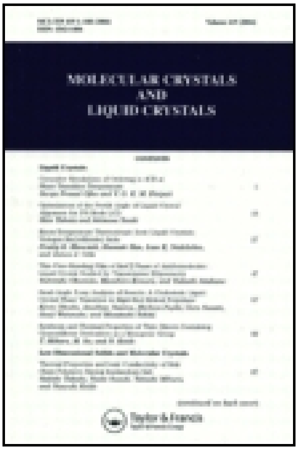

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Electric Field Aligned Photo-Polymer Films for Liquid Crystal Display

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Electric Field Aligned Photo-Polymer Films for Liquid Crystal Display

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Oriented photopolymer films were obtained by using electric field alignment of the cinnamoyl side groups near the glass transition temperature of poly(vinyl)cinnamate (PVCN) followed by photo-polymerization using unpolarized UV light. In this way the induced anisotropy could be fixed and was subsequently shown to lead to a well aligned liquid crystal texture. The combination of electric field and UV light offers a solution to the pretilt angle problem for photo-aligned substrates.

Keywords: Photopolymerization; Unpolarized UV light; Photo-induced alignment; Polyvinylcinnamate; Electric field alignment

INTRODUCTION

There has been a lot of research on alignment techniques[1-4] for liquid crystals since the introduction of LCD's (liquid crystal display). Especially the rubbing method is widely used for the production of liquid crystal devices because it is suitable for LCD mass production in industries. However due to its contact nature the rubbing method also causes problems. It introduces either dust which is harmful for ultra-clean production lines[5] or surface electric charges which can be detrimental for transistor liquid crystal displays (TFT-LCD's). In addition it limits the realization of a wide-view angle and high resolution. To solve such problems, subpixell controllable processes using non-contact methods have been considered like the oblique evaporation of SiO_x, surfactant treatment, Langmuir Blodgett films and photo-polymerization using polarized UV light. Among these methods, the latter seems to be the most promising one[6]. It not only allows clean surfaces but also the creation of fine subpixells on surfaces for wide-view angle applications. The mechanism of photo-induced alignment of polyvinylcinnamate (PVCN) is based on the selective [2+2] cycloaddition of the cinnamoyl groups. Photo-polymerization of the cinnamoyl groups of PVCN in the direction of the UV polarization gives PVCN films optical anisotropy through the unreacted side chains. These unreacted side groups, that are aligned in a direction normal to the UV polarization, are known to align liquid crystals through van der Waals forces[6]. The major problems of this method are a very small pretilt angle and a weak anchoring between the liquid crystal molecules and the alignment layer. Recently it was shown that it is possible to increase the pretilt angle by introducing either a polar structure at the cynnamoyl group (like florinate cinnamoyl groups[7-8]) or an external field during UV irradiation[9-10].

In this paper we present a new method for aligning liquid crystal molecules using an electrically poled- and optically stabilized photopolymer film. The polymer poling method has been used in retardation films[11], nonlinear polymer films[12] or liquid crystal polymers[13]. By applying an electric field at a temperature near the glass transition of the polymer (T_g), we introduced an optical anisotropy in the polymer films. The alignment was consequently fixed by cross-linking with unpolarized UV light. It is important to note that this method in nature is different from Linearly Photo Polymerized (LPP) UV alignment. The LPP method is based on selective [2+2] cycloaddition of the cinnamoyl groups whereas our method is based on aligning the cinnamoyl group at the surface in an external electric field using the dipole moment of the carbonyl group. As the electric field is a vector quantity, both direction and amplitude of the field can be used to align the polymer side chains in plane and out of plane. LPP films usually have an anisotropy without a polar direction[7] whereas the EPP films not only have an anisotropy with a polar axis, necessary to manipulate the pretilt angle at the surface, but they also yield a retardation by the poling throughout the bulk of the polymer. Such a pre-aligned polymer film has the functionality of an in-cell retardation film. The retardation can be controlled by the strength of the applied electric field, the thickness of the polymer film, and the strength of the electric dipole moment of the side chains.

EXPERIMENT

Samples were prepared by spin- or dip- coating using 0.3 to 2wt%-concentrated solutions of PVCN in chloroform on ITO coated glass substrates that were etched to make two ITO electrodes 3mm apart. The samples were heated to T_g of the polymer and an in-plane electric field of 0.1 to 1.0 KV/cm was applied. After prealigning for 30 minutes, the films were crosslinked by unpolarized UV light from a 150W Xenon lamp, keeping the electric field constant. The films were cooled down to room temperature after the photo-polymerization.

The induced optical anisotropy of the PVCN films were investigated after and during alignment by a precise birefringence set-up with an accuracy of 10^{-6} radians.

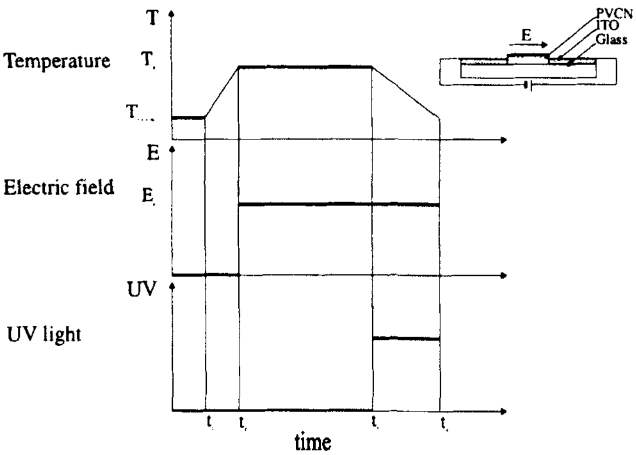

FIGURE 1, Aligning and stabilization cycle in the EPP films

RESULTS AND DISCUSSION

Upon heating amorphous polymers such as PVCN undergo a glass-rubber transition at a glass transition temperature (T_g). On further heating the elastic behavior diminishes and a shear stress will cause viscous flow to predominate over elastic deformation. It is known that below the glass transition this polymer shows several transitions where the side chains or local segments can freely move or oscillate[14]. These transitions can be detected by studies of mechanical damping, nuclear magnetic resonance, or electric loss measurements. Our birefringence measurements presented below show the appearance of a field driven secondary transition. In figure 2, we plot the relative birefringence (i.e. the difference in birefringence in the presence and absence of the electric field) for different values of the applied field as a function of temperature. It can be seen that the relative birefringence has a peak at T_s which is about 15 degrees below T_g. T_s is the secondary transition temperature at which the side chains can be oriented in the direction of the electric field. Note that this transition is field driven and appears above a threshold field (0.5KV/cm). For glassy amorphous polymers T_s can be calculated[14] from the relaxation process associated with it (so called β relaxation): $T_s \approx 0.75 * T_g = 52.5°C$, which is in fairly good agreement with our measured value T_s=56°C.

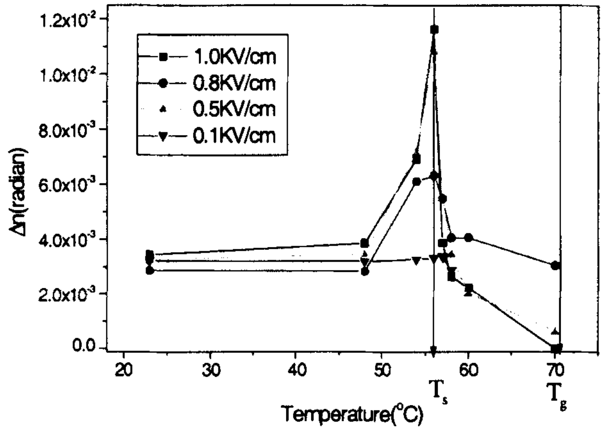

FIGURE 2, Relative birefringence of a 200nm thick EPP film as a function of temperature. Data are measured at different applied fields.

Considering the thermal fluctuations at room temperature and the rather low electric field that was applied to the EPP film, one does not expect to see any induced birefringence in this film. However, in thin PVCN films it is possible to get a phase separation between the polar side chains and the non-polar backbones, leading to a sheet-like arrangement [15] in which the side chains are locally ordered. This means that before any field treatment the PVCN film has a kind of domain structure in which the side chains within a domain are aligned but the domains are randomly distributed in the PVCN film. When an electric field is applied to this polymer, both individual side chains and the domains reorient. The major anisotropy contribution then comes from the domain reorientation. In this picture, the EPP film, before crosslinking, is similar to a ferroelectric film. In fact the temperature behavior of the EPP film (figure.2) is often observed in ferroelectrics[16].

The temperature dependence of the anisotropy has already been observed in poled polymers[17]. The maximum anisotropy in a plasma-poled NLO-chromophore film was obtained at T_g-17°C by using *in situ* second harmonic generation[18] and in our case the maximum birefringence of the PCVN film was measured at T_g-15°C. These kinds of polymers have chromophore side groups with a planar structure resulting in a locally ordered micro-phase[19] which can respond to the applied electric field.

As a secondary test of the reorientation of the side chains at the secondary transition, we performed *in situ* measurements of the birefringence as a function of applied electric field (Figure 3). Figure 3 shows that even at 35 degrees below T_g, one can reorient the side chains (secondary transition). However, as one would expect in this case, the threshold electric field increases from 150 to 250 volts. Both of these experiments indicate that by applying an electric field the side chains become aligned.

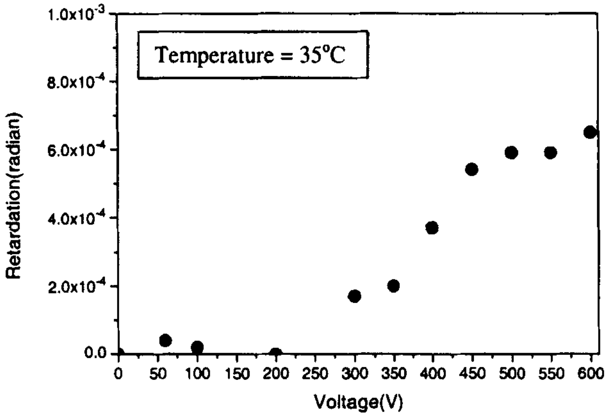

FIGURE 3, The retardation of EPP film *in situ* measured showing the electric field driven transition at 35°C

To determine the direction of the side chain with respect to the applied electric field, one should realize that the birefringence measurement detects the average direction of the long axis of the side chain "S"(see figure 4), whereas the electric field interacts with the average direction of the electric dipole of the side chain, "P". Though two directions not necessarily coincide, in the bulk of the film the components of "S" perpendicular to "P" should average out to zero, leading to an optical axis in the direction of the applied field.

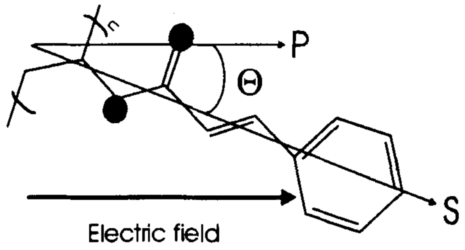

FIGURE 4. Scheme of electric dipole of cinnamoly group, "P" directed with an angle θ=17° with respect to the long axis of the side chains "S".

Using the simulation program MOPAC[20], we calculated the electric dipole, P= 2.8 Debye to be directed with an angle of θ=17° with respect to the long axis of the side chains "S".

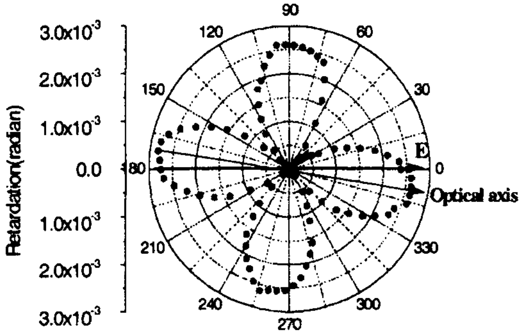

FIGURE 5, Retardation of EPP film prepared unpolarized UV and poling at 56°C shows that the optic axis of the film deviated from electric field direction.

Figure 5 shows the anisotropy of the PVCN film which is crosslinked with unpolarized UV light during poling at 56°C. The deviation of the maximum birefringence from the direction of the electric field by about 10 degrees indicates that the optical axis of the film does not coincide with the direction of the applied field. This is in contrast to what one would expect(see above), and will be further investigated.

We also studied the alignment of 5CB molecules in twisted or parallel cells using EPP films. The cells were well aligned and show different alignment structures and anchoring energies depending on UV exposure time[21].

In summary, using electric fields it is possible to align the side chain of a photopolymer and this alignment can be fixed by crossliking with unpolarized UV light. The onset of the side group alignment can be observed by the sudden increase of the film birefringence at temperatures below the T_g of the polymer.

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