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Photoinduced ordering and alignment properties of polyvinylcinnamates

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First order reaction kinetics have been accurately fitted to birefringence data taken on polyvinylcinnamate samples during polarized UV exposure. The peak measured value of 0·0136 is about three times smaller than that found in rubbed polymers. However the measured azimuthal anchoring energy ($4{\cdot}2 \times 10^{-6}\,\mathrm{J\,m^{-2}}$) is about two orders of magnitude less than rubbed polymers. Thus it is suggested that the photoinduced ordering at the surface of polyvinylcinnamates may be different to that measured in the bulk.

1. Introduction

The vast majority of commercial liquid crystal displays use rubbed polymer alignment to achieve a pretilted planar anchoring of the nematic director at each surface. The mechanism for this alignment is an anisotropic van der Waals interaction which is caused by surface ordering induced by the rubbing of the polymer [1]. However the use of rubbing has major drawbacks. Firstly, the process itself is hard to control and requires very accurate tolerances in pile deformation especially when a high pretilt is required. Also the rubbing leads to scratches in the polymer surface which are observed in the microscopic nematic texture and lead to a reduced contrast ratio. Finally, rubbing creates a large static charge which can cause cross-track shorts or failure of thin film transistors. Hence there is much interest in alternative technologies which can provide alignment without the need to make contact with the surface. These techniques include Langmuir–Blodgett film disposition [2], oblique evaporation [3] and grating alignment [4, 5].

One further technique involves the use of polymers in which ordering can be induced by polarized incident radiation. This process is non-contact and so does not lead to sample contamination. Furthermore it allows subpixellation via either alignment direction or by anchoring energy. Broadly speaking, two different approaches have been adopted. The first relies on the light-induced reorientation of a chromophore such as an azobenzene dye in a polyimide host [6] or a chromophore attached directly to a surface [7]. The second approach is to deplete the concentration of a starting material by a reaction whose rate depends on the direction of the polymer with respect to the polarization direction of the incident radiation. Examples include photo-deimidization of polyimide films [8] and photo-crosslinking of polyvinylcinnamate [9].

In this paper we present results based on the latter technique. The kinetics of the exposure are followed by monitoring birefringence and comparison is made with predictions from first order reaction kinetics. We also measure the azimuthal anchoring strength of a nematic liquid crystal on these surfaces and comment on its relationship with the photoinduced ordering.

2. Modelling of reaction kinetics

It is now well understood that the dominant photoreaction in polyvinylcinnamate (PVCi) is the cycloaddition of two cinnamate side groups (species A) from different polymer chains to form a truxinic acid derivative (species B) as shown in figure 1. The cinnamate groups have significant UV dichroism and dielectric anisotropy

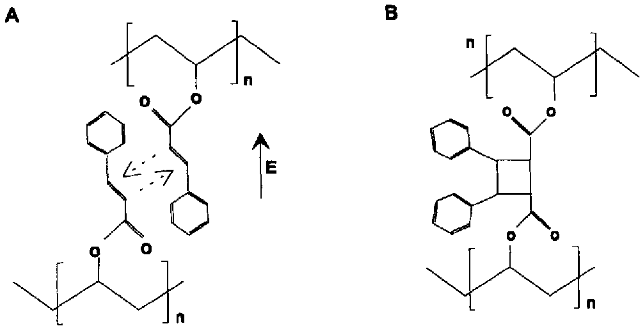

Figure 1. Polyvinylcinnamate polymer (A) and photoproduct (B).

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due to electron delocalization extending from the benzene through the adjacent double bond to the carboxyl group. Therefore the absorption of a photon and the resulting cycloaddition is most probable when the photon polarization is in the direction shown in figure 1. Polarized UV irradiation of an initially amorphous film will lead to a selective depletion of cinnamate groups aligned parallel to the polarization axis. The polarizability anisotropy of the reaction product (B) is assumed to be much less than the cinnamate and so it is the direction of the residual cinnamate groups (A) which dictates the macroscopic birefringence axis and the liquid crystal alignment. Reaction kinetics can therefore be monitored by real time measurement of film birefringence. The evolution of birefringence during exposure is modelled as follows.

The reaction kinetics are assumed to be pseudo-first order, and the rate of reaction is further assumed to depend on the angle between the long axis of the cinnamate group and the plane of polarization of light. The orientation of each cinnamate side chain in the polymer is described by its polar angles θ and ϕ. Thus the rate equation is:

$$\frac{\mathrm{d}[\mathrm{A}]_{\theta,\phi}}{\mathrm{d}t} = -k[\mathrm{A}]_{\theta,\phi} f(\theta,\phi) \tag{1}$$

The expression takes its simplest form if light is incident from a direction such that $\theta = 90°$, and with the polarization vector aligned along the axis $\theta = 0°$ (see figure 2), the rate equation becomes in this case,

$$[\mathrm{A}]_{\theta,\phi} = K \exp(-kt\cos^2\theta) \tag{2}$$

For the analysis of the induced birefringence, both the total residual concentration of cinnamate groups in the sample, and their degree of orientation must be determined at each point in time. The orientation is defined by the scalar order parameter S, given by:

$$S = \frac{1}{2}(3\langle\cos^2\theta\rangle - 1) \tag{3}$$

Note that in the present work, the cinnamate residues are selectively depleted from a fixed orientation. The limiting distribution under long exposure to light will consist of cinnamate groups distributed with circular symmetry, perpendicular to the polarization vector of the incident light. The order parameter in this case will increase from 0 to $-0{\cdot}5$ during the exposure. We define the integrals:

$$\begin{aligned} P &= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \sin\theta \exp(-t\cos^2\theta)\,\mathrm{d}\theta\,\mathrm{d}\phi \\ &= 2\pi\frac{\pi^{1/2}\,\mathrm{Erf}(t^{1/2})}{t^{1/2}} \\ Q &= \int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \sin\theta\cos^2\theta \exp(-t\cos^2\theta)\,\mathrm{d}\theta\,\mathrm{d}\phi \\ &= 2\pi\left(\frac{\pi^{1/2}\,\mathrm{Erf}(t^{1/2})}{2t^{3/2}} - \frac{1}{t\exp t}\right) \end{aligned} \tag{4}$$

in terms of which:

$$[\mathrm{A}]_{\mathrm{total}} = KP \tag{5}$$

and

$$S = \frac{1}{2}\left(\frac{3Q}{P} - 1\right) \tag{6}$$

In the above equations, the constant factor k has been incorporated into a re-scaled value of t for convenience. Erf is the error function. The concentration of A and the order parameter are plotted as a function of time in figure 3. The concentration falls to a value of about $0{\cdot}1$ in this time period, while the order parameter is seen to rise more quickly to a value close to $-0{\cdot}5$. The photoinduced birefringence can now be calculated from these quantities. For comparison with previous authors, we have considered the approximation

$$\Delta n \approx S[\mathrm{A}]_{\mathrm{total}} = K'(3Q - P) \tag{7}$$

This equation is equivalent to the more complex expression given in [10], although they base their analysis

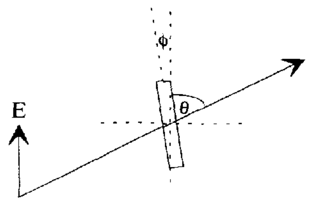

Figure 2. Definition of chromophore orientation with respect to the polarization vector of the incoming radiation.

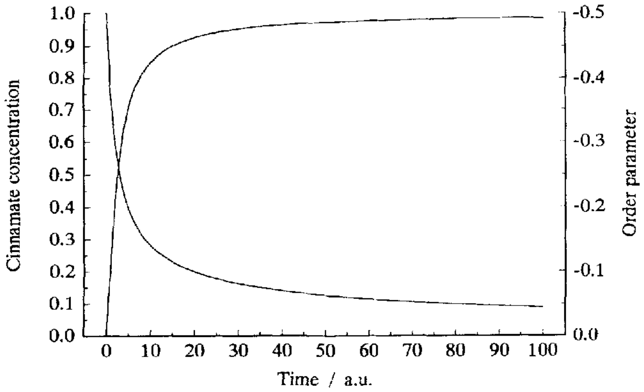

Figure 3. Calculated cinnamate concentration and order parameter as a function of time.

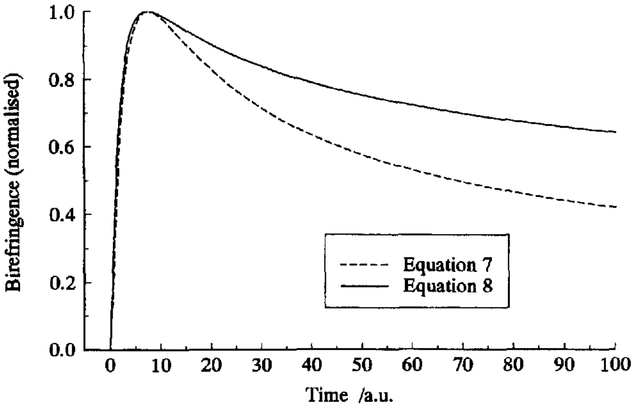

Figure 4. Comparison of birefringence calculated using equation (7) (dashed line) and equation (8) (solid line).

on the concentration of photoproduct rather than that of residual starting material. However, a better approximation is likely to be [11]

$$\Delta n \approx S[\mathrm{A}]_{\mathrm{total}}^{1/2} \tag{8}$$

Equations (7) and (8) are compared in figure 4. The maximum birefringence has been scaled to unity in each case and the time unit for equation (7) has been re-scaled so that the observed maxima coincide. It can clearly be seen that equation (8) predicts a larger birefringence for exposures beyond these maxima.

3. Experimental techniques and results

3.1. *Induced birefringence during exposure*

The configuration for measuring induced birefringence during exposure is shown in figure 5. The sample consisted of a 100 nm thick layer of PVCi on a 3 mm thick fused silica substrate. The material was obtained from Aldrich Chemicals. The layer was formed by spin coating at 3000 rpm for 30 s using a 6% solution in propylene glycol monomethyl ether acetate. Baking the samples at 90°C for 30 min ensured removal of all solvent. Exposure of the film was carried out using a beam from a HeCd laser operating at 325 nm with a polarization direction as shown. The beam was spatially filtered and then apertured to 2 mm diameter so that the reflection from the back face of the sample did not coincide with the incident beam. This prevented the formation of standing waves which would have led to a non-uniform exposure through the depth of the film. Fused silica substrates were used as conventional indium–tin oxide coated glass was found to exhibit significant photoinduced retardation. A final precaution was the choice of exposure wavelength (325 nm). This was well away from the peak of the cinnamate absorption ($13{\cdot}9\,\mu\mathrm{m}^{-1}$ at 274 nm) and thus ensured a low film absorbance ($0{\cdot}13\,\mu\mathrm{m}^{-1}$) and a near uniform intensity through the 100 nm layer.

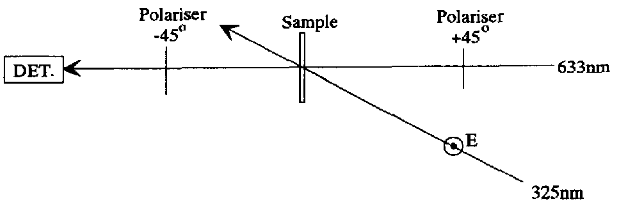

Figure 5. Configuration of apparatus used to measure photoinduced birefringence during exposure.

During exposure, the birefringence was monitored using a HeNe laser (632·8 nm) and two crossed polarizers arranged at ±45° to the polarization of the HeCd beam. This probing wavelength was chosen as it was far removed from any intrinsic absorption bands in either the starting compound or photoproduct. The intensity at the photodetector is given by

$$I = I_0 \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \tag{9}$$

where λ is the probing wavelength, Δn is the birefringence and d is the sample thickness (measured using a Dektak surface profiler). I_0 is the intensity measured with parallel polarizers and an unexposed sample. Thus measurement of I allowed Δn to be calculated. Figure 6 shows a typical set of data. The birefringence was seen to rise to a maximum of 0·0136 at an exposure of $2{\cdot}45\,\mathrm{J\,cm}^{-2}$ followed by a slow decrease. The solid line is the best fit to the data using equation (8) and shows excellent agreement across the entire data range. Equation (7) could not be fitted to the data. Hence it can be concluded that the birefringence is more closely proportional to $[\mathrm{A}]_{\mathrm{total}}^{1/2}$ rather than $[\mathrm{A}]_{\mathrm{total}}$. These data were taken using an exposure intensity of $130\,\mathrm{mW\,cm}^{-2}$. Data taken at lower intensities confirmed that there were no non-linear processes occurring and that only the total exposure was of importance.

By comparison of data with theory it is noted that

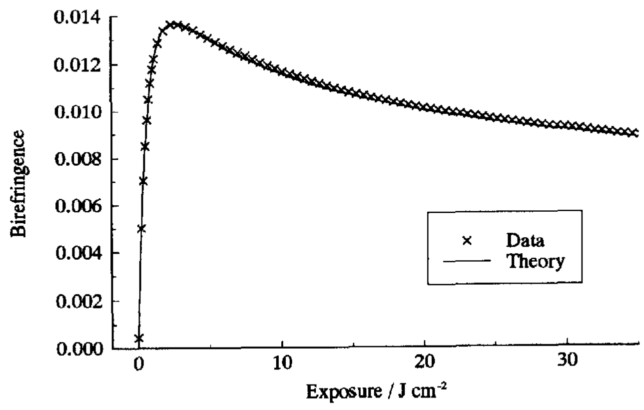

Figure 6. Photoinduced birefringence versus exposure. Solid line is theory, crosses are data.

the maximum birefringence of 0·0136 occurs when the cinnamate concentration is only 0·324 and when the order parameter is $-0·400$ (using equations (5) and (6)). The maximum order parameter that is possible for the starting compound is $-0·5$, i.e. when all cinnamate side chains lie in the plane perpendicular to the polarization direction of exposure. If this condition existed with a cinnamate concentration of unity, then a birefringence of 0·0525 would be expected. Hence the birefringence obtained via polarized UV exposure is only 26% of that which would be expected from a perfect uniaxially stretched film of PVCi.

Further comparisons with theory reveal that the cinnamate concentration at the maximum exposure ($35\,\mathrm{J\,cm^{-2}}$) is only 0·0886 which implies that nearest neighbour reactions are unlikely. It is therefore remarkable that the assumption of first order kinetics with a fixed reaction rate is valid in this dilute regime. Even at very long exposures ($450\,\mathrm{J\,cm^{-2}}$), the reaction did not cease and the birefringence continued to fall. Furthermore, it was noted that the ordering could always be removed by rotation of the HeCd beam polarization. Thus the cinnamate groups, even at very low concentrations will always be susceptible to further reaction. This is in agreement with other work [10].

3.2. *Anchoring energy of alignment*

It is of great interest to measure the azimuthal anchoring energy of a nematic on a PVCi surface and relate it to the exposure energy. This was achieved by the following method. Substrates were exposed to different irradiation energies and were then constructed into cells consisting of one photo-ordered surface and one rubbed polyimide surface which is assumed to be infinitely anchored. Care was taken to avoid any post-exposure of the PVCi surface during the exposure of the UV curing edge seal. The polarization direction of exposure of the PVCi surface was arranged to be parallel to the rubbing direction on the polyimide surface. Thus the alignment direction on the PVCi surface was expected to be perpendicular to the rubbing direction and a 90° twisted nematic structure should be obtained. In practice, a twist angle less than 90° was obtained due to the competition between the bulk twist energy and the finite anchoring energy of the PVCi surface. The azimuthal anchoring energy (W_ϕ) can be found from the liquid crystal twist angle (ϕ) by [12]

$$W_\phi = \frac{2k_{22}\phi}{d\sin 2\phi} \qquad (10)$$

where d is the cell gap and k_{22} is the twist elastic constant. The cell gap was measured prior to filling by measuring the spacing of interference fringes obtained using a spectrometer. Large cell gaps ($20\,\mu\mathrm{m}$) were used so that the observed twist angle was the same as the liquid crystal twist angle. The former was measured by rotation of the analyser until white light extinction was obtained within the area of the exposed spot. Before this was done the rubbing direction was set parallel to the input polarizer by extinction of the unexposed regions (which formed a non-twisted structure). Figure 7 shows the calculated anchoring energy as a function of exposure for a set of data taken on a $20·8\,\mu\mathrm{m}$ cell which was filled with E7 in the isotropic phase and then cooled to room temperature. The PVCi surface contained 12 exposure spots, and twist angles of between 0·0° and 84·0° were measured. For very low exposure energies, the twist angle was zero which corresponds to an energy of $\leqslant k_{22}/d$. Thus the saturation of data points at this energy is due to the true anchoring energy being less than that required to induce a twist bifurcation. For longer exposures, the anchoring energy rises until it saturates at a value of $4·0\times10^{-6}\,\mathrm{J\,m^{-2}}$. This occurs at an exposure of $53\,\mathrm{J\,cm^{-2}}$ which is much larger than the exposure which induces maximum birefringence ($2·45\,\mathrm{J\,cm^{-2}}$). Thus it would appear that the functional relationship between the birefringence and the anchoring energy is complex. A possible explanation is that the dynamics of the cycloaddition reaction are altered at the surface of the PVCi compared to the bulk. The anchoring energy is derived from an anisotropic van der Waals interaction and only depends on the first few molecular layers of the polymer, whereas the induced birefringence is averaged through the entire film thickness. Similar alignment properties were measured using films of thicknesses ranging from 30 nm to $1\,\mu\mathrm{m}$ which further demonstrates that only the surface layers are of importance. Films baked at three different temperatures prior to exposure (90°C, 150°C and 200°C) were also found to possess the same anchoring energy which confirms that the

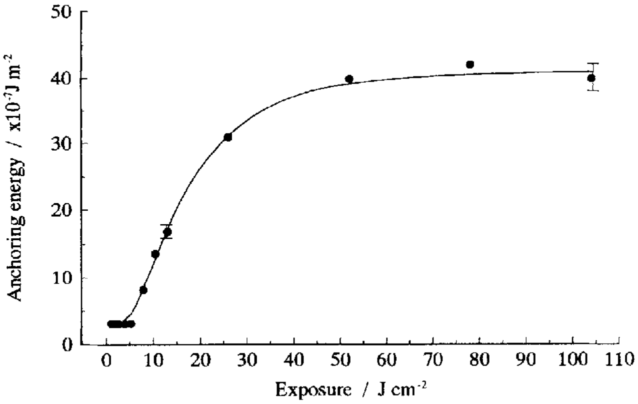

Figure 7. Azimuthal anchoring energy of E7 on a polyvinylcinnamate substrate as a function of exposure. Solid line is for guidance only.

distribution of cinnamate side chains in the starting structure cannot be optimized by annealing.

The maximum anchoring energy obtained for these PVCi films ($4{\cdot}2 \times 10^{-6}\,\mathrm{J\,m^{-2}}$) is much less than that measured for a typical rubbed polyimide ($5{\cdot}0 \times 10^{-4}\,\mathrm{J\,m^{-2}}$ [13]). Retardation measurements on rubbed polymers have shown that the surface region can possess a typical birefringence of 0·046 [14]. This is 3·4 times larger than the bulk value obtained for PVCi and could be many more times larger than the birefringence at the surface of the PVCi film. If a linear relationship between anchoring energy and surface birefringence was assumed, then we would conclude that the PVCi films studied here have a surface birefringence of only 0·0004, a small fraction of the bulk value.

Finally, we report on assessment of the stability of the photoinduced ordering in PVCi. In one test, a sample received a post exposure bake at 130°C for 30 min before filling. No change in anchoring energy was measured in comparison to a control sample. Once filled, the alignment was thermally stable below 100°C. Doubts over the stability of the nematic E7 prevented tests at much higher temperatures. Optical stability was tested by constructing complete cells with polarizers and exposing them to a powerful lamp with the same spectral profile as daylight. After a total exposure of $1{\cdot}6 \times 10^{3}\,\mathrm{J\,cm^{-2}}$, the anchoring energy of the PVCi surface had dropped to 89% of its original value. However it is anticipated that this problem can be practically solved by modifying the characteristics of the polarisers in order to prevent any transmission below 350 nm.

4. Conclusions

The dynamics of the 2 + 2 cycloaddition reaction occurring in polyvinylcinnamate and the resulting alignment properties have been studied. The modelling of the evolution of birefringence during exposure shows an excellent comparison with data even in the regime of low cinnamate concentration. Thus we believe that the assumption of first order kinetics with a fixed reaction rate is an accurate model of this photoreaction. The excellent agreement also suggests that other reaction products are either insignificant or are formed with the same reaction kinetics.

Anchoring energies were found to be disappointingly low considering that the birefringence was only 3·4 times lower than that typically measured in rubbed polymer films. It was therefore concluded that the ordering occurring at the surface is significantly less than that measured for the bulk. Also the fact that the anchoring is optimized at much higher exposures than the birefringence suggests that the surface layer has a slower reaction rate. A possible explanation is that the surface layer of cinnamate groups have an initial preferred orientation out of the surface, close to $\theta = 0$ (quasi-one-dimensional ordering). These groups would then be almost orthogonal to the polarization vector of the exposing radiation and would therefore undergo a much slower reaction. Furthermore, their preferential orientation would lead to a much lower degree of in-plane ordering. Therefore to improve the anchoring strength we must either raise the polarizibility anisotropy of the cinnamate groups or, more importantly, make the surface layer behave in the same manner as the bulk.

With reference to device applications, the lower anchoring energy of PVCi compared to rubbed polyimide is not a problem in many configurations, as the nematic material can often be pitch matched to the required cell twist angle. One further requirement for a device alignment layer is that it should possess a significant pretilt. This has not yet been obtained using PVCi materials. However, it has been shown that tilt state selection can also be readily achieved by the use of fringing fields [15]. Indeed this form of selection is most effective in materials where the pretilt is exactly zero, a condition which is hard to achieve with rubbed polymers.

Therefore photoinduced ordering in PVCi now offers a viable non contact alternative to rubbed polyimides for the alignment of nematics.

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