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J. Phys. Chem. B, **2008**, 112 (47), 14857-14862 • DOI: 10.1021/jp806967x • Publication Date (Web): 30 October 2008

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A Theoretical Study of the Charge Transfer Behavior of the Highly Regioregular Poly-3-hexylthiophene in the Ordered State

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Received: August 5, 2008; Revised Manuscript Received: September 25, 2008

We use quantum mechanical (QM) methods to interpret the charge transport properties of the self-assembled poly-3-hexylthiophene (P3HT) molecules along the intrachain and interchain directions. Our approach is illustrated by a hopping transport model, in which we examine the variation of the electron-coupling strength (transfer integral) with the torsional angle and the intermolecular distance between two adjacent thiophene segments. We also simulate the packed P3HT structures at various values of temperature and regioregularity via the molecular dynamics (MD) simulations. The MD results indicate that with decreasing the molecular regioregularity and/or increasing temperature, the P3HT backbone chains experience a larger distortion of the thiophene rings out of coplanarity, and thus the charge mobility along the main chains is reduced. However, as long as the P3HT molecules remain in the ordered lamellar state due to the presence of the π - π interaction, the resultant mobility along the π - π interchain direction is still significantly less than that along the intrachain direction. Accordingly, the main charge transfer route within the P3HT ordered domains is along the intrachains instead of the interchains.

Introduction

Organic thin-film transistors (OTFTs), which are used to be the main current switching and control units, have been applied in lots of electron devices such as large-area thin sensor, electronic paper, and active matrix display.^{1–3} Among these applications, promoting the efficiency of charge transport within the organic layers plays a key role. The charge carrier transport properties critically depend on the packing order of the molecules in the system. Recently, particular interest has been dedicated to OTFTs based on highly regioregular poly-3-hexylthiophene (rr-P3HT) because of the fact that the rr-P3HT molecules can pack orderly to form a lamellar structure via π - π interchain stacking.^{4,5} Accordingly, charge delocalization in these ordered lamellae occurs not only along the conjugated main chains, but also along the π - π stacking direction of the thiophene rings between neighbored chains.

Experimentally, it has been shown that rr-P3HT can reach a high charge mobility of $0.1 \text{ cm}^2/\text{V}\cdot\text{s}$ in the ordered state.^{6–8} Some of the key factors that affect the charge carrier mobility in the ordered structure are the molecular regioregularity, molecular weight, temperature, and processing conditions. For example, Sirringhaus et al. reported that the self-assembled P3HT lamellae in the field-effect transistors can adopt two different orientations with respect to the substrate, which are illustrated in Figure 1, by tuning the molecular regioregularity and processing conditions.⁹ When the P3HT regioregularity is low (81% of head-to-tail linkages), the formed lamellae in the spin-coated films are preferentially parallel to the substrate and provide a one-dimensional charge transfer route mainly along the intrachains. However, in samples with high regioregularity (>91%), the ordered P3HT molecules tend to pack to form the

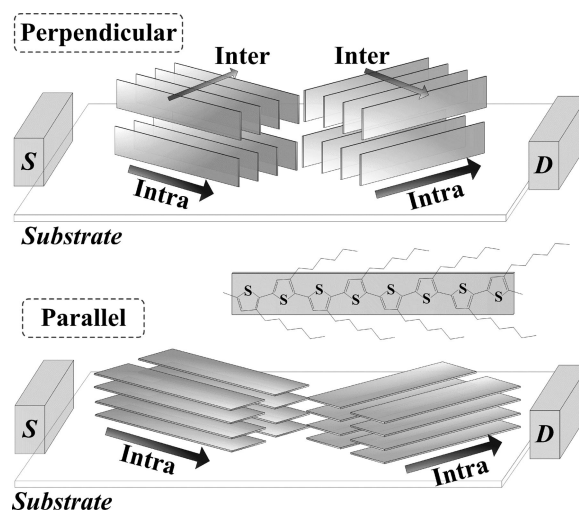


Figure 1. Schematic plot of the two different orientations of the self-assembled P3HT lamellae with respect to the substrate. The arrows denote the interchain and intrachain transfer directions, respectively.

lamellae perpendicular to the substrate, and thus the field-induced charge carriers can be transported via both intrachain and interchain (π - π stacking) directions. They reported that a significant increment of the charge mobility to a value as high as $0.1 \text{ cm}^2/\text{Vs}$ can be achieved by varying the orientation of the ordered lamellae from parallel to perpendicular with respect to the substrate. This result may lead to the conclusion that the charge transport along the π - π stacking interchains plays a dominant factor in the high carrier mobility of rr-P3HT in the field-effect transistors.¹⁰ However, it should be noted that varying the P3HT molecular regioregularity not only results in the different packing orientations of the lamellae (i.e., dimensionality of the charge transfer route) but also strongly affects the chain conformation and chain packing. A few studies have shown that increasing the molecular regioregularity can lead to

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a more rod-like (trans) chain conformation with extended π -conjugation as well as more dense packing of chains along the π - π stacking direction.^{11–17} For example, McCullough et al. employed molecular mechanics and ab initio calculations to examine the conformation of P3HT with different head-to-tail and head-to-head configurations.¹⁴ They observed that the existence of head-to-head coupling significantly causes the torsional angle between two thiophene rings to deviate out of coplanarity. In contrast, the thiophene rings with a head-to-tail configuration tend to adopt a coplanar (trans) conformation, which leads to a larger value of conjugation length and red-shift of absorption spectrum. Moreover, it has also been shown that in the P3HT the torsional angle between thiophene rings is strongly associated with the alkyl side chain packing.¹⁸ With increasing the temperature, the alkyl side chains experience a conformational disordering from trans to a combination of gauche and trans and thus act as a trigger to induce the disordering in the main-chain conformation. Through the torsional rotation about the ring–ring bonds, the conjugation length can be effectively shortened. Accordingly, one cannot exclude the possibility that the more coil-like chain conformation, by decreasing the P3HT regioregularity and/or increasing the temperature, may reduce significantly the charge transport property along the intrachain direction, which thus also attributes to the decrease in the field-effect mobility. In fact, Zen et al. investigated the effects of molecular weight and annealing of P3HT on the performance of field-effect transistors.¹⁹ They observed that the mobility shows the same decreasing trend with increasing temperature and decreasing molecular weight. The significant blue-shift of the solid-state absorption spectra with decreasing molecular weight indicates that the P3HT backbone chains with a lower molecular weight suffer a larger distortion, hence the main-chain conformation plays the most dominating role in controlling the charge transport in the P3HT layers.

As manifested above, despite the experimental studies that have addressed how the charge mobility is influenced, the issue of whether the high carrier mobility of rr-P3HT in the field-effect transistors is mainly attributed to the charge transfer route via intrachain or interchain still remains unconcluded yet. In this paper, we thus aim to theoretically examine how the charge transport properties along the intrachains and interchains, respectively, are affected by the chain conformation and chain packing within the ordered lamellae. In particular, we artificially vary the torsional angle between two conjugated thiophene segments (τ) along the main chain to resemble the local deformation created by the molecular stereoregularity and/or temperature, and we calculate the transfer integral values of both hole and electron as a function of τ . For simplicity, we choose each segment as the smallest repeated unit in the main chain, that is, two thiophene rings in a trans conformation, and vary the rotational angle between two segments (τ). Note that the value of $\tau = 0^\circ$ and 180° denotes a cis and trans conformation, respectively, of the two neighbored thiophene rings. By varying the torsional angle between two segments (τ), how the charge carrier mobility along the main chain is affected by the local rotational degree about the ring-to-ring bonds can be manifested. In analyzing the charge transport properties along the π - π stacking interchains, we consider two segments separated in a distance D . Each segment also consists of two thiophene rings in a trans conformation. By varying the intermolecular distance D , we investigate the influence of molecular packing on the transfer integrals of hole and electron along the interchains. Our results indicate that the charge transfer integral along the interchain direction between 3.8 and 4.0 Å, which is the typical

range of intermolecular distance in the P3HT systems, is significantly less than that along the intrachain direction even when the torsional angle deviates from a trans conformation of 180° to 140° . Accordingly, the resultant field-effect mobility in the ordered state is mainly dominated by the charge transport through the main-chains instead of the interchains. Moreover, in order to examine the influence of molecular regioregularity and temperature on the local distortion degree of the ring-to-ring bonds along the backbone chains as well as the interchain packing, we simulate the equilibrated P3HT structures at various values of regioregularity and temperature via the molecular dynamics simulations. We observe that with decreasing the regioregularity to 50 and/or increasing the temperature to 500 K, a larger deviation of the torsional angle out of 180° to $\pm 37^\circ$ between the thiophene rings along the main-chains can be reached when the P3HT molecules still remain in the ordered lamellar state.

Theoretical Methods and System

In this paper we adopt a hopping model to describe the charge transport properties along both the directions of intrachains and interchains in the P3HT system. At room temperature, the motion of the carriers can be described as a sequence of uncorrelated hopping processes, and the relationship of the carrier mobility μ and the charge transfer rate (hopping probability per unit time) k_{CT} can be obtained via the Einstein relation given as follows,

$$\mu = \frac{ea^2}{k_B T} k_{CT} \quad (1)$$

where k_B , T , e , and a correspond to the Boltzmann constant, temperature, electronic charge, and the transport distance. Apparently, the mobility of the carriers is directly proportional to the charge transfer rate k_{CT} . According to the semiclassical Marcus theory,^{20–26} the charge transfer rate k_{CT} between the neighbored segments can be expressed as follows,

$$k_{CT} = \frac{2\pi}{\hbar^2} t^2 \sqrt{\frac{1}{4\lambda\pi k_B T}} \exp\left[-\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right] \quad (2)$$

where \hbar is Planck's constant, and λ is the inner reorganization energy due to the hole/electron-vibration interactions. ΔG° is the difference of the Gibbs free energy of the system before and after the charge hopping process and is equal to zero since the segments are identical. As seen in eq 2, the transfer rate k_{CT} is proportional to the square of the transfer integral t , which represents the electron coupling strength of the adjacent segments and can be estimated within the Marcus–Hush two-state model.^{20,23–26} The transfer integral of a given system is related to the energetic splitting of the electronic level, which is attributable to the segment interaction. In each of the isolated segments, the HOMO (highest occupied molecular orbital) is a π -bonding orbital delocalized over the segment with energy ϵ of this state. When the two segments approach each other and the HOMO of each segment starts to interact, new HOMO and HOMO – 1 are formed. Thus, the energetic splitting due to the segment interaction is equal to the energy difference of the HOMO and HOMO – 1 in the interactive segment pairs. The transfer integral t of hole is thus given by the following,

$$t_{\text{hole}} = \frac{1}{2} \sqrt{(E_{\text{H}} - E_{\text{H}-1})^2 - (\epsilon_1 - \epsilon_2)^2} \quad (3)$$

As the energy for each isolated segment is equal, that is, $\epsilon_1 = \epsilon_2$, eq 3 becomes

$$t_{\text{hole}} = \frac{E_{\text{H}} - E_{\text{H}-1}}{2} \quad (4)$$

where E_{H} and $E_{\text{H}-1}$ denote the energy level of HOMO and HOMO - 1, respectively. Similarly, the transfer integral of electron (t_{el}) can be obtained via the difference of LUMO (lowest unoccupied molecular orbital) and LUMO + 1 of the interactive segment pairs, as given in eq 5,

$$t_{\text{el}} = \frac{E_{\text{L}+1} - E_{\text{L}}}{2} \quad (5)$$

The above theoretical model has been successfully used to describe the conductive properties of organic transistors such as the pentacene systems.^{20–22}

All of the above electronic energy levels were carried out using the MP2/6–311G (d,p) quantum mechanical calculations. The MP2 (Møller–Plesset second-order perturbation theory) is based on the Hartree–Fock method but including the electron correlation terms. Hence, it is suitable to describe the long-range interactions of organic molecular pairs, such as π – π interaction.²⁷ To give more accurate results of the charge coupling strength along the interchain direction (coupling through space), we chose a relatively large basis set 6–311G (d,p). The 6–311G indicates that 6 Gaussian functions are used to describe the core orbitals, and the valence orbitals are represented by 5 Gaussian functions (3 Gaussians in the contracted part, 1 in the outer part and 1 in the diffuse part). The use of (d,p) polarization function attempts to describe the anisotropic charge distribution of each molecule. As the MP2/6–311G (d,p) quantum mechanical calculation is often accompanied with huge computational time and memory resource, here we ignore the existence of the alkyl side chains, which has been shown to be negligible on the resultant HOMO and LUMO state calculations.

We employ the molecular dynamics (MD) method with the PCFF (polymer consistent force field)²⁸ to simulate the equilibrated P3HT structures at various values of regioregularity and temperature. In particular, the simulation system contains 4 P3HT molecules with 16 thiophene rings per chain, and each P3HT molecule is artificially set as an infinite chain to avoid the influence of the end-group liberation. To set the chain infinite, we artificially set one end atom of the P3HT molecule to connect with the imaged chain head atom in the next periodical box.²⁹

All the simulations were carried out in the isothermal–isobaric ensemble (NPT) with the time step equal to 1 fs, and the system pressure was set at 0.0001 GPa (1 atm). Initially, the 4 P3HT molecules were set to form a lamellar structure with an interchain separation distance of 4.0 Å and 17 Å along the π – π stacking and side-chain packing directions, respectively.^{11,30,31} Prior to simulation, the steepest descent minimization method was adopted to relax and equilibrate the initial structures. The minimized system was then relaxed and followed by a series of annealing processes. The annealing temperature was first raised from 300 to 500 K at a rate of 20 K/ps, and then quenched

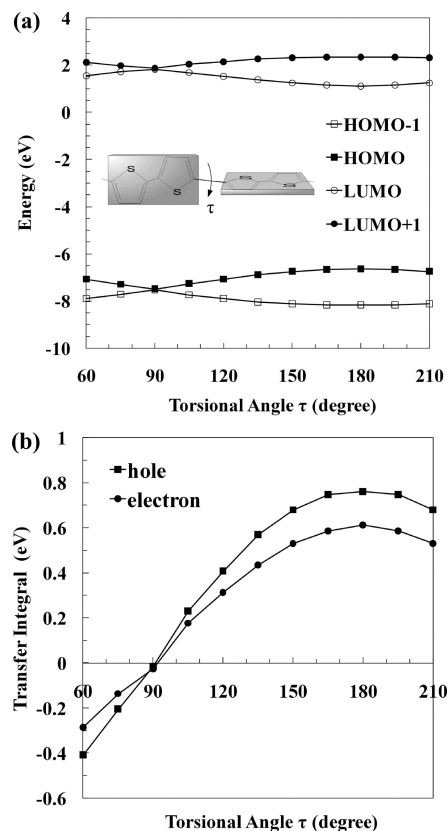


Figure 2. (a) The calculated energy levels of HOMO - 1, HOMO, LUMO, and LUMO + 1 as a function of the torsional angle τ of the two conjugated segments. (b) The transfer integrals of electron and hole along the intrachains as a function of the torsional angle τ of the conjugated segments.

to 300 K at the same rate. This annealing cycle was repeated five times to ensure that the system had been equilibrated. Finally, it was followed by a long relaxation period of 1.5 ns (1.5×10^6 time steps) at the setup temperature of each system and checked if the variation of the system temperature is smaller than 1%. After these processes were performed, so that the system energy had reached the equilibrium value, then 500 ps more of simulation is taken, and the trajectory is collected to analyze the averaged interdistance of the neighbored chain and to get the distribution profile of the torsional angle of the neighbored thiophene rings.

Results and Discussion

Figure 2a displays the calculated four energy levels of HOMO - 1, HOMO, LUMO, and LUMO + 1 for two conjugated segments, which consist of two thiophene rings in a trans conformation per segment, as a function of the torsional angle τ . From these calculated energy levels, we obtain the transfer integrals of hole and electron along the intrachains via eqs 4 and 5, and we plot them as a function of τ in Figure 2b. As can be seen clearly, both charge carriers of hole and electron have a maximum value of transfer integral at $\tau = 180^\circ$, that is, when the neighboring thiophene rings are in a trans conformation. As τ deviates from 180° , both the transfer integrals of hole and electron decrease progressively to the minimum value of 0 when the neighbored thiophenes are located in a perpendicular direction ($\tau = 90^\circ$). When τ ranges between 180° and 90° , the electron coupling strength (transfer integral) is positive with the bonding interaction (front orbital coupled with the same phase). As τ deviates further smaller than 90° , a negative value of the

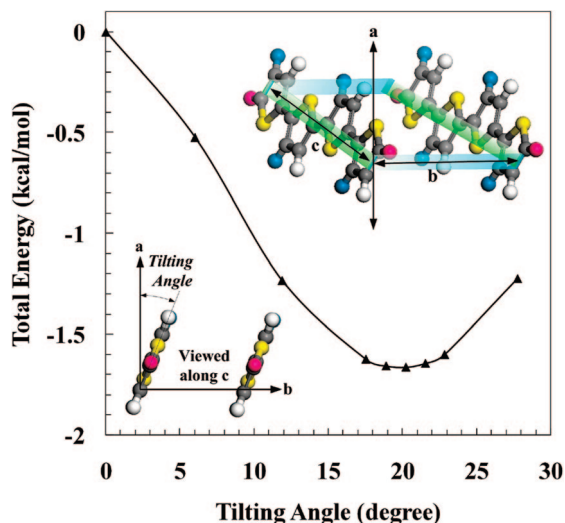


Figure 3. The relative total energy of two cofacial thiophene dimers as a function of the tilting angle with respect to the energy when the tilting angle is equal to 0° . The gray, white, yellow, blue, and red beads denote the carbon, hydrogen, sulfur, alkyl group, and head/tail group.

transfer integral indicates an antibonding interaction (front orbital coupled with the inverted phase) of the corresponding frontier orbital. The sign of transfer integral only indicates the combination type of the frontier orbital. As manifested in eqs 1 and 2, the charge carrier mobility is proportional to the square of transfer integral. Hence, both the charge carriers have largest value at $\tau = 180^\circ$ and smallest value at $\tau = 90^\circ$. Moreover, the hole transfer integral is larger than the electron transfer integral whatever the torsional angle τ . This is mainly due to the fact that the frontier orbital of the LUMO in polythiophene segments always has one more node than the HOMO wave function. Qualitatively speaking, the lower the number of nodes in the wave function of a given frontier level in the isolated segments, the larger the splitting of that level (the transfer integral) in the interactive segments. Therefore, the LUMO splitting is expected to be smaller than the HOMO splitting.^{23,26}

To illustrate the influence of intermolecular separation, we consider two cofacial thiophene dimers, which belong to the adjacent molecules, respectively, and have the conjugated-plane tilting angle equal to 20° . The tilting angle is defined as the angle between the conjugated thiophene-ring plane and the \vec{a} axis, as shown in Figure 3. The reason why a tilting angle of 20° is chosen can be rationalized clearly in Figure 3, where the plot of the calculated total energy of two cofacial thiophene dimers as a function of the tilting angle (while keeping the interchain distance fixed at 3.8 \AA) shows a minimum when the conjugated planes are substantially tilted 20° . Indeed, DeLongchamp et al. have also confirmed this tilting structure by both theory and experiment.³² We then fix the tilting angle of these two thiophene dimers at 20° and examine the evolution of the calculated transfer integrals of hole and electron as a function of the distance D in Figure 4. Similarly, the transfer integral of hole is larger than that of electron no matter what the interchain distance is. Because of the fact that the overlapping degree of π -atomic orbitals along the intermolecular direction decreases with an increase in the separation distance, both transfer integrals of hole and electron display an exponential decay with the interchain distance D . This result may point to the conclusion that one can get relatively large mobility of hole and electron along the interchain direction as long as the molecules keep closer. However, a significantly large

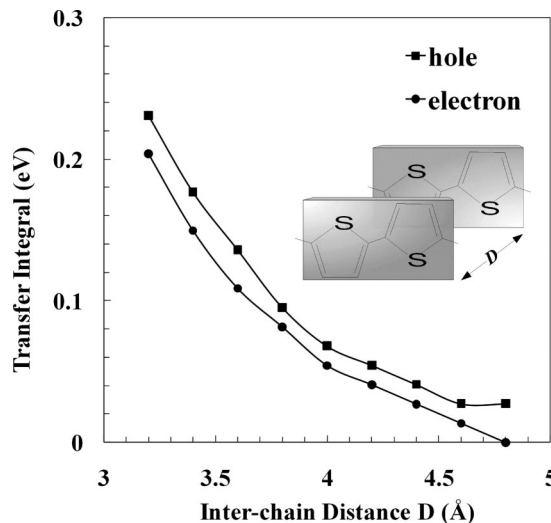


Figure 4. The transfer integrals of electron and hole along the interchains as a function of the intermolecular separation distance D .

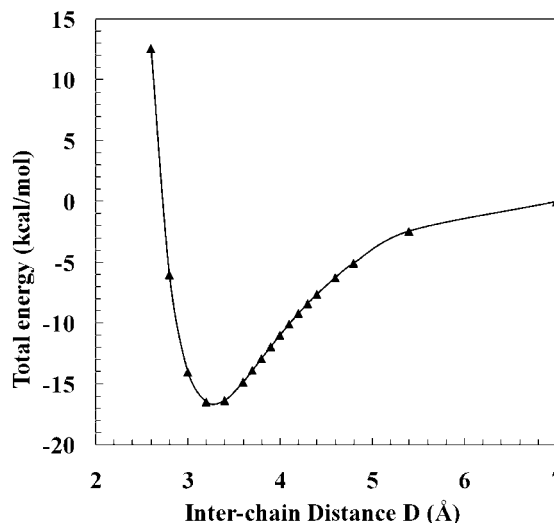


Figure 5. The calculated total energy of two thiophene dimers as a function of the separation distance D .

repulsive force is often accompanied with too closely packing molecules. Figure 5 illustrates the calculated total energy of two thiophene dimers as a function of the distance D , from which the distance when the dimers have the lowest energy is around 3.4 \AA . As the distance becomes closer than 3.4 \AA , the rapidly increasing free energy makes the two dimers hard to keep together. Note that here we ignore the existence of the alkyl side chains linked to the thiophene rings. When considering the effects of the alkyl side chains, an average distance of ca. 3.8 \AA between the intermolecular layers has been obtained by both experiments^{30,31} and our MD simulation results, which will be presented later. By varying the typical range of the intermolecular distance between 3.8 and 4.0 \AA , we observe that the transfer integral in Figure 4 ranges between 0.1 and 0.07 eV , which is significantly smaller than that along the intrachain direction even when the torsional angle of the thiophene rings has a large deviation of 40° out of coplanarity of 180° , as shown in Figure 2b. To clarify, when the thiophene torsional angle deviates from 180 to 140° , the resultant transfer integral along the main-chain is reduced from 0.7 to 0.5 eV , thus a significant decrease of the charge mobility to $1/2$ is reached. However, the

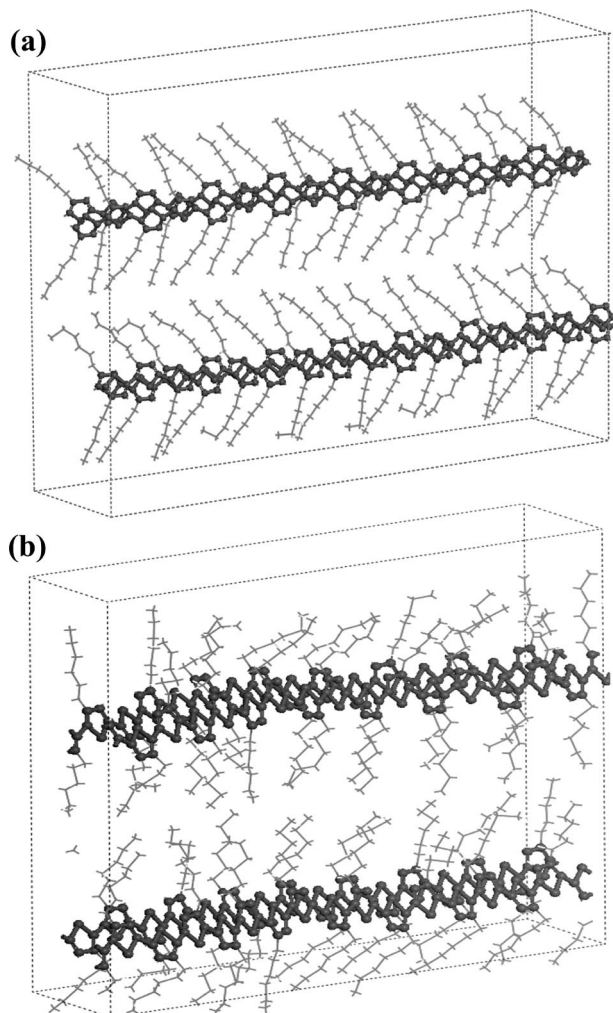


Figure 6. The equilibrated structures of the 4 P3HT molecules with 16 thiophene rings per chain and regioregularity value equal to (a) 100% and (b) 50%, respectively, simulated at 300 K via MD method.

charge transport route along the intrachain direction is still dominant in controlling the charge transport in the ordered P3HT layers.

So far, we have manifested the effects of the local distortion degree of the thiophene ring-to-ring bonds along the backbone chains and the intermolecular distance on the charge carrier mobility along the intrachain and interchain directions, respectively. The remaining issue is how the torsional degree of the backbone rings and the interchain packing are influenced by the molecular regioregularity, molecular weight, and temperature, as these factors have been proven to be important in affecting the resultant charge mobility experimentally. To illustrate these effects, we employ a molecular dynamics simulation method to obtain the energy-minimized molecular structure of 4 P3HT molecules with 16 thiophene rings per chain at a regioregularity value of 100 and 50%, and temperature at 300 and 500 K, respectively. It should be noted that here we do not examine the longer P3HT chains, as the associated simulation is too time-consuming. However, as has been suggested by Zen et al.,¹⁹ the effect of decreasing the molecular weight on the charge mobility is analogous to increasing the temperature. Figures 6 and 7 display the typical molecular structures and the distribution of the torsional angle between the thiophene rings τ , respectively, simulated at 300 K and various values of regioregularity. With a decrease in the regioregularity, we observe an increasing degree of the irregular

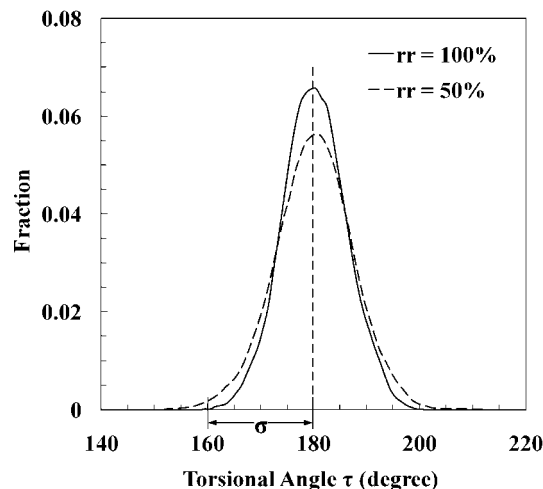


Figure 7. The distribution profile of the torsional angle τ between the thiophene rings for the 4 P3HT molecules with 16 thiophene rings per chain and various values of regioregularity at 300 K.

TABLE 1: List of the Interchain Spacing within the Lamellar Thiophene-ring Planes (a), the Interchain Spacing Due to the π - π Stacking (b), the Backbone Chain Length with 16 Thiophene Rings (c), and the σ Value of the Torsional Angle τ , at Various Values of the Molecular Regioregularity (rr) and Temperature

	rr = 100%, 300 K	rr = 100%, 500 K	rr = 50%, 300 K	rr = 50%, 500 K
<i>a</i> (Å)	19.78	19.80	19.88	19.98
<i>b</i> (Å)	3.78	3.99	3.91	4.00
<i>c</i> (Å)	57.23	57.21	56.22	56.47
σ (degree)	21.5	25.5	29.5	37

packing of the side chains (Figure 6) as well as a broader distribution of the rotational angle between the backbone thiophene rings out of coplanarity of $\tau = 180^\circ$ (Figure 7). A similar trend when the temperature increases to 500 K has also been observed. To illustrate the broadening degree of the τ distribution, we use a parameter of σ , which is defined as a width that the possible τ value for the backbone thiophene rings falls between $180^\circ \pm \sigma$. In Table 1 we list the interchain spacing within the lamellar thiophene-ring planes (*a*), interchain spacing due to the π - π stacking (*b*), the backbone chain length with 16 thiophene rings (*c*), and the σ value in the torsional angle (τ) distribution profile, as a function of the molecular regioregularity and temperature. We observe that the interchain spacing due to the π - π stacking (*b*) increases, whereas the backbone chain length (*c*) decreases with decreasing the molecular regioregularity and/or increasing temperature. For the variation regime of the interchain spacing *b* listed in Table 1 between 3.8 and 4.0 Å, the transfer integral along the interchains in Figure 4 ranges between 0.1 and 0.07 eV. Regarding the effects of temperature and molecular regioregularity on the transfer integral values along the intrachains, it is worthy to note that when the temperature is lower (300 K), decreasing the regioregularity from 100% (all head-to-tail) to 50% (half-random mixed with head-to-head and head-to-tail) causes a slight increase of the τ distribution regime from $180 \pm 21.5^\circ$ to $180 \pm 29.5^\circ$. When increasing temperature to 500 K, a more significant increase of the τ distribution regime from $180 \pm 25.5^\circ$ to $180 \pm 37^\circ$ is obtained by varying the regioregularity from 100 to 50%. These results manifest the fact that decreasing the regioregularity and/or increasing the temperature enable the thiophene ring-to-ring bonds to suffer a larger deviation of the torsional angle out of 180° ; therefore

the resultant charge carrier mobility along the main-chains when the P3HT molecules still remain in the ordered lamellar state is reduced. Moreover, varying temperature (or molecular weight) has a more profound effect on the charge mobility than varying molecular regioregularity. If we adopt the deviation of the torsional angle between thiophene rings τ out of coplanarity of 180° as large as $\pm 37^\circ$ when the regioregularity decreased to 50% and temperature raised up to 500 K, then the resultant transfer integral along the intrachains in Figure 2b decreases from 0.7 to 0.5 eV, which is still larger than that along the π - π stacking direction.

Finally, it should be pointed out that though we have theoretically confirmed that the charge transfer route along the intrachains instead of the π - π interchains is mainly dominant within the lamellar domains; this result does not exclude the importance of the π - π interaction. As has been clearly revealed by experiments, the fact that the P3HT molecules can pack to form a lamellar ordered state is mainly attributed to the π - π interaction.^{9,10,31} Thereafter, the ordered P3HT molecules adopt a more coplanar conformation of the thiophene rings as well as a more dense packing along the π - π direction. Comparing with the disordered state, the charge carrier mobility when the P3HT molecules remain in the ordered state is significantly enhanced, which, however, is still reached through the transfer route along the intrachains.

Conclusion

We employ the molecular dynamics and quantum mechanical methods to examine the molecular conformation behavior and the charge transport properties of the self-assembled rr-P3HT molecules into an ordered lamellar state. In particular, we focus on the effects of the chain conformation and chain packing on the charge transfer behavior along the intrachains and π - π interchains, respectively. We adopt a hopping transport model and calculate the transfer integral, which is correlated to the charge transfer rate and charge mobility, based on the Marcus-Hush two-state model. We find that when the molecules experience the π - π attractive interaction and remain in the ordered lamellae, decreasing the molecular regioregularity and/or increasing the temperature can cause a certain deviation degree of the thiophene rings out of coplanarity and hence a decrease in the charge carrier mobility along the main-chain direction. However, the resultant mobility is still larger than that along the π - π interchain direction. Accordingly, we conclude that the main dominating charge transport route within the P3HT ordered domains is along the intrachain instead of the interchain direction. On the basis of this important finding, it is reasonable to suggest that in order to improve the charge mobility in the field-effect transistors, simply tuning up the lamellar orientation to have additional π - π transfer route may not be the key issue. One should also consider the effects associated with the existence of the disordered domains and grain boundary, as most of the polymers can not self-assemble to form 100% ordered lamellae.

Acknowledgment. This work was supported by the National Science Council of the Republic of China through grant NSC 96-2221-E-002-019.

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