

Large photoinduced birefringence observed over a wide spectral range in an amorphous azopolymer

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The birefringence spectrum $\Delta n(\lambda)$ for an amorphous azopolymer synthesized in the Institute of Optical Materials and Technologies is measured in a wide wavelength region – from 390 to 700 nm. High values of Δn are established – from 0.02 at the longer wavelengths up to 0.05 close to 400 nm. Hence, the polymer could be used in applications such as polarization holographic gratings and diffractive optical elements with unique polarization properties usable in the entire visible range.

Keywords: spectral birefringence, high photoinduced birefringence, azopolymer

INTRODUCTION

Optical anisotropy is a property of the medium which varies depending on the direction of propagation of the optical wave. In contrast, isotropy implies identical properties in all directions. Anisotropy of absorbance is referred as “dichroism” (ΔD) and anisotropy of the refractive index – as “birefringence” (Δn). Anisotropy can also be linear or circular, inherent or photoinduced. Most interesting for practical applications is the photoinduced linear birefringence. Based on it, efficient polarization phase gratings can be recorded (up to 100 % diffraction efficiency), whereas for absorption gratings (when dichroism is used), the maximal theoretical efficiency is limited to 6.25 % [1].

Photoinduced birefringence has been found in various inorganic and organic materials, but one of the most efficient are the azobenzene polymers and therefore they have numerous applications, especially in the field of polarization holography [1–6]. The photoinduced effects in them arise from two main processes: selective *trans*–*cis* isomerization followed by reorientation of the *trans*-azobenzenes.

Usually the value of birefringence is measured at fixed laser wavelengths – either of reading or recording laser. However there are some cases, where it is critical to know the birefringence over a broad spectral range. An example is polarization

diffraction grating used in a device (spectral Stokesmeter) measuring the polarization state of light, i.e. the four Stokes parameters, simultaneously for a number of wavelengths [7, 8]. Its diffraction efficiency at a given wavelength is closely related with the birefringence value for the same wavelength.

Although reports can be found of recording in azopolymers at wavelengths outside the typical 440–500 nm range – either in the UV [9], or in the yellow and red [10], very few researchers present data about the spectral birefringence [11]. Therefore, we believe our study will be of interest to the scientific community and will clarify the dependence of Δn on the wavelength.

EXPERIMENTAL

Azopolymer synthesis and sample preparation

The polymer we use is a side-chain azopolymer denoted as P₁. Its chemical structure is shown in Fig. 1. The synthetic procedure is briefly described below.

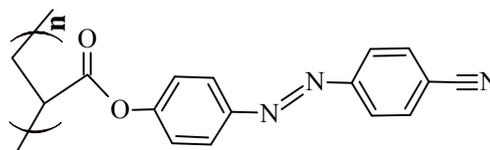


Fig. 1. Structure of the azopolymer P₁ used in the present study.

Initially azo chromophore 4-(4-hydroxyphenylazo)benzonitrile was prepared by

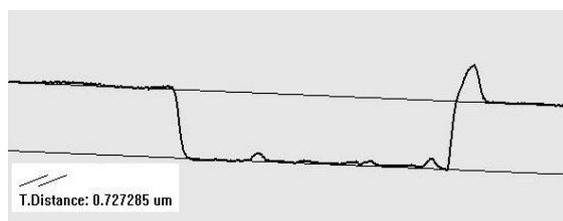
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dissociation of 4-aminobenzonitrile and coupling with phenol using standard technology. Then by etherification with acryloyl chloride the azo dye monomer was obtained. Finally, the polymer was synthesized by radical-type polymerization [12]. The differential scanning calorimetry (DSC) data indicate glass transition temperature $T_g = 106$ °C. The polymer is amorphous and its weight average molecular weight is $M_w = 1.46 \times 10^4$ g/mol, as measured by gel-permeation chromatography (GPC).

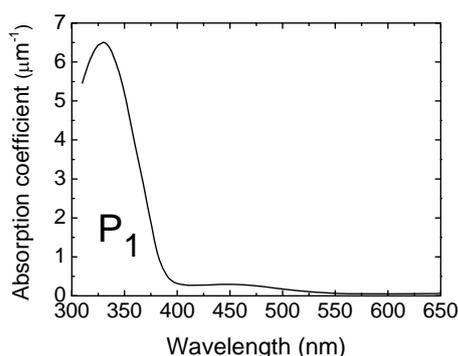
In order to prepare thin films for optical testing, 20 mg of the polymer were dissolved in 200 μ l of 1,2-dichloroethane, i.e. at concentration of 100 g/L. Then the solutions were spin coated at 1500 rpm on glass substrates to produce films with uniform thickness.

Thickness measurement and spectrophotometric characterization

As it will be seen in the next section, the thickness is an important characteristic of the photosensitive films, as it is directly used in the calculation of the birefringence. Hence, its value has to be determined precisely. For this purpose we employed a high-precision Talystep profilometer with 1 nm vertical and 0.1 μ m horizontal



(a)



(b)

Fig. 2. (a) Thickness profile of a thin film prepared from the azopolymer P₁; (b) Spectrum of absorption of the same thin film.

resolution, additionally upgraded with a digital recording device. A typical scan over the film

surface is presented in Fig. 2a. The “valley” corresponds to a region where the polymer layer has been removed. Thus the thickness of the film is $d = 730$ nm, assuming uncertainty of the measurement of ± 1 %.

The spectral measurements required to determine the absorbance and also the spectral variation of the birefringence are performed on a Varian Cary 5E spectrophotometer. The device has a spectral range from 200 to 3300 nm, i.e. in the UV/VIS/NIR parts of the spectrum. Figure 2b shows the absorption spectrum of a thin film from P₁ before irradiation.

Birefringence recording setup

To induce birefringence in the sample, an expanded vertically polarized beam from a Diode-Pumped Solid State (DPSS) laser at 473 nm was used. The beam diameter after the collimator is 8 mm and the intensity is approximately 25 mW/cm². The azopolymer film is placed behind an aperture with 5 mm diameter in order to ensure a more uniform light distribution over the irradiated area of the film. To control *in situ* the birefringence value Δn , the sample is placed between two crossed polarizers with axes oriented at $\pm 45^\circ$ with respect to the vertical and a probe He-Ne laser beam ($\lambda = 633$ nm) is passed through this system. The intensity of the transmitted beam is given by [2]:

$$I = I_0 \sin^2 \left(\frac{\pi d \cdot \Delta n}{\lambda_{\text{He-Ne}}} \right) \quad (1)$$

where I_0 is the intensity of the probe beam before the exposure and at parallel polarizers, d is the thickness of the film and $\lambda_{\text{He-Ne}}$ is the wavelength of the probe He-Ne beam. From Eq. (1) the value of birefringence can be easily determined as

$$\Delta n = \frac{\lambda_{\text{He-Ne}}}{\pi d} \cdot \arcsin \sqrt{I/I_0} \quad (2)$$

The intensity is measured in real time during the experiment and the irradiation continues until saturation of I and respectively Δn is reached. In our case this time is about 30 min. Shortly after the exposure has been stopped, the value of the birefringence at 633 nm is calculated using Eq. (2): $\Delta n (633 \text{ nm}) = 0.0235$.

RESULTS AND DISCUSSION

In order to determine the spectrum of birefringence, three spectra have to be measured, corresponding to transmission of the sample placed between:

1. **crossed** polarizers **after** the exposure – $T_{\perp}^{\text{exp}}(\lambda)$;

2. **crossed** polarizers **before** the exposure – $T_{\perp}^{\text{non-exp}}(\lambda)$;

3. **parallel** polarizers **before** the exposure – $T_{\parallel}^{\text{non-exp}}(\lambda)$.

For an isotropic sample we would expect $T_{\perp}^{\text{non-exp}}(\lambda) = 0$. However, although the sample is isotropic before the exposure, this spectrum has very small, but non-zero values. They are probably due to stray light in the spectrophotometer compartment or scattering from the sample. Thus, in order to take these effects into account, we have to subtract this spectrum from the first one (after the exposure). So finally we can express the spectral birefringence in terms of the three spectra, using Eq. (2) as:

$$\Delta n(\lambda) = \frac{\lambda}{\pi d} \cdot \sin^{-1} \sqrt{\frac{T_{\perp}^{\text{exp}} - T_{\perp}^{\text{non-exp}}}{T_{\parallel}^{\text{non-exp}}}} \quad (3)$$

Note, that in this expression, the wavelength is not a constant, as it is in Eq. (2).

The birefringence spectrum calculated using the last equation is shown in Fig. 3. The value of Δn for 633 nm is indicated by an arrow and is equal to 0.0233. This value coincides very well with the

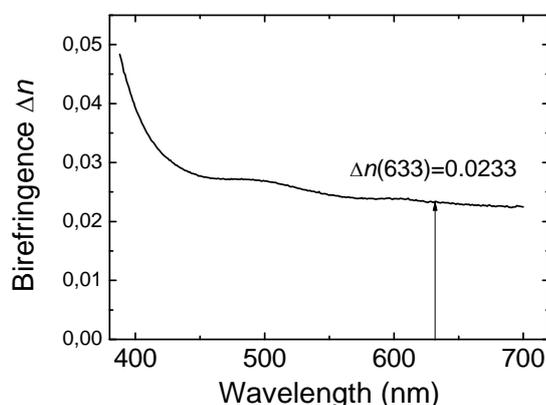


Fig. 3. Spectral birefringence obtained after irradiation of 730 nm thick film from azopolymer P₁ with linearly polarized light ($\lambda = 473$ nm, $I = 25$ mW/cm²) for 30 min.

value obtained at the end of recording (0.0235), which means the two methods of measuring Δn – as time series at fixed wavelength, and in the spectral domain – give compatible results.

In this case the data for $\Delta n(\lambda)$ are given for visible light (390–700 nm), but the range of measurement can be easily expanded. To cover the

UV, it is essential to replace the glass substrates with quartz. Both for UV and NIR, polarizer and analyzer with broad spectral operating range have to be used.

We would like to point out that the shape of the curve for $\Delta n(\lambda)$ obtained by us is similar to the one reported by Lachut *et al.* [11] in bis-azo polymer, in spite of the different wavelength region. The trend in both cases is that the birefringence is higher at shorter wavelengths and approaches a constant value at longer wavelengths.

In our further studies, we intend to expand the range of measurement both in the UV and NIR, in order to confirm this trend and to address the telecommunication band (1300–1500 nm), which is important for many applications as planar waveguides, optoelectronic devices, etc.

CONCLUSIONS

In summary, we present data for the spectral dependence of the photoinduced birefringence Δn for an azopolymer over a wide wavelength band, covering the entire visible part of the spectrum (390–700 nm). As the birefringence at a given wavelength is closely related to the diffraction efficiency on holographic recording, this method gives a fast estimate whether an azopolymer can be used as a media for polarization diffraction grating suitable for certain wavelength range.

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REFERENCES

1. L. Nikolova, P. S. Ramanujam, *Polarization Holography*, Cambridge Univ. Press, Cambridge, 2009.
2. T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.*, **23**, 4309 (1984).
3. M. Eich, J. H. Wendorff, *Makromol. Chem.–Rapid Comm.*, **8**, 467 (1987).
4. A. Natansohn, P. Rochon, *Chem. Rev.*, **102**, 4139 (2002).
5. L. Nedelchev, T. Todorov, L. Nikolova, Tz. Petrova, N. Tomova, V. Dragostinova, *Proc. SPIE*, **4397**, 338 (2001).
6. D. Ilieva, L. Nedelchev, Ts. Petrova, N. Tomova, V. Dragostinova, L. Nikolova, *J. Opt A: Pure Appl. Opt.*, **7**, 35 (2005).
7. T. Todorov, L. Nikolova, *Opt. Lett.*, **17**, 358 (1992).
8. T. Todorov, L. Nikolova, G. Stoilov, B. Hristov, *Appl Opt.*, **46**, 6662 (2007).

9. P. S. Ramanujam, L. Nedelchev, A. Matharu, *Opt. Lett.* **28**, 1072 (2003).
10. P. S. Ramanujam, O. B. Jensen, P. Tidemand-Lichtenberg, *Opt. Express*, **21**, 1812 (2013).
11. B. L. Lachut, S. A. Maier, H. A. Atwater, M. J. A. de Dood, A. Polman, R. Hagen, S. Kostromine, *Adv. Mater.*, **16**, 1746 (2004).
12. G. Martinez-Ponce, Ts. Petrova, N. Tomova, V. Dragostinova, T. Todorov, L. Nikolova, *J. Opt. A: Pure Appl. Opt.*, **6**, 324 (2004).

ГОЛЯМО ФОТОИНДУЦИРАНО ДВУЛЪЧЕПРЕЧУПВАНЕ НАБЛЮДАВАНО В ШИРОК СПЕКТРАЛЕН ДИАПАЗОН В АМОРФЕН АЗОПОЛИМЕР

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(Резюме)

В статията са представени експериментални данни за спектъра на двулъчепречупване $\Delta n(\lambda)$ за аморфен полимер, синтезиран в Института по Оптически Материали и Технологии към БАН. Измерването е в широк спектрален диапазон – от 390 до 700 nm. Установени са високи стойности на Δn : от 0,02 за дълговълновата част на спектъра, до 0,05 в близост до 400 nm. От това следва, че полимерът е подходящ за приложения от типа на поляризационни холографски решетки и дифракционни оптични елементи с работна област, обхващаща целия видим спектър.