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Optically-controlled Alignment of Liquid Crystals on Alignment Layer (PWD) Containing Azo-group

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To align liquid crystals on an alignment layer, the rubbing method is generally used. But it has some problems such as the generation of dust, and the difficulty of the quantitative control of rubbing intensity. To overcome these problems, we developed new photo-active mixture of w-dye (see the Fig. 1(a)) and PVA which can be applied as an alignment material for liquid crystal display (LCD). Using this polymer, we made cells and observed properties of a photo-alignment layer and LC alignment. From these results, we discussed the mechanism of LC and polymer alignment by UV irradiation in photo-alignment layer. We show that this new alignment material may be used in commercial LCDs.

Keywords: LCD; photo-alignment; UV; LC-pretilt; order parameter

I. INTRODUCTION

For obtaining liquid crystal displays (LCD) of good characteristics, liquid crystals on the surface of substrate should be uniformly aligned. To do this, some technologies [1-2] have been developed. Among them, a rubbing method has been used generally in industry because of its capability of mass production and treatment of large areas, but it also has disadvantages such as the generation of dust, and static electricity and the difficulty of quantitative control of the rubbing strength because of many randomly attached rubbing fibers (about 10⁸ piece/m²) [3] on rubbing cloth.

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To overcome these problems, Schadt et al. [4-7] suggested a new alignment technology; photo-alignment utilizing photo-chemical reaction of a photo polymers. Authors have reported using PVCN (polycinnamate) [8] or PVMC (polyvinyl 4-methoxycinnamate) [4], polysiloxane [9], and PVA doped with an azo dye (methyl orange) [10]. Those materials have fundamental properties to align LCs. To be applied to the commercial LCDs, however, they need more development of high order-parameter of LC, good thermal stability, and easy LC-pretilt generation. Polyimide materials using photo-alignment method have been also used to align LCs [11, 12], but those materials take too much to obtain good alignment.

To eliminate these problems, we developed a new mixture of PVA and dye containing an azo-group as the LC-alignment layer (abbreviated to PWD) in which PVA has optimum thermal stability and the dye reacts easily to UV light. In this paper, we described the properties of the photo-alignment layer, the effects on LCs, and thermal stability of LC-pretilt.

II. EXPERIMENT

The PVA and w-dye (1 wt%, PVA: w-dye = 1:4) are blended into DI water as shown in Figure 1 and a small amount of fenoxal is added into PWD to improve the film formation. To make samples for retardation measurement, we coated quartz plates with PWD. To investigate the LC pretilt angle, we made antiparallel cells. Photo polymer solution was spin-coated onto ITO-coated glass substrate to make thin layer and fixed through heat treatment.

a)w-dye(4,4'-bisarylazo-biphenyl)

-/. ..

FIGURE 1 The molecular structure of w-dye and PVA (PWD).

The photopolymer coated substrate was irradiated with linearly polarized light (see Fig. 2) and then this substrate was assembled. Liquid crystal, ZLI-2293 (MERCK), was injected into the cell. The LC pretilt is measured by using an improved crystal rotation method [13]. A Xenon lamp is used to align the dye molecules on an alignment layer. The irradiation incident angle relative to the normal direction of the substrate is 45° as shown in Figure 2. To study the microscopic changes of the dye-polymer (PWD) in an alignment layer, the optical retardation was measured as a function of UV exposure energy. For this experiment, we made quartz plates coated with a PWD layer of about 1500 Å thickness to prevent multi-reflection effect [14] in an alignment layer when the retardation is measured. To observe the degree of trans-cis isomerization, we measured spectra of PWD by measuring the UV absorption. We also obtained the second rank order parameter according to dichroism of guest dyes in order to measure the extent of LC alignment in LC cell [15], and measured the change of LCpretilt as a function of annealing temperature to see the possibility of PWD application to commercial liquid crystal display (LCD).

III. RESULT AND DISCUSSION

a) Alignment Characteristics of PWD After UV Exposure

The retardation values as a function of UV energy are shown in Figure 3. The value after UV exposure increase from zero to a certain value as a function of UV energy as shown in Figures 3(a) and (b). Here, we postulate that the retardation is mainly the result of dye molecules because the structure of dye is composed of many benzene rings which are the main contribution to retardation value. From this result, we assume that the dye

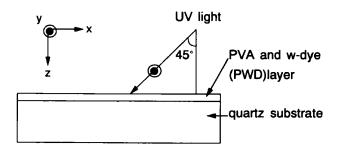


FIGURE 2 UV exposure method on the substrate.

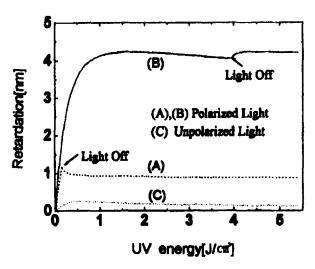


FIGURE 3 Retardation change as a function of UV exposure energy. (A), (B) Retardation change when the polarized UV light is exposured to the PWD substrate, (C) Retardation change when the unpolarized UV light is exposured to the PWD substrate.

molecules in the alignment layer are randomly aligned before the exposure of UV light, but the dye molecules are aligned by polarized UV light and the direction of alignment is perpendicular to the polarized direction of UV light. In case of Figure 3(a), when the UV light is cut off before the retardation is saturated, the value decreases slightly. From this result, we believe that the relaxation results from trans-cis photo isomerization and cis-state return to the original state (trans-state) after UV cutoff. But, in case of Figure 3(b) when the UV light is cut off in the saturated region, the value increases slightly. In this region, the number of trans-state molecules perpendicular to the polarization is larger than that of molecules parallel. Those surround molecules affect them of cis-state, and these turn to trans-state making the retardation increase.

On the other hand, the retardation after exposing with non-polarized light is very small (about zero) compared to the value after exposure of polarized UV light, as shown in Figure 3(c). From this result, we know the UV light without polarized component forces dye molecules to align randomly without a certain alignment direction in layer.

The absorbance of dichroic ratio is obtained as a function of wavelength as shown in Figure 4. In case of Figure 4(a), the absorbance values under the different conditions, which the direction of polarizer is parallel (A_{\parallel}) or perpendicular (A_{\perp}) , is almost same. It means that the dye in alignment layer is aligned randomly before UV-exposure. When the polarized UV-light is

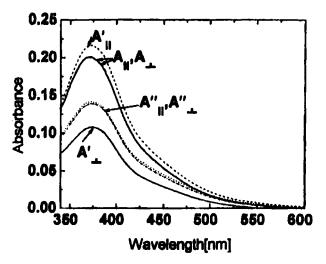


FIGURE 4 Absorbance of PWD as a function of wavelength. (a) A_{\parallel} , A_{\perp} : absorbance before exposure of UV light, (b) A_{\parallel}' , A_{\perp}' : absorbance after exposure of linearly polarized UV light, (c) A_{\parallel}'' , A_{\perp}'' : absorbance after exposure of non polarized UV light.

exposed to the substrate, the dichroic ratio between a parallel (A_{\parallel}) and a perpendicular (A_{\perp}) is larger than that before UV-exposure. In particular, the parallel absorbance (A'_{\parallel}) is large absorbance like Figure 4(b). From this result, we believe the polymer after UV-exposure is uniformly aligned perpendicularly to polarized direction of UV light. Moreover, if the non-polarized UV-light is exposed to the polymer substrate, there is no difference between A_{\parallel} and A_{\perp} (see Fig. 4(c)). Here we see the non-polarized UV-light can not contribute to the alignment of uni-direction in the alignment layer.

(b) LC Alignment Characteristics on PWD Layer

To measure the extent of LC-alignment, we obtained the dichroic absorption of dye mixed with liquid crystal. Here, we measured the order parameter of dye (4,4'-bisarylazo-biphenyl), defined second rank order parameter, P. We can easily estimate the extent of LC alignment from this method. We injected the mixture of dye and liquid crystal, and then measured the dichroic absorption of dye. The second rank order parameter can be calculated by

$$P = \frac{A_{B\parallel} - A_{B\perp}}{A_{B\parallel} + 2A_{B\perp}},$$

where P, $A_{B\parallel}$, and $A_{B\perp}$ are second rank order parameter, absorbance parallel and perpendicular to linearly polarized light, respectively.

Moreover, we obtained the LC order parameter (called by second rank order parameter) as a function of UV energy to look into the alignment of molecules in LC bulk as shown in Figure 5. We can see the order parameter is saturated over $0.5 \, \text{J/cm}^2$. Comparing relation between retardation and LC order parameter, these values of UV exposure energy up to saturation region are almost same. From this result, we know that the alignment of molecules in LC bulk is dominated by aligned dye molecules in an alignment layer. In case of this order parameter, the absolute value is similar to the value obtained by rubbing process. Thus, we see that there is no difference for an LC alignment-extent in azimuthal direction between photo alignment and rubbing alignment.

To investigate the dissolution of PWD layer in LC, we prepared glass which was coated with PWD and baked at the temperature of 110°C for 30 minutes. We dipped the substrate in LC, and we observed no change of color of LC in 20 days.

(c) Thermal Stability of Photo-alignment Using PWD

For the application to commercial LCD, the LC-pretilt is very important parameter for electro-optical property in LCD. We controlled LC-pretilt as a function of UV energy. As a result, we certified that the LC-pretilt angle

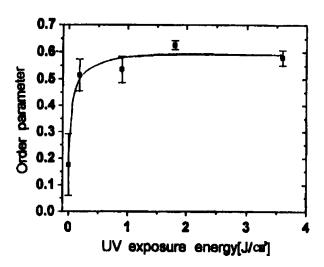


FIGURE 5 The relation of second rank order parameter as a function of UV energy.

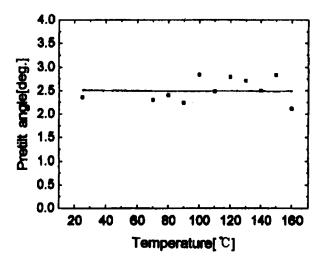


FIGURE 6 Curing temperature dependence of pretilt angle after injection of liquid crystal.

can be controlled up to 4 degrees [16]. Figure 6 shows the thermal stability as a function of curing temperature. At each temperature, cells are cured for 10 minutes. From this result, we know the alignment layer using PWD give thermal stability up to 140°C-150°C. In these regions, we believe that this PWD have a good possibility to realize LCD of TN type with a optimum LC-pretilt angle and a good thermal stability.

IV. CONCLUSION

We made the new material mixtured with w-dye (4,4'-bisarylazo-biphenyl) and PVA, and it has a good alignment characteristic for LC's alignment. For alignment property, we consider the dye molecules are aligned perpendicular to polarization direction of UV light, and LCs are aligned to the same direction. Moreover we show that our material by using two times UV exposrute method have an optimum LC-pretilt angle and good thermal stability for the commercial LCD.

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