Improving Liquid Crystal Alignment Ability and UV Sensitivity in Photodecomposition Polyimide Film

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A liquid crystal alignment film with fewer processes capable of imparting anisotropy was developed using a polyimide, which utilized the cleavage of a cyclobutane ring by irradiation of polarized UV light at 254 nm. When an aromatic diamine with alkylene in the molecular center was used, an even methylene number of diamines showed superior liquid crystal alignment ability compared with diamines with an odd methylene number. Additionally, a diamine containing a molecular structure with a pre-imidized imide group adjoined to a cyclobutane ring was extremely effective in improving liquid crystal alignment ability and sensitivity to polarized UV light.

Keywords: FFS-mode, Photodecomposition polyimide, Liquid crystal alignment ability, UV sensitivity

1. Introduction

Liquid crystal displays (LCD) in smartphones, tablets and computers are not easily disarranged when pressed because many of them employ in-plane switching (IPS) and fringe-field switching (FFS) modes. Rubbing has been replaced by photoalignment as the method for treating alignment in liquid crystal alignment films used in LCD technology owing to the benefits of contrast and viewing angle. From the perspective of stability in backlight, and UV light when curing the sealant adhesive, we have been developing a photodecomposition polyimide capable of imparting anisotropy by irradiating polarized UV light at 254 nm [1-4]. If a process that grants anisotropy to the polyimide is shorter, then LCD manufacturing costs can be reduced. Therefore, a short-processed photodecomposition polyimide capable of imparting anisotropy has been developed by irradiating polarized UV light to cleave a cyclobutane ring with a specified direction

after coating a substrate with polyamic acid solution; subsequently, it is pre-baked at approximately 80 °C to remove the solvent, and then post-baked at approximately 230 °C and imidized [5]. Additionally, when a solution of partially imidized polyamic acid-polyimide copolymer was used before coating the substrate during the same processes, it was confirmed that a superior liquid crystal alignment ability could be imparted with a small dosage of irradiated polarized UV light [6]. In this study, we investigated the relationship between the molecular structure derived from diamine and liquid crystal alignment ability. We also investigated in detail the relationship between the rate of imidization in a solution state, liquid crystal alignment ability, and UV sensitivity.

2. Experimental

2.1. Materials

Scheme 1 shows cyclobutane-1,2,3,4-tetra-

Scheme 1. Synthesis of polyamic acids.

Scheme 2. Synthesis of polyamic acid-polyimide copolymers.

carboxylic dianhydride (CBDA),
 1,4-diaminobenzene (DB),
 1,2-bis(4-aminophenoxy)ethane (BAP2M),
 1,4-bis(4-aminophenoxy)butane (BAP4M),
 1,5-bis(4-aminophenoxy)pentane (BAP5M),
 1,6-bis(4-aminophenoxy)hexane (BAP6M),
 1,7-bis(4-aminophenoxy)heptane (BAP7M), and
 1,9-bis(4-aminophenoxy)nonane (BAP9M)
 purchased as the raw materials required to
 synthesize polyamic acid. Additionally, Scheme 2

shows Diamine A, which was synthesized as the
 raw material required to synthesize a polyamic
 acid-polyimide copolymer [6].

2.2. Synthesis of polyimide derivatives

Diamine was weighed in a four-necked flask
 equipped with a stirrer; subsequently,
N-methyl-2-pyrrolidone (NMP) was added and
 stirred to dissolve/disperse the diamine. The
 four-necked flask was immersed in a water bath

Fig. 1. FFS mode electrode-attached substrate.

and cooled, and CBDA was added while the solution was stirred. The leftover NMP was added to achieve a polymer concentration 10–12 wt%, and the solution was stirred at 23 °C for 3–8 h. When the total amount of diamine was 100 mol%, it was added to the solution to achieve a CBDA weight of 92–96 mol% and adjusted to achieve a viscosity of 130–370 mPa·s at a post-reaction solution temperature of 25 °C. The obtained solution was fractionated in a conical flask containing a stirring rod and added in the order of NMP and a butyl cellosolve (BCS) to achieve a polymer concentration of 4.5–5 wt% and BCS amount of 30 wt% and stirred for 2 h at 23 °C to obtain a polymer solution for evaluating the alignment of the liquid crystals. Using the experimental procedure above, we obtained seven types of polyamic acid solutions (Scheme 1) and four types of polyamic acid-polyimide copolymer solutions (Scheme 2).

2.3. Fabrication of liquid crystal cells

After filtering the polyamic acid and polyamic acid-polyimide copolymer solutions through a 1.0 μm filter, they were deposited onto an FFS mode electrode-attached glass substrate via spin coating. Subsequently, they were pre-baked on a hot plate at 70 °C for 90 s. Subsequently, polarized UV light was irradiated from a vertical direction onto the substrate using lithography equipment APL-L050121S1S-APW01 manufactured by Ushio Inc. through a 240LCF wavelength selector filter and a 254 nm-type polarizer. The plane of

polarization of the polarized UV light onto the substrate is inclined at 10° from the top IZO electrode (3rd layer), as shown in Fig. 1. The exposure dose of polarized UV light was measured using the UVD-S254SB luminometer developed by Ushio Inc. and configured to the range 250–1500 mJ/cm² at a wavelength of 254 nm. Subsequently, the substrate was post-baked for 30 min using an infrared oven set at 230 °C to obtain a substrate with a 100-nm-thick polyimide film with treated alignment. Additionally, to obtain a counter substrate, the same procedures above were applied to a glass substrate bearing a 4-μm-tall columnar spacer on which an ITO electrode was formed on the reverse side, resulting in a substrate with an alignment-treated polyimide film. These two polyimide film-attached substrates were paired to print a sealant with a shape that left behind a liquid crystal injection inlet on one side of a substrate with polyimide film. The sealant was then faced opposite to the polyimide film side of the other substrate so as to be parallel with the plane of polarization of the polarized UV light, where the two were pasted together and pressure bonded. Subsequently, the sealant was allowed to harden, thus producing an empty cell with a cell gap of 4 μm. The MLC-7026-100 liquid crystal (Negative LC manufactured by Merck & Co., Inc.) was injected into the empty cell through a low-pressure injection method, and the injection inlet was sealed, obtaining an FFS-mode liquid crystal cell. Subsequently, the obtained FFS-mode liquid crystal cell was heated at 120 °C for 30 min,

Fig. 2. Evaluation procedure of LC alignment ability.

left overnight at 23 °C, and then used to evaluate the liquid crystal alignment ability.

2.4. Evaluation of LC alignment ability

Using the FFS-mode liquid crystal cell, an AC voltage of 16 Vpp was applied for 96–168 h at a frequency of 30 Hz under a constant temperature of 70 °C. Subsequently, the space between the top IZO electrode (3rd layer) and the bottom IZO electrode (1st layer) of the liquid crystal cell was short-circuited and left overnight at 23 °C. Subsequently, the polarizer angle was measured by installing the liquid crystal cell between the two polarizers in a cross Nicols arrangement, and rotating the polarizer and analyzer while maintaining cross Nicols at each of the upper and lower regions of the curved electrode shown in Fig. 2. The amounts of change from the initial directional alignment of the liquid crystal's molecules, represented as $\Delta\theta_1$ and $\Delta\theta_2$, are

calculated using the procedures above, and added together to obtain $\Delta\theta$ —the index for the liquid crystal alignment ability [7].

3. Results and discussion

Table 1 shows the results of the measurements of $\Delta\theta$, after a liquid crystal cell made from polyamic acid was AC-driven for 168 h. When the exposure doses of polarized UV light were set to 600, 900, 1200, and 1500 mJ/cm², the lowest values of $\Delta\theta$ were observed when exposed to the dosage of 1500 mJ/cm² across all samples, and the liquid crystal alignment ability was shown to be greater than that of liquid crystal cells manufactured with a small exposure dosage. When comparing BAP2M through to BAP9M, which possess an alkylene chain in the molecular structure derived from diamine, a molecular structure with an even methylene number produced a significantly smaller $\Delta\theta$ value than a molecular

Table 1. Results of $\Delta\theta$ of polyamic acids after AC driving for 168 h.

Polyamic acid		$\Delta\theta$ (°)			
Tetracarboxylic anhydride	Diamine	Exposure dose of Polarized UV light (mJ/cm ²)			
		600	900	1200	1500
CBDA	DB	1.25	0.94	0.65	0.54
CBDA	BAP2M	0.42	0.25	0.13	0.13
CBDA	BAP4M	0.39	0.25	0.18	0.15
CBDA	BAP5M	0.94	0.62	0.54	0.51
CBDA	BAP6M	0.46	0.27	0.20	0.15
CBDA	BAP7M	2.01	1.05	0.61	0.44
CBDA	BAP9M	1.34	0.75	0.51	0.37

Table 2. Results of $\Delta\theta$ of polyamic acid-polyimide copolymers after AC driving for 96 h.

Polyamic acid-polyimide copolymer			$\Delta\theta$ (°)							
Tetracarboxylic anhydride	Diamine Diamine A : BAP4M = p : q	Imidization rate in solution (%)	Exposure dose of Polarized UV light (mJ/cm ²)							
			250	400	600	800	900	1000	1200	1500
CBDA	0 : 100	0	-	-	-	-	0.21	-	0.16	0.13
CBDA	10 : 90	9.7	-	-	-	-	-	-	0.20	0.16
CBDA	30 : 70	24.6	-	0.08	0.11	0.15	-	0.20	0.22	-
CBDA	40 : 60	30.3	0.03	0.03	0.07	0.24	-	-	-	-
CBDA	60 : 40	39.5	0.04	0.02	0.10	1.55	-	-	-	-

structure with an odd methylene number, confirming the even-odd effect. Factors related to the liquid crystal alignment ability of the liquid crystal alignment film in the IPS-mode LCD include viscoelastic behavior of the surface of the liquid crystal alignment film before and after AC driving, azimuthal anchoring energy, and uniaxial orientation of the polymer chain of the liquid crystal alignment film [7-11]. With these results alone, it is difficult to isolate the main factor that caused the even-odd effect. However, we inferred that the cause for the appearance of the even-odd effect in the $\Delta\theta$ value was that the principal polyimide chain was more likely to bend at least in the molecular structures of BAP2M through to BAP9M when the methylene number is odd, making the uniaxial orientation of the principal polyimide chain more likely to be disturbed.

Table 2 shows the results of the measurements of $\Delta\theta$, after a liquid crystal cell made from polyamic acid, or polyamic acid-polyimide copolymer was AC-driven for 96 h. The rate of imidization in the solution state was calculated from the mole ratio of CBDA and Diamine A. When observing the exposure-dose dependence of polarized UV light in $\Delta\theta$, the $\Delta\theta$ value is smallest for the samples p:q=0:100, 10:90 under dosage of 1500 mJ/cm². However, the $\Delta\theta$ value is smallest for the samples p:q=30:70, 40:60, 60:40 under dosage of 400 mJ/cm². From these results, it is considered that the sensitivity to polarized UV light is improved when the copolymerization ratio of Diamine A in the total amount of diamine is 30 mol% or more. It is known that a cyclobutane ring derived from CBDA is easily cleaved by irradiated polarized UV light when the imidization ratio in the two adjoining imide groups is higher [12]. Additionally, in this experimental process, as the

substrate was only heated up to 70 °C before being irradiated with polarized UV light after coating the substrate with a polyamic acid solution or polyamic acid-polyimide copolymer solution, it is considered that almost no imidization reaction would occur at this temperature. Therefore, we inferred that there is a threshold where UV light sensitivity is improved in this process in the range where the imidization rate is between 9.7% and 24.6% in the solution state. Additionally, the absolute value of $\Delta\theta$ is improved if the copolymerization ratio of Diamine A in the total amount of diamine is higher.

4. Conclusion

It is shown that an even methylene number in the molecular structures in BAP2M through to BAP9M resulted in a greater liquid crystal alignment ability. Additionally, increasing the copolymerization ratio of Diamine A in the total amount of diamine was effective in improving the liquid crystal alignment ability. Furthermore, a liquid crystal alignment film with excellent UV sensitivity was obtained when the copolymerization ratio of Diamine A was 30 mol% or more.

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