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PAGES: 89-96

ORIGINAL PDF URL: <https://dergipark.org.tr/tr/download/article-file/45262>

Photoinduced Optical Anisotropy of Photosensitive Polymer Films

Rıdvan KARAPINAR¹, Mary O'NEILL²

Abstract

In this study, the optical anisotropy of the photosensitive polymer films was studied as a function of exposure time of linearly polarized ultraviolet (UV) laser light. The anisotropy of the polymer films is due to the photoinduced intermolecular effect under the influence of the UV light. The photoalignment mechanism was investigated on the polymer films by using twisted nematic liquid crystal structures. Twisted nematic liquid crystal structures were examined by a polarizing microscope.

Keywords: Photoinduced anisotropy, Photosensitive polymers films, Liquid crystal alignment.

Özet

Bu çalışmada ışığa duyarlı polimer filmlerin optiksel anizotropisinin çizgisel kutuplanmış morötesi lazer ışığının uygulanma süresine göre değişimi incelendi. Bu tür polimer filmlerin anizotropisi morötesi ışığın soğurumu sonucu oluşan ışık etkimeli moleküler etkiden ileri gelmektedir. Polimer filmlerdeki fotoyönelim mekanizması bükümlü nematik sıvı kristal yapılar kullanılarak araştırıldı. Bükümlü nematik sıvı kristal yapılar polarize mikroskopla incelendi.

Anahtar kelimeler: Işık etkimeli anizotropi, Işığa duyarlı polimer filmler, Sıvı kristal yönelim.

1. Introduction

Uniform alignment of the liquid crystal molecules on the polymer surfaces is essential for the fabrication of liquid crystal displays. Many techniques have been developed to produce planar alignment of liquid crystals. Among these, the control of the liquid crystal alignment by a polarized UV laser light has attracted much

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interest because of the importance in electro-optic applications. The photoinduced reorientation process yields some structural changes on the photosensitive materials upon UV illumination (Marusii and Reznikov, 1993, 161-168). Thus, the photosensitive polymer films have been used as alignment layers for liquid crystal displays. Polyvinyl cinnamate (PVCi) and its derivatives in thin film forms are well known to provide such alignment (Schadt et al., 1995, 3240-3249; Bryan-Brown and Sage, 1996, 825-829). However, one of the drawbacks of PVCi was found to be the lack of thermal stability due to its low glass transition temperature. That is why, recently new types of photoalignment polymers have also been employed to generate variable orientation directions on polymer layers (Schadt and Seiberle, 1997, 397-400, Jackson et al., 1999, 38-47). In the present study we report photoinduced optical anisotropy in some photosensitive polymer films and discuss the mechanism of the photoinduced anisotropy using photopolymerization process model.

2. Experiment and method

The syntheses of the polymers investigated are described in our previous work [Hindmarsh et al., 1999, 439-446]. Chemical structures of the polymers (1) and (2) are shown in Figure 1. These polymers are polymethacrylate derivatives of hydroxycoumarin. Thin films were deposited by first spin coating at 2000 rpm for 30 s using 6% solution of the polymer in cyclopentanone and curing at 87 °C for 30 minute to remove the solvent. All thermal treatments were performed in the oven under a flowing nitrogen gas condition. The thickness of the films was measured using a surface profile measuring system [Dektak 3ST Auto1 Surface Profiler]. The thickness of the layers was controlled (ranged from 100 nm to 300 nm) with varying

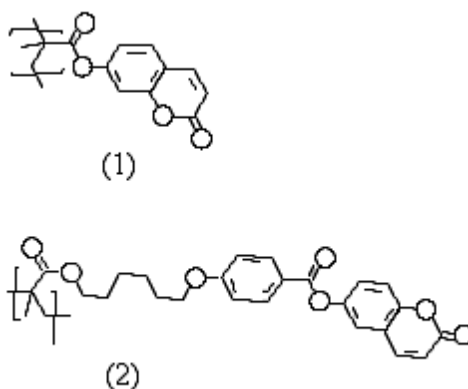


Figure 1. Chemical structures of photocrosslinkable polymers (1) and (2).

rotation speed of the spin coater. The UV absorption spectra of the photopolymer film was obtained using a UV scanning spectrometer [Philips PU8720].

The photoinduced anisotropy of the films was created by linearly polarized argon ion laser irradiation. The pumping laser beam operating at 300.5 nm was expanded by using a beam expander in order to prevent the formation of standing waves which would led to a non-uniform exposure through the depth of the film. Irradiation was performed at room temperature. The optical anisotropy in the photopolymer layers was measured by probing a He-Ne laser beam (632.8 nm) under crossed polarizers. One of the crossed polarizers was arranged to make an angle of 45° with respect to the polarization direction of the pumping beam. The wavelength of the He-Ne laser beam does not perturb the photoinduced optical anisotropy since its value is far away from any intrinsic absorption bands in either starting photopolymer or its photoproduct. In order to analyze the optical anisotropy of the photosensitive films, the samples were placed between the crossed polarizers. The light intensity of the He-Ne laser beam passed through the polymer sample was detected by a photodetector. The signal taken from the photodetector was processed by a phase sensitive lock in amplifier and was recorded by a computer. The transmitted intensity (I) of the probe beam through the crossed polarizer system is given by;

$$I = I_0 \sin^2 \left(\frac{\pi \Delta n d}{\lambda} \right) \quad (1)$$

where λ is the wavelength of the probing He-Ne laser beam. Δn is the birefringence of the polymer sample and d is its thickness. I_0 is the intensity of the laser light passing through the pairs of parallel polarizers and unexposed sample. Thus the measurement of the intensity of the transmitted light allows to determine the optical birefringence of the polymer samples.

3. Results and discussion

The optical absorption spectrum of the polymer sample (1) is shown in Figure 2. The sample exhibits a maximum of absorption at 322 nm. It was observed that the intensity of the absorption peak decreased significantly as a function of the UV irradiation time. This may be due to the photogenerated (2+2) cycloaddition of side chains belonging to different main chains. Thus photocycloaddition appears to be dominant process occurring in the films.

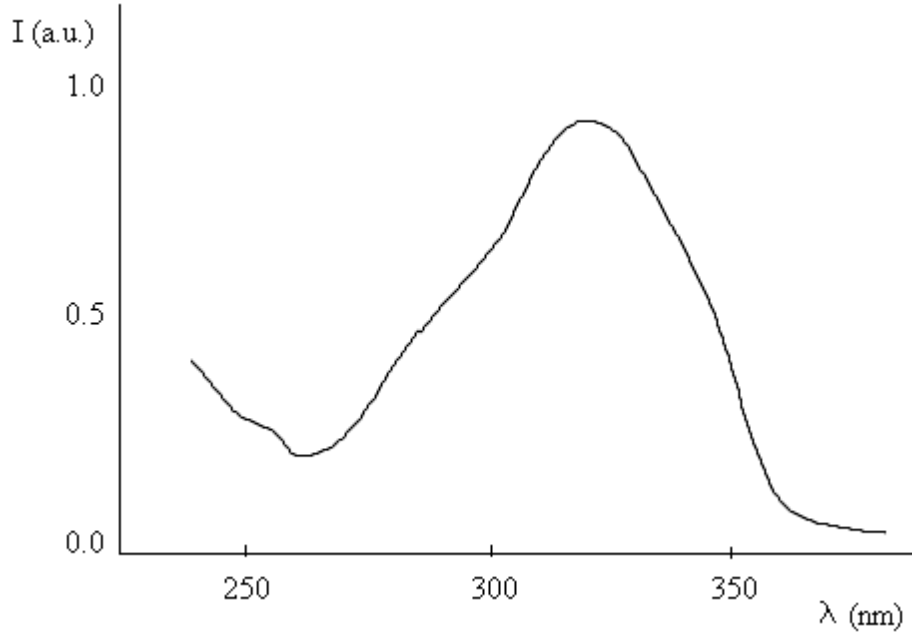


Figure 2. UV-visible absorption spectrum of the photopolymer sample.

The optical anisotropy of the sample was plotted as a function of the UV exposure time as shown in Figure 3. No optical anisotropy was detected prior to exposure, since the molecules are isotropically distributed. However, after UV irradiation optical anisotropy increased rapidly and reached at maximum and then decreased slowly as exposure time increases. The polarized UV exposure causes to a selective depletion of side chain groups aligned parallel to the UV polarization direction. Thus, the time dependence of the optical anisotropy can be explained by the preferred depletion of side chain molecules (Kim et al., 1998, 5644-5650). The possibility of a photopolymerization of molecules oriented a specific direction should be proportional to the number of photons whose polarization direction match with that direction. If the direction of the polarization is along x direction, the time dependent angular distribution of the photosensitive molecules can be written as;

$$N(\theta, \phi, t) = N_0(\theta, \phi) \exp(-\alpha t \cos^2 \theta \cos^2 \phi) \quad (2)$$

where $N_0(\theta, \phi, t)$ is the initial angular distribution of the molecules and α is a constant proportional to the intensity of the UV light. The optical retardation of the

photopolymer films polymerized by linearly polarized UV light can be given as;

$$\delta(t) = C \int_0^{2\pi} \int_0^{\pi/2} \frac{1}{2} (3 \cos^2 \phi - 1) N(\theta, \phi, t) \sin \theta d\theta d\phi \quad (3)$$

where C is a constant related to the refractive index of the film. In a two-dimensional system in which all molecules lie in a plane parallel to the x - y plane, Eq. (3) can be rewritten as follows:

$$\delta(t) = C \int_0^{2\pi} (2 \cos^2 \phi - 1) [1 - \exp(-\alpha t \cos^2 \phi)] d\phi \quad (4)$$

Eq. (4) indicates that the optical anisotropy rapidly increases with the exposure time and becomes saturated in long exposures. Experimental data was found to be in good agreement with the findings of Eq. (4). Thus, the mechanism of the photoinduced optical anisotropy can be explained in terms of the photopolymerization process having angular dependence.

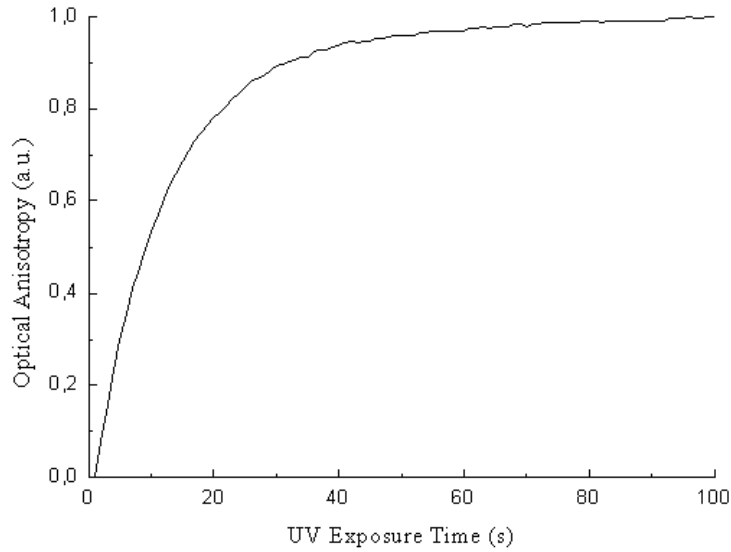


Figure 3. Optical anisotropy of the polymer sample (2) as a function of exposure time.

It was observed that polymer sample type (1) exhibits an induced optical anisotropy upon the UV irradiation. However, this anisotropy disappeared almost instantly on removal of the irradiation (Figure 4). This indicates that there is a

degree of photoinduced anisotropy, but the photochemical crosslinking reaction is inhibited due to steric hindrance attributable to the absence of a spacer unit in the side chain. These photosensitive polymers with reversible photoinduced anisotropy are promising materials for real-time recording and image processing. The inclusion of a spacer gives flexibility and freedom of movement to side chains. Thus, when the sample is exposed to the linearly polarized UV light, the crosslinking reaction may take place between neighboring side chains. As a result linear photopolymerization leads to a preferred depletion of side chain molecules which are parallel to the UV polarization direction.

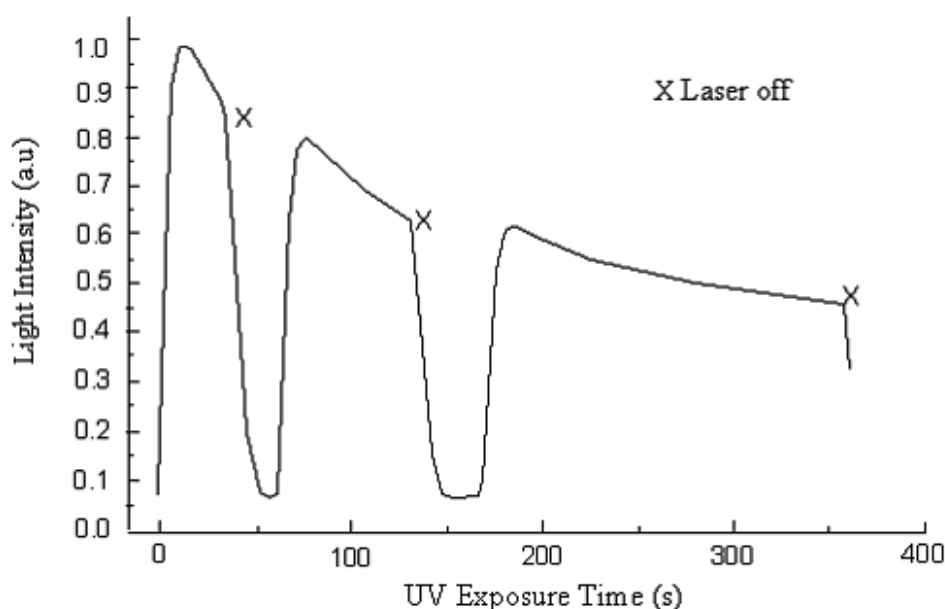


Figure 4. Exposure time variation of light intensity of the photopolymer sample (1).

The photopolymer films have unique properties such as good thermal stability and very suitable for liquid crystal alignment layers. To investigate the photoalignment behavior of the liquid crystal, the twisted nematic cells were constructed. By using a metallized target mask, the photoalignment areas which are exposed to light with different exposure times were obtained in the polymer film. Twisted nematic cells of thickness 13 μm were constructed using one exposed photopolymer layer and one rubbed polyimide layer. The cells were filled with the nematic liquid crystal E202. The twisted structures were obtained in such a way that the rubbing direction on the polyimide layer was perpendicular to the alignment

direction on the photopolymer layer. Optical images of the test cells were taken with a polarizing optical microscope and camera. Macroscopic photograph of twisted nematic cell showing the optical white states between crossed polarizers is displayed in Figure 5. In the figure bright spots are UV exposed areas and the background is homogenous alignment.

Photoalignment mechanism still has not been understood fully. It was proposed the template effect of the dimerized species is responsible for the liquid crystal alignment (Schadt et al., 1995, 3240-3249). However, it was also suggested that isomerization reaction is the real reason for the alignment (Ichimura et al., 1996, 992-995). Generally, anisotropic distribution of the polymer side chains induced by linearly polarized laser light is responsible for the alignment of liquid crystal molecules. The anisotropy of the polymer side chains results in anisotropic interaction with the contacted liquid crystal molecules which induce an easy axis on the polymer surface.

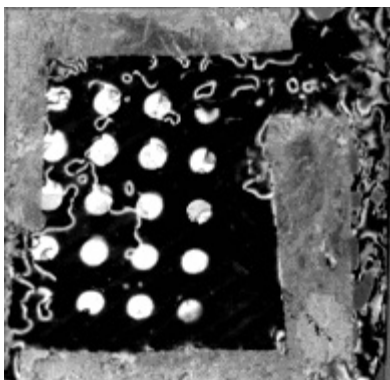


Figure 5. A micrograph of a typical twisted nematic structure.

4. Conclusion

In this study the optical anisotropy of the polymers containing coumarin in the side chain were investigated as a function of UV illumination. It was shown that linearly polarized UV irradiation on the coumarin polymers induced optical anisotropy of the polymer films and these photosensitive polymer films can be used for the alignment layers for nematic liquid crystals.

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