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OFET Characteristics of Stretched Poly(3-hexylthiophene) Films

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We investigated the field-effect characteristics of mechanically stretched regio-regular poly(3-hexylthiophene) (P3HT) on a supporting poly(vinyl alcohol) (PVA) film. After stretching the P3HT/PVA film, large dichroism was observed in the polarized UV-Vis absorption spectra. The stretched P3HT films were applied parallel or orthogonal to the conduction channel of the transistor. The field-effect mobility was highly anisotropic, with larger mobility along the stretched direction of the films. The mobility increased with increasing stretch ratio (S_r) for the parallel devices but decreased for the orthogonal devices.

Key Words : Polythiophene, Stretching, OFET, Molecular Orientation

1 Introduction

Organic field-effect transistors (OFETs) are promising candidates for use in flexible, large-area and low-cost electronic devices, and they have undergone extensive improvements in recent years. Solution-based processes, such as spin-coating, casting, inkjet printing and screen printing, have attracted considerable attention as highly efficient methods for fabrication of OFET devices.^{1,2)} Great effort has been devoted to the development of solution-processable transistor materials and the process techniques for solution-processed OFETs. Recently, a variety of newly developed soluble organic semiconductors have been reported as high performance solution-processable transistor materials.³⁻⁵⁾ In many cases, the high performance of solution-processed OFETs is due to their well-ordered molecular arrays in their active layers. The hydrophobic intermolecular interaction between alkyl chains leads to enhanced molecular orbital overlap between neighboring molecules, which can enhance carrier mobility in the OFET devices. Molecular ordering in the thin film transistors is also achieved by physical methods such as rubbing and photoalignment method.⁶⁻⁸⁾ Mechanical stretching method (also referred to as the hot drawing method) is also one of the most fundamental and promising techniques for processing uniaxially oriented polymer films.⁹⁻¹¹⁾ However, there are very few reports about OFET devices using stretching method.

In this paper, we investigate the OFET characteristics of the mechanically stretched regio-regular poly(3-hexylthiophene) (P3HT) polymer films. We select P3HT as a test polymer because it is one of the most popular and well defined organic semiconductors used for solution-processable organic transistors.¹¹⁻¹³⁾

2 Experimental

P3HT ($M_w = 87,000$) with a head-to-tail content of $>97\%$ was purchased from Aldrich Chemical Co. and used as received. The PVA film (film thickness = 70 μm) was donated by Polatechno Co., Ltd. and cleaned by sonication in ethanol. Chloroform (Aldrich Chemical Co.) was purified by using an Al_2O_3 short column just before use.

To determine the stretch ratio (S_r), we marked the back side of a PVA substrate in intervals of approximately 1 cm. A thin film of P3HT was deposited on the supporting PVA substrate by spin coating a 0.4 wt% solution of P3HT in chloroform at 2000 rpm for 30 sec. This sample film was kept at 65 $^\circ\text{C}$ for 30 min and then mechanically stretched at the stretching speed of 9 cm

Fig. 1 Schematic illustrations of (a) the bottom-contact type OFET device based on the stretched P3HT film applied (b) orthogonally and (c) parallel to the electric field.

min^{-1} . S_r was defined as $S_r = r_{//}/r_0$, where $r_{//}$ and r_0 are distances between the marks to the stretched direction after and before stretching, respectively.

The “bottom-contact” (bottom source and drain contact, bottom gate contact) type OFET devices (Fig. 1) were fabricated as follows. Heavily doped n^+ -Si (100) wafers with a thermally grown insulating SiO_2 layer (210 nm thick) were used as the substrates. Gold drain and source electrodes (50 nm thick) were patterned on the Si/ SiO_2 substrate using a photolithography technique. For a typical device, the drain-source channel length (L) and width (W) were 10 μm and 2.0 cm, respectively. The stretched and unstretched P3HT/PVA films were applied by pressing to the device in the desired orientations.

Polarized UV-Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrometer under ambient conditions. The dichroic ratio (R_d) was determined using the equation $R_d = A_{//\text{max}}/A_{\perp\text{max}}$, where $A_{//\text{max}}$ and $A_{\perp\text{max}}$ are absorbances at λ_{max} obtained for incident lights with electric vectors polarized parallel and orthogonal to the stretched direction of the films, respectively.

The electrical properties of the OFET devices were measured using an Agilent 4155C semiconductor parameter analyzer under ambient conditions. Field-effect mobility was calculated in the saturated regime ($V_d = -100$ V) of the drain current. The current on/off ratio ($I_{\text{on}}/I_{\text{off}}$) was determined from the maximum (I_{on}) and minimum (I_{off}) value of the I_d .

3 Results and Discussion

Figure 2 shows polarized UV-Vis absorption spectra of the stretched P3HT/PVA film ($S_r = 1.9$). $A_{//}$ and $A_{\perp}$ represent the absorption spectra observed for the plane-polarized light with electric vectors parallel and orthogonal to the stretching direction of the P3HT/PVA film, respectively. For unstretched film, $A_{//}$ and $A_{\perp}$ are essentially the same, suggesting that P3HT is randomly oriented in the unstretched film. After stretching the P3HT/PVA film, large dichroism was observed in the region from 400 to 700 nm with $R_d = 3.92$. Since the transition dipole moment of polythiophene is generally polarized along the polythiophene backbone, P3HT is considered to be oriented parallel to the stretching direction.

Figure 3 shows the relationship between R_d and S_r obtained with the stretched P3HT film on the supporting PVA film. The value of R_d increases with increasing the S_r value and reached 9.1 at $S_r = 3.7$. The supporting PVA film tore when the S_r value exceeded approximately 4.0. These results are consistent with the various π -conjugated polymers.⁹⁻¹¹⁾

Bottom-contact type OFET devices were fabricated with unstretched and stretched P3HT/PVA films. Figure 4 represents typical plots of I_d vs. V_d at various gate voltages for the OFET devices based on the stretched P3HT film ($S_r = 3.4$) applied parallel to the electric field. The channel conductance increases as V_g becomes more negative, meaning that the P3HT film behaves as a p -type semiconductor. The field-effect

Fig. 2 Polarized UV-Vis absorption spectra of the stretched P3HT films ($S_r = 1.9$) on the PVA substrates. $A_{//}$ (solid line) and $A_{\perp}$ (broken line) represent the spectra obtained for incident light with electric vectors polarized parallel and orthogonal to the stretching direction of the P3HT/PVA films, respectively.

Fig. 3 Dependence of R_d on S_r for the stretched P3HT/PVA film.

mobility calculated using I_d in the saturation regions was $6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with $I_{\text{on}}/I_{\text{off}} = \sim 10^5$ and $V_{\text{th}} = -13$ V. This value of mobility is several times higher than that of the orthogonal film, while the values of V_{th} were almost the same.

Relationship between field-effect mobility and S_r obtained with the OFET devices with the unstretched ($S_r = 1.0$) and stretched P3HT films applied orthogonally and parallel to the electric field is shown in Fig. 5. For the unstretched P3HT-based device, the field-effect mobility was about $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility increased with increasing S_r value for the parallel devices but decreased for the orthogonal devices. This suggests that the intramolecular charge migration in the polymer backbone is faster than intermolecular charge migration. Interestingly, this charge migration direction is different from small molecules-based high performance OFETs. For small molecules, it is accepted that charge migration in the film with perpendicularly oriented molecules occurs via the overlapping of frontier molecular orbitals between the neighboring molecules.¹⁴⁾ Further investigations about the charge migration mechanism are underway.

Fig. 4 I_d vs. V_d curves at different gate biases for the OFET devices with the stretched P3HT film ($S_r = 3.4$) applied parallel to the electric field.

Fig. 5 Relationship between field-effect mobility and S_r obtained with the OFET devices with the unstretched ($\triangle$) and stretched P3HT films applied ($\square$) parallel and ($\circ$) orthogonal to the electric field.

4 Conclusion

In summary, we have successfully fabricated OFETs with mechanically stretched P3HT films acting as the active layers. After stretching the P3HT film, large dichroism was observed in the polarized UV-Vis absorption spectra. The field-effect mobility was highly anisotropic, with larger mobility along the stretched direction of the films. The mobility increased with the

stretch ratio (S_r) for the parallel devices, while it decreased as the S_r value increased for the orthogonal devices. The mechanical stretching method is a promising technique for the processing of uniaxially oriented π -conjugated polymer films in order to fabricate high performance OFETs.

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