New Method for Determining the Distribution of Birefringence and Linear Dichroism in Polymer Materials Based On Polarization-Holographic Grating

Barbara Kilosanidze, George Kakauridze, Levan Nadareishvili, Yuri Mshvenieradze

Abstract—A new method for determining the distribution of birefringence and linear dichroism in optical polymer materials is presented. The method is based on the use of polarization-holographic diffraction grating that forms an orthogonal circular basis in the process of diffraction of probing laser beam on the grating. The intensities ratio of the orders of diffraction on this grating enables the value of birefringence and linear dichroism in the sample to be determined. The distribution of birefringence in the sample is determined by scanning with a circularly polarized beam with a wavelength far from the absorption band of the material. If the scanning is carried out by probing beam with the wavelength near to a maximum of the absorption band of the chromophore then the distribution of linear dichroism can be determined. An appropriate theoretical model of this method is presented. A laboratory setup was created for the proposed method. An optical scheme of the laboratory setup is presented. The results of measurement in polymer films with two-dimensional gradient distribution of birefringence and linear dichroism are discussed.

Keywords—Birefringence, graded oriented polymers, linear dichroism, optical polymers, optical anisotropy, polarization-holographic grating,

I. Introduction

THE different methods are used for measuring birefringence and linear dichroism. The most widely used methods of birefringence measurement are the methods based on polariscopes - polarimeters [1]-[3]. However, the existing methods generally require a priori know the orientation of the anisotropy axes in the test sample and moreover they are labour-consuming, difficult to be automated, require a long time.

Linear dichroism has a long history and a wide range of applications, all requiring a means of orienting the sample [3]-[5]. Recently different techniques have developed to measure birefringence and linear dichroism with using polarization information which provide more molecular structural information than available from unpolarized absorption spectra. These techniques take advantages of both absorption differences and refractive index differences for polarized light.

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An experimental setup for linear dichroism measurements using Fourier-transform infrared spectroscopy (FTIR) in combination with a photoelastic modulator (PEM) is described in [6].

These techniques provide a powerful set of tools for studying molecular dynamic processes, studying and characterization in inorganic chemistry, polymer chemistry, material science, and biochemistry.

Therefore, the development of more technological method of measuring the distribution of birefringence and linear dichroism in optical transparent materials, such as polymer films oriented with complex manner, the natural and artificial crystals, etc. is very important.

In this paper, a new and convenient polarimetric method based on the polarization holographic grating [7]-[9] is presented for determining the distribution of birefringence and linear dichroism in samples of optical polymer materials, by measuring the ratio of the intensities of the diffraction orders of monochromatic light passing through the sample and diffracting on the grating. We have developed an appropriate theoretical model of the proposed method and have created a laboratory setup. As an example of the method we show the results of our measurements on polymer films with two-dimensional gradient distribution of optical parameters.

II. Theoretical Model

The anisotropy of optical parameters appears in polymer materials in case of mechanical stresses, stretching, including gradient stretching, an ununiform thermal action, when using special chemical methods, also the polarization-sensitive materials under the action of polarized light [7], [10], [11].

Let us consider the possibility of determining the complex birefringence (birefringence and linear dichroism) in polymer materials on an example of polymer materials with the gradient distribution of optical parameters. Materials having complex birefringence can be described by the Jones matrix [12].

$$M_G = \begin{pmatrix} \exp{-iKd\hat{n}_x} & 0 \\ 0 & \exp{-iKd\hat{n}_y} \end{pmatrix} \qquad (1)$$

Here $\hat{n}_x$ and $\hat{n}_y$ are complex birefringence coefficients of the material along the x and y axes ($\hat{n} = n - in\tau$, n - refractive index, τ - extinction coefficient), $\Delta n = n_y - n_x$,

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$\Delta n\tau = n\tau_y - n\tau_x$; d is the thickness of the sample, K is the coefficient depending on the mechanism that gives rise to an anisotropy of the optical parameters.

Let us note that the materials have a pure birefringence in spectral range away from the absorption band. Therefore, for the separate determination of the birefringence and linear dichroism the probing beams with different wavelengths may be used, namely, a wavelength away from the absorption band of the chromophore of the material is used for determining birefringence, and a wavelength close to the absorption maximum of the chromophore for determining linear dichroism.

The advantage of such an approach is the fact that, in a general case of the simultaneous determination of birefringence and linear dichroism, there is the need to know the orientation of the anisotropy axis. But the task is much more complicated in case of searching for the anisotropy axis, and even more at the variable character of anisotropy.

Matrix (1) can be represented as a multiplication of two matrices.

$$M = M_{BR}M_{LD} = \exp(-iKdn_x)\exp(-Kdn\tau_x) \qquad (2)$$

$$\cdot \begin{pmatrix} 1 & 0 \\ 0 & \exp(-Kd\Delta n) \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & \exp(-Kd\Delta n\tau) \end{pmatrix}$$

Here M_{BR} and M_{LD} are matrices describing birefringence ($\Delta n = n_y - n_x$) and linear dichroism ($\Delta n\tau = n\tau_y - n\tau_x$), respectively. Matrices in (2) are diagonal matrices, i.e. they are commutative, and therefore the multiplication result is independent on the sequence of the multipliers.

Let us illuminate the sample of the material by right circularly polarized probing light beam with the wavelength far from the absorption band of the chromophore. The Jones vector of illuminating beam is $\begin{pmatrix} 1 \\ i \end{pmatrix}$. After passing through the sample, the polarization state of light is transformed into the following form

$$\psi_{BR} = M_{BR}\begin{pmatrix} 1 \\ i \end{pmatrix} = \exp-iKdn_x\begin{pmatrix} 1 & 0 \\ 0 & \exp-iKd\Delta n \end{pmatrix}\begin{pmatrix} 1 \\ i \end{pmatrix} \qquad (3)$$

$$= \exp-iKdn_x\begin{pmatrix} 1 \\ i\exp-iKd\Delta n \end{pmatrix}$$

The polarization-holographic grating is suggested to be used for determining the distribution of birefringence and linear dichroism in polymer materials. Such a grating is obtained by recording with two orthogonally circularly polarized beams on the special polarization-sensitive material. The grating of such a kind divides an incident light beam on the orthogonal circular basis. The Jones matrix of such a grating is presented in [8], [9]:

$$M_C = M_0 + M_{-1,C} + M_{+1,C}$$

Here matrix M_0 is responsible for forming the nondiffracted order, matrices $M_{-1,C}$ and $M_{+1,C}$ are responsible for forming -1 and +1 orders, respectively,

$$M_{\mp 1,C} \approx A_{\pm 1}\begin{pmatrix} 1 & \mp i \\ \mp i & -1 \end{pmatrix}, \qquad (4)$$

where $A_{\pm 1}$ is a coefficient depending on the wavelength of grating recording, on the thickness of the recording medium, on anisotropic reaction of the medium and the intensity of the recording beam.

In case of applying such a grating, the use of a circularly polarized probing beam eliminates the necessity of knowing orientation of the anisotropy axes of the sample relative to the laboratory system, because the result of diffraction on such a grating does not depend on the orientation of the polarization plane of an incident beam [8], [9]. This gives the possibility of obtaining a picture of any complex distribution of birefringence and linear dichroism on the sample surface.

The transformed light beam (3) diffracts on the C grating and the Jones vectors of ∓ 1 diffracted orders are derived from multiplication of the appropriate Jones matrices (4) by the Jones vector (3) of the incoming wave.

$$\psi_{\mp 1} = A_{\mp 1}\exp-iKdn_x\left(1\mp\exp-iKd\Delta n\right)\begin{pmatrix} 1 \\ \mp i \end{pmatrix} \qquad (5)$$

The following expression for intensities of these beams was obtained from (5)

$$I_{\mp 1} = A_{\mp 1}A_{\mp 1}^*\left(1\pm\exp-iKd\Delta n\right)\left(1\pm\exp iKd\Delta n\right) \qquad (6)$$
$$= 4A_{\mp 1}A_{\mp 1}^*\left(1\pm\cos Kd\Delta n\right)$$

Here $A_{-1}A_{-1}^* = A_{+1}A_{+1}^*$. The intensities ratio is

$$\frac{I_{+1}}{I_{-1}} = \frac{1-\cos Kd\Delta n}{1+\cos Kd\Delta n} \qquad (7)$$

As a result we have obtained from (7) the following expression for determining birefringence

$$\Delta n = \frac{1}{Kd}\left(\arccos\frac{\frac{I_{+1}}{I_{-1}}-1}{\frac{I_{+1}}{I_{-1}}+1} + 2\pi m\right) \qquad (8)$$

As follows from (8), we can determine the distribution of birefringence of an arbitrary area of the sample by measuring ratio of the intensities I_{-1}/I_{+1} of the orders of diffraction on C grating, taking into account the wavelength of the probing light beam and the order of the interference band ($m = 0, 1, 2, ...$). This order can be determined experimentally by counting sequential blanking of +1 and -1 diffraction orders when the sample is shifted from zero fringe to the area under

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investigation.

It is important to note that the use of the ratio of the intensities of the diffraction orders significantly reduces the requirements on the stability of the source power as the measurement of the intensities of these orders is carried out simultaneously. It should be also note that the diameter of the probing beam can be quite small compared to the changing of birefringence that leads to the increase in the measurement accuracy. The proposed method enables the distribution of birefringence to be obtained by scanning the sample surface.

For materials having linear dichroism we have from (3)

$$M_{LD} = \exp(-iKdn_x)\exp(-Kdn\tau_x)\begin{pmatrix} 1 & 0 \\ 0 & \exp(-Kd\Delta n\tau) \end{pmatrix} \quad (9)$$

Let us also irradiate a sample of the material having a linear dichroism by the right circularly polarized light beam with a wavelength close to the maximum of the absorption band of the chromophore.

After passing through the sample the corresponding Jones vector has the following form.

$$\psi_{LD} = M_{LD}\begin{pmatrix} 1 \\ i \end{pmatrix} \quad (10)$$

$$= \exp-iKdn_x \exp(-Kdn\tau_x)\begin{pmatrix} 1 \\ \exp-Kd\Delta n\tau \end{pmatrix}$$

The light beam (10) also incident on the polarization-holographic grating with matrices (4) which are responsible for forming -1 and +1 diffraction orders. As a result we obtain the following Jones vectors for ∓1 diffraction orders

$$\psi_{\mp 1} = A_{\mp 1}\exp-iKdn_x \exp-Kdn\tau_x\left(1 \pm \exp-Kd\Delta n\tau\right)\begin{pmatrix} 1 \\ \mp i \end{pmatrix} \quad (11)$$

The intensities of these beams are

$$I_{\mp 1} = 2A_{\mp 1}A_{\mp 1}^*\exp(-2Kdn\tau_x)\left[1 \pm \exp(-Kd\Delta n\tau)\right]^2 \quad (12)$$

In (12) $A_{-1}A_{-1}^* = A_{+1}A_{+1}^*$.
For the ratio of the intensities we have

$$\frac{I_{-1}}{I_{+1}} = \frac{\left[1 + \exp(-Kd\Delta n\tau)\right]^2}{\left[1 - \exp(-Kd\Delta n\tau)\right]^2} \quad (13)$$

and we get the following expression for linear dichroism from (13)

$$\Delta n\tau = \frac{1}{Kd}\ln\left|\frac{\sqrt{\frac{I_{-1}}{I_{+1}}}-1}{\sqrt{\frac{I_{-1}}{I_{+1}}}+1}\right| \quad (14)$$

The expression (14) includes a module of the logarithm argument because the argument represents the ellipticity of the

light beam which passes through the sample and according to [8] it is equal to $\varepsilon = \left|\frac{\sqrt{I_{-1}} - \sqrt{I_{+1}}}{\sqrt{I_{-1}} + \sqrt{I_{+1}}}\right|$, $0 \le \varepsilon \le 1$.

As follows from (14) for the determination of linear dichroism in any area of the sample it is necessary to measure simultaneously the ratio of the intensities I_{-1}/I_{+1} of ∓1 orders of diffraction on the polarization holographic grating, taking into account the wavelength of the probing light.

Thus, this approach enables the birefringence and linear dichroism regardless of the orientation of the anisotropy axes of the sample to be determined, as only the circularly polarized light is used for sensing. In this case the light with a wavelength in the absorption band of the chromophore is used for determining dichroism and we can use the light with a wavelength outside the absorption band for determining birefringence.

III. EXPERIMENTAL RESULTS

To check experimentally the theoretical model, a laboratory setup was created, the optical scheme of which is presented on Fig. 1:
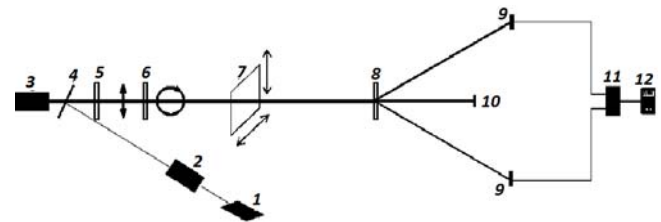

Fig. 1 Optical scheme of the laboratory setup for determining the distribution of birefringence and linear dichroism: 1 – laser with λ = 442 nm; 2 – laser with λ = 532 nm; 3 – laser with λ = 635 nm; 4 - semi-transparent mirror; 5 - Glan prism; 6 - quarter-wave plate; 7 – sample; 8 – polarization-holographic diffraction grating; 9 – photodetectors; 10 - opaque screen; 11 – analog division unit; 12 - digital indicator

Three lasers are used: laser 1 (with wavelength of 442 nm), laser 2 (532 nm) and laser 3 (635 nm); the power of each laser was about 5 mW. Glan prism 5 is placed on the path of the probing beam for obtaining linearly polarized radiation with the degree of linear polarization close to 100%. Then the beam passes through the quarter-wave plate 6 for the given wavelength, oriented so that the beam will be right-hand circularly polarized. The sample 7 is mounted in a two-dimensional scanning device and is illuminated by a formed light beam.

If a transmission area of the sample exhibits birefringence, the polarization of the transmitted light beam is changed and it becomes elliptically polarized. The degree of ellipticity unambiguously depends on the value of birefringence. Let us note that this is true in case of studying a sample outside the spectral absorption band of the material.

The beam that passed through the sample comes on the polarization holographic grating 8, which forms +1 and -1 diffraction orders and nondiffracted zero beam. As shown in

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the theoretical model, the ratio of the intensities of the diffracted beams unambiguously determines the value of the birefringence in the illuminated sample area. High quality photodetectors 9 were used for simultaneous measurement of the intensities. Zero beam is blocked by an opaque screen 10. In the process of moving the sample along the horizontal axis the order of the interference fringe was determined.

For the direct measurement of the intensities ratio of the diffracted beams the analog block of the intensity division 11 was used on the basis of high-speed microscheme of analog division AD734, which provides measurement accuracy of 0.1% and has a large dynamic range. The value of the intensity ratio was displayed on the digital display 12.

The two-dimensional scanning device, in which the sample was fixed, gives the possibility of moving the sample along two axes in the laboratory coordinate system, with a range of movement along a horizontal axis 60 mm, and along a vertical axis 30 mm. Thus we have the possibility of obtaining the distribution of birefringence and linear dichroism throughout the sample.

For experimental check the samples of polymer films based on polyvinyl alcohol (PVA) have been used, in which two types of dichroic dyes - Methylene blue and Rhodamine 6G have been introduced with various concentrations. The samples without dye were also investigated. Some of the samples were in an undeformed (isotropic) state; the other ones were polymeric films with gradient artificial birefringence investigated by us [13]-[15].

Absorption spectra of isotropic samples were obtained. According to these spectra three lasers with wavelengths of 442 nm, 532 nm and 635 nm were included in the optical scheme of the laboratory setup.

This makes it possible to measure birefringence far from the absorption band of the chromophore: laser of 635 nm was used for the samples based on chromophore Rhodamine 6G, and to determine linear dichroism in the same sample a laser at 532 nm was used. For the sample based on the chromophore Methylene blue we used a laser at 442 nm to determine the birefringence and a laser at 635 nm to determine linear dichroism in the same sample. For samples without chromophore the birefringence was determined for two wavelengths of 532 nm and 635 nm.

As an illustration, the curves of the distribution of birefringence Δn and linear dichroism $\Delta n\tau$ on the surface of the isotropic samples, and also on the surface of samples with different modes of gradient orientation are presented on Figs. 2-7 for different samples.

Fig. 3 The distribution of Δn and $\Delta n\tau$ in the sample based on PVA with dye methylene blue, the concentration of dye is 0.1%; the sample is isotropic; the thickness is 50 micrometers, a wavelength of the probing beam: (a) 442 nm; (b) 635 nm

Fig. 4 The distribution of Δn in the sample based on PVA; the sample is isotropic; the thickness is 420 micrometers, a wavelength of the probing beam: (a) 635 nm; (b) 532 nm

Fig. 5 The distribution of Δn and $\Delta n\tau$ in the sample based on PVA with dye Rhodamine G6, the concentration of dye is 0.3%; uniaxial stretching 400%; the thickness is 100 micrometers, stretching speed 5 mm/sec; temperature 90^{0}C; a wavelength of the probing beam: (a) 635 nm; (b) 532 nm
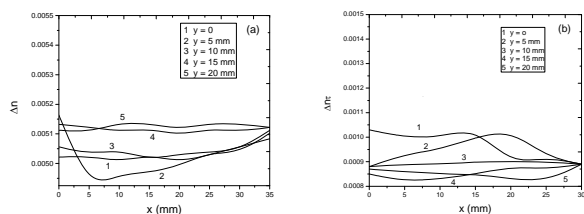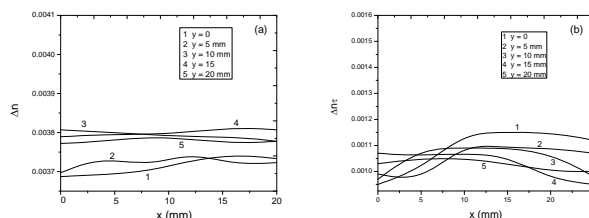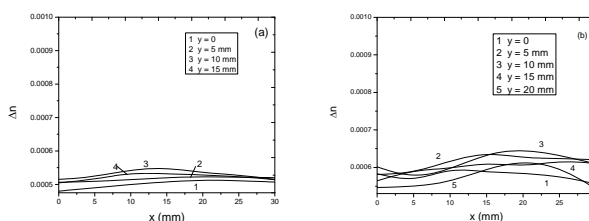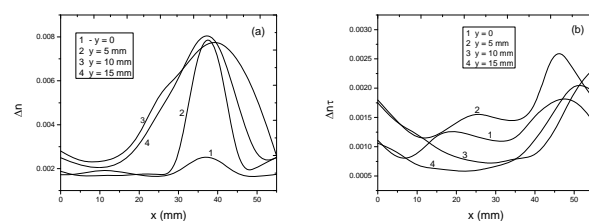
Fig. 2 The distribution of birefringence Δn and linear dichroism $\Delta n\tau$ in the sample based on PVA with dye rhodamine G6, the concentration of dye is 0.15%; the sample is isotropic; the thickness is 50 micrometers, a wavelength of the probing beam: (a) 635 nm; (b) 532 nm
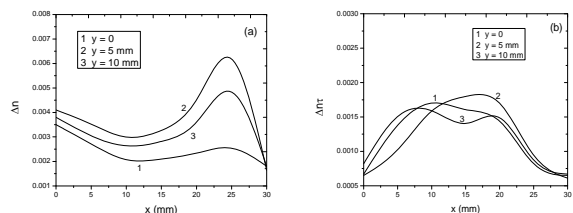
Fig. 6 The distribution of Δn and $\Delta n\tau$ in the sample based on PVA with dye Rhodamine G6, the concentration of dye is 0.3%; uniaxial stretching 200%; the thickness is 110 micrometers, stretching speed 5 mm/sec; temperature 90^{0}C; a wavelength of the probing beam: (a) 635 nm; (b) 532 nm

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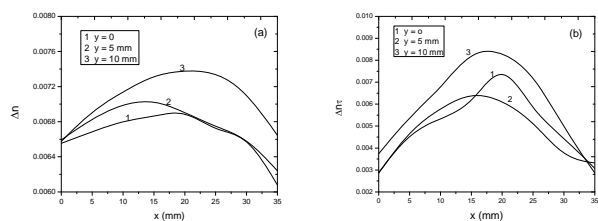International Journal of Chemical and Molecular Engineering
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Fig. 7 The distribution of Δn and $\Delta n\tau$ in the sample based on PVA with dye Methylene blue, the concentration of dye is 0.1%; uniaxial stretching 200%; the thickness is 25 micrometers, stretching speed 5 mm/sec; temperature 90^0C; a wavelength of the probing beam: (a) 442 nm; (b) 635 nm
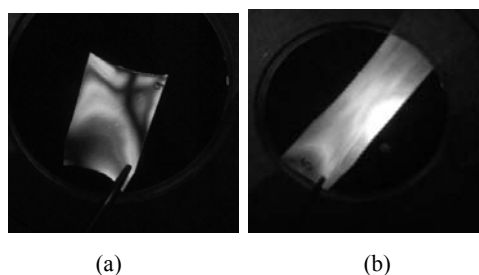

(a)   (b)

Fig. 8 Photos of the samples placed between crossed polarizers: (a) sample in Fig. 6; (b) sample in Fig. 5

As can be seen from Figs. 2-4 the change of Δn and $\Delta n\tau$ does not exceed 2×10^{-4} for isotropic samples. Small fluctuations of Δn and $\Delta n\tau$ are caused by thickness inhomogeneity of the film and by inhomogeneity of drying. For the stretched samples it follows from Figs. 5-7 that the change in values of Δn over the sample surface reaches 6×10^{-3} and the change of $\Delta n\tau$ reaches 5×10^{-3}. At the same time there is a sufficiently large inhomogeneity of the parameter distribution on the surface of the samples, which coincides closely with the diagrams of gradient stretching of the sample.

At a probing wavelength of 442 nm (outside the absorption band of the chromophore) for the sample in Fig. 7 (a), the intensities ratio I_{+C}/I_{-C} is equal to 0.069 in point of the sample with coordinates $x = 20$ mm, $y = 10$ mm and we obtained $\Delta n = 0.0074$ and $\Delta n\tau = 0.0014$. For a probing wavelength of 635 nm (close to the absorption peak) for the same point of the sample in Fig. 7 (b) the intensities ratio I_{+C}/I_{-C} is equal to 0.608 and $\Delta n = 0.0053$ and $\Delta n\tau = 0.0085$. This confirms the eligibility of the theoretical model on the separate determination of Δn and $\Delta n\tau$.

Fig. 8 shows the samples with the most characteristic distribution Δn and $\Delta n\tau$ placed between crossed polarizers. The interference fringes of zero and first orders are observed.

Let us note that the diameter of the probing beam can be quite small in comparison with the scale of measurement of optical parameters which increases measurement accuracy.

The proposed method is more technological and simple in comparison with the existing methods for determining the birefringence and linear dichroism and it enable the measurements to be carried out regardless of the orientation of the axis of deformation of the sample and also in case of a complex distribution of the axes of anisotropy in the sample.

This method has a sufficiently high sensitivity and as can be seen it reveals even small changes in the optical parameters of the polymer films caused by errors in the technology of manufacturing films.

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