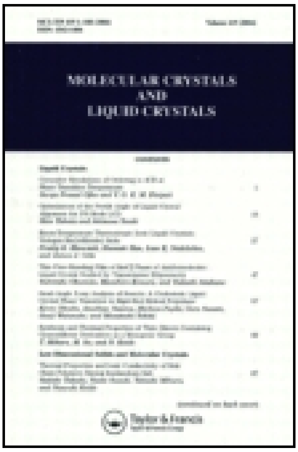

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Photoinduced Orientation of Azobenzene Groups in Polymer Films. Characterization by UV/Visible Spectroscopy

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We study the kinetics of the photoinduced orientational ordering of two methacrylic polymers containing different azobenzene groups with both electron-donor and electron-acceptor substituents under irradiating them at two different wavelengths. For the experimental study of the orientational distribution in polymer films, we use the method based on absorption measurements. It is found that azofragments are oriented by either the photoorientation or photoselection mechanism depending on the wavelength. The components of the order parameter tensor of azobenzene fragments are estimated for the initial state and after different doses of irradiation.

Keywords Absorption spectra; azopolymers; orientational order

1. Introduction

In the past few years, azo-dye-containing polymer systems have been the subject of intense researches due to their potential applications in photonics, optoelectronics, and optical signal processing [1,2]. One of the main interests in these polymer systems is their birefringence properties when they are irradiated with a linearly polarized light [3]. This birefringence comes from the reorientation of azobenzene groups through *trans*-*cis*-*trans* isomerization cycles which lead to an excess of photochromic entities oriented perpendicularly to the laser polarization direction. When the laser is turned off, a large part of the photoinduced orientation is preserved (between 60% and 80%) in polymers containing azobenzene side chains [4,5]. Amorphous azobenzene-based polymers with a high glass transition temperature (T_g) are better candidates for this procedure.

The time dependence of the photoinduced orientation in azobenzene polymers has been explained by Dumont *et al.* using a theoretical model which takes the population in both the *trans* and *cis* metastable states into account [6–8]. This model considers that the polarized light induces a selective optical pumping ("angular hole-burning (AHB)") followed by angular reorientations (AR) during the direct *trans*-*cis* and reverse *cis*-*trans* photoisomerizations and the *cis*-*trans* thermal back-relaxation. As a result, two mechanisms are cooperated in proportions depending

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on molecular parameters and on irradiation conditions. The first mechanism is related to the angular selectivity of the photoexcitation which produces *angular hole burning*. This selective depletion of the ground state is common in all photochromic materials. If photoproducts are thermally and photochemically stable, the saturation of hole burning leads to a total depletion of the initial state. The second mechanism occurs when the photochromism is thermally or optically reversible (like the *trans-cis* photoisomerization of the majority of azobenzene derivatives). In that case, molecules undergo a great number of photoisomerization cycles resulting in a kind of mechanical stirring which induces a random-walk rotation of azochromophores. This process known as *angular redistribution* leads to the accumulation of molecules perpendicularly to the polarization of the exciting light. More generally, after a great number of photoisomerization cycles, these two processes tend to minimize the probability of optical excitation.

In the past decade, several groups of scientists had studied the influence of the molecular architecture on the orientational characteristics of photochromic polymers. In a recent study, Sekkat *et al.* [9] have investigated the photoinduced orientation in an azobenzene-containing polyglutamate film. An anisotropy in the *cis* isomer orientation has been found, when the film was irradiated with a linearly polarized UV light (360 nm), and a theoretical model has described the time dependence of this anisotropy. Furthermore, Natansohn *et al.* [10,11] have studied the time dependence of the birefringence of a poly[4-[2-(methacryloyloxy)ethyl] azobenzene] film (called pMEA) using polarized UV (360 nm) or visible (514.5 nm) light. A similar birefringence has been measured for the two wavelengths, but its value was lower than that observed in various polymers containing polar azobenzene groups. The pump irradiance and the temperature dependences of the photoinduced anisotropy in a pMEA polymer film have also been studied and compared with simple theoretical predictions [12]. By using the irradiation with the polarized light of two different wavelengths, Yaroshchuk *et al.* [13] found that the photoinduced anisotropy kinetics can be dominated by either the photoorientation (angular redistribution of *trans* chromophores) or photoselection (angular selective *trans-cis* isomerization) mechanism depending on the wavelength.

In this work, we are concentrated on the features of the azochromophore orientation determined by the above-discussed mechanisms of the photoinduced ordering. There are two azopolymers of different structures used in this study, and the exposure of samples at two different wavelengths has induced the alignment of azobenzene chromophores. For the experimental study of the orientational distribution in polymer films, we used the method based on absorption measurements. This method has the indisputable advantage, because the order parameters of various molecular groups can be estimated from the results of these measurements.

2. Experimental Section

Materials

We used the poly[4-(methacryloyloxy)-4′-nitro-azobenzene] (P1) and poly[4-(methacryloyloxy)-4′-methoxy-azobenzene] (P2) differing by the donor/acceptor nature of end substitutes of the side-chain azochromophore. Figure 1 shows the general formula of these compounds.

The synthesis of these polymers has been described in a previous publication [14]. It is based on the free-radical polymerization of corresponding azomonomers

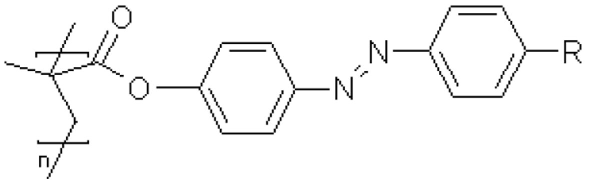


Figure 1. Chemical structure of the polymers.

with AIBN as a free radical initiator. The synthesized polymethacrylates are characterized by elemental analysis and ^{1}H NMR spectroscopy [14]. The results are in agreement with the proposed structures. Molecular weights of polymers were determined by gel permeation chromatography. The data for number-average molar mass M_n are presented in Table 1. The phase transitions were studied by polarization differential scanning calorimetry (DSC). The phase transition temperatures are presented in Table 1.

Film Preparation

To prepare thin films, the polymer was dissolved in chloroform, and the solution was deposited by spin-coating onto quartz slides. Films were then heated for 30 min at 80°C to remove any remaining solvent. The film thickness of about 300–500 nm was measured with a profilometer. The optical quality of films strongly depends on their thickness. As a rule, thin films ($d < 500$ nm) are uniform and have good optical properties.

Methods

The photoordering processes were initiated by the irradiation with polarized light directed normally to the films. Two different wavelengths were used to pump the samples:

1. $\lambda_{ex1} = 365$ nm, from a mercury lamp, selected by an interference filter and polarized with a Glan prism. The light intensity I was varied in the range 4–10 mW/cm^2.
2. $\lambda_{ex2} = 480$ nm from an Ar+laser ($I \approx 20$ mW/cm^2).

As it will be shown below, the line $\lambda_{ex1} = 365$ nm corresponds to the strong absorption of azochromophores, whereas the line $\lambda_{ex2} = 480$ nm lies on the wing of the UV/visible absorption band. In all cases, the polarization of light was chosen along the x axis of the Cartesian coordinate system with the x and y axes parallel to the verges of the rectangular polymer film and the z axis normal to this film.

Table 1. Characteristics of the polymers under study

Polymer	R	T_g, K	M_n, g/mol	λ_{max}, nm
P1	NO_2	435	5600	355
P2	OCH_3	432	5900	340

Particularly, UV/visible spectroscopy allows us to get a valuable preliminary information for estimating the order parameters of azochromophores and of other molecular fragments [15–16].

We perform 2D dichroism measurements in the UV/visible spectral range. The UV/vis absorption measurements were carried out with the use of a S2000 diode array spectrometer from Ocean Optics Co. The samples were set normally to the testing light from a low-intensity deuterium lamp. A Glan–Thomson prism was used to polarize a probe beam.

The optical densities, D_x and D_y, corresponding to x and y in plane polarizations, are measured with a probe beam propagating perpendicularly to the sample. The third component, D_z, is estimated by the *total absorption (TA) method* which presumes the conservation of the total absorption $D_{tot} = D_x + D_y + D_z$. D_{tot} can be easily obtained, if the sample is uniaxial at some instant of time t_0 with an out-of-plane orientation of the axis of anisotropy, say, x [14]. Then

$$D_{tot} \equiv D_x(t_0) + D_y(t_0) + D_z(t_0) = D_x(t_0) + 2D_y(t_0) \tag{1}$$

If the number of azobenzene units in the *trans* configuration remains constant at each instant of time t, D_z can be estimated as

$$D_z(t) = D_{tot} - D_x(t) - D_y(t) \tag{2}$$

where $D_x(t)$ and $D_y(t)$ are experimentally measured. Then, the diagonal terms of the tensor of orientational order S_{ij} can be estimated. For example,

$$S_{xx} = \frac{D_x - \frac{1}{2}(D_y + D_z)}{D_x + D_y + D_z} \tag{3}$$

The components S_{yy} and S_{zz} can be obtained by a cyclic permutation in expression (3).

The total absorption method can be applied in some experimental situations described below.

3. Results

UV-Vis Spectroscopy. In our study, we used polymers containing azobenzene groups with electron-donor and electron-acceptor substituents, which strongly absorb in the visible region of the electronic spectrum. Figure 2 shows the absorption spectrum in the 300–600 nm regions of a P1 and P2 film before irradiation. These UV-vis spectra displays a high-intensity $\pi \rightarrow \pi^*$ band in the UV (at 324 nm) and a low-intensity $n \rightarrow \pi^*$ band in the visible region (at 450 nm). These bands are characteristic of “azobenzene type molecules” in Rau’s classification [17]. Considering the absorption spectra of *trans*- and *cis*-azobenzene [18], the band at nearly 345 nm corresponds essentially to the absorption of the *trans* isomers while the band at 450 nm is mainly due to the absorption of the *cis* isomers. The wavelength of the maximum of the $\pi \rightarrow \pi^*$ absorption band, λ_{max}, is presented in Table 1 for two homologs.

1. *Irradiation with Polarized UV Light* ($\lambda_{\mathrm{ex1}} = 365$ nm)

First, we consider a polymer containing push-pull chromophore P1. The in-plane optical densities, D_x and D_y, of P1 films have been measured. The significant

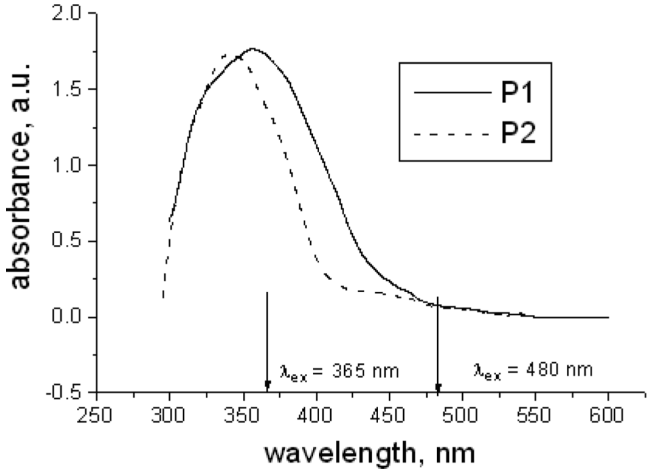
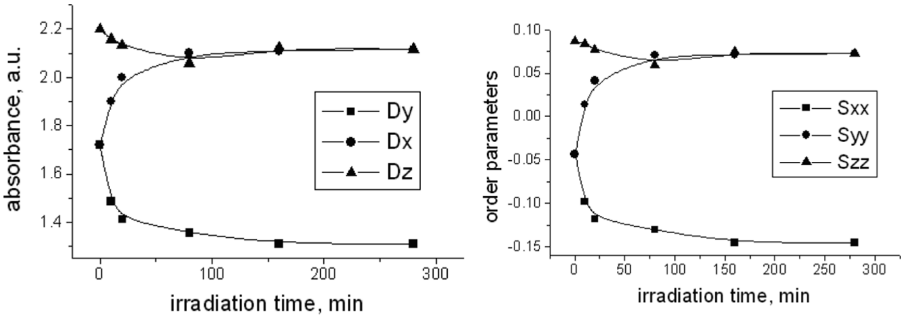


Figure 2. UV-visible absorption spectra of polymer films.

photoinduced changes of the optical density were detected in this polymer at its irradiation with polarized UV light at $\lambda_{ex1} = 365$ nm. Figure 3a represents the results of absorption measurements for P1 film before the irradiation and after subsequent irradiation steps. After the irradiation, D_y is above D_x and the azochromophores are aligned along the *y* direction that is perpendicular to **E**. The kinetics of D_x and D_y can be assigned to reorientation mechanism [19, 20,], since measurements are made after the full relaxation of *cis* isomers. In this case, the fraction of *cis* isomers is neglible and the out-of-plane absorption coefficient D_z depicted in Figure 3a can be estimated by using Eq. (2) after the calculation of D_{tot} in the photosaturated state, where $D_y^{(st)} = D_z^{(st)}$.

The values of D_x, D_y, and D_z are used to calculate order parameters as described above in the experimental section. The results are presented in Figure 3b. Before the irradiation, $S \equiv S_{zz} = 0.08$ and $S_{xx} = S_{yy} = -S_{zz}/2 = -0.04$ (positive uniaxial order along *z*). In the first steps of irradiation, S_{xx}, S_{yy}, and S_{zz} are different because of



(a) (b)

Figure 3. a) Experimentally measured D_x, D_y and calculated D_z kinetics and b) order parameters components as a function of the irradiation time τ_{ex} at $\lambda_{ex1} = 365$ nm ($I = 5$ mW/cm^2, *x* polarization) for polymer P1.

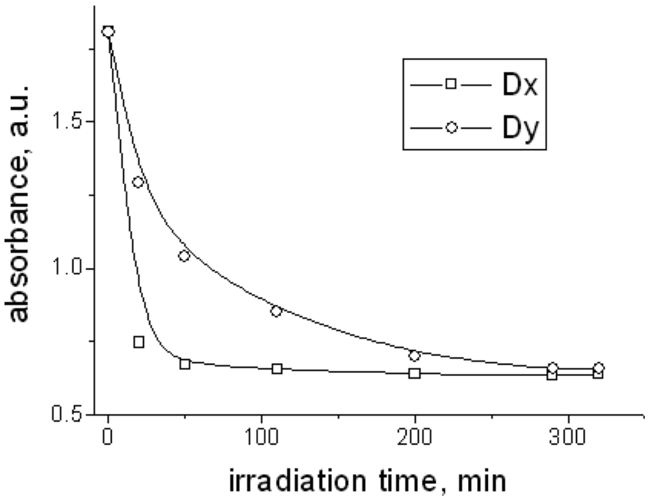


Figure 4. Experimentally measured D_x, D_y kinetics for polymer P2. Irradiation with $\lambda_{ex1} = 365\,\text{nm}$ ($I = 5\,\text{mW/cm}^2$, x polarization).

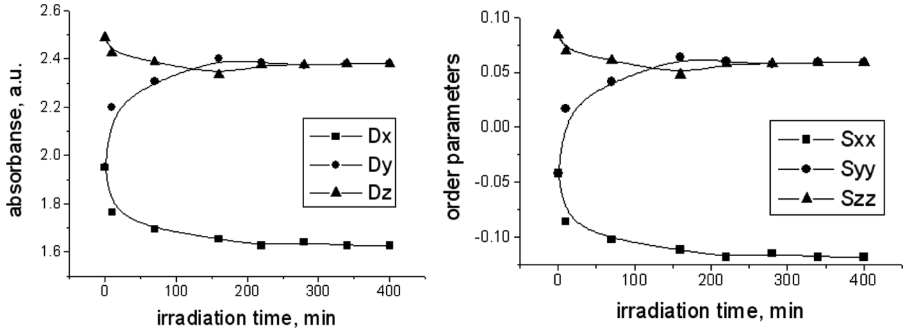
a biaxial order. At the saturation, $S \equiv S_{xx} = -0.145$ and $S_{yy} = S_{zz} = -S_{xx}/2 = 0.073$ (uniaxial negative order along x).

The $D_x(t)$ and $D_y(t)$ curves for P2 are presented in Figure 4. In contrast to the case presented in Figure 3a, the simultaneous decrease of these curves clearly indicates that the azobenzene chromophores are oriented by the angular photoselection mechanism [19, 20]. The conversion of *trans* isomers in the long-lived *cis* form first in the direction of light polarization $\mathbf{E}_{ex}$ and then in all other spatial directions may explain the isotropic order realized in P2 film at high radiation doses. On the initial stage of the irradiation, we observe the biaxial alignment which transforms, with irradiation dose, in the spatially isotropic distribution.

Note that the TA method cannot be applied for P2 because of the strong exhaustion of *trans* chromophores possible for rather stable *cis* isomers. This automatically excludes conditions needed for the TA method.

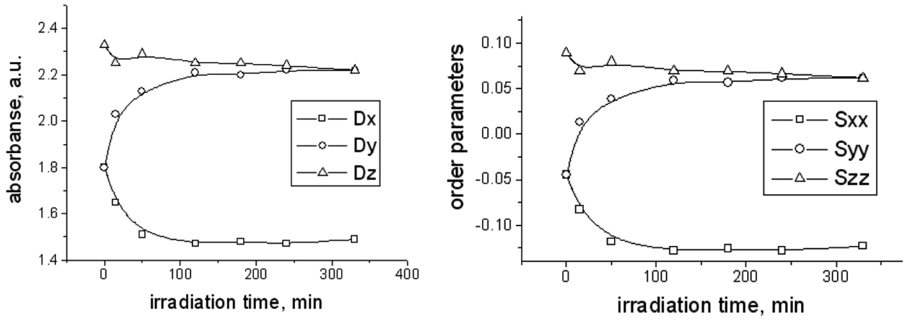
2. *Irradiation with Polarized Visible Light ($\lambda_{ex2} = 480\,nm$)*

The values of D_x and D_y absorption components for polymers P1 and P2 corresponding to various exposure times with $\lambda_{ex2} = 480\,\text{nm}$ excitation (x-polarization) are presented in Figures 5a and 6a, respectively. The observed behavior is similar to the case of the 365-nm irradiation for P1. Hence, the kinetics of D_x and D_y can be assigned to the reorientation mechanism. The D_z components have been estimated by the total absorption method. These data can be used to calculate order parameter components for each irradiation step, as it was done in case of $\lambda_{ex1} = 365\,\text{nm}$ irradiation. The $S_{xx}(t)$, $S_{yy}(t)$, and $S_{zz}(t)$ curves are shown in Figure 6a and 6b for P1 and P2, respectively. Before the irradiation, $S \equiv S_{zz} = 0.084$ and $S_{xx} = S_{yy} = -S_{zz}/2 = 0.042$ for P1 and $S \equiv S_{zz} = 0.09$ and $S_{xx} = S_{yy} = -S_{zz}/2 = 0.045$ for P2. At the saturation, the uniaxial oblate distribution of azochromophores with the x ordering axis realized in the stationary state of irradiation is characterized by the scalar $S \equiv S_{xx} = -0.118$ for P1 and $S \equiv S_{xx} = -0.123$ for P2. We observe similarities



(a) (b)

Figure 5. a) Experimentally measured D_x, D_y and calculated D_z kinetics and b) order parameters components as a function of the irradiation time τ_{ex} at $\lambda_{ex1} = 480\,\text{nm}$ ($I = 15\,\text{mW/cm}^2$, x polarization) for polymer P1.



(a) (b)

Figure 6. a) Experimentally measured D_x, D_y and calculated D_z kinetics and b) order parameters components as a function of the irradiation time τ_{ex} at $\lambda_{ex1} = 480\,\text{nm}$ ($I = 15\,\text{mW/cm}^2$, x polarization) for polymer P2.

between two methacrylic azopolymers having chromophores with substituents of different nature under their irradiation with $\lambda_{ex2} = 480\,\text{nm}$. This allows us to assume that the excitation of azochromophores by the action of polarized light with a wavelength which lies in the visible region of the *cis* isomers absorption stirs the reversible *cis-trans*-isomerization to the activity and leads to the accumulation of the optically active *trans* form. As a result of such an irradiation, azochromophores are oriented perpendicularly to the polarization direction of the exciting light by the photoorientation mechanism.

Conclusions

In this paper, we have studied the photoinduced ordering processes in methacrylic azopolymers having substituents of different nature in side-chain chromophores. The irradiation of polymer films by polarized light with different wavelengths from the absorption region of both *trans* and *cis* isomers leads to the orientation of azochromophores by different mechanisms. In a polymer with acceptor substituents

(NO_2) in azobenzene moieties, the lifetime of *cis* isomers is short, and numerous *trans-cis-trans*-isomerization cycles are accompanied by a rotation of azochromophores. Thus, under the irradiation by actinic light of both wavelengths, azobenzene groups are oriented by the photoorientation (angular redistribution) mechanism. The orientation of azochromophores containing donor substituents (OCH_3) occurs by the angular hole burning mechanism in case of the irradiation by light with $\lambda_{ex} = 365\,nm$ (absorption region of *trans* isomers). Whereas the angular redistribution mechanism takes place in case of the irradiation by light with $\lambda_{ex} = 480\,nm$ (absorption region of *trans* isomers), when the reversible *cis-trans*-isomerization is activated. We have additionally calculated the out-of-plane absorbance D_z and the absorption order parameters S_i in the photoorientation regime. It is shown that $S_{xx} = 0.118$–0.145, and the uniaxial negative order along x is formed.

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