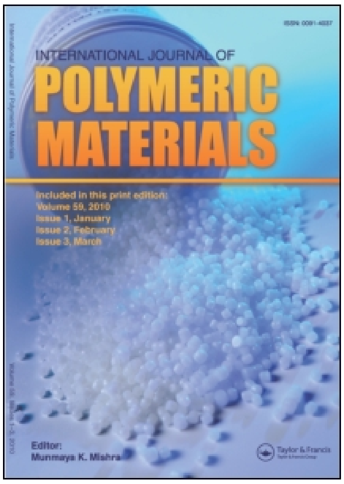

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The Structure and Properties of Thermally Treated Polyester Films

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The structure and properties of highly birefringent polyester (PET) films annealed at 120°C for different intervals of time are investigated. In the present of a polarizer, the Michelson interferometer is used to determine the refractive indices and the birefringence of the samples. For accurate results, the refractive indices are determined at different angles of incidence, and the average is taken. The effect of annealing time on the optical properties is investigated. The results show that the refractive indices and the birefringence increase as the time of thermal treatment increases. The values of refractive index difference (birefringence) are confirmed by those obtained directly from another optical technique. The obtained values of refractive indices and birefringence are utilized to calculate some optical and structural parameters important in characterizing the investigated PET films. Relationships between the obtained parameters and annealing time are given for illustration. The study shows that the Michelson interferometer can be considered as important tool in investigating thick and highly birefringent polyester films.

Keywords: birefringent polyester films, annealing, Michelson interferometer, refractive indices, birefringence, optical properties

INTRODUCTION

In oriented polymers, the refractive indices along the orientation direction and at right angle to it are different. That is, oriented polymers are birefringent and optically anisotropic. The molecular mechanism responsible for the variation in the optical properties is clarified by observation of the birefringence. Birefringence depends

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on molecular orientation in polymers as it contains contributions from the polarizabilities of all molecular units in the sample. It is thus a rapid and powerful tool for the study of morphological characteristics of defined polycrystalline polymers [1]. Optical anisotropy can be produced by thermal treatments, mechanical drawing, solid-state extrusion, and other treatments. It gives valuable information for characterization of polymers on the molecular level. It is worth nothing that the degree of orientation could vary significantly from one polymer to another depending on the polymer history during manufacture and subsequent processing operations. Polyester is a good moldable, fiber and film forming material because of its high glass transition temperature (70–80°C) and high crystalline melting point (>250°C). It is, therefore, one of the most important industrial polymers [2–3].

The optical properties of polymer films have been investigated in many publication using several experimental tools [4–7], although interferometery [8–16] is the most accurate one. The interferometric techniques measure the optical path difference over the entire visible spectrum as well as interference order in the image of the examined object. The thickness, refractive indices, birefringence and the other optical parameters can be determined. The highly coherent light obtained from the laser source has made it particularly easy to create new interferometric configurations. Pluta [10–11] used the variable wavelength technique to measure the optical parameters of different materials. Lloyd's interferometer was applied by Hamza et al. [12] to determine thickness and refractive indices of thin films. Medhat et al. [13] obtained fringes of equal tangential inclination by curved-induced birefringence. Sadik et al. used a general interferometric approach based on variable incident angle for refractive index and thickness measurement of birefringent single-medium [14] and multi-medium objects [15]. Shabana [16] determined the thickness and refractive index of isotropic polypropylene films using different interferometric techniques.

The present work focuses on using the Michelson interferometer to measure the refractive indices and the birefringence of free-standing, thick, and highly birefringent polyester films annealed at 120°C for different intervals of time. The refractive index difference (birefringence) is confirmed by another optical technique used to determine the birefringence directly. The optical principles are given and the mathematical formulae are derived. Certain optical and structural parameters such as the mean polarizability per unit volume, surface reflectivity, optical orientation function, and orientation angle are also obtained as functions of thermal treatment.

THEORETICAL CONSIDERATIONS

The refractive indices and the birefringence can be determined from the analysis of the obtained fringe patterns depending on the applied interferometric technique. The principle of Michelson interferometer makes it a necessity to slowly vary the length of the film through which the interference beam passes. A greater length of film is obtained as it is rotated by an angle (θ). The change in path length is related to the measured fringe transmissions by the following equation:

$$2n_a\, d_a\,(\theta) + 2n_f\, t_f\,(\theta) = m\,\lambda \tag{1}$$

where m is the collected number of fringe transmissions, λ is the wavelength of light used, n_a and n_f are the refractive indices of air and film, respectively, $d_a\,(\theta)$ is the distance traveled in air, $t_f\,(\theta)$ is the film thickness and θ is the angle of rotation of the film. Equation 1 can be rearranged and used together with some basic mathematics to calculate the refractive index of the examined film as follows [17]:

$$n_f = \frac{(2t_f - m\lambda)(1 - \cos\theta)}{2t_f(1 - \cos\theta) - m\lambda} \tag{2}$$

Equation 2 can be applied to determine the refractive indices $n_f^{\parallel}$ and $n_f^{\perp}$ if a polarizer is introduced in the optical path between the laser source and the beam splitter. The collected number m changes according to the polarization direction, parallel or perpendicular to the axis of the film.

The direct determination of birefringence, in the present work, is based on recording the intensity ratio $\mathbf{I}/\mathbf{I_o}$, where $\mathbf{I}$ and $\mathbf{I_o}$ are the intensity of light reaches the power meter and that just before striking the sample, respectively. When the polarized light strikes the samples, and the plane of polarization makes an angle of 45° with the axis of the sample, the electric vector can be resolved into parallel and perpendicular components. The two waves are passing through the sample with different velocities. As a result, a phase change in the emerging light is observed. This change of phase is directly proportional to the intensity of light $\mathbf{I}$ as follows:

$$\mathbf{I}/\mathbf{I_o} = \sin^2(\delta/2) \tag{3}$$

The phase difference δ is related to the optical path difference, $t_f\,(n_f^{\parallel} - n_f^{\perp})$, via the well-known equation:

$$\delta = \frac{2\pi}{\lambda} t_f\,(n_f^{\parallel} - n_f^{\perp}) \tag{4}$$

Since the birefringence Δn_f is taken as the difference between $n_f^{\parallel}$ and $n_f^{\perp}$, it can then be given from the combination of equations 3 and 4, as follows:

$$\Delta n_f = \frac{\lambda}{\pi t_f} \sin^{-1}(\mathbf{I}/\mathbf{I_o})^{1/2} \tag{5}$$

The obtained values of $n_f^{\parallel}$ and $n_f^{\perp}$ are utilized for calculating the following optical parameters:

The mean polarizability per unit volume, $\overline{P}$, is estimated from the relation

$$\overline{P} = \frac{3}{4\pi} \frac{(\overline{n}_f^2 - 1)}{(\overline{n}_f^2 + 2)} \tag{6}$$

where $\overline{n}_f$ is the mean refractive index of the examined sample.

The surface reflectivity of a polymer for light at normal incidence can be estimated from Fresnel equations and knowledge of mean refractive index $\overline{n}_f$. Thus the percentage reflection R (in air) is given by [2]

$$R = \left(\frac{\overline{n}_f - 1}{\overline{n}_f + 1}\right)^2 \times 100 \tag{7}$$

The refractive indices and the birefringence are also utilized for calculating the optical orientation function $P_2(\theta)$ and the orientation angle θ. The orientation function $P_2(\theta)$ is estimated by Hermans [18] and Ward [19] from the following equation:

$$P_2(\theta) = \frac{\Delta n_f}{(\Delta n_f)_{max}} \tag{8}$$

where $(\Delta n_f)_{max}$ is the maximum birefringence of the fully oriented polymer. Its value was previously determined [18] to be 0.24 for polyester. The orientation factor $[\Delta n_f/(\Delta n_f)_{max}]$ is related to the polarizabilities $\varphi^{\parallel}$ and $\varphi^{\perp}$ according to the following relation [20]

$$\frac{\varphi^{\parallel} - \varphi^{\perp}}{\varphi^{\parallel} + 2\varphi^{\perp}} = \left[\frac{\Delta\alpha}{3\alpha_o}\right] P_2(\theta) \tag{9}$$

and the polarizability was given by Stein and Wilkes [21] from the relation

$$\varphi^{\parallel} = \frac{n_f^{\parallel^2} - 1}{n_f^{\parallel^2} + 2} \tag{10}$$

and an analogous equation for $\varphi^{\perp}$. $(\Delta\alpha/3\ \alpha_o)$ is a quantity depending on the molecular structure.

The orientation angle (θ), the angle between the sample axis and that of the polymer units, is determined from the following equation [19]:

$$P_2(\theta) = 1 - \frac{3}{2}\sin^2\theta \tag{11}$$

SAMPLES PREPARATION

In this work polyethyleneterephthalate (PET) polyester sheet of thickness 194 μm was used. A set of samples was annealed at 120°C for different intervals of time (0, 3, 6, 9, 12, and 15 h) using a Fisher Scientific Oven, Model 655G. The annealed samples were quenched in air at room temperature and then were left in a desiccator for 24 h.

EXPERIMENTAL TECHNIQUES AND RESULTS

Set-up of Michelson Interferometer

The optical set-up of the well-known Michelson interferometer is shown in Figure 1. Prior to setting up the experiment, the laser was warmed up for at least one hour to eliminate any possible fringe or intensity variations. For accurate optical alignment, the components should be carefully arranged. A laser source of wavelength 632.8 nm was used and a polarizer was inserted in front of it to enable the determination of both refractive indices $n_f^{\parallel}$ and $n_f^{\perp}$. The sample is then mounted, in the path of the transmitted beam, on a rotational component holder so that it is exactly perpendicular to the optical path. The light rays spread out when 18 mm convex lens is placed between the polarizer and the beam-splitter. The counted number of fringe transmissions changes by rotating the holder.

This method of interference is suitable for studying free-standing, homogeneous, and not cloudy films. It overcomes the problems of thick and highly birefringent materials. Moreover, the samples are investigated in air with no need for immersion liquids.

Set-up for a Direct Measurement of Birefringence

The optical set-up of this system is shown in Figure 2. The unpolarized light is incident on an ideal linear polarizer placed at an angle of 45° with the incident beam of light. A second identical ideal polarizer, or analyzer, is introduced at 90° relative to the first. The irradiance **I** that

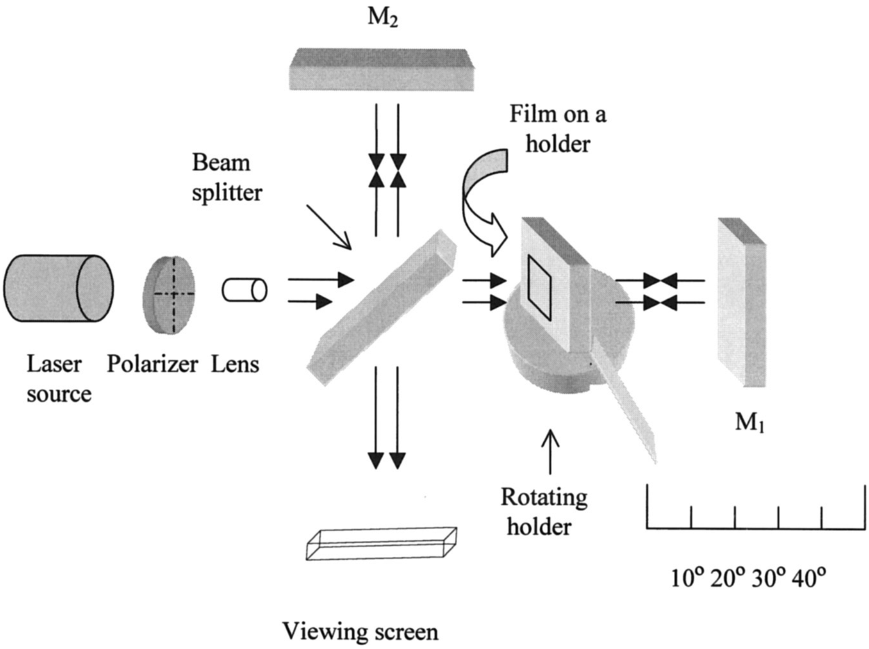

FIGURE 1 Optical set-up of the Michelson interferometer for determining refractive indices and birefringence of anisotropic polymers.

reaches the detector changes from zero to positive reading when the anisotropic polyester sample is introduced between the two polarizers, whereas the maximum irradiance $\mathbf{I_o}$ is taken, by the detector, in the absence of the sample. By the knowledge of the wavelength of the laser light and the sample thickness, the birefringence Δn_f can be calculated.

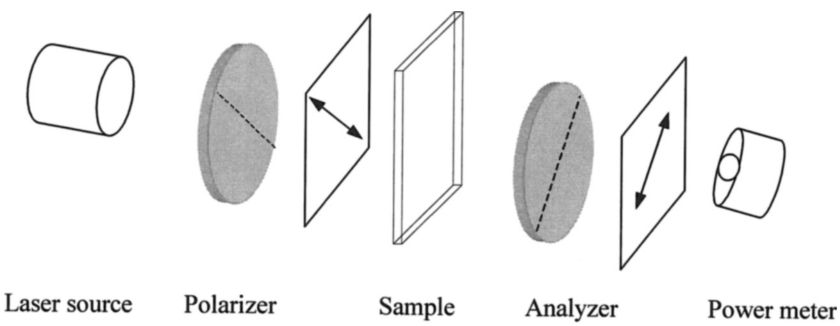

FIGURE 2 Optical set-up for direct measurement of birefringence.

EXPERIMENTAL RESULTS

Refractive Indices and Birefringence Measurements

Polyester films annealed at 120°C for 0, 3, 6, 9, 12, and 15 h were investigated. The Michelson interferometer has been devised, in the presence of an ideal polarizer, to estimate the refractive indices in the two principal vibration directions parallel and perpendicular to the axis of the examined samples. This method requires that the film under investigation must neither scatter nor absorb the light passing through it. The optical path length of one of the interfering beams changes as an effect of the rotation of the holder to certain degree. As a result, the number of times the fringe pattern restored to its original state is counted. As long as the minima and maxima can be clearly distinguished accurate measurements can be made. It is also very important to make sure that the counted number of fringe transmissions is absolutely correct. This can be done by centering the interference pattern on a viewing screen and by selecting a reference line on a millimeter scale at the boundary between the bright and the dark fringes. The values of the refractive indices are calculated using equation 2 with the knowledge of the wavelength of the laser source and the thickness of the examined samples. The refractive index $n_f^{\parallel}$ for each sample is calculated at different angles of rotation, and then the average is taken in order to minimize errors. By changing the polarization direction to a position normal to the sample axis, and by repeating the experimental procedures at several angles of incidence, the refractive index $n_f^{\perp}$ of each sample is calculated. The interference patterns seem not perfectly symmetrical or sharp due to the presence of the sample in the light path.

The values of the refractive indices $n_f^{\parallel}$ and $n_f^{\perp}$ for the unannealed sample and those annealed for different intervals of time are given in Table 1. The value of birefringence for each of the examined samples is taken as the difference between $n_f^{\parallel}$ and $n_f^{\perp}$ and is given in Table 1. Figure 3 shows the relationship between the refractive indices $n_f^{\parallel}$ and $n_f^{\perp}$ and the annealing time. The refractive index $n_f^{\parallel}$ increases, whereas $n_f^{\perp}$ decreases with increasing annealing time. This means that the molecules rearranged in the parallel direction more than in the perpendicular one.

Direct Measurements of Birefringence

The optical arrangement shown in Figure 2 was used for the direct determination of birefringence. A power meter was used to measure

TABLE 1 Values of Annealing Time, Refractive Indices, and Birefringences Using Michelson Method and the Direct Method

Annealing time (hour)	Refractive indices $n_f^{\parallel}$	Refractive indices $n_f^{\perp}$	Michelson method $(n_f^{\parallel} - n_f^{\perp}) \times 10^{-3}$	The direct method $\Delta n_f \times 10^{-3}$
0	1.6897	1.6303	59.4	59.9
3	1.7097	1.6153	94.4	95.0
6	1.7235	1.6042	119.3	119.7
9	1.7357	1.5942	141.5	142.1
12	1.7458	1.5855	160.3	160.9
15	1.7554	1.5782	177.2	177.8

the intensities of light **I** and $\mathbf{I_o}$. Several readings were recorded and their average was taken for greater accuracy. The birefringence Δn_f of each sample was then calculated using equation 5, and their values are also given in Table 1. In comparison, the obtained values of birefringence, using both methods, are nearly equal. The difference between them may arise from the difficulty of investigating the same restricted area of the sample. The birefringence, obtained by the two methods, was drawn as a function of the annealing time as shown in Figure 4. They increase as the annealing time increases. The

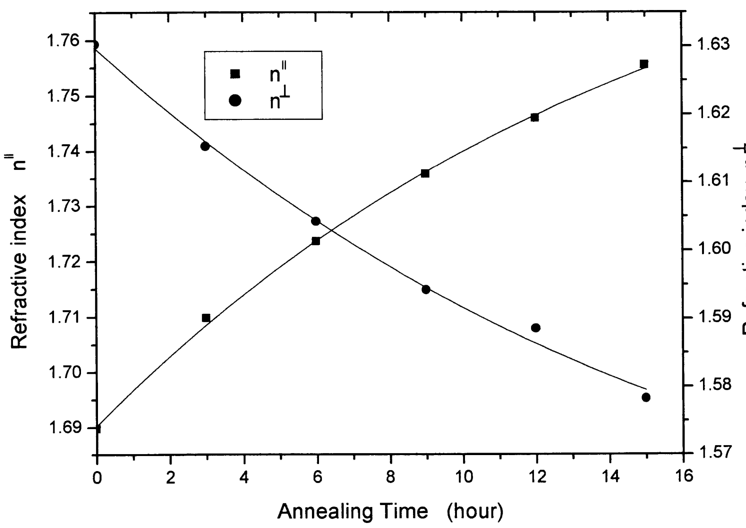

FIGURE 3 The relationship between refractive indices $n_f^{\parallel}$ and $n_f^{\perp}$ and annealing time.

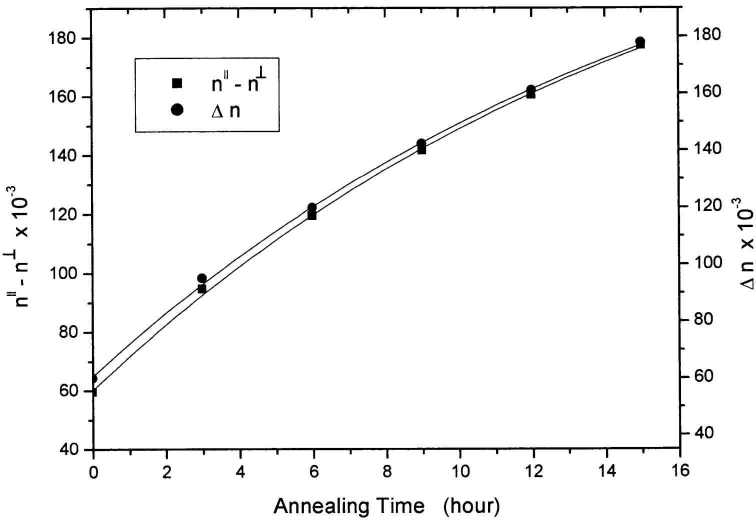

FIGURE 4 The birefringence, by the two methods, as a function of the annealing time.

crystallization and densification occuring at 120°C are the major reasons for the increased refractive index and birefringence.

Refractive Index-Structure Correlation

The values of the refractive indices $n_f^{\parallel}$ and $n_f^{\perp}$ and the birefringence values are utilized for calculating important optical and structural parameters for the characterization of the examined polyester samples. The mean polarizability per unit volume $\overline{P}$ and the surface

TABLE 2 Values of Annealing Time, Mean Polarizability per Unit Volume, Surface Reflectivity, Orientation Function, and Orientation Angle

Annealing time (hour)	$\overline{P} \times 10^{-3}$	R	$P_2(\theta) \times 10^{-2}$	θ
0	88.10	6.156	24.75	45.06
3	88.38	6.191	39.33	39.47
6	88.52	6.209	49.71	35.36
9	88.63	6.225	58.96	31.52
12	88.71	6.235	66.79	28.05
15	88.83	6.252	73.83	24.67

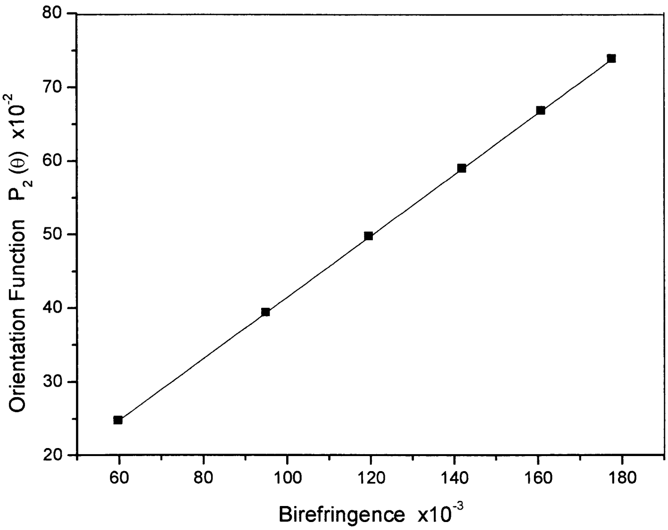

FIGURE 5 The relationship between optical orientation function $P_2(\theta)$ and birefringence.

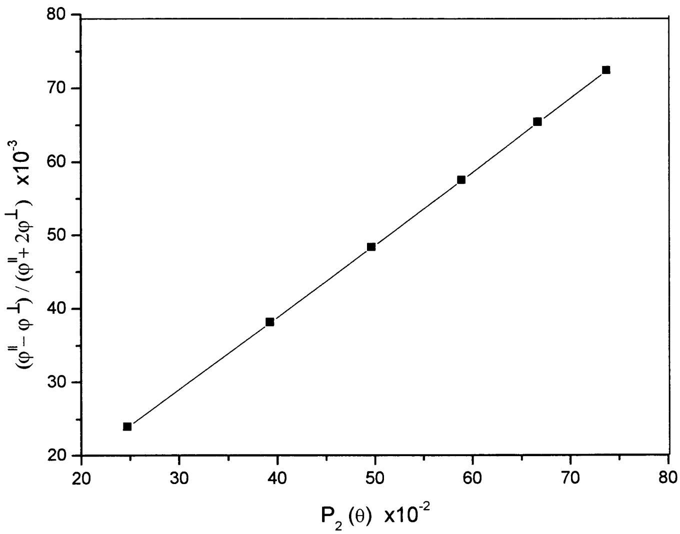

FIGURE 6 The polarizability factor $[(\varphi^{\parallel}-\varphi^{\perp})/(\varphi^{\parallel}+2\varphi^{\perp})]$ versus the optical orientation function $P_2(\theta)$.

reflectivity R are calculated using equations 6 and 7, respectively. The results of these parameters are given in Table 2.

The optical orientation function $P_2(\theta)$ and the orientation angle (θ) are calculated from equations 8 and 11, respectively. The values of $P_2(\theta)$ and θ are also given in Table 2. In contrast to the optical orientation function, the orientation angle decreases with increasing birefringence. The relationship between optical orientation function $P_2(\theta)$ and the birefringence is given in Figure 5. The factor $(\Delta\alpha/3\ \alpha_o)$ is also calculated from the relation between the polarizability factor $[(\varphi^{\parallel} - \varphi^{\perp})/(\varphi^{\parallel} + 2\varphi^{\perp})]$ and the optical orientation function $P_2(\theta)$; see Figure 6. Its value is 98.76×10^{-3}.

Significant variation in the obtained values of refractive index and birefringence, and hence in the optical properties of polyester films, is demonstrated as an effect of thermal treatment. The crystallization temperature has been detected at as low as 113.5°C for PET [22]. Hence, PET does crystallize measurably and even the fraction of polymer that remains amorphous becomes more dense upon annealing at 120°C. The crystalline areas give to PET high modulus of rigidity, elasticity, and ultimate tensile strength, whereas the amorphous areas give the samples the flexibility, recovery, elongation, and swelling. As a result, thermal treatment may produce new physical structure of certain semi-crystalline polymers, important in industry.

CONCLUSIONS

1. Two optical systems have been used to investigate highly birefringent polyester films, annealed for different times, via the determination of their optical properties.
2. Michelson interferometer was utilized, in the presence of an ideal polarizer, to determine the refractive indices and birefringence of the examined samples.
3. In contrast to the refractive index $n_f^{\perp}$, the refractive index $n_f^{\parallel}$ and the birefringence increased with increasing annealing time.
4. The optical orientation function linearly increased with increasing birefringence.
5. The arrangement of Michelson system offers the determination of the optical parameters, where they are hardly investigated by the conventional microscopic interferometers.
6. The Michelson method has the advantages of investigating thick specimens (>100 μm), and highly birefringent materials.
7. The values of birefringence were confirmed by those obtained from another simple optical system, used to determine the birefringence directly.

8. The laser source has the advantage of getting accurate measurements because a restricted area of the sample can be selected for investigation. Moreover, its highly coherent light has made it particularly easy to create new interferometric configurations.

As a result, the used optical systems have been established as making important contribution to investigate the optical properties of highly birefringent polyester films. They can be considered as important tools in the field of polymer physics.

REFERENCES

[1] Samules, R. J. (1974). *Structured Polymer Properties*, Wiley, New York.
[2] Hemsley, D. A. (1989). *Applied Polymer Light Microscopy*, Elsevier, London.
[3] Boder, G. (1991). *Structural Investigation of Polymers*, Ellis Horwood Ltd., Chichester, UK.
[4] Harrick, N. J., *Appl. Optics*. **10**, 2344 (1971).
[5] Liu, X., Liang, P., Zhang, W., and Tang, Y., *Optics & Laser Technology*. **30**, 85 (1998).
[6] Matthews, R. G., Ajji, A., Dumoulin, M. M., and Prud'homme, R. E., *Polym. Eng. and Sci.* **39** (12), 2377 (1999).
[7] Russo, R., *Polym. Testing*. **20**, 283 (2001).
[8] Barakat, N. and Hamza, A. A. (1990). *Interferometry of Fibrous Materials*, Hilger, Bristol.
[9] Pluta, M. (1993). *Advanced Light Microscopy*, Elsevier, Amsterdam, London, New York and Tokyo, Chapter 3.
[10] Pluta, M., *Optics and Laser Tech*. **20**, 81 (1998).
[11] Pluta, M., *Optica Applicata*. **21**, 2 (1991).
[12] Hamza, A. A., Mabrouk, M. A., Ramadan, W. A., and Emara, A. M., *Opt. Comm.* **225**, 341 (2003).
[13] Medhat, M., Hendawy, N. I., and Zaki, A. A., *Optics & Laser Technology*. **35**, 31 (2003).
[14] Sadik, A. M., Ramadan, W. A., and Litwin, D., *J. Meas. Sci. Tech.* **14**, 1753 (2003).
[15] Litwin, D., Sadik, A. M., Shabana, H. M., Sitarek, S. The full paper was accepted for publication in the proceedings of SPIE.
[16] Shabana, H. M., *Polym. Testing*. **23**, 695 (2004).
[17] Instruction Manual and Experimental Guide for the PASCO Scientific (1990). USA.
[18] Hermans, P. H. (1946). *Contributions to the Physics of Cellulose Fibres*, North-Holland, Amsterdam.
[19] Ward, I. M., *J. Polym. Sci. Polym. Symp.* **53**, 9 (1977).
[20] Cunningham, A., Davies, G. R., and Ward, I. M., *Polymer*. **15**, 743 (1974).
[21] Stein, R. S. and Wilkes, G. L. (1975). *Structure and Properties of Oriented Polymers*, Applied Science, London, pp. 57.
[22] Ezquerra, T. A., Sics, I., Nogales, A., DenChev, Z., and Balta-Calleja, F. J., *Euro. Phys. Lett.* **59** (3), 417 (2002).