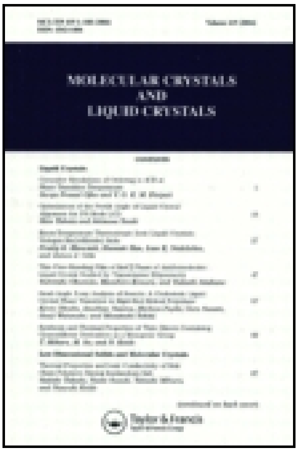

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Propagation of Polarized Light Through Azobenzene Polyester Films

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Propagation of Polarized Light Through Azobenzene Polyester Films

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When elliptically polarized light of appropriate wavelength corresponding to *trans-cis-trans* isomerisation process is incident on thin films of azobenzene polyesters, a helical structure is induced. We investigate the propagation of the exciting light beam (self-induced) as well as a probe light beam outside the absorption band through the polyester films. Investigations are carried out in one amorphous and one liquid crystalline polyester. We show that amorphous polyester after irradiation behaves like classical helical material.

Keywords: azobenzene; polymers; chirality; anisotropy; polarization

INTRODUCTION

There is a considerable academic and commercial interest in azobenzene polymers due to their possible application in the area of high-density optical storage of information. When azobenzene containing films are irradiated with linearly polarized light, a large linear birefringence is found to result [1-4]. This birefringence was found to be stable even after the exciting light was switched off, forming the basis for optical storage [5-7]. In addition, several new phenomena have been discovered in azobenzene polymers. A strong surface relief profile has been found to result when the films are irradiated with polarized light [8,9]. Surface relief gratings have also been found to arise when two orthogonally polarized beams are used to irradiate the film [10]. A novel biphotonic process was found to occur in some azobenzene polymers requiring photons of different wavelength [11-14]. We reported the appearance of circular anisotropy in liquid crystalline azo-polyesters on irradiation with circularly polarized light, even though the material was a racemic mixture [15,16]. We have also shown that a rotation of the azimuth of the incident elliptically polarized light arises when both liquid crystalline and amorphous azo-polymers are irradiated [17,18]. Iftime et al. [19] have reported the formation of chirality in azobenzene containing methacrylate systems.

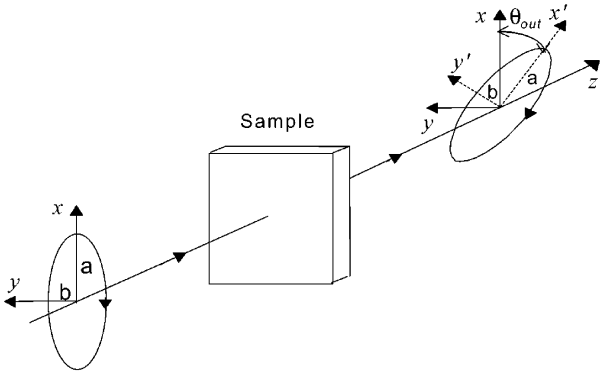


FIGURE 1. Propagation of polarized light through an anisotropic sample.

Let an elliptically polarized light of appropriate wavelength and with semiaxes ↦ and ↕ be incident on the film. (Fig. 1). Let the major axis of the ellipse be along the *X*-axis with the azimuth $\theta_{\text{in}} = 0$. This incident light orients the azobenzene chromophores through repeated *trans-cis-trans* isomerization perpendicular to the incident polarization. In this case, more molecules are oriented perpendicular to the major axis ↦ of the incident light and results in the formation of an optical axis. Once an optical axis is generated, further propagation of light is influenced by this process, rotating the azimuth of the light. The azimuth of the new polarization ellipse is rotated by an angle $\theta_{\Delta z}$

$$\theta_{\Delta z} = \frac{1}{2}\arctan\left[\frac{2ab}{a^2-b^2}\sin(2\delta\Delta z)\right] \tag{1}$$

where δ is the phase difference given by $\pi\Delta n / \lambda$, Δn being the birefringence, and λ the wavelength of the incident light; Δz is the layer thickness. In other words, the new polarization ellipse is rotated to an angle $\theta_{\Delta z}$ with respect to the optical axis at the front surface. Thus propagating through the sample, the incident light induces an optical axis that gradually rotates along the thickness of the film. This results in the formation of a helical structure, similar to that of a cholesteric material. (We denote the rotation of the exciting beam as θ, and the rotation of a probe He-Ne beam as ψ). We have examined the passage of polarized light through a series of azobenzene copolyesters of type **E1aP(x)12(1–x),** where x varies from 0 to 1. When $x = 0$, the polyester E1a12 is mesogenic, and for $x = 1$, the polyester **E1aP** is amorphous. There is a gradual transition from the liquid crystalline to the amorphous state as x increases from 0 to 1. In this article, we show that light propagation displays different systematics in the amorphous polyester, **E1aP**, and the liquid crystalline polyester, **E1a12**.

THEORY

Azzam and Bashara [20,21] have discussed in great detail the evolution of the ellipse of polarization as it propagates through an anisotropic medium. The differential propagation matrix N as introduced by Jones is defined as

$$N = \lim_{\Delta z \to 0} \frac{M(z,\Delta z) - I}{\Delta z} \tag{2}$$

where $M(z, \Delta z)$ is the Jones matrix of a thin slice of the anisotropic medium with a thickness of Δz. The differential equation for the Jones vector ε is given by

$$\frac{d\varepsilon}{dz} = N\varepsilon \tag{3}$$

Azzam and Bashara [21] show that the ellipse of polarization of the light beam can be determined by a single complex variable

$$\chi = \varepsilon_2 / \varepsilon_1 \tag{4}$$

where ε_1 and ε_2 are the projections of the Jones vector ε along any pair of basis polarization states. The geometry of the problem dictates that circularly polarized basis states be used. In this representation, the incident light is given by

$$\chi_0 = \tan(\varepsilon + \pi / 4)\exp(-i2\theta) \tag{5}$$

where the ellipticity of the light $e = \tan(\varepsilon) = b / a$ and the azimuth of the light is given by θ. Azzam and Bashara [20] derive the following master equation:

$$\frac{d\chi}{dz} = -n_{12}\chi^2 + (n_{22} - n_{11})\chi + n_{21} \tag{6}$$

where n_{ij} are the elements of $\boldsymbol{N}$.

For the case of an inhomogeneous, isotropic medium such as a cholesteric system, the rotation of the azimuth, θ is given by αz where $\alpha = 2\pi / P$, P being the pitch of the helix, z is the thickness of the layer and

$$N = \delta_0 \begin{bmatrix} 0 & i\exp(2\alpha z) \\ i\exp(-2\alpha z) & 0 \end{bmatrix} \tag{7}$$

Substituting Eq. (7) in Eq. (6), one gets

$$\frac{d\chi}{dz} = (-i\delta_0 \exp(i2\alpha z))\chi^2 + i\delta_0 \exp(-i2\alpha z) \tag{8}$$

A particular solution of Eq. (8) is of the form

$$\chi = K\exp(-i2\alpha z) \tag{9}$$

In the case of the photoinduced chiral structure, it has been shown [17] that

$$\alpha = \frac{2e_0\delta_0}{(1 - e_0^2)} \tag{10}$$

The ellipticity of the light is the same as that of the incident light inducing the chiral structure, however the azimuth is rotated. We term this self-induced rotation.

In the general case, when the ellipticity and/or the azimuth of the exciting beam is different from that of a probe beam, the solution has the form

$$\chi = u(z)\exp(-2i\alpha z) \tag{11}$$

However $u(z)$ is not a constant along the direction of propagation, and there is a change in both the ellipticity and azimuth of the probe beam. The solution in this case is given by

$$\chi(z,\chi_0)=\frac{(\beta+i\alpha\tan(\beta z))\chi_0+i\delta\tan(\beta z)}{i\delta\tan(\beta z)\chi_0+\beta-i\alpha\tan(\beta z)}\exp(-i2\alpha z) \tag{12}$$

where

$$\beta=\delta\left[\left(\frac{\alpha}{\delta}\right)^2+1\right]^{1/2};\delta=\delta_0\lambda_0/\lambda \tag{13}$$

λ and λ_0, being the wavelength of the probe and exciting beam, respectively.

One can calculate the ellipticity e_{out} and the azimuth ψ_{out} of the output polarization ellipse using

$$e=\frac{|\chi|-1}{|\chi|+1} \tag{14}$$

and

$$\psi=-\frac{1}{2}\arg(\chi) \tag{15}$$

EXPERIMENTAL

The structure of the amorphous polyester, **E1aP**, and its mesogenic counterpart, **E1a12**, are shown in Fig. 2. The main structural difference between **E1aP** and **E1a12** is borne in their polyester backbone. **E1aP**

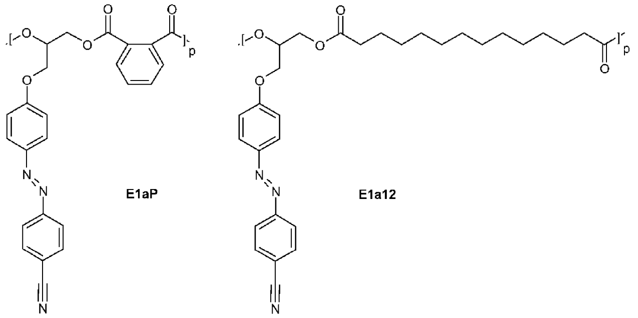
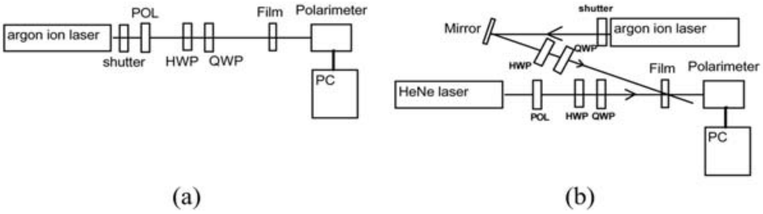


FIGURE 2. Chemical structure of **E1aP** and **E1a12**.

comprises aromatic 1,2-phenylene units, which create a stiff main chain with no domain structure. Thus the polyester is amorphous. **E1a12** possesses a non-aromatic flexible backbone primarily composed of methylene units. Both polyesters contain cyanoazobenzene attached via a single methyleneoxy (-CH_2O-) unit, as side chain to the main polyester backbone. Azobenzene polyesters, **E1aP**, **E1a12** and **E1aP(*x*)12(1–*x*)**, were readily synthesized via base-catalysed (K_2CO_3), *in vacuo*, melt-transesterification of 3-[4-((4-cyanophenyl)azo)-phenoxy]-1,2-propanediol with the appropriate diphenyl diester. For example, melt-transesterification of the diol with a stoichiometric amount of diphenyl phthalate afforded **E1aP** whilst **E1a12** was generated in the presence of diphenyl tetradecanedioate [22]. Classical Williamson's etherification between 3-bromo-1,2-propanediol and 4-[4-(cyanophenyl)azo]-phenol, in the presence of anhydrous potassium carbonate and boiling acetone, furnished the desired 3-[4-((4-cyanophenyl)azo)-phenoxy]-1,2-propanediol. A differential scanning calorimetry (DSC) analysis of **E1aP** discloses a glass transition at 107 °C. When examined in a polarization microscope, a film of the mesogenic polyester, **E1a12**, displays randomly distributed domains with sizes between 0.5 and 2 μm. Unfortunately, the liquid crystalline phase is not well developed and difficult to identify through polarization microscopic examination. However, differential scanning calorimetry (DSC) measurements indicate that the material is in either a nematic or a poorly ordered smectic phase [4].



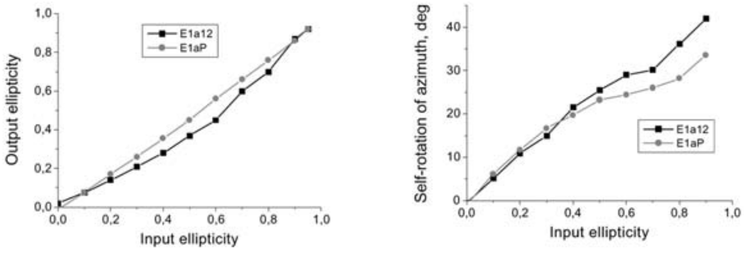
(a) (b)

FIGURE 3. (a) Experimental set-up for measuring the self-induced rotation. In the figure, POL is a polarizer, HWP, a half-wave plate, QWP, a quarter-wave plate and PC is a personal computer. (b) The film is irradiated by an argon laser, whose polarization state can be controlled by quarter- and half-wave plates and probed by a He-Ne laser.

The polyesters were spin coated (25 mg in 150 μl trichloroethanol) on clean glass substrates. Film thickness was measured with Filmetrics thickness measuring equipment and predominantly found to lie between 1 and 2 μm. The experimental set-up for measuring self-induced rotation is shown in Fig. 3a; for measurements on films excited with an argon laser and probed with a He-Ne laser, the set-up shown in Fig. 3b was utilized. An argon ion laser at 488 nm was used as the exciting light; a half-wave plate and a quarter-wave plate were used for setting the ellipticity and azimuth of the incident light. For the probe beam, a He-Ne laser at 633 nm was used. The ellipticity and azimuth of the probe beam was controlled independently through a set of half- and quarter-wave plates. After passing through the film, the polarization state of the emergent beam was measured using a ThorLabs polarimeter. For static measurements, the films were illuminated till the process reached saturation values. For dynamic experiments, the Stokes' parameters were measured as a function of time. An argon laser power of 50 mW was used in these measurements, corresponding to an intensity of approximately 700 mW/cm^2. The absorbance of **E1aP** at 488 nm is measured to be 0.02, and at 633 nm is 0.005. The absorbance of **E1a12** at 488 nm is 0.2, and at 633 nm is 0.09.

DISCUSSION

a) Self-induced rotation:



(a) (b)

FIGURE 4. (a) Dependence of the output ellipticity on the input ellipticity for self-induced polarization changes. (b) Dependence of the induced rotation angle on the input light ellipticity for self-induced effects.

Figure 4a shows the output ellipticity as a function of the input ellipticity after the argon ion laser beam is allowed to pass through the film. It can be seen that the output ellipticity is the same as the input ellipticity for the case of the amorphous film, **E1aP**, whereas for the liquid crystalline polyester, **E1a12**, there is a deviation from the linear response. A straight line fit of the output ellipticity in **E1aP** as a function of input ellipticity gives a correlation coefficient of $R = 0.9996$, while a fit to the **E1a12** data gives a correlation coefficient of $R = 0.9868$. Fig. 4b shows the rotation of the azimuth of the elliptically polarized light as a function of the input ellipticity for **E1aP** and **E1a12**. The phase difference δ_0 for the photoinduced helical structures can be calculated from Eq. (10) and is shown in Fig. 5.

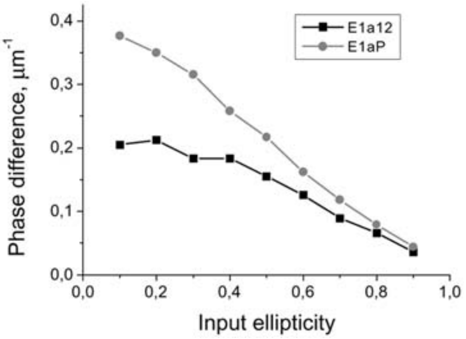
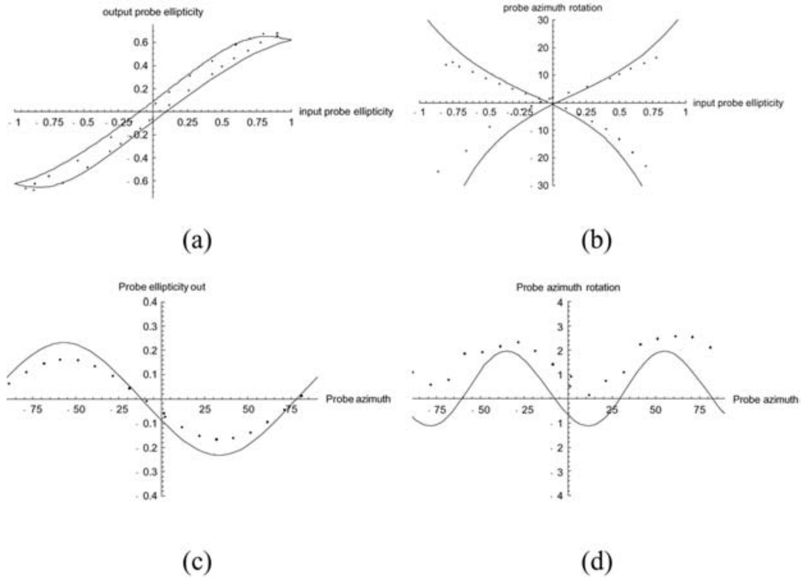


FIGURE 5. Phase difference δ_0 calculated as a function of the input ellipticity from Fig. 4b.

b) Probe-beam measurements:

Two types of measurements were performed: 1) input probe beams with azimuths $\psi_{in} = 0$ and $\psi_{in} = 90°$ and different ellipticities between −1 and +1; and 2) a linearly polarized probe beam with different polarization azimuths, $\psi_{in.}$ For the probe beam measurements, it is necessary to use Eq. (12) and $\chi_{0,}$ in this case, represents the incident light given by Eq. (5). α can be calculated using Eq. (10), and β, δ from Eq. (13). In all cases, the ellipticity of the exciting argon laser beam e_0 is equal to –0.5 and its azimuth is 90° (vertical). Fig. 6a shows the calculated and experimental output ellipticity as a function of the input ellipticity. The output ellipticity was calculated using Eq. (14). The value of $\delta_{0,}$ calculated from Eq. (10) was 0.217 μm^{-1} for a film thickness of 1.4 μm. It is seen that the agreement between the experimental and calculated values is very good. We also examined the rotation of the azimuth of the probe beam as a function of the input ellipticity of the probe beam using Eq. (15) (Fig. 6b). The experimental points closely follow the calculated theoretical curve. We also have measured the output probe ellipticity as a function of the input probe azimuth and the rotation of the probe azimuth for different input probe azimuth (Figs. 6c and 6d). In all cases, the experimental and theoretical values show the same trend. Thus in all these cases, the amorphous polyester, **E1aP**, behaves like a classical helical medium after irradiation with elliptically polarized light.



(a) (b)

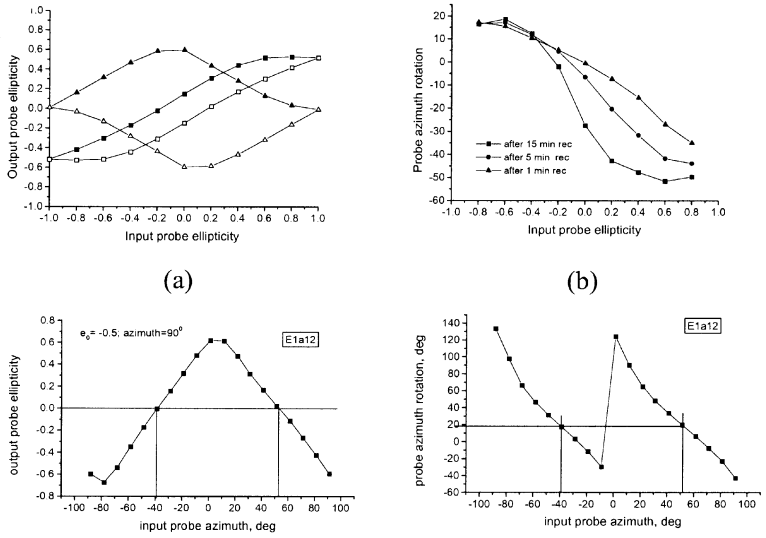
(c) (d)

FIGURE 6. (a) Experimental and theoretical dependence of the output ellipticity of the probe beam on its input ellipticity for input azimuths 0° and 90° obtained for $e_0 = -0.5$ for the amorphous polyester **E1aP**. The theoretical curves are calculated with $\delta_0 = 0.217\ \mu\text{m}^{-1}$. (b) Experimental and theoretical dependence of the output azimuth of the probe beam on its input ellipticity. (c) Experimental and theoretical dependence of e_{out} on the azimuth of a linearly polarized probe beam. (d) Experimental and theoretical dependence of the rotation of the polarization azimuth of the probe beam.

Interestingly, a completely different picture is exhibited for the liquid crystalline polyester, **E1a12**. Fig. 7a shows the output ellipticity of the probe beam as a function of its input ellipticity, when the input ellipticity of the exciting argon beam is held constant at –0.5 and the azimuth at 90°. For low exposure time, the system behaves in much the same way as the amorphous polyester, **E1aP**. However, for increased exposure times, a large output ellipticity results even when the input ellipticity is zero. The azimuthal rotation (Fig. 7b) also shows an interesting behaviour, as a function of the input ellipticity. In the case of negative ellipticities, the maximum rotation is achieved with short exposures. However, for positive ellipticities, there is a considerable temporal development. We believe that this behaviour may be related to the presence of small mesogenic domains in the film. An examination of the film through a polarization microscope reveals domains with sizes 0.5 – 2 μm with random orientations. The experimental results suggest that the photoinduced changes are different from those detected in the amorphous films. The directors of the birefringent domains are randomly oriented before irradiation. During the illumination, the intrinsic birefringence of each domain changes the polarization of the incident light and new directors of the domains are created. The optical axes in the input plane of these individual birefringent domains have different orientation and the changes induced in the directors are also randomly oriented. For short exposure times, we believe that only those molecules that are not bound in a domain are influenced by the incident light, behaving like an amorphous sample. However, longer exposure times allow a reorientation of entire domains to take place, and results in a loss and reformation of domain-like structures. In this case, the induced anisotropy is also higher. Fig. 7c shows the output ellipticity as a function of the input probe azimuth. The input beam in this case is linearly polarized, i.e., possesses zero ellipticity. The output beam has zero ellipticity for incident azimuths of –40° and +53°. For these two angles, the film behaves like a half-wave plate. Fig. 7d shows the azimuthal rotation as a function of input probe azimuth and reveals a rotation of approximately 20°. By increasing the thickness of the film, we believe that a rotation of 90° can be easily achieved which can form the basis for a novel light controlled optical switch.

CONCLUSION

We have examined the propagation of polarized light through thin films of a family of homopolysters with azobenzene side chains. We find that a chiral structure can be induced in all the cases when irradiated with elliptically polarized light. The propagation of polarized light in



(a) (b)

(c) (d)

FIGURE 7. (a) Experimental dependence of the output ellipticity of the probe beam on the input ellipticity obtained for $e_0 = -0.5$ for a liquid crystalline polyester **E1a12**. The filled black squares are the values after irradiation of the film for 5 min. The filled black triangles are the values after irradiation for 15 min. (b) Temporal evolution of the rotation of the azimuth of the probe beam as a function of input ellipticity in a film of **E1a12**. The filled triangles are obtained after 1 min of irradiation, filled circles after 5 min of irradiation and filled squares after 15 min of irradiation. (c) Dependence of the output ellipticity on the input azimuth of the probe beam in a film of **E1a12**. The straight line represents zero output ellipticity and thus represents a linearly polarized output beam. (d) Dependence of the rotation of azimuth on the input azimuth. The horizontal straight line corresponds to the rotation of plane polarized light with azimuths of –40° and +53° derived from Fig. 8c

amorphous structures follows the classical theory proposed by Azzam and Bashara, whereas in liquid crystal structures, a behaviour that is strongly dependent on the irradiation time is detected. A very large rotation of a linearly polarized probe beam at 633 nm is obtained when a thin film of the azobenzene polyester is irradiated with elliptically polarized argon laser light at 488 nm. We believe that this process can also be observed in other photoanisotropic materials, and can form the basis of a novel optical switch.

Acknowledgments

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