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Anchoring of a liquid crystal on a photoaligning layer with varying surface morphology

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We report the studies of the photoalignment properties of fluorinated polyvinylcinnamate (PVCN-F) films. The influence of film preparation and UV light irradiation conditions on anchoring properties were investigated. We have studied surface director reorientation in a magnetic field for various exposures and surface conditions. The results obtained show that both the preparation conditions and exposure time determine surface morphology, which in turn affect the value of anchoring energy. For small concentration of the PVCN-F in a spin-coated solution the surface of the aligning film is rather smooth, and the value of anchoring energy $\bar{W}_\varphi = 10^{-5}$ J m^{-2} is presumably determined by a physico-chemical interaction. Higher concentration of the PVCN-F results in rough irregularities on the surface, and the value of the anchoring value increases due to a predominant contribution of the Berreman-type anchoring up to 7×10^{-5} J m^{-2}.

1. Introduction

Photoalignment using polarized irradiation of a polymer film has been the subject of extensive research since the discovery nearly a decade ago of optical control of liquid crystal (LC) anchoring [1–4]. This non-rubbing technique is based on producing an axis of anisotropy on the surface of a photosensitive polymer by irradiation with polarized UV light. This photoalignment method considerably simplifies LC device fabrication and has advantages over the common rubbing alignment technique (no electrostatic charge or dust contamination of the aligning surface after treatment). Another surprising peculiarity of this photoalignment technique is the possibility of controlling LC anchoring energy with the aligning surface. An excellent review of up-to-date achievements in the area of photoalignment of LCs is presented in [5].

It is well known that film preparation conditions critically affect the final aligning properties of rubbed polymers. This is of special concern for photoaligning materials that provide a smaller anchoring energy than do rubbed polymers. The aim of the present work is to clarify the influence of preparation conditions on the aligning properties of polyvinylcinnamate, which is one of the most popular photoaligning material [6–8]. In particular, we studied the dependence of anchoring on exposure time, polymer concentration in the solution and spin-coating velocity.

2. Experiments and results

We studied the aligning properties of fluorinated polyvinylcinnamate (PVCN-F) [9]. PVCN-F consists of a polyvinyl alcohol main chain with photosensitive side groups based on fluorinated cinnamic acid. Side groups with their long axes parallel to the light polarization undergo photo-crosslinking under linearly polarized UV light. This leads to anisotropic distribution of long axes both of the non-crosslinked cinnamic groups and of the cyclobutane photoderivatives. This structure provides a homogeneous planar or tilted LC alignment perpendicular to the polarization of the UV light.

PVCN-F films were deposited by spin-coating of a solution of polymer on glass substrate covered with indium tin oxide. The concentration of the polymer in the solvent varied in the range 0.1 to 3.0 wt %, and the velocity of spin-coating varied between 500 and 3000 rpm. The obtained films were cured at 150°C for 1 hour. After curing, the films were exposed to linearly polarized UV light from a Hg-lamp, incident normally to the film surface. The polarization of the UV light was formed by

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a quartz lens and polarizing Glan–Thomson prism. The intensity of the UV light in the plane of the PVCN-F film was about 6 mW cm^{-2}.

The alignment of the LC on PVCN-F film was examined in combined cells assembled from a reference substrate and the test substrate. The reference substrate was covered by a rubbed polyimide layer and provided strong planar alignment of the LC. The test surface was covered with PVCN-F film. The direction of rubbing on the reference surface was perpendicular to the vector of UV light polarization. The thickness of the cell was controlled by 60 μm and 10 μm spacers. The cells were filled with LC 5CB at room temperature along the direction of rubbing on the reference surface.

Observation in the polarizing microscope showed a domain structure pointing to a degenerate planar alignment in non-irradiated areas of the test surface. In the irradiated areas of the test surface we found a homogeneous planar alignment with a light-induced easy axis parallel to the direction of rubbing on the reference surface. Such LC alignment corresponded to a direction of the light-induced easy axis perpendicular to the incident light polarization.

We studied a director reorientation on a non-irradiated test surface in a magnetic field, **H**, vs. PVCN-F concentration, $c_{\mathrm{PVCN\text{-}F}}$, in the solution during spin-coating and velocity ω of spin-coating. The combined cell ($L = 60\,\mu\mathrm{m}$) was placed between the magnet poles and crossed polarizers. The magnetic field was parallel to the planes of the cell and perpendicular to the LC director. The reference surface faced toward the He-Ne laser test beam whose polarization was parallel to the director on the reference surface.

The application of the magnetic field caused director reorientation in the cells and the appearance of light beyond the analyser. The dependences $\varphi(\mathbf{H})$ for different values of $c_{\mathrm{PVCN\text{-}F}}$ and the fixed value $\omega = 1000$ rpm are depicted in figure 1. It can be seen that the character of the director reorientation depends on the concentration $c_{\mathrm{PVCN\text{-}F}}$. At the low concentration $c_{\mathrm{PVCN\text{-}F}} = 0.1$ wt % the reorientation of the director on the test surface begins at a rather high field, $\mathbf{H} \approx 0.2$ T. The twist angle reaches the value $\varphi = 10°$ at $\mathbf{H} \approx 0.25$ T. Rotation of the analyser restored a dark state at a fixed position of the polarizer. Thus the director was reoriented on the test surface, and the light polarization followed the director in the cell (Maugiun regime) [10]. The reorientation angle, φ, was equal to the angle of the rotation of analyser in this case. We could not obtain darkness on rotating the analyser at higher fields. Thus, the Maugiun regime was not valid at $\mathbf{H} > 0.25$ T. At higher concentrations of $c_{\mathrm{PVCN\text{-}F}}$ the Maugiun regime was valid up to $\varphi \approx 90°$, and the threshold of the reorientation increased with the increase of $c_{\mathrm{PVCN\text{-}F}}$.

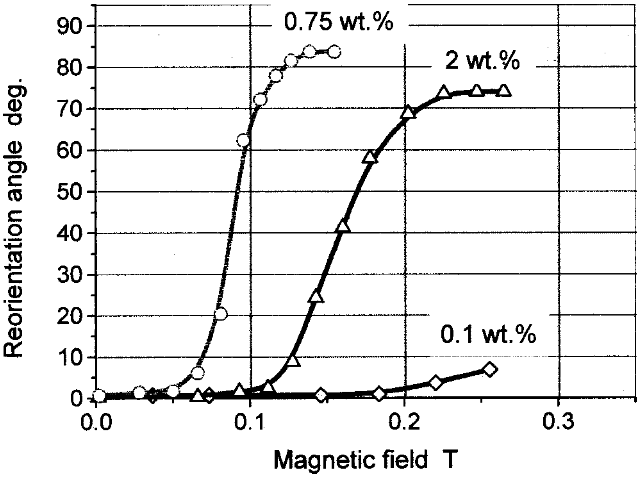


Figure 1. Reorientation angle of the LC director vs. magnetic field strength **H**.

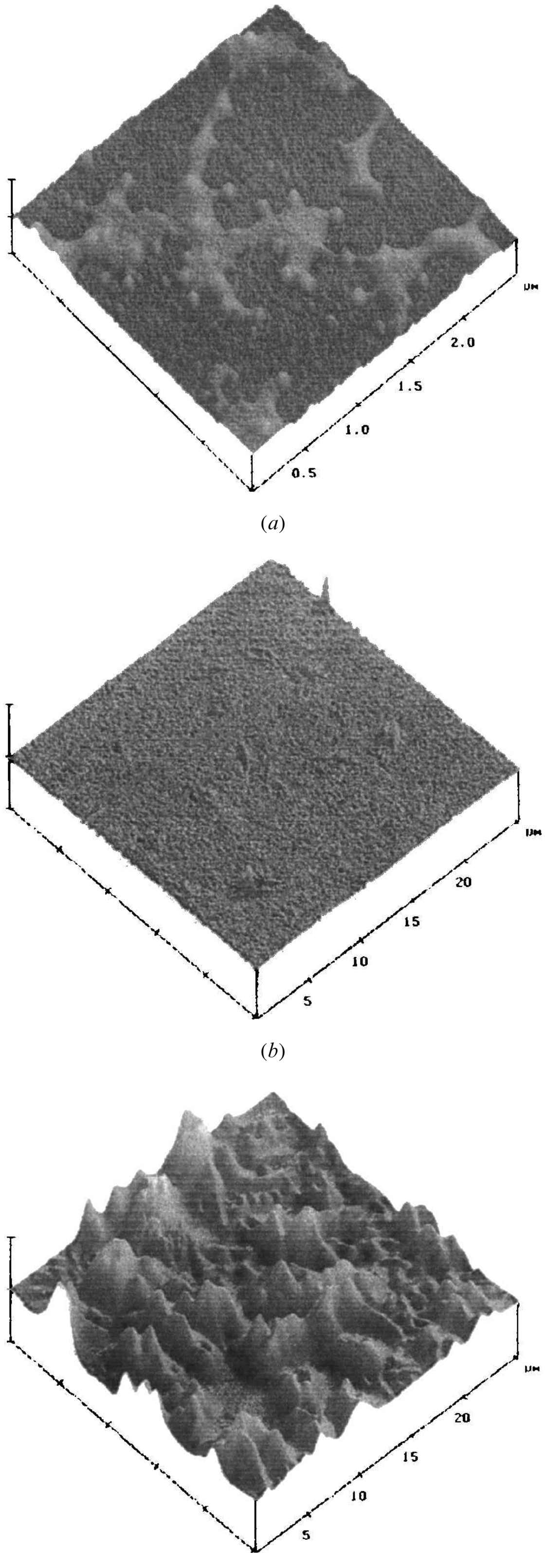
The dependences $\varphi(\mathbf{H})$ shown in figure 1 could also be obtained by changing the parameter ω and keeping $c_{\mathrm{PVCN\text{-}F}}$ constant. Thus, the changing of $c_{\mathrm{PVCN\text{-}F}}$ at fixed ω is equivalent to the changing of ω at fixed $c_{\mathrm{PVCN\text{-}F}}$ in the range $c_{\mathrm{PVCN\text{-}F}} = 0.5$–4% and $\omega = 500$–4000 rpm.

We considered that the results obtained could be explained by different morphologies of the test surface at different values of ω and $c_{\mathrm{PVCN\text{-}F}}$. To check this, the test substrates were studied by atomic force microscopy (AFM) before and after UV irradiation at different values of $c_{\mathrm{PVCN\text{-}F}}$. The AFM measurements were made in contact mode at constant force. The surface structure obtained for different polymer concentrations $c_{\mathrm{PVCN\text{-}F}}$ exhibited a great difference. Figures 2(*a*–*c*) show the topographic structure of polymer films with $c_{\mathrm{PVCN\text{-}F}} = 0.1$, 0.75 and 2 wt %, respectively.

In figure 2(*a*) it can be seen that at low value of PVCN-F concentration, $c_{\mathrm{PVCN\text{-}F}} = 0.1$ wt %, the surface is incompletely covered with polymer, and the parts of the surface covered with polymer are flatter than the ITO surface. The characteristic size of regions covered with PVCN-F was about 1 μm. At $c_{\mathrm{PVCN\text{-}F}} > 0.1$ wt %, polymer completely covers the ITO surface; UV irradiation of the surfaces with either polarized or non-polarized UV light does not change its morphology.

At the concentration $c_{\mathrm{PVCN\text{-}F}} = 0.75$ wt % we obtained a continuous layer of PVCN-F with characteristic hills of size 0.2–0.3 μm and heights of the order 0.01 μm figure 2(*b*). The average distance between the hills also is about 0.2–0.3 μm. We found no evidence of changes in surface morphology after UV irradiation of the surfaces with either polarized or non-polarized UV light.

Further increase of concentration results in a strongly inhomogeneous PVCN-F surface. The concentration $c_{\mathrm{PVCN\text{-}F}} = 2$ wt % produced surface inhomogeneities with



(*a*)

(*b*)

(*c*)

Figure 2. AFM pictures of the PVCN-F surface: $c_{\text{PVCN-F}} =$ (*a*) 0.1, (*b*) 0.75, (*c*) 2 wt %.

characteristic size 0.5 μm and height 0.2 μm. The distance between inhomogeneities was about 0.5 μm, figure 2 (*c*). Further increase of the polymer concentration up to 5 wt % did not influence the surface roughness. UV irradiation of the surfaces with polarized or non-polarized UV light caused a reduction of the inhomogenity height to 130 nm without apparent changes in their lateral size. In agreement with the authors of [11], we found no anisotropy in the surface morphology after irradiation. The absence of *macroscopic* surface anisotropy in the films means that LC photoalignment is dominantly determined by *microscopic* anisotropy in the irradiated polymer.

We studied the influence of surface morphology on the value of the azimuthal anchoring energy of the LC on the PVCN-F films. We used the combined twisted cell method described in detail in [12]. The combined cell was assembled so that the surfaces easy axes were orthogonal to each other. The twist angle φ between the directions of the director on the aligning substrates was measured as a function of concentration $c_{\text{PVCN-F}}$. The azimuthal anchoring energy, $\bar{W}$, was estimated from the formula [12]

$$\bar{W} = \frac{2k_{22}\varphi}{L \sin 2\varphi} \qquad (1)$$

where $k_{22} = 3.1 \times 10^{-12}$ N is a twist elastic constant of 5CB [13].

The results of the measurements of $\bar{W}(c_{\text{PVCN-F}})$ are presented in the table. The dependence $\bar{W}(c_{\text{PVCN-F}})$, and the AFM data, indicate a strong influence of surface morphology on the value $\bar{W}$. The measurements for a surface incompletely covered by polymer ($c_{\text{PVCN-F}} = 0.1$ wt %) gave the effective value $\bar{W} = 22 \times 10^{-6}$ J m^{-2}. We obtained a smaller value, $\bar{W} = 10 \times 10^{-6}$ J m^{-2}, for the flat surface ($c_{\text{PVCN-F}} = 0.75$ wt %) and a rather strong anchoring, $\bar{W} = 70 \times 10^{-6}$ J m^{-2}, for the rough surface ($c_{\text{PVCN-F}} = 2$ wt %) for the same exposure. Anchoring with ITO gives a contribution to the effective value of anchoring energy. Below we restrict our consideration to the completely covered PVCN-F films.

Table. Dependence of the anchoring energy $\bar{W}_\varphi$ of LC on the PVCN-F surface, and of the average amplitude of the surface relief, on the polymer concentration $c_{\text{PVCN-F}}$.

Polymer concentration, $c_{\text{PVCN-F}}$/wt %	Average amplitude of the surface relief/nm	Anchoring energy, $\bar{W}_\varphi \times 10^{-6}$ J m^{-2}
0.1	30	22
0.75	10	10
2	200	72

3. Discussion

In order to understand the results obtained we need to take into account that the formula (1) was derived for a flat aligning surface; an irregular surface relief should change the energy needed for surface director reorientation. Therefore, the expression (1) gives an effective value $\bar{W}$, comprising both a traditional component W_φ and the component W_B determined by surface morphology. Surface *microscopic* inhomogeneities, the size of which is comparable to the molecular size, can result in the decrease of the LC order parameter near the surface and, in turn, in the decrease of the anchoring energy. On the other hand, *macroscopic* inhomogeneities can effectively increase the anchoring energy. According to the Berreman model [14, 15], a sinusoidal relief on the aligning surface gives a contribution W_B to the effective anchoring energy, $\bar{W} = W_\varphi + W_B$, where W_φ is the physico-chemical contribution. In the case of a sinusoidal relief the value W_B increases as a second power of the amplitude A of the surface undulation:

$$W_B = k_{22} A^2 \left(\frac{2\pi}{\Lambda} \right)^3 \qquad (2)$$

where k_{22} is the Frank elastic constant and Λ is the period of the sinusoidal surface modulation.

In our case we cannot directly apply Berreman's model, because the surface modulation is two-dimensional and irregular; however, we can make some qualitative estimates. Suppose that the profile of the surface modulation is given by $z = Af(x, y)$, where the 0z-axis is perpendicular to the polymer surface, A is the magnitude of the modulation, and the characteristic length of the inhomogeneity is Λ. If the ratio A/Λ is small enough and the anchoring is strong, i.e. the director follows the surface profile at the surface, the director modulation is proportional to A/Λ. Since the contribution of the director deformation to the volume density of the total free energy of a LC is proportional to $(\partial n_i/\partial x_j)^2$, the excess of the free energy density due to the surface modulation should be proportional to A^2/Λ^4. To obtain this excess, we must integrate the volume density of free energy over the cell thickness. This integration cancels Λ^{-1} and we find that the free energy per unit area is proportional to A^2/Λ^3. Thus, these simple speculations show that the functional dependence of the LC free energy excess upon the A and Λ values, on the surface with arbitrary relief, is the same as for the sinusoidal modulated surface. Therefore formula (2) may be used for a qualitative description of the anchoring on the studied surfaces with different morphologies.

At the concentration $c_{\text{PVCN-F}} = 0.75$ wt % the parameters appeared to be $A = 0.005$ µm and $\Lambda = 0.5$ µm, so that the ratio $A/\Lambda = 10^{-2}$ is very small. In this case formula (2) is valid and gives the value $W_B \approx 1.5 \times 10^{-7}$ J m^{-2}, which is much smaller than the measured value $\bar{W} = 10 \times 10^{-6}$ J m^{-2}. Therefore, it is reasonable to suppose that at this concentration the anchoring energy is predominantly determined by the physico-chemical interaction, i.e. $\bar{W} \approx W_\varphi$.

As the concentration $c_{\text{PVCN-F}} = 2$ wt % we estimate the surface parameter as $A = 0.1$ µm and $\Lambda = 0.5$ µm. Now we get from (2) the value $W_B \approx 60 \times 10^{-6}$ J m^{-2}, which in turn leads to $\bar{W} = W_\varphi + W_B \approx 70 \times 10^{-6}$ J m^{-2}, surprisingly close to the measured value, $\bar{W} = 72 \times 10^{-6}$ J m^{-2} with the dominating contribution of surface morphology.

4. Conclusions

Our study clearly shows the crucial roles of the polymer concentration and spin-coating velocity on the surface morphology of PVCN-F surfaces. By varying these parameters one can obtain either smooth or rough aligning surfaces. At the same time, UV exposure does not modify the macroscopic structure of the surface but produces just a microscopic anisotropy of the surface. For a low concentration of the PVCN-F ($c_{\text{PVCN-F}} = 0.75$ wt %) in a spin-coating solution, the surface of the aligning film is rather smooth, and the value of the anchoring energy $\bar{W}_\varphi = 10 \times 10^{-6}$ J m^{-2} is presumably determined by a physico-chemical interaction. A higher concentration ($c_{\text{PVCN-F}} = 2$ wt %) results in rough irregularities on the surface, and the value of the anchoring value increases due to a predominant contribution of Berreman-type anchoring.

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