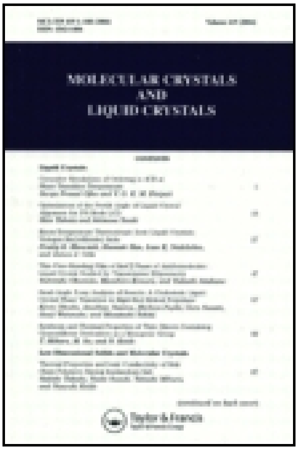

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Photo-Alignment using Adsorbed Dichroic Molecules

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Photo-Alignment using Adsorbed Dichroic Molecules

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In this paper we report photo-alignment using low molecular weight dichroic materials. We produced photo-alignment by exposing thin films of dichroic materials such as methyl red, 4,4′-dihydroxyazobenzene and 4,4′-biphenol to linearly polarized light. The irradiation generates a preferred orientation of liquid crystals perpendicular to the polarization direction. The mechanism of the photo-alignment process was studied. Alignment appears to be produced by a single mono-layer of the dichroic material adsorbed on the substrate. Polarized exposure produces anisotropic desorption and distribution of the remaining dichroic material. Photo-alignment of these materials requires the presence of polar groups in the molecules. Strong adsorption and stable alignment can be achieved by properly matching the chemical characteristics of the dichroic and surface materials. We hope to adjust the energy and tilt angle of the alignment layer by simply adsorbing mixtures of different dichroic materials.

Keywords: liquid crystal; photo-alignment; dichroic materials

INTRODUCTION

The alignment of bulk liquid crystal is determined by the orientational distribution of the molecules on the surface mono-layer.[1] There are many ways to generate an ordered surface. Mechanical rubbing of a polyimide film is the most widely used method[2] but the rubbing process can introduce scratches and other damage to the surface. Also, alignment by the anisotropic polymer chains is not homogeneous on the molecular level. In recent years, the photo-alignment process has become a promising substitution for rubbing. It provides an easy to control non-contact method to achieve alignment.[3] There are several different ways of producing photo-induced anisotropy that lead to the alignment of liquid crystals: photo-polymerization,[4-6] photo-decomposition,[7] photo-isomerization,[8,9] etc. One of the most interesting phenomena among these studies is the alignment of the liquid crystal by the liquid crystal itself. Reznikov, et al.[10] have observed homogeneous planar alignment of liquid crystal 5CB on a fused quartz surface by exposure with linearly polarized UV light. They have proposed that light-induced reorientation of the adsorbed liquid crystal molecules contributes to such an effect.

Usually photosensitive materials are either chemically attached to the substrate surface[11] or incorporated into the polymer chains.[12] We have reported previous work on the study of the photo-alignment effect of methyl red.[13] The mechanism of photo-alignment of adsorbed methyl red molecules on an ITO substrate is postulated to be cis/trans isomerization. In this paper we report on other dichroic materials coated on bare ITO glass and PVA substrates and their alignment following polarized broadband UV irradiation. Our study on the photo-alignment behavior of a variety of dichroic materials adsorbed on non-photosensitive surface exposed to linearly polarized visible or ultraviolet light has lead to a very interesting conclusion.

EXPERIMENTAL

All chemicals were obtained from Aldrich. PVA (89% hydrolyzed) was dissolved in water to form a solution of 2%(wt) concentration. The solution was spin-coated on ITO/glass or quartz substrates to form a PVA film with an average thickness of 8mm. The PVA coated substrates were dried in an oven at 100°C for 1 hr. Dichroic materials were dissolved in isopropanol (i-PrOH) at various concentrations. The solution was spin-coated on both bare ITO/glass and PVA substrates under the same conditions. Film thickness can be adjusted by using solutions of different concentrations. The substrates coated with dichroic materials were irradiated with polarized light. An Ar^+ laser (Ion Laser Technology) was used for polarized visible light (501nm) irradiation of methyl red. A Xe lamp (Oriel 6266) was used for polarized broadband UV light irradiation at an average intensity of $5x10^{-4}$ W/cm^2 for all the other dichroic materials. Rubbed Polyimide (Nissan, SE3510) with low pretilt angle on ITO/glass was used as the reference substrate. The irradiated substrates and reference substrates were assembled into TN test cells with the setup shown in figure 1. The polarization direction is 45° off from the rubbing direction of the Polyimide (PI). Plastic spherical spacers (47 mm) were used to maintain uniform cell gap. The test cells were then filled with pentylcyanobiphenyl (5CB, from Merck) at 50°C. The filled cell was slowly cooled down to room temperature to minimize the effect of

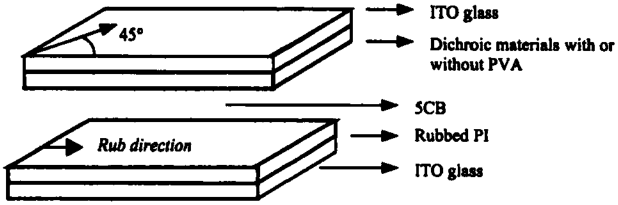


FIGURE 1 Setup for the test cell

flow-induced alignment. The alignment direction of the liquid crystal induced by the photo-exposed film was examined between crossed polarizers. Solutions of dichroic materials were also spin-coated on PVA/quartz substrate to record UV-vis spectra using a UV/vis/NIR (Perkin-Elmer Lambda 19) spectrometer. The absorption of PVA was subtracted when taking the spectrum.

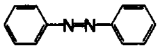
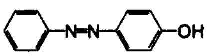
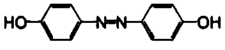
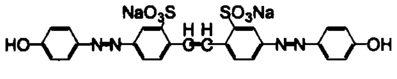
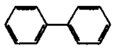
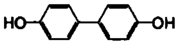
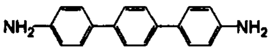
RESULTS AND DISCUSSION

All the dichroic materials we studied produced alignment direction perpendicular to the polarization direction of the irradiation light. Table 1 lists the results of some materials we tested.

We found that all dichroic materials listed in the table showed some alignment effect on proper substrates except azobenzene and biphenyl, which had no alignment effect on any of the tested substrates. Brilliant Yellow (BY) produced very strong alignment effect on PVA. All tested dichroic materials had fair solubility in the liquid crystal 5CB. When filling the cell with liquid crystal 5CB under isotropic state, we noticed that part of the surface film was dissolved by the liquid crystal. Therefore, one may say that only a mono-layer of

TABLE I

The photo-alignment effect of various dichroic materials adsorbed on both ITO glass and PVA substrates.

Name	Structure	Effect on different substrates	
		ITO glass	PVA
azobenzene		No	No
4-phenyl azophenol		No	Moderate
4,4'-dihydroxy azobenzene		Poor	Good
Brilliant Yellow		Poor	Good
Biphenyl		No	No
4,4'-biphenol		Poor	Good
4,4'-diamino terphenyl		No	Poor

the dichroic molecules adsorbed directly to the surface of the substrate remains. The anisotropy of this monolayer generated by polarized light irradiation induces the alignment of liquid crystal. Therefore the ability of these molecules to strongly adsorb on the surface of the substrate is a primary requirement for photo-alignment. Molecules having strong polar functional groups are therefore more effective for photo-alignment. Materials like azobenzene that do not have polar functional groups will not show photo-alignment after PUV irradiation while materials such as Brilliant Yellow produce very strong alignment.

We also noticed that molecules with polar functional groups usually show weak alignment effect or no effect at all on ITO glass substrates while having better aligning ability on PVA substrates. The 89% hydrated PVA is highly polar and produces stronger adsorption than ITO. The intermolecular interaction between the substrate and the adsorbed molecules is indicated by a red shift of the absorption peak of the UV-vis spectrum of the adsorbed species. As shown in figure 2, The λ_{max} of 4,4′-dihydroxyazobenzene adsorbed on PVA is at 400nm, while the λ_{max} of 4,4′-dihydroxyazobenzene in hexane is at 280nm. The intermolecular interaction between the hydroxyl groups of the molecule with the substrate results in a red shift of the absorption peak. The stronger the interaction, the more the peak shifts. As shown in figure 3, the λ_{max} for BY on ITO is at 380nm, while the λ_{max} for BY on PVA is at around 430nm. Therefore the interaction between BY

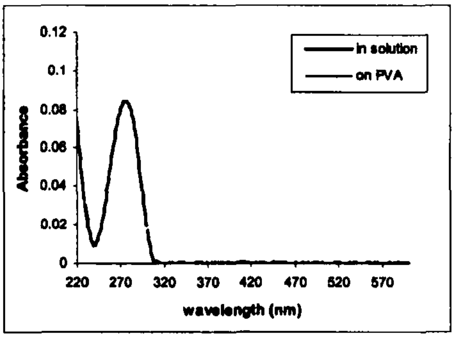


FIGURE 2 The spectra of 4,4′-dihydroxyazobenzene in hexane solution and on PVA substrate.

molecules and PVA is stronger than the interaction between BY molecules and ITO surface.

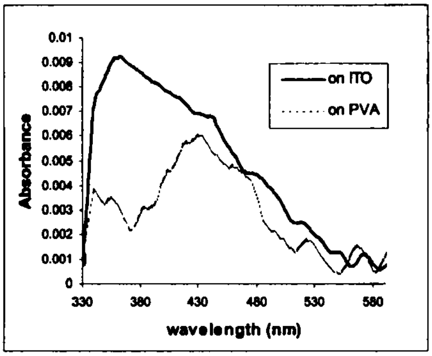


FIGURE 3 The spectra of adsorbed Brilliant Yellow on ITO and PVA surfaces.

The intermolecular interaction between adsorbed molecules and the substrate also influences the stability of the alignment effect. The alignment on ITO substrates is generally not as stable as that on PVA substrates. Alignment on ITO disappears after several weeks under room temperature while the alignment on PVA remains stable indefinitely at room temperature or even after heating up to 80°C for five hours. The alignment effect of adsorbed BY on cross-linked gel substrate is very strong and is thermally stable after heating to 150°C for one hour.

In order to study the mechanism of the photo-alignment process with adsorbed dichroic materials, we monitored the change of absorption spectrum of adsorbed 4,4'-dihydroxyazobenzene on PVA with polarized broadband UV (PUV) irradiation. Before exposure, the molecules are distributed isotropically on the surface, which is indicated by identical spectra parallel and perpendicular to the polarization direction. The anisotropy appears after exposure for five minutes and increases with increasing exposure time. As shown in figure 4, the absorption peak does not shift with exposure. Also, the

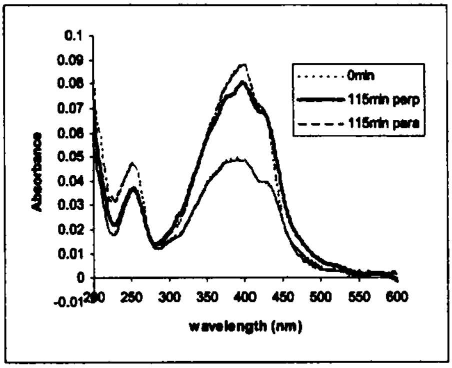


FIGURE 4 The change of absorption spectrum of 4,4′-dihydroxyazobenzene film on PVA with PUV exposure.

PVA film remains isotropic after PUV exposure. The peak absorption of the adsorbed materials perpendicular to PUV direction (A_{perp}) does not change much with irradiation while the absorption parallel to PUV direction (A_{para}) decreases with increasing exposure time. This clearly indicates a photo-induced selective desorption process resulting in elimination of molecules parallel to the PUV direction as opposed to an isomerization process which would result in an increase of A_{perp}. Due to the strong interaction between the adsorbed molecules and substrate surface, the remaining molecules maintain their original orientation. This process yields an anisotropic distribution of the adsorbed dichroic molecules, which in turn generates a uniform alignment of liquid crystal 5CB. There is no evidence indicating a cis/trans isomerization which would show a peak shift with increasing exposure. Figure 5 shows the anisotropy generated by PUV exposure.

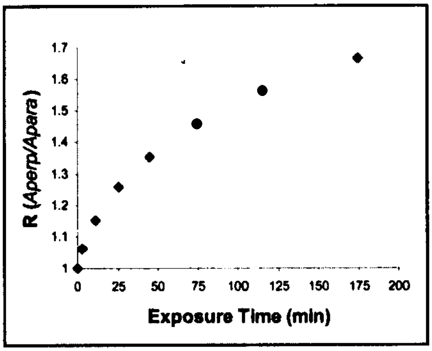


FIGURE 5 The generation of dichroism on 4,4'-dihydroxyazobenzene film on PVA with PUV exposure.

The ratio (R) of the A_{perp} to A_{para} is used as an indication of the anisotropy of the substrate surface. R increases with increasing irradiation time, asymptotically approaching a maximum. We predict R will eventually decrease as molecules adsorbed perpendicular to the PUV direction begin to desorb.

Since the presence of the azo group in 4,4'-dihydroxy-azobenzene and cis/trans isomerization do not seem to contribute to this photo-alignment process, it is natural to test the alignment effect of the structurally similar 4,4'-biphenol. The adsorbed 4,4'-biphenol on PVA shows a strong photo-alignment effect for liquid crystal. Another dichroic material 2,2'-diamino-terphenyl also shows the alignment effect on PVA substrate. Cis/trans isomerization is clearly not required for this type of photo-alignment.

Azobenzene lacks polar groups on either end of the phenyl ring. Consequently, there is no strong adsorption on the substrate. Figure 6 indicates no significant red shift of absorption peak for azobenzene on PVA as compared to its solution spectrum. After selective desorption by polarized UV light the rest of the azobenzene molecules redistribute themselves relatively freely on the substrate surface, resulting in an isotropic distribution and subsequently no alignment effect. The peak absorbance of azobenzene decreases with exposure time, but no difference between A_{perp} and A_{para} is observed (The experimental results are shown in figure 7). Both decrease equally with time, indicating an isotropic distribution of molecules on the substrate surface.

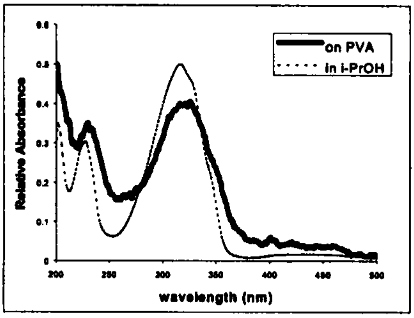


FIGURE 6 Absorption spectra of azobenzene in isopropyl alcohol solution and on PVA

Normal exposure to PUV of suitable adsorbed dichroic materials generates uniform azimuthal alignment of liquid crystals. A second

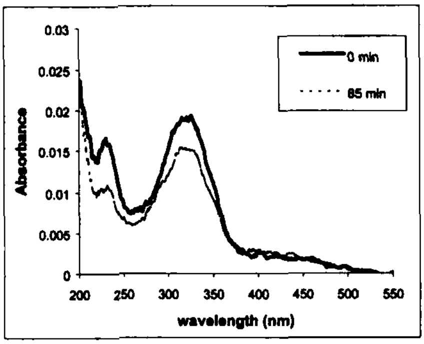


FIGURE 7 Change of absorption spectrum with PUV irradiation for azobenzene adsorbed on PVA

oblique exposure is needed to produce pretilt.[7] Our group is currently researching control of the pretilt of these photo-aligning films. We hope to eventually adjust the energy and pretilt of the alignment layer freely by simply mixing different types of molecules.

CONCLUSION

The photo-alignment process of a series of low molecular weight dichroic materials adsorbed on different substrates was studied. Polarized light induced anisotropic desorption together with the intermolecular interaction between the adsorbed material and the substrate result in an anisotropic distribution of the adsorbed molecules on the substrate surface which aligns the liquid crystal 5CB perpendicular to the polarization direction of the PUV light. An effective and stable alignment can be produced by properly matching the chemical characteristics of the dichroic and surface materials.

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