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Observation of 3-D Birefringence Distribution of Polymer Thin Film by Near-Field Optical Microscope

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Abstract. According to development of optical engineering, the measurement accuracy of optical components and materials has become more important. For example, birefringence in polymer thin film is an essential issue for development of liquid crystal display. In this study, after a PVA (poly vinyl alcohol) film was embedded by photopolymer and cut by ultramicrotome, a cross-sectional birefringence distribution of cut film was observed by birefringence contrast scanning near-field optical microscopy (B-SNOM). As a result, three dimensional birefringence ratios were calculated and birefringence of parallel to stretching direction was larger than that of vertical one. This result shows that cross-sectional birefringence distribution is yielded by inhomogeneous distribution of molecular alignment in film material according to asymmetry stretching.

1. Introduction

By the recent development of nanotechnology, the importance of observation and analysis in the micro region of object increases, and related researches are widely carried out. An birefringence measurement is effective for evaluation of polymer materials of optical components, and also for observation of biopolymer. Especially, a PVA (polyvinyl alcohol) film is polarizing material of the LCD (Liquid Crystal Display) panel. An evaluation of optical characteristics by the observation of birefringence distribution is very important, since it is directly related to display qualities such as angle of visibility, contrast, and colour tone reproducibility. However, research and development for such evaluation have not been advancing in present state, because an observation technique of birefringence distribution at cross section in the thickness direction has not been established.

In this study a birefringence distribution in the film cross section was directly observed using birefringence near field optical microscope (B-SNOM) [1], after it was cut off using the ultramicrotome which is widely used for highly precise cross sectional cutting in the field of electron microscope.

2. Principle of birefringence measurement

Schematic drawing of birefringence contrast scanning near-field optical microscope (B-SNOM) used in the study is shown in Figure 1. A measurement based on the heterodyne interferometry[2] is performed using frequency stabilized axial Zeeman laser (SAZL) which emits right- and left-handed circularly polarized lights with frequency difference. The heterodyne interferometry has a property of the high-speed and high-precise quantitative measurement. Using the optical intensity which synchronized for beat frequency between two components of SAZL, amplitude of beat frequency components I_x, I_y are detected by lock-in amplifier, and DC component I_{DC} with a low-pass filter is detected. Therefore, the phase retardation Δ and azimuth angle ϕ of birefringence can be calculated using I_x, I_y and I_{DC} as following equations:

$$\Delta = \sin^{-1}\left(\frac{\sqrt{I_x^2 + I_y^2}}{I_{DC}}\right) \tag{1}$$

$$\phi = \frac{1}{2}\tan^{-1}\left(\frac{I_x}{I_y}\right) \tag{2}$$

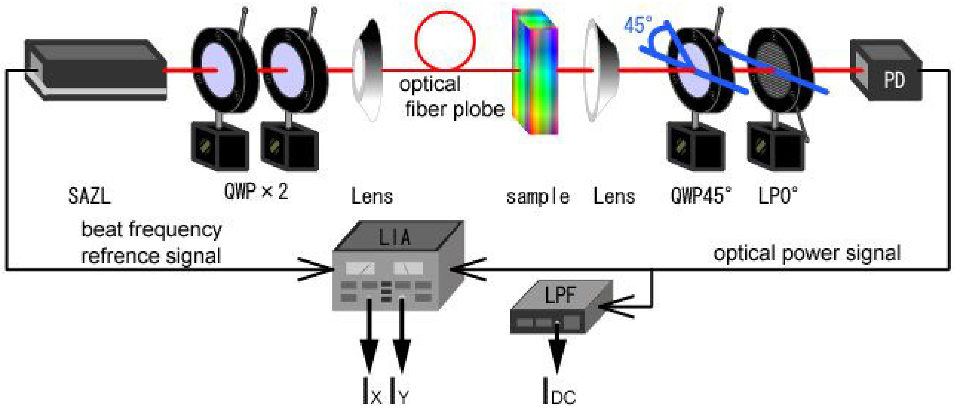


Figure 1. Schematic drawing of birefringence contrast scanning near-field optical microscope (B-SNOM): SAZL(Stabilized Axial Zeeman Laser); QWP(Quarter wave plate); PD(Photo detector); LPF(Low pass filter.

3. Film cutting and sample preparation

The sample cross section was exposed using the ultramicrotome[3] in order to observe the cross section of PVA film. A film was embedded by the resin in order to fix a film slice in the ultramicrotome as shown in Figure 2. As a resin for embedding, ultraviolet curing resin of epoxy polymer and urethane acrylate oligomer which is heat hardening resin was compared. As a result, the ultraviolet curing resin is suitable because the embedding finishes in a short period of time, and there is low thermal effect on the hardening. The thin film of sample was developed on a slide glass by collecting the sample with a tweezer, after cutting by steel knife. The optimization of tool angle and clearance angle was performed using a steel knife. A small irregularity and brake in the cut section were observed, when it was cut off at the tool angle sharper than 35 deg. Since both embedding resin and PVA are soft, this is because the vibration of knife due to a cutting resistance was induced at the small tool angle.

A PVA film was fabricated by dropping PVA solution on glass substrates and drying. The birefringence in a PVA film is induced in proportion to the film stretching. The film which was exfoliated from the glass substrates was extended by the drawing machine. It was heated by the warm wind in order to stretch a film over 70 ° C which is glass transition temperature of PVA. The stretching speed was about 5mm/sec, and the stretching ratio of the sample was set at 1, 3, and 5 times.

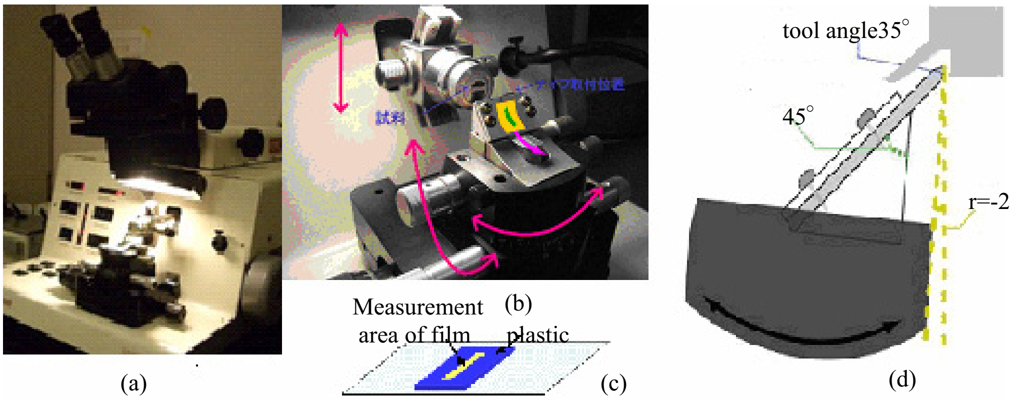


Figure 2. Preparation of sample. (a) picture of ultramicrotomes (b) the schematic of cutting process (c) sample schematic (d) knife and sample

4. Experimental results

Since the deformation and stress in the cutting of sample induce the birefringence of PVA film which is not originally included, the cutting condition with low effect is important for evaluation of cross section in the film. Then, an optimum condition of cutting repeat count and speed with low effect for the cutting were obtained using the PVA film without stretching. Birefringence images of the film cross section after the cutting is shown in Figure 3. The birefringence distributions at the film and resin parts were different each other until 15 times of the cutting repeat count as shown in Figure 3(a). In the slice of 20 cutting times shown in Figure 3(b), the birefringence distribution in the whole area of the image was indistinct within 5deg. or less. Therefore, it became clear that the cutting counts with the knife limits to be 15 times.

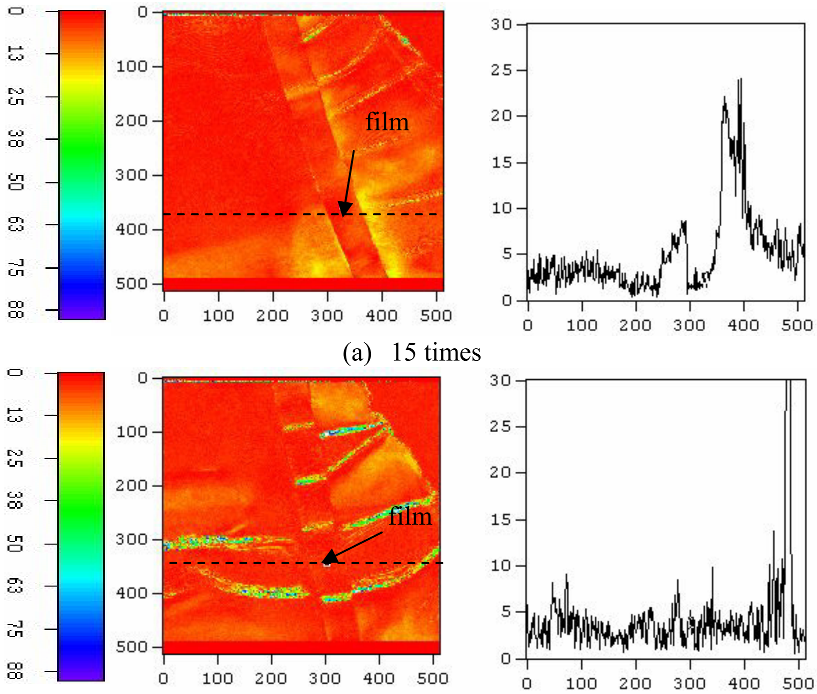
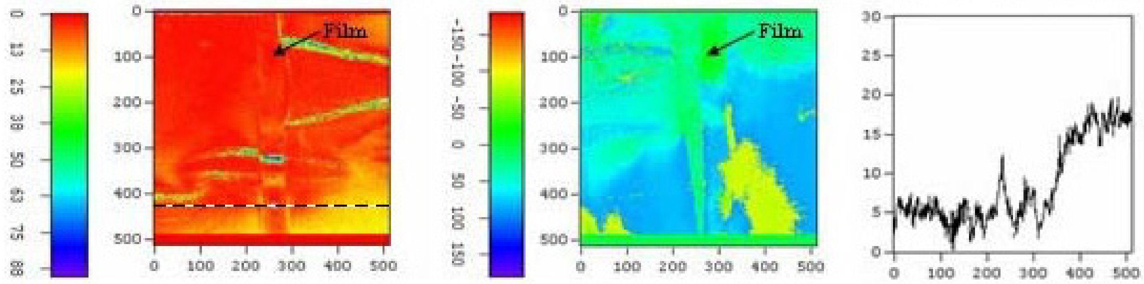
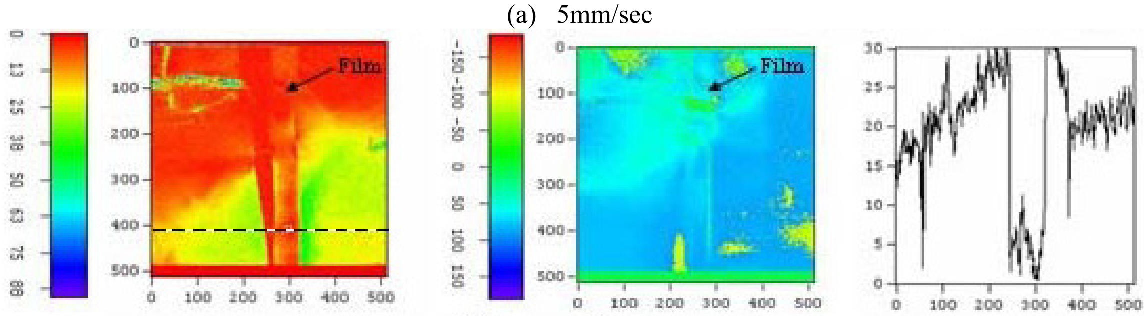


Figure 3. The effect brought in by cutting repeat count.
(a) cutting 15 times and (b) cutting 20 times.

The birefringence by deformation and stress of the cut section may be induced, because the force applied between sample and knife increases as the cutting speed. The birefringence distributions for changing the cutting speed are shown in Figure 4. The birefringence was almost held at 10deg. or less in the cutting speed under 0.5mm/sec, while the birefringence over 15deg. occured when the cutting speed was set at 5mm/sec. Therefore, the cutting speed should be as slow as 0.5mm/sec.



(a) 5mm/sec



(a) 0.5mm/sec

Figure 4. The effect brought in by cutting velocity.
(a) 5mm/sec and (b) 0.5mm/sec.

The birefringence which arises in the PVA film is proportional to the stretching ratio on film stretching [4]. Then, the increase in the birefringence for the change of the stretching ratio was examined. The measurement direction is defined as shown in Figure 5. The birefringence ΔX in the cross section which is perpendicular to the film stretching direction is measured from the X direction. Similarly, the birefringence ΔY corresponds to the plane parallel to the drawing direction, and ΔZ means the birefringence parallel to the film plane. The birefringence observed from the each direction is given by following equations.

$$\text{Retardation in X direction: } \Delta_x = n_y' - n_z'$$

$$\text{Retardation in Y direction: } \Delta_y = n_x' - n_z'$$

$$\text{Retardation in Z direction: } \Delta_z = n_x' - n_y'$$

The retardations in the X, Y, and Z directions for stretched sample film were measured by the B-SNOM. The result is shown in Figure 6. It was normalized by the measurement of the mean value of retardation in a film at every 10μm thickness. From the result, it was found that the birefringence approximately increased as the increment of stretching ratio. The difference of the birefringence according to the observation direction was clarified. The vector diagram expressed by three orthogonal vectors in normalizing ΔY and ΔZ with ΔX is shown in Figure 7. In the case of the uniaxial stretching in the X direction, refractive index n_x in the X direction increases as shown in Figure 8, because the molecule is orientated in the direction in which the object is extended. On the other hand, both of the refractive index n_y and n_z in Y and Z directions decrease.

Therefore, ΔY and ΔZ increases, while ΔX should become small in comparison. In the result of the experiment, the tendency of ΔX<ΔY predicted at sample #3, #4, #5, and #8 was able to be confirmed.

In the meantime, birefringence difference of all directions is almost equal in the sample #6. The sample #7 became ΔX >ΔY, which is different from the prediction. This might be because the slight difference of the stretching state occurred between front and back surface by heating from upper side on the film stretching.

From observation results of the birefringence distribution in the cross section, it was categorized as a sample with large birefringence at internal part of film or with that at film surface. The case in which the birefringence near the surface was large is shown in Figure 9. The Δ in the table of Figure 9 represents the mean value δ of the retardation at every 10 μm thickness of the film. In this figure, it can be estimated that the stress in the Y direction was generated, while the film is extended in X direction, because the mean value of ΔX is larger than that of ΔY in the whole area of film. And also, we can see that ΔX decreased near the left side surface of the figure, while there was a portion where ΔY increased near the surface. It can be supposed that ΔY increases at this part, since there was a small stress component by strong orientation in the X direction on the stretching.

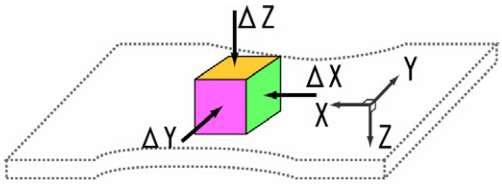


Figure 5. Measurement direction.

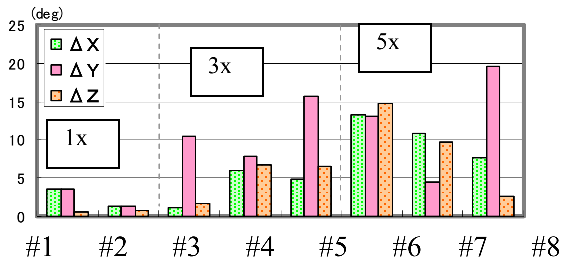


Figure 6. Retardation of PVA film as a function of drawing ratio.

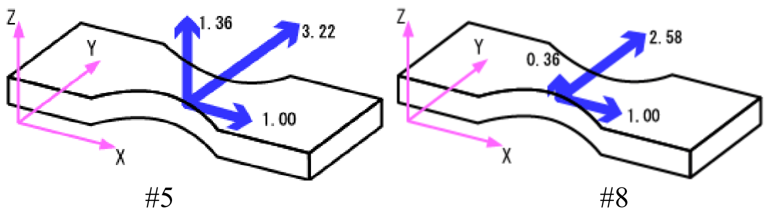


Figure 7. Schematic diagram of relative birefringence image.

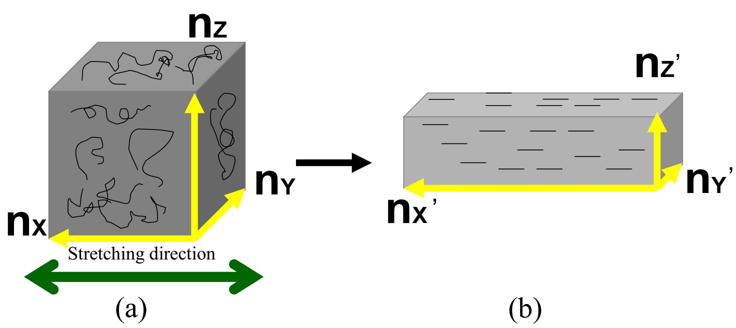
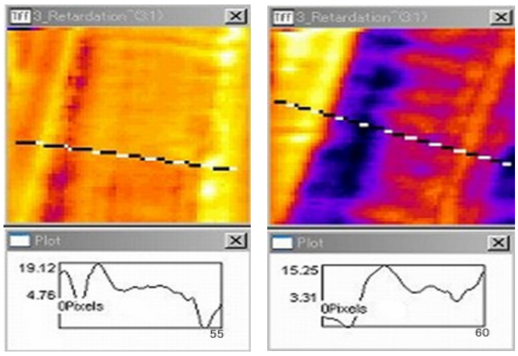


Figure 8. Schematic image of generation of birefringence.



(a) X direction image (b) Y direction image

	t(μm)	δ(deg)	SD of δ.	**Δ(deg)**
Δ X	16.6	15.1	2.5	**9.1**
Δ Y	18.4	12.4	2.4	**6.8**

Figure 9. Birefringence distribution of PVA(#3). Image area is (94.4μm×94.4μm).

5. Conclusion

In this study, the highly resolved observation of film cross section was carried out using birefringence near field optical microscope, and following conclusions were obtained.

(1) The cross sectional observation was performed by the cutting with the ultramicrotome, after the PVA film was embedded. The method using the ultraviolet curing epoxy resin was suitable for embedding of film.

(2) As a result of measuring the birefringence of the film with different stretching ratios, the birefringence increased in proportional to the stretching ratio.

(3) It was possible to verify the prediction that birefringence Y of the parallel cross section to stretching direction is larger than that X in the vertical section.

(4) It was found that there were two tendencies in the distribution of the birefringence in the film cross section. That is, they are the case in which the birefringence near the film surface is large and the case in which that of the film inside is large. It is estimated that the stretching along stretching direction was carried out, when ΔY is larger than ΔX by this originating from stretching condition.

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