Interfacial properties of free-standing poly(3-hexylthiophene) films

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Using full atomistic classical molecular dynamics simulations, the interfacial properties of free-standing poly(3-hexylthiophene) (P3HT) films have been investigated. The orientations of different parts of the P3HT chain and the surface tensions of the films were calculated in a temperature range of 540 K–600 K. At the liquid/vacuum interface, the P3HT chain shows ordering by exposing hexyl groups at the interface, while the chain backbone lays flat with the thiophene ring preferentially tilt toward the surface. At the interface, the terminal methyl groups of hexyl side chains are in excess compared to the ethylene groups or thiophene rings. The surface tension of P3HT in its melt state shows similar temperature dependence to that of polymers that have long alkyl side chains. The surface tension values are comparable to those polymers that expose methyl or ethylene groups on the surface. The surface tension values determined for the melt state are lower than the experimental reported values for crystalline P3HT films, as expected. © 2012 American Institute of Physics.

I. INTRODUCTION

Over the past three decades, conjugated polymers have received a great deal of interest mainly due to their potential applications in solar cells, light-emitting diodes, and field-effect transistors. Polymer-based devices, especially solvent-processable ones, have numerous potential advantages—such as low cost, light weight, high flexibility, and easy processability—compared to inorganic semiconductor devices. Among the conjugated polymers, poly(3-hexylthiophene) (P3HT) is a particularly good candidate because it offers good conductivity and solubility. In P3HT, the thiophene backbone provides good electrical conductivity and charge carrier mobility, while the hexyl side chains provide good solubility and processability of the polymer without significantly affecting its electrical and optical properties.

The performance of P3HT-based devices is strongly dependent on the structural packing, morphology, and interfacial properties of the P3HT. In order to improve the efficiency of these devices, understanding the structural and dynamical properties of P3HT molecules in the bulk and at interfaces at the molecular level can be very important. Though both bulk and interfacial properties of P3HT are equally important, most of the previous studies have focused mainly on understanding its bulk properties. Among them, many computational studies have emphasized the electronic structure, charge transport, and structural properties of P3HT in bulk. Similarly, most of the previous experimental studies have investigated the structure, packing, morphology, and charge carrier transport properties of P3HT in bulk. However, there are relatively few reported experimental studies on the surface and interfacial properties of P3HT. These experimental studies have primarily focused on the orientation of the thiophene-ring backbone of the P3HT at the polymer/air and polymer/substrate interfaces, but less attention has been given to the orientations of the hexyl side chains at interfaces. For device applications, it is of particular interest to pinpoint which part of the P3HT chain contributes primarily to the interface; this crucial piece of information is missing from the literature. Furthermore, to the best of our knowledge, there has been no computational study in the literature that specifically addresses the structure and orientation of P3HT chains at interfaces.

In addition, to obtain better structural ordering, most thin films that are solution processed are thermally annealed and the surfaces may have a tremendous impact on the final structural ordering of these films. For P3HT films, thermal annealing is mostly done below the bulk melting temperature. However, in a recent experimental study, the annealing of P3HT on a hydrophobized substrate above its bulk melting temperature resulted in a pronounced surface-induced ordering of P3HT chains. Similarly, Guru et al. observed maximum order in poly(3-alkylthiophene) film when it is heated above its melting temperature and then recrystallized just below its melting temperature. This approach seems to be promising in generating highly ordered P3HT films, since annealing above the melting temperature removes the residual stress resulting from spin-coating processes. What is missing in these studies is how the structure of the amorphous region of the semi-crystalline film, which significantly affects the electrical transport in the system, changes due to the annealing of the film above its melting temperature. It is probably reasonable to assume that the amorphous region of the semi-crystalline film may have similar structure to the melt if the film was prepared by annealing it above its melting temperature. It is also very likely that the surface groups that are present at the surface in the melt state would also be preferred in the solid state of the film after annealing. It is thus important to understand the structure of a P3HT film in a melt state in order to elucidate the structure and morphology of the amorphous region and also the surface properties of the crystalline film, which is the main motivation for our present work.

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In the present work, we are also interested in determining the surface tension of a P3HT melt as a function of temperature. The surface tension is a thermodynamic parameter that plays an important role in determining properties such as wetting, coating, blending, and adhesion. A polymer film usually achieves a thermodynamically equilibrium surface by minimizing the surface energy either by minimizing the surface area and/or by exposing group of atoms that are energetically favorable to the interface. The orientation of these group of atoms at the interface controls most of the interfacial properties of the film. An understanding of the surface properties of P3HT at the molecular level, leading to structure-property relations, is a prerequisite to the design of a suitable P3HT film for a given application whenever interfacial phenomena are involved. Though the surface tension is clearly an important parameter, there exist very few experimental studies (and no computational studies, to the best of our knowledge) that have reported surface tension values for P3HT films in the solid state, and none that do so for the melt state.

In this paper, we report the results of molecular dynamics simulations describing the structural and surface properties of free-standing P3HT melt thin films. We examine the orientations of P3HT chains at liquid/vacuum interfaces as well as interfacial width, surface roughness, and surface tension as a function of temperature. In Sec. II, we will discuss our simulation methodology, including the details of our simulation procedures and surface tension calculations. The results and discussion – the mass and number density profile, the orientational ordering, interfacial width, surface roughness, and the surface tension – are presented in Sec. III. The summary and conclusions are given in Sec. IV.

II. METHODOLOGY

A. Force field description and simulation details

In this work, we used the force field proposed by Huang et al. for melt P3HT and validated by the same group. In this force field, the total potential energy of the system is represented as a sum of four types of potentials: bond-stretching, angle-bending, torsion, and non-bonded interactions. Huang et al. adopted the force field parameters from several different sources. For the backbone chain, equilibrium bond lengths, angles, and partial charges were based on the model of Marcon and Raos for tetrathiophene, while the dihedral potential parameters were based on the results of ab initio calculations of 3HT oligomers by Darling et al. The force field parameters for the hexyl group were taken from the optimized potential for liquid simulations—all atom (OPLS-AA) force field for n-alkanes. The van der Waals interactions are described by the Lennard-Jones potential, \( U_{ij}^{LJ} = 4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] \), and the parameters for the LJ diameter \( \sigma_{ij} \) and the interaction strength \( \epsilon_{ij} \) were also obtained from the OPLS-AA force field. The interaction parameters \( \sigma_{ij} \) and \( \epsilon_{ij} \) for the heteroatomic interactions are specified by the geometric mean of the homoatomic parameters, as is the case with the OPLS-AA force field. The non-bonded interactions (LJ + Coulombic) are evaluated for all intermolecular interactions and for intrachain interactions between atoms separated by three bonds or more. For intrachain interactions between atoms separated by three bonds, the interaction potential is reduced by a factor of 2, following the OPLS-AA force field paradigm.

In this study, we consider 100% regioregular P3HT chains consisting of 100 chains with 10 monomers per chain; thus, the total number of atoms is 25 200. The initial configuration of the P3HT system was generated by randomly placing the P3HT chains in a cubic periodic simulation box of dimensions \( L_x = L_y = L_z = 67.5 \text{ Å} \), corresponding to a density of 0.898 gm/cm\(^3\). The initial equilibration of the P3HT system was carried out in two steps – first the system was run in the NPT ensemble at a temperature of 600 K, far above the melting temperature of P3HT, and at a pressure of 20 atm for 5 ns, which allowed the system to adjust to its melt density at this temperature. The system was further equilibrated in the NVT ensemble for 5 ns at the same temperature. Once equilibrium in the NVT ensemble was reached, a P3HT film with surfaces in the \((x, y)\) plane was created by removing the periodicity along the \(z\)-direction, resulting in a new box with dimensions \( L_x = L_y = 68.0 \text{ Å} \) and \( L_z = 102.0 \text{ Å} \). To ensure that periodic images of the resulting film did not interact in the \(z\)-direction, the simulation box dimension along the \(z\)-direction was significantly increased to \( L_z = 202.0 \text{ Å} \). The P3HT film was then run in the NVT ensemble at temperatures between 540 K and 600 K, in increments of 20 K, well above the melting temperature of P3HT (Refs. 27, 35, and 18, 36–38) and well below its degradation temperature (693 K). All simulations were carried out using the LAMMPS simulation package. The equations of motion were integrated using the velocity-Verlet algorithm using a time step of 1 fs. For both NPT and NVT ensembles, a Nosé-Hoover thermostat with a damping time of 100 fs was used to maintain the temperature of the system. For the NPT ensemble, an additional Nosé-Hoover barostat with a 1 ps damping time was used to keep the pressure of the system at 1 atm. For the non-bonded interactions, the cutoff radius was fixed at 12 Å and the long-range Coulomb interactions (beyond the cutoff radius) were calculated using the particle-particle/particle-mesh Ewald algorithm. The surface tension calculations required the P3HT film system to be equilibrated for a long time—70 to 100 ns, depending on the temperature. The surface tension was calculated following the procedure described below.

B. Surface tension and tail correction calculation

At a given temperature, the surface tension, \( \gamma_p \), of the P3HT melt system was calculated during the simulation using the following Kirkwood-Buff equation:

\[
\gamma_p = \frac{L_z}{2} \left[ \langle p_z \rangle - \frac{\langle p_z \rangle^2 + \langle p_z \rangle}{2} \right].
\]

where \( \langle p_z \rangle \) and \( \langle p_z \rangle^2 + \langle p_z \rangle \) are normal and tangential pressure components, respectively. The angle brackets denote time average and the factor of 1/2 exists to account for the symmetry in the simulation box. The surface tension calculated using Eq. (1) does not take into account the contribution of the Lennard-Jones interaction beyond the cutoff radius. The “tail
correction, $\gamma_{\text{tail}}$, to the surface tension can be calculated from the mass density profile $\rho(z)$ (Ref. 43) as

$$
\gamma_{\text{tail}} = \frac{\pi}{2} \int_{-\infty}^{\infty} \int_{-1}^{1} \int_{r_c}^{\infty} r^3 \frac{dU(r)}{dr} g(r)(1 - 3s^2)(\rho(z)\rho(z - sr) - (\rho_G(z))^2)drdsdz,
$$

(2)

where $U(r)$ is the pairwise potential, $g(r)$ is the radial distribution function, $r_c$ is the cutoff for the dispersion terms in the non-bonded interactions, $s = \cos(\theta)$ in cylindrical polar coordinates, and $\rho_G(z)$ is a Gibbs dividing surface.\(^{44}\) The Gibbs dividing surface is defined by

$$
\rho_G(z) = \frac{\rho_l + \rho_v}{2} + \frac{\rho_l - \rho_v}{2} \text{sgn}(z),
$$

(3)

where $\rho_l$ and $\rho_v$ are the averaged densities of the liquid and the vacuum phases, respectively. In Eq. (2), for our case, the radial distribution function is assumed to be $g(r) = 1$ for $r \geq r_c$. Based on previous simulation studies,\(^{45,46}\) we fit $\rho(z)$ to an error function

$$
\rho(z) = \frac{\rho_l - \rho_v}{2} \left( \text{erf} \left( \frac{(|z_0| - |z|)}{\sqrt{2}\Delta} \right) + 1 \right),
$$

(4)

where $z_0$ is the position of the Gibbs dividing surface and $\Delta$ is the interfacial width. The overall surface tension of the system is given as the sum of the surface tension of the simulation result and the tail correction: $\gamma = \gamma_p + \gamma_{\text{tail}}$.

III. RESULTS AND DISCUSSION

A. Density profiles

1. Mass density profiles

One of the simplest ways to characterize the interface is by calculating the mass density profile, which is easily accessible to simulations and can also be determined in experiments. Here, we calculated the mass density profile of the film at four different temperatures from 540 K to 600 K in intervals of 20 K. The mass density at a given value of $z$, $\rho(z)$, is calculated by partitioning the simulation cell into bins along the $z$-direction, with bin thickness $\Delta z = 1$ Å, and summing the masses of atoms in each bin per partitioned volume.

Figure 1 shows time-averaged mass density profiles of P3HT film at four different temperatures. The mass density profiles show two symmetric and smooth liquid/vacuum interfaces. The observed stable and smooth interfaces are good indications of the applicability of the force field parameters we used in describing the P3HT film. Furthermore, at a given temperature the middle region of the film shows an approximately constant mass density (cf. region IV of Figure 6), which is expected to correspond to the bulk liquid density of P3HT at that given temperature. To compute the bulk liquid density, $\rho_b$, at each temperature, we took the region in which the density is essentially constant and calculated the average density within this region. The calculated bulk densities at different temperatures are tabulated in Table I and are also shown in the inset of Figure 1. As can be seen in the inset, the predicted bulk density of P3HT decreases linearly from 0.852 g/cm\(^3\) at 540 K to 0.787 g/cm\(^3\) at 600 K.

![Figure 1](image-url)
sides of the film surface were calculated, and the average value of the two surfaces is tabulated in Table I. As shown in Table I, the roughness increases with increasing temperature due to thermal fluctuations. At each temperature, the roughness, $W$, is found to be slightly greater than the interfacial width, $\Delta$. Though the two parameters are interchangeably used to characterize surface roughness, the variation is due to the fact that $\Delta$ does not take the lateral structure of the rough surface into account while $W$ does.

To better characterize the topology of the film at liquid/vacuum interfaces, an isochore profile was constructed by taking the height of each grid ($H_i$) with respect to the average height ($\overline{H}$). In Figure 2, isochore plots of the top surface of the film at 540 K and 600 K are shown. As can be seen, for both temperatures, the fluctuation in surface height with respect to the average height is in the range of $\pm 10$ Å. However, more pronounced peaks and valleys are observed at 600 K than at 540 K, as expected from the roughness results.

The observed density peak at the boundary of the interface in Figure 1 can be explained better by investigating the number density of the different components of the P3HT chain and is presented below.

2. Segment number density profiles

Compared to linear polymer chains, the P3HT chain has a relatively complex structure due to rigid thiophene rings on the backbone and long flexible hexyl side chains that are terminated with methyl groups. To determine how the different components of the P3HT chain are distributed throughout the film, the number density of thiophene rings, methyl groups, and hexyl side chains have been calculated. The segment number density at a given value of $z$ is calculated by partitioning the simulation cell into bins along the $z$-direction (with slab thickness $\Delta z = 3.0$ Å) and summing over the number of target groups in each bin per partitioned volume. This slab thickness is chosen in order to obtain good statistics within the film profile. For each group of atoms (thiophene ring, methyl group, and hexyl group), we took the geometric center as representative of the groups’ respective positions.

The number density profile of thiophene rings and methyl and hexyl groups at two representative temperatures, 540 K and 600 K, are shown in Figure 3. On the vacuum side, methyl groups show higher number density than hexyl groups and thiophene rings. The snapshot shown in Figure 4 also confirms the methyl groups are in excess at the liquid/vacuum interface. The three number densities meet around the Gibbs dividing surface, and the trend is reversed on the liquid (bulk) side, where the thiophene rings dominate over methyl and hexyl groups. In addition, there is a peak in the ring number density profile at the boundary of the interface, similar to the peak we observed in the mass density profile in Figure 1. This means there is an enhanced thiophene ring density at the boundary of the interface, indicating thiophene ring ordering at the interface that is more pronounced at lower temperatures.

From the above observations, we can conclude that P3HT forms a stable structure at the liquid/vacuum interface by exposing the hydrophobic part of the chain (methyl groups) to the vacuum side and the hydrophilic part (thiophene rings) to the liquid side. Recent molecular dynamics simulation studies of the small molecule 4-methylpyridine at the liquid/vacuum interface showed similar number density profiles. The observed enhanced number density profile of the nitrogen atoms on pyridine was attributed to the segregation of the nonpolar part (the methyl groups) from the polar part (pyridine) at the interface, which can be thought of as a result of the presence of the hexyl group. Furthermore, in normal alkanes, the methyl groups are excess at the vacuum (air) side, of liquid/vacuum interfaces, as opposed to the liquid (bulk).
side.\textsuperscript{50} Since P3HT has a rigid backbone which would constrain the orientation of the hexyl groups, in order to have higher number density of methyl groups at the liquid/vacuum interface, the plane of the thiophene rings close to the interface should be tilted towards the normal to the surface, while the chain preferentially lays parallel to the surface. This should induce better packing of the thiophene rings close to the interface, which will in turn result in increasing the thiophene ring density considerably at the boundary of the interface, as is evidenced in both Figures 1 and 3. This warrants a quantitative description of the orientation of the different segments of the P3HT chain at the interface, presented in detail in Subsection III B.

B. Molecular orientation

The differences observed in segment number density profiles for different parts of the P3HT chain and the enhanced thiophene ring density at the interfaces of the film have both structural and thermodynamic origins. The thermodynamic origin has been already briefly discussed above in terms of the difference in polarity between the different parts of the P3HT chain. To qualitatively elucidate the structural origin of these differences, we have calculated the orientational order parameter of the thiophene rings, backbone segments, hexyl side chains, and methyl groups of the chain. This will allow us to compare our simulation results with experiment, as the orientational ordering of different parts of P3HT at the interface can be measured using different experiential techniques. For example, using sum-frequency generation vibrational spectroscopy, the methylene and methyl groups at the interface can be easily probed.\textsuperscript{51} Near-edge x-ray absorption fine structure spectroscopy (NEXAFS) (Refs. 22–24) can also be used to determine the orientation of thiophene ring and hexyl groups at the interface. It is therefore possible to directly compare our simulation results with experiment. The orientational order parameter can be calculated using the second-order Legendre polynomial, which is given by

\[ P_2(z) = \frac{1}{2} (3 \cos^2(\theta) - 1), \tag{6} \]

where \( \theta \) is the angle between the \( z \) axis, i.e., normal to the interface, and a vector used to describe the orientation of each of the different parts of the P3HT chain. The orientational vector for the four different parts of the P3HT chain is defined as follows. (1) Backbone segment: the vector originating from the first carbon atom on the thiophene ring and ending at the first carbon atom on the neighboring thiophene ring, as shown in Figure 5(a). (2) Thiophene ring: the vector originating from the thiophene sulfur atom and ending at the carbon atom on the thiophene ring that connects the thiophene ring to a hexyl group, as shown in Figure 5(b). (3) Hexyl group: the vector originating from carbon atom on the thiophene ring (which bonds thiophene ring to its hexyl group) and ending at the carbon atom on the methyl group, as shown in Figure 5(c).

In order to compare with experiment, the orientation of the C–C bonds in the hexyl group is also determined. (4) Methyl group: the vector originating from the carbon atom of the methyl group and ending at the center of the hydrogen atoms of the methyl group, as shown in Figure 5(d). The average, \( \langle \rangle \), is taken over all possible orientations and time steps within a specified slice of width, \( \Delta z = 3.0 \text{ Å} \), over a given region in the \( z \)-direction. The value of the order parameter \( P_2(z) \) is thus 1 when the orientational vector is perpendicular to the surface, while 0 may imply random orientation and \( -0.5 \) implies that the orientational vector is parallel to the surface.

In order to better quantify the orientational ordering of the different components of the P3HT chain within the film, we have divided the film into four regions, and calculated the normalized probability distribution of the angle \( \theta \), \( P(\theta) \), in each region. We calculated \( P(\theta) \) in each region by partitioning \( \theta \) values from 0 to \( \pi \) into bins of width \( \Delta \theta = \pi/60 \) and summing over the number of angles that lie between \( \theta \) and \( \theta + \Delta \theta \) in each bin and normalizing it with respect to the total number of possible orientations. We would like to point out that since both the mass and number density profiles exhibit symmetry, the \( P(\theta) \) reported for the interfacial part of the film in the present work was calculated using the top side of the film.
1. Backbone segment orientation

Figure 6 shows the average orientational order parameter $P_2(z)$ of the backbone segments at two representative temperatures, 540 K and 600 K. The average ring number density is also shown in the same figure as a reference for identifying the different regions of the film. In order to correlate the behavior of $P_2(z)$ with the ring number density, we have divided the film into four regions separated by broken vertical lines in the figure: (I) the vacuum region, where the ring number density is below 10%; (II) the 90–10 region, where the number density decreases from 90% to 10% of the bulk density; (III) the dense region, which extends from the end of the 90–10 region to the first minimum of the ring density oscillation; and (IV) the bulk region, which is everything else.

In Figure 6, in the bulk region for both temperatures, $P_2(z) \approx 0$, implying that the backbone segments are close to a random orientation in this region. In regions II and III, $P_2(z) < 0$ indicates that the backbone lies preferentially parallel to the surface. Note that the order parameter $P_2(z)$ shows a deep minimum at the boundary of the two interfaces. In region I, $P_2(z) > 0$ suggests that the backbone segments on the outer side of the interface are oriented preferentially normal to the surface. A more detailed analysis of the data shows that the backbone segments at chain ends are the ones that dominate region I, since they want to expose the hydrogen atoms at the chain ends and experience less steric hindrance to do so. The orientational order parameter calculation for the hydrogen atoms at the chain ends (not shown here) shows the hydrogen atoms to be sticking out of the surface and dominating the vacuum side of the interface.

Clearly, the degree of orientational order at the interface is higher at lower temperatures and correlates very closely with the amplitude of the peak in the ring number density in region II. Because the ordering in regions II and III is not very strong, the amplitude of the peak in the ring number density is small. However, the amplitude in both the orientation and ring number density increases with decreasing temperature and may significantly increase as the crystallization temperature is approached; at this point, this is beyond the time scale of standard molecular dynamics simulations for polymers such as P3HT with very slow dynamics.

Figure 7 shows the angular probability distribution, $P(\theta)$, for the backbone segments in regions II, III, and IV at 540 K and 600 K. In the bulk region at both temperatures, $P(\theta)$ shows a broad normal (Gaussian) distribution. Therefore, the orientation of the backbone in the bulk region is random. The peak position at 540 K is slightly off from $\pi/2$, which may be due to the fact that some chains are participating in both
the interfacial and bulk regions of the film, with the effect becoming observable as the temperature is lowered. In regions II and III for both temperatures, $P(\theta)$ shows a narrower Gaussian distribution with a higher peak than the bulk region. The narrower distribution and higher peak in the middle of the distribution indicate that the backbone segments prefer to orient more parallel to the surface, in agreement with what we concluded above based on the orientational order parameter. Furthermore, at 540 K, region III serves as a transient region by displaying a distribution that is between regions II and IV. At 600 K, region III (which is not part of the interfacial region at 540 K) has become part of region II (same $P(\theta)$), which agrees with the observed increase in interfacial width with increasing temperature.

2. Thiophene ring orientation

Figure 8 shows the average orientational order parameter $P_2(Z)$ and the respective average number densities of the thiophene rings at 540 K and 600 K. In the bulk region, for both temperatures, $P_2(Z) \approx 0$ implies that the orientation of the thiophene rings is essentially random. In regions II and III, $P_2(Z) > 0$ indicates a preference of the thiophene rings to be oriented normal to the surface. However, the value of the order parameter is small, hence the ordering is weak. In region I, the implication of $P_2(Z) < 0$ may not be immediately obvious. As pointed out above, region I is dominated by chain ends, with the hydrogen atom at a chain end sticking out of the surface. Since the thiophene ring vector defined in Figure 5(b) is almost perpendicular to the orientation of the hydrogen atom at a chain end, the ring vector should orient parallel to the surface, as confirmed by the negative $P_2(Z)$ value, for the hydrogen atom to stick out of the surface. This is also consistent with the orientation of the backbone with respect to the ring vector at the vacuum region.

We also calculated the percentage of thiophene rings that preferentially expose sulfur atoms towards the surface normal in different regions of the film. When the angle between the thiophene ring vector and the surface normal (i.e. the $z$-axis) is less than $\pi/2$, the ring is considered to be preferentially exposing its sulfur atom towards the surface normal. At 540 K, the percentage of thiophene rings that expose sulfur atoms towards the surface normal are 45%, 49%, and 50% for the 90–10 region, dense region, and bulk region, respectively. The corresponding values at 600 K is 45%, 48%, and 50%. Therefore, at the interface, most of the thiophene rings expose to the surface the carbon atom that connects the thiophene ring to the hexyl group so that the hexyl group can easily stick out to the surface.

Though our results are for a P3HT film in a melt state, they contain implications for a P3HT film in a solid state, and comparing our results to experimental results for solid P3HT film is fully justified. Using NEXAFS for regioregular P3HT thin films at air/film interfaces, several average tilt-angle measurements of thiophene ring have been reported. Ho et al. found tilt angles for spin-casted thin film, using different solvents, of 57°–60° and drop-cast thin-film P3HT of 59°. Hao et al. investigated the orientation of the thiophene ring for different thin-film samples. The measured average tilt angles are 62°, 72°, and 70° for samples spin coated at high speed, low speed, and dip coated, respectively. Moreover, investigations of the effect of annealing on the orientation for different solution concentrations show average tilt angles in the ranges 55°–58° and 59°–62° for the thin films before and after annealing, respectively.

In spin-coating processes, the rate of solvent evaporation is proportional to the film thickness. The difference in spin coating may lead to different microstructures of the processed thin films because the final microstructure is mainly a result of the competition between rate of solvent evaporation and interfacial tension. For regioregular P3HT films prepared with spin coating the thiophene ring orientation can vary depending on the spin-coating parameters. More face-on conformations are obtained using fast spin speeds and high solution concentration. Spin-coated thin films of P3HT prepared with slow spin-coating rates, slow solvent evaporation rates, and annealed above the melting temperature result in the most thermodynamically stable orientations. At the polymer-air interface, the thiophene rings adopt a highly ordered edge-on orientation. Our simulation were conducted in the melt state; thus, the thin films can easily attain a thermodynamically stable state. The orientations of the thiophene rings at the interfaces we obtained are consistent with the experimentally observed thiophene ring orientations for P3HT thin films that are thermodynamically stable.
3. Hexyl group orientation

Figure 9 shows the hexyl group orientational order parameter and the corresponding number density for 540 K and 600 K. The orientational order parameter of the C–C bonds in the hexyl group is also shown in the figure and displays the same orientation as the hexyl group. The orientation of the hexyl groups is consistent with our proposed picture of the orientation of a P3HT chain in a thin film—random orientation in the bulk region and in the surface region (regions II and III), backbone segments preferentially orient parallel to the surface, with thiophene rings slightly tilted toward the surface normal, and the hexyl groups preferentially orient parallel to the surface normal ($P_2(z) > 0$).

The angular distributions, $P(\theta)$, for hexyl groups in regions II, III, and IV at 540 K and 600 K are shown in Figure 10. In the bulk region, for both temperatures, $\theta$ has a broad Gaussian distribution with peak value at $\pi/2$, which implies that the hexyl groups have random orientations. In region II, $\theta$ shows Gaussian distributions skewed to small values of $\theta$ ($\theta < \pi/2$) and has a peak at $\theta \approx 51^\circ$ and an average value of $\theta \approx 65^\circ$, which agrees very well with the strong orientational ordering in this part of the film as predicted from the orientational order parameter calculation above. In region III, the $\theta$ distribution is close to Gaussian, with the peak slightly shifted towards small values of $\theta$, indicating that hexyl groups should show weak orientational ordering, confirmed above by a smaller orientational order parameter value in this region of the film.

For P3HT thin films at the film/air interface using NEXAFS, Ho et al. determined the hexyl group orientation by measuring average hexyl C–C orientation relative to the film plane. They found that the average tilt angle is in the range of 49°–52° for different samples. Despite the P3HT films being in different states (melt and solid state), both experimental measurement and simulation show that the hexyl groups at the interface have significant orientational ordering.

4. Methyl group orientation

The orientational order parameters of methyl groups and the corresponding angular distributions at 540 K and 600 K are shown in Figure 11 and Figure 12, respectively. Both the orientational order parameter and the angular distribution in different parts of the film exactly follow the behavior that we described above for the hexyl groups. This should be of no surprise, since the methyl groups are attached to the hexyl groups and are thus sterically constrained to a great extent to follow the orientation of the hexyl groups.

FIG. 9. Orientational order parameter profile, $P_2(z)$ (circles), and number density profile (stars) of hexyl groups at 540 K (left) and 600 K (right). Also shown in the figure is the order parameter for the C–C bonds in the hexyl group (rectangles).

FIG. 10. Probability distributions of tilt-angle $\theta$ of hexyl groups in region II (stars), region III (triangles), and bulk region (circles) at 540 K (left) and 600 K (right).

FIG. 11. Probability distributions of tilt-angle $\theta$ of methyl groups in region II (stars), region III (triangles), and bulk region (circles) at 540 K (left) and 600 K (right).
From the density and orientation calculations, we can confidently draw the following conclusions: at the interface, the P3HT chain lies preferentially parallel to the surface with the thiophene rings tilted towards the surface normal and the hexyl groups sticking out toward the surface so that the methyl groups are preferentially exposed to the surface (cf. Figure 4). In the bulk region, the P3HT chain shows almost perfectly random orientation. The transition from random orientation in the bulk to orientational ordering at the interface seems to have resulted in an enhancement of the number of thiophene rings at the boundary of the interface, which in turn induces a denser region than the bulk. Based on this observation, we should expect the surface tension properties of a P3HT film to be dominated by the surface properties of the hexyl part of the chain and less on the thiophene backbone, which is confirmed by our surface tension calculations presented below.

C. Surface tension

Figure 13 shows the running time average of the surface tension calculated using Eq. (1), i.e., without the tail correction, for four different temperatures. As can be seen in the figure, to get reliable surface tension data takes at least 50 ns of simulation time even at the highest temperature studied. This clearly demonstrates the slow dynamics of the P3HT chains in the film, which is common among polymer chains with rings and side chains. We ran the simulations until the time variation of the surface tension did not seem to change any more and calculated the average over the last 10 ns. The corresponding tail correction to the surface tension was calculated using Eq. (2). For comparison, the surface tension with and without the tail correction are shown in Figure 14. The contribution of the tail correction to the surface tension is significant but does not change the qualitative trend of the surface tension as a function of temperature.

The simulation result shows that the surface tension monotonically decreases with increasing temperature. As shown in Figure 3, the hydrophobic hexyl side chains are dominant at the surface and contribute to the observed low surface tension values of the P3HT melt. This indicates that water, which has a very high surface tension of around 72 mN m$^{-1}$ will not wet a P3HT surface, as confirmed by experiment.$^{54}$

To the best of our knowledge, there are no theoretical or experimental surface tension values available for melt P3HT in the literature. However, for solid-state P3HT, experimental reported values from contact-angle measurements are in the range of 21–36 mN m$^{-1}$. $^{28–30}$ The differences in the reported experimental surface tension values may be due to the differences in molecular weight, morphology (crystallinity) of

FIG. 11. Orientational order parameter profile, $P_2(z)$ (circles) and number density profile (stars) of methyl groups at temperatures (a) 540 K and (b) 600 K.

FIG. 12. Probability distributions of the tilt-angle $\theta$ of the methyl groups region II (stars), region III (triangles), and bulk region (circles) at 540 K (left) and 600 K (right).
sample, and the temperature at which measurements were done. Surface tension calculated from contact-angle measurement is an indirect way of determining the surface tension, and this might cause large discrepancies in the reported experimental surface tension values. Moreover, as we discussed earlier, depending on the thin-film processing conditions, the thiophene rings can have face-on or edge-on orientations which will determine whether the thiophene rings or the methyl groups are exposed to the surface. Hence, this can contribute to the large differences observed in reported surface tension values of P3HT films.

In an attempt to compare the simulation surface tension values with experiment, the surface tension data were fit by a linear regression, as shown by the solid line in Figure 14. The line fits the data very well, with a very high linear correlation coefficient of 0.998. The temperature coefficient of −0.072 m N m⁻¹ K⁻¹ found in this study is similar to the values found for polymers that have side chains similar to P3HT (Ref. 55) and also to other polymers. While we are well aware that we should not extrapolate the fit below the crystallization temperature of P3HT, we can not resist making the following compelling argument to have a crude estimate of the surface tension of P3HT at room temperature. Although the bulk crystallization temperature of P3HT is around 400 K, the hexyl side chains, which dominate the surface morphology of the film, do not crystallize until they are cooled far below their thermodynamic melting point of 333 K. We can thus safely assume that the hexyl side groups of a P3HT film should maintain their melt properties at least up to this temperature and that the error we incur by extrapolating the fit to this point should not be significant. To be on the safe side, we can assume the extrapolated value of the surface tension to room temperature (i.e., 34.5 m N m⁻¹) to be an upper bound to the true value at room temperature since the surface tension below the crystallization temperature of the side chains may be monotonically decreasing with temperature. Though this hypothesis is open to experimental verification, the predicted surface tension value of 34.5 m N m⁻¹ is as argued at the upper end of the experimental range.

IV. SUMMARY AND CONCLUSIONS

The structural and interfacial properties of melt P3HT free-standing films were investigated using all-atomistic molecular dynamics simulations. Mass density and number density profiles of the films and orientational ordering for different parts of the P3HT chain segments in the films were calculated. The number density profile revealed that the surface was mainly covered by the methyl groups. At the boundary of the bulk and interfacial regions, a peak in the mass density profile was observed, which was more pronounced at lower temperatures than higher temperatures. At this boundary the thiophene ring number density was found to be higher than in the bulk region due to the interface effect which induced more ordering to the thiophene rings that are at and close to the interface. At the interface, the thiophene rings preferentially expose the carbon atoms that connect the thiophene rings to the hexyl groups rather than the sulfur atoms. The orientational ordering calculations show both methyl and hexyl groups sticking out to the surface with strong orientational ordering observed at vacuum side of the interface. The thiophene ring segments orient parallel to the surface with the thiophene ring plane preferentially tilted toward normal to the interface.

The equilibrated surface tension value at a given temperature was obtained by running the simulation for at least 50 ns. The surface tension shows similar temperature dependence as that of polymers with alkyl side chains. The simulation-measured surface tension of melt P3HT is smaller than all experimentally reported values for crystalline P3HT films.

Though computationally very expensive, our future work will focus on the effect of chain length on the reported interfacial properties and also on the structure and dynamics of supported P3HT films on different substrates. To circumvent the computational cost, we plan to represent the alkyl side chains with a united atom model that will significantly reduce the computational cost.
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