

## CHOLESTERIC LIQUID CRYSTALLINE CHARACTER ON THE SURFACE OF CHITOSAN/POLYACRYLIC ACID COMPOSITES\*

Yan-ming Dong\*\*, Yu-song Wu and Mian Wang

Department of Materials Science & State Key Laboratory for Physical Chemistry of Solid Surfaces,  
Xiamen University, Xiamen 361005, China

**Abstract** The cholesteric liquid crystalline structure in chitosan/polyacrylic acid composite films was studied by surface techniques. A periodical lamellar-like structure was observed in the permanganic acid etched film surface by both scanning electron microscopy (SEM) and atomic force microscopy (AFM), instead of the thumb-print texture which can be detected with polarized optical microscopy. It is suggested that the periodical lamellar-like structure is induced by the etching selectivity between cholesteric layers due to different molecular arrangement on the film surface. Four kinds of perpendicular disclinations, i.e.  $\chi \rightarrow \tau + \lambda^+$ ,  $\chi \rightarrow \lambda^- + \tau^+$ ,  $\chi \rightarrow \tau^- + \tau^+$  and  $\chi \rightarrow \lambda^- + \lambda^+$ , were found in the composite films from SEM observations. The smallest periodicity of lamellar-like structure (equals to half pitch) is 20~40 nm measured with AFM.

**Keywords** Chitosan, Cholesteric order, Liquid crystalline, Fingerprint texture, Lamellar structure, SEM, AFM

### INTRODUCTION

Chitosan is a semi-rigid chain polymer which can form lyotropic liquid crystals in appropriate solvents<sup>[1]</sup>. As most natural polymeric liquid crystals, the mesophase of chitosan has been found to have an internal twist structure and is classified as cholesteric. A typical cholesteric texture, the so called thumb-print texture, can be observed in concentrated chitosan solutions. The technique for investigating cholesteric texture is generally restricted to polarizing optical microscopy. However, the scale of the texture is often at the limit of the optical microscope.

Thomas<sup>[2]</sup>, Wood<sup>[3]</sup> and Hudson<sup>[4]</sup> developed the technique of crystal lamellar decoration which enables high resolution visualization of liquid crystalline texture. After crystallization, lamellae can be readily imaged with good contrast in thin film using bright field transmission electron microscope (TEM), revealing a map of the molecular director field in the nematic mesophase of a thermotropic aromatic polyester. Chen *et al.*<sup>[5]</sup> observed many kinds of disclinations in the nematic mesophase of another aromatic polyester with a RuO<sub>4</sub> staining technique by TEM. The pattern of the decorating crystal lamellae for polyester mesophase was also revealed using an etching technique in scanning electron microscope (SEM) by Ford<sup>[6]</sup>, Windle<sup>[7]</sup> and Dong<sup>[8]</sup>.

For lyotropic polymers, electron microscopy can not be used for the direct observation of mesophase in solution because of the evaporation of solvents in the vacuum of the electron microscope, but the liquid crystalline texture can be investigated after solidification of the solvents by polymerization. Tsutsui<sup>[9]</sup>, Nishio<sup>[10]</sup> and Huang<sup>[11]</sup> studied some polypeptide/alkene monomer systems and some cellulose derivative/alkene monomer systems with this technique. Huang<sup>[12]</sup> also used atomic force microscopy (AFM) to observe the texture of the cellulose derivative/polyacrylic acid composites.

\* This work was supported by the National Natural Science Foundation of China (No. 29974023) and Natural Science Foundation of Fujian (No.29910006).

\*\* Corresponding author: Yan-ming Dong (董炎明), E-mail: ymdong@jingxian.xmu.edu.cn

Received May 4, 2000

This aim of contribution is to exploit the power of both electron microscopy and atomic force microscopy in the study of the organization in chitosan liquid crystals, of which there have been relatively few studies.

## EXPERIMENTAL

Chitosan with a degree of deacetylation of 84% (determined by an acid-base titration method) and a viscosity average molecular weight of  $7.4 \times 10^5$  was supplied by Xiamen Second Pharmaceutical Factory (China).

15 wt% chitosan solution in acrylic acid (including 5% benzoin ethyl ether as initiator and a small amount of water which is necessary for solvation) was prepared and kept in darkness for 5 days. The resulting homogeneous solution was then sandwiched between two small pieces of glass slides and photopolymerized to form solidified chitosan/polyacrylic acid (CS/PAA) composite films with a thickness of about 0.5 mm. One of the glass slides was removed to expose the surface of the films. Then, the films were etched in a solution of 1%  $\text{KMnO}_4$  in 2:1 mixture of  $\text{H}_2\text{SO}_4$  (concn.) and  $\text{H}_3\text{PO}_4$  (85%) for different time (30 min for shallow etching and 60 min for deep etching) at ambient temperature.

The films were observed under an Olympus polarized optical microscope (POM) directly and also by using a Hitachi S-520 SEM after sputtering with gold on the film surface and a Digital Instruments Nanoscope IIIa AFM directly or after sputtering with gold or coating with carbon.

## RESULTS AND DISCUSSION

### Observation of Thumb-Print Texture with POM

The critical concentration for lyotropic liquid crystal formation from chitosan/acrylic acid solutions was determined to be 8 wt%. The solutions were isotropic for concentration lower than 8 wt% and biphasic in the concentration of 8 wt%~19 wt%. So the 15 wt% CS/PAA composite films exhibited cholesteric order in mesophase domains. It is well known that cholesteric liquid crystals consist of ordered molecular layers which spontaneously twist. When the planes of layers are vertical to the film surface, a pattern with alternative black and white streaks (i.e. retardation lines) presents under POM (see Fig. 1). It is so called the thumb-print texture.

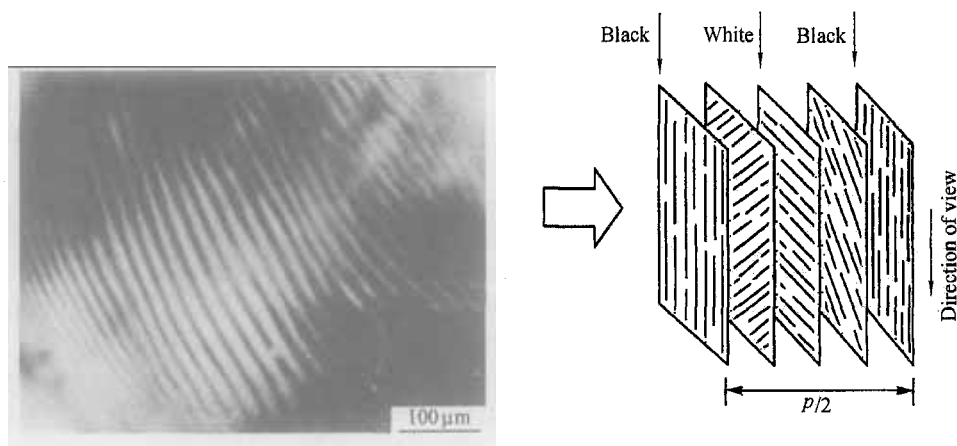


**Fig. 1** Schematic representation of thumb-print superstructure and polymer chain orientation for cholesteric liquid crystal solution of chitosan, where  $p$  is the pitch

The periodicity of the streaks in thumb-print texture corresponds to the half pitch of the cholesteric phase, therefore the pitch of CS/PAA composites can be measured with POM. The values of pitch varied from a few microns to several tens of microns. In some domains, it can be seen that the pitch varied continuously from one side to the other, the half pitch at the lower right corner was about 4  $\mu\text{m}$  and the half pitch at the upper left corner

was about 40  $\mu\text{m}$  (see Fig. 2a). From Fig. 2(b), the half pitch at the lower right corner was about 4  $\mu\text{m}$ , but the pitch at the upper left corner was too small to be distinguished, and was regarded as so called planar texture.

There are three reasons for the variation of pitch. First, the layers may be on the tilt. The greater the degree of tilt is, the smaller the pitch that will be observed. Secondly, there were some distributions in structure parameters such as molecular weight or degree of deacetylation of chitosan. Thirdly, a so called “structure hysteresis”, i.e. some of the characteristics of crystal remain in the texture of liquid crystal phase, occurred during solvation.

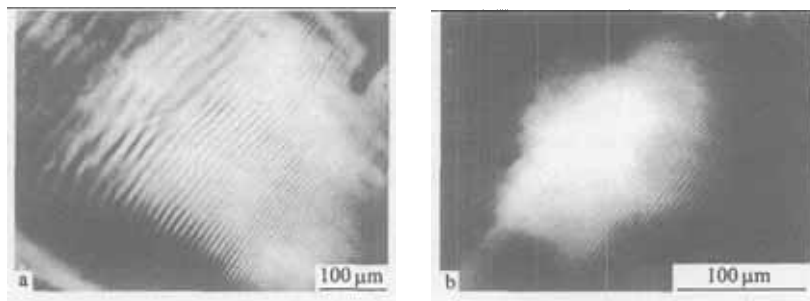


**Fig. 2** POM microphotographs of the CS/PAA composites prepared from the cholesteric liquid crystalline solution (15 wt%)

### **Observation of Lamellar-Like Structure with SEM**

Actually the structure in the scale close to 1  $\mu\text{m}$  is difficult to observe with POM. Therefore, electron microscopy was introduced. Although TEM has high resolution, the sectioning artifacts arising from shrinkage and deformation stress in ultrathin slices are difficult to avoid. On the other hand, permanganic etching technique have proved to be a reliable and fruitful preparation technique of specimen for SEM in the study of both conventional crystalline polymers such as polyolefins<sup>[13, 14]</sup> and nematic liquid crystalline polymers such as polyesters<sup>[6]</sup> with less artifacts and easier explanation of the surface topography. So in this article, permanganic etching was developed to investigate the structure of cholesteric order for chitosan. The active species in permanganic etchant is thought to be  $\text{O}_3\text{MnOSO}_3\text{H}^{[15]}$ . The etchant attacks different environments along specific pathways producing oxidized fragments, which are soluble in the liquid etchant. The resulting etched surface can then be examined by both SEM and AFM. Checking the texture of the CS/AA solution, the solidified CS/PAA composite film and the etched CS/PAA composite film with POM, it can be seen that no serious change of texture has happened after photo-polymerization and subsequent etching.

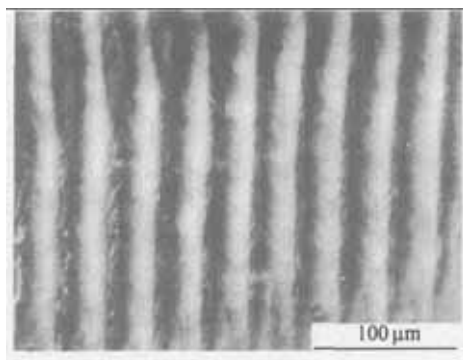


**Fig. 3** SEM microphotograph of CS/PAA composite film prepared from 15 wt% CS/AA solution, showing the typical lamellar-like structure

Figure 3 demonstrates the lamellar-like structure in the solidified composite films after permanganic etching observed by SEM. The periodicity (in the scale of few microns) of the lamellar-like structure in the composite

films coincides with the typical half pitch of the cholesteric phase measured by POM. The lamellar-like structure can therefore be regarded as the same structure named thumb-print texture observed with POM.

When the solidified films with thumb-print texture are subjected to permanganic etching, attack tends to be selective between layers due to different molecular arrangement. The chains which lie on the film surface are rather easier to access, because of chain scission, solvation of the resulting fragments and exposure of inner chains. On the other hand, the chains whose direction is perpendicular to the surface of the film are rather more resistant to degradation, because of the formation of an array of oxidized end groups (usually  $-\text{COOH}$ ) after the first attack. The lamellar-like structure therefore can be formed by this mechanism whose schematic representation is shown in Fig. 4. According to this mechanism, the "lamellae" indicate the regions where the directors are parallel to the surface. It must be noted that this has the inverse appearance to POM microstructures, i.e., the dark streaks illustrate the regions where directors are normal to the surface and the bright streaks illustrate the regions where directors are parallel to the surface (see Fig. 1, except that it happens to be parallel to polarizer or analyzer). It implies that the dark streaks under POM will be the bright "lamellae" under SEM.

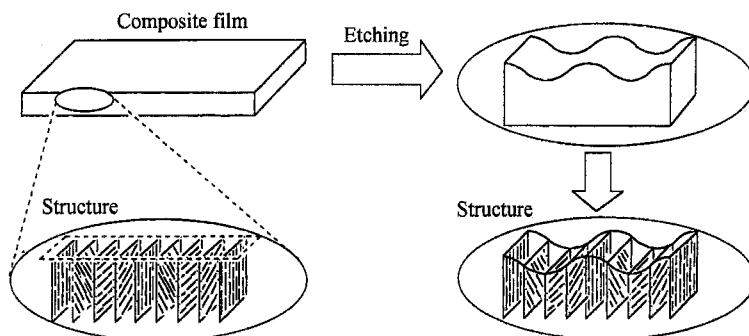


Fig. 4 The model of the mechanism for permanganic etching of CS/PAA composite films

In addition to the regular lamellar-like structure, a multi-disclination lamellar-like structure is demonstrated in Fig. 5(a). The detail of this structure is shown in Fig. 5(b). In Fig. 5(b), some pairs of perpendicular disclinations  $\chi \rightarrow \bar{\tau} + \lambda^+$  (marked by A) and  $\chi \rightarrow \lambda^- + \bar{\tau}$  (marked by B) can be found simultaneously. A more complicated multi-disclination pattern is illustrated in Fig. 5(c). Figure 5(d) is the director map for local area of Fig. 5(c).  $a_1/a_2$  is a pair of perpendicular disclinations,  $\chi \rightarrow \bar{\tau} + \tau^+$ , and  $b_1/b_2$  is another pair of perpendicular disclinations,  $\chi \rightarrow \lambda^- + \lambda^+$ .

#### Observation of Lamellar-Like Structure with AFM

Although normal SEM provides an improvement in imaging power over POM, the lamellar-like structure whose size is smaller than  $10^{-1} \mu\text{m}$  is hard to detect. Therefore AFM, an even more powerful surface microscopy, was used.

AFM is one of the scanning probe techniques which was first reported by Binnig *et al.* in 1986<sup>[16]</sup> and has been applied in the studies of polymer surface<sup>[17]</sup>. As indicated in Fig. 6, the lamellar-like structure with  $1/2p \approx 0.5 \mu\text{m}$  can be observed. The magnitude of this structure was only slightly smaller than what was observed with POM or SEM. We believe that these observations were all from one kind of structure. The height from peak to valley also can be measured to be about 50 nm. The schematic representation of mechanism of AFM determination for CS/PAA composite film is illustrated in Fig. 6.

Some smaller lamellar-like structures with  $1/2p = 20\text{--}40 \text{ nm}$  are further shown in Fig. 7. From Fig. 7(a), it can be seen that the baseline noise of uncoated surface is evident because of the flexibility of polymer chains. This situation can be improved by sputtering Au on the film surface, the result is shown in Fig. 7(b). The resolution increases obviously, but sputtering Au concurrently causes undesirable gold granules (about 5 nm) to be produced. Coating carbon instead of gold, the microstructure become more clear (Fig. 7c), because the granularity of carbon is smaller than that of gold. The height difference from local peak to valley is measured to

be about 2 nm, near 1/10 of the space of lamellae. This implies that the shallow coating of carbon (~50 nm, judged according to color) did not destroy the contrast of the image.

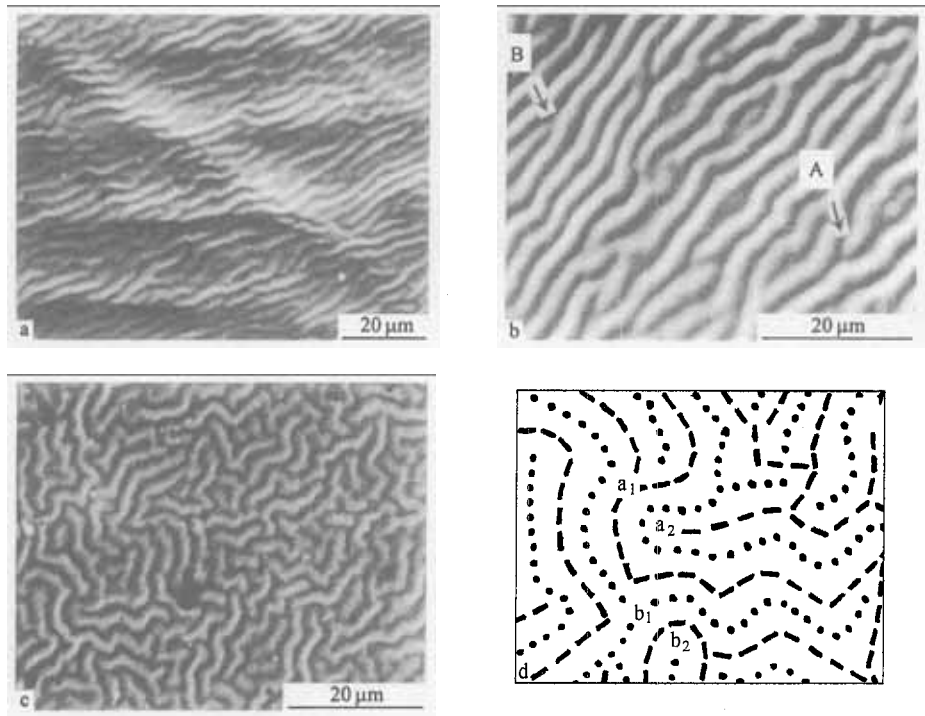


**Fig. 5** SEM microphotographs of CS/PAA composite films prepared from 15 wt% CS/AA solution, showing the multi-disclination lamellar-like structure (a), (b) and (c) were observed in the different regions of the same film. (b) is the detail of the structure of (a). (d) is the local director map of (c) (in the lower left corner). The dashes represent the directors parallel to the paper plane, while the dots represent the directors perpendicular to the paper plane.

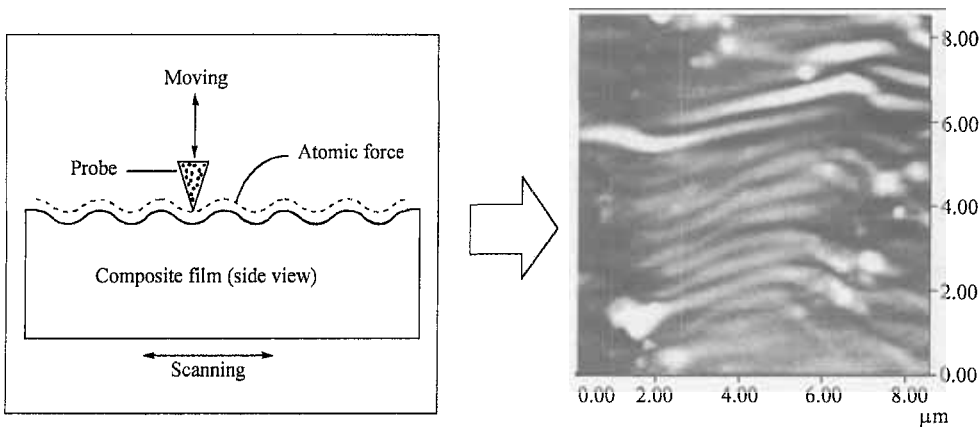


**Fig. 6** Schematic representation of AFM determination mechanism for CS/PAA composite film and resulted AFM microphotograph (two dimensional image) of the CS/PAA composite film without coating (deeply etched for 60 min)

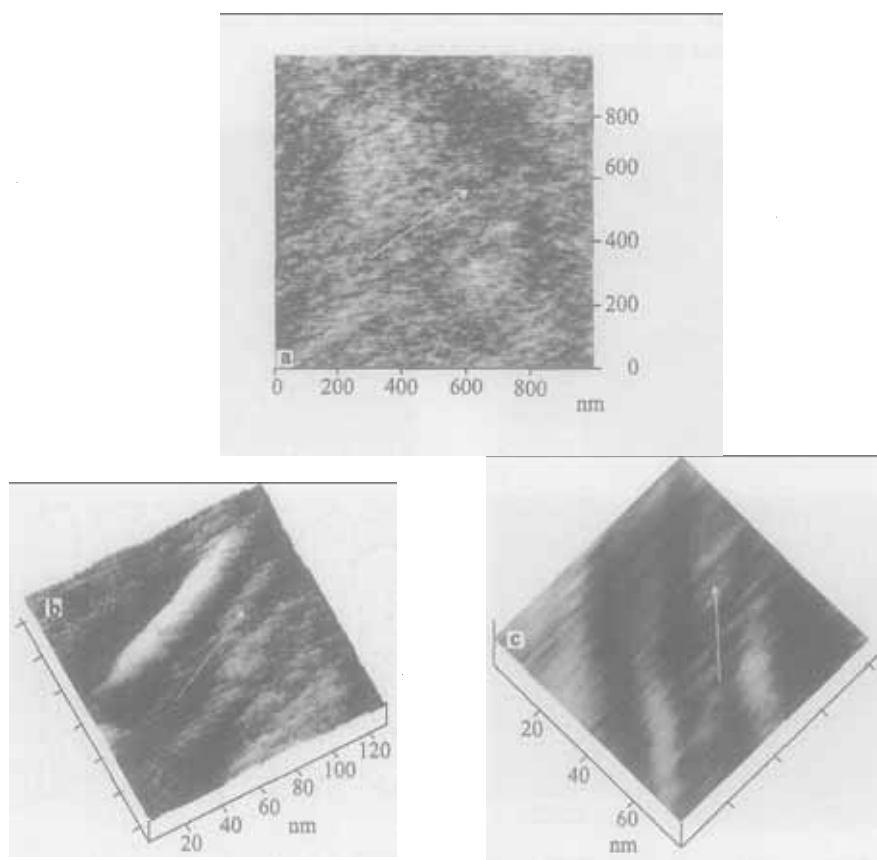


**Fig. 7** AFM microphotographs of the CS/PAA composite film (shallowly etched for 30 min) (a) without coating, two dimensional image; (b) sputtering Au, three dimensional image; and (c) coating C, three dimensional image. The arrows represent the direction of the lamellae. The bands parallel to the bottom frame with the width of about 4~5 nm are not lamellae, they are only the baseline noise.

From the results obtained in this contribution, we suggest that there are cholesteric structures in very different scales for CS/PAA composite films. Normally the thumb-print texture in the scale of  $10^0\sim10^1\ \mu\text{m}$  can be observed directly with POM. The lamellar-like structure in the scale of  $10^0\sim10^1\ \mu\text{m}$  can also be easily detected with permanganic etching and SEM technique. Further, with the help of AFM, the lamellar-like structure in the scale of  $10^1\sim10^2\ \text{nm}$  was found. Actually, the different level of structure may exist in the same film. The exposure of different level of structure depends on the deepness of etching.

**Acknowledgements** The authors thank Dr Zhao-xiong Xie for performing AFM.

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