

# DC Image Sticking in Liquid Crystal Displays Caused by Polyimide Anion Radicals

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## ABSTRACT

We investigated the anion radical effect from aromatic imide groups in polyimide alignment layers of liquid crystal cells by means of electron spin resonance and absorption measurements. We found anion radicals generated by ultra-violet or blue light irradiation shows a clear correlation to DC image sticking.

## 1 INTRODUCTION

Providing materials that enable a stable liquid crystal device is imperative for their use applications such as LCDs. We have worked to elucidate the mechanism of the deterioration of LCD qualities and to improve the light stability of LCD materials [1].

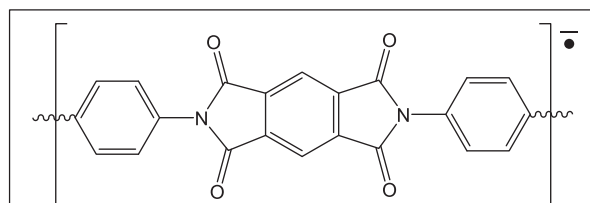
The LCD defects of area image sticking could be categorized into two types, a DC-type and an AC-type defect. Ionic impurities in liquid crystals or residual DCs are believed to be the origin of the DC-type defects of LCD for long time [2-4]. On the other hand the AC-type image sticking is said to arise from the misalignment of the LC molecules. There has been some controversy between DC type and AC type on the defect type of Flexoelectric effect [5-7]. We will restrict our subject in this study into a DC-type area image sticking. Most of the reports concerning the DC-type defects refer to adsorption and desorption of ions at the interface of LC and alignment layers or charge accumulation [4,8-13]. Most studies were conducted by investigating the kinetics of electrical signals response such as voltage, current, etc. Physical phenomena as well as the chemical species, which would be responsible for the defects of LCD, are not definitive and somewhat ambiguous.

We studied LCD image sticking phenomena by the combination method of photo-physics and photo-chemistry which are normally applied in molecular science [14-17]. We assumed a process on the occurrence of a defect of LCD by light irradiation listed as following [1]:

- (1) Photo-excitation on LC mixture and poly-imide (PI) alignment layer.
- (2) Generation of transient charges and species.
- (3) Charge accumulation, LC degradation, or insulation breakdown of PI.
- (4) Occurrence of display defects.

By direct photo-kinetics measurement of LC cells to detect a chemical intermediate, we have successfully

observed the anion radical of the aromatic imide chromophore (N,N'-Bis(4-alkylphenyl)-1,2,4,5-benzenetetracarboxylic 1,2:4,5-Diimide (**1**) as shown in Figure 1 [18]) in PI alignment layer by using electron spin resonance (ESR) and absorption spectroscopic techniques. To the best of our knowledge, this is the first study reporting the specific chemical intermediate in LC cells in explicit way. Our study revealed that the anion radical of (**1**) is one of a chemical species causing DC-type image sticking, and opens the new viewpoint to develop higher LCD quality.



**Fig. 1** Schematic chemical structure of the anion radical of the aromatic imide chromophore (**1**). The anion radical is formed by one electron reduction of the parent chromophore (**1**).

## 2 EXPERIMENT

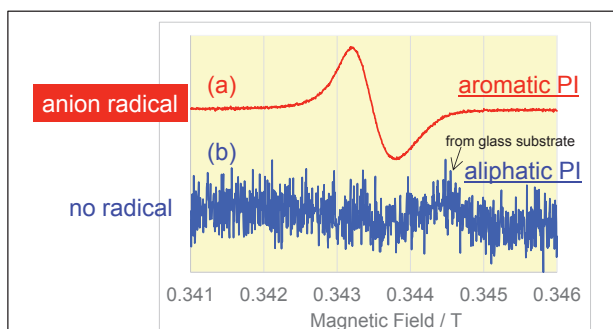
We prepared all LC and PI materials by ourselves basically. We also fabricated LC cells by ourselves for evaluation.

Image sticking were measured under the standard means of the LCD industrial field as described previously [19]. Conventional electron spin resonance (ESR) measurements were performed using a setup as reported elsewhere [13]. Imide anion signals from UV to near IR region were measured using UV-vis (JASCO V-750) spectrometer attached with absolute reflectance measurement unit (ARSV-916) with some modification. The parameters of anion radical of (**1**) and DC image sticking were obtained with employing the same LC cells.

### 3 RESULTS AND DISCUSSIONS

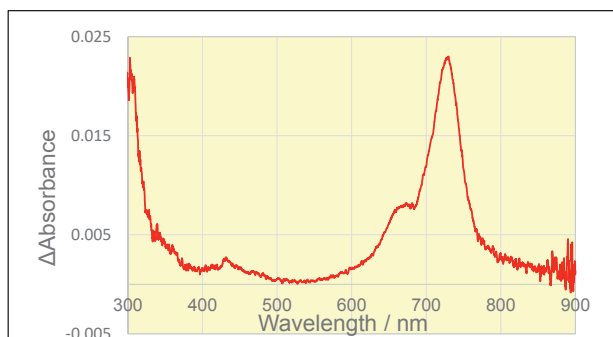
#### 3.1 ESR Measurements

Since electron spin resonance (ESR) is the spectroscopy detecting an unpaired electron in a material, it is a very powerful method to yield the information of radical species. Figure 2a shows the X-band (9 GHz) continuous wave (CW) ESR spectrum of anion radical of aromatic imide (1) in PI alignment layer after UV ( $\lambda > 320$  nm) irradiation. Although we performed the same experiments for aliphatic PI layer, only the signal from the glass substrate was observed as shown in Figure 2b for comparison. The broad radical signal was observed only for the PI including the chromophore (1). The signal intensities and the lifetimes drastically depend on the constituents of PI materials. The central band position of the anion radical of (1) in Figure 2a was observed at lower magnetic field relatively in comparison with that for normal aromatic hydrocarbons. The observed total line width was consistent with the previous report [20].



**Fig. 2** CW-ESR spectrum of anion radical of aromatic imide chromophore (1) formed by UV irradiation ( $\lambda > 320$  nm) in PI alignment layer (a). Only the signal from the glass substrate were observed for aliphatic PI (b).

The anion radical formation of (1) is probably due to the consequences of photo-induced electron transfer reactions with certain electron donors such as (di)amines, LC single compounds, chemical impurities, and so on [17], although we have not detected any signals from counter cation radicals yet presumably due to their short lifetimes.



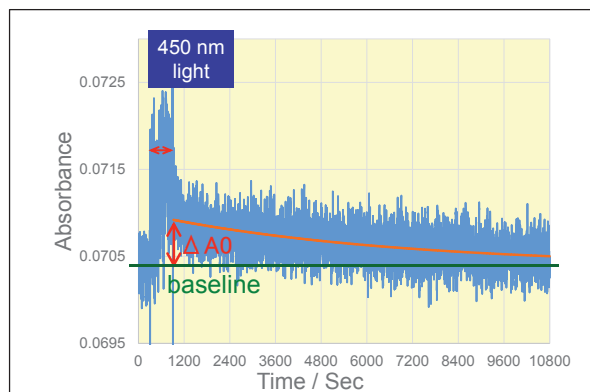
**Fig. 3** Absorption spectrum of anion radical of aromatic imide chromophore (1) formed by UV irradiation ( $\lambda > 320$  nm) in PI alignment layer.

#### 3.2 Absorption Spectra of Imide Anion Radical

Since we have detected only one broad band for aromatic PI in ESR experiments, we carried out absorption measurements. Figure 3 shows the absorption spectrum of anion radical of aromatic imide (1), which is obtained by taking the difference between the spectra before and after UV irradiation ( $\lambda > 320$  nm), in PI alignment layer. Although the observed absorption bands were slightly red-shifted, the spectral pattern on the whole of the region was clearly in accord with the one reported previously created by electrochemical reduction in polar solvent [18]. So we verified the formation of the anion radical of (1) upon UV irradiation.

#### 3.3 Time-Profile Measurements at 730 nm

Since the anion radical signals of (1) in PI alignment layer of LC cells were normally too weak to measure the absorption spectra in broad wavelength region as described in the previous section, we needed to perform time-profile measurements at 730 nm corresponding to the strongest absorption wavelength of the anion of (1).

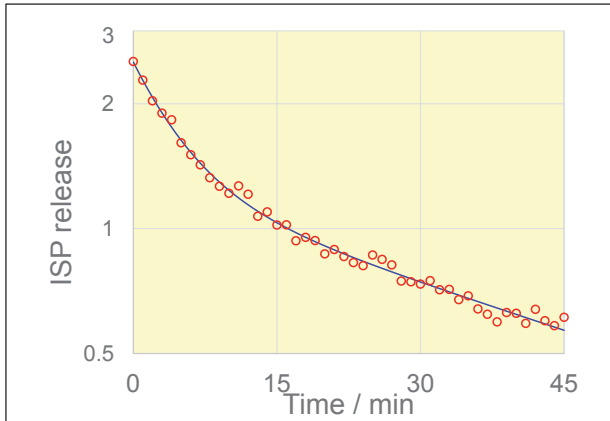


**Fig. 4** Typical time-profile of absorbance at 730 nm for a LC cell with a blue light ( $\lambda = 450$  nm).

Figure 4 shows the typical time-profile of the absorbance monitored at 730 nm. The absorbance surely increased with the irradiation of 450 nm blue light, and decreased gradually after the light was turned off. These observation correspond to the formation and decay of the anion radical of the chromophore (1), respectively. The generation of the anion radical in the PI layer even occurs with irradiating by blue light. A decay curve was analyzed by a single exponential function, and the initial intensities and the lifetimes of the anion radical signals were obtained for various LC cells. The lifetimes for most samples were around 100 minutes depending on both LC and PI materials.

#### 3.4 DC-ISP Release

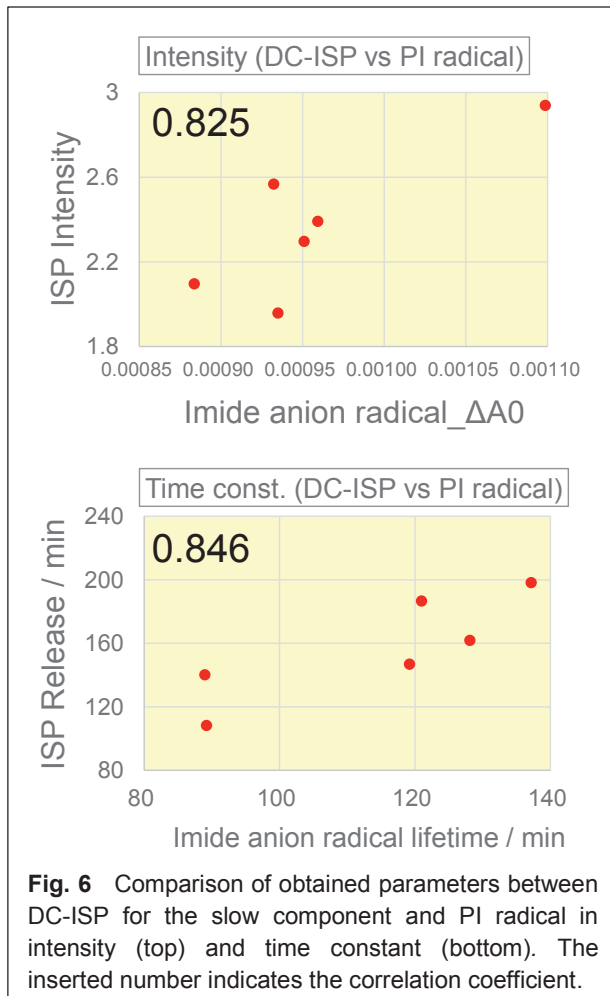
A time-profile of the release of image sticking for a FFS cell was measured at 30 Hz driving. The image sticking parameter (ISP) is defined by



**Fig. 5** Typical time-profile of ISP release, which shows double exponential decay. The slow component turned out to relate to the anion radical. The vertical axis is represented in logarithmic scale.

$$ISP = \frac{|Bs - Br|}{Br} \quad (\text{Eq. 1})$$

where  $Br$  is the average of luminance of the reference area and  $Bs$  is the average of luminance of the stress area [19]. The most time-profiles showed double exponential decay



**Fig. 6** Comparison of obtained parameters between DC-ISP for the slow component and PI radical in intensity (top) and time constant (bottom). The inserted number indicates the correlation coefficient.

curves typically as shown in Figure 5. The intensity ratio between the fast and slow components depended on LC cells, which is probably ascribed to several factors like the materials employed, an initial quality of each LC cell, and the extent of a kind of stress applied. When we had applied extensive stress on LC cells, a fast component having the time constant of a few minutes dominated the ISP and a slow component was covered almost completely. We assigned the slow component on the ISP release to the anion radical of (1) as described in the next section in detail. The fast component would presumably arise from mobile ions as reported in previous studies [4,8-13].

### 3.5 Correlation between Radical and DC-ISP

To confirm the contribution of the imide anion radical of (1) in PI to DC-ISP, we have checked the correlation between these parameters obtained with the cells of a FFS mode. Figure 6 shows the correlation between the slow component on DC image sticking and the anion radical in intensity (Figure 6 top) and in time constant (Figure 6 bottom) for some LC sells with different LC materials. Obviously we can see strong positive correlation between them, indicating that the anion radical of (1) is one of the causative chemical species of DC image sticking. The results of Student's t-test for correlation coefficients are less than 5 % for both intensity and time constant indicating the enough statistical significance. Our observation suggests that the LCD degradation especially in an initial stage would be triggered by the formation of the aromatic imide anion radical of (1) in PI layer.

## 4 CONCLUSIONS

In this paper we have reported the anion radical of the aromatic imide chromophore (1) in PI alignment layers in LC cells by means of ESR and absorption spectroscopies. We have found that the anion radical was formed by the light irradiation even with 450 nm blue light and have verified that the anion radical is one of the chemical species originating a DC-type image sticking.

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