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Liquid crystal photoalignment properties of polymethylphenylsilane

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Abstract

Polymethylphenylsilane (PMPS), prototype of polysilanes, is considered as photoaligning material for liquid crystals (LC). The LC photoalignment on PMPS is characterized by the singular low exposure energy ($E \le 50$ mJ) necessary to produce LC alignment. Dependence of the azimuthal anchoring energy W_a on the exposure time τ_{exp} is non-monotonous; curve $W(\tau_{exp})$ sharply increases, goes through a maximum and decreases to the values close to zero. The easy axis of LC alignment is induced in the direction of light polarization. Possible microscopic mechanisms of LC photoalignment on PMPS layers are discussed. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

A method of liquid crystal (LC) alignment with the photocurable layers was proposed at the end of the past decade. In experiments of Ichimura et al. [1], non-polarised light of different wavelengths was used to cause reversible homeotropic-planar reorientation of a LC on the LB films containing azobenzene moieties. Later on, Dyadyusha et al. [2] on polyvinylcinnamate (PVCN) and Gibbons et al. [3] on azo-polymers showed that curing of orienting photosensitive layers with polarized light may cause "inplane" orientation of LC. In the current decade, LC aligning properties of polymers containing other pho-

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tosensitive groups were revealed and studied. For instance, Schadt [4] observed LC photoalignment on the layers of coumarin-containing polymers, West et al. [5] reported photoalignment properties of polyimide layers, etc. Such materials differ in the light energy values necessary for recording, values of induced birefringence and absorption dichroism, LC aligning parameters.

In Ref. [6], we reported for the first time the peculiarities of LC photoalignment on the polysilane films. These polymers are very promising for various applications due to their unusual electrical, photoelectronic, and nonlinear optical properties [7]. In our experiments, we used polymethylphenylsilane (PMPS), a prototypical polysilane. Its physical properties have been studied rather extensively [8]. First investigations showed that PMPS differ from the

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common photoaligning polymers with the singular photosensitivity and non-monotonous dependence of the LC anchoring parameter on the irradiation dosage. New aspects of LC alignment on PMPS layers were considered in Refs. [9,10].

In this paper, there are summarized results of our investigations of LC photoalignment properties of PMPS. The possible alignment mechanisms are discussed.

2. Experimental

PMPS was dissolved in dichlorethane (concentration is 15 g/l). The prepared solution was filtered and spin-coated on the glass substrates. The films prepared in this way were kept at the temperature of 50° C for 1 h to provide a complete evaporation of the solvent. Thickness of the films estimated with a profilometer by Tencor Instruments was 50–80 nm. Films were irradiated with a polarized light of the high-pressure mercury lamp. Irradiation time was 0.1–15 min at the light intensity in the sample position of 5 mW/cm². Using these substrates, LC cells with a cell gap of 20 μ m were fabricated. We have prepared two types of cells, namely:

- 1. both substrates are coated with photopolymer (symmetrical cells);
- one substrate is covered with photopolymer and the other one with rubbed polyimide layer (combined cells).

Filling of the cells was done at room temperature with LC ZLI 4801-000 ($T_c = 95^{\circ}$ C) produced by Merck.

Sufficiently good quality of LC alignment was observed in both types of the cells. A homogeneous planar as well as a twisted planar LC textures were observed. It is worth noting that a twisted structure was realized only for the short-time irradiation of PMPS substrates (Fig. 1). This is an evidence for the strong dependence of the anchoring energy on the exposure.

To estimate an azimuthal anchoring energy, we measured a twist angle in the combined cell. To study the dependence of anchoring energy on the exposure, combined multi-domain cells were fabri-



Fig. 1. Cell filled with LC ZLI4801-000 among the crossed polarizers. Bottom substrate is covered by the rubbed polyimide, wereas the upper one by the irradiated PMPS layer. Polarization direction of the light on upper substrate is perpendicular to the rubbing direction on bottom substrate. Irradiation time in the domains 1, 2 and 3 is 0, 2 and 20 min., respectively.

cated. The domains differed only in the irradiation time of a PMPS substrate. Direction of the UV light polarization was fixed; the angle between polarization direction (photocured substrate) and rubbing direction (rubbed substrate) was 45°. Twist angle φ in the domains was measured using polarizing microscope. The azimuthal anchoring energy W was found from the LC twist angle φ by the formula

$$\xi \sin 2(\varphi - \alpha) = 2\varphi, \tag{1}$$

derived in Ref. [11]. In Eq. (1), α is the angle between direction of orientation induced by rubbed substrate and the polarization of the exciting light, $E_{\rm exc}, \ \xi = Wd/K$ is the anchoring parameter, where d and K are the cell gap and LC orientational elastic constant, respectively. Dependence $W(\tau_{exp})$, calculated from the experimental curve $\varphi(\tau_{exp})$ using values $\alpha = 45^{\circ}$, $d = 20 \ \mu m$ and $K = 10^{-12}$ N in Eq. (1), is shown in Fig. 2. In contrast to the prototypical photo-orientant PVCN, where curve $W(\tau_{exp})$ saturates at some τ_{exp} value [12], dependence $W(\tau_{exp})$ for PMPS is strongly non-monotonic. It reaches a maximum at short-time exposures and goes down when irradiation time increases. Extremely short irradiation dosage (less then 50 mJ), in comparison to known photoalignment materials, was required for reaching the maximum values of anchoring energy. The value $W_{\text{max}} = 1.2 \times 10^{-6} \text{ J/m}^2 \text{ for PMPS was several}$ times lower than that for the photo-oriented PVCN substrate [12]. In addition, in contrast to PVCN as



Fig. 2. Dependence of the azimuthal anchoring energy of LC ZLI4801-000 on polymethylphenylsilane substrate on the irradiation time.

well as to the vast majority of photo-orientants, easy axis of LC alignment on PMPS was induced parallel to E_{exc} .

Thermostability of the induced alignment on PMPS was tested by the comparison of LC textures in a cell before and after keeping it in an oven at different temperatures. Such observations revealed fairly poor thermostability; for example, heating of the combined cells up to 70°C led to the relaxation of the twisted structure.

3. Discussion

LC photoalignment is usually associated with a photoinduced anisotropy in orienting films, which can be revealed in a spectral dichroism or birefringence [13]. It reflects the anisotropy of the orientational molecular distribution, appearing due to the absorption dichroism of photosensitive moieties. For such dichroic fragments, efficiency of the phototransformation depends on the angle between transition moment of a chromophor and direction of the polarization of the actinic light. This results in the anisotropic distribution of the initial absorbing fragments and dichroic photoproducts. The most efficient reaction in azo-polymers is *trans-cis* isomerisation of azobenzene derivatives; in cinnamate polymers, both *trans-cis* isomerisation and photodimerisation of cinnamoyl units are essential. Main photoreaction in the photosensitive polyimides is supposed to be decomposition of polyimide chains.

It is commonly accepted that LC photoalignment is caused by anisotropic molecular interaction of LC with the photo-oriented surface of the polymer film. Different types of molecular interaction in LC-polymer interface (dispersion, dipole–dipole, and steric) seem to be important for LC alignment [14]. The role of each of them depends on the chemical structure of LC and polymer molecules, their conformation, presence of the dipole groups, a type of the surface molecular aggregation, etc. Molecular photoaligning mechanisms are well studied both in azobenzene and in cinnamate-containing polymers. Anisotropic "inplane'' distribution of photosensitive groups and some photoproducts is the main factor of the homogeneous planar alignment of LC on the films of these polymers [1-5,15,16]. Presence of strong dipole groups in the chromophors improves quality of the "in-plane" LC alignment [17].

Melecular photoaligning mechanism could be also expected in PMPS. Photoinduced decomposition of the weak σ -conjugated silane chains (chain scission) is a common reaction for polysilanes [7,8]. The photodestructive reaction under the irradiation with polarized UV light occurs, most probably, on segments of a silane chain favorably oriented with respect to the direction of the light polarization. Such photoselection can induce anisotropy in the initially isotropic distribution of the segments. Interaction of LC molecules with anisotropically destroyed segments of polymer chains can cause LC alignment. However, assuming that the described mechanism is only one mechanism of LC alignment, it is difficult to explain both a substantial difference in photosensitivities and in the recording kinetics of the anchoring energy in PMPS and in typical photo-orientants. Besides, the value of photoinduced birefringence reflecting the anisotropy of the molecular distribution is incredibly low in PMPS films. Following our results, the value of Δn is less than 5 10⁻⁴. For comparison, the order of magnitude of Δn in the azobenzene polymers and PVCN is 10^{-1} [13] and 10^{-2} [12,16], respectively. The light-induced dichroism detected with authors of Ref. [9] is also incredibly low. The explanation of these facts should be evidently founded in the unique properties of PMPS.

PMPS is a typical representative of polysilanes, well-known organic photoconductors. In these materials, the quantum efficiency of charge carrier photogeneration and the hole drift mobility are of the order of 10^{-4} cm²/Vs [18], which is unusually high. The charge carrier transport in polysilanes is believed to be controlled by the charge hopping through the intrinsic states derived from segments of the silane main chain. Photogenerated ion pairs in PMPS normally have rather short lifetime at room temperature (of the order of tens of microseconds [8]). Under the applied electric field, they can dissociate into free charge carriers contributing to photocurrent. As was recently shown [19,20], irradiation with UV light results in appearing of the pairs with a long lifetime and being even stable at room temperature. They are located in the deep traps, which appears at the ends of the "cut-off" parts of the macro-chains due to the scission process.

Since a distribution of the decomposed domainlike segments in the case of irradiation with polarized light should be anisotropic, one can expect an anisotropic distribution of the deep traps. In turn, it could cause the creation of preferentially oriented stable ion pairs possessing dipole moments. In other words, some sort of photoelectret state can be realized on the irradiation with polarized light [21]. Anisotropic distribution of such ion pairs can be an important factor for LC alignment.

Some experimental results obtained with a method of thermally stimulated luminescence [20] show that proposed photoalignment mechanism is reasonable. For instance, excitation energy of the long-life pairs was approximately equal to the energy needed for the induction of maximal anchoring. Besides, low activation energy of the deep traps agrees well with a poor thermostability of the induced alignment.

In contrast to the intermolecular dipoles, playing the role in molecular mechanism of LC alignment, the dipoles described above are created by cooperative charges. Assuming it, one can say that the new possible photoalignment mechanism is of electrical origin. This mechanism can essentially enhance ''in-plane'' anchoring on the PMPS film. Further studies are required to prove this hypothesis.

4. Conclusions

The LC alignment on the films of polymethylphenylsilane, a prototypical polysilane, was stu-

died. High photosensitivity and non-monotonous dependence of the anchoring on irradiation time characterize this alignment. This can be an evidence for the new photoalignment mechanism in polymer materials. Taking into account a high photoconductive ability of PMPS and photogeneration of the stable ion pairs, one can conclude that LC alignment on PMPM might be partially caused by the mechanism of electrical origin. We associate it with the system of dipoles locating on the stable ion pairs. Angular "in-plane" distribution of the appearing dipoles is supposed to be anisotropic on the irradiation with polarized light. Proposed mechanism could be realized also in other classes of photoalignment materials having essential photoconductivity, for example, in polyimides. One can predict a new interesting application of LC, if this hypothesis will be confirmed; it will make possible visualization of the structure of surface charges by LC lavers.

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