Molecular Arrangements of Regioregular and Regiorandom Poly(3-hexylthiophene): Molecular Dynamics Simulations

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We studied the effects of regioregularity of the poly(3-hexylthiophene) (P3HT) molecules on the order of molecular arrangement in the P3HT lamellar structure using molecular dynamics simulations. We found that the RR-P3HT molecule shows the aligned molecular arrangement in the ordered lamellar structure, while the RRa-P3HT molecule produces disorders in the π-π interchain stacking due to the formation of disordered network of intermolecular interactions between alkyl side chains of the P3HT molecules. RR-P3HT gains more stabilization energy with respect to the intermolecular interactions than RRa-P3HT due to the formation of ordered lamellar structure in the former system. The order of molecular arrangement in the P3HT lamellar structure is considered to be controlled by the intermolecular interactions between the alkyl side chains.

Key words: Poly(3-hexylthiophene), Molecular dynamics simulation, Organic semiconductor, Molecular orientation, Regioregularity, Organic field effect transistor

1. INTRODUCTION

π-Conjugated polymers have received much attention in the field of organic devices since they possess excellent electrical and opto-electrical properties and easy processability. Among them, poly(3-hexylthiophene) (P3HT) exhibits relatively high carrier mobility and has been widely applied to polymer-based field-effect transistors and organic solar cells. Its transport and optical properties are known to depend on regioregularity of P3HT. A film consisting of regioregular (RR) P3HT molecules shows higher mobility than that consisting of regiorandom (RRa) P3HT molecules. The RR-P3HT forms an ordered structure: Two-dimensional (2D) conjugated sheets formed via intermolecular π-π stack of thiophene main chains are separated by layers of alkyl side chains. This structure is called lamellar structure in the field of conjugated polymers. The RRa-P3HT shows amorphous nature. The degree of order of molecular arrangement in P3HT films has been considered to play a dominant role in determining their properties. However, the microscopic features of disordered molecular arrangement arising from the low regioregularity have not yet been fully elucidated, in particular, from the theoretical point of view.

In this work, we study the effects of regioregularity of the P3HT molecules on the order of molecular arrangement in the P3HT lamellar structure using molecular dynamics (MD) simulations. Furthermore, we also investigate a factor which causes the disorder in the molecular arrangement.

2. SIMULATION DETAILS

We constructed two model systems for simulating equilibrated P3HT lamellar structures using the crystal structure of RR-P3HT. The systems contain 42 dodecamers of RR-P3HT (Figure 1a) and RRa-P3HT (Figure 1b), respectively. The chain ends of dodecamers are capped by hydrogen atoms.

All the MD simulations were performed using the GROMACS 4.5.4. The general amber force field (GAFF) was employed. In order to determine the atomic charges for the P3HT molecules, we performed quantum chemical calculations of the isolated dodecamers at the HF/6-31G* level for optimizing molecular geometries and fitting the electrostatic potential at selected points according to the Merz-Singh-Kollman scheme using the Gaussian 09
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3. RESULTS AND DISCUSSIONS

The total potential energies of the model systems for RR- and RRa-P3HT are plotted as a function of time in Figure 2. They show a stable energy fluctuation with an average value. The direction is defined by the two polymer backbone chains. The model systems were simulated at constant temperature (300 K) and pressure (1 bar) under three-dimensional periodic boundaries condition. The Nose-Hoover thermostat and the Martyna-Tuckerman-Tobias-Klein isotropic barostat were used for the temperature and pressure controls, respectively. The simulation systems were subjected to some steps of energy optimization using the steepest decent method before starting the MD simulations. The simulations were carried out for 4 ns with the time integration step of 0.5 fs.

In order to analyze the order of molecular arrangement of RR- and RRa-P3HT molecules, we defined two variables: The first one characterizes variation in the directions of thiophene rings. $\Delta \phi_{\text{avg}}$ is the mean deviation angle in the normal vectors of the planes of thiophene rings from their averaged value. The second one characterizes variation in the directions of polymer backbone chains. $\Delta \theta_{\text{chain}}$ is the mean deviation angle in the directions of the polymer chains from their averaged value. The direction is defined by the two carbon atoms attached to the terminal hydrogen atoms in the chains. $\Delta \phi_{\text{avg}}$ and $\Delta \theta_{\text{chain}}$ were calculated for each 2D conjugated sheet in the original cells.

Table 1 summarizes the total potential energies and intra- and inter-molecular interaction energies of each system. They were obtained by averaging them in the rage of 3.7 and 4.0 ns. The total energy of system for RR-P3HT is smaller than that of RRa-P3HT due to energy differences of both intra- and inter-molecular interactions. Electrostatic interaction is a dominant contribution to the energy difference in the intramolecular interaction between the two systems. The two structural isomers, RR-P3HT and RRa-P3HT, have different charge distributions. Thus, this is considered to cause the change in the potential energy within the P3HT molecules. On the other hand, the energy difference in the intermolecular interactions between the two systems is mainly dominated by the order of molecular arrangement of P3HT in their lamellar structures: it results in more intermolecular stabilization energy in the RR-P3HT system.

Figure 3 shows MD snapshots of each system at 4 ns of simulation time. As seen in the figure, the model system for RR-P3HT shows an ordered lamellar structure, while the model system for RRa-P3HT shows a disordered π-π stacking and a waving of the sheets. Table 2 summarizes $\Delta \phi_{\text{avg}}$ and $\Delta \theta_{\text{chain}}$ of each sheet in the two systems. They were obtained by averaging them in the rage of 3.7 and 4.0 ns. The values in parentheses are the standard deviations of the angles. The average values and standard deviations of $\Delta \phi_{\text{avg}}$ and $\Delta \theta_{\text{chain}}$ in the RRa-P3HT system are greater than that in the RR-P3HT system (Table 2). This means that molecular orientations of P3HT represented by these angles are disordered in the RRa-P3HT system. Our results of MD simulations are consistent with experimental results: According to references 8 and 11, the P3HT molecules with high regioregularity form an ordered lamellar structure, while the P3HT molecules with lower regioregularity show amorphous structure.

Figure 4 shows alkyl side chain arrangements in the RR- and RRa-P3HT systems at 4 ns. Regularly arranged alkyl side chains in the RR-P3HT molecules form an ordered network of intermolecular interactions (Figure 4a). Thus, the RR-P3HT can pack orderly and closely to form the lamellar structure. On the other hand, in the RRa-P3HT molecules, the random attachment of the alkyl chains to carbon atoms at the beta positions in the thiophene rings results in the formation of disordered network of intermolecular interactions between the alkyl side chains. This brings about disorder in the molecular arrangement of RRa-P3HT. Therefore, the intermolecular interactions of alkyl side chains are considered to control the order of molecular arrangement in the P3HT lamellar structure.

Table 2. Orientation angles of P3HT molecule in the lamella structure.

<table>
<thead>
<tr>
<th>System</th>
<th>Sheet Num.</th>
<th>$\Delta \phi_{\text{avg}}$ (degree)</th>
<th>$\Delta \theta_{\text{chain}}$ (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR-P3HT</td>
<td>1</td>
<td>7.0 (3.9)</td>
<td>0.8 (0.5)</td>
</tr>
<tr>
<td>RRa-P3HT</td>
<td>1</td>
<td>1.3 (1.4)</td>
<td>0.9 (0.9)</td>
</tr>
</tbody>
</table>

Table 1. Total potential energies and their components.

<table>
<thead>
<tr>
<th>System</th>
<th>Total Potential Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RR-P3HT</td>
<td>28 054</td>
</tr>
<tr>
<td>RRa-P3HT</td>
<td>48 774</td>
</tr>
</tbody>
</table>

Figure 2. Total potential energies of the model systems for regioregular and regiorandom P3HTs as a function of time.
4. CONCLUSIONS
We studied the effects of regioregularity of the P3HT molecules on the order of molecular arrangement in P3HT lamellar structure using molecular dynamics simulations. We found that the system of RR-P3HT shows the aligned molecular arrangements in the ordered lamellar structure, and the system of RRa-P3HT shows disordered molecular arrangements, consistent with experimental results. Furthermore, we found that RR-P3HT gains more stabilization energy with respect to the intermolecular interactions than RRa-P3HT due to the formation of ordered lamellar structure in the former system. The order of molecular arrangement in the P3HT lamellar structure is considered to be controlled by the intermolecular interactions between the alkyl side chains of P3HT molecules.

ACKNOWLEDGEMENT
This work was partly supported by JSPS KAKENHI (No. 22340080).

5. REFERENCES


(Received January 10, 2012; Accepted April 5, 2012)