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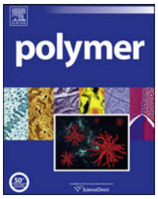

Liquid crystal alignment property of polystyrene derivatives containing dual photoreactive side groups

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ABSTRACT

We synthesized a series of polystyrene derivatives having the dual photoreactive side moieties, 4-(4-cyanophenylazo)phenoxymethyl and methyl cinnamate-4-oxymethyl, for the application of photoalignment materials. Stable and homogeneous planar LC cells having pretilt angles adjustable from 0.5° to 5° were obtained from these polymer films having molar contents of cinnamate and azobenzene groups in the ranges of 100–80 and 0–20 mol%, respectively, through the irradiation of linearly polarized ultraviolet (LP-UV) light to crosslink the cinnamate groups, followed by the irradiation of linearly polarized visible (LP-Vis) light to induce the isomerization of the azobenzene groups. The electro-optical and LC alignment properties of the LC cells were found to be affected by the molar composition of the photoreactive side groups and the exposure energies of LP-UV and LP-Vis light.

1. Introduction

Liquid crystal (LC) alignment has attracted considerable interest in scientific research as well as practical applications in the liquid crystal display (LCD) industry [1–10]. The mechanical rubbing of polyimide (PI) [11–22] and polystyrene (PS) [23–31] substrates has been widely studied as a method of fabricating LC alignment layers, due to its simplicity and rapidity, where the LCs are normally aligned parallel and perpendicular with respect to the rubbing direction, respectively. However, the rubbing process has disadvantages such as electrostatic charge, dust generation, and physical damage to the alignment layer surfaces. Moreover, the pretilt angle of LC molecules on the alignment layer surfaces cannot be easily controlled using the rubbing technique.

Noncontact methods of LC alignment have been investigated in order to overcome the disadvantages of the rubbing method [2–6,10]. Photoalignment has been taken a notice of promising noncontact alignment techniques to be used for the next generation LC display applications, including flexible ones, due to its various advantages such as its cleaness, suitability for large glass substrates, and unrestrictedness to surface morphology. A number of polymers containing various photoreactive groups for photoisomerization [32–39], photodimerization [40–51], and photodegradation [52–54] have been studied for photoalignment layers. In particular, polymers containing cinnamate groups can produce stable and homogeneous planar LC alignment from their [2 + 2] photoaddition reaction upon their exposure to linearly polarized ultraviolet (LP-UV) light [10,40–43] and their LC alignment properties, such as their aligning ability, alignment direction, and pretilt angle, were found to be affected by the incidence angle and exposure energy of the UV light [3,40,55–57]. Anisotropic surfaces on polymers containing azobenzene groups can be produced by the *E*–*Z* isomerization of these azobenzene groups through the irradiation of UV and visible light [32–37] and the pretilt angles of the LC molecules on these films can be easily controlled from 90° to 0° by changing the incidence angle and irradiation energy of the light [58,59]. Furthermore, polymers, such as polysiloxanes [60,61] and poly(amide–imide)s [62], and layer-by-layer (LBL) film [63] containing the two photoreactive groups, azobenzene and cinnamate groups, have been used as photoalignment layers to control the pretilt angles of the LC cells.

Recently we could prepare very stable LC cells having good electro-optical (E-O) properties from the polystyrene derivatives having additional aromatic side groups including photoreactive coumarin groups through the rubbing alignment process [51,64,65], while we could not get any stable LC alignment layers from the non-contacting photoalignment process [51,64]. In this study, we found that stable LC cells could be prepared from polystyrene derivatives having cinnamate side groups as the alignment layers through the UV irradiation. When the LC cells were prepared from the polystyrene derivatives having both cinnamate and azobenzene side groups, pretilt angles could be adjustable from 0.5° to 5° and the electro-optical performance was found to be improved.

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The synthesis and characterization of these polymers and the E-O properties of the LC cells fabricated using these photoirradiated polymer films are discussed in this paper.

2. Experimental

2.1. Materials

4-Chloromethylstyrene and potassium carbonate were purchased from Aldrich Chemical Co. and nematic LC (ZLI-5900-000) was purchased from Merck Co. *N*,*N*′-Dimethylacetamide (DMAc) was dried over molecular sieves (4 Å). Methanol was dried by refluxing with calcium hydride followed by distillation. Tetrahydrofuran (THF) was dried by refluxing with benzophenone and sodium followed by distillation. 4-Chloromethylstyrene (Aldrich) was purified by column chromatography on silica gel using hexane as an eluent to remove any impurities and inhibitors (*tert*-butylcatechol and nitroparaffin). Poly(chloromethylstyrene) (PCMS of $M_n = 11\,800$ and $M_w/M_n = 1.75$) was obtained through the conventional free radical polymerization of purified 4-chloromethylstyrene (10 g, 65.8 mmol) using 2,2′-azobisisobutyronitrile (AIBN, Junsei Chemical Co. Ltd., 2.0 wt% based on monomer) in dried THF (20 mL) under a nitrogen atmosphere [66]. AIBN was purified by recrystallization using methanol. All other reagents and solvents were used as-received.

2.2. Preparation of methyl 4-hydroxycinnamate (4-MHC)

Methyl 4-hydroxycinnamate was synthesized by refluxing 4-hydroxycinnamic acid (10 g, 61 mmol) in absolute methanol (100 mL) with 2–3 drops of concentrated H_2SO_4 for 24 h. The solution mixture was poured into water (500 mL) and the pH adjusted to 7 using sodium bicarbonate solution. The white precipitate was filtered out and washed thoroughly with water to remove any methanol and 4-hydroxycinnamic acid. The product was obtained in above 80% yield after dried under a vacuum overnight.

4-MHC ^{1}H NMR ($CDCl_3$): $\delta = 3.80$ (s, 3H, –OCH_3), 5.37 (s, 1H, *H*O–PhH–), 6.30 (d, 1H, –CH=C*H*CO–), 6.86 (m, 2H, OH–Ph*H*–), 7.43 (m, 2H, –Ph*H*–CH=CH–), 7.64 (d, 1H, –PhH–C*H*=CH–).

2.3. Preparation of 4-(4-cyanophenylazo)phenol (4-CPAP)

Sodium nitrite (5.0 g, 72.5 mmol) in water (30 mL) was slowly added dropwise to 4-cyanoaniline (9.1 g, 77.0 mmol) dissolved in 25 vol% sulfuric acid (150 mL), and the reaction mixture was stirred for 1 h below 0 °C. Then, the solution mixture was added to phenol (9.1 g, 97 mmol) in acetic acid (30 mL) below 0 °C and stirred for 1 h. Dilute sodium hydroxide solution was added to the reaction mixture until the supernatant solution was neutralized. The dark brown precipitate was collected by filtration and recrystallization was carried out in methanol to obtain the dark brown crystals (yield: 80%).

4-CPAP ^{1}H NMR ($CDCl_3$): $\delta = 5.26$ (s, 1H, *H*O–PhH–), 6.97 (d, 2H, OH–Ph*H*–), 7.72 (d, 2H, –Ph*H*–CN), 7.90 (d, 2H, –N=N–Ph*H*–), 8.15 (d, 2H, –Ph*H*–N=N–).

2.4. Preparation of polystyrene derivatives containing cinnamate side group (PS-CIN) and polystyrene derivatives containing cinnamate and azobenzene side groups (PS-CINAZOs)

A mixture of 4-MHC (1.05 g, 5.92 mmol, 180 mol% compared with PCMS) and potassium carbonate (0.91 g, 6.58 mmol) in *N*,*N*′-dimethylacetamide (DMAc, 10 mL) was heated to 80 °C. PCMS (0.5 g, 3.29 mmol) solution in DMAc (10 mL) was added to the mixture and then magnetically stirred at 80 °C for 3 h under nitrogen atmosphere. The solution mixture was cooled to room temperature and then poured into methanol to obtain a white precipitate. The precipitate was further purified by reprecipitating it several times from DMAc solution into methanol and then washed with water to remove any potassium carbonate and remaining salts. The product was obtained in above 80% yield after dried under a vacuum overnight. The degree (%) of substitution was calculated by comparing the singlet at 3.7–3.9 ppm (3H) with the backbone peak at 1.0–2.1 ppm (3H), which includes the contribution of the residual poly(chloromethylstyrene) and found to be almost 100%. This polymer was designated as PS-CIN.

PS-CIN ^{1}H NMR ($CDCl_3$): $\delta = 1.0–2.1$ (m, 3H, –CH_2–C*H*–Ph–), 3.7–3.9 (s, 3H, –CH=CH–COOCH_3), 4.7–5.1 (s, 2H, –Ph–CH_2–O–), 6.1–6.3 (s, 1H, –CH=C*H*–COOCH$_3$), 6.3–6.7 (m, 2H, –CH$_2$–CH–Ph*H*–CH$_2$–O–), 6.7–7.0 (m, 2H, –CH$_2$–CH–Ph*H*–CH$_2$–O–), 7.0–7.5 (m, 4H, –O–Ph*H*–CH=CH–), 7.5–7.7 (s, 1H, –Ph–C*H*=CH–CO–) (Fig. 2(b)).

PS-CIN IR (KBr, cm^{-1}): 3015 (C–H in aromatic), 2925 (asymmetric aliphatic C–H), 2852 (symmetric aliphatic C–H), 1638 (C=C in cinnamate), 1602 (C=C in phenyl ring), and 1452 (C=C in phenyl ring).

The following procedure was used to synthesize all of the PS-CINAZOs. The synthesis of PS-CINAZO20 is given as an example, where 20 indicates the molar % of the azobenzene containing monomeric unit in the heterosubstituted polymer is 20, in which case 80 molar % of this polymer is the cinnamate containing monomeric unit. A mixture of 0.146 g of 4-CPAP (0.66 mmol, 20 mol% compared with PCMS) and 0.468 g of 4-MHC (2.63 mmol, 80 mol% compared with PCMS) and potassium carbonate of 0.91 g (6.58 mmol, 200 mol% compared with PCMS) in *N*,*N*′-dimethylacetamide (DMAc, 10 mL) was heated to 80 °C. PCMS (0.5 g, 3.29 mmol) solution in DMAc (10 mL) was added to the mixture and then magnetically stirred at 80 °C for 6 h under a nitrogen atmosphere. The solution mixture was cooled to room temperature and then poured into methanol to obtain a red precipitate. The precipitate was further purified by reprecipitating it several times from DMAc solution into methanol and then washed with water to remove any potassium carbonate and remaining salts. The product was obtained in above 70% yield after dried under a vacuum overnight. The degrees (%) of substitution of chloromethyl groups into the 4-(4-cyanophenylazo)phenoxymethyl group and methyl cinnamate-4-oxymethyl group were calculated by comparing the singlets at 4.6–5.0 ppm (2H) and singlet at 3.7–3.9 ppm (3H) with the backbone peak at 1.0–2.1 ppm (3H) which included the contribution of the residual poly(chloromethylstyrene) and were found to be about 20% and 80%, respectively.

PS-CINAZO20 ^{1}H NMR ($CDCl_3$): $\delta = 1.0–2.1$ (m, 3H, –CH_2–C*H*–Ph–), 3.7–3.9 (s, 3H, –CH=CH–COOCH_3), 4.6–5.0 (s, 2H, –Ph–CH_2–O–), 6.1–6.3 (s, 1H, –CH=C*H*–COOCH$_3$), 6.3–6.5 (m, 2H, –CH$_2$–CH–Ph*H*–CH$_2$–O–), 6.5–6.9 (m, 2H, –CH$_2$–CH–Ph*H*–CH$_2$–O–), 6.9–7.2 (m, 4H, –O–Ph*H*–N=N–, –O–Ph*H*–CH=CH–), 7.3–7.5 (s, 1H, –Ph–C*H*=CH–CO–), 7.5–7.7 (m, 1H, Ph*H*–N=N–Ph*H*–), 7.7–7.9 (m, 1H, –Ph–N=N–Ph*H*–) (Fig. 2(c)).

PS-CINAZO20 IR (KBr, cm^{-1}): 3015 (C–H in aromatic), 2925 (asymmetric aliphatic C–H), 2852 (symmetric aliphatic C–H), 2225 (C≡N in azobenzene), 1638 (C=C in cinnamate), 1602 (C=C in phenyl ring), and 1452 (C=C in phenyl ring).

The heterosubstituted polymers, designated as PS-CINAZO#, where # is the molar content (%) of 4-(4-cyanophenylazo)phenoxymethyl group containing monomeric units in the polymer (then 100 − # is the molar content (%) of methyl cinnamate-4-oxymethyl group containing monomeric units) were synthesized using the same procedure as that used for the preparation of PS-CINAZO20 except for the amounts of 4-CPAP and 4-MHC in the reaction. For example, PS-CINAZO15 was prepared using 0.110 g of 4-CPAP (0.49 mmol, 15 mol% compared with PCMS) and 0.499 g of

4-MHC (2.80 mmol, 85 mol% compared with PCMS), and PS-CINAZO10 was prepared using 0.073 g of 4-CPAP (0.33 mmol, 10 mol% compared with PCMS) and 0.527 g of 4-MHC (2.96 mmol, 90 mol% compared with PCMS), with a slight excess amount of potassium carbonate (0.91 g, 6.58 mmol, 200 mol% compared with PCMS). These heterosubstituted polymers, PS-CINAZO15 and PS-CINAZO10, were obtained in yields above 70%.

2.5. *Film preparation*

Solutions of the PS-CIN and PS-CINAZO#s in $CHCl_3$ (2 wt%) were prepared. These solutions were filtered using a PTFE membrane with a pore size of 0.45 μm. Thin films of the polymers were prepared by spin-coating (2000 rpm, 30 s) them onto $1.5 \times 1.5\ cm^2$ ITO coated glass substrates. These films were obliquely irradiated using a 200 W high pressure Hg–Xe lamp (66902, Oriel Instruments) equipped with bandpass filter and attached to power supply (69911, Oriel Instruments) which is schematically shown in Fig. 5(a). The incidence angles of LP light were 30, 45, and 60°, respectively. Dichroic polarizer (27320, Oriel Instruments) was used to irradiate the films with linearly polarized ultraviolet (LP-UV) and linearly polarized visible (LP-Vis) light. The intensity of the irradiated light was measured by optical power meter (UM-10, Minolta) equipped with a photosensor.

2.6. *LC cell assembly*

Twisted nematic (TN) and antiparallel LC cells were fabricated using the linearly polarized photoirradiated polymer films in the oblique direction with respect to the polymer surfaces onto ITO coated glass slides. The TN LC cells were made by assembling the films together orthogonally with respect to the polarization direction of incident light for the photoirradiated film using spacers with a thickness of 6.5 μm. The antiparallel LC cells were constructed by assembling the films together antiparallel with respect to the polarization direction of incident light for the photoirradiated film using spacers with thicknesses of 6.5 and 50 μm. The LC cells were filled with a nematic LC, ZLI-5900-000 (Merck Co., $n_e = 1.6327$, $n_o = 1.5011$, and $\Delta\varepsilon = 15.5$, where n_e, n_o, and $\Delta\varepsilon$ represent the extraordinary refractive index, ordinary refractive index, and dielectric anisotropy, respectively), in the isotropic state in order to avoid creating flow alignment by the capillary action. The manufactured LC cells were sealed with epoxy.

2.7. *Instrumentation*

^1H NMR measurements were carried out on a Bruker AVANCE at 300 MHz. Gel permeation chromatography (GPC) was used to measure the molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the synthesized polymer with respect to polystyrene standards using tetrahydrofuran (THF) as an eluent and a UV detector. Differential scanning calorimetry (DSC) measurements were carried out on a TA instruments 2920 at heating and cooling rates of 20 °C/min under a nitrogen atmosphere. Thermal gravimetric analysis (TGA-2050, TA instrument) was used to investigate the thermal stability of the polymer samples. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. The FTIR spectra were recorded at a resolution of 4 cm^{-1} and interferograms were accumulated 64 times. The UV–Vis spectra of the polymer films were taken on a Perkin Elmer Lamda 20 spectrometer. The electro-optical properties of the LC cells were investigated using an optical apparatus equipped with a He–Ne laser, a polarizer, an analyzer, and a photodiode detector. The cell gap was measured before filling the LCs using a spectrophotometer (Ocean optics Inc., S 2000). The pretilt angle of the antiparallel LC cell was measured by the crystal rotation method [67,68]. The azimuthal anchoring energy of the LC cells was calculated using a torque balance equation written as

$$E_\varphi = K_{22}\frac{2 \times (\Phi - \Delta\varphi)}{d_e \sin(\Phi - \Delta\varphi)}$$

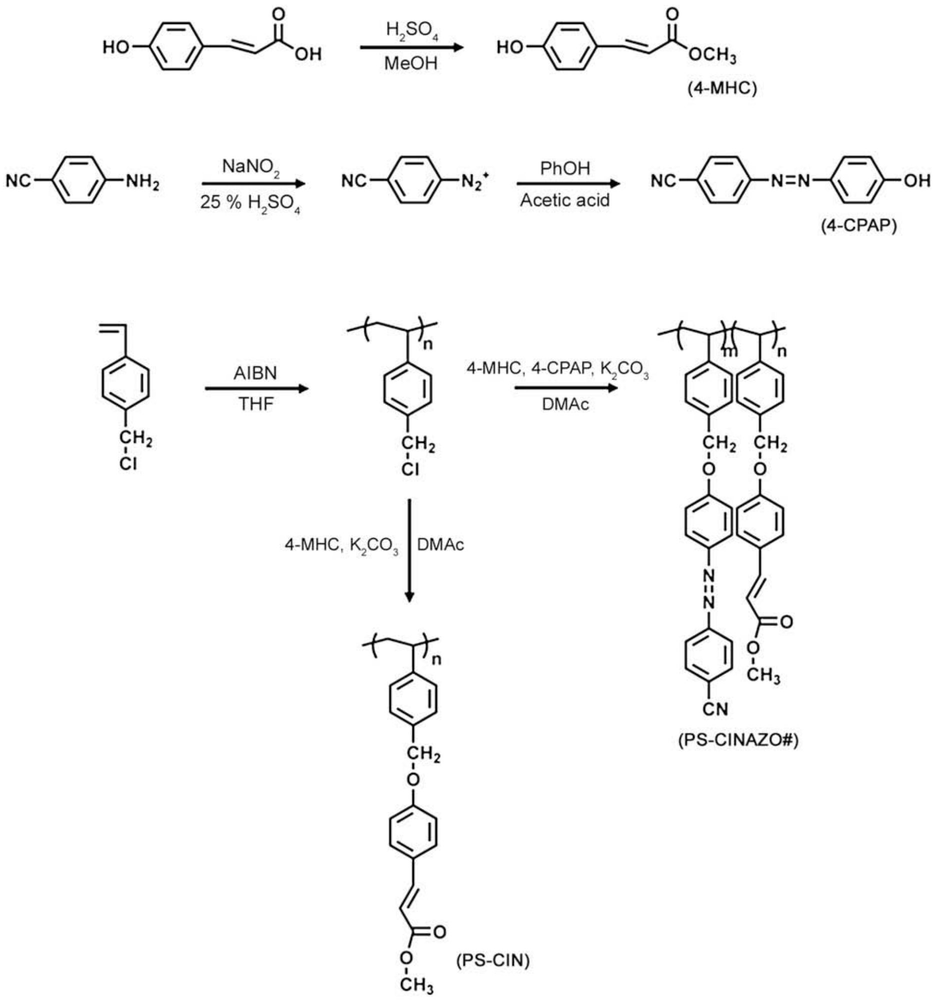
where K_{22} is the elastic constant of liquid crystal, d_e is the cell gap measured using the spectrophotometer, Φ is the intended twist angle, and $\Delta\varphi$ is the actual twist angle. The actual twist angle was determined as reported by others [69,70]. The LC alignment direction of the antiparallel LC cells was investigated by measuring the angular dependence of the absorbance of a dichroic dye (disperse blue 1), which was dissolved at 1 wt% in ZLI-5900-000, using an optical apparatus equipped with a He–Ne laser, a polarizer, and a photodiode detector as a function of the rotation angle of the samples [21]. The contact angles were measured with a Kruss DSA10 contact angle analyzer equipped with drop shape analysis software. The Owens–Wendt's equation was applied to calculate the surface energies from the contact angles [71]. The response time and voltage–transmittance (V–T) of the TN LC cells were measured using the previously reported method [72]. The threshold voltage (V_{th}) and driving voltage (V_{on}) in the V–T curve are defined as the voltages at which the transmittance was decreased to 90% and 10% of the initial transmittance value, respectively. The rising (T_r) and falling (T_f) response times for the white-to-black and black-to-white changes are defined as the times corresponding to the transition from 10% to 90% transmittance and vice versa [72]. POM images of LC cell were taken using an optical microscope (Nikon, ECLIPSE E600 POL) equipped with a crossed polarizer and digital camera (Nikon, COOLPIX995).

3. Results and discussion

Fig. 1 shows the synthetic route to the methyl cinnamate-4-oxymethyl-substituted polystyrenes (PS-CIN) and 4-(4-cyanophenylazo)phenoxymethyl and methyl cinnamate-4-oxymethyl-substituted polystyrenes (PS-CINAZO). The heterosubstituted polymers (PS-CINAZO) with different degrees (%) of substitution were obtained by varying the amounts of 4-CPAP and 4-MHC in the reaction. The characteristic peaks of chloromethyl in PCMS at 4.2–4.6 ppm completely disappeared in the ^1H NMR spectra of the PS-CIN and PS-CINAZO20, indicating that all of the chloromethyl groups in these polymers were changed to phenoxymethyl containing side groups by the reaction with 4-CPAP and 4-MHC in the polymer analogous reactions, as shown in Fig. 2. The degrees of substitution of the polymers were calculated from the ^1H NMR data by comparing the peaks integrals of the 4-(4-cyanophenylazo)phenoxymethyl and methyl cinnamate-4-oxymethyl side groups and the backbone.

The FTIR spectra of PS-CIN and PS-CINAZO# were measured and the peaks were identified with the aid of those of other polymers containing azobenzene and cinnamate side groups reported by others (Fig. 3) [73]. The IR peaks representing the characteristic bands of the stretching vibrational mode of the C≡N group in the 4-(4-cyanophenylazo)phenoxymethyl side group and the C=C group in the methyl cinnamate-4-oxymethyl side group were observed at 2225 and 1638 cm^{-1}, respectively. In particular, the intensity of the characteristic band of the stretching vibrational mode of the C≡N group in the azobenzene side group at 2225 cm^{-1} increases as the molar content of the azobenzene containing monomeric unit in PS-CINAZO increases.

The average molecular weights (M_n) of the PS-CIN and PS-CINAZO#s synthesized from the PCMS ($M_n = 11\,800$) were always larger than 16 300 (Table 1), indicating that the polymer modification from PCMS to the products gave rise to an increase in the



Where # is the mole percent of the azobenzene containing monomeric unit.

Fig. 1. Synthetic route to the polystyrene derivatives containing photoreactive side groups.

average molecular weights of the polymers, as expected. These polymers were soluble in polar aprotic solvents such as NMP, DMF, and DMAc and in many organic solvents having low boiling points such as THF, $CHCl_3$, and so on.

The thermal properties of these polymers were investigated by DSC and TGA (Table 1). All of the polymers including PCMS were found to be amorphous, since only glass transitions were observed in their DSC thermograms. As the content of the azobenzene

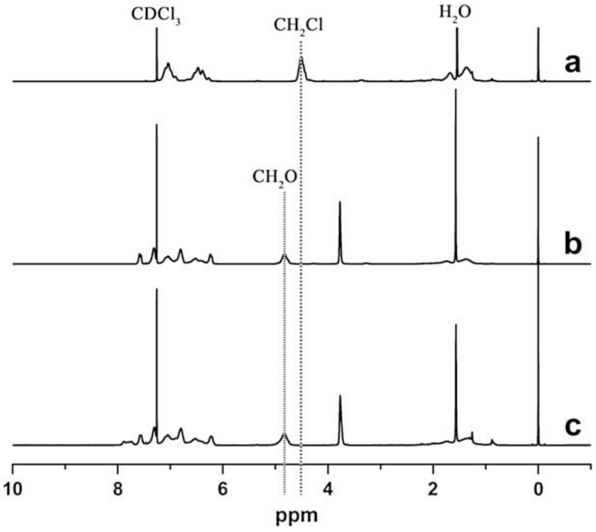


Fig. 2. ^1H NMR spectra of the (a) PCMS, (b) PS-CIN, and (c) PS-CINAZO20.

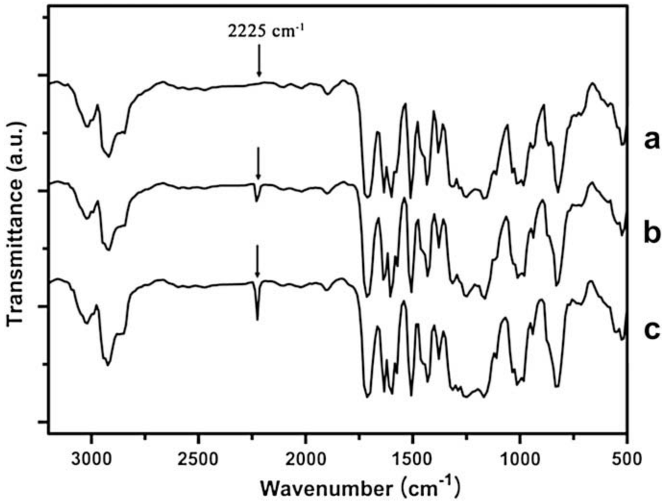


Fig. 3. FTIR of spectra of the polymers ((a) PS-CIN, (b) PS-CINAZO10, and (c) PS-CINAZO20).

Table 1
Results of the characterization of the polymers using ^{1}H NMR, GPC, DSC, and TGA.

Polymer designation	Mole percent of azobenzene moiety (%)	Mole percent of cinnamate moiety (%)	M_n[a]	M_w/M_n[a]	T_g (°C)	$T_{d,90\%}$ (°C)[b]
PCMS			11 800	1.75	106	308
PS-CIN	0	100	16 300	1.89	112	345
PS-CINAZO10	10	90	16 600	2.06	113	351
PS-CINAZO15	15	85	17 100	2.07	120	352
PS-CINAZO20	20	80	17 900	1.66	123	355

[a] Obtained from GPC using THF as solvent with respect to monodisperse polystyrene as standards.

[b] The decomposition temperature ($T_{d,90\%}$) is defined as 10 wt% loss.

containing monomeric unit increased from 0 to 20%, the glass transition temperature (T_g) increased from 112 °C for PS-CIN to 123 °C for PS-CINAZO20. As the molar content of the azobenzene side group increased from 0 to 20%, the decomposition temperature ($T_{d,90\%}$) of the polymers increased from 345 °C for PS-CIN to 355 °C for PS-CINAZO20. Overall, the incorporation of the 4-(4-cyanophenylazo)phenoxymethyl group into the PS-CINAZO# increased the glass transition temperatures (T_g) and thermal decomposition temperatures ($T_{d,90\%}$).

The characteristic bands of the absorption of the PS-CIN and PS-CINAZO# films were investigated by UV–Vis spectroscopy (Fig. 4). The absorption bands characterized by the π–π^* transition of the cinnamate moiety at 297 nm (λ_{max}) and π–π^* transition of the azobenzene moiety at 373 nm (λ_{max}) in the side groups were observed. As the content of the azobenzene containing monomeric unit in PS-CINAZO# increases from 0% for PS-CIN to 20% for PS-CINAZO20, the intensity of the azobenzene peak increases and that of the cinnamate peak decreases.

Fig. 5 shows the FTIR and UV–Vis spectra of the PS-CIN films irradiated with linearly polarized ultraviolet (LP-UV) light with different energies using experimental setup of polarized irradiation in the oblique direction of 30° with respect to the PS-CIN surfaces which is schematically shown in Fig. 5(a). The FTIR spectra of the PS-CIN film irradiated with LP-UV light of 0.972 J/cm^2 clearly shows a decrease in the intensity of the characteristic band of the stretching vibration of the C═C bond in the cinnamate group at 1638 cm^{-1}. This decrease is attributed to the [2 + 2] cycloaddition reaction of the C═C bond in the cinnamate group through the UV irradiation, as reported by others [40–43]. Similarly, a decrease in the intensity of the peaks from the cinnamate groups (λ_{max} = 297 nm) was observed in the UV–Vis spectra of the PS-CIN films upon increasing the UV exposure energy, as shown in Fig. 5(c).

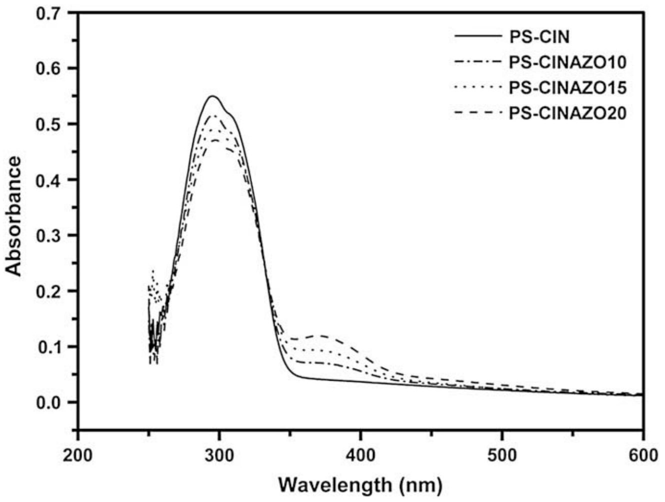


Fig. 4. UV–Vis spectra of the PS-CIN and PS-CINAZO# films.

We also tried to observe the photoisomerization behavior of the azobenzene groups in the PS-CINAZO# films irradiated with LP-UV and/or LP-Vis light using UV–Vis spectroscopy. When the PS-CINAZO20 film was irradiated with LP-Vis light, the intensity of the azobenzene band (λ_{max} = 373 nm) characterized by the π–π^* transition of the *trans* form increases as previously described in other reports [74–76]; as the exposure energy of LP-Vis light increases from 0 to 0.2 J/cm^2, the intensity of the *trans* azobenzene band at 373 nm increases (Fig. 6). The intensity increase of the *trans* azobenzene band might be caused by the orientation change in E isomer, breaking aggregations, and/or mixing Z isomers through the irradiation of LP-Vis light, while we don't have any clear

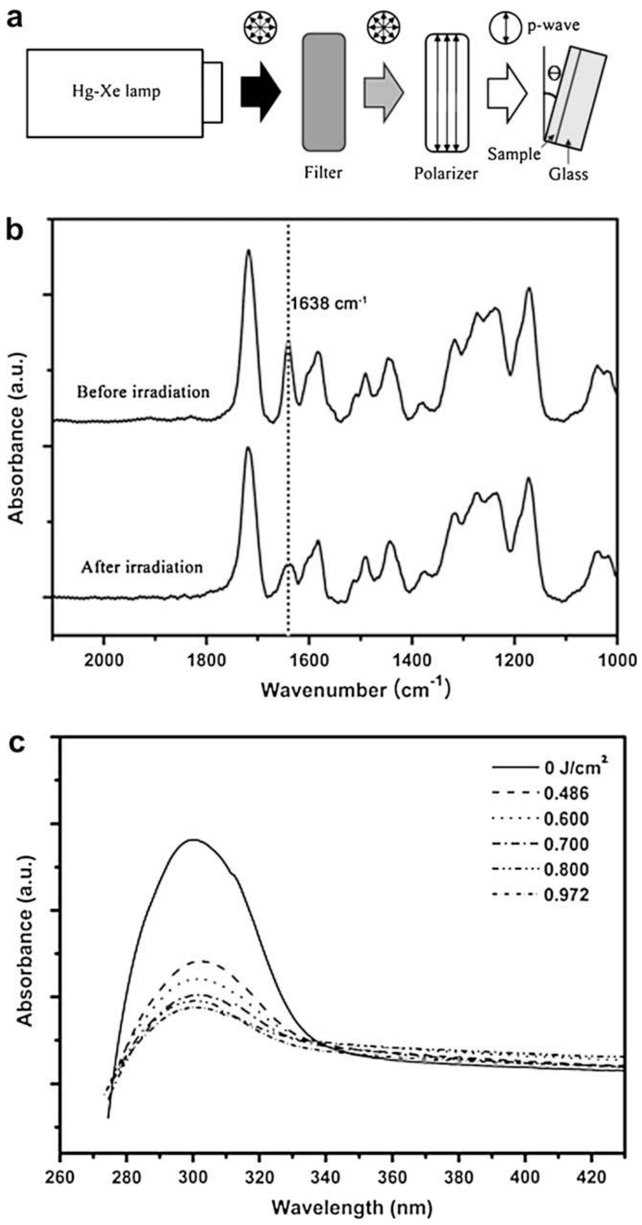


Fig. 5. (a) Schematic diagram of experimental setup of polarized oblique irradiation, (b) FTIR, and (c) UV–Vis spectra of the PS-CIN films irradiated with LP-UV light with different energies in the oblique direction of 30° with respect to the polymer surfaces.

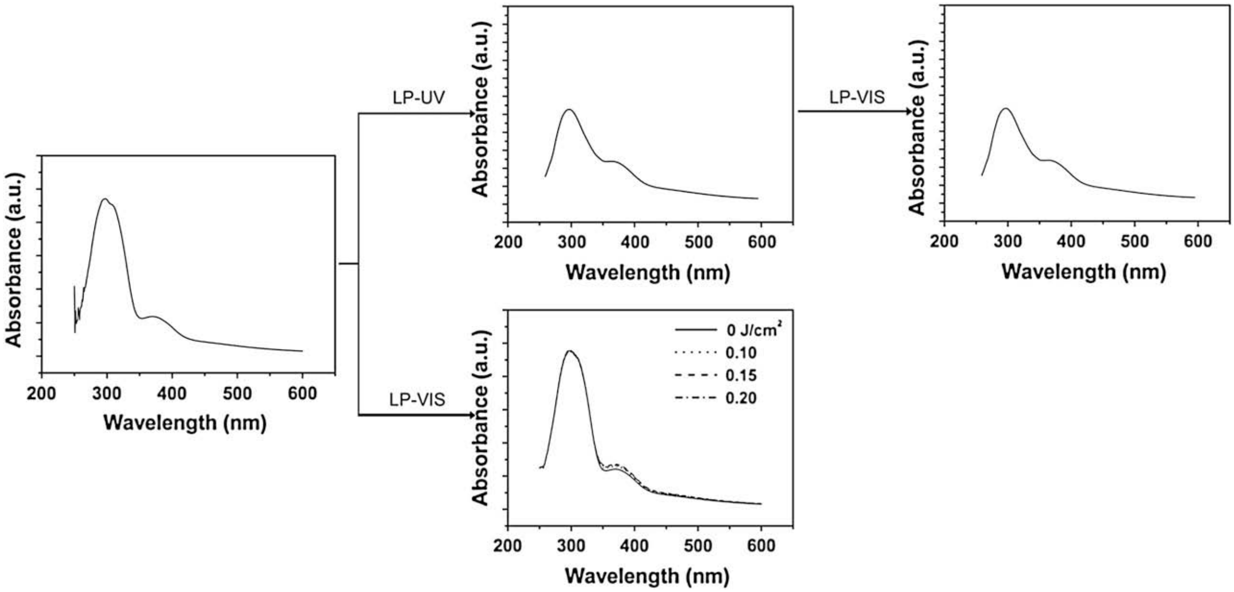


Fig. 6. UV–Vis spectra of the PS-CINAZO20 films irradiated with LP-UV and/or LP-Vis light in the oblique direction of 30° with respect to the polymer surfaces.

answer; we could not observe any distinguishable changes of the polymer films irradiated with LP-UV and/or LP-Vis light with different energy as explained in the later part of this paper. On the contrary, we could not observe the intensity changes of the azobenzene band characterized by the n–π^* transition of the *cis* form possibly because the extinction coefficients of n–π^* absorptions for the *cis* isomer is too small [74]. Furthermore, we could not observe any intensity changes of the azobenzene band when PS-CINAZO20 was irradiated with LP-Vis light after first being irradiated with LP-UV light. The crosslinked networks generated by the intermolecular [2 + 2] cycloaddition reaction of the cinnamate groups might prevent or hinder the isomerization of the azobenzene groups, especially in the bulk phase of the polymer film. However we believe that the isomerization and/or another reaction occurs on the surface of the film and the pretilt angles of the liquid crystal increase when PS-CINAZO20 is irradiated with LP-Vis light after first being irradiated with LP-UV light.

The LC aligning ability of the antiparallel LC cells made from the polymer films irradiated with LP-UV light in the oblique direction of 30° with respect to the polymer surfaces was determined by observing the transmitted intensity of a LP He–Ne laser beam passed through the LC cells between crossed polarizers as a function of the rotation angle of the samples (Fig. 7(a)) [40,51,63]. Homogeneous planar and parallel LC alignment with respect to the polarization direction of the incident UV light was observed from the LC cell made from the PS-CIN film, resulting from their alignment polymers having cinnamate moieties, as reported by others [55–57]. A UV exposure energy larger than about 0.25 J/cm^2 was required to make the LC cell show homogeneous planar LC aligning ability. This value is close to the normal exposure energies needed for the preparation of stable LC cells using other cinnamate containing polymer films as the alignment layers. For example, homogeneous planar LC alignments were observed from the LC cells made from polyimide containing cinnamate side groups [73] irradiated with a UV exposure energy of 0.5 J/cm^2 and polymethylmethacrylate containing cinnamate side groups [40] irradiated with UV exposure energies of 0.05–1.5 J/cm^2. As the UV exposure energy increases from 0 to 0.972 J/cm^2, the contrast ratio (the ratio of the maximum transmittance to the minimum transmittance) of the LC cell made from the PS-CIN film increases. UV

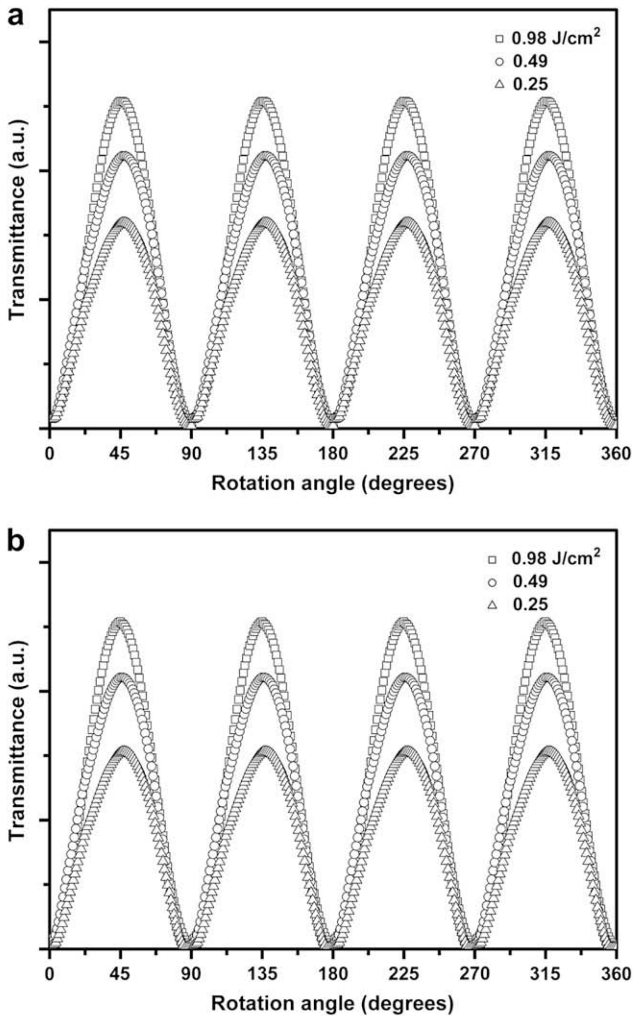


Fig. 7. Angular dependence of the transmitted light intensity of a LP He–Ne laser through the antiparallel LC cells made from UV irradiated (a) PS-CIN and (b) PS-CINAZO20 films in the oblique direction of 30° with respect to the polymer surfaces between crossed polarizers.

irradiation of about 0.972 J/cm^2 gave rise to the maximum contrast ratio for the LC cell made from the PS-CIN film. The LC cells made from the PS-CINAZO20 films irradiated with LP-UV light also show homogeneous planar and parallel LC alignment with respect to the polarization direction of the incident UV light; as the UV exposure energy increases from 0 to 0.972 J/cm^2, the contrast ratio of the LC cells also increases, as shown in Fig. 7(b). These results indicate that the PS-CIN and PS-CINAZO# films irradiated with LP-UV light can produce LC cells having good LC aligning ability from the cycloaddition reactions of the cinnamate moieties.

The LC cells made from the PS-CIN and PS-CINAZO# films by the successive irradiation in the oblique directions of 30° of LP-UV light with an energy of 0.972 J/cm^2 and LP-Vis light with energies in the range of 0.05–0.2 J/cm^2 showed homogeneous planar LC alignment behavior in the photoimages of the antiparallel LC cells shown in Fig. 8. The LC alignment direction of the antiparallel LC cells made from the PS-CIN and PS-CINAZO# films by the successive irradiation of LP-UV light of 0.972 J/cm^2 and LP-Vis light of 0.2 J/cm^2 was found to be parallel (maximum absorbance along the 0° ↔ 180°) with respect to the polarization direction of the incident light, according to the polar diagrams of the absorbance of the dichroic dye (disperse blue 1) in the LC cells. Therefore, the LC alignment direction derived from LP-UV irradiation was maintained after the LP-Vis irradiation. When we increased the content of azobenzene groups in PS-CINAZO# to more than 20 mol%, the LC cells made from these polymer films using the same photoalignment process showed poor LC alignment behavior. Possibly, the competition between the homogeneous planar LC alignment from the cinnamate part upon the irradiation of LP-UV light and the homeotropic LC alignment (or the increase of the pretilt angle) from the azobenzene part upon the irradiation of LP-Vis light. Azobenzene groups are known to induce homeotropic LC alignment or to increase the pretilt angle of LCs on the polymer surfaces through the irradiation of LP-Vis light [60–63]. We tried to compare the alignment ability of these LC cells by measuring their anchoring energy. The azimuthal anchoring energy values of the LC cells made from PS-CIN and PS-CINAZO# films irradiated with LP-UV light of 0.972 J/cm^2, LP-Vis light of 0.2 J/cm^2 successively and LP-UV light of 0.972 J/cm^2 only are all about $\sim 10^{-6}$ J/m^2 close to those of photoirradiated films of other polymers for photoalignment studies [3], while we could not observe any differences of the azimuthal anchoring energy values between the LC cells made from PS-CIN and PS-CINAZO# films with the resolution of our equipment.

The pretilt angles of the antiparallel LC cells fabricated with the polymer films were measured, in order to determine the effect of the exposure energy of LP-UV and/or LP-Vis light on the LC alignment direction (Fig. 9). We could not measure the pretilt angles of the LC cells made from the polymer films irradiated with a UV energy less than 0.25 J/cm^2 or those of the LC cells made from the PS-CINAZO# films having a molar content of azobenzene groups larger than 20 mol%, due to their poor LC alignment behavior. The pretilt angles of all of the LC cells made from the polymer films irradiated with UV energies in the range of 0.6–0.972 J/cm^2 were almost identical within about 0.5° independent of the incidence

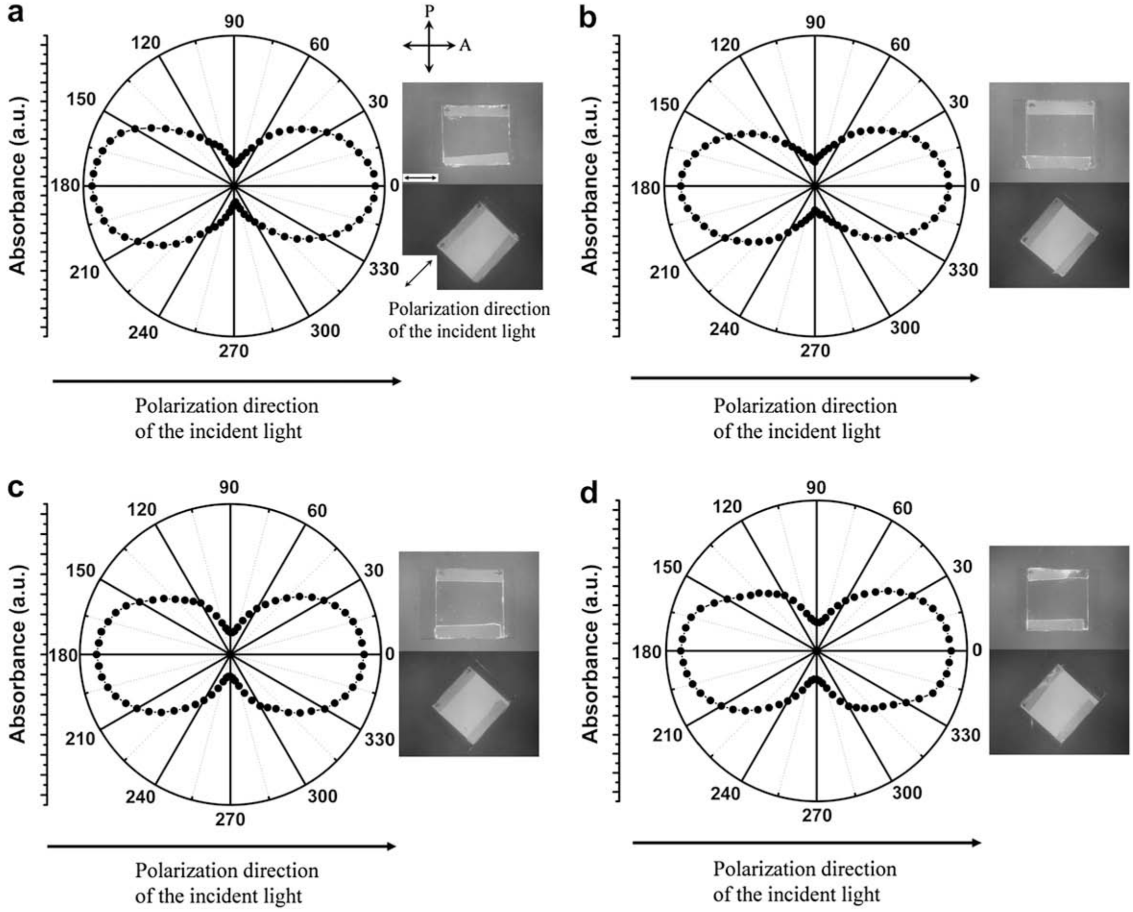


Fig. 8. Polar diagram of the absorbance of a disperse blue 1 in antiparallel LC cells made from (a) PS-CIN, (b) PS-CINAZO10, (c) PS-CINAZO15, and (d) PS-CINAZO20 films by the successive irradiation in the oblique directions of 30° of LP-UV light of 0.972 J/cm^2 and LP-Vis light of 0.2 J/cm^2 as a function of angle of the samples and photoimages of their fabricated LC cells.

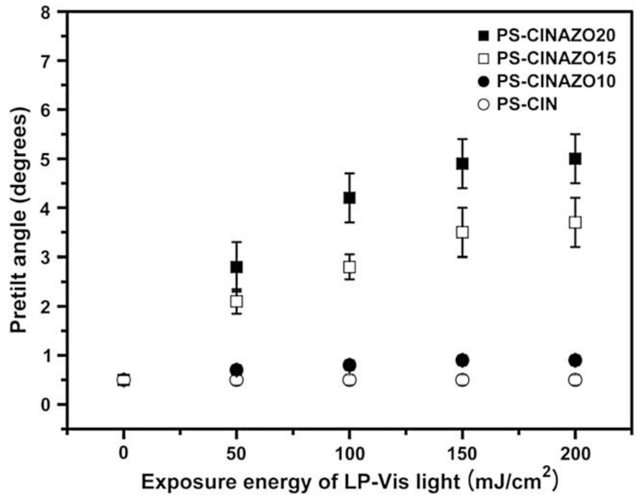


Fig. 9. Observation of the pretilt angles of the LC cells made from polymer films by the successive irradiation in the oblique direction of 30° of LP-UV light of 0.972 J/cm^2 and LP-Vis light as a function of exposure dose of LP-Vis light.

angle, the exposure energy of LP-UV light, and the composition of the polymer. Also, the pretilt angles of the LC cells made from the PS-CINAZO# films by the successive irradiation of LP-UV and LP-Vis light were almost identical independent of the incidence angles (30, 45, and 60°) of LP-Vis light. For example, the pretilt angles of LCs on the PS-CINAZO20 films irradiated with LP-UV light of 0.972 J/cm^2 in the oblique direction of 30° and LP-Vis light of 0.2 J/cm^2 in the oblique directions of 30, 45, and 60°, respectively, are all about 5°. However, the pretilt angles on the PS-CINAZO# films made from the successive irradiation in the oblique direction of 30° of LP-UV light of the same energy of 0.972 J/cm^2 and LP-Vis light having different exposure energy values were found to be affected by the composition of the polymers and the exposure energy of LP-Vis light (Fig. 9). For example, as the exposure energy of the visible light in the oblique direction of 30° increases from 0 to 0.2 J/cm^2 for the PS-CINAZO20 films, the pretilt angle of LCs increases from 0.5° to 5°. Also, when the molar content of azobenzene side groups increases from 0 to 20% for the LC cell made from polymer films by the successive irradiation of UV light of 0.972 J/cm^2 and visible light of 0.2 J/cm^2, the pretilt angles on the polymer films increase from 0.5° to 5°. We tried various characterization techniques such as Raman, attenuated total reflection (ATR), electron spectroscopy for chemical analysis (ESCA), grazing incidence X-ray diffraction (GIXD), and surface energy measurements to investigate the effect of the structure change of the azobenzene group in the PS-CINAZO# irradiated with LP-UV and/or LP-Vis light on the pretilt angle of LCs on the polymer surfaces. However, we could not observe any distinguishable changes of the polymer films irradiated with LP-UV and/or LP-Vis light with different energy. Even the surface energy values of these films were almost identical. For example the surface energy values of PS-CINAZO20 films irradiated with LP-UV and/or LP-Vis light with different energies are all identical about 47.8 mJ/m^2. Possibly very minor changes of the azobenzene groups on the surface through the irradiation of LP-Vis light, which is not distinguishable with the resolution of experimental devices we have, affect the pretilt angles. However, the azobenzene side groups in the PS-CINAZO# can be used to adjust the pretilt angles of the LC cells and can improve the electro-optical (E-O) properties of the LC cells as shown in the next paragraph.

Table 2
Voltage–transmittance and response time values of the LC cells made from the photoirradiated films.

Sample	Voltage–transmittance (V)			Response time (ms)		
	V_{th}	V_{50}	V_{on}	T_r	T_f	Response time
PS-CIN[a]	2.09	2.62	4.12	20	39	59
PS-CINAZO10[b]	2.05	2.50	3.90	19	38	57
PS-CINAZO20[b]	1.90	2.24	3.04	17	35	52

[a] Irradiation of LP-UV light of 0.972 J/cm^2.
[b] Successive irradiation of LP-UV light of 0.972 J/cm^2 and LP-Vis light of 0.2 J/cm^2.

The E-O properties of the LC cells with a cell gap of about 7 μm made from the polymer alignment films were determined by measuring the voltage–transmittance (V–T) and response time values. Fig. 10 clearly shows that the TN LC cells made from the PS-CIN, PS-CINAZO10, and PS-CINAZO20 films by the successive irradiation in the oblique directions of 30° of LP-UV light of 0.972 J/cm^2 and LP-Vis light of 0.2 J/cm^2 have good E-O properties. Using these results, the V_{th} and V_{on} values of this LC cell made from PS-CINAZO20 film were found to be 1.90 V and 3.04 V, respectively (Table 2). For comparison, the V_{th} and V_{on} values of the LC cells fabricated using the PS-CIN films irradiated with LP-UV light of 0.972 J/cm^2 only were found to be 2.09 V and 4.12 V, respectively, which are larger than those obtained from the PS-CINAZO20 film. We also found that the response time (about 52 ms) of the LC cell made from the photoirradiated PS-CINAZO20 film is faster than that (about 59 ms) of the LC cell made from the photoirradiated PS-CIN film. It has been reported that LC alignment films having larger pretilt angles have faster response times in various LCD modes, such as the TN (twisted nematic), OCB (optically compensated bend), and NBB (no-bias-bend) modes [77–79]. Therefore, the response time of the LC cell made from the PS-CINAZO20 film having a pretilt angle of approximately 5° by the successive irradiation of LP-UV and LP-Vis light is faster than

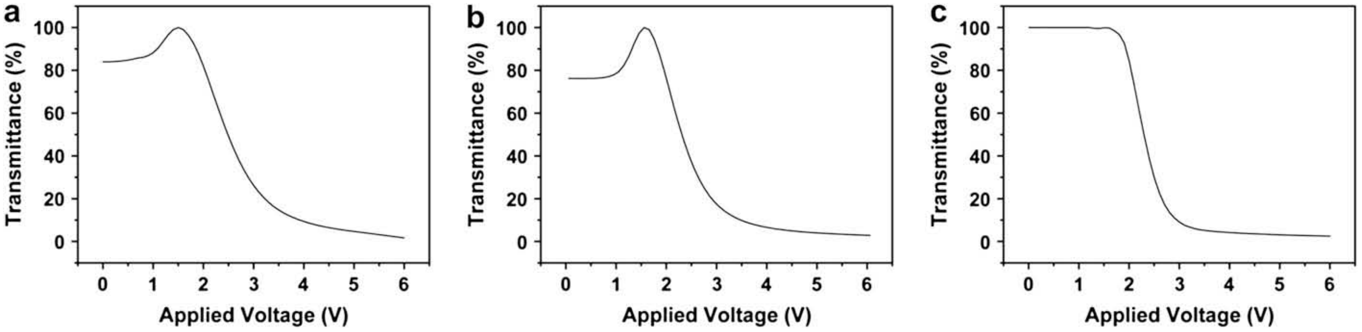


Fig. 10. Voltage–transmittance curves of the LC cells fabricated with photoirradiated (a) PS-CIN, (b) PS-CINAZO10, and (c) PS-CINAZO20 films irradiated with LP-UV light of 0.972 J/cm^2 and LP-Vis light of 0.2 J/cm^2 in the oblique direction of 30° successively with respect to the polymer surfaces.

that of the LC cell fabricated with the PS-CIN film having a pretilt angle of about 0.5°.

4. Conclusions

We synthesized a series of polystyrene derivatives containing both photocrosslinkable cinnamate groups and photoisomerizable azobenzene groups. These polymers were synthesized through the reaction of polychloromethylstyrene with different amounts of 4-(4-cyanophenylazo)phenol and methyl 4-hydroxycinnamate groups. Stable and homogeneous planar LC cells could be prepared from these polymer films through the photoalignment process. The pretilt angle, V_{th}, V_{on}, and response time of the LC cell made from the polymer films containing only cinnamate groups through the irradiation of LP-UV light were 0.5°, 2.09 V, 4.12 V, and 59 ms, respectively, and those of the LC cell made from the polymer alignment layers having molar contents of cinnamate and azobenzene groups of 80 and 20 mol% prepared by the successive irradiation of LP-UV and LP-Vis light were 5°, 1.90 V, 3.04 V, and 52 , respectively. Therefore, the incorporation of azobenzene side group into the polymers increases the pretilt angle of the LCs and improves the electro-optical performance of the LC cell.

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References

[1] Kohki T, Masaki H, Mitsuhiro K, Nobuyuki I, Ray H, Masanori S. In: Gray GW, Goodby JW, Fukuda A, editors. Alignment technologies and applications of liquid crystal devices. New York: Taylor & Francis; 2005.
[2] Ichimura K. Chem Rev 2000;100:1847–74.
[3] O'Neill M, Kelly SM. J Phys D Appl Phys 2000;33:R67–84.
[4] Schadt M. Annu Rev Mater Sci 1997;27:305–79.
[5] Almeria N, Paul R. Chem Rev 2002;102:4139–76.
[6] Chaudhari P, Lacey J, Doyle J, Galligan E, Lien S-CA, Callegari A, et al. Nature 2001;411:56–9.
[7] Kim J-H, Yoneya M, Yokoyama H. Nature 2002;420:159–62.
[8] Varghese S, Narayanankutty S, Bastiaansen CWM, Crawford GP, Boer DJ. Adv Mater 2004;16:1600–5.
[9] Lee YJ, Choi JG, Song I-K, Oh JM, Yi MH. Polymer 2006;47:1555–62.
[10] Schadt M, Schmitt K, Kozinkov V, Chigrinov V. Jpn J Appl Phys 1992;31:2155–64.
[11] Ghosh MK, Mittal KL. Polyimides: fundamentals and applications. New York: Marcel Dekker; 1996.
[12] Feller MB, Chen W, Shen TR. Phys Rev A 1991;43:6778–92.
[13] Van Aerle NAJ, Tol AJW. Macromolecules 1994;27:6520–6.
[14] Lee KW, Paek S-H, Lien A, Durning C, Fukuro H. Macromolecules 1996; 29:8894–9.
[15] Weiss K, Woll C, Hohm E, Fiebranz B, Forstmann G, Peng B, et al. Macromolecules 1998;31:1930–6.
[16] Stohr J, Samant MG, Cossy-Favre A, Diaz J, Momoi Y, Odahara S, et al. Macromolecules 1998;31:1942–6.
[17] Meister R, Jerome B. Macromolecules 1999;32:480–6.
[18] Ge JJ, Li CY, Xue G, Mann IK, Zhang D, Wang S-Y, et al. J Am Chem Soc 2001;123:5768–76.
[19] Kim D, Oh-e M, Shen YR. Macromolecules 2001;34:9125–9.
[20] Chae B, Kim SB, Lee SW, Kim SI, Choi W, Lee B, et al. Macromolecules 2002;35:10119–30.
[21] Hahm SG, Lee TJ, Chang T, Jung JC, Zin W-C. Macromolecules 2006;39:5385–92.
[22] Vaughn KE, Sousa M, Kang D, Rosenblatt C. Appl Phys Lett 2007;90:194102/1–194102/3.
[23] Geary JM, Goodby JW, Kmetz AR, Patel JS. J Appl Phys 1987;62:4100–8.
[24] Ishihara S, Wakemoto H, Nakazima K, Mastuo Y. Liq Cryst 1989;4:669–75.
[25] Seo D-S, Muroi K-I, Isogomi T-R, Matsuda H, Kobayashi S. Jpn J Appl Phys 1992;31:2165–9.
[26] Seo D-S, Yoshida N, Kobayashi S, Nishikawa M, Yabe Y. Jpn J Appl Phys 1995;34:4876–9.
[27] Schwab AD, Agra DM, Kim J-H, Kumar S, Dhinojwala A. Macromolecules 2000;33:4903–9.
[28] Oh-e M, Hong S-C, Shen YR. Appl Phys Lett 2002;80:784–6.
[29] Lee SW, Chae B, Kim HC, Lee B, Choi W, Kim SB, et al. Langmuir 2003;19: 8735–43.
[30] Lee SW, Yoon J, Kim HC, Lee B, Chang T, Ree M. Macromolecules 2003;36:9905–16.
[31] Hahm SG, Lee TJ, Lee SW, Yoon J, Ree M. Mater Sci Eng B 2006;132:54–8.
[32] Akiyama H, Kudo K, Ichimura K, Yokoyama S, Kakimoto M, Imai Y. Langmuir 1995;11:1033–7.
[33] Ichimura K, Morino S, Akiyama H. Appl Phys Lett 1998;73:921–3.
[34] Wu Y, Kanazawa A, Shiono T, Ikeda T, Zhang Q. Polymer 1999;40:4787–93.
[35] Yaroshchuck O, Agra DMG, Zakrevskyy Y, Chien L-C, Lindau J, Kumar S. Liq Cryst 2001;28:703–7.
[36] Furumi S, Ichimura K. Adv Funct Mater 2004;14:247–54.
[37] Xiao S, Lu X, Lu Q. Macromolecules 2007;40:7944–50.
[38] Ichimura K, Tomita H, Kudo K. Liq Cryst 1996;20:161–9.
[39] Hahm SG, Lee SW, Lee TJ, Cho SA, Chae B, Jung YM, et al. J Phys Chem B 2008; 112:4900–12.
[40] Ichimura K, Akita Y, Akiyama H, Kudo K, Hayashi Y. Macromolecules 1997;30: 903–11.
[41] Kawatsuki N, Matsuyoshi K, Hayashi M, Takatsuka H, Yamamoto T. Chem Mater 2000;12:1549–55.
[42] Chae B, Lee SW, Ree M, Jung YM, Kim SB. Langmuir 2003;19:687–95.
[43] Uchida E, Kawatsuki N. Macromolecules 2006;39:9357–64.
[44] Jung KH, Hyun S-Y, Song D-M, Shin D-M. Opt Mater 2003;21:663–6.
[45] Shin D-M, Song D-M, Kim YB. Mater Sci Eng C 2004;24:127–30.
[46] Li X-D, Zhong Z-X, Lee SH, Ghang G, Lee M-H. Jpn J Appl Phys 2006;45:906–8.
[47] Obi M, Morino S, Ichimura K. Chem Mater 1999;11:1293–301.
[48] Trenor SR, Shultz AR, Love BJ, Long TE. Chem Rev 2004;104:3059–78.
[49] Kim C, Trajkovska A, Wallace JU, Chen SH. Macromolecules 2006;39:3817–23.
[50] Kim C, Wallace JU, Trajkovska A, Ou JJ, Chen SH. Macromolecules 2007; 40:8924–9.
[51] Kang H, Kwon K-S, Kang D, Lee J-C. Macromol Chem Phys 2007;208:1853–61.
[52] Sung S-J, Lee J-W, Kim H-T, Park J-K. Liq Cryst 2002;29:243–50.
[53] Xu C, Shiono T, Ikeda T, Wang Y, Takeuchi T. J Mater Chem 2003;13:669–71.
[54] Zhong Z-X, Li X, Lee SH, Lee M-H. Appl Phys Lett 2004;85:2520–2.
[55] Kawatsuki N, Ono H, Takatsuka H, Yamamoto T, Sangen O. Macromolecules 1997;30:6680–2.
[56] Lee SW, Chang T, Ree M. Macromol Rapid Commun 2001;22:941–7.
[57] Lee SW, Ree M. J Polym Sci Polym Chem 2004;42:1322–34.
[58] Furumi S, Nakagawa M, Morino S, Ichimura K. J Mater Chem 2000;10:833–7.
[59] Furumi S, Ichimura K. Thin Solid Films 2006;499:135–42.
[60] Gu HW, Xie P, Shen D-Y, Fu P-F, Zhang J-M, Shen Z-R, et al. Adv Mater 2003;15:1355–8.
[61] Gu HW, Xie P, Fu P-F, Zhang T-Y, Zhang R-B. Adv Funct Mater 2005;15:125–30.
[62] Hamciuc E, Sava I, Bruma M, Kopnick T, Schulz B, Sapich B, et al. Polym Adv Technol 2006;17:641–6.
[63] Zhang L, Peng Z, Yao L, Lv F, Xuan L. Liq Cryst 2008;35:163–71.
[64] Kang H, Kang D, Lee J-C. Liq Cryst 2008;35:1005–13.
[65] Kang H, Park JS, Kang D, Lee J-C. Macromol Chem Phys 2008;209:1900–8.
[66] Odian G. Principles of polymerization. New York: Wiley; 2004 [chapter 3].
[67] Kmetz AR, Nehring J. In: Sprokel GJ, editor. The physics and chemistry of liquid crystal devices. New York: Plenum Press; 1980.
[68] Witter V, Bauer G, Berreman DW. Phys Lett A 1976;56:142–4.
[69] Jerome B. Rep Prog Phys 1991;54:391–451.
[70] Fonseca JG, Galerne Y. Appl Phys Lett 2001;79:2910–2.
[71] Owens DK, Wendt RC. J Appl Polym Sci 1969;13:1741–7.
[72] Boer WD. Active matrix liquid crystal displays: fundamental and applications. Amsterdam: Elsevier; 2005.
[73] Lee SW, Kim SI, Lee B, Choi W, Chae B, Kim SB, et al. Macromolecules 2003;36:6527–36.
[74] Sekkat Z, Knoll W. Photoreactive organic thin films. San Diego: Academic Press; 2002.
[75] Liu Z-F, Loo BH, Baba R, Fujishima A. Chem Lett 1990:1023–6.
[76] Lee WJ, Kim W, Song K. Polymer(Korea) 2005;29:308–13.
[77] Yeung FS-Y, Kwok H-S. Appl Phys Lett 2006;88:063505/1–063505/3.
[78] Yeung FS-Y, Xie F-C, Wan JT-K, Lee FK, Tsui OKC, Sheng P, et al. J Appl Phys 2006;99:124506/1–124506/4.
[79] Yeung FS-Y, Li YW, Kwok H-S. Appl Phys Lett 2006;88:041108/1–041108/3.