Anisotropic charge transport in highly oriented films of semiconducting polymer prepared by ribbon-shaped floating film

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Fabrication of large area and uniform thin films with preferred edge-on orientation is highly demanded for flexible organic electronic devices. In this work, utilization of a newly designed slider in the floating film transfer method to assist unidirectional film spreading led to the fabrication of uniform and macroscopically edge-on oriented ribbon-shaped floating films (15 cm × 2 cm) having very large optical anisotropy (>20). The results pertaining to the in-plane grazing angle incident X-ray diffraction (GIXD) and φ-scan measurements revealed the well-stacked polymer backbone conformation with edge-on orientation without any inter-mixing of face-on oriented counterparts. Optical anisotropy dependent charge transport in organic field effect transistors using anisotropic poly(3,3‴-didodecyl-quaterthiophene) films has also been shown, and the results are supported by polarized electronic absorption and GIXD measurements. *Published by AIP Publishing.* https://doi.org/10.1063/1.5000566

Recent years have witnessed intense investigations for solution-processable conjugated polymers (CPs) due to their application potential in the area of printed electronics.[1,2] Interest in CPs was geared considering their features like mechanical flexibility, self-assembly, and tuning of their electronic functionality. Inherent 1-dimensionality and extended π-conjugation of CPs render them highly susceptible to molecular self-assembly in a condensed state. Unidirectional alignment of CP macromolecules is highly desired for the facile in-plane charge transport along the orientation direction resulting in improved performance of organic field effect transistors (OFETs). Performance of the devices based on CPs stringently depends on their film morphology, leading to the proposal of various film fabrication techniques.[3–5] A number of methods have been proposed to orient CPs; however, most of them use shear forces resulting in face-on orientation. At the same time, the existing possibility of physicochemical damages to the underlying soft polymeric layers also cannot be ruled out.[6,7] However, direct deposition of thin films via slow solvent evaporation from the polymer solution inherently results in thermodynamically favored edge-on orientation of CPs, which is highly favorable for planar devices like OFETs.[3,8,9]

We have reported a facile and low-cost strategy for fabricating oriented thin films of CPs on hydrophilic viscous liquid substrates and named as the floating film transfer method (FTM).[4,9] In this method, film formation takes place by simultaneous rapid spreading and compression of the film by dragging force posed by the viscous liquid substrate as reported earlier in detail.[9–11] In this work, a ribbon-shaped FTM is being reported which provides very large area and highly oriented thin floating films. At the same time, these macroscopically oriented films exhibit very small variation in the film thickness as well as orientation intensity. The in-plane grazing angle incident X-ray diffraction (GIXD) measurement was carried out to probe the arrangement of the polymeric backbones. In addition, OFETs were also fabricated using such oriented films to probe the implication of observed optical anisotropy on the anisotropic charge carrier transport.

Poly(3,3‴-didodecyl-quaterthiophene) (PQT) with molecular weight ($M_W = 10\,010$ g/mol) and a polydispersity index (PDI) of 2.28 was synthesized as per our previous publication which was used as representative CP in the present work.[12] PQT polymer solution 2% (w/w) was prepared by dissolving in super dehydrated chloroform (Wako, Japan) with the maximum water content of 0.001%. A custom-made slider consisted of polytetrafluoroethylene was designed and used to provide directionality while film spreading. The slider was dipped in a rectangular tray in such a manner that half of its slope was immersed in the viscous liquid substrate as shown schematically in Fig. 1. The viscosity of the liquid substrate plays a dominant role and decides not only the thickness but also the molecular orientation which was optimized as reported earlier.[10] We have used a mixture of ethylene glycol and glycerol in the ratio of 3:1 as an optimized viscous liquid substrate and 25 μl of the polymer solution was dropped in the center of the slider. This dropped polymer solution rapidly spreads and expands in the form of a ribbon up to 15–20 cm from the drop point. However, unlikely to our standard FTM reported previously,[9] spreading, in this case, took place only in one direction due to the tilted bottom wall of the slider (Fig. 1). Orientation was qualitatively verified by the naked eye using a polarizing film followed by its transfer on the glass slides (1.1 cm × 2.5 cm) by stamping for quantitative analysis. Spin-coated films were also prepared from 0.5% (w/w) PQT solution in chloroform by spin coating at 3000 rpm for

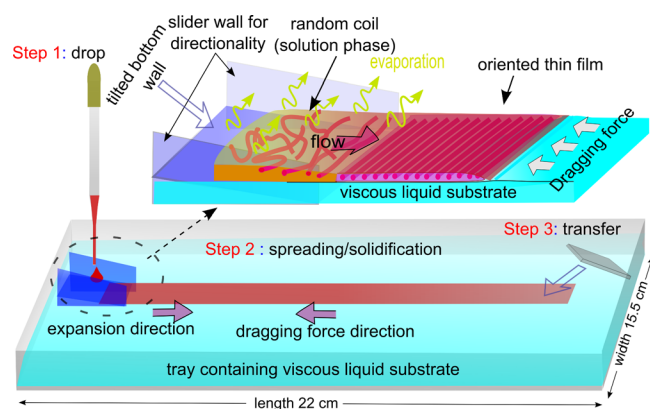a)Electronic addresses: tripathi-atul@edu.life.kyutech.ac.jp and shyam@life.kyutech.ac.jp

FIG. 1. Schematic illustration for the fabrication of ribbon-shaped oriented FTM films and its orientation mechanism.
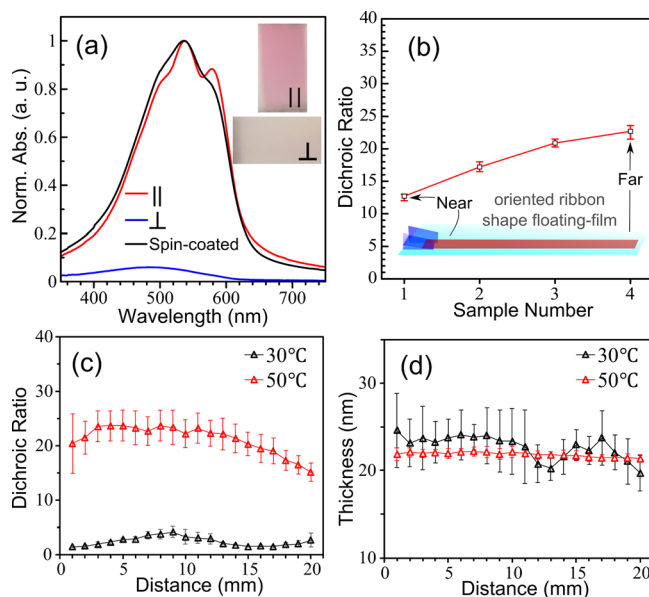

FIG. 2. (a) Polarized electronic absorption spectra of the oriented film and (b) variation of DR from near to far with samples taken at an equidistant interval in a 15 cm long ribbon-shaped oriented film. Variation in DR (c) and film thickness (d) of the oriented film cast on a glass substrate with an area of $2 \times 2\,cm^2$. The inset in (a) is the photograph of the oriented film transferred on a glass slide with $\parallel$ and $\perp$ orientations. The dark color shows parallel ($\parallel$) and almost colorless shows perpendicular ($\perp$) orientation when the angle of the polarizer was rotated from 0° to 90°. The error bar represents maxima and minima (b) and standard deviation (c) and (d).

120 s for comparison. PQT coated glass substrates were annealed at $60\,^\circ C$ for 5 min in order to ensure the complete evaporation of any remaining solvent. Polarized electronic absorption spectra were measured with a UV-visible-near infrared spectrophotometer (JASCO V-570) equipped with Glan Thomson prism. In order to quantify the molecular orientation and optical anisotropy in the FTM processed films, the optical dichroic ratio (DR) was also estimated from the polarized optical absorption spectrum. Optical DR was defined as $DR = A_\parallel/A_\perp$, where $A_\parallel$ and $A_\perp$ are the absorption maximum (λ_{max}) of the film along the $\parallel$ and $\perp$ directions of the orientation, respectively.[10] The thickness measurement was carried out with the help of interference microscopy (Nikon Eclipse LV150) to determine the extinction coefficient followed by thickness estimation using peak absorbance during positional mapping.

Figure 2(a) exhibits the polarized electronic absorption spectra of the oriented ribbon-shaped FTM as well as spin-coated thin films of PQT. The spin-coated PQT film exhibits a featureless absorption spectrum with ill-defined vibronic modes as compared to that of oriented films. On the other hand, parallel oriented PQT thin films exhibit clear peaks at λ_{max} around 537 nm and 580 nm along with a shoulder at 505 nm. The presence of a well-defined vibronic peak around 580 nm represents the formation of higher structural ordering in the condensed state and enhanced π–π lamella stacking.[13] DR of the oriented film shown in Fig. 2(a) was found to be 22. Interestingly, Pandey *et al.*[13] have also reported orientation in the PQT films by our conventional FTM but DR was considerably low along with less pronounced vibronic features. Such a high resolution of the 0–0 vibronic transition at 580 nm indicates the higher planarization of polymeric chains and enhanced molecular ordering due to higher unidirectional orientation.[14]

Absorption spectra of the films with $\perp$ orientation are featureless with λ_{max} at 489 nm and are very similar to that in solution, which clearly indicates the presence of randomly distributed polymer chains.[9,15] Macroscopic orientation in this work can be gauged by the fact that a single drop (25 μl) of polymer solution leads to the formation very large (15 cm $\times$ 2 cm) ribbon-shaped and oriented FTM films. Since molecular orientation in the FTM films results from the synergistic interaction between the solvent evaporation and viscous drag by the liquid substrate, it is obvious to have some

variation in the observed DR at such a large scale oriented film which is shown in Fig. 2(b). A perusal of this figure corroborates that observed DR at the distal end (far) of the film is relatively high as compared to that at the proximal end (near) from the solution dropping point. It is attributed to the fact that progressing film towards the distal end has to pass through the additional dragging force posed by the viscous liquid substrate before their solidification. The homogeneity of the thin films in terms of their thickness and molecular orientation plays a crucial role in controlling the final device performance. Figures 2(c) and 2(d) show the variation in DR and thickness at intervals of 1 mm in the oriented film with a point source photonic analyzer connected with the computer controlled mobile stage for holding the PQT coated glass substrate. It can be seen that the thickness of the FTM films fabricated at $50\,^\circ C$ is rather uniform (variation ± 1 nm) as compared to that prepared at $30\,^\circ C$ having relatively large thickness inhomogeneity (variation ± 6 nm) in the latter case. Relatively less uniformity in the films fabricated at a lower temperature could be associated with the slow solvent evaporation and non-uniform expansion.

In-plane GIXD measurements were also taken in order to analyze the conformation of the backbones in the FTM processed films as shown in Fig. 3(a). Measurements were taken by casting the oriented films on a bare silicon wafer following the measurement geometry [inset of Fig. 3(a)].[7,16] It can be seen that all of the diffraction peaks related to lamellar alkyl-stacking are absent and only 010 peak associated with π-π staking appeared at 21° in the as-cast film when the incident X-ray was $\parallel$ ($\chi = 90^\circ$) to the orientation direction.[17,18] Interestingly, the same peak at 21° completely
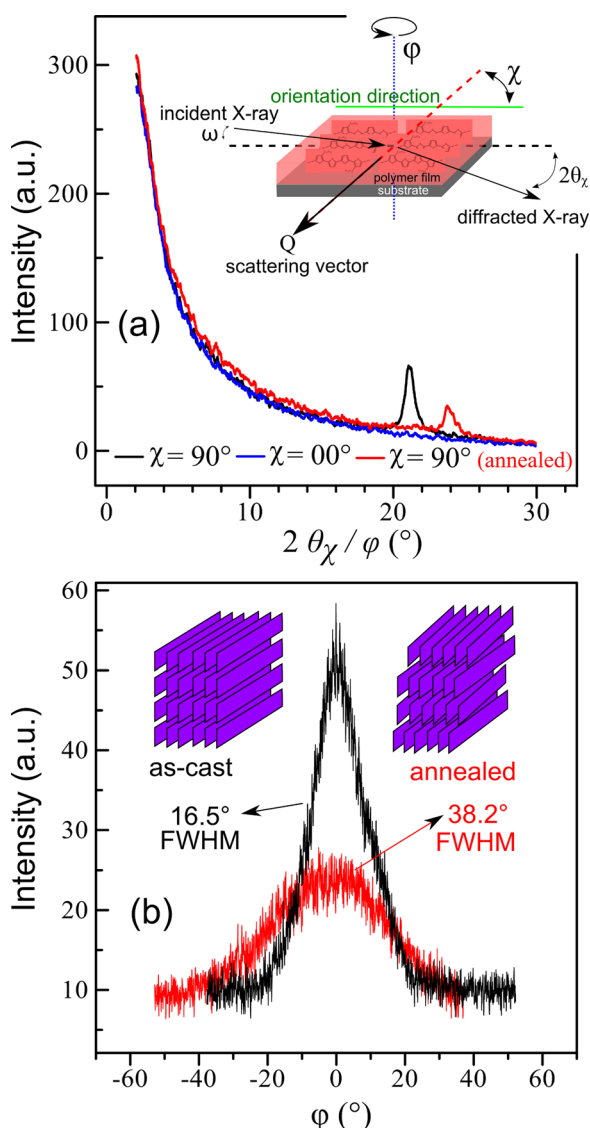
FIG. 3. (a) In-plane GIXD of the oriented PQT film before and after thermal annealing, (b) φ scan of the 010 peak of as-cast and annealed oriented films. GIXD along $\chi = 0°$ and $\chi = 90°$ represents the diffraction pattern along the perpendicular and parallel to the orientation directions, respectively. The inset in (a) presents the experimental geometry for the in-plane GIXD set-up and the inset in (b) is the schematic view of the orientation pattern in the edge-on oriented film before and after annealing.

disappears when the incident X-ray was $\perp$ ($\chi = 0°$) to the orientation direction. These results imply that the polymers are uni-directionally oriented with conjugation as well as the π–π staking axis is in-plane of the substrate (edge-on orientation).[9] This is crucial for devices like OFETs, where charge transport takes place at the insulator/semiconductor interface and the presence of any alkyl sidechains in the channel direction acts as resistive barriers for hopping of the charge carriers.[19]

It has been reported that PQT exhibits liquid crystalline (LC) behavior and alkyl side-chains melt around 130 °C.[20] In our case, when the as-cast highly oriented film was annealed at LC phase transition temperature for 5 min, the 010 peak shifted at 24° representing more dense packing in the films. Since there was no remarkable change in the extent of orientation after annealing, this could have originated from the disturbance in the polymer stacking. In order to probe this,

φ-scan was also performed for 010 peak of as-cast and annealed films as shown in Fig. 3(b). The φ-scan yielded a full width at half maximum (FWHM) of 16.5° in the as-cast film which increased drastically to 38.2° for annealed films. This clearly indicates that although the π–π stacking goes under more dense state once annealed, however, there was a disturbance in the molecular arrangement during π–π stacking. It is also worth noting here that these values of FWHM are very close to oriented poly(3-hexylthiophene) prepared by mechanical rubbing and friction transfer techniques; however, those methods yielded face-on orientation with alkyl chains laying in-plane to the substrate.[21,22]

OFETs were fabricated by stamping the oriented PQT films on CYTOP coated SiO_2/Si(p++) substrates with the capacitance of 8 nF/cm^2, followed by washing with isopropanol and drying in air for 15 min to remove any remaining liquid substrate adhered with the stamped film. Later, source and drain contacts were evaporated at 10^{-6} Torr with nickel shadow mask having the channel length and width of 20 μm and 2 mm, respectively, as schematically shown in Fig. 4(a). Electrical characterization was made under dark with a computer-controlled electrometer (Keithley-2612) at 10^{-3} Torr. Field effect mobility (μ) and other parameters were extracted in the saturation region as reported earlier.[23] Charge transport was evaluated for PQT in both the orientation directions, viz., with the channel || to orientation and channel $\perp$ to orientation directions [Fig. 4(a)]. Parallel and perpendicular OFETs were fabricated on the same substrates and in similar device configurations in order to pinpoint the implication of molecular orientation only and avoiding the substrate-dependent deviations. Figure 4(b) shows the typical I-V characteristics with a clear p-type behavior, where higher output currents (I_{DS}) were observed when the channel was || as compared to devices with the channel $\perp$ with respect to the orientation direction of the polymer backbone. Figure 4(c) shows the transfer characteristic of the same OFETs (DR = 22) with average (maximum) μ of 0.026 (0.029) cm^2/Vs and 0.0025 (0.0014) cm^2/Vs along the || and $\perp$ directions, respectively. All of the OFETs using oriented PQT films exhibited nearly similar on/off ratios typically in the order of 10^5 and 10^4 for || and $\perp$ films, respectively. As discussed above, the possibility of fabricating PQT films with variable optical anisotropies by controlling the film casting conditions under ribbon-shaped FTM encouraged us to explore the implication of extent of molecular orientation on the anisotropic charge transport. To accomplish this, OFETs were fabricated using oriented PQT films with varying optical anisotropy and DR dependent μ for parallel ($\mu_{||}$) and perpendicular oriented ($\mu_{\perp}$) PQT films as shown in Fig. 4(d). It can be clearly seen that mobility anisotropy ($\mu_{||}/\mu_{\perp}$) increases with the increasing DR, which clearly indicates the significance of increasing the molecular orientation on the charge transport. Biniek *et al.*[22] have reported that nature of the molecular orientation and extent of their distribution (edge-on/face-on) in CPs play a dominant role in controlling the charge carrier transport anisotropy ($\mu_{||}/\mu_{\perp}$). Therefore, almost one order of magnitude change in ($\mu_{||}/\mu_{\perp}$) for PQT films at high DR is in good agreement with the GIXD results, where a well-stacked edge-on conformation was clearly seen.

The angular dependent μ measurement was carried out, where the orientation direction of the highly oriented film (DR = 22) was changed against the channel direction
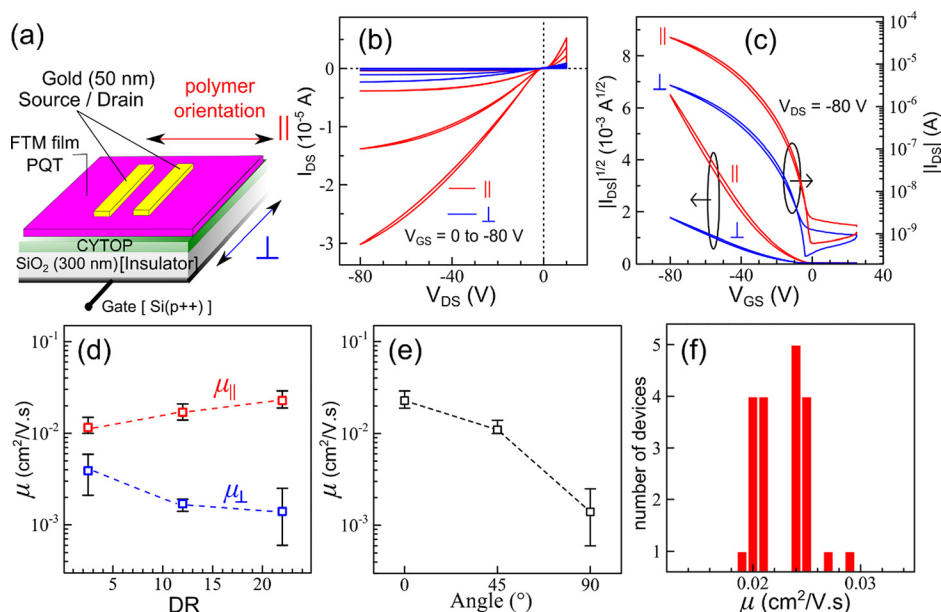
FIG. 4. Device schematic of the fabricated OFET (a), their output (b), and transfer curves (c) using the oriented PQT film having the DR of 22. Variation in μ for the OFETs using oriented PQT of variable DR (d), where $\mu_{||}$ and $\mu_{\perp}$ represent the μ along the $||$ and $\perp$ directions, respectively. PQT film with low DR ($\sim$2) was cast at 30 °C while that with intermediate DR ($\sim$12) was cast at the proximal end of the oriented ribbon-shaped film prepared at 50 °C. Angle dependent μ with respect to channel direction (e) and μ histogram at DR 22 (f). Error bar represents maxima and minima in (d) and (e).

[Fig. 4(e)]. The average drop in μ at 45° and 90° was 2 and 16 times, respectively, with respect to $\mu_{||}$. This small drop in $\mu_{45°}$ in comparison to $\mu_{\perp}$ can be well correlated with the fact that π–π stacking has a dominant role in the charge transport when combined together with the long-axis,[24] whereas low $\mu_{\perp}$ in such highly oriented films can be ascribed due the presence of only π–π stacking. We also found a low deviation in the μ histogram for $\mu_{||}$, which clearly indicates the high homogeneity in films [Fig. 4(f)]. It is worth mentioning that reported benchmark μ of PQT is 0.1 cm²/Vs by spin coating and other deposition techniques, which is relatively high as observed in this work.[17,24,25] Although this has been well acknowledged in the past that μ in OFETs stringently depends on many other parameters such as gate dielectric, dielectric/semiconductor interface, and molecular weight of the CPs, their optimization is beyond the scope of this work.[26] In an interesting report on charge transport in PQT, Pingel *et al.*[14] have emphasized that M_W and PDI both play a dominant role in controlling the charge transport. There was about three orders of magnitude change in the μ depending on the M_W and PDI. Therefore, relatively low M_W and high PDI of PQT in our case could be one of the possible reasons for the 1-order lower μ.

In conclusion, we have demonstrated a cost-effective method for the fabrication of large area, uniform, and highly oriented floating films. It has been shown that oriented films of PQT up to 15 cm in length can be easily cast with just 25 μl of the polymer solution. Polarized electronic absorption spectra of the oriented PQT films exhibited very high optical anisotropy of DR = 22. Investigation pertaining to the film uniformity in terms of the extent of orientation and thickness revealed high uniformity for the films fabricated under optimized casting conditions. In-plane GIXD results also clarified the well-stacked backbone conformation with ideal edge-on orientation. At the same time, φ-scan suggested that although PQT shows a thermotropic LC phase but main chains are ideally aligned in edge-on conformation without any thermal treatment at LC phase transition temperature. DR dependent charge transport anisotropy has also been demonstrated and is well correlated with the results of polarized electronic absorption spectroscopy as well as GIXD supporting the fact that the increase in DR leads to increased $\mu_{||}$, decreased $\mu_{\perp}$, and vice versa.

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