

Exposure and temperature dependences of contact angle of liquid crystals on photoaligning surface

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We report on first studies of wetting of liquid crystal on photoaligning surface. We observed strong light-induced variations of a contact angle of a liquid LC 5CB on a photoaligning surface of fluoro-polyvinyl-cinnamate (PVCN-F) and we connected these variations with changes of PVCN-F polarity. We also present drastic changes of the contact angle of a nematic liquid crystal (MLC-6080) on the PVCN-F surface in a vicinity of temperature anchoring transition of liquid crystal from homeotropic orientation to planar one. We did not find any peculiarities in temperature dependence of the contact angle of isotropic liquid (glycerol) on PVCN-F and of nematic liquid crystal on pure glass in the same temperature range. It allows us to suggest that rearrangement of LC molecules and flexible fragments in the LC-polymer interface are responsible for the change of surface tensions both of LC and polymer and the observed jump of the contact angle.

Keywords: nematic liquid crystal, photoalignment, PVCN-F, contact angle.

1. Introduction

Orientation of liquid crystals (LCs) on various surfaces has been actively investigating in the last decades [1–5] due to necessity of perfectly aligned panels in LCD industry and because of serious fundamental aspects of LC various anchoring phenomena. One of advanced orientation techniques implies photosensitive polymer layers irradiated with polarised UV-light [3–5]. Polarised UV-exposure induces anisotropy in polymer layers leading to formation of easy orientation axis on irradiated polymer surface [3–5]. Parameters of photoinduced alignment (direction of the easy axis, pretilt angle, anchoring energy) can be effectively controlled by changing the UV light polarisation and exposure.

Polymers with cinnamoyl-containing side fragments and different side-chains are the most popular and studied photoaligning materials [6–8]. UV-produced cross-linking of side fragments and their reorientation perpendicular to polarisation of UV-light are considered, the main mechanisms of formation of light-induced easy axis in these materials [6]. At the same time we found a non-monotonic dependence of the pretilt of LC 4-*n*-pentyl-4'-cyanobiphenyl (5CB) on fluoro-polyvinyl-cinnamate (PVCN-F) [7] which cannot be explained by known models [9]. We assumed the observed increase in the pretilt at long UV-exposure to be caused by light-induced changes of polarity of the PVCN-F surface. Since surface tension of a liquid on contacting surface is directly connected with a polarity of a surface [10], the study of the LC contact angle behaviour on a photoaligning surface can give important information about influence of UV-exposure on the polarity of the surface. Besides,

investigations of the contact angle attracted our attention in the connection with our recent observations of a thermally-induced anchoring transition of LC MLC-6080 from the homeotropic alignment to the planar one on the PVCN-F layer [8]. We suggested that the cause of this effect is the temperature-dependent competition between aligning abilities of the main chain fragments and flexible photosensitive fragments which concentration depends on UV-exposure. According to empirical Creagh's conception [1,2] the homeotropic alignment of LC is realised at $\gamma_S < \gamma_{LC}$ while the planar alignment occurs at $\gamma_{LC} < \gamma_S$ (γ_S is the surface tension of the substrate and γ_{LC} is the surface tension of LC). Therefore, one can expect a peculiarity of the contact angle in the vicinity of the light-induced anchoring transition.

Here, we report on the first studies of the wetting of liquid crystal on a photoaligning surface. We observed strong light-induced variations of the contact angle of the liquid crystal 5CB on the PVCN-F surface and we connected these variations with the changes of polarity of the photoaligning surface after UV irradiation. We also present drastic changes of the contact angle of a nematic liquid crystal (MLC-6080) on the PVCN-F surface in a vicinity of temperature anchoring transition of liquid crystal from the homeotropic orientation to the planar one.

2. Materials and samples

We used nematics LCs 5CB (clearing point $T_C = 35^\circ\text{C}$) and MLC-6080 ($T_C = 95^\circ\text{C}$), both from Merck, and polymer PVCN-F from the Institute of Bioorganic Chemistry and Petrochemistry (Kyiv, Ukraine) in our studies. PVCN-F films were prepared by spin coating of the polymer solution

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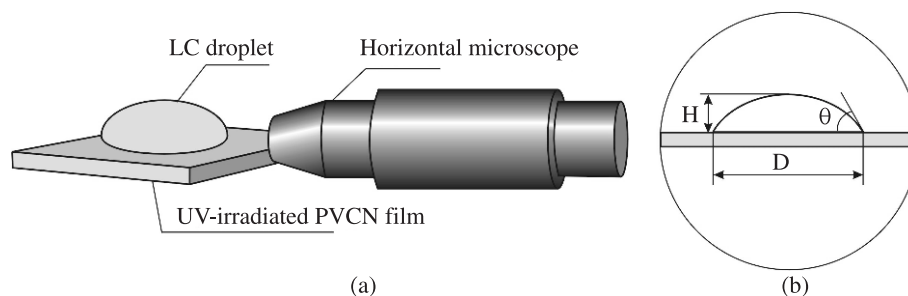


Fig. 1. Set up for determination of geometry of a liquid crystal droplet.

in dichlorethane (concentration 15 g/l) on a glass substrate covered with ITO. The deposited film was cured at 80°C during one hour to remove the solvent residuals. Different strip-like regions of the PVCN-F films were exposed with linearly polarized UV light (the power density $P = 15 \text{ mWcm}^2$, during different times $t_{exp} = 5, 10, 60, 18, 900$, and 1800 s).

To measure the contact angle θ of the LC on differently exposed PVCN-F regions, small droplets of the nematic of the same size were deposited in the irradiated regions by a tube capillary with 0.5-mm diameter. After several minutes the droplets acquired the stable shapes which linear dimensions (the diameter D and the height H) were measured in a horizontal microscope (Fig. 1), and the contact angle θ was calculated according to the formula [10]

$$\cos \theta = \left[\left(\frac{D}{2} \right)^2 - H^2 \right] / \left[\left(\frac{D}{2} \right)^2 + H^2 \right] \quad (1)$$

To measure the temperature dependences $\theta(T)$, the substrates with the PVCN-films were put on a hot stage (MikRa-600, Ukraine), which allowed us to control the temperature of the polymer surface with the accuracy of 0.5°C.

3. Experimental results and discussion

The exposure dependences of the contact angle θ_{LC} measured at the room temperature and at the temperature above the clearing point are shown in Fig. 2. Both dependences are non-monotonic, the short exposure region and the long one are characterised with essential pretilt whereas almost planar alignment is observed in an intermediate region. The contact angle in the isotropic phase is smaller than in the nematic phase that corresponds to regular monotonic decrease in the surface tension with the increase in temperature [10].

The obtained dependences $\theta_{LC}(t_{exp})$ are qualitatively the same as the exposure dependence of the pretilt angle $\theta_{pr}(t_{exp})$ previously reported in Ref. 7. In that paper we found that the short-exposed and the long-exposed PVCN-F surfaces are much more polar than the PVCN-F surface irradiated with the intermediate exposure. Inasmuch as the contact angle of isotropic liquid on a rigid surface usually increases with the increase in the polarity of this surface, one can suggest with confidence that the dependence $\theta(t_{exp})$ is governed by photochemical changes of the polarity of

PVCN-F. At the same time, the last studies shown that the cross-linking of fluorocinnamoyl side fragments and their reorientation perpendicular to polarisation of UV-light through consequent trans-cis-trans-... isomerization are the main microscopic mechanisms of photo-transformation of the PVCN-F [7]. In this concern, the pretilt angle is associated with the concentration of the fluorocinnamoyl side fragments and the initial decrease in the pretilt angle (short exposure regime) is governed by decreasing number of side fragments due to their cross-linking. This process is accompanied by the lowering the surface polarity since the conjugation between phenyl ring and carbonyl group is broken by the cross-linking. The long exposure results in a reverse transition of the fluorinated truxinic and truxillic isomers of the cross-linked fragments to the initial fluorocinnamoyl side fragments. It leads to the recovery of the surface polarity and renovation of the pretilt and the contact angles.

Thus, our results show an evident correlation between the pretilt value and the surface tension of the aligning substrate; the bigger contact angle θ_{LC} and the polarity of the surface are the higher pretilt angle θ_{pr} is. In some sense this conclusion appears to be complementary of the empirical Creagh's conception [1,2]. Our observations show that the gradual change of the surface energy of rigid surface can describe not only the limiting cases of LC orientation ($\theta_{LC} = 0, 90^\circ$) but also control the tilt of LC between planar and homeotropic alignment.

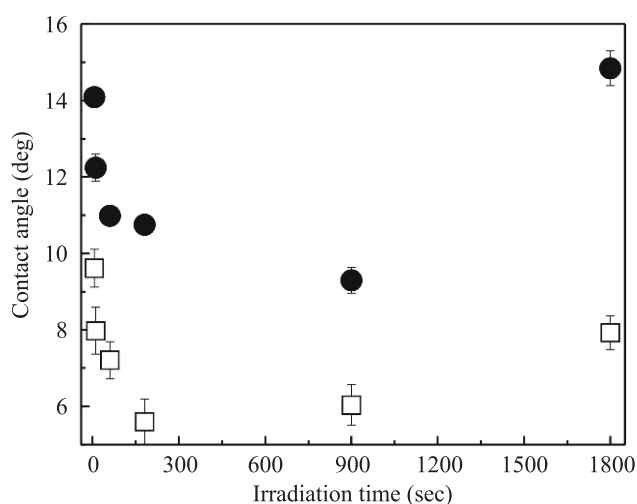


Fig. 2. Exposure dependence of θ_{LC} . Full circles – $T = 24^\circ\text{C}$, open squares – $T = 57^\circ\text{C}$.

The surface tension is associated with the work required to extract a molecule from the bulk to the surface. It is reasonable to suggest that in liquid crystals this work also depends on the both orientational ordering and LC molecules orientation at the boundary. In this case the orientational ordering and the pretilt θ_{pr} should contribute to the contact angle θ_{LC} . To check this suggestion we measured the temperature dependence of the contact angle of LC MLC-6080 on PVCN-F surface in the vicinity of the anchoring transition from a homeotropic to a tilted alignment, which was observed in Ref. 8. The results of these measurements are presented in Fig. 3.

The temperature dependence of the intensity of light passed through the crossed polarizers and the LC cell in between is also depicted in the figure, the keen rise of the light behind the output polarizer in the temperature region $T_{anch} \in (40-55^\circ\text{C})$ corresponds to the anchoring transition of the LC MLC-6080 from homeotropic to tilted alignment. One can see the sharp jump of the contact angle at the temperature of the anchoring transition. At the same time, the analogous measurements of the contact angle of MLC-6080 on the glass surface and of the glycerol (isotropic liquid) on the PVCN-F surface did not show any peculiarities of the dependences $\theta_{LC}(T)$ and $\theta_{glycerol}(T)$ (Fig. 4). In addition, we did not observe the anchoring transition of MLC-6080 on the glass substrate.

Smooth dependence of the contact angle of LC on a glass substrate, i.e., the absence of the anchoring transition, allows us to say that there are no peculiar changes of the surface energy of LC around T_{anch} . This means that decrease in the orientational ordering of LC itself cannot explain the drastic temperature changes of θ_{LC} and θ_{pr} around T_{anch} , and that the role of the PVCN-F surface is crucial. On the other hand, the fact of that there are no peculiarities of the dependence of the contact angle of glycerol on the glass substrate testifies of the absence of specific changes of the surface tension of PVCN-F in the actual temperature region. Thus, we can state that the anchoring transition is accompanied with a strong jump of the contact angle with the

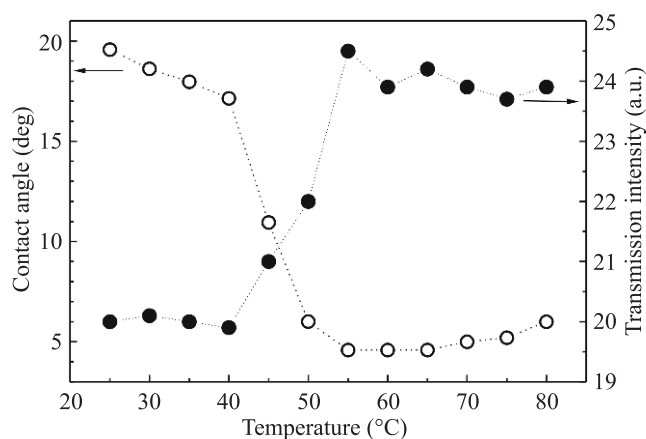


Fig. 3. Dependences of a contact angle of θ_{LC} (open circles) and of transmission intensity (full circles) on temperature.

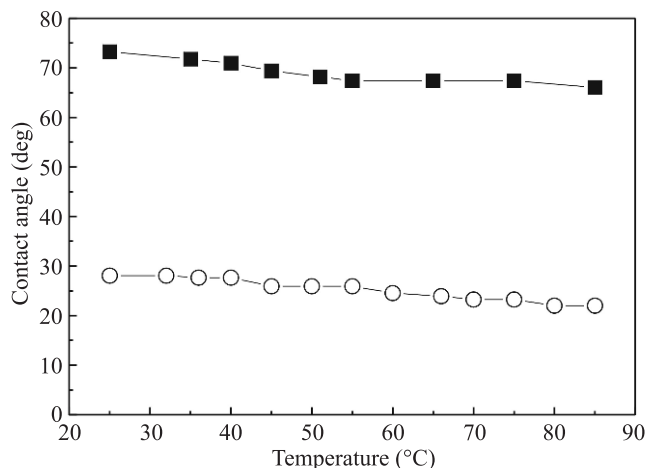


Fig. 4. Temperature dependences of a contact angle of glycerol (full squares) on PVCN-F surface and of MLC-6080 on glass substrate (open circles).

orientational interaction between LC molecules and polymer moieties at the LC-polymer interface being responsible for the both effects. In the low-temperature region, cinnamoyl fragments are aligned perpendicular to the polymer surface and preferably that causes homeotropic alignment of LC. The increase in temperature results in randomization of the angular distribution and depression of the homeotropic affinity of the side-chains assemble. At the same time, the temperature rise does not change the arrangement of the main chains that encourage the planar alignment. At the anchoring transition temperature, the planar aligning property of the main chain grows prevailing. Rearrangement of LC molecules and flexible fragments at the LC-polymer interface evidently changes the amount of work required to pull out a molecule from the LC bulk to the surface. It results in the change of surface tensions of both the LC and the polymer and, in turn, causes the observed sudden change of the contact angle.

4. Conclusions

We observed strong light-induced variations of a contact angle of a liquid LC 5CB on a photoaligning surface of PVCN-F and we connected these variations with the changes of polarity of PVCN-F. We also present drastic changes of the contact angle of a nematic MLC-6080 on the PVCN-F surface in a vicinity of temperature anchoring transition of liquid crystal from homeotropic orientation to planar one. We did not find any peculiarities in temperature dependence of the contact angle of isotropic liquid (glycerol) on PVCN-F and of nematic liquid crystal on pure glass in the same temperature range. It allows us to suggest that rearrangement of LC molecules and flexible fragments in the LC-polymer interface are responsible for the change of surface tensions both of LC and polymer and the observed jump of the contact angle.

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