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Macroscopic self ordering of solution processible poly(3,3′′′-dialkylquaterthiophene) by floating film transfer method

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Ordering and alignment of π-conjugated polymer chains are highly desirable for high performance and long life organic electronic devices. We report here self assembly of ordered and aligned solution processible Poly(3,3′′′-dialkylquaterthiophene) (PQT-12) polymer at macroscopic level using Floating Film Transfer Method (FTM). PQT-12 polymer film is formed over solution of ethylene glycol and glycerol at different temperatures viz. 22, 26, 33, and 38 °C. PQT-12 films formed by FTM technique are further characterized for optical and morphological properties. UV-vis absorption (for polarize and unpolarize light) and surface topography/phase imaging are carried out by using UV-vis spectrometer and atomic force microscope (AFM), respectively. UV-vis spectra show the polymer chains alignment perpendicular to the film propagation direction and it is well supported by AFM images. The effect of temperature on ordering and alignment of PQT-12 shows 33 °C as an optimum temperature for alignment of polymer chains (a little compromise in ordering). The heating of polymer films at 110 °C for 2 h in ambient causes significant changes in UV-vis absorbance spectra, optical anisotropy, and AFM topography/phase imaging. Our studies provide better understanding of ordering and alignment of PQT-12 chains and also disordering on heating. This work further provides a facile and user-friendly technique for the long range ordered self assembly of PQT-12, which shows enormous potential for various electronic applications. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4817288]

I. INTRODUCTION

Conjugated polymers are emerging candidates for the construction of the active layers of organic electronic devices, because they offer the possibility for various flexible and large-area electronic applications through cost-effective techniques.[1–8] Organic light emitting diodes, organic solar cells, and organic field effect transistors (OFETs) are the most technologically interesting devices and recently developed by using various conjugated polymers.[9,10] The performance of these devices strongly depends on the structural order alignment of the semiconducting molecules.[11–13] Therefore, the study of film morphology of active layer is essential for high performance organic devices.

Tsumura and co-workers fabricated first organic field-effect transistors (OFETs) in 1986 by using electro-polymerization technique to get uniform organic polymer film.[14] After that, several attempts were made to get uniform and ordered film in order to improve the organic device properties.

The formation of an active layer of organic semiconductor is a key step in fabrication of OFETs or other electronic devices.[15,16] Therefore, a deposition technique with precise control over the molecular/chain ordering, film morphology and crystalline orientation of semiconductor domains is highly desirable.[17] Various methods have already been used to control the aforementioned properties in Π-conjugated polymers, such as rubbing technique, Langmuir-Blodgett technique, liquid crystalline self-organization, and friction transferred techniques.[18–21] However, these techniques are complicated and need skill to get better ordering of the molecules or polymer chains. Recently, our group explored a facile method "Floating Film Transfer Method (FTM)"[22] to provide an ordered polymer film on hydrophilic liquid surface and transferring to a substrate by simple lifting method. The floating film transfer method proposed is similar to one for depositing Langmuir-Shieffer (LS) film although there is no surface-pressure application to make a compact film. The FTM can also be extended for fabrication of large area thin film based devices.[38]

Recently, a new class of polythiophene, poly(3,3′′′-dialkylquaterthiophene) (PQT-12) (cf. Fig. 1) has attracted much more interest due to higher stability in air and processibility in comparison to other regioregular poly(3-alkylthiophene)s (PATs) such as poly(3-hexylthiophene) (P3HT). In addition, this molecule also shows large π conjugation and

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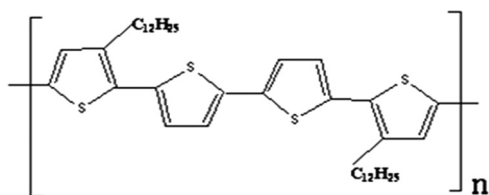
FIG. 1. Molecular structure of PQT-12.

liquid crystals phase at a certain temperature range below its melting point.[23,24] The crystalline domains are reported in properly conditioned thin film of PQT-12, which consists of both π-π stacking and the interlayer stacking of backbones (with an additional ordering from side chain interdigitation).[23–25] These properties make its potentially possible to manipulate its morphologies to enhance device performance through technique like LS (Langmuir-Shieffer) or recently by FTM.

Temperature dependency of molecular packing of the poly (3-alkylthiophene)s family polymers have been well investigated for effect on ordered and crystal structures.[23,26,27] These results, however, give information an average over volume that might contain different phase components. Study of alignment with ordering by using optical anisotropy and surface morphology of PQT's film under polarized, unpolarized UV-vis spectroscopy and atomic force microscopy may lead to better understanding of the nature of the chains organization. No any details related to large scale aligned fine structures with temperature is reported so far. Moreover, no report is available of atomic force microscope (AFM) topography, phase imaging, and polarized UV-vis spectroscopy studies of large scale aligned films of PQT-12.

In this work, we present FTM technique for the self assembly of ordered and aligned PQT-12 film formed at different temperatures. PQT-12 films are characterized for thermal properties by using differential scanning calorimetry (DSC) thermogramme, and unpolarized light UV-vis is used to study the effect of temperature on the π-π stacking, the interlayer stacking of backbones, and additional ordering from side chain interdigitation. Further, polarized light UV-vis spectroscopy is carried out to study the temperature effect on polymer chain ordering/alignment and AFM technique to study the effect of temperature on topography/phase image of films. Ordering/alignment of PQT-12 polymers are confirmed by using polarized and unpolarized light UV-vis spectra and AFM images. We have also investigated the optical and morphological properties of the heat treated samples of PQT-12 at 110 °C (between the liquid crystalline phases). Our study shows a simple technique for processible conjugated polymer film formation for the ordered self assembled polymer backbone arrangement with example of PQT-12 for organic electronic devices.

II. EXPERIMENTAL

A. Materials and synthesis methods

The monomer used for synthesis of PQT-12 was synthesized in accordance to modified Knochel method[28] and the literature.[23]

To a dry 50 ml vial, ground Mg powder (168 mg, 7.0 mM) was placed in Ar globe box. 7.0 ml of 0.5 M LiCl/THF solution and a drop of 1.0 M diisobutylaliminium hydride/hexane solution were cannulated to the mixture. Then, a solution of 2-bromo-3-dodecylthiophene (930 mg, 2.8 mM) in 5 ml THF was slowly poured in the mixture followed by warming at 55 °C for 1 h. After continuous stirring for 4 h, the obtained Grignard reagent was cooled down to room temperature. The Grignard reagent was slowly added via cannula at −10 °C to another fresh dry 50 ml vial filled with a mixture of 5,5′-dibromo-2,2′-dithiophene (330 mg, 1.0 mM) with 10 mol. % Ni(dppp)Cl$_2$ (158 mg, 0.3 mM). Further solution was warmed up to 50 °C and left for 2 days under stirring. After cooling to room temperature, the reacted mixture was quenched with saturated aqueous NH$_4$Cl solution and washed with 0.1 M HCl solution followed by brine. Sample was purified by column chromatography on silica gel and recrystallized from a mixture of methanol and isopropanol to obtain a yellow product.

FeCl$_3$-mediated oxidative coupling polymerization has been used to obtain PQT-12.[29,30] 1 mM of monomer dissolved with 5 ml dichlorobenzene was added to a dry 50 ml vial bottle filled with FeCl$_3$ (4.0 mM) in 20 ml of dichlorobenzene, under 0 °C. Further it was warmed up to 40 °C under stirred for overnight. After quenching the reactant in 1 M HCl, a solution of 1 M NH$_4$Cl and chloroform was added and separated organic layer was mixed with a fresh 1 M NH$_4$Cl solution. It was warmed up to 70 °C under stirring followed by washing with 1 M EDTA/aq for several times. The organic layer was reprecipitated in MeOH, again dissolved in chloroform, and reprecipitated in acetone to obtain PQT-12 polymer as a dark brown powder.

B. Sample preparation

PQT-12 film was prepared by using FTM as mentioned in the electronic supplementary information.[38] All substrates were ultrasonically cleaned and dried in air at 50 °C for 1 h before using for the UV-vis and AFM sample preparation. UV-vis samples were prepared on glass/quartz substrate of dimension 1 cm × 2.5 cm. Si with 100 nm SiO$_2$ deposited layer substrates of dimension of 1 cm × 1 cm was used for AFM samples preparation without surface modification. All UV-vis and AFM samples were dried at 50 °C for 60 min in air after transferring the film over glass/quartz and SiO$_2$ substrate.

C. Characterization

DSC thermogramme (Mettler-Toledo model 823) was used to study thermal property and detection of different phases. Unpolarized and polarized light UV-vis spectra were recorded to see the effect of temperature and order parameter "O," respectively, of polymer films using JASCO V-570 spectrophotometer equipped with a Glan Thomson polarizer. The order parameter "O" was calculated from the dichroic ratio "D" of UV-vis absorption spectra using the equation:

$O = \frac{D-1}{D+2}, D = \frac{A_p}{A_o}$, where A_p and A_o are the absorption intensities for the lights polarized parallel (p-polarization) and orthogonal (o-polarization). The order parameter "O"
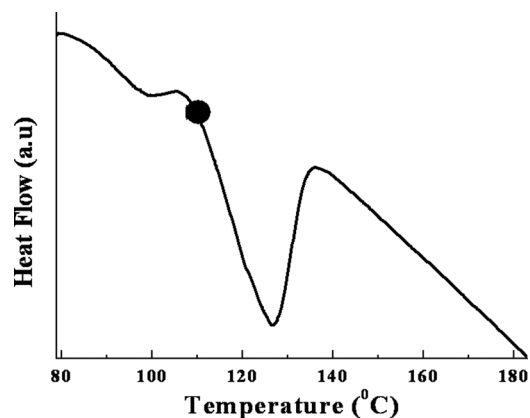
FIG. 2. DSC thermogramme of PQT 12 in N_2 environment; heating rate 10 °C/min.

indicates the degree of orientation of polymer chains, so that zero corresponds to the isotropic state and unity corresponds to the ideal oriented state.

Surface topographies and phase imaging of PQT-12 films formed by FTM at different temperature were transferred over SiO_2 substrates and investigated under tapping mode of AFM (JEOL SPM5200). All the images were obtained by using probes purchased from Olympus (OMCL-AC200TSC3).

III. RESULTS AND DISCUSSION

A. DSC study

It has been already reported in literature that phase transition in PQT-12 polymer from solid to liquid crystal involves only the melting and disordering of side chains while the backbone stacking remains in ordered state (retains π-π stacking).[24] The DSC thermogramme of as synthesized PQT-12 polymer taken in N_2 environment showed two endotherms (cf. Fig. 2) for transitions supporting the observation reported in the literature. The two endotherms at 101 °C and 127 °C clearly showed the liquid crystal property of PQT-12 polymer by changing the phase from crystalline solid to anisotropic liquids (melting and disordering of side chain) and from anisotropic to isotropic liquid phase (melting and disordering of backbone stacking of polymer chains), respectively. It was further confirmed by UV-vis studies.

B. UV-vis study

Fig. 3(a) represents the original recorded picture of PQT-12 circular film of 7.5 cm diameter, floating on surface of hydrophilic liquid surface (mixture of ethylene glycol and glycerol). In every attempt, we found 7 ± 0.5 cm diameter circular film by using 20 μl amount solution of 10 mg/ml PQT-12 sample in chloroform. Fig. 3(b) represents the UV-vis spectra of same PQT-12 film transferred from three different positions along the radius from centre to circumference (one from centre to 1 cm "inner side," second 1–2 cm "mid side" and third 2–3 cm "outside" over the glass substrates (1 cm × 2.5 cm dimension)). The increase in absorbance reveals that the increase in thickness along the radial directions of the film. Further, we also observed the UV-vis absorbance variation with change in polarization angle of incident light. Here, we used polarized light source to investigate the optical anisotropy in the PQT-12 FTM films. The
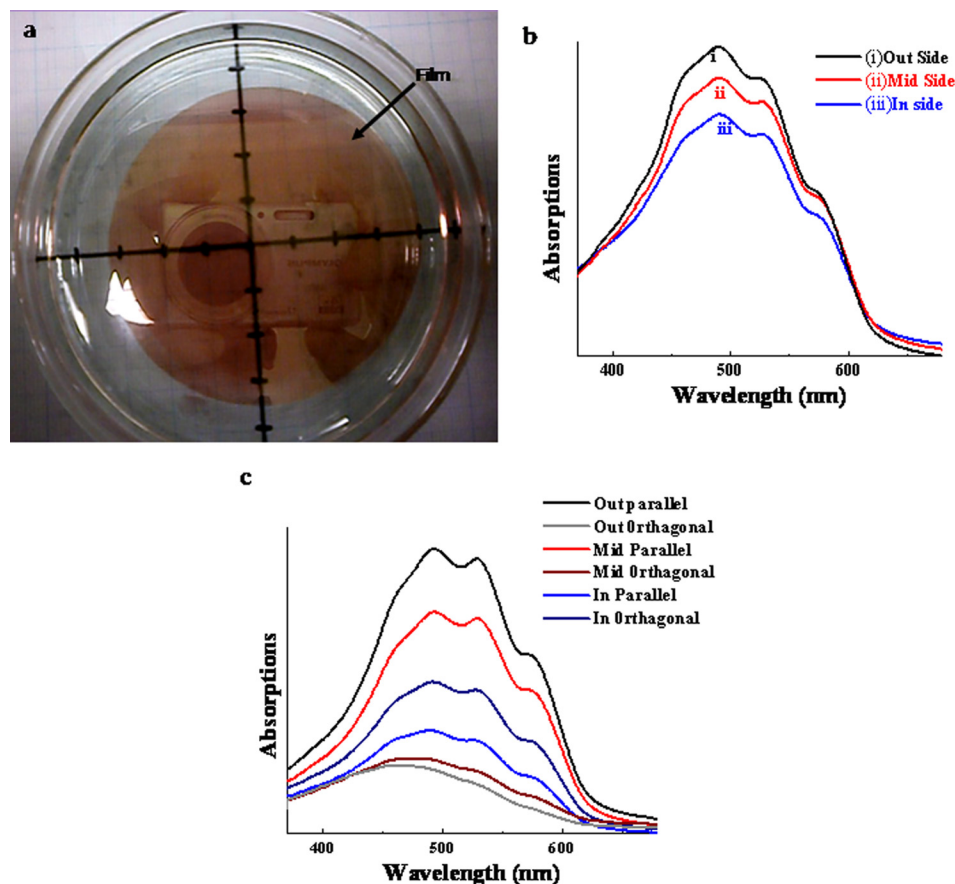

FIG. 3. (a) Picture of PQT 12 film over liquid surface. UV-vis. spectra of PQT 12 (b) unpolarized light (c) polarized light.

TABLE I. Mean radius vs. dichroic ratio (order parameter).

Position of film	Mean radius	Dichroic ratio	Order parameter
Out side	2.5 cm	3.78	0.480
Mid side	1.5 cm	2.64	0.353
In side	0.5 cm	0.70	−0.176

study of polarized light UV-vis of these samples reveal the increase in absorbance spectra for zero degree position of polarizer (plane of polarization of light is parallel to length of substrate) or p-polarization and decrease for 90° position of polarizer (plane of polarization of light is orthogonal to length of substrate) or o-polarization (cf. Fig. 3(c)). The PQT-12 film made by FTM technique with p-polarization showed well defined peaks at 531 nm and 575 nm, which show the ordered and long conjugated polymer back-bones.[31,32] On the other hand; with the o-polarization, these peaks are not well defined. This behavior was same for all the three positions (out, mid, and in-side cf. Figs. 3(a) and 3(b)) of the PQT-12 FTM films. Fig. 3(c) clearly shows the absorption spectrum of PQT-12 films strongly depends on the type of polarization. The absorption spectra of PQT-12 FTM films (cf. Fig. 3(c)) show optical anisotropy. The calculated dichroic ratios for mean radius = {(Outer Radius + inner Radius)/2} and order parameters of every sample are given in Table I.

Further, our findings as shown in Fig. 3 and Table I are explained with the help of scheme (cf. Figs. 4(a)–4(c)). Fig. 4(a) is a schematic diagram to represent the film as shown in Fig. 3(a). The increase in absorption along the radial direction (as shown in cf. Fig. 3(b)) is showing the increase in thickness along the radial direction from centre to outer circumference. This increase in thickness can be understood by the nature of chloroform and mixture solution on

which PQT-12 film is initially forming. Chloroform is hydrophobic in nature while liquids used for film formation provides hydrophilic surface. This opposite nature leads to chloroform spread rapidly with polymer in uniform manner in all the directions over hydrophilic surface. It formed circular film over the liquid surface after evaporation of chloroform with decreasing thickness from circumference to centre. This reveals the formation of disc type (circular) film over hydrophilic surface with decreasing thickness from circumference to centre and supports the result obtained in Fig. 3(b).

It has already reported that the maximum absorption of linearly polarized light occurs along the polymer chain length direction and minimum (almost zero) in orthogonal direction.[21] We designed a scheme (cf. Figs. 4(a)–4(c)) to explain the data obtained in the Fig. 3(c) and Table I using directional absorption property of polymer. One can presume the circular alignment of polymer chains in the film as shown in Fig. 4(a). If this film is placed directly in the path of linearly polarized light (linear polarization is in Y direction, light propagation is in X directions and plane of the film is in X direction) as shown in the Fig. 4(b), then polymer chains component parallel to Y direction will absorb the linearly polarized light. If we take three parts of this film, one from outside, second from mid side, and third from inside according to our sample preparation for UV-vis, then the polymer chains over the substrate will look like as shown in Fig. 4(c) and this will represent our original sample schematic diagramme. The obtained spectra as shown in Fig. 3(c) change in dichroic ratio and order parameter value (Table I) may be explained by using our presumptions. It is well known that the isotropic film shows dichroic ratio as 1. The change in dichroic ratio can be explained in following way:

As shown in Fig. 4(c-i), the parallel component of polymer chains in out-side sample is much more interacting with
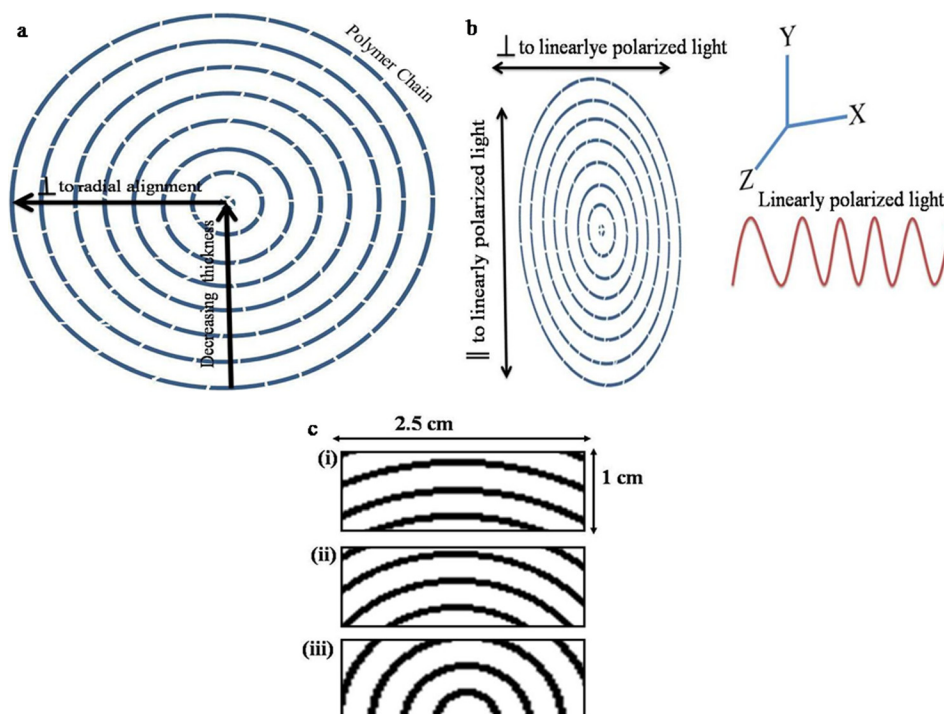

FIG. 4. (a) Schematic diagram of PQT-12 film with chain alignment direction (b) Schematic diagramme for plane polarized light absorption. (c) Schematic diagramme for align polymer film sample made for UV-vis measurement (i) outside, (ii) mid side, and (iii) inside.

p-polarize light in comparison to o-polarize light due to low curvature. This parallel component leads to the maximum absorption for p-polarize light while there is also some absorption for o-polarize light due to the curvature. Therefore, this sample shows dichroic ratio 3.78 with order parameter 0.48. The parallel component of polymer chains is decreasing and perpendicular component is increasing for p-polarize light (Figs. 4(b) and 4(c)) due to increase in curvature of polymer chains for rest samples taken from mid and inside of the circular film. This leads to the decrease in dichroic ratio along the radius of the discotic film.

Sample from inside (cf. Fig. 4(c-iii)) shows reverse trend of absorption (maximum for o-polarize light) in comparison to rest two samples (outside and mid side). This could be possible only in the case of more parallel component of polymer chain are for o-polarize light (in orthogonal) in comparison to the p-polarize light. Our presumptions of circular alignment of polymer chains explain the observed spectra and decreasing value of dichroic ratio and ordered parameter (cf. Table I) from circumference to centre very successfully.

Fig. 5(a) represents the normalized UV-vis spectra of (i) PQT-12 in chloroform, (ii) FTM film of PQT-12 at 38 °C, and (iii) FTM film of PQT-12 at 22 °C. Red shift of the highest absorption peak with some well resolved vibration peaks of FTM film of PQT-12 formed at 22 °C and 38 °C in comparison to PQT-12 in chloroform reveal the formation of well ordered films for FTM. While FTM film formed at 22 °C shows red shift and well resolved vibrations peaks (531 and 575 nm) in comparison to film formed at 38 °C. This reveals the more ordered coplanar conformation of chains along its backbone due to π-π stacking and well side chain ordering also.[31–33] The peak appearing at 461 nm on right shoulder for the films formed at 22 °C and 38 °C is due to presence of non stacked/amorphous polymer chains (possibility some amorphous

form also exist). The increase in absorption 461 nm formed at 38 °C is attributed to increase of non stacked polymer chains percentage at higher temperature.

To study the angle dependent absorption (optical anisotropy) of FTM film (formed at 26 °C from outside the discotic film), we used different angle of polarized light source. The absorption shows linear changes with change in angle of polarizer (Plane of polarization of light) (Fig. 5(b)). This shows maximum absorption when polarizer is set at 0° and sample length is parallel to this. The absorption decreases with change in polarizer angle and reaches minimum (not 0 due to circular alignment of polymer chain) for orthogonal to its length. This optical anisotropy phenomena reveal the polymer backbone alignment, which contribute maximum along the sample length and minimum along orthogonal to its length. The change in absorption with change in polarizer angle is linear as shown in the inset of Fig. 5(b).

The polarized (p-polarized and o-polarized) and unpolarized light source for UV-vis study (cf. Fig. 5(c)) reveals the maximum absorption for p-polarized light and minimum for o-polarized light. The unpolarized light absorptions just lie in between these two. Normalization of UV-vis spectra in Fig. 5(c) has been represented in the Fig. 5(d) and discloses the effect of polarized light and unpolarized light. The red shift with well resolved vibration peaks in spectra for p-polarization light confirms the presence of well ordered parallel polymer chain structure as already discussed previously. The o-polarization of light spectra shift toward blue with decrease in resolution of vibration peaks on right shoulder. The blue shifting of absorption peak for o-polarization of light reveals the presence of non stacked PQT-12 chain.[34] The unpolarized light absorption peak lies between these two.

Fig. 6 represents the systematic study of temperature dependent optical anisotropy by using p-polarized light and
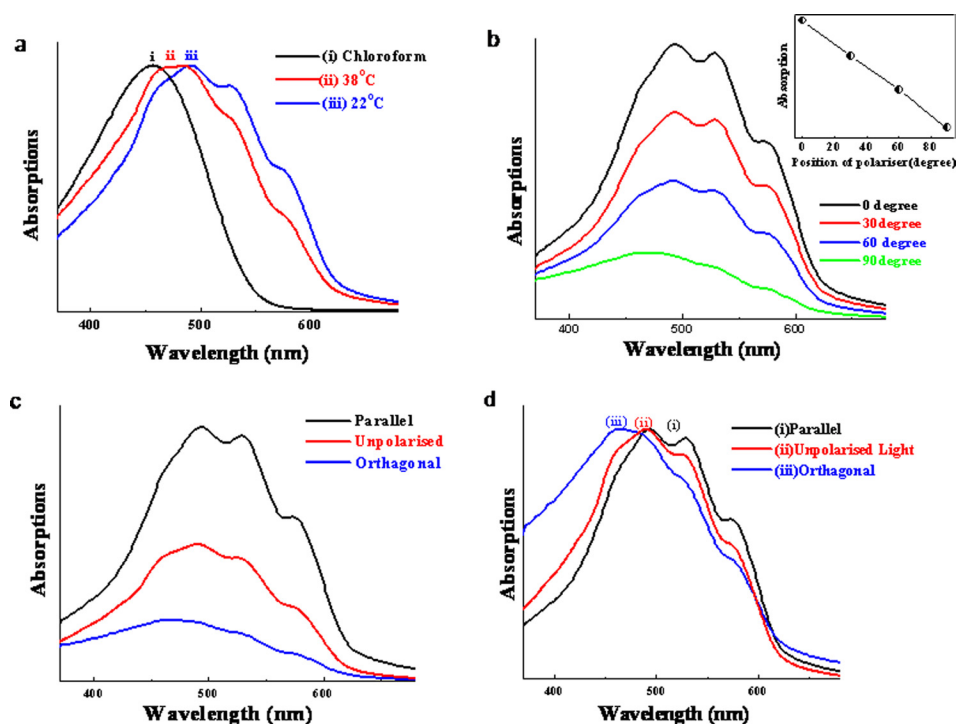

FIG. 5. (a) Normalized UV-vis spectra of (i) PQT-12 in chloroform (ii) FTM film formed at 38 °C (iii) FTM film formed at 22 °C. (b) Polarize UV-vis spectra of PQT-12 films formed at 26 °C with changing the plane of polarization of light. Inset shows the linear change in absorption with change in position of polarizer (c) Polarized and unpolarized light UV-vis spectra of PQT-12 film formed at 26 °C (d) Normalized UV-vis spectra of PQT 12 formed at 26 °C by FTM.
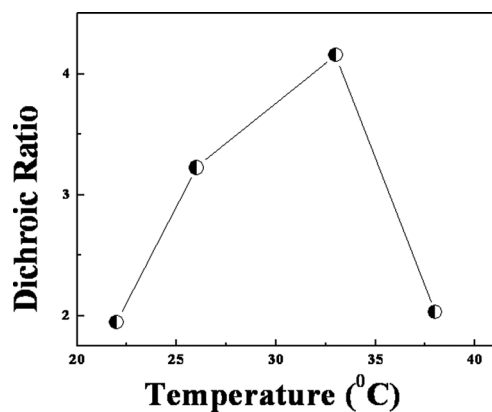
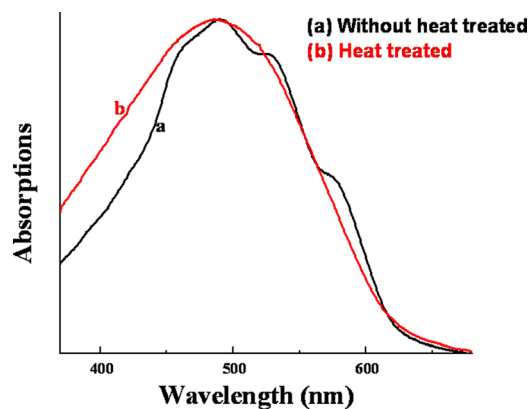FIG. 6. Dichroic ratio vs. temperature used for the formation of FTM film.

FIG. 7. Normalized unpolarized light UV-vis of PQT-12 (a) without heat treated (b) Heat treatment at 110 °C for 2 h in air and cooled at normal cooling rate.

o-polarized light spectra of PQT-12 film formed at 22, 26, 33, and 38 °C from the maximum align region of polymer chains viz. outside the discotic film. The increase in dichroic ratio is observed with increase in temperature and it attained maxima before decreasing with increasing temperature, which reveals the existence of optimum temperature for maximum alignment of polymer chains. The result obtained in Fig. 6 can be explained as follows:

It was observed that temperature controlled the viscosity of liquid surface (at which film was formed) and evaporation rate of chloroform over surface of the liquid. At low temperature, viscosity of liquid was higher and chloroform evaporation rate was slow in comparison to higher temperature, i.e., 33 °C. This high viscosity restricted the polymer chains backbone propagation orthogonal to radial direction and slow evaporation rate provided more time to self assemble the PQT-12 chains (supported by well resolved shoulder peaks in UV-vis spectra cf. Fig. 5(a-iii)). Further reduction in viscosity with rise in temperature caused random motion of chains and high evaporation rate provided less time to self assemble the chains (supported by less resolved shoulder peaks cf. Fig. 5(a-ii)). It was observed that 33 °C is optimum temperature which provided suitable viscosity and time for maximum alignment of polymer chains among four chosen temperatures for preparing the samples.

C. Effect of temperature on UV-vis spectra in liquid crystal phase

Fig. 7 shows the normalized unpolarized light UV-vis spectra of PQT-12 film formed at 26 °C over glass substrate reveals the presence of vibration peak as right shoulder. After heat treatment of the same film at 110 °C (in liquid crystal phase) for 2 h, the shoulder peaks disappears, however highest absorption peak remains the same. This may leads to loss of side chain ordering in liquid crystal phase, however, the backbone stacking remains in order state at 110 °C.

D. The film morphology transferred at different temperatures

The AFM morphology taken from centre of circular film[38] reveals the circular alignment of the polymer chains

as per the given scheme in Fig. 4. A very significant property charge mobility is reported maximum along the back bone and minimum along orthogonal to polymer chain (electrical anisotropy). One can fabricate high performance OFETs by taking care of electrical conduction along the polymer backbone. This property motivated us to investigate the morphology of maximum linear aligned (low curvatures) region of film viz. outside of the circular film. The morphologies of the films transferred at different temperatures over SiO₂ are presented in Figs. 8(a)–8(d) using AFM.

The objective of this study was again to examine the effect of temperature on morphology and alignment of crystal domain structures of the PQT-12 and further to establish correlations between AFM images with optical spectra, so that one can fabricate directly high performance electronic devices. The AFM topography and phase imaging do not show clearly the aligned polymer chains, however, it shows linear alignment of lamella of polymer chains.

The AFM results can be interpreted and correlated with Fig. 5 and supplementary information.[38] The unpolarized light UV-vis spectra of these samples show a correlation in the decrease in the side chains ordering and the resolution of shoulder's vibration peaks. The PQT-12 film formed at 22 °C shows the maximum resolved vibration peaks on right shoulder while 38 °C shows minimum among the four temperatures.[38] This observation is also supported by AFM studies. All the AFM images (cf. Figs. 8(a)–8(d)) show the closely packed domains of lamellar structure with additional ordering from side chains. The AFM topography and phase imaging of the film formed at 22 °C reveal the formation of large domains of lamellar structure with well additional side chain ordering (cf. Figs. 5(a) and S3) as already supported with UV-vis spectra. Rise in temperature causes decrease in size of domains of lamellar structure (cf. Figs. 8(b)–8(d)) resulted decrease in additional ordering from side chains. Rise in temperature and decrease of PQT-12 domains also cause the increase in alignment up to 33 °C (also supported in cf. Fig. 6 and supplementary information[38]). Further rise in temperature causes decrease in alignment of the polymer chains. We got maximum alignment for chains in the film formed at 33 °C (cf. Fig. 8(c)), which is also supported in polarized light UV-vis spectra.[38] These results suggest
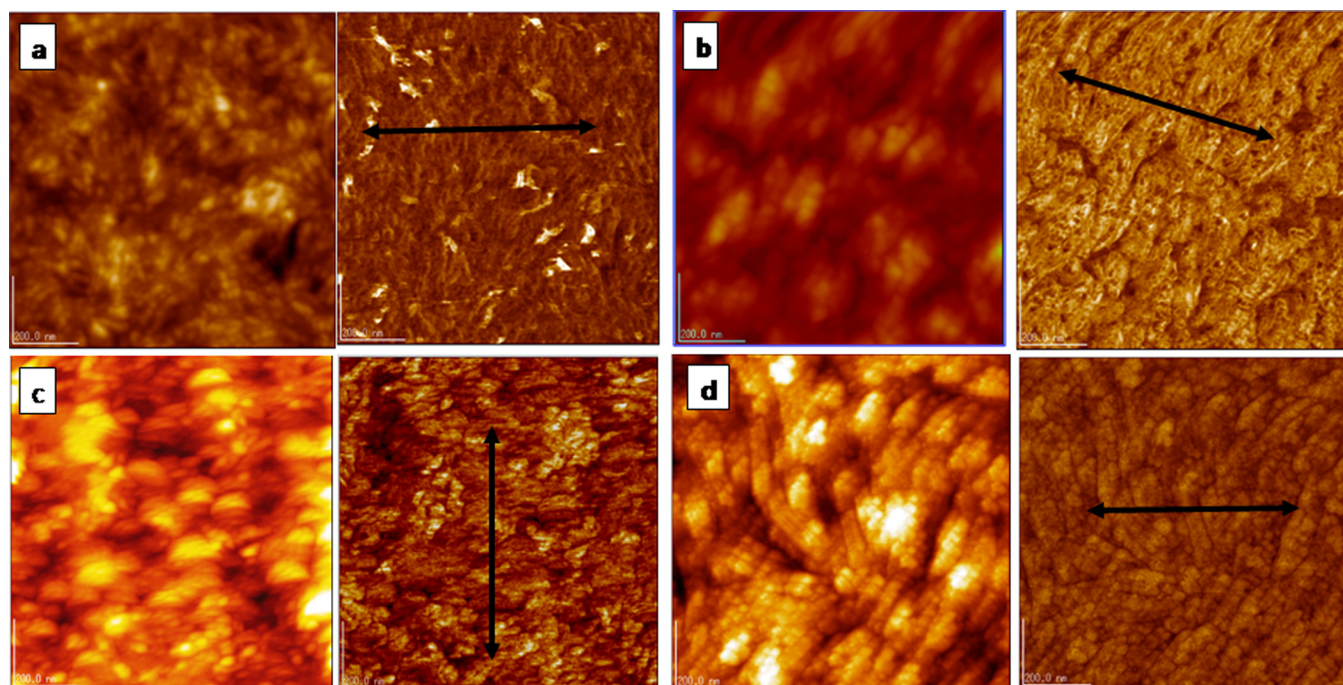
FIG. 8. AFM topographic (left column) and phase (right column) images of PQT-12 films formed on unmodified substrates. The morphology of the films formed at (a) 22 °C, (b) 26 °C, (c) 33 °C, and (d) 38 °C. Double head arrow indicates the perpendicular direction of polymer chain backbone in the film.

that temperature plays very important role in alignment of PQT-12 chains and ordering of side chains in FTM films. Optimization of temperature is essential for achieving highly aligned polymer with suitable ordering of side chain.

It has already been reported that charge mobility along the back bone of polymer chain is more in comparison to orthogonal to its backbone. This is a significant property of conjugated polymers and formation of ordered polymer film is important step for high performance electronic devices. Above results show the π-π stacking of the aligned PQT molecules, resulting in the formation of ordered films. This property also allows the possible development of more aligned chains of this material just by increasing the size of discotic film over the liquid surface.

E. Effect of temperature on polymer alignment in liquid crystal phase

The DSC thermogramme (cf. Fig. 2) revealed the liquid crystalline property of PQT-12 which exists in between the temperatures 101 °C and 127 °C. Further, we tried to study the effect of heat treatment on ordering of the side chain and correlation of AFM morphology with polymer alignment in liquid crystal (LC) phase. Highest aligned polymer film (obtained at 33 °C) was heated at 110 °C (between LC phases) for 2 h and cooled in air. The AFM topography and phase imaging show decrease in size of PQT-12 domains and alignment of polymer chains (cf. Fig. 9). Probably, the loss in size of domain was caused due to the loss in side chain ordering as shown in Figure 9 and loss in alignment caused the loss in dichroic ratio from 4.15 to 2.22.[38]

The results found after the heat treatment contradict the already reported results of polythiophene derivative after similar heat treatment. The contradiction of results probably

due to the hydrophobic nature of the substrate and plane of polymer backbone alignment, which is reported just perpendicular to the substrate.[35–37] However, for hydrophilic surface plane, alignment of the polymer backbone is reported parallel to the surface.[21] In our case, the surface provided by liquid is hydrophilic and we use the unmodified surface of SiO_2/glass for transferring the films. So the plane of polymer backbone will remain parallel to the substrate surface. Combining the results of Figs. 7 and 8, we found that the heating between LC phase (101 to 127 °C) causes melting of side chain ordering as already discussed above and cooling in ambient did not give much time for ordering of the chain.

Thus, our technique is very easy and usefull for getting polymer alignment with ordering. This technique clearly showed align and ordered polymer structure formation and did not require any heat treatment for ordering of polymer chains or enhancing the ordering as previous results show such requirements.
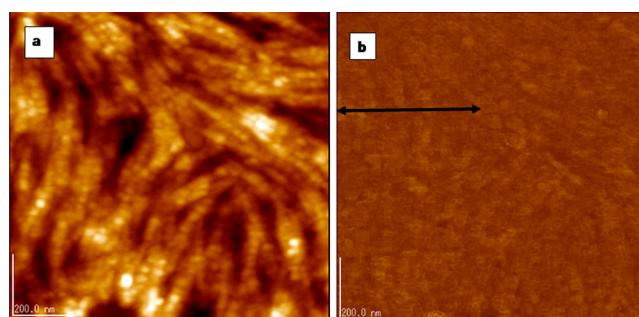

FIG. 9. AFM (a) topography (b) Phase imaging of PQT-12 film heat treated at 110 °C for 2 h in air and cooled with normal cooling rate in air. Double head arrow indicates the perpendicular direction of polymer chain backbone in the film.

IV. CONCLUSION

We have systematically studied the thermal, optical, and morphological properties of solution processible polymer poly(3,3‴-dialkylquaterthiophene) film formed by our novel floating film transfer method. FTM is a cheap and facile technique for deposition of ordered PQT-12 discotic films. Our studies also revealed that the chains alignment depends on the mean radius or minimum curvature of discotic films. The alignment of the polymer chains was characterized by UV-vis and AFM measurements. UV-vis spectra supported the alignment of polymer and further showed by AFM images. We have also studied the effect of temperature on alignment of PQT-12 films made by this technique. It was found that 33 °C is an optimum temperature for the maximum alignment of the polymer chains, which showed best dichroic ratio. Since FTM involved the liquid surface for the formation of films, therefore, one can control the alignment of polymer chains just by small heating of liquid for desired alignments. Further heat treatment at 110 °C (between LC phases, i.e., 101 to 127 °C) for 2 h of the PQT-12 samples formed at 33 °C showed clear picture of parallel lamellar structure in AFM topography and loss in ordering of side chains under unpolarized light UV-vis spectrum. The heat treatment also decreased the alignment of polymer chains with decrease in dichroic ratio. We believe that our study will be useful for the synthesis of ordered PQT-12 films and similar polymers; further for the development of organic electronic devices and to improve the performance and control of various parameters of the devices.

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[38]See supplementary material at http://dx.doi.org/10.1063/1.4817288 for details of formation of PQT-12 film by FTM method (S1) and characterization using unpolarized, polarized lights UV-vis of as deposited sample (S2 and S3), polarized light UV-vis study of heat treated sample (S4), and AFM study of film outside (S5), and centre (S6).