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Liquid Crystal Alignment Behaviors of Polystyrene Derivatives Containing Coumarin Moieties

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We synthesized a series of polystyrene derivatives containing coumarin side groups, poly(7-(4-vinylbenzyloxy)coumarin) (P7COU#) and poly(7-(4-vinylbenzyloxy)4-phenylcoumarin) (P7COU4P#), where # is the molar content of 7-hydroxycoumarin and 7-hydroxy-4-phenyl coumarin, respectively, using polymer analogous reaction, in order to study the effect of the 7-hydroxycoumarin and 7-hydroxy-4-phenyl coumarin side groups on the liquid crystal (LC) alignment properties. The LC alignment behavior of these two series was investigated by photoalignment or rubbing alignment. The LC cells made from photoirradiated P7COU# and P7COU4P# films showed homogeneous planar LC alignment. We found that LC aligning ability of the LC cells made from rubbed P7COU# and P7COU4P# films were affected by the structure and molar content of coumarin side groups. For example, anchoring energy of the LC cell fabricated with rubbed P7COU82 (7×10^{-5} J/m^2) and P7COU4P81 (7×10^{-7} J/m^2) film was increased drastically and slightly compared to polystyrene (10^{-7}–10^{-8} J/m^2), respectively. Particularly, anchoring energy of the LC cell made from rubbed P7COU# having more than 51 mol % of the 7-hydroxycoumarin as a side groups is comparable to that of the conventional polyimide in the LCD industry.

Keywords Alignment; coumarin; liquid crystal; polystyrene

1. Introduction

Extensive researches about liquid crystal (LC) alignment have been performed with great interest in scientific research as well as in the liquid crystal display (LCD) industry. Among the many techniques proposed for LC alignment, rubbing alignment [1, 2] and photoalignment [3, 4] have been mainly recognized as a LC alignment process using polymeric films. Polyimide (PI) [5] and polystyrene (PS) [6–10] have been primarily studied as a polymeric alignment layer in rubbing techniques. Generally, the LC cell made from rubbed PI and PS film has been known to parallel and perpendicular LC alignment with respect to the rubbing direction, respectively. Among the many mechanisms proposed by other research groups,

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physico-chemical interaction [6, 11, 12] and microgroove effect [13–16] mechanisms have been mainly considered as a mechanism of LC alignment. In particular, not only interaction between LC molecules and micro and/or nanogroove but physico-chemical interaction between LC molecules and oriented chemical groups in main and side chain have been important role in LC alignment behavior [17].

Recently, photoalignment, one of the alternative approaches to the conventional method, as a type of noncontact LC alignment using photopolymer has taken a notice of promising alignment layer. Because photoalignment technique is a highly producible process due to clean process, adaptiveness to large glass, and unrestrictedness to surface morphology. A number of photoreactive polymers, which are photoisomeric [18–20], photodimeric [21–26], and photodegradable [27–29] polymers, have been studied for LC alignment in past decades. Especially, photoreactive polymer containing coumarin group has been considered as a candidate in advanced LC alignment layer due to good thermal property and uniform LC aligning ability [24–26].

In this paper, we examined the LC aligning behavior and molecular orientation for two series of polymeric materials, poly(7-(4-vinylbenzyloxy)coumarin) (P7COU#) and poly(7-(4-vinylbenzyloxy)4-phenylcoumarin) (P7COU4P#). Here, we discussed about relationship between LC alignment property and molar content, structure of coumarin side group using rubbing and photoalignment techniques.

2. Experimental Part

2.1. Materials

7-Hydroxycoumarin, 7-hydroxy-4-phenyl coumarin, 4-chloromethylstyrene, and potassium carbonate were purchased from Aldrich chemical Co. and nematic LC (ZLI-5900-000) was purchased from Merck Co. 4-Chloromethylstyrene (Aldrich) was purified by column chromatography on silica gel using hexane as an eluent to remove any impurities and inhibitors such as *tert*-butylcatechol and nitroparaffin. Poly(chloromethylstyrene) (PCMS of $M_n = 34\,000$ and $M_w/M_n = 2.13$) was obtained through the conventional free radical polymerization of the purified 4-chloromethylstyrene (8.0 g, 52.6 mmol) using 2,2′-azobisisobutyronitrile (AIBN) (2.0 wt % based on monomer) in dried THF (50 mL) under a nitrogen atmosphere. AIBN (Junsei Chemical Co., Ltd.) was used as an initiator. AIBN was purified from crystallization using methanol. *N*,*N*'-dimethylacetamide (DMAc) was dried over molecular sieves (4 Å). Tetrahydrofuran (THF) was dried by refluxing with benzophenone and sodium followed by distillation. All other reagents and solvents were used as received.

2.2. Poly(7-(4-vinylbenzyloxy)coumarin) [P7COU#]

The potassium salt of 7-hydroxycoumarin was prepared by reacting 7-hydroxycoumarin (0.533 g, 3.29 mmol) with potassium carbonate (0.909 g, 6.58 mmol) in a purified 50 mL DMAc. After mixture of the potassium salt of 7-hydroxycoumarin was stirred in DMAc (50 mL) at 80°C for 1 hr, the DMAc solution (50 mL) of the PCMS (0.5 g, 3.29 mmol) was added in this flask. The mixture was magnetically stirred at 80°C for 3 hr under nitrogen atmosphere. After the mixture was cooled to room temperature, it was poured into methanol. The bright-gray precipitate was filtered out, it was reprecipitated several times with methanol. It was washed with water to remove potassium carbonate and remaining salts and then dried under vacuum overnight. Reaction conditions and synthesis results

Table 1. Characterization results of the polymers

Polymer designation	Degree of substitution (%)	M_n[a]	M_w/M_n[a]	T_g (°C)	T_d (°C)[b]
PCMS	0	34,000	2.13	106	250
P7COU31	31	36,000	2.58	124	254
P7COU51	51	35,000	2.48	124	261
P7COU65	65	36,000	2.58	127	265
P7COU82	82	41,000	2.34	132	275
P7COU4P15	15	36,000	2.22	138	280
P7COU4P44	44	37,000	2.56	145	285
P7COU4P57	57	38,000	2.48	147	292
P7COU4P81	81	42,000	2.20	150	300

[a]Obtained from GPC using THF as solvent with respect to monodisperse polystyrene as standard.
[b]Decomposition temperature (T_d) was defined as 1 wt% loss.

of the P7COU# are summarized in Table 1. The P7COU# was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and characterized by ^{1}H NMR spectroscopy.

P7COU# ^{1}H NMR (DMSO-d_6, δ, ppm): 1.0-2.4 (m, 3H, −C*H*$_2$−CPh*H*−), 4.8-5.2 (s, 2H, Ph−C*H*$_2$−O−), 6.0-6.2 (d, 1H, −OCOC*H*=CH−), 6.2-6.6 (m, 1H, −OPh*H*−), 6.6-7.6 (m, 6H, Ph*H*CH$_2$−, −OPh*H*−), and 7.6-8.0 (d, 1H, −OCOCH=C*H*−).

The degree of substitution was found to be about 82 %. This was calculated by comparing the doublet at 7.6–8.0 ppm with the backbone peak at 1.0–2.4 ppm which included the contribution of residual poly(chloromethylstyrene). This polymer was designated as P7COU82 (Table 1).

The copolymers were prepared from the same procedure, which was used for P7COU82, except that less than 100 mol-% of 7-hydroxycoumarin was used. For example, P7COU31, P7COU51, and P7COU65 were prepared with 7-hydroxycoumarin of 0.213 g (1.32 mmol), 0.320 g (1.97 mmol), and 0.427 g (2.63 mmol), respectively, using slight excess amounts of potassium carbonate (0.909 g, 6.58 mmol, and 200 mol-% compared with PCMS).

2.3. Poly(7-(4-vinylbenzyloxy)4-phenylcoumarin) [P7COU4P#]

The potassium salt of 7-hydroxy-4-phenyl coumarin was prepared by reacting 7-hydroxy-4-phenyl coumarin (0.784 g, 3.29 mmol) with potassium carbonate (0.909 g, 6.58 mmol) in a purified 50 mL DMAc. After mixture of the potassium salt of 7-hydroxy-4-phenyl coumarin was stirred in DMAc (50 mL) at 80°C for 1 hr, the DMAc solution (50 mL) of the PCMS (0.5 g, 3.29 mmol) was added in this flask. The mixture was magnetically stirred at 80°C for 3 hr under nitrogen atmosphere. After the mixture was cooled to room temperature, it was poured into methanol. The white precipitate was filtered out, it was reprecipitated several times with methanol. It was washed with water to remove potassium carbonate and remaining salts and then dried under vacuum overnight. Reaction conditions and synthesis results of the P7COU4P# are summarized in Table 1. The P7COU4P# was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and characterized by ^{1}H NMR spectroscopy.

P7COU4P# ^{1}H NMR (DMSO-d_6, δ, ppm): 1.0–2.4 (m, 3H, −C*H*$_2$−CPh*H*−), 4.8–5.2 (s, 2H, Ph−C*H*$_2$−O−), 6.2–6.7 (m, 2H, −OPh*H*−), 6.0–6.2 (d, 1H, −OCOC*H*=CH−), and 6.7–7.6 (m, 10H, Ph*H*CH$_2$−, −OPh*H*−, CH=CPh*H*).

The degree of substitution was found to be about 81%. This was calculated by comparing the doublet at 6.0–6.2 ppm with the backbone peak at 1.0–2.4 ppm which included the contribution of residual poly(chloromethylstyrene). This polymer was designated as P7COU4P81 (Table 1).

The copolymers were prepared from the same procedure, which was used for P7COU4P81, except that less than 100 mol-% of 7-hydroxy-4-phenyl coumarin was used. For example, P7COU4P15, P7COU44, and P7COU4P57 were prepared with 7-hydroxy-4-phenyl coumarin of 0.314 g (1.32 mmol), 0.469 g (1.97 mmol), and 0.626 g (2.63 mmol), respectively, using slight excess amounts of potassium carbonate (0.909 g, 6.58 mmol, 200 mol-% compared with PCMS).

2.4. Film Preparation and Alignment Process

Fused silica substrates were washed with acetone, isopropyl alcohol, and pure water. P7COU# and P7COU4P# and PCMS were dissolved in $CHCl_3$, these solutions were filtered using a PTFE membrane of pore size 0.45 μm. The polymer films were prepared by spin-coating (2000 rpm, 30 sec) in $CHCl_3$ (3 wt%) onto indium tin oxide coated glass substrates. Spin-coated films were baked at 80°C for 1 hr. The polymer coated substrates were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corp.). The rubbing density equation is written as $L/l = N[(2\,\pi rn/60v)\text{-}1]$, where L is the total length of the rubbing cloth (mm), l is the contact length of the circumference of the rubbing roller (mm), N is the cumulative number of rubbings, n is the speed (rpm) of the rubbing roller, r is the radius (cm) of rubbing roller, and the v is the velocity (cm/s) of the substrate stage [9,17]. Photoreaction was conducted by irradiating 200W high-pressure mercury lamp (66902, ThermoOriel Instruments) equipped with interference filter at 290 nm and attached to power supply (69911, ThermoOriel Instruments). Dichroic polarizer was used to irradiate with linearly polarized ultraviolet (LP-UV). The intensity of irradiated LP-UV light was measured by UV detector (UM-10, Minolta) with a sensor.

2.5. LC Cell Assembly

All of the twisted nematic (TN) and antiparallel LC cells were fabricated by incorporating either photoalignment or rubbing alignment. The TN and antiparallel LC cells were fabricated using spacers of thickness of 6.5 and 50 μm, respectively. The cells were filled with same nematic LC, ZLI-5900-000 (Merck Co., $n_e = 1.6327$ $n_o = 1.5011$, and $\triangle\varepsilon = 15.5$, where n_e, n_o, and $\triangle\varepsilon$ represent the extraordinary refractive index, ordinary refractive index, and dielectric anisotropy, respectively), by capillary action. The manufactured LC cells were sealed with epoxy glue.

2.6. Instrumentation

^{1}H NMR measurement was carried out on a JEOL-LA at 300MHz. The samples were dissolved with deuterated solvent (tetramethylsilane as an internal reference). Gel permeation chromatography (GPC) was used to measure the molecular weight and polydispersity index of synthesized polymer with respect to PS standard using $CHCl_3$ as an eluent. Differential scanning calorimeter (DSC) measurement was carried out on TA instruments 2920 at a heating and cooling rate of 10°C/min under nitrogen atmosphere at a flow rate of 60 cm^3/min. Glass transition temperature was determined from the onset temperature of the

small transition region in the thermogram obtained in the second heating. Thermal gravimetric analysis (TGA-2050, TA instrument) was used to investigate thermal stability of polymer samples. Samples were heated from room temperature to 800°C at the heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 80 cm^3/min. UV-Vis spectra were acquired using Perkin Elmer Lamda 20 spectrometer. Fourier transform infrared (FTIR) measurement was carried out on Perkin Elmer Spectrum 2000 spectrometer in the transmission mode. Polarized FTIR measurement was carried out on Perkin Elmer Spectrum 2000 spectrometer equipped with a polarizer. FTIR spectra were recorded 4 cm^{-1} resolution as a function of the rotation angle of polarizer and interferograms were accumulated 256 times. The electro-optical property of LC alignment was investigated using optical apparatus equipped with He-Ne laser, polarizer, analyzer, and photodiode detector. The anchoring energy was measured from TN LC cell using optical apparatus equipped with photoelastic modulator (PEM-90TM, HINDS instruments) with a modulation frequency of 50 kHz, a polarizer and analyzer pair, photodiode detector, lock-in amplifier (Stanford Research Systems, SR 830 DSP), digital voltmeter (KEITHLEY, Model 2000 multimeter), and stage controller (Mark-202, Sigma Koki Co.) [30]. Anchoring energy of the LC cells was calculated using torque balance equation. Torque balance equation is 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 LC, the d_e is the cell gap measured using spectrophotometer, Φ is intended twist angle, and $\triangle\varphi$ is actual twist angle. The actual twist angle was determined by comparing a theoretical curve to the experimental curve derived from the transmitted laser intensity, as reported by others [31]. The cell gap was measured before LC filling using spectrophotometer (Ocean optics Inc., S2000). POM images of the LC cell were taken from an optical microscope (Nikon, ECLIPSE E600 POL) equipped with crossed polarizer and digital camera (Nikon, COOLPIX 995).

3. Results and Discussion

Figure 1 shows synthetic routes to the PS derivatives containing 7-hydroxycoumarin (P7COU#) and 7-hydroxy-4-phenyl coumarin (P7COU4P#) side groups. PCMS was obtained by the conventional free radical polymerization of chloromethylstyrene using 2,2′-azobisisobutyronitrile (AIBN). P7COU# and P7COU4P# were obtained by the reaction of

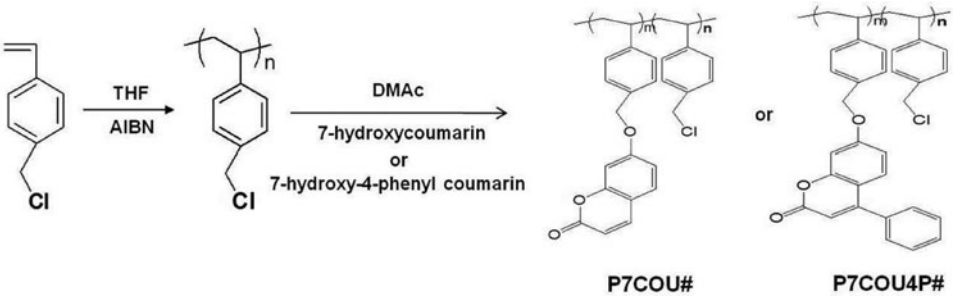

Figure 1. Synthetic route to poly(7-(4-vinylbenzyloxy)coumarin) (P7COU#) and poly(7-(4-vinylbenzyloxy)4-phenylcoumarin) (P7COU4P#), where # is the molar content of 7-hydroxycoumarin and 7-hydroxy-4-phenyl coumarin, respectively.

poly(chloromethylstyrene) with 7-hydroxycoumarin and 7-hydroxy-4-phenyl coumarin via polymer analogous reaction, respectively. The maximum conversions from chloromethyl to the coumarin chromophore are about 80%, respectively. The characterization results for the polymers using GPC, DSC, and TGA measurements are listed in Table 1. The average molecular weights (M_n) of these synthesized polymers were always larger than 34 000 from the GPC measurement, indicating that polymer modification from PCMS to P7COU# and P7COU4P# gives rise to increase of average molecular weights of polymers, as expected. However, the average molecular weights were smaller than the theoretical molecular weights of P7COU# and P7COU4P#. Since these molecular weights were measured using GPC, which only provides the relative molecular weight not the absolute molecular weight, a direct comparison might not be valid. Nevertheless, an increase in the average molecular weights of polymers indicates little or no backbone cleavage in polymer modification from PCMS to P7COU# and P7COU4P#. These polymers are soluble in many medium-polarity solvents having low boiling points, such as THF and chloroform, and in aprotic polar solvents, such as DMF, NMP, and DMAc.

The thermal properties of these polymers were investigated using DSC and TGA. Primarily, the PCMS shows amorphous behavior because of only one small transition at around 106°C. The P7COU# and P7COU4P# also exhibit amorphous behavior because of formation of atactic structure and existence of the short spacer to prevent crystallization. T_gs of the P7COU# and P7COU4P# were observed in the range of 124–132°C and 138–150°C, respectively. T_gs of the P7COU4P# are higher than those of the P7COU# due to the existence of the inflexible and aromatic structures (7-hydroxy-4-phenyl coumarin) to reduce side chain motion. As the molar content of the 7-hydroxycoumarin and 7-hydroxy-4-phenyl coumarin increased, T_g of the copolymers increased. TGA was used to determine the thermal stability for the P7COU# and P7COU4P# (Table 1). The decomposition temperature (T_d) defined as 1 weight percent loss was compared. At first, T_d of the PCMS is about 250°C. T_ds of the P7COU# and P7COU4P# were observed in the range of 250–275 and 280–300°C, respectively. T_ds of the P7COU4P# are higher than those of P7COU#. As the molar content of coumarin increased, the T_d of the copolymers increased. These results show that thermal characteristics are affected by the structure and molar content of coumarin side groups.

Figure 2 shows UV-Vis spectra measured from photoirradiated (a) P7COU82 and (b) P7COU4P81 film with LP-UV light with various exposure energies. The wavelength of maximum absorbance peaks (λ_{max}) are about 320 and 328 nm on P7COU82 and P7COU4P81 film, respectively, due to absorbance of the coumarin chromophore in the side groups. λ_{max} results for P7COU82 and P7COU4P81 show that incorporation of 7-hydroxy-4-phenyl coumarin group gives rise to bathochromic shift of λ_{max} about 8 nm. This is arises from the results of reduction of energy gap between HOMO and LUMO (red shift arises from short-path transition to π^* antibonding orbitals which occur in the ultraviolet region for a coumarin chromophore), if the phenyl ring is added. On UV irradiation of P7COU82 and P7COU4P81 film, as the UV irradiation energy increased, intensity of absorbance peak (λ_{max}) decreased by [2+2] cycloaddition of the C=C bond in the coumarin chromophore. As shown in the intensity difference of absorbance peak, the yield of the photoproduct of the P7COU4P81 is relatively lower compared with that of P7COU82. Incorporation of 7-hydroxy-4-phenyl coumarin having relatively bulky and rigid structures gives rise to disruption of molecular packing arrangement by steric configuration. This significantly may decrease the photoreactivity of double bonds in the coumarin chromophore with UV light.

Uniformly homogeneous alignment for LC cell fabricated with photoirradiated P7COU82 film was observed by polarized optical microscopy, whereas aligning ability

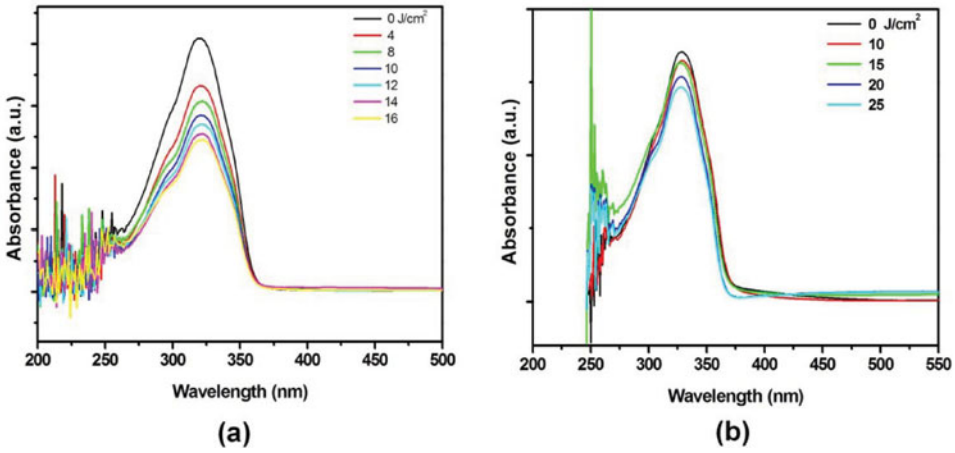

Figure 2. UV-Vis spectra measured from (a) P7COU82 and (b) P7COU4P81 film irradiated with LP-UV light with various exposure energies.

of the LC cell fabricated with P7COU4P81 film was not uniformly good in whole area (images not shown). Angular dependence of the transmittance was observed by optical apparatus equipped with He-Ne laser in order to investigate LC aligning ability accurately. Figure 3 shows the angular dependence of transmittance of monitoring source through TN LC cell made from photoirradiated (a) P7COU82 and (b) P7COU4P81 film as a function of rotation angle of samples. Before irradiated with LP-UV on P7COU82 and P7COU4P81 film, a uniform alignment of TN LC cell was not observed by monitoring transmittance of the LC cell. Homogeneous planar alignment of LC cell fabricated with photoirradiated P7COU82 film was observed after irradiating with UV exposure energy more than about 5 J/cm^2. When irradiated with UV exposure energy about 16 J/cm^2, LC cell made from the photoirradiated P7COU82 film have good LC aligning ability. However, planar

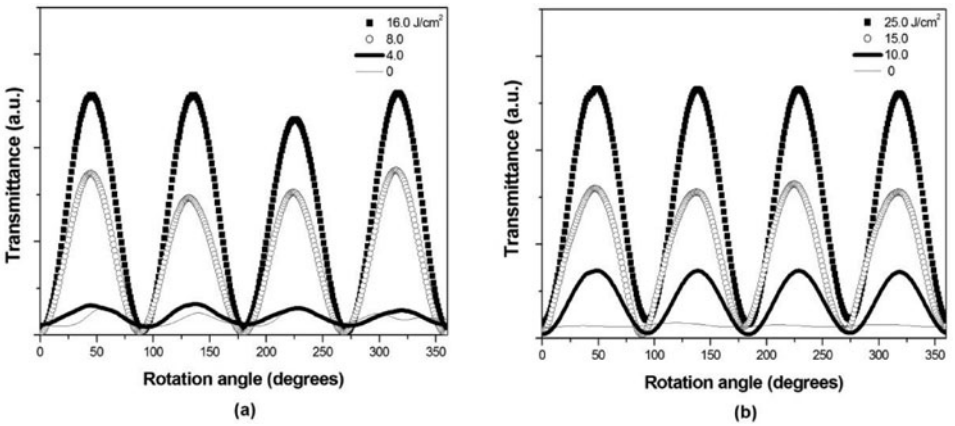

Figure 3. (a) Angular dependence of transmitted light intensity of a LP He-Ne laser through a LC cell made from (a) P7COU82 and (b) P7COU4P81 film. Exposure doses were 0(–), 4(—), 8(○), and 16(■) J/cm^2 for P7COU82 and 0(–), 10(—), 15(○), and 25(■) J/cm^2 for P7COU4P81 film, respectively.

alignment of LC cell made from photoirradiated P7COU4P81 film was observed after irradiating with UV exposure energy more than about 10 J/cm^2. As irradiated with UV exposure energy about 25 J/cm^2, LC cell made from the photoirradiated P7COU4P81 film had highest contrast ratio of the maximum transmittance to minimum transmittance. The LC molecules on P7COU82 and P7COU4P81 films are oriented perpendicular with respect to the LP-UV irradiation direction (data not shown). We cannot closely examine correlation between molecular structure of the copolymers (P7COU# and P7COU4P#) and LC alignment property. We believe that LC molecules interact anisotropically with the oriented segment of photoproduct and the oriented segment of remaining molecule (undimerized coumarin ring and poly(chloromethylstyrene) via π–π and/or dipole–dipole and/or van der Waals interaction.

Antiparallel LC cells made from rubbed P7COU82 film with a rubbing density of 250 and photoirradiated P7COU82 film with UV exposure energy of 16 J/cm^2, and photoirradiated P7COU4P81 film with UV exposure energy of 25 J/cm^2, respectively, in order to examine the annealing effect of LC cell. Figure 4 represent polar diagram for the transmittance of monitoring source through the annealed LC cell made from rubbed P7COU82 film for 10 min as a function of rotation angle of samples. As shown in Fig. 4, transmittance behavior of monitoring source through the LC cell made from rubbed P7COU82 film with a rubbing density of 250 and photoirradiated P7COU82 film with UV exposure energy of 16 J/cm^2 is similar at various temperature such as room temperature, 100, and 150°C, although the T_g of P7COU82 is about 132°C. Similarly, polar diagram of monitoring source passed through the LC cell made from photoirradiated P7COU4P81 film with UV exposure energy of 25 J/cm^2 have maintained at annealing temperature of 200°C above the T_g (150°C) of P7COU4P81 (data not shown). However, when the annealed time at 150 and 200°C was longer than 1 hr, the LC cells fabricated with the rubbed/photoirradiated P7COU82 and photoirradiated P7COU4P81 film showed random planar LC alignment behavior with birefringenced. On the other hand, good uniformity of the planar LC alignment behavior was maintained over the whole area when the annealing temperature was lower than the T_g. We did not observe polar diagram for the transmittance of the LC cell fabricated with rubbed P7COU4P81 film. Because LC aligning ability of the LC cell made from rubbed P7COU4P81 film was not good in whole area.

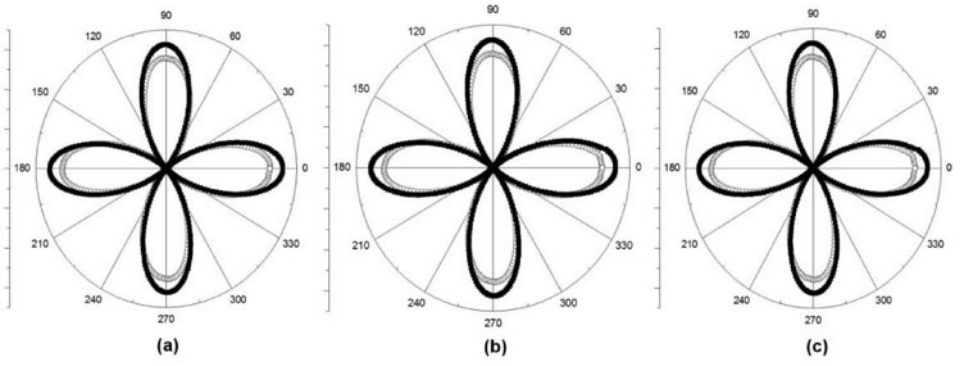

Figure 4. Polar diagram of the light intensity of antiparallel LC cell made from P7COU82 film annealed at (a) room temperature (b) 100°C/10min and (c) 150°C/10min with a rubbing density of 250 and UV exposure energy of 16 J/cm^2 as a function of rotation angle of analyzer (■: rubbing alignment, □: photoalignment).

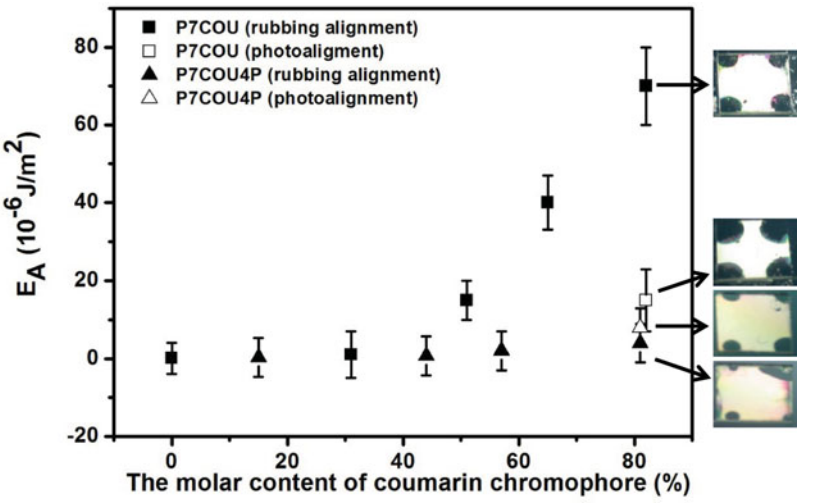

Figure 5. Anchoring energy of TN LC cells fabricated with rubbed and photoirradiated P7COU# and P7COU4P# films as a function of the molar content of coumarin chromophore.

Anchoring energy of LC cell fabricated with rubbed and photoirradiated P7COU# and P7COU4P# film was measured using same method as previously reported [30, 31]. Figure 5 shows anchoring energy of LC cells fabricated with rubbed and photoirradiated P7COU# and P7COU4P# films as a function of molar content of coumarin chromophore. At first, anchoring energy of the LC cell fabricated with photoirradiated P7COU82 film is in the level of $\sim 10^{-5}$ J/m^2. This value is as much as that of the LC cell made from photoirradiated coumain polymer films, as previously reported [32]. Anchoring energy of the LC cell fabricated with photoirradiated P7COU4P81 film is about 3×10^{-6} J/m^2. Anchoring energy of the LC cell made from rubbed poly(chloromethylstyrene) (PCMS) film with a rubbing density of 250 is estimated to 10^{-7} to 10^{-8} J/m^2. This value is similar with that of the LC cell fabricated with rubbed PS film in previous reports [6–9]. Anchoring energy of the LC cell made from rubbed P7COU# increased as the molar content of 7-hydroxycoumarin side group increased. Particularly, anchoring energies of the LC cell fabricated with rubbed PS derivatives containing more than 51 mol% of the 7-hydroxycoumarin (P7COU82, 65, and 51) with a rubbing density of 250 are larger than 10^{-5}J/m^2 (1×10^{-5} to 7×10^{-5} J/m^2). These anchoring energies of P7COU#s (P7COU82, 65, and 51) are comparable with those of conventional PI (from $\sim 10^{-5}$ to $\sim 10^{-3}$ J/m^2) in the LCD industry. However, anchoring energies of the LC cells fabricated with rubbed PS derivatives containing 7-hydroxy-4-phenyl coumarin with a rubbing density of 250 are about 10^{-7}J/m^2. The anchoring energies of the LC cells made from rubbed P7COU4P#s (P7COU4P81, 57, 44, and 15) with a rubbing density of 250 were measured in the range from 3×10^{-7} to 7×10^{-7} J/m^2. The anchoring energy of the LC cell fabricated with rubbed P7COU4P# was slightly increased, as the molar content of 7-hydroxy-4-phenyl coumarin increased. Conclusively, anchoring energy of rubbed P7COU# is higher than that of rubbed P7COU4P#s indicating that anchoring energy values are depended on the molecular structure and molar content of coumarin side group.

Figure 6 shows polarized FTIR spectra of (a) rubbed P7COU82 film with a rubbing density of 150 and (b) photoirradiated P7COU82 film with UV exposure energy of 16

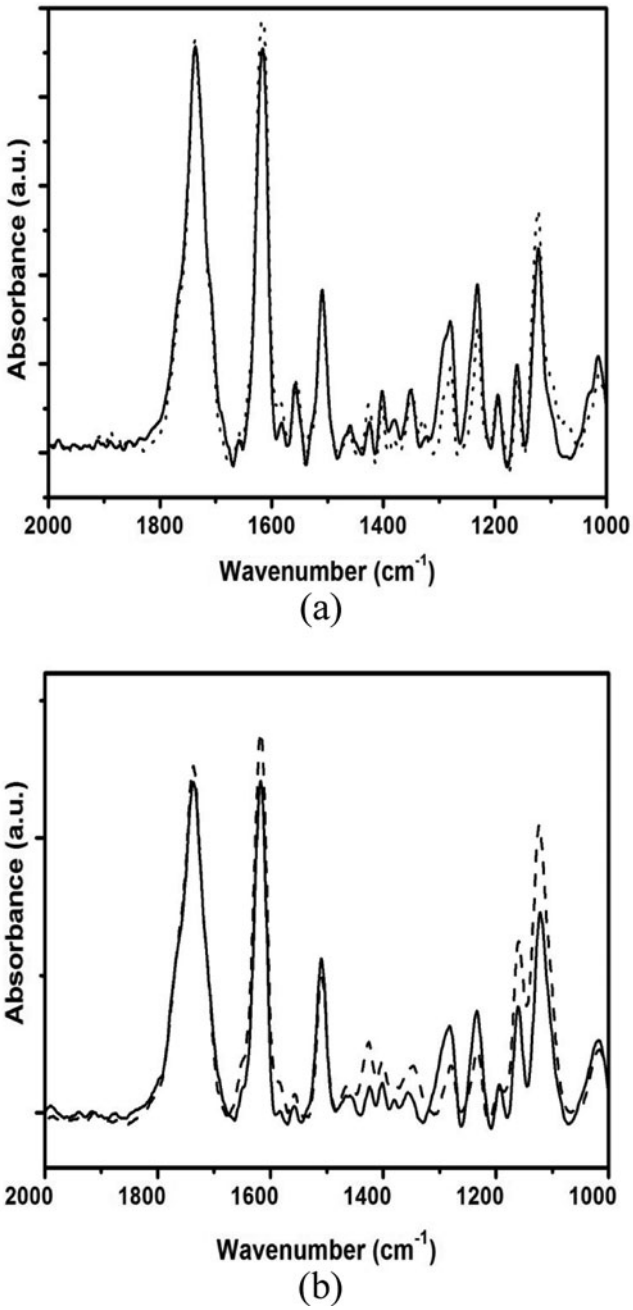

Figure 6. FTIR dichroic spectra of (a) rubbed P7COU82 film with a rubbing density of 150 and (b) photoirradiated P7COU82 film with UV exposure energy of 16 J/cm^{2}on Si-wafer. Solid and dotted line indicate FTIR spectra with IR source perpendicular with respect to the rubbing direction and with IR source parallel with respect to the rubbing direction, respectively.

J/cm^2 on Si wafer with the IR monitoring light perpendicular and parallel to the rubbing and photoirradiation direction. Absorbance peaks at 1732, 1614, 1401, and 1159 cm^{-1} individually represent the stretching vibration of C=O, the stretching vibration of C=C, the stretching vibration of C=C (cis form), and the stretching vibration of unconjugated ester. Spectra not shown, IR spectra of unrubbed and unphotoirradiated P7COU82 film show no dichroic aspect for IR light. But, IR spectra of (a) rubbed and (b) photoirradiated P7COU82 film represent dichroic aspect for polarized IR light. Anisotropy of intensity of absorbance of the IR spectra results from in-plane orientation of molecules on the film. That is, absorbance of specific vibrational IR peaks of rubbed and photoirradiated P7COU82 film depends on whether perpendicular or parallel to IR light. However, data not shown, FTIR spectra of rubbed and photoirradiated P7COU4P81 film represent no dichroic aspect for polarized IR light. We could not observe distinct changes of spectra of rubbed and photoirradiated P7COU4P81 films. Dichroic aspects for polarized IR light of rubbed P7COU82 film imply anisotropic molecular orientation of rubbed and photoirradiated P7COU82 surface and isotropic molecular orientation of rubbed and photoirradiated P7COU4P81 surface.

To further study, a close examination about correlation between molecular orientation in polymer chain and LC alignment property was performed by measuring absorbance mode of linearly polarized infrared spectroscopy equipped with rotatable polarizer as a function of rotation angle of polarizer. A comparison of intensity of absorbance of interested IR peak was recorded as a polar diagram which is represented as a function of rotation angle of polarizer. Figure 7 shows polar diagram of specific vibrational IR peaks of rubbed P7COU82 with a rubbing density of 150 and photoirradiated P7COU82 film with UV exposure energy of 16 J/cm^2, measured by polarized infrared spectroscopy, as a function of rotation angle of polarizer. The stretching vibration of C=C at 1614 cm^{-1}, the symmetric stretching vibration of C−O−C at 1125 cm^{-1} of rubbed and photoirradiated P7COU82 film are stronger than that of any other direction as the IR light is perpendicular to the rubbing direction. Intensity of absorbance of interested four vibrational IR peaks is the strongest as the direction of IR source is perpendicular to the rubbing and photoirradiation direction. The result of the polarized FTIR spectroscopy of rubbed and photoirradiated P7COU82 film indicates that 7-hydroxycoumarin segment as a side chain and molecular segment of phenyl ring as a main chain is oriented preferentially perpendicular to the rubbing and photoirradiation direction. In this study, we intentionally used a nematic LC with a positive dielectric anisotropy, ZLI-5900-000, because this LC has been used widely for the LC cells showing homogeneous planar LC alignment behavior. Unfortunately, the detailed structures and compositions of this LC are not available from the company. Generally, LC molecules are composed of cyclic mesogenic structure such as phenyl and/or cyclohexyl groups, and polar terminal groups (positive LC, $\Delta\varepsilon > 0$) such as CN, F, or other dipolar groups. Possibly, the π–π and/or dipole–dipole interactions between the mesogenic groups and the aromatic groups on the polymer layers would affect the LC alignment behaviors. In our polymer system, the LC molecules interacts with the parallely oriented vinyl backbone, interacts with the perpendicularly oriented styrene and coumarin side groups. In viewpoint of relationship between LC alignment property and molecular orientation, ordering tendency can be effectively ensembled from vinyl and styrene backbone to coumarin side chains and then LC molecules can be strongly anchored at the polymer-LC interface due to the favorable anisotropic π–π and/or dipole–dipole interactions between LC molecules and the side groups preferentially oriented perpendicular with respect to the rubbing and photoirradiation direction. Therefore, molecular orientation of backbone and side chain gives rise to high anchoring energy of

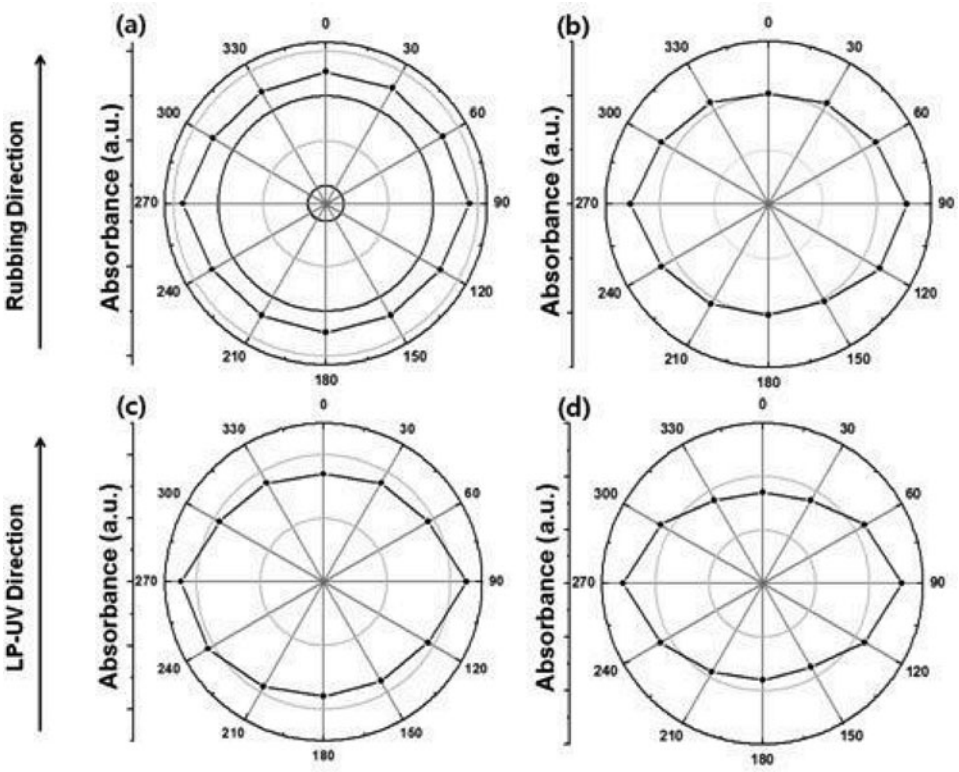

Figure 7. Polar diagram of specific vibrational IR peaks of rubbed P7COU82 ((a) υ(C═$C_{benzene}$) at 1614 cm^{-1} and (b) υ(C−O−C) at 1125 cm^{-1}) film with a rubbing density of 150 and photoirradiated P7COU82 ((c) υ(C═$C_{benzene}$) at 1614 cm^{-1} and (d) υ(C−O−C) at 1125 cm^{-1}) film with UV exposure energy of 16 J/cm^2, measured by polarized infrared spectroscopy, as a function of rotation angle of polarizer.

the LC cell fabricated with rubbed and photoirradiated P7COU82 film. However, data not shown, absorbance intensity of the stretching vibration of C═C at 1614 cm^{-1}, the symmetric stretching vibration of C−O−C at 1125 cm^{-1} of rubbed P7COU4P81 film are nearly same on any other direction, indicating that orientational order of polymer chains on P7COU4P81 film is different from that of P7COU82 film. Because, additional 4-phenyl group in the side 7-hydroxy-4-phenylcoumarin can disturb the perpendicular orientation of the side group which in turn can interfere with the π–π interactions between the aromatic side groups on the rubbed surface and LCs. The difference of molecular anisotropy at rubbed surface leads to have a gap of the anchoring energy between P7COU82 and P7COU4P81 cell. We concluded that P7COU82 showing molecular in-plane anisotropy on rubbed surface strongly anchored with LC, whereas P7COU4P81 showing molecular isotropy on rubbed surface very weakly anchored with LC.

4. Conclusions

Poly(7-(4-vinylbenzyloxy)coumarin) (P7COU#) and poly(7-(4-vinylbenzyloxy)4-phenylcoumarin) (P7COU4P#) were prepared by changing the feed ratio of 7-hydroxycomarin and 7-hydroxy-4-phenyl coumarin with poly(chloromethylstyrene) using

polymer analogous reaction, respectively. P7COU4P# having bulky phenyl ring between photoreactive double bond on the coumarin ring give rise to increase of UV irradiation energy and decrease of yield of the photoproducts compared to P7COU#. We found that the LC cell made from rubbed P7COU# film have a good LC aligning ability (strong anchoring behavior), whereas that fabricated with rubbed P7COU4P# have a poor LC aligning ability (weak anchoring behavior), respectively. The strong anchoring behavior of P7COU# was ascribed to the increased π–π and/or dipole–dipole interactions between polymer films and LC by anisotropic molecular orientation and weak anchoring behavior of P7COU4P# was ascribed to the disturbance of the π–π and/or dipole–dipole interactions between the aromatic side groups on the rubbed surface and LCs by additional 4-phenyl group in the side 7-hydroxy-4-phenylcoumarin.

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