

Reactive mesogen photoalignment on photopolymerizable composite layer

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Abstract. The volume photoanisotropy (photoinduced birefringence) and surface photoanisotropy (LC photoalignment) of compositions of LC monomer – benzaldehyde polymer upon polarized UV radiation have been revealed and investigated. A high quality of photoalignment is confirmed by an extreme value of birefringence and low imperfection of phase plates fabricated on the basis of LC monomer on composite layer.

1. Introduction

Liquid crystal (LC) photoalignment arises as a result of irradiation of aligning layer by linearly polarized light without any additional treatment of the material surface [1]. Such contact-free method makes possible to avoid typical disadvantages of rubbing method (dust, electrostatic charging, etc.), besides it allows to form multidomain aligning layer with different local orientation of LC director achieving by rotation of polarization plane of the activating light.

As aligning materials photocrosslinking polymers have the best prospects as the aligning molecular structures formed during the irradiation are appeared to be included in insoluble polymer network [2]. In previous works [3–5] we reported on LC photoalignment on the surface of photocrosslinking polymers, containing benzaldehyde groups in the side chain that upon linearly polarized UV irradiation create the molecular structures with a high anisotropic polarizability. But the azimuthal anchoring energy of the photoalignment for these materials is insufficient ($\sim 10^{-5}$ J/m²) to form defectless multidomain phase LC films. The problem can be partially solved using an effect of photostimulated rubbing alignment [6]. Photocrosslinking makes the material insoluble, that allows to create polymer relieves with multidomain LC alignment [7]. Nevertheless this method just discrete changing of LC director orientation makes possible and the number of the orientations is limited.

In order to find the other opportunity to increase an azimuthal anchoring energy of the photoalignment in the present work we investigated photoanisotropy of composite material LC - monomer - benzaldehyde polymer (LC–B composition). Expected positive effect was connected with a partial alignment of LC monomer in the composite layer by photoproducts of benzaldehyde side groups of the polymer component.

2. Experiment

The experiments were performed with methacrylate polymers of M-series having different content of benzaldehyde fragments and LC monomer RMM-491 (Merck). The composition components were dissolved in the required ratio in toluene. Thin aligning layers (0.1 – 0.15 μ m) were obtained by spin-coating without baking upon elevated temperature. Photoinduced birefringence of the composite layers



(0.5 – 0.6 μm), formed by exposing to linearly polarized radiation of a mercury lamp was measured by sample probing by laser beam ($\lambda = 650 \text{ nm}$) as it is described in [8].

To study the photoalignment process LC monomer was coated on exposed composite layer and was polymerized with UV radiation to fix induced alignment. The transmittance coefficient T versus rotational angle of the sample placed between cross linear polarizers was measured and its birefringence was calculated according to:

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

where $\Delta T = T_{\text{max}} - T_{\text{min}}$, l – the LC layer thickness, λ – wavelength of the probing laser beam ($\lambda = 650 \text{ nm}$). The LC anisotropy axis direction (alignment direction) was determined by comparison of the experimental angle dependences for the examined sample and the reference one. The sample thickness was determined using interference microscope. The quality of the alignment of LC molecules was estimated by quality parameter that can be calculated as:

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

3. Photoinduced birefringence

The total flux of linearly polarized radiation (300 mW/cm^2) creates a negative photoinduced birefringence in the layers of the compositions (Fig. 1), it corresponds to lower value of the refractive index for the light with \mathbf{E} -vector parallel to polarization of the activating radiation ($\delta n = n_{\parallel} - n_{\perp} < 0$).

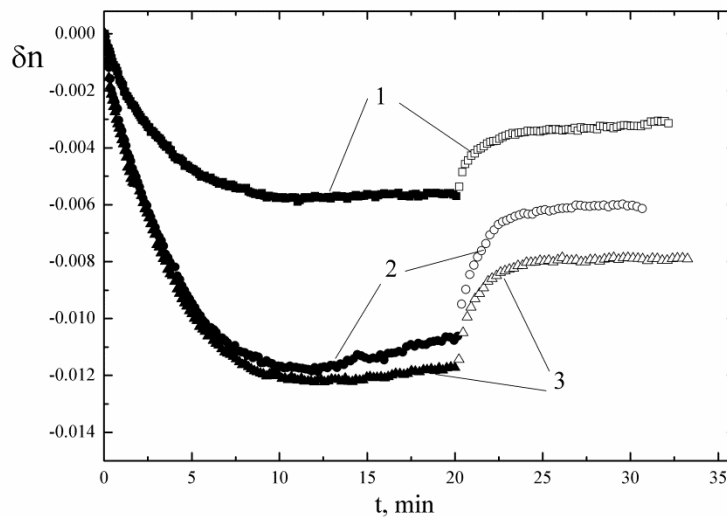


Figure 1 The kinetics of photoinduced birefringence recording and its dark behavior for the layers of LC-B composition (10:1 by weight) with different content of benzaldehyde groups in polymer: 10 (1), 20 (2), and 40 (3) mol. %

The positive ($\delta n > 0$) birefringence of the composite layers is observed upon linearly polarized irradiation in the restricted spectral region and under less intensity (20 mW/cm^2), respectively, by using cut filter transmitting light with a wavelength more than 300 nm . And the time of exposure appeared to be sufficiently smaller (Fig. 2, curve 1). Upon dark relaxation the value of the negative birefringence decreases (Fig. 1) whereas the positive one increases (curve 2).

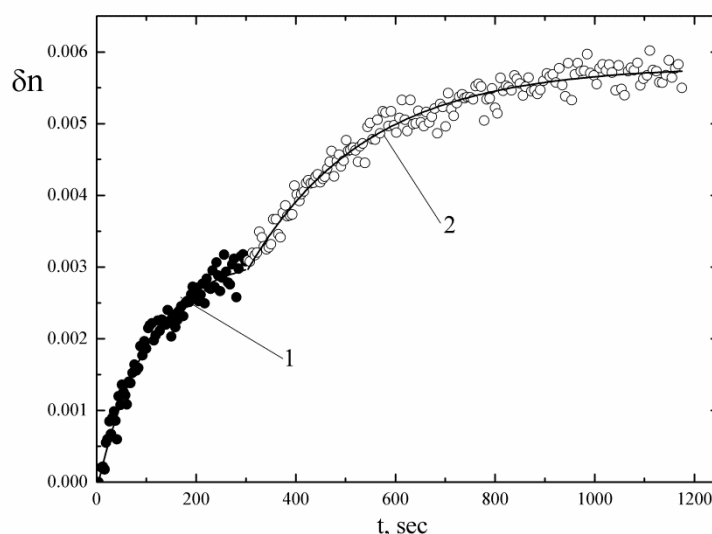


Figure 2 Kinetics of the photoinduced birefringence of the layer of LC-B composition with the components' ratio 6:1 (1) and its postexposure amplification (2)

Proper photoinduced birefringence of the benzaldehyde polymers consists of two basic components: non-stable negative birefringence and stable positive one [8]. The negative component of the birefringence foregoes positive one in the kinetics curves and lasts over a long period of time just upon high contents of benzaldehyde groups in macromolecules, i.e. upon their high concentration in polymer layer. As a rule values of both components are about $10^{-4} - 10^{-3}$, and just upon high concentration of benzaldehyde fragments the negative birefringence exceeds value of 0,001 [9].

The positive component of photoinduced birefringence of the benzaldehyde polymers is formed by anisotropic products of photoreduction of benzaldehyde groups, included in crosslinks. The negative component arises due anisotropic (predominantly perpendicular to **E**) distribution of residual benzaldehyde fragments and the process of rotational chaotization makes the negative photoanisotropy rapidly decreasing [10].

The negative photoinduced birefringence of the composite layers (Fig. 1) arises during LC monomer photocuring and after its completing. According to the data of the wet development of irradiated composition layers, 5 minutes exposure time is quite enough to make the layers insoluble. It is hard to believe that the non-stable negative anisotropy of the ensemble of residual benzaldehyde fragments is able to align LC monomer, all the more after its curing. Therefore more probable reason of the negative birefringence forming in the composite materials is a phototransformation of mesogen centers of LC monomer and its polymer after curing that decrease their anisotropy.

The positive photoinduced birefringence of the composition layer (Fig. 2) might be considered as a result of LC monomer photoalignment effect. Actually the anisotropic axis direction in this case is determined by orientation of long axes of anisotropic products of benzaldehyde fragments along **E**, so the LC alignment does [4]. It is also proved by dark growth of the birefringence, that may be caused by finite duration of the alignment process, exposure time that is sufficiently less than curing time (5 min) and the absolute value of birefringence that exceeds considerably the values of the positive birefringence of pure benzaldehyde polymers.

4. Photoalignment of LC monomer

The strong photoalignment effect was demonstrated by experiments of LC monomer coating onto thin ($0.1 - 0.15 \mu\text{m}$) composite layers, irradiated beforehand by linearly polarized light in the presence of the cutting filter. The effect appeared in the same time limits as for recording of the positive birefringence in composition layers (Fig. 2). It should be noted that there was no photoalignment effect upon total light flux exposure. Fig. 3 shows the dependences of birefringence of the cured LC monomer photoaligned on composite layers.

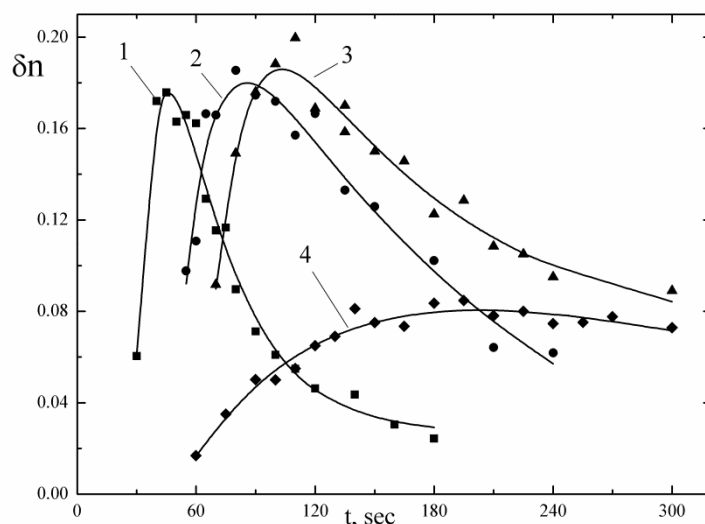


Figure 3 The kinetics of birefringence of LC layers aligned by composite layers upon different ratio LC – B: 10:1 (1), 7:1 (2), 5:1 (3), 3:1 (4). Polymer component contains 10 mol.% of benzaldehyde fragments

The dependences demonstrate dramatic growth of δn to the maximal value, and then relatively gradual decreasing of its value is observed. Maximal value of δn corresponds to the limit of anisotropy of cured LC monomer, it indicates to a low defectiveness of LC polymer film and high azimuthal anchoring energy. Low-intensity excitation $\lambda > 300 \text{ nm}$ could make for creating of aligning benzaldehyde groups' photoproducts ahead of LC molecules' polymerization. In this case rotational mobility of LC and its alignment remains. At the same time the total light flux could polymerize LC quickly to prevent its alignment.

Applied potentialities of the photoalignment effect on the composite layers have been confirmed by polymeric retarder producing with radial director orientation based on linearly polarized irradiation of rotating photoalignment layer (Fig. 4).



Figure 4 The photo of LC film with radial director orientation in-between cross linear polarizers

5. Conclusion

Photosensitive composite material consisting of LC monomer and benzaldehyde-containing polymer has demonstrated a photoalignment effect under linearly polarized irradiation $\lambda > 300$ nm. Anchoring energy created by the material suffices for high quality alignment of the LC monomer layer. Co-axis photoinduced birefringence corresponds to assumption of partial alignment of LC molecules by benzaldehyde groups' photoproducts as a cause of the effective photoalignment.

References

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