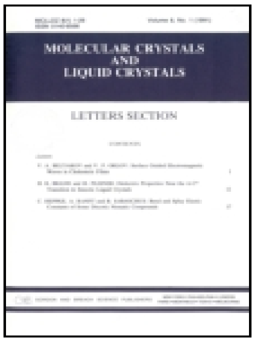

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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**To cite this article:** Toshiaki Miura, Taiki Ito & Takeshi Shimomura (2016) Molecular dynamics simulation on the nanofiber formation of conducting polymers in solutions, Molecular Crystals and Liquid Crystals, 629:1, 248-253, DOI: 10.1080/15421406.2015.1096994

**To link to this article:** http://dx.doi.org/10.1080/15421406.2015.1096994

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 629, 248–253
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# Molecular dynamics simulation on the nanofiber formation of conducting polymers in solutions

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**ABSTRACT**
We study the initial nucleation dynamics of poly (3-hexylthiophene) (P3HT) in solution, with particular regard to the effect of rigid backbone length on the ordering dynamics. We carried out Langevin dynamics simulation, and found that the initial nucleation processes of P3HT in solution begin with the ring ordering, followed by the main chain ordering. In the meantime, ordering of side chains was slow and induced by the packing of main chains. This basic ordering mechanism is common regardless of chain length of P3HT in this study, although the longer chain systems showed slower growth than the shorter chain systems. Our simulation results demonstrated the unique and universal ordering features of comb-like polymers with flexible side chains and rigid main chains in the initial crystallization processes.

**KEYWORDS**
P3HT; conducting polymer; nanofiber; crystallization; simulation

## Introduction

Polymer semiconductors, such as poly (3-hexylthiophene) (P3HT) have attracted much attention in recent years. They are widely applied for organic electronic devices. Some kinds of these conjugated polymers form nanofiber structures from solutions at certain conditions [1–18]. The formation of nanofibers is a complicated structure formation process and many unresolved problems remain on basic ordering physics. Recently, we have investigated the initial nucleation process of P3HT in solution by simulations and revealed the detailed ordering mechanisms, especially focusing on the role of rigid main chains and flexible side chains [19]. These simulation results showed that the initial nucleation processes consist of fast processes of ring ordering or main chain ordering and a slow process of side chain ordering. In our previous study, the degree of polymerization of P3HT was 10. Since the chain length is an important factor in the order formation of chain molecules, it would be important to study the ordering dynamics with longer chain length. Another problem was the effect of potential details. In our previous study, we used a semi-empirical method to evaluate the electric charges, but it would be important to evaluate them by more accurate ab-initio methods. In this paper, we studied the initial crystallization processes of P3HT whose degree of

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This paper was originally submitted to *Molecular Crystals and Liquid Crystals*, Volumes 620–622, Proceedings of the KJF International Conference on Organic Materials for Electronics and Photonics 2014.

polymerization was 20 and electric charges were assigned by an ab-initio method. We compared these results with the previous results to verify the universality of ordering mechanisms.

## Model

The simulations of structure formation of P3HT in solution were performed using the Langevin dynamics method. The Langevin dynamics is suitable for studying the slow ordering processes of polymers in solution, since the lack of a large number of solvent molecules significantly reduces the simulation time. The screening effect of electrostatic interactions by solvent molecules was considered by using dielectric constant of solvent molecules. In this study, we used GROMACS 4.5.6 [20], in which the force field we used was generalized Amber force field. In the previous study [19], we used MOPAC 6 for the calculation of electric charges. In this study, the electric charges were determined by Gaussian 09 [21], in which the point charges were assigned using RESP. The degree of polymerization of P3HT was 20 and the number of P3HT in the simulation box was 16. The box size was 20.0 nm and the periodic boundary condition was applied. The relative dielectric constant was 4.33, which corresponds to that of anisole solvent. Initial states were prepared by randomly allocating P3HT molecules in the simulation box. Since the Langevin dynamics is based on a kind of coarse-grained model, we used the reduced unit for time scales. In the case of reduced unit for alkane chains, 1 reduced time corresponds to 2.01 ps. We have observed the structure formation processes at constant temperature (300K) and volume until $t = 37500$. The time step of simulation was 0.00025.

For the analysis of ordering processes, we calculated three kinds of orientation order parameters, which are the normal vectors of thiophene rings, the main chain vectors and the side chain vectors, respectively (Fig. 1). Orientation order parameters are calculated by $<3\cos^2\theta-1>/2$, in which $\theta$ is the angle formed by two chain vectors. The details of calculation are reported elsewhere [19]. These three order parameters can be further classified into three types; the global order, the intermolecular local order, and the intra order. The global orders are obtained by averaging over all bond pairs in the entire system region except for

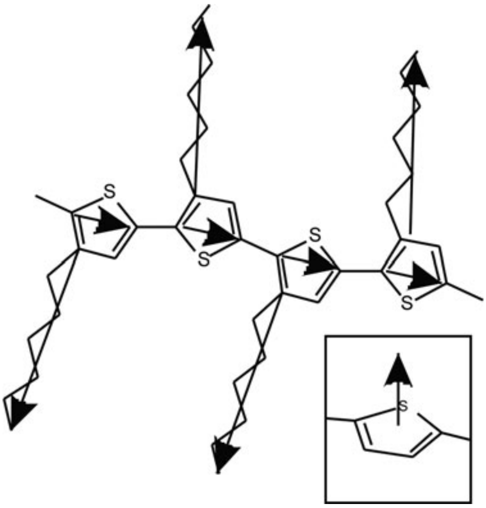

**Figure 1.** Schematic of main chain and side chain vectors. Normal vector of a thiophene ring is illustrated in a rectangular.

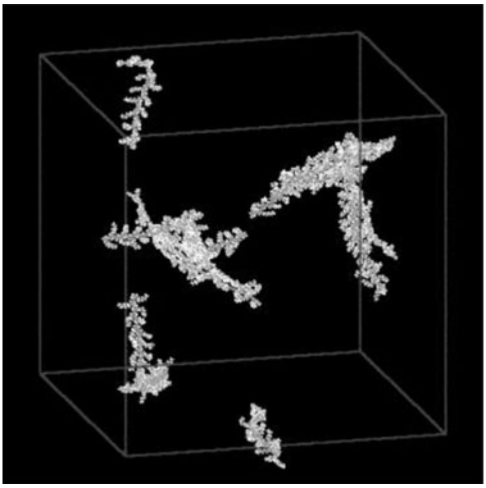

**Figure 2.** Example of assembled structure of P3HT at t = 37500.

bond pairs within the same molecules. The intermolecular local orders are obtained by averaging only for the pairs of neighbor bonds of different chain molecules. In our simulation, we regard two bonds to be in the neighbor region when the distance between them is less than 0.5 nm for main chains and 1.0 nm for side chains. The intramolecular local orders are obtained by averaging over the pairs of bonds within the same molecules. In the calculations of these orders, we carried out ten simulation runs from the different initial states and obtained the average values.

## Results and discussions

An example of obtained structures of P3HT 20mer (P3HT-20) solutions after a long time (t = 37500) is shown in Fig. 2. P3HT molecules assembled and form crystal nuclei. To elucidate the initial nucleation process in microscopic levels, we have calculated the time evolution of various order parameters and compared these results with those of P3HT 10mer (P3HT-10) reported previously [19]. In Fig. 3, we showed the time evolution of orientation order of normal vectors of thiophene rings. Black lines indicate the results of

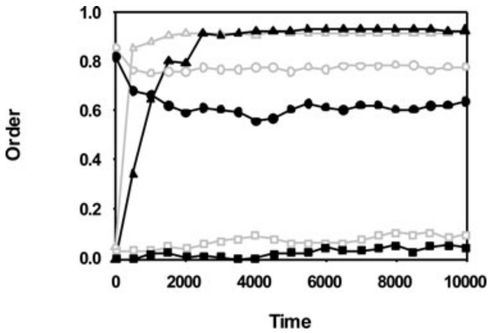

**Figure 3.** Time evolution of the orientation order of the thiophene ring. Black and gray lines indicate P3HT-20 and P3HT-10, respectively. Circles, triangles, and squares indicate the intramolecular, the intermolecular local, and the global orders, respectively.

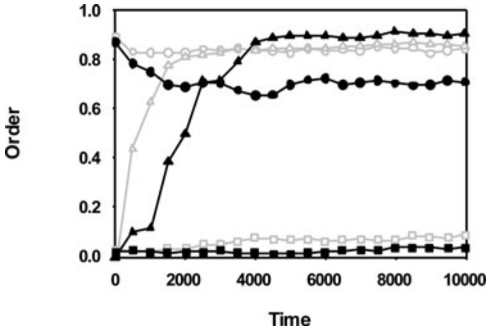

**Figure 4.** Time evolution of the orientation order of the main chains. Lines and symbols are the same as those in Fig. 3.

P3HT-20, and gray lines indicate those of P3HT-10. Circles, triangles, and squares indicate intramolecular, intermolecular local and global orders, respectively. The intermolecular local order of P3HT-20 increased rapidly at the beginning of crystallization until t = 2000. This behavior was similar to that of P3HT-10 except for the time scale. The longer chain system showed slower ordering dynamics. On the other hand, intramolecular order decreased in the initial period. The decrease of intramolecular order resulted from the slight fluctuation of planar backbones, which were subjected to bending or torsion stress from other neighboring molecules. The development of global order was very slow, because many crystal nuclei which took various directions remained in the simulation period. Existence of many crystal nuclei at various directions reduces the value of average global order considerably.

Next, we showed the time evolution of orientation orders of main chains in Fig. 4. The order parameters of main chains increased until t = 4000. The growth speed of P3HT-20 was slower than that of P3HT-10. In the case of P3HT-20, the intermolecular local order of main chains showed higher order than the intramolecular order in the intermediate and late periods after t = 3000. On the other hand, in the case of P3HT-10, the saturated value of main chains of intermolecular local order was almost the same as intramolecular one. For long polymer chains, initial crystal nuclei often formed by partial assembly as shown in Fig. 5 (a). Unstacked parts of polymer molecules outside the crystal nuclei were easier to bend, which caused the slightly lower values for intramolecular orientation orders.

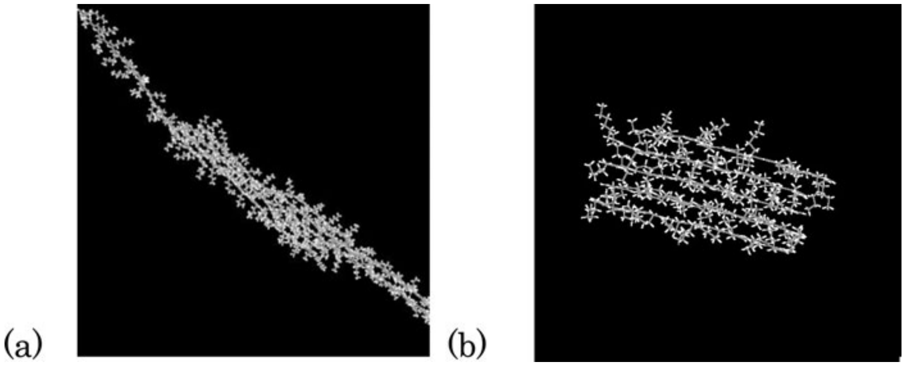

**Figure 5.** Snapshot of initial crystal nuclei of P3HT-20 (a) and P3HT-10 (b). Side view, parallel direction of thiophene rings.

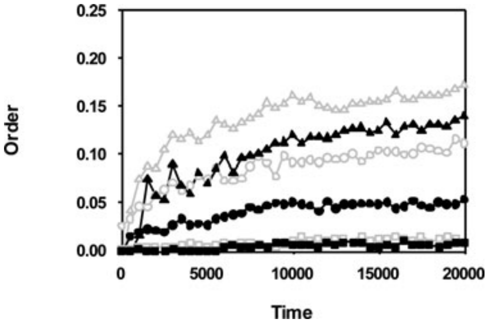

**Figure 6.** Time evolution of the orientation order of the side chains. Lines and symbols are the same as those in Fig. 3.

Figure 6 showed the time evolution of orientation orders of side chains. The order parameters of side chains showed slower growth than those of main chains. The intermolecular local orders increased gradually in the late period for both P3HT-20 and P3HT-10. The intramolecular order also showed the similar slow growth as the intermolecular order. These results suggest that the ordering of side chains is induced only after the stacked structure of main chain backbone is sufficiently developed.

For comparison of these ordering dynamics, the time evolution curves of the intermolecular local and global orders are fitted by a single exponential function given by $1-A_1 \exp(-t/\tau_1)$. Although improved fittings might be obtained by summation of several exponential functions in some cases, fittings by a small number of parameters would be convenient for comparison between different curves at first approximation. We have summarized the fitting results in Table 1. These results on the local orders suggested the following mechanism in the initial crystallization process. Initially, the neighboring thiophene rings aligned each other in a very short time. Then the neighboring main chains arranged chain directions each other within a short time scale, which was more than several times longer than that of ring alignment. In this study, we have changed both the chain length and the method of charge assignment at once and obtained the common ordering behaviors. Hence, the difference in charge calculation methods would not affect the fundamental features, but only the quantitative aspects.

Thus, in the nucleation process of P3HT nanofibers, the planar shape and strong interactions between thiophene rings played an important role. On the other hand, flexible side chains had not ordered well and took various directions in the initial period. Ordering of side chains proceeded after the formation of stacked layer structures, which confined the side chains into limited free spaces. The time scale of side chain ordering was almost several times longer than that of main chain ordering. This made the growth of ordered structure for the

**Table 1.** Growth times and amplitudes of various order parameters.

| | | P3HT-20mer | | P3HT-10mer | |
|---|---|---|---|---|---|
| | | $\tau_1$ | $A_1$ | $\tau_1$ | $A_1$ |
| local order | ring | 860 | 0.93 | 100 | 0.81 |
| | main chain | 2100 | 0.92 | 590 | 0.74 |
| | side chain | 5500 | 0.14 | 2600 | 0.16 |
| global order | ring | 4900 | 0.044 | 4900 | 0.12 |
| | main chain | 17000 | 0.11 | 9500 | 0.14 |
| | side chain | 16000 | 0.014 | 11000 | 0.018 |

side chain directions more difficult than the growth perpendicular to ring plane, which might lead to anisotropic growth of crystal nuclei. Hence, this study revealed that the chain length of main backbone affects the ordering rates, but it does not significantly alter the basic ordering mechanism in the range of this study.

## Summary

In summary, we have investigated the crystallization dynamics of P3HT in solutions at different main chain length by Langevin dynamics simulations. We found that the initial nucleation processes of P3HT in solution began with the ring ordering, followed by the main chain ordering and the side chain ordering. In the meantime, ordering of side chains was slow and induced by the packing of main chains. These basic ordering mechanisms were common for both short and long P3HT molecules except for values of time scales, in which the longer chain systems showed slower growth than shorter chain systems. Thus, our simulation results demonstrated the universal ordering features of comb-like chain molecules of flexible side chains and rigid main chain rings in the initial nucleation period.

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