Application of Refractive Index Measurements to Polymer Analysis

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Synopsis

The availability of a simple experimental technique for determining the three principal refractive indices of an anisotropic film (here defined as the trirefringence technique) makes possible a wide range of optical criteria for evaluating property and processing variables. The present study considers different applications of the refractive index information in order to show the versatility and practical utility of the technique. For example, a normalization procedure is developed which determines equivalent optical anisotropic states of films. This allows films produced by different multiaxial fabrication processes to be compared. Similarly, procedures are described for characterizing the crystallinity, the angular optical distribution in the plane of the film, and other interesting applications of the refractive index information.

INTRODUCTION

The availability of a simple experimental technique for determining the three principal refractive indices of an anisotropic film (here defined as the trirefringence technique) makes possible a wide range of optical criteria for evaluating property and processing variables. The present study considers different applications of the refractive index information in order to show the versatility and practical utility of the technique. For example, a normalization procedure is developed which defines equivalent optical anisotropic states of films. This allows films produced by different multiaxial fabrication processes to be compared. Similarly, procedures are described for characterizing the crystallinity, the angular optical distribution in the plane of the film, and other interesting applications of the refractive index information.

The "trirefringence" technique, involves a clever application of the Abbé refractometer. The idea was originally developed by Okajima and Koizumi[1] in 1939, but went unrecognized, probably because of the advent of the second World War. In 1958, Z. W. Wilchinsky and P. L. Mercier reinvented the technique as was reported by Schael.[2,3] Schael obtained the refractive indices of films produced by several fabrication procedures, showed the relation of their average refractive index to density, and considered some optical relations between the refractive indices. Samuels[4] applied the trirefringence technique to oriented hydroxypropylcellulose (HPC) and extended the optical equations of Schael.

However, no detailed description of the technique has been given by any of these authors. In order to facilitate the application of the technique for use by others, a detailed description of the experimental procedure is also given in this article along with a description of the general principles of the measurement.

APPLICATIONS OF REFRACTIVE INDEX INFORMATION

Refractive Index and Crystallinity

The refractive index N is a measure of the change in velocity of a light wave as it goes from one medium to another. It is directly related to the molecular state of the material it traverses and thus can be related to the density of that material. The refractive index is also directly related to the dielectric constant of the material. Although the refractive index N is not a tensorial property, it can be treated as such through the dielectric constant relationship. Hence, for a solid body the refractive index may be treated as a second-order tensor. When this is done, it is found that the upper N^2 and lower $(1/N^2)$ bound of the refractive index tensor coincide; hence, they are no different from the refractive index N.[5] Thus, N^2, N, and $(1/N^2)$ will all relate similarly to the property under investigation.

When two materials are mixed, the average refractive index of the mixture, $\overline{N}$ (where

$$\overline{N} = (N_x + N_y + N_z)/3 \qquad (1)$$

and x, y, and z are three mutually perpendicular directions in the sample), will be directly proportional to the average refractive index and volume fraction of each of the components of the mixture. For a two-phase system of crystalline and noncrystalline polymer,

$$\overline{N} = \overline{N}_c V_c + \overline{N}_{AM}(1 - V_c) \qquad (2)$$

where $\overline{N}_c$ is the average refractive index of the crystal; $\overline{N}_{AM}$ is the average refractive index of the noncrystalline polymer; V_c is the volume fraction of crystals; and $(1 - V_c) = V_{AM}$ = the volume fraction of the noncrystalline polymer. $\overline{N}_c$
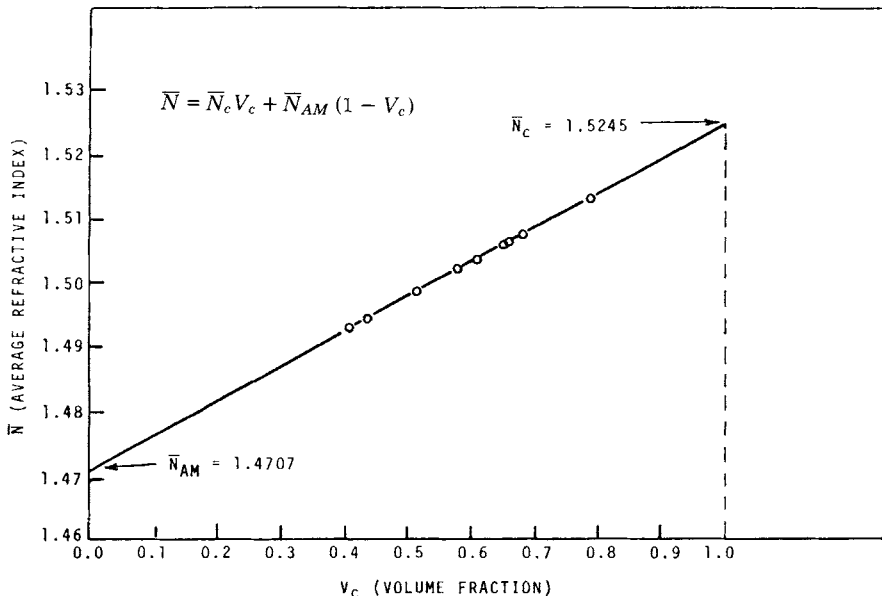

Fig. 1. Relation between average measured refractive index, $\overline{N}$, and the measured volume fraction, V_c, for cast and annealed isotactic polypropylene films.

TABLE I
Optical Properties of Drawn Water-Cast HPC Films

Property	Elongation, %					
	0	50	100	150	200	250
N_z (exp.)	1.4860	1.4868	1.4878	1.4895	1.4906	1.4910
N_y (exp.)	1.4860	1.4845	1.4832	1.4824	1.4816	1.4812
$N_{x(1)}$ (exp.)	1.4821	1.4822	1.4819	1.4818	1.4818	1.4812
$N_{x(2)}$ (exp.)	1.4821	1.4820	1.4822	1.4820	1.4821	1.4822
N_x (Av.)	1.4821	1.4821	1.4821	1.4819	1.4820	1.4817
Δ_{zy} (Abbé) $\times 10^3$	0	2.3	4.6	7.1	9.0	9.8
Δ_{zy} (microscope) $\times 10^3$	0	1.70	4.61	6.89	8.11	9.24
Δ_{zx} (Abbé) $\times 10^3$	3.9	4.7	5.7	6.6	8.6	9.3
Δ_{yx} (Abbé) $\times 10^3$	3.9	2.4	1.1	0.5	-0.4	-0.5
$\overline{N}$ (calc.)	1.4847	1.4845	1.4844	1.4846	1.4847	1.4847

and $\overline{N}_{AM}$ are absolute values for the polymer, and hence, act as constants in the equation.

Figure 1 shows the average refractive index of a series of cast and annealed isotactic polypropylene films plotted against the volume fraction of the films.[6] The average refractive index of these films was calculated from the refractive indices measured in the Abbé refractometer using eq. (1). The volume fractions were obtained from the measured film densities using the expression,

$$V_c = \frac{(d - d_{AM})}{(d_c - d_{AM})} \qquad (3)$$

where d is the measured density, d_c is the crystal density (0.936), and d_{AM} is the noncrystalline density (0.850). As seen in Figure 1, a plot of $\overline{N}$ against V_c is definitely linear. Also, the two limiting values of the plot yield the average component refractive indices $\overline{N}_c$ and $\overline{N}_{AM}$.

Equation (1) is independent of orientation. That is, no matter how one redistributes the phases, the average refractive index remains the same so long as the volume fraction of each phase is the same. Thus, whether a sample is isotropic or highly oriented, so long as the volume of crystals remains the same, $\overline{N}$ will not change. N_x, N_y, and N_z will change, and this will yield information about the anistropy of the sample, but $\overline{N}$ will be constant with constant V_c.

The data from drawn films of hydroxypropylcellulose (HPC),[4] tabulated in Table I and plotted in Figure 2, illustrate this point. These films have planar orientation. Thus, as the films are drawn in the z direction, N_z increases, N_y decreases, and N_x remains constant (Fig. 2). Since the crystallinity is not changing in these samples, $\overline{N}$ does not change during the orientation (Table I) although N_z and N_y do change considerably. Thus, crystallinity as well as anisotropy information can be obtained provided the refractive index in all three directions in the film is obtained.

Refractive Index and Anisotropy

Birefringence

Characterization of the three refractive indices of a film yield considerable information about the anisotropy of the film. The most obvious information
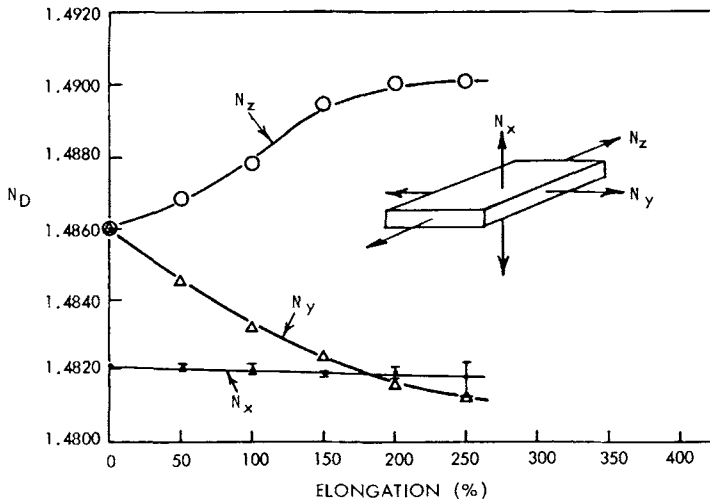
Fig. 2. Effect of deformation on the refractive indices of water-cast HPC Film.[4]

one obtains from N_x, N_y, and N_z, besides the average refractive index $\overline{N}$, is a measure of the birefringence in all three directions of the film. That is,

$$
\begin{aligned}
\Delta_{zy} &= N_z - N_y \\
\Delta_{zx} &= N_z - N_x \\
\Delta_{yx} &= N_y - N_x
\end{aligned}
\tag{4}
$$

The birefringence has traditionally been measured using a compensator and a microscope. This measures the difference in refractive index directly and gives no indication of the absolute values of the refractive indices themselves. The compensator technique is simple, however, and in the absence of an equivalently simple refractive index technique, it was the most reasonable optical method to use from a practical point of view. Again, conventionally, the birefringence in the plane of the film, Δ_{zy}, has generally been measured, while the other two birefringences have been neglected. This has occurred because the technique for measuring the birefringence through the film thickness involved a more elaborate film tilting and plotting technique. The trirefringence technique eliminates these difficulties and allows direct access to all three birefringence values (see section on Experimental Trirefringence Procedure p. 1402 ff).

The determination of all three birefringences from the measured refractive indices and their behavior with extension can be illustrated by the hydroxy-propylcellulose data.[4] The HPC film values of Δ_{zy}, Δ_{zx}, and Δ_{yx} calculated from eq. (4) by use of refractive indices from the Abbé refractometer, and the value of Δ_{zy} determined by the compensator method in a polarizing microscope with a quartz compensator, are shown in Table I and Figure 3. For the planar-oriented, undrawn, water-cast HPC film, the value of Δ_{zy} obtained from both the microscope and the Abbé refractometer is zero. With no other optical data available, a zero birefringence would indicate that the cast film is randomly oriented. An x-ray diffraction pattern taken with the x-ray beam normal to the surface of the film seemed to verify that conclusion. Only by also examining the properties of the film through the thickness can the planarity of the film be
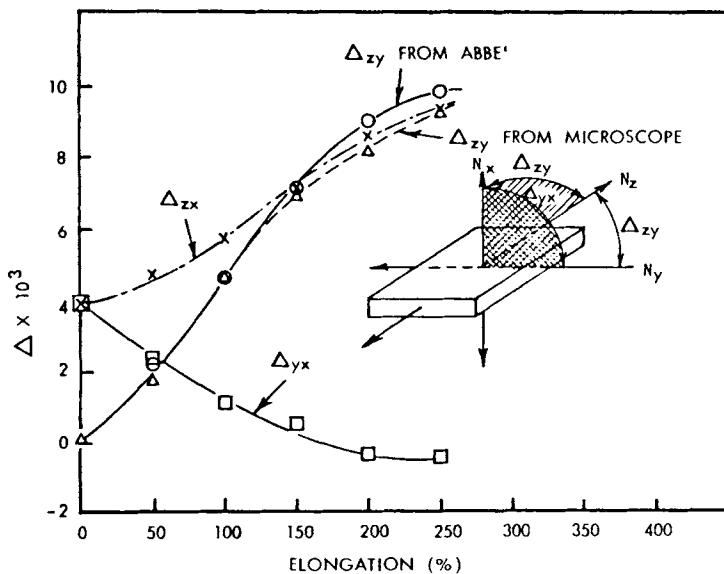
Fig. 3. Effect of deformation on birefringences of water-cast HPC film. $\Delta_{zy} = N_z - N_y$; $\Delta_{zx} = N_z - N_x$; $\Delta_{yx} = N_y - N_x$.

established.   A randomly oriented film would show $\Delta_{zy} = \Delta_{zx} = \Delta_{xy} = 0$; however, the planar film shown in Figure 4 has $\Delta_{zy} = 0$, but $\Delta_{zx} = \Delta_{yx} \neq 0$.   As extension proceeds and the cast film becomes oriented, Δ_{zx} approaches the value of Δ_{zy}, while Δ_{yx} approaches zero.   Thus, in the limit of complete orientation of the HPC molecular chains, planar and uniaxial orientation become indistinguishable.

Birefringence is thus an important measure of orientation.   It has been used as the anisotropic indicator which, when coupled with x-ray and crystallinity measurements, can yield information about the orientation behavior of the
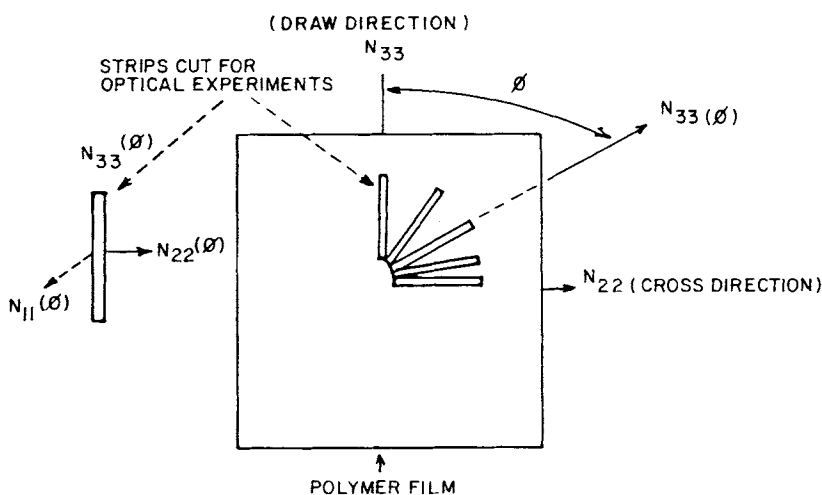

Fig. 4. Schematic representation of nomenclature for refractive index distribution measurements.

noncrystalline phase of the polymer.[7]   The refractive indices yield so much more information about the polymer film, however, that limiting measurement to just the birefringence is unduly prohibitive.   The ease of the trirefringence technique now makes such a measurement restriction unnecessary.

Refractive Index Distribution

The trirefringence technique makes a complete description of the refractive index distribution in the plane of a film possible.   Since the refractive index is a measure of the anisotropy of the film, characterization of the refractive index as a function of the angle around the film will be quite instructive.

Figure 4 shows the principle behind this measurement.   Strips are cut from the film under investigation with the long axis of the strip aligned at different angles, ϕ, from the principal reference axis as defined by the fabrication process (e.g., draw direction for a uniaxial extension).   The three refractive indices, N_x, $N_y(\phi)$, $N_z(\phi)$, are then determined from each strip in the Abbé refractometer using the trirefringence technique.   This will yield two values of $N_z(\phi)$ and $N_y(\phi)$ for each angle ϕ of the film, and numerous values of N_x (which is the refractive index through the film, and hence, is single valued in this measurement).   Averaging of these measured values at each ϕ angle increases the accuracy of the data.   The measured refractive index distribution in the plane of the film can then be plotted on polar paper to give a visual display of the anisotropy.

Figures 5–7 show visual displays of the refractive index distribution of several different polymer films.   Figure 5 compares the refractive index distribution obtained from a highly oriented uniaxially drawn (635% extension at 110°C)
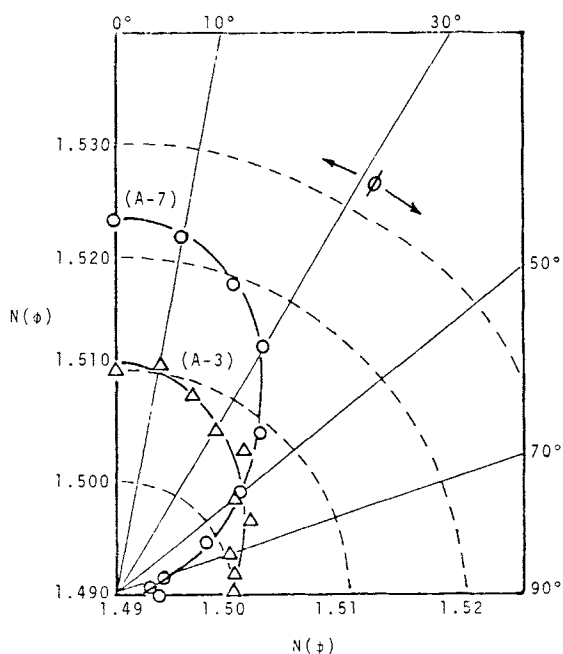

Fig. 5. Polar plot of the refractive index distribution of uniaxially oriented isotactic polypropylene films.
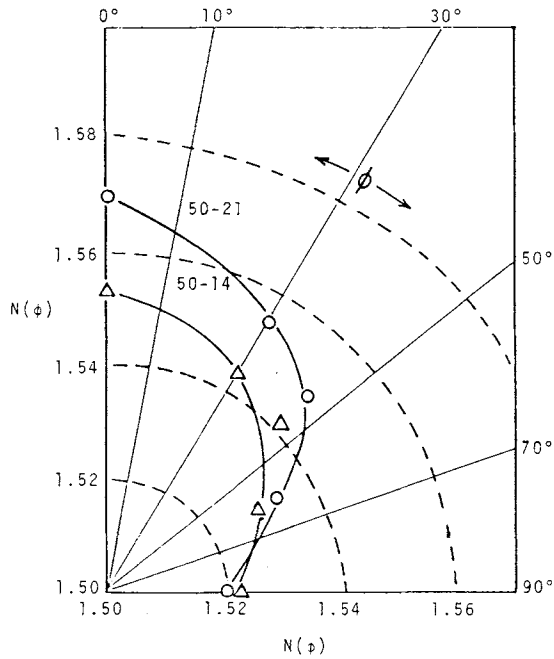
Fig. 6. Polar plot of the refractive index distribution of uniaxially oriented polyethylene films.

isotactic polypropylene film (A–7), with a less oriented uniaxially oriented film (A–3) drawn under the same conditions (73% extension at 110°C).[8]   If the films were unoriented, the refractive index would be the same at all angles and the curve would follow a constant refractive index circle (dashed line).   Instead, the samples are oriented in the machine direction (0°), with the more highly drawn sample having the highest refractive index in the 0° stretch direction.   The bi-
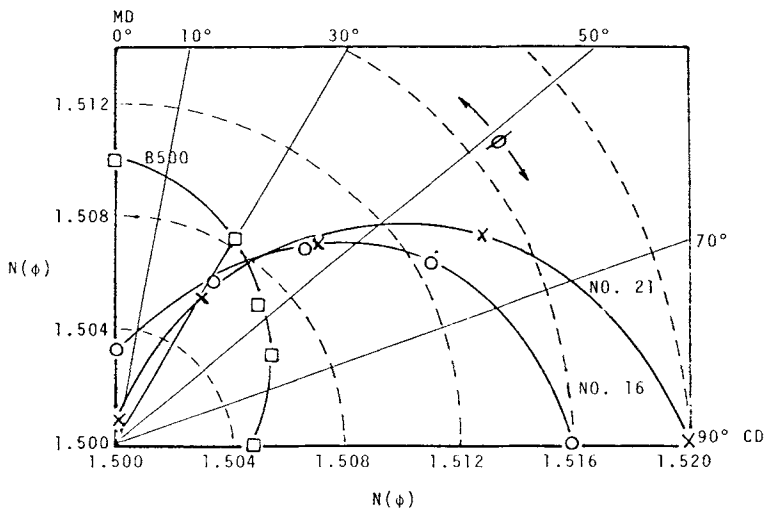

Fig. 7. Polar plot of the refractive index distribution in the Z–Y plane of multiaxially drawn isotactic polypropylene films.

refringence, Δ_{zy}, of these samples is simply the refractive index at $0°$ ($N_\parallel$) minus the refractive index at $90°$ ($N_\perp$) of the film.

Figure 6 shows the refractive index distribution from two uniaxially oriented films of polyethylene. It can be seen at a glance from the refractive index distributions that film (Nos. 50–21) is more oriented in the machine ($0°$) direction than film (Nos. 50–14), and that the range of refractive index values for polyethylene is different than from polypropylene. Both polyethylene films were drawn at $120°C$, with (Nos. 50–14) drawn 3×, and (Nos. 50–21) drawn 6.5×.

Figure 7 shows the refractive index distribution from differently processed isotactic polypropylene films. That the distributions of these films are different depending on the process can be seen immediately by examination. Film Nos. 16 and 21 obviously have their highest refractive index (orientation) in the cross direction ($90°$), while the Hercules B500 polypropylene film sample has its highest refractive index in the machine direction ($0°$). The B500 film was prepared by a bubble process and the $0°$ direction was defined here as the roll direction of the film package. This film is seen to be somewhat more oriented in the roll direction ($0°$) than in the cross direction. If this film were completely balanced in the plane of the film, the distribution would follow a dashed circle. Instead, this particular sample has a slight orientation in the roll direction

$$[\Delta_T = (N_\parallel - N_\perp) = 5.2 \times 10^{-3}]$$

Film Nos. 16 and 21 were prepared by sequential drawing, with hot drawing in the machine direction and subsequent transverse drawing in the tenter. Film No. 16 was drawn approximately 5.4× in the machine ($0°$) direction and 9.2× in the ($90°$) cross direction. Film No. 21 was drawn approximately 4.5× in the machine ($0°$) direction and 11.2× in the ($90°$) cross direction. The refractive index distributions from these samples are obviously different from each other and very different from the B500 and uniaxially drawn film distributions shown previously. Here again, the film with the highest draw in the cross direction (No. 21) had the highest refractive index value at $90°$.

The optical uniaxial indicatrix can be described by an analytic expression having the form[5,9]:

$$N(\phi) = N_\perp + (N_\parallel - N_\perp) \cos^2(\phi) \qquad (5)$$

Here, $N_\parallel$ is the refractive index direction parallel to the given reference axis, $N_\perp$ is the refractive index perpendicular to the reference axis, and $N(\phi)$ is the refractive index measured at an angle ϕ to the reference axis. This equation predicts the complete refractive index distribution in the plane of the film from only two measured refractive index values, $N_\parallel$ and $N_\perp$, the refractive index at $0°$ and $90°$).

Figure 8 is a plot of the uniaxially oriented isotactic polypropylene refractive index data from Figure 5, plotted according to eq. (5). The data definitely satisfy the equation, as a linear relationship holds for both samples. Figure 9 is a plot of the uniaxially oriented polyethylene refractive index data from Figure 6. Again, eq. (5) is satisfied. One important aspect of eq. (5) is that all of the angular data can now be used to get the best value of $N_\parallel$ and $N_\perp$, thus increasing the accuracy of the technique. When $\cos^2\phi = 1.0$, $\phi = 0°$, and $N(0°) = N_\parallel$. When $\cos^2\phi = 0.0$, $\phi = 90°$, and $N(90°) = N_\perp$. Thus, by getting the best fit of all the angular data, accurate $N_\parallel$ and $N_\perp$ values are obtained.
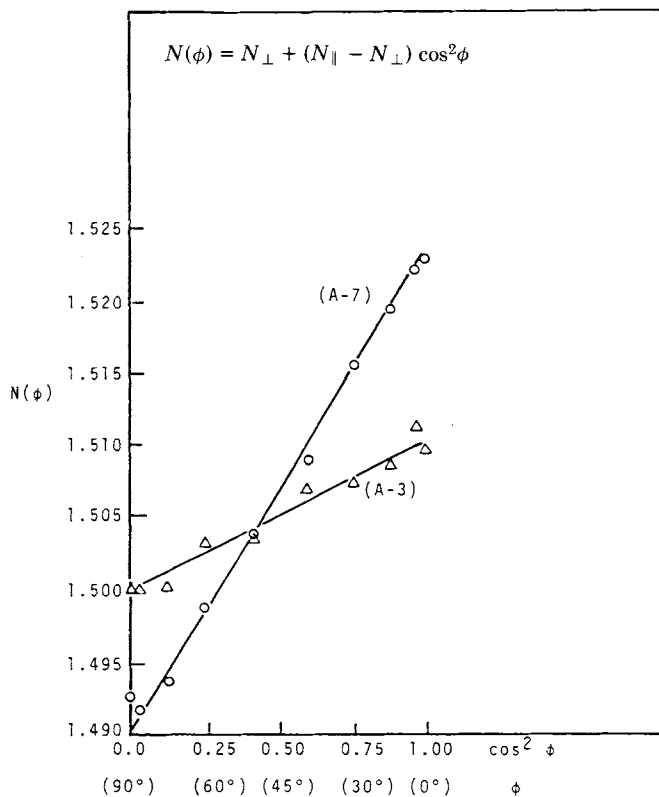
Fig. 8. $N(\phi)$ vs. $\cos^2 \phi$ for uniaxially oriented isotactic polypropylene films.

Figure 10 shows another important feature of the indicatrix expression [eq. (5)]. Here the angular data of the multiaxially drawn isotactic polypropylene films from Figure 7 are plotted according to eq. (5). The refractive index distributions in the zy plane of these films are seen to follow eq. (5) quite well. This is a consequence of the fact that the optical tensor is second-order and only the diagonal elements contribute to the field. Thus, as long as the principal optic axes are identified in the plane of the film, eq. (5) will hold. For the B500 film, the roll direction corresponded to the extinction direction, hence, the principal directions in the film are the roll direction (0°) and transverse to the roll direction (90°). These principal directions in the plane of the film are easily identified from the polar plot (Fig. 7). Similar considerations apply to the sequentially drawn films. Here, however, the principal optic axis is in the transverse direction. Thus, the lines in Figure 10 for sample Nos. 16 and 21, have a negative slope to satisfy eq. (5). If the orientation were random in the zy plane for any of these films, a horizontal line parallel to the abscissa would have been obtained.

Refractive Index Distribution and Molecular Orientation

The refractive index distribution is a reflection of the molecular orientation of the crystalline and noncrystalline components which compose the film. The measurement technique described previously shows how the refractive index
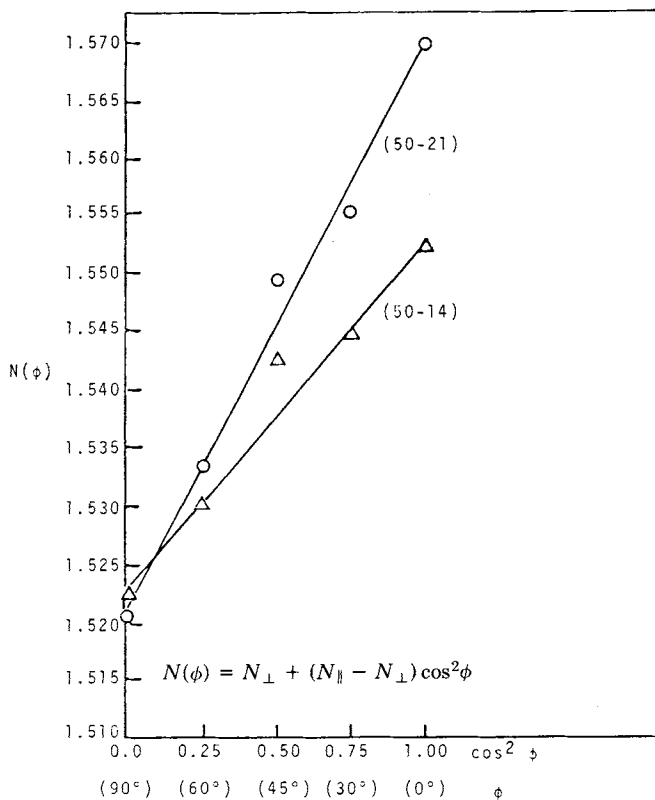
Fig. 9. $N(\phi)$ vs. $\cos^2\phi$ for uniaxially oriented polyethylene films.

distribution can be measured and described *for a given film*. Each film must be measured separately in order to describe its optical properties.

What is needed is some method of relating the refractive index distribution of one film to that of another film. In order to do this, it is necessary to relate the macroscopic optical indicatrix to the microscopic molecular structure.

This has been done for the case of uniaxial orientation.[9] The molecular orientation of the film is defined by three measureable parameters, V_c, f_c, and f_{AM}. Here, V_c is the volume fraction of crystals, f_c is the orientation function for the crystals, and f_{AM} is the orientation function for the noncrystalline chains.[7] To describe the optical properties, two intrinsic birefringences (Δ°_c and Δ°_{AM}) characterizing the optical properties of the crystal and noncrystalline elements are also necessary. These are constants intrinsic to the molecular structure and can be determined experimentally.[7,9] Once determined for a polymer, such as isotactic polypropylene, they need not be determined again.

The expression relating the refractive index, $N(\phi)$, to these molecular parameters has the form:

$$N(\phi) = \overline{N} + 2/3[V_c\Delta^\circ_c f_c + (1 - V_c)\Delta^\circ_{AM} f_{AM}]F(\phi) \qquad (6)$$

Here, $F(\phi) = (3\cos^2\phi - 1)/2$, where ϕ is the macroscopic angle around the film as defined earlier (see Fig. 4). Figure 11 shows the relation between the refractive index distribution for a series of uniaxially oriented films predicted from eq. (6)
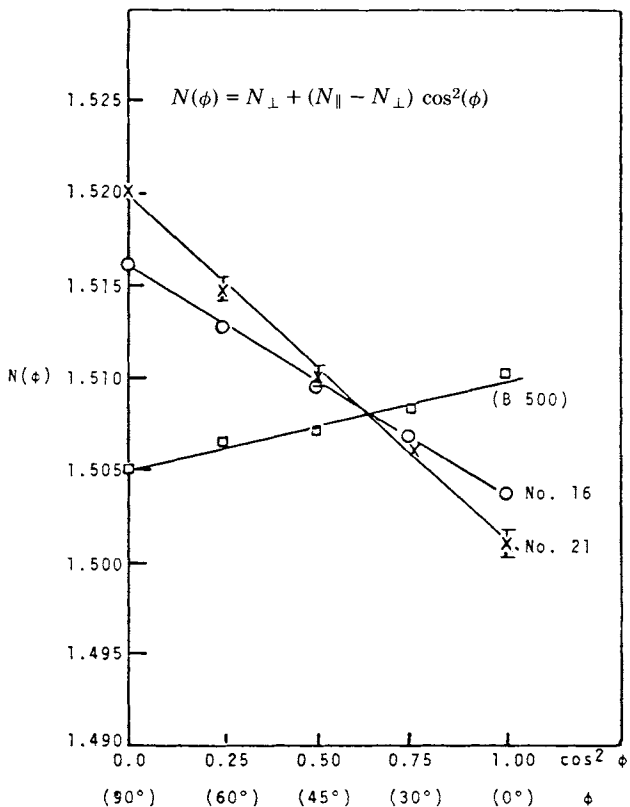
$$N(\phi) = N_\perp + (N_\| - N_\perp)\cos^2(\phi)$$

Fig. 10. $N(\phi)$ vs. $\cos^2\phi$ for multiaxially drawn isotactic polypropylene films.

using the measured values of V_c, f_c, f_{AM} (solid lines), and the experimentally determined refractive index values.[9] The fit here is quite satisfactory.

These orientation parameters $(V_c,\ f_c,\ f_{AM})$ also relate to other physical properties of the films and thus act as a link between the fabricated anisotropic structure and the observed physical properties of the fabricated film.[7] Unfor-
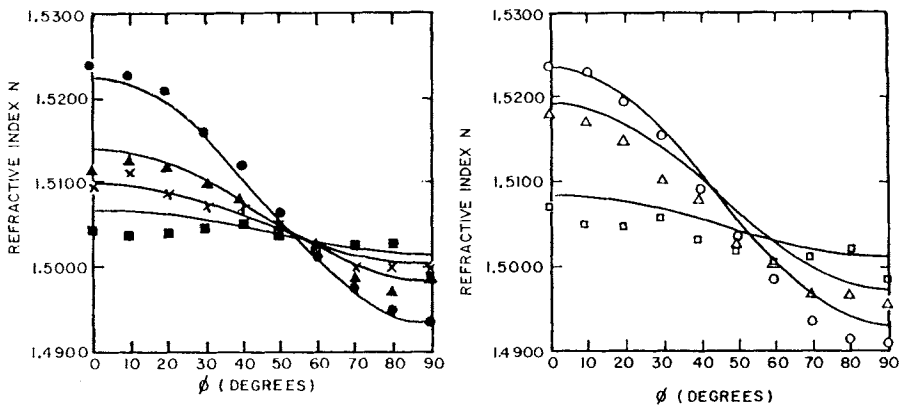

Fig. 11. Relation between the predicted and experimental refractive index distribution for a series of isotactic polypropylene films. Solid line is the predicted curve, the points are experimental.[9] ■, A–1; ×, A–3; ▲, A–4; ●, A–6; □, A–2; △, A–5; ○, A–7.

tunately, this relation has only been solved for the uniaxial case; hence, biaxial film behavior cannot be predicted from the molecular parameters.

Optical Comparison of Fabrication Processes

Normalized Optical Equations

Different fabrication processes can be considered as different paths to equivalent anisotropic molecular states.[7] In the same way, different fabrication processes can also lead to equivalent anisotropic optical states. Although equivalent anisotropic optical states do not guarantee equivalent molecular orientation states [remember from eq. (6) the optical state is a function of three variables V_c, f_c, and f_{AM}], a comparison of properties from films produced by different fabrication processes and having equivalent optical states would be useful for visualizing related processes.

Even within a given process, a characterization of equivalent optical anisotropic states can be informative. Figure 2 shows the change in the three refractive indices, N_x, N_y, and N_z, with extension for hydroxypropylcellulose. By plotting the three refractive indices against the draw ratio, the planar orientation character of the deformation became obvious, since N_x remained constant while N_z and N_y changed. Figure 12 shows a similar kind of plot, but now for a uniaxial orientation process. Two uniaxial orientation series are shown: the series A films[8] and a series reported by Schael.[3] (Note: Schael defines x as the draw direction and z as the through direction in his article. His nomenclature has been changed in this article for consistency).

The refractive index data in Figure 12 show both film processes are uniaxial, since $N_x = N_y \neq N_z$ as the sample is drawn to different extensions. The conditions of fabrication of these two series of films was different, however, since
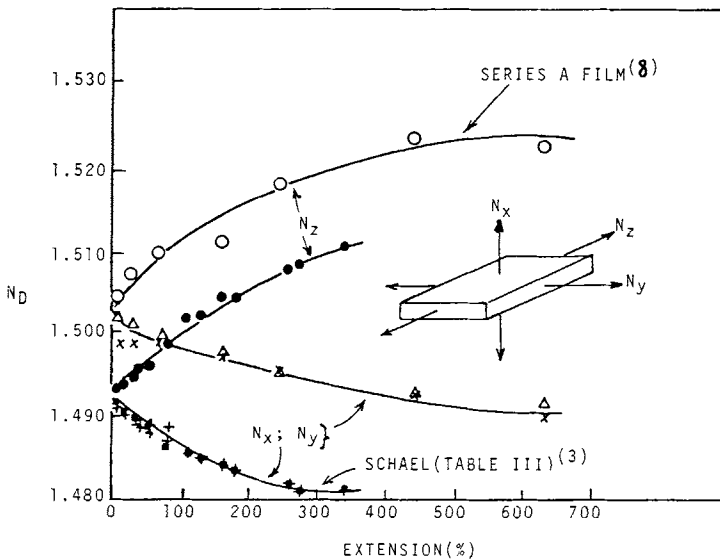

Fig. 12. Effect of deformation on the refractive indices of uniaxially oriented isotactic polypropylene films.

they were produced at different locations, at different times, and with different process equipment. An example of these differences is the different average refractive index values of the two series of films. This is a consequence of the different fraction of crystals in the two series of drawn film (see Fig. 1).

The crystallinity of each of these films and their refractive index distribution can be calculated from their N_x, N_y, and N_z values using eqs. (1), (2), and (5). However, although each film can be described in this way, it would be useful if the optical data could be normalized to some optically anisotropic equivalent state by eliminating the effect of variable crystal fraction so that only the anisotropy of the two series of films could be compared.

Consider now the problems inherent in characterizing multiaxial draw processes. Here the fabrication variables become so complicated that any normalization process which would yield criteria for comparing the film products would be useful.

The availability of the three mutually perpendicular principal refractive indices of a film provides the necessary experimental data for setting up an anisotropic optical normalization procedure. The birefringence of a film which has the same crystallinity as the experimental film sample, but in which both the crystalline and noncrystalline elements are fully oriented, can be defined as the optical reference state. That is,

$$N_\parallel^\circ = n_{\parallel,c}^\circ V_c + n_{\parallel,AM}^\circ V_{AM}$$

$$N_\perp^\circ = n_{\perp,c}^\circ V_c + n_{\perp,AM}^\circ V_{AM} \tag{7}$$

$$(N_\parallel^\circ - N_\perp^\circ) = \text{reference state birefringence}$$

Where $N_\parallel^\circ$ is the theoretical limit for the average parallel refractive index of fully oriented crystalline and noncrystalline chains of a given volume fraction V_c; $N_\perp^\circ$ is the theoretical limit for the average transverse refractive index of fully oriented crystalline and noncrystalline chains of a given volume fraction V_c; $(N_\parallel^\circ - N_\perp^\circ)$ is the maximum average refractive index difference possible for a given volume fraction of crystals if all the chains are fully oriented; $n_{\parallel,p}^\circ$, $n_{\perp,p}^\circ$ are the parallel and perpendicular refractive indices of the crystalline and noncrystalline elements ($p = c$,AM); and $V_{AM} = (1 - V_c)$, is the volume fraction of noncrystalline chains.

By defining the limits in this way [eq. (7)], the crystallinity effect is eliminated and only the optical anisotropy contributes to the result.

The fraction of the total refractive index of the sample oriented in a given film direction can then be defined as

$$f(N_i) = \frac{N_i - N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ} \tag{8}$$

where N_i is the measured refractive index in the i direction, and $i = x, y,$ and z; and $(N_i - N_\perp^\circ)$ is the refractive index difference between the ideal transverse refractive index, $N_\perp^\circ$, and that actually present in the sample in the i direction, N_i.

For this definition of $f(N_i)$ the following orthogonality relation holds (Appendix A):

$$f(N_x) + f(N_y) + f(N_z) = 1 \tag{9}$$

This orthogonality relation means that determination of any two $f(N_i)$ values will immediately determine the third. This in turn leads to a simple plotting method which relates samples prepared by different processes to an equivalent anisotropic optical state.

Isotactic polypropylene can be used as an example of the method. By means of the trirefringence technique, N_x, N_y, and N_z are determined for a given film. Then from Figure 1 and eqs. (1) and (2)

$$\overline{N} = (N_x + N_y + N_z)/3 \tag{10}$$

and

$$V_c = \frac{\overline{N} - 1.4707}{(0.0538)}$$

Also for isotactic polypropylene

$$N_{\parallel}^{\circ} = n_{\parallel,c}^{\circ} V_c + n_{\parallel,AM}^{\circ} V_{AM} = 1.5439\, V_c + 1.5107\, (1 - V_c)$$

$$N_{\perp}^{\circ} = n_{\perp,c}^{\circ} V_c + n_{\perp,AM}^{\circ} V_{AM} = 1.5148\, V_c + 1.4507\, (1 - V_c) \tag{11}$$

Where the molecular refractive indices $n_{\parallel,p}^{\circ}$ and $n_{\perp,p}^{\circ}$ ($p = c$,AM) were obtained from intrinsic optical data (Appendix B).

By use of eqs. (10) and (11) and the three measured refractive indices, N_x, N_y, and N_z, eq. (8) can then be calculated for the film:

$$f(N_z) = \frac{N_z - N_{\perp}^{\circ}}{N_{\parallel}^{\circ} - N_{\perp}^{\circ}}$$

$$f(N_y) = \frac{N_y - N_{\perp}^{\circ}}{N_{\parallel}^{\circ} - N_{\perp}^{\circ}}$$

$$f(N_x) = \frac{N_x - N_{\perp}^{\circ}}{N_{\parallel}^{\circ} - N_{\perp}^{\circ}}$$

These normalized optical data may then be used to compare the anisotropic optical properties of films prepared by different process variables.

Triangular Plots of Normalized Optical Data

The orthogonality relation that exists between the three fractional optical parameters, $f(N_i)$, dictates that a knowledge of any two of the fractions will determine the third. This immediately suggests a triangular plotting procedure which will illustrate the relationship between the three fractions.

Figure 13 is just such a plot for the uniaxially oriented isotactic polypropylene films shown in Figure 12, along with other uniaxially oriented films reported by Schael.[3] The z direction is the machine direction (MD), the y direction is the cross direction (CD), and the x direction is the through direction (TD) of the films. The ordinate and abscissa of the plot vary from 0.0 to 1.0, the upper and lower limits of $f(N_i)$. The values of $f(N_z)$ are plotted along the vertical axis, and the values of $f(N_y)$ are plotted along the horizontal axis. To complete the triangle, a line is then connected between $f(N_z) = 1$, where orientation is perfectly parallel to the z axis, to $fN(y) = 1$, where full orientation would be parallel to the y axis. Three lines are then drawn within the triangle connecting each apex of the triangle to the midpoint of the opposite side. Each of these lines represents a uniaxial orientation line, since any point along one of these lines will have the
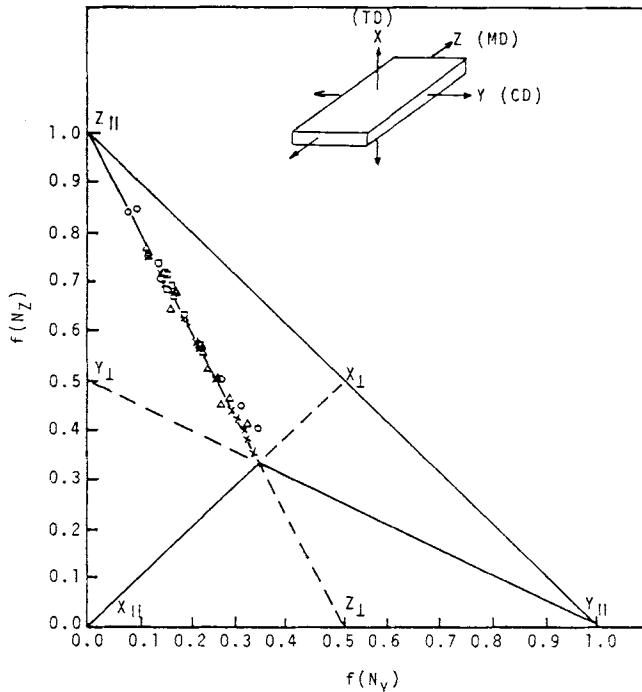
Fig. 13. Refractive index characterization of uniaxially oriented isotactic polypropylene films. O, Series A, drawn film[8]; △, Schael, Table I[3]; □, Schael, Table II (selected)[3]; ×, Schael, Table III.[3]

refractive index parallel to that axis with the other two perpendicular refractive indices equal to each other. Where the three lines intersect, $f(N_y) = f(N_z) = f(N_x)$. Thus, the point of intersection of the three lines identifies the completely unoriented state.

The isotactic polypropylene film data all fall along the z axis line in Figure 13. The z axis was defined as the extension direction for these uniaxially oriented films. Films with equivalent optical anisotropy may be identified by their equivalent position along the z-axis line. Since the optical anisotropy is a general measure of the total molecular orientation in the film, the relative orientation within the different films can be assessed by the position of the sample on the z-axis line.

Films which behave as though they have planar orientation with extension (see Fig. 2) are also easily identified with the triangular plot. Here, $f(N_x)$ will be a constant for all samples (where x is the through direction) since for planar orientation N_x does not change with extension. Under this restriction, all of the points will fall along a line perpendicular to the x-axis line. Figure 14 shows normalized optical data from isotactic polypropylene films simultaneously drawn on a T.M. Long stretcher to different draw ratios at 300°F.[3] The data for two groups of the films fall along a line of constant $f(N_x)$; $[f(N_x) = 0.15]$. Although the orientation within the plane of these films varies $[f(N_z)$ and $f(N_y)$ change], the refractive index through the film thickness remains essentially constant $[f(N_x) = 0.15]$. The third set of data for the simultaneously drawn film falls around a different $f(N_x)$ line $[f(N_x) = 0.265]$ with one point from these data approaching the other two sets. Whether either of these $f(N_x)$ values are related
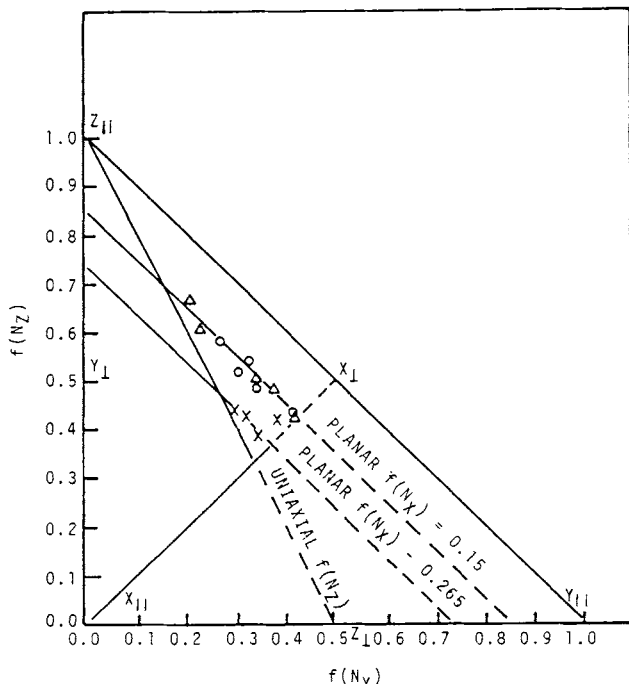
Fig. 14. Refractive index characterization of simultaneously drawn isotactic polypropylene films. O, Schael,[3] Table I (group 1); △, Schael,[3] Table I (group 2); X, Schael,[3] Table I (group 4).

to a particular set of desirable film properties is not known, but it is interesting that essentially constant through refractive index with differing orientation within the plane of the film was achieved by the process.

Figure 15 shows normalized optical data for films produced by other multiaxial film processes as reported by Schael.[3] Here some of the data were produced on the T.M. Long stretcher by sequential drawing, while the rest were produced from the same 10-mil polypropylene sheet at 300°F by a combination of simultaneous and sequential drawing. The interesting feature of these data is that the optical properties of these samples fall around a planar line having an $f(N_x)$ value of 0.14. Since much of the simultaneously drawn film data (Fig. 14) falls along a similar valued planar line [$f(N_x) = 0.15$], these results suggest that either attempts were made to produce similar films from the three processes or the T.M. Long stretcher can impose a limiting x-direction orientation by the nature of its operation.

Obviously, depending on the process variables, points can fall all over the normalized optics triangle during multiaxial draw. Thus, the four values represented by crosses in Figure 14 not only represent films which are closer to unoriented or uniaxial than the other samples in the figure, but also show the kind of scatter of values one might normally expect from such a complex fabrication process.

Correlations with Fabrication Draw

The normalized optical data may also be used in conjunction with the fabrication variables to determine the effect of these variables on film properties. For
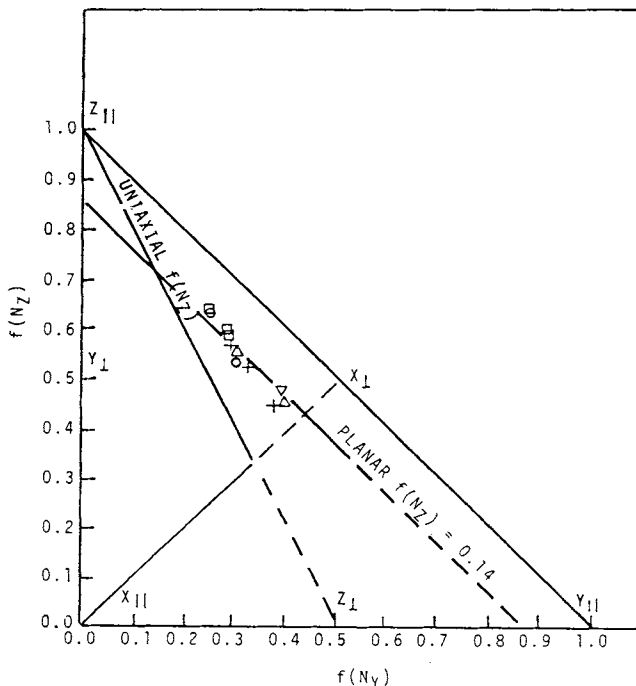
Fig. 15. Refractive index characterization of sequentially, and simultaneous–sequentially drawn isotactic polypropylene films. O, sequential, Table I, part 1; △, sequential, Table I, part 2; □, sequential, Table I, part 3; +, simultaneous–sequential, part 1; ▽, simultaneous–sequential, part 3 (ref. 3).

multiaxial processes, these data can be plotted on perspective paper, so that three parameters can be examined simultaneously.

Figure 16 is a three-dimensional plot of some of the fabrication variables used to produce the simultaneously drawn films examined in Figure 14. Here the two draw ratios reported by Schael[3] are plotted along the horizontal axes, while $f(N_z)$ is plotted along the vertical axis. Since from Figure 14, all of Schael's (group 1) and (group 2) data have essentially the same refractive index through the film, only one refractive index term, $f(N_z)$, should be needed to observe any trend. Examination of Figure 16 shows that the greater the draw in the z direction with respect to that in the y direction, the greater will be $f(N_z)$. Thus, if the percent elongation of y is held constant at some draw such as 200%, and the percent elongation in the z direction is increased, $f(N_z)$ will increase with increasing z-direction draw. Similarly, if $f(N_z)$ is held constant at some draw such as 500% extension and elongation increased in the y direction toward the equal biaxial draw line, $f(N_z)$ will decrease with increasing y-direction draw. In fact, observation of Figures 14 and 16 suggests that $f(N_z)$ may be proportional to the ratio of the elongation in the z direction, $[\%E(z)]$, to that in the y direction, $[\%E(y)]$, for the first two sets of simultaneously drawn data, where the through-direction fraction is essentially constant.

Figure 17 is a plot of the biaxial draw ratio $[\%E(z)/\%E(y)]$ against $f(N_z)$. As suggested by Figures 14 and 16, $f(N_z)$ is found to be directly proportional to the biaxial draw ratio for the two sets of data in which the orientation through the film thickness was essentially constant. The one optical value for which group 4 draw data[3] was available and which had a different through direction orien-
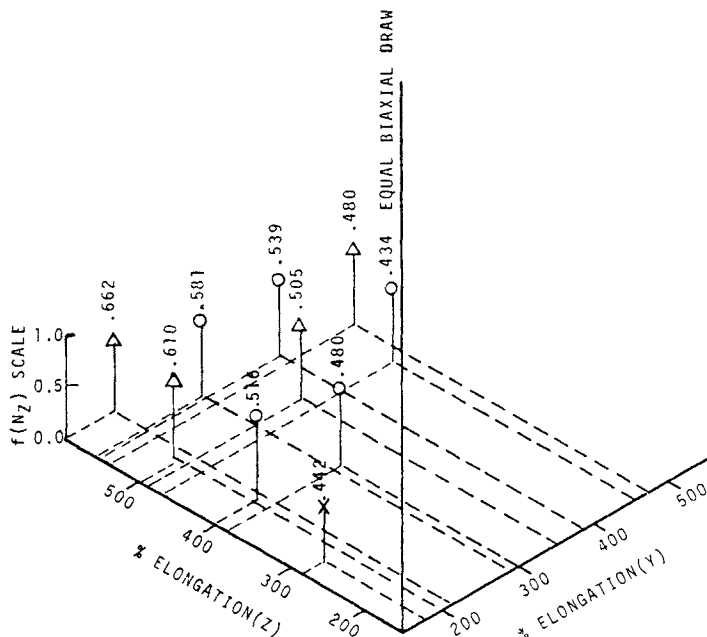
Fig. 16. Effect of simultaneous draw at 300°F in the ZY plane on the normalized refractive index, $f(N_Z)$, of isotactic polypropylene film. O, Schael,[3] Table I (group 1); Δ, Schael,[3] Table I (group 2); X, Schael,[3] Table I (group 3).

tation from the other data sets falls off this proportionality line, as would be expected. Thus, by use of the normalized fractional refractive indices, considerable insight can be gained about the workings of a fabrication process.

Since normalized optical data from three different biaxial fabrication processes are available, the relation between the draw ratios and the resulting optical anisotropy of the films produced by these different processes can now be compared. Figures 18 and 19 show three-dimensional plots of the optical anisotropy as a
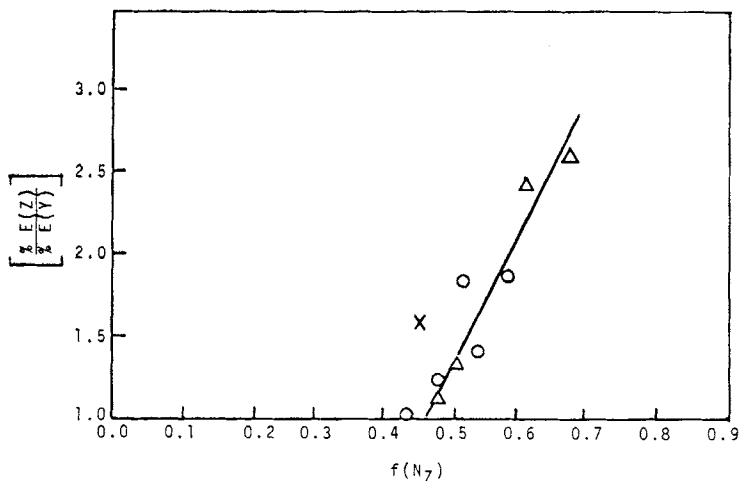

Fig. 17. Relation between the biaxial draw ratio, $[\%E(z)/\%E(y)]$ and the normalized refractive index, $f(N_z)$, for simultaneously drawn isotactic polypropylene film. O, Schael,[3] Table I (group 1); Δ, Schael,[3] Table I (group 2); X, Schael,[3] Table I (group 4).
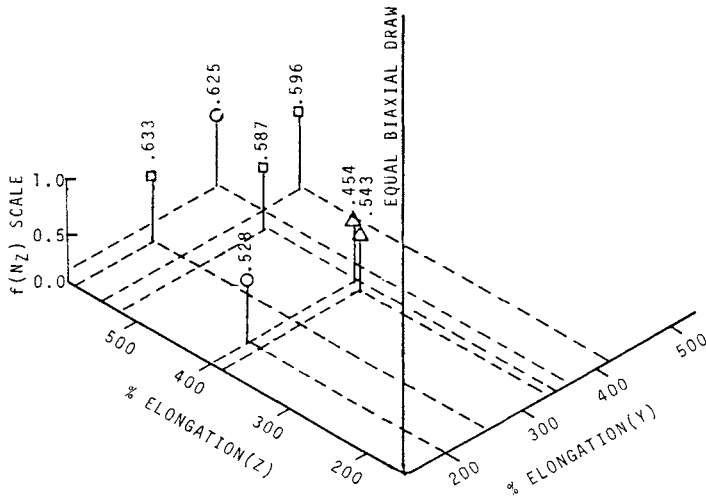
Fig. 18. Effect of sequential draw at 300°F in the zy plane on the normalized refractive index, $f(N_z)$, of isotactic polypropylene film.

function of biaxial draw for the sequentially drawn (Fig. 18) and simultaneously sequentially drawn (Fig. 19) films.   Only a few points are available from each of these processes, and although the data trends seem generally similar to those observed for the simultaneous draw process (Fig. 16), the results are far from conclusive.

If Figures 18 and 19 are overlaid onto Figure 16, it becomes obvious that similar orientation occurs at equivalent draw ratios for both the simultaneous–sequential draw process and the simultaneous-only draw process (a rather surprising result) but that different draw ratios are required to get equivalent optical anisotropy with the sequential draw process.   Since the general trends of the data from all
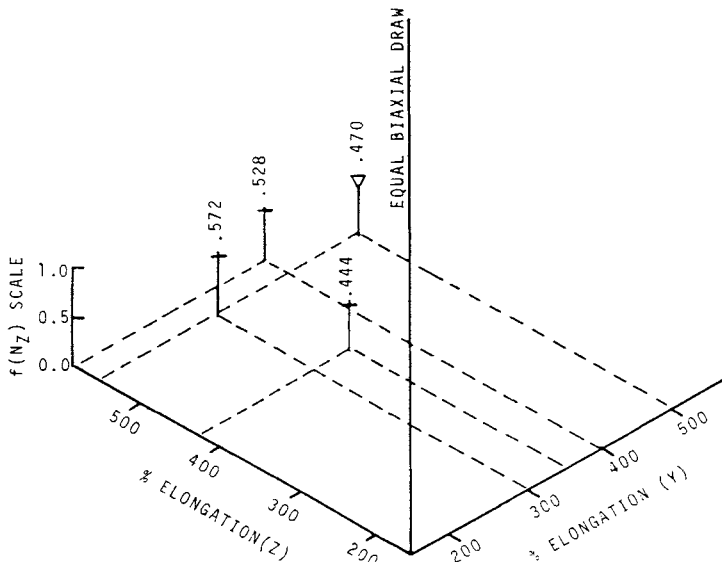

Fig. 19. Effect of simultaneous–sequential draw at 300°F in the zy plane on the normalized refractive index, $f(N_z)$, of isotactic polypropylene film.
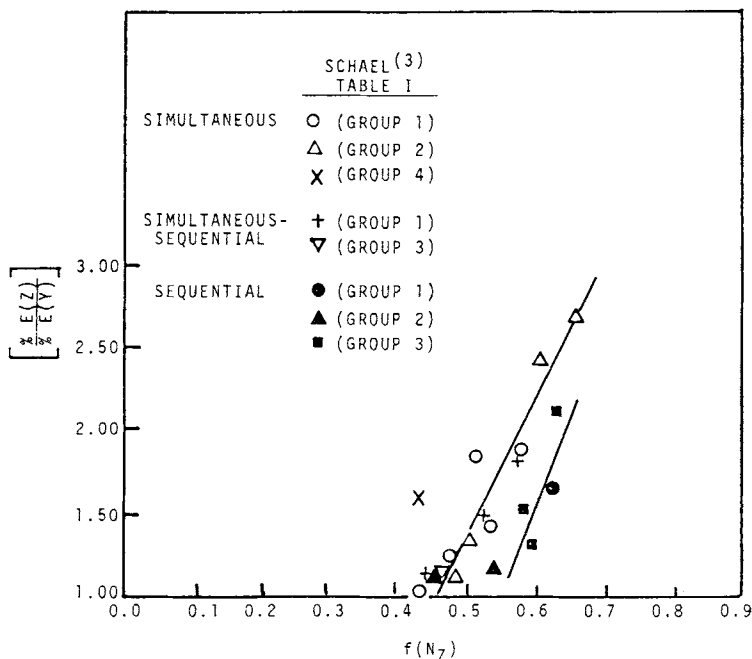
Fig. 20. Relation between the biaxial draw ratio, [%E(z)/%E(y)], and the normalized refractive index, $f(N_z)$, for films produced by different drawing processes.

three processes are the same and $f(N_x)$ has approximately the same constant value for all three sets of films (see Figs. 14 and 15), the biaxial draw ratio data from all three processes is plotted against the normalized optical anisotropy along the z-draw direction, $f(N_z)$, in Figure 20.

The results in Figure 20 substantiate the observations made by overlying Figures 16, 18, and 19. The optical anisotropy follows the same draw ratio relationship for the simultaneous–sequential fabrication process as it does for the simultaneous process. The data from the sequential fabrication process, while following a similar trend for the change in optical anisotropy with biaxial draw ratio, requires different amounts of biaxial draw than the other two processes to achieve an equivalent optical anisotropy. Thus, different fabrication processes can be compared by using normalized optical data as characterization criteria.

EXPERIMENTAL TRIREFRINGENCE PROCEDURE

General Principle of Measurement

Okajima and Koizumi[1] made a detailed study of the optical trirefringence technique, including a geometric ray analysis and a test of the system with mica. The analysis provided by Wilchinsky and Mercier, though less sophisticated, amply describes the principles of the technique as follows[10]:

Let the three principal directions in a film be designated x, y, and z, and the principal refractive indices N_x, N_y, and N_z. These are defined as the refractive indices measured with plane polarized light having its electric vector parallel to the x, y, and z directions, respectively. Consider a film placed between the
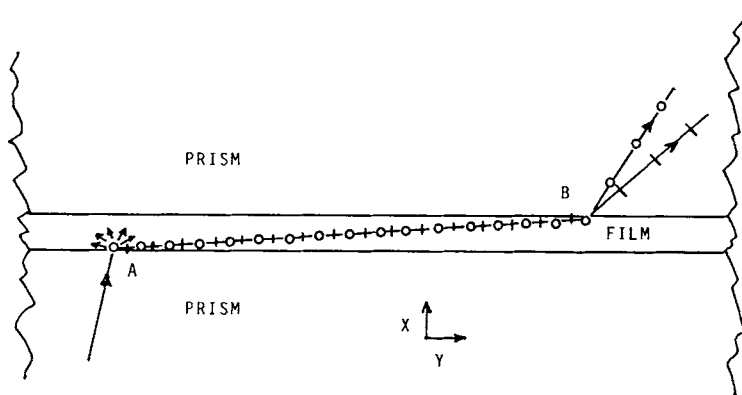
Fig. 21. Diagram showing position of film between prisms of ABBE refractometer. Polarized components of limiting rays are refracted separately at B.[10]

prisms of a refractometer as indicated in Figure 21. The refractive index of the prisms is greater than those of the film. This is to prevent total reflection at the film–prism interface. Unpolarized light, on emerging from the lower prism, is scattered at the diffusing surface of the prism in contact with the film at A. Because of the birefringent nature of the film, the light in the film is, in general, no longer unpolarized. The rays scattered at A and traveling in the xy plane of the film will consist of two sets of plane polarized rays, one set having electric vectors in the xy plane and the other having electric vectors perpendicular to this plane.

The beam from A to B in the figure represents a bundle of rays traveling very nearly in the y direction. For one set of the constituent rays, the electric vector is in the z direction; for the other set, the direction of the electric vector can be closely approximated as the x direction. The error resulting from this approximation is negligible. On entering the upper prism at B, these two sets of rays are refracted through different angles. By means of an analyzer, each of these sets of rays is transmitted, in turn, and the corresponding refractive indices N_z and N_x are measured in the usual manner. The refractive index, N_y, can be measured when the positions of the film's y and z directions are interchanged in the refractometer.

To facilitate obtaining a sharp optical image, an inert contact liquid between the film and prisms is recommended. The refractive index of this liquid must be greater than the refractive index being measured, otherwise total reflection of the desired limiting rays will occur in the film at the film–liquid interface at B.

Thus, by the application of a higher refractive index oil to the polymer film and the simple attachment of a rotatable polaroid film analyzer to the refractometer eyepiece, the Abbé refractometer is converted into a powerful tool for determining all three refractive indices of a film.

Experimental Technique

Measuring Instrument and Sample Mounting Procedures

The Abbé-Refractometer "trirefringence" technique is a direct, easy to use, accurate method for measuring the refractive indices of films. A Zeiss Opton
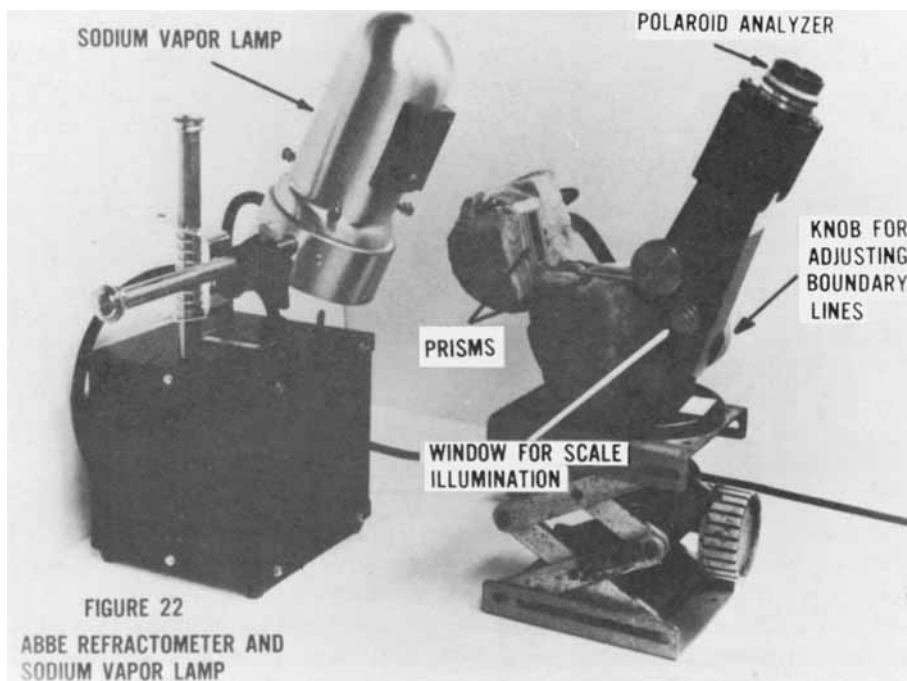
Fig. 22. ABBE refractometer and sodium vapor lamp.

Zomess model G-110 Abbé refractometer with a rotatable film analyzer mounted on the eyepiece constitutes the measuring instrument (Fig. 22) used in this study. The refractive index range with the standard prisms is 1.3–1.7.

The film to be measured is cut large enough to cover the measuring prism (the measuring prism is 10×35 mm). It is important to note that the entire prism should be covered by the sample. (It was found that the ideal sample size is 40×30 mm because then the same piece of film can be used when the sample is rotated as described later in this article.) If the sample does not cover the entire measuring prism, lateral incident light may reduce the contrast of the boundary line. If a large enough sample cannot be obtained, the open part of the measuring prism can be masked from light by a black paper cover.

Once the sample is cut and ready, a drop of immersion fluid is placed on the measuring prism. The immersion fluid should have a higher refractive index (n_D) than the film to be measured. For polypropylene films, Dow silicone oil $(n_D$ 1.52–1.54) was used. For higher refractive index films like polyethylene $(n_D$ 1.54–1.56), a mixture of the same silicone oil with α-chloronaphthalene (a common immersion fluid, n_D 1.632) may be used. A mixture of approximately one part silicone oil to two parts α-chloronaphthalene will give a refractive index of about 1.59–1.61. The exact refractive index of the mixture can be obtained in the Abbé refractometer before using it with films.

It is important that the immersion fluid "wet" the film thoroughly and evenly if accurate results are desired. α-Chloronaphthalene and some other immersion fluids were found not to wet the film properly when used alone. Uneven, hard to see boundary lines were obtained giving scattered results. Once the proper wetting immersion fluid has been identified, it is evenly dispersed on the mea-
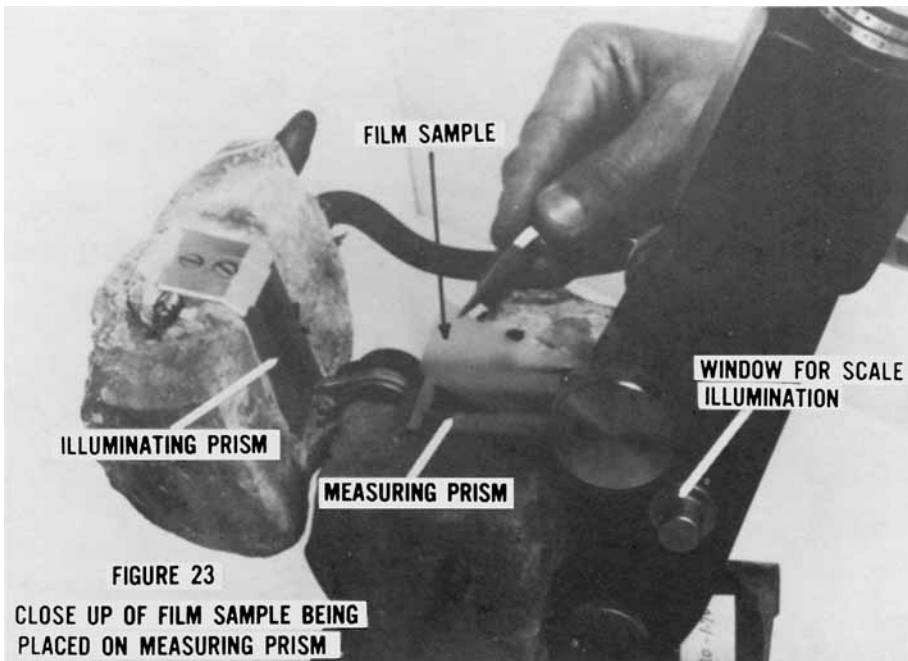
Fig. 23. Closeup of film sample being placed on measuring prism.

suring prism. The film is then placed on the prism, being careful not to get air bubbles under the film (Fig. 23). A drop of immersion fluid is placed on the exposed surface of the film and spread thinly over it. The illuminating prism is then carefully folded down into place. The refractive index is now ready to be read.

For measuring the refractive indices of polypropylene and polyethylene films, it is necessary to use a monochromatic light source (Fig. 22) in conjunction with the refractometer. A sodium vapor lamp (sodium spectral D line; wavelength 589.3 mμm) was used for this purpose. (The model used in these tests was an SLA-5c from Geo. W. Gates and Co., Franklin Square, Long Island, NY, ordered through Fisher Scientific Co.) With the sample set up in the refractometer as previously described, the sodium lamp is brought close to the light-admission aperture of the illuminating prism.

The refractive indices are read in the Abbé using the following procedure. The rotatable Polaroid film holder mounted above the eyepiece (Fig. 24) is removed. The knurled ring is then turned until the crosshairs are clearly defined in the upper illuminated field of view. This simultaneously brings the refractive index scale in the lower field of view into sharp focus [Fig. 25(a)]. The eyepiece is then replaced with the polarized eyepiece 0° mark aligned with the reference mark (see degree settings and reference mark position in Figure 24). The polarized eyepiece has settings for 0°, 30°, 60°, and 90°.

With the sample set up as previously described the refractive indices may now be determined. The light (from the sodium lamp) enters through the aperture of the illuminating prism and penetrates the film (Fig. 23). Via a reflecting mirror, the light passes through the measuring prism and a lens to the image boundary line in the field of view of the eyepiece. By rotating the boundary
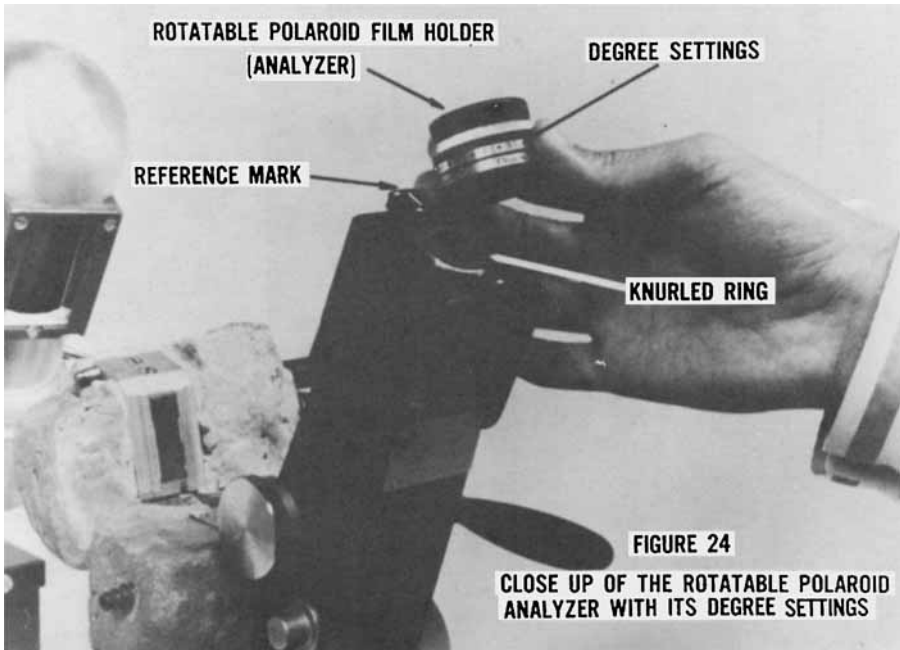
Fig. 24. Closeup of rotatable Polaroid analyzer with degree settings.

adjustment knob (the large lower knob on the right side of the Abbé, Fig. 22), the boundary line between the light and dark fields can be centered at the intersection point of the crosshairs [Fig. 25(b)]. Once the crosshairs are set, the refractive index is read directly from the scales located below the field of adjustment. The refractive index scales can be illuminated for easier reading by directing a light source (an intense microscope light works well) to the window located in the middle of the Abbé on the left-hand side (Fig. 22).

Determination of Sample Film Refractive Indices

Before wetting, a sample the film is first examined. If samples received are not identified as to their machine or draw direction, a reference direction must be found. This is done by placing the sample film between two pieces of Polaroid material that are "crossed" so that no light shows through.

If the film sample is balanced, i.e., exhibiting identical properties in all directions around the film, nothing will be seen but a dark background when the sample film is rotated to any angle between the crossed polarizers when placed over a lightbox (or some other light source). If a sample of uniaxial film (drawn in a single direction) is placed between the same two pieces of crossed Polaroids and rotated, the sample will be extinguished (turns black) at a certain position. It will be found that the extinction positions for any one sample are 90° apart; extinction occurs four times during a complete rotation of the film. It is important that one of the extinction directions is defined as the reference direction (0°) and thereafter used as the reference direction (0°) for all other angle cuts made. When the machine direction is specified for a sample, the extinction
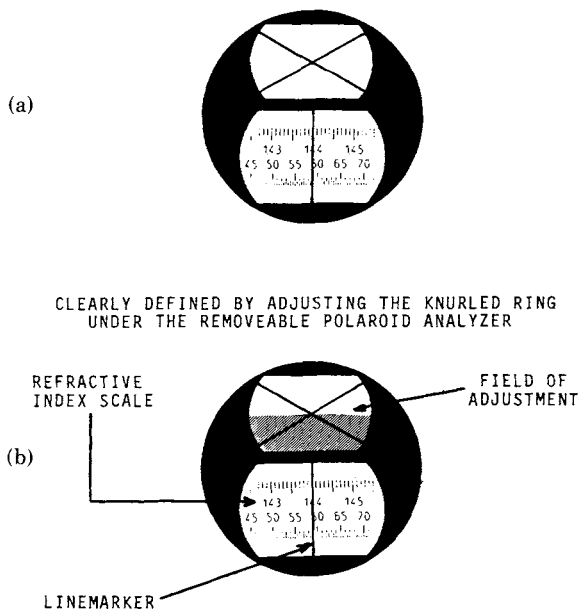
FIELD OF VIEW IN ABBE REFRACTOMETER

(a)

CLEARLY DEFINED BY ADJUSTING THE KNURLED RING
UNDER THE REMOVEABLE POLAROID ANALYZER

REFRACTIVE
INDEX SCALE

FIELD OF
ADJUSTMENT

(b)

LINEMARKER

Fig. 25. Field of view in ABBE refractometer. (a) Crosshairs clearly defined by adjusting knurled ring under removeable Polaroid analyzer. (b) Boundary line in the field of adjustment.

direction most nearly coinciding with this direction is generally chosen as the 0° direction.

A 40 × 30-mm sample is cut in this 0° reference direction. This film is then carefully placed on the refractometer with the 0° direction aligned as closely as possible parallel to the long axis of the measuring prism. With the film properly placed in the refractometer, using the proper immersion oil, four refractive index measurements are now obtained from a single film sample.

The first reading is with the Polaroid anlayzer in the 0° direction (Fig. 24). For the second reading, the sample remains in the same position and the Polaroid
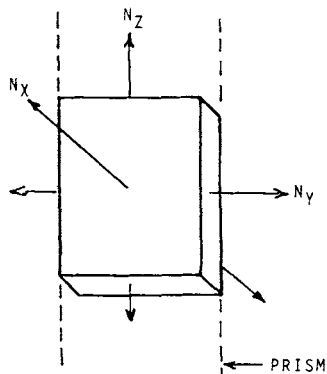
N_Z

N_X

N_Y

PRISM

Fig. 26. Cut-away view of film with N_z direction being the machine (and draw) direction.

analyzer is rotated to the 90° setting (Fig. 24). A second reading is then taken as before. For the third reading, the sample film is now rotated 90° in the refractometer and the Polaroid analyzer is reset in the 0° position. Finally, for the fourth reading, the sample is again left untouched and the Polaroid analyzer is rotated to the 90° setting. Figure 26 defines the three measurement directions. The first reading taken (the Polaroid analyzer in the 0° setting and the sample in the 0° direction) was in the through (N_x) direction. The second reading taken (Polaroid analyzer rotated to 90° setting and the sample in the 0° direction) was in the cross (N_y) direction. The third reading taken (film rotated 90° and the Polaroid analyzer on 0° setting) was another through (N_x) direction reading. The fourth reading (the film position unchanged and the Polaroid analyzer rotated to the 90° setting) was in the machine or orientation direction (N_z). This yielded the three refractive indices required for a quantitative description of the optical axiality. Figure 27 (with Table II) shows the results from a single film sample of oriented high-density polyethylene (Nos. 50–21) that had been cast and drawn to 6.5×. The measurements were made on a 0° cut in the orientation direction (in this case, the orientation and machine directions were the same).

To determine the optical distribution around the axis of the film, samples can be cut at several angles around the orientation direction. Using the 0° (machine) direction as the reference direction, individual strips can be cut at various angles ϕ around the film (Fig. 4). Each strip is treated as a separate sample and measured as described previously. The data from each strip can then be tabulated as shown in Figure 28 and Table III.
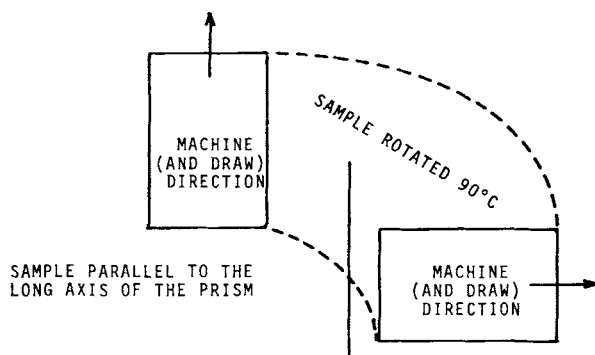

Fig. 27. Refractive index readings from a single 0° cut strip of polyethylene.

TABLE II
Tabulated Data for Figure 27

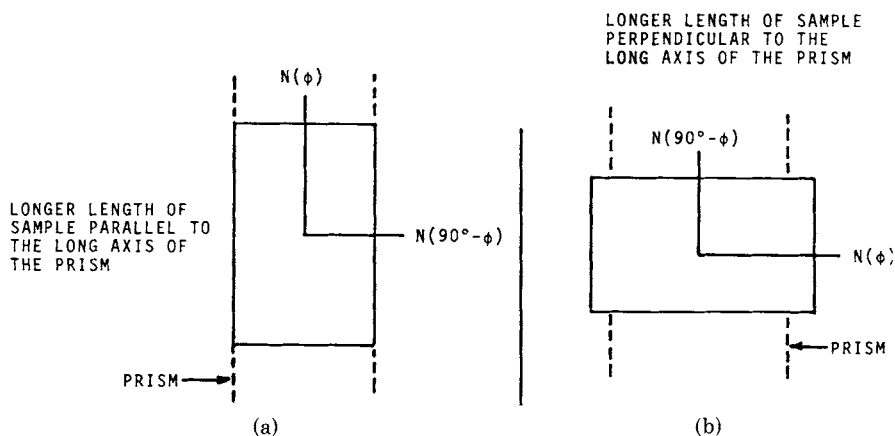|			Sample Rotated 90°	
Fabrication direction	Through direction, N_x	Cross direction, N_y	Through direction, N_x	Machine direction (draw direction), N_z
Polaroid analyzer setting,°	0	90	0	90
Refractive index reading	1.5188	1.5202	1.5215	1.5710

Fig. 28. Measured refractive indices from a polyethylene sample (Nos. 50–21) cut around angles. (a) Longer length of sample parallel to long axis of prism. (b) Longer length of sample perpendicular to long axis of prism. See Table II.

TABLE III
Tabulated Data for Figure 28

Cut strip angle, ϕ	A Direction		B Direction	
	Analyzer, 0°	Analyzer 90°	Analyzer 0°	Analyzer 90°
0°	1.5188	1.5202^5	1.5215	1.5710^1
30°	1.5190	1.5314^4	1.5180	1.5551^2
45°	1.5185	1.5520^3	1.5180	1.5465^3
60°	1.5195	1.5552^2	1.5190	1.5355^4
90°	1.5185	1.5685^1	1.5200	1.5210^5

Refractive Index Averages around Film Plane

$\phi,°$	Number	Refractive index average
0	1	1.5698 ± 0.001
30	2	1.5552 ± 0.0001
45	3	1.5493 ± 0.003
60	4	1.5335 ± 0.002
90	5	1.5206 ± 0.0004 N_x (through) average 1.5191 ± 0.002

There is a direct relationship between the refractive indices measured from the film samples cut at different strip angles. For example, the strip cut at the angle, $\phi = 0°$, placed in the refractometer with the long axis perpendicular to the prism axis (B direction), with the Polaroid analyzer set at 90°, should give the same reading from the refractometer as the strip cut at the angle $\phi = 90°$, placed in the refractometer with its long axis parallel to the prism axis (A direction), with the Polaroid analyzer set at 90°. The complementary strip cut angles, (ϕ), that directly correspond with each other, can be calculated by using the following formula for the refractive indices in the plane of the film: $N(\phi) = N(90° - \phi)$. This is indicated by the corresponding superscript numbers (1–5) in Figure 28 (a). Thus, with the Polaroid analyzer set at 90° in all cases, the $\phi = 30°$ strip placed in direction B was averaged with the $\phi = 60°$ strip placed in direction A

(the 30° cut = 90° − 30° cut = 60°). The 45° cut placed in directions A and B were averaged together and should be the same (45° cut = 90° −45° cut = 45°). The 60° cut placed in direction B was averaged with the 30° cut placed in direction A. The 90° cut placed in direction B was averaged with the 0° cut placed in direction A. The average refractive indices around the film plane are shown in Figure 28 (b). Having two measured values for each ϕ angle increases the accuracy of the data used for correlating with the fabrication variables and end-use properties of the film.

The refractive index through the film is obtained when the Polaroid analyzer is set at 0° at all times. Since the through refractive index remains constant for all the strip data, ten through-direction values are obtained [Fig. 28(a)]. By averaging these ten values an accurate measure of the through refractive index is also obtained [Fig. 28(b)].

CONCLUSIONS

The "trirefringence" technique is a simple, direct method for determining the refractive indices in all three principal directions (machine, cross, and through directions) of a film. The modified Abbé refractometer is a low-cost piece of equipment, the measurements are rapid (a few minutes), and the resulting optical information is excellent for evaluation of practical film problems.

The applicability of the optical trirefringence data to practical film evaluation has been demonstrated. The kind of film information that can be generated from the trirefringence data includes the following:

(1) the percent crystallinity of the film;
(2) the birefringence in all three principal directions of the film;
(3) the refractive index distribution in the plane of the film; and
(4) normalized optical anisotropy parameters.

There are a large number of fabrication processes (uniaxial draw, biaxial draw, film blowing, tentering) used to produce commercial film. Within each of these fabrication processes, a wide range of variables (temperature, rate, extension) may be used. Since the function of all of these processes is to rearrange the internal molecular architecture to achieve desired properties, and since the range of available structures is limited, equivalent anisotropic states can be produced either by the different fabrication processes or, within a given process, by the selection of different process variables.

Criteria are needed to assess what process conditions lead to equivalent anisotropic states if excessive on-line experimentation is to be prevented. This optical information can be used for assessing equivalent optical anisotropic states. In this way, the relation between the products of different fabrication techniques can be evaluated, and the advantages and disadvantages of the different processes assessed.

APPENDIX A

Proof of the $f(N_i)$ Orthogonality Relation

$$\frac{N_x - N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ} + \frac{N_y - N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ} + \frac{N_z - N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ} = 1 \tag{A-1}$$

$$\left[\frac{(N_x - N_\perp^\circ)}{N_\perp^\circ} + \frac{(N_y - N_\perp^\circ)}{N_\perp^\circ} + \frac{(N_z - N_\perp^\circ)}{N_\perp^\circ}\right]\left(\frac{N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ}\right) = 1$$

$$\left[\left(\frac{N_x}{N_\perp^\circ}\right) - 1 + \left(\frac{N_y}{N_\perp^\circ}\right) - 1 + \left(\frac{N_z}{N_\perp^\circ}\right) - 1\right]\left(\frac{N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ}\right) = 1$$

$$\left[\left(\frac{N_x}{N_\perp^\circ} + \frac{N_y}{N_\perp^\circ} + \frac{N_z}{N_\perp^\circ}\right) - 3\right]\left(\frac{N_\perp^\circ}{N_\parallel^\circ - N_\perp^\circ}\right) = 1$$

$$(N_x + N_y + N_z) - 3N_\perp^\circ = (N_\parallel^\circ - N_\perp^\circ)$$

$$N_x + N_y + N_z = (N_\parallel^\circ + 2N_\perp^\circ) \tag{A-2}$$

Dividing both sides of eq. (A-2) by 3 yields:

$$\overline{N} = (N_x + N_y + N_z)/3 = (N_\parallel^\circ + 2N_\perp^\circ)/3 \tag{A-3}$$

and from eq. (A-3):

$$\overline{N} = \overline{N}$$

APPENDIX B

Calculation of Molecular Optics for Isotactic Polypropylene

$$\overline{N}_c = (n_{c \text{ axis}} + n_{a \text{ axis}} + n_{b \text{ axis}})/3$$

but

$$n_{a \text{ axis}} \cong n_{b \text{ axis}} = n_{\perp,\text{cryst}}$$

$$\therefore \overline{N}_c = (n_{c \text{ axis}} + 2n_{\perp,\text{cryst.}})/3 = 1.5245 \text{ (from Fig. 1)} \tag{B-1}$$

$$\Delta_c^\circ = (n_{c \text{ axis}} - n_{\perp,\text{cryst.}}) = 0.0291 \tag{B-2}$$

Where Δ_c° is the intrinsic birefringence of the crystal.[7]

$$\therefore n_{c \text{ axis}} = 0.0291 + n_{\perp,\text{cryst.}} = \Delta_c^\circ + n_{\perp,\text{cryst.}} \tag{B-3}$$

Substituting eq. (B-3) into (B-1) yields

$$\overline{N}_c = (\Delta_c^\circ + n_{\perp,\text{cryst.}} + 2n_{\perp,\text{cryst.}})/3 = (\Delta_c^\circ + 3n_{\perp,\text{cryst.}})/3$$

$$3n_{\perp,\text{cryst.}} = 3\overline{N}_c - \Delta_c^\circ$$

$$n_{\perp,c} = \overline{N}_c - 0.333\Delta_c^\circ \tag{B-4}$$

$$= 1.5245 - 0.333 (0.0291)$$

$$= 1.5148$$

Substituting eq. (B-4) into (B-3) yields

$$n_{c \text{ axis}} = 1.5439 = n_{c,\parallel}$$

Similarly for the noncrystalline chains:

$$\overline{N}_{\text{AM}} = (n_{\parallel,\text{AM}} + 2n_{\perp,\text{AM}})/3 = 1.4707 \text{ (from Fig. 1)} \tag{B-5}$$

$$\Delta_{\text{AM}}^\circ = (n_{\parallel,\text{AM}} - n_{\perp,\text{AM}}) = 0.060 \tag{B-6}$$

Where Δ°_{AM} is the intrinsic birefringence of the noncrystalline element.[7]

$$\therefore n_{\parallel,AM} = \Delta^{\circ}_{AM} + n_{\perp,AM} \tag{B-7}$$

Substituting eq. (B7) into (B5) yields

$$n_{\perp,AM} = \overline{N}_{AM} - 0.333 \, \Delta^{\circ}_{AM}$$

$$= 1.4707 - 0.333 \, (0.060) \tag{B-8}$$

$$= 1.4507$$

Substituting eq. (B8) into (B7) yields

$$n_{\parallel,AM} = 1.5107$$

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