45.3: Azo Dye Materials for the Alignment of Liquid Crystal

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In this paper, the photo-induced alignment of liquid crystal on an azo dye film is discussed for the liquid crystal display (LCD) applications. This is a non-contact technique to align the liquid crystals so that the dust particles and static charges generated by the rubbing process can be eliminated. To prepare for the photo-alignment layer, the azo dye film is exposed to a linearly polarized or non-polarized light. As a result of the dipole absorption, the photo-induced molecular distribution is non-uniform and has an angular dependence. Consequently, since the dispersion forces between the dye and the liquid crystal molecules dominate, the induced orientation of the liquid crystal molecules is possible. The oblique incidence of the light exposure will also favour a non-zero pretilt angle. We find that the order parameter associated with the aligned liquid crystal medium is high, and very good contrast has been measured in the Twist Nematic (TN) LCD.

1. INTRODUCTION

The alignment layers for the liquid crystal displays (LCDs) and other liquid crystal (LC) devices are usually based on the polyimide film of 10-50 nm thick. Conventionally, the alignment of liquid crystals is induced by the mechanical rubbing or brushing. However, the tiny particles and static charges are generated in this process, which have been reported as one of the major causes in the defective displays. The cross contamination problem is also very difficult to minimize. For the active-matrix liquid crystal displays (AMLCDs), these problems are unforgiving.

On the other hand, the photo-alignment technology is a clean and non-contact process. The photo-alignment layer is first exposed to the polarized or non-polarized light, and a molecular order is induced in the photo-alignment layer. Although the order parameter as a measure of this photo-induced transformation is often not large, we find that it is possible to induce a good homogeneous orientation of the liquid crystal and a non-zero pretilt angle. This process is compatible with the clean-room requirement and the fabrication of the AMLCDs. In addition, it is an effective mean to fabricate the multi-domain structures for the wide viewing angle LCDs.

Currently, there are several groups of materials suitable for this purpose, such as the polyvinylcinnamate, polyimide and liquid crystalline side-chain polymers. Historically, the photo-induced anisotropy recorded in the polyvinylcinnamate was first demonstrated in 1977 [1]. This material was then applied to align the liquid crystal molecules, and very promising results had been obtained [2-3]. However, the homogenous alignment cannot be restored after a number of thermal cycles. The thermal stability and the compatibility with the LCD manufacturing are the primary issues one has to solve for this material.

The second material, which had successfully induced the alignment of the liquid crystals, was the azo dyes mixed with a polyimide [4]. The thermal stability has been improved and become comparable to the polyimide matrix. Recently, the polyimide derivatives, which have cross-linked with the dyes, have shown very impressive alignment characteristics [5-7]. Since these materials have the similar stable characteristics as the polyimide, much research efforts have been undertaken in this direction. However, the high exposure energy is usually required for the polyimide derivatives and the free radicals are generated by the photo-dissociation. The impact due to these free radicals to the LCD life time has not been fully understood. Moreover, the photo-induced alignment depends on the exposure time and energy density. The induced order parameter will decrease gradually for the prolong exposure time and high energy density. In the early development of photo-alignment technology, the liquid crystalline side-chain polymer [8-9] and photo-stable azo dye polymer mixtures [10] had also drawn an attention.

In this paper, we shall study the azo dye materials, which can be the effective and stable alignment agents on their own. This alternative material can be made very sensitive, water-soluble, metal-free, thermal and UV stable. Nevertheless, since the liquid crystal is a weak electrolyte, the synthetic dyes of low molecular weight may be dissolved very slowly. This is a long term issue to scrutinize although the dissolution rate is extremely slow and is virtually unnoticeable for those synthetic dyes used in the photo-induced alignment experiments. Any inter-molecular hydrogen bond introduced in the dye molecules may help minimize this problem. Synthetic dyes can also be cross-linked in a polymeric main chain. This however may reduce the order parameter drastically and cause the disclination lines in the liquid crystal medium.

In the following sections, we propose for the first time the fluorinated dyes for the photo-induced alignment of liquid crystals. We discover that the sulphonated groups on one hand can help stabilize the dye molecules on different substrates, even at an elevated temperature. Whereas the fluorinated substitutes on the other hand can minimize the ionic dissociation associated with the carbonyl groups, and hence they improve the voltage holding ratio. In addition, these dye molecules are photochemical and thermal stable. They also exhibit the promising characteristics for the super fluorinated liquid crystals and the AMLCDs. TN-LCDs using these materials have been fabricated and tested in our laboratory, and the results are encouraging.

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2. PHOTO-INDUCED ALIGNMENT OF LIQUID CRYSTAL

Azobenzene derivatives, used in the experiments are shown in Fig. 1. When the azo dye molecules are optically pumped by a polarized light beam, the energy absorbed for the transformation is proportional to the square of the cosine θ , the angle between the transition dipole moments of the molecules and the direction of the polarized light. In other words, this probability distribution is non-uniform and has an angular dependence. Therefore, the azo dye molecules that have their transition dipole moments parallel to the direction of the polarized light will absorb most of the photon energy. It may give rise to the molecular reorientation and transformation. When the illumination light source is removed, these induced molecular changes relax to the thermal equilibrium state. This dark relaxation is often governed by the internal mean field associated with the molecules and domain structures. In some cases, long-lasting anisotropic dichroism and optical retardation can be photo-induced and the associated order parameter as a measure of these effects is large. These have been attributed to the photo-isomerization of azo dyes molecules. Well-established theoretical and experimental results have also been reported [11-15].

Yet, it is not clear whether the photo-isomerization is central in the photo-induced alignment of liquid crystals. According to the recent reports, it may be due to the ratchet mechanism, which induces a translational or rotational net transport of dye molecules [16-18]. Therefore, torque for example can be coupled to induce a twist deformation of liquid crystal medium. Nevertheless, how the liquid crystal molecules interact with the surface azo dyes layer is crucial to understand the surface-induced alignment mechanism. It is doubtful that the ordering is simply due to the “nematic-like interaction” between the liquid crystal and dyes molecules. Because we find that the order parameter of liquid crystal medium is not often related to that of the azo dyes alignment layer.

In the present discussion, we follow Pedersen's treatment [11] to show that our azo dyes have undergone isomerization. Accordingly, based on mean-field theory and the dynamic balance equations for the two-level transitions, the initial rate of change of optical anisotropy is given by

$$\frac{d\Delta n}{dt} = K' I \quad (1)$$

where I denotes the power density of pump beam. K' is a material constant, which depends on the transition coefficient, polarizabilities and initial order parameter.

So, the effects due to the isomerization cannot be neglected. It is believed that the dipole moment associated with the isomerized dyes molecules plays an intricate role in the alignment of liquid crystal.

3. EXPERIMENT

The dye molecules, which were synthesized for the studies of photo-induced alignment, were shown in Fig. 1. The precursor was 4,4'-diamino-3,3'-biphenyldisulfonic acid. Then it was azo-coupled with the 2-hydrobenzoic acid for SD1 or with *o*-trifluoromethylphenol for SD-2. The purity and yield were good.

To measure the induced optical anisotropy, the polarization vector of the pump beam at 488nm was 45° with respect to that of the probe beam at 632.8nm. A cross-polarization setup was used (see Fig. 2). The pump source was an Ar-ion laser from Ion Laser Technology.

Fig. 1 Synthetic azo dyes

Fig. 2 Experimental setup to measure the induced optical anisotropy

To prepare for the photo-alignment layer, a thin film of the synthetic dye was first spin-coated on top of the glass substrate. After the soft baking, this solid dye film was then irradiated by the polarized UV light (from a 1000 W Oriel Xenon arc lamp). The UV sheet polarizer was also

purchased from Oriel Instruments to obtain the linearly polarized UV light, and the polarized intensity at 365nm was about 6 mW/cm². This sheet polarizer can be eliminated however, if the photo-alignment layer is exposed by the non-polarized light at an oblique incidence. To fabricate the TN-LCD for the comparison, the polyimide from Chisso Corp and liquid crystal mixture E7 from Merck KGaA were used. The cell gap was 5μm.

Fig. 3 Absorption spectra of SD1 and SD2

4. RESULTS AND DISCUSSION

In this paper, the synthetic disazo dyes exhibit a photo-induced order when it is exposed to the polarized UV light, and the absorption spectra of SD1 and SD2 are shown in Fig. 3. The corresponding peaks are 366.6nm and 385.9nm respectively. The absorption is due to the electronic conjugation. The presence of the donor (azo-groups) and acceptor (trifluoromethyl, sulfonic, carboxyl and hydroxyl groups) strongly intensify this process [19]. The capability to accept electrons can be enhanced when the carboxyl groups are substituted by the fluorinated groups. So a sizeable increase in the voltage holding ratio has been measured in fluorinated-substituted SD2. A further significant improvement has also been found in our latest metacrylate-substituted SD1. In both cases, the photo-induced alignment of liquid crystal is very good after the substitution.

Fig. 4 FTIR spectra of SD1 before (solid) and after (dot) UV exposure

In Fig. 4, Azo dye SD1 was excessively exposed to UV light of 30 J/cm². Based on our latest results and these FT-IR spectra, it suggests that the concentration of cis-isomers is low, and that the isomers are very stable after the UV exposure.

Fig. 5 The initial rate of change of optical anisotropy

Due to the molecular dispersion forces between the dye and the liquid crystal molecules, a homogeneous orientation of the bulk liquid crystal is induced. Yet, the physical origin is not clear since the order parameter of aligned liquid crystal medium is much higher compared with that of the azo dyes alignment layer. We discovered that certain organic photochemical stable substances, illuminated by a linearly polarized or non-polarized light, showed a much higher degree of the induced molecular order than those found in an active photochemical molecular layer. For SD1, the experimental data and the theoretical fit are plotted in Fig. 5. The molecular order, which was evaluated by the photo-induced optical anisotropy, became saturated when the exposure energy reached the critical value (see Fig. 6). Both the initial rate of change of optical anisotropy and its saturated value are roughly proportional to the power density of the illumination source. This linear dependence is a unique signature of absorption-induced reorientation, which is consistent with the published results [11, 13].

In addition, it was possible to induce the photo-alignment of the liquid crystals, using the obliquely incident non-polarized light. In this case, the molecular order in the photo-alignment layer increases with the exposure energy. The preferred orientation of the liquid crystal molecules is usually parallel to the plane of oblique incidence and the final orientation depends on the interaction between the liquid crystal and the dye molecules. Thus the expensive UV-polarizers can be eliminated and the whole production process of the photo-alignment layer can be considerably simplified. In Fig. 7, the transmission voltage curves of the TN-LCD using SD1 and polyimide PIA3744 as the alignment layer are compared. The transfer characteristics are similar and very good contrast as the result of homogenous alignment can be measured directly. It is greater than 70 at the normal incidence.

Fig. 6 The dynamic change of optical induced anisotropy

Fig. 7 The comparison of azo dye SD1 and polyimide PIA3744 for TN-LCD

5. CONCLUSION

The photo-stable azo dyes, which exhibit the effect of the photo-induced molecular ordering, are promising candidates for the photo-induced alignment of liquid crystal. These materials, which require low exposure energy and power densities, have many attractive properties: negligible photo-chemical degradation, good adhesion to the glass substrates, thermal stability and sufficiently high holding ratio. In addition, the photo-polymerization of the azo dyes has further improved the thermal and UV stabilities, and voltage holding ratio. These results will be published elsewhere.

6. ACKNOWLEDGMENTS

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