

Photoalignment in PVCi Film

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Keywords

Photoalignment of Liquid Crystals, Photo-Induced Anisotropy, Polyvinylcinnamate

P hotoalignment is an important technique for the fabrication of liquid crystal devices. This method enables the liquid crystal molecules to be aligned by linearly polarized ultraviolet light. Polyvinylcinnamate is a photoreactive polymer and allows for a control of liquid crystal alignment due to the photoinduced optical anisotropy. In this paper the results of the influence of linearly polarized ultraviolet laser light on the surface properties of thin polyvinylcinnamate films are reported.

Introduction

Polyvinylcinnamate (PVCi) is one of the earliest synthetic photoresists and the design of some photopolymers has been inspired by this polymer. PVCi is well known for the sensitivity to ultraviolet (UV) light. The photochemical reaction which occurs upon photopolymerization of PVCi with unpolarized UV light has been first studied by Egerton et al. [1]. However, the photochemical reaction by a linear polarized light has been studied by Schadt et al. [2]. It has been shown that photoinduced chemical transformation of PVCi leads to induction of birefringence upon exposure UV irradiation [3-5]. PVCi has a polyvinyl backbone with cinnamoyl side chains and crosslinks are formed by photocycloaddition between excited polymer-bound cinnamoyl group of one polymer chain with a ground state cinnamoyl group belonging to another chain when exposed to UV light. Under the irradiation by linear polarized UV radiation, the side chains with long axes parallel to the polarization direction of the incoming electric field (E) undergo photocrosslinking (Figure 1). Thus, it is able to undergo efficient crosslinking due to [2 + 2] photocycloaddition of two cinnamate side groups from different polymer chains, leading to a cyclobutyne ring and the insolubility of the material [6].



Fig. 1. Photocrosslinking between PVCi molecules.

PVCi has been widely investigated not only as a basic study but also as a material for device applications. Recently the first vapor-phase deposition PVCi has been reported by using initiated chemical vapor deposition [7]. From the practical point of view, the important feature of this photopolymer is the alignment of liquid crystals (LCs) on these layers. It has been reported that the PVCi derivatives induce the alignment of LCs on the substrate surface upon irradiation with linearly polarized UV light [8-11]. Uniform alignment of LCs is a prerequisite for the fabrication of electro-optical displays. Traditionally, displays have been fabricated by using mechanically-rubbed polymer alignment layers deposited on glass substrates. However, the displays produced by rubbing method suffer from restricted viewing angles due to the uniaxial nature of the LC alignment. It also causes surface electric charges which can damage thin film transistors. That is why there is widespread interest in viable alternative technologies. The photoalignment is one of the promising techniques for the production of LC devices. The use of PVCi photoalignment layer and its alignment properties have attracted considerable research interest. However, PVCi has some limitations such as the low-order parameter of LC alignment, poor thermal stability and low pretilt angle. Therefore, new types of photoalignment materials including coumarin polymers which give better alignment have been synthesized [12].

Experimental Method

To prepare PVCi thin films, polymer was dissolved in propylene glycol monomethyl ether acetate at a concentration of 6% in weight and was spin coated at 3000 rpm for 30 s onto indium tin oxide (ITO) coated substrates. The substrates were baked at 90°C for 30 min to remove the solvent. Thermal treatments were performed in the oven under a flowing nitrogen gas condition. The thickness of the layers ranged from 100 nm to 350 nm was controlled with varying rotation speed of the spin coater. The film thickness was measured using a surface profile measuring system [Dektak 3ST Auto1 Surface Profiler]. UV absorption spectra were obtained by using a UV scanning spectrometer.

The optical anisotropy in the PVCi films was measured by using an experimental set-up which is shown in Figure 2. To induce the photoinduced anisotropy, the polymer coated surfaces were exposed by linearly polarized argon ion laser irradiation. The UV laser beam has wavelength of 300.5 nm and power of 20 mW and its polarization direction (E) is shown in figure. The UV laser beam was expanded by using a beam expander (BE) which is a quartz lens in order to prevent the formation of standing waves which may cause a non-uniform exposure through the film. The UV irradiation was performed at room temperature. Since the ITO coated glass plates showed significant photoinduced retardation, the fused silica substrates were used for the optical anisotropy experiments.

In order to monitor the intensity of the laser light, the PVCi film was placed between two crossed polarizers in the path of a He-Ne laser beam (632.8 nm). During the UV exposure, the photoinduced optical anisotropy was monitored using crossed polarizers (P_1 , P_2) arranged at \pm 45 degrees with respect to the polarization direction of the exposure beam. The light intensity of the laser beam passed through the PVCi film was detected by a photodetector (D), processed by a phase sensitive lock-in amplifier and recorded by a computer (C).



Fig. 2. Experimental set-up to measure optical anisotropy of the PVCi film.

Twisted alignment of nematic LC cells was produced using a one-side rubbing method, in which one side of a glass substrate was coated with polyimide layer, which was subsequently rubbed unidirectonally and the other side with PVCi. The polarization direction of exposure of the PVCi film was arranged to be perpendicular to the rubbing direction on the polymer layer. Thus the alignment direction on the PVCi surface was perpendicular to the rubbing direction on the polyimide surface.

As a nematic LC material, cyanobiphenyl mixture BL001 (Merck) was used. This material has high clearing point (60 °C). The cells were filled with the material at 65 °C by the capillary action. The filled cells were then cooled slowly to room temperature at a rate of 0.2 °C/min. The film thickness of 13 µm was obtained by using Mylar spacers. Twisted nematic LC cells were observed through crossed polarizers under the polarizing microscope.

Results and Discussion

Figure 3 shows isotropic UV-absorption spectrum of a 100 nm thick PVCi film. As can be seen from the figure, the PVCi film exhibits a maximum absorption at 294 nm. It has been reported that this absorption peak disappears with progressing photopolymerization [2]. The absorbance peak value is far away from wavelength of the UV exposure beam. Dimerization of cinnamate group can cause crosslinking by cyclobutane ring formation by UV irradiation. Thus cyclobutane ring formation is confirmed by the changes in the UV spectra of PVCi [13].



Fig. 3. UV absorption spectrum of the PVCi film.

PVCi photopolymer exhibits a photoinduced optical anisotropy upon UV irradiation. The intensity of light at the photodetector is given simply by

$$I = I_0 \sin^2(\frac{\pi \Delta nd}{\lambda}) \tag{1}$$

where λ is the wavelength of the incoming light beam, Δn is the birefringence and d is the thickness film, l_0 is initial the intensity of the light. The typical time-dependence behavior of the photoinduced optical anisotropy is shown in Figure 4. The optical anisotropy rapidly increases at the beginning, reaches a maximum and then decays very slowly. The anisotropy of the polymer films is due to the photoinduced crosslinking intermolecular effect under the influence of linearly polarized UV light. Prior to UV exposure, the cinnamate acid side chains are isotropically distributed. Polarized UV irradiation of an initially amorphous film will lead to a selective depletion of cinnamate groups aligned parallel to the polarization direction of UV light. Thus, it can be considered that UV light is selectively absorbed by PVCi molecules that have their side chains (cinnamate groups) parallel to the polarization direction of the polarized UV light. The mechanism of the photoinduced optical anisotropy can be explained in terms of the photopolymerization process [14]. The possibility of photopolymerization of molecules oriented a specific direction is proportional to the number of photons whose polarization direction along that direction. The optical anisotropy of the photopolymer is given as

$$\delta(t) = C \int_{0}^{2\pi} \int_{0}^{\pi/2} \frac{1}{2} (3\cos^2 \varphi - 1) N(\theta, \varphi, t) \sin \theta \, d\theta \, d\varphi \tag{2}$$

where C is a constant related to the refractive index of the photopolymer film. $N(\theta, \phi, t)$ is the time-dependent angular distribution of the photosensitive molecules. Eq. (2) indicates that the optical anisotropy rapidly increases with the exposure time. The photopolymerization leads to a preferred depletion of side chains which are parallel to the UV polarization direction.



Fig. 4. Optical anisotropy as a function of UV exposure time.

In order to check the alignment direction of the twisted nematic LC cell, transmission of the cell was monitored while rotating the sample between crossed polarizers under the polarizing microscope. It was found that the molecular alignment direction on the substrate is perpendicular to the polarization direction of the UV light. A macroscopic picture of the twisted nematic LC cell between parallel polarizers is shown in Figure 5. The UV exposed spots seems dark in the figure.



Fig. 5. Macroscopic picture of the LC cell.

For the electro-optic applications it is important to know anchoring energy. The anchoring energy (*W*) is related to the twist angle (ϕ) and is given as follows [15].

$$W = \frac{2K_{22}\phi}{d\sin 2\phi} \tag{3}$$

where K_{22} is the twist elastic constant and d is the thickness of the film. So, the anchoring energy can be calculated by measuring the twist angle. For the measurement of ϕ , the rubbing direction on the substrate with polyimide layer was set to parallel to the input polarizer by extinction of the unexposed regions. Thus, twist angle was determined by rotation of the analyzer until white-light extinction was obtained within the area of the exposed spot. Using the value of the twist elastic constant from the literature the anchoring energy was calculated. The elastic constants strongly depend on temperature [16] and $K_{22} = 8.8 \times 10^{-12}$ N was used for T = 20 °C at which this experiment was performed. In the measurements, typical value of the anchoring energy obtained for the BL001/PVCi system is about 3.1×10^{-5} J/m². This value is in the same order of other nematic materials. Figure 6 shows the variation of anchoring energy with the twist angle. From the figure it is clear that PVCi photopolymer initially shows a gradual increase of the anchoring energy with twist angle followed by a sudden increase to a maximum value. Twist angles are function of the UV exposure time, hence optical anisotropy. Thus, the anchoring energy increases with increasing optical anisotropy of the PVCi film. The anchoring energy is not only due to the optical anisotropy of photopolymer but also adsorbing LC molecules on the polymer surface. The polarizing microscopy observation confirmed that there was a planar alignment with nematic schlieren texture in the UV exposed region of the alignment layer. The LC molecules on the surface of the UV exposed regions are perpendicular to the irradiated UV polarization. This alignment is due to the anisotropic van der Waals interaction between LC molecules and the optical anisotropy arising from the photoinduced side chain distribution on the PVCi films.



Fig. 6. Anchoring energy as a function of twist angle.

There are some theoretical models for anchoring energies of LCs. It has been reported the anchoring energy on photopolymer layer is influenced by the anisotropic van der Waals interaction and additional steric interaction [17]. It has been shown that anchoring energy increases exponentially with increasing optical anisotropy of the PVCi film, since the photoinduced alignment varies continuously with the UV exposure time [18]. It has been also reported that subsequent exposures of alignment layer may lead to a continuous reorientation of the alignment direction. Different kinds of orientation have been also reported in photopolymers with coumarin in the side chains [19].

PVCi has ability to align LC unidirectionally and to generate pretilt angle for avoiding the appearance of reverse tilt disclinations [20]. The surface alignment of LC multilayers formed by evaporation on PVCi film has been observed by threedimensional surface profiler. Photoinduced anisotropy of partially exposed PVCi film has been visualized as a topological image of LC multilayers [21].

Application of photoalignment technology to LC on silicon micro-displays and their performance has been reported. A threestep photo-exposure method has been developed to solve problems with alignment disturbances on reflective silicon panels [22]. For the production of LC displays, the quality of the orienting polymer layers depends on numerous technological factors. Film production parameters such as polymer baking duration, photopolymerization time and dose of UV light are important for the performance of the LC alignment [23]. Thus the success of the photoalignment depends on the film production procedure.

Conclusions

The photoalignment of LCs is of technological interest, because the ability of ordering of the polymer molecules leads to LC display applications. This method eliminates the need for mechanical rubbing which limits the yield of active matrix displays. On the other hand, different alignment patterns can also be achieved on the same polymer layer. Another interesting behaviour of photoalignment is the possibility of changing the preferred orientation by changing the polarization direction of the UV radiation. The change in the photoinduced anisotropy is due to main change in the molecular morphology of the photopolymer. PVCi is a classical negative photoresist where crosslinks are formed by photocycloaddition between polymer-bound cinnamoyl groups. The UV irradiation leads to anisotropic arrangement of cyclobutane molecules with their long axis lying perpendicular to the polarization direction of the UV light. The anisotropic crosslinking of side chains of this photopolymer with linearly polarized UV light gives unidirectional alignment in the azimuthal plane of the film. Thus the LC molecules align homogeneously on these films. The LC alignment on the PVCi surface is caused by the anisotropic van der Waals interaction between the LC molecules and the optical anisotropy arising from the photoinduced side chain distribution.

Acknowledgement

The author would like to thank Professor M.O'Neill of Hull University for valuable advice and discussions.■



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