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Electrically Aligned Photo-Polymer Films for Liquid Crystal Alignment

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The photo and electric field alignment of thin film of polyvinylcinnamate (PVCN) is shown to be considerably enhanced by using a combination of both methods. ITO-coated glass substrates were covered with a PVCN film using spin or dip coating and then heated above the glass transition temperature of PVCN. The alignment was induced by applying an electric field and stabilized by [2+2] cycloaddition of the polymer using a linearly polarized UV light. The anisotropy of the aligned polymer films was checked by measuring linear birefringence. Without crosslinking, the anisotropy of the electrically aligned films is very weak. Crosslinked PVCN films using polarized UV light in the absence of any external fields lead to a better anisotropy than the aligned film by an electric field. The anisotropy is however increased substantially when the aligned PVCN films were crosslinked in the presence of a field.

Keywords: Photopolymerization; Linearly polarized UV light; Polyvinylcinnamate; Electric field

INTRODUCTION

During the last 20 years, different alignment techniques for liquid crystals have been developed. Among them, the rubbing method is widely used for the production of liquid crystal devices. However due to its contact nature the rubbing method has two main disadvantages. 1) it introduces dust which is harmful for ultra-clean production lines. 2) it causes surface electric charges which can damage thin film transistors that are essential in the thin film transistor liquid crystal displays (TFT-LCDs).

Therefore non-contact processes have been considered in order to prevent the contamination such as the oblique evaporation of SiO_x , surfactant treatment, Langmuir Blodgett films, and photo-polymerization using polarized UV light. Despite many studies to explain the alignment mechanism of liquid crystal on a surface, it is still not clear what kind of surface forces drive liquid crystals into a certain direction.

The alignment induced by rubbing is thought to be the result of topological⁽¹⁾ or anisotropic molecular interactions⁽²⁾. Topological theory was also used to understand the SiO_x surface⁽³⁾. A surfactant-coated surface was experimentally determined to yield a polar and dispersive force⁽⁴⁾, which drives the order of the liquid crystals at the interface. This is also applicable to alignment mechanisms using Langmuir Blodgett films with small molecules or polymers.

Among these non-contact aligning methods, the most promising and attractive one seems to be the introduction of anisotropy by photo-polymerization using a linearly polarized UV light⁽⁵⁾. The photo-polymerization of the cinnamoyl groups of PVCN takes place in the direction of the polarization of the UV. This selective [2+2] cycloaddition gives PVCN films optical anisotropy through unreacted side chains, which have optical birefringence. These unreacted side groups being aligned opposite to the polarized UV light are known to align liquid crystals through van der Waals forces⁽⁶⁾. This optical method has many merits compared to the others. It is possible to make fine subpixels on surfaces to give wide view angle LCD's as well as keeping the command layer for alignment clean.

In this paper we present a method to increase the anisotropy of the PVCN alignment layer. By applying an electric field at a temperature above the glass transition of the polymer we could align the polymer film. Consequently the alignment was fixed by cross-linking with linearly polarized UV light. The aligned polymer films show an anisotropy bigger than the films prepared just by linearly polarized UV irradiation.

EXPERIMENT

Samples were made using a solution of PVCN in chloroform with concentrations from 0.3% to 2wt%. The ITO coated glasses were etched to make two ITO electrodes with 3mm gap in between. The PVCN films were prepared by spin- or dip- coating using the glass substrates. The thickness of the PVCN films was controlled by the concentration of the PVCN solution and spin speed.

The samples were heated on a heating stage above the glass transition temperature of PVCN ($T_g = 70^\circ\text{C}$). When the temperature was stabilized, the electric field was turned on for 30 minutes to get pre-aligning of the cinnamoyl groups of the polymers. These pre-aligned films were then fixed by photo-polymerization by a linearly polarized UV light using a Xenon lamp. The

applied electric field was kept at 100V per 1mm while the polymer films were being cross-linked and cooled at a rate of 1.3 °C per minute on a well controlled heating stage. The angle between the electric field and the polarization of the UV light was varied between 0° to 180°. The PVCN films were also only irradiated by the UV light without an electric field in the same conditions as with an electric field to investigate temperature effects. After the cycloaddition of the photo-polymer, the optical anisotropy was measured using a birefringence set-up⁽⁷⁾.

RESULTS AND DISCUSSION

The anisotropy of the PVCN films was measured by the birefringence set-up in figure 1. The lock-in measures the first and second harmonic intensity of the modulated and transmitted beam as a function of the azimuthal angle. The retardation of the two components parallel and perpendicular to the photo-elastic modulator (PEM) axis was calculated using the equations in ref.7

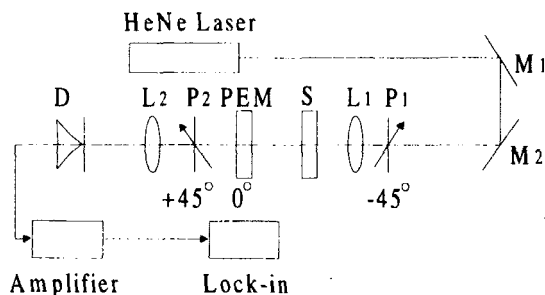


FIGURE 1 Birefringence set-up. M1, M2, mirror; P1, P2, polarizer; L1, L2, lens; S, sample rotating stage; PEM, photo-elastic modulator; D, detector.

In order to study the effect of the thermal fluctuations of the polymer on the alignment of the cinnamoyl groups, we prepared a series of identical samples when the cross-linking was done at different temperatures. Figure 2 shows the anisotropy of PVCN film as a function of the photo-polymerization temperature. It can be seen that the anisotropy of the PVCN film reduces by increasing the photo-polymerization temperature. This can be explained by considering that, even below T_g , the backbone of the polymer is somewhat flexible and therefore the probability of the cross-linking of the proper double bonds in the polarization of UV light reduces due to the thermal fluctuations of the backbone. Another important factor is the thermal fluctuations of the side

groups which are excited far below T_g and are partly responsible for the reduction of the anisotropy.

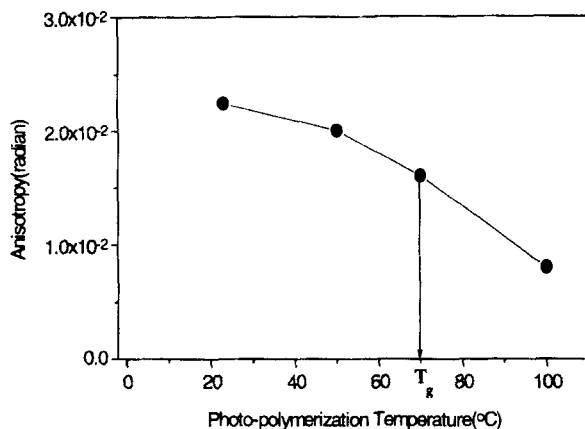


FIGURE 2 The anisotropy of PVCN film as a function of photo-polymerization temperature.

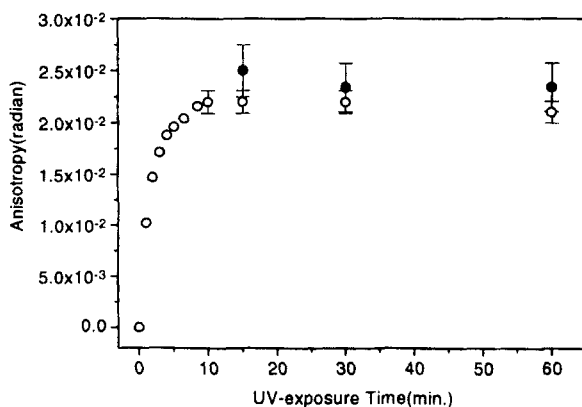


FIGURE 3 The anisotropy of PVCN films measured at room temperature as a function of the UV-exposure time. The open circles represent the anisotropy from the sample exposed to the polarized UV light at room temperature and the solid circles show the anisotropy from the ones exposed to the UV light above the T_g of PVCN in the presence of an electric field.

The anisotropy of the PVCN films at room temperature as a function of the UV -exposure time is shown in figure 3. The open circles are representing the anisotropy of the samples which were exposed to polarized UV light at room temperature, whereas the solid ones show the anisotropy of the samples which were exposed to the UV above T_g of the polymer in the presence of an electric field. Note that in both cases the birefringence measurements were performed at room temperature. It can be clearly seen that the anisotropy of the electric field-assisted PVCN film is higher than the UV-exposed film and it saturates for exposure times above 10 minutes. The increase of the anisotropy of the electric field-aligned PVCN films can be described as follows; above T_g , the backbone of the polymer is flexible and each cinnamoyl group of PVCN has a permanent dipole moment which can be aligned in the direction of the electric field. UV exposure fixes these aligned side chains. Therefore the total anisotropy of the sample increases due to two different mechanisms: selective cycloaddition of the side chains by polarized UV exposure and alignment of the side groups by an electric field. However our simulation based on a MOPAC⁽⁸⁾ computational program shows that the carbonyl group in the cinnamoyl group gives a dominant contribution to the whole electric dipole in side chains which are tilted by an angle of 45 degrees with respect to the long axis of the side chain. Note that in the birefringence measurement, one measures the anisotropy which results from the interaction of the optical field with the side chain (i.e. birefringence measurement probes the long axis of the side chain). Therefore in the samples with dipole moments of the side chain aligned parallel to the electric field, the measured anisotropy has a maximum at an angle, which is defined by the direction of the average dipole moment and the long axis of the side chain.

However since the early anisotropy measurements of UV-exposed-PVCN films, it is known that the UV-exposed-PVCN films have an anisotropy perpendicular to the UV polarization. Hence the total anisotropy results from two different sources and depends on the angle between the UV polarization and the electric field. Figure 4 shows the induced anisotropy of the PVCN film as a function of the angle between the UV polarization and the electric field. It can be seen that the anisotropy is maximum for an angle of about 75 degrees.

The aligned PVCN films were used to make liquid crystal cells. The alignment of the nematics on these films is qualitatively improved compared to the cells with only UV-exposed films. However the cells also show interesting domain structures in the direction of the applied electric field which are the subject of our present research.

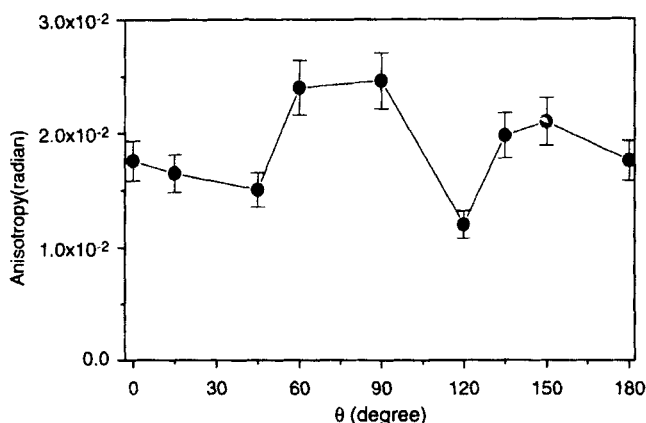


FIGURE 4 The induced anisotropy of PVCN film as a function of the angle, θ between the UV polarization and the electric field.

CONCLUSION

Using an electric field, we succeeded to align the side chains of PVCN above the glass transition temperature. The alignment was fixed using cross-linking of the side chains by a polarized UV light.

We found that the maximum anisotropy is achieved when the polarization of the UV light makes an angle of about 75 degrees with respect to the direction of the electric field. The aligned PVCN films cause a better alignment of nematic liquid crystals, however there are interesting domain structures that should be studied in detail.

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