PHYSICAL REVIEW E, VOLUME 63, 061807

Effect of rigidity on the crystallization processes of short polymer melts

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(Received 25 October 2000; published 25 May 2001)

Order formation in crystallization processes of the dense melts of chain molecules has been studied by the coarse-grained molecular dynamics method. For semirigid molecules, the parallel orientation and elongation of chains take place simultaneously. However, for semiflexible molecules, long induction periods are observed. Time evolution studies of local order parameters indicated that two different processes occur, which implies that a precondition exists. For flexible molecules, the structures become mostly amorphous at certain sharp threshold conditions of chain rigidity. It was determined that the rigidity of the main chains strongly influences the dynamic behavior of crystallization for dense melts, particularly in the early stage.

DOI: 10.1103/PhysRevE.63.061807 PACS number(s): 61.41.+e, 81.10.Aj

I. INTRODUCTION

Order formation processes during the crystallization of polymer systems have been extensively studied from both experimental and theoretical points of view. The crystallization phenomena of polymer systems have various unique features in their ordering processes and morphology that are not observed in other molecular systems [1]. When polymer systems are supercooled, they form lamella structures that consist of regularly folded polymer chains. Crystallization initially occurs principally through homogeneous nucleation. After crystal nuclei are created by thermal fluctuations, crystals grow on the surfaces of these nuclei. In some dense polymer systems, the formation of higher order structures such as spherulite is also observed. Many experimental studies have attempted to explore these complex phenomena of crystallization processes using various methods such as calorimetry, spectroscopy, scattering, and microscopy. The results provide valuable information on the evolution of the overall order structure. The crystallization of polymers has also been studied by means of computer simulations. Simulations are useful for examining the dynamical behavior of a single polymer chain. Examples include the secondary nucleation on a growth surface of a polymer crystal [2] or the formation of a crystal nucleus in dilute polymer solutions [3,4]. Difficulties in the numerical simulation of polymer crystallization are due to the slow dynamics of the systems being studied and the numbers of interactions between the many polymers which must be included in the calculations. Hence, in comparison to dilute solution systems or the growth surface process, the simulation of the crystallization of dense polymer melts has not been fully studied, except in the cases of static crystal structures and for melting point properties [5–7]. Recently, order formation processes during the induction period and the early stage of the crystallization process of polymer melts have attracted interest. There are some experimental reports which suggest that the parallel ordering of polymer segments increases during the induction period of crystallization [8,9]. Although this concept seems reasonable to some extent, it requires further experimental or simulation studies to clarify what occurs during the induction period. Simulations for studying the dynamical aspects of order formation in the crystallization process have been attempted for polyethylene melts [10–12]. These studies used the united atom model of polyethylene in order to investigate the trans-gauche transition of main chains. The simulation results showed that the number of trans segments increased before crystal growth occurred. However, these behaviors are not always clear due to fluctuations of the order parameters, and it also remains unclear whether these are universal properties of chain molecules or features specific to the model polyethylene systems. Thus, the order formation process during the crystallization of polymer melts is not fully understood. Another interesting feature of the crystallization of polymer melts is its similarity to the isotropic-nematic transition of liquid crystals. If long sequences of rigid trans conformation are required for the crystallization of polymer melts, these sequences can be regarded as mesogen groups of liquid crystal molecules. In that sense, details of the trans-gauche conformation are not essential, and we may regard the rigidity of polymer chains as one important parameter that determines how crystallization proceeds. Rigid rodlike polymers might form nuclei more easily than less rigid chains because the rigid chains can easily associate in their elongated state. On the other hand, crystallization could be suppressed as a result of the lack of chain mobility. Hence, it is likely that crystallization processes strongly depend on the rigidity of polymer chains. To the best of our knowledge, there have been no studies which examine this effect in the dense melts of chain molecules. Thus, further in-depth analysis is necessary in order to understand the microscopic features of order formation during crystallization. In this study, we have employed the coarse-grained polymer model that includes a parameter to control the rigidity of main chains. We carried out the molecular dynamics simulation for the crystallization processes of the model melts of chain molecules. We found that the degree of crystallization or the order parameters show a sharp transition at certain thresholds of chain rigidity. Our study also indicates that the time evolution of order formation is influenced by the rigidity of the main chains, particularly in the induction period.

II. MODEL

We used the molecular dynamics method to study the simulation of the crystallization process of dense melts

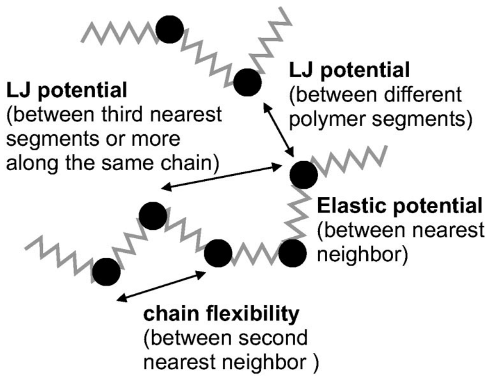

FIG. 1. The schematic picture of coarse grained polymer model. Here modified LJ potential was introduced to control chain flexibility between second nearest segments along the same polymer chain.

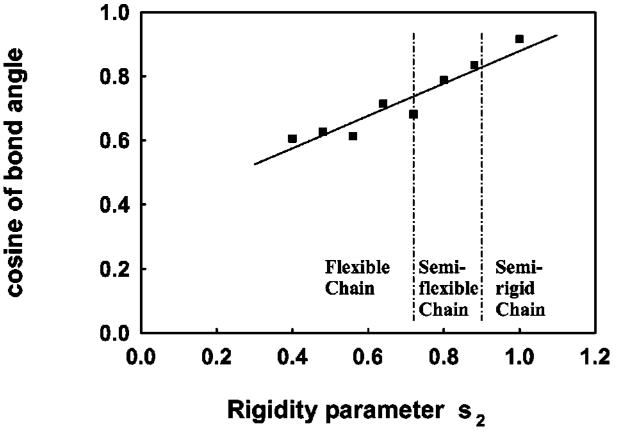

FIG. 2. The relation between the rigidity parameter s_2 and the angle correlation of two successive bond vectors.

[13,14]. In order to investigate the universal behavior of chain molecules, we adopted a coarse-grained model in which the segments are represented by beads; these segments are connected to each other by springs as shown in Fig. 1. We applied the Lennard-Jones (LJ) type potential given by $U(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$, for the interaction between the segments, except for the interaction between nearest-neighbor or second-nearest-neighbor segments along the same chain. We employed dimensionless reduced units, in which the length and energy are scaled by the strength (ϵ) and the length scale (σ) of the LJ interaction, respectively. The time scale is also scaled by $(m\sigma^2/\epsilon)^{1/2}$, where m is the mass of one segment. For the interaction between the nearest-neighbor segments of the same chains, we used a harmonic potential given by $U(b)=k(b-b_0)^2$. The chain rigidity can be introduced using various methods. It may be possible to control the distribution of chain conformation by changing the potential energy of the trans and gauche states or the potential barrier between trans and gauche states in the united atom alkane model. However, these parameters are not a direct measurement of chain rigidity but rather are related in a more complicated manner. Instead, we added additional interactions between the second-nearest-neighbor segments of the same chains. This interaction has the LJ-type potential given by $U(r)=4\epsilon[(s_2/r)^{12}-(s_2/r)^{6}]$, in which the chain rigidity can be easily controlled by the value (s_2) of the interaction range. In our model, we used the same value for the strength parameter (ϵ) as for the LJ potential. Strictly speaking, the difference in the interaction between second-nearest-neighbor segments may cause a slight difference in the average bond length. We think that it can be negligible, as the difference is less than 10% in our simulation range. For the simulation of chain molecules, it is important to consider how the geometrical constraints of the main chains where a chain cannot cross another contribute to the slow dynamics of dense melt systems. This can be achieved by choosing values for the equilibrium spring length that are sufficiently lower than the diameter of the segments. In that case, the excluded volume effect of the chain segments prevents bond crossing. In our simulations, parameter values were 1.0 for the segment diameter σ, 0.4 for the equilibrium bond length b_0, and 9000 for the elastic constant k of the bond springs in reduced units. The number of segments in one chain molecule is 20 in our simulation. Initially, the number of chain segments appears to be rather small considering the fact that simulations of polymer dynamics in melts have been carried out with more than 100 chain segments [15,16]. However, in the case of the simulation of crystallization, there are some restrictions. One is that the attractive LJ potential has to be included in order to achieve crystallization at low temperature, which results in a higher segment density in the melting state than that of polymer melts with purely repulsive LJ potential. Another factor is that the size of the simulation box should be sufficiently large that the fully extended chain in the crystal state should not exceed the periodic boundary conditions. The latter condition is particularly critical and we had to compromise the chain length to some extent in order to satisfy it. In our simulation, the initial system size was a cubic region with a length of 12.5 in reduced units, which was chosen to be greater than the length of the fully extended chains. Periodic boundary conditions are applied to the simulation box. A large number of chain molecules were placed in this region so that the number density became 1.64. Then we prepared the initial states by thermally equilibrating these oligomer melts at temperatures well above the crystallization temperature. For simulations of the crystallization processes, the temperatures of the systems were suddenly quenched to low temperatures. Both the temperature and pressure were kept constant using the Nose-Hoover methods.

III. RESULTS AND DISCUSSION

In order to examine the properties of the rigidity parameter s_2, we first calculated the correlation of the bond vectors in dilute solution. In Fig. 2, we show the average cosine angle of two successive bond vectors along the chain. In this simulation, the chain length was 50 and the temperature was 6.0 in reduced units. We varied the value of the parameter s_2 between 0.4 and 1.0. As shown in this figure, the angular correlation linearly increases as the parameter s_2 approaches 1.0. In the case of $s_2=1.0$, the value of the average cosine is 0.92 and the chain conformation is nearly rodlike, while the

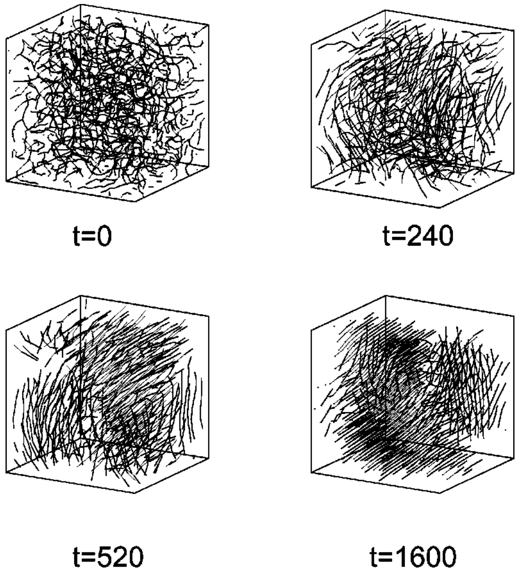

FIG. 3. Typical crystallization process of semirigid chain melts.

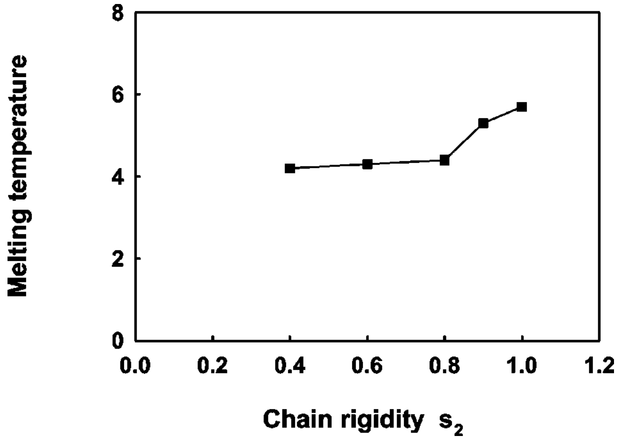

FIG. 5. Relationship between the chain rigidity and the melting temperature.

chain can be regarded as almost flexible for $s_2 = 0.4$. Thus, it was confirmed that the parameter s_2 is an appropriate variable for controlling the chain rigidity in future simulations. In Fig. 3, we show a typical crystallization process for semirigid chain melts. The crystallization regions grow gradually after cooling and finally become large domains. Although it is possible to form a large single crystal domain from appropriate initial states, in many cases the crystal structure consists of several domains and some amorphous regions. Unlike crystallization growth from dilute solutions, many crystal nuclei appear for dense melts under very rapid cooling conditions. These nuclei form crystal regions, each with a different orientation. Some of them are absorbed into other larger crystal domains, but the rest remain as defects. In Fig. 4, we demonstrate the typical dependence of the initial state in the ordering processes. Here, we prepared many samples of the melts and observed their crystallization processes. In order to compare each sample, we calculated both a global orientation order and a local orientation order, which are widely used in polymer simulations. The global orientation order is defined as the average of the order parameter $\langle 3\cos^2\theta - 1\rangle/2$, where θ is the angle formed by two bond vectors of the main chains. In this case, the averaging included all bond pairs in the entire system region. The local orientation order is similar to the global orientation parameter except that the averaging of bond pairs is only calculated for adjacent bonds. In our simulation, we regard two bonds to be adjacent when the distance between them is less than 1.5. As shown in Fig. 4, the time evolution of the local order parameter does not depend significantly on the initial state. However, in the case of the global order parameter, the time evolution and final orientation order are strongly affected by the initial state. Since there are such large fluctuations in the evolution of the global order parameters, it may not be sufficient to discuss the evolution curves of only one sample. Therefore, we decided to prepare many samples and use the average evolution curves. Although this requires significant computational resources, we are thus able to estimate the effect of various external conditions on the crystallization processes of melts. In this report, we use the average of about 10 samples. It is well known that the crystallization processes are affected by the degree of supercooling. Hence, in order to simulate each crystallization process at the same degree of supercooling, we first examined the melting temperature with various chain rigidities. For the determination of melting points T_m, we prepared a well-ordered crystal state and observed the orientation order and the system volume at various temperatures. These values show a large change at T_m, and the simulation results are summarized in Fig. 5. As shown in this figure, the melting point increases slightly as the chains become rigid. In our later simulations, we decided to observe the crystallization processes at the temperature of $0.7T_m$.

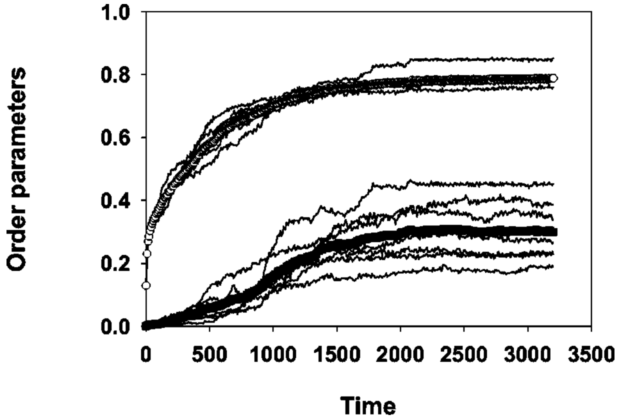

FIG. 4. Development of order parameters during the crystallization processes for various initial melts. Filled squares indicate the global order parameters averaged over many samples. The open circles indicate the local order parameters averaged over samples. Solid lines indicate each crystallization process for various initial melts.

Next, we examined how the rigidity of chains affects the crystallization time evolution and structure. In Fig. 6, we show the influence of rigidity on the final crystal order at $T = 0.7T_m$. Here, the global order and the local order are plot-

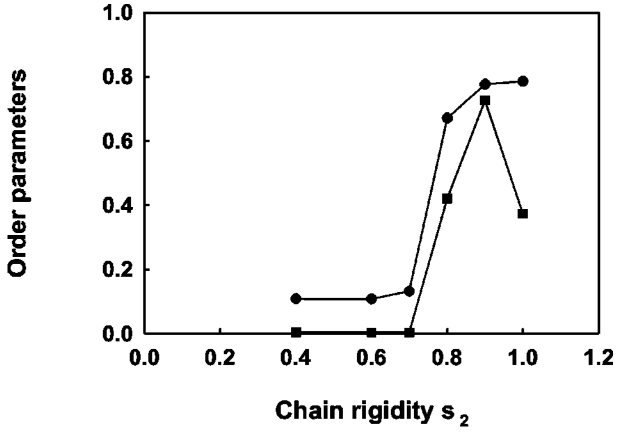

FIG. 6. Relationship between the rigidity of main chains and the final crystallization order. Circles are for the local order; squares are for the global order.

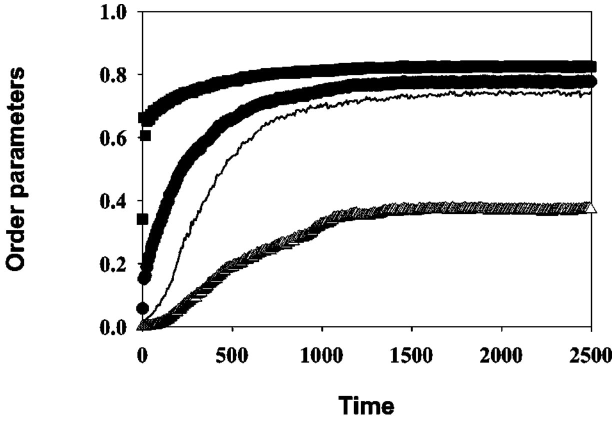

FIG. 7. Order formation processes of semirigid chain melts. Filled square are for intrachain local order parameter; filled circle are for interchain local order parameter; open triangles are for global order parameter; solid lines are for the degree of crystallization.

ted on the same chart. For flexible chains where s_2 is near 0.4, we cannot observe large crystal domains. These flexible chain melts were frozen without forming a distinct ordered structure, and the value of the global order parameter approached zero. However, when the main chains became rigid beyond a certain threshold of rigidity, the formation of an ordered structure began sharply. It is also interesting that the local order parameter increases slowly in the range of s_2 between 0.8 and 1.0, while the global order parameter shows a maximum at 0.9. This is due to the formation of smaller domains that have different orientation orders than the main ordered domain. We shall return to this point later.

In previous arguments, we used the global order parameter and the local order parameter. In order to closely examine the relationships between the local chain conformation, the local chain association and the domain growth of crystals, we defined the following parameters. One is the degree of crystallization, which is defined as the ratio of the number of bonds that belong to the crystal domain to the number of all bonds in the system. Here the crystal domain is defined as the group of segments whose bond vectors are within the distance of 1.5 apart and the orientation difference between bond vectors is less than 5°. We did not include any group of less than 20 segments among the crystal domains. Other defined parameters include the intrachain local order parameter and the interchain local order parameter. They have a definition similar to the local order parameter except that they are calculated only for the same chains or different chains, respectively. Using these order parameters, we investigated the order formation process during the initial period of crystallization. In Fig. 7, we show the crystallization behavior of semirigid chain melts. The simulation parameters are $s_2 = 1.0$ and $T = 4.0$ $(= 0.7T_m)$. In the case of semirigid molecules, chains extend very rapidly after cooling, as shown in the time evolution of the intrachain local order parameter. The local chain alignment, which is represented by the interchain local order parameter, proceeds on a slightly longer time scale than the extension of single chains. Although the development of the global order parameter is slower than that of the two local order parameters, it seems likely that the local chain alignment and the global crystallization processes take place almost simultaneously for semirigid melts. In this case, the induction period of the crystallization processes was not clearly evident from the time evolution curves of the order parameters. We show the crystallization processes of semiflexible chain melts in Fig. 8. The simulation parameters are $s_2 = 0.8$ and $T = 3.0$ $(= 0.7T_m)$. As the chains become more flexible, the crystallization processes slow down. In addition, the time evolution curves of the order parameters exhibit different behaviors from those of the semirigid melts. On cooling, the chains become straight, to some extent, within a short time range of 300. Then, the development of intrachain local order gradually reduces the speed. At a time of 800, the crystal domains begin to grow slowly as shown by the development of the global order parameter. The growth of crystal domains is accompanied by chain realignment and packing, which leads to the second acceleration of the development of local intra-chain order in the time range between 1000 and 2000. Thus, in the case of semiflexible chain melts, the induction period for crystallization can be clearly observed. Another interesting feature is the degree of crystallization. In Fig. 7, the degree of crystallization of semirigid melts reaches 0.75, which means that most of the

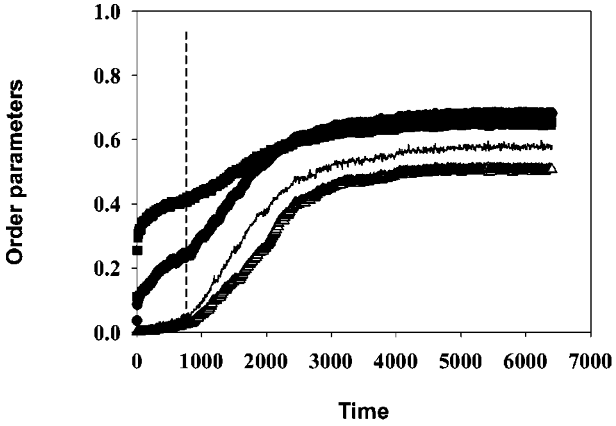

FIG. 8. Order formation processes of semiflexible chain melts. Symbols are the same as Fig. 7.

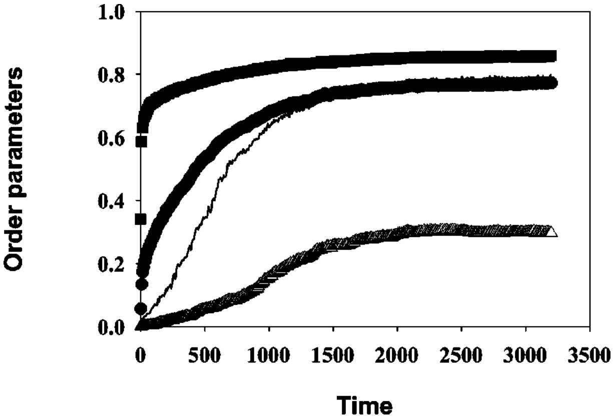

FIG. 9. Order formation processes of semirigid chain melts at $T=3$. Symbols are the same as Fig. 7.

chains belong to the crystal domains. However, the degree of crystallization of semiflexible melts was 0.58 in Fig. 8, although the value of the global order parameters is slightly higher than that of the semirigid melts. In the case of semirigid melts, chains easily associate with each other and form crystal regions, but this condition promotes nuclei formation. Competition between the nuclei prevents the development of global order.

In the above discussion, we have examined the crystallization processes at the same degree of supercooling. It may be helpful to consider the crystallization processes at different degrees of supercooling. In Fig. 9, we showed the crystallization processes of semirigid chain melts ($s_2=1.0$) at a lower temperature $T=3.0$ $(=0.53T_m)$, which is the same temperature as the condition given in Fig. 8. As shown in this figure, the final values of the intrachain local order parameter and the degree of crystallization become slightly larger than those obtained at $T=0.7T_m$, while the final value of the global order parameter decreases. The simulation results at a higher temperature of $T=5.0$ $(=0.88T_m)$ also confirm these temperature dependencies. Hence, in this range of supercooling, the global orientation order of the crystal increases as the growth temperature becomes higher. However, apart from the difference in the final values of order parameters, the dynamic behaviors of order parameters remain almost the same in this temperature range. Both the time scale of the local chain orientation and that of the global alignment slow down equally and we cannot observe any distinct changes in the relationship between the developments of local and global orientation orders.

In this study, we have mainly focused on the effect of chain rigidity at certain temperature conditions of the same quench degree. Since the simulations of crystallization from melts require heavy computational resources, simulations of the crystallization behaviors at very small quench temperatures remain as future tasks. Simulations with longer polymer chains would be preferred as well. However, it is very difficult at present to simulate the slow crystallization processes of the entangled melts of long polymers. Thus, we have neglected the formation of the folding structure and have concentrated on the relationship between the development of the internal molecular order and the overall system order. We consider that the simulations on short polymer melts would give us some keys to the elucidation of the order formation dynamics of real polymer systems in the early stage of crystallization.

IV. CONCLUSION

In summary, we have investigated the crystallization processes of dense melts of chain molecules, mainly focusing on the effect of chain rigidity. We found that the final crystal order drops sharply below a certain threshold of chain rigidity. The ordering dynamics during the crystallization are also affected by chain rigidity. In the case of semirigid chain melts, the change of single chain conformation and the parallel orientation of chains take place almost simultaneously. It is very difficult to distinguish these processes from the observation of order parameters. However, in the case of semiflexible chain melts, we can observe a long induction period and two different processes in the development of local order parameters. One of them is the stretching of single chain molecules, which occurs on a short time scale. The other is the chain association and packing that leads to the formation of crystal domains, which requires a longer time scale for melts. The latter process causes the reacceleration of the time evolution of the local intrachain order parameter for semiflexible chain melts. These results support the consideration that in the crystallization of the molecules with large internal degrees of freedom, a preparatory process is necessary within the molecules before the overall ordering processes can begin. However, these processes are not always clearly detectable even by monitoring the microscopic properties of chains as in the case of the semirigid chain melts. In the case of further flexible chain melts, most of the regions become amorphous and we cannot observe any distinct crystal domains. It is also observed that the final local order of the crystal increases as the chains become rigid, while the final global order of crystal takes its maximum value at a certain rigidity of main chains. Thus, our study indicates how the rigidity of chains affects the ordering dynamics in the early stage of the crystallization processes of short polymer melts.

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