Optical Anisotropy of Polyimide

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Synopsis

Optical anisotropy of polyimide films prepared from polyamic acid solutions was investigated by conoscopic observation and refractive index measurements. The conoscopic figure (crossed pattern) characteristic of a negative uniaxial crystal with its optic axis perpendicular to the film plane was observed for samples imidized on substrates. Uniaxial drawing of a polyamic acid cast film with 40 wt % solvent gave a highly oriented sample with an elongation of more than 80%. This sample had a conoscopic figure characteristic of a positive uniaxial crystal with its optic axis equivalent to the molecular *c* axis (parallel to the film plane). A large optical anisotropy (birefringence 0.18) was observed in the film plane. The TE-mode refractive index (parallel to the film plane) ranged from 1.64 to 1.82 at a wavelength of 633 nm according to the sample rotation. These values corresponded to the refractive indices perpendicular and parallel to the *c* axis, respectively. The optical system change of the polyimide film was explained in terms of the uniaxial orientation of the in-plane oriented molecular *c* axis.

INTRODUCTION

Recently, much attention has been devoted to polyimides as lightguide materials because of their thermal and environmental stability.[1–4] Low loss waveguides (below 0.1 dB/cm) were obtained from polyimides containing hexafluoroisopropylidene (6F) groups.[3] In addition to lowering the optical loss, it is necessary to control the refractive index when fabricating optical waveguides.

Polyimide films exhibit a large optical anisotropy. This anisotropy is quantitatively assessed by determining the refractive indices of the two polarizations, parallel (n_{TE}) and perpendicular (n_{TM}) to the film plane.[1–3,5] The difference between n_{TE} and n_{TM} is explained by the in-plane orientation of the molecular chains in spun-on polyimide films.[5,6] This shows the possibility of refractive index control by molecular orientation.

Poly[*N,N'*-bis(phenoxyphenyl)-pyromellitimide] (PMDA-ODA, DuPont Kapton) is an aromatic polyimide (PI) that is widely used due to its good thermal, electrical, and mechanical properties. The optical anisotropy and the molecular order have been investigated by many authors.[5–11] Although the anisotropy of n_{TE} has not yet been reported.

In this study, the optical anisotropy of the polyimide (PMDA-ODA) films is investigated by means of conoscopic observation. The conoscopic figures are explained in terms of the uniaxial orientation of the in-plane oriented molecular *c* axis. Furthermore, the refractive indices (n_{TE} and n_{TM}) of highly oriented and also nearly isotropic polyimide films are presented.

EXPERIMENTAL

Solutions (12 wt %) of polyamic acid (PAA) in dimethylacetamide were made from pyromellitic dianhydride (PMDA) and oxydianiline (ODA). The

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solutions were spin-coated onto glass slides. After casting under different conditions, PAA cast films were thermally cured to PI films.

PAA cast films were uniaxially drawn under constant loads using a Toyoseiki Strograph T tensile test machine while the temperature was raised to 160°C.

The samples were observed using a Nikon Microphot-FX polarizing microscope. Refractive indices (n_{TE} and n_{TM}) were measured at a wavelength of 633 nm using a Metricon PC-2000 prism coupler. Wide-angle X-ray diffraction photographs were taken using a Rigaku Rotaflex with nickel-filtered CuKα radiation at power settings of 40 kV and 200 mA.

RESULTS

Conoscopic Observation

The optical anisotropy of polymer films is easily observed by polarizing microscopy. In particular, conoscopy gives information concerning optical crystal forms and suggests molecular alignments.

The results of the conoscopic observation of PAA and PI films during their cast and cure processes are schematically summarized in Figure 1. The PAA concentration (wt %) and the thickness (μm) of the sample on the substrate (glass slide) were calculated from the sample weight using the final weight of the cured PI film. Several kinds of conoscopic figures were observed during the processes. The conoscopic figure depended on the PAA concentration and the cast conditions, e.g., on substrate or off substrate.

Conoscopic figures with a crossed pattern were observed for PAA films cast on substrates with higher concentrations, as shown in Figure 2. This pattern is typical for the uniaxial crystal with the optic axis perpendicular to the film

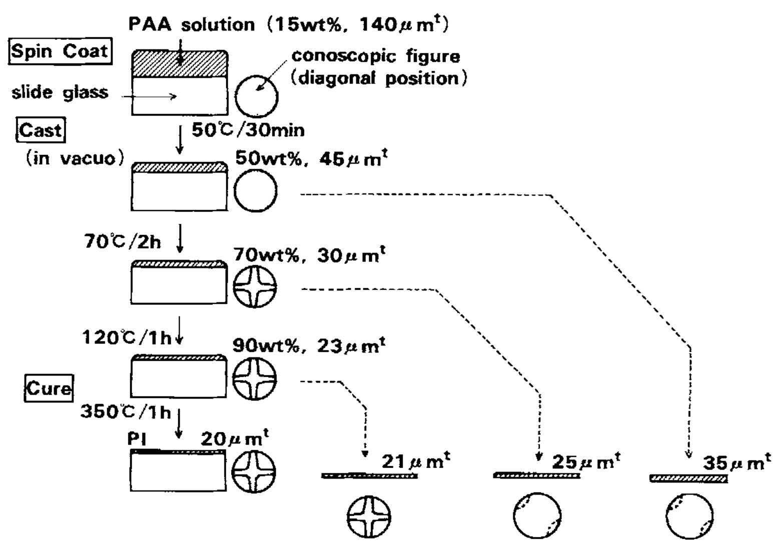


Fig. 1. Conoscopic observation of polyamic acid and polyimide films during their cast and cure processes. —►: on substrate; - -►: off substrate.

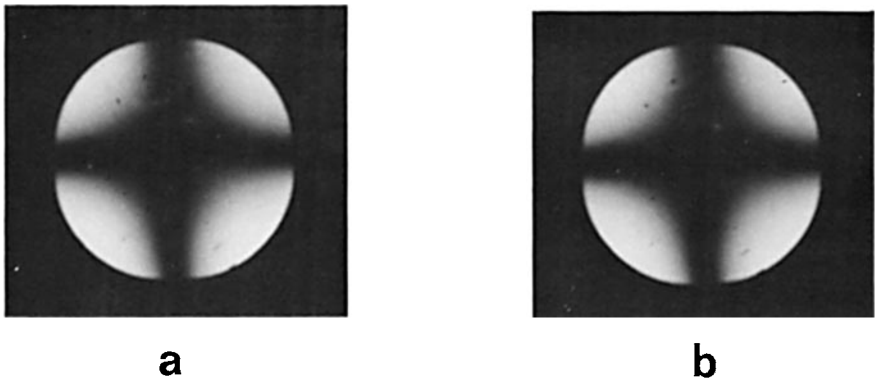


Fig. 2. Conoscopic figure of polyamic acid film cast on substrate. (a) diagonal position, (b) extinction position.

plane. Figure 3 shows the concentration change of the PAA films cast on substrates at different temperatures and in different atmospheres. The anisotropic PAA cast films showing a conoscopic figure with a crossed pattern were obtained on substrates at concentrations of more than 55 wt %, irrespective of the casting temperature and the atmosphere. The volume loss due to solvent evaporation is in one dimension, i.e., the film thickness decreases, but the film surface area on the substrate does not change. The shrinkage stress in the film plane causes this optical anisotropy.

As shown in Figure 4(a), conoscopic figures with a crossed pattern were also observed for PI films cured on substrates. The optic axis is perpendicular to the film plane. Insertion of a $\lambda/4$ plate showed that these PI films were optically negative and uniaxial.

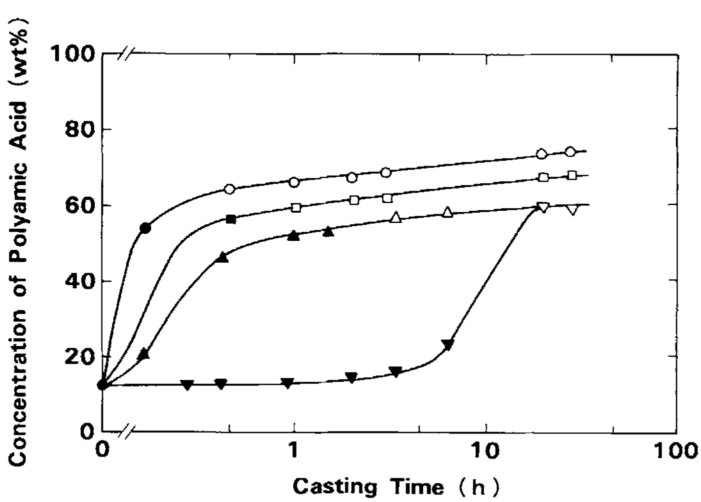


Fig. 3. Concentration of polyamic acid cast on substrate as a function of casting time. Casting conditions: ○ ● 70°C in vacuo; □ ■ 50°C in vacuo; △ ▲ 20°C in vacuo; ▽ ▼ 20°C in a nitrogen atmosphere. Open symbols: anisotropic. Filled symbols: isotropic.

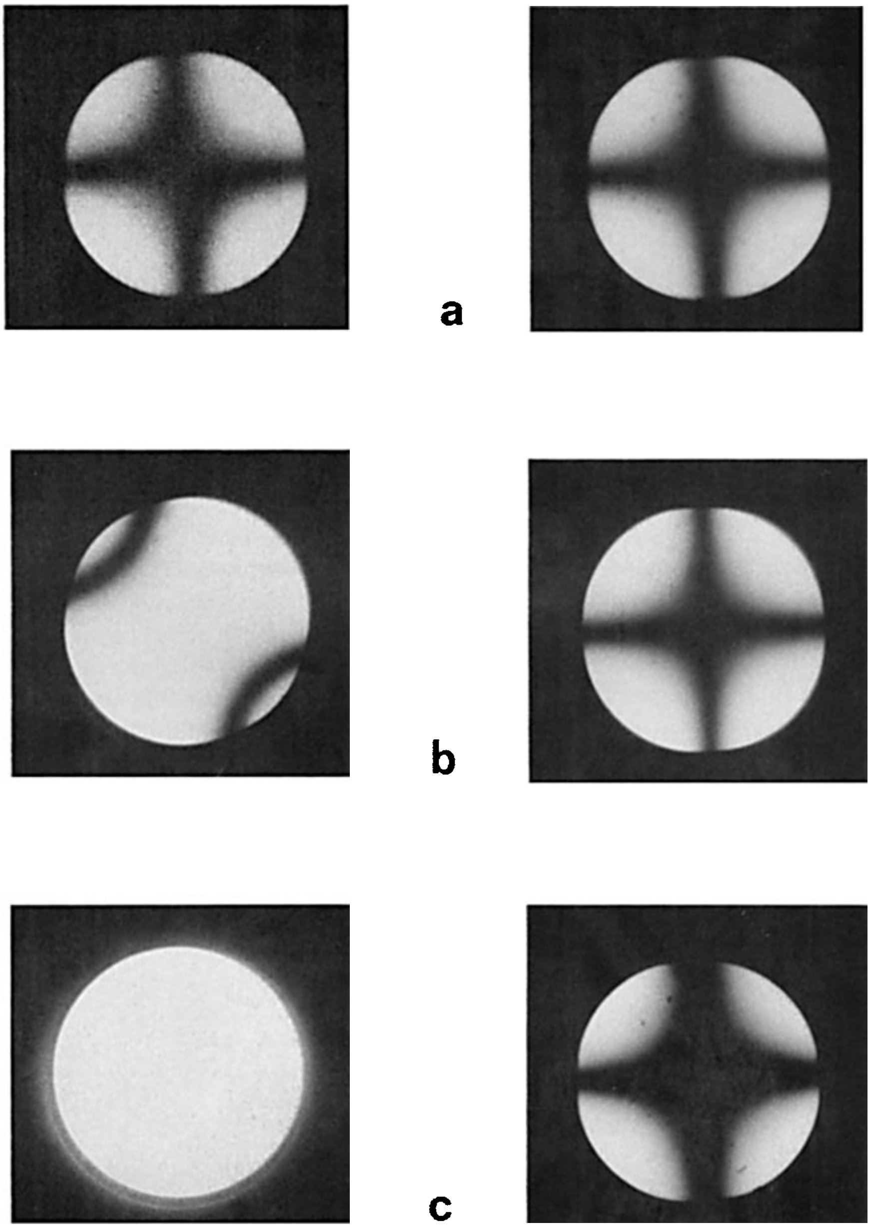


Fig. 4. Conoscopic figures of polyimide films. (a) on substrate; (b) and (c) under inhomogeneous shrinkage. Left side: diagonal position, right side: extinction position. Fig. 4-2. Conoscopic figures of polyimide films; (d) uniaxially drawn, elongation 30%; (e) uniaxially drawn, elongation 83%; (f) off substrate. Left side: diagonal position, right side: extinction position.

When PAA cast films were cured in a free-standing form (off substrate) after the initial casting, the conoscopic figure depended on the PAA concentration of the cast film removed from the substrate. PAA cast film with a high concentration (90 wt %) produced a conoscopic figure with a crossed pattern

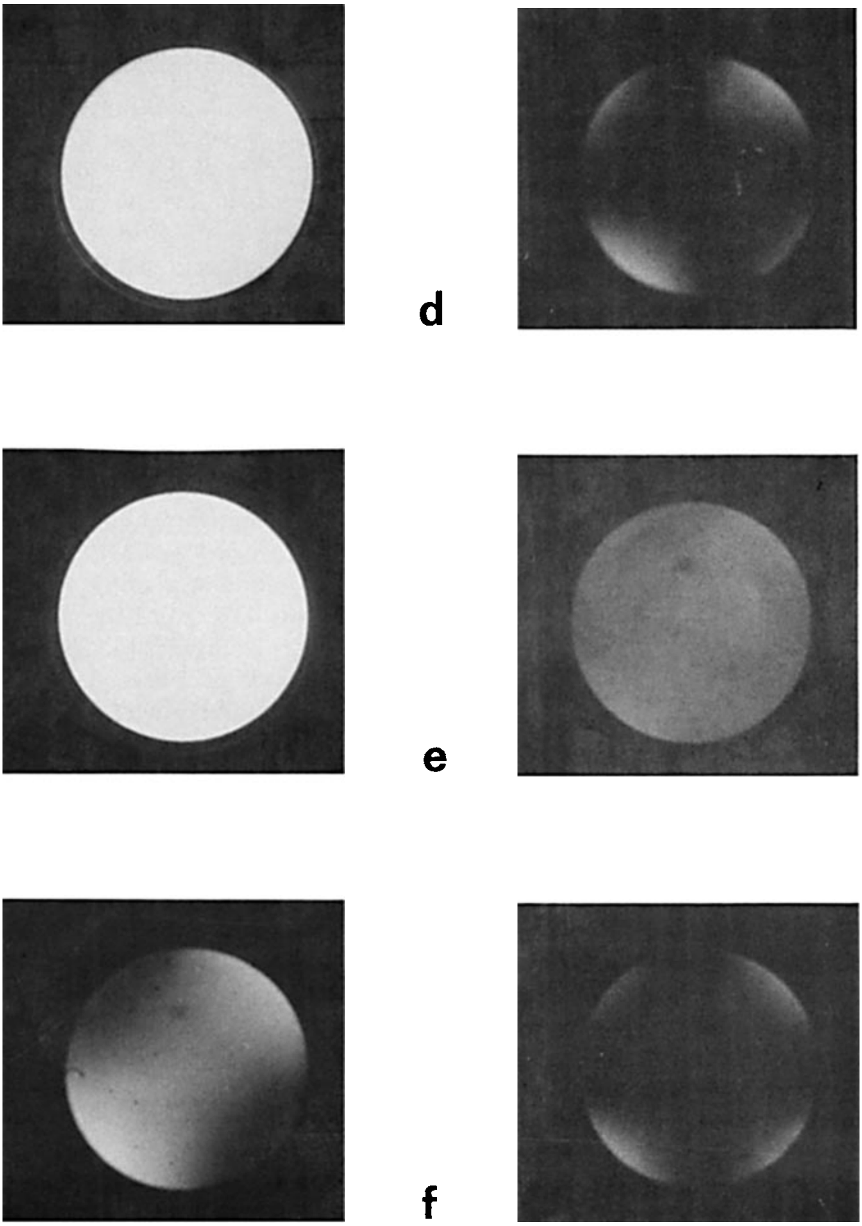


Fig. 4. (*Continued from the previous page.*)

as with PI film cast on a substrate. The PAA cast films with lower concentrations (e.g., 50 and 70 wt %) gave a conoscopic figure with an ambiguous pattern [Fig. 4(f)]. These samples were nearly isotropic in bulk. When the solvent content is high the optical anisotropy caused on the substrate is reduced in the free-standing form during imidization.

After the initial casting at 120°C PAA cast films were removed from the substrates, sandwiched between glass slides, and cured at 350°C for 1 h in vacuo. In this case inhomogeneous shrinkage occurred in the film plane and the conoscopic figures characteristic of a biaxial crystal were observed as shown in Figures 4(b) and (c). When the PAA cast film was sandwiched between plane electrodes and cured under an electrostatic field of more than 0.1 MV/cm, no shrinkage occurred in the film plane, although the film thickness decreased. This is due to electrostatic attraction and/or electrolytic adhesion. A conoscopic figure with a crossed pattern was observed in the electrode area. While a conoscopic figure characteristic of a biaxial crystal was observed outside the electrode area owing to the inhomogeneous shrinkage in the film plane. Under crossed polarizers a clear boundary was observed around the electrode area, because the electrode area was a dark field, while the area outside the electrode was a light field.

Uniaxially drawn samples were prepared as follows. After initial casting at 50°C for 1 h the PAA cast film was removed from the substrate, cut to a size of 10 × 38 mm, and set on the tensile test machine. A constant load was applied to the sample and the temperature was then raised from room temperature to 160°C (upper temperature limit of the apparatus) at an average heating rate of 4°C/min. The initial stress was changed in the range of 3 to 4 MPa. Highly drawn samples were obtained owing to the high solvent content of the starting material, i.e., 40 wt %. The maximum elongation was 83%. After the drawing the samples were cured at 350°C for 1 h. The conoscopic figures are shown in Figures 4(d) and (e). These figures are characteristic of a crystal with its optic axis parallel to the film plane. Insertion of a $\lambda/4$ plate showed that these samples were optically positive and uniaxial.

Refractive Index

The optical anisotropy of PI films is quantitatively assessed by determining refractive indices of the two polarizations, parallel (n_{TE}) and perpendicular (n_{TM}) to the film plane. The optical anisotropy in the film plane is also checked by measuring the n_{TE} by rotating the sample. The full-prism coupling geometry for the measurements is shown in Figure 5. The values of n_{TE} and n_{TM} are plotted as a function of the sample rotation angle in Figure 6 for 3 samples prepared under different conditions; i.e., (a) off substrate, (b) on substrate, and (c) uniaxially drawn.

The PI film prepared off substrate is isotropic in the film plane, because the n_{TE} is independent of the sample rotation angle. This sample had a conoscopic figure with an ambiguous pattern [Fig. 4(f)]. The n_{TE} and n_{TM} are almost equal. This means that this sample is nearly isotropic in bulk. The refractive index of the isotropic PI film is 1.70 at a wavelength of 633 nm.

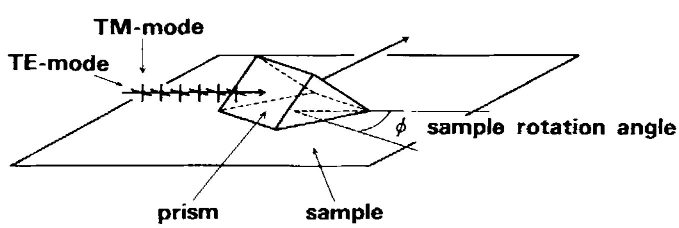


Fig. 5. Full-prism coupling geometry for refractive index measurements.

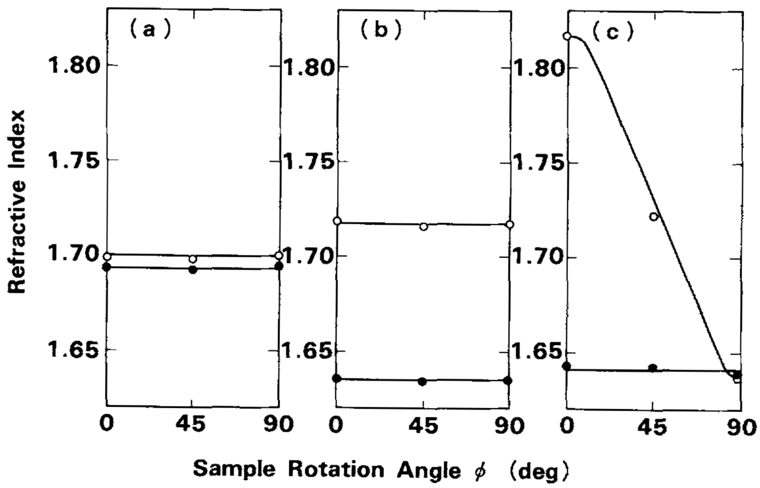


Fig. 6. Refractive index of polyimide film as a function of sample rotation angle. (a) off substrate, (b) on substrate, (c) uniaxially drawn (elongation 83%, draw direction $\phi = 0°$). Open circles: n_{TE}, filled circles: n_{TM}; wavelength 633 nm.

The n_{TE} and n_{TM} for the sample indicating a conoscopic figure with a clear crossed pattern [Fig. 4(a)] are shown in Figure 6(b). This sample is also isotropic in the film plane, but highly anisotropic in the out-of-plane. The n_{TE} (1.72) and n_{TM} (1.64) coincided with those obtained by Russell et al.[5]

The uniaxially drawn sample with a maximum elongation of 83% shows a large anisotropy in the film plane as shown in Figure 6(c). The values of n_{TE} parallel and perpendicular to the draw direction were 1.82 and 1.64, respectively.

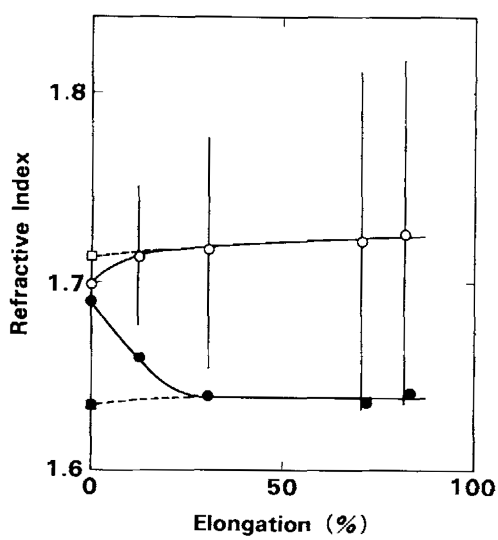


Fig. 7. Refractive index of uniaxially drawn polyimide. Circles: uniaxially drawn samples, squares: samples prepared on substrate; open symbols: n_{TE}, filled symbols: n_{TM}; wavelength 633 nm.

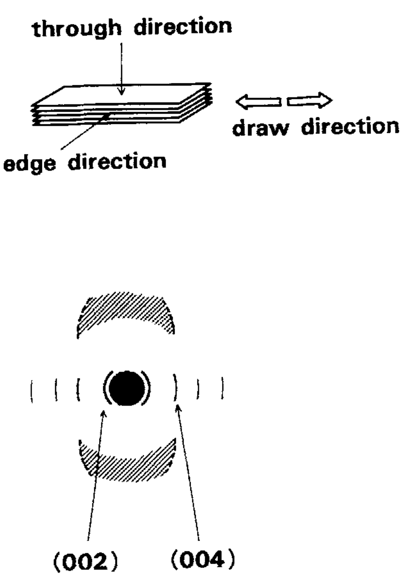
The birefringence of this sample reached 0.18 in the film plane. This value is comparable to that for dolomite.

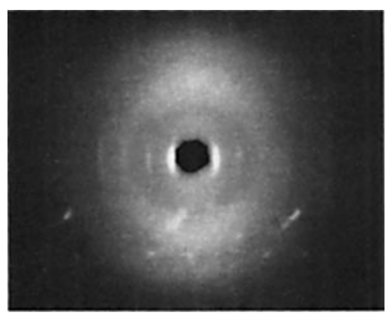
Figure 7 shows the n_{TE} and n_{TM} as a function of elongation. The sample with an elongation of 0% corresponds to the sample prepared under no stress, i.e., off substrate. The vertical line of n_{TE} shows the range of n_{TE} due to the anisotropy in the film plane. The upper and lower limits of the line are the values of n_{TE} parallel and perpendicular to the draw direction, respectively.

The n_{TE} and n_{TM} are nearly equal to 1.70 for the isotropic PI film (0% elongation). The n_{TE} increases and the n_{TM} decreases as the sample is elongated. Above an elongation of 30% the average n_{TE} and n_{TM} level off to 1.72 and 1.64, respectively. These average values are nearly equal to those for the sample prepared on a substrate. The range of n_{TE} due to the anisotropy in the film plane increases as the sample is elongated and becomes nearly constant at about 80% elongation.

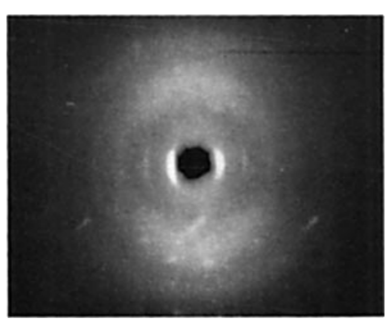
Wide-Angle X-Ray Diffraction

Wide-angle X-ray diffraction photographs of a uniaxially drawn PI film (elongation 72%) are shown in Figure 8. The drawn film (27 μm in thickness) was cut to a size of 2 $\times$ 10 mm. A stack of 10 cut films was used for the measurements. The photographs were taken with the incident beam normal to the film plane (through direction) and to the film edge (edge direction). Figure





a



b

Fig. 8. Wide-angle X-ray diffraction photographs of uniaxially drawn polyimide film. Elongation 72%.

8 shows that reflections due to intramolecular and intermolecular order are anisotropic for both incident beam directions. The reflections of (002), (004), etc., due to intramolecular order were clearly observed. These patterns show that the molecular chains are oriented parallel to the film plane and also to the draw direction.

DISCUSSION

The PAA and PI films prepared on substrates had a conoscopic figure with a clear crossed pattern as shown in Figure 2 and Figure 4(a). This pattern shows that the optic axis is perpendicular to the film plane. Usually the optic axis is equivalent to the crystal *c* axis. So, the molecular *c* axis might be considered to be perpendicular to the film plane. But this is not the case.

In the normal preparation of PAA and PI films it is known that an in-plane orientation arises from the use of a substrate.[5-8] Solvent evaporation and dehydration due to imidization occur during the cast and cure processes. The stress due to volume losses combined with the good adhesion of the polymer to the substrate leads to a molecular orientation parallel to the film plane. Removal of the PAA films from the substrates prior to imidization permits a free shrinkage and produces isotropic samples.

In our work the in-plane orientation of the PI film prepared on a substrate was not confirmed directly by means of wide-angle X-ray diffraction, because no clear diffraction patterns were observed. But the measurements of n_{TE} and n_{TM} showed that the sample was highly anisotropic in the out-of-plane and isotropic in the film plane as seen from Figure 6(b). Both n_{TE} (1.72) and n_{TM} (1.64) coincided with the corresponding average values (Fig. 7) of the uniaxially drawn sample in which the molecular *c* axis was confirmed to be parallel to the film plane by the wide-angle X-ray diffraction patterns (Fig. 8). This shows that the molecular *c* axis is not perpendicular (not equivalent to the optic axis), but parallel to the film plane.

Figure 9 shows side views of the index surfaces of the PI films. The left side view shows the index surface for the PI film prepared on a substrate. The optic

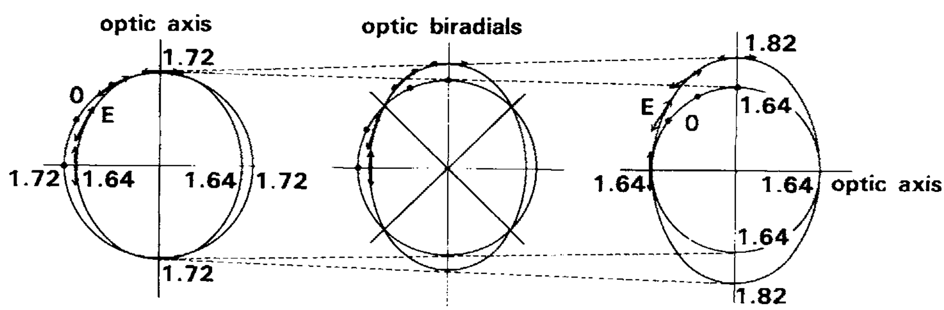


Fig. 9. Index surfaces of polyimide films prepared under different conditions. Left side: on substrate, center: under inhomogeneous shrinkage, right side: uniaxially drawn; O: ordinary light, E: extraordinary light.

axis is perpendicular to the film plane. The n_{TE} (1.72) is the refractive index of ordinary light and the value is the average of the refractive indices parallel ($n_{c\parallel}$) and perpendicular ($n_{c\perp}$) to the molecular *c* axis, because the *c* axis is parallel to the film plane and isotropic in the film plane. The n_{TM} (1.64) is the refractive index of extraordinary light and is equal to the $n_{c\perp}$. Both indices are independent of the sample rotation angle as seen from this figure. In this case the optical system is negative and uniaxial and the conoscopic figure with the crossed pattern is observed from the direction normal to the film plane [Fig. 4(a)].

The index surface for the uniaxially drawn PI film is shown in the right side of Figure 9. In this case the molecular *c* axis is equivalent to the optic axis. This optical system is positive and uniaxial. The conoscopic figures are shown in Figures 4(d) and (e). The n_{TM} (1.64) is the refractive index of ordinary light and independent of the sample rotation. The n_{TE} is the refractive index of extraordinary light and depends on the sample rotation angle. The maximum and minimum n_{TE} are obtained at directions parallel and perpendicular, respectively, to the optic axis (draw direction). The maximum n_{TE} (1.82) is the $n_{c\parallel}$ and the minimum n_{TE} (1.64) is the $n_{c\perp}$, i.e., equal to the n_{TM}. Using these values the refractive index for isotropic PI film can be calculated to be $(n_{c\parallel} + 2n_{c\perp})/3 = 1.70$. This coincides with the observed value.

Isotropic orientation of the *c* axis in the film plane gives a negative uniaxial system, while uniaxial orientation in the film plane produces a positive uniaxial system. As an intermediate state the biaxial system exists as shown in the center of Figure 9. This optical system is obtained by a partially uniaxial orientation of the *c* axis in the film plane due to an inhomogeneous stress. The conoscopic figures are shown in Figures 4(b) and (c).

The optical system of the PI film depends on the uniaxial orientation of the in-plane oriented molecular *c* axis.

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