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PHOTO-ORIENTATION IN AZOBENZENE CONTAINING POLYBUTADIENE BASED POLYMER

D. Rais[a,*], S. Nešpůrek[a,b], Y. Zakrevskyy[c], J. Stumpe[c], Z. Sedláková[a],
M. Studenovský[a]

[a]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic
[b]Chemical Faculty, Technical University of Brno, Purkynova 118, 612 00 Brno, Czech Republic
[c]Fraunhofer Institute for Applied Polymer Research, Science Campus Golm,
Geiselbergstr. 69, D-14476 Potsdam, Germany

The photochemical behavior of a liquid crystalline polymer based on HO-terminated telechelic polybutadiene Krasol LBH 3000 grafted with 5-(4-{[4-(octyloxy)phenyl]azo}phenoxy)pentane-1-thiol units was studied. The photochemically induced trans-cis-trans isomerization cycles of azobenzene groups resulted in their local reorientation upon irradiation with linearly polarized UV light of He-Cd laser. The irradiation led to a reorientation of the azobenzene chromophores perpendicular to the electric field vector and in this way to the induction of stable anisotropy represented by a maximum of dichroic ratio of 5.6 at 325 nm. The resulting dichroism and birefringence was quite stable. Erasing of the orientation was carried out by the irradiation with 365 nm light of Hg-lamp. Upon irradiation with polarized and non-polarized light of the lamp, the polymer film went to a completely disordered state. Further irradiation with the linearly polarized laser beam led again to the induction of anisotropy.

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1 Introduction

Reversible optical data storage based on organic photochromic materials is a promising approach in photonics. The phenomenon of photo-induced isomerization of azobenzene groups provides interesting features to materials that contain them. Irradiating the material with linearly polarized light of proper wavelength, the azobenzene chromophore changes their spatial orientation [1-4]. In this way anisotropy – dichroism and birefringence – is generated. This process can find its applications in optical switching [5], digital and holographic data storage [6] and optical modulators [7]. The polymeric surrounding of the azobenzene moieties provides the temperature and temporal stability of the spatial organization of the chromophores. Another desired feature of such materials as optical memories is the possibility of a large number of reversible writing and erasing cycles. However, the anisotropy induced in many azobenzene containing polymers (polymers containing azobenzene chromophores covalently attached to the main chain) is not very stable, especially at higher temperatures. In this article, we present a new azobenzene containing polymer class with promising properties for the fabrication of optical memories. It was synthesized based on a pre-polymer from which linear copolymers or polymer networks can be prepared (thus by reactions of its terminal hydroxyl groups with isocyanate groups of diisocyanate or triisocyanate derivatives).

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[*] Corresponding author: david.rais@atlas.cz

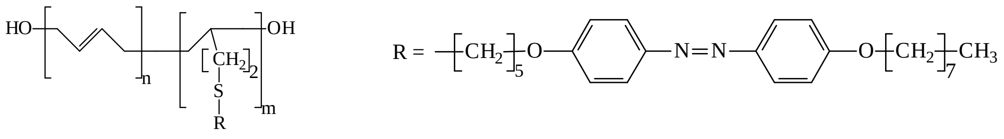

Fig. 1. The structure of the polymer.

In this way, the properties, such as the stability of the orientation at higher temperatures, of the polymer could be fine-tuned for needs of particular application.

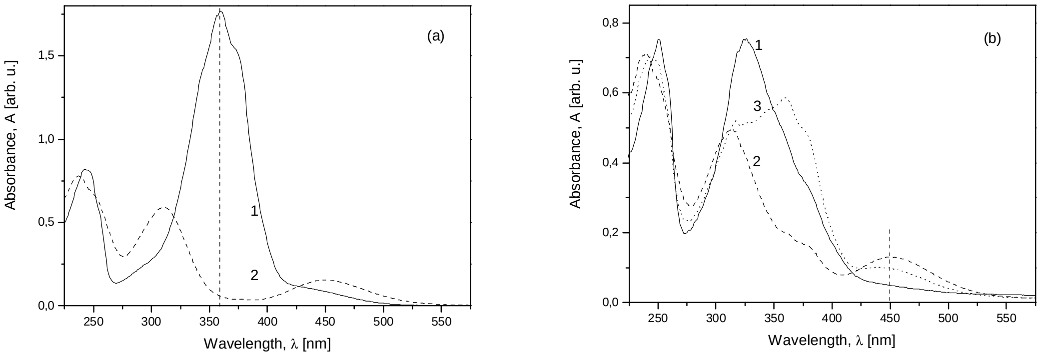

Fig. 2. Absorption spectra of the polymer in solution (a) and as thin film (b) before (1 – full lines) and after (2 – dashed lines) UV irradiation at 365 nm. The vertical lines mark the wavelengths used for the analysis of the lifetimes. The dotted line (3) in Fig. 2b represents the spectrum of thin film after 4 h relaxation. Curve 1 represents also the spectrum after thermal isomerization to the initial state.

2 Experimental

The photochromic polymer (see Fig. 1) was prepared by the addition of a 4'-octyloxy-4-pentyloxythiol azobenzene to polybutadien Krasol LBH 3000 at 60 °C in the presence of azobisisobutyronitrile as initiator. The thiol functionalized azobenzene group was prepared by a five-step synthesis, which will be described elsewhere. Its molar and weight averages of molar mass was $M_n = 12000$ g/mol and $M_w = 14000$ g/mol, respectively. The content of the azobenzene side groups was 36 mol %.

The glass transition temperature T_g was found around 10 °C by DSC measurements. The polymer showed two first order phase transitions during heating, one at 62 °C with enthalpy change $\Delta H = 2.433$ J/g and another one at 98 °C with $\Delta H = 10.8$ J/g. Both are attributed to the formation of liquid-crystalline phases. Similar transitions were observed also upon cooling.

For the measurements of the optical properties in tetrahydrofuran, a solution containing 0.03 mg of the polymer per 1 ml was prepared. Irradiation of the solution was carried out with the non-polarized light of Hg-lamp using a 365 nm filter whereas the power density after the filter was 10 mW/cm^2.

Films of the polymer were prepared by spin-coating onto quartz glass substrates using a chloroform solution (concentration 25 mg of the polymer per 1 ml of the solvent and at 1000 rpm). The prepared films were kept at room temperature at least for 24 hours allowing the solvent to evaporate The optical anisotropy in the films was induced by linearly polarized light of a He–Cd laser with a wavelength of 325 nm and a power density of 10 mW/cm^2 at normal incidence. Erasing of the information was realized by the irradiation with polarized and non-polarized light of Hg-lamp (with a 365 nm filter and a power density after filter of 10 mW/cm^2).

The thermal cis-trans isomerization kinetics in spin-coated films and in THF solutions were measured with the Perkin-Elmer Lambda 950 UV/Vis spectrometer after UV irradiation using the lamp with the band filter with maximum at 365 nm at various temperatures. The UV irradiation was performed until establishing the steady state; thus, polymer films and polymer solutions were exposed for 11 min and for 2 min, respectively. To achieve a homogenous excitation in the whole volume, the solution was stirred during the exposure. The time evolution of optical absorbance was detected at $\lambda = 450$ nm. The thermal cis-trans isomerization kinetics were found to be first order processes (in thin films at long relaxation time approximation). Thus, the momentary concentration $n(t)$ of the cis-form in the time t fulfilled the relation $n(t) = n(0)\exp(-t/\tau)$, where $n(0)$ is the concentration at the beginning of the cis-trans isomerization and τ is the time constant of the process, which followed the Arrhenius type of the dependence

$$\tau = \nu_0^{-1}\exp(E_A / RT)\,, \tag{1}$$

where ν_0 is the frequency factor and R stands for the universal molar gas constant and E_A is the activation energy of the cis-trans isomerization.

The development of polarized absorption spectra with the growing irradiation dose was recorded for two polarization directions, one of them was parallel (indexed by || sign) to the polarization of the pumping light, and the other was perpendicular (⊥). The measurements were performed at room temperature using a Perkin-Elmer Lambda 19 UV/Vis spectrometer equipped with Glan-Thompson polarizers, driven by computer-controlled stepper motors. Dichroic ratio D (the ratio of absorbencies $A_\perp/A_\parallel$ at selected wavelength) was used to express the magnitude of the anisotropy.

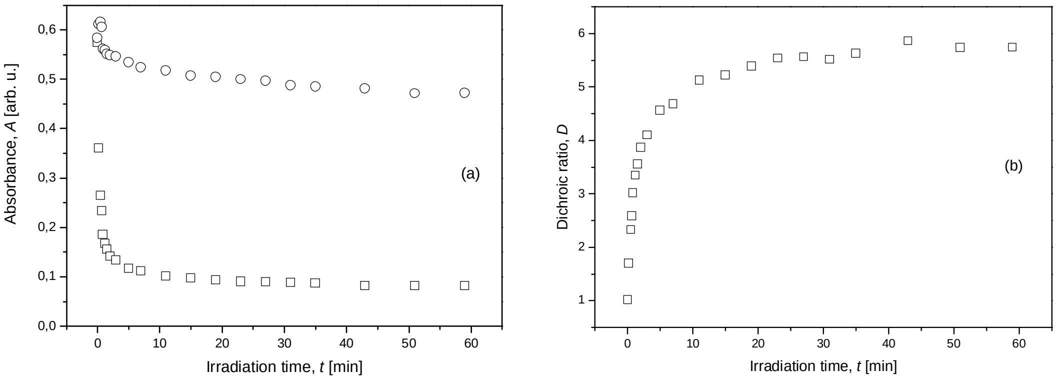

Fig. 3. Development of the dichroism upon irradiation by linearly polarized light $\lambda = 325$ nm (He-Cd laser). (a) - Absorbance values in parallel (squares) and perpendicular polarization direction (circles) (measured at 329 nm). (b) - The resulting dichroic ratio.

3 Results and discussion

3.1 Thermal cis-to-trans isomerization

The absorption spectra of the polymer before and after UV exposure recorded at room temperature are shown in Fig. 2a. The initial solution contained exclusively the trans isomer, but the steady state upon irradiation at 365 nm is characterized by a high proportion of the cis formic chromophore. The spectrum shows the main maximum at $\lambda = 356$ nm which corresponds to π-π^* transitions of trans isomer of azobenzene chromophore. After the irradiation by UV light ($\lambda = 365$ nm) the cis-form with characteristic maxima at $\lambda = 310$ nm and 450 nm was observed. The reaction was reversible with a time constant of about $\tau = 10$ h at room temperature. The activation energy and the frequency factor of the thermal cis-trans isomerization were determined using Eq. (1) as $E_A = 97$ kJ/mol and $\nu_0 = 3.9\times10^{13}$ Hz.

The spectrum of thin polymer film before UV irradiation shows maxima at λ =326 nm which corresponds to π-π* transitions in azobenzene chromophore. UV irradiation results in change of the spectrum characterized by maxima at λ = 313 and 450 nm indicating the formation of the cis isomer. It shows a quite complicated kinetic behavior with respect to the trans-cis photoisomerization and in photo-induced distortion of H aggregates shifting the spectrum temporally to longer wavelengths with a maximum at 358 nm characteristic for non-aggregated trans isomers. At the beginning, the thermal cis-trans isomerization was accompanied by the increase of absorbance band with the maximum λ = 358 corresponding to isolated trans isomers (see spectrum measured 4 h after the UV irradiation – curve 3 in Fig. 2b). At longer decay times this peak shifted to λ = 326 nm which can be set to the aggregation of azobenzene units. In order to avoid possible problems with the determination of the time constant with respect to the complex spectral change in the range of the π-π* band, the kinetics of the thermal cis-trans isomerization were measured at λ = 450 nm.

The ratio between the peak intensity of the σ-σ* transition (at 240 nm) and the intensity of the π-π* transition provides information on the orientation of the azobenzene chromophores, because the σ-σ* transition is not sensitive to the orientational order in contrast to the π-π* transition [1]. The ratio was about 1:2 in solution (cf. Fig. 2a) and about 1:1 in thin film (see Fig. 2b). This indicates that the azobenzene chromophores preferred the homeotropic (perpendicular to the film surfaces) orientation in thin film. The peak intensities of the cis form (at 240, 310 and 450 nm) in solution (cf. dashed line in Fig. 2a) are in almost the same relationship as in the thin film (see dashed line in Fig. 2b).

The thermal cis-trans isomerization process shows a kinetics characteristic for a unimolecular reaction similar to that in solution with characteristic lifetime τ = 9.7 h at room temperature. The activation energy and the frequency factor were found to be E_A = 98 kJ/mol and $\nu_0 = 1.1\times10^{13}$ Hz (at long time approximation).

3.2 Kinetics of orientation by linearly polarized light

The irradiation with linearly polarized light (λ = 325 nm) causes a reorientation of azobenzene chromophores inducing anisotropy in the film.(see Fig. 3). The azobenzene molecules underwent a number of trans-cis-trans isomerizations in the steady state that led to their reorientation perpendicular to the electric field vector. At the beginning (during first 70 s), the dichroism grew very fast and almost linearly with the exposure time. After that the speed of the growth is decreased and after about 30 min of the irradiation, the dichroism reached a saturation value (D = 5.6). However, there was a preference in the homeotropic reorientation. This shows that boundaries strongly influenced the alignment in the film. The time stability of the dichroism developed by this irradiation procedure was checked after 5 days keeping the films at room temperature under day light; the value of D decreased by only 1 %.

4 Conclusions

A new liquid crystalline polymer based on the HO-terminated telechelic polybutadiene Krasol LBH 3000 grafted by 5-(4-{[4-(octyloxy)phenyl]azo}phenoxy)pentane-1-thiol was prepared. The irradiation with linearly polarized or non-polarized UV light (λ = 365 nm) (brought the film to a disordered state. Irradiation with linearly polarized light of 325nm generated dichroism of about 5.6 in the film. However, irradiation with 365 nm removed completely the dichroism developed by previous polarized irradiation. Erased films were ready for a further re-writing of anisotropy by polarized light.

Acknowledgements

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