to be stored as a form of elastic potential energy, [26–29]. The evolution of the banded texture from its formation to its disappearance is over a short time scale relaxation.

However, it is difficult to obtain more details of

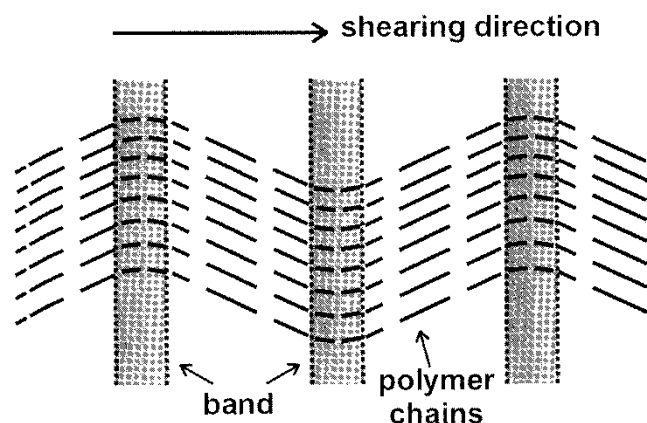


Figure 4. Schematic representation of the orientation of polymer chains in the banded texture.

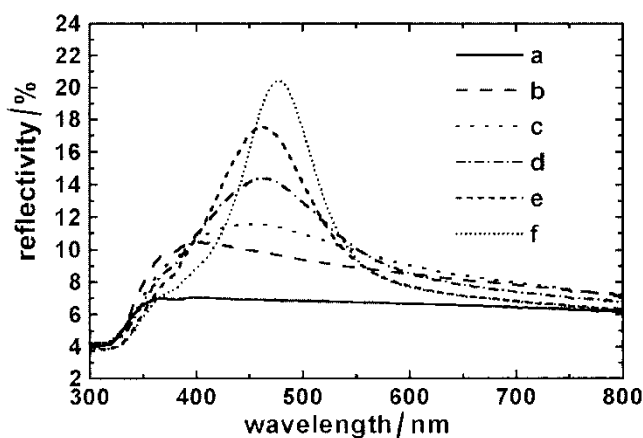


Figure 5. Reflection spectra of the 51.5 wt% (E-CE)C/AA LC oriented solution film with different relaxation times: (a) 0, (b) 1, (c) 2.8, (d) 10, (e) 26, (f) 56 min.

structural variation over a longer time relaxation process from POM observation. Therefore, the rheo-optical method is used to measure the variation of optical properties of the cholesteric structure during relaxation. The shift of λ_{max} during relaxation of the sheared (E-CE)C/AA cholesteric LC solution film is shown in figure 5. It can be seen that the selective reflection peak in the spectrum disappears after shearing, which indicates that the (E-CE)C/AA cholesteric LC structure is destroyed by the shearing and is transformed to a nematic phase (curve a in figure 5). After the oriented solution film is relaxed for 1 min, the reflection peak reappears but is very weak and broad (curve b in figure 5). When the solution is relaxed for 10 min, the reflection peak is much narrower (curve d in figure 5) than when the solution relaxes for 1 min, which indicates a large change in the reflection peak during

Table. The wavelength, λ_{max} and the intensity of the reflection for the 51.5 wt% (E-CE)C/AA LC oriented solution film with various relaxation times.

Relaxation time/min	$\lambda_{\text{max}}/\text{nm}$	Intensity of reflection/%
Before shearing	479	20.61
1	397	10.50
1.9	437	11.05
2.8	450	11.54
3.6	460	12.13
6.4	465	13.43
10	461	14.39
26	463	17.54
41	474	19.57
56	478	20.42
71	479	20.57
87	479	20.78
100	479	20.84
117	479	20.90

the relaxation and suggests that the cholesteric structure is restored very quickly. Subsequently, the peak becomes sharper and sharper as the relaxation time increases (figure 5). From the table, it can also be seen that the λ_{\max} shifts to longer wavelengths with increased relaxation time, and the intensity of the reflection peak increases gradually.

When the oriented solution film is relaxed for about 56 min, λ_{\max} shifts back to the original position before shearing, as shown in curve f in figure 5, which suggests that the cholesteric structure is totally recovered. After this time, λ_{\max} is constant and only the strength of the reflection peak grows slightly with time (see the table). Thus, the relaxation process of sheared (E-CE)C/AA cholesteric LC solution can be regarded as complete within about 1 h. Similar results have also been reported by Asada *et al.* [4]. The variation in shape and intensity of the reflection peak, as well as the position of the λ_{\max} , in the reflection spectra of the sheared (E-CE)C/AA cholesteric LC solution, indicates that the cholesteric order with the planar texture is gradually regained during the relaxation. Hongladarom and Burghardt have also found that the selectively reflected light of an HPC cholesteric solution becomes more intense with increasing relaxation time by measuring the birefringence and flow visualization [6].

Furthermore, it is found that λ_{\max} is not proportionally increased with relaxation time. Figure 6 gives the curves of λ_{\max} vs. relaxation time for (E-CE)C/AA oriented solution films with varying concentration; this shows similar trends for λ_{\max} variation with relaxation time at the different concentrations.

Figure 7 shows details of the λ_{\max} variation of the 50.5 wt% (E-CE)C/AA LC oriented solution film. The variation of the λ_{\max} with relaxation time (t_r) can be divided into three stages. From t_0 to t_1 , λ_{\max} increases with the t_r in stage I. From t_1 to t_2 , λ_{\max} decreases with

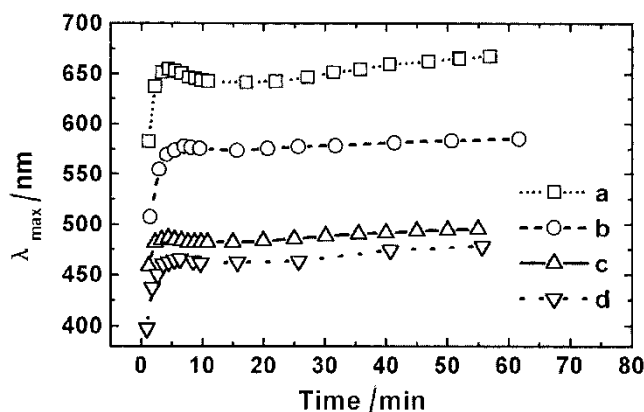


Figure 6. The dependence of λ_{\max} on relaxation time for (E-CE)C/AA LC oriented solution films of different concentrations; (a) 46, (b) 48, (c) 50.5, (d) 51.5 wt%.

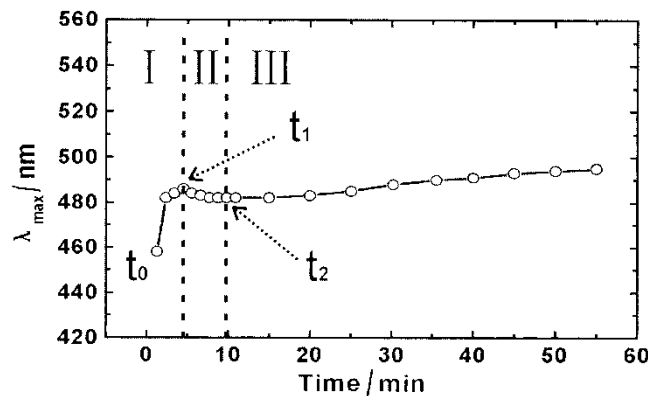


Figure 7. The dependence of λ_{\max} on relaxation time t_r for the 50.5 wt% (E-CE)C/AA oriented solution film. From t_0 to t_1 (about 1 to 5 min), λ_{\max} increases with t_r (stage I). From t_1 to t_2 (about 5 to 10 min), the λ_{\max} beyond decreases with t_r (stage II). Finally, λ_{\max} increases with the t_r in stage III after t_2 (above 10 min).

t_r in stage II; finally, λ_{\max} again increases with t_r in stage III beyond t_2 .

3.2. Relaxation process model

The results of these experiments indicate that the structure of the (E-CE)C/AA LC oriented solution films is markedly changed during relaxation. From the relationship between λ_{\max} and P , a model for the structural variation during the relaxation of the LC oriented solution films after shearing may be proposed (figure 8).

Before the solution film is sheared, the cholesteric phase exhibits the planar texture, in which the helix axes are normal to the film surface, figure 8(a). The cholesteric phase, at this time, exhibits selective reflection properties with vivid colours. Under the shearing, the polymer chains are oriented along the

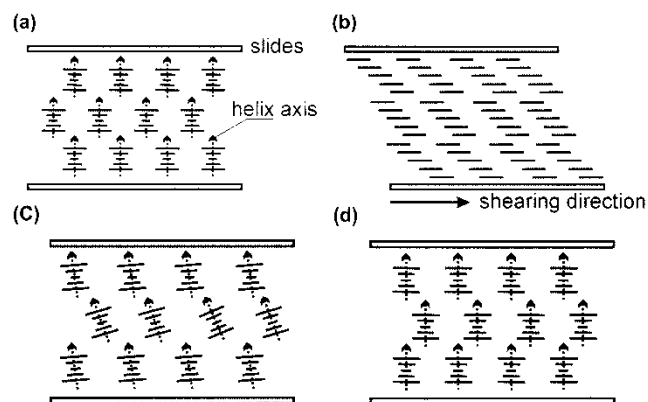


Figure 8. Schematic representation of the structural changes to the cholesteric order during the relaxation process of the oriented solution films.

shearing direction and the mesophase transforms to the nematic phase, figure 8(b); the selective reflection is lost, with the disappearance of the vivid colours. Upon shearing cessation, the oriented (E-CE)C chains recoil on increasing relaxation time, which is associated with the elastic restoring forces due to a reorganization of the director field [14–16]. A banded texture is then formed and disappears very quickly. The (E-CE)C chains then self-assemble into the cholesteric order again, driven by the helical twist power of chiral LC macromolecules. The appearance of the reflection peak (curve b in figure 5) suggests that the system begins to reassemble to the cholesteric structure after relaxation of 1 minute. Because the shearing is in one direction, the average direction of the helix axes of the cholesteric structure aligns oblique to the film surface in the same direction figure 8(c). This is in agreement with the results of Pochan [2, 3, 5] and Asada [4]. Pochan *et al.* have found that the helix axis oblique angle is increased with increasing shear rate. Asada *et al.* have adopted a model for calculating the absorbance spectrum under applied shear with after cessation the shear; their computer-fitting curve agrees well with experimental data. From the data, it has been shown that the helix axis oblique angle decreases with the time [4].

In addition to the twist power, the anchoring power is a factor that can regulate the molecular arrangement. It is well known that the glass slides have homogeneous anchoring power, which influences the orientation of polymer chains near the slide surface inducing them to be parallel to the film surface. So with the combination of the twist power and the anchoring power, the helix axes of the reordered cholesteric domains quickly align normal to the surface in the region close to the slide surface. The helix axes in domains far from the slide surface align normal to the film surface more slowly because of the lower anchoring power effect. This accords with the study of flow-induced nematic LC films and it has been found that molecular orientation of the relaxed systems varies markedly with different boundary anchoring conditions [30, 31]. As more and more helix axes change their alignment from being oblique to normal to the film surface, the shape of the reflection peak in the spectrum becomes sharper and the intensity of the reflection also increases. It is proposed, therefore, that at the beginning of the relaxation process the average direction of the helix axes changes from oblique to perpendicular to the film surface, driven by both the helical twist power and the homogeneous anchoring power of the glass slide surface, and φ increases gradually.

According to the equation $\lambda_{\max} = nP \sin \varphi$, the value of λ_{\max} is proportional to n , P and $\sin \varphi$. Figure 9 shows that there is only very small decrease in the mean

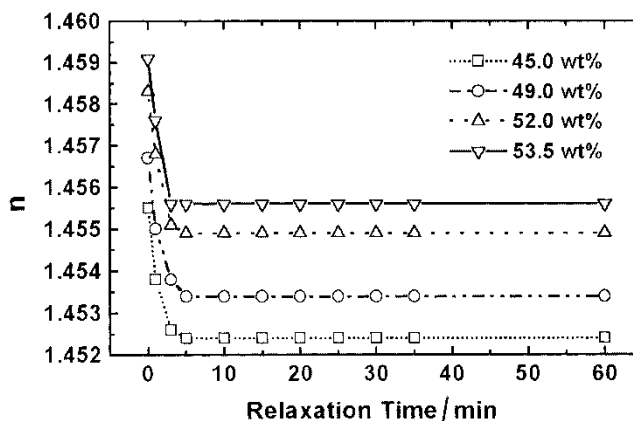


Figure 9. Variation of the mean refractive index during the relaxation process.

refractive index during the relaxation (less than 0.5%) and change in the mean refractive index ceases after $t_r = 5$ min. Therefore, n may be treated as a constant during the relaxation and it is suggested that only the variations of P and $\sin \varphi$ are related to the variation of λ_{\max} . When $t_0 < t_r < t_1$ (stage I), the angle θ between the direction of the average helix axes and the film surface is less than 82° and is increased during the relaxation; this means that the angle φ is smaller than 90° , figure 10(a), and increases with increasing t_r . Therefore, λ_{\max} shifts to longer wavelengths with increasing

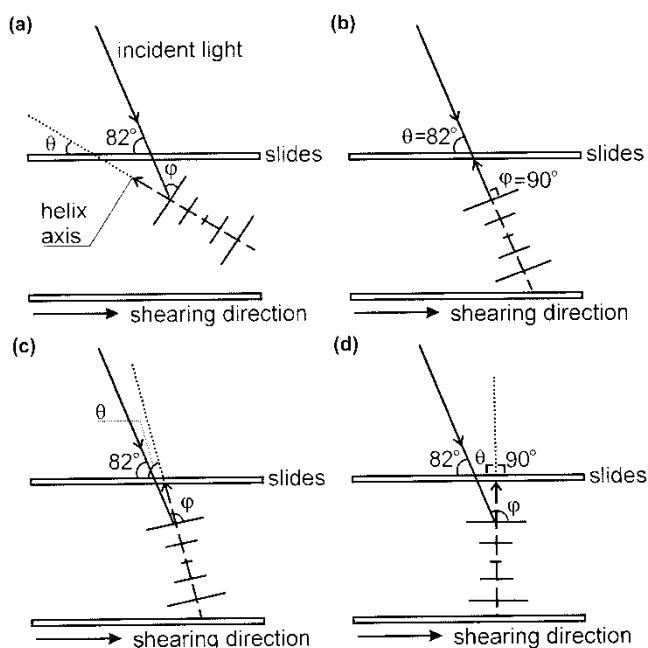


Figure 10. Schematic representation of the variation of the helix axis direction during the relaxation process of the oriented solution films: (a) $t_r < t_1$, (b) $t_r = t_1$, (c) $t_1 < t_r < t_2$ and (d) $t_r > t_2$.

relaxation time in this stage. When $t_r = t_1$, the angle θ becomes 82° , figure 10(b), which means that $\varphi = 90^\circ$ and $\sin \varphi = 1$, and the λ_{\max} is increased to the maximum value. When $t_1 < t_r < t_2$ (stage II), the angle θ becomes greater than 82° , which means that the angle φ is larger than 90° , figure 10(c), and $\sin \varphi$ is again less than 1. This results in the shift of λ_{\max} towards shorter wavelengths with increasing relaxation times.

The helix axes in all domains reorganize and align in increasingly ordered arrangement by effect of the combined action of the twist and anchoring powers; so the shape of the reflection peak in the spectra becomes sharper and the intensity of the spectra increases (as shown in figure 5 and the table). When $t_r = t_2$, the cholesteric order with planar texture is restored and the average direction of the helix axes is perpendicular to the film surface, figure 8(d). In stage III, $\theta = 90^\circ$, $\varphi = 82^\circ$ and $\sin \varphi = \sin 82^\circ$, figure 10(d); therefore, the shift of λ_{\max} results from the increase of helical pitch P in this stage. It is well known that the definition of pitch length is the distance along the helix axis in which the director is rotated to 360° . The pitch may be influenced by two factors; (a) the distance between neighbouring 'molecular layers' and (b) the twisting angle between the molecular directors of neighbouring 'molecular layers' (angle α). Therefore, the increasing of P may result from the increase of the distance between neighbouring 'molecular layers' or the decrease of the angle α , or both. After a relaxation time of close to 1 h, the λ_{\max} shifts completely back to the

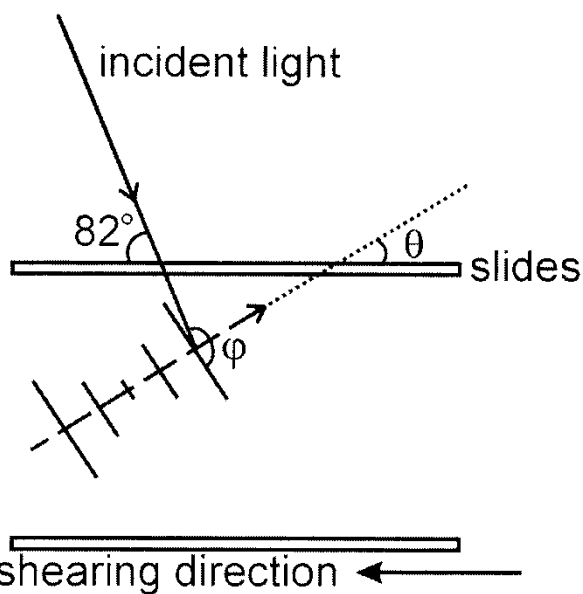


Figure 11. Schematic representation of the helix axis direction when the solution film in figure 10(a) is rotated to 180° .

original position before shearing (see the table), which suggests that the cholesteric order is completely recovered.

When the angle θ is less than 90° (stages I and II), the average direction of the helix axis is oblique to the film surface; the angle φ between the incident light and the 'molecular layers' of the cholesteric phase will be changed if the oriented solution film is rotated (changing the position, see figure 1) and the λ_{\max} will also be shifted. If the position shown in figure 10(a) is rotated from 0° to 180° , φ is changes from $<90^\circ$ to $>90^\circ$ (figure 11) and $\sin \varphi$ is changes accordingly from less than 1 to 1, then less than 1 again. Therefore, λ_{\max} will be changed with the sample rotation. When $t_r \approx t_2$, the angle θ is about 90° , the angle φ is a constant of 82° , and λ_{\max} is a constant with rotation of the sample, figure 10(d).

Figure 12 shows the variation of λ_{\max} with the sample rotation of the oriented solution film after relaxation for 1 minute. It can be seen that λ_{\max} varies markedly with the sample rotation angle and the variation ($\Delta\lambda_{\max}$) is 25 nm when the cholesteric LC oriented solution film is rotated by 360° . It can be calculated that the angle θ is about 63° when the relaxation time is 1 min. $\Delta\lambda_{\max}$ decreases with increasing relaxation time and is only 4 nm when the oriented solution film is relaxed for 10 min, which means that the angle θ is 88° and the helix axis is almost perpendicular to the film surface. Therefore, the change of the helix axis direction is the main factor (the increase of θ) that cause the shift of the λ_{\max} in stages I and II. After a long relaxation time, the average direction of the helix axes is perpendicular to the film surface and is unchanged

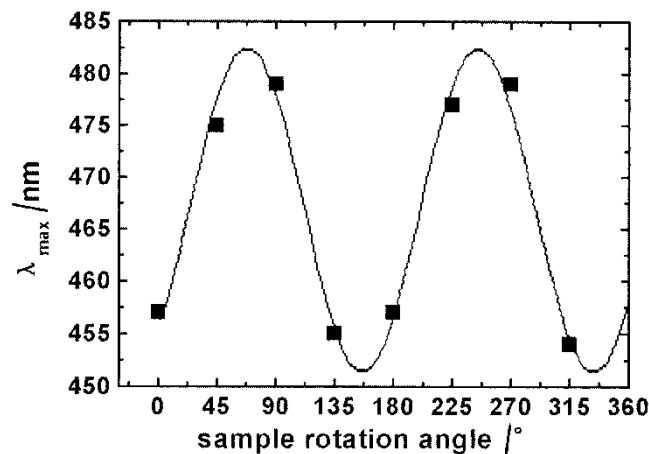


Figure 12. Variation of λ_{\max} vs. the sample rotation angle of the frozen 50.5 wt% (E-CE)C/AA oriented solution film [(E-CE)C/PAA film], after relaxation for 1 min; solid squares are obtained by experiment and the line is simulated.

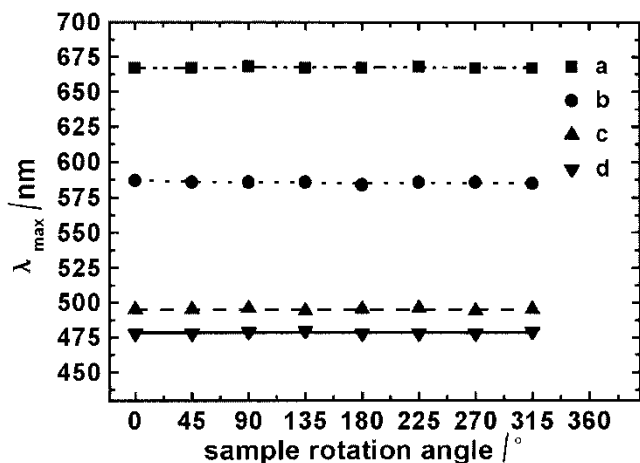


Figure 13. Curves of λ_{\max} vs. sample rotation angle for the (E-CE)C/AA oriented solution films of different concentration, after relaxation for 60 min: (a) 46, (b) 48, (c) 50.5 (d) 51.5 wt %.

with further increase in relaxation time. Therefore, the λ_{\max} is not changed with rotation of the sample (figure 13).

Structural variation during the relaxation is also confirmed by the TEM observation of the frozen (E-CE)C/AA oriented solution films—the (E-CE)C/PAA films—

for different relaxation times. In our previous studies, the planar texture exhibits a periodic lamellar structure by TEM; this is formed as alternating dark and bright striations, when the cutting direction is parallel to the helix axes, and the distance between neighbouring lamella is equal to half the pitch length [11]. Similar structures have been observed in other cholesteric LC phases. It is generally believed that the morphology of the lamellar structure results from the periodicity of molecular orientation and characterizes the cholesteric structure [32–34]; it is never found in the isotropic phase [33].

Figure 14(a) shows the morphology of the oriented film after relaxation for 3 s; the cholesteric structure has been destroyed and there is no any periodic lamellar structure, confirming that the cholesteric structure is transformed to the nematic state by shearing. However, some weak lamellar structures are formed after the oriented solution film is relaxed for 1 min, figure 14(b), which indicates that the cholesteric structure has begun to recover. On increasing the relaxation time, the cholesteric order is gradually restored and the periodic lamellar structure is increasingly more regulated. Figure 14(c) shows that the periodic lamellar structure becomes very ordered after a relaxation time of 10 min. The original cholesteric order is completely restored

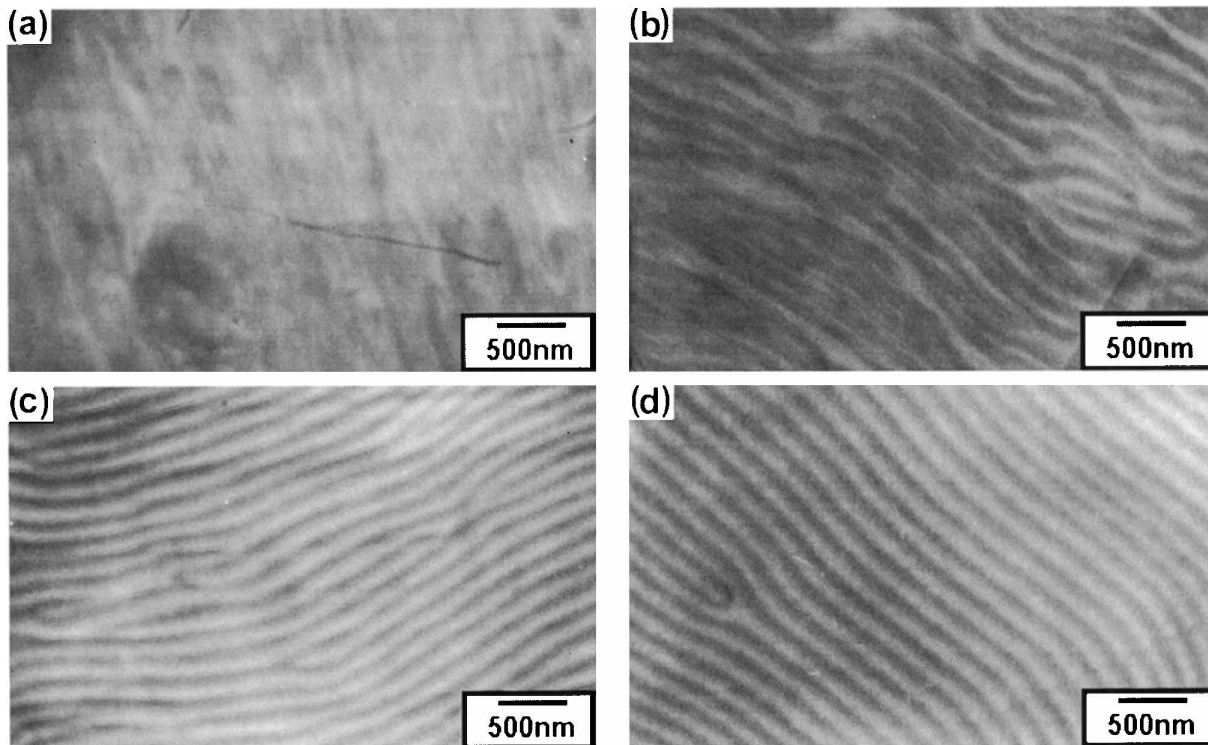


Figure 14. TEM micrographs of the frozen 50.5 wt % (E-CE)C/AA oriented solution film after relaxation for (a) 3 s, (b) 1 min, (c) 10 min and (d) 56 min; the sections are perpendicular to the shearing direction.

after the oriented solution film has been relaxed for about 56 min, Figure 14 (d). Furthermore, the periodicity of the lamellar structure (half pitch) is about 150 nm ($t_r=1$ min), 159 nm ($t_r=10$ min) and 165 nm ($t_r=56$ min), respectively, which confirms that the pitch gradually increases during relaxation.

4. Conclusions

The cholesteric structure with planar molecular arrangement of solution films is destroyed by shearing, and transforms to the nematic phase. After cessation of shearing, a banded texture is quickly formed, but is unstable and disappears after several minutes. The shape of the reflection peak in the spectrum then becomes very sharp within a short time (about 10 min), and becomes increasingly sharper with the relaxation time. Both the position of the λ_{\max} and the intensity of the reflection peak in the spectrum are increased with relaxation time, which indicates that the (E-CE)C chains are gradually reformed to cholesteric order with the planar texture during the relaxation, driven both by the twist power and the homogeneous anchoring power. The average direction of the helix axes is firstly varied from oblique to normal to the solution film surface, in which the molecular arrangement with planar texture is reconstructed. Then, the helix axes are held normal to the film surface and the pitch alone increases continually until the cholesteric order is completely restored after a long time of relaxation (about 56 min).

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References

- [1] REY, A. D., 1996, *Rheol. Acta*, **35**, 400.
- [2] MARSH, D. G., and POCHAN, J. M., 1973, *J. chem. Phys.*, **58**, 2835.
- [3] MARSH, D. G., POCHAN, J. M., and ERHARDT, P. F., 1973, *J. chem. Phys.*, **58**, 5795.
- [4] ASADA, T., TODA, K., and ONOGI, S., 1981, *Mol. Cryst. liq. Cryst.*, **68**, 231.
- [5] POCHAN, J. M., and MARSH, D. G., 1972, *J. chem. Phys.*, **57**, 1193.
- [6] HONGLADAROM, K., and BURGHARDT, W. R., 1998, *Rheol. Acta*, **37**, 46.
- [7] DERFEL, G., 1983, *Mol. Cryst. liq. Cryst. Lett.*, **92**, 41.
- [8] REY, A. D., 1996, *Phys. Rev. E*, **53**, 4198.
- [9] ONOGI, S., and ASADA, T., 1980, *Rheology*, edited by G. Astarita, G. Marrucci, and G. Nicolais, (New York: Plenum), p. 127.
- [10] DE VRIES, H., 1951, *Acta Crystallogr.*, **4**, 219.
- [11] JIANG, S. H., and HUANG, Y., 1993, *J. appl. polym. Sci.*, **50**, 607.
- [12] HUANG, Y., YANG, Y. Q., and PETERMAAN, J., 1998, *Polymer*, **39**, 5301.
- [13] WANG, L., and HUANG, Y., 2002, *Macromolecules*, **35**, 3111.
- [14] BURGHARDT, W. R., and FULLER, G. G., 1990, *J. Rheol.*, **34**, 959.
- [15] WANG, J., and LABES, M. M., 1992, *Macromolecules*, **25**, 5790.
- [16] RITI, J.-B., and NAVARD, P., 1998, *J. Rheol.*, **42**, 225.
- [17] JIANG, S. H., HUANG, Y., and SHEN, J. R., 1995, *J. macromol. Sci., polym. Phys. Ed.*, **B34**, 357.
- [18] NISHIO, Y., and TAKAHASHI, T., 1984, *J. macromol. Sci.-Phys.*, **B23**, 483.
- [19] NAVARD, P., 1986, *J. polym. Sci., polym. Phys. Ed.*, **24**, 435.
- [20] FRIED, F., and SIXOU, P., 1988, *Mol. Cryst. liq. Cryst.*, **158B**, 163.
- [21] HARRISON, P., NAVARD, P., and CIDADE, M. T., 1999, *Rheol. Acta*, **38**, 594.
- [22] ZHAO, C. T., CAI, B. L., XU, M., and ZHANG, G. L., 1998, *Macromol. Chem. Phys.*, **199**, 1485.
- [23] PISKEN, S. J., NOLDENAERS, P., BERGHMANS, S., and MEWIS, J., 1992, *Macromolecules*, **25**, 4759.
- [24] GLEESON, J. T., LARSON, R. G., MEAD, D. W., KISS, G., and CLADIS, P. E., 1992, *Liq. Cryst.*, **11**, 341.
- [25] LARSON, R. G., and MEAD, D. W., 1992, *Liq. Cryst.*, **12**, 751.
- [26] HORIO, H., ISHIKAWA, S., and ODA, K., 1985, *J. appl. polym. Sci., appl. polym. Symp.*, **41**, 269.
- [27] MARRUCCI, G., 1985, *Pure appl. Chem.*, **57**, 1545.
- [28] MARSANO, E., CARPANETO, L., and CIFERRI, A., 1989, *Mol. Cryst. liq. Cryst.*, **177**, 93.
- [29] MAFFETTONE, P. L., GRIZZUTI, N., and MARRUCCI, G., 1989, *Liq. Cryst.*, **4**, 385.
- [30] RUTHS, M., STEINBERG, S., and ISRAELACHVILI, J. N., 1996, *Langmuir*, **12**, 6637.
- [31] JANIK, J., TADMOR, R., and KLEIN, J., 1997, *Langmuir*, **13**, 4466.
- [32] BUNNING, T. J., VEZIE, D. L., LLOYD, P. F., HAALAND, P. D., THOMAS, E. L., and ADAMS, W. W., 1994, *Liq. Cryst.*, **16**, 769.
- [33] HUANG, Y., LOOS, J., YANG, Y. Q., and PETERMANN, J., 1998, *J. polym. Sci., polym. Phys.*, **36**, 439.
- [34] BOUDET, A., MITOV, M., BOURGERETTE, C., ONDARCUHU, T., and CORATGER, R., 2001, *Ultramicroscopy*, **42**, 9657.