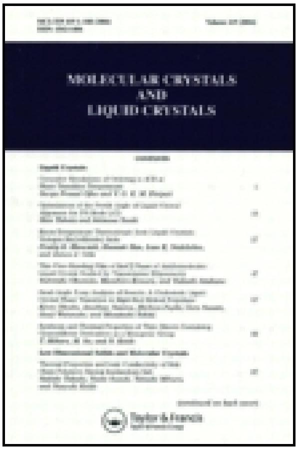

Molecular Crystals and Liquid Crystals

Photoreorientation in Liquid Crystalline Side-Group Polysiloxane with Azobenzene Derivative Admixture

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Photoreorientation in Liquid Crystalline Side-Group Polysiloxane with Azobenzene Derivative Admixture

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The photoreorientation effect in thin films of a liquid crystalline side-group polysiloxane with an azobenzene derivative admixture of the pseudo-stilbene type is presented. The film is introductory homogenously aligned in a typical liquid crystal cell of 3 μm in thickness due to rubbed polyimide coatings. The molar concentration of the azobenzene derivative, calculated per monomeric mesogenic units of the polysiloxane, is equal to 0.021 M/M and corresponds to 2 wt%. The exposure with linearly polarized light results in a reorientation of the azobenzene derivative and the 4′-cyano biphenyl side groups of the liquid crystalline polymer perpendicular towards the electric field vector of the incident light. Caused due to the reorientation process the degree of order is decreased from 0.73 to 0.44.

Keywords: azobenzene derivative; liquid crystalline polysiloxane; photoisomerization; photoreorientation

INTRODUCTION

Amorphous or liquid crystalline polymers with aromatic azobenzene side groups attract much attention because of their potential applications in optical data storage, as aligning layer or in optical components [1–7]. The azobenzene derivatives exist in two isomeric

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forms: the elongated *E* form and the bent *Z* form [8]. The *trans* isomer is thermodynamically more stable than the *cis* one. In the darkness the *Z* azobenzene derivatives are found in the *trans* form. Light absorption results in fast *trans–cis* and *cis–trans* photoisomerization processes during less than one picosecond [9]. The reverse *cis–trans* isomerization can occur as deactivation process of the excited state, photochemically or thermally from the *cis* isomeric form between the ground states of the *cis* and *trans* forms. The decay constant for the azobenzene derivatives ranges from milliseconds to minutes [9,10], whereas donor-acceptor substitution results in short life times of *cis* isomers. The photoisomerization of azobenzene derivatives was studied in the polymeric systems where the azobenzene moiety was mixed or chemically connected to a polymeric backbone [11]. It was found that isomerization of azobenzenes in polymer matrices requires a sufficient amount of free volume depending on the azobenzene type, the isomerization mechanism, and the polymeric matrix as well [12,13].

Photoorientation is a process of molecular redistribution as a result of the irradiation with polarized light. The photoisomerization process plays the basic role in the photoorientation of photochromic polymers with mesogenic and azobenzene side groups [6,14–18]. The probability of photon absorption depends on the mutual orientation between the electric field vector of the incident light and the absorption dipole transition moment of the azobenzene group. Consequently, the azobenzene moieties absorb polarized light angular selectively, resulting in the angular-selective formation of the *cis* isomer. This process is named photoselection [19]. During the illumination with polarized light the azobenzene groups undergo many isomerization cycles. Caused by the rotational diffusion, which is more efficient in the case of the *cis* isomeric form, the long axis of the *trans* isomer changes its direction in each isomerization cycle slightly. As a result of photoisomerization, photoselection, and rotational diffusion, the *trans* azobenzene moieties tend to orient perpendicularly to the electric field vector of the incident light. Short-range interactions between the photoisomerizing and the mesogenic side groups can induce the redistribution of the latter ones as well. In the glassy state of polymers the induced linear dichroism and birefringence are usually long term stable below T_G. If the photochromic sample is introductory anisotropic and the electric field vector of the incident light makes a non-zero angle with the optical axis, a photoreorientation process can be realized. As a result, a new orientation of the photoisomerizing and the mesogenic groups can be obtained [15–17]. But there is always a competition between the initial order and the reorientation tendency, which depends on the aligned polymer matrix, the type and the amount of the azobenzene moiety, the exposure wavelength and the power density.

The photoreorientation effect can be observed not only for liquid crystalline copolymers with photoisomerizing groups chemically bounded to the main chain of the polymer but also for polymers with the azobenzene derivatives mixed with the side-group polymers. Recently, photoreorientation of liquid crystalline side-group polysiloxane doped with azobenzene derivative of pseudo-stilbene type has been reported [20]. Another example of such system is described in the present paper.

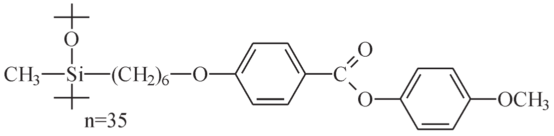
EXPERIMENTAL

Liquid crystalline side-group polysiloxane (PS6) was synthesized via hydrosilation of alkene type mesogen with commercially available poly(methylhydrogensiloxane) with an average degree of polymerization equal to 35 (Merck, Germany) [21]. The chemical structure of PS6 is given in Figure 1.

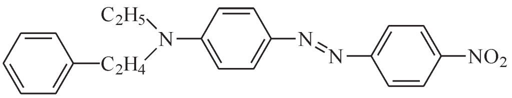
The following mesophase sequence was established from DSC scans [22]:

glass – 278 – Smectic A – 319 – nematic – 381 – isotropic phase.

The mesophase type and the transition temperatures were checked by the observations under polarizing microscope equipped with a hot stage [23]. At room temperatures, the polymer looses its plastic



PS6



EPANA

FIGURE 1 Chemical structures of liquid crystalline side-group polysiloxane (PS6) and azobenzene derivative admixture (EPANA).

properties, and resembles closely the glassy state, what can indicate the presence of some introductory vitrification process.

The chemical structure of the azobenzene derivative of the pseudo-stilbene type, 4-(N-ethyl-N-phenethylamino)-4′-nitroazobenzene (EPANA), is presented in Figure 1. It was mixed with PS6 at the concentration equal to 2 wt%. This corresponds to the molar concentration equal to 0.021 M/M (as calculated per monomeric mesogenic units of the polysiloxane).

Homogenous film of the polymer and the admixed molecules, PS6-EPANA, become planar aligned in one direction using typical liquid crystal cells (Merck, Darmstadt). The glass walls of the "sandwich" cell were covered with PI aligning-layers. The spacing distance was equal to 3 μm. The cell was filled at temperatures corresponding to the isotropic phase ($T > 385\,K$) for 24 hours, due to capillary forces. The optical quality and the uniaxiality of the sample were checked under polarizing microscope.

As light source, a diode-pumped frequency-doubled Nd:YAG laser (120 mW, Coherent, Inc.) was used. The transmitted intensity during the irradiation was recorded by a diode array spectrometer TIDAS (J&M Analytische Mess- und Regeltechnik GmbH, Aalen, Germany). The laser beam ($\lambda = 532\,nm$) with irradiation intensity of $10\,W/cm^2$ illuminated the circle area of the sample of about 2 mm in the diameter length. The electric field vector of the polarized light created an angle equal to 45° with respect to the optical axis of the sample, as it is shown in Figure 2. The irradiation of the sample was performed at room temperature (295 K) in different spots during 7 to 60 seconds. After this procedure, the angular-dependent, polarized absorption spectra were recorded by using microscope spectrometer (Zeiss, Oberkochen) working in the UV and visible range. The polarization plane of the spectrometer was rotated between 0 and 180° with a step equal to 9°.

RESULTS

The absorption band of the pseudo-stilbene type azobenzene derivatives in the visible range is attributed to the $\pi \rightarrow \pi^*$ transition connected with an intramolecular charge transfer transition [8]. This transition is strongly polarized along the long axis of the molecule given by the line between 4 and 4′ positions of the pseudo-stilbene. The absorption maximum of EPANA in PS6 was found at 515 nm. It is slightly blue-shifted comparing to that value found of a similar compound without phenyl ring in the diethylamino group [20].

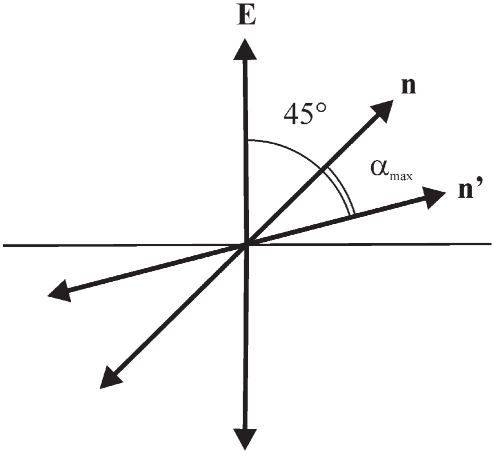


FIGURE 2 Geometry of laser irradiation in the sample spots: **E** – electric field vector of the laser light, **n**, **n**′ – vectors describing the preferred orientation of EPANA molecules and the side-groups of PS6 before and after irradiation.

Taking into account the huge power of the actinic light, it can be supposed that the temperature in the irradiated spot increases considerably. If the sample is overheated above the SmA-N transition point than the fast cooling, after breaking the illumination, will give an inhomogeneous orientation of the mesogenic side-groups and the pseudo-stilbene type molecules. Such an effect is not observed in the present case. Thus, it can be assumed that the photoreorientation process occurs below the SmA-N transition point, and that this process is intensified by the increase of the temperature in the sample during the illumination.

The maximum of the angular absorbance as a function of the polarizer's angular rotation of EPANA in PS6, recorded by using microscope spectrometer, is presented in Figure 3. The figure contains the data for five sample spots, obtained for different irradiation times. The experimental data are fitted with a curve describing the angular dependence of the absorbance in uniaxial systems having the optical axis parallel to the cell surface [20]:

$$A(\alpha) = -\lg\left[10^{-A_{\max}}\cos^2(\alpha-\alpha_{\max}) + 10^{-A_{\min}}\sin^2(\alpha-\alpha_{\max})\right], \qquad (1)$$

where $A_{\max}$ and $A_{\min}$ are the absorbances for the spectrum polarized in the direction of the preferred orientation of the absorbing molecules, described by the angle $\alpha_{\max}$, and perpendicularly to this direction, respectively.

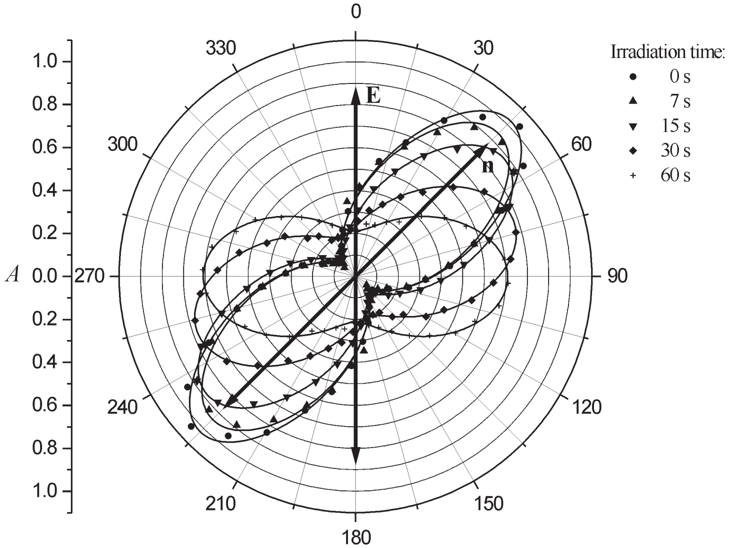


FIGURE 3 Absorbance at maximum of the spectrum (515 nm) of EPANA in PS6 (2 wt%) as a function of angular rotation of the polarizer.

The experimental data fit well to the theoretical curve, which suggest an axially symmetric distribution of EPANA molecules in the irradiated spots. The observations of the induced optical anisotropy under polarizing microscope confirm the cooperative reorientation of the mesogenic groups, as it was found previously [20]. It is seen from Figure 3 that the effective reorientation of the optical axis occurs after a short induction period during the first 7 seconds of irradiation. The illumination of the sample for 60 seconds results in a new distribution where a preferable orientation of the photoisomerizing molecules and the mesogenic groups is established perpendicularly to the electric field vector of the incident light. This is indicated by the homogenous extinction of the irradiated spot and homogenous interference color between crossed polarizers when rotating the sample.

The absorbances, $A_{\max}$ and $A_{\min}$, the average absorbance, $A_{av} = \frac{1}{3}(A_{\max} + 2A_{\min})$, the absorption anisotropy, $S = (A_{\max} - A_{\min})/(A_{\max} + 2A_{\min})$, and the reorientation angle, $\alpha_{\max}$, obtained from fitting procedure, are collected in Table 1. Additionally, the time evolution of these parameters is presented in Figure 4. The average absorbance, A_{av}, practically is not changed due to the irradiation and is independent on the duration of exposure whereas the absorption anisotropy decreases from 0.73 to a stationary value equal to 0.44. This

TABLE 1 Maximum, Minimum, and Average Absorbances (515 nm), Reorientation Angle, and Absorption Anisotropy of EPANA in PS6 (2 wt%) for Different Irradiation Time, Obtained from Fitting Procedure

t[s]	A_{max}	A_{min}	A_{av}	α_{max} [°]	S
0	1.022	0.111	0.415	0.0	0.73
7	0.941	0.116	0.391	−0.1	0.70
15	0.882	0.120	0.374	7.1	0.68
30	0.779	0.199	0.392	26.0	0.49
60	0.708	0.213	0.378	45.0	0.44

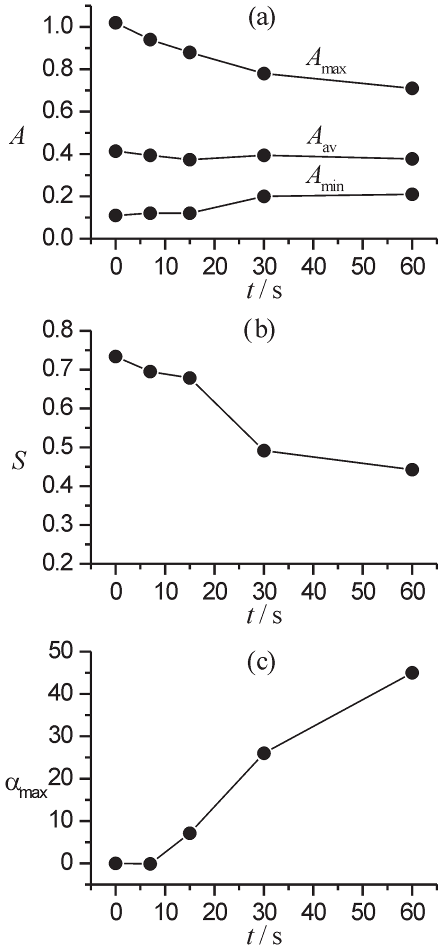


FIGURE 4 Absorbances (a), absorption anisotropy (b), and reorientation angle (c) of PS6-EPANA layer as functions of irradiation time.

indicates that the axially symmetric molecular distribution is preserved during the photoreorientation, and the process should be treated as a collective reorientation of the mesogenic ester side groups and the azobenzene molecules. Such a collective reorientation can be described by the direction of the symmetry axis of the molecular distribution, given by $\alpha_{\max}$. In this connection, one can draw an analogy between the photoreorientation process in PS6 admixed with EPANA and the Freédericksz electrooptical effect in liquid crystals [24]. Photoreorientation processes similar to those presented by PS6-EPANA mixture were observed for glassy state of liquid crystalline poly(acrylate) and poly(methacrylate) copolymers containing azobenzene groups [15,25].

CONCLUSION

The light-induced reorientation was observed in aligned films of a smectic side-group polysiloxane with azobenzene derivative of the pseudo-stilbene type admixture. The reorientation of the photoisomerizing molecules and the mesogenic groups occurs as a collective effect, which can be described as the reorientation of the symmetry axis of molecular distribution. The photoreorientation process is performed at room temperature in the smectic phase of PS6. At this temperature the polymer looses its plastic properties, connected with the introductory vitrification process in the material. The reorientational changes in the sample are stable at room temperature for a long period of time.

In contradiction to the case of the photoorientation in the glassy state of azobenzene containing polymers, a relatively low molar concentration of about 2% is sufficient for the reorientation process in side-group polysiloxane in its liquid crystalline state. From the other side, the photoreorientation of PS6-EPANA mixture aligned in a "sandwich" cell requires much higher irradiation intensities (about 50 times) compared the azobenzene copolymers.

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