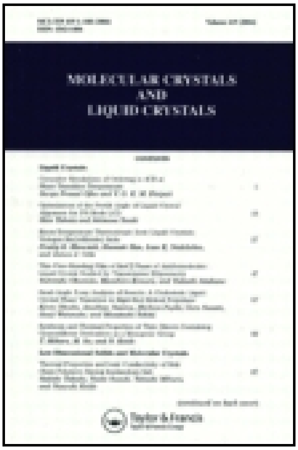

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Alignment of Nematic Liquid Crystals on Poled Photo-Polymer Films

A. Rastegar [a] [b] , M. W. Kim [a] , I. Drevenšek Olenik [a] , P. De Witte [b] , R. Nolte [b] & Th. Rasing [a]

[a] Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525ED, Nijmegen, The Netherlands

[b] Nijmegen SON Research Institute for Molecular Structure, Design and Synthesis, University of Nijmegen, Toernooiveld 1, 6525ED, Nijmegen, The Netherlands

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Alignment of Nematic Liquid Crystals on Poled Photo-Polymer Films

A. RASTEGAR[ab], M. W. KIM[a], I. DREVENŠEK OLENIK[a],
P. DE WITTE[b], R. NOLTE[b] and TH. RASING[a]

[a]*Research Institute for Materials, University of Nijmegen, Toernooiveld 1, 6525ED Nijmegen, The Netherlands and* [b]*Nijmegen SON Research Institute for Molecular Structure, Design and Synthesis, University of Nijmegen, Toernooiveld 1, 6525ED Nijmegen, The Netherlands*

We have studied the alignment of nematic liquid crystals on Electrically Poled Photopolymer (EPP) films. Polarization microscopy studies show different textures in the planar and Twisted Nematic (TN) cells that were made of an EPP substrate and a rubbed-polyimide (**PI**) substrate. The EPP films exhibit a small pretilt angle of 3 to 5 degrees depending on the cell configuration. In contrast to the small anisotropy of the EPP film compared to Linearly Photo Polymerized (LPP) films, the azimuthal anchoring strength of the EPP films is larger than that of LPP films and depends on the UV exposure time. The alignment of EPP films in the TN cells is stable for months whereas the alignment of the LPP films is destroyed within three days.

Keywords: Photo induced alignment; PVCN; electrically poled photopolymer; surface anchoring

INTRODUCTION

The alignment of liquid crystals on a substrate has been an important issue since the invention of the first Liquid Crystal Display (LCD). Since then many alignment methods for liquid crystal molecules on a substrate have been studied[1-4]. Among them, the rubbing method is the most frequently used in the production of LCD's due to its simplicity and low cost. However rubbing has its own back draws of producing static charge and dust that makes it unfavorable for high density applications that are manufactured in ultra clean environments[5]. In the search for non contact methods two different approaches of photo-induced alignment were introduced by Schadt *et. al.* [6] and Gibbons *et. al.* [7] The essence of the Gibbons *et. al.* approach is the reorientation with UV light of a dye molecule embedded in the liquid crystals. Schadt *et. al.* used polarized UV light to induce anisotropy in a photo-polymer (Poly(Vinyl) Cinnamate) (PVCN). When nematic liquid crystals were deposited on the Linearly Photo Polymerized (LPP) films they aligned normal to the polarization of the applied UV light. Cycloaddition of the cinnamoyl group was considered to be responsible for this induced anisotropy. [6]

In a recent work[8], we proposed a new method of photo-assist alignment of liquid crystals on Electrically Poled Photo-polymer (EPP) films. This method is based on the alignment of the polar side chains of a photo polymer by poling it in a static electric field and stabilizing the induced alignment by using unpolarized UV light. The detailed procedure of the preparation and optical properties of these EPP films is described somewhere else[9] in this issue.

The aim of the present work is to discuss the alignment of the nematic liquid crystals in cells that were prepared with these EPP films.

EXPERIMENT

The EPP substrates were prepared by using ITO coated glasses that were etched to form two electrodes 3mm apart. PVCN was purchased from Aldrich[10] and was used without further purification. A solution of (2 w%) PVCN in chloroform was deposited on the substrate by spin or dip coating. The thus formed PVCN films were then baked at 100 °C for one hour. A 1 kV/cm DC electric field was applied for 10 min. to pole the side chains of the photo polymer while the substrate temperature was kept fixed at 60 °C (10 degrees below the glass transition temperature of PVCN). A 150 W Xe- arc lamp was used to apply *unpolarized* UV light to crosslink the PVCN films. The UV intensity within the absorption interval of ($250nm<\lambda<350$ nm) was 0.15 mW/cm^2 at the sample position. The electric field and temperature was kept constant during photo polymerization. Samples with different exposure times were prepared.

Planar and twisted nematic (TN) cells of an EPP substrate and a rubbed Polyimide (PI) substrate with a thickness of 6μm were prepared. In TN cells, the rubbing direction of the rubbed surface was placed at 90 degrees with respect to the direction of the applied electric field in the EPP film. Planar cells in the parallel and antiparallel configurations (rubbing direction parallel and antiparallel to the applied electric field) were prepared. Cells were filled with 5CB at room temperature (24 °C) or in its isotropic phase at 40 °C. The cells were filled in such a way that the LC flow was in the direction of the rubbing.

Some of the rubbed Polyimide substrates were supplied by Philips[11] the rest was prepared in our lab. Azimuthal surface anchoring strengths were measured by measuring twist angles in TN cells. The pretilt angle was measured in planar cells by the rotating sample method[12].

RESULTS AND DISCUSSIONS

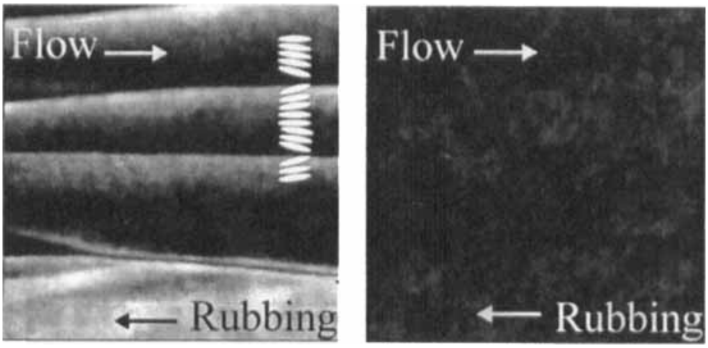
Optical polarization microscopy shows that EPP films align 5CB liquid crystals both in planar and TN cells. However the liquid crystal textures strongly depend on the UV exposure time and the flow direction of the LC during the filling process. For an exposure time of 10 to 30 minutes a defect free or a striped texture can be observed in the planar cells depending on the flow direction and the direction of the EPP substrate compared to the rubbed PI substrate. When the rubbing direction is parallel to the applied electric field in the EPP layer, a homogenous defect free texture is obtained in the parallel planar cell. In the antiparallel planar cells, a stripe texture appears in the direction of the flow. The stripes are elongated over the whole length of the cell (12mm) and have an average width of 400 μm.

In this interval of UV exposure time, the stripe texture always appears no matter at which temperature the cell is filled, at room temperature or in the isotropic phase of the LC. However in the limit of long UV exposure times (30 to 60 min) no stripe textures can be seen both in the parallel and antiparallel planar cells. Instead a defect free homogeneous texture is achieved. (see Fig. 1).

Planar cells	UV exposure time 10 to 30 min.	UV exposure time 30 to 60 min
$E \uparrow\uparrow R$, $R \uparrow\uparrow F$	Homogeneous texture	Homogeneous texture
$E \uparrow\downarrow R$, $R \uparrow\uparrow F$	Stripe texture	Homogeneous texture

Table1- Observed textures in planar cells under crossed polarizers. E is applied electric field, R is rubbing direction and F is the flow direction. Arrows indicate the (anti)parallel direction.

In the planar cells which were prepared by using a linearly polarized photo polymer (LPP) substrate and a rubbed PI substrate, no stripe texture was observed for any exposure time. Table-1 shows a summary of the observed textures in the planar cells.



A B

FIGURE 1 Microphotograph of the liquid crystal textures in the planar cell under crossed polarizers. A)- stripe texture in an antiparallel planar cell. The EPP surface was stabilized by 10 min. unpolarized UV exposure White ellipses are a representation of the molecular orientation within each stripe. B)-Texture in the same cell. The EPP surface was stabilized by 60 min. unpolarized UV exposure.

The stripe textures were also observed in TN cells in which the EPP substrate was exposed for 10 min. to unpolarized UV light and the flow direction was parallel to the applied field of the EPP substrate and normal to the rubbing direction. When a similar cell was filled with the flow direction parallel to the rubbing no TN structure was achieved, instead the cell aligned parallel to the flow direction. For an EPP substrate exposed to 60 min. unpolarized UV, a stripe free TN texture was achieved regardless of the direction of the flow. Table-2 shows a summary of the observed textures in the TN cells.

TN cells	UV exposure time 10 to 30 min.	UV exposure time 30 to 60 min.
$E \perp R$, $E \uparrow\uparrow F$	Stripe texture	Homogeneous texture
$E \perp R$, $R \uparrow\uparrow F$	Parallel alignment	Homogeneous texture

Table2- Observed textures in TN cells under crossed polarizers. E is applied electric field, R is rubbing direction and F is the flow direction. Arrows indicate the (anti)parallel direction. ⊥ indicates normal direction.

Further analysis of the stripe textures showed that the liquid crystal molecules are aligned within a stripe as shown in Fig. 1. At the center of the stripes, the molecules are aligned parallel to the direction of the stripe whereas towards the edge of the stripe they display a continuously increasing tilt. The stripes are separated by domain walls.

Having two different textures in the parallel and antiparallel planar cells indicate two different pretilt angles on the rubbed PI substrate and the EPP substrate. By using the cell rotation method [12] we measured the pretilt angle of 5CB on the PI surface in a PI-PI antiparallel rubbed cell to be $\theta_{PI} = +1.25°$. Taking this value as a reference value we measured the pretilt angle of 5CB on the EPP surface in a parallel planar cell as $\theta^{p}_{EPP} = -3°$ and in the antiparallel planar cell as $\theta^{a}_{EPP} = -6°$ (for 10 min. UV exposure time). In the case of LPP films, it is known[13] that the pretilt angle depends on the UV exposure time.

Experiments are in progress to measure the dependence of the pretilt angle on the UV exposure time in our EPP films.

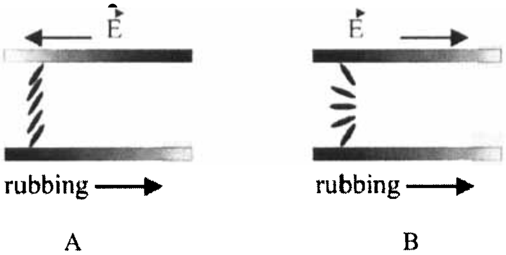


FIGURE 2 The alignment of the liquid crystal molecules in the antiparallel(A) and parallel(B) planar cells.

The liquid crystal molecules align differently in the parallel and antiparallel planar cells as shown in Fig. 2. Similar alignments in planar cells with LPP films were observed[14] but no stripe texture appeared in these cells.

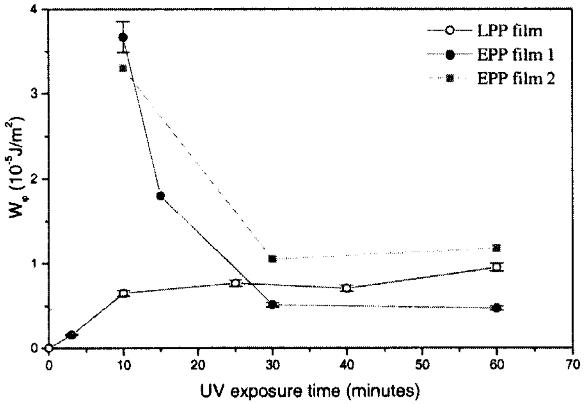


FIGURE 3 Azimuthal anchoring strength of 5CB in the EPP and LPP films. Two different measurements in the EPP cells with different rubbed PI substrates are shown.

Figure 3 shows the azimuthal surface anchoring strength of 5CB on the EPP films of PVCN as a function of UV exposure time. The azimuthal surface anchoring strength was obtained by measuring the twist angles in EPP TN cells.

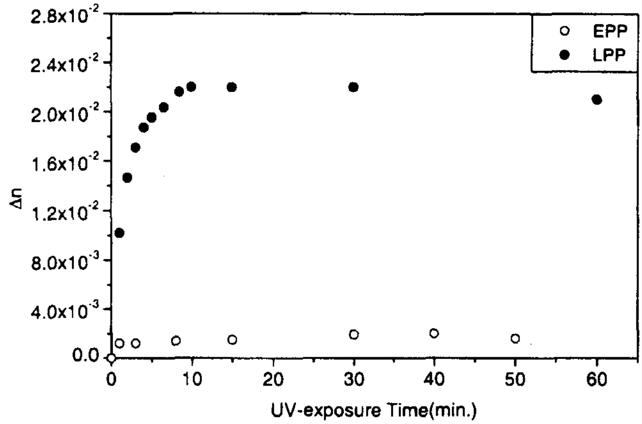


FIGURE 4 The linear birefringence of the LPP and EPP films vs. the UV exposure time

We added similar measurements for LPP films for comparison. As can be seen in Fig. 3, the surface anchoring of the LPP films increases monotonously towards a saturation limit for long UV exposure times whereas the, originally much higher, surface anchoring of the EPP films decreases towards the same limiting value for long UV exposure times. This behavior is in contrast to the measured linear birefringence of the LPP and EPP films as a function of UV exposure time. As shown in Fig. 4, the birefringence of the LPP films increases towards a saturation limit for long UV exposure times, in a similar way as the surface anchoring strength in these films (see Fig. 3). The birefringence of the EPP films is almost an order of magnitude smaller than that of the LPP films and, importantly, remains almost constant with increasing UV exposure time.

The observations above indicate that the surface characteristics of the EPP films are totally different from those of LPP films. In the LPP films α-truxillate cycloaddition of the cinnamoyl group by polarized UV light is considered to be responsible for inducing an anisotropy in the LPP film normal to the direction of the polarization of the applied UV light.

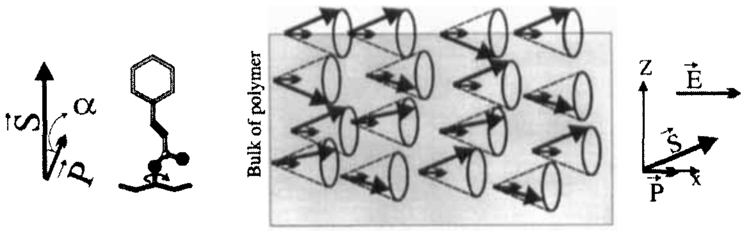


FIGURE 5 The surface structure of the EPP film before cross linking and presentation of the relation between the direction of the electric dipole and the symmetry axis of the side chain

In contrast, in the EPP films not the unpolarized UV light but the electric field does introduce an anisotropy (see Fig. 5), aligning the average direction of the electric dipole of the side chain "P" parallel to the field. Therefore before the cross linking by unpolarized UV light, the symmetry axis of the side chain "S", stays on a cone around the dipole moment "p". (Fig. 5)

By using MOPAC93[15], a molecular orbital calculation program, we have calculated the average dipole moment of the cinnamoyl group to be P=2.8 D, directed with an angle α= 17° with respect to the symmetry axis of the side chain[16]. The symmetry of the system requires that in the bulk of the polymer, the projection of the side chains in all directions vanishes except in the direction of the applied electric field. However at the interface, due to strong steric interactions in the bulk, side chains prefer to stay on the surface. Therefore on the surface there is an excess of side chains which are tilted with an angle θ_s with respect to the surface. Note that θ_s is the angle between the side chain and its projection on the surface and therefore it can get values from θ_s =0° when the side chain is laying on the surface up to the average calculated angle α =17° (i.e. $0<\theta_s<\alpha=$ 17°). This result is in good agreement with our Surface Second Harmonic Generation (SSHG) measurements[17] which gives θ_s = 12° ±5° for PVCN films before UV exposure.

When the surface of the EPP films is exposed to unpolarized UV light, two major different photo processes can occur: cis-trans isomerization and cycloaddition of the cinnamoyl group[18]. In contrast to the LPP films where α- truxillate cycloaddition of the cinnamoyl group is considered to be the most important mechanism in inducing anisotropy in the LPP films[6], we believe that β- truxinate cycloaddition happens between the adjacent cinnamoyl groups which are aligned in the direction of the electric field. Note that according to the work of Egreton *et.al*[18] β- truxinate is the major isomer (60%) of the PVCN photoproducts. Therefore the cycloaddition does not induce an anisotropy itself but fixes the aligned side chains. That is why the linear birefringence of the EPP films does not change strongly with UV exposure time. (see Fig. 4).

Hence cycloaddition of the side chains at the surface also reduces the measured pretilt angle of $\theta_s = 12°$ before applying the UV light to a value of $\theta_s = 3°$ to 6° as we measured in planar cells. Another effect of the crosslinking by UV light is the modification of the surface adsorption on the PVCN film. As we have shown in one of our recent SSHG studies[19] the surface adsorption energy of liquid crystal molecules on the PVCN decreases by increasing UV exposure time. This explains the vanishing of the flow effects for the long exposure times.

Finally the stability of the aligned cells in time is one of the major differences between the EPP and LPP films. Our EPP TN cells remained stable during the past 8 months whereas the LPP TN cells lost their alignment within a few days!

In conclusion, we have demonstrated a new method of photo-induced alignment by using Electrically Poled Photopolymer (EPP) films. These films show larger surface anchoring energies compared to the LPP films prepared by the linearly polarized UV method and therefore the alignment in the EPP cells is much more stable than in the LPP cells. It will be possible to control the direction of the pretilt angle by controlling the direction of the applied electric field.

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