Polarization holographic gratings in side-chain azobenzene polyesters with linear and circular photoanisotropy

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We investigate thin phase polarization holographic gratings recorded with two waves with orthogonal linear polarizations in materials in which illumination with linearly/circularly polarized light gives rise to linear/circular birefringence. The theoretical analysis shows that the presence of circular photoanisotropy changes significantly the diffraction characteristics of the gratings. The intensities of the waves diffracted in the +1 and −1 orders of diffraction and their ratio depend substantially on the reconstructing-wave polarization. Experiments with films of side-chain liquid-crystalline azobenzene polyester that is a photoanisotropic material of the considered type confirm the unusual polarization properties. It is shown that polarization holography may be used for real-time simultaneous measurement of photoinduced linear and circular birefringence.

Key words: Polarization holographic gratings, photoanisotropy, side-chain azobenzene polyesters.

1. Introduction

Photoanisotropic materials are widely investigated for optical storage and processing applications. The most promising of them seem to be azo-dye–polymer systems because of the large value of the photoinduced birefringence in them. Different types of azo dyes have been used, dissolved or chemically linked to a polymer.1–15 These systems differ in the sensitivity and stability of the induced effects. In all of them the appearance of only linear anisotropy was reported. It is due to trans–cis isomerization and reorientation of the azobenzene moieties and parts of the polymer chains. Holographic gratings recorded in these types of materials (with linear photoanisotropy) have been investigated, and their polarization properties are well known.16–19

Recently we found that, in films of side-chain azobenzene polyesters,8 circular birefringence (optical activity) can also be induced if the exiting light is circularly polarized.20 For the present we do not know the exact mechanism of inducing the optical activity. However, it is clear that it influences the characteristics of the holographic gratings recorded in these films. In this work we make a theoretical analysis, based on the Jones matrices method, of thin phase holographic gratings in materials with both linear and circular photoanisotropy. We also report experiments on polarization gratings recorded in films of side-chain liquid-crystalline azobenzene polyester.8,15

2. Theory

The optical transmittance of a nonabsorbent birefringent material with optical activity is given by

\[ T = \exp(i\hat{K}z), \]  

where the wave matrix \( \hat{K} \) in a coordinate system related to the optical axis is

\[ \hat{K} = \frac{2\pi}{\lambda} \begin{bmatrix} n_1 & -i\Delta n_{\text{cir}} \\ i\Delta n_{\text{cir}} & n_2 \end{bmatrix}. \]  

Here, \( n_1 \) and \( n_2 \) are the principal refractive indices in the absence of optical activity, \( \Delta n_{\text{cir}} = (n_t - n_c)/2, n_t \)
and $n_r$ being the refractive indices for the left- and right-circular, respectively. The matrix equation (2) can be written in the form

$$\hat{K} = \frac{2\pi}{\lambda} \hat{n} + \Delta \hat{K}, \quad \Delta \hat{K} = \frac{2\pi}{\lambda} \begin{bmatrix} \Delta n_{\text{lin}} & -i \Delta n_{\text{cir}} \\ i \Delta n_{\text{cir}} & -\Delta n_{\text{lin}} \end{bmatrix},$$  \hspace{1cm} (3)$$

where $\hat{n} = (n_1 + n_2)/2$ and $\Delta n_{\text{lin}} = (n_1 - n_2)/2$.

Let the medium be initially isotropic, and illumination with polarized light gives rise to both linear and circular anisotropy. We assume that the induced linear birefringence axis is parallel to the polarization ellipse axis of the exciting light. We also assume that $\Delta n_{\text{lin}}$ is proportional to the difference of the intensities of the light components polarized along and perpendicularly to this axis, and that $\Delta n_{\text{cir}}$ is proportional to the difference of the intensities of the left- and right-circularly polarized components. That is,

$$\Delta n_{\text{lin}} = L(a^2 - b^2) = L\sqrt{S_1^2 + S_2^2},$$  \hspace{1cm} (4)$$

$$\Delta n_{\text{cir}} = CI - I_r = CS_3,$$  \hspace{1cm} (5)$$

where $L$ is the response constant for the linear anisotropy, $C$ is the constant for the circular anisotropy, $a$ and $b$ are the semiaxes of the polarization ellipse, $I_1$ and $I_r$ are the intensities of the left- and right-circular components of light, respectively, and $S_1, S_2,$ and $S_3$ are the Stokes parameters.

Let a holographic grating be recorded in this material with two plane waves with orthogonal linear polarizations, vertical and horizontal [Fig. 1(a)]. It is well known that in this case the resultant light field is constant in intensity and with a spatially modulated state of polarization. Let the scheme of the recording be symmetrical and the two recording waves be of equal intensities. Then the Jones vector of the resultant light field in the coordinate system $(x, y)$ with axes inclined at $\pm 45^\circ$ to the vertical is

$$\mathbf{E} = \sqrt{2} \begin{bmatrix} \cos(\delta/2) \\ i \sin(\delta/2) \end{bmatrix},$$  \hspace{1cm} (6)$$

where $I$ is the total light intensity, $\delta/2 = (2\pi/\lambda)\sin \theta$ $x'$, $\delta$ is the phase difference between the two recording waves, and $x'$ is the horizontal axis. The periodic modulation of the state of polarization corresponding to Eq. (6) is shown in Fig. 1(b). The polarization changes gradually from linear, along $x$, to left circular, linear along $y$, right circular, linear along $x$, and so on. If only linear anisotropy is induced in the material, the regions illuminated with circularly polarized light remain isotropic. The properties of this type of polarization holographic gratings are described in Ref. 18. In the general case, when circular anisotropy is also induced, left- and right-circular polarization causes different changes in the optical constants of the material, and the type of the recorded anisotropic structure is different. Then the spatially modulated anisotropic changes in the refractive index are

$$\Delta n_{\text{lin}} = L\sqrt{S_1^2 + S_2^2} = LI \cos \delta,$$  \hspace{1cm} (7)$$

$$\Delta n_{\text{cir}} = CS_3 = CI \sin \delta.$$  \hspace{1cm} (8)$$

The matrix $\Delta \hat{K}$, corresponding to the recorded polarization grating, is

$$\Delta \hat{K} = \frac{2\pi}{\lambda} \begin{bmatrix} \Delta n^l \cos \delta & -i \Delta n^c \sin \delta \\ i \Delta n^c \sin \delta & -\Delta n^l \cos \delta \end{bmatrix},$$  \hspace{1cm} (9)$$

where $\Delta n^l = LI$ and $\Delta n^c = CI$ are the amplitudes of the modulation of the photoinduced linear and circular birefringence, respectively, in the periodic anisotropic structure. To analyze the diffraction at this grating, one has to calculate the matrix $\mathbf{T} = \exp(i \Delta \hat{K} z)$. In the general case, $\mathbf{T}$ is

$$\mathbf{T} = \begin{bmatrix} \cos N + i \Delta \varphi^l \cos \delta & \sin N \Delta \varphi^c \sin \delta/N \\ -\Delta \varphi^c \sin \delta/N \cos N - i \Delta \varphi^l \cos \delta \sin N/N \end{bmatrix}.$$  \hspace{1cm} (10)
where
\[
\Delta \varphi^l = \frac{2\pi}{\lambda} \Delta n^l z, \quad \Delta \varphi^c = \frac{2\pi}{\lambda} \Delta n^c z,
\]
\[
N = \sqrt{\Delta \varphi^c \cos \delta + \Delta \varphi^c \sin \delta}.
\]

The matrix \( \hat{T} \) can be simplified in the following cases:

(i) \( \Delta n^c = 0 \) and \( \Delta n^l \neq 0 \); that is, only linear birefringence is induced. Diffraction at polarization gratings recorded in these types of materials is described in Ref. 18. There are many orders of diffraction; the corresponding light intensities do not depend on the polarization. For the waves diffracted in the \( \pm 1 \) orders the gratings act as a \( \lambda/2 \) plate with the fast axis at \( 45^\circ \) from the vertical.

(ii) \( \Delta n^c \neq 0 \) and \( \Delta n^l = 0 \) (only circular birefringence is induced). Then \( \Delta \varphi^l = 0 \) and \( N = \Delta \varphi^c \sin \delta \), and \( \hat{T} \) becomes
\[
\hat{T} = \begin{bmatrix}
\cos(\Delta \varphi^c \sin \delta) & \sin(\Delta \varphi^c \sin \delta) \\
-\sin(\Delta \varphi^c \sin \delta) & \cos(\Delta \varphi^c \sin \delta)
\end{bmatrix}.
\] (11)

It can be seen that there are again many orders of diffraction, and the corresponding intensities do not depend on the polarization. When the incident light is linearly polarized, the waves diffracted in the \( \pm 1 \) orders have linear polarizations rotated to \( 90^\circ \) with respect to the initial one.

(iii) \( \Delta n^c = \Delta n^l \neq 0 \). Then \( \Delta \varphi^l = \Delta \varphi^c = \Delta \varphi \) and \( N = \Delta \varphi \), and \( \hat{T} \) turns out to be
\[
\hat{T} = \begin{bmatrix}
\cos \Delta \varphi + i \sin \Delta \varphi \cos \delta & \sin \Delta \varphi \sin \delta \\
-\sin \Delta \varphi \sin \delta & \cos \Delta \varphi - i \sin \Delta \varphi \cos \delta
\end{bmatrix}.
\] (12)

It is seen that there are only \( \pm 1 \) orders of diffraction. If the incident light is linearly polarized and its polarization azimuth is \( \alpha \), the intensity \( I_{\pm 1} \) will depend on \( \alpha \) as follows:
\[
I_{\pm 1} = \frac{1}{2} I_0 \sin^2 \Delta \varphi (1 \pm 2 \alpha),
\] (13)

where \( I_0 \) is the incident intensity and \( \alpha \) is measured in the coordinate system of the matrix of Eq. (12). That is, \( I = I_0 \sin^2 \Delta \varphi \) (diffraction efficiency as much as 100%) for the polarization corresponding to one of the recording waves, and \( I = 0 \) for the orthogonal polarization. Furthermore, whatever the incident light polarization is, one of the diffracted waves has vertical polarization and the other has horizontal polarization.

In the general case \( \Delta n^c \neq \Delta n^l \neq 0 \) the polarization characteristics are not as in cases (i) and (ii) nor as in case (iii). The intensities of the diffracted waves depend on the polarization but do not fall to zero. If we assume small photoanisotropic changes \( N \ll 1 \), a linear approximation can be done; that is, \( \cos N = 1 \) and \( \sin N/N = 1 \), and we have
\[
\hat{T} = \begin{bmatrix}
1 + i \Delta \varphi^l \cos \delta & \Delta \varphi^c \sin \delta \\
-\Delta \varphi^c \sin \delta & 1 - i \Delta \varphi^l \cos \delta
\end{bmatrix}.
\] (14)

For the Jones vector of the waves diffracted in the \( \pm 1 \) orders we obtain
\[
E_{\pm 1} = \sqrt{I_0} \begin{bmatrix}
\frac{\Delta \varphi^l}{2} \cos \alpha \pm \frac{\Delta \varphi^c}{2} \sin \alpha \\
\frac{\Delta \varphi^c}{2} \cos \alpha \mp \frac{\Delta \varphi^l}{2} \sin \alpha
\end{bmatrix}.
\] (15)

The corresponding intensities are
\[
I_{\pm 1} = \frac{1}{2} I_0 (\Delta \varphi^l + \Delta \varphi^c)^2 - 2 \Delta \varphi^l \Delta \varphi^c \sin 2\alpha; \quad (16)
\]

that is, \( I \) is maximum when the incident light polarization coincides with the polarization of one of the recording waves \( \alpha = \pm 45^\circ \) and minimum for the orthogonal polarization. Figure 2 shows the dependences \( \eta_{\pm 1}(\alpha) = I_{\pm 1}(\alpha)/I_0 \) for \( \Delta \varphi^l = 0.02 \) and different values of \( \Delta \varphi^c \). From Eq. (15) it is also seen that, if the polarization azimuth of the incident wave is \( \alpha_{\text{in}} = 45^\circ \), then \( \alpha_{\pm 1} = -45^\circ \) and vice versa. If \( \alpha_{\text{in}} = -45^\circ \), then \( \alpha_{\pm 1} = 45^\circ \); that is, the diffracted wave’s polarization is orthogonal to that of the incident and the directly transmitted waves. For larger values of \( \Delta \varphi^c \) and \( \Delta \varphi^l \), more than one term of the series \( \cos N \) and \( \sin N/N \) can be taken into account. The next approximation is \( \cos N = 1 - N^2/2 \) and \( \sin N/N = 1 - N^2/6 \). It can be shown that these new terms do not change the type of the polarization characteristics [Eq. (15)] for the \( \pm 1 \) order of diffraction but influence only the ratio \( I_{\text{max}}/I_{\text{min}} \).

3. Experiment

Polarization holographic gratings with two waves that have orthogonal linear polarizations, vertical and horizontal, were recorded on films made of

![Fig. 2. Theoretical dependence of the diffraction efficiency \( \eta \) on the polarization azimuth of the reconstructing wave for \( \Delta \varphi^l = 0.02 \) and different values of \( \Delta \varphi^c \): 0 (curve 1), 0.02 (curve 2), and 0.005 (curve 3).](image-url)
liquid-crystalline polyester, prepared as described below.\(^5\) The polyester, P8a12, was synthesized by transesterification in the melt of mesogenic 2-(4-4-

\[\begin{align*}
\text{cyano-phenylazo-phenoxo-octyl-1,3-propanediol and diphenyl tetradecanedioate under vacuum at elevated temperature, as recently described.}^{15}
\end{align*}\]

P8a12 was recovered after cooling as a benzene solution, precipitated into methanol, filtered, and finally dried at room temperature under vacuum. Solution \(^{13}\)C NMR spectroscopic analysis indicated the polyester main chains to be linear with the detectable structural features expected from the precursors. The intrinsic viscosity of P8a12 at 30 °C in tetrahydrofuran was measured to be 0.38 dL/g. Size-exclusion chromatographic analysis performed also in tetrahydrofuran on polystyrene gel columns with differential refractometric detection and narrow molecular mass polystyrene calibration standards disclosed the polyester molecular mass to be Gaussian in shape with number and weight average molecular masses of 35,000 and 63,000 g mol, respectively. The absolute weight average molecular mass was determined to be 47,000 g mol by low-angle laser light scattering. Both the mesogenic diol and the corresponding polyester have the characteristic transition with the maximum at 365 nm and an \(\varepsilon_{\text{max}}\) of approximately 20,000 L cm mol (in tetrahydrofuran). We obtained films of the liquid-crystalline polyester by dissolving 2 mg of P8a12 in 100 µL of chloroform and casting the solution on a clean glass substrate. The thickness of the films is estimated to be \(\sim 5\) µm. We established that illumination with linearly (circularly) polarized light induces linear (circular) anisotropy in these films.

4. Results and Discussion

The gratings were recorded at 488 nm [Ar\(^+\) laser], the recording light intensity was 60 mW cm\(^{-2}\), and the exposure time was 20 min. The reconstruction was done with a He–Ne laser beam, at the Bragg angle. Its wavelength is outside the absorption band of the polyester, and it does not influence the recording. Its polarization direction was rotated with a λ/2 plate. We measured the diffraction efficiency in the +1 order, \(\eta_{\text{+1}} = I_{\text{+1}}/I_0\), where \(I_0\) is the incident intensity, and its dependence on the incident light polarization azimuth \(\alpha\) during recording and after the Ar\(^+\) laser was switched off. Figure 3 shows the experimental curves \(\eta_{\text{+1}}(\alpha)\) measured at \(t_1\), during the last minute of recording, \(t_2\) 60 min after recording, and \(t_3\) 24 h after recording. The polarization azimuth is measured in the same coordinate system, inclined at 45°. It is seen that there is a very strong polarization dependence: \(\eta_{\text{+1}}\) is maximum for \(\alpha = -45^\circ\) [horizontal polarization, coinciding with the polarization of the corresponding Ar\(^+\) beam] and minimum for \(\alpha = 45^\circ\).

From these maximum and minimum values of \(\eta_{\text{+1}}\) we determined [using Eq. (16)] the values of \(\Delta \varphi^L\) and \(\Delta \varphi^C\) at \(t_1, t_2,\) and \(t_3\) (see Table 1). It is seen that, after a slight decrease during the first minutes after recording, \(\Delta \varphi^C\) and \(\Delta \varphi^L\) [that is, \(\Delta n^C\) and \(\Delta n^L\)] increase considerably during the following 24 h. The growth of \(\Delta n^L\) seems to be greater; the ratio \(\Delta \varphi^L/\Delta \varphi^C\) changes from 3 to 3.5.

In order to register the evolution of \(\Delta \varphi^L\) and \(\Delta \varphi^C\), during recording and after it, we set the He–Ne beam polarization at 45° and split the +1-order diffracted beam by means of a Wollaston prism. The polarization of the beams after the Wollaston prism are vertical and horizontal; that is, they correspond to the minimum and the maximum values of the curves \(\eta(\alpha)\) in Fig. 3. Then, the intensities of these beams are \(I_\text{h} = k\eta_{\text{max}}I_0/2\) and \(I_\text{v} = k\eta_{\text{min}}I_0/2\), with \(k\) depending from the losses in the Wollaston prism. Figures 4(a) and 4(b) show the experimental curves \(\eta_{\text{max}}(t)\) and \(\eta_{\text{min}}(t)\) measured in real time for two different recording intensities, 60 mW cm\(^{-2}\) and 8 mW cm\(^{-2}\). From the values \(\eta_{\text{max}}(t)\) and \(\eta_{\text{min}}(t)\) we can obtain, using Eq. (16), the curves \(\Delta \varphi^L(t)\) and \(\Delta \varphi^C(t)\). The results are shown in Figs. 5(a) and 5(b). It is seen that the kinetic curves for \(\Delta \varphi^L(t)\) and \(\Delta \varphi^C(t)\) are different. Furthermore, the ratio \(\Delta \varphi^L(t)/\Delta \varphi^C(t)\) depends on the writing intensity. The circular birefringence is better pronounced at higher intensity. The maximum values of the linear and the circular birefringence obtained from these experiments (with the film thickness taken to be 5 µm) are 2.10 \(^{-2}\) and 4.10 \(^{-3}\), respectively.

The azobenzene polyesters are, to our knowledge, the only material exhibiting significant photo-induced

| Table 1. Values of the Photoinduced Anisotropic Phase Difference Caused by Linear \(\Delta \varphi^L\) and Circular \(\Delta \varphi^C\) Birefringence |
|---------------------------------|-------|-------|-------|
| Anisotropic Phase Difference (rad) | \(t_1\) = 0 | \(t_2\) = 1 | \(t_3\) = 24 |
| \(\Delta \varphi^L\) | 0.35 | 0.32 | 0.53 |
| \(\Delta \varphi^C\) | 0.11 | 0.09 | 0.15 |

Fig. 3. Experimental dependence of the diffraction efficiency \(\eta\) on the polarization azimuth \(\alpha\) of a He–Ne reconstructing beam; the recording intensity is 60 mW cm\(^{-2}\) and \(\lambda = 488\) nm: (curve 1) after 20 min of recording, (curve 2) 1 h after the recording, (curve 3) 24 h after the recording. The experimental values are marked with the signs. The solid curves are calculated following Eq. (16); the data for \(\eta_{\text{max}}\) and \(\eta_{\text{min}}\) were taken from Table 1.
circular birefringence. The origin of this circular anisotropy is not clear to us at the moment. It certainly needs more extensive investigations. Photo-induced anisotropy in materials is usually investigated by polarimetry. However, using polarimetric methods, one can make real-time measurement of the induced linear or circular anisotropy separately using linearly or circularly polarized exiting light. Polarization holography makes it possible to measure the evolution of both types of birefringence induced simultaneously. Thus we think that this method can be useful for the study of the photoprocesses in materials sensitive to polarization.

5. Conclusion
We have made a theoretical analysis of the diffraction at thin phase polarization holographic gratings recorded with two waves with orthogonal linear polarizations in materials in which both linear and circular birefringence are induced on illumination. The theory predicts unusual polarization characteristics; the intensities in the ±1 orders of diffraction and their ratio depend on the reconstructing light polarization. We have observed this peculiarity by recording polarization gratings in films of a sidechain liquid-crystalline polyester. As the maximum and the minimum of the diffracted waves intensities are unambiguously related to the values of photoinduced linear ($\Delta n_{\text{lin}}$) and circular ($\Delta n_{\text{cir}}$) birefringence, we have shown that polarization holography can be used for real-time simultaneous investigation of $\Delta n_{\text{lin}}$ and $\Delta n_{\text{cir}}$.

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