

Novel Photoinduced Alignment Material Consisting of Aromatic Polyamide for Liquid Crystal Display Device

by

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Abstract

Uniform and stable alignment of liquid crystal (LC) molecules was achieved on the films of aromatic polyamides exposed to the linearly polarized UV light, although these polyamides had no common photoreactive group such as cinnamoyl, coumarin or azo chromophore. This paper describes the LC photoalignment characteristics of the novel type of LC photoalignment materials consisting of aromatic polyamides. The polyamides with excellent sensitivity have been found, which could induce the uniform and unidirectional LC alignment by irradiation of linearly polarized 313 nm light with $0.2 \sim 0.5 \text{ J cm}^{-2}$.

Keywords: *Liquid crystal, Photoinduced alignment, Aromatic polyamide, Material for display device.*

1. Introduction

In liquid crystal display (LCD) device, the alignment control of liquid crystal (LC) molecules is one of the most important subjects to characterize the quality of a display. Usually, polyimide thin films formed on the substrate with electrode are mechanically rubbed with rayon or nylon rolls to achieve the unidirectional alignment of LCs in the rubbing direction. However, the rubbing method may cause static charge, dust or scratches on the LC cell, which lower the production yield or the quality of LCDs. The LC alignment using a linearly polarized ultraviolet (UV) light exposure, *i.e.* LC photo-alignment, is one of the favorable candidates to overcome the above problem. For the photoalignment materials, three kinds of polymer systems have been mainly proposed, which exhibited the anisotropic photoreaction on irradiation of linearly polarized UV light. The first of them is based on the photo-isomerization of polymers containing azobenzene¹⁾ or stilbene²⁾ moiety, and the second utilizes the anisotropic photo-dimerization of cinnamoyl or coumarin unit³⁾ which is covalently bonded to the polymer backbone. The third is based on the anisotropic photodegradation of polyimide films⁴⁾. However, the sensitivity of these

materials by UV irradiation and the stability of aligned LC in the cell are still not sufficient for practical applications as the LC photoalignment layers.

Thus, we have investigated the several polymers to find out a new material, which have enough sensitivity for UV light and thermal and optical stability of aligned LC in the cell. As the component of the polymer backbone, fully aromatic polyamides were selected because of their thermal stability and durability to LC molecules. Then, it was found unexpectedly that the irradiation of linearly polarized UV light on ordinary aromatic polyamide films induced the uniform and stable alignment of LC molecules, even if these polyamides had no typical photoreactive group such as cinnamoyl or azo chromophore.

This paper deals with the novel photo-induced LC alignment phenomenon of aromatic polyamide films, and the effect of chemical structure on their LC photoalignment characteristics, in order to find out the advantageous structure for enhancing LC alignment.

2. Experiments

2.1 Materials

Several aromatic polyamides, PA-1 ~ PA-25 listed in Tables 1 and 3, were prepared from the corresponding monomers according to the conventional direct

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polycondensation of the Higashi-Yamazaki method⁵⁾ or the polycondensation of diacid dichloride with diamine.

A typical procedure to prepare PA-1 is as follows: Under nitrogen atmosphere, 27.51 g of 4-(4'-aminophenoxy)benzoic acid (120.0 mmol) and 16.46 g of 3-aminobenzoic acid (120.0 mmol) were dissolved in 147 ml of N-methyl-2-pyrrolidinone (NMP). After adding 23.3 ml of pyridine and 75.5 ml of triphenyl phosphate, the solution was stirred at 100°C for 10 h. Then, the mixture was poured into excess amounts of methanol to precipitate the polymer, and the reprecipitation from its NMP solution into methanol was carried out to afford 33.28 g of the desired copolyamide, PA-1. The composition, x/y, of PA-1 was measured to be 50/50 mol% by ¹H-NMR spectrum.

2.2 Evaluation for photo-induced LC alignment

The evaluation of photoinduced LC alignment for the obtained polyamides was carried out as follows: The polymer films (thickness: ca. 1000 Å) were formed on glass substrates with ITO electrode by spin-coating of the polymer solutions (polymer content: 5 wt.%) in NMP/butyl cellosolve (4/1 wt. ratio), and the substrates were annealed at 180°C for 1 h. The linearly polarized UV light (254 or 313 nm) were exposed from the normal direction to the substrates, where a 700 W super-high pressure mercury lamp was used as UV light source, and a band-pass filter for each wavelength and a UV polarizer were employed. The irradiation intensity was measured with ORC UV light measure model MO-01 (detector UV-25, UV-31 or UV-35). Then, two of the substrates were composed in 6 μm cell gap by spherical spacers, whose directions of electric vectors of incident light

were parallel each other. In order to investigate the details of the uniformity of LC alignment, the nematic LC (ZLI-2293, Merck, clearing point: 85°C) was injected in the isotropic phase. The size of LC-cells is 30mm×30mm. The uniformity of LC photoalignment was estimated in terms of microscopic observation.

The alignment qualities were classified into 4 grades, A to D, as follows; A: uniform and unidirectional alignment without defect, B: unidirectional alignment with few defects, C: unidirectional alignment with a lot of defects, D: multi-domain alignment.

3. Results and discussion

3.1 LC photoalignment properties of polyamides with or without cinnamoyl group

At first, we attempted to investigate the aromatic polyamides containing an ordinary photoreactive chromophore, such as cinnamoyl component, in expectation to show the thermal stability of aligned LC. For this purpose, the comparison of the photoinduced LC alignment characteristics of aromatic polyamides with and without a cinnamoyl group was performed. Table 1 illustrates the chemical structures of three kinds of polyamides with their molecular weights, thermal stability and solubility. The obtained polyamides were soluble in aprotic polar solvents such as dimethylformamide (DMF) and N-methyl-2-pyrrolidinone (NMP) at r.t., as shown in Table 1. Also, they were thermally stable and observed no glass transition up to 350 °C in the measurement of differential scanning calorimetry (DSC).

Table 1 Structure and characterizations of polyamides.

Code	Structure	Molecular weight ^{a)}		Thermal behavior / °C		Solubility ^{a)}			
		Mn×10 ⁻³	Mw×10 ⁻³	Td(5%) ^{b)}	Td(10%) ^{b)}	CHCl ₃	THF	DMF	NMP
PA-1		30.8	55.9	428.7	466.0	×	×	○	○
PA-2		7.3	15.5	376.2	424.0	×	×	○	○
PA-3		4.0	9.4	373.4	431.1	×	×	○	○

a) Number-average molecular weight (Mn) and weight-average molecular weight (Mw), determined by gel permeation chromatography with polystyrene standards.

b) Temperatures of 5% and 10% weight loss, respectively, determined by thermogravimetry.

c) ○: soluble at r.t., ×: insoluble.

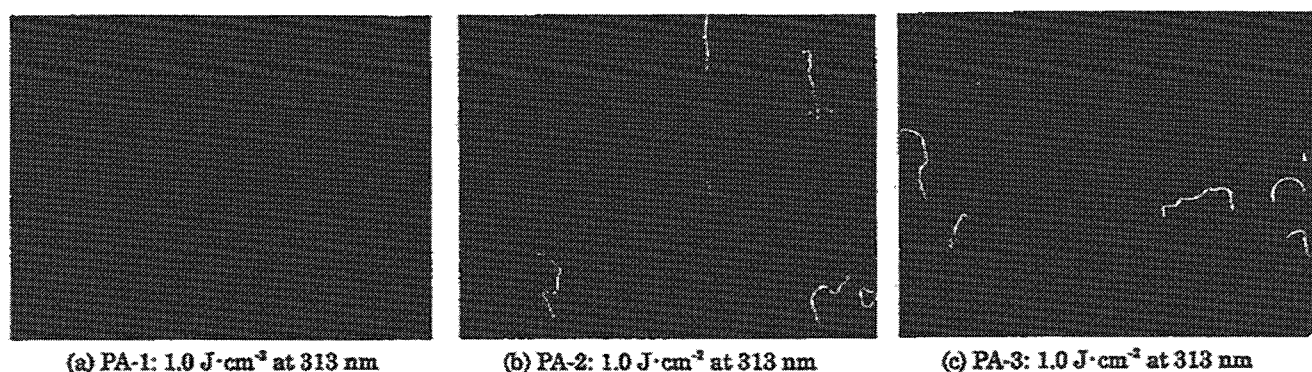


Fig. 1 Microphotographic texture of LC alignment on (a) PA-1, (b) PA-2 and (c) PA-3.

Table 2 Grade of LC alignment quality* as a function of exposed light energy.

Code	254nm			313nm					
	1.0	5.0	10 (J·cm ⁻²)	0.1	0.2	0.5	1.0	5.0	10 (J·cm ⁻²)
PA-1	B	A	A	C	B	A	A	A	A
PA-2	B	A	A	—	—	—	B	A	A
PA-3	B	B	—	—	—	—	B	B	A

When the films of PA-2 and PA-3 containing a cinnamoyl group were irradiated by polarized UV light with 5–10 J·cm⁻², the uniform LC alignment was induced on the film, the direction of which was perpendicular to the electric vector of linearly polarized light, as expected³. However, unexpectedly, the photoinduced LC alignment was also observed for the films of PA-1, although it had no typical photoreactive group such as cinnamoyl unit. In this case, the alignment was induced in the same direction as the cases of PA-2 and PA-3.

Figure 1 indicates the LC alignment on linearly polarized UV exposed films of PA-1, PA-2 and PA-3, where the irradiation energy is 1.0 J·cm⁻² at 313 nm. PA-1 showed the uniform and defect-free alignment in all area of the cell, however, the LC alignment with a few defects was observed for PA-2 and PA-3. The grade of LC alignment quality on these polyamide films was summarized in Table 2. Namely, it was found that PA-1 had the higher sensitivity than PA-2 and PA-3, and the defect-free alignment was achieved only at 0.5 J·cm⁻² in this system. Therefore, it was thought that the sensitivity of PA-1 was preferred over the conventional photoalignment materials.

In order to investigate what kind of photoreaction took place in this system, the UV-Vis absorption and the differences of the subtraction spectra between parallel and perpendicular

directions were measured for PA-1 and PA-3. As shown in Fig. 2 (c), the absorption spectra of PA-3 having cinnamoyl groups significantly changed after UV exposure. This behavior can be explained by the photo-dimerization and/or photo-isomerization of cinnamoyl units⁶. Furthermore, Fig. 2 (d) indicates the optical anisotropy in the PA-3 film was obviously induced by irradiating polarized UV light. However, in the case of PA-1 having no typical photoreactive group, the spectra changed little and the optical anisotropy was also little induced as shown in Fig. 2 (a) and (b), although LC molecules could sensitively receive the some change of the film surface induced by polarized light exposure. These results suggested that the photoreaction took place at only the surface of polyamide film, therefore, the spectral change could not be detected. Thus, such a optically small change on the film surface greatly affects the alignment behavior of liquid crystals, but makes the detailed analysis extremely difficult.

In general, the photo-Fries rearrangement and photo-oxidative degradation are well known as the photoreactions of aromatic polyamide⁷. In fact, when KaptonTM (fully aromatic polyimide) and nylon-6,6 (fully aliphatic polyamide) were exposed by linearly polarized light of 254, 313 or 365 nm much enough, the uniform alignment of liquid crystals could never be induced. Since the photo-Fries rearrangement does not occur for polyimide and aliphatic poly-

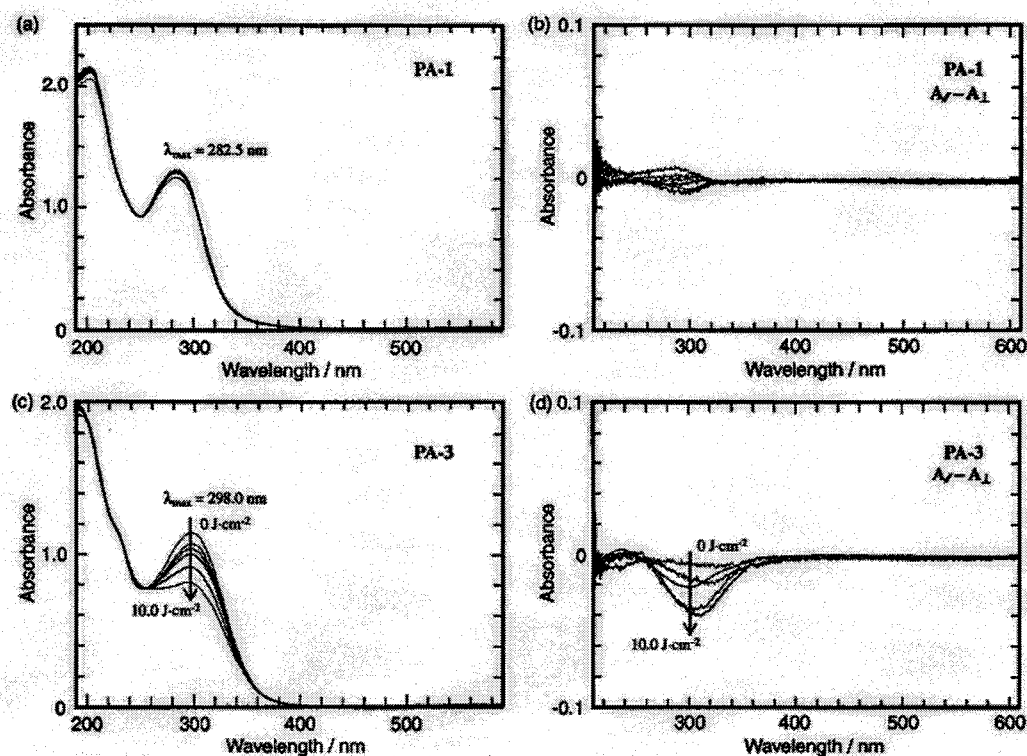


Fig. 2 Changes of the UV-Vis absorption spectra and the subtraction spectra of PA-1 and PA-3 films with the increase of the irradiation energy of linearly polarized ultraviolet light at 313 nm: (a) and (c), the ultraviolet absorption spectra of PA-1 and PA-3 films, respectively; (b) and (d), the subtraction spectra ($A_{//} - A_{\perp}$) of PA-1 and PA-3, respectively, when exposing 0, 0.5, 1.0, 2.0, 5.0, 10.0 $\text{J}\cdot\text{cm}^{-2}$ of linearly polarized light at 313 nm.

amide, the present photoinduced LC alignment phenomena of aromatic polyamides possibly must be related to the photo-Fries rearrangement. But it was difficult to understand that only the photo-Fries rearrangement induced the LC alignment, according to the result that PA-1 was pretty more sensitive than PA-2 and PA-3. In order to confirm the validity of our consideration described above, we investigated the photoalignment properties in the case that the film of PA-1 was irradiated with polarized UV light in vacuum and nitrogen. As a result, the uniformity of LC alignment was remarkably lowered as compared with the case that it was irradiated in air. Furthermore, temperature dependence of the sensitivity of LC photoalignment was observed, namely, higher temperature induced higher sensitivity. These results suggest that the photoreaction of this system is accelerated in the presence of oxygen, and that the anisotropic photo-oxidation mainly induces such a LC alignment.

3.2 Effect of chemical structure of polyamide on the LC photoalignment property

In order to reveal the effect of chemical structure on the LC photoalignment characteristics, several kinds of aromatic

polyamides were prepared and the LC alignment qualities after UV exposure were evaluated by the same procedure. For the preparation of LC alignment layer on the glass substrates, polymers should be soluble in an organic solvent. However, most aromatic polyamides, for example, poly(*p*-phenylene terephthalamide), tend to be insoluble. Therefore, this evaluation will be limited to compare some aromatic polyamides. The copolymerizations sometimes afford soluble polyamides, although the homopolymers composed of each monomer unit are insoluble. In addition, the introduction of *m*-phenylene unit in the main-chain or substituents on the phenylene ring is generally effective to improve the solubility. Thus, taking these into account, we prepared the aromatic polyamides PA-4 ~ PA-25 listed in Table 3, which exhibited the good solubility in DMF and NMP.

As shown in Table 3, slight modifications of main-chain structures of these aromatic polyamides largely alter the sensitivity to the exposed UV light for the uniform LC photoalignment. For example, the direction of amide unit influenced the sensitivity for the LC alignment as compared PA-6 with PA-7, and as compared PA-14 with PA-15. 4,4'-Diphenyl ether unit seemed to be effective to improve the

Table 3 Grade of LC alignment quality after exposure of light of $1.0 \text{ J} \cdot \text{cm}^{-2}$.

Code	Structure	254nm	313nm
PA-4		B	B
PA-5		A	A
PA-6		B	B
PA-7		B	A
PA-8		A	A
PA-9		B	B
PA-10		B	B
PA-11		A	C
PA-12		C	B
PA-13		C	B
PA-14		B	C
PA-15		C	A
PA-16		B	B
PA-17		A	A
PA-18		B	A
PA-19		A	A
PA-20		B	A
PA-21		B	A
PA-22		B	C
PA-23		A	C
PA-24		D	D
PA-25		D	D

sensitivity, but 3,4'-diphenyl ether and 4,4'-diphenyl thioether units decreased the sensitivity as compared among the polyamides PA-6 ~ PA-12. In addition, the introduction of

benzophenone unit greatly decreased the sensitivity (PA-13), although this unit has been known to accelerate a photoreaction as a sensitizer⁸⁾. Probably, in this case, a large absorption coefficient of benzophenone unit would prevent the anisotropic photoreaction to achieve the LC alignment, like as the cinnamoyl unit in PA-2 and PA-3.

On the other hand, the introduction of cyclohexane unit (PA-11) and 2,2-diphenylpropane unit (PA-22 and PA-23) influenced the wavelength of the exposed UV light, namely for these polyamides the irradiation of 254 nm light was more effective to obtain the uniform LC alignment than that of 313 nm light. By the irradiation of 365 nm light, all of these polyamides did not induce the LC alignment. Furthermore, in the cases of PA-24 and PA-25 containing aliphatic chain, LC photoalignment or anisotropy on film surface was not induced at all. From these results, the backbone structure consisted of phenylene or cyclohexane ring with amide linkage is thought to be essential to obtain the LC photoalignment.

In these investigations, it was also noticed that the introduction of methyl groups on the phenylene rings improved the sensitivity as a LC photoalignment layer. For examples, Table 4 shows the differences of grades of LC photoalignment as a function of irradiation energy for the polyamides consisted of similar structures with and without methyl group. In particular, PA-19 exhibited the highest sensitivity among these polyamides investigated in this study, where $200 \text{ mJ} \cdot \text{cm}^{-2}$ of 313 nm light was enough to induce the uniform and unidirectional LC alignment. Such a high sensitivity with a wide range of wavelength is useful for a development of the practical photoalignment layer. However, the structural tendency to exhibit such an excellent LC photoalignment ability has not yet been clarified as well as the photoalignment mechanism, which is now in progress.

Table 4 Grade of LC alignment quality of polyamides as a function of exposed light energy.

Code	Structure	254nm			313nm				
		0.25	5.0	1.0 ($\text{J} \cdot \text{cm}^{-2}$)	0.1	0.2	0.25	0.5	1.0 ($\text{J} \cdot \text{cm}^{-2}$)
PA-16		C	C	B	—	—	C	B	B
PA-17		B	A	A	—	—	B	B	A
PA-18		B	B	B	—	—	B	A	A
PA-19		B	A	A	B	A	A	A	A

3.3 Stability of LC photoalignment on polyamide films

To examine the stability of the obtained LC photoalignment on PA-1, the following investigations were carried out. After aging the LC cell at 120°C for 6 hours, the LC alignment quality was observed under a polarized optical microscope. Secondly, after irradiating visible ray to the LC cell for 40 hours using Xe lamp, the wavelength of which is longer than 300 nm, the similar observation was carried out. As a result, the uniformity of LC alignment was completely held in the both cases. Therefore, it was confirmed that the thermal and optical stability of LC alignment was very high in this photoalignment system.

4. Conclusion

The new class of LC photoalignment materials consisted of aromatic polyamides were found out, which gave the uniform and stable LC alignment by the irradiation of linearly polarized UV light, although they had no typical photoreactive group such as cinnamoyl moiety. The effects of chemical structures of aromatic polyamides on the LC photoalignment ability were also investigated. It was revealed that the sensitivity and the suitable wavelength for the LC photoalignment greatly depended on the main-chain structure, and that some polyamides exhibited the excellent sensitivity to wide wavelength of UV exposure. In particular, 4,4'-diphenyl ether and 3,3'-dimethyl-4,4'-diphenylmethane units in the main chain were very effective for the improvement of the sensitivity in this LC photoalignment system. Otherwise, the introduction of light-absorbing groups such as benzophenone or cinnamoyl group, which possessed a large absorption coefficient, decreased the sensitivity. In addition, the induced LC alignment exhibited high thermal and optical stability enough for practical applications.

We believe, these phenomena of the aromatic polymers must be classified into a new category of photoinduced alignment materials and bring about the practical application due to their high sensitivity and stability of LC alignment.

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