

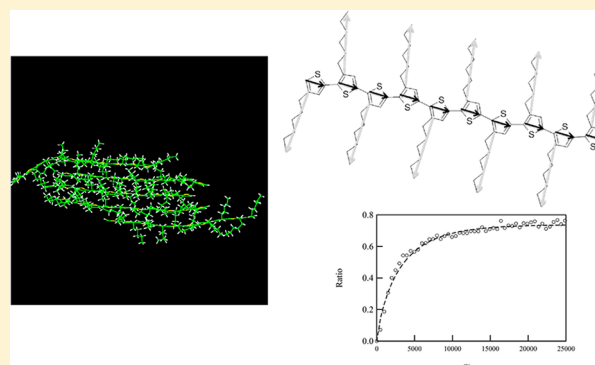
Simulation Study of the Initial Crystallization Processes of Poly(3-hexylthiophene) in Solution: Ordering Dynamics of Main Chains and Side Chains

Yuumi Takizawa,[†] Takeshi Shimomura,^{*,†} and Toshiaki Miura^{*,‡}

[†]Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

[‡]National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 2, 1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

ABSTRACT: We study the initial nucleation dynamics of poly(3-hexylthiophene) (P3HT) in solution, focusing on the relationship between the ordering process of main chains and that of side chains. We carried out Langevin dynamics simulation and found that the initial nucleation processes consist of three steps: the ordering of ring orientation, the ordering of main-chain vectors, and the ordering of side chains. At the start, the normal vectors of thiophene rings aligned in a very short time, followed by alignment of main-chain end-to-end vectors. The flexible side-chain ordering took almost 5 times longer than the rigid-main-chain ordering. The simulation results indicated that the ordering of side chains was induced after the formation of the regular stack structure of main chains. This slow ordering dynamics of flexible side chains is one of the factors that cause anisotropic nuclei growth, which would be closely related to the formation of nanofiber structures without external flow field. Our simulation results revealed how the combined structure of the planar and rigid-main-chain backbones and the sparse flexible side chains lead to specific ordering behaviors that are not observed in ordinary linear polymer crystallization processes.



1. INTRODUCTION

Recently, poly(3-hexylthiophene) (P3HT) has attracted much attention as a material for polymer semiconductors with potential applications in field-effect transistors owing to its high carrier mobility. In particular, since synthesis methods for obtaining highly controlled regioregularity in side chains have been reported,^{1,2} the mobility increased markedly because the thiophene rings of the main chain can maintain their coplanar position, and the π -electron-conjugated structure along the main chain can be developed without any steric hindrance between side chains in head-to-tail regioregularity. Furthermore, the control of regioregularity leads to P3HT molecules forming a highly ordered self-organizing structure through π - π interaction between thiophene rings.

The P3HT nanofibrous structure crystallized from certain types of poor solvent has been investigated vigorously^{3–20} and is expected to be used in hyperfine transistors of flexible and printable organic devices owing to its unique configuration. The dimensions of this nanofiber are 2–15 nm in width and several micrometers in length, and the aspect ratio is more than 100. Structural properties such as the diameter and branching properties of the conductive nanofibers are affected by molecular weight, chain length, type of solvent, and preparation temperature, which complicate self-organization processes.

Moreover, there remain many unresolved problems on the details of ordering mechanisms.

Structure formation processes of polymer systems have been extensively studied by computer simulations.^{21–37} In particular, simulations of crystallization processes have been mainly studied for linear polymer systems, and side chains are usually obstacles to obtaining ideal crystals from these systems. Alternatively, P3HT, which has a complex structure with a rigid-main-chain backbone and flexible side chains, may have unique features in relation to crystallization processes compared with conventional linear polymers. Because the side chains of P3HT vary in flexibility and in their interactions with the rigid backbone, they should play different roles in structure formation during crystallization processes. It is also worth noting that anisotropic nanofiber structures of nanometer-scale diameter are spontaneously formed without requiring an external flow. The formation of fibrous structures is related to the extreme difference in growth rate among various crystallographic axes.

For studying the structure formation dynamics of these complicated polymer systems, molecular dynamics simulation

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can be a useful tool. However, simulations of structure formation in some solutions are usually more difficult than those in a vacuum, because solution systems contain many solvent molecules. In addition, organic solvent molecules, such as anisole, which consists of 16 atoms, are considerably larger than the solvent water; hence, these solvent molecules make the simulation time extremely long. Therefore, we here used Langevin dynamics simulation in which the effects of random fluctuation and frictional forces are included.^{34,35} The screening effect of electrostatic interaction with solvent molecules was considered using the dielectric constant of solvent molecules. These simulation results would provide information on the basic nucleation and growth mechanism of crystallization of P3HT solutions. Although there are many simulation studies on the static structure of P3HT crystals,^{38–41} its crystallization dynamics in solution has not been systematically investigated until now. Hence, in this study, we carried out molecular simulations of crystallization of P3HT in solutions, and considered the effects of rigid backbone rings and flexible side chains on the ordering dynamics, particularly focusing on the role of shape, strong interaction of thiophene rings, and interaction of side chains.

2. MODEL

We performed Langevin dynamics simulation to investigate the structure formation processes of P3HT in solutions, particularly on the initial nucleation dynamics. Nanofibers of P3HT are generally prepared in solutions such as *p*-xylene, chloroform, and anisole. However, the explicit solvent model requires considerable simulation time for the study of dynamic processes. The Langevin dynamics method is suitable for clarifying the basic mechanism of structure formation in solutions. In this study, we used GROMACS 4.5.4,⁴² in which the force field we used was the generalized Amber force field, and the electric charges were determined using MOPAC 6. The cutoff distance of pairwise forces was 1.0 nm. The degree of polymerization of P3HT was 10, and the number of P3HT molecules in the system was 32. The size of the simulation box was 15.0 nm, and the periodic boundary condition was applied. Since we studied the formation of isolated crystal nuclei in the solution, the finite size effect on the stability of the crystalline phase would be negligible in this condition. The relative dielectric constant inside the simulation box was 4.33, which corresponds to that of the anisole solvent. Since the Langevin dynamics is based on a kind of coarse-grained model, in which the effects of solvent molecules are included indirectly, it would be preferable to express the time scale in dimensionless reduced units.^{35,42} In this study, we used the reduced dimensionless units for alkane chains, in which 1 reduced time unit corresponds to 2.01 ps.²¹ The actual scaling factors between the reduced units and real units might be changed by various solvents. Initial states were prepared by randomly allocating P3HT molecules in the simulation box. Then, we observed the structure formation processes at a constant temperature (300 K) and volume until $t = 25\,000$. The time step of simulation was 0.000 25. We carried out 10 simulation runs from the different initial states and examined the average properties.

In order to analyze the ordering processes, we calculated the orientational order parameters of the main chains and side chains. In the calculation of main-chain orders, we used the main chain vector that connects the t2 carbon and t5 carbon of thiophene. In the calculation of side-chain orders, we used the

side-chain vector that connects the 3-carbon of thiophene and the carbon at the end of the side chain. The main-chain and side-chain vectors are shown in Figure 1. An orientational order

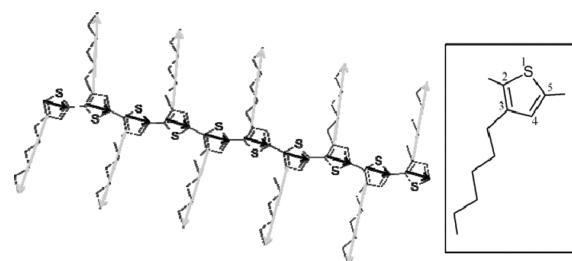


Figure 1. For the analysis of the chain order of P3HT, we used the main-chain vector and side-chain vector. The main-chain vectors are indicated by black arrows. The side-chain vectors are indicated by gray arrows.

parameter is given by $\langle 3 \cos^2 \theta - 1 \rangle / 2$, in which θ is the angle formed by two corresponding chain vectors. A global order parameter is defined by averaging over all chain vector pairs in the entire system except for chain vector pairs within the same molecules. The global order parameter of main chains or side chains is useful for the estimation of overall ordering processes. An intermolecular local order parameter is obtained by averaging only the pairs of neighbor chain vectors of different molecules. In our simulation, we regarded two chain vectors to be in the neighboring region when the distance between their centers was less than 0.5 nm for main chains and 1.0 nm for side chains. The intermolecular local order parameter of main chains or side chains is useful for the observation of nuclear formation and growth of the crystal interface. An intramolecular local order parameter is obtained by averaging over the pairs of bonds within the same molecules.

We also calculated the orientational order of the normal vector of the thiophene ring to investigate the role of the planar ring in the ordering dynamics. The relationship between ring orientation and stacking process would give us more detailed information on chain alignment. For the calculation of normal vectors, we used the cross product of two vectors. One is the vector that connects the t3 carbon and sulfur atom of the thiophene ring, and the other is the vector that connects the t4 carbon and sulfur atom of the thiophene ring. Global, intermolecular local, and intramolecular local order parameters of normal vectors were calculated using the same procedure as those of chain vectors.

Crystallization processes during the formation of P3HT nanofibers can also be traced effectively on the basis of crystallinity. Crystallinity is the ratio of the number of main chains that belong to the crystals to the number of all the main chains in the system. In our simulation, a crystal domain is defined as the group of main-chain vectors that are within 0.5 nm of each other and whose orientation difference is less than 15° . We did not include any group of less than 15 segments among the crystal domains.

3. RESULTS AND DISCUSSION

The structure formation processes of P3HT are shown in Figure 2. In the initial state ($t = 0$), P3HT molecules are randomly distributed in the solution. In the initial period, $2500 < t < 5000$, P3HT molecules slowly assemble. Small crystal nuclei are formed at approximately $t = 15\,000$. For a better

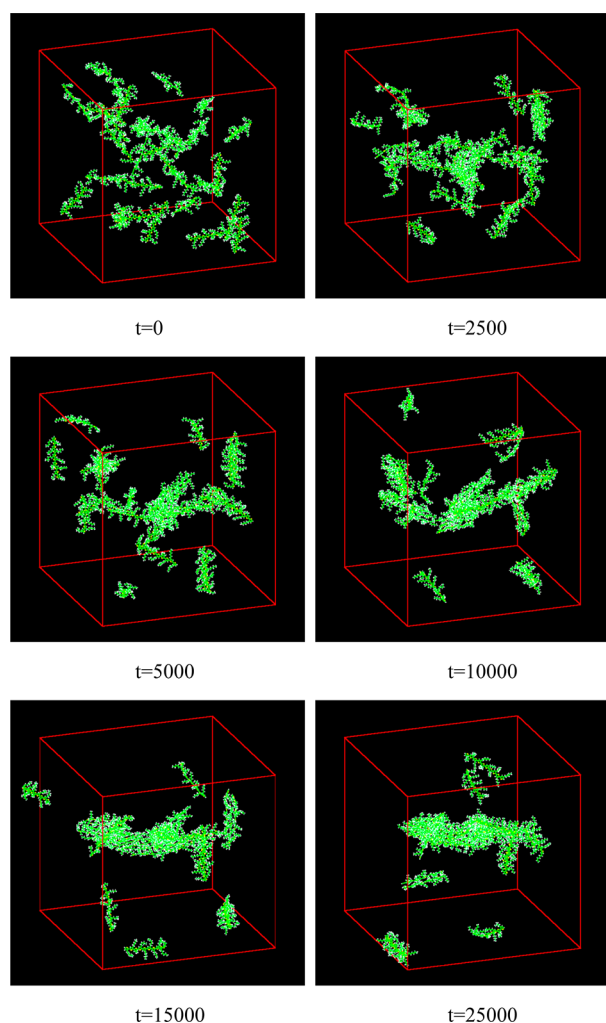


Figure 2. Example of structure formation processes of P3HT molecules. In solutions, crystallization processes are slow owing to the screening effect and random forces of solvents. Small crystal nuclei were formed at approximately $t = 15\,000$.

perspective of the initial crystal nuclei, the ordered region of P3HT at $t = 25\,000$ is shown in Figure 3. Figure 3a shows the top view, which is observed from the direction perpendicular to the thiophene ring, and Figure 3b shows the side view, which is observed from the direction parallel to the thiophene ring and main chains. These figures indicate that the initial crystal nuclei

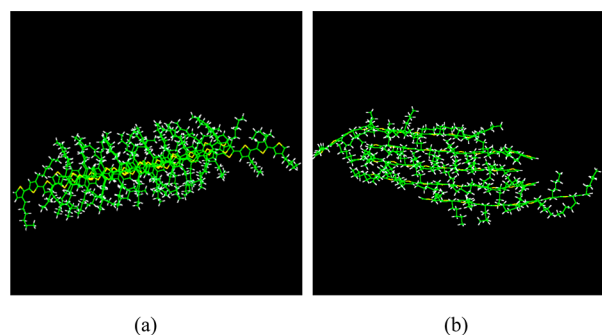


Figure 3. Images of initial crystal nuclei. (a) Top view, perpendicular direction of thiophene rings. (b) Side view, parallel direction of thiophene rings.

grew through the stacking of thiophene rings. The lateral position and direction of main chains in each layer are almost ordered, but the directions of side chains are not completely aligned in the initial periods.

From Figure 4, we examined the stacking direction of thiophene rings during the crystallization processes. Here, we

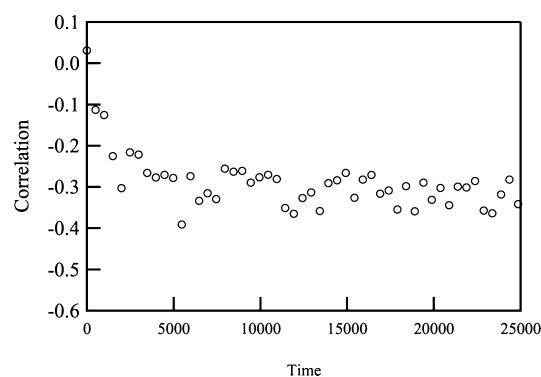


Figure 4. Ordering process of stack layers. The vertical axis shows the correlation of direction of thiophene rings between the nearest upside or downside layers. In the initial period, the correlation is near zero, which indicates that the P3HT molecules stack randomly. Then, P3HT molecules rapidly adjust their arrangement, and they prefer stacking alternately.

evaluated the ring direction as 1 or -1 when two adjacent thiophene rings take the same direction or the opposite direction, respectively. When the rings stack randomly, the ring direction value approaches 0, whereas it approaches -1 when the rings stack alternately. The simulation result was -0.31 , which indicated that the thiophene ring of P3HT preferred stacking in the opposite ring direction in each layer. This result was also consistent with the well-known crystal structure of P3HT bulk systems.

Next, we examined the time evolution of various order parameters to clarify the initial nucleation processes at the microscopic level. In Figure 5, we showed the time evolution of orientational order parameter for a normal vector of thiophene rings. The intermolecular local order parameter increased rapidly at the start of crystallization until $t = 1000$ and then

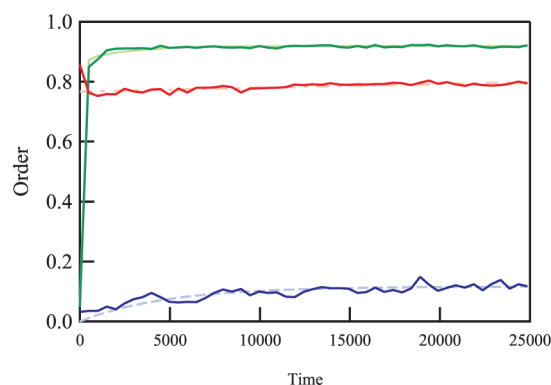


Figure 5. Time evolution of the orientational order of the thiophene ring. Red, green, and blue solid lines indicate intramolecular, intermolecular local, and intermolecular global orders, respectively. The intermolecular local order of the normal vector of the thiophene ring shows a sharp increase at the start of crystallization. The dashed line indicates the fitting curve.

saturated to almost 1.0 after $t = 1000$. On the other hand, the global order parameter increased quite slowly and did not saturate by $t = 25\,000$. The value of about 0.1 at $t = 25\,000$ shows that the crystalline order on a large scale did not appear from the global viewpoint. The orientation of normal ring vectors is closely related to the formation of stack layers. For the analysis of crystallization processes, it would also be important to investigate the ordering of main chains and side chains. Figure 6 shows the time evolution of order parameters

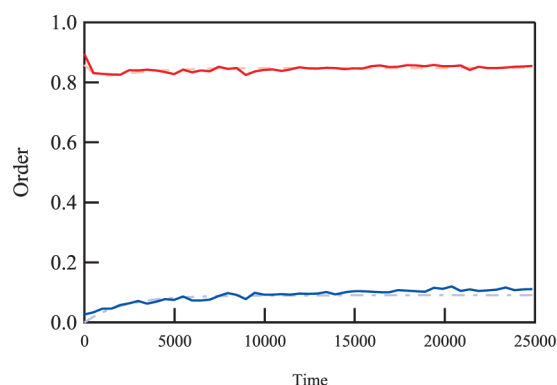


Figure 6. Time evolution of intramolecular orientation order of main chains and side chains. The red and blue solid lines indicate the main chains and side chains, respectively. The conformation of the main chains of single molecules is not affected largely during the crystallization processes. On the other hand, the orientation order of the side chain inside single molecules showed very slow ordering behaviors. The dashed line indicates the fitting curve.

for intramolecular local orders, which is suitable for observing changes in single-polymer conformation during crystallization processes. The intramolecular local order parameter of main chains slightly decreased before $t = 1000$. This is caused by the slight bending of the main chains that are out of the stacking regions owing to the decrease in surface area. On the other hand, the intramolecular local order of side chains showed a different behavior. Although it corresponds to the short-range order, the increase is extremely slow and the value remains small at $t = 25\,000$. Figure 7 shows the time evolution of order parameters for intermolecular local orders of the main and side

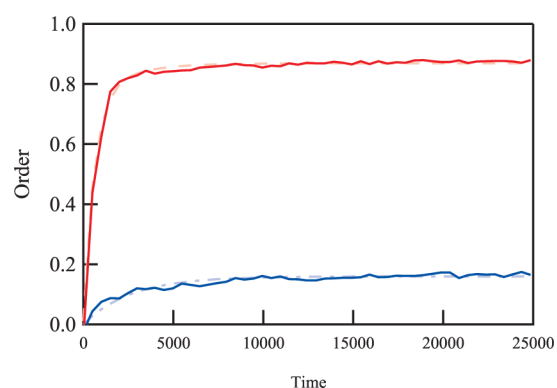


Figure 7. Time evolution of intermolecular local orientation order of main chains and side chains. The red and blue solid lines indicate the main chains and side chains, respectively. The order parameter of main chains increased markedly and rapidly in the initial periods. However, its growth is slightly slower than that of normal vectors of thiophene rings, as shown in Figure 5. The dashed line indicates the fitting curve.

chains. The order parameter of main chains increased rapidly until $t = 2500$, and the saturated value was almost the same as the intramolecular value. This coincidence indicates that the thiophene rings order at a high degree of about 0.8 with no difference in intramolecular or intermolecular attribution even at the initial small crystal nuclei. Alternatively, the order parameter of side chains increased more slowly than that of main chains, and it seemed to be impossible to achieve a high value comparable to that of main chains. In Figure 8, we show

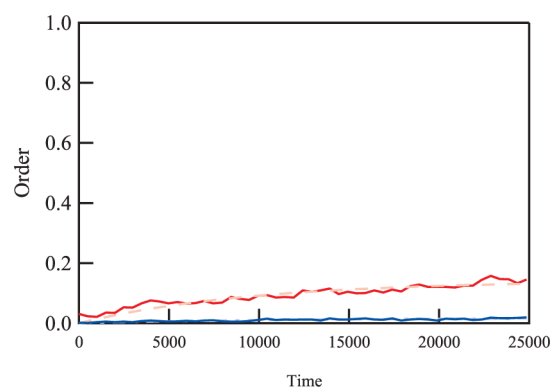


Figure 8. Time evolution of the intermolecular global orientation order of main chains and side chains. The red and blue solid lines indicate the main chains and side chains, respectively. Because the initial crystal nuclei are still small at $t = 25\,000$ and other small clusters are randomly distributed in solutions, the global order parameters are small. The dashed line indicates the fitting curve.

the time evolution of global order parameters of the main and side chains. Because the P3HT molecules did not assemble into one cluster during the simulation, the global order parameters are considerably smaller than the local order parameters. In addition, although the global order of main chains steadily increased, the global order of side chains was almost zero during simulation. Because the global order parameter does not increase with the formation of small aggregates or crystallization in random directions, it would be preferable to use different parameters to monitor such growth processes. In Figure 9, we show the time evolution of crystallinity, which shows a slow but steady growth, which is different from the case of global order parameters. This tendency means that the system is in the polycrystalline state during the simulation.

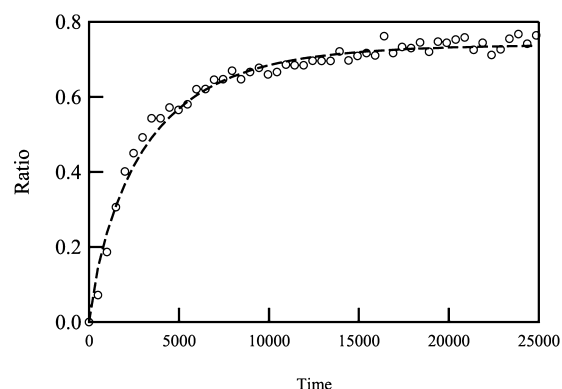


Figure 9. Time evolution of crystallinity. The growth speed of crystallinity is slightly lower than that of intermolecular local order of main chains. Crystallinity steadily increased in the initial period, which is quite in contrast to the growth of global order parameters.

The results showed that it took a longer time for the crystal nuclei to grow than the local order of main chains. In the crystallization of polymer systems, the time evolution of crystallinity $C(t)$ is often expressed by the stretched exponential function given by $C(t) = A - A \exp(-(t/\tau)^n)$, in which the exponent n depends on the crystallization processes. From our results, the parameters were determined as $A = 0.72$, $n = 1$, and $\tau = 3100$, and then $C(t)$ was fitted by a normal exponential function. In our simulation, we examined the initial nucleation within a limited simulation time and we did not investigate the secondary growth of crystallization; hence, the analysis was applied to the formation dynamics of initial crystal nuclei. For the investigation of crystallization growth in the intermediate or late periods, we suggest that monitoring be carried out using larger systems for a longer time at a higher threshold of a criterion of crystal domains.

The time evolution curves of the global or local order parameters are expressed by a single exponential function $A_1 [1 - \exp(-t/\tau_1)]$ or a double exponential function $A_1 [1 - \exp(-t/\tau_1)] + A_2 [1 - \exp(-t/\tau_2)]$. We summarized the fitting results in Table 1. The time evolution of intermolecular local

Table 1. Relaxation Times and Amplitudes of Various Order Parameters

	τ_1	A_1	τ_2	A_2
local order (direction of ring)	100	0.81	2500	0.049
global order (direction of ring)	4900	0.12		
intramolecular order (side chain)	7100	0.090		
local order (main chain)	590	0.74	2100	0.12
local order (side chain)	2600	0.16		
global order (main chain)	9500	0.14		
global order (side chain)	11000	0.018		

order of main chains and that of the normal vector of rings are better fitted by a double exponential function. In contrast, other order parameters can be fitted by a single exponential function. These findings suggest the following mechanism of initial nuclei formation, as schematically illustrated in Figure 10. At the start of structure formation, the neighboring thiophene rings aligned in a very short time ($\tau = 100$, Figure 10a). Then, the neighboring main chains arranged their directions with respect to each other within a short time ($\tau = 590$, Figure 10b), which took more than 5 times longer than the ring alignment. At this time, side chains were not yet ordered and remained in various directions. The ordering of side chains proceeded after the formation of the stack layer structure, which packs the side chains into limited free spaces (Figure 10c). The side chain ordering took almost 5 times longer than the main chain ordering.

Hence, the simulation results revealed that the initial nucleation of P3HT in solution consists of various ordering processes, namely, ring ordering, main-chain ordering, and side-chain ordering. The time scales of these three ordering processes are markedly different. The planar shape and strong interaction between thiophene rings play an important role in the initial nucleation processes. These factors caused the anisotropic nuclei growth, in which P3HT molecules stack perpendicularly to the thiophene ring plane, but the growth in other directions, namely, the side-chain direction, was rarely observed. In the case of polymers with an axial symmetry, such as polyethylene melts, crystal nuclei showed an ellipsoid structure. In addition, the side chains of P3HT also play an

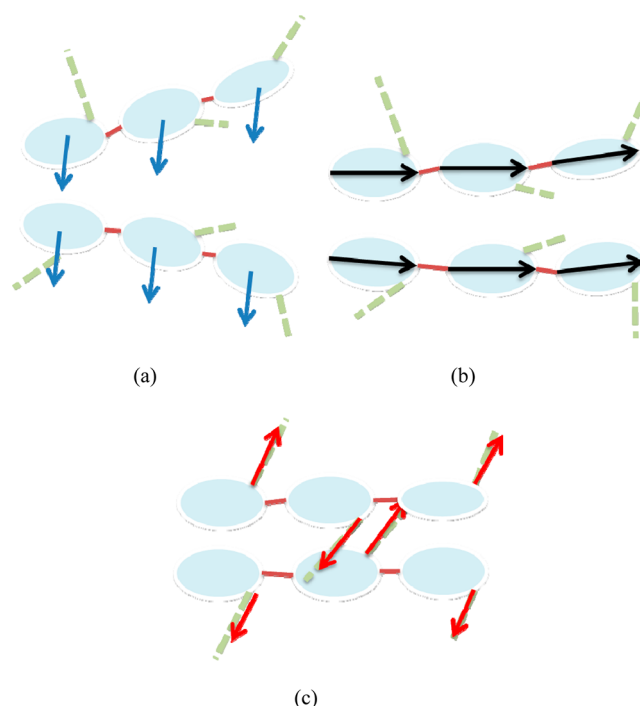


Figure 10. Schematic illustration of the ordering mechanism of P3HT in solutions. (a) At the start, the neighboring thiophene rings aligned the normal vectors. (b) Next, the neighboring main chains arranged their directions. At this stage, side chains were in various directions. (c) Finally, formation of the layer structure of main chains limited the free space of side chains, which caused the alignment of flexible side chains.

important role in anisotropic nucleation growth. Because the ordering of side chains was extremely slow, the side chains were in various directions at the initial nucleation period. These side chains acted as buffer spaces, and the growth of an ordered structure in the side-chain directions became more difficult than growth perpendicular to the ring plane.

Note that the strong thiophene ring interaction and rigidity of main chains have another role in side chain ordering. In general, branched polymers show a lower crystallinity. For example, branched polyethylene systems showed an extremely slow chain ordering, as shown in Figure 11. This system consists of a branched polyethylene and the degree of polymerization of the main chain is 40, with 10 side chains

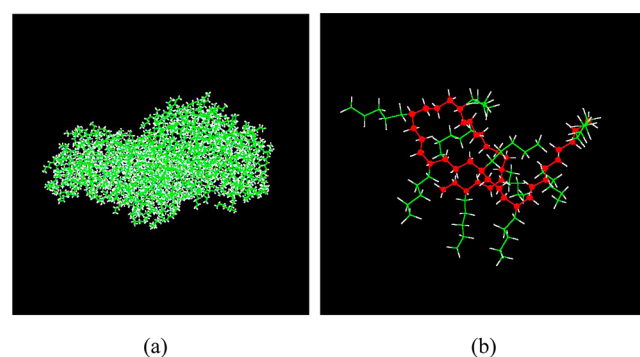


Figure 11. Images of crystal of branch polyethylene. (a) Overall structure. Since there are too many side chains, crystallization is markedly inhibited. (b) Conformation of single branch polyethylene in the assembled structure. The red part indicates the main chains.

of five carbon length. This simulation result was obtained by molecular dynamics simulation in a vacuum, but we suppose that the final structure would not be significantly changed in solution simulation for the static properties. The alignment of main chains competed with that of side chains in these branched systems. This inhibited the stretching of main chains owing to the random local ordering of side chains in various processes including the main chain and side chain pairs. The conformation of the main chain is shown in red in this figure, which was almost a random coil structure. Thus, the rigidity and chain stretching of the main chain is very important for side chain polymer systems to form regular crystal structures.

Next, we will consider the relationship between experimental results. In Figure 12, we show the scattering function of

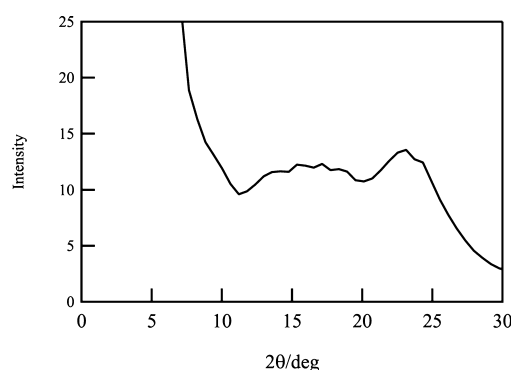


Figure 12. Scattering function of crystal nuclei obtained from simulations. The peak at 23° corresponds to the interlayer distance.

structures obtained from Figure 3. The scattering profile is in good agreement with the results observed from X-ray scattering experiments. The peak at $2\theta \approx 23^\circ$ corresponds to the interlayer distance of 0.38 nm along the longitudinal direction, which is related to the (0, 2, 0) peak.^{1,43} The strong anisotropic shapes in the crystal nuclei might also be related to the long fiber formation, in which the fiber direction is the same as the direction of thiophene ring stacking.

Next, we will mention the effects of potential details. For the study of structure predictions or polymorphism of crystal phases, potential details might become an essential factor, since the bulk structures are strongly affected by the weak differences in energies of the various competing phases. However, our study intended to investigate the dynamics of initial nucleation of nanofibers, in which fluctuations of the structure formation are considerably large due to the large free volume around polymers. Therefore, the dynamics are discussed from the ensemble average of many random initial states. In this case, the generalized Amber force field would be effective for the clarification of basic ordering dynamics as a first step. We suppose that these potential details would become more significant in some kinds of future works, such as precise analysis of nanofiber structures in the late periods. The effect of solvent polarization is another factor which is not considered in this study. These factors might become important for the future study on the effects of various solvent types such as good or poor solvents on the structure formation processes.

Thus, the simulation results provide qualitative explanations to some extent. However, there remain some problems mainly owing to the restrictions of simulation. Because the simulation with a large degree of polymerization of P3HT is difficult, we used low-molecular-weight systems for the first step. Hence, the

bending structure of main chains in the crystals was impossible to observe in this simulation model. Thus, we concentrated our analysis on the initial nucleation processes, particularly the mechanism of local structure formation. It would also be interesting to estimate the effects of side-chain structure in more detail, in order to fully understand the crystallization processes of P3HT systems, which are characterized by a strong planar main-chain backbone and flexible-side-chain systems. In this study, we considered the nucleation dynamics in solutions. In the case of crystallization from melts, the limited free volume and entanglement effect might suppress the polymer motion, while lack of solvent molecules might accelerate the aggregation. These effects would affect the actual time scale of order formation, but we suppose that the basic ordering mechanisms would not be significantly different in melt crystallization. The mechanism of secondary crystal growth from the nuclei interface would be another interesting topic to study to understand long-fiber formation, because the control of lateral growth and branch structure is important for the preparation of nanofiber structures of P3HT systems. Our simulation results revealed the roles of ring ordering, main-chain ordering, and side-chain ordering in the formation of crystal nuclei. These would be a useful step toward understanding the structure formation of polymer nanofibers.

4. CONCLUSIONS

In summary, we have investigated the crystallization dynamics of P3HT in solutions. We carried out Langevin dynamics simulation using random initial solutions and observed the initial nucleation processes. The scattering profile of initial crystalline domains showed good agreement with the experimental results, which indicated that the stacking structure of the main-chain rings was initially formed. The simulation also confirmed that the thiophene ring of P3HT preferred stacking in the opposite ring direction in each layer. We found that the initial nucleation processes for P3HT in solution begin the ring ordering, followed by main-chain ordering and side-chain ordering. At the start, the neighboring thiophene rings aligned in a very short time. Then, the neighboring main chains arranged their directions with respect to each other, which took more than 5 times longer than the ring ordering. In these fast ordering processes, the planar shape and strong interaction between thiophene rings played an important role. In the meantime, the side chains were not yet oriented. The ordering of side chains occurred through the packing of main chains. When one side of the alkyl chains is fixed, this geometrical constraint often suppresses the crystallization processes. Formation of a regular stack structure of main-chain rings made it easy for the side chains to align, which resulted in the slow order formation in the late period. The side-chain ordering took almost 5 times longer than the main-chain ordering. The slow ordering dynamics of side chains is one of the factors that cause anisotropic nuclei growth, during which the crystalline domain grows faster in the direction of the normal vectors of rings than in that of side-chain vectors. Thus, our simulation results indicated that the combined structure of flexible side chains and rigid-main-chain rings caused the three ordering steps in the initial nucleation period and contributed to the anisotropic structure formation of nanofiber structures.

AUTHOR INFORMATION

Corresponding Author

*Phone: (+81)-29-861-3460. E-mail: miu@ni.aist.go.jp (T.M.), simo@cc.tuat.ac.jp (T.S.).

Notes

The authors declare no competing financial interest.

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