Implication of Molecular Weight on Optical and Charge Transport Anisotropy in PQT-C12 Films Fabricated by Dynamic FTM

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ABSTRACT

Large area (>20 cm x 2 cm) oriented thin films of PQT-C12 with varying molecular weight and polydispersity index (PDI) were fabricated by ribbon-shaped floating film transfer method aiming towards their application as active semiconductor element of organic field effect transistors (OFETs). Investigation on the influence of the molecular weight and PDI upon the extent of molecular alignment and anisotropic charge transport were systematically carried out. It has been demonstrated that high molecular weight in combination with low PDI not only leads to high a very high optical anisotropy >10 but also high charge carrier anisotropy with the hole mobility of about 0.07 cm^2/Vs for OFETs using parallel oriented PQT-C12 thin films. Such structure-property correlation are highly beneficial for development of high performance organic electronic devices by synergistic and amicable tuning of the optoelectronic anisotropies and polymer synthetic variables.

KEYWORDS: molecular orientation, semiconducting polymers, poly (quaterthiophene), floating film transfer, molecular weight, field-effect transistor

INTRODUCTION

Recent past has witnessed that conjugated polymers (CPs) have contributed highly for the development of the organic electronic devices such as organic field effect transistor (OFETs),[1,2] organic light emitting diodes (LEDs)[3–5] organic solar cell,[6,7] and organic photodetectors[8,9]. Main focus has been directed towards development of flexible and low-cost organic electronic devices owing to the flexibility and solution processability of the CPs[9–11]. Amongst organic electronic devices, OFETs bear the fascination for the research and development being the integral part of many devices owing to their amplifying and switching actions[12]. Commercialization of organic electronic devices not only demand for the high performance OFETs but also amicable solutions for the issues such as enhancement in field effect mobility,[13] operational stability,[14] surface passivation[15,16] and high reproducibility[17,18]. One-dimensionality of CPs in combination with extended π-conjugation offers inherent tendency of molecular self-assembly, which concomitantly influences the charge transport in these materials. Therefore, fabrication of thin films of these materials highly depends not only upon conditions of the film fabrication but also post treatments in order to promote the extent and nature of molecular self-organizations[19–21]. In the recent past, efforts have been directed to control the molecular weight and distribution of CPs in order to have in-depth insight about their implication on the final device performance, especially in the area of OFETs. It has been reached at a common consensus that charge carrier mobility increases as a function of increasing molecular weight as emphasized by various research groups[19,21–23]. A dramatic influence of molecular weight on charge transport in poly(3-hexylthiophene) based OFETs have been clearly demonstrated by Kline et al, where there was nearly 4 orders of magnitude increase in the field effect mobility (10^{-6}-10^{-2} cm^2/Vs) upon increasing the molecular weight of this polymer from 3.2 kDa to 33.8 kDa.[19]

Apart from controlling the molecular weight of CPs, other approaches like design and development novel polymeric systems have also been attempted aiming towards imparting other functionalities in OFETs along with promoting the charge transport[24,25]. In the meantime, efforts for decreasing the threshold voltage and stable n-channel charge transport in OFETs have also been demonstrated by amicably controlling the crystalline domains and molecular design of novel CPs[26,27]. Molecular self-assembly of CPs plays a dominant role in controlling the final device performance, but providing directionality to the ordered domains especially in the channel direction is highly desired for enhancing the performance of OFETs. A number of methods such as mechanical rubbing,[28] friction transfer,[29] strain alignment,[30] high temperature rubbing [31] and roll transfer printing[32] etc. have been already used to align the CPs. Although, these techniques are successful in aligning the macromolecules by applying the external force but intriguing problems such as mechanical damage, static charge accumulation, solubility of underlying layer, material wastage during thin film fabrication must be solved amicably. In order to solve these issues, our group have developed a simple and cost-effective floating film transfer method (FTM) where, a thin and oriented floating film of CPs is first cast upon orthogonal liquid substrate followed by its transfer to any desired substrate[33,34]. In this method, molecular orientation of the fabricated thin films can be controlled by controlling and optimizing the casting parameters depending on the nature of polymeric backbone like concentration of polymer solution, casting temperature and viscosity of liquid substrate[35-36].

Fabrication of large area homogeneous thin films is highly desired for the acceleration of commercialization efforts of organic electronic devices. In this context, we have improvised the conventional FTM by introducing the custom made slider consisted of Teflon for providing the directionality during film spreading under FTM[37]. Utilization of custom made slider during the film

casting in FTM led to fabrication of large area rectangular films (> 2 cm X 20 cm), which we named as ribbon shaped FTM[38]. In this work, a dual approach pertaining to the optimization of synthetic parameters of CP under investigation in combination with fabrication of its large area oriented thin films by ribbon-shaped FTM have been applied for the investigation of anisotropic charge transport. In the first approach, synthesis of poly(dodecyl-quaterthiophene) (PQT-C12) as representative CP with varying molecular weight and polydispersity index (PDI) was conducted by varying the synthesis parameters. In the second approach, large area oriented thin films of the synthesized CPs were prepared by ribbon-shaped FTM followed by fabrication of OFETs. Efforts have been directed to delineate the role of molecular weight and PDI on the extent of molecular orientation and their implications on the anisotropic charge transport.

2. EXPERIMENTAL DETAILS

2.1 Materials and methods.

Chemicals like methanol, ethylene glycol, glycerol, ferric chloride, hexane, super dehydrated chloroform and 28 % ammonia solutions etc. were purchased from Wako Chemicals Japan. Starting materials for the synthesis of PQT-C12, 3,3'''-didodecyl-quarterthiophene and octadecyltrichlorosilane (OTS) for surface treatments were purchased from Sigma-Aldrich and used as received without any further purification. A Glan-Thomson prism polarizer (GYPC-10-19SN, Sigma-Kouki, Japan) with UV-visible spectrophotometer (JASCO, V570) was used for the measurement of polarized absorption spectrum. Thickness of thin films fabricated was measured by interference microscopy (Nikon Eclipse LV-150). Molecular weights and their distributions in terms of polydispersity index (PDI) of PQT-C12 were

estimated by gel permeation chromatography (GPC) (TOSOH HLC-8320; GPC-EcoSEC) using polystyrene standard for molecular weight calibration, chloroform solvent and refractive index detector. Nuclear magnetic resonance (NMR) spectrum (JEOL, 500 MHz) of the PQT-C12 was measured at room temperature in $CDCl_3$ using tetramethylsilane as internal standard.

2.2 Synthesis of PQT-C12.

PQT-C12 of different molecular weight and PDI were used as an active organic semiconductor for the investigation of optical as well as electrical anisotropy. PQT-C12 was chemically synthesized by $FeCl_3$ mediated oxidative polymerization as per reported procedures[36,49]. In a typical procedure, 0.65 gm of ferric chloride and 20 ml hexane were added in a three neck round bottom flask fitted with condenser and dropping funnel. To this slurry stirred at room temperature under continuous N_2 flow, 170 mg (0.5 mmol) of 3,3'''-Didodecyl-2,2':5',2'':5'',2'''-quaterthiophene dissolved in 20 ml of chlorobenzene was added using dropping funnel at two different rates of 0.2 ml/min and 2.0 ml per min at room temperature. Reaction mixture was stirred at room temperature under N_2 flow for 3 hours. After this, polymerization was continued by heating the solution containing the quaterthiophene monomer and $FeCl_3$ catalyst at two different temperatures of 40°C and 60°C. After 18 hours of polymerization, solution was brought to room temperature followed by quenching of polymerization by adding 200 ml of methanol containing 10% HCl leading to precipitation. Precipitate was collected by filtration followed by washing with ample methanol to remove catalyst and monomeric impurities. Since it was doped polymer, dedoping was conducted by dissolving the polymer in chloroform (100 ml) and adding 100 ml aqueous ammonia solution (14 %) followed by stirring the mixture at 50°C for 30 min. This process was repeated 3 times and finally, chloroform fraction containing the polymer was separated by separating funnel.

Concentration of the chloroform solution followed by re-precipitation led to the un-doped PQT-C12, which was finally purified by soxhlet extraction by hexane to remove the soluble oligomeric impurities. Thus, four different type of CPs named as **PQT-C12-A** (0.2 ml/min@40°C), **PQT-C12-B** (2.0 ml/min@40°C), **PQT-C12-C** (0.2 ml/min@60°C) and **PQT-C12-D** (2.0 ml/min@60°C) have been synthesized in this work. Poor solubility of PQT-C12 with relatively higher molecular weights in $CDCl_3$ (**B**, **C** and **D**) led to the measurement of proton NMR spectra of **PQT-C12-A** only, which is being shown. ^{1}H NMR of PQT-C12-A ($CDCl_3$, ppm): δ 7.12 (d, 2H), 7.05 (d, 2H), 6.99 (s, 2 x C2-H of alkyl substituted thiophene ring), 2.72 (t, 2 x **CH₂**-$C_{11}H_{23}$ of alkyl chain), 1.60 (2 x CH_2-**CH₂**-$C_{10}H_{21}$ of alkyl chain), 1.20 (m, 18 x CH_2), 0.80 (m, 2 x CH_3). This proton NMR confirms the structural identity of the synthesized PQT-C12 with molecular structure as shown in the Fig. 1(c).

2.3 Thin film fabrication.

Spin coating and ribbon-shaped FTM has been employed for the fabrication of thin films of four different samples of PQT-C12 on glass and SiO_2/Si substrates for optical characterization and OFET fabrication, respectively. Polymer in super dehydrated chloroform solutions were prepared in 1 % and 0.5 % (w/w) for making the thin films by ribbon shaped FTM and spin coating, respectively. Oriented ribbon-shaped thin films were prepared as per our earlier publication[38]. Typically, 15-20 µl of polymer solution in chloroform was dropped on the hydrophilic liquid substrate in center of the assisting slider, which was placed towards one edge of partly filled rectangular tray. An optimized condition of FTM like Ethylene glycol-glycerol (3:1) as hydrophilic liquid substrate, 1 % (w/w) polymer solution in chloroform and 40°C temperature of liquid bath was used for all of polymer samples synthesized in this work. Dried oriented thin films of PQT-C12 formed after evaporation of chloroform, was finally transferred on desired substrate by stamping for further characterization and device fabrication. On the other hand, spin

coated thin film of polymers was also prepared by spinning at 3000 rpm for the duration of 120 seconds. Thin film fabrication by ribbon-shaped FTM has been shown schematically in the figure 1(a). Relatively lower concentration of the polymer solution in combination of high spinning speed was used for spin coating in order to avoid very large mismatch between the thickness of spin coated and FTM processed thin films. Anisotropic thin films of PQT-C12 films prepared by ribbon shaped FTM were transferred on glass substrate for investigation of orientation using polarized absorption spectroscopy. Polarized absorption spectra was measured by rotating the polarizer angle 0° and 90° during the measurement. Extent of molecular orientation was quantitated in terms of dichroic ratio (DR $= \frac{A_\parallel}{A_\perp}$) and calculated by the absorption spectra at 0° ($\parallel$) at λ_{max} divided by absorption spectra at 90° ($\perp$) at λ_{max}.
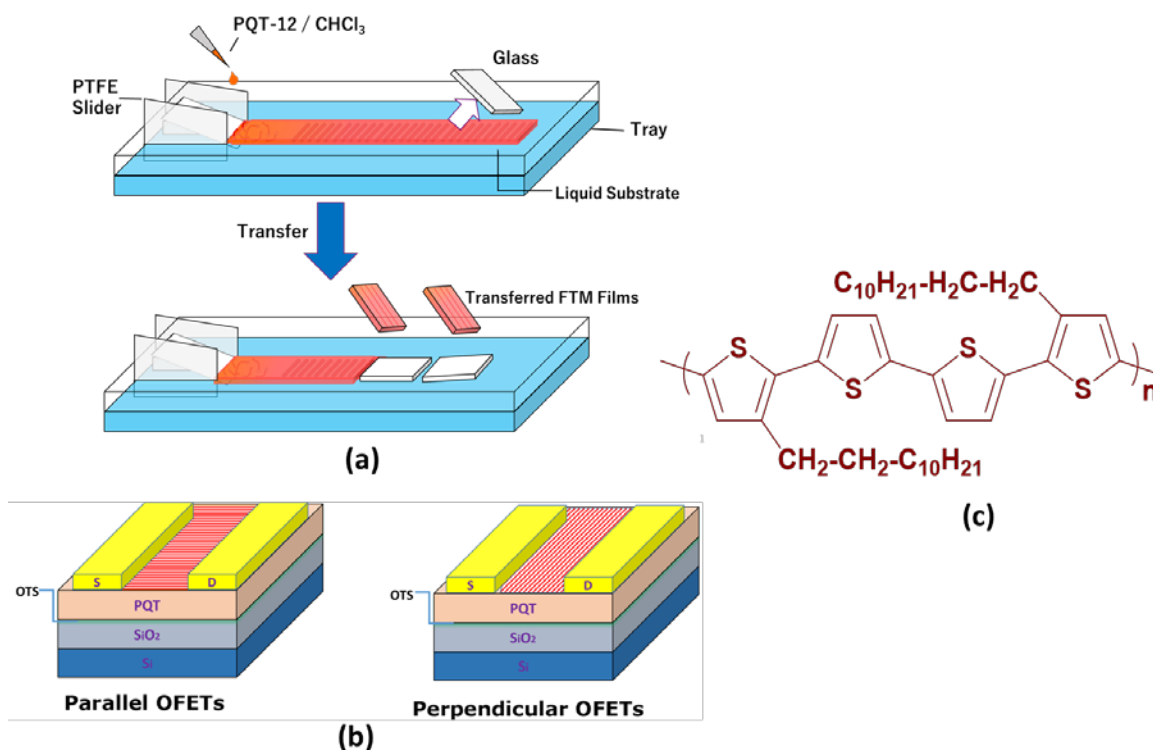

Figure 1. Schematic representation of oriented thin film fabrication by ribbon-shaped FTM (a), device architecture of parallel/perpendicular OFETs (b) and chemical structure of PQT-C12 (c).

2.4 Fabrication and Characterization of OFETs.

PQT-C12 with varying molecular weight and PDI were used for investigation of anisotropic charge transport by fabricating OFETs in bottom gate top contact (BGTC) device architecture, which is shown in the Fig. 1(b). For making the OFETs, highly doped Si substrate was used with 300 nm SiO_2 layer as gate insulator. Before transferring the oriented films of PQT-C12 processed by FTM, surface of the SiO_2 was treated by self-assembled monolayer of OTS on the SiO_2 surface. Surface treatment was conducted by dipping ultrasonically cleaned SiO_2/Si substrate in 2 mM solution of OTS in dehydrated toluene at 90°C for 2 hours followed by annealing at 130°C for 30 mins. The estimated dielectric capacitance (Ci) was 10 nF/cm^2. Orientated thin films formed by FTM were then transferred on OTS treated SiO_2 surface by stamping. OFETs with parallel and perpendicularly oriented PQT-C12 films were then completed by thermal evaporation of 50 nm gold electrode (source and drain), while confirmation of the direction of orientation by a polarizer film. Thermal evaporation was conducted at the base pressure 10^{-6} torr using nickel shadow mask having the channel length and width of 20 µm and width 2 mm, respectively. Electrical characterization was done by computer controlled 2 channel source measure unit (Keithley-2612) in vacuum with pressure 10^{-3} torr.

3. RESULT AND DISCUSSION
3.1 Polymer synthesis.
Molecular weight and PDI plays a dominant role in controlling the charge transport of CPs. Advent of solution processable polythiophene class of CPs by introduction alkyl chains led to the development of different synthetic methods like radical polymerization, electrochemical polymerization and regiocontrolled chemical synthesis. Amongst these methods, FeCl$_3$ catalyzed chemical synthesis is most suitable for large-scale synthesis owing to its simplicity and higher polymer yield.[39] Difficulty in the

regio-specific control during polymerization and importance of regioregularity on facile charge carrier transport led to the popularity and most versatile application of regioregular poly(3-alkylthiophenese) (P3ATs) in organic electronic devices[40,41]. One of the plausible and amicable solutions for regiocontrolled synthesis is to first prepare a regioregular block of oligomer followed ther polymerization using simple FeCl₃ mediated chemical synthesis, which resulted in to the emergence of alkyl-substituted poly(quaterthiophene) (PQT)[23]. Synthetic conditions like monomer to catalyst ratio, temperature, choice of solvent and speed of addition plays a dominant role in controlling the molecular weight and PDI of the P3ATs prepared by FeCl₃ mediated chemical polymerization[39]. In this work four types of PQT-C12 have been synthesized by FeCl₃ mediated chemical polymerization of 3,3'''-didodecyl-2,2':5',2'':5'',2'''-quaterthiophene by varying the temperature (40ºC and 60ºC) and rate of addition (0.2 ml/min and 2.0 ml/min) of FeCl₃ suspension in hexane to the monomer solution taken in the chlorobenzene. Effort was also directed for the synthesis of PQTs at 80ºC but very small yield along with insolubility in chloroform led to confine our detailed investigations on only four types of PQT-C12 prepared in this work. GPC analysis result of the CPs under investigation have been summarized in the table 1. A perusal of the table 1 pertaining to the GPC analysis corroborates that chemical polymerization using FeCl₃ led to appreciably good yield of PQT-C12 under all of the synthetic conditions. Observed molecular weights are although lower than P3ATs, which is due to the bulkiness of the quaterthiophene radical cation formed during polymerization. Observed values of molecular weights are in agreements with the commercially available products having molecular weight in the range of 10,000-40,000[42]. Higher rate of addition of the catalyst in the monomer led to higher molecular weights of the CPs but with relatively decreased polymer yield. Very slow rate of addition although gave higher polymer yields but at the same time leads to polymers with relatively low molecular weights. Decrease in molecular weight under slow addition could be attributed to the faster chain termination during polymerization.

Therefore, relatively lower temperature with higher rate of addition seems to make a balance for quality of the obtained polymer with good molecular weight and narrow distribution.

Table 1: Influence of synthetic conditions on the polymerization of 3,3'''-Didodecyl-2,2':5', 2'': 5'',2'''-quaterthiophene with FeCl$_3$

Polymer	Temperature	Rate of addition	Yield	Mn	Mw	Mw/Mn
PQT-C12-A	40℃	0.2 mL / min	79.5 %	10766	24156	2.2
PQT-C12-B	40℃	2 mL / min	76.8 %	19564	40500	2.1
PQT-C12-C	60℃	0.2 mL / min	87.3 %	15252	30965	2.0
PQT-C12-D	60℃	2 mL / min	79.6 %	16153	55865	3.5

3.2 Optical characterization

3.2.1 Non-polarized absorption spectra.

Four differently prepared PQT-C12 were subjected to electronic absorption spectral characterization using their thin films fabricated by spin coating in order to investigate the implication of molecular weight and PDI on their optical behavior. Figure 2 exhibits normalized solid-state electronic absorption spectra of four PQT-C12 polymers synthesized under different synthetic conditions along with summarization of optical parameters in the table 2. Amongst polymer under investigation, PQT-C12-D having highest weight average molecular weight (Mw) and PDI exhibits absorption maximum (λ_{max}) at 538 nm and vibronic shoulder at 592 nm. Spectral behaviour is very similar with slight bathochromic shift to that of reported for the commercial PQT-C12 (purchased from American Dye Source) as reported by Cha et al[42]. It is interesting to note that PQT-C12-B have relatively lower (Mn) and narrow molecular weight distribution (PDI=2.1) as compared to that of PQT-C12-D, although exhibits nearly similar λ_{max} and optical band edge but pronounced vibronic shoulder. This could be attributed to the enhanced π-π

molecular orbital overlap and assistance in molecular packing due to narrow distribution in the weight and number of the polymeric chains. It can also be seen from the normalized solid-state electronic absorption spectra that increase in the molecular weight of the PQT-C12 not only leads to monotonic red shift in the optical absorption edge but also pronounced vibronic shoulders. A similar behavior of implications of the molecular weight on bathochromic shift in the λ_{max} and pronounced vibronic features for PQT and P3HT as a function of increasing molecular weight have also been observed by Pingle et al and Zen et al, respectively[43,44] . They advocated that in the CPs with high and medium molecular weight, absorption spectral feature almost resemble to each other and spectral feature starts to degrade (becoming featureless) with blue shift in the λ_{max} in the case of samples, when moving from higher to lower molecular weight fractions.
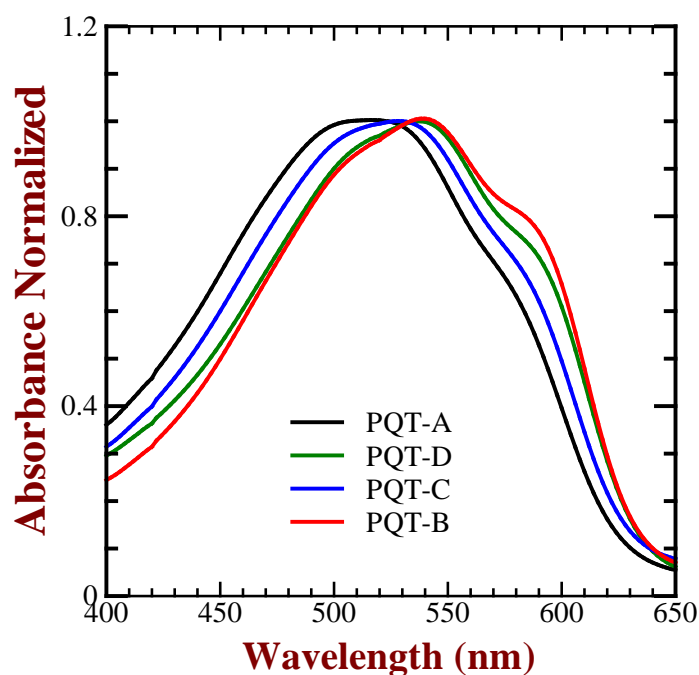

Figure 2. Electronic absorption spectra of spin-coated thin films of PQT-C12 with varying molecular weight and PDI.

3.2.2 Polarized absorption spectra.

It has been previously reported that our newly developed ribbon shaped FTM provide very large area oriented films and extent of orientation depends on the nature of the polymeric backbone of CPs[36,45]. Oriented thin films of PQT-C12 having different molecular weight and PDI were subjected to polarized electronic absorption spectral investigation using Glan-Thomson prism. Results of polarized electronic absorption spectra of these PQT-C12 films prepared by ribbon shaped FTM have been shown in the Figure 3 along with summarization of optical parameters in the table 2. That

Table-2 Optical parameters for isotropic spin coated and anisotropic ribbon shaped FTM films for various PQT-C12 samples deduced from the electronic absorption spectra.

Conjugated polymers	Film fabrication conditions	Absorption maximum (nm)	Dichroic ratio	Vibronic shoulder (nm)
PQT-C12-A	Spin coating	518		586
	FTM parallel	544	4.8	586
	FTM perpendicular	532		590
PQT-C12-B	Spin coating	538		586
	FTM parallel	550	11.1	588
	FTM perpendicular	538		592
PQT-C12-C	Spin coating	528		578
	FTM parallel	536	5.3	582
	FTM perpendicular	496		582
PQT-C12-D	Spin coating	538		590
	FTM parallel	546	6.1	586
	FTM perpendicular	532		590

It can be clearly seen that irrespective of molecular weight and PDI, FTM films exhibited a bathochromic shift in the λ_{max} in the case of parallel orientation as compared to their corresponding spin coated counterparts indicating extension of effective π-conjugation after the molecular orientation. Amongst

the four differently prepared PQT-C12, one of polymer (PQT-C12-B) with appreciably higher molecular weight along with lower PDI exhibited λ_{max} at 550 nm associated with the π-π^* electronic transition, which is 12 nm red shifted as compared to its spin coated counterparts. At the same time, it has not only exhibited highest optical anisotropy (DR=11.1) but also highly pronounced vibronic shoulder appearing at 588 nm. Unlike other CPs like P3ATs and PBTTT, which have used for molecular orientation, relatively fewer efforts have been directed for orienting PQTs using methods like role transfer and FTM including our group with DR in the range of 4-6[46]. To the best of our knowledge, this is one of the highest DR observed for PQT-C12-B having moderately high molecular weight and narrow PDI.
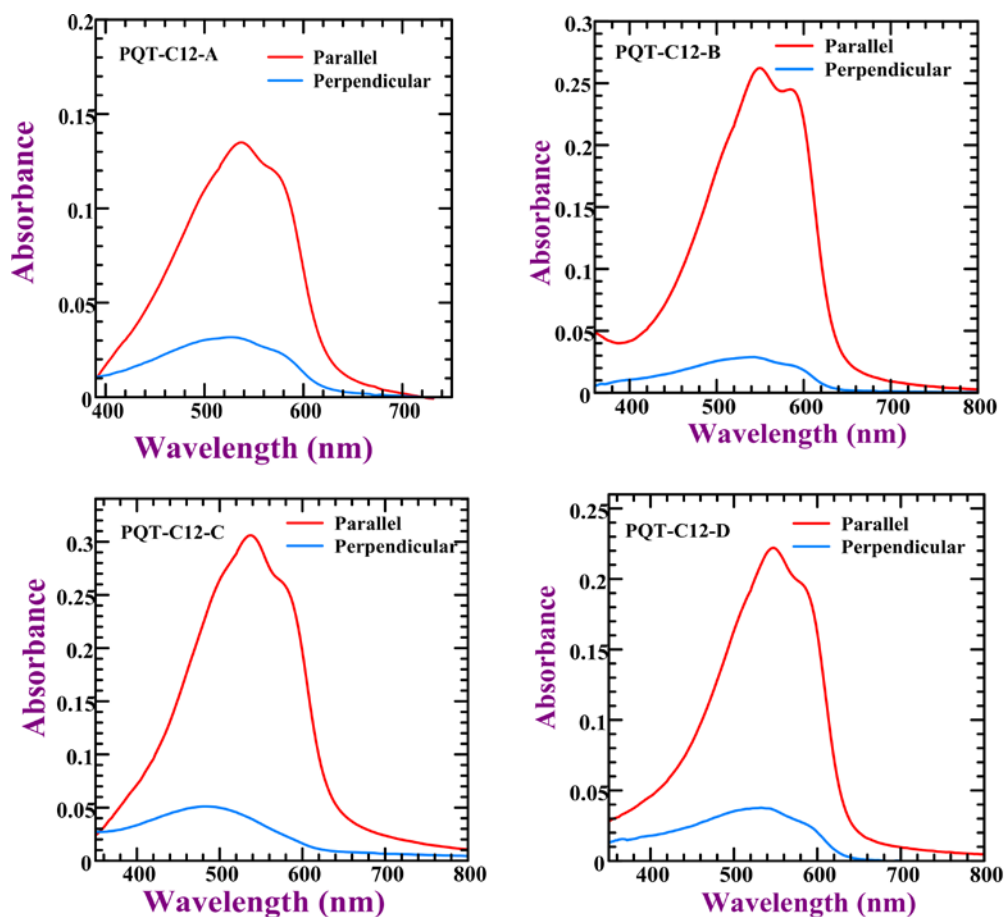

Figure 3. Polarized electronic absorption spectra of oriented thin films PQT-C12 with varying molecular weights prepared by ribbon-shaped FTM on glass substrate.

A perusal of the table 2 corroborates that increase the molecular weight of PQT-C12 leads to a general tendency of increase in the extent of molecular orientation and optical anisotropy. Pronounced enhancement in the molecular orientation leading to very high optical anisotropy for the PQT-C12-B could be attributed to the higher molecular weight in combination of narrow distribution. In spite of highest molecular weight represented by polymer PQT-C12-D, it exhibited relatively decreased extent of molecular orientation (DR=6.1) as compared to PQT-C12-B, which might of associated with very high value of PDI. In the case of P3HT, there was not only a monotonic decrease in crystallinity but also blue-shift in the λ_{max} as a function of decreasing molecular weight, which was explained considering the fact that lower molecular weight chains are in more disordered amorphous state and exhibit less plainrised backbone conformation[47,48]. Most probably, higher extent of low molecular weight amorphous chains present in the PQT-C12-D poses a dragging force to orienting higher molecular weight chains leading to overall hampered optical anisotropy (DR=6.1).

3.3 Anisotropic charge transport

In order to investigate the anisotropic charge transport in oriented thin films of PQT-C12 prepared under different synthetic conditions, OFETs in the BGTC device configuration were fabricated and subjected to electrical characterization. Figure 4(a) depicts the schematic illustration of the OFET in its BGTC device architecture, where oriented/non-oriented PQT-C12 thin films fabricated by ribbon-shaped FTM were used in the channel as active organic semiconductor. For the investigation of anisotropic charge transport, direction of the oriented films was first confirmed by polarizer film followed by its transfer on OTS treated SiO_2/Si gate insulator in order to assign the direction of orientation. The top source-drain electrodes were then thermally evaporated using shadow mask by placing the mask in parallel and perpendicular with respect to the orientation direction. A typical output characteristics for the parallel

and perpendicular OFETs using one of the polymer PQT-C12-B having highest optical anisotropy (DR=11.1) is shown in the Fig. 4 (b). It exhibits a clear p-type electrical transport upon application of the gate bias from 0 to -80 V. Apart from p-type behavior, it also shows clear difference in parallel and perpendicular drain currents at respective gate bias, which reflects the anisotropic charge transport. There was about an order of magnitude higher drain currents at each respective gate bias in the OFETs bearing parallel oriented films as compared to that of their corresponding perpendicularly oriented thin film counterparts. This was attributed to the facile charge transport due to orientation of the polymeric chains in channel direction. Best performance was also exhibited by the FET based on parallel oriented thin films of PQT-C12-B having hole mobility and on/off ratio of 0.07 cm^2/V.s and 10^6, respectively. At the same time, this also exhibits mobility anisotropy of 10.5, which matches very well with the optical anisotropy of 11.1.

Electronic parameters of OFETs such as charge mobility (μ) and on/off ratio were estimated from the transfer characteristics as shown in the Figure 4 (c). Transfer characteristics clearly reveal the implication of molecular orientation on the anisotropic charge transport. Field effect mobility was calculated at the condition, when it operates in saturation region by using the equation 1

$$I_{DS} = \frac{W}{2L}\mu C_i (V_{GS} - V_{TH})^2 \hspace{2cm} [1]$$

Where, I_{DS}, W, L, μ, C_i, V_{GS} and V_{TH} are source-drain output current, channel length, channel width, capacitance of gate insulator, gate to source voltage and threshold voltage, respectively. Electronic parameters such as mobility of parallel OFETs ($\mu_{\parallel}$), perpendicular OFETs ($\mu_{\perp}$), on/off ratio (I_{ON}/I_{OFF}), and mobility anisotropy ($\mu_{\parallel}/\mu_{\perp}$) deduced from the transfer curves of the OFETs fabricated using different PQT-C12 samples are summarized in the table 3.
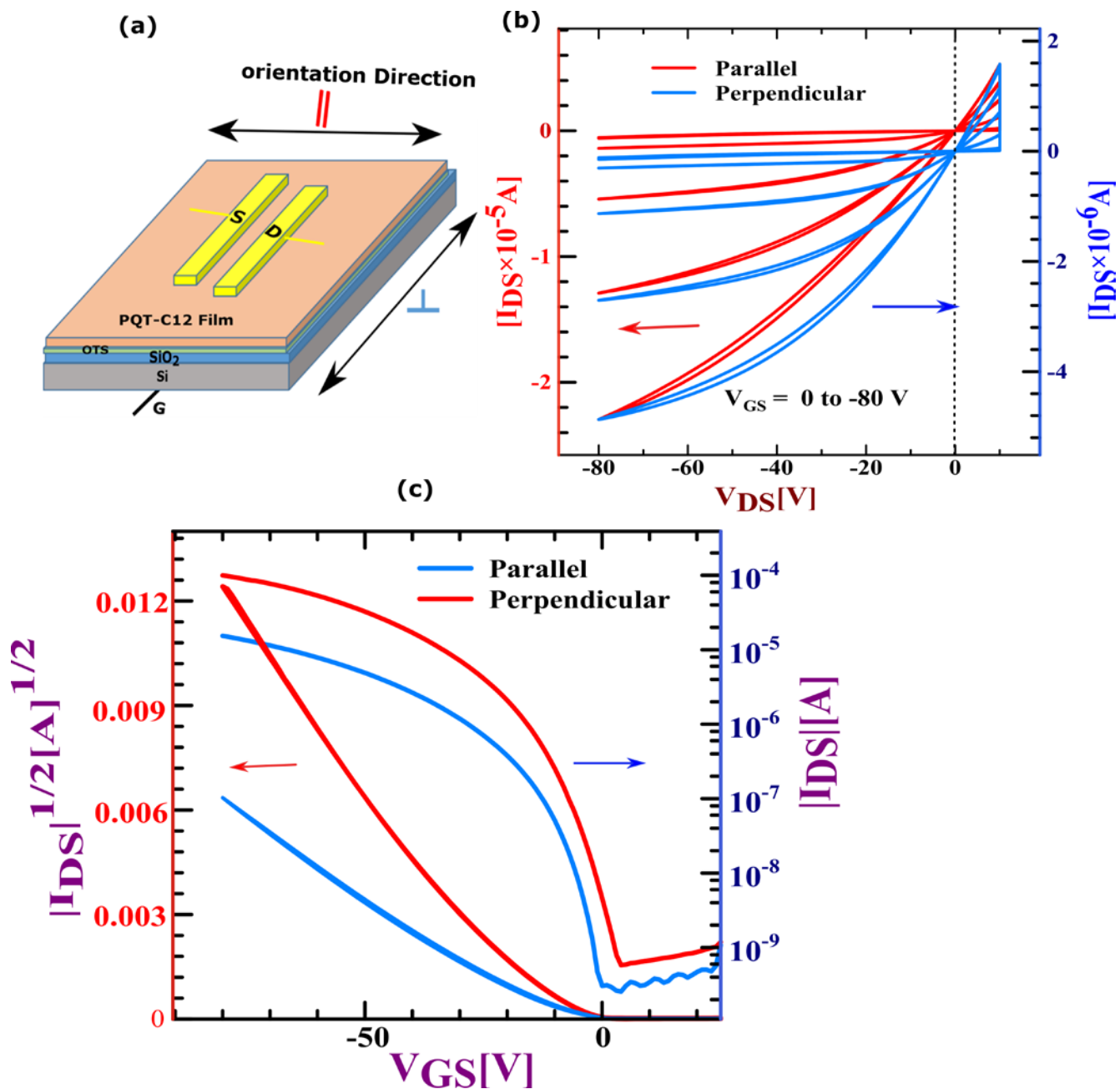
Figure 4. Device architecture of fabricated OFETs (a), representative output characteristics (b) and transfer characteristics (c) at gate bias of -80 V for the OFETs fabricated using parallel and perpendicularly oriented PQT-C12-B films.

Table-3 Device parameters deduced from OFETs prepared by thin films of PQT-C12 fabricated by ribbon-shaped FTM. Values shown in the parantheses represents the average values of the parameters taken for the four independent devices.

Polymer samples	$\mu_{\parallel}$ (cm^2/Vs)	$\mu_{\perp}$ (cm^2/V.s)	$\mu_{\parallel}/\mu_{\perp}$	I_{ON}/I_{OFF}	DR
PQT-C12-A	5.2×10^{-3} (4.0×10^{-3})	2.5×10^{-3} (2.4×10^{-3})	2.1 (1.7)	10^4	4.0 (3.9)
PQT-C12-B	6.7×10^{-2} (6.6×10^{-2})	6.4×10^{-3} (6.3×10^{-3})	10.5 (10.4)	10^6	11.1 (10.3)
PQT-C12-C	8.3×10^{-3} (8.2×10^{-3})	9.3×10^{-4} (9.4×10^{-4})	8.9 (8.7)	10^5	7.7 (6.6)
PQT-C12-D	3.9×10^{-2} (3.3×10^{-2})	5.3×10^{-3} (5.0×10^{-3})	7.4 (6.6)	10^5	6.1 (5.6)

A perusal of the table 3 clearly corroborates that increase in the molecular weight of PQT-C12 leads to increase in all of the electronic parameters like charge carrier mobility, mobility anisotropy and on/off ratio following the same trends of the optical anisotropy. Contrary to this, in spite of higher molecular weight of PQT-C12-D, as compared to that of PQT-C12-B, it exhibited hampered charge carrier mobility of 3.9 $\times10^{-2}$ cm^2/Vs and mobility anisotropy of 7.4. This could be explained considering the wide molecular distribution (PDI=3.5) in the PQT-C12-D and low molecular weight fraction present in the polymer matrix with rich amorphous domains poses a dragging force to long molecular weight chains undergoing facile orientation. That is why, it not only exhibits reduced optical anisotropy but also these amorphous rich domains hinders the charge transport leading to reduced charge carrier mobility and extent of the mobility anisotropy. The value of mobility 6.7$\times10^{-2}$ cm^2/Vs shown by parallel OFET using PQT-C12 is higher as compared to that reported by Ong.et al (Mn =17000) and our group (Mn=10,000)

previously with reported mobility of 0.02 -0.05 cm^2/Vs and 0.03 cm^2/Vs, respectively, which could be attributed to the combined effect of high molecular weight and low PDI [38,49].
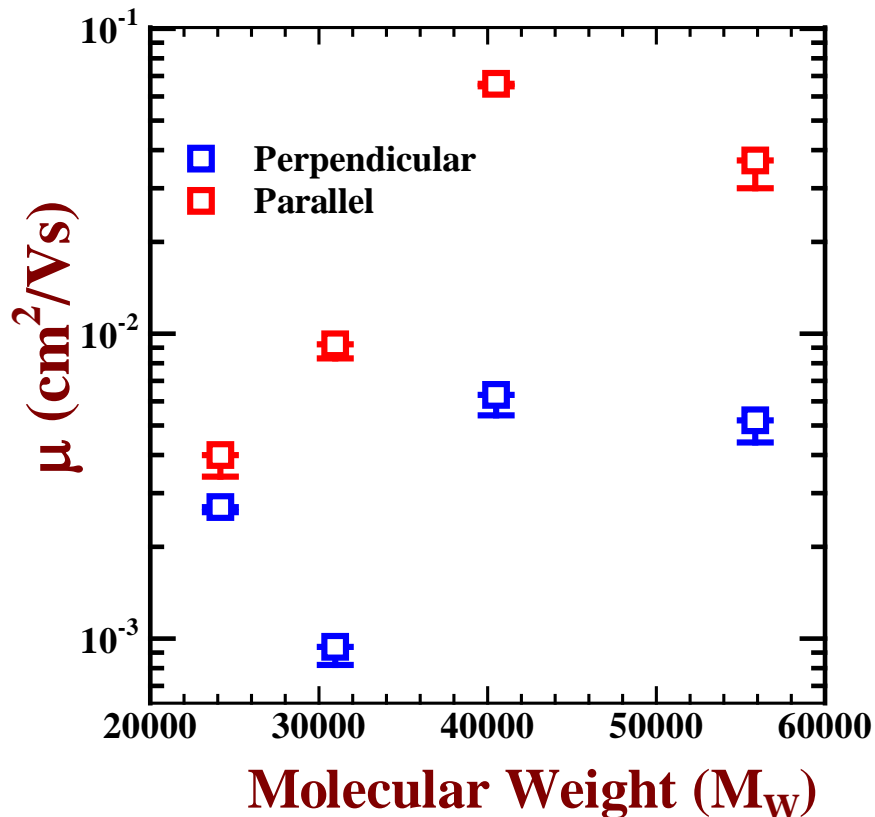

Figure 5. Molecular weight dependence of the charge carrier mobility for the oriented thin film PQT-C12 prepared by ribbon-shaped FTM.

In order to visualize the implications of molecular weight on anisotropic charge transport, a number of devices were fabricated using oriented thin films of PQT-C12 prepared under different synthetic conditions having different molecular weights and PDI. Results of the charge carrier mobilities for the parallel and perpendicular OFETs utilizing PQT-C12 samples under investigation has been shown in the Figure 5. It can be clearly seen from the figure that charge carrier mobility monotonically increases as a function of increasing molecular weight up to the weight average molecular weight of about 40,000. Further increase in the molecular weight was not found to be beneficial rather it was

decreased due to large molecular weight distribution as discussed earlier. This monotonic increase in the in mobility as function of molecular weight could also be attributed to the charge trapping at the end, the density of chemical defects, promotion of molecular self-assembly and variation in energy level because of PDI etc[19]. It has also been reported by Menon et al that regioregularity in polymer chain play an important role for enhancement in mobility because of molecular self-assembly driven chain packing[50]. The decrease in the mobility of PQT-C12-D having higher PDI (3.5) might be attributed to the fact that longer chain statically provide longer conjugation length and smaller polymer chains with rich amorphous domains present the matrix acts as trap site hampering the charge transport[50]. OFET based on low molecular weight sample (PQT-C12-A) exhibited not only small optical anisotropy with DR of 4.0 but also highly hampered electrical anisotropy of 2.1 only explaining the importance of molecular orientation on facile charge carrier transport.

Synthetic control of molecular weight and PDI of CPs are not only important for the investigation of molecular orientation and anisotropic charge transport as discussed above but also bears tremendous application potentials in the area of optoelectronic devices and sensing. Importance of the PDI and molecular weight of CPs on the device performance of polymer LEDs was probed by Menon et al, where it was demonstrated that CPs with low molecular weight and PDI exhibited about two orders of magnitude higher external quantum efficiency as compared to their higher molecular weight and PDI counteparts[50]. In an interesting report, Koppe et al[51] emphasized that a judicious balance between molecular weight and regioregularity is highly desired for high performance bulk-heterojunction solar cells. It was clearly shown that best solar cell performance was obtained using average molecular weight CPs, where too high or low molecular weight polymers exhibited deteriorated device performances, which was explained by differential aggregation kinetics. Implications of molecular weight and its

distribution in chemical sensing and biosensing have also been widely addressed by many research groups. Sato et al[52] have also reported about the fluoresecence-based detection of ss-DNA by studying the fluorescence quenching due to formation of polyelectrolyte complex with conjugated polymers. They remarked that there was a need of optimum balance between the molecular weight and degree of polymerization in order to have optimum detection by highest quenching due to complexation. In an interesting report of chemical vapor sensing by polystyrene/carbon black composite Li et al[53] have emphasized that extent of PDI should be decided by the nature of applications. In this report they clearly demonstrated that a higher value of PDI was relatively more advantageous for responsivity of organic vapor sensing, which was boosted about 20 times upon increasing the PDI of the polystyrene matrix from 2.5 to 7.6. It was explained considering the fact that low molecular weight polymeric fractions undergo easy swelling leading to enhanced response for the organic vapor sensing.

5. CONCLUSION

In Summary, four different batches of PQT-C12 class of CPs with varying molecular weight and PDI have been successfully synthesized by controlling the rate of addition of catalyst and temperature during FeC_3 mediated oxidative chemical polymerization. Large area oriented thin films of these polymers up to the size of 20 cm in length and 2 cm in width were prepared by ribbon-shaped FTM followed by their utilization as active semiconducting element to fabricate OFETs and investigation of their anisotropic charge carrier transport. It has been shown that under identical thin film fabrication conditions, extent of orientation increases as a function of increasing molecular weight reaching >10 for the polymer PQT-C12-B having high molecular weight and narrow PDI. In spite of highest molecular weight exhibited by polymer PQT-C12-D, it showed a bit decrease in the charge carrier mobility from 0.07 cm2/Vs to 0.04 cm^2/Vs. The decrease in the hole mobility was attributed to the higher PDI (3.5), which was explained

considering the fact that longer chain statically provide longer conjugation length and smaller polymer chains with rich amorphous domains present in the matrix acts as trap sites hampering the charge carrier transport. Therefore, a judicious control of molecular weight and its distribution is highly desired for the improved molecular orientation and anisotropic charge transport.

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