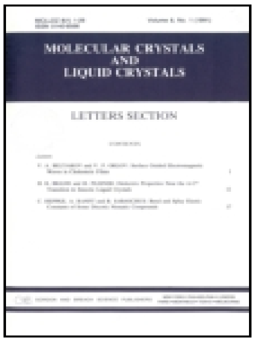

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Polystyrene Blend Alignment Layers for High Pretilt Angle Control

Hyo Kang[a] and Daeseung Kang[b]

[a]Department of Chemical Engineering, Dong-A University, Saha-gu, Busan , Republic of Korea; [b]Department of Electrical Engineering, Soongsil University, Dongjak-gu, Seoul , Republic of Korea

ABSTRACT

We prepared blend alignment layer based on 4-ethylphenoxymethyl-substituted polystyrene (P4EP) and polystyrene containing 7-hydroxycoumarin (P7COU) for liquid crystal (LC) alignment. Stable and uniform vertical LC cells having pretilt angles adjustable from 90° to 81.2° were obtained from these polystyrene films having molar contents of P4EP and P7COU in the ranges of 100–70 and 0–30 mol%, respectively. The LC alignment behavior was well correlated with the wettability of the polymer films. These polystyrene blends having good solubility in many organic solvents and their films having low process (curing) temperature can be candidates for LC alignment layer in the flexible display. This study contributes to the latest efforts to develop new alignment layers for pretilt angle control.

KEYWORDS

Alignment; liquid crystal; pretilt angle; polystyrene

Introduction

The pretilt angle control of liquid crystal (LC) has been extensively studied due to the scientific and technical interest in liquid crystal displays (LCDs) industry. In particular, it is desired to improve image quality and electro-optical (E-O) performance in LCD applications. Recently, several techniques have been developed to control the pretilt angle of LCs on the alignment layer surfaces, so as to be applied in several LCD modes; rubbing techniques of the polyimide surfaces [1, 2], photoirradiation using the photoresponsive alignment layer [3], ion beam treatments of the organic/inorganic hybrid alignment layer [4–7], blending of two kinds of polyimides for planar and vertical LC alignment [8–11], stacking of the alignment layers [12–14], and nano and/or micro-structures using lithographic techniques [15, 16]. Recently, Rosenblatt et al. and we reported that pretilt angles on polyimide films can be controlled by changing the baking temperature of the polyimide films from 230 to 290°C, rubbing density, and composition of the blends [11, 17–20].

Recently, we have found that 4-ethylphenoxymethyl-substituted polystyrene (P4EP) shows vertical LC alignment [21] and polystyrene derivatives containing 7-hydroxycoumarin (P7COU) exhibits enhanced planar LC alignment on rubbed film [22], respectively. In this study, we control the pretilt angle of the LC on these polystyrene blend films, P4EP having vertical alignment and P7COU having planar alignment, by changing the blending ratio ranging from 90/10 to 10/90, using the rubbing method. Moreover, changes of the pretilt angles

CONTACT Hyo Kang ✉ hkang@dau.ac.kr Department of Chemical Engineering, Dong-A University, 37 Nakdong-Daero 550beon-gil, Saha-gu, Busan 604-714, Korea.

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were found to be strongly related to changes of the surface wettability. The surface properties of polystyrene films giving different pretilt angles were investigated using contact angle measurements.

Experimental part

Materials

4-Ethylphenoxymethyl-substituted polystyrene (P4EP of $\overline{M_n} = 34,100$ and $\overline{M_w}/\overline{M_n} = 2.40$, $T_g = 49°C$) [21] and polystyrene derivatives containing 7-hydroxycoumarin (P7COU of $\overline{M_n} = 41,000$ and $\overline{M_w}/\overline{M_n} = 2.34$, $T_g = 132°C$) side groups [22] were synthesized using same method as described previously. All other reagents and solvents were used as received.

P7COU^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-).

P4EP^1 H NMR (CDCl$_3$): 1.0–1.2 (t, 3H, -O-Ph-CH$_2$-CH_3), 1.2–1.5 (m, 2H, -CH_2-CH-Ph-), 1.6–2.1 (m, 1H, -CH$_2$-CH-Ph-), 2.4–2.7 (m, 2H, -Ph-CH_2-CH$_3$), 4.6–5.0 (s, 2H, -Ph-CH_2-O-), 6.2–6.7 (m, 2H, -O-PhH-CH$_2$-CH$_3$), 6.7–6.9 (m, 2H, -O-PhH-CH$_2$-CH$_3$), 6.9–7.2 (m, 4H, -CH-PhH-CH$_2$-O-).

Polymer blend and film preparation

Polymer blends were prepared by precipitating 5 wt% solution containing in a weight ratio, 90/10, 70/30, 50/50, 30/70, and 10/90 of each component (P4EP and P7COU), into isopropyl alcohol. Polymer blends (P4EP and P7COU) were prepared from chloroform solutions. Blended polymers were dissolved in CHCl$_3$, these solutions were filtered using a polytetrafluoroethylene (PTFE) membrane of pore size 0.45 μm. Thin films of the blended polymers were prepared by spin-coating (2000 rpm, 30 sec) onto 20 × 20 mm^2 ITO coated glass substrates. Polyimide (PI, Nissan Chemical SE-7492K) alignment agents were spin coated (3000 rpm, 40 sec) onto 0.02 m × 0.02 m ITO coated glass substrates. The PI films were prebaked at 80°C for 15 min and then were fully baked at 220°C for 45 min.

Alignment process and LC cell assembly

The polymer films were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corp.). The rubbing density equation is written as $L/l = N[(2\pi rn/60v) - 1]$, where L is the total length of the rubbing cloth (mm), l the contact length of the circumference of the rubbing roller (mm), N the cumulative number of rubbings, n the speed (rpm) of the rubbing roller, r the radius (cm) of rubbing roller, and v the velocity (cm/s) of the substrate stage [23]. All of the antiparallel LC cells were fabricated using rubbed polymer film onto ITO-coated glass slides. Antiparallel LC cell were fabricated by assembling polymer films together orthogonally and antiparallel with respect to the rubbing direction using spacers of thicknesses of 6.5 and 50 μm, respectively. The LC cells were filled with a nematic LC, 4-n-pentyl-4′-cyanobiphenyl (5CB, $n_e = 1.736$, $n_o = 1.5442$, 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.

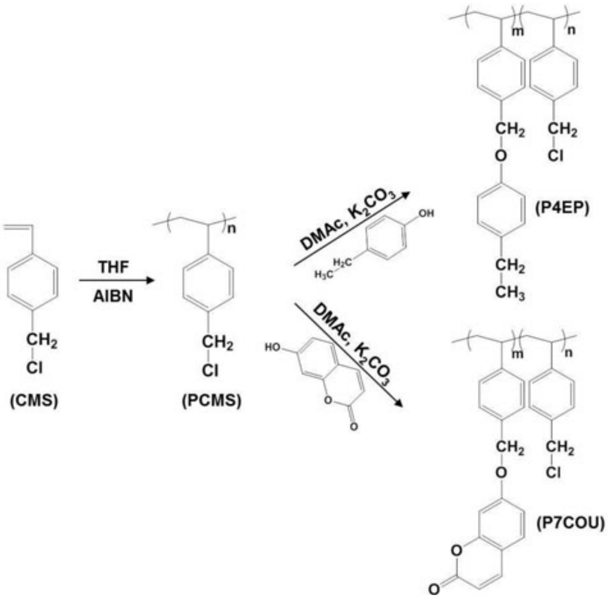

Figure 1. Synthetic route of 4-ethylphenoxymethyl-substituted polystyrene (P4EP) and polystyrene derivatives containing 7-hydroxycoumarin (P7COU).

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 ($\overline{M_n}$) and molecular weight distributions ($\overline{M_w}/\overline{M_n}$) of synthesized polymer with respect to polystyrene standards using chloroform ($CHCl_3$) as an eluent and UV detector at 254 nm. The optical transmittance of the polymer films was obtained using UV-Vis spectroscopy (Perkin Elmer Lamda 20 spectrometer). For the UV-Vis spectroscopy of polymer, the polymer films were prepared by spin-coating onto ITO coated glass substrates. The contact angles of distilled water on the polymer films were determined with a Kruss DSA10 contact angle analyzer equipped with drop shape analysis software. The electro-optical property of LC alignment was investigated using optical apparatus equipped with He-Ne laser, polarizer, analyzer, and photodiode detector. The pretilt angle of antiparallel LC cell was measured by rotating the LC cell by the crystal rotation method [24]. The cell gap was measured before LC filling using spectrophotometer (Ocean optics Inc., S 2000). Polarized optical microscopy (POM) images of LC cell were taken from an optical microscope (Nikon, ECLIPSE E600 POL) equipped with crossed polarizer and digital camera (Nikon, COOLPIX995).

Results and discussion

Figure 1 shows the synthetic route of 4-ethylphenoxymethyl-substituted polystyrene (P4EP) and polystyrene derivatives containing 7-hydroxycoumarin side groups (P7COU), respectively. Poly(chloromethylstyrene) (PCMS) was obtained by free radical polymerization of 4-chloromethylstyrene using 2,2′-*azobisisobutyronitrile* (AIBN) as an initiator in tetrahydrofuran (THF) and then P4EP and P7COU were obtained by the reaction of PCMS with 4-ethylphenol and 7-hydroxycoumarin in *N,N*′-dimethylacetamide (DMAc) using polymer analogous reactions in previous reports, respectively [21, 22]. Molar content of

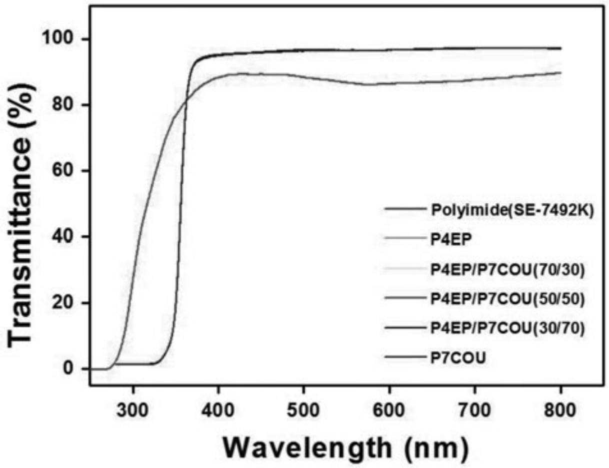

Figure 2. UV-Vis transmittance spectra of polystyrene derivatives and polyimide (SE-7492K) alignment layers onto quartz substrates.

4-ethylphenoxymethyl and 7-hydroxycoumarin containing side group of the polymers were about 100% and 82%, respectively. In this experiment, polystyrene blend films were prepared from a mixture fabricated with 90 and 10, 70 and 30, 50 and 50, 30 and 70, 10 wt% of P4EP and 90 wt% of P7COU, respectively.

Quantitative analysis of transparency of P4EP, P7COU, and blend (P4EP/P7COU(70/30), P4EP/P7COU(50/50), and P4EP/P7COU(30/70)) films was evaluated using UV-Vis spectra to investigate the possibility for the surface coating applications (Fig. 2). At first, the transmittance value of the coated blend as well as P4EP, P7COU film onto glass substrate is about 96% at a specific wavelength of 550 nm, which is similar with that of bare glass substrate. This value is higher than that (87%) of the widely used polyimide (SE-7492K) film as a LC alignment layer. Conclusively, the optical transparency in the visible light region of the blend polymer films was still sufficient for them to be used as optical materials for display applications.

Figure 3 shows POM images of the LC cells made from rubbed polymer films, (a) P4EP, (b) P4EP/P7COU(90/10), (c) P4EP/P7COU(70/30), (d) P4EP/P7COU(50/50), (e) P4EP/P7COU(30/70), and (f) P4EP/P7COU(10/90) using 5CB, respectively. The vertical LC alignment behavior of the P4EP, P4EP/P7COU(90/10), and P4EP/P7COU(70/30) was observed. These LC cells fabricated from the rubbed polymer blend films have maintained a vertical LC alignment for more than several months since we first made the LC cell. As the weight content of the P7COU in the polymer blend was increased, the defect area of the vertical LC alignment was slightly observed. When the weight content of the 4EP was larger than 50%, the LC cells fabricated with the polymer blend ((d) P4EP/P7COU(50/50), (e) P4EP/P7COU(30/70), and (f) P4EP/P7COU(10/90)) film showed planar LC alignment behavior having defect area.

The pretilt angles of the antiparallel LC cells fabricated with the polymer films were measured, in order to determine the effect of the weight content of the P4EP and P7COU on the LC alignment direction (Fig. 4). At first, the pretilt angle of the LC cell from only P4EP was found to be very high approximately 90°. When the weight content of P7COU increases from 0 to 30% for the LC cell made from polymer films, the pretilt angles on the polymer films decrease from approximately 90° to 81.2°. We could not measure the pretilt angles of the

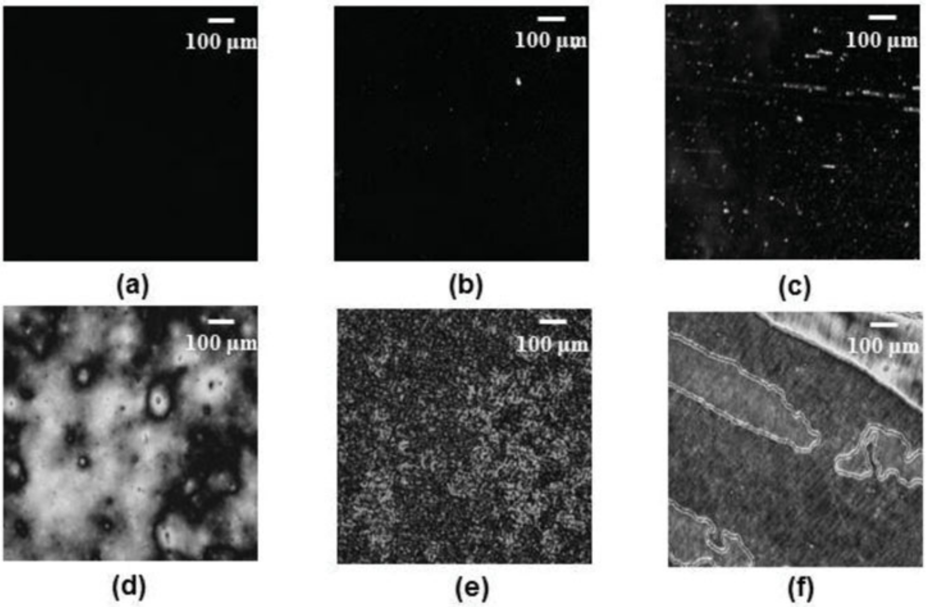

Figure 3. POM images of the LC cells made from rubbed polymer films ((a) P4EP, (b) P4EP/P7COU(90/10), (c) P4EP/P7COU(70/30), (d) P4EP/P7COU(50/50), (e) P4EP/P7COU(30/70), and (f) P4EP/P7COU(10/90)) using 5CB.

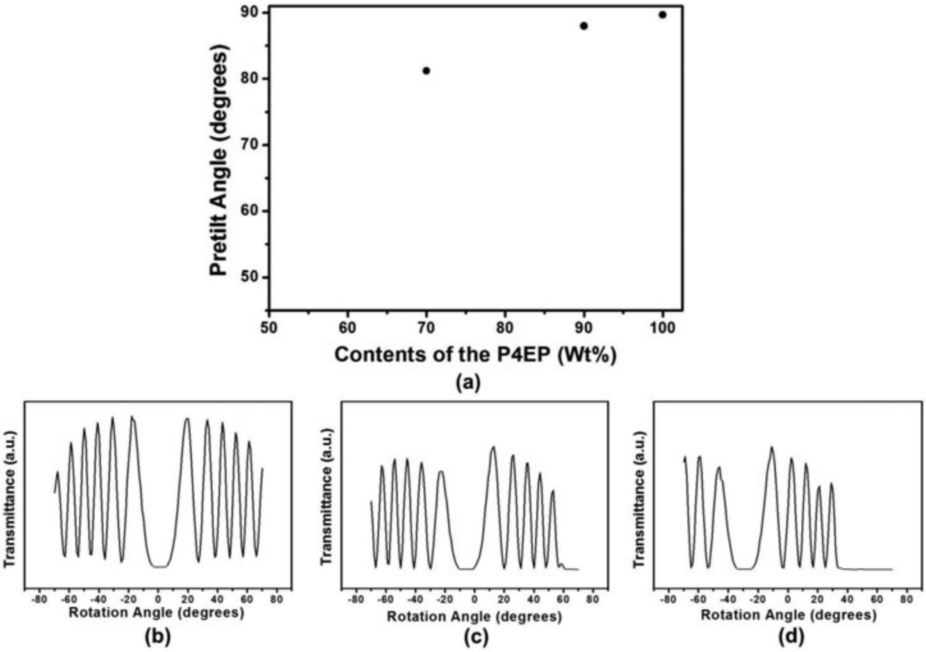

Figure 4. Observation of the (a) pretilt angles of the LC cells fabricated with rubbed blend films based on P4EP and P7COU using 5CB as a function of blending ratio and relationship between the transmittance and the incident angle in various LC cell ((b) P4EP, (c) P4EP/P7COU(90/10), and (d) P4EP/P7COU(70/30)) fabricated with the polystyrene derivatives films for measuring pretilt angles.

Table 1. Water contact angle and pretilt angle of the polymer blend films.

Polymer designation	Water contact angle (°)[a]	Pretilt angle (°)[b]
P4EP	88	89.7
P4EP/P7COU(90/10)	86	88.0
P4EP/P7COU(70/30)	84	81.2
P4EP/P7COU(50/50)	79	–[c]

[a] Measured from static contact angles.
[b] Measured from the antiparallel LC cells made from rubbed polymer films using crystal rotation method.
[c] Cannot be measured due to the poor LC alignment.

LC cells made from the polymer blend films having a weight content of P7COU larger than 50 wt%, due to their poor LC alignment behavior. The thermal stability of the LC cell made from the P4EP, P4EP/P7COU(90/10), and P4EP/P7COU(70/30) film was estimated from the pretilt angle after heating for 1 hr at 150°C, respectively. The distinguishiable difference of pretilt angle of the LC cells made from polymer film having vertical LC aligning ability cannot be observed, indicating that the pretilt angle of these LC cell was found to be maintained even at the high temperature. This is well above the glass transition temperature of P4EP, even though the molecular motion of P4EP occurred at approximately 49°C.

The contact angle values on polymer blend films according to the weight content of the P4EP and P7COU were measured to study the effect of the wettability on the pretilt angle of LCs (Table 1). We adopted distilled water contact angles on the blend polymer films in static mode. The contact angle values on polymer blend films increase with the increase of weight content of the P7COU indicating that the changes of pretilt angles are strongly related with the changes of wettability on polymer films as described by others [25, 26]; They are 88, 86, 84, and 79° at P4EP, P4EP/P7COU(90/10), P4EP/P7COU(70/30), and P4EP/P7COU(50/50), respectively.

Recently, considerable effort has been made to develop the LC alignment layers on the plastic substrates for flexible LC displays [27]. All of the LC cells made from the polymer blend films on plastic substrates exhibit similar LC alignment behavior compared with the LC cells made from same alignment films on ITO substrates as previously shown in Fig. 3 and their POM images are shown in Fig. 5. We found that the LC cells fabricated using the polymer blend films on plastic substrates show pretilt angle behaviors. For example, pretilt angle value (approximately 81°) for this LC cell made from P4EP/P7COU(70/30) film showed were maintained after bending it 100 times. Therefore, these films can be considered as candidate LC alignment layers for flexible LC displays.

Conclusions

We prepared a series of blend polystyrene films composed of 4-ethylphenoxymethyl-substituted polystyrene (P4EP) and polystyrene derivatives containing 7-hydroxycoumarin (P7COU). Stable and vertical LC cells could be prepared from these polymer films through the rubbing process. The pretilt angle of LC was controlled using LC cells made from rubbed polystyrene blend films by changing the mixing ratio. For example, the pretilt angle of the LC cell made from the P4EP films was about 90° and that of the LC cell made from the blend alignment layers having weight contents 4-ethylphenoxymethyl and 7-hydroxycoumarin groups of 70 and 30 wt% was approximately 81.2°. These polymers could be a good candidate as an alignment layer for flexible LC display applications because they have low processing temperatures and stable bending performances.

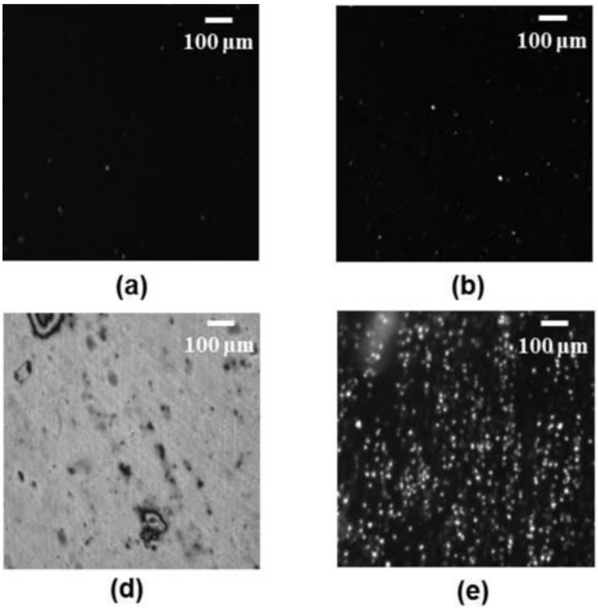

Figure 5. POM images of the LC cells made from rubbed polymer films ((a) P4EP, (b) P4EP/P7COU(90/10), (c) P4EP/P7COU(70/30), (d) P4EP/P7COU(50/50), (e) P4EP/P7COU(30/70), and (f) P4EP/P7COU(10/90)) on plastic substrates using 5CB.

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