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FEATURE ARTICLE

Photoalignment of liquid crystals: basics and current trends

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The review describes the status of the studies and the recent achievements in the field of photoalignment of liquid crystals. An update classification of photoaligning materials and exposure schemes, and analyzes of the relationship between the molecular structure of the materials and characteristics of LC alignment are provided. In addition, bulk mediated photoalignment and combination of photoalignment with other alignment methods are discussed. Along with traditional, recently proposed applications of the photoalignment technique are considered.

1. Introduction

The combination of long range orientational ordering and relatively free movement of anisotropic molecules in liquid crystals (LCs) makes these materials unique. This combination leads to exceptional sensitivity of LCs to electric and magnetic fields that initiated a booming growth of liquid crystals science and the development of a powerful LCD industry in the 1970s and 1980s. In such devices aligned layers of LCs are commonly used and the alignment is usually set by a rigid substrate with an anisotropic surface. Due to a long-range orientational interaction, the preferable alignment of a liquid crystal given by the surface extends into the liquid crystal bulk on a macroscopic scale. As this takes place, the orientational elasticity “smooths out” orientational inhomogeneities that are unavoidably present at the surface. It allows one to obtain liquid “single-crystals” in cells with a thickness varying from several to hundreds of micrometres.

The axis of preferable alignment of molecules in the LC is called a director of the LC, \vec{d} . Anisotropic interaction between the LC and the aligning surface determines the direction of the easy alignment axis of a LC on the aligning surface, \vec{e} . The director of the LC, \vec{d} , coincides with the direction of the easy axis \vec{e} , if the director is not affected by any elastic torque. The easy axis is given by azimuthal φ and zenithal θ angles (Fig. 1). The zenithal angle θ is often called a pretilt angle of the LC on the aligning surface. Depending on value of the pretilt, planar ($\theta = 0^\circ$), homeotropic ($\theta = 90^\circ$) and tilted ($0^\circ < \theta < 90^\circ$) alignments are distinguished. The strength of the alignment is characterized by anchoring energy, W , that determines the energy needed to deviate the director, \vec{d} , from the easy axis, \vec{e} , on a certain angle. One can differentiate between the anchoring energy related to deviation of the director in the azimuthal plane (azimuthal anchoring energy, W_φ) and the anchoring energy related to the deviation in the zenithal (polar) plane (polar anchoring energy, W_θ). The biggest industrial challenge is to obtain a uniform planar or tilted alignment of LCs with the required pretilt angle and anchoring energy and high alignment stability.

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At first the experimentalists simply rubbed the glass substrate on a piece of paper or leather.¹⁻³ Similarly, in the first twist electro-optic devices the liquid crystals were aligned by rubbing transparent electrodes.^{4,5} However, the rubbing technique became much more reliable when the glass substrate was covered with a rubbed polymer layer.

The rubbing of polymers turned out to be a very convenient technique and it is now widely used both in small scientific labs as well as large LCD factories. This method is still actively used in the LCD industry for the alignment treatment of LCD substrates with a linear size exceeding 3 meters. Enormously expensive rubbing machines of several meters width provide precise pressure and accurate motion of the rubbing roll over the glass substrate in this case.

Despite the apparent achievements of the rubbing technology, it has some serious drawbacks which became obvious from the first steps of its application and appeared to be crucial for the production of last generation LCDs and miniature LC telecommunication devices. These drawbacks follow from the contact type of the rubbing technology. Movement of the rotating rubbing roll over the polymer surface leads to accumulation of static charges and generation of fine dust particles that can diminish the fundamental characteristics of the device and are dangerous for its operation. For instance, accumulation of static electricity may destroy transistors or diodes driving the LCD. The application of the rubbing technology for large LCDs faced additional difficulties connected with the precise control of the rubbing characteristics over huge substrate areas. Using this method is also problematic in the case of projection displays, because rubbing traces become visible, when the formed image is magnified. Other problems may arise when rubbing is used in miniature telecommunication devices where there is a need to align LC in the thin gaps of the light waveguides. Finally, this method in principle cannot be used to align LCs in closed volumes.

Limitations of the rubbing technique caused the search for alternative methods of LC alignment. Among the developed methods, the so-called photoalignment method shows the greatest industrial prospects. In its original sense, this procedure involves a light treatment of the substrates, which acquire the ability to align liquid crystals (surface mediated photoalignment). To realize this effect, the substrate must contain a layer of photosensitive material whose molecules (fragments) and/or their photoproducts are capable of orientational ordering under

the light irradiation. Due to anisotropic interfacial interaction this ordering determines direction of easy orientation axis of the adjacent LC. So, based on this effect, LC alignment can be controlled by light action on the aligning layer. Alignment of a LC can be obtained by processing separate aligning substrates as well as assembled cells, either empty or filled with LC. The latter possibility very favorably distinguishes the photoalignment from many other methods of LC alignment, which are inapplicable for mechanically inaccessible volumes.

The photoalignment effect was first described in 1988 by Ichimura *et al.* in ref. 6 in which a LC alignment was controlled by light in the zenithal plane. The authors of ref. 6 found that the light irradiation of the aligning substrate grafted with monolayers of azobenzene resulted in homeotropic-to-planar reorientation of the LC due to *trans-cis* isomerization of azobenzene molecules. By varying the wavelength of light the authors changed direction of the reaction of *trans-cis* isomerization, and thus realized reversible switching of LC alignment. Shortly after publication of Ichimura's results, the groups from the USA (Gibbons *et al.*⁷), Russia/Switzerland (Schadt *et al.*⁸) and Ukraine (Dyadyusha *et al.*^{9,10}) almost simultaneously demonstrated LC photoalignment in an azimuthal plane of the aligning substrate. The latter results have been particularly important because they provided a real alternative to the rubbing technology.

The advantages of this contactless technology are evident. In contrast to the rubbing technique, neither excess charge nor dust ends up on the substrates. Photoalignment technology provides effective control of basic anchoring parameters: easy orientation axis, pretilt angle and anchoring energy. Besides this, the photoalignment technique promises new advanced applications of liquid crystals in telecommunications and organic electronics, in which the use of rubbing technique is very problematic.

Therefore, studies of photoaligning effects, synthesis of photoaligning materials and development of different photoalignment technologies for mass production have become one of the hottest topics of applied liquid crystals science. Throughout the twenty years of active work, various classes of photoaligning materials and irradiation procedures have been investigated, new photoalignment effects have been discovered, and mechanisms of LC alignment have been comprehensively studied. The photoalignment technique has gained popularity in liquid crystal labs.

Recently, truly revolutionary events associated with the industrial application of the photoalignment technology occurred. In 2009, Sharp Corp. announced development of a photoalignment based LCD operation mode.¹¹ One year later, this technology was accomplished at the world largest factory of this corporation for production of LCD panels of 10th generation. Some other applications of photoalignment are also close to practical implementation.

Actual applications of photoalignment provide new incentives for research in this field. Development of advanced photoalignment processes, synthesis of new photoalignment materials and fundamental studies of the mechanisms of photoalignment continue to be in a focus of interest of researchers and engineers dealing with LCs.

Since the discovery of photoalignment, more than a thousand papers were published and hundreds of patents were issued. The flow of the publications about different aspects of

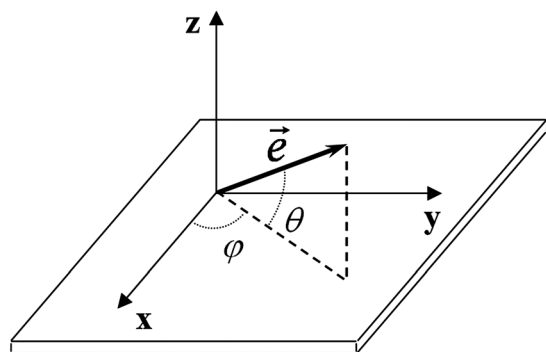


Fig. 1 Orientation of easy alignment axis.

photoalignment and technology is still very intensive and requires analysis and generalization. At the same time, available reviews^{12,13} on photoalignment of LCs were published decade ago and the first book on this topic¹⁴ is focused on selected aspects of photoalignment. The present review will help readers to get an idea of the status of the studies and the recent achievements in the field. The review provides an updated classification of aligning materials and exposure schemes and analyzes the relationship between the molecular structures of the photoaligning materials and characteristics of LC alignment. In addition, we consider bulk mediated alignment and combination of photoalignment with other alignment technologies. Finally, along with traditional, new applications of photoalignment techniques are considered.

The structure of the review is as follows. In the first chapter we describe the principles of the surface-mediated photoalignment, *i.e.* a photoalignment of LCs on the surfaces which become anisotropic due to a light irradiation. We illustrate the basic procedures of the LC photoalignment and review the photoaligning materials, paying the most attention to newly developed ones. The main photoaligning mechanisms are also considered. The second chapter is devoted to bulk-mediated photoalignment, *i.e.* the alignment of LC on a boundary surface that appears due to a light impact on the liquid crystal. In the third chapter we consider briefly various applications of photoalignment technology and its combination with other aligning methods.

2. Surface mediated photoalignment

Surface mediated photoalignment of liquid crystals arises on the adjacent surfaces treated with light. In a narrow sense, the term “photoalignment” exactly denotes this phenomenon. This section gives a survey of exposure schemes, photoaligning materials and mechanisms of this type of photoalignment.

2.1. Photoirradiation procedures

To align a LC by light, in the simplest case, the substrate with a layer of photosensitive material is exposed to a linearly polarized exciting light at its normal incidence on the substrate (Fig. 2). Typically, the spectrum of the exciting light lies in a near-ultraviolet or visible range, but deep ultraviolet light¹⁵ and even near-infrared light¹⁶ is used for irradiation of some peculiar materials.

The linearly polarized exciting light initiates orientationally selective photoexcitations of the molecules (fragments) of the aligning material leading to their bulk and surface orientational ordering. The mechanisms of this ordering will be considered in section 2.3. The order induced in the aligning film and the characteristics of the “LC-substrate” interaction determine orientation of easy axis of LC. In most photoaligning materials the easy axis is induced in the direction *perpendicular* to the exciting light polarization, \vec{E}_{exc} (direction \vec{e}_{s1} in Fig. 2a). However, there are many groups of materials providing alignment with the in-plane projection of easy axis, \vec{e}_s , *parallel* to \vec{E}_{exc} (direction \vec{e}_{s2} in Fig. 2a), at least for some range of exposure doses. This issue is discussed in section 2.2.

Disadvantage of the normal light beam incidence on the substrate is that it does not provide an unambiguous assignment

of the LC pretilt direction. On the untreated surface the pretilt, if any, is conically degenerated. Irradiation at the normal incidence with polarized light breaks this rotational symmetry, although the pretilt remains two-fold degenerated (see Fig. 2b). This degeneracy can be removed during filling of LC in a cell^{17,18} or by application of a magnetic field during the irradiation.^{19,20} In more convenient way, the two-fold degeneracy is removed by breaking the zenithal symmetry of the aligning surface order by oblique irradiation of the photoaligning surface. This approach was first proposed by Schadt *et al.*²¹ for “parallel” photoaligning materials, *i.e.* materials with $\vec{e}_s \parallel \vec{E}_{\text{exc}}$ (Fig. 3a). In case of “perpendicular” materials ($\vec{e}_s \perp \vec{E}_{\text{exc}}$) the oblique irradiation cannot remove the two-fold degeneracy of the pretilt. To break the symmetry of the photoaligning surface in this case, two-stage exposure techniques were developed. First, Hashimoto *et al.*²² proposed applying two exposures with mutually perpendicular directions of light polarization (Fig. 3b). The first exposure at the normal or oblique incidence of the beam with s-polarization generates in-plane orientational order with the out-of-plane symmetry that induces two-fold degenerated tilted LC alignment. The second exposure with p-polarized light at oblique incidence brings an out-of-plane asymmetry of the orientational order and sets the unambiguous direction of LC pretilt.

The method of breaking the out-of-plane symmetry of the photoaligning surface by the asymmetrical light treatment^{21,22} was later expanded and modified. Reznikov *et al.*²³ suggested exposure schemes in which a p-polarized light at the second exposure was replaced with unpolarized light. Furthermore, instead of two exposures one can use a single oblique exposure by partially polarized light; in case of $\vec{e}_s \perp \vec{E}_{\text{exc}}$ the beam should be

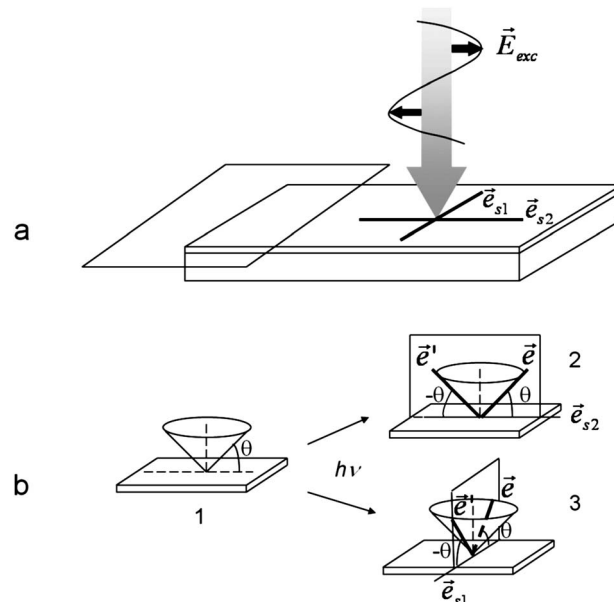


Fig. 2 Photoalignment procedure: case of normal exposure. (a) Exposure geometry and the in-plane projection of easy axis induced for “perpendicular” ($\vec{e}_s \perp \vec{E}_{\text{exc}}$) and “parallel” ($\vec{e}_s \parallel \vec{E}_{\text{exc}}$) material. (b) Schemes demonstrating conical degeneration of easy axis on the non-irradiated photoaligning film (1) and its two-fold degeneration on the irradiated films (2, 3). Schemes 2 and 3 correspond to “parallel” and “perpendicular” material, respectively.

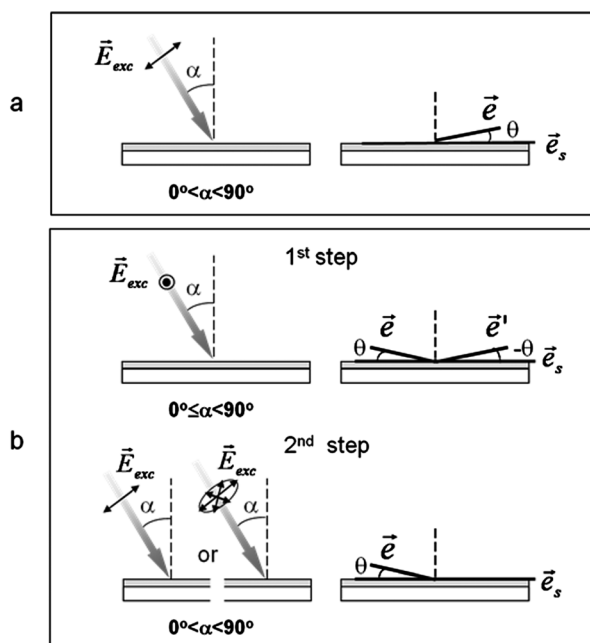


Fig. 3 Photoalignment procedure: the case of oblique exposure. (a) Exposure geometry providing non-degenerate tilted alignment on “parallel” materials. (b) A two-step exposure scheme providing non-degenerate tilted alignment on “perpendicular” materials. The first exposure transforms conically degenerated alignment into two-fold degenerated alignment, while the second exposure removes completely the degeneration.

preferably p-polarized, while s-polarization component should prevail when $\vec{e}_s \parallel \vec{E}_{exc}$.²⁴

Finally, single oblique irradiation with unpolarized light may also result in a tilted alignment.^{25–27} The problem of this method, especially for the materials with low pretilt, is to induce sufficiently strong anisotropy in plane of the aligning film to get a uniform LC alignment. This is usually achieved by utilization of high incident angles of the exciting beam²⁸ and this procedure is especially effective for deviation of LC director from homeotropic alignment.^{29,30} The result of application of non-polarized oblique irradiation also depends on the photoaligning materials. To our knowledge, the best results with this type of exposure demonstrate azopolymers.^{31,32} This is probably due to the high dichroism of azo fragments and their ability to reorient perpendicularly to the polarization of light, *i.e.*, to accumulate in the direction of light propagation in case of non-polarized light.

The optical elements and the aligning substrates are motionless during the irradiation in the above described methods. Recently, several schemes in which the substrate with the photoaligning material is moved while irradiated are suggested. Sonehara *et al.*³³ realized roll-to-roll translation of flexible substrates under luminous flux. It allowed implementation of continuous manufacturing of optical films. Kimura *et al.*^{34,35} translated the photoaligning material under the normally incident polarized light whose intensity was spatially modulated by passing the light through the proximity mask with the periodic slits. The slits were oriented perpendicularly to the sample translation direction so that all parts of the aligning substrate underwent multiple passes through the “light-shadow” borders. Passage of such boundaries

led to the unidirectional sweeping of the photoreaction fronts over the surface and generated surface asymmetry. As a result, a pretilt angle appeared with the projection on the aligning surface, which coincided with the translation direction of the substrate. The value of pretilt angle depended on the translation speed. Using this process the authors achieved pretilt angle 5 times larger than in the case of oblique irradiation. The important fact was that the pretilt was extremely stable in time. Another advantage of this process is that it avoids shadowing effect emerging for the oblique irradiation of bumpy substrates or the substrates covered with masks. Because of the analogy with rubbing procedure, the developed process was called as optical rubbing.

Entire substrate or its part can be exposed by using proximity photo-masks. The mask processes are commonly involved to realize patterned alignment. It is worth noting that patterning of LC alignment with the aid of light is much easier to realize than with the aid of rubbing. No laborious lithography processes should be applied. Moreover, since optical rewriting is possible on many photoaligning materials, number of mask processes can be minimized. The domain size of the micro-patterning can be as small as 1 μm , and both easy axis and anchoring energy can be patterned. Finally note that photoalignment allows us to create unique patterns, which are very difficult if not impossible to achieve by conventional LC alignment techniques. For example, Chen *et al.*³⁶ described radial and azimuthal alignment patterns created by irradiation of rotating substrates through segmental masks. Based on these substrates unique LC devices can be constructed.

2.2 Basic photoaligning materials

Photoaligning materials contain photosensitive species with angularly dependent absorption. As a rule, these species are anisometric and their transition dipole moments are preferably oriented along their long geometrical axis. The photosensitive species can be physically or chemically adsorbed on the substrate (Fig. 4a–d), blended with a polymer (Fig. 4e), chemically linked to polymer molecules as a part of side or main polymer chain (Fig. 4f) or be a component of polyelectrolyte multilayers (Fig. 4h and 4i). The photoaligning layers of small molecules are commonly formed by casting from solution,^{37–39} Langmuir–Blodgett technique,⁴⁰ and methods of chemical grafting.^{6,41,42} Polymer films are usually formed by a spin-coating or printing.¹⁴ Polyelectrolyte films are produced by layer-by-layer wet coating.^{43–45}

Photoaligning materials are usually classified according to prevailing photochemistry of photosensitive groups. On this basis one can distinguish three main groups of the materials.

The first group includes materials undergoing *trans-cis* photoisomerization (Fig. 5a). This reaction is reversible; *cis*-isomers can be transferred back to the *trans*-state by irradiation with a light of proper wavelength or by thermal activation. This group of materials primarily includes azo-compounds in the form of small molecules,^{6,38,40,46} molecular dopants in polymer matrices^{7,47} and azo-polymers.^{27,32,48–51} To this group we also assign sulfonated diazo-dyes,^{38,46} although possibility of *trans-cis* isomerisation in these molecules is under discussion. Other *trans-cis* photoisomerizable species employed for LC photoalignment are stilbenes.⁵²

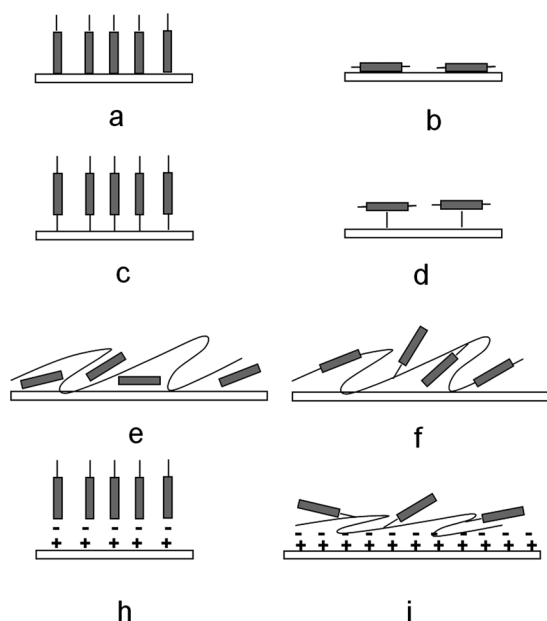


Fig. 4 Structures of photoaligning materials: (a, b) physically and (c, d) chemically adsorbed layers of small photosensitive molecules; (e) polymer blends of small photosensitive molecules; (f) polymers containing photosensitive fragments in main and side polymer chains; (h, i) polyelectrolyte multilayers containing photosensitive groups, correspondingly, in the form of low-molecular-weight and polymeric ions.

The second group comprises materials (commonly, polymers) susceptible to irreversible photo-destruction, such as chain scission, photooxidation, *etc.* The targets of these reactions usually are aromatic fragments of main or side polymer chains. For example, Fig. 5b shows chain scission reaction of polyimides.[†] In addition to polyimides,^{53–57} polysilanes,^{58,59} polystyrene, polyesters and some other aromatic polymers¹⁵ exhibit photoalignment due to the photodestruction.

The third group includes various photocrosslinkable substances, which can also be used in the form of small molecules,^{37,39,41} polymers,^{8–10} and polymer blends.⁶⁰ The majority of these materials undergo photo-crosslinking of a cycloaddition type. The [2 + 2] cycloaddition is typical for cinnamate,^{8–10} coumarin,^{21,61–63} chalconyl,⁶⁴ tetrahydrophthalimide⁶⁵ and maleimide^{65,66} photosensitive groups. In some of these materials, such as cinnamates and chalcones, [2 + 2] cycloaddition is accompanied with *trans-cis* isomerization.^{67,68} In the materials with rigid molecular structure, such as coumarin, tetrahydrophthalimide and maleimide, *trans-cis* isomerization is not possible and at high exposure doses their photodestruction becomes essential.⁶³ The photochemical reactions of cinnamate and coumarin species are schematically presented in Fig. 5c and 5d, respectively. The photoalignment ability of anthracenyl containing polymers is caused by [4 + 4] cycloaddition of these species⁶⁹ (Fig. 5e). The diphenylacetylene photosensitive groups in other photoaligning polymers⁷⁰ undergo the photodimerization, which presumably includes 1,2,3-triphenylnaphthalene, 1,2,3-triphenylazulene, and others photoproducts.

[†] We consider here the polyimides, which do not contain additional photosensitive groups.

Recently, good photoaligning properties of methacrylamidoaryl methacrylates were found.^{71,72} Crosslinkings in these materials are formed due to radical photopolymerization of methacryloyl groups accompanied with photo-Fries rearrangements (Fig. 5f).⁷³

The listed reactions do not exhaust the whole variety of types of photochemical reactions leading to photoalignment. For example, spiropyrans, which demonstrate good photoalignment effect, undergo ring opening/closure of their [4 + 2] π -electronic system.⁷⁴ The photo-Fries reaction, the same as in methacrylamidoaryl methacrylates,⁷³ seems to be an important alignment factor for many aromatic compounds.

One can assign materials containing several photosensitive fragments of different nature to a separate group. The materials combining the fragments undergoing *trans-cis* isomerization and polymerization,^{75,76} *trans-cis* isomerization and [2 + 2] cycloaddition,^{77,78} and [2 + 2] cycloaddition and polymerization^{37,79,80} are described.

Absolute majority of photoalignment materials are organic compounds, and only recently two examples of inorganic photoaligning materials—diamond-like carbon films⁸¹ and chalcogenide glass^{82,83} were reported. Despite the fact that the mechanisms of photoalignment are not well established for these materials, their exclusive thermal stability, unusual optical and dielectrical properties make them very promising for specific applications.

From a practical standpoint, each of these classes of materials has advantages and disadvantages. The azo-compounds usually give excellent LC alignment at low exposure dose, which can be less than 0.05 J. However, this alignment is not stable enough against heat and light because of reversible photochemistry and orientational disordering of azo fragments. Among azo materials sulfonated diazodyes stand out; they demonstrate high thermal stability and exceptionally high azimuthal anchoring, $W_\phi \geq 10^{-4}$ J m⁻² for the azo dyes vs. 10^{-8} – 10^{-6} J m⁻² for azopolymers,¹⁴ comparable to the anchoring on rubbed polyimides. However, hygroscopicity and electrolytic nature are serious problems hindering practical application of these materials.

Photodestructive polyimides usually reveal sufficiently high anchoring energy, $W_\phi \geq 10^{-5}$ J m⁻².^{84,85} At the same time, the pronounced image sticking and display flicker are characteristic of these materials. The essential advance in development of these materials with low sticking has been claimed recently.⁸⁶

Comparison analysis shows that the photo-crosslinking materials demonstrate the best industrial prospect. They may combine rather good photosensitivity and high resistance of LC alignment to heat and light, because of irreversible photochemistry and strongly restricted molecular motions. The azimuthal anchoring energy of the photo-crosslinking materials is usually in the range of 10^{-5} – 10^{-6} J m⁻²,^{87,88} but higher values, $W_\phi \geq 10^{-5}$ J m⁻², were reported for some polymethacrylate-based coumarins⁶³ and cellulose-based cinnamates.⁸⁹ Apparently, the aligning materials present on the market belong to this class of photo-crosslinking materials.

2.3. Influence of photoaligning materials structure on characteristics of LC alignment

Molecular structure of photoaligning materials predetermines their photoaligning properties. In particular, molecular design

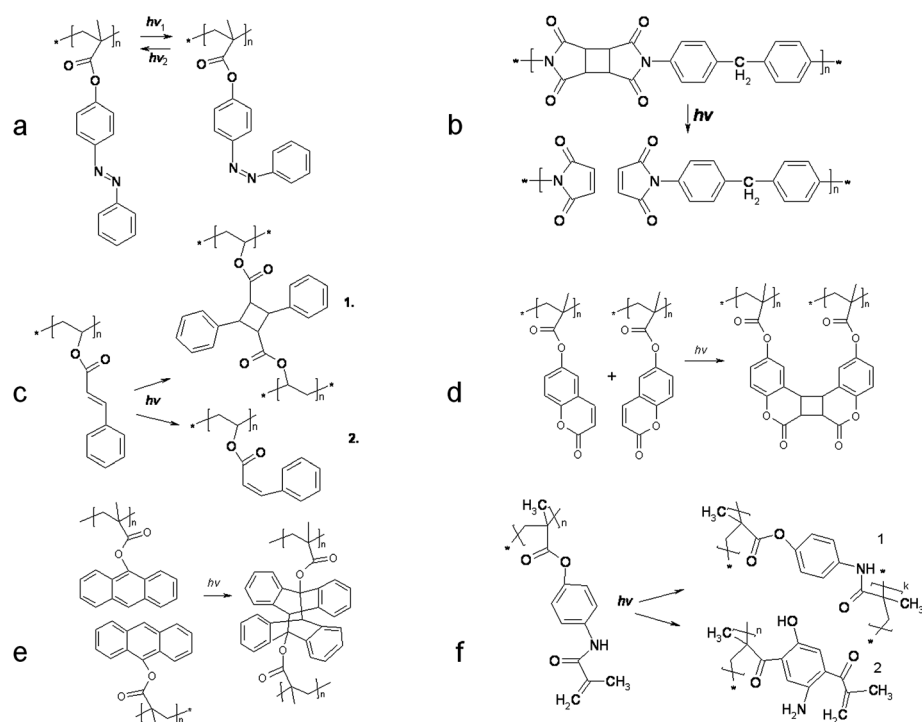


Fig. 5 Photoreaction schemes for the compounds representing different classes of photoaligning materials. (a) *Trans-cis* isomerization of azobenzene groups; (b) photodecomposition of polyimides; (c) (2 + 2) photocycloaddition (1) and *trans-cis* isomerization (2) of cinnamate groups; (d) (2 + 2) photocycloaddition of coumarin groups; (e) [4 + 4] cycloaddition of anthracenyl species; (f) photopolymerization (1) and photo-Fries rearrangements (2) in methacrylamidoaryl methacrylates.

allows us to predict the direction of easy axis on the irradiated surface. Reznikov *et al.*⁹⁰ showed that the direction of easy axis in azimuthal plane, \vec{e}_s , depends upon the position of cinnamate fragments in side polymer chains. If these fragments were attached to a macromolecule by the end which was closer to C=C bond (direct attachment), then the alignment perpendicular to polarization of light (“perpendicular” alignment, $\vec{e}_s \perp \vec{E}_{\text{exc}}$) was observed. In contrast, the attachment of cinnamate fragments to the opposite end (inverse attachment) resulted in the alignment parallel to polarization of light (“parallel” alignment, $\vec{e}_s \parallel \vec{E}_{\text{exc}}$). We agreed above to call the corresponding materials “perpendicular” and “parallel”. It has been suggested that the alignment direction is determined by the direction of the geometrical anisotropy axis of the crosslinked fragments resulting from the [2 + 2] cycloaddition of cinnamate moieties of the polymer (Fig. 6). Obi *et al.*⁹¹ and Kawatsuki *et al.*⁹² found other cinnamate polymers demonstrating “parallel” LC alignment. These polymers, as well as some of cinnamate monomers,³⁷ gave both “parallel” and “perpendicular” alignment, depending on the exposure dose. Selected photoaligning cinnamate structures are presented in Table 1, an updated and concentrated version of Tables 2–5 in ref. 13.

Both “parallel” and “perpendicular” alignments are also typical for coumarin side-chain polymers^{62,63} (Table 1). Comparing presented structures and directions of the photoalignment on these materials allows us to note several regularities. First of all, the ability for “parallel” alignment of polymers with coumarin and inverse cinnamate species increases if a flexible spacer is introduced between these species and the polymer backbone. A different trend for the polymer P11, *i.e.* its

“perpendicular” alignment at long-term exposure, can be explained by the photo-destruction clearly detected in this polymer,⁶³ which commonly supports “perpendicular” LC alignment.⁷³ The result for P4 suggests that a “parallel” alignment can also be obtained for polymers with direct cinnamate species if they are attached to a backbone through the spacer with mesogenic structure.

The parallel photoalignment was also found for polyimide P13,^{84,94} Table 1. Besides, the polyimides containing azobenzene⁹⁵ and stilbene⁹⁶ chromophores are described, which change the alignment direction \vec{e}_s by 90°, correspondingly, with excitation wavelength and exposure dose.

By manipulating the structure of molecules, one can also change the position of the easy axis in zenithal plane. The pretilt angle can be adjusted by attaching to photosensitive molecules the hydrophobic groups such as fluorine, alkyl, alkoxy, fluoroalkyl, fluoroalkoxy and others. These fragments can be attached as terminal groups of photosensitive side chains,^{17,37} as individual side chains^{72,97} or fragments of main polymer chains. They can also be mixed with the photoaligning materials.^{57,60,98}

Photosensitive fragments of organic photoaligning materials have aromatic groups commonly forming π conjugation with other parts of these fragments that determines the absorption spectrum of the fragments. Therefore, the rate of photo-degradation of photoaligning materials is rather sensitive to the structure of these aromatic fragments. For example, in polyimide P12 (Table 1), replacement of cyclobutane ring by benzene ring increases exposure dose of effective degradation by a factor of 10.⁸⁴

The way of connecting photosensitive fragments to the polymer chain is important. For example, the position of azobenzene

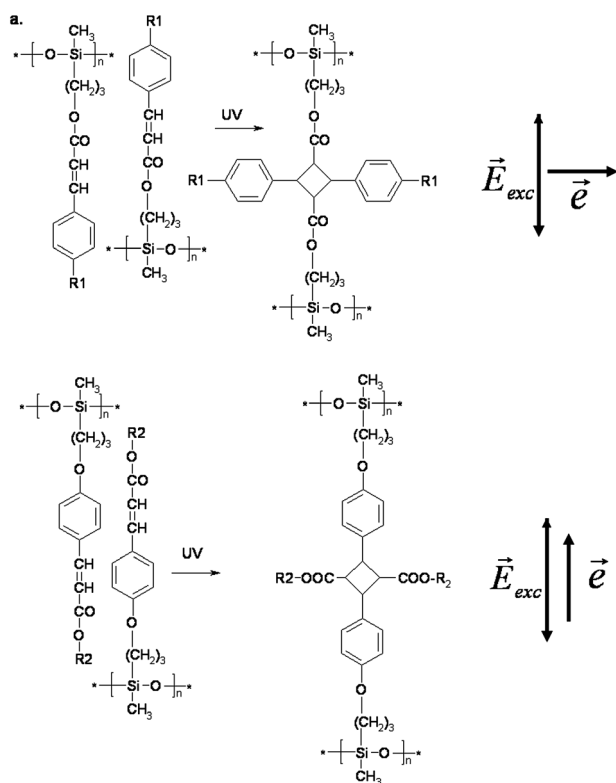


Fig. 6 Photoreaction schemes for the polymers containing side-chain cinnamate fragments with (a) direct and (b) inverse attachment.

fragments in the main chain results in enhancement of photo- and thermal stability of LC alignment. In turn, attachment of these fragments to a side chain amplifies the reaction rate and the photoinduced ordering. This position also provides a larger controlling range of LC pretilt angles.⁵⁰ According to ref. 49, the attachment of azobenzene in *ortho* position results in much higher photosensitivity and thermal stability of the alignment than the attachment in *para* position. Flexible spacers, used to attach the fragments to the macrochain, affect the rate of photoinduced ordering and liquid crystallinity of the photoaligning polymers.⁹⁹

The molecular weight of photoaligning polymer is also an important factor that affects photoalignment properties. Increase of the molecular weight often improves thermal stability of photoalignment due to the reduced mobility of the polymer chains. At the same time, molecular weight may affect rate of photoreactions and photoordering, especially in the case of main chain localization of photosensitive fragments.¹⁰⁰ Fei *et al.*¹⁰¹ described homeotropic to planar alignment transition with the increasing molecular mass of fluorinated polymer.

2.4. Basic photoalignment mechanisms

The photoaligning effect occurs due to anisotropic interaction of a LC with the orientationally ordered aligning film. As commonly believed, the major mechanism of this interaction is a short-range anisotropic interaction of LC molecules with the anisotropic orientationally ordered species on the photoaligning

surface. Van der Waals, dipole-dipole, π - π stacking, hydrogen bonding or steric interactions may contribute to the anchoring, depending on molecular structure of LC and photoaligning material. Due to the long-range interaction in mesophases, the surface induced alignment extends to the LC bulk resulting in homogeneous alignment of the whole LC cell.^{102–105} Besides, morphology of the aligning surface can contribute to the anisotropic interaction between a LC and aligning layer.^{106,107}

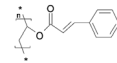
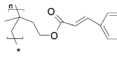
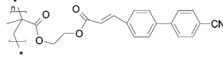
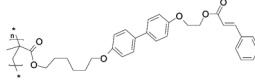
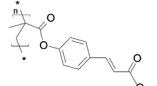
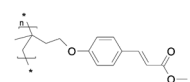
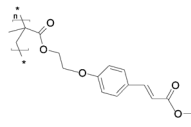
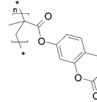
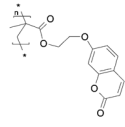
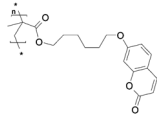
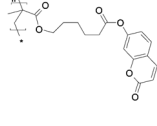
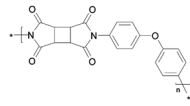
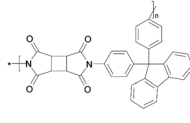
A distinctive feature of photoalignment is that in contrast to the rubbing treatment the light irradiation orientationally orders not only the polymer surface, but also the bulk of the polymer film. Therefore, to clarify the basic mechanisms of LC photoalignment it is quite important to know the features of the molecular photoordering in the photoaligning film.

Studying azopolymers, Dumont and Sekkat^{108,109} considered two main mechanisms of photoorientation of anisotropic azo-fragments, which can be generalized for other photoaligning materials. In case of reversible photochemical reaction or non-reactive photoexcitation, the photosensitive species experience many acts of photoexcitation and relaxation accompanied with their random-walk rotation. This process, known as *angular redistribution*, leads to accumulation of photosensitive species in the direction perpendicular to the polarization of the exciting light, \vec{E}_{exc} , in which the absorption of these species is minimal. The mechanism of angular redistribution is common for azo-materials^{99,108} and acts as supplementary one in cinnamates.⁶⁸ In the case of irreversible photochemical reactions, the photosensitive species are out of the game after photo-transformations. Because of absorption dichroism, the angular distributions of the photo-transformed species becomes anisotropic that results in producing of the easy axis, usually perpendicular to \vec{E}_{exc} . This mechanism is called *angular photoselection* or *angular hole burning*. It dominates in a vast majority of materials undergoing photocrosslinking, photo-Fries rearrangement, and photodecomposition.

A special photoselection process may occur in adsorbed layers of photosensitive molecules. The anisotropy of these layers may be induced by the angularly selective photostimulated desorption. As in the case of irreversible photochemical reactions, this process may cause anisotropic depletion of photosensitive molecules.^{110,111}

In many cases, in addition to ordering of initial photosensitive groups, it is necessary to take into account ordering of their photoproducts. This is particularly important for cinnamates, coumarins and chalcones, whose molecules form anisotropic crosslinking groups after irradiation. In these materials, the photoordered photosensitive groups and their crosslinking products contribute to LC alignment. The anchoring forces associated with these two ensembles of oriented moieties may act in one direction or in perpendicular directions. The magnitudes of these forces and their dependencies on the light exposure can be different, but both contributions are important to explain all peculiarities of LC photoalignment. For example, the competition of these two mechanisms with mutually perpendicular alignment directions may explain the “parallel” alignment or change of the alignment direction by 90° with the exposure dose in some photoaligning materials.^{62,63,91,92} Usually the “parallel” alignment is attributed to crosslinking fragments while the “perpendicular” alignment is associated with intact

Table 1 Selected photoaligning polymers and corresponding types of LC alignment

Designation	Molecular structure	LC alignment		References
		Short exposure	Long exposure	
Cinnamates				
P1		⊥	⊥	8–10
P2		⊥	⊥	90
P3		⊥	⊥	93
P4			⊥	92
P5		⊥		91
P6				90
P7				91
Coumarins				
P8			⊥	62
P9				62
P10				62
P11			⊥	63
Polyimides				
P12		⊥	⊥	94
P13				84,94

photosensitive groups. Note that it is difficult to separate contributions of these mechanisms if they cause alignment in the same direction. The most prominent representative of such materials is polyvinylcinnamate (PVCN), the first

photocrosslinking material for which the photoalignment effect was discovered.^{8–10} Despite rather convincing arguments for the contribution of crosslinking fragments in LC alignment,^{68,112} some researchers hold the view that the alignment is caused by

the orientational order of cinnamate fragments whereas the role of the crosslinking fragments is limited to fixing this order.⁶⁷

In many polymeric photoalignment materials, especially in LC polymers with low glass transition temperature, T_g , the ordering of initial photosensitive groups and their photoproducts is accompanied with the ordering of non-photosensitive fragments of side and main polymer chains.^{113,114} This collective orientation driven by spontaneous self-organization enhances and stabilizes the photoordering in polymers.^{114,115} Moreover, the intrinsic ordering may also superpose with a light-induced ordering on the surface of photoaligning film and thus affect a position of light-induced axis of easy alignment.^{32,116}

As we noted above, the topography of the aligning surface also contributes to photoalignment. The authors of ref. 100 and 101 assume that regardless of the alignment treatment roughness anisotropy on substrates' surface occurs. Alignment of LC along the direction of lower roughness, as expected from Berreman's calculation, is suggested to be a universal feature of all alignment films. The authors of ref. 106 and 107 hold the view that anisotropy of the roughness determines direction of LC alignment, while the magnitude of the anchoring energy is mainly determined by the anisotropic molecular interaction of LC and aligning material.

3. Bulk mediated photoalignment

In the previous chapter we considered photoalignment phenomena caused by formation of an anisotropy axis due to photochemical reaction in the boundary alignment layers deposited on the substrate. Physical origin of these phenomena is the formation of the anisotropic angular distribution of anisotropic polymer fragments or small molecules on the surface by polarized light. Similar effects appear when a photoaligning film is produced due to formation of anisotropic layer of molecules that come from the LC bulk and are adsorbed by the surface due to absorption of light. A layer of adsorbed molecules is always present on the boundary surface^{117,118} and an active molecular exchange happens between the adsorbed layer and the LC bulk.^{119–122} Since the molecules involved in this process are anisometric, dichroic and angularly ordered in the LC bulk, the irradiation of the filled cell with a polarized light results in a stationary anisotropic angular distribution of the molecules in the adsorbed layers. In consequence, the light-induced axis of easy alignment appears on the adsorbed film. The light-induced effects associated with formation of the easy alignment axis in the layer of adsorbed molecules due to molecular exchange between the LC bulk and adsorbed layer are usually called *bulk-mediated photoalignment*. The distinctive feature of the bulk-mediated photoalignment is that it is achieved *in situ* upon irradiation of the filled LC cell. Below we review the experimental studies and the theoretical model of bulk-mediated photoalignment.

3.1. Photoaligning procedure and characteristics of bulk-mediated photoalignment

Bulk-mediated photoalignment was first reported by Voloshchenko *et al.* in 1995.¹²³ It was found that irradiation of a planar cell filled with LC 5CB doped by azo-dye Methyl Red (MR), with a polarized light in the absorption band of MR resulted in

a photoalignment of LC on an isotropic surface of PVCN film. The authors of¹²³ observed very stable in time and temperature light-induced twist structures in the combined cells made of the rubbed substrate (reference surface) and of the substrate covered with PVCN layer (tested surface). These twist structures were formed in the areas of the cell irradiated by a green laser beam at its normal incidence on the cell and the polarization \vec{E}_{exc} perpendicular or at the angle 45° to the director, \vec{d} . Formation of the twist structures pointed at the producing of easy alignment axes on the tested surface. The dependence of the twist angle on the exposure time allowed authors to find that the direction of the light-induced easy axis, \vec{e} , is almost *parallel* to the direction of the light polarization and the anchoring energy is of the order of 10^{-7} – 10^{-5} J m⁻².

A polymer PVCN is not sensitive to a visible light. Therefore, to explain the observed results a new mechanism, different from the mechanism of the traditional surface-mediated photoalignment has to be suggested. The authors supposed that this mechanism is connected with a light-induced adsorption of the excited MR molecules on the isotropic polymer surface. More particularly, it was suggested that phototransformation of the MR molecules located close to the surface results in the significant change of their adsorption ability. Komitov *et al.* supposed that light absorption of *trans*-isomers near the substrates causes their transformation to *cis* form and the consequent adsorption of *cis*-isomers by the surface.¹²⁴ Later, the detailed studies of Francescangeli *et al.* by X-ray reflectometry and half-leaky guided mode optical technique confirmed that in the case of 5CB doped with MR the layers of spontaneously adsorbed MR molecules and photoadsorbed MR molecules are formed on a PVCN surface.¹²⁵ Since MR molecules are anisotropic and dichroic ones and are in the anisotropic matrix, the light-induced adsorption should be anisotropic and sensitive to the polarization of exciting beam. The following studies^{126,127} confirmed these suggestions.

The direction of the light-induced easy axis due to the light-induced adsorption is determined by the maximum of the angular distribution of the adsorbed MR molecules on the substrate. This maximum is determined by the angular distribution of the MR molecules near the surface, *i.e.* by the order parameter of the LC near the surface.

Later, Magyar *et al.*¹²⁸ and Reznikov *et al.*¹²⁹ observed bulk-mediated planar photoalignment of pure LC 5CB on a fused quartz surface in the filled cell upon illumination with polarized UV light in the absorption band of the LC molecules. Unlike a dye-doped LC, where LC aligns preferably *parallel* to \vec{E}_{exc} , the director of LC in the irradiated area was close to the direction *perpendicular* to \vec{E}_{exc} . The authors supposed that these phenomena are caused by a light-induced rearrangement of the LC layer spontaneously adsorbed on the surface. In particular, it was suggested that the absorption dichroism of LC molecules could result in anisotropic desorption of these molecules from the surface that yields anisotropy of the adsorbed layer with the axis *perpendicular* to \vec{E}_{exc} .

The observation of the LC alignment perpendicular to \vec{E}_{exc} in the cells with pure LC, supposedly due to the light-induced desorption of LC molecules, pointed to the possibility of the analogous effect in a dye doped LC. The following studies showed that in the case of LC doped with MR a light-induced

desorption from spontaneously adsorbed MR layer resulted in the alignment of the LC *perpendicular* to \vec{E}_{exc} at low exposures. A light-induced adsorption mechanism that tends to align LC *parallel* to \vec{E}_{exc} is manifested at higher exposures.^{123,125–127,130–132}

The ordering of dye molecules complicates the picture of formation of easy alignment axis in a nematic phase. This process is simplified significantly if a cell with the dye doped LC is irradiated in the isotropic phase¹³⁰ when there is no molecular ordering in the bulk and on the surfaces. In this case irradiation of the LC cell and its consequent cooling to the nematic phase results in formation of good planar alignment with the direction of the easy axis either exactly perpendicular (low exposure doses) or exactly parallel to the polarization \vec{E}_{exc} .

It should be noted that the details of the formation of bulk-mediated easy alignment axis strongly depend on the origin of the substrate. According to,^{133–139} a dark adsorption does not occur on the substrates that are not coated with a PVCN. Moreover, the authors of^{133–139} found that in the case of polyvinyl-alcohol films and some homeotropically aligning layers a long exposure results in ripple structures with the periods of the order of 100 nm and microgrooves oriented along \vec{E}_{exc} .

In addition to controlling the direction of the easy axis in the azimuth plane, the bulk-mediated photoalignment technique allows adjusting orientation of the axis in the zenithal plane. A smooth control of the pretilt angle is possible by controlling the parameters of the ripple structure in the cell with initial homeotropic alignment of a LC.¹⁴⁰ According to ref. 140, the period of this structure is about 300 nm and the amplitude of the relief depends on the exposure and changes in the range 80–150 nm, providing a planar anchoring due to the Berreman mechanism. The combination of initial homeotropic alignment in the cell and the variable Berreman forces result in an equilibrium tilted alignment. The authors of ref. 140 controlled the pretilt in the range 24°–63.5° with this technique. Additional opportunities to control the pretilt angle arise, if we use a LC with negative dielectric anisotropy and apply a bias electric field during light irradiation.¹⁴¹ This allowed authors to control the pretilt angle in the range 90°–50°. A sharp switching from initial homeotropic alignment to final planar alignment is possible in the LC cells doped with MR and oligomeric nanoparticles. The homeotropic alignment induced by these particles is changed to a planar alignment by the light-induced adsorption of MR dopant.¹⁴²

3.2. Mechanisms of bulk-mediated photoalignment

The current model of the easy alignment axis formation by the bulk-mediated photoalignment of MR-doped LC on PVCN surface is presented in ref. 132. According to the model, the light-induced exchange of dye molecules due to adsorption/desorption mechanism in the presence of the light-induced bulk torque results in deviation of preferable alignment of adsorbed dye molecules from the initial direction. At first it leads to the drift of the initial easy axis away from the vector \vec{E}_{exc} due to light-induced desorption of the dye molecules from the surface at low exposures. Then the light-induced adsorption begins to dominate and longer exposures result in the drift of the easy axis toward \vec{E}_{exc} (Fig. 7).

The model¹³² describes the experimental data collected in ref. 123, 126 and 129–131 well for PVCN aligning surfaces although it does not take into account the changes in the morphology of the adsorbed MR layers clearly observed on polyvinyl-alcohol films and several homeotropic alignment layers after long exposures.^{133,142–144} SEM and AFM techniques detected smooth layers of adsorbed molecules on these surfaces at the exposures corresponding to director reorientation perpendicular to \vec{E}_{exc} and the layers with well oriented ripples at the exposures corresponding to alignment toward \vec{E}_{exc} . According to ref. 134 and 141 the adsorbed layer consists of a large number of adsorbed *cis*-isomers of MR molecules with their long axes perpendicular to the ripples. The ripples themselves are parallel to the direction \vec{E}_{exc} and contribute to the final alignment due to the Berreman mechanism. The origin of the ripple structures is not finally set and the authors of ref. 133 associate them with the interference between the exciting beam and its surface scattering. The ripple structures were not observed on the PVCN surfaces. Supposedly, the exposure doses in the cells with PVCN surfaces were not high enough to form notable microgrooves. It is also likely that a well-established layer of spontaneously adsorbed MR molecules is required for formation of the ripple structure that was not the case of PVCN surface.

Moreover, although Lee *et al.*¹³³ showed that the light-induced desorption of dye molecules does not play essential role in the case of polyvinyl-alcohol films, they also observed the formation of the easy alignment axis parallel to \vec{E}_{exc} at short exposures. The authors of ref. 133 suggested that excited MR molecules near the surface undergo a series of transformations, including photoisomerization, three-dimensional reorientation, diffusion and finally adsorption onto the substrate with the long axes perpendicular to both the polarization and propagation directions of the impinging light. In our opinion, this model requires further development and additional experimental and theoretical studies.

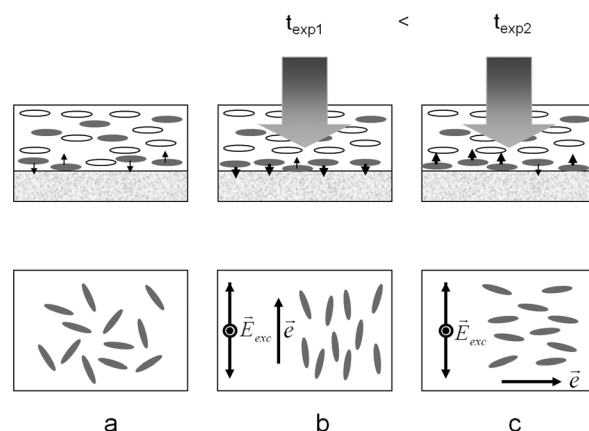


Fig. 7 Bulk-mediated photoalignment in isotropic phase of liquid crystal. (a) Exchange by dye molecules between boundary surface and a LC; no preferable alignment. (b) Light-induced desorption of dye molecules results in easy alignment axis perpendicular to \vec{E}_{exc} at short exposures. (c) Photo-adsorption causes easy alignment axis parallel to \vec{E}_{exc} at long exposures.

4. Applications of photoalignment

4.1. Application in display technologies

Application of photoalignment is primarily associated with the alignment of liquid crystals in LCDs. The first publication where the advantages of the photoalignment technology for LCD industry were clearly demonstrated was the work by Schadt *et al.*,²¹ in which high-resolution pretilt controlled pattern in the plane of the display was produced by irradiation through a proximity mask to fabricate free of alignment defects multi-pixels structure. This principle was further used to expand the viewing angle of LCDs.^{22–24} The photoalignment also provides good opportunities for improvement of other types of LCDs such as liquid-crystal-on-silicon (LCOS) microdisplays, ferroelectric LCDs, stereoscopic and transmissive LCDs. The details of these applications can be found in a recent book by Chigrinov *et al.*¹⁴

A unique possibility of effective control of an easy axis, including reversible changes of LC alignment in the filled cell, allowed researchers to suggest a number of new, rather exotic types of LCDs which are almost impossible to fabricate by traditional technologies. Developing ideas primarily proposed by Ichimura *et al.*,^{6,25} Muravski *et al.*¹⁴⁵ realized an optically rewritable display based on a surface mediated photoalignment. The authors used the photoaligning diazodyes allowing big number of reorientations with polarized light. Fuh *et al.*¹⁴⁶ reported different optically rewritable LCDs, in which the image is written, erased, and rewritten due to a bulk-mediated photoalignment. In ref. 147 a polarizer free, electrically switchable and optically rewritable display is fabricated based on dye-doped polymer-dispersed LC. Due to a bulk-mediated alignment the adsorbed dye in the illuminated region aligns the LC homeotropically and thus produces a transparent pattern on the scattering background without any polarizers. The photoinduced patterning can be erased and then recorded again by desorption and re-adsorption of the dye using thermal and optical treatments, respectively. Combination of bulk mediated hybrid photoalignment and homeotropic alignment in one pixel allowed authors of ref. 148 to fabricate LCD with controllable viewing-angle, which switches between two images by changing viewing angle.

Recent studies have shown the universality of the photoalignment method. In addition to nematics, it appeared to be quite effective for chiral nematics,¹⁴⁹ ferroelectric LCs¹⁵⁰ and discotics.^{151,152} As stated in the next subsection, the method also shows high efficiency for reactive LCs and lyotropic LC materials, which can be applied in the technology of optical films.

Despite high potential of photoalignment technique, this method has not found practical application for several decades. This was mainly associated with the shortcomings of existed photoaligning materials. These materials demonstrated insufficient thermal, light and temporal (aging) stability of LC alignment. The other important problem which had prevented application of the photoaligning materials in LCD industry was a residual image of the previous frame of LCD (so called *image sticking effect*). This effect is caused by two main reasons. The first one is accumulation of electric charges nearby the photoaligning surfaces that relaxes slower than the frame changes.¹⁵³ Second, rather weak anchoring energy of the photoaligning

materials results in deviation of the director from the easy alignment axis by external torque that in its turn leads to the drift (gliding) of the easy axis.^{154–157,132}

Several approaches to solve these problems were recently proposed. First of all, we should mention optical rubbing,^{34,35} discussed in section 2.1. It provides LC alignment with very stable pretilt angle that is fundamentally important for conventional TN LCDs. Another important step in perfection of photoaligning layers is their stabilization by reactive mesogens (RM).¹⁵⁸ With this approach, the photoaligning layer aligns a thin layer of RM, which, in turn, aligns a LC. In this case the photoaligning film with insufficiently stable photoinduced order is replaced by the layer of RM whose orientational order is firmly fixed due to photo-crosslinking. Basically, this approach allows strong stabilization of LC alignment on practically any photoaligning material providing alignment of RM.

A breakthrough in practical application of photoalignment has occurred recently. It is primarily associated with development and industrialization of photoalignment based multi-domain vertical alignment (MVA) mode (so named UV2A mode). The UV2A eliminates protrusions and slit electrodes, which reduce the aperture ratio of pixels and cause light leaks. Because of this, the UV2A drastically improved transmittance, contrast ratio and response time compared to the conventional MVA mode.¹¹ Furthermore, LG Corp. recently claimed development of image sticking free photoaligning materials for the in-plane switching (IPS) mode.¹⁵⁹ Finally, using the method of photoalignment, Arisawa company has developed a patterned retarder (commercial name Xpol), giving the opportunity to get a 3D image on virtually any modern LCD display.¹⁶⁰ We are confident that the LCD industry is on the verge of new astonishing applications of photoalignment.

4.2. Application in photonics and electronics

The restrictions of the rubbing alignment technique are critical for many modern photonic applications that require LC alignment of high microscopic uniformity and fine alignment patterning. Besides this, alignment on relief, curved and flexible substrates as well as in confined volumes is often necessary. Photoalignment is an indispensable method for these applications.

In particular, the application of the photoalignment technique is highly effective for producing anisotropic films for optical retarders and dichroic polarizers. As such, reactive mesogens and lyotropic liquid crystals are commonly used. Using suitable photoalignment materials one can align these LCs very well. Also, one can readily pattern LC alignment that allows one to realize patterned retarders and polarizers particularly needed for development of stereoscopic and transmissive LCDs.^{160–166}

Examples of photonic devices based on the photoaligned layers of LCs are electrically controlled Fresnel lenses,^{167–169} polarization convertors,^{170,171} and optical gratings.^{172–178}

The possibility of aligning LCs by light in micro-volumes opens new horizons for their applications in miniature LC telecommunication devices such as waveguides, optical switches and routers, *etc.* Photoalignment technology has already been successfully applied for alignment of LCs in a submicrometre-sized rib

waveguides and electrically driven waveguide-coupled micro-resonators with the LC cladding layer.¹⁷⁹

The photoalignment technique is also a unique tool to achieve LC alignment in mechanically inaccessible volumes. Presumably, the first attempt to photoalign LC in the droplets of polymer dispersed liquid crystals was done by Nazarenko *et al.*¹⁸⁰ Recently, the photoalignment technique was successfully applied to align LC in glass micro-tubes and in photonic crystal fibers.^{181,182} LC configuration in these samples can be readily controlled and patterned by photoirradiation.¹⁸³

The past decade has also seen great interest in application of LCs in electronic devices such as organic light emitting diodes (OLED), organic thin film transistors (OTFT), photovoltaic cells, *etc.* Use of aligned layers of semiconducting LCs enables to increase charge carrier mobility, which improves performance of corresponding devices. Besides this, it allows one to obtain polarized electroluminescence from those materials. Such sources of polarized light are particularly interesting as backlights for brighter and more efficient LCDs. Photoalignment finds increasing application in this area. OLED and OTFT devices based on photoalignment technology are described in ref. 184–187 and ref. 188, respectively.

4.3. Combination of photoalignment with other alignment methods

New application possibilities of photoalignment technology are opened by its combination with other methods of LC alignment. Irradiation with polarized light in the absorption band of a polyimide changes easy axis direction and anchoring energy generated by rubbing.^{189,190} Non-polarized light may also widely vary anchoring energy on the rubbed aligning layers.^{190,191} Yamaguchi and Sato¹⁹² applied this effect for development of a unique method for patterning LC alignment in the azimuthal plane. Providing illumination through the transparent filter the authors recorded continuous grey scale images in the cells combining alignment layers with a weak (patterned) and strong (non-patterned) anchoring (Fig. 8). Similar approach was applied to develop optical security device containing two or three latent



Fig. 8 Gray scale image recorded in LC cell combining rubbed aligning layers with a weak (patterned) and strong (non-patterned) anchoring made of polyvinylcinnamate and polyimide, respectively. The patterning was realized by providing illumination through the grey scale transparency filter. The LC cell is viewed between a pair of (a) crossed and (b) parallel polarizers. The cell is kindly presented by R. Yamaguchi.

images visualized using one or two polarizers.¹⁹³ Photoalignment can also be beneficially combined with another efficient non-mechanical technique—ion/plasma beam alignment.^{194,195} Combination of these techniques allowed development of anisotropic multifunctional films for in-cell applications and produced well aligned RM films for LCD compensators, achromatic retarders and dichroic polarizers.^{196,197}

5. Conclusions

After more than 20 years history the LC alignment by light has become a routine part of laboratory practice and found its application in LCD technology. It is indispensable tool for producing highly uniform or multiform director structures of various kinds of LCs. These structures can be realized on microscopic, curved and flexible substrates, and in confined volumes. Many years of hard work of scientists and engineers were marked by development of highly effective materials and processes providing a strong anchoring, stable pretilt, and negligibly weak image sticking. This allowed improvement of the basic characteristics of conventional LCDs and suggested new display devices such as multistable and optically rewritable LCDs. Furthermore, recent studies demonstrate that photoalignment is a highly potential method for many photonic and electronic applications; it can be successfully used in technology for producing anisotropic optical films, various telecommunication devices, and thin film electronic devices such as OTFTs and OLEDs. New applications may arise from recent observation of a LC alignment on inorganic materials. Finally, many opportunities are opened up by combining the photoalignment with other methods of LC alignment such as rubbing and ion/plasma beam alignment. Based on these combinations, unique systems of optical recording, security devices, multifunctional films for LCDs have been proposed.

In this review it was impossible to cover all aspects of photoalignment of LCs. Surface mediated alignment effects such as the alignment on photo-induced relief gratings^{7,198,199} and complex effects caused by photoalignment and photorefractive effects were beyond the focus of our discussion.²⁰⁰ Considering bulk mediated alignment we are limited only to the alignment effects in LC cells caused by anisotropy of the boundary surfaces. Therefore, many exciting phenomena connected with a light induced/controlled anisotropy in the LC bulk (*e.g.*, orientational photo-ordering in LC polymers with photosensitive side chains,²⁰¹ mixtures of LC with dyes²⁰² or polymers with photoalignable fragments,²⁰³ *etc.*) are not addressed in the present review.

We also have not discussed here dielectric properties of the photoaligning layers, as well as dielectric and electro-optical properties of corresponding LC cells. Finally, we did not discuss the role of photoalignment technique in the progress of surface physics of liquid crystals. This interesting and multiform problem deserves a separate review.

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