

FLUORESCENCE ANISOTROPY MEASUREMENTS OF ORIENTED POLYMERS

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Abstract

Fluorescence anisotropy area scans of sheet and film specimens have been carried out using a fiber optic sensor that contains polarizing optical elements. Measurements on polyethylene terephthalate food packaging, which contains the fluorescent dye benzoxazolyl stilbene, are presented. In one case, a sheet cut from the side of a blow molded bottle displayed variation in biaxial orientation as a function of distance from the neck of the bottle. In another case, a thin film of shrink wrap material showed uniform biaxial orientation over the scanned area.

Introduction

Fluorescence anisotropy measurements yield information about the orientation of the absorption dipole moment of a fluorescent dye. (1,2) The measurement has been used to measure molecular orientation in polymer melts, and in solid polymer films and fibers.(2-6) For characterizing polymer systems, a dye is incorporated into the polymer matrix by mixing dye and resin at low levels of dye concentration, less than 100 ppm by weight. In some cases, the polymer molecule contains fluorescent moieties that eliminate the need for adding a fluorescent dye. Also, the fluorescent dye can be covalently bonded or "tagged" to the polymer molecule.(2)

The anisotropy measurement employs excitation light polarized with a fixed spatial relationship with respect to the principal orientation axes of the film or sheet. Orientation factors are obtained from the emitted fluorescent light, which is analyzed for its polarization. Fluorescence anisotropy, r , is defined as

$$r = \frac{I_{vv} - I_{vh}}{I_{vv} + 2I_{vh}} \quad (1)$$

where I_{vv} and I_{vh} are respectively vertically and horizontally polarized fluorescent light which are produced by vertically polarized excitation light. A coordinate system depicting the polarization directions is shown in Figure 1 where z is defined as the direction of resin flow; $I_{vv} = I_{zz}$ and $I_{vh} = I_{zx}$.

Molecular models yield a relationship between r and fluorescent dye orientation.(2-4,6) Orientation is defined by θ and ϕ angles of the dye absorption dipole moment where θ and ϕ are spherical coordinates of the laboratory

reference coordinate system of Figure 1. In general,

$$r = f(\langle \cos^2 \theta \rangle, \langle \cos^2 \phi \rangle, \frac{\tau_f}{\tau_r}) \quad (2)$$

where τ_f is the fluorescence decay time and τ_r is the rotational relaxation time of the molecule.(1-4) The term τ_f/τ_r appears because a molecule with small τ_r relative to τ_f will randomize its orientation before radiating fluorescence and, therefore, show no anisotropy. The ideal situation is $\tau_r \gg \tau_f$, for which the molecule is stationary while it fluoresces. Usually, $\tau_r \approx \tau_f$ for which some reorientation of the molecule occurs during fluorescence emission. Interpretation of r measurements must take into account effects attributed to the τ_f/τ_r ratio. The measurements reported here are made at room temperature for which τ_f/τ_r is constant.

If a resin undergoes extensional flow in the z direction, then dependence on ϕ is eliminated because of axial symmetry. In this case, fluorescence anisotropy r is given as

$$r_{cw} = r(\infty) + [r(0) - r(\infty)] \left(\frac{\tau_f}{\tau_r} + 1 \right)^{-1} \quad (3)$$

where

$$r(0) = \frac{[2 \langle P_2^2 \rangle + \langle P_2 \rangle] P_2(\cos \delta)}{2 \langle P_2 \rangle + 1} \quad (4)$$

and

$$r(\infty) = \langle P_2 \rangle P_2(\cos \delta) \quad (5)$$

where P_2 is the second Legendre orientation term,

$$P_2(\cos \theta) = \frac{(3 \cos^2 \theta - 1)}{2} \quad (6)$$

and δ is a molecular constant, the angle between the absorption and emission dipoles of the dye.(1) The subscript cw refers to measurements obtained using continuous illumination, and the brackets $\langle \rangle$ indicate averages over space.

A description of fluorescence anisotropy and its application to orientation studies of biaxially oriented films is presented in reference 3. In order to characterize biaxially oriented films, at least two anisotropy measurements, for which excitation light is polarized perpendicular to each other, need to be made.(3) The value of anisotropy obtained for each direction is a measure of the orientation in that direction.

This paper is a continuation of work that was presented at this meeting in 1998.(7) In that paper we described the design and application of a sensor which can be used for rapid and simultaneous acquisition of I_{vv} and I_{vh} at temperatures customary for polymer processing, up to 300 °C. The sensor head contains polarizing optics for polarizing the excitation light and for analyzing fluorescence polarization. It can be conveniently mounted adjacent to an extruded film or sheet for real-time monitoring or for acquiring area scans of fluorescence anisotropy off-line. Here, we present the results of scans obtained from a blow molded bottle and from a biaxially stretched film. In both cases the resin is polyethylene terephthalate.

Experimental Procedure

Fluorescence Anisotropy Sensor. Sensor design is shown in [Figure 2](#) and is described in more detail in reference 7. The sensor head has a square cross section (2.54 cm) in order to maintain a recognizable direction of the light polarization. Light exiting this sensor is polarized with direction parallel to a side of the square. Excitation light is produced by a suitable light source such as a laser, xenon arc lamp or halogen lamp. The sensor head contains a Glan-Taylor polarizer consisting of two calcite crystals separated by a fixed air space of approximately 0.1 mm. Both I_{vv} and I_{vh} are obtained from this arrangement. Excitation light is transmitted by the optical fiber in the central channel of the sensor and becomes vertically polarized by the calcite polarizer. The same calcite crystals analyze polarization of the fluorescence. Because of its birefringence, the calcite crystal separates the fluorescence into horizontal and vertical components. The horizontal polarization reflects off the interface between the two polarizers to the mirror and into the left channel where an optical fiber collects it for transmission to the detector. The vertical component of fluorescence is transmitted straight through the calcite crystal to the optical fiber in the central channel and then to the detector. The I_{vv} and I_{vh} signals are sent through a light chopper, then detected by a photomultiplier, and separated by a gated photon counter. A full description of the detection apparatus is presented in the previous publication.(7)

The sensor head can deliver either vertically or horizontally polarized excitation light. The optical fibers of [Figure 2](#) designated as “light source” and “alternate light source” produce excitation beams that are perpendicular to each other. By alternating the excitation light between these two light paths, mutually perpendicular polarized excitation light beams are produced and are used to obtain anisotropy values associated with mutually perpendicular directions in the specimen, e. g. the machine and transverse directions of an extruded resin.

The standard uncertainty in anisotropy values reported in this paper is 1.5 %.

The specimens consisted of polyethylene terephthalate doped with benzoxazolyl stilbene (BOS). They were extracted from two consumer products, a blow molded bottle and the shrink wrap around the lid of a food container. In both cases the BOS was mixed with the resin in order to give the product the distinctive blue BOS fluorescent color. The mass fraction of BOS in these products was estimated from the fluorescence intensity to be in the range $(200 \text{ to } 300) \times 10^{-6}$. The dimensions of the shrink wrap are 2 cm by 6 cm by 0.08 mm thick, and for the bottle they are 6.5 cm square by 0.55 mm thick. The bottle piece was cut from the side near the bottom at a position that was 20 cm from the top and 5 cm from the bottom.

A spectrum of BOS fluorescence is shown in [Figure 3](#) where fluorescence intensity versus wavelength is plotted for BOS in PET at room temperature for excitation at 365 nm. The standard uncertainty of the fluorescence data is 0.1%. For anisotropy measurements, the dye was excited at 365 nm and I_{vv} and I_{vh} were detected by integrating light over the wavelength range from 400 to 650 nm. The light source was a xenon arc lamp that was filtered using a 365 nm bandpass filter.

Scans of anisotropy were obtained by mounting the specimen on a translating x-y stage with the sensor head placed directly above the specimen. The distance between the sensor head and specimen was less than 1 mm. All measurements were made at room temperature. Area scans were carried out by moving the sensor head in 5 mm increments between measurement positions. The scan pattern thus established was a two dimensional 5 mm square mesh.

Results

[Figures 4 and 5](#) are contour plots of anisotropy measurements on a piece cut from the side of the blow molded bottle. [Figure 4](#) is for excitation light polarized in the x direction, and [Figure 5](#) is for excitation polarized in the y direction. The increasing y direction points from the bottom to the top of the bottle. The data show gradual shifts in anisotropy as a function of y. For y polarized excitation, anisotropy increases with increasing y, and for x polarized excitation, anisotropy decreases with increasing y. At maximum y, the two sets of anisotropy values overlap. Also, the contour plots show regions of relatively high gradients in anisotropy that can be interpreted as regions possessing high stress gradients. A portion of these data are shown in another view in [Figure 6](#) where we have plotted anisotropy versus distance in the y direction for x = 40 mm. We see that the two curves converge to a common value at large y. We conclude that the blow molding

process produces biaxial orientation that is approximately equal in the x and y directions for large y, but diverges as the resin is blown to the bottom of the bottle. While still biaxially oriented at the bottom of the bottle, the measurements indicate that there is more orientation in the x direction than in the y direction. A larger orientation in the x direction is produced in the bottle during radial expansion that creates tangential extensional stress.

Anisotropy measurements for the shrink wrap are shown in Figure 7. Between crossed polarizers, the shrink wrap shows distinct light transmission when oriented at 45° with respect to the polarizer axes of polarization, characteristic of biaxial orientation. Rotation away from 45° renders a very sharp transition to dark at all other orientations. This observation indicates that the specimen was cut from a larger sheet of biaxially oriented film. The effect of birefringence on the anisotropy measurements has been shown to be small.(3) Figure 7 contains plots of the anisotropy for excitation polarized in the x and y directions respectively. The data are presented as anisotropy versus distance in the y direction, where the y axis is in the direction of the long dimension of the specimen, which is a ribbon 6 cm long by 2 cm wide. Each plot contains four curves corresponding to x = 0, 5, 10, and 15 mm. The results for both x and y polarized excitation show uniform orientation with y polarization displaying a slightly broader distribution of anisotropy values. We visually examined the positions that yielded the outlying data points of Figure 7 and found that those regions contained wrinkles or other stretch marks that were visible between crossed polarizers.

It is helpful to illustrate biaxial orientation in a matrix format.(3) For example, the fluorescence measurements on the shrink wrap film specimen can be expressed as a 2 x 2 matrix of averaged fluorescence intensities,

$$I_{ij} = \begin{bmatrix} 3.2 & 1 \\ 1 & 3.2 \end{bmatrix}$$

where the intensities have been normalized with respect to the off diagonal components I_{12} and I_{21} . I_{11} and I_{22} are Iv for x and y polarized excitation respectively and are indicators of specimen orientation in the x and y directions. The standard deviations of the I_{11} and I_{22} averages are 2 % and 7 % respectively.

For the blown bottle at y = 0, after averaging the intensities we have

$$I_{ij} = \begin{bmatrix} 3.26 & 1 \\ 1 & 2.29 \end{bmatrix}$$

and at y = 55 mm

$$I_{ij} = \begin{bmatrix} 2.76 & 1 \\ 1 & 2.69 \end{bmatrix}$$

where the standard deviation of these averages is 8 %.

The relationships between the matrix elements and the average cosine orientation factors have been derived and discussed by Monnerie and co-workers.(3) In general, I_{ij} are functions of both the second and fourth moment of the orientation distribution function.

In summary, we have used a new fluorescence anisotropy sensor to measure orientation and to obtain orientation scans in processed polyethylene terephthalate film and blow molded bottle products. Using two excitation light beams, polarized perpendicular to each other, we examined biaxial orientation. Although these measurements were carried out off line, the sensor can be mounted on a process line for real-time monitoring. It can be used at operating temperatures up to 300 °C.

References

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Keywords: fluorescence anisotropy, optical sensor, molecular orientation, polyethylene terephthalate.

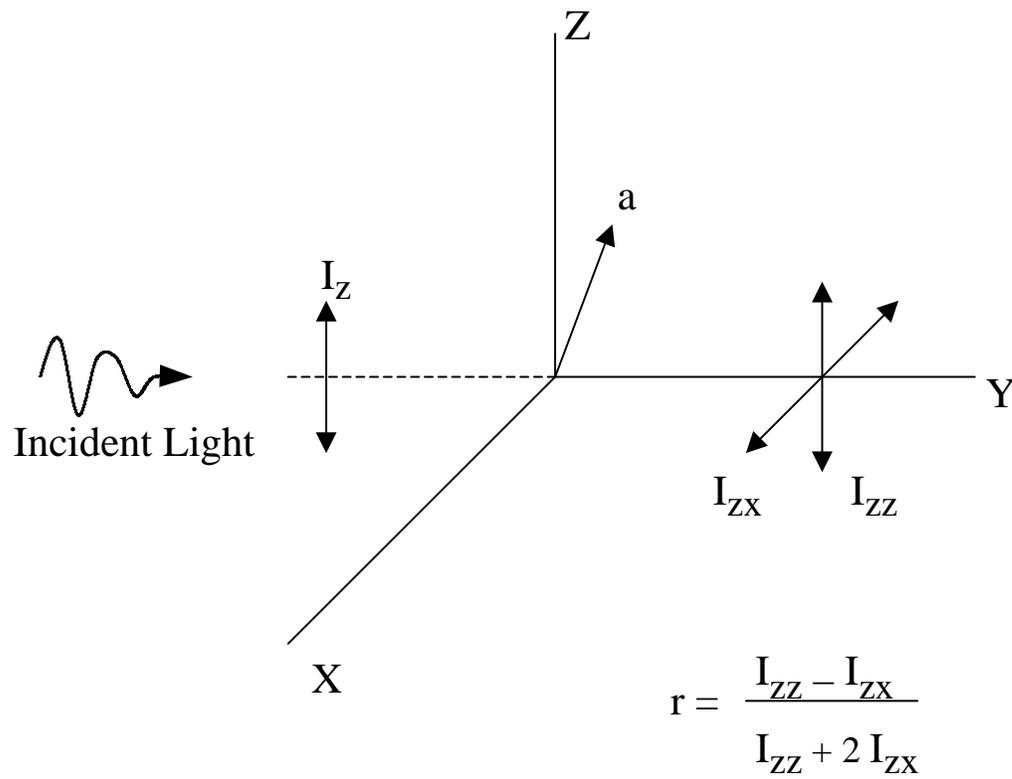


Figure 1. The laboratory coordinate system is shown.
 Here, $I_{zz} = I_{vv}$ and $I_{zx} = I_{vh}$.

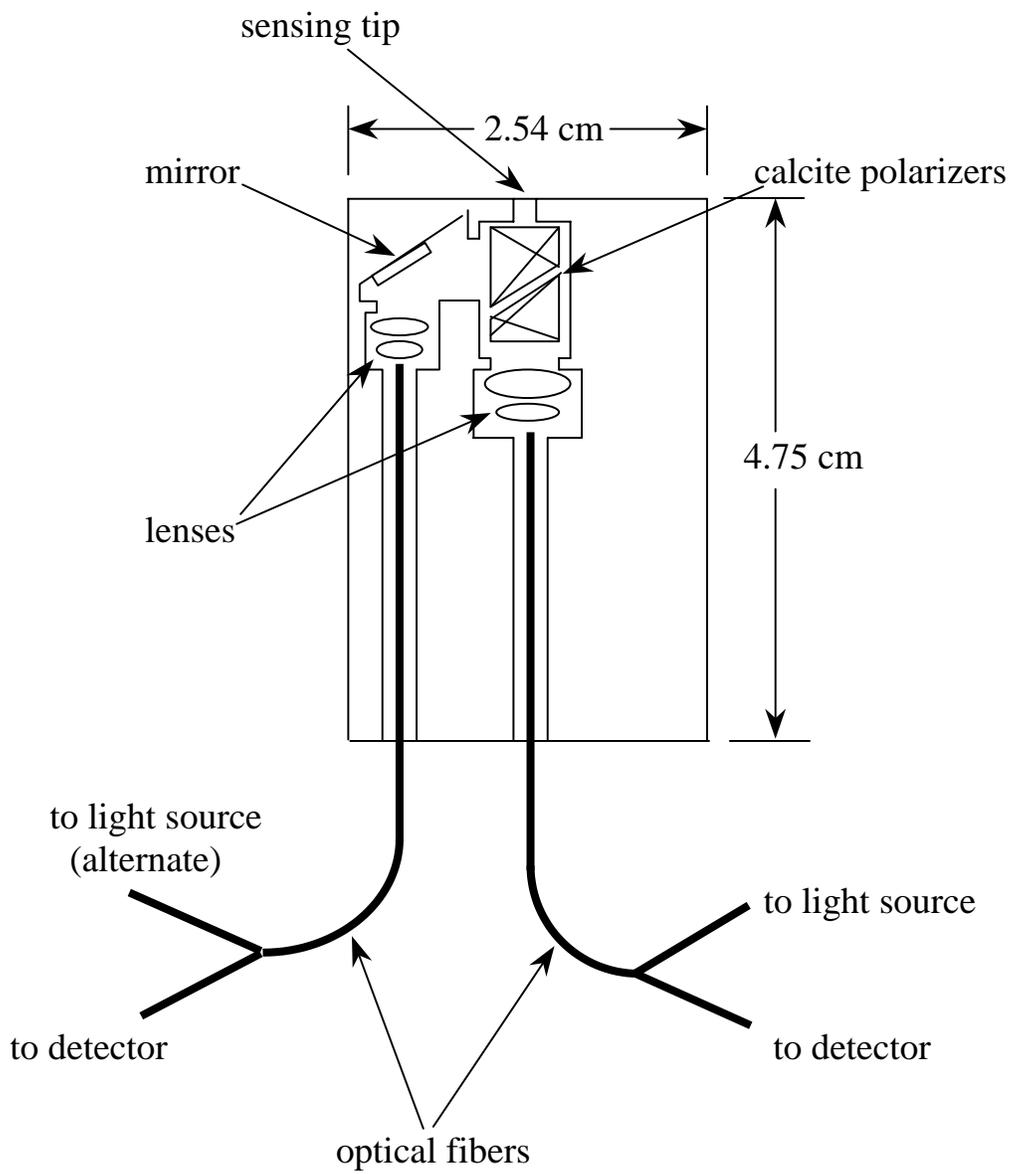


Figure 2. A schematic of the anisotropy sensor head is shown.

Benzoxazolyl Stilbene

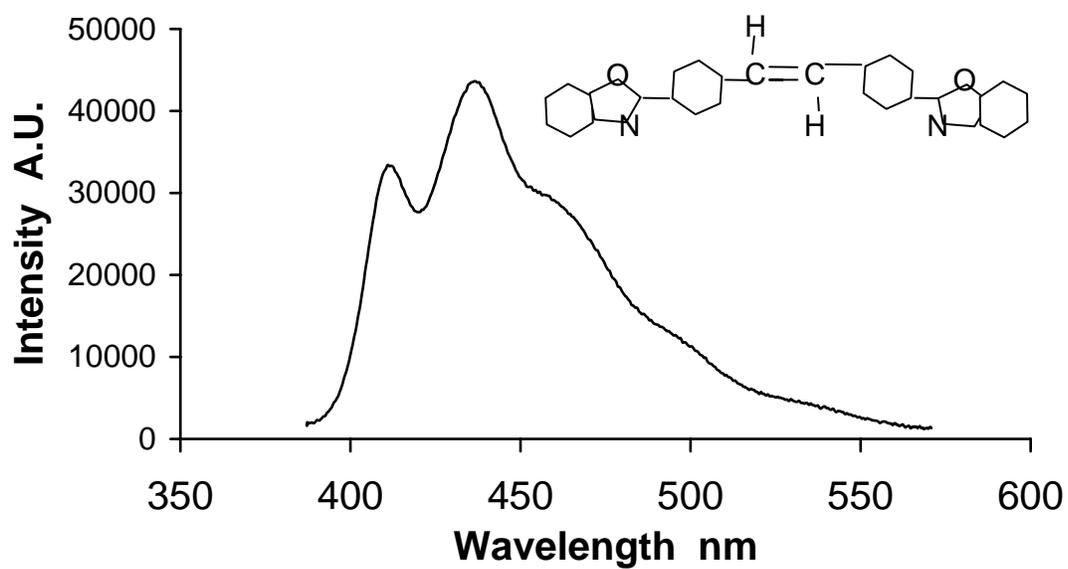


Figure 3. The fluorescence spectrum of BOS in PET is shown.

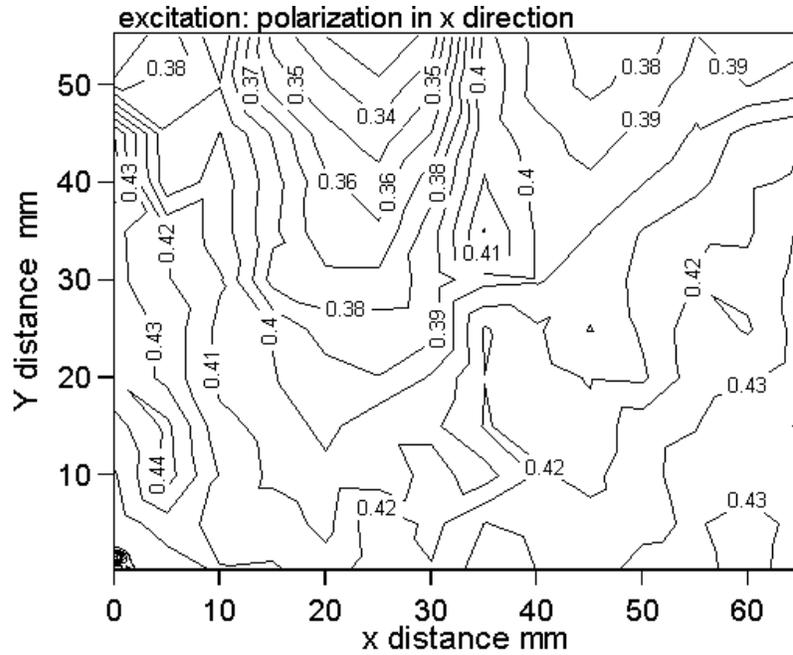


Figure 4. A contour plot of anisotropy for x polarized excitation is shown for a scanned area of 55 x 65 mm.

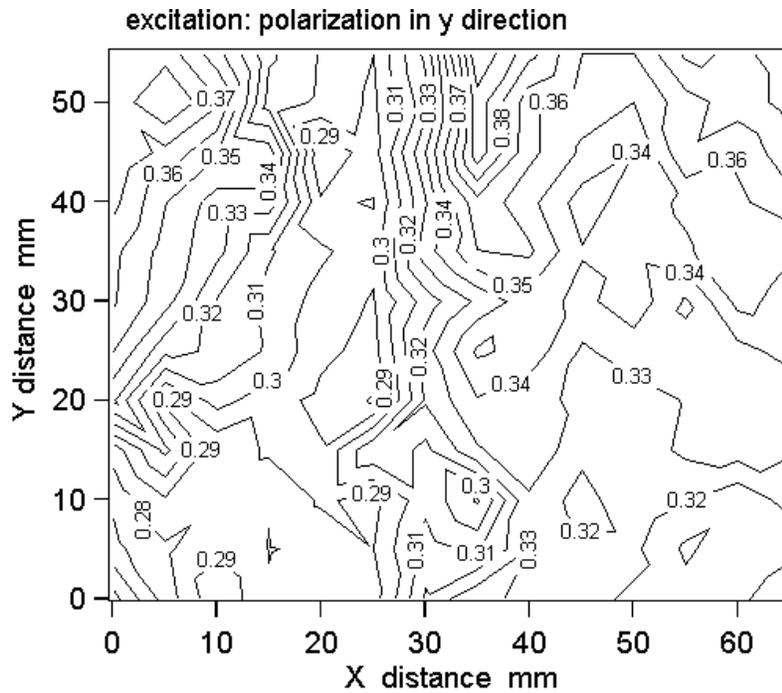


Figure 5. A contour plot of anisotropy for y polarized excitation is shown for a scanned area of 55 by 65 mm.

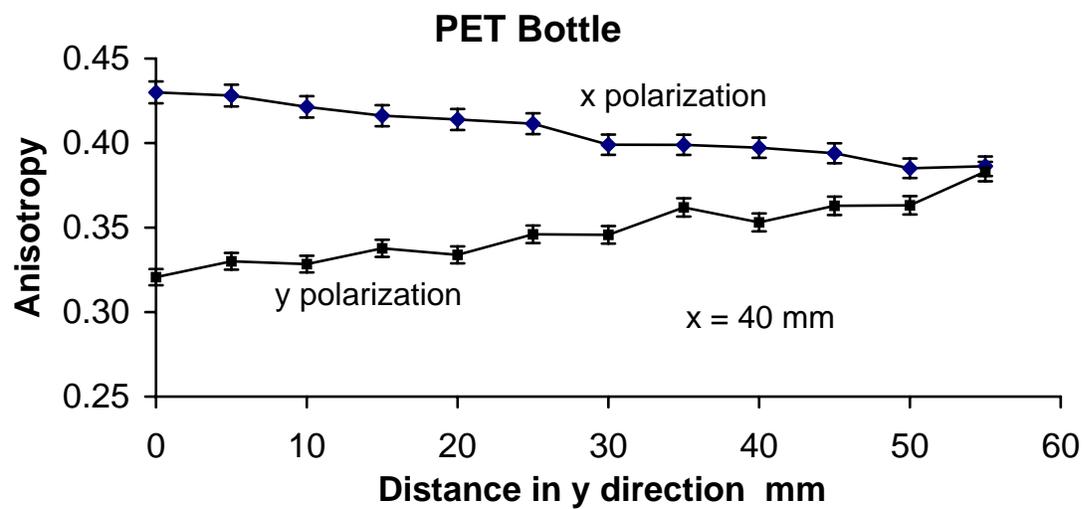


Figure 6. Anisotropy versus distance in y direction for excitation polarized in x and y directions. Data for fixed x position.

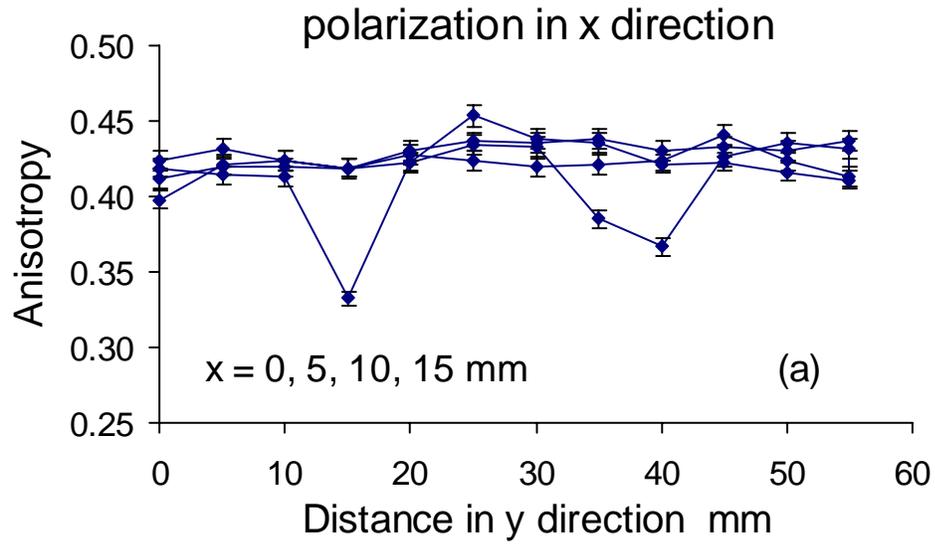


Figure 7(a). Anisotropy versus distance in y direction for four values of x.

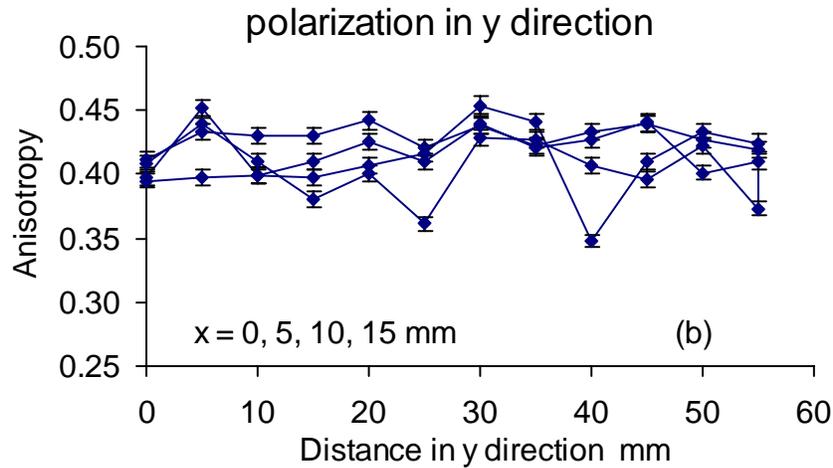


Figure 7. Anisotropy versus distance for (a) excitation in x direction and (b) excitation in y direction. Scans are for four x positions. Data for PET shrink wrap material.