



4th International Conference Photonics and Information Optics, PhIO 2015, 28-30 January 2015

## Photosensitive polymers for liquid crystal alignment

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### Abstract

The peculiarities of alignment of liquid crystal (LC) materials by the layers of photocrosslinkable polymers with side benzaldehyde groups are considered. The investigation of mechanism of photostimulated alignment by rubbed benzaldehyde layer is performed. The methods of creation of multidomain aligning layers on the basis of photostimulated rubbing alignment are described.

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Peer-review under responsibility of the National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)

*Keywords:* photosensitive polymer; photocrosslinking; photoalignment; photostimulated rubbing alignment.

### 1. Introduction

Reversible and irreversible photochemical reactions are widely used for the creation of anisotropy of intermolecular forces on the surface of the polymer and low-molecular photosensitive layers to align liquid crystalline (LC) materials. Linearly polarized irradiation can create an orientational anisotropy of photosensitive molecules and/or their photoproducts, as well as segments of polymer chains [Yaroshchuk et al. (2012), Cojocariu et al. (2004), Obi (1999), Hasegawa et al. (1995)]. Arised orientational order can lead to the certain type of LC alignment, called photoalignment. For practical applications of photosensitive polymers as aligning materials the induced surface anisotropy have to be stable to thermal and light impact and action of liquid media (including LC). Such stability can be provided by photocrosslinking when the aligning molecular structures are included in polymer network to prevent their rotational mobility. Being contactless and capable to form local fields of different director orientation the photoalignment method seems quite attractive for the fabrication of various LC devices. Nevertheless numerous technological requirements contradict with each other; this causes limited choice of photoaligning

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materials for industrial applications from one side and stimulates new investigations to realize the same functions by alternative methods from the other. In the present work we focus on the effect of photostimulated LC alignment after mechanical rubbing of the layers of photocrosslinking polymers, containing benzaldehyde groups in the side chain (photostimulated rubbing alignment), and on possibilities of its practical applications similar to photoaligning materials.

The photosensitivity of the benzaldehyde polymers proves itself in effective photocrosslinking due to attachment of the products of photoreduction of the benzaldehyde groups to macromolecules. Under linearly polarized UV irradiation the materials demonstrate the photoinduced birefringence [Mahilny et al. (2011)] and the effect of LC photoalignment [Kazak et al. (2008)], both appeared to be stable to light, heat and liquid media impact [Mahilny et al. (2008)]. The azimuthal anchoring energy of photoalignment is about  $10^{-5}$  J/m<sup>2</sup>, and the anisotropy axis lies along the electric vector of activating radiation [Mahilny et al. (2013)]. Sufficiently greater energy has been achieved after rubbing of the layer of benzaldehyde polymer and then exposing it to nonpolarized UV radiation [Mahilny et al. (2009)].

## 2. Experiment

The experiments were performed with methacrylate polymers B- and M-series having the benzaldehyde side groups. Thin aligning layers (0.08 – 0.12 μm) were obtained by spin-coating. After drying the polymeric layers were treated by exposing to linearly-polarized radiation of a mercury lamp or by rubbing and subsequent irradiation with nonpolarized light of the lamp, the intensity of nonpolarized light being (600±20) mW/cm<sup>2</sup>. Polarization of the radiation was realized using a quartz Wire-Grid polarizer (polarization degree P≈100%, transmission coefficient ≈50%). A thin (~ 0.8 μm) LC monomer (RMM-491, Merck) layer was coated on exposed benzaldehyde aligning layer and was polymerized with UV radiation. The transmittance coefficient T versus rotational angle of the sample placed between cross linear polarizers was measured and its birefringence was calculated according to:

$$|\delta n| = \frac{\delta}{l} = \frac{\lambda}{\pi l} \arcsin \sqrt{\Delta T}, \quad (1)$$

where

$$\Delta T = T_{max} - T_{min},$$

$\delta$  is path difference between ordinary and extraordinary beams,

$l$  is LC layer thickness,

$\lambda$  is wavelength of the probing laser beam ( $\lambda = 650$  nm).

The LC anisotropy axis direction was determined by comparison of the experimental angle dependences for the examined sample and the reference one.

The quality of the alignment of LC molecules was estimated by quality parameter that can be calculated as:

$$q = \frac{T_{max} - T_{min}}{T_{max}} \quad (2)$$

Photocrosslinking of the benzaldehyde polymers was studied with the help of characteristic curves – the dependences of relative height of polymer photorelief  $l_{rel}$ , formed upon UV irradiation of the layer and subsequent wet development on exposure doze H ( $l_{rel} = l/l_0$ , where  $l$  – photorelief height,  $l_0$  – the initial thickness of the layer).

## 3. Photoalignment and photostimulated rubbing alignment

For the first time LC photoalignment by benzaldehyde polymers was used by the authors [Kazak et al. (2008)] to fabricate controllable diffraction grating. Appearance of aligning properties of benzaldehyde polymers of B-series being rubbed and then UV exposed was described for the first time in [Mahilny et al. (2009)]. Then the same

properties were observed for polymers of M-series [Muravsky et al. (2010)]. These papers as well as [Trofimova et al. (2013)] describe practical possibilities of the materials and do not consider the mechanism of the surface anisotropy formation excluding a brief mention of supposed role of photocrosslinking. To confirm it we have compared exposure dependences of the effectiveness both of photoalignment and photostimulated rubbing alignment (Fig. 1a), and characteristic curves of photocrosslinking (Fig. 1b).

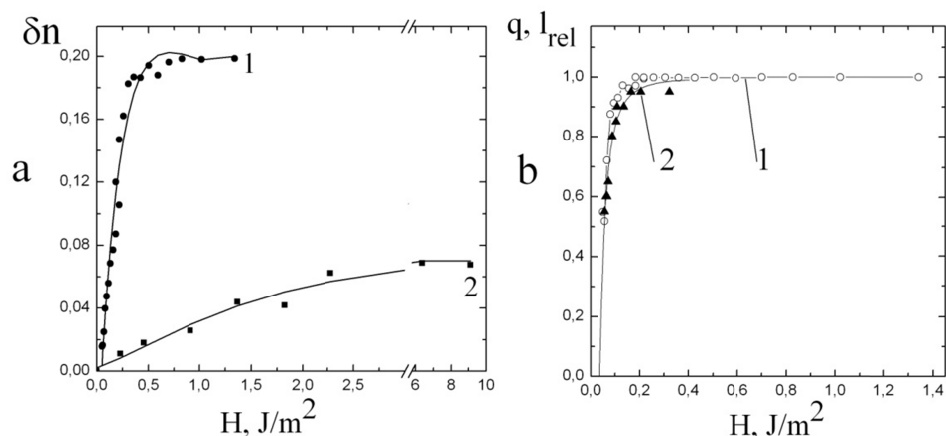


Fig. 1. Exposure dependences of the characteristics of the polymer B-15: (a) – birefringence of LC on the rubbed layer (1) and after linearly polarized irradiation without rubbing (2); (b) – quality parameter of LC on the rubbed aligning layer (1) and characteristic curve of B-15 layer (2).

Non-polarized exposure of the rubbed aligning layer causes a sharp increase of LC birefringence that reaches maximal value of  $\sim 0.2$  at exposure dose of  $0.5 J/cm^2$  (Fig. 1a, curve 1). If non-rubbed layer is exposed to the polarized radiation the LC birefringence increases considerably slower and its maximal value is sufficiently lower ( $\sim 0.07$ , Fig. 1a, curve 2). The spectra of UV absorption of the aligning polymer layer during its exposure show that  $\delta n$  of the LC layer reaches its maximum at a deep photoconversion of the benzaldehyde groups, whereas upon photostimulated rubbing alignment it occurs after phototransformation of just 10-15% of the photosensitive fragments (Fig. 1a, curve 1). The kinetics of quality parameter  $q$  agrees with the characteristic curve (Fig. 1b).

Photoalignment is assumed to be related with the ensemble of anisotropic molecular photoproducts formed upon polarized irradiation of the layer and oriented mainly along electric vector of activating light [Mahilny et al. (2013)]. The higher the concentration of the anisotropic photoproducts the higher the effect of photoalignment. Stimulation of the rubbing alignment under UV irradiation correlates rather with the process of photocrosslinking. Actually the relative thickness of the relief formed under wet development  $I_{rel}$  can be considered as the insoluble material fraction (gel-fraction) consisting of polymer chains united in the network by crosslinks. Due to high efficiency of benzaldehyde photoattachment the gel-fraction reaches the value of 1 (Fig. 1b, curve 2) at a relatively low level of photoconversion (low value of  $H$ ). Almost simultaneously the birefringence  $\delta n$  of LC monomer layer (Fig. 1a, curve 1) and the quality parameter  $q$  of its alignment (Fig. 1b, curve 1) achieve maximal values. Further increasing of  $H$  value causes the growth of photoproduct concentration and the photoalignment efficiency enhances, it tends to saturation at 100% of photoconversion of benzaldehyde groups. The distinctive feature of the photoalignment – its insensibility to overexposure that was mentioned earlier [Mahilny et al. (2013), Trofimova et al. (2014)].

The photoalignment method provides LC layers birefringence of a small value denoting about lower azimuthal anchoring energy, and the defectiveness of LC monomer layer is observed to be pretty high (Fig. 2a). Meanwhile photostimulated rubbing alignment creates LC layer without visible defects (Fig. 2b) and demonstrate one of the essential properties of photoaligning materials – azimuthal anchoring energy growth under irradiation. This property appeared to be useful for fabrication of the aligning layers with alternating tilt angle due to the competition between homeotropic and planar alignment [Ho et al. (2007)].

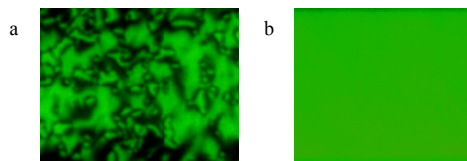


Fig. 2. Microscopic images of LC layer aligned by photoalignment (a) and rubbing (b) methods.

The effect of photostimulated rubbing alignment may be related to a higher orientational order of the benzaldehyde photoproducts in comparison with the case of polarized irradiation of non-rubbed layer. But our experiments show that LC is aligned along the rubbing direction, whereas other polymers having benzene rings in the side chain align LC perpendicular to the rubbing direction [Kang et al. (2009)]. Moreover the alignment direction remains the same for every possible polarization orientation of stimulating light.

LC alignment can be formed by the ensemble of main chain segments, oriented statistically by rubbing, if these segments consist of polar groups, as in polyimides [Yang et al. (2007)]. Ester groups included in the methacrylate chain of the benzaldehyde polymers have considerable polarity. The oriented ensemble of the main chain segments with ester groups is supposed to be formed by rubbing also in this case, providing the basis for LC alignment along rubbing direction. Enhancement of azimuthal anchoring energy upon UV irradiation can be considered as a result of increasing of the order parameter in the ensemble of oriented main chain segments. A decrease of the surface roughness of the benzaldehyde polymer layers upon UV irradiation is revealed in [Muravsky et al. (2010)]. It indicates of a deformation of near-surface material and may be caused by crosslinks forming under irradiation. As a result of rubbing such deformation can become anisotropic. Actually the side benzaldehyde groups of the “oriented” segments are directed predominately perpendicular to the rubbing line. UV exposure of the rubbed surface creates in the polymer network the ensemble of crosslinks preserving the angular distribution of benzaldehyde fragments originating these crosslinks. This must lead to stronger compression of the network in the direction perpendicular to the rubbing line.

Photostimulated rubbing alignment of the benzaldehyde polymers allows to form multidomain LC structures with a high alignment quality. Photocrosslinking being in the basis of the effect makes the rubbed layer insoluble. The layer insolubility and the alignment ability of LC molecules develop almost simultaneously (Fig. 1b). This allowed to propose the method of creation of locally inhomogeneous orientation of LC director on the surface of polymer nanorelieves, that formed by coating, rubbing, exposing through photomask and wet development of additional polymer layers [Trofimova et al. (2013)]. In such structures open areas of the surface of each layer implement LC alignment.

Process flow of patterned aligning layer fabrication is illustrated in Fig. 3.

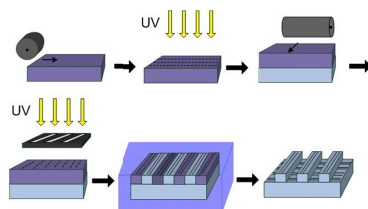


Fig. 3. Fabrication of multidomain aligning surface on the basis of photostimulated rubbing alignment with wet development of upper layers.

The 1st layer (~ 80 nm) is obtained by spin-coating of polymer solution on glass substrate. Five-minute baking at 90°C is enough to remove residual solvent. The polymeric layer coated undergoes the procedure of rubbing by cloth in a certain direction. Then the rubbed layer is exposed to non-polarized UV radiation of a mercury lamp. The 2nd polymeric layer is coated on photo-treated surface of the 1st layer and baked. The rubbing of the 2nd layer is carried out as well in another direction different from the rubbing direction of the 1st aligning layer. The second UV non-

polarized exposure is performed through photomask. Then non-exposed areas of the 2nd layer are removed by wet development in organic solvent. They open areas of the surface of the 1st aligning layer. Thus two alignment directions are created (Fig. 3).

Upon photocrosslinking of the rubbed benzaldehyde polymers an insensitivity of the surface anisotropy to repeated rubbing in another direction together with subsequent irradiation appears. This makes it possible to create multidomain aligning layers that doesn't need additional layer coating and its wet development. The procedure of fabrication becomes simplified – Fig. 4.

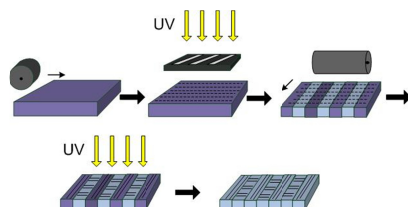


Fig. 4. Multidomain aligning layer fabrication process on the basis of photostimulated rubbing alignment with multiple rubbing.

#### 4. Conclusion

The investigation of photostimulated rubbing LC alignment by the layers of benzaldehyde polymers in comparison with photocrosslinking and photoalignment has been carried out. The correlation between aligning properties of rubbed polymer surface enhanced by UV radiation and its photocrosslinking has been established. Such photostimulation of LC alignment was related to anisotropic deformation of the rubbed polymer layer that increases the order parameter of the ensemble of the segments of main methacrylate chains. The schemes of fabrication of multidomain aligning layers on the basis of nanorelieves and multiple rubbing have been presented.

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