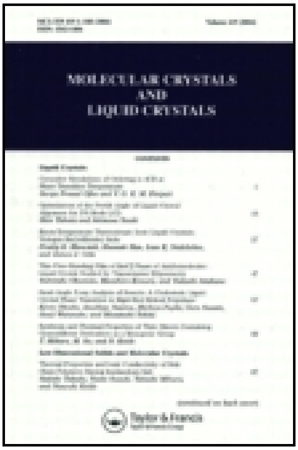

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Surface Versus Bulk Anisotropy of Photo-Sensitive Poly(vinyl cinnamate) Alignmet Layers

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Surface Versus Bulk Anisotropy of Photo-Sensitive Poly(vinyl cinnamate) Alignmet Layers

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Reaction kinetics and orientational anisotropy of poly(vinyl cinnamate) (PVCN) alignment layers photo-co-polymerized with linearly polarized UV light were probed by measurements of linear dichroism (LD) and surface optical second-harmonic generation (SSHG). The results show that the bulk and the surface properties of PVCN films are very similar and suggest that in PVCN there are no specific surface photochemical processes, which could presumably reduce the anchoring of liquid crystals on PVCN substrates. The azimuthal surface anchoring energy coefficient of nematic liquid crystal 5CB in contact with our substrates was of the order of 10^{-6} J/m^2 and strongly depended on the procedure used to measure it. This can be explained by a presence of various memory effects on the LC/PVCN interface, which strongly affect the alignment ability of the PVCN layers.

Keywords: surface alignment; photo-sensitive materials; surface-anchoring

INTRODUCTION

Photo-assisted methods of preparation of polymeric alignment layers for liquid crystals provide substrates with a similar extent of the induced structural anisotropy as the conventional rubbing technique[1-5]. In contrast to this similarity, the photo-aligned layers generally provide much weaker azimuthal surface anchoring strenght as the rubbed ones[2,3,6,7]. The origin of this generally observed difference between the rubbed and the photo-polymerized substrates is still not fully understood.

The interaction of a polymeric layer with liquid crystals primarily depends on its surface structure. From this point of view a possible source of different anchoring effects can be different surface properties of the substrates. These can presumably origin from the fact that rubbing technique is most effective on the surface of the polymer, while axially selective photo-chemical modification takes place predominantly in the bulk. Additional reactions and steric restrictions on the surface can considerably reduce the corresponding photo-chemical changes. To clarify this aspect and to resolve its relation with surface anchoring we performed a comparative investigation of the surface and the bulk properties of the linearly photo-polymerized (LPP) poly(vinyl cinnamate) (PVCN) alignment layers. The bulk properties were extrapolated from the measurements of the linear dichroism (LD) in the UV absorption spectra, while the surface properties were deduced from the surface optical-second harmonic generation (SSHG) experiments. The aligning effect of the substrates on liquid crystals was probed by mesauring the azimuthal surface anchoring energy coefficient W_φ of the nematic liquid crystal 4'-n-pentyl-4-cyanobiphenyl (5CB) in contact with the substrates.

EXPERIMENTAL

PVCN (Aldrich) was dissolved at various concentrations in chloroform. Clean fused silica or glass plates were dipped in the solution for few seconds and then dried at the edge of the filter paper. The plates were then baked for 1 hour at 90°C. The thickness of the adsorbed PVCN films was determined from their UV absorbance at 275 nm and ranged from 20 nm (LD measurements) up to 200 nm (SSHG measurements). The co-polymerization of the cinnamoyl side chains was induced by UV light from either the 150W Xe discharge lamp or the Hg lamp of a similar output power in the UV region. The UV polarizer was mounted between the lamp and the sample.

The LD measurements as well as the SSHG measurements were performed in-situ during the co-polymerization. The UV absorption spectra were detected on HP 8453 spectro-photometer. The activation UV light from the Hg lamp, passing the UV polarizer, entered the sample in direction of 20° with respect to the sample normal. In purpose to measure the absorption anisotropy, a second UV polarized was mounted inside the spectrometer behind the sample position and was rotated between the two orthogonal directions with respect to the polarization of the activation UV light.

The SSHG measurements were performed by using 100 fs long light pulses of 800 nm wavelength from the mode-locked Ti:sapphire laser. The average power of the incident laser beam was 500 mW and was focused onto the sample to a spot of about 100 μm in diameter. The incident beam entered the sample at 45° with respect to the sample normal and the specularly reflected second harmonic light was detected by a photomultiplier mounted after the appropriate spatial and spectral filtering. The sample was mounted on a rotation stage in air and illuminated for some definite time interval with the UV light at normal direction. Then the UV source was switched off and the azimuthal dependence of the SSHG signal was measured. After this the UV light source was switched on again and the photo-polymerization continued.

Measurements of the surface anchoring energy were performed in 6 μm thick flat glass cells. For measurements in twisted configuration[7], one of the glass plates was coated with a rubbed polyimide layer and another with a UV exposed PVCN film. The easy axes of the plates were orthogonal. For the measurements based on observation of the thickness of the Neel disclination walls[3], both plates were covered with UV exposed PVCN layers and had the same orientation. The cells were filled with 5CB by capillary action at room temperature – i.e. in the nematic phase. To probe the effect of nematic-isotropic phase transition on the surface anchoring, the cells were heated to 50°C and then fast cooled down back to room temperature and measured again.

RESULTS AND DISCUSSION

The absorption spectrum of PVCN is characterised by a broad peak at 275 nm[8,9]. Another reference wavelenght is at 250 nm, which is the isosbestic point for trans-cis isomerization reaction of the cynnamoyl side chains[10]. During exposure of the sample to linaerly polarized (LP) UV light the absorbance at both of these wavelenghts reduces as a consequence of the photo-induced isomerization and dimerization (cross-linking) reactions.

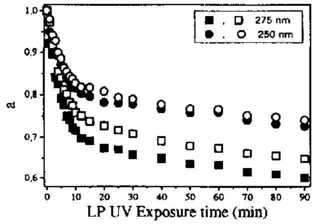

Fig. 1. Anisotropic reduction of absorption at two reference wavelengths during LP UV exposure: solid symbols – relative absorbance of light polarized in direction parallel to the polarization of the activation UV light, open symbols – relative absorbance of light polarized in direction perpendicular to the polarization of the activation UV light.

Due to selective absorption of the activation UV light the reduction is larger for the spectrometric light polarized in direction parallel to the activation UV light (Fig. 1). The corresponding linear dichroism is for that reason negative with respect to the UV polarization direction.

In thin PVCN films the cinnamoyl groups are presumed to be oriented predominantly in direction parallel to the surface[8]. The absorbance of cis-cynnamoyl groups at 275 nm is for a factor of 1.77 lower than the absorbance of trans-cynnamoyl groups, while the dimerized groups are supposed to have a negligible absorbance at both 275 nm and 250 nm[8,10]. From this data and the observed modification of the absorbance it is possible to calculate the relative concentrations and surface-in plane order parameters of various conformational forms of the side chains. Extension of the material balance equations of Egerton at al.[8] to the case of anisotropic photo-polymerization yields to the following equations for the relative decrease of the absorbance

$$
\begin{aligned}
a_{II}^{(275)} &= \frac{A_{II}^{(275)}(t)}{A^{(275)}(t=0)} = \frac{2}{N_o}\int_0^{2\pi}\left(N_t(\varphi)+\beta N_c(\varphi)\right)\cos^2\varphi d\varphi \\
a_{\perp}^{(275)} &= \frac{A_{\perp}^{(275)}(t)}{A^{(275)}(t=0)} = \frac{2}{N_o}\int_0^{2\pi}\left(N_t(\varphi)+\beta N_c(\varphi)\right)\sin^2\varphi d\varphi
\end{aligned}
\qquad (1)
$$

and

$$
\begin{aligned}
a_{II}^{(250)} &= \frac{A_{II}^{(250)}(t)}{A^{(250)}(t=0)} = \frac{2}{N_o}\int_0^{2\pi}\left(N_t(\varphi)+N_c(\varphi)\right)\cos^2\varphi d\varphi \\
a_{\perp}^{(250)} &= \frac{A_{\perp}^{(250)}(t)}{A^{(250)}(t=0)} = \frac{2}{N_o}\int_0^{2\pi}\left(N_t(\varphi)+N_c(\varphi)\right)\sin^2\varphi d\varphi
\end{aligned}
\qquad (2)
$$

where *A* is absorbance, *N(φ)* the concentration of the specifically oriented side chains, N_0 the initial concentration of the trans-side chains, β a ratio of the absorptivities of the cis and trans forms and φ measures the orientation of the cinnamoyl molecular absorption axis with respect to the activation UV light. The indeces *t* and *c* denote trans and cis forms respectively.

The relative concentrations of various species can be calculated as

$$
\begin{aligned}
n_t &= \frac{1}{N_0}\int_0^{2\pi} N_t(\varphi)d\varphi = \frac{1}{2(1-\beta)}\left[\left(a_{II}^{(275)}+a_{\perp}^{(275)}\right)-\beta\left(a_{II}^{(250)}+a_{\perp}^{(250)}\right)\right], \\
n_c &= \frac{1}{N_0}\int_0^{2\pi} N_c(\varphi)d\varphi = \frac{1}{2(1-\beta)}\left[\left(a_{II}^{(250)}+a_{\perp}^{(250)}\right)-\left(a_{II}^{(275)}+a_{\perp}^{(275)}\right)\right], \\
n_d &= \frac{1}{N_0}\int_0^{2\pi} N_a(\varphi)d\varphi = 1-\frac{1}{2}\left[a_{II}^{(250)}+a_{\perp}^{(250)}\right]
\end{aligned}
\qquad (3)
$$

where *d* denotes dimerized groups. The result is given in Fig. 2. After 90 min of LP UV exposure the concentration of the trans groups reduces to about 50% of its initial value. The cis and the dimerized groups are formed in about similar amount. The photo-reactions are extensive in the first 10 minutes of the UV exposure, while afterwards the reaction kinetics considerably slows down. This second slow process is usually related to dimerization, but in our PVCN films, however, both photo-reaction processes show a very similar kinetics.

The surface in-plane order parameters $Q=<cos2\varphi>$ of the trans and the cis groups are calculated from absorbance modifications as

$$Q_t=\frac{1}{N_0 n_t}\int_0^{2\pi} N_t(\varphi)\cos 2\varphi d\varphi=\frac{1}{2n_t(1-\beta)}\left[\left(a_{II}^{(275)}-a_{\perp}^{(275)}\right)-\beta\left(a_{II}^{(250)}-a_{\perp}^{(250)}\right)\right],$$

$$Q_c=\frac{1}{N_0 n_c}\int_0^{2\pi} N_c(\varphi)\cos 2\varphi d\varphi=\frac{1}{2n_c(1-\beta)}\left[\left(a_{II}^{(250)}-a_{\perp}^{(250)}\right)-\left(a_{II}^{(275)}-a_{\perp}^{(275)}\right)\right]. \qquad (4)$$

The order parameter of dimers can not be deduced, as we have no information on their absoption anisotropy. The result of the calculation is given in Fig. 3. The order parameter of the trans and cis groups have opposite signs and the magnitude of Q of the trans groups increases with incresing exposure while the magnitude of Q of the cis groups decreases. This is because the latter are formed on behalf of the former and it shows that photo-generated cis groups are oriented in a similar direction as the initial parent trans groups. After 90 minutes of LP UV exposure the order parameters of both have a value of about 0.1.

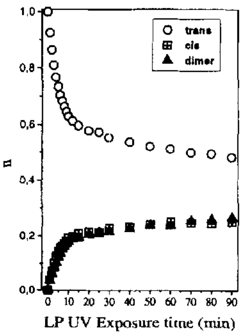

Fig. 2. Relative concentration of various conformational forms of cinnamoyl side groups as a function of the LP UV exposure.

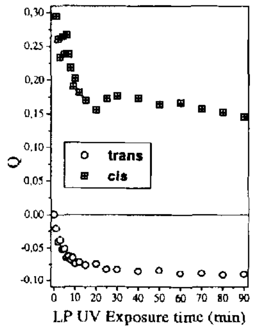

Fig. 3. In-plane orientational order parameter of trnas and cis forms of cinnamoyl side groups as a function of the LP UV exposure.

Our surface optical second-harmonic measurements on PVCN films are extensively described elsewhere[11,12]. They provide information on the surface relative concentration of the trans-cinnamoyl groups and on their surface in-plane order parameter. The results are given in Fig.4 and Fig. 5. and are quite similar to the results of the LD measurements. As the SSHG measurements were performed by using a different UV light source (Xe-lamp) as in LD measurements (Hg-lamp), some relatively small variations in the details of the photokinetics presumably originate from different spectra of the excitation light. Despite this difference, the characteristic two step nature of the photo-reaction process (initial fast depopulation and the following slower decay) is evident also on the surface. It is also notable that the surface order parameter attains very similar magnitudes as the bulk one. From these observations we conclude that the surface and the bulk photoreaction kinetices of the PVCN are very similar. On contrary to the propositions found in the literature[2,3], it seems that there is no specific surface reactions which would crucially affect the surface photo-polymerization process and consequently the anchoring of liquid crystals on the PVCN substrates.

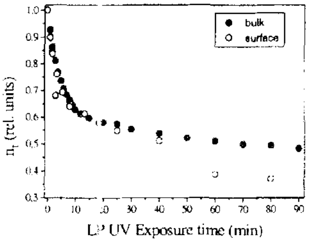

Fig. 4. Relative concentration of trans cinnamoyl groups as a function of the LP UV exposure time: solid circles – bulk, open circles - surface.

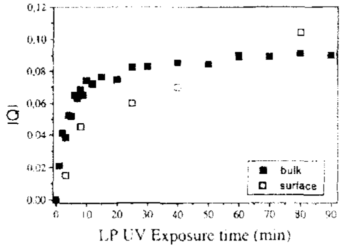

Fig.5. In-plane orientational order parameter of trans cinnamoyl groups as a function of the UV exposure: solid squares - bulk, open squares - surface.

Fig. 6 and Fig. 7 show the results for azimuthal surface anchoring energy coefficient W_φ of 5CB in contact with PVCN layers for various exposures of the layers to the LP UV light. In twisted configuration W_φ rapidly increases in the beginning of the exposure, and then a more slow increase takes place. For a layer prepared by 80 min of exposure the value of $W_\varphi=1.4\cdot 10^{-5}$ J/m^2 is attained. Measurements by the Neel wall method, however, gave much lower values of W_φ. In this case (Fig. 7) W_φ about linearly increases with increasing exposure time and reaches a magnutude of $W_\varphi=1.2\cdot 10^{-6}$ J/m^2 for 80 minutes of exposure. When the sample is heated to the isotropic phase and then cooled back to room temperature again, the surface anchoring considerably decreases and seems to be practically independent on the UV exposure time. These results demonstrate that the observed values of W_φ can be strongly influenced by the procedure used to measure them and that abroupt heating to the isotropic phase can destroy the photoalignment. This suggests on the presence of various memory effects in the PVCN/5CB interface.

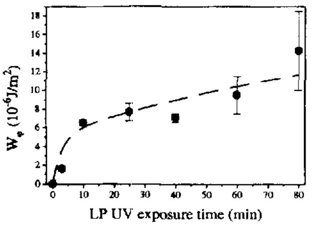

Fig. 6. Azimuthal surface ancho-ring energy coefficient versus LP UV exposure time as determined from measurements in twisted cell. The dashed line is just a guide to the eye.

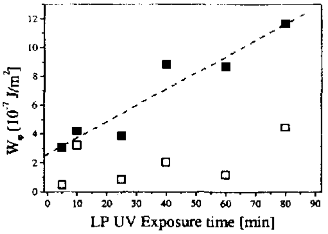

Fig. 7. Azimuthal surface anchoring energy coefficient versus LP UV exposure time as determined from measurements of the width of the disclination lines (Neel walls): solid squares – measurement before heating of the sample to the isotropic phase, open squares – after heating to the isotropic phase.

CONCLUSIONS

We found that the surface and the bulk photo-reaction kinetices of the trans-cinnamoyl side groups of the PVCN are quite similar. The initial fast decrease of the concentration of these groups $n_t(t)$ is followed with a subsequent much slower decrease. Also the surface and the bulk in-plane orientational order parameters of the trans-cinnamoyl groups $Q=<cos2\varphi>$ change in a similar manner and rich maximal values of about 0.12, which is similar to the rubbed polyimide layers. Measurements of the azimuthal surface anchoring energy coefficient W_φ of the liquid crystal 5CB in contact with the substrates showed that the dependence of $W_\varphi(t)$ is correlated with the behaviour of $Q(t)$ for the trans-cinnamoyl side groups. The observed values of $W_\varphi \sim 10^{-6} J/m^2$ are, however, much lower than in case of polyimide layers and strongly depend on procedure used to measure them and on the hystory of the sample. These observations suggest on the presence of various memory effects on the LC/PVCN interface, which very probably reduce the alignment ability of the PVCN substrates.

Acknowledgments

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