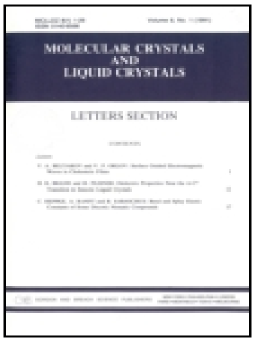

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Photoalignment Behavior on Polystyrene Films Containing Coumarin Moieties

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We synthesized a series of polystyrene derivatives containing coumarin side groups, poly(6-(4-vinylbenzyloxy)coumarin)(P6COU#), where # is the molar content of 6-hydroxycoumarin using polymer modification reaction, in order to study the effect of the 6-hydroxycoumarin side groups on the liquid crystal (LC) alignment properties. The LC alignment behavior of these polymers was investigated using photoalignment method. The LC cells made from photoirradiated P6COU# films exhibited homogeneous planar LC alignment with a pretilt angle of approximately 0°. We found that LC aligning ability of the LC cells made from photoirradiated P6COU# films was affected by the molar content of 6-hydroxycoumarin side groups. For example, the azimuthal anchoring energy of a P6COU80 compared to P6COU25 is about 1×10^{-5} *J/m*^{2} *and* 5×10^{-7} *J/m*^{2}*, respectively. The electro-optical characteristics of the LC cells fabricated with P6COU80 films such as voltage holding ratio and residual DC voltage, threshold voltage, driving voltage, and response time were as good as those fabricated from rubbed polyimide films, the most commonly used LC alignment layers.*

Keywords Coumarin; liquid crystal; photoalignment; polystyrene

1. Introduction

Extensive researches about liquid crystal (LC) alignment techniques and materials have been studied with great interest in scientific field as well as in the liquid crystal display (LCD) industry. Among the several techniques proposed for uniform orientation of the LC molecules, rubbing alignment [1, 2] and photoalignment [3, 4] have been mainly recognized on the LC alignment process using polymeric films. Rubbed polyimide (PI) [5] having parallel LC aligning ability with respect to the rubbing direction and polystyrene (PS) [6–10] having perpendicular LC aligning ability with respect to the rubbing direction have been primarily studied as a polymeric alignment material, respectively. Among the several mechanisms proposed by other research groups, physico-chemical interaction [6, 11, 12] and groove effect [13–16] mechanisms have been mainly considered as a mechanism of LC alignment. In particular, not only relationship between LC molecules and micro- and/or nanoscale groove but physico-chemical interaction between LC molecules and oriented

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*Address correspondence to Dr. H. Kang, Department of Chemical Engineering, Dong-A University, Nakdong-Daero 550beon-gil, Saha-gu, Busan, 604-714, Republic of Korea. E-mail: hkang@dau.ac.kr chemical groups on surface of the alignment materials have known to play an important role in determining the LC alignment behavior [17].

Photoalignment, one of the alternative approaches to the conventional contact method such as rubbing alignment, as a type of noncontact method using photoreactive polymer has taken a notice of promising alignment technique. Because photoalignment technique is a highly producible process due to its various advantages such as clean process, adaptiveness to large glass, and unrestrictedness to surface morphology. Recently, a number of photoreactive polymers, which are photoisomeric [18–20], photodimeric [21–26], and photodegradable [27–29] polymers, have been studied for LC alignment. Especially, photoreactive polymers containing coumarin group have been recognized as a candidate in next generation LC alignment materials due to the good thermal properties and uniform LC aligning abilities [24, 25].

In this paper, we examined the LC aligning behavior of polymeric alignment materials, poly(6-(4-vinylbenzyloxy)coumarin)(P6COU#). Here, we discussed about relationship between LC alignment behavior and molar content of coumarin side group using photoalignment techniques. The synthesis and characterization of these polymers and the detailed electro-optical properties of the LC cells made from P6COU# films are included.

2. Experimental Part

2.1. Materials

6-Hydroxycoumarin, 4-chloromethylstyrene, and potassium carbonate were purchased from Aldrich Chemical Co. *N,N′*-Dimethylacetamide (DMAc) was dried over molecular sieves (4 Å). 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 such as *tert*-butylcatechol and nitroparaffin. Poly(chloromethylstyrene) (PCMS of $M_n = 28\ 000$ and $M_n/M_w = 2.12$) was obtained through the conventional free radical polymerization of the purified 4-chloromethylstyrene (10.0 g, 65.8 mmol) using AIBN (2.0 wt% based on monomer) in dried THF (50 mL) under a nitrogen atmosphere. 2,2’-Azobisisobutyronitrile (AIBN, Junsei Chemical Co., Ltd.) was used as an initiator. AIBN was purified from crystallization using methanol. All other reagents and solvents were used as received.

2.2. Preparation of Polystyrene Derivatives Containing Coumarin Side Groups (P6COU#)

A mixture of 6-hydroxycoumarin (0.85 g, 5.92 mmol, 180 mol% compared with PCMS) and potassium carbonate (0.91 g, 6.58 mmol) in DMAc (20 mL) was heated to 70°C. A PCMS (0.5g, 3.29 mmol) solution in DMAc (10 mL) was added to the mixture and then magnetically stirred at 70°C for 3 hr under a 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 several reprecipitations from the DMAc solution into methanol and then washed with water to remove potassium carbonate and any remaining salts. The product was obtained in above 80% yield after drying overnight in a vacuum.

Table 1. Synthesis and LC alignment properties of polystyrene derivatives containing coumarin side groups

Polymer designation	Degree of substitution (%)	M_n[a]	M_n/M_w[a]	T_g (°C)	Pretilt angle (degree)[b]	LC alignment direction (degree)[c]
PCMS	0	28 000	2.12	106	0	90 ↔ 270
P6COU25	25	30 000	2.30	138	0	90 ↔ 270
P6COU42	42	32 000	2.25	136	0	90 ↔ 270
P6COU59	59	33 000	2.38	136	0	90 ↔ 270
P6COU80	80	33 000	2.22	136	0	90 ↔ 270

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

[b] Measured from the antiparallel LC cell fabricated with photoirradiated polymer films using crystal rotation method.

[c] Measured from the angular dependence of the absorbance of a dichroic dye dissolved in 5CB on the rotation angle of the samples.

^{1}H NMR (DMSO-d_6): $\delta = 1.0$–2.4 (m, 3H, –CH_2—CPhH—), 4.8—5.2 (s, 2H, Ph—CH_2—O—), 6.0–6.2 (d, 1H, –OCOCH = CH–), 6.2–6.6 (m, 1H, —OPhH—), 6.6–7.6 (m, 6H, PhHCH$_2$—, —OPhH—), 7.6–8.0 (d, 1H, —OCOCH=CH—).

IR (Si-wafer): 1732 (C=O), 1614 (C=C in benzene ring), 1125 cm^{-1} (C(C=O)—O).

The degree of substitution was found to be about 80%. 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 P6COU80 (Table 1).

Other PS derivatives containing coumarin side groups were synthesized from the same procedure used for the preparation of P6COU80 except for differing amounts of 6-hydroxycoumarin in the reaction. For example, P6COU59, P6COU42, and P6COU25 were prepared with 6-hydroxycoumarin of 0.533 g (3.29 mmol), 0.426 g (2.63 mmol), and 0.268 g (1.65 mmol), respectively, using slight excess amounts of potassium carbonate (0.909 g, 6.58 mmol, 200 mol% compared with PCMS).

2.3. *Film Preparation and LC Cell Assembly*

Solutions of P6COU#s and PCMS in CHCl$_3$ (2 wt%) were prepared. These solutions were filtered using a PTFE membrane with a pore size of 0.45 μm. The polymer films were obtained by spin-coating (2000 rpm, 30 sec) onto ITO-coated glass substrates. The film thickness was measured using ellipsometer (Auto gain ellipsometer L116B, Gaertner). Photoalignment process of the films was also conducted by irradiating under a 200 W high-pressure mercury lamp (66902, ThermoOriel Instruments) equipped with an interference filter at 290 nm and attached to a power supply (69911, ThermoOriel Instruments). A dichroic polarizer was used to irradiate with linearly polarized UV (LPUV). The intensity of the LPUV was 6 mW/cm^2. The exposure dose of irradiated LPUV was measured with a UV detector (UM-10, Minolta) equipped with a sensor. Twisted nematic (TN) and antiparallel LC cells were fabricated using the photoirradiated polymer films onto 2 cm × 2 cm ITO-coated glass slides. TN and antiparallel LC cells were made by assembling the films together orthogonally and antiparallel with respect to the polarization direction of LPUV for the photoirradiated polymer films using spacers with a thickness of 6.5 and 50 μm, respectively. The LC cells were filled with a nematic LC, 4-*n*-pentyl-4′-cyanobiphenyl (5CB, $n_e = 1.7360$, $n_o = 1.5442$, and $\Delta\varepsilon = 14.5$, where n_e, n_o, and $\Delta\varepsilon$ represent extraordinary refractive indexes, ordinary refractive indexes, and dielectric anisotropy, respectively), in an isotropic state in order to avoid creating flow alignment through capillary action, and were then sealed with epoxy.

2.4. Instrumentation

^{1}H NMR measurement was carried out on a JEOL-LA at 300 MHz. Gel permeation chromatography (GPC) was used to measure the molecular weight (M_n) and molecular weight distributions (M_n/M_w) of the synthesized polymer with respect to PS standards using THF as an eluent and a UV detector. Differential scanning calorimeter (DSC) measurements were carried out on a TA Instruments 2920 at a heating and cooling rate of 10°C/min under a nitrogen atmosphere. FTIR spectra were recorded at a resolution of 4 cm^{-1} and interferograms were accumulated 64 times. UV-Vis spectra of the polymer films were taken on a Perkin Elmer Lamda 20 spectrometer. The electro-optical property of LC cells was investigated using an optical apparatus equipped with a He–Ne laser, polarizer, analyzer, and photodiode detector. 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) dissolved in 5CB at a concentration of 1 wt% on the rotation angle of the samples using optical apparatus equipped with a He-Ne laser, a polarizer, and a photodiode detector [17]. The pretilt angle of antiparallel LC cell was measured by rotating the LC cell along the LC alignment direction by the crystal rotation method [26]. The azimuthal anchoring energy was measured from the TN LC cells using an optical apparatus equipped with a photoelastic modulator (PEM-90 TM, HINDS instruments) with a modulation frequency of 50 kHz, a pair of polarizer and analyzer, 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.) [27]. 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, the d_e is the cell gap measured using the spectrophotometer, Φ is the intended twist angle, and $\Delta\varphi$ the is actual twist angle. The actual twist angle was determined by comparing a theoretical curve to the experimental curve derived from transmitted laser intensity as reported by others [28]. The voltage–transmittance (*V–T*) was measured from the LC cell using the same method as that reported by others [29, 30]. The threshold voltage (V_{th}) in the *V-T* curve are defined as the voltages at which the transmittance was increased to 10% of the initial transmittance value [29, 30]. The rising (T_r) and falling (T_f) response times for the white-to-black and black-to-white changes, respectively, are defined as the time to transition from 10% to 90% transmittance and vice versa [29,30]. The total response time (T_t) is determined by the average of T_r and T_f. The cell gap was measured before LC filling using spectrophotometer (Ocean optics Inc., S 2000). The polarized optical microscopy (POM) images of the LC cell were taken using

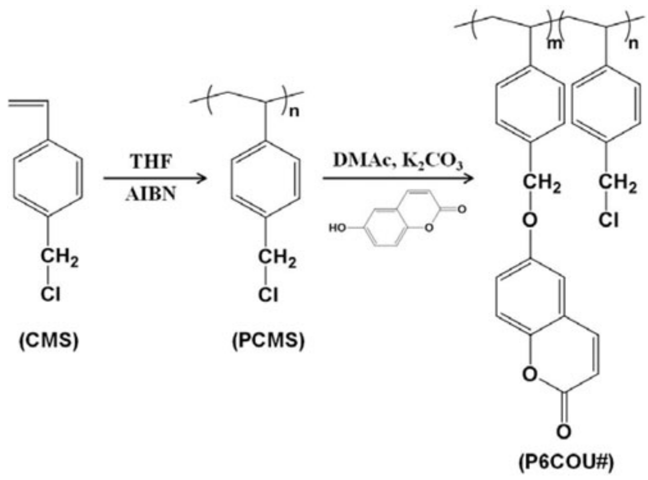

Figure 1. Synthetic route of polystyrene derivatives containing 6-hydroxycoumarin side groups (P6COU#), where # indicates the mole percent of 6-hydroxycoumarin containing monomeric units in the polymer.

an optical microscopy (Nikon, ECLIPSE E600 POL) equipped with a polarizer and digital camera (Nikon, COOLPIX995).

3. Results and Discussion

Figure 1 shows synthetic routes to the PS derivatives containing 6-hydroxycoumarin side groups (P6COU#). PCMS was obtained by the conventional free radical polymerization of chloromethylstyrene using AIBN. P6COU#s were obtained by the reaction of poly(chloromethylstyrene) with 6-hydroxycoumarin via polymer modification reaction, respectively. The maximum conversions from chloromethyl group to the coumarin chromophore are about 80%. The characterization results for the polymers using GPC and DSC measurements are listed in Table 1. The average molecular weights (M_n) of these synthesized polymers were always larger than 30 000 from the GPC measurement, indicating that polymer modification from PCMS to P6COU# 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 P6COU#. 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 P6COU#. These polymers are soluble in many medium-polarity solvents having low boiling points, such as THF and $CHCl_3$, and in aprotic polar solvents, such as DMF, NMP, and DMAc.

The thermal properties of these polymers were investigated using DSC measurement as shown in Fig. 2. At first, the PCMS shows amorphous behavior because of only one small transition at around 106°C. The P6COU# also exhibit amorphous behavior because of formation of atactic structure and existence of the short spacer to prevent crystallization. T_gs of the P6COU# were observed in the range of 136–138°C, respectively. T_gs of the P6COU# are higher than that of the PCMS due to the existence of the inflexible and aromatic structures to reduce side chain motion.

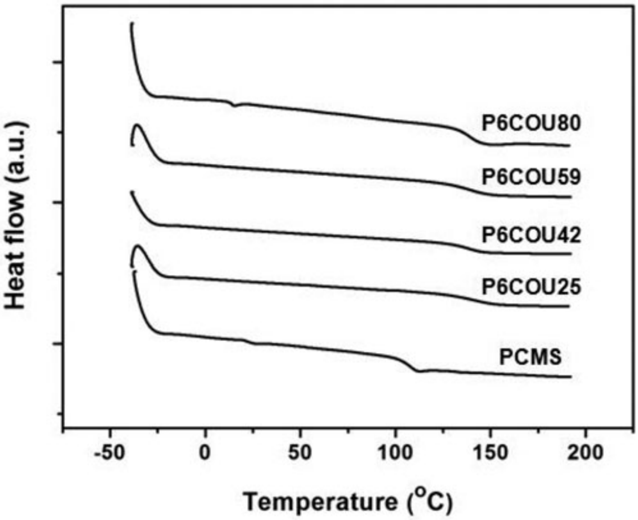

Figure 2. DSC thermogram of the polymers.

Quantitative analysis of transparency of P6COU# films having thickness of about 100 nm were evaluated using UV-Vis spectra to investigate the possibility for the surface coating applications (Fig. 3). The transmittance value of the P6COU# film is similar with that of bare glass substrate. For example, regardless of the molar content of 6-hydroxycoumarin moiety in the polymers, the transmittance of the P6COU# films is above 96% at 550 nm, which is similar with that of bare glass substrate. Conclusively, the optical transparency of all of the films in the visible light region is good enough to be used as optical materials for flexible display devices.

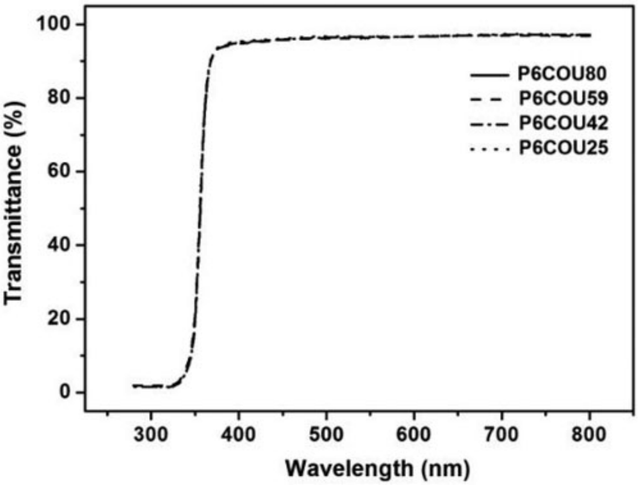

Figure 3. UV-Vis spectra of the P6COU# films on glass substrates prepared by a spin-coating method.

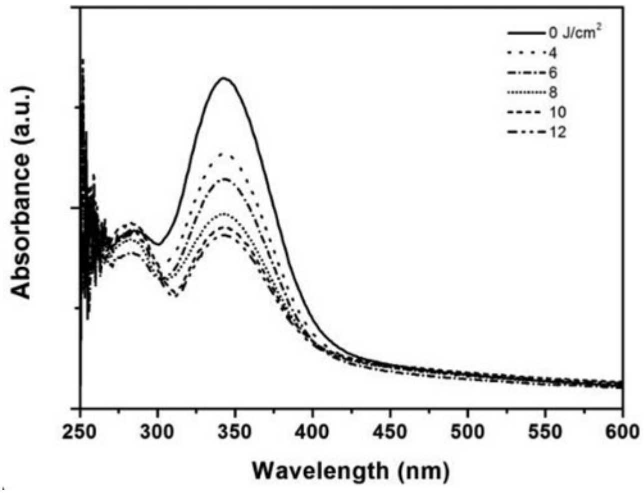

Figure 4. UV-Vis spectra measured from P6COU80 film irradiated with LPUV light with various exposure energies.

Figure 4 shows UV-Vis spectra measured from photoirradiated P6COU80 film with LPUV light with various exposure energies. The wavelength of maximum absorbance peaks (λ_{max}) are about 343 nm on P6COU80 film due to the absorbance of the coumarin chromophore in the side groups. On UV irradiation of P6COU80 film, as the UV irradiation energy increased, intensity of absorbance peaks (λ_{max}) decreased by [2+2] cycloaddition of the C=C bond in the coumarin chromophore.

Uniformly homogeneous planar alignment for LC cell fabricated with photoirradiated P6COU80 film was observed by POM (image not shown). The pretilt angle of the LC cell made from photoirradiated P6COU80 film is approximately 0° (Table 2). Angular dependence of the transmittance of monitoring source through TN LC cell made from photoirradiated P6COU80 film was also observed by optical apparatus equipped with He–Ne laser in order to investigate LC aligning ability accurately (Fig. 5). Before irradiated with LPUV on P6COU80 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 P6COU80 film was observed after irradiating with UV exposure energy more than about 4 J/cm^2. When irradiated with UV exposure energy about 12 J/cm^2, LC cell made from the photoirradiated P6COU80 film have good LC aligning

Table 2. Voltage holding ratio (VHR), residual DC voltage (R-DC), voltage-transmittance, and response time value of the LC cell made from polymer film

			Voltage-transmittance (V-T)			Response time (ms)		
Sample	VHR (%)	R-DC (mV)	V_{th}	V_{50}	V_{on}	T_r	T_f	T_t
P6COU80	99	30	1.10	1.33	1.75	13	23	36
PI	99	30	1.08	1.30	1.70	12	24	36

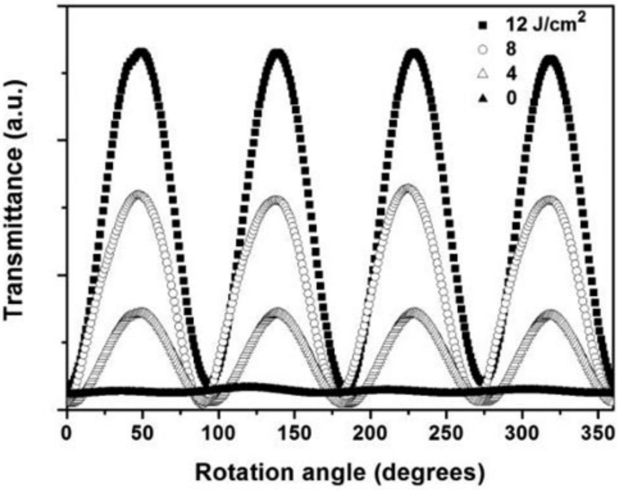

Figure 5. Angular dependence of transmitted light intensity of a LP He–Ne laser through a LC cell made from photoirradiated P6COU80 film.

ability. The antiparallel LC cells made from photoirradiated films of P6COU80 showed maximum absorbances along the 90°↔270° direction by monitoring the polar diagrams of the absorbance of the dichroic dye (disperse blue 1) in the LC cells as a function of rotation angle of samples indicating that the LC molecules on P6COU80 films are oriented perpendicular with respect to the LPUV irradiation direction, possibly, although others reported that coumarin containing polymers give the parallel LC alignment with respect to the LPUV irradiation direction [31]. Since the LC alignment direction on the coumarin containing acrylate-based polymer films can be affected by various factors such as polymer structure such as spacer length, regioisomerism and UV irradiation condition, and others [24–32]. We further observed the LC alignment direction on other copolymer films, P6COU25, P6COU42, and P6COU59, irradiated with UV exposure energy about 4, 8, and 12 J/cm^2 to investigate the effect of the 6-hydroxycoumarin group on the LC alignment behavior. The LC molecules on all polymer films are oriented perpendicular with respect to the LPUV irradiation direction (Table 2). However, we cannot clearly determine correlation between molecular structure of the atactic styrene based copolymers (P6COU#) having an oxymethyl spacer between phenyl ring and coumarin ring in the side group and LC alignment properties. The LC (5CB) molecules used in this study are composed of biphenyl group and polar terminal groups such as cyano group. We believe that 5CB molecules interact anisotropically with the oriented segment of photoproduct and the oriented segment of remaining molecule such as undimerized coumarin ring and poly(chloromethylstyrene) on the P6COU# films via π–π and/or dipole–dipole and/or van der Waals interaction.

Azimuthal anchoring energy values of the LC cell fabricated with photoirradiated P6COU# film was measured using same method as previously reported [35,36]. Figure 6 shows anchoring energy values of LC cells fabricated with photoirradiated P6COU# films as a function of molar content of coumarin chromophore. At first, anchoring energy of the LC cell fabricated with photoirradiated P6COU25 film is in the level of $\sim 10^{-7}$ J/m^2 similar with that of rubbed PS film [8]. Anchoring energy of the LC cell fabricated with photoirradiated P6COU42 and P6COU59 film is about 6×10^{-6} and 8×10^{-6} J/m^2, respectively. However,

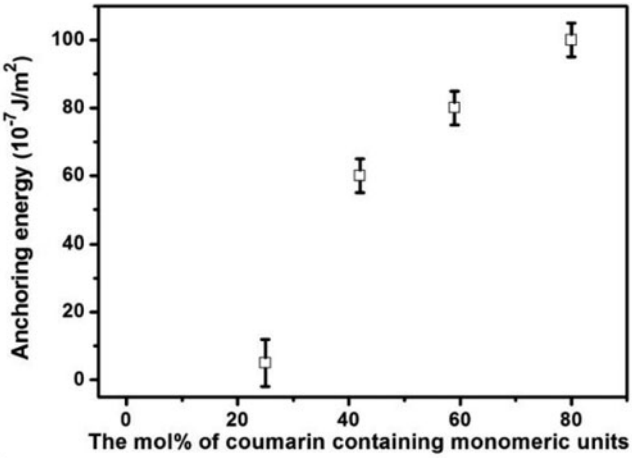

Figure 6. Azimuthal anchoring energy of TN LC cells fabricated from photoirradiated P6COU# films as a function of the mole percent of coumarin containing monomeric units.

anchoring energy of the LC cell fabricated with photoirradiated P6COU80 film is in the level of ∼10^{-5} J/m^2. This value is as much as that of the LC cell made from photoirradiated coumain polymer films and comparable with those of conventional PI (from ∼10^{-5} to ∼10^{-3} J/m^2) in the LCD industry, as previously reported [1,37]. Conclusively, anchoring energy values of the LC cell made from photoirradiated P6COU# increased as the molar content of 6-hydroxycoumarin side group increased.

Antiparallel LC cells made from photoirradiated P6COU80 film with UV exposure energy of 12 J/cm^2 in order to examine the thermal stability of LC cell. Figure 7 represent polar diagram for the transmittance of monitoring source through the LC cell made from photoirradiated P6COU80 film as a function of rotation angle of samples. Transmittance behavior of monitoring source through the LC cell made from photoirradiated P6COU80 film with UV exposure energy of 12 J/cm^2 is similar at various temperature such as room temperature, 150, and 200°C, although the T_g of P6COU80 is about 136°C, indicating that LC aligning ability have maintained at annealing temperature of 200°C above the T_g (136°C) of P6COU80. Conclusively, LC aligning ability of annealed P6COU80 LC

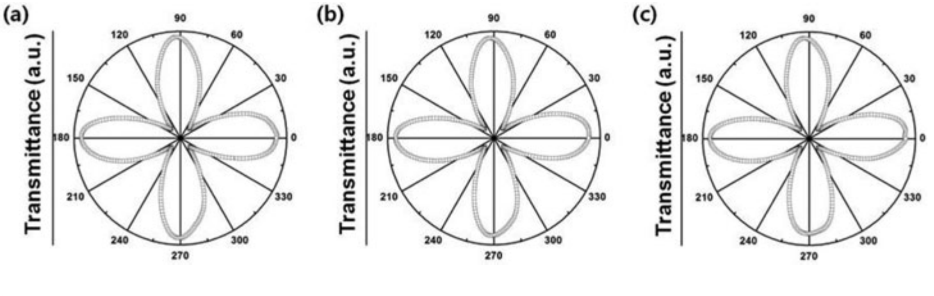

Figure 7. Polar diagram of the light intensity of antiparallel LC cell from photoirradiated P6COU80 film annealed at (a) room temperature, (b) 150°C/10 min, and (c) 200°C/10 min with an irradiation energy of 12 J/cm^2 as a function of rotation angle of samples.

cell have maintained above T_g, although the molecular motion of main and side chain of P6COU80 has been taken place above T_g.

The electro-optical performance of the LC cells having the same cell gap of about 6.5 μm was determined by measuring the *V–T* and response time values using the same conditions (Table 2). The V_{th}, V_{on}, and response time of the photoirradiated P6COU80 film were 1.10 V, 1.75 V, and 36 ms, respectively, are close to those of rubbed PI in the LCD industry, 1.08 V, 1.70 V, and 36 ms, respectively.

Recently, there are increased attentions on the development of flexible LC displays using plastic substrates [38]. The LC cells made from the P6COU80 film on flexible polyethylene terephthalate (PET) substrate also show the planar LC alignment behavior. Furthermore, the LC cell on the PET showed very consistent planar LC aligning ability maintaining an extremely low pretilt angle of about 0° after bending it 100 times (data not shown). Therefore, P6COU80 can be considered as candidate optical materials for flexible displays, such as in planar alignment mode and applications.

4. Conclusions

Poly(6-(4-vinylbenzyloxy)coumarin)(P6COU#, where # is the molar content of coumarin side groups in%) were prepared by changing the feed ratio of 6-hydroxycomarin with poly(chloromethylstyrene) using polymer modification reaction. Stable and homogeneous planar LC cells could be prepared from these polymer films through the photoalignment process. The LC alignment properties, such as azimuthal anchoring energy, were found to be affected by the molar content of the coumarin side groups in the PS derivatives containing coumarin side groups. For example, as the molar content of coumarin side groups increased from 25% to 80%, the azimuthal anchoring energy increased from 5×10^{-7} to 1×10^{-5} J/m^2. The strong anchoring behavior of P6COU80 was ascribed to the increased π–π and/or dipole–dipole interactions between polymer films and LC molecules by anisotropic molecular orientation. The electro-optical properties such as the threshold voltage, driving voltage, and response time of the LC cell fabricated with the photoirradiated P6COU80 film was as good as that of the LC cell fabricated with the commercial PI film in the LCD industry, indicating that these cells can be used for practical LC display applications including flexible displays.

Acknowledgments

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