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Textures and defects in lyotropic liquid crystals of ethyl-cyanoethyl cellulose

Y. Huang[a]; J. R. Shen[b]
[a] Laboratory of Cellulose and Lingocellulosics Chemistry, Guangzhou Institute of Chemistry, Guangzhou, China [b] Department of Polymer Materials Science and Engineering, South China University of Technology, Guangzhou, China

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Textures and defects in lyotropic liquid crystals of ethyl-cyanoethyl cellulose

by Y. HUANG*

Laboratory of Cellulose and Lingocellulosics Chemistry,
Guangzhou Institute of Chemistry, Academia Sinica, P.O. Box 1122,
Guangzhou 510650, China

and J. R. SHEN

Department of Polymer Materials Science and Engineering,
South China University of Technology, Guangzhou 510641, China

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Textures and defects in ethyl-cyanoethyl cellulose [(E-CE)C]/dichloroacetic acid (DCA) cholesteric liquid crystalline solutions and in (E-CE)C/polyacrylic acid (PAA) composites were observed and studied by polarizing microscopy and electron microscopy. The existence of χ, λ and τ disclinations were observed in the mesophase with disk-like and band-like textures. Pairs of disclinations with different signs were also found in the mesophase with the band-like texture. Domain walls were observed in (E-CE)C/PAA composite films with cholesteric order by TEM. The orientation of polymer chains in the vicinity of the core of the disclinations is discussed.

1. Introduction

Textures and defects of liquid crystalline polymers (LCPs) are one of the most interesting topics in LCP research. The textures and defects are known very well for small molecular liquid crystals [1], but the arrangement and the orientation of LCP chains in the liquid crystalline state are still not well understood. Most LCPs can be crystallized and their morphology and structure in the semi-crystalline solid is closely related with the structural features of the liquid crystalline state before crystallization. The crystalline structures of some LCPs have been reported [2]. However, the relationship of the processing, the structures and the properties is far from understood for most of the LCPs.

There are many small scale structures found in textures of LCPs. These structures are very complicated for cellulose and its derivative liquid crystalline phase because it is cholesteric. For example, lyotropic liquid crystals of ethyl-cyanoethyl cellulose show multi-texture behaviour [3]; that is, the texture varies with the concentration and the temperature. To study the textures and the defects of liquid crystals, polarizing microscopy is one of the most useful methods, in which they are directly observed. In many cases, however, some fine structure of LCPs which cannot be clearly observed by optical microscopy can be seen by electron microscopy [4–6].

The liquid crystalline state has to be frozen if electron microscopy is used to study the structures of the liquid crystalline phase. In the polypeptide/vinyl monomer and cellulose derivative/vinyl monomer systems, the cholesteric liquid crystalline state can be solidified by polymerizing the solvent [7–9]. Ethyl-cyanoethyl cellulose [(E-CE)C] can form a cholesteric liquid crystalline phase in acrylic acid (AA) and (E-CE)C/polyacrylic acid (PAA) composites with a cholesteric structure can be prepared by polymerizing the AA [10, 11]. The structure of the cholesteric liquid crystalline phase of (E-CE)C may be studied by observing the morphology and structure of the (E-CE)C/PAA composites with electron microscopy. In this report, the textures and defects of cholesteric liquid crystalline phase in (E-CE)C/dichloroacetic acid (DCA) and (E-CE)C/acrylic acid (AA) solutions are studied by polarizing microscopy and electron microscopy.

2. Experimental

The (E-CE)C was prepared by the reaction of ethyl cellulose and acrylonitrile. The molecular formula is as follows:

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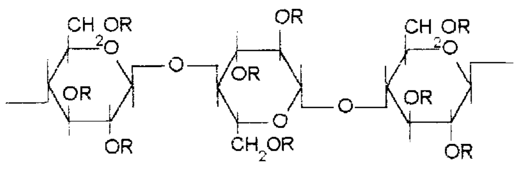
* Author for correspondence.



$R = H, CH_2CH_3, CH_2CH_2CN$

The degree of ethyl-substitution was about 2·1 and for cyanoethyl- about 0·43. The molecular weight of (E-CE)C M_n, measured by a gel permeation chromatography (GPC)(HPLC, Waters-209), was 7×10^4. The AA and the DCA were chemically pure reagents and the AA was distilled at 50°C in vacuum before use.

The (E-CE)C was mixed with DCA at room temperature and the solutions were sealed in a test-tube. The solutions were laid aside at room temperature for over one week, after which they were heated at 50°C for about 10 h. The solution was then sandwiched between a microscope slide and a cover glass to form a solution film about 10–30 μm in thickness and the specimen sealed with solid wax. The textures and defects of the cholesteric liquid crystalline phase were observed by polarizing microscopy (Leitz, Orthoplan POL, Germany) after the specimen had been stored at room temperature for 24–48 h.

The (E-CE)C was mixed with AA and some initiators at room temperature and the mixture was allowed to sit for one week to form a homogeneous system. The transparent solutions were sandwiched between two glass slides to form the solution films which were about 0·1–1·0 mm in thickness. The specimen was sealed with solid wax and stored in the dark until use. The photopolymerization was conducted by inserting the specimen into the ultraviolet chamber with a 250 W high intensity mercury arc lamp until complete polymerization to form (E-CE)C/polyacrylic acid (PAA) composites. The solutions for photopolymerization contained 2 wt % benzophenone as photo initiator (with respect to the solvent AA) and 0·5 wt % *N,N*-methylaniline as promoter. The (E-CE)C/PAA composites were sectioned to super-thin films after they were embedded in epoxy resin and observed by a transmission electron microscope (TEM) (Jeol 100 CX-II, Japan).

3. Results and discussion

Cholesteric liquid crystals consist of layers of ordered molecules and can be generally looked upon as a spontaneously twisted nematic phase and considered to be locally uniaxial about the director. However, the twist removes the local cylindrical symmetry and the structure should be looked upon as a continuously twisted biaxial phase [11]. The defects in cholesteric liquid crystals can result from the singularity (non-continuity) of the local director of the layers and the singularity of the axis of helices. The rotation axes of the axial disclinations in cholesteric liquid crystals can be parallel to the axis of the helices, which is called the χ disclination. The disclination, in which the rotation axis is normal to the axis of the helices, can be called disclination λ, in which the rotation axis is parallel to the local director, and disclination τ, in which the rotation axis is perpendicular to the local director. The disclination χ simply results from the singularity of the local director and is similar to the axial disclination in nematic phase. The disclination λ results from the singularity of the axis of the helices instead of the singularity of local directors because the rotation axis is parallel to the local director. The disclination τ is a singular line of the axis of the helices and the local directors. The disclination χ can take any shape but a disclination λ or τ has to be a straight line [12].

In the (E-CE)C/DCA cholesteric liquid crystalline solutions, the mesophase shows multi-texture behaviour, exhibiting different textures with variation of concentration [3]. When the liquid crystalline phase is non-continuous, the disk-like texture with concentric, bright and dark rings, or helix, appears in the solution. When the liquid crystalline phase just becomes continuous, the band-like texture with parallel bright and dark strips and the pseudo-isotropic texture generally appear in the solution [13]. With further increase in concentration, the planar texture with vivid colours can form in the solution, the colour of the solution shifting from red to blue with increasing concentration [14]. The mesophase shows a polygonal texture at very high concentration.

χ disclinations are similar to the nuclei or the filaments in a nematic phase and may be built by the same process. In the beginning of the formation of (E-CE)C/DCA cholesteric liquid crystalline solutions with increasing concentration, the mesophase is non-continuous and generally shows a disk-like texture [3]. The χ disclination with a strength $S = 1$ exists in the disk-like texture (see figure 1). The layers of ordered polymer chains, which are normal to both the film surface and the radial directions, are bent to form concentric rings or helix. Figure 2 gives the configuration of the director in the vicinity of the core of the disclination in the disk-like texture. Indeed, there are

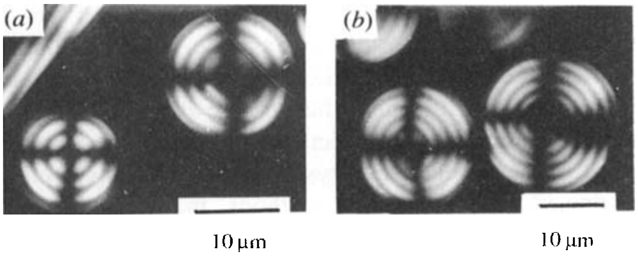


Figure 1. Polarized light micrographs of the 28·6 wt % (E-CE)C/DCA liquid crystalline solution, (*a*) concentric rings and (*b*) helix.

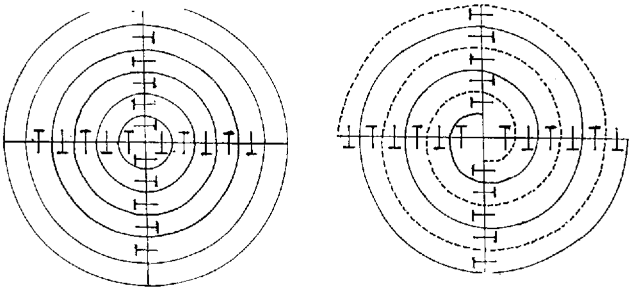


Figure 2. The configuration of the director in the vicinity of the core of the disclination in the disk-like texture.

splay, twist and bend deformations in the disk-like texture. The orientation direction of polymer chains rotate with the pitch of the cholesteric along the radial directions, that is, the axes χ. The orientation direction of the polymer chains in the layers of ordered polymer chains on the circle with the same diameter, however, is splayed when polymer chains are normal to the film surface and bent when they are parallel to the film plane. There is a singularity in the centre of the disk-like texture.

In the band-like texture, many kinds of disclinations can be observed. The disclination λ and the disclination τ are often found. Figure 3 shows the disclination $\lambda(1/2)$ and $\lambda(-1/2)$ observed with a microscope with crossed-polarizers, and the scheme of local directors is given. Those two kinds of disclinations are often observed in the interface regions between the liquid crystalline and isotropic phases. The $\tau(1/2)$ and $\tau(-1/2)$ disclination may also be observed in some interface regions (see figure 4). In the $\lambda(1/2)$ disclination, the rotation axis is parallel to the local director but in the $\tau(1/2)$ disclination, it is perpendicular to it. Therefore, there is no singularity in the $\lambda(1/2)$ disclination but a singularity with high energy exists in the $\tau(1/2)$ disclination.

In general, the λ and τ disclinations appear in the regions neighbouring the isotropic phase, which suggests that the appearance of these two kinds of disclination requires high energy. In the biphasic solution with the anisotropic and isotropic phases, the interface region between phases has high energy. In order to decrease the energy of the interface, the non-continuous phase can become spherical so that there is the smallest interfacial surface between two phases. In the interfacial region with an arc shape, there is sufficient energy to form disclinations within the liquid crystalline phase because of the existence of the interfacial tension. The λ and τ disclinations with strength of 1/2 or $-1/2$ depend on topological constraints, which are imposed by boundary conditions of the mesophase. The strength of disclinations is generally $-1/2$ when the mesophase is a continuous phase and 1/2 when the mesophase is a non-continuous phase.

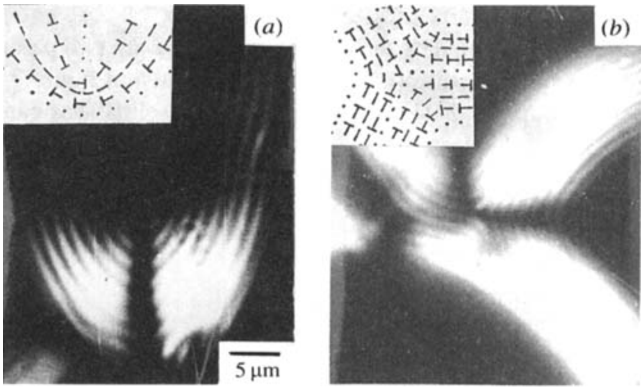


Figure 3. λ disclinations in the (E-CE)C/DCA cholesteric liquid crystalline solutions with the strength $S=(a)$ 1/2 and (b) $-1/2$.

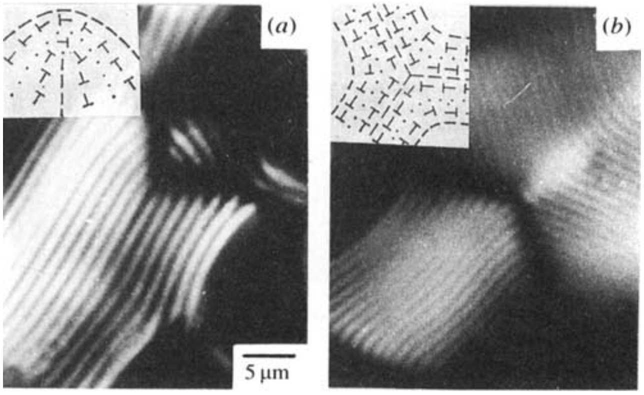
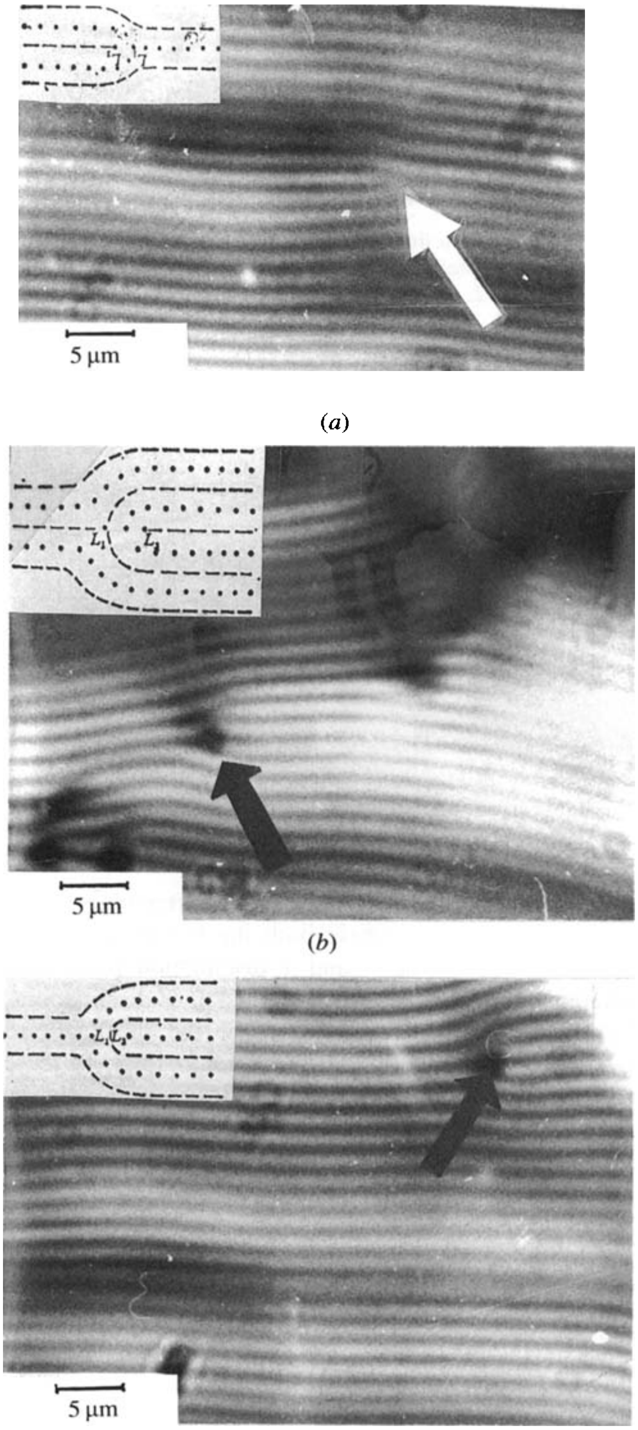


Figure 4. τ disclinations in the (E-CE)C/DCA cholesteric liquid crystalline solutions with the strength $S=(a)$ 1/2 and (b) $-1/2$.

The χ disclination which is composed of a λ, τ disclination pair with different signs is often observed in the liquid crystalline phase with the band-like texture. Figure 5 gives some λ and τ disclination pairs with different signs. Figure 5 (a) shows a pair of disclinations, $\chi \rightarrow \tau^{+} + \lambda^{-}$, (b) shows a pair of the disclinations, $\chi \rightarrow \tau^{-} + \tau^{+}$ and (c) is the $\chi \rightarrow \lambda^{+} + \lambda^{-}$ pair. In these pairs of disclinations, the normal distance of the rotating axes of the disclinations τ and λ with different signs must be times of a constant $d=P/4$, where P is the pitch of the cholesteric phase. $d=P/4$ in figure 5 (a), and $d=P/2$ in (b) and (c). The existence of these λ and τ disclination pairs with different signs should decrease the energy of the system. In theory, the deformation energy of one disclination which exists in isolation approaches infinity [15]. Consequently, the existence of the disclination pairs with different signs are often observed. The pairs of the disclinations observed above are stable if the axial direction is not changed in the cholesteric liquid crystalline phase.

Groups of disclinations or pairs of disclinations can be observed in some areas of the liquid crystalline phase. In figure 6, two pairs of disclinations, $\chi \rightarrow \lambda^+ + \lambda^-$, exist together (indicated by the arrow). Also there are two pairs of $\chi \rightarrow \tau^- + \tau^+$ disclinations together shown in figure 7. Such groups of disclinations or pairs of disclinations can be found in many areas of the liquid crystalline phase, which suggests that such arrangements lower the elastic energy of the system.

In some (E-CE)C lyotropic liquid crystalline systems, the pitch is very small and the disclinations in the cholesteric liquid crystalline phase cannot be observed directly by polarizing microscopy. However, the characteristics of cholesteric order and disclinations of the cholesteric liquid crystalline phase can be frozen-in by fast polymerization of the solvent in (E-CE)C/vinyl monomer liquid crystalline solutions. By using a transmission electron microscope, it can be found that the disclination and pairs of disclinations similar to those observed by polarizing microscopy exist in the (E-CE)C/polymer composites with cholesteric order. Figure 8 shows a disclination with strength 1/2 in the (E-CE)C/polyacrylic acid (PAA) composite with cholesteric order observed by



(*a*)

(*b*)

(*c*)

Figure 5. Pairs of disclinations with different signs in the (E-CE)C/DCA cholesteric liquid crystalline solutions, (*a*) $\chi \rightarrow \tau^+ + \lambda^-$, (*b*) $\chi \rightarrow \tau^+ + \tau^-$ and (*c*) $\chi \rightarrow \lambda^+ + \lambda^-$.

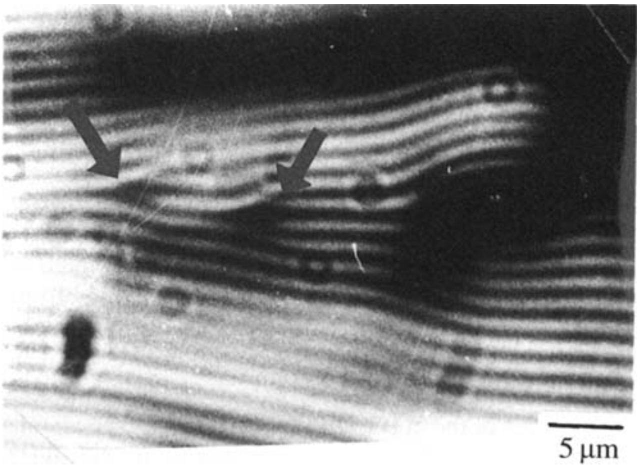


Figure 6. Two pairs of $\chi \rightarrow \lambda^+ + \lambda^-$ disclinations in the (E-CE)C/DCA cholesteric liquid crystalline solution.

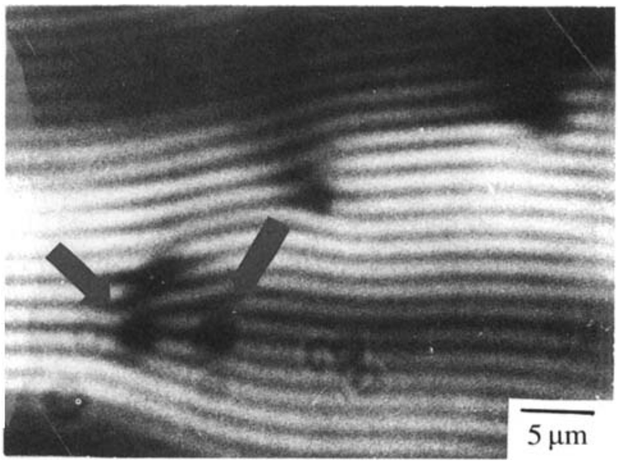


Figure 7. Two pairs of $\chi \rightarrow \tau^+ \tau^-$ disclinations in the (E-CE)C/DCA cholesteric liquid crystalline solutions.

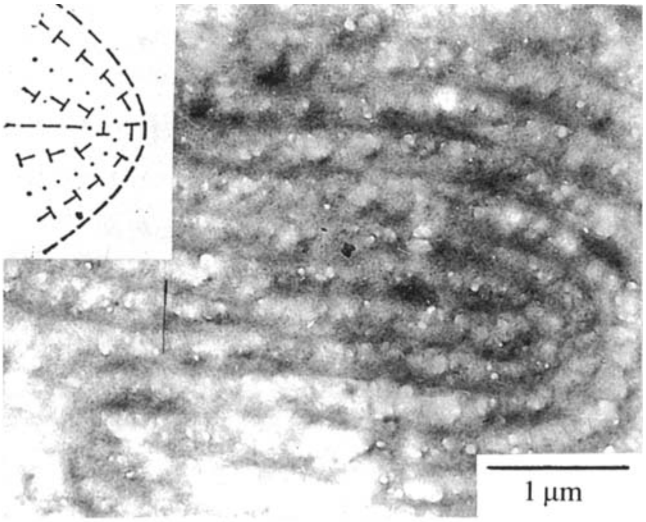


Figure 8. The τ disclination with strength $S = 1/2$ in the (E-CE)C/PAA composites observed by TEM.

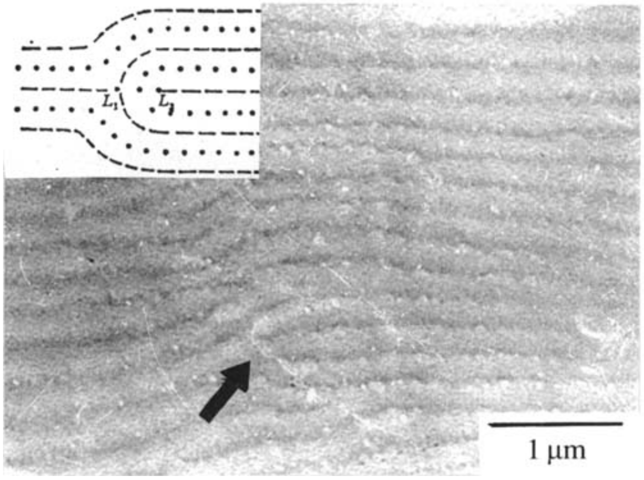


Figure 9. The pair of $\chi \rightarrow \tau^+\tau^-$ disclination in the (E-CE)C/PAA composites observed by TEM.

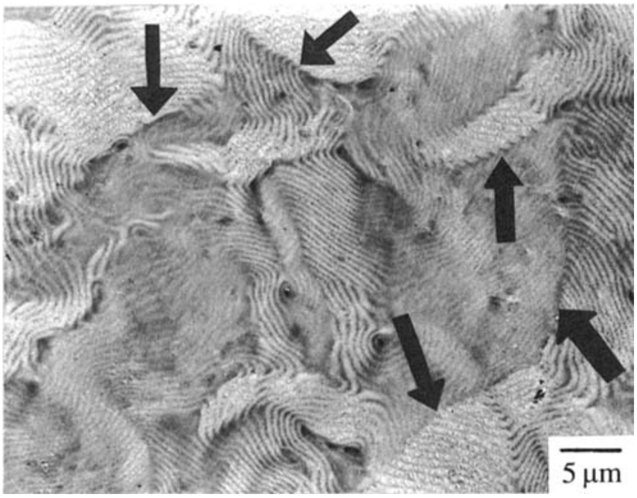


Figure 10. TEM micrograph of the (E-CE)C/PAA composite with 40 wt % (E-CE)C.

the electron microscopy. Other kinds of disclinations are also observed in the composites. In many cases, moreover, pairs of the disclinations (see figure 9) and groups of disclinations can be observed. The results observed by transmission electron microscopy, therefore, completely agree with those observed by polarizing microscopy.

The domain walls can also be observed from (E-CE)C/PAA composite films with cholesteric order by TEM. Many domain walls are observed in figure 10 (indicated by the arrow) and the lamellation beside the wall is very clear, which means that polymer chains in domains beside the wall are very well ordered. The orientation direction of the cholesteric helix axes is the same within the domains. The directions of the lamellae on both sides of the wall, however, are obviously different, which implies that the orientation of the cholesteric helix is changed across the wall. From the variation of the direction for the lamellation, the direction of the helicoidal axes can rotate through any angle inside or outside the film surface plane across the domain wall.

The disclinations observed above by electron and optical microscopy have been observed in small molecule cholesteric liquid crystals [16]. The structural characteristics of the lytropic cholesteric liquid crystalline phase of cellulose derivatives, therefore, can be considered to be the same or similar to those of small molecule cholesteric liquid crystals.

4. Conclusions

In the (E-CE)C/DCA cholesteric liquid crystalline solutions, the mesophase generally shows a disk-like texture when it is non-continuous at relatively low concentration, and a χ disclination with strength $S = 1$ can be observed. The existence of λ and τ disclinations in the interfacial region between the liquid crystalline and the isotropic phases can be observed. Within the mesophase with a band-like texture, pairs of τ and λ disclinations with different signs are often observed and the normal distance of the rotating axes of the τ and λ disclinations with different signs in the pairing must be a constant distance, i.e. a multiple of $P/4$.

In the (E-CE)C/acrylic acid (AA) cholesteric liquid crystalline solutions, the cholesteric order can be frozen in the (E-CE)C/PAA composites by polymerizing the AA. TEM can be used to study the morphology and structure of the composites to reveal the features of the cholesteric order. Many disclinations are observed in the composites by TEM, which are similar to those observed by polarizing microscopy in the (E-CE)C/DCA systems.

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