Photo-Orientation Phenomena in Photochromic Liquid Crystalline Azobenzene-Containing Polymethacrylates with Different Spacer Length

Alexey Bobrovsky,* Valery Shibaev, Alexey Piryazev, Denis V. Anokhin, Dimitri A. Ivanov, Olga Sinitsyna, Vera Hamplova, Miroslav Kaspar, Alexej Bubnov

Synthesis and investigation of the phase behavior and photo-optical properties of two chiral liquid-crystalline polymers with azobenzene-containing side groups having different spacer lengths, 6 and 10 methylene groups (PMAzo-6 and PMAzo-10, respectively) are described. Formation of different smectic phases and high-temperature cholesteric phase is studied by polarizing optical microscope, differential scanning calorimetry, and X-ray investigations. It is shown that UV-irradiation induces effective reversible $E$–$Z$ photoisomerization in polymer solutions and films. Atomic force microscopy (AFM) study reveals substantial changes in the surface topography of the polymer PMAzo-6 film after UV-irradiation, whereas PMAzo-10 surface remains the same. Irradiation by polarized light (457 nm) results in photo-orientation process in polymer films consequential in significant alignment of the chromophores in direction perpendicular to the polarization plane of the incident light. A significant difference is found in thermal stability of the photoinduced alignment; an annealing of PMAzo-10 irradiated samples results in a slight decrease of dichroism values (down to 0.57); whereas the dichroism increases up to very high values (0.91) for PMAzo-6.

1. Introduction

Photochromic liquid-crystalline (LC) polymers represent a promising type of smart materials with high potential for a large variety of applications in optics and optoelectronics.[1,2] Among different types of photochromic fragments incorporated in polymer matrices, the azobenzene moieties are the most remarkable chromophores...
2. Experimental Section

2.1. Synthesis of MAzo-6 and MAzo-10 Monomers

Design of MAzo-6 monomer as starting material for resulting polymethacrylate was done according to general synthetic procedure represented in Figure 1. Detailed description of the specific reactions and steps together with 1H-NMR spectra of the intermediates and final products are presented in the Supporting Information. Monomer MAzo-10 was prepared by similar way and its molecular structure was confirmed by measurements of 1H-NMR spectra acquired on a spectrometer Varian 300 MHz in deuterochloroform as well.

The chemical purity of both materials was checked by high pressure liquid chromatography, which was carried out using a silica gel column (Biosphere Si 100-5 μm, 4 × 250, Watrex) with a mixture of 99.9% of toluene and 0.1% of methanol as an eluent, and detection of the eluting products by a UV–vis detector (λ = 290 nm). The chemical purity was found between 99.5% and 99.7%.

2.2. Polymerization

Photochromic polymers were prepared by a radical polymerization of corresponding methacrylic monomers (see the previous section) in benzene solution in the presence of 2 wt% (to monomer) of azobisisobutyronitrile (AIBN). After 3 d storage at 65 °C, the solvent was evaporated and solid product was washed several times by boiling ethanol. Yield of polymerization was about 70%. Such relatively low yield is explained by competing radical transfer reaction promoted by azobenzene fragment. During polymer synthesis, a lot of low-molar-mass products (dimers, short oligomers) are formed. Molecular masses (Mn) and polydispersity of polymers (Mw/Mn) were determined by gel permeation (GPC) chromatography using "Knauer" instrument.

2.3. Mesomorphic Behavior, Structural Properties, and Selective Light Reflection

The phase transition temperatures of the monomers and polymers were measured by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 8500. Dry nitrogen was purged through the DSC cell in order to stabilize the temperature. Standard aluminum pans with about 10 mg of sample material were used. The measurement program started from heating the sample from room temperature to 260 °C at a 10 °C min⁻¹ rate, followed by isothermal segment for 1 min, cooling to room temperature, another isothermal segment, and a second heating ramp.

Polarizing optical microscope (POM) investigations in order to determine the type of existing mesophases were performed using LOMO P-112 and Carl Zeiss Discovery V8 polarizing microscopes equipped by Mettler TA-400 heating stage. UV cut-off filter was used for preventing E–Z isomerization of azobenzene chromophores during POM observations.

In order to determine the mesophase structure, the X-ray diffraction studies were performed on monomers using Bruker Nanostar system (CuKα radiation, Vantec 2000 area detector,
MRI TCPU H heating stage), working in a transmission mode, and Bruker GADDS system (CuKα radiation, HiStar area detector) working in a reflection mode. In both systems, the temperature stability was 0.1 K. Powder samples (for Nanostar) were prepared in thin-walled glass capillaries (1.5 mm diameter); partially oriented samples for the experiments in reflection mode were prepared as droplets on a heated surface.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments were performed on polymethacrylate samples at the ID-10 beamline at European Synchrotron Radiation Facility (ESRF) (Grenoble, France). Diffraction patterns were collected with a Pilatus 300k detector (172 × 172 µm² pixel size). The wavelength of 1.24 Å was used. The measurements were performed on thin films deposited on Si substrate at an incidence angle of 0.2° that allows X-ray beam to probe all the thin film volume. The modulus of the scattering vector \( |s| = 2\sin\theta/l \), where \( \theta \) is Bragg angle, was calibrated using seven orders of Ag behenate for WAXS and three orders for small angle X-ray scattering (SAXS). In situ heating ramps were performed with a Linkam heating stage. For in situ UV-irradiation, Herolab UV-8S/L lamp (254&365 nm wavelength, 680 and 950 µW cm⁻²) placed directly above the sample at ~5 cm distance was used. Integration of 2D WAXS patterns was performed with home-made routines built in Igor Pro software (WaveMetrics Ltd.).

Thin polymer films were deposited on Si substrate by spin-coating using solutions in chloroform at 10 mg mL⁻¹ concentration with 1000 rot min⁻¹ speed to obtain film thickness of ~100 nm. In order to completely remove all traces of chloroform, the spin-coated films were kept at room temperature for 1 d. Fibers were drawn from the molten drop at a temperature of 190 °C.

For selective light reflection study, the polymer films were prepared between two glass plates coated with polyvinyl alcohol and rubbed in one direction in order to achieve a good planar alignment. The film thickness was predetermined by the use of 20 µm thick Teflon spacers. Before investigation, the films were annealed during 30 min 10 °C below the clearing point followed by slow cooling down (1° min⁻¹). Transmittance spectra were recorded by Hitachi U3400 UV–vis–atomic force microscopy (near infrared) spectrophotometer.

The surface morphology of polymer films was investigated with FemtoScan scanning probe microscope in semicontact mode of atomic force microscopy (AFM) in air at room temperature.
2.4. Photo-Optical Investigations

Thin polymer films for photo-optical experiments were obtained by spin-coating using chloroform solutions of different concentrations. In order to completely dry, the spin-coated films were kept at room temperature for 1 d. The film thickness was estimated from the UV-vis spectral data to be in the range of 100–200 nm.

Photochemical investigations were performed using an optical setup equipped with a DRSh-350 ultrahigh pressure mercury lamp and MBL-N-457 diode laser (457 nm, CNI Laser). To prevent the heating of the samples due to the IR irradiation of the mercury lamp, a water filter was introduced in the optical scheme. To assure the plane-parallel light beam, a quartz lens was applied. Using the filters, a light with the wavelengths 365 and 436 nm was selected. The intensity of light was measured by LaserMate-Q (Coherent) intensity meter and was equal to \( \approx 2.0 \text{ mW cm}^{-2} \) (365 nm), \( \approx 1.0 \text{ mW cm}^{-2} \) (436 nm) for lamp and \( \approx 0.3 \text{ W cm}^{-2} \) for laser.

Spectral measurements were performed using Unicam UV-500 UV–vis spectrophotometer with a linearly polarized laser beam (Glan–Taylor prism controlled by computer program). The dichroism values, \( D \), of the polymer films were calculated from the spectra using the following Equation (1)

\[
D = \left( A_p - A_{\perp} \right) / \left( A_p + A_{\perp} \right)
\]

where \( A_p \) and \( A_{\perp} \) are the absorbance parallel and perpendicular to the preferred azobenzene chromophore orientation direction, respectively.

In order to study the out-of plane photo-orientation phenomena, the angular distribution of the polarized absorbance spectra had been measured at an angle of about 45° with respect to the film layer normal.

3. Results and Discussion

3.1. Phase Behavior of the Polymethacrylates

The molecular distribution characteristics of the polymers and their phase behavior are presented in Table 1. According to the polarizing optical microscopy observations and DSC data, both polymethacrylates possess two LC mesophases (cf. Figures S1–S3 in the Supporting Information). At high temperatures, the textures of both polymers reveal the cholesteric phase, which is characterized by focal conics or planar textures with oily streaks and possesses a selective light reflection in the near-IR spectral range (Figure S4, Supporting Information). At lower temperatures, values of \( \lambda_{\text{max}} \) of both polymers have tendency to increase, demonstrating helix untwisting due to the formation of smectic order fluctuations. The low-temperature phase of PMAzO-6 polymethacrylate has an unspecific texture (Figure S2, Supporting Information), whereas PMAzO-10 polymethacrylate forms a fan-shaped texture after prolonged annealing (Figure S3, Supporting Information).

GIWAXS was employed to explore the mesophase structure of both polymers. Figure 2 shows 2D GIWAXS diffraction pattern measured on a thin polymer film prepared by spin-coating and subsequently annealed at 150 °C overnight. The diffraction pattern contains information on two different molecular organization levels: a series of peaks in the small-angle region reflects the layer-like organization of the mesogens at a large scale, whereas the broad peak (halo) at wide angles (4.4 Å) corresponds to local organization of the mesogen in the direction perpendicular to the mesogen long axes, similarly to liquid-like order.

For PMAzO-6 polymethacrylate, a group of diffraction peaks in the small-angle region infers the formation of a particular layer-like structure (Figure 2a). It can be suggested that layers possess a wavy interface, which gives rise to splitting of the 110 and 210 reflexes about the meridional direction of the pattern. Comparing obtained results with the literature data, it is possible to conclude that this phase has a structure similar to the so-called SmC* mesophase. In this rather exotic phase, the mesogens are organized in undulated smectic layers with a liquid-like order within the layers.

The cell parameters of PMAzO-6 polymethacrylate are as follows: \( a = 43.3 \text{ Å}, b = 26.9 \text{ Å}, \gamma = 78° \). In Table 2, the calculated and experimental \( d \)-spacing values are presented. There is a good match between the experimental and calculated values, obtained by fitting experimental peaks and by modeling the X-ray pattern from fitted lattice. Figure 3a schematically represents a possible model for corresponding molecular arrangement and the observable diffraction peaks. It is noteworthy that the mesogen length is close to one half of the corresponding unit cell parameter (i.e., the \( a \)-parameter). The number of mesogens per layer was calculated from the macroscopic density measured by flotation method (1.13 g cm\(^{-3}\)) and was found to be equal to six.

While comparing the mesogen-length and \( a \)-parameter, it is possible to observe the difference which can
be related to mesogen tilt inside the layer. Additional experimental evidence for the inclination of the side-chain segments in the structure of PMAzo-6 polymethacrylate can be obtained from X-ray measurements on uniaxially oriented samples (i.e., fibers). Indeed, a 2D diffraactogram given in Figure S5 (Supporting Information) clearly exhibits azimuthal splitting of the halo at 4.4 Å. The tilt of separated parts of scattering from 90° direction indicates the mesogen packing in chevron-like structures, i.e., they form a wave-like layer.

PMAzo-10 polymethacrylate also forms a bilayered structure, which however can be considered as a conventional. This can be confirmed by observation of several orders of the smectic peak (cf. Figure 2b) with the fundamental distance of 85.18 Å. This value was obtained by extrapolation of the diffraction orders because corresponding peak is located out of experimental range of our equipment. The diffraction peak positions are given in Table 3, and the phase structure is schematically shown in Figure 3b.

The temperature-dependent GIWAXS patterns correlate well with the DSC data (cf. Figure S6 in the Supporting Information). The N*–I phase transition at high temperatures were not observed on the integrated X-ray patterns due to absence of the halo peak within the measurement range. Two smectic phases observed below the transition to the N* phase were designed as the SmX(1)* and SmX(2)* phases, respectively. The transition between these two smectic phases (at 138 °C) visible on the corresponding DSC trace (Figure S2b, Supporting

### Table 2. Calculated and experimental d-spacing values for 2D unit cell of PMAzo-6 polymethacrylate.

<table>
<thead>
<tr>
<th>Miller indices</th>
<th>d [Å] (experimental value)</th>
<th>d [Å] (calculated value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 1</td>
<td>24.8</td>
<td>24.8</td>
</tr>
<tr>
<td>2 0</td>
<td>21.1</td>
<td>21.1</td>
</tr>
<tr>
<td>3 0</td>
<td>14.1</td>
<td>14.1</td>
</tr>
<tr>
<td>2 1</td>
<td>18.5</td>
<td>18.5</td>
</tr>
</tbody>
</table>
Information), gives rise to a substantial modification of
the X-ray diffractogram.

Thus, the first, second, fourth, and fifth orders of the
fundamental smectic peak disappear from the patterns
(cf. Figure S6b in the Supporting Information). Since
the positions of the remaining diffraction peaks did not
change, this modification reflects the internal layer reor-
ganization, which may be induced by enhanced mobility
of the alkyl chains. Therefore, the observed structural evol-
ution may consist of modification of the relative thick-
ness of the sublayers pertinent to the mesogen and alkyl
regions of the system, without changing the total smectic
layer thickness.

### Table 3. Calculated and experimental interlayer distances obtained for smectic SmX(1)^* and SmX(2)^* phases for PMAzo-10

<table>
<thead>
<tr>
<th>Order number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>Diffuse halo</th>
</tr>
</thead>
<tbody>
<tr>
<td>d, exp., [Å], SmX(1)^*</td>
<td>–</td>
<td>42.78</td>
<td>28.02</td>
<td>20.94</td>
<td>17.19</td>
<td>14.23</td>
<td>4.45</td>
</tr>
<tr>
<td>d, calc., [Å], SmX(1)^*</td>
<td>85.18</td>
<td>42.59</td>
<td>28.39</td>
<td>21.29</td>
<td>17.03</td>
<td>14.19</td>
<td>–</td>
</tr>
<tr>
<td>d, exp., [Å], SmX(2)^*</td>
<td>–</td>
<td>–</td>
<td>28.02</td>
<td>–</td>
<td>–</td>
<td>14.23</td>
<td>4.45</td>
</tr>
<tr>
<td>d, calc., [Å], SmX(2)^*</td>
<td>83.18</td>
<td>41.81</td>
<td>28.02</td>
<td>21.13</td>
<td>16.99</td>
<td>14.23</td>
<td>–</td>
</tr>
</tbody>
</table>

### 3.2. Influence of E–Z Photoisomerization of the
Azobenzene Chromophores in Polymer Films on the
Mesophase Behavior

The main absorbance peaks of the polymethacrylate
films demonstrate asymmetric shoulders (Figure 4
and Figure S7 (Supporting Information)), that could be
explained by the formation of the aggregates.\(^{[18,25]}\) UV-
irradiation of polymethacrylate films induces E–Z isomer-
ization of azobenzene chromophores which is confirmed
by significant changes in absorbance spectra presented in
Figure 4 and Figure S7 (Supporting Information). Strong
decrease in absorbance corresponding to \(\pi-\pi^*\) electronic
transition (337 nm) and increase in peak intensity for

![Figure 4. a) Spectral changes under UV-irradiation of amorphousized film of PMAzo-6 polymethacrylate (365 nm, 4.5 mW cm\(^{-2}\)). b) Spectral changes under visible irradiation of UV-irradiated fresh film (436 nm, \(\approx\)2.0 mW cm\(^{-2}\)). c) Kinetics of absorbance changes.](image)
n–π* electronic transition (≈450 nm) are clearly observed in the spectra.

According to results obtained by X-ray scattering, the smectic structure of thin annealed films of PMAzo-6 polymethacrylate gradually disappears during UV-irradiation (Figure 5a). This effect is associated with a decrease in the azobenzene groups’ anisometry during E–Z isomerization. The Z-isomers having low anisometry destroy the LC-order. The decrease of smectic 110 peak intensity for PMAzo-6 polymethacrylate is well described by the exponential law (Figure 5b, red curve), whereas for PMAzo-10 polymethacrylate, a substantial deviation from exponential law has been found. The characteristic transition time calculated from fitting process was found to be about 6 min. Annealing of the films induces recovery of the initial LC-state.

Photoinduced phase transition in PMAzo-6 polymethacrylate enables to control surface topography of polymer films. Figure 6a,b shows AFM scans of the polymer film surface before and after UV-irradiation. Ridge-like structures (with width of 740 ± 110 nm and the height of 60 ± 20 nm) were observed on the film surface before UV-irradiation. In the direction perpendicular to the ridges, periodic height changes with a step length of 90–150 nm have been found. The latter is associated with the smectic order in PMAzo-6 polymethacrylate as it disappears after UV-irradiation, and is reforming back after annealing. After UV-irradiation, the ridges are broadened; their average height increases to 130 ± 30 nm (Figure 6b). The mean-square roughness of the surface grows from 20 to 60 nm.

In contrast, PMAzo-10 polymethacrylate films have smooth isotropic surface, consisting of polymer blobs with the height of ≈1 nm and the size of ≈30 nm in the surface plane (Figure S8a, Supporting Information). The films contain some bumps and pores (Figure S9b, Supporting Information), which probably get up during the preparation process. No significant changes of the surface morphology of PMAzo-10 polymethacrylate film were observed after UV-irradiation.

Thus, spacer length plays a very significant role in the topography changes under UV-irradiation of polymer films. Probably, separation of the chromophores from the polymer backbone by the longer flexible spacer in PMAzo-10 polymethacrylate completely suppresses formation of any features in surface topography as well as their changes during E–Z photoisomerization.

3.3. Photo-Orientation and Reorientation Processes in Polymer Films under Polarized Light Action

Irradiation of amorphousized spin-coated polymethacrylate films by polarized blue light (457 nm laser)
induces photo-orientation process, i.e., alignment of azobenzene chromophores in direction perpendicular to the polarization plane of the incident light. This effect becomes apparent as strong dichroism in absorbance of the polarized light (Figure 7a, b and Figure S9 (Supporting Information)). It is noteworthy that rate of the dichroism growth is a little bit higher for PMAzo-6 polymethacrylate (Figure 7c). The obtained values of the dichroism are very large and noticeably higher than for the previously studied polyacrylate with the same chromophore (0.75 vs 0.57).[18]

A significant difference was found in thermal stability of the photoinduced dichroism. Thus, annealing of the irradiated samples of PMAzo-10 polymethacrylate at 120 °C (temperature corresponding to the SmX(1)* phase) leads to slight decrease in dichroism values (to 0.57), whereas for PMAzo-6 polymethacrylate, D values increases up to 0.91. This thermal behavior of the irradiated films is completely different in comparison with the previously studied polyacrylate with the same chromophore (0.75 vs 0.57).[18]

A significant difference was found in thermal stability of the photoinduced dichroism. Thus, annealing of the irradiated samples of PMAzo-10 polymethacrylate at 120 °C (temperature corresponding to the SmX(1)* phase) leads to slight decrease in dichroism values (to 0.57), whereas for PMAzo-6 polymethacrylate, D values increases up to 0.91. This thermal behavior of the irradiated films is completely different in comparison with the previously studied polyacrylate with the identical chromophore structure.[18] For the polyacrylate, an annealing was found to fully disrupt photoinduced alignment due to the transition to homeotropic state (with chromophores oriented along normal to the film plane).

Alternate rotation of polarization plane of excitation light allows one to realize many cycles of chromophore reorientation in both amorphousized and annealed polymer films (Figure 8). At each irradiation cycle, polarization plane is rotated by 90° with respect to the previous one. Important peculiarities, namely the decrease of the orientation rate and maximal achievable dichroism value after first irradiation cycle (~0.6 instead ~0.75) can be observed in Figure 8b, c. This phenomenon is associated with partial out-of-plane chromophore orientation which is confirmed by measurements of the polarized absorbance spectra of the film tilted by 45° with respect to the probe beam (Figure S10, Supporting Information). Reorientation occurs through the out-of-plane oriented state (at ~60 s of irradiation) for both amorphousized and annealed films. Investigation of the reorientation phenomena in amorphous and annealed LC polymer films showed that in annealed films, reorientation proceeds is slower but the maximal values of D remain about the same (Figure 9), i.e., LC state of the film slows down the rate of the reorientation, but does not suppress chromophore alignment.

Thus, irradiation of polymer films enables to achieve strong uniaxial alignment of the chromophores with extremely high values of the photoinduced dichroism. Alternate rotation of polarization plane of excitation light during photo-orientation experiments allows making many cycles of chromophore reorientation. Investigations of the kinetics of this process have revealed influence of
LC-order of the films on the rate of this process, however the values of the photoinduced dichroism are the same for amorphous and LC-films.

4. Conclusions

Two new azobenzene containing chiral monomers and corresponding LC polymethacrylates with azobenzene-containing side groups with different spacer length, 6 and 10 methylene groups (PMAzo-6 and PMAzo-10, respectively) were obtained. Their mesomorphic behavior and photo-optical properties were studied. POM, DSC, and X-ray investigations reveal formation of different smectic phases and a broad temperature range of the cholesteric phase.

UV-irradiation induces effective reversible \(E\text{--}Z\) photoisomerization in polymer solutions and films. As was shown by AFM study, UV-irradiation of polymer films results in noticeable changes in the surface topography of PMAzo-6 polymethacrylate film, whereas for PMAzo-10 polymethacrylate film, surface remains unchanged. Irradiation by polarized blue light (457 nm) results in photo-orientation process in polymer films resulting in significant alignment of the chromophores in direction perpendicular to the polarization plane of the incident light. The significant difference was found in thermal stability of the photoinduced alignment; an annealing of the irradiated samples of PMAzo-10 polymethacrylate leads to slight decrease in dichroism values (to 0.57), whereas
for PMAzo-6, polymethacrylate dichroism increases up to very high values (0.91).

For the first time, the reorientation process in azobenzene-containing polymers induced by polarized light with alternate changing of the direction of the polarization plane was studied. A possibility of performing cycles of reorientation without any fatigue has been demonstrated. Further studies related to this topic are in progress now and will be presented elsewhere.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements: This research was supported by the Russian Foundation for Basic Research (grant nos. 16-03-00455, 16-29-05140, study of photo-optical properties of PAAzo) by the Russian Science Foundation (14-13-00379, study of the phase behavior of the polymers) and Scholarships of the President of the Russian Federation for young scientists and graduate students (№ SP-2238.2016.1, study of the mesophases structure by X-ray). Authors (V.H. and A.B.) greatly acknowledge the financial support of the MEYS LH15305 and the CSF 16-12150 research projects.

Conflict of Interest: The authors declare no conflict of interest.

Received: March 11, 2017; Revised: April 17, 2017; Published online: ; DOI: 10.1002/macp.201700127

Keywords: azobenzene; liquid crystalline polymers; photo-isomerization; photo-orientation phenomena