Liquid Crystal Alignment Properties on Polyamide Films Bearing a Phenylenediacryloyl Moiety in the Main Chain

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Soluble photosensitive polyamide, which has a photoreactive 1,4-phenylenediacryloyl (PDA) moiety in the main chain with biphenyl side groups, was synthesized with high molecular weights. The polymer produced high quality films through conventional spin-casting and dry processing with relatively good thermal stability. The photochemical reactions of the polyamide in the films were investigated by UV-Vis spectroscopy; the polymer in the film demonstrated excellent photoreactivity to UV light. Linearly polarized ultra-violet light (LPUVL) irradiation induced anisotropic reorientations of the polymer chains in the film as a result of direction-selective photoreaction of the PDA moieties. The polyamide thin films were found to have excellent unidirectional orientation ability as a result of photo-exposure with LPUVL; the direction-selective photoreaction of the PDA moiety in the main chains induced alignment of nematic liquid-crystals (LCs) on the surface. The pretilt behaviors of the LC molecules on the LPUVL irradiated film surfaces were controlled by both the exposure dose of LPUVL and the annealing temperature.

Keywords LCD; nematic liquid-crystal; phenyleneacryloyl moiety; photosensitive polyamide; pretilt angle; unidirection alignment

Introduction

Several photoinduced liquid-crystal (LC) alignment concepts have been of wide interest in both academia and the LC flat panel display (LCD) device industry because these concepts can be used to prepare a rubbing-free LC alignment layer for LCD devices. Some photoinduced LC alignment concepts have been reported [1–8] and reviewed [9,10]. The photoinduced LC alignment concepts using linearly polarized ultraviolet light (LPUVL) irradiation can be categorized into three classes of materials according to the photochemical reaction responsible for the photoalignment, as follows [9,10].

The first class involves azobenzene dye containing materials [1–3,9,10]. Azobenzene dyes undergo photoinduced isomerization from the *trans*-isomer to the *cis*-isomer and the reverse. LC alignment behavior using LPUVL irradiation on polymer surfaces containing

azobenzene side groups has been reported by several research groups. The second class includes materials containing [2+2] photodimerizable moieties such as cinnamate [4], styrylpyridine [5], chalcone [6], and coumarin [7] moieties. The photodimerization generates crosslinks in the polymer via cyclobutane ring formation, leading to insolubilization of the polymer film. Poly(vinyl cinnamate) (PVCi), a representative photoalignment material, and its derivatives in films have been reported to align LC molecules in the direction perpendicular to the electric vector of the LPUVL when exposed to LPUVL. The third class includes LC alignment induced by photodegradation caused by LPUVL irradiation [8]. Hasegawa and coworkers reported photoalignment of polyimide by LPUVL at 257 nm irradiation [11].

Nevertheless, these approaches still are not feasible for mass production of LCDs due to several unsolved problems, including low thermal stability, low anchoring energy, low pretilt angle, limited processability with ultraviolet (UV) light exposure, and the lack of availability of suitable materials. Thus, there remains a significant challenge to delivering high performance materials suitable for LPUVL induced LC aligning films.

In this study, a novel photosensitive polyamide containing the *p*-phenylenediacryloyl (PDA) moiety in the main chain with biphenyl groups as a side chain was synthesized by solution polymerization, which exhibited good solubility and processability. The photoreactivity and photoalignment characteristics of the polyamide films were investigated using spectroscopic methods. In addition, the alignment behavior and pretilt angle of LC molecules were investigated on the polymer films treated with various LPUVL exposures. In addition, the pretilt angles of LC molecules on the annealed films also were investigated.

Experimental

Materials and Measurements

3,5-diminobezoic acid, *p*-toluenesulfonic acid monohydrate (TsOH), di-tert-butylcarbonate [(Boc)$_2$], *N,N*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 1,4-phenylenediacrylic acid, triphenylphospine (TPP), pyridine (Py), and 4-phenylphenol were purchased from Aldrich Company and used without purification. N-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure and under nitrogen atmosphere.

^{1}H NMR spectra were obtained at room temperature with a Bruker AM 300 spectrometer. For the synthesized polyamide, the inherent viscosity was measured in NMP at 25°C using an Ubbelohde suspended level capillary viscometer by a method described in the literature [12]. The glass transition temperature (T_g) and degradation temperature (T_d) of each film were measured using a differential scanning calorimeter (DSC) (model DSC 220CU, Seiko, Japan) and a thermogravimeter (model TGA7, Perkin-Elmer, USA), respectively. UV-visible absorption spectra were obtained as a function of the exposure dose using a Hewlett-Packard 8453 spectrophotometer with or without a dichroic polarizer (Oriel, model 27320). Optical phase retardation was measured using an optical set up consisting of a photoelastic modulator (PEM) (Hinds Instruments, model PEM90), as described elsewhere [13]. The LC alignment in the cell was examined by measuring the absorption of the linearly polarized He-Ne laser beam (632.8 nm wavelength) as a function of the rotational angle of the cell, thereby allowing the construction of polar diagrams. For these measurements, the LC cell was installed perpendicular to the incident laser beam direction. The pretilt angle, α, of the LC molecules was measured using a crystal rotation apparatus.

Synthesis of 3,5-di-tert-butoxycarbonylaminobenzoic Acid

A solution of [(Boc)$_2$] (5.2 g, 23.9 mmol) and dried NMP (10 ml) was added dropwise to a stirred solution of 3,5-diaminobezoic acid (1.65 g, 10.9 mmol) and dried NMP (40 ml) at 0°C under nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature, poured into 500 ml of cold water, and extracted with ethyl acetate. The combined organic layer was dried over magnesium sulfate, followed by evaporation and drying for 24 h at 80°C under vacuum. The solid obtained was recrystallized from ethyl acetate and hexane to produce a 94% yield of 3,5-di-*tert*-butoxycarbonylaminobenzoic acid (3.6 g, 10.2 mmol). ^{1}H NMR (DMSO-d6, δ): 12.81 (s, 1H, -O*H*), 9.48 (s, 2H, -N*H*-), 7.87 (t, 1H, Ar*H*), 7.70 (d, 2H, Ar*H*), 1.48 (s, 18H, -C(C*H*$_3$)$_3$).

Synthesis of Biphenyl-3,5-diaminobenzoate

3,5-Di-*tert*-butoxycarbonylaminobenzoic acid (3.5 g, 9.9 mmol), 4-phenylphenol (2.09 g, 11.9 mmol), and DCC (2.5 g, 11.9 mmol) were dissolved in dry methylene chloride along with DMAP catalyst (0.15 g, 1.23 mmol), and the reactant mixture was stirred at ambient temperature for 12 h. After stirring, the reaction solution was filtered and the solvent removed by rotary evaporation. The residue was purified using column chromatography [SiO$_2$, MC/ethyl acetate (45:1 in volume)] to yield biphenyl-3,5-di-tert-butoxycarbonylaminobenzoate (4.1 g, 8.1 mmol, yield 82%). ^{1}H NMR (DMSO-d6, δ): 9.84 (s, 2H, -N*H*), 8.36–8.27 (m, 3H, -Ar*H*-), 8.05–7.96 (m, 4H, -Ar*H*-), 7.80–7.75 (m, 2H, -Ar*H*-), 7.69–7.63 (m, 3H, -Ar*H*-), 1.79 (s, 18H, -C(C*H*$_3$)$_3$). The obtained biphenyl-3,5-di-tert-butoxycarbonylaminobenzoate (4.0 g, 7.9 mmol) and TsOH (33.2 g, 0.17 mol) were dissolved in dry NMP and THF. The reaction mixture was stirred at room temperature for 24 h, poured into 500 ml of cold water, and extracted with ethyl acetate three times. The combined organic layer was dried over magnesium sulfate, followed by rotary evaporation. The residue was purified using column chromatography [SiO$_2$, ethyl acetate/hexane (3:2 in volume)] to yield biphenyl-3,5-diaminobenzoate (BP). The monomer was purified to polymerization grade by recrystallization from ethanol (1.88 g, 6.2 mmol, yield 78%). ^{1}H NMR (DMSO-d6, δ): 7.74–7.67 (m, 3H, -Ar*H*-), 7.51–7.46 (m, 2H, -Ar*H*-), 7.40–7.38 (m, 2H, -Ar*H*-), 7.31–7.28 (m, 2H, -Ar*H*-), 6.65 (d, 2H, -Ar*H*), 6.17 (s, 1H, -Ar*H*), 5.34 (s, 4H, -N*H*$_2$).

Synthesis of Poly[oxy(4-biphenyl-3,5-benzoate)oxy-1,4-phenylenediacryloyl] (PBP-PDA)

PBP-PDA was synthesized from the direct polycondensation of PDA and BP as follows [14]. A mixture of 1,4-phenylenediacrylic acid (1.08 g, 4.9 mmol), BP (1.50 g, 4.9 mmol), 40 mL of NMP/Py (v/v 5 4/1), and TPP (2.59 g, 9.9 mmol) was stirred at room temperature under nitrogen for 2 h. The reaction mixture was heated to 100°C for an additional 12 h. Thereafter, the reaction solution was poured into hot methanol with vigorous stirring, producing PBP-PDA polyamide as a powder precipitate with 92% yield.

LC Cell Fabrication

The polyamide solution was spin-cast onto indium tin oxide (ITO) glasses for optical retardation and LC cell assembly. The polyamide films adhered to glass slides were irradiated by LPUVL at various exposure doses. Here, the LPUVL exposure was conducted with the film positioned with a tilt angle of 0°, where the tilt angle is the angle between the film

plane and the propagation plane of the LPUVL. Some of the polyamide films irradiated with LPUVL at 1.5 J/cm^2 were thermally annealed in a cumulative step manner from room temperature to 150°C using the regime, 35°C/10 min, 60°C/10 min, 90°C/10 min, 120°C/10 min, and 150°C/10 min, and then they were cooled back to room temperature. LC cell assemblies were constructed from the annealed films. Using these polymer films, LC cells were assembled and filled with 4-pentyl-4-biphenylcarbonitrile (5CB) containing 1.0 wt% of a dichroic dye (Disperse Blue 1) using a capillary technique.

Results and Discussion

Photoreactive PBP-PDA polyamide containing a PDA moiety in the main chain was synthesized using PDA and BP monomer from direct polycondensation, modifying the procedure reported previously (see Scheme 1) [14]. The obtained polymer was characterized by ^{1}H-NMR. Figure 1 shows the ^{1}H NMR spectrum of the synthesized PBP-PDA polyamide. The BP monomer had its characteristic proton peak of amine groups at 5.34 ppm while the PBP-PDA polyamide did not reveal any proton peak originating from the amine groups of the BP monomer and showed a characteristic amide proton peak at 10.61. Measured inherent viscosity of the polyamide in NMP at 25°C using an Ubbelhode-type viscometer was 1.21 dL/g. Considering the ^{1}H NMR spectra and inherent viscosity, it can be inferred that the polyamide was successfully synthesized with a reasonably high molecular weight. Glass transition (T_g) and degradation temperatures (T_d) were measured using DSC and TGA. Investigation of PBP-PDA revealed a 283°C T_d and a 113°C T_g.
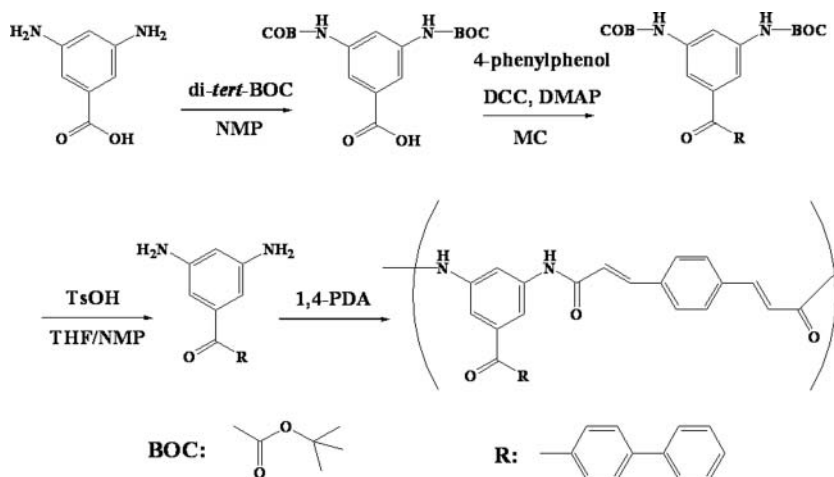
Scheme 1. Synthetic scheme and chemical structure of the BP monomers and the photoreactive PBP-PDA polyamide.

Figure 2 shows UV-vis spectra measured from PBP-PDA polyamide films irradiated with UV light at various exposure doses. The PBP-PDA polymer exhibited an absorption maximum at 353 nm ($= \lambda_{max}$). This UV absorption might originate from the photosensitive PDA group in the polymer. The absorption peak intensity at $\lambda_{max} = 353$ nm decreased drastically with increasing exposure dose up to 6.0 J/cm^2 and then remained nearly constant with further increasing exposure doses. The absorption peak $\lambda_{max} = 353$ shifted to 348 nm at 0.25 J/cm^2, and blue-shift increased with increasing exposure dose. This might be due
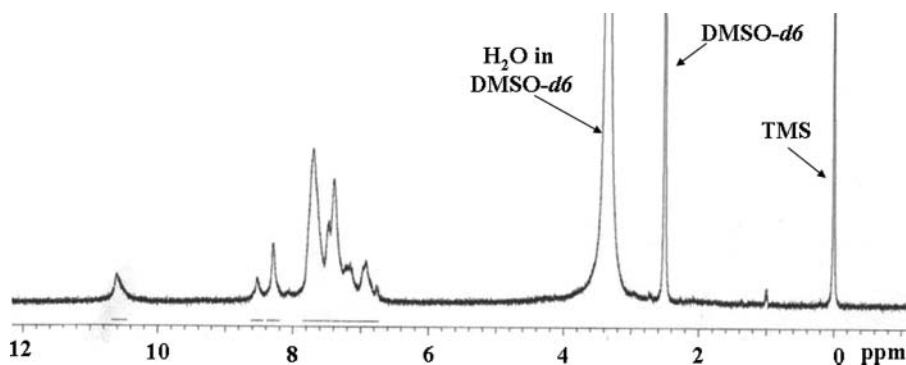
Figure 1. ^{1}H NMR spectrum of the photoreactive PBP-PDA polyamide.

to photoreactions, such as [2+2] cycloaddition and/or *trans-cis* isomerization of the PDA chromophore in the films.

Egerton et al. reported that the PDA moiety in the polymer films undergoes photodimerization through a hydrolysis experiment of UV irradiated PPDA, which is a polyester of PDA with 1,4-bis(2-hydroxyethoxy)cyclohexane [15]. Vargas et al. [17] and Ikeda et al. [18] also reported that polymer films containing the PDA moiety in the main chain become crosslinked photochemically via [2+2] cycloaddition. Moreover, the absorption peak $\lambda_{max} = 353$ shift to 348 nm was attributed to shortening of conjugation length as a result of the reaction of the double bond converting into a cyclobutane ring.

For the polymer films exposed to the linearly polarized UV light, the dichroic ratio was monitored as a function of UV-exposure dose. Here, the dichroic ratio is estimated from the following equation:

$$\text{Dichroic ratio} = (A_\perp - A_{//})/(A_\perp + A_{//}) \tag{1}$$

where $A_\perp$ and $A_{//}$ are the absorbances of the polymer film at λ_{max} as measured by a linearly polarized probing UV light perpendicular to and parallel with, respectively, the electric vector of LPUVL used in the exposure. As shown in Fig. 3(A), PBP-PDA polyamide films exposed to LPUVL consistently revealed a positive dichroic ratio for 0.0–3.0 J/cm^2.
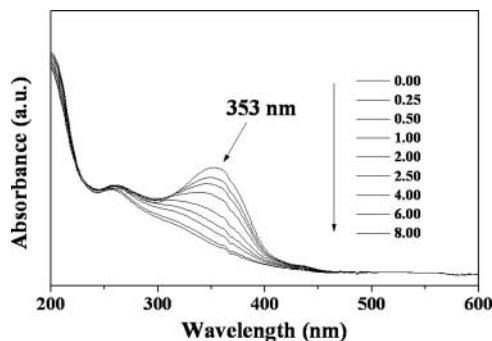

Figure 2. UV spectra of photoreactive PBP-PDA polymer films irradiated with unpolarized UV light (260–380 nm) at varying exposure doses.
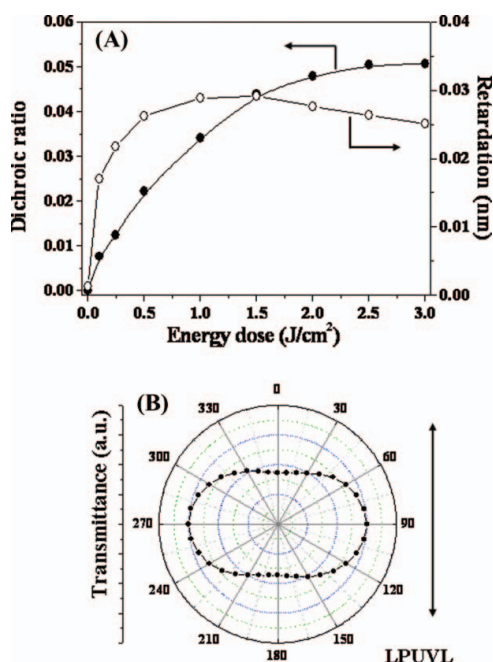
Figure 3. (A) Dichroic ratios and retardation measured from PBP-PDA films irradiated by LPUVL with various exposure energies; (a) dichroic ratio (•), (b) retardation (○). (B) Polar diagram of transmitted light intensity [(in-plane birefringence) × (phase)] taken from the optical phase retardation measurement of a PPDA-C4BZ film irradiated with LPUVL at 1.5 J/cm^2 as a function of the angle of rotation of the film.

The dichroic ratio increased gradually with increasing exposure dose to reach 0.051 at 3.0 J/cm^2. The obtained dichroic ratio values are similar to those of previous reported results [20–22]. This indicates that PDA moieties located parallel to the electric vector of LPUVL were consumed more rapidly than those positioned perpendicularly. The direction-selective consumptions of PDA moieties might take place via [2+2] cyclo-addition. In addition, the low values of dichroic ratio might come from the remaining disordered PDA moieties in the polymer film.

Optical birefringence was measured using a PEM system with a He-Ne laser (632.8 nm). Fig. 3(B) shows a representative polar diagram of the transmittance with respect to angle of rotation of LPUVL-exposed PBP-PDA films from optical phase-retardation measurements, which was measured for the polyamide film irradiated with LPUVL at 1.0 J/cm^2. The optical axis of the LPUVL-exposed polyamide film in this study lie along the 90–270° direction, which is at an angle of 90° with respect to the polarization direction of LPUVL (0–180°). The measured optical birefringences are plotted in Fig. 3(A) as a function of exposure dose. For the PBP-PDA film, the optical birefringence increased sharply with increasing exposure dose, reaching 0.026 at 0.5 J/cm^2. Then, the birefringence remained constant with further increase of exposure dose. Here, the UV-exposed polyamide films exhibited a positive in-plane birefringence generated by exposure to LPUVL. The positive birefringence might come from two major factors. (1) Polymer chains reorientation induced by selective [2+2] photodimerization by LPUVL irradiation. This means that photodimerization of PDA moieties in the main chain requires movement of the polymer chains [13].

Thus, the reorientation of polymer chains causes positive birefringence of LPUVL irradiated films [5]. (2) The remaining *trans*-isomer of the PDA moieties has a relatively large polarization along its longer axis compared to its products from direction-selective photoreaction. This means that PDA moieties located parallel to the electric vector of the LPUVL were consumed selectively by [2+2] photodimerization. As a result of photoreaction, the PDA moieties positioned perpendicular to the electric vector of LPUVL remained greater than the parallel ones. It turns out that such remaining *trans*-isomers of PDA moieties contribute to creation of positive birefringence. Together these factors may contribute to the generation of positive birefringence. However, these factors may compete against each other, meaning, the overall birefringence may be controlled by one predominant factor or a combination of these factors.

Polar diagrams constructed from the LC cells fabricated with LPUVL irradiated films of the PBP-PDA polyamide were measured. The polar diagram of LCs on the surface of the PBP-PDA polyamide at 1.5 J/cm^2 with LPUVL exposed films is shown in Fig. 4. Similar polar diagrams were obtained for other LC cells fabricated from the polyamide films irradiated with LPUVL at various exposure doses. For an LC cell with a PBP-PDA polyamide film, the LC molecules were aligned along the perpendicular direction with respect to the electric vector of LPUVL, independent of LPUVL exposure dose. These results suggest that the selective photoreaction by LPUVL irradiation induced preferential LC molecule alignment. Using polyesters containing a PDA moiety in the main chains, Kawatsuki et al. [19] and Song et al. [20] reported that the perpendicular LC alignment was caused by the interaction between the LCs and the nonphotoreacted PDA group that was perpendicular to the electric vector of LPUVL. Considering these results, it is reasonable that the LC alignment is primarily controlled by the remaining PDA moiety after LPUVL exposure. And, polymer chain reorientation by selective photodimerization may be a minor factor in LC alignment.

Pretilt angle for the PBP-PDA polyamide was measured for the LC cells fabricated from films irradiated with various exposure doses of LPUVL by means of the crystal rotation method. For PBP-PDA polyamide films, pretilt angles varied in the range of 1.8–4.2°, depending on the exposure dose of LPUVL irradiation. As shown in Fig. 5(A), pretilt
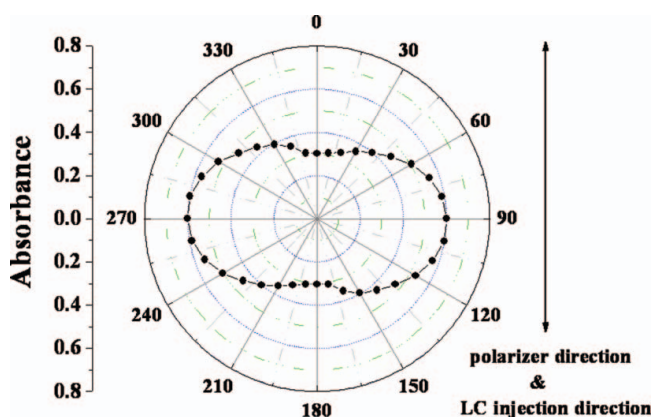

Figure 4. Polar diagrams of the absorption of linearly polarized visible light (632.8 nm wavelength) by LC cells fabricated with PBP-PDA films irradiated with LPUVL at 1.5 J/cm^2 as a function of the angle of rotation of the LC cells.
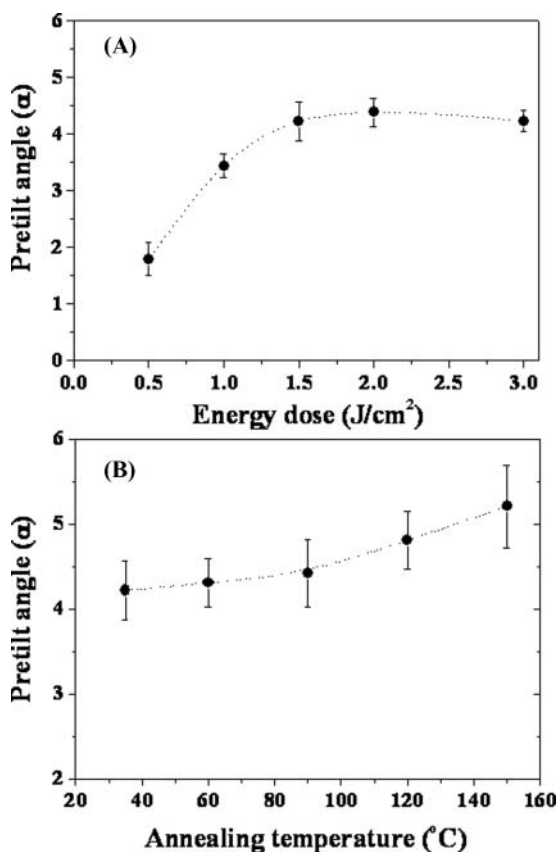
Figure 5. Pretilt angle variations of LCs measured for LC cells fabricated from PBP-PDA films. (A) The PBP-PDA films were exposed to LPUVL at various exposure doses. (B) The PBP-PDA films were irradiated with LPUVL at 1.5 J/cm^2 and annealed using a stepped heating regimen (45°C/10 min, 60°C/10 min, 90°C/10 min, 120°C/10 min, and 150°C/10 min).

angle initially increased with increasing exposure dose but leveled off above 1.5 J/cm^2. Pretilt angle of the PBP-PDA polyamide was also measured for the LC cells fabricated from films irradiated with 1.5 J/cm^2 of LPUVL, which were subsequently annealed at various temperatures. The obtained pretilt angle as a function of annealing temperatures is presented in Fig. 5(B). Pretilt angle of LC cells using annealed polyamide films increased with increasing annealing temperature. These pretilt angle variations can be understood as due to the changes in the orientations of the biphenyl side groups in the film surfaces that result from thermal annealing. Furthermore, all cells fabricated from annealed films reveal polar diagrams very similar to that observed for the cell of non-annealed films, independent of annealing.

Conclusions

A photosensitive polyamide with a photoreactive PDA moiety in the main chain and biphenyl side groups was synthesized by direct solution polycondensation. The polymers produced high quality films through conventional spin-casting and dry processing with

respective T_g and T_d values of 102 and 283 °C. Overall, the polyamide was synthesized at reasonably high molecular weights. The polymer film has an excellent photoreactivity to UV light. The dichroic ratio of the film due to linearly polarized UV light increased with increasing exposure dose. However, birefringence of the film reached the maximum values at 1.0 J/cm² exposure dose. By irradiation of LPUVL, the PDA moiety in the polymer main chain undergoes selective [2+2] photodimerization and induces reorientation of the polymer main chains. For the synthesized polyamide film, the direction-selective photoreaction of the PDA moiety in the main chains and the unreacted PDA moiety are believed to induce the alignment of LC molecules on the surface. The direction of LC alignment is perpendicular to the LPUVL. The pretilt behaviors of the LC molecules on the LPUVL irradiated polyamide films were controlled by both the exposure dose of LPUVL and the annealing temperature. In conclusion, this novel PBP-PDA polyamide is a good candidate material for applications in the LCD industry.

Acknowledgments

References

[1] Ichimura, K., Akiyama, H., Ishizuki, N., & Kawanishi, Y. (1993). *Macromol. Rapid Commun.*, *14*, 813.
[2] Akiyama, H., Kudo, K., & Ichimura, K. (1995) *Macromol. Rapid Commun.*, *16*, 35.
[3] Gibbons, W. M., Shannon, P. J., Sun, S. T., & Swetlin, B. J. (1991). *Nature*, *351*, 491.
[4] Schadt, M., Schmitt, K., Kozinkov, V., & Chigrinov, V. (1992). *Jpn. J. Appl. Phys.*, *31*, 2115.
[5] Lee, S. W., Chang, T. H., & Ree, M. (2001). *Macromol. Rapid Commun.*, *22*, 941.
[6] Jung, K. H., Moon, J. H., Song, D. M., & Shin, D. M. (2001). *Mol. Cryst. Liq. Cryst.*, *371*, 443.
[7] Jackson, P. O., O'neill, M., Duffy, W. L., Hindmarsh, P., Kelly, S. M., & Owen, G. (2001). *J. Chem. Mater.*, *13*, 694.
[8] Wang, Y., Xu, C., Kanazawa, A., Shiono, T., Ikeda, T., Matsuki, Y., & Takeuchi, Y. (1998). *J. Appl. Phys.*, *84*, 4573.
[9] Ichimura, K. (2000). *Chem. Rev.*, *100*, 1847.
[10] O'Neill, M., & Kelly, S. M. (2000). *J. Phys. D: Appl. Phys.*, *33*, R67.
[11] Hasegawa, M., & Taira, Y. (1995). *J. Photopolym. Sci. Technol.*, *8*, 241.
[12] Chae, B., Lee, S. W., Ree, M., & Kim, S. B. (2002). *Vibrat. Spectrosc.*, *29*, 69.
[13] Lee, S. W., & Ree, M. (2004). *J. Polym. Chem., Part A., Polym. Chem.*, *42*, 1322.
[14] Choi, K. H., Lee, K. H., & Jung, J. C. (2001). *J. Polym. Chem., Part A., Polym. Chem.*, *39*, 3818.
[15] Reiser, A., & Egerton, P. L. (1979). *Macromolecules*, *12*, 670.
[16] Egerton, P. L., Trigg, J., Hyde, E. M., & Reiser, A. (1981). *Macromolecules*, *14*, 100.
[17] Vargas, M., Collard, D. M., Liotta, C. L., & Schiraldi, D. (2000). *J. Polym. Sci. Polym. Chem. Ed.*, *38*, 2167.
[18] Ikeda, T., Lee, C. H., Sasaki, T., Lee, B., & Tazuke, S. (1990). *Macromolecules*, *23*, 1691.
[19] Kawatsuki, N., Sai, I., & Yamamoto, T. (1999). *J. Polym. Sci.: Part A: Polym. Chem.*, *37*, 4000.
[20] Song, S., Watabe, M., Adachi, T., Kobae, T., Chen, Y., Kawabata, M., Ishida, Y., Takahara, S., & Yamaoka, T. (1998). *Jpn. J. Appl. Phys.*, *37*, 2620.
[21] Chae, B., Lee, S. W., Kim, S. B., Lee, B., & Ree, M. (2003). *Langmuir*, *19*, 6039.
[22] Furumi, S., Nakagawa, M., Morino, S., & Ichimura, K. (2000). *Polym. Adv. Technol.*, *11*, 427.