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Surface-induced alignment of pentacene by photo-alignment technology for organic thin film transistors

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A series of highly soluble maleimide-based polymers with photoreactive pendant group were synthesized and used as a gate dielectric insulator for organic thin film transistors. Photoalignment properties were characterized by UV-visible spectroscopy and the alignment of liquid crystals. Photopolymerization of polymer-coated organic thin film transistors with linearly polarized UV light induces anisotropy in field-effect mobility. The gate dielectric insulator based on the photoalignable maleimide shows higher field-effect mobility and on/off current ratio than those from a SiO_2 gate dielectric insulator with the values of 0.3 cm^2 V^{-1} s^{-1} and 10^4, respectively. Our results demonstrate that the photo-induced anisotropy of alignment films to control the molecular order of semiconducting pentacene is a promising technology for improving the performance of organic thin film transistors.

Introduction

Organic semiconducting materials are of current interest in organic light-emitting diodes (OLEDs),[1] photovoltaic cells,[2] and organic thin film transistors (OTFTs)[3] for all organic-based flexible display. The applications of OTFTs include low-end display driving circuits[4] and low-cost memory devices for smart cards and identification tags.[5,6] The advantage of OTFTs is easy design of the semiconductor materials and gate dielectric insulator materials for improving the key parameters such as field-effect mobility, on/off current ratio, and threshold voltage. Among the p-type semiconductor materials such as oligothiophenes, benzodithiophene dimer, pentacene, phthalocyanine, and poly(3-alkylthiophene)s, pentacene is a promising candidate material for OTFTs due to its high field-effect mobility, good semiconducting behavior, and environmental stability.[7,8] Carrier mobilities approaching 2.7 cm^2 V^{-1} s^{-1} have been reported for pentacene-based OTFTs with inorganic dielectrics and on/off current ratios between 10^4 and 10^8.[9] The control of orientational order and crystallization of organic semiconductor materials have been proven to be important factors for determining the performance of OTFTs.

Several methods have been developed in order to control the orientational order of liquid crystal (LC) molecules for the application of electro-optic devices and organic semiconductor films for the anisotropic characteristics of carrier mobility. These include mechanical stretching,[10] liquid-crystalline self organization,[11] rubbing,[12] and interface treatments between the semiconductor and gate dielectric insulator.[13] The groups of Reznikov[14] and Schadt[15] have reported photo-induced alignment of LCs using polyvinylcinnmates (PVCi) as alignment layers. Exposure to linear polarized UV light (LPUVL) leads to preferential crosslinking along the polarization direction, resulting in the homogeneous alignment of LCs with the director oriented perpendicular to the direction of polarization. Thermal stability of the photoalignment layer is an important factor to obtain highly aligned pentacene thin films during vacuum deposition. While the PVCi films demonstrated the principal of photoalignment of LCs, their commercial potential is limited due to their low thermal stability. Maleimide-based polymers have high glass transition temperatures (T_g) above 200 °C and thermal stability.[16] So, we used a maleimide-incorporated homopolymer and alternating copolymer with polystyrene backbone as a gate dielectric insulator in order to align the pentacene thin films during vacuum deposition for enhanced mobility. Recently, the photoalignment technique using polyimides (PI) has been reported for the preparation of highly ordered organic semiconducting films.[17] However, to our knowledge, no report has been made using poly(maleimide) and poly(maleimide-*alt*-styrene) derivatives as gate dielectric insulators, aligning the pentacene semiconductor in OTFTs.

In this article, we report the synthesis of novel poly(maleimide)-based photoalignment materials, improved anisotropy in field-effect mobility, and the results of measurements of their electro-optical properties in OTFTs.

Results and discussion

The synthetic routes of the nomomer and polymers are shown in Scheme 1. 4-Fluorobenzoyloxycinnamic acid (**1**) was

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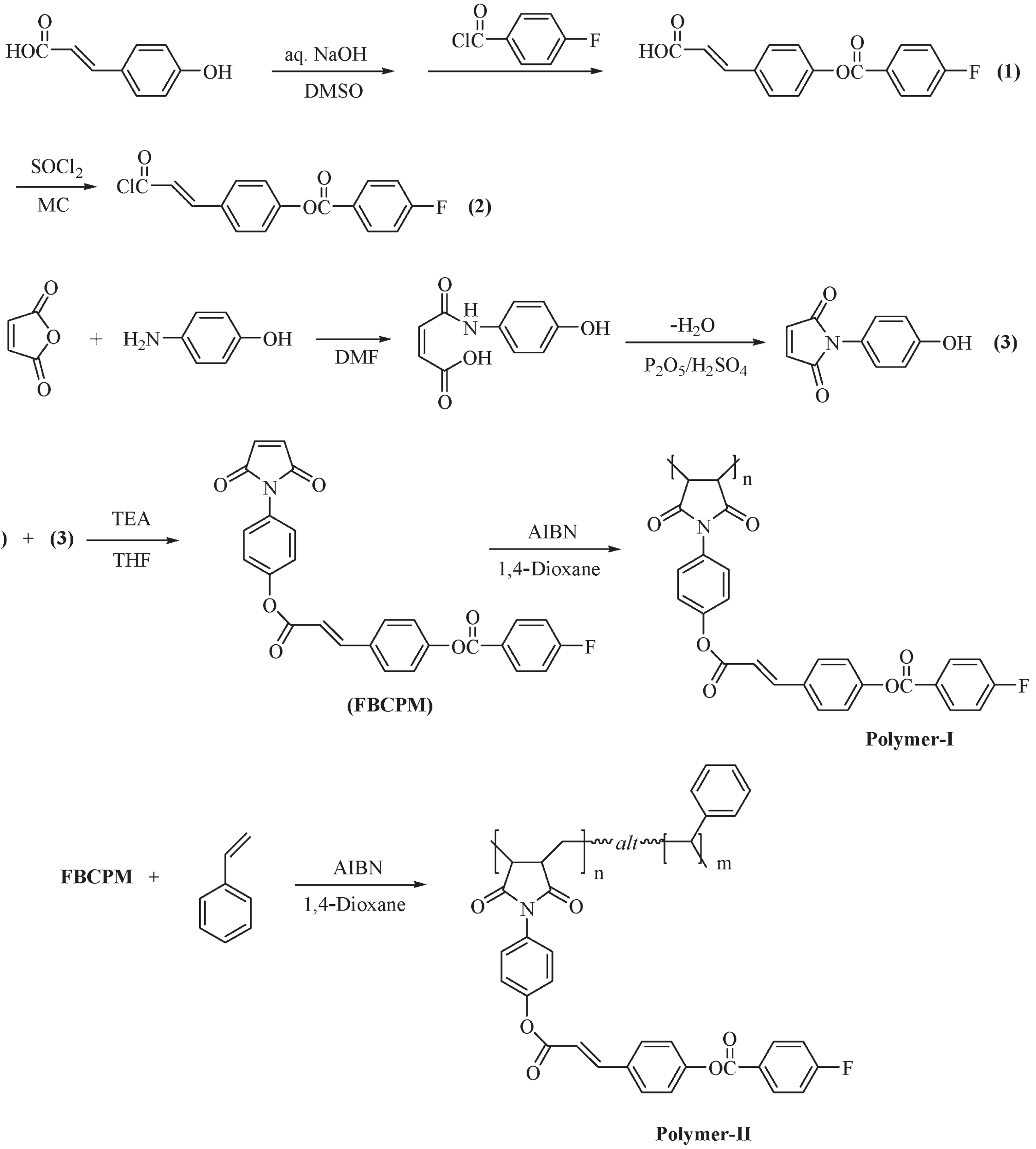

Scheme 1

obtained by esterification of 4-hydroxycinnamic acid with 4-fluorobenzoyl chloride in the presence of sodium hydroxide in DMSO and H_2O. *N*-Hydroxyphenylmaleimide (**3**) was synthesized *via* two steps. First, a clear amic acid solution was obtained by reaction of maleic anhydride with 4-aminophenol in DMF. Phosphorus pentaoxide and sulfuric acid in DMF were added to the amic acid solution to obtain *N*-hydroxyphenylmaleimide. 4-Fluorobenzoyloxycinnamic acid was reacted with thionyl chloride, and the corresponding acid chloride (**2**) was dropped into the *N*-hydroxyphenylmaleimide and triethylamine in methylene chloride solution to give monomer **FBCPM** containing a photoreactive moiety. Two kinds of photoreactive polymers were synthesized by free radical polymerization as shown in Scheme 1. The intermediates, monomer, and resulting polymers were characterized by ^{1}H, ^{13}C NMR, elemental analysis, UV-visible spectroscopy, gel permeation chromatography, DSC, and TGA.

Fig. 1 show the ^{1}H NMR spectra of **FBCPM** and **Polymer-I**. The vinylic proton peak from the maleimide unit of **FBCPM** appears at 7.18 ppm as indicated by the circle in Fig. 1(a). The double bond in maleimide changes to a single bond during the free radical polymerization, and consequently the vinylic proton peak at 7.18 ppm completely disappeared as seen in Fig. 1(b), while the new single bond proton peaks appeared at 3.87–3.32 ppm as marked in Fig. 1(b) for **Polymer-I**.

Table 1 summarizes the polymerization results, molecular weights, and thermal data of **Polymer-I** and **Polymer-II**. The copolymer composition of **Polymer-II** was calculated by ^{1}H NMR spectroscopy. Typically, maleimide-based monomers undergo homopolymerization with great difficulty and

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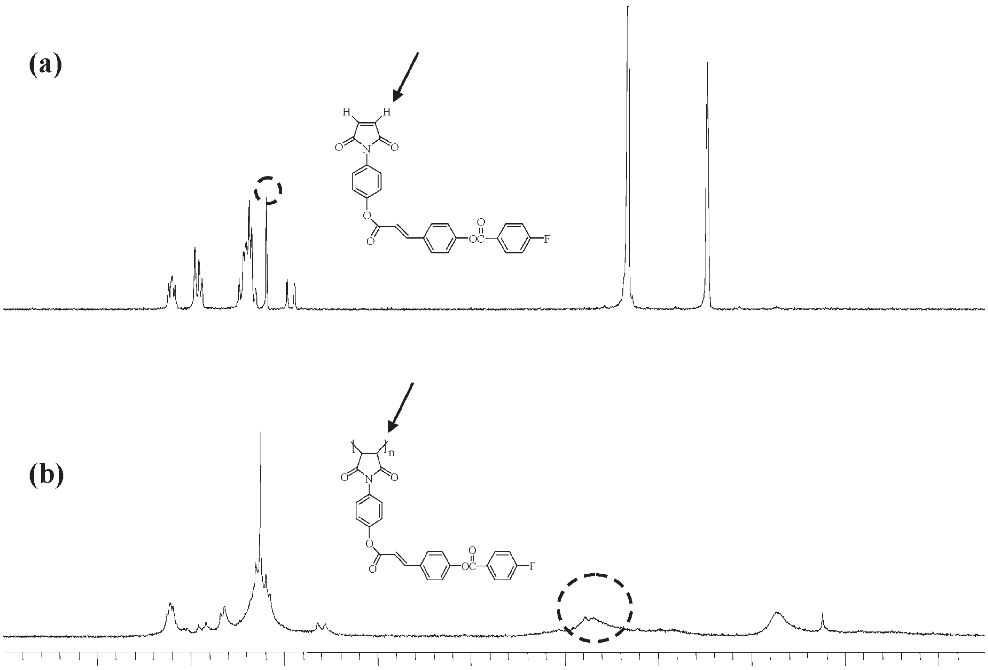

Fig. 1 ^1H NMR spectra of **FBCPM** (a) and **Polymer-I** (b) in $CDCl_3$.

Table 1 Polymerization results and thermal properties of polymers

Polymer	Feed composition [FBCPM]	Feed composition [St]	Yield (%)	Copolymer composition[a] [FBCPM]	Copolymer composition[a] [St]	M_w[b]	PDI	DSC/°C	TGA[c]/°C
Polymer-I	100	0	90	100	0	18000	1.3	134	315
Polymer-II	50	50	89	50.4	49.6	25000	1.7	137	353

[a] Determined by ^1H NMR spectroscopy. [b] M_w and PDI of the polymers were determined by GPC using polystyrene standards. [c] TGA was measured at the temperature of 5% weight loss for the polymers.

copolymerize with electron-rich monomers. Further, they are known to form alternating copolymers with maleimide and styrene monomers.[18,19] Polymerization yields, weight average molecular weights (M_w), and polydispersities of the polymers were found to be in the ranges 90%, (1.8–2.5) × 10^4, and 1.3–1.7, respectively.

Since semiconductor thin films are, in general, evaporated above room temperature and even at 100 °C, the thermal stability of gate dielectric insulators is important for device fabrication and the long-term operating stability of OTFTs. Fig. 2 shows the DSC and TGA thermograms of **Polymer-I** and **Polymer-II**. The thermal stabilities of **Polymer-I** and **Polymer-II** were investigated using TGA under a nitrogen atmosphere. **Polymer-II** exhibits higher thermal stability than **Polymer-I**: they exhibit 5% loss of weight at 353 and 315 °C, respectively. The glass transition temperatures (T_g) of **Polymer-I** and **Polymer-II** are about 134 °C and 137 °C, respectively.

Fig. 3(a) shows the UV-visible spectra of **Polymer-I** film irradiated with UV light at various exposure doses. **Polymer-I** exhibits an absorption maximum (λ_{max}) at 292 nm. This absorption band originates from the photoreactive cinnamate groups in the polymer. The absorption peak intensity at 292 nm drop dramatically with increasing exposure dose up to 5.0 J cm^{-2}. These results indicate that the **Polymer-I** is very reactive to UV light. Similar UV-visible spectral changes on UV irradiation were observed for **Polymer-II** as shown in Fig. 3(b).

Dichroic UV-visible absorption spectra of **Polymer-I** and **Polymer-II** films irradiated with LPUVL at 1.0 J cm^{-2} are shown in Fig. 4. All the irradiated films exhibit stronger absorption in directions perpendicular to the electric vector of the LPUVL than in directions parallel to the electric vector of the LPUVL. The dichroic ratio (DR) was determined from the absorption ($A_\perp$) at maximum absorption wavelength with UV-visible light linearly polarized perpendicular to the electric vector of the LPUVL and that ($A_{//}$) measured with UV-visible light linearly polarized parallel to the electric vector of the LPUVL, which leads to eqn (1).

$$DR = (A_\perp - A_{//})/(A_\perp + A_{//}) \quad (1)$$

The dichroic ratios for films irradiated with LPUVL at 1.0 J cm^{-2} are 0.063 for **Polymer-I** and 0.061 for **Polymer-II** as shown in the inset of Fig. 4(b). This result indicates that the cinnamoyl moieties oriented parallel to the direction of LPUVL are consumed more rapidly than those positioned perpendicular to the LPUVL. Consequently, the unreacted

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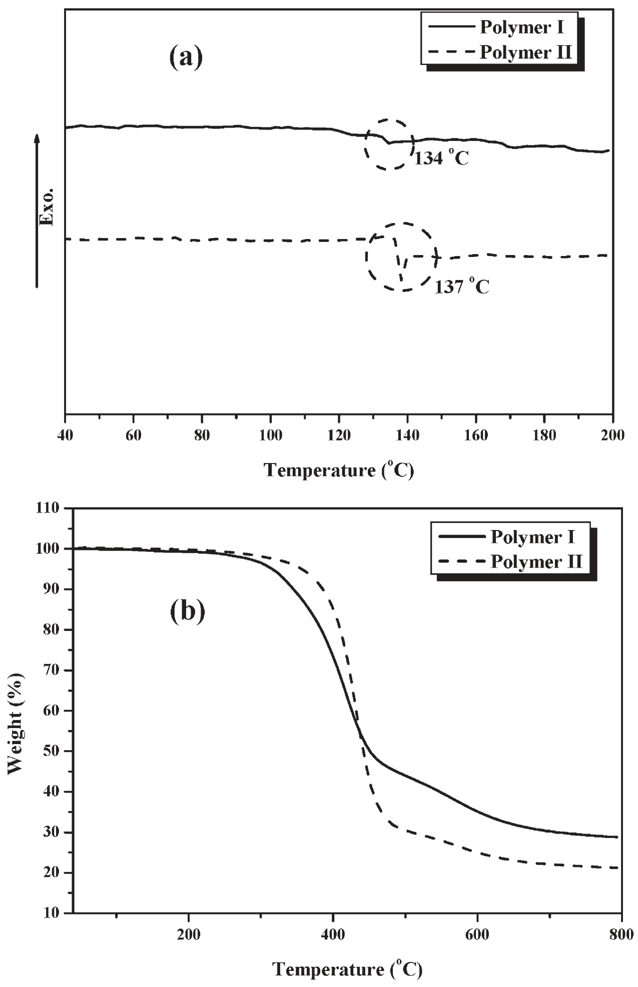

Fig. 2 DSC (a) and TGA (b) curves of **Polymer-I** and **Polymer-II** (at a heating rate of 10 °C min^{-1}).

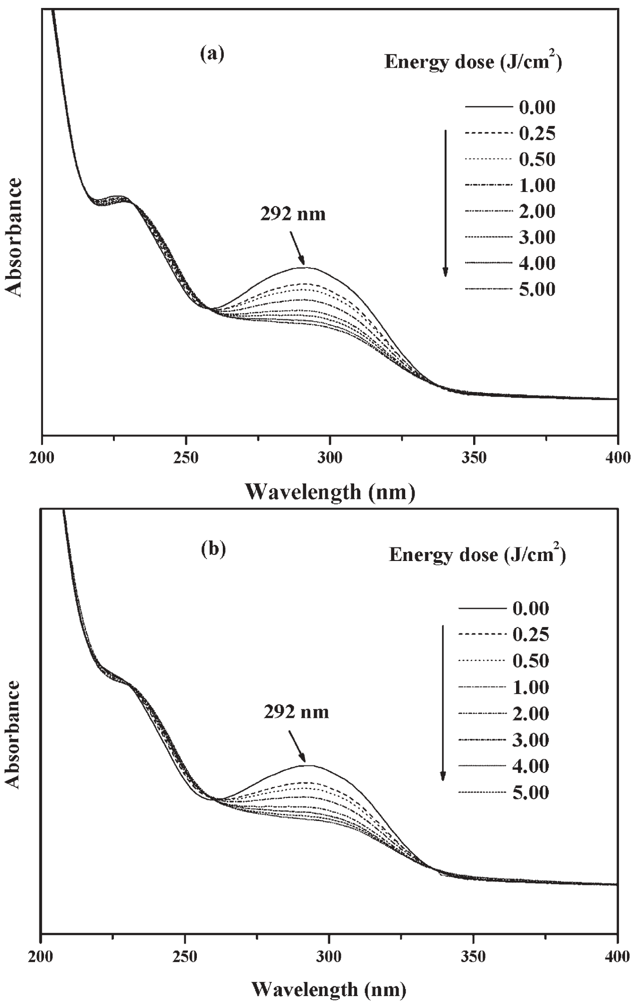

Fig. 3 UV-visible absorption spectra of **Polymer-I** (a) and **Polymer-II** (b) films irradiated with unpolarized UV light (365 nm) at varying exposure doses.

cinnamoyl moieties in a film irradiated with LPUVL preferentially lie in a direction perpendicular to the electric vector of the LPUVL.

To evaluate the performance of **Polymer-I** and **Polymer-II** as a gate dielectric insulator for aligning the pentacene semiconductor in OTFTs, we fabricated OTFT devices with spin-coated photoreactive polymers on a SiO_2 gate dielectric insulator as illustrated in Fig. 5(a). This device has a channel length and width of 100 μm and 2 mm, respectively and a gate dielectric layer with a thickness of 100 nm. Due to the leakage current to the gate electrode in **Polymer-I** and **Polymer-II** films, it was difficult to measure the characteristics of OTFTs. Therefore, the resulting photoreactive polymers were spin coated on a SiO_2 gate dielectric insulator to facilitate the alignment control of pentacene molecules with a 100 nm thickness. Two kinds of electrode were employed to observe the influence of anisotropic exposure of LPUVL to the photoreactive polymer films. The electrodes were designed for the source/drain to be aligned parallel or perpendicular to the direction of LPUVL, respectively, as shown in Fig. 5(b).

Fig. 6 shows the I_D–V_{DS} characteristics for various gate-source voltages (V_{GS}), and $\sqrt{I_D}$–V_{GS} and $\log(I_D)$–V_{GS} characteristics of **Polymer-I** along with the parallel (a) and perpendicular (b) orientation of pentacene thin films with respect to the source and gate electrodes. For similarly treated films (see details in the Experimental section), the LC molecules were aligned perpendicular to the direction of LPUVL, which corresponds to the LC director parallel to the source and drain electrodes. Based on the results from both liquid crystal and pentacene, we conclude that the alignment mechanism of pentacene molecules during the thermal evaporation is similar to that of LC molecules observed using the photoalignment materials as shown in Fig. 7.[15] These results are consistent with our measured anisotropy in carrier mobility. When the orientation of pentacene molecules is parallel to the direction of current flow, the field-effect mobility is higher than when the orientation of pentacene is perpendicular to the direction of current flow. From the $\sqrt{I_D}$–V_{GS} and $\log(I_D)$–V_{GS} characteristics, field-effect mobility ($\mu_{//}$) and on/off current ratio of **Polymer-I** were up to 0.3 cm^2 V^{-1} s^{-1} and 10^3 for a width/length ratio (W/L) of 20 with a parallel orientation of pentacene thin films. However, the field-effect mobility ($\mu_\perp$) of **Polymer-I** with a perpendicular orientation of pentacene molecules between source and drain electrodes was 0.05 cm^2 V^{-1} s^{-1}. The FET characteristics

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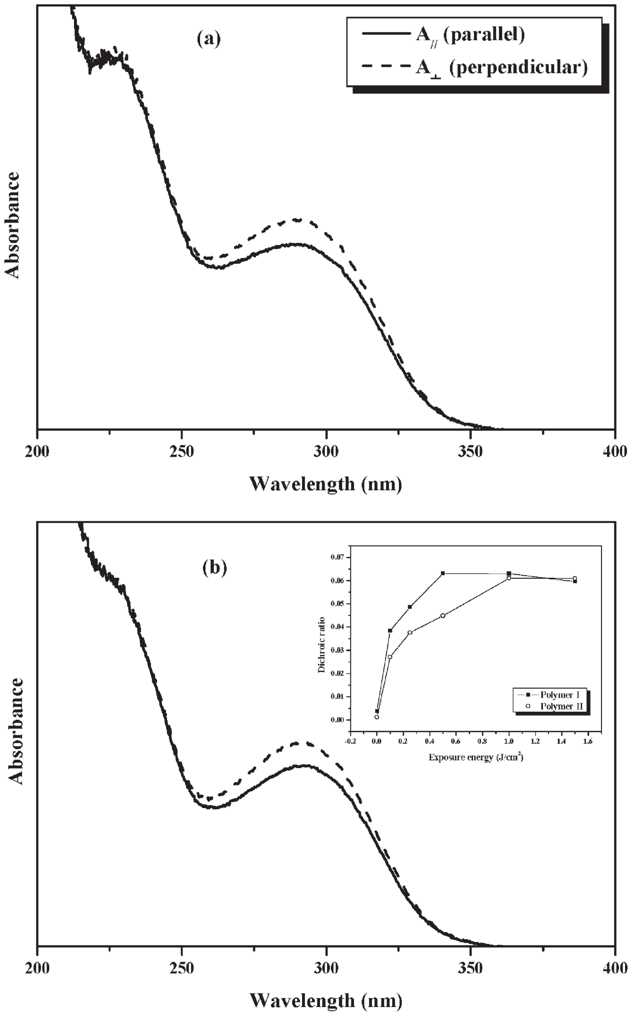

Fig. 4 Dichroic UV-visible absorption spectra of **Polymer-I** (a) and **Polymer-II** (b) films irradiated with LPUVL at 1.0 J cm^{-2}: (- - -), measured with light polarized perpendicular to the electric vector of the LPUVL; (—), measured with light polarized parallel to the electric vector of the LPUVL.

of **Polymer-II** showed a lower field-effect mobility of 0.12 $cm^2 V^{-1} s^{-1}$ than **Polymer-I**. This result can be expected from the lower photo-crosslinking density of **Polymer-II** compared to **Polymer-I** in a repeating unit of the polymer backbone. The field-effect mobilities, on/off current ratios, and subthreshold voltages of **Polymer-I**, **Polymer-II**, and SiO_2 for comparison as a gate dielectric insulator are summarized in Table 2.

Conclusions

This study focused on the improvement of FET characteristics by controlling the orientational order of pentacene molecules used as a semiconductor layer, by employing a photoalignable gate dielectric insulator. Photosensitive maleimide-based polymers with a high thermal stability were synthesized through free radical polymerization. Thin polymer films were treated using linearly polarized UV-light with 365 nm wavelength. The photoalignment properties were characterized by UV-visible spectroscopy and the alignment of LC molecules. For both LCs and pentacenes, the average orientation of the molecules' long axis was perpendicular to the direction of UV polarization. When the maleimide-based photoalignment polymers are used as a gate dielectric insulator and, at the same time, as an alignment layer for the organic semiconducting material, the field-effect mobilities and on/off ratios are in the range of 0.12–0.3 $cm^2 V^{-1} s^{-1}$ and 10^3–10^4. In addition, the OTFTs fabricated from aligned pentacene exhibit a significant anisotropy in device performance. The device with photoaligned polymers also shows highly improved OTFT characteristics, compared to the SiO_2 only device as a gate insulator. Our results demonstrate that photoalignment is a promising method for the preparation of highly ordered organic semiconducting films.

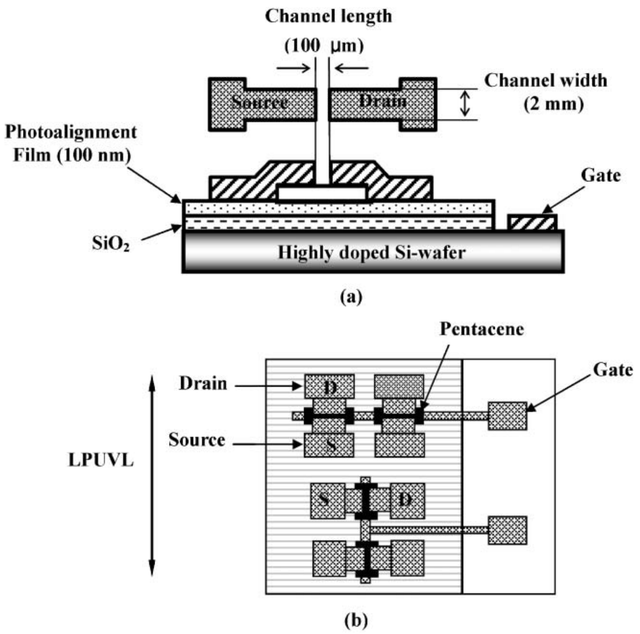

Fig. 5 Schematic diagram of top-contact OTFT fabricated with a photoalignment polymer layer on SiO_2 insulator (a) and two types of source and drain electrode to the direction of LPUVL (b).

Experimental

Materialsl

4-Hydroxycinnamic acid, 4-fluorobenzoyl chloride, maleic anhydride, and 4-aminophenol were purchased from Aldrich Co., and used without further purification unless otherwise noted. *N*,*N*-Dimethylformamide (DMF) was stirred with $MgSO_4$ overnight and distilled under reduced pressure. Tetrahydrofuran (THF) and 1,4-dioxane were dried over sodium metal and distilled under a nitrogen atmosphere. Methylene chloride was distilled over calcium hydride under a nitrogen atmosphere. 2,2′-Azobisisobutyronitrile (AIBN) initiator was recrystallized from methanol and dried in a vacuum oven.

Measurements

The number-average molecular weights (M_n) and the weight-average molecular weights (M_w) of the synthesized polymers

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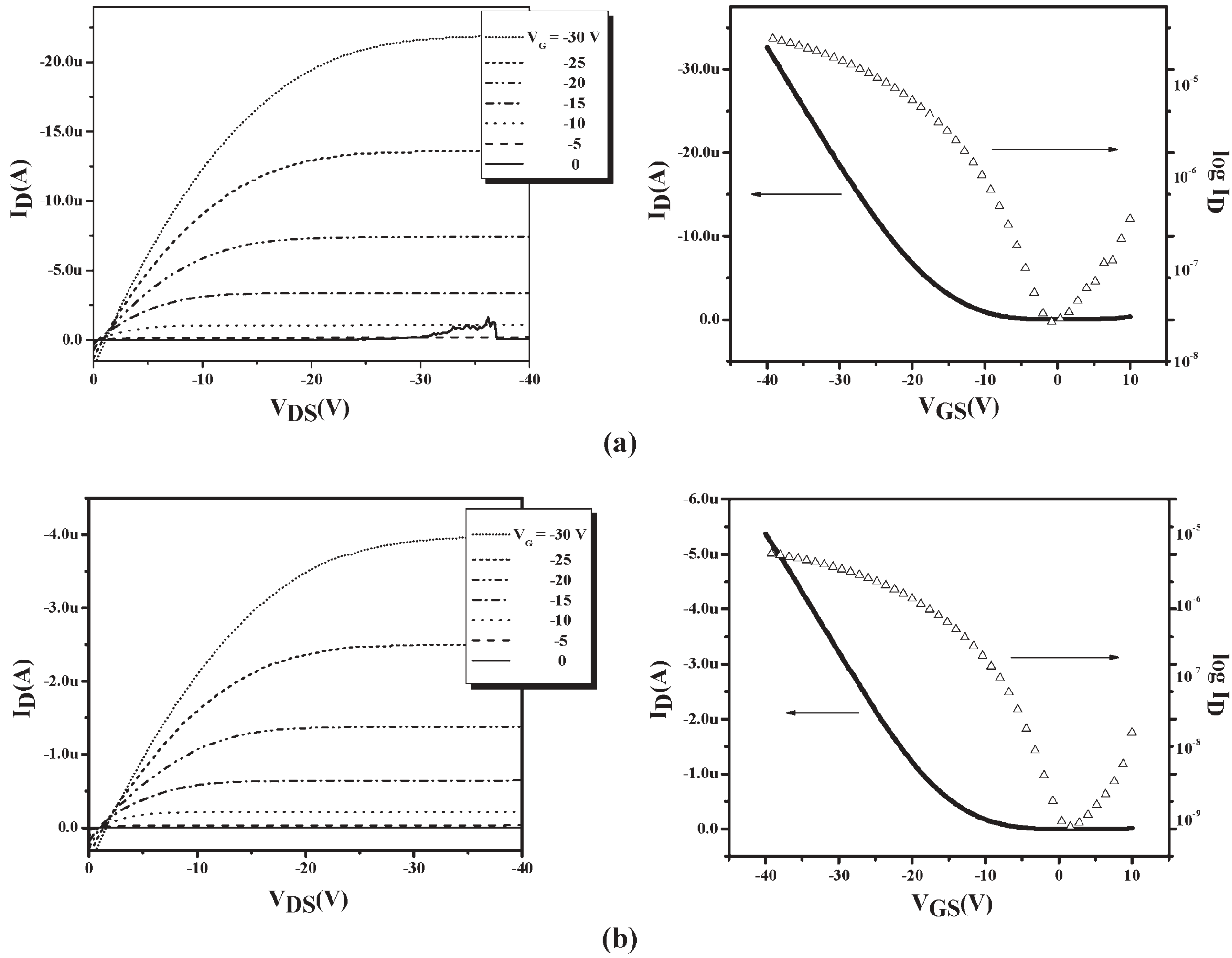

Fig. 6 The I_D–V_{DS} output characteristics and transfer characteristics about **Polymer-I** when current is $\mu_{//}$ (a), when current is $\mu_{\perp}$ (b).

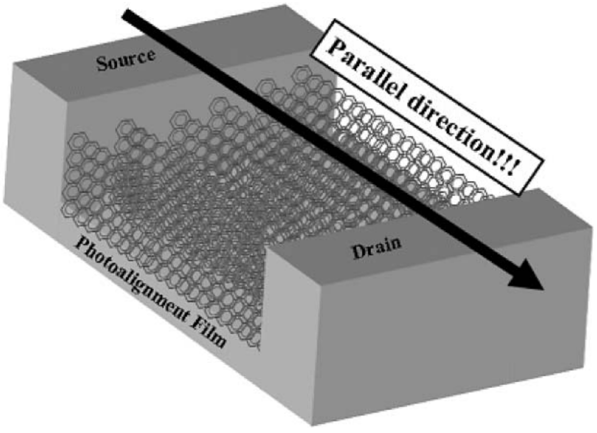

Fig. 7 Schematic orientation of pentacene molecules on photoalignment layer.

were measured using gel permeation chromatography (GPC, Agilent Technologies; Agilent 1100 series) calibrated with polystyrene standards. Glass transition temperatures (T_g) were measured in the range of 40–200 °C using a differential scanning calorimeter (DSC) (METTLER TOLEDO; DSC 822^e). Degradation temperatures (T_d) were determined under a nitrogen atmosphere using a thermogravimetric analyser (TGA) (METTLER TOLEDO; TGA/SDTA 852^e). The thickness of films was measured with an Alpha-Step IQ surface profiler (KLA Tencor, San Jose, CA). A UV cross-linker (UVItec, model CL-508) that exposes a beam of 365 nm wavelength as the UV light source for irradiating the polymer films was employed. To generate LPUVL, a polarizer (PUM-51) was used. UV-visible spectra were determined using a Shimadzu Model 2401 spectrophotometer.

Synthesis of 4-fluorobenzoyloxycinnamic acid (1)[20]

4-Hydroxycinnamic acid (16.42 g, 0.1 mol) was dissolved in dimethylsulfoxide (100 mL) and water (100 mL), in which sodium hydroxide (8.8 g, 0.22 mol) has been dissolved. 4-Fluorobenzoyl chloride (15.86 g, 0.1 mol) was slowly added at 0 °C with vigorous stirring. After the reaction was allowed to proceed for 2 h at room temperature, the reaction mixture was neutralized to pH 6–7 by using dilute hydrochloric acid. The solid intermediate obtained by filtering was thoroughly washed with water. The product was vacuum dried and recrystallized in methanol to yield 4-fluorobenzoyloxycinnamic acid (17.44 g, yield: 72%). ^{1}H NMR (DMSO-d$_6$,

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Table 2 Characteristics of OTFT devices fabricated as photoalignment polymers coated onto SiO_2 and SiO_2 gate insulator

Gate Insulator	Direction of current	Mobility/cm^2 V^{-1} s^{-1}	I_{off}/A	S·S/V decade^{-1}	I_{on}/I_{off}
Polymer-I/SiO_2	$\mu_{//}$	0.3	2.56×10^{-8}	5.9	10^3
	$\mu_{\perp}$	0.05	7.8×10^{-10}	5.8	10^4
Polymer-II/SiO_2	$\mu_{//}$	0.12	4.7×10^{-10}	2.8	10^4
	$\mu_{\perp}$	0.12	9.88×10^{-10}	3.8	10^4
SiO_2		0.21	4.28×10^{-11}	1.2	10^5

200 MHz): δ (ppm) 8.22–8.18 (m, 2H, aromatic protons), 7.77 (d, 2H, aromatic protons), 7.60 (d, 1H, vinylene proton), 7.41 (t, 2H, aromatic protons), 7.32 (d, 2H, aromatic protons), 6.52 (d, 1H, vinylene proton). Mp: 227–228 °C.

Synthesis of *N*-hydroxyphenylmaleimide (3)[21]

A three-necked flask equipped with a Teflon stirrer and a thermometer was injected with nitrogen gas through a nitrogen purge tube and cooled with cold water to maintain its temperature below 15 °C. 4-Aminophenol (7 g, 0.064 mol) was added into a solution of maleic anhydride (7.55 g, 0.077 mol) in DMF (20 ml), which was stirred for about 2 h in a water bath below 15 °C with a nitrogen purge so as to obtain a clear amic acid solution. Then, a mixture containing phosphorus pentaoxide (3.7 g, 0.013 mol), sulfuric acid (1.77 g, 0.018 mol), and 30 mL of DMF was added dropwise into the amic acid solution during a period of 1 h. The resulting mixture, after stirring at 80 °C for about 6 h, was cooled and poured into 500 mL of ice water to obtain a precipitate, which was washed with deionized water and recrystallized in isopropyl alcohol and further dried in a vacuum to obtain *N*-hydroxyphenylmaleimide (8.71 g, yield: 72%). ^{1}H NMR (DMSO-d$_6$, 200 MHz): δ (ppm) 9.66 (s, 1H, –OH), 7.09 (s, 2H, vinylene protons in maleimide), 7.03 (d, 2H, aromatic protons), 6.80 (d, 2H, aromatic protons). Mp: 187 °C (lit: 185–186 °C).

Synthesis of *N*-(4-(4-fluorobenzoyloxycinnamoyl)oxyphenyl)-maleimide (FBCPM)[20]

A round bottomed flask containing 4-fluorobenzoyloxycinnamic acid (5.44 g, 0.019 mol), methylene chloride (50 mL) and thionyl chloride (6.8 g, 0.057 mol) was held under a nitrogen atmosphere. The reaction was carried out at 40 °C until a transparent solution was obtained. After the reaction, the solvent and thionyl chloride were removed under vacuum, and the obtained product, 4-fluorobenzoyloxycinnamoyl chloride, was used without further purification for the next reaction. In a round bottomed flask, *N*-hydroxyphenylmaleimide (3.97 g, 0.021 mol) was dissolved in 40 mL of THF, then triethylamine (2.3 g, 0.023 mol) was added, and agitation was carried out for 30 minutes. Afterwards 4-fluorobenzoyloxycinnamoyl chloride in methylene chloride was slowly added dropwise with vigorous agitation at 5 °C. After the exhaustion of 4-fluorobenzoyloxycinnamoyl chloride, the reaction was carried out for 24 h. Then, it was poured into a mixture of water (400 mL) and methanol (400 mL), and the precipitate was filtered off. The product was washed using water and methanol, and followed by vacuum drying to give *N*-(4-(4-fluorobenzoyloxycinnamoyl)oxyphenyl)maleimide (8.3 g, yield: 95%). ^{1}H NMR (DMSO-d$_6$, 200 MHz): δ (ppm) 8.23–8.16 (m, 2H, aromatic protons), 7.94–7.87 (m, 3H, aromatic protons), 7.47–7.30 (m, 8H, aromatic protons and vinylene proton in cinnamate), 7.18 (s, 2H, vinylene protons in maleimide), 6.91 (d, 1H, vinylene proton in cinnamate). ^{13}C NMR (DMSO-d$_6$, 500 MHz): δ (ppm) 169.91, 164.93, 163.44, 152.40, 149.57, 145.74, 134.73, 132.98, 132.85, 131.83, 130.11, 129.09, 128.04, 122.61, 122.43, 117.21, 116.35, 116.06. Anal. Calcd for $C_{26}H_{16}FNO_6$: C, 68.27% ; H, 3.53% ; N, 3.06% ; Found: C, 67.22% ; H, 2.11% ; N, 3.06%. Mp: 250–252 °C.

Synthesis of poly[*N*-(4-(4-fluorobenzoyloxycinnamoyl)-oxyphenyl)maleimide] (Polymer-I)

In a 50 mL Schlenk flask were placed *N*-(4-(4-fluorobenzoyloxycinnamoyl)oxyphenyl)maleimide (1 g, 2.2 mmol), AIBN (0.05 g, 0.3 mmol) and 20 mL of 1,4-dioxane. The oxygen dissolved in 1,4-dioxane was removed by a degassing process with a nitrogen freeze–thaw cycling method. The polymerization mixture was stirred at 90 °C for 24 h under a nitrogen atmosphere. After the polymerization was over, solvent was removed to about 10 mL and the polymerization mixture was poured into 300 mL of methanol to precipitate. The precipitated polymer was collected by filtration and washed with methanol. Then, vacuum drying was carried out to obtain 0.9 g (yield: 90%) of poly[*N*-(4-(4-fluorobenzoyloxycinnamoyl)-oxyphenyl) maleimide] (**Polymer-I**). ^{1}H NMR (DMSO-d$_6$, 200 MHz): δ (ppm) 8.38–7.78 (5H, aromatic protons), 7.74–7.10 (8H, aromatic and vinylene protons), 7.10–6.71 (1H, vinylene proton).

Synthesis of poly[(*N*-(4-(4-fluorobenzoyloxycinnamoyl)-oxyphenyl)maleimide)-*alt*-styrene] (Polymer-II)

In a 50 mL Schlenk flask were placed *N*-(4-(4-fluorobenzoyloxycinnamoyl)oxyphenyl)maleimide (1 g, 2.2 mmol), AIBN (0.06 g, 0.37 mmol) and 24 mL of 1,4-dioxane. The oxygen dissolved in 1,4-dioxane was removed by a degassing process with a nitrogen freeze–thaw cycling method. The polymerization mixture was heated up to 90 °C. Then, 0.23 g (2.2 mmol) of styrene was added and the reaction was carried out for 24 h under nitrogen atmosphere. After the polymerization was over, solvent was removed to about 10 mL and the polymerization mixture was poured into 300 mL of methanol to precipitate. The precipitated polymer was collected by filtration and washed with methanol. Then, vacuum drying was carried out to obtain 1.1 g (yield: 89%) of poly[(*N*-(4-(4-fluorobenzoyloxycinnamoyl)oxyphenyl)maleimide)-*alt*-styrene] (**Polymer-II**). ^{1}H NMR (DMSO-d$_6$, 200 MHz): δ (ppm) 8.38–7.78 (5H, aromatic protons), 7.74–6.71 (14H, aromatic and vinylene protons).

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LC cells fabrication

The polymer films were prepared by spin-coating with 5 wt% polymer solutions (dissolved in 1-methoxy-2-propanol acetate) either onto quartz for UV-visible spectroscopy or onto glass substrates for the fabrication of LC cells, and followed by drying for 1 h at 130 °C. Paired substrates treated by the LPUVL were assembled antiparallel with respect to each polarization direction of the LPUVL and separated with 5 μm glass sphere spacers. A nematic LC, 4′-phenyl-4-biphenylcarbonitrile (Aldrich Co.), containing 1.0 wt% Disperse Blue 1 (Aldrich Co.) as a dichroic dye, was injected into the cells.

Acknowledgements

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