Backbone Arrangement in "Friction-Transferred" Regioregular Poly(3-alkylthiophene)s

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ABSTRACT: The regioregular highly head-to-tail-coupled poly(3-alkylthiophene) (HT-P3AT) films were prepared by a *friction-transfer technique*. Polarized UV−vis absorption spectroscopy and grazing incidence X-ray diffraction (GIXD) were used to study the polymer molecular arrangement in the friction-transferred HT-P3AT films, and scanning electron microscopy (SEM) was used to observe the film surface morphology. The polarized UV−vis absorption spectra show a large dichroism regarding the drawing direction of friction-transfer. The order parameter is evaluated close to unity, which is the ideal orientation state. GIXD measurements show that alkyl side chains lie in the film plane, and the polymer backbones are well-ordered along the drawing direction of friction-transfer within 10° for poly(3-hexylthiophene) and 13° for poly(3-dodecylthiophene) in the film plane. The polymer backbones form a layered structure with the stacking of thiophene rings normal to the film surface. The polymer molecules in the friction-transferred films are ideally arranged three-dimensionally.

Introduction

Organic materials with a large π-conjugated electron system have been attracting much attention as new electronic and optoelectronic substances mainly used for active semiconducting layers in light-emitting diodes,[1,2] photovoltaic cells,[3] and field-effect transistors.[4−7] There are unique features that the organic materials can offer, including turning of electronic functionality, easy structural modifications, possibility of self-assembly, and mechanical flexibility. These properties can be exploited for the fabrication of large-area, low-weight, and low-cost disposable electronic products. Conjugated polymers are promising organic materials due to their excellent electrical and optical properties, reasonable chemical stability, and easy processability and allow low-cost and low-temperature fabrication. Moreover, conjugated polymer molecules are expected to exhibit anisotropic properties because the intrinsic characteristic of conjugated polymers originates from the electrons delocalized along the polymer backbone (main chain).[8−15] However, those films prepared without using a polymer arrangement technique exhibit isotropic properties. Various methods have been applied to arrange polymers, such as a rubbing technique,[11] the Langmuir−Blodgett (LB) technique,[10] and liquid crystalline (LC) self-organization.[13] It was reported that the LC-conjugated polymer molecules, poly(9,9-dioctylfluoren-*co*-bithiophene), on preoriented substrates were arranged regularly with the polymer backbone and that this arrangement was applied to high-performance electronic devices.[13] Thus, arranging the backbone of a conjugated polymer is essential for fabricating organic devices.

Here we suggest a simple technique for conjugated polymer film preparation with the polymer backbone arrangement. The friction-transfer technique using poly(tetrafluoroethylene) (PTFE) was proposed by Wittman and Smith in 1991.[16] They demonstrated the deposition of a thin film of PTFE on clean metal or glass surfaces by squeezing and drawing a PTFE block on those suitable substrates and observed highly oriented polymer backbones along the drawing direction of the friction-transfer by transmission electron microscopy (TEM)[16] and X-ray analysis.[17] The friction-transfer technique is useful for direct film preparation of solid-state materials and enables arrangement of polymer backbones. Tanigaki et al. had applied the friction-transfer technique to the film preparations of both insoluble and soluble conjugated polymers, such as polysilane (PS), poly(*p*-phenylene) (PPP), poly(*p*-phenylene-vinylene) (PPV), and their derivatives. Some successful results have been obtained in various conjugated polymers; the conjugated polymer films prepared by the friction-transfer technique exhibited high in-plane anisotropic properties.[18−20]

In this study, we apply the friction-transfer technique to prepare highly oriented films of regioregular highly head-to-tail-coupled poly(3-alkylthiophene)s (HT-P3ATs). HT-P3ATs are one of the most promising conjugated polymers because of their high charge carrier mobility in the range $10^{-4}-10^{-1}$ cm^{2}V^{-1}s^{-1}.[6,7] Although several attempts to orient the polymer backbone in HT-P3AT films have been made,[10,11,14,15] these films have shown relatively low in-plane anisotropies so far. Here we show high in-plane anisotropies in HT-P3AT films due to well-ordered polymer backbones induced by the friction-transfer technique.

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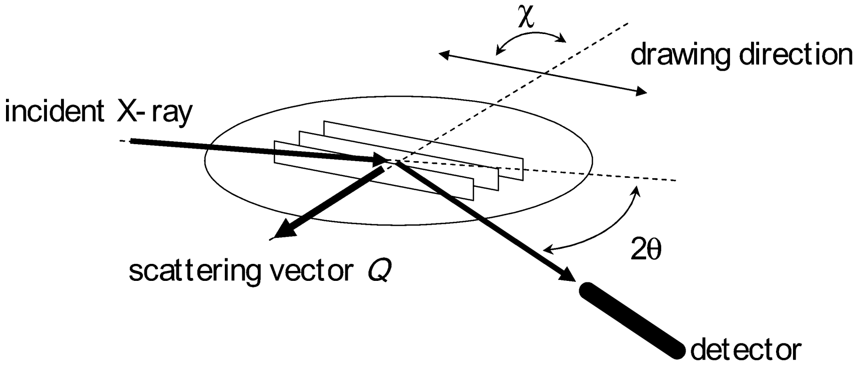
Scheme 1. Geometry of Grazing Incident X-ray Diffraction Measurements



Experimental Section

The regioregular poly(3-hexylthiophene) (P3HT) and poly(3-dodecylthiophene) (P3DDT) with more than 98% head-to-tail-coupling (Aldrich Chem. Co.) were used as purchased. The HT-P3AT films were prepared on quartz and silicon substrates by the friction-transfer technique. Each of the HT-P3AT powders was compressed into pellets, with an applied load of 1250 kgf/cm^2 under dynamic vacuum. The friction-transfer process was carried out by squeezing and drawing a pellet of each HT-P3AT with a contact area of 0.1 cm^2 on the substrate heated at 150 °C for P3HT and 100 °C for P3DDT. The applied load for squeezing was 30 kgf/cm^2, and the drawing speed was 1 m/min. The films thus prepared had an area of 1.5 cm^2 (pellet width of 1.0 cm × drawing length of 1.5 cm) and a thickness of less than 100 nm. The molecular arrangements, the polymer backbone in particular, in the friction-transferred HT-P3AT films were evaluated by polarized ultraviolet−visible absorption spectroscopy (Shimadzu MPS2000 with Glan-Tomson polarized prism) and grazing incidence X-ray diffraction[21−24] (X-ray Research Lab, Rigaku Co. Ltd.). The surface morphology of the friction-transferred HT-P3AT films was observed by scanning electron microscopy (Zeiss LEO1550).

For optical measurement, the films friction-transferred on quartz substrates were investigated by polarized ultraviolet−visible (UV−vis) spectroscopy. The order parameter, O, was calculated from the dichroic ratio, D, of UV−vis absorption using the following equation: $O = (D - 1)/(D + 2)$, $D = A_p/A_o$, where A_p and A_o are the absorption intensities for the lights polarized parallel (p-polarization) and orthogonal (o-polarization) to the drawing direction of friction transfer, respectively. The order parameter O indicates the degree of orientation, so that zero corresponds to the isotropic state and unity corresponds to the ideal oriented state.

For structure analysis, the films friction-transferred on silicon wafers were studied by grazing incidence X-ray diffraction (GIXD). The X-ray diffraction measurements were performed by an advanced thin-film X-ray diffraction system—grazing incidence in-plane diffractometer (ATX-G) with focused Cu Kα radiation ($\lambda = 1.540\,56$ Å). The angle of incidence was adjusted close to the critical angle for total reflection against the substrate. The X-ray scattering vector Q, which is defined as the difference between the scattered and incident X-ray wave vectors, was positioned parallel to the film surface. The angle between the scattering vector Q and the drawing direction of friction-transfer was defined as χ, which was kept constant during the $\theta-2\theta$ scan. The molecular arrangement was determined by measuring the scattered intensity with χ. χ scans were carried out at a constant 2θ. Changes in scattered intensity at a fixed 2θ correspond to the distribution of arrangement of the reflecting plane (see Scheme 1). The structure of HT-P3AT had been investigated by several groups.[8−10,25] It has been reported that HT-P3AT are in the semicrystalline form, with a mixture of amorphous and crystalline fractions. The crystalline structure is composed of planar backbones of polythiophene stacked on top of each other with a stacking distance of 3.8 Å. The alkyl side chains extend to the space between neighboring polymers of which the separation distance depends on the alkyl side-chain length (P3HT = 16−18

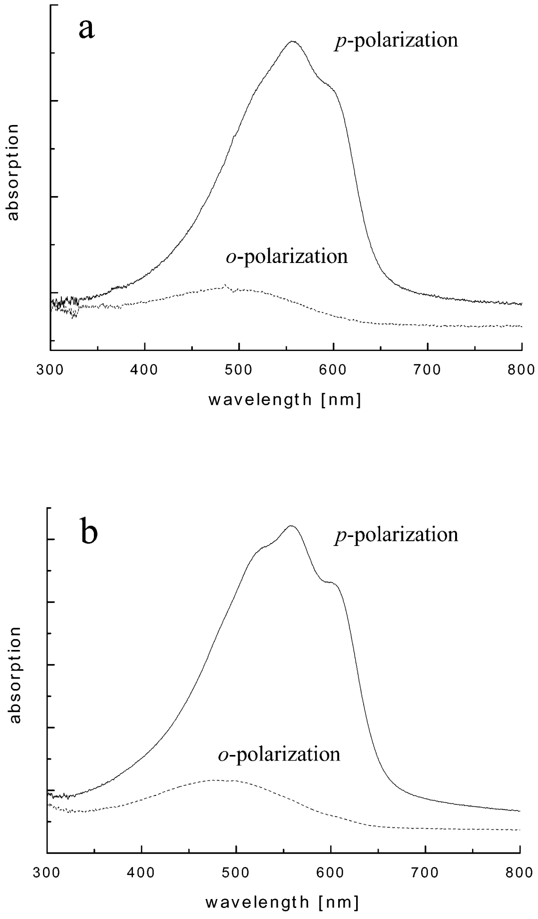


Figure 1. Polarized ultraviolet−visible absorption spectra of the friction-transferred P3HT (a) and P3DDT (b) films. p-polarization is defined as the light polarized parallel to the drawing direction of friction-transfer, and o-polarization is orthogonal to p-polarization.

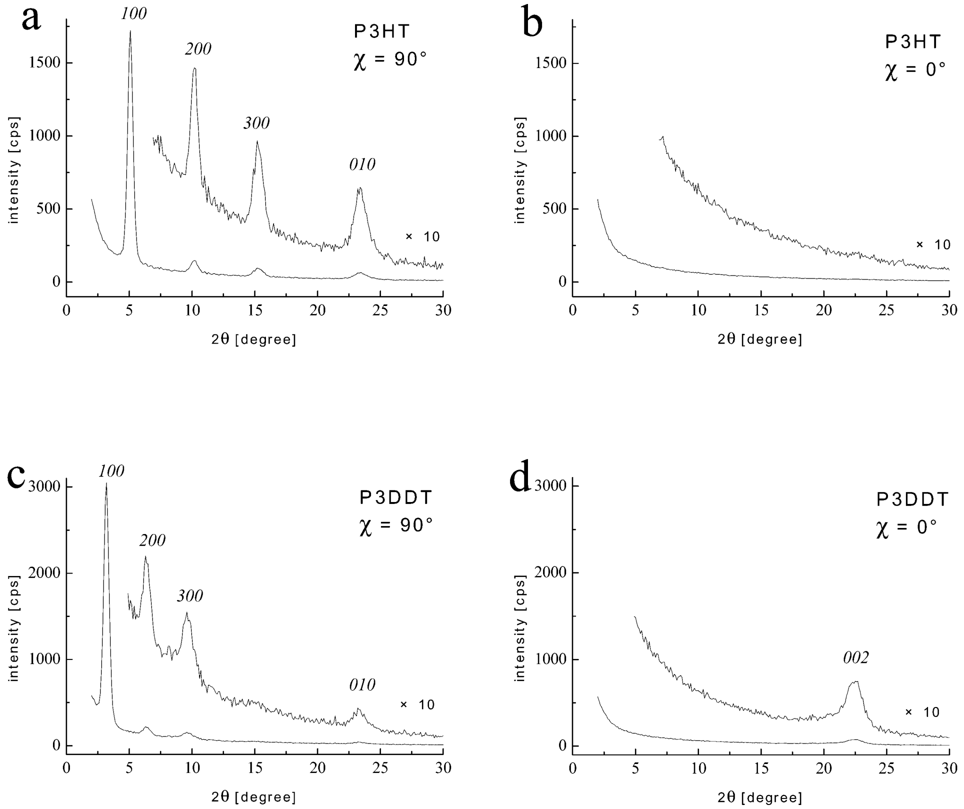


Figure 2. Grazing incidence diffraction pattern of friction-transferred P3HT (a, b) and P3DDT (c, d) films, with *Q* orthogonal ($\chi = 90°$) to the drawing direction of friction transfer (a, c) and with *Q* parallel ($\chi = 0°$) to the drawing direction of friction transfer (b, d).

Å, P3DDT = 25−27 Å). Hereafter, we refer to the alkyl side chains direction as the *a*-axis, the π-stacking direction, which is perpendicular to the planar thiophene rings, as the *b*-axis, and the polymer backbone (main chain of polythiophene) direction as the *c*-axis.

Results and Discussion

Figure 1 shows the polarized UV−vis absorption spectra of the friction-transferred P3HT (a) and P3DDT (b) films on quartz substrates. Since the UV−vis absorption of π-conjugated polymers assigned to the $\pi-\pi^*$ transition is very sensitive to the direction of polarization of incident light, one can use polarized light to probe the structural anisotropy in the films. The absorption spectra show different profiles depending on the type of polarization. The P3HT (Figure 1a) with p-polarization showed an absorption maximum at 560 nm and shoulders at 524 and 610 nm, which are assigned as the well-ordered and long conjugated polymer backbones. With the o-polarization, on the other hand, only a single peak at around 485 nm was observed. The absorption spectra of P3DDT (Figure 1b) showed a similar anisotropy to those of the P3HT. Compared to the friction-transferred films, the films prepared by casting and spin-coating did not show anisotropy in absorption. These results indicated that the polymer backbones in the friction-transferred HT-P3AT films were arranged parallel to the drawing direction of friction-transfer. The dichroic ratio *D* at 560 nm, the maximum absorption with p-polarization, was 10−100, and the order parameter *O* calculated from *D* was 0.75−0.97. Such high uniaxial arrangement of polythiophene backbones is not once reported in the HT-P3AT films prepared by other polymer backbone arrangement methods, such as the rubbing technique.[11]

Figure 2 shows the in-plane grazing incidence X-ray diffraction patterns of the friction-transferred HT-P3AT films on single-crystal silicone wafers. The orthogonal ($\chi = 90°$) diffraction pattern of the P3HT film shows two sets of reflection: the three low-angle diffraction peaks indexed *h*00 ($h = 1-3$) and the peak indexed 010 (Figure 2a). The former are associated with the crystallographic direction along the alkyl side chains (*a*-axis), and the latter is associated with the π-stacking direction of the backbones consisting of polythiophene (*b*-axis). The orthogonal diffraction pattern of the P3DDT film also shows the *h*00 and 010 reflections (Figure 2c). From the *h*00 reflection of HT-P3ATs, it is clear that the inter-layer spacing between polymers was increased with the increase in alkyl side-chain length. Since the 010 reflection is independent of the side-chain length, it can be attributed to the stacking distance of plane backbones of polythiophene.[25] Since these diffractions were observed in-plane, it is suggested that both the *a*- and *b*-axes are in the film plane. As described before, the *a*- and *b*-axes perpendicularly intersect each other, and the polarized UV−vis spectra have revealed that the *c*-axis aligned along the drawing direction of friction-transfer. These results show the presence of two molecular arrangements in the film: one with the *a*-axis aligned in the film plane and the other with the *b*-axis aligned in the film plane. The friction-transferred HT-P3AT film and solution-processed HT-P3AT film differ largely, by means of the peak intensity ratio of the 100 reflection and the 010 reflection. Within the solution-processed HT-P3AT films, it is reported that the 010 reflection is dominant in the in-plane structure. Therefore, on the whole, the *a*-axis must be parallel to the scattering vector *Q* in the friction-transferred HT-P3AT film. Although the conventional measurement system with

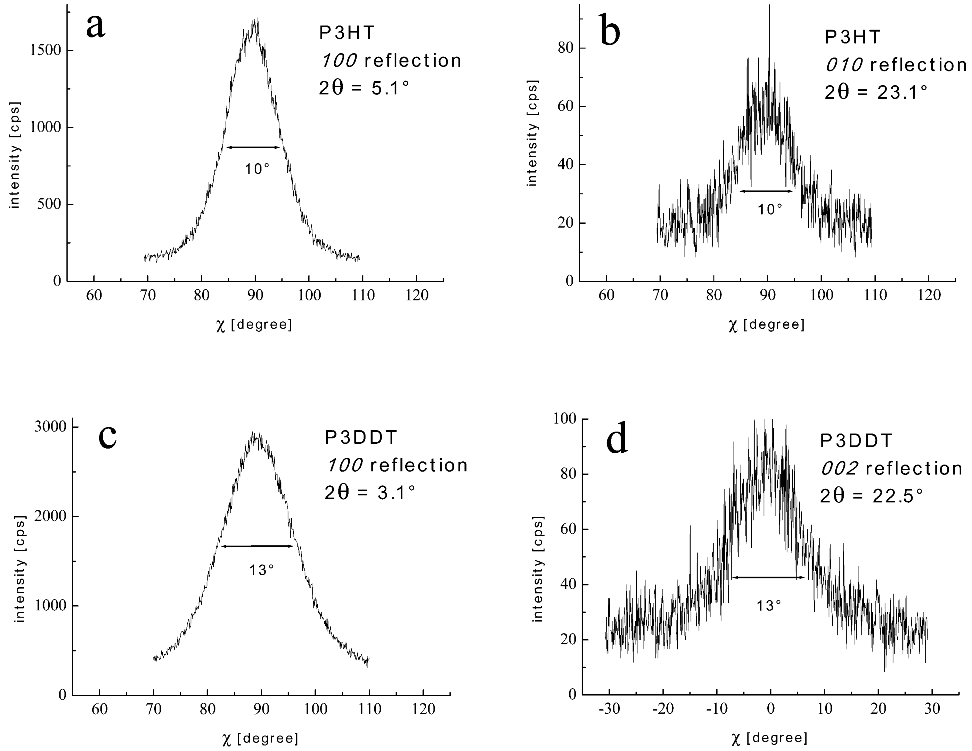


Figure 3. Distributions of arrangement of reflecting plane in the friction-transferred P3HT (a, b) and P3DDT (c, d) films. The angle χ dependence of (a) P3HT orthogonal 100 reflection at approximately $\chi = 90°$ scan with fixed $2\theta = 5.1°$, (b) P3HT orthogonal 010 reflection at approximately $\chi = 90°$ scan with fixed $2\theta = 23.1°$, (c) P3DDT orthogonal 100 reflection at approximately $\chi = 90°$ scan with fixed $2\theta = 3.1°$, and (d) P3DDT parallel 002 reflection at approximately $\chi = 0°$ scan with fixed $2\theta = 22.5°$.

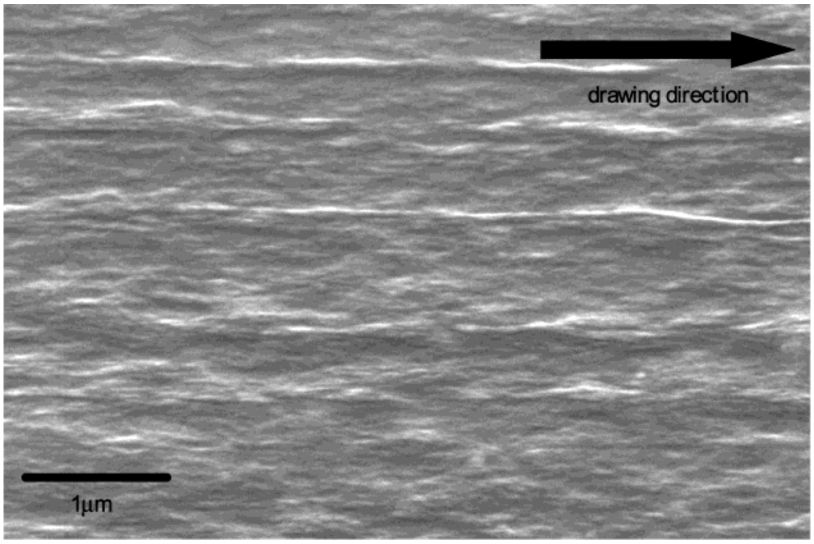
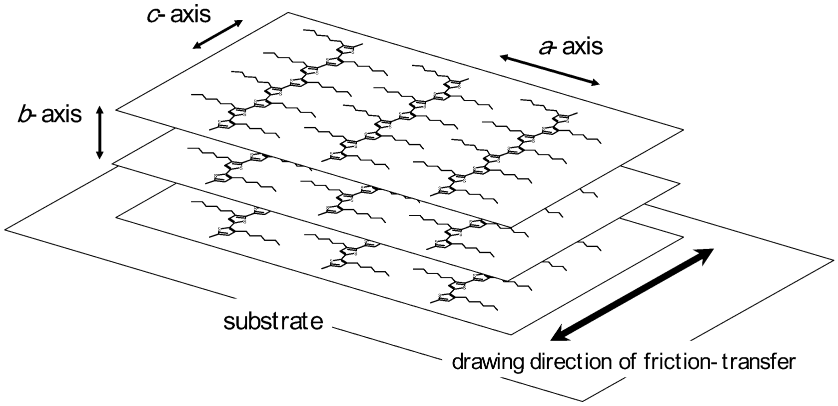


Figure 4. SEM image of the friction-transferred P3HT film on silicon substrate. The drawing direction of friction transfer is indicated by the arrow.

vertical X-ray diffraction cannot detect any reflection peaks because of a thickness value smaller than the detection limit, we have confirmed that polymers in the film plane are arranged with the *a*-axis dominant by introducing energy-dispersive grazing incidence X-ray diffractometry for the whole reciprocal lattice space measurement[17] (the details will be reported separately). From these viewpoints, we conclude that the *a*-axis lies in the film plane, and the *b*-axis is normal to the film surface.

The parallel ($\chi = 0°$) diffraction pattern of the P3HT film shows no *h*00 and 010 reflections (Figure 2b). This indicated that both the *a*- and *b*-axes are perpendicular to the drawing direction of friction-transfer and the *c*-axis is parallel to the drawing direction of friction-transfer, which are consistent with the results of the polarized UV−vis absorption spectra. The parallel diffraction pattern of the P3DDT film shows only a reflection indexed 002, centered at a 2θ angle of 22.5° (Figure 2d). Since the *a*- and *b*-axes are perpendicular to the drawing direction of friction-transfer, the reflection observed as a peak at 22.5° can be attributed to the 00*l* reflection from the *c*-axis. Therefore, the 002 reflection observed here could correspond to the fiber period (distance of two thiophene rings in a backbone) of 7.98 Å. This is a first observation of the meridional reflection by grazing incidence X-ray diffraction without using synchrotron radiation. Thus, the HT-P3AT mol-

Scheme 2. Schematic Structure for Polymer Molecular Arrangement in Friction-Transferred HT-P3AT Film



ecules in friction-transferred films can be crystallized considerably. In fact, all the diffraction patterns of the friction-transferred HT-P3AT films did not show a broad peak at $2\theta = 15°-30°$ from amorphous fraction, which is shown strongly in the diffraction patterns of the solution-processed HT-P3AT films.

We found that the diffraction patterns strongly depended on the angle χ between the scattering vector Q and the drawing direction of friction-transfer. Changes in the scattering intensity at the fixed scattering angle 2θ indicate the distribution of arrangement of the reflecting plane to the drawing direction of friction-transfer. The half-width of the distribution of the P3HT orthogonal 100 reflection was estimated to be 10° (Figure 3a), and that of the P3HT orthogonal 010 reflection was also found to be 10° (Figure 3b). This might be the first observation of the in-plane distribution of the arrangement of HT-P3AT molecules in the film by X-ray diffraction. These results show that the polymer backbones (*c*-axis) in the friction-transferred film are well-ordered in the drawing direction of friction-transfer. The friction-transferred P3DDT orthogonal 100 reflection distribution was 13° (Figure 3c). The P3DDT parallel 002 reflection had a distribution of 13°, which was the same as the P3DDT orthogonal 100 reflection distribution (Figure 3d). It is interesting to note that the parallel 002 reflection has the same distribution as the orthogonal 100 reflection despite a different χ. The HT-P3AT molecules in friction-transferred films are excellently arranged in not only the drawing direction of friction-transfer but also orthogonally.

Figure 4 shows a SEM image of the friction-transferred P3HT film on the silicon substrate. The friction-transferred P3HT film has a uniform surface morphology, which is clearly different from that of the friction-transferred PTFE film. The friction-transferred PTFE film surface consists of numerous submicrometer-periodic grooves.[15−20] The applications of friction-transferred PTFE films have shown that these films have in-plane electrical properties caused by surface topological features. On the other hand, this uniform surface morphology of friction-transferred HT-P3AT films offers attractive advantages as an active semiconducting layer with an intrinsic in-plane anisotropy in electronic devices.

Conclusions

We have revealed that the HT-P3AT molecules in friction-transferred films are considerably crystallized and ideally arranged three-dimensionally (see Scheme 2). Thus, the friction-transfer technique is very useful for the preparation of a molecularly arranged film of conjugated polymers that does not involve a solution process. Amundson et al. have reported the in-plane anisotropic carrier mobility of a bilayer film of P3HT on friction-transferred PTFE.[15] We have also observed the in-plane anisotropic carrier mobility in friction-transferred-HT-P3AT-film field-effect transistors.[26] The electrical properties are also affected by the molecular arrangement. In this study, we demonstrated that the friction-transferred HT-P3AT films have a large anisotropy. Fabrication of some new devices functionalized by the high optoelectronic anisotropy of active semiconducting layers is currently under way.[27]

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