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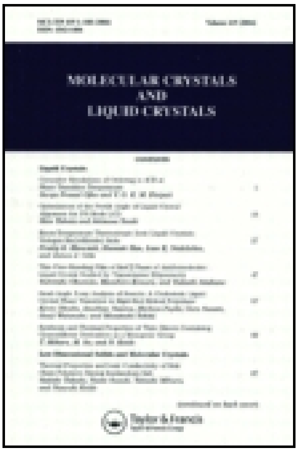

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Preferable Molecular Orientation of Poly(3-hexylthiophene) on Self-Assembled Monolayers: Molecular Dynamics Simulation

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Preferable Molecular Orientation of Poly(3-hexylthiophene) on Self-Assembled Monolayers: Molecular Dynamics Simulation

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Using molecular dynamics simulations, we theoretically investigate the molecular orientation of poly(3-hexylthiophene) (P3HT) on hydrophobic and hydrophilic self-assembled monolayers (SAMs). In particular, we study the effects of roughness at the SAM surfaces on the molecular orientation of P3HT molecules put on the surface. The energetically preferable molecular orientation does not change by the roughness we introduced. The roughness induces more frequent transition between the edge-on and face-on orientations, when a small number of P3HT molecules are put on the hydrophobic SAM.

Keywords Molecular dynamics simulation; molecular orientation; organic field-effect transistor; π-conjugated polymer; self-assembled monolayer

Introduction

Organic field-effect transistors (OFETs) have attracted much attention due to their excellent properties [1,2]. The orientations of molecules or polymers at the interface between organic semiconductor layers and gate insulators have much influence on carrier mobility in the devices. The surfaces of gate insulators have often been functionalized by self-assembled monolayers (SAMs). Poly(3-hexylthiophene) (P3HT) is one of typical polymers used in OFETs and other organic devices. P3HT is known to take an edge-on or face-on orientation at the interface [3–7], where the former orientation shows higher carrier mobility than the letter one [3]. Although the control of the molecular orientation is crucial to improve the device performance, the microscopic mechanism to determine the molecular orientation remains open question.

We have theoretically investigated the preferable molecular orientation of P3HT on hydrophobic and hydrophilic SAMs using molecular dynamics (MD) simulations [8] as well as the bulk properties of this polymer [9]. In Ref. [8] we assumed that the SAMs have a flat surface. In this work, we focus our attention on how roughness at the surface affects the molecular orientation of P3HT molecules put on the surface. This is because the actual interfaces are considered not always perfectly flat and smooth even after SAM

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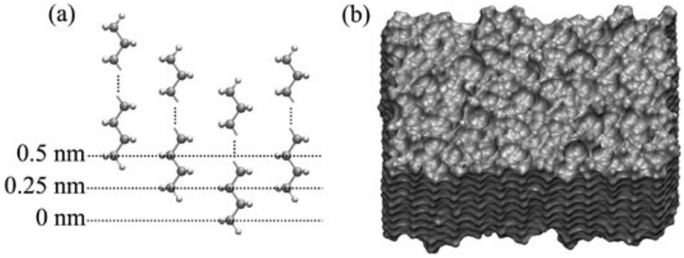

Figure 1. Modeling of the SAM with rough surface. (a) Manner of shifts of the alkane molecules. (b) Equilibrated structure of CH_3-terminated SAM.

treatment. For example, it is reported that SiO_2, a typical gate dielectric, thermally grown on crystalline Si takes an amorphous structure [10].

Calculation Method

We constructed the model system of the hydrophobic SAM by means of the two-dimensional aggregate of linear alkanes with 19 carbon atoms. For the hydrophilic SAM, one of the end groups in each alkane was replaced from the CH_3 to NH_2 group. In order to make the SAM surfaces rough, 76 and 52 alkanes among total 182 ones were initially translated 0.25 and 0.5 nm along the direction normal to the surface, respectively (Fig. 1(a)). Then, before constructing combined P3HT-SAM model systems, the SAM systems were equilibrated alone with anchoring the chain-end carbons of the alkanes on the side opposite to the SAM surfaces (Fig. 1(b)) [8]. A P3HT polymer chain was modeled by a long oligo(3-hexylthiophene) with 12 repeating units. Hereafter, we simply refer to the oligomer model as P3HT.

We performed two kinds of MD simulations. In the first one, we simulated the equilibrated structures of the model systems containing 28 P3HT molecules arranged in the edge-on or face-on manner on the SAMs and analyzed their potential energies. In these cases, the MD simulations were performed at a constant volume and temperature (300 K) under two-dimensional periodic boundary condition for 6 ns. The second kind of simulation investigated the dynamic behavior of limited numbers of the P3HT molecules on SAMs. The simulations were performed at higher temperature of 600 K for 4ns to make the dynamical features clear. All the calculations were carried out using the GROMACS 4.5.4 [11] with the general amber force field (GAFF) [12]. Details in calculation method were described in [8].

Results and Discussion

Potential Energy Analysis

Based on the time dependence of the energy fluctuation, the combined systems of P3HT and SAM are considered to archive their equilibrated structures by the MD simulations for 6 ns. When we examine the MD snapshots of the system at 6 ns, the P3HT molecules keep the edge-on or face-on orientation even on the rough surfaces both in the CH_3- and NH_2-termnated SAMs, although the roughness gives rise to disorder to some extent in the packing of P3HTs compared to the flat surfaces at the same temperature.

Table 1. Total potential energies and their components in the P3HT-SAM model systems in the unit of kJ/mol. The values in parentheses indicate the difference between the rough and flat SAM surfaces.[a)]

SAM	P3HT orientation	Total pot. energy	Intermolecular interactions: P3HT-P3HT	Intermolecular interactions: P3HT-SAM	Other components
CH_3-terminated	edge-on	52 616 (1 328)	−16 262 (63)	−825 (70)	69 703 (1 195)
	face-on	54 181 (1 452)	−14 030 (354)	−1 011 (18)	69 222 (1 080)
NH_2-terminated	edge-on	48 757 (1 161)	−16 140 (171)	−1 127 (−91)	66 024 (1 081)
	face-on	49 726 (1 052)	−14 191 (262)	−1 517 (25)	65 434 (765)

[a)] The values for the flat SAM surfaces are listed in Ref. [8].

Table 1 summarizes the total potential energies and their components at the equilibrated structures by averaging these quantities in the range between 5.7 and 6.0 ns. We found that the most basic features do not change by introducing the roughness: (i) The edge-on orientation is preferable to the face-on orientation in the both kinds of the SAMs because the former gains more P3HT-P3HT intermolecular interactions. (ii) The face-on gains more intermolecular interactions between the P3HT and SAMs. (iii) The P3HT-SAM intermolecular interactions are stronger in the NH_2-termnated SAM than CH_3-termnated SAM. When we compare the intermolecular interaction between the rough and flat surfaces in more detail (the values in parentheses in Table 1), the rough surface increase both the P3HT-P3HT and P3HT-SAM interactions in all the model systems, except for the NH_2-terminated SAM system with the P3HT molecules in the edge-on manner. The surface roughness prevents the close contact of the P3HT with the SAM surfaces. It also gives rise to the disorder between molecular packing of the P3HT molecules.

Dynamic Behavior of P3HT on the SAMs

In order to characterize the molecular orientation of the P3HTs on the SAM surface, we calculated “orientation angle” by averaging, over every thiophene rings, the angles of the molecular planes of the thiophene rings against the SAM surface. The edge-on and face-on orientations give large and small values of this angle, respectively. Figure 2 plots the time variation of the orientation angles for the CH_3-terminated SAM with the rough surface.

As seen in Fig. 2(a), the system of two P3HT molecules stacked together frequently changes the orientation angle. This indicates the frequent switches between the face-on and edge-on orientations. The system with the four stacked molecules also switches the orientations at 1.4 and 3.7 ns. The six stacked molecules keep the edge-on orientation. The rough surface of the CH_3-terminated SAM makes the switch of molecular orientation easy compared with the flat surface. In the flat surface, we observed only two switches for the two stacked case and no switch for the four stacked case [8].

The behaviors on the NH_2-terminated SAM surface are basically same between the rough and flat surfaces. The two stacked molecules keep the face-on orientation after

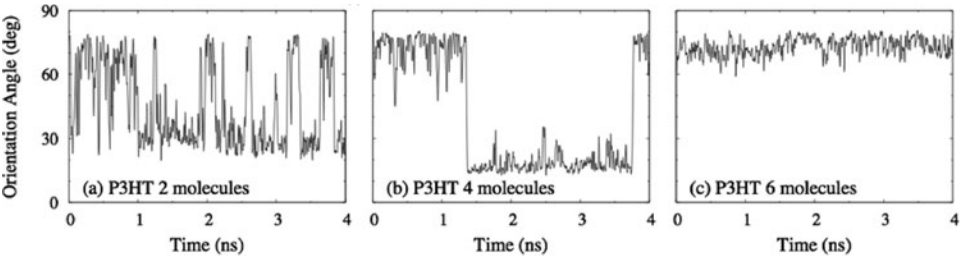

Figure 2. Orientation angles as a function of simulation time. (a)–(c): two, four, and six stacked P3HT molecules, respectively on the CH_3-terminated SAM with rough surface. See text for the definition of the orientation angle.

changing promptly from the initial edge-on orientation. The four and six stacked molecules keep the edge-on orientation.

Summary

Using MD simulations, we theoretically investigated the molecular orientation of P3HT on the hydrophobic and hydrophilic SAMs. In particular, we elucidated the effects of roughness at the SAM surfaces on the molecular orientation. The energetically preferable molecular orientation does not change by the roughness we introduced. The roughness induces the more frequent transition between the edge-on and face-on orientations, when a small number of P3HT molecules are put on the hydrophobic SAM. It also gives rise to the disorder between molecular packing of the P3HT molecules.

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