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Liquid Crystal Alignment Behavior and OTFT Performance of Poly(3-hexylthiophene) Blends with Comb-Like Poly(oxyethylene)

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Abstract: Alignment characteristics of nematic liquid crystal (LC) on the surface of conjugated semi-conducting polymer blends with a comb-like polymer were studied. Conoscopic polarized optical microscope images show vertical alignment of LC on the blend films regardless of blend ratio. The LC alignment behavior on the blended film surface can be explained by a preponderance of comb-like polymers at the film surface. The mobility values of organic thin film transistors (OTFT) prepared with the blend film as an active layer are found to be similar to those with a pure conjugated semi-conducting polymer film. This result suggests a novel route for effectively reducing the amount of active semi-conducting polymer without significant deterioration of charge carrier mobility in an OTFT device. Since the LC alignment can be controlled on the surface of channel layer of OTFT by employing the polymer blend as the semi-conducting layer, the LC alignment and OTFT performance with the blend composition can be investigated simultaneously.

Keywords: polymer blend, comb-like polymer, surface property, liquid crystal alignment, organic thin film transistor.

Introduction

Comb-like poly(oxyethylene) with regularly arranged alkylsulfonyl side chains has been known to show very low surface energy (20-23 mN/m), close to those of poly(dimethylsiloxane) and poly(tetrafluoroethylene), which are the most commonly used polymers for low surface energy applications.[1-7] In particular, comb-like polymers can be used to adjust the surface properties of general polymers through polymer blending methods.[8-10] Polymer blending has also been employed for controlling surface properties of the blend film to induce liquid crystal (LC) alignment[5-7] and for improving electrical properties in organic thin film transistors (OTFT).[11] Polymer blends based on semi-conducting and insulating polymers used in OTFT have been studied to effectively improve the charge carrier mobility by adjusting film morphology, air stability, and mechanical strength.[12] Therefore, the polymer blending approach is important as an alternative and efficient method to modify surface properties of the film for LC alignment and for improving electrical properties of OTFTs.

For the past twenty years, OTFTs have attracted many researchers due to their potential capability of producing large scale and flexible devices owing to their easy and low cost fabrication.[13-15] Solution processable semi-conducting polymers such as poly(3-hexylthiophene) (P3HT) have been of interest, because they can be easily processed to form the polymer channel layer of OTFT by coating or ink-jet printing.[16-18] Recently, liquid crystal-on-organic field effect transistor (LC-on-OTFT) sensory devices with P3HT was reported as viable practical applications.[19] The LC-on-OTFT devices were fabricated by mounting LC molecules on the polymer channel layer of OTFT. Results showed that the presence of LC molecules on the channel layer caused enhanced drain currents due to a strong dipole effect of LC molecules and resulting in detection of extremely low level gas flows. The alignment of LC molecules on a surface of the channel layer is, therefore, an interesting subject for enhancement of drain currents in LC-on-OTFT. The LC alignment on the channel layer of OTFT can be controlled by employing the polymer blend of P3HT as a semi-conducting layer. In this study, polymer blends of semi-conducting P3HT with comb-like poly(oxyethylene) were investigated to understand effects of the blend composition on surface and electrical properties when the blend film was used as a channel layer in OTFT devices.

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Experimental

The chemical structure of poly[oxy(*n*-octylsulfonylmethyl)ethylene] (CH_3-8SE), a comb-like polymer, is shown in Figure 1, and it was synthesized according to a previously reported procedure.[1-7] Poly(3-hexylthiophene) (P3HT; M_w=50,000 g/mol), chlorobenzene, and diiodomethane were purchased from Sigma-Aldrich and were used without further purification. A nematic LC, 4-*n*-pentyl-4′-cyanobiphenyl (5CB), was received from Merck.

In order to prepare LC cells in which nematic LCs are sandwiched between two glass plates, a thin P3HT/CH_3-8SE blend film was spin-coated as an alignment layer on the glass plates. After cleaning with acetone, ethanol, and distilled water several times, glass plates were treated with hexamethyldisilazane (HMDS). Mixtures of P3HT and CH_3-8SE with different weight ratios of 100/0, 80/20, 60/40, 40/60, and 20/80 were dissolved in chlorobenzene with a concentration of 1 wt%. After filtering through a 0.45 μm polytetrafluoroethylene (PTFE) syringe filter, the solutions were spin-coated on the HMDS modified glass substrates at a rate of 2000 rpm for 60 s. They were then annealed at 200 °C for 30 min. LC cells were fabricated by assembling these glass plates together using spacers with a thickness of 4.79 μm. Nematic LC was injected into the LC cell using capillary action at a temperature above the nematic to isotropic transition temperature.

Bottom-gate and top-contact OTFT devices were fabricated on highly doped p-type Si with a 300 nm SiO_2 dielectric layer. Si/SiO_2 substrates were coated with P3HT/CH_3-8SE blend films using identical cleaning and coating conditions as described above. For source and drain electrodes, 50 nm Au electrodes were deposited on the P3HT/CH_3-8SE blend films by thermal evaporation. All procedures were carried out in a dry argon gas filled glove box. Electrical characteristics of OTFT devices were measured using a Keithley 4200 parameter analyzer in a glove box in the dark under an argon atmosphere.

The conoscopic polarized optical microscope (POM) images of LC cells were obtained at a scale of 200×magnification using an optical microscope (Eclipse E600 POL, Nikon) equipped with a polarizer and a digital camera. Surface topology of the polymer films was determined using tapping mode atomic force microscopy (AFM; SPA 400, Seiko) employing a silicon nitride cantilever with a resonance frequency of 320 kHz and a spring constant of 42 N/m. X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo Scientific) was conducted using an AlK_α radiation source operating at a constant power of 100W (15 kV and 10 mA). The binding energies were calibrated using the C 1s peak at 285.0 eV as a reference. For photoelectron spectra acquisition, the constant analyzer energy mode was employed at 40 eV and a step of 0.1 eV at a takeoff angle of 90°. The static contact angles of deionized water and diiodomethane were measured at room temperature using a Kruss DSA 10 contact angle analyzer that interfaced with drop shape analysis software. Contact angles for each sample were measured more than six times on three independently prepared films, and the values were averaged. The Owens-Wendt-Rabel-Kaelble method was used to calculate the surface energy of the polymer blend films.[20,21]

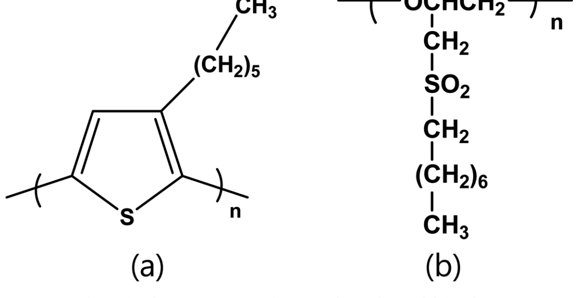

Figure 1. Chemical structures of (a) poly(3-hexylthiophene) (P3HT) and (b) poly[oxy(*n*-octylsulfonylmethyl)ethylene] (CH_3-8SE).

Results and Discussion

Chemical structures of two polymers of the blend P3HT/CH_3-8SE are shown in Figure 1. P3HT is a highly conjugated semi-conducting polymer with an aromatic backbone and an alkyl side chain. CH_3-8SE, which is a comb-like polymer with well ordered side chain structures, has been reported to show a very low surface energy. The low surface energy of CH_3-8SE results in induction of vertical alignment of nematic liquid crystals on its surface.[5-7] Since CH_3-8SE has been used to tune surface properties by blending with other polymers,[8-10] we investigated the effects of the surface properties of this comb-like polymer on the electrical properties of OTFTs made of P3HT/CH_3-8SE blends.

First, we investigated alignment characteristics of nematic LCs on the surface of the P3HT/CH_3-8SE blend film. Figure 2 shows conoscopic POM images of LC cells prepared with a pure P3HT film and P3HT/CH_3-8SE blend films as LC alignment layers. As shown in the conoscopic images of Figure 2,

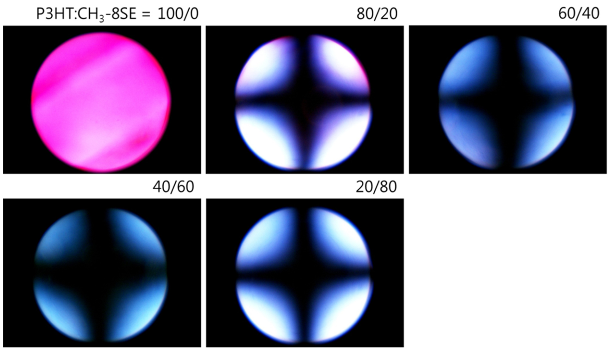

Figure 2. Conoscopic polarized optical microscope images of LC cells prepared with P3HT/CH_3-8SE blend films as an alignment layer: P3HT/CH_3-8SE blend ratios of 100/0 (pure P3HT), 80/20, 60/40, 40/60, and 20/80.

Table I. Surface Properties of P3HT/CH_3-8SE Blends

P3HT/CH_3-8SE	Contact Angle [degrees][a]		Surface Energy (mN/m)[b]	Surface Roughness RMS (nm)
	Water	Diiodomethane		
100/0	105.2 (0.8)	52.6 (1.3)	32.8	1.2
80/20	106.0 (1.1)	63.7 (1.9)	26.6	1.7
60/40	106.1 (2.1)	64.5 (1.2)	26.1	1.4
40/60	106.8 (1.5)	64.1 (1.4)	26.3	0.9
20/80	107.5 (2.2)	68.5 (1.8)	23.9	2.1

[a] Standard deviations are given in parentheses. [b] Calculated using Owens-Wendt-Rable-Kaelble method.

5CB shows a planar arrangement with the pure P3HT alignment film, whereas all blend films of P3HT/CH_3-8SE induce a vertical LC alignment regardless of their blend ratio. P3HT chains have strong interactions with LC molecules through van der Waals or π-π interactions, leading to a planar arrangement of nematic LCs. However, CH_3-8SE, which is a comb-like polymer with well-ordered aliphatic side chains, induces a vertical LC arrangement through weak interactions of side chains with LCs and steric repulsion.[22] The vertical alignment of the nematic LC observed on the surface of the blend films could be caused by differences in surface energy between polymers in the blends.[23,24] Due to its comb-like structure, CH_3-8SE (23.9 mN/m) has a lower surface energy than P3HT (32.8 mN/m). Interestingly, values of surface energy for the P3HT/CH_3-8SE films are similar for all blended films, as shown in Table I. These findings indicate that if the blend films contain CH_3-8SE, they have relatively lower values of surface energy regardless of blend composition. These results are in good agreement with the observations of conoscopic POM images of P3HT/CH_3-8SE blends where vertical alignment of 5CB is found for all blend compositions. Therefore, the LC alignment behavior on the surface of P3HT/CH_3-8SE blend films may be explained by surface domination of CH_3-8SE chains with lower surface energy. CH_3-8SE domains in the blend films may exhibit more influence on the LC alignment than P3HT domains since CH_3-8SE chains can induce vertical LC alignment through molecular interactions of extended alkyl side chains.

XPS was employed to determine the amount of sulfur from the thioether (-S-) of P3HT and from the sulfone group (-SO_2-) of CH_3-8SE at the surface of P3HT/CH_3-8SE blended films. The XPS S2p core level spectrum of the P3HT/CH_3-8SE (80/20) blend film is shown in Figure 3(a). S2p binding energies of a sulfur atom in the sulfone group are found at 166.9 and 168.1 eV, whereas those of thioether are at 163.1 and 164.3 eV. Figure 3(b) provides ratios of sulfur atoms from two polymers in the blends plotted as a function of CH_3-8SE content. The amount of sulfur atoms in the sulfone group increases with CH_3-8SE content in the blends as expected, however the rate of increase is quickly reduced when the CH_3-8SE content exceeds 40 wt%. This result indicates that CH_3-8SE chains are predominantly located at the surface for most P3HT/CH_3-8SE blend films. It is suggested, therefore, that the vertical LC alignment is strongly

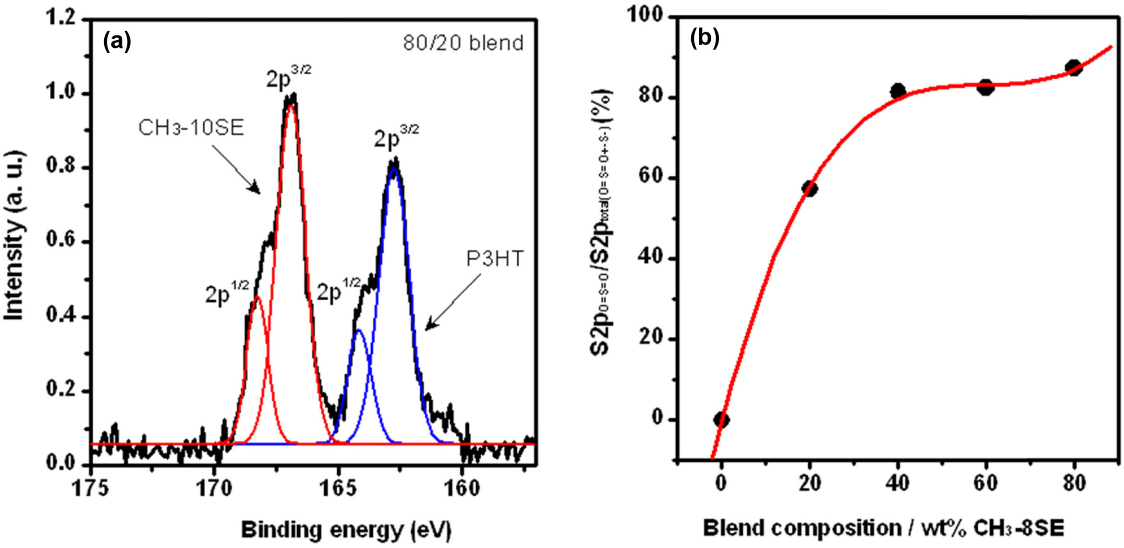

Figure 3. (a) XPS S2p core level spectra of P3HT/CH_3-8SE (80/20) blend film and (b) plot of ratio of sulfur from CH_3-8SE to all sulfur from the sample as a function of CH_3-8SE amount.

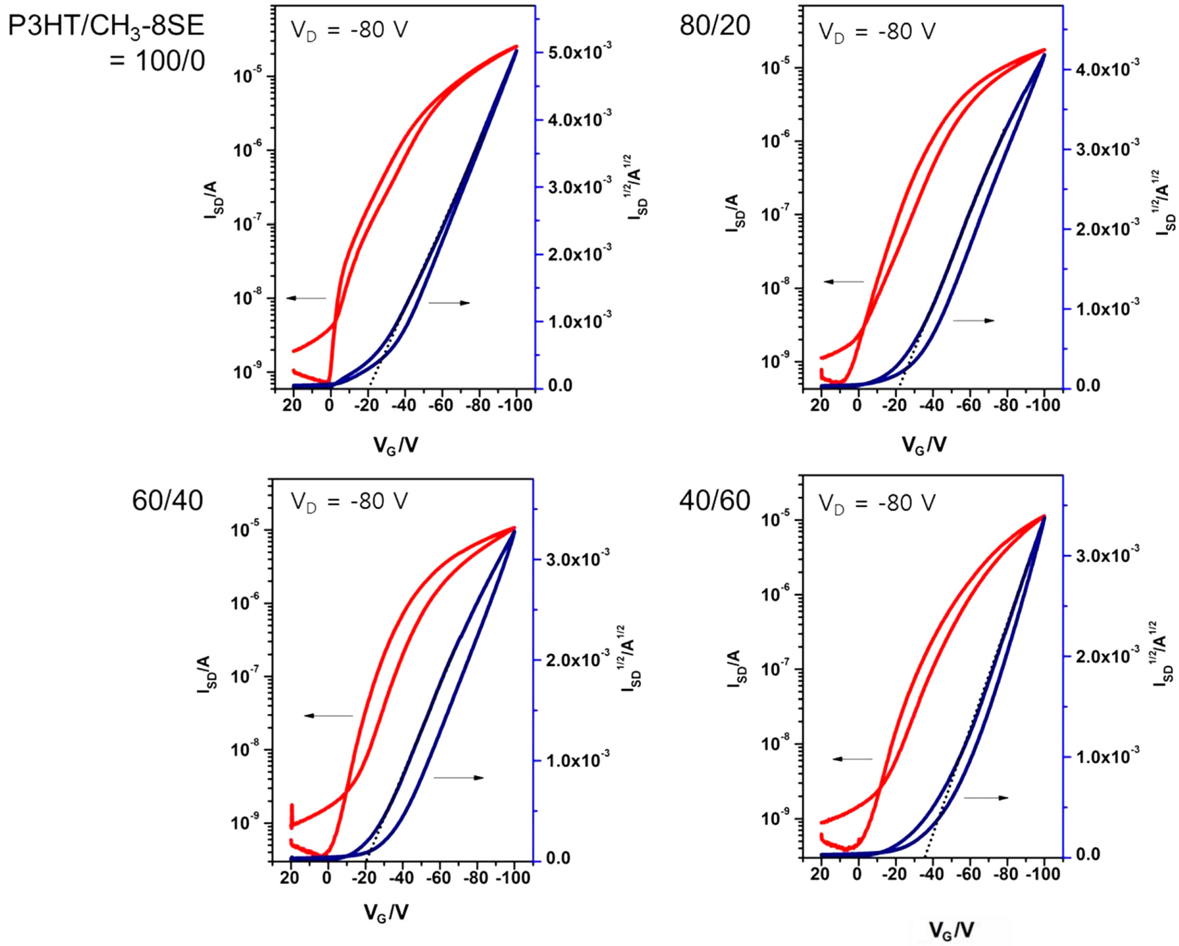

Figure 4. Transfer characteristics of OTFT prepared with P3HT/CH_3-8SE blend film as an active layer: P3HT/CH_3-8SE blend ratios of 100/0 (pure P3HT), 80/20, 60/40, and 40/60.

affected by the presence of CH_3-8SE domains at the surface of the blends.

Table II. Electrical Properties of OTFTs with P3HT/CH_3-8SE Blend Films

P3HT/CH_3-8SE	μ [$cm^2V^{-1}s^{-1}$][a]	V_t [V]	I_{on}/I_{off}
100/0	0.04 (0.010)	-18.6 (4.4)	10^4
80/20	0.03 (0.010)	-22.6 (2.7)	10^4
60/40	0.02 (0.010)	-25.6 (4.8)	10^4
40/60	0.03 (0.005)	-36.7 (3.4)	10^4
20/80[b]	-	-	-

[a]Standard deviations are given in parentheses. [b]Not available.

Figure 4 shows transfer characteristics of OTFTs prepared with a P3HT/CH_3-8SE blend film as an active layer. Electrical properties of OTFT devices were derived from transfer curves of Figure 4 in a saturation regime for devices with pure P3HT and three P3HT/CH_3-8SE blend films. The field effect mobility (μ), threshold voltage (V_t), and on/off current ratio (I_{on}/I_{off}) of the devices are listed in Table II. Mobility values of OTFTs with P3HT/CH_3-8SE blends are found to be similar to that with pure P3HT except for the 20/80 blend. The OTFT made with a 20/80 blend did not work as a transistor device. Although there is a difference between the surface properties of pure P3HT and those of blends containing CH_3-8SE (as evidenced by LC alignment characteristics and XPS results), no clear correlation was found between the electrical properties of OTFTs and the blend composition. This suggests that a percolation path exists in the blend films, thus allowing efficient charge transport through the channel regardless of the amount of P3HT. However, the threshold voltage (V_t) of the devices decreases with increasing comb-like CH_3-8SE polymer in the blend because the resistance at the interface of the blend film may change with the amount of comb-like CH_3-8SE chains. Although the comb-like polymer induces a vertical alignment of LC molecules, it does not have much influence on the electrical properties of the OTFT. However, there exists a percolation threshold required for stable OTFT performance and high interfacial resistance between P3HT and CH_3-8SE polymers in the OTFT

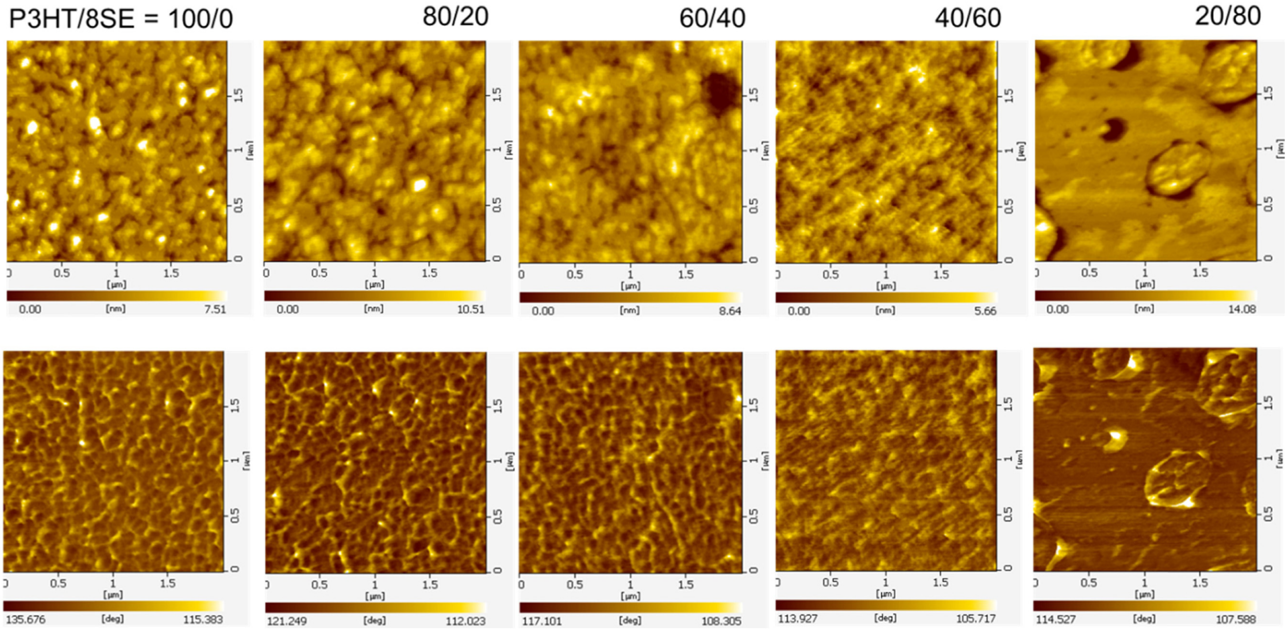

Figure 5. AFM height (upper) and phase (lower) images of the surfaces of P3HT/CH_3-8SE blends: P3HT/CH_3-8SE blend ratios of 100/0 (pure P3HT), 80/20, 60/40, 40/60, and 20/80.

active layer. This result suggests that OTFT performance can be maintained at a level similar to that of pure P3HT (100%) even though a blend of P3HT (40%)/CH_3-8SE (60%) is used.

Morphologies of P3HT domains in P3HT/CH_3-8SE blend films were investigated using tapping mode atomic force microscopy (AFM). Figure 5 shows AFM surface topology and phase images of P3HT/CH_3-8SE blend films cast on HMDS modified SiO_2 substrates. The surfaces of pure P3HT (100/0) and P3HT/CH_3-8SE blend films were mostly flat with uniform domain structures where RMS roughness values are below 2.1 nm (Table I). It was observed from phase image pictures of Figure 5 that the pure P3HT film could form a well defined short fibrillar texture in which fibril-like crystalline domains were interconnected within the films. P3HT blends with CH_3-8SE still maintain the short fibrillar morphology, although CH_3-8SE was incorporated into the P3HT matrix. This result explains why the field effect mobilities of P3HT/CH_3-8SE blend films are similar to that of pure P3HT film in OTFTs. However, AFM surface topology and phase images of the P3HT/CH_3-8SE (20/80) blend film are clearly different from other P3HT/CH_3-8SE blends (Figure 5). This finding indicates that the P3HT/CH_3-8SE blend may form a different morphology as the amount of CH_3-8SE becomes larger than 80% in the blend. It is suggested for the P3HT/CH_3-8SE blends with lower CH_3-8SE content that CH_3-8SE chains do not hinder parallel lamellar stacks of P3HT domains during crystallization, resulting in interconnected fibril-like crystalline domains. However, as the amount of CH_3-8SE becomes larger, the blends form a disconnected morphology of P3HT fibrillar domains, resulting in isolated P3HT crystalline structures within the CH_3-8SE matrix. These results explain why the OTFT device made of the P3HT/CH_3-8SE (20/80) blend film does not work even though the blend film exhibits surface properties similar to those of other P3HT/CH_3-8SE films.

Conclusions

Alignment characteristics of nematic LCs on the surface of P3HT/CH_3-8SE blends were studied. Conoscopic POM images of LC cells show a vertical alignment for all blend films regardless of blend ratios. The LC alignment behavior on the surface of P3HT/CH_3-8SE blend films may be explained by domination of CH_3-8SE chains with lower surface energy. CH_3-8SE domains in the blend films may exhibit more influence on the LC alignment than P3HT domains since CH_3-8SE chains can induce vertical LC alignment through molecular interactions of extended alkyl side chains. XPS data support these findings by showing that CH_3-8SE chains are dominantly located at the surface for most P3HT/CH_3-8SE blend films.

The mobility values of OTFTs prepared with the P3HT/CH_3-8SE blend film as an active layer are found to be similar to that with a pure P3HT film. Although there is a difference in surface properties between pure P3HT and the blends containing CH_3-8SE, as evidenced by LC alignment characteristics and XPS results, no clear correlation was found between the OTFT electrical properties and the blend composition. P3HT blends with CH_3-8SE still maintain a short fibrillar morphology, although the comb-like polymer CH_3-8SE was incoporated into the P3HT matrix. CH_3-8SE induces vertical alignment of LC molecules, however, it does not have much influence on the electrical properties of OTFTs. This suggests that LC alignment on the channel layer of OTFT can be controlled without deterioration of charge carrier mobility of the device by employing P3HT blend as a semi-conducting layer. This result may be useful in improving the performance of LC-on-OTFT sensory devices. Since the mobility values of OTFT prepared with the P3HT blend are similar to those with a pure P3HT film, this study provides a novel route for effectively reducing the amount of active P3HT semi-conducting polymer without deterioration of the electrical property of OTFT.

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