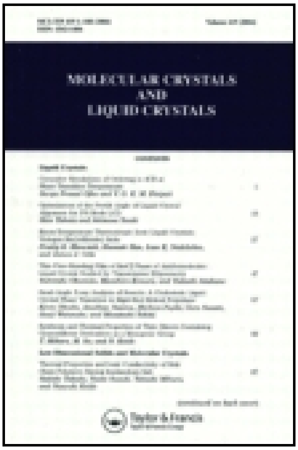

Molecular Crystals and Liquid Crystals

Azodyes as Photo-Alignment Materials for Liquid Crystals

Boris Umanskii [a] , Nikolai Novoseletskii [a] , Sofia Torgova [a] & Galina Dorozhkina [a]

[a] Federal State Unitary Enterprise, State Research Center, Moscow, Russia

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AZODYES AS PHOTO-ALIGNMENT MATERIALS FOR LIQUID CRYSTALS

*Boris A. Umanskii**, *Nikolai V. Novoseletskii, Sofia I. Torgova, and Galina N. Dorozhkina*
Federal State Unitary Enterprise, State Research Center, NIOPIK B. Sadovaya 1/4, Moscow 123995, Russia

The photo-generation of optical anisotropy by irradiation of linearly polarized light was investigated for spin-coated films of individual insoluble in liquid crystals (LC) azodyes and the same dyes incorporated in polymer matrix. The different soluble in LC azodyes were also investigated as orienting agents. The photo-alignment of azodyes was studied in the bulk of guest-host LC samples in the cells with different surfaces of glass plates.

Keywords: azodyes; chemical structure; H-bonds; liquid crystals, photo-alignment

INTRODUCTION

For the fabrication of liquid crystal displays (LCD) the uniform alignment of liquid crystals (LC) is indispensable. Mechanically rubbed polyimide films are generally used to achieve the uniform alignment. The unidirectional LC alignment is typically produced by the surface rubbing techniques of the polymeric LC alignment layers [1,2]. This method, however, has several problems such as the generation dust particles and electrostatic charges. To resolve these problems rubbing-free techniques are desired.

Recently, it has been reported many investigations of LC alignment obtained by irradiation of linearly polarized UV light [3–5]. One type of photo-aligning materials is based on photo-isomerization of azo-containing chromophore. Such materials are used as orienting films, which can be individual azodyes, polymers with azodye fragments and azodyes incorporated

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*Coresponding author. Tel.: (007-095) 408-87-72, E-mail: uman@aha.ru in polymer matrix. For such films were used azodyes insoluble in LC. Moreover LC alignment could be achieved on nonphotosensitive substrates by azodyes dissolved in LC matrix [6–9].

Previously we have investigated the orienting ability of different azodye films, the influence of chemical structure of different solvents used for spin-coating on the LC photo-aligning characteristics and electro-optic properties of twist nematic photoaligned cells [10–13]. The aim of this work is to analyze the influence of chemical structure of azodyes used as photo-orienting layers and dissolved in the bulk of LC matrix on their aligning capability.

EXPERIMENTAL

The chemical structures of the investigated azodyes are given in the table. All compounds were synthesized in NIOPIK except X and XVIII which are standard chemical indicators (products of NPO “Biochemreactive”). Some of the dyes (I–XIV) are soluble in liquid crystals, so for our experiments they were just dissolved in LC with definite percentage. The other dyes (XV–XVIII) are insoluble in liquid crystals therefore they were used either as individual dye films or they were incorporated into polymer layers (polyamide acid – PAA).

As a nematic liquid crystal material was used ZhK-1289 (commercial product of NIOPIK). For soluble dye we have investigated the influence of dye concentration on the type of LC orientation. For other investigations we used 0.4% solutions of azodyes in LC matrix.

For investigation of aligning capability of insoluble in LC azo-dyes incorporated in polymer matrix the aligning films of compositions of azodyes with PAA were formed on glass substrates by spin-coating of the polymer-azodye solutions in three different solvents, namely dimethylformamide (DMF), N-methylpirrolydone (N-MPD) and ethylcellosolve (ECS). Then coated substrates were annealed at 180°C for 1 hour.

For the investigation of aligning capability of soluble azodyes glass substrate coated with pure PAA were prepared. For the compound X (Methyl Red) we have investigated the influence of the cell surface nature on its ability to orient LC. For this purpose we prepared six different surfaces of the cell: glass plates coated with indium-tin oxide (ITO), polyamide acid (PAA), polyacrilic acid (PAcA), polyvinylalcohol (PVA), bare glass plates and bare quartz plates.

LC cells were fabricated by assembling of two substrates by gluing with epoxy glue. Calibrated spacers gave the cell’s thickness equaled 12 μm. After that empty cells with photosensitive substrates were irradiated by a polarized light beam directed normally to the plates and then they filled with LC material. Another group of LC cells without photosensitive substrates were filled with LC dopped by azodye at the temperature, higher than clearing point of LC. Then they were irradiated with a polarized light.

For irradiation we used 250 W high-pressure mercury lamp. The irradiation time was 1–30 min, the light intensity was 60 mW/cm^2. The dose of radiation was varied by changing of the time for exposure. The band-pass filter (460 nm) and Glan polarizer were used for getting required light conditions.

RESULT AND DISCUSSION

The main mechanism of photo-alignment by azodyes, as it is known from literature, is cis-trans isomerisation under UV-light [6]. According to our experimental results this property is necessary, but not enough. As one can see from the table, the irradiation by linearly polarized UV light of compounds I–IX doesn't show any LC alignment while irradiation of the compounds X–XVIII results in LC alignment. Moreover, when insoluble azodyes were used as orienting films even the chemical structure of the solvents used for spin coating procedure played a very important role. For example, the dyes XVI, XVII with the solvents N-MPD and DMF leads to homeotropic LC orientation, while solvent ECS results to planar orientation. The dye XV leads to planar orientation with every solvent mentioned above.

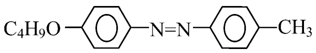
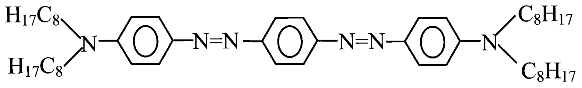
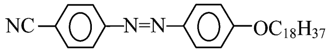
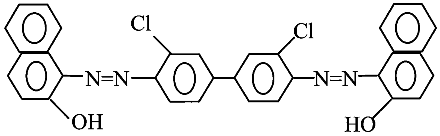
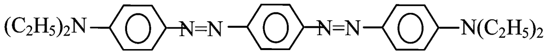
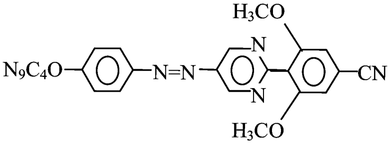
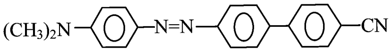
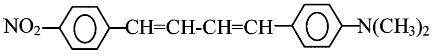
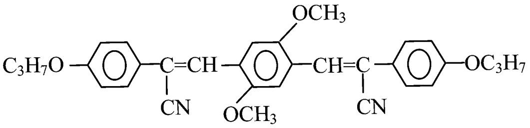
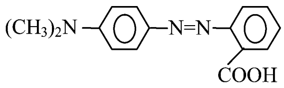
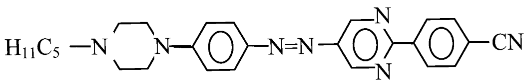
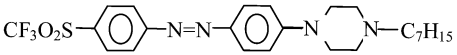
The main difference in the chemical structure in-between compounds XVI, XVII and XV is the presence in the last one the substituents which are the donors of the protons for hydrogen bonds (H-bonds) formation, namely carboxyl and hydroxyl substituents (Table). From the point of view of H-bonds formation it is also possible to explain the influence of the solvents. Solvent ECS is the strong donor of protons, so it is able to form H-bonds with the surface and with compounds XVI, XVII as well.

From these facts follow that formation of H-bonds plays a crucial role on the aligning capability of azodyes due to the ability to preserve orientation by the increasing of anchoring energy. Thus the chemical nature of the substituents in the photosensitive molecule and the chemical nature of the solvent used for spin coating as well determine the type of LC orientation.

When azodyes are soluble in LCs the probability of their practical application as orienting agents in LCD manufacturing is negligible. However, the investigation of the LC photoinduced alignment on nonphotosensitive substrates of the cell filled with LC dopped by photosensitive dye is very useful for elucidation of the mechanism of alignment by photoisomerised molecules.

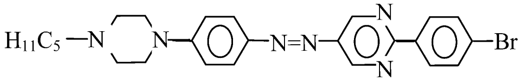
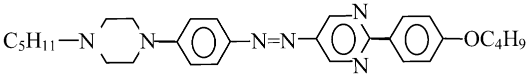
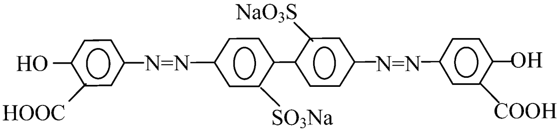
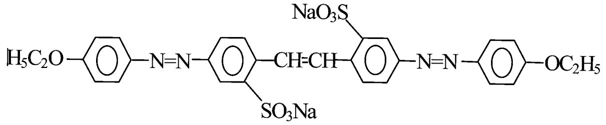
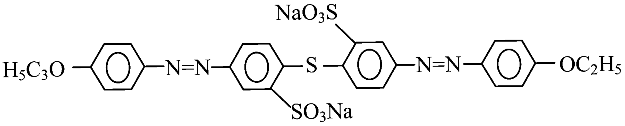
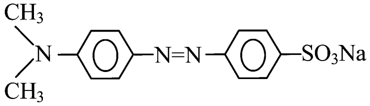
We have studied some azodyes dissolved in LC matrix. It is evident from the Table that among investigated soluble azodyes some of them result to

TABLE Chemical Formulae of Investigated Azo-Dyes

N/N	Chemical formulae	Orientation
I		no
II		no
III		no
IV		no
V		no
VI		no
VII		no
VIII		no
IX		no
X		yes
XI		yes
XII		yes

(Continued)

TABLE (*Continued*)

N/N	Chemical formulae	Orientation
XIII		yes
XIV		yes
XV		yes
XVI		yes
XVII		yes
XVIII		yes

LC alignment (compounds X–XIV) while others don't exhibit any photoinduced alignment. Analysis of the structure of these dyes makes it possible to relate the presence of some substituents with the aligning ability of the dyes. Among dyes investigated we have revealed only two such substituents: piperasene fragment and carboxyl one. Both of these fragments are able to form H-bonds with the surface containing hydroxyl. As it was mention above we used LC cells with different type of surfaces. On the substrates coated with PAA, PVA, PacA and for bare glass and bare quartz which have hydroxyl-groups on the surface after irradiation with linearly polarized light the photoinduced alignment arise due to the photoisomerization of dye molecules attached to the surface by H-bonds. While on the substrates coated with ITO, which have no hydroxyl-groups and don't form

H-bonds with azodyes no alignment arises under irradiation by linearly polarized light. We can conclude, that photoisomerisation of dye molecules in the bulk of LC doesn't cause LC alignment.

We have also investigated some derivatives of stilbene soluble in LC matrix (compounds VIII-IX), which also exhibit cis-trans isomerisation under UV light. No any photoinduced alignment with stilbene derivatives has been found.

It is necessary to underline that azodye Methyl Red (compound X) which has carboxyl group results to photoinduced planar or twist orientation only if its concentration is less than 0,5% (wt). For 1% (wt) concentration after irradiation with linearly polarized light the homeotropic LC orientation arises. For concentrations more than 1,5% (wt) the homeotropic orientation arises after a time without any irradiation. The dyes with piperasene fragment (compounds XI–XIV) always result to planar orientation. Since the cells were filled with LC by self-flow method (LC flows into the cell under capillary forces) LC cells have either quasi-planar orientation due to the flow during the filling of the cells or they have no any orientation at all. Then the cells were irradiated by linearly polarized UV light, were the vector of polarization is along LC director in quasi-planar cells. In the non-oriented cells the direction of light polarization vector has no matter and so for identity we have chosen it along flow direction.

The irradiated cells content LC either in nematic or in isotropic phase. In the case of irradiation the cells with LC in nematic phase with random orientation the planar orientation of LC arises with the director perpendicular to the light polarization vector. When the quasi-planar cells are irradiated at the temperature below clearing point the twist orientation arises. But if these quasi-planar cells were irradiated at the temperature above clearing point and after irradiation they cooled to room temperature, then the uniform planar orientation arises with director perpendicular to the initial one.

This fact we explain by the presence of birefringence of LC layer in nematic phase. It means that under irradiation of the cells with LC in nematic phase the photoinduced alignment firstly arise on the closer substrate due to the strong light scattering in nematic phase. For the cells with random orientation unidirectional alignment on the closer surface induces LC alignment over whole bulk of LC. After that the linearly polarized light effects on the second substrate with the same direction of polarization vector and photoinduced alignment arise on the second surface. As a result the orientation of the cell becomes planar.

For the cells with quasi-planar orientation photoinduced alignment on the closer surface arise perpendicular to the direction of light polarization vector while on the second surface the initial orientation remains unchanged. Thereforet twist orientation arises. After that vector of polarization of linearly polarized light propagating through the twisted LC layer is turning on 90° and on the second surface photoinduced alignment arises parallel to the initial quasi-planar orientation. Thus twist orientation originally arose remains unchanged with further irradiation by linearly polarized light.

In the case of irradiation of the cells with LC in isotropic phase the light scattering is significantly less then in nematic phase so both surfaces are irradiated by linearly polarized light under the same conditions. As a result the uniform planar LC orientation arise with the director perpendicular to the light polarization vector.

CONCLUSION

We have investigated the influence of chemical structure of azodyes on their aligning capability for dyes soluble and insoluble in LCs. It was shown that formation of H-bonds between azodyes and surfaces has a crucial factor on aligning capability of azodyes. It was found that random orientation of LC dopped by azodyes after irradiation with linearly polarized light is transformed to planar orientation while quasi-planar orientation of LC is transformed to twist one.

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