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Non-monotonic exposure dependence of the pretilt angle and surface polarity of the photo-orientant F-PVCN

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We report on the first observation of a *non-monotonic* UV exposure dependence of the pretilt angle of a liquid crystal on a photoaligning surface. We found this non-monotonic dependence on fluorinated poly(vinyl cinnamate) (PVCN-F) surface while non-fluorinated PVCN revealed a monotonic decrease of the pretilt angle with exposure. These dependences correlate with light-induced changes of the polarity of PVCN-F and PVCN surfaces. The obtained data point to an important role of the surface polarity and the light-induced changes in mechanisms of pretilt angle generation on photoaligning materials.

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1. Introduction

The operation of liquid crystal (LC) devices requires uniform orientation and reproducible pretilt of the LC director on aligning surfaces. Traditional methods of LC alignment involve mechanical rubbing of the aligning polymer surfaces [1]. Last decade, Gibbons *et al.*, Reznikov *et al.* and Schadt *et al.* proposed alternative, photoaligning techniques [2–5]. Their techniques use polarized light to induce an anisotropy in a photosensitive aligning layer. The light-induced anisotropy of the irradiated layer causes the appearance of the easy orientation axis, **e**, of the LC director on a photosensitive surface.

Poly(vinyl cinnamates) (PVCNs) are among the most studied of photoaligning materials [3–7]. Their irradiation with polarized UV light provides high quality homogeneous alignment of nematic LCs. The main photochemical reactions in these materials are light-induced crosslinking of cinnamate side fragments and their *trans–cis* isomerization (figure 1) [4, 6, 7]. The photoaligning properties of PVCNs are caused mainly by crosslinking [8]. This process is sensitive to the polarization of incident light because of the strong dichroism of cinnamate groups, resulting in anisotropy of the irradiated surface.

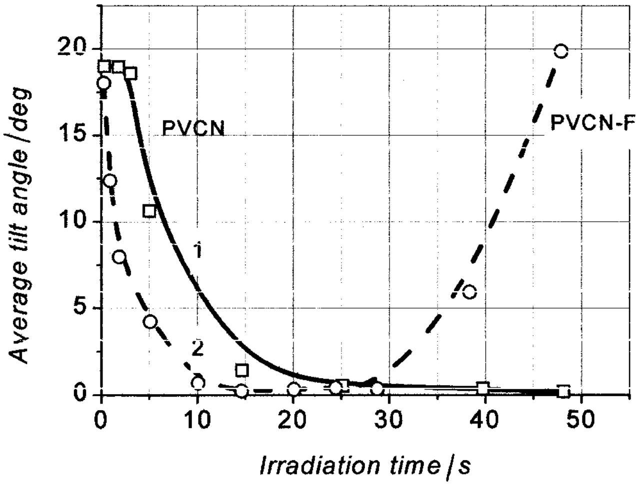

Figure 1. Pretilt angle vs. irradiation time for PVCN and PVCN-F.

The tilted alignment of a LC on a PVCN surface was first observed by Kobayashi *et al.* [9] and Dyadyusha *et al.* [10–12]. It was shown that the pretilt angle, θ, *monotonically* decreases with UV exposure, finally approaching zero. It was suggested that the cinnamate fragments are responsible for oblique LC orientation, and that cyclobutane photo-derivatives have a planar

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aligning ability [10]. Thus, a decrease of pretilt angle with UV exposure is explained by changes of the concentration between cinnamate and cyclobutane fragments and their spatial distributions. This model predicts a monotonic decrease of the pretilt angle with UV exposure that was observed in [10].

In this work we report on the first observation of a *non-monotonic* dependence of the LC pretilt angle on a fluorinated PVCN surface. The results indicate that the elementary microscopic photoprocesses in poly(vinyl cinnamates) cannot be explained by the model [10] where the exposure behaviour of the pretilt was reduced to competition between two photochemical processes—crosslinking and *trans–cis* isomerization of cinnamate fragments. We believe that an additional elementary photo-process is the light-induced change of polarity of the PVNC surface.

2. Experimental and results

We studied the aligning properties of PVCN and *para*-fluorinated PVCN (PVCN-F). Polymer films were produced by spin coating of the polymer solution in dichloroethane (concentration $10\,\mathrm{g\,l^{-1}}$) on a glass substrate; the films were cured at 150°C for one hour. The films were then exposed to linearly polarized UV light (Hg lamp) incident normal to the film surface. The intensity of UV in the plane of the polymer film was about $60\,\mathrm{W\,m^{-2}}$.

The alignment of the LC was tested in combined parallel LC cells made from a reference and test surfaces, with liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB, Merck) in between. Calibrated polymer spacers set the cell thickness $L = 60\,\mu\mathrm{m}$. The reference surface was covered with rubbed polyimide layer SE7492 (Nissan Chemical) that provided strong planar anchoring with a pretilt angle $\theta_{\mathrm{ref}} = 0.5°$. Test surfaces were made from the materials under study.

It is known that a pretilt of the director on photoaligning materials is, if anything, double degenerated [12]. To break this degeneracy, the cells were filled in the nematic phase; in this case the degeneracy was broken because of the flow orientation of the LC. The direction of the flow was chosen to give antiparallel alignment of the LC in the cell. The pretilt angle on PVCN was determined from the measured average pretilt in the cell and the known pretilt on the tested surface by a rotation technique [10, 13].

The results of the measurements are shown in figure 1. The cell with the PVCN layer exhibited monotonic decrease of the pretilt angle with increasing exposure time (curve 1). Poor alignment with a large fluctuation of the director on the test surface and wide disinclination lines were observed at the short exposure ($t_{\mathrm{exp}} < 10$ s). Increase of the exposure resulted in improvement of the alignment (visible anchoring fluctuations and orientational defects disappeared at $t_{\mathrm{exp}} > 15$ s) and decrease of the pretilt angle to a value $\theta_{\mathrm{test}} \approx 0.5°$, constant up to the maximum exposure time $t_{\mathrm{exp}} = 60$ s. We found no deterioration of the alignment as the exposure time increased.

The dependence of the pretilt angle on exposure was non-monotonic on the PVCN-F surface (curve 2). The pretilt angle reached zero in the range 10–30 s, then increased to the initial value of $\theta_{\mathrm{test}} \approx 20°$ after 50 s exposure. The observed non-monotonic behaviour of the pretilt angle was not previously observed for any photoaligning materials.

3. Discussion

The non-monotonic behaviour of the pretilt angle on a PVCN-F surface cannot be explained by known models, and we need to search for additonal factors, which can regulate the photoalignment properties. It is known that polar groups of an aligning surface usually produce tilted alignment [1]. Therefore, we supposed that light-induced changes of the surface polarity may be responsible for the exposure dependence of the pretilt. To check this idea we carried out the following qualitative experiment.

The glass substrates covered with PVCN and PVCN-F films were divided into three regions irradiated by UV light for different times $t_{\mathrm{exp}} = 0$, 10 and 60 s. After irradiation we sprinkled the film with a carbon-based powder from a laser printer cartridge; the powder was then shaken off and the film surfaces were examined. On the PVCN film the powder particles adhered only to non-irradiated areas, and they did not adhere in the irradiated areas, figure 2 (photo (*a*)). On the PVCN-F film the powder adhered to the surface not only in the non-irradiated area but also in the region of longest exposure, figure 2 (*b*).

The laser printer powder possesses a very high polarizability and adheres to polar surfaces. Therefore, from figures 1 and 2 one can make the following conclusions. Both non-irradiated PVCN and non-irradiated PVCN-F surfaces are polarized. The UV irradiation changes the initial polarity of the PVCN and PVCN-F surfaces in different ways; the irradiation only decreases the polarity of the PVCN surface, while the polarity of the PVCN-F surface, after the decrease at the short exposure, rises again. Thus, there is a correlation between the exposure dependences of the surface polarity and the pretilt angle on PVCN and PVCN-F surfaces. This correlation supports our suggestions of a role for surface polarity in the exposure dependence of the pretilt angle on the surfaces studied.

To understand the microscopic nature of the surface polarity of PVCNs, and the mechanisms of its changes

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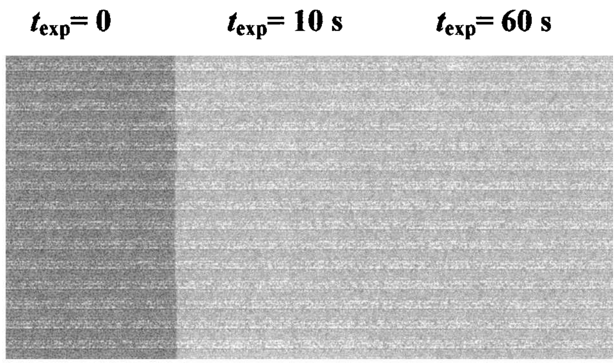
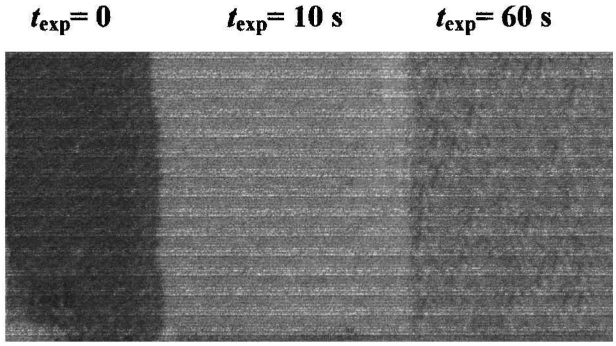


a) PVCN



b) PVCN-F

Figure 2. The toner powder on (*a*) the PVCN film, and (*b*) the PVCN-F film after different exposure times.

with exposure to UV light, additional studies are necessary. At the present stage, we can propose the following model. We presume that in this study the difference in the exposure dependence of the surface polarity is due to the difference in stability of PVCN- and PVCN-F-photodimers. The UV-induced crosslinking of cinnamate fragments produces cyclobutane fragments from both polymers (figure 3). These fragments have lower polarities than cinnamate groups, since the conjugation between phenyl ring and carbonyl group is broken by the crosslinking. The crosslinking process therefore results in a monotonic decrease of the surface polarity and the pretilt angle in the first stage of UV exposure for both PVCN and PVCN-F films (figure 1). In the case of the PVCN film, further irradiation leads to no essential change in aligning and polar properties. This points to a high photochemical stability of the cyclobutane fragments produced from PVCN, namely truxinic and truxillic esters. In the case of PVCN-F, the longer exposure leads to the reappearance of the pretilt angle and polarity of the surface. This indicates that fluorinated truxinic and truxillic esters of the cyclobutane fragments from PVCN-F are photo-unstable. We suppose that a reverse photochemical process takes place, resulting in the recovery of the initial fluorocinnamoyl fragments; this leads to the increase of surface polarity and pretilt angle at long UV exposure.

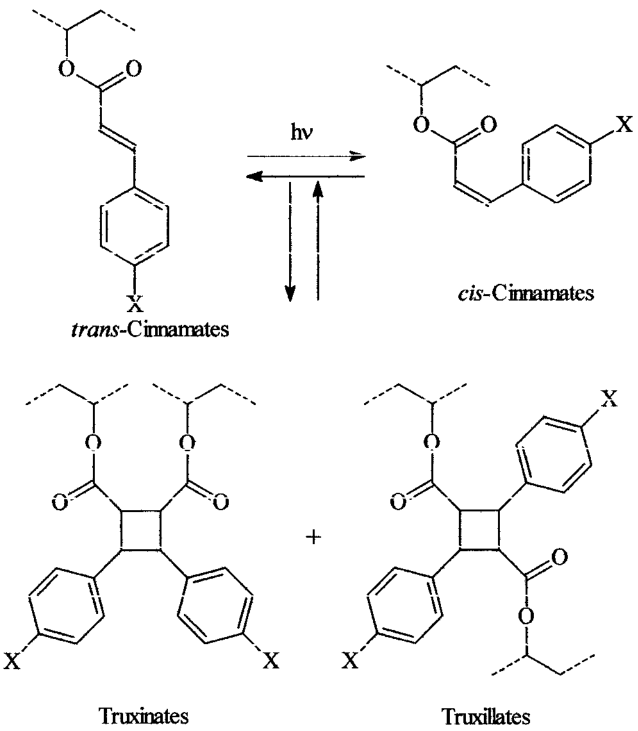


Figure 3. Chemical structures and photochemical transformations of PVCN and PVCN-F.

4. Conclusions

We have observed the non-monotonic UV exposure dependences of the pretilt angle on photoaligning material. We found that the initial decrease of pretilt angle on the PVCN-F surface at the start of irradiation changes to an increase on longer exposure. This dependence correlates with non-monotonic changes of the polarity of the initially polarized PVCN-F surface. This correlation is also observed for the PVCN surface where a monotonic decrease of the pretilt angle with exposure is accompanied by a decrease of surface polarity. These results point to an important role of the surface polarity and its light-induced changes in mechanisms of pretilt angle generation on photoaligning materials.

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References

[1] Cognard, J., 1982, *Alignment of Nematic Liquid Crystals and their Mixtures* (New York: Gorgon & Breach).

[2] Gibbons, W., Shannon, P., Sun, S.-T., and Swetlin, B., 1991, *Nature*, **49,** 351.

[3] Dyadyusha, A., Kozenkov, V., Marusii, T., Rezinikov, Yu., Reshetnyak, V., and Khizhnyak, A., 1991, *Ukr. Phys. J*., **36,** 1059.

[4] Schadt, M., Schmitt, K., Kozenkov, V., and Chigrinov, 1992, *Jpn. J. appl. Phys*., **31,** 2155.

[5] Marusii, T., and Reznikov, Yu., 1993, *Mol. Mater*., **3,** 161.

[6] Obl, M., Morino, S., Ichimura, K., 1998, *Jpn. J. appl. Phys*., **38,** L145.

[7] Ichimura, K., Akita, Y., Akiyama, H., Hayashi, H., and Kudo, K., 1996, *Jpn. J. appl. Phys*., **35,** L992.

[8] Ichimura, K., Akita, Y., Akiyama, H., Kudo, K., and Hayashi, H., 1997, *Macromolecules*, **30,** 903.

[9] Hashimoto, T., Sugiyama, T., Katoh, K., Saitoh, T., Suzuki, H., Iimura, Y., and Kobayashi, S., 1995, *SID 95 Dig*, 877.

[10] Dyadyusha, A., Khizhnyak, A., Marusii, T., Reshetnyak, V., Reznikov, Yu., and Yaroshchuk, O., 1995, *Mol. Cryst. liq. Cryst*., **263,** 339.

[11] Dyadyusha, A., Marusii, T., and Reznikov, Yu., 1995, *Proc. SPIE*, **2731,** 151.

[12] Duadyusha, A., Khizhnyak, A., Marusii, T., Reshetnyak, V., Reznikov, Yu., and Park, W.-S., 1995, *Jpn. J. appl. Phys*., **34,** L1000.

[13] Baur, G., Wittwer, V., and Berreman, D., 1976, *Phys. Lett*., **56A,** 142.

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