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Fine structure in cholesteric fingerprint texture observed by scanning electron microscopy

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Summary

The fine structure in some cholesteric fingerprint textures of cyanoethyl chitosan (CNCS)/acrylic acid solution and photo-solidified CNCS/polyacrylic acid composite film was studied using scanning electron microscopy (SEM), small angle light scattering (SALS) and polarizing optical microscopy (POM). Permanganic etching was developed to reveal the cholesteric liquid crystalline textures in the composite films. A schematic model was presented to explain this kind of fine structure. The directors within each cholesteric molecular layer did not orient in nematic-like order, but varied their orientation by an ill-defined period.

Introduction

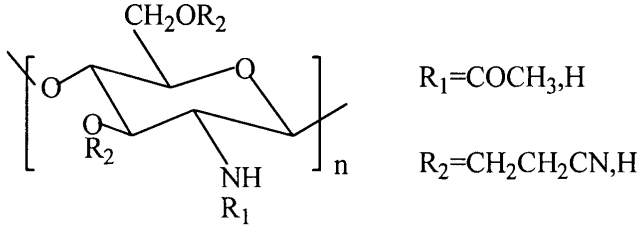
Most of the natural polymers such as polypeptides, DNA, RNA, cellulose derivatives and so on can form cholesteric lyotropic liquid crystal (1,2). The techniques for investigating cholesteric structure and morphology are generally restricted to polarizing optical microscopy (POM), X-ray diffraction and small angle light scattering (SALS). Optical examination hints at a wealth of detail smaller than the wavelength of light which is invariably present in cholesteric lyotropic liquid crystalline polymers. Therefore, the electron microscopy and atomic force microscopy have been used to conduct these structure and morphology investigations (3-5). The periodic lamellar structure in the cholesteric phase was observed. Nevertheless, the preparation of specimen for these techniques was ultra-microtome. The reason for forming the contrast in ultrathin slices was still under debate, and the sectioning artifacts arising from shrinkage and deformation stress in ultrathin slices were difficult to avoid. On the other hand, permanganic etching technique have proved to be a fruitful preparation technique of specimen for scanning electron microscopy (SEM) in the study of both conventional crystalline polymers such as polyolefine (6, 7) and nematic liquid crystalline polymers such as aromatic polyesters (8) with less artifacts and easier explanation of surface topography. In this article, permanganic etching was developed to investigate the structure of cholesteric order which is much more complicated than nematic order.

Chitin and most of its derivatives can form cholesteric lyotropic liquid crystals in the appropriate solvents (9,10). A typical texture observed in their mesophase under POM was well-known fingerprint texture which presented regular retardation lines. Actually the retardation lines are not always successive. Besides that the disclinations often interrupt

the lines (11), the local discrete or disorder of retardation lines in some fingerprint texture was frequently encountered, which made the explanation of morphology complicated. These delicate details of fingerprint texture have been revealed by using permanganic etching and SEM in this paper.

Experimental

O-Cyanoethyl chitosan (CNCS) was synthesized by the reaction of chitosan (degree of deacetylation 84%; molecular weight, 2.34 X 10^6) and acrylonitrile at room temperature using alkali preswollen method (12). The chemical structure is as follows:



Scheme 1. The chemical structure of cyanoethyl chitosan

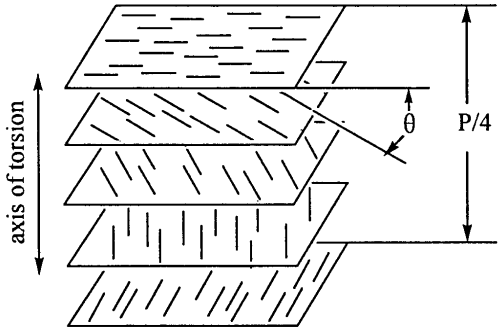
The degree of substitution was 1.59, measured by a HERAEUS CHN-O-RAPID elemental analyzer.

15wt% CNCS solution in acrylic acid (AA) (including 5% glycol diacrylate as crosslinker and a small amount water which was necessary for solvation) was prepared and kept in darkness for a week. The solution was then sandwiched between two small pieces of glass slides, and the textures were observed by an OLYMPUS polarizing optical microscope. Subsequently the same solution was photopolymerized to form solidified CNCS/polyacrylic acid (PAA) composite film. It was shown by checking the film that the liquid crystalline textures kept unchanged after photopolymerization. One of the glass slides was removed to expose the surface of the film. After that, the films were etched by a solution of 1% $KMnO_4$ in 2:1 mixture of H_2SO_4 (conc.) and H_3PO_4 (85%) for 30 minutes at room temperature. A HITACHI S520 scanning electron microscope was used for the observation of this film.

Results and discussion

CNCS solution has a distinctive cholesteric helicoidal structure with a spontaneous twist of the molecular orientation around an axis vertical to director. Robinson and co-workers have extensively characterized the structure of the PBLG mesophase (13). The model proposed by Robinson is shown diagrammatically in scheme 2. In this model, there are a number of layers of nearly molecular thickness. In each layer, the polymer molecules orient preferentially in one-dimensional nematic order. The direction of orientation of the molecules rotates with a small constant angle in the same manner from one layer to the next.

When the layers lie on the solution surface, i.e. the helical axes are perpendicular to the solution surface, a pseudo-isotropic texture will be seen by POM. But when the layers are vertical to the solution surface, i.e. the helical axes are parallel to the solution surface,



Scheme 2. Schematic representation of polymer chain orientation for cholesteric liquid crystals, after Robinson (ref. 13)

the fingerprint texture can be seen if the pitch is larger than the resolution of POM. A typical fingerprint texture of CNCS/AA solution is shown in Figure 1a. The characteristics of cholesteric texture can also be frozen-in by fast photo-polymerization of the solvent in CNCS/vinyl monomer liquid crystalline solutions. Figure 1b demonstrates the fingerprint texture on the solidified composite films observed by SEM, which had very similar appearance as optical texture in Figure 1a, but had completely different forming mechanism.

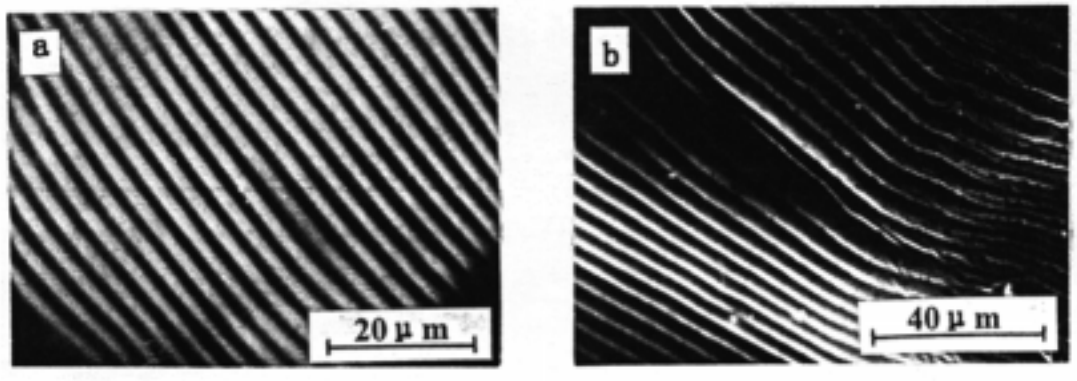
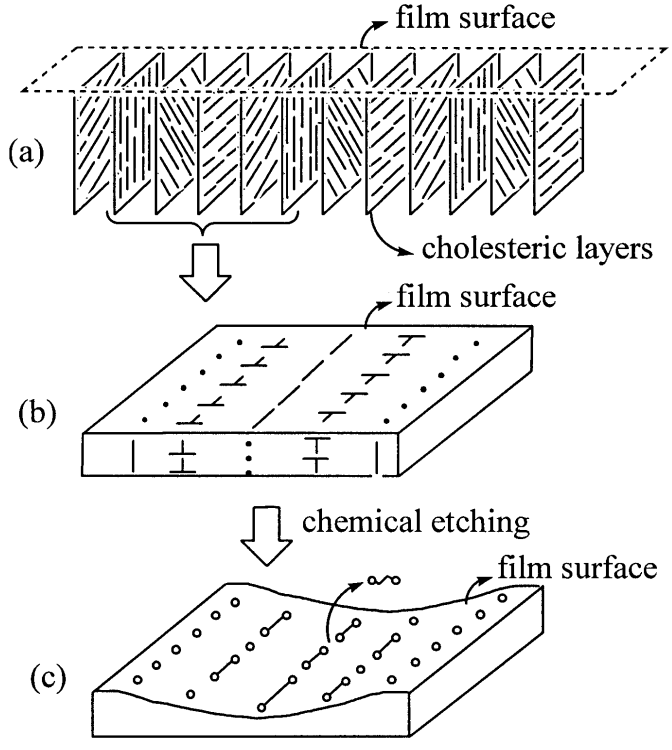


Figure 1. Micrographs of fingerprint texture. (a) POM micrograph of 15% CNCS/AA solution; (b) SEM micrograph of CNCS/PAA film (after permanganic etching)

When the solidified films with fingerprint texture were rendered for permanganic etching, it gave good selectivity between layers due to different molecular arrangement. The molecules which lay on the surface of the film were rather easier to be attacked, because of chain scission and solvation of the resulting fragments. On the other hand, the molecules which were normal to the surface of the film were rather more resistant to degrade, because of an array of oxidized end groups (usually --COOH). Consequently obvious topography in SEM measurement can be noted. Scheme 3 is schematic representation of this mechanism. According to this mechanism, the dark streaks

indicated the regions where molecular directors were parallel to the surface and the bright streaks indicated the regions where directors were vertical to the surface. It must be noticed that it was in the opposite way in POM photography, i.e., the dark streaks illustrated the regions where directors were vertical to the surface and the bright streaks illustrated the regions which directors were parallel to the surface but neither to polarizer nor to analyzer. It implies that the dark streaks under POM will be bright under SEM, vice versa.

From Figure 1b, it can also be noticed that there were two regions with rather different resolution, which were on the bottom left and on the top right respectively. The latter region presented better resolution, but some cracks and holes can be observed. The variation may be explained by the different depth of etching on different regions even though in the same specimen. However, it is certain that on both regions there were no interested fine structure along the direction of layer lines that will be discussed later.



Scheme 3. Model of the mechanism for permanganic etching of CNCS cholesteric phase. (a) The arrangement of layers in fingerprint texture of CNCS/PAA composite film; (b) The director map of the film; (c) Schematic description of the film after etching. The circles represent oxidized end groups. A chain scission is seen detaching itself from the film surface after being cut by the etchant

Sometimes more details can be noticed in fingerprint texture. A phenomenon which was usually observed was the overlap of two fingerprint domains with different orientation direction and perhaps different pitch, shown in Figure 2. Normally the two fingerprint domains were in different layers in thickness, for instance one lay close to the upper glass slide, and the other lay on the vicinity of the lower glass slide. Nevertheless, this phenomenon did not relate to the fine structure of fingerprint texture. It was simply the superposition of two typical textures.

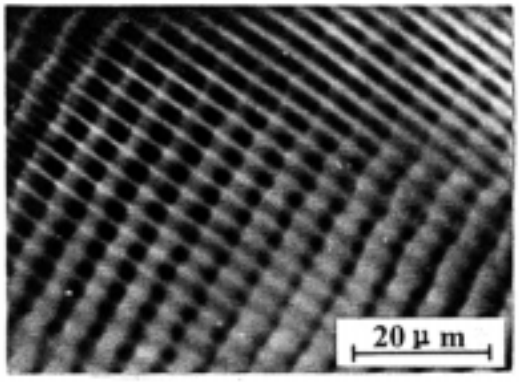


Figure 2. POM micrograph of 15%CNCS/AA solution, showing the superposition of two typical fingerprint domains

Another phenomenon on which this article focuses was shown in Figure 3a. The retardation lines in some fingerprint textures were not continuous. Some periodic variations occurred along the retardation lines. SALS technique was used to prove the presence of fine structure. The SALS determination of the same specimen demonstrated a four-spot scattering pattern. (Figure 3b). Two sharp dots in smaller angle with stronger intensity can be used to calculate the average pitch $\overline{P}$ according to the equation [14] as follow:

$$n\lambda = \overline{P} \cdot \sin\theta_{max}$$

where n is interference order; λ, the wavelength of the laser (632.8nm); θ_{max}, scattering angle in maximum intensity. The average pitch in Figure 3 calculated both from POM and SALS was about 7 μ m.

It is of interest to notice that another two weak and diffuse scattering spots appeared in larger angle of equatorial reflection (strictly speaking, there was a small angle departure from equatorial reflection). From the two spots, a periodic space of about 1 μ m can be evaluated on the basis of the equation described previously.

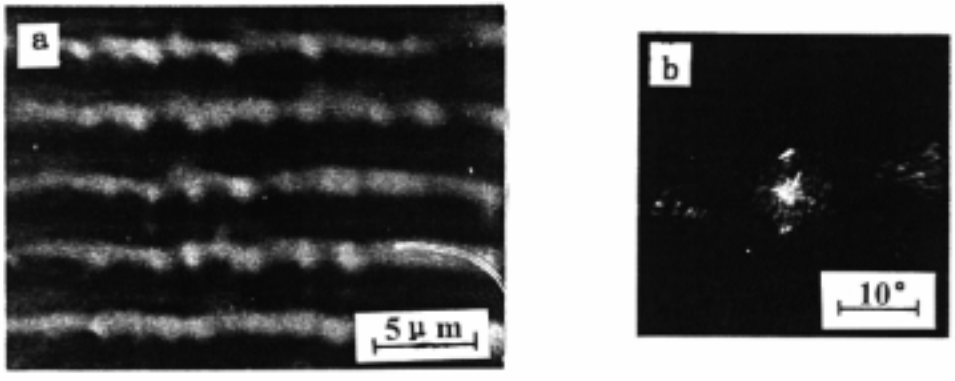


Figure 3. Fine structure of some fingerprint texture. (a) POM micrograph of 15% CNCS/AA solution, showing the discrete retardation lines; (b) SALS pattern of the same specimen as (a), showing both the meridianal and equatorial reflections

Because of limited resolution, no further details can be seen from POM photography. SEM was used to reveal the delicate details of fingerprint texture. The results were shown in Figure 4.

From Figure 4a, regular distinct layer lines can be seen. The reason of forming contrast was mentioned previously (see also Scheme 3). The permanganic etching concurrently caused the contrast along layer lines to take place. Figure 4b further reveals the fine detail. The black and white region along the direction of layer lines represented again the concave and convex region respectively. According to the mechanism of permanganic etching, a model of forming mechanism of fine structure in fingerprint texture is illustrated in Scheme 4. It implied that the directors twisted in two ways, i.e. along the axes and within the layer planes. The former way was regular and long range order (space was about 3.5 μ m); and the latter way was rather irregular and ill-defined short range order (space was about 1 μ m measured both by SALS and SEM). In these textures, the polymer molecules in each layer did not orient in nematic-like order, but rotated continuously. Hence it can be looked upon as that there were twist dislocations within layers. However the forming reason is still remained to approach.

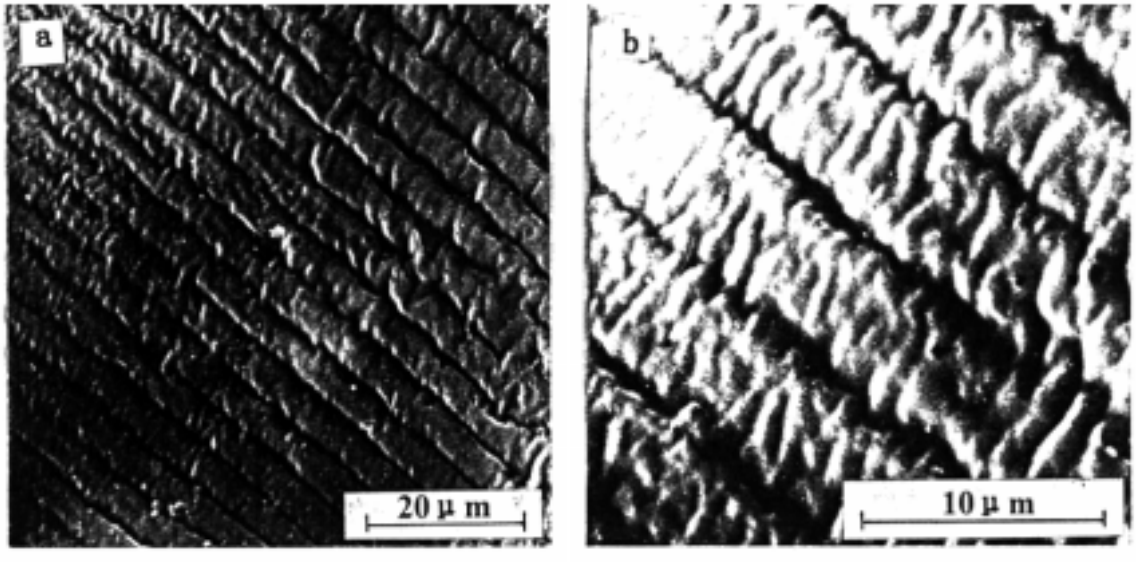
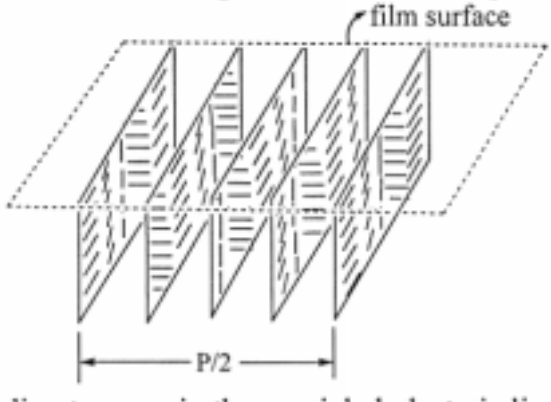


Figure 4. SEM micrographs of fine structure in fingerprint texture of CNCS/PAA composite film which was prepared from the same solution as Figure 3. (a) and (b) of this figure are in different magnification of same specimen



Scheme 4. The director map in the special cholesteric liquid crystalline texture

Conclusion

The foundation of cholesteric structure which is well known is the torsion of molecular layers in which directors orient preferentially in only one dimensional order. Now a novel characteristic of some cholesteric texture of chitin derivative was shown. The directors within the layers changed their orientation continuously to form a rather complicated director map.

Acknowledgement

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