Liquid crystals photoalignment by films of side-chain azobenzene-containing polymers with different molecular structure

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ABSTRACT

Liquid crystals photoalignment on the films of several side-chain azobenzene-containing polymers with various molecular structures was studied. Kinetics of the alignment and realignment of the liquid crystals director under irradiation by the polarized light was investigated and a comparison of the rates of polymers’ azobenzene moieties reorientation and director realignment were performed. The degree of the orientation, stability of the alignment, the possibility of multiple reorientation and other parameters of the photoinduced processes occurring in polymers films and liquid crystal cells were studied in detail. A rubbing technique was applied as alternative method for LC-alignment using these azobenzene-containing polymers. It was shown that the studied azobenzene-containing polymers can be considered as a photocontrollable command surfaces for the application in display technology and optoelectronics.

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1. Introduction

The main approach for alignment of liquid crystal (LC) mixtures for display application is the rubbing method [1–3]. Usually, indium tin oxide (ITO) coated glass substrates are covered by thin polyimide layer followed by rubbing with textile, cloth or special roller. Anisotropy of the surface energy originating from the polymer surface topography or microscopic molecular structures of the polymer coating has been proposed for alignment origin [4–6]. It should be pointed out, that the rubbing technique has a number of disadvantages, such as an appearance of electrostatic charges, dust particles etc. This process does not lead itself to the manufacture of multidomain alignment layers that are necessary to increase the limited viewing angle in the LC displays.

A relatively new alternative method for aligning of LC materials is photoalignment [7–9]. This technique implies the creation of aligning layer by using photochromic low-molar-mass or polymer film in the form of coating irradiated by polarized light (Scheme 1). Polarized light induces an uniaxial orientation of photochromic moieties and such irradiated layer can work as “command surface” [9] and orient nematic (or smectic) LC-director of low-molar-mass liquid crystal in the same direction.

There are many papers devoted to the study of the different photoalignment materials and mechanism of alignment phenomena. Mostly studied materials for this purpose can be divided into the two types, cinnamoyl-, coumarin-containing polymers [10,11] and azobenzene based materials [12–29]. Cinnamoyl fragments undergo under UV-irradiation two main thermally irreversible processes, E–Z isomerization and {2+2} photocycloaddition, whereas azobenzene photochromes are characterized by reversible E–Z isomerization. For both types systems a polarized light induces selective excitation of photochromes oriented along polarization direction. After selectively excited photoreaction some degree of anisotropy (orientation of chromophores) in polymers films is appeared. Chromophores orientation leads to surface energy anisotropy which is quite enough for LC director alignment. Resulting alignment direction in the case of azobenzene-containing systems is a perpendicular to the polarization plane of the light used for photoalignment. For the photocrosslinkable polymer coatings parallel LC alignment is observed, and, in some cases, alignment switching between perpendicular and parallel alignment takes place frequently during polarized light action [29,30].

Despite a large number of papers devoted to the problems of photoalignment, there is a lack of information about the usage of azobenzene-containing side chain LC polymers for liquid crystals alignment. In the present paper we have performed a detailed comparative study of photoalignment processes on substrates coated by several LC and one amorphous azobenzene-containing polymers having different spacer lengths, type of the mesophase and structure of aromatic cores:
The photoalignment behaviour of the polymers Pazo4M, Pazo6M, Pazo10M and PA10HAzo* was studied in the present paper for the first time.

A number of commercially available LC nematic mixtures were used for alignment study. In order to determine quality and degree of LC-director alignment the nematic mixtures were doped by dichroic merocyanine dye ASh253 [31].

According to polarizing optical microscopy and DSC data, polymer Pazo is amorphous, polymer Pazo4M forms only nematic phase, another polymers, Pazo6M, Pazo10M and PA10HAzo* are characterized by smectic phases (Table 1).

Thus, the main goal of this work is to compare different photoaligning substrates and find optimal polymer structure for achieving good uniform LC-alignment, best reorientation capability and high stability of obtained LC-alignment. Another interesting topic of our investigation is a study of the possibility of using above-mentioned compounds for LC-alignment by conventional rubbing and comparison this technique with photoirradiation by polarized light.

2. Experimental

2.1. Materials

Polymer Pazo (poly[1-[4-(3-carboxy-4-hydroxy-phenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt) by Aldrich was used as received.

Monomer Azo4M and Azo10M were synthesized by Kostromin and Stakhanov [32], we express our thanks for providing these substances. Synthesis of monomer A10HAzo* was described in [33]. Monomer Azo6M was synthesized by us using standard techniques [34].

Photochromic polymers Pazo4M, Pazo6M, Pazo10M and PA10HAzo* were synthesized by a radical polymerization of corresponding acrylic monomers in benzene solution in the presence of 2 wt.% (with respect to monomer) of AIBN. After 3 days storage at 65 °C the solvent was evaporated and solid product was washed several times by boiling ethanol. Yield of polymerization was 60–70%. Such relatively low yield is explained by competing radical transfer reaction promoted by azobenzene fragment. Molecular masses and polydispersity of polymers as determined by GPC chromatography using instrument “Knauer” are listed below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>(M_w) (g/mol)</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pazo4M</td>
<td>(\sim 19,500)</td>
<td>2.1</td>
</tr>
<tr>
<td>Pazo6M</td>
<td>(\sim 13,700)</td>
<td>1.9</td>
</tr>
<tr>
<td>Pazo10M</td>
<td>(\sim 3,4000)</td>
<td>2.3</td>
</tr>
<tr>
<td>PA10HAzo*</td>
<td>(\sim 12,400)</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Values of molar masses are relatively low in comparison with other acrylates and methacrylates without azobenzene fragments. It is explained by the high value of the chain transfer constant with respect to a double \(N=N\) bond of photochromic monomers. This effect is associated with the formation of a stable hydrazyl radical [35,36].

The photoaligning properties of these polymers were compared with well-known low-molar-mass azobenzene-containing substance having good well-studied photoaligning properties (SD1) [7].

The photoalignment behaviour of amorphous polymer Pazo only for polyelectrolyte complex layered structures was successfully described in [16], but we did not find any paper concerning photoalignment properties of the pure Pazo films.

Table 1

<table>
<thead>
<tr>
<th>Substance</th>
<th>(T_g) (°C)</th>
<th>Phase transitions (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pazo</td>
<td>–*</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Pazo4M</td>
<td>58</td>
<td>N 158-159 I</td>
</tr>
<tr>
<td>Pazo6M</td>
<td>48</td>
<td>SmA 133-136 I</td>
</tr>
<tr>
<td>Pazo10M</td>
<td>41</td>
<td>SmA 164-167 I</td>
</tr>
<tr>
<td>PA10HAzo*</td>
<td>–*</td>
<td>Cr 118 SmC* 145 SmA* 154 N* 194 I</td>
</tr>
</tbody>
</table>

* Glass transition was not detected.
2.1.1. Study of phase behaviour of azobenzene-containing polymers

The phase transition temperatures of the polymer were detected by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 thermal analyzer (a scanning rate of 10 K/min).

The polarizing optical microscope investigations were performed using a Mettler TA-400 thermal analyzer and a LOMO P-112 polarizing microscope.

2.1.2. Cells preparation and LC-photoalignment study

For investigation of LC-alignment the glass or quartz cells with a gap of 30 μm predetermined by Teflon spacers were prepared. Before assembling of cells the glass (or quartz) substrates were spin-coated by chlorophorm solution of azobenzene-containing polymers (with concentration of 1–5 mg/ml). For PAzo and SD1 methanol was used as a solvent. Thickness of the films was estimated by AFM method (NTEGRA, NT-MDT, Russia) and was in most cases 15–50 nm depending on the polymers concentration. For study of the chroomophore reorientation films with a thickness of about 300 nm were prepared. After that, prepared cells were irradiated using a special optical set up equipped with a DRSh-250 ultra-high pressure mercury lamp. To prevent the heating of the samples due to the IR irradiation of the mercury lamp, a water filter was introduced in optical scheme. In most cases we have used polarized polychromatic light (PPL) of lamp due to its highest intensity (~15 mW/cm²) and presence of Hg-lines inducing photoorientation process very efficiently (365 nm, 405 nm and 436 nm). Presence of long-wavelength lines (405 and 436 nm) shifts photostationary equilibrium to E-form preventing disruption of photooriented polymer structure by bent-shaped Z-isomer. In some cases, using the interference filters a light with the wavelengths 365 nm and 436 nm were selected in the case of Hg lamp. Glan–Taylor prism was used as a polarizer. The intensity of light was measured by LaserMate-Q (Coherent) intensity meter.

After 10–20 min of PPL irradiation the cells were filled with the mixture containing nematic mixture MLC6816 (cyclohexane derivatives) or E48 (cyanobiphenyl derivatives), both from Merck. In order to estimate degree of LC-orientation 0.1 wt.% of dichroic dye ASΗ253 was added (absorbance maxima is 610 nm in MLC6816 host).

The linearly polarized spectra of the film samples were studied with a TIDAS spectrometer (J&M) equipped with rotating polarizer (Glan–Taylor prism controlled by computer program).

The dichroism values, D, of the empty or filled films were calculated from the spectra using the following Eq. (1):

\[
D = \frac{A_\parallel - A_\perp}{A_\parallel + A_\perp}
\]

where \(A_\parallel\) and \(A_\perp\) is polarized absorbance along and perpendicular to the preferred chromophores orientation, respectively.

3. Results and discussion

3.1. Photoorientation phenomena in thin spin-coated films of azobenzene-containing polymers

Before investigations of LC-alignment properties, let us consider some aspects of the photoorientation phenomena in thin spin-coated films of azobenzene-containing polymers and SD1. Spin-coating allows one to obtain amorphous films of all polymers because rate of solvent evaporation is very high that is preserve films from LC order formation. Photoorientation processes in SD1 and polymer PA10HAzo* were described in detail in [7,15,37], respectively.

As seen from the normalized absorbance spectra in Fig. 1a, all polymers possess absorbance maxima corresponding to π–π* electronic transition in the UV spectral range, whereas absorbance in the visible spectral region is negligible. It is noteworthy that for LC-photoalignment in most cases we have used very thin films of polymers having absorbance below ~0.01 at wavelengths corresponding to π–π* electronic transition.

Fig. 1b and c shows kinetics of dichroism growth during irradiation with polarized polychromatic light (PPL) of mercury lamp for polymers PAzo and PAzo4M. For all polymers and SD1 PPL irradiation induces photoorientation of azobenzene moieties in direction perpendicular to polarization plane of incident light. For the amorphous ionogenic polymer PAzo maximum value of photoinduced
dichroism is about 0.12, whereas for nematic polymer PAzo4M value D is two times higher. It is noteworthy, that annealing of irradiated PAzo films slightly decreases dichroism (Fig. 1a), whereas for PAzo4M noticeable increase of dichroism values was found (Fig. 1b). This effect is well-known and described in the literature as the so-called “gain effect” [38]. The gain effect is associated with formation of the nematic phase during annealing leading to improved uniaxial orientation in the system.

For irradiated films of polymers subsequent changing of the polarized light direction in direction perpendicular to the initial induces reorientation of chromophores (Fig. 1b). This effect was observed for all studied polymers, and many cycles of reorientation are possible.

### 3.2. LC-photoalignment in cells prepared using azobenzene-containing polymers and SD1

Fig. 2a demonstrates the polarized absorbance spectra of nematic mixture MLC6816 doped by dichroic dye ASH253 in PPL irradiated cell prepared using glass substrates coated by PAzo4M. Polarized spectra and polar diagram in Fig. 2b give good representation of a nice uniaxial alignment of LC molecules inside irradiated cells. Direction of orientation is completely coincides with direction of azobenzene moieties orientation and perpendicular to the polarization plane of the incident light used for photoalignment. Values of dichroism, D, corresponding to absorbance of dichroic dye (at 610 nm) for all photoalignment substances are listed in the first column of Table 2. As seen from Table 2, values of D are almost the same and lie between 0.66 and 0.72, within experimental error of dichroism calculation. It is noteworthy, that conventional method of LC-alignment, namely rubbing of polyvinyl-alcohol-coated substrates gives the similar results (Table 2). Nevertheless, according to polarizing optical microscopy of aligned cells photoalignment provides more homogeneous orientation, without stretches and dust, if compare with rubbing technique.

Irradiation with monochromatic light of wavelengths 365 nm and 436 nm qualitatively showed the same results, but due to the lower light intensity more prolonged irradiation is necessary for alignment.

LC alignment for all cells containing MLC6816, i.e. mixture of cyclohexane derivatives, is stable. Cells filled by nematic mixture E48 showed good alignment only with ionogenic PAzo or SD1 photoaligning layers. Another azobenzene-containing polymer induces only poor (or unstable in time) LC-orientation due to the partial solubility of alignment layer.

### 3.3. Study of LC-director reorientation in photoaligned cells

We have investigated kinetics of reorientation and realignment of LC-director under PPL with polarization axis perpendicular to the initial direction. For this purpose two cells based on quartz substrates spin-coated with PAzo were prepared. Both cells were irradiated by PPL during 10 min. The first cell was filled by mixture MLC1686 doped with dichroic dye ASH253, whereas, the second cell was filled by MLC6816 without any additive. The first cell was selected for study of kinetics of LC-director realignment measured by dichroism of dichroic dye at 610 nm. The second cell was used for a study of azobenzene moieties reorientation, because the nematic mixture MLC6816 without dye does not absorb light within the range of the azobenzene absorbance.

Dichroic dye dichroism (at 610 nm) changing during realignment is shown in Fig. 3. During the first 5 min of irradiation dichroism value is almost unchanged, then, suddenly and fast decreases, going through the zero, and after 10 min of irradiation reaches steady negative value. The negative sign of the dichroism corresponds to LC-director oriented perpendicular to the initial orientation. It is noteworthy, that such “threshold” behaviour was found for all polymer photoalignment coatings studied in this paper.

Kinetic curve of azobenzene moieties reorientation (at 364 nm) has completely different smooth shape (Fig. 3). Dichroism start to decrease after the first seconds of irradiation and drops to zero after only 2 min of irradiation. After 10 min D values reach the steady negative values. Comparison of these two curves in Fig. 3 gives us opportunity to compare kinetics of both processes. Thus, LC-director reorientation process has threshold-like behaviour or noticeable “activation energy barrier” because after irradiation of only 5 min the degree of azobenzene units reorientation became

### Table 2

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Photoalignment</th>
<th>Reorientation</th>
<th>Rubbing</th>
<th>Reorientation after rubbing</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA</td>
<td>D1</td>
<td>−0.11</td>
<td>0.69</td>
<td>−0.63</td>
</tr>
<tr>
<td>SD1</td>
<td>0.67</td>
<td>−0.11</td>
<td>0.69</td>
<td>−0.63</td>
</tr>
<tr>
<td>PAzo4M</td>
<td>0.66±0.03</td>
<td>−0.61±0.03</td>
<td>0.65</td>
<td>−0.30</td>
</tr>
<tr>
<td>PAzo4M</td>
<td>0.72±0.04</td>
<td>−0.70±0.02</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>PAzo6M</td>
<td>0.69</td>
<td>−0.64</td>
<td>0.55</td>
<td>0.53</td>
</tr>
<tr>
<td>PAzo10M</td>
<td>0.71</td>
<td>−0.42</td>
<td>0.65</td>
<td>0.62</td>
</tr>
<tr>
<td>PAzo10A</td>
<td>0.72</td>
<td>−0.79</td>
<td>−0.79</td>
<td>−0.79</td>
</tr>
</tbody>
</table>

a No any preferred orientation was found.
b Average numbers and errors were obtained by the statistical treatment of cyclic irradiation data. In all other cases errors of D estimation was less than ±0.05.
c No reorientation takes place.

---

**Fig. 2.** (a) Polarized absorbance spectra of nematic mixture in cell prepared using PAzo4M as photoaligning substrate. (b) Corresponding polar diagram of absorbance. Before filling cell was irradiated by PPL for 10 min.
very high; at the same time the realignment of LC-director was not initiated yet.

All systems, except low-molar-mass compound SD1 and polymers PAzo10 M and PA10HAzo° demonstrate good reorientation ability under cycles of PPL irradiation with alternating direction of the polarization [see Table 2 and Fig. 4]. The origin of reorientation suppression for SD1, PAzo10 M and PA10HAzo° coatings is still unclear. Probably, LC molecules of low-molar-mass nematic mixture induce a “memory effect” and mesogenic azobenzene groups of the polymer “remember” the position achieved after first irradiation cycle.

3.4. LC-alignment using the rubbing and subsequent photoinduced reorientation of the LC-director

We have studied an influence of rubbing by cloth as alternative method of using these azobenzene-containing substances for LC-alignment. In order to reproduce results, several cells each having rubbed coatings were prepared. As clearly seen from Table 2 rubbing technique allows one to obtain a good orientation in the case of SD1, PAzo, and PAzo10 M. For other systems lower values of dichroism and poor reproducibility of alignment were observed. Polarizing spectroscopy measurements reveal small values of dichroism and poor reproducibility of alignment were observed. Polarizing spectroscopy measurements reveal small values of dichroism induced for SD1 coating by rubbing; from the other hand we did not find any dichroism for polymer systems. In order to find a plausible explanation of this difference AFM investigation of rubbed coating are planned for the future.

It is interesting to note that subsequent irradiation of cells with PPL having polarization direction coinciding with rubbing direction gives positive results only for SD1 coating (Table 2). For polymer coating, a complete reorientation does not take place (Fig. 5). In other words, rubbing and formation of surface relief formed during this process plays a crucial role in LC alignment. Subsequent orientation of azobenzene moieties can not change significantly the alignment direction.

3.5. Photopatterning of photoalignment coatings for latent image recording

A possibility of photopatterning of cells coated by different azobenzene-containing substances was demonstrated. For this purpose a cell was first irradiated by PPL with definite polarization direction. Then, the cell was irradiated using the mask with PPL having polarization rotated by 45° or 90° with respect to the initial polarization.

Fig. 6 shows the photos of the photopatterned cell prepared using PAzo4 M as photoalignment coating filled with the nematic mixture containing dichroic dye. Image of letters “МГУ”, which mean the Russian abbreviation of “Moscow State University” can
not be seen without a polarizer. The image becomes visible when the polarizer is placed on the top of the cell. Moreover, polarization rotation changes the image from the positive to the negative.

4. Conclusion

In summary, several azobenzene-containing compounds including side-chain LC polymers were studied from the point of view of LC-photoalignment ability. Kinetics of alignment and realignment were studied and the rates of azobenzene moieties reorientation and LC-director realignment were compared. It was shown that the amorphous and nematic polymers PAzo and PAzo4M posses a high degree of orientation, good stability, and possibility of multiple reorientation. These polymers can be considered as very promising materials for application in display technology and optoelectronics.

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References