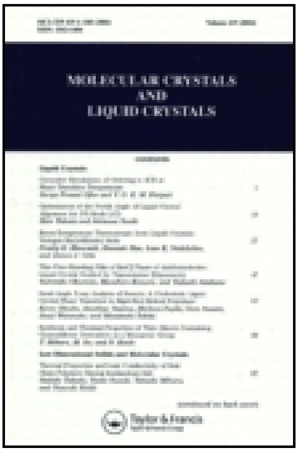

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Photoreaction and Photoalignment Behavior of Novel Polyamic-Ester Derivative Containing a Photo-Crosslinkable Group

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This paper describes the photoalignment behavior of liquid crystals (LCs) on a photoalignment layer containing a new photosensitive polyamic-ester derivative (PAE) under several fabricating conditions. Irradiating PAE films with a linearly polarized (LP) UV light at temperatures over 160°C dramatically accelerated the photoreaction and photoinduced optical anisotropy. Furthermore, an improvement of the LC alignment quality was observed on PAE films when films were irradiated over 160°C.

Keywords Photoalignment; photoreactive polymer

Introduction

To fabricate liquid crystal displays (LCDs), a uniform LC alignment is required. Mechanical rubbing of a polyimide film, which is the most common process for the LC alignment in LCD industries, involves some problems such as non-uniformity in large size LC alignment, and the presence of dust and scratches upon rubbing. To overcome these problems, photoinduced alignment of nematic LCs has recently received much attention because it is the most promising candidate to realize large scale LC alignment without any defects. This technique is based on the anisotropic photoreaction of the alignment films by the use of polarized light [1]. Additionally, the key technologies of photoalignment involve photosensitive materials and fabrication process. High photosensitivity of alignment materials is strongly required in order to put photoalignment to mass-production.

A wide range of photoreactive polymers including azobenzene-containing compounds [2], polyvinyl cinnamate derivatives [3], and polyimides (PIs) [4] have been investigated for the LC photoalignment layer. Among them, PI showed best properties as the LC alignment layer, exhibiting good alignment ability and electric properties, and high thermal stability. However, large exposure energy is generally required in order to achieve sufficient LC

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alignment quality on PI films. This is because the photoinduced optical anisotropy of PI films is based on the photodegradation of the materials.

In contrast, polyvinyl polymers containing photo-crosslinkable side groups, such as cinnamate, coumarin, and chalcone moieties show high photosensitivity compared to photodecomposition of PI, and can be used as the LC photoalignment layer using linearly polarized (LP) UV light [5]. Additionally, photosensitive PIs with photo-crosslinkable side groups have been synthesized [6,7].

In this paper, we report on a new photoreactive polyamic-ester derivative containing *p*-phenylene diacrylate for LC photoalignment layer. The influence of the exposure condition on the photoreactivity and LC alignment behavior were investigated.

Experimental

Materials and Characterization

Chemical structure of PAE is depicted in Fig. 1. PAE was prepared by the poly-condensation reaction with 2,2-bis (4-aminophenyl)-hexafluoropropane, *p*-phenylene diacrylic acid and 2,5-bis (ethoxycarbonyl) terephthalic acid chloride. Polymer composition was measured by ^{1}H-NMR. The number average molecular weight (M_n) of PAE determined by the gel-permeation chromatography was about 31,000. Heat imidization reaction of PAE detected using thermo-gravimetric analysis started around 240°C.

Photoreaction

Three fabrication processes for fabricating the alignment layer are illustrated in Figs. 2a–c. To prepare the alignment layer, PAE was dissolved in N-Methyl-2-pyrrolidone (NMP)/ Butyl-cellosolve (BCS) mixed solvent and then spin-coated onto quartz or ITO glass substrates. After pre-baking at 80°C for 5 min, film thickness was controlled at 30-50 nm. The photoreaction was performed under several conditions (Fig. 2) using an ultrahigh-pressure Hg lamp equipped with Glan-Taylor polarizing prisms and cut filter under 290 nm to obtain LPUV light with an intensity of 14 mWcm^{-1} at 365 nm. The degree of photoreaction was estimated by monitoring the decrease in absorbance at 340 nm using UV spectroscopy.

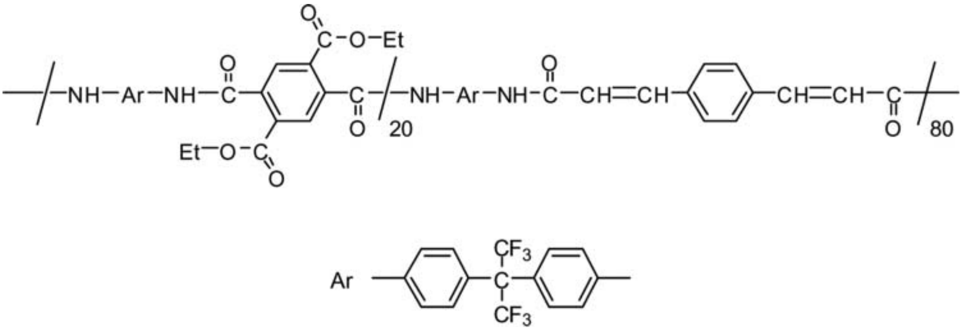

Figure 1. Chemical structure of PAE.

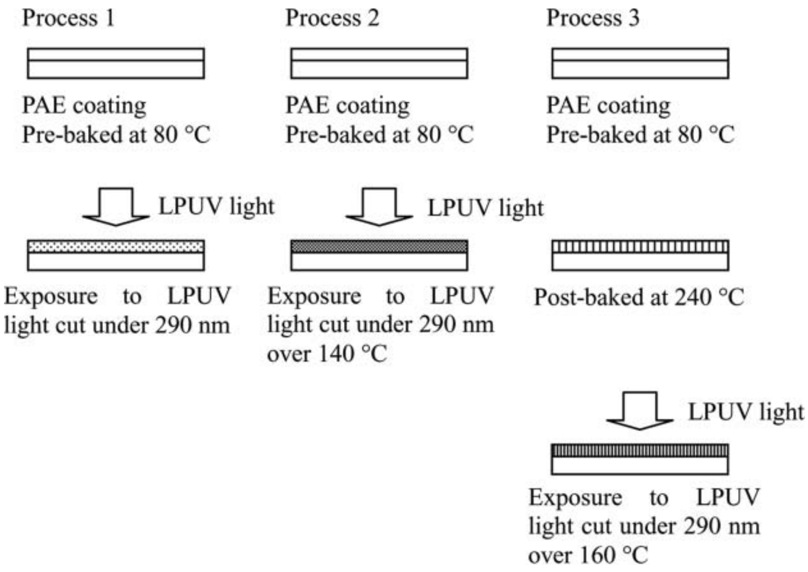

Figure 2. Three types of fabrication process for the photoalignment layer.

The photoinduced optical anisotropy, ΔA, which was evaluated using the polarization absorption spectra, is expressed as eq. 1.

$$\Delta \mathrm{A} = \mathrm{A}_{||} - \mathrm{A}_{\perp} \tag{1}$$

where $\mathrm{A}_{||}$ and $\mathrm{A}_{\perp}$ are the absorbances parallel and perpendicular to the polarization (**E**) of the LPUV light.

To evaluate an LC alignment behavior, an anti-parallel LC cell was fabricated using two photoreacted films. The 12.5 μm-thick LC cell was filled with a nematic LC mixture (ZLI-4792: Merck Japan, Ti = 102°C) doped with 0.1 wt% of dichroic dye of DB14 (Ardrich) at 110°C and then cooled slowly. The alignment direction of the dye was measured by a polarized UV-vis spectroscopy and LC alignment quality was evaluated by polarized optical microscopy (POM) observation of the LC cell.

Results and Discussion

Photoreaction

Figure 3a shows the changes in the absorption spectrum of a PAE film upon irradiating with LPUV light at rt. (*Process 1*). It reveals that the absorption around 340 nm gradually decreases when exposure dose increases. A new absorption band around 270 nm appeared, which increased until the exposure dose was 3.0 J/cm^2. After additional exposure over 3.0 J/ cm^2, absorption band around 250 nm increased. Additionally, two isosbectic points at 300 nm and 270 nm were observed, which appeared during the course of irradiation with varying exposure dose. This indicates that the [2+2] photodimerization of the *p*-phenylene diacrylate group firstly proceeds from one side and then to the other side of the diacrylate group stepwise as exposure dose increased.

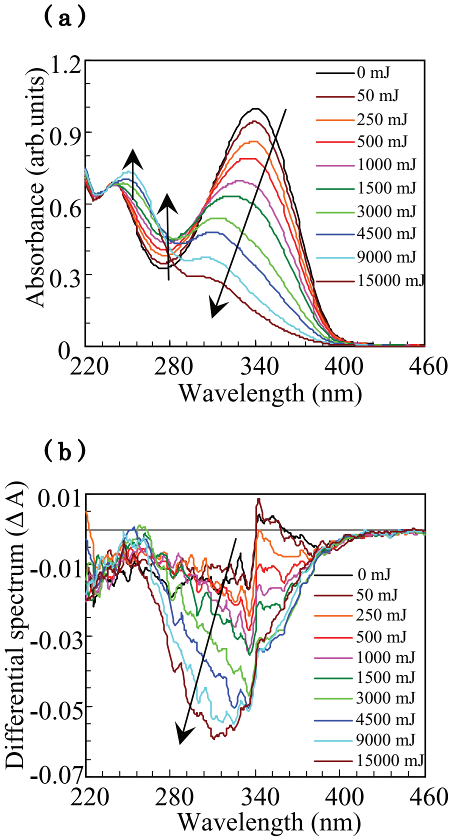

Figure 3. (a) Absorption spectral changes of PAE film irradiated with UV light at rt. as a function of exposure dose. (b) Differential spectrum after LPUV irradiation at rt. as a function of exposure dose.

Since the photoreaction of the *p*-phenylene diacrylate group occurred axis-selectively [8], a photoinduced negative optical anisotropy of the film appeared as shown in Fig. 3b. In the early stage of photoreaction until film was irradiated 3.0 J/ cm^2, the negative dichroism was observed around 340 nm. Further exposure to the film led to blue shift of ΔA that also might be due to the stepwise photoreaction of *p*-phenylene diacrylate group.

The effect of irradiation temperature on photoreaction behavior of PAE was investigated by irradiating films under heating at various temperatures. Figure 4 plots the degree of the photoreaction and induced ΔA as a function of exposure temperature when films were irradiated for 250 mJ/cm^2 (*Process 2*). The photoreaction of PAE accelerated drastically when the irradiation temperature was 140°C and then proceeded gradually as exposure temperature increased. The estimated photosensitivity improves by 8 times at 240°C, as compared to that at rt.. Since the mobility of PAE main chain improves at elevated temperatures, exposing at elevated temperatures accelerate the photodimerization of PAE film. Furthermore, the photoinduced negative ΔA at 340 nm increased when the irradiation temperature increased, especially at 180°C and higher. Figure 5 shows the photoinduced ΔA as a function of exposure dose when films were irradiated at 240°C. Negative optical anisotropy was observed around 340 nm and maximum ΔA increased from −0.0097 at rt. to −0.0323 at 240°C. It should be mentioned that the maximum ΔA was obtained when

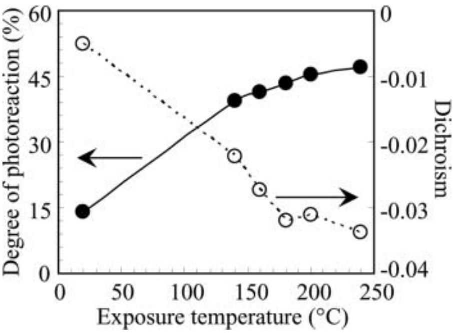

Figure 4. The degree of photoreaction of the *p*-phenylene diacrylate group (black circles), and dichroism ($A_\parallel - A_\perp$) at 340 nm after LPUV irradiation as a function of exposure dose (white circles).

the exposure energy was 250 mJ/cm^2 due to the accelerated photoreaction. The increased ΔA could be attributed to the thermally enhanced molecular reorientation [5]. Similar increase in the photoinduced optical anisotropy was observed other photo-crosslinkable polymer films [9]. Additionally, further exposure to the film led to blue shift and spread of ΔA wavelength band as in the case of photoreaction at rt., that might be attributed to the stepwise photoreaction of *p*-phenylene diacrylate group.

LC Alignment

The LC alignment behavior on PAE film was evaluated using parallel LC cells. Figures 6a–c display the POM image of LC cells using alignment layer of PAE irradiated with 50 mJ/cm^2, 250 mJ/cm^2 and 500 mJ/cm^2 at rt., respectively (*Process 1*). Because irradiating a PAE film with LPUV at rt. leads to negative optical anisotropy due to the axis-selective [2+2] photodimerization, LC alignment direction is perpendicular to **E** of LPUV light. This is caused by a decreased interaction between LC molecules and photo-crosslinked main chain parallel to **E**. However, LC alignment obtained using alignment layer fabricated by process 1 was not uniform regardless of the exposure energy as shown in Figs. 6a–c, where the disclination lines were observed.

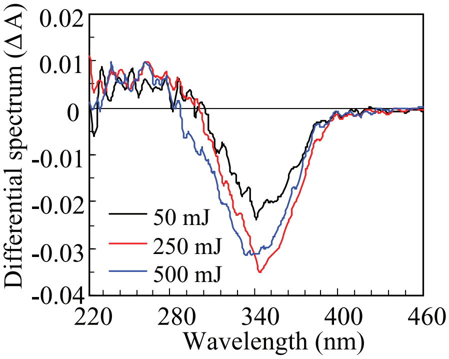

Figure 5. Differential spectrum after LPUV irradiation at 240°C as a function of exposure dose.

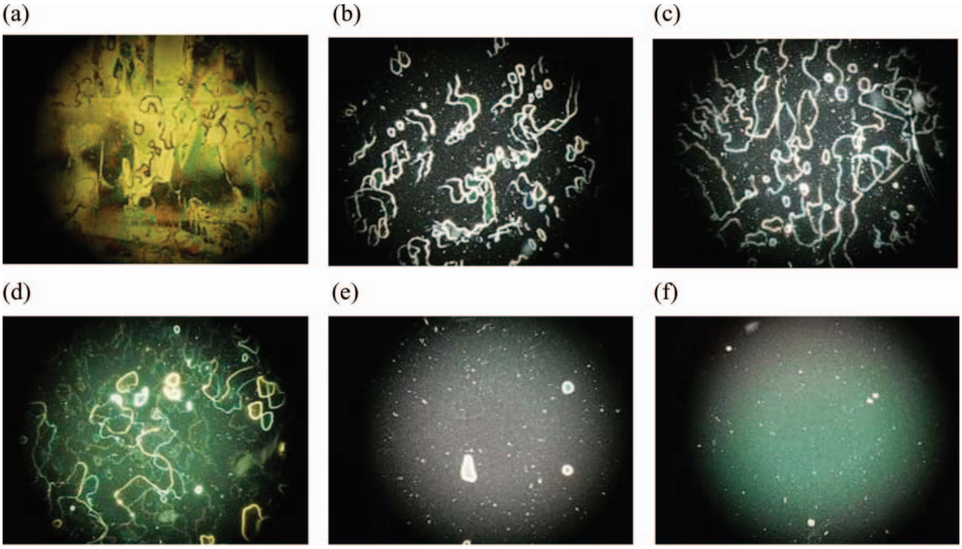

Figure 6. POM photograph of LC cells using PAE film irradiated with LPUV at different exposure doses, (a) PAE irradiated for 50 mJ/cm^2 at rt., (b) PAE irradiated for 250 mJ/cm^2 at rt., (c) PAE irradiated for 500 mJ/cm^2 at rt. (d) PAE irradiated for 50 mJ/cm^2 at 240°C, (e) PAE irradiated for 250 mJ/cm^2 at 240°C, (f) PAE irradiated for 500 mJ/cm^2 at 240°C.

In contrast, improved LC alignment quality was observed when using alignment layers fabricated by process 2. Figures 6d–f display the POM image of LC cells using alignment layer of PAE irradiated with 50 mJ/cm^2, 250 mJ/cm^2 and 500 mJ/cm^2 at 240°C respectively. Especially, uniform LC alignment was obtained when the PAE film was irradiated for 500 mJ/cm^2 (Fig. 6f). Additionally, influence of the exposure temperature on the LC alignment quality was investigated. Figures 7a-c display POM photographs of LC cells when the PAE films were exposed for 250 mJ/cm^2 at various temperatures. The LC alignment became uniform when the exposure temperature was higher than 160°C. This also suggests that the increased photoinduced optical anisotropy of PAE films accompanied by the increased photoreactivity at elevated temperatures played an important role in the improvement of the LC alignment quality. However, uniform LC alignment was not achieved

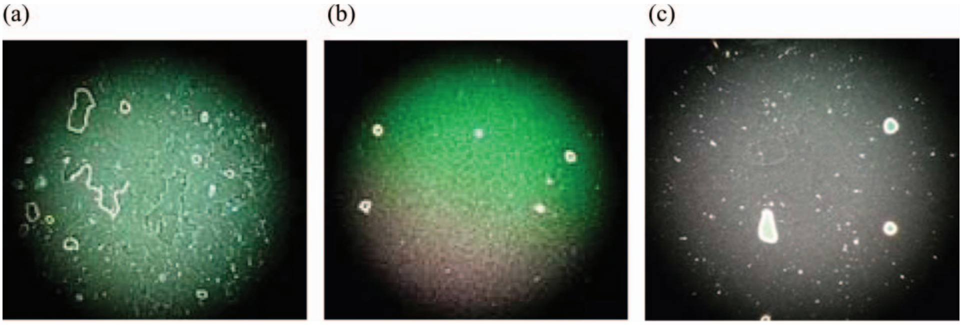

Figure 7. POM photograph of LC cells using PAE film irradiated for 250 mJ/cm^2 at different temperatures, (a) PAE irradiated at 140°C, (b) PAE irradiated at 160°C, (c) PAE irradiated at 240°C.

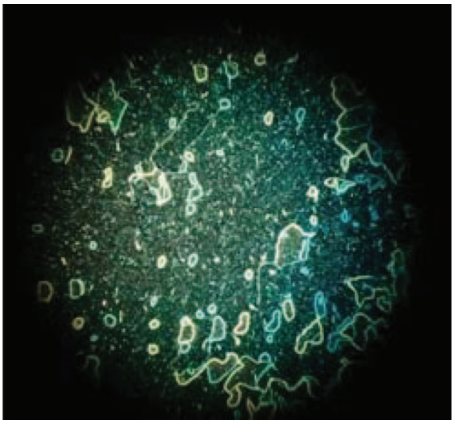

Figure 8. POM photograph of LC cells using PAE irradiated for 250 mJ/cm^2 at 160°C after post-baked at 240°C.

when the PAE films were exposed to LPUV with 250 mJ/cm^2 at 160°C after the imidization reaction (*Process 3*) as shown in Fig. 8. This is because that process 3 could not increase the photoinduced optical anisotropy.

Conclusion

In summary, a new photo-crosslinkable polyamic-ester derivative containing *p*-phenylene diacrylate for photoalignment layer was developed. Since the degree of photoreaction of PAE film was controlled by varying the exposure temperature of the film, an improvement of LC alignment quality using low irradiation dose of LPUV was achieved due to the improved mobility of polymer chain before the imidization reaction. This result indicates that this irradiation process can be very useful for improvement of the throughput of alignment process in mass production of photo-crosslinkable high performance polymers.

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