

# Investigation and control of charge transport anisotropy in highly oriented friction transferred polythiophene thin films

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## ABSTRACT

Highly oriented thin films of poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] PBTTT were prepared by friction transfer technique followed by their characterization using polarized absorption spectroscopy, angle-dependent polarized Raman spectroscopy and X-ray diffraction techniques. Orientation in high molecular weight ( $M_w$ ) polymers is hampered by chain folding/entanglements, which limits their macromolecular orientation. Interestingly, utilizing high molecular weight PBTTT ( $M_w > 50$  kDa) and friction transfer technique, successful fabrication of highly oriented thin films with very high dichroic ratio ( $\sim 30$ ) was demonstrated. Role of the substrate's surface energy and their impact on the field-effect mobility ( $\mu$ ) of the oriented thin films was comprehensively investigated. Influence of annealing of the thin films as prepared on the bare and self-assembled monolayer (SAM) treated  $\text{SiO}_2$  surface exhibiting differential trends of  $\mu$  was systematically investigated. This was explained by partial and complete conformational transformation of macromolecule on bare and SAM treated  $\text{SiO}_2$  surface, respectively, after their annealing beyond liquid crystalline phase transition temperature as revealed by in-plane and out-of-plane XRD results. On bare  $\text{SiO}_2$  optimum  $\mu$  up to  $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  along the backbone orientation was obtained for the thin films annealed to  $120 \text{ }^\circ\text{C}$ , where as it reached up to  $0.36 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  on SAM treated  $\text{SiO}_2$  after annealing at  $200 \text{ }^\circ\text{C}$ . Finally, a charge transport mechanism was proposed taking evidences from the anisotropic optical and electrical characteristics of the friction transferred PBTTT films in to consideration.

**Keywords:** Semiconducting polymer; orientation; dichroic ratio; electrical anisotropy; surface energy dependent charge transport mechanism; Friction Transfer.

## 1. Introduction

Organic semiconductors are promising candidates for flexible electronics due to their excellent electrical and optical properties.<sup>1-3</sup> Considerable efforts have been made to improve the charge transport in thin films of organic semiconductors by tuning their chemical structure or processing techniques aiming towards enhancing their crystallinity.<sup>4,5</sup> Conjugated polymers (CPs) offer better solution processability, device reproducibility and solution rheology over the small-molecule organic semiconductors.<sup>2,6-8</sup> Utilizing the quasi 1-dimensional nature of CPs is amongst one of the best possible means for improving the carrier transport by uniaxially orienting them along the source and drain electrodes of an organic field-effect transistor (OFET). Orientation methods for CPs are generally categorized by the physical state in which it was processed such as processing in solution-state or in the solid-state.<sup>2</sup> Solution processing made the device fabrication possible at low-cost and low-temperature, nonetheless, there are some limitations such as need for good solubility of the CPs, surface wettability, and in some techniques pre-aggregation in solution is essential for orientation.<sup>9,10</sup> At the same time need for the halogenated organic solvents for film fabrication may also create serious health and environmental hazards during large-scale production.<sup>2,11</sup> Friction transfer is a solvent free processing method to orient CPs and is effectively utilized to overcome these issues.<sup>12-14</sup> There are reports on the high optical anisotropy of such thin films and their impact on controlling the anisotropic charge transport.<sup>13-15</sup>

Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT) is one of the rigid rod-like polymers extensively studied in the past 10 years due to its high field-effect mobility ( $\mu$ ).<sup>16,17</sup> The increase in  $\mu$  of PBTTT has been widely observed after annealing of the thin films above its liquid crystalline (LC) temperature.<sup>16,18</sup> At the same time, its charge transport is highly sensitive

to the substrate characteristics primarily the surface energy.<sup>17,19</sup> Taking this into consideration, friction transferred PBTTT thin films fabricated on low and high surface energy substrates were annealed below and above its LC phase transition temperature in order to investigate the influence of the polymer ordering on their optoelectronic properties. Here high energy substrates represent bare glass, bare SiO<sub>2</sub> or bare Si substrates and some of them were treated with hexamethyldisilazane (HMDS) in order to decrease their surface energy by forming the self-assembled monolayer (SAM).<sup>17</sup> Since bare Si has also few nanometers of native oxide on its top surface, therefore, henceforth in this manuscript both Si and SiO<sub>2</sub> surfaces will be termed as oxide surface. In this work, oriented thin films of PBTTT were fabricated by friction transfer method and macromolecular orientation was investigated by various characterization techniques, such as polarized UV-visible absorption spectroscopy, angle-dependent Raman spectroscopy, X-ray diffraction (XRD), grazing incident X-ray diffraction (GIXD) and measurement of mobility anisotropy ( $\mu_{\parallel}/\mu_{\perp}$ ; where  $\mu_{\parallel}$  and  $\mu_{\perp}$  are field-effect mobility along and orthogonal to the backbone orientation direction respectively) by fabricating OFETs.

It was noticed that in the case of untreated substrates,  $\mu_{\parallel}$  and  $\mu_{\parallel}/\mu_{\perp}$  increased as a function of annealing temperature up to ~120 °C followed by a decreasing trend beyond this temperature. Contrary to this, for substrates having SAM exhibited a consistent increase in the  $\mu_{\parallel}$  with the annealing temperature but  $\mu_{\parallel}/\mu_{\perp}$  followed rather the opposite trend. Polarized-absorption spectroscopy can probe the presence of macromolecular anisotropy only but not their conformation and film crystallinity, which play a crucial role in charge transport. Therefore, the variation in  $\mu_{\parallel}$  and  $\mu_{\parallel}/\mu_{\perp}$  with the annealing temperature was correlated with the corresponding XRD and GIXD measurements. Finally, a plausible charge-transport mechanism was proposed based on the evidences obtained from temperature and interface dependent anisotropic charge transport.

## 2. Experimental Section

### *Materials and Thin-film fabrication:*

PBTTT with  $M_w > 50$  kDa (product code: 753971-250MG) was purchased from Sigma Aldrich. Dehydrated HMDS and the solvents were procured by Sigma Aldrich and Wako Chemicals Japan, respectively. The substrates (glass, Si and Si/SiO<sub>2</sub>) were thoroughly cleaned with acetone, isopropanol and ultrapure water by sonicating 10 minutes in each solvent followed by annealing at 150 °C for 1 h under ambient conditions. For SAM treatment, cleaned and dried substrates were covered with HMDS droplets and placed in a closed glass petri dish and kept at 50 °C for 1 h followed by sonication in dehydrated chloroform for 5 min and annealing at 150 °C for 1 h. The polymer pellet was prepared according to the method reported earlier.<sup>20</sup> Thin films of PBTTT were cast using friction transfer technique on the desired substrates by drawing the polymer pellet on it at a constant speed of 50 mm/min with a fixed squeezing load of 3 kgf/cm<sup>2</sup> kept at the top, as schematically shown in **Figure 1(a)**. All of the thin-film characterizations except electrical characterization were performed under ambient conditions.

### *Optical characterization:*

Absorption spectroscopy: The electronic absorption spectra of thin films coated on glass substrate were measured by dual beam spectrophotometer (JASCO V-570). A Glan-Thompson prism was placed between sample and the illumination source in order to measure polarized absorption spectra.

Polarized Raman spectroscopy: Polarized Raman spectra of the thin films coated on glass substrate were recorded using Raman spectrometer (JEOL NRS-4100). The linearly polarized laser beam ( $\lambda$

= 532 nm) was focused on the sample by a  $100\times$  objective lens associated with an attenuator with optical density of 3. For optimum signal-to-noise ratio an exposure time of 5s, and five accumulations were used to obtain the data. Samples were rotated with respect to the polarization direction of the laser source and spectra were measured at the angles of  $0^\circ$ ,  $30^\circ$ ,  $60^\circ$ , and  $90^\circ$ . In order to correlate macromolecular orientation with the angle dependent polarized Raman spectra, power of the laser source was kept constant at 10 mW throughout the measurement.

GIXD and XRD measurements: The index of refraction less than one, signifies that at grazing incident angle ( $\omega$ ) from the sample surface below critical angle ( $\omega_c$ ),  $\omega < \omega_c$ , X-rays go through total external reflection.<sup>21</sup> As a consequence, there is an evanescent wave within the refracting medium, which propagates parallel to the flat surface. Rapid decay of evanescent field amplitude leads to higher surface sensitivity of X-rays in this mode, with penetration depth of few nanometers. Thus, keeping X-ray at the angle  $\omega (< \omega_c)$  from a rotating plane of the surface favors the detailed analysis of the surface and near surface structures and known as in-plane GIXD measurement. On the other hand, when any two of X-ray source, sample, and detector are rotated out-of-plane of the sample surface and following Bragg diffraction condition, the structure along the depth of the sample is analyzed, it is termed as  $\theta$ - $2\theta$  or out-of-plane XRD measurement.<sup>22</sup> In this work, for structural analyses of the thin films, friction transferred PBTTT films on bare/HMDS treated silicon substrates were subjected to in-plane GIXD and out-of-plane XRD measurements, the schematic diagrams of the measurement techniques are shown in **Figure 2**(a, b). In-plane GIXD ( $\varphi$ - $2\theta$  scan) and out-of-plane XRD ( $\theta$ - $2\theta$  scan) measurements were performed by the Rigaku smart lab and Rigaku X-ray diffractometer, respectively with Cu-K $\alpha$  radiation source ( $\lambda = 1.54 \text{ \AA}$ ). During in-plane GIXD measurements the sample and detector were rotated with angle of  $\varphi$  and

$2\theta\chi$ , respectively, while keeping  $\omega$  and the scattered angles at 0.14 and 0.28, respectively from the sample surface. In the in-plane GIXD measurement, the angle between the scattering vector and drawing direction ( $\chi$ ) was kept around  $0^\circ/90^\circ$  to probe anisotropy in the macromolecular arrangement in the thin film. During out-of-plane XRD measurement the X-ray source and detector were rotated with angle of  $\theta$  and  $2\theta$  respectively from the sample surface. To see the distribution in macromolecular arrangement,  $\phi$ -scan or rocking curve measurement corresponding to specific peak was performed. It was carried out by keeping the source and detector fixed corresponding to certain  $2\theta\chi$ , while the substrate was rotated along  $\phi$ -direction, **Figure 2(a)**.

*Device fabrication and characterization:*

OFETs were fabricated in the bottom gate top contact device architecture on highly doped silicon wafers with 300 nm thick thermally grown  $\text{SiO}_2$  acting as the dielectric layer with a capacitance ( $C_i$ ) of  $10 \text{ nF/cm}^2$ . For device fabrication and optical characterizations, films were annealed to various temperatures for 3 – 5 min in Argon-atmosphere followed by slow cooling to room temperature. Further, to complete the OFETs, Gold electrodes were thermally evaporated on the friction transferred PBTTT thin film (deposition rate  $\sim 1.5 \text{ \AA/s}$  under pressure of  $\sim 10^{-6}$  Torr). A nickel shadow masks with channel length and width of  $20 \text{ }\mu\text{m}$  and  $2 \text{ mm}$ , respectively, was utilized to pattern the source and drain electrodes. The OFETs were characterized under mild vacuum with pressure  $\sim 10^{-2}$  Torr, through a two channel source-measure unit (Keithley 2612).

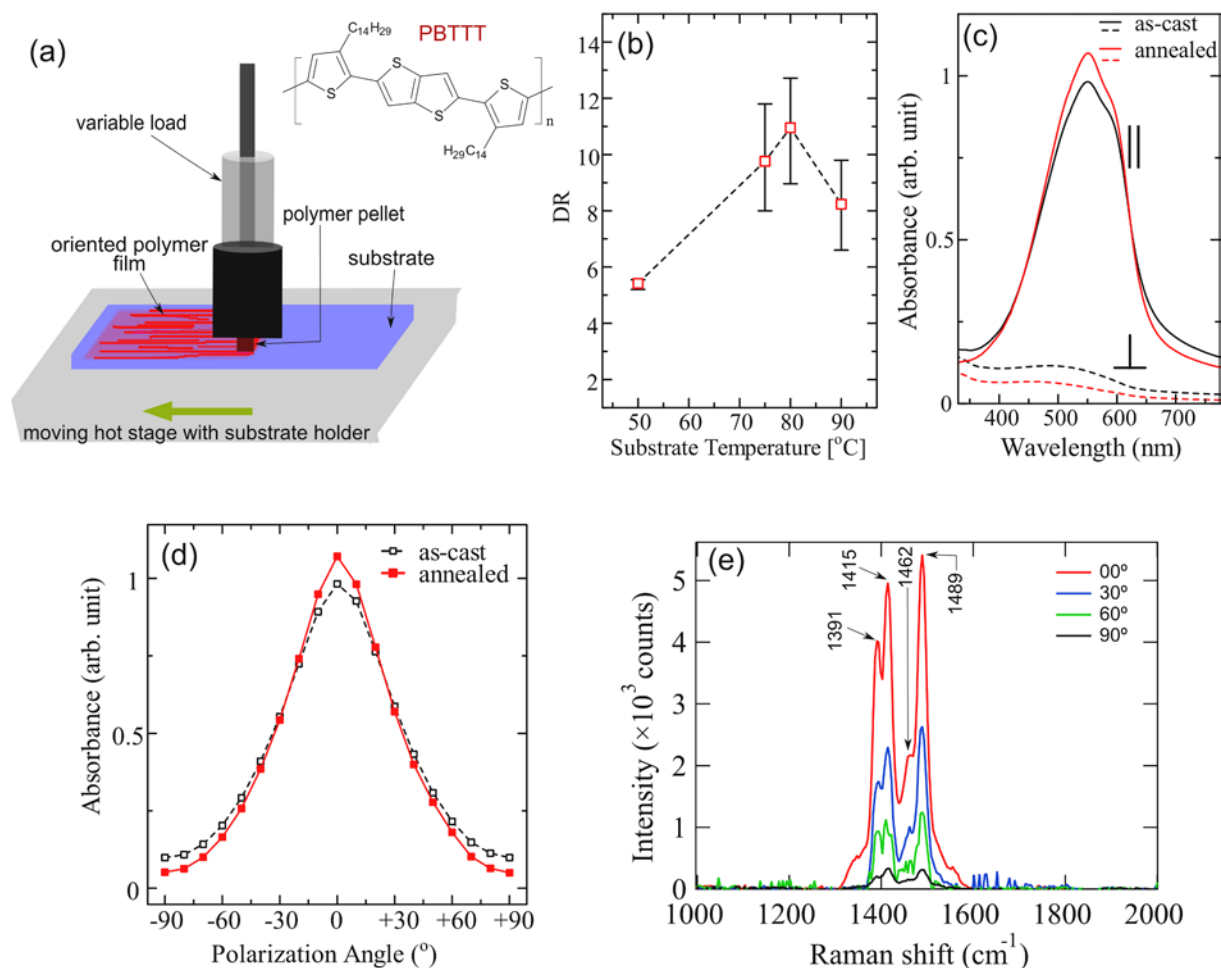
### **3. Results and Discussion**

To fabricate a highly oriented thin film of PBTTT by friction transfer method, the film casting parameters such as, drawing speed, squeezing load, and substrate temperature, play dominant roles

and they were optimized. It was found that low squeezing load and slow drawing speed resulted in high orientation, therefore, they were fixed to be 3 kgf/cm<sup>2</sup> and 5 cm/min, respectively, while optimum substrate temperature was found to be 80 °C as shown in **Figure 1(b)**. Polymer orientation of the fabricated thin films was characterized by polarized electronic absorption spectroscopy and the results are shown in **Figure 1(c)**. Since transition dipole moment for the optically induced  $\pi$ - $\pi^*$  transition is aligned along the polymer backbone, therefore, linearly polarized light is absorbed maximum, when the polarization direction was aligned parallel ( $\parallel$ ) to the polymer backbone orientation resulting in the highest value of absorbance (maximum absorption value at  $\lambda_{\text{max}}$ ), which decreases by moving the polarization direction away from the backbone orientation direction and reaches to the minimum, when they were orthogonal ( $\perp$ ) to each other. The optical anisotropy was calculated in terms of the dichroic ratio (DR) =  $A_{\parallel}/A_{\perp}$ , where  $A_{\parallel}$  and  $A_{\perp}$  are maximum absorbance of the respective absorption spectra with polarized light  $\parallel$  and  $\perp$  to the polymer orientation direction. The maximum absorbance along the drawing direction confirmed the orientation of polymers to be along the drawing direction. Average DR of the as-prepared films was found to be  $10.95 \pm 0.89$ . The DR further increases and reaches up to  $27.62 \pm 2.46$  upon annealing above LC temperature 180 °C.<sup>16,23</sup> Annealing temperature dependent DR is summarized in **Table 1**. It is worth to note that DR values were not significantly affected by the surface energy of the substrate. Such high DR values corresponds to the highly anisotropic and unidirectional arrangement of the PBTTT backbones in the thin film with order parameter (OP) of  $\sim 0.9$ , where  $OP = (DR - 1)/(DR + 2)$ . The OP signifies the extent of orientation and its minimum (0) and maximum (1) values corresponds to the ideal isotropic and ideal anisotropic films, respectively. It can be clearly seen that absorption spectra in  $\perp$  direction do not have any vibronic shoulders (featureless) as shown in **Figure 1(c)**, which clearly reflects that  $\perp$  spectrum is



originated from the randomly lying polymeric chains, withstanding chain twisting/folding or entanglement, having large distribution in conjugation lengths similar to the solution phase absorption spectrum, as shown in **Figure S1** (supplementary information). Similar observation was also reported by Brinkmann group for highly oriented thin films of poly(3-hexylthiophene).<sup>24</sup> The absorption peak ( $\lambda_{\text{max}}$  for  $\perp$ -absorption spectrum) of the as-cast film appeared at 508 nm, which was blue-shifted by 52 nm after annealing to 180 °C because ordered polymeric chains serve as a template for remaining randomly lying polymers in the film, when alkyl side chains recrystallize during the cooling process, leading to simultaneous increase in  $A_{\parallel}$  and decrease in  $A_{\perp}$ .<sup>16,18,25</sup> Consequently upon annealing the DR increased. Moreover, it was also observed that annealing beyond 180 °C the magnitude of increment in DR was smaller.



**Figure 1.** (a) Schematic representation for the Friction Transfer method and the inset represents the molecular structure of PBTTT. (b) Effect of substrate temperature on orientation, when the stage speed and load were kept constant to 50 mm/min and 3 kgf/cm<sup>2</sup>, respectively. (c) Polarized absorption spectra of the as-cast and annealed (180 °C) friction transferred PBTTT film and (d) absorbance at  $\lambda_{\max}$  (for  $\parallel$  absorption spectrum) versus polarization angle for angle dependent polarized absorption spectra. (e) Angle dependent Polarized Raman spectra of similar thin film. All of these characterizations were performed on the bare glass substrate.

**Table 1.** The values of charge transport parameters and optical anisotropy obtained for friction transferred PBTTT films cast on different substrates and annealed at different temperatures with  $V_{DD} = -80$  V;  $V_{GS} = -40$  to  $+40$  V (for bare SiO<sub>2</sub>) or  $-80$  to  $+40$  V (for HMDS treated SiO<sub>2</sub>). The thin films were cast with optimized coating parameters as shown in Figure 1. All the statistics were calculated with three or more separate films.

Annealing temperature (°C)	$\mu_{\parallel}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{\perp}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_{\parallel}/\mu_{\perp}$	$I_{on}/I_{off} \approx$ (along backbone orientation)	DR
	<b>bare SiO<sub>2</sub></b>				<b>bare glass</b>
as-cast	0.008 ± 0.0003	(4.68 ± 0.2) × 10 <sup>-5</sup>	< 200	10 <sup>3</sup>	10.95 ± 0.89
120	0.026 ± 0.04	(2.70 ± 0.16) × 10 <sup>-5</sup>	~ 10 <sup>3</sup>	10 <sup>5</sup>	15.96 ± 1.25
150	0.023 ± 0.002	(4.64 ± 2.9) × 10 <sup>-5</sup>	~ 500	10 <sup>5</sup>	19.37 ± 0.71
180	0.017 ± 0.005	(5.24 ± 1.3) × 10 <sup>-5</sup>	> 200	10 <sup>4</sup>	27.62 ± 2.46
200	0.012 ± 0.003	(1.04 ± 0.23) × 10 <sup>-5</sup>	~ 200	10 <sup>4</sup>	24.17 ± 2.85
	<b>HMDS treated SiO<sub>2</sub></b>				<b>HMDS treated glass</b>
200	0.334 ± 0.03	0.016 ± 0.004	> 20	10 <sup>6</sup>	22.6 ± 1.66

Angle-dependent peak absorbance as shown in **Figure 1(d)** reflects the orientation uniformity in friction transferred film and decrease in absorption intensity in both sides of 0° (clockwise and counter-clockwise) on annealing, supports the same hypothesis that the randomly lying polymers

are getting templated during recrystallization. To the best of our knowledge, the obtained DR in PBTTT is among the highest reported values for PBTTT (see comparison in Table S1 of supporting information). In general, orientation techniques using shear force, DR is susceptible to molecular weight ( $M_w$ ) of the CPs and falls with an increase in  $M_w$  due to chain folding and entanglement.<sup>2,10,26,27</sup> Using high temperature mechanical rubbing technique, high DR was obtained for lower  $M_w$  PBTTT samples but with increase in  $M_w > 45$  kDa the orientation decreased below 10.<sup>27</sup> Whereas the present study was conducted with commercially available high  $M_w$  PBTTT ( $M_w > 50$  kDa, Sigma Aldrich), which resulted in high DR, thereby suggesting that this technique can efficiently orient high  $M_w$  polymers too, which is one of the important requirements for the facile charge transport. To examine the uniaxial alignment of PBTTT macromolecules further, these films were also characterized by the angle-dependent polarized Raman spectroscopy and results are shown in the **Figure 1(e)**, while the major Raman bands corresponding to different bond stretching are listed in **Table 2**.<sup>16,28</sup> When polarization direction of the incident laser lies along the PBTTT orientation direction ( $00^\circ$ ), it interacts with the maximum number of C-C and C=C bonds resulting in higher output Raman signal corresponding to each bond. This intensity decreases gradually and reaches to minimum, when they were orthogonal ( $90^\circ$ ). Since the power of the laser source was kept constant throughout the measurement, therefore, gradual decrease in the peak intensities corresponds to the macromolecular orientation present in the thin-film. Further analysis of different peak intensities of angle dependent polarized Raman spectra resulted in variation their ratios, i.e., intensity ratios of corresponding peaks in  $00^\circ$  and  $90^\circ$  spectra which is listed in **Table 2**. The variation in the ratios can be attributed to difference in the stretching direction of different peaks and it is also being reinforced by the maximum ratio corresponding

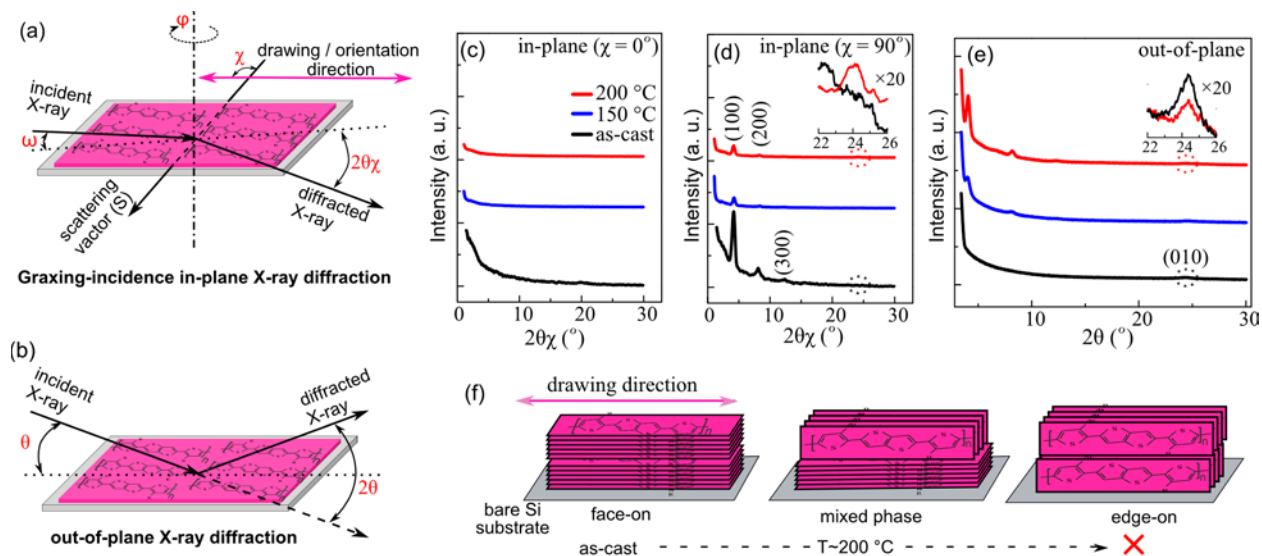
the thiophene C-C stretch, which is more aligned with the backbone orientation direction compared to other bond stretchings.

**Table 2.** Raman peak assignment for PBTTT and relative peak intensities of parallel and orthogonal Raman spectra as shown in the **Figure 1(e)**.

Peak	Frequency (cm <sup>-1</sup> )	Assignment <sup>a)</sup>	Ratio of peak intensity for 00° and 90° spectra
$\nu_1$	1391	thiophene C-C stretch	19.28
$\nu_2$	1415	thienothiophene C=C stretch	14.96
$\nu_3$	1462	inter-ring thiophene C-C stretch	14.98
$\nu_4$	1489	thiophene C=C stretch	17.40

<sup>a)</sup>Reference for peak assignments was taken from density functional theory (DFT) simulation reported by Gao et al.<sup>28</sup>

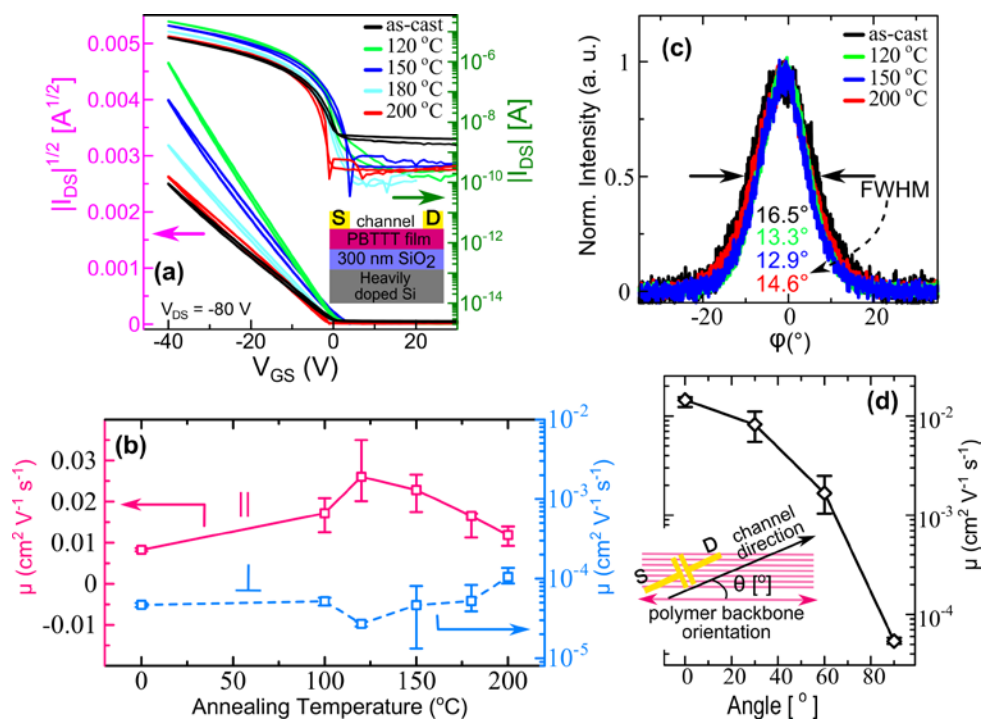
To analyze the macromolecular arrangement, in-plane GIXD and out-of-plane XRD measurements were performed as per the geometry shown in **Figure 2(a, b)**. It can be seen from **Figure 2 (c – e)** that in case of the samples as-prepared and annealed below LC temperature for friction transferred PBTTT thin-film on bare oxide substrate, series of diffraction peaks (h00) corresponding to alkyl-stacking is observed for in-plane GIXD and are absent in the out-of-plane GIXD. This clearly reflects that macromolecules in the as-prepared thin films adopted face-on orientation and upon annealing above the LC temperature (130-140 °C),<sup>16</sup> where side chain melts to reorganize the crystalline domains leading to the observed conformational change in the thin film.



**Figure 2.** Geometry of in-plane GIXD measurement (a) and out-of-plane XRD measurements (b). In-plane GIXD profile of friction transferred PBTBT film, as-cast and annealed at different temperatures on bare oxide substrate with scattering vector parallel ( $\chi = 0^\circ$ ) (c) and orthogonal ( $\chi = 90^\circ$ ) (d) to the drawing direction, out-of-plane XRD pattern of the films (e) and schematic representation for conformational change in the film after annealing (f).

A closer look at XRD patterns reveals that peak intensity of (h00) decreases in the in-plane and increases in out-of-plane mode with the increase in the annealing temperature  $\geq 150^\circ\text{C}$ , while just opposite trend was observed for the (010) diffraction peak corresponding to  $\pi$ - $\pi$  stacking. These results clearly suggest that there is a gradual change in the conformation of PBTBT from face-on dominated to edge-on dominated depending on the annealing temperature. It is worth to note here that at  $200^\circ\text{C}$ , the intensity of the (h00) diffraction peak is observable in both of the in-plane and out-of-plane modes, therefore, partly the PBTBT macromolecules can be considered to recrystallized in edge-on conformation. Moreover, since (010) diffraction peak did also not diminish completely in the out-of-plane mode at  $200^\circ\text{C}$ , it suggests that some face-on oriented crystallites also remained in the film.<sup>29</sup> The possible conformational changes in the orientation of the crystallites with temperature are schematically shown in **Figure 2(f)**.

To examine the impact of these highly oriented thin films of PBTTT on the charge transport, OFETs were fabricated in the bottom gate top contact geometry as schematically shown in the inset of **Figure 3(a)**. The saturation  $\mu$  and other electronic parameters were extracted from the transfer curves ( $I_{DS} - V_{GS}$ ) as described earlier.<sup>30</sup> The OFETs were fabricated with the thin films as-cast and annealed at different temperatures (100 °C to 200 °C) and their transport characteristics are shown in **Figures 3(a, b)** along with summarization of the device parameters in **Table 1**. A perusal of the anisotropic optical and electrical characteristics clearly reveals that the  $\mu$  did not increase consequently with the increase in DR. In spite of exhibiting the maximum DR for the films annealed to 180 °C, the  $\mu_{\parallel}$  was lower compared to films annealed at lower temperatures (**Table 1**). Consistent increment in the  $\mu_{\perp}$  was also observed with annealing beyond LC temperature, which can be attributed to increase in edge-on oriented macromolecules in the thin film as shown in the **Figure 3(b)**. However, more than two orders of  $\mu_{\parallel}/\mu_{\perp}$  was maintained even after annealing to 200 °C, which confirms the presence of face-on oriented crystallites near dielectric interface as this has been well examined that in edge-on oriented PBTTT thin-films,  $\mu_{\parallel}/\mu_{\perp}$  lies within one order of magnitude,<sup>2,31</sup> and these results are consistent with the observation made by XRD measurements. Therefore, we anticipate that during annealing, the evolution of edge-on conformation starts from the top surface of the film and the templating process to be similar to the case of orientation templating in the ribbon-phase of PBTTT,<sup>32,33</sup> which has been as schematically represented in the **Figure 2(f)**.



**Figure 3.** (a) Representative transfer curves of OFETs, and (b) statistical variation in  $\mu$  for friction transferred PBT TT on bare oxide substrate and annealed at different temperatures. Inset in (a) represents schematic of OFET. (c) Rocking curve for the (100) diffraction peak measured in orthogonal in-plane GIXD mode keeping  $\chi \approx 90^\circ$  for friction transferred PBT TT on bare oxide substrate. (d) The trend of the  $\mu$  with respect to channel orientation angle, the films were annealed at  $180^\circ\text{C}$  and the OFETs' architecture were same as inset (a). Inset of (d) represents the angle-dependent channel fabrication.

In order to explain the annealing temperature dependent variation in  $\mu$  more explicitly, the rocking curve of the (100) diffraction peaks appeared in orthogonal in-plane GIXD pattern ( $\chi=90^\circ$ ) of the thin-films were also measured and the results are shown in **Figure 3**(c). The full width at half maximum (FWHM) of these peaks corresponds to the distribution in the backbone orientations. On annealing, the FWHM decreased to  $12.9^\circ$  at  $150^\circ\text{C}$  and on further annealing at  $200^\circ\text{C}$  it reaches up to  $14.6$ . This represents that the in-plane stacking of the alkyl chains increased for annealing up to  $\sim 150^\circ\text{C}$  and further annealing at  $200^\circ\text{C}$  led to decrease in this stacking.

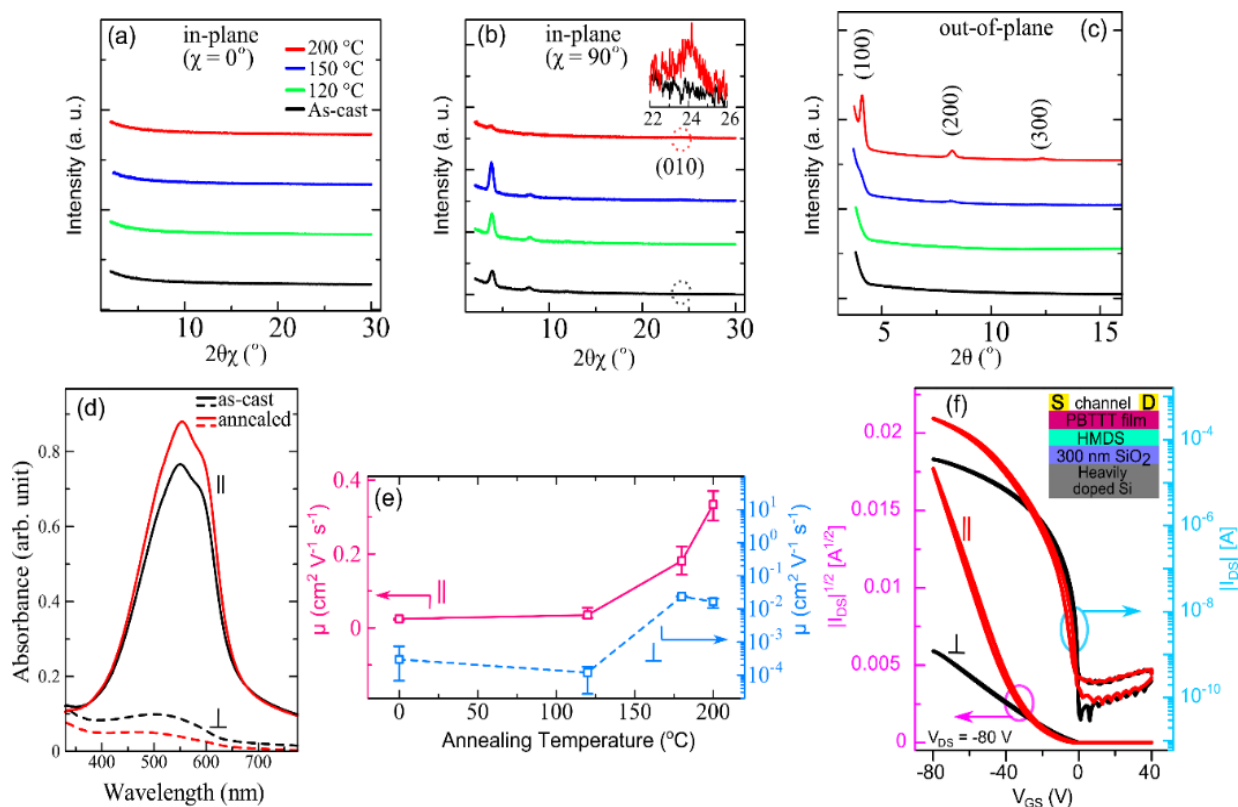
For thin-films fabricated on the bare oxide surface, it is clear that with increase in annealing temperature beyond LC temperature, evolution of mixed-phase in the thin film led to decrease in corresponding  $\mu_{\parallel}$  and  $\mu_{\parallel}/\mu_{\perp}$ , as shown in the **Figure 3** and **Table 1**. It is worth mentioning here that face-on oriented fractions remained even after annealing at for longer time (10 minutes) as shown in **Figure S2** (supplementary information). Although the exact cause of this observed behavior not yet completely clear, however, since the PBTTT films are on the bare oxide surface and according to morphological investigations by Kline et al.,<sup>18</sup> we assume that this rigidity in the face-on oriented crystallites must be arising from the chemical interaction between thiophene rings and reactive groups on the bare oxide surface. At the same time, it was also overserved that detaching the film from oxide surface was rather tough before as well as after annealing clearly follows the above fact based on results by Kline et al. Further, in order to demonstrate the coexistence of high optical and electrical anisotropy of friction transferred thin film, angle dependent  $\mu$  were measured for the thin-films possessing maximum DR (films annealed at 180 °C), where the source-drain direction was rotated on the same substrates to reduce the variations in device to device performances as shown in the **Figure S3** (supporting information). High output current was observed along the orientation direction, which decreased while moving towards 90°, confirming the highly anisotropic transport in the oriented polymer thin-films. The extracted  $\mu$  in the OFETs fabricated at different configuration are shown in **Figure 3(d)** and representative transfer characteristics are shown in **Figure S4** (supporting information).

PBTTT is a well-known material to exhibit high  $\mu$  on SAM treated substrates because of low surface energy.<sup>19,23</sup> However, because of the high contact angle of the octadecyltrichlorosilane (OTS) treated surface,<sup>34,35</sup> it was difficult to have uniformly adhered film, while squeezing the



PBTTT pellet. Therefore, to examine the origin of this low  $\mu$  and reasons behind the incomplete transformations of macromolecular conformation from face-on to edge-on, treatment of SiO<sub>2</sub> surface was performed using a mild SAM agent, HMDS that results in to relatively lower contact angle in comparison to OTS treated surfaces. Such a difference in surface energy between SAM treated SiO<sub>2</sub> substrates affects the interplay between molecule–substrate and molecule–molecule interactions in their own way. However, following the assumptions and results by Kline et al.,<sup>18</sup> we believed if this behavior was originated because of the oxide surface, HMDS treated surface would be suitable model for the investigation pertaining to the nature of macromolecular conformation adopted as a function of the annealing temperature.

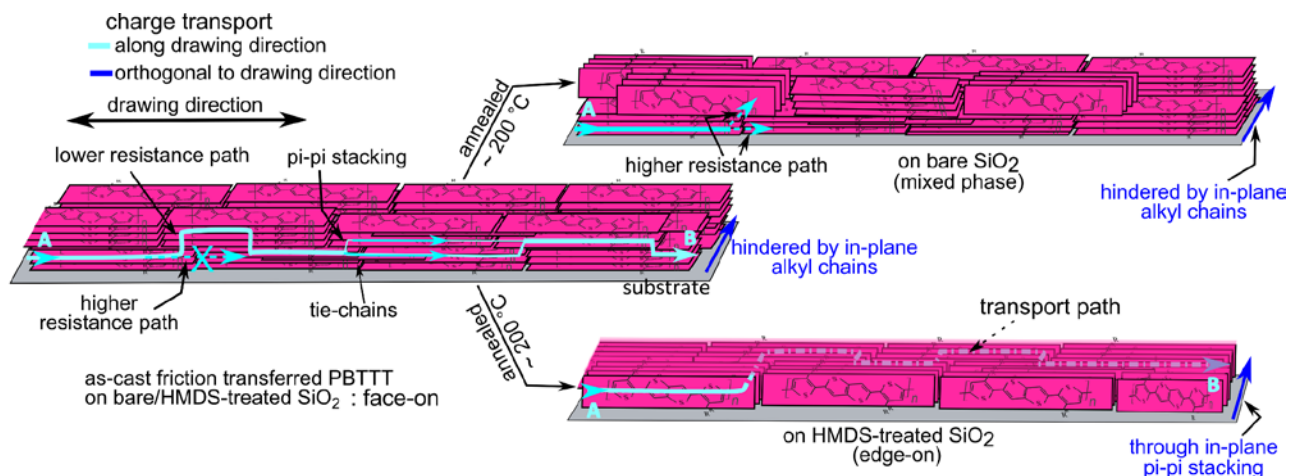
Results of in-plane GIXD and out-of-plane XRD of as cast and annealed films of friction transferred PBTTT on HMDS treated substrate as shown in **Figure 4**, clearly revealed the almost complete transformations from the face-on to edge-on after annealing the thin-films  $\sim 200$  °C. The diffraction peaks (h00) of lamellar stacking of alkyl side chain was observed in the out-of-plane mode and diffraction peak (0k0) related to  $\pi$ - $\pi$  stacking was observed in the in-plane mode. At the same time, average  $\mu_{\parallel}$  of PBTTT films on HMDS treated SiO<sub>2</sub> reaches up to  $0.33 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and  $\mu_{\perp}$  to  $0.016 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  (see **Table 1** and **Figure 4**), which is comparable to other reported mobility values for PBTTT on OTS substrates and it has also been well demonstrated by Umeda et al. that decreasing surface energy of the substrates resulted in an increase in the  $\mu$  of PBTTT based OFETs.<sup>2,17</sup>



**Figure 4.** In-plane GIXD profile of friction transferred PBTTT film on HMDS treated Si substrate, as-cast and annealed at different temperatures with scattering vector parallel (a) and orthogonal (b) to the drawing direction and their out-of-plane (c) XRD pattern. Representative polarized absorption spectra of the oriented friction transferred PBTTT film fabricated on HMDS treated glass and annealed to 200 °C (d). Statistical variation in  $\mu$  for the thin films cast on HMDS treated SiO<sub>2</sub> and annealed to different temperatures (e). Representative transfer curves for OFETs with channel parallel and perpendicular to the backbone orientation direction fabricated with the thin films annealed at 200 °C with the device architecture as shown in the inset (f).

Results obtained pertaining to the differential nature of macromolecular conformations attained depending on the nature of surface and annealing temperature along with evidences from anisotropic charge transport of OFETs, a plausible charge transport mechanism for the friction transferred PBTTT thin films have been proposed, which is schematically shown in the **Figure 5**. Structure of the friction transferred thin film was compared to slipped stacks or brickwork like film structure.<sup>36</sup> In such structure, complete face-on orientation may lead to high  $\mu_{\parallel}$  compared to

mixed-phase of face-on and edge-on. In the former case, the charge carriers traverse through the inter-layer of  $\pi$ - $\pi$  stacking, when a high resistance path (between polymer chains or domains) is encountered. However, in the latter case, the charge carriers face additional high resistance path due to presence of alkyl chains between two layers. Hence, for the efficient charge transport, the thin films should possess an optimum macromolecular orientation and conformation. This agrees well with the films annealed to 120 °C (on bare SiO<sub>2</sub>), which possessed higher orientation compared to as-cast thin films and complete face-on conformation of macromolecules. In the case of HMDS treated SiO<sub>2</sub>, annealing the film beyond LC temperature ( $\sim$  200 °C) led to almost complete edge-on oriented thin film, resulting in to higher in-plane  $\mu_{\parallel}$ . Along with conformational transformation at 200 °C, increment in domain size, extensively reported as intrinsic nature of PBTTT to form large domains, when the thin-films annealed beyond LC temperature on SAM treated substrate, should also be taken into consideration to interpret increase in  $\mu_{\parallel}$ .<sup>19,23</sup> Interestingly, in the optimized conditions for films annealed to 120 °C on bare silicon oxide,  $\mu_{\parallel}$  and  $\mu_{\parallel}/\mu_{\perp}$  exceeded some previous reports for the same material in which the thin films possessed edge-on conformation and the dielectric substrates were given SAM treatment.<sup>37,38</sup> Therefore, the improved  $\mu_{\parallel}$  and  $\mu_{\parallel}/\mu_{\perp}$  in this case can solely be attributed to the higher orientation.



**Figure 5.** Schematic representation for cross-sectional view of the charge transport mechanism in as-cast and annealed friction transferred PBTTT thin films and substrate's surface energy dependent macromolecular conformation possessed by the thin films. In the bottom-right part of the figure only the bottom layer of the film is represented for better understanding.

## Conclusion

Highly oriented thin films of PBTTT ( $M_w > 50$  kDa) were fabricated by the friction transfer technique. The uniaxial orientation of polymers was characterized using UV-visible electronic absorption spectroscopy and polarized Raman spectroscopy. A high value of DR ( $27.62 \pm 2.46$ ) was obtained by optimizing the casting and annealing conditions. The film's crystallinity was systemically analyzed by XRD and GIXD measurements. Generally, PBTTT thin films show improved  $\mu$ , when they are annealed beyond the LC temperature. However, in this work role of substrate's surface energy in microstructural change in annealed thin films and their consequence on  $\mu$  were exhaustively studied. It was observed that on high surface energy substrate, i.e., bare oxide surface, initially, the  $\mu_{\parallel}$  and  $\mu_{\parallel}/\mu_{\perp}$  increased with an increase in annealing temperature but beyond LC temperature they decreased, which was attributed to the evolution of mixed-phase in the thin film causing a high resistance path to the field-effect charge transport. Through optimum annealing of the films at 120 °C,  $\mu_{\parallel}$  of  $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  with high  $\mu_{\parallel}/\mu_{\perp} \sim 1000$  were obtained,

which signify that such thin films can be easily complied with low temperature fabrication processes. On the other hand, for lower surface energy substrate, i.e., HMDS treated SiO<sub>2</sub>,  $\mu_{\parallel}$  reached up to 0.36 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with  $\mu_{\parallel}/\mu_{\perp} > 20$  after annealing the thin-films at 200 °C. Further, a possible charge transport mechanism was proposed to interpret the effect of surface property and annealing temperature on anisotropic charge transport in friction transferred PBTTT thin films.

## **ASSOCIATED CONTENT**

**Supporting Information.** The following files are available free of charge. Comparative absorption spectra of PBTTT in solution and friction transferred thin films, table of comparative optical anisotropy, XRD and GIXD of friction transferred PBTTT on oxide surface annealed for longer durations, digital image of large area friction transferred thin films and representative output and transfer curve for OFET.

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The manuscript was written through consent of all authors. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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# TOC Graphic

