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Photoinduced circular anisotropy in side-chain azobenzene polyesters

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Abstract

We report for the first time the inducing of large circular anisotropy in previously unoriented films of side-chain azobenzene polyesters on illumination with circularly polarized light at a wavelength of 488 nm. The circular dichroism and optical activity are measured simultaneously in real time at two wavelengths, 488 nm and 633 nm. The photoinduced optical activity has been measured to be $> 10^4$ deg/cm and the circular dichroism has been found to be on the order of 0.3. © 1997 Elsevier Science B.V.

1. Introduction

The photoisomerization of azobenzene derivatives is widely studied in solution [1] and in polymer films [2–5]. It is well known that if the illumination is done with linearly polarized light it can induce a significant linear anisotropy in the sample due to selective trans-cis isomerization and/or reorientation of the dye molecules. Linear birefringence up to $\Delta n_{\text{lin}} = 0.025$ has been measured in several azo dye/polymer systems [2,5]. In 1990 Kakichashvili reported the photoinduction of circular dichroism in films of azo dye doped gelatine [6]. The effect is considerably small and it is supposed that it is related to the gelatine matrix. Liquid crystalline me-

dia for information storage based on light-induced conversions between isotropic and optically active state with circular birefringence up to 3×10^{-4} is described in [7]. We report here a very large photoinduced circular anisotropy – circular dichroism and optical activity – in initially isotropic films of a Liquid crystalline side-chain azobenzene polyester induced on illumination with a circularly polarized Ar laser beam.

2. Experiment

2.1. Preparation of the polyester films

The polyester, P6a12, was synthesised by transesterification in the melt of mesogenic 2-[6-(4-(4-

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cyanophenylazo)phenoxy)-hexyl]-1,3-propanediol and diphenyl tetradecanedioate under vacuum at elevated temperature as recently described [5]. P6a12 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 P6a12 at 30°C in tetrahydrofuran was measured to be 0.33 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 distribution to be Gaussian in shape with number and weight average molecular masses of 17 000 and 43 000 g/mol respectively. Both the mesogenic diol and the corresponding polyester have the characteristic $\pi-\pi^*$ transition with the maximum at 365 nm and an ε_{max} of approx. 20 000 l/cm mol (in tetrahydrofuran). 5 mg of P6a12 was dissolved in 100 μl of chloroform and solution cast onto glass substrates. After drying, a microscope cover slide was glued on using index matched glue, in order to protect the film. The film thickness is estimated to be about 5 μm . It was established that illumination with linearly polarized light at 488 nm induces large linear birefringence in these films [8].

2.2. Polarimetric setup and method of measurement.

The polarimetric setup used to investigate the photoinduced circular anisotropy in the films is shown in Fig. 1. The changes in the optical properties of the sample S are induced by an Ar laser beam (1) with $\lambda = 488$ nm, circularly polarized by a Babinet-Soleil compensator B. The photoinduced changes are measured at two wavelengths: 488 nm and 633 nm, the measuring beams are both linearly polarized at 45° by P₂ and P₃. The intensity I_2 of beam 2 (0.3 mW) is much smaller than that of beam 1 (I_1); the photoshutter C opens it for 100 ms every 2 s, so we suppose that its influence is negligible. After the sample, beam 2 is split by a Wollaston prism W in two beams, with vertical and horizontal polarizations, so that detectors R₆ and R₇ measure the

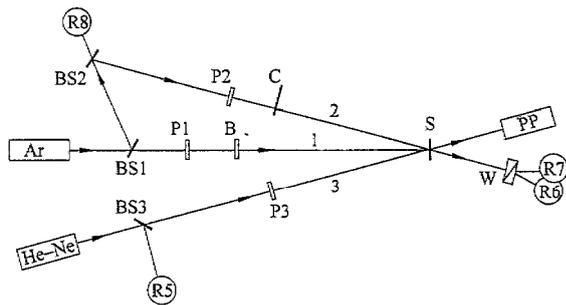


Fig. 1. Experimental setup, Ar, He-Ne: lasers, PP: photopolarimeter, BS1, BS2, BS3: beam splitters, R5 ÷ R8: photosensors, P1 ÷ P3: polarizers, B: Babinet-Soleil compensator, C: shutter, S: sample, W: Wollaston prism

intensities of the corresponding light components. The intensity and the polarization of the He-Ne beam after the sample are measured by a 4-detector photopolarimeter PP, that measures simultaneously the four Stokes parameters of light (S_0 , S_1 , S_2 and S_3) [9]. Detectors R₅ and R₈ are used to compensate for the laser instabilities.

If the circularly polarized Ar beam induces circular anisotropy in the sample, for the Jones matrix describing its transmittance we can write (in circular coordinates)

$$T = \begin{pmatrix} t_l e^{i\varphi_l} & 0 \\ 0 & t_r e^{i\varphi_r} \end{pmatrix} \quad (1)$$

where t_l and t_r are the amplitude transmittances for the left and right components of light and φ_l and φ_r the corresponding phase delays proportional to the refractive indices n_l and n_r . In the general case the linearly polarized measuring beams will become elliptically polarized and will be rotated. In order to determine the circular dichroism and birefringence one has to know all the Stokes parameters of the transmitted light. For our geometry (measuring beams polarized at 45°) we have:

$$\begin{aligned} S_0 &= t_l^2 + t_r^2 & S_1 &= 2t_r t_l \sin(\varphi_l - \varphi_r) \\ S_2 &= 2t_r t_l \cos(\varphi_l - \varphi_r) & S_3 &= t_l^2 - t_r^2 \end{aligned} \quad (2)$$

and from the measured values of S_i we determine the angle of polarization rotation in the sample

$$\alpha = \frac{\varphi_l - \varphi_r}{2} = \frac{1}{2} \arctg\left(\frac{S_1}{S_2}\right) \quad (3)$$

and the transmittance for the left and right circular components:

$$T_l = t_l^2 = \frac{S_0 + S_3}{2}; \quad T_r = t_r^2 = \frac{S_0 - S_3}{2} \quad (4)$$

For $\lambda = 488$ nm from the signals at detectors R_6 and R_7 we can determine only S_0 and S_1 . However, if there is no circular dichroism and the measuring beams retain their linear polarization after the sample, we can write in Eq. (2) $T_l = T_r$ and therefore

$$\alpha = \frac{\varphi_l - \varphi_r}{2} = \frac{1}{2} \arcsin\left(\frac{S_1}{S_0}\right) \quad (5)$$

3. Results and discussion

Illumination with a circularly polarized Ar beam causes an increase of the average optical transmittance $T_{av} = (T_l + T_r)/2$ of the sample for 488 nm as well as for 633 nm (Figs. 2 and 3). At 488 nm this effect is larger when the exciting beam right circularly polarized. It is seen that the circularly polarized Ar beam induces a large optical activity in the film – significant rotation of the polarization azimuth of both the measuring Ar (Fig. 4) and He-Ne (Fig. 5) beams are observed. The optical activity is larger for the blue light. At 488 nm its maximum value is ~ 6 deg/ μm , that results in a circular birefringence

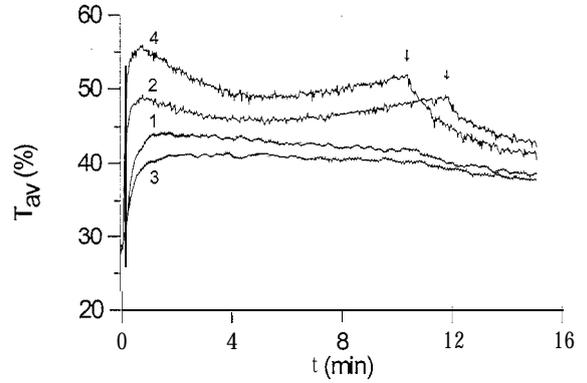


Fig. 3. The same curves as in Fig. 2, measured at 633 nm.

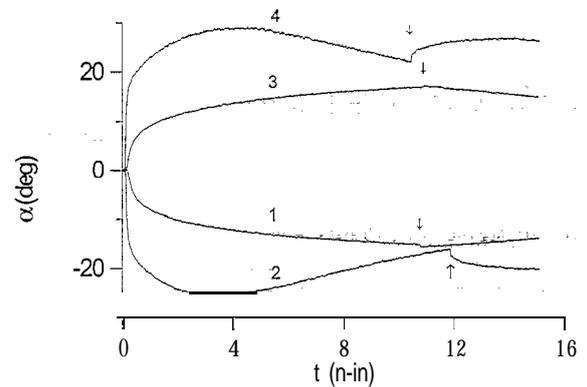


Fig. 4. The rotation of the polarization azimuth at 488 nm induced on illumination with circularly polarized Ar beam 1 and measured with linearly polarized beam. Left circular polarization of beam 1: curve 1 – $I = 1.5$ mW, and curve 2 – $I = 20$ mW. Right circular polarization of beam 1: curve 3 – $I = 1.5$ mW, and curve 4 – $I = 20$ mW.

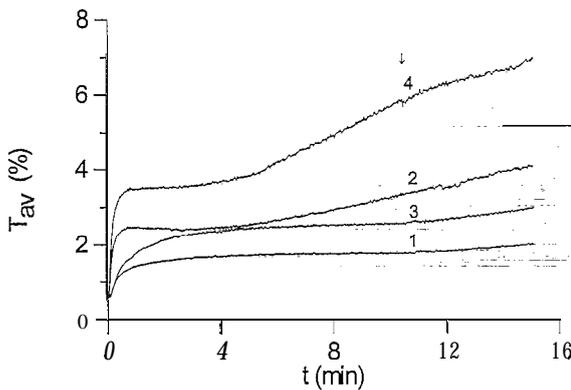


Fig. 2. The changes in the average transmittance T_{av} at 488 nm on illumination with circularly polarized Ar beam. Left circular polarization of beam 1: curve 1 – $I = 1.5$ mW and curve 2 – $I = 20$ mW. Right circular polarization of beam 1: curve 3 – $I = 1.5$ mW and curve 4 – $I = 20$ mW.

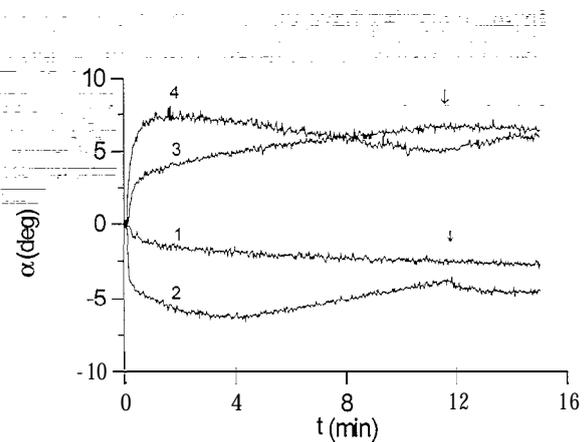


Fig. 5. The same curves as in Fig. 4, measured at 633 nm.

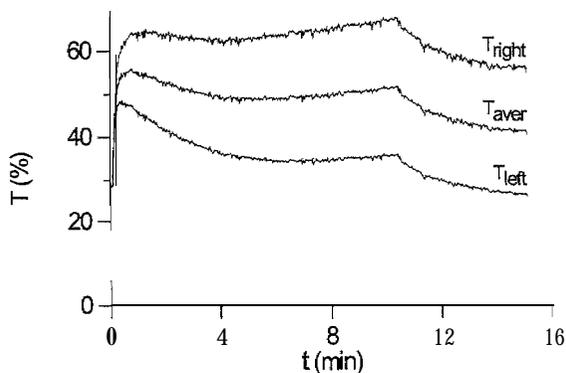


Fig. 6. The changes in the optical transmittances for the left (T_{left}) and right (T_{right}) circularly polarized component of light at 633 nm and the average transmittance $T_{\text{av}} = (T_{\text{left}} + T_{\text{right}})/2$ on excitation with a right circularly polarized Ar laser beam, 20 mW.

$\Delta n_{\text{cir}} \sim 0.01$. The sign of the rotation depends on the type of the circular polarization of the exciting beam (left or right). After the excitation is switched off (marked with arrows) the induced rotation changes slightly during the first minutes and after that remains stable for months. Fig. 6 shows the changes in the optical transmittances at 633 nm for the left T_l and right T_r circularly polarized components of light. It is seen that a large circular anisotropy in the transmittances is also induced. As no visible polarization dependence of the scattering or the reflectance of the film is observed we consider this anisotropy as due to the photoinduced circular dichroism in the film. The measured value of the circular dichroism is $AD = \lg(T_r/T_l) = 0.28$. It remains stable for months.

In summary, we have observed, for the first time to our knowledge, the photoinducing of a large circular birefringence $\Delta n_{\text{cir}} = 10^{-2}$ (optical activity $> 10^4$ deg/cm) and circular dichroism ($AD \sim 0.3$) in films of a side-chain azobenzene polyester that are initially isotropic. The exact mechanism of inducing

this anisotropy is not clear to us for the moment. It is well known that light induces trans-cis isomerization and reorientation of the azobenzene groups. At 488 nm both the trans and the cis form absorb [10]. We suppose that illumination with circularly polarized light initiates a photoenantiomerization of the azobenzenes (and the whole side-chains) through the reversible trans-cis isomerization. We also suppose that this process triggers physical changes in the liquid crystalline structure of the film that amplify the effect of the photochemical reaction. Understanding the nature of this effect certainly requires more detailed experiments.

Acknowledgements

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References

- [1] A.M. Makushenko, B.S. Neporent, O.V. Stolbova, *Opt. Spektrosk.* 31 (1971) 557.
- [2] T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.* 23 (1984) 4309.
- [3] Z. Sekkat, M. Dumont, *Synthetic Metals* 54 (1993) 373.
- [4] I.D. Shatalin, V.I. Kakichashvili, Sh.D. Kakichashvili, *Pisma ZTF* 13 (1987) 1051.
- [5] S. Hvilsted, F. Andruzzi, C. Kulinna, H.W. Siesler, P.S. Ramanujam, *Macromolecules* 28 (1995) 2172.
- [6] Sh.D. Kakichashvili, *Pisma ZTF* 16 (1990) 28.
- [7] B.S. Udayakumar, G.B. Schuster, *J. Org. Chem.* 58 (1993) 4165.
- [8] N.C.R. Holme, P.S. Ramanujam, S. Hvilsted, *Appl. Opt.*, submitted.
- [9] T. Todorov, L. Nikolova, *Opt. Lett.* 17 (1992) 358.
- [10] P.S. Ramanujam, S. Hvilsted, I. Zebger, H.W. Siesler, *Macromol. Rapid Commun.* 16 (1995) 455.