

Light-induced optical activity in optically ordered amorphous side-chain azobenzene containing polymer

M. IVANOV, I. NAYDENOVA, T. TODOROV, L. NIKOLOVA, T. PETROVA, N. TOMOVA and V. DRAGOSTINOVA Central Laboratory of Optical Storage and Processing of Information,

Bulgarian Academy of Sciences, Sofia 1113, PO Box 95, Bulgaria

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Abstract. We report the appearance of circular birefringence (optical activity) in amorphous side-chain azobenzene polymer films on illumination with circularly polarized light. The effect is observed only if an optical axis is previously created in the film with the help of linearly polarized light. The photoinduced optical activity is believed to be due to changes in the polymer structure initiated by a circular momentum transfer from the circularly polarized light to the azobenzene chromophores.

1. Introduction

Azobenzene-containing polymers have been intensively investigated as optical storage media [1-6]. Usually the interest in these materials is related to the large linear birefringence which can be induced in them through photoreorientation of the azobenzene side chains in directions perpendicular to the light polarization direction and finally to photoinduced ordering of the whole polymer.

Recently, we reported [7, 8] the appearance of significant photoinduced circular birefringence (optical activity) in azo-polymers on illumination with circularly polarized light. The effect is observed in liquid-crystalline side-chain cyanoazobenzene polyesters without chiral groups. We believe that it is initiated by a circular momentum transfer from the circularly polarized light to the azobenzene chromophores. Evidence for this phenomenon was first reported by Santamato *et al.* [9]. In low molecular nematic liquid crystals it gives rise to a collective rotation of the molecules which causes a continuous rotation of the polarization azimuth of light passing through the sample. In azobenzene-containing polymers the mesogenic azobenzene side chains are attached to the polymer backbones and cannot accomplish free precession. The circular momentum transfer leads to a torque and to changes in the whole polymer structure. It gives rise to chirality and to the observed photoinduced optical activity. Until now this phenomenon has been observed only in liquid crystalline azobenzene polymers. We think that it is related to the presence of ordering in the polymer films before illumination.

In this paper we present some experimental results that support this idea. We show that optical activity can also be induced in amorphous azobenzene-containing polymers if they are previously ordered by illumination with linearly polarized light.

2. Experimental

2.1. The samples

The experiments are done with films of 4-(4-hydroxyphenylazo)benzonitrile/ methylmethacrylate copolymer. The structure of this copolymer is shown in figure 1. Its synthesis is described in [10]. The concentration of the chromophore is 23 mol.% The films are spin coated and are $3 \mu m$ thick.

2.2. Experimental set-up

The experimental set-up is shown in figure 2. We used an Ar-laser excitation beam ($\lambda = 488 \text{ nm}$, $I = 10 \text{ mW cm}^{-2}$) with different polarization states: linear,





Figure 2. Scheme of the optical set-up. Ar is the exciting Ar beam; P—linear polarizers; $\lambda/2$ and $\lambda/4$ —wave plates; He–Ne is the probe beam; S—sample; PP— the 4-detector Stokesmeter. The angle between beams 1 and 2 is small and they are both normal to the film plane.

with polarization directions at 0° , 45° and 90° with respect to the vertical and left and right circular. A He–Ne beam was used as a probe beam; it was linearly polarized at 45° .

The polarization of the probe beam passing through the sample S was measured by a photopolarimeter (PP). This device measures simultaneously the four Stokes parameters of light S_j (j = 0, 1, 2, 3) in real time [11, 12] and makes it possible to record the time evolution of the light polarization azimuth θ and ellipticity *e* during the illumination and after it. θ and *e* are calculated from the measured values of S_j using the formulae:

$$\theta = \frac{1}{2}\arctan\left(\frac{S_2}{S_1}\right),\tag{1}$$

 $e = \tan\left[\frac{1}{2} \arcsin\left(\frac{S_3}{S_0}\right)\right].$ (2)

Additionally, in the cases in which the exciting light was with vertical or horizontal polarization we were able to determine the induced linear birefringence Δn using:

$$\Delta n_{\rm lin} = \frac{\lambda \delta}{2\pi d}.\tag{3}$$

Here *d* is the film thickness, $\lambda = 633$ nm is the wavelength of the probe beam and δ is the phase difference between the vertical and horizontal components of the measuring beam passing through the sample and is calculated from the Stokes parameters S_2 and S_3 :

$$\delta = \arctan \frac{S_3}{S_2}.\tag{4}$$

2.3. Experimental results

In the experiment presented in figure 3 we first illuminated the sample with circularly polarized light. No changes in the azimuth (shown in the figure) or the ellipticity of the probe beam were observed. After 60 s the exciting light polarization was changed to linear, at 45° . It was previously established that linearly polarized light induces large linear birefringence in these films. However, since the He–Ne beam polarization direction coincides with the induced optical axis, the probe beam remains linearly polarized at 45° . Then the Ar light polarization was changed to circular again. This time a considerable rotation of the polarization azimuth is observed during the first 5 s, after which the effect is slowly erased.

In the next two experiments the sample was first illuminated with vertically or horizontally polarized light, then with left circularly polarized light. Between the two types of illuminations the exciting light was switched off, as shown with arrows in figures 4 and 5. In figure 4 (curves 1 and 2) we have plotted the evolution of the anisotropic phase difference δ during the experiments. Figure 5 shows the corresponding curves for the photoinduced changes in the polarization azimuth. As is seen, the linearly polarized light induces considerable birefringence. The sign of $\delta = 2\pi (n_{ver} - n_{hor})d/\lambda$ depends on the direction of the linear polarization. It is positive for horizontal polarization (in this case $n_{ver} > n_{hor}$) and negative for vertical polarization ($n_{ver} < n_{hor}$). This means that the induced birefringence is negative as usually expected for azobenzene materials. The maximum value of Δn



Figure 3. Rotation of the probe beam azimuth θ . The excitation beam is circularly polarized during the first 60 s, then it is linear at 45°, and circular again after another 60 s. The arrows point to the moments when the change of the excitation polarization occurs.



Figure 4. The evolution of the anisotropic phase delay δ induced in the sample during the experiment. The film is first illuminated with horizontally (curve 1) or vertically (curve 2) polarized Ar light, then the excitation is switched off for 20 s, and after that the Ar beam is with left circular polarization.

at 633 nm calculated from this curve for the 3 μ m thick film is ≈ 0.04 . A very small linear dichroism is also induced, which is responsible for the small rotation of the polarization azimuth during this illumination (figure 5). Both linear dichroism and birefringence are considerably stable when the Ar beam is stopped. When the exciting light polarization is switched to left circular, a significant rotation of the azimuth is observed. The sign and the value of this rotation do not depend on the direction of the previously induced optical axis. At the same time the linear birefringence is gradually erased. As the exciting light is circularly polarized the



Figure 5. Rotation of the probe beam azimuth θ . The values of θ are measured during the experiment described in figure 4.

polarization rotation cannot be due to linear dichroism. We conclude therefore that the effect is due to photoinduced circular birefringence (optical activity). The induced optical activity remains stable if the exciting beam is switched off for a few seconds (figure 5), otherwise it is erased (as in figure 3).

In the next two experiments the sample was first exposed to a horizontally polarized Ar beam and then the beam polarization was changed to left or right circular. The evolution of the polarization azimuth of the probe He–Ne beam during these experiments is shown in figure 6. The sign of the polarization rotation is determined by the handness of the exciting beam polarization. Left circularly polarized Ar light induces a left-hand rotation and right circularly polarized light induces a right-hand rotation. The rotation power is $\approx 2^{\circ} \mu m^{-1}$; in both cases it remains stable after switching off the Ar laser. The induced optical activity is reciprocal—if the probe beam is sent back through the sample its initial polarization is recovered.

4. Discussion

As discussed above, the induction of optical activity on illumination with circularly polarized light has been observed until now only in liquid crystalline azobenzene polymers and not in amorphous polymers containing the same chromophores. It suggests the idea that the phenomenon is related to the pre-existence of ordering in the films; this belief is strongly supported by the experimental results presented here. It also indicates that the appearance of optical activity is not directly due to the photoinduced processes with the azobenzenes themselves but rather to changes in the structure of the whole polymer. We believe that these structural changes are the result of a circular momentum transfer from the exciting circularly polarized light to the ordered azobenzenes. As the latter are attached to the polymer chains they can only be rotated through a limited angle. In liquid crystalline polymers each domain has a director; this director is determined by the orientation of the mesogenic azobenzenes. If the circularly polarized light



Figure 6. Evolution of the probe beam azimuth θ . Left and right circularly polarized excitation induces correspondingly left or right optical activity in the preliminary ordered sample.

induces rotation of the directors and the rotation angle depends on the coordinate z—along the light propagation direction—the birefringence axis will be gradually rotated through the sample and this will result in the appearance of chirality. It was similar in the amorphous polymers in which we previously induced an optical axis. It is known that the large photoinduced linear birefringence in amorphous azo-polymers is associated not only with the reorientation of the azobenzenes but also with ordering of the polymer chains. If the circularly polarized light causes rotation of the previously induced axis and this rotation is z dependent, the resulting structure will be chiral and the film will exhibit optical activity. Further illumination with circularly polarized light destroys the birefringence axis and makes the film isotropic; this is why the effect is erased with large exposures (figure 3)

4. Conclusion

In summary, we have shown that circular birefringence can be induced in amorphous polymers as well, if an optical axis is previously created in the polymer films by illumination with linearly polarized light. As the observed optical activity is significant $(2^{\circ}\mu m^{-1})$ and it is stable in the dark, this light induced effect can find interesting applications, for example in polarization holography, polarization optical elements, etc.

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