

MORPHOLOGICAL STUDY ON THE ORIENTED CHITOSAN FILM OBTAINED FROM PRE-SHEARED LIQUID CRYSTALLINE SOLUTION IN DICHLOROACETIC ACID

Zhong-ming Hu¹, Li-heng Wu^{2*}, Da-cheng Wu³ and Shou-xi Chen¹

¹ State Key Laboratory of Polymer Physics and Chemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

² China Textile Academy, Beijing 100025, China

³ Textile College, Sichuan University, Chengdu 610065, China

Abstract The oriented chitosan films obtained from pre-sheared liquid crystalline chitosan/dichloroacetic acid (DCA) solutions were studied by means of polarized optical microscopy (POM), scanning electron microscopy (SEM), infra-red dichroism technique and wide angle X-ray diffraction (WAXD). The shear induced band texture in the film was found to correspond to the sinusoidal fibrillar microstructure along the shearing direction on the basis of POM and SEM observations. The sinusoidal fibril was found to be lying within the film plane. The model of chitosan molecular orientation in the pre-sheared film with band texture can be established assuming that the main chain orients in the shearing direction and the side group is perpendicular to the shearing direction. The WAXD azimuthal scanning at $2\theta = 20^\circ$ indicates that the (002) plane orients perpendicular to the shearing direction.

Keywords Chitosan, Morphology, Orientation, Shear induced band texture, Liquid crystalline solution

INTRODUCTION

Chitosan is the deacetylated product of chitin after alkali treatment. It has been found that chitosan and some of its derivatives can exhibit lyotropic cholesteric liquid crystalline behavior at suitable concentrations^[1, 2]. Since then, studies on the liquid crystallinity of chitosan have been carried out. Sakurai *et al.*^[3] determined the unit cell parameters of chitosan crystal and studied the molecular chain packing in the unit cell of crystal for the chitosan film prepared from the liquid crystalline solution of chitosan/formic acid. Sakurai *et al.*^[4, 5] also tried to make chitosan fibers from lyotropic liquid crystalline solutions of chitosan/formic acid which had been concentrated from dilute solutions. They found that high degree of crystallinity and orientation can be achieved for chitosan through liquid crystalline solution spinning. Some other studies have also been carried out on the mesophases of chitosan derivatives^[6-9]. For the system of chitosan/dichloroacetic acid (DCA), we have reported the influence of molar mass and degree of deacetylation of chitosan on the liquid crystalline behavior of chitosan in DCA^[10] as the well as phase transition^[11] and its kinetics of chitosan/DCA^[12].

The orientation behavior of liquid crystalline polymer (LCP) in an external field and its corresponding orientation structure are of theoretical and practical importance. The band texture formation is very common for main-chain LCP in its melt or in solution after cessation of shearing, and occasionally it can also be found in side-chain LCP^[13-16]. Recently, Harrison *et al.*^[17] presented a clear and comprehensive review on the development of understanding about the structure and evolution of band texture from studies over the last 20 years. Despite some conflicting ideas regarding the exact structure of the band texture in the literature, the band texture is a periodic variation of the director field in the direction of shear. For main-chain LCP it has been

* Corresponding author: Li-heng Wu (吴立衡)

Received July 31, 2000; Revised September 7, 2000; Accepted September 25, 2000

shown that this kind of alternating bright and dark band texture observed by POM corresponds to the periodic zigzag^[17-21] or sinusoidal^[22-25] supermolecular structures of the microfibrils aligned in parallel with each other but normal to the long dimension of the bands. The structure often contains an in-phase, out-of-plane component to the periodicity. Ding *et al.*^[26, 27] have calculated the theoretical birefringence patterns associated with these two typical supermolecular structure models and found that both models are reasonably supported by the microphotographs of polarized optical microscopy (POM). It seems to be difficult to establish what are the factors leading to the zig-zag or sinusoidal microstructure of the band texture.

In the present work, we report on the basis of POM and SEM observations the sinusoidal fibrillar microstructure of chitosan films with band texture obtained from a pre-sheared liquid crystalline chitosan/DCA solution. The orientation of the chitosan film was also studied by infra-red dichroism and wide angle X-ray diffraction (WAXD).

EXPERIMENTAL

The commercial chitosan (Kexin Chemical Company, China) was further deacetylated using 40% aqueous NaOH solution at 90°C under N₂ atmosphere. The degree of deacetylation of the resultant chitosan sample is 89% determined by FTIR, and M_n is approximately 1.6×10^6 . This chitosan sample was used in the following experiments. The critical concentration for this chitosan sample to form a liquid crystalline phase in DCA has been measured to be 10% (in weight) in our previous work^[10].

The chitosan/DCA solution of concentration 18% (weight percent) was prepared by mixing chitosan and DCA at room temperature and then sealed tightly for storage. The solution was sheared between two slides just by hand within two days following the preparation of the solution and the resultant liquid film was put into ethanol for coagulation. The film thus obtained was denoted as Fa film, which was successively neutralized with 4% aqueous NaOH solution then rinsed with deionized water till it was neutral and finally air-dried. This dried film was denoted as Fb. The obtained solid films were about 10 μm thick. The sample for wide angle X-ray diffraction (WAXD) study was a stack of about 20 pieces of films with the same pre-shearing direction.

The texture of pre-sheared chitosan films was observed with a Leitz Laborlux 12 polarizing optical microscope (POM). Small angle light scattering (SALS) experiment for the film was conducted by using a SALS instrument made in this institute with a 632.8 nm wavelength He-Ne gas laser. The Hv scattering pattern of the film was photographically recorded.

The pre-sheared chitosan film Fb was torn along the pre-shearing direction and the longitudinal fracture surface was coated with Au and then observed under a Cambridge 250 Stereo Scan scanning electron microscope (SEM).

Infra-red dichroism measurements of the shear-oriented films were made using a Nicolet 400D Fourier transform IR spectrometer with a Perkin-Elmer gold wire grid polarizer at a resolution of 2 cm^{-1} .

WAXD spectrum was recorded by using a Rigaku D/Max- γ A X-ray generator with nickel-filtered CuK α radiation. Scattered X-ray intensities were measured by a scintillation counter. The slit system was set at DS/RS/SS = 0.5°/0.15 mm/0.5°. Scans for the pure chitosan film Fb were conducted along the equator and meridian in the θ geometry with the pre-shearing direction being vertical. The scan for azimuthal diffraction was taken at the 2θ angle at which the maximum diffraction peak appeared. The azimuthal scan range is 0–180° from meridian through equator at a speed of 8 degree/min.

RESULTS AND DISCUSSION

The critical concentration of the chitosan sample used here to form a liquid crystalline phase in DCA has been found to be 10% (in weight) in our previous work^[10]. The 18% chitosan/DCA solution exhibits band texture after cessation of shearing as observed by POM under crossed polarizers. Figure 1(a) shows the POM microphotograph of the band texture in the film Fa at the position of the shearing direction parallel to the direction of polarizer. The band spacing was found to be about 1 μm . The SALS Hv pattern for the band texture shown in

Fig. 1(a) gives a typical grating diffraction pattern with two scattered lobes normal to the bands, which indicates the formation of a periodic structure aligning along the shearing direction after the cessation of pre-shearing. The bands appear to be in pairs and the number of bands is changed when the film specimen is rotated relative to the polarizers. Figure 2 shows the POM microphotographs of the pre-sheared film Fa under crossed polarizers when the film is rotated to different angles relative to the orthogonal position. In the latter case the shearing direction is parallel to the polarizing direction of the polarizer or the analyser. In the orthogonal position the paired bands appear as fine black ones and the band spacing is about $1\text{ }\mu\text{m}$ on average, as found in Fig. 2(a). By rotating the film specimen with respect to the crossed polarizers, each paired band merges into one gradually (from Fig. 2a to Fig. 2c). At a certain angle, about 28° as shown in Fig. 2(c), every two adjacent bands have equal spacing, while the number of bands becomes half of that at the orthogonal position. Comparing this experimental observation with the theoretical birefringence images for the sinusoidal model calculated by Ding *et al.*^[26, 27], the microstructure associated with the shear-induced band texture in the chitosan film can be ascertained as a sinusoidal structure rather than a zig-zag one. The maximum angular divergence between the local director and the shearing direction is about 28° .

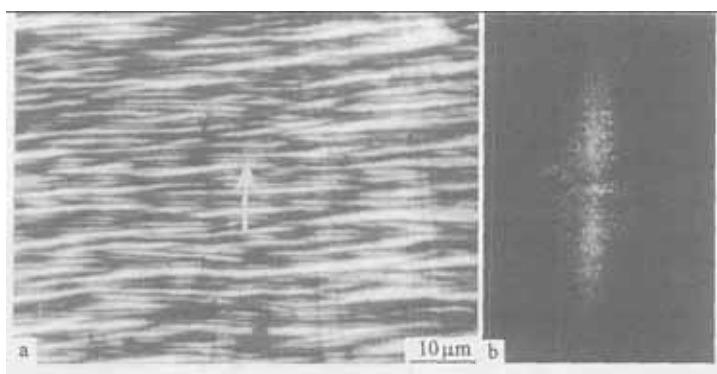


Fig. 1 (a) POM micrograph of the band texture in the film Fa with the shearing direction parallel to the polarizer direction and (b) corresponding SALS Hv pattern, the arrow indicates the shearing direction

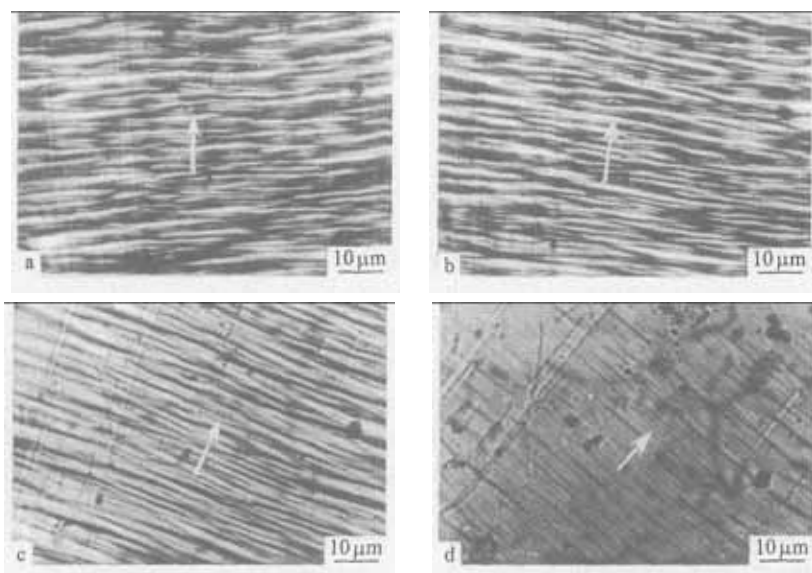


Fig. 2 POM microphotographs of the pre-sheared film Fa under crossed polars when the film is rotated at different angles relative to the orthogonal position of shearing direction which is parallel to the polarizer direction, (a) 0° , (b) 10° , (c) 28° and (d) 45° , the arrows indicate the shearing direction

In order to obtain further morphological information of the pre-sheared chitosan film with band texture, SEM observation was performed on the fracture surface of Fa film specimen torn along the pre-shearing direction. The SEM observations were made at different angles to the fracture surface of the film, which is illustrated schematically in Fig. 3. In Fig. 3(a), the crosstie-like structure spreading on the fracture surface along the shearing direction indicates that the sinusoidal fibrils lie approximately in the plane of the film. From Fig. 3(b), the regular pleated structure consisting of periodic sinusoidal fibrils running in the direction of pre-shearing is clearly seen. In Fig. 3(c) with higher magnification than Fig. 3(a) and 3(b), the periodic sinusoidal fibrils can be seen more clearly. The morphology observed does not seem to contain the contribution of an in-plane, out-of-plane component to the periodicity as Patnaik^[24] and Fischer *et al.*^[25] found in the films cast from lyotropic solutions. The period of the sinusoidal structure is about 2 μm measured from the SEM microphotographs in Fig. 3. This value is in agreement with that of band spacing obtained from the POM observation at the orthogonal position.

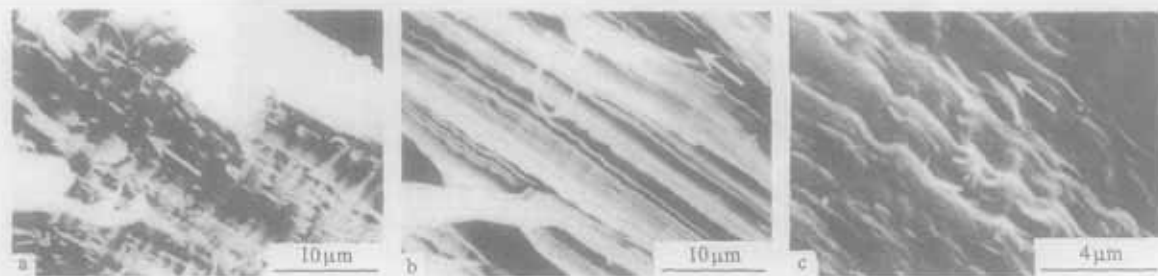
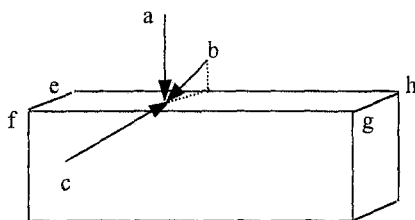


Fig. 3 SEM micrographs of the fracture surface of the film Fa torn along the shearing direction at different observation angles relative to the fracture surface e, f, g, h as indicated in the schematic (a) top view; (b) decline view; (c) side view

Figure 4 is the polarized FTIR spectra of film Fa and Fb respectively, where $A_{//}$ and $A_{\perp}$ are the absorbances for radiation polarized parallel and perpendicular to the shearing direction, respectively. Here it should be noted that the film Fa consists of chitosan-DCA complex in which the side group NH_2 of chitosan molecules is in the form of NH_3^+ , while film Fb consists of pure chitosan molecules after neutralization with dilute alkali solution^[28]. In the FTIR spectrum, the band at 1155 cm^{-1} is assigned to the bridge C—O stretching vibration^[29, 30]. The band at 1533 cm^{-1} in Fig. 4(a) and that at 1595 cm^{-1} in Fig. 4(b) are assigned to NH_3^+ and NH_2 deformation vibration^[29, 30], respectively. As can be seen in Fig. 4, the bridge C—O stretching vibration band exhibits parallel dichroism and the NH_3^+ and NH_2 deformation vibration bands exhibit perpendicular dichroism. The dichroism of the bridge C—O stretching band and NH_2 or NH_3^+ deformation bands reflects the orientation feature of chitosan main chain axis and the side group, respectively. As the transition moment of bridge C—O stretching is directed along the main chain axis of chitosan, the ratio $A_{//}/A_{\perp} > 1$ for this band indicates that the main chain saccharide ring tends to orient parallel to the shearing direction. The transition moments of NH_2 and NH_3^+ deformation are in the direction of the C—N bond and the ratios $A_{//}/A_{\perp} < 1$ for these bands indicate that the NH_2 and NH_3^+ side groups are oriented normal to the shearing direction. Now a model can be established for chitosan molecular orientation in the pre-sheared film with band texture, i.e., the main chain orients in the shearing direction and the

side group is perpendicular to the shearing direction. This orientation feature of the chitosan film is different from that of the cellulose film recovered from an anisotropic solution reported by Kamide *et al.*^[30] where the bridge C—O vibration appeared perpendicular to the shearing direction and the intramolecular hydrogen bonds were oriented parallel to the shearing direction, possibly due to the distorted helical structure of the cellulose molecular chain. The values of the dichroism function R_f can be regarded as a relative measure of the molecular orientation^[31],

$$R_f = (R - 1)/(R + 2)$$

where R is the measured dichroic ratio of a certain IR absorption band, for the bridge C—O stretching vibration band and NH_3^+ and NH_2 deformation vibration bands in films Fa and Fb are listed in Table 1. A comparison of the values of R_f for the films Fa and Fb indicates that the neutralization with 4% aqueous NaOH solution leads to a weakening of the orientation of chitosan molecule in the pre-sheared film to some extent.

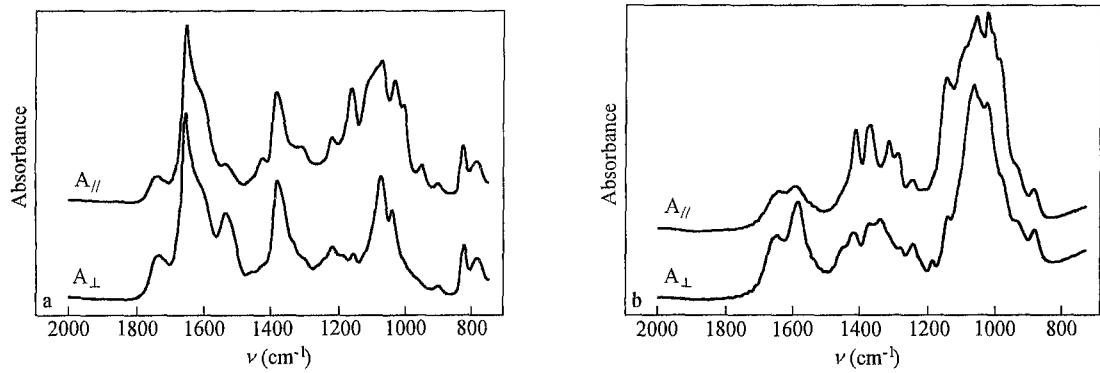


Fig. 4 Polarized FTIR spectra of the films (a) Fa and (b) Fb

Table 1. FTIR dichroism of film Fa and Fb

Film sample	$\nu(\text{cm}^{-1})$	$A_{//}$	$A_{\perp}$	Dichroism	Dichroic function (R_f)
Fa	1155	1.17	0.31	//	0.48
	1533	0.32	0.97	⊥	-0.29
Fb	1155	1.58	0.52	//	0.36
	1595	0.42	1.04	⊥	-0.25

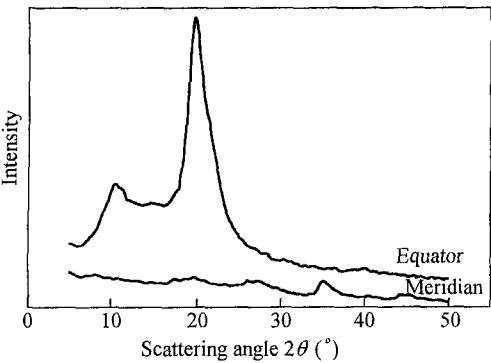


Fig. 5 WAXD equator and meridian intensity curves of the film Fb

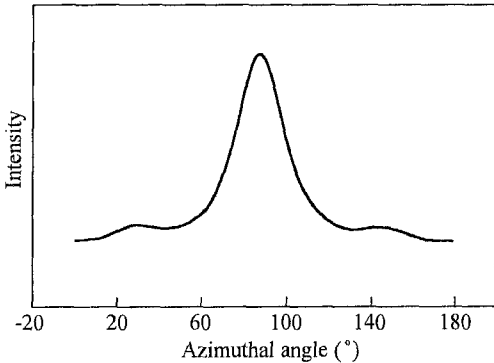


Fig. 6 Azimuthal scanning curve of the film Fb at $2\theta = 20^\circ$

The WAXD intensity curve of film Fb obtained by scanning along equator and meridian are shown in Fig. 5, which appears similar to those of a pure chitosan film of Sakurai *et al.*^[3] obtained from liquid crystalline chitosan/formic acid solution. Based on the Miller indices Sakurai *et al.* determined for the pure chitosan film they obtained, as shown in Table 4 of their paper^[3], the first equatorial reflection in Fig. 5 could be assigned as (100) and the second more distinctive equatorial reflection as (002). Figure 5 indicates that the reflection intensities of (100) and (002) at the equator are far stronger than those at the meridian. More clearly, the azimuthal scanning curve at $2\theta = 20^\circ$, as shown in Fig. 6, shows a clear reflection peak at the equator. It indicates that the (002) plane has its normal oriented perpendicular to the shearing direction. However, the peak is relatively broad and its width is about 75° estimated from the azimuthal scanning curve, which may be caused by the orientation relaxation during coagulation and drying without tension and successive neutralization processes.

ACKNOWLEDGMENT The authors wish to express their gratitude to Professor Qian, R.Y. for helpful discussions.

REFERENCES

- Ogura, K., Kanamoto, T. and Sannan, T., "Proceeding of 2nd Int. Chitin Chitosan Conf.", Japan, 1982, 39
- Terbojevich, M., Cosano, A., Conio, G., Marsano, E. and Bianchi, E., *Carbohydr. Res.*, 1991, 209: 251
- Sakurai, K., Shibano, T., Kimura, K. and Takahashi, T., *Sen-Igak Kaishi*, 1985, 41(9): T-361-T-368
- Sakurai, K., Takahashi, T. and Sen-Igak Kaishi, 1988, 44(3): 149
- Sakurai, K., Miyata, M. and Takahashi, T., *Sen-Igak Kaishi*, 1990, 46(2): 791
- Rout, D.K., Pulapura, S.K. and Gross, R.A., *Macromolecules*, 1993, 26: 5999
- Rout, D.K., Pulapura, S.K. and Gross, R.A., *Macromolecules*, 1993, 26: 6007
- Rout, D.K., Barman, S.P., Pulapura, S.K. and Gross, R.A., *Macromolecules*, 1994, 27: 2945
- Dong, Y.M. and Li, Z.Q., *Acta Polymerica Sinica*, 1998, (3): 282
- Hu, Z.M., Li, R. X., Wu, D.C., Liu, H. B., Sun, Y.S. and Wu, L.H., *Acta Polymerica Sinica*, 2000, (1): 46
- Hu, Z. M., Li, R.X., Wu, D.C., Sun, Y.S., Liu, H.B. and Wu, L.H., *Chem. J. Chinese Uni.* (in Chinese), 1999, 20(1): 153
- Hu, Z.M., Wu, L.H., Wu, D.C. and Chen, S.X., *J. Appl. Polym. Sci.*, in press
- Xu, G.Z., Wu, W., Shen, D.Y., Hou, J.A., Zhang, S.F., Xu, M. and Zhou, Q.F., *Polymer*, 1993, 34: 1818
- Zhou, Q.F., Wan, X.H., Zhu, X.L., Zhang, F. and Feng, X.D., *Mol. Cryst. Liq. Cryst.*, 1993, 231: 107
- Song, W.H., Chen, S.X., Jin, Y.Z. and Zhang, S.F., *Acta Polymerica Sinica*, 1999, (1): 80
- Hu, Z.M., Chen, S.X. and Zhang, S.F., Qian, R.Y., *Liq. Cryst.*, in press
- Harrison, P. and Navard, P., *Rheol. Acta*, 1999, 38: 569
- Kiss, G. and Porter, R.S., *J. Polym. Sci., Polym. Phys. Ed.*, 1980, 18: 267
- Hu, S.R., Xu, M., Li, J., Qian, B.G., Wang, X. and Lenz, R.W., *J. Polym., Sci., Polym. Phys. Ed.*, 1985, 23: 2387
- Chen, S.X., Jin, Y.Z., Hu, S.R. and Xu, M., *Polym. Commun.*, 1987, 28: 208
- Chen, S.X., Jin, Y.Z., Qian, R.Y. and Cai, L.Y., *Makromol. Chem.*, 1987, 188: 2713
- Donald, A.M. and Windle, A.H., *J. Mater. Sci.*, 1983, 18: 1143
- Viney, C., Donald, A.M. and Windle, A.H., *J. Mater. Sci.*, 1983, 18: 1136-1142
- Patnaik, S.S., Bunning, T.J. and Adams, W.W., *Macromolecules*, 1995, 28: 393
- Fischer, H., Miles, M.J. and Odell, J.A., *Macromol. Rap. Commun.*, 1994, 15: 815
- Ding, J.D., Feng, J. and Yang, Y.L., *Polym. J.*, 1995, 27: 1132
- Ding, J.D., Hu, Y.H. and Yang, Y.L., *Polym. Adv. Tech.*, 1997, 8: 155
- Hu, Z.M., "Study on the Lyotropic Liquid Crystalline Chitosan", Dissertation, Sichuan University, 1998, 2
- Jiang, T.D., "Chitin" (in Chinese), Chinese Environmental Science Press, Beijing, 1995, p.72
- Kamide, K. and Miyamoto, I., Okajima, K., *Polym. J.*, 1993, 25: 453
- Li, H.M. and Shen, D.Y., *Spectroscopy and Spectral Analysis* (in Chinese), 1988, 8(1): 16