Development of a Novel Azobenzene Diamine Compound for Photoalignment Film with High Transmittance

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Abstract A novel azobenzene compound for isomerization type photoalignment film has been developed. It has 4-aminophenethyl groups at both sides of azobenzene core. Photoalignment film (PAF) containing it shows high transmittance and almost the same alignment-ability compared with our conventional isomerization type PAF.

Keywords: High transmittance LCD, photo alignment film, photo isomerization, azobenzene compound

1. Introduction

Controlling the direction of liquid crystal (LC) molecules in specific alignment is essential for fabricating LC displays (LCDs). In the current industrial manufacturing process for LCDs, the most widely used technique to obtain uniform alignment of LC is rubbing of polyimide (PI) substrate. However, the rubbing alignment method has some disadvantages such as generation of static charge1 and dusts, damages arising from scratches on PI surface because PI surface and rubbing cloth are contacted directly in the rubbing method. It diminishes visual quality of assembled LCDs. Therefore, some non-contact alignment methods have been developed2-8. Among them, a photo-alignment method, in which alignment ability for LC is induced by irradiation of linear polarized ultra violet light (LPUV) to polymer substrate, has attracted much attention because of its high productivity and uniformity. The photo alignment film (PAF) is classified into three types: an isomerization type2-3, a dimerization type4 and a degradation type5, according to alignment-ability generation mechanism. Since it is frequently observed that the degradation type of PAF generates unnecessary over decomposed product during UV irradiation process8, the isomerization type of PAF is more preferable to simplify the manufacturing process of LCD, which can omit degradation materials removal steps, and we have put isomerization type PAF into practical production for fringe field switching (FFS) LCDs. PAF we developed (JNC-PAF) shows large anisotropy and high alignment-ability (Figure 1). Azobenzene diamine (1) has been used extensively as a monomer of polyamic acid (PAA) in isomerization type PAF11-14. However, it suffers from lower transmittance compared with the other types of PAF due to the absorption property of azobenzene structure. Generally, absorption spectrum of azobenzene is partly including visible region (380-780 nm)2-14. Therefore, PAF consists of azobenzene decreases transmittance in visible region of LCD device that isomerization type PAF is applied. Thus, increasing transmittance of isomerization type PAF leads to realize

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a higher performance LCD device. Here, we report a novel azobenzene diamine (2) and isomerization type PAF utilizing 2 as a monomer in it with high transmittance and alignment-ability\textsuperscript{15}.

2. Experiments

2.1 Materials

<General>
All commercial materials and solvents were used directly without further purification. All reactions were performed under N\textsubscript{2} atmosphere. Irradiation of LPUV was carried out by ML-501C/B (Ushio Co.) combined with a linear polarizing plate. Irradiation energy of LPUV was adjusted by controlling exposure time based on light intensity measured by actinography UIT-150 (Ushio Co.) and UVD-S365 (Ushio Co.).

<Procedure for preparation of PAA solution>
5,5’-(octane-1,8-diyl)-bis(isobenzofuran-1,3-dione) (3) (2.457 g, 6.05 mmol) was added to a solution of 2 (2.543 g, 6.05 mmol) in dry N-methyl-2-pyrrolidone (NMP) (65 g) at 10 °C. The reaction mixture was stirred at ambient temperature for 12 h. Then, 2-butoxyethanol (BE) (30 g) was added to the solution at ambient temperature. The solution was heated to 60 °C and stirred until the viscosity of the solution decreased to 35 mPa·s. After the reaction, the solution was cooled to ambient temperature and filtrated by a membrane filter (PTFE, pore: 0.20 µm). PAA was obtained as a 5% (w/w) solution in NMP/BE (PAA-B).

By means of the similar preparation method using 3 and 1, PAA-A was obtained.

<Typical procedure for preparation of PAF>
The PAA solution was spin-coated (thickness: approx. 100 nm) on a glass substrate. The coated substrate was irradiated by LPUV (2.0 J/cm\textsuperscript{2} at 365 nm) at normal incidence after a prebake process (60 °C × 80 sec.). Then, the substrate was post-baked (220 °C × 30 min.) to proceed thermal imidization reaction.

2.2. Characteristics

Transmittance of PAF formed on glass substrate was measured by UV-VIS absorption optophotometer (V-660, JASCO Co.). AC image sticking (AC IS) level\textsuperscript{16} and contrast ratio (CR) of test FFS-LCD cell, which has PAF, were measured in order to evaluate alignment ability of PAFs. The fabrication process of the test FFS-LCD is as follows; PAF is formed on glass substrate equipped with FFS electrodes, then, two substrates with identical PAF are bound with a certain cell gap using spacers (d=3.5 µm). The polarized direction of LPUV irradiated to each PAF is parallel. The cell is filled with a LC mixture ($\Delta n=0.10$, $\Delta\varepsilon=-3.7$) and the inlet is sealed with UV curable resin. AC IS level is defined as a change rate of transmittance in V-T curve before and after AC stress at the same driving voltage (Figure 3). CR is defined as a ratio of brightness in white state and black state. Additionally, VHR (voltage holding ratio) measurement of test IPS-LCD according to the Shimazakiet al.\textsuperscript{17} was conducted to confirm reliability of assembled LCD. Small AC IS level, large CR and high VHR value are demanded for high performance LCD device.

3. Results and discussion

3.1 Molecular design and synthesis of 2

The novel compound (2) is designed to have shifted $\lambda$ max to invisible region. Importantly, we can tailor ring substitution patterns of azobenzene derivatives to have preferable $\lambda$ max\textsuperscript{18}. The compound 2 has two 4-aminophenethyl groups at both para positions of azobenzene. HOMO-LUMO energy gap of 2 is predicted to be larger than that of 1, since conjugated system of the azobenzene unit in 2 is not directly connected to amino groups (Figure 4).

The synthesis of 2 is shown in scheme 1. First, N-mono(2,2,2-trifluoroacetyl)-1,2-bis(4-aminophenyl)ethane (4) was dimerized oxidatively using NaBO\textsubscript{3}(H\textsubscript{2}O)\textsubscript{4} and B(OH)\textsubscript{3} in AcOH\textsuperscript{19}. Subsequent detrifluoroacetylation\textsuperscript{20} of 5 under basic condition afforded 2 (77% yield in 2 steps).

The UV absorption spectra of 1 and 2 are shown in Figure 5. The $\lambda$ max wave length of 2 (334 nm) is shorter than that of 1 (375 nm), reflecting its larger HOMO-
LUMO energy gap. Further, the longest limitation of absorption region of 2 is less than 400 nm. PAF prepared from 2 is expected to have shorter wavelength absorption compared with PAF from 1.

3.2 Transmittance and alignment-ability

The compositions of PAA used in this study are shown in Table 1. The transmittance spectra of PAFs prepared from each PAA solution on glass substrate are shown in Figure 6. The average transmittance (380-600 nm) of PAF B which was prepared from PAA-B is improved compared with that of PAF A which was prepared from PAA-A (92% vs 86%). Additionally, the shoulder of transmittance curve of PAF A is around visible region of wavelength, 420 nm, on the other hand, that of PAF B is shorter than 400 nm, since \( \lambda_{\text{max}} \) of the azobenzene core of PAF B is shifted to shorter wave length. This result is in accordance with our molecular design concept. Application of PAF B is one of solutions to the coloring problem arising from use of azobenzene derivatives monomer when it is applied to high transmittance LCD.

Measurement results of CR and AC IS level are shown in Figure 7. AC IS level of test cell in which PAF B was applied is superior to that of PAF A, although PAF B shows a little worse CR than PAF A. Importantly, these results indicate that azobenzene core of compound 2 can isomerize and induce alignment-ability by irradiation of LPUV as well as 1 in PAA backbone. In addition, there was no significant difference between VHR values of two test cells (Figure 8). Overall, alignment-ability of PAF B is comparable in degree to that of PAF A.

3.2 Optimization of irradiation spectrum

At first, the high-pressure mercury lamp was used as the light source for LPUV in comparative experiments. The high-pressure mercury lamp shows sharp peaks at
303, 313, 365 nm in its emission spectrum, which is different to the $\lambda_{\text{max}}$ of 2 (334 nm). Therefore, it is assumed that the alignment-ability of the PAF B can be improved by optimizing the irradiation spectrum for the isomerization wavelength. For that purpose, LPUV light source, which was used for preparation of test FFS-cell using PAA B, was replaced with the metal halide lamp. The emission spectra of those two lamps are shown in Figure 9. The metal halide lamp generates wide spectrum and shows stronger intensity at around 334 nm. To compare alignment-ability dependence on light source, the AC IS level and CR of test FFS-LCD cells which are made from PAA B irradiated by different light source were evaluated. The results are shown in Figure 10 and 11. The CR increased by using the metal halide lamp, although the AC IS level was the same level as using high-pressure mercury lamp. It indicates that the isomerization efficiency which is directly related with alignment ability of 2 in the PAA-B is able to be enhanced by optimization of the light source.

4. Conclusion

In summary, an improvement in transmittance of isomerization type PAF has been archived. The newly developed PAF containing the novel azobenzene compound (2) with elongated structure has almost the same alignment-ability and reliability compared with conventional isomerization type PAF. Since 2 has large HOMO-LUMO energy gap, its wave length of $\lambda_{\text{max}}$ is shifted to the invisible region. The absorption property of PAF B prepared from 2 shows similar improved tendency of optical performance. A higher performance LCD device can be fabricated utilizing PAF B.

References

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