"Molecular orientation observed in sheared specimens is due entirely to plastic deformation."

Strain-Induced Molecular Orientation in Sheared Polycarbonate

by

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ABSTRACT

Characterization of molecular orientation was done on polycarbonate samples previously deformed in plane simple shear. Birefringence and extinction angle values and x-ray data indicated the presence of molecular orientation. Measurements done on undeformed samples showed no evidence of orientation indicating that the orientation in the deformed sample is strain-induced. A theoretical expression giving birefringence as a function of draw ratio was derived using the pseudo-affine hypothesis. Good agreement was found with the birefringence data. Comparison with samples deformed in uniaxial tension showed that for the same draw ratio, samples deformed in simple shear had higher birefringence.

INTRODUCTION

Certain studies (Ward, 1962, 1967 and 1977; Gurnee, 1954) have already shown that plastic deformation induces molecular orientation in polymers. Most of these studies have been conducted on specimens deformed in uniaxial tension (De Rudder and Filisko, 1977; Falkai and Hinrichsen, 1977) or compression (Kramer, 1974). With the development of the plane simple shear test (Boni, 1981; G'sell et al., 1982), the characterization of shear-induced molecular orientation has become possible, particularly because simple shear testing has proven to be unaffected by artifacts such as necking or crazing (Boni, 1981; Gopez, 1983).

For this study, polycarbonate, a transparent amorphous polymer was chosen. The transparency of this polymer allows the use of refractive index and birefringence measurements, while its amorphous nature simplifies the analysis because only one phase is present at temperatures below its melting point.

Polycarbonate specimens deformed in simple shear testing at ambient temperature were used. The mechanical response of polycarbonate to simple shear testing was already reported in previous articles (Gopez, 1984 a and b).

The objectives of this study are:

a) to measure and describe strain-induced molecular orientation in polycarbonate deformed in simple shear;

b) to correlate the data obtained with existing models of molecular orientation; and,

c) to compare the results with those obtained in uniaxial tension.

EXPERIMENTAL PROCEDURE

Material

The polymer used in this study is a commercial grade bisphenol A polycarbonate (Makrolon). A schematic diagram of the monomer structure is given in Figure 1. Polycarbonate has very little tendency to crystallize and has a glass transition temperature T_g = 145°C. It is, therefore, in its glassy state at room temperature (23±1°C) where most of the straining and measurements were carried out. Polycarbonate is transparent, with a refractive index of 1.586 (DIN 53491) and a coefficient of transmission of visible light equal to 0.85 (DIN 5036). Wide angle x-ray diffraction indicates that the material used is essentially amorphous (Gopez, 1984a).

The material was received in the form of 9-mm thick extruded plates. Initial birefringence was approximately $5\,10^{-5}$ indicating that no molecular orientation was induced by the hot extrusion process. In the undeformed state, it may be said that the molecular chains of the material used are randomly oriented.

Techniques and Theoretical Considerations

Sample Preparation

Polycarbonate specimens were first deformed in plane simple shear at room temperature using the test method developed by Boni (1981, G'sell et al., 1982). The sheared portions were then cut away by sawing and abraded with emery paper (500 and 1200P Grit) on a metallographic grinder. The cut samples were mounted with low melting point wax on cylindrical holders for ease in grinding and to insure that flat parallel surfaces were obtained on samples. Scratches due to the grinding operation were removed by polishing with diamond paste. These samples were used for optical and x-ray measurements.

Deformation Geometry of Simple Shear

Figure 2 shows a parellelipiped undergoing simple shear. A detailed description of simple shear deformation is given elsewhere (Gopez, 1984a), so only the important features will be recalled in this section.

Planes in the solid which are perpendicular to the Ox_2 axis are translated parallel to the Ox_1 axis. x_1 x_3 planes are referred to as shear planes. The stress is applied in the direction of Ox_1, also called the stress axis. It is quite clear from the diagram that no deformation takes place in the Ox_3 direction. Plane strain conditions prevail in simple shear. The x_1 x_2 plane, on which deformation takes place will be referred to as the plane of deformation. Shear stress and shear strain are defined as shown in the figure.

Figure 3 shows what happens to a circle inscribed on the x_1 x_2 plane if it undergoes simple shear. The unit circle is transformed into an ellipse showing that the principal strain axes should correspond to the major and minor axes of the ellipse. The principal strain axes thus rotate during straining, with the angle α varying with shear strain γ as follows (Boni, 1981; G'sell et. al., 1982):

$$\alpha = \tan^{-1}(2/\gamma)$$

The principal strains may also be defined from the figure by means of the draw ratios (length of an axis of the ellipse/circle radius). The major principal strain is defined by λ_z and the other principal strain is λ_y. In terms of the prevailing shear strain (G'sell et al., 1982):

$$\lambda_z = \frac{1}{2}(\gamma+\sqrt{\gamma^2+4})$$

$$\lambda_y = \frac{1}{2}(-\gamma+\sqrt{\gamma^2+4})$$

$$\lambda_x = 1 \text{ (no deformation)}$$

where x, y, z are axes coinciding with the principal strain axes. Oy and Oz rotate as straining proceeds while Ox corresponds with Ox_3.

The samples were cut such that measurements were carried out on the plane of deformation ($x_1 x_2$).

Optical Characterization

In the undeformed state, a transparent polymer does not show any evidence of optical anisotropy (i.e., birefringence) due largely to the random orientation of its molecular chains. Molecular orientation in the deformed state is usually indicated by birefringence.

The birefringence Δn in the plane of deformation ($x_1 x_2$) of sheared specimens was measured with a Berek compensator (30 orders) mounted on a transmission optical polarizing microscope. The orientation of the principal axes of the refractive indices was also determined with a graduated rotating stage by looking for the extinction position. Appendix A gives more details on birefringence and its measurement.

Birefringence values were measured at ambient temperature.

X-ray Diffraction

Transmission x-ray diffraction of the samples was done with a flat film camera. A copper (Cu Kα) source (λ = 1.54A°) was used with a generator (Philips) set at 60 kV and 16 mA. Film-to-specimen distance was fixed at 40 mm and exposure time was 30 minutes. Beam diameter was 0.5mm and a nickel (Ni) filter was used.

Due to the amorphous nature of the specimens, the diffraction patterns showed characteristic halos. For isotropic specimens the intensity of the primary halo does not change along its circumference. Any intensity variation indicates presence of molecular orientation (Kakudo and Kasai, 1972). For patterns from deformed specimens, these variations were measured with a light meter.

Other data on molecular orientation was obtained by using x-ray diffraction results to draw pole figures for two specimens. This was done by Messrs. Beautemps and Jarry at the Rhone-Poulenc Research Center.

RESULTS

Refractive Index Ellipsoid

The refractive index ellipsoid is defined by the principal axes of the refractive indices (Bruhat, 1959). These are three orthogonal directions which correspond to the extremal values of the refractive indices in an optically anisotropic material (see Appendix A for more details). It can be shown that differences in refractive indices in a body are linked to the existence of polarizable units in the material (Mills, 1972; Stein and Wilkes, 1975). In polymers these units are considered to be covalent bonds in the central molecular chain or functional molecular groups (such as phenyl radicals). These units are assumed to have an inherent polarizability p_1 along the main axis (usually taken parallel to the main chain axis) and a secondary polarizability p_2 in any other perpendicular direction. These units have therefore been described to be anisotropic but transversally isotropic (Ward, 1967 and 1975). If these units are preferentially oriented in one direction, a birefringent system is produced in which the refractive index n_1 in the orientation direction is higher than in the perpendicular direction n_2. The refractive index n_3 perpendicular to the first two directions will be the same as n_2. This system is then defined by a single birefringence value $\Delta n_{12} = n_1 - n_2$ with $\Delta n_{13} = \Delta n_{12} = 0$. In this case, the refractive index ellipsoid will have two equal axes n_2. and n_3. The experimental determination of birefringence in a plane containing the principal axis corresponding to n_1 will fully characterize the system.

In the case of simple shear the x_1 x_2 plane as represented by Figure 2 was chosen for measurements. Since it contains two principal strain axes, it should contain the major principal axis of refractive indices. The position of this axis was determined by placing the specimen between crossed polars and looking for the extinction position. At extinction the principal axes are parallel to the optical axes of the two polarizers. The stress axis was taken as the reference axis; and the acute angle retained as the angle of orientation. This parameter indicates the orientation of the major principal refractive index axis, or the major axis of the projection of the ellipsoid on the plane of measurement.

Results are shown by Figure 4 which gives the variation of the extinction angle with plastic shear strain (γpl). The extinction angle decreases with increasing plastic strain.

On the same figure, the variation of the angle α, between the principal strain axis and the stress axis (Ox_1), with plastic strain has been drawn. This is given by $\alpha = 1/2 \tan^{-1} (2/\gamma)$ and is represented by the curve in the figure. It is to be noted that the extinction angle varies in the same way as the angle α.

Birefringence values obtained with sheared specimens are given in Table 1. White light was used and an equivalent wavelength of 565mm was used in the computations. The maximum draw ratio λ corresponding to the plastic shear strain has also been reported in Table 1. Figure 5 shows graphically the variation of birefringence Δn with plastic shear strain γpl. Birefringence does not appear to be a linear function of plastic shear strain.

Measured birefringence values for sheared polycarbonate are all positive. This indicates that the refractive index along the molecular alignment direction becomes bigger than refractive index in the perpendicular direction. Looking at the birefringence expression (see section on p. 80) will show that for birefringence to be positive, $p_1 > p_2$. Hence the inherent polarizability of polycarbonate along the molecular chain axis must be p_1, greater than the inherent polarizability p_2 in a perpendicular direction. This is confirmed by looking at the structure of a polycarbonate monomer (Figure 1). No bulky side groups are present and two phenyl groups can be seen on the main chain. Phenyl groups are very polarizable (Gurnee, 1954; Rudd and Gurnee, 1957; Mills, 1972). At this point, it can already be said that the major refractive index axis of polycarbonate (as given by the extinction angles) should correspond to the molecular alignment direction.

In the case of polystyrene, negative birefringence was observed and this was later attributed to phenyl side groups attached to the molecular chain (Gurnee, 1954; Kramer, 1974).

Table 1: Birefringence Values

Sample Number	Plastic Shear strain, γ pl	Maximum draw ratio, λ	Birefringence n x 10^2
175	0.22	1.12	1.76 1.77 1.80 1.83
195	0.44	1.24	2.08 2.09 2.09 2.12
29	0.62 0.64	1.36 1.37	3.18 3.19
223	0.72	1.42	3.18 3.37 3.39
8	0.75 0.76	1.44 1.45	3.59 3.64
7	0.80	1.48	4.07 3.88
5	0.89 0.91	1.54 1.55	4.27 4.47
24	0.96 0.97	1.59 1.60	4.61 4.58
224	0.97	1.60	4.52 4.67 5.61
14	1.05	1.65	4.78 4.81

It is to be noted that birefringence increases rapidly with plastic strain. The values obtained ($\Delta n = 5\ 10^{-2}$ at $\lambda = 1.65$ for example) are of the same order of magnitude as those obtained for polycarbonate deformed in tension at room temperature, $\Delta n = 4.5\ 10^{-2}$ for an extension ratio $\lambda = 2$ (Falkai and Hinrichsen, 1977). At the same value of draw ratio birefringence values obtained in tension seem to be lower than those for simple shear.

The birefringence of hot drawn polycarbonate (T > 150°C) is even lower; $\Delta n = 8\ 10^{-4}$ at $\lambda = 10$ (de Rudder and Filisko, 1977) and $\Delta n = 1\ 10^{-2}$ at $\lambda = 2$ (Falkai and Hinrichsen, 1977).

X-ray Diffraction

Figure 6a shows the x-ray diffraction pattern from an undeformed polycarbonate sample. The amorphous halo has uniform circumferential intensity and this confirms the absence of any molecular orientation (Kakudo and Kasai, 1972). A pattern from a deformed sample (Figure 6b) shows the same halo but with varying circumferential intensity. The angle between the molecular alignment axis and the stress axis (vertical on the pattern) was determined with the help of a light meter. The pattern was rotated about an axis corresponding to the primary x-ray beam to measure the variation of the intensity along the circumference of the halo. A plot of the intensity (arbitrary units) as a function of the azimuthal angle θ is shown on Figure 7. The stress axis was taken as reference, $\theta = 0$. The molecular alignment with respect to the stress axis is given by the point of minimum intensity.

The diffraction patterns obtained for the deformed specimens correspond to that for a biaxial orientation (Kakudo and Kasai, 1972) or for a fibrous orientation (Guinier, 1956). The azimuthal direction corresponding to the minimum diffracted intensity on the pattern corresponds with the principal orientation axis of the polymer chains (Kakudo and Kasai, 1972). For the different specimens studied the azimuthal angles are also plotted on Figure 4. It is to be noted that the extinction angle, the azimuthal angles corresponding to the polymer chain alignment and the angle α corresponding to the major principal strain axis all vary in a similar manner.

DISCUSSION

Models of Molecular Orientation

Strain-induced molecular orientation or texture in polymers has been described by two theories, the "affine" deformation theory (Kuhn and Grun, 1942; Treloar, 1954 and Gurnee, 1954) and the "pseudo-affine" theory (Kratky, 1933; Ward, 1962, 1967 and 1971).

In the affine deformation theory, (initially proposed for rubbers), the material is considered to be composed of a jumble of flexible chains. Each of these chains is made up of free-jointed links or segments which are more or less able to move. In this model molecular orientation is described by taking the orientation of the end-to-end vectors of all the molecular chains. As the material is deformed, the orientation of the end-to-end vectors is changed while the links in the molecular chain rearrange themselves due to stress or entropy factors (Treloar, 1954; Ward, 1967 and 1975). This model requires a statistical description of the flexible chain configuration. Based on this an expression for birefringence as a function of strain has been obtained (Kuhn and Grun, 1942).

$$\Delta n = \frac{2\pi}{45} \frac{(n^2+2)^2}{n} N (p_1 - p_2)(\lambda^2 - 1/\lambda)$$

where n = average refractive index (or refractive index in the isotropic state)

N = number of chains per unit volume

p_1 and p_2 = primary (along the principal axis) and secondary (perpendicular direction) polarizability of a segment

λ = draw ratio (or extension ratio)

Since there are many possible configurations for the segments in a given molecular chain, the average orientation of these segments will be much lower than the orientation of the end-to-end vectors of the chains, particularly for strains between 100 percent and 200 percent (Gupta and Ward, 1967 and 1968; Ward, 1975). As such birefringence increases slowly with strain (see Figure 8).

In the pseudo-affine theory, on the other hand, all of the segments (chain units) are considered to change their orientation as a function of the induced strain. Each of these segments also possesses different polarizabilities along the chain axis and in perpendicular directions (Ward, 1967, 1971 and 1975). This model ignores any change in the length of the segments during deformation.

In the pseudo-affine theory the chain segments change their orientation with the strain while in the affine theory, the end-to-end chain vectors change their orientation. The pseudo-affine theory thus predicts a more rapid development of the birefringence with the strain. It gives a birefringence vs draw ratio curve which is concave downward and which passes above the same curve as predicted by the affine theory (Figure 8).

The affine theory has been found to describe very well the development of molecular orientation in rubbers (Kuhn and Grun, 1942; Treloar, 1954; Ward, 1977) and in rubbery amorphous polymers (at temperatures above the glass transition temperature, Tg) (Perrena et al., 1980; Ward, 1967 and 1977; Foot and Ward, 1975; De Vries, 1982) but it has been found inadequate for glassy amorphous polymers (Ward, 1975 and 1977). In the case of semi-crystalline polymers, analysis of orientation is more complicated due to the presence of two phases (amorphous and crystalline) and due to the difficulty in determining the birefringence contribution from each of these phases (Wilkes, 1971; Samuels, 1974; Stein and Wilkes, 1975).

Studies on glassy amorphous polymers have shown that the pseudo-affine theory can be used to describe the molecular orientation due to plastic strain (Foot and Ward, 1975; Perrena et al., 1980). Ward (1975 and 1977) has shown that at low temperatures (below Tg) experimental data are in agreement with the pseudo-affine theory, while at high temperatures, the affine theory agrees better with the data. These studies were done mostly on amorphous polyethylene terephthalate (PET). For semi-crystalline polyments, the pseudo-affine theory seems to be a good first approximation for strain-induced molecular orientation (Ward, 1975 and 1977; Stein and Wilkes, 1975).

A Theoretical Calculation of the Birefringence due to Simple Shear

Using the pseudo-affine theory, an expression of the birefringence as a function of shear strain will now be derived. The details are given in Appendix B, and only the principal developments of the solution will be given in this section.

The following hypotheses were used:

(1) the material is composed of chain segments which change their orientation during straining such that the axes of symmetry of the segments undergo the same changes in orientation as lines (or vectors) drawn on the solid being deformed (the pseudo-affine hypothesis).

(2) there is no change in volume during deformation.

(3) there is no change in the length of segments during deformation.

(4) the segments are transversally isotropic, with a polarizability p_1 along their axis and a polarizability p_2 in any direction perpendicular to the axis.

Shear deformation may be represented by a vector $\vec{p}'(x',y',z')$ changing its orientation due to the macrosopic strain in system of axes corresponding to the principal strain axes. In this system, Oxyz, z is the axis of maximum elongation while y is the axis of maximum compression. This system of axes rotates during straining due to the large physical strains involved. Since there is plane strain, the draw ratio λ_x along a direction perpendicular to the deformation plane is equal to 1 (no normal strain along x).

The maximum draw ratio is $\lambda_z = \lambda = 1/2\,(\gamma + \sqrt{\gamma^2 + 4})$ and the draw ratio along the other axis is $\lambda_y = 1/\lambda = 1/2\,(-\gamma + \sqrt{\gamma^2 + 4})$

with γ being the shear strain. In the deformed state the vector $\vec{p}'(x',y',z')$ is moved to another orientation represented by $\vec{p}(x',y',z)$. The primed coordinates x',y',z' give the position of the vector before deformation while the x, y, z coordinates give the position after deformation (Figure 9).

The change in the orientation of vector $\vec{p}'$ may be given as a function of the angles ϕ' and θ', which are respectively, the angle between the $x'y'$ projection of the vector and the Ox' axis and the angle between the vector and the Oz' axis.

These relationships are given by:

$$\tan\phi = \left(\frac{1}{\lambda}\right)\tan\phi'$$

$$\text{and } \tan\theta = \tan\theta'\frac{1}{\lambda}\;\frac{\sqrt{1+\lambda^{-2}\tan^2\phi'}}{\sqrt{1+\tan^2\phi'}}$$

where $\lambda = \lambda_z$

and the angles ϕ and θ (without primes) are the angles after deformation has taken place.

The apparent polarizabilities along the given axes may now be obtained (after Ward, 1962).

$$p_x = p_1\cos^2\phi\sin^2\theta + p_2(\sin^2\phi + \cos^2\phi\cos^2\theta)$$

$$p_y = p_1\sin^2\phi\sin^2\theta + p_2(\cos^2\phi + \sin^2\phi\sin^2\theta)$$

$$p_z = p_1\cos^2\theta + p_2\sin^2\theta$$

where p_1 and p_2 are polarizabilities of the segment and θ and ϕ are the previously defined angles.

By the Lorentz-Lorenz equation (Stein and Wilkes, 1975) these apparent polarizabilities may be related to the refractive indices in the same directions.

$$\frac{n_i^2-1}{n_i^2+2} = \frac{p_i}{3} \quad \text{(in MKSA units)}$$

(where i = x, y or z).

The birefringence $(n_i - n_j)$ is given by:

$$\frac{6n}{(n^2+2)^2} \Delta n = \frac{p_i - p_j}{3}$$

by using the following approximations:

$$n_i + n_j = 2n$$
$$n_i - n_j = n$$
$$(n_i^2 + 2)(n_j^2 + 2) = (n^2 + 2)^2$$

These expressions are valid for a single polarizable element. For N elements, birefringence may be written as:

$$\Delta n = \frac{N}{18} \frac{(n^2+2)^2}{n} \overline{(p_i - p_j)}$$

where N is the number of polarizable elements, n is the refractive index in the isotropic state, and $\overline{(p_i - p_j)}$ is the average difference in polarizability in the i and j directions for the population of segments.

In the yz plane the birefringence corresponding to the values measured in this study should be given by

$$\Delta n_{zy} = \frac{N(n^2+2)^2}{18 \quad n} \overline{(p_z - p_y)}$$

where the average $\overline{(p_z - p_y)}$ is taken for N chain segments in the deformed state.

Using the previously derived expressions for p_z and p_y,

$$\overline{(p_z - p_y)} = (p_1 - p_2)\left[1 - \overline{\sin^2\theta} - \overline{\sin^2\theta \sin^2\phi}\right]$$

where $\overline{\sin^2\theta}$ and $\overline{\sin^2\theta \sin^2\phi}$ are functions of the average values of the angles θ and ϕ and consequently of the shear strain.

Orientation birefringence due to simple shear is therefore written as:

$$\Delta n_{zy} = \frac{N}{18} \frac{(n^2+2)^2}{n} (p_1 - p_2)\left[1 - \overline{\sin^2\theta} - \overline{\sin^2\theta \sin^2\phi}\right]$$

with the average quantities given by expressions in Appendix B.

It is to be noted that in the case of uniaxial tension the term $\left[1 - \overline{\sin^2\theta} - \overline{\sin^2\theta \sin^2\phi}\right]$ reduces to $\left[1 - 3/2 \, \overline{\sin^2\theta}\right]$, Hermans (1946) orientation function, because the angle $\phi = \phi'$ and $\overline{\sin^2\phi} = 1/2$ (Kuhn and Grun, 1942; Ward, 1962).

Analytical solutions for $\overline{\sin^2\theta}$ and $\overline{\sin^2\theta\ \sin^2\phi}$ turned out to be difficult to obtain so numerical solutions were used instead. Figure 10 gives the variation of the orientation factor as a function of the draw ratio. Orientation birefringence varies proportionately with the orientation factor.

$$\Delta n = C\,[1-\overline{\sin^2\theta} - \overline{\sin^2\theta\sin^2\phi}]$$

where

$$C = \frac{N}{18}\,\frac{(n^2+2)^2}{n}\,(p_1-p_2)$$

and only N varies in the expression for C.

Comparison with Uniaxial Tension

For comparison, birefringence values due to uniaxial tension were obtained. A cylindrical specimen was strained to necking at ambient temperature and a nominal strain rate $\dot{\varepsilon} = 10^{-3}\ s^{-1}$. By measuring the diameter of the specimen at different points in the necked area, the local strain was obtained from the expression $\varepsilon = 2\ln(D_o/D)$ and the draw ratio $\lambda = \exp\ \varepsilon$. The results are also shown in Figure 11. A value of $C = 0.131$ likewise gives a theoretical $\Delta n-\lambda$ curve in good agreement with experimental data. This gives the same values of C for both tension and simple shear and appears to lend additional support to the pseudo-affine theory. The parameter C is also referred to as Δn_{max} (Ward, 1962).

Other Indications of Molecular Orientation

Diffraction patterns of deformed specimens have halos of low intensity in two diametrally opposed areas (see Figure 6). This variation in intensity is due to the molecular alignment (Kakudo and Kasai, 1972) in a direction perpendicular to the direction of maximum diffraction. The diffracted intensity is increased in a direction perpendicular to the fiber (or molecular chain) alignment. At large strains, this type of orientation approaches a fibrous orientation (Guinier, 1956; Kakudo and Kasai, 1972; Samuels, 1974). From Figure 4, the direction of molecular alignment as determined by X-ray diffraction coincides well with the major refractive index axis and the major principal strain axis.

More data on molecular orientation were obtained by constructing pole figures* (Guinier, 1956, Kakudo and Kasai, 1972) for two values of plastic strain. For these measurements, cylindrical samples (diameter = 2mm) were machined carefully from calibrated parts of sheared specimens. Figure 12 gives the pole figures for plastic shear strains $\gamma_{pl} = 0.32$ and 1.0. The $x_1 x_2$ plane perpendicular to the plane of the pole figures is the plane on which birefringence measurements and flat chamber x-ray diffraction were carried out. These pole figures confirm the existence of a direction of molecular alignment. The symmetry of the texture with respect to the plane of measurement ($x_1\ x_2$) is also shown by the figures.

Effects of Temperature on Molecular Orientation

Data indicate the validity of the pseudo-affine theory for glassy polycarbonate. To see if the affine theory is valid at high temperature (T > Tg), specimens were de-

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* We acknowledge the assistance of Messrs. Beautemps and Jarry of the "Centre de Recherche des Carrieres (St. Fons)" of Rhone Poulenc in the tracing of these pole figures.

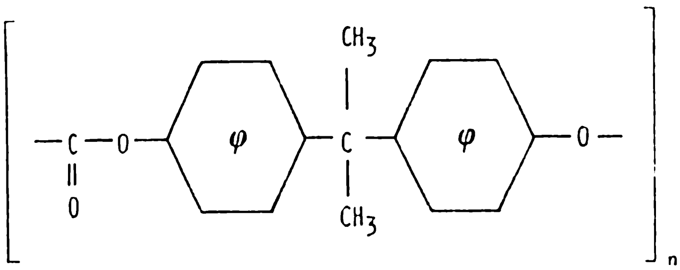


Figure 1: Schematic diagram of the structure of a polycarbonate monomer.

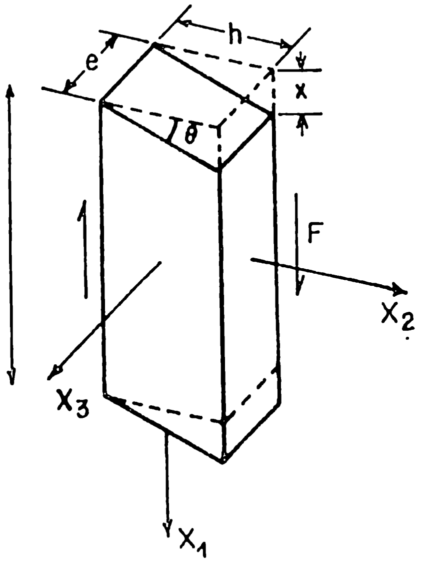


Figure 2: Deformation geometry of plane simple shear.

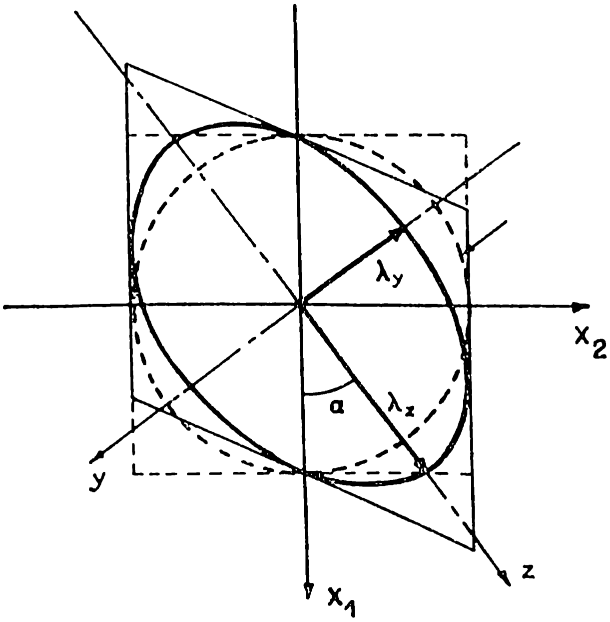


Figure 3: Deformation geometry on the plane of deformation in simple shear.

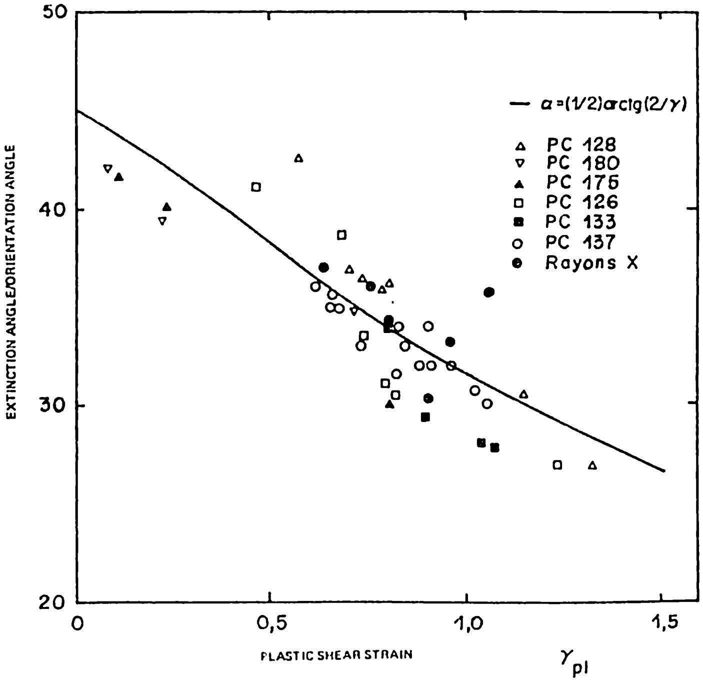


Figure 4: Orientation of the major principal axis of refractive indices as a function of plastic shear strain. X-ray data give direction of molecular alignment while the $\alpha = 1/2 \ \tan^{-1} (2/\Upsilon)$ curve indicates orientation of major principal strain axis.

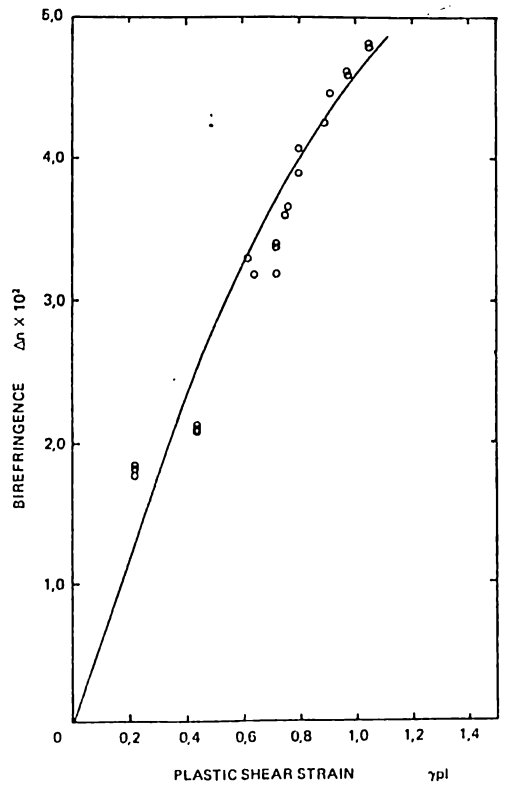
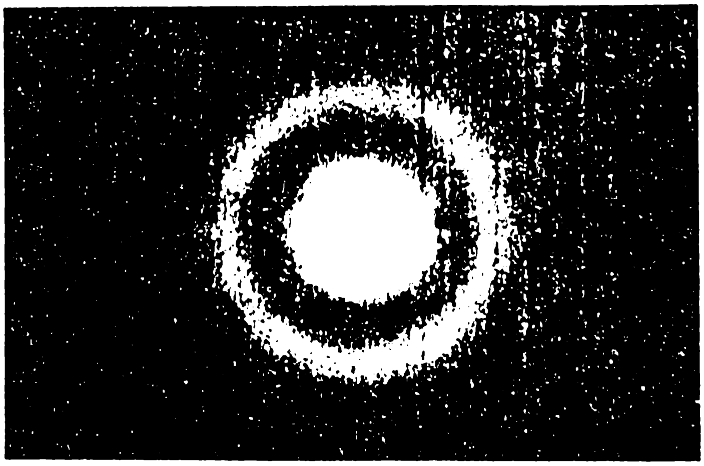
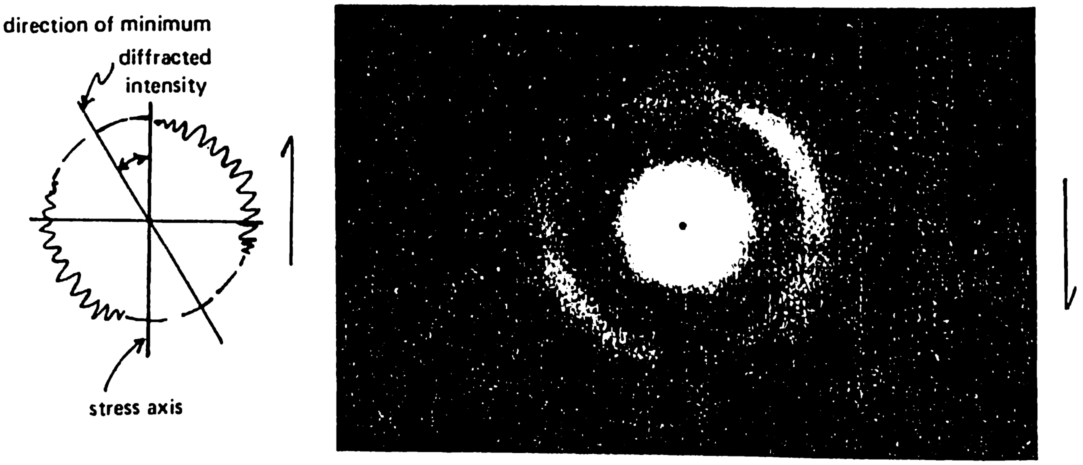


Figure 5: Birefringence vs. plastic shear strain.



a) underformed sample



b) deformed sample

$\gamma_{pl} = 0,63$

Figure 6: X-ray diffraction patterns.

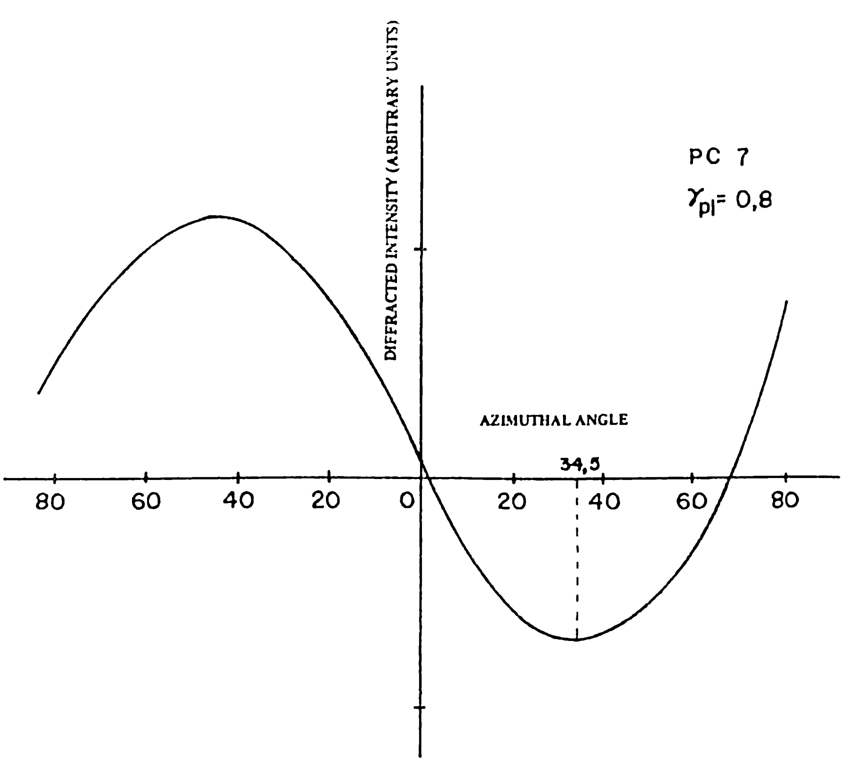


Figure 7: Diffracted intensity vs. azimuthal angle in an x-ray diffraction pattern.

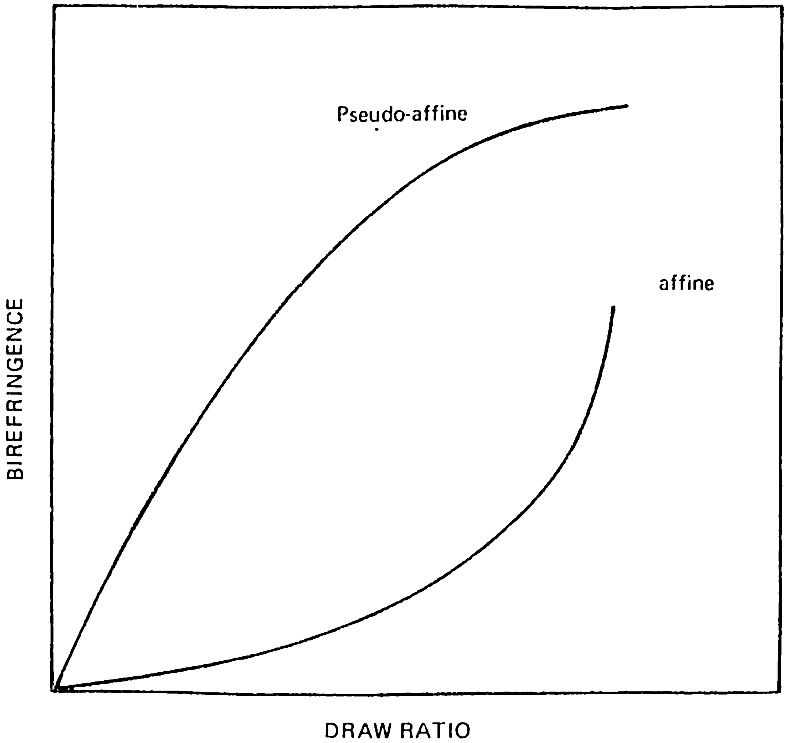


Figure 8: Birefringence-draw ratio curves for pseudo-affine and affine theories (after Ward, 1975; De Vries, 1982).

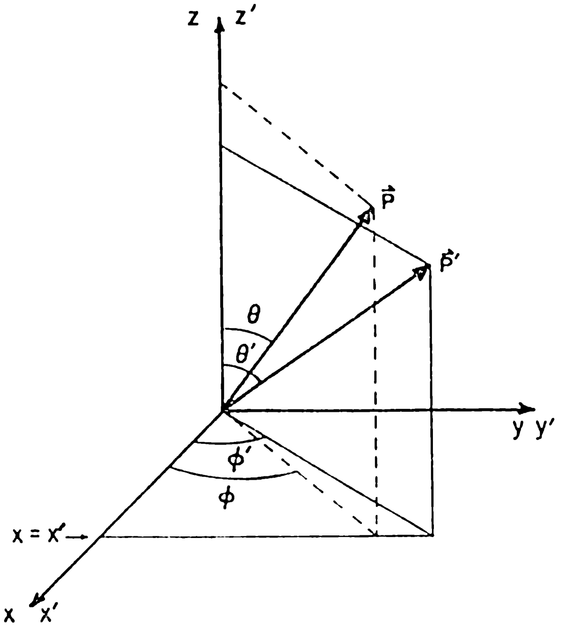


Figure 9. The change in the Orientation of a Vector in a body undergoing plane simple shear.

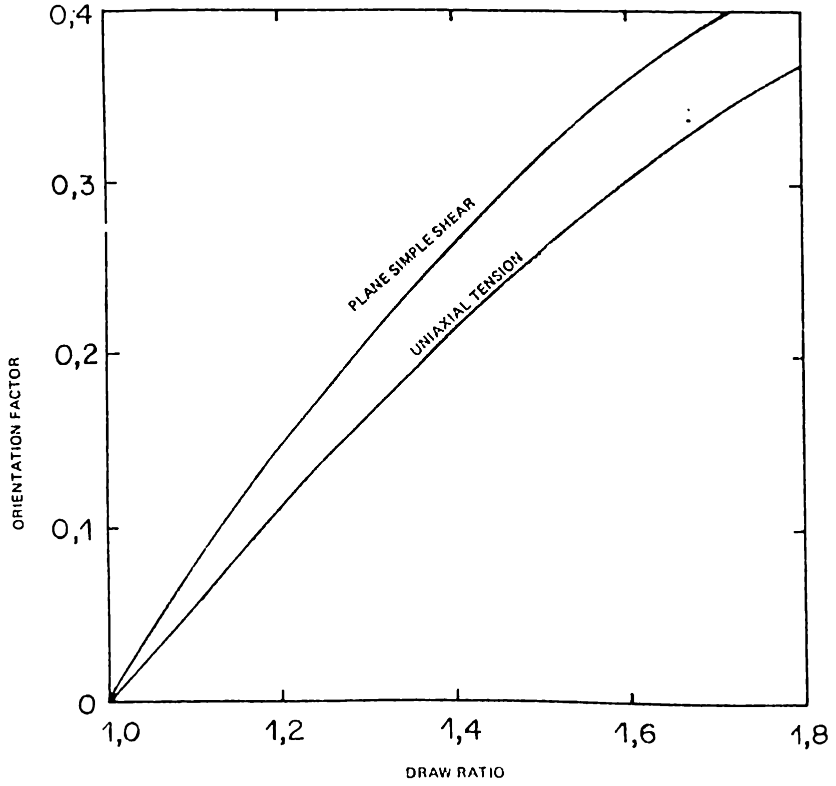


Figure 10: Orientation factor vs draw ratio for plane simple shear and uniaxial tension.

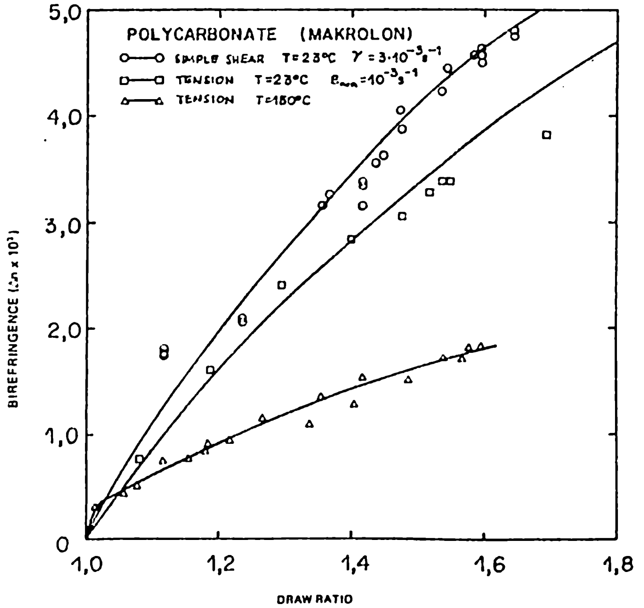


Figure 11: Birefringence data, at room temperature compared with the theoretical Δn vs λ curves in plane simple shear and uniaxial tension. Birefringence data for hot draw polycarbonate (lowest curve).

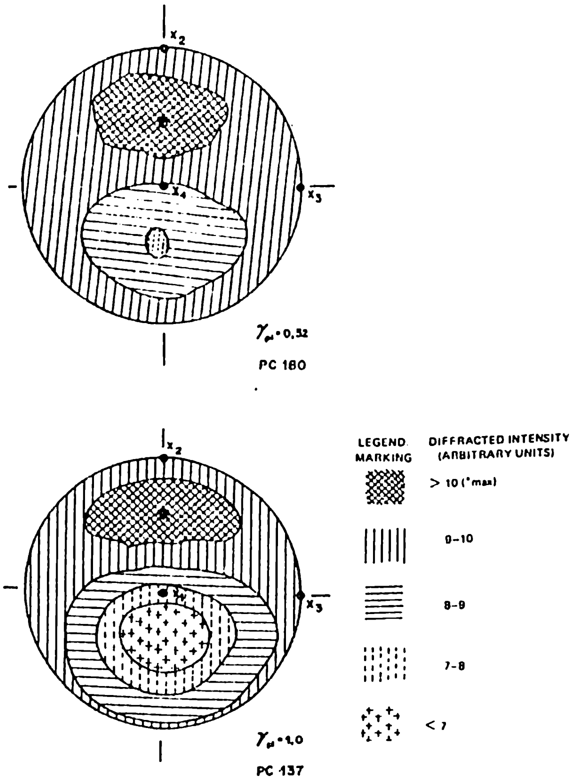


Figure 12: Pole figures of sheared polycarbonate.

formed in uniaxial tension at 150°C (Tg = 145°) and birefringence values obtained for different draw ratios. Results are also shown on Figure 11. Birefringence values at 150°C are less than half the values at 23°C. The $\Delta n - \lambda$ curve is however, still concave downward. Validity of the affine theory should have been affirmed by a curve which is concave upward. It is possible that the temperature at which straining was done (150°C) was still too low to allow the molecular segments enough free volume to conform to the affine theory. Experiments at higher temperatures could not be done because polycarbonate undergoes thermal decomposition at around 155°C. It can still be said however, that deformation at high temperature induces less molecular orientation.

CONCLUSIONS

Birefringence data and x-ray diffraction results indicate that simple shear deformation induces molecular orientation in glassy polycarbonate. Measurements on undeformed specimens indicate the absence of any orientation in the undeformed state. Birefringence is very weak ($5\ 10^{-5}$) and x-ray diffraction gives a pattern with a characteristic halo of uniform intensity. Molecular orientation observed in sheared specimens is thus due entirely to plastic deformation.

The direction of molecular alignment was deduced from x-ray data, while the optical extinction angle indicates the position of the major principal axis of refractive indices (Figure 4).

The principal axis of refractive indices rotates towards the shear stress axis as strain increases. The major axis of the refractive index ellipsoid also seems to coincide with the principal strain axis of the Eulerian strain tensor for simple shear.

The positive birefringence values indicate that the polarizability of a polycarbonate monomer along its chain axis must be higher than in any other perpendicular direction.

Pole figures further confirm the presence of molecular orientation.

The data obtained fits the $\Delta n - \lambda$ curve obtained by using the pseudo-affine theory. This fit was obtained by adjusting a parameter in the birefringence expression. The same value of this parameter was obtained for both simple shear and uniaxial tension. An attempt was made to see if the $\Delta n - \lambda$ data at high temperature correlated with the affine theory. The data showed a $\Delta n - \lambda$ curve which is concave downward.

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APPENDIX A. BIREFRINGENCE DETERMINATION

Birefringence

The measurement of optical anisotropy is an often-used procedure for the characterization of molecular orientation in polymers, and is particularly useful for transparent amorphous polymers. Optical anisotropy is essentially due to the differences in the inherent polarizabilities of the material. Since polarizability is a tensorial quantity, the resulting optical properties may vary according to the direction in which they are measured. Polarizability $\overline{\overline{p}}$ relates an electric dipole $\vec{m}$ to the local electric field $\vec{E}$ by the expression (Gaudaire, 1969; Mills, 1972).

$$m_i = p_{ij}E_j \qquad i,j = 1,2,3$$

For a polymer chain segment (consisting of a covalent bond), the interaction between electrons in the bond with the electric field would be more intense if the field oscillated parallel to the bond axis than if the oscillations were in a plane perpendicular to the bond axis (Figure A1). This interaction reduces the velocity of incident light by a quantity defined by the corresponding refractive index, n (Stein and Wilkes, 1975). Polarizability and refractive index are related by means of the Lorenz-Lorentz equation (Mills, 1972, Stein and Wilkes, 1975).

$$\frac{n^2-1}{n^2+2} = \frac{P}{3} \qquad \text{(in MKSA units)}$$

In the case of a polymer with molecular orientation, the molecular chains are aligned in parallel directions and this results in a difference in the refractive index values on the plane of orientation. This difference in refractive indices $\Delta n = n_1 - n_2$ is called birefringence. In this expression, n_1 is an extremal value of the refractive index (usually in a direction parallel to the molecular orientation) and n_2 is the refractive index in a direction perpendicular to n_1 in the plane of measurement (Bruhat, 1959; Stein and Wilkes, 1975). Taking n_1 as the refractive index along the direction of molecular alignment and n_2 as the index in a perpendicular direction, a third refractive index n_3 may be defined in a direction perpendicular to the first two. These three external refractive index values may then be used to define a refractive index ellipsoid:

$$\frac{x^2}{n_1^2} + \frac{y^2}{n_2^2} + \frac{z^2}{n_3^2} = 1$$

This ellipsoid may be drawn in a set of reference axes x, y, z such that Ox, Oy and Oz are parallel to directions 1, 2 and 3, respectively (Bruhat, 1959). The Ox, Oy and Oz

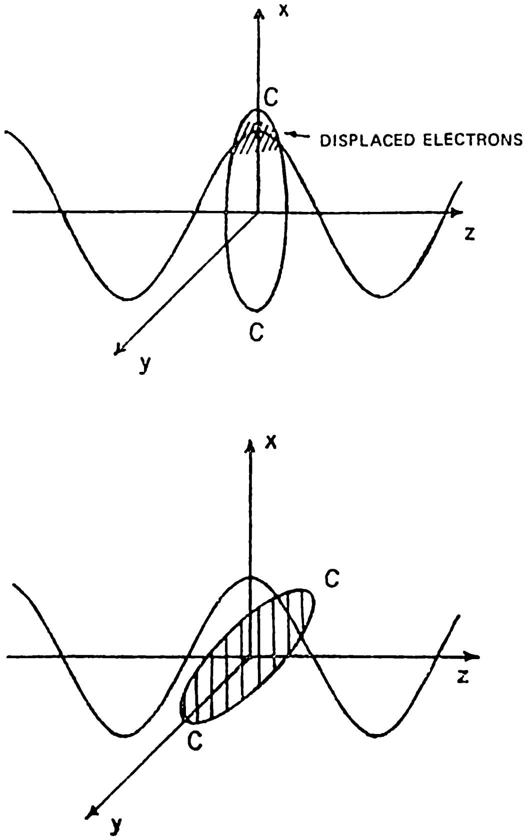

Figure A1: Interaction of a Covalent Bond (C-C) with an Electromagnetic Wave (after Stein and Wilkes, 1975).

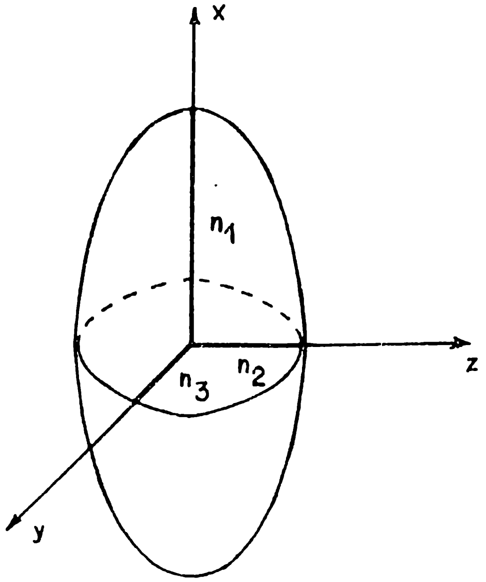

Figure A2: Ellipsoid of Refractive Indices.

axes are called the principal axes of refractive indices (Figure A2). In most cases, the polarizable units (e.g. covalent bonds in a molecular chain) are considered to be transversally isotropic (Ward, 1962 and 1967). This is equivalent to saying that $n_2 = n_3$ and the system is fully defined with a single birefringence value $\Delta n_{12} = n_1 - n_2$ with $\Delta n_{13} = \Delta n_{12}$ and $\Delta n_{23} = 0$. In this case a proper choice of the plane of measurement will enable an experimental determination of the birefringence value which defines the system. The plane of measurement must be chosen such that it contains the projection of the biggest ellipse of the refractive index ellipsoid (the xy or xz plane in Figure A2). Depending on the values of n_1 and n_2, the birefringence may be positive ($n_1 > n_2$) or negative ($n_1 < n_2$). Birefringence is positive if the polarizability along the molecular chain segments in a polymer is greater than that in perpendicular directions. It is negative in the reverse case. The latter has been observed in cases where the side groups on the molecular chains are very polarizable groups (polystyrene for example).

In simple shear the x_1 x_2 plane (see Figure 3) is the plane on which deformation takes place and consequently the plane on which molecular orientation should be most evident. This plane was chosen for measurements. The Δn value on this plane should fully characterize the refractive index ellipsoid of the material.

Measurement of Birefringence

The schematic diagram on Figure A3 shows the compensation method of birefringence determination, a method used in this study of sheared polycarbonate. This method is based on the fact that polarized light going through a birefringent sample suffers an optical delay δ given by (Stein and Wilkes, 1975):

$$\delta = \frac{e}{\lambda} \Delta n$$

where e = specimen thickness

λ = wavelength of polarized light

Δn = birefringence

When a birefringent specimen is placed between crossed polars the intensity of transmitted light varies with the specimen position with respect to the optical axes of the polarizers. If the principal refractive index axes of the specimen are parallel to the optical axes of the polarizers, no light is transmitted. This is called the extinction position, and there are four such positions. These are found by turning the specimen about an axis corresponding to the light beam (Ox on Figure A3). At 45° to these extinction angles, the intensity of transmitted light is maximum. This is called the diagonal position or the position of maximum illumination.

The optical delay is measured in a diagonal position by using a material of known birefringence which is equal to and opposite the birefringence of the specimen. This is called compensation. It is achieved when the transmitted light is extinguished by proper adjustment of the compensator. The wavelength in the calculations is fixed by the light used. If white light is used, an equivalent wavelength λ_{eq} = 565 nm is used for the calculations (VISHAY Micromeasures).

A typical procedure consists in first determining the position of the principal refractive index axes by looking for an extinction position. A diagonal position is then found (by turning 45° with respect to the extinction position) and the compensator is used to measure the amount of optical delay.

In our study, a 30-order Berek compensator was used. This is essentially a quartz piece whose thickness is varied by rotation of the piece about an axis perpendicular to the light beam.

There are other methods of birefringence determination: by transmission (Stein and Wilkes, 1975), the Babinet compensation technique (Bruhat, 1959; Wilkes, 1971), and a refractometer method (Samuels, 1974.)

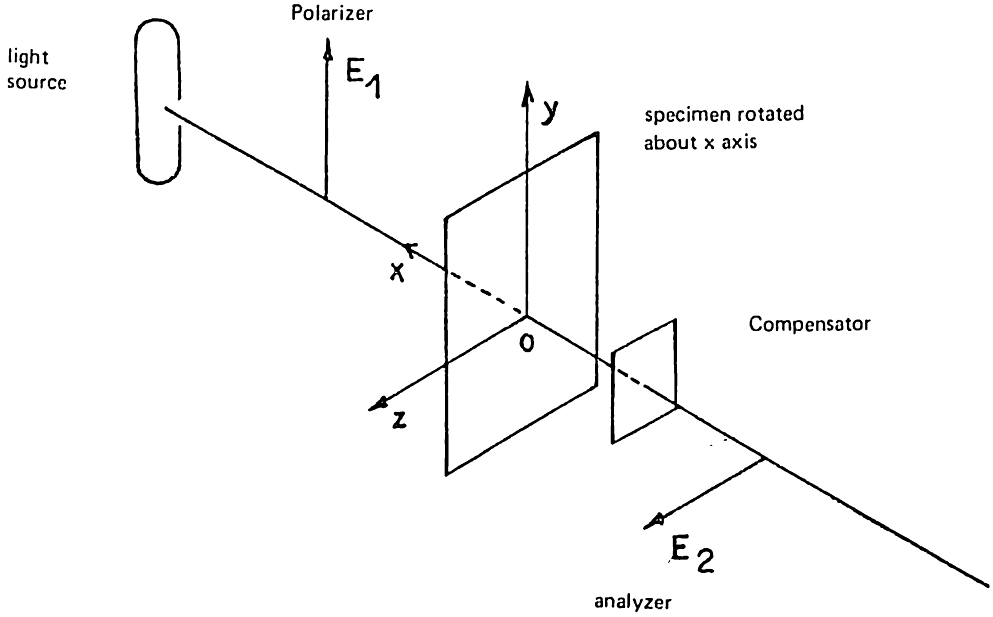

Figure A3. Schematic Diagram of Compensation Method

APPENDIX B. CALCULATION OF ORIENTATION BIREFRINGENCE DUE TO SIMPLE SHEAR

General Comments

We have adopted the pseudo-affine hypothesis (Kratky, 1933; Ward, 1962 and 1967) which seems to better account for molecular orientation in glassy polymers. The affine theory (Kuhn and Grun, 1942; Gurnee, 1954, Treloar, 1954), which was initially proposed for rubber does not seem to describe orientation in polymers unless these are at temperatures above the glass transition temperature (Tg). At these temperatures, the polymers are said to be in the "rubbery" state (Ward, 1977).

The pseudo-affine hypothesis states that each element on the molecular chain of an initially isotropic polymer develops a dipole moment due to the action of incident light and is oriented under the effect of the applied macroscopic strain (Ward, 1967, 1971 and 1975).

Calculations to define the relationships between the strain due to simple shear and the resulting birefringence were done and a comparison was drawn with the case of uniaxial tension.

Geometry of Simple Shear Deformation

Figure B1 shows the geometry of deformation in simple shear, with x_1 x_2 being the plane of deformation and Ox_1 being the shear stress direction. A set of reference axes x, y, z which turns with the principal strain axes are used in the derivation. The deformation is planar (plane strain) and the draw ratio λ_x in the x direction is unity (no deformation in this direction). Denoting the draw ratios along Oy and Oz by λ_y and λ_z respectively, conservation of volume gives:

$$\lambda_y \lambda_z = 1$$

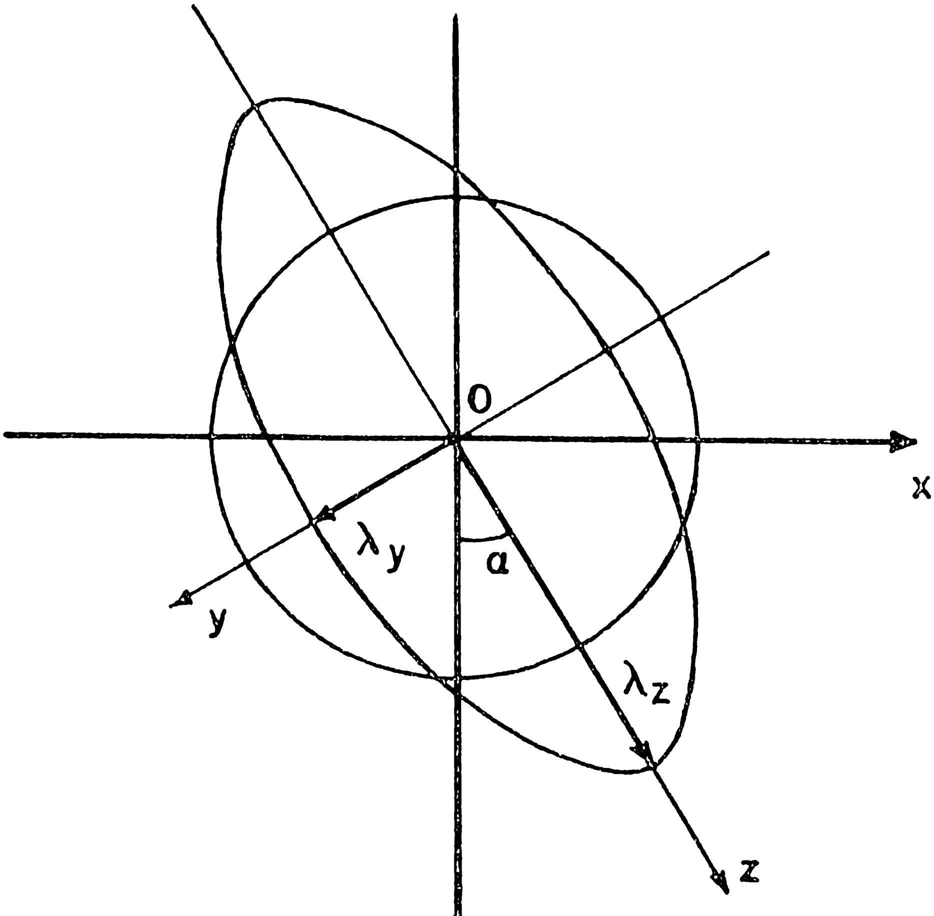

Figure B1: Deformation Geometry of Plane Simple Shear

Since Oz is the major principal strain axis, λ_z is the bigger draw ratio and will be simply designated as λ . This, together with the previous expression yields:

$$\lambda_z = \lambda \qquad\qquad \lambda_y = 1/\lambda$$

Consider now a molecular chain element in a set of reference axes x, y, z. For simplicity, the element will be chosen such that all its components are positive. Under the action of simple shear this vector $\vec{p}'(x',y',z')$ will rotate to a new position $\vec{p}(x,y,z)$ (Figure 9). It will be assumed that no change takes place in the magnitude of the vector (if this vector represents a covalent bond in a molecular chain, this is not unreasonable). The transformation equations relating the position in the deformed state to the initial position are now written as:

$$z = \lambda z'$$
$$y = (1/\lambda)y'$$
$$x = x'$$

The following trigonometric relationships may also be defined:

$$\tan\phi' = y'/x' \text{ and } \tan\phi = y/x = (1/\lambda)\tan\phi'$$

where ϕ' is the angle between the projection of vector $\vec{p}'$ on the $x'y'$ plane and the Ox' axis and ϕ is a similar angle for vector $\vec{p}$.

For the angle θ' between vector $\vec{p}'$ and the Oz' axis and the angle θ between $\vec{p}$ and Oz, the following relationships may be written:

$$\tan\theta' = (x'/z')\sqrt{1+\tan^2\phi'}$$
$$\tan\theta = (x'/\lambda z')\sqrt{1+\tan^2\phi'}$$
$$\tan\theta = \tan\theta'(1/\lambda)\frac{\sqrt{1+\lambda^{-2}\tan^2\phi'}}{\sqrt{1+\tan^2\phi'}}$$

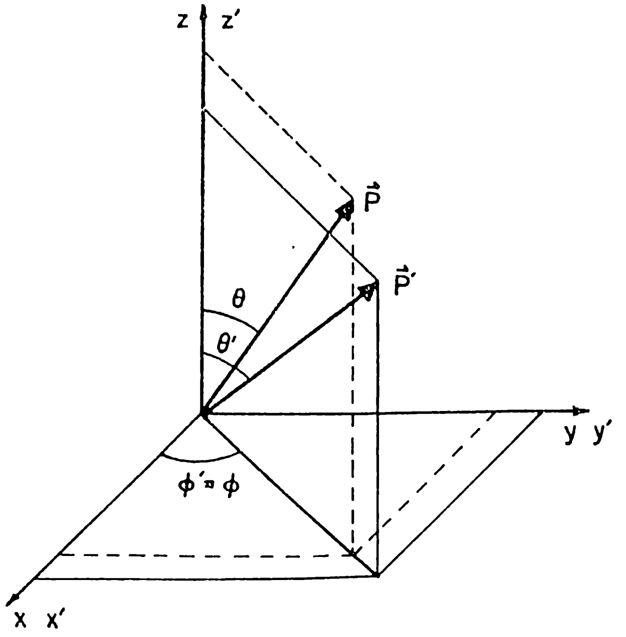

Figure B2: Change in the Orientation of a Vector in Body in Uniaxial Tension

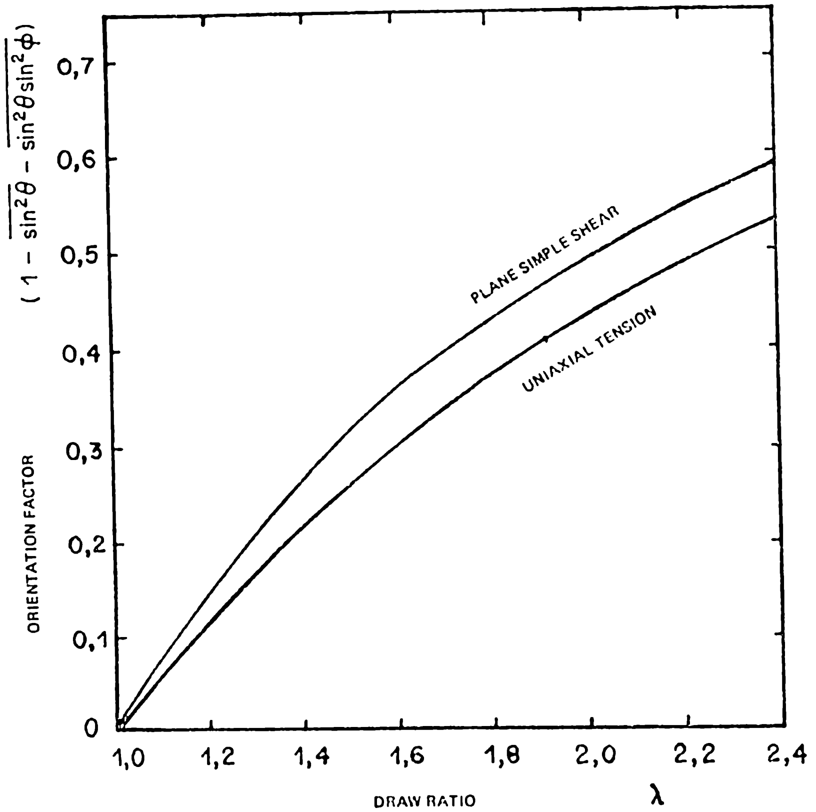

Figure B3: **Orientation Factor vs Draw Ratio for Plane Simple Shear and Uniaxial Tension**

Optical Description

The material is assumed to be composed of polarizable units which are transversally isotropic. These units may be covalent bonds on the polymer molecular chain and may acquire a dipolar moment $\vec{m}_1$ along a given direction (such as the chain axis) and another moment $\vec{m}_2$ in a direction perpendicular to the first one.

Electrical polarizability is given by the expression (Gaudaire, 1969):

$$p_1 = \vec{m}_1/\varepsilon_0\vec{E}_1 \text{ and } p_2 = \vec{m}_2/\varepsilon_0\vec{E}_2$$

where p_1 and p_2 are the polarizabilities along $\vec{m}_1$ and $\vec{m}_2$ and $\vec{E}_1$ and $\vec{E}_2$ are the corresponding components of the local electric field and $\vec{m}_1$ and $\vec{m}_2$ are the polar moments due to the external electric field. These moments are perpendicular to each other with direction 1 very often parallel to the molecular chain axis.

The apparent polarizabilities along the reference axes x, y, z (in Figure 9) are now obtained by a double projection:

a) of the field $\vec{E}$ along direction of polarization 1 (the chain axis) or direction 2 (perpendicular to the chain axis),
b) and of the resulting dipolar moments $\vec{m}$ along the reference axis.

The following expressions are obtained (Ward, 1962):

$$\begin{aligned} p_x &= p_1 \cos^2\phi \sin^2\theta + p_2(\sin^2\phi + \cos^2\phi\cos^2\theta) \\ p_y &= p_1 \sin^2\phi \cos^2\theta + p_2(\cos^2\phi + \sin^2\phi\cos^2\theta) \\ p_z &= p_1 \cos^2\theta + p_2 \sin^2\theta \end{aligned}$$

The expressions originally obtained by Ward (1962) differ slightly from those given above due to a permutation of axes.

These polarizabilities may now be linked to the corresponding refractive indices by the Lorentz-Lorenz equation.

$$\frac{n_i^2 - 1}{n_i^2 + 2} = \frac{P_i}{3} \quad \text{(in MKSA units)}$$

where p_i is the polarizability of polarizable unit along the i^{th} direction and n_i is the refractive index in the same direction.

The birefringence $(n_i - n_j)$ with i being perpendicular to the j direction is then given by:

$$\frac{n_i^2 - 1}{n_i^2 + 2} - \frac{n_j^2 - 1}{n_j^2 + 2} = \frac{p_i - p_j}{3}$$

since birefringence values are very often small (from 10^{-4} to 10^{-2}), the following approximations may be used.:

$$n_i + n_j = 2n$$
$$(n_i^2 + 2)(n_j^2 + 2) = (n^2 + 2)^2$$

These together with the birefringence expressions gives:

$$\frac{6n}{(n^2 + 2)^2} \Delta n = \frac{(p_i - p_j)}{3}$$

where $\Delta n = n_i - n_j$ is the birefringence. For N polarizable elements the above expression becomes:

$$\frac{6n}{(n^2+2)^2} \Delta n = N \frac{\overline{(p_i - p_j)}}{3}$$

and rearranging:

$$\Delta n = \frac{N}{18} \frac{(n^2+2)^2}{n} \overline{(p_i - p_j)}$$

In this expression, n is the refractive index of the material in the isotropic (undeformed) state while $\overline{(p_i - p_j)}$ is average difference in polarizabilities for all the N elements.

The birefringence Δn on the yz plane must therefore be given by:

$$n_{zy} = \frac{N}{18} \; \frac{(n^2+2)^2}{n} \; \overline{(p_z - p_y)}$$

with $\overline{(p_z - p_y)}$ being taken for N elements in the deformed state. The expressions for the apparent polarizabilities are now used:

$$\overline{p_z} = p_1 - (p_1 - p_2)\overline{\sin^2 \theta}$$

$$\overline{p_y} = (p_1 - p_2)\overline{\sin^2\phi \sin^2 \theta} + p_2$$

We therefore obtain:

$$\overline{p_z - p_y} = (p_1 - p_2)(1 - \overline{\sin^2\theta} - \overline{\sin^2\phi \; \sin^2\theta})$$

To obtain the relationship between birefringence and strain (through the draw ratios) the average values in the expression for $\overline{(p_z - p_y)}$ must first be obtained.

Average Values

For a given function $f(\theta, \phi)$ the average value in three-dimensional space is given by:

$$f = \frac{\int_0^{2\pi} \left[\int_0^{\pi} f(\theta,\phi) \sin\theta' d\theta' \right] d\phi'}{\int_0^{2\pi} \left[\int_0^{\pi} \sin\theta' d\theta' \right] d\phi'}$$

The average values if $\sin^2\theta$ and $\sin^2\theta \; \sin^2\phi$ must be obtained. Due to the periodicity of these functions only the following intervals will be considered: $0 \leqslant \theta \leqslant \frac{\pi}{2}$ and $0 \leqslant \phi \leqslant \frac{\pi}{2}$. The resulting expressions are:

$$\overline{\sin^2\theta} = \frac{\int_0^{\frac{\pi}{2}} \int_0^{\frac{\pi}{2}} \sin^2\theta(\theta',\phi') \sin\theta' d\theta' d\phi}{1 \cdot \frac{\pi}{2}}$$

$$\overline{\sin^2\theta \; \sin^2\phi} = \frac{\int_0^{\frac{\pi}{2}} \int_0^{\frac{\pi}{2}} \sin^2\theta(\theta',\phi') \sin^2\phi(\phi') \sin\theta' d\theta' d\phi'}{1 \cdot \frac{\pi}{2}}$$

where $\sin^2\theta \; (\theta',\phi')$ and $\sin^2 \phi \; (\phi')$ indicate that these expressions must be given as functions of θ' and ϕ' defined in the reference system x', y', z' in which the calculations are being done.

The analytical solution to the above expressions has turned out to be difficult to obtain. Numerical solutions have therefore been obtained. The following are the transformed expressions for programming:

$$\overline{\sin^2\theta} = \frac{\sum\limits_{\theta'_i=\theta'_1}^{\theta'_N}\left[\sum\limits_{\phi'_i=\phi'_1}^{\phi'_N} \sin^2\theta_i(\theta'_i,\phi'_i)\,\sin\theta'_i\right]\cdot\frac{\pi}{2}\cdot\frac{\pi}{2}}{\frac{\pi}{2}}$$

$$\text{or}\qquad \overline{\sin^2\theta} = \frac{\pi}{2}\sum_{\theta'_i=\theta'_1}^{\theta'_N}\left[\sum_{\phi'_i=\phi'_i}^{\phi'_N} \sin^2\theta_1\,(\theta'_i,\phi'_i)\,\sin\theta'_i\right]$$

where

$$\sin^2\theta(\theta',\phi') = \frac{1}{\frac{1}{\tan^2\theta}+1} = \frac{1}{\left[\frac{\lambda^2(1+\tan^2\phi')}{\tan\theta'\left(1+\frac{\tan^2\phi'}{\lambda^2}\right)}\right]+1}$$

The other expression becomes:

$$\overline{\sin^2\theta\sin^2\phi} = \frac{\pi}{2}\sum_{\theta'_i=\theta'_1}^{\theta'_N}\left[\sum_{\phi'_i=\phi'_1}^{\phi'_N} \sin^2\theta_i(\theta'_i,\phi'_i)\,\sin^2\phi_i(\phi')\,\sin\theta'_i\right]$$

where $\sin^2\theta(\theta',\phi')$ is the same expression as before,

$$\text{and}\quad \sin^2\phi\,(\phi') = \frac{1}{\frac{\lambda^2}{\tan^2\phi'}+1}$$

Birefringence in Uniaxial Tension

The derivation for this case using the pseudo-affine theory has already been done by Ward (1962) and is being given here for comparison. The geometric conventions proposed by Kuhn and Grun (1942) are used here and only the principal equations will be given.

Figure B2 shows a vector representing a molecular chain element changing its orientation due to tensile deformation. The vector $\vec{p}'$ (x',y',z') represents the undeformed state and its position after deformation is given by $\vec{p}$ (x,y,z). In this case the x',y',z' and x, y, z axes are practically identical. The magnitude $\vec{p}$ is also assumed to be unaffected by the strain and the constant volume hypothesis applies.

The tensile stress axis coincides with the Oz' axis and the draw ratio along this axis is denoted by λ. The draw ratios along the Ox' and Oy' axes are equal (tranverse structural isotropy) and from constant volume, we obtain, $\lambda_x' = \lambda_y' = 1/\sqrt{\lambda}$

The angle made by the vector with the Oz' axis varies according to (Kuhn and Grun, 1942; Treloar, 1954, Ward, 1962):

$$\tan\theta = \lambda^{-3/2}\tan\theta'$$

where θ' is the angle before deformation and θ the angle after deformation.

The angle between the projection of the vector on the $x'y'$ plane and the Ox' axis does not change since $\lambda_{x'} = \lambda_{y'}$. This is the essential difference in the deformation geometries of simple shear and uniaxial tension.

By the same reasoning as that for the case of simple shear:

$$\Delta n \ \alpha \ (1 - \overline{\sin^2\theta} - \overline{\sin^2\theta \sin^2\phi})$$

but $\overline{\sin^2\theta} = 1/2$ since ϕ' does not vary with strain and the above expression is reduced to (Hermans, 1946; Ward, 1962):

$$\Delta n \ \alpha \ (1 - 3/2 \ \overline{\sin^2\theta})$$

The full expression is:

$$\Delta n = \Delta n_{max} \ (1 - 3/2 \ \overline{\sin^2\theta})$$

where $(1\text{-}3/2 \ \overline{\sin^2\theta})$ is often called Hermans orientation factor after Hermans (1946) who first derived this expression. This expression may also be found as:

$$\Delta n = \Delta n_{max} \ (1/2) \ (3 \ \overline{\cos^2\theta} - 1)$$

Since $\overline{\sin^2\theta}$ is no longer a function of ϕ' (as was the case for simple shear) this average may be calculated both analytically and numerically.

The numerical solution is:

$$\overline{\sin^2\theta} = \frac{1}{N}\,\frac{\pi}{2} \sum_{\theta'_i=\theta'_1}^{\theta'_N} \sin^2\theta_i(\theta'_i)\,\sin\theta'_i$$

with $\sin^2\theta(\theta') = \dfrac{1}{\dfrac{1}{\lambda^{-3}\tan^2\theta'} + 1}$

The analytical solution (Ward, 1962) is:

$$\overline{\sin^2\theta} = \frac{K}{(1\text{-}K^2)^{3/2}} \ \cos^{-1}\left[K - K\sqrt{(1 - K^2)}\right]$$

with $K = \lambda^{-3/2}$

The birefringence expression becomes:

$$\Delta n = \Delta n_{max} \frac{3}{2} \left[\frac{1}{1 - K^2} - \frac{K \cos^{-1} K}{(1-K^2)^{3/2}} - \frac{1}{3} \right]$$

Results

The general expression for birefringence is:

$$\Delta n = \frac{N\,(n^2+2)^2(p_1-p_2)}{18\ n}\,[1-\overline{\sin^2\theta}-\overline{\sin^2\theta\sin^2\phi}]$$

This may be rewritten as:

$$\Delta n = C\ [1-\overline{\sin^2\theta} - \overline{\sin^2\theta\ \sin^2\phi}]$$

$$\text{where } C = \frac{N\,(n^2+2)^2}{18\quad n}\,(p_1-p_2) = \Delta n_{max}$$

The term in the brackets is referred to as the orientation factor. For uniaxial tension it reduces to Hermans orientation factor.

The numerical solutions were obtained by integration of the expressions with an Apple II microcomputer. Thirty-three increments in θ and ϕ were used. The results are given in Figure B3 which shows a plot of the orientation factor vs. draw ratio for both uniaxial tension and simple shear. Both curves show an increase in orientation (and consequently of Δn) with increasing draw ratio. The curves are also concave downward as predicted by the pseudo-affine theory and it appears that for the same draw ratios molecular orientation due to simple shear is stronger.