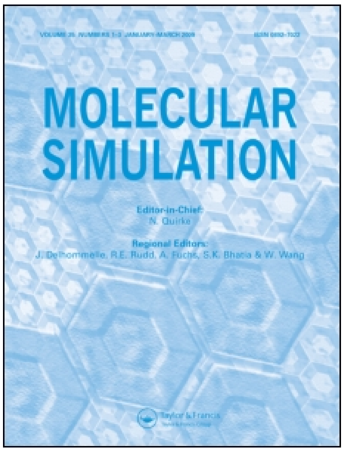

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Order Formation Dynamics in the Early Stage of Melt Crystallization of Polymer Systems

Toshiaki Miura[a]; Ryoichi Kishi[a]; Akira Kaito[a]; Masuhiro Mikami[a]
[a] National Institute of Advanced Industrial Science and Technology, Ibaraki, Japan

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Order Formation Dynamics in the Early Stage of Melt Crystallization of Polymer Systems

TOSHIAKI MIURA*, RYOICHI KISHI, AKIRA KAITO and MASUHIRO MIKAMI

National Institute of Advanced Industrial Science and Technology, AIST Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-0065, Japan

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Order formations dynamics during the crystallization processes of chain molecules have been studied by means of coarse-grained molecular dynamics simulations, mainly focusing on the early nucleation processes. In order to examine the nucleation and fluctuation dynamics in the early regime, we prepared dense melts of flexible chains which contained rigid extended chains as nucleating agents. A long induction time of the melt crystallization was observed for samples with a low nuclei concentration. For both each individual process and for the ensemble average, we present a precise analysis of the time evolution of the orientation order and crystallinity. A stretched exponential form expresses the time evolution curves for low nuclei concentration region. It was found that for the crystallization of chain molecules, the rigid extended chains play a significant role in the ordering dynamics.

Keywords: Molecular dynamics; Polymer; Chain; Crystallization; Nucleation; Induction time

INTRODUCTION

In recent years, simulations of the crystallization processes of polymer systems have been studied by many researchers [1–9]. The Sequenced connectivity of polymer or chain molecular systems adds several unique ordering features not present in the crystallization dynamics of other low molecular systems. Since the molecules have large numbers of internal degrees of freedom, the relations between the local order formation and the overall ordering processes are important factors in understanding the crystallization dynamics of chain molecules. In addition, the co-operative motion of chain molecules plays a significant role in the case of a dense melt. Although the crystallization dynamics of chain molecules have been extensively investigated for the dilute solution or the crystal surface, crystallization processes from dense melts that contain no solvent molecules are still not fully explored [5–9]. This is because the simulations must consider both the extremely slow dynamics of the ordering processes and the large numbers of interactions between chain molecules. Hence, for the study of these melt crystallization processes, it may be helpful to use appropriate coarse-grained models and clarify the universal features in the ordering mechanisms. The coarse grained approaches have provided fundamental and systematic information on the role of the intrinsic properties of molecules or intermolecular interactions.

In previous studies, we have examined the effect of chain rigidity on the early crystallization processes [10]. We found that the chain rigidity has a primary influence on the time evolutions of order parameters, and that the degree of crystallization shows sharp transition at a certain threshold of chain rigidity. For semi-flexible chains, induction periods were observed, in which the time evolution of local order parameters indicated the two different scale processes occur. Although these results give us some insight on the role of internal molecular factors on the crystallization dynamics, many points still remain to be clarified, especially issue involving the nucleating phenomena and detailed behaviors in these long induction periods. The difficulty lies partly in the fact that the chain rigidity promote

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*Corresponding author. Address: National Institute of Advanced Industrial Science and Technology, AIST Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-0065, Japan. E-mail: miu@ni.aist.go.jp

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the crystallization but the ordering process often becomes too rapid to distinguish the various levels of ordering processes. On the other hand, the flexibility easily leads to amorphous structures and ordering processes become hard to observe. Thus, in order to consider the fluctuation and nucleating processes in the induction periods, efficient modeling is necessary. Since associated extended chains become crystal nuclei, which then induce the development of ordering structures, it may be effective to study a model system of flexible chain melts that contain some rigid molecules as crystallization nuclei. Under this condition, the time scales of the chain stretching processes and that of intermolecular co-operative ordering processes are separated, and we can easily examine the nucleating processes. In a recent study, we have reported these crystallization processes induced by rigid molecular nuclei, and have clarified the nuclei concentration dependence of the crystallization dynamics [11]. The long induction periods were observed for the samples of 5% nuclei concentration. Since the order formations in these systems depend on the random concentration fluctuation of nuclei molecules, the order evolution curves of each simulation run largely fluctuate around the averaged order evolution curves. Hence, it is important to include sufficient number of samples in order to reduce statistical errors. It would be also interesting to examine the relation between the averaged dynamics and the single process. In this study, we explored the simulations of the induced crystallization processes of short chain molecules with many simulation runs, and analyzed in detail the ordering dynamics, focusing on systems that show a long induction period.

MODEL

The model and method of the coarse-grained molecular dynamics simulations in this study are almost the same as reported previously [10,11]. We adopted the beads–springs model that is characterized by the chain connectivity and the chain rigidity. The chain connectivity is introduced by the harmonic potentials between the nearest-neighbor segments along the same chain molecules, as given by $U(b) = k(b - b_0)^2$. We applied the Lennard–Jones (LJ)-type potential given by $U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ for the interactions between each segment, except for the pairs between nearest-neighbor or second-nearest-neighbor segments along the same chain. The chain rigidity is introduced by a controlled interaction between the second-nearest-neighbor segments, which is given by the soft-sphere repulsive potential $U(r) = 4\varepsilon[(s_2/r)^{12} - (s_2/r)^6] + \varepsilon \quad \text{when} \quad r < 2^{1/6}s_2$. Detailed features of this polymer model have been reported previously [10]. In our simulations, the parameter values of the model were 0.4 for b_0, and 9000 for k. The values of parameter s_2 were 0.4 for the flexible chains and 1.0 for the extended nuclei molecules. The parameters and results are expressed in dimensionless reduced units. Hence, the rigid molecular nuclei have the same kind of interaction between flexible chain molecules but have different potentials for internal bending only. In this study, flexible chains are chosen as completely flexible. Thus, without rigid molecular nuclei, flexible chains would be difficult to order spontaneously under supercooled conditions. The cutoff length of LJ potential was chosen as 3.0. In this study, we selected short chain systems in order to reduce the calculation time. Hence, the formation of the folded structure is beyond the scope of this study, and we have concentrated on other features, such as the initial nucleation processes of the rigid segments. The number of segments per one chain molecule was 20, the number of chains in the system was 160, and the initial system size was a cubic region with a length of 12.5. We ensured that the size of the simulation box was greater than the length of the fully stretched rigid nuclei molecules, since interactions with their mirror image molecules must be avoided under periodic boundary conditions. The initial states were prepared by thermally equilibrating the systems that contained both rigid nuclei molecules and flexible chain molecules at a temperature of 7.0. Then we suddenly chnged the temperature of the system to 3.0 by velocity scaling, and kept both the temperature and pressure constant during the crystallization processes using the Nose–Hoover method. The volume was changed isotropically. The mass of the thermostat was 3200, the external pressure was 0.007 and its mass parameter was 1.0. The equations of motion are integrated using a forth-order predictor–corrector method with a time step of 0.0008. We carried out simulations for many runs from different initial states in order to reduce the variance of the data in the time evolution curves of the order parameters.

RESULTS AND DISCUSSION

For the analysis of the simulation results, we calculated various order parameters and the degree of crystallization. The order parameters of the molecular orientation are given by $< 3\cos^2\theta - 1 > /2$, where θ is the angle formed by two bond vectors of chain molecules. Averages can be taken among various set of bond pairs. In this study, we used three kinds of orientation orders, which are global order, inter-local order and intra-local order. The global order is defined as the averaged value for all bond pairs in the entire system region except for bond pairs within the same molecules. The inter-local order is the averaged value for the pairs of adjacent bonds, but exclude the pairs within the same molecules. In our simulation, we regard two bonds to be adjacent when the distance between them is less than 1.5. The intra-local order is the averaged value for the pairs of adjacent bonds along the same main chains. We also calculated the degree of crystallization, which is the ratio of the number of segments that belong to the crystal domains to the total number of all segments. The crystal domain is the group of segments whose bond vectors are within 1.5 of each other and whose orientation difference is less than 10 degrees. We did not include in the crystal domains any groups of segments whose number was less than 50.

In Fig. 1, we show the time evolution curves of order parameters during the crystallization processes for the high concentration of rigid nuclei molecules. Here, we carried out four simulation runs from the different initial configurations and the order parameters were calculated as the ensemble average. Since this system includes 40% of rigid molecules, the orientation orders increase very rapidly just after the temperature jump. It seems that the global order and the local orders evolve almost simultaneously for the high concentration region of rigid nuclei.

On the other hand, as shown in Fig. 2, the systems that contain 5% rigid molecules have a remarkably long induction time in the early crystallization processes. Here, we carried out eleven simulation runs from different initial configurations and the order parameters were calculated as an ensemble average. This figure is used on the same conditions as reported previously [11], but the simulation runs in this study were doubled, which makes the evolution curves smoother and reduces the unnecessary dips due to occasional fluctuation noises. As shown in this figure, the orders of flexible chains increased negligibly at first stage. In the meantime, the inter-local order of rigid chains was fluctuating and increased gradually, which corresponds to the nucleation processes. After time 6000, all three of the intra-local, inter-local, and global order parameters of the flexible chains began to increase concurrently along with the global order of the rigid molecules. In this case, one rigid molecule alone was not sufficient to induce the crystallization, since other molecules around the stretched rigid chains remained disordered in that period. The long induction period observed corresponds to the time required to form a nucleus cluster of a certain size by an association of the stretched rigid chains. Direct observation might shed light on these behaviors.

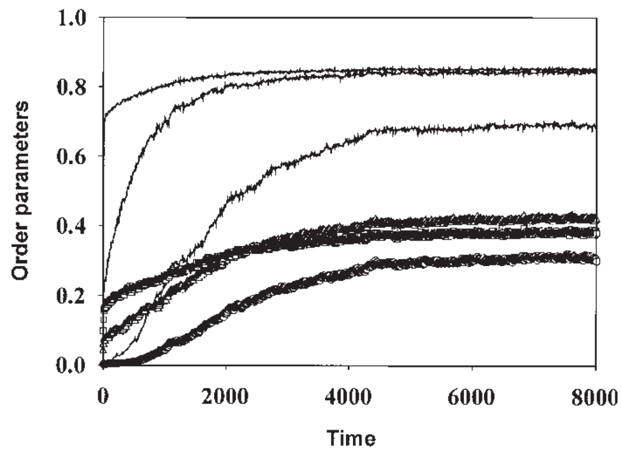

FIGURE 1 Time evolution curves of order parameters of the system with 40% rigid molecules. The lines indicate the order parameters of rigid molecules that function as crystal nuclei. The top line, middle line and bottom line indicate the intra, inter-local and global order parameters, respectively. The marks indicate the order parameters of flexible chains. The squares, triangles and circles indicate the intra, inter-local and global order parameters, respectively.

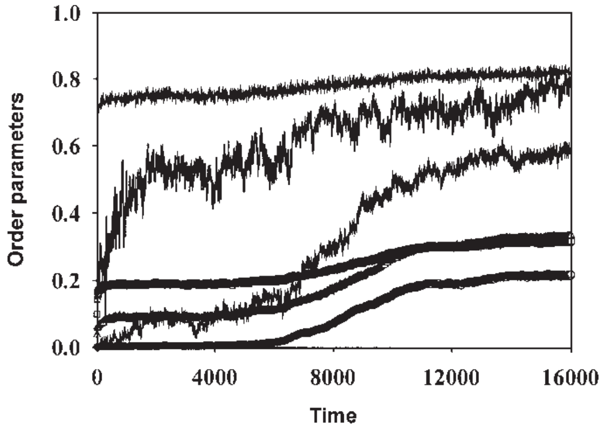

FIGURE 2 Time evolution curves of order parameters of the system with 5% rigid molecules. The symbols are the same as those in Fig. 1.

In Fig. 3, we show examples of the crystallization processes of a system that contains 5% rigid molecules, which showed a long induction period. The molecules in the box were randomly arranged at time 0 (Fig. 3a). At time 5600 (Fig. 3b), some rigid molecules had associated by random fluctuation, while the flexible chains remained almost disordered at the initial stage. At time 8000 (Fig. 3c), the rigid molecules had formed crystal nuclei and some flexible chains had begun to organize. At time 16,000 (Fig. 3d), the most of the chain molecules had oriented to single direction, and the crystallization process was almost completed.

Since there are large fluctuations in the evolution curves for the low concentration region of the nuclei molecules, it would be interesting to compare each of the simulation runs. In Fig. 4, we show the time development of the global orders of the flexible chains that contains 5% rigid molecular nuclei. The open circles indicate the averaged values, which is the same as that plotted in Fig. 3. The results of each simulation runs are shown in thin solid lines. As indicated in this figure, the actual simulation runs have a very large

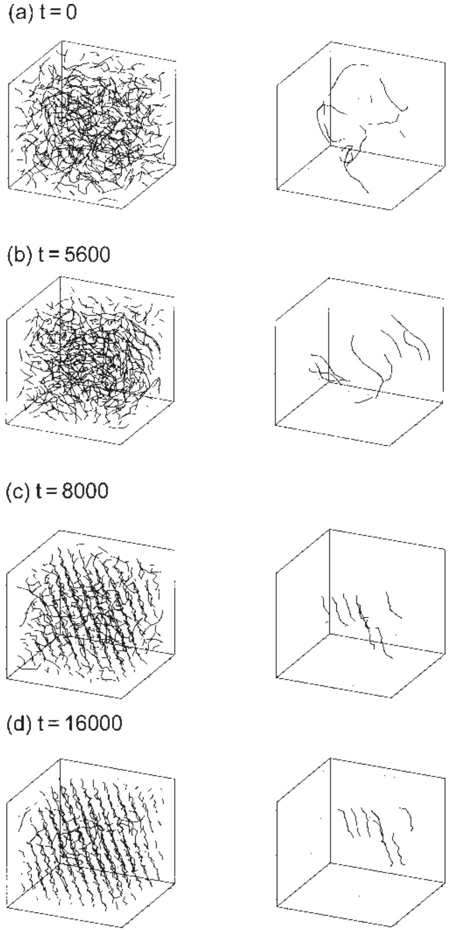

FIGURE 3 Examples of crystallization processes of flexible chain molecules which contain, 5% rigid molecules. (a), (b), (c), and (d) are the snapshots of developments at time 0, 5600, 8000, 160,000, respectively. In each figure, the left picture indicates the whole molecules and the right picture indicates the rigid extended molecules.

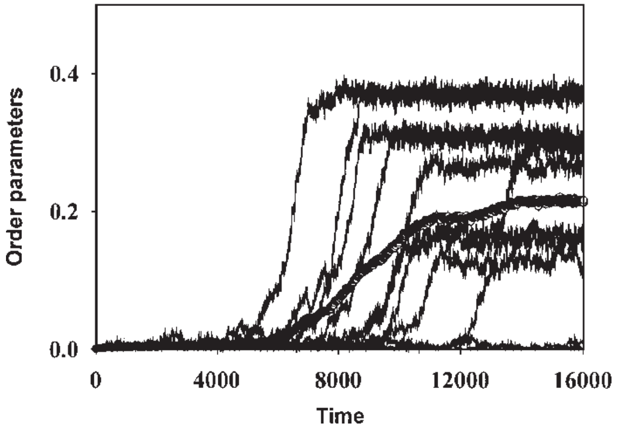

FIGURE 4 Comparison of the averaged time evolution curve and each individual evolution curve. The orientation order shown here is the global order parameters of the flexible chains for the system with 5% rigid molecules.

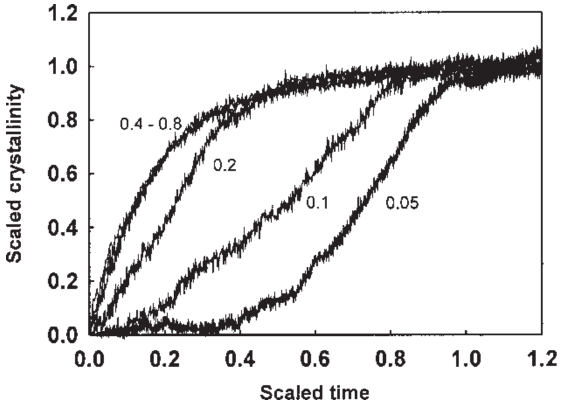

FIGURE 5 Time evolution curves of the crystallinity at different concentrations of rigid molecules are shown at a scaled unit. The curves of 0.4, 0.6 and 0.8 concentrations belong to the same master curve, whereas in the low concentration regions the curves are differently shaped.

variance both in the final value of the order and the incubation time. The formation of the crystal nuclei is purely stochastic process of accidental association, which leads to a large difference in the incubation times. In general, the mobility of the supercooled chain molecules decreased as the time passe, which might have caused low orientation orders for the samples that started the crystallization with longer incubation time. However, there are some occasions during which crystallization takes place with a longer incubation time and a moderate degree of orientation orders. Since the averaged evolution curves are not significantly altered when there are sufficient numbers of samples, the averaged values would be suitable for the comparison with different concentration conditions.

In Fig. 5, we show the scaled evolution curves of the degree of crystallization for various concentrations of rigid molecules. Here, the unit of the final equilibrium values approximately scales the reduced degree of crystallization, and the reduced time is scaled by the approximate time required to complete the crystallization. These curves are averaged over many simulation runs. As shown in this figure, the ordering processes of the systems that contain 40, 60 and 80% rigid molecules fit to the same master curve. In the case of these high-concentration samples, crystallizations begin very rapidly just after cooling. The ordering processes seem to be almost spontaneous, and the induction period of the crystallization processes was not evident from these time evolution curves. In Fig. 6, we depict a comparison of yhe simulation data and the fitting curve for 60% rigid nuclei condition. The simulation data is best fitted by a single exponential curve given by $C = 1 - \exp(-t/0.19)$. The fact that all these evolution curves can be fitted to a certain exponential master curve suggests that the ordering processes are generally based on the same mechanism, in which small order fluctuations grow spontaneously from thermodynamically unstable states. On the other hand, below the concentration region of 10 or 20%, the time evolution curves take on a different shape. They do not show any initial rapid growth.

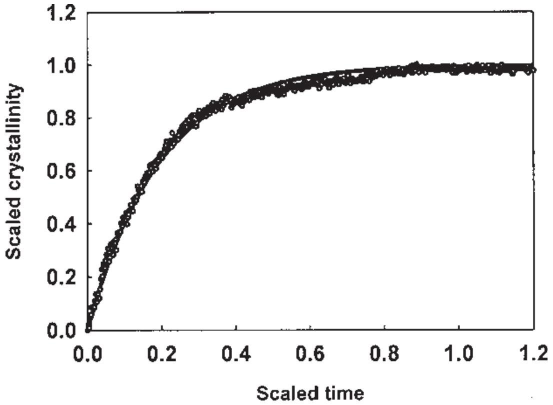

FIGURE 6 Averaged time evolution curve of the crystallinity for the system that contains 60% rigid molecules. Simulation data are indicated as open circles, and the fitting curves are indicated as a solid line.

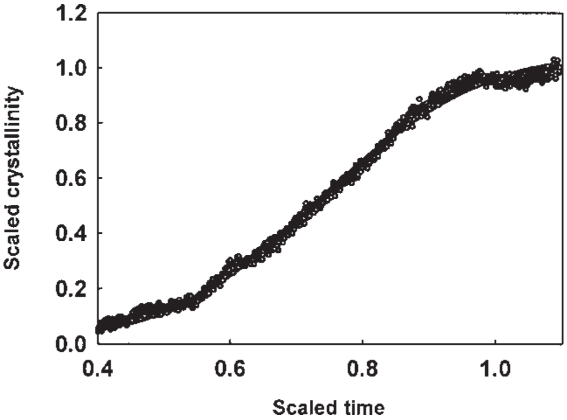

FIGURE 8 Averaged time evolution curve of the crystallinity for the system that contains 5% rigid molecules. Simulation data are indicated as open circles, and the fitting curves are indicated as a solid line.

Comparison of simulation data and fitting curve for the condition of 10% rigid nuclei is shown at Fig. 7. In this case, the time evolution curve becomes a sigmoidal one. The curve is now best fitted by a stretched exponential curve given by $C = 1 - \exp(-t^{2.3}/0.29)$. Although this expression is similar to the Avrami equations in polymer crystallization, an exact comparison would be difficult since the simulation volume is small and the chain length is limited. However, these growth curves illustrate the intrinsic features of diffusion and aggregation limited dynamics in the low nuclei concentration region. When the concentration of rigid nuclei becomes further diluted to as 5% rigid nuclei, for example the long induction period can be observed. The evolution curves remains sigmoidal as well, but the exponent of the stretched exponential equation changes slightly. In Fig. 8, we show the comparison between the simulation data and the fitting curves. Here, because the induction periods are long, those data we displayed only for the time rage when the crystallization growth is dominant. The fitting curve is given by $C = 1 - \exp(-(t - 0.3)^{2.8}/0.15)$. We think that a longer simulation time may be necessary to determine the precise values of the fitting, since there was a sign of a slight increase even at the reduced time 1.0. However, the basic behaviors would remain the same with a longer simulation and additional ensembles. Since the fluctuation of order evolution is very large for the 5% nuclei samples, we show an example of fitting curve for the result of a single simulation run in Fig. 9. In this figure, the induction time range between 0 and 0.6 is omitted in order to magnify the region of crystal growth. The individual evolution curves are also a sigmoidal shape and the fitting curve is given by $C = 1 - \exp(-(t - 0.64)^{3.1}/0.01)$. Although the value of the incubation time varies between each sample, the Avrami exponent of the stretched exponential form remains around 3. These gradual order formation processes indicate that the systems are in a metastable condition in the initial states, where the ordering

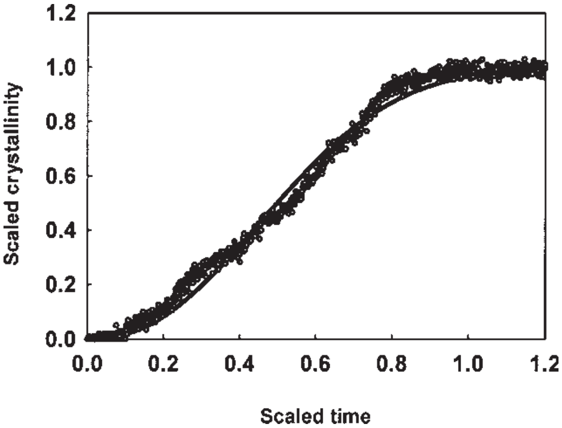

FIGURE 7 Averaged time evolution curve of the crystallinity for the system that contains 10% rigid molecules. Simulation data are indicated as open circles, and the fitting curves are indicated as a solid line.

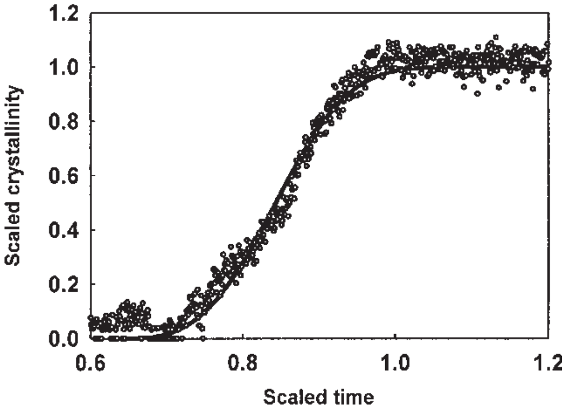

FIGURE 9 Example of time evolution curve of the crystallinity which was obtained by a single simulation run. The system contains 5% rigid molecules. Simulation data are indicated as open circles, and the fitting curves are indicated as a solid line.

dynamics depends on the formation of critical nuclei by random fluctuations. In this simulation, the flexible chains are considered makes them completely flexible, which are very hard to crystallize without nucleating agents. This leads to the relatively high concentration of rigid molecular nuclei in order to crystallize. We think that if the main chains were semi-flexible and had some degree of rigidity, the required concentration of nucleating agents would become smaller as in the actual experimental cases.

CONCLUSION

We have studied the melt crystallization dynamics of the short chain molecules, in which the rigid molecular nuclei induce the ordering processes. While the samples with a high concentration of rigid nucleus molecules showed rapid and spontaneous ordering dynamics, the samples with a low concentration of rigid nucleus molecules showed clear long induction periods, during which only the inter-local order of rigid molecules developed. To precisely analyze the fluctuation and nucleation behaviors in the low nuclei concentration regions, we used many, simulation runs. The time evolution curves of the degree of crystallization are of a single exponential form in the high concentration region and a stretched exponential form in the low concentration region. These reflect the difference in crystallization dynamics, whether the ordering starts from the unstable state or from the metastable state. The behaviors in the low concentration condition suggest that the formations of some kinds of critical nuclei, which involve the parallel orientation of extended rigid segments, are necessary for the inducement of the overall crystallization. The simulation results also suggested that in the case of the chain molecules, the rigid stretched molecules play an important role in the crystallization dynamics.

Acknowledgements

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