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# Improvement of Liquid Crystal Alignment Using Novel Photo-Activators

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Photo-activator is a kind of additive that can improve the anchoring energy by attacking some of the bonds of polyimide (PI). Photo-activators were synthesized from the reaction of cyclohexanone oxime with three different anhydrides, respectively. Each activator generates different active radicals when irradiated. These fragmented and activated radicals are responsible for the liquid crystal (LC) alignment of PI film. The reactivity was confirmed through UV-Visible spectroscopy. All the three photo-activators had characteristic bimodal-shaped absorption peaks at 270~280 nm. The photo-fragmentation reactions were completed within 1 min of UV irradiation, which implies that the activators are highly reactive to UV light. The short reaction time is very useful for liquid crystal display (LCD) factory applications. The photo-activator using crotonic anhydride (CAP) showed the highest surface anchoring energy, of  $6.92 \times 10^{-5}$  J/m<sup>2</sup>, compared to that of the other activators and that obtained by rubbing methods;  $(1.11 \times 10^{-5}$  J/m<sup>2</sup>). This result was obtained due to resonance stabilization from the allyl radicals of CAP. The photo-activator using acetic anhydride (AAP) reached its maximum anchoring energy in less than 3 min of irradiation, which is the shortest optimum irradiation time. Considering the fact that this process does not require additional procedure and time, the photo-activators can be considered an innovate additive.

Keywords: Liquid Crystal Display, Photo-Activator, Photo-Alignment, Anchoring Energy.

# **1. INTRODUCTION**

Since the operation of LCD is based on LC alignment and its variation in the panel, the electro-optical properties of LCD panels are determined by the shape and characteristics of LC.<sup>1, 6–8, 11</sup> Improving the stability of LCD is an important factor because it preserves the superior electrooptical properties of the panel to maintain high definition and performance.<sup>1, 2, 6–8, 10, 11</sup> The uniform and stable LC alignment is a prerequisite and can be achieved by inducing anisotropy on the surface of the alignment layer. For this purpose, the rubbing method was widely used until recently.<sup>1, 2, 6–8, 10, 11</sup>

To overcome the limitations of mechanical rubbing, photo-alignment has been proposed as a non-contact alternative. The anisotropic intermolecular interactions between the alignment surfaces and LC in the photo-alignment method are strong enough to hold the LC on the alignment surfaces.<sup>3</sup> The photo-alignment methods are capable of minimizing the pixels accompanied by the high definition of LCD and the division of pixels necessary for a wide viewing angle. The commonly used photo-alignment

methods include photo-dimerization, photo-isomerization, and photo-decomposition.

Photo-activation is a new concept in the photo-alignment technique. To facilitate the photo-reactions, we use fast fragmentation reactions employing photo-activators. The reactive radicals can be used to orient the LC by the formation of alkyl groups on the PI surfaces. Because the manufacturing lead times are directly related with productivity in the LCD process, along UV irradiation time can be a limitation when compared with the rubbing method.<sup>4</sup> Therefore, in this paper, we propose novel photo-activators that can react faster and improve the anchoring energy compared to that obtained in the existing rubbing methods.

## 2. EXPERIMENTAL DETAILS

## 2.1. Synthesis of Photo-Activators

The three kinds of anhydride (0.011 mol), were respectively dissolved in  $30 \sim 50$  ml of hexane or dimethyl formamide (DMF), with cyclohexanone oxime (0.01 mol), followed by the addition of one drop of 57% perchloric acid. The mixture was stirred by shaking and left to stand for 24~28 hrs at 20~23 °C. At the same time,

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**Figure 1.** Synthetic schemes of photo-activators (AAP, HAP, and CAP) from cyclohexanone oxime.

the round-bottom flasks were respectively wrapped in aluminum foil several times. The mixture was then diluted with water and extracted with hexane, and the phase containing the product was separated, and removed with a small amount of water with 98.5% anhydrous sodium sulfate. Finally, the mixture was filtered using a filter paper to remove the precipitate. Thereafter, the solvent was removed at a temperature not exceeding  $25 \sim 30$  °C.

When synthesizing AAP, DMF was used as the solvent. The mixture was then diluted with ethyl acetate (EA) to 10 times the volume of DMF, and washed with water several times. Then, the solvent, EA, was removed at a temperature not exceeding  $25\sim30$  °C.<sup>5</sup> Figure 1 shows the three synthesis reactions. To compare the alignment properties according to the different structures of photoactivators, three anhydrides were selected.

#### 2.2. Fabrication of LC Cell

The photo-alignment solution was prepared in volume proportions of NMP:  $\gamma$ -butyrolactone: 2-butoxyethanol = 8:1:1. TN PI (JSR) (15 wt%) and photo-activator (5 wt%) were then added to the above solution. These were then coated on indium tin oxide (ITO) glass using a spin coater (Midas 1200T) for 10 s at 1000 rpm and 20 s at 3000 rpm. The coated substrates were pre-baked at 80 °C for 2 min to vaporize the solvent and then baked at 200 °C for 15 min.

To align the LC, 1000 W intensity LPUV (66921, Newport) and  $310 \sim 400$  nm polarizer (1026819, Newport) were used in parallel direction. After passing through the polarizer, the UV intensity was 1.5 mW/cm<sup>2</sup>. If the time required for the photo-alignment process exceeds 10 min, it cannot be shown as an improvement in terms of time. Hence, it was measured only up to 10 min.

Two substrates that were prepared in the same conditions were placed in parallel direction and sealed using a UV hardening agent (NOA 68) with 5.5  $\mu$ m spacer. The LC material (ML-0643,  $\Delta \varepsilon = 6.9$ ,  $\Delta n = 0.1023$ , Merck) mixed with a chiral dopant (R-811, Merck) was injected between the cell gap by the capillary method at 100 °C. Finally, all the edges of the cell were sealed with a UV hardener to prevent the leakage of LC.

#### 2.3. Measurement of Alignment Properties

The photo-activators were measured using a UV-Visible spectroscope (Agilent 8453) to analyze the reactivity as a function of UV irradiation time through observance of its absorbance change. A <sup>1</sup>H-NMR spectrometer (Bruker Biospin 400 MHz FT-NMR spectrometer) was used with d-CDCl<sub>3</sub>, and the data were compared with the graph of MestRe-C and Chemdraw program.

Contact angle (phoenix 300, SEO), anchoring energy, and pretilt angle measurements were carried out on the LC cells. For contact angle, the PI and photo-activator were dropped on a non-treated silicon wafer, or DI water was dropped on the wafer coated with PI.



Figure 2. IR spectra of AAP, HAP, and CAP.

Azimuthal anchoring energy was measured from the angular difference between the force of the dopant and photo-alignment.<sup>9, 12</sup> For pretilt angle, the polarizer rotation method and extended Jones matrix were used.<sup>1, 12</sup> The twist angle was set at 50°, and other conditions also used same LC with anchoring energy when calculated.

## 3. RESULTS AND DISCUSSION

The structure of all the activators were confirmed from the FT-IR and <sup>1</sup>H-NMR spectra; shown in Figures 2 and 3, respectively. In the IR spectra, the characteristic bonds of each activator were examined. In particular, C=O (1715 cm<sup>-1</sup>) and N-O (1515 cm<sup>-1</sup> and 1345 cm<sup>-1</sup>) commonly appeared for all the activators.

Since all the activators had similar structures, the spectra were compared for a common double peak: the cyclohexane ring ( $2.37 \sim 2.55$  ppm) in the <sup>1</sup>H-NMR spectrum. With integration, peaks corresponding to the characteristic allyl bond of CAP appeared at 5.88 ppm and 7.07 ppm at the same area. Further, HAP showed a relatively strong peak at 1.31~1.6 ppm due to its large hexyl group. The peak at 7.25 ppm is characteristic of CDCl<sub>3</sub>.

UV-Visible spectroscopy was performed to observe the absorbance changes, which indicate the reactivity of the photo-activators to UV light. As shown in Figure 4, the absorbance drastically declined within several seconds in all the spectra. This implies that the photo-activators



Figure 3. <sup>1</sup>H-NMR spectra of AAP, CAP, and HAP.





**Figure 4.** Changes in the UV-Vis spectra of AAP, HAP, and CAP after 5 min of UV irradiation.

were highly reactive to UV and disintegrated into radicals. The common bimodal peaks appeared at  $270 \sim 280$  nm and are indicated by dotted line. These peaks remained even after irradiation. The characteristic peak appeared due to the common N–O–C==O–C bond in the photoactivators. The photo-fragmentation of AAP and HAP completed within 1 min, while the CAP photo-fragmented in 5 min. Even when these activators were added to TN PI at 5 wt%, the photo-fragmentation reactions completed rapidly within 1 min. Interestingly, the photo-fragmentation of CAP required the longest irradiation time because of the relatively high stability of its allyl radicals.

During the experiment, we found the possibility that surface roughness can affect the anchoring energy. Thus,

 Table I.
 Maximum anchoring energy of photo-activators using TN PI with UV irradiation time.

Activator	Maximum anchoring energy $(\times 10^{-5} \text{ J/m}^2)$	Irradiation time (min)
AAP	3.46	3
HAP	3.68	8
CAP	6.92	10

we measured the contact angle. The contact angles for each photo-activator and TN PI on silicon wafer were measured to observe the changes on the surface of the PI film. The contact angle of DI water droplet on silicon wafer was 6.3104° and was used as a reference. The HAP demonstrated the largest angle, of 21.459°, while AAP had the smallest, contact angle of 8.765°. The large contact angle of HAP resulted from its characteristic hydrophobic hexyl groups.

When TN-PI-coated silicon wafers were used, after irradiation, all the contact angles remarkably increased due to hydro-phobization of the surface. Carbon dioxide gas, which generated from the irradiated photo-activators, evaporated from the surface of the PI films during photoirradiation. As a result, unsaturated C=C bonds were formed on the surface, which rendered the surface more hydrophobic and rough. We found the possibility that fragmented parts were located on the surface of the PI films and could affect the surface interactions with LC.

As shown in Table I and Figure 5, CAP showed the highest anchoring energy, of  $6.92 \times 10^{-5}$  J/m<sup>2</sup>, at 10 min of irradiation. This is outstanding result as compared to that obtained in the rubbing method,  $(1.11 \times 10^{-5} \text{ J/m}^2)$ . Moreover, shortening the irradiation time to 10 min is very

![](_page_3_Figure_7.jpeg)

Figure 5. Anchoring energy of photo-activators (AAP, HAP, and CAP).

meaningful and useful in terms of productivity and efficiency. AAP and HAP respectively showed their maximum anchoring forces at 3 min and 5 min of irradiation. The shortest irradiation time was achieved due to the methyl radicals of AAP that can react faster than the other activators. Allyl radicals are more stable than methyl radicals are; this indicates that prolonged irradiation makes the surface of the films more random.

Furthermore, all the cells had similar pretilt angles of  $8 \sim 9^\circ$ , which did not exceed 10°. When the cells were treated by the rubbing method before photo-alignment, the pretilt angles slightly decreased to  $7 \sim 9^\circ$ .

### 4. CONCLUSION

Three novel photo-activators were synthesized to improve the LC properties and were characterized by FT-IR, <sup>1</sup>H-NMR and UV-Vis. All the photo-activators demonstrated fast degradation and high reactivity. Moreover, the photo-activators exhibited similar pretilt angles of about  $8 \sim 9^{\circ}$  when mixed with TN PI. Further, the contact angle increased due to surface hydro-phobization through evaporation of carbon dioxide by UV irradiation. All the three activators achieved maximum anchoring energy within 10 min. The CAP-containing PI films showed the highest surface anchoring force, of  $6.92 \times 10^{-5}$  J/m<sup>2</sup>, which is around twice of that of the others. Considering the UV irradiation time, and the average figures of the usual photo-alignment process and rubbing process, the novel photo-activators can be efficient photo-alignment additives, sufficiently applicable to the LCD process.

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