Influence of Backbone Structure on Orientation of Conjugated Polymers in the Dynamic Casting of Thin Floating-Films

Manish Pandey[a,*], Shyam S. Pandey[a], Suichi Nagamatsu[b,c], Shuzi Hayase[a,b], and Wataru Takashima[a,b*]

[a]Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu 808-0196, Japan

[b]Research Center for Advanced Eco-fitting Technology, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Kitakyushu 808-0196, Japan

[c]Department of Computer Science and Electronics, Kyushu Institute of Technology, 680-4 Kawazu, Iizuka, 820-8502, Japan

Corresponding Authors

Manish Pandey and Wataru Takashima

Graduate School of Life Science and Systems Engineering
Kyushu Institute of Technology
Hibikino 2-4, Wakamatsu, Kitakyushu,
Fukuoka, 808-0196, Japan
Tel/Fax: +81-93-695-6235

E-mail: pandey-manish@edu.life.kyutech.ac.jp , wtakashima@life.kyutech.ac.jp

1

Abstract

Dynamic casting of conjugated polymer films on liquid-substrate is a unique method which provides thin floating-film and can be easily transferred on a desired substrate by stamping. The important feature in this procedure is associated with the formation of thin polymeric film during compression and solidification controlled by viscous drag of liquid substrate and solvent evaporation of the polymer, respectively. Lyotropic liquid-crystalline (LC) characteristics of conjugated polymer possibly assist to orient the polymer chain in one direction. It is found that this method produce highly oriented thin films (dichroic ratio >5) of thiophene-based conjugated polymers such as PBTTT-C14, PQT-C12 and non-regiocontrolled poly(3-hexylthiophene) NR-P3HT. On the other hand, weak orientation intensity in regioregular poly(3-hexylthiophene) RR-P3HT was found. The mechanism for this diverse orientation in thiophene-based conjugated polymers is discussed in correlation with the backbone chemical structure and lyotropic LC phase transition during the floating-film formation.

Keywords: Floating-film, conjugated polymer, molecular orientation, polarized spectra, lyotropic liquid-crystalline phase

1. Introduction

Traditionally conjugated polymers (CPs) with extended π-conjugation like polypyrrole, polythiophene, polyaniline etc. are a class of one-dimensional (1D) functional polymeric materials in both of the electronic and photonic characteristics. Inspired by very high electrical conductivity of graphene sheet, there are also reports about the two dimensional CPs by extending the π-conjugation in the two dimensions by chemical modifications of the main polymeric chains via logical molecular design [1,2]. The use of this one-dimensional function is a possible key-technology for the polymer based organic electronics. Ongoing research and development in this area is expected towards the proliferation of the flexible and anisotropic photo-electronics, which is difficult and costly by implementing the crystalline inorganic semiconductors. The active use of strong anisotropic function of the conjugated organic semiconducting polymers may lead to the development of unique anisotropic optoelectronic devices. A variety of procedures towards the fabrication of oriented thin films of conjugated polymers have been proposed and investigated in detail by many researchers in the recent past [3]. Most of the large scale orientation have been achieved by using shear forces to align the conjugated polymer such as mechanical rubbing, friction transfer, strain alignment [4–6]. These shear forces are not suitable for fabricating device with multilayer architectures as they affect the morphology of underlying layers as well as the substrates. Therefore solution based methods to prepare highly oriented conjugated polymers can resolve such problems especially when the oriented film can be prepared and transferred independently. Developing such method should resolve both the problems as they will not damage the substrate and multilayers of oriented films can be easily processed [7–11]. Taking the advantage of inherent one-dimensionality, it is possible to promote the high degree of molecular orientation of conjugated

3

polymer by utilizing their liquid-crystalline (LC) characteristics. Thermotropic LC phase transition has been already used for the domain formation of aligned polymers to achieve the high carrier transport.

We have reported a unique characteristics of molecular orientation as clearly evidenced by optic and electronic anisotropy in a film formed by the dynamic casting of floating-film of conjugated polymer on liquid-substrate named as floating film transfer method (FTM) [7–9,12–14] . The unique concepts in this procedure is not only to cast a thin-film on liquid substrate [10,11] but also to solidify the film coincidentally during spreading the solution, leading to the well-orientation of conjugated polymers. Not only a variety of conjugated polymers can be oriented into a similar direction tangential to the film propagation [12] but also anisotropic functions in optics [15] and electronics [14] has been demonstrated as anisotropic organic devices. The orientation intensity depends upon the casting conditions such as liquid substrate viscosity, concentration of polymer solution, temperature etc. In spite of optimization of these film forming conditions under dynamic film casting, it varies with the nature of conjugated polymers under investigation. Even under the best tuning of the casting condition, it was found that the regioregular poly(3-hexylthiophene) (RR-P3HT) shows a weak orientation. We have carefully chosen the conjugated polymers of polythiophene family in order to clarify the orientation characteristics by dynamic-FTM. Non-regiocontrolled (NR)-P3HT, RR-P3HT, poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT-C14) and Poly(3,3'''-didodecyl-quarterthiophene) (PQT-C12) have been employed for the thin film fabrication and characterization by dynamic-FTM in this work owing to their structural similarity. A possible origin for the observed differential orientation intensities has been discussed amicably by taking the molecular structure of the polymeric main chain in to

4

consideration.

2. Experimental Details

In this work, RR-P3HT, NR-P3HT, PQT-C12 and PBTTT-C14 having chemical structure as shown in the Fig. 1 have been employed as the target thiophene-based conjugated polymers for investigating orientation characteristics in dynamic-FTM. PBTTT-C14 and dehydrated chloroform (CHCl$_3$) were purchased from Aldrich Co. Ltd. USA. Other conjugated polymers such as polymers, RR-P3HT, NR-P3HT and PQT-C12 were chemically synthesized according to the literature procedures [16–18]. All the synthesized conjugated polymers were purified by using EDTA or Soxhlet extraction as per earlier publications [19,20]. Regioregularity of the synthesized polymers have been estimated by 1H-NMR at aryl methylene region [21,22].

Dynamic casting of floating-film was carried out under tuning the casting condition as per our earlier publication [23]. For the purpose of obtaining the high degree of orientation, the solution concentration, the viscosity of liquid-substrate and the temperature of both the liquid-substrate and the solution were selected optimally to get the maximum orientation. The casting condition optimized for respective polymers to achieve highest optical dichroic ratio (DR) has been summarized in Table 1. All of the solutions were prepared to dissolve the target polymer powder in dehydrated CHCl$_3$ as the solvent. Viscosity of the liquid substrate was tuned by mixing deionized water/ethylene glycol or ethylene glycol/glycerol in the optimized ratio [23]. As shown in Fig. 2, these solvent mixtures were poured in a 15 cm-diameter petri-dish to use as liquid-substrate. At the center of the liquid-substrate, one drop (about 15μL) of the target polymer solution was dropped by a micropipette, which swiftly spread over the liquid-substrate

5

forming a floating-film at the same time. Oriented floating-film was then transferred on a white glass with a dimension of (1 cm x 2.5 cm) followed by the measurement of polarized electronic absorption spectra. Spin coated films of similar thickness were also prepared by spin coating. All of the polarized absorption spectra were measured through Glan-Thomson prism with UV-Vis-NIR spectrophotometer (JASCO V-570). Optical DR representing the extent of orientation has been calculated as per our earlier publication [21]. Thickness of all the films were found to be in between 20-50 nm measured by interference microscopy (Nikon Eclipse LV150).

3. Results and Discussion

FTM is one of the facile casting/coating methods for the fabrication of oriented thin films. In the dynamic-FTM procedure, a thin floating film is first formed by dropping a very small amount (about 15uL) of conjugated polymer solution on a hydrophilic liquid-substrate followed by its transfer to a desired solid substrate. This stamping like procedure is similar to the Langmuir-Schaefer technique. The unique and key-feature in this casting procedure is to form the floating-film during concentration followed by its solidification dynamically. The compressive/expansive force offered by the liquid substrate while spreading the floating film along with the coincidental solvent evaporation leads to the self-alignment. The seamless transition from the solution phase into the solid phase should go through lyotropic liquid-crystalline (LC) phase if the solidified material has LC characteristics. The compression/expansion behavior on liquid-substrate plays a role as shear force to promote the macromolecules orientation and could be responsible for providing oriented films as shown in schematic Fig. 2. Several conjugated polymers have been reported to have lyotropic LC phase suitable for dynamic-FTM [24]. For all the oriented floating-films, the direction of orientation

is tangential to the propagation direction of the dropped solution. This indicates that the orientation mechanism is essentially the same for all the conjugated polymers in this study.

A possible explanation to cause this orientation lies in the balance between the spreading and solidification speed. If the spreading speed is higher than the solidification speed, the floating parts disperse into small flakes. Contrary to this, in the opposite case where speed of solidification is higher than the spreading, the solidifying part propagates towards outside with continuous formation of floating-films although the orientation is not always to be high [21]. The spreading speed of floating solution is controlled by the viscosity of liquid substrate, speed of solidification and the concentration of solution [23]. The spreading behavior also appends tangential pressure into the solidifying parts as the shear force. The high concentration of polymer solution generates the lyotropic LC phase due to the strong inter-macromolecular interaction. The compressive/expansion force induces the shear force to align macromolecules into the same direction with seamless solidification, leading to the orientation of floating-film on the liquid substrate.

Fig. 3 shows the polarized absorption spectra of thin films of NR-P3HT and RR-P3HT prepared by dynamic-FTM. The non-polarized spectra of respective spin-coated films have also been shown for the comparison. It can be clearly seen that films prepared by dynamic-FTM exhibits clear optical dichroism for both the thiophene-based conjugated polymers. As shown in Fig. 3 (a), large DR of 5.8 has been estimated for NR-P3HT which was collaterally due to the mismatch of λ_{max} for the parallel and the perpendicular-polarized electronic absorption spectra. It is interesting to note that in the perpendicularly polarized spectrum of NR-P3HT there is featureless absorption spectral behavior having λ_{max} around 475 nm which

7

is quite similar to that of spin-coated one. It is reported that NR-P3HT is consisted of the mixture of crystalline as well as amorphous parts [25]. Intensity of the perpendicular absorption possibly correlates with the extent of amorphous region in the oriented NR-P3HT film existing as non-oriented part. Contrary to NR-P3HT, spin-coated films of RR-P3HT typical exhibits main peak in the electronic absorption around 520 nm with well-defined vibronic shoulders around 550 nm and 610 nm. Interesting in the oriented films of RR-P3HT where there is strong molecular ordering and vibronic shoulder appearing around 550 nm becomes more pronounced corresponding to the main π-π* electronic transition in the polymer main chain [5,26]. To consider the high regioregularity and the high crystallinity of RR-P3HT, the difference in the spectral profile of the perpendicular one is also explained by the essential difference in the perpendicular modes of dipole moments on conjugated main-chain.

A perusal of electronic absorption spectra of spin-coated and FTM films of RR-P3HT reveals that main peak of the spin-coated film appears at 516 nm with vibronic shoulders at 550 nm and 602 nm as shown in Fig. 3 (b). Besides this, the parallel polarized absorption peaked at 554 nm with shoulders at 525 nm and 602 nm is similar to that observed for the solution cast films [26]. All the vibronic peaks located at almost the similar wavelength indicates that essentially the same vibronic modes appear by simply change in the Huang-Rhys parameter [27]. Observed red-shift in RR-P3HT films is attributed to the switch of the main-transition mode from 0-2 to 0-1. It is well-known that the slow growth of crystalline domain in RR-P3HT promotes the evolution of lower vibronic modes due to the fibrous crystalline domain formation [28]. In particular the growth of 0-0 modes in RR-P3HT is discussed by Spano by correlating with the electronic structure of excitonic bandwidth (W) with intermolecular coupling transition energy, Ep, by Equation 1 as shown below [29].

8

$$\frac{A_{0-0}}{A_{0-1}} \approx \left(\frac{1 - 0.24 \frac{W}{E_p}}{1 + 0.073 \frac{W}{E_p}} \right)^2$$

(1)

Where A_{0-0} and A_{0-1} represents the corresponding intensities of the 0-0 and 0-1 transitions.

The growth of low vibronic mode essentially represents the extension of conjugation length on the polymer main chain. Observed difference in the absorption profile of RR-P3HT films from those in NR-P3HT is simply explained that RR-P3HT macromolecules maintain rather well-stretched conformation owing to the dynamic-FTM procedure due to its relatively slow casting as compared to spin-coating. It can be seen that vibronic modes in both of the parallel and perpendicularly polarized RR-P3HT, at the same energy level with only differing in their intensity. This difference in the intensity of vibronic modes is simply due to the changes in the relative conjugation lengths.

Solid-state electronic absorption spectra of spin-coated and FTM-processed thin films of conjugated polymers PQT-C12 and PBTTT-C14 are shown in the Fig. 4. The optical and dichroic parameters are shown in the Table 2. The polarized absorption spectra in both films exhibit high optical dichroism having a DR of 6.4 and 5.1 for the PQT-C12 and PBTTT-C14, respectively. These DR values are higher as compared to that of RR-P3HT films (1.5). Although there is only a little difference in the chemical structure of polymeric main chain in both of the conjugated polymers, a similar vibronic shoulders were appeared in the thin films prepared by dynamic-FTM. As compared to their spin-coated counterparts, both of these polymers show a bathochromic shift of 7 nm-14 nm which is relatively smaller as compared to those for the RR and NR-P3HT (about 45 nm). In the normalized absorption spectra, it can be

9

seen that vibronic shoulders are more pronounced in the parallel polarized spectra as compared to those of their spin-coated counterparts for both polymers. This could be associated with the consistent expansion of conjugation length by dynamic-FTM. The structural expansion of polymer chain by dynamic-FTM can be assigned as the promotion of conformational expansion owing to the nematic LC phase with appropriate share force during the solidification. It should be noted that both of PBTTT-C14 and PQT-C12 are reported to show a clear thermotropic LC phase transition by DSC analyses.[18,30] Relatively high performance of carrier transport in these polymers is explained by the good alignment of macromolecules with thermal annealing assisted by the thermotropic LC characteristics in these polymers [18,30,31].

Orientation intensity varies with the conjugated polymer as well as the casting condition as listed in table 2. In order to verify the role of polymeric backbone, it is necessary to compare their relative orientation characteristics under identical casting condition. Taking this point in to consideration we fixed the casting condition utilized for PQT-C12 giving maximum DR and results are shown in the Fig. 5. It can be seen from Fig. 5 that DR values for RR-P3HT, NR-P3HT and PBTTT-C14 is much less than that achieved by optimized conditions as already shown in Fig. 3, Fig. 4 and table 2. Although, these three conjugated polymers have less orientation under similar casting conditions where, PBTTT-C14 exhibits the effective improvement of DR after optimizing the casting parameters under dynamic-FTM as shown in the table 2. For RR-P3HT DR still stays low irrespective of the casting conditions. These results also indicate that basic nature of polymeric backbone and their inherent characteristics seems to play a vital role for orientation, which reflects in differential DR values under the dynamic-FTM.

A perusal of Fig. 3, Fig. 4 and Table 2 pertaining to the orientation characteristics reveals that orientation strength in RR-P3HT is quite small (DR=1.5) as compared to the other

10

thiophene-based conjugated polymers in this study. In spite of the fact that we attempted dynamic-FTM for RR-P3HT obtained from different commercial sources such as Merck (Iisicon SP001) and Aldrich (Electronic grade), but obtained DRs with all the RR-P3HTs were also found low. It should be noted that the large DR can be obtained with NR-P3HT having the same chemical structure. These facts suggest that the high regioregularity in RR-P3HT inhibits the further promotion of polymer chain orientation. In contrast, completely regioregular conjugated polymers of PBTTT-C14 and PQT-C12 can easily orient in dynamic-FTM as described above. These findings also suggest that structural feature in RR-P3HT resist the promotion of macromolecular alignment into the same direction in dynamic-FTM. The regioregularity in NR-P3HT was estimated to be 80 %, which is lower as compared to that of typical 90-95 % in RR-P3HT.[17,21] This indicates that almost one by 5 units of thiophene ring shows non-regioregular (head-to-head or tail-to-tail) coupling in NR-P3HT. Against this, such mismatch occurs about one by 10-20 units in case for RR-P3HT. This comparison helps us to suggest the orientation mechanism which has been schematically represented in the Fig. 6.

In order to explain the differential orientation behaviors for NR-P3HT and RR-P3HT as evident by very large differences in their respective DR, we have to consider their differential inter-molecular interactions associated with the packing of macromolecules in the solid-state. The regioregular part of the P3HT molecular framework attains the fish-bone like structure by the alkyl side chains as schematically shown in Fig. 6 (a). These side-chains will interdigitate to the neighbor macromolecules due to the zipper effect [25,32]. The fish-bone structure forces to switch the movable direction of neighboring interdigitated-macromolecules, alternately. This behavior provides the locking force to prevent the sliding action of neighboring macromolecules in highly condensed solution. In particular, the regioregular part of main chain

11

in RR-P3HT strongly forms this interlocking structure by the zipper effect. Against this, for NR-P3HT there are still existing some parts forming amorphous structure. The relative low regioregularity also reduces the interlock formation even in the condensed state as schematically shown in Fig. 6 (b). This provides the free sliding motion for NR-P3HT unlike RR-P3HT. In contrast, the base unit in PBTTT-C14 and PQT-C12 forms point-symmetrical substituents unlike the fish-bone structure as shown schematically in Fig. 6 (c). This enables no inter-digitation among the individual macromolecules and making the neighboring macromolecules capable for free slide. The higher freedom of sliding motion between the neighboring macromolecules provides effective orientation of macromolecules with strong stretching of main chain into the same direction by shear force in lyotropic LC phase.

It is interesting to note that the thermotropic LC phase transition characteristics in poly(3-alkylthiophene)s has been well discussed till the end of '90s by many researchers.[32–34] After the discovery of the synthetic method to attain very high regioregularity the research for structural and electronic characteristics of NR-P3HT (chemically synthesized with FeCl$_3$) was strongly reduced.[35] This suggests that RR-P3HT seems not to show clear LC phase transition unlikely NR-P3HT. Against this, PBTTT-C14 and PQT-C12 are focused in their thermotropic LC characteristics and discussed about their contribution for achieving the high carrier transport [36,37]. It should be noted that the correlation between the behaviors for thermotropic LC transition and lyotropic LC transition in conjugated polymers has not been clearly discussed yet. However, PPV derivatives have also been reported to show both of lyotropic and thermotropic LC characteristics [24,38]. Other lyotropic like behaviors in conjugated polymer also have been reported [39]. Interestingly such polymers exhibit clear molecular orientation and optical anisotropy in the films prepared by the dynamic-FTM. Therefore, dynamic-FTM is

12

expected to be one of the important key-technologies for the quick and facile fabrication of oriented thin-film using lyotropic LC phase transition characteristics in conjugated polymers.

4. Conclusion

The orientation characteristics of NR-P3HT, RR-P3HT, PBTTT-C14 and PQT-C12 prepared by dynamic-FTM has been investigated by taking their structure-property correlation into consideration. It has been shown that all of the thiophene-based conjugated polymers show the clear optical anisotropy except RR-P3HT having very small DR of 1.5. This has been explained in terms of the possibility of lyotropic LC phase formation during the solution concentration in dynamic-FTM. The strong zipper effect generated by the highly regioregular conformation with fish-bone structure in RR-P3HT resists the LC phase formation, This tendency of reduced lyotropic LC phase formation hampers the driving force towards its orientation in the dynamic-FTM. Conclusively although dynamic-FTM provides the oriented thin-films of conjugated polymers but their orientation ability depends upon the strength of lyotropic LC characteristics.

References

[1] D.F. Perepichka, F. Rosei, Extending Polymer Conjugation into the Second Dimension, Science. 323 (2009) 216–217. doi:10.1126/science.1165429.

[2] X. Guo, M. Baumgarten, K. Müllen, Designing ??-conjugated polymers for organic electronics, Prog. Polym. Sci. 38 (2013) 1832–1908. doi:10.1016/j.progpolymsci.2013.09.005.

13

[3]   M. Brinkmann, L. Hartmann, L. Biniek, K. Tremel, N. Kayunkid, Orienting semi-conducting pi-conjugated polymers, Macromol. Rapid Commun. 35 (2014) 9–26. doi:10.1002/marc.201300712.

[4]   L. Hartmann, K. Tremel, S. Uttiya, E. Crossland, S. Ludwigs, N. Kayunkid, C. Vergnat, M. Brinkmann, 2D versus 3D crystalline order in thin films of regioregular poly(3-hexylthiophene) oriented by mechanical rubbing and epitaxy, Adv. Funct. Mater. 21 (2011) 4047–4057. doi:10.1002/adfm.201101139.

[5]   S. Nagamatsu, W. Takashima, K. Kaneto, Y. Yoshida, N. Tanigaki, K. Yase, K. Omote, Backbone arrangement in "friction-transferred" regioregular poly(3-alkylthiophene)s, Macromolecules. 36 (2003) 5252–5257. doi:10.1021/ma025887t.

[6]   B. O'Connor, R.J. Kline, B.R. Conrad, L.J. Richter, D. Gundlach, M.F. Toney, D.M. DeLongchamp, Anisotropic structure and charge transport in highly strain-aligned regioregular poly(3-hexylthiophene), Adv. Funct. Mater. 21 (2011) 3697–3705. doi:10.1002/adfm.201100904.

[7]   T. Morita, V. Singh, S. Nagamatsu, S. Oku, W. Takashima, K. Kaneto, Enhancement of transport characteristics in poly(3-hexylthiophene) films deposited with floating film transfer method, Appl. Phys. Express. 2 (2009) 111502. doi:10.1143/apex.2.111502.

[8]   T. Morita, V. Singh, S. Oku, S. Nagamatsu, W. Takashima, S. Hayase, K. Kaneto, Ambipolar transport in bilayer organic field-effect transistor based on poly(3-hexylthiophene) and fullerene derivatives, Jpn. J. Appl. Phys. 49 (2010) 0416011–0416015. doi:10.1143/JJAP.49.041601.

[9]   T. Ohtomo, K. Hashimoto, H. Tanaka, Y. Ohmori, M. Ozaki, H. Kajii, Improved carrier balance and polarized in-plane light emission at full-channel area in ambipolar heterostructure polymer light-emitting transistors, Org. Electron. 32 (2016) 213–219. doi:10.1016/j.orgel.2016.02.037.

[10]   J. Noh, S. Jeong, J.-Y. Lee, Ultrafast formation of air-processable and high-quality polymer films on an aqueous substrate., Nat. Commun. 7 (2016) 12374. doi:10.1038/ncomms12374.

[11]   J.C. Hu, Y. Shirai, L.Y. Han, Y. Wakayama, One-step fabrication of large-scaled indium tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)/poly(3-hexylthiophene-2,5-diyl): 6,6 -phenyl-C61-butyric acid methyl ester multi-layered

structure, Thin Solid Films. 554 (2014) 46–50. doi:10.1016/j.tsf.2013.04.098.

[12] D. Arnaud, R.K. Pandey, S. Miyajima, S. Nagamatsu, R. Prakash, W. Takashima, S. Hayase, K. Kaneto, Fabrication of large-scale drop-cast films of π-conjugated polymers with floating-film transfer method., Trans. Mater. Res. Soc. Japan. 38 (2013) 305–308. doi:10.14723/tmrsj.38.305.

[13] A. Dauendorffer, S. Nagamatsu, W. Takashima, K. Kaneto, Optical and transport anisotropy in Poly (9, 9'-dioctyl-fluorene-alt-bithiophene) films prepared by floating film transfer method, Jpn. J. Appl. Phys. 51 (2012) 055802. doi:10.1143/jjap.51.055802.

[14] M. Pandey, S. Nagamatsu, S.S. Pandey, S. Hayase, W. Takashima, Enhancement of carrier mobility along with anisotropic transport in non-regiocontrolled poly (3-hexylthiophene) films processed by floating film transfer method, Org. Electron. 38 (2016) 115–120. doi:10.1016/j.orgel.2016.08.003.

[15] A. Dauendorffer, S. Miyajima, S. Nagamatsu, W. Takashima, S. Hayase, K. Kaneto, One-step deposition of self-oriented β-phase polyfluorene thin films for polarized polymer light-emitting diodes, Appl. Phys. Express. 5 (2012). doi:10.1143/APEX.5.092101.

[16] R.H. Lohwasser, M. Thelakkat, Toward perfect control of end groups and polydispersity in poly(3-hexylthiophene) via catalyst transfer polymerization, Macromolecules. 44 (2011) 3388–3397. doi:10.1021/ma200119s.

[17] S. Amou, O. Haba, K. Shirato, T. Hayakawa, M. Ueda, K. Takeuchi, M. Asai, Head-to-tail regioregularity of poly(3-hexylthiophene) in oxidative coupling polymerization with FeCl3, J. Polym. Sci. Part A Polym. Chem. 37 (1999) 1943–1948. doi:10.1002/(SICI)1099-0518(19990701)37:13<1943::AID-POLA7>3.0.CO;2-X.

[18] B.S. Ong, Y. Wu, P. Liu, S. Gardner, High-Performance Semiconducting Polythiophenes for Organic Thin-Film Transistors, J. Am. Chem. Soc. 126 (2004) 3378–3379. doi:10.1021/ja039772w.

[19] M.R. Andersson, D. Selse, M. Berggren, H. Järvinen, T. Hjertberg, O. Inganäs, O. Wennerström, J.-E. Österholm, Regioselective polymerization of 3-(4-octylphenyl)thiophene with FeCl3, Macromolecules. 27 (1994) 6503–6506. doi:10.1021/ma00100a039.

[20] M. Trznadel, a Pron, M. Zagorska, R. Chrzaszcz, J. Pielichowski, Effect of Molecular

Weight on Spectroscopic and Spectroelectrochemical Properties of Regioregular Poly(3-hexylthiophene), Macromolecules. 31 (1998) 5051–5058. doi:10.1021/ma970627a.

[21] M. Pandey, S. Nagamatsu, S.S. Pandey, S. Hayase, W. Takashima, Orientation Characteristics of Non-regiocontrolled Poly (3-hexyl-thiophene) Film by FTM on Various Liquid Substrates, J. Phys. Conf. Ser. 704 (2016) 12005. doi:10.1088/1742-6596/704/1/012005.

[22] R.D. McCullough, R.D. Lowe, M. Jayaraman, D.L. Anderson, Design, synthesis, and control of conducting polymer architectures: structurally homogeneous poly(3-alkylthiophenes), J. Org. Chem. 58 (1993) 904–912. doi:10.1021/jo00056a024.

[23] M. Pandey, S.S. Pandey, S. Nagamatsu, S. Hayase, W. Takashima, Controlling Factors for Orientation of Conjugated Polymer Films in Dynamic Floating-Film Transfer Method, J. Nanosci. Nanotechnol. 17 (2017) 1915-1922.

[24] M. Hamaguchi, K. Yoshino, Z. Jin, Z. Li, T. Honda, T. Sasada, R.M. Orientation, M. Hamaguchi, K. Yoshino, J. Peng, B. Yu, L.S. Microscope, F. Kao, S. Chou, Lyotropic Behavior of Poly (2 , 5-dinonyloxy-p-phenylenevinylene), Jpn. J. Appl. Phys. 33 (1994) L1689–L1692. doi:10.1143/jjap.33.l1689.

[25] C. Yang, F.P. Orfino, S. Holdcroft, A Phenomenological Model for Predicting Thermochromism of Regioregular and Nonregioregular Poly(3-alkylthiophenes), Macromolecules. 29 (1996) 6510–6517. doi:10.1021/ma9604799.

[26] W. Takashima, S.S. Pandey, T. Endo, M. Rikukawa, N. Tanigaki, Y. Yoshida, K. Yase, K. Kaneto, Photocarrier transports related to the morphology of regioregular poly(3-hexylthiophene) films, Thin Solid Films, 2001: pp. 334–342. doi:10.1016/S0040-6090(01)01109-9.

[27] T.W. Hagler, K. Pakbaz, K.F. Voss, A.J. Heeger, Enhanced order and electronic delocalization in conjugated polymers oriented by gel processing in polyethylene, Phys. Rev. B. 44 (1991) 8652–8666. doi:10.1103/PhysRevB.44.8652.

[28] A. Kumar, W. Takashima, K. Kaneto, R. Prakash, Nano-dimensional self assembly of regioregular poly (3-hexylthiophene) in toluene: Structural, optical, and morphological properties, J. Appl. Polym. Sci. 131 (2014). doi:10.1002/app.40931.

[29] F.C. Spano, Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films, J. Chem. Phys. 122 (2005).

16

doi:10.1063/1.1914768.

[30]   I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. Macdonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M.L. Chabinyc, R.J. Kline, M.D. McGehee, M.F. Toney, Liquid-crystalline semiconducting polymers with high charge-carrier mobility., Nat. Mater. 5 (2006) 328–333. doi:10.1038/nmat1612.

[31]   M.L. Chabinyc, M.F. Toney, R.J. Kline, I. McCulloch, M. Heeney, X-ray scattering study of thin films of poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene)., J. Am. Chem. Soc. 129 (2007) 3226–3237. doi:10.1021/ja0670714.

[32]   K. Tashiro, Y. Minagawa, M. Kobayashi, S. Morita, T. Kawai, K. Yoshino, Structure and thermochromic solid-state phase transition of poly(3-alkylthiophene): [3] effects of alkyl side chain length on the phase transitional behavior, Synth. Met. 55 (1993) 321–328. doi:10.1016/0379-6779(93)90952-s.

[33]   T.J. Prosa, J. Moulton, A.J. Heeger, M.J. Winokur, Diffraction line-shape analysis of poly(3-dodecylthiophene): a study of layer disorder through the liquid crystalline polymer transition, Macromolecules. 32 (1999) 4000–4009. doi:10.1021/ma981059h.

[34]   K.C. Park, K. Levon, Order-disorder transition in the electroactive polymer poly(3-dodecylthiophene), Macromolecules. 30 (1997) 3175–3183. doi:10.1021/ma961322j.

[35]   R.D. McCullough, S. Tristram-Nagle, S.P. Williams, R.D. Lowe, M. Jayaraman, Self-orienting head-to-tail poly(3-alkylthiophenes): new insights on structure-property relationships in conducting polymers, J. Am. Chem. Soc. 115 (1993) 4910–4911. doi:10.1021/ja00064a070.

[36]   L. Biniek, N. Leclerc, T. Heiser, R. Bechara, M. Brinkmann, Large scale alignment and charge transport anisotropy of pBTTT films oriented by high temperature rubbing, Macromolecules. 46 (2013) 4014–4023. doi:10.1021/ma400516d.

[37]   Y. Wu, P. Liu, B.S. Ong, T. Srikumar, N. Zhao, G. Botton, S. Zhu, Controlled orientation of liquid-crystalline polythiophene semiconductors for high-performance organic thin-film transistors, Appl. Phys. Lett. 86 (2005) 1–3. doi:10.1063/1.1894597.

[38]   M. Hamaguchi, K. Yoshino, Liquid crystalline behavior and optical properties of poly (2, 5-dinonyloxy-p-phenylenevinylene), Japanese J. Appl. Physics-Part 1 Regul. Pap. Short Notes. 33 (1994) L1478-1481. doi:10.1143/jjap.33.l1478.

[39]   M.S. Park, A. Aiyar, J.O. Park, E. Reichmanis, M. Srinivasarao, Solvent evaporation

17

induced liquid crystalline phase in poly(3-hexylthiophene), J. Am. Chem. Soc. 133 (2011) 7244–7247. doi:10.1021/ja110060m.

Figure and Table captions

Table 1: List of the casting condition to obtain optimum DR by dynamic-FTM for polymers under investigation.

Table 2: Optical parameters for spin-coated and dynamic-FTM fabricated thin films various conjugated polymers used in this work.

Figure 1: Chemical structure of thiophene-based conjugated polymers utilized for present investigation.

Figure 2: Schematic representation of film formation process in FTM procedure.

Figure 3: Polarized electronic absorption spectra of oriented FTM (parallel: red, perpendicular: blue) and non-oriented spin-coated (black) films of NR-P3HT (a) and RR-P3HT (b) prepared by dynamic-FTM.

Figure 4: Polarized electronic absorption spectra of oriented FTM (parallel: red, perpendicular: blue) and non-oriented spin-coated (black) films of PQT-C12 (a) and PBTTT-C14 (b) prepared by dynamic-FTM.

Figure 5: Orientation intensity (DR) of all the polymer-films prepared under the identical casting condition for PQT-C12 to provide highest orientation.

Figure 6: Schematic skeletal drawing of possible intermolecular packing images for (a) RR-P3HT, (b) NR-P3HT and (c) PBTTT-C14/PQT-C12, respectively. Ovals in (a) represent disordered (amorphous) regions.

Table 1: List of the casting condition to obtain optimum DR by dynamic-FTM for polymers under investigation.

Polymer	Concentration of polymer in chloroform (wt/wt)	Temperature	Liquid substrate[*]
NR-P3HT	1.0	25 °C	Eg:Gl = 3:1
RR-P3HT	1.0	42 °C	Wt:Eg = 1:2
PBTTT-C14	1.0	70 °C	Gl
PQT-C12	1.0	25 °C	Eg:Gl = 2:1

* mixing ratio in volume. Eg, Gl and Wt are ethylene glycol, glycerol and deionized water, respectively.

Table 2: Optical parameters for spin-coated and dynamic-FTM fabricated thin films various conjugated polymers used in this work.

Polymer	Conditions	DR	Absorption Maximum	Vibronic shoulders (nm)
NR-P3HT	Spin-Coated	-	479 nm	-
	FTM-Perpendicular	5.8	465 nm	-
	FTM-Parallel		525 nm	602 nm
RR-P3HT	Spin-Coated	-	516 nm	550 nm, 602 nm
	FTM-Perpendicular	1.5	550 nm	525 nm, 602 nm
	FTM-Parallel		554 nm	525 nm, 602 nm
PQT-C12	Spin-Coated	-	524 nm	503 nm, 574 nm
	FTM-Perpendicular	6.4	523 nm	574 nm
	FTM-Parallel		538 nm	503 nm, 574 nm
PBTTT-C14	Spin-Coated	-	538 nm	592 nm
	FTM-Perpendicular	5.1	540 nm	592 nm
	FTM-Parallel		545 nm	592 nm

Figure 1: Chemical structure of thiophene-based conjugated polymers utilized for present investigation.
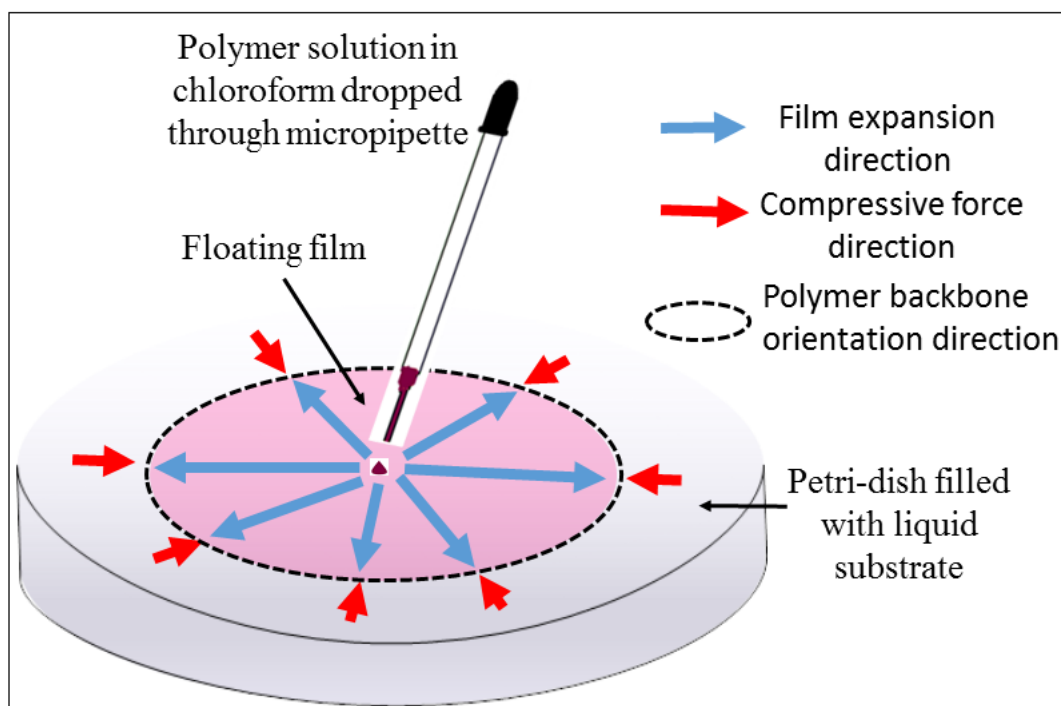
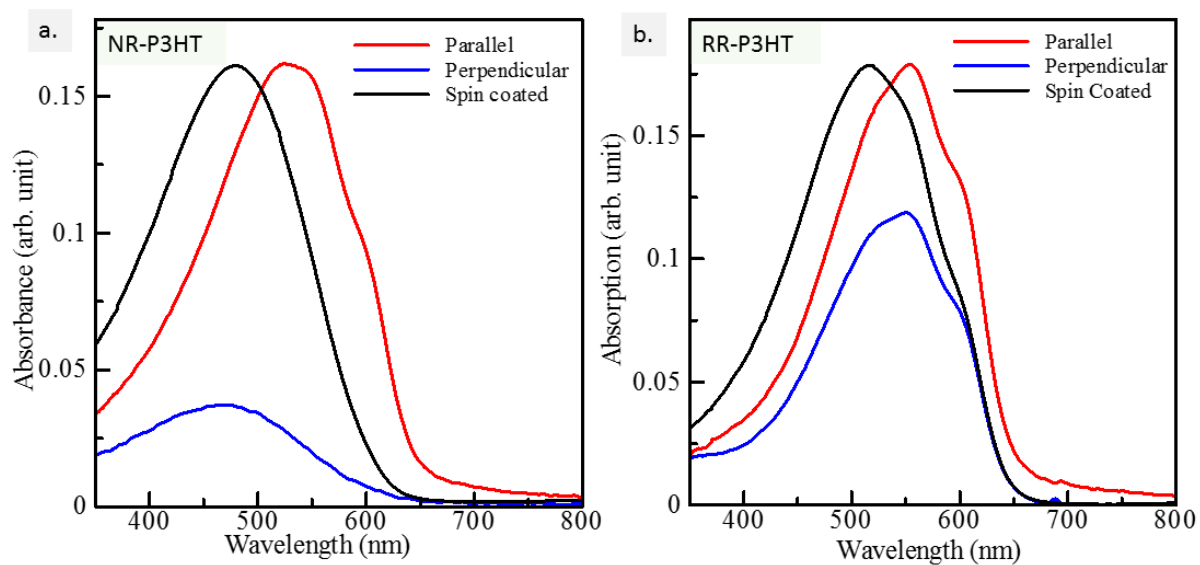**Figure 2**: Schematic representation of film formation process in FTM procedure.

Figure 3: Polarized electronic absorption spectra of oriented FTM (parallel: red, perpendicular: blue) and non-oriented spin-coated (black) films of NR-P3HT (a) and RR-P3HT (b) prepared by dynamic-FTM.
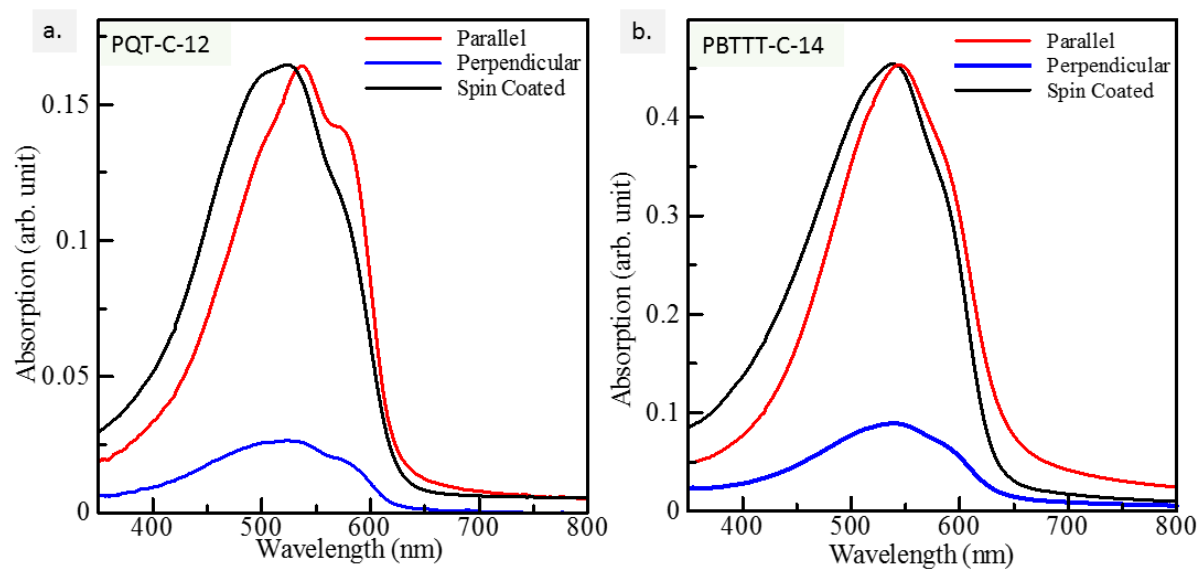
Figure 4: Polarized electronic absorption spectra of oriented FTM (parallel: red, perpendicular: blue) and non-oriented spin-coated (black) films of PQT-C12 (a) and PBTTT-C14 (b) prepared by dynamic-FTM.
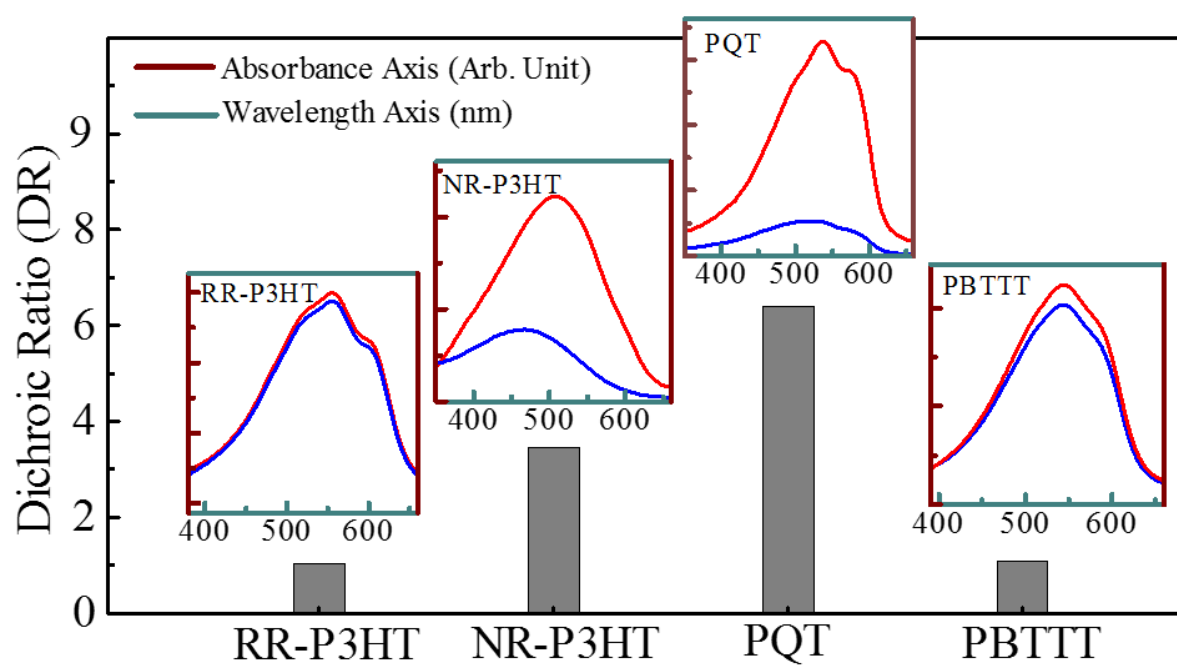
Figure 5: Orientation intensity (DR) of all the polymer-films prepared under the identical casting condition for PQT-C12 to provide highest orientation.
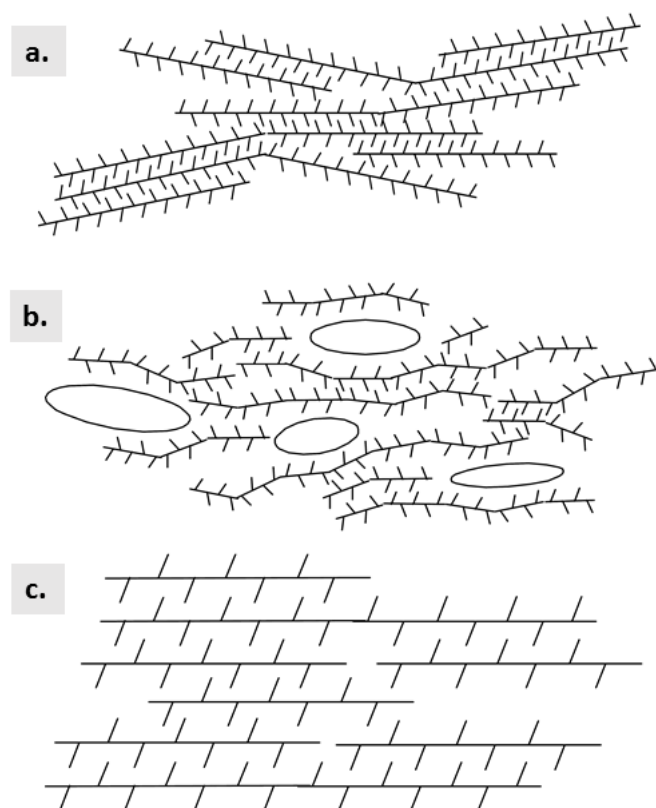
Figure 6: Schematic skeletal drawing of possible intermolecular packing images for (a) RR-P3HT, (b) NR-P3HT and (c) PBTTT-C14/PQT-C12, respectively. Ovals in (a) represent disordered (amorphous) regions.